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BHABHA ATOMIC RESEARCH CENTRE

PARTITIONING OF ACTINIDES FROM HIGH ACTIVE WASTE SOLUTION OF PUREX ORIGIN:  
COUNTER-CURRENT EXTRACTION STUDIES USING TBP AND CMPO

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# PARTITIONING OF ACTINIDES FROM HIGH ACTIVE WASTE SOLUTION OF PUREX ORIGIN: COUNTER-CURRENT EXTRACTION STUDIES USING TBP AND CMPO

## ABSTRACT

*A solvent extraction scheme has been formulated for the partitioning of actinides from PUREX high level waste (HLW). The scheme is based on the results of earlier studies carried out with simulated waste solutions. In the present studies, the scheme was tested with high active waste (HAW) solution generated during the reprocessing of spent fuel from research reactors using laboratory scale mixer-settlers. The proposed process involved two-step extraction using tri-n-butyl phosphate (TBP) and octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO). In the first step, uranium, neptunium and plutonium were removed from the waste using TBP as extractant. The minor actinides left in the raffinate were extracted using a mixture of CMPO and TBP in the second step. The results showed complete extraction of actinides from the waste solution. Plutonium and neptunium extracted in TBP, were stripped together using a mixture of hydrogen peroxide and ascorbic acid in 2 M nitric acid medium, leaving uranium in the organic phase. Uranium can later be stripped using dilute nitric acid. Actinides extracted in CMPO-TBP phase were stripped using a mixture of formic acid, hydrazine hydrate and citric acid. The stripping was quantitative in both the stripping runs.*

*An additional extraction step for the preferential recovery of uranium, neptunium and plutonium from the waste solution using TBP is a modification over the conventional TRUEX process. Selective stripping of neptunium and plutonium from the loaded TBP, leaving bulk of uranium in the organic phase, has an advantage of separating neptunium and plutonium from large quantities of uranium. The extraction of uranium using TBP eliminates the possibility of third phase and undesired loading of CMPO-TBP in the following step. Use of citrate-containing strippant allows the recovery of actinides from loaded CMPO-TBP mixture without causing any reflux of the actinides during stripping. The process has been developed with due consideration to minimising the generation of secondary wastes. The proposed strippants are effective even in presence of HDBP, a major degradation product of TBP. Chemicals used in the process are commonly available and can be destroyed with conventional methods without generation of hazardous residues.*

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## 1. INTRODUCTION

Reprocessing of spent fuel generates radiotoxic high level waste (HLW) which contains more than 99% of the total non-volatile fission product activity generated in the nuclear fuel cycle<sup>(1)</sup>. Fission product activity includes  $^{90}\text{Sr}$ - $^{90}\text{Y}$ ,  $^{95}\text{Zr}$ - $^{95}\text{Nb}$ ,  $^{99}\text{Tc}$ ,  $^{106}\text{Ru}$ - $^{106}\text{Rh}$ ,  $^{134,137}\text{Cs}$ ,  $^{144}\text{Ce}$ - $^{144}\text{Pr}$ ,  $^{147}\text{Pm}$ ,  $^{152,154,155}\text{Eu}$ , etc. In addition to the fission products, the waste also contains actinide elements like uranium, neptunium, plutonium, americium and curium. These actinides are of great environmental concern and render the final immobilised waste form hazardous for millions of years. If the actinides from the HLW are partitioned prior to its immobilisation, hazard of the solidified waste will be reduced to a level below that of natural uranium ore within few hundred years<sup>(2,3)</sup>. Incidentally, the isotopes of actinides have reasonably high cross sections for transmutation with fast neutrons<sup>(4-6)</sup>. This makes the destruction of these radionuclides possible through transmutation in a nuclear reactor.

Earlier solvent extraction studies<sup>(7-13)</sup>, carried out with simulated HLW solutions, had shown the feasibility of partitioning the actinides from HLW. Based on these studies, a scheme was formulated as shown in Fig.1. The process involves two extraction steps and uses tri-n-butyl phosphate (TBP) and octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide [ $\text{O}(\phi)\text{D}(\text{iB})\text{CMPO}$  or simply  $\text{CMPO}$ ] as the extractants. In the first step, major fraction of uranium is removed from the waste solution using TBP as extractant. During this 'uranium depletion step', neptunium and plutonium are also removed from the waste after adjusting their oxidation states. The raffinate from this step is contacted with CMPO for the removal of

americium and curium as well as the traces of uranium, neptunium and plutonium. The alpha activity in the raffinate from this extraction step will be only few nCi/l and the raffinate can be considered as a non-alpha waste.

Neptunium and plutonium from the loaded TBP phase are selectively recovered using a mixture of hydrogen peroxide and ascorbic acid in nitric acid medium as strippant. Uranium left in the TBP phase can be recovered using dilute nitric acid. A mixture of formic acid, hydrazine hydrate and citric acid is used to strip extracted actinides from CMPO phase. Lean organic phases generated in the process can be recycled after a wash with alkali carbonates like sodium carbonate.

An additional step for the preferential recovery of uranium, neptunium and plutonium using TBP as the extractant, the selective recovery of neptunium and plutonium from loaded TBP and the recovery of americium and other actinides from CMPO-TBP mixture using common complexing agent are the salient features of the proposed process. The process was tested using laboratory scale mixer-settlers, with high active waste (HAW) solutions generated during the reprocessing of spent fuel from research reactors. The present report describes the results of these studies in detail.

## 2. EXPERIMENTAL

### 2.1. Materials

#### *Waste Solution:*

The studies were carried out with HAW solution originated from the reprocessing of spent fuel from research reactors. Since HLW is expected to contain higher concentrations of the actinides, the HAW solution was spiked with required quantities of uranium, neptunium and plutonium. The total volume of the waste was ~4 litres. The acidity of the waste was ~2 M.

#### *Extractants:*

TBP was procured from M/s. Bharat Vijay Chemicals, India and used without further purification. CMPO used in the experiments was indigenously synthesised and purified<sup>(14)</sup> in the Bio-Organic Division of this Centre. The purification was carried out using basic alumina column for reducing the proportion of acidic impurities below 0.02 wt%. The structure and the purity of the product was ensured by infrared (IR) and nuclear magnetic resonance (NMR)

spectroscopy. The purity of CMPO was further confirmed by determining the distribution ratios of americium ( $D_{Am}$ ) from pure nitric acid solutions. A solution containing 0.2 M CMPO and 1.2 M TBP in n-dodecane was used to determine  $D_{Am}$  from 3.0 M and 0.01 M nitric acid solutions. The distribution ratio was ~22 from 3.0 M nitric acid at an organic to aqueous phase ratio of 1:1 and the same was <0.02 from 0.01 M nitric acid solution. These values were comparable with those reported in literature<sup>(15)</sup>.

Dodecane (~93% C<sub>12</sub>, Specific gravity 0.751, refractive index 1.42, aromatics <0.1%, distillation range 160°-210°C), procured from M/s.Transware Chemia Handelsgesellschaft, Hamburg, Germany, was used as a diluent without further purification.

#### *Neptunium tracer:*

<sup>237+238</sup>Np was prepared by irradiating <sup>237</sup>Np at APSARA reactor. The irradiated target containing nearly 800 µg of neptunium was dissolved in 6 M HCl. The feed for the extraction run using TBP was spiked with this neptunium tracer before the run. During the stripping of neptunium and plutonium from the loaded TBP, the organic feed was spiked with <sup>237+238</sup>Np after extracting it into 30% TBP. (Neptunium was oxidised to Np(VI) using potassium dichromate prior to this extraction.)

#### *Reagents:*

All the reagents used in the studies were of analytical reagent grade. Chemicals which are available only in solution form were analysed using standard volumetric techniques. Hydrogen peroxide solution was estimated by titration against 0.1 M ceric sulphate solution in 2.0 M nitric acid medium, using ferroin indicator. Acids and bases like nitric acid, formic acid, hydrazine hydrate, etc. were estimated by potentiometric titrations using standard alkali and acid.

#### *Feed Solutions:*

The waste solution, spiked with uranium, neptunium and plutonium, formed a feed for the counter-current extraction studies using TBP as the extractant. Potassium dichromate was added to the feed for adjusting the oxidation states of neptunium and plutonium. The final concentration of potassium dichromate in the feed was 0.01 M. Uranium-lean raffinate generated in this run was used as feed for the counter-current extraction studies using CMPO-TBP mixture.

The loaded TBP phase generated in the counter-current extraction run was used as organic feed for counter-current stripping studies after spiking it again with <sup>237+238</sup>Np. Similarly,



loaded CMPO-TBP solutions generated during the extraction run was used as feed for counter-current stripping studies. (The lean organic phase generated in the latter studies was washed using sodium carbonate solution.)

## 2.2. Equipment

Counter-current studies were carried out using six-stage mixer-settlers, fabricated from polyacrylic sheets. The capacity of the mixer was ~30 ml and that of the settler was ~130 ml for each stage. The mixer-settler was installed in a fume hood cell with 5" thick lead shield, with lead-glass window mounted on it for viewing the operations. The mixing of the phases was carried out mechanically using 12 V electrical motors. In general, mixing time was about 2.5 minutes and settling time was about 10 minutes, in all the experiments.

