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SOLVENT DISTILLATION STUDIES FOR A PUREX REPROCESSING PLANT

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ABSTRACT

A distillation system has been developed for regeneration of Purex solvent and will be implemented for the first time in a reprocessing plant. The results are described and analyzed, with emphasis on laboratory experiments which were made with a radioactive plant solvent. Particularly the distillation provides a good separation of solvent degradation products, which was verified by measurements of interfacial tension and plutonium or ruthenium retention.

INTRODUCTION

The Purex process is used today in France to reprocess light water reactor fuel. Tributylphosphate (TBP), whose extractive properties have been known since 1944 (1) is the industrial solvent. In French Purex process operations, the TBP is diluted to 30% by volume with a mixture of highly branched alkanes with 10 to 14 carbons and with about 70% of branched dodecanes (2). Because of the high burnups of light water reactor fuel (33,000 $\mathrm{Mwd/T^{-1}}$ and more), the TBP solvent receives large radiation doses that result in degradation of the solvent molecules. Radiation-induced degradation of TBP to form dibutylphosphate (DBP) is well known (3), but radiolytic degradation of the diluent is less understood.

Laurylbutylphosphoric acid (4), hydroxamic acids (5,6), oximes (7), or enols (8) have been proposed as degradation products of the Purex solvent system. Further developments are needed for optimum recycle of the Purex solvent.

Our goals for the solvent management are to preserve properties and quality of the TBP solvent, and to avoid excessive solvent treatment in order to minimize volumes of organic wastes. Three methods have been used to maintain Purex process solvent quality: (1) intensive chemical methods of regeneration, (2) specific management of solvent streams, and (3) regeneration of solvent components by distillation.

Solvent regeneration by chemical methods has been employed since the inception of the Purex process, but few improvements have been made, despite numerous attempts with various reagents. We previously reported attempts to improve some of the classical alkaline treatments (2).

Good solvent management in a Purex plant will include diluent washing of high-level radioactive aqueous streams and optimum solvent and diluent routing between extraction cycles. To minimize radiolytic degradation of TBP, diluent scrubbers equivalent to three counter-current stages are installed at all the aqueous phase outlets of the extraction units. The very high partition coefficient of TBP (9) allows for low diluent flow rates (a few percent of the aqueous stream), so that it is unnecessary to recover these diluent streams for separate treatment. They are, therefore, systematically added to the solvent stream, which results in an increase in the volume of the organic phase, and a decrease of TBP content. Thus, it is necessary to adjust the TBP content by adding concentrated TBP, and to remove TBP-diluent in each cycle.

For a plant reprocessing 800 tons of fuel per year, the one-time-through spent solvent is about 1300 $m^3 \cdot year^{-1}$. It is uneconomical to consider this solvent as a single-use product to be discharged to the wastes. Figure 1 shows one possible strategy for managing the solvent. It consists of a distillation system and a distribution system where the distillates are sent to the most active cycles in the following sequence: uranium cycles → plutonium cycles → first plutonium cycle → overall excess.

Distillation

Other reports (10,11,12) have shown that classical distillations of degraded TBP solvent is not satisfactory. The resident in the boiler darkens rapidly and tends to decompose above 145° C in vacuo, consequently, the distillate was slightly colored. To minimize residence time, flash distillation has been studied (8,13), but the inherent formation of aerosols limits the purification. Other works, with a classical boiler to recover the diluent (14,15), and a project with rotating evaporators (16) shows that distillation is widely used at laboratory or at pilot scale to improve regeneration of the TBP solvent.

A distillation system has been developed and will be implemented for the first time on the industrial scale in plants under construction in France. Distillation (Fig. 1) performs three major functions: (1) separation of the components of the TBP diluent mixture to restore the quality of the diluent required to scrub the aqueous streams, and of the concentrated TBP to adjust the solvent concentration in all the extraction cycles; (2) removal of certain degradation products that are detrimental to extraction operations; and (3) elimination of beta-gamma activity in the TBP solvent to allow recycle to the purification cycles. To limit the thermal decomposition of TBP

