Fission Product Decontamination Factors for Plutonium Separated by PUREX from a Low-Burnup, Fast-Neutron Irradiated Depleted UO2

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**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 (DUO2) target were conducted. The sample was a DUO2 pellet (0.256 wt% 235U) irradiated to a low-burnup (4.43 ± 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 (TBP) in a kerosene diluent. The first experiment characterized Pu DFs for a single stage extraction and back-extraction, while the second experiment had multiple stages with the goal of achieving greater Pu recovery. The benchtop scale PUREX process had overall Pu recoveries of (83 ± 9)% and (99.7 ± 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) process could give indications of material origins, but that a broad 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, Darby 1954, Irish 1957, Stoller 1961, Benedict 1982). These sources generally report overall beta or gamma DFs of up to 108 with Pu recoveries of 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 106Ru and 95Zr (Stoller 1961). A compilation of distribution data for PUREX extraction processes provides data for U, Th, and Pu in a variety of concentrations (Siddall 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 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 (HNO3) have been reported for U, Pu, Zr, Nb, Ru, and the rare earth elements, but vary with HNO3 concentration and U saturation in TBP (Sherwood 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 (DUO2) was irradiated in a pseudo-fast neutron spectrum at the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory (Swinney 2014). The DUO2 pellet, containing fission products (FPs) and Pu, was dissolved in HNO3 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):

Equation 1

|  |  |  |
| --- | --- | --- |
|  |  | (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, , deposited in the organic (TBP) phase for a single element, assuming a volume ratio between the aqueous and organic phases, , is given by Equation 2.

Equation 2

|  |  |  |
| --- | --- | --- |
|  |  | (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 extracted. Conversely, “back-extraction” is the process by which a desired solute is extracted out of an organic solution through contact with an immiscible aqueous solution. Both extraction and back-extraction will also be termed “stage”, where mass transfer occurs between two sufficiently mixed immiscible liquid phases. “Scrubbing” is the transfer of 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, the measured effectiveness of a PUREX cycle is described by the DF, which is ideally determined by DCs and measure the effectiveness with which a contaminant, , is removed from a product. The product of interest in this work is Pu, and the DF is defined by Equation 3.

Equation 3

|  |  |  |
| --- | --- | --- |
|  |  | (3) |

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 (> 107) for industrial scale PUREX compared to the benchtop scale version presented here because of an additional scrubbing step as well as a larger number of stages (Stoller 1961, Benedict 1982).

Industrial processes often report either an overall DF value, or a DF value for a 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 DUO2 sample.

1. **Experiment**

A commercially acquired pellet containing 12.9 ± 0.1 mg of DUO2 was irradiated over the course of three months with two shutdown periods in the HFIR. The final burnup was 4.43 ± 0.31 GWd/tHM (Swinney 2015) and was determined by measuring the 137Cs activity. The irradiation produced 0.24 ± 0.01 mg of Pu as measured by ICP-MS. After the short-lived radioisotopes had opportunity to decay, the irradiated pellet was shipped to Texas A&M University.

The kerosene and TBP (>99%) used for these experiments were acquired from Alfa Aesar (Haverhill, Massachusetts, USA), NaNO2 was acquired from Aldrich Chemistry (St. Louis, Missouri, USA), 69% nitric acid was acquired from Mallinckrodt Chemicals (St. Louis, Missouri, USA), and iron sulfamate (40.26%) was acquired from Strem Chemicals (Newburyport, Massachusetts, USA).

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 (Zakrzewski 2013, Canberra 2013a). Canberra’s software package GENIE-2000 version 3.2.1 (Canberra 2013b) was used to collect spectra while the samples were inside a lead tomb. The same detector was used to count 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 HNO3 was added to the flask, 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 H2, CO2, Kr, Br2, I2 and N2O were captured in the cold trap containing molecular sieves that were chilled by liquid nitrogen. In order to reduce the amount of activity per sample, 500 μl from the dissolution solution was diluted to 5.0 ml and the concentration was changed to 4 M HNO3. 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.

The “working” solution was prepared by transferring a 500 μl aliquot of stock solution and 0.5 mg of NaNO2 to a 15 ml centrifuge tube. The tube was subsequently stirred and covered to retain the resulting NO2 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 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.

Each extraction and back-extraction mixed organic and aqueous solutions with unequal volumes. The solution being added always contained an extra 200 μl to reduce the chance of accidentally pipetting both phases. For example, if TBP were being added to the working solution described above, 700 μl would be added initially and 500 μl 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). All results presented below have been corrected to those that would be expected for equal volumes between aqueous and organic solutions during both extraction and back-extraction. Results are also corrected to zero hold-up volume.

*Experiment 1.* The purpose of the first experiment was to quantify product recovery and DF values for a single stage extraction and back-extraction of Pu. U(VI) and Pu(IV) were extracted and decontaminated by contacting the prepared working 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 contacting the physically separated TBP solution with a solution of 0.024 M ferrous [Fe(II)] sulfamate in 0.75 M HNO3. The working solutions 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 recover a large fraction of Pu. Utilizing the results from the first experiment, it was determined that contacting the prepared working solution four times with TBP would extract over 90% of the Pu. Therefore, this experiment had four extraction stages with the prepared working solution. The four TBP solutions were then collected into a single vial, and contacted three times with a 4 M HNO3 in a 0.024 M ferrous sulfamate solution. These three contacts were then collected into a single vial.

