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Purex Process Solvent Literature Review

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PUREX PROCESS SOLVENT
LITERATURE REVIEW

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Research and Engineering

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INTRODUCTION

The purpose of this document is to summarize the data on Purex process solvent presently published in a variety of sources. Extracts from these various sources are presented herein and contain the work done, the salient results obtained, and the original, unaltered conclusions of the author of each paper. Three major areas are addressed: solvent stability, solvent quality testing, and solvent treatment processes.

CONCLUSIONS

A number of conclusions were reached from the work carried out with respect to Purex process solvent.

SOLVENT STABILITY

- Tributyl phosphate (TBP)-kerosene solvent is degraded by either heat or radiation.
- The amount of radiation required to cause observable degradation is known.
- The products of degradation have been identified.
- The effects of degradation products on solvent performance have been demonstrated.
- The stability of various classes of hydrocarbons in relation to nitration and radiolytic degradation has been determined.

SOLVENT QUALITY TESTING

Several tests for solvent quality have been devised. However, in general, they do not detect minor changes unless those changes are part of a long-term trend. However, major changes in solvent quality, e.g., the ability of the solvent to effect decontamination factor (DF) of the products, are detectable in some instances.

SOLVENT TREATMENT

Treatment of used Purex process solvent has been studied extensively. It has been concluded generally that:

- Washes with sodium carbonate and/or sodium hydroxide remove radioactivity but are not effective in removing the compounds responsible for forming the complexes with the fission products. Increases in contact time and/or temperature improve fission product removal.
- Dilute nitric acid alone is of little value as a solvent wash reagent.
- The use of a calcium hydroxide wash following a sodium carbonate wash was detrimental to solvent quality.
- Washing with a mixture of sodium carbonate and potassium permanganate has proved a very effective treatment for used solvent.
- Alkaline hydroxylamine treatment gives solvent DF comparable to permanganate carbonate mixture.
- Washing with hydrazine solution is comparable to washing with sodium carbonate as far as fission product removal is concerned.
- Treatment of used solvent with a macroreticular resin produces solvent of excellent quality.
- Distillation by flashing at reduced pressure or vacuum fractionation appears impractical as a solvent treatment method.

DOCUMENT EXTRACTS

Following are extracts from 34 published documents. The shortened title of each document is followed by a document identification number. Complete identification of each document is given in Extract Bibliography.

CHEMICAL STABILITY OF PUREX PROCESS SOLVENT (1, HW-34501)

Data obtained during a study to demonstrate the effect of nitric and nitrous acid on Shell Spray Base (E-2342) diluent and diluent plus 30% by volume TBP at 71°C are shown in Table 1.

TABLE 1. Chemical Effects of Nitrite Ion on Diluent or Diluent Plus TBP at 71°C.

Description	Exposure Time, hr	Uranium Distribution Value	Uranium Transfer Rate		Dispersion Time, sec	Coalescence Time, sec
			K	R ^a		
"As Received" Shell Spray Base Versus 2.25M HNO ₃	163	0.0051	14.24	1.11	68	19
"As Received" Shell Spray Base Versus 2.25M HNO ₃ , 0.01M NaNO ₂	144	0.055	9.24	0.70	57	30
"As Received" Shell Spray Base + 30% vol TBP (CO ₂ washed) Versus 2.25M HNO ₃	139	0.008	11.69	0.97	80	46
"As Received" Shell Spray Base + 30% vol TBP (CO ₂ washed) Versus 2.25M HNO ₃ + 0.01M NaNO ₂	139	0.028	13.00	1.02	62	53
"As Received" Shell Spray Base + 30% vol TBP (CO ₂ washed) Versus 2.25M HNO ₃ + 0.1M NaNO ₂	139	0.19	10.01	0.79	45	55

^a Ratio of uranium transfer rate constant, K, to rate constant of standard solvent.

The conclusions reached from these and other experiments are as follows:

- TBP solutions (30%) in Shell Spray Base, Soltrol-170, Bayol-D, and Ultrasene were found to be satisfactorily stable at 71°C in nitric acid concentrations up to 6.0M, providing nitrous acid is excluded.
- In the presence of nitrous acid, the above solvents (or the diluents alone) are unstable when in contact with aqueous nitric acid at 71°C and react at rates which increase with increasing nitric acid concentration. Soltrol-170 shows greater resistance to attack than does Shell Spray Base.
- The effect of nitrous acid in promoting chemical instability can be eliminated by the addition of nitrite inhibitors to aqueous phases to be contacted with an organic phase. Experiments have shown that 0.2M urea or 0.2M sulfamic acid completely eliminates effects due to nitrous acid.
- Nitrous acid is not a catalyst but enters directly into the reactions. By analysis, nitrite esters, nitroso compounds, and oxidation products are found among the impurities in solvents exposed to combined nitric acid-nitrous acid attack.
- The impurities resulting from the chemical decomposition of Shell Spray Base cause increases in uranium distribution coefficients (K_d) under dilute C Column conditions, increases in coalescence times, lowering of the uranium transfer rate, lowering of dispersion time, enhanced fission product retention by the solvent, and enhanced foaming during the course of uranyl nitrate (UNH) calcination.
- The aromatic content of diluents of the Shell Spray Base type seems to have little effect on the solvent as regards its use in a Purex-type process. This seems to be due to impurities arising from the aromatic constituents being among those readily removed by aqueous carbonate washing.

IMPURITIES IN USED SOLVENT (2, HW-34502)

A direct analysis of recycled Uranium Recovery Plant solvent (20% by volume TBP in Shell E-2342 diluent) was made to determine type, source, and properties of impurities generated in the solvent and present in the solvent after it has been in use for some time. This work was directed toward the separation and identification of the impurities by compound class. Impurities originating from the diluent were positively identified as:

- Aliphatic nitro compounds, resulting from nitration by nitric or nitrous acid.
- Aliphatic carboxylic acids, resulting from oxidation reactions of nitric or nitrous acid.
- Aliphatic nitroso compounds, produced by the action of nitrous acid on secondary nitro compounds.

Impurities originating from the diluent and whose presence are strongly indicated, but have not been positively identified, are:

- Aromatic compounds, probably nitro and nitroso.
- Ketones or aldehydes which may be intermediates in oxidation reactions leading to carboxylic acid formation.

Impurities originating from TBP are:

- Dibutyl phosphate (DBP) resulting from hydrolysis of TBP.
- Tributyoxyethyl phosphate, present originally as an impurity in TBP.
- Two additional phosphorus compounds not specifically identified.

Uranium Kd measurements on the chromatographically separated fractions show that impurities arising from the diluent are the principal cause of deterioration in solvent quality. The fractions containing phosphate esters were among those having no deleterious effect.

Separations were not sufficiently complete to evaluate the effect of impurities on an individual basis. Using butyl nitrite and nitropropane as stand-ins for the nitrite esters and nitro compounds may be relatively innocuous.

Of the various impurities found in the recycled solvent, only DBP can be removed efficiently by a dilute carbonate wash solvent treatment procedure. However, failure to find more than trivial amounts of material of an aromatic character among the impurities indicates these are removed. It seems probable that a portion of the organic acids and nitroso compounds are also removed.

The uranium Kd values shown in Table 2 indicate that impurities derived from the diluent are primarily responsible for chemical deterioration in the solvent. Fractions I and K contain no phosphorus compounds and yield the highest Kd. These fractions are mixtures and could not be further resolved so that the effect of individual components could be estimated separately. These fractions differ, however, in that fraction I contains nitrite esters and this may account for the higher Kd observed. A comparison of fractions C and D lends credence to this hypothesis in that nitrite esters are a major impurity in fraction D. Further indication that nitrite esters may be deleterious was obtained when addition of 1% by volume butyl nitrite raised Kd of a 30% TBP (vacuum distilled) Shell Spray Base solution from 0.004 to 0.33.

Aliphatic nitro compounds constitute a major portion of impurities identified in these fractions. Their separation from other impurities is not complete enough to estimate their effect, taken singly. The addition of 1 and 2% by volume nitropropane to 30% TBP (vacuum-distilled) Shell Base, however, produced little change in the Kd, so it is not believed that their effect is serious. Nitropropane, admittedly, is not necessarily representative of these compounds because of its comparatively low molecular weight.

TABLE 2. Composition of Fractions Separated From Used Uranium Recovery Plant Solvent.

Fraction	Kd ^a	Description of Fraction Composition
B	0.002	Contains the aromatic nitro and nitroso compounds, an unidentified carbonyl compound, and small amounts of TBP.
C	0.0013	Nearly pure TBP, trace of nitroso compound indicated by Lieberman test.
D	0.06	Impure TBP. Strong evidence for nitrite ester presence. Unidentified carbonyl compound (ketone or aldehyde) also present.
E	0.018	Impure tributoxyethyl phosphate. Unidentified carbonyl compound (above) as well as nitro and nitroso compounds detected.
F-G	---	Impure tributoxyethyl phosphate.
H	0.059	Contains unidentified phosphorus compound. Strongly acid to indicator paper and shows acid C=O and OH bands in infrared. Aliphatic nitro compounds are also present.
I	1.08	No phosphate esters. Strongly acid, contains acid C=O and OH in infrared. Strong evidence for presence of nitrite ester. Positive nitroso test by Lieberman reaction. Strong aliphatic nitro compound absorption in infrared.
J	0.035	Contains unidentified phosphorus compound different from fraction H. Contaminated by small amounts of impurities listed from fraction I.
K	0.205	No phosphate esters. Moderately acid to indicator paper, contains acid C=O and OH bands in infrared. Positive nitroso test by Lieberman reaction. Aliphatic nitro compounds present.
L	---	Same as fraction I.
M	---	Eluted with 6.0M HCl. Yellow in color, sweet odor. Not separable from aqueous phase and, therefore, not further identified.

^aResult of an equal volume contact of the organic with 1 g/l uranium (as UNH) followed by analysis of the clear organic layers for uranium. The samples are 30% TBP containing 2% by volume of the impurity. These samples are normally washed with carbonate prior to test. For these samples, the carbonate wash was omitted.

The nitro compounds may be offensive only in that being chemically very reactive, their presence results in formation of secondary reaction products having much worse characteristics. In alkaline media, the nitro compounds enolize and are very reactive in this form. It may be significant, in this connection, that 2.0M NaOH washing raises, rather than lowers, the Kd of impure solvent. Continued recycling of these reactive substances may lead to formation of secondary reaction products which would otherwise never appear, e.g., reaction with nitrous acid to yield nitroso compounds or nitrolic acids.

High molecular weight carboxylic acids are known to behave as surface active agents. Some are known to form comparatively insoluble salts with heavy metals and this may be a factor in crude formation and in fission product retention.

STABILITY OF PUREX SOLVENT TO RADIATION AND CHEMICAL ATTACK (3, HW-38263)

The influence of variables affecting solvent degradation rate was found to be:

- The rate of solvent deterioration due to chemical action in systems representative of those in the Purex Plant was studied as a function of the variables involved. The rate of deterioration was directly proportional to the concentration of acid, directly proportional to the concentration of nitrate ion, and proportional to the square root of the concentration of nitrite ion. These observations can be expressed as the rate law

$$dK/dt = K (H^+) \cdot (NO_3^-) (NO_2^-)^{0.5}$$

where dK/dt is the rate at which the "C" contact extraction coefficient* increases as a function of time and the concentrations of reactants are those present in the aqueous phase before equilibration.

- The rate of solvent deterioration due to chemical action was double for each 5°C temperature increase.
- Soltrol-170 diluent resisted chemical attack a factor of two better than Shell E-2342 diluent. The stability of Ultrasene was about the same as that of Shell E-2342, and the stabilities of Bayol-D and AMSCO-125-90W were about the same as that of Soltrol-170.

*The organic phase (30% TBP-diluent) was contacted with an equal volume aqueous phase containing 1.0 g/l uranium (as U⁴⁺) in water. The organic phase was then analyzed for uranium and the extraction coefficient calculated. Duplicate determinations usually agreed to within 30%. When using pure TBP and unused diluent, the extraction coefficient was found to be about 0.065. Experience in the Uranium Recovery Plant has shown that operating difficulties arise when this extraction coefficient is in the region of 0.02.

- Radiation produced no appreciable solvent deterioration until the solvent received a dose of 20 Wh/l, a factor of 8 higher than estimated for the dose received by the solvent during its lifetime in the Purex Plant. The deterioration occurring between 20 and 200 Wh/l was due to the action of radiation on TBP rather than the diluent. Somewhere between 200 and 400 Wh/l, damage to the diluent begins to produce serious deleterious effects.

These conclusions allow a calculation of the equilibrium level of the solvent deterioration products in the Purex Plant. With the plant operating at 60°C under specific conditions* with Soltrol-170 as diluent, this level should not be high enough to hinder plant operation. With the same flowsheet and diluent at 70°C, however, the level of the deterioration products would exceed that necessary to hinder plant operation.

Of the tests of solvent quality employed in this work, the "C" contact extraction coefficient test was found to be best for studying solvent quality as a function of chemical or radiation damage.

* R. E. Smith, "Purex Chemical Flowsheet HW 3", HW-31373, General Electric Co., Richland, WA, April 6, 1954.

RADIATION EFFECTS ON ORGANICS IN SOLVENT EXTRACTION OF FUELS (4, Nuc. 17, 1957)

In TBP-naphtha solvent systems for processing irradiated reactor fuels, a noticeable drop in DF may occur at radiation doses as low as 0.5 Wh/l. However, significant radiation damage begins to affect the performance of the solvent extraction system materially at exposures of 10 to 30 Wh/l, as shown by uranium, plutonium, and fission product retention in the solvent (Table 3), as well as by a drop in the DF from fission products (Table 4).

TABLE 3. Effect of Solvent Irradiation on Uranium Retention.^a

Extraction Cycle	Uranium Remaining in Solvent, mg/ml			
	No Irradiation (control)	3.5 Beta Wh/l	17.5 Beta Wh/l	35 Beta Wh/l
After 1st strip	4.63	4.41	6.61	4.92
After 2nd strip	0.006	0.078	0.344	0.432
After 3rd strip	0.0002	0.001	0.190	--
After 4th strip	0.0002	0.0002	0.095	0.430

^aSolvent: TBP in oleum-treated AMSCO special naphtha 1.
Strip: Demineralized water.

NOTE: Solvent irradiated to level shown, equilibrated with nitric acid-UNH solution to form uranium-bearing solvent having uranium concentration of 35 mg/ml, and stripped with double-volume batches of demineralized water.

TABLE 4. Gamma Radiation Effects on Solvent Extraction With TBP.

Radiation Exposure Wh/l	Uranium DF	Beta Activity of Used Solvent, cpm/ml
0	5,000	550
2.4	1,300	225
4.3	2,200	110
27	220	4×10^3
30	600	1.3×10^5
280	21	1.4×10^5

The ultraviolet spectra of irradiated TBP-naphtha solvent indicated that a radiation exposure of 12 Wh/l did not greatly affect the material. Therefore, it can be assumed that the deleterious effects of radiation damage occur at exposures of 20 to 30 Wh/l. The controlling factor, however, may be radiation-induced emulsifiers or insoluble compounds that would impair or possibly prevent operation of the first solvent extraction cycle.

Some G values (i.e., number of molecules affected per 100 eV of energy absorbed) for the decomposition of saturated hydrocarbon formations are as follows: hydrogen = 4.2, methane = 0.22, and polymer in n-heptane = 1.7. In general, the G value of H_2 decreases with increasing chain length to about 3.5; the G value for CH_4 increases with the number of methyl groups; and the G value for the amount of starting material permanently altered varies from 4 to 8. This indicates that the saturated hydrocarbons are not particularly stable toward radiation but are not particularly subject to chain polymerization reactions.

For the formation of peroxides, carbonyls, and acids in oxygen-saturated n-heptane, the G values are: $R_1OOR_2 = 2.2$, $ROOH = 1.2$, $H_2O_2 = 0.3$, carbonyl = 2.0, $COOH = 0.4$, for a total of 6.1. This is in close agreement with the value for the amount of material permanently altered.

SOLVENT WASHING WITH BASIC PERMANGANATE (5, HW-50379)

A basic potassium permanganate solvent wash was found to be very effective in reducing the residual fission product activity of used TBP solvent (TBP diluted by a suitable hydrocarbon). The mechanism has since been determined to involve coprecipitation of manganese dioxide in the solvent phase and subsequent adsorption of the fission product-complexing ligand.

Potassium permanganate scavenging of used Purex process solvent reduced the zirconium-niobium and ruthenium gamma activity by as much as 80- and 11-fold, respectively. These results were obtained by an equal volume, 20-minute contact with 0.01M KMnO_4 in 3 wt% Na_2CO_3 solution at 50°C, conditions which appeared to be near optimum. The zirconium-niobium and ruthenium DF were better by factors of 5 and 2, respectively, than those obtained in 3 wt% Na_2CO_3 solution alone under otherwise comparable conditions.

Changing any of the following variables from the above values as indicated reduced the zirconium-niobium DF by 2 to 3.5 and the ruthenium DF by 1.5:

- Reducing the KMnO_4 concentration of 0.001M
- Reducing the temperature to 25°C
- Reducing the contact time to 5 minutes
- Reducing the aqueous-to-organic ratio from 1.0 to 0.05.

The effectiveness of the permanganate over the normal carbonate was decreased to zero after three throughputs of solvent because of the complete reduction of the KMnO_4 . This is a short life compared with that of Na_2CO_3 scrub (normally used for about 20 to 30 organic throughputs).

Other miscellaneous information about potassium permanganate behavior is listed below:

- The KMnO_4 dKd was 0.034.
- KMnO_4 scavenging did not increase uranium or plutonium retention in the solvent.

- MnO_2 collected at the interface. It could be readily dissolved in dilute nitric acid by adding reducing agents such as ferrous or nitrite ions.
- Unreacted KMnO_4 in the organic phase was quickly reduced to MnO_2 by a dilute nitric acid wash. It could also be washed out readily by water or 3 wt% Na_2CO_3 solution.

A TEST FOR SOLVENT QUALITY (6, DP-237)

In the TBP-kerosene extraction process for the recovery of uranium and plutonium from irradiated fuel, the solvent may be degraded to form materials that limit the extent to which certain fission products can be removed. Some of these degradation products (1) arise from the kerosene diluent used in the solvent, (2) are not removed from the solvent by caustic washing, and (3) form very strong complexes with zirconium. Hence, a practical way to test for solvent quality would be to measure the essentially irreversible extraction of zirconium.

A method referred to as the Zirconium Index Test (Z test) was devised to give a measure of the degradation products that appear in the solvent. The Z value (number obtained from this test) makes it possible to predict the performance of the solvent in the extraction process.

In the Z test a zirconium tracer solution is adjusted to a specified concentration of inactive zirconium and is equilibrated with the TBP-kerosene solvent. The solvent is then scrubbed three times with 3M nitric acid, and a sample of the solvent is counted for zirconium beta activity. The concentration of zirconium retained in the solvent is calculated from the known ratio in the tracer of radioactive zirconium to total zirconium. The Z value is then the concentration of zirconium retained by the solvent in moles per million liters.

The precision of the Z test was determined from four results on solvent of low Z value and from 10 results on solvent of high Z value. The low Z values gave an average of 44 and a standard deviation of 1.5 (3.4%). The high Z values gave an average of 261 and a standard deviation of 3.5 (1.3%).

TBP AND ITS DILUENT SYSTEMS (7, IEC50)

One factor which makes TBP one of the most important solvents for processing nuclear fuels is its chemical stability. However, degradation reactions give butyl acid phosphates which may react with metal ions being separated and must, therefore, be kept at low concentrations. Because radiation damage may lead to similar products, radiolysis, not only of pure TBP but also its mixtures with various diluents, was examined in detail.

Qualitative Observations

Preliminary distillation of TBP, given an exposure of 250 Wh/l (about 10^8 r), gave evidence of butyl alcohol and ether, DBP and monobutyl phosphate (MBP), and a high molecular weight polymer. Distillations carried out at 21-mm mercury and at less than 1-mm mercury yielded the same products. Phosphoric acid was not found in any samples given an exposure up to 250 Wh/l. TBP, severely degraded at 3000 Wh/l, gave a sirupy mass from which phosphoric acid was extracted. No peroxides were detected whether or not air was present.

Approximate yields of off-gas expressed as G values were: hydrogen 2.5, butane plus butene 0.08 (total), propane 0.05, ethane 0.02, and methane 0.05.

DBP Yield From Pure TBP

The liquid products of the radiolysis, especially DBP, is formed in much larger amounts than any other compound (Tables 5 and 6).

G values for MBP at the above exposures are 2.2 and 1.5 for dry and wet TBP, respectively.

DBP Yield From TBP Diluent System

The DBP yields were not significantly changed by dilution of dry TBP with iso-octane to concentrations of 75, 40, 30 and 10% TBP, water saturated solutions, or the substitution of other paraffin hydrocarbons, e.g., Soltrol-170, for iso-octane.

TABLE 5. Radiolysis of Pure and Diluted TBP.
[Dose, 250 Wh/l ($\sim 10^8$ r), 1.25 MeV gamma]

TBP	DBP		MBP		Butyl Alcohol	
	Yield, g/Wh	G value	Yield, g/Wh	G value	Yield, g/Wh	G value
Dry	0.14	1.8	0.02	0.3	0.02	0.7
Water satd. ^a	0.091	1.2	0.02	0.3	0.01	0.4
With 50% butyl alcohol	0.093	1.2	0.01	0.2	----	---
Dry, with 70% iso-octane	0.15	1.9	0.03	0.5	0.02	0.7
Water-satd. with 70% iso-octane	0.11	1.4	0.03	0.5	----	---

^aSaturation results in a mole ratio of $H_2O/TBP \sim 1$.

By contrast, use of benzene as a diluent gave a lower yield of DBP. As benzene is added, the yield drops rapidly to about one sixth that of pure TBP. The stability and protective action of a benzene ring as part of the molecule being irradiated is well known in radiation chemistry. Merely employing the benzene as a diluent is also effective.

Carbon tetrachloride as a diluent gave higher DBP yields which increase as the concentration of carbon tetrachloride increases (Table 7). The yield of DBP is based on the energy absorbed by the TBP. This does not account for the energy imparted to its molecules from hot radicals produced from irradiated carbon tetrachloride which has a high free radical yield and consequently is able to transfer gamma energy absorbed through collisions of these free radicals to other molecules. Hence the strong dependence of the DBP yield on carbon tetrachloride concentration. The fact that the DBP yield in a TBP-hydrocarbon system does not vary with the diluent concentration must indicate that free radical yields for iso-octane and Soltrol-170 are low and comparable with that of TBP. Table 8 gives some of the free radical yields previously obtained.

TABLE 6. Radiolysis of TBP and Its Mixtures.
(Dry systems, 0.6-1.0 MeV gamma)

TBP	Dose, r	DBP ^a		Butyl Alcohol ^a		Chloride ^b	
		Yield, g/Wh	G value	Yield, g/Wh	G value	Yield, g/Wh	G value
Pure	10 ⁴	0.65	7	-----	-----	-----	-----
	10 ⁶	0.13	1.7	0.014	0.5	-----	-----
	10 ⁷	0.13	1.7	0.016	0.5	-----	-----
	10 ⁸	0.13	1.7	0.02	0.7	-----	-----
30% in iso-octane	10 ⁴	1.05	13	-----	-----	-----	-----
	10 ⁵	0.27	3.4	0.4	14	-----	-----
	10 ⁶	0.17	2.3	0.04	1.4	-----	-----
	10 ⁷	0.17	1.8	0.02	0.7	-----	-----
	10 ⁸	0.17	2.3	0.02	0.7	-----	-----
30% in Soltrol-170	10 ⁴	0.8	10	-----	-----	-----	-----
	10 ⁵	0.24	3.1	0.4	14	-----	-----
	10 ⁶	0.13	1.7	0.05	1.8	-----	-----
	10 ⁷	0.16	2.0	0.03	1.0	-----	-----
	10 ⁸	0.16	2.2	0.03	1.0	-----	-----
30% in carbon tetrachloride	10 ⁴	4.1	52	-----	-----	0.39	29
	10 ⁵	1.3	17	0.4	14	0.14	11
	10 ⁶	0.78	10	0.04	1.4	0.088	6.6
	10 ⁷	2.3	31	0.01	0.4	0.068	5.1
	10 ⁸	1.1	14	0.001	0.04	0.041	3.1

^aYields based on energy absorbed by TBP.

^bYields based on energy absorbed by carbon tetrachloride.

TABLE 7. Effect of Dry TBP Concentration
in Diluent Mixtures.

TBP Vol%	Chloride Yield		DBP Yield	
	g/l	Y, g/Wh	g/l	Y, g/Wh
In CCl ₄ ; dose, 1.0×10^7 r; 0.6 to 1.0 MeV gamma				
0	2.46	0.069	---	---
10	2.57	0.080	4.4	1.8
30	1.60	0.064	7.6	1.0
75	0.68	0.071	6.8	0.37
99	0.41	0.15	5.6	0.23
100	---	---	3.8	0.15
In benzene; dose, 8.7×10^7 r; 1.25 MeV gamma				
2			0.10	0.025
10			0.62	0.029
20			1.56	0.036
30			2.60	0.041
50			5.75	0.054
80			15.5	0.091
90			22.7	0.12
96			27.7	0.14
99			31.7	0.15

TABLE 8. Free Radical Yields From
Gamma Radiolysis
(Radium Source)

Compound	Free Radicals Produced/ 100 eV
Carbon Disulfide	0.85
Benzene	1.8
Toluene	3.1
Ethylbenzene	9.0
Nitrobenzene	4.5
n-Heptane	9.9
n-Octane	11.4
Cyclohexane	14.3
Methanol	24.0
Ether	24.5
Ethyl acetate	32.0
Chlorobenzene	17.5
o-Dichlorobenzene	30.0
Ethyl bromide	28.0
Chloroform	57.5
Carbon tetachloride	70.0

Chloride Yield

Chloride production was measured as a function of carbon tetrachloride concentration in its mixtures with TBP. Chloride yield was constant from 0 to 75% TBP carbon tetrachloride (Table 7), but increased by a factor of almost 20 at 99%.

For the pure carbon tetrachloride system the yield was increased when water or oxygen was present. As seen from Table 9, in the TBP-carbon tetrachloride system the presence of dissolved oxygen or water did not affect the chloride yield at a dose of 10^7 r.

Effect of Uranium and Nitric Acid

The presence of uranium and nitric acid reduced DBP yields (Table 10) more than the similar effect from adding water to TBP. The gas produced in TBP saturated with UNH was about 30% less than for pure TBP. The chloride yields are slightly higher in the presence of uranium and nitric acid.

Application to Fuel Processing

In terms of total radiation damage, TBP can be considered a normal organic compound. One compound, DBP, is produced in considerably higher yield than any other. Although this compound is an objectionable impurity in TBP used for solvent extraction of plutonium or uranium, the amount of radiation received in most processing applications is less than 0.1 W/l. The small amount of DBP formed under such conditions is not objectionable. A concentration buildup can be prevented by periodically washing the solvent with an alkaline solution. The limitations imposed by higher radiation exposures to the solvent are well known.

TABLE 9. Effect of Dissolved Air and Water on Chloride Yield.
(Irradiated CCl_4 , 0.6-1.0 MeV gamma)

CCl_4	Dose, r	Chloride	
		G/l	Y, g/Wh absorbed by CCl_4
Air satd.	10^5	0.064	0.18
	10^6	1.0	0.28
	10^7	2.5	0.069
Water satd.	10^7	4.1	0.11
Degassed	6.8×10^5	0.49	0.20
	7.8×10^6	0.78	0.027
	8.6×10^7	3.3	0.011
With 30% TBP			
Air satd.	10^7	1.6	0.064
Water satd.	10^7	1.7	0.069
Degassed	10^7	1.7	0.069
With 40% TBP			
Air satd.	10^7	1.3 ^a	0.064
Degassed	9.4×10^6	1.7	0.086

^aInterpolated from Table 7.

TABLE 10. Chloride and DBP Yields.
(In two-phase and single-phase systems
irradiated with ^{60}Co gamma rays)

System ^a	Dose, R	Yield, g/Wh		
		Cl^-	DBP initial	DBP after 3 days ^b
Two-phase, 30% TBP in CCl_4 aqueous $\text{UO}_2(\text{NO}_3)_2$	10^4	0.27	1.0	1.3
	2×10^5	0.36	0.3	0.9 ^c
Single-phase, 30% TBP in CCl_4 equili- brated with aqueous $\text{UO}_2(\text{NO}_3)_3$	10^4	0.24	0.8	0.8
	2×10^5	0.35	0.24	0.9 ^c
	4×10^5	0.33	0.15	0.6 ^c

^aAqueous phase consisted of 0.7M $\text{UO}_2(\text{NO}_2)_3$ and 2M HNO_3 .

^bCorrected for chemical hydrolysis (~ 0.004 g DBP/l/day).

^cAfter 2 days.

SOME ASPECTS OF THE CHEMISTRY OF KEROSENE AND RELATED INERT DILUENTS RELEVANT TO EXTRACTION PLANT USE (8, AERE-R-3501)

Chemical study of the inert diluent (odorless kerosene) used in the TBP extraction process received scant attention in early studies. Under particular conditions and after long periods of solvent recycling, however, some signs of solvent degradation become apparent, including: (1) retention of uranium, plutonium and fission products in the washed solvent phase; (2) poor phase separation; and (3) reduction in DF.

Composition of Kerosene and Related Compounds

Crude oil varies enormously in composition and properties, but the composition from a given field normally remains fairly constant. Each crude is a mixture of thousands of hydrocarbons conveniently classified as paraffins, naphthenes, and aromatics. Olefinic groups are rarely found in crude oils and acetylenic groups never.

Nonhydrocarbon Constituents of Petroleum

Mercaptans, open-chain sulphides, and cyclic sulphides have been found in petroleum and both straight- and branched-chain varieties identified. Thiophenes and aromatic thiols have been identified in cracked petroleum fractions but not in naturally occurring petroleum. Only the alkyl mercaptans of low molecular weight are soluble in aqueous alkalies.

Nitrogen occurs chiefly as quinolines and pyridines with alkyl or cycloalkyl groups attached. Nonbasic nitrogenous material occurs mainly as pyrrole or porphyrin derivatives.

Oxygen occurs chiefly as carboxylic acids (including acid anhydrides) and phenols.

The ash content of crude petroleum varies between 0.01 to 0.05% by weight. Oil-soluble salts of petroleum acids probably account for the bulk of this.

Hydrocarbon Constituents of Petroleum

Paraffins - Saturated hydrocarbons with the empirical formula C_nH_{2n+2} . For further convenience they are subdivided into normal paraffins, which contain a straight -C-C-C-C- structure and branched-chain paraffins, which contain a branched carbon skeleton.

Olefins - Unsaturated hydrocarbons are referred to as olefins and contain a -C=C- linkage.

Naphthenes - Saturated hydrocarbons containing one or more rings, each of which may have one or more paraffinic side chains, referred to as naphthenes or cycloparaffins; only C_5 and C_6 rings are encountered in any quantity.

Aromatics - Includes those hydrocarbons containing one or more aromatic nuclei, such as benzene or naphthalene, which may be linked up with substituted naphthene rings and/or paraffinic side chains.

Composition of Odorless Kerosene

A combined mass spectrum, ultraviolet and infrared examination of a sample of Shell kerosene from Windscale showed the following:

<u>Components</u>	<u>wt%</u>
Straight-chain paraffins	62
Naphthenes	26
Branched-chained paraffins	7
Aromatics	5
Olefins	Nil

An elemental analysis of a sample gave the result C, 85.45 wt%: H, 14.74 wt% which corresponds to an atomic H/C figure of 2.05.

The specification for Shell Mex/B.P. odorless kerosene allows:

Unsaturation - Less than 0.5 g bromine to react with 100 g sample.

