

# Fission Product Decontamination Factors for Plutonium Separated by PUREX from a Low-Burnup, Fast-Neutron Irradiated Depleted UO<sub>2</sub>

Paul M. Mendoza<sup>a,b</sup>, Sunil S. Chirayath<sup>a,b,\*</sup>, Charles M. Folden III<sup>c</sup>

<sup>a</sup>Nuclear Security Science & Policy Institute (NSSPI)

<sup>b</sup>TAMU Department of Nuclear Engineering

<sup>c</sup>Cyclotron Institute

Texas A&M University, College Station, Texas 77840

---

## Abstract

Experimental investigations to determine fission product separation from actinides (U and Pu) while employing the Plutonium Uranium Recovery by Extraction (PUREX) process to purify plutonium produced in a fast neutron irradiated depleted uranium dioxide (DUO<sub>2</sub>) target were conducted. The sample was a DUO<sub>2</sub> surrogate pellet (0.256 wt% <sup>235</sup>U) irradiated to a low-burnup ( $4.43 \pm 0.31$  GWd/tHM) that was PUREX processed 538 days after neutron irradiation. Decontamination factors (DF) for the elements U, Mo, Ru, Ce, Sm, Sr, Pm, Eu, Nd, Pd, and Cd were measured in two experiments using 30 vol.% tri-n-butyl phosphate in a kerosene diluent. The first experiment characterized Pu DFs for a single contact extraction and back-extraction, while the second experiment had multiple contacts with the goal of achieving greater Pu recovery. The benchtop scale PUREX process had overall Pu recoveries of  $(83 \pm 9)\%$  and  $(99.7 \pm 4.2)\%$  for the first and second experiments, respectively.

*Keywords:* PUREX, Decontamination Factor, Depleted Uranium

---

## 1. Introduction

*Background.* In a recent publication, our group suggested that investigation of trace contaminants in plutonium recovered using the Plutonium Uranium Recovery by Extraction (PUREX) could give indications of material origins, but that a broad

---

\*Corresponding author

Email address: sunilsc@tamu.edu (Sunil S. Chirayath)

5 study of many elements would be necessary (Chirayath 2015). Descriptions of  
various PUREX processes are provided in many sources with explanations of  
chemistry including flow sheets and decontamination factors (DFs) (Lanham 1950,  
Arker 1954, Chandler 1954, Reas 1957, Stoller 1961, Benedict 1982). These sources  
generally report overall beta or gamma DFs of up to  $10^8$  with Pu recoveries of  
10 99.7% for industrial scale reprocessing facilities. While distribution coefficients  
(DC) for the various process steps of PUREX have been previously reported,  
details about elemental DFs for PUREX cycles have been largely limited to the  
major activity contributors, such as  $^{106}\text{Ru}$  and  $^{95}\text{Zr}$  (Stoller 1961). A compilation of  
distribution data for PUREX extraction processes provide data for U, Th, and Pu  
15 in a variety of concentrations (Prout 1957). DCs for Zr, rare earth metals, Pu, and  
Th are also available (Alcock 1957, Best 1957, Hesford 1957, Scargill 1957, Alcock  
1958, Best 1959, Hesford 1959). Additionally, Ga has been studied for separation  
(Collins 2000) because it is a common contaminant in weapons-grade Pu.

Although a DC, coupled with process information, can be used to calculate a  
20 reasonable estimate of DF (Colburn 1939, Sherwood 1952, Long 1967, Perry  
2008), variability of DCs under different system conditions give rise to uncertainty  
in calculated results. For example, DCs between tri-n-butyl phosphate (TBP) and  
nitric acid ( $\text{HNO}_3$ ) have been reported for U, Pu, Zr, Nb, Ru, and the rare earth  
elements, but vary with  $\text{HNO}_3$  concentration and U saturation in TBP (Sherwood  
25 1952, Stoller 1961). These sources also derive mathematical correlations between  
DC and DF, but experimental PUREX DFs for a large number of individual  
elements were not provided.

