Gamma and alpha radiolysis of TBP solvent*

GAO Yang (高杨),^{1,2,†} ZHENG Wei-Fang (郑卫芳),² CAO Xiao-Ming (曹晓明),¹ and CHEN Shao-Lei (陈少雷)¹

¹Fundamental Science on Nuclear Safety and Simulation Technology Lab,

Harbin Engineering University, Harbin 150001, China

²Department of Radiochemistry, China Institute of Atomic Energy, Beijing 102413, China

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In light of the problem of radiolysis of the solvent system in PUREX (plutonium uranium recovery by extraction) process, γ and α irradiation stabilities of tributylphosphate (TBP)/*n*-dodecane/nitric acid system were studied using ⁶⁰Co γ -rays and α particles from ²³⁸Pu. The main degradation products, dibutyl phosphate (HDBP) and monobutyl phosphate (H₂MBP) were detected by the gas chromatography-mass spectrometry (GC-MS), and the degradation products that could not be easily removed by the washing procedure were measured by the Pu retention. Effects of the absorbed dose, the HNO₃ concentration, and the cumulative dose on the irradiation stability of the systems were investigated. The yields of HDBP, H₂MBP and the Pu retention increased with the absorbed dose. The HNO₃ concentration affected significantly on the yield of HDBP, but had little impact on the output of H₂MBP and Pu retention. For a similar absorbed dose, the Pu retention of the solvent by alpha irradiation is larger than that by gamma irradiation.

Keywords: PUREX process, TBP solvent, Irradiation degradation, Degradation product

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I. INTRODUCTION

In the PUREX (plutonium uranium recovery by extraction) process for reprocessing spent nuclear fuel, the tributylphosphate (TBP) solvent extraction system suffers radiation and chemical degradation, resulting in the formation of a series of degradation products. It has been recognized that the main products of TBP radiolysis are dibutylphosphoric acid (HDBP), monobutyl phosphoric acid (H₂MBP), phosphoric acid, hydrogen, and methane, which can usually be removed through alkali washing. However, the principal impurities originating from the diluents, i.e. nonpolar hydrocarbon mixtures, nitroalkane and its derivatives [1, 2], cannot be removed by aqueous alkalis in the solvent washing systems. These degradation products can cause various physical and chemical damage, and performance of the solvent deteriorates, which is demonstrated by poor phase separation, decrease of the mass transfer coefficient of uranium and plutonium, and retention of the fission products in the uranium and plutonium product streams.

Since the early 1960s, researchers in USA, UK, France and other countries have investigated irradiation stability of the solvent extraction systems in the PUREX process, which covers the determination and measurement of degradation products, the degradation mechanism, the hypothesis of metal complexing agents, the effects of diluent, water, acid, metal ion, temperature, atmosphere, etc. Most studies regarding the TBP radiolysis mechanism focus on the generation mechanism of HDBP and H_2MBP [3–6]. Burr [3] proposed a mechanism for HDBP formation based on decay of the TBP carbon-centered radical. Zaitsev *et al.* [4] reported that dissociative electron capture by TBP can produce butyl radical

and HDBP. Wilkinson and Williams [6] found that H_2MBP and phosphoric acid were the direct degradation products of TBP, rather than decomposition of HDBP. It has been suggested that hydroxamic acid [7, 8], nitroparaffin [9], carbonyl compound [10], and acid phosphate ester [11, 12] should be responsible for retention of fission products. Canva [13], Nowak [14], and Bellido [15] studied the effect of various diluents on the TBP degradation. They agreed that CCl₄ accelerates the process of degradation products. Burger and McClanahan [16], Williams and Wilkinson [17] reported independently a decrease in the yields of HDBP or acid phosphate for the water saturated TBP system. Becker *et al.* [18] and Kulikov *et al.* [19] reported an increase or a decrease in the yield of HDBP in the presence of uranium, respectively.

