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# STUDIES ON THE PARTITIONING OF ACTINIDES FROM HIGH LEVEL WASTE USING A MIXTURE OF HDEHP AND CMPO AS EXTRACTANT

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## ABSTRACT

The paper describes the extraction and stripping behavior of actinides and lanthanides *viz.* americium, plutonium, uranium, cerium, and europium using a mixture of di-(2-ethylhexyl)phosphoric acid (HDEHP) and octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) in n-paraffin as extractant. The extractant mixture combines the advantages of both the extractants for the partitioning of actinides from PUREX High Level Waste (HLW) solution. The extraction studies have been carried out from nitric acid medium as well as with simulated uranium-lean PUREX-HLW solution as relevant to Pressurized Heavy Water Reactor (PHWR) fuel reprocessing. The extracted actinides are stripped using a mixture of diethylenetriaminepentaacetic acid (DTPA), formic acid and hydrazine hydrate, leaving lanthanides in the organic phase. The

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lanthanides are subsequently stripped using a mixture of DTPA and sodium carbonate. The behavior of cesium, strontium, ruthenium, and zirconium is also studied using this mixed extractant.

*Key Words*: High level waste; Actinides; Fission products; Lanthanides; Solvent extraction; CMPO; HDEHP; DTPA

## INTRODUCTION

Trivalent actinides can be separated from lanthanides by the TALSPEAK process (1) developed for the recovery of actinides from High Level Waste (HLW). This process uses di-(2-ethylhexyl)phosphoric acid (HDEHP) as extractant for the separation of actinides and lanthanides. The extracted actinides can be selectively stripped from the organic phase using a solution of polyaminocarboxylic acid like diethylenetriaminepentaacetic acid (DTPA) in a buffer medium. (DTPA forms stronger complexes with actinides than lanthanides.) The extraction of the actinides and lanthanides into HDEHP requires a low feed acidity (pH $\sim$ 2). The initial lowering of the feed acidity of the highly acidic PUREX-HLW can be avoided, if HDEHP is used along with a neutral extractant like octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO), which is capable of extracting trivalent actinides and lanthanides even from moderately concentrated nitric acid solutions (2,3). In the TRUEX process (2,4), which uses a mixture of CMPO and tri-n-butyl phosphate (TBP) as an extractant, the extracted trivalent actinides are stripped using dilute nitric acid. If a mixture of these extractants is used in the partitioning process, CMPO will prove to be effective in extracting the metal ions from HLW solution, whereas HDEHP will be the active constituent of the extractant mixture during the stripping. Selective stripping of the extracted actinides should then be possible using a solution of DTPA under low acid conditions (as in TALSPEAK process). Such a mixture of HDEHP and CMPO would find an application in the partitioning of actinides from HLW, as it combines the merits of both the extractants and eliminates an additional step for the trivalent actinide-lanthanide group separation.

The feasibility of using this extractant mixture for the partitioning of actinides from HLW is investigated in the present work. The studies are carried out from pure nitric acid medium as well as from uranium-lean simulated PUREX-HLW as relevant to Pressurized Heavy Water Reactor (PHWR) fuel reprocessing. The studies involve extraction of actinides (americium, plutonium, and uranium), lanthanides (cerium and europium), and other fission products like cesium, strontium, ruthenium, and zirconium. The extraction was followed by their stripping, using buffer solutions containing citric acid or DTPA, at various acidities (pH). Studies have been carried out mainly with a mixture of 0.3 M HDEHP and 0.2 M CMPO in n-paraffin.





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## EXPERIMENTAL

### Materials

HDEHP and n-paraffin used in the studies were procured from M/s. Fluka AG, Switzerland, and M/s. Tamilnadu Petro, Chennai, India, respectively, and were used without further purification. Solvent extraction grade CMPO (<0.02 wt.% of acidic impurities) used in these studies was indigenously synthesized and purified as reported elsewhere (5).

The composition of simulated HLW is shown in Table 1 and is based on the fission product inventory of spent fuel from PHWR with a burn-up of 6,500 MWd/Te of $UO_2$ and 3 years of cooling (6). Quantity of waste produced is assumed to be 800 liters/Te of fuel. Inert constituents like sodium and corrosion products like iron, chromium, and nickel were added in the quantities anticipated in the PHWR-HLW solutions. As proposed in the earlier process for actinide partitioning (7), potassium dichromate (0.01 M) was also added to HLW for oxidation of plutonium and neptunium to their hexavalent state. Urnaium content of this HLW was lowered to a concentration level of <10 mg/l by repeatedly contacting it with fresh 30% TBP in n-paraffin at an organic toaqueous phase ratio of 1:1. This

***Table 1.*** Composition of Simulated High-Level Waste Solution

| 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* | 0.0283 |
| Technetium* | 0.1813 | Samarium | 0.1638 |
| Ruthenium | 0.4638 | Europium | 0.0226 |
| Rhodium* | 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 |

*Lanthanum was added for promethium, molybdenum for technetium, and cobalt for rhodium.
**Corrosion products.





