Contract No:

This document was prepared in conjunction with work accomplished under Contract No. 89303321CEM000080 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

Disclaimer:

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U.S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied:

1) warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or
2) representation that such use or results of such use would not infringe privately owned rights; or
3) endorsement or recommendation of any specifically identified commercial product, process, or service.

Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.

Savannah River
National Laboratory®

Evaluation of Niowave's Proposed Solvent Washing Approach

M. S. Mills

T. S. Rudisill

August 2021

SRNL-STI-2021-00362, Revision 0

DISCLAIMER

Evaluation of Niowave's Proposed Solvent Washing Approach

M. S. Mills
T. S. Rudisill

August 2021

Savannah River National Laboratory®

REVIEWS AND APPROVALS

AUTHORS:

Signature on file, signed 8/30/21

_____

M. S. Mills, Nuclear Materials Systems   Date

Signature on file, signed 8/31/21

_____

T. S. Rudisill, Actinide & Separations Science   Date

TECHNICAL REVIEW:

Signature on file, signed 8/31/21

_____

E. A. Kyser, Actinide & Separations Science, Reviewed per E7 2.60   Date

APPROVAL:

Signature on file, signed 8/31/21

_____

J. M. Duffey, Manager   Date
Actinide & Separations Science

Signature on file, signed 8/31/21

_____

D. S. Lowry, Manager   Date
Nuclear Materials Systems

Signature on file, signed 8/31/21

_____

K. E. Zeigler, Director, Nuclear Materials Processing   Date

Signature on file, signed 8/31/21

_____

A. S. Poore, SRNL Mo-99 Program Manager   Date

ACKNOWLEDGEMENTS

EXECUTIVE SUMMARY

Niowave, Inc., is a domestic supplier of medical and industrial isotopes from uranium (U) and radium (Ra). The company has recently entered into a cooperative agreement with the U.S. Department of Energy's National Nuclear Security Administration (NNSA) and plans to deploy a superconducting electron accelerator (LINAC) to fission U for molybdenum-99 (^{99}Mo) production without the need for a nuclear reactor or highly enriched uranium (HEU). NNSA provided funding to the Savannah River National Laboratory (SRNL) to support Niowave in this effort.

Niowave will chemically process the irradiated material for recovery and purification of valuable isotopes, beginning with the dissolution of targets in nitric acid (HNO$_3$). A modified Plutonium Uranium Reduction Extraction (PUREX) process will be implemented for the recovery of U. The PUREX process utilizes a tributyl phosphate (TBP) in normal paraffin hydrocarbon (NPH) solvent which, when contacted with the nitric acid feed, extracts actinides into the organic phase. Ionizing radiation and nitric acid cause degradation of both the TBP and NPH. The principal degradation products of TBP are dibutyl phosphate (DBP) and monobutyl phosphate (MBP), which decrease U stripping efficiencies. NPH degradation products include a variety of oxidation and nitration products, which tend to affect phase separation and may retain certain short-lived fission products. A solvent washing process has been proposed to treat the degraded solvent by contacting it with 4 wt% sodium carbonate (Na$_2$CO$_3$) followed by contact with 0.1 M HNO$_3$ to neutralize residual alkalinity. The carbonate wash is effective at removing DBP and MBP but does not remove long chain degradation products derived from the solvent.

SRNL evaluated the application of the solvent washing process for Niowave at the proposed solvent:carbonate volume ratio (O:A) of 1:1.14 and with a reduced proportion of carbonate at an O:A ratio of 1:0.5. To do so, solvent was contacted with nitric acid and irradiated to the anticipated single pass radiation dose of 394 gray (Gy) and 10x and 100x the anticipated dose to demonstrate the impact of multiple recycles on the solvent quality. The solvent of all three doses was washed at the proposed O:A ratio and alternate O:A ratio of 1:0.5. The quality of the solvent was evaluated based on recommendations for similar processes at the Savannah River Site including DBP concentration, interfacial tension (IT), and disengagement time.

A DBP concentration < 30 ppm is recommended for process solvent. Irradiated unwashed solvent at all three doses was found to have a significant concentration of DBP; 490 ± 50 ppm at 394 Gy. However, the washing process at both O:A ratios evaluated was found to effectively remove DBP below the limit of detection for all three doses.

An IT > 3 dyne/cm is recommended. Irradiated unwashed solvent at all three doses was found to have an IT exceeding this metric including 7.0 ± 0.4 dyne/cm at 394 Gy. Washed solvent at both O:A ratios evaluated also has an IT exceeding this metric at all three doses. At the anticipated dose and 10x the anticipated dose, the IT of washed and unwashed solvent is not statistically distinguishable, however, at 100x the anticipated dose, the ITs of both washed solvents were less than that of the unwashed solvent. This indicates a potential negative impact from the washing process on IT at higher radiation doses.

The disengagement times of all unwashed and washed solvents were slightly less than or statistically indistinguishable from that of fresh solvent. This is desirable and indicates there is no negative impact from the process on disengagement time. Additionally, the disengagement times of washed solvents at both O:A ratios were indistinguishable from that of unwashed solvent at each radiation dose evaluated. Since degradation products that impact IT and disengagement time are not removed by carbonate washing, these results indicate that they are not generated in significant quantities within the range of conditions evaluated.

It is recommended that Niowave frequently or continuously wash the process solvent since this work indicates that a significant amount of DBP will be generated. Additionally, Niowave should frequently monitor the quality of process solvent. Accumulation of DBP may indicate that the carbonate solution is at or approaching the end of its life while declining IT may indicate that the solvent should be treated with alumina or replaced. Additionally, Niowave should monitor the alpha and beta-gamma activities of the carbonate and acid wash solutions; a limit should be defined, and the solutions should be replaced if the activities exceed these values. Niowave should also monitor the alkalinity of the carbonate wash solution and free acid of the acid wash solution; a limit should be defined for these and the solutions should be replaced when depleted below these values. Finally, Niowave may consider reducing the ratio of carbonate to solvent. Although this was not found to provide any advantages or disadvantages in solvent quality, it could allow them to reduce the volume of the carbonate tank and the volume of waste per carbonate discard.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

µg	microgram
A	aqueous
cm	centimeter
DBP	dibutyl phosphate
g-force	gram or gravitational acceleration (981 cm/s^2)
Gy	gray
HEU	highly enriched uranium
hr	hour
IT	interfacial tension
L	liter
LINAC	superconducting electron accelerator
M	molar
MBP	monobutyl phosphate
mL	milliliter
Mo	molybdenum
mol	mole
NNSA	National Nuclear Security Administration
NPH	normal paraffin hydrocarbon
O	organic
ppm	parts per million
PUREX	Plutonium Uranium Reduction Extraction
Ra	radium
rpm	revolutions per minute
s	second
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
TBP	tributyl phosphate
U	uranium
vol%	volume percent
wt%	weight percent

1.0 Introduction

1.1 <u>Background</u>

Niowave, Inc., is a domestic supplier of medical and industrial isotopes from uranium (U) and radium (Ra). The company has recently entered into a cooperative agreement with the U.S. Department of Energy's National Nuclear Security Administration (NNSA) to produce molybdenum-99 (^{99}Mo) without the use of highly enriched uranium (HEU). The United States currently produces very little ^{99}Mo and, therefore, imports essentially all of its supply from foreign producers, some of which still use HEU in the production process. The continuity of the ^{99}Mo supply has also been an issue in the recent past. A majority of the research reactors used to irradiate targets that produce much of the world's supply of ^{99}Mo are over 40 years old. Aging infrastructure and planned and unplanned outages of some of these reactors have resulted in ^{99}Mo supply interruptions. NNSA's support to the cooperative agreement participants is based on a 50% government/50% commercial cost-share basis [1], with initial NNSA contributions up to a total of $25 million for each project. In addition to the financial support provided directly to the commercial businesses, NNSA has also funded national laboratory support to assist in the commercialization of the ^{99}Mo production processes. The Savannah River National Laboratory (SRNL) is currently providing support to Niowave, which plans to deploy a superconducting electron accelerator (LINAC) to fission U for ^{99}Mo production without the need for a nuclear reactor or HEU [2].

