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Validation of the flow-sheet proposed for reprocessing of AHWR spent fuel: counter-current studies using TBP

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ABSTRACT

A solvent extraction based flow-sheet, for reprocessing of spent fuel arising from Advanced Heavy Water Reactor (AHWR) for separation of uranium, plutonium and thorium using 5% TBP in *n*-dodecane, has been tested using laboratory scale mixer-settlers. Simulated feed solution containing thorium, uranium and plutonium in the concentration levels expected in feed solutions of AHWR spent fuel reprocessing is prepared using plutonium, natural uranium and thorium nitrate. Quantitative extraction of uranium and plutonium is achieved under experimental conditions leaving bulk of thorium in the raffinate. Co-extracted thorium from the organic phase is scrubbed using 3.00 M HNO_3. Separation of plutonium from uranium is achieved by chemical reduction employing a mixture of hydroxylamine nitrate and hydrazine nitrate in nitric acid. Results show quantitative partitioning. Uranium from the plutonium lean organic phase is stripped using 0.01 M HNO_3. The results clearly established the validity of the proposed flow-sheet.

Keywords: AHWR; Uranium; Plutonium; Thorium; TBP; Solvent extraction

1. Introduction

Advanced Heavy Water Reactor (AHWR) is designed to utilize (Th, Pu)O_2 as fuel in its initial core and both (^{233}U,Th)O_2 and (Pu,Th)O_2 in a single cluster in the equilibrium core. This reactor is a first of its kind for early introduction of thorium into the power scenario and has many built-in passive safety features [1–3]. It is designed to extract maximum power from thorium [4]. Spent fuel from AHWR is expected to contain about 2% to 4% fissile materials *viz.* ^{233}U and plutonium. Reprocessing of spent (Th, Pu)O_2 fuel pins from AHWR offers challenges to the separation chemists as the fuel pins have to be processed for the separation of three components i.e., in-bred ^{233}U, residual Pu and Th from each other and also from fission products.

No well developed method exists in literature for the separation of U, Pu and Th from irradiated fuels. Solvent extraction studies in batch mode were reported earlier from our laboratory using simulated solution equivalent to spent fuel composition of irradiated (Th,Pu)O_2 fuel arising from AHWR to evolve a process scheme for a three-component separation [5,6]. Studies clearly indicated the feasibility of using 5% TBP in *n*-dodecane solvent for selective extraction of uranium and plutonium from the feed solution containing 100 g/l thorium. Conditions for scrubbing of co-extracted thorium and reductive partitioning of plutonium from uranium were also evaluated. Hydroxyl amine nitrate (HAN) along with hydrazine was studied in detail to establish and optimize the

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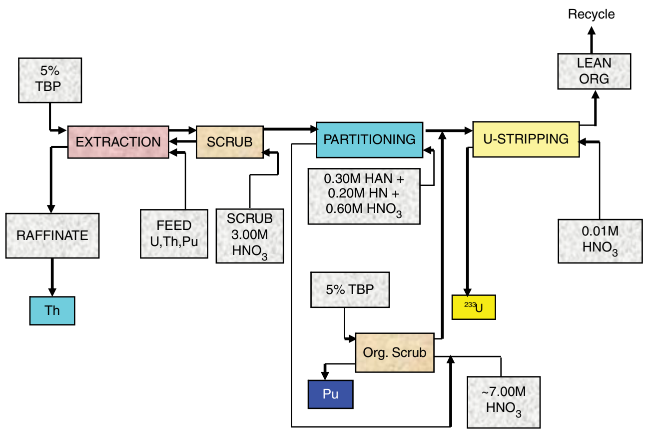

Fig. 1. Flow-sheet proposed for reprocessing of AHWR spent fuel.

striping parameters. Even though HAN was selected as the choice of reductant due to the large-scale experience, efficacy of a few other potential alternatives were also reported [6]. Based on co-current extraction data a flow-scheme was proposed for a three-component separation as shown in Fig. 1. and the same is validated in the present work using laboratory scale mixer settlers housed in specially designed glove-boxes using simulated solution containing thorium, natural uranium and plutonium in concentration levels expected in feed solutions of AHWR spent fuel reprocessing.

