Summary Report on Gamma Radiolysis of TBP/n-dodecane in the Presence of Nitric Acid Using the Radiolysis/Hydrolysis Test Loop

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INL
Idaho National Laboratory

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Idaho National Laboratory
Fuel Cycle Research & Development
Idaho Falls, Idaho 83415

http://www.inl.gov

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SUMMARY

Design and installation has been completed for a state-of-the-art radiolysis/hydrolysis test loop system. The system is used to evaluate the effects of gamma radiolysis and acid hydrolysis on the stability and performance of solvent extraction process solvents. The test loop is comprised of two main sections; the solvent irradiation and hydrolysis loop and the solvent reconditioning loop. In the solvent irradiation and hydrolysis loop, aqueous and organic phases are mixed and circulated through a gamma irradiator until the desired absorbed dose is achieved. Irradiation of the mixed phases is more representative of actual conditions in a solvent extraction process. Additionally, the contact of the organic phase with the aqueous phase will subject the solvent components to hydrolysis. This hydrolysis can be accelerated by controlling the system at an elevated temperature. At defined intervals, the organic from the irradiation/hydrolysis loop will be transferred to the solvent reconditioning loop where the solvent is contacted with scrub, strip, and solvent wash solutions which simulate process flowsheet conditions. These two processes are repeated until the total desired dose is achieved.

Since all viable solvent extraction components in an advanced fuel cycle must exhibit high radiolytic and hydrolytic stability, this test loop is not limited to any one solvent system but is applicable to all systems of interest. Also, the test loop is not limited to testing of process flowsheets. It is also a valuable tool in support of fundamental research on newly identified extractants/modifiers and the impact of gamma radiation on their stability in a dynamic environment. The investigation of the radiolysis of a TBP/n-dodecane process solvent in contact with aqueous nitric acid has been performed. These studies were intended to confirm/optimize the operability of the test loop system. Additionally, these data are directly applicable to numerous other solvent extraction processes containing TBP that are being developed to support advanced aqueous separations processes. Initial experimental results are consistent with existing literature reports regarding TBP/n-dodecane radiolysis. Additionally, the gamma dose rate has been characterized within the test loop and analytical methods have been developed for the characterization and quantification of radiolytic degradation products.

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ACRONYMS

AMUSE   Argonne Model for Universal Solvent Extraction

CINC   Costner Industries Nevada Corporation

GC-FID   Gas chromatography with flame ionization detection

HDBP   Dibutylphosphoric acid

HMBP   Monobutylphosphoric acid

INL   Idaho National Laboratory

NIKIMT   Research and Development Institute of Construction Technology

O/A   Organic to aqueous phase ratio

PUREX   Plutonium Uranium Reduction EXtraction

TBP   Tri-n-butylphosphate

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SEPARATIONS CAMPAIGN

SUMMARY REPORT ON GAMMA RADIOLYSIS OF TBP/N-DODECANE IN THE PRESENCE OF NITRIC ACID USING THE RADIOLYSIS/HYDROLYSIS TEST LOOP

1.   Introduction

A test loop system has been designed and installed at the Idaho National Laboratory (INL) to evaluate the effects of gamma radiolysis and acid hydrolysis on the stability and performance of solvent extraction process solvents. Since all preferred solvent extraction processes must exhibit high radiolytic and hydrolytic stability, this test loop will not be limited to any one solvent system but will be applicable to all systems of interest. The effects of radiolysis/hydrolysis on a particular solvent extraction flowsheet or solvent component are evaluated by re-circulating an aqueous/organic dispersion through the solvent irradiation loop until a desired absorbed gamma dose is achieved and then passing the irradiated organic solvent through the applicable scrub, strip, wash, etc. stages of the flowsheet. The conditioned organic solvent is then dispersed with a fresh aqueous solution and subjected to another cycle in the solvent irradiation loop. This process is repeated until a desired total absorbed dose is achieved.

2.   Description of the Solvent Radiolysis and Hydrolysis Test Loop

The design, construction, and installation of the solvent radiolysis and hydrolysis test loop have been described previously.[1] The irradiation source (see Figure 1) is a MDS Nordion GammaCell 220 Excel self-contained ^{60}Co gamma irradiator. The gamma dose rate is approximately 10.3 kGy/hr (1.03 MRad/hr) in the center of the sample chamber. The solvent irradiation loop is based upon a coil of borosilicate glass tubing (0.375" OD, 0.202" ID) which is placed in the gamma irradiator sample chamber. During the solvent irradiation, the aqueous and organic phases are mixed using a centrifugal contactor (CINC V-02, USA) with the entrance to the inside of the rotor plugged. The plug on the entrance to the interior of the rotor prevents phase separation within the

