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Separation and Recovery of Uranium, Neptunium, and Plutonium from High Level Waste Using Tributyl Phosphate: Countercurrent Studies with Simulated Waste Solution

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ABSTRACT

The present work deals with countercurrent extraction studies on the partitioning of uranium, neptunium, and plutonium using 30% tributyl phosphate (TBP) from simulated high level waste solution generated during reprocessing of spent uranium fuel from pressurized heavy water reactors. The oxidation states of neptunium and plutonium were adjusted either by 0.01 M potassium dichromate or 0.01 M dioxovanadium ion. Neptunium and plutonium, extracted in the TBP phase, were stripped together using a mixture containing 0.05 M ascorbic acid and 0.25 M hydrogen peroxide in 2.0 M nitric acid solution. Although dioxovanadium ion is more effective for proper adjustment of the oxidation states of plutonium and neptunium, subsequent recovery of these actinides from loaded TBP is better if potassium dichromate is used for the valency adjustment. Results of the stagewise analysis of extraction and stripping of actinides using mixer-settlers are presented.

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INTRODUCTION

The high level waste (HLW) generated during reprocessing of spent uranium fuel from nuclear reactors contains the fission products in bulk and small amounts of actinides like uranium, neptunium, plutonium, americium, and curium. The HLW solutions are immobilized in a vitreous matrix for ultimate disposal in deep geological repositories. Partitioning of actinides from HLW has been proposed to reduce the long-term hazards of vitrified product. Solvent extraction techniques are under development for the removal of actinides from HLW solutions by using various types of reagents. Octyl-(phenyl)-*N*,*N*-diisobutylcarbamoylmethylphosphine oxide (CMPO) is one of the most promising extractants for actinide partitioning because of its ability to extract trivalent transplutonics like americium, in addition to uranium, neptunium, and plutonium, from HLW solutions (1–6).

A high concentration of uranium in a waste solution leads to the formation of a third phase with CMPO solutions even in the presence of tributyl phosphate (TBP) used as a phase modifier. In addition, a high concentration of uranium in the feed lowers the extraction of other actinides due to excessive loading of the CMPO phase. These problems can be avoided by introducing a uranium depletion step using 30% TBP prior to the CMPO extraction step (7). TBP also extracts neptunium and plutonium if they are in either the tetravalent or hexavalent state. With a proper adjustment of oxidation states, it is possible to remove neptunium and plutonium from HLW during the uranium depletion step. This will avoid the distribution of neptunium and plutonium into different streams during subsequent partitioning of the HLW when CMPO is used as an extractant.

Sodium nitrite has been used to adjust the oxidation state of plutonium to Pu(IV) in the PUREX process. Nitrous acid can be used to adjust the oxidation states of neptunium for its recovery from the dissolver solution (8). Maintaining the concentration of nitrous acid is critical for effective oxidation of neptunium to Np(VI). Equilibrium favors the formation of inextractable Np(V) with a high concentration of nitrous acid. In the case of HLW, the concentration of nitrite ion may not remain constant due to radiolysis of nitric acid. Potassium permanganate and potassium bromate cannot be used because the former reacts with CMPO and the latter is not generally preferred for plant-scale operations. Cerium cannot be considered because Ce(IV) is not stable in nitric acid. Furthermore, Ce(IV) as well as Ce(III) are extractable in CMPO and cause undesirable loading of the CMPO phase. Among other reagents, dichromate ion can oxidize neptunium and plutonium (9) to the hexavalent state. Dioxovanadium ion is another reagent suitable for adjustment of the oxidation states (10). In the present work, dichromate and dioxovanadium ions were used for adjustment of the oxidation states.

Neptunium(VI) and plutonium(IV or VI) extracted in TBP can be stripped simultaneously by reducing them to inextractable Np(V) and Pu(III), respectively, leaving uranium in the TBP phase. This was achieved in our earlier batch studies with simulated as well as actual HLW using a solution containing ascorbic acid and hydrogen peroxide in 2.0 M nitric acid (11). Neptunium and plutonium from the aqueous product are present in the same concentration range and can be separated using techniques like ion exchange. Uranium left in loaded TBP can easily be recovered using dilute nitric acid. Lean TBP can be recycled after a carbonate wash which removes residual actinides and acidic degradation products.

In the present work the feasibility of the above process was tested by countercurrent studies using mixer-settlers. The behavior of actinides during their extraction and stripping was studied in detail through stagewise analysis.