2. Experimental

2.1. Reagents

Tri-*n*-butyl phosphate obtained from Bharat Vijay Chemicals, India was purified by contacting it with 2% solution of sodium carbonate for the removal of acidic impurities. It was then washed with distilled water. Diluent *n*-dodecane (~93% C_{12}, sp. gr. = 0.751, refractive index = 1.42) supplied by M/s. Transware Chemia Handelsgeselschaft, Hamburg, Germany was used as such without any further purification.

Stock solution of uranium (100.00 g/l) was prepared in 0.10 M HNO_3 from AR grade uranyl nitrate hexahydrate procured from BDH Chemicals, England. Nuclear grade thorium nitrate procured from Indian Rare Earths Ltd., India was used to make a stock solution of thorium (400.00 g/l) in water. Ion-exchange purified plutonium (^{239}Pu isotopic content >92%) from PUREX stream was used to prepare a stock solution of 12.00 g Pu /l in 4.00 M HNO_3.

Hydroxylamine (50% solution in water) supplied by Merck Schuchardt OHG, Germany and hydrazine hydrate (99% solution) from s.d. fine Chem. Ltd., Mumbai, India were neutralized by nitric acid solution to prepare the partitioning reagent *viz.* 0.30 M hydroxyl amine nitrate (HAN) + 0.60 M HNO_3 + 0.20 M hydrazine nitrate (HN).

All other chemicals used in the present studies were of analytical reagent grade.

2.2. Mixer-settler units

Mixer-settler units fabricated from poly acrylic sheets were used. The capacity of each mixer was ~30 ml and that of the settler was ~130 ml. The mixing chambers had bottom inlets for organic and aqueous feeds. Solutions were fed at required rates using peristaltic pumps. Mixing was done by 12 V DC motors. Solutions were fed to the mixer-settler by pumping air at predetermined rates using peristaltic pumps kept outside the fume hood/glove box. Mixing time of 2–3 min and settling time of 8–12 min were generally maintained in all the experiments.

2.3. Preparation of feed solution

Feed solution used in the extraction studies was prepared by mixing appropriate quantities of uranium, plutonium and thorium from their stock solutions so as to get final concentrations 2.00, 2.00 and 100.00 g/l respectively. Sodium nitrite (0.03 M) was added to maintain the oxidation of Pu as Pu(IV) during extraction step. Calculated quantities of aluminium nitrate and conc. hydrofluoric acid were also added to get their final concentrations as 0.10 and 0.03 M respectively. The acidity of the feed was adjusted to 3.50 M HNO_3. 3.00 M HNO_3 was used for thorium scrubbing during the counter current extraction experiment.

2.4. Analyses

Thorium in the aqueous phase was analysed either by complexometric titration with EDTA or by spectrophotometrically using thoron as colour developing reagent [7]. Uranium was analysed spectrophotometrically using 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (Bromo-PADAP) as chromogenic reagent [8]. Plutonium from aqueous samples was extracted into thenoyltrifluoroacetone (TTA) in xylene after proper adjustment of the oxidation state and acidity. The extracted plutonium was determined radiometrically using alpha proportional counter. For the estimation of plutonium from TBP, it was stripped into aqueous phase by reducing to Pu^{3+} with ferrous solution. The aqueous phase was then analysed using radiometry. The concentration of nitric acid in the sample was determined by acid base titration after complexing Th/Pu/U with potassium oxalate using potentiometry.

2.5. Counter-current experiments

2.5.1. Extraction

Twelve stage mixer-settler unit was used during extraction cum scrub run of which eight stages were used for extraction and the remaining four stages were used for scrubbing the small amounts of co-extracted thorium in the organic phase using 3.00 M HNO_3. The scheme used in extraction cum scrub run is shown in Fig. 2. Flow rates of 6.0 and 3.0 ml/min were maintained during this extraction cum scrub run for organic and aqueous feed solutions whereas 1.0 ml/min was maintained for 3.00 M HNO_3 used as scrub stream. The mixer settler unit was initially filled with 3.00 M HNO_3 and 5% TBP in *n*-dodecane and the same solutions were used to adjust the flow rates. Once the required rates were achieved the nitric acid solution at feed point was replaced by aqueous feed solution prepared above. During the run, exit samples were collected intermittently till the steady state condition is ascertained by analyzing uranium, plutonium and thorium. Run was continued to collect the sufficient loaded organic (~5 l) for partitioning run. At the end of the run stage samples were collected. These samples were analyzed for uranium, plutonium thorium and acidity using the methods described above.

