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THE CHEMISTRY OF RUTHENIUM
AND ZIRCONIUM IN THE PUREX
SOLVENT EXTRACTION PROCESS*

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ABSTRACT. The literature on the chemistry of ruthenium and zirconium in nitric acid solution — tri-n-butyl phosphate/diluent media is reviewed. The structure and composition of ruthenium and zirconium species are described. The available data on extraction of these two elements, pertinent to the Purex process, are summarized and distribution coefficients are tabulated. The effects of process conditions on the separation of uranium and plutonium from these two elements are discussed.

1. INTRODUCTION

Most of the methods used for reprocessing irradiated nuclear fuel are based on solvent extraction from a nitric acid medium. Precipitation and ion exchange are used for the final purification of uranium and plutonium, but only to a limited extent. Depending on the composition of the spent fuel, different solvents and salting agents are selected. The most common separation processes are the Redox process, which uses methyl isobutyl ketone for extraction and aluminium nitrate as a salting agent, and the Purex process, which employs tri-n-butyl phosphate (TBP) and nitric acid for these functions.

There are many variations of the Purex separation process. In the most common version the uranium and plutonium are extracted into an organic solvent

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in the first solvent extraction cycle, while most of the fission products remain in the aqueous phase (raffinate), so that with the aid of multistage contactors complete separation potentially can be achieved.

However, two elements, ruthenium and zirconium, complicate satisfactory decontamination of products in the reprocessing of irradiated fuel by Purex solvent extraction. These elements accompany the fissile materials (uranium and plutonium), get into the subsequent extraction cycles, and consequently end up in the low-activity waste stream.

The inability to effect a separation of uranium and plutonium from ruthenium lies in the diversity of ruthenium compounds and their extraction coefficients in the nitric acid solutions and the sensitive equilibria between the compounds, which are affected by even slight differences in extraction conditions. The differences in extractabilities are enough to cause significant changes in the decontamination factors with small changes in conditions. Zirconium, and its daughter niobium, create difficulties primarily because they react with small quantities of radiolytic and hydrolytic degradation products of TBP and of diluents and are retained in the solvent, reducing the decontamination factor and complicating solvent recycle. For these reasons, the chemistry of ruthenium and zirconium compounds in nitric acid and organic solvent media is of very special significance.

In this review the literature on ruthenium and zirconium chemistry that is relevant to the Purex process is described. Although there were extensive studies in the 1950s, there are still many gaps in the knowledge of the chemistry of these two elements. The available data that will be summarized have to be regarded with some caution, especially where there is no direct evidence to support the reported hypotheses. Nevertheless,. the data can be utilized, if only partially, in developing advanced solvent extraction techniques for nuclear fuel reprocessing.

2.   RUTHENIUM

2.1. Introduction

Ruthenium belongs to the platinum group metals and shows one of the largest ranges of valence states, from 8^+ as in RuO_4 to zero in carbonyls. The principal valence states (and the most relevant to the Purex process) are 2^+ and 3^+. The ground state configuration of Ru^0 is $4d^7 5s$ and for Ru^+ and Ru^{2+} the configurations are, respectively, $4d^7$ and $4d^6$ [1].

Ruthenium (II) forms a large number of complexes, almost invariably six-coordinated, although five-coordinated compounds like $[Ru(CO)_2Cl_3]$ or $RuCl_2L_3$ (L = phosphine or arsine) also exist [2, 3]. The six-coordinated

complexes are extremely stable because Ru^{2+}, with the d^6 configuration, obeys the 18-electron rule when octahedrally co-ordinated and additionally stabilized by π-bonding ligands. All the complexes are diamagnetic, indicating that Ru(II) has the low spin, $(t_{2g})^6$, configuration [4]. Ruthenium (III) is also low spin with a magnetic moment within the range 1.8–2.2 μ_B at room temperature[1]. The electronic configuration can be approximately described as $(t_{2g})^5$ [3, 4].

Ligands found in ruthenium complexes include halide, hydroxide, ammonia, amines and other non-nitrogen ligands. They are numerous and a list of them can be found in Griffith [4]. Many cationic, neutral and anionic complexes are known. Since ruthenium (II) is a very strong π-donor [5], it will form very strong bonds with good π-acceptors like NO, CO, SO_2 and, to a lesser extent, N_2. Complexes formed by ligands that rely on only σ-electron donation, e.g. amines, are considerably less stable than those involving π-electrons. The ruthenium in the oxidation state (III) is a weaker π-donor and does not complex with the NO or N_2 group.

A special peculiarity of ruthenium is the extraordinarily stable species $(RuNO)^{3+}$, ruthenium nitrosyl, and the formation of a great many (~ 100) nitrosyl complexes. The Ru-NO bond is exceedingly difficult to break by substitution or oxidation-reduction (even by boiling in mineral acids), whereas the analogous osmium (II) complexes are easily oxidized. There have been some contradictory opinions in the literature on the valence states of ruthenium in the Ru-NO group [6].

Currently [3], NO in RuNO is considered to bond formally as NO^+. It is assumed that the NO group donates an electron to Ru (III) and that RuNO is equivalent to a bivalent Ru(II) complex containing NO^+ [7]. This idea is supported by diamagnetism of the RuNO complexes [3, 5, 6]. The infra-red spectra and bond length data indicate that two-electron pairs in the two orbitals formed by overlap of the filled d_{xz} and d_{yz} orbitals with the two empty π^* of NO^+ orbitals are responsible for strengthening the Ru-N bond and considerably weakening the N-O link (Table I). The bonding electrons are, in a sense, partially donated from the filled metal d orbitals to the empty ligand NO π^* orbital (the process is known as metal-to-ligand π-bonding or back-bonding). The Ru-N distance in $[Ru(NO)]^{3+}$ complexes varies from 1.7 to 2.0 Å, depending on the complex [4], and is sufficiently short to be consistent with the formation of the bonding, $Ru = N^+ = O$. (The Ru-N bond distance in $[Ru(NH_3)_6]^{2+}$ is approximately 2.14 Å.) The N-O distance in $RuNO^{3+}$ is between 1.10 and 1.15 Å [4], which, in comparison with the N-O distance in NO(g), 1.14 Å, and in NO^+, 1.06 Å, also suggests considerable back-bonding.

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[1] One Bohr magneton (μ_B) = 9.723 $\times$ 10^{-21} erg/G.

TABLE I.   INFRA-RED SPECTRA AND BOND LENGTH DATA OF N-O
Reprinted, with permission, from Ref. [5].

	NO	NO^+	$Na_2[RuNO(NO_2)_4OH] \cdot 2H_2O$
$NO(cm^{-1})$	1878	2200	1907
N-O distance ($\overset{\circ}{A}$)	1.14	1.06	1.13
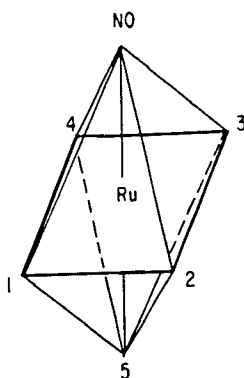
FIG.1.   *Octahedral structure of ruthenium nitrosyls. Positions 1, 2, 3 and 4 are stable, and position 5 is labile.*

Only one NO group is found in the complexes of ruthenium nitrosyl that can occur in cationic, anionic or neutral forms of octahedral arrangements (Fig. 1). The presence of the RuNO group is indicated by a strong band in the infra-red spectrum in the range 1930−1845 cm^{-1} [8].

Tetravalent ruthenium (the form of radioruthenium that may also be present in the dissolved fuel) forms relatively few complexes. They are of octahedral structure, which is characteristic for the $(t_{2g})^4$ configuration [3].

2.2. Ruthenium nitrosyls

During the dissolution of irradiated nuclear fuel in nitric acid the ruthenium mainly passes into solution in the form of various nitrato, nitro and mixed nitratonitro complexes[2] of trivalent ruthenium nitrosyls ($RuNO^{3+}$). They are complexed with hydroxo and aquo ligands and are of the general formula:

$$[RuNO(NO_3)_x(NO_2)_y(OH)_z(H_2O)_{5-x-y-z}]^{3-x-y-z}$$

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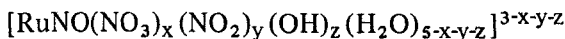
[2]   A prefix nitro denotes the presence of a monovalent −NO$_2$ radical; a nitrato compound contains the monovalent −NO$_3$ radical.

The nitrosyl group has a strong trans-effect, manifesting itself in the labilization of the ligand bond in trans-position to it on the co-ordinate L-Ru-NO (where L is a neutral or acid ligand, e.g. OH⁻ [9]). The postulate that four relatively stable positions and one labile position exist agrees with the observation that there are only one mononitrato, two dinitrato (cis and trans, Fig. 2), one trinitrato and one tetranitrato ruthenium species.
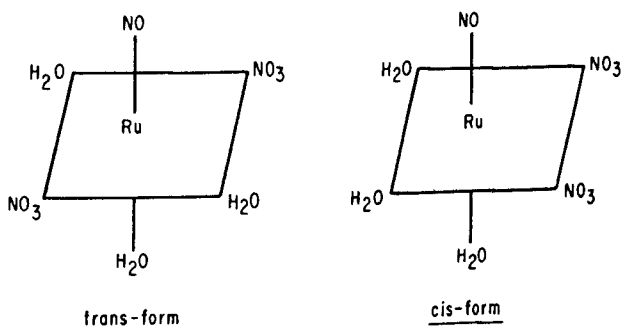
FIG.2.   Cis and trans-dinitrato ruthenium nitrosyl complexes.

All the isolated RuNO complexes show the diamagnetism expected for an octahedral arrangement around the ruthenium atom. The formation and inter-conversion reactions are slower for complexes containing the nitro ligands than for ones with nitrato groups, and thus slow reactions ($t_{1/2}$ = 1 to 30 days at 20°C) [10] characterize substitutions involving the nitro ligand on $RuNO^{3+}$. In contrast, reactions with nitrato ligands occur with $t_{1/2}$ = 10 to 60 min at 20°C [10]. Once formed, however, nitro complexes show greater stability than their nitrato analogues, e.g. they are more difficult to oxidize to RuO_4.

2.3. Nitrato complexes of ruthenium nitrosyl

The aquo-nitrato complexes were first prepared by Joly [11] in 1889 and then neglected for some fifty years. The existence of tri, di and mononitrato complexes has been established by Fletcher et al. [12], Wallace [13] and Scargill et al. [14]. In 1960–61 Wallace isolated the complexes existing in nitric acid media by cation and anion exchange techniques and assigned the following formula to them:

$$[RuNO(NO_3)_x(H_2O)_{5-x}]^{3-x}$$
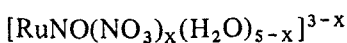
with x = 3, 2, 1, 0.

TABLE II. RATES OF NITRATION AND AQUATION REACTIONS AT 25°C

Reprinted, with permission, from Ref. [14].

| | Rate Constant ($\times 10^3$) min^{-1} | | | |
| | HNO$_3$ Conc. during Nitration | | HNO$_3$ Conc. during Aquation | |
Reaction	6.1M	8.1M	6.1M	8.1M
mono- $\rightleftarrows$ cis-di-	1.65	3.0	0.70	0.72
mono- $\rightleftarrows$ trans-di	8.1	13.5	4.3	4.5
cis-di- $\rightleftarrows$ tri-	17.9	32.5	11.1	11.7
trans-di- $\rightleftarrows$ tri-	74.0	144	36.5[a]	37.4
tri- $\rightleftarrows$ tetra-	17.0	68	102	270

[a]Rudstam [15] found 25×10^{-3} min^{-1} for this rate constant at 20°C in 0.95M HNO$_3$.

