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CHAPTER 5

SIMPLE DETERMINATION OF TBP AND DBP IN HIGHLY RADIOACTIVE LIQUID WASTE SOLUTION AND PLUTONIUM NITRATE SOLUTION

5.1 INTRODUCTION

The simple, safe and sensitive determination of TBP and DBP in the aqueous solutions of reprocessing streams concerning evaporation processes has been required for the studies on the dissolution and the degradation of TBP in aqueous solutions.

Gas chromatography may be the most suitable method to rapidly determine the trace amount of organic compounds. Brodda[1], Ladrille[2] and Lee[3] have reported the applications of gas chromatography to the determination of DBP. Their methods, however, require derivetization of DBP by reactions such as esterification or silylation prior to the gas chromatographic determination because of the poor volatility of DBP. These operations are so tedious and time-consuming that they may not be appropriate to the rapid determination.

Recently it was found that an OV-17 liquid phase coated on Tenax GC was available for the direct determination of dicarboxylic acid as its underivatized form[4, 5]. In this work, gas chromatographic conditions including column packing materials ; liquid phase coated Tenax GC has been investigated to allow the simultaneous determination of TBP and DBP without the derivetization of DBP. The recovery of TBP and DBP from the aqueous phase in the reprocessing streams containing FPs or plutonium has been also examined.

5. 2 EXPERIMENTAL

5. 2. 1 Reagents

Standard aqueous solutions of TBP (100 mg/l) and DBP (1000 mg/l) were prepared by dissolving TBP (>97 %) and DBP (>95 %) of Tokyo

Kasei Chem. Ind. Ltd. in water. Other reagents used were of analytical-reagent grade.

5. 2. 2 Extraction of TBP and DBP

A 3-ml of sodium hydroxide solution (10 %) was added to 5 ml of the aqueous solution containing the FP elements (ca. 50gFP/l, 2M HNO_3). After the precipitate was removed by filtration, the acidity of the supernatant was made 3M in nitric acid. TBP and DBP contained in the supernatant were extracted by vigorous shaking with chloroform (1:1, v/v) for a few minutes. For the solutions from the aqueous product streams of plutonium, 2 ml of sodium hydroxide solution (30 %) was added to 5 ml of the sample solution containing 50-100 mg plutonium (1M nitric acid) in order to precipitate the plutonium. The other operations were as already described. All operations were carried out in a glove-box or in a radioactively shielded space.

5. 2. 3 Gas Chromatography

A Shimadzu Model GC-14A Gas Chromatograph equipped with a hydrogen flame ionization detector (FID) and flame photometric detector (FPD), and Chromatopac C-R4A data processor were used. A glass column of 1. 0 m. × 2. 6 mm. I. D. was packed with 5 % OV-101, 5 % OV-17 or 5 % OV-25, and 0. 5 m., 1. 0 m. × 2. 6 mm. I. D. columns with 1 % PEG-20M. Tenax GC (80-100 mesh) was employed as a solid support. A solution coating technique[4] was used for the preparation of the packing and column conditioning was carried out for 10 hours in a N_2 carrier gas at 260° for PEG-20M and at 270° for the other packings. The operating conditions were as follows; column temp.: 220°, injection port temp. and detector temp.: 300°, carrier gas flow: 50 ml/min. Certain amounts of TBP and DBP dissolved in n-hexane or chloroform were injected into the column with a 1μl syringe.

RESULTS AND DISCUSSION

5.3.1 Comparison of Columns

Table 5.1 gives the numbers of theoretical plates and the separation factors (ratio of retantion time) of TBP/DBP in different columns. The separation factors obtained suggest that only OV-17 and PEG-20M are suitable for the simultaneous analysis of TBP and DBP. Table 5.1 also indicates that the number of theoretical plates for TBP in OV-17 was greater than that in PEG-20M, whereas that for DBP in PEG-20M was greater than that in OV-17. The retention times of TBP and DBP in PEG-20M were 3.61 (min.) and 13.44 (min.), respectively, whereas those in OV-17 were 5.27 (min.) and 2.47 (min.), respectively. This implies a reverse order of effusion of TBP and DBP in both columns. The sensitivities of DBP relative to TBP were 0.035 and 0.128 in OV-17 and PEG-20M, respectively. It can be concluded that the PEG-

Tabel 5.1 Numbers of theoretical plate and separation factors

	Number of theoretical plate		Separation factor
Column	TBP	DBP	TBP & DBP
OV-101	9.73	9.11	0.01[a)]
OV-17	30.73	7.53	0.73
OV-25	14.66	15.15	0.02[a)]
PEG-20M	16.07	50.00	1.81

a) TBP and DBP were not separated.

20M column is the most appropriate for the simultaneous determination of TBP and DBP.

5.3.2 Determination of TBP and DBP

The limits for determination of TBP and DBP by FID were 1 ng and 5 ng, respectively, while those by FPD were 0.2 ng and 1 ng, respectively. It was found that the FID response was consistently linear over a wide range up to 10^4 ng of both TBP and DBP whereas the FPD one showed linearity within a narrower range between 0.2 ng - 10^3 ng for TBP and between 1 ng - 10^2 ng for DBP. The determination of DBP with FPD, however, can rather give a reproducible quadratic curve with a range to 10^3, which is sufficient for the practical requirements for DBP determinations. The relative standard deviations for seven replicate measurements of TBP and DBP were, respectively, 4.1 % at 10 ng and 5.3 % at 50 ng when FID was employed, whereas those on FPD were 3.2 % at 10 ng and 5.2 % at 50 ng. Fig. 5.1 gives a typical chromatograms of 1.0 m long PEG-20M column.

5.3.3 Recovery of TBP and DBP from Aqueous Solutions

Previous studies suggested that separation of DBP from TBP by chloroform was satisfactory after DBP was back-extracted to the aqueous phase[3)]. This implies that TBP and DBP dissolved in an aqueous phase may be simultaneously extracted by chloroform with high recovery. The recoveries of TBP and DBP in nitric acid

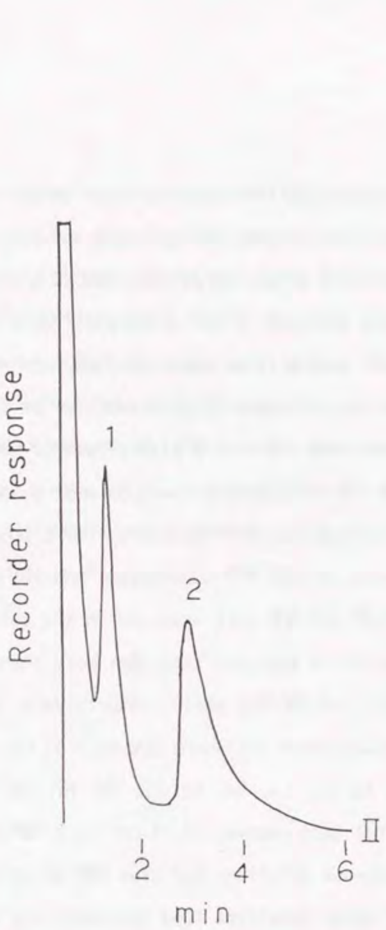

Fig. 5.1 Separations of TBP and DBP. Column: 1%PEG-20M on TenaxGC (2.6 mm i.d); column length: 1.0 m.; column temp.:220° ; injection port temp.: 300° ; detector temp.:300° ; carrier gas flow:50ml/min(N_2); H_2:0.6kg/cm^2; air:0.5kg/cm^2; 1=TBP 10ng, 2=DBP 50ng.

solutions with a wide range of concentrations (1M-6M) were examined by the procedure given. The average recoveries for TBP and DBP within the above acidic range were 96±3% and 92±6%, respectively. It was observed in the solutions from the reprocessing streams that a large portion of DBP, mainly generated as a radioactive degradation product or as a hydrolysis product of TBP, was converted into a precipitate of DBP metal complexes. This sort of precipitate could be also a source of the third phase6) during evaporation. Therefore, it is important to analyze DBP contained in both the supernatant and the precipitate. The recoveries of TBP and DBP were examined in the solutions including FP elements. It was confirmed that more than 95% and 86% of TBP(100 mg/l) and DBP(500 mg/l), respectively, were recovered from the solutions including 500 mg/l of Fe, Zr, Ru, Cr, Y, Se, Sr, Mo, Pd, Ag, Cs, La, Ce, Sm, Eu, Gd, Ni, Cd, Rb, Nd and Ba. This implies that good recoveries of not only TBP/DBP freely contained in the aqueous solutions but also DBP contained in the precipitate of DBP metal complexes from the solutions containing various metal ions can be achieved using the proposed procedures. The result suggests that DBP present in a precipitate as a complex may be converted into free DBP by making the solutions alkaline.

5.3.4 Determination of TBP and DBP in Practical Samples

The accuracy of the method was examined by analyzing practical samples to which known amounts of TBP and DBP had been added. The analytical results of standard-added samples are given in the Table 5.2. The values found agreed well with the amounts added. Fig. 5.2 shows the chromatograms of TBP and DBP including a precipitate recovered from the practical samples. The time required for one determination of TBP and DBP in the aqueous solutions from HRLW streams and PuN streams were ca. one hour and 40 minutes, respectively. It is concluded that TBP and DBP in the aqueous solution of reprocessing streams can be determined by gas chromatography without any interferences.

Table 5.2 Determination of TBP and DBP recovered from practical samples

Sample	TBP added (mg/l)	TBP[a] found (mg/l)	DBP added (mg/l)	DBP[a] found (mg/l)
HRLW[b] ca. 50gFPs/l 2M HNO_3	100	94±5	100	90±5
Plutonium nitrate[b] 30g/l, 2M HNO_3	100	93±5	100	86±7

a) Mean value ± av. dev. for 5 results.

b) TBP and DBP originally contained in the solutions were negligible.

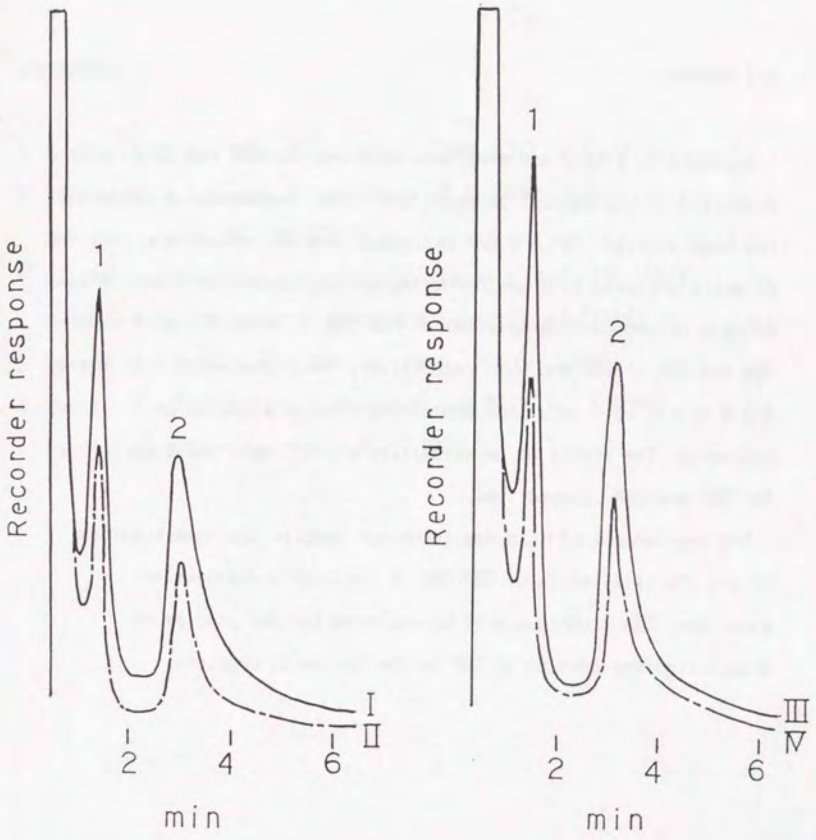

Fig. 5.2 Gas chromatograms of TBP and DBP recovered from practical samples.TBP/DBP were recovered from standard TBP and DBP-added samples of HRLW(I,II) and plutonium nitrate(III,IV).I-1:TBP 20 mg/l,I-2:DBP 100 mg/l; II-1:TBP 10 mg/l,II-2:DBP 50 mg/l; III-1:TBP 30 mg/l, III-2:DBP 150 mg/l; IV-1:TBP 15 mg/l, IV-2:DBP 75 mg/l; column:1% PEG-20M on Tenax GC (1.0 m×2.6 mm i.d.) column temp.:220° ; injection port temp.:300° ; detector temp.:300° ; carrier gas flow:50ml/min(N_2), 0.6kg/cm^2(H_2), 0.5kg/cm^2(air).

5.4 SUMMARY

A method to simply and simultaneously analyze TBP and DBP dissolved in the aqueous phase of spent fuel reprocessing streams has been studied. TBP and DBP extracted into chloroform are directly analyzed by a gas chromatograph equipped with FID or FPD using a column packing material of PEG-20M on Tenax GC. More than 95% and 85% of TBP and DBP, respectively, were recovered from the 2-3 M nitric acid solutions containing fission products or plutonium. The limits of detectability are 0.2 mg/l and 1 mg/l for TBP and DBP, respectively.

The development of this new technique enables the investigation of the characteristics of TBP/DBP in the highly radioactive solutions. The technique will be employed for the studies of dissolution/degradation of TBP in the following chapters.

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PART 2

STUDIES ON RADIOLYSIS OF DISSOLVED TBP AND WATER IN HIGHLY RADIOACTIVE AQUEOUS SOLUTIONS

CHAPTER 6

SOLUBILITY OF TBP IN PLUTONIUM NITRATE SOLUTION AND HIGHLY RADIOACTIVE LIQUID WASTE SOLUTION

6.1 INTRODUCTION

TBP used for the extractive reprocessing of spent nuclear fuel could slightly be left in aqueous solutions after the rinsing processes of PUREX reprocessing. It is required to know the solubility of TBP in the actual solutions of reprocessing for the study of behavior of dissolved TBP in evaporation processes. The studies about TBP solubility in the simple aqueous systems with varying solvents, temperature, concentrations of nitric acid[1,2] and other electrolytes has been reported. The data have been reviewed[3]. There have been, however, no literature information on the solubility of TBP in PuN solution. On the other hand, estimation of the solubility in solutions containing FPs from the data reported must be difficult because the effect of electrolytes on solubility in a mixture of plural electrolytes differs from that in solutions containing a single electrolyte. In this study, the variation in solubility of TBP with concentrations of the species involved or with temperature in the solutions of evaporation processes, namely PuN solution and HRLW solution, has been investigated. The effects of those factors are also discussed for the clarification of the dissolution properties of TBP.

6.2 EXPERIMENTAL

6.2.1 Reagents

TBP (purity >99%)[Tokyo Kasei Kogyo Co. LTD.] was used as received. PuN solutions used in these experiments were prepared from the plutonium nitrate recovered at the Tokai Reprocessing Plant. The PuN was purified with anion exchange resin in nitrate

form. The concentrations of a few foreign elements present were less than 50 ppm. Other reagents used were of analytical reagent grade.

6.2.2 Procedures

Plutonium nitrate solutions (5-235 g/l) with varying nitric acid concentrations (0.9-8M) were prepared; whereas, the various concentrations of FPs in 1.5-8.3 M nitric acid were prepared from HRLW of the Tokai Reprocessing Plant. Undissolved particles present in FP-containing samples were filtered off. The preparation of TBP-saturated solutions were prepared by adding 0.2 ml of TBP (100%) to 10ml of the solutions of PuN or HRLW, corresponding to a slight excess of TBP relative to the approximate solubilities of TBP in the solutions, after undissolved particles present in the solutions had been filtered off for HRLW. The undissolved TBP was removed by filtration with double layer JIS-5C filter after vigorous shaking for 15 min.. It was confirmed before the experiment that the excess TBP can be quantitatively removed by the filtration. The determination of TBP in solutions of PuN or HRLW was performed by the method described in Chapter 5. The validity of the proposed method for determining the solubility of TBP was confirmed by observing the solubility in nitric acid solution or in uranyl nitrate solution, which were in accord with the reported value[4,5]. The concentrations of major components in the PuN solutions or HRLW solutions used were determined by controlled-potential coulometry for plutonium (Chapt. 4), ICP spectrometry for metal elements (e.g. Tc in Chapt. 3), and potentiometric titration for free nitric acid [16]. Table 6.1 lists the major elements in the HRLW used. The concentration of plutonium in PuN solution was determined after the removal of excess TBP since a slight amount of plutonium moves to the organic phase of the excess TBP during the dissolution of TBP in aqueous phase. With respect to the temperature effect on the solubility of TBP in PuN solutions, TBP was added to the solutions 3 hours after controlling temperature, which was confirmed to be adequate for reaching stable oxidation states of plutonium. The oxidation states and the effect of temperature on the Pu-NO_3^- complex were investigated by the spectrometry described in Chapter 4 using a photometer (Hitachi U3410) with an absorption cell thermostated at a given temperature (25°-100°)±0.5°.