In the current work, 12.9 mg of depleted uranium dioxide (DUO<sub>2</sub>) was irradiated in a pseudo-fast neutron spectrum at the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory. The DUO<sub>2</sub> pellet, containing FP and Pu, was dissolved in HNO<sub>3</sub> and subjected to two different PUREX experiments for DF characterization and Pu product recovery. Aqueous solutions were analyzed at each step with Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The experimental work used benchtop scale methods to isolate a large fraction of Pu, measure DFs for FPs, and measure overall gamma DFs as part of a larger project to develop forensic radioanalytical capabilities at Texas A&M University.

*Terminology.* A DC is defined as the concentration ratio between the organic (org) and aqueous (aq) phases as shown in Equation 1, and describes the equilibrium distribution of a species in the system during PUREX separation processes (Benedict 1982):

$$DC = \frac{c_{org}}{c_{aq}} \quad (1)$$

where c is the concentration of the specific species in the indicated phase. DCs are specific to an element and vary widely with the concentration and temperature of the solvents. They are also affected by saturation of U and Pu in the system and, in some cases, time since solution preparation (Stoller 1961, Simpson 2010). For PUREX, the fraction of mass,  $f_{org}$ , deposited in the organic (TBP) phase for a

single element, assuming a volume ratio between the aqueous and organic phases,  $V_R$ , is given by Equation 2.

50

$$f_{org} = (1 + DC^{-1}V_R^{-1})^{-1} \quad (2)$$

This is termed “extraction”, where a desired solute is extracted out of an aqueous solution through contact with an immiscible liquid phase. Ideally, a large fraction of desired solutes are extracted into the organic phase, while a small fraction of undesired solutes are left in the aqueous phase. Conversely, “back-  
55 extraction” is the process by which a desired solute is extracted out of an organic solution through contact with an immiscible aqueous solution. “Scrubbing” occurs to transfer a large fraction of impurities to a second phase while having a minimal transfer of desired constituent.

After several cycles of Pu extraction/scrubbing/back-extraction are complete,  
60 the measured effectiveness of a PUREX cycle is described by the DF, which is fundamentally determined by DCs and measure the effectiveness with which a contaminant,  $j$ , is removed from a product. The product of interest in this work is Pu, and the DF is defined by Equation 3.

$$DF_j = \frac{\frac{c_j}{c_{Pu}}|_{initial}}{\frac{c_j}{c_{Pu}}|_{final}} \quad (3)$$

65 Initial and final refer to the values before and after purification, respectively.  
DFs are also characteristic of different process cycles, and may have larger values (  
> 10<sup>7</sup>) for industrial scale PUREX compared to the benchtop scale version  
presented here (Stoller 1961, Benedict 1982).

Industrial processes report either an overall DF value, or a DF value for a  
70 single isotope. What is needed for forensics purposes is DFs for individual FP  
contaminants, which is why elemental DF values were obtained for a benchtop  
scale PUREX process performed on a DUO<sub>2</sub> surrogate sample.

## 2. Experiment

A commercially acquired pellet containing  $12.9 \pm 0.1$  mg of DUO<sub>2</sub> was  
75 irradiated over the course of three months with two shutdown periods in the  
HFIR. The final burnup was  $4.43 \pm 0.31$  GWd/tHM (Swinney 2015) and was  
determined by measuring the <sup>137</sup>Cs activity. The irradiation produced an ICP-MS  
measured  $0.237 \pm 0.008$  mg of Pu. After the short lived radioisotopes had  
opportunity to decay, the irradiated pellet was shipped to Texas A&M University.

80 The kerosene and TBP (>99%) used for these experiments were acquired  
from Alfa Aesar (Haverhill, MA, USA), NaNO<sub>2</sub> was acquired from Aldrich  
Chemistry (St. Louis, MO, USA), 69% nitric acid was acquired from Mallinckrodt  
Chemicals (St. Louis, MO, USA), and iron sulfamate (40.26%) was acquired from  
Strem Chemicals (Newburyport, MA, USA).

85 The pellet, both prior to dissolution and after, was counted with a Canberra  
HPGe detector model number CC4018 which was connected to a Canberra Lynx  
multichannel analyzer (Canberra 2013, Zakrzewski 2013). Canberra's software

package GENIE-2000 version 3.2.1 (Canberra 2013) was used to collect spectra while the samples were inside a lead tomb. The same detector was used to count  
90 the various process solutions. Inductively coupled plasma mass spectrometry (ICP-MS) was also conducted for aqueous samples using a PerkinElmer NexION 300X quadrupole ICP-MS (PerkinElmer 2009).

