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ATOMIC ENERGY COMMISSION

SEPARATION OF TRIBUTYL PHOSPHATE FROM DEGRADED
SOLVENTS USING SOLVENT EXTRACTION TECHNIQUE

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बंबई, भारत
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ABSTRACT

A solvent extraction method is described for the recovery of Tributyl Phosphate (TBP) from degraded process solvents. The method involves the separation of TBP and shell solt(SST) from 30% TBP/SSP mixture by thorium nitrate extraction leading to the formation of a heavy phase (Third phase) which contains essentially TBP. The equilibrium experiments revealed that by utilizing Thorium feeds of concentrations above 525 g/L in water at 1:1 ratio, a 30% TBP/SST mixture can be effectively separated into TBP and SST fractions with light SST phase having about 3% TBP. Using single stage mixer settler experiments, the feasibility of continuous separation of the three phases was assessed. Since there is a tendency for the degraded products of the diluent to seek the TBP phase, additional treatment steps would be necessary for their removal if the TBP is to be reused. Activated charcoal was investigated for this purpose. If purification of the TBP is not envisaged the volume of the organic waste generated in processing plants could be reduced by separating the diluent and TBP and only the TBP could be sent as concentrated waste.

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1. INTRODUCTION

Among the aqueous processes used for treating the irradiated fuel elements, Purex process using Tributyl Phosphate (TBP) in a diluent as extractant has been widely employed on an industrial scale. In addition, TBP is also used for recovery/refining of uranium from the ores and for its separation from rare earth elements. In spite of many merits of TBP as a solvent, it is vulnerable to chemical and radiation damage⁽¹⁾. Even though its radiation and chemical stability can be considered to be reasonably good, when compared to most of the other organic solvents, however, during protracted use even moderate radiation and chemical damages can lead to a gradual deterioration in the process performance. The radiolysis of TBP and the diluent leads to the formation of various compounds like Dibutyl Phosphate (DBP), Monobutyl Phosphate (MBP), nitroparaffins, carbonyl compounds etc. (2, 3, 4). Polymerization of some of these products has also been reported⁽⁵⁾. In the purex process, the presence of DBP in TBP increases the extraction of uranium, plutonium, zirconium and Ruthenium by this solvent and makes complete stripping of these elements extremely difficult⁽⁶⁻⁹⁾. The presence of DBP affects the Zirconium decontamination seriously⁽⁷⁾. Under intense radiation fields TBP & DBP undergo further damage to form MBP and phosphoric acid in extreme cases leading to precipitate formation

in process equipments⁽¹⁰⁾. Traces of TBP present in aqueous product streams might find their way into product evaporators where the thermal decomposition leads to the formation of a heavy organic phase and solid degradation products which could accumulate Pu, Zr and U and cause problem in subsequent cycles^(11, 12). In some processes especially in ore refining plants⁽¹³⁾ extraneous matter like compressor oil, lubricants etc. find their way into process streams and tend to accumulate in TBP streams affecting its characteristics. In order to mitigate these problems, the solvent is generally washed with sodium carbonate and sodium hydroxide solutions before recycling in the purex process. This step removes DBP and MBP but does not improve the diluent quality⁽¹⁾. In addition, solvent clean up by sorption techniques using fresh MnO_2 , Al_2O_3 ⁽¹⁴⁾, ZrO_2 ⁽¹⁵⁾, Titania⁽¹⁶⁾, activated charcoal⁽¹⁷⁾, macro reticular anion exchangers⁽¹⁸⁾ etc. have been reported. Liquid scrubbing using ethanalamines have been investigated⁽¹⁹⁾. Improvements in the extraction properties of TBP have been reported when the degradation products are esterified with diazo methane⁽²⁰⁾. Various distillation techniques have been tested successfully for the purification of used TBP solvent^(1, 19). In spite of these efforts, the solvent quality deteriorates over protracted use and has to be discarded periodically. Depending upon the capacity of the processing plants the annual inventory of TBP is generally of the order of several tons. Hence, it will be worthwhile to explore the possibility of recovering the TBP from spent solvents with a view to either purify it or to reduce the volume of the degraded TBP so that the waste volume can be smaller.

The Eurowat Process⁽²¹⁾ developed by the Eurochemic Centre envisages the ultimate disposal of the degraded TBP by formation of a third phase by acid saturation using concentrated phosphoric acid or dissolution of TBP by anhydrous phosphoric acid. The authors report that on loading the TBP in a diluent with concentrated phosphoric acid, a third phase is formed which contains essentially all the TBP and the degraded products. When anhydrous phosphoric acid is used only two phases are formed as the anhydrous phosphoric acid dissolves the TBP and degraded products leaving a diluent phase which is free from impurities. It has however been reported⁽¹⁶⁾ that TBP separated even from pure TBP/OK by this method has high metal retention properties, particularly for Zirconium and Plutonium. Acid equilibration technique leading to third phase formation has been utilized for the development of analytical methods for TBP estimation⁽²²⁾ and other applications⁽²³⁾.

