Desalination and Water Treatment
www.deswater.com

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doi: 10/5004/dwt.2012.2738

38 (2012) 146–150
January

Taylor & Francis
Taylor & Francis Group

Removal of dissolved Tri *n*-butyl phosphate from aqueous streams of reprocessing origin: engineering scale studies

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Received 17 February 2011; Accepted 21 July 2011

ABSTRACT

Tri-*n*-butyl phosphate is extensively used in aqueous reprocessing of spent nuclear fuel for separating the fissile elements from fission products and other wastes. Presence of tri-*n*-butyl phosphate in these acidic aqueous solutions leads to a limitation with respect to evaporation of these streams for achieving volume reduction. Process development for removal of dissolved tri-*n*-butyl phosphate from acidic solutions has been addressed in the present work using solvent extraction route. Batch studies were followed with continuous runs using Combined Airlift based Mixer-Settler Unit (CAL-MSU). These studies have revealed that the dissolved TBP in aqueous solutions can be brought down from 160 ppm to 15 ppm using dodecane with a maximum loading of 3.6% TBP. All these studies on CAL-MSU have demonstrated the applicability of diluent in removing dissolved TBP from reprocessing aqueous solutions. The results obtained reveal an alternate method for stripping out dissolved TBP from reprocessing solutions thereby achieving higher volume reduction factors during evaporation by avoiding the "Red oil" formation.

Keywords: TBP removal; nitric acid; CAL-MSU; n-dodecane; solvent extraction; red oil formation

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1. Introduction

The PUREX process is used for recovering plutonium and uranium from spent nuclear fuel. In this process, spent fuel is dissolved in the nitric acid which results in the formation of uranium and plutonium nitrates. These nitrates are selectively extracted from irradiated fuel using 30% tri *n*-butyl phosphate (TBP) in *n*-dodecane as the solvent. During this solvent extraction process, the plutonium and uranium gets preferentially extracted into the organic phase while most of the metals and fission products retained in the aqueous phase [1]. The loaded organic is further subjected to a series of separation steps to achieve the desired purity of the nuclear material. The concentration of nitric acid used in this process varies from 0.01 M to 4 M.

Such multi cycle solvent extraction processes encompass continuous extraction and stripping operations that are invariably carried out in pulsed columns. Depending on the operating conditions the aqueous phase emanating out of these columns will have entrained organic and dissolved TBP content. As some of these aqueous streams

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Proceedings of DAE-BRNS Biennial Symposium on Emerging Trends in Separation Science and Technology, Kalpakkam, India, March 1–4, 2010

need to be evaporated before they are fed to the subsequent cycle or to be stored as waste pending further treatment/disposal, the organic content associated with the aqueous phase needs to be minimized to avoid red oil formation during evaporation. While entrained organic can be minimized by giving adequate settling time in the settlers and down stream equipment, reduction in dissolved TBP needs to be addressed in a specialized manner. Removal of such dissolved TBP is of direct interest in reprocessing processes as this would enable manifold evaporation of aqueous stream without any operational difficulties.

Steam stripping and adsorption on suitable exchangers are some of the processes considered for this purpose. Many investigators have studied different processes for TBP removal in the past. Pandey et al. have removed dissolved TBP from the aqueous solutions using Amberlite XAD-4 resin [2]. The various factors affecting the adsorption rates and breakthrough curves in batchwise and semi-continuous fixed bed adsorber have also been studied. Misra et al. have simultaneously removed dissolved DBP and TBP as well as uranyl ions from aqueous solutions using Micellar-enhanced ultrafiltration technique [3]. The entire study was carried out using sodium dodecyl sulphate as an anionic surfactant. Causse and Faure have used acidic surfactants for removal of TBP from metallic surfaces [4]. Different formulations have been prepared using nonionic surfactants as active molecule for maximum adsorption on TBP/water interface in their work. Chang et al. have separated TBP from aqueous solution using the foam separation method with the help of anionic surfactant like sodium dodecyl sulfate and a cationic surfactant like cetyl trimethyl ammonium bromide [5]. Zilberman et al. have carried out regeneration of irradiated and actual spent solvent by steam distillation [6]. The single and two-step continuous processes of solvent distillation were performed for recovery of 30% TBP in diluent.

Distillation cannot be used for recovery of TBP because of its high boiling point, low stability at high temperature, low concentration in large volume of acidic solutions and other economic reasons. While adsorption process leads to generation of secondary waste and is not economically feasible. The advantages of using solvent extraction over the other two are continuous and selective extraction, reusability of solvent and waste minimization.

