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SUBJECT: Some Effects of Radiation on Solvent Extraction Processes

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DISCLAIMER

Some Effects of Radiation on Solvent Extraction Processes

ABSTRACT

The yield of total acid, G_{acid}, in the radiolysis of tributyl phosphate-Amsco 125-82 solutions is 2.7 times the electron fraction of TBP, or approximately 2.7 times the weight fraction of TBP, per 100 ev of energy absorbed by the solution. Dibutyl phosphoric acid, DBPA, constitutes about 85% of the acid. Radiolysis of TBP also results in the conversion of about 0.9 molecules of TBP to a polymer per 100 ev of energy absorbed.

Uranium extraction-stripping tests with an 8 stage spinner column have shown that one mole of uranium is retained in the organic phase during the stripping operation per mole of DBPA added prior to the extraction operation. This is at least twice as much uranium as would be expected on the basis of a compound of the composition $UO_2(DBP)_2$. On the basis of a tentative molecular weight of 843 g/mole, the polymer retains in the organic phase during stripping operations about 1.2 moles of uranium per mole of polymer added prior to extraction. In addition to polymer and acids, condensed phase radiolysis products include olefins, whose yield, expressed as $G_{c=c}$, or number of double bonds formed per 100 ev of energy absorbed, decreases from ca 4 to 1 as the TBP concentration increases from 4.5 to 100 wt %.

Among newer extractants being examined for use in radiochemical reprocessing, diethyl carbonate, DEC, has been tested for uranium retention and fission product decontamination properties. After irradiation to the 400 watt-hr/liter level, the uranium retention by DEC on stripping is decreased, rather than increased. Although γ-decontamination was adversely affected, β-decontamination was essentially unaffected by irradiation to this level.

INTRODUCTION

After partial burn-up, it is necessary to remove fuels from nuclear reactors in order to remove fission products. The process most widely used to effect this removal is solvent extraction, in which process the fissile or fertile elements (uranium, thorium, plutonium) transfer from an aqueous phase to an organic extractant solution while the fission products remain in the aqueous solution. Like other organic compounds, the extractant is subject to decomposition by radiation from the fission products. We shall be concerned with some of the effects of the radiolysis products on the extraction process.

TRIBUTYL PHOSPHATE - AMSCO 125-82 SYSTEMS

Tributyl phosphate (TBP) in a kerosene-like diluent is the most widely used of the many possible extractants (4,5,12,13,16); its radiolysis has been studied extensively (1,7,8,9,11,14,15,17). Some of the known deleterious effects of radiation on TBP extraction processes are 1) retention of uranium and plutonium in the organic phase during stripping operations, 2) extraction of some of the fission products (particularly Zr, Ru, and possibly I_2), 3) formation of a very insoluble thorium compound, which has necessitated the addition of a filtration step to the Thorex Process when high burn-up, short decayed fuels are processed, and 4) emulsion formation, which increases phase separation time, thereby decreasing column efficiency.

Neglecting gases, the principal product of the radiolysis of TBP is dibutyl phosphoric acid (DBPA). Monobutyl phosphoric acid (MBPA) and H_3PO_4 are formed in considerably smaller quantities. DBPA is known to be one of the principal causes of trouble in radiochemical reprocessing. For example, it forms a solvent-soluble complex with uranium, presumably uranyl dibutyl phosphate; with thorium, on the other hand, it forms a compound that is very insoluble in aqueous or organic phases. The solubility of the compound, probably thorium

tetra-dibutyl phosphate, in TBP-kerosene solution is less than 0.04 g/liter (17).

DBPA accounts for about 85% of the total acidic products from the radiolysis of TBP-kerozene solutions. Yield studies, Figure 1, show that

$$G_{acid} = 2.7\ F^{e}_{TBP}, \qquad (1)$$

where F^{e}_{TBP} is the electron fraction of TBP in the kerosene solution. To a close degree of approximation, $F^{e}_{TBP} \tilde{=} W_{TBP}$ = weight fraction of TBP in the solution. If the radiation dose density, D, is expressed in terms of watt-hr/liter, then the molarity of the acidic product may be expressed as

$$\underline{M}_{acid} = 9.20 \times 10^{-4}\ DW_{TBP}, \qquad (2)$$

or

$$W_{acid} = 9.20 \times 10^{-7}\ DW_{TBP}\ \frac{(\text{M Wt of acid})}{\text{\% solution}} \qquad (3)$$

Using $W_{TBP} = 0.4$, corresponding to the approximately 40% TBP in Amsco 125-82 used in the Thorex Process first cycle extraction column (5), it can be shown that the thorium compound will start precipitating when the radiation dose exceeds about 0.38 watt-hr/liter.

