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# Recovery of Neptunium from Highly Radioactive Waste Solutions of Purex Origin Using Tributyl Phosphate

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## ABSTRACT

The present work deals with the extraction of neptunium into the TBP/dodecane phase under conditions relevant to highly radioactive waste solutions, along with uranium and plutonium, by oxidizing it to the hexavalent state using 0.01 M $K_2Cr_2O_7$ and subsequently recovering it by selective stripping. Three types of simulated HLW solutions, namely sulfate-bearing (SB, in ~0.3 M $HNO_3$) and nonsulfate wastes originating from the reprocessing of fuels from pressurised heavy water reactors (PHWR) and fast breeder reactors (FBR) (both in 3.0 M $HNO_3$), have been employed in this study. Very high extraction of U(VI), Np(VI), and Pu(VI) was obtained from PHWR and FBR-HLW solutions, whereas extraction was less but reasonably high from the SB-HLW solution. The uptake of cerium at tracer level concentrations in the millimolar range (encountered in HLW solutions) and from the simulated HLW solutions containing 0.01 M $K_2Cr_2O_7$ by 30% TBP has shown that its extraction takes place only at tracer level concentrations and not at millimolar levels. The stripping of the metal ions from the loaded organic phase was done with a mixture of 0.01 M ascorbic acid and 0.1 M $H_2O_2$ in 2.0 M $HNO_3$ at organic to aqueous phase ratios of 1:1, 2:1, and 4:1. Quantitative recovery of neptunium and plutonium was achieved. Based on these results, a scheme was formulated for the recovery of neptunium, and it was tested using

the actual high level waste solution originating from the reprocessing of research reactor fuels.

## INTRODUCTION

The alpha-emitting long-lived nuclides contained 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. In the last ten years a considerable amount of work has been carried out worldwide on the partitioning of actinides from acidic waste solutions using various extracting agents (1–8). Octyl(phenyl)-*N*-*N*-diisobutyl-carbamoylmethylphosphine oxide (CMPO) has been adjudged as the best reagent for this purpose because of its ability to extract even trivalent actinides without any feed adjustment (1–6). Neptunium, which normally exists in the inextractable pentavalent state, has a very low distribution ratio ($D$) even with CMPO. Since $^{237}Np$ is one of the longest-lived nuclides among the actinides present in HLW solutions, its separation, recovery, and transmutation will minimize the problems of long-term surveillance of the vitrified waste to a great extent. Kolarik and Horwitz (9) and Mincher (10) 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 scheme for the partitioning of minor actinides from HLW solutions using either solvent extraction or an extraction chromatographic technique (1–3) employing CMPO, we incorporated a uranium depletion step using 30% tributyl phosphate (TBP) in dodecane. The present study deals with the recovery of neptunium during the uranium depletion step from three types of simulated HLW solutions: sulfate-bearing (SB), pressurized heavy water reactor (PHWR), and fast breeder reactor (FBR) HLW, and also the actual HLW solution originating from the reprocessing of research reactor fuels. The SB-HLW is the stored waste which contains a considerable amount of sulfate ions, arising from the ferrous sulfamate used for reducing Pu(IV) to Pu(III) in the partitioning stage. These wastes have been stored under low acid conditions. The other HLW solutions utilized here are generally salt-free and at an acidity of about 3 M. The recovery of neptunium has been achieved by its oxidation to the extractable hexavalent state using potassium dichromate and subsequently extracting it into 30% TBP. The extraction behavior 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 removing uranium, neptunium, and pluton-

ium together or removing neptunium and plutonium in one fraction and uranium in another fraction.