EXPERIMENTAL

Materials

The composition of the simulated waste used for our studies is shown in Table 1. The composition is based on a fission product inventory of spent

TABLE 1
Composition of Simulated High Level Waste Solution (acidity = 3.0 M)

Constituent	Concentration (g/L)	Constituent	Concentration (g/L)
Selenium	0.0123	Barium	0.3088
Rubidium	0.0745	Lanthanum	0.2638
Strontium	0.1863	Cerium	0.5325
Yttrium	0.0990	Praseodymium	0.2438
Zirconium	0.7713	Neodymium	0.8625
Molybdenum	0.7313	Promethium[a]	0.0283
Technetium[a]	0.1813	Samarium	0.1638
Ruthenium	0.4638	Europium	0.0226
Rhodium[a]	0.1275	Gadolinium	0.0165
Palladium	0.2675	Terbium	0.0005
Silver	0.0186	Dysprosium	0.0002
Cadmium	0.0159	Uranium	18.325
Tin	0.0151	Sodium	3.0
Antimony	0.0047	Iron	0.5
Tellurium	0.1028	Chromium	0.1
Cesium	0.5438	Nickel	0.1

[a] Lanthanum was added for promethium, molybdenum for technetium, and cobalt for rhodium.

fuel from a pressurized heavy water reactor with a burn-up of 6500 MWd/Te of UO_2 and 3 years of cooling. The quantity of waste produced is assumed to be 800 L/Te of fuel. Inert constituents (such as sodium) and corrosion products (like iron, chromium, and nickel) were added in the quantities anticipated in the actual PHWR-HLW solutions. The uranium concentration in the simulated waste solution was ~18 g/L. Dioxovanadium solution was prepared by dissolving vanadium pentoxide (V_2O_5) in 3 M HNO_3. All the chemicals used were of Analytical Reagent grade. The waste solution was spiked with neptunium ($^{237+238}Np$) and plutonium (mainly ^{239}Pu). The concentration of neptunium in the spiked waste was 0.1–0.2 mg/L and that of plutonium was 2–4 mg/L. $^{237+238}Np$ was prepared by irradiating ^{237}Np at the Apsara research reactor of this Centre and obtained in radiochemically pure form in the tetravalent state (12). TBP was obtained from Bharat Vijay Chemicals, India, and purified as discussed earlier (13). Dodecane was supplied by Transware Chemia Handelsgeselschaft, Hamburg, Germany, and was used without further purification.

Mixer-Settlers

The mixer-settlers used for the countercurrent runs were fabricated from polyacrylic sheets. The capacity of each mixer was 30 mL and that of the settler was 130 mL. Peristaltic pumps were used for feeding the liquids. Mechanical stirrers were used for mixing the liquids.

Extraction and Stripping Procedure

Uranium, neptunium, and plutonium were extracted from the simulated PHWR-HLW by 30% TBP in *n*-dodecane. The studies were carried out in the presence of 0.01 M $K_2Cr_2O_7$ and 0.01 M VO_2^+. The details of the scheme are presented in Figs. 1 and 2. The HLW feed was diluted to about 33% due to mixing with the scrub. The mixing and settling times were 2.9 and 12.3 minutes, respectively, in each stage. The loaded TBP phase was stripped with a mixture containing 0.05 M ascorbic acid and 0.25 M H_2O_2 in 2.0 M HNO_3. The strippant was introduced at two points as shown in Figs. 3 and 4. The aqueous product was scrubbed with 30% TBP. The equilibrium conditions were determined by periodic checks of total activity in the exit streams of the organic and aqueous phases. Samples were collected from various stages as well as from the exit streams at the end of each run and then analyzed for actinides.

Analysis

Uranium in the organic samples was analyzed spectrophotometrically either by the thiocyanate method (14) or by the 2-(5-bromo-2-pyridylazo)-5-diethyl-