1.2 <u>Niowave ^{99}Mo, U Utilization Process</u>

The Niowave production process for ^{99}Mo uses triuranium octoxide (U_3O_8) pellets as the target material in the LINAC. Molybdenum-99 is one of the predominate U fission products generated during pellet irradiation. After cooling for nominally one day, the pellets are dissolved in nitric acid (HNO_3) to prepare a feed solution for the purification and recovery of the U. The U is purified using a modified Plutonium Uranium Reduction Extraction (PUREX) solvent extraction process designed to recover the actinides in the U product stream, shown in Figure 1-1. The modified PUREX process utilizes a tributyl phosphate (TBP) in normal paraffin hydrocarbon (NPH) solvent. The ^{99}Mo is not extracted by the TBP solvent and is rejected to the raffinate. The raffinate is subsequently processed for the recovery of the ^{99}Mo and other isotopes of interest. The U in the product solution from the PUREX process is precipitated as an oxalate which is calcined to U_3O_8 for pellet fabrication.
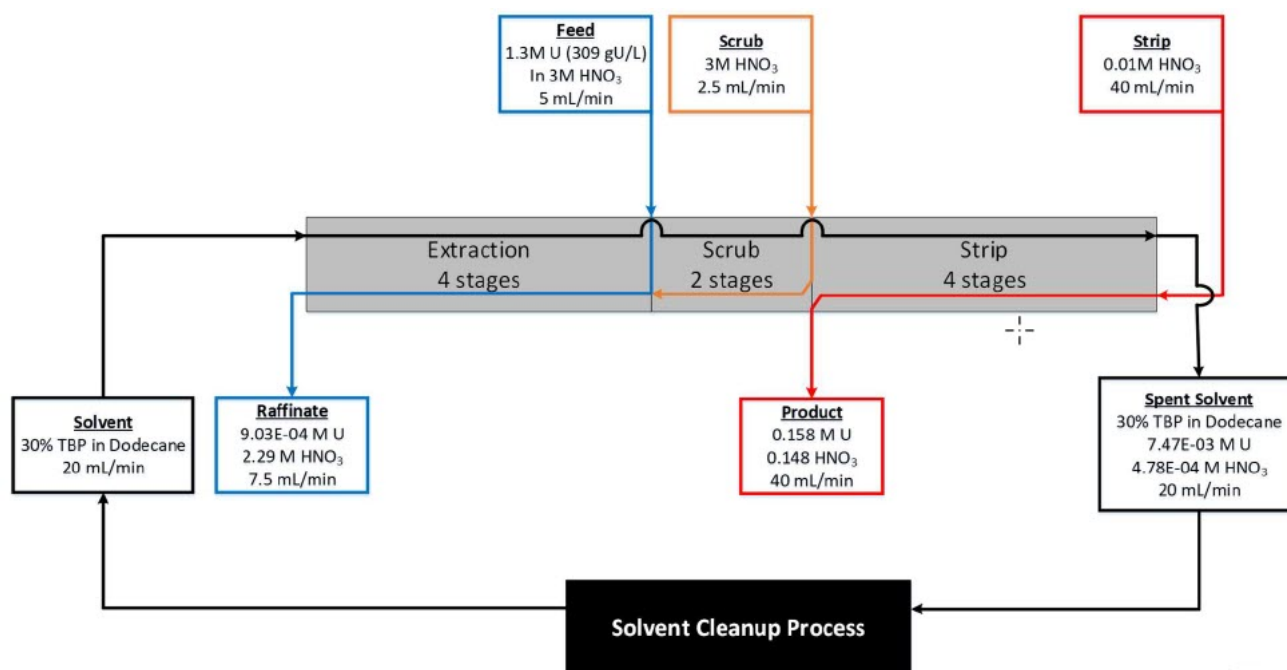
Figure 1-1. Preliminary Niowave Modified PUREX Process for U Recovery

1.3 Degradation of TBP/NPH Solvent

A mixture of 30 vol% TBP and 70 vol% NPH solvent will be used in the modified PUREX process for the recovery of the actinides in the U product stream. When the solvent is contacted with ionizing radiation and nitric acid, both the TBP and NPH components undergo degradation. The principal degradation products of TBP are dibutyl phosphate (DBP) and monobutyl phosphate (MBP), which are formed by acid hydrolysis and radiolysis decomposition [3]. These combine with actinide and fission product ions forming strong complexes, which decrease the stripping metal recovery and decontamination efficiencies and can sometimes cause physical problems [4]. The NPH diluent degrades to various oxidation and nitration products including long-chain nitro, nitrite, and nitroso hydrocarbons. Additional NPH degradation products include alcohols, unsaturated alcohols, nitro alcohols, nitro alkenes, esters, and long-chain organic acids, which tend to affect phase separation and may retain certain short-lived fission products [4, 5].

Processing with degraded solvent results in issues including product losses, lower fission product decontamination, reduced extraction efficiencies, poorer separations, higher recovered solvent activity, and increased interfacial "crud" levels. Additionally, product losses and decontamination factors are five to twenty times worse with untreated recycled solvent than with fresh solvent [6].

1.4 Solvent Washing Process

The degraded TBP/NPH solvent is to be treated by single stage contact with aqueous 0.4 molar (M) (4 wt %) sodium carbonate (Na_2CO_3). The purpose of the Na_2CO_3 solvent wash is to remove DBP and MBP, degradation products of TBP, and radioactive contaminants from the solvent. The carbonate washed solvent is then contacted with dilute (nominally 0.1 M) HNO_3 to neutralize any residual alkalinity from the carbonate wash [5].

The proposed Niowave solvent washing process, represented in Figure 1-2, is to use an organic (O) solvent to aqueous (A) carbonate volume fraction (O/A) of 0.88 (O:A ratio of 1:1.14), followed by dilute acid neutralization with an O/A of 1 (O:A ratio of 1:1).
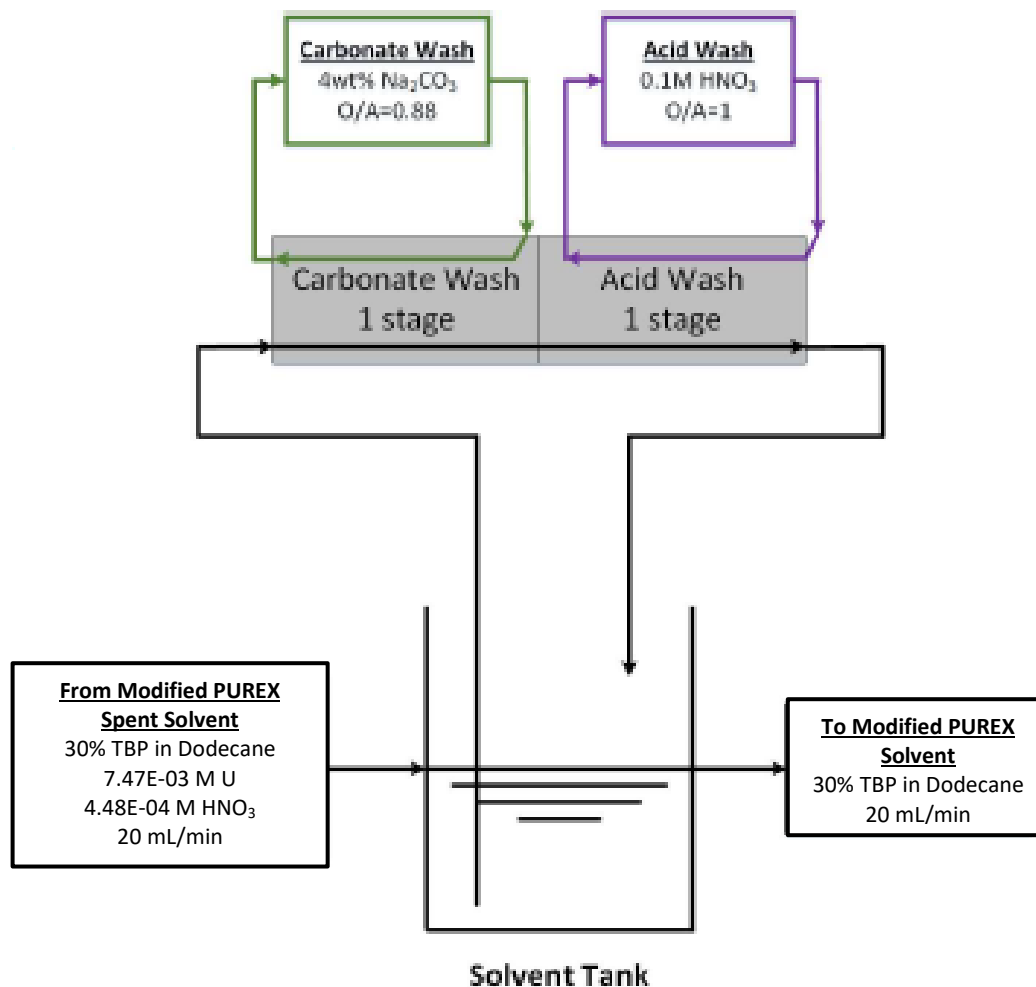
Figure 1-2. Preliminary Niowave Solvent Treatment Process

1.5 Objectives

The objective of this work is to determine if the above-described solvent washing process is an effective treatment of degraded TBP/NPH solvent. An effective treatment will remove degradation products from the solvent that are generated from contacting the solvent with radiation and nitric acid. This will allow the solvent to be recycled in the modified PUREX solvent extraction process with minimal to no loss of efficacy in separating actinides from the aqueous feed stream.