Figure 1.   MDS Nordion GammaCell 220 gamma irradiator.

centrifugal contactor. The annular mixing region of the centrifugal contactor may be purged with inert gas, if necessary. The organic and aqueous phases used are metered into the mixing region of the contactor at the desired organic to aqueous phase ratio (O/A). The mixed phases are pumped through the irradiator test loop by a magnetic drive gear pump. The mixed phases flow through the glass coil in the irradiator sample chamber, through the water bath, and return to the inlet of the centrifugal contactor where the phases are mixed and circulated back through the loop. An in-line tube mixer (TAH Industries, Inc.) is used to provide additional phase mixing in the test loop. The in-line tube mixer is placed between

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the outlet of the gear drive pump and the inlet of the irradiation loop.   The flowrate of the dispersion is in the range of 1.5 L/min in order to maintain turbulent flow and keep the phases dispersed. The radiolysis/hydrolysis test loop is equipped with pressure gauges and thermocouples before and after the gamma irradiator. Two flow sight glasses are used to monitor the extent of mixing in the test loop. The two phases continue to circulate until the desired dose is obtained. A view of the radiolysis/hydrolysis test loop is shown in Figure 2.

The temperature inside the sample chamber is ~45 °C due to the decay heat of the ^{60}Co source. Lower temperature irradiations are possible by using the off-gas of a liquid nitrogen dewar and a control valve interfaced to a temperature controller to maintain a temperature below 45 °C in the sample chamber. The lower limit for the operating temperature has not been determined, but irradiations at 10 °C are possible. A temperature-controlled water bath (external to the sample chamber) is used to maintain the desired temperature of the test solutions outside of the irradiator sample chamber. The sampling port permits samples to be withdrawn from the test loop in order to monitor the conditions during an irradiation. To facilitate hydrolysis of the solvent in the test loop, this setup will allow the solution to be maintained at an elevated temperature throughout testing if desired.

Figure 2. View of radiolysis/hydrolysis test loop showing gamma irradiator (center foreground), centrifugal contactor (right), recirculation pump (center), and temperature-controlled water bath (center back).

3.   Determination of Effective Gamma Dose Rate in Test Loop

The gamma dose rate at the center line of sample chamber was determined using Fricke dosimetry [2]. However, there is a spatial dependence for dose rate in the sample chamber, and the irradiation loop fills the entire chamber. Further, only a fraction of the solution in the test loop resides in the radiation field at any given time. Thus to measure absorbed dose to the irradiated solution, a liquid dosimeter was developed that could be pumped through the test loop. The effective dose rate in the gamma radiolysis test loop was determined using a methyl red dosimetry solution.[3-5] The methyl red dosimeter is based upon the bleaching of an irradiated methyl red solution, observed as a change in the optical density of the solution as a function of absorbed dose.

The absorption spectra of a of an air-saturated, aqueous 3.7E-4 M methyl red solution adjusted to pH 12.5 with NaOH irradiated at the centerline position of the gamma irradiator for various amounts of time are shown in Figure 3.   The absorbed gamma dose to the methyl red solution is calculated using the dose rate at the centerline position as determined by Fricke dosimetry. The absorbance maximum occurs at approximately 430 nm, and decreases with increasing absorbed dose.

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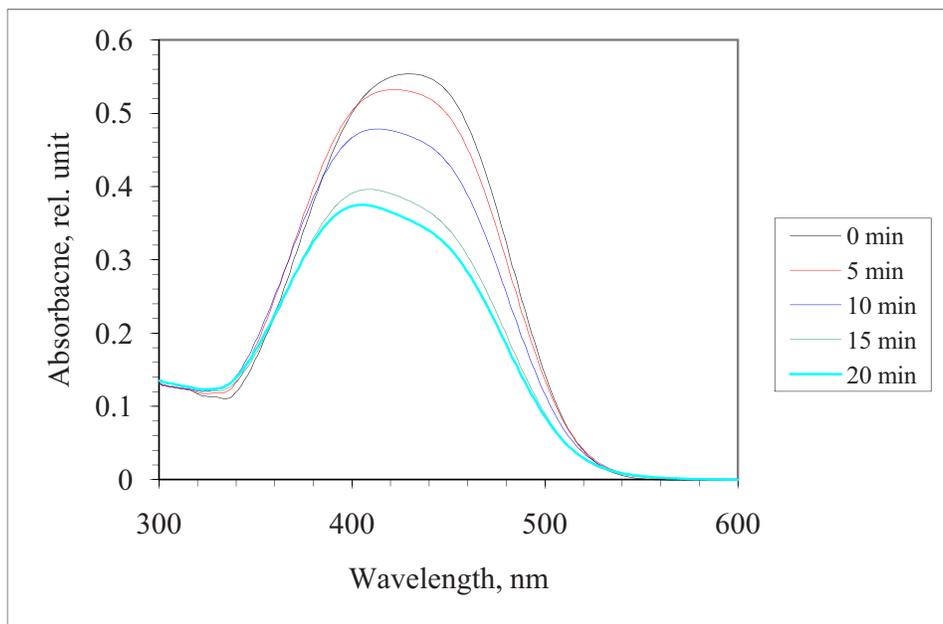
Figure 3. Methyl Red dose calibration spectra.

