

CONTINUOUS REMOVAL OF RADIOLYTIC PRODUCTS FROM TBP  
EXTRACTION SYSTEMS

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In the actinide separation process using TBP as extractant, hydrolytic and radiolytic reactions cause a gradual decomposition of the extractant, resulting in the formation of degradation products which can affect process performance adversely. The TBP diluent has to be cleaned from these degradation products before it is reused. This paper deals with a procedure for solvent cleanup, using a fourstage continuous contactor for increasing the scrubbing efficiency.

## INTRODUCTION

In the reprocessing of spent fuel by the Purex Process, tributyl phosphate (TBP) is used as the extractant, being diluted with an aliphatic hydrocarbon, usually n-dodecane<sup>1,2</sup>.

Depending on the irradiation level of the organic phase, TBP is decomposed resulting in some undesired compounds which affect the performance of the whole process. The primary degradation product is HDBP and its formation can be significant under certain conditions.  $H_2MBP$  and  $H_3PO_4$  are slightly found. In addition, the acid hydrolysis of TBP is superimposed on the radiolysis, increasing the rate of the decomposition reaction.

HDBP acts on the effectiveness of the extraction system by strong complex formation with plutonium and zirconium, decreasing plutonium and uranium stripping, zirconium removal and promoting the highly troublesome crud formation. Besides HDBP,  $H_2MBP$  and  $H_3PO_4$  also are formed, but in very low amounts<sup>3-5</sup>. Some of these products also have complexing properties for metals, in particular for tetravalent ions. A solvent cleanup process should be necessary before solvent recycle, to remove the retained products, and TBP and diluent degradation products. Commonly, an alkaline washing is used with good efficiency mainly for acid degradation products of TBP. The disadvantage of this process is  $Na_2CO_3$  consumption by residual  $HNO_3$  in the solvent, resulting in a large volume of medium activity waste (MAW). Other compounds including hydrazine carbonate or oxalate have been used as scrub solution<sup>6</sup>. An advantage of this method is the reduction of waste volume, since hydrazine can be subsequently destroyed by electrooxidation, giving a salt-free MAW. A process using solid adsorbents has also been reported for solvent cleanup<sup>7</sup>. In this paper a procedure for continuous counter-current washing, using a four stage mixer-settler is presented, to improve the alkaline washing efficiency and allowing safety and better performance for the system.

EXPERIMENTAL

Materials

A 30 vol.% technical grade TBP diluted in n-dodecane was selected as organic phase.

Solvent A: freshly prepared 30 vol.% TBP/n-dodecane, without any treatment. Prior to use, it has been equilibrated with 1M  $\text{HNO}_3$ .

Solvent B: 30 vol.% TBP/n-dodecane coming from continuous uranium separation experiments, after uranium back-extraction with 0.01M  $\text{HNO}_3$ .

Solvent C: Uranium loaded 30 vol.% TBP/n-dodecane. This solvent was stored for up to 60 d. Uranium was only reextracted with 0.01M  $\text{HNO}_3$  just before the scrubbing experiment is done.

Solvent D: simulated organic phase from a reprocessing spent fuel. To simulate this solution 30 vol.% TBP/n-dodecane was previously washed with 5% w/v  $\text{Na}_2\text{CO}_3$  solution, O/A=10:1 and equilibrated with 1M  $\text{HNO}_3$ . This solution was irradiated in a  $^{60}\text{Co}$  source for about 6 h, at a dose rate of  $0.37 \text{ kGy h}^{-1}$ , and then, contacted with irradiated uranyl nitrate solution. The resulting organic phase with uranium and some fission products, mainly Zr and Ru, have been used for cleanup experiments.