Aromatic compounds - Combined aromatic and unsaturated compounds not to exceed 2% by volume when determined by a sulphuric acid extraction method.

A more detailed analysis of a U.S. equivalent, Ultrasene, has been given as:

<u>Component</u>	<u>wt%</u>
n-paraffins below C ₁₀ total	< 0.2
n-decane	1
n-undecane	4
n-dodecane	14
n-tridecane	16
n-tetradecane	4
n-pentadecane	1
n-paraffins above C ₁₅ total	< 1
Total n-paraffins	40
Total branched and cycloparaffins	60
Total aromatics	0.5
Total olefins	0.01

The bulk of the crude oil supplied to Europe is classified as a mixed paraffin-naphthene base. An analysis of a C₅ - 200°C fraction has been given as:

<u>Component</u>	<u>wt%</u>
Aromatics	11.8
Paraffins	67.5
Naphthenes	20.7

While this agrees well with the overall analysis of the crude oil itself, it must be remembered that odorless kerosene has a boiling range of 180 to 240°C and may not contain exactly the same relative proportions of paraffins to naphthenes because of the varying distribution of the hydrocarbon types throughout the boiling range of the crude. The bulk of the aromatic content will certainly have been removed during the oleum treatment which is given to odorless kerosene.

The following hydrocarbons have been definitely identified in a kerosene from Ponca City (200 to 230°C).

<u>Hydrocarbon</u>	<u>Boiling Point, °C</u>	<u>Fraction, wt%</u>
Dodecane	216	13.6
2,3,4-tetramethyl benzene	205	1.1
tetralin	207.6	0.3
1-methyltetralin	234.4	0.7
2-methyltetralin	224	0.7
Naphthalene	217	0.5
1-methylnaphthalene	245	0.8
2-methylnaphthalene	241	<u>1.8</u>
Total		19.5

An analysis of another fraction, having a boiling range from 180 to 230°C gave the following:

<u>Component</u>	<u>wt%</u>
Normal paraffins	24
Branched paraffins	14
Monocyclic paraffins	33
Dicycloparaffins	11
Mononuclear aromatics	16
Dinuclear aromatics	2

Liquid-Phase Nitration of Aliphatic Hydrocarbons

Reactions most likely to occur with the inert diluent are nitration and oxidation; these may be independent or consecutive. Kerosene requires only mild reaction conditions for some nitration to occur and, in the laboratory, it is readily demonstrated that kerosene undergoes extensive oxidation as well as nitration by boiling 20% nitric acid.

Studies of the nitration of hydrocarbons produced the following generalizations regarding the reaction of aliphatic hydrocarbons with aqueous nitric acid in the liquid phase:

- Quaternary carbon atoms are particularly difficult to nitrate. Tertiary hydrogen atoms are replaced more easily than secondary ones while primary hydrogen atoms react more slowly. There is some disagreement as to the position where nitration occurs with the higher aliphatic paraffins.
- Reaction is slow but the rate is increased at elevated temperatures.
- Nitration is accompanied by considerable oxidation, and nitric acid is lost as elementary nitrogen.
- Polynitroalkanes are formed.
- The nitration of saturated aliphatic hydrocarbons with nitric acid is easier than with aromatic compounds. The aliphatic side chains of aromatic hydrocarbons tend to nitrate more easily than the corresponding saturated hydrocarbon due to the activating effect of the aromatic ring. Cyclic saturated hydrocarbons with tertiary carbon atoms are relatively easily nitrated with dilute nitric acid.
- It is likely that the action of nitric acid on aliphatic hydrocarbons is mixed, with concurrent formation of nitration and oxidation products. The rate of nitration depends on (1) temperature, (2) pressure, and (3) concentration of acid, and these do not influence the nature of the products obtained.
- It was shown experimentally that nitric acid in the absence of nitrogen oxides had little effect on either normal or isoparaffins, cycloparaffins, or side-chain alkyl benzenes. In the presence of nitrogen oxides, the chemical action increases with increasing nitrogen dioxide content.

- When bicyclic naphthenes consisting of two six-membered rings or one six-membered and one five-membered ring are nitrated, tertiary nitro compounds are formed in which the nitro group is attached to the carbon atom common to both rings.
- Unsaturated hydrocarbons undergo nitration fairly readily giving predominantly mononitro compounds.

It can be judged from the above that no accurate forecast as to the nature of the products obtained by nitration of kerosene-TBP mixture can be made without more detailed knowledge of the nature of the hydrocarbons concerned.

Work already carried out on the radiolysis of TBP-kerosene-nitric acid mixtures has mainly been concerned with the buildup of MBP and DBP in the system. It was generally assumed that similar, although not necessarily identical, reaction products will be produced during radiation-induced nitration as by the thermal reaction, and that the presence of radiation will increase the extent of degradation.

Purification Treatments for Kerosene and Other Inert Diluents

Purification treatments for kerosene are usually based on processes which will separate or concentrate according to the size or type of molecule. Regular distillation alone will not separate pure hydrocarbons from petroleum and one or more other methods must be used.

The following points apply whenever a pretreatment of any kind is suggested or when a washing treatment is introduced for the removal of degradation products.

- Completeness of purification treatment.
- Interconversion of different classes of hydrocarbons under processing conditions such as:
 1. The removal of deleterious products, e.g., sulfur, nitrogen and asphalts by caustic and sulfuric acid treatment of diluents.

2. The possibilities of a purification step, e.g., sulfuric acid treatment, causing composition changes via isomerization, polymerization, etc.

Alternate Solvents

From time to time, solvents other than kerosene have been proposed as inert diluents for TBP. These have been mainly synthetic products from the chemical or the petroleum-refining industries and thus differ from kerosene, which is essentially of natural origin. Their cost is invariably greater than that of kerosene. The main alternatives to kerosene that have been proposed comprise:

- Petroleum alkylates
- Hydrogenated olefin polymers (including conjunct polymers)
- Straight-chain hydrocarbon mixtures
- Hydrogenated Fischer-Tropsch hydrocarbons.

The process used to prepare the items listed above and the products themselves are described with regard to their structural makeup. Also, an Appendix is included which gives a number of examples of the products resulting from the liquid-phase nitration of various hydrocarbons.

RADIOLYTIC AND CHEMICAL STABILITY (9, DP-517)

The chemical and radiolytic degradation of 21 high purity hydrocarbons in the molecular weight range of kerosene indicated that olefins and certain aromatic hydrocarbons are major precursors of zirconium ligands (Table 11). The aromatic-cycloparaffins (mixed type), tetrahydronaphthalene and indan, and the olefins, 1-undecene, 1-dodecene, and 1-hexadecene, were highly unstable to the degradation procedure as measured by zirconium retention or Z values. In addition, tetrahydronaphthalene, indan, and 1-hexadecene formed stable emulsions during the post-degradation washes. The instability of mixtures of 1-dodecene and n-dodecane was a direct function of the concentration of 1-dodecene. The stabilities of mixtures of aromatic-cycloparaffins (mixed type) and n-dodecane were not simple functions of the aromatic content, and in the case n-dodecane-indan mixtures, the results were completely anomalous. Dilute mixtures of indan in n-dodecane were as stable as pure n-dodecane.

The alkylbenzenes tested ranged from stable to moderately unstable. The position of the alkyl groups on the benzene ring had no significant effect on the stability of these compounds. The aromatic compounds were highly colored after degradation and, in general, the intensity of color increased with increasing zirconium retention.

The compounds tested in the isoparaffin, cycloparaffin, and normal paraffin classes were comparatively stable. A synthetic kerosene made from the relatively stable pure compounds was also stable.

TABLE 11. Stabilities of Pure Hydrocarbons^a

Class Compound ^b	Radiolytic ^c			Chemical ^d		
	Stable	Moderately Unstable	Unstable	Stable	Moderately Unstable	Unstable
Normal paraffins:						
n-dodecane	x			x		
Isoparaffins:						
2,2,4,6,6-pentamethylheptane	x			x		
2,2,4-trimethylpentane	x			x		
2,3,5-trimethylhexane	x			x		
Cycloparaffins:						
n-butylcyclohexane	x			x		
cis-decahydronaphthalene	x			x		
trans-decahydronaphthalene	x			x		
cyclohexane ^e	x			x		
Olefins:						
1-undecene			x			x
1-dodecene			x			x
1-hexadecene			x			x
2,5-dimethyl-trans-3-hexene						x
Aromatic hydrocarbons:						
isobutylbenzene	x			x		
sec-butylbenzene				x		
1-methyl-4-tert-butylbenzene	x				x	x
1,3-dimethyl-5-ethylbenzene	x				x	x
1,2-diethylbenzene		x		x	x	
1,2,4,5-tetramethylbenzene	x					
5% naphthalene in n-dodecane		x			x	
Aromatic-Cycloparaffins (mixed type):						
tetrahydronaphthalene		x				x
indan			x			x

^aStability was divided into three classes according to the ratio, Z value of pure compound/Z value of n-dodecane. The range for each group is as follows: stable, <2; moderately unstable, 2-8; very unstable, >8.

^bFrom the National Bureau of Standards except where noted. Impurities certified to be <0.2M%.

^cIrradiated to 10^7 rad $\pm$ 10% in contact with 4M HNO₃ - 0.1M HNO₂.

^dContacted with 4M HNO₃ - 0.1M HNO₂ for 2 days at 70°C.

^eEastman white label grade.

PURIFICATION OF IRRADIATED TBP BY DISTILLATION IN KEROSENE-TYPE DILUENT (10, MSE 9)

Preliminary Treatment of Solvent

A solution containing 30% by volume TBP in AMSCO 125-82 was contacted with aqueous solutions containing 1.3M uranium and 1.84N nitric acid. The two phases were irradiated to a dose of 120 Wh/l to the organic phase. The organic was stripped by successive contacting with 0.01N nitric acid. After eight strip contacts, the organic composition was natural uranium - 3.29 g/l, TBP - 32.1% by volume, H^+ - 0.01M, and H_2O - 2.1 g/l.

Vacuum Fractionation

Attempts to distill the irradiated solvent at either 20 or 50 mm of mercury (reflux temperature 85 to 130°C), in a column containing 40 theoretical plates, were unsuccessful. The distillate was colored greenish-yellow, and the pot material rapidly became a thick, black slurry. Copious quantities of light ends collected in the cold trap.

A sample of the irradiated material was washed with sodium carbonate solution in an attempt to eliminate residual uranium and acidic radiolysis products which may have caused decomposition during the distillation. The fractional distillation of this sample was also unsuccessful.

Rapid Volatilization

If the radiolysis products causing decomposition during the distillation were high-boiling materials, it could be possible to evaporate the TBP and AMSCO 125-82 rapidly under high vacuum. The low temperature and short residence time could prevent thermal decomposition. It could also be desirable to separate the TBP and diluent by this method and then to fractionally distill them separately. The separation of these two materials by a simple evaporation was possible due to the large difference in their boiling points.

Flash distillations were performed on the materials outlined below:

- Control (unirradiated 30% by volume TBP in AMSCO) unwashed
- Unwashed irradiated solvent

- Control (unirradiated 30% by volume TBP in AMSCO) washed with sodium carbonate
- Irradiated solvent washed with sodium carbonate.

The wash was an aqueous solution of 10% sodium carbonate by weight. The volume ratio of solvent to sodium carbonate was 2 to 1, with six washes being performed.

In all cases, the AMSCO fraction vaporized between 35 and 110°C with 90% distilling between 40 and 60°C. The TBP fraction distilled between 110 and 120°C. All rapid volatilizations were performed at approximately 0.5 mm mercury.

Fractional Distillations of Products From Rapid Volatilizations

The conditions of the distillations are given in Table 12. The reflux temperature for the AMSCO fraction increased from 85 to 126°C at 50 mm mercury, and was 170 and 195°C for the TBP fraction at 20 and 50 mm of mercury, respectively.

TABLE 12. Conditions for Distillations.

Material	Charge, g	Reflux Ratio	Operating Pressure, mm Hg	Boil up, ml/hr
AMSCO 125-82				
Unirradiated, unwashed	1030	10/1	50	580
Irradiated, unwashed	970	10/1	50	560
Unirradiated, washed	1017	10/1	50	650
Irradiated, washed	878	10/1	50	620
TBP				
Unirradiated, unwashed	583	5/1	20	185
Irradiated, unwashed	518	5/1	20	287
Unirradiated, washed	554	10/1	50	780
Irradiated, washed	556	10/1	50	635

In all cases, the fractional distillations proceeded smoothly. All of the AMSCO fractions were water-white except two. The fractions boiling between 123 and 124.6°C (88 to 92% distilled) from the two irradiated samples had a slight green color.

The TBP fractions from the rapid volatilizations were water-white initially but yellowed after standing about 1 day. When fractionated the pot material turned dark and the distillate had a tan cast. No solid material was observed in the pot.

It was observed in all the TBP fractionations that when the distillation was approximately 70% complete the pot material decomposed. This could be due to the buildup in concentration in the pot of some species, which could cause a rapid decomposition of the pot material, or a superheating of the pot material which could not be detected by the pot thermometer because of a very low liquid level in the still pot. When decomposition of the TBP occurred, it was quite rapid and large amounts of gas were evolved.

Solvent Extraction Studies. Extraction-strip contacts made with ^{233}U and ^{106}Ru - ^{106}Rh shows that the characteristics of the distilled, irradiated fractions are reasonably comparable to distilled, unirradiated fractions. The benefit of washing with Na_2CO_3 was evident but it appeared to benefit the irradiated solvent to a greater extent.

EXTRACTION PERFORMANCE OF DEGRADED PROCESS EXTRACTANTS (11, ORNL-TM-27)

Effect of TBP on Degradation of AMSCO 125-82 With Nitric Acid

Many of the anomalous extraction properties of 1M TBP in AMSCO 125-82 are caused by products resulting from nitration of the diluent. Nitro-paraffins (e.g., RCH_2NO_2) gave the same infrared spectrum and performed in ^{95}Zr - ^{95}Nb extraction tests similarly to nitric acid degraded AMSCO 125-82. The degradation was accomplished either by irradiating or by heating an intimately mixed two-phase system of solvent and nitric acid. The solvent phase was AMSCO 125-82 alone or in combination with TBP. Irradiation was by ^{60}Co gamma radiation.

Degradation of the AMSCO 125-82 was shown to be more severe when TBP was present than when it was not. This is presumed to be a consequence of nitrate and nitrite extraction by TBP increasing the opportunity for nitration and of stabilization of the nitro groups by complexing with TBP. The degradations by irradiation and by heating were essentially equivalent with respect to effects detected by ^{95}Zr - ^{95}Nb extraction, by total organic nitrogen analysis, and by spectrophotometric nitroparaffin analysis.

The effects of different irradiation conditions and subsequent treatments on zirconium-niobium extraction by the solvents are compared in Table 13. Results are shown for irradiation of 1M TBP in AMSCO 125-82, irradiation of AMSCO 125-82 alone, and irradiation of AMSCO 125-82 alone followed by addition of fresh TBP at 1M.

When TBP was present during irradiation, zirconium extraction was high with the unscrubbed solvent, then dropped considerably after carbonate scrubbing to remove the low-weight acids DBP and MBP, and rose again sharply after calcium hydroxide treatment.

TABLE 13. ^{95}Zr - ^{95}Nb Extraction Test.

Irradiation, Wh/l		^{95}Zr - ^{95}Nb in Organic Phase ^a , cps/ml	
Irradiated 1M TBP - AMSCO 125-82	As Irradiated	Carbonate Washed	Carbonate: Calcium Hydroxide Washed
25	4500	1000	2500
50	5000	1500	5000
75	5200	2000	6700
Irradiated AMSCO			
25	500	500	50
50	600	500	100
75	500	500	150
Fresh 1M TBP: Irradiated AMSCO			
25	2300	700	400
50	2700	1200	1000
75	2100	1100	1000

^aInitial aqueous phase: 2M HNO_3 , 10^4 cps/ml ^{95}Zr - ^{95}Nb , extractions at phase ratio organic to aqueous = 1, room temperature, 10-minute contact time.

When AMSCO 125-82 was irradiated alone, the degradation-induced zirconium extraction was much lower although still significant. Sodium carbonate scrubbing had little effect but zirconium extraction was almost eliminated by the calcium hydroxide treatment. The latter effect can be reconciled with the marked enhancement of extraction with TBP present by noting that the solid calcium hydroxide is known to sorb a portion of the impurities, but with limited capacity. When the impurity concentration is high, the amount sorbed is relatively unimportant, but when it is low nearly all may be sorbed.

When fresh TBP was added to the irradiated AMSCO 125-82, all three extractions were higher than those for the degraded diluent alone, higher than could be accounted for by the additional extraction by TBP itself. This resulted from (1) the presence in the untreated solution of impurities in the fresh TBP reagent, and (2) the interaction between TBP and diluent degradation products to give synergistically enhanced extraction.

It seems clear that degradation occurred in the diluent and was much more severe when TBP was present. It is very likely that the complexing of TBP with HNO_3 and nitroparaffins increased the total yield. Extraction of HNO_2 by TBP may also be important.

The increased zirconium extraction after calcium hydroxide treatment is explained in terms of the following tautomeric equilibria of primary and secondary nitroparaffins. Since tertiary nitroparaffins have no enolizable hydrogen atom, they do not undergo these reactions and do not contribute to the extraction power of the solvent.

In acidic media, the equilibrium of reaction 1 is far to the left (the keto form), and/or the rate of equilibration is slow. Reaction 2 occurs in basic media. Its equilibrium is farther to the right (salt of the enol form), and its rate of equilibration is relatively fast. Moreover, both the rate and the position of equilibrium vary with different bases. Contact with calcium hydroxide produces more of the enol salt,

and more rapidly, than does contact with sodium carbonate or sodium hydroxide (Table 14). Thus, on treatment with calcium hydroxide, a large proportion of the nitro groups enolize, and, on acidification, remain as enols long enough to be effective in extracting the zirconium.

TABLE 14. Rate of Extraction of Sodium From Alkaline Solution.

Organic phase: 1M TBP-AMSCO irradiated 90 Wh/l, then scrubbed with 0.2M $\text{Na}_2\text{CO}_3(2X)$, 2.6M $\text{NaCl}(2X)$, all at phase ratio = 1 and for 10 minutes.

Aqueous phase: 1M NaOH, phase ratio = 1

Room temperature:

Time of Contact, hr	Sodium Extracted ^a , N
0.17 (10 min)	0.0046
0.5	0.0051 ^b
1.0	0.006
4.0	0.009
16.0	0.013 ^c

^aCalculated from analysis of 2M HNO_3 used to strip sodium from the organic extract.

^bAfter contact of the organic phase with 200 g/l, solid $\text{Ca}(\text{OH})_2$ for 30 minutes, the calcium analysis was 0.024 N.

^cAfter contact of the organic phase with 5 g/l, solid $\text{Ca}(\text{OH})_2$ for 16 hours, the calcium analysis was 0.08 N.

Degradation by Exposure to Boiling HNO_3

Boiling, with an equal volume of 2M HNO_3 under total reflux, degraded AMSCO 125-82 severely enough for its degradation products to extract ^{95}Zr - ^{95}Nb strongly even without the presence of TBP. Data in Table 15 compare the zirconium-niobium extraction behavior of 1M TBP in AMSCO 125-82 and AMSCO 125-82 alone as a function of reflux time. Prior to use, both solvents were scrubbed with Na_2CO_3 , to remove DBP and MBP from the TBP solvent, and then with $\text{Ca}(\text{OH})_2$ to "develop" the nitrohydrocarbons as extractants. Extraction by the 1M TBP-AMSCO degraded for 4 hours was matched by that of AMSCO alone degraded for about 22 hours, again demonstrating the accelerated diluent nitration caused by the presence of TBP.

TABLE 15. ^{95}Zr - ^{95}Nb Extraction Test with TBP-AMSCO 125-82
After Exposure to Boiling 2M Nitric Acid.

Reflux Time, hr	^{95}Zr - ^{95}Nb Activities in Organic Phase, cps/ml	
	1M TBP-AMSCO 125-82	AMSCO 125-82
4	7300	0
16	--	1200
24	--	9600

Radiation Versus Boiling HNO_3 : Estimates of Nitration
Product Concentrations

Ultraviolet Absorption Spectra. Nitroparaffins give the same infrared spectrum (and perform in ^{95}Zr - ^{95}Nb extraction tests in the same way) as AMSCO 125-82 degraded with nitric acid. Studies have been made of nitroparaffin spectra in the ultraviolet to find whether such measurement would also be useful in examining the type and extent of solvent degradation. Preliminary testing with degraded TBP-AMSCO solutions showed much interference at the 280- μ band, but at the higher intensity band (205- μ in the author's system) reproducible results were obtained. Conformity of the nitrodecane 205- μ band to Beer's law was shown over the range 0 to 0.0005M nitrodecane.

The absorbance and, therefore, the concentration of nitroparaffin, was found to increase linearly with amount of exposure for both the AMSCO and TBP-AMSCO. This was true whether the exposure was to irradiation or boiling nitric acid.

Nitrogen Analysis. Chemical analysis for organic-phase nitrogen was obtained for a few AMSCO and AMSCO-TBP samples degraded by either irradiation or boiling nitric acid. The limited data indicate a fairly constant proportionality of nitro groups to total nitrogen regardless of degradation type. The 1M TBP-AMSCO solution irradiated for 90 Wh/l contained 0.2M nitrogen. The concentration of total nitrogen in the solvent does not necessarily indicate the concentration of active or potentially active extractant because the analyses make no distinction between primary,

secondary, or tertiary nitroparaffins, or between other nitrogen-containing compounds.

Titration. Simple two-phase titration with aqueous sodium hydroxide to differentiate between the tertiary compounds and the acids was unsuccessful.

Zirconium-Niobium Extraction Stoichiometry

Approximate zirconium extraction coefficients with degraded AMSCO 125-82 signified a combining ratio of 4 for extractant to extracted zirconium. Such a conclusion is reasonable since tetravalent zirconium and monobasic nitroparaffin acids are involved.

Decomposition of HNO_3 During Irradiation

Degradation of HNO_3 by irradiation has been the subject of previous investigation. The G values reported for the degradation of nitric acid by irradiation have varied from 5 to 10. The present data corrected for chemically combined nitrogen are represented by a line with slope G value of 5.

Formation of HNO_2 During Irradiation

The aqueous HNO_2 concentration increased during irradiation reaching 0.03 to 0.04M at 90 Wh/l. No analyses were made for HNO_2 in the organic phase so the total amount formed during the treatment could not be calculated. In addition to the nitrohydrocarbons formed by HNO_3 -diluent reaction, it is possible that additional amounts could be contributed by nitrosation with HNO_2 . One mechanism could involve formation of a nitroso compound ($-\text{CH}-\text{N}=\text{O}$), with accompanying enolization to the oxime ($-\text{C}-\text{NOH}$), and oxidation of both to the nitrocompound ($-\text{CNO}_2$).

Formation of DBP

A rough estimate has been made of DBP formed during irradiation of 1M TBP solution, contacted with 2M HNO_3 , to a dose of 90 Wh/l. The irradiated organic phase, scrubbed free of HNO_3 , was shaken for 16 hours with an excess of 1M NaOH. Another portion of the HNO_3 -free organic was further

scrubbed with Na_2CO_3 to remove DBP and it, too, was shaken with excess NaOH. The base consumed in each test was determined by back titration with HCl. The difference, giving an approximation of the DBP, was 0.06 eq/l. At the 90 Wh/l dose, this concentration of DBP formed represents a G value of approximately 2.

PUREX PROCESS PERFORMANCE VERSUS SOLVENT EXPOSURE AND TREATMENT (12, NSE 17)

Equilibrium Model

The simple form of the model states that the final concentration of some degradation product, A, in washed solvent is the sum of that which was produced in one pass through the solvent extraction banks, and which lived through one pass through the solvent washers, plus the successively diminishing contributions from passes that had been through the washers previously in successively more times. The implicit assumption is that a given degradation product behaves the same in successive exposures to the wash solution.

This converging series is obtained:

$$\begin{aligned} \text{equilibrium} &= \frac{Ra}{DFa} + \frac{Ra}{(DFa)^2} + \frac{Ra}{(DFa)^3} \\ &+ \dots + \frac{Ra}{(DFa)^n} = \frac{Ra}{DFa-1} \end{aligned}$$

where:

Ra = production rate of A per pass through the extraction system

DFa = DF A_{in}/A_{out}, in solvent washing and n approaches infinity in continuing operation.

Both Ra and DFa depend on many factors. Pertinent points are:

1. The relative efficiency of washing is measured by the term DFa-1. For example, DF of 1.1 and 1.02 have been measured for some activity species in solvent. (A DF of 1.1 is five times as good as the DF of 1.02).

2. DBP may be of small influence to long-term stability of operation compared to the effect of some material that is produced in apparently negligible amounts. For example, the equilibrium value of DBP, produced in large yield but for which a washing DF of 20 is easily obtained, would be about the same as the equilibrium value of a material with a DF

of 1.02, if the production rate of this poorly decontaminated material is as much as 0.11% that of the DBP.

3. At these low DF in solvent washing, a great many passes through the system are needed before equilibrium is reached. Weeks or months could be involved in large systems with only one or two circulations of solvent per day.

The slow rates of recovery observed in plant work are quite consistent with the rates estimated from solvent washing data. For all practical purposes, recovery rates from some ruthenium-retaining species are so low by the normal washing system that the solvent may be considered permanently damaged unless drastic solvent cleaning techniques are used.

Solvent Quality and Decontamination Performance

The first definitive illustration of the influence of solvent quality on performance was found with the large banks by a simple graph of first cycle decontamination versus solvent activity, with zirconium-niobium and ruthenium treated separately. The DF used for this purpose is based on the average activity of ruthenium or zirconium-niobium sent to the plutonium and uranium product streams (1BP and 1CU, respectively) and may be calculated from normal DF as:

$$\frac{1}{DF} = \frac{1}{2} \left[\frac{1}{DF_{Pu}} + \frac{1}{DF_U} \right]$$

Use of this "mean" DF eliminates many of the apparent wide variations in decontamination to the individual end streams.

Relations Between Solvent Activity and Performance

Experimental data for solvent activity versus decontamination with Ultrasene diluent fell largely in fairly narrow bands.

Some implications of this are:

1. Activity of the washed solvent was an index to the potential DF that could be obtained, e.g., the equilibrium activity in the circulating washed solvent was proportional to the ligands that could depress the DF.

2. The comparatively narrow spread in DF (about a factor of 2) for a given washed solvent activity showed that most of the common process changes (flow ratios, uranium saturation, etc.) did not effect a large change in performance indicating that solvent quality was of prime importance.

3. Sustained periods of comparatively low solvent activity showed that increased degradation due to the long residence time with the large banks did not overwhelm the solvent washing capabilities.

4. If solvent quality were preserved, the large solvent extraction banks inherently could give better DF than the smaller banks.

5. The effect of recycle of aqueous and organic streams could not be predicted:

- Solvent containing high DBP gave drastic decreases in zirconium-niobium DF but the DBP was easily removed in solvent washing so that there was rapid recovery and no long-term influence on the solvent.
- Some solvent recycles caused severe discontinuities in DF and solvent activity, with slow recovery. In a few cases dissolved paint, hydraulic oil, and other offstandard materials have contributed to this behavior.
- Some aqueous recycles were innocuous while others, when blended with feed on a routine basis, gave steady increases in solvent activity and decreases in DF with slow recovery.

6. The data suggest that both the ruthenium and zirconium-niobium DF consists of two components:

- A constant DF, approached at low solvent activity, which represents the limiting DF available in the system.
- A DF term, approached at high activities, that is inversely proportional to the abundance of ligands, as measured by the activity of the fission product retained in the washed solvent.

Diluent Effects: Adakane and Ultrasene

There was a definite improvement in DF from ^{95}Zr - ^{95}Nb when Adakane was substituted for Ultrasene, though several other factors were changed at the same time. Also, a great deal of care has been taken to avoid contaminating the Adakane with degraded solvent from recycle streams, and plant conditions generally were modified in an effort to preserve the quality of the Adakane. Experience with the two diluents can be interpreted as follows:

1. The mean DF for ^{95}Zr - ^{95}Nb were three to five times higher with Adakane than Ultrasene at a given concentration of zirconium in the solvent.
2. Zirconium activity in the raw spent solvent was comparable for the two diluents. This activity could result primarily from degradation of TBP to DBP and might not be influenced by the diluent.
3. Zirconium activity in the washed solvent was generally lower with Adakane, indicating that Adakane forms less of the zirconium-retaining ligands.
4. Ruthenium behavior with respect to DF and levels in the solvent was unchanged with the two diluents.

Solvent Activity and Chemical Concentration

Solvent activity was used as an index to solvent quality and the abundance of degradation products, but the actual chemical concentration of a fission product is a better measure if feeds of different irradiation levels and cooling times are processed. Activities should be normalized

to account for decay time or they should be converted to chemical concentration because:

1. The specific activities of the zirconium and ruthenium in the process are determined by the ^{95}Zr and ^{103}Ru plus ^{106}Ru , respectively, and these active isotopes are less than 10% of the total elemental concentrations after comparatively short cooling times.

2. A given solvent activity can signify a wide gamut of chemical concentrations and solvent qualities. The retention of 2M Ci/l of zirconium or ruthenium activity in the solvent with feed at 100 days cooling time would indicate far superior solvent than the retention of this same activity with the same fuel cooled to 400 days.

Washed Solvent Activity and Final Product Streams

There are some definite relationships between first cycle solvent and fission product activities in the uranium and plutonium product streams from the second solvent extraction cycles.

1. From 3 to 6% of the activity in washed first cycle solvent used for 1BS (organic scrub stream) is stripped out under 1B and 1C bank conditions. This material is abnormal in its extraction behavior and tends to carry through under the conditions in the second cycles to a greater extent than normal ruthenium species. The ruthenium in plant end streams, at times of poor quality first cycle solvent, does not exhibit the extraction behavior of normal nitrato-nitrosyl ruthenium species.

2. Second cycle solvents have had little effect on the ruthenium in the end streams.

3. Correlation between ^{95}Zr - ^{95}Nb activity in the end streams and the first cycle solvent is apparent above a zirconium concentration of $2 \times 10^{-8} \text{ M/l}$ in the solvent.

Solvent Indices

Numerous empirical tests have devised to measure some aspect of solvent quality. These include:

1. Disengaging ratio with caustic - The surfactant concentration or soap-forming potential in solvent is determined by measurement of the stability of an organic continuous emulsion. The bulk disengaging time of a solvent is compared to that of virgin solvent and recorded as a ratio.
2. Interfacial tension with caustic - A more direct measure of surfactant concentration is the measurement of the interfacial tension of a solvent with a caustic solution used to scrub the solvent.
3. Permanganate demand - An index that is a normalized measure of the reducing strength of solvent.
4. Z value - A measure of the concentration of zirconium which is irreversibly extracted by solvent from $3M\ HNO_3$. As the Z value increases, solvent extraction DF would be expected to decrease.
5. Polarographic diffusion current - This is a measure of the total reducible species at a dropping mercury electrode at a half wave potential which is approximately the same as for the reduction of nitro, nitrate, carbonyl, and carboxyl groups. The diffusion current was found in laboratory tests to be directly proportional to Z value on the same solvent.

The following relations may be inferred by comparison of plant performance and concurrent solvent tests results:

1. Minor changes in solvent determined by any of the tests are of questionable significance unless they are one step in a long-term trend. Data have been found to be a consistent indication of solvent quality only at the extremes. There have been no cases of good Purex solvent with high permanganate demands (greater than $10\ \mu M/\ell$), or poor solvent with low permanganate demand (less than $5\ \mu M/\ell$). Also, there have been

no cases of good Purex solvent with high disengaging ratios (greater than 3), and low interfacial tension (less than 5 dynes/cm) or of poor solvent with low disengaging ratios and high interfacial tensions.

