Gamma and alpha radiolysis of TBP solvent: Postprint

Authors: GAO Yang, Weifang Zheng, CAO Xiao-Ming, CHEN Shao-Lei

Date: 2023-06-18T00:00:00+00:00

Abstract

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.

Full Text

Preamble

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]

[1]Fundamental Science on Nuclear Safety and Simulation Technology Lab, Harbin Engineering University, Harbin 150001, China
[2]Department of Radiochemistry, China Institute of Atomic Energy, Beijing 102413, China

(Received May 12, 2014; accepted in revised form July 19, 2014; published online December 20, 2014)

Abstract: In light of the problem of radiolysis of the solvent system in the PUREX (plutonium uranium recovery by extraction) process, the gamma and alpha irradiation stabilities of the tributylphosphate (TBP)/n-dodecane/nitric acid system were studied using ^{60}Co gamma rays and alpha particles from ^{238}Pu. The main degradation products, dibutyl phosphate (HDBP) and monobutyl phosphate (H_2MBP), were detected by gas chromatography-mass spectrometry (GC-MS), and the degradation products that could not be easily removed by the washing procedure were measured by Pu retention. Effects of the absorbed dose, HNO_3 concentration, and cumulative dose on the irradiation stability of the systems were investigated. The yields of HDBP, H_2MBP, and Pu retention increased with the absorbed dose. The HNO_3 concentration significantly affected the yield of HDBP but had little impact on H_2MBP production and Pu retention. For a similar absorbed dose, Pu retention in the solvent after alpha irradiation was larger than that after gamma irradiation.

Keywords: PUREX process, TBP solvent, Irradiation degradation, Degradation product
DOI: 10.13538/j.1001-8042/nst.26.S10303

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. The main products of TBP radiolysis are recognized to be dibutylphosphoric acid (HDBP), monobutylphosphoric acid (H_2MBP), phosphoric acid, hydrogen, and methane, which can usually be removed through alkali washing. However, principal impurities originating from the diluents—namely nonpolar hydrocarbon mixtures, nitroalkane and its derivatives [1, 2]—cannot be removed by aqueous alkalis in the solvent washing systems. These degradation products cause various physical and chemical damage, and the performance of the solvent deteriorates, demonstrated by poor phase separation, decreased mass transfer coefficients for uranium and plutonium, and retention of fission products in the uranium and plutonium product streams.

Since the early 1960s, researchers in the USA, UK, France, and other countries have investigated the irradiation stability of solvent extraction systems in the PUREX process, covering the determination and measurement of degradation products, degradation mechanisms, hypotheses of metal complexing agents, and the effects of diluent, water, acid, metal ions, 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 direct degradation products of TBP, rather than decomposition products of HDBP. It has been suggested that hydroxamic acid [7, 8], nitroparaffin [9], carbonyl compounds [10], and acid phosphate esters [11, 12] should be responsible for retention of fission products. Canva [13], Nowak [14], and Bellido [15] studied the effect of various diluents on TBP degradation, agreeing that CCl_4 accelerates the degradation process, while aromatic diluents decrease the yields of degradation products. Burger and McClanahan [16] and Williams and Wilkinson [17] independently reported a decrease in HDBP or acid phosphate yields for water-saturated TBP systems. Becker et al. [18] and Kulikov et al. [19] reported an increase or decrease in HDBP yield in the presence of uranium, respectively.

Thus far, most investigations of TBP degradation have been carried out using gamma rays or electron beams, with only a few studies 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, finding that HDBP yield was highest for CCl_4 and that aromatic diluents provided the best protection for TBP against radiolysis. Lloyd and Fellows [21] determined the formation rates of 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, finding that the effect of alpha and gamma irradiation on distribution coefficients for Pu^{4+} and Zr^{4+} was identical. Ladrielle et al. [22] reported that the difference in HDBP yield by alpha and gamma irradiation was small and that there is a linear relationship between HDBP yield and TBP concentration.

In this work, the gamma and alpha irradiation stabilities of the TBP/n-dodecane/nitric acid system were studied with ^{60}Co gamma rays and alpha particles from ^{238}Pu. The main degradation products, HDBP and H_2MBP, were determined accurately by gas chromatography-mass spectrometry (GC-MS), and the degradation products of the diluent that could not be easily removed by the washing procedure were measured indirectly by Pu retention. The effects of absorbed dose, aqueous nitric acid concentration, and cumulative absorbed dose on the irradiation stability of the TBP system were discussed.

