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Studies on the Development of a Flow-Sheet for AHWR Spent Fuel Reprocessing Using TBP

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The present paper describes the results of solvent extraction studies carried out in batch mode to collect data on distribution of uranium, plutonium, and thorium using 5% TBP in n-dodecane. Extraction studies are carried out from feed solutions having bulk thorium containing aluminum and fluoride ions in ~3.00–4.00 M nitric acid at concentration levels anticipated in feed solutions during Advanced Heavy Water Reactor (AHWR) spent fuel reprocessing. Studies are carried out under varied experimental conditions. Parameters such as organic to aqueous phase ratio during extraction, concentration of nitric acid for scrubbing co-extracted thorium from loaded organic phase etc., are studied in detail. Hydroxylamine nitrate is selected for reductive stripping of plutonium in preliminary studies. Reagent mixture containing 0.30 M HAN + 0.60 M HNO_3 and 0.20 M N_2H_4 is found to be optimum for plutonium partitioning. This paper also describes the extraction and stripping of uranium and plutonium in co-current mode. The extraction behavior of relevant fission products is studied from a simulated feed solution. A preliminary study on a few commercially available reducing agents is also included. These data are useful in developing a flow-scheme for the recovery of uranium and plutonium from spent fuel originating from AHWR.

Keywords AHWR; HAN; PUREX; solvent extraction; spent fuel reprocessing; TBP; THOREX

INTRODUCTION

Solvent extraction data play a pivotal role in designing flow-schemes for the reprocessing spent fuels from nuclear reactors. In India, rich experience exists in reprocessing of spent fuel from thermal, research, and power reactors based on natural uranium fuel which contains ~0.71% fissile ^{235}U. The average burn-up of the spent fuel in these pressured heavy water rectors is generally ~6700 mega watt days per tonne. Because of the poor uranium resources, attention is being focused on the utilization of abundant thorium (1,2). In the context of thorium utilization, all-round research and development activities are in progress in many laboratories of the country to address fuel cycle issues (3–14). Advanced Heavy Water Reactor (AHWR) which utilizes (Th, Pu)O_2 as fuel is a first of its kind for early utilization of thorium for power generation (15). This reactor has many built-in passive safety features and is designed to extract maximum power from thorium. Spent fuel from AHWR is expected to contain ~2 to 4% fissile materials viz. ^{233}U and plutonium. Reprocessing of the spent fuel from AHWR is a challenge to a closed fuel cycle where the three components viz. in-bred uranium, plutonium, and residual thorium are required to be separated from the bulk of the fission products. Scarce data is only available (16,17) on the separation of individual actinides from such a three-component system and no data is available on the separation of these actinides from actual irradiated (Th-Pu)O_2 fuels. Such a scheme is essential for closing the AHWR fuel cycle.

The present paper aims at the basic data generation on three components viz. U, Th, and Pu, prior to counter-current extraction runs on a laboratory scale. Batch equilibration studies are carried out using 5% TBP in n-dodecane from nitric acid medium containing Al^{3+} and F^- ions which are added to simulate thoria dissolution conditions employing THOREX dissolvent of 13.00 M HNO_3 0.03 M fluoride and 0.10 M $Al(NO_3)_3$ (4). In order to gain confidence, co-current extraction studies are also carried out from simulated feed solutions with the above composition. Even though co-current extraction leads to higher impurity uptake, it can be used for estimating the number of stages required for counter-current extraction. Based on these data a flow-sheet is proposed for the three component separation from spent (Th-Pu)O_2 fuel from AHWR.

EXPERIMENTAL

Reagents and Chemicals

Tri-n-butyl phosphate (TBP) obtained from M/s. Bharat Vijay Chemicals, India and n-dodecane (~93% C_{12}) supplied by M/s. Transware Chemia Handelsgeselschaft, Hamburg, Germany are used as such without any further purification. Stock solution of uranium

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(100.00 g/L) is made 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 is used to make the stock solution of thorium (400.00 g/L) in water. Ion-exchange purified plutonium from PUREX stream is used to prepare a stock solution (12.000 g/L in 4.00 M HNO_3) for preparing the feed solution for extraction studies.

Hydroxylamine (50% solution in water) supplied from 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 desired concentrations of hydroxylamine nitrate (HAN) and hydrazine nitrate (HN) solutions. Commercially available reagents viz. acetohydroxamic acid (AHA), ferrous ammonium sulphate (FAS), tert-butylhydroquinone (TBH), and ascorbic acid (AA) are used as such for partitioning of plutonium from uranium.

All other chemicals used are of analytical grade.

Batch Experiments

Extraction

Feed solutions for extraction studies are prepared by mixing a required volume of the actinide stock solutions in HNO_3 medium, so as to get a final concentration of ~100 g/L thorium and the required concentration of uranium and plutonium. Aluminum nitrate and sodium fluoride solutions are also added in the feed solutions to get a final concentration of $Al^{3+} = 0.10$ M, $F^{-} = 0.03$ M which are added to simulate dissolution conditions of irradiated thoria fuel during AHWR spent fuel reprocessing. The final acidity of the feed solution is adjusted between 3.00–4.00 M HNO_3. Extraction of uranium and plutonium is also studied from feed solutions at varying concentrations. Extraction studies are carried out using 5% TBP in n-dodecane as extractant without acid equilibration.

In all batch extraction experiments a known volume (generally 2 mL to 10 mL) of aqueous feed solutions are contacted with organic phase at different organic to aqueous phase ratios varying from 1 to 3 for about 15 min. which is found to be sufficient to attain equilibrium for the TBP solvent system. Phases are separated and assayed for desired components.

Scrubbing

Loaded organic phase obtained from extraction experiments is used for scrubbing thorium with nitric acid of different concentrations varying from 1.00–4.00 M. In these experiments also the contact time of ~15 min. is maintained. Aqueous and organic phases are assayed for desired components.