6.3 RESULTS AND DISCUSSION

6.3.1 Variation in Solubility of TBP with Concentration of Plutonium or FP Metal-Ions

The solubility of TBP in nitric acid solutions with varying concentrations of plutonium or FP metal-ions was investigated. Figure 6.1 gives the solubility at the concentration of PuN from

Table 6.1 Concentrations of major metal elements in highly radioactive liquid waste solutions

Element	HRLW1 (M)	HRLW2 (M)	Element	HRLW1 (M)	HRLW2 (M)
Na	2.6×10^{-1}	2.0×10^{-1}	Mo	6.3×10^{-3}	4.2×10^{-3}
Fe	6.4×10^{-2}	5.4×10^{-2}	Cr	5.8×10^{-3}	7.6×10^{-3}
Nd	1.4×10^{-2}	1.3×10^{-2}	Tc	5.1×10^{-3}	6.0×10^{-3}
Zr	9.9×10^{-3}	8.8×10^{-3}	Pd	4.8×10^{-3}	2.8×10^{-3}
U	8.0×10^{-3}	8.4×10^{-3}	Sr	4.4×10^{-3}	4.4×10^{-3}
Ru	7.9×10^{-3}	8.0×10^{-3}	Pr	3.5×10^{-3}	2.8×10^{-3}
Ba	7.3×10^{-3}	5.8×10^{-3}	La	3.1×10^{-3}	2.6×10^{-3}
Ce	7.1×10^{-3}	7.2×10^{-3}	Sm	2.7×10^{-3}	2.5×10^{-3}
Ni	6.8×10^{-3}	6.8×10^{-3}	Y	2.2×10^{-3}	2.2×10^{-3}

0 to 1M. The solubility in the pure nitric acid system and that in ferric nitrate are also shown. The values shown in the figure are the mean of two separate determinations. The largest average deviation was 5%. Setschenow[10] described the equation for the solubility of TBP as follows;

$$\log S_o/S = kC \qquad (1)$$

where S_o is the molar solubility of TBP in pure water and S is that of TBP in a given concentration C of electrolyte simply acting for the salting-out of TBP. A plot of log S vs concentration of an ion under the condition of constant concentration of a foreign species is expected to show a linear relation referring to the relation between S_o/S and ions in the ternary system[11]. As shown in Fig. 6.1, the plot of log S vs the concentration of Pu(IV) at a constant HNO_3 concentration shows a linearity at low plutonium concentrations (0 - 0.1M) where most of TBP may be dissolved as the form combining with HNO_3[3,13], independent of interaction with Pu(IV) as an electrolyte mentioned above. Log S in PuN, however, levels off with increasing concentration of plutonium. The same tendency was reported in the pure nitric acid system, extending the range of its concentration beyond 1M[3,6]. Higgins et al. indicated that the lack of linearity was due to a specific interaction between the organic and its electrolyte[6]. The levelling off in

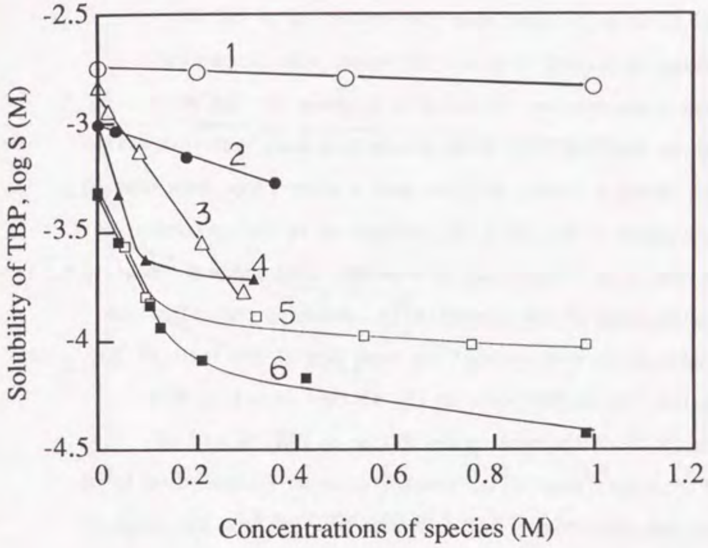

Fig. 6.1 Effect of species involved in aqueous solutions on TBP solubitity; 1: HNO_3, 2: Fe(III) in 8M HNO_3, 3: Pu(III) in 0.6M HNO_3, 4: Pu(IV) in 3M HNO_3, 5: Pu(IV) in 8M HNO_3, 6: Pu(IV) in 6M HNO_3.

the solubility of TBP at high plutonium concentrations may be due to the dissolution form of some TBP-Pu complexes, namely $Pu(NO_3)_n^{(4-n)+} \cdot TBP$, because the solubility of the complexes is expected to be significant when the solubility of $TBP-HNO_3$ complex(es), discussed in 6.3.2, decreases with increasing plutonium concentration. It would be evidence for the above explanation that Pu(III), which should have much less interaction with TBP, shows a linear relation over a wider range than that in Pu(IV) as shown in Fig. 6.1. The solubility vs the concentration of iron, where no interaction is expected, also shows a linearity over a wide range of the concentration. Assuming that plutonium simply acts as an electrolyte, the logarithm of the ratio of TBP molar solubility in PuN solution (S) to that in nitric acid solution (S_o') at the same concentration of HNO_3 should be inversely proportional to the concentration of Pu according to Eq. (1). The following linear relation was obtained from the range of plutonium concentration of 0 - 0.1M in Fig. 6.1.

$$\mathrm{Log}\ S/S_o' = -6.0[\mathrm{Pu(IV)}] \qquad (2)$$

where [Pu(IV)] is the concentration (M) of Pu(IV). S_o' given in the literature cited[1] was used. The solubility of TBP in 3M HNO_3 solutions with varying concentration of FP metal-ions is shown in Fig. 6.2 together with that in ferric nitrate solutions and zirconium nitrate solutions. The largest deviation in the

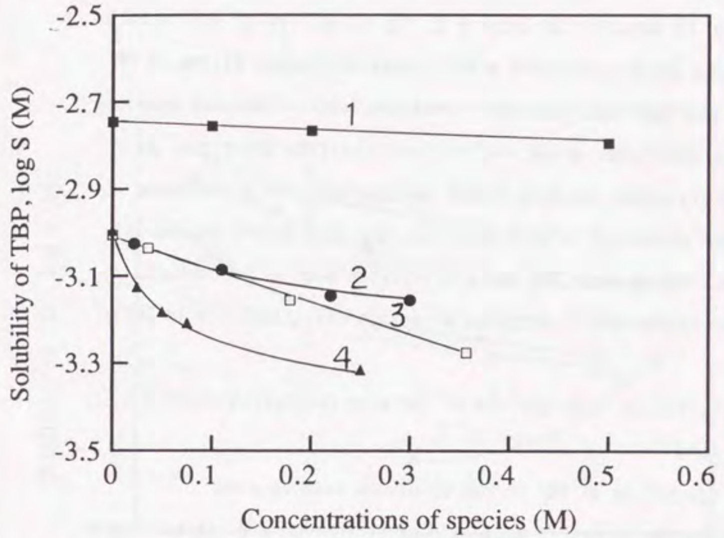

Fig. 6.2 Effect of species involved in aqueous solutions on TBP solubitity; 1:HNO_3, 2: Zr(IV) in 8M HNO_3, 3: Fe(III) in 3M HNO_3, 4: FP/metal-ions in 3M HNO_3 (HRLW1).

mean value shown in the figure was 5%. The concentration of species for diluted HRLW is given as total molecules of FP metals per liter. The original HRLW solution is estimated to be 0.5M as total FP metals from Table 6.1. The solubility of TBP in HRLW solutions which levels off with increasing concentrations of FP metal-ions apparently shows a trend similar to that in zirconium nitrate solutions, while that in ferric nitrate solutions, as previously shown, shows a linear relationship. This indicates that TBP dissolved in HRLW solutions may also have some specific interactions between TBP and electrolytes such as zirconium, because zirconium(IV) provides a certain extractability to TBP[12].

6.3.2 Variation in Solubility of TBP with Concentration of Nitric Acid

The solubility of TBP in PuN solutions with varying concentration of nitric acid is plotted in Fig. 6.3. It was found that the variation in TBP solubility with nitric acid concentration at low plutonium concentrations (approximately 0.1M) shows a similar relationship to that in nitric acid (1-8M). Since the dissolution of TBP in PuN solutions at low Pu concentration is predominantly dependent upon the HNO_3 other than the dependency on Pu given in Eq.(2), the solubility of TBP in solutions containing 0 - 0.1M of plutonium may be expressed in Eq.(3) by approximation of the curve of TBP in HNO_3 in Fig. 6.3 and Eq.(2).

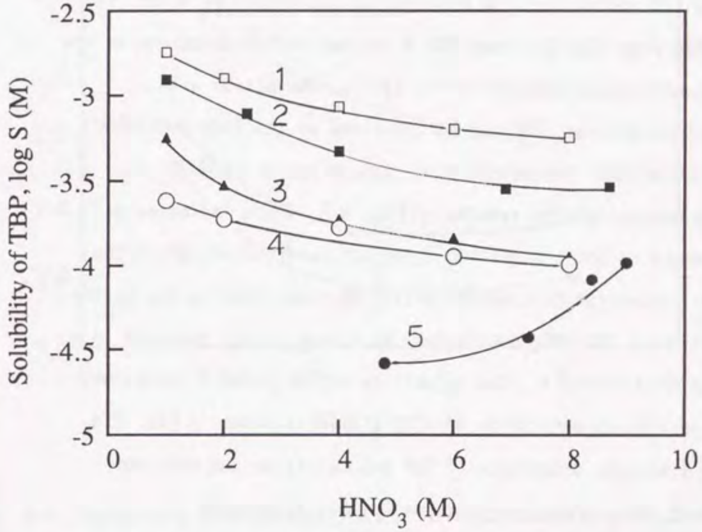

Fig. 6.3 Variation in TBP solubility with nitric acid concentration; 1: HNO_3, 2: 4.2×10^{-2}M Pu(IV), 3: 1.0×10^{-1}M Pu(IV), 4: 3.1×10^{-1}M Pu(IV), 5: 9.8×10^{-1}M Pu(IV).

$$\mathrm{Log}\ S = -2.8 - 0.15[HNO_3] + 0.0091[HNO_3]^2 - 6.0[Pu(IV)] \quad (3)$$

In comparison with the experimental result shown in Fig. 6.3, this empirical formula can describe the solubility of TBP in less than 0.1 M of PuN (in 1-8M HNO_3) solutions within 6% error. It is probable from Fig. 6.1 that TBP dissolved in PuN solutions at low Pu concentrations apparently has little interaction with plutonium; whereas, TBP may be dissolved as the form combining with H_2O or HNO_3 depending on the concentration of HNO_3[3, 13] taking acconut of the results in Fig. 6.3, which indicates a dependency on HNO_3. A salting-in effect observed of TBP in the higher concentration range of nitric acid may also be due to the formation of TBP-HNO_3 complex(es) as Alcock et al. reported in a nitric acid system[13]. The solubility of TBP in HRLW solutions with varying concentration of nitric acid is shown in Fig. 6.4, where a similar dependency of TBP solubility on the HNO_3 was observed. This indicates that the solubility depends predominantly upon the formation of TBP-HNO_3 complex(es) at the high concentration of HNO_3. The form of TBP-HNO_3 complex(es) would be dependent on the concentrations of HNO_3/H_2O. It may vary from TBP•H_2O to HNO_3•TBP•H_2O, HNO_3•TBP, $2HNO_3$•TBP and $3HNO_3$•TBP with increasing the concentration of HNO_3, inferring from the earlier report of solubility of HNO_3/H_2O in TBP[9, 13].

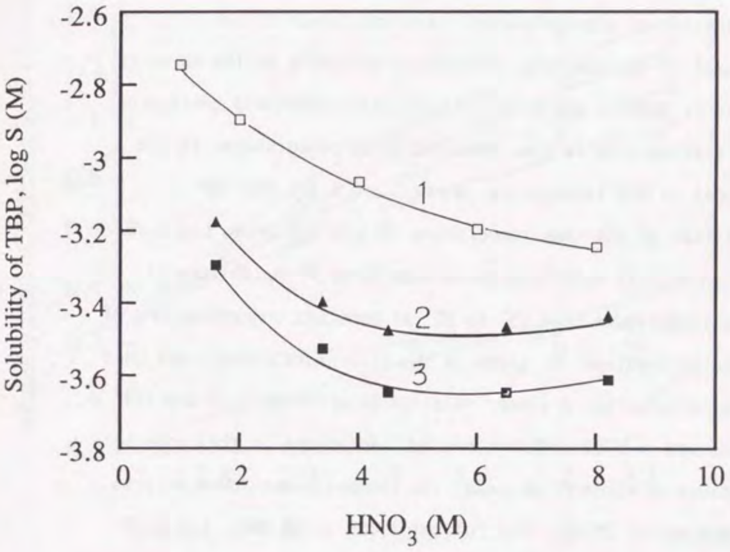

Fig. 6.4 Variation in TBP solubility with nitric acid concentration; 1: HNO_3, 2: HRLW1 diluted by a factor of 2, 3: HRLW1 (no dilution).

6.3.3 Effect of Temperature on the Solubility of TBP

The logarithm of the ratio of TBP molar solubility in pure water (S_o) to the molar solubility of TBP in a given concentration of electrolyte (S) is proportional to the reciprocal of the absolute temperature according to the equation proposed by McDevit and Long[7]. Log S_o/S in solutions containing plural electrolytes is also expected to be proportional to the reciprocal of the temperature, where S_o and S are the TBP solubilities at the same temperature. Figure 6.5 shows Log S_o/S of TBP in several solutions containing Pu or FP metal-ions at varying temperature from 25° to 90° at constant concentrations of the species involved. S_o given in the literature cited[3] was used for the calculation. A linear relation between log S_o/S and 1/T was observed in HRLW solution and HNO_3 solutions in the range of temperature of concern; whereas, the linearity was found only at low temperature, 25-55°, for PuN solutions in 5M HNO_3. Log S_o/S deviates from the linear relation with increasing temperature in PuN solutions, particularly at higher concentrations of Pu. This can be due to the change in the Pu ionic form in the solutions depending upon the increase in temperature. Figure 6.6 shows the absorption spectra of plutonium nitrate observed at 25° and 90°. It is apparent that the spectrum, specially the absorbance at 480 nm of Pu(IV), in 5M HNO_3 at 90° is rather closer to that of the same concentration of Pu(IV) at 25° in 6M HNO_3 than that in 4M HNO_3. This implies that the complexing formation with NO_3

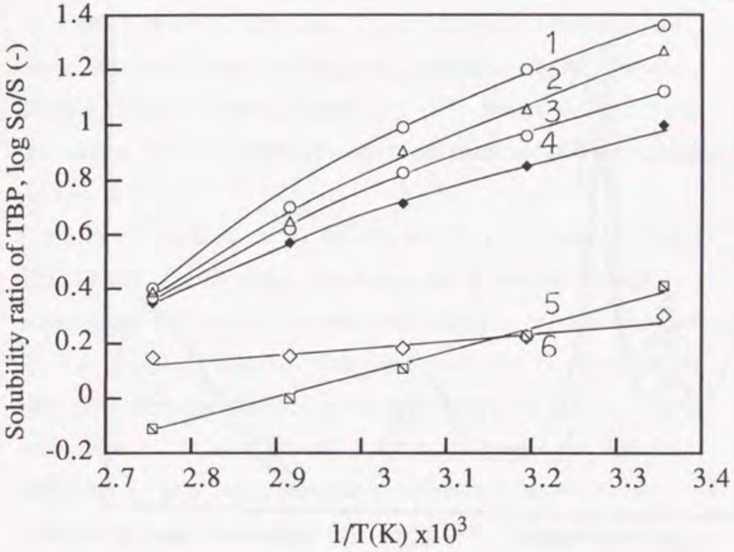

Fig. 6.5 Effect of temperature on TBP solubility; 1: 4.2×10^{-1}M Pu(IV) in 5M HNO_3, 2: 2.1×10^{-1}M Pu(IV) in 5M HNO_3, 3: 1.3×10^{-1}M Pu(IV) in 5M HNO_3, 4: 4.2×10^{-2}M Pu(IV) in 5M HNO_3, 5: 5M HNO_3, 6: HRLW2 in 1M HNO_3.