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uranium-lean HLW solution was then spiked with tracer quantities of $^{241}$Am, Pu (mainly as $^{239}$Pu), $^{233}$U, $^{137}$Cs, $^{90}$Sr, $^{95}$Zr, $^{106}$Ru, $^{144}$Ce, and $^{152+154}$Eu as per the requirements of each experiment.

In the studies with pure nitric acid solutions, plutonium was converted to Pu(IV) and Pu(VI) using sodium nitrite and potassium dichromate, respectively, before spiking. The loaded organic feed for the stripping studies was prepared by contacting the extractant with uranium-lean HLW spiked with necessary actinides, lanthanides and other fission products.

All the studies were carried out at an organic to aqueous ratio of 1:1, with a contact time of 10 minutes. (Scouting experiments showed that contact of 10 minutes was sufficient for reaching the equilibrium.)



### Analysis

$^{241}$Am, $^{137}$Cs, $^{95}$Zr, $^{106}$Ru, $^{144}$Ce, and $^{152+154}$Eu in the aqueous as well as organic phases were assayed by gamma spectrometry using 62 c.c. HPGe detector coupled with 4 K multichannel analyzer. In the extraction studies from nitric acid solutions, plutonium, and uranium (as $^{233}$U) analysis in both the phases was carried out by direct radiometry using alpha proportional counter. In the case of the experiments with simulated HLW solutions, plutonium in the aqueous phase was extracted into 0.5 M TTA in xylene and TTA phase was analyzed radiometrically. The analysis of plutonium in the organic phase from these experiments was carried out by direct radiometry. $^{90}$Sr in the organic as well as aqueous phase was analysed on a gas-flow beta proportional counter.

## RESULTS AND DISCUSSION

### Extraction Studies

The distribution ratios for Am(III), Pu(IV), Pu(VI), U(VI), Ce(III), and Eu(III) from nitric acid solutions with varying concentration (0.5 to 4.0 M), using a mixture of 0.3 M HDEHP and 0.2 M CMPO in n-paraffin as an extractant, are presented in Table 2. As expected, distribution ratios for tetravalent and hexavalent species are found to be higher than those for trivalent species. The table shows that the extraction, in general, decreases with increasing concentration of nitric acid. The high extraction observed at lower concentration of nitric acid is clearly by HDEHP, an acidic extractant. At higher concentration of nitric acid, the effectiveness of HDEHP decreases and that of CMPO increases, with nitric acid acting as a salting-out agent. However, the extraction of various species with this mixture at higher acidity is lower than that reported with TRUEX solvent (5). This



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***Table 2.*** Extraction of Actinides and Lanthanides by HDEHP-CMPO Mixture from Nitric Acid Medium

| $[HNO_3]$ (M) | Distribution Ratios (D) | | | | | |
|---|---|---|---|---|---|---|
| | Am(III) | Ce(III) | Eu(III) | Pu(IV) | Pu(VI) | U(VI) |
| 0.5 | 36.61 | 45.47 | 48.83 | 3093.2 | 934.4 | 39.95 |
| 1.0 | 7.74 | 7.20 | 12.79 | 2845.4 | 404.5 | 37.98 |
| 2.0 | 2.56 | 3.19 | 3.67 | 2588.1 | 261.9 | 34.31 |
| 3.0 | 2.13 | 1.93 | 2.55 | 2113.4 | 163.0 | 32.50 |
| 4.0 | 1.78 | 1.25 | 1.90 | 1754.2 | 136.4 | 28.46 |

1. Extractant: 0.2 M CMPO + 0.3 M HDEHP in n-paraffin
2. Phase Ratio = 1:1
3. Contact time = 10 minutes.



lowering of extraction may be due to interaction between HDEHP and CMPO. Alkylphosphoric acids are known to have a tendency to form mixed systems like HX.S, $HX_2$.S, and $H_2X_2$.S, resulting in the decrease of the active concentrations of the reagents (8). The tendency appears to be more pronounced at higher acidity, where the complexing ability of CMPO is suppressed substantially because of the presence of HDEHP.