The waste was transferred from the hot cell to the feed containers using suction. Peristaltic pumps were used for feeding the liquids. The equilibrium conditions were ascertained through periodic checking of the activity in the exit organic and aqueous streams. Samples were collected from each stage at the end of the runs.

## 2.3. Analysis

Analysis of the various elements was carried out using radiometry, spectrophotometry and inductively coupled plasma - atomic emission spectroscopy (ICP-AES). The acidity of the aqueous as well as organic samples was determined by potentiometric titration using standard sodium hydroxide solution.

The total alpha activity was assayed radiometrically using  $2\pi$  argon gas flow proportional counter standardized against  $^{239}\text{Pu}$ . Plutonium in the aqueous samples was analysed radiometrically either by direct plancheting or after selective extraction of plutonium into thenoyl trifluoroacetone (TTA). Americium and individual fission products were determined by gamma spectrometry using high purity germanium (HPGe) detector (60 c.c.) coupled to 4K multichannel analyser.

Since HAW was spiked with  $^{238}\text{Np}$ , neptunium could be analysed using gamma ray spectrometry. Nevertheless for its analysis from the aqueous samples collected during the extraction step, it was essential to separate neptunium from radioactive fission products.

Neptunium was first extracted in TBP and the extracted neptunium was analysed by gamma spectrometry using a HPGe detector.

Uranium was analysed spectrophotometrically using 2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol (Bromo-PADAP) method<sup>(16)</sup>. Wherever necessary, it was first extracted into tri-n-octyl phosphine oxide (TOPO) to avoid the interference from other metal ions in the waste solutions. Chromium was analysed by ICP-AES. Organic samples were treated with nitric acid and perchloric acid mixture before the analysis for destroying the organic material.

### 3. RESULTS AND DISCUSSION

#### 3.1. Extraction Studies

HLW generated during the reprocessing of spent fuel contains small quantities of various actinides like uranium, neptunium, plutonium, americium and curium. Neutral bifunctional organophosphorus extractants like CMPO are capable of extracting trivalent, tetravalent and hexavalent actinides from nitric acid solution and can be used for the partitioning of the actinides from HLW<sup>(7-13, 17-19)</sup>. Among all the metal ions present in HLW, concentration of uranium is very high compared to that of the others. The extraction of large quantities of uranium from the waste solutions by CMPO leads to the formation of a third phase<sup>(20,21)</sup> due to the limited solubility of uranium-CMPO complex in the aliphatic diluents like n-dodecane. Although the formation of the third phase can be suppressed with the use of suitable phase modifiers like TBP, the tendency cannot be completely eliminated at high concentration of uranium in the waste solution. Moreover, uranium in HLW causes undesired loading of CMPO and in turn, adversely affects the extraction of other actinides, especially the trivalent ones like americium<sup>(7)</sup> and curium. This makes the removal of uranium from HLW essential, prior to the use of CMPO for extraction.

#### *Extraction using TBP:*

In the present studies, 30% TBP in n-dodecane was used as extractant for depleting uranium from the waste solution. Neptunium and plutonium also can be removed from the waste solution during this step, by adjusting their oxidation states to either (IV) or (VI), both the states being extractable in TBP<sup>(11,22)</sup>. Various ions, which can be considered for adjusting the oxidation states, include ceric, dioxovanadium, dichromate, permanganate, bromate, persulphate and nitrite, etc. In spite of the capability of these ions to oxidise/reduce neptunium and plutonium,

some of these ions pose limitation on their own use in the partitioning of actinides. Among the above reagents, cerium could not be used as it is extractable in CMPO, which is to be used for the removal of trivalent actinides in the following step. High extraction of this extraneous cerium will cause additional loading of CMPO phase, adversely affecting the extraction of actinides. Bromate was not used because of its highly toxic and corrosive nature. Permanganate could not be used as it reacts with CMPO<sup>(23)</sup>. The use of persulphate ions was avoided because it would generate corrosive product like sulphate ions. Nitrite can catalyse the oxidation of neptunium provided it is present in very low concentrations<sup>(24)</sup>. In presence of high concentration of nitrite ions, neptunium remains in inextractable pentavalent state. Since it is difficult to control the concentration of nitrite ions in the waste stream from PUREX process, nitrite ions could not be used for valence adjustment. Dioxovanadium ions, which can be used for efficient extraction of neptunium and plutonium into TBP, its presence in the organic phase led to incomplete stripping of neptunium<sup>(11)</sup>. This left only dichromate ions as the candidate for the adjustment of the oxidation states. Potassium dichromate oxidises both the ions to their hexavalent states.

Based on the above observations, the extraction of actinides in TBP was carried out in presence of 0.01 M potassium dichromate. Scheme used for this extraction is presented in Fig.2. The scheme involves 4 stages of extraction and 2 stages of scrubbing. The feed and the extractant were passed at phase ratio of 1:1, with flow-rates of 4.5 ml/min. The loaded TBP was subjected to a scrub with 2.0 M nitric acid for the removal of extracted fission products. The scrub was carried out at an organic to aqueous phase ratio of 3:1. The flow rate of the scrubbing solution was 1.5 ml/min. The HAW feed was diluted to an extent of about 33% due to the mixing of scrub.

Results of the stage-wise analysis, presented in Fig.2, show that the concentration of uranium is reduced to ~4 mg/l, which corresponds to a removal of ~99.9%. Plutonium was removed to an extent of ~93%. No neptunium was detected in the raffinate. (Three stages were adequate for the complete removal of neptunium from the waste solution.) Among the fission products, cerium was extracted to an extent of ~10% (Fig.3). This relatively high extraction of cerium was probably due to its partial oxidation to the extractable tetravalent state. Ruthenium was extracted to an extent of ~1%. Acidity of aqueous phase was reduced from 2.01 to 1.70 M. ICP-AES analysis showed that nearly 32% of chromium was extracted in TBP. (Dichromate is known to be extractable in TBP as  $H_2Cr_2O_7 \cdot 2TBP$ <sup>(25)</sup>.)

### *Extraction using CMPO:*

The raffinate of the above extraction step contained mainly trivalent actinides and traces of uranium and plutonium. CMPO can extract all these species without any feed adjustment of the waste. Nitrates of trivalent actinides ions like Pu(III) and Am(III) are extracted in CMPO as trisolvated species  $[M(NO_3)_3 \cdot 3CMPO]^{(6)}$ . Nitrates of uranium, plutonium and neptunium in tetravalent and hexavalent states are extracted as disolvated species like  $M(NO_3)_4 \cdot 2CMPO$  and  $MO_2(NO_3)_2 \cdot 2CMPO^{(26)}$ . The extractability of trivalent, tetravalent and hexavalent actinides by CMPO has been used for their partitioning from HLW in TRUEX process<sup>(18,19,27)</sup>.

Since CMPO has a tendency to form a third phase with high concentration of extracted metal ion, it is always used along with a suitable phase modifier of polar nature like tri-n-butyl phosphate (TBP)<sup>(19,21,28)</sup>. Although the uranium content of the waste solution can be lowered through the introduction of the uranium depletion step<sup>(7,9,11)</sup>, the uranium-lean HLW contains substantial quantities of extractable trivalent and tetravalent fission products. Extraction of these metal ions into CMPO can lead to a third phase formation. This makes the use of phase modifier like TBP along with CMPO mandatory during the extraction of residual actinides even from uranium-lean waste solution.

The present studies use a solution of 0.2 M CMPO and 1.2 M TBP in n-dodecane as extractant and is similar to that used in TRUEX process. The extraction was carried out at an phase ratio of 1:1, with flow rates of 4.5 ml/min (Fig.4). The loaded extractant was scrubbed with a dilute nitric acid (0.1 M) at a phase ratio of 3:1 to reduce its acid content. The analysis showed no alpha activity in the raffinate. While plutonium was removed in 2 stages, americium required 3 stages for its complete removal (Fig.4). All the lanthanides accompanied the actinides during extraction as shown in Fig.5. Nearly 16% of ruthenium was extracted during this step. Acidity of the waste was reduced to ~1.2 M. The scrub was effective in lowering the acidity of the loaded CMPO-TBP from 0.55 M (stage 3) to 0.28 M.

### 3.2. Stripping Studies

#### *Stripping from loaded TBP:*

Neptunium and plutonium are extracted from HLW as hexavalent ions in the presence of dichromate ions. The extracted neptunium and plutonium can be stripped from the TBP phase by reducing them to their pentavalent and trivalent states, respectively. Uranium can then be

stripped with dilute nitric acid solution. Neptunium and plutonium are present in waste solution in low concentrations. Due to the high extent of extraction, the concentration of these actinides in the TBP phase should also be in the same range. It is advantageous to strip neptunium and plutonium together leaving uranium in the organic phase. This would separate neptunium and plutonium from large quantity of uranium.

PUREX process uses either ferrous or uranous ions for the reduction of Pu(IV) to inextractable Pu(III) in the partitioning step. Both of these reagents could not be employed in the present process, as the use of former leads to a reduction of neptunium to extractable Np(IV) and that of the latter involves an introduction of undesirably large quantity of uranium. Other reducing agents that find application in nuclear industry include hydrazine, hydroxylamine, ascorbic acid, etc. Hydrogen peroxide also can be used as a strippant as it reduces Np(VI)<sup>(29)</sup> as well as Pu(VI)<sup>(30,31)</sup>. Our earlier studies have shown that neptunium and plutonium can be preferentially stripped<sup>(22,11)</sup> by reducing them to inextractable Np(V) and Pu(III), respectively, using a solution containing 0.25 M hydrogen peroxide and 0.05 M ascorbic acid in 2.0 M nitric acid medium. (Uranium left in the loaded TBP can be easily stripped using dilute nitric acid.) In the present studies, loaded TBP generated in the extraction step was subjected to stripping using the similar reducing mixture.