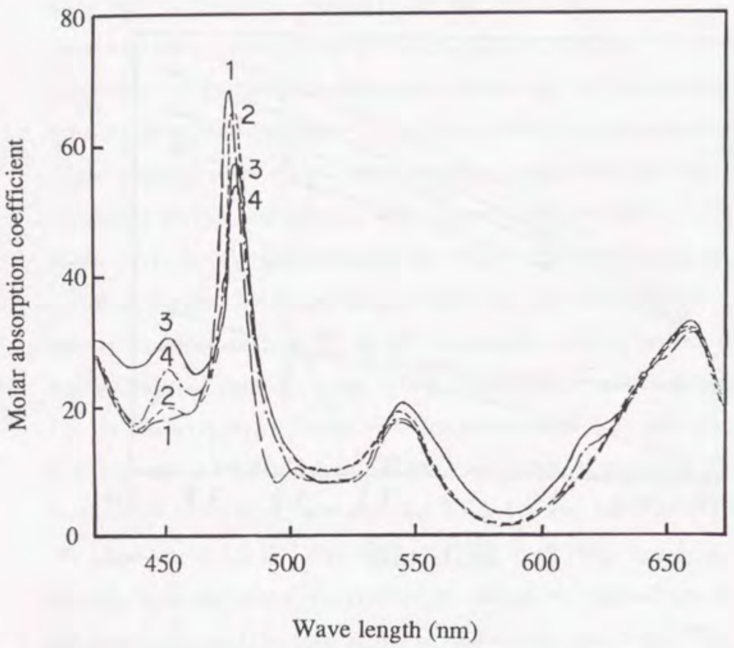

Fig. 6.6 Absorption spectrum of plutonium; 1: 4M HNO_3 at 25˚ , 2: 5M HNO_3 at 25˚ , 3:5M HNO_3 at 90˚ , 4: 6M HNO_3 at 25˚ .

increases with rising temperature, which is generally in accord with the previous study[14]. Lipis et al. reported that $Pu(NO_3)_3^+$, $Pu(NO_3)_4$ and $Pu(NO_3)_5^-$ were the principal complexes, respectively, at 3.8M, 5.6M and 7.1M of HNO_3[15]. It is probable based on the above discussion that the principal complex in 5M HNO_3 becomes $Pu(NO_3)_4$ with increasing temperature. This change in ionic form, decreasing the ionic strength, would increase solubility as shown in Fig. 6.5.

A plot of log S_o/S vs 1/T for the PuN at a low concentration of HNO_3 (0.6M) is a straight line except for a portion at high temperature with nearly the same slope as that in water as shown in Fig. 6.7. This suggests that the dissolution is predominantly dependent upon the dissolution in water where TBP-H_2O is concerned[8, 9]. It also implies that the dissolution of TBP in PuN solution at a low concentration of HNO_3 is an exothermic reaction because the same is true of water[9]. The decrease in log S_o/S observed at high temperature is pronounced at higher concentration of plutonium. Table 6.2 indicates that the composition of Pu(VI) becomes appreciable with decreasing concentrations of plutonium at high temperature. The change in ionic form shown above would be the reason for the relative decrease in log S_o/S with rising temperature observed at the higher concentration of plutonium, because log S_o/S is proportional to the number of ions and to the square of the valence of the ions involved[11].

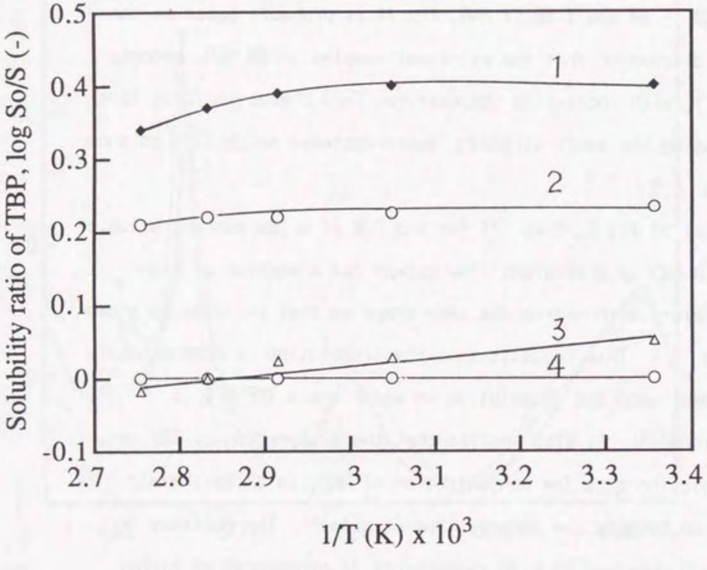

Fig. 6.7 Effect of temperature on TBP solubility; 1: 1.0×10^{-1}M Pu in 0.6M HNO_3, 2: 2.1×10^{-2}M Pu in 0.6M HNO_3, 3: 1M HNO_3, 4: water.

Table 6.2 Distribution of Pu oxidation states in 0.6M HNO_3

Temp. (C)	Pu (M)	Pu(IV)$^{a)}$ (%)	Pu(VI)$^{a)}$ (%)
90	0.021	24	76
	0.105	54	46
25	0.021	100	0
	0.105	100	0

a) Calculated from spectra obtained three hours after controlling temperature.

6.4 SUMMARY

The solubility of TBP in solutions of PuN and HRLW with varying several parameters was investigated. An empirical formula describing the solubility of TBP in PuN solutions in the range of 0-0.1M Pu and 1-8M HNO_3 was obtained. The following items have become apparent in the present study. (1) Plutonium simply acts as an electrolyte in the range of 0-0.1M Pu for the salting-out of TBP; whereas, different tendency in the dissolution of TBP was observed with increasing the concentration of Pu, which is presumably due to the interaction between Pu(IV) and TBP because the TBP solubility in Pu(IV) solutions shows different tendency from that in Pu(III) solutions, which has much less interaction with TBP. (2) The variation in S in PuN solutions (0-0.1M Pu) with nitric acid concentration shows almost the same tendency as that in HNO_3 solution where S is the molar solubility of TBP in a given concentration of the electrolyte (Pu). This suggests that TBP is dissolved in the form combining with H_2O/HNO_3. (3) A dependency of S on FP metal-ions in HNO_3 for HRLW solution similar to that for PuN was observed. (4) A plot of log S_o/S vs 1/T gives a nearly linear relation for the solutions of HRLW or low concentration of PuN where S_o is the molar solubility of TBP in pure water. The plot (log S_o/S vs 1/T) deviates from the linear relation at high temperature presumably due to the change in ionic form of Pu when the concentration of Pu is increased.

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CHAPTER 7

DEGRADATION OF TBP IN PLUTONIUM NITRATE SOLUTION

7.1 INTRODUCTION

It is of importance to know the degradation behavior of TBP dissolved in aqueous solutions from the discussion on the formation of the complex, organic compounds, as mentioned in Chapter 1.

Little information is available about the degradation of TBP occurring in aqueous single-phase system although the studies on the degradation of TBP have lasted three decades and those results were summarized by Schultz et al.1). Becker et al. investigated TBP degradation by both hydrolysis and radiolysis in nitric acid system with ^{90}Sr-^{90}Y source2,3). It was shown that TBP concentration exponentially decreased by radiolysis with increasing total dose. Clay reported that the chemical attack upon dissolved TBP would be due to radiation-produced hydroxyl radicals because G(DBP) declined with increasing undissociated HNO_3 acting as a hydroxyl radical scavenger4). These suggest that the TBP radiolysis occurring in solutions containing dissolved species such as Pu and FPs would be more complicated and unpredictable because some chemical reactions between the dissolved substances and hydroxyl radicals may be involved. In this chapter, the study of TBP radiolysis in PuN solutions as an alpha radiolysis of TBP in the actual solutions of nuclear fuel reprocessing is described.

7.2 EXPERIMENTAL

7.2.1 Reagents

TBP (purity >99%) and n-dodecane (purity >99%)[Tokyo Kasei Kogyo Co. LTD.] were used as recieved. Plutonium solutions used

in these experiments were prepared from the PuN solutions recovered at the Tokai Reprocessing Plant and from high purity metal (NBL126 >99.9%). The former was purified by anion exchange method in nitrate form and left fourteen days to get equilibrium of radiolytically generated HNO_2. The concentrations of a few foreign elements present were less than 50ppm. Other reagents were of analytical-reagent grade.

7.2.2 Procedures

The concentrations of Pu and free nitric acid in the solutions studied varied from 10 g/l to 175 g/l and from 0.9M to 8M, respectively.

The total concentration, the oxidation states and the isotopic compositions of Pu were determined by the controlled-potential coulometry, the spectrophotometry as shown in Chapter 4 and mass spectrometry, respectively, whereas the concentration of free nitric acid was determined by the potentiometric titration after precipitation of Pu by the addition of KF5). Nitrous acid contained in PuN solutions was determined by the spectrophotometry6). TBP-saturated solutions were prepared as described in Chapter 6. The degradation rates were obtained by periodically determining the concentrations of TBP. TBP in the aqueous Pu solution was extracted with chloroform (1:1, v/v) and determined by the gas chromatography shown in Chapter 5.

7.2.3 Estimate of Absorbed Energy

It was assumed that all the energy of alpha and beta particles emitted from plutonium was completely absorbed in the liquid. The energy from gamma ray was neglected because that was apparently small relative to the total decay energy of Pu used. The isotopic compositions and alpha/beta-radiation energy released were given in Table 7.1.

7.3 RESULTS AND DISCUSSION

7.3.1 Effect of Plutonium on the Degradation Rate of TBP

The TBP degradation in different concentrations of Pu obtained under the same concentration of nitric acid (7.8M) are given in Fig. 7.1. It seems to be difficult to separate exactly the hydrolytic contribution from the radiolysis because both involve chemical reactions, for instance, a reaction with HNO_3 where HNO_3 would act as a scavenger for radiation-produced OH radicals and also would act as a reactant in the hydrolysis. Hence, the degradation dealt with here refers to the all-around reactions though the contribution due to hydrolysis must be relatively small at ambient temperature. The literatures cited[7,15] showed that the amount of HDBP generated in TBP was proportional to the energy that the system absorbed. The similar proportionality in TBP degradation would be expected because HDBP should be the

Table 7.1 Isotopic compositions and $\alpha(\beta)$-radiation energy of PuN used

	PuN1			PuN2		
Isotopes	Wt%	Conc.[a] (Bq/ml)	Energy (Wh/l)	Wt%	Conc.[a] (Bq/ml)	Energy (Wh/l)
^{238}Pu	1.4	8.85×10^{7}	0.0777	0.0015	9.48×10^{4}	8.32×10^{-5}
^{239}Pu	55.9	1.28×10^{7}	0.0105	97.9	2.24×10^{7}	0.0185
^{240}Pu	24.1	2.02×10^{7}	0.0167	2.06	1.73×10^{6}	1.39×10^{-3}
^{241}Pu	13.0	4.99×10^{9}	0.0168	0.012	4.54×10^{6}	1.5×10^{-5}
^{242}Pu	5.6	8.12×10^{4}	6.36×10^{-5}	0.001	14.5	1.1×10^{-8}
			0.122(Total)			0.020(Total)

a) Radioactivity concentrations when total Pu is 10.0 mg/ml.

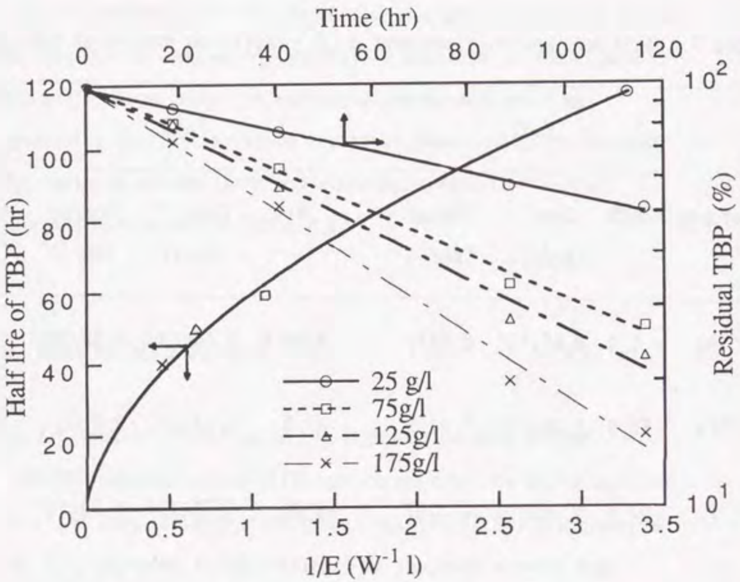

Fig. 7.1 Degradation rate of TBP vs reciprocal of power due to α / β decay, 1/E, in PuN solutions. E/[Pu]: 0.0122 W/g, [HNO_3]: 7.8M, The initial concentrations of TBP are 45±2mg/l, 40±2mg/l, 37±2mg/l and 37±2mg/l for 25g/l, 75g/l, 125g/l and 175g/l of PuN, respectively.

major degradation product of TBP. Together with the results in Fig. 7.1 indicating the first-order kinetics, the degradation of TBP could be described as ($-dC_{TBP}/dt=kEC_{TBP}$), where E is absorption rate of alpha/beta decay energy in the solutions (W/l). The half life of TBP in each solution is also plotted in the Fig. 7.1 as a function of reciprocal of E. In the figure, however, it can not be seen that the half life is proportional to 1/E. That implies the above assumption may not be valid. In Fig. 7.2 the degradation is expressed as a function of the energy that the system absorbed. These would give the possibility of the degradation of TBP depending on the Pu concentration. The relationship in Fig. 7.1 is approximated by the following empirical formula, which must be valid in the particular Pu solution (PuN1, E/[Pu]:0.0122 W/g).

$$t_{1/2}(hr) = 10.25\{(1+45.1/E)^{1/2}-1\} \qquad (1)$$

The expression including the dependence on Pu concentration will be discussed later.

7.3.2 Effect of Nitric Acid on the Degradation Rate of TBP

Clay et al. reported the effect of undissociated HNO_3 on G(DBP) [4]. They suggested the decrease in G(DBP) with the increase of [HNO_3] is due to the fact that radiation-produced OH radicals originating from water[4, 12] are scavenged by undissociated HNO_3

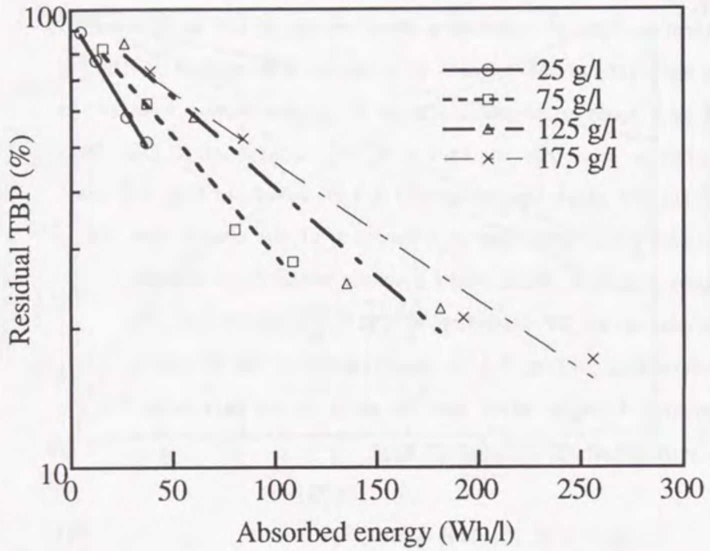

Fig.7.2 Dependence of TBP degradation rate on plutonium concentration. $[HNO_3]$: 7.8M

as shown in Eq. (2), because the dissolved TBP is chemically attacked by OH radicals.

$$OH + HNO_3 \rightarrow H_2O + NO_3 \qquad (2)$$

It is also known the fraction of undissociated HNO_3 steeply rises with increasing HNO_3 concentration[12]. The G(DBP) in 0.5M, 2M and 4M of nitric acid solutions were, for instance, presented 1.87, 1.33 and 0.49 by Clay et al.. The same effect in PuN was investigated under the condition of the constant Pu concentration (25/75 g/l). However, the description of the degradation of TBP by G-value, which is defined the number of TBP molecules decomposed when the whole aqueous system containing TBP absorbs 100 eV, may not be appropriate for the aqueous solution system, because G-value much depends on the concentration of TBP, namely initial solubility of TBP. The decrease of the degradation rate of TBP is expressed by a half life and plotted as a function of free HNO_3 in Fig. 7.3. Approximately linear relationship is observed and the following equations are empirically obtained.