2. Permanganate demand of the solvent generally increases with diminishing DF from zirconium-niobium.

3. Disengaging ratios less than 2 had little significance, but above this value they gave excellent correlation with ruthenium DF.

4. The Z value procedure works well for cold solvent but is severely limited with solvent containing a high ruthenium background.

Feed Activity and Solvent Degradation

The radiolytic degradation rate obviously is a function of fission product activity in the feed solution to the 1A solvent extraction bank. Plant data can be interpreted as follows:

1. The bulk of the ^{95}Zr - ^{95}Nb and ruthenium activities in the solvent, before and after washing, varies approximately as the second power of the feed activity.

2. The squared relation between feed and solvent activities may really show a linear dependency of chemical concentration in the solvent, hence degradation rate, on feed activity.

3. A limit can be placed on feed activity (hence fuel cooling time) that allows stable performance on one side and rapidly deteriorating operation on the other.

The responses of solvent activity to feed activity can be separated into several components which may be classified as washable, responsive core, and bound activities. Washable activity is that which has a high DF in solvent washing and so does not affect the long-term equilibrium appreciably. The responsive core represents degradation products with DF in the range of 1.05 to 1.20 which come to equilibrium slowly but still level out in the period of a few days to several weeks. Bound activities require months to reach equilibrium.

The activity history of a charge of Adakane diluent is an example of the influence of the various solvent degradation components. The solvent washing system consisted of caustic-carbonate solution in the first stage, acid in the second stage, and carbonate in the third stage. The following observations can be made:

1. There are responses in the various solvent concentrations of fission products to the rises in feed activity near the end of each campaign, and these are overlaid on a gradual accumulation of solvent degradation products that decreases the solvent quality.

2. Washable ^{95}Zr - ^{95}Nb is generally larger in the second campaign and does not decrease even during an extended period at low feed activity. ^{95}Zr - ^{95}Nb in the washed solvent recovered from the high point in the first campaign. The increase in washable ^{95}Zr - ^{95}Nb is probably due to the accumulation of a species that increases the extractability of ^{95}Zr - ^{95}Nb in the process and releases activity in the washers without being removed itself.

3. Ruthenium in the washed solvent does not decrease appreciably during the extended period of low feed activity in the second campaign. Possible explanations are:

- The degradation product that holds the ruthenium has a very low DF in solvent washing, so the level in the solvent is fixed essentially by the most radioactive feed to which it has ever been exposed.
- The combination of a low production rate and a low DF caused sufficient lag in the growth of the degradation product during the exposure to high activity feed so that the degradation product only reached the equilibrium value characteristic of low activity feed.

4. Of significance is the relatively small change in solvent quality during the low feed activity campaign as compared to the high feed activity campaign. If the decreased rate of change in quality

represents the approach to an equilibrium, then this solvent charge may give satisfactory performance for many more campaigns.

5. The rather abrupt increases in washed solvent ^{95}Zr - ^{95}Nb content at the times of highest feed activity are primarily credited to physical inefficiencies in the solvent washing system and inability to change the aqueous wash solutions rapidly enough.

Solvent Washing Variables

Many laboratory results on DF of solvent activity are not significant to plant operation because the activity is merely stripped from the complexing agent, which remains in the solvent to affect the next extraction pass. Even high removal of both activity and the complexing agent may not be significant to plant operation if the complexing agent is removed easily in the plant washers. For example, increasing the DF for the DBP from 20 to 40 makes little difference at equilibrium in the amount or influence of DBP fed back into the process in the washed solvent.

Solvent Recovery Reagents

Numerous reagents have been tested in the laboratory or in the process, chiefly NaOH , Na_2CO_3 , HNO_3 , KMnO_4 , $\text{Ca}(\text{OH})_2$, NH_2OH , and amino alcohols (alkanolamines). In addition, physical methods such as filtration, centrifugation, absorption, and distillation have been used. In general, distillation has proven to be the only method that will generate solvent of good quality from solvent of extremely poor quality. Contacting with aqueous washes (with final filtration) has been the standard treatment at Savannah River Plant. Several generalizations can be made:

1. In any given solvent, there is a core concentration of ruthenium and ^{95}Zr - ^{95}Nb , which appears inversely proportional to the quality of the solvent. This activity is very slightly removed by the aqueous reagents commonly used in solvent washing. The core ruthenium activity is removed with a DF of less than 1.02 in Na_2CO_3 , less than 1.05 in NaOH , and less than 1.1 in KMnO_4 - Na_2CO_3 . There is some evidence that this

material distributes in alkaline solution according to normal extraction laws so that, at these low DF, the wash solution is essentially saturated with core material after contact with an equal volume of solvent and will remove no more until the wash solution is changed. The core ^{95}Zr - ^{95}Nb appears to be removed 5 to 10 times more effectively than core ruthenium for a given reagent.

2. Alkanolamines will effectively extract ruthenium activity and ruthenium complexing agents from solvent in the laboratory. To be efficient with solvent, they had to be used without aqueous dilution, which leads to difficulties because TBP and undiluted alkanolamines are mutually soluble to a variable extent depending on the complexity of the alkanolamine.

3. Permanganate-carbonate solution removes complexing agents both by oxidation and by absorption on the MnO_2 that is formed. As a result, there is little apparent wash saturation effect.

4. Alkaline hydroxylamine solution gave superior DF in laboratory solvent recovery tests (about comparable to permanganate).

5. Nitric acid alone is of little use as a wash reagent except as an emulsion eliminator.

Order of Reagents

The order of aqueous solutions in the solvent washers had a large effect on the DF from ^{95}Zr - ^{95}Nb with a great improvement when the sequence in the three washers is changed from base-base-acid to base-acid-base.

1. If a change in solvent conditions from acid to base to acid is considered a unit washing cycle, the original conditions of acid solvent from the extraction banks going through first and second stage alkaline washers, then a final acid washer and back to the acid solvent extraction system, is really equivalent to only one unit cycle. On the other hand, acid solvent going to a first stage alkaline washer, a second stage acid washer, a third stage alkaline washer, and back to the acid banks has been effectively through two unit wash cycles.

2. Other benefits of the changed sequence are that the solvent goes through the final filter in an alkaline condition and is stored in an alkaline condition pending return to the extraction system, hence minimizing acid hydrolysis of TBP to DBP.

Mixing Time

Decontamination from fission products is a function of contact time between the organic and the aqueous wash solution and proper design of a solvent washing facility must consider the effect of time. Points pertinent to the contact time selected are:

1. In a typical laboratory contact test between plant solvent and a basic wash solution, there is a continuing transfer of zirconium activity from solvent to aqueous. The DF is roughly 4 after 1 minute, 10 after 6 minutes, and increases further with continued contact.

2. There is only a very brief period of intimate mixing in the plant turbo-mixers, equivalent to somewhere between 15 seconds and 1 minute, although total residence time can be several hours. However, overall DF of 100 for ^{95}Zr activity in plant spent solvent are obtained in three short laboratory contacts and DF almost this large are obtained in the plant.

3. Decontamination from ruthenium increases slowly with increasing mixing time, but to a lesser extent than with zirconium. The DF were 1.4 after 5 seconds, 1.7 after 10 minutes, and 2.0 after 1 hour.

4. For both zirconium and ruthenium, there is clear evidence that, in extended contact, the continued removal of activity does not represent a DF of the complexing agent in the solvent.

5. Excessive contact times in solvent washing are not necessarily good. Deleterious effects from excessive contact with strong caustic solutions in enhancing zirconium retention have been reported.

Wash Change Frequency

The importance of the frequency of wash changes in the operation of continuous washers has been demonstrated frequently. Three related washing characteristics have been observed in solvent washing operations.

1. Solvent washing DF for fission products (for portions of solvent contacted with a single wash solution) decrease with successive use of the wash solution.

2. Measurable quantities of normal degradation and fission products are re-extractable by fresh solvent from used wash solutions, both acid and alkaline.

3. The buildup of degradation products and uranium compounds in a wash solution increases the stability of alkaline emulsion thereby increasing entrainment from an alkaline washer. The entrainment, in turn, decreases the efficiency of the next washer by further transmission of the emulsion if the next stage is basic or by dissolution and re-extraction of degradation products if the next stage is acid.

Temperature of Wash Solution

Temperature of a solvent wash system plays an important part in its performance. Alkaline washers are generally maintained between 35 and 55°C while acid washers should be below 35°C. These conditions are based on the following:

1. With alkaline washers, increased temperature gives better phase separation and increased removal of activity at constant mixing times. The magnitude will vary greatly depending on the quality of the solvent, the reagent used, and the age of the wash solution.

⁹⁵Zr-⁹⁵Nb DF increases at least threefold as temperature increases from 25 to 55°C for solvent washing in an alkaline medium at mixing times less than 10 minutes. Ruthenium DF also improved but generally by less than a factor of 2.

2. Temperatures above 55°C are avoided for the alkaline washers because the solvent flash point is being approached and there is concern over the increased rate of alkaline hydrolysis of TBP and over the possibility of degradation of diluent.

3. Acid washers should be operated at temperatures below 35°C to prevent deleterious nitration and dealkylation reactions with the solvent. No significant improvements in DF have been observed in the laboratory by the use of a 50°C second-step acid wash.

TBP DECOMPOSITION PRODUCT BEHAVIOR IN POST-EXTRACTIVE OPERATIONS
(13, NSE 17)

The presence of dibutyl phosphoric acid (HDBP) in solvent extraction systems based on TBP and the tendency of this decomposition product to complex with uranium, zirconium, iron, aluminum, and other ions are well known. Several of these complexes are quite strong, poorly soluble in aqueous media, and markedly affect solvent extraction performance. Their physical form, particularly zirconium DBP, may be that of a gum which can be either interfacially active or impair the function of moving equipment.

Solubility Ratio of Uranyl DBP

The distribution of $\text{UO}_2(\text{DBP})_2$ between the aqueous and organic phases will, in part, determine whether DBP is retained in the organic phase or accompanies the major portion of uranium further in the extraction cycle.

The solubilities of $\text{UO}_2(\text{DBP})_2$ in the system TBP-AMSCO:1.05M HNO_3 and TBP-AMSCO:0.04M HNO_3 are given in Table 16. While the solubilities in the aqueous phases are not too different, there is a considerable decrease in organic-phase solubility at the lower acid and at lower TBP concentrations. The $\text{UO}_2(\text{DBP})_2$ distribution ratios are also shown in Table 16. At both acid concentrations, the decrease in distribution ratio with a decrease in TBP concentration is relatively sharp.

TABLE 16. Solubility of Uranyl DBP in TBP-AMSCO.

Initial HNO_3 Conc. in Aqueous Phase, <u>M</u>	TBP Conc. in AMSCO, wt%	$\text{UO}_2(\text{DBP})_2$, <u>M</u>		Distribution Ratio, U_a
		Aqueous Phase	Organic Phase	
1.05	1	1.6×10^{-3}	7.0×10^{-3}	4
1.05	10	8.0×10^{-3}	2.0×10^{-1}	250
1.05	20	6.0×10^{-4}	4.0×10^{-1}	650
0.04	1	4.0×10^{-4}	1.3×10^{-5}	0.03
0.04	10	4.0×10^{-4}	7.0×10^{-3}	25
0.04	20	2.0×10^{-4}	5.0×10^{-2}	250

Uranium Distribution as a Function of HDBP Concentration

The effect of HDBP on the uranium Kd was determined at various TBP concentrations. The Kd are shown in Table 17. It may be calculated that the amount of uranium extracted is too great for complexes with DBP to uranium ratio greater than one. All complexes previously described have DBP to uranium ratios of 2 or greater. Hence, it appears that a new complex containing TBP is present.

TABLE 17. Distribution of Uranium Between TBP-AMSCO and 0.04M HNO_3 as a Function of HDBP Concentration.

TBP Conc, wt%	Initial HDBP Conc, M/l	Uranium Kd
26.0	10^{-5}	2×10^{-1}
11.7	10^{-5}	6×10^{-2}
5.9	10^{-5}	1×10^{-2}
2.7	10^{-5}	3×10^{-3}
26.0	10^{-4}	2×10^{-1}
11.7	10^{-4}	6×10^{-2}
5.9	10^{-4}	2×10^{-2}
2.7	10^{-4}	7×10^{-3}
26.0	10^{-3}	3×10^{-1}
11.7	10^{-3}	9×10^{-2}
5.9	10^{-3}	8×10^{-2}
2.7	10^{-3}	7×10^{-2}

Phosphate Extraction with Kerosene

Tributyl phosphate can be removed from an aqueous stream by washing with diluent. The Kd for TBP between AMSCO and dilute UNH-nitric acid is 290 over the concentration range 10^{-2} to 10 mg/l phosphorus in the aqueous phases.

Kinetic studies showed that an 18-second residence time was required to reach 95% of equilibrium and 60 seconds to reach full equilibrium for the extraction of TBP from water with AMSCO.

Equilibration of pilot-plant feed stock, distilled water, or deionized water with AMSCO revealed the presence of an aqueous favoring phosphate species. The species was not identified other than to determine that it is acidic and has an extraction coefficient less than one.

Zirconium Oxide Absorption

The strong affinity of zirconium for phosphate and DBP provides a basis for the separation of degraded phosphate from UNH solutions. It has been shown that in dilute acid solution hydrated zirconium oxide is stable and functions as an anion exchanger. In tests of uranium absorption capacity, dilute UNH nitric acid solutions were passed through HZO-1 ion exchanger with no detectable change in uranium concentration. The capacity of the exchanger for TBP was only 0.16 $\mu\text{M/g}$.

The capacity of the HZO-1 for HDBP was 0.4 and 0.7 meq/g at flow rates of 122 and 25 $\ell/\text{hr/lb}$. The resin capacity in the latter case was reduced to 0.003 meq/g in the presence of 0.02M $\text{UO}_2(\text{NO}_3)_2$. Further tests on the absorption capacity of zirconium oxide produced the results in Table 18. The effect of flow rate is marked. The diffusion of the relatively large phosphate species into the particle apparently controls the adsorption in the concentration in the plateau region.

A normal first cycle evaporator product was found to contain 34 mg/ ℓ of phosphorus. This was processed through HZO-1 at 3.5 $\ell/\text{hr/lb}$. The phosphate DF ranged from 14 to 85. DF increased with decreasing flow rate.

TABLE 18. Absorption of Degraded Phosphate on HZO-1 (-50 to +60 Mesh).

Condition	Experiment 1	Experiment 2
Flow rate, $\ell/\text{hr}/\text{lb}$	3.15	1.38
Effluent sample size, $\text{m}\ell$	23	18
Influent PO_4^{3-} , mg/ℓ	12.8	23.3
Effluent PO_4^{3-} , mg/ℓ		
Sample:		
1-2	2.76	1.81
15	3.56	1.80
20	3.52	1.76
25	3.43	1.69
30	3.36	--
35	3.41	--
Average DF	3.7	13.2

Regeneration of crystals can be accomplished by elution with basic solution. Results of a partial elution are given in Table 19. Approximately 69% of the phosphorus loaded was removed in samples 1 through 6.

TABLE 19. Regeneration of HZO-1 With 0.2N NaOH.

Sample	Flow rate, $\ell/\text{hr}/\text{lb}$	PO_4^{3-} , mg
1	2.53	136
2	2.99	336
3	3.29	73
4	1.32	179
5	2.74	31
6	2.74	54

PERFORMANCE AND DEGRADATION OF DILUENTS FOR TBP AND THE CLEANUP OF DEGRADED SOLVENTS (14, NSE 17)

The useful life of hydrocarbon-TBP solvent systems is limited by the formation of unidentified compounds formed by the interaction of nitric and nitrous acids with the hydrocarbon under the influence of radiation or at elevated temperatures. Unlike the decomposition products of TBP, these degradation products are not removed by aqueous alkalis in the solvent wash systems, but slowly accumulate and reduce the performance of the solvent to the point where it has to be discarded and replaced by a fresh charge. Degraded solvents show poor phase separation, decreased mass transfer coefficients for uranium, etc., retention of fission products in the solvent after aqueous alkaline washing, and leakage of fission products into the uranium and plutonium product streams.

Chemistry of Diluent Degradation

Method of Assessment. Use of the Z value as an index for the measurement of metal retention in degraded solvents (i.e., the number of moles of zirconium retained by 10^9 g of solvent after carrying out a standardized test involving the extraction of zirconium into the solvent followed by extensive scrubbing of the solvent with 3M nitric acid) has been widely adopted for laboratory studies of solvent degradation. Substitution of ^{181}Hf for ^{95}Zr results in an essentially equivalent test. A performance index has been used for the comparison of diluents:

$$\text{Performance Index} = \frac{\text{H value of diluent}}{\text{H value of standard diluent}}$$

Role of Nitrous Acid in the Degradation of the Inert Diluent. The species involved in the thermal degradation of the diluent is nitrous acid. The degradation of 20% TBP-odorless kerosene by 4M nitric acid at 70°C required an induction period of 40 hours, during which time nitrous acid was produced. The degradation reaction was suppressed completely in the presence of sulphamic acid or urea or similar nitrous acid scavenger in the aqueous phase. Nitrous acid, like nitric

acid, is strongly extracted by TBP and this facilitates the attack on the hydrocarbon. The presence of air in the system reduced the amount of degradation, probably by oxidation of the nitrous acid. Degradation was reduced by a factor of 3 when keeping the reaction vessel open to the atmosphere; by 10 when sparging air through both phases; and by 20 when operating at 30°C rather than at 60°C.

Nature of the Complexing Materials Formed by Nitric Acid

Degradation of Diluents. There is some evidence to suggest that hydroxamic acids $RCONHOH$ (where R is alkyl) are one of the main complexing species. The precursors to the complexing species are primary nitrohydrocarbons. These may be formed from:

- nitration of -- CH_3 groups in hydrocarbon chains
- nitration of alkyl side chains in aromatics and naphthenes
- nitration of terminal ethylenic linkages in olefins
- ring opening of naphthenes.

Primary nitroparaffins are converted to hydroxamic acids by:

- acidification (Victor Meyer Reaction), as the main product
- aci-salt formation with alkalies, followed by reacidification (Nef Reaction), as a side reaction. The main products in this latter reaction are nitrolic acids, which are not in themselves strong complexing agents.

Experimental data indicate:

- The concentration of hydroxamic acid builds up in the organic phase on solvent recycle to a small but steady value, being lost from the system by hydrolysis as hydroxylamine.
- Prolonged alkaline washing increases this steady-state concentration.
- Hydroxamic acid in recycled solvent forms complexes such as zirconium tetrahydroxamate which remain in the organic phase.

Cleanup and Decontamination Procedures

Removal of Complexing Species. There is agreement that the removal of nitroparaffins from the solvent reduces the metal retention capacity to acceptable limits. Thus, the removal or destruction of nitroparaffins is the essential step in a cleanup procedure.

Only hypochlorites and permanganate solutions were found to be effective. Chlorination of the solvent and some filtration difficulties have mitigated against the extensive use of these processes. The alkanolamines were shown to be suitable reagents. They owe their effectiveness to: (1) their low solubility in TBP-kerosene, and (2) preferential extraction of nitro compounds from the solvent by salt formation. The conversion of nitroparaffins to the sodium salt of the aci-form is normally a slow process requiring many days to go to completion, whereas salt formation with alkanolamines is complete within a few minutes. The process would be relatively expensive for plant use, due to: (1) the high volume ratio of alkanolamine to solvent required, (2) loss of TBP due to its solubility in the alkanolamine phase, and (3) the high cost of alkanolamine and the expense for its recovery.

Removal of Uranium Retained in the Solvent. Decontamination of retained uranium arising from hydrocarbon degradation has been studied. Uranium(VI) is known to give an intensely yellow peruranate complex when hydrogen peroxide is added to alkaline ($\text{CO}_3^{=}$ or OH^-) solutions of uranium. The peruranate complex is more stable than the carbonate or insoluble uranate complexes which are formed under the same conditions in the absence of peroxide. Alkaline peroxide removed the uranium from degraded solvents considerably faster than alkaline washes alone.

Pretreatment Processes for Odorless Kerosene and Comparisons of Alternative Diluents

Various simple treatments that might improve the performance of odorless kerosene as diluent have been assessed.

Steam Distillation. Whereas straight distillation had very little effect on the composition and stability of odorless kerosene, steam distillation produced more encouraging results. At atmospheric pressure, some 25% by volume of odorless kerosene remained involatile in steam and this residue was shown to be five times less stable than the parent material to nitric acid, i.e., the high boiling hydrocarbons were more unstable than the low boiling fractions. In the volatile fractions, the first 10% of the distillation was three times more stable than the undistilled material and the stability fell off as distillation continued.

Sulfuric Acid Treatments. Odorless kerosene has already had an oleum washing treatment at the refinery. Typical samples of odorless kerosene were given further sulfuric acid treatments. The stability could be increased twofold in this way but with excessive contact some mercaptanlike compounds were produced which possessed metal retaining properties. The upgrading of odorless kerosene by sulfuric acid is due to removal of unsaturation and isomerization of branched-chain paraffins and naphthenes to more stable structures.

Alternative Diluents. Paraffins extracted from kerosene by urea-adduction showed an improvement factor of 3 over the parent diluent but this was much lower than that of n-dodecane itself. The urea-adducted hydrocarbons constituted about 40% by volume of the feed diluent and performance could be further improved by factors of 1.5 and 3.5 by additional steam distillation and sulfuric acid washing, respectively. It is suggested that the reason why the urea-adducted paraffins do not equal the performance of n-dodecane is due to the presence of: (a) high molecular weight n-alkanes, and (b) straight-chain olefins, and not due to the small concentration of those isoparaffins present since these have a high stability to nitric acid.

Certain isoparaffins are more stable than odorless kerosene toward nitric acid. Both an alkylate and a hydrogenated propylene tetramer have better stability (six and five times, respectively) compared with odorless kerosene.

The conjunct polymers of simple olefins were examined and found to be more stable than odorless kerosene by factors of up to 12. Conjunct polymers are mixtures of fully saturated branched chain hydrocarbons with a complex structure prepared by contacting olefins with concentrated sulfuric acid.

A gas chromatographic examination of diluents of possible interest identified certain individual hydrocarbons in very complex mixtures, e.g., monomethyl-substituted paraffins in kerosene fractions. From the composition of the different diluents, the performance of the diluents with composition and chemical structure was rationalized. The conclusions reached confirm that unsaturates, aromatics, and naphthenes are compounds to be avoided.

PROPERTIES OF DEGRADED TBP-AMSCO SOLUTIONS AND ALTERNATIVE EXTRACTANT-DILUENT SYSTEMS (15, NSE 17)

Among the effects caused by solvent 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 solvent activity levels by stripping extracted fission products and preventing buildup of low molecular weight acidic products which are primarily from hydrolysis of the extractant, e.g., strongly extracting DBP formed from TBP.

Two methods were employed to degrade the solvent phase: (1) a ^{60}Co source was used to irradiate an agitated two-phase system, the aqueous phase being initially 2M HNO_3 and the radiation power being approximately 2.25 W/l ; (2) the solvent was boiled with 2 to 8M HNO_3 under total reflux with agitation produced by the boiling.

The degraded solvent is customarily used to extract metal ions, usually fission product ^{95}Zr - ^{95}Nb , from aqueous HNO_3 , and the ability of the extracted metals to withstand subsequent stripping with HNO_3 is one of the common measures of degradation. However, it has been observed that the curves showing metal ion extraction and those showing retention ability are nearly always parallel when using the test procedure described below. Only the metal extraction ability of the solvent is described.

Extraction test procedure: (1) make the degraded solvent 1M in TBP and scrub twice with an equal volume of 2.2M aqueous Na_2CO_3 to remove low molecular weight acids, primarily DBP and MBP (10 minutes each contact); (2) contact 30 minutes with solid calcium hydroxide, about

50 g solid/l of organic phase, and separate from solid; (3) contact with metal tracer solution (e.g., ^{95}Zr - ^{95}Nb) in nitric acid solution and measure the extraction.

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

Extraction of ^{95}Zr - ^{95}Nb by the "as-degraded" solvent rose rapidly with the extent of irradiation, and is attributable largely to acidic DBP, etc., derived from the TBP. The small residuum of ^{95}Zr - ^{95}Nb extractants remained after scrubbing with sodium carbonate, increased in quantity nearly linearly with irradiation. Treatment with calcium hydroxide after sodium carbonate increased the ^{95}Zr - ^{95}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.

Importance of Nitroparaffins

A sample of AMSCO 125-82 was severely degraded by boiling with an equal volume of 8M nitric acid under total reflux for about 6 hours. A part of the organonitrogen products from the degradation reaction were sorbed on chromatographic grade alumina. After removal from the alumina the material analyzed 75.2% carbon, 12.6% hydrogen, and 2.7% nitrogen.

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).

Samples of purified organonitrogen compounds were added, at concentrations up to 0.3M, to undegraded 1M TBP-AMSCO solutions, and the resulting mixtures were tested for ^{95}Zr - ^{95}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. Solvent containing caprylohydroxamic acid ($\text{C}_7\text{H}_{15}\text{CONOH}$) extracted ^{95}Zr - ^{95}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 ($C_8H_{17}ONO_2$) and decyl nitrite ($C_{10}H_{21}ONO$) did not extract increased amounts of ^{95}Zr - ^{95}Nb , with or without the calcium hydroxide treatment.

Extraction Mechanism

If either or both the nitroparaffin enol and 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 actually be accomplished by a trace component. However, a single test suggests that a significant fraction of the nitroparaffin was involved at one time in hafnium extraction.

Other extraction mechanisms were proposed on the basis of trace-level extractions. Zirconium extraction by nitroparaffin enols was questioned, and it was proposed that the effective extractants are hydroxamic acids derived from the nitroparaffin enols by rearrangement in the acid solution. A zirconium-hydroxamic acid adduct was shown to be more stable than hydroxamic acid in acid solution. Direct evidence for the existence of hydroxamic acids in these systems has not yet been obtained.

Solvent Cleanup

Whether the actual extraction and retention of fission products in degraded solvents is affected by enol nitroparaffin, by hydroxamic acids derived therefrom, or by other related components, such extraction correlates with the concentration of nitroparaffin present. 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.

Solid Sorption. Current solvent treatment in processing plants using TBP involves combinations of washings with acidic solutions, alkaline solutions, and, occasionally, alkaline permanganate solutions. 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. Absorption of these on the solid manganese dioxide 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. The two sorbants were tested on a 1M TBP-AMSCO solution exposed in the presence of nitric acid to 45 Wh/l irradiation.

Both solids showed similar sorption patterns in room temperature tests. Impurities causing 50 to 60% of the ^{95}Zr - ^{95}Nb extraction by the irradiated, carbonate-scrubbed solvent were easily sorbed. Removal of another fraction causing 20 to 25% of the ^{95}Zr - ^{95}Nb extraction was achieved by further relatively large addition of solid; but, even at the highest solids level used, the solvent retained 20 to 25% of its ^{95}Zr - ^{95}Nb extraction power. To achieve equivalent performance, it was necessary to use 10 to 20 times more alumina than manganese dioxide. Efficiency of cleanup by manganese dioxide increased when the accompanying sodium carbonate concentration was increased from 0.1 to 0.5M. 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.

Liquid Scrubbing. Solvent cleanup with a liquid scrub rather than with a solid has definite operational advantages. In studies involving nearly 100 liquids, or in some cases, liquid and solid combinations, most effective cleanup was achieved by ethanolamine. The amine forms salts with the nitroparaffins which have significant solubility in the amine

phase. Table 20 compares stepwise scrubbing of the degraded solvent with both 0.5N aqueous sodium hydroxide and 100% ethanolamine. The organic phase was scrubbed with successive batches of fresh scrub solution. After being scrubbed, the treated organic was used to extract ^{95}Zr - ^{95}Nb from a 2M HNO_3 tracer solution. The amine-scrubbed material decreased in extraction ability with each of the first four scrub steps, and after the fourth step, 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 steps. The extraction after four steps was still several times that obtained with the fresh TBP-AMSCO.

TABLE 20. Comparison of Sodium Hydroxide and Ethanolamine Cleanup of a Degraded Solvent.

Scrub Steps	^{95}Zr - ^{95}Nb Extraction by Organic Phase cps/ml	
	As Scrubbed	After $\text{Ca}(\text{OH})_2$
No cleanup		4000
After cleanup with 0.5N 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
Extraction by fresh 1M TBP in fresh AMSCO 125-82		
	70	70

Distillation

Low pressure flash distillation appears at present to be the best method for partial or total repurification of TBP-AMSCO 125-82 solutions decomposed by radiation. This is based on laboratory studies of molecular and rapid (not flash) distillation of degraded 30% by volume TBP-AMSCO 125-82 solutions. Both molecular distillation at $\sim 70^{\circ}\text{C}$, which corresponds to $\sim 10^2 \mu$ TBP vapor pressure, and rapid pot-to-pot distillation at 110 to 120°C , corresponding to $\sim 5 \times 10^2 \mu$ TBP vapor pressure, showed that the degradation products remained as a pot residue.

Extraction tests showed essentially no distillation of materials that affect the zirconium, niobium, ruthenium, or uranium extraction properties of the 30% by volume TBP-AMSCO 125-82 organic solution.

Improving the Stability of AMSCO 125-82

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

AMSCO can be improved by destroying, prior to process use, some of the sites which are reactive to nitric acid. Experimentally this has been done by scrubbing the AMSCO before use with concentrated sulfuric acid and 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 ($>95\%$) or when oleum is added to the concentrated acid for use at room temperature. Whereas, the 1M TBP in unpretreated AMSCO (after 8 hours of nitric acid degradation) showed a hafnium extraction coefficient of 16, those in AMSCO pretreated with 96, 98 or 100% sulfuric acid showed coefficients of 0.3, 0.15, and 0.03, respectively. Thirty percent TBP in AMSCO pretreated

with 100 and 105% acid at room temperature and with 95.6% acid at 50°C for 30 minutes, all had extraction coefficients of ~ 0.15 even after 24 hours of degradation. The sulfuric acid apparently acts to destroy the active sites by sulfonation to sulfuric acid-soluble byproducts 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 1M TBP and then boiled for 24 hours with 2M nitric acid, was as stable as AMSCO pretreated with 100 and 105% sulfuric acid at room temperatures.

Alternative Diluent Investigations

Because most solvents now in use have structures at least as complicated as those in AMSCO 125-82 (and apparently less stable), it is difficult to make comparisons between data obtained at one operating site and those obtained at another. The trend is toward use of simple, relatively pure, more stable, normal hydrocarbons, e.g., n-dodecane.

In addition to aliphatic compounds, a number of aromatics have been examined since they help 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.

Table 21 shows the performance of a number of diluents in the usual carbonate-calcium hydroxide tests after degrading a solution 1M in TBP for 4 hours 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. Stability of alkylbenzenes with two side chains apparently depended upon the particular isomer or purity.

TABLE 21. Performance of Degraded Diluents.

Diluent	Flash point (closed cup), °F	⁹⁵ Zr- ⁹⁵ Nb cps/ml (Calcium test)
Alkyl Benzenes		
Methyl (toluene)	40	110
1,2-dimethyl (o-xylene)	63	100
1,3-dimethyl (m-xylene)	63	100
1,4-dimethyl (p-xylene)	63	100
1,2,4-trimethyl (pseudocumene)	125	100
1,2,3-trimethyl (heminellitene) 73%	124	400
96%		>6000
1,2,3,4-tetramethyl (prehnitene)	163 ^a	200
1,2,3,5-tetramethyl (isodurene)	155 ^a	1400
Ethyl	59	500
Diethyl (mixtures)	138 ^a	4000, 10000
Triethyl (mixture)		140
Propyl	86	80, 450
Isopropyl (cumene)	102	30, 4000
Diisopropyl (mixture)	170	>6000
Triisopropyl	170	>6000
n-butyl	160 ^a	125
sec-butyl	126	130
tert-butyl	140 ^a	120
iso-butyl		45
Tetralin	171	decomposes
1-methyl-4-isopropyl (paracymene)	138	4000
sec-amyl	~150 ^a	170
tert-amyl (1,1-dimethylpropyl)		130
n-hexyl		120
Cyclohexyl		>6000
n-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
n-decane	115	1000
2,2,5-trimethylhexane		80
n-dodecane	165	125
n-hexadecane		140

^aOpen Cup.