Experiments on Reductive Partitioning of Pu

Reductive partitioning of plutonium from uranium is carried out from uranium and plutonium loaded organic phase generated from the extraction experiments. HAN is studied in detail as partitioning agent in the presence of hydrazine nitrate (HN) at low concentrations of nitric acid. Optimization of the partitioning agent is carried out through batch experiments where the concentrations of HAN (0.10–0.30 M) as well as HNO_3 (1.00–3.00 M) are varied. Fixed concentration of HN (0.20 M) is used as a scavenger for HNO_2. In order to get a higher concentration of Pu in the aqueous product during reductive stripping, experiments are also conducted on different organic to aqueous phase ratios ranging from 1 to 8.

Stability of Pu as Pu^{3+} in $HAN + HNO_3 + HN$ Medium

In order to study the stability of Pu in its trivalent state in aqueous medium containing $HAN + HNO_3 + HN$, experiments are carried out in which Pu^{4+} is reduced to Pu^{3+} state in aqueous medium containing 0.30 M HAN + 0.20 M HN at a concentration level of ~2 g/L at different concentrations of nitric acid viz. 0.30, 0.60, 1.50, and 3.50 M separately. In each case the stock solutions of Pu^{3+} are made in 10 mL. Extraction of Pu from these aqueous phases is studied as a function of time (upto 28 days) using 30% TBP in n-dodecane as extractant. In these experiments, 1 mL of the aqueous phase is contacted with 2 mL of the organic phase (30% TBP in n-dodecane) for about 15 min. Solutions are separated after centrifuging and organic phases in each case are analysed for Pu concentration.

Batch Extraction in Co-Current Mode

In these experiments, 2 mL of the feed solution is contacted with 2 mL and 4 mL of the organic phase containing 5% TBP in n-dodecane in separate extraction vials for ~15 min. After equilibration the organic phases are separated from each vial and analysed for each component using standard procedures. To the separated aqueous phase, fresh lots of organic solvent is added at a desired phase ratio. Twelve successive contacts are given to check the extraction of uranium, plutonium, and thorium.

Alternate Reducing Agents

To compare the efficacy of Pu partitioning, a few commercially available reducing reagents are tested. In these experiments, 0.10 M of each reagent in 2.00 M HNO_3 is used as aqueous phase for reductive stripping in batch mode. The concentration of nitric acid is purposely kept at 2.00 M to retain maximum uranium in the organic phase. A few batch experiments are also carried out where HN along with nitric acid is used as partitioning agent. The stripping behavior is compared with dilute nitric acid (0.60 M and 0.90 M) alone.

Behavior of Fission Products

In order to check the distribution behavior of fission products during the extraction of uranium and plutonium from feed solution of AHWR spent fuel reprocessing using 5% TBP in n-dodecane, a batch experiment is carried out using feed solution containing $[Th] = 100.10\,g/L$, $[Pu^{4+}] = 2.080\,g/L$, $[UO_2^{2+}] = 2.040\,g/L$, $[Al^{3+}] = 0.11\,M$, $[F^-] = 0.03\,M$ at $\sim$3.50 M HNO_3. Diluted aliquot of a High Level Liquid Waste sample from the PUREX process is spiked to the above solution to get composite fission product activity. Organic and aqueous phases are contacted at 1:1 phase ratio for about 15 min. After equilibration, the phases are separated and assayed for individual fission product activity using gamma spectrometry.

Analysis

Thorium and uranium are analysed spectrophotometrically using thoron (18) and 2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol (Bromo-PADAP) method (19) respectively. Plutonium from aqueous samples is first extracted into thenoyltrifluoroacetone (TTA) in xylene after proper adjustment of the oxidation state and acidity. The extracted plutonium is determined radiometrically using an alpha proportional counter. For the estimation of plutonium from TBP, it is stripped into the aqueous phase by reducing to Pu^{3+} with ferrous solution. The aqueous phase is then analysed in the same way as above. Individual fission product gamma activities are assayed using a 62 cc HPGe detector coupled to a 4 K multichannel analyzer.

RESULTS AND DISCUSSION

During the initial THOREX campaign (4,5), 5% TBP in n-dodecane was used in reprocessing of irradiated thoria from CIRUS reactor for the recovery of in-bred ^{233}U alone from feed solutions having $\sim$200 g/L Th and mg/L ^{233}U with mCi/L fission product activity from nitric acid containing trace amounts of fluoride and aluminium ions. Since AHWR fuels are having an average enrichment of 3.5% Pu, 10% TBP in n-dodecane was selected initially for the extraction of plutonium and uranium leaving the bulk thorium in the aqueous phase. Concentration of thorium in these preliminary experiments was kept about 100 g/L to limit the fissile content to less than 7 g/L to maintain an ever safe concentration from the criticality viewpoint. Counter-current studies with feed solutions containing 100.000 g/L thorium at 3.50 M acidity were initiated at 1:1 aqueous to organic phase ratio to study the extraction behavior. During extraction runs the third phase was observed when the liquid in the mixer settler unit was drained at the end of the run. Hence, in further studies only 5% TBP is used as extractant as it is well established that this solvent will not lead to third phase formation at any loading conditions.

Table 1 shows the distribution ratios of uranium, plutonium, and thorium in 5% TBP in n-dodecane from feed solutions containing varying concentrations of uranium and plutonium containing 100.000 g/L thorium from 3.00–4.00 M nitric acid in the presence of fluoride and aluminium ions at concentration range anticipated in feed solutions from AHWR spent fuel reprocessing. Results indicate that the distribution ratios of uranium, plutonium, as well as thorium in 5% TBP in n-dodecane are lowered with increase in the concentration of uranium in the feed. In spite of this, the extraction of uranium is good even at the concentration level of 10.000 g/L. Although the distribution ratio of plutonium is lowered, extraction can be

TABLE 1
Extraction of UO_2^{2+}, Pu^{4+} and Th using 5% TBP in n-dodecane

Experimental parameters

Feed: HNO_3 containing varying conc. of uranium and plutonium and 100.000 g/L Th in presence of 0.10 M Al^{3+} and 0.03 M F^- ions, Organic to aqueous phase ratio (O:A) = 1:1, Contact time = 15 min.