So far, most investigations about the TBP degradation have been carried out using gamma-rays or electron beams, only a few studies were performed using alpha particles with high linear energy transfer (LET). Barney and Bouse [20] used plutonium in the organic phase as the radiation source and studied alpha radiolysis of TBP solutions in different types of diluents. They found that the yield of HDBP was the highest for CCl₄, and the aromatic diluents gave the best protection for TBP against radiolysis. Lloud and Fellows [21] determined the formation rates of the principal degradation products produced by Pu(IV) loading in TBP solutions as a function of temperature. Kulikov et al. [19] studied the radiation chemistry of 30% TBP solutions in vacuum, air or inert gas, and found that the effect of alpha and gamma irradiation on the distribution coefficients for Pu⁴⁺ and Zr⁴⁺ was identical. Ladrielle *et al.* [22] reported that the difference in HDBP yield by alpha and gamma irradiation was small and there is a linear relationship between the HDBP yield and TBP concentration.

In this work, gamma and alpha irradiation stabilities of TBP/*n*-dodecane/nitric acid system were studied with ⁶⁰Co γ -rays and alpha particles from ²³⁸Pu. The main degradation

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[†] Corresponding author, gaoyang@hrbeu.edu.cn

products, HDBP and H_2MBP of TBP were determined accurately by means of gas chromatography-mass spectrometry (GC-MS), and the degradation products of the diluent, being not easily removed by the washing procedure, were measured indirectly by Pu retention. The effects of the absorbed dose, the concentration of aqueous nitric acid, and the cumulative absorbed dose on the irradiation stability of the TBP system were discussed.

II. EXPERIMENTAL

A. Irradiation

1. Gamma irradiation

A 30 vol% TBP/*n*-dodecane was prepared and purified by equal-volume scrubs with 5wt% Na₂CO₃, 0.1 M HNO₃, and distilled water. Solutions of 30% TBP/*n*-dodecane were equilibrated with 1–5 M HNO₃. The organic phases were irradiated to 100–1000 kGy in a 4.8×10^{15} Bq (0.13 MCi) ⁶⁰Co γ -ray source in air at room temperature. The dose rates were measured by potassium dichromate dosimeter.

2. Alpha irradiation

Plutonium stock solutions were purified by pyridine anion exchange, yielding 10 g/L ²³⁸Pu(IV) products in HNO₃. A certain amount of Pu(NO₃)₄ solution was diluted with HNO₃, and mixed with an equal volume of 30% TBP/*n*-dodecane. Acidity of each Pu(NO₃)₄ solution was the same as the preequilibrated acidity of the contacted organic phase. The organic solutions were separated and sealed in centrifuge tubes for a period of time. Due to the extremely low penetration of α particles released by ²³⁸Pu, the absorbed dose was calculated by assuming that all the decay radiation from the plutonium dissolved in the organic phase was absorbed by the organic phase. The decay energy of ²³⁸Pu is 0.54 W/g, and the absorbed dose is the product of the decay energy (W/g) of ²³⁸Pu, the ²³⁸Pu concentration (g/L) in the organic phase, and the irradiation time (s).

B. Analysis

1. Gas chromatography-mass spectrometry (GC-MS) array

A Varian 4000 GC-MS was used. The main degradation products from the TBP solvent are of high boiling points. They cannot be gasified easily. So, the organic solutions after γ irradiation were treated via a methyl-esterification reaction for GC-MS analysis. The analysis conditions are as follows: injection temperature, 300 °C; carrier flow, 10 mL/min; split ratio, 50 : 1; sample size, 1 µL; 110 °C \rightarrow 180 °C (hold time = 5 min), program rate, 8 °C/min; 180 °C \rightarrow 200 °C (hold time = 10 min), program rate, 5 °C/min. The mass spectrometry condition is as follows: electron impact (EI) ion source; ion source temperature, 300 °C, electron energy, 70 eV; scanning area, 20-50 m/z.

2. Plutonium retention test

Each γ -irradiated sample was contacted with an equal volume and acidity of HNO₃ loading ²³⁹Pu (IV) tracer (50 mg/L) for 15 minutes. The organic phase was back extracted six times with equal volumes of 0.1 M dimethyl hydroxy-lamine (DMHAN)-0.15 M monomethyl hydrazine (MMH)-0.3 M HNO₃, and then scrubbed three times with equal volumes of successively 5wt.% Na₂CO₃, 0.1 M HNO₃ and distilled water. The plutonium concentration extracted in the organic phase or retained in the solvent after scrubbing was estimated by injecting a 50-µL aliquot in a scintillation solution for radiometric measurements with a Beckman LS-6000LL liquid scintillation counter. The plutonium retention of each sample was characterized by the ratio of alpha counter (plutonium concentration) in a fixed aliquot of organic phase after washing to that before stripping.