Samples of the pellet were prepared as described below. The sample was added to a round-bottom flask and 5.0 ml of 8 M HNO<sub>3</sub> was added to the flask,  
95 which was heated to 50 °C with constant 100 rpm stirring for 2 hr. This solution will be referred to as the “dissolution solution”. The flask was connected to a cold trap with the help of Schlenk line. The fission product gases such as H<sub>2</sub>, CO<sub>2</sub>, Kr, Br, I and N<sub>2</sub>O were captured in a cold trap containing molecular sieves that were chilled by liquid nitrogen. In order to reduce the amount of activity per sample,  
100 500 µl from the dissolution solution was diluted to 5.0 ml and the concentration was changed to 4 M HNO<sub>3</sub>. From this solution, referred to as the “stock solution”, 0.5 ml aliquots, containing ~1% of the pellet, were used in benchtop scale PUREX experiments described in the two subsections below. The total activity concentration of the stock solution was approximately 80 µCi/ml.

105 Experiments started by transferring a 500 µl aliquot of stock solution and 0.5 mg of NaNO<sub>2</sub> to a 15 ml centrifuge tube. The tube was subsequently stirred and covered to retain the resulting NO<sub>2</sub> gas. The solution was left overnight so that Pu(III) was completely oxidized to Pu(IV). During extraction and back-extraction, both experiments had the aqueous and organic phases mixed on a vortex mixer for  
110 15 min at 1500 rpm, after which the two phases were allowed to settle and

separate. The phases were physically separated into two different vials through careful pipetting.

Each extraction and back-extraction mixed organic and aqueous mixtures with unequal volumes. The solution being added always contained an extra 200  $\mu\text{l}$  to  
115 reduce the chance of accidentally pipetting both phases. For example, if TBP were being added to the stock solution described above, 700  $\mu\text{l}$  would be added initially and 500  $\mu\text{l}$  removed. This excess volume will be referred to as hold-up volume in similar fashion to the differential extraction experiment described by Long (Long 1967).

120 *Experiment 1.* The purpose of the first experiment was to quantify product recovery and DF values for a single contact extraction and back-extraction of Pu. U(VI) and Pu(IV) were extracted and decontaminated by contacting the prepared stock solution with a solution of 30 vol.% TBP with a kerosene diluent. After mixing and separation of the two phases, Pu(IV) was reduced to Pu(III) and back-extracted by  
125 contacting the physically separated TBP solution with 0.75 M  $\text{HNO}_3$  in a 0.024 M ferrous sulfamate solution via oxidation of Fe(II). The stock solution both before and after TBP contact, as well as the final solution containing back-extracted Pu, were analyzed with ICP-MS.

*Experiment 2.* The purpose of the second experiment was to extract a large fraction  
130 of Pu. Utilizing the results from the first experiment, it was determined that contacting the prepared stock solution four times with TBP would extract over 90% of the Pu. Therefore, this experiment had four TBP contacts with the prepared stock solution. The four TBP solutions were then collected into a single

vial, and contacted three times with a 4 M  $\text{HNO}_3$  in a 0.024 M ferrous sulfamate  
135 solution. The three contacts were then collected into a single vial.

In order to ensure minimal U back-extraction, the  $\text{HNO}_3$  concentration for  
this experiment was increased to 4 M because higher concentrations reduce the  
degree to which U is back-extracted (Stoller 1961). Three contacts of the ferrous  
sulfamate solution ensured complete back-extraction of Pu, while the higher nitric  
140 acid concentration minimized back-extraction of U. The same solutions as  
described in the first experiment were analyzed with ICP-MS.

The four contact extraction three contact back-extraction process described  
above for the second experiment will be referred to as a cycle. The combined  
ferrous sulfamate solution containing back-extracted Pu underwent a second cycle  
145 to verify the repeatability of the process and for comparison with the first cycle.  
The final solution Pu was reset with the addition of 0.5 mg of  $\text{NaNO}_2$  to convert  
all the Pu(III) to Pu(IV).

### 3. Results

All results are presented for equal contact volumes between aqueous and  
150 organic solutions for both extraction and back extraction. Results are also depicted  
for a zero holdup volume.