Composition of feed			Distribution ratio		
HNO_3 (M)	U (g/L)	Pu (g/L)	U	Pu	Th
3.50	0.00	Trace	–	1.27	<0.1
	1.000	Trace	4.42	1.21	<0.1
	2.500	Trace	2.72	1.18	<0.1
	5.000	Trace	2.65	1.09	<0.1
	7.500	Trace	2.50	0.96	<0.1
	10.000	Trace	2.21	0.72	<0.1
4.00	4.000	0.000	2.89	–	<0.1
	4.000	2.050	3.24	1.22	<0.1
	4.000	4.220	2.97	1.18	<0.1
	4.000	6.110	3.11	1.21	<0.1

TABLE 2
Extraction of UO_2^{2+}, Pu^{4+} and Th from HNO_3 medium using 5% TBP in n-dodecane

Experimental condition
Feed: Nitric acid containing U, Pu Th in presence of Al^{3+} and F^- ions, Extractant: 5% TBP n-dodecane, Volume of aqueous phase: 2 mL, Contact time: 15 min.

			Distribution ratio		
S. No.	Feed composition	Phase ratio	D_U	D_{Pu}	D_{Th}
1	[Thorium] = 100.000 g/L [Plutonium] = 1.970 g/L [Uranium] = 2.000 g/L	2:1	2.88	1.15	<0.1
	$[Al(NO_3)_3]$ = 0.10 M [HF] = 0.03 M $[HNO_3]$ = 3.50 M	3:1	2.65	1.14	<0.1
2	[Thorium] = 100.000 g/L [Plutonium] = Trace level [Uranium] = 4.000 g/L	2:1	2.36	1.41	<0.1
	$[Al(NO_3)_3]$ = 0.10 M [HF] = 0.03 M $[HNO_3]$ = 3.50 M	3:1	2.34	1.27	<0.1

improved in actual practice by employing higher organic to aqueous phase ratios of 2:1 or 3:1.

The results from the experiments carried out at a higher organic to aqueous phase ratios of 2:1 and 3:1 are shown in Table 2. Distribution ratios of uranium, plutonium, and thorium remained similar to those obtained from the experiments using the phase ratio of 1:1.

During the extraction step co-extracted thorium is required to be scrubbed using appropriate concentration of nitric acid. Table 3A shows the release of plutonium in the aqueous phase from a plutonium loaded 5% TBP-n-dodecane phase containing plutonium alone at an organic to aqueous phase ratio of 1:1 using varying concentrations of nitric acid (0.50–4.00 M HNO_3). Distribution ratios obtained for plutonium are also given in the same table. Similar scrubbing experiments are also carried out using the loaded organic phase generated from extraction experiments using feed solutions containing U, Pu, and Th at concentration levels of the feed solution corresponding to AHWR spent fuel reprocessing. Trends in the distribution ratios are observed to be more or less similar in both cases. These results are given in Table 3B.

Subsequent to extraction, stripping studies are carried out. Reductive stripping of plutonium by HAN is considered due to its proven performance in many PUREX plants. HAN has been used in combination with nitric acid and HN (20). The reduction of Pu^{4+} (21) per the following reaction

$$2NH_3^+OH + 2Pu^{4+} \rightarrow 2Pu^{3+} + N_2 + 2H_2O + 4H^+ \quad (1)$$

Table 4 gives the results of the reductive stripping of plutonium from an organic phase loaded with Pu alone.

TABLE 3A
Scrubbing of Pu from Pu-loaded 5% TBP in n-dodecane phase using different concentration of HNO_3

Experimental parameters
Conc. of Pu in organic feed used for scrubbing studies = 2.130 g/L, [This organic feed for scrubbing experiment was prepared by contacting 3 mL pure Pu solution $[Pu^{4+}]$ = 5.260 g/L at 3.50 M HNO_3 twice with 3 mL of 5%TBP in n-dodecane and mixing both the loaded organic phases to get the mix organic phase]
Phase ratio: 1:1, Volume: 2 mL for each phase, Contact time: 15 min.

$[HNO_3]$, M used for Scrubbing	4.00	3.00	2.00	1.00	0.50
D_{Pu}	1.33	1.09	0.58	0.20	0.05

TABLE 3B

Scrubbing of Pu from Pu-loaded 5% TBP in n-dodecane phase using different concentration of HNO_3: Studies from synthetic AHWR feed solution

Experimental parameters

Conc. of Pu in organic feed used for scrubbing studies = 1.340 g/L [This organic feed was prepared by contacting 6 mL synthetic AHWR feed solution with [Th] = 100.100 g/L, $[Pu^{4+}]$ = 2.080 g/L, $[UO_2^{2+}]$ = 2.040 g/L, $[Al^{3+}]$ = 0.11 M, $[F^-]$ = 0.03 M at 3.50 M HNO_3 twice with 3 mL 5%TBP in n-dodecane and mixing the loaded organic phases]

Phase ratio: 1:1, Volume: 2 mL for each phase, Contact time: 15 min.

$[HNO_3]$, M used for Scrubbing	4.00	3.00	2.00	1.00	0.50
D_{Pu}	1.00	0.91	0.32	0.29	0.07

Two different concentrations of HAN (0.20 and 0.30 M) are used in varying concentrations of nitric acid (0.30–1.00 M). Nitric acid concentration lower than 0.30 M is not considered as plutonium undergoes hydrolysis (22) under these conditions. Results indicate plutonium stripping above 99% when the concentration of nitric acid is below 0.80 M. These concentrations of HAN are sufficiently higher than that required for the stoichiometric reduction of Pu used in the study. At both concentrations of HAN, marginally less stripping of Pu is noticed when 1.00 M HNO_3 is used.

