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PROPERTIES AND CLEANUP OF DEGRADED
TBP
TRIBUTYL PHOSPHATE-AMSCO SOLUTIONS AND
THE RELATIVE STABILITIES OF ALTERNATIVE
EXTRACTANT-DILUENT SYSTEMS

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OAK RIDGE NATIONAL LABORATORY

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SOLUTIONS AND THE RELATIVE STABILITIES OF
ALTERNATIVE EXTRACTANT-DILUENT SYSTEMS

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ABSTRACT

The formation and chemical properties of the major degradation products of several diluents in contact with acid nitrate solutions have been studied, together with (1) methods for purifying degraded diluents, (2) methods of pretreating the diluent to minimize degradation, and (3) the relative stability of several extractant-diluent systems. Emphasis was on Amsco 125-82, a specially treated naphtha used extensively at ORNL as a diluent for tributyl phosphate, a prominent extractant in liquid-liquid extraction systems used to recover uranium from aqueous solutions containing many elements.

Accelerated degradation of the diluent, usually containing 1 M tributyl phosphate (TBP), was induced by boiling with nitric acid or by irradiating (Co^{60} gamma rays) while agitating the solvent phase with nitric acid. Nitroparaffins, RNO_2 , were the major degradation products and were formed at twice the rate when TBP was present during degradation. Under the conditions of degradation, a 100-whr/liter exposure was practically equivalent to 11 hr of boiling with 2 M HNO_3 , as shown by Zr-Nb⁹⁵ extraction, total organic nitrogen analysis, and spectrophotometric analysis.

Extraction from acid solution of certain fission products, for example, Zr-Nb but not ruthenium, increased markedly after the degraded solvent had been treated with alkaline reagents, and a test employing solid calcium hydroxide was developed to estimate the extent of diluent degradation. The alkaline treatment converted a significant fraction of the nitroparaffin to the enol form. There was synergistic extraction of Zr-Nb⁹⁵ by the combination of TBP and degraded diluent.

The degraded diluents can be cleaned up by scrubbing with alkanolamines to remove nitroparaffin-amine salts or by contacting with activated alumina. Both methods have doubtful economy, and the latter requires solids handling.

Low-pressure flash distillation is an effective, inexpensive method for partial or total repurification of degraded TBP-Amsco mixtures.

Pretreating Amsco 125-82 by scrubbing with concentrated sulfuric acid before degrading with hot nitric acid improved its stability.

The stabilities of a number of alternative aliphatic and aromatic diluents were determined. With aliphatic diluents, the configuration most stable against nitration is the simplest, for example, n-dodecane. Aromatic diluents increase the radiation stability and extraction selectivity of TBP. The stabilities of the simple alkylbenzenes against nitration vary widely with the number of alkyl groups, their type and their position, but a mixture of diethylbenzenes low in the para isomer, and some of the polymethylbenzenes, did not form fission product extractants in routine tests. Also, nitration of the benzene ring does not produce extractants for Zr-Nb⁹⁵.

1. INTRODUCTION

In recovering uranium, plutonium, or thorium, for example, from "spent" fuel elements by solvent extraction, deterioration of the extractant phase contributes to unsatisfactory operation. The extent of degradation varies with the exposure of the organic extractant phase to radiation and reactive chemicals during the processing of the aqueous feed, which contains the uranium and fission products, plus other constituents. Most of the feeds encountered now and in the past have been prepared from fuels irradiated to 1000 Mwd/ton or less and cooled for relatively long times before processing. However, it is anticipated that future power reactor fuels will be irradiated to as high as 10,000 to 20,000 Mwd/ton and that in the first cycles of the Purex- or Thorex-type solvent extraction processes, the organic reagents will be exposed to aqueous feed solutions that are ten times more radioactive than present-day feeds.

Among the effects caused by the degradation products are poor separation of the valued metals from contaminants, poor phase separations, loss of metal values to waste streams, and increased activity levels in the recycled organic extractant. To counteract these effects a solvent cleanup operation is used, first, to reduce the activity level and then, if possible, to remove the degradation products from the organic stream. The current solvent cleanup methods involve a combination of alkaline and acid washes, sometimes in conjunction with alkaline permanganate treatment. At low levels of degradation this scrubbing is generally sufficient to maintain acceptable radioactivity levels in the reagent-diluent mixture by stripping extracted fission products and by preventing buildup of low-molecular-weight acidic products which are primarily from hydrolysis of the extractant, for example, the strongly extracting dibutylphosphate (DBP) formed from the tributyl phosphate (TBP).