## EXPERIMENTAL

### Materials

TBP procured from M/s Bharat Vijay Chemicals, India, was purified by contact with a dilute solution of sodium hydroxide and subsequently washing with water. Dodecane (~93% C-12) was obtained from Transware Chemia Handelgeselscaft, Hamburg, Germany, and used untreated as the diluent (11). 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 (12–14). The radioactive tracer $^{238}Np$ was prepared by irradiating $^{237}Np$ at the Apsara research reactor of this Centre and dissolving the target in 6 M HCl. The acidity was adjusted to 1 M, and $Fe^{2+}$ nitrate solution (9) was added to make it 0.02 M with respect to $Fe^{2+}$. Neptunium in the tetravalent state was extracted with 0.5 M thenoyltrifluoroacetone (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. Each target of $^{237}Np$ contained nearly 800 μg Np. The tracer solutions thus prepared contained large amounts of Np; its concentration in the extraction experiments was kept at ~0.01 mM.

The radioactive tracer solutions of uranium and plutonium were assayed by liquid scintillation counting. While assaying plutonium in the 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 sodium iodide (Tl) detector. The total alphas in the samples were estimated by direct planchetting on a SS planchet and counting in an alpha proportional counter. Plutonium alpha activities were assayed by extracting plutonium in 0.5 M TTA/xylene and directly planchetting the organic phase. Uranium was analyzed spectrophotometrically using the 2-(5-bromo-2-pyridylazo)-5 diethyl-aminophenol (Bromo-PADAP) method for the aqueous phase (15) and using the thiocyanate method (16) for the organic phase.

In one of the extraction experiments, the aqueous phase contained either $^{237}Np$ (~0.04 mM) or $^{238}Np$ tracer (~0.01 mM Np) along with 0.01 M $K_2Cr_2O_7$ in nitric acid. Extraction with 30% TBP resulted in same distribution coefficients ($D$). This confirmed that the behavior of $^{237}Np$

alone in the millimolar range and the behavior of the tracer $^{238}Np$ (containing about 0.01 mM Np) are similar.

$^{238}Np$ tracer added to the actual HLW solution was estimated by gamma spectrometry using a HPGe detector coupled to a 4 k multichannel analyser. To avoid the interference due to large amounts of fission product activities, neptunium in the aqueous phase was estimated after reducing it to the tetravalent state with $Fe^{2+}$ and extracting it in 0.5 M TTA/xylene. Analysis of neptunium in the organic phase was carried out directly. The material balance in each system was better than 95%. The error limit in the estimation of activities was generally less than 2%. The compositions of the three simulated waste solutions are given in Table 1.

## Extraction Procedures



One milliliter of the feed solution (one of the three simulated HLW solutions) containing 0.01 M $K_2Cr_2O_7$ was spiked with $^{233}U$, $^{238}Np$, or $^{239}Pu$ tracer. The waiting period for completion of the reaction was maintained between 10 and 15 minutes, and then an equal volume of 30% TBP/dodecane was added to it. The solutions were equilibrated by slow rotation for 30 minutes in a thermostated bath at 25 ± 0.1°C. After equilibration, the solutions were centrifuged. The phases were then separated and pipetted for radioassay. In all the extraction studies with neptunium, Np(V) was used for initial spiking. Conversion of Np(IV) to Np(V) was achieved by taking Np(IV) in 1.0 M $HNO_3$ and heating it on a water bath at about 60°C for 4 hours. The fraction of neptunium not converted to Np(V) was removed by repetitive extraction with a mixture of 0.2 M CMPO + 1.2 M TBP in dodecane until the $D$ value for neptunium remained constant at ~0.05. Four CMPO extractions achieved a reproducible low $D$ for neptunium (10). In other extraction experiments, Np(V) tracer was added to 1 mL simulated HLW solutions containing (a) $K_2Cr_2O_7$ with a concentration varying between 0.0 to 0.01 M and (b) $NaNO_2$ with a concentration varying between 0.0 to 0.05 M. These solutions were contacted with equal volumes of 30% TBP. The equilibration, settlings, and radioassay were carried out as discussed above.

