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Tert-butyl hydroquinone: A promising reductant of plutonium for process and analytical applications

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ABSTRACT

Tert-butyl hydroquinone (TBH) has been evaluated as a plutonium reductant for reprocessing and analytical applications. The effect of nitric acid concentration on plutonium reduction efficiency of TBH and its recycling are investigated under conditions prevailing in the uranium purification cycle of the PUREX process. A solvent extraction method has been developed for the separation of trace concentrations of uranium (3–30 μg/mL) from plutonium solution (10–12 mg/mL) obtained on dissolution of plutonium oxide in HNO_3 containing traces of HF. The method involves the selective extraction of U(VI) with a mixed solvent comprising 1% trialkyl phosphine oxide (TRPO) + 1.1 M tri-*n*-butyl phosphate (TBP) + 0.4 M TBH solution in *n*-dodecane from 3 M HNO_3–0.4 M N_2H_4, while reducing Pu(VI)/Pu(IV) to inextractable Pu(III) using salt-free reductants TBH (organic phase) and hydrazine (aqueous phase). A decontamination factor of ~150 with respect to Pu has been achieved. This method has been adopted for routine analysis of uranium in PuO_2 samples by Inductively Coupled Plasma–Atomic Emission Spectroscopy (ICP-AES).

Keywords: Uranium; Plutonium; TBP; *Tert*-butyl hydroquinone; Reductant

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1. Introduction

The PUREX process has been in use worldwide for almost five decades. It employs 1.1 M tri-*n*-butyl phosphate (TBP) solution in *n*-dodecane as the solvent and is based on the principle of co-extraction of Pu(IV) and U(VI) as $Pu(NO_3)_4\cdot 2TBP$ and $UO_2(NO_3)_2\cdot 2TBP$ from ~3 M HNO_3 [1]. Mutual separation of U and Pu is achieved by reducing Pu(VI)/Pu(IV) to inextractable Pu(III) without affecting the oxidation state of U. An aqueous U(IV) solution stabilized with 0.2 M hydrazine at 1 M HNO_3 is introduced in the partitioning column to strip Pu from the U bearing organic phase that leaves the column. Back extraction of uranium is carried out by contacting the organic phase with 0.01 M HNO_3. The solvent after this cycle is generally sent for sodium carbonate wash to remove the degradation products of TBP. The aqueous dilute and impure U product is fed to evaporators for concentration (300–350 g/L) and after conditioning at ~1 M HNO_3 with U(IV)-hydrazine, which reduces Pu(IV) to Pu(III), is fed to the compound contactor where U is again extracted by 1.1 M TBP-*n*-dodecane to a higher saturation level leaving Pu(III) and fission products as impurities in the aqueous phase. U of the loaded solvent is stripped into the aqueous phase with 0.01 M HNO_3 in another column. The final purified U product is con-

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centrated, precipitated as ammonium diuranate, filtered and calcined to get U_3O_8 powder. Whereas the practice of using U(IV)-hydrazine mixture does not lead to any additional burden on the volume of secondary waste, it adds to the uranium processing load thereby affecting plant throughput. Also, the use of hydrazine in nitric acid medium forms ammonium nitrate/azides which are explosive in nature. In view of these problems, there is a need to improve the present step of U purification as a part of spent nuclear fuel reprocessing.

Plutonium oxide and uranium oxide are the main products of the PUREX process and are used in the manufacture of ceramic oxide fuels for nuclear reactors. The chemical quality control requirements of PuO_2 product involve the determination of exact quantity of uranium, which is usually present in the range of 300–3000 ppm in plutonium oxide. The commonly used spectroscopic analytical methods like spectrophotometry and Inductively Coupled Plasma–Atomic Emission Spectrometry (ICP-AES) for uranium determination in plutonium oxide, suffer severe interference from Pu matrix [2,3]. Therefore, the chemical separation of the trace uranium present in plutonium oxide becomes mandatory prior to its determination. Conventionally, solvent extraction and ion exchange methods are employed for this purpose [4,5]. The solvent extraction method involves the selective extraction of U(VI) by tri-*n*-octyl phosphine oxide (TOPO) after reduction of Pu(VI)/Pu(IV) to inextractable Pu(III) with ferrous sulphamate; the ion-exchange method involves the selective adsorption of the anionic species of uranium, e.g. $UO_2Cl_3^-$ and $UO_2Cl_4^{2-}$ on anion exchange resin from 6 to 8 M HCl after reduction of Pu(VI)/Pu(IV) to Pu(III) using $NH_2OH{\cdot}HCl$ – $SnCl_2$ reducing mixture. Although these methods demonstrate effective separation of U from Pu, they suffer from the limitation of generation of aqueous analytical waste in undesirable form that contains significant amounts of Pu (~10–12 mg per sample analysis). Recovery of Pu from such waste solutions prior to their final disposal requires additional efforts.