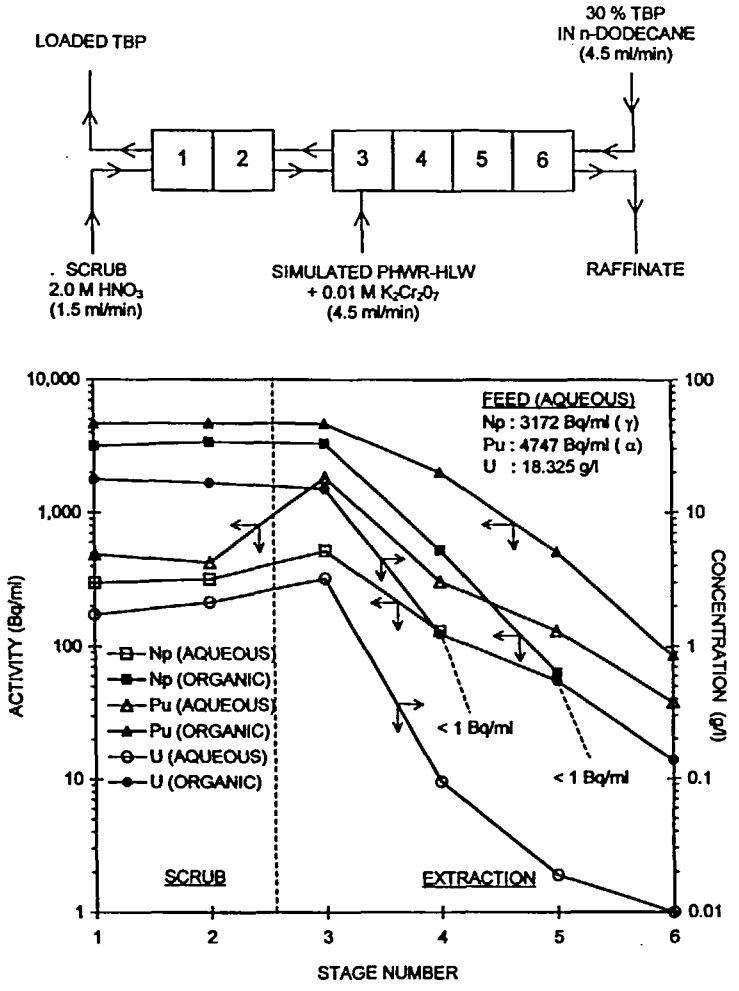

FIG. 1 Extraction of actinides from simulated PHWR-HLW by 30% TBP in the presence of 0.01 M potassium dichromate.

aminophenol (Bromo-PADAP) method (15). The latter method is suitable for determining uranium at the ppm level. Uranium in the aqueous samples was first extracted with tri-*n*-octyl phosphine oxide (TOPO) in benzene to avoid interference from other metal ions and then analyzed by either of the above methods, depending upon its concentration.

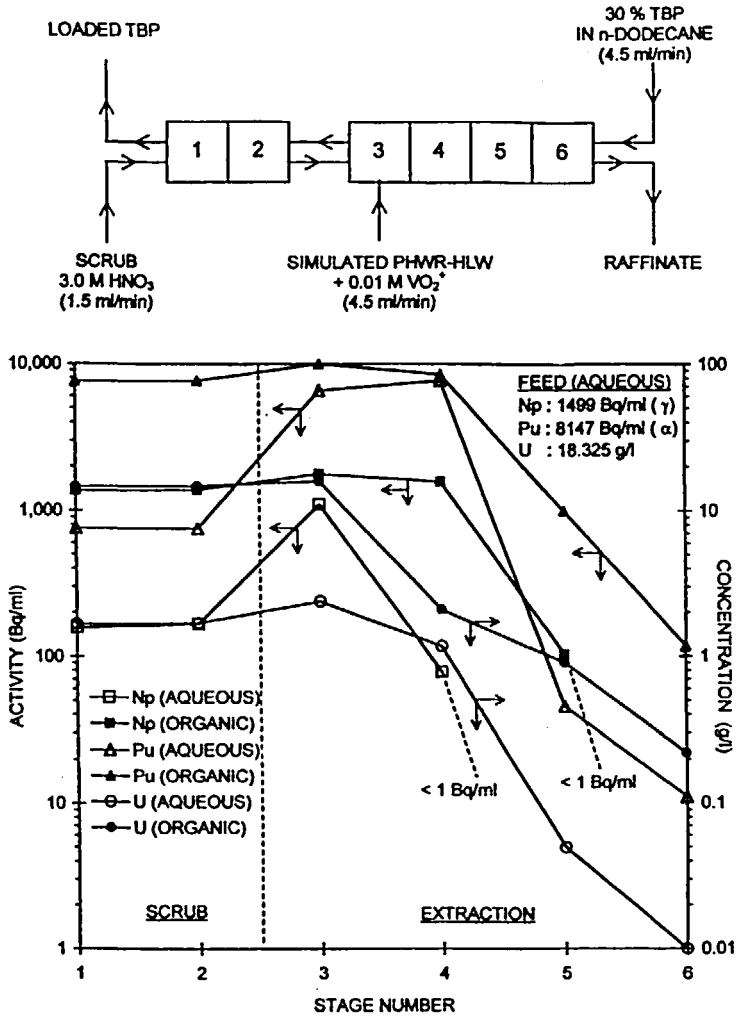

FIG. 2 Extraction of actinides from simulated PHWR-HLW by 30% TBP in the presence of 0.01 M dioxovanadium ion.