2.0 Experimental

2.1 Solvent and Solution Preparation

The following solutions were prepared:
1. 3 M HNO_3;
2. 0.1 M HNO_3;
3. 30 vol% TBP in 70 vol% dodecane; and
4. 4 wt% Na_2CO_3.

A single volume of fresh solvent was contacted with three separate equal volumes of fresh 3 M nitric acid in a separatory funnel and allowed to equilibrate each time for ~5 minutes. This was done to saturate the solvent with HNO_3 to produce acid hydrolysis degradation products in the solvent before and during irradiation.

The anticipated radiation dose to the solvent is 394 gray (Gy) during each solvent extraction cycle [7]. The acid-contacted solvent was split into three equal volumes and irradiated to the anticipated dose, 10x the anticipated dose (3,940 Gy), and 100x the anticipated dose (39,400 Gy), respectively. Solvent was irradiated to 10x and 100x the anticipated dose to demonstrate the effect of the washing process on solvent that had been recycled multiple times through the Niowave system.

2.2 Solvent Washing

The Niowave process will utilize 2-centimeter (cm) diameter centrifugal contactors at a nominal speed of 3,000 revolutions per minute (rpm) (i.e., ~100 g-force) and a total residence time of ~15 s, which includes both mixing and separation, for both carbonate washing and neutralization. Due to the short contact time in the centrifugal contactors, the organic and aqueous phases may not equilibrate. Therefore, to better represent the Niowave process, experiments were performed by mixing the phases for ~10 s with a vortex mixer followed by immediately centrifuging of the phases at ~216 g-force for 15 s. The higher g-force and longer time in the centrifuge was selected to ensure complete phase separation and allow time for the centrifuge to reach full speed.

These experiments were performed at the proposed solvent:carbonate ratio of 1:1.14 and with a reduced amount of aqueous at a solvent:carbonate ratio of 1:0.5. The ratio of carbonate to 0.1 M HNO_3 was held constant, as shown in Table 2-1 below.

Table 2-1. Organic:Aqueous Ratios Evaluated

-	Solvent:Carbonate	Solvent:Acid	Carbonate:Acid
Proposed	1:1.14	1:1	1:0.877
Reduced Aqueous	1:0.5	1:0.439	1:0.877

For each dose at both O:A ratios evaluated, solvent was washed in small batches and the washed solvent samples were combined and mixed after washing to provide a uniform solvent sample for analysis.

2.3 Solvent Quality Measurements

Criteria for acceptable solvent quality in PUREX processes were developed by the Savannah River Laboratory (SRL) (predecessor to SRNL) for the Savannah River Site's (SRS's) F and H Canyon facilities [3]. Solvent quality was evaluated based on interfacial tension (IT), DBP concentration, and solvent residual activity after a laboratory extraction-strip test. The SRS criteria are shown in Table 2-2. Note that these criteria are specific to SRS processes. These may not be ideal metrics for the Niowave process. Niowave should develop and refine their own quality criteria, however, the SRS recommendations represent a good baseline.

Table 2-2. Solvent Quality Criteria Limit Recommendations

Parameter	Limit
Interfacial Tension (IT)	> 3.0 dynes/cm
DBP Concentration	< 30 parts per million (ppm)
Pickup (after stripping)[1]	< 10^4 disintegrations per minute per milliliter (dpm/mL) alpha

The experiments for this work were maintained clean (i.e., non-radiological) so pickup tests were not performed on the solvent. IT and DBP concentrations were determined to evaluate the various solvents. Additionally, disengagement time was evaluated. Disengagement time had historically been used to evaluate the quality of SRS solvent but was generally abandoned in favor of IT due to the subjectivity involved and difference in perspective between different operators. This aspect was minimized by having the same two individuals measuring disengagement time for all tests. A quantitative criterion for disengagement time was not found but qualitatively, an effective solvent will have a low disengagement time and disengagement time can be used to compare solvents of different radiation doses and O:A ratios.

A description of each criterion and quantification method used for this work is provided below. Detailed step-by-step instructions on how to determine solvent interfacial tension and disengagement time were previously provided to Niowave [8].

2.3.1 Dibutyl Phosphate Concentration
DBP has historically been found to be generated in substantial quantities via acid hydrolysis and radiolysis decomposition in PUREX cycle operations at SRS. U and Pu have a stronger affinity for DBP than TBP and DBP has a high solubility for the organic phase. Therefore, DBP in the Niowave process solvent would result in decreased stripping efficiencies proportional to 0.5 to 1 moles (mol) of U per mol of DBP. This depends on whether U is complexed with 2 mol of DBP or 1 mol of DBP and 1 mol of TBP [3].

The DBP concentration was determined using the standard addition method for hydrogen nuclear magnetic resonance (HNMR) spectroscopy. This was done for all unwashed and washed solvents. For each dose and O:A ratio evaluated, a total volume of 1.2 mL was prepared with (a) the solvent; (b) the solvent plus nominally 10 µg/mL DBP; and (c) the solvent plus nominally 20 µg/mL DBP. The prepared samples were provided to the SRNL NMR analyst who determined the DBP concentrations of the samples.

2.3.2 Interfacial Tension
Interfacial tension is a measure of the solvent and aqueous phases' ability to separate from each other. A low interfacial tension results in longer separation times and reduction in stage efficiency and product purity. Interfacial tension reduction is caused by nitric acid oxidation and radiolysis degradation products, which are long carbon chain compounds derived from NPH or TBP dimers or trimers. These IT reducing components are not removed via carbonate washing and require alumina absorption for removal [3].

SRL developed an analytical method for determining the solvent interfacial tension of solvent samples from SRS processes [9]. This method was adapted for these experiments but relies on the same fundamental principles [8].

Solvent was loaded into a test tube. A 1.00-mL Hamilton syringe was connected to tubing with a 20-gauge blunt point syringe tip via Luer Lock fittings.[2] The entire syringe, tubing, and manifold assembly was filled

---

[1] This specification was specific for SRS Pu recovery. Niowave should develop their own criteria specific to their process if this metric is used.
[2] Hamilton #91050 N720 NDL syringe tip was used.

with 4 wt% Na_2CO_3 solution such that the system was free of any air bubbles. The 1.00-mL syringe was configured in a KD Scientific Model 101 Syringe Pump as depicted in Figure 2-1 below.

Figure 2-1. Syringe and Syringe Pump Configuration

The blunt point syringe tip was positioned and held about ¼" below the surface of the solvent in the middle of the tube as simulated in Figure 2-2.

Figure 2-2. Blunt Point Syringe Position in Test Tube [3]

The syringe pump was set to a rate of 4.00 mL/hr and turned on. A drop of carbonate solution would form on the tip of the syringe submerged beneath the solvent. At the moment that the drop fell from the tip, a stopwatch was started. This process was repeated for at least 10 drops with the lap button pressed for each drop to capture the time for that drop to form and fall.

The average drop time was used to calculate the average volume of a drop using Equation *(1)*.

$$V_A = F \frac{t}{3600 \; {}^s\!/_{hr}}$$

(1)

Where,

V_A = Average volume of a drop, mL
F = Syringe pump flowrate, mL/hr
t = Average time for a drop to form and fall, s

The average drop volume is then used to calculate the IT using Equation *(2)* [9].

---

[3] Test tube is dry in simulated example. Syringe tip was held ¼" below solvent surface.

$$\gamma = \frac{V_A(\rho_A - \rho_O)gf}{D} \qquad (2)$$

Where,

γ = Interfacial tension, dyne/cm
ρ_A = Density of aqueous (sodium carbonate), g/mL
ρ_O = Density of organic solvent, g/mL
D = Outside diameter of blunt tip needle, cm
f = Fraction of ideal drop that falls, unitless

The following expression represents the fraction of an ideal drop which actually falls.

$$f = C_1 + C_2\, log\left(\frac{V_A}{D^2}\right) + C_3 \left(log\left(\frac{V_A}{D^2}\right)\right)^2 \qquad (3)$$

Where,

$C_{1,2,3}$ = Constants, unitless

The constants are as follows:

Table 2-3. Fraction of Ideal Drop Constants

$\dfrac{V_A}{D^2}$	C_1	C_2	C_3
<1.5	0.26056	0.021385	-0.02267
>1.5	0.2754	-0.0157	-0.0002357

2.3.3 Disengagement Time

Disengagement time is the time it takes for the organic and aqueous phases to completely separate, beginning immediately after mixing. This had been used to evaluate solvent quality at SRS facilities but had poor reproducibility from operator to operator due to the subjectivity involved in judging when phase separation was complete. The IT method was developed to replace the disengagement time method since IT and disengagement time are inversely related [3, 9]. Although IT and disengagement time are related, these test methods are not necessarily redundant since the IT is determined between the solvent and aqueous Na_2CO_3 while the disengagement time is between the solvent and aqueous HNO_3.[4]

To determine the disengagement time, 5 mL of 3 M HNO_3 and 5 mL of solvent were added to a small separatory funnel. The funnel was sealed and vigorously shaken for ~30 s. Two individuals independently measured the time from when shaking ceased to when they judged phase separation to be complete with stopwatches. The shaking of solvent and HNO_3 and measuring of disengagement time was performed five times per solvent.