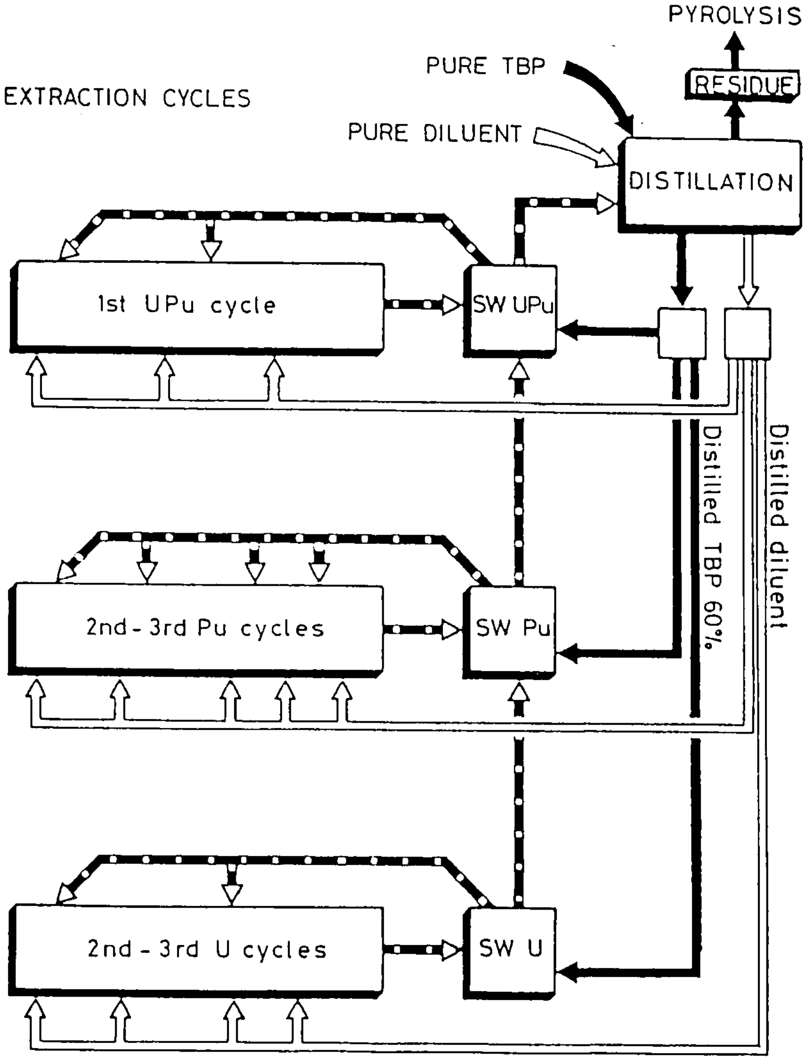


Fig. 1. Solvent management with distillation.

and to prevent the formation of tars, distillation is conducted under reduced pressure at moderate temperature and in thin film evaporators with short residence time and without formation of aerosols.

The distillation equipment (Fig. 2) includes: washing to remove sodium salts; a dehydration unit which operates under reduced pressure; an evaporation unit to vaporize 95% of the solvent, leaving 5% of active residue (consisting of TBP enriched in degradation products); a rectification column for separation of diluent and TBP concentrated to about 60 to 80%; and a unit for washing of concentrated TBP with aqueous NaOH.

Full development of the distillation process involved the usual three activities of: (1) laboratory scale (about 1:1000) with real solvents from plants taken in the first extraction cycle, (2) pilot-plant scale (1:20) with TBP solvents contaminated with uranium, and (3) full-scale prototype operating with totally inactive solvent.

Laboratory Development. The 1:1000 scale distillation unit is constructed of glass and does not permit extrapolation for full-scale operation in stainless-steel equipment; but the principle, and especially the chemical conditions, are quite identical. The 1:1000 scale facility includes the following features (Fig. 3): concurrent flow primary evaporator; packed demister to decontaminate vapor reaching the rectification column with multiknit metal packing; counterflow finishing evaporator; and double-wall rectification column (silver-plated vacuum design to ensure adiabatic conditions) filled with multiknit metal packing.

Two different 1st Purex cycle plant solvents were distilled. Table 1 lists experimental conditions and results. Distillation produces two decontaminated solvent fractions: a distillate which is pure diluent (Table 2), and a concentrate with a TBP concentration of 60 to 80 vol %. Distillation produces also a residue containing degradation products and organometallic complexes.

Two tests were developed and applied to determine the quality of the distilled TBP solvent. First, tests of ruthenium and plutonium retention after several scrubbing steps were performed. Second, settling tests and interfacial tension measurements with aqueous 0.5 M NaOH solution were performed. For all these tests and measurements, a 30% TBP solvent was prepared by adding either pure diluent or pure TBP to the appropriate distillate.

Solvents were well decontaminated of complexing agents responsible for ruthenium and plutonium retention (Tables 3 and 4). Results are very different for ruthenium and plutonium extractants, and suggests that the nature of the complexing agents is different for ruthenium and plutonium.

Results of interfacial tension and settling time tests for distillate and concentrate are very good and close to those of reference TBP solvent (Table 5).