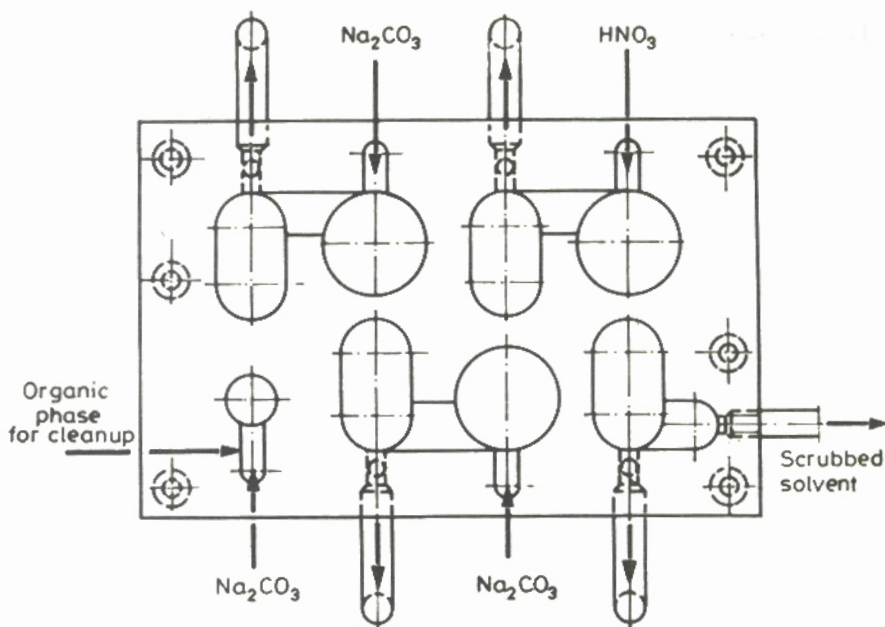


Fig. 1. Solvent scrubbing contactor scheme

#### Equipment and procedure

Batch washing experiments were conducted using lab scale borosilicate glass cylindric funnels. Ten volumes of organic phase and one volume of aqueous phase were mixed, at 1500 rpm for 30 min using a mechanical stirrer. The phases were allowed to separate for 60 min. Then the organic phase was equilibrated with 1M  $\text{HNO}_3$  and sampled for analysis.

Continuous countercurrent solvent washing studies were performed with a four-stage plexiglass mixer-settler. Each transfer unit consists of a  $37.3 \text{ cm}^3$  capacity mixing chamber and an equal capacity of settling chamber, except for the first transfer unit, which has a smaller mixing chamber capacity ( $7.7 \text{ cm}^3$ ). The contactor scheme is shown in Fig. 1. The organic

phase is pumped to the first mixer chamber and flows through the 4 mixing and settling chambers. The 5% w/v sodium carbonate scrub solution is feed into the 1st, 2nd and 3rd mixing chambers, leaving by the settling chamber of each transfer unit. The last mixing chamber is used for feeding 1M  $\text{HNO}_3$  to reestablish the acid equilibrium of the solvent washed.

#### Analytical control

In all experiments the HDBP content was controlled by a gas chromatographic method<sup>8</sup>.

#### RESULTS AND DISCUSSION

Initially, normal alkaline batch solvent washing tests with a 5% w/v sodium carbonate solution, as described in section "Equipment and procedure" were previously done in order to compare with the continuous scrubbing. These experiments were performed with solvents A and B. The HDBP content was reduced to <5 ppm, confirming the expected results.

For continuous operation, some exploratory studies using a 4-stage mixer-settler were planned to develop operating procedures, and to check the hydrodynamic behavior of the system and also to search for operational problems. During the tests, this system was used to scrub TBP/n-dodecane (solvent A) in order to remove some HDBP present in the TBP received from the manufacturer.