The extraction of Ce in the presence of 0.01 M $K_2Cr_2O_7$ by 30% TBP was studied from 1 mL nitric acid (concentration between 0.3 to 3.0 M) containing Ce either at the tracer level or in the millimolar range as well as from the simulated waste solutions. The volume of the TBP phase taken was the same as that of the aqueous phase. The equilibration was carried out as discussed above.

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[a] | — | 0.0990 | 0.0738 |
| 5. Zirconium | — | 0.7713 | 0.8221 |
| 6. Molybdenum | — | 0.7313 | 1.0921 |
| 7. Technetium[a] | — | 0.1813 | 0.2622 |
| 8. Ruthenium | 0.0001 | 0.4638 | 0.8131 |
| 9. Rhodium[a] | — | 0.1275 | 0.2622 |
| 10. Palladium[a] | — | 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[a] | — | 0.0283 | 0.0531 |
| 23. Samarium | — | 0.1638 | 0.3060 |
| 24. Europium | — | 0.0226 | 0.0318 |
| 25. Gadolinium | — | 0.0165 | 0.0657 |
| 26. Terbium[a] | — | 0.0005 | 0.0113 |
| 27. Dysprosium[a] | — | 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. Aluminum | 5.710 | — | — |
| 6. Calcium | 1.000 | — | — |
| 7. Sulfate | 14.320 | — | — |

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

## 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. The stripping agents used are given in Tables 6 through 17 along with their concentrations and other details. In the cases where repetitive contacts of fresh strip solutions were used, the organic phase was removed to a fresh equilibration tube after each contact, and aqueous phase containing the stripping agents was added to that tube. The contact time during stripping was 15 minutes, and the time between successive contacts was between 15 and 20 minutes. The assay of the activities in the separated organic and aqueous phases was done as discussed earlier.

At present, detailed studies on the kinetics of extraction and stripping have not been carried out. It is planned to take up these studies using Akufve and then to decide the type of equipment to be utilized.



## RESULTS AND DISCUSSION

The extraction of uranium, neptunium, and plutonium in the presence of 0.01 M $K_2Cr_2O_7$ by 30% TBP/dodecane (Table 2) shows the order of extraction to be U > Np > Pu, which follows the order of the effective cationic charges, i.e., 3.2, 3.0, and 2.9, respectively, of the actinyl $MO_2^{2+}$ ions (17). 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 the latter contains large amounts of sulfate ions and has a low acidity of only 0.3 M. Except in the case of extraction of Pu from SB-HLW, where $D$ was about 1.3, reasonably high $D$ values have been obtained in all other systems. It is possible to remove and recover uranium, neptunium, and plutonium quantitatively from HLW

TABLE 2
Extraction of Uranium, Neptunium, and Plutonium from Simulated Waste Solutions in the Presence of 0.01 M $K_2Cr_2O_7$ by 30% TBP. Organic to Aqueous Phase Ratio = 1:1

| | Distribution ratio | | |
|---|---|---|---|
| Aqueous feed | 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 |

solutions by oxidizing the latter two metal ions to the hexavalent state by using 0.01 M $K_2Cr_2O_7$ and extracting them into 30% TBP/dodecane. To optimize the concentration of $K_2Cr_2O_7$ required for this purpose, the extraction of neptunium was carried out from simulated PHWR-HLW solution by 30% TBP at varying $K_2Cr_2O_7$ concentrations. From the results (Table 3), it can be concluded that even 0.005 M $K_2Cr_2O_7$ is sufficient to oxidize Np to the extractable hexavalent state. However, in all the present studies, its concentration was always maintained at 0.01 M.