The results of uranium stripping under similar conditions are shown in Table 5. In these batch experiments, concentration of uranium is varied in the concentration range as expected in the loaded TBP phase in the first extraction cycle of AHWR spent fuel reprocessing. As concentration of nitric acid in the partitioning reagent decreases, uranium release to the aqueous phase increases which accompany the plutonium stream during partitioning. Based on these results, the concentration of nitric acid in the partitioning reagent is fixed in the range of 0.30–0.60 M for efficient Pu partitioning though under these conditions uranium back extraction is unavoidable.

TABLE 4

Optimization of strippant (HAN + HNO_3) for Pu stripping from Pu loaded 5%TBP phase

Experimental parameters

Organic feed: $[Pu^{4+}]$ = 1.510 g/L, Organic to aqueous Phase ratio: 1:1, Volume: 2 mL each, Contact time: 15 min.

Strippant composition (M)		
HAN	HNO_3	Pu-stripping (%)
0.20	0.30	99.92
	0.60	99.56
	0.80	98.95
	1.00	97.25
0.30	0.30	99.94
	0.60	99.75
	0.80	99.18
	1.00	97.54

Table 6 gives the results on partitioning of plutonium using 0.20 and 0.30 M HN in the presence of varying concentrations of nitric acid (0.30–1.00 M). The results clearly illustrate slower kinetics of Pu stripping when HN alone in nitric acid is used as strippant. More than 99% stripping is achieved in 0.30 M HNO_3 (lowest HNO_3 concentration limit to avoid Pu hydrolysis), but this requires around 72 h. At 10 min. < 92% stripping is only achieved. Moreover, stripping may be due to reduced nitrate concentration in the aqueous phase. Hence a study is conducted to understand the kinetics of stripping and also the effect of nitrate concentration in the aqueous phase.

The results of Pu stripping from Pu loaded TBP phase carried out using lower concentrations of nitric acid and nitric acid +HN are shown in Fig. 1. The figure presents the percentage stripping of Pu as a function of log time. These results indicate that stripping is a function of nitrate ion concentration rather than the effect of HN.

Reductive stripping of Pu is studied from the uranium loaded organic phase using varying concentration of HAN and nitric acid. The results are given in Table 7. The results indicate that HAN in the concentration range of 0.10 to 0.30 M is an effective reducing agent at lower acidities (<1 M). At very low acid concentration >70% uranium is also stripped along with Pu. Hence, re-extraction of uranium from the stripped aqueous product with TBP is necessary to separate plutonium from uranium.

The effect of higher organic to aqueous phase ratio is studied in a set of experiments to look into the feasibility of obtaining a concentrated Pu product. In these studies

TABLE 5
Stripping behaviour of uranium from organic phase using mixture of HAN and HNO_3

Experimental parameters
Organic Phase: U loaded in 5% TBP, Aqueous phase: HAN + HNO_3, Phase ratio: 1:1, Volume: 2 mL, Contact time: 15 min.

Strippant composition (M)		$[UO_2^{2+}]$ in organic feed (g/L)	Conc. of U in the aq. phase at equilibrium (g/L)	Conc. of U in the org. phase at equilibrium (g/L)
HAN	HNO_3			
0.30	0.30	2.000	1.740	0.530
	0.60		1.570	0.680
	0.80		1.010	1.050
	1.00		1.000	1.070
	0.30	3.000	2.620	0.780
	0.60		2.240	1.000
	0.80		1.650	1.380
	1.00		1.590	1.550
	0.30	4.000	3.390	0.900
	0.60		2.810	1.400
	0.80		2.220	1.870
	1.00		2.100	2.060

0.20 M HN is added as a holding reductant along with 0.30 M HAN for stripping Pu from the organic phase as HN is reported to be a better scavenger (20) for HNO_2. Results from these experiments are given in Table 8. Organic to aqueous phase ratios are varied in the range of 1 to 8. Results indicate that lower acidities of 0.30–0.60 M is an optimum range for operation. Even though a higher organic to aqueous phase ratio is capable of retaining more of uranium in the organic phase, hydrodynamic parameters may not be suitable beyond a ratio of 5.

TABLE 6
Reductive stripping of Pu from loaded TBP phase using HN and HNO_3

Experimental parameters
Organic feed: $[Pu^{4+}]$: 1.700 g/L, organic to aqueous phase ratio: 1:1, Volume: 2 mL each.

Strippant composition (M)		Percent Pu-stripping after	
HN	HNO_3	10 min	72 h
0.20	0.30	92.41	99.74
	0.60	86.00	99.27
	0.80	80.94	98.84
	1.00	67.29	97.81
0.30	0.30	92.71	99.77
	0.60	82.59	99.75
	0.80	81.65	99.31
	1.00	70.00	98.57

Table 9 gives the extraction studies of uranium from an aqueous phase containing HAN + HNO_3 and HN along with Pu^{3+} under conditions similar to that obtained from partitioned plutonium product solutions after adjusting the acidity to 3.50 M. Results show the possibility of complete partitioning of Pu from uranium by providing the

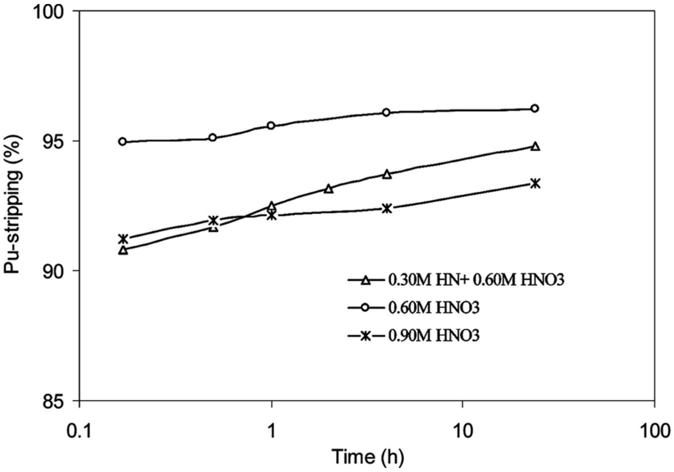

FIG. 1. Stripping of Pu from Pu loaded TBP phase using HNO_3 and its mixture with HN as a function of time [Organic feed: $[Pu^{4+}]$: 0.659 g/L, Phase ratio: 1:1, Volume: 5 mL for each phase].