Grossi reported the use of organic soluble hydroquinones as reductants for Pu(VI)/Pu(IV) to Pu(III) and Np(VI) to Np(V) from nitric acid medium [6]. It was observed that quantitative reduction of plutonium (>99.99%) could be easily achieved using 2, 5-di-*tert*-pentylhydroquinone ($DTPQH_2$) as the reductant in the acidity range 0.3–3 M HNO_3 by maintaining Pu-reductant concentration ratio as 1–10. The large concentrations of uranium (~100 g/L) in the aqueous phase had no influence on the reduction behavior of plutonium. The reduction kinetics for both Pu(IV) and Pu(VI) ions in the aqueous phase was favorable and further improved at elevated temperature (50°C). Grant et al. evaluated the use of this class of reagents for the reduction of plutonium in the organic phase during the process development studies on U-Th-Pu spent fuels [7]. Earlier, in our laboratory, a combination of *N,N*-diethylhydroxylamime (DEHAN) and *tert*-butyl hydroquinone (TBH) were found to be effective for selective extraction of uranium over Pu from high level waste solution at ~1 M HNO_3 [8]. There are reports suggesting the rapid reoxidation of Pu(III) to Pu(IV) by the HNO_2 extracted by TBP towards the organic phase [7] resulting in the reduced separation factor (SF) of U with respect to Pu. It was, therefore, of interest to explore organophilic reductants like substituted hydroquinones.

The focus of the present work is to optimize the chemical conditions for the selective extraction of uranium over plutonium in the (i) uranium purification cycle of the PUREX process, and (ii) trace U assay of PuO_2 using a non salt forming organic soluble reductant, TBH.

2. Experimental

2.1. Materials

Pu (principally ^{239}Pu, ~10^{-5} M) was purified by 2-thenoyltrifluoroacetone (HTTA) extraction method and used after ascertaining the radiochemical purity by alpha as well as gamma spectrometry [9]. ^{233}U tracer (~10^{-4} M) was purified by anion exchange to eliminate the daughter products of ^{232}U [10]. TBH (purity: 98%) from Loba Chemie, India, was used as received. Other reagents such as TBP, TOPO and n-dodecane were of extraction grade and were used without further purification.

2.2. Dissolution of plutonium oxide powder

Approximately 700 mg PuO_2 powder was digested in 15 mL of concentrated HNO_3 – 0.1 M HF at 100°C in a 50 mL Teflon beaker. The resulting solution was quantitatively transferred to 50 mL volumetric flask and made to volume with using 1 M HNO_3. The solution was assayed for Pu and HNO_3 concentrations by coulometry and potentiometry respectively [11,12]. Pu concentration was found to be 12.3 g/L, while HNO_3 concentration was 5.1 M.

2.3. Extraction experiments

Solvent extraction experiments were carried out by equilibrating equal volumes (unless stated otherwise) of the organic and aqueous phases in 15-mL capacity glass vials for 10 min at ambient temperature. Pu and U assay of the phases were done by radiometry using alpha-scintillation counting system coupled with ZnS(Ag) detector for Pu; while liquid scintillation counting system was used for ^{233}U. The assay of ^{233}U samples for uranium purification cycle containing ~300 g/L of natural U, were corrected for background contribution due to large concentrations of uranium and its decay products. Distribution ratio (D_M) was defined as the ratio of analytical concentration of Pu or U (expressed in terms of counts per unit time per unit volume) in the organic phase to that of the aqueous phase.

Material balance and reproducibility of the extraction data was within error limits (±5%). Uranium analysis after extraction from PuO_2 samples was done by ICP-AES [13]

3. Results and discussion

3.1. Evaluation of TBH as reductant in uranium purification cycle

Solvent extraction experiments were carried out to investigate the effect of aqueous phase acidity (1–3 M HNO_3) on the performance of TBH as reductant for plutonium. Fig. 1 clearly demonstrates that with the increased aqueous phase acidity, the efficiency of TBH to reduce Pu(VI)/Pu(IV) decreases. This behaviour can be attributed to the oxidation of TBH with nitric acid forming *tert*-butyl quinine (deep yellow in colour) and HNO_2. Nitrous acid so formed oxidises Pu(III) to Pu(IV) resulting in enhanced extraction of Pu(IV) with TBP [7].