Third phase formation is a commonly encountered phenomenon when mineral acids or tetravalent metal nitrates like Pu, Th, Zr etc. are extracted in TBP systems especially when their concentrations in organic phase are very high⁽²⁴⁾. This is generally attributed to the limited solubility of the TBP complexes of these tetranitrates in the diluents used⁽²⁵⁾. When the limiting solubility of the solute is reached in the TBP diluent mixture, the organic phase splits into two distinct immiscible layers, one having a high TBP and metal nitrate content and the other being mostly the diluent used. This limiting concentration of metal nitrate beyond which the third phase formation occurs is dependent on the acidity, temperature, the nature and

concentration tetravalent element, the type of the diluent and the concentration of TBP employed⁽²⁴⁾. This mode of separation of TBP from diluent has been examined several years ago⁽²⁶⁾, when some compounds like $\text{Th}(\text{NO}_3)_4$, $\text{ZrO}(\text{NO}_3)_2$, FeCl_3 and CaCl_2 were studied for this purpose. The main object of these studies has been to produce a diluent free from radioactivity and from phosphorus contamination such that it can be reused in fuel reprocessing or stored in a solid matrix^(16, 26).

A TBP recovery method from the degraded solvent employing metal nitrate saturation technique could be advantageous since the diluent and the TBP could be separated using a solvent extraction method by properly choosing the metal nitrates which could be subsequently stripped from the organic phase. The main disadvantages of this technique would be the carry over of the degraded impurities with TBP phase and small losses of TBP to diluent phase. However, this method of separation of TBP could be employed in combination with methods like distillation or solid sorption on activated charcoal etc. for purification of TBP.

This report deals with the separation of TBP and shell solt (SST) from the TBP/SST mixture by thorium nitrate extraction leading to third phase formation. The report also includes a summary of efforts made to purify a chemically degraded process solvent.

2. SEPARATION OF TBP FROM TBP/SST MIXTURES BY $\text{Th}(\text{NO}_3)_4$ LOADING

Extensive data are available on the formation of third phase during the extraction of Thorium by TBP dissolved in aliphatic diluents^(27, 28) which has also been reviewed by Kertes⁽²⁴⁾. The extraction capacity

of TBP for Thorium nitrate is sufficiently high such that at high concentrations, $\text{Th}(\text{NO}_3)_4$ can be loaded into TBP from water and also can be stripped with water by adopting suitable volume ratios.

To start with, equilibrium experiments were conducted to arrive at ideal conditions for maximum separation of TBP and SST by Thorium nitrate loading, and based on the results, an extraction scheme was proposed and tested in a laboratory single stage mixer settler unit with fresh 30% TBP in SST and a chemically degraded solvent.

2.1 Experimental

2.1.1 Reagents

- (a) Thorium Nitrate obtained from Indian Rare Earths Ltd. was used in all the experiments.
- (b) Tributyl Phosphate (from Morsanto Chemicals, USA) diluted with shell solT (Shell-Netherland) was used in all the experiments.
- (c) Pure Plutonium (IV) stock conditioned with H_2O_2 in 8 M HNO_3 was used for the Plutonium retention tests performed for degraded TBP solutions.
- (d) Activated charcoal from BD H (UK) was used in the purification experiments.

2.1.2 Equilibrium experiments : The extractions were carried out in separating funnels by taking appropriate volumes of aqueous feed solution and the organic extractant and manually shaking for 5 minutes. The three layers were separated and after centrifugation were analysed.

2.1.3 Analytical Procedures : The samples were analysed for Acidity, Density, Thorium content and also TBP content in the two organic layers.

(a) Estimation of free acid was carried out by first complexing Thorium with preneutralised saturated potassium oxalate solution and titrating

the resultant solution with standard alkali⁽²⁹⁾.

(b) Density was measured by weighing 250 λ aliquot of the sample.

(c) The aqueous and organic Thorium estimations were done by EDTA titration with xylenol orange as indicator⁽³⁰⁾.

(d) The TBP contents of the organic phases were determined by acid equilibration technique using 9 & 8.5 M HNO_3 ⁽³¹⁾. The thorium present in the organic sample was removed by water and 5% Na_2CO_3 prior to acid equilibration.