A plot of the absorbance at 430 nm versus absorbed gamma dose for the data shown in Figure 3 is shown
in Figure 4.
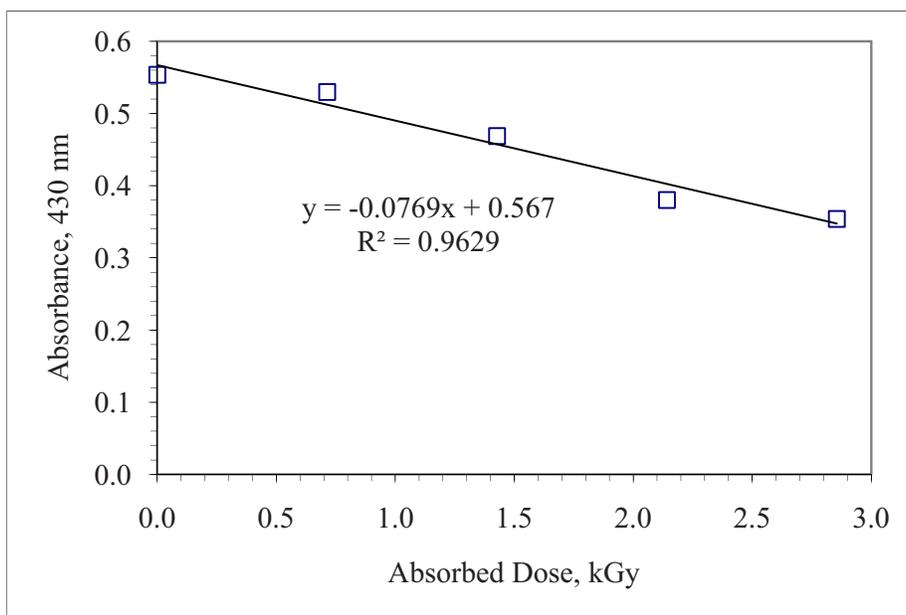
Figure 4. Absorbance of methyl red solution at 430 nm versus absorbed dose.

The absorption spectra of the same composition methyl red solution irradiated in the gamma radiolysis
test loop is shown in Figure 5. The change in absorbance at 430 nm and the slope of the methyl red
calibration curve (see Figure 4) are used to calculate the absorbed dose at each time point.

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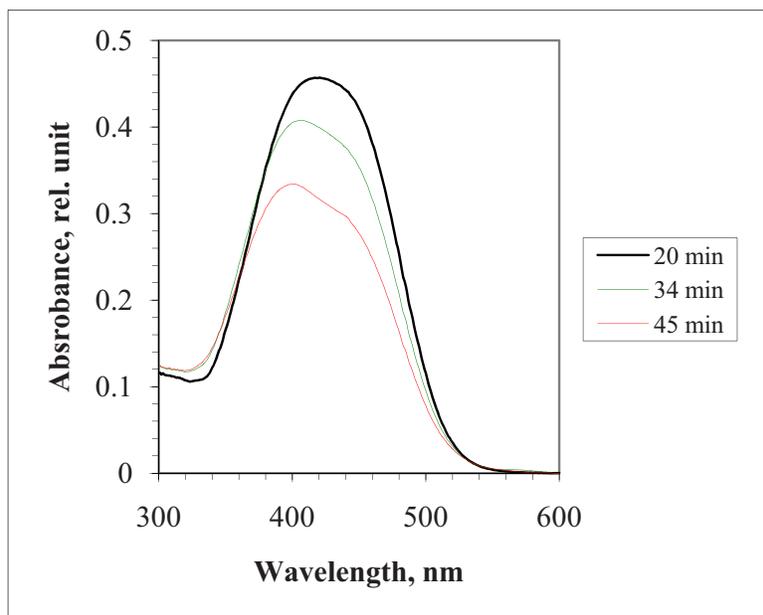
Figure 5. Methyl red absorption spectra in radiolysis test loop.