As Cathers (9) has indicated, deleterious effects are observable when radiation dose densities have increased to 0.1 to 0.5 watt-hr/liter, corresponding, for example, to 7.14×10^{-4} to 3.57 to 10^{-3} wt % radiolytic acids (DBPA, MBPA, H_3PO_4) in TBP-Amsco 125-82 solutions.

Laboratory studies have been performed to determine the effect of DBPA and radiolytic polymer on uranium distribution coefficients and phase separation times. In these experiments, purified DBPA or polymer isolated from TBP that had been irradiated to 1900 watt-hr/liter were added in known quantities to pure TBP to the concentrations indicated in Figure 2. The TBP plus addend was then diluted to 25% W/V in Amsco and contacted with 2 volumes of 2 $\underline{M}$ HNO_3 - 0.2 $\underline{M}$ $UO_2(NO_3)_2$. Data plotted in Figure 2 were obtained with an 8 stage (calibrated) spinner column and express the ratio of uranium in the stripped organic stream to that in the aqueous product stream. The effects of both DBPA and polymer on retention of uranium by the organic phase during stripping

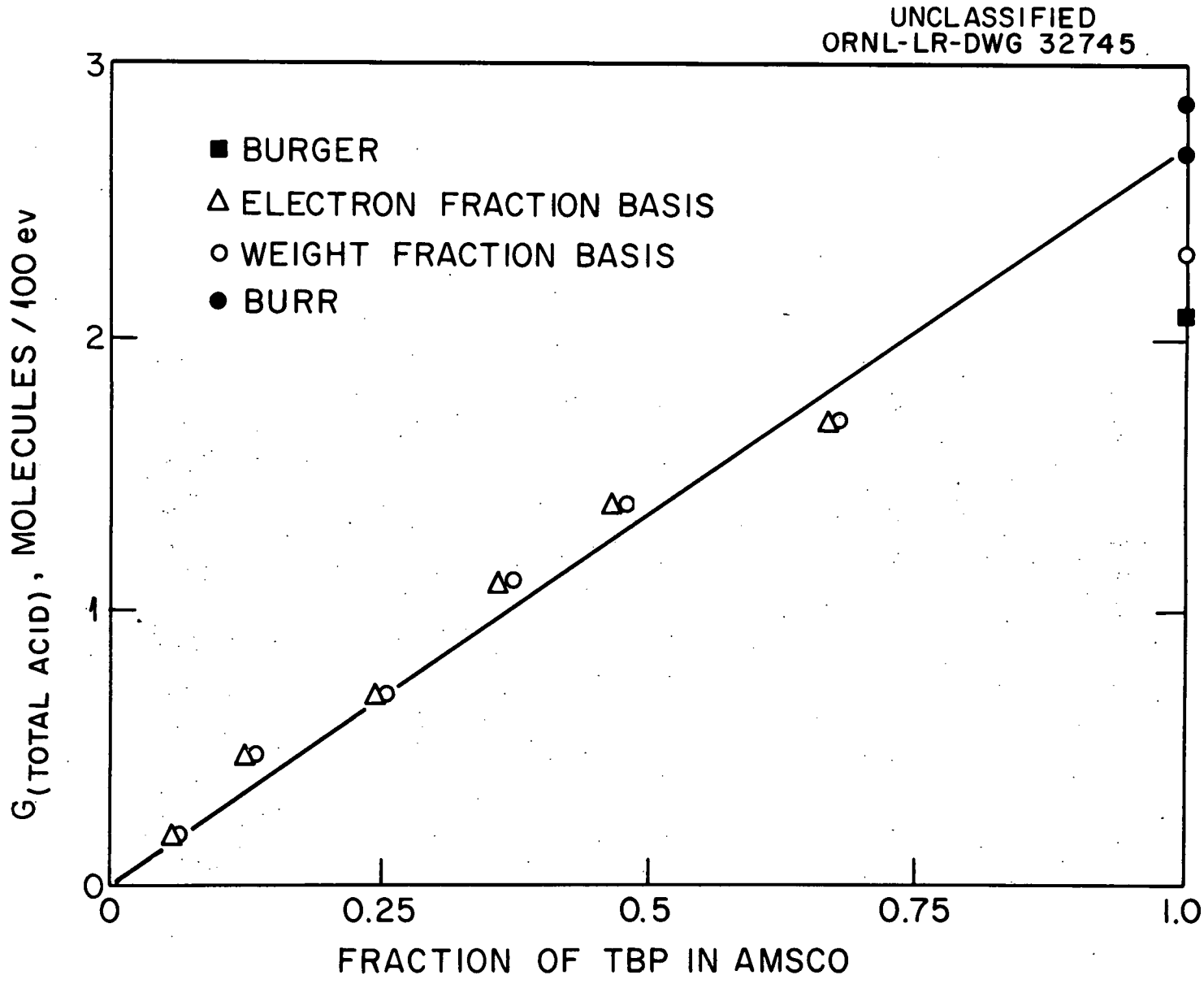

Figure 1: Acid Yield in the Hydrolysis of TBP-Amsco 125-82 Solutions: Dose: - 1.60×10^{13} ergs/kg solution (Approx. 400 watt-hr/liter).

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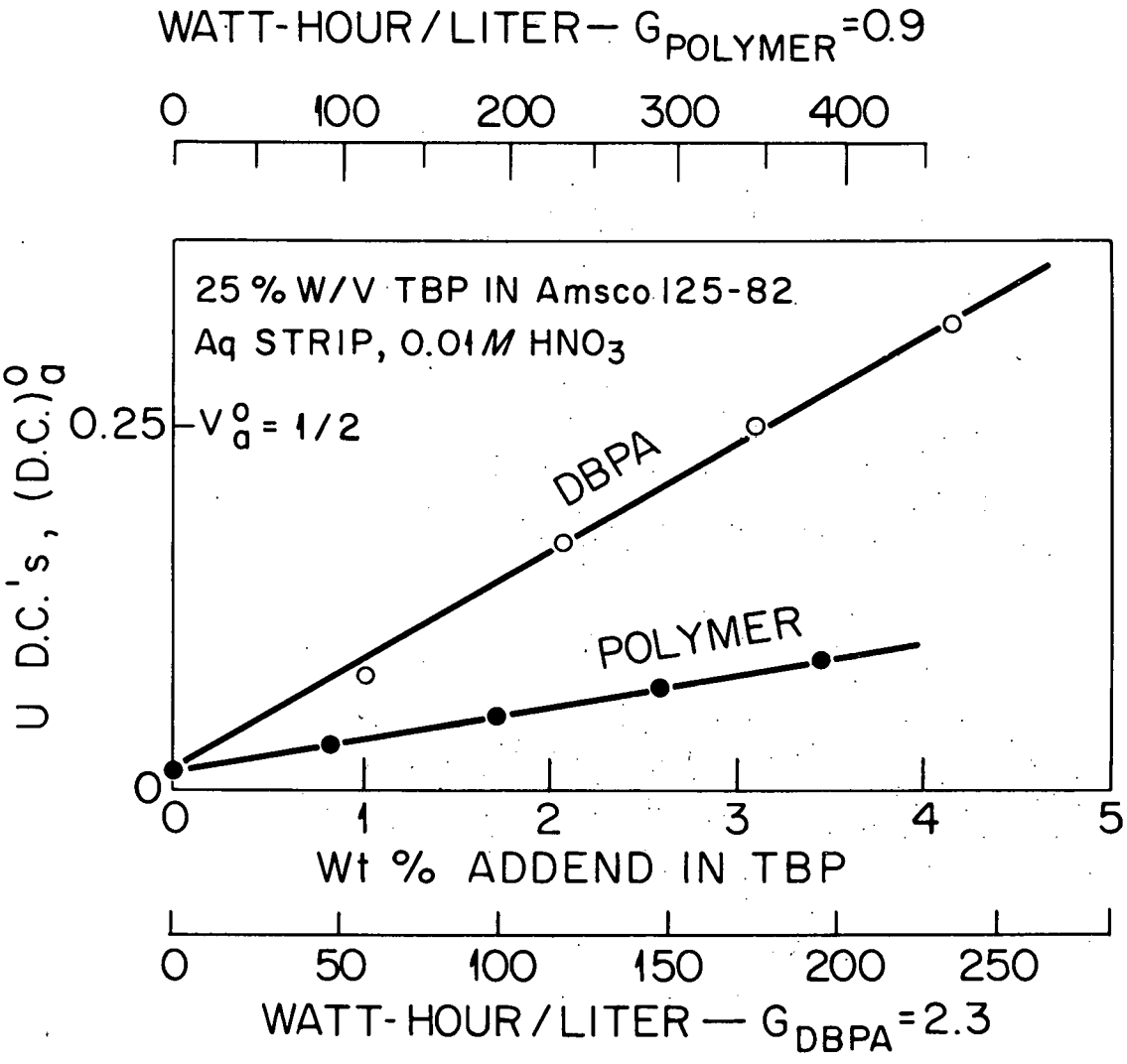