To investigate the effect of other reagents on the oxidation of Np(V) to Np(VI) in the waste solutions, $NaNO_2$ was used. When $NaNO_2$ was added to a solution containing Np(V) in 3.0 M $HNO_3$, the $D$ value increased from 0.004 (in the absence of $NaNO_2$) to 0.4 in the presence of 0.01 or 0.05 M $NaNO_2$ (Table 4). A similar increase in $D$ values has been reported by Kolarik and Horwitz (9) while extracting Np(V) in the presence of $NaNO_2$ by 0.2 M CMPO + 1.2 M TBP in dodecane. In a recent publication, Tochiyama et al. (18) suggested a catalyzed oxidation of neptunium in the nitric acid–TBP system in the presence of nitrous acid.

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 |

Our studies with all three waste solutions show that the $D$ value for Np (Table 4) decreases as the $NaNO_2$ concentration increases from 0.01 to 0.05 M. In the absence of $NaNO_2$, the $D$ values of Np in PHWR- and FBR-HLW solutions (which have an acidity of 3.0 M) are much higher (more than 100 times) as compared to the $D$ value in pure 3.0 M $HNO_3$ without any metal ions. The $D$ value for Np in SB-HLW is much lower than those in PHWR- or FBR-HLW, but this is again higher than that in pure 3.0 or pure 0.3 M $HNO_3$ ($D < 10^{-3}$). It could be inferred from the $D$ values that neptunium, which was expected to be in the inextractable pentavalent state under HLW conditions, actually undergoes disproportionation, resulting in such higher $D$ values. However, when 0.01 or 0.05 M $NaNO_2$ is added to the waste solutions, the $D$ value for Np decreases with increasing $NaNO_2$ concentration. Although it is not possible to give a definite explanation for the contradictory behavior of $NaNO_2$ in HLW solutions as compared to that in pure $HNO_3$, it appears that the addition of $NaNO_2$ under the waste conditions (with several metal ions and corrosion products) reduces Np(VI) to Np(V), resulting in lower $D$ values.

Among the other oxidizing agents, potassium permanganate was not tried because it reacts with CMPO (9) which will be used for the partitioning of the remaining actinides (Am, Cm, etc.) from the TBP raffinate. Potassium bromate is not preferred for plant-scale operations.

Smith and Moore (19) reported the separation of radiocerium by oxidizing it to the tetravalent state with $K_2Cr_2O_7$ and extracting it into TTA/xylene. Ce(IV) is extracted into the 30% TBP phase along with U, Np, and Pu. To assess the behavior of Ce under waste conditions, we carried out the extraction of Ce at tracer and at millimolar levels in different acidities as well as in the three simulated waste solutions. As can be seen from Table 1, the concentration of Ce is at the tracer level in SB-HLW whereas it is in the millimolar range in the other two wastes. It is clear from Table 5 that at both concentration levels, the $D$ of Ce in the presence of 0.01 M $K_2Cr_2O_7$ in 30% TBP increases with an increasing concentration of $HNO_3$. The $D$ values in millimolar concentrations of Ce are over an order of magnitude lower than those at the tracer level.

In the case of simulated PHWR- and FBR-HLW solutions, the lower $D$ values of ~0.03 suggest negligible uptake of Ce by TBP from these waste solutions. However, in the case of SB-HLW solution, $D$ of nearly 1, which indicates a significant uptake of Ce in the TBP phase. Thus, high extraction of Ce at tracer level concentrations agrees well with the findings of Smith and Moore (19). However, negligible extractions at the millimolar level were observed. Right now it is not possible to explain the difference in behavior of Ce at tracer and millimolar levels.

TABLE 5
Extraction of Cerium from Nitric Acid and Simulated HLW Solutions in the Presence of 0.01 M $K_2Cr_2O_7$ by 30% TBP. Organic to Aqueous Phase Ratio = 1:1

| | Distribution ratio for Ce | | | | |
|---|---|---|---|---|---|
| | From $HNO_3$ solution at cerium concentration | | From simulated waste solutions | | |
| Acidity | 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 |