HLW is expected to contain significant quantity of uranium, which may lead to formation of a third phase when contacted with a mixture of CMPO and HDEHP in n-paraffin. Moreover, uranium in HLW will cause undesired loading of CMPO and will adversely affect the extraction of other actinides, especially the trivalent ones like americium and curium. In the next set of experiments, the extraction of Am(III), Ce(III), and Eu(III) was studied from 3.0 M nitric acid medium containing varied concentration of uranium. Table 3 clearly shows the lowering of extraction for all the three species with increasing concentration of uranium. The distribution ratio for Am(III) is as low as 0.47 for the uranium concentration of 12.0 g/l in the feed. With the uranium content of the feed >12 g/l, the phase disengagement was observed to be poor. Moreover, the material balance for the americium activity was found to be unsatisfactory (the difference exceeding 10%). The third-phase formation was distinctly observed for uranium concentrations above 30 g/l in the feed.

The mixed extractant, when contacted with simulated PHWR-HLW containing ~18 g/l uranium with an acidity of 3.0 M nitric acid (Table 1), resulted in crud formation due to precipitation of some of the extracted metal ions. This makes the removal of uranium from HLW essential prior to its contact with the mixed extractant. Uranium can be removed from HLW solution by extraction with TBP. (Plutonium and neptunium can also be extracted along with uranium by converting them to their hexavalent states using potassium dichromate as oxidizing agent (7).) The distribution ratios for Am(III), Ce(III), Eu(III), U(VI), and Pu(VI) from



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***Table 3.*** Extraction of Actinides and Lanthanides by HDEHP-CMPO Mixture from 3.0 M Nitric Acid Medium in Presence of Uranium

| [Uranium] (g/l) | Distribution Ratios (D) | | |
|---|---|---|---|
| | Am(III) | Ce(III) | Eu(III) |
| 0 | 2.13 | 1.93 | 2.55 |
| 1.0 | 1.82 | 1.69 | 2.37 |
| 2.0 | 1.56 | 1.53 | 1.94 |
| 4.0 | 1.34 | 1.37 | 1.52 |
| 8.0 | 0.68 | 1.03 | 1.26 |
| 12.0 | 0.47 | 0.72 | 0.92 |

1. Extractant: 0.2 M CMPO + 0.3 M HDEHP in n-paraffin
2. Phase Ratio = 1:1
3. Contact time = 10 minutes.



uranium-lean HLW with the mixed extractant at different acidities are presented in Table 4. (The residual plutonium in uranium-lean PHWR-HLW, being present in hexavalent state, extraction of plutonium was studied only for Pu(VI).) As in the case of pure nitric acid medium, the extraction for all the species except cerium is observed to be lowered with increasing concentration of nitric acid. Although the extraction of Am(III) and Eu(III) is affected marginally when extracted from waste solution, the extraction is significantly affected in the case of hexavalent metals ions. The difference in the extraction behavior may be due to the extraction of various species present in macro amounts in the waste solution. Nevertheless, the extraction of actinides is acceptably high for their removal from HLW solution. The increase in the extraction of cerium may be due to its possible oxidation to the more extractable tetravalent state.

***Table 4.*** Extraction of Actinides and Lanthanides by HDEHP-CMPO Mixture from Uranium-Lean Simulated PHWR-HLW

| $[HNO_3]$ (M) | Distribution Ratios (D) | | | | |
|---|---|---|---|---|---|
| | Am(III) | Ce(III) | Eu(III) | Pu(VI) | U(VI) |
| 1.50 | 2.93 | 9.12 | 6.26 | 35.58 | 2.34 |
| 2.50 | 2.46 | 7.66 | 3.76 | 16.07 | 1.90 |
| 3.10 | 1.89 | 6.56 | 2.28 | 12.93 | 1.82 |

1. Extractant: 0.2 M CMPO + 0.3 M HDEHP in n-paraffin
2. Phase Ratio = 1:1
3. Contact time = 10 minutes



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The extraction of other fission products like cesium, strontium, ruthenium, and ziroconium was investigated in separate experiments using this mixed extractant. The extraction of alkali and alkaline earth metals like cesium and strontium is observed to be very low from 3.0 M nitric acid solution as well as from uranium-lean PHWR-HLW ($H^+ \sim 3.0$ M), with a distribution ratio of $<10^{-2}$. Similar low extraction is observed for ruthenium with a distribution ratio of $<10^{-2}$ from nitric acid as well as simulated waste solution. The respective distribution ratios for zirconium are 3.42 and 3.12, indicating its extraction along with actinides and lanthanides into the mixed extractant.

The change in the acidity of the feed during the extraction was less than 0.01 M, which shows that the uptake of the acid by the mixed extractant is much less compared to that in the case of TRUEX solvent (9). The interaction between the two extractants discussed earlier may be the cause of low uptake of acid in the organic phase.