II. Experimental

1. Gamma Irradiation

A 30 vol% TBP/n-dodecane solution was prepared and purified by equal-volume scrubs with 5 wt.% Na_2CO_3, 0.1 M HNO_3, and distilled water. Solutions of 30% TBP/n-dodecane were equilibrated with 1-5 M HNO_3. The organic phases were irradiated to 100-1000 kGy in a 4.8×10^{15} Bq (0.13 MCi) ^{60}Co gamma-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 ^{238}Pu(IV) products in HNO_3. A certain amount of $Pu(NO_3)_4$ solution was diluted with HNO_3 and mixed with an equal volume of 30% TBP/n-dodecane. The acidity of each $Pu(NO_3)_4$ solution was the same as the pre-equilibrated 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 alpha particles released by ^{238}Pu, the absorbed dose was calculated by assuming that all decay radiation from the plutonium dissolved in the organic phase was absorbed by the organic phase. The decay energy of ^{238}Pu is 0.54 W/g, and the absorbed dose is the product of the decay energy (W/g) of ^{238}Pu, the ^{238}Pu concentration (g/L) in the organic phase, and the irradiation time (s).

3. Analysis

Gas Chromatography-Mass Spectrometry (GC-MS) Analysis A Varian 4000 GC-MS was used. The main degradation products from the TBP solvent have high boiling points and cannot be easily gasified. Therefore, the organic solutions after gamma irradiation were treated via a methyl-esterification reaction for GC-MS analysis. The analysis conditions were as follows: injection temperature, 300 °C; carrier flow, 10 mL/min; split ratio, 50:1; sample size, 1 μL; temperature program from 110 °C to 180 °C (hold time = 5 min) at 8 °C/min, then from 180 °C to 200 °C (hold time = 10 min) at 5 °C/min. The mass spectrometry conditions were: electron impact (EI) ion source; ion source temperature, 300 °C; electron energy, 70 eV; scanning range, 20–50 m/z.

The GC fingerprints of HDBP and HDBP/H_2MBP standards and the gamma-irradiated 30% TBP/n-dodecane solution contacted with 3 M HNO_3 are shown in Fig. 1 [Figure 1: see original paper]. The peak at 7.2 min corresponds to HDBP in Fig. 1(a), and the peak at 4.0 min indicates H_2MBP 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 H_2MBP, respectively. The peak at 4.0 min in Fig. 1(c) appears more like a small interfering peak than a characterized peak. The huge peak right after the small H_2MBP peak corresponds to the diluent n-dodecane in the solution. To further determine the two main degradation products of the TBP solutions, especially H_2MBP, the three strong peaks of the irradiated sample were analyzed by MS. The MS spectrum shows that the molecular weights of the three peaks are 182, 224, and 266 u, which are consistent with the molecular weights of H_2MBP, HDBP, and TBP, respectively. Therefore, it can be confirmed that the peaks at 4.0, 7.2, and 10.4 min in Fig. 1(c) are H_2MBP, HDBP, and TBP, with peak areas of 2.26×10^4, 4.40×10^5, and 1.22×10^6, respectively.

Plutonium Retention Test Each gamma-irradiated sample was contacted with an equal volume and acidity of HNO_3 loading ^{239}Pu(IV) tracer (50 mg/L) for 15 minutes. The organic phase was back-extracted six times with equal volumes of 0.1 M dimethyl hydroxylamine (DMHAN)-0.15 M monomethyl hydrazine (MMH)-0.3 M HNO_3, and then scrubbed three times with equal volumes of successively 5 wt.% Na_2CO_3, 0.1 M HNO_3, 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 into 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 counts (plutonium concentration) in a fixed aliquot of organic phase after washing to that before stripping.

The plutonium retention method for alpha-irradiated samples was similar to that used for gamma-irradiated samples. The only difference was that the alpha-irradiated sample itself contained ^{238}Pu(IV), so no separate Pu extraction step was needed.

4. Reagents

Tributylphosphate and nitric acid from Beijing Chemical Reagent Company, n-dodecane from Alfa Aesar (A Johnson Matthey Company), and dimethyl hydroxylamine from CIAE (>97.7% pure) were used. All reagents, unless specified, were of analytical reagent grade.

III. Results and Discussion

A. Gamma-Irradiated Samples

1. GC-MS Study The peak areas of TBP, HDBP, and H_2MBP were measured for all samples. The peak areas of HDBP and H_2MBP for the 30% TBP/n-dodecane/3M HNO_3 solvents irradiated to different doses are shown in Fig. 2 [Figure 2: see original paper]. The amount of DBP increases linearly with dose, while MBP yield depends little on dose. In general, the larger the absorbed dose, the more serious the TBP solvent radiolysis.