INVESTIGATIONS TO DETERMINE THE EXTENT OF DEGRADATION OF TBP/ODORLESS KEROSENE SOLVENT IN THE NEW SEPARATION PLANT, WINDSCALE (16, NSE 17)

Batch Irradiation Experiments

Batch irradiations of 20% by volume TBP/OK*, previously washed with sodium carbonate solution, were performed. The irradiated solvents were centrifuged, washed with 0.01N nitric acid, and examined by infrared analysis or by the test.

Chemistry of Degradation Products. In one of the experiments, 20% by volume TBP/OK was stirred with an aqueous phase of 3N nitric acid containing uranium (170 g/l), zirconium nitrate (3×10^{-3} M) and sodium nitrite (1×10^{-3} M). The detectable products of degradation, i.e., nitro compounds, organic nitrates, and carbonyl-containing materials, accumulate at a linear rate with increasing total dose while the capacity to retain zirconium increases in a nonlinear fashion. If it is assumed that one molecule of zirconium is complexed by one molecule of ligand, the concentration of ligand species can be calculated (Table 22). These values are much less than the concentrations of the primary products identified by infrared analysis. These observations indicate the detectable "primary" products of irradiation are not responsible for fission product retention in process solvents.

TABLE 22. Concentration of Irradiation Products in a Sample of 20% by Volume TBP/OK.

(Dose = 7.5 Wh/l)

$R-NO_2$, M/l	$RONO_2$, M/l	RCO_2H , M/l	$RCOR_1$, M/l	Ligand, ^a M/l
5×10^{-3}	2.8×10^{-2}	1×10^{-2}	7.4×10^{-2}	1.7×10^{-5}

^aCalculated assuming a 1:1 zirconium to ligand ratio.

*The OK (odorless kerosene)(Shell B.P. Ltd.) used has the following constitution: n-paraffins, 60%; isoparaffins, 7%; naphthenes, 32%; aromatics, 1%; unsaturates, 0.1%.

A series of compounds representing both primary and possible secondary products were synthesized and tested for their ability to retain zirconium under processing conditions. The compounds were dissolved in 20% by volume TBP/OK at concentration levels expected in degraded solvents and were subjected to the Z test. Results are shown in Table 23. None of the "primary" products, individually or collectively, cause appreciable fission product retention and of the "secondary" products only dodecyl hydroxamic acid showed high ability to retain zirconium under simulated process conditions. Further work showed naphthenic and oleic hydroxamic acids to display the same behavior, and that the zirconium complexes remained stable in contact with 3N nitric acid for 2 hours. When TBP/OK containing $5 \times 10^{-5} \text{M}$ C_{12} -hydroxamic acid was compared with degraded solvent ($Z = 50,000$) in a batch extraction, backwash, and solvent wash cycle, it was found that the retained activity in the former material was only 10% of that in the degraded solvent, and a solution of 10^{-3}M C_{12} -hydroxamic acid in TBP/OK gave only 30% the retention of the degraded solvent.

Radiation Yields of Degradation Products. A preliminary investigation of the dependence of radiation yield (G value) on the different chemical and physical environments encountered in the first extractor was made. Where one phase was irradiated separately, it was equilibrated with the other phase before the radiation period. The results are given in Table 24.

Comparison of the series of experiments with gamma-radiation (Experiments 1 through 6) and beta-radiation (Experiments 7 through 10) indicates that dose rate and solvent-to-aqueous ratio (S/A) affect the determined G value, although results of the same order of magnitude were obtained.

Experiments 7, 8, and 9 show the influence of nitrite level in the aqueous feed. A tenfold rise in nitrite ion concentration in the feed causes a fourfold rise in the radiation yield of ligands.

TABLE 23. Zirconium Retention of 20% by Volume
TBP/OK Containing Added Synthetic Materials.

Class of compound	Formula	Initial molarity	Z Number
20% TBP/OK alone		--	30
<u>Primary Products</u>			
Ketone	$\text{CH}_3\text{COC}_9\text{H}_{19}$	2×10^{-2}	30
Carboxylic acid	$\text{C}_7\text{H}_{15}\text{COOH}$	4×10^{-2}	350
Nitro alkane	$\text{C}_{12}\text{H}_{25}\text{NO}_2$	2×10^{-2}	130
Alkyl nitrite	$\text{C}_{12}\text{H}_{25}\text{ONO}$	2×10^{-2}	100
Alkyl nitrate	$\text{C}_{12}\text{H}_{25}\text{ONO}_2$	2×10^{-2}	150
<u>Secondary Products</u>			
Nitro olefin	$\text{C}_{10}\text{H}_{21}\text{CH} = \text{CHNO}_2$	2×10^{-2}	220
Nitrolic acid	$\text{C}_2\text{H}_5\text{CH}(\text{NO})\text{NO}_2$	4×10^{-2}	200
Hydroxamic acid	$\text{C}_{11}\text{H}_{23}\text{CONHOH}$	1×10^{-2}	4×10^5
Nitro alcohol	$\text{C}_{10}\text{H}_{21}\text{CH}(\text{OH})\text{CH}_2\text{NO}_2$	5×10^{-3}	50
DBP	$(\text{C}_3\text{H}_7\text{O})_2\text{POH}$	2×10^{-3}	30
DBP	$(\text{C}_3\text{H}_7\text{O})_2\text{POH}$	2×10^{-3}	30
Alkyl nitrate	$\text{C}_{12}\text{H}_{25}\text{ONO}_2$	2×10^{-2}	30
Nitro alkane	$\text{C}_{12}\text{H}_{25}\text{NO}_2$	2×10^{-2}	30
Carboxylic acid	$\text{C}_7\text{H}_{15}\text{COOH}$	2×10^{-2}	30
Ketone			
Hydroxamic acid, contacted 2 hours with 3M HNO_3		3×10^{-5}	60
Zirconium complex of hydroxamic acid, contacted 2 hours with 3M HNO_3		3×10^{-5}	3.4×10^3

^aCalculated assuming that zirconium to ligand ratio = 1:1

TABLE 24. Batch Irradiations of 20% TBP-OK-3N HNO_3 -0.7M- $\text{UO}_2(\text{NO}_3)_2$ Systems.

Conditions of Irradiation					Radiation yield (G value), M/l					
System examined	Radiation	Dose rate, Wh/l	Total dose, Wh/l	Temp., °C	Zirconium ligand ^a	RNO_2	RONO_2	RCO_2H	RCOR_1	Nitrite level in feed, M/l
1 Two phases stirred; S/A = 2.7	γ	2.9	31	41.5	3.9×10^{-4}	0.9	1.9	1.4	3.1	0
2 Two phases under settled conditions; S/A = 2.6	γ	2.9	31	41.0	1.8×10^{-3}	2.2	1.9	0.7	0.5	0
3 Equilibrated organic phase stirred and irradiated alone	γ	2.9	31	41.0	1.8×10^{-4}	1.3	1.7	2.0	3.7	0
4 Equilibrated organic phase alone (not stirred)	γ	2.9	31	42.5	1.9×10^{-3}	2.3	1.9	0.7	0.5	0
5 Two phases settled and air sparged (but not mixed); S/A = 2.7	γ	2.9	31	43	6.2×10^{-4}	1.3	1.9	1.2	3.1	0
6 Two phases settled and nitrogen sparged (but insufficiently to mix); S/A = 2.7	γ	2.9	31	43	6.1×10^{-4}	2.5	1.4	2.1	Not detected	0
7 Two phases stirred and organic phase recirculated, aqueous phase continuous flow containing 2×10^{-4} molar sodium nitrite; S/A = 5	β	0.03	9.0	26	2.0×10^{-4}	Not detected	3.1	---	5.0	2×10^{-4}
8 As 7 with 2×10^{-3} continuous aqueous feed molar in sodium nitrite	β	0.03	9.5	26	9.2×10^{-4}	Not detected	5.3	---	5.0	2×10^{-3}
9 As 7 with 2×10^{-2} continuous aqueous feed molar in sodium nitrite	β	0.03	9.0	26	3.3×10^{-3}	10	4.4	---	4.4	2×10^{-2}
10 Settled phases irradiated together; S/A = 5	β	0.03	16	26	5.2×10^{-4}	---	---	---	---	0
11 Aqueous phase irradiated alone and then extracted	β	0.01	3	26	6.5×10^{-5}	---	---	---	---	0

^aCalculated assuming that zirconium to ligand ratio = 1:1

In the absence of nitrite ion, more degradation of the solvent occurs under settler conditions than under mixer conditions (Experiments 1 and 2). This may be due in part to the buildup of nitrite (produced by radiation) in the static system, and it is noted that air or N_2 sparging, which would destroy or remove nitrite, reduces the radiation yield. The smaller ratio of nitro to carbonyl groups produced under stirred conditions, when compared with static irradiation, supports this view. (Experiments 1 and 3, 2 and 4, Table 24.)

Comparison of Experiments 4 and 2 indicates that the presence of the aqueous phase has a negligible effect on total yield of ligands for conditions of equal irradiation. Another experiment (Experiment 11, Table 18) in which the aqueous feed was equilibrated with solvent and separated prior to irradiation, followed by re-equilibration with the original unirradiated solvent phase, showed a low yield of ligands.

If a nominal dose to the solvent in the first extractor is assumed to be 0.04 Wh/l/cycle, and the G values for the mixer and settler conditions are as shown in Table 18, it is calculated that 8.5×10^{-9} M/l/cycle of ligands (as determined by the Z test) are produced by radiolysis. It is believed that a single pass through the solvent wash contactors removes the zirconium-complexed ligands by a factor which varies with the degree of degradation. Taking a mean DF of 2, it is estimated that after 500 cycles through the first coextraction cycle, the ligands produced would retain approximately 25 μ Ci/l of retained zirconium/niobium when measured at the feed to the alkali washers. This value appears to be high, being 25 times the operating level with fresh solvent.

Recycle Experiment

The initial object of the experiment was to circulate 20% by volume TBP/OK containing uranium and zirconium through a radiation field, a back-wash section, and an alkaline wash section (sodium carbonate, sodium hydroxide, and nitric acid). Later the apparatus was modified to include multistage extraction and stripping with solvent wash contactors.

Both the absolute level of ^{95}Zr - ^{95}Nb activity and the ^{95}Zr - ^{95}Nb activity calculated as a percentage of the feed input were examined. The experiment was subdivided thus:

- Period A: 0 to 240 cycles. During the period solvent saturation fluctuated and control of feeds was poor.
- Period B: 240 to 320 cycles. A period of steady running during which a steady increase in the activity levels of the solvent streams occurred.
- Period C: 320 to 380 cycles. A period of steady running. A bulk addition of solvent (20% of the total charge) was made and may account for a fall in activity at this point.
- Period D: 380 to 480 cycles. A period of steady running in which a further increase in ^{95}Zr - ^{95}Nb activity levels of the recycled solvent streams occurred. At 480 cycles, the washed solvent was yellow in color, contained organic nitrate esters and carboxylic acids, and appeared to be heavily degraded.
- Period E: 480 to 640 cycles. At 480 cycles, a 10-step scrub section was introduced and the solvent charge was diluted by 60% with fresh solvent. A slow fall in the solvent raffinate activity levels occurred during the following 160 cycles.

The overall interpretation of the experiment is a steady increase in the retained activity level of the solvent raffinate streams from 0 to 480 cycles. The introduction of the 10-step scrub section then caused a gradual reduction of the solvent activity level. Evidently, the strong acid condition and uranium loading of the scrub flow removes activity not removed by the more dilute acid in the strip contactor, despite the higher S/A in the latter.

The effects of solvent degradation on ^{95}Zr - ^{95}Nb behavior are shown in Table 25. In this table, the operation of the recycle test equipment with fresh solvent is compared with solvent recycled for 600 cycles and with two samples of solvent degraded by batch irradiation in gamma-field. All the results are conditions of 90% uranium solvent saturation at the feed plate.

TABLE 25. Effects of Solvent Degradation on ^{95}Zr - ^{95}Nb in the First Cycle.^a

Source of solvent	DF for Zr/Nb					Activity of solvent, as percentage input ^b			Scaled activity to new plant	
	Extraction	Strip	Total over Ext.-Strip 1 ^(c)	Back-wash	First Cycle overall	HA wash system, %	Unwashed solvent, %	Washed solvent, %	Unwashed solvent, $\mu\text{Ci}/\ell$	Washed solvent, $\mu\text{Ci}/\ell$
Fresh 20% by volume TBP/OK	9×10^2	5	4.5×10^3	2.5	1.2×10^4	< 7	0.03	0.004	0.06	0.1
20% TBP/OK after 600 cycles in the experiment (total dose 60 Wh/ ℓ)	7×10	4.6	3.2×10^2	13.7	4.4×10^3	1.5	0.3-0.6	0.2-0.4	6-12	4-8
20% TBP/OK batch irradiated to 30 Wh/ ℓ	---	---	2.8×10^2	3.5	1.0×10^3	3.0	0.6	0.2	12	4
20% TBP/OK batch irradiated to 60 Wh/ ℓ	4.8×10	3.6	1.7×10^2	7.9	1.5×10^3	1.4	0.8	0.6	17	12

^aTemp: 23°C, all results taken for the same condition of uranium saturation of solvent, 90% at feed plate.

^bPercentage = $\frac{\text{solvent activity} \times \text{flowrate}}{\text{aqueous feed activity} \times \text{flowrate}} \times 100$

^cFirst Extractor

Using solvent exposed for 600 cycles, a threefold decrease in DF for ^{95}Zr - ^{95}Nb to the first cycle aqueous product was observed. At the same time, there is a ten- to twentyfold rise in the ^{95}Zr - ^{95}Nb activity level of the unwashed first cycle solvent raffinate, and a decrease in the efficiency of activity removal by the first cycle coextraction solvent wash system. A net increase of forty- to eightyfold in the ^{95}Zr - ^{95}Nb activity of the recycle solvent was recorded.

Data obtained by physicochemical tests on fresh solvent and batch-degraded solvents are shown in Table 26.

Ruthenium Behavior in Degraded Solvents

Separate batch experiments were carried out with fresh (10- to 40-hour aged) dissolver feed using a series of degraded solvents to determine the effect of solvent degradation on ruthenium behavior under process conditions.

The results are tabulated (Table 27) for fresh solvent, for solvent recycled in the solvent degradation apparatus, and for three samples of solvent degraded by continuous gamma-radiolysis. Data from the Windscale pilot plant, when operated with the same dissolver feed, are shown for comparison.

Only in heavily degraded solvents are significant effects observed, there being some fall in ruthenium DF in the first contactor and some decrease in the efficiency of solvent cleanup by alkali washing. With solvent recirculated for 600 cycles, although ^{95}Zr - ^{95}Nb effects are appreciable, ruthenium behavior is little affected.

Remedial Measures for Solvent Degradation

The solvent degradation pattern of an existing processing plant be improved by installing an improved wash procedure for ligand removal or changing the diluent to one less susceptible to chemical and radiolytic attack.

Many reagents are efficient for activity removal, but there is evidence that the ligands responsible for complexing activity often pass through the wash system as solvent soluble (sodium) salts, and are recirculated to pick up activity again in the first contactor. Hence,

TABLE 26. Physiochemical Tests on Degraded Solvents.

Source of Solvent	Infrared analysis, wt%				Settling Time ^a (Aqueous in Organic), sec	Windscale Z test
	(C ₁₂) NO ₂	(C ₁₂) CO ₂ H	(C ₅) ₂ C=O	C ₁₂ (NO ₃)		
Fresh 20% TBP/OK	nd	nd	nd	nd	40	36
Solvent batch irradiated to 30 Wh/l	0.05	0.06	0.33	0.28	46	2500
Solvent batch irradiated to 60 Wh/l	0.09	0.13	0.65	0.58	58	10,000
Solvent batch irradiated to 70 Wh/l	0.12	0.17	0.85	0.78	61	20,000

^a The settling test is carried out as follows. A paddle stirrer (1500 rpm) was used to disperse the phases, (20% TBP/OK), and UO₂(NO₃)₂ (300 g/l) in the 3N HNO₃ in a 50-ml measuring cylinder at 28°C. The time for the phases to disengage is given.

TABLE 27. Ruthenium Behavior in Degraded Solvents.^a

Solvent used	DF for ruthenium		Activity of $^{103} + ^{106}\text{Ru}$, $\mu\text{Ci}/\ell$	
	P.S. 1 ^b	HA wash system ^c	Unwashed solvent P.S. 2 raffinate	Washed (recycle) solvent
Fresh 20% TBP/OK	2.0×10^3	40	0.30	0.009
Solvent degraded for 600 cycles in the recycle experiment. Total dose 60 Wh/ ℓ ^d	1.9×10^3	47	0.41	0.009
Solvent irradiated 20 Wh/ ℓ with nitric acid	1.3×10^3	50	0.41	0.008
Solvent irradiated 35 Wh/ ℓ with nitric acid	1.3×10^3	20	0.29	0.015
Solvent irradiated 60 Wh/ ℓ with nitric acid	7.8×10^2	7.7	0.9	0.12
Performance of the Windscale pilot plant with the same feed and fresh 20% TBP/OK	1.5×10^3	11-60	0.4-1.5	0.023-0.035

^aBatch contacting with fresh dissolver stock feed containing: uranium, 314 g/ ℓ ; ^{95}Zr - ^{95}Nb , ~ 10 Ci/ ℓ ; $^{103} + ^{106}\text{Ru}$, ~ 5 Ci/ ℓ ; and HNO_3 , 3.0N.

^bFirst extractor.

^cHighly active solvent wash system.

^dNot allowing for solvent replacement. Estimated dose including replacements = 20 Wh/ ℓ .

attention has been focused on the ability of reagents to remove ligands from the solvent. The results from laboratory studies are shown in Table 28. The cheaper reagents, e.g., Na_2CO_3 , NaOH , and HF , are not very effective for ligand removal and their efficiency for activity removal falls off as solvent degradation increases. Alkaline permanganate is an effective scavenger of activity and ligands, and its efficiency varies little with the degree of solvent degradation. However, laboratory studies in small-scale counter-current equipment showed that MnO_2 sludges accumulated in settler aqueous phases; appreciable quantities of MnO_2 were carried in the solvent phase (20 mg/l), and this solid was only slowly removed by subsequent nitric acid washes.

Various alkanolamines, mono-, di-, and tri-ethanolamines and tri-isopropanolamine were excellent reagents for activity removal and for ligand removal; the efficiency of ligand removal varied little with the degree of solvent degradation. The TBP content of the solvent is depleted in the first pass and emulsions sometimes occurred in subsequent acid washes. The alkanolamines are expensive and poor results are obtained with diluted solutions or when the alkanolamine solutions are recycled.

Distillation procedures appear an attractive method to clean up solvent. Simple vacuum distillation of 20% by volume TBP/OK yields a kerosene-rich fraction followed by a TBP-rich heel. The ligands produced by degradation have a finite volatility and distillation conditions must be chosen with care to give good fractionation and disentrainment, and still minimize thermal degradation by having a low residence time at elevated temperatures.

A steam flash vaporization procedure was investigated. The preheated solvent is injected into superheated steam which vaporizes the solvent and acts as a carrier medium; unvolatilized material is separated in a cyclone. The residence time of solvent in the heated zone is only a few seconds. At temperatures of operation above 170°C , the finite volatility of the ligands leads to poor cleanup of degraded solvent. However, using lower temperatures, DF for ligand of 10 to 40 with residues of 1 to 6% have been achieved on small-scale equipment.

TABLE 28. Cleanup Procedures for Degraded Solvents - Summary of Laboratory Work.^a

Conditions	DF zirconium	DF zirconium ligand	Comments
0.1M Na ₂ CO ₃	10	2	Varies with degree of degradation
0.1M NaOH	10	2	Varies with degree of degradation
1M Na ₂ CO ₃	13	2	
1M NaOH	15	3	
0.23M KMnO ₄ in 0.25M Na ₂ CO ₃	>100	10-15	Efficient at different levels of degradation; MnO ₂ carry over
100% triethanolamine	>100	20-40	Efficient at different levels of degradation; some emulsions; TBP depleted; expensive
10% triethanolamine in 0.1M NaOH	20	4	
0.1M NaF in 0.1M HNO ₃	>100	1	Complete removal of zirconium
Vacuum distillation	>1000	3	Tarry pot residues tend to decompose; DF for ligands depend on distillation temperature
Steam flash vaporization	>1000	Up to 40	DF for ligands depend on operating temperature and percentage residue

^a All experiments on heavily degraded (60 Wh/l) solvent washed at 60°C for 30 minutes at S/A ratio of 1.

The magnitude of solvent degradation effects also depends on the nature of the diluent. It is well established that the order of susceptibility of hydrocarbons to thermal and radiolytic degradation is olefins > naphthenes > isoparaffins > n-paraffins. Evidence on the behavior of aromatic hydrocarbons is conflicting. A range of diluents was investigated in a standard radiation test in which solvent is irradiated in a mixer compartment in contact with a continuously renewed aqueous feed containing uranium, nitric acid, and nitrite ion. The results show an order of stability expected from their known constitution. British OK behaves well compared with other kerosene fractions but is inferior to alkylated products and n-dodecane.

CHANGES TO PLUTONIUM EXTRACTION BEHAVIOR OF TBP AND ALKYLAMINES THROUGH IRRADIATION (17, NST 3)

Solvent extraction with TBP kerosene is at present the only practical method adopted in the reprocessing of irradiated fuels. Although alkylamines, such as trioctyl amine, have come to receive increasing attention for possible use in reprocessing, the data are not included in this abstract.

Some extraction separation in reprocessing is performed under intensive radiation from fission products. The extractant is affected, resulting in such unfavorable effects as decrease in separation efficiency and formation of emulsions.

Plutonium was studied to examine changes in its behavior in irradiated TBP/(distilled white) kerosene and to examine the possibility of its use in the direct recovery of plutonium under intensive radiation.

Experimental

TBP was diluted to 30% by volume with kerosene and was irradiated to 2.6×10^8 r.

Nonirradiated, as well as extractant irradiated to different degrees, were mixed with equal volumes of an aqueous solution containing a tracer amount of plutonium with 0.03M/l sodium nitrate in 3N nitric acid, and mechanically stirred for 5 minutes at room temperature (25°C).

The organic phase was scrubbed after extraction with 3N nitric acid. Stripping was carried out with 0.1N nitric acid solution containing 0.03M/l of ferrous sulfamate. The Kd scrubbing percentage, and stripping percentage were calculated. Phase separation time was measured to show the quantitative degree of separation into aqueous and organic phases after mixing.

Results

Changes to Plutonium Extraction Behaviors of TBP/Kerosene Through Irradiation. As shown in Table 29, a significant decrease in the Kd was observed with irradiation to 10^7 r, and then at 10^8 r, it was found increased far beyond the previous range.

TABLE 29. Changes of Distribution Ratio of Plutonium in Irradiated TBP/Kerosene.

Organic phase:	30 volume % TBP/kerosene
Aqueous phase:	Tracer amount of plutonium nitrate in 3N HNO ₃ containing 0.03M NaNO ₂
Volume ratio:	O/A=T
Temperature:	25°C

Irradiation, r	Kd
0	12.5
3.4×10^4	8.2
3.6×10^5	7.1
3.0×10^6	6.5
3.6×10^7	5.7
2.6×10^8	62.0

The decrease in Kd can be considered to be due to the decomposition of TBP and the large increase of 10^8 r to the formation of polymer which complexes strongly with plutonium.

The changes in plutonium behavior in the scrubbing and stripping steps caused by irradiation are indicated in Table 30. The scrubbing percentage was observed to increase with irradiation up to 10^7 r, and then at 10^8 r, it decreased dramatically. The changes in scrubbing percentage are in good agreement with the corresponding Kd data in the extraction step.

The stripping percentage decreased gradually under irradiation up to 10^7 r and then dropped markedly at 10^8 r irradiation.

Since below 10^7 r, the changes are more marked for Kd and scrubbing percentage than with stripping percentage, the detrimental effects of radiation to TBP/kerosene on its plutonium extraction properties appear predominantly in the extraction and scrubbing steps rather than in the stripping step.

TABLE 30. Changes to Plutonium Behavior
Through Irradiation of TBP/Kerosene.

Scrubbing: 3N HNO ₃ Stripping: 0.1N HNO ₃ containing 0.03M ferrous sulfamate Volume ratio: O/A=1 Temperature: 25°C		
Irradiation, r	Scrubbing, %	Stripping, %
0	4.3	85
3.4×10^4	11.0	84
3.6×10^5	13.5	77
3.0×10^4	14.5	75
3.6×10^7	15.0	73
2.6×10^9	1.5	19

The results for the elements extracted with regard to degree of affect on extraction behavior by radiation were:

1. ⁹⁵Zr-⁹⁵Nb, characterized by increasing K_d and decreasing stripping percentage
2. ¹⁰⁶Ru-¹⁰⁶Rh by increasing K_d
3. plutonium by decreasing K_d and increasing scrubbing percentage
4. uranium by increasing K_d and decreasing stripping percentage
5. thorium and ¹⁴⁴Ce-¹⁴⁴Pr, by decreasing stripping percentage.

It may be concluded from the above results that losses of plutonium during extraction increase with irradiation of TBP/kerosene at irradiations below 10^7 r, and that at irradiations as high as 10^8 r, this solvent is no longer usable.

Radiation Effects on Fission Product Decontamination of Plutonium

To clarify the radiation effect on the separation of plutonium from fission products, the hypothetical DF of a single stage was calculated as a measure of separation. Experimental data were substituted into

Equations (1) through (4) where DF_{ex} , DF_{sc} , DF_{st} and $DF_{overall}$ denote the DF in extraction, scrubbing, stripping, and the overall process, respectively.

$$DF_{ex} = \frac{Kd(Pu)(1 + Kd(\text{fission products}))}{Kd(\text{fission products})(1 + Kd(Pu))} \quad (1)$$

$$DF_{sc} = \frac{100 - \text{scrubbing \% (Pu)}}{100 - \text{scrubbing \% (fission products)}} \quad (2)$$

$$DF_{st} = \frac{\text{stripping \% (Pu)}}{\text{stripping \% (fission products)}} \quad (3)$$

$$DF_{overall} = D_{ex} \cdot D_{sc} \cdot D_{st} \quad (4)$$

The results of calculation reveal that the DF-determining nuclide, or the nuclide having the smallest DF in gross fission products, was ^{95}Zr - ^{95}Nb in the case of irradiated TBP.

The results calculated for these DF-determining fission products are shown in Table 31.

TABLE 31. Effect of Radiation on the DF of ^{95}Zr - ^{95}Nb for Plutonium in TBP Systems.

Irradiation, r	Overall DF
10^4	4×10^3
10^5	9×10^2
10^6	3×10^2
10^7	8×10
10^8	2×10

For ^{95}Zr - ^{95}Nb in the TBP system, DF decreases markedly with an increase in irradiation indicating increasingly ineffective separation. The decreasing tendency of $DF_{overall}$ is not so large for ^{106}Ru - ^{106}Rh and ^{144}Ce - ^{144}Pr as for ^{95}Zr - ^{95}Nb in the TBP system after irradiation.

It may be concluded that the DF for separation between fission products and plutonium decreases markedly with irradiation.

Phase Separation

The degree of phase separation into organic and aqueous phases plays an important role in the mixing efficiency of an actual extractor and can also be taken as a measure of solvent degradation. A large increase of phase-separation time with irradiation was observed in the extraction of ^{95}Zr - ^{95}Nb . Plutonium extraction with nonirradiated TBP showed good phase separation. At 10^8 r irradiation, the phase separation time increases by a factor of 2.

No emulsion was observed in the course of this study with tracer concentration of plutonium.

Conclusion

It was observed that with TBP system, the losses of plutonium increase in the extraction and scrubbing steps with increasing irradiation up to 10^7 r, and that this solvent is no longer usable for the separation of plutonium when irradiation reaches 10^8 r.

The fission product DF for plutonium also decreases markedly with irradiation in the TBP system.

PREDICTIONS OF THE BEHAVIOR OF FIRST CYCLE SOLVENT DURING THE REPROCESSING OF HIGHLY IRRADIATED FUEL (18, ORNL-TR-1902)

Solutions of 30% by volume TBP in diluent were equilibrated with aqueous UNH solutions contained $3M$ nitric acid and 82 g/l uranium and then irradiated by ^{60}Co gamma radiation. After irradiation, samples of the organic phase were contacted with an aqueous phase, containing $10^{-3}M$ $\text{Zr} + ^{95}\text{Zr} - ^{95}\text{Nb}$, 9 g/l uranium, and $3M$ nitric acid. The zirconium K_d of the irradiated solutions increased in all cases with the dose, but the values obtained at low doses were clearly less than those measured for nonirradiated solutions.

The parasitic extraction of zirconium by solvents containing HDBP was verified, i.e., a continuous increase in zirconium K_d as a function of HDBP between 0 and $2 \times 10^{-2}M$. The K_d for zirconium in the absence of HDBP was equal to 0.26×10^{-2} . At $2 \times 10^{-2}M$ HDBP, the K_d increased to 4×10^{-1} . Between 1 and 5 mrad exposure, the yield of HDBP varies between 0.5 and 0.9 molecule formed per 100 eV of energy.

Experiments showed that irradiation of the organic phase between 0 and 5 mrads increased the extraction of ruthenium from the aqueous phase only moderately. When the aqueous phase is irradiated separately, a similar effect on K_d occurs. Thus, HDBP has only a minor effect on the extraction of ruthenium.

Plutonium(IV) was found to extract slightly better into irradiated solvent. Stripping of the plutonium(IV) with $0.01M$ HNO_3 was not appreciably affected at doses below 5 mrad, but becomes more difficult at higher doses. If uranium(IV) stabilized by hydrazine is used in the stripping medium, the effect of solvent irradiation is low for doses up to 3 mrad. Mixer-settler experiments with a solution of 30% by volume TBP containing $0.12M$ HNO_3 , 83 g/l uranium, and 387 mg/l plutonium irradiated to 2 mrad, gave excellent partitioning results.

Organic solutions, after equilibration with $3M$ HNO_3 and 82 g/l uranium and irradiated between 0 and 5 mrad, were contacted with $0.013M$ HNO_3 . After the first strip, no difference was found between the 0 and 5 mrad

exposure. After the second strip, the retention of uranium increased slightly with dose and after the third strip, the retention in the irradiated organic was greater than that of the nonirradiated organic by up to 60%. It was shown that the residual uranium in an organic phase, after five or six strips, increased over nonirradiated solvent as follows:

- At 100 mrad, by a factor of 150.
- At 50 mrad, by a factor of 100.
- At 2 mrad, by a factor of 2 to 5.

The effect of irradiation on stripping ^{95}Zr - ^{95}Nb and ruthenium was:

- The K_d for ^{95}Zr - ^{95}Nb were about 10 times higher than those obtained for extraction and vary similarly with the dose.
- The K_d for ruthenium is low and is not affected by the dose.

Although ruthenium is unaffected by solvent irradiation in the first cycle coextraction column, the same is not true for ^{95}Zr - ^{95}Nb , as shown in Table 26.

TABLE 26. Effect of Solvent Irradiation on ^{95}Zr - ^{95}Nb Radioactivity in Process Streams.