TABLE III. THE TEMPERATURE DEPENDENCE OF THE RATE CONSTANTS (ACIDITY = 0.95M HNO$_3$)

Reprinted, with permission, from Ref. [15].

$$RuNO(NO_3)_3(H_2O)_2 \underset{k_{DT}}{\overset{k_{TD}}{\rightleftarrows}} RuNO(NO_3)_2(H_2O)_3$$

$$RuNO(NO_3)(H_2O)_4 \underset{k_{NM}}{\overset{k_{MN}}{\rightleftarrows}} RuNO(H_2O)_5$$
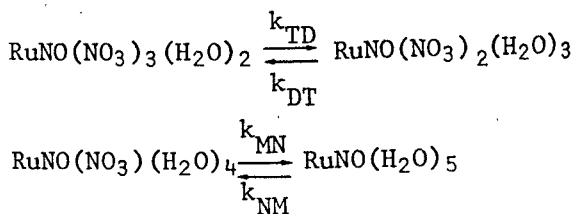
Temperature	k_{TD} (min^{-1})	k_{DT} (min^{-1})	k_{MN} (min^{-1})	k_{NM} (min^{-1})
10°C	0.0065	0.00096	----	----
20°C	0.025	0.0024	0.0041	0.0025
30°C	0.068	0.0058	0.012	0.0085

TABLE IV. THE ACIDITY DEPENDENCE OF THE RATE CONSTANTS

Reprinted, with permission, from Ref. [15]. t = 20°C.

HNO$_3$ Acidity	k_{TD}[a] (min^{-1})	k_{DT}[a] (min^{-1})	k_{MN}[a] (min^{-1})	k_{NM}[a] (min^{-1})
0.95M	0.025	0.0024	0.0041	0.0025
1.92M	0.019	0.0058	0.0046	0.014
3.80M	0.018	0.013		
7.11M	0.020	0.053		

[a]See Table III for definitions of rate constants.

TABLE V. THE INFRA-RED SPECTRA OF TRINITRATO AND TETRANITRATO COMPLEXES OF RuNO

Reprinted, with permission, from Ref. [14].

Complex	NO$^+$ ν_{st}	-ONO$_2$					H$_2$O	
		ν_4	ν_1	ν_2	ν_6	ν_3	ν_{st}	ν_{bend}
Trinitrato	1945 s	1508 s	1265 s,b	968 s,b	783 w	765[a] w	3140 s,b	1620 vw / 1670 w
Tetranitrato	1945 s	1518 s	1265 s,b	965 s,b	783 w	763[a] w	3134 m,b	1673 w

s = strong; w = weak; v = very; b = broad; m = medium; st = stretching vibration.
[a]Alternatively, this band may be due to a rocking vibration of coordinated water.

Later Scargill et al. [14] separated and identified the cis and trans-dinitrato complexes and also the tetranitrato by cation exchange, paper chromatography and extraction techniques. The assignment of the cis and trans-dinitrato was based on the differences in their rates of formation from the mononitrato complex. The rate is governed by a trans-nitrato effect (i.e. the more favourable electron distribution occurs when the subsequent NO$_3^-$ group attaches in trans-position) and thus the trans-complexes form faster and are more stable. Rates of nitration and aquation reactions were also measured and are given in Table II [14]. The temperature and the acidity effects on the rate constants of the interchange reactions between different complexes are given in Tables III and IV and are taken from Rudstam's studies [15]. It can be seen that the rate of conversion of the trinitrato complexes, the most extractable species, to other

TABLE VI.   FRACTION OF RUTHENIUM IN DIFFERENT NITRATO
COMPLEXES OF RuNO AT EQUILIBRIUM IN SOLUTIONS OF HNO_3
AT 20°C (Ru conc. ~0.1M)

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Communities, Luxembourg, P.O.B. 1003. Tabulated by Amavis et al. [17];
data of Fletcher et al. [16].

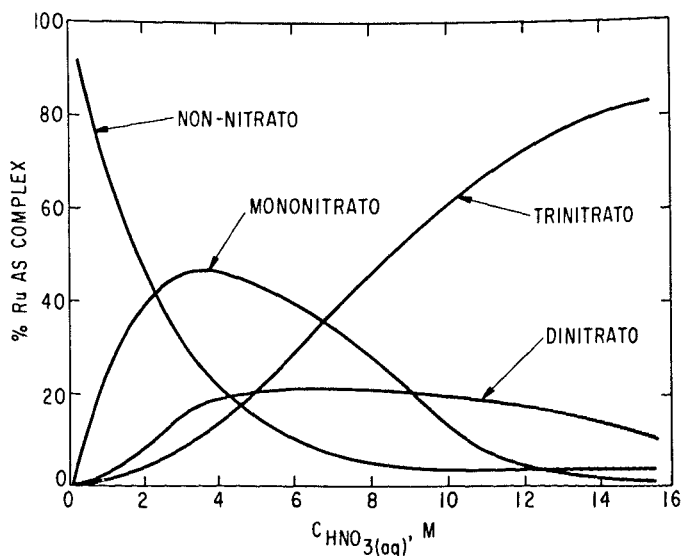|	HNO_3								
	0.1M	1M	3M	4.6M	7.5M	8.7M	9.2M	11.3M	14.5M
Trinitrato	0	0.035	0.07	0.18	0.42	0.505	0.555	0.705	0.81
Dinitrato	0	0.03	0.15	0.20	0.19	0.215	0.20	0.185	0.13
Mononitrato	0.05	0.235	0.46	0.44	0.315	0.23	0.195	0.065	0.02
Non-nitrato	0.95	0.70	0.32	0.18	0.075	0.05	0.05	0.045	0.04

FIG.3.   *Composition of solutions of (RuNO) nitrato complexes at equilibrium in nitric acid.*

nitrato compounds is slow; the half-time for the conversion is approximately 30 min at 25°C [16]. The infra-red spectra of tri and tetra-nitrato complexes were determined by Scargill et al. and are presented in Table V.

Pentanitrato complexes are not known, contrary to some earlier interpretations by Fletcher et al. [14].

In nitric acid solutions the fractions of different nitrato complexes of $RuNO^{3+}$, $[RuNO(NO_3)_x(H_2O)_y(OH)_{5-x-y}]^{y-2}$ will depend on the nitrate ion concentration in the solution. The proportions of the various complexes at equilibrium in solutions of HNO_3 at 20°C for a ruthenium concentration of ~0.1M are given in Table VI [17] and illustrated in Fig. 3. In solutions of uranium and HNO_3, such as found in reprocessing plants, the equilibrium proportions of nitrato complexes have been determined as follows [18]:

Number of Nitrato (NO_3) Groups	Proportion (%) in	
	$1.25M\ UO_2(NO_3)$ and $3M\ HNO_3$[a]	$3M\ HNO_3$
0 } 1 }	11	4.5 30
2 cis	28.5	29
2 trans	19	21.5
3	38.5	14
4	5	1

[a]Total is 102%, which can be attributed to experimental error.

2.4. Nitro complexes of ruthenium nitrosyl

In the presence of nitrous acid the relatively weakly bound nitrato groups can be slowly replaced by the more nucleophilic nitro groups, e.g.

$$[RuNO(NO_3)_2(H_2O)_3]^{1+} + 2\ NO_2^- \rightleftharpoons [RuNO(NO_2)_2(H_2O)_3]^{1+} + 2\ NO_3^-$$
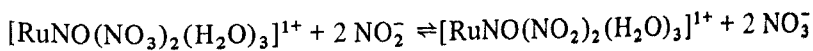
Nitro complexes of ruthenium nitrosyl are of the general formula:

$$[RuNO(NO_2)_x(H_2O)_y(OH)_z]^q$$
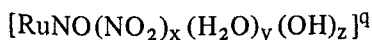
where $x + y + z = 5$ and $q = 3 - x - z$. They were first studied by Joly in 1889 [11], but their structure was established only much later by X-ray diffraction techniques [19].

Trinitrocomplexes of ruthenium nitrosyls have low stability in solutions [20]. On hydrolysis, they are converted into the more stable dinitronitrosyls. Brown [10] also reported the existence of mononitro compounds.

TABLE VII. WAVE NUMBERS OF THE MAXIMA OF THE ABSORPTION
BANDS OF THE NO AND OH GROUPS IN [RuNO(NO$_2$)$_2$A$_2$OH] FOR
VARIOUS LIGANDS A [20]

Compound	Ligand A	ν_{NO}(cm^{-1})	σ_{OH}(cm^{-1})	ν_{OH}(cm^{-1})
[Ru(NO)(NO$_2$)$_2$(H$_2$O)$_2$(OH)]	H$_2$O	1873	971	3322
[Ru(NO)(NO$_2$)$_2$(NH$_3$)$_2$(OH)]	NH$_3$	1867	958	3470
[RuNO(NO$_2$)$_2$Py$_2$OH]	Py[a]	1850	945	3525
[RuNO(NO$_2$)$_2$(TBPO)$_2$OH]	TBPO[b]	1830	--	--

[a]Py--pyridine.

[b]TBPO--tributyl phosphine oxide.

2.4.1. Dinitroruthenium nitrosyls

The complex of the formula [RuNO(NO$_2$)$_2$(OH)(H$_2$O)$_2$] can be obtained
from sodium tetranitroruthenium nitrosyls by the action of dilute nitric acid at
60°C [10]. The infra-red spectrum of it gives 1873 cm^{-1} for the frequency of the
stretching vibrations of the nitrosyl group. The water molecules in this complex
can be replaced by some other ligands, and that would have a significant influence
on the electron density distribution in the molecule. Thus, when the ligands are
in the cis-position relative to the nitrosyl group, the strength of the Ru-N bond
in RuNO decreases with increase in the donor properties of the ligands in the
order[3] H$_2$O < NH$_3$ < Py < TBPO [20]. There is a simultaneous change in the
strength of the bond between the OH group in the trans-position to the NO and
Ru, as indicated by the change shown in Table VII, in the frequencies of the
stretching and bending vibrations of the hydroxyl group.

The dinitroruthenium nitrosyl in nitric acid solutions undergoes slow
nitration (with t$_{1/2}$ ~ 1 day), rendering as the final product a mixture of
nitratonitro and nitrato complexes of the RuNO [10].

2.4.2. Tetra and higher nitro complexes of ruthenium nitrosyl [20]

The reaction of potassium, sodium or rubidium nitrites with chlorides,
chloronitrosyls or nitrato-nitrosyls of ruthenium gives tetranitrohydroxoruthenium
nitrosyl, M$_2$[Ru(NO)(NO$_2$)$_4$(OH)] where M = Na, K or Rb. These complexes
decompose endothermically at temperatures higher than 200°C by liberation

---

[3] Py is pyridine, TBPO is tri-n-butylphosphine oxide.

TABLE VIII.   PROPERTIES OF THE TETRANITROSYLS OF RUTHENIUM [20]

Compound	Color	Refractive Indices	Frequency of the stretching vibrations of the NO group (cm^{-1})
$Na_2[Ru(NO)(NO_2)_4(OH)]\ H_2O$	yellow	$n_p=1.593$ $n_m=1.596$ $n_g=1.726$	1905
$K_2[Ru(NO)(NO_2)_4(OH)]$	yellowish orange	$n_p=1.626$ $n_m=1.655$ $n_g=1.737$	1900
$Rb_2[Ru(NO)(NO_2)_4(OH)]$	orange	$n_p=1.630$ $n_m=1.734$	1890
$(TOAH)_2[Ru(NO)(NO_2)_4(OH)]$[a]	dark orange	~ 1.410	1875

[a] TOAH is trioctylammonium

first of water (from hydroxo group), and later at higher temperatures of MNO_3 and MNO_2. At approximately 350°C exothermic decomposition of RuNO takes place, forming RuO_2. The properties of the tetranitrosyls of ruthenium are given in Table VIII [20]. As is evidenced by the decrease in frequency of the NO stretching vibration, the strength of the bond between the nitrosyl group and ruthenium slightly decreases as the outer sphere cation is replaced in the order $Na^+ < K^+ < Rb^+$; the weakest bond is that with rubidium in the outer sphere.