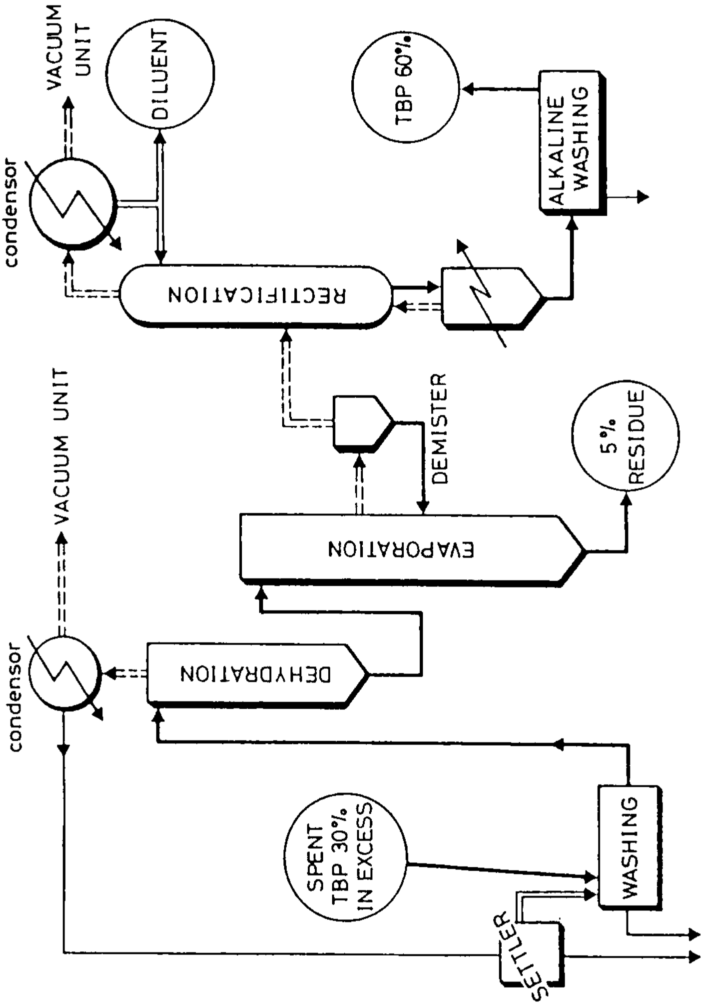


Fig. 2. Distillation unit.

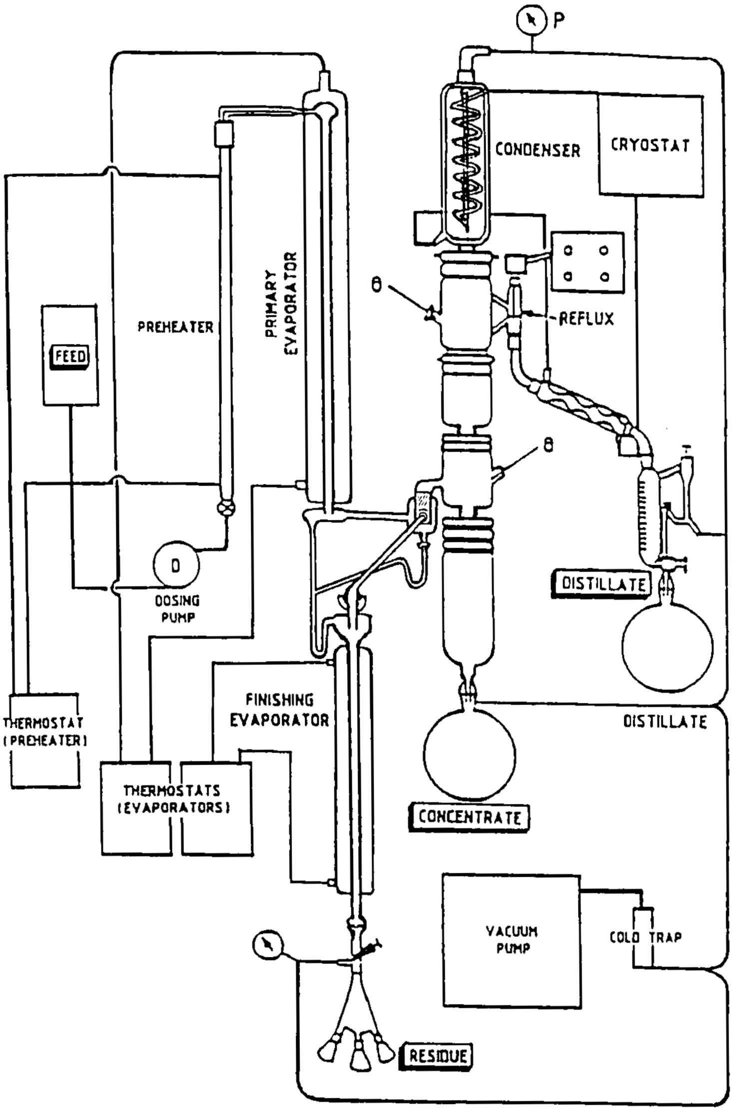


Fig. 3. Scale 1/1000 pilot unit.