Process Streams	No Solvent Degradation	Solvent Degradation by Fuel Exposed to	
		10,000 MWD/T	25,000 MWD/T
HAP	1	1.1	1.5
HSP	1	1.3	2.5
IBU	1	1.8	5.0

Solvent irradiated to 25 mrad retains three times as much plutonium as fresh solvent during the partitioning cycle.

The retention of uranium in the organic phase, during stripping, will be almost doubled for fuel irradiated to 30,000 MWD/T.

The extraction of fission products can be lowered by:

- Increasing the saturation
- Decreasing the TBP concentration
- Lowering the acidity
- Lowering the total nitrate concentration
- Lowering the temperature.

These parameters can only be manipulated over narrow ranges and solvent degradation causes an increase in the extraction of fission products which cannot be offset by such manipulation. However, contamination of the final product can be avoided by fixing the contamination outside the solvent phase or stabilizing the solvent.

Solvent stabilization can be accomplished, to a degree, by adding an aromatic compound, e.g., diethylbenzene to the diluent. It was found that degradation in the first cycle coextraction column is clearly less in the case of Solvesso-100 (which contains aromatics) than in the case of Shell-Sol-T. This is due to the stabilizing effect on the TBP of the aromatic diluent. In tests where a 30% by volume solution of TBP in Solvesso-100 loaded with 80 g/l uranium and equilibrated with 3M HNO_3 was irradiated to 100 mrad, the extraction of zirconium is less by a factor of 10 to 100 than when Shell-Sol-T or dodecane is used as the diluent. However, when Solvesso-100 was kept in contact with nitric acid, a continual formation of gas was observed. The increase in iodine number of the diluent after irradiation was much faster in the case of Solvesso-100 than with aliphatic diluents.

Washing Shell-Sol-T or dodecane with concentrated sulfuric acid had no appreciable effect as far as the capability of irradiated solvent to extract zirconium and its subsequent decontamination were concerned.

For a 30% by volume TBP solution, there is an almost linear relation between the amount of HDBP present and the K_d of uranium at 0.1M nitric acid. Studies were performed with mixtures of TBP and tri-lauryl amine to

determine the effects of washing on zirconium retention during irradiation. The tests and results are not included, since they are not strictly applicable to the Purex process. It was concluded, however, that:

- The extraction of ^{95}Zr - ^{95}Nb is increased by a factor of 2 by the presence of triauryl amine for doses less than 50 mrad, but the solvent can be decontaminated by a carbonate wash, as effectively as the TBP system.
- At high doses, greater than 50 mrad, the contamination becomes comparable for the two systems and carbonate treatment of the solvent still provides a high degree of decontamination.
- The degradation of diluent is effected in a favorable way by the presence of triauryl amine; if not by its existence, by the possibility of better decontamination of the solvent.

Two methods of pretreatment of coextraction cycle feed immediately after dissolution (to alter the form of the fission products so that they will be in a noncomplexing form with respect to the products of solvent degradation) were investigated:

- Heating the coextraction cycle feed with hydrazine hydrate - the transformation of ruthenium to an inextractable form was completed in 1 hour.
- Selective precipitation of zirconium with mandelic acid - it was found that the precipitation of zirconium with mandelic acid: (1) did not change appreciably the K_d with 30% by volume TBP in diluent for uranium, plutonium, ruthenium or zirconium; and (2) radically suppressed the contamination of the solvent by zirconium; and (3) produced a slight lowering of the beta and gamma radioactivity of the coextraction cycle feed solution (about 3%).

Outside the use of a centrifugal contactor during decontamination, there is no truly unique method capable of resolving all solvent degradation problems. Three approaches were tested:

- the total and selective precipitation of zirconium, which could be done by mandelic acid
- the use of an aromatic diluent, which is less susceptible to nitration to serve as a radiochemical protector for TBP.
- a change in the process to the use of TBP-trilauryl amine as the solvent.

STABILITY OF HNO_3 -TBP-DILUENT SYSTEMS -- BIBLIOGRAPHY OF DATA UP TO JUNE 1966 (19, ORNL-TR-1901)

This bibliographic study addressed the problem of degradation of solvent, TBP and its diluents, in reprocessing irradiated fuels under well-defined conditions. Results of the different authors were compared to determine whether the data in the literature permit the prediction of the performance of the process with any fuel that might be treated.

Radiolysis of TBP

The anion PO_4^{3-} is stable during irradiation of TBP, the rupture of a P-O bond being much less probable than that of a C-O bond. This fact is evidenced by the low yields of butanol generally observed: G value of ~ 0.13 molecule transformed per 100 eV of irradiation.

Pure TBP. The principal product formed by irradiation is HDBP. The G value of HDBP varies from 1.5 to 2.4. The yield of formation of MBP is about 10 times less. $\text{P}(\text{OH})_3$ is obtained only with doses greater than 1000 mrad.

In addition, gaseous products are formed (saturated hydrocarbons and olefins); but the amounts are much less than would be expected from the organic fractions lost in the formation of acid. The G values of H_2 published are quite close to those of HDBP, i.e., 1.1 to 2.5.

A high molecular weight polymer is formed having a molecular weight of 840 and a titrametric acidity of 6% by weight. A G value of 0.9 to 2.5 can be calculated. Small quantities of butyl ether are formed but no peroxide is observed in the presence or absence of air.

A delayed effect of irradiation has been observed; the G value for HDBP doubles in several days due to causes other than photolysis or hydrolysis.

TBP in Diluent. The addition of water to TBP in diluent causes a drop in the G value of HDBP (from 1.8 to 1.2). Diluting the TBP by 50% in butanol produces the same effect.

There is general agreement that the aromatic diluents that increase the radiolytic stability of TBP decrease the G value of HDBP. In the case of benzene, the G value for HDBP is 1.54; with toluene, 1.97 (as compared to 2.25 for pure TBP); in Solvesso 100, 0.3 (as compared to 0.75 in AMSCO 125-82). The stabilization is attributed to the ring of electrons on the benzene nucleus.

With aliphatic diluents, the situation is more complex. The G value for HDBP increases when TBP is diluted with CCl_4 (30 as compared with 1.7 for pure TBP); but when TBP is diluted with iso-octane, no change was observed.

The protective effect by certain substances on the radiolytic decomposition of TBP increases in the following order: cyclohexene < toluene < diphenyl-methane < benzene < diphenylether < -methyl naphthalene < naphthalene < diphenyl < phenanthrene < cyclo-octatetracene. The saturated compounds hexane, cyclohexane, and dodecane sensitize the degradation of TBP.

With CCl_4 diluent, nitric acid lowered the G value for HDBP. However, the G value increased with the concentration of HNO_3 in TBP irradiated without diluent from two- to fivefold. In the above system, nitric acid was decomposed with a G value of 20. For pure nitric acid, the G value is between 0.2 and 1.5. AMSCO 125-82 equilibrated with 2M HNO_3 gave a G value of 0.7 for MBP.

In the case of TBP in a diluent and equilibrated with HNO_3 , H_2MBP has G values close to those for HDBP and sometimes greater.

The presence of $\text{UO}_2(\text{NO}_3)_2$ at saturation in TBP lowers the G value for HDBP as well as for gas (the latter by 30%).

Performances of the Solvent as a Function of the Degradation of TBP

The degradation compound of TBP which lowers performance most markedly is DBP.

Behavior of DBP Compared with the Solvent. DBP at 0.05M has a K_d in kerosene (at equilibrium with 1M HNO_3) of 2, in dodecane, 10; and in benzene, 30. At a concentration of 10^{-3}M its K_d in kerosene is only 0.1.

In the system, 20% by volume TBP in diluent, DBP is easily extracted at all acidities and even at low concentration:

$$\begin{aligned} K_d &\approx 20 \text{ for } 0.5\text{M DBP and } 1\text{M } \text{HNO}_3 \\ K_d &\approx 15 \text{ for } 10^{-5}\text{M DBP and } 1\text{M } \text{HNO}_3 \\ K_d &\approx 2 \text{ for } 0.05\text{M DBP and } 0\text{M } \text{HNO}_3 \end{aligned}$$

MBP is 100 to 1000 times less extractable:

$$\begin{aligned} K_d &\approx 0.5 \text{ for } 0.07\text{M } \text{H}_2\text{MBP and } 1\text{M } \text{HNO}_3 \\ K_d &\approx 10^{-3} \text{ for } 0.07\text{M } \text{H}_2\text{MBP and } 0\text{M } \text{HNO}_3 \end{aligned}$$

Both HDBP and H_2MBP are dimers in the aqueous and the organic phase. The reaction $2 \text{HDBP}_{(o)} \rightleftharpoons (\text{HDBP})_{2(o)}$ has the following equilibrium constant

$$\log K = 0.75$$

Furthermore, HDBP is complexed in the organic phase with TBP:

Combinations with Cations. Stripping of uranium(VI) into an aqueous phase with dilute HNO_3 is disturbed by the presence of HDBP. The existence of a complex dimer $[\text{UO}_2(\text{NO}_3)\text{DBP} \cdot \text{TBP}]_2$ with $\log K = 12.5$ is postulated

An HDBP concentration of 10^{-2}M in 30% TBP could cause the K_d in 0.04M HNO_3 to go from 0.1 to about 1, and that between 10^{-3} and 10^{-2}M HDBP there is an appreciable effect.

Complexes formed by uranium and plutonium with H_2MBP as well as with the polymer are not soluble to either of the two phases.

Zirconium is extracted slightly in highly acid media as $\text{Zr}(\text{NO}_3)_4 \cdot (\text{TBP})_2$ or $\text{Zr}(\text{NO}_3)_4 \cdot \text{TBP}$. However, HDBP is extracted to a considerable extent in the form $\text{Zr}(\text{NO}_3)_2 \cdot (\text{DBP} \cdot \text{HDBP})_2$. TBP must be 5×10^4 times as high as HDBP to produce the same extraction for zirconium. When a 20% solution of TBP in contact with $\text{UO}_2(\text{NO}_3)_2$ in HNO_3 is subjected to a level of radiation from fission products of 1 W/l, 36 mg/l/hr of HDBP ($1.8 \times 10^{-4}\text{M}$) is formed. Traces of zirconium are extracted by 20% TBP with a K_d of 0.5 from 2M HNO_3 and a K_d of 0.23 from 4M HNO_3 . Only $2 \times 10^{-5}\text{M}$ HDBP is sufficient to furnish an equivalent extraction.

It has been found also that zirconium is retained by HDBP; moreover, complexes are formed with zirconium by the HDBP-producing emulsions which seriously disturb the disengaging time of the phases.

Elimination of the Degradation Products of TBP. For HDBP, the most efficient treatment is washing with the alkaline solution Na_2CO_3 which removes more than 90% of the HDBP. Decontamination from HDBP of 99% of the activity has been obtained by passing a solvent through a 14-micron fritted glass filter.

HDBP can be directly absorbed from organic solutions on some oxides, e.g., Al_2O_3 , ZrO_2 , and SiO_2 . Conclusions relative to adsorption include:

- Removal of fission products which are only entrained in the solvent is relatively easy; removal of fission products complexed by the degradation products of the solvent, primarily zirconium, is more difficult.
- A preliminary filtration holds back only the fission products forming insoluble complexes in the two phases.

- Successive treatments with Na_2CO_3 are very effective for the removal of fission products complexed with HDBP, provided that this contact is followed by a complete separation of the phases, operating with at least equimolar quantities of Na_2CO_3 (with respect to HDBP), and repeating the operation several times.
- Filtration after alkaline wash removes the insoluble complexes formed during the course of the treatment.
- Washing with HNO_3 after the alkaline wash, without an effective separation of the phases, potentially redissolves the degradation products in the organic phase.
- Treatment with KMnO_4 seems to be only as effective as preliminary filtration in that it removes only the fission products which are not complexed by the degradation products.

Finally, Na_2CO_3 treatment which is effective for zirconium has only a partial effect for decontamination from ruthenium and even with heating to 90°C , 25% of the ruthenium activity cannot be removed.

A reducing treatment of the organic phase showed a low reaction rate. In addition, the reaction is only partial and leaves more of the ruthenium behind in the solvent phase than the alkaline treatments. The same is true when operating at 90°C with a 0.5M hydrazine nitrate solution adjusted to a pH of 12 by Na_2CO_3 . Similarly, the use of other complexes forming insoluble compounds affords no improvement. The reagents used must not affect the TBP and the diluent. Thus, strong oxidizing agents such as permanganate considered as a treatment for ruthenium in the aqueous phase, and the use of NaNO_2 or NO_2 treatment attempted at the Savannah River Plant, carry some attendant risks.

Degradation of the Diluent

Removal of all HDBP from the degraded solvent does not necessarily bring it back to its initial performance. A used solvent of 33.5% TBP in kerosene containing 0.37 g/l of HDBP retained 0.63 g/l of uranium in

the organic phase (after six stages of stripping); 0.01 g/l of HDBP in a fresh solvent retained 0.001 g/l of uranium under the same conditions. The same new solvent after being treated in a Podbielniak extractor contains only 0.04 g/l HDBP but retains 0.46 g/l of uranium. After treatment by washing with carbonate, it contains only 0.02 g/l HDBP but still retains 0.45 g/l of uranium. Thus, about 0.44 g/l of the uranium retained (from 0.63 g/l) is not due to HDBP, and HDBP appears as the least serious cause of the degradation of the solvent. The degradation products of the diluent were not removed by the alkaline washes and accumulated in the solvent.

Products Formed. The principal criterion of the degradation of a solvent is to measure the Z (or H) value which is the number of moles of zirconium (or of hafnium) retained by 10^9 l of solvent.

The Z value increases both by irradiation and by the chemical action of HNO_3 which is favored by increasing temperature. It appears that nitration of the diluent is caused by HNO_2 , for on one hand it occurs after a period of induction and on the other hand it can be suppressed by the presence in the aqueous phase of stabilizers of the hydrazine type or by bubbling oxygen into the organic phase. The formation of nitro and nitroso compounds when kerosene-type diluents are heated in the presence of 5M HNO_3 was not observed until the mixture was adjusted to 0.1M in HNO_2 . The rate of degradation in the presence of HNO_2 increases with temperature and the total nitrate concentration in the solvent phase. TBP does not seem to play any role since it acts only on the solvent for the HNO_3 and HNO_2 .

It has been hypothesized that the rate of reaction for the degradation of the diluent would be of the type:

$$\frac{d(E - E_{\text{TBP}} - E_{\text{HDBP}})}{dt} = K [\text{HNO}_3]^m [\text{HNO}_2]^n$$

From experimental work, m is about 3.7 and n is about 0.47 (E is the experimental value for the Kd which indicates that the effect of HNO_3 is greater than that of HNO_2).

The principal product would simply be nitro compounds of the type $R-CH_2-NO_2$ and would be formed either by irradiating to 100 Wh/g or boiling 11 hours in contact with $2M$ HNO_3 .

The extraction would take place by enolization:

In acid media, equilibria 1 and 2 are such that we have essentially the Keto form; on the contrary, in a basic media, equilibrium 2 is displaced toward the right with a rate much larger for $Ca(OH)_2$ than for Na_2CO_3 . Hydrolysis by placing in an acid media liberates the noncombined enol form in equilibria 3 (displaced upwards) which then complexes the zirconium in the organic phase. Thus, after alkaline treatment increased retention of zirconium results in spite of the elimination of HDBP.

The products responsible for zirconium retention have been assumed to be hydroxamic acids of the type $R-CONHOH$. In the current study, hydroxamic acid in excess of $10^{-3}M$ was not found. This accounts for only 30% of the solvent degradation as measured by Z value. Conclusions are:

1. The concentration of hydroxamic acid in the organic phase reaches a low but stable value controlled by a hydrolysis step which converts it to the hydroxylamine form.
2. Prolonged alkaline washes increase the steady-state concentration by the formation of the acid form with the nitroparaffin $R-NO_2$, followed by reacidification by the NeF reaction.
3. Hydroxamic acid in recycled solvents forms complexes such as the tetrahydroxamate of zirconium which are held in the organic phase.

Comparative Behavior of Diluents

The aromatic diluents have certain advantages:

- solubilization of metallic salt complexes
- increase in the extractive capacity of TBP
- improvement in the radiolytic stability of TBP.

On the other hand, while the aromatic compounds may be more sensitive to nitration, the point remains controversial. An aromatic diluent will be attacked by HNO_3 preferentially on the side chain and under certain conditions on the nucleus itself. In the latter case, the nitrate compound cannot be enolized because there is no hydrogen in the alpha position. It was confirmed with the pure products that the nitrated compound cannot then extract fission products.

Solutions containing 1M TBP in a variety of aromatic diluents were degraded by boiling for 4 hours with HNO_3 . The solutions were scrubbed with a mixture of Na_2CO_3 - $\text{Ca}(\text{OH})_2$ and contacted with a zirconium solution. The aromatic diluents are variable in behavior with respect to nitration ranging from low molecular weight and pure compounds that have Z values comparable to dodecane, to mixtures like Solvesso-100 which are degraded about 60 times greater.

Diethylbenzenes (DEB) were studied as diluents. Tests with commercially available DEB showed that after degradation by HNO_3 , they do not appreciably extract fission products. A more precise study has shown that the meta DEB is more stable than the ortho and para. The rate of degradation is actually two times greater for the latter two isomers. Even so, the meta DEB forms at least six degradation products. The three main products are: 3-ethylacetophenone (I), 1-nitroethylbenzene (II), and a little ethyl benzoic acid. Using the above as 0.4M solutions in DEB, there was no appreciable extraction of uranium. When used as 0.4M solutions in 1M TBP, compound (I) had no effect on the uranium K_d while (II) slightly depressed it just as the degraded solution does.

DEB is degraded two to five times more rapidly by HNO_3 in the presence of TBP. This can be attributed to the extraction of nitrate and nitrite by the TBP as in the case of the aliphatic diluents. The phase separation time is doubled by nitrate degradation of DEB, but no change was observed in the flash point.

Results obtained at Harwell with different aliphatic diluents showed n-dodecane to be the form most stable to nitration.

Treatment of Degraded Solvents

Most of the studies were conducted on an investigation of:

- treatment giving the best DF and the greatest purification of degraded solvent
- the best stabilizing treatment for the solvent before operation.

Decontamination and Purification Treatments for the Solvent. Economical reagents like Na_2CO_3 , NaOH or HF , although they are effective for removal of HDBP, prove to be less effective for the removal of complexing agents formed from the diluents. The efficiency diminishes further as the degradation of the solvent increases.

The effectiveness of alkaline permanganate has been demonstrated, but has the inconvenience of forming MnO_2 which partially goes into the organic phase.

When a solvent has been degraded badly and retains large quantities of uranium(VI), alkaline washes do not prove sufficient. However, alkaline peroxides rapidly remove the uranium.

Ethanolamines form slightly soluble salts with the nitroparaffins that provide satisfactory cleanup. However, the ethanolamines are expensive and sometimes emulsions are produced during later acid scrubs.

Another economic technique consists of contacting the degraded diluent with activated alumina, precipitated manganese dioxide, or activated carbon (charcoal). The maximum DF requires large quantities of solids (10 times more Al_2O_3 than MnO_2); and in the case of charcoal, for example, the quantities required are such that the adsorber retains a great deal of TBP.

Molecular distillation tests under reduced pressure have shown that to avoid thermal degradation it is necessary that the operation be very rapid. The process of flash distillation gives better results since it provides a good separation of the degradation products without increasing their amount. The residence time of the solvent in the heated zone (around 170°C) does not exceed several seconds, in fact, even fractions of a second.

Study of the Stabilization of the Solvent. It is necessary to stabilize the extractant without changing its extraction properties, by avoiding the introduction of foreign compounds to the system capable of changing the properties, or of forming derivatives that can change these properties.

The rate of degradation of AMSCO 125-82 has been reduced by a factor of about 40 by scrubbing it with concentrated H_2SO_4 (greater than 95%) at 50°C, or after degradation by boiling with 2M HNO_3 and then washing in the cold with concentrated H_2SO_4 . Since AMSCO is a mixture of aliphatic hydrocarbons C_{12} - C_{14} , containing branched chain compounds, it is capable of forming nitro derivatives. The sulfuric treatment destroys the sites that are particularly vulnerable to HNO_3 .

Distillation is not only to be considered as a method of decontamination and cleanup of degraded solvent, but also a method of purification of solvent. Each operation of distillation makes it possible to keep only the nitration resistant fractions. Good results were obtained by sorting the stable fractions of odorless kerosene by distillation.

Conclusions

It is necessary to distinguish two types of degradation:

- that of TBP, alone or in the presence of different compounds (and in particular of the diluents)
- that of the diluent, alone or in the presence of TBP and other compounds (and in particular of HNO_3).

Problem of Diluent. The problem of diluent is complicated in nitric acid media because a minor product of the degradation or of the nitration can have such a complexing effect on certain fission products, and an organic substance formed in traces in an organic media of diverse composition is difficult to remove in a simple way.

It can be concluded that aliphatic diluents are generally considered more stable than the aromatic diluents because the latter are nitrated more easily. Dodecane is often considered as a reference because it has a remarkable stability toward nitration. However, the aromatic compounds have an advantage of stabilizing the TBP.

As for pretreatment and regeneration of the diluent, flash distillation is a simple, effective, and economic technique. In practice it permits choosing only the fractions that are desired without creating additional degradation because the residence time in the apparatus is negligible, and the operation does not introduce any foreign reactants.

Problems of TBP Degradation. The problems of the degradation of TBP have a more direct implication on the performance of the process. In the course of a single cycle, before any regeneration of solvent is possible, the radiation dose in the first cycle coextraction column may be such that the process performance may be adversely affected immediately.

THE INFLUENCE OF RADIOLYSIS OF TBP ON THE PLUTONIUM BEHAVIOR IN THE PUREX PROCESS AT HIGH PLUTONIUM CONTENT (20, KFK-691)

The deleterious effects of solvent irradiation appear where fuel is processed after exposure to several thousand mwd/t, at which point the radiation load on the solvent is on the order of less than 0.1 Wh/l. By applying the Purex process to fuel elements with an exposure of 50,000 mwd/t or more and cooling times of 100 days, the radiation exposure to the solvent is on the order of 1 Wh/l. Therefore, it can be expected that the decomposition makes itself observable in unacceptable amounts, especially by the unsatisfactory stripping of plutonium from the solvent and lower plutonium purity.

The formation of HDBP by the radiolysis of TBP was examined for undiluted TBP or in mixtures (TBP-CCl₄, TBP-C_nH_{2n+2}, TBP-C₆H₆), which were irradiated partly acid and water-free and partly equilibrated with dilute nitric acid or water. The data are scanty on the formation of HDBP at the equilibrium presence of an aqueous phase during conditions existing in the extraction process. Both single-phase irradiation and the irradiation of mixed phases (organic/aqueous) have been studied to approach the real conditions. Besides the formation of HDBP, the influence of HDBP on the stripping of plutonium in the organic phase was investigated, and possibilities were explored extensively to avoid plutonium losses.

Single-Phase Irradiation

The organic phase was brought into equilibrium with 3M HNO₃, and the aqueous phase removed. Only the organic phase (HNO_{3org} = 0.3M) was irradiated.

Mixed-Phase Irradiation

Organic and aqueous phases (i.e., water containing nitric acid of different concentrations) in a volume ratio of 1 to 1 were contacted and mixed violently during the irradiation. In contrast to the single-phase irradiation, a constant exchange of radiolysis products was possible within both phases.

Radiation with alpha, beta, and gamma rays was accomplished in an individual radiation to study the radiolytic effects.

- Alpha radiation: The radiation of the system 20% by volume TBP- C_nH_{2n+2} with alpha rays was obtained by spiking the system with plutonium. A solution of 20% by volume TBP was loaded with plutonium, and the organic phase separated. After standing for from 2 to 41 days analyses were made.
- The beta irradiation source consisted of 20 curies of ^{90}Sr contained in a double stainless-steel shell with a very thin window (0.075 mm) on one end.
- A ^{60}Co radiation source was used as the source of gamma rays.

Absence of air to the sample was possible for all irradiations. The temperature was 25°C for the single-phase irradiation and 29°C for the mixed-phase irradiation.

Determination of Plutonium Retention by Repeated Stripping

The irradiated solvent sample was mixed with an aqueous plutonium nitrate solution (2.4 g/l plutonium(IV), 0.4 M HNO_3) for 20 minutes at 25°C and was thereby loaded with plutonium. To determine the plutonium retention, the organic plutonium solution was washed an equal volume of 0.4M HNO_3 (20 min., 25°C). The backwash was repeated five times with an equal volume of fresh water solution. After the fourth or fifth backwash, the organic phase had an almost constant plutonium content (plutonium total). The plutonium retention was defined as follows: from the plutonium content of the organic phase after the fifth back extraction (plutonium total) the portion of the plutonium bound in the TBP was subtracted. This permits the calculation of the plutonium concentration in the aqueous phase after the fifth back extraction by using the partition coefficient for nonirradiated material. The plutonium retention is obtained by the difference formula:

$$Pu_{ret} = Pu_{total} - Pu_{TBP}$$

Formation of HDBP by Radiolysis

Single-Phase Irradiation. After standing for 8, 12, and 15 days, the organic phase containing plutonium (36.47 g/l, 0.3M HNO_3) samples were taken and analyzed for HDBP. The formation rate (g/l HDBP) per Wh/l dose could be calculated and stated as g/Wh. A formation rate of 0.034 to 0.027 g/Wh was shown for the range of 16 to 30 Wh/l. Because of the limited number of samples used, it cannot be determined if there was a real decrease in the rate of formation or only a scatter of the analytical values. The G value for HDBP formation was calculated on the basis that the total dose was absorbed in the system TBP-hydrocarbon to be 0.43 to 0.33 (molecules HDBP/100 eV of absorbed energy) with an average of 0.36.

For a loading of the solvent by plutonium of about 8 g/l and an approximate contact time of plutonium in the extraction, scrub, and stripping section of 1 hour, the dose received from the alpha radiation of plutonium will be 1.9×10^{-2} Wh/l. At an average formation rate of 0.03-g HDBP/Wh this gives the formation of about 6×10^{-4} g HDBP/l per pass. Thus, the portion of the HDBP from radiation is insignificant compared to the amount arising from beta and gamma radiation.

Solvent loaded with HNO_3 (0.3M HNO_3 organic) was irradiated by beta or gamma rays to a total dose of 2 to 8.6 Wh/l. A linear line could be drawn through the measured points for beta and gamma radiolysis. However, the HDBP concentration after longer irradiations does not increase linearly with dose. At a dose of 3 to 4 Wh/l, a decrease in the formation rate is clear. The formation rate (total concentration/total dose) decreases from 0.037 (at 2 Wh/l) to 0.029-g HDBP/Wh (at 8.6 Wh/l). For a water-saturated system, a value of 0.033-g HDBP/Wh (TBP + HC) was obtained.

Mixed-Phase Irradiation

In one research sequence, organic (20% by volume TBP-HC), and an inorganic phase (HNO_3 of different concentrations in a 1:1 volume ratio) were mixed violently during the irradiation. At all of the lower acid strengths (water, 0.4M HNO_3) a considerable part of the HDBP is found in the aqueous phase, i.e., in the system 20% by volume TBP-dodecane/water

the organic phase contains only 22%, and the inorganic phase 78% of the HDBP formed. At 0.8M HNO_3 , the HDBP concentration of the aqueous phase is however, less than 10% of that in the organic phase.

From the HDBP concentration and the radiation dose (taken by TBP-HC), a formation rate of 0.16 g HDBP/Wh is obtained for the system with 0.8M HNO_3 as aqueous phase (volume ratio o/a = 1). The corresponding formation rates with 1.5M or 3M HNO_3 are 0.23 and 0.22 g HDBP/Wh. Depending on the conditions under which the two-phase irradiations took place, very different values resulted for the HDBP yield:

Mixing under extensive exclusion of O_2 (introduction of argon)	0.060 g/Wh
Stirred mixing, admission of O_2 possible	0.10 g/Wh
Stirred mixing, introduction of O_2	0.14 g/Wh
Turbulent mixing, constant addition of O_2 to the mixed phases	0.22 g/Wh

For all tests organic and aqueous phases (3M HNO_3 , o/a = 1) were intensively mixed.

It is possible that the HDBP can form from two different methods: as the primary product through radiolysis of TBP or as a secondary product as a result of hydrolysis of oxidation products of TBP, perhaps of a type containing acylbonds $\text{CH}_3\text{-CO-O-PO}(\text{CC}_4\text{H}_9)_2$, which in the presence of O_2 are formed by the reaction of a TBP radical with acid. In strongly acid medium, the hydrolysis of the acylbond proceeds further than in a weakly acid solution. In this way, the demonstrated dependence of the total yield HDBP/Wh on the acidity of the aqueous phase could come about.

Influence of Radiation on Plutonium Retention

Alpha Radiolysis. 20% by volume TBP in dodecane was loaded with 31.5 and 36.5 g/l plutonium and after standing for from 2 to 21 days the back extractable plutonium was removed by washing six times with 0.4M HNO_3 . The amount of retention calculated as the specific plutonium retention in g Pu/Wh was 0.025 g Pu/Wh ($\pm 15\%$).

Gamma Radiolysis. After mixed-phase irradiation samples were brought to equilibrium with plutonium(IV) solution, the retention was measured by back extraction. In a dose range of 0.4 to 4.8 Wh/l (TBP + HC) during a mixed-phase irradiation with 0.4M HNO_3 , a retention of 0.09- to 0.1 g Pu/Wh was obtained and at 3M HNO_3 the retention was 0.15 g Pu/Whr. For the alpha and gamma mixed-phase irradiation, the linear relationship expected from theoretical considerations between the retention of plutonium and the irradiation dose was demonstrated.

The mol ratio Pu:HDBP was calculated from the HDBP concentration and the plutonium retention. For the mixed-phase irradiations, the ratio averaged between 0.5 and 0.6 and indicated a composition of $\text{Pu}(\text{HDBP} \cdot \text{DBP})(\text{NO}_3)_3$ or $\text{Pu}(\text{DBP})_2(\text{NO}_3)_2$.

Influence of Uranium(VI) on the Plutonium Retention

Since uranium(VI) also forms HDBP complexes, the degree of influence on the plutonium retention is of interest. With no uranium present, 110 mg Pu/Whr of DBP in 1 l of 20% by volume TBP is held back, this amount is reduced by 8.4/1 ratio U/Pu (50 g/l U, 6 g/l Pu) to 61.3 mg Pu/Wh and at a 100:1 ratio U/Pu (50 g/l U, 0.5 g/l Pu) to 5 mg Pu/Wh. The Plutonium loss at an irradiation dose of 1 Wh/l lies on the order of 1%.

Influence of Uranium(IV) and Other Wash Solutions on Plutonium Retention

The irradiation of 20% by volume TBP-dodecane (0.3M HNO_3) forms about 0.03 g/l HDBP/Wh/l. This amount increases during the irradiation of a two-phase mixture of solvent and aqueous solution (1.5 to 3M HNO_3) to 0.22 g/l HDBP. A solvent with the latter DBP content holds at least 0.11 g/l plutonium bound in the organic phase which is not removed by the usual back extraction media. It was expected that the plutonium retention in the organic phase would be inhibited by concurrent four valent metal ions, such as uranium(IV).

The use of a uranium(IV) wash solution substantially reduced the plutonium concentration of a solvent irradiated to 4.4 Wh/l after different nitric acid strips. Organic, which was loaded with 5 g/l plutonium

and irradiated extremely heavily (130 Wh/l, alpha rays), shows qualitatively the same behavior. In all cases, the uranium(IV) displaced the bound plutonium from the organic phase by reduction and/or substitution.

Experiments with other hydroxylamine and hydrogen peroxide wash solutions showed unsatisfactory results concerning the decrease of plutonium retention in an irradiated TBP solution.

