**Fission Product decontamination factors for plutonium separated by PUREX from a low-burnup, pseudo-fast-neutron irradiated depleted UO2**

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Abstract

Experimental investigations to determine fission product (FP) and actinide (uranium and plutonium) separation while employing the Plutonium Uranium Redox Extraction (PUREX) process to purify plutonium in neutron-irradiated uranium dioxide targets were conducted. The sample processed was low-burn-up (4.93 ± 0.132 GWd/tHM) depleted uranium dioxide (DUO2) surrogate pellet (0.28 ± 0.002 wt.% 235U). Decontamination factors for U, Mo, Ru, Ce, Sm, Sr, Pm, Eu, Nd, Pd, Cd, Ba and Sn for a two-step PUREX cycle using 30 vol.% tri-n-butyl phosphate in a kerosene diluent with low uranium concentrations in 4 M nitric acid were determined. These values were consistent with of previously reported distribution coefficient values. Decontamination factors for each of the above elements were determined for a single extraction back-extraction cycle as well as a four contact extraction coupled with a three contact back extraction. Results were determined with mass spectrometry. The laboratory scale PUREX cycle employed had an overall 94% Pu recovery with an overall activity decontamination factor of ~20 for the single contact and ~5 for the multiple contact schemes.

1. Introduction

In a recent publication, our group suggested that investigation of PUREX-processed plutonium for trace contaminates could give indication of material origins, but that a broad study of many elements would be necessary (Chirayath, Osborn et al. 2015). Descriptions of various PUREX processes are provided in many sources (Reas 1957, Stoller and Richards 1961, Benedict, Levi et al. 1982) with explanations of chemistry including flow sheets, while other sources give decontamination factors (DFs) for PUREX (Gresky 1950, Arker 1954, Chandler 1954). These sources generally report overall beta or gamma decontamination factors (DFs) of up to ~108 with plutonium recoveries of 99.7% for industrial-scale reprocessing facilities. While distribution coefficients (DC) for the various process separation 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 ruthenium and zirconium. A compilation of distribution data for PUREX extraction processes provide DC information for uranium, thorium, and plutonium in a variety of concentrations (Prout 1957). DCs for Zr, rare earth metals, plutonium, and thorium are also available (Alcock, Bedford et al. 1957, Best, McKay et al. 1957, Hesford, McKay et al. 1957, Scargill, Alcock et al. 1957, Alcock, Best et al. 1958, Best, Hesford et al. 1959, Hesford, Jackson et al. 1959). Although a DC (coupled with process information) can be used to calculate a reasonable estimate of DF (Colburn 1939, Sherwood and Pigford 1952, Long 1967, Perry and Green 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 nitric acid concentration and uranium saturation in TBP. These sources also derive mathematical correlations between DC and DF, but experimental PUREX DFs for individual elements were not provided. Additionally

In the current work, a 12.9 mg depleted uranium dioxide (DUO2) pellet (0.28 ± 0.002 wt.% 235U) was irradiated in a pseudo-fast neutron spectrum at the High Flux isotope Reactor at Oak Ridge National Laboratory. The DUO2 pellet, containing FP and weapons-grade plutonium, was subjected to three PUREX decontamination steps and the aqueous process solutions analyzed at each step with Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The experimental work used benchtop-scale methods to isolate the maximum amount of plutonium, measure DCs for fission products, and measure three-step DFs as part of a larger project to develop forensic radioanalytical capabilities at Texas A&M University.

1. Definitions

A DCs is defined as the concentration ratio between the organic (“org”) and aqueous (“aq”) phases as shown in Equation 1, and describes the steady-state distribution of any species in the system (Benedict, Levi et al. 1982):

Equation Distribution coefficient.

|  |  |  |
| --- | --- | --- |
|  |  | 1 |

where 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 uranium and plutonium in the system and even time since preparation of the solution (Stoller and Richards 1961, Michael and Jack 2010). For PUREX, the fraction of mass *forg* deposited in the organic (TBP) phase for a single element (assuming equal contact volumes) is given by Equation 2.