(e) Assessment of the quality of the solvent was made by either 'Z' test or Pu retention test. In the case of Z test, the Windscale method⁽¹²⁾ was used and the value was expressed as moles per billion litre. The Z values reported on the basis of Windscale method were higher by a factor of about 100 than those obtained when Savannah River Laboratory⁽³²⁾ procedure was used. The discrepancy could be due to the difference in the concentration of Zr (IV) carrier used⁽²³⁾. However, due to practical difficulties involved in Z test, Pu retention test was used as the alternate method to compare the results. The method involved contacting of Pu(IV) (10 mg/l) in 3M HNO_3 with an equal volume of acidic test solvent and scrubbing the loaded solvent three times with 0.1M HNO_3 at 1:2 ratio. The lean solvent was then counted for alpha using alpha proportional counter. The Pu retention was given as moles per billion litres. The forward Kd values were also determined by alpha counting of appropriate phases. Always control tests with fresh TBP were carried out for comparison. In all these experiments, Thorium if present in the organic sample was first removed by water and alkali wash.

2.2 Experimental results and discussion

The equilibrium data were collected only at room temperature and results of the extraction pattern of Thorium from water, 1M, 2M and 3M HNO_3 and its effect on TBP in the organic phase are presented in Tables 1 to 4. The values reported are above the threshold point at which the third phase formation occurs. It is seen from the results in Table 1 that when the TBP is saturated with Thorium beyond this threshold point the TBP content of the light phase decreases slowly so much so that when a 525 g/l solution of Thorium in water is used as feed at 1:1 ratio, the outgoing SST phase contained only about 3% TBP and the third phase contained about 77% TBP, the rest being SST. From the Thorium extraction experiments in presence of acid it can be seen that the threshold concentration of Th for the third phase formation is lowered when the acidity is increased which has already been reported by several authors⁽²⁷⁾. But the TBP content in the SST phase depended mainly on the Thorium concentration and not on nitric acid concentration. In the regions above 400 g/L Th feeds, the influence of Nitric acid was negligible and it did not alter the settling characteristics also to any significant extent, in the case of pure TBP.

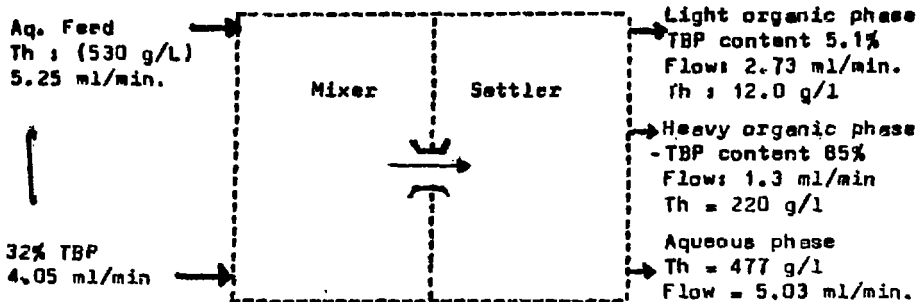
From these results it can be concluded that by utilizing Thorium feeds of concentrations above 525 g/L in water at 1:1 ratio, a 30% TBP/SST mixture can be effectively separated into TBP and SST fractions, with the outgoing SST phase having about 3% TBP. After taking into consideration the volume factors involved it was worked out that the TBP loss to SST phase was about 7% of total TBP input.

2.3 Mixer Settler Experiments

Based on the results, mixer settler experiments were planned with a single stage mixer settler unit to assess the feasibility of continuous separation of three phases. Initially only fresh TBP was used to standardize the conditions.

2.3.1 The mixer settler unit: A sketch of the glass mixer settler unit used in these experiments is shown in Fig. (1). The unit had a mixer volume of 20 ml and settler volume of 100 ml. The aqueous and organic streams were introduced at the bottom of the mixer. The mixed phase entered the middle of the settler through a tunnel port connecting the mixer and settler. The mixing in the mixer was achieved by means of vacuum pulsing through glass tubes of 0.6 mm dia. The pulse frequencies and amplitudes were so chosen that the entire mixer volume is occupied by the mixed phases. The settling in the settler was by gravity only. The settler had three exit ports. The aqueous raffinate and the middle phase exits were connected to vented tees whose heights controlled the inter-phase levels of different layers in the settler. During the operation, it was ensured that the heavy organic phase was at the same level as the interconnection port of the mixer and settler. This was necessary to prevent any bypassing of feed organic stream to the settler zone. The organic and aqueous streams were fed to the unit using metering pumps.

