Separation of Trivalent Actinides from High-Active Waste


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Abstract

A typical high-active waste (HAW) arising from reprocessing of \((U_{0.3}Pu_{0.7})C\) fuel irradiated to the burn-up of 155 GWd/Te in a fast breeder test reactor (FBTR) was characterized. Partitioning of trivalent actinides from HAW was demonstrated using a solvent, 0.2 M n-octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) - 1.2 M tri-n-butylphosphate (TBP) in n-dodecane (n-DD), in a mixer settler. The results established quantitative separation of trivalents (Am(III) + Ln(III)) from HAW and recovery (> 99 %) using a citric acid-nitric acid formulation. The mutual separation of lanthanides and actinides from the stripped product was studied by using bis(2-ethylhexyl)diglycolamic acid (HDEHDGA), synthesized in our laboratory.

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Keywords: High active waste; Trivalent actinide partitioning; Lanthanide-actinide separation; glycolamic acid; carbamoylmethylphosphine oxide; solvent extraction

1. Introduction

The PUREX process has been in vogue, worldwide, for the recovery of uranium and plutonium from the spent nuclear fuel. The process involves liquid-liquid extraction of U(VI) and Pu(IV) from the spent nuclear fuel dissolver solution by using a solution of tri-n-butylphosphate (TBP) in n-dodecane (n-DD) [1]. The raffinate rejected after the extraction of uranium and plutonium is known as high-active waste (HAW), which is a complex
mixture of several elements such as the radioactive actinides, short and long-lived fission products and stable fission products. Since the trivalent lanthanides, neptunium and transplutonium elements are inextractable by tri-n-butylphosphate, they are rejected to HAW.

Partitioning and Transmutation (P&T) [2, 3] of trivalent actinide is being considered in many countries as a viable method for the safe management of high-level liquid waste (HLLW). Partitioning is usually carried out by liquid-liquid extraction of trivalent actinides and chemically similar lanthanides from HLLW followed by lanthanide-actinide separation. There are several reagents such as the organophosphorous compounds, amides, and diglycoamides [4-10] have been proposed as potential candidates for actinide partitioning. Horwitz et al. [6] introduced a TRUEX process, in which the trivalents are selectively extracted in to a solution of 0.2 M n-octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO)- 1.2 M tri-n-butylphosphate (TBP) in n-dodecane (n-DD). Thrust in the utilization of CMPO over other reagents for minor actinide partitioning is due to the fact that the TRUEX solvent enjoys a well-established co-ordination chemistry of trivalents and well-examined system over few decades [4-6].

During minor actinide partitioning, the lanthanides are also co-extracted into organic phase along with trivalent actinides. However, for transmutation, the mutual separation of trivalent lanthanides and actinides is necessary; otherwise, the lanthanides acts as neutron poisons while transmuting the actinides in fast reactors. The separation of lanthanides(III) from actinide(III) or vice versa is a challenging task due to the similarity in the chemical and extraction behavior of 4f- and 5f- elements [7,8]. Several methods have been reported in literature that exploits the presence of spatially extended 5f-orbitals in actinides [9-13] for mutual separation of actinides from lanthanides. In this context, we synthesized bis(2-ethylhexyl)diglycolamicacid (HDEHDGA) and studied for the extraction of Eu(III) and Am(III) from nitric acid medium [14,15]. These diglycolamic acids are acid derivatives of alkyl-3-oxapentane, emerging as promising candidates for lanthanide-actinide (Ln-An) separations. Unlike the other reagents in-use for Ln-An separation, the diglycolamic acids are made up of CHON- atoms and they are completely miscible in n-dodecane.

The aim of the present paper is three fold. Initially, we report the chemical characterization of genuine high active waste (HAW) arising from reprocessing of nuclear fuel (U0.3Pu0.7)C, irradiated to the burn-up of 155 GWd/Te in a fast breeder test reactor (FBTR). This is followed by the results of mixer-settler studies carried out on partitioning of trivalent actinides from fast reactor HAW (155 GWd/Te) by using 0.2 M CMPO-1.2 M TBP/n-DD. Finally, we also report the summary of mixer-settler studies carried out for the mutual separation of Am(III) from Eu(III) from the citric acid medium by using 0.1 M HDEHDGA/n-DD.