The dependence of the peak areas of HDBP and H_2MBP on HNO_3 concentration at an absorbed dose of 500 kGy is shown in Fig. 3 [Figure 3: see original paper]. The peak area of HDBP increases when the HNO_3 concentration is 1–2 M but decreases from 2 M to 5 M, where the HDBP yield is lowest. The HNO_3 concentration affects the peak area of H_2MBP only slightly. In literature on TBP solutions, the role of aqueous nitric acid has been a focus of debate. Nowak et al. [23] reported that yields of HDBP in solutions of 30% TBP/n-dodecane contacted with 0.5 M and 3 M HNO_3 were 0.032 and 0.037 M, respectively. Clay and Witort [24] found that due to reaction of OH • radicals with undissociated nitric acid in competition with OH • radical attack on TBP, the production of HDBP decreased with increasing HNO_3 concentration. Our result is consistent with the latter.

2. Pu Retention Test Figure 4 [Figure 4: see original paper] plots Pu retention of the radiolyzed TBP solvents versus dose at an HNO_3 concentration of 3 M. Pu retention increases with dose. As shown in Fig. 5 [Figure 5: see original paper], variation of Pu retention is very small across the acidic HNO_3 range studied in this work.

In reprocessing plants, TBP solvent undergoes a washing process to remove degradation products prior to reuse. The recycle procedure of the solvent system was simulated as shown schematically in Fig. 6 [Figure 6: see original paper]. In general, the more times the solvent is recycled, the more serious the retention of plutonium becomes (Fig. 7 [Figure 7: see original paper]). The degradation products of the TBP solvent cannot be easily removed by the washing procedure, causing gradual deterioration of the extraction behavior of the solvent.

B. Alpha-Irradiated Samples

Figure 8 [Figure 8: see original paper] plots Pu retention of the radiolyzed solvents as a function of the alpha absorbed dose. From 100 kGy to 500 kGy, Pu retention increases slowly from 2.22% to 4.05%, then rises dramatically to reach 37.52% at 1000 kGy. High dose is responsible for the apparent increase in degradation product yield. The strong complexation capability and resistance to removal by alkali washing give rise to increased plutonium retention in the organic phase solvents. Under similar absorbed dose and the same equilibrated HNO_3 concentration conditions, Pu retention of the 30% TBP/n-dodecane solution after alpha radiation can be compared with that after gamma radiation. At low doses, the irradiation results from the two radiation sources differ little, with plutonium retention in samples exposed to alpha particles being slightly larger. At high doses, Pu retention after alpha radiolysis is significantly higher than after gamma radiolysis, especially at 1000 kGy where Pu retention of the former is more than two times that of the latter.

The effect of equilibrated HNO_3 concentration on Pu retention is illustrated in Fig. 9 [Figure 9: see original paper]. Similar to gamma-irradiated samples, Pu retention depends little on HNO_3 concentration. From 1 M to 5 M, Pu retention fluctuates between 4% and 6%. As shown in Table 1 , Pu retention in the alpha-irradiated solvent is 6–12 times greater than that in the gamma-irradiated solvent.

IV. Conclusion

The irradiation stability of the 30% TBP/n-dodecane solution was studied with samples exposed to ^{60}Co gamma rays or alpha particles from plutonium dissolved in the organic phase. Using gas chromatography-mass spectrometric analysis of the gamma-irradiated organic phase, the two main degradation products HDBP and H_2MBP were determined. The results showed that the influences of absorbed dose and HNO_3 concentration on the amount of HDBP were much larger than those on H_2MBP. The HDBP yield increased with dose, and the

HDBP yield at low HNO_3 concentration was larger than at high HNO_3 concentration. Pu retention of the samples was measured to estimate yields of degradation products that cannot be easily removed by washing procedures and have strong complexation with metal ions. It was found that the larger the absorbed dose, the more serious the radiolysis of the TBP solution; however, Pu retention depended less on aqueous HNO_3 concentration than on absorbed dose. In simulations of the real solvent system recycle procedure, retention of plutonium in the organic phase increases with irradiation time.

For the alpha-irradiated samples, only Pu retention was tested due to their high radioactivity. The results indicated that Pu retention increased slowly before 500 kGy, after which it began to increase rapidly. At high doses, the degree of alpha radiolysis was significantly more serious than that of gamma radiolysis. Similar to gamma irradiation, the effect of HNO_3 concentration on Pu retention was very small. Further research will be conducted with other diluents.