The plutonium retention method for α -irradiated samples is similar to that used for the γ -irradiated samples. The only difference is that the α -irradiated sample itself contains ²³⁸Pu (IV), hence no need to perform a separate Pu extraction step.

C. Reagents

Tributylphosphate and nitric acid from Beijing chemical reagent company were used. n-dodecane from Alfa Aesar, A Johnson Matthey company was used. Dimethyl hydroxylamine from CIAE (> 97.7% pure) was used. All the reagents used, unless specified, were of AR grade.

III. RESULTS AND DISCUSSION

A. Gamma-irradiated samples

1. GC-MS study

GC fingerprints of the HDBP and HDBP/H₂MBP standards and the γ -irradiated 30% TBP/*n*-dodecane solution contacted with 3 M HNO₃ are shown in Fig. 1. The peak at 7.2 min corresponds to HDBP in Fig. 1(a), and the peak at 4.0 min indicates H₂MBP in Fig. 1(b). From Figs. 1(a) and 1(b), the peaks in Fig. 1(c) at 10.4, 7.2 and 4.0 min correspond to TBP, HDBP and H₂MBP, respectively. The peak at 4.0 min in Fig. 1(c) looks more like a small interfering peak than a characterized peak. The huge peak right after the small H₂MBP peak corresponds to the diluent *n*-dodecane in the solution. To further determine the two main degradation products of the TBP solutions especially H₂MBP, the three strong peaks of the irradiated sample were analyzed by MS. The MS spectrum shows that molecular weights of the three peaks are



Fig. 1. Gas chromatographic fingerprints of different samples irradiated to 1000 kGy by^{60} Co γ -rays.

182, 224 and 266 u, which are consistent with the molecular weight of H₂MBP, HDBP and TBP, respectively. Therefore, it can be sure that the peaks at 4.0, 7.2 and 10.4 min in Fig. 1(c) are H₂MBP, HDBP and TBP, with peak areas of 2.26×10^4 , 4.40×10^5 and 1.22×10^6 , respectively.

The peak areas of TBP, HDBP and H_2MBP of all samples were measured. The peak areas of HDBP and H_2MBP of the 30% TBP/*n*-dodecane/3M HNO₃ solvents irradiated to different doses are shown in Fig. 2. It can be seen that the amount of DBP increases linearly with the dose, while MBP yield depends little on the dose. In general, the larger the absorbed dose is, the more serious the TBP solvent radiolysis is.

Dependence of the peak areas of HDBP and H_2MBP on concentration of HNO₃ acid at absorbed dose of 500 kGy are shown in Fig. 3. The peak area of HDBP increases when the HNO₃ concentration was 1–2 M but decreases from 2 M to 5 M, where the HDBP yield is the lowest. The HNO₃ concentration affects the peak area of H_2MBP just a little. In literary over the TBP solution, the role of aqueous nitric acid has been a focus of debate. Nowak *et al.* [23] reported that yields of HDBP in the solutions of 30% TBP/*n*-dodecane contacted with 0.5 M and 3 M HNO₃ were 0.032 and 0.037 M, respec-



Fig. 2. Effect of γ -ray dose on the yields of HDBP and H₂MBP in 30% TBP/*n*-dodecane contacted with 3M HNO₃.



Fig. 3. Effect of aqueous HNO_3 concentration on yields of HDBP and H_2MBP in 30% TBP/n-dodecane irradiated to 500 kGy.

tively. Clay and Witort [24] found that due to reaction of OHradicals with undissociated nitric acid in competition with the OH- radical attack of the TBP, the production of HDBP decreased with increasing HNO₃ concentration. Our result is close to the latter.



Fig. 4. Effect of γ -ray dose on Pu retention in 30% TBP/*n*-dodecane contacted with 3 M HNO₃.

2. Pu retention test

Figure 4 plots Pu retention of the radiolyzed TBP solvents vs. the dose at HNO_3 concentration of 3 M. The Pu retention increases with the dose. In the range of the acidic HNO_3 in this work, as shown in Fig. 5, variation of the Pu retention is very small.