Figure 2: Effect of Dibutyl Phosphoric Acid (DBPA) and Radiolytic Polymer from TBP on Uranium Retention by the Extractant during Stripping Operations.

are linearly dependent on concentration and, therefore, on dose density. In the dose density correlation, equations similar to 1 and 2 were used, $\underline{M}_{acid}$ in these equations being replaced by $\underline{M}_{DBPA}$ or $\underline{M}_{Polymer}$ and G_{acid} by G_{DBPA} or $G_{Polymer}$. For G_{DBPA} a value of 0.85 G_{acid} was used; for $G_{Polymer}$ (actually the number of molecules of TBP converted to polymer per 100 ev of energy absorbed) an experimental value of 0.9 was used. This was determined from the irradiation of TBP to the 1900 watt-hr/liter level; Burr (8) has reported values of 1.50 and 2.47.

The data of these experiments can be used to calculate the uranium loss due to complexing with DBPA or polymer, wherein pertinent terms are defined as follows.

X_f = concentration of uranium in the extraction cycle aqueous feed, $\underline{M}$;

X_w = concentration of uranium in the extraction cycle aqueous waste, $\underline{M}$;

Y = concentration of uranium in the extraction cycle organic product and stripping cycle organic feed, $\underline{M}$;

X = concentration of uranium in the stripping cycle aqueous product, $\underline{M}$;

Y_w = concentration of uranium in the stripping cycle organic waste, $\underline{M}$;

F = aqueous extraction cycle feed rate;

Q = organic extraction and stripping cycle flow rates;

S = aqueous stripping cycle flow rate.

From a uranium balance across the spinner column we may write

$$Y_w = \frac{\frac{Q}{S}\left(\frac{Y_w}{X}\right)}{\frac{Q}{S}\left(\frac{Y_w}{X}\right) + 1} Y \qquad (4)$$

for the stripping operation in the absence of added DBPA or polymer, and a similar expression for the case of added DBPA or polymer. We may express the increase in uranium retention in the organic phase, during the stripping operation, due to the presence of the addend as

$$Y'_w - Y_w = \frac{\frac{Q}{S}\left[\left(\frac{Y_w}{X}\right)' Y' - \left(\frac{Y_w}{X}\right) Y\right]}{\left[\frac{Q}{S}\left(\frac{Y_w}{X}\right)' + 1\right]\left[\frac{Q}{S}\left(\frac{Y_w}{X}\right) + 1\right]}; \qquad (5)$$

the prime refers to the system containing the addend. With the conditions X_f = 0.2 M, (Y_w/X) and Y as listed in Table 1, (Q/S) = 0.5, and (Q/F) = 0.5, it may be seen that the retention of uranium in the organic phase persists through an 8 stage stripping operation and that the uranium retention is about twice that expected on the basis of a compound $UO_2(DBP)_2$. For each mole of DBPA added to the system prior to extraction, one mole of uranium is retained after 8 stages of stripping.