The U and Pu recovery after back-extraction for the first and second  
experiments are shown in Table 1. The DCs for U and Pu were determined by  
analyzing the stock solution both before and after extraction for experiment 1.  
155 These were determined to be  $26.7 \pm 2.9$  and  $11.6 \pm 1.1$ , for U and Pu respectfully.



Experiment 2 successfully recovered about 93% of the original Pu with less than 1% of the original U.

Table 1 Recoveries of U and Pu for the different experiments.

	Pu Recovery	$\pm$	U Recovery	$\pm$
Experiment 1	0.834	0.095	0.112	0.013
Experiment 2 Cycle 1	0.997	0.042	0.068	0.003
Experiment 2 Cycle 2	0.930	0.046	0.066	0.003
Overall Experiment 2	0.927	0.060	0.0045	0.0003

160        Approximately 10% of the U in the TBP phase was back extracted with a single contact of 0.75 M HNO<sub>3</sub> in a 0.024 M iron sulfamate solution in experiment 1. Experiment 2 had much smaller U back extraction due to the higher molar concentration of HNO<sub>3</sub> in the back extraction solution (Benedict 1982). This can also led to lower Pu recovery because 4 M HNO<sub>3</sub> much more rapidly oxidizes Fe(II), the agent which reduces Pu, with NO<sub>2</sub><sup>-</sup> than 0.75 M HNO<sub>3</sub> (Stoller 1961).  
165        This is also emphasized in the differences in Pu recovery between cycle 1 and cycle 2 of experiment 2, where cycle 2 back extraction utilized a Fe(II) solution that was a day older.

170        The DF calculations utilized concentration ratios between contaminants that were normalized to the Pu concentration per Equation 3, with the initial solution as the stock solution and the final solution as the back-extracted Pu. Both experiment 1 and experiment 2 first cycle DF values are shown in Table 2. Cycle 2 of experiment 2 is not depicted because of the low signal in the mass spectrometry machine for these samples.

175

Table 2 Decontamination factors for single and multiple contacts PUREX.

Element (Z)	Exp. 1	$\pm$	Exp. 2 C1	$\pm$	Isotopes Used
-------------	--------	-------	-----------	-------	---------------

<b>Rb (37)</b>	39.0	5.9	11.8	0.8	<sup>85</sup> Rb
<b>Sr (38)</b>	282.5	42.5	84.6	5.9	<sup>90</sup> Sr
<b>Mo (42)</b>	5.7	0.8	1.9	0.2	<sup>97,98,100</sup> Mo
<b>Ru (44)</b>	59.2	6.4	16.6	2.5	<sup>101,102,104</sup> Ru
<b>Pd (46)</b>	65.0	14.3	8.9	1.2	<sup>110</sup> Pd
<b>Cd (48)</b>	73.6	17.4	22.1	2.5	<sup>112</sup> Cd
<b>Cs (55)</b>	176.6	28.0	52.9	3.9	<sup>133</sup> Cs
<b>Ce (58)</b>	42.5	16.3	11.5	4.9	<sup>140,142</sup> Ce
<b>Nd (60)</b>	19.2	2.1	5.9	0.4	<sup>143</sup> Nd
<b>Pm (61)</b>	12.8	1.9	3.9	0.3	<sup>147</sup> Pm
<b>Sm (62)</b>	11.5	1.5	3.6	0.3	<sup>151</sup> Sm
<b>Eu (63)</b>	10.0	1.4	3.6	0.3	<sup>154</sup> Eu
<b>U (92)</b>	7.4	1.2	14.7	0.9	<sup>238</sup> U

Exp 2 DF goes down b/c experiment guaranteed for it to go down

180 The common trend is that DF decreases from experiment 1 to experiment 2.  
The major exception is U, which has a higher DF value. This is expected due to the change in HNO<sub>3</sub> concentration in the iron sulfamate solution as discussed above. The rest of the elements have lower DF values because of multiple extraction and back extraction steps.

185 Figure 1 shows theoretical DFs as a function of extraction step and volume ratio. This shows how DF decreases with increasing the number of contacts. Representative DC values corresponding to Pu(IV) and the FPs were chosen to produce Figure 1. The number of contacts decreases DF because less and less product is removed with each extraction, while the amount of contaminant  
190 removed is approximately equal.