$$t_{1/2} = 11.4C_{HNO3} + 22.0 \quad : 25\ g/l \qquad (3)$$

$$t_{1/2} = 7.0C_{HNO3} + 9.8 \quad : 75\ g/l \qquad (4)$$

7.3.3 Chemical Retardation Effect on the Radiolysis of TBP

As is shown above, the half life of TBP can dramatically

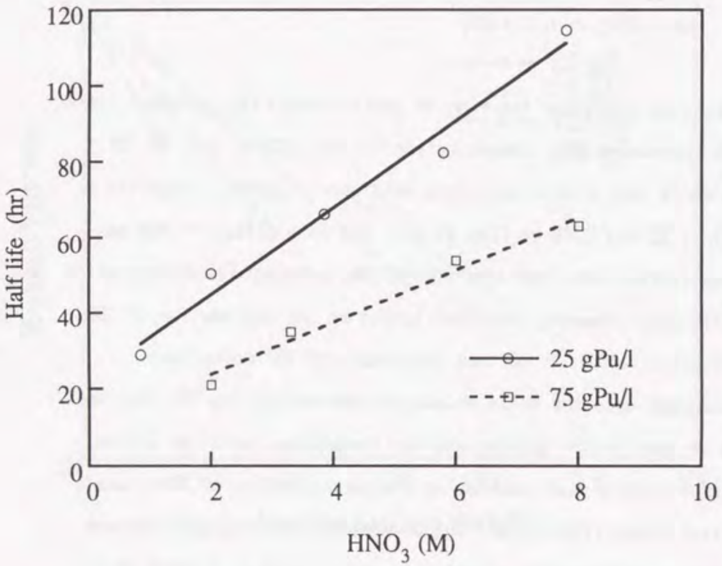

Fig.7.3 Dependence of TBP degradation on nitric acid in PuN. The initial concentrations of TBP in 25gPu/l are 150±7mg/l, 80mg±4/l, 50±3mg/l, 40±2mg/l and 40±2mg/l for 1M, 2M, 4M, 6M and 7.8M of HNO_3 respectively, whereas those in 75gPu/l are 50±3mg/l, 45±2mg/l 40±2mg/l and 40±2mg/l for 2M, 3.3M, 6M and 8M of HNO_3, respectively.

decrease with increasing the concentrations of plutonium nitrate or with decreasing that of nitric acid. Stieglitz et al. reported that G(DBP) significantly decreased in the presence of uranium though their experiment was performed in organic/aqueous system. Mahlman gave the evidence that the reaction between NO_3^- and OH radicals most probably does not occur[8]. Hence, Pu^{4+} and HNO_2 as major species other than undissociated HNO_3 could react with radicals in PuN solution. Assuming that the former is a OH radical scavenger as the undissociated HNO_3, the following reaction would occur because OH behaves as an oxidation radical.

$$Pu^{4+} + OH + H_2O \rightarrow PuO_2^{+} + 3H^{+} \qquad (5)$$

The above reaction was also given to explain the mechanism of Pu oxidation by X-rays in PuN solutions[13]. The difference of the degradation rates of TBP due to the oxidation state of Pu, Pu(III) and Pu(IV), was investigated, as the oxidation of Pu(III) with OH was expected to be faster than that of Pu(IV) based on the fact that the latter involves formation of Pu-oxygen bonds. Pu(III) was electrochemically prepared in the presence of 0.005M of sulfamic acid. It was confirmed that the concentration of sulfamic acid gave no significant effect on the degradation of TBP in Pu(IV) nitrate solution. Table 7.2 gives the result indicating that Pu(III) probably scavenges OH radicals more rapidly than Pu(IV) does. This implies the probability of reaction between TBP and OH decreases due to the scavenge with Pu(III)/Pu(IV). TBP degradation rates were also examined in different concentrations of Pu (54 g/l, 10 g/l) but the same power of radiation (0.11W/l) using PuN2 and another PuN. The dependence of the degradation of TBP on Pu concentration can be seen in Fig. 7.4. HNO_2 is primarily formed by the reactions of NO_3^- and H, the direct reduction of NO_3^- with α particles, and the radiolysis of undissociated HNO_3(10, 12). The initial yield of nitrite increases with increasing acid concentration and a maximum concentration is reached, depending on the concentration of nitric acid and dose[10, 11]. The saturation of HNO_2 may be attained after the solution absorbed 2×10^{20} eV/ml[11], which is approximately equivalent to three days standing for the Pu solution used (PuN1). The degradation of TBP in PuN solution containing HNO_2 was investigated after the PuN solution was left to stand for more than 5 days. To see the effect of HNO_2, on the other hand, the degradation of TBP in two other solutions was measured, one was oversaturated with HNO_2 and the other contained no HNO_2, both had the same concentration of Pu. The results shown in Table 7.3 indicate no significant effect of HNO_2 on the degradation.

7.3.4 Quantification of Retardation Effect on the Degradation of TBP

Table 7.2 Effect of Pu oxidation states on TBP degradation

Oxidation state	Pu(III)	Pu(IV)
Half life[a] (hr)	79	50

a) The concentrations of Pu and HNO_3 were 10 g/l and 0.90M, respectively.

Table 7.3 Effect of HNO_2 on TBP radiolysis in PuN[a]

HNO_2 (mg/l)	Half life (hr)
200 [b]	48
85 [c]	48
0 [d]	49

a) The concentrations of Pu and HNO_3 were 10 g/l and 0.95M, respectively. b) HNO_2 shown was the initial concentration just after the preparation. c) HNO_2 radiolitically generated was chemically at equilibrium, determined by spectrophotometry. d) HNO_2 present in PuN was decomposed by the addition of equivalent sulfamic acid.

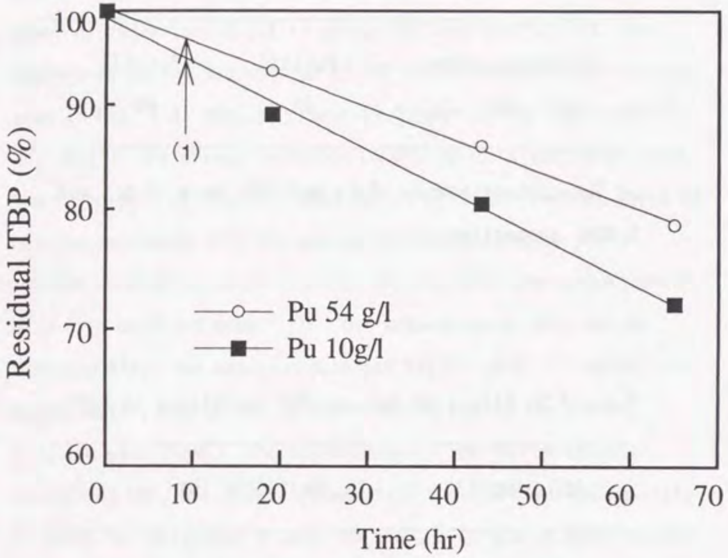

Fig.7.4 Degradation of TBP in the same power of radiation. [HNO_3]: 3.0M,
(1) Both solutions absorb 1 Wh/l.

Based on the assumption that the retardation by undissociated HNO_3 is independent of Pu concentration, the following equation is obtained from Eq.(1) and Eq.(3) normarizing at the common point of (7.8M, 25 g/l); $t_{1/2}$=11.2hr.

$$t_{1/2}(hr) = (1.03C_{HNO_3} + 2.0)\{(1+45.1/E)^{1/2}-1\} \qquad E/[Pu]:\ 0.0122\ W/g \quad (6)$$

The $t_{1/2}$ values in 75 gPu/l calculated from Eq.(6) are 24.7, 43.6 and 62.4 hr. in 2M, 5M and 8M of HNO_3 system, respectively, which are in good agreement with the experimental results given in Fig. 7.3. This implies the validity of the above assumption.

Another description of the retardation effect is necessary because Eq.(6) is available for the limited condition of E/[Pu]=0.0122 W/g. Fig. 7.5 gives a general expression of the degradation rate of TBP as a function of Pu concentration obtained from Eq.(6) when PuN solutions uniformly absorb the same radiation dose, 1 Wh/l. The relationship is valid on the assumption that Pu concentration is a dominant factor under the condition of constant HNO_3. The degradation rates at 1 Wh/l absorption in the two PuN solutions, having different concentration, are plotted in Fig. 7.5. The plot fitting on the curve (Fig. 7.5) suggests validity of the assumption above stated.

The G(TBP) at 1 Wh/l absorption in TBP-saturated solution are calculated from the relation given in Fig. 7.5 and the solubility

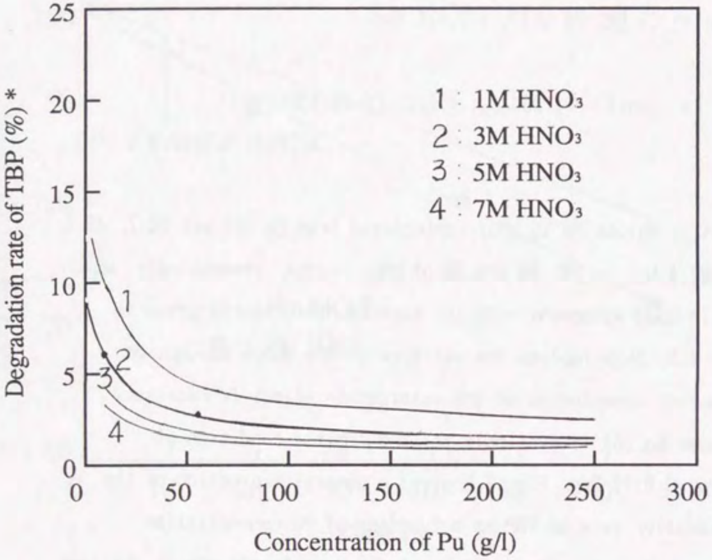

Fig.7.5 Degradation rate of TBP in PuN. * Calculated from Eq.6 when each PuN solution absorbs 1Wh/l. • Plots obtained from Fig. 7.4

of TBP in several PuN solutions in order to know the degree of the retardation effect by undissociated HNO_3 and plutonium. It can be seen in Table 7.4 that the G(TBP) become extremely small with the increase in the concentrations of HNO_3 and Pu although the above definition of the G(TBP) depends on the solubility of TBP.

Table 7.4 G-value of TBP degradation

	Pu concentration (g/l)		
HNO_3 (M)	10	30	235
1.0	3.3×10^{-1}	1.3×10^{-1}	-
3.0	1.0×10^{-1}	3.6×10^{-2}	-
5.0	4.4×10^{-2}	1.3×10^{-2}	2×10^{-3}
7.0	2.3×10^{-2}	7×10^{-3}	1×10^{-4}

7.5 SUMMARY

The degradation of TBP dissolved in PuN solutions was experimentally investigated. The items elucidated in the present study are as follows: (1) The degradation of TBP in PuN solutions indicates first-order kinetics. It is, however, observed that the TBP degradation depends upon Pu concentration. (2) The presence of undissociated HNO_3 decreases TBP degradation rate in PuN. The half life of TBP in PuN solution increases linearly with increasing the concentration of HNO_3. The retardation by undissociated HNO_3 is almost independent of Pu concentration. (3) No significant effect of HNO_2, generated by radiolysis, was observed. (4) The retardation of the degradation of TBP can be described as a function of Pu concentration and HNO_3. The general expression of the function was presented as shown in Fig. 7.5. (5) The G(TBP) values calculated from Fig. 7.5 and the solubility values of TBP become extremely small when the concentrations of HNO_3 and Pu increase. (6) The retardation would be due to the OH radical scavenging by Pu and the Pu(III)/Pu(IV) give different degradation rates of TBP.

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CHAPTER 8

DEGRADATION OF TBP IN HIGHLY RADIOACTIVE LIQUID WASTE SOLUTION

8.1 INTRODUCTION

The investigation of the degradation of TBP in beta(gamma) radiation system is also important for the same reasons shown in Chapter 1 and Chapter 7. Further investigations on not only the degradation of TBP but also the formation rate of its degradation products have been required for the study of the formation of organic compounds in the evaporation processes of the PUREX reprocessing.

As stated before, little information about TBP degradation occurring in aqueous single-phase systems has been reported. It was probably certain that an appreciable portion of the radiolysis of TBP was initiated by hydroxyl radicals according to the discussion shown in the previous chapter and other reports [1, 2]. The degradation of TBP occurring in HRLW solutions may be more complicated than that in PuN because some chemical reactions between OH radical and FP metal-ions/undissociated HNO_3 would be involved. Becker et al., on the other hand, investigated TBP radiolysis in a nitric acid system, where the rate of DBP generation was not in accord with that of TBP degradation[3, 4], but no further discussion was given. In this study, the degradation rate of TBP dissolved in HRLW solution from the reprocessing as a beta(gamma) radiolysis has been investigated. An explanation of the degradation has also been examined in order to predict the degradation in various HRLW solutions. Further, the formation of DBP and other degradation product(s) of TBP in the solution was studied.

8.2 EXPERIMENTAL

8.2.1 Reagents

TBP (purity >99%) and n-dodecane (purity >99%) [Tokyo Kasei Kogyo Co. LTD.] were used as received. Other reagents were of analytical reagent grade.

8.2.2 Procedures

The various concentrations of FPs in 1.5-8.3M nitric acid were prepared from the HRLW of the Tokai Reprocessing Plant. TBP-saturated solutions were prepared by the method shown in Chapter 6. The radiolysis rates were obtained by the same way shown in Chapter 7. TBP in the aqueous sample solutions was determined by the analysis method shown in Chapter 5. DBP resulting from TBP degradation was simultaneously determined with TBP after appropriate preparation of sample as described in Chapter 5. HRLW solutions were characterized after a certain dilution or separation, followed by gamma spectrometry for gamma emitters, ICP spectrometry for metal elements, isotopic dilution mass spectrometry for Pu, and alpha spectrometry for Cm, whereas, the concentrations of free nitric acid and nitrous acid were determined by potentiometric titration and colorimetry, respectively. ^{90}Sr-^{90}Y, which predominantly emits energy in HRLW, was determined by the method given in Chapter 2.

8.2.3 Estimate of Absorbed Energy

A small volume of sample (4.4 ml, 15mm i.d.x25mm h) was used because of the limitation of activity dealt with in the shielded hot cell. Hence, the absorbed energy was estimated by the stopping power in the system. The energy loss of electrons in the sample cell used was estimated from the collision between electrons, which is the predominant interaction among beta particles5). The stopping power of the particles in materials is given by the Bethe-Bloch equation6). The rate of energy loss of beta particles in the sample was estimated from the approximate solution of the equation with the Runge-Kutta method7) assuming that the average beta energy of each radionuclide is representative for the beta energy emitted. The calculation was made for radionuclides contributing to more than 1% of all the exothermic reactions occurring in the HRLW. It was confirmed that the energy emitted from these radionuclides comprises 99% of the total energy of HRLW. The rates of energy loss were estimated as 1.00, 1.00, 1.00, 1.00, 1.00, 0.87, 0.84, and 0.80 for Ce-144, Sr-90, Cs-134, Cs-137, Eu-154, Y-90, Pr-144 and Rh-106, respectively. It was assumed that all the energy of alpha particles emitted from Am, Cm and Pu were completely absorbed in the system. The energy from gamma rays was neglected because the absorption of gamma energy in the apparatus used was apparently small relative to the total decay energy. The concentration and absorbed energy of each radionuclide estimated by the above calculation are given in Table 8.1. The concentrations of major inactive metal ions are also shown in the table.