2.5.2. Partitioning

The uranium and plutonium loaded organic phase from above extraction cum scrub experiment is subjected to partitioning step where separation of plutonium and uranium is achieved by reducing plutonium to its inextricable trivalent state using hydroxyl amine nitrate in nitric acid solution. In this step, eight stage mixer settler unit was used, of which four stages were used for reductive partitioning using a mixture of 0.30 M HAN + 0.60 M HNO_3 containing 0.20 M HN whereas remaining four stages were used for the re-extraction of uranium that gets released to the aqueous phase during partitioning. A nitric acid solution containing ~7.00 M was fed in the fifth stage mixer to increase the acidity of the aqueous phase to ~3.50 M for near complete extraction of uranium into 5% TBP in *n*-dodecane phase. Organic streams containing uranium i.e., U-1 (organic scrub stream) and U-2 (Pu lean organic stream) were collected separately. The scheme used for partitioning experiment is shown in Fig. 3.

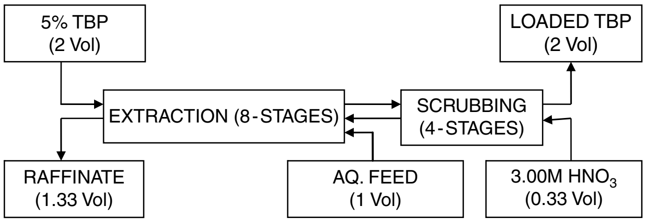

Fig. 2. Scheme used in counter-current extraction cum scrub experiment.

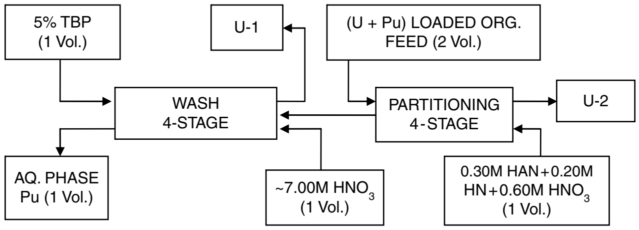

Fig. 3. Scheme used for partitioning of U and Pu.

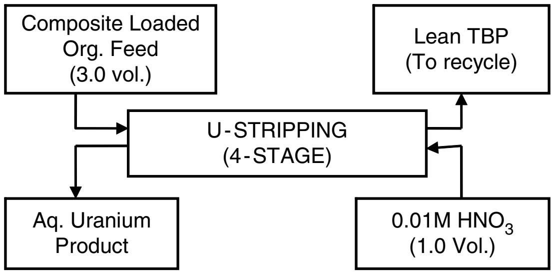

Fig. 4. Scheme used in uranium stripping step.

2.5.3. Stripping of uranium

Organic scrub stream and Pu lean organic stream obtained from partitioning run were mixed to get a composite uranium bearing organic phase which was used for uranium stripping using 0.01 M HNO_3. In this experiment, 4-stage mixer settler unit was operated. The organic to aqueous flow rates used for this stripping experiment was maintained at 3:1. The details of the scheme used for uranium stripping is shown in Fig. 4.

3. Results and discussion

Based on batch data reported earlier [6], a flow-scheme was proposed (Fig. 1) for the separation of three components *viz.* U, Pu and Th, in which selective extraction of uranium and plutonium was suggested from bulk of thorium using 5% TBP in *n*-dodecane. Reductive partitioning of plutonium from uranium was suggested by a mixture of HAN, HN and HNO_3. The flow-scheme was initially tested in counter-current mode in fume hood with tracer amounts of Pu and actual amounts of U and Th to adhere to the safety limits of Pu handling in fume hoods and also to establish the system performance prior to moving the equipment to a glove-box where actual concentrations of Pu can be tested [9].