Uranium(IV) as wash solution was also tested in countercurrent experiment with mixer-settlers. In these 20% by volume TBP-dodecane (1.2 Wh/l ^{60}Co irradiation) was used. The dose of 1.2 Wh/l is on the order of the irradiation exposure of the solvent anticipated for the reprocessing of fuel elements from fast breeder reactors with an exposure of 80,000 MWD/T and a cooling time of 100 days. A solution containing 0.1M plutonium(IV) nitrate, 0.9M UNH, and 3M HNO_3 was extracted with irradiated TBP-dodecane. The organic solution containing 6.7 g/l plutonium and 67 g/l uranium was backwashed countercurrently (10 stages) with an aqueous solution of 0.006M uranium(IV) and 0.3M HNO_3 ; a plutonium loss of 0.015 occurred. Through suitable utilization of uranium(IV) nitrate solution in the HC-extractor, the plutonium(IV) bound in the organic phase can be reduced to insignificance in the product solution.

DBP COMPOUNDS OF ZIRCONIUM (21, RJIC14)

It has been found that in the extraction of tracer quantities of zirconium from aqueous solutions with low concentrations of nitric acid (ionic strength 2) by solutions of dibutyl hydrogen phosphate (DBHP) or HA in toluene, the compound $\text{Zr}(\text{NO}_3)_2(\text{HA}_2)_2$ is formed in the organic phase.

If, however, a 0.1M solution of DBHP in toluene is brought repeatedly into contact with equal volumes of an aqueous solution containing 0.1M zirconium nitrate in 2M nitric acid, the composition of the organic phase saturated with zirconium corresponds to a compound with the simplest formula $\text{Zr}(\text{NO}_3)_2\text{A}_2$. The same compound was isolated in the acid hydrolysis of nondiluted DBP in the presence of a 0.25M solution of $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ in 2-5M HNO_3 at 50°C.

Experiments were carried out to define the composition of the DBP compounds of zirconium formed in the extraction. Normal decane was used as diluent for the DBHP.

It was found that, irrespective of the composition of the original aqueous (0.2-6M HNO_3 ; 50 to 600 mg/l zirconium) and organic (0.6 to 1.6 g/l DBHP in n-decane) solutions, the reaction of DBHP with macroquantities of zirconium in all instances leads to the formation of either precipitates or a third (liquid) phase. The formation of the third phase (in the form of a heavy, oily, colorless liquid, which usually separated as fine droplets on the surface of the glass equipment used) is observed only at a [DBHP]:[Zr] ratio in the original solution >8 to 10. The separation of the precipitates or the third phase does not take place only when the ratio [DBHP]:[Zr] >>8 to 10. At [DBHP]:[Zr] ≥ 2 , the DBHP during the extraction is distributed between the aqueous, organic, and solid (third) phases, whereas zirconium is found only in the organic and solid (third) phases, but is not found in the aqueous phase.

Composition of the Precipitates of the DBP Compounds of Zirconium Obtained from 6M HNO₃

In the absence of strong complex-forming reagents, the state of zirconium in aqueous solutions is determined by the concentration of the metal and hydrogen ions. The reaction of zirconium with DBHP was studied both in 6M HNO₃, in which zirconium at $[Zr] = 0.5$ to 5 g/l, is present chiefly as the monomer, and in 0.25M HNO₃, in which zirconium at the same concentrations is present chiefly in polymeric form.

Solutions of zirconium in 6M HNO₃ with metal concentrations in the range 0.59 to 5 g/l were mixed with solutions of DBHP in HNO₃ with the same concentration, containing 1.66 to 6.5 g/l precipitant. N, the ratio of the absolute quantities of DBHP and zirconium in the solutions, was carried over the widest possible range. The formation of precipitates or separation of liquid phase generally took place while the solutions were being mixed. Since the original and final quantities of zirconium and DBHP in the solutions are known, the molar ratio DBHP:Zr = n in the precipitates was readily calculated.

The results (Table 33) show that only zirconium is detected in the solutions in an excess of zirconium ($N = 0.044$ to 1.06), and only DBHP in an excess of DBHP ($N = 5.34$ to 28.6). At $N = 2.64$, neither zirconium nor DBHP is found in the solution. In the range $N = 0.044$ to 0.53 , the composition of the precipitates remains fairly constant ($n = 2$), but with increase in N from 1.06 to 8.08 , the value of n also increases to $n = 4$. With further increase in N to ~ 13 to 14 , the composition of the precipitates remains unchanged ($n = 4$). In the range $N \geq 13$ to 14 , a liquid phase separates instead of the precipitates, and n increases sharply to 6. The boundary of the transition between the precipitate and the second liquid phase could not be established exactly.

In 6M HNO₃, zirconium reacts with DBHP to form three compounds, two of which (1:2 and 1:4) are solid at 25°C, whereas the third (1:6) is liquid. The conditions of formation of the DBP compounds of zirconium are determined by the value of N. In the range $N = 1.06$ to 7.19 , the 1:2 and 1:4 compounds are precipitated in varying proportions.

TABLE 33. Zirconium and DBHP in Solutions and Precipitates.

Mixed Solutions				Mother-Liquor			Molar Ratio DBHP:Zr	
Zirconium		DBHP		Volume, ml	Zr Conc., g/l	DBHP Concn., g/l		
Volume, ml	Concn., g/l	Volume, ml	Concn., g/l				in Original Solutions, N	in the Precipitates, n
HNO ₃ Concentration 6M								
103.2	5.0	20	2.63	123.2	4.10	<0.02	0.044	2.06
34.4	5.0	20	2.63	54.4	2.95	<0.02	0.132	2.00
100	5.0	90	6.08	190	2.00	<0.02	0.47	1.96
8.6	5.0	20	2.63	28.6	1.13	<0.02	0.53	2.11
4.3	5.0	20	2.63	24.3	0.46	<0.02	1.06	2.20
1.72	5.0	20	2.63	21.72	<0.002	<0.02	2.64	2.64
0.86	5.0	20	2.63	20.86	<0.002	1.01	5.34	3.21
40	1.08	400	1.66	440	<0.002	0.72	6.61	3.46
400	0.59	900	4.39	1300	<0.002	1.55	7.19	3.54
62	0.98	175	6.51	237	<0.002	2.32	8.08	4.19
0.43	5.0	20	2.63	20.43	<0.002	1.60	10.56	4.00
40	1.08	400	3.43	440	<0.002	2.21	13.68	4.00
60	1.08	400	4.92	460	<0.002	2.32	13.10	6.00
80	0.98	400	6.51	480	<0.002	3.21	14.3	5.84
40	0.98	400	6.51	440	<0.002	4.64	28.6	6.16
HNO ₃ Concentration 0.25M								
2	0.88	4	2.98	6	<0.002	1.11	2.93	1.29
1	0.88	4	2.98	5	<0.002	1.82	5.86	1.38
80	0.88	400	2.98	480	<0.002	2.12	7.30	1.06

NOTE: Change in the concentrations of zirconium and DBHP in the original solutions and in the volumes of the solutions within the ranges indicated, and also the order of mixing of the solutions, have no influence on the compositions of the precipitates.

Chemical analysis showed that all the precipitates contain NO_3 groups; the ratio $\text{Zr}:\text{NO}_3 = 1.2$, irrespective of the value of n . For $n = 2, 4$, and 6 , the ratios of $\text{Zr}:\text{NO}_3:\text{DBHP}$ defined the formula of the DBP compounds of zirconium as: $\text{Zr}(\text{NO}_3)_2\text{A}_2$, $\text{Zr}(\text{NO}_3)_2\text{A}_2 \cdot (\text{HA})_2$, and $\text{Zr}(\text{NO}_3)_2 \cdot \text{A}_2(\text{HA})_4$.

Compositions of the Precipitates of the DBP Compounds of Zirconium Obtained from 0.25M HNO_3

In the precipitates obtained from solutions containing polymeric forms of zirconium, $\text{Zr}:\text{DBHP} \approx 1:1$ and n remains almost unchanged in the range $N = 2.57$ to 7.30 . The DBP compounds obtained from 0.25M HNO_3 contain up to 0.2 NO_3 group per zirconium atom. Under the conditions studied, the chief structural unit is assumed to be a fourmembered zirconium ring, and the compound can be assigned the formula $[\text{Zr}_4(\text{OH})_{12}\text{A}_4]$ or $[\text{Zr}_4\text{O}_4(\text{OH})_4\text{A}_4]$ if the zirconium atoms are joined not by hydroxo-bridges but by oxo-bridges. The NO_3 groups are apparently not coordinated, but are absorbed by the highly developed surface of the gelatinous precipitate.

Solubility of DBP Compounds of Zirconium

The DBP compounds of zirconium are insoluble in 0.25M and 6M HNO_3 . The compounds with $n = 1$ and $n = 2$ are insoluble in n -decane. The solubility of $\text{Zr}(\text{NO}_3)_2\text{A}_2 \cdot (\text{HA})_4$ in n -decane at 25°C was found to be $1.86 \times 10^{-2}\text{M}$. When $\text{Zr}(\text{NO}_3)_2\text{A}_2 \cdot (\text{HA})_2$ and a $\text{Zr}(\text{NO}_3)_2\text{A}_2 \cdot (\text{HA})_2 + \text{Zr}(\text{NO}_3)_2\text{A}_2$ mixture with $n = 3.55$ was dissolved in n -decane, it was observed that at equilibrium, the DBHP:Zr ratio in the solutions increased to $n = 6$, whereas in the precipitates, it decreased and approached the value $n = 2$. A similar phenomenon was observed when $\text{Zr}(\text{NO}_3)_2\text{A}_2 \cdot (\text{HA})_2$, $\text{Zr}(\text{NO}_3)_2\text{A}_2$, and their mixtures were dissolved in solutions of DBHP in n -decane.

The solubility of the DBP compounds of zirconium with $n = 2$ and 4 increases with increase in concentration of DBHP in n -decane (Table 34). The precipitates dissolve until the $\text{Zr}:\text{DBHP}$ ratio in the solution approaches 1:6. The solubility data show that not only $\text{Zr}(\text{NO}_3)_2\text{A}_2$, but also $\text{Zr}(\text{NO}_3)_2\text{A}_2 \cdot (\text{HA})_2$, is insoluble in n -decane, and that both compounds are also insoluble in n -decane-DBHP mixtures. When these compounds are

dissolved in n-decane-DBHP mixtures, the DBP compound with $n = 6$, which is the only soluble DBP compound of zirconium, is formed. A similar phenomenon is observed when $\text{Zr}(\text{NO}_3)_2\text{A}_2 \cdot (\text{HA})_2$ is dissolved in n-decane; this DBP compound disproportionates to $\text{Zr}(\text{NO}_3)_2\text{A}_2$ and $\text{Zr}(\text{NO}_3)_2\text{A}_2 \cdot (\text{HA})_4$, after which the latter dissolves.

In the study of the solubility of the compound with $n = 1$ in n-decane-DBHP mixtures, the precipitate absorbs DBHP from the solution (Table 34).

TABLE 34. Solubility of DBP Compounds of Zirconium in DBHP-n-Decane Mixtures at 25°C.

DBHP Concentration g/ℓ		Concentration of Zirconium After Dissolution, g/ℓ	Ratio DBHP:Zr in the Solution
In Original Solutions, N	After Dis-solution		
$\text{Zr}(\text{NO}_3)_2\text{A}_2 \cdot (\text{HA})_2$			
0	1.85	0.13	6.14
1.0	3.76	0.26	6.23
1.63	5.64	0.40	6.07
3.0	10.72	0.80	5.78
$\text{Zr}(\text{NO}_3)_2\text{A}_2$			
0.66	0.84	0.063	5.78
3.98	6.85	0.52	5.78
DBP Compound of Zirconium* with n = 1			
0.1	0.04	< 0.002	--
0.6	0.06	< 0.002	--
1.5	0.13	< 0.002	--
3.4	0.21	< 0.002	--

* ~0.5 g of precipitate dissolved in 15 ml solvent.

Mechanism of the Extraction of Zirconium by DBHP

The results of the determination of the compositions of the DBP compounds of zirconium and their solubilities indicate that in $\text{Zr-HNO}_3\text{-H}_2\text{O-DBHP-n-decane}$ system under conditions in which the zirconium is present in the monomeric form, the compound extracted is a DBP compound with the composition $\text{Zr}(\text{NO}_3)_2\text{A}_2\cdot(\text{HA})_4$. The experiments on the extraction showed that, irrespective of the value of N, contact between the aqueous and organic phases leads to the immediate formation of precipitates or a third phase. It was observed visually that in a large excess of DBHP, the precipitates dissolve partly or completely (if $N \gg 8$ to 10) when the phases are brought into contact. The formation of the DBP compounds evidently takes place initially in the aqueous phase. With a sufficient excess of DBHP, $\text{Zr}(\text{NO}_3)_2\text{A}_2$ and $\text{Zr}(\text{NO}_3)_2\text{A}_2\cdot(\text{HA})_2$ are converted completely into $\text{Zr}(\text{NO}_3)_2\text{A}_2\cdot(\text{HA})_4$; this compound is subsequently distributed between the phases. In aromatic diluents (benzene or toluene), in addition to $\text{Zr}(\text{NO}_3)_2\text{A}_2\cdot(\text{HA})_4$, DBP compounds with $n = 4$ and 2 may also be extracted.

MACRORETICULAR ION EXCHANGE RESIN CLEANUP OF PUREX
PROCESS TBP SOLVENT (22, ARH-SA-58)

The merits of the macroreticular ion exchange treatment for cleaning up Purex process solvent stand out clearly. Particularly noticeable are the low fission product content and plutonium retention number of the resin-treated extractant; both values are substantially lower than those for alkaline permanganate-washed plant solvent. The plutonium retention number has traditionally been considered a sensitive measure of the presence of deleterious diluent and/or TBP degradation products in used Purex process solvent. The colorless appearance of the resin-treated TBP extractant and its very low plutonium retention number are convincing evidence that the ion exchange procedure effectively removes these degradation products. It is truly a "solvent cleanup" method and not just a mechanism for removing radioactivity.

The other properties listed in Table 35 (TBP concentration, density, etc.) all confirm that ion exchange treatment neither removes nor adds components to the Purex solvent which affect its hydraulic and chemical performance as an extractant for uranium and plutonium. (Variation of a factor of 2 in disengaging time with the apparatus used is not regarded as significant.)

Other conclusions from the study include:

- Strong base (A-26 and A-29) resins sorbed HDBP and fission products ^{106}Ru , ^{95}Zr , and ^{95}Nb much more strongly than did either Amberlyst A-21 (weak base) or Amberlyst 15 (cation exchanger) resins. (Amberlyst A-26 resin was selected for further study because of its slightly greater stability at elevated temperatures.)
- Affinity of hydroxide-form A-26 resin for radoruthenium was slightly greater than that for ^{95}Zr , ^{95}Nb , or HDBP; however, batch distribution ratios for all these solutes were greater than 500.

- Kinetics of sorption of fission products and HDBP from used Purex solvent by A-26 resin were significantly faster at 40°C than at 25°C. Kinetics of fission product and HDBP uptake by A-26 resin also increased with decreasing resin particle size.
- Of many reagents tested for this purpose, 1 to 4M NaOH and 1 to 3M HNO₃ - 0.05M HF solutions were best for eluting fission products and HDBP from A-26 resin.
- High capacity of A-26 resin for sorbing extractant impurities was indicated in very preliminary column runs. Physical and chemical properties of the effluent solvent in these runs were equal to or superior to those of Hanford Purex Plant carbonate-washed material.

TABLE 35. Properties of Ion Exchange-Treated Purex Solvent.

Test/Property	Plant 1CW ^a	Plant 100 ^b	Ion Exchange-Treated, Bed Volumes		Laboratory Prepared Solvent
			119	195	
TBP, vol%	29.6	29.2	28.8	29.9	30.0
Color	Yellow	Yellow	Colorless	Colorless	Colorless
Density	0.8111	0.8122	0.8108	0.8114	0.8126
Fission product Content, $\mu\text{Ci}/\ell$					
Zirconium	90.0	3.4	0.62	0.35	-
Niobium	98.0	2.1	0.69	0.54	-
Ruthenium	170.0	9.0	1.2	3.0	-
Disengaging time, sec	37.0	61.0	28.0	50.0	67.0
Uranium extraction, Kd	4.6	14.2	14.1	17.6	17.4
Plutonium retention number	2070.0	50.0	6.0	9.0	23.0

^aTypical plant used solvent.^bTypical plant washed solvent.

SOLVENT STABILITY IN NUCLEAR FUEL PROCESSING:
CYCLE IRRADIATION STUDIES OF 15 VOLUME PERCENT
TBP - n-DODECANE (23, ORNL-4618)

Irradiation Procedure

One volume of freshly prepared 15% by volume TBP in n-dodecane was added to 0.5 volume of 0.38M $\text{UO}_2(\text{NO}_3)_2$ --3M HNO_3 . The mixed phases were irradiated for the equivalent of solvent radiation doses of about 0.3, 1, and 2 Wh/l, respectively. After irradiation and separation of the phases, the organic phase was stripped of its uranium content by five consecutive contacts with 0.5 volume of 0.01M HNO_3 and washed twice with 0.5 volume of 0.3M Na_2CO_3 and once with 0.2 volume of 0.1M HNO_3 . The complete procedure was repeated until the solvent had received an integrated radiation dose of 6 to 10 Wh/l. Samples of the organic and aqueous phases were taken periodically after each step. The organic samples taken after the carbonate--nitric acid wash treatment were reloaded with uranium before the ^{95}Zr and ^{106}Ru extraction and retention tests were run.

Zirconium Extraction and Retention Tests

Extraction of zirconium by the solvent was measured by contacting aliquots of uranium-containing solvent from the irradiation contact and of carbonate-washed solvent (reloaded with uranium) with the following solution for 5 minutes:

<u>Constituent</u>	<u>Concentration</u>
Uranium	10 g/l
HNO_3	3M
Zirconium	0.9 g/l
^{95}Zr - ^{95}Nb	$\sim 8 \times 10^5 \text{ counts min}^{-1} \text{ ml}^{-1}$

The phases were separated and a gross gamma count was made of each phase. The organic phase was then stripped by five consecutive contacts with 0.01N HNO_3 , each at a phase ratio of 1:1, and a gross gamma count was made of the stripped solvent. The zirconium extraction coefficient

was calculated by assuming that all gamma activity in the organic phase in excess of the activity arising from uranium was due to ^{95}Zr , and that about 40% of the ^{95}Zr - ^{95}Nb activity in the original feed was due ^{95}Zr .

Ruthenium Extraction and Retention Tests

Three molar nitric acid containing about 0.3 g of ruthenium per liter, ^{106}Ru tracer ($\sim 1 \times 10^6$ cpm/ml) and 10 g U/l were shaken with a sample of uranium-bearing solvent from the irradiation-extraction step. After phase separation, the ruthenium concentration was determined. Ruthenium retention in the organic phase was measured after five consecutive contacts with 0.01N HNO_3 . Similar extraction-stripping tests were made using samples of the carbonate--nitric acid--washed solvent after the solvent had been loaded with uranium.

Plutonium Extraction and Retention Tests

Plutonium extraction and retention tests were made with samples of the solvent extract obtained from the irradiation-extraction step and with the carbonate-washed solvent after it had been reloaded with uranium.

Retention of Uranium

There was a small increase in the amount of uranium retained by the solvent after stripping as the radiation dose per cycle was increased from 0.3 to 2 Wh/l cycle (Table 36). The quantity of uranium retained by solvent receiving a dose of 0.3 Wh/l cycle was essentially the same as for solvent that had not been irradiated during extraction. Presumably the higher retention at greater radiation doses was due to the presence of HDBP. However, the quantity of retained uranium did not increase with cycling indicating that the carbonate wash treatment efficiently removed the HDBP.

TABLE 36. Effect of Irradiation on Uranium Extraction and Retention.

Solvent Radiation Dose, Wh/l/cycle	Uranium in Stripped Solvent (avg.), mg/l
0.0 (unirradiated solvent)	1.0
0.3	0.6
1.0	3.3
2.0	14.0

Extraction and Retention of Zirconium

As shown in Table 37, solvent that had been irradiated to 1 or 2 Wh/l/cycle evidenced an increased ability to extract ^{95}Zr . The average ^{95}Zr extraction coefficient obtained with unirradiated solvent was 0.012 which did not increase with irradiation to a level of 0.3 Wh/l/cycle. However, solvent irradiated to 1 or 2 Wh/l/cycle gave ^{95}Zr coefficients of 0.027 and 0.036, respectively, or a factor of 2 to 3 higher than that obtained with unirradiated solvent.

TABLE 37. Results of Zirconium Extraction and Retention Tests.

Solvent Radiation Dose Wh/l/cycle	^{95}Zr Extraction Coefficient (Average)	% of Original ^{95}Zr Retained (Average)
Organic Samples Taken After Irradiation Contact		
0.0	0.012	0.57
0.3	0.011	0.20
1.0	0.027	0.81
2.0	0.036	0.70
Organic Samples Taken After Carbonate--Nitric Acid Wash		
0.0	0.012	0.57
0.3	0.008	0.23
1.0	0.011	0.48
2.0	0.012	0.56

Irradiated solvent washed with a sodium carbonate solution gave coefficients equal to, or less than, those obtained with unirradiated solvent. These results indicate that the degradation products responsible for the increased extraction (HDBP) were effectively removed by the alkaline wash treatment.

Extraction and Retention of Ruthenium

Irradiation up to a dose of 2 Wh/l/cycle had no effect on the extraction and retention of ruthenium. Both the ^{106}Ru extraction coefficients obtained with unirradiated (control) solvent and those obtained with solvent that had been irradiated to about 0.3, 1, and 2 Wh/l/cycle were about 0.002 as shown in Table 38. From 0.11 to 0.16% of the ^{106}Ru in the feed was retained by the stripped solvent; variations within this range showed no dependence on solvent radiation dose.

TABLE 38. Results of Ruthenium Extraction and Retention Tests.

Solvent Radiation Dose Wh/l/cycle	^{106}Ru Extraction Coefficients (Average)	% of Original ^{106}Ru Retained (Average)
Organic Samples Taken After Irradiation Contact		
0.0	0.0022	0.16
0.3	0.0020	0.11
1.0	0.0022	0.15
2.0	0.0023	0.16
Organic Samples Taken After Carbonate--Nitric Acid Wash		
0.0	0.0022	0.16
0.3	0.0020	0.11
1.0	0.0020	0.15
2.0	0.0019	0.14

Extraction and Retention of Plutonium

The quantities of plutonium extracted or retained by the solvent after stripping were the same for unirradiated solvent and for solvent irradiated up to 2 Wh/l/cycle. After extraction, each solvent had a plutonium concentration of about 0.4 g/l. This concentration was reduced to less than 5×10^{-5} g/l by stripping the organic phase with ferrous sulfamate solution.

Measurements of Surface Tension and Interfacial Tension

The cyclic irradiation had essentially no effect on either the surface tension of the regenerated solvent or the interfacial tension between the solvent and the aqueous uranium feed solution.

Cyclic Irradiation

The effects of irradiation on solvent properties are summarized in Table 39. Irradiation of 15% by volume TBP-dodecane at 0.3 Wh/l/cycle to an integrated dose of about 6.5 Wh/l had no apparent adverse effect on solvent performance. The quantities of uranium, plutonium, zirconium, and ruthenium that were extracted and retained were the same as those observed for unirradiated solvent. Increasing the dose level to 1 and 2 Wh/l/cycle increased the ^{95}Zr extraction efficiencies by factors of 2 and 3, respectively, and caused only a retention of uranium. However, cycling caused no build-up of the effects; they were apparently caused by the presence of HDBP, which would be formed in significant amounts at these irradiation levels. The carbonate wash treatment, which removed HDBP effectively from the solvent, eliminated the irradiation effects; that is, the performance of the washed solvent was equivalent to that of unirradiated solvent. In each test, phase separation was rapid and well-defined. Even at the highest irradiation level (2 Wh/l/cycle), there was no evidence of the formation of solids (e.g., precipitation of the zirconium salt of HDBP, which has a low solubility).

TABLE 39. Cyclic Irradiation Tests
With 15% TBP-Dodecane.

Test	Exposure, Wh/l/cycle	Number of Cycles	Total Exposure, Wh/l	Effect on Extraction Properties
1	0.29 to 0.34	20	6.5	No change observed
2	0.93 to 1.01	10	9.5	Quantity of zirconium was twice that obtained for unirradiated solvent; stripped solvent retaining 3 mg U/l.
3	1.94 to 2.02	3	5.9	Quantity of zirconium extracted was three times that obtained for unirradiated solvent; stripped solvent retained 14 mg U/l.

These tests do not show the effects of extended use of solvent in a processing plant. This can lead to a slow accumulation of degradation products in the solvent phase that may impair solvent performance. These degradation products usually derive primarily from the reaction of nitric acid with the diluent, the reaction rate (and thus the accumulation of degradation products) increasing when the extraction process is conducted at elevated temperatures and/or in a high radiation field. The use of normal hydrocarbons (principally dodecane) as process diluents has greatly decreased the extent of problems arising from diluent degradation; but, if necessary, the solvent can be purified periodically by distillation to remove degradation products.

INVESTIGATION ON THE NATURE OF DEGRADATION PRODUCTS
IN THE SYSTEM 20 VOL.% TBP-DODECANE-NITRIC ACID

I. ENRICHMENT OF COMPLEXING PRODUCTS AND INFRARED STUDY (24, ISEC 1971)

Samples of 20 vol.% TBP-dodecane were equilibrated (volume ratio organic:aqueous phase = 1) with water or nitric acid (concentration: 0.2, 0.5, 0.75, 1.0, 2.0, 3.0, 4.0, and 5.0M), and the organic phase was irradiated. The radiation power was 0.6 W/l, and the temperature was 30 to 35°C. After irradiation, the low molecular weight acid products, such as MBP and DBP, were removed by scrubbing with 1M sodium carbonate solution. Then the degraded solvent was contacted for 10 minutes with a hafnium tracer solution in 3M nitric acid at a phase ratio of unity. An "H-number", i.e., an index giving the number of moles of hafnium retained in 10^9 l of degraded solvent, was used as a measure of solvent degradation.

Effect of Nitric Acid Concentration During Irradiation

The concentration of nitric acid during the irradiation proved to be very important for the formation of extracting agents. The H-number for samples irradiated to a total dose of 40 Wh/l was 75 if the system had been equilibrated with water, and increased to 170 and 950 for solvents with organic nitric acid concentrations of 0.02 and 0.04M, respectively, during irradiation. For final $\text{HNO}_3(\text{org})$ concentrations of 0.45 and 0.55M, the corresponding H-numbers were as low as 9 and 6, respectively. Apparently two counteracting processes take place: at low nitric acid concentration, considerable amounts of complexing products are formed, which are suppressed or destroyed at high nitric acid concentrations. At the same irradiation level, there is a roughly linear relationship between nitroparaffin and nitric acid concentrations. It may be concluded that no direct relation exists between the presence of nitroparaffins and the extraction of hafnium.

Enrichment of Complexing Agents by Molecular Distillation

Five hundred ml of solvent (equilibrated with 0.5M nitric acid) were irradiated to a total dose of 40 Wh/l. After scrubbing with 1M sodium carbonate solution, water, and 0.5M nitric acid the sample had an H-number of 1000. High-vacuum molecular distillation at 10^{-2} mm mercury and 40°C gave a distillate and a residue with H-number of 450 and 6700, respectively. Further enrichment was achieved by a second and third distillation of the respective residues resulting in a concentrated residue (H-number 72,000). Marked infrared absorptions at 1550 and 1640 cm^{-1} indicate the presence of equal amounts of nitroparaffins and nitrate esters in residues 1 and 2, while the extraction powers differed significantly. This again suggests that nitroparaffins have no influence on the retention of hafnium. A substantial peak occurs at 1720 cm^{-1} after the second distillation which is even more intense with the third residue. Absorptions at 1720 cm^{-1} are generally assigned to the carbonyl function. In the spectrum of residue 3, further peaks at 1615 and 1660 cm^{-1} are emerging and are also tentatively assigned to the carbonyl group, e.g, in diketones. It is obvious from the present results that the high extracting power can be related to carbonyl compounds rather than nitroparaffins.

Conclusions

The degradation products responsible for the retention of fission products can be characterized as follows:

- As scrubbing with sodium carbonate solution is ineffective in removing the compounds, the substance may be either a weak acid, or a sodium salt with a high solubility in the organic phase.
- The volatility is lower than that of TBP, pointing to a high molecular weight.
- No relationship was found between the presence of primary nitroparaffins and the specific action with respect to hafnium or zirconium. An increase of the extraction power was noted in cases where infrared absorptions due to the carbonyl function had increased.

- The concentration of complexing agents even after high radiation doses (40 Wh/l is of the order of 10^{-6} mole/l, while monofunctional degradation products such as nitroparaffins and unsubstituted ketones are formed at a rate that is higher by a factor of 1000.

INFRARED SPECTROSCOPIC STUDY OF THE ZIRCONIUM COMPLEX OF DBP (25, RJIC 16)

To investigate the nature of the bonds and the structures of the previously isolated zirconium complexes of DBP or HA with the composition $\text{Zr}(\text{NO}_3)_2\text{A}_2$ (compound I), $\text{Zr}(\text{NO}_3)_2(\text{HA})_2$ (compound II), and $\text{Zr}(\text{NO}_3)_2\text{A}_2(\text{HA})_4$ (compound III), infrared spectroscopy was used. The absorption spectra were obtained in the frequency range 400 to 4000 cm^{-1} . The assignments of the infrared absorption bands are given in Table 40. The spectrum of DBP saturated with nitric acid shows a decrease of the $\text{P} = \text{O}$ stretching vibrations by about 10 cm^{-1} . The 2250-cm^{-1} and 2650-cm^{-1} absorptions bands, characterizing the DBP dimer, hardly change. The spectrum has a number of bands characteristic of the vibrations of the nitric acid molecule, in particular, a set of bands due to the vibrations of nitrate groups with partially covalent bonds.

The spectrum resembles the spectra of molecular compounds of TBP and also those of diheptyl phosphinic acid in nitric acid. The results indicate the formation of a molecular compound by the DBP dimers with nitric acid via an additional hydrogen bond between the $\text{P} = \text{O}$ oxygen atom in DBP and the hydrogen atom in nitric acid.

The spectra of compounds I, II, and III show significant changes compared with those of DBP and DBP saturated with nitric acid owing to the powerful interaction between the reactants. As for zirconium nitrate, the spectra of all the compounds show absorptions bands due to nitrate groups bound by partly covalent bonds.

In the spectrum of compound I, there are no 2250 and 2650 cm^{-1} DBP absorption bands corresponding to the OH stretching vibrations and no broad band at 1723 cm^{-1} , which is probably also associated with the vibrations of the same OH groups.

Instead of the 1235 cm^{-1} stretching vibration band of the $\text{P} = \text{O}$ groups in DBP, an intense and complex band is observed in the region of 1120 cm^{-1} . This intense band is superimposed on bands at 1123 and 1149 cm^{-1} of moderate intensity observed in the spectrum of free DBP and associated with the deformation vibrations of the butyl group. The remaining absorption bands undergo smaller changes, which in the spectrum of compound I, indicate the formation of a zirconium nitrate-DBP complex.

TABLE 40. Wave Numbers (cm^{-1}) of the Maxima and the Assignment of the Absorption Bands in the Infrared Spectra.