Plutonium from aqueous samples was first extracted into thenoyltrifluoroacetone (TTA) in xylene after proper adjustment of the oxidation state and acidity. The extracted plutonium was radiometrically determined using an alpha proportional counter. For the estimation of plutonium from TBP, it was stripped into the aqueous phase by reducing it to Pu(III) with ferrous solution.

The aqueous phase was then analyzed in the same way as above. ^{238}Np, which was the only gamma activity in the simulated waste solution during the uranium depletion step, was analyzed on a single channel analyzer using a NaI(Tl) detector.

Analysis of chromium and vanadium in the raffinate was carried out using ICPAE spectroscopy.

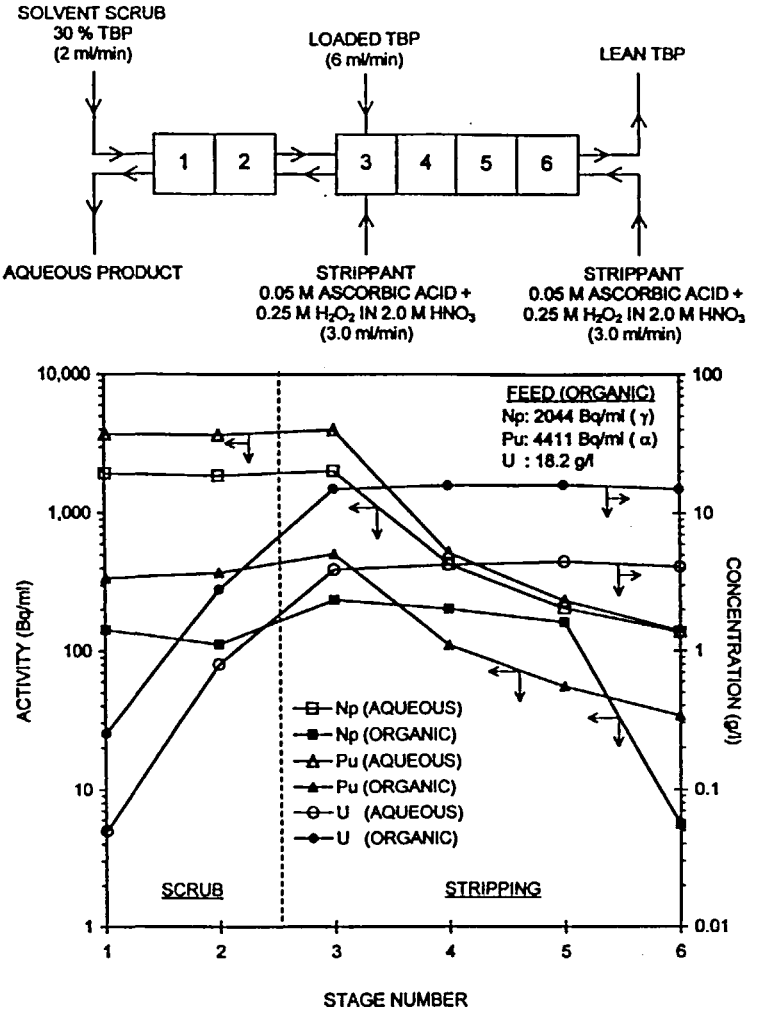

FIG. 3 Stripping of actinides from loaded TBP (extracted in the presence of 0.01 M $K_2Cr_2O_7$).