When solvent extraction was first recognized as a desirable method for the purification of atomic energy metals, much effort was spent on evaluating the effects of type and structure of reagents and diluents on extraction performance. Tributyl phosphate became the preferred reagent, and a number of commercial diluents, primarily saturated aliphatic hydrocarbons, passed the performance requirements for use with the low-activity-level feed solutions then being processed. Much of the subsequent supporting

research involved studies of the extractant, the effects of whose degradation frequently overshadowed the properties of the parent reagent. Meanwhile there was a strong tendency to label the diluents "inert." In the period beginning about 1954, the prospect of treating feeds at much higher activity levels, coupled with some bad operating experiences, again focussed the attention of a number of U.S. and foreign laboratories on the diluents.¹⁻⁵⁸

It is difficult to correlate the diluent degradation and cleanup data from the various processing sites, for while most of them use TBP as the active extractant, all use different supporting diluents. Although all the diluents are primarily saturated aliphatic hydrocarbon mixtures, some are characterized by substantial quantities of cyclic paraffins, some by high aromatic hydrocarbon content, some by relatively high degrees of unsaturation, and all have differing chain lengths and type of branching. Further, the solvent recovery procedure is frequently blamed for poor process results in cases where improper operation is probably the true offender, for example, improper feed preparation, unusual column operating conditions, introduction of contaminants by recycle of waste streams during periods of high metal-value losses, and subjection of the extractant to severe degradation by improper operation of equipment such as intercycle evaporators.

This paper deals first with the degradation behavior of the diluent in a single system, that of TBP-Amsco 125-82. The experiments led to the conclusion that nitroparaffins, RNO_2 , formed from the Amsco 125-82, were the major degradation products. The specifics of their chemical reactions offer an explanation of the observed behavior of degraded solvents,* a basis for suggesting possible alternative cleanup methods, and a guide in the selection of new diluents less susceptible to nitration.

*The complexing properties of some of these degradation products or related compounds are being examined in other applications, for example, in fission product extraction and feed pretreatment.^{59,60-62}

2. EXPERIMENTAL METHODS

Two methods were employed to degrade the solvent (extractant plus diluent) phases: (1) A 10,000-curie Co^{60} source was used to irradiate an agitated two-phase system,⁶³⁻⁶⁵ the aqueous phase being initially 2 M HNO_3 , and the radiation power being approximately 2.25 w/liter. (2) The solvent was boiled with 2 to 8 M HNO_3 under total reflux, the agitation being done by the boiling.

Tributyl phosphate was present during many of the degradations. Since the interest was primarily with the diluent and its properties, the degraded solvent was usually scrubbed with 0.2 M Na_2CO_3 to remove the low-molecular-weight acid products derived from TBP. Such scrubbing had been shown previously^{22,27} to restore TBP, degraded by either of the above methods, nearly to its original extraction behavior as measured in the present test procedure.

The degraded solvent is customarily used to extract metal ions, usually fission product Zr-Nb^{95} , from aqueous nitric acid, and the ability of the extracted metals to withstand subsequent stripping with nitric acid is one of the common measures of degradation.^{15,16,50} However, it has been observed here that the curves showing metal ion extraction and those showing retention ability are nearly always parallel when using the test procedure described below. To simplify the presentation of data, only the ability of the solvent to extract metallic cations is described in this paper.

Extraction-test procedure: (1) Make the degraded solvent 1 M in TBP and scrub twice with an equal volume of 0.2 M Na_2CO_3 to remove low-molecular-weight acids, primarily DBP and MBP (10 min for each contact). (2) Contact 30 min with solid calcium hydroxide, about 50 g of the solid per liter of organic phase, and separate from solid. (3) Contact the regenerated solvent with metal tracer solution (e.g., Zr-Nb^{95}) in nitric acid solution and measure the extraction. An equal volume of tracer solution containing 10^4 counts sec^{-1} ml^{-1} in 2 M HNO_3 is customarily used. The extraction of metal ion increases with increasing degradation.

Several tracer elements may also be used in the extraction test. Much of the testing was done with Zr-Nb⁹⁵. (The separation of the two elements is possible but tedious.) Where the testing continues over a period of time it is simpler to use the ⁴⁰Zr⁹⁵/⁶⁰Nb⁹⁵ equilibrium mixture. The niobium extraction coefficient is about a tenth of that for zirconium, and, when degradation is low, little is extracted in proportion to zirconium. Hafnium-181, though extracting with a coefficient nearer to that of niobium than to that of zirconium, has also been utilized, particularly in some tests where degradation is severe.¹⁵

Elemental analyses were performed by the ORNL Analytical Division: calcium and sodium by flame photometry of solutions obtained by stripping the elements from the organic extracts with 2 M HNO₃; nitrogen by the Kjeldahl method; carbon and hydrogen by combustion; sulfur by total decomposition of the organic phase and conversion to sulfate. Infra-red and ultraviolet absorption measurements were made, also by the ORNL Analytical Division, using Beckman IR7, and Cary model 14 recording spectrophotometers.