2.3.2 Experimental results and discussion: Extraction scheme used is given below, along with flow rates and final results.



The aqueous feed flow rate was kept higher than that of organic to avoid any maloperation due to slight variation in the flows. When 1:1 ratio was used, even a slight change in the aqueous and organic flows resulted in improper saturation of TBP phase leading to higher TBP loss in SST phase.

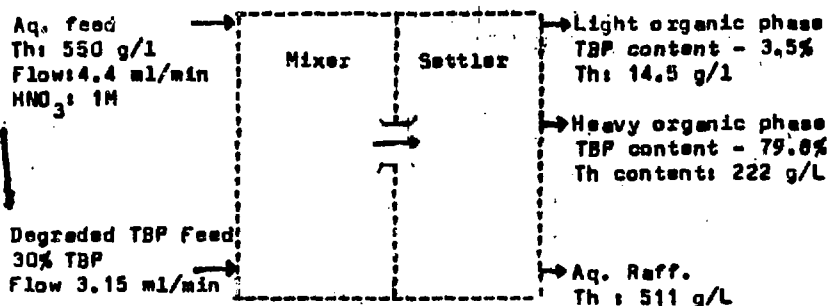
During the run, it was found that the phase separation was satisfactory. The input/output material balance for flow rates, Thorium and TBP were checked for 15 to 20 min. period on a continuous basis. The agreement was satisfactory. These results are given in Table 5.

From the results it can be seen that the total loss of TBP to SST phase was about 11%. The Thorium from Heavy organic and the light organic phases could easily be stripped with water and recycled after concentration.

Encouraged by these results, this separation technique was applied to a chemically degraded solvent from the uranium purification facility. The solvent was dark red in colour and the TBP content was about 43%. This was diluted to 30% with shell solvent and was washed repeatedly with hot 5% Na_2CO_3 solution and water. To start with, its third phase formation tendency was

studied in the laboratory under the ideal conditions recommended in the case of fresh TBP. The 30% TBP solvent was contacted with 550 g/l Th in water at 1:1 ratio. The resultant phases were analysed for all the relevant data. In addition, the light yellow SST phase and the dark red heavy phase were also subjected to Pu retention tests and Z tests to assess the behaviour of degradation products. These data are presented in Table 6. This degraded solvent was then subjected to a continuous separation in a mixer settler as per scheme given in the case of fresh TBP. For this purpose, the degraded TBP was adjusted to 30% and washed in bulk with hot NaOH and Na₂CO₃ before use.

However, the run was not satisfactory as settling problems were very severe. The settling could be improved by introducing nitric acid in the aqueous feed and by increasing the settler residence time. It has been reported⁽¹³⁾ that in Uranium (VI) and nitric acid systems, the saturation with Uranium leads to the ejection of less soluble impurities from the Heavy TBP phase in the form of cruds which accumulate in the org. - aqueous interface. Such phenomenon was observed in the case of thorium saturation also. The mixing was also not very satisfactory due to the viscous nature of the solvent. The mixing improved by switching over to alternate compressed air and vacuum pulsing of the probes, in place of suction and venting as used before. The changed scheme is given below along with results.



As can be seen the TBP content in the Light Organic phase is about 3.5%. The middle phase contained some crud and required filtration for their removal. The mixing and settling characteristics had improved considerably.

The Light organic phase was pale yellow in colour and the middle phase was dark red in colour indicating that all the degraded products tend to follow the Heavy organic phase. Pu retention tests and Z tests were conducted to assess the quality of the incoming and outgoing solvent phases. These results are presented in Table 7. The data in Table 6 and 7 indicate that though concentration of TBP could be effected by this step, additional steps would be required to improve the quality of the solvent. With this in view, an effort was made to improve the quality of the solvent with the help of activated charcoal.

3. CLEAN UP OF A CHEMICALLY DEGRADED TBP SOLVENT

Various attempts to improve the quality of the spent solvent using solid sorption techniques have been reported in literature. Activated Bauxite, Alumina powder, silica gel etc. have been used in uranium ore Refineries⁽³³⁾. Activated charcoal has been found to be effective in improving the colour and quality of the solvent⁽¹³⁾. However, losses have been reported⁽¹⁷⁾ during

the charcoal treatment of irradiated TBP. Charcoal has been tested for its use to remove the entrapped organic solvents from aqueous fuel reprocessing wastes⁽³⁴⁾. Pilot Plant scale operations have been described⁽¹³⁾ for the solvent clean up using powdered and granular charcoal in ore refineries. The general operational techniques involved the passing of the spent solvent through columns packed with charcoal.