The results of the extraction experiment showed that a considerable quantity of dichromate was extracted into 30% TBP, which may interfere with the stripping of neptunium and plutonium. Hence, it is necessary for the strippant to destroy the extracted oxidising agent during the reduction of plutonium and neptunium. Special provisions were made to ensure complete destruction of the extracted dichromate during the stripping. The strippant was fed through two inlets as shown in the schematic in Fig.6. Each portion of the strippant was passed at a flow rate half that of the organic phase, maintaining the total input of the strippant same as that of loaded TBP. With this arrangement, major portion of the extracted dichromate should be destroyed immediately after the entry of the organic feed into the mixer-settler. This four-stage stripping was supplemented by a two-stage solvent scrub with 30% TBP to reduce the uranium losses to the aqueous phase. The organic to aqueous phase ratio for the scrub was 1:3. The flow-rates for the organic feed, strippant and scrub were 4.8, 2.4 (each stream) and 1.6 ml/min, respectively. Results presented in Fig.6 show that >99% of plutonium and >95% of neptunium were stripped from the TBP phase. Uranium release to the aqueous product was only 0.05%.

While cerium was completely stripped, nearly 17% of the extracted ruthenium remained in the organic phase (Fig.7). Chromium was completely released during this stripping.

#### *Stripping from loaded CMPO-TBP:*

Loaded CMPO-TBP contains 0.24 M acid even after scrubbing it with dilute nitric acid (0.1 M). Conventional TRUEX process uses dilute nitric acid as a strippant for the recovery of trivalent actinides from loaded CMPO-TBP. Our earlier studies carried out with simulated waste solutions under these conditions showed high degree of reflux of americium<sup>(8)</sup> due to the extracted acid. Although the reflux could be reduced using a two-step stripping<sup>(9)</sup>, it led to a two-fold increase in the volume of the secondary waste. Moreover, a separate step using oxalic acid for the removal of plutonium also added to the volume of secondary waste. The volume of the secondary waste will be reduced considerably, if americium and plutonium are recovered in a single step without allowing reflux of americium to take place. This necessitates the development of a suitable reagent which can strip americium as well as plutonium simultaneously from the CMPO-TBP phase even in presence of high quantity of extracted acid.

The use of water soluble diphosphonic acids for stripping the actinides from TRUEX solvent with high acid content has been reported in the literature<sup>(32)</sup>. Although these complexing agents can be finally destroyed, they generate phosphoric acid as one of the end products. Another strippant being studied for the same purpose is a less common chemical called tetrahydrofuran tetracarboxylic acid<sup>(33)</sup>. In the present studies, the selection of reagents was restricted to common chemicals, which can be destroyed with conventional methods and do not leave any hazardous inorganic residue on destruction.

This could be achieved with the use of a solution of a complexing agent in buffer medium. The buffering action of the aqueous phase reduces the effective acidity of the organic phase and the complexing agent effectively strips the metal ions from the CMPO-TBP phase. The complexing agents used in these studies include citric acid, diethylenetriamine pentaacetic acid (DTPA), ethylenediamine tetraacetic acid (EDTA) and oxalic acid. It was seen from the batch studies that either citric acid or DTPA dissolved in a mixture of formic acid and hydrazine hydrate can be efficiently used for the simultaneous stripping of americium and plutonium from the CMPO-TBP phase<sup>(12,13)</sup>. This strippant can be tailor-made for quantitative recovery of actinides from the loaded CMPO-TBP phase having different acidities by changing its formic

acid and hydrazine hydrate contents. It is effective even in the presence of HDBP<sup>(12 22)</sup>, which is a major degradation product of TBP.

Based on the above studies, a mixture of 0.4 M formic acid, 0.4 M hydrazine hydrate and 0.1 M citric acid was used for the stripping of actinides from loaded CMPO-TBP phase in the present work. The stripping was carried out at a phase ratio of 1:1 and involved 6 stages of stripping (Fig.8). The flow for both the phases was maintained at 4.5 ml/min. The strippant was very effective in recovering americium and plutonium as well as lanthanides from the organic phase. Data presented in Fig.8 show that three stages were sufficient for complete stripping of alpha activity. Similarly, lanthanides were also completely stripped from the organic phase in three stages (Fig.9). Results showed no reflux of any of these species. Ruthenium showed incomplete stripping with nearly half of it remaining in the organic phase. Uranium, which was present in trace quantity, continued to remain in the organic phase. Quantitative stripping of americium, plutonium and lanthanides was due to effective complexing of these species by citric acid under low acid conditions. Acidity of the organic phase was lowered from 0.28 M to less than 0.10 M due to the buffering action of formic acid and hydrazine hydrate. The pH of the aqueous product was nearly 4. No crud formation was observed in any of the stages during the stripping.

The lean organic phase contained traces of uranium and ruthenium and required washing with alkali carbonate, if it is to be recycled. The washing was carried out using 0.25 M sodium carbonate solution with flow rates of 4.8 ml/min for each phase (Fig.10). Uranium was completely stripped in the second stage of this six-stage washing run. About 3% of the extracted ruthenium was left in the CMPO-TBP phase even after the alkali wash. Although the stripping of ruthenium was incomplete, the decreasing trend shown by the profile in Fig.10 clearly suggests that complete washing of ruthenium would be possible with the increase in the number of stages of the mixer-settler.

Overall distribution of actinides and some of the fission products during the runs is presented in Table 1. The material balance of various species was better than 95%. The lanthanides accompany trivalent actinides during the extraction and stripping. The actinides in the citrate containing aqueous product from the stripping of loaded CMPO-TBP can be separated from lanthanides using methods like extraction chromatography. Acidic organophosphorus

extractants have been used for the separation of actinides and lanthanides<sup>(34)</sup>. Batch and column studies carried out with the secondary streams generated during the partitioning experiments with simulated waste solutions showed that the actinides and lanthanides can be extracted from the citrate containing aqueous product (pH~4), on 2-ethylhexyl-2-ethylhexyl phosphonic acid (KSM-17) sorbed on an inert support (chromosorb-102)<sup>(35)</sup>. Extracted americium and cerium could be separated from the rest of the lanthanides like promethium and europium by gradient elution using nitric acid. These results are concurrent with those carried out from pure nitric acid solution<sup>(36)</sup>. Further separation of americium from cerium can be accomplished by extraction chromatography using di-(2-ethylhexyl) phosphoric acid (HDEHP) as an extractant<sup>(35)</sup>. Alternately, it can be achieved by chemical or electro-oxidation<sup>(37)</sup> of cerium followed by solvent extraction using TBP or KSM-17.

#### 4. CONCLUSION

The partitioning of actinides from HAW solution is possible using a two-step solvent extraction process. The process had reduced the alpha activity of the waste solution below detectable levels. Major fraction of uranium, neptunium and plutonium was removed from the waste solution using TBP as extractant with dichromate used as oxidising agent. Americium and traces of other actinides were removed quantitatively from the raffinate of the above step using CMPO-TBP as extractant. Quantitatively stripping of neptunium and plutonium, extracted in TBP phase, was possible using a reducing mixture containing hydrogen peroxide and ascorbic acid. The stripping of actinides extracted in CMPO-TBP phase was achieved using citrate containing buffer solution.

Although the scheme uses CMPO as one of the extractant as in the TRUEX process, the present process has been modified in many respects. The extraction step using TBP avoids excessive loading of CMPO, to be used later for the extraction of trivalent actinides. Selective stripping of neptunium and plutonium from loaded TBP, leaving uranium in the organic phase offers an advantage of separation of neptunium and plutonium from large quantities of uranium. Aqueous product containing neptunium, plutonium (and small quantity of uranium) can be concentrated and the separation of the individual actinides can be achieved using conventional techniques like ion-exchange<sup>(38)</sup>. Uranium left in the TBP phase can be stripped with dilute nitric acid.



The citrate containing strippant used for the recovery of actinides, extracted in CMPO-TBP phase, is very efficient in stripping the actinides. Unlike that in the conventional process which uses dilute nitric acid as a strippant for trivalent actinides, no reflux of americium was observed during the stripping. Since americium and plutonium are simultaneously stripped with this strippant, no additional step is required for the stripping of plutonium from CMPO-TBP phase. Consequently, the process generates less volumes of secondary wastes compared to that in the conventional process. The strippant used in this partitioning scheme is effective even in presence of HDBP<sup>(12,22)</sup>, which is a major degradation product of TBP. The chemicals used in the process are commonly available chemicals and can be destroyed with conventional methods without generation of hazardous residues. These residues as well as the sodium carbonate stream from the final wash of the solvent can be considered as fission product wastes and disposed by conventional immobilisation methods like cementation, polymerisation or bitumenisation.