3. NATURE OF THE DEGRADATION

It will be expedient to preface considerations of the nature of the diluent degradation with a description of the effects of bases, especially calcium hydroxide, on degraded solvents. The marked effect of calcium hydroxide on solvents containing nitroparaffins, first noted in tests of cleanup by sorption on solids, is the basis for the sensitive test for the degree of nitration described above and has aided in the identification and interpretation of the role of the nitroparaffins in the behavior of degraded solvents.

3.1 Effects of Sodium Carbonate Scrubbing and Calcium Hydroxide Treatment on Extraction Behavior

Figure 1 shows the extractability of Zr-Nb tracer by a series of solvent samples degraded by gamma irradiation in the presence of nitric acid. Extraction by the "as-degraded" solvent rose rapidly with the extent of irradiation and is attributable largely to acidic DBP, etc., derived from the TBP. A smaller residuum of Zr-Nb extractants remained

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Fig. 1. Extraction Performance 1 M TBP/Amsco 125-82 Irradiated While Being Agitated with 2 M HNO_3 .

after scrubbing with sodium carbonate, in quantity increasing nearly linearly with irradiation. These extractants may include both neutral compounds and acid compounds of molecular weight too high for extraction into the aqueous scrub, and they may derive from the TBP, from impurities originally accompanying the TBP, and from the diluent.

Treatment with calcium hydroxide after sodium carbonate (Fig. 1) increased the Zr-Nb extraction at all except the lowest irradiation levels, and at the higher irradiation levels increased the extraction above that of the "as-degraded" solvent. During such treatment calcium is extracted, and the amount extracted by a given degraded solvent increases with contact time. This can be explained in terms of the tautomeric equilibria of nitroparaffins. (A primary nitroparaffin is shown; secondary nitroparaffins undergo the same reactions, but tertiary nitroparaffins and nitrobenzenes do not, having no alpha-hydrogen atom for the enolization. Further, a diluent molecule may have more than one nitro group, and each may enolize provided that there is an available hydrogen atom.)

NITROPARAFFIN EQUILIBRIA

In acid media the equilibrium of reaction (1) is far to the left (the keto form), and/or equilibration is slow. The equilibrium of reaction (2) in basic media is farther to the right (enol salt form), and equilibration is moderately fast. On shift to an acid medium, hydrolysis (reaction 3)

gives the free enol form in much larger amount than is obtained through reaction (1). Both the position of equilibrium and the equilibration rate in reaction (2) vary with different bases. Calcium hydroxide produces the enol salt more rapidly and in greater ultimate amount than does sodium carbonate (Table 1), lithium hydroxide, or sodium hydroxide solution; strontium and barium hydroxide solutions are less effective. With the assumption that either or both the enol and enol-salt forms readily extract Zr-Nb, these equilibria give a qualitative explanation of the different extraction curves in Fig. 1.

It may be noted that all the diluents involved in the foregoing discussion were 1 M in TBP. It is important that all comparisons be made with solutions comparable to each other, since TBP appears to give a large synergistic enhancement of Zr-Nb extraction by degraded diluent (Table 2).

Table 1. Sodium and Calcium Extraction by Degraded Solvent

Solvent Pretreatment: 1 M TBP-Amsco 125-82 irradiated 90 whr/liter, scrubbed with 0.2 M Na_2CO_3 (2 $\times$), 2 M HNO_3 (2 $\times$), 2.6 M NaCl (2 $\times$), all at phase ratio = 1 for 10 min

Sodium Extraction Test: Pretreated solvent contacted with 1 M NaOH at phase ratio = 1 for indicated time

Calcium Extraction Test: Pretreated solvent shaken with solid calcium hydroxide

Time of Contact	Extraction (Normality in Organic Phase)	
	Sodium	Calcium
10 min	0.0046	
30 min	0.0051	0.024
1 hr	0.006	
4 hr	0.009	
16 hr	0.013	0.08

Table 2. Synergistic Extraction by Degraded TBP-Amsco

Extractant	Approx. Nitrogen Molarity	Extraction from 2 M HNO_3 , 10^4 counts $\text{sec}^{-1} \text{ ml}^{-1}$ of Zr-Nb ⁹⁵ after Na_2CO_3 -Ca(OH) ₂ , scrubbing
Fresh 1 M TBP-fresh Amsco	0	100
Degraded Amsco (boiled with 2 M HNO_3 for ~15 hr)	~0.1	700
Fresh 1 M TBP in degraded Amsco 125-82 (boiled with 2 M HNO_3 for ~18 hr)	~0.1	8500

3.2 The Deleterious Effects of Nitroparaffins

A sample of Amsco 125-82 was severely degraded by boiling with an equal volume of 8 M HNO_3 under total reflux for about 6 hr. A part (possibly all) of the organonitrogen products from the degradation reaction were sorbed on chromatographic-grade alumina. The alumina was washed first with petroleum ether to remove undegraded diluent, and next with acetone to remove the sorbed material. Acetone was removed from the wash by evaporation, leaving a product consisting of 75.2% C, 12.6% H, and 2.7% N.