Table 8.1 Major components and absorbed energy of highly radioactive liquid waste solutions

Sample	HRLW1		HRLW2	
	Conc.	Absorbed energy	Conc.	Absorbed energy
FPs	(Bq/ml)	(Wh/ml)	(Bq/ml)	(Wh/ml)
Ce-144	$5.7*10^{7}$	$7.2*10^{-7}$	$1.7*10^{7}$	$2.1*10^{-7}$
Sr-90	$4.6*10^{9}$	$1.4*10^{-4}$	$2.2*10^{9}$	$7.1*10^{-5}$
Cs-134	$3.3*10^{8}$	$8.3*10^{-6}$	$1.1*10^{7}$	$2.7*10^{-6}$
Cs-137	$4.8*10^{9}$	$1.4*10^{-4}$	$2.3*10^{9}$	$6.9*10^{-5}$
Eu-154	$8.2*10^{7}$	$2.6*10^{-6}$	$3.6*10^{7}$	$1.1*10^{-6}$
Y-90	$4.6*10^{9}$	$6.3*10^{-4}$	$2.2*10^{9}$	$3.1*10^{-4}$
Pr-144	$5.7*10^{7}$	$9.5*10^{-6}$	$1.7*10^{7}$	$2.9*10^{-6}$
Rh-106	$6.9*10^{7}$	$1.1*10^{-5}$	$2.5*10^{7}$	$3.7*10^{-6}$
Actinides	(Total:Bq/ml) $9.5*10^{8}$	(Wh/ml) $5.8*10^{-5}$	(Total:Bq/ml) $4.9*10^{8}$	(Wh/ml) $3.0*10^{-5}$
Total		(Wh/ml) $1.0*10^{-3}$		(Wh/ml) $4.9*10^{-4}$

Sample	HRLW1	HRLW2		HRLW1	HRLW2
Element	(g/l)	(g/l)	Element	(g/l)	(g/l)
Na	6.0	2.3	Ru	0.8	0.4
Fe	3.6	1.5	La	0.7	0.3
U	1.9	1.0	Tc	0.5	0.3
Ce	1.0	0.5	Ni	0.4	0.2
Ba	1.0	0.4	Cr	0.3	0.2
Pd	1.0	0.6	Ag	0.06	0.1
Zr	0.9	0.4	Br	0.02	0.01

8.3 RESULTS AND DISCUSSION

8.3.1 Retardation Effect of TBP Degradation by Nitric Acid

The effect of nitric acid concentration on the TBP degradation in HRLW solutions was investigated under the condition of constant concentrations of FP metal-ions. The degradation dealt with in this study refers to the all-around reactions including hydrolysis as stated in Chapter 7, although the contribution to the degradation of TBP due to the hydrolysis in the system at ambient temperature is negligibly small; about 10^{-4} hr^{-1} of rate constant[8]. Fig. 8.1 shows that the degradation rate of TBP is influenced by the concentration of HNO_3 in spite of the fact that little effect of NO_3^- in TBP degradation is observed, which is consistent with the results of the literature source cited[9]. Mahlman concluded that this phenomenon was due to the fact that the reaction between hydroxyl radicals and NO_3^- most probably did not occur. In Fig. 8.2, the half life of TBP is plotted as a function of free HNO_3, where the presence of HNO_3 predominantly retards the TBP degradation. This is also consistent with another literature source[2] where the G(DBP) values in 0.5M, 2M and 4M of nitric acid solutions were, for instance, presented as 1.87, 1.33 and 0.49. In the report Clay et al. suggested that the chemical attack upon dissolved TBP in aqueous solution was due to the

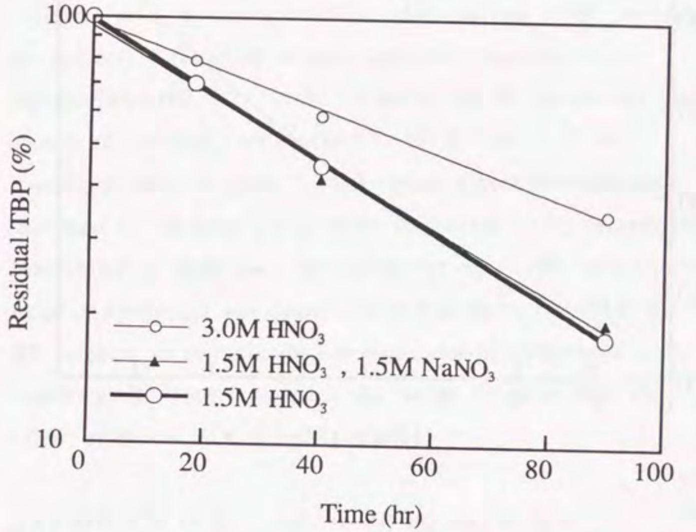


Fig. 8.1 Effect of HNO_3 and NO_3^- on TBP degradation in HRLW. The HRLW used was HRLW1 diluted by a factor of 6.7.

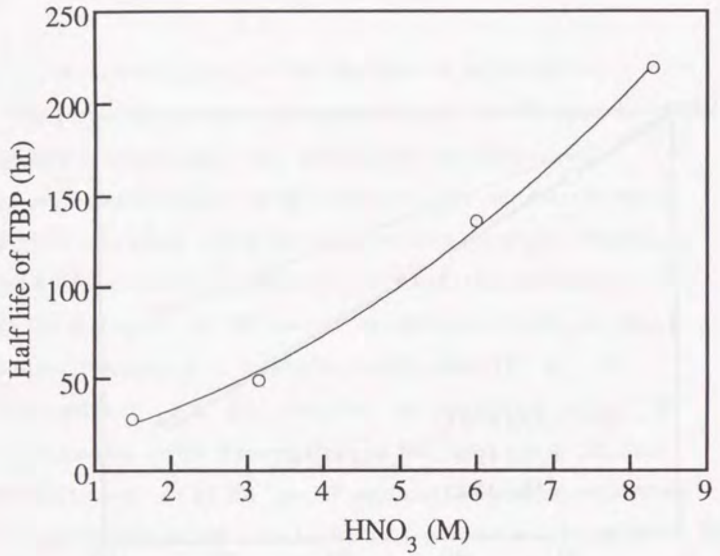


Fig. 8.2 Dependence of TBP degradation on nitric acid in HRLW. The HRLW used was HRLW1 diluted by a factor of 5.

radiation-produced hydroxyl radicals originating from water and that this attack was in competition with the reaction between undissociated HNO_3 and the hydroxyl radicals. The results of our experiment could also be evidence that TBP is predominantly attacked by OH in HRLW solution.

Nitrous acid, primarily formed by the reactions of NO_3^- and H, the radiolytic reduction of NO_3^-, and the radiolysis of undissociated $HNO_3$10, 11) could influence the TBP degradation rate because of its high rate constant ($>10^9$ M^{-1} sec^{-1}) of the reaction with OH radicals12), although no significant influence was found in PuN solutions as shown in Chapter 7. The degradation rate of TBP in HRLW1 where the concentrations of HNO_2 were in the range of 10-50 mg/l was compared with that in another HRLW1 after HNO_2 present in the solution was decomposed by sulfamic acid. No significant difference was observed, which indicates that the effect of NOx in HRLW is negligible.

8.3.2 Effect of FP Metal-Ions on TBP Degradation Rate

The effect of FP metal-ion on TBP degradation was investigated by the same way as that used in the experiment for PuN. The TBP degradation rates at different concentrations of FP metal-ions obtained under the same nitric acid concentration (3.0M) are given in Fig. 8.3. The solutions used were prepared by appropriately diluting HRLW1. Based upon the results, it appeared that the first-order kinetics of the degradation of TBP could be

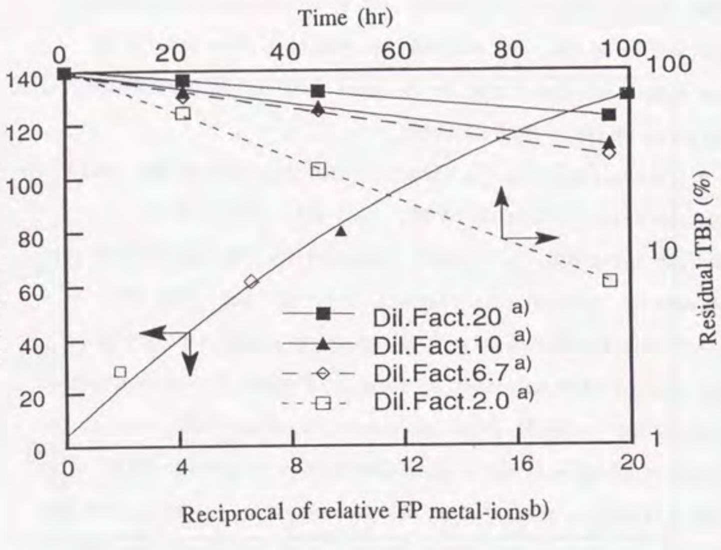


Fig. 8.3 Degradation rate of TBP and half life vs reciprocal of relative concentration of FP metal-ions. (HNO_3:3M) a) Dilution factors relative to HRLW1. Solutions were prepared by diluting HRLW 1. b)"Relative concentration of FP metal-ions" is defined as the ratio of gross concentration of FP metal-ions in the solutions to that in HRLW1.

expressed as $-dC_{TBP}/dt=kEC_{TBP}$ where E represents the absorption rate of energy in the solutions and C_{TBP} stands for the concentration of TBP, because the literature cited[13, 14] showed that the amount of HDBP, a major degradation product of TBP, was in proportion to the energy the system absorbed. In this regard, the half-lives of TBP in different solutions are expected to be proportional to 1/E. Figure 8.3 also shows the relationship between the half life and the reciprocal of the relative concentrations of FP metal-ions. It is obvious from the figure that the half-life is not proportional to 1/E when the relative concentration of FP metal-ions is replaced by E., which is almost the same as that detected in PuN solution. This suggests the possibility of the TBP degradation depending on the concentration of FP metal-ions. In Fig. 8.4 the degradation rate as the residual percentage of TBP is plotted against the energy that each system absorbed. The solid line indicates the degradation of TBP in 3 molar nitric acid calculated from another literature source cited[3]. This may be evidence that FP metal-ions influence the degradation rate of TBP.

8.3.3 Kinetics of Retardation Effects on TBP Degradation

Plutonium retarded TBP degradation in PuN solution as shown in Chapter 7. Stieglitz et al. reported that G(DBP) significantly decreased in the presence of uranium though obtained in org./aq. system. This indicates that the degradation of TBP in HRLW

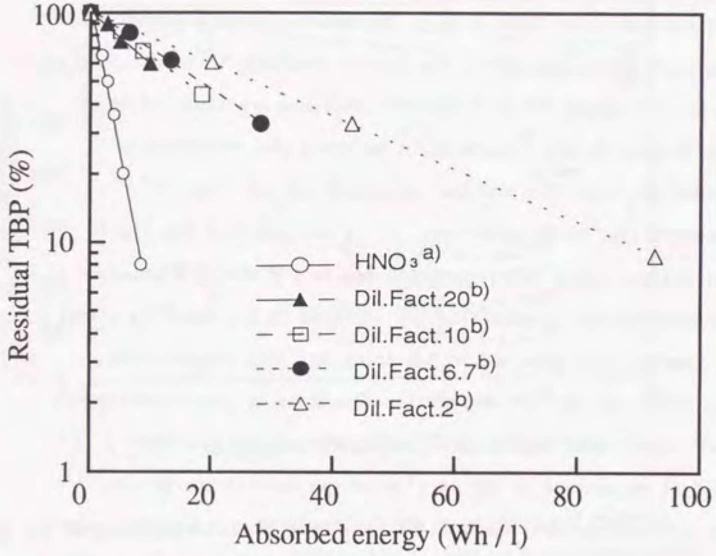


Fig. 8.4 Dependence of TBP degradation rate on concentration of FP metal-ions. (HNO_3: 3M) a) Calculated from literature data[3] b) Dilution factors corresponding to those in Fig. 8.3.

solution cannot be expressed by only E even under a constant HNO_3 concentration. Some of the FPs and the other metal ions would act as OH radical scavengers as well as the undissociated HNO_3.

$$M^{n+} + OH \rightarrow M^{(n+1)+} + OH^- \qquad (1)$$

Sasahira et al.[15] and McIntosh et al.[16] reported that the higher oxidation states of elements such as Ce(IV), Cr(VI) and Ru(VIII) were shifted to lower oxidation states in the nitrate system due to nitrous acid originating from gamma radiolysis. It has been assumed that the retardation of TBP degradation in HRLW is predominantly due to the OH scavenging by other elements involved. Table 8.2 gives the half-lives of TBP in HRLW2 diluted by a factor of 2 to which the following nonactive compounds were respectively added ; $Ce(NO_3)_3 \cdot 6H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$, $RuNO(NO_3)_3$, $Pd(NO_3)_2$, $AgNO_3$, $Zr(NO_3)_2 \cdot 2H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $Ba(NO_3)_2$, $CsNO_3$, NaBr, $Na_2MoO_4 \cdot 2H_2O$, NH_4TcO_4, $La(NO_3) \cdot 6H_2O$ and $Nd(NO_3)_3 \cdot 6H_2O$. TBP was added to each solution after it was allowed to stand for two weeks in order to stabilize the oxidation states of the above metal ions to be reached. It was found that only the solutions containing the elements of Ag, Pd, Br, Ru and Ce, having higher potentials in the redox systems of Ag(I)/Ag(II), Pd(II)/Pd(IV), Br(I)/Br(0), Ru(III)/Ru(IV) and Ce(III)/Ce(IV) than that of NOx, showed significant differences in the half life of TBP. This suggests the validity of the above hypothesis because the above

Table 8.2 Effect of metal ions on TBP degradation

Added$^{a)}$	$t_{1/2}$ (hr)$^{b)}$	Added$^{a)}$	$t_{1/2}$ (hr)$^{b)}$
None	26.2	Ba	26.1
Ce	26.7	Fe	26.2
Cr	26.1	Cs	26.1
Ru	26.7	Br	43.2
Pd	34.4	Mo	26.1
Ag	34.4	Tc	26.0
Zr	26.2	Nd	26.2
La	26.1		

a) Each element was added to HRLW2 diluted by a factor of 2 ($3M\ HNO_3$) as 1 g/l* (* Br: 3.5 g/l), where [TBP] is 86 mg/l.

b) Half-life of TBP

elements can easily be oxidized by the reaction (1). The other elements having lower potentials in the redox systems, e.g. Fe(II)/Fe(III), than that of NOx are thought to be present as higher oxidation state(s), so that those are difficult to be oxidized by OH.

An estimation of the effects of those ions on TBP degradation was made by a kinetic study. The ratio (W_{TBP}) of TBP-OH reaction to all the reactions with OH can be described by the following equation when TBP-OH reaction competes with other OH radical scavenging reactions.

$$W_{TBP} = k_{TBP}[TBP] \,/\, (\, k_{TBP}[TBP] + k_{HNO_3}[HNO_3] + \Sigma k_{I_i}[I_i] \,) \quad (2)$$

Here, k_{TBP}, k_{HNO_3}, and k_{I_i} are bimolecular rate constants of the reactions of TBP-OH, HNO_3-OH and I_i(one of FP metal-ions)-OH, respectively. In the experiment described above, each element, I_i, was added to the HRLW2 diluted by a factor of 2 where the concentration of TBP (86 mg/l), HNO_3 (3M) and the other components such as FP metal-ions were constant. In the above system, G(TBP), the number of TBP molecules decomposed at 1 Wh/l absorption when the entire aqueous system absorbs 100 eV, is given by the following equations[17].

$$G(TBP) = G(OH) \cdot W_{TBP}$$

$$1/G(TBP) = (1/G(OH))(K + k_{I_i}[I_i]/k_{TBP}[TBP]) \qquad (3)$$

where K, constant, is $1 + (k_{HNO_3}[HNO_3] + \sum_{i \neq j} k_{I_j}[I_j]) / k_{TBP}[TBP]$.

Thus a plot of 1/G(TBP) vs $[I_i]/[TBP]$ would yield a straight line with a slope of $k_{I_i}/(k_{TBP} \cdot G(OH))$, which gives k_{I_i} when the values of k_{TBP} and G(OH) are known. The value of k_{TBP} can also be estimated by the same approach using the following equation.

$$1/G(TBP) = (1/G(OH))(K' + k_{HNO_3}[HNO_3]/k_{TBP}[TBP]) \qquad (4)$$

where K', constant, is $1 + (\sum k_{I_i}[I_i] / k_{TBP}[TBP])$.
From the slope of nearly straight curves shown in Fig. 8.5, $G_{OH}=3$ [18] and k_{TBP} (1.1×10^{10} M^{-1} sec^{-1} obtained from Fig. 8.6 and k_{HNO_3} (5.3×10^{7} M^{-1} sec^{-1} [19]), k_{I_i} (I_i = Ce, Ru, Br, Pd and Ag) are 3.1×10^{8}, 3.1×10^{8}, 1.8×10^{9}, 4.0×10^{9} and 4.0×10^{9} M^{-1} sec^{-1}, respectively. The rate constant of the Ce reaction with OH radicals obtained, for instance, is in fairly good agreement with other published value, 3×10^{8} [12]. Clay and Witort showed the kinetic constant for the reaction between TBP and OH in a single aqueous solution system with gamma source (1.3×10^{10} M^{-1} sec^{-1})[2]. It should be noted that the kinetic constant, k_{TBP}, we obtained from Fig. 8.6 is in good agreement with the above literature value. The G(TBP) in the HRLW2 diluted by a factor of 2 (3M HNO_3) was calculated as 0.088 from the half-life in Table 8.2; whereas,

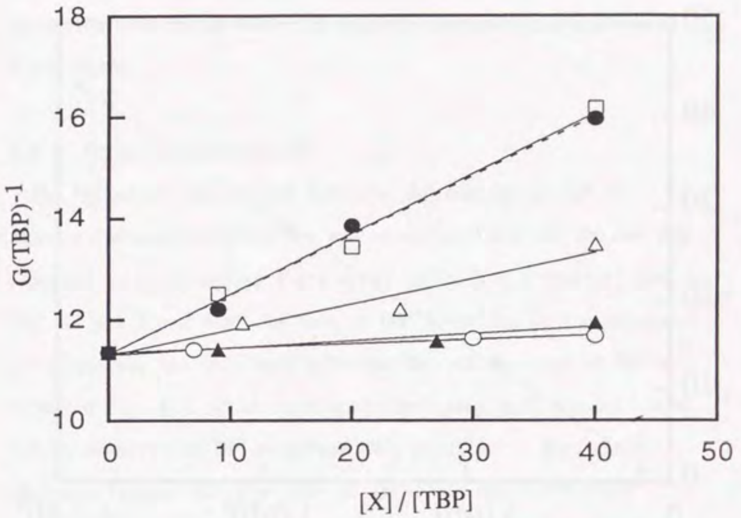


Fig. 8.5 Reciprocal plots for TBP degradation in HRLW solutions of different concentrations of X. X: ○Ce, △Br, □Ag, ●Pd and ▲Ru. The HRLW used was HRLW2 diluted by a factor of 2.