TABLE 7
Reductive stripping of Pu using a mixture of HAN + HNO_3

Experimental conditions
Organic feed: 5% TBP in n-dodecane loaded with uranium and plutonium Organic to aqueous phase ratio (O: A) = 2:1, Contact time: 15 min.

Organic feed			Strippant		% Stripping	
$[UO_2^{2+}]$ (g/L)	$[Pu^{4+}]$ (g/L)	HNO_3 (M)	HAN (M)	HNO_3 (M)	U	Pu
2.586	1.419	0.09	0.10	0.30	71.50	99.74
2.586	1.419	0.09	0.10	1.00	39.06	91.04
2.586	1.419	0.09	0.10	3.00	14.08	35.45
2.294	1.991	0.10	0.20	0.30	54.23	99.65
2.294	1.991	0.10	0.30	0.30	45.03	99.75

TBP re-extraction step. Based on these studies 0.30 M HAN in 0.30–0.60 M HNO_3 range containing 0.20 M HN is selected as the partitioning agent.

The results on the stability of Pu as Pu^{3+} in HNO_3 + HAN + HN medium at three different concentration of nitric acid are given in Fig. 2. In these experiments 30% TBP in n-dodecane is used as an extractant which extracts Pu as Pu^{4+} from the aqueous nitrate medium. The plots show that Pu extraction remains constant and very low due to its stability in the trivalent state. At least up to 28 days almost all Pu remained in Pu^{3+} state. Any conversion to tetravalent state should have shown an increased extraction in the TBP phase. These results are in concurrence with literature data reported earlier (20). As expected, extraction increases with increasing concentration of nitrate in the aqueous phase due to a salting out effect. These results clearly indicate that after co-stripping of uranium and plutonium to aqueous phase using a partitioning reagent (HAN + HN + HNO_3), the aqueous phase nitric acid concentration can be adjusted in the range of 3.00–3.50 M to extract uranium to TBP phase leaving Pu^{3+} in the aqueous phase. A small concentration of Pu is co-extracted to the organic phase in its tri valent state.

Results of batch studies carried out using a few potential reducing agents (16,17,23,24) for the partitioning

TABLE 8
Partitioning of Pu and U from organic phase at varying organic to aqueous phase ratio

Experimental conditions
Feed: 5% TBP n-dodecane phase generated from mixer-settler experiment containing $[UO_2^{2+}] = 1.380$ g/L, $[Pu^{4+}] = 0.858$ g/L and $[H^+] = 0.09$ M, Organic to aqueous phase ratio (O: A) = varying, Contact time = 15 min.
Partitioning reagent conc. = 0.30 M HAN + 0.20 M HN in varying concentration of HNO_3

$[HNO_3]$ in HAN + HN medium	An	% of An in stripped organic phase at phase ratio (O/A)					
		1:1	2:1	3:1	5:1	7:1	8:1
0.30 M	[Pu]	0.48	0.61	1.47	3.15	5.80	8.31
	$[UO_2^{2+}]$	29.71	50.00	63.77	73.19	81.16	89.13
0.60 M	[Pu]	0.93	2.06	3.95	6.52	12.93	15.29
	$[UO_2^{2+}]$	40.17	56.82	71.01	78.62	87.36	91.27
1.00 M	[Pu]	2.74	5.34	7.79	18.67	26.06	29.30
	$[UO_2^{2+}]$	57.25	68.84	78.26	85.51	92.38	93.12
2.00 M	[Pu]	17.66	25.14	33.91	56.90	61.59	63.10
	$[UO_2^{2+}]$	68.85	75.81	84.78	89.12	93.89	94.28
3.50 M	[Pu]	28.45	51.75	53.26	58.89	64.97	66.05
	$[UO_2^{2+}]$	82.43	87.16	90.54	92.56	96.19	96.62

TABLE 9

Extraction of uranium from aqueous phase containing HAN + HNO_3 + HN using 5% TBP in n-dodecane

Experimental conditions

Feed: Aqueous phase adjusted to 3.50 M HNO_3 containing U and Pu in presence of varying concentration of HAN and 0.20 M HN.
Phase ratio (O: A) = 1:1, 2) Contact = 15 min.

Feed					Organic phase			% Extraction	
			Acidity (M)						
HAN (M)	U (g/L)	Pu (g/L)	Initial	Adjusted	U (g/L)	Pu (g/L)	HNO_3 (M)	U	Pu
0.10	1.827	2.641	0.30	3.50	1.731	0.126	0.01	94.74	4.77
0.20	1.659	2.645	0.30	3.50	1.571	0.034	0.01	94.70	1.28
0.30	1.377	2.648	0.30	3.50	1.305	0.026	0.02	94.77	0.98

of plutonium from uranium are given in Table 10. As explained in the experimental section, feed used in these experiments is loaded organic from counter-current extraction runs. For comparison, the concentration of each reagent is kept at 0.10 M in 2.00 M nitric acid medium. Higher concentration of nitric acid is selected to study the retention of uranium in the organic phase. TBH and FAS show highest efficiency of stripping for Pu. Based on the Pu retention values in the organic phase, the efficiency of stripping is found to be in the order TBH > FAS > AHA > AA > HAN.