In laboratory studies, batch experiments were conducted with activated charcoal to assess the extent of purification effected and the TBP loss incurred during the process.

3.1 Experimental

The red solvent was treated with hot 5% Na_2CO_3 solution 3 times at 1:1 ratio and then with 1M NaOH three times at 1:1 ratio.

The separation of layers was carried out after prolonged settling each time. Alkali solution containing about 3% alcohol gave better settling characteristics. The treated solvent which still retained its colour was washed with water and TBP content of the solvent was about 43%. This TBP was used in all the experiments and the quantity of charcoal used was about 1 gm/10 ml of the solvent (unless otherwise specified). The TBP percentage was estimated after each contact to assess the loss of TBP to the charcoal. The treated solvent was also subjected to Pu retention tests. The preliminary experiments revealed that the intensity of the red colour of the solvent decreased considerably on treatment with charcoal. The treated solvent when subjected to Pu retention test, indicated a decrease in the value as compared to untreated sample and this decrease was proportional to the decrease in the intensity of

the red colour in the sample in all cases. Fresh TBP in shell solvent was used in control experiments for comparing TBP loss, forward Kd of Pu and Pu retention values. The charcoal treatment studies were done at even low TBP concentrations after dilution with SST to arrive at ideal conditions as it was felt that the concentration of purified TBP could be increased by Third phase technique.

3.2 Experimental Results

The results in Table 8 show the percentage TBP loss per charcoal contact for fresh 10%, 20%, 30% and 40% TBP in shell solvent and Pu retention values obtained. Similar results obtained for chemically degraded TBP are given in Table 9. In this case, the quantity of charcoal used was proportional to the TBP content of the test solution and not to the total volume of the solution. With regard to TBP loss, the amount of TBP entrapped by the charcoal remains more or less constant over the range tested as given in Table 8. In Table 9, the results indicate that the Pu retention values are reduced by a factor of 3 to 5 times the original values when treated with charcoal. However, these values are much higher as compared to the values obtained in the case of fresh TBP/SST solutions (Table 8). Repeated contacts with charcoal gave TBP solutions which were almost colourless having low plutonium retention values but the TBP loss was also considerable. In order to assess the extent to which the TBP can be separated and purified a scheme was devised which comprised of two charcoal treatment steps in combination with a single third phase formation step and the red solvent was subjected to these steps of purification and separation. The scheme used is given in chart 1 alongwith results. As can be seen from the results the heavy phase Pu

retention values could be decreased by a factor of about 10. However, these values are still much higher than those obtained for fresh TBP (Table 8).

The Pu retention values obtained for light phase indicate that the diluent fraction can also be recovered free from impurities, by repeated treatment with charcoal.

4. CONCLUSIONS

From these studies it can be concluded that solvent extraction techniques can be conveniently used for the separation of TBP and the diluent. Since there is a tendency for the degraded products of the diluents to seek the TBP phase, it will be necessary to adopt a subsequent purification step for the complete removal of the degradation products, if the TBP is to be reused. The diluent fraction can also be recovered for reuse after charcoal treatment. If no further recovery of the TBP is envisaged, the volume of the organic waste generated in the plant could be considerably reduced by separating the diluent and the TBP and only the TBP phase could be sent for the ultimate disposal as it will retain most of the degradation products. Most of the results reported here have been obtained with TBP solvent wastes from uranium purification facility. Further studies using recycled purex process solvents are yet to be conducted.

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Table 1

**VARIATION OF TBP CONCENTRATION IN THE HEAVY
ORGANIC PHASE AND THE LIGHT ORGANIC PHASE
DUE TO THORIUM SATURATION**

Aq. feed acidity = Nil
Org. feed 30% TBP in SST

Volume 30 ml: 30 ml (approx.)
Contact time: 5 mts.

No.	AQ. Feed		After Equilibrium						
	Th g/L	Aq. Raffinate	Middle org. phase				Light org. phase		
		Sp. gr.	Th g/L	Sp. gr.	Th g/L	TBP %	Sp. gr.	Th g/L	TBP %
1	217.8		183.9						29.20
2	266.3	1.350	199.2	1.074	127.7	51.2	0.846	36.3	21.30
3	290.4					55.0			12.50
4	314.7	1.408	229.8	1.149	148.1	61.6	0.829	42.4	12.80
5	363.1	1.505	288.6	1.220	183.9	67.6	0.788	15.3	8.05
6	411.5	1.578	337.1	1.251	189.0	71.0	0.796	14.8	5.95
7	459.9	1.663	377.9	1.282	209.4	75.6	0.785	10.2	4.30
8	508.3	1.724	418.8	1.297	222.2	77.2	0.779	9.2	3.00
9	580.0					79.8			2.60

Table 2

**VARIATION OF TBP CONCENTRATION IN THE HEAVY
ORG. PHASE AND THE LIGHT ORGANIC PHASE DUE
TO THORIUM SATURATION**

Aq. feed acidity = 1.0M HNO₃
Org. feed 30% TBP in SST

Volumes 30ml:30ml (approx.)
Contact time: 5 mts.