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TABLE 1

PERCENTAGE DISTRIBUTION OF ELEMENTS

ELEMENTS	EXTRACTION STEP USING TBP			EXTRACTION STEP USING CMPO-TBP			
	TBP RAFFINATE	AQUEOUS PRODUCT (I)*	TBP#	CMPO RAFFINATE	AQUEOUS PRODUCT (II)**	AQUEOUS PRODUCT (III)***	LEAN CMPO
U	0.06	0.05	99.89	<0.01	<0.01	0.06	<0.01
Np	<0.01	96.40	3.60	<0.01	<0.01	<0.01	<0.01
Pu	6.73	92.46	0.81	<0.01	6.73	<0.01	<0.01
Am	~100	<0.01	<0.01	<0.01	100.46	<0.01	<0.01
Ce	90.68	9.37	<0.01	<0.01	88.72	<0.01	<0.01
Eu	~100	<0.01	<0.01	<0.01	101.32	<0.01	<0.01
Ru	98.72	1.07	0.25	82.91	7.42	5.02	0.54
Cr	67.65	32.40	<0.01	50.18	15.24	3.33	2.43

# Uranium to be stripped with dilute nitric acid

\* Strippant: 0.25 M H<sub>2</sub>O<sub>2</sub> + 0.05 M ascorbic acid in 2.0 M HNO<sub>3</sub>