Infrared analysis showed bands with the degradation product which did not occur with the original Amsco 125-82 at 6.4 and 7.4 μ , typical of nitroparaffins, and at 5.8 and 2.8 μ , typical of oxidation products (carbonyl, carboxyl, and hydroxyl).

Purified organonitrogen compounds were added, at concentrations up to 0.3 M, to undegraded 1 M TBP-Amsco solutions, and the resulting mixtures were tested for Zr-Nb extraction. Solvents containing 1-nitrooctane ($\text{C}_8\text{H}_{17}\text{NO}_2$) and 2-nitrooctane [$\text{C}_7\text{H}_{14}(\text{CH}_3)\text{NO}_2$] showed little extraction after sodium carbonate treatment and enhanced extraction after calcium hydroxide treatment (Fig. 2), in considerable parallel with the behavior of degraded solvent shown in Fig. 1. Solvent containing caprylohydroxamic acid ($\text{C}_7\text{H}_{15}\text{CONOH}$) extracted Zr-Nb strongly, but extraction was not enhanced by calcium treatment, and the hydroxamic acid was noticeably unstable in nitric acid solutions. Solvents containing octyl nitrate

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Fig. 2. Extraction with TBP/Amsco-Nitrooctane Mixtures.

($C_8H_{17}ONO_2$) and decyl nitrite ($C_{10}H_{21}ONO$) did not extract increased amounts of Zr-Nb, with or without the calcium hydroxide treatment.

The concentrations of nitroparaffin in degraded Amsco 125-82 have been estimated by ultraviolet spectrophotometry and by total organic nitrogen determinations.⁵ The ultraviolet spectra of simple nitroparaffins give an intense band at around 200 $m\mu$, as did also a number of samples of Amsco and TBP-Amsco exposed for varying times to boiling nitric acid or to gamma irradiation in the presence of nitric acid⁶³⁻⁶⁵ (Fig. 3). The absorbance, attributed to nitroparaffin concentration, increased linearly with exposure time. Since 100 whr of irradiation per liter appeared to be nearly equivalent to 11 hr of refluxing with 2 M HNO_3 , the irradiation dose scale at the top of Fig. 3 was arbitrarily adjusted to make the slope for the diluent radiation damage match that for the diluent chemical damage, and this resulted in good agreement of the single TBP-diluent chemical-damage point with the TBP-diluent radiation damage. The slopes indicate that nitration was at least twice as fast in the presence of TBP, probably because of nitrate and nitrite extraction by the TBP,⁶⁶ and perhaps also from stabilization of the nitroparaffins by complexing with the TBP.*

Chemical analyses of organic-phase nitrogen in several of the degraded solutions indicated a fairly constant ratio of total nitrogen to nitro-groups as indicated by spectrophotometry. These include about half of the test points in Fig. 3. The right-hand scale, "Approx. Nitrogen Analysis," was fitted smoothly to these points, for general comparison.

3.3 Extraction Mechanism

As suggested above, if either or both the nitroparaffin enol and the enol-salt can complex zirconium, niobium, and hafnium readily, then all of the extraction behavior of the diluent can be accounted for on this basis. This hypothesis is difficult to test because of the extremely low concentrations usually involved, such that the extractions might

*While the degradation of TBP is enhanced by the presence of metal ions,¹⁷ some preliminary testing by boiling 1 M TBP-Amsco with 2 M HNO_3 containing uranium and zirconium salts did not appear to increase diluent degradation.

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Fig. 3. Correlation of Type of Degradation with Absorbance.

actually be accomplished by a trace component. However, the following single test at higher concentration suggests that a significant fraction of the nitroparaffin was involved at one time in hafnium extraction.

In this test, 1 M TBP/Amsco, refluxed for 6 hr with 2 M HNO_3 , then scrubbed with sodium carbonate solution, showed 0.1 M organic-phase nitrogen by chemical analysis. After 30 min of contact with solid calcium hydroxide, it contained 0.005 M Ca, presumably in association with at least 0.01 M extractant, indicating at least 10% enolization. Equilibration with 0.1 M Hf in 2 M HNO_3 gave 0.001 M Hf in the organic phase. (The hafnium was traced with Hf^{181} at 10^4 counts $\text{sec}^{-1} \text{ ml}^{-1}$; several tests at different activity levels indicated equilibrium between the tracer and the cold hafnium.) The combining ratio of organic ligand to hafnium is probably greater than 1:1, and previous data⁵ indicate that it may be 4:1. Assuming that this ratio holds, the 0.001 M Hf extraction represents combination with about 0.004 M extractant. This is about 40% of the nitroparaffin enol concentration indicated by the calcium extraction and hence strongly indicates extraction of the hafnium by the nitroparaffin enol itself, rather than by any compound derived from the nitroparaffin transiently and in only trace amounts. Three successive scrubs with equal volumes of fresh 2 M HNO_3 left 0.0003 M Hf in the extract, with nearly equal forward and backward distribution coefficients, $E_a^0 = 4$ to 5, confirming that equilibrium was reached and that all of the initial 0.001 M Hf was held by ligands with the same magnitude of complexing power as was the last 0.0003 M Hf retained in the extract.