2. Experimental

2.1. Materials

All the chemicals and reagents used in the study were of analytical grade. The chemicals, citric acid (CA) and diethylenetriaminepentaacetic acid (DTPA) were purchased from LOBA chemicals, Mumbai. n-Octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) was obtained from NCL, Pune. HDEHDGA was synthesized by the procedure described elsewhere [14]. (152+154)Eu in the form of EuCl₃ was purchased from Board of Radiation and Isotope Technology, Mumbai and ²⁴¹Am(III) was obtained from Bhabha Atomic Research Centre, India. High-active liquid waste was received from the CORAL pilot plant, IGCAR.

2.2. Characterization of HAW (155GWd/Te)

The procedure adopted for determining various elements and radioisotopes present in HAW is described in detail elsewhere [16]. Briefly, the concentration of nitric acid was determined by titrimetric method. The gamma
emitting isotopes were assayed using HPGe detector coupled with multi-channel analyzer (MCA). Plutonium was estimated by solvent extraction with theonyltrifluoroacetone (HTTA) followed by the determination of alpha activity. Uranium was analyzed by both spectrophotometry and HPLC methods. Neptunium was estimated by neutron activation analysis. The radioactivities of americium and curium were determined by alpha counting technique and alpha spectrometry. The other elements present in this waste were determined by ICP-AES.

2.3. Mixer-Settler run

The high-active liquid waste arising from reprocessing of (U0.3Pu0.7)C fuel irradiated to the burn-up of 155 GWd/Te in a fast breeder test reactor was received from the CORAL pilot plant, IGCAR. The waste was characterized as described above. The extraction of trivalents from HAW was performed by passing the feed (HAW) and organic phase (0.2 M CMPO-1.2 M TBP/n-DD) in a counter current mode in a 16-stage mixer settler, as illustrated in figure 1. Mixing of the organic and aqueous phases was achieved by air pulsing in the column by applying vacuum and pressure alternatively with the help of a solenoid valve operated by a cyclic timer. The aqueous and organic solutions were fed into the mixer settler at a constant flow rate of 4.5 ml per minute by means of metering pumps equipped with precise flow control. Steady state was attained in four hours. The system was operated for ~7 hrs. Samples were taken from organic and aqueous phases of all stages for obtaining the radioactivity profile in the mixer settler run. The organic and aqueous phases were collected at the outlet. The organic phase obtained after extraction was known as loaded organic and the aqueous phase was known as raffinate in this case.

![Fig 1. Illustration of the mixer-settler and the conditions employed for extraction and stripping.](image)

(a) For minor actinide partitioning: Number of stages 1-16, conditions for extraction and stripping: Aq. feed: HAW solution, flow rate 4.5 mL/min, Organic:0.2 M CMPO-1.2 TBP/n-DD, flow rate 4.5 mL/min. Loaded organic: organic phase after the extraction of trivalents, flow rate 4.5 mL/min. Aqueous strip: 0.1 M CA-0.1 M HNO₃, flow rate 4.5 mL/min
(b) For lanthanide-actinide separation: Number of stages 1-20, conditions for extraction and stripping: Aqueous feed: 0.1 M CA+ 0.1 HNO₃ spiked with ^{152+154}Eu(III) and ^{241}Am(III) tracers and was adjusted to pH 3, flow rate 3 mL/min. Organic: 0.1 M HDEHDGA/n-DD, flow rate 3 mL/min. Loaded organic: 0.1 M HDEHDGA/n-DD containing Eu(III) and Am(III), flow rate 3 mL/min. Aqueous Strip: 0.01 M DTPA + 0.025 M CA adjusted to pH 1.5, flow rate 3 mL/min

The lanthanides and actinides were recovered from the loaded organic in a counter current extraction process using the same mixer settler in a separate run (illustrated in figure 1). The stripping formulation was composed of 0.1 M citric acid (CA) and 0.1 M HNO₃. The aqueous and organic phases were fed into the mixer settler at a constant flow of 4.5 mL/min for 7 hours. The aqueous and organic samples were taken from various stages for
constructing the radioactivity profile. The organic phase obtained after back extraction was known as lean organic and the aqueous phase was known as aqueous product. The sampling devices, electronic gadgets, flow controls and other electronic/mechanical components required for the run were either fabricated or assembled in-house for successful operation in hot cells.