2.4 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2. Signature of the E7 technical reviewer on the final document signifies completion of the design verification review. The completed checklist is retained in the Electronic Laboratory Notebook.

---

[4] The IT and disengagement methods could be used with an aqueous phase of either carbonate or nitric acid.

3.0 Results and Discussion

Supplemental data are provided in Appendix A.

3.1 <u>Unwashed Solvent</u>

3.1.1 DBP Concentration

The DBP concentrations of unwashed solvents are shown in Table 3-1 and represented in Figure 3-1 below.

Table 3-1. DBP Concentrations of Unwashed Irradiated Solvents

Solvent	DBP Concentration ± 95% Uncertainty (ppm, μg/g)
394 Gy	490 ± 50
3,940 Gy	560 ± 50
39,400 Gy	620 ± 50
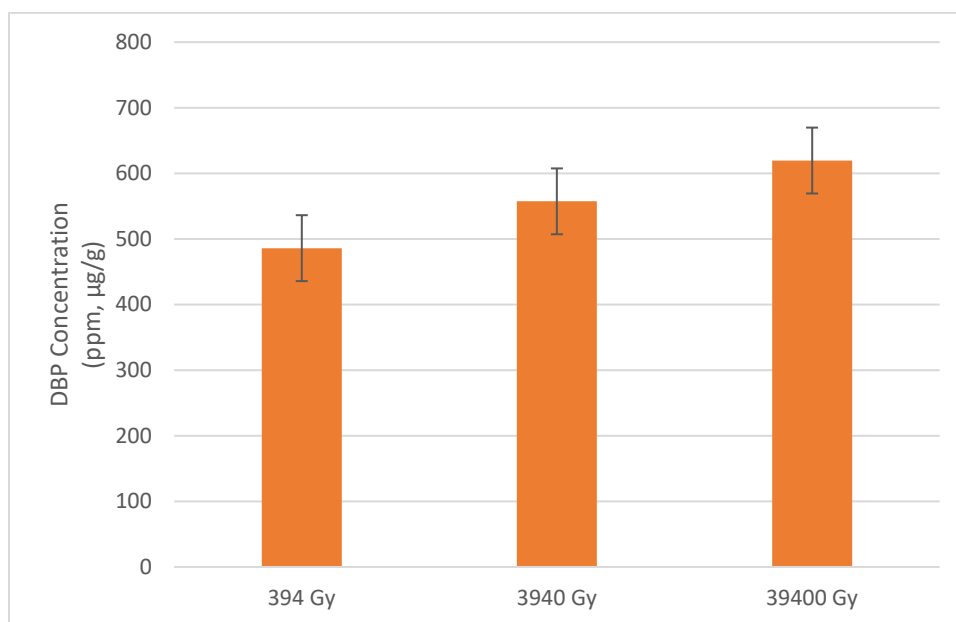
Figure 3-1. DBP Concentrations of Unwashed Solvents

For all three doses of unwashed irradiated solvent, the DBP concentration is much greater than the recommendation provided in Table 2-2 of 30 ppm and is considered significant. For example, a buildup of 403 ppm DBP in F Canyon solvent was recognized as the cause of Pu buildup in process carbonate wash solution [3]. This will reduce U stripping efficiency, which could compound if the DBP is not removed. This supports the need for frequent or potentially continuous washing of the solvent to remove DBP.

Additionally, the DBP concentration appears to be linear with the log of dose, as shown in Figure 3-2, although the uncertainty margins are very close. This could indicate that acid hydrolysis from the 3 M HNO_3 has a more significant impact on DBP generation than the radiation dose.

9
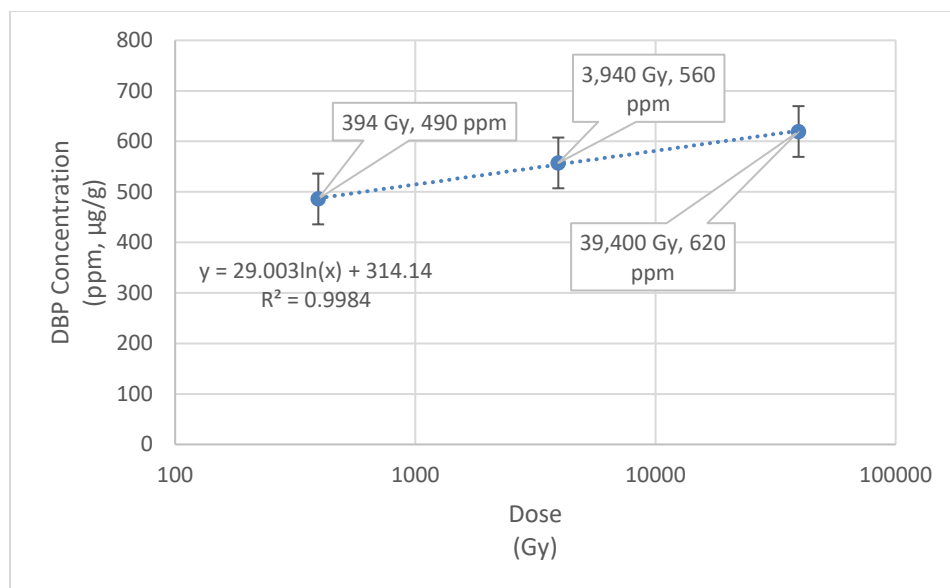
Figure 3-2. DBP Concentrations of Unwashed Solvent with Semi-Log Trendline

3.1.2 Interfacial Tension

The interfacial tensions of unwashed solvents are shown in Table 3-2 and represented in Figure 3-3 below. Also included is the measured interfacial tension of fresh (non-acid contacted and unirradiated) solvent for comparison.

Table 3-2. Interfacial Tensions of Unwashed Irradiated Solvents

Solvent	Interfacial Tension ± 95% Uncertainty (dyne/cm)
Fresh Solvent	7.1 ± 0.4
394 Gy	7.0 ± 0.4
3,940 Gy	6.9 ± 0.4
39,400 Gy	6.9 ± 0.4

Figure 3-3. Interfacial Tensions of Irradiated Unwashed Solvents

For all three doses of unwashed irradiated solvent, the interfacial tension is above the minimum specified in Table 2-2 of 3 dyne/cm. The differences in IT at all three doses and fresh solvent are statistically indistinguishable, indicating that there is no discernable impact from radiation dose. These results imply that the long carbon chain compounds derived from NPH or TBP dimers or trimers are not generated in significant quantities within this range of conditions. This is promising for the Niowave process since these compounds are not removed by alkaline washing.

3.1.3 Disengagement Time

The disengagement times of unwashed solvents were measured twice, more than two months apart. For all doses the measurements were statistically different. The disengagement times measured for both dates are shown in Table 3-3 and represented in Figure 3-4 and Figure 3-5 below. Also included is the measured disengagement time of fresh (non-acid contacted and unirradiated) solvent for comparison.