Various reagents have been tried for stripping Np and Pu from the organic phase. In this context, since the reduction of Np(VI) to Np(V) by $H_2O_2$ in dilute nitric acid is fast and that of Np(V) to Np(IV) is very slow (20), it was decided to use a dilute solution of $H_2O_2$ at different $HNO_3$ concentrations to study the stripping behavior of Np from the TBP phase. The data in Table 6 suggest that in the presence of 0.1 M $H_2O_2$, and by varying the $HNO_3$ concentrations between 0.1 to 2.0 M, more than 98% of Np could be stripped. It was decided to carry out stripping of Np at various organic to aqueous phase ratios using 0.1 M $H_2O_2$ + 2.0 M $HNO_3$ as the strippant. Table 7 shows that the total Np stripped (after four contacts) decreases with increasing organic to aqueous phase ratios, but even at a ratio of 6:1, a major portion of Np (~87%) has been stripped.

Extraction studies of Ce in the presence of $K_2Cr_2O_7$ by 30% TBP (Table 5) have shown that $D$ for Ce was ~1 only in the case of SB-HLW. Stripping of Ce from this TBP phase was carried out with 0.1 M $H_2O_2$ in 0.5, 1.0, and 2.0 M $HNO_3$ to examine its behavior during the stripping of Np. Table 8 shows that almost quantitative stripping of Ce was achieved in three contacts. Thus, it is concluded that under conditions where Ce is extracted into the organic phase, it is stripped along with Np.

Since the reduction of Pu(VI) to Pu(IV) in the presence of $H_2O_2$ in nitric acid is fast even at room temperature (20), it was expected that under the stripping conditions of Np, Pu would be held up in the TBP phase. Our results (Table 9) suggest that a substantial portion of the Pu is stripped into the aqueous phase, although the amount decreases with increasing $HNO_3$ concentration. As an example, from the TBP phase containing Pu extracted from the simulated PHWR-HLW solution, the total percentages

TABLE 6
Stripping of Neptunium from Loaded TBP Phase (originally extracted from simulated HLW solutions in the 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

| | % Np stripped, reagents used | | | |
|---|---|---|---|---|
| Contact | 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 |



of Pu stripped were 99.9, 94.5, 85.7, and 67.9 for $HNO_3$ concentrations of 0.1, 0.5, 1.0, and 2.0 M, respectively. These results suggest that although Np can be stripped almost quantitatively by a mixture of $H_2O_2$ and $HNO_3$, the aqueous phase will not be free of Pu. In fact, it will contain considerable amounts of Pu.

TABLE 7
Stripping of Neptunium from Loaded TBP Phase (originally extracted from simulated PHWR-HLW in the 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 $HNO_3$

| | % Np stripped | | | |
|---|---|---|---|---|
| Contact | 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 the 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

| | % Ce stripped, reagents used | | |
|---|---|---|---|
| Contact | 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 the 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

| | % Pu stripped, reagents used | | | |
|---|---|---|---|---|
| Contact | 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 |

It was decided to strip both Np and Pu quantitatively in the same fraction after further reducing Pu(IV) to the inextractable trivalent state. Ascorbic acid was chosen for this purpose. However, the stripping of Pu with ascorbic acid alone in 2 M $HNO_3$ did not give a quantitative recovery. A mixture of ascorbic acid and $H_2O_2$ in 2 M $HNO_3$ was the best combination for the complete recovery of Pu. Table 10 shows that solutions containing 0.01 M ascorbic acid and 0.1 M $H_2O_2$ at varying $HNO_3$ concentrations between 0.1 to 2.0 M could strip Pu from the TBP phase almost quantitatively. Further, we investigated the stripping of Pu from the TBP phase at various organic to aqueous phase ratios using a strippant mixture containing 0.1 M ascorbic acid and 0.1 $MH_2O_2$ in 2.0 M $HNO_3$. Even at a high organic to aqueous phase ratio of 4:1, quantitative stripping of Pu was achieved in four contacts (Table 11). The stripping of Pu in the absence of ascorbic acid is also given in the same table for the purpose of comparison.