The hexanitro complex exists, which is very striking. It is formed when ruthenium nitrosyls are treated with an excess of KNO_2, but not with $NaNO_2$ or NH_4NO_2. The infra-red spectra of the product contain no bands in the range $1830-1930\ cm^{-1}$ characteristic of ruthenium nitrosyl and no bands due to water or a hydroxy group. This compound forms $K_2[Ru(NO)(N)_2)_4(OH)]$ on heating, but an excess of KNO_2 solution converts it back to the hexanitro complex. According to Pichkov et al. [20], it is unlikely that the very firmly bound NO group is displaced from the inner sphere by the nitro group; more likely it is oxidized to the NO_2 group.

The nitro group is less firmly bound to ruthenium than the nitrosyl group but, owing to the ability of the nitro group to form dative and donor-acceptor bonds with ruthenium [13, 20], is more firmly bound than other acid ligands of the series: $NO_2^- > (C_2O_4, SO_4^{2-}, etc.) > NO_3^- > F^- > ClO_4^-$ [20]. According to Pichkov et al. [20], the ruthenium nitrosyls containing four nitro groups are

TABLE IX. NITRATION OF SOME RuNO NITRO COMPLEXES

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Complex	Rate Constant at 25°C (M^{-1} h^{-1})	Activation Energy[a] (kcal/mole)	Product
1,2 dinitro	0.043	17.5	1,2-dinitro-3-nitrato
1-nitro	0.11	23.8	1-nitro-3-nitrato
1,3 dinitro	1.0	22.4	1,3-dinitro-2-nitrato
1-nitro-3-nitrato	0.1	22.4	1-nitro-2,3-dinitrato

[a]Activation energies calculated from the rate constants at 0°C and 25°C, $E = 14.9 \cdot \log (k_{25}/k_0)$, kcal $mole^{-1}$.

TABLE X. AQUATION OF SOME RuNO NITRO COMPLEXES.

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Complex	Rate Constant at 25°C (M^{-1} h^{-1})	Activation Energy[a] (kcal/mole)	Product
1-nitro-3-nitrato	0.47	23.5	1-nitro
1,2-dinitro-3-nitrato	0.21	19.7	1,2-dinitro
1,3-dinitro-2-nitrato	2.7	21.8	1,3-dinitro
1-nitro-2,3-dinitrato	1.7	22.0	1-nitro-3-nitrato

[a]Activation energies calculated from the rate constants at 0°C and 25°C, $E = 14.9 \cdot \log k_{25°C}/k_{0°C}$, kcal $mole^{-1}$

the most stable toward substitution. The inner sphere substitution begins at increased temperatures in reactions with acids of a high displacing power. And so in the reaction of $[Ru(NO)(NO_2)_4(OH)]^{2-}$ with 1M HCl the chloride ions do enter the inner sphere, forming chlororuthenium nitrosyls. However, the reactions of $[RuNO(NO_2)_4OH]^{2-}$ with nitric and perchloric acids give $[Ru(NO)(NO_2)_2(H_2O)_2(OH)]$; that is, NO_3^- and ClO_4^- do not enter the inner sphere.

Aqueous solutions of tetranitro complexes of ruthenium are stable to hydrolysis at room temperature. However, at increased temperatures, the rate of hydrolysis is not negligible, and at $70°C$ the pH of $0.001M$ $Na_2[Ru(NO)(NO_2)_4(OH)]$ changes from 6.1 to 3.5, apparently due to the gradual introduction of hydroxo groups into the inner sphere of the ruthenium nitrosyl. The reaction is reversed by treating the hydrolysed solutions with sodium nitrite. Pentanitro complexes of RuNO are unknown.

2.5. Mixed nitronitrato complexes of ruthenium nitrosyl

A mononitrodinitrato complex was obtained by Brown [10] when oxides of nitrogen $(NO + NO_2)$ were passed through a solution of ruthenium nitrosyl nitrato complexes in 6M HNO_3 at $50°C$. Joon [21] separated some nitro and mixed nitronitrato complexes and studied their conversion rates (Tables IX and X). The compounds were separated by extraction chromatography; their composition with respect to ruthenium, nitrite and nitrate was determined by spectrophotometric methods. The structure of isolated species has been inferred on the basis of the determined ratios of $Ru : NO_2^- : NO_3^-$ and their extractability. The cis-complexes were differentiated from trans-complexes as having the higher dipole moment and therefore being the less extractable (non-polar molecules are more readily extractable into TBP). Species with four $(NO_2^- + NO_3^- = 4)$ nitronitrato groups have not been found, except when only one type of ligand is present.

2.6. Tetravalent ruthenium

Ruthenium (IV) species can also be formed during the dissolution of irradiated fuel in nitric acid. Some of them probably exist as binuclear oxygen-bridge compounds, –Ru-O-Ru [22]. They can undergo hydrolysis to form $[RuO_{aq}]^{2+}$.

Ruthenium (IV) nitrates, of prominent brown colour, are practically non-extractable by TBP. The distribution coefficient for 30% TBP is $D_{Ru(IV)} < 10^{-3}$ [22, 23]. Thus, their presence reduces the total amount of ruthenium extracted. They are extractable to a higher degree by dibutyl phosphate, a hydrolysis product of TBP. High acid conditions oppose the formation of a Ru(IV)–DBP complex. In the most favourable condition (3.3M stock solution diluted to 0.1M HNO_3 and extracted immediately) the distribution coefficient of these species by 2% (0.1M) DBP in kerosene is $D_{Ru(IV)} \cong 0.07$; from 1M HNO_3 solution D_{Ru} is approximately equal to 10^{-3}. If the solution is allowed to age for 1–2 hours, polymers of Ru(IV) are formed and the extractability into DBP is reduced [22]. The adverse effect of radiation on ruthenium decontamination is probably not due to the action of DBP on Ru(IV).

2.7. Extraction by tri-n-butyl phosphate

Extractability of different nitrato or nitro complexes or ruthenium nitrosyl varies, and therefore the equilibrium between the species is critical for decontamination of uranium and plutonium from ruthenium. It has been observed that nitrato complexes are generally about twice as extractable as nitro complexes and that among the ruthenium complexes the trinitrato complexes are the most extractable in TBP [14, 24, 25]. During the dissolution of irradiated fuel more nitro complexes than nitrato may be produced. Under typical plant conditions (2 to 4M HNO_3, 10^{-2} to 10^{-3}M HNO_2) 30 to 70% of the total ruthenium in the solution used as feed to the first extraction cycle may be in the form of nitro complexes rather than nitrato complexes [18]. Thus, some of the ruthenium extracted into TBP may be in the form of nitro or mixed nitronitrato complexes. On the other hand, Joon et al. [26] attributed the extractability and retention of ruthenium in TBP mainly to dimers of the general composition $[RuNO(H_2O)(NO_3)_3]$, $[RuNO(H_2O)(NO_2)(NO_3)_2]_2OH^-$ and $[RuNO(NO_2)(NO_3)_2(OH)]_2$.

Dibutyl phosphate, sometimes present in TBP due to radiolysis and hydrolysis, does not extract ruthenium nitrosyl complexes to any significant degree, e.g. $D_{Ru} < 10^{-5}$ at 20°C for 2% DBP and 3M HNO_3 [22].

2.7.1. Mechanism of extraction

The extraction may occur by two different mechanisms [27–29]. One involves direct metal-TBP co-ordination, and the other hydrogen bonding with TBP. Hydrogen bonding is relatively weak (4–7 kcal) as compared with about 100 kcal for a covalent linkage and can be as easily ruptured as formed [29].

There is a dispute concerning the nature of ruthenium complexes extracted by TBP from nitric acid media. Hallaba and Azzam [29] favour (RO)$_3$-PO-Ru bonding, where two TBP groups displace the aquo groups in a
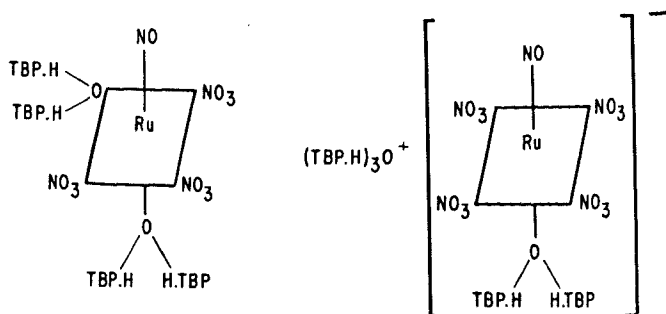
FIG.4. *Hydrogen bonding of TBP groups to either aquo groups or the hydronium ion* [27, 31, 32].

TABLE XI.   COMPARISON OF INFRA-RED BANDS OF TBP-
SOLVATED AND TBP-COMPLEXED TRINITRATO
NITROSYLRUTHENIUM[a]

Reprinted, with permission, from Ref. [27].

D_3 org.	$RuNO(NO_3)_3(TBP)_2$	Assignment	
~ 3400	--	ν_{OH} from H_2O	
1935 m	1930 m	NO	
1640 w	--	H_2O	
1530 s	1525 s	ν_4 nitrato	monodentate
1530 s	1263 s	ν_1 nitrato	
1241 m, sh	--	P = O bonded to H_2O	
--	1183 v.s	P = O bonded to Ru	
956 m	952 m	ν_1 nitrato	

[a]Other bands found for TBP itself were present in both
spectra.

RuNO complex. Furthermore, Zvjagintsev et al. [30] observed the effect of
the inner sphere substitution; the nature of the internal ligand influenced the
extraction coefficients. On the other hand, Fletcher et al. [27, 31] and
Joon [32] believe that TBP groups are attached by hydrogen bonding to either
aquo groups or the hydronium ion as shown in Fig. 4. This mechanism is
consistent with their extraction data and is confirmed by IR measurements.
The infra-red bands of solvated TBP (D_3 org) and TBP-complexed trinitrato
ruthenium nitrosyl are given in Table XI.

The probable mechanism [29, 33] is that labile TBP solvates are formed
initially, and then the TBP slowly enters the inner positions. The labile solvates
may be formed by TBP entering the labile trans-position, though they could
also be formed by hydrogen bonding of TBP to H_2O or H_3O^+ ligands. The
process of moving TBP into one of the cis-positions is slow, since it involves a
displacing of ligands. On this basis, tetranitrato complexes should be less
extractable than trinitrato, and this has indeed been found [25, 33] except by
Fletcher and Scargill [34].