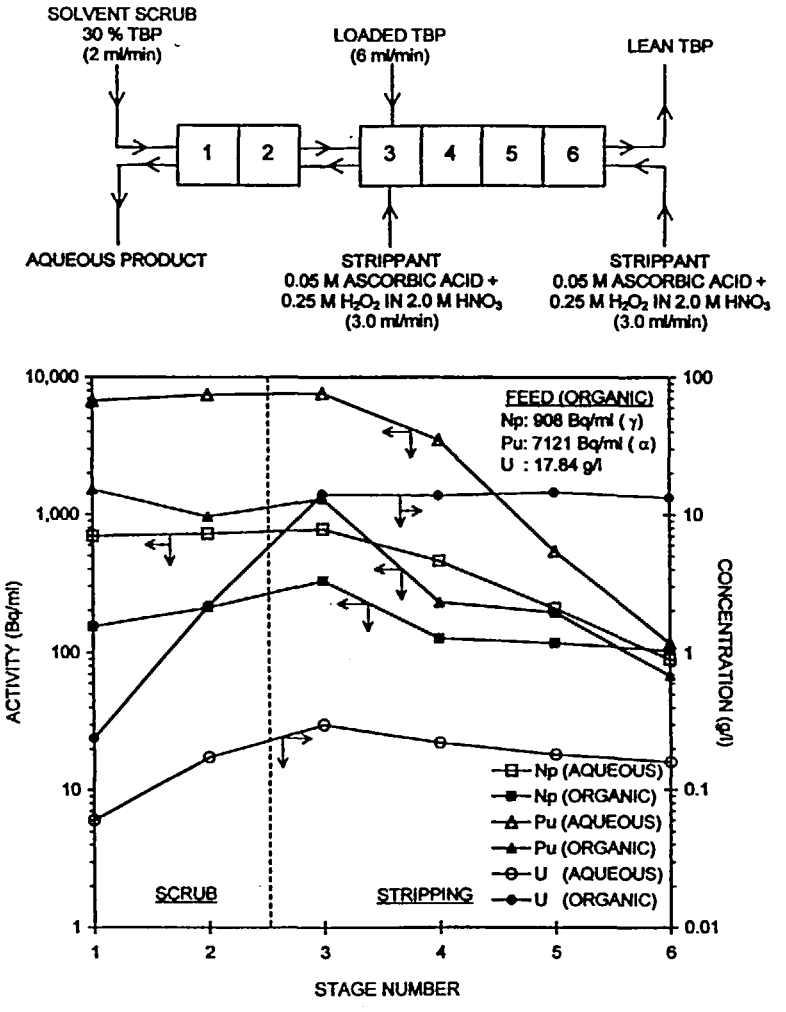

FIG. 4 Stripping of actinides from loaded TBP (extracted in the presence of 0.01 M VO_2^+).

RESULTS AND DISCUSSION

As seen in our batch studies (11) using 30% TBP, neptunium exhibits high extraction with a distribution ratio of ~13 from HLW solutions in the presence of 0.01 M $K_2Cr_2O_7$. Potassium dichromate oxidizes neptunium and plutonium to their hexavalent state. Although the extraction of Pu(VI) is lower than that

of Pu(IV), the distribution ratio is sufficiently high (>5) for quantitative extraction of plutonium from HLW solutions. Dioxovanadium ion also oxidizes neptunium to Np(VI). Its advantage lies in the fact that oxidation of Pu(III) to Pu(IV) by dioxovanadium ion is a fast reaction, but its further oxidation to Pu(VI) is a slow reaction. Since the distribution ratio of Pu(IV) in TBP is higher than that of Pu(VI), this should result in a higher extraction of plutonium.

The stagewise extraction patterns for uranium, neptunium, and plutonium in the presence of 0.01 M $K_2Cr_2O_7$ and 0.01 M VO_2^+ are presented in Figs. 1 and 2. The extraction behaviors of uranium and neptunium were observed to be similar in both cases. The concentration of uranium was reduced from 18 g/L to a very low value of ~10 mg/L after four extraction stages (~99.9% removal). No ^{238}Np gamma activity was detected in the raffinate. In the case where $K_2Cr_2O_7$ was used as the oxidizing agent, plutonium in the raffinate was found to be ~1% of that in the feed, whereas in the case of VO_2^+ as the oxidizing agent, plutonium, being in the tetravalent state, showed an improved extraction of about 99.8%. No appreciable release of uranium, neptunium, and plutonium was observed from the organic phase during scrubbing in either case. These results show that dichromate as well as dioxovanadium ion can be used for the extraction of actinides from HLW; the latter is more effective because of the high extraction of plutonium. The reason for the slight reflux of actinides observed in the third and fourth stages during their extraction in the presence of dioxovanadium ion (Fig. 2) is not clear. It may be due to interference from cation–cation complexes. Dioxovanadium ion is known to form such complexes with actinides (16).