Table 1. Permanency of the Retention of Uranium by Dibutyl Phosphoric Acid in a 25% TBP-Amsco 125-82 Solution*

Concn. of DBPA, M	Uranium Distribution Coefficient, $\frac{Y_w}{X} = E_a^o$	Equivalent Radiation Dose, Watt-hr/liter	Organic Phase U Concn., Y, M	U-Retention Due to DBPA, M	Moles U Lost Per Initial Mole DBPA
0.00000	0.011	0	0.354	0.0000	0.00
0.01225	0.08	63	0.391	0.0131	1.07
0.02450	0.17	125	0.391	0.0287	1.17
0.03675	0.25	188	0.391	0.0415	1.13
0.04900	0.32	251	0.391	0.0520	1.06

*See Text for experimental conditions.

Table 2. Permanency of the Retention of Uranium by Polymer Produced During Irradiation of TBP in a 25% TBP-Amsco 125-82 Solution*

Concn. of Polymer,** M	Uranium Distribution Coefficient, $\frac{Y_w}{X} = E_a^o$	Equivalent Radiation Dose, Watt-hr/liter	Organic Phase U Concn., Y, M	U-Retention Due to Polymer, M	Moles U Lost Per Mole of TBP Initially Present as Polymer**
0.00000	0.011	0	0.354	0.00000	0.000
0.00813	0.03	106	0.340	0.00309	0.380
0.01626	0.05	212	0.340	0.00636	0.391
0.02439	0.07	318	0.340	0.00957	0.392
0.03252	0.09	424	0.340	0.01271	0.391

* See Text for experimental conditions.

** The concentration of polymer is expressed in units of TBP since the only molecular weight determination, 843 g/mole, is very tentative. Approximately 0.9 molecules of TBP are converted to polymer per 100 ev of energy absorbed.

The quantitative correlation of uranium retention with radiolytic polymer concentration is given in Table 2. Here agin, the retention is large, even after an 8 stage stripping operation, and corresponds to ca 0.4 moles of uranium per molecule of TBP contained in the polymer. If the tentative, average molecular weight of polymer is used, namely 843 g/mole, retention corresponds to ca 1.2 moles of uranium per mole of polymer.

Further information on the effects of radiation on uranium losses in TBP-Amsco solvent extraction were obtained from an experiment in which 0.37 volume of an aqueous solution of 1.3 M $UO_2(NO_3)_2$ - 1.84 M HNO_3 was stirred with 1 volume of 30% TBP in Amsco 125-82 while being irradiated to the 125 watt-hr/liter level in a 10 kilocurie cobalt-60 source. After stripping the organic phase with four 0.32 volume and four 0.8 volume of 0.01 M HNO_3, the uranium content had decreased to an average of 3 g/liter; i.e., 2.7% of the uranium remained in the organic phase.

It should be noted that some of the fission product elements may compete favorably with uranium in forming complexes or compounds with DBPA or radiolytic polymer. Such competition can greatly reduce the extent of decontamination.

Formation of olefinic compounds in irradiated TBP-hydrocarbon solutions has been recognized for some time (9). Recently, yields for double bond formation have been calculated from measurements of iodine numbers. A summary of results is given in Table 3. It is apparent that radiolysis of TBP-Amsco 125-82 solutions yields an ample quantity of unsaturated hydrocarbon with which radioactive iodine may react, thereby resulting in solvent contamination that can be removed only with difficulty.

Table 3. Olefin Formation During Radiolysis of TBP-Amsco 125-82 Solutions

Solution Composition, % W/V	Dose Density, Watt-hr/liter	Increase in I_2 Number*	$G_{c=c}$
4.5	400	14.2	3.37
10	400	13.4	3.17
20	400	11.4	2.70
30	400	11.4	2.70
45	400	10.5	2.49
60	400	8.1	1.92
100	400	4.2	1.00
15	200	8.6	4.08
25	200	7.7	3.65

* Determined by Wij method

OTHER EXTRACTANTS

Many organic compounds, such as phosphates, phosphonates, phosphinates, phosphine oxides, primary -, secondary -, and tertiary amines, have been tested for possible utility in extracting uranium from sulfate ore leach liquors (2,3,6,10). Some of these compounds have been examined as extractants in nitric acid systems employing carbon tetrachloride as diluent (6). At present, we are trying to determine the effects of radiation on uranium retention and fission product decontamination by typical examples of these various classes of extractants. One of these examples is diethyl carbonate, DEC.