TABLE XII. EXTRACTION COEFFICIENTS OF RUTHENIUM NITROSYL COMPLEXES

Assumed Complex	Temp (°C)	[HNO$_3$] M	TBP (vol %)	Diluent	[Ru] M	D_{Ru}[a]	Ref
dinitrato	20	1	21.0	Nysolin 160/200[b]	$<10^{-7}$	0.18	15
	20	1	30.0	Nysolin 160/200	$<10^{-7}$	0.22	15
	20	1	31.2	Nysolin 160/200	$<10^{-7}$	0.39	15
	20	1	40.9	Nysolin 160/200	$<10^{-7}$	0.54	15
	20	1	50.0	Nysolin 160/200	$<10^{-7}$	0.63	15
dinitrato	0	1	30	kerosene	10^{-3}	12.5	24
	0	3	30	kerosene	10^{-3}	0.5	24
trinitrato	0	1	10	kerosene	$\sim 10^{-4}$	11.0	27
	0	3	15	kerosene	$\sim 10^{-4}$	0.9	27
	0	3	20	kerosene	$\sim 10^{-4}$	1.5	27
	0	4	30	kerosene	$\sim 10^{-4}$	0.95	27
	0	3	30	kerosene	$\sim 10^{-4}$	3.5,2.6	27
trinitrato	20	1	10.0	Nysolin	$<10^{-7}$	2.4	15
	20	1	21.0	Nysolin	$<10^{-7}$	19.5	15
	20	1	30.0	Nysolin	$<10^{-7}$	39.0	15
	20	1	31.2	Nysolin	$<10^{-7}$	45.1	15
	20	1	40.9	Nysolin	$<10^{-7}$	88.0	15
	20	1	50.0	Nysolin	$<10^{-7}$	150.0	15
	--	1	20	kerosene	$5 \cdot 10^{-2}$	0.15	28
	--	2	20	kerosene	$5 \cdot 10^{-2}$	0.09	28
	25	3	20	kerosene	--	0.3	34
trinitrato[c]	37	3	30	"Adakene 12"[d]	--	0.42[c]	45
	65	3	30	"Adakene 12"	--	0.1[c]	45
tetranitrato	0	3.05	30	kerosene	$\sim 10^{-4}$	8.2,12	27
	0	2.95	10	kerosene	10^{-4}	2.1	27
	25	3.00	20	kerosene	--	0.9	34
tri & tetra nitrato	--	3	10	n-dodecane	$5 \cdot 10^{-5}$	0.131	35
	--	3	15	n-dodecane	$5 \cdot 10^{-5}$	0.422	35
	--	3	20	n-dodecane	$5 \cdot 10^{-5}$	0.548	35
tri & tetra nitrato	0	4	30	kerosene	$8.5 \cdot 10^{-3}$	1.2	27
	0	3	30	kerosene	$2.5 \cdot 10^{-4}$	4.2	27
	0	3	20	kerosene	$2.5 \cdot 10^{-4}$	1.8	27
	0	3	15	kerosene	$2.5 \cdot 10^{-4}$	1.1	27
	0	1	10	kerosene	$8.5 \cdot 10^{-3}$	15.0	27
dinitro	20	0.1	30	kerosene	$5 \cdot 10^{-3}$	2.04	10
	20	1.0	30	kerosene	$5 \cdot 10^{-3}$	1.70	10
	20	3.0	30	kerosene	$5 \cdot 10^{-3}$	0.506	10
dinitro(cis)	20	1.0	30	n-dodecane	$5 \cdot 10^{-5}$	0.0155	21

TABLE XII. (cont.)

Assumed Complex	Temp (°C)	[HNO₃] M	TBP (vol %)	Diluent	[Ru] M	D_{Ru}	Ref
dinitro(trans)	20	1.0	30	n-dodecane	$5 \cdot 10^{-5}$	0.0477	21
dinitro–mono nitrato	--	3	10	n-dodecane	$5 \cdot 10^{-5}$	0.0078	35
	--	3	15	n-dodecane	$5 \cdot 10^{-5}$	0.0141	35
	--	3	20	n-dodecane	$5 \cdot 10^{-5}$	0.0467	35
1 nitro -2,3-dinitrato	20	1	30	n-dodecane	$5 \cdot 10^{-5}$	7.28	21
mononitro– dinitrato	20	5	30	kerosene	$5 \cdot 10^{-3}$	0.8	10
1,2 dinitro– 3-nitrato	20	1	30	n-dodecane	$5 \cdot 10^{-5}$	5.25	21
1,3 dinitro– 2-nitrato	20	1	30	n-dodecane	$5 \cdot 10^{-5}$	10.74	21

[a] $D_{Ru} = [Ru]_{ORG} / [Ru]_{AQ}$.

[b] Nysolin––Mainly paraffinic kerosene.

[c] In the presence of 1.5M $UO_2(NO_3)_2$

[d] Adakene=straight-chain paraffins.

The extraction coefficients have been reported to depend on the concentration of the free TBP to the second or third power, indicating that two or three TBP molecules are coordinated to the ruthenium complexes [15, 21, 24, 28, 29, 35], except for Fletcher et al. [27, 31] who reported fourth and fifth power. Shevchenko and Zhdanov [36] have pointed out the need to be aware of the difficulties entailed in analysing the dependence of distribution coefficients on extractant concentration. Since concentrations of TBP are expressed as volume percentages or molarities, the changes in total volume relative to total number of moles, which are considerable at high TBP concentrations, must be taken into account in the mass action law based on molarities. The differences between the true and the apparent solvation numbers may be approximately $\pm 0.08\ C_T$ (C_T = concentration of TBP in volume per cent). In addition, there are deviations from ideal solution, even at relatively low TBP concentrations in inert diluents. These deviations can be expressed as activity coefficients [37, 38].

There is also no generally accepted method of calculation of the concentration of free TBP represented by [free TBP]. Fletcher et al. [27] calculated it from the equation:

$$[\text{free TBP}] = [\text{TBP}]_{ORG} - [\text{HNO}_3]_{ORG}$$

TABLE XIII.   DISTRIBUTION COEFFICIENTS OF SOME RuNO-NITRO COMPLEXES BY TBP/n-DODECANE, RUTHENIUM CONCENTRATION $\sim 5 \times 10^{-5} M$

A revision of a table in Ref. [21], reprinted with permission.

Complex[a]	Extraction coefficient, D_{Ru}, at 20°C
1,2 dinitro	$1.3 \times 10^{-6} (\text{TBP } eff)^{3}$ [b]
1-nitro	$3.1 \times 10^{-6} (\text{TBP } eff)^{3}$
1,3 dinitro	$4 \times 10^{-6} (\text{TBP } eff)^{3}$
1 nitro-3 nitrato	$3.5 \times 10^{-5} (\alpha_{NO_3^-})^{-0.5} (\text{TBP } eff)^{3}$
1,2 dinitro-3-nitrato	$4.4 \times 10^{-5} (\alpha_{NO_3^-})^{-0.5} (\text{TBP } eff)^{3}$
1,3 dinitro-2-nitrato	$9 \times 10^{-5} (\alpha_{NO_3^-})^{-0.5} (\text{TBP } eff)^{3}$
1-nitro-2,3-dinitrato	$6.1 \times 10^{-4} (\alpha_{NO_3^-})^{-1} (\text{TBP } eff)^{3}$

[a] Structures of the complexes have been assigned according to Figure 1.

[b] $\text{TBP } eff = [\text{TBP}_{eff}] = [\text{TBP}_{initial}]^{(1-0.08 \cdot C_{HNO_3}^{aq})}$ [in vol%], $\alpha_{NO_3^-}$ is the nitrate ion activity, and $(HNO_3)_{aq}$. is given in [mole ℓ^{-1}].

Rozen and Moiseenko [39] give the following equation for calculating TBP:

$$[\text{free TBP}] = \frac{[\text{TBP}]_{initial}}{1 + 0.9 [HNO_3]^2 + 0.004 [HNO_3]^4}$$

Also, the free TBP concentration has been taken as the concentration of $TBP \cdot H_2O$ complex [21], which does not seem to be justified. On the basis of the existence of two forms of nitric acid-TBP solvates, $TBP \cdot HNO_3$ and $TBP \cdot 2 HNO_3$, Egorov et al. [40] have derived the following expression:

$$[\text{free TBP}] = \frac{[\text{TBP}]_{initial}}{[1 + K_1 (H^+)aq (NO_3^-)aq + K_2 (H^+)^2 aq (NO_3^-)^2 aq (1 + \Delta V)]}$$

where [TBP]$_{initial}$ is the initial concentration of TBP in the organic phase, K_1 is the equilibrium constant for the formation of TBP·HNO$_3$, K_2 is the equilibrium constant for the formation of TBP·2HNO$_3$, (H$^+$)aq is the concentration of hydrogen ion in the aqueous phase, (NO$_3^-$)aq is the equilibrium nitrate ion concentration in the aqueous phase, and ΔV is the change in volume during the extraction process. This is the most complete equation and the only one taking into account the change in volume.

2.7.2. Extraction coefficient data

Values of the extraction coefficents for various complexes of ruthenium nitrosyl are given in Tables XII and XIII. The extraction data are presented as the ratio of the equilibrium concentration of the element in the organic phase to its equilibrium concentration in the aqueous phase, unless otherwise noted. The complexes have different solvating power and hence different extractabilities. The extraction coefficients depend upon the concentration of TBP, the nature of the diluent, the concentrations of nitric acid, nitrous acid and nitrate ion, and also temperature.

The extraction data for the RuNO nitrato and nitro complexes indicate that it is only the free, uncomplexed TBP that is available for the extraction of these complexes. Neither TBP·HNO$_3$ nor TBP·H$_2$O appears to be involved in the extraction of ruthenium complexes. The distribution coefficients (D$_{Ru}$) increase with increasing free TBP concentration according to the general relation:

$$D_{Ru} = k \cdot [NO_3^-]_{aq}^x \, [\text{free TBP}]_{aq}^b$$

where k and x are constants, depending on the types of extraction complexes and conditions of extraction, and b is the number of TBP molecules in the extracted complexes. Usually, b is an integer (approximately two or three) although not necessarily so [35].

The effect of nitric acid concentration on D$_{Ru}$ is illustrated in Fig. 5. A maximum in extractability occurs at a certain concentration of HNO$_3$, which is explained on the basis of a combination of salting action and competition between nitric acid and ruthenium complexes for solvent molecules [28]. Metal nitrates influence D$_{Ru}$ in three ways: (1) by acting as salting agents, (2) at higher concentrations, by changing the ionic strength of the aqueous solutions, and (3) by shifting the equilibrium to higher nitrato complexes. A decrease in extracting temperature is accompanied by an increase of D$_{Ru}$ [16, 41], which can be attributed to the exothermic character of the extraction by TBP as well as to changes in equilibrium between the more and the less extractable species (Fig. 6). The presence of nitrous acid also influences the extraction by converting nitrato complexes to less-extractable nitro forms.
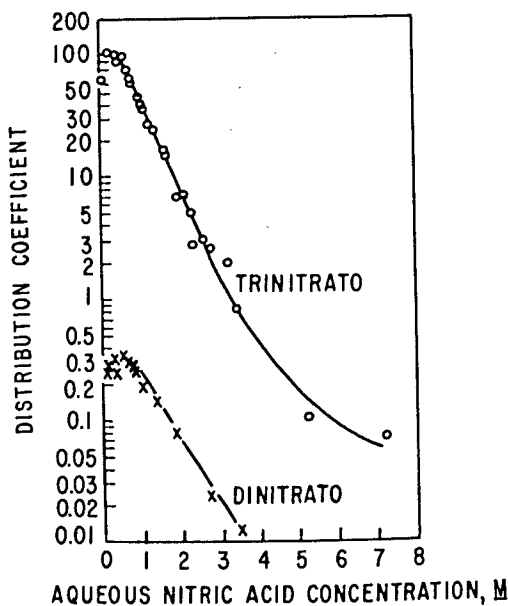
FIG.5.   The dependence of the extraction coefficients of (RuNO) nitrato complexes at 20°C and 30% TBP [15] on nitric acid concentration.
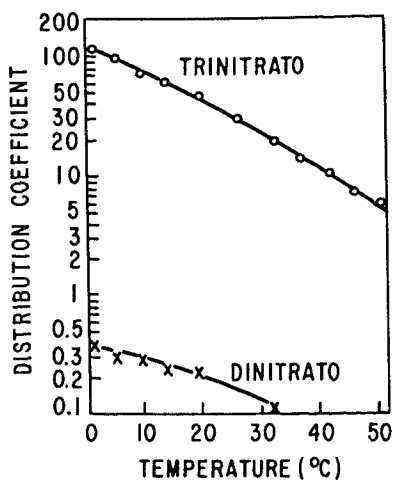

FIG.6.   The temperature dependence of the distribution coefficients of (RuNO) nitrato complexes (30% TBP, 1M HNO₃) [15].
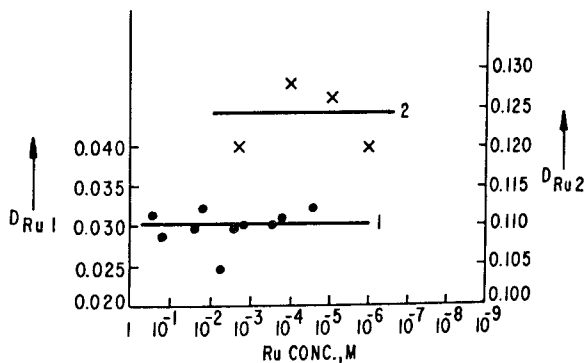
FIG. 7.   Variation of D_{Ru} with ruthenium concentration $(10^{-5}-10^{-1})$ [29].
1 — 20% TBP/0.4M HNO₃ 10 min mixing time [29];
2 — Fletcher's results. 30% TBP/3M HNO₃ for 30 s mixing at $0°C$ [11].