\*\* Strippant: 0.4 M formic acid + 0.4 M hydrazine hydrate + 0.1 M citric acid

\*\*\* Strippant: 0.25 M Na<sub>2</sub>CO<sub>3</sub>

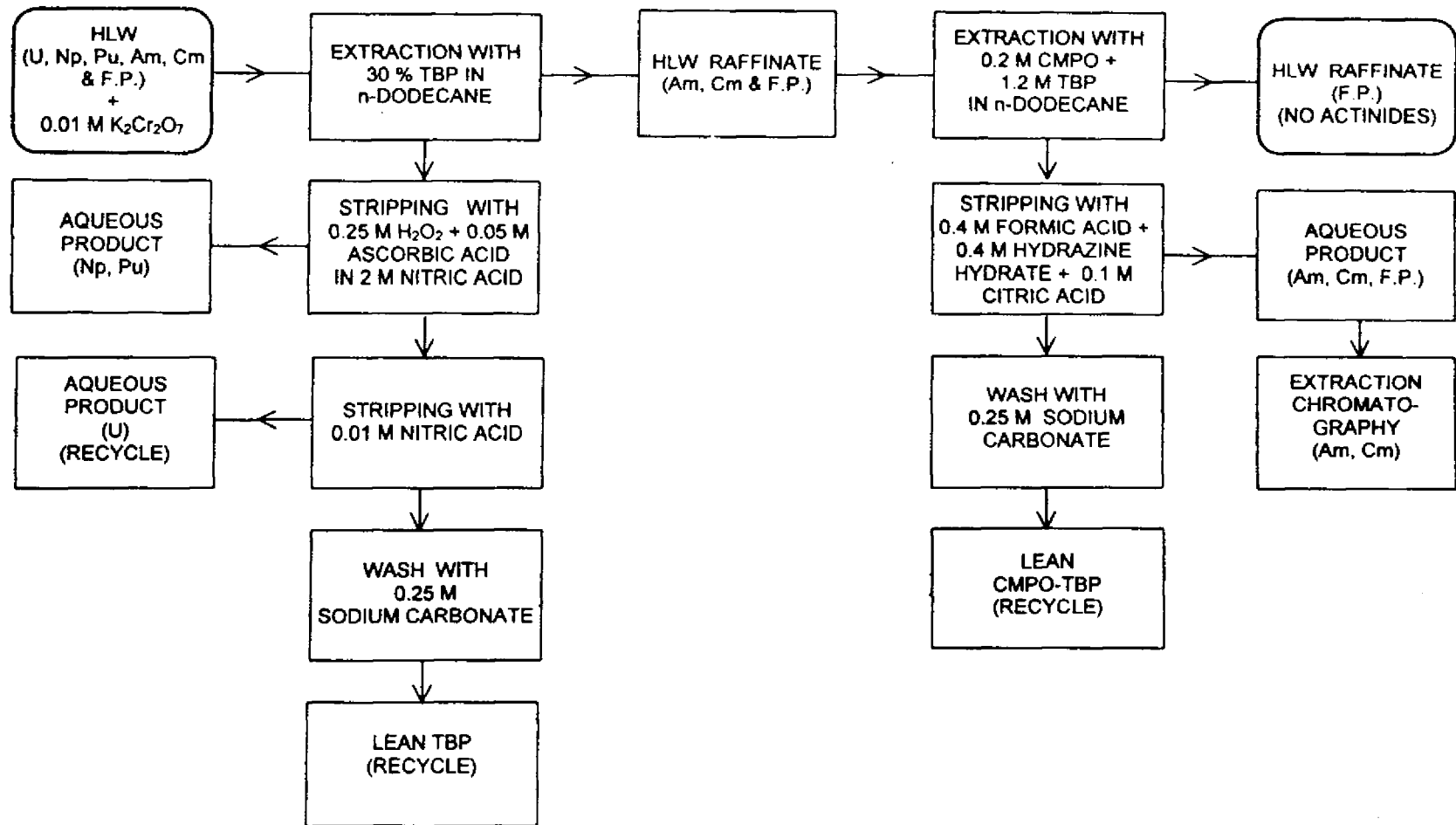


FIG.1. SCHEME FOR PARTITIONING OF ACTINIDES FROM HLW USING TBP AND CMPO AS EXTRACTANTS

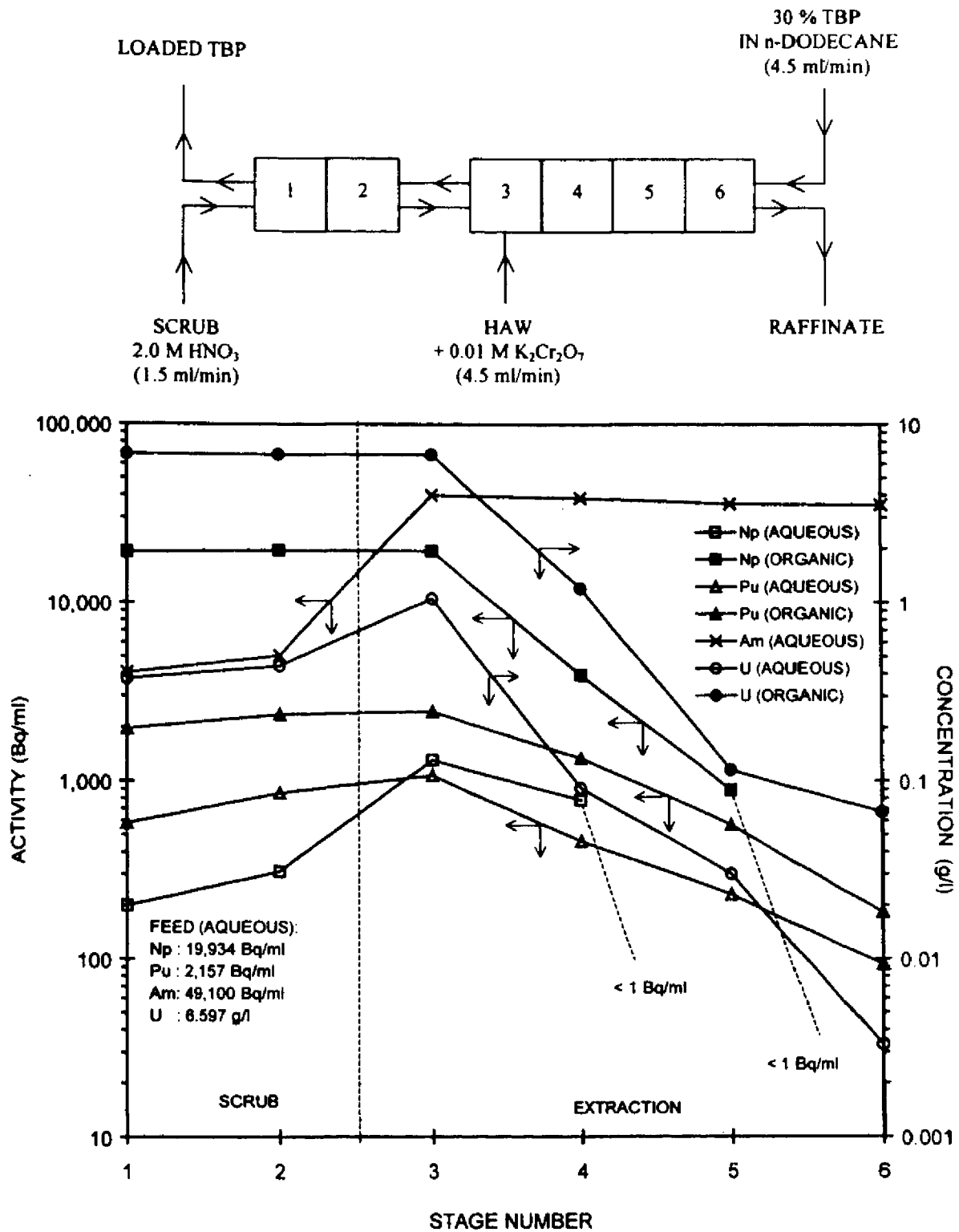
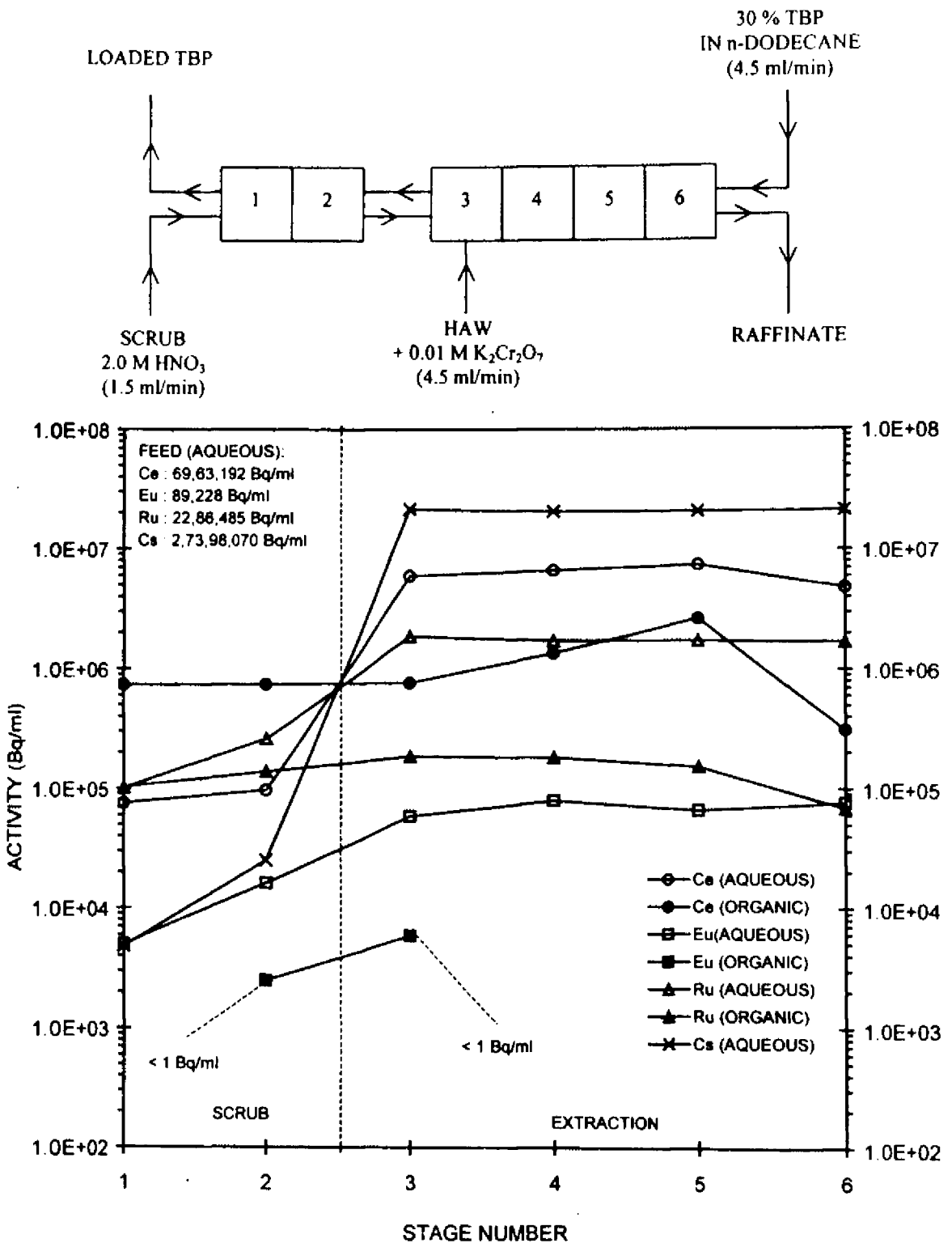
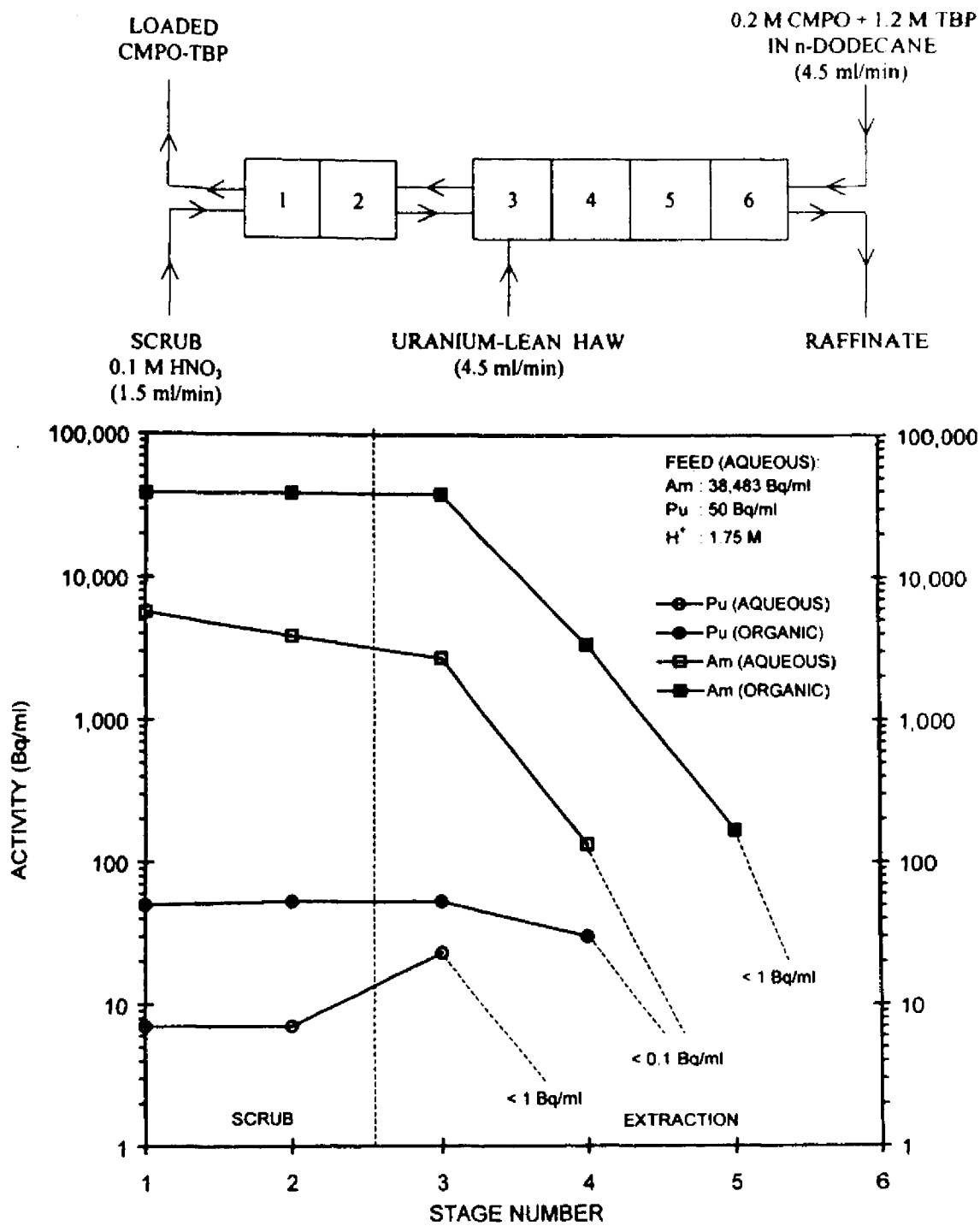