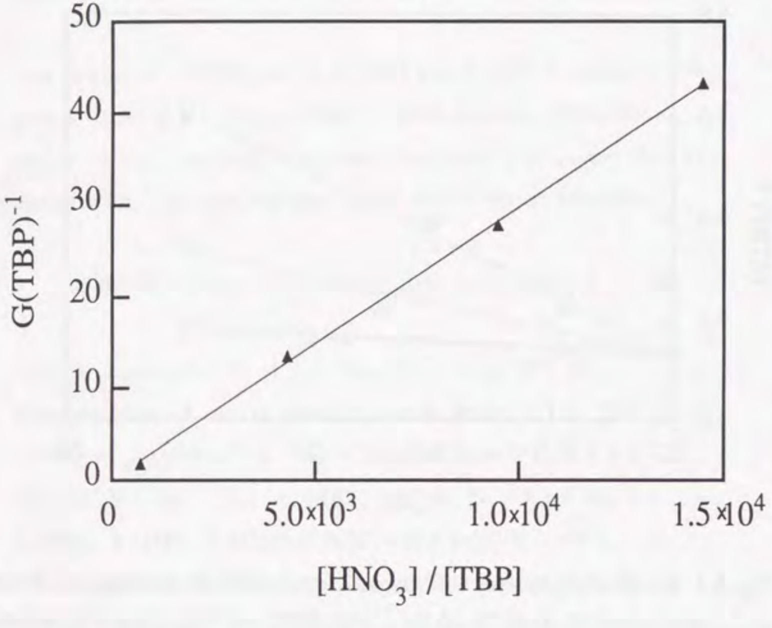


Fig. 8.6 Reciprocal plots for TBP degradation in HRLW solutions of different concentration of HNO_3. HRLW used was the diluted HRLW1 by a factor of 10.

that for the same TBP concentration, i.e., 86 mg/l in FP-free 3M HNO_3 solution, was estimated as 0.26 from the published data3). The ratio of these G-values, 0.34, would be explained with W_{TBP}, estimated from Eq. (2) with the contributions of ions/species as shown above.

8.3.4 Formation Rate of DBP

The formation rate of DBP with the degradation of TBP in aqueous radioactive solutions was investigated since the DBP was expected to be formed as a principal radiolytic product of the TBP. It was found that the rate of DBP formation in the aqueous solutions was not in accord with the degradation rate of TBP as shown in Fig. 8.7, which is almost consistent with the published result observed in TBP-dissolved HNO_3 solution3). More rapid decomposition of DBP than that of TBP could cause the above phenomenon. Thus the decomposition rate of DBP was investigated. It was reported that DBP was precipitated as complexes with some ions such as Zr^{4+} and Ru^{4+} in the HRLW solutions20). A complex between Pu and DBP was also confirmed to be precipitated in acidic solutions. The half life of the decomposition of DBP in a precipitate formed in a HRLW solution was observed approximately 10^2 times that of TBP (in 3M HNO_3) regardless of the nitric acid concentration, which implies that the decomposition rate of the precipitated DBP is negligibly small relative to that of TBP. The above result (Fig. 8.7) must, therefore, be explained by the

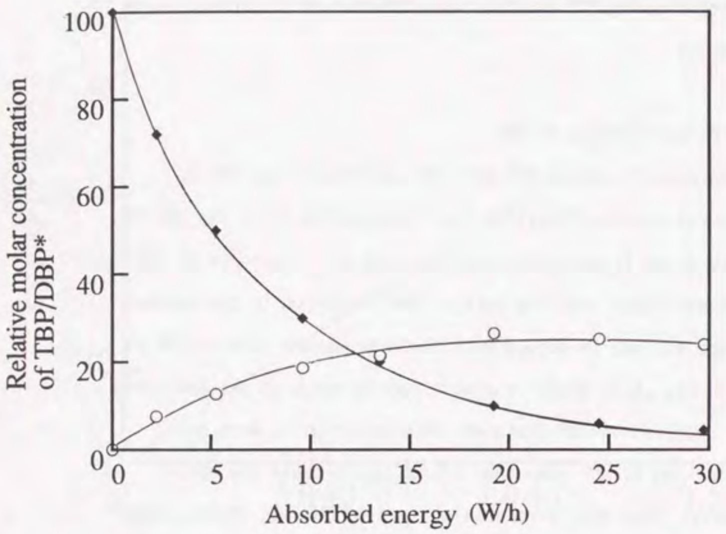


Fig. 8.7 Formation of DBP with degradation of TBP. HRLW used was HRLW1 diluted by a factor of 6.7 (HNO_3: 1.5M). *Initial TBP concentration is given 100.

different phenomenon such as the formation of other degradation products. No significant H_2MBP was detected at the radiolytic degradation of TBP. A gas chromatogram for the degradation products of irradiated TBP in aqueous solution obtained with a flame photometric detector, which selectively detected phosphorus compounds, is shown in Fig. 8.8. Undefined peak(s) between TBP and DBP growing up during the degradation of TBP are observed. This suggests the presence of a relatively large portion of different degradation.

8.3.5 Identification of Another Major Degradation Product

The following formation would be presumed. The addition of oxygen to the radical site of β or γ carbon position of TBP, $(BuO)_2\text{-PO-CH}_2\text{-CH}\bullet\text{-CH}_2\text{-CH}_3$ or $(BuO)_2\text{-PO-CH}_2\text{-CH}_2\text{-CH}\bullet\text{-CH}_3$ formed possibly by the reaction with OH, would provide different degradation product(s) from DBP because that to the radical site of α carbon results in the decomposition of TBP radical into DBP[2]. A total ion chromatogram of degradation products was obtained (Fig. 8.9) by a gas chromatograph-mass spectrometric determination (GCMS) although a different column from that for the previous experiment shown in 8.3.4 was used in order to observe chromatogram of higher resolution. The mass spectrum of the largest peak in undefined peaks, observed next to TBP, was shown in Fig. 8.10. The possible fragment ions estimated from the Fig. 8.10 were given in Fig. 8.11 referring the literature cited[21].

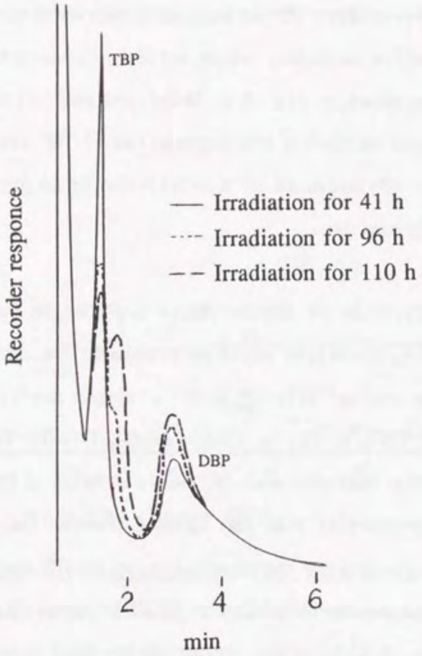


Fig. 8.8 Gas chromatogram of degradation products of TBP. Aqueous solution containing TBP was irradiated (0.5 w/l). TBP and degradation products were extracted by chrloform. Column. 1% PEG-20M on Tenax GC (1.0 m×2.6 mm i.d.) column temp.:220° ; injection port temp.:300° ; detector temp.:300° ; carrier gas flow:50ml/min(N_2), 0.6kg/cm^2(H_2), 0.5kg/cm^2(air).

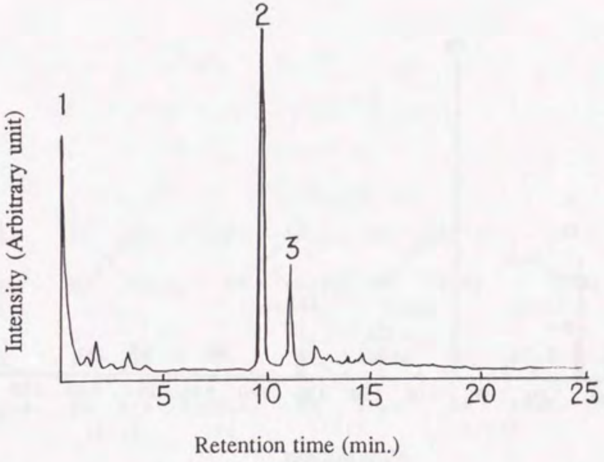


Fig. 8.9 Total ion chromatogram of degradation products of TBP. Degradation products were extracted with chloroform. Recovered organic phase was concentrated to near dryness under He atmosphere. After dissolved with methanol sample was measured with Shimadzu GCMS-QP1000. GC:Injection port temp. 250° Column: DB-1, 15m×0.53mm ID, df=1.5μm, Column temp. 70° (1min)→10° /min→300° He:25ml/min.(carrier), 5ml/min.(make-up), Separator temp.(GC-MS interface):300° MS: Ionization temp.250° Ionization:EI, 70eV, 60μA. Peak1 :methanol+chloroform, Peak2:TBP, Peak3:undefined.

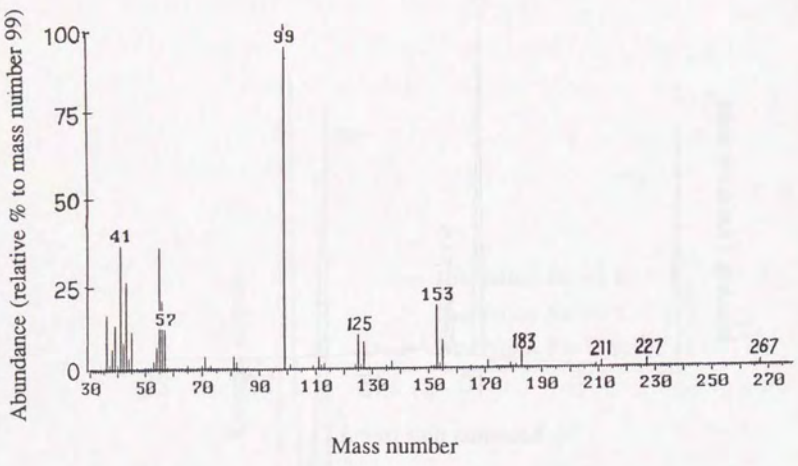


Fig. 8.10 Mass spectrum of peak 3 in Fig. 8.9 observed under the same condition as shown in Fig. 8.9. Scan range:35-600, Scan interval: 3 sec..

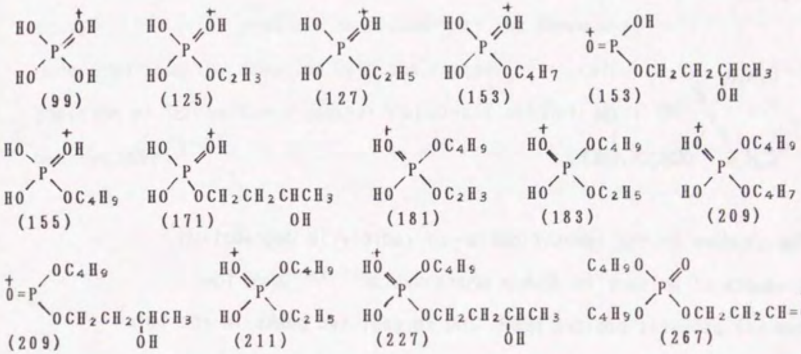
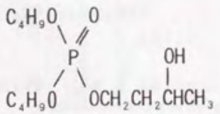
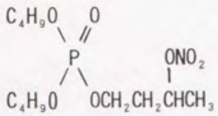


Fig. 8.11 Possible fragment ion corresponding to each mass number

Almost the same mass spectrum was obtained as a degradation product of PUREX solvent[21] although both the organic/aqueous phases were irradiated. The detailed study on the estimate of the molecular structure from the fragmentation was discussed in the study. This indicates that the molecular structure of the degradation product in this experiment is likely as follows:



The studies on the identification of radiolytic degradation products of solvent in double phase system[21, 22] gave four typical products besides HDBP. The largest two peaks in the total ion chromatogram reported were the same compound as that shown above and the following compound.



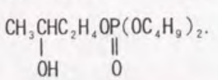
The former one would be produced by the addition of oxygen to the radical site of γ carbon position of TBP as discussed above, whereas the latter one could be produced as follows;

$$R + NO_3 \rightarrow RONO_2$$

where R stands for $(BuO)_2$-PO-CH_2-CH_2-CH•-CH_3. Under the condition of low concentration of HNO_3 (1.5M in this experiment) and rich oxygen, it is probable that the proportion of former product is larger. From both the present work and the previous study[21, 22], it is possibly concluded that the compoud(s) generated from the reaction with the radical of γ carbon position of TBP is the principal radiolysis product(s) of TBP besides HDBP.

8.4 SUMMARY

Degradation of TBP dissolved in aqueous solutions of HRLW solutions from nuclear fuel reprocessing was investigated under various conditions. The following points were elucidated (1) The degradation of TBP in HRLW solutions was retarded by the presence of undissociated HNO_3 and the elements involved having higher redox potentials than that of NOx such as Ce, Ru, Ag, Pd and Br. (2) The retardation is almost accounted for by their contributions to the kinetics of the reactions with OH radicals. (3) The difference in the G-values of TBP dissolved in FP metal-ion free HNO_3 solution published and that in the HRLW at the same concentration of HNO_3 can be also explained by the fraction of the TBP-OH reaction in all the reactions with OH radicals. (4) The formation rate of DBP was found not to be in accord with the degradation rate of TBP. This is due to the fact that degradation product(s) of TBP other than DBP is appreciably formed in aqueous radioactive solutions. The major/typical one was identified by GCMS as



$CH_3\underset{\overset{|}{OH}}{C}HC_2H_4O\underset{\overset{\|}{O}}{P}(OC_4H_9)_2$.

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CHAPTER 9

RADIOLYTICALLY GENERATED HYDROGEN AND OXYGEN FROM PLUTONIUM NITRATE SOLUTION

9.1 INTRODUCTION

The hydrogen generation by alpha radiolysis in nitric acid solutions was investigated with plutonium[1-3], curium-244[1] and polonium-210[4]. Bibler et al.[1] pointed out that the $G(H_2)$ with ^{244}Cm/^{210}Po was consistently higher than that with Pu without further discussion, as shown in Chapter 1. On the other hand, Bibler et al. also studied the mechanism of oxygen generation in the alpha radiolysis. He presented a view divergent from the previous suggestion that the effect of plutonium on the oxygen generation, namely, the plutonium-catalyzed decomposition of hydrogen peroxide stated by Kazanjian et al.[3], was incorrect. We have reinvestigated the radiolytic evolution of hydrogen/oxygen gases, specially focusing on the effect of plutonium concentration on the alpha radiolysis.

Many studies of the gamma radiolysis of neutral and acidic aqueous nitrate solutions have been reported[5-8]. Becker et al. showed the presence of the effect of solution height in the practical solutions of highly beta, gamma-radioactive waste[6]. This effect may be due primarily to the reaction between molecular hydrogen and OH radicals[1,6]. No information about the effect in PuN solutions has been, however, reported. In the present study, the effect of solution height on the hydrogen generation in PuN solutions was also investigated.