The suitable mixing speed for using a 5% w/v sodium carbonate solution was found to be 1250 rpm. The stream flow-rates of 600-400 ml  $\text{h}^{-1}$  for the organic phase and

TABLE 1

Continuous solvent

Run No	Organic feed solution					
	Type	[HDBP], ppm	[U], g.l <sup>-1</sup>	<sup>95</sup> Zr, c/min.ml <sup>-1</sup>	<sup>103</sup> Ru, c/min.ml <sup>-1</sup>	Gross $\gamma$ , c/min.ml <sup>-1</sup>
1	Solvent A	28	-	-	-	-
2	Solvent A	39	-	-	-	-
3	Solvent C	1484	1.0	-	-	-
4	Solvent D	48	2x10 <sup>-1</sup>	4670	5410	24840
5	Solvent D	61	2x10 <sup>-1</sup>	5550	5780	25500
6	Solvent D	48	2x10 <sup>-1</sup>	4670	5410	24840
7	Solvent B	19	-	-	-	-

n.d. = Not detected.

20-40-60 ml h<sup>-1</sup> for the aqueous phase also gave no interfacial problem in the settlers.

After the exploratory tests had been completed, seven definitive experiments with TBP/n-dodecane of different origin were carried out. The data from these studies are shown in Table 1.

The earlier two experiments were accomplished with freshly prepared 30 vol.% TBP, diluted in n-dodecane directly from the stock tank, using an O/A ratio of 20 and 30. In both experiments, the HDBP was reduced to undetectable level (<5 ppm), as expected, since the distribution coefficient of NaDBP salt can be estimated to be 0.001<sup>7</sup>.

In the 3rd run, spent 30 vol.% TBP/n-dodecane (solvent C) with greater amounts of HDBP was used. HDBP was

## cleanup experiments

Stream flow-rate		Scrubbed solvent				
Organic ml.h <sup>-1</sup>	Aqueous, [HDBP], ml.h <sup>-1</sup>	[HDBP], ppm	[U], g.l <sup>-1</sup>	<sup>95</sup> Zr, c/min.ml <sup>-1</sup>	<sup>103</sup> Ru, c/min.ml <sup>-1</sup>	Gross γ, c/min.ml <sup>-1</sup>
400	20	<5	-	-	-	-
600	20	<5	-	-	-	-
400	20	<5	2x10 <sup>-2</sup>	-	-	-
600	20	<5	9x10 <sup>-4</sup>	110	470	640
400	20	<5	5x10 <sup>-5</sup>	120	50	120
600	40	<5	2x10 <sup>-4</sup>	n.d.	n.d.	90
600	40	<5	-	-	-	-

also removed to undetectable levels and no interfacial problems have been observed.

In the experiments performed using a simulated spent fuel reprocessing organic phase (solvent D), no decrease in solvent cleanup effectiveness was observed (Table 1). The HDBP content was reduced from ~50 to <5 ppm, even in solvent containing metal ions. The sodium carbonate wash was effective in activity removal, with a decontamination factor of 10<sup>2</sup> for ruthenium and 10 for zirconium. On the other hand, the decontamination factor for uranium was 10<sup>3</sup>. These results were obtained for an O/A ratio equal to 20, with decreasing values for O/A = 30.

These samples for analytical control were taken from time to time from the cleaned solvent delivered to the receiver tank, at 30 min intervals and the last sample after system shutdown, after two hours operation. The

levels of gross gamma, Ru, Zr counting, and HDBP content in the solvent after washing were, in all samplings, constant, irrespective of the operation time.

The last experiments were accomplished with spent organic phase coming from the uranium extraction process (solvent B). The washing mixer-settler was directly connected to the organic phase stream of uranium stripping mixer-settler. In spite of the organic flow rate oscillation of the stripping mixer-settler, hydrodynamic equilibrium was maintained during 8 hours of operation and no problem was noted. The HDBP concentration was reduced to <5 ppm at any moment, showing the workability of a continuous cleanup process to solvent recycle.

The solvent cleanup using conventional sodium carbonate scrubbing has the advantage of long time experience in operating plants and the use of innocuous chemicals. The continuous washing has the advantage of being slightly more effective for HDBP removal as compared to batch operation, which is also time consuming. The studies will be continued for testing other scrubbing solutions, mainly to improve the decontamination of long-chain organic compounds and to eliminate the waste treatment problems generated.

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