Other extraction mechanisms have been and may be proposed, at least for the trace-level extractions. British workers^{8,15} question the extraction of zirconium by nitroparaffin enols and propose that the effective extractants are hydroxamic acids, derived from the nitroparaffin enols by rearrangement in the acid solution. They have shown a zirconium-hydroxamic acid adduct to be more stable than the hydroxamic acid is in acid solution. Direct evidence for the existence of hydroxamic acids in these systems has not yet been obtained, except for possible infrared identification at about 10^{-5} M in certain solvents degraded by batch radiolysis.

4. SOLVENT CLEANUP: REMOVAL OF THE NITROPARAFFINS

Whether the actual extraction and retention of fission products in degraded diluents is effected by enol nitroparaffin, by hydroxamic acids derived therefrom, or by other related components, such extraction correlates with the concentration of nitroparaffin present, and the elimination of nitroparaffins also eliminates the objectionable extraction. Accordingly, nitroparaffin concentration is used in the present study as a measure of diluent degradation, and solvent cleanup is defined as removal of the nitroparaffins.

While cleanup is somewhat simplified by this definition, it is still in strong contrast to the mere stripping out of the extracted and retained metals. That operation may reduce solvent activity levels, but it does not generally remove the extractants which remain to extract fission products again and recontaminate the solvent on recycle.

Several studies of solvent cleanup methods have been made at ORNL and elsewhere,^{*} but only three approaches will be discussed here:

(1) sorption of nitroparaffins on activated solids, (2) partitioning the nitroparaffins into liquid scrubbing reagents, and (3) distillation of the pure TBP-Amsco mixture away from the nitroparaffin.

4.1 Solid Sorption

Current solvent treatment in processing plants using TBP involves combinations of washings with acid solutions, alkaline solutions, and occasionally, alkaline permanganate solutions.⁴⁹ While each of these acts to remove degradation products of the TBP, only the alkaline permanganate treatment removes significant amounts of diluent degradation products from the organic phase. The absorption of degradation products from the diluent on the solid manganese dioxide that is formed during the scrubbing accounts for the cleanup, and the effectiveness of the treatment depends on temperature, amount of solid, alkalinity and degree of degradation. Activated alumina will also sorb diluent degradation products and as described above was used to collect enough of the degradation

* Pertinent references on solvent cleanup are: 1, 2, 6, 9, 15, 20, 34, 37, 43, 44, 46, 49, 56.

products to be identified as nitroparaffins. The two sorbants have been tested briefly⁶ on a 1 M TBP-Amsco solution which had been exposed in the presence of nitric acid to 45 whr of irradiation per liter. Principal interest was in the ability of the solids to decrease Zr-Nb extraction by the irradiated solvent. Results (Fig. 4) are compared on the basis of grams of alumina added to, or grams of manganese dioxide formed in, each liter of treated solvent.

The two solids showed similar sorption patterns in room-temperature tests. Impurities causing 50 to 60% of the Zr-Nb extraction by the irradiated, carbonate-scrubbed solvent were easily sorbed. Removal of another fraction causing 20 to 25% of the Zr-Nb extraction was achieved by further relatively large additions of solid, but, even at the highest solids levels used, the diluent retained 20 to 25% of its Zr-Nb extraction power. To achieve equivalent performance, it was necessary to use 10 to 20 times more alumina than manganese dioxide. The efficiency of cleanup by manganese dioxide increased when the accompanying sodium carbonate concentration was increased from 0.1 to 0.5 M. Raising the temperature to 50°C caused increased consumption of manganese dioxide, probably in removal of more organic material, but had no significant effect on the performance of alumina. Predrying of the alumina and variation of its particle size from +100 to -325 mesh were also without significant effect.

4.2 Liquid Scrubbing

Solvent cleanup with a liquid scrub rather than with a solid has definite operational advantages. In studies^{1,2,15,28} involving nearly a hundred liquids, or in some cases, liquid and solid combinations, the most effective cleanup was achieved by ethanolamine. The amine forms salts with the nitroparaffins, and these salts have significant solubility in the amine phase. Table 3 compares stepwise scrubbing of the degraded solvent with both 0.5 N NaOH and 100% ethanolamine. In each test series the organic phase was scrubbed with successive batches of fresh scrub solution, each equal in volume to the organic phase. After being scrubbed, the treated organic was used to extract Zr-Nb⁹⁵ from a 2 M HNO₃ tracer solution. The amine-scrubbed material decreased in extraction ability with each of the first four scrub stages, and, after the

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Fig. 4. Comparison of Cleanup by Alkaline Permanganate Solutions and by Activated Alumina.

fourth stage, the extraction ability of the treated solvent was almost indistinguishable from that of fresh TBP-Amsco. With the ordinary caustic scrubbing there was some initial decrease in extraction ability, but no further decrease was noted in the third and fourth stages. The extraction after four stages was still several times that with the fresh TBP-Amsco.