DBP	DBP sat with HNO_3	$\text{Zr}(\text{NO}_3)_2\text{A}_2$	$\text{Zr}(\text{NO}_3)_2\text{A}_2$ $\cdot (\text{HA})_2$	$\text{Zr}(\text{NO}_3)_2\text{A}_2$ $\cdot (\text{HA})_4$	Assignment of Absorption Band
470 s	470 sb	475 m	475 m	470 s	CH and CC deformation vibrations
525 s	525 sb	530 m	530 w	525 s	
550 m	550 mb	553 m	550 m	550 m	
---	---	605 w	603 w	600 w	Zr-O vibrations
---	---	---	---	644 m	
---	---	---	---	679 m	
727 m	730 m	728 m	725 m	733 m	CH rocking vibrations $\text{N}_3(\text{ONO}_2)$
---	740 w	---	---	---	
776 m	778 m	771 m	772 m	783 w	P-O-(C)
804 m	804 m	804 m	804 m	804 m	Non-planar CH deformation vibrations
---	---	---	---	837 vw	
---	---	---	---	853 w	
843 w	---	860 w	855 w	863 vw	Bound PO
912 m	910 w	923 w	915 w	913 w	CH ₃ fanwise rocking vibrations
---	---	---	---	952 w	
---	---	1042 s	1042 s	1041 vs	$\nu_2(\text{ONO}_2)$
1031 vs	1031 vs	---	---	---	(P)-O-C
1063 w	1063 w	1072 vs	1071 vs	1062 vs	
---	---	1112 s	1110 s	1105 vw	Bound PO
---	---	1130 vs	1126 s	1127 w	
1123 m	1122 w	---	---	1153 w	CH ₂ and CH ₃ deformation vibrations
1149 m	1151 w	1210 vw	1220 vw	---	
---	---	1233 vw	---	1237 vw	P = O stretching vibrations
1235 s	1225 s	---	---	---	
---	---	---	---	1270 vw	$\nu_1(\text{ONO}_2)$
---	---	1275 m	1273 w	1306 vw	
---	---	---	---	1391 m	CH ₃ sum. deformation vibrations
1386 m	1393 m	**	**	---	
---	---	---	---	1439 w	CH ₃ antisym. deformation vibrations
1470 m	1469 m	**	**	1470 m	
---	---	1543 vw	1540 vw	---	$\nu_4(\text{ONO}_2)$
---	---	1558 vw	1556 vw	1558 m	
---	---	1572 s	1573 s	---	b(H ₂ O) deformation vibrations of H ₂ O molecules
---	1653 m	---	---	---	
---	1662 m	---	---	1642 m	b(OH) deformation vibrations of OH groups
1673 mb	---	1615 vw	1614 vw	---	
1723 mb	---	1751 vw	---	---	$\nu(\text{NH})$ stretching vibrations of OH groups in acid
---	---	---	---	2250 mb	
2250 mb	2300 mb	---	2350 wb	2720 mb	$\nu(\text{CH})$ stretching vibrations of CH groups
2650 mb	2750 mb	---	2610 vw	---	
2880 s	2880 s	**	**	2880 s	$\nu(\text{OH})$ stretching vibrations of OH groups in water
2920 w	2920 w	---	---	2920 w	
2940 w	2940 w	---	---	2940 w	
2980 s	2970 s	---	---	2980 s	
---	3430 sb	---	---	3470 vw	

NOTE: m = moderate intensity, s = high intensity, vw = very low intensity, vs = very high intensity, w = low intensity, st = band satellite, b = broad band, sp = sharp band.

* The assignment of the absorption band is given in the text.

** Absorption bands of liquid paraffin.

associated with the deformation vibrations of the butyl group. The remaining absorption bands undergo smaller changes, which in the spectrum of compound I, indicate the formation of a zirconium nitrate-DBP complex.

The spectrum of compound II is similar to that of compound I, which is evidence of a similarity in their structures. A distinctive feature of the spectrum of compound II is the presence of weak absorption in the region of the stretching vibrations of OH groups. The 2350 and 2610 cm^{-1} bands are somewhat displaced and weakened compared with the corresponding DBP absorption bands, but their presence in the spectrum indicates the existence in compound II of hydrogen-bonded DBP molecules. This constitutes the principal difference between compounds II and I, indicating definite differences in their structures.

In the absorption spectrum of compound III, the fundamental bands characteristic of DBP are also considerably displaced. In the region corresponding to $\text{P}=\text{O}$ stretching vibrations, a number of bands of low or moderate intensity are observed (at 1105, 1127, 1153, and 1237 cm^{-1}). The $(\text{P})-\text{O}-\text{C}$ band has a frequency of 1063 cm^{-1} and in the region of 1040 cm^{-1} absorption, caused mainly by $\nu_2(\text{ONO}_2)$ vibrations of nitrate groups, appears. There is some change in the absorption due to the vibrations of the nitrate groups, which affects mainly the 1558 cm^{-1} band. The spectrum of compound III also shows several additional absorption bands of low or moderate intensity, which have no direct analogues in the spectra of other similar compounds (644, 679, 837, 853, 952, and 1439 cm^{-1}). These bands are probably caused by the formation of additional bonds between the molecules of DBP, zirconium nitrate, and compound III.

The structures of the compounds can probably be represented by the following formulae:

This agrees with the experimental data obtained. X-ray diffraction study of the compounds shows that they are amorphous. The last member of the zirconium-DBP compounds considered (compound III) differs significantly from compounds I and II. As shown above, under normal conditions it is a viscous liquid with chemical properties different from those of compounds I and II. Possibly it exists as the monomer, the structure of which is described by the formula:

INFRARED SPECTROSCOPIC STUDY OF DBP COMPOUNDS OF UNH (26, RJIC 16)

The reaction of UNH with DBP (HA) in nitric acid solutions gives compounds shown by chemical analysis to have compositions corresponding to the ratios $U:NO_3:A = 1:0:2$ (I), $1:1:4$ (II), and $1:1:2$ (III). Under normal conditions, compound I is a pale-yellow, almost white friable powder, and compounds II and III are dark-yellow oily liquids.

Compound I has been regarded as a salt in which the $P-O-UO_2^{2+}$ bond has increased covalent character, of the same order as that of the $P-O-H$ bond. The possible existence of a strong bond of the $P=O \rightarrow UO_2^{2+}$ type, leading to a displacement of the band due to the $P=O$ stretching vibrations from 1220 cm^{-1} in the free acid to 1124 cm^{-1} . The dependence of the distribution constant of uranium(VI) on the concentration of nitric acid in the aqueous phase in the extraction by DBP was described on the assumption that the extractable forms are $UO_2A_2(HA)_2$ and $UO_2(NO_3)_2 \cdot (HA)_2$.

It is possible that the solution also contains compound I at low concentrations of HA and HNO_3 . Coordination saturation of UNH is brought about by molecules of the diluent, so that the formula of the compound is $UO_2A_2S_2$, where S represents the diluent.

The solid polymer I was isolated and was obtained in crystalline form. Information on the nature of the reaction of HA with metals and the structure of the compounds formed can be obtained from a study of the infrared absorption spectra of these compounds. The infrared absorption spectra of the DBP compounds of UNH were studied, and the assignment and relative intensities of the absorption bands are given in Table 41.

The absorption bands of greatest interest are those corresponding to the vibrations of the main groups $P-OH$, $P-OC$, and $P=O$.

TABLE 41. Wave Numbers (cm^{-1}) of the Maxima and Interpretation of the Absorption Bands in the Infrared Spectra of Compounds of Uranyl with Dibutyl Hydrogen Phosphate.

DBP	Dibutylphosphato-compounds of Uranyl			Assignment of Absorption Bands
	I	II	III	
	440 vw	440 vw	440 vw	
470 s	469 v med	469 br med	465 v med	CH and CC bending vibrations
525 s	520 br med	525 br w	525 br med	
550 med	555 v med	555 br med	555 br med	
	576 v med	575 br w	575 br med	U-O vibrations
727 med	737 v med	737 v med	738 v med	CH rocking vibrations
776 med	795 vw	783 w	790 med	P-O-(C)
804 med	819 vw	819 vw	810 w	out-of-plane CH bending $\nu_6\text{ONO}_2$
			830 w	
843 w	864 v med	858 br med	860 br med	P=O bound
912 med		910 vw		CH ₃ wagging vibrations
	938 vs	938 vs	933 vs	UO_2^{2+} stretching vibrations
	967 vw		963 w	
			998 vw	
	1002 vw	1002 vw	1010 w	
1031 vs				P-O-C free
1063 w	1036 vs	1035 vs	1035 vs	P-O-C free
	1070 vs	1075 vs	1070 vs	CH ₂ and CH ₃ bending vibrations
1123 med				
1149 med	1128 vs	1128 vs	1128 vs	P=O bound
	1200 w	1200 w	1200 w	P=O free
	1240 w	1240 w	1230 w	
1235 s				
	1272 w	1270 w	1275 w	$\nu_1\text{ONO}_2$
	1312 w	1310 w	1310 w	
		1400 br s	1390 vs	symmetric CH ₃ bending vibration, ν_{HNO_3}
1386 med*		1450 br w	1450 vw	
		1478 vs	1470 vs	antisymmetric CH ₃ bending vibration
1470 med*				
		1650 w	1520 w	$\nu_4\text{ONO}_2$
			1540 med	H ₂ O bending vibrations
			1650 w	
			1680 w	bending vibrations of OH group, ν_{OH}
1673 med			1730 w	
1723 med				
			2300 br med	stretching vibrations of OH group, ν_{OH}
			2600 br med	
2250 br med				
2650 br med		2880 s	2880 s	stretching vibrations of CH group, ν_{CH}
		2920 w	2920 w	
2880 vs*		2940 w	2940 w	
2920 w		2980 vs	2980 s	
2940 w				
2980 vs				
	3180 w		3050 w	stretching vibrations of OH group, ν_{OH}
			3200 w	
	3400 w	3500 br w	3450 br s	
			3800 w	

* Absorption bands of liquid paraffin.

The spectra of compounds I, II, and III show intense bands at 1036, 1070, and 1128 cm^{-1} , and very weak bands at 1200 and 1240 cm^{-1} . The intense band with highest frequency at 1128 cm^{-1} corresponds to the vibrations of the bound $\text{P}=\text{O}$ HA group. The $(\text{P})-\text{O}-\text{C}$ band also undergoes a marked displacement, to 1036 cm^{-1} , 1070 cm^{-1} . The direction of the displacement of the band is in accordance with the usual scheme corresponding to the inductive effect on the formation of bonds with phosphoryl oxygen. An important feature of the spectrum of compound I is the absence of absorption in the range 2250 to 2750 cm^{-1} . The spectrum of HA in this range shows absorption bands corresponding to the stretching vibrations of the OH groups of the acid. The absence of the bands at 2250 to 2750 cm^{-1} in the spectrum of compound I indicates that this compound does not contain OH groups. Thus, compound I is evidently a salt of DBHP containing a bond of the $\text{U}-\text{O}-\text{P}$ type. In addition, the compound contains a bond of the $\text{U}\cdots\text{O}=\text{P}$ type, probably formed with the anion of a second molecule of the acid. These two bonds with one uranium atom apparently cannot be formed with a single HA molecule, since the resulting four-membered chelate structure would be extremely strained. The structural unit of compound I should then be

From the requirements of electrical neutrality, however, the number of bonds of the type $\text{U}-\text{O}-\text{P}$ should be doubled, and from the requirements of coordination saturation of the UNH the number of bonds of the type $\text{U}\cdots\text{O}=\text{P}$ should also be doubled, so that the structural unit of compound I is:

The terminal oxygen atoms of this structure can obviously form additional bonds with the neighboring uranyl groups, forming chain polymer of the type

The suggestion that compound I has a polymeric structure agrees with the low solubility of this compound in organic solvents of the benzene or decane type, in which it forms gelatinous precipitates.

The spectra of the liquid compounds II and III differ from that of compound I; they contain additional bands and show various differences in the range corresponding to the fundamental groups of the phosphates. The spectra of both compounds contain additional bands and show various differences in the range corresponding to the fundamental groups of the phosphates. The spectra of both compounds contain absorption bands corresponding to the vibrations of nitric acid molecules, and there is an increase in the intensity of the 1200 cm^{-1} band corresponding to the stretching vibrations of a $\text{P}=\text{O}$ group taking part in hydrogen bonding. The spectra of compound II also contain the absorption bands of DBP. In view of the change in the state of aggregation on going from compound I to compounds II and III, it may be assumed that the latter are formed by the partial or complete breakdown of the polymeric structure of compound I in 6M nitric acid solution and the attachment, to each separate fragment of compound I, of a molecule of nitric acid (compound III) or molecules of nitric acid and DBP (compound II). The introduction of acidic hydroxyl groups makes possible the production of both intramolecular and intermolecular hydrogen bonds, by means of which more or less extensive associates may be formed.

Polymerization is apparently not as extensive in compounds II and III as in compound I. The chief difference between compounds II and III and compound I is the absence of a complex polymeric structure and the attachment of molecules of nitric acid and DBP to the individual fragments of polymer I.

THORIUM AND IRON DBP (27, RJIC 16)

The influence of nitric acid concentration on the composition of the thorium DBP which separates when aqueous nitric acid solutions of thorium nitrate and DBHP or HA are mixed has not been documented. The compound ThA_4 , insoluble in water, is obtained by mixing aqueous solutions of the sodium salt of DBHP and of thorium nitrate. ThA_4 is also formed after the readily volatile part of a heterogeneous mixture of aqueous $\text{Th}(\text{NO}_3)_4 + \text{TBP}$ is distilled off. DBHP precipitates ThA_4 from 1M HNO_3 .

When aqueous solutions of thorium nitrate containing 0.2M HNO_3 and DBHP are mixed, the precipitate differs markedly from that formed when 6M HNO_3 solution of thorium nitrate and DBHP are mixed. After being dried at 40°C , the first is a white free-flowing powder, whereas the second is an amorphous waxy mass. The composition of thorium DBP at a given acidity of an aqueous solution does not depend on the ratio of the reactants DBHP and thorium (N). A precipitate of composition of ThA_4 separates from 0.2M HNO_3 , $\text{ThA}_4 \cdot 2\text{HA}$ from 6M HNO_3 .

The precipitates formed at room temperatures do not contain the NO_3 group or water. The value of N was varied within wide limits: 0.42 to 14.8 when precipitates were produced from 0.2M HNO_3 , and 0.6 to 24 when precipitates were from 6M HNO_3 . The composition of the precipitates was determined from the amounts of DBHP and thorium in the solutions before and after precipitation and by analysis for DBHP, thorium, and NO_3^- ions.

The difference in composition of the precipitates isolated from 0.2 and 0.6M HNO_3 can be explained by the fact that DBHP readily forms hydrogen bonds both with water molecules and with one another. In 0.2M aqueous HNO_3 , the structure of the water is not destroyed and this hinders the formation of bonds between DBHP molecules. As a result, the Th^{4+} ion reacts with monomeric species of DBHP. In 6M aqueous HNO_3 , however, the structure of the water is broken down, and the DBHP is evidently predominantly in the form of a dimer. In the formation of precipitate, a molecule of the dimer (H_2A_2) adds to ThA_4 . ThA_4 and $\text{ThA}_4 \cdot 2\text{HA}$ are sparingly soluble

in aqueous solutions of HNO_3 . When 0.2M HNO_3 is used and there is an excess of one component above the stoichiometric quantity, the second component is not observed. For 6M HNO_3 when there is an excess of one of the components, analytically determinable amounts of thorium and DBP remain in the solutions. ThA_4 is almost insoluble in pure n-decane and also in mixtures of n-decane + 3 g/l DBHP the solubility of ThA_4 is 0.025 g/l. When the concentration of DBHP in n-decane is increased from 1.1 to 8.0 g/l, the solubility of $\text{ThA}_4 \cdot 2\text{HA}$ increases approximately linearly from 0.006 to 0.053 g/l.

Iron(III) DBP is reported to have the composition FeA_3 . This compound is poorly soluble in water and in benzene. The solubility in the benzene + 20% TBP mixture is 40 mg/l.

When solutions of iron(III) nitrate in 0.2 or 6M HNO_3 (~ 16 g Fe/l) were mixed with solutions of DBHP in HNO_3 of corresponding concentration ($[\text{DBHP}] \sim 4$ g/l) at room temperature, a white precipitate slowly separated (over 24 hours). Its composition was FeA_3 and was independent of the acidity of the aqueous solution and of the ratio of DBHP to iron of 0.2 to 16. As with thorium, when one of the components was in excess, the proportion of the other component in the solution was independent of the acidity.

MACRORETICULAR ANION EXCHANGE RESIN CLEANUP
OF TBP SOLVENTS (28, ARH-SA-129)

Strong base macroreticular anion exchange resins (e.g., Amberlyst A-26) remove fission products, DBP acid, and diluent degradation products from used TBP extractants. Column tests with both unwashed Hanford Purex Plant 30% TBP-normal paraffin hydrocarbon solvent demonstrate the following.

Solvent Flow Rate

Table 42 summarizes conditions and results of column runs made to study effects of flow rate and solution residence time on A-26 resin cleanup of Purex process solvent. Resin bed performance is primarily a function of solution residence time rather than flow rate. Solvent cleanup is excellent at residence times of 10 to 30 minutes (2 to 6 bed volumes per hour).

TABLE 42. A-26 Resin Treatment of Purex Process Solvent --
Effects of Flow Rate and Residence Time.

Flow Rate Gal ft ² /hr	Residence Time, Min	Average Effluent Solvent		
		C/Co ^a		Plutonium Retention Number
		⁹⁵ Zr- ⁹⁵ Nb	¹⁰⁶ Ru- ¹⁰⁶ Rh	
5.0	30.0	0.0027	0.0031	63
10.8	14.6	0.0062	0.0026	35
11.3	10.0	0.0081	0.0194	41
20.8	7.7	0.0257	0.0202	140
10.0	6.7	0.0272	---	---

NOTE: Data are for passage at 40°C of 50 to 100 column volumes of Purex ICW (first cycle) solutions through beds of 14 to 50 mesh, OH-form A-26 resin (height to diameter ratio = 4).

^aConcentration in ICW/concentration in effluent.

Capacity Tests

The capacity of A-26 resin for sorbing fission products from Purex process solvents depends strongly on the HDBP concentration (as measured by plutonium retention number) of the solvent. For feed containing little HDBP (low plutonium retention number), as much as 10,000 to 15,000 μCi of ^{95}Zr - ^{95}Nb and ^{106}Ru - ^{106}Rh could be loaded without significant breakthrough of any radioisotope. Conversely, with a feed whose plutonium retention number was a high 90,000, 17% breakthrough of ^{106}Ru - ^{106}Rh occurred after only 960 μCi of ^{106}Ru - ^{106}Rh were loaded.

The plutonium retention number of all the effluent solvent produced in one run was less than 100, comparable to that of carbonate-washed used solvent. Resin-treated solvent generated in some of the other capacity tests had plutonium retention numbers in the range 1600 to 4000. However, such solvent was produced only after breakthrough of fission product activity.

Cyclic Load-Elution Tests

Sequential load-elution tests were performed to study A-26 resin performance and life under such cyclic conditions and to evaluate effectiveness of various elution schemes for removing fission products.

No truly effective eluent for removing all the fission product activity from A-26 resin has been found. But a combination of 8 to 9 column volumes each of 3M HNO_3 -0.025M HF and 1M NaOH solutions removes 55 to 60% of the ^{95}Zr - ^{95}Nb and 80 to 100% of the ^{106}Ru - ^{106}Rh . Removal of this much activity still permits highly satisfactory load cycle performance. The low plutonium retention numbers of the effluent solvent in subsequent load cycles indicate that the combination of HNO_3 -HF and NaOH eluents also provides satisfactory removal of HDBP.

Mixer-Settler Tests with Resin-Treated Solvent

Decontamination and physical performance of resin-treated ICW solvent under continuous countercurrent conditions was indicated in early batch tests to be comparable to that of carbonate-washed extractant.

Countercurrent runs in standard mixer-settlers simulated flowsheet conditions of the Hanford Purex Plant first cycle coextraction column. Three extractants were tested: A-26 resin-treated 1CW solvent, plant carbonate-washed 1CW solvent, and laboratory-prepared and -washed 30% by volume TBP-normal paraffin hydrocarbon. Performance of the former extractant equaled or exceeded that of the latter two on all counts.

Resin Type and Form

Other macroreticular strong base anion exchange resins (e.g., Amberlyst A-29 and A-641) can be used in place of OH-form Amberlyst A-26 resin for cleaning up used Purex process solvent. Approximately 75 column volumes of typical 1CW were passed downflow (at 40°C and four column volumes per hour through a 12.5-m² bed of 16- to 50-mesh, OH-form, A-641 resin. The resin bed removed 98 to 99% of all the fission products in the influent solvent; all the effluent was water-white and its plutonium retention number was about 50.

In the as-received Cl-form, A-26 resin does not efficiently sorb fission products from used Purex solvent. Limited test data suggest the CO₃-form A-26 resin is as effective as OH-form resin for this purpose.

Sorption of Yellow Color Bodies

In addition to sorbing HDBP and fission products from used solvent, both OH- and CO₃-form A-26 resins remove yellow color bodies from the TBP solution. Capacity of the OH-form A-26 resin for producing waterwhite effluent from typical 1CW solvent is about 550 column volumes. The yellow compounds desorb readily when the resin bed is eluted with HNO₃-HF solution. Additional yellow-colored material elutes when the NO₃-form is converted to the OH-form.

The yellow color bodies are thought to be nitration products of the normal paraffin hydrocarbon diluent. In A-26 resin treatment of degraded Purex process solvent, it is important to recognize that breakthrough of yellow color occurs long before breakthrough of either HDBP or fission products. Properties, especially plutonium retention number, of the resin-treated solvent do not appear to be significantly affected by the presence or absence of the yellow-colored compounds.

Resin Treatment of Degraded Diluent

Evidence exists to show that nitration products (or compounds derived therefrom; e.g., hydroxamic acids) of nonstraight-chain paraffinic diluents, e.g., Shell E-2342 or Soltrol-170, are responsible for increased fission product retention by washed TBP solvents. Straight-chain paraffins are much more resistant to nitration, and their nitration products are not particularly troublesome.

Tests were made to determine if A-26 resin would remove deleterious diluent degradation products. For this purpose, 30 column volumes of degraded Soltrol-170 were passed downflow (at 40°C and two column volumes per hour) through a 21.5-mx bed of OH-form A-26 resin. Influent and effluent plutonium retention numbers were 1200 and 550, respectively, corresponding to removal of about half of the undesirable ligands.

Mechanism of Fission Product Sorption

It has been suggested that: (1) TBP retention of nitrosylruthenium is due to dimeric species such as $[\text{Ru}(\text{NO})(\text{H}_2\text{O})(\text{NO}_3)_2]_2$, $[\text{Ru}(\text{NO})(\text{H}_2\text{O})(\text{NO}_2)(\text{NO})_3]_2(\text{OH})_2^-$, and $[\text{Ru}(\text{NO})(\text{NO}_2)(\text{NO}_3)_2]_2(\text{OH})_2^-$. Presumably the latter two species might undergo ion exchange with the A-26 resin; (2) strong sorption of ^{95}Zr and ^{95}Nb from 1CW solution onto A-26 resin occurs through neutralization of positively charged colloidal species; and (3) reactions such as

and

account for the removal of the zirconium and niobium.

MACRORETICULAR ANION EXCHANGE RESIN CLEANUP
OF TBP SOLVENTS (29, TRANS. AM. NS)

Certain macroreticular strong-base anion exchange resins (e.g., Rohm and Haas Company A-26 resin) strongly sorb fission product ruthenium, zirconium, and niobium; DBP acid; and yellow-color bodies from used Purex process 30% by volume TBP solvent. Application of such resins in routine cleanup of TBP extractants is potentially attractive to eliminate or, at least, minimize the large volumes of radioactive waste generated by presently used wash procedures.

Tests with used Purex 1CW solvent, both before and after carbonate washing, have been concerned primarily with determining the capacity of A-26 resin for sorbing solvent contaminants. Applicability of the A-26 resin for removal of DBP and residual plutonium from spent Hanford Plutonium Reclamation Facility (PRF) 20% TBP-CCl₄ solvent has been demonstrated.

In capacity tests, unwashed 1CW solvent containing 15 to 1800 $\mu\text{Ci}/\ell$ ⁹⁵Zr-⁹⁵Nb and 70 to 340 $\mu\text{Ci}/\ell$ ¹⁰⁶Ru-¹⁰⁶Rh was passed downflow (40°C, five to six column volumes per hour) through a 21.5-ml (1.9-cm-diameter by 7.6 cm-high) bed of 14- to 50-mesh, hydroxide-form A-26 resin. In each of three successive load cycles, 16,000, 3100, and 11,000 μCi of ⁹⁵Zr-⁹⁵Nb, and 11,000, 2000, and 4000 μCi of ¹⁰⁶Ru-¹⁰⁶Rh, respectively, were loaded after passage of 2200, 750, and 1500 bed volumes of 1CW solvent. Load cycles were terminated when the concentration of fission products in the effluent exceeded about 10% of the influent activity level. After the first load cycle, elution at 25°C with eight and six bed volumes, respectively, of 3M HNO₃ -0.05M HF and 4M NaOH removed only about 25% of the fission products. After the second load cycle, elution at 40°C with 16 and 14 bed volumes, respectively, of the HNO₃-HF and NaOH solutions removed 80% of the ¹⁰⁶Ru-¹⁰⁶Rh and 63% of the ⁹⁵Zr-⁹⁵Nb loaded in both the first two cycles. In all load cycles, breakthrough of yellow color occurred after passage of 400 to 500 column volumes of 1CW solution. As measured by plutonium retention numbers, breakthrough of DBP did not occur in any load cycle.

For routine cleanup of Purex process solvent, A-26 resin can probably be used most effectively in tail-end treatment of carbonate-washed first-cycle extractant. The resulting solvent can then be used in all Purex process cycles. With feed containing, 25 to 50 $\mu\text{Ci}/\ell$ ^{95}Zr - ^{95}Nb and 50 to 100 $\mu\text{Ci}/\ell$ ^{106}Ru - ^{106}Rh , the capacity of the resin could be high enough (5,000 to 10,000 bed volumes) to permit use on a once-through basis, thus avoiding unattractive elution steps. For convenient disposal, spent resin can be incinerated at temperatures above 500°C.

Hydraulic and fission product decontamination performance of resin-treated ICW solvent in miniature centrifugal contactor runs under modified Purex process first-cycle conditions was equal or superior to that of the 30% TBP-dodecane control solvent.

Used PRF solvent, after one extraction cycle, contains about 0.5 mg/ ℓ plutonium and 10^{-4} M DBP. A 6-inch-diameter by 4-foot-high bed of hydroxide-form A-26 resin is proposed for routine treatment of the solvent. Judging from laboratory data, this size resin bed (operated at 40°C and two column volumes per hour) will treat over 500 bed volumes of PRF solvent to yield effluent containing about 0.2 mg/ ℓ plutonium and $<10^{-5}$ M DBP.

INVESTIGATION OF THE DEGRADATION PRODUCTS OF THE SYSTEM
20% VOL.TBP-DODECANE-NITRIC ACID.
II. ANALYSIS OF PRODUCTS (30, KFK-1373)

Radiolytic Decomposition of TBP

In the radiolytic decomposition of TBP, TBP is formed as the chief product, along with a small amount of MBP. Radiolytic products found in addition to these phosphoric acid esters include hydrogen, lower hydrocarbons, as well as high molecular polymeric compounds. Particularly troublesome in the extraction process is HDBP, since it is able to form complexes with zirconium, plutonium(IV), uranium(VI), and niobium. This leads to a loss of uranium and plutonium and in extreme cases to the formation of precipitates with zirconium.

These phosphoric acid esters can be successfully removed from the organic phase with an alkaline wash, causing only temporary deterioration in the solvent.

Radiolytic Decomposition of the Diluent

Aliphatic carbonyl, nitro, nitrito and carboxyl compounds are formed in the radiolysis of the diluent and cannot be removed by an alkaline wash from the organic phase, so that they slowly increase in concentration. A long-term deterioration of the solvent is ascribed to these substances. These radiolysis products cause difficulties particularly through their tendency to form stable complexes with zirconium. As a consequence, there is an increased retention of fission products combined with a lowering of the DF for product streams.

Earlier Investigations of the Complex-Forming Decomposition Products of the Diluent

It is reported that nitroalkanes are responsible for the increased tendency to form complexes with heavy metal ions. These compounds appear in an aci-form, which is in the following equilibrium with the neutral form:

An irradiated sample of 20% TBP/80% alkane was treated with solid $\text{Ca}(\text{OH})_2$ after an Na_2CO_3 wash. Its zirconium-retention number was then determined. It was found that the test samples have a very much greater (factor of 3) at 75 Wh/l retention number than samples which have only been washed with an Na_2CO_3 solution.

As $\text{Ca}(\text{OH})_2$ forms enol-salts of nitroalkanes much faster and in greater amount than Na_2CO_3 , it was assumed that enol-salt is the complex-forming radiolysis product of the TBP/alkane mixture. However, experiments with synthetic nitroalkanes gave negative results. Their retention powers proved relatively small.

English research indicated that hydroxamic acids, which arise from the nitroalkanes as intermediates by secondary reactions, are the effective complex-forming decomposition products. Their production can be explained by the Victor Meier or Nef reactions.

Nitroparaffin

H^+ Victor-Meier-
Reaction

Aci-Form
 H^+

Nef-
Reaction

Mixture of:

Hydroxamic acids form stable complexes with metals, especially zirconium. However, it has not yet proved possible to demonstrate their presence in an irradiated TBP/dodecane sample, because they are hydrolysed to hydroxylamine. It was nevertheless believed that indications of the occurrence of hydroxamic acids in irradiated samples had been obtained from ultraviolet spectroscopic investigations. Also a solution with a high zirconium-retention number was obtained by simply adding small amounts (10^{-4}) of hydroxamic acid to a TBP/HC mixture. No such effect was obtained by adding other substances, e.g., oximes or nitrolic acids.

To determine which hypothesis was valid, it was first necessary to find optimum conditions for the production of the complexing agents and also to enrich them because they only occurred in very small quantities (10^{-5} M). Samples of 20% TBP/80% dodecane were brought into equilibrium with equal volumes of HNO_3 of different concentrations and irradiated with a ^{60}Co source. After an alkali wash, the retention number of the organic phase was determined.

The experiments showed that the production of the complexing agents occurs preferentially at low HNO_3 concentrations (0.04M). At high HNO_3 concentrations, the yield is small.

The formation of nitroalkanes, on the other hand, increases almost linearly with the HNO_3 concentration. They cannot, therefore, be primarily responsible for the increased complexing power of degraded solvent.

Experimental

Enrichment of the Complexing Agents by Distillation. The first stage of this work was to enrich the complex-forming radiolysis products in an irradiated TBP/dodecane sample.

1. Reagents - TBP was purified by washing with a 1M Na_2CO_3 solution and then with water. The fraction which came over at 0.2-mm mercury and 80°C in a subsequent vacuum distillation was then used. Normal dodecane (>99% gas-chromatographic purity) was used without further treatment.

2. Irradiation - 500 ml of a solution of 20% TBP and 80% dodecane was equilibrated with an equal quantity of 0.5M HNO and irradiated for 494 hours at an irradiation dose of 0.6 W/l, giving a total dose of 296 Wh/l. After the irradiation, the sample was washed with a 1M Na₂CO₃ solution for the removal of HDBP, H₂MBP, and H₃PO₄, and the complex-forming decomposition products were further enriched by a high-vacuum molecular distillation.
3. High-Vacuum Molecular Distillation - A pressure of less than 10⁻³ Torr is used. To bring the substances as quickly as possible to the vaporization temperature, the so-called "falling film" principle was used.
4. Determination of the Retention Number - An estimate of the extent of degradation of an irradiated solvent is obtained by the determination of the zirconium or hafnium retention number which gives the number of moles of zirconium or hafnium which are combined in the organic phase by 10⁹ l of solvent.