It is known that in the PUREX process, stripping of Pu from the TBP phase in the presence of dibutyl phosphoric acid (DBP) in the organic phase leads to the formation of a Pu–DBP–TBP synergistic complex. This results in incomplete removal of Pu from the organic phase. To investigate the stripping behavior of Pu under the conditions of HLW, Pu was extracted from PHWR-HLW solution by 30% TBP containing 2 g/L DBP and subsequently stripping with 0.01 M ascorbic acid + 0.1 M $H_2O_2$ at acidities of 0.1 and 2.0 M with an organic to aqueous phase ratio of 4:1. Almost complete stripping of Pu from a loaded organic phase (Table 12)



TABLE 10
Stripping of Plutonium from Loaded TBP Phase (originally extracted from simulated PHWR-HLW in the 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

| | % Pu stripped using reagents | | | |
|---|---|---|---|---|
| Contact | 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 the 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 $HNO_3$

| | | % Pu stripped | | |
|---|---|---|---|---|
| Stripping reagent | Contact | O:A = 1:1 | O:A = 2:1 | O:A = 4:1 |
| 0.1 M $H_2O_2$ + 0.01 M ascorbic acid | I | 91.26 | 85.32 | 37.40 |
| + 2.0 M $HNO_3$ | 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 |



suggests that the presence of DBP in the organic phase will not create any serious problems in the stripping of Pu. Under these experimental conditions, Np should behave in a similar manner.

The effect of other reducing agents such as hydroxylamine and hydrazine on the stripping of Pu from the TBP phase at an organic to aqueous

TABLE 12
Stripping of Plutonium from Loaded TBP + DBP Phase (originally extracted from simulated PHWR-HLW solutions in the presence of 0.01 M $K_2Cr_2O_7$). Organic Phase = 30% TBP Containing 2 g/L 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

| | | % Pu stripped from loaded TBP + DBP phase | |
|---|---|---|---|
| Stripping reagent | Contact | $HNO_3$: 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 |

phase ratio of 4:1 was also studied and compared with $H_2O_2$ in 2.0 M $HNO_3$ (in the absence as well as in the presence of 0.01 M ascorbic acid). It can be seen from Table 13 that although the stripping of Pu from the TBP phase follows the order hydroxylamine > hydrazine > hydrogen peroxide in the absence of ascorbic acid, the order is reversed in the presence of ascorbic acid. Quantitative stripping of Pu could be achieved using only the stripping mixture containing 0.01 M ascorbic acid + 0.1 M $H_2O_2$ acid in 2.0 M $HNO_3$. 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 together is possible using a mixture of ascorbic acid, $H_2O_2$, and $HNO_3$ as the strippant.

The stripping behavior of uranium from the loaded TBP phase under conditions favorable for the stripping of Np and Pu was also investigated in detail. Using the strippant mixture of 0.01 M ascorbic acid and 0.1 M $H_2O_2$ in 0.1 or 2.0 M $HNO_3$ and at an organic to aqueous phase ratio of 4:1, it was observed that at an acidity of 2.0 M only about 7% of the uranium was stripped whereas at 0.1 M $HNO_3$ ~31% of the uranium was stripped into the aqueous phase after four contacts (Table 15). This results in an aqueous phase containing substantial but incomplete amounts of uranium along with neptunium and plutonium. Complete removal of uranium is possible only after additional washings of the TBP phase with very dilute nitric acid.