No	AQ. Feed		After Equilibrium											
			AQ Raffinate			Middle Org. phase				Lt. Org. phase				
	HNO ₃ M	Th g/L	HNO ₃ M	Sp. gr.	Th g/L	HNO ₃ M	Sp. gr.	Th g/L	TBP %	HNO ₃ M	Sp. gr.	Th g/L	TBP %	
1	1.0	121.0												29.30
2	"	169.4	0.95			0.176	"							28.90
3	"	217.8	1.00		163.4	0.176		Turbid third phase						20.60
4	"	266.3	0.90	1.369	194.1	0.250	1.130	142.4	59.0	0.100	0.804	21.4	13.30	
5	"	314.7	0.98	1.439	229.6	0.250	1.181	155.8	65.7	0.075	0.793	17.4	9.45	
6	"	363.1	1.06	1.517	240.9	0.250	1.224	178.8	70.8	0.080	0.798	24.0	7.50	
7	"	411.5	0.78	1.574	318.6	0.230	1.250	194.1	73.0	0.055	0.792	12.7	5.90	
8	"	459.9	0.88	1.639	352.4	0.230	1.270	199.2	75.1	0.055	0.783	10.2	4.75	
9	"	508.3	0.83	1.729	404.6	0.230	1.294	214.5	77.2	0.055	0.777	9.2	3.35	

Table 3

**VARIATION OF TBP CONCENTRATION IN THE HEAVY
ORG. PHASE AND THE LIGHT ORGANIC PHASE DUE TO
THORIUM SATURATION**

Aq. Feed acidity = 2.0 M HNO_3
Org. feed 30% TBP in SST

Volumes 30 ml:30ml (approx.)
Contact time 5 mts.

No.	AQ. Feed		After Equilibrium										
			AQ Raffinate				Middle Org. phase				Light org. phase		
	HNO_3 M	Th g/L	HNO_3 M	Sp.gr.	Th g/L	HNO_3 M	Sp.gr.	Th g/L	TBP %	HNO_3 M	Sp.gr.	Th g/L	TBP %
1	2.0	169.4			127.5		Just turbid	48.3					
2	"	217.8	1.80	1.335	163.2	0.35	0.990	137.7	59.0	0.140	0.828	24.5	14.7
3	"	266.3	1.86	1.415	209.2	0.40	1.173	163.3	62.0	0.100	0.810	20.4	19.0
4	"	314.7	1.86	1.465	250.0	0.40	1.221	183.6	69.0	0.070	0.798	15.8	7.6
5	"	363.1	2.03	1.562	301.1	0.38	1.232	199.0	72.4	0.050	0.786	12.7	5.3
6	"	411.5	2.06	1.648	352.2	0.40	1.269	209.2	75.0	0.040	0.779	10.2	4.3
7	"	459.9	2.06	1.711	367.9	0.40	1.288	219.4	76.9	0.040	0.777	7.7	3.6
8	"	508.3	2.06	1.787	439.0	0.40	1.300	222.0	76.9	0.030	0.774	9.2	2.9

Table 4

**VARIATION OF TBP CONCENTRATION IN THE HEAVY
ORG. PHASE AND THE LIGHT ORGANIC PHASE DUE TO
THORIUM SATURATION**

Aq. Feed acidity = 3.0 M HNO₃
Org. feed 30% TBP in SS

Volumes 30 ml; 30ml(approx.)
Contact time 5 mt.

No.	AQ. Feed		After Equilibrium										
			AQ Raffinate			Middle Org. phase				Lit. Org. phase			
	HNO ₃ M	Th g/L	HNO ₃ M	Sp. gr.	Th g/L	HNO ₃ M	Sp. gr.	Th g/L	TBP %	HNO ₃ M	Sp. gr.	Th g/L	TBP %
1	3.0	169.4			127.5			40.6	Just turbid				
2	"	217.8	2.71	1.362	163.2	0.40	1.149	153.0	63.0	0.160	0.818	22.4	12.5
3	"	266.3	2.75	1.443	209.2	0.40	1.201	173.4	67.5	0.120	0.800	15.3	9.1
4	"	314.7	2.80	1.498	250.0	0.40	1.226	183.6	71.6	0.090	0.792	12.3	6.9
5	"	363.1	2.86	1.588	298.6	0.38	1.257	199.0	73.8	0.070	0.786	8.7	4.9
6	"	411.5	2.66	1.627	324.1	0.40	1.268	206.6	73.8	0.055	0.781	10.2	4.9
7	"	459.9	2.66	1.674	357.3	0.38	1.281	214.3	74.2	0.055	0.778	9.7	4.1
8	"	484.1	2.61	1.678	362.4	0.40	1.283	214.3	76.9	0.050	0.779	9.2	4.1