FIG.2. EXTRACTION OF ACTINIDES FROM HAW USING TBP



**FIG.3. EXTRACTION OF FISSION PRODUCTS DURING PARTITIONING OF ACTINIDES USING TBP**



**FIG.4. EXTRACTION OF ACTINIDES FROM URANIUM-LEAN HAW USING CMPO-TBP**



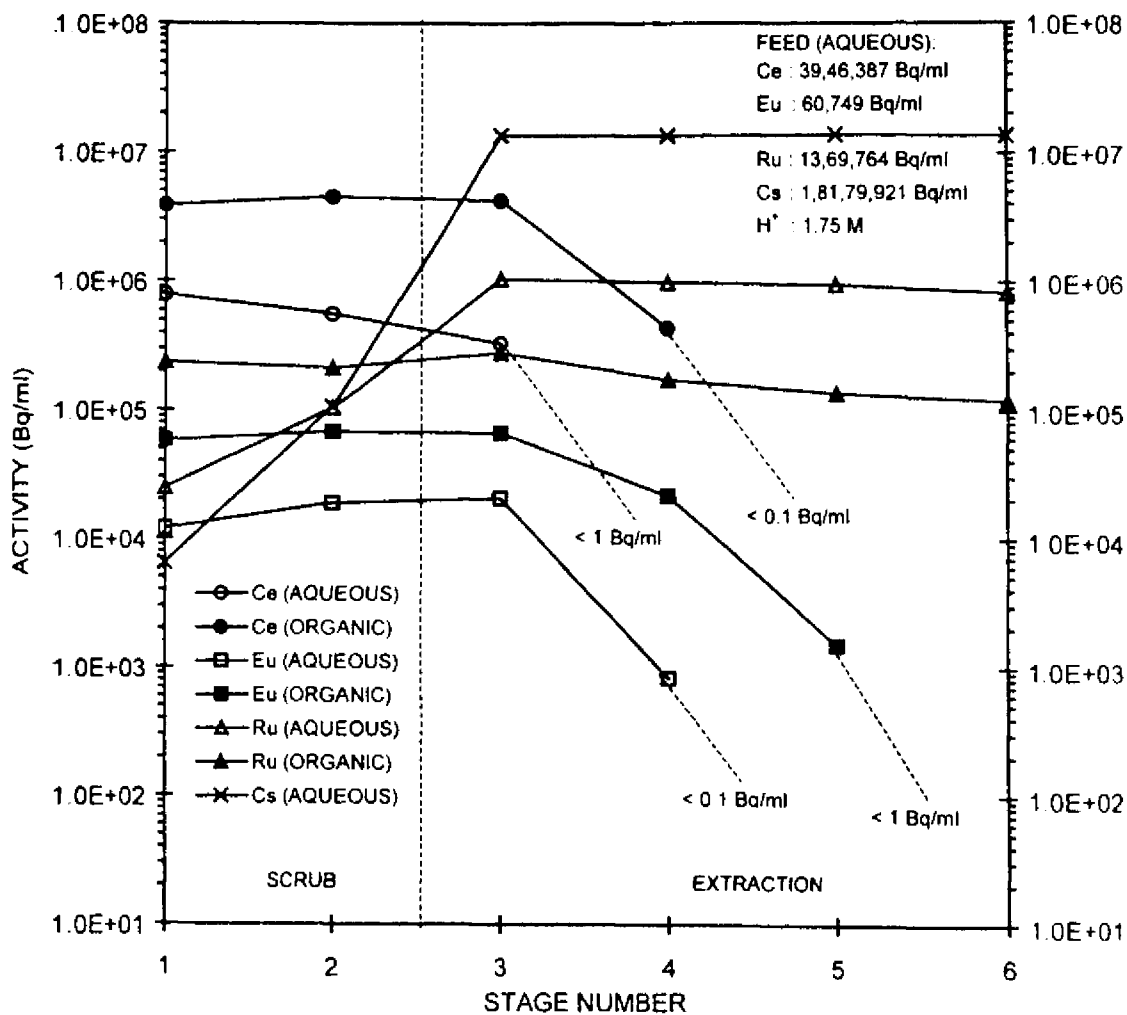
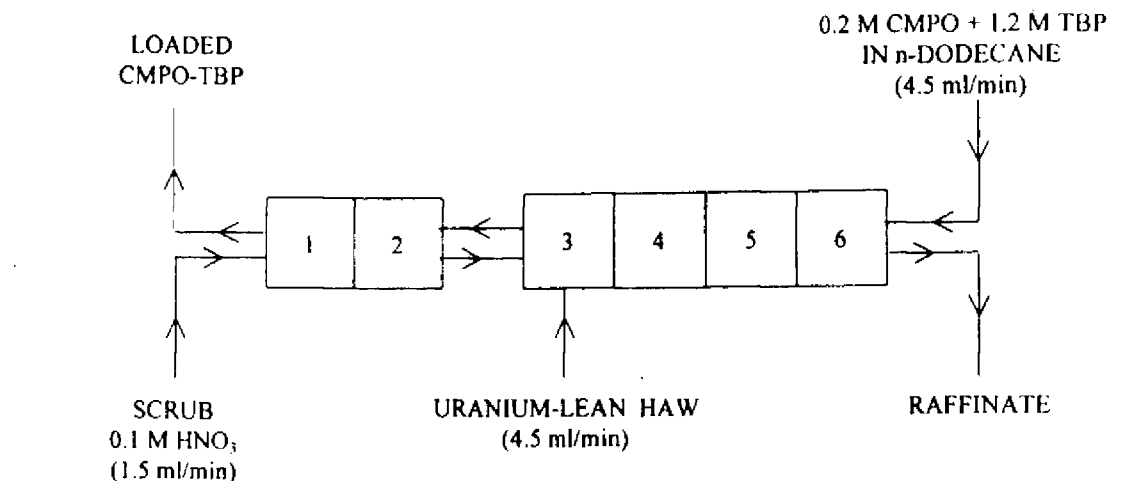
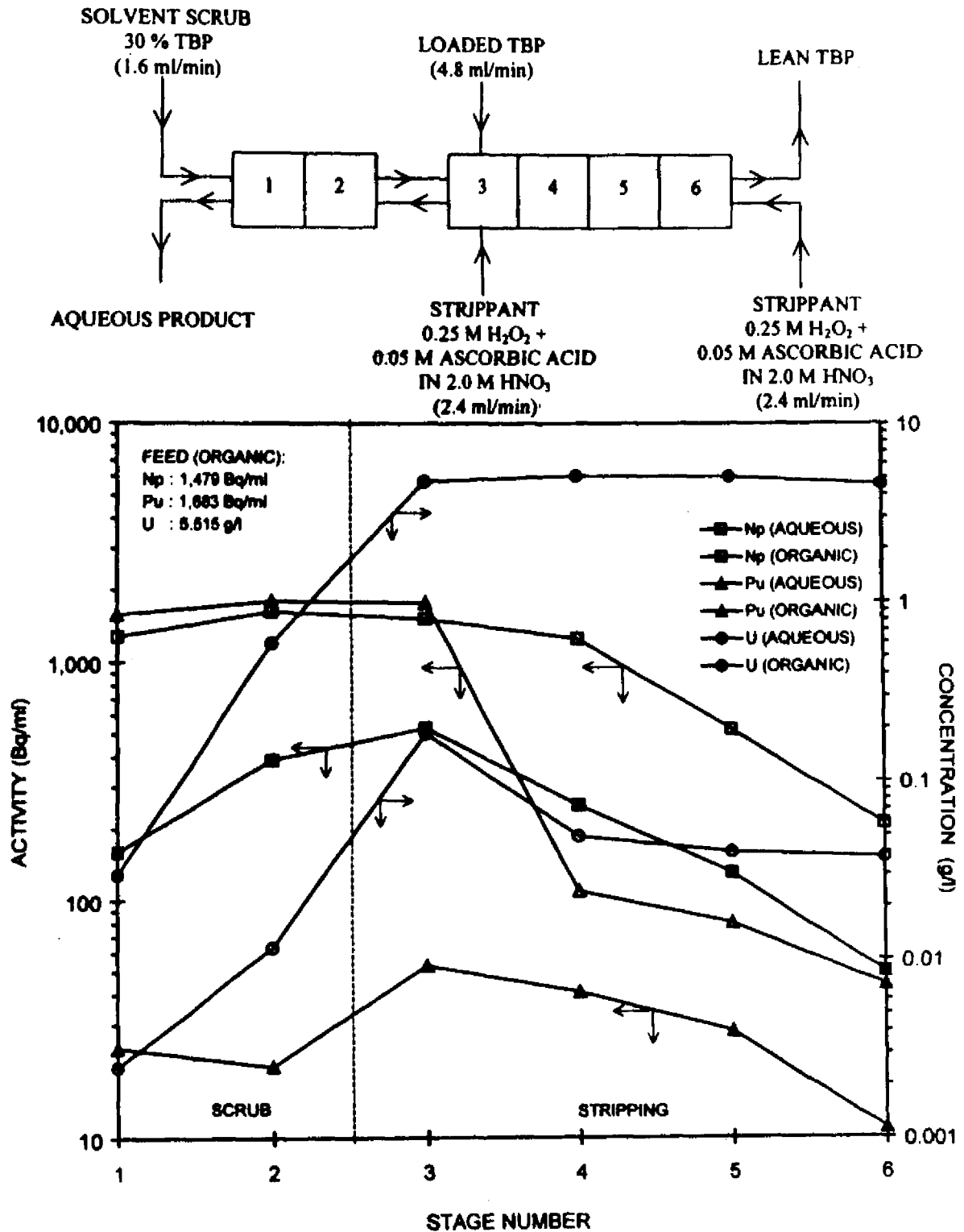
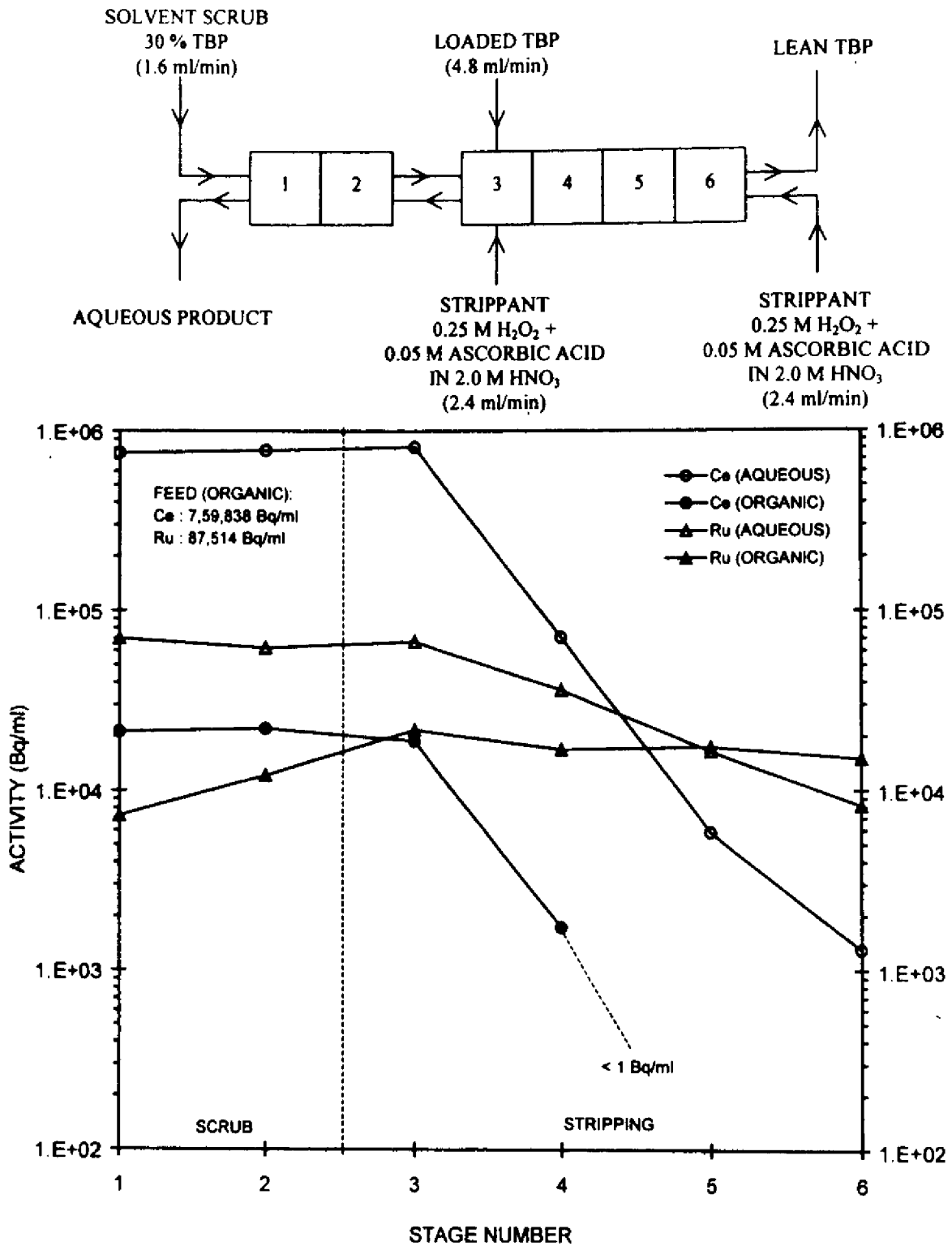