A plot of absorbed dose versus exposure time is shown in Figure 6. The slope of a linear best-fit line corresponds to the effective dose rate in the gamma radiolysis test loop. The effective gamma dose rate is 4.52 ± 0.65 kGy $\cdot$hr^{-1}
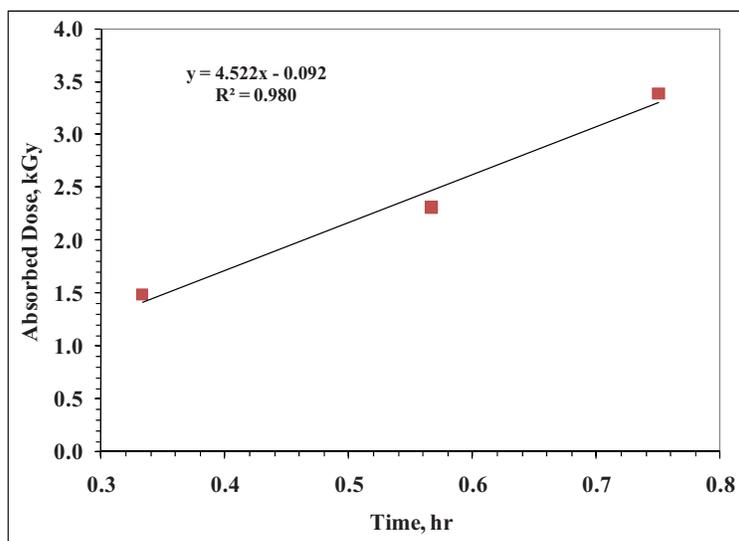
Figure 6. Plot of absorbed dose versus exposure time for a methyl red solution circulated through the radiolysis test loop. The slope of the linear best-fit is the effective gamma dose rate in the test loop. The effective gamma dose rate is 4.52 ± 0.65 kGy$\cdot$hr^{-1}.

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4.   Radiolysis Testing of TBP/n-Dodecane Solvent System

The test loop is comprised of two main sections; the solvent irradiation and hydrolysis loop and the solvent reconditioning loop. The sections are operated independently in a batch mode. In the solvent irradiation and hydrolysis loop, aqueous and organic phases are mixed and circulated through a gamma irradiator until the desired absorbed dose is reached. Irradiation of the mixed phases is more representative of actual conditions in a solvent extraction process. Additionally, the contact of the organic phase with the aqueous phase will subject the solvent components to hydrolysis. This hydrolysis can be accelerated by controlling the system at an elevated temperature. At defined intervals, the organic from the irradiation/hydrolysis loop will be transferred to the solvent reconditioning loop where the solvent is contacted with scrub, strip, and solvent wash solutions which simulate process flowsheet conditions. These two processes are repeated until the total desired absorbed dose is achieved.

The initial testing in the radiolysis/hydrolysis test loop utilized tributylphosphate (TBP) dissolved in n-dodecane. The TBP solvent system was chosen as the initial test solvent because it is one of the most common organic extractants used in nuclear separations. The TBP/alkane diluent system has received extensive attention in the scientific literature for at least the last forty years. The radiation chemistry of the TBP was recently reviewed by Mincher *et al.*.[6] A TBP/n-dodecane flowsheet was modeled as a reference point for the initial test in the radiolysis/hydrolysis loop. The basis for the model was taken from a typical PUREX flowsheet for the recycle of spent light water reactor fuel. This flowsheet (see Figure 7) provided the input for the AMUSE modeling with simplified aqueous feed (dissolved nuclear fuel) solutions and is used to evaluate the solvent extraction performance of the TBP/n-dodecane solvent as a function of absorbed gamma dose.
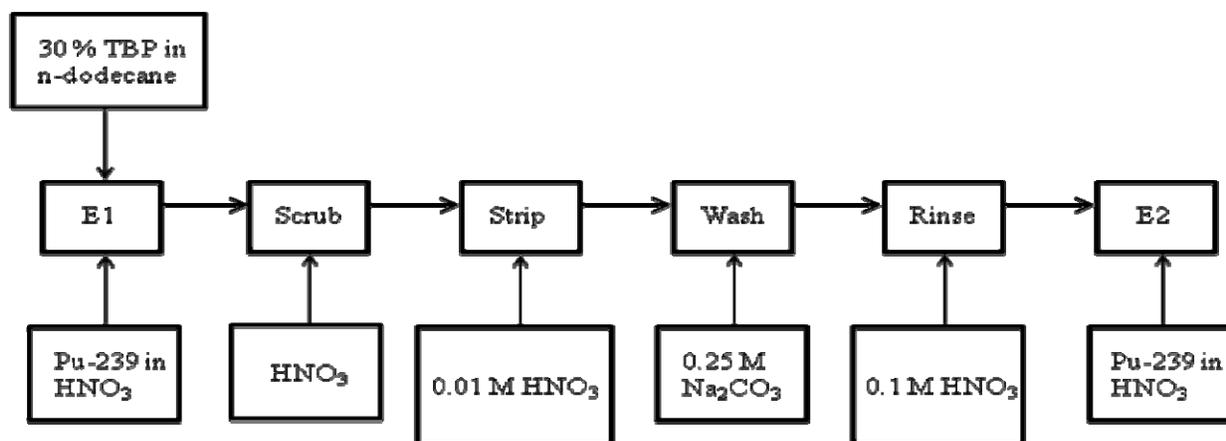
Figure 7. Schematic diagram of flowsheet used to evaluate the effects of gamma radiolysis on a 30 % TBP solvent.