The work presented in this paper aims to study the removal of dissolved organic from acidic solutions by solvent extraction technique using *n*-dodecane on an industrial scale. The choice of the solvent was restricted to *n*-dodecane, since it is used as a diluent in the PUREX process. The choice of contactor was restricted to those that can be amenable for in-cell application in radioactive environment.

Various kinds of centrifugal extractors, extraction columns and mixer-settlers have been extensively used for aqueous waste stream treatment in nuclear fuel reprocessing [7]. However, the mixer-settler was most preferred in this case because of its characteristics like low headroom, simplicity, low maintenance and hydrodynamic stability [8]. The present study has been directed towards minimizing the *n*-dodecane requirement, with a view of recycling it to the main PUREX process. The performance of the developed process has been studied using indigenously developed mixer-settlers with passive mixing elements, to enable direct adoption for active application. The Combined Air Lift based Mixer-Settler Unit (CAL-MSU) has been used to remove dissolved TBP from aqueous acidic solutions. The benefits of using CAL-MSU for the present study are absence of moving parts because of air-lift based mixing making it suitable for radioactive use, vigorous mixing of two phases by appropriate design of the nozzle, provision of end-settlers to take care of any entrainment in terminal streams and operation flexibility when required. Hence, the main objective of this work is maximum removal of dissolved TBP using CAL-MSU with organic waste minimization.

2. Materials and methods

2.1. Feed preparation

All the chemicals used for preparation of the bulk quantity of solutions were of commercial grade as available in the radiochemical plants. TBP, nitric acid and *n*-dodecane used were of analytical grade and supplied by Prabhat chemicals, Mumbai, India. Their purity was around 97%, 70% and 95% respectively.

2.1.1. Aqueous feed

Two types of aqueous feed representing two typical streams of reprocessing origin namely high acidity feed (3 M) and low acidity stripped product (0.3 M) were prepared. The 0.3 M HNO_3 was prepared by adding 14 M HNO_3 into de-mineralized water and agitating the vessel contents for about 20 min. 30% TBP in *n*-dodecane (plant grade) was added in A/O ratio of 2:1 and mixed thoroughly for a period of about 2 h. The solution was transferred into decant and the phases were allowed to separate overnight followed by gravity settlement. The separated aqueous phase was transferred into another tank which served as feed to the mixer-settler. The feed preparation tank was fitted with an interphase detection device so as to ensure that no entrained organic goes along with the aqueous phase. 3 M HNO_3 feed was also prepared in a similar manner.

2.1.2. Organic feed

The organic feed was prepared by diluting 30% TBP in *n*-dodecane with neat *n*-dodecane to get the desired initial concentration of 3–6% TBP in *n*-dodecane. As the objective of this work was to minimize the use of the solvent, *n*-dodecane loaded upto 6% TBP was used for TBP removal. Hence, *n*-dodecane containing different concentrations of TBP (ranging from 3–6%) was used as the organic feed.

2.2. Analysis of TBP

The concentration of TBP in the organic phase was determined by gas chromatography (GC) and in the aqueous phase by high performance liquid chromatography (HPLC) as described in detail in Bajoria et al. [9]. Each sample was analyzed thrice to check the reproducibility of results. The deviation in the results obtained is precise within ±2%.

2.3. Experimental methods

Laboratory scale batch experiments have been carried out to determine equilibrium values, followed by engineering scale mixer-settler runs to study the performance of the process on full scale.

2.3.1. Batch equilibration studies

As one of the objectives of the work was to minimize the organics generated from the treatment process, it was imperative to know the extent of TBP concentration in *n*-dodecane phase beyond which the organic would have to be rejected. Therefore, batch studies were carried out to ascertain the distribution values of TBP in pure *n*-dodecane, 3.6% TBP and 6% TBP at an A/O ratio of 6:1. Specific A/O ratio was chosen so as to achieve a good overall performance of the mixer-settler banks using a minimum amount of *n*-dodecane.