Table 3. Comparison of Sodium Hydroxide and Ethanolamine Cleanup of a Degraded Solvent

Scrub Stage	Zr-Nb ⁹⁵ Extraction by Organic Phase (counts sec ⁻¹ ml ⁻¹)	
	As Scrubbed	After Ca(OH) ₂
No Cleanup		
		4000
After Cleanup with 0.5 N Sodium Hydroxide		
1	800	3000
2	325	1000
3	300	600
4	300	600
After Cleanup with 100% Ethanolamine		
1	400	2500
2	200	800
3	150	70
4	70	70
Blank: Extraction by Fresh 1 M TBP in Fresh Amsco 125-82		
	70	70

Visually, there was also an indication of solvent cleanup in that the salts of the nitroparaffins are highly colored (orange to yellow), and, only after ethanolamine scrubbing did all the color report to the scrubbing phase.

A principal disadvantage of cleanup with ethanolamine is the relatively high reagent costs. The costs of a gallon each of 1 M TBP-Amsco and ethanolamine are about \$1.50 and about \$2.00, respectively. Therefore,

if, during processing, each gallon of TBP-Amsco requires 1 gallon ethanolamine for effective cleanup, then the cost for the scrub solution would be about \$2.00, or about 50 cents more than if the 1 M TBP were discarded without cleanup. The cost would be reduced if the degradation were not so severe as to require cleanup of the total solvent stream during each cycle, or if the amine solution could be recovered. On the other hand, if the extractant phase requires a greater than equal volume of scrub phase and if the amine cannot be recycled the costs will increase. This will be accompanied by increased costs for handling larger volumes of waste. In addition, there is a significant distribution of TBP to the ethanolamine phase. When contacting an equal volume of 0.5 to 1.0 M TBP in Amsco 125-82, the distribution appeared to be solubility-limited at about 0.05 M TBP (about 13 g/liter) in the ethanolamine. This loss of TBP is equivalent to about 6 cents per gallon of ethanolamine used.

4.3 Distillation

Low-pressure flash distillation appears at present to be the best, and possibly cheapest, method for the partial or total repurification of TBP-Amsco 125-82 solutions that have been decomposed by radiation in systems containing H_2O , HNO_3 , and $UO_2(NO_3)_2$. This statement is based on laboratory studies of molecular and rapid (not flash) distillation of 30% TBP-Amsco 125-82 solutions degraded in two ways: (1) by irradiation to the 122-whr/liter level in a nominal 10,000-curie Co^{60} source while being agitated with an aqueous phase containing 1.84 M HNO_3 and 310 g of uranium per liter in the ratio 2.7 vols of organic per volume of aqueous solution, and (2) by use in processing irradiated reactor fuels in the ORNL solvent extraction (Thorex) pilot plant. Both molecular distillation at about $70^\circ C$, which corresponds to about $10^2 \mu$ of TBP vapor pressure, and rapid pot-to-pot distillation at 110 to $120^\circ C$, corresponding to about $5 \times 10^2 \mu$ of TBP vapor pressure, showed that the degradation products detectable as nitro or similar compounds by fission product extraction-scrub-strip tests remained as a pot residue; that is to say, they are much less volatile than the hydrocarbon diluent or the TBP. Extraction tests showed almost no distillation of materials that affect the Zr, Nb, Ru, or U extraction properties of the 30% TBP-Amsco 125-82 extractant mixture.^{9,10,67}

On the basis of these tests, a specially designed flash distillation unit has been proposed by Weinrich and Associates (Fig. 5) to handle 150 liters of TBP-diluent solution per hour. This unit provides for heating the solution to 160°C, preferably after contacting with dilute Na_2CO_3 solution to remove HNO_3 and uranium, feeding the solution to a packed column at a pressure of 55-60 mm Hg, and flashing the diluent and TBP into two separate fractions. TBP, removed as a side stream, will contain some diluent, perhaps 10% diluent-90% TBP. The remaining diluent will be taken off the top of the still.

Costs of building and operating the flash distillation unit are estimated to be 11 to 15 cents per gallon of feed, including taxes, insurance, amortization, and general overhead, or \$0.078 per gallon exclusive of these costs. For comparison, and at purchase costs of \$0.34/gal, special treated naphtha and \$4.29/gal technical grade TBP, the initial cost of 30% TBP in Amsco 125-82 is about \$1.50/gal.