The effect of varied nitric concentration on the radiolytic degradation of TBP dissolved in n-dodecane was evaluated using the radiolysis test loop. Three nitric acid concentration (0.9 M. 1.4 M and 3.0 M HNO_3) were studied. An organic to aqueous phase ratio (O/A ratio) of 1.0 ± 0.1 was used during the test. The test loop temperature was maintained at 25 °C during the irradiation. Samples of the aqueous and organic phases were removed periodically (every 48 – 72 hours of operation). Table 1 describes the irradiations performed.

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Table 1. List of TBP irradiations performed using 30 % TBP/n-dodecane solvent in contact with various
concentrations of nitric acid.

Irradiation	Start Date	End Date	[HNO_3], M	Total absorbed dose, kGy
1	08/03/2009	08/07/2009	0.9	385
2	12/22/2009	01/04/2010	1.4	1418
3	02/02/2010	02/05/2010	1.4	539
4	03/04/2010	03/09/2010	1.4	506
5	03/18/2010	03/29/2010	1.4	649
6	04/02/2010	04/07/2010	3.0	539
7	04/15/2010	04/26/2010	3.0	1169
8	05/19/2010	06/07/2010	3.0	2048
9	06/08/2010	06/28/2010	0.9	2158
10	06/29/2010	07/13/2010	1.4	1536

The density of the organic solvent was determined by weighing 1 mL samples of solvent in triplicate.
The un-irradiated solvent (0 kGy absorbed dose) was equilibrated three times with the appropriate HNO_3
solution prior to the density determination. All solvent samples were centrifuged for approximately ten
minutes to minimize any entrained aqueous phase. The lack of a statistically significant change in the
measured density of the organic solvent indicates no appreciable amount of the diluent was lost due to
evaporation during the course of the irradiation.

4.1   Measurement of Pu-239 Distribution Ratios

In order to gauge the effect of gamma radiolysis upon the extraction performance of the TBP solvents
used in this study, plutonium distribution ratios were measured as a function of absorbed dose. All
chemicals were reagent grade or better (Sigma Aldrich). Aqueous solutions were prepared using de-
ionized water. All analyses are performed in triplicate unless otherwise noted.

The extent of extraction is determined by calculating the distribution ratio, D = [Pu]org/[Pu]aq. The
concentration of Pu in the organic and aqueous phases is determined by liquid scintillation counting using
a Ultima Gold liquid scintillation cocktail (PerkinElmer). Prior to studying the radiolysis of the solvent,
the acidic degradation products were removed from the organic solvent by washing three times with 0.25
M $Na_2(CO_3)_2$. Following the caustic wash, the solvent was acidified by contacting with 0.1 M HNO_3.
Omission of the solvent clean-up resulted in unreasonably high measured values of D_{Pu} at low
concentrations of HNO_3. The acid dependence of the measured values of D_{Pu} for the extraction of Pu-239
by 30% TBP dissolved in n-dodecane is shown in Figure 8. The measured values of D_{Pu} as a function of
nitric acid concentration agree well with previous literature reports.[7-10]

The flowsheet shown in Figure 7 (vide supra) is employed to evaluate the extraction behavior of Pu-239
radiotracer using the TBP solvent samples generated in this study. The results of the flowsheet tests for
solvent irradiated in the presence of 0.9 M, 1.4 M, and 3.0 M HNO_3 are presented in Tables 2 – 4,
respectively. In each case, the wash and rinse distribution ratios are not reported for the un-irradiated
solvent because the low amount of activity reporting from the stripping contact precludes an accurate
determination of the Pu activity in those samples.