The results were found to be encouraging. Hence to test the proposed flow-sheet under near realistic concentrations of uranium, plutonium and thorium, laboratory scale counter-current extraction and stripping runs were carried out in specially designed glove-boxes. Under proposed flow conditions, the experiments were carried out till steady state conditions were reached. The results of each step are given below.

The extraction of uranium and plutonium was carried out using the flow scheme given in Fig. 2. During the experiment, the exit organic as well as aqueous phases were analysed intermittently for uranium, plutonium and thorium till it reached steady state conditions. After getting steady value for these constituents, the run was continued for five more hours. Stage wise profile and results from this experiment at steady state conditions are given in Fig. 5a and b, and Table 1. From the organic phase profile shown in Fig. 5a it can be seen that the extraction of uranium is sharp and completed in lesser number of stages due to its high distribution ratio in the experimental conditions where as Pu extraction is completed in more number of stages due to its lesser affinity to the organic phase in comparison to uranium. Thorium concentration in the extracted phase is almost constant due to its very high concentration even though its affinity is the lowest. During the acid scrubbing of the loaded organic phase the affinities of the ions are more pronounced and thorium is preferentially scrubbed out from the organic phase. Fig. 5b shows the aqueous profile of the ions during extraction and scrubbing. The results are in conformity with extraction data. The aqueous exit sample has the highest Th concentration with minimum U and Pu loss. In the scrub section, thorium is removed maximum close to the feed point where as U and Pu concentration remained mostly constant. These results indicate quantitative extraction of uranium and plutonium under the experimental conditions. Thorium contamination of about 210 mg/l is observed in the organic extract.

The composite organic phase generated from the extraction cum scrub run had the concentration of uranium, plutonium and thorium of 1.38, 0.858 and 80 mg/l respectively and had ~0.09 M HNO_3. During reductive partitioning of plutonium from uranium in four stages under the experimental conditions, uranium gets released to the aqueous stream partly. In order to increase the concentration of nitrate in this aqueous phase, a 7.00 M HNO_3 stream was introduced in fifth stage which enhanced the acidity of the aqueous phase to ~3.50 M thereby enabling the extraction of uranium back to organic phase. This organic stream (U-1) was found to have major portion of uranium compared to Pu lean organic stream (U-2) coming out of the partitioning stage and collected separately. The results obtained are given in Table 2.

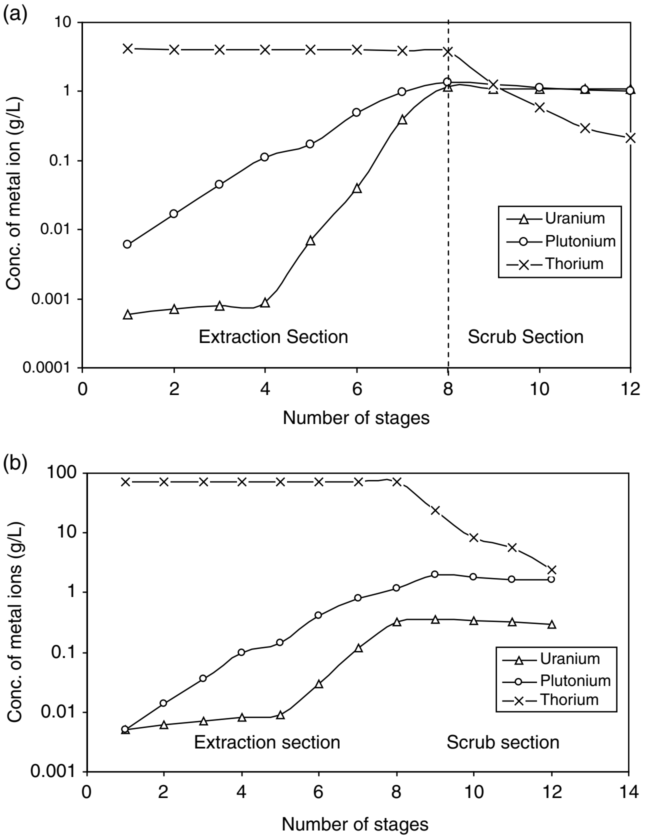

Fig. 5. (a) Stage-wise profile of U, Pu and Th in organic phase. (b) Stage-wise profile of U, Pu and Th in aqueous phase.