Table 3-3. Disengagement Times of Unwashed Irradiated Solvents

Solvent	Disengagement Time ± 95% Uncertainty – 2/10/21 (s)	Disengagement Time ± 95% Uncertainty – 4/22/21 (s)
Fresh Solvent	35.1 ± 0.7	-
394 Gy	32.3 ± 0.4	30.1 ± 0.5
3,940 Gy	33.0 ± 0.4	30.6 ± 0.5
39,400 Gy	34.3 ± 0.5	32.1 ± 0.7
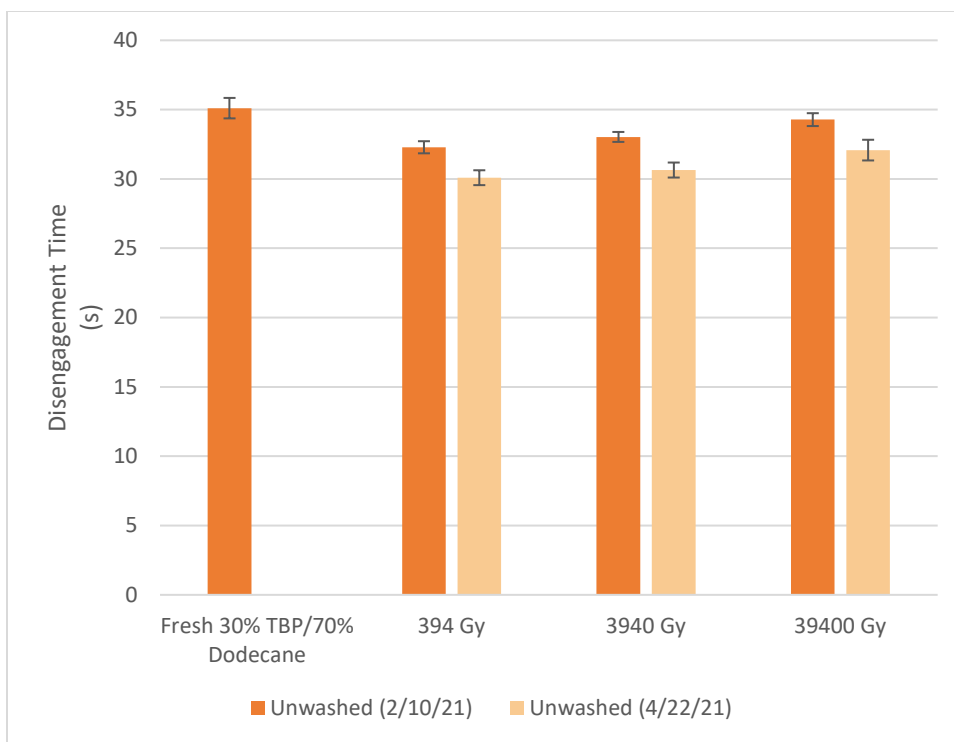
Figure 3-4. Disengagement Times of Unwashed Solvents
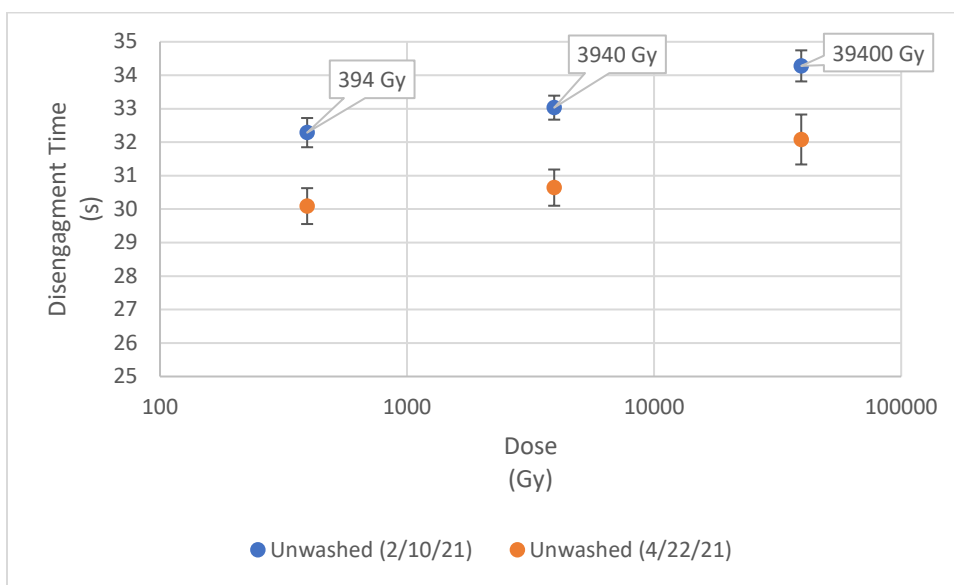
Figure 3-5. Semi-Log Plot of Disengagement Time of Unwashed Solvents

The disengagement times trend higher with increasing dose; however, the disengagement time for irradiated solvent is lower than that of fresh solvent for all measurements and is not a matter of concern. The disengagement times measured on 4/22/21 averaged 2.3 s shorter than those originally measured on 2/10/21. This is a small margin but is statistically distinguishable for all doses. This difference could be a result of

the time between measurements but more likely reflects an underrepresentation of uncertainty due to the subjectivity of the disengagement time method.

3.2 Proposed Solvent:Carbonate Ratio of 1:1.14

3.2.1 DBP Concentration

DBP was not detectable in the solvent at any dose evaluated. This is shown with the associated uncertainty in Table 3-4.

Table 3-4. DBP Concentrations of Solvent:Carbonate Ratio of 1:1.14

Solvent	DBP Concentration (ppm, μg/g)
394 Gy	0
3,940 Gy	0
39,400 Gy	0

*DBP concentration uncertainty is ± 5 ppm at a 95% confidence interval for all doses.

These results indicate that the proposed solvent washing process will be effective at removing the significant amount of DBP generated from the process, which is necessary to maximize U recovery efficiency.

3.2.2 Interfacial Tension

Solvent washing will not remove the degradation products that decrease interfacial tension but the impact of the washing process on IT was investigated. The interfacial tensions of an O:A ratio (carbonate) of 1:1.14 are shown in Table 3-5 and represented with the ITs of unwashed solvent in Figure 3-6 below. Also included is the measured interfacial tension of fresh (non-acid contacted and unirradiated) solvent for comparison.

Table 3-5. Interfacial Tensions of Solvent:Carbonate Ratio of 1:1.14

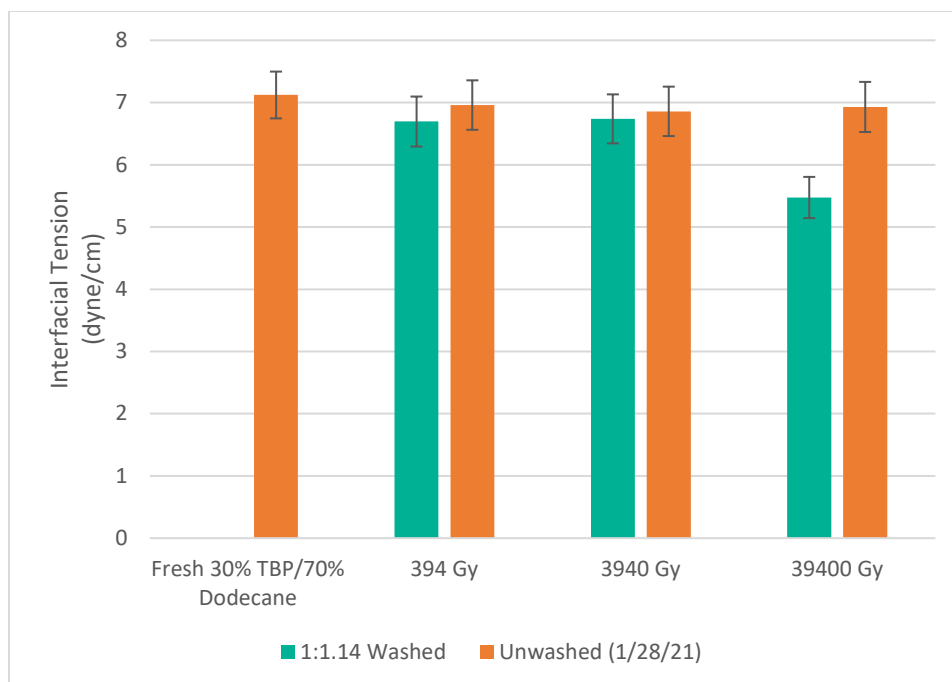| Solvent	Interfacial Tension ± 95% Uncertainty (dyne/cm)
Fresh Solvent	7.1 ± 0.4
394 Gy	6.7 ± 0.4
3,940 Gy	6.7 ± 0.4
39,400 Gy	5.5 ± 0.3

Figure 3-6. Solvent:Carbonate Ratio of 1:1.14 Interfacial Tension

For all three doses of washed solvent at the proposed solvent:carbonate ratio of 1:1.14, the interfacial tension is above the minimum recommendation specified in Table 2-2 of 3 dyne/cm. The differences in IT between the washed solvent and unwashed solvent at 394 Gy (anticipated dose) and 3,940 Gy are statistically indistinguishable. However, the washed solvent at 39,400 Gy is 1.4 ± 0.7 dyne/cm lower than the unwashed solvent and 1.6 ± 0.7 dyne/cm lower than fresh solvent, although it is still above the minimum recommendation and is acceptable.