The aqueous product (in citric acid medium) obtained after the minor actinide partitioning acts as a feed for solution for the mutual separation of lanthanides from actinides. To understand the separation behavior of lanthanides and actinides from citric acid medium, the extraction behavior of Eu(III) and Am(III) was studied using 0.1 M HDEHDGAn-DD as extractant. The details are described elsewhere [15]. The mixer-settler studies were performed by co-extraction of Eu(III) and Am(III) from citric acid medium in a counter-current mode using a 20-stage mixer-settler (illustrated in figure 1). The operation of the mixer-settler was similar to the 16-stage mixer-settler used for minor actinide partitioning. The organic phase was composed of 0.1 M HDEHDGAn-DD and aqueous phase was 0.1 M CA+0.1 M HNO3 spiked with (152+154)Eu(III or 241Am(III) tracer, adjusted to pH 3. The solutions were fed to the mixer-settler at a constant flow rate of 3 mL/min. The system was operated for six hours. Back extraction of Am(III) alone from the loaded organic phase was performed by using a solution of 0.025 M CA+0.01 M DTPA adjusted to pH 1.5 in a separate run.

3. Results and discussion

3.1. Characterization of HAW

Characterization of HAW is a challenging task of determining various elements and radionuclides present in a complex mixture of multi-elemental matrix. Majority of the elements and radionuclides present in high-active waste arising from reprocessing of nuclear fuel (U0.3Pu0.7)C irradiated to the burn-up of 155 GWd/Te were determined by a suitable procedure. The results are summarized in table 1. Our findings indicate that the alpha activity is essentially contributed by 241Am, 242Cm and 239Pu and the 𝛽-𝛾 activity by 137Cs and 106Ru. The concentration of corrosion products such as iron, nickel and additives such as sodium are significant.

3.2. Mixer-settler studies for minor actinide partitioning

We developed a method for partitioning of trivalent actinides from the fast reactor dissolver solution by using a solution of 0.2 M CMPO-1.2 M TBP/n-DD. The details of the method developed in our laboratory are described elsewhere [17]. Based on that method, the mixer-settler run was performed with real HAW (155 GWd/Te) and the results are described below. The separation and recovery of trivalent actinides during this run was monitored by the 𝜋-emitting radionuclides present HAW. The gamma spectra of the feed, aqueous raffinate, loaded organic, lean organic and aqueous product are shown in figures 2 to 4. The lower energy spectrum of feed (from 50 keV to 200 keV) was enlarged and displayed in figure 2. All the peaks present in the gamma spectra are characterized and assigned to the characteristic radioisotope. Essentially, the feed contains the gamma emitting isotopes of cesium (134Cs, 137Cs), cerium (144Ce), europium (154Eu, 155Eu), ruthenium (106Ru), antimony (125Sb), and americium (241Am). It is also observed that corrosion products such as 60Co and 54Mn are present. The radioactivities of the isotopes present in HAW are shown in table 1.

The gamma spectrum of the raffinate obtained after the extraction of trivalents is compared with the feed in figure 2. The gamma emissions characteristic to the trivalents namely, 241Am, 155Eu, 154Eu, and 144Ce, are insignificant in the raffinate as compared to those in the feed (figure 2a) (note: both are counted for different time intervals). Table 1 shows the quantity of different radionuclides extracted in CMPO phase. It is observed that extraction of trivalents (Am(III) and Eu(III)) from the feed is more than 99%. Stage sample analysis obtained from the mixer settler run also confirmed that the extraction was complete in 6 stages.
Fig 2. Gamma spectra of the feed (a) and aqueous raffinate (b). *The data in (a) and (b) are represented in arbitrary units. This is due to the fact that the samples are counted for different time intervals in order to get substantial counts for the analysis of the radionuclides that are present in negligible amounts (especially after extraction). Moreover, the aliquots volumes taken for analysis were also different.

Table 1. Isotopic and elemental composition of HAW arising from reprocessing of \((U_{0.3}Pu_{0.7})C\) fuel irradiated to a burn-up of 155 GWd/Te. [16].