Among the reagents used, FAS is not studied further as it will introduce sulphate ions in subsequent process streams that may cause corrosion in addition to the contribution of iron impurity. TBH and AHA have shown good performance in the reductive partitioning of Pu. TBH is organic soluble and can reduce the Pu in the organic phase. The use of hydroquinone has been reported to be effective for the partitioning of Pu from the loaded TBP phase (16). Limitations on its use in counter-current studies are also reported. Both these reagents have not yet been studied in plant scale application. AA, a complexing reagent, is also not preferred in the plant scale operation. HAN is used (20) in the PUREX process and enough operating experience on the plant scale is available. It has been shown that at higher acidity it shows a degraded performance. In

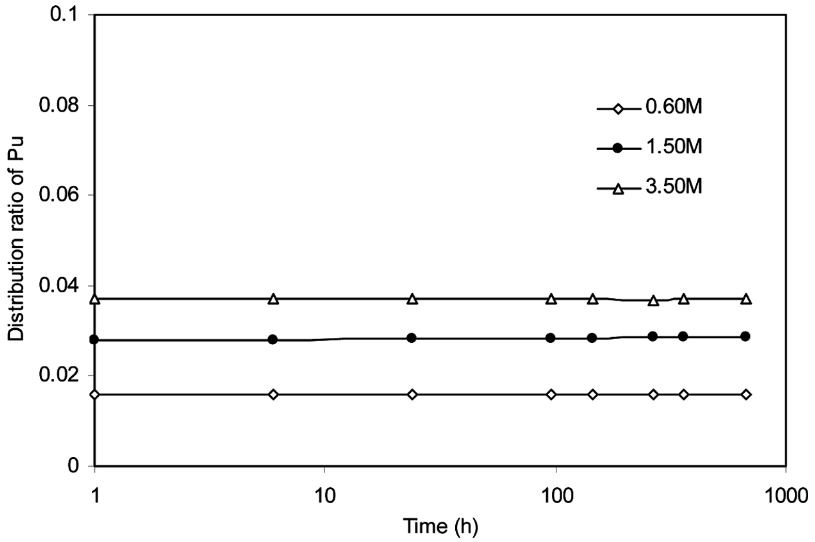

FIG. 2. Stability of Pu as Pu^{3+} in aqueous medium containing HAN + HNO_3 + HN [Experimental parameters: Aq. phase: HNO_3 containing 0.30 M HAN + 0.20 M HN, Concentration of Pu in Aq. phase: 2.000 g/L, Extractant: 30% TBP in n-dodecane, Phase ratio 1:1, Contact time 15 min.].

TABLE 10
Reductive partitioning of Pu from U from 5% TBP phase using various reagents

Experimental conditions
Initial concentration of actinides in the organic feed: [Pu] = 0.800 g/L, $[UO_2^{2+}] = 1.380$ g/L, $[H^+]_{org} = 0.09$ M, Organic to aqueous phase ratio (O/A): 1, Volume of each phase = 2 mL, Contact Time = 15 min, Concentration of each reagent: 0.10 M in 2.00 M HNO_3

	Retention in organic phase (%)	
Reagents	Plutonium	Uranium
AHA	3.38	57.97
HAN	12.46	57.98
FAS	0.09	52.90
TBH	0.01	66.66
AA	8.88	53.62

the proposed flow-sheet of AHWR spent fuel processing, 5% TBP in n-dodecane is being used as extractant which does not extract nitric acid to the same extent as 30% TBP in n-dodecane. Additionally, in the presence of uranium and plutonium, acid extraction will be reduced. Hence, it is preferred for Pu partitioning.

The results of decontamination with respect to some relevant fission products are shown in Table 11. Results indicate the decontamination factors of the order of 10^3 for all the fission products relevant to reprocessing. During the experiment, though Sr analysis is not carried out, its behavior is expected to be similar to that of Cs.

Table 12 shows the concentration profile of U, Pu, and Th in feed, organic phases, and final raffinate in successive contacts in the co-current mode at 1:1 and 1:2 O/A phase ratios using 5% TBP in n-dodecane. It is clear from the data that the extraction efficiency decreases in the order U > Pu > Th. In both cases uranium can be extracted quantitatively in less than 7 contacts whereas for >99.5% extraction of Pu, nine and seven stages are required when the organic to aqueous phase ratios of 1:1 and 2:1 are used respectively. In case of thorium, it can be seen that almost a constant uptake of ~5 g/L is observed throughout successive extractions when a 1:1 O/A is used. Slow decrease towards the end stages may be due to change in the total nitrate content of the feed. Variation of thorium extraction by 5% TBP is clearly discernible in case of 1:2 phase ratio. In this case, extraction of thorium passes through a maximum due to increase in the availability of free TBP after the major uptake of uranium and plutonium. Decrease in the end stages is due to decrease in total nitrate as in 1:1 case.

Based on these studies a flow-scheme is proposed (Fig. 3) for three component processing of irradiated (Th-Pu)O_2 spent fuel arising from AHWR.

TABLE 11
Distribution of fission products during extraction

Experimental parameters
Feed: Aqueous phase containing [Th] = 100.100 g/L, $[Pu^{4+}] = 2.080$ g/L, $[UO_2^{2+}] = 2.040$ g/L, $[Al^{3+}] = 0.11$ M and $[F^-] = 0.03$ M at 3.50 M HNO_3 spiked with FPs from diluted PUREX-HLLW, Extractant: 5% TBP in n-dodecane, Phase ratio: 1:1, Volume: 2 mL for each phase, Contact time: 15 min.

	Activity in equilibrated phases (mCi/L)		
Fission product	Organic phase	Aqueous phase	Distribution ratio
^{144}Ce	$<8 \times 10^{-5}$	0.850	$<10^{-3}$
^{137}Cs	$<2 \times 10^{-5}$	0.200	$<10^{-3}$
^{106}Ru	$<2 \times 10^{-4}$	0.210	$<10^{-3}$
^{95}Nb	ND	0.007	$<10^{-3}$

TABLE 12

Extraction of uranium, plutonium and thorium in Co-current mode using 5% TBP in n-dodecane

Experimental conditions

Feed used for Extraction: 3.50 M HNO_3 containing [Th] = 100.000 g/L, [[UO_2^{2+}] = 2.000 g/L, [Pu^{4+}] = 2.000 g/L, $Al(NO_3)_3$ = 0.10 M and HF = 0.03 M, Contact time: 15 min. each.