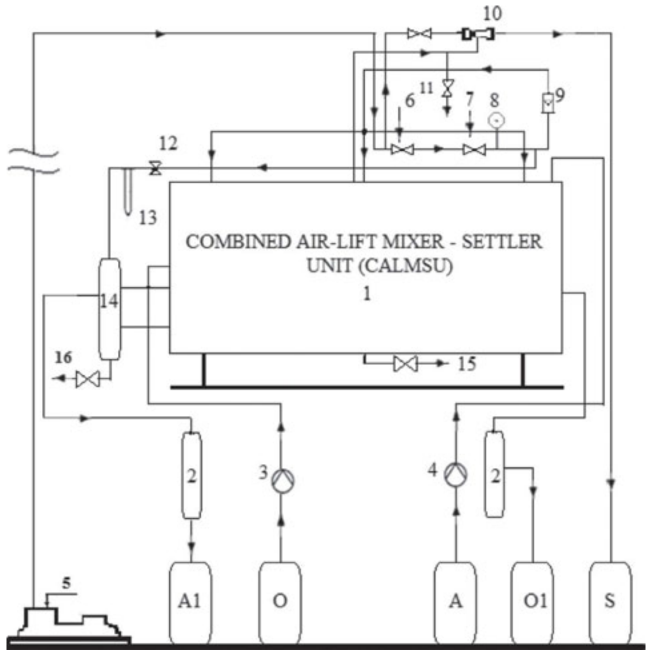
Pure *n*-dodecane, 3% TBP in *n*-dodecane and 6% TBP in *n*-dodecane were used separately as the organic phase. The different concentrations of TBP loaded *n*-dodecane were used as the organic solvent to study the extent of TBP removal at different loading of *n*-dodecane. The aqueous feed was TBP dissolved in 0.3 M HNO_3. The aqueous and the organic phase was taken at an A/O ratio of 6:1 in the separating funnel and mechanically shaken for 30 min. The contents of the funnel were then left for gravity settling resulting in separation of the two equilibrated phases. Both the phases were sampled individually and were analyzed for their TBP concentration.

The concentration of nitric acid in the aqueous phase was monitored by using the titration method. The nitric acid was titrated with 0.3 M NaOH solution using phenolphthalein as an indicator. The color change at end point was from colorless to pale pink. The uncertainty reported in results was ≤0.1%.

2.3.2. Engineering scale studies

The engineering scale runs were carried out in an inactive test facility. The test facility comprised of a 10 stage mixer-settler, feed tanks, raffinate tanks and metering pumps for delivering the required feed rate to the mixer-settler. The mixer-settler has been adequately instrumented to observe and control set parameters and also to identify key parameters for actual operations.

In line with the requirement of radioactive services, the mixer-settler used in this study has passive mixing elements that are virtually maintenance free. A 10 stage CAL-MSU contactor unit made of SS 304 l with a maximum capacity of 80 LPH has been used in this study [10]. The innovatively designed static mixing element CAL-MIX (Combined Airlifting and Mixing) uses air to create high turbulence effecting both phase dispersion and interstage transfer during the solvent extraction process. The CAL-MSU has been provided with two end-settlers to minimize the presence of entrained phase in the outlet streams. The schematic of the experimental set-up with all necessary connections is shown in Fig. 1.



1. CAL-MSU
2. Density pot
3. Organic phase-Varicon Pump
4. Aqueous phase-Varicon Pump
5. Compressor
6. Valve
7. Pressure regulator
8. Pressure gauge
9. Air-Rotameter
10. Air ejector
11. Vent-off sampling port
12. Pressure regulating valve
13. Manometer
14. Interphase Pot
15. Mixer-settler drain valve
16. Interphase pot drain valve.

O: Organic phase reservoir
A: Aqueous phase reservoir
A1: Extract phase collector
O1: Raffinate phase collector
S: Vent-off gas stripper.

Fig. 1. Schematic of the mixer-settler.

The mixer-settler was operated in countercurrent mode with a maximum A/O ratio of 6:1. Each run was carried out for about 10–13 h continuously. Hourly sampling of the outlet streams were carried out to estimate the time to reach steady state. After achieving steady state, stagewise sampling was carried out to study the concentration profile across the contactor.

3. Results and discussion

3.1. Batch studies

The results of the batch equilibrium experiments are summarized in Table 1. The results revealed that the organic phase needs to be rejected at a maximum TBP concentration of around 4%. Therefore, further studies were carried out with an inlet concentration of about 3.6% and the outlet concentration less than 4% TBP. This was carried out to test the extent of removal at a loading of about 4%. Starting with an initial 0% conc. of TBP would entail processing of very large quantity of simulated waste (1 l of dodecane would need ~250 l of aqueous to get a concentration of about 4% TBP in organic phase).

It was also found that the concentration of nitric acid in the aqueous feed was constant (0.3 M) during the extraction process. As the concentration of the nitric acid was very less in the aqueous phase, it was not extracted by TBP present in the organic phase. Bajoria et al. has obtained the same results and mentioned that transfer of nitric acid into the organic phase increases with the concentration of the nitric acid in the aqueous phase [9]. The distribution coefficient for nitric acid at equilibrium when contacted with different percentages of TBP in diluent has also been determined. The solubility of TBP in the aqueous phase as a function of TBP concentration in the organic phase in equilibrium is also reported in their work.