FIG.5. EXTRACTION OF FISSION PRODUCTS DURING PARTITIONING OF ACTINIDES USING CMPO-TBP



**FIG.8. STRIPPING OF NEPTUNIUM AND PLUTONIUM FROM LOADED TBP**



**FIG.7. STRIPPING OF FISSION PRODUCTS FROM LOADED TBP**

LOADED CMPO-TBP  
IN n-DODECANE  
(4.5 ml/min)

LEAN  
CMPO-TBP

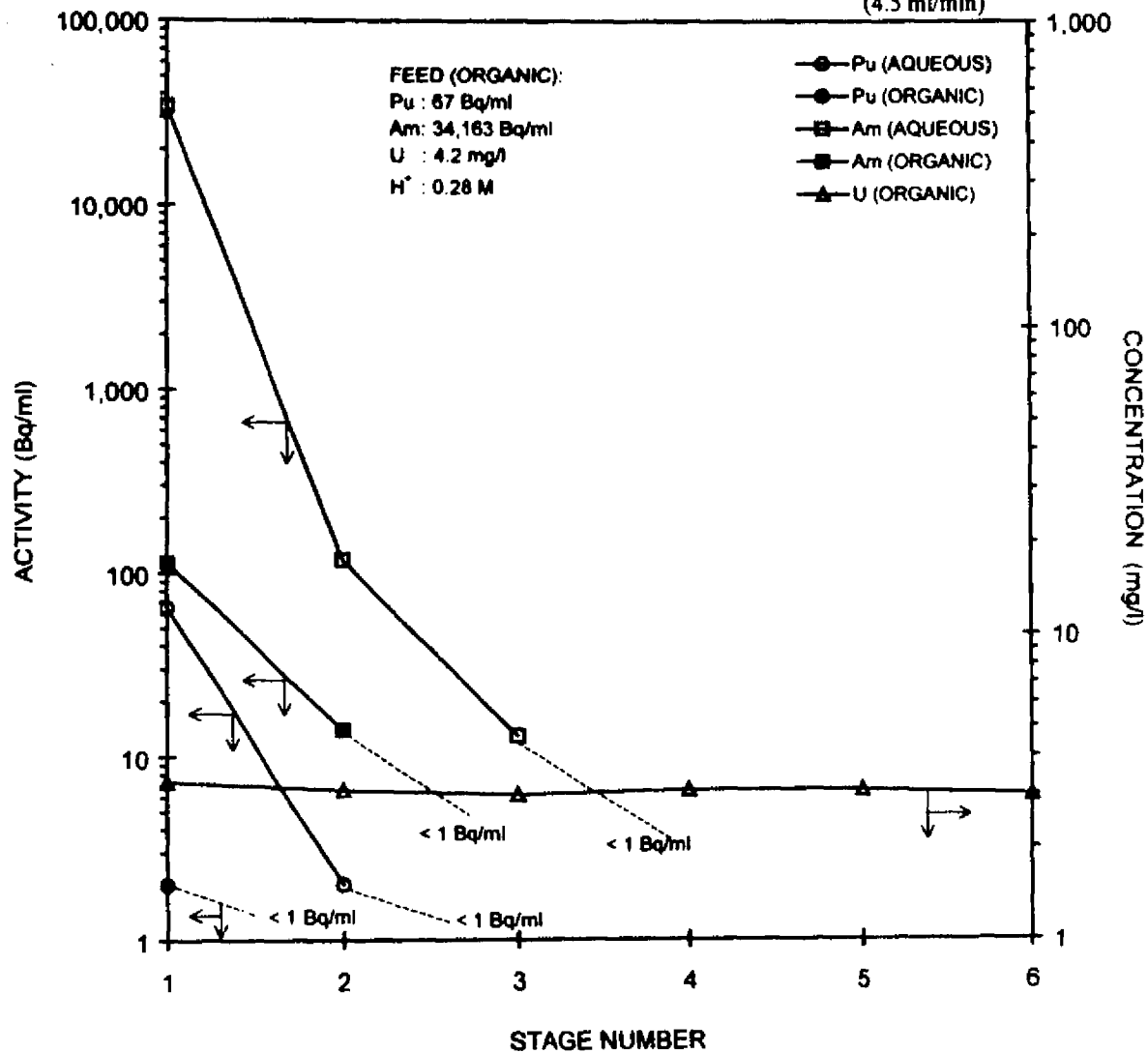
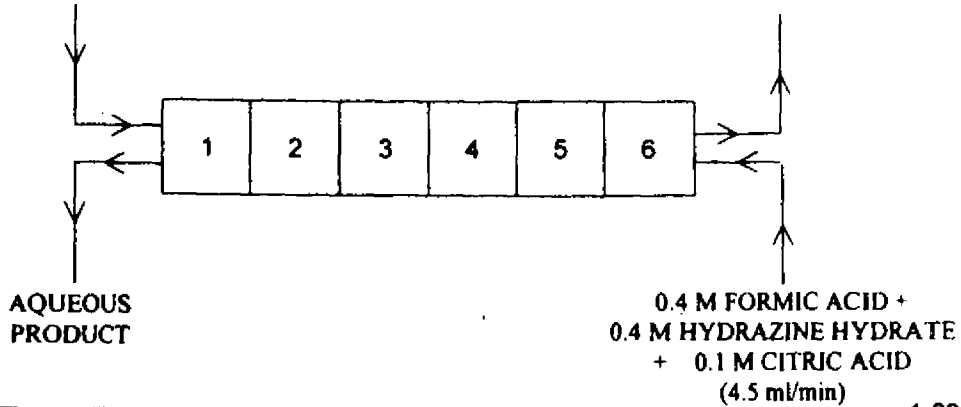


FIG.8. STRIPPING OF ACTINIDES FROM LOADED CMPO-TBP

LOADED CMPO-TBP  
IN *n*-DODECANE  
(4.5 ml/min)