In order to ensure minimal U back-extraction, the HNO3 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 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 to verify the repeatability of the process and for comparison with the first cycle. The ending solution of the first cycle Pu was “reset” with the addition of 0.5 mg of NaNO2 to convert all Pu(III) to Pu(IV).

1. **Results**

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 working solution both before and after extraction for experiment 1. These were determined to be 26.7 ± 2.9 and 11.6 ± 1.1, for U and Pu respectively. Experiment 2 successfully recovered approximately 93% of the original Pu with less than 1% of the original U remaining.

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

|  |  |  |
| --- | --- | --- |
|  | Pu Recovery | U Recovery |
| Experiment 1 | (83.4 ± 9.5)% | (11.2 ± 1.3)% |
| Experiment 2 Cycle 1 | (99.7 ± 4.2)% | (6.8 ± 0.3)% |
| Experiment 2 Cycle 2 | (93.0 ± 4.6)% | (6.6 ± 0.3)% |
| Overall Experiment 2 | (92.7 ± 6.0)% | (0.45 ± 0.03)% |

In experiment 1, approximately 10% of the U in the TBP phase was back-extracted with a single contact of a solution of 0.024 M iron sulfamate in 0.75 M HNO3. Experiment 2 had much smaller U back-extraction due to the higher molar concentration of HNO3 in the back-extraction solution (Benedict 1982). This can potentially led to lower Pu recovery because the stability of ferrous ion decreases as the concentration of nitric acid increases (Stoller 1961). This is due to the increased concentration of nitrite in solution (Stoller 1961). The half-life of the ferrous ion in the back-extraction solution of experiment 2 was estimated with the published data to be approximately 4 days (Stoller 1961). The effect is shown 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.

The DF calculations utilized concentration ratios between contaminants that were normalized to the Pu concentration per Equation 3, with the initial solution being the working solution and the final solution being 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 shown because the data were below background for these samples. The low DF values reported were expected due to reasons described above: the extraction and back-extraction were performed without intermittent scrubbing, and the number of stages was low.

Table 2 Decontamination factors for single and multiple contacts PUREX. Results have been corrected to equal contact volumes between aqueous and organic solutions during both extraction and back-extraction, as well as zero hold-up volume.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Element (Z) | Exp. 1 | ± | Exp. 2 Cycle 1 | ± | Isotopes Used |
| Rb (37) | 39.0 | 5.9 | 11.8 | 0.8 | 85Rb |
| Sr (38) | 282.5 | 42.5 | 84.6 | 5.9 | 90Sr |
| Mo (42) | 5.7 | 0.8 | 1.9 | 0.2 | 97,98,100Mo |
| Ru (44) | 59.2 | 6.4 | 16.6 | 2.5 | 101,102,104Ru |
| Pd (46) | 65.0 | 14.3 | 8.9 | 1.2 | 110Pd |
| Cd (48) | 73.6 | 17.4 | 22.1 | 2.5 | 112Cd |
| Cs (55) | 176.6 | 28.0 | 52.9 | 3.9 | 133Cs |
| Ce (58) | 42.5 | 16.3 | 11.5 | 4.9 | 140,142Ce |
| Nd (60) | 19.2 | 2.1 | 5.9 | 0.4 | 143Nd |
| Pm (61) | 12.8 | 1.9 | 3.9 | 0.3 | 147Pm |
| Sm (62) | 11.5 | 1.5 | 3.6 | 0.3 | 151Sm |
| Eu (63) | 10.0 | 1.4 | 3.6 | 0.3 | 154Eu |
| U (92) | 7.4 | 1.2 | 14.7 | 0.9 | 238U |

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 HNO3 concentration in the iron sulfamate solution as discussed above. The rest of the elements have lower DF values because of the four extraction and three back-extraction steps in cycle 1 of experiment 2 compared to one extraction and one back extraction in experiment 1.

This is shown in Figure 1, where theoretical DFs as a function of extraction step and volume ratio for a product with a DC of 10 and a contaminant with a DC of 0.1 are shown. Higher numbers of contacts decrease DF because less and less product is extracted with each step, while the amount of contaminant extracted is approximately equal. Experiment 2 DF values decrease relative to experiment 1 DF values because of this.



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

1. **Conclusions**

Two PUREX experiments were conducted. The first experiment determined DC values for Pu, U 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 Pu and U recoveries for experiment 1 were (83.4 ± 9.5)% and (11.2 ± 1.3)%, respectively, while the same values for experiment 2 cycle 1 were (99.7 ± 4.2)% and (6.8 ± 0.3)%, respectively. DF values were measured for 12 fission product elements. DF values were lower than those typically found in industrial scale PUREX plants due to multiple extraction and back-extraction steps without an intermittent scrubbing step.

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