TABLE XIV.   VARIATION OF THE RATIO OF $D_{Ru\ tracer}/D_{Ru\ macro}$ WITH [TBP] AT CONSTANT 0.5M HNO₃ [29]

TBP (M)	$D_{Ru\ tracer}$ $(1.5 \cdot 10^{-8}M)$	$D_{Ru\ macro}$ $(1.65 \cdot 10^{-3}M)$	Ratio, $D_{Ru\ tracer}/D_{Ru\ macro}$
0.546	0.2	0.02	10
0.728	0.3	0.03	10
1.09	0.55	0.06	9.2
2.18	0.8	0.24	7.5

    The distribution coefficients are basically independent of the ruthenium concentration (within 10%) over the range 10^{-5}-M (Fig. 7) [11, 22, 29]. This can be attributed to the existence of mononuclear ruthenium species. However, comparison of the distribution coefficients of ruthenium in tracer amounts $(10^{-8}M)$ and macro amounts $(10^{-3}M)$ shows that they differ by a factor of 10 (Table XIV) [29]. This cannot be explained by changes in the molar activity coefficient of the distributing element alone, since the ionic strength due to $(RuNO)^{3+}$ does not vary much at such low concentrations; the observed results may be due to impurities in TBP and diluents.

2.7.3. Discussion

In some of the extraction data, presented in Tables XII and XIII, there is an unfortunate omission of important information, such as the phase contact time, temperature or any indication of whether specified nitric acid concentrations are initial or equilibrium values. Since acids and salts are also extracted by TBP to some extent, appreciable differences among values from different studies cannot be easily illuminated. In addition, only very few values can be compared since in most cases they refer to different extraction conditions. However, it can be observed that higher values are reported in the earlier studies (Table XII).

A value for the ruthenium distribution coefficient for all the ruthenium species in equilibrium in 3M HNO_3, extracted into 30% TBP/n-dodecane, is $D_{Ru} \approx 0.12$ at 20°C [42], which is in agreement with our determination of $D_{Ru} \approx 0.13$ [23]; the equilibrium solution contains besides ruthenium nitrosyl nitrates and nitro complexes, Ru(IV) to an extent of 10^{-4} M (characteristic brownish colour) [22, 23].

Among the *nitrato* complexes of RuNO, trinitrato and tetranitrato complexes have been found to be the most extractable. Dinitrato and mono-nitrato have been reported to extract poorly. In the case of the *nitro* complexes of RuNO, the dinitro complex is more extractable than higher nitro complexes, but its extraction coefficient is still low. Mixed *nitronitrato* species are more extractable than nitro compounds (Table XIII).

Significant differences in the reported values of the overall extraction coefficient, D_{Ru}, or the extraction coefficient of individual species may be due to: (1) the differences in experimental equilibration time, which is not always specified; (2) impurities or hydrolysis products of solvents and diluents, some of which might be much more powerful extracting agents than TBP and become particularly important at tracer ruthenium concentrations; (3) incomplete separation of different ruthenium complexes; (4) the presence of different portions of ruthenium complexes (either in equilibrium or not); and (5) incorrect identification of their structure.

2.8. Possible methods of suppressing extractability of ruthenium

The extent of extractability of some of these ruthenium species, primarily trinitrato complexes, from nitric acid solutions is responsible for complications in the Purex process. The overall behaviour of fission product ruthenium in the Purex process is largely controlled by the ruthenium nitrosyl nitrates. To obtain the optimum conditions for ruthenium decontamination, the overall extractability of the ruthenium species has to be minimized. This can be achieved by adjusting (1) acidity (concentrations of nitric acid and nitrous acid), (2) concentration of solvent, (3) temperature, (4) aqueous-solvent contact time, and (5) chemical treatment.

Since the maximum of D_{Ru} occurs at 0.5M HNO_3 [15, 29], operating at higher concentrations of nitric acid seems to be desirable. Moreover, treatment with nitrous acid has been found to improve ruthenium decontamination since it converts nitrato species to the much less extractable nitro complexes. However, the limit of conversion appears to be 90% [43]. This incomplete conversion could be the reason for treatment with nitrous acid resulting in an improvement by only a factor of two in process solutions [44] compared with improvement by a factor of 50 in laboratory solutions (20% TBP, 0.5 to 1M HNO_3) [43]. An increase in the temperature of the extraction process should also be beneficial because it leads to a decrease of the extraction coefficient, D_{Ru} [41, 44–46]. Another possibility is the use of more dilute solvent (e.g. 3% TBP) [46, 47]; however, this would also decrease the amount of uranium and plutonium extracted.

A reduction in aqueous-solvent contact time to 2–5 seconds is expected to reduce the extractability of ruthenium, since the rate-controlling process in the overall extraction of this element involves chemical equilibria among different ruthenium nitrosyl species, which are established slowly. Half-lives of 10 to 60 minutes for nitrato complexes and $t_{1/2}$ of 1 to 30 days for nitro ligands at 20°C have been measured [22]. Also, the time of formation of solvates is longer than the residence time expected in centrifugal contactors, e.g. a conversion of the aquo-complexed ruthenium nitrosyl nitrate into the corresponding TBP-complexed compound has a half-time of 3 minutes (the reverse reaction has a $t_{1/2} \sim 6$ min) [22]. The time of ~3 hours is required to reach constant D_{Ru}. In fact, when the mixer-settlers in the decontamination cycle at the Savannah River Plant were replaced with centrifugal contactors, the decontamination factor from ruthenium increased by a factor of two and the bound ruthenium in washed solvent decreased by a factor of eight due to decreased solvent degradation [48].

Chemical treatments to either eliminate ruthenium (by volatization or precipitation) or to convert it to less extractable form (by oxidizing or complexing) have been tried but without success [49, 50]. Oxidizing agents, like ozone, oxidize ruthenium to a non-extractable tetravalent state, but the reaction does not stop there; the volatile tetroxide RuO_4 is formed, which is very difficult to handle [51]. Hydrogen peroxide has been used but it decomposes in the nitric acid solution and hence is not very efficient for converting ruthenium nitrosyl species to the Ru(III) state. Hydrazine and similar reducing agents are unsuitable in the first extraction cycle to displace NO group since plutonium also undergoes reduction to unextractable Pu(III), but can be of some value in the uranium purification cycle.

No ruthenium complexing agent has been found that would reduce the extractability of this fission product into TBP and would not, at the same time, inhibit plutonium extraction [49].

Further discussion regarding the improvement of combined decontamination from ruthenium and zirconium appears in the Conclusions section.

3. ZIRCONIUM

3.1. Introduction

The chemistry of zirconium is complicated by the ability of zirconium to form co-ordination bonds and by the variety of different modes of bonding in the complexes formed. Zirconium exists exclusively in the tetravalent state. In aqueous solutions, zirconium can be surrounded by a large variety of ligands – in particular, those containing oxygen, e.g. OH^-, H_2O and NO_3^-. Complexes of the type $Zr(H_2O)_n^{4+}$ are formed, even in highly acidic solutions. Zirconium forms several types of bridging and non-bridging bonds with OH^- and O^{2-}, but the radical, ZrO^{2+}, is unlikely to exist [3].

Zirconium also forms polymers and colloids. The 8-coordination number can be found in these complexes, e.g. in polynuclear zirconium, the water molecule completes the co-ordination of double hydroxo-bridged compounds.
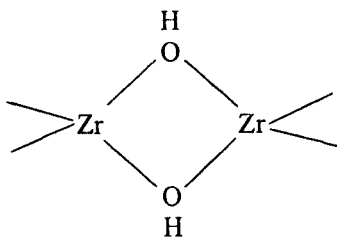
The existence of polynuclear compounds of zirconium affects significantly the chemical behaviour of the element in aqueous and organic phases. They form in non-negligible amount in solutions with zirconium concentrations greater than 10^{-4}M.

The two most common nitrates of Zr are zirconyl nitrate, $(ZrO(NO_3)_2 \cdot 2H_2O)$, which is rather readily formed from dilute nitric acid, and the hydrated tetranitrate, $(Zr(NO_3)_4 \cdot 5H_2O)$, obtained from strong nitric acid. Other hydrates of these two nitrates have also been reported. In addition to hydrates, the anhydrous oxy-nitrate, $ZrO(NO_3)_2$, and tetranitrate, $Zr(NO_3)_4$, can be prepared. Solution studies indicate the possible existence of anionic species $Zr(NO_3)_5^-$ and $Zr(NO_3)_6^{2-}$ [3].

In solutions with low nitric acid concentration complexes with the OH^- group prevail and polymers are produced. At higher nitric acid concentrations the hydroxy groups are replaced with NO_3^- ligands. Thus, in solutions with a

nitrate ion concentration near 5M most of the zirconium may be in the form of the tetranitrato complex, in rapid equilibrium with anionic species (e.g. $Zr(NO_3)_6^{2-}$) and lower nitrato forms (e.g. $Zr(OH)_2(NO_3)_2$). The proportions of these vary, depending upon the concentrations of zirconium, nitric acid and nitrate ion.
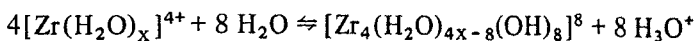
3.2. Extraction

3.2.1. Irreproducibility of extraction results

The difficulties with the study of zirconium behaviour in extraction processes come from the irreproducibility of the results [52]. The extractability of zirconium from nitric acid solutions depends on the 'history' and the method of preparation of the solutions. Depending on the zirconium concentration and the H^+ concentration, the zirconium complexes may undergo hydrolysis and/or polymerization to produce polynuclear complexes whose structure depends on the composition and nature of the initial solutions. The differences in the D_{Zr} values obtained from forward and back-extraction studies indicate that an equilibrium does not always exist in these solutions but that there are varying amounts of the different inextractable forms of zirconium in the aqueous phase. The relative amounts of inextractable and extractable forms are unchanged (D_{Zr} unchanged) when solutions are diluted and extracted immediately. However, the attainment of true equilibrium must be verified by extraction from both directions, and not on the basis of the absence of changes in D_{Zr} with time as determined by extraction from the aqueous phase. The rate of conversion of inextractable form to extractable form increases with increasing concentration of HNO_3. Sarsenov et al. [54] studied the extractability of zirconium nitrate as a function of the nature of the compound used to prepare initial solution. Zirconium nitrate and hydrolysed zirconium nitrates of different compositions were used as the starting materials for the preparation of nitric acid solutions with identical zirconium and nitric acid contents; the extractability differed by as much as a factor of two.