TABLE 13
Stripping of Plutonium from Loaded TBP Phase (originally extracted from simulated PHWR-HLW in the presence of 0.01 M $K_2Cr_2O_7$) Using Various Reagents. Organic to Aqueous Phase Ratio = 4:1

| | % Pu stripped, using reagents | | | | | |
|---|---|---|---|---|---|---|
| | 0.05 M $NH_2OH \cdot HCl$ 2.0 M $HNO_3$ | | 0.05 M $NH_2NH_2 \cdot H_2SO_4$ 2.0 M $HNO_3$ | | 0.1 M $H_2O_2$ 2.0 M $HNO_3$ | |
| Contact | 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 the 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

| | | % Np stripped | | |
|---|---|---|---|---|
| Stripping reagent | Contact | 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 the 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

| | | % U stripped | | |
|---|---|---|---|---|
| Stripping reagent | Contact | 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 |

In the next experiment, uranium, neptunium, and plutonium were added together to the simulated PHWR-HLW solution containing 0.01 M $K_2Cr_2O_7$, and their extraction with 30% TBP was carried out at an organic to aqueous phase ratio of 1:1. The stripping of the loaded TBP phase was carried out with two stripping mixtures:

$$0.01\ \text{M ascorbic acid} + 0.1\ \text{M } H_2O_2 + 0.1\ \text{M } HNO_3 \quad (1)$$

$$0.01\ \text{M ascorbic acid} + 0.1\ \text{M } H_2O_2 + 2.0\ \text{M } HNO_3 \quad (2)$$

at the organic to aqueous phase ratio of 4:1. By using Mixture (1), more than 99% of the neptunium and plutonium were recovered after four contacts (Table 16). This fraction also contained nearly 35% of the uranium. The remaining 65% of the uranium was present in the TBP phase. A dilute $HNO_3$ washing is necessary for the complete recovery of uranium. By using Mixture (2), nearly 99% of the neptunium and plutonium were released from the TBP phase in four contacts, together with ~6% of the uranium. This aqueous phase was given a scrub with 30% TBP at an



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 the 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 $H_2O_2$ + | I | 4.66 | 15.52 | 73.18 |
| 0.01 M ascorbic acid | 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 $H_2O_2$ + | I | 2.03 | 46.78 | 31.87 |
| 0.01 M ascorbic acid | 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 |

organic to aqueous phase ratio of 1:4, which resulted in an aqueous phase containing only Np and Pu.

Based on the above data, a flow sheet (Fig. 1) for the removal and recovery of neptunium and plutonium was prepared and employed while using the actual HLW solution generated during the reprocessing of re-