Table 1
Composition of different streams at steady state condition during extraction

Analyte	Concentrations		
	Feed	Raffinate	Loaded organic phase
$[HNO_3]$, M	3.66	3.52	0.06
[Th], g/l	100.02	71.29	0.210
[U], g/l	2.00	<0.001	1.004
[Pu][a], g/l	2.01	0.0048	1.008
$[Al^{3+}]$, M	0.10	0.07	–
$[F^-]$, M	0.03	0.02	–

[a] Total Pu concentration.

Stage wise profile of U, Pu and Th in aqueous as well as organic phases is given in Fig. 6a and b. Fig. 6a presents the stage wise profile of uranium, plutonium and thorium in the aqueous phase. This profile has a profound influence on entry and exit of various streams at different stages. Composite organic phase is introduced at Stage 5

Table 2
Composition of aqueous and organic streams during partitioning run at steady state condition

Analyte	Concentrations			
	Composite organic phase	Pu product stream	Pu lean organic stream	
			U-1[a]	U-2[b]
[HNO_3], M	0.09	3.40	0.09	0.05
[Th], g/l	0.21	0.18	0.080	ND
[U], g/l	1.38	0.01	2.19	0.27
[Pu][c], g/l	0.858	0.8575	0.0046	1×10^{-5}

[a] Organic used for scrubbing after adjusting aqueous phase acidity to ~3.50 M HNO_3.
[b] Pu lean organic stream.
[c] Total Pu concentration.

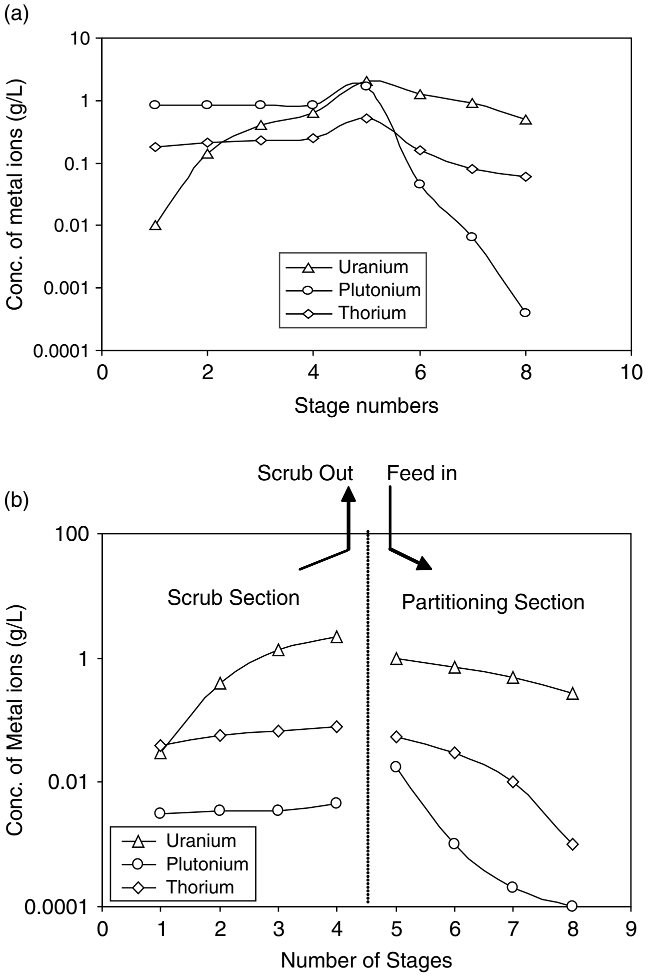

Fig. 6. (a) Stage-wise profile of U, Pu and Th in aqueous phase in partitioning. (b) Stage-wise profile of U, Pu and Th in organic phase in partitioning.