3.2.2. The effect of the polymerization of zirconium on its extraction

The existence of polynuclear compounds largely determines the chemical behaviour of zirconium in both aqueous and organic phases. Many anions may serve as bridges, but such bonds are formed preferentially by hydroxyl, oxygen and polydentate anions. The appearance of OH^- bridging is assumed to be due to the transfer of hydrogen ions out of the first co-ordination sphere, e.g. in the case of tetramer formation:

$$4[Zr(H_2O)_x]^{4+} + 8 H_2O \rightleftharpoons [Zr_4(H_2O)_{4x-8}(OH)_8]^8 + 8 H_3O^+$$

The hydroxo bridges in these polymers change into bridging oxo groups with time. This process is irreversible.

The extraction behaviour of the polynuclear species depends on their nature and the nature of the extractant; some of the polynuclear species have been found to be extractable. Formation of the non-extractable zirconium polymers naturally reduces the effective extraction coefficients of this element. Some of the non-extractable polynuclear compounds are in equilibrium with the monomeric forms and transform into extractable polymeric forms as a result of shifting of the equilibrium as the monomers are extracted into the organic phase [54].
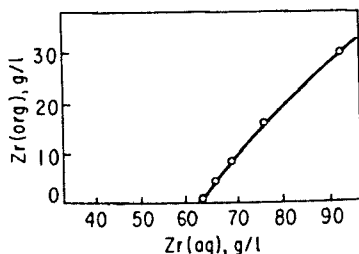
FIG.8.   Distribution of zirconium between 100% TBP and zirconium solution in 4M HNO₃, showing the presence of non-extractable polymers. Initial concentration of zirconium in the aqueous phase was 123 g/l ($V_{org}: V_{aq} = 3:1$) [54].
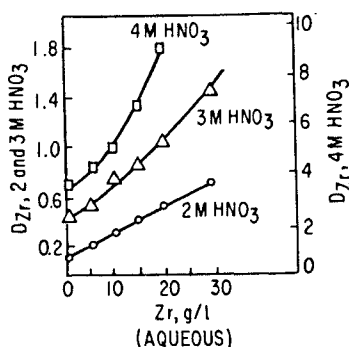
FIG.9.   Effect of stable polynuclear compounds on distribution coefficient of extractable form of zirconium. Initial concentration of extractable form of zirconium: 10 g/l [54].

In nitric acid solutions with higher zirconium concentrations (greater than 10^{-2} M), different very stable polynuclear complexes are formed which are not in equilibrium with monomeric forms. These stable polynuclear complexes do not react with colorimetric indicators, nor are they separated by cation exchange.

No zirconyl or OH groups have been detected in these polymers. Infra-red spectra indicate a Zr-O-Zr bond, and dialysis experiments indicate a polymerization factor of 4. Thus, these are oxopolymers of zirconium. Although their exact structures have not been determined, they are known to be non-extractable by TBP under any conditions, and part of the metal always remains in the aqueous phase (Fig. 8). However, they do exert a salting action on zirconium monomer extractions (Fig. 9). The same applies to zirconium solutions aged under conditions of low acidity.

It was previously believed that zirconium was extracted only in the form of monomers. However, it is now recognized that zirconium can also transfer into the organic phase in the form of hydroxy and sulphate polymers but not as oxy-polymers. For example, polynuclear zirconium compounds with a Zr : OH ratio of 2 : 1 are extracted from aqueous solutions of low acidity and high concentrations of $LiNO_3$ [55].
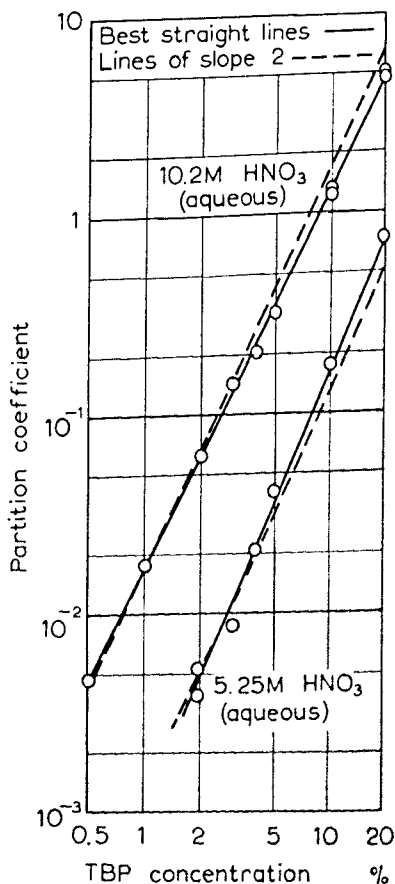

FIG.10. *Partition coefficient of zirconium as a function of TBP concentration, expressed in volume per cent. Reprinted with permission from Ref.* [57].
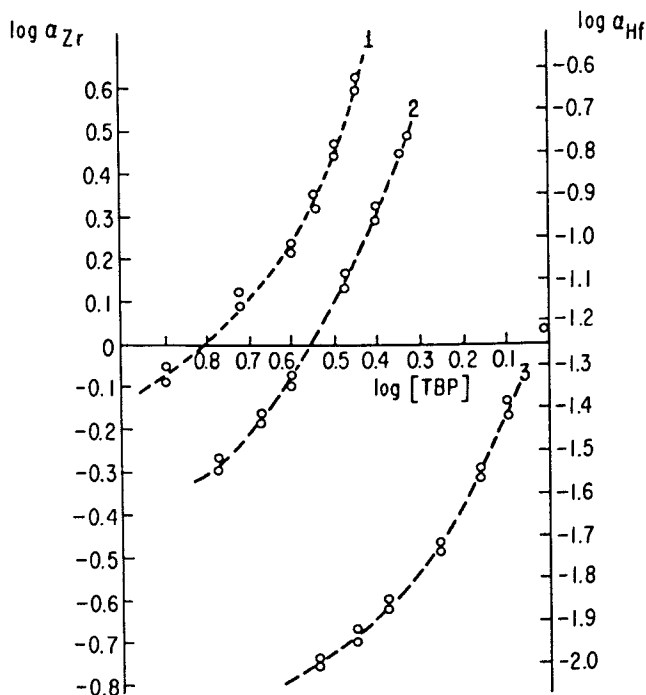
FIG.11. Dependence of zirconium distribution constants on the tributyl phosphate concentration [61]. *1 –* [HNO$_3$] *= 5M; 2 –* [HNO$_3$] *= 4M; 3 –* [HNO$_3$] *= 3M.*

$$[TBP]_0 = \frac{[TBP]_{initial}}{(1 + K_1 [H^+]_{aq}[NO_3^-]_{aq} + K_2 [H^+]_{aq}^2 [NO_3^-]_{aq}^2)(1 + \Delta V)}$$

3.2.3. Mechanism of extraction of zirconium from nitric acid solutions by TBP

The results of earlier work on the mechanism of zirconium extractions were contradictory and the number of TBP molecules solvating the zirconium nitrates was in dispute. Some believed that only one TBP molecule entered the complex [56], whereas others found the presence of disolvates [57–60] (as indicated in Fig. 10). Egorov et al. [61] have reported that formation of mono or di-solvates of zirconium nitrate with TBP depends on the concentration of the free solvent (Fig. 11).[4] They found that at low concentrations of free TBP the slope log D_{Zr} versus log (free TBP) is unity and that at higher concentrations it is approximately two. This observation indicates that during extraction from nitric acid in the range 3–7M, initially monosolvates, $Zr(NO_3)_4 \cdot TBP$, and later di-solvates, $Zr(NO_3)_4 \cdot 2TBP$, are formed.

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[4] Note that he uses the concentration of the free solvent (see caption to Fig. 11), but actually zirconium does not compete with HNO$_3$ for TBP (see Extraction Coefficient Data section below and Ref. [62]).

By thermodynamic analysis of the experimental data, Solovkin in his later work [63] showed that the extraction takes place with the formation of the following compounds in the organic phase:

$$Zr(NO_3)_4 \cdot 2TBP, \; Zr(OH)(NO_3)_3 \cdot 2TBP$$

and

$$Zr(OH)_2(NO_3)_2 \cdot 2TBP$$
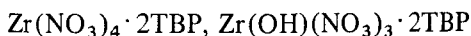
He described the extraction of zirconium by the equation:

$$Zr(OH)_i^{4-i} + (4-i)NO_3^- + 2TBP \rightleftharpoons Zr(OH)_i(NO_3)_{4-i} \cdot 2TBP$$

where $i \leqslant 4$, and calculated the extraction coefficients, which were in good agreement with published data. In addition, the formation of tri-solvates, $Zr(NO_3)_4 \cdot 3TBP$ [60], which slowly establish an equilibrium with a more highly solvated species of unknown composition, was found, together with other types of solvates like $Zr(NO_3)_4 \cdot n(HNO_3)_m \cdot TBP$ where n, m = 1 or 2 [59].

Zirconium hydroxide nitrates are extracted from the non-acidic solutions as monosolvated polymers:

$$[ZrOH(NO_3)_3 \cdot TBP]_2, \; [Zr(OH)_2(NO_3)_2 \cdot TBP]_n$$
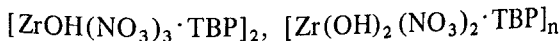
where n = 2 to 4 [64]. In these complexes, infra-red spectroscopic studies have established that the TBP is co-ordinated to the central atom.

3.2.4. Extraction coefficient data

In contrast to UO_2^{2+}, $RuNO^{3+}$, PuO_2^{2+}, Pu^{4+} or Pu^{3+}, the extraction coefficient of zirconium shows a continuous increase as the acidity of the aqueous phase increases (Fig. 12). Thus, zirconium does not appear to compete with HNO_3 for TBP as the former ions do, and the distribution coefficient of zirconium increases with an increase in the concentration of TBP(Fig. 10); in the case of Ru, in contrast, the distribution coefficient depends on the concentration of free TBP. The D_{Zr} values increase with acidity, even though the concentration of free TBP remains constant. The increase of D_{Zr} with the concentration of HNO_3 may arise from several different sources: (1) further nitration of zirconium complexes, according to:

$$[ZrO(H_2O)_n NO_3]^+ + NO_3^- \rightleftharpoons [ZrO(H_2O)_{n-1}(NO_3)_2] + H_2O$$

or

$$[Zr(H_2O)_m(NO_3)_2]^{2+} + 2NO_3^- \rightleftharpoons [Zr(H_2O)_{m-2}(NO_3)_4] + 2H_2O$$
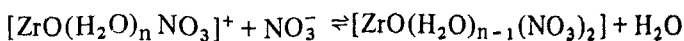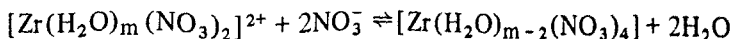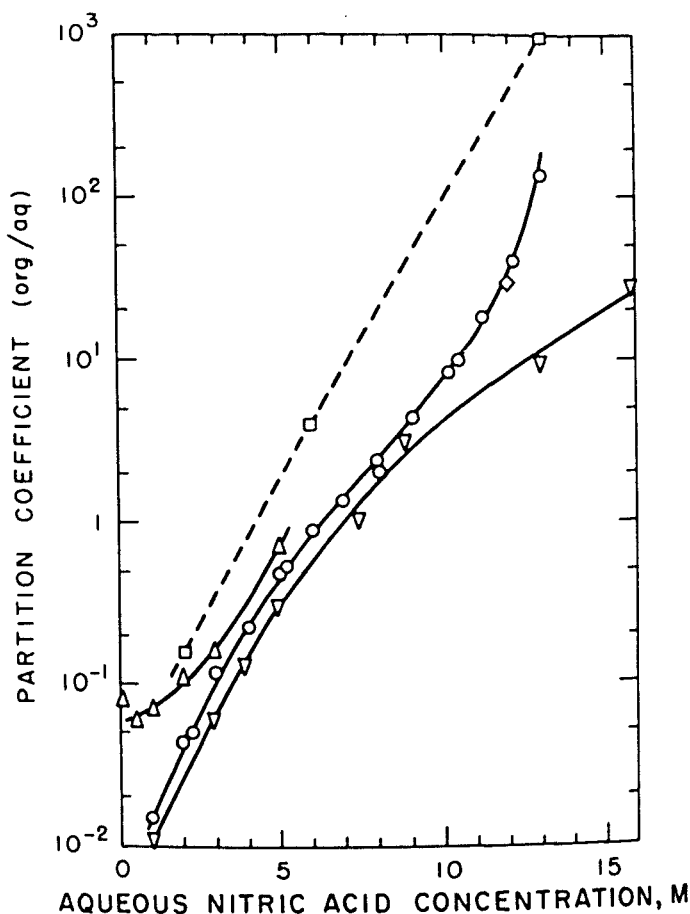
FIG.12. *Extraction of zirconium from HNO₃ systems.*
○ *19% TBP in kerosene* [57]; ▽ *30% TBP in CCl₄* [68]; △ *TBP in Varsol* [70]; □ *100% TBP* [71]; ◇ *25% TBP in benzene* [71].