Figures 3 and 4 show the stripping of neptunium and plutonium from loaded TBP generated in the extraction runs with a mixture of 0.05 M ascorbic acid and 0.25 M H_2O_2 in 2.0 M HNO_3. Under these conditions, plutonium is reduced to inextractable Pu(III), whereas neptunium is reduced to inextractable Np(V). Its further reduction to extractable Np(IV) is a slow reaction.

TBP extracts various metal ions through solvation. Potassium dichromate is known to be extractable in TBP, probably as the disolvate species $H_2Cr_2O_7 \cdot 2TBP$ (17). In countercurrent stripping, extracted dichromate may interfere with the reduction of neptunium and plutonium and lead to reflux (reextraction) of the stripped species. In our extraction runs, ~18% of chromium and ~3% of vanadium were found to be extracted in the TBP phase. To ensure immediate and complete destruction of the extracted oxidizing agent, the stripping solution was fed through two inlets as shown in Figs. 3 and 4. Each of the two aqueous phases was passed at a flow rate half that of the organic phase, thereby maintaining the total input of the strippant to be the same as that of loaded TBP.

Figure 3 shows that neptunium and plutonium were quantitatively stripped from TBP loaded with actinides from simulated HLW containing 0.01 M $K_2Cr_2O_7$. All stages show high plutonium and neptunium activity in the aqueous phase compared to the organic phase. The concentrations of neptunium and plutonium in the TBP phase were appreciably lowered in the third stage, which was the entry point for fresh strippant. Although a major fraction of $H_2Cr_2O_7$ present in the TBP phase would have been destroyed in this stage, traces of $H_2Cr_2O_7$ seem to have remained in the TBP phase and affected the stripping of neptunium in the next two stages. Destruction of this $H_2Cr_2O_7$ in the sixth stage by fresh strippant might have resulted in further improvement in the stripping of neptunium. About 99.6% of neptunium and 99% of plutonium were stripped from the TBP phase. The solvent scrub was effective in lowering the uranium content of the aqueous product. The concentration of uranium in the aqueous product was only 0.05 g/L, which corresponds to a release of only 0.3% of uranium from the organic feed.

The stripping of neptunium and plutonium, extracted from simulated HLW in the presence of 0.01 M VO_2^+, is shown in Fig. 4. Although plutonium was stripped quantitatively, stripping of neptunium was incomplete with nearly 15% of neptunium left in the exiting TBP phase. The last three mixer-settler stages showed an almost constant neptunium content in the organic phase, which may be due to the presence of extractable Np(IV). Vanadyl ion is known to react with ascorbic acid through the formation of an intermediate V(III) species (18), and V(III) in turn can reduce Np(V) to Np(IV) (19). This will lead to incomplete recovery of neptunium. The concentration of uranium in the aqueous product was low (~0.06 g/L). Comparison of the results shows that if simultaneous recovery of neptunium and plutonium is sought (leaving uranium in the TBP phase), then dioxovanadium is not suitable for adjusting the oxidation states during the uranium-depletion step.

CONCLUSION

A uranium-depletion step using 30% TBP as the extractant quantitatively removes uranium, neptunium, and plutonium from simulated PHWR-HLW. The uranium concentration in the waste solution is reduced to ~10 mg/L. This avoids the formation of a third phase and a high uranium loading of CMPO which is used in the subsequent step for the removal of trivalent actinides. Use of 0.01 M $K_2Cr_2O_7$ or 0.01 M VO_2^+ leads to practically complete removal of neptunium by 30% TBP. More than 99% of the plutonium can be extracted in the presence 0.01 M $K_2Cr_2O_7$, whereas the extraction is ~99.8% in the presence of VO_2^+. The extraction trend shows the possibility of further improvement in the extraction of plutonium if an adequate number of extraction stages are provided.

Although the use of dioxovanadium ion for adjusting the oxidation states leads to improved extraction of plutonium, recovery of neptunium from the TBP phase with a mixture containing 0.05 M ascorbic acid and 0.25 M H_2O_2 in 2.0 M HNO_3 is incomplete. For quantitative stripping to be possible, potassium dichromate should be used to adjust the oxidation states during the extraction step.

The uranium-depletion step can be included as a regular feature in a reprocessing plant since all the reagents are compatible with the PUREX process.

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