Conventional feed composition for U-purification cycle is ~300–350 g/L U + 10–20 ppm Pu in 0.75–1.0 M HNO_3 and extractant (TBP) concentration is 1.1 M in *n*-dodecane. The organic-to-aqueous phase volume ratio (V_{org}/V_{aq}) is maintained at 3. Based on these observations, it was decided to use 0.4 M TBH as the organic soluble reductant for extraction experiments under the conditions of uranium purification cycle. Table 1 shows that uranium extraction increases with acidity from ~50% (0.75 M HNO_3) to 60% (1 M HNO_3) in contrast to Pu extraction that is negligible i.e. ≤1% and ~3% at 0.75 M and 1 M HNO_3 respectively. This suggested that 0.4 M TBH is effective for Pu reduction/decontamination in uranium purification cycle.

It was desirable to test the reusability of TBH under process conditions. Recycling studies of the organic phase (1.1 M TBP + 0.4 M TBH/*n*-dodecane) were carried out using Pu tracer + 300 g/L U at 1 M HNO_3 as the aqueous phase. D_{Pu} values were determined in different stages. The loaded organic phase containing U was stripped with 0.01 M HNO_3. The lean organic phase was used for subsequent extraction cycle with the fresh aqueous phase.

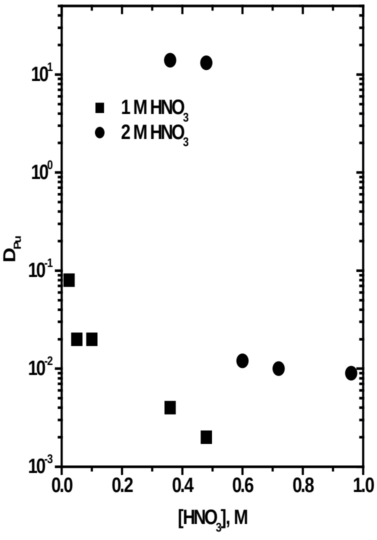

Fig. 1. D_{Pu} as a function of TBH and nitric acid concentration . Extractant 1.1 M TBP/*n*-dodecane, temperature 25°C.

Table 1
Distribution data of uranium and plutonium as a function of acidity. Extractant = 1.1 M TBP + 0.4 M TBH/*n*-dodecane; [U] = 300 g/L; V_{org}/V_{aq} = 3; temperature = 25°C

HNO_3 (M)	D_U	D_{Pu}
0.75	0.34	2.4×10^{-3}
1.0	0.45	1.0×10^{-2}

Table 2
Recycling test of TBH. Extractant = 1.1 M TBP + 0.4 M TBH/*n*-dodecane; [U] = 300 g/L; $[HNO_3]$ = 1 M; V_{org}/V_{aq} = 3; temperature = 25°C; duration = 72 h

Cycle No.	D_{Pu}
I	1.0×10^{-2}
II	1.2×10^{-2}
III	1.3×10^{-2}
IV	1.5×10^{-2}

Four subsequent extractions were performed using the same organic phase in duration of 72 h. Table 2 shows marginal increase in D_{Pu} values in every cycle. These studies, however, indicate that it may be possible to recycle TBH in U-purification cycle of the PUREX process. It is mentioned in the literature that these types of reductants can be regenerated by simple contact with $Na_2S_2O_4$ solution in 0.1 N N_2H_4-H_2O [6]. The excess of TBH or its degradation product, *tert*-butyl quinine present in the aqueous phase can be removed by anion exchange resin.

3.2. Evaluation of TBH as reductant in chemical quality control analysis of PuO_2

1 mL of the Pu stock solution (12.3 g/L Pu, 5.1 M HNO_3, cf. Section 2.2) was diluted to 3 mL with 2 mL of 0.3 M HNO_3 + 0.6 M N_2H_4 so as to adjust the resulting solution to 3 M HNO_3 + 0.4 M N_2H_4. This solution was equilibrated with 3 mL solution of 1% TRPO + 1.1 M TBP in *n*-dodecane, containing varying concentrations of TBH, by magnetic stirring for 15 min. The phases were allowed to settle for 10 min. The organic and the aqueous phases were assayed for Pu concentration.