9.2 EXPERIMENTAL

9.2.1 Reagents

Plutonium solutions used in these experiments were prepared from PuN solutions recovered at the Tokai Reprocessing plant and

also from high purity metal (NBL126>99.9%). PuN was purified by an anion exchange method in nitrate form. The concentrations of foreign elements were less than 10 mg/l. Two different isotopic compositions of plutonium used, shown in Table 9.1, were obtained from four repeated determinations by mass spectrometry after the purification of the plutonium by the anion exchange method. Other reagents were of analytical reagent grade. The concentrations of argon, hydrogen and oxygen gases used were 99.999%, 100ppm (in Ar balance gas) and 100 ppm (in Ar balance gas), respectively.

9.2.2 Method

A carefully studied procedure and repeated measurements were used. A 40.0 ml sample of PuN solution was placed in a stainless steel cylindrical reaction vessel(3.6cmϕ). PuN solutions degassed by bubbling argon gas for 30 min. were allowed to stand for 12 hours in the vessel after the system was closed. The argon gas with generated gases in the gas phase was displaced by new argon gas after starting vibration of the vessel. The vibrator (50 Hz) attached to the outside of the vessel was confirmed to be effective for complete removal of bubbles attached to the inner surface of the vessel. The gases generated in the gas phase were circulated with argon in a closed line by a pump once every 30 min., when the concentrations of hydrogen/oxygen gases were measured by a gas chromatograph (Shimadzu Model GC-14A) with a

Table 9.1 Isotopic compositions and α/β-radiation energy of PuN solutions used

Sample	Isotopes (Wt%)					Absorption rate of energy (W/l)[a]
	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu	
No. 1	1.17	62.83	23.51	8.46	4.01	0.105
No. 2	0.0037	74.37	19.50	4.22	1.88	0.0523

a) Energy when total Pu is 10 g/l.

column (Molecular Sieve 5A) and a detector of TCD. The amount of gases was calculated using the concentration, the volume of the circulation system and the gas pressure. The effect of temperature was corrected when the solutions were heated. The measured values, which showed a linear relationship between the amount of generated gas and irradiated time, were adopted for results. A slight amount of oxygen contributed by air was corrected using the initial value of oxygen contained in the argon carrier gas. The reliability of the circulation system was confirmed with standard H_2 and O_2 gases. The G-values of H_2/O_2 shown in this paper refer to the apparent G-values calculated from the gases passing into the gas phase. The G(H_2) from identical independent experiments varied less than 5%, whereas those for oxygen varied less than 10%. The solutions were not agitated except for the above vibration, because poor reproducibility was observed when the solutions were agitated and also exact expression for the agitation seems to be difficult.

9.3 RESULTS AND DISCUSSION

9.3.1 Effect of Plutonium on Hydrogen Generation

The effect of the presence of cations on the hydrogen generation in water was reported[10], where the decrease of G(H_2) results from reactions between cations and e_{aq}[1]. The predominant reaction for the hydrogen generation in an acidic solution is H + H[9]. Pu(IV) is expected to be involved in the hydrogen generation as shown in the following reaction.

$$H + Pu(IV) \rightarrow Pu(III) + H^+ \qquad (1)$$

In the presence of nitric acid or nitrate ion, the following reaction[1,3] of H with NO_3^- can also competitively occur with a recombination reaction of H.

$$H + NO_3^- \rightarrow NO_2 + OH^- \quad (2NO_2 + H_2O \rightarrow NO_2^- + NO_3^- + 2H^+) \qquad (2)$$

The values for $G(H_2)$ in nitric acid solutions containing plutonium are plotted in Fig. 9.1 as a function of nitrate concentration because the nitrate must be the predominant anion in the given system. The above G-values plotted are the average of five independently determined data points, which agreed within 6%. Published values with ^{244}Cm[1] are also plotted. The results at higher concentrations of plutonium are in agreement with the published values[2,3]. The curves/plots, however, indicated that $G(H_2)$ at lower concentration of plutonium came closer to the values in ^{244}Cm. In addition, the low concentration of plutonium did not decrease $G(H_2)$ as much as the higher concentration did. Assuming that $G(H_2)$ at 0M Pu corresponds to that in ^{244}Cm, $G(H_2)$ at a certain concentration of nitrate (4.2M) was plotted in Fig.

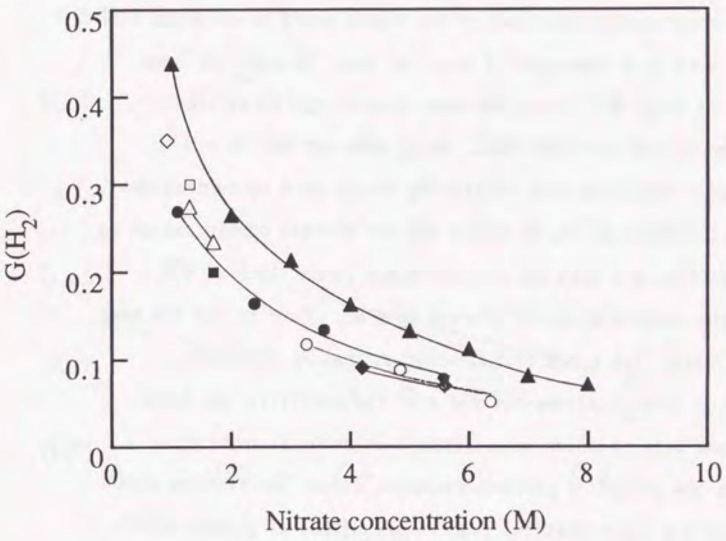

Fig. 9.1 Dependence of $G(H_2)$ on nitrate concentration in α radiolysis.
▲:HNO_3-244Cm, ref.(4), □:9.3 gPu/l, ◇:13 gPu/l, △:18.5 gPu/l,
●:30 gPu/l, ■:37 gPu/l, ○:100 gPu/l, ◆:160 gPu/l.

9.2 against $[Pu(M)]^{1/3}$. The assumption is based on the fact that curium is not chemically involved in the reaction with OH because Cm has only an oxidation state, (III), in the given system. The linear relationship observed in the figure would be evidence that Pu(IV) acts as a scavenger of H out of spur, in much the same manner in which NO_3^- obeys the same theoretical curve. The fraction of undissociated HNO_3, which does not act as a H scavenger, increases with increasing nitric acid concentration16). Hence, the plots of the G-values against nitrate concentration as shown in Fig. 9.1 does not provide exact comparisons of $G(H_2)$ since the concentration of nitrate as a NO_3^- form is not the same in all cases. Two kinds of PuN solutions having different plutonium concentrations but the same radioactivity for both alpha and beta emission were prepared in order to accurately confirm the effect of plutonium concentration. The results shown in Table 9.2 imply that the significant effect of plutonium(IV) on $G(H_2)$ appears to be certain.

Pu(VI) generated by heating solutions is said to possibly result in a positive influence on the hydrogen generation probably accompanied by its reduction, although no evidence has been reported. At a high concentration of Pu(VI), the reduction of PuO_2^{2+} by a reaction with radiolytically generated $H_2O_2$19) would increase the hydrogen generation, because the rate of reaction between H and H_2O_2 which interferes with the hydrogen generation would be reduced. Rabideau et al., however, stated

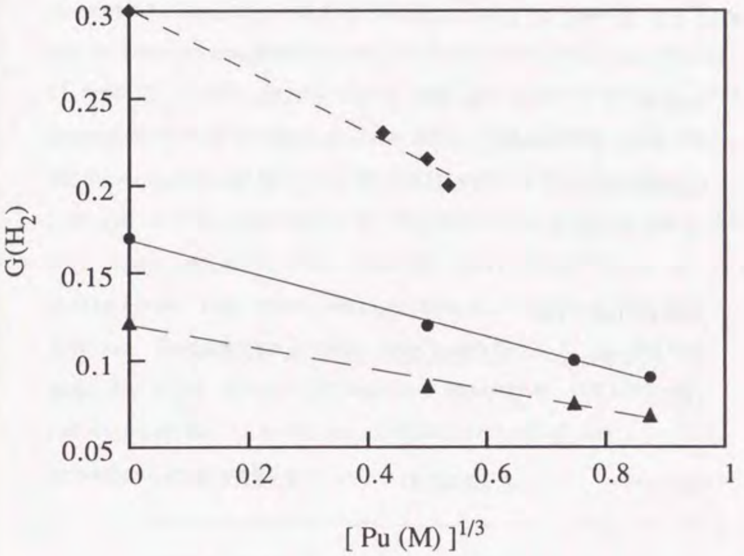

Fig. 9.2 Relationship between $G(H_2)$ and plutonium(IV) concentration. Total nitrate concentrations of solutions are ◆:1.7 M, ●:4.2 M and ▲:4.8 M.

Table 9.2 Effect of plutonium(IV) on hydrogen generation

Sample[a]	No. 1	No. 2
Concentration of Pu(IV)(g/l)	18.5	37.1
Absorption rate of α/β energy (W/l)	0.172/0.022	0.172/0.022
$G(H_2)$[b]	0.23±0.01	0.20±0.01

a) Isotopic compositions of sample No. 1 and No. 2 were identical to those shown in Table9.1. The concentration of HNO_3 and total nitrate were 1.10 M and 1.72 M, respectively, for both the samples. The difference in $[NO_3^-]$ was adjusted by the addition of $NaNO_3$.

b) Mean value±av. dev. for 6 repeated determinations.

that the concentration of H_2O_2 decreased with increasing temperature[13]. This implies that the decrease in the concentration of H_2O_2, not Pu(VI), may increase the hydrogen generation. The effect of heating on $G(H_2)$ was investigated by either keeping the temperature of PuN solution at 70° or cooling it from 70° to 25°. In the latter case the fraction of Pu(VI) was decreased from 45 percent to less than a few percent. (The rest of the fraction was Pu(IV).) No significant difference was observed in $G(H_2)$ regardless of the heating as shown in Table 9.3. This result indicates either that the above effect can be negligible or that other reactions giving a negative bias are involved. The reaction between PuO_2^{2+} and H would, for instance, occur[19], which reduces the hydrogen generation. The chemical reduction of Pu(VI) by H_2 may also be involved at low concentration of nitric acid[17].

9.3.2 Dependence of Hydrogen Released on the Height of Solution

It has been proposed that the effect of the height of solution on hydrogen released is due to the following reaction[5];

$$H_2 + OH \rightarrow H_2O + H. \qquad (3)$$

Assuming that the above explanation is true, the effect under alpha radiation is expected to be less than that under beta/gamma

Table 9.3 Effect of heating solution on hydrogen generation[a]

$G(H_2)$ at 25°	$G(H_2)$ at 70° [b]	$G(H_2)$ at 70° [c]
0.36±0.01	0.36±0.01	0.35±0.01

a) Concentrations of Pu and HNO_3 were 10.0 g/l and 0.6 M, respectively. Pu(VI) was confirmed to be 45% of total Pu at 70. The value shown is mean±av. dev. for 4 repeated determinations.

b) Temperature of solution was kept at 70.

c) Solution was cooled from 70° to 25.

radiation because apparent G(OH) under alpha radiation observed out of tracks is small relative to that under beta/gamma radiation(12). On the other hand, a certain fraction of OH would be scavenged by plutonium in solutions as shown in Chapter 7, so that the concentration of plutonium also may be involved in the effect of the height of solution. The G-values of molecular hydrogen ($G(H_2)$) on varying the solution height were investigated, where the volume of solution remained unchanged(40 ml). Specht et al. suggested that the corrosion products of stainless steel catalyzed the recombination of H_2 with O_2(14). The G-value for the same solution height with additional thin stainless steel foil soaked was investigated. No significant difference was found, which implies that the stainless steel did not significantly work as a catalyst in this experiment. Values for $G(H_2)$ as a function of the solution height are shown in Fig. 9.3, where the G-values decrease almost linearly with a small slope. It is obvious that two PuN solutions having the same concentration of plutonium but different concentrations of nitric acid showed a significant difference in the effect of the solution height. It is probable that this is due to the difference in the concentration of undissociated nitric acid known to be an OH scavenger(15), which should decrease the reaction (3). It was also confirmed that the effect of solution height under alpha radiation was apparently less than that under gamma radiation. These results can also be considered evidence for the validity of the above explanation for

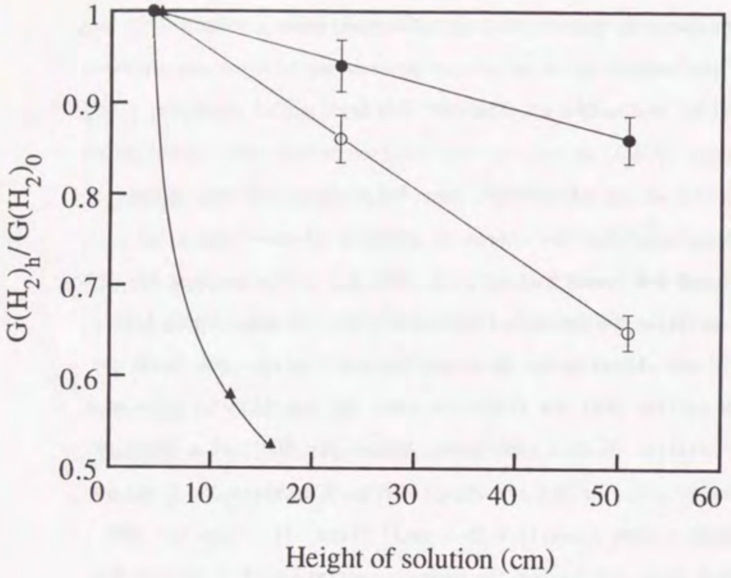

Fig. 9.3 Dependence of $G(H_2)$ on height of solution. ●:4.2M HNO_3, ○:0.7 M HNO_3, ▲:^{60}Co irradiation without stirring, ref.(6). Subscripts h and o represent solution height of h cm and 4 cm for Pu/ 5 cm for ^{60}Co, respectively.

the effect of the solution height. The dependence of the effect of solution height on plutonium was investigated at the same concentration of OH radicals. Two plutonium nitrate solutions having the same concentration of alpha/beta emitters but different concentrations of plutonium (shown in Table 9.2) were used. A small but significant contribution of plutonium to the decrease in the effect of solution height was found as shown in Fig. 9.4. This may be in accord with the conclusion that Pu(IV) scavenges OH as stated in the previous study. Assuming that the effect of the solution height is due only to the reaction (3), $G(H_2)_h$, the G-value for a height of h is described by the following equation;

$$G(H_2)_h = G(H_2)_o - G(H_2)_d$$

where $G(H_2)_o$ and $G(H_2)_d$ are the G-values at a position having no effect of solution height (4 cm for this experiment) and that of decomposed H_2 by reaction (3), respectively. Thus, divided by $G(H_2)_o$,

$$G(H_2)_h/G(H_2)_o = 1 - G(H_2)_d/G(H_2)_o$$

$G(H_2)_d$ is described by $G(OH)\cdot W$, where W is the fraction of the reaction between OH and H_2 in all the reactions scavenging OH.