Since the degradation products that reduce solvent IT are not removed by solvent washing, the washing process was not anticipated to improve IT. The IT of the washed solvent was measured nonetheless to understand the impact of the washing process on solvent IT. These results indicate that, with the proposed washing parameters, the washing process may have a negative impact on solvent IT, especially at higher radiation doses.

3.2.3 Disengagement Time

Because disengagement times and IT are both indicators of degradation products that are not removed by solvent washing, disengagement time was similarly not anticipated to be improved from washing but was still investigated to understand the impact of the washing process. The disengagement times of the solvent:carbonate ratio of 1:1.14 are shown in Table 3-6 and represented with the disengagement times of unwashed solvent in Figure 3-7 and Figure 3-8 below.

Table 3-6. Disengagement Times of Solvent:Carbonate Ratio of 1:1.14

Solvent	Disengagement Time ± 95% Uncertainty (s)
394 Gy	32.5 ± 0.2
3,940 Gy	31.6 ± 0.5
39,400 Gy	31.8 ± 0.5
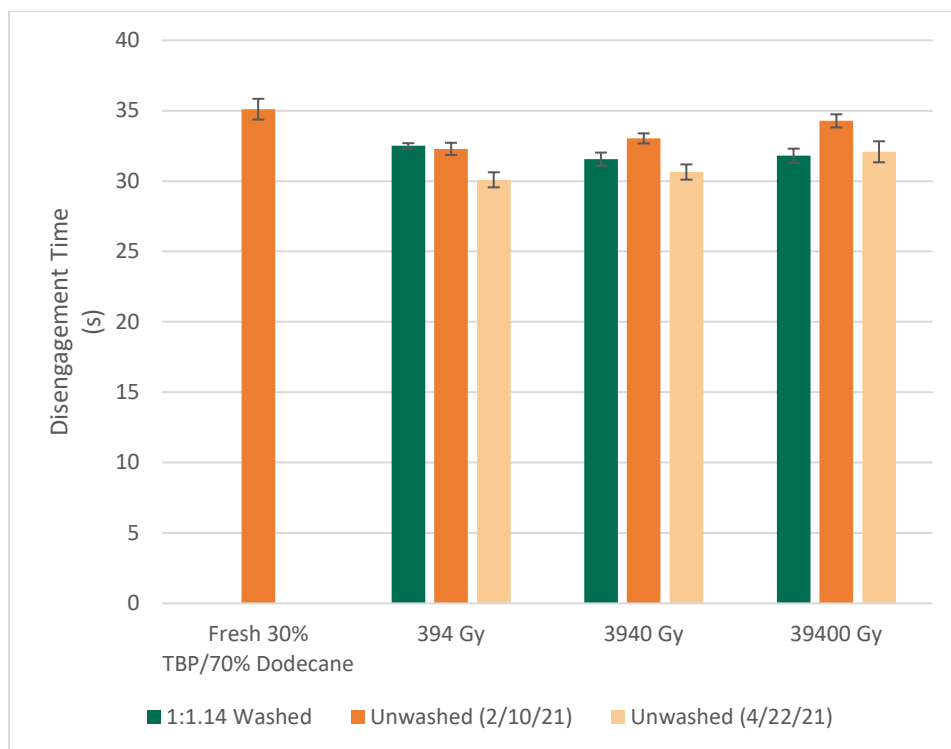
Figure 3-7. Solvent:Carbonate Ratio of 1:1.14 Disengagement Times
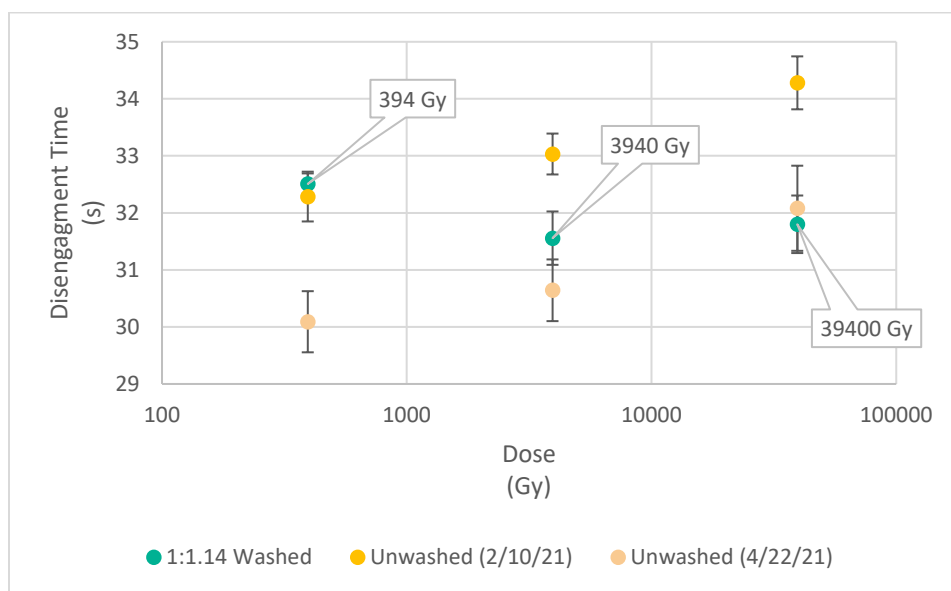
Figure 3-8. Semi-Log Plot of Solvent:Carbonate Ratio of 1:1.14 Disengagement Times

The disengagement time of washed solvent with a solvent:carbonate ratio of 1:1.14 is slightly higher at 349 Gy than at 3,940 Gy (1.0 ± 0.6 s) but is not statistically distinguishable from that at 39,400 Gy. Additionally, the disengagement time of the washed solvent at all doses is within the margin of uncertainty for that of the unwashed solvent for one of the two measurements made. Therefore, no significant impact from the washing process on disengagement time is discernable.

3.3 <u>Solvent:Carbonate Ratio of 1:0.5</u>

Since the proposed solvent:carbonate ratio of 1:1.14 was effective at removing DBP below detectable limits but may cause a negative impact on IT, a reduced proportion of carbonate to solvent at a solvent:carbonate ratio of 1:0.5 was evaluated to determine if it would still be effective at removing DBP while reducing any potential negative impact on IT.

3.3.1 DBP Concentration

DBP was not detectable in the solvent at any dose evaluated. This is shown with the associated uncertainty in Table 3-7.

Table 3-7. DBP Concentrations of Solvent:Carbonate Ratio of 1:0.5

Solvent	DBP Concentration (ppm, μg/g)
394 Gy	0
3,940 Gy	0
39,400 Gy	0

*DBP concentration uncertainty is ± 5 ppm at a 95% confidence interval for all doses.

These results indicate that a reduced proportion of 4 wt% Na_2CO_3 will remain effective at removing the significant amount of DBP generated from the process.

3.3.2 Interfacial Tension

The interfacial tensions with a solvent:carbonate ratio of 1:0.5 are shown in Table 3-8 and represented with the ITs of unwashed solvent in Figure 3-9 below. Also included is the measured interfacial tension of fresh (non-acid contacted and unirradiated) solvent and washed solvent at the proposed solvent:carbonate ratio of 1:1.14 for comparison.

Table 3-8. Interfacial Tensions of Solvent:Carbonate Ratio of 1:0.5

Solvent	Interfacial Tension ± 95% Uncertainty (dyne/cm)
Fresh Solvent	7.1 ± 0.4
394 Gy	7.1 ± 0.5
3,940 Gy	6.8 ± 0.4
39,400 Gy	5.5 ± 0.4