	Concentration of actinide in organic phase					
	1:1			2:1		
Sample	[UO_2^{2+}]	[Pu^{4+}]	[Th]	[UO_2^{2+}]	[Pu^{4+}]	[Th]
O-1	1.414 g/L	1.154 g/L	5.650 g/L	0.812 g/L	0.586 g/L	2.810 g/L
O-2	0.524 g/L	0.549 g/L	5.590 g/L	0.183 g/L	0.168 g/L	3.000 g/L
O-3	0.105 g/L	0.209 g/L	5.410 g/L	0.052 g/L	0.077 g/L	3.380 g/L
O-4	0.037 g/L	0.075 g/L	4.990 g/L	0.026 g/L	0.026 g/L	3.170 g/L
O-5	0.016 g/L	0.032 g/L	5.180 g/L	0.016 g/L	0.013 g/L	3.490 g/L
O-6	0.002 g/L	0.012 g/L	5.270 g/L	0.005 g/L	0.004 g/L	3.250 g/L
O-7	ND	0.004 g/L	5.260 g/L	ND	0.001 g/L	3.420 g/L
O-8	ND	0.002 g/L	4.480 g/L	ND	0.650 mg/L	2.990 g/L
O-9	ND	0.001 g/L	4.680 g/L	ND	0.410 mg/L	2.910 g/L
O-10	ND	0.810 mg/L	4.580 g/L	ND	0.240 mg/L	2.710 g/L
O-11	ND	0.340 mg/L	4.540 g/L	ND	0.090 mg/L	2.140 g/L
O-12	ND	0.220 mg/L	4.530 g/L	ND	0.070 mg/L	2.060 g/L
Final Raffinate	ND	ND	40.000 g/L	ND	ND	26.400 g/L

ND: Below detection limit.

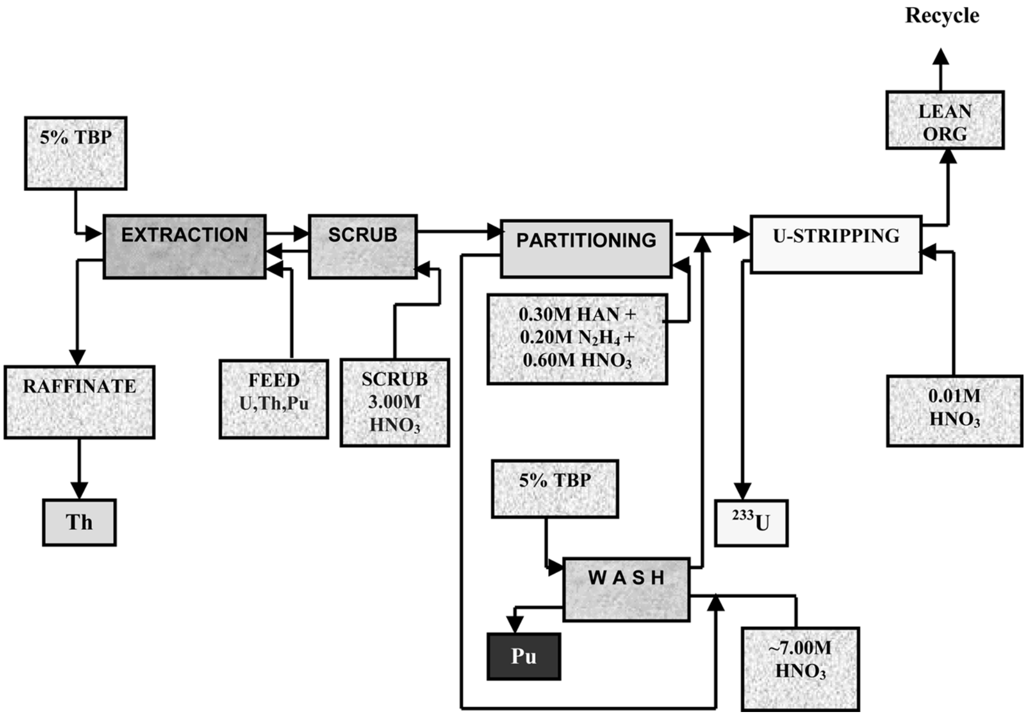

FIG. 3. Schematic flow-sheet for three component separation from AHWR spent fuel.

CONCLUSIONS

Batch extraction studies under simulated spent fuel composition of irradiated (Th-Pu)O_2 fuel arising from AHWR were carried out to evolve a process scheme for a three-component separation. Studies clearly indicate 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 are evaluated. HAN along with HN is studied in detail to establish and optimize the striping parameters. Even though HAN is selected as the choice of reductant due to the large-scale experience, efficacy of a few other potential alternatives are also reported. Based on the co-current extraction data a flow-scheme is proposed for a three-component separation.