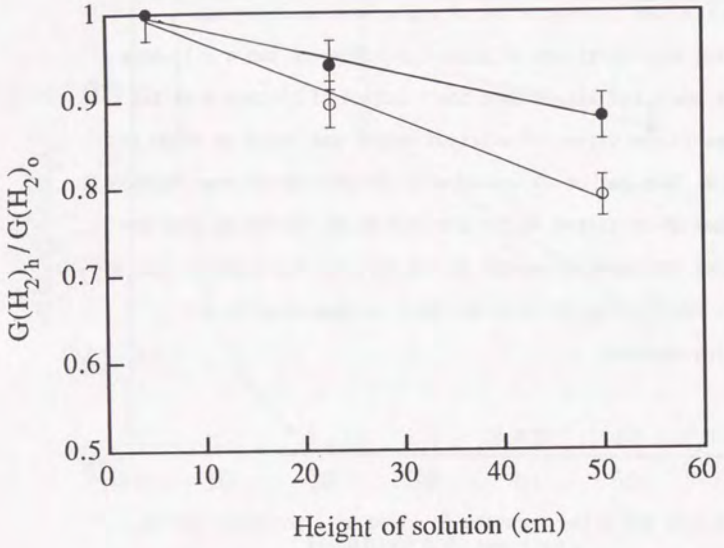

Fig. 9.4 Effect of plutonium(IV) on relation between $G(H_2)_h/G(H_2)_o$ and solution height. ●:37.1 gPu/l, ○:18.5 gPu/l, Concentrations of HNO_3, total nitrate and absorption rate of α / β energy are 1.1 M, 1.72 M and 0.194 W/l.

$$G(H_2)_h/G(H_2)_o = 1 - G(OH) \cdot W/G(H_2)_o$$

The OH radicals in this system would primarily react with undissociated HNO_3 and plutonium(IV), referring to the previous work3).

$$\begin{aligned} & G(H_2)_h/G(H_2)_o \\ & \quad = 1 - G(OH)/G(H_2)_o \cdot k_{H2}[H_2]/(k_{HNO3}[HNO_3] + k_{Pu}[Pu] + k_{H2}[H_2]) \\ & \quad \fallingdotseq 1 - G(OH)/G(H_2)_o \cdot k_{H2}[H_2]/(k_{HNO3}[HNO_3] + k_{Pu}[Pu]) \qquad (4) \end{aligned}$$

where k_{H2}, k_{HNO3} and k_{Pu} are bimolecular rate constants of the reactions of OH-H_2, OH-HNO_3 and OH-Pu, respectively. $[H_2]$ represents the apparent concentration of H_2 involving the effect of the shape of the same volume of solution on the hydrogen generation. $[H_2]$ can be regarded to be approximately proportional to $G(H_2)_o \cdot h$ because $G(H_2)_h$ almost linearly decreases with increasing h as shown in Fig. 9.4. Since G(OH) is constant in the given solutions,

$$G(H_2)_h/G(H_2)_o = 1 - K \cdot h/(k_{HNO3}[HNO_3] + k_{Pu}[Pu]) \qquad (5)$$

It was found that a good fit can be obtained for both the straight lines shown in Fig. 9.3 when a certain value was taken for the constant K in the equation (5), where k_{HNO3} and k_{Pu} are, respectively, $5.3 \times 10^7\ M^{-1}sec^{-1}$ 18) and $2 \times 10^9\ M^{-1}sec^{-1}$ that was estimated by the same manner shown in 8.6 (Chapter 8) with the result of Fig. 7.5 in Chapter 7. It was also confirmed that equation (5) with the same value for K fairly satisfied the straight lines shown in Fig. 9.4. This implies that the effect of solution height in plutonium nitrate solutions would be due to the reaction (3). In the above approach, however, a contradiction may be found when k_{H2-OH} and the concentration of H_2 in the solution estimated from the its solubility in water are substituted for equation (4). Thereby, the effect of solution height may not completely be explained by only the reaction (3).

9.3.3 $G(O_2)$ for Plutonium Nitrate Solution

Both Kazanjian et al.[3] and Sheppard[2] showed that $G(O_2)$ decreased continuously with increasing nitric acid concentration up to 10 M. That was explained by the following plutonium-catalytic reaction that was predominant among the reactions producing oxygen[3].

$$2H_2O_2 \xrightarrow{Pu} O_2 + 2H_2O \qquad (6)$$

$G(O_2)$ decreased with increasing NO_3^- because nitrous acid, the main radiolysis product of HNO_3, rapidly reacted with H_2O_2. Bibler, however, showed apparently inconsistent results, namely that $G(O_2)$ increased with increasing NO_3^-, based on the following predominant reaction.

$$NO_3^- \xrightarrow{\alpha} NO_2^- + O \quad (O + O \rightarrow O_2) \qquad (7)$$

He suggested that the difference was due to the fact that a sizeable fraction of gases can remain in solution because of the absence of agitation of the solution. He also indicated that the direct decomposition of HNO_3 was not occurring in the alpha radiolysis. Although the gas generated was collected without agitation of the solution except for vibrating the solution in this work, good agreement with other literature results was observed in the hydrogen generation as shown previously. Figure 9.5 shows $G(O_2)$ plotted against NO_3^- obtained with a relatively high concentration of plutonium (100-210g/l) where literature data are also plotted. It was found that our results nearly agreed with the $G(O_2)$ observed with ^{244}Cm or $^{244}Cm + ^{239}Pu$[1] and that of ^{210}Po[4]. The following reactions for $G(O_2)$, however, must be involved at higher concentration of nitric acid other than reaction (7), since the fraction of undissociated HNO_3 rises steeply with increasing HNO_3 concentration[16].

$$HNO_3 + OH \rightarrow H_2O + NO_3 \qquad (8)$$

$$(\text{subsequently, } NO_3 \rightarrow NO_2 + 1/2O_2)$$

The results shown in Fig. 9.5 agreed with the literature data in

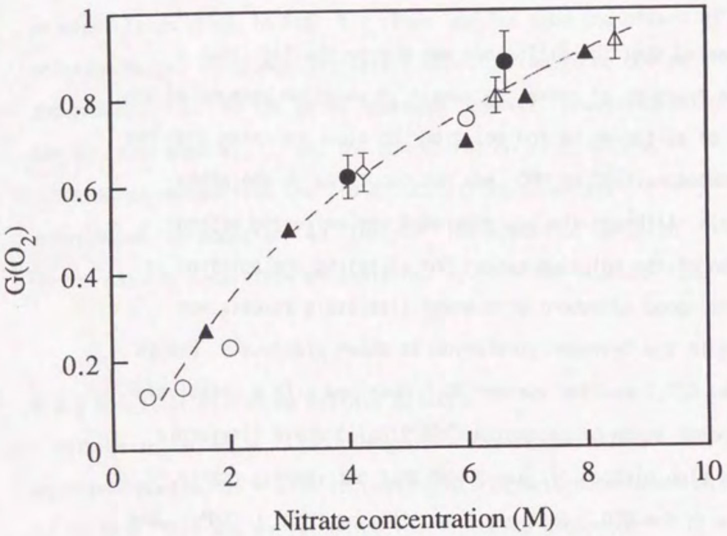

Fig. 9.5 Dependence of G(O$_2$) on nitrate concentration in α radiolysis. △:210 gPu/l, ◇:160 gPu/l, ●:100 g/l, ○:HNO$_3$-^{210}Po, ref.5, ▲:HNO$_3$-^{244}Cm, ref.6.

spite of the fact that the concentrations of NO$_3^-$ and HNO$_3$ varied widely, which suggests the presence of both reactions (7) and (8). Although no explanation for the disagreement in G(O$_2$) between the previous published literature[2, 3] and Bibler's[1] has been offered here, the trend that G(O$_2$) increases with increasing nitrate concentration, which Bibler also showed, is concluded to be correct.

9.4 SUMMARY

Hydrogen and oxygen gases radiolytically generated in a nitrate system by alpha-radiation were investigated. The following points were elucidated: (1) Plutonium (IV) is involved in the G-value for the hydrogen generation. The difference in G-values in a ^{244}Cm-HNO_3 solution and a Pu(IV)-HNO_3 solution can be explained by the presence of Pu. (2) Heating PuN solution, by which Pu(VI) was formed, showed no significant difference in the hydrogen generation. (3) Radiolytic evolution of hydrogen in PuN solutions depends upon a height of the solution in a vessel, although this dependence is apparently less than that observed under gamma radiation. (4) A reaction between OH and H_2 would be involved in the effect of the solution height. The presence of undissociated HNO_3 and Pu(IV), which are thought to be primary scavengers of OH radicals, significantly influences the effect. (5) It was reconfirmed that $G(O_2)$ increased with increasing NO_3^- system in accord with the relation between $G(O_2)$ and NO_3^- in the ^{244}Cm/^{210}Po-HNO_3 system.

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Chapter 10

CONCLUSION

The investigation of the characteristics of the highly radioactive process solutions has been of importance for the safety study of the PUREX reprocessing process, as stated in Chapter 1. This dissertation focused on some problems, namely the establishment of some pertinent anlytical techniques, the investigation of the solubility of TBP and the radiolysis of TBP/water in the highly radioactive aqueous solutions, which had remained in the overall studies on the characterization of process solutions of reprocessing.

Part 1, Chapters 2-5, disclosed the analytical techniques for determining some important nuclides/elements/species of concern in the highly radioactive solutions.

Determination of ^{90}Sr in HRLW solutions from nuclear fuel reprocessing was discussed in Chapter 2. The nuclides including ^{90}Y possibly interfering with this method, ^{106}Ru, ^{134}Cs, ^{137}Cs, ^{144}Ce, ^{144}Pr, ^{147}Pm, ^{154}Eu, ^{123}Sn and ^{125}Sb, were quantitatively removed by co-precipitation with ferric hydroxides during the alkaline precipitation stage, leaving ^{90}Sr in the supernatant in the presence of inactive strontium as the hold-back carrier. ^{90}Y freshly grown from the ^{90}Sr recovered as a carbonate precipitate from the supernatant was measured by Cerenkov radiation counting. It was confirmed that the recovery of an appreciably large amount of ^{90}Sr enabled the determination of ^{90}Sr in HRLW within three hours with an error of less than 5%.

The establishment of this method contributes to the exact calorific evaluation of HRLW solutions because Y^{90} accounts for appreciable fraction in the all calorific value in the solution.

Chapter 3 described an analytical method for technetium (^{99}Tc) in solutions from spent fuel reprocessing processes. The technetium in HRLW was roughly isolated from other elements by changing the acidity of the sample solution to make it alkaline in a manner similar to that for ^{90}Sr. After making the supernatant liquid acidic, inductively coupled plasma emission spectrometry (ICPES) with a Tc II 261.00 nm line was employed for subsequent measurements. The decontamination factors were found to be more than 10^4 for FPs. It was found that this method can be applied to practical samples with relative standard deviations of about 2% at 9 mg/l and 5% at 0.9 mg/l of technetium.

From this study determination of ^{99}Tc, which chemically characterizes the highly radioactive solutions because of its large content and its unique behavior in PUREX reprocessing, was established.

Precise determination methods of determining plutonium content and its oxidation states with controlled-potential coulometry and spectrophotometry were described in Chapter 4. The reliability of determining a high concentration of plutonium has been improved by introducing the coulometry. It was confirmed that the impurities involved in the plutonium product of a general PUREX process such as neptunium, chromium and americium, which interfered with the conventional titration method, did not affect the proposed controlled-potential coulometry. The precise determination of oxidation states was also established by spectrophotometry with a sophisticated spectrum analysis flow.

A combination of these two methods enables more exact and detailed characterization of the PuN solution.

In Chapter 5 is shown the simultaneous determination of TBP and DBP in the aqueous phase of spent fuel reprocessing streams. It was confirmed that TBP and DBP extracted into chloroform were directly measured by a gas chromatograph with FID or FPD and a column packing material of PEG-20M on Tenax GC. No particular preparation is required. It was found that this method can be applied to samples not only of the solutions containing TBP/DBP but also the solutions having a precipitate of a DBP-metal compound. The limits of detectability were confirmed to be 0.2 mg/l and 1 mg/l for TBP and DBP, respectively.

The development of this simultaneous technique facilitates the investigation of the characteristics of TBP/DBP in the highly radioactive solutions.

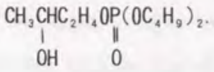
Together with earlier analytical studies in the same area, almost all analytical items necessary for the characterization of highly radioactive solutions of PUREX reprocessing have been completed by the present work. Those methods established in Part 1 were employed in the studies of dissolution/radiolysis of Part 2.

Based upon the requirement stated in Chapter 1, the radiolysis of dissolved TBP and water in the solutions of reprocessing was dealt with in Part 2 of this study.

Chapter 6 describes the solubility of TBP in solutions of PuN and HRLW with variation of several parameters. An empirical formula which can approximately describe the solubility of TBP in PuN solutions in the range of 0-0.1M Pu and 1-8M HNO_3 was obtained. The estimate of the TBP solubility in the actual reprocessing solutions at various conditions turns out to be possible as the result of this study. The other items elucidated are as follows. (1) Plutonium simply acts as an electrolyte in the range of 0-0.1M Pu for the salting-out of TBP while the dissolution of TBP showed a different tendency with an increasing concentration of Pu, which may be due to the interaction between Pu(IV) and TBP. (2) Almost the same tendency was observed in the variation in TBP solubility in PuN solutions (0-0.1M Pu) with nitric acid concentration as that in HNO_3 solution. (3) A dependency of TBP solubility on FP metal-ions was observed in HNO_3 for HRLW solution similar to that for PuN. (4) The logarithm of the ratio of TBP solubility in water to that in the solutions of interest was nearly proportional to 1/T for HRLW solution or for low concentration of PuN solution. That deviates from the linear relation at high temperature when the concentration of PuN is increased, which is explained by the change in the ionic form of Pu.

In Chapter 7, the degradation rate of TBP in PuN solutions at various conditions was found in this study. The following items have become apparent; (1) The degradation of TBP in PuN solutions depends upon the plutonium concentration, although it indicates first-order kinetics. (2) The half life of TBP increases linearly with increasing HNO_3 concentration in PuN solution. The retardation by undissociated HNO_3 is almost independent of Pu concentration. (3) A significant effect of HNO_2, generated by radiolysis, on TBP degradation was not observed. (4) The retardation of the degradation of TBP can be described only by the concentration of Pu and HNO_3. (5) The G(TBP) in PuN solutions decreases extremely with increasing concentration of Pu and HNO_3. (6) Taking into account the fact that Pu(III)/Pu(IV) produces different degradation rates of TBP, plutonium besides undissociated HNO_3 would be involved in the retardation due to OH radical scavenging by Pu.

Degradation of TBP dissolved in aqueous solutions of HRLW solutions from nuclear fuel reprocessing is dealt with in Chapter 8. The following items were proven. (1) The degradation of TBP in HRLW solutions is retarded by the presence of undissociated HNO_3 and elements involved having higher redox potentials than that of NOx such as Ce, Ru, Ag, Pd and Br. (2) The retardation is nearly accounted for by their contributions to the kinetics of the reactions with OH radicals. (3) The difference in the G(TBP) FP metal-ion free HNO_3 solution and that in the HRLW at the same concentration of HNO_3 is explicable by the fraction of the TBP-OH reaction in all the reactions with OH radicals. (4) The formation rate of DBP was not in agreement with the degradation rate of TBP which implies that the degradation product(s) of TBP other than DBP is formed in appreciable amounts in aqueous radioactive solutions. The major one was identified as



$$CH_3\underset{\displaystyle OH}{\underset{|}{C}}HC_2H_4O\underset{\displaystyle O}{\underset{\|}{P}}(OC_4H_9)_2.$$

Finally, Chapter 9 describes the radiolytic generation of hydrogen and oxygen gases in plutonium nitrate solution. The following points can be concluded. (1) Plutonium (IV) is involved in the $G(H_2)$, which can explain the difference in G-values in ^{244}Cm-HNO_3 solution and Pu(IV)-HNO_3 solution. (2) Heating plutonium nitrate solution, by which Pu(VI) was formed, caused no significant difference in hydrogen generation. (3) The dependence of radiolytic evolution of hydrogen upon the height of the solution in a vessel is apparently found to be less than that observed under gamma radiation. (4) A reaction between OH and H_2 would be involved in the effect of the solution height. The presence of undissociated HNO_3 and Pu(IV), which are thought to be primary scavengers of OH radicals, significantly influences the effect. (5) Inconsistent results have been reported for the oxygen generation in plutonium nitrate solution. Hence it was reconfirmed that G(O_2) increased with increasing NO_3^-, which is in accord with the reported relation between G(O_2) and NO_3^- in the ^{244}Cm/^{210}Po-HNO_3 system.

Throughout the studies given in Part 2, detailed information about the dissolution and radiolysis of TBP was obtained, which is absolutely necessary and important when the knowledge of the formation of organic phase of TBP complexes in evaporation processes is extended to the practical system of nuclear fuel reprocessing. In addition, several matters on radiolysis of water involved in the reprocessing solutions, which has been ambiguous and disagreed in the past studies, has been clarified.

It must be noted that the concentration of TBP normally observed in the solutions just before the evaporation process was negligibly small compared with the solubility obtained in this study. In other words, the rinsing with diluent does work well in the present PUREX process. Yet, assuming that significant amount of TBP is dissolved in the solutions to be concentrated, the information on the solubility is of importance, as stated before. It was found in Chapter 8 that the degradation of TBP resulted in the formation of not only DBP but other product(s) giving an appreciable yield. These must be involved in the formation of organic phase. To find more detailed/exact characteristics of organic compounds in the actual system, an extensive study on the

solubility of TBP in the presence of such degradation products may be required as a future work. The exothermic reactions of the TBP complexes including such degradation products in nitrate solutions must also be a future subject to be investigated.

Although a further study may be necessary for the complete explanation for the effect of solution height, it was confirmed that the G(H_2) in the plutonium solutions present in an actual vessel was appreciably smaller than that expected before, due to the effect. It can be said that the safety evaluation on hydrogen generation so far made is too severe due to the lack of available information on the effect of solution height. More realistic evaluation based on this study is expected for the future safety evaluation on this matter.

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