Figure 3-9. Solvent:Carbonate Ratio of 1:0.5 Interfacial Tension

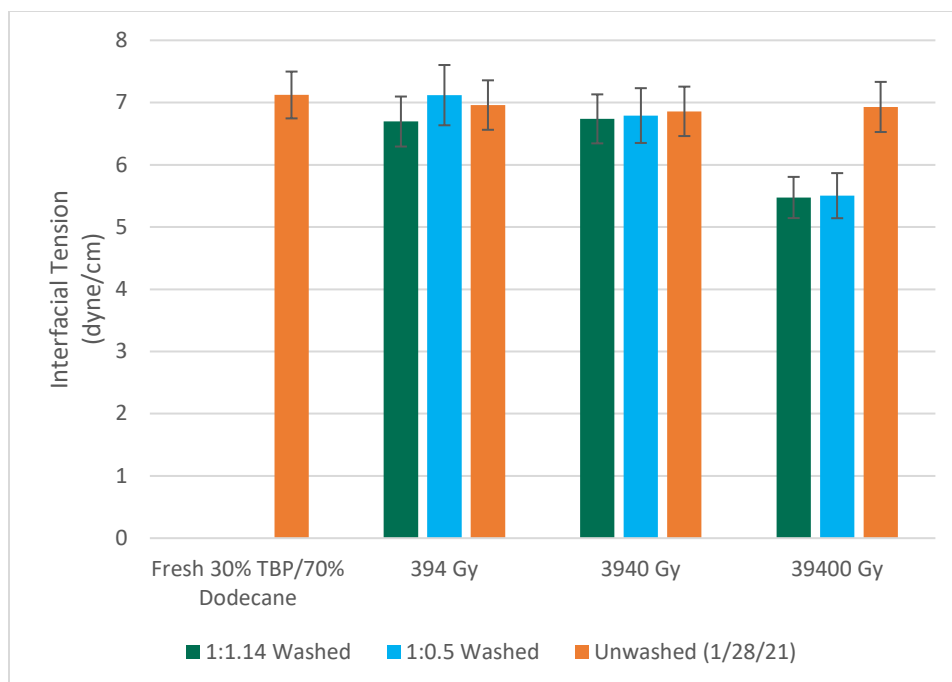The IT with a solvent:carbonate ratio of 1:0.5 is not statistically distinguishable at any radiation dose evaluated from that at the proposed ratio of 1:1.14 and does not appear to provide any advantage or disadvantage with respect to improving IT. For all doses, the IT is above the minimum recommendation of 3 dyne/cm. Similar to the IT with the proposed ratio, the IT at 1:0.5 is within the margin of uncertainty to that of fresh solvent at 394 Gy and 3,940 Gy but is distinguishably lower at the highest dose evaluated of 39,400 Gy.

3.3.3 Disengagement Time

The disengagement times of the solvent:carbonate ratio of 1:0.5 are shown in Table 3-9 and represented with the disengagement times of unwashed solvent and washed solvent at the proposed solvent:carbonate ratio of 1:1.14 for comparison in Figure 3-10 and Figure 3-11 below.

Table 3-9. Disengagement Times of Solvent:Carbonate Ratio of 1:0.5

Solvent	Disengagement Time ± 95% Uncertainty (s)
394 Gy	33.0 ± 0.4
3,940 Gy	33.5 ± 0.7
39,400 Gy	34.9 ± 0.9
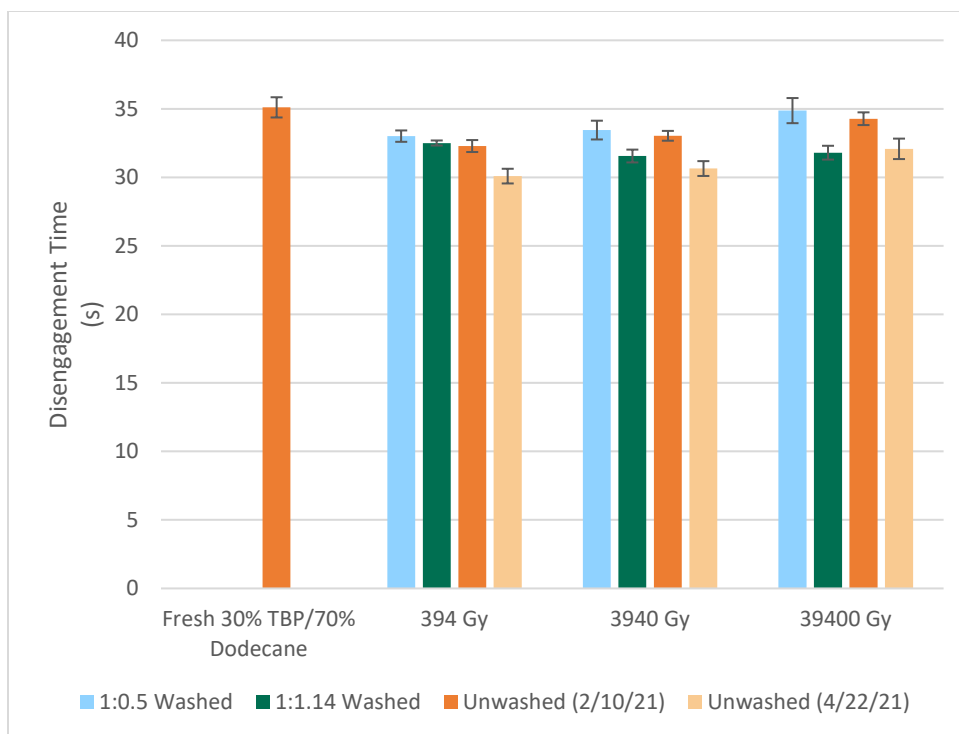
Figure 3-10. Solvent:Carbonate Ratio of 1:0.5 Disengagement Times
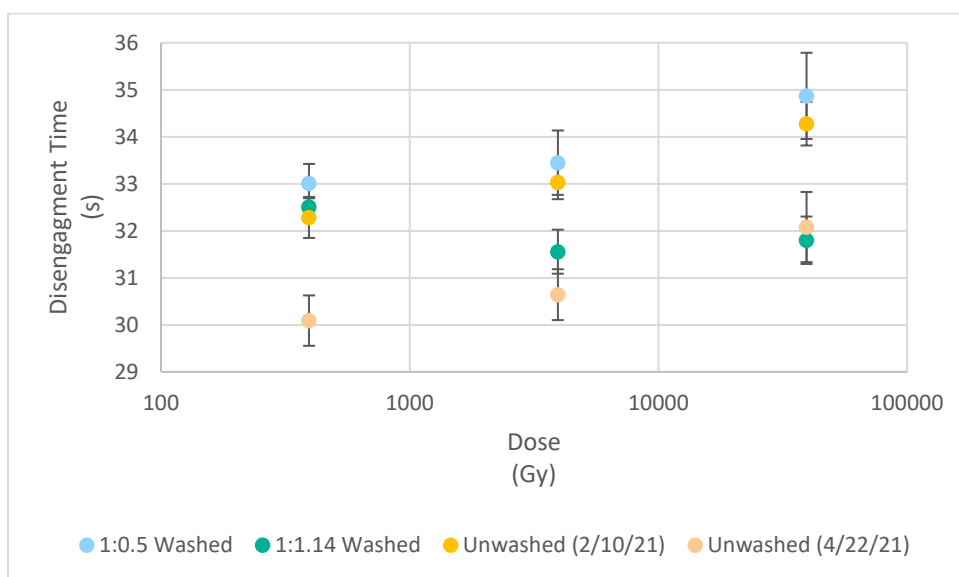
Figure 3-11. Semi-Log Plot of Solvent:Carbonate Ratio of 1:0.5 Disengagement Times

The disengagement time of washed solvent with a solvent:carbonate ratio of 1:0.5 is not statistically distinguishable from that of unwashed solvent (2/10/21) and washed solvent at the proposed solvent:carbonate ratio of 1:1.14 at 394 Gy. The disengagement times with a solvent:carbonate ratio of 1:0.5 at 3,940 Gy and 39,400 Gy are within the margin of uncertainty of unwashed solvent (2/10/21) as well but are slightly higher than those with the proposed ratio of 1:1.14, although the differences are not significant. These results indicate that reducing the solvent:carbonate ratio to 1:0.5 did not distinguishably improve disengagement time and provides no advantage with respect to doing so.

4.0 Conclusions

This work indicates that a significant amount of DBP will be generated in Niowave's process PUREX solvent. The DBP should be removed to maximize U recovery efficiency. Niowave's proposed solvent washing process was demonstrated to effectively remove DBP below detectable limits. This supports the need for Niowave to frequently or continuously wash the process solvent to keep U process losses manageable.

The interfacial tension of representative unwashed solvent was found to be acceptable at all radiation doses evaluated and statistically indistinguishable from the interfacial tension of fresh solvent. This is promising because carbonate washing does not remove degradation products that are represented by lower interfacial tension. The proposed solvent:carbonate ratio was found to have no discernable impact on interfacial tension at 394 Gy or 3,940 Gy but caused a reduction in interfacial tension at 39,400 Gy. This could indicate that the washing process itself may have a negative impact on the interfacial tension of the process solvent after many cycles.

The disengagement time of unwashed solvent was surprisingly found to be slightly improved (i.e., lower) relative to that of fresh solvent. The washed solvent disengagement time was not found to be discernably improved or reduced at any radiation dose evaluated.

A reduced ratio of carbonate to solvent was evaluated with a solvent:carbonate ratio of 1:0.5. This was also found to effectively remove DBP below detectable limits. However, this resulted in no discernable improvement in interfacial tension or disengagement time relative to the proposed ratio.

5.0 Recommendations

Niowave may consider reducing the ratio of carbonate to solvent. Although this was not found to provide any significant advantage or disadvantage in solvent quality, it could allow them to reduce the volume of the carbonate tank and the volume of waste per carbonate discard.