Equation Percent deposition in the TBP phase.

|  |  |  |
| --- | --- | --- |
|  |  | 2 |

After several cycles of plutonium extraction/decontamination are complete, 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 is removed from a product. In this work, the product of interest is plutonium, and the DF is defined by Equation 3.

Equation Decontamination factor for a single contaminate.

|  |  |  |
| --- | --- | --- |
|  |  | 3 |

where represents the contaminant of interest and “initial” and “final” refer to the values before and after purification, respectively. DFs are also characteristic of different process cycles, and will have much greater numerical values (typically ~107) in industrial systems, since most industrial processes report *overall* DFs. An overall DF (), by definition, would be described with Equation 4:

|  |  |  |
| --- | --- | --- |
|  |  |  |

where *J* is the number of contaminant species. Industrial processes typically report DFs with regard to total gamma or total beta activity since these are readily determined; otherwise, each contaminant must be quantified. In practice, is a strong function of the pool of contaminants used for the calculation.

|  |  |  |
| --- | --- | --- |
|  |  |  |

The relationship between individual DFs, individual contaminant concentrations, and is given by Equation 5:

|  |  |  |
| --- | --- | --- |
|  |  | 5 |

where *I* is [\*\*\*definition of *I*]. Equation 6 gives for an equal volume liquid-liquid separation between nitric acid and TBP:

|  |  |  |
| --- | --- | --- |
|  |  |  |







where *DCPu* is [\*\*\*definition of *DCPu*]. The numerator inside the large summation for Equation 6 is constant for all contaminants. The largest influences on are contaminants with large *initial* concentrations and contaminants with large DCs. For example, if a process has 30 contaminants each with a DC of 0.001 and perfect plutonium recovery, then would be 1000. If a single contaminant DC value were changed to 0.01, then would be 772, and if that same value were changed to 0.1, then would be 250, which is a 25% or 75% decrease in for a single step. This effect worsens as the number of contaminants accounted for decreases and as the spread between DF values increase, which is why individual decontamination factors are necessary. with respect to gamma counts and elemental DFs will be reported, but will not be calculated from each other for reasons stated above.

Figure 1 shows calculated decontamination factors for one and two contacts of TBP as a function of volume ratio assuming constant hypothetical DC across all volume ratios and a DC for plutonium of 10. This plot assumes that the second contact of TBP is combined with the first contact. Note that the second contact results in a decreased DF, even though the recovery of plutonium is improved. Additionally, volume plays a significant role in DF, although different volume ratios will affect how close uranium is to its solubility limit. Extremely large DF can be achieved with minimal TBP solution (McHenry, Posey et al. 1963), although this will adversely affect plutonium recovery. The experiments described below utilized four contacts with a volume ratio of 1.4.



Figure 1 Decontamination factors as a function of volume ratios for first and second contact.

1. Experimental

How was the sample prepared? I was not on the project at this point

How was the sample irradiated? I was not on the project at this point

How were the chemical acquired? I was not on the project at this point

A commercially acquired pellet containing 12.9 ± 0.1 mg of depleted UO2 was irradiated over the course of three months with two shut down periods in the HFIR flux spectrum to about 3000 MWd/t. The burn-up was determined by measuring the 137Cs activity. This produced 0.237 ± 0.008 mg of Pu. After the short lived radioisotopes had opportunity to decay, the irradiated pellet was shipped to Texas A&M University and transferred to a round-bottom flask. 5.0 ml of 8 M HNO3 was added to the flask, which was heated to 50° C with constant 100 rpm stirring for two hours. This solution will be referred to as the “dissolution solution.” a containing that 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, 0.5 ml aliquots (referred to as the “stock solution” and containing ~1% of the pellet) were used in a benchtop-scale PUREX process described below. The activity concentration of the stock solution was approximately 80 μCi/ml.