The fraction of the total plant throughput of TBP-diluent that would have to be distilled would depend on plant operating and radiation dose conditions. If the dose were high, for example, 0.1 whr per liter per pass, as experienced in the first cycle of the Thorex pilot plant, and if only one extractant stream were used for both cycles of extraction, then it would be necessary to distill 100% of the organic solution on each pass through the plant. On the other hand, if separate extractant streams for the two cycles were used, the plant inventory might require purification only once per ten passes of extractant through the plant. In any event, only one still would be needed to produce high quality TBP and diluent.

5. IMPROVING THE STABILITY OF AMSCO 125-82

Amsco 125-82 is a specially prepared aviation naphtha, a type of solvent which is generally considered to be among the most stable of the commercial aliphatic hydrocarbons. Yet, as shown above, Amsco can be degraded severely under several different conditions. When it is considered that Amsco 125-82 is composed of as many as 17 compounds in the C_{12} - C_{14} range³⁹ and that many of these are highly branched, it is not surprising that such degradation is possible.

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Fig. 5. Flash Distillation Systems for TBP-Amsco (excluding reflux streams).

Amsco can be improved by destroying, prior to process use, some of the sites reactive to nitric acid.⁶⁸ Experimentally this has been done two ways: (1) by scrubbing the Amsco before use with concentrated sulfuric acid; and (2) by preliminary nitric acid degradation followed by sulfuric acid cleanup.

Sulfuric acid scrubbing is more effective when Amsco is warmed while contacting with the concentrated acid (more than 95%), or when oleum is added to the concentrated acid for use at room temperature. In Fig. 6, the treated Amsco and untreated Amsco were made 1 M in fresh TBP and then degraded up to 24 hr by boiling with 2 M HNO_3 . Degradation was followed as previously by conversion of nitroparaffins to the enol form, through the sodium carbonate and calcium hydroxide treatments, and extraction of tracer (Hf^{181}). Whereas the solution in unpretreated Amsco, after 8 hr of nitric acid degradation, showed a hafnium extraction coefficient of $E = 16$, those in Amsco pretreated with 96%, 98%, or 100% sulfuric acid showed coefficients of 0.3, 0.15, and 0.03, respectively. Solutions in Amsco pretreated with 100% and 105% acid at room temperature and with 95.6% acid at 50°C for 30 min all had extraction coefficients of but about 0.15, even after 24 hr of degradation. The sulfuric acid apparently acts to destroy the active sites by sulfonation to sulfuric acid-soluble by-products or by rearrangement of the molecule to a more stable configuration. No sulfur has been detected in the diluent after treatment.

Amsco degraded with nitric acid, scrubbed with concentrated sulfuric acid at room temperature, made to 1 M in TBP and then boiled for 24 hr with 2 M HNO_3 was as stable as Amsco pretreated with 100 and 105% sulfuric acid at room temperature or with 95.6% acid at higher temperatures. This treatment makes use of the fact that sulfuric acid will partition nitroparaffins away from the bulk Amsco. (Such scrubbing is not practical on the 1 M TBP solution containing nitroparaffin, for the TBP also distributes to the sulfuric acid.)

The limit to cleanup suggested by the data of Fig. 6 is apparently real. Amsco was recovered from the 24-hr degraded 1 M TBP solutions by extracting the TBP and nitroparaffin with concentrated sulfuric acid. The recovered Amsco was again made 1 M in fresh TBP and subjected to an

Fig. 6. Acid Cleanup of Amsco 125-82.

additional 24-hr degradation with 2 M HNO_3 , and subsequent testing again gave a hafnium extraction coefficient of about 0.15. Repetition of the cycle four additional times produced the same amount of extractants during each 24-hr degradation. Apparently after the initial treatments to remove or deactivate the sites susceptible to easy nitration the bulk of the Amsco degraded at a consistently low rate.

This behavior has significance with respect to the distillation method of cleanup, for such treatment could constitute not only cleanup but gradual "purification" of the Amsco diluent. In other words, Amsco that has been degraded and distilled several times should be much less susceptible to degradation than the original stock.

6. INVESTIGATIONS OF ALTERNATIVE DILUENTS

Because most solvents now in use have structures at least as complicated as those in Amsco 125-82 (and apparently less stable), it is extremely difficult to make comparisons between data obtained at one operating site and those obtained at another. Further, different lots of the same diluent frequently have different compositions. The trend toward use of simple, relatively pure, more stable, normal hydrocarbons, e.g., n-dodecane, is encouraging, as is the effort of the petroleum industry to supply these at more reasonable prices than in the past.⁶⁹

Here, as at other laboratories, there is a program of systematic testing of alternative diluents. In addition to aliphatic compounds, a number of aromatics have been examined because these provide certain advantages in some solvent extraction systems. They help, for example, in solubilizing metal-salt complexes with some useful aromatic solvent extraction reagents, in increasing extraction ability of reagents such as TBP, in imparting greater radiation stability to the extracting reagent, and in improving the ability of reagents such as TBP to separate uranium from fission products.