<table>
<thead>
<tr>
<th>Elements</th>
<th>Quantity (µg/mL)</th>
<th>Elements</th>
<th>Quantity (µg/mL)</th>
<th>Elements</th>
<th>Quantity (µg/mL)</th>
<th>Radioisotopes</th>
<th>Activity (µCi/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitric acid</td>
<td>4.6 M</td>
<td>Nitric acid</td>
<td>4.6 M</td>
<td>Palladium</td>
<td>8.7</td>
<td>⁶⁰Co</td>
<td>16.3</td>
</tr>
<tr>
<td>Plutonium</td>
<td>3.6</td>
<td>Europium</td>
<td>3</td>
<td>Silver</td>
<td>&lt;5</td>
<td>¹⁰⁶Ru</td>
<td>698</td>
</tr>
<tr>
<td>Uranium</td>
<td>222</td>
<td>Molybdenum</td>
<td>202</td>
<td>Strontium</td>
<td>32</td>
<td>¹²⁵Sb</td>
<td>43</td>
</tr>
<tr>
<td>Neptunium</td>
<td>&lt; 2</td>
<td>Chromium</td>
<td>884</td>
<td>Ruthenium</td>
<td>82</td>
<td>¹³⁴Cs</td>
<td>121</td>
</tr>
<tr>
<td>(Am+Cm)</td>
<td>77</td>
<td>Dysprosium</td>
<td>&lt; 5</td>
<td>Zirconium</td>
<td>3</td>
<td>¹³⁷Cs</td>
<td>4190</td>
</tr>
<tr>
<td>Lanthanum</td>
<td>56</td>
<td>Iron</td>
<td>3602</td>
<td>Calcium</td>
<td>316</td>
<td>¹⁴⁴Ce</td>
<td>325</td>
</tr>
<tr>
<td>Neodymium</td>
<td>162</td>
<td>Gadolinium</td>
<td>6</td>
<td>Magnesium</td>
<td>20</td>
<td>¹⁵⁴Eu</td>
<td>37.5</td>
</tr>
<tr>
<td>Cerium</td>
<td>87</td>
<td>Manganese</td>
<td>368</td>
<td>Sodium</td>
<td>16800</td>
<td>⁶⁰Co</td>
<td>16.3</td>
</tr>
<tr>
<td>Praseodymium</td>
<td>38</td>
<td>Nickel</td>
<td>787</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Samarium</td>
<td>38</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The trivalents present in the present extracted organic phase was recovered by using a solution of 0.1 M citric acid in 0.1 M nitric acid, in a counter-current extraction process. The gamma spectra of loaded organic and lean organic are compared in figure 3a and 3b, respectively. It is observed that the gamma peaks characteristic to \(^{241}\)Am, \(^{155}\)Eu, \(^{154}\)Eu, and \(^{145}\)Ce in the lean organic are negligible. The gamma spectrum of the aqueous product is displayed in figure 4. It shows all the peaks corresponding to \(^{241}\)Am, \(^{155}\)Eu, \(^{154}\)Eu, and \(^{144}\)Ce isotopes. Quantitative analysis of the data from figures 3 and 4 showed that recovery of lanthanides is \(\sim 99\%\) (table 1). The stage sample analysis of the mixer settler stripping run confirmed that the back extraction was complete in 10 stages. The demonstration run thus established that the quantitative recovery of trivalents using a CMPO-TBP solution. The estimation of \(^{241}\)Am in the sample was also determined by alpha counting of raffinate, loaded and
lean organic, and product stream. The analysis indicated that loading of $^{241}\text{Am}$ in 0.2 M CMPO-1.2 M TBP/n-DD was quantitative and the $^{241}\text{Am}$ in the raffinate is negligible (<100 nCi/mL). Analysis of $^{241}\text{Am}(\text{III})$ in the product showed that the recovery was > 95%. Lower value in this case could be due to the interference of citric acid salt deposit in the product during analysis.

![Gamma spectra of the loaded organic (a) and lean organic (b).](image)

*Fig 3. Gamma spectra of the loaded organic (a) and lean organic (b).* 
*The data in (a) and (b) are represented in arbitrary units. This is due to the fact that the samples are counted for different time intervals in order to get substantial counts for the analysis of the radionuclides that are present in negligible amounts (especially after extraction). Moreover, the aliquots volumes taken for analysis were also different.

![Gamma spectrum of aqueous product](image)

*Fig 4. Gamma spectrum of aqueous product*

Table 2. The percentage of extraction and stripping of some radioisotopes during minor actinide partitioning

<table>
<thead>
<tr>
<th>Radioisotopes</th>
<th>Percentage of extraction from HAW</th>
<th>Percentage of stripping from loaded CMPO phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Europium-154</td>
<td>&gt; 99.9</td>
<td>&gt; 99.9</td>
</tr>
<tr>
<td>Cerium-144</td>
<td>&gt; 99.9</td>
<td>&gt; 99.9</td>
</tr>
<tr>
<td>Americium-241</td>
<td>&gt; 99.9</td>
<td>&gt; 99.9</td>
</tr>
<tr>
<td>Cesium-137</td>
<td>negligible</td>
<td>-</td>
</tr>
<tr>
<td>Antimony-125</td>
<td>&lt; 1</td>
<td>-</td>
</tr>
<tr>
<td>Ruthenium-106</td>
<td>30</td>
<td>10</td>
</tr>
</tbody>
</table>