Diethyl carbonate is a very weak complexing agent for uranium. Extraction requires highly salted, but only modestly acidic feed solution. Good extraction of uranium from 1.5 to 1.75 M $Al(NO_3)_3$ and 1 M HNO_3 can be obtained. These conditions provide uranium distribution coefficient, $D.C._a^o$ (organic phase concentration/aqueous phase concentration), of approximately 2 if the uranium concentration in the feed is in the order of 0.2 M.

A sample of DEC irradiated to the 400 watt-hr/liter level and an unirradiated control sample were contacted with equal volumes of an aqueous feed containing 0.172 M $UO_2(NO_3)_2$, 1.57 M $Al(NO_3)_3$, 0.99 M HNO_3, and the fission products (F.P.) shown in Table 6. Values of uranium $D.C._a^o$, Table 4, show that the irradiated DEC may have extracted uranium somewhat better than did the unirradiated sample. Measurements of radioactivity showed the irradiated DEC to extract less β-activity but more γ-activity than the unirradiated control.

The two DEC solutions, irradiated and unirradiated, were scrubbed to determine whether the fission products could easily be back-washed into the aqueous phase. This back washing occurred to a very large extent in both cases. The scrub solution had a composition nearly the same as that of the aqueous solution from the extraction operation, namely 0.060 M $UO_2(NO_3)_2$, 1.87 M $Al(NO_3)_3$, 0.56 M HNO_3 (see Table 4 for comparison). As a result, the compositions of irradiated and unirradiated DEC changed only slightly during scrubbing, except for fission product activity.

Comparison of stripping data, Table 5, shows that the irradiated DEC retained less uranium than did unirradiated DEC. This is just the opposite of the situation that prevails with TBP-kerosene diluent solutions wherein the radiolytically formed DBPA holds uranium in the extractant phase during stripping operations.

In general, radiolysis products do not have a very deleterious effect on extraction of uranium and its separation from fission products (Table 4, 5, 6), except for decontamination from γ-active elements. At the present time we can say that DEC is superior to TBP-kerosene systems from the standpoint of uranium retention, but we do not yet have a good control for comparison of decontamination of fission products. This is due, primarily to use of batch contacting in the experiments with DEC whereas work with TBP-kerosene solutions has been performed with multistage, countercurrent equipment.

Table 4. Experimental Conditions, Diethyl Carbonate Extraction Test*

	Organic Phase	Aqueous Phase	$D.C._a^g$
		Unirradiated DEC	
Relative Volume	1.05	0.95	-
Uranium, M	0.0997	0.0535	1.86
HNO_3, M	0.065	0.62	0.105
		Irradiated DEC	
Relative Volume	1.03	0.97	-
Uranium, M	0.113	0.0458	2.47
HNO_3, M	0.046	0.50	0.092

*Feed: 0.172 M $UO_2(NO_3)_2$; 1.57 M $Al(NO_3)_3$; 0.99 M HNO_3;
Fission Products as in Table 6; Relative Volume = 1
Extractant: DEC; Relative Volume = 1

Table 5. Experimental Conditions, Diethyl Carbonate Stripping Test*

	Organic Phase	Aqueous Phase	$D.C._a^o$
		Unirradiated DEC	
Relative Volume	1	1	-
Uranium, M	(0.0174)**	0.0972	0.18
HNO_3, M	-	0.49	-
		Irradiated DEC	
Relative Volume	1	1	-
Uranium, M	(0.00955)**	0.1055	0.0905
HNO_3, M	-	0.52	-

*Feed: Organic phase from scrubbing operation; Relative Volume = 1; Strip: 0.01 M HNO_3; Relative Volume = 1

** Calculated by difference on basis of feed and product compositions.

Table 6. Effects of Radiation on Fission Product Distribution During Extraction with Diethyl Carbonate*

	Gross β	Gross γ	Zr-Nb γ	Ru^{106} γ	TRE** β
Feed, (c/min-mg U) x 10^{-4}	4.63	2.93	2.14	0.249	3.20
Dist. Coeff. on Extraction					
($D.C._a^o$) x 10^2: Unirradiated	2.53	2.30	2.64	4.70	2.84
: Irradiated	1.04	5.38	6.36	10.4	0.0178
Decontamination Factor					
: Unirradiated	700	370	315	170	1060
: Irradiated	520	85	76	22	1080

* See text and Table 4 and 5 for conditions.

** Total rare earth elements.

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