## Stripping Studies

Citric acid in presence of formic acid and hydrazine hydrate can strip actinides and fission products even in presence of acidic impurities like dibutyl phosphoric acid (HDBP) (9). The constituents of this strippant can be destroyed by conventional methods without the generation of any hazardous residue. The similar strippant containing even 0.5 M citric acid at varied pH (2 to 4) could not strip actinides from the loaded HDEHP-CMPO mixture. In the further studies, a stronger complexing agent like DTPA was used in place of citric acid.

In the next set of experiments, the stripping of Am(III), Ce(III), Eu(III), and Pu(VI) was carried out using a mixture of 0.05 M DTPA, 0.4 M formic acid, and 0.4 M hydrazine hydrate at varying pH of 2 to 4. Table 5 shows the difference in the stripping behavior of Am(III), Ce(III), and Eu(III). It is seen that Am(III) is more easily stripped compared to Ce(III) and Eu(III). Although it is possible to strip more than 85% of Am(III) in a single contact at pH 4, the release of Ce(III) is less than 5%. The release of Eu(III) is ~30% under similar conditions. Complete stripping of Am(III) is achieved in the second contact. The table also shows the stripping behavior of plutonium, and it is seen that about 80% of plutonium could be stripped using this mixture at pH 4.0 in a single contact. In the second contact, plutonium could be stripped completely. The aqueous phase after first contact was analyzed for the acidity (pH) in each case. Table 5 shows that the change in pH of the strippant is marginal.

The stripping behavior of zirconium, extracted in the mixed solvent from uranium-lean simulated PHWR-HLW ($H^+ \sim 3$ M), was studied using the same strippant at pH 4. No stripping of zirconium was observed even after two contacts. This shows that the stripping of actinides will not be accompanied by that of zirconium.



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***Table 5.*** Stripping of Americum, Cerium, and Europium from HDEHP-CMPO Using DTPA as a Function of pH

| pH of Strippant | | %Stripping | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Contact I | | | | Contact II | | | |
| Before Contact | After First Contact | Am (III) | Ce (III) | Eu (III) | Pu (VI) | Am (III) | Ce (III) | Eu (III) | Pu (VI) |
| 2.00 | 1.83 | 0.91 | 0.61 | 0.53 | — | 2.94 | 2.12 | 0.91 | — |
| 2.50 | 2.30 | 6.41 | 1.00 | 2.80 | — | 11.00 | 2.74 | 7.40 | — |
| 3.00 | 2.82 | 19.88 | 1.79 | 4.80 | 4.99 | 39.98 | 3.16 | 12.49 | 8.80 |
| 3.50 | 3.34 | 53.23 | 2.15 | 10.04 | 10.52 | 75.13 | 3.19 | 28.47 | 18.45 |
| 4.00 | 3.73 | 85.86 | 4.40 | 30.81 | 79.85 | ∼100 | 10.11 | 58.24 | ∼100 |

1. Extractant: 0.2 M CMPO + 0.3 M HDEHP in n-paraffin
2. Feed for extraction: Uranium-lean simulated PHWR-HLW
3. Strippant: 0.4 M hydrazine hydrate + 0.4 M formic acid + 0.05 M DTPA
4. Phase Ratio = 1:1
5. Contact time = 10 minutes.

Table 6 shows the distribution ratios and the separation factors for Am(III), Ce(III), and Eu(III) based on the first contact. These results indicate a very high separation factor (∼136) between americium and cerium, especially at the high pH of 4.0. The separation factor between americium and europium is ∼14 under

***Table 6.*** Distribution Ratios and Separation Factors as a Function of pH of the Strippant for Trivalent Lanthanides and Actinides (Calculated*)

| | Distribution Ratio (D) | | | Separation Factor ($\alpha$) | |
|---|---|---|---|---|---|
| pH of Strippant | Am(III) | Ce(III) | Eu(III) | Ce/Am | Eu/Am |
| 2.0 | 108.90 | 162.90 | 187.70 | 1.50 | 1.72 |
| 2.5 | 14.60 | 99.00 | 34.71 | 6.78 | 2.38 |
| 3.0 | 4.03 | 54.87 | 19.83 | 13.62 | 4.92 |
| 3.5 | 0.88 | 45.51 | 8.96 | 51.72 | 10.18 |
| 4.0 | 0.16 | 21.73 | 2.25 | 135.81 | 14.06 |

*Based on the results reported in Table 5
1. Extractant: 0.2 M CMPO + 0.3 M HDEHP in n-paraffin
2. Feed for extraction: Uranium-lean simulated PHWR-HLW
3. Strippant: 0.4 M Hydrazine hydrate + 0.4 M formic acid + 0.05 M DTPA
4. Phase Ratio = 1:1
5. Contact time = 10 minutes.