Table 3 indicates the influence of TBH concentration (present in 1 % TRPO + 1.1 M TBP/*n*-dodecane) on the reduction of Pu(VI)/Pu(IV) at 3 M HNO_3 + 0.4 M N_2H_4. The D_{Pu} decreases from 5.1×10^{-2} (0.2 M TBH) to 1.1×10^{-2} (0.4 M

Table 3
Distribution data of Pu with varying concentration of TBH in the organic phase; Organic phase: 1% TRPO + 1.1 M TBP/*n*-dodecane; aqueous phase: 3 M HNO_3–0.4 M N_2H_4; $V_{org}/V_{aq} = 1$

TBH (M)	Pu_{org} (μg/mL)	Pu_{aq} (μg/mL)	D_{Pu}
0.2	192.3	3802	5.1×10^{-2}
0.3	119.5	3915	3.0×10^{-2}
0.4	45.8	4038	1.1×10^{-2}
0.5	46.4	4041	1.1×10^{-2}

TBH) and then remains unchanged thereafter. Similarly, uranium recovery was ascertained by extracting U(VI) in a single step with 3 mL 1 % TRPO + 1.1 M TBP + 0.4 M TBH/*n*-dodecane from aqueous phase containing 12.3 mg Pu spiked with known amounts of uranium (5 and 15 mg) and adjusted to 3 M HNO_3 + 0.4 M N_2H_4. It should be noted that uranium extraction experiments were done at 3 M HNO_3 to ensure a sufficiently high value of $D_{U(VI)}$ (~106.5) and its quantitative extraction by the extractant mixture. The extracted uranium of the organic phase was stripped into the aqueous phase with 0.8 M oxalic acid at organic-to-aqueous phase volume ratio, V_{org}/V_{aq} of 2.

Under the experimental conditions, uranium recovery was found 99.4±0.4% both at 5 and 15 μg U level in the presence of 12.3 mg Pu (Table 4). The aqueous phase was assayed for U and Pu concentrations to compute U recovery and its decontamination factor (DF) against Pu. The decontamination factor from Pu was found to be ~150 (Table 5). These studies suggest that TBH efficiently reduces Pu(VI)/Pu(IV) to Pu(III) in 3 M HNO_3 + 0.4 M N_2H_4. Hydrazine acts as holding reductant for TBH in the organic phase as well as stabilizes Pu(III) against oxidation in the nitric acid medium.

Table 4
Recovery of uranium from the dissolved solution of PuO_2. Organic phase: 1 % TRPO + 0.4 M TBH + 1.1 M TBP/*n*-dodecane; aqueous phase: 3 M HNO_3 + 0.4 M N_2H_4; $V_{org}/V_{aq} = 1$

U added (μg)	U recovered (μg)	Recovery (%)	Average recovery (%)
5	4.98	99.6	99.4(± 0.4)
5	4.95	99.0	
15	14.98	99.9	
15	14.87	99.1	

Table 5
Decontamination factor (DF) of uranium over plutonium after selective uranium extraction

Sample	U (μg/mL)	Pu (μg/mL)	Pu/U ratio	DF
Before separation	6.24	12.3×103	1971	150.4
After separation	1.98	26.01	13.1	

The extent of U recovery and its decontamination with respect to Pu achieved by this separation method are adequate for developing an ICP-AES based analytical method for the estimation of trace concentrations of U in plutonium oxide samples. This is the primary aim of this investigation. The aqueous waste produced in the U–Pu separation, containing a significant amount of Pu (10–12 mg per separation) is compatible with the PUREX process streams and hence can be easily recycled in Pu reconversion operation. This will be the major advantage of the present analytical method.

4. Conclusions

Tert-butyl hydroquinone (TBH) has been evaluated as a plutonium reductant for reprocessing and analytical applications. The data presented in this paper appears encouraging for probable use of TBH as a non-salt forming reductant in the uranium purification cycle of the PUREX process. It helps in improving the throughput of the process. Using TBH, a solvent extraction method has been developed for the separation of trace concentrations of uranium (3–30 μg/mL) from plutonium solution (10–12 mg/mL) obtained on dissolution of plutonium oxide in HNO_3 containing traces of HF. The method involves the selective extraction of U(VI) with a mixed solvent comprising 1% TRPO +1.1 M TBP + 0.4 M TBH/*n*-dodecane from 3 M HNO_3 + 0.4 M N_2H_4. Under the optimized conditions, Pu is reduced to inextractable Pu(III) using salt-free reductants TBH (organic phase) and N_2H_4 (aqueous phase). This method has been adopted for ICP-AES routine analysis of uranium in PuO_2 samples.

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