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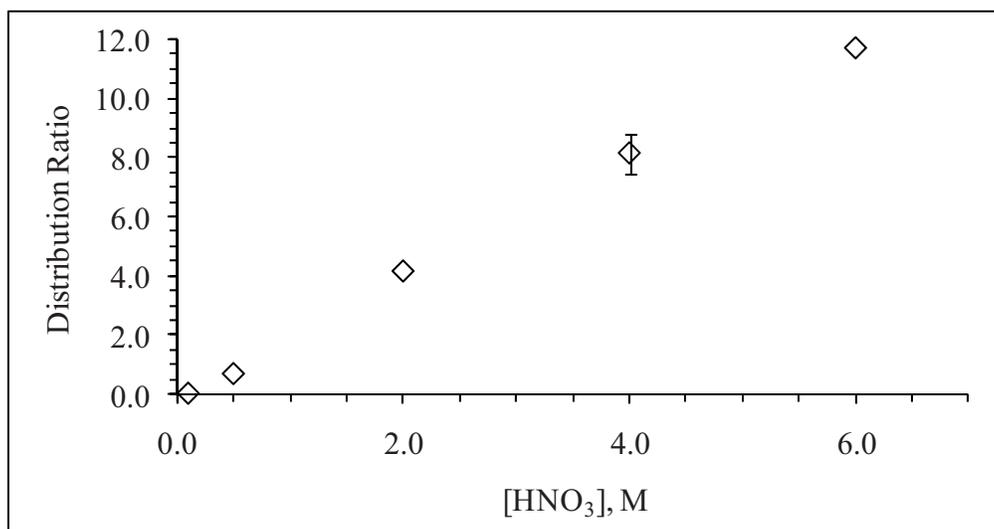
Figure 8. Acid dependence of the measured values of D_{Pu} for the extraction of Pu-239 by 30 % TBP dissolved in n-dodecane.

The most important data to consider in Tables 2 – 4 are the values of D_{Pu} for the E1, Strip, and E2 contacts. For all acidities studied, increasing absorbed gamma dose results in increasing values for the E1 and Strip contacts distribution ratios. This behavior is consistent with the generation of acidic degradation products from the radiolytic decomposition of TBP dissolved in n-dodecane. As expected, the essentially constant value of the distribution ratio measured for the E2 contacts as a function of absorbed dose indicates that the carbonate wash effectively removes the acidic degradation products of TBP radiolysis.

Table 2. Pu-239 distribution ratios for the different sections of the solvent evaluation flowsheet as a function of absorbed dose for a 30 % TBP solution irradiated in contact with 0.9 M HNO3.

Absorbed Dose, kGy	Pu-239 Distribution Ratios					
	E1	Scrub	Strip	Wash	Rinse	E2
0	3.21 ± 0.07	1.71 ± 0.08	1.42 ± 0.07	ND	ND	2.57 ± 0.13
76.9	7.16 ± 0.09	9.03 ± 0.83	6.50 ± 0.43	1.02 ± 0.01	6.21 ± 0.25	2.32 ± 0.02
185	9.76 ± 0.26	13.0 ± 0.4	10.3 ± 1.1	0.89 ± 0.11	7.51 ± 1.19	2.37 ± 0.07
306	11.6 ± 0.2	14.9 ± 1.1	17.7 ± 0.8	0.70 ± 0.27	4.73 ± 1.55	2.48 ± 0.47
385	12.5 ± 0.1	14.6 ± 2.7	20.4 ± 0.5	0.24 ± 0.01	4.74 ± 0.95	2.21 ± 0.02

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Table 3. Pu-239 distribution ratios for the different sections of the solvent evaluation flowsheet as a
function of absorbed dose for a 30 % TBP solution irradiated in contact with 1.4 M HNO_3.

Absorbed Dose, kGy	Pu-239 Distribution Ratios					
	E1	Scrub	Strip	Wash	Rinse	E2
0	3.25 ± 0.04	1.92 ± 0.02	0.84 ± 0.02	ND	ND	1.77 ± 0.05
109	6.85 ± 0.18	8.34 ± 0.03	10.4 ± 0.5	2.06 ± 0.79	7.60 ± 0.54	2.56 ± 0.07
544	14.5 ± 0.1	21.4 ± 0.9	19.2 ± 0.5	1.77 ± 0.31	3.35 ± 0.42	2.99 ± 0.25
1196	17.4 ± 0.6	30.7 ± 0.4	16.4 ± 0.7	0.39 ± 0.15	1.31 ± 0.46	2.20 ± 0.08

Table 4. Pu-239 distribution ratios for the difference sections of the solvent evaluation flowsheet as a
function of absorbed dose for a 30 % TBP solution irradiated in contact with 3.0 M HNO_3. Only
duplicate contacts performed.