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these conditions. These results show the possibility of separating actinides from other fission products from uranium-lean HLW. In actual process, the europium contamination of the aqueous stream containing actinides can be reduced by introducing a solvent scrub for the aqueous product stream with the same mixed extractant.

Although the mixed solvent used in these experiments does not extract acid to any significant extent, a few experiments were carried out that involved a prior scrubbing of the organic phase before the stripping. In these experiments, the organic phase, contacted with uranium-lean HLW spiked with americium, cerium, and europium, was scrubbed using either distilled water or a buffer solution containing formic acid and hydrazine hydrate (pH 4). Two contacts with these scrubbing solutions at a phase ratio of 1:1 were followed by contacts with the usual strippant containing DTPA, formic acid, and hydrazine hydrate (pH 4). Results showed that the stripping of americium, cerium and europium is not influenced by this scrub.

Removal of americium from the organic phase will leave major fraction of the lanthanides in the organic phase. Stripping of this lanthanide fraction from the organic phase was studied using sodium hydroxide and sodium carbonate either alone or in the presence of DTPA. Results of these studies are presented in Table 7. Use of sodium hydroxide resulted in the precipitation during the stripping, whether used alone or in presence of DTPA. Sodium carbonate, when used alone, led to poor phase disengagement. But when it was used in presence DTPA, more than 98% of the lanthanides and zirconium could be stripped in a single contact, without any precipitation or phase disengagement problems. The activity could be completely removed from the organic phase in the second contact with a mixture of sodium carbonate and DTPA. The lean-organic phase, which is in sodium form, may be regenerated by contacting it with moderately concentrated nitric acid and reused.

***Table 7.*** Solvent Cleanup Using Various Reagents

| Reagents | Contact I | Contact II |
|---|---|---|
| 0.5 M NaOH | Resulted in precipitation | — |
| 0.25 M $Na_2CO_3$ | Phase disengagement poor | Resulted in precipitation |
| 0.5 M NaOH + 0.05 M DTPA | Resulted in precipitation | — |
| 0.5 M $Na_2CO_3$ + 0.05 M DTPA | Excellent phase disengagement with stripping of >98% activity | Excellent phase disengagement with no detectable activity in the organic phase |

1. Extractant: 0.2 M CMPO + 0.3 M HDEHP in n-paraffin
2. Phase Ratio = 1:1
3. Contact time = 10 minutes





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The extraction studies with the mixed extractant were also carried out at a lower concentration of HDEHP in the mixture to assess its influence on the actinide/lanthanide extraction and separation. A lowered concentration of HDEHP in the extractant (0.2 M HDEHP and 0.2 M CMPO in n-paraffin) shows higher extraction (nearly twice) for both actinides and lanthanides as compared to that obtained with a mixture of 0.3 M HDEHP and 0.2 M CMPO in n-paraffin used as extractant. This improvement in the extraction may be due increase in the active concentration of CMPO (8). The stripping studies on Am(III), Ce(III), and Eu(III) extracted from nitric acid medium (3.0 M) into the mixed extractant with lower HDEHP concentration of 0.2 M showed that nearly 90% of Am(III) and 60% of Eu(III) are stripped in a single contact with a mixture of DTPA, formic acid, and hydrazine hydrate (pH $\sim$ 3.5) used as a strippant. The stripping of cerium under these conditions was only $\sim$2%. Similar studies carried out with a DTPA containing strippant at pH 4.0 showed still higher stripping of europium ($\sim$75%) along with americium (>95%). The stripping of cerium continued to be low and was only $\sim$5%. These results show that although americium can be separated from cerium, substantial quantity of europium will accompany the americium product when lower concentration of HDEHP is used in the mixed extractant. However, these experiments reveal various possibilities in evolving flow sheets with different concentration levels of HDEHP in CMPO.

## CONCLUSION

The mixture of HDEHP and CMPO is tested as an extractant for the removal of actinides from uranium-lean HLW in the present studies. It is seen that the actinides can be extracted from solutions of HLW at higher acid concentration using the mixed extractant. The trivalent actinides extracted in HDEHP-CMPO phase can further be selectively stripped using a mixture of DTPA, formic acid, and hydrazine hydrate leaving bulk of the lanthanides in the organic phase. Plutonium is also stripped along with the trivalent actinides. Trivalent lanthanides left in the organic phase can be recovered using a mixture of DTPA and sodium carbonate. This mixed solvent may find useful applications in the partitioning of actinides from waste solutions.

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