Table 1. Results of laboratory distillations of spent solvents.

Nature of the solvent	1st solvent	2nd solvent
Sampling origin	Before treatment	After treatment
^{106}Ru + ^{106}Rh content at the day of sampling (Ci.m^{-3})	14	2
Number of days before distillation	≈500	≈130
Operative conditions:		
Flow rate (l.h^{-1})	0.45	0.64
Pressure (at the condenser) mbar	3.5	1
Thermofluid temperature for:		
primary evaporator	162	164
finishing evaporator	179	179
Results:		
Residue rate (% of feed)	5.5	4.3
% vol TBP in concentrate	63	88.4
Decontamination factors		
^{106}Ru:		
DF on concentrate	>7.9 E6	5.4 E3
DF on distillate	>6.1 E6	2.9 E3
Alpha Emitters:		
DF on concentrate	Not measured	>3.2 E4
DF on distillate	Not measured	>1.6 E4

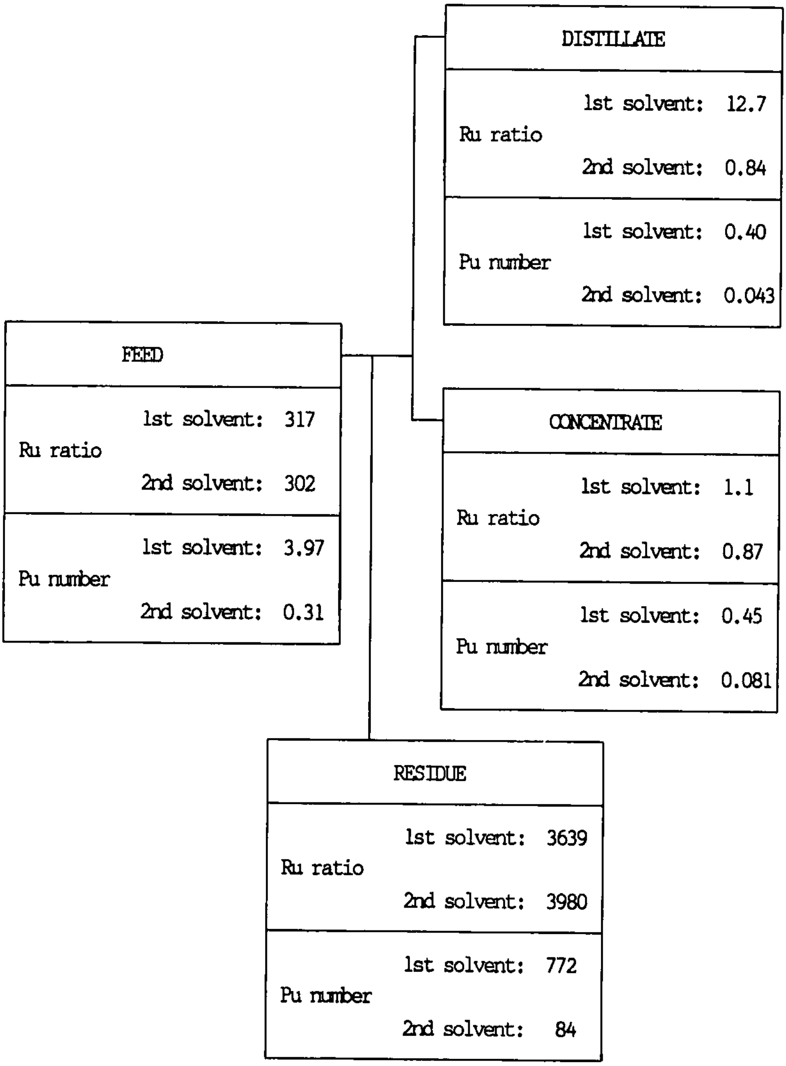
Table 2. Comparison of virgin diluent and distillate composition
(gas chromatographic analysis)

Compound	Virgin Diluent	Distillate*
C10H22	1.4%	2%
C11H24	22.5%	23%
C12H26	74.7%	74%
C13H28	1.4%	1%

*Distillate obtained from first spent solvent. Distillation in 1/1000 pilot facility.