Absorbed Dose, kGy	Pu-239 Distribution Ratios					
	E1	Scrub	Strip	Wash	Rinse	E2
0	4.1	3.6	3.9	ND	ND	2.3
412	12	16	15	1.7	5.1	2.9
575	12	16	15	2.0	4.8	3.0
761	11	21	14	0.9	3.7	2.2
1169	16	21	10	0.6	3.1	2.1

4.2   Determination of TBP Concentrations

The concentration of TBP in the organic solvent was determined by gas chromatography with flame
ionization detection (GC-FID) using a method similar to that reported by Krishnamurthy and
Sipahimalani [11]. The organic samples were analyzed directly using an Agilent 7890 gas chromatograph
equipped with a XTI-5 (30 m x 0.25 mm ID x 0.25 mm df) column. The GC oven used a temperature
profile of 80 °C – 300 °C at a rate of 10 °C/min. The retention time for TBP was 16.35 min.

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The variation in the concentration of TBP in the TBP/n-dodecane solvent irradiated in the presence of 0.9 M, 1.4 M, and 3.0 M HNO$_3$ as a function of absorbed dose is presented in Figure 9. These data show that over the course of the irradiation experiment the concentration of TBP in the solvent mixture decreases by approximately 5 % (v/v). These data show that there is no dependence of the radiolytic degradation of TBP upon the nitric acid concentration present in the aqueous phase. The analysis of the irradiated organic solvent for other degradation products is ongoing. The ion chromatography method based upon the work of Dodi and Verda [5] is the basis of the HDBP and HMBP analyses.
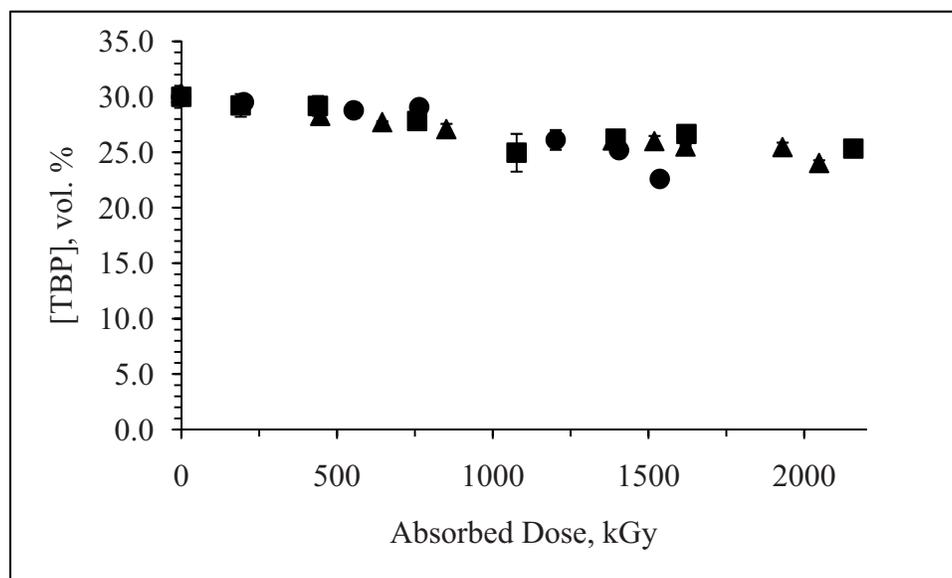

Figure 9. Concentration of TBP (vol. %) versus absorbed dose determined by GC-FID for irradiations performed with 0.9 M (squares), 1.4 M (circles), and 3.0 M (triangles) nitric acid.

4.3   Evaluation of g-values for Radiolytic Degradation of TBP

The efficiency of the conversion of absorbed radiation energy (gamma rays) into chemical products (radiolytic degradation products) is defined as the G-value, in units of $\mu mol \cdot J^{-1}$ ($J = Gy \cdot kg^{-1}$). The analytically determined TBP concentrations may be used to calculate a $-G_{TBP}$ for the destruction of TBP due to gamma irradiation. A plot of TBP concentration versus absorbed dose and the linear best fit to the concentration data for the irradiation of 30 % TBP/n-dodecane solutions in the presence of 0.9 M , 1.4 M, and 3.0 M HNO$_3$ is shown in Figure 10. The slope of the best-fit line corresponds to the G-value; $-G_{TBP}$, for the destruction of TBP. The determined G-values for the destruction of TBP in the presence of 0.9 M, 1.4 M, and 3.0 M HNO$_3$ are $-G_{TBP}$ = -0.097 $\pm$ 0.023, -0.148 $\pm$ 0.026, and -0.112 $\pm$ 0.010 $\mu mol \cdot J^{-1}$, respectively. Since there is no evidence of a dependence of the radiolytic degradation of TBP upon the aqueous nitric acid concentration, the average value of $-G_{TBP}$ for the destruction of TBP due to gamma irradiation is $-G_{TBP}$ = -0.119 $\pm$ 0.026 $\mu mol \cdot J^{-1}$.