Table 5

**RESULTS OF MIXER SETTLER EXPERIMENTS
WITH FRESH TBP**

AQ. Feed:
Th = 530 g/L
Sp.Gr. = 1.891

Org. Feed
TBP/SST = 32.5%

1. Analytical Results

No.	AQ. Raff.		Light organic phase			Heavy org. phase		
	Sp. gravity	Th g/L	Sp. gravity	Th g/L	%TBP	Sp. gravity	Th g/L	%TBP
1	1.823	477.2	0.800	15.3	7.5	1.281	215.5	83.6
2	1.810	472.6	0.792	13.0	5.9	1.284	215.5	83.6
3	1.813	472.6	0.791	13.4	6.0	1.286	213.1	84.8
4	1.812	472.6	0.785	12.0	5.1	1.288	220.1	84.0
5	1.813	477.2	0.784	12.0	5.1	1.296	220.0	84.8

2. Flow Rate Stability

No.	Inlet flows ml/min		Outlet flows ml/min	
	Aq. Feed	Org. Feed	Aq. Raffinate	Org. combined
1	5.20	4.15	4.90	4.20
2	5.25	4.05	5.13	4.17
3	5.25	4.05	5.03	4.03

3. Thorium Material Balance

No.	Duration of measurement mts.	Input Th gms.	Output Thorium gms			Total output Th in gms.
			Aq. Raff.	Heavy org. phase	Light org. phase	
1	20	55.12	46.3	5.39	0.77	52.46
2	15	41.76	36.4	3.63	0.55	40.80
3	15	41.76	36.0	4.29	0.49	40.78

Table 5 (contd.)

4. TBP Material Balance

No.	Duration of measurement mts.	Input TBP, ml	heavy phase TBP ml.	Light org. phase TBP ml.	Output (total) TBP ml.
1	20	26.60	20.90	3.48	24.38
2	15	19.50	13.86	2.35	16.21
3	15	19.50	16.54	2.09	18.63

Table 6

**RESULTS OF THORIUM SATURATION EXPERIMENTS
ON CHEMICALLY DEGRADED TBP**

AQ. Feed	Raff.	Heavy phase	Light Org.
Th: 513 g/L	Th: 469 g/L	Th: 217 g/L	Th: 9.04 g/L
Sp.gr. = 1.920	Sp.gr. = 1.852	Sp.gr. 1.295	Sp.Gr. 0.805
		TBP: 75%	TBP: 3.8%

no.	Sample	Plutonium		Z number
		Forward Kd.	Pu retention no.	
1	Degraded organic TBP made to 30% with SST and alkali washed	7.06	66.98 $\times 10^2$	170.40 $\times 10^2$
2	Diluent phase after third phase formation and removal of Thorium	0.23	24.26	51.79
3	Heavy organic phase after removal of Thorium and adjustment of TBP to 30%	7.81	74.96	229.19

Table 7

**RESULTS OF M. S. UNIT EXPERIMENT WITH
CHEMICALLY DEGRADED SOLVENT**

AQ. Feed	Reff.	Heavy Org. phase	Light org. phase
Th: 550 g/L	Th: 511 g/L	Th: 222 g/L	Th : 14.5 g/L
Sp.Gr. = 1.899	Sp.Gr. 1.879	Sp.Gr. 1.293	Sp.gr. 0.845
HNO ₃ : 1M		TBP = 79.8%	TBP : 3.5%

No.	Sample	Plutonium		Z number
		Forward Kd	Pu retention %	
1	Alkali washed degraded TBP feed to mixer settler	6.03	74.05	32.76
2	Exit light organic phase after removal of Thorium	0.27	16.80	29.48
3	Exit heavy organic phase after removal of Thorium and adjustment of TBP to 30% with SST	5.63	99.29	137.19

Table 8

LOSS OF TBP DUE TO CHARCOAL TREATMENT

Pu Extraction

Feed AQ : Pu = 12 ug/ml
HNO₃ = 3.0M
ORG : TBP (Fresh)
Vol. Ratio: 1:1
Time of contacts: 30 mts.