Table 3. Typical ruthenium ratios and plutonium numbers of distilled UP2 plant TBP solvent
(TBP 30% solvent prepared by adding either pure diluent or pure TBP)

Pu reference number: Fresh solvent: 0.27
Fresh solvent + alkaline wash: 0.035



FEED

Ru ratio	1st solvent:	317
	2nd solvent:	302
Pu number	1st solvent:	3.97
	2nd solvent:	0.31

DISTILLATE

Ru ratio	1st solvent:	12.7
	2nd solvent:	0.84
Pu number	1st solvent:	0.40
	2nd solvent:	0.043

CONCENTRATE

Ru ratio	1st solvent:	1.1
	2nd solvent:	0.87
Pu number	1st solvent:	0.45
	2nd solvent:	0.081

RESIDUE

Ru ratio	1st solvent:	3639
	2nd solvent:	3980
Pu number	1st solvent:	772
	2nd solvent:	84

Table 4. Decontamination factors in complexing agents responsible for ruthenium and plutonium solvent retention for distilled plant solvents

DISTILLATE		
Ru D.F.	1st solvent:	33
	2nd solvent:	402
Pu D.F.	1st solvent:	13
	2nd solvent:	8

CONCENTRATE		
Ru D.F.	1st solvent:	345
	2nd solvent:	377
Pu D.F.	1st solvent:	10
	2nd solvent:	4

Table 5. Interfacial tension and settling time ratio of distilled UP2 plant TBP solvents

Interfacial tension reference: Fresh solvent: 10.4
in mN/m Fresh solvent + alkaline wash: 10.7

DISTILLATE		
Interfacial Tension	1st solvent:	11.2
	2nd solvent:	11.3
Settling time ratio	1st solvent:	1.0
	2nd solvent:	1.0

FEED		
Interfacial Tension	1st solvent:	5.5
	2nd solvent:	9.9
Settling time ratio	1st solvent:	4.5
	2nd solvent:	1.8

CONCENTRATE		
Interfacial Tension	1st solvent:	10.8
	2nd solvent:	10.2
Settling time ratio	1st solvent:	1.8
	2nd solvent:	1.3

RESIDUE		
Interfacial Tension	1st solvent:	*
	2nd solvent:	2.1
Settling time ratio	1st solvent:	∞ *
	2nd solvent:	∞ *

* No settling (stable emulsion)

Flash points of the first and second solvent distillates and the virgin diluent were 59°, 63°, and 60° ± 1° C, respectively. The flashpoint of the distilled diluent tends to rise, so the distillates can be recycled without increased risk.

1/20th Pilot Plant Scale. Since 1981, more than 35 m^3 of solvent have been successfully distilled in the pilot plant. The distilled TBP solvent was recycled to an uranium pilot unit operating with pulsed columns; improved hydrodynamic behavior was observed.

In other pilot plant tests, 2 m^3 of low-activity spent solvent from the French La Hague Purex Plant were distilled. Decontamination factors for ^{106}Ru and uranium were both $>10^3$. The flashpoint of distilled diluent was slightly increased over that of virgin diluent, thus the distilled diluent can be recycled without risk.

Plant Scale Distillation Unit (Prototype). The distillation unit is designed to handle 1300 m^3 of solvent per year. Since 1985 more than 1200 m^3 of solvent have been distilled.

The following performance requirements were achieved: (1) solvent dehydration: <1 $g.l^{-1}$ water; (2) evaporation rate: 95%; (3) recovered diluent: $<0.02\%$ TBP; (4) concentrated TBP: $\geq 60\%$ TBP; and (5) DF (U as a tracer): $>10^3$.

CONCLUSION

The substantial amounts of TBP solvent used in large reprocessing plants are such that considerable care must be paid to solvent management to limit the generation of organic wastes. Intensive treatment by chemical regeneration serves to increase the useful life of the TBP solvent.

General solvent management, combined with a distillation unit under reduced pressure, also helps to recycle the two components of the TBP solvent at a low activity level. Distillation also serves to remove degradation products that are generally responsible for poor hydrodynamic behavior and for the holdup of radioactive products such as plutonium, zirconium, and ruthenium. From a safety standpoint, the flashpoint of the distilled diluent tends to rise. It can therefore be recycled without risk.

Solvent quality must be maintained over a long period. Yet it is clear that the complete behavior of all the solvent degradation products is still poorly controlled; that only the full-scale plant experiment, with complete recycling, will confirm improved solvent cleanup performance.

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