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REFERENCES

1. Srinivasan, M.; Kimura, I. (eds.). (1990) Thorium utilization, Proceedings of the Indo-Japan Seminar on Thorium Utilization, December, 10–13, Bombay, India.
2. Anantharaman, K.; Shivakumar, V.; Saha, D. (2008) Utilization of thorium in reactors. *Journal of Nuclear Materials*, 383: 1191.
3. Anantharaman, K.; Ramanujam, A.; Kamath, H.S.; Majumdar, S., Vaidya, V.N.; Venkataraman, M. (2000) Thorium based Fuel Reprocessing and Refabrication Technologies and Strategies, INSAC-2000 on Power from Thorium: Status, Strategies and Directions, Mumbai, India, 1: 107.
4. Srinivasan, N.; Nadkarni, M.N.; Balasubramaniam, G.R.; Chitnis, R.T.; Siddiqui, H.R. (1972) Pilot plant for the separation of ^{233}U at Trombay, BARC Report-643.
5. Balasubramaniam, G.R.; Chitnis, R.T.; Ramanujam, A.; Venkatesan, M. (1977) Laboratory studies on the recovery of uranium-233 from irradiated thorium by solvent extraction using 5% TBP Shell Sol-T as solvent, BARC Report-940.
6. Chitnis, R.T.; Rajappan, K.G.; Kumar, S.V.; Nadkarni, M.N. (1979) Cation Exchange Separation of Uranium from thorium, BARC Report-BARC-1003.
7. Mukherjee, A.; Kulkarni, R.T.; Rege, S.G.; Achuthan, P.V. (1982) Anion exchange separation of uranium from thorium for the tail-end purification of ^{233}U in THOREX process. Board of Research in Nuclear Sciences. Radiochemistry and radiation chemistry symposium, Pune, India, Paper No. SC-12, December 7–11.
8. Ramanujam, A.; Dhami, P.S.; Gopalakrishnan, V.; Mukherjee, A.; Dhumwad, R.K. (1989) Separation and Purification of uranium product from thorium in THOREX process by precipitation technique, BARC Report-496.
9. Achuthan, P.V.; Janardanan, C.; Vijayakumar, N.; Kutty, P.V.E.; Mukherjee, A.; Ramanujam, A. (1993) Studies on the separation of thorium and uranium on variously cross linked Dowex 50 W Resins, BARC Report-E/09.
10. Govindan, P.; Palamalai, A.; Vijayan, K.S.; Raja, M.; Parthasarathy, S.; Mohan, S.V.; Subba Rao, R.V. (2000) Purification of ^{233}U from thorium and iron in the reprocessing of irradiated thorium oxide rods. *Journal of Radioanalytical and Nuclear Chemistry*, 246 (2): 441.
11. Chitnis, R.R.; Dhami, P.S.; Ramanujam, A.; Kansara, V.P. (2001) Recovery of ^{233}U from irradiated thorium fuel in THOREX process using 2% TBP as extractant. BARC Report-E/030.
12. Achuthan, P.V.; Dhami, P.S.; Dakshinamoorthy, A.; Diwakar, D.S.; Vijayan, K.; Kannan, R.; Sumankumar Singh, Jambunathan, U.; Dey, P.K. (2003) Analysis of irradiated thoria dissolved solution. BARC Report-I/002.
13. Mishra, R.K.; Sengupta, P.; Kaushik, C.P.; Taygi, A.K.; Kale, G.B.; Raj, K. (2007) Studies on immobilization of thorium in barium borosilicate glass. *J. Nuclear. Materials*, 360: 143.
14. Sinha R.K.; Kakodkar, A. (2006) Design and Development of the AHWR-the Indian thorium fuelled innovative nuclear reactor. *Nuclear Engineering and Design*, 236: 683.
15. Kutty, T.R.G.; Khan, K.B.; Achuthan, P.V.; Dhami, P.S.; Dakshinamoorthy, A.; Somayajulu, P.S.; Panakkal, J.P.; Arun Kumar; Kamat, H.S. (2009) Characterisation of ThO_2-UO_2 pellets made by co-precipitation process. *Journal of Nuclear Materials*, 389: 351.
16. Grant, G.R.; Morgan, W.W.; Mehta, K.K.; Sargent, F.P. (1980) Heavy Element Separation for Thorium-Uranium-Plutonium Fuel. In: *Actinide Separation, ACS Symposium Series 117*, Navratil, J.D.; Schulz, W.W., eds.; Washington, D.C., 351–369.
17. Schulz, W.W. (1965) Pacific Northwest Laboratory Report, BNWL-57.
18. USAEC report, TID No. 1015, method 1218710. (1954) Thorium, Spectrophotometric Thoron Method.
19. Das, S.K.; Rege, S.G.; Mukherjee, A.; Ramanujam, A.; Dhumwad, R. K. (1991) Direct spectrophotometric method for the determination of microgram quantities of uranium with Bromo-PADAP in aqueous and organic waste streams of PUREX and THOREX processes. BARC Report-539.
20. Malvyn Mckibben, J.; Bercaw, J.E. (1971) Hydroxylammine nitrate as a plutonium reductant in the PUREX Solvent Extraction Process. USAEC Report DP-1248, *E.I.DUPONT DE NEMOURS & COMPANY, SAVANNAH RIVER LABORATORY, AIKEN, S.C.* 29801, Jan.
21. Schulz, W.W.; Burger, L.L.; Navratil, J.D.; Bender, K.P. (1990) *Science and Technology of Tributyl Phosphate, Vol. 3*; CRC Press, Inc.: Boca Raton, Florida.
22. Wei, Y.; Kumagai, M.; Takashima, T.; Bruggeman, A.; Gysemans, M. (1999) A rapid elution method of tetravalent plutonium from anion exchanger. *J. Nucl. Sci. Technol.*, 36 (3): 304.
23. Chitnis, R.R.; Wattal, P.K.; Ramanujam, A.; Dhami, P.S.; Gopalkrishnan, V.; Mathur, J.N.; Murali, M.S. (1998) Separation and recovery of uranium, neptunium and plutonium from high level waste using tributyl phosphate: Counter-current studies with simulated waste solution. *Sep. Sci. Technol.*, 33 (12): 1887.
24. Taylor, R.J.; May, I.; Wallwork, A.L.; Denniss, I.S.; Hill, N.J.; Galkin, B.Ya.; Zilberman B.Ya.; Fedorov, S.Yu. (1998) The application of formo- and aceto-hydroxamic acids in nuclear fuel reprocessing. *J. Alloys Compds.*, 534: 271.