Charcoal contact

Amt. of activated charcoal=1.0g
Vol. of TBP : 10.0 ml
Time of contact: 30. mts.

S.No.	TBP content(%)	Pu Kd(Forward)	Plutonium Retention no. $\times 10^4$	After charcoal treatment TBP content (%)
1	10.70	2.09	0.13	7.90
2	19.50	3.60	0.39	17.90
3	32.60	6.02	0.55	30.10
4	39.00	6.80	1.51	36.50
5	60.00	6.96	3.62	-

Table 9

RESULTS OF CHARCOAL TREATMENT OF DEGRADED TBP

Pu Extraction (for PNO)

Charcoal contact

AQ. Feeds: Pu = 12 μ g/ml
 $\text{HNO}_3 = 3M$

Time of contact: 30 mts.

Org. Chemically degraded TBP

Vol. Ratio = 1:1

Time of contact: 30 mts.

No.	Before charcoal Treatment			After charcoal Treatment	
	TBP content (%)	Pu retention number	Amount of charcoal/10 ml of solvent	TBP content (%)	Pu retention no.
1	11.0	24.96 $\times 10^2$	0.25	9.9	4.39 $\times 10^2$
2	21.8	69.19	0.50	20.6	13.55
3	30.8	117.44	0.75	29.3	33.75
4	43.2	156.78	1.00	41.8	39.13

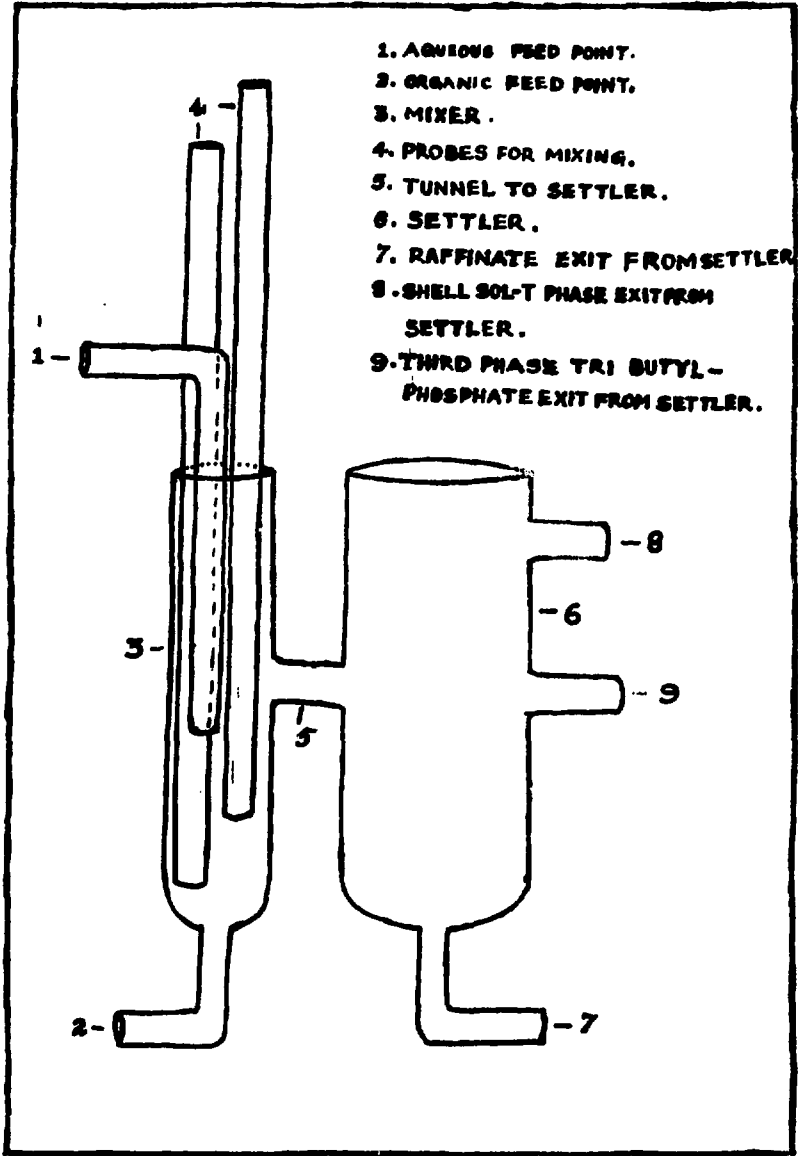


FIG. 2.

CHART 1

Suggested Scheme for the Separation and Purification of
TBP from a Chemically degraded solvent