The flow chart for a PUREX cycle for the experiments is shown in Figure 2 below, and the boxed numbers are intended to help make the steps clearer. Each experiment started with transferring a 500 μl aliquot of stock solution and 0.5 mg of NaNO2 to a 15 ml centrifuge tube. The tube was subsequent stirred and covered to retain the resulting NO2 gas. The solution was left overnight so that NO2 gas completely oxidized Pu(III) to Pu(IV). U(VI) and Pu(IV) were extracted and decontaminated by contacting the aliquot with a solution of 30 vol.% TBP with a kerosene diluent. Pu(IV) was then reduced to Pu(III) and extracted and back-extracted by contacting the TBP solution with dilute HNO3 in a 0.024 M ferrous sulfamate solution via oxidation of Fe(II). , U UAfter the back extraction of Pu(III), the solution was prepped for another cycle of Pu decontamination with the addition of more NaNO2.

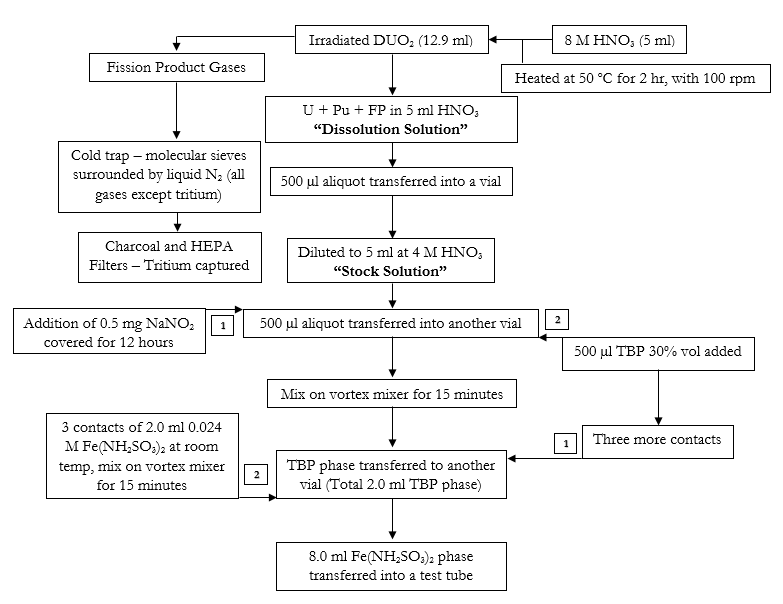


Figure Flow chart for the experiment. See the main text for a discussion.

This 500 μl aliquot was then contacted by TBP at room temperature. The volume of TBP was kept as close to 500 μl as possible, but usually an additional 200 μl was added. The concentration remained the same with 30% by volume TBP diluted with kerosene. When a larger volume of TBP was contacted with stock solution the extra was added to reduce the chance of accidentally pipetting HNO3. Similarly, comparable contact volumes were used during the plutonium and uranium separation.

Both sets of extractions had the aqueous and organic phase mixed on a vortex mixer for 15 min at 1500 rpm, and then allowing the two phases to settle and separate. The sample was additionally centrifuged and carefully pipetted to physically separate the two phases into two different vials. For the PUREX cycles, TBP was contacted with the stock solution multiple times to ensure the quantitative recovery of heavy metal from the stock solution with the TBP collected in a single vial.

The pellet, both prior to dissolution and after, was counted with a standard HPGe detector with a Pb shield. The same detector was used to count the various process solutions. GENIE software was used to analyze spectrum and samples were typically encased in a lead tomb. Inductively coupled plasma mass spectrometry (ICP-MS) was also conducted for some samples using a PerkinElmer NexION 300X quadrupole ICP-MS.

1. Results and Discussion

A second and third plutonium extraction/back-extraction was carried out in the same manner as the four-contact experiment described above. The goal of these experiments was to continually decontaminate, while maintaining large plutonium recovery with simple processes. The second extraction/back-extraction had a 90% plutonium recovery with an additional 95% of the uranium remaining in the organic phase. The third step had dismal back-extraction due to Fe(II) catalytically oxidizing to Fe(III) with NO2- (Stoller and Richards 1961).

The decontamination factor calculations utilized concentration ratios between contaminants that were normalized to the plutonium so that volume changes due to processing were negated. Both the single- and