and was allowed to move as a counter current flow to Stage 8 where the partitioning agent was introduced. Thus in the partitioning section the aqueous phase is in contact with the organic phase with increasing concentration of metal ions from Stage 8 to 5. This is well reflected in the increasing concentration of all the ions from Stage 8 to 5. Sharp change was observed with Pu as it is converted to Pu(III) which is almost completely stripped near the point of introduction of loaded TBP where it meets the partitioning agent. At Stage 4 the aqueous phase acidity was altered by introducing nitric acid. This was necessitated to recover the U which was also co-stripped with Pu in significant amounts. The 5% TBP phase introduced at stage 1 during its counter current passage through 1 to 4 stages almost quantitatively pickup the U and to a lesser extent Th leaving behind the inextractable Pu(III) in the aqueous phase. Fig. 6B presents the corresponding stage wise profile of the two separate organic phases, *viz.* feed and scrub, employed counter currently. The feed phase while passing through Stages 5 to 8 meet the partitioning agent moving from 8 to 5. Sharp decrease of Pu from Stage 5 to 8 is brought about by the change in Pu valency where as the decrease in Th and U is based on the affinity of the nitrate concentration of the stream. The scrub stage from 1 to 4 show sharp pickup of uranium from 5 to 1 and slow pick up of thorium and practically no pickup of Pu(III).

The results from the uranium stripping of composite organic phase (U-1 + U-2) using 0.01 M HNO_3 are given in Table 3 which show quantitative stripping of uranium at an organic to aqueous phase ratio of 3:1. The stage wise profile of uranium in stripping run is given in Fig. 7. From both organic and aqueous phase it can be seen that almost quantitative stripping is achieved in two to three stages.

The analysis of the three product streams obtained using the proposed flow sheet is given in Table 4. The purity of individual components with respect to other actinides can be improved to desired level using

Table 3
Composition of aqueous and organic streams during uranium stripping run at steady state condition

Analyte	Concentrations		
	Composite organic feed (U-1 + U-2)	U-product stream	Lean organic phase
[HNO_3], M	0.06	0.17	ND
[Th], g/l	0.04	0.11	ND
[U], g/l	1.47	4.42	ND
[Pu][a], g/l	0.001	0.004	$<1 \times 10^{-4}$

Flow ratios—Organic feed: strip = 6:2, ND = not detected.
[a] Total Pu concentration.

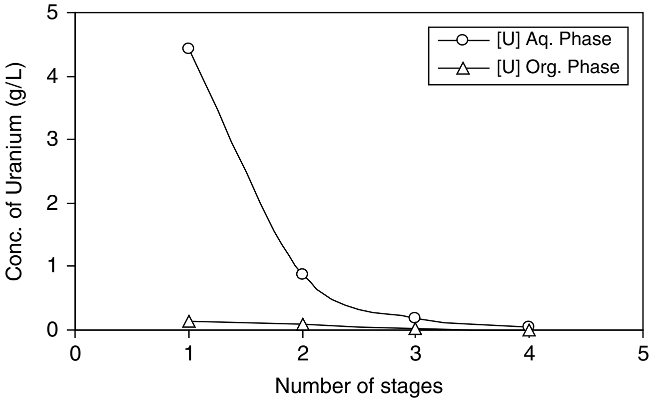

Fig. 7. Stage wise profile of U in stripping.

Table 4
Analysis of three product stream after separation

Concentration (g/l)		
Th-stream	Pu-stream	U-stream
[Th]: 71.29	Pu: 0.8575	U: 4.42
[U]: 0.001	U: 0.01	Pu: 0.004
[Pu][a]: 0.0048	Th: 0.18	Th: 0.109

[a] Total Pu concentration

conventional techniques such as solvent extraction, precipitation and ion-exchange. During the course of the above experiments, neither third phase formation nor crud formation were encountered at any stage of the runs.

4. Conclusions

Above results clearly illustrate the efficacy of 5% TBP in *n*-dodecane in the selective extraction of uranium and plutonium from bulk of thorium present in feed solutions from AHWR spent fuel reprocessing. Chemical reduction using a combination of HAN, HN and dil. HNO_3 was found to be effective in stripping of Pu from loaded organic. Co-stripped uranium in the partitioning step could be selectively back extracted using TBP and finally the uranium product in the TBP phase could be recovered with dilute acid. The laboratory scale mixer settler operations described above could establish the flow ratios and the number of stages needed for the separation of the three components, *viz.* U, Pu and Th, into individual streams and established the validity of the proposed flow-sheet.

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