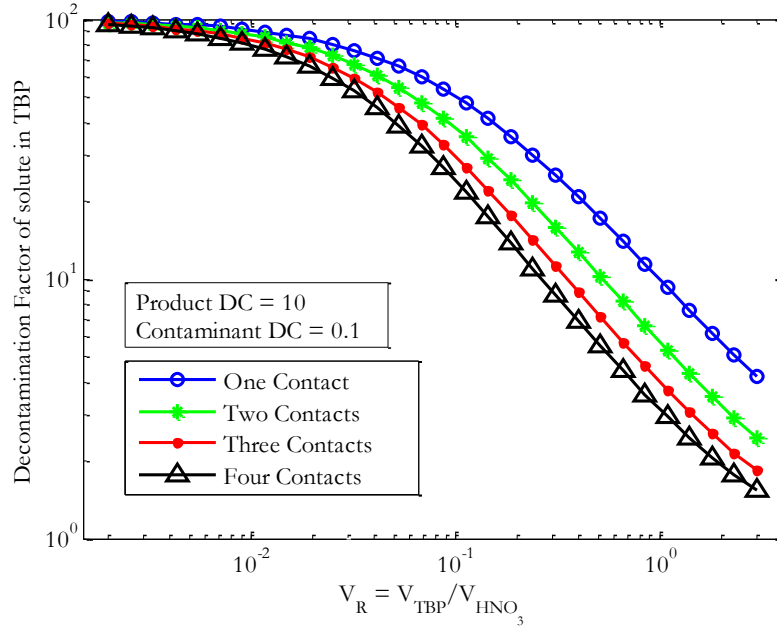


Figure 1 DFs as a function of volume ratios for the first to fourth contact in TBP.

#### 4. Conclusions

Two PUREX experiments were conducted. The first experiment determined DC values for U, Pu, and several FPs. The second experiment utilized these values to recover over 92% of the Pu while recovering less than 1% of the U. Overall U and Pu recovery for experiment 1 were  $(11.2 \pm 1.3)\%$  and  $(83.4 \pm 9.5)\%$  while the same values for experiment 2 cycle 1 were  $(6.8 \pm 0.3)\%$  and  $(99.7 \pm 4.2)\%$ . DF values for  $^{133}\text{Cs}$  were determined to be  $(176.6 \pm 28.0)\%$  and  $(52.9 \pm 3.9)\%$  for experiment 1 and experiment 2 cycle 1 respectively. DF values were lower than industrial scale PUREX plants due to multiple extraction and back extraction steps without an intermittent scrubbing step. Future experiments will utilize a scrubbing stage in the PUREX process.