(2) conversion of inextractable polymeric forms to extractable forms, which is higher at greater concentrations of nitric acid, and (3) the formation of DBP as a result of hydrolysis and radiolysis of TBP and the subsequent formation of Zr-DBP complexes.

The controlling factor in the extraction is actually the total nitrate ion concentration; the partition coefficients in the presence of nitric acid alone are the same as those for mixtures of HNO₃ with sodium nitrate (Table XV). With other elements, e.g. Ru and U, there is always an increase in extraction corresponding to an increase in the concentration of the free TBP when sodium nitrate replaces nitric acid (see the discussion on ruthenium extraction). On the other hand, in the presence of uranyl nitrate the extraction of zirconium falls considerably with increasing $UO_2(NO_3)_2$ concentration since uranyl nitrate is itself extractable and competes for TBP with Zr (Table XVI).

TABLE XV.   EXTRACTION OF ZIRCONIUM IN THE PRESENCE OF SODIUM NITRATE

19 vol.% 0.69M TBP in kerosene. Reprinted, with permission, from Ref. [57].

Concentration (M)			Distribution Coefficient (org/aq)	
HNO_3 (aq)	$NaNO_3$ (aq)	HNO_3 (org)	Mixtures	HNO_3 only[a]
1.00	0.0	0.115	0.015	--
0.99	1.0	0.205	0.05	(0.045)
0.99	2.0	0.27	0.12	(0.12)
0.99	3.0	0.33	0.25	(0.23)
0.99	4.5	0.41	0.64	(0.65)
0.99	6.0	0.48	1.41	(1.40)
2.00	0.0	0.28	0.045	--
2.00	1.0	0.37	0.14	(0.12)
2.00	2.0	0.42	0.26	(0.23)
2.00	3.0	0.47	0.48	(0.49)
1.98	4.0	0.51	0.66	(0.89)
1.98	4.5	0.54	0.74	(1.12)
1.98	5.0	0.56	1.06	(1.40)

[a] In the presence of nitric acid only at a concentration equal to $C_{HNO_3} + C_{NaNO_3}$.

The values of the distribution coefficients of zirconium with TBP are given in Table XVII and are shown on Figs 10 and 12. The distribution coefficients indicate that a satisfactory decontamination from zirconium should be achieved in the Purex process, but in reality plant data show incomplete separation [48]. This may be partially due to chemical additives and impurities. In addition, the formation and interconversion of zirconium complexes and polymers takes place gradually during the extraction and determines the decontamination from this element. The retention of zirconium by the solvent and possible remedies for this problem are discussed in the next section.

TABLE XVI.   EXTRACTION OF ZIRCONIUM IN THE PRESENCE OF
URANYL NITRATE

19 vol.% 0.69M TBP in kerosene.   Reprinted, with permission, from Ref.[57].

Concentration				Distribution Coefficient (org/aq)
HNO_3 (aq) (M)	$UO_2(NO_3)_2$ (aq) (M)	HNO_3 (org) (M)	$UO_2(NO_3)_2$ (org) (M)	Zirconium
2.00	0.000	0.28	0.000	0.045
1.97	0.0235	0.15	0.156	0.0185
1.97	0.086	0.11	0.24	0.0072
1.98	0.21	0.07	0.30	0.0047
5.00	0.000	0.61	0.000	0.55
5.02	0.0045	0.44	0.099	0.50
5.12	0.087	0.15	0.27	0.134
5.37	0.32	0.03	0.35	0.076
4.95	1.01	0.02	0.36	0.024

3.3. Retention of zirconium in solvent in the Purex process

It has been observed during the reprocessing of nuclear fuel that the efficient
separation of fission products by extraction with TBP deteriorates with time.
The decontamination factor for zirconium drops when zirconium starts to
accumulate near the feed point as an interface precipitate [72]. A possible
explanation is that the solvent and diluent both undergo radiolysis and hydrolysis,
yielding primary and secondary degradation products which complex zirconium
to form both very extractable compounds and compounds insoluble in both the
solvent and aqueous phases.

The nature of the degradation products of the solvent and diluent responsible
for the retention of zirconium in the organic phase is still a matter of dispute.
The primary degradation products of the extractant, TBP, are phosphates, e.g.
DBP (dibutyl phosphate), MBP (monobutyl phosphate) and H_3PO_4. The ratio
of MBP to DBP formed increases from 1/10 to 1/2 with increased dose of
radiation [74]. These phosphates form complexes with zirconium which are
soluble in the diluents used with TBP systems and cause retention of this element
in the organic phase. Competition between uranium, plutonium(IV), zirconium
and niobium for the DBP and MBP is illustrated in Table XVIII [24]. The
formation constants of these complexes are in the relative order $Pu(IV) > Zr$
$> Nb > UO_2^{2+}$ [24][5] However, since the uranium concentration predominates,

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[5] The stability of the complexes increases in the following sequence $Zr^{4+} > Pu^{4+} >$
$> UO_2^{2+} > RuNO_3^{3+} > Nb^{5+}$ [73].

TABLE XVII. THE EXTRACTION COEFFICIENTS OF ZIRCONIUM, D_{Zr}

Temp (°C)	TBP (vol %)	Diluent	HNO$_3$ (M)	D_{Zr}	Ref
	19	kerosene	0.98	0.015	57
			2.02	0.045	57
			3.01	0.120	57
			4.01	0.23	57
			4.96	0.49	57
			6.04	0.90	57
23	20	saturated hydrocarbons (fraction boiling at 170–240°C)	0.5	0.0089	65
			1.04	0.019	65
			1.94	0.044	65
			2.84	0.084	65
			3.74	0.167	65
			5.7	0.58	65
			9.0	4.7	65
40	20	saturated hydrocarbons	0.4	0.004	65
			1.1	0.019	65
			2.0	0.053	65
			2.9	0.121	65
			5.58	0.64	65
70	20	saturated hydrocarbons	0.58	0.012	65
			1.0	0.04	65
			1.82	0.099	65
			3.5	0.38	65
			5.4	0.78	65
	50	white spirit	4	0.48–0.52	66
			5	1.5–1.7	66
			6	5.1–5.4	66
			7	8.8–9.3	66
	5	benzene	3	0.007	67
	10		3	0.026	67
	20		3	0.07	67
	40		3	0.17	67
	5	decane	3	0.01	67
	10		3	0.032	67
	20		3	0.13	67
	40		3	0.24	67

TABLE XVII. (cont.)

Temp (°C)	TBP (vol %)	Diluent	HNO$_3$ (M)	D$_{Zr}$	Ref
~20	30	carbon tetrachloride	1.0	0.011	68
20	30	carbon tetrachloride	1.5	0.0095	68
20	3)	carbon tetrachloride	2.0	0.042	68
20	30	carbon tetrachloride	2.9	0.063	68
30	100	none	3.0	0.22	69

especially near the feed point, the extraction of zirconium and niobium is reduced, owing to competition for extractant in the organic phase and the low rates of complex formation with DBP or MBP. In solvent extraction stages where the uranium concentration is low, DBP and MBP complex zirconium.

It has been found that addition of DBP decreases the zirconium decontamination factor but does not result in precipitation, whereas the addition of MBP-DBP mixture also leads to precipitation [72, 74]. Therefore, it would seem that DBP is responsible for the reduction of the zirconium decontamination factor, that MBP (and H$_3$PO$_4$) is primarily responsible for the presence of precipitate[6], and that both are consequently responsible for the increased radiation exposure of the TBP. The literature contains little information [75] on zirconium(IV) monobutyl phosphate, but it is known that zirconium phosphate is one of the most insoluble phosphates, even in nitric acid.

The extraction of zirconium by DBP was studied by Hardy and Scargill [76] and others [47,77,78]. Figures 13 and 14 illustrate variations of D$_{Zr}$ with DBP and with HNO$_3$ concentrations. The distribution coefficient shows a maximum value at about 4M HNO$_3$; this behaviour is different from the case of zirconium extraction by TBP for which the distribution coefficient increases steadily with HNO$_3$ concentration, Fig. 12. Even very small amounts of DBP in the diluent extract zirconium strongly. For example, for the extraction of trace zirconium by 20% TBP (0.69M) values of D$_{Zr}$ are 0.05 at 2M HNO$_3$ and 0.23 at 4M HNO$_3$, whereas to obtain corresponding values of D$_{Zr}$ with DBP under similar conditions requires only 2×10^{-5} M DBP (3×10^{-3} vol.% impurity).

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[6] At larger uranium concentrations the zirconium precipitate is not formed [74].