Niowave should frequently monitor the quality of the washed solvent. Accumulation of DBP may indicate that the carbonate solution is at or approaching the end of its life while declining IT may indicate that the solvent should be treated with alumina or replaced. Additionally, Niowave should monitor the carbonate and acid wash solutions for total alpha and beta-gamma activity. Activity limits should be established. After these are exceeded, the solutions should be changed out. Finally, Niowave should monitor the carbonate alkalinity and acid wash free acid. Similarly, limits should be established for these and after the solutions are depleted below these limits they should be changed out.

Further experiments may be useful to better understand the impact of many recycles on solvent quality. This was explored by evaluating 10x and 100x the anticipated single pass radiation dose, however, the impact of frequent contact with 3 M HNO$_3$ is not represented. Additionally, the impact of recycling the carbonate on washing efficacy could be evaluated.

6.0 References

[1]   "American Medical Isotopes Production Act of 2011," ed: S.99, 112th Congress, 1st Session, 2011.

[2]   (2021). *Niowave*. Available: https://www.niowaveinc.com/

[3]   D. J. Reif and J. H. Gray, "Good Solvent Criteria (U)," Savannah River Laboratory, WSRC-RP-91-477, 1991.

[4]   O. K. Tallent, J. C. Mailen, and K. D. Pannell, "PUREX Diluent Degradation," Oak Ridge National Laboratory, ORNL/TM-8814, 1984.

[5]   H. E. Shook, "Solvent Degradation Products in Nuclear Fuel Processing Solvents," Savannah River Laboratory, DP-1759, 1988.

[6]   D. J. Reif and H. E. Shook, "Solvent Dedgradation and Cleanup in Reprocessing Reactor Fuel and Target Elements," Savannah River Laboratory, DPST-84-749, 1984.

[7]   M. S. Mills, C. G. Verst, and T. S. Rudisill, "Evaluation of Proposed Solvent Washing Approach for NIOWAVE's Uranium Recovery Solvent Extraction Process," Savannah River National Laboratory, SRNL-L6100-2020-00028, 2020.

[8]   M. S. Mills and T. S. Rudisill, "Proposed R&D Directions for Solvent Washing Experiments," Savannah River National Laboratory, SRNL-L6100-2021-00008, Rev. 0, 2021.

[9]   D. J. Reif, "Solvent Quality Test," Savannah River Laboratory, DPST-85-877, 1985.

Appendix A. Supplemental Information and Data

Uncertainty

Uncertainties associated with calculated quantities are determined using the root sum of squares (RSS), shown in the following equation.

$$u_Y = \sqrt{\sum_{i=1}^{i=N}\left(u_{x_i}\frac{\partial Y}{\partial x_i}\right)^2} \qquad (4)$$

Where,

u_Y = Total uncertainty associated with variable Y, units of Y
u_{x_i} = Uncertainty associated with variable x_i, units of x_i
x_i = Variable of which Y is a function

The random uncertainty associated with a variable is quantified using a 95% confidence interval. For small repetitions of measurements (i.e., less than 30), a t-test is used to determine the confidence interval which is calculated using the "CONFIDENCE.T" function in Microsoft Excel.

The total uncertainty associated with a measured variable is determine by calculating the RSS of the random uncertainty and equipment uncertainty, shown in the Equation below.

$$u_T = \sqrt{u_E{}^2 + u_R{}^2} \qquad (5)$$

Where,

u_T = Total uncertainty
u_E = Uncertainty associated with equipment (systematic uncertainty)
u_R = Random uncertainty (statistical uncertainty)

Equipment

The following equipment was used to determine solution densities, IT drop volumes, and disengagement times.

Equipment	Model	Accuracy	Density	IT Drop Volume	Disengagement Time
Balance	Mettler Toledo MS304S	$u_m = \pm\ 0.0002$ g	x		
Electronic Pipette	Rainin E4 XLS 1000 μL	$u_v = \pm\ 0.008$ mL	x		
Syringe Pump*	KD Scientific 101	$u_F = \pm\ 0.005$ mL/hr		x	
Stopwatch*	Std. iPhone Stopwatch	$u_v = \pm\ 0.005$ s		x	x

* Manufacturers accuracy was not determined. These are assumed to be limited by display resolution. The balance and pipette accuracies are provided by the manufacturers.

Densities

Densities were measured by weighing 1.000 mL of solution for several repetitions. Density is calculated by the following equation.

$$\rho = \frac{m}{V} \qquad (6)$$

Where,

ρ = The calculated density, g/mL
m = Mass measured by analytical balance, g
V = Volume of material as measured by an electronic pipette, mL (This was always 1 mL)

Table A-1. Densities of Non-Solvent Solutions

Solution	Density ± 95% Uncertainty (g/mL)
Stock DBP	1.075 ± 0.010
Stock Dodecane	0.754 ± 0.006
1950 µg DBP/mL Standard	0.759 ± 0.006
100.8 µg DBP/mL Standard (1/20/21)	0.757 ± 0.006
100.8 µg DBP/mL Standard (4/26/21)	0.747 ± 0.008
4 wt% Na_2CO_3 (1/28/21)	1.050 ± 0.010
4 wt% Na_2CO_3 (2/10/21)	1.045 ± 0.009
4 wt% Na_2CO_3 (4/22/21)	1.043 ± 0.011
0.1 M HNO_3	1.01 ± 0.009

Table A-2. Densities of Unirradiated and Irradiated Unwashed Solvents

Solution	Density ± 95% Uncertainty (g/mL)
Fresh 30% TBP/70% Dodecane*	0.824 ± 0.007
Acid Contacted Unwashed*	0.844 ± 0.008
394 Gy Unwashed (1/20/21)	0.839 ± 0.007
394 Gy Unwashed (4/22/21)	0.842 ± 0.007
3940 Gy Unwashed (1/20/21)	0.841 ± 0.007
3940 Gy Unwashed (4/22/21)	0.841 ± 0.007
39400 Gy Unwashed (1/20/21)	0.842 ± 0.007
39400 Gy Unwashed (4/22/21)	0.838 ± 0.007

*Unirradiated

Table A-3. Solvent:Na_2CO_3 Ratio of 1:1.14 Densities

Solution	Density ± 95% Uncertainty (g/mL)
394 Gy	0.824 ± 0.007
3940 Gy	0.822 ± 0.007
39400 Gy	0.824 ± 0.007

Table A-4. Solvent:Na_2CO_3 Ratio of 1:0.5 Densities

Solution	Density ± 95% Uncertainty (g/mL)
394 Gy	0.816 ± 0.010
3940 Gy	0.818 ± 0.009
39400 Gy	0.822 ± 0.009

Interfacial Tension - Drop Volumes

Table A-5. Unwashed Solvents IT Drop Volumes

Solution	Drop Volume ± 95% Uncertainty (mL)
Fresh 30% TBP/70% Dodecane*	0.01109 ± 0.00009
Acid Contacted Unwashed*	0.01158 ± 0.00019
394 Gy Unwashed	0.01161 ± 0.00007
3940 Gy Unwashed	0.01155 ± 0.00010
39400 Gy Unwashed	0.01169 ± 0.00010

*Unirradiated

Table A-6. Solvent:Na_2CO_3 Ratio of 1:1.14 IT Drop Volumes

Solution	Drop Volume ± 95% Uncertainty (mL)
394 Gy	0.01077 ± 0.00012
3940 Gy	0.01075 ± 0.00004
39400 Gy	0.00886 ± 0.00011

Table A-7. Solvent:Na_2CO_3 Ratio of 1:0.5 IT Drop Volumes

Solution	Drop Volume ± 95% Uncertainty (mL)
394 Gy	0.01106 ± 0.00012
3940 Gy	0.01064 ± 0.00006
39400 Gy	0.00884 ± 0.00005

Distribution

kristine.zeigler@srnl.doe.gov
jonathan.duffey@srnl.doe.gov
gene.daniel@srnl.doe.gov
harris.eldridge@srnl.doe.gov
jarrod.gogolski@srnl.doe.gov
eddie.kyser@srnl.doe.gov
betty.mealer@srnl.doe.gov
tracy.rudisill@srnl.doe.gov
douglas.lowry@srnl.doe.gov
matthew.mills@srnl.doe.gov
james.klein@srnl.doe.gov
anita.poore@srnl.doe.gov
fernando.fondeur@srnl.doe.gov
nicholas.karay@srnl.doe.gov
robert.pierce@srnl.doe.gov
thomas.shehee@srnl.doe.gov
christopher.verst@srnl.doe.gov
Records Administration (EDWS)