3.3. Decontamination of ruthenium

Among the radioactive isotopes, significant amount of ruthenium-106 was extracted by the CMPO-TBP solution (table 2). The analysis of the feed and lean organic organic after the run indicates that nearly ~20% of $^{106}\text{Ru}$ is retained in the lean organic phase. Decontamination of radioactive ruthenium from lean organic phase was studied using several aqueous based reagents, ion exchange resins and inorganic sorbents to identify the best suitable formulation [18]. Among the various reagents examined, sodium hydroxide, sodium carbonate are
promising candidates for the removal of radioactive ruthenium from the organic phase. The initial radioactivity of \(^{106}\text{Ru}(\text{III})\) in the lean organic phase was about 150 \(\mu\text{Ci/mL}\). Nearly, 95% could be removed in 10 contacts using these reagents. Further treatment with adsorbents such as alumina and Dowex 1X4 (OH- form) quantitatively decontaminated the radioactive ruthenium from the lean organic phase.

3.4. Lanthanide-actinide separation studies

The aqueous product obtained after minor actinide partitioning was a solution of trivalent actinides and lanthanides in 0.1 M CA-0.1 HNO\(_3\) medium. Therefore, we developed a method for the mutual separation of trivalent actinides and lanthanides from 0.1 M citric acid medium by using a CHON-based diglycolamic acid, bis(-2-ethylhexyl)diglycolamic acid (HDEHDGA) in n-DD. The conditions required for complete extraction and recovery was optimized by the batch studies reported elsewhere [15]. The results showed that quantitative extraction of \(\text{Am(III)}\) and \(\text{Eu(III)}\) from 0.1 M citric acid medium was achieved in 2-3 contacts with the use of 0.1 M HDEHDGA/n-DD, at pH 3. The mutual separation of \(\text{Am(III)}\) and \(\text{Eu(III)}\) was achieved by using the optimized reagents composed of 0.01 M DTPA-0.025 M CA. Based on the optimized conditions, the mixer-settler run was performed. As expected, the extraction of \(\text{Am(III)}\) and \(\text{Eu(III)}\) from 0.1 M CA at pH 3 in 0.1 M HDEHDGA/n-DD was quantitative in two contacts. The mixer-settler results for the separation of \(\text{Am(III)}\) from \(\text{Eu(III)}\) present in the loaded organic phase was performed by using 0.01 M DTPA-0.025 M CA at pH 1.5. The results are shown in figure 5. It is observed that more than 96% of \(\text{Am(III)}\) could be recovered from the loaded organic phase after 20-stages of stripping in a mixer-settler. However, the stripping of \(\text{Eu(III)}\) was only 2%. The results, therefore, confirmed the feasibility of using HDEHDGA/n-DD for the mutual separation of lanthanides and actinides from citric acid medium.

![Fig 5. Back extraction profile of \(\text{Am(III)}\) and \(\text{Eu(III)}\) in a 20 stage mixer-settler. Loaded organic phase: 0.1 M HDEHDGA/n-DD containing Eu(III) and Am(III). Stripping aqueous phase: 0.01 M DTPA CA+0.025 M CA, adjusted to pH 1.5. Flow rate: Loaded organic 3 mL/min, stripping aqueous phase 3 mL/min.](image-url)
4. Conclusions

The high active waste arising from reprocessing of the nuclear fuel (U0.3Pu0.7)C irradiated to the burn-up of 155 GWd/Te in a fast breeder test reactor (FBTR) was characterized. Partitioning of trivalent actinides from HAW was demonstrated using a solution of 0.2 M CMPO-1.2 M TBP in n-DD. The results confirmed the quantitative separation and recovery (>99%) of trivalents (Am(III)+ Ln (III)) from HAW. The trivalents were extracted in six stages and stripped in 10 stages using the citric acid-nitric acid formulation. The radioactive ruthenium carried to the lean organic phase was decontaminated with sodium hydroxide or sodium carbonate solution. A method was developed for the mutual separation of Am(III) and Eu(III) from 0.1 M citric acid medium by using a solution of 0.1 M HDEHDGA/n-DD. Quantitative extraction of Am(III) and Eu(III) from 0.1 M citric acid medium was achieved in 2 contacts with the use of 0.1 M HDEHDGA/n-DD, at pH 3. The recovery of Am(III) alone from the loaded organic phase was achieved using 0.01 M DTPA-0.025 M CA at pH 1.5 in 20-stages of a mixer-settler.

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References