Table 1
Summary of the batch equilibrium studies

S. No.	Conc. of HNO_3 (M)	A/O Ratio	Conc. of TBP in aq. feed (ppm)	Conc. of TBP in dodecane (%)	Conc. of TBP in raffinate (ppm)
1	0.3	6:1	176	0	<5
2	0.3	6:1	176	3	68
3	0.3	6:1	176	6	174

3.2. Engineering scale studies

The mixer-settler was operated smoothly in a countercurrent mode with aqueous as the continuous phase. The runs were carried out uninterrupted for about 10–13 h continuously. Stable interphase positions could be achieved throughout the period of operation. The summary of the runs is given in Table 2. The mixer-settler was observed to have stable concentration profile after about 4 h of operation, as shown in Fig. 2. After achieving stable operation, the concentration profiles across the mixer-settler were also observed as given in Fig. 3. While runs 1–3 were taken with an A/O ratio of 6:1, the last run was taken with an A/O ratio of 1:1. However, the overall organic hold-up for the run was maintained at 6:1. This was to study the performance at a lower A/O ratio.

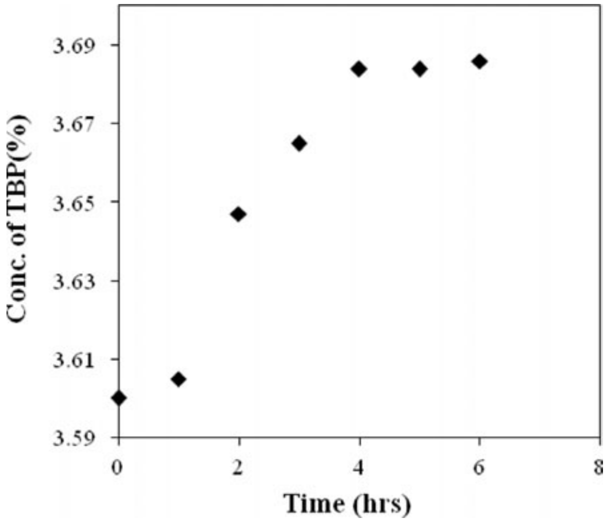


Fig. 2. Transient concentration gradient - loaded organic phase.

Table 2
Summary of CAL-MSU runs

Run No.	Conc. of aq. HNO_3 (M)	A/O Ratio	TBP in aq. Feed (ppm)	Initial conc. of TBP in dodecane (%)	TBP in raffinate (ppm)	Final conc. of TBP in dodecane (%)
1	0.3	6:1	160	0	15	1.4
2	0.3	6:1	162	3.6	25	3.70
3	3	6:1	193	3.67	40	3.82
4	0.3	1:1	158	3.6	15	3.70

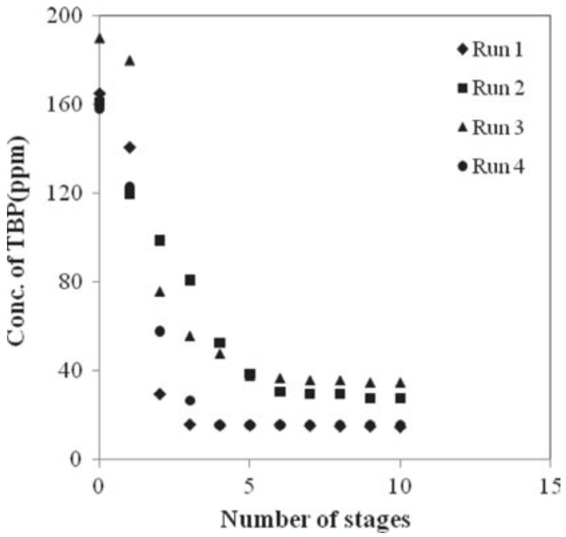


Fig. 3. Stagewise steady state concentration profile (Aqueous phase).

The maximum extraction of TBP from aqueous nitric acid was achieved in only 3 stages in the run with neat *n*-dodecane as solvent because of high concentration gradient of TBP. Lower A/O ratio of 1:1 resulted in better performance, owing to higher availability factor. Higher A/O ratio of 6:1 with 3.6% TBP in *n*-dodecane was seen to require about 5 to 6 stages and the concentration of TBP retained in the raffinate was ~40 ppm.

4. Conclusions

Batch study concludes that dodecane reloaded upto 4% could be reused for extraction of TBP from aqueous waste. From the stability profile, it can be concluded that at the given operating conditions the CAL-MSU stabilization time is four hours. Maximum extraction was observed using A/O ratio 1:1 on mixer-settler. From the concentration profile of all runs, it is proved that around 5 stages are required with A/O ratio of 1:1 for TBP removal from the aqueous waste. These studies have conclusively demonstrated, the efficiency of CAL-MSU in removing dissolved TBP from acidic aqueous solutions using *n*-dodecane. The results obtained reveal a deployable method for removing dissolved TBP from acidic aqueous solutions of spent nuclear fuel reprocessing.

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