LEAN  
CMPO-TBP

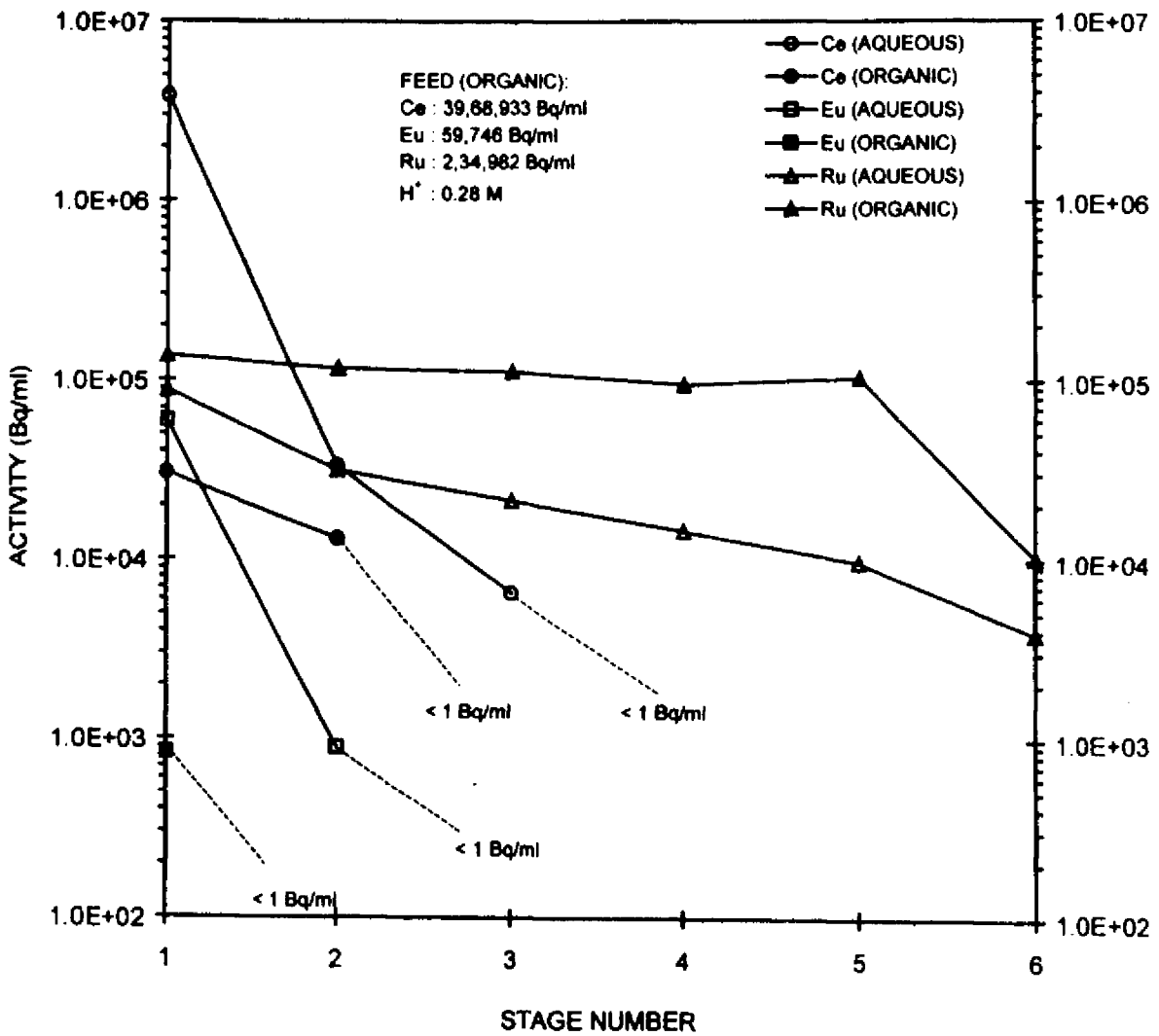
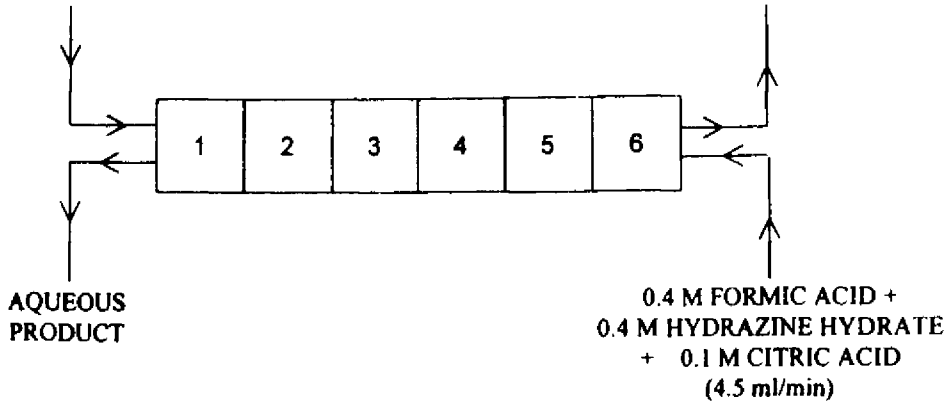


FIG.9. STRIPPING OF FISSION PRODUCTS FROM LOADED CMPO-TBP

LEAN CMPO-TBP  
IN n-DODECANE  
(4.8 ml/min)

WASHED  
CMPO-TBP

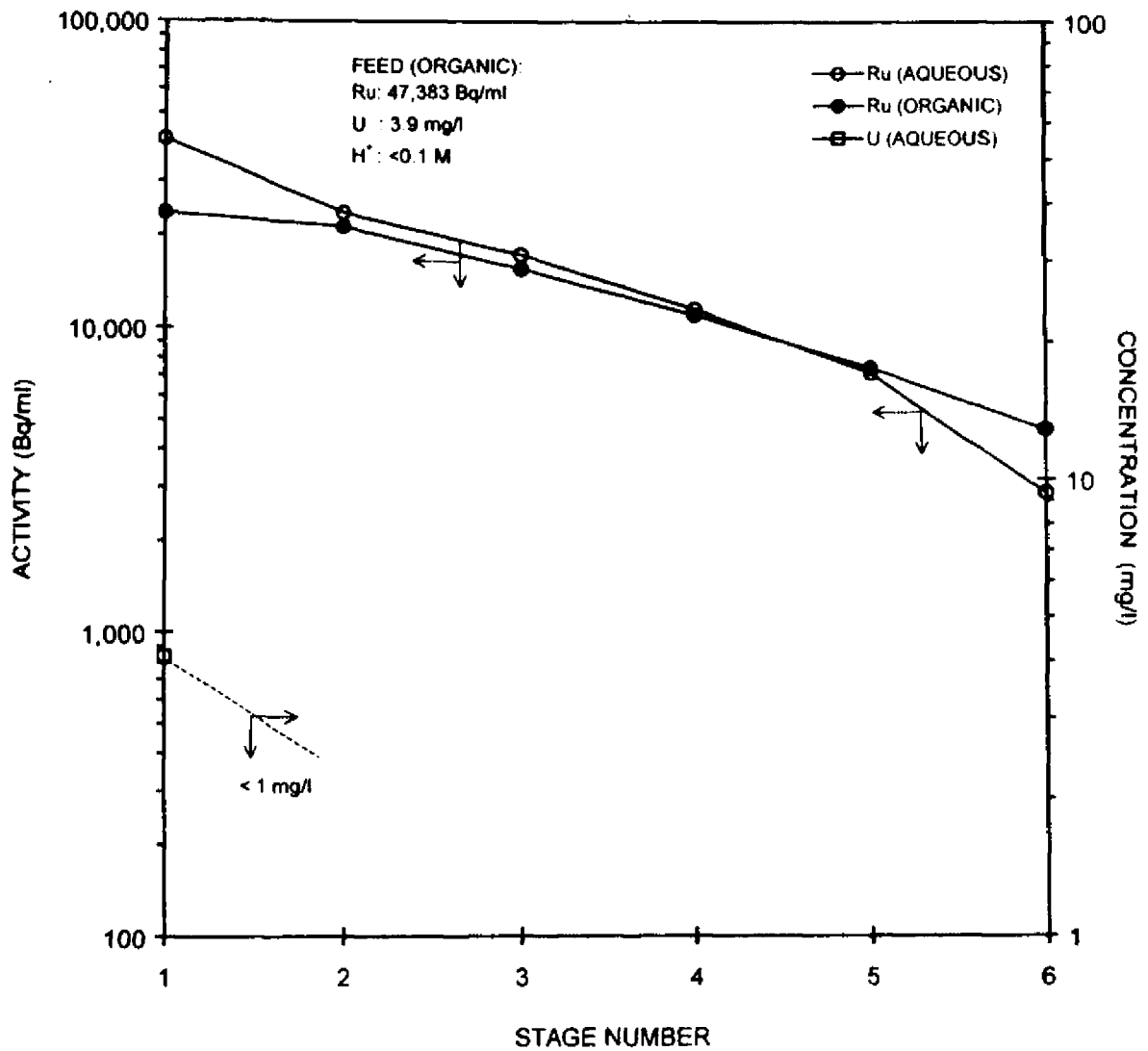
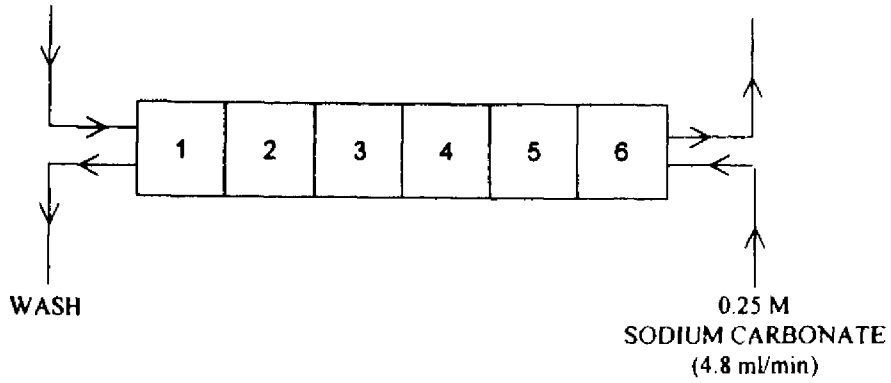


FIG.10. WASHING OF LEAN CMPO-TBP USING ALKALI

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