Nitric acid attacks the aromatic (aryl-alkyl) diluents at points along the aliphatic side chain and, under some conditions, at points on the benzene ring itself. As with the aliphatic diluents, the calcium hydroxide used in evaluating degradation reacts only with those nitro groups that can enolize. Thus, nitro groups on the ring should not form

calcium salts nor lead to the extraction of fission products. Tests with pure compounds confirmed this assumption. Consequently, the term "stability of the aryl-alkyl diluents," as used in this section refers to the formation of primary and secondary nitro groups on the alkyl side chains, not to nitration of the benzene ring itself.

Table 4 shows the performance of a number of diluents in the usual carbonate-calcium hydroxide tests after degrading a solution 1 M in TBP for 4 hr in boiling nitric acid. All the simple aliphatic hydrocarbons tested were more stable than untreated Amsco 125-82, but the sulfuric-acid-scrubbed Amsco was of comparable stability. The stability of the aromatic diluents tested varied widely with structure. Benzene, the various methylbenzenes, the monoalkylbenzenes, and triethylbenzene usually had stabilities comparable to that of n-dodecane. The stability of alkylbenzenes with two side chains apparently depended upon the particular isomer or purity. Mixed diethylbenzenes from different sources gave widely differing stabilities. Gas chromatograms and infrared spectra show major differences that have not yet been interpreted.* The one mixture of diisopropylbenzenes was very unstable. Benzenes with single but cyclic side chains (tetrahydronaphthalene and cyclohexylbenzene) were also poorly stable. The indication that isobramching in monoalkylbenzenes may be favorable needs further substantiation. (Triisopropylbenzene was very unstable.)

It should be noted that although aromatic diluents have higher densities and viscosities than do the ordinary aliphatic diluents (e.g., d is about 0.86 for diethylbenzene vs d equal to about 0.76 for Amsco 125-82), satisfactory physical performance has been achieved in several continuous countercurrent solvent extraction applications.⁷⁰⁻⁷²

Several of the stable diluents have flash points acceptable for use in most plants ($\geq 140^\circ\text{F}$). Finally, although nitration of the benzene ring

*It has since been shown by the authors that m-diethylbenzene is about as stable as n-dodecane with respect to formation of fission product extractants during nitration. The ortho and para isomers, however, are much less stable. The most stable of the commercial diethylbenzenes were shown by the gas chromatographic analyses to have the highest meta isomer content.⁷³

Table 4. Performance of Degraded Diluents

Diluent	Flash Point (Closed Cup) °F	Zr-Nb ⁹⁵ γ (c/s/ml) (Calcium Test)
Alkyl Benzenes		
Methyl (toluene)	40	110
1,2-Dimethyl (<u>o</u> -xylene)	63	100
1,3-Dimethyl (<u>m</u> -xylene)	63	100
1,4-Dimethyl (<u>p</u> -xylene)	63	100
1,2,4-Trimethyl (pseudocumene)	125	100
1,2,3-Trimethyl (hemimellitene) 73% 96%	124	400 >6000
1,2,3,4-Tetramethyl (prehnitene)	163 ^a	200
1,2,3,5-Tetramethyl (isodurene)	155 ^a	1400
Ethyl	59	500
Diethyl (mixtures) (Ref 73)	138 ^a	4000, 10000
Triethyl (mixture)		140
Propyl	86	80,450
Isopropyl (cumene)	102	30,4000
Diisopropyl (mixture)	170	>6000
Triisopropyl	170	>6000
<u>n</u> -Butyl	160 ^a	125
<u>sec</u> -Butyl	126	130
<u>tert</u> -Butyl	140 ^a	120
<u>iso</u> -Butyl		45
Tetralin	171	decomposes
1-Methyl-4-isopropyl (paracymene)	138	4000
<u>sec</u> -Amyl	~150 ^a	170
<u>tert</u> -Amyl (1,1-dimethylpropyl)		130
<u>n</u> -Hexyl		120
Cyclohexyl		>6000
<u>n</u> -Nonyl		180
Dodecyl (branched mixtures)		220
Solvesso-100	118	>6000
Solvesso-150	150	>6000
Aliphatic Hydrocarbons		
Amsco 125-82	128	4000
Amsco 125-82 (H ₂ SO ₄ scrubbed)	128	100
<u>n</u> -Decane	115	1000
2,2,5-Trimethylhexane		80
<u>n</u> -Dodecane	165	125
<u>n</u> -Hexadecane		140

^a Open cup.

does not form Zr-Nb extractants, the factors influencing such nitration and the resulting effect on diluent properties, including safety, need further study.

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