References

[1] Neace J C. Diluent degradation products in the Purex solvent. Separ Sci Technol, 1983, 18: 1581-1594. DOI: 10.1080/01496398308056116
[2] Tripathi S C, Bindu P, Ramanujam A. Studies on the identification of harmful radiolytic products of 30%TBP-n-dodecane-HNO_3 by gas liquid chromatography. Formation of diluent degradation products and their role in Pu retention behaviour. Separ Sci Technol, 2001, 36: 1463-1478. DOI: 10.1081/ss-100103561
[3] Burr J G. The radiolysis of tributyl phosphate. Radiat Res, 1958, 8: 214-221. DOI: 10.2307/3570477
[4] Wilkinson R W, Williams T F. The radiolysis of tri-n-alkyl phosphates. J Chem Soc, 1961, 4098-4107. DOI: 10.1039/JR9610004098
[5] Zaitsev V D, Protasova E L, Khaikin G I. Kinetics of primary electron-ion pair recombination in liquid trialkyl phosphate radiolysis. High Energ Chem+, 1993, 27: 28-34.
[6] Zaitsev V D, Protasova E L, Khaikin G. I. Radiation-chemical behavior and spectral characteristics of solvated electrons in liquid trialkyl phosphates. High Energ Chem, 1994, 28: 21-
[7] Huggard A J, Warner B F. Investigation to determine the extent of degradation of TBP/odorless kerosene solvent in the new separation plant, Windscale. Nucl Sci Eng, 1963, 17: 638-650.
[8] Lane E S. Performance and degradation of diluents for TBP and the cleanup of degraded solvents. Nucl Sci Eng, 1963, 17:
[9] Blake C A Jr, Davis W Jr, Schmitt J M. Properties of degraded TBP-Amsco solutions and alternative extractant-diluent system. Nucl Sci Eng, 1963, 17: 626-637.
[10] Stieglitz L. Investigation on the nature of degradation products in the system 20 vol. tributyl phosphate-dodecane-nitric acid I. Enrichment of complexing products and infrared study. Proccedings of the international solvent extraction conference, 1971, 155-159.

[11] Becker R, Baumgartner F, Stieglitz L. Identification of complexing radiolytic products of the PUREX systems (20% TBP-Dodecane-HNO_3). Kernforschungzentrum, Karlsruhe, West Germany, 1977, KFK-2304.

[12] Tripathi S C, Ramanujam A, Gupta K K. Studies on the identification of harmful radiolytic products of 30%TBP-n-dodecane-HNO_3 by gas liquid chromatography II. Formation and characterization of high molecular weight. Separ Sci Technol, 2001, 36: 2863-2883. DOI: 10.1081/ss-100107634

[13] Canva J and Pages M. Effects of protection and of sensibilization in the decomposition radiolytic of the phosphate tributyl. Radiochim Acta, 1965, 4: 88-91. DOI: 10.1081/ss-100107634

[14] Nowak M, Nowak Z, Rochon A. Thin-layer chromatographic examination of the radiolysis of TBP-diluent-nitric acid systems. Radiochem Radioa Let, 1974, 20: 47-58.

[15] Bellido A V, Rubenich M N. Influence of the diluents on the radiolytic degradation of TBP in TBP, 30%(v/v)-diluent-HNO_3 systems. Radiochim Acta, 1984, 36: 61-64. DOI: 10.1524/ract.1984.36.12.61

[16] Burger L L and McClanahan E D. Tributyl phosphate and its diluent systems. Ind Eng Chem, 1958, 50: 153-156. DOI: 10.1021/ie50578a025

[17] Williams T F and Wilkinson R W. The radiolysis of tri-n-butyl phosphate and allied systems. A.E.R.E. Report C/R 2179,

[18] Becker R, Stieglitz L, Bautz H. Investigation of the radiolytic TBP degradation under PUREX process conditions. 1983, KFK-3639.

[19] Kulikov I A, Kermanova N V, Vladimirova M V. Radiolysis of TBP in the presence of plutonium and uranium. Sov Radiochem, 1983, 25: 330-336.

[20] Barney G S and Bouse D G. Alpha radiolysis of tributyl phosphate: effect of diluents. 1977, ARH-ST-153.

[21] Lloyd M H, Fellows R L. Alpha radiolysis and other factors affecting hydrolysis of tributyl phosphate. 1985, ORNL/TM-

[22] Ladrielle T, Wanet P, Lemaire D, et al. Alpha and gamma induced radiolysis of tributylphosphate. Radiochem Radioa Let, 1983, 59: 355-363.

[23] Nowak Z. Radiolytic degradation of extractant-diluent systems used in the PUREX process. Nucleonika, 1977, 22: 155-172.

[24] Clay P G, Witort M. Radiolysis of tri-n-butyl phosphate in aqueous solution. Radiochem Radioa Let, 1974, 19: 101-107.

[25] Barelko E P, Solyanina I P, Tsvetkova Z I. Radiation-chemical stability of TBP in solutions of hydrocarbons. Soviet Atomic Energy, 1966, 21: 946-950. DOI: 10.1007/BF01885923

Note: Figure translations are in progress. See original paper for figures.

Source: ChinaXiv —Machine translation. Verify with original.