Results - A short-path distillation was carried out at 40, 50, 60, and 90°C. The hafnium retention number of the residue obtained at each temperature was determined. The hafnium retention number rose with rising temperature. A fraction of the complexing substances could still be removed from the residue by an alkaline wash.

The results of the high-vacuum molecular distillation are given in Table 43.

TABLE 43. Increase in the Hafnium Retention Number of the Residue After Distillation, With Rising Temperature.

Sample	Hafnium Retention Number as Obtained/Carbonate Washed	
	a	b
Residue at 40°C	not determined	
Residue at 50°C	11200	3850
Residue at 60°C	19400	8450
Residue at 90°C	24200	9150

A preliminary composition of the residue from distillation could be obtained by infrared-spectroscopy. The bands due to nitroalkanes, carbonyl compounds, and phosphoric acid esters were found. This shows that high molecular compounds are involved since any readily volatile phosphoric acid esters would already have been removed by the distillation.

Extractive Separation of the Distillation Residue. The distillation residue (90°C) was separated into three fractions by an extraction process for further investigations.

1. Separation Procedure - The distillation residue was first dissolved in ether and then extracted with 1M Na_2CO_3 solution. The inorganic phase was separated and acidified with 2M HCl . It was then extracted three times with ether. The ether extract was dried over Na_2CO_3 and the ether distilled off to produce an " Na_2CO_3 extract". The organic phase remaining after this extraction was extracted three times with water. After removal of the ether the residue was designated "neutral phase".

Hydrochloric acid was added to the aqueous phase to convert the compounds present as sodium salts to the acid form so that they could be back-extracted into the organic phase with diethyl ether. The ether solution was dried and the ether distilled off giving a " H_2O extract".

2. Investigation of the Separate Fractions - The three fractions obtained were investigated separately. To establish in which fraction the complexing agents had been enriched, the K_d for Hf^{4+} was determined. This is defined as:

$$K_d = \frac{Hf \text{ (organic phase)}}{Hf \text{ (inorganic phase)}}$$

The K_d provides, in contrast to the hafnium retention number, a qualitative indication of the complexing power of a sample under test.

- Neutral Phase - The neutral phase constituted 94% by weight of the original sample, and its complexing power was small. A K_d of 0.5 was obtained. Repeated with 3M HNO_3 removed part of the activity from the organic phase.

The principal components of the neutral phase were long-chain neutral carbonyl compounds, phosphoric acid esters, and alkanes having a small extractive power.

- H_2O Extract - The H_2O extract represented 2.4% of the original sample. It contained acid compounds which have high complexing power. They cannot be removed by a Na_2CO_3 wash since their sodium salts have a high solubility in the organic phase.
- Na_2CO_3 Extract - The Na_2CO_3 extract constituted the smallest part of the original sample, viz. 0.6%. The presence of carbonyl compounds, phosphoric acid esters and alkyl chains was confirmed, and the presence of a chelate complex indicated.

Summary. It was possible to concentrate the complexing agents into two fractions, as water extract and sodium carbonate extract.

The substances in both extracts interfere with reprocessing. Their complexing power for heavy metals causes an increased retention of fission products and reduction in the D_f of the product stream.

The products in the H_2O extract are not removed under the conditions of the Na_2CO_3 wash. They therefore become enriched in the process. It is probable that they are responsible for the long-term deterioration of the solvent.

Mass-Spectrometric Investigation of the H₂O Extract. For further study, the H₂O extract was separated gas-chromatographically and the individual compounds were mass-spectrometrically identified.

A series of substances was found at fairly low gas-chromatographic column temperatures, which could be identified as carboxylic methyl esters. All of these contained a fairly long alkyl chain, e.g., C₇H₁₅COOCH₃ and C₉H₁₉COOCH₃.

The remaining constituents of the H₂O extract were phosphoric acid esters. Since the sample had been esterified with diazomethane before investigation, the original compound must have contained an acidic hydroxyl group.

The fragment (CH₃O)(C₄H₉O)P(OH)₂ was identified, and the following general structure can be assumed for the phosphoric acid esters originally present in the H₂O fraction:

Other observations showed the possible presence of:

- Methyl and butyl ester groups.
- Chain branching in the second alkyl group, possibly from the following fragment which could be produced by the splitting off of C₄H₈OH:

mass - 265

As fragmentation occurs, preferentially at a point of branching, the presence of a branched alkyl group is indicated.

- A hydroxyl group still present on the second alkyl group.

The fragments probably have the following structures

The following decomposition scheme could account for the fragments described.

As both elimination of water and onium (CH_2OH) cleavage are fragmentation reactions which usually occur with alcohols, it can be deduced that there is a hydroxyl group in the compound. The molecular weight of the compound then probably amounts to 338.

All other phosphate esters found in the H_2O extract likewise possess an acidic hydroxyl group and an unchanged butyl group. They differ solely in their second alkyl group. As a rule, a hydrogen atom in the butyl group originally present has been replaced by an alkyl radical, produced by radiolysis of the diluent. In this way, branched alkyl residues are often formed, some with functional groups such as hydroxyl. Apart from the carboxylic acid esters which are found at low column temperatures, all the other components of the H_2O extract which can be detected gas-chromatographically are such long-chain, acid phosphate esters.

CLEANUP OF THE PUREX PROCESS TBP SOLVENT BY
MACRORETICULAR ION EXCHANGE RESIN
(31, Radiochimica Acta 22)

Used Purex process solvent from both pilot plant (10% by volume TBP in alkane) and from plant (30% by volume TBP) was used to test the efficiency of Amberlyst A-26 and A-29 resin cleanup. Kd ratios for ^{95}Zr - ^{95}Nb or ^{106}Ru - ^{106}Rh were defined as follows:

$$K_d = \frac{\text{radioactivity on resin per g of air dried resin}}{\text{radioactivity in solution per ml solution}}$$

Kd ratios of ^{106}Ru - ^{106}Rh on both resins (resin size, 22 to 30 B.S.S.) were higher for pilot-plant solvent at 40°C than at 25°C as shown below:

<u>Temperature,</u> <u>°C</u>	<u>Contact</u> <u>Time,</u> <u>min.</u>	<u>^{106}Ru-^{106}Rh</u> <u>Kd</u>	
		<u>A-26 Resin</u>	<u>A-29 Resin</u>
25	30	55	35
25	90	70	65
40	30	70	55
40	90	85	85

The Kd of ^{106}Ru - ^{106}Rh for the plant solvent at 40°C is lower and remains so after long contact time (45 and 60 for 30- and 90-minute contact times with A-26 resin at 40°C). This indicates that there is a temperature effect on distribution kinetics and that background histories of the solvents have a marked effect on the distribution data. The effect of the background histories may be due to the variation in the amounts of three different types of (ruthenium-NO) complexes present.

The Kd ratios for ^{95}Zr - ^{95}Nb given below for pilot-plant solvent are also higher at 40°C than at 25°C.

Temperature, °C	Contact Time, min.	^{95}Zr - ^{95}Nb A-26 Resin	Kd Ratios A-29 Resin
25	30	25	15
15	90	40	45
40	30	30	22
40	90	80	65

The effects of resin particle size (22 to 30 B.S.S.) on Kd ratios produced somewhat anomalous results, indicating an influence of specific radionuclides and resin type.

The Kd ratios for radionuclides in pilot-plant solvent were found to be influenced strongly by solvent pretreatment. For example, the following Kd values for ^{106}Ru - ^{106}Rb were obtained using A-26 resin at a 30-minute contact time:

<u>Solvent Pretreatment (20 to 25°C)</u>	<u>Kd</u>
None (pH = 0.5)	40
Washed with 1M sodium carbonate (resulting solvent pH = 5)	14
Alkali washed followed by 1M nitric acid wash (resulting pH = 0.5)	8

Similar observations to those above were obtained with A-29 resin. The findings indicate that the washing removes that portion of radio-activity which is responsive to washing, leaving a bound fraction which is less responsive to ion exchange removal.

The tests were repeated at 40°C. Although the results indicated some irregularities, the Kd values in each case are higher than those obtained at 20°C.

The same investigation was carried out with plant solvent at 40°C. The ^{106}Ru - ^{106}Rh Kd values for A-26 resin at a 30-minute contact time were:

Solvent Pretreatment, 40°C	Kd
None (pH = 0.5)	47
Washed with 1M sodium carbonate (pH = 5)	90
Alkali washed followed by 1M nitric acid wash (pH = 0.5)	20

The fact that the Kd ratio of the alkaline-washed solvent has the highest Kd value has not been explained. The differences in the behavior of pilot-plant and plant solvent have been ascribed to the difference in histories of the two solutions, e.g., solvent and diluent compositions, number of recycles, total contact time, radiation exposure dose to the organic phase, and age after use in the process.

To compare the retention of ruthenium complexes in both pilot-plant and plant solvent, solvent samples were washed exhaustively with sodium carbonate at 60°C. The results are shown in Table 44.

It can be seen that the plant solution is less responsive to alkali washing and retains a higher amount of ruthenium complex.

To get an indication of the response of the bound fraction of the ruthenium complex toward A-26 resin, 2 g instead of 0.25 g of resin was contacted with exhaustively washed plant solution. The data presented indicate that the bound fraction of the ruthenium complex, irrespective of the kinetics and equilibrium, is quite responsive to A-26 resin at a pH of 5.0 and 40°C.

TABLE 44. Retention of ^{106}Ru - ^{106}Rh at Different Stages of Alkaline Washing of the Pilot Plant and Plant Solutions.

Stages of Washing	Pilot-Plant Solution		Plant Solution	
	cpm/ml of org. phase	Activity left in org. phase % of the blank	cpm/ml of org. phase	Activity left in org. phase % of the blank
Solution as supplied (Blank)	118	--	119,510	---
Normally washed solution (washed with equal volume of 1M Na_2CO_3 at 20°C for 5 min.)	50	41.7	71,790	60.1
1st wash with equal vol of 1M Na_2CO_3 at 60°C for 80 min.	28	23.3	57,380	48.0
2nd wash with equal vol of 1M Na_2CO_3 at 60°C for 80 min.	33	27.9	51,170	42.8
3rd wash with equal vol of 1M Na_2CO_3 at 60°C for 80 min.	21	17.4	44,150	36.0

Response of the so-called bound fraction of ruthenium-complex remaining in cpm/ml of plant solution after exhaustive washing toward 2.0 grams A-26 resin contacted at 40°C is shown in Table 45.

The lower K_d values for 2.0-g sample, compared to those for 0.25-g sample are not necessarily due to exhaustive washings. An increase in the amount of solid is equivalent to a decrease in solution concentration, and K_d values are likely to decrease.

TABLE 45. Distribution Coefficients for Bound Ruthenium as a Function of Times.

Contact time, min	cpm/ml in the org. phase for ^{106}Ru - ^{106}Rh	Activity left in the org. phase % of the blank at 0 min. contact time		Kd	Kd values for contacting 0.25 gram A-26 at 40°C with 10 ml normally washed solution
0	42,810		(35.8) ^a	--	--
10	10,280	24.0	(8.6)	14.9	79.3
30	7,730	18.0	(6.5)	21.7	90.3
60	6,140	14.3	(5.1)	28.9	109.8
90	5,360	12.5	(4.5)	33.9	113.6
120	4,310	10.0	(3.6)	43.6	118.9
240	1,920	4.5	(1.6)	104.9	---

^aFigures within parentheses indicate percent left in the organic phase in terms of the activity in the supplied plant solution as blank.

REACTION OF PLUTONIUM(IV) WITH DBHP IN AN ORGANIC PHASE
(32, RJIC21)

There is no published information on the nature of the reaction of plutonium(IV) with DBHP (DBP or HA) in solutions of TBP in various organic diluents. The presence of appreciable quantities of DBP in the TBP-diluent system leads to a marked increase in the DF of plutonium for its extraction from nitric acid solutions.

Organic solutions of plutonium(IV) were prepared by extracting the metal from 3M nitric acid solutions by 10 vol % TBP-diluent (CCl_4 or hydrocarbon) mixtures. The spectrophotometric titration (room temperature, absorption bands at 492 and 726 nm) was carried out using solutions of DBP in the same diluents. The reaction between plutonium(IV) and DBP in organic solutions takes place in less than 10 seconds.

The absorption spectra obtained in the titration of plutonium(IV) with DBP in TBP diluent show several isosbestic points which indicate the formation of a stable complex of plutonium(IV) and DBP. The change in the optical density of the solutions shows that the optical density becomes constant at a molar ratio $\text{DBP}:\text{Pu(IV)} = N \approx 2$. The reaction between plutonium(IV) and DBP in organic solutions can be represented by the equation:

At $N < 2$, the spectra of solutions of $\text{Pu}(\text{NO}_3)_4 \cdot 2\text{HA}$ in CCl_4 and hydrocarbon are practically identical. At $N > 2$, however, the formation of a flocculent pink precipitate of plutonium(IV) DBP in the TBP-hydrocarbon system leads to a change in the absorption spectrum and the appearance of a sharp inflection on the plot of optical density against A in the region of $N \approx 2$. In the TBP- CCl_4 system, plutonium(IV) DBP precipitates are not formed at any values of N .

The stability constant (K_H) of the complex of plutonium(IV) with DBP, formed by reaction (1), was calculated from the equation:

$$K_H = \frac{[\text{Pu}(\text{NO}_3)_4 \cdot 2\text{HA}][\text{TBP}]^2}{[\text{Pu}(\text{NO}_3)_4 \cdot 2\text{TBP}][\text{HA}]^2} \quad (2)$$

In the calculations, the concentration of the TBP was taken as equal to the concentration in the original solution. The exponent of $[\text{HA}]$ was found graphically from the slope of the straight line $\log [\text{HA}] - \log [\text{Pu}(\text{NO}_3)_4 \cdot 2\text{HA}]$. The exponent of $[\text{HA}]$ in Eq. (2) is close to 1, which does not correspond to the stoichiometric coefficient of the proposed equation for the reaction.

The difference between the calculated coefficient and that corresponding to the stoichiometry of the equation (<1) must be due to the high degree of dimerization of DBP in the TBP diluent systems. The degree of dimerization of DBP in organic solvents is low in pure TBP, but it increases sharply in CCl_4 and hydrocarbons and in these diluents DBP is present chiefly as a dimer.

Calculations of the stability constant of the complex $\text{Pu}(\text{NO}_3)_4 \cdot 2\text{HA}$ in solutions of TBP in CCl_4 and hydrocarbon are in Table 46.

The numerical values of the concentrations of the complexes $\text{Pu}(\text{NO}_3)_4 \cdot 2\text{HA}$ and $\text{Pu}(\text{NO}_3)_4 \cdot 2\text{TBP}$ were calculated. The results are given in Table 47.

Table 47 shows that K_H for $\text{Pu}(\text{NO}_3)_4 \cdot 2\text{HA}$ in a 10% solution of TBP in CCl_4 or hydrocarbon remains constant up to $N = 2$. The average value of K_H at $N \leq 2$ is $(3.30 \pm 0.14) \times 10^{-2}$ for a solution of TBP in CCl_4 and $(8.20 \pm 0.25) \times 10^{-2}$ for a solution of TBP in hydrocarbon.

It was shown that the values of N at which plutonium(IV) DBP is precipitated are determined by the concentration of TBP in hydrocarbon (Table 47): with an increase in the concentration of TBP from 1 to 30 vol %, the value of N increases from 0.4 to 14.5. A compound of DBP with plutonium(IV) is not precipitated from solutions containing 40% TBP, irrespective of N .

TABLE 46. Calculation of the Stability Constant of the Complex $\text{Pu}(\text{NO}_3)_4 \cdot 2\text{HA}$ in Solutions of TBP in CCl_4 and Hydrogen.

$[\text{HA}], \text{M}$	N^a	C_D^b	C_T^c	K_H^d
TBP (10 vol%)- CCl_4 System				
0	---	0	$6.20 \cdot 10^{-3}$	---
$7.16 \cdot 10^{-4}$	0.18	$3.5 \cdot 10^{-4}$	$5.86 \cdot 10^{-3}$	350
$3.30 \cdot 10^{-3}$	0.53	$1.30 \cdot 10^{-3}$	$4.92 \cdot 10^{-3}$	356
$5.51 \cdot 10^{-3}$	0.80	$2.65 \cdot 10^{-3}$	$3.62 \cdot 10^{-3}$	328
$7.76 \cdot 10^{-3}$	1.25	$3.66 \cdot 10^{-3}$	$2.54 \cdot 10^{-3}$	316
$9.90 \cdot 10^{-3}$	1.60	$4.55 \cdot 10^{-3}$	$1.71 \cdot 10^{-3}$	312
$1.19 \cdot 10^{-2}$	1.96	$5.20 \cdot 10^{-3}$	$1.00 \cdot 10^{-3}$	326
$1.45 \cdot 10^{-2}$	2.32	$5.85 \cdot 10^{-3}$	$0.40 \cdot 10^{-3}$	490
$1.65 \cdot 10^{-2}$	2.67	$6.02 \cdot 10^{-3}$	$0.18 \cdot 10^{-3}$	705
TBP (10 vol%)-Hydrocarbon System				
0	---	---	$6.86 \cdot 10^{-3}$	---
$9.48 \cdot 10^{-5}$	0.14	$4.70 \cdot 10^{-4}$	$6.36 \cdot 10^{-3}$	868
$7.72 \cdot 10^{-4}$	0.25	$8.50 \cdot 10^{-4}$	$5.67 \cdot 10^{-3}$	802
$4.04 \cdot 10^{-3}$	0.59	$1.80 \cdot 10^{-3}$	$4.72 \cdot 10^{-3}$	815
$5.54 \cdot 10^{-3}$	0.81	$2.73 \cdot 10^{-3}$	$3.79 \cdot 10^{-3}$	846
$6.42 \cdot 10^{-3}$	0.94	$3.16 \cdot 10^{-3}$	$3.36 \cdot 10^{-3}$	882
$9.58 \cdot 10^{-3}$	1.40	$4.65 \cdot 10^{-3}$	$1.87 \cdot 10^{-3}$	836
$1.39 \cdot 10^{-2}$	1.93	$6.15 \cdot 10^{-3}$	$3.70 \cdot 10^{-4}$	822

^aN = Ratio TBP to plutonium(IV).^bC_D = Concentration of complex $\text{Pu}(\text{NO}_3)_4 \cdot 2\text{HA}$.^cC_T = Concentration of complex $\text{Pu}(\text{NO}_3)_4 \cdot 2\text{TBP}$.^dK_H = Equilibrium constant.

TABLE 47. Influence of the Concentration of TBP in Hydrocarbon on the Precipitation of Plutonium(IV) DBP.

Concentration in the Original Solution		Concentration of DBP at the start of precipitation g/l	N ^a
TBP, vol%	Pu, g/l		
1	0.11	0.04	0.4
2	0.22	0.18	0.8
5	1.09	1.82	1.8
10	1.80	3.70	2.3
15	1.36	3.37	2.8
20	1.30	4.23	3.7
25	1.24	4.37	4.1
30	1.76	22.40 ^b	14.5 ^b
40	2.14	38.00 ^b	20.0 ^b

^aN = Ratio DBP to plutonium(IV).^bNo precipitate formed.

At the same time, at a constant TBP concentration (10 vol%) the limiting value of N, above which plutonium(IV) DBP is precipitated, depends on the concentration of plutonium(IV) in the solutions. At a plutonium concentration 0.05 to 0.67 g/l⁻¹ and N = 1.8, a precipitate is not formed. At N = 2, a precipitate appears in solutions containing more than 0.38 g/l plutonium. In solutions containing 0.21 g/l plutonium, a precipitate was found at N = 2.4, and in solutions containing 0.11 g/l plutonium or less, a precipitate was not formed even at N = 5.

The rate of precipitation of plutonium(IV) DBP from solutions of TBP in hydrocarbon is determined by many factors. The decrease in the concentration of plutonium in the solution (c_t , g/l) as a function of the logarithm of the reaction time t (the time interval from the moment when the solutions were mixed to the time t , hours) is almost linear throughout the entire range of t . Thus, the possibility of formation of the plutonium(IV) DBP precipitate in the TBP hydrocarbon system and the degree of precipitation of plutonium from the solution are determined by the concentrations of TBP, DBP, and plutonium, and by the reaction time. In the

the case of 10% TBP solution, plutonium(IV) DBP separates rapidly from solutions containing ≤ 0.2 g/l plutonium at $N \geq 2$, but at a plutonium concentration 0.2 g/l a considerable excess of DBP ($N \geq 2$) and a long reaction time are required. At $t = 100$ to 200 hours and $N = 2.5$, practically all the plutonium can be precipitated; if its concentration in the solution ≥ 0.78 g/l.

The plutonium(IV) DBP precipitates were analyzed for plutonium, DBP, and nitrate ion. The DBP:plutonium ratios in the precipitates (N) are given in Table 48.

Table 48 shows that, irrespective of N (in the range 2.5 to 18) the value of $\underline{n}$ in the precipitates is close to 2. The precipitates also contain NO_3 groups (two NO_3 groups per plutonium atom). The plutonium(IV) DBP insoluble in solutions of TBP in hydrocarbon has the composition $\text{Pu}(\text{NO}_3)_2\text{A}_2$.

The reflectance spectra of the precipitates confirm that the $\text{Pu}(\text{NO}_3)_2\text{A}_2$ obtained from organic and aqueous solutions are identical.

TABLE 48. Composition of the Plutonium(IV) DBP Formed in the TBP (10 vol%) Hydrocarbon System, $t = 2$ hours.

Concentration After the Solutions Were Mixed, g/l		N^a	Concentration in the Mother-Liquors, g/l		N^b
Plutonium	DBP		Plutonium	DBP	
0.60	1.31	2.5	0.21	0.50	2.03
0.86	1.90	2.5	0.29	0.45	2.20
1.54	3.40	2.5	0.57	1.35	2.15
1.98	4.44	2.5	0.73	2.02	1.93
1.65	5.82	4.0	0.55	3.69	2.10
2.01	10.30	5.9	0.56	6.88	2.19
1.63	15.60	10.9	0.44	12.60	1.95
1.44	22.80	18.0	0.34	20.30	2.20

$^a N$ = Ratio DBP to plutonium(IV) in solution.

$^b N$ = Ratio DBP to plutonium(IV) in precipitates.

$\text{Pu}(\text{NO}_3)_2\text{A}_2$ is soluble in benzene and at a concentration in this solvent equal to 0.4 g/l (calculated as the metal) the solution forms a gel. Cryoscopic measurements showed that in the concentration range 0.25 to 0.4 g/l (calculated as the metal) in benzene, $\text{Pu}(\text{NO}_3)_2\text{A}_2$ exists in the form of a polymer having an average degree of polymerization, $\alpha \approx 11$ (molecular weight $\approx 8.8 \times 10^3$).

The infrared spectra of plutonium(IV) DBP were recorded in the wave number range 700 to 4,000 cm^{-1} , and were compared with the infrared spectrum of pure DBP. Differences in the spectrum indicate the formation of a compound of plutonium with DBP containing NO_3 groups. This is also indicated by the analogy which can be drawn between the compounds $\text{Pu}(\text{NO}_3)_2\text{A}_2$ and $\text{Zr}(\text{NO}_3)_2\text{A}_2$.

In examining the possible structure of $\text{Pu}(\text{NO}_3)_2\text{A}_2$, the formation of two types of bond between the metal atom and the DBP molecules must be assumed; through the phosphoryl oxygen atom plutonium...O = P and the free oxygen atom of the DBP anion plutonium - O - P = O. The ionized $\text{P}^{\text{O-}}$ group can be coordinated in different ways. The properties of phosphoric acids indicate that the DBP molecule most probably acts as a bridging ligand, capable of forming chain or three-dimensional polymeric structures. Thus the structure of the compound $\text{Pu}(\text{NO}_3)_2\text{A}_2$ can be represented as follows:

A NEWLY DEVELOPED SOLVENT WASH PROCESS IN NUCLEAR FUEL
REPROCESSING DECREASING THE WASTE VOLUME
(33, Kerntechnik, 18)

To minimize the volume of radioactive waste resulting from solvent regeneration by the classical sodium carbonate treatment, a cleanup procedure employing hydrazine or hydrazonium carbonate combined with fine cleaning over lead oxide in silica gel solid bed columns is suggested. Hydrazine can then be decomposed into nitrogen and water by anodic oxidation. The concentration of degradation products not removed during alkaline treatment is reduced by more than an order of magnitude in the following lead oxide fine cleaning step.

Experimental Results of Solvent Treatment by Liquid Wash

DF for HDBP and fission products are compiled in Table 49. The data represent results from solvent samples from the Wiederaufarbeitungsanlage Karlsruhe (WAK) and the "MILLI" highly shielded miniature extraction facility, Institute of Hot Chemistry, Karlsruhe. The samples were stirred thoroughly for 5 minutes in a mixing vessel with 0.1M sodium carbonate or with hydrazine of 0.1 to 0.2M at a volume ratio of 50 to 1 solvent to wash. Table 49 also displays the DF of fission products for various washing cycles of pilot-plant solvent and the increase in DF achieved with increasing wash temperatures. Operating temperatures of 50°C are feasible. Results obtained during inactive runs in a HolleyMott-type mixer-settler of the WAK design are listed in row 3. At a contact time of 10 minutes, DF of above 100 were achieved.

Experimental Results with Solid-Bed Lead-Oxide Columns

TBP of 20% by volume was irradiated with a ^{60}Co source at a total dosage of 40 Wh/l. Subsequently, degradation products soluble in water were first removed by treatment with 1M Na_2CO_3 and 0.5M nitric acid. Afterwards, the solvent was passed through a solid bed column with 90% by weight silica gel layered with 10% by weight lead oxide. To measure the effectiveness of the lead oxide treatment as to removal of higher-order and dimer phosphoric acid esters, the extraction of hafnium nitrate was studied.

TABLE 49. DF for HDBP, Zirconium, Niobium, Ruthenium and Rhodium.

Feed	Contact Time, min.	Cleaning Solution	DF for HDBP	
WAK solvent Zr/Nb 1.5 $\mu\text{Ci}/\ell$	5	0.1M Na_2CO_3	= 100	
Ru/Rh 8 $\mu\text{Ci}/\ell$ HDBP 270 $\mu\text{g}/\ell$	5	0.1M $\text{N}_2\text{H}_5\text{OH}$	= 100	
Unirradiated solvent HDBP 400 $\mu\text{g}/\ell$	10	0.1 to 0.2M Na_2CO_3 $(\text{NH}_4)_2\text{CO}_3$	> 100	
			DF for Fission Products	Temp., $^{\circ}\text{C}$
MILLI solvent Zr/Nb = 5 Ci/ℓ Ru/Rh	5	0.2M $\text{N}_2\text{H}_5\text{OH}$	2.5 (1st Stage) 4.8 (2nd Stage) 15 (3rd Stage)	25
			6.5 (1st Stage) 11 (1st Stage)	50 75

The results are presented in Table 50. After putting through 10 column volumes of solvent, the extraction of hafnium was 14 times lower than that of untreated solvent.

TABLE 50. Cleaning Factors with Respect to Dimer and Higher Order Phosphoric Acid Esters.

Throughput (Number of Column Volumes), ml	Hafnium Extracted after Cleaning, cpm/ml	Cleaning Factor
0 (0)	92000	-
16 (1.06)	387	238
39 (2.6)	838	109
60 (4)	850	108
81 (5.4)	2476	37
105 (7)	8299	11
129 (6.5)	5464	16
151 (10.1)	6496	14

TOWARD CLARIFICATION OF COMPLEXFORMING RADIOLYSIS PRODUCTS OF THE PUREX SYSTEM (20% TBP-DODECANE-HNO₃) (34, KFK-2304)

The lifetime of Purex solvent extraction system is limited by radiolytic and hydrolytic decomposition of the solvent and diluent. The decomposition products of TBP can be removed from the process by an alkali wash. However, materials of an unknown nature are not removable by carbonate washing and increase in concentration with time. The consequences are an increase in the retention of fission products, especially zirconium, lost uranium and plutonium as well as the formation of emulsions and difficult of phase separation.

There are several hypotheses regarding the nature of these compounds. They may be: (1) nitro compounds, which form from the diluent and in their enol form bound with zirconium either in the form of a salt or an adduct complex in the organic phase, (2) hydroxamic acids which arise from the aliphatic nitro compounds or secondary reactions such as the VictorMeier or the Nef Reaction; or (3) acidic long-chain and higher molecular weight phosphate esters as possible complex formers.

Five hundred milliliters of a mixture of 20% TBP and 80% dodecane were irradiated with an equal amount of 0.5M nitric acid, in a ⁶⁰Co source to a dose of 0.6 W/l. The temperature was 30 to 35°C, and the inorganic phase was changed frequently. After the irradiation, the lower molecular weight acidic decomposition products such as MBP and DBP were removed first from the organic phase by an alkali wash. The lower boiling components were removed by molecular distillation of 90°C and 10⁻³ Torr, and the complex formers remained in the residue.

The distillation residue was separated by liquid chromatography into fractions with essentially individual compounds which could be identified. Dichlormethane, acetic acid, and methanol were used as elution agents. The complex former was concentrated in the methanol fractions by this procedure. The partition coefficients of the other fractions were so low that there is a high probability no complex formers would be found.

To clarify their chemical properties, all fractions were analyzed by a combination of gas chromatography and mass spectrometry. Fractions resulting from the chromatographic separation may be combined into three groups:

1. The nonpolar components which represent 45% or about half of the effluent samples and lie in the first three fractions. The question raised by these compounds is whether they are exclusively the radiolysis products of the diluent, such as paraffins, olefins, and ketones.

2. The four fractions in which the neutral phosphate esters lay could be combined into a second group. This represented 35% of the effluent. Monomers and dimeric phosphate esters besides some polyphosphates are the chief components of these fractions. As dimeric products, such compounds as two phosphate groups bound to a single alkyl group in one molecule, were identified. The dimeric compounds which could be identified appeared to be isomers of dimeric TBP. The presences of pyrophosphate esters was proven.

3. The complex-forming radiolysis products, which occur in both of the methanol fractions and comprised 20% of the effluent, was the third group. Some TBP and DBP are contained in this fraction. As the complex formation proceeds, the long-chain monomeric and dimeric phosphate esters are formed principally. These decomposition products are responsible for greater impairment of irradiated solvent than the others. Presumably, long-chain polycarbonyl compounds in the enol form in small amounts are the chief components of the second methanol fraction to be highly retentive to fission products. In that state, they form stable chelate complexes with four valent metals. The troublesome influence of these polycarbonate compounds, even considering their low concentration, is comparable with that of the acid phosphate esters.

The magnitude of the part played by the nonvolatile compounds in the methanol fraction, which are not detectable by gas chromatography, remains open. The amount of the nonvolatile component, determined thermogravimetrically, contained 31.7% phosphate esters and 19.9% polycarbonyl compounds, and amounts to 14% of the eluted sample.

The high molecular components in the phosphate fraction were separated further by gas chromatography by this method into two fractions which had a maximum of molecular weights of 800 and 1005. This corresponds approximately to oligomeric phosphate esters which are the result of the addition of three and sometimes four TBP molecules. The infrared spectra shows only the characteristic absorption bands of phosphate esters.

The work could be summarized as follows:

1. The complex formers could be separated on the basis of their low volatility through a molecular distillation and found in the distillation residue.
2. The distillation residue was separated liquid chromatographically into nine fractions and it was possible to concentrate the complex former into two polar fractions.
3. The chemical composition of a single fraction could be determined by a combination of gas chromatography and mass spectrometry. Of special interest was the composition of either complex forming fractions which was shown as a long chain phosphate ester. In subordinate amounts are found polycarbonyl compounds which are responsible for the increased retention of fission products.
4. The high molecular weight component of the phosphate ester fraction could be separated gas chromatographically and was identified as an oligomeric phosphate ester.

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