TABLE XVIII. *EXTRACTION FROM ACID SYSTEMS* [24]

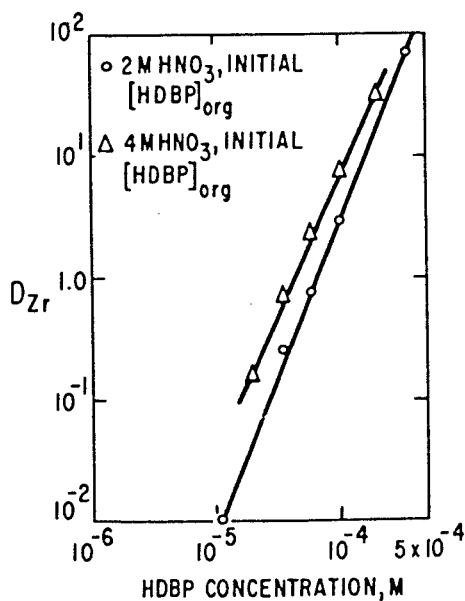| *Two-phase system with aqueous HNO3*	*Uranium VI*	*Niobium*	*Zirconium*	*Pu(IV)*
A. Fundamental systems				
1. 20% TBP + diluent	Strong at ~1M HNO3 Weak at ~0.1M HNO3	$D_{Nb} \sim 0.01$ for 6M HNO3	$D_{Zr} \sim 1$ for 6M HNO3	$D_{Pu}(max)=20$ at 7M HNO3
2. HDBP + diluent	Strong at all acidities	Stronger than U	Stronger than U and Nb	Strong in 'absence of U
3. H2MBP + diluent	Ppts. at ~3 x 10^{-3}M H2MBP	Weak	Much stronger than U and Nb weakly affected by presence of U Ppts. at 10^{-3}M MBP with 10^{-3}M Zr	Strong in presence of U
4. H2MBP + HDBP + diluent with and without TBP		Extraction enhanced over separate phosphate esters		
B. Process systems				
5. 20% TBP + diluent with U	D_u decreases as [U] increases	Too low to be significant	80% U-saturation of TBP reduces D_{Zr} by ~9 at 2M HNO3 and by ~6 at 6M HNO3	U-saturation of TBP reduces D_{Pu}, *e.g.* by a factor of 2.2 at 1.5M HNO3 for 37% saturation
6. 20% TBP + diluent with U and traces of H2MBP and HDBP	--	Strongly repressed by the presence of U		--
7. Same as (6), with Pu	--	Pu retention decreases Nb and Zr retention		--

FIG.13.   The variation of D_{Zr} with HDBP concentration in toluene.   Reprinted with permission from Ref. [76].
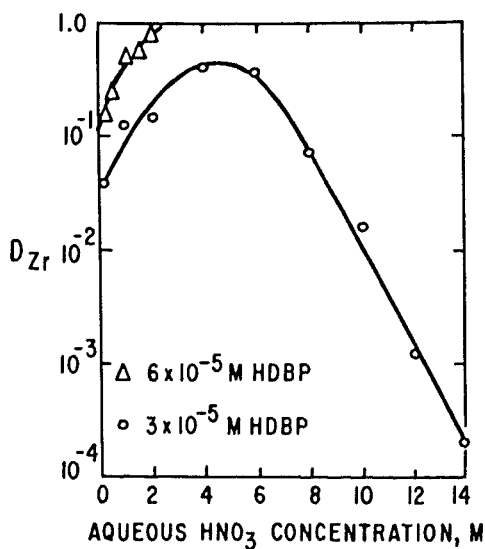

FIG.14.   The variation of D_{Zr} with HNO_3 concentration for two different solutions of HDBP in toluene.   Reprinted with permission from Ref. [76].

TABLE XIX.   CONCENTRATIONS OF TBP TO GIVE
EQUIVALENT EXTRACTION OF ZIRCONIUM FROM
HNO_3 SOLUTION

Reprinted, with permission, from Ref. [76].

Solvent	Diluent	Concentration (M)
(a) D_{Zr}=0.2 at 3M HNO_3		
TBP	Kerosene	1.38
HDBP	Toluene	3×10^{-5}

$$\text{Ratio } \frac{[TBP]}{[HDBP]} \approx 5 \times 10^{4}$$

Solvent	Diluent	Concentration (M)
(b) D_{Zr}=10^{-2} at 10M HNO_3		
TBP	Kerosene	2.7×10^{-2}
HDBP	Toluene	3×10^{-5}

$$\text{Ratio } \frac{[TBP]}{[HDBP]} \approx 10^{3}$$

At higher concentrations of HNO_3 (e.g. $> 10M$), the effect is less pronounced (Table XIX). (The possible effect of the diluent is ignored as probably negligible as compared with DBP effect.)

The degradation products of a common diluent for TBP, odourless kerosene, are organic nitrates, nitroparaffins, aldehydes, ketones and carboxylic acids. These are possibly also responsible for zirconium retention in degraded solvents. Blake et al. [79] consider that nitroparaffinenol adducts or salts lead to metal retention. Stieglitz [80], however, has not found any relation between the concentration of nitroparaffins and the degree of retention, using hafnium in the test. According to Lane [81] and Huggard and Warner [82], none of the primary degradation products cause Zr/Nb retention. These authors found that hydroxamic acids, a secondary degradation product, show a powerful retention capability. Hydroxamic acids are assumed to be formed from primary nitroparaffins by rearrangement (Victor Meyer reaction) or reacidification (Nef reaction) (Fig. 15). The presence of carbonyl groups has been found by infra-red analysis [80, 82] in compounds
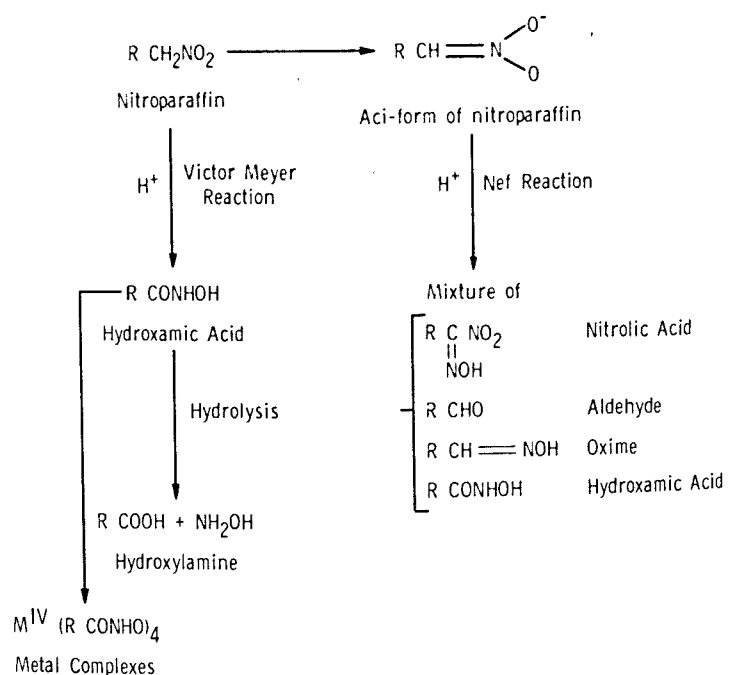
FIG.15.   *Conversion of nitroparaffins to hydroxamic acids. Reprinted with permission from Ref.* [81].

responsible for increased metal retention by degraded solvent. Stieglitz suggested that these were ketones, although they could be equally well assigned to the carbonyl group in hydroxamic acids [83].

Healy and Pilbeam [42] investigated the effects of hydroxamic acids on metal retention in the organic phase under both simulated and actual fuel reprocessing conditions. In recycled solvent there has not been positive identification of hydroxamic acids since their concentration is probably below the detectable level (10^{-6} M). They found that hydroxamic acids could have appreciable effects on zirconium retention if present in concentrations of at least 10^{-3} M, but at such concentrations they would be easily detected. At these concentrations they also should have a much larger effect than DBP if they are not destroyed by nitrous acid. Cao et al. [84] reported a $D_{Zr} \geqslant 1000$ for 0.1M hydroxamic acids. No synergic effects were observed. Thus, it is likely that hydroxamic acids are not the only complexing agents for zirconium and that some other species must also be responsible for metal retention in degraded TBP-diluent solutions.

3.4. Possible methods of improving the decontamination from zirconium

Limiting the irradiation of the organic phase and thereby the formation of radiolytic degradation products of the organic phase, which are responsible for retention of zirconium in the solvent, improves the performance of the Purex process. This reduction can be accomplished by carrying the process out in short residence time (centrifugal) contactors. The use of those contactors also limits extraction time and reduces the amount of zirconium extracted, several minutes being required for the equilibrium state to be established [54].

Chemical treatments represent another possibility for improved decontamination from zirconium. Zirconium can be eliminated by a final absorption on silica gel, by complexing it as the fluoride before the extraction, or by providing a reagent that competes for the organic degradation products by rapidly forming strong complexes. Scandium and molybdenum ions were reported to be such complexing agents [72, 73]. Fluoride complexes zirconium very strongly, even in concentrated nitric acid, and the use of fluoride has been studied [85–87]. Small amounts of hydrogen fluoride are added to the feed for the first extraction to avoid precipitation of zirconium by MBP. The monofluoride complex, ZrF^{3+}, is extractable whereas ZrF_2^{2+} and ZrF_3^{+} are not, and hence conversion of ZrF_3^{+} to higher complexes is desired. However, the fluoride ions depress the extraction of plutonium and the allowable concentration of fluoride is limited to only about twice the zirconium concentration. Moreover, concentrations of fluoride greater than 10^{-2} M appreciably enhance the corrosion of stainless steel. Aluminium is introduced into the feed to reduce corrosion effects and to improve plutonium extraction by competing for fluoride ions. Even a strongly irradiated fuel containing large concentrations of zirconium can be treated with combinations of F^- and Al^{3+} to improve zirconium removal.

Swanson [86] has found that not only does the addition of fluoride improve decontamination from zirconium, but the addition of oxalic acid, EDTA or inactive zirconium to the feed solution also produces this effect. The addition of inactive zirconium was reported to improve decontamination by a factor of four for radiozirconium and by a factor of two for ruthenium [73]. The use of hafnium has also been suggested since it can serve as a neutron poison at the same time [73]. However, most of the chemical treatments suffer from a disadvantage of introducing foreign ions which complicate waste management.

4. CONCLUSIONS

We have discussed, separately, conditions for optimum decontamination from ruthenium and zirconium (sections 2.7 and 3.4). In the Purex process,

however, simultaneous decontamination from these two elements is desired. The following process conditions can be adjusted and should be optimized to minimize the extractability and retention of both zirconium and ruthenium[7] in the organic phase:

(1) Acidity

Unfortunately, the ruthenium extraction coefficient decreases (for $HNO_3 > 1M$) whereas the zirconium extraction increases with an increase of nitric acid concentration. A concentration of HNO_3 in the range of 2–3M is a reasonable compromise. Zones of two acidities in the scrubbing section were suggested, a high-acid zone to remove ruthenium and a low-acid part to remove zirconium [45].

(2) Concentration of TBP

For more dilute solvents the D_{Ru} and D_{Zr} are both lower; additionally, the radiolytic and chemical degradation of the extractant is reduced, and thus also the zirconium retention.

(3) Temperature

Extraction coefficients of ruthenium and niobium (always accompanying zirconium) decrease with increasing temperature, but D_{Zr} has a minimum at 28–31°C [41]. The gross gamma decontamination was found to increase by operating at higher temperature (50°C) [44–46, 90]. Also, dual-temperature processing can be advantageous [91].

(4) Use of two solvents

A two-solvent system that has been tested successfully uses TBP, which gives good decontamination from ruthenium and methyl isobutylketone (MIBK), which separates zirconium from uranium [92]. However, this is not a practical solution.

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[7] The presence of DBP does not affect the ruthenium extraction, as Bruce [88] and Brown et al. [22] have shown, although reactions of ruthenium nitrosyl with DBP might occur after prolonged contact times to produce complexes soluble in organic solutions [89].

(5) Chemical treatment

Any chemical treatment that is independently effective for ruthenium or zirconium could be applied, but only as a last resort, since candidates usually lead to corrosion problems and add to waste volume and difficulties in waste solidification [49, 50, 86, 89]. Specific effects on the recovery of uranium and plutonium must be considered, including possible operational difficulties such as product reflux in scrubbing sections.

(6) Solvent cleaning

Owing to the deleterious effect of small amounts of solvent degradation products on decontamination, frequent and efficient solvent cleaning should result in improved removals of zirconium.

(7) Extraction time

Improvement in the decontamination of uranium and plutonium from ruthenium and zirconium might be achieved when the process is performed in short residence time contactors [45, 48, 90] due to the differences in the rates of extraction of these elements. In a non-equilibrated system the distribution coefficient of one (or both) of the solutes may vary, resulting in changes in the separation factor with time. The extraction of uranium and plutonium is diffusion-controlled and reaches 99% of the equilibrium state in 0.6–6 seconds [93, 94]. On the other hand, the rate-controlling process in the extraction of zirconium and ruthenium involves conversion among different chemical species and the formation of solvates. These processes are much slower than diffusion across a phase boundary, and equilibrium may not be reached for several minutes or more [10, 54]. The difference in effective extraction rates may, thus, provide a basis for improved separation of uranium and plutonium from these fission products.

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