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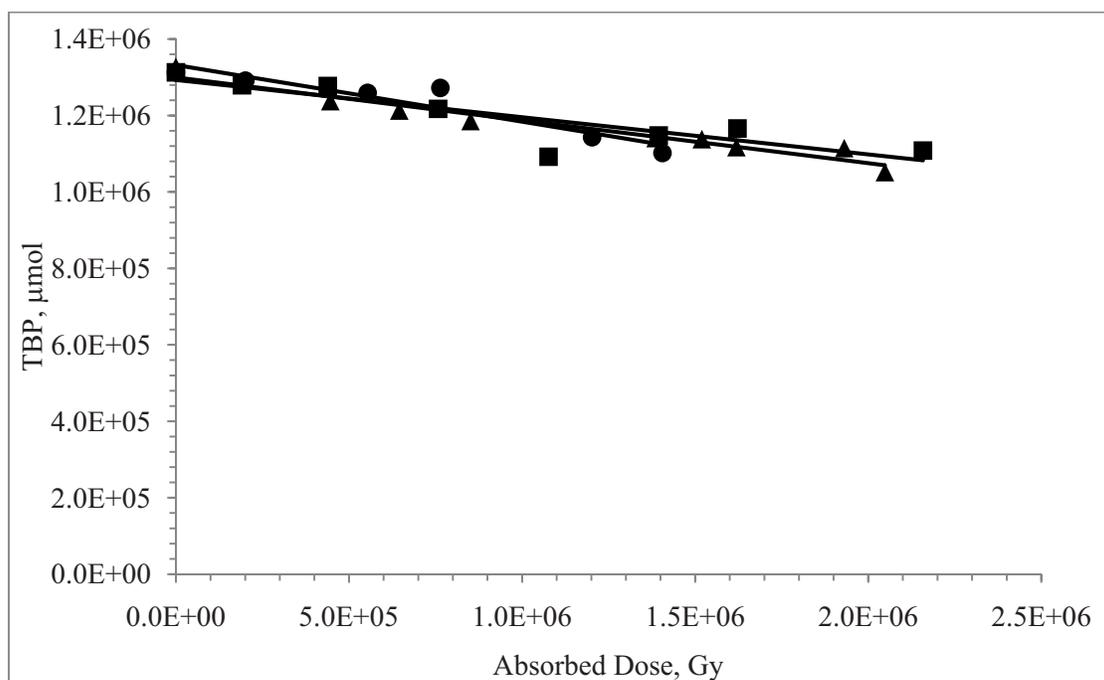
Figure 10. Plot of μmol TBP versus absorbed dose for irradiations performed with 0.9 M (squares), 1.4 M (circles), and 3.0 M (triangles) nitric acid. The slopes of the linear best-fit lines correspond to the g-value for the decomposition of TBP. The determined G-values for the destruction of TBP in the presence of 0.9 M , 1.4 M, and 3.0 M HNO_3 are $-G_{TBP}$ = -0.097 ± 0.023, -0.148 ± 0.026, and -0.112 ± 0.010 μmol·J^{-1}, respectively.

5.   Conclusions

Design and installation has been completed for a state-of-the-art radiolysis/hydrolysis test loop system, which will be used to evaluate the effects of gamma radiolysis and acid hydrolysis on the stability and performance of solvent extraction process solvents. Investigations of the radiolysis of a TBP/n-dodecane process solvent in contact with aqueous nitric acid have been completed. These studies have confirmed the operability of the test loop system.

It is well-known that the highest yield TBP radiolysis product is HDBP.[6] Assuming that HDBP is the only radiolysis product formed, the value of -G_{TBP} = -0.119 μmol·J^{-1} determined in this work agrees well with reported G-values for the production of HDBP which fall in the range of 0.07 – 0.12 μmol·J^{-1}. Since it is known that HMBP is also a degradation product formed via gamma radiolysis of TBP, this assumption is not strictly valid. Ongoing experiments are focusing on the determination of HDBP and HMBP product yields for comparison to literature values and TBP decomposition rates. Furthermore, results of this work demonstrate that the extent of radiolytic degradation of TBP/n-dodecane solvents is independent of nitric acid concentration.

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6.   Acknowledgements

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