Fig. 5. Effect of HNO₃ concentration on Pu retention in 30% TBP/*n*-dodecane irradiated to 500 kGy by 60 Co γ -rays.

In the reprocessing plant, TBP solvent goes through a washing process to clean it from degradation products prior to its reuse. The recycle procedure of the solvent system is simulated, as shown schematically in Fig. 6. In general, the more number of times the solvent is recycled, the more serious the retention of plutonium is (Fig. 7). The degradation products of the TBP solvent cannot be removed easily by the washing procedure, and this causes gradual deterioration of the extraction behavior of the solvent.



Fig. 6. Flow diagram of the recycle radiation procedure of the 30% TBP/n-dodecane contacted with HNO₃.

B. Alpha-irradiated samples

Figure 8 plots Pu retention of the radiolyzed solvents as a function of the α absorbed dose. From 100 kGy to 500 kGy, the Pu retention increases slowly from 2.22% to 4.05%. Then it increases dramatically to reach 37.52% at 1000 kGy. High dose is responsible for apparent increase in degradation products yield. The strong complex capability, and the nature of not-ease-to-remove by alkali wash, giving rise to increased plutonium retained in the organic phase solvents. Under similar absorbed dose and the same balanced HNO₃ concentration conditions, the Pu retention of the 30% TBP/*n*-dodecane solution after α radiation can be compared with that after γ radiation. It can be seen that at low doses, the irradiation results of the two radiation sources differ little from each other, with the retention of plutonium in the samples exposed to α



Fig. 7. Effect of cumulative γ -ray dose on the Pu retention in 30% TBP/*n*-dodecane contacted with 3 M HNO₃.

particles being slightly larger. At high doses, the Pu retention after α radiolysis is significantly higher than that of γ radiolysis, especially at 1000 kGy where the Pu retention of the former is over two times more than that of the latter.



Fig. 8. Effect of the α absorbed dose on the Pu retention in 30% TBP/*n*-dodecane contacted with 3 M HNO₃.

Effect of the balanced HNO₃ concentration on the Pu retention is illustrated in Fig. 9. Similar to the γ -irradiated samples, the Pu retention depends little on the HNO₃ concentration. From 1 M to 5 M, the Pu retention fluctuates between 4% and 6%. Besides, as shown in Table 1, Pu retention in the α -irradiated solvent is 6–12 times more than that in the γ -irradiated solvent.



Fig. 9. Effect of the HNO₃ concentration on the Pu retention in 30% TBP/n-dodecane for the α dose of 500 kGy.

Pu retention in the γ irradiated solvent

Pu retention in the α irradiated solvent

0.0065

0.0400

0.0068

0.0630

TABLE 1. The comparison of the	e Pu retention in	the γ and α irradiated	solvents for the al	osorbed dose 500 kGy	
Nitric acid concentration (M)	1	2	3	4	5

0.007

0.0596

0.0045

0.0532

IV.	CONCLUSION	

Irradiation stability of the 30% TBP/*n*-dodecane solution was studied with samples exposed to 60 Co γ -rays or α -particles from plutonium dissolved in the organic phase. Using gas chromatography-mass spectrometric analysis of the γ -irradiated organic phase, the two main degradation products HDBP and H₂MBP were determined. The results showed that influences of the absorbed dose and the HNO₃ concentration on the amount of HDBP were much larger than that of H₂MBP. The HDBP yield increased with the dose, and the HDBP yield at low HNO₃ concentration was larger than that at high HNO₃ concentration. Pu retention of the samples was measured to estimate yields of the degradation products that cannot be removed easily by wash procedure and with

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strong complexation on metal ions. It was found that the larger the absorbed dose, the more serious the radiolysis of the TBP solution was, however, the Pu retention depended less on the aqueous HNO_3 concentration than the absorbed dose. In simulations of the real solvent system recycle procedure, the retention of plutonium in the organic phase increases with the irradiation time.

0.0273

0.0405

For the α -irradiated samples, only the Pu retention was tested due to their high radioactivity. The results indicated that the Pu retention increased slowly before 500 kGy, where it begins to increase rapidly. At high doses, the α radiolysis degree was significantly more serious than that of the γ radiolysis. Similar to the γ -irradiation, the effect of HNO₃ concentration on the Pu retention was very small. Further research will be made with other diluents.

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