## References

- 205 Alcock, K., F. Bedford, W. Hardwick and H. McKay (1957). "Tri-n-butyl phosphate as an extracting solvent for inorganic nitrates—I: Zirconium nitrate." Journal of Inorganic and Nuclear Chemistry 4(2): 100-105.
- 210 Alcock, K., G. Best, E. Hesford and H. McKay (1958). "Tri-n-butyl phosphate as an extracting solvent for inorganic nitrates—V: Further results for the tetra- and hexavalent actinide nitrates." Journal of Inorganic and Nuclear Chemistry 6(4): 328-333.
- Arker, A. J. (1954). "Terminal Report on Purex Program in KAPL Separations Pilot Plant." Knolls Atomic Power Laboratory.
- 215 Benedict, M., H. Levi and T. Pigford (1982). "Nuclear chemical engineering." Nucl. Sci. Eng. 82(4).
- Best, G., E. Hesford and H. McKay (1959). "Tri-n-butyl phosphate as an extracting agent for inorganic nitrates-VII: The trivalent actinide nitrates." Journal of Inorganic and Nuclear Chemistry 12(1): 136-140.
- 220 Best, G., H. McKay and P. Woodgate (1957). "Tri-n-butyl phosphate as an extracting solvent for inorganic nitrates—III The plutonium nitrates." Journal of Inorganic and Nuclear Chemistry 4(5): 315-320.
- Canberra. (2013). "Genie 2000 Basic Spectroscopy Software." Retrieved 4/6/2016, from
- 225 [http://www.canberra.com/products/radiochemistry\\_lab/pdf/G2K-BasicSpect-SS-C40220.pdf](http://www.canberra.com/products/radiochemistry_lab/pdf/G2K-BasicSpect-SS-C40220.pdf).
- Canberra. (2013). "Standard Electrode Coaxial Ge Detectors (SEGe)." Retrieved 4/6/2016, from
- 230 <http://www.canberra.com/products/detectors/pdf/SEGe-detectors-C40021.pdf>.
- Chandler, D. O. D. a. J. M. (1954). "Terminal Report for the ORNL Pilot Plant Investigation of the Purex Process." Oak Ridge National Laboratory USAEC Report ORNL -1519.
- 235 Chirayath, S. S., J. M. Osborn and T. M. Coles (2015). "Trace Fission Product Ratios for Nuclear Forensics Attribution of Weapons-Grade Plutonium from Fast and Thermal Reactors." Science & Global Security 23(1): 48-67.
- Colburn, A. P. (1939). "Simplified calculation of diffusional processes." general consideration of two-film resistances 35: 211-236.
- 240 Hesford, E., E. Jackson and H. McKay (1959). "Tri-n-butyl phosphate as an extracting agent for inorganic nitrates—VI Further results for the rare earth nitrates." Journal of Inorganic and Nuclear Chemistry 9(3-4): 279-289.
- 245 Hesford, E., H. McKay and D. Scargill (1957). "Tri-n-butyl phosphate as an extracting solvent for inorganic nitrates—IV Thorium nitrate." Journal of Inorganic and Nuclear Chemistry 4(5): 321-325.

- Lanham, W. B. and A. T. Gresky (1950). "Purex Process Laboratory Development." Oak Ridge National Laboratory USAEC Report ORNL-717.
- 250 Long, J. T. (1967). Engineering for nuclear fuel reprocessing, New York : Gordon and Breach Science Publishers, [1967].
- PerkinElmer. (2009). "PerkinElmer NexION 300X quadrupole ICP-MS." Retrieved 4/6/2016, from  
 255 [https://partners.perkinelmer.com/Content/DealerSalesInfo/Product%20Lines/Inorganic/ICP-MS/Brochures/NexION%20300%20BRO\\_DEF.pdf](https://partners.perkinelmer.com/Content/DealerSalesInfo/Product%20Lines/Inorganic/ICP-MS/Brochures/NexION%20300%20BRO_DEF.pdf).
- Perry, R. H. and D. W. Green (2008). Perry's chemical engineers' handbook, 8th ed, New York : McGraw-Hill, [2008]. 8th ed. / prepared by a staff of specialists under the editorial direction of editor-in-chief, Don W. Green, late editor, Robert H. Perry.
- 260 Prout, W. (1957). Equilibrium Distribution Data for PUREX and Similar Extraction Processes.
- Reas, W. (1957). The PUREX Process-A Solvent Extraction Reprocessing Method For Irradiated Uranium.
- 265 Scargill, D., K. Alcock, J. Fletcher, E. Hesford and H. McKay (1957). "Tri-n-butyl phosphate as an extracting solvent for inorganic nitrates—II Yttrium and the lower lanthanide nitrates." Journal of Inorganic and Nuclear Chemistry 4(5): 304-314.
- Sherwood, T. K. and R. L. Pigford (1952). Absorption and extraction, 2d ed,  
 270 New York : McGraw-Hill, 1952.
- Simpson, F. M. and D. J. Law (2010). Nuclear Fuel Reprocessing - INL/EXT-10-17753, Idaho National Laboratory (INL). Sponsoring Organization: DOE - NE.
- Stoller, S. and R. Richards (1961). "Reactor Handbook, Volume II, Fuel Reprocessing." Inter science Publishers, Inc., New York.
- 275 Swinney, M. (2015). Experimental and Computational Assessment of Trace Nuclide Ratios in Weapons Grade Plutonium for Nuclear Forensics Analysis. Doctor of Philosophy, Texas A&M University.
- Zakrzewski, B. and V. Jordanov (2013). "Versatility of Modern Digital Signal Processing: LYNX® - A Platform for Global Spectroscopy Applications." Digital Nuclear Spectroscopy: 87.
- 280