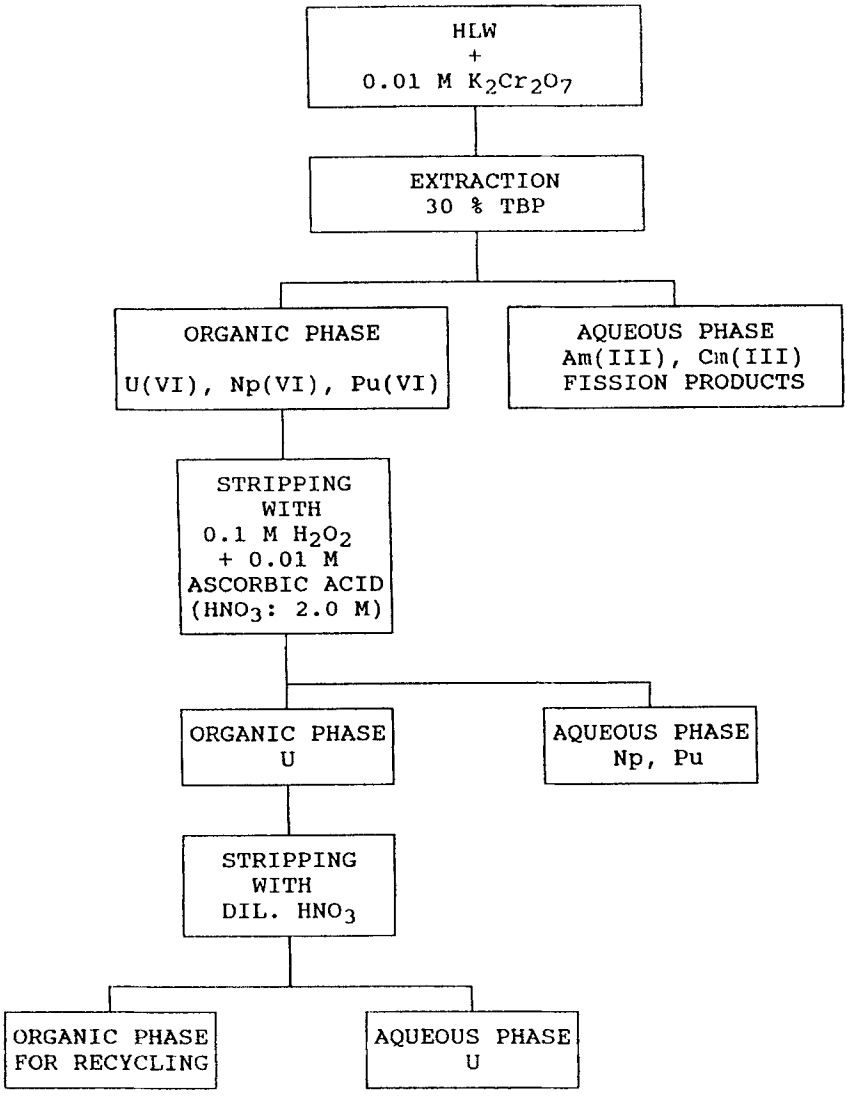


FIG. 1 Flow sheet for the partitioning of neptunium, plutonium, and uranium from high level waste solution.

TABLE 17
Extraction and Stripping of Uranium, Neptunium, and Plutonium from Actual HLW by 30% TBP

| *Extraction*[a] | | |
|---|---|---|
| Metal ion | Distribution ratio | % Extraction |
| U(VI) | 17.91 | 94.71 |
| Np(VI) | 14.46 | 93.53 |
| Pu(VI) | 9.338 | 90.33 |

| *Stripping*[b] | | | |
|---|---|---|---|
| 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 |

[a] Organic to aqueous phase ratio = 1:1.
[b] Stripping reagent = 0.1 M $H_2O_2$ + 0.01 M ascorbic acid + 2.0 M $HNO_3$. Organic to aqueous phase ratio = 4:1.



search reactor fuels. The solution was spiked with $^{238}Np$ for easy and efficient assay of Np in the actual HLW solutions. The concentration of Np was in the range of about 0.02 mM. Extraction of uranium, neptunium, and plutonium was carried out in the presence of 0.01 M $K_2Cr_2O_7$ at an organic to aqueous phase ratio of 1:1. The results of replicate experiments are given in Table 17 and are in fair agreement with those obtained while using synthetic HLW solutions. The $D$ values were found to be 17.7, 14.4, and 9.3 for U, Np, and Pu, respectively, suggesting the 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 a mixture containing 0.01 M ascorbic acid and 0.1 M $H_2O_2$ in 2.0 M $HNO_3$ at an organic to aqueous phase ratio of 4:1. Nearly 99% of the Np and Pu has thus been recovered. Separation of Np from Pu can be achieved by employing well-known procedures.

The addition of 0.01 M $K_2Cr_2O_7$ to HLW solutions leads to about 0.5% of the Cr in the final vitrified waste product. This amount is within the normally acceptable limits of Cr in glass.

## CONCLUSION

Quantitative extraction of neptunium and plutonium along with uranium from simulated SB-, PHWR-, FBR-HLW, and the actual HLW solutions

by 30% TBP could be achieved by oxidizing neptunium and plutonium to the extractable hexavalent state using 0.01 $K_2Cr_2O_7$. More than 99% of the neptunium and plutonium has been recovered from the loaded TBP phase using the strippant mixture of 0.01 M ascorbic acid and 0.1 M $H_2O_2$ in 2.0 M $HNO_3$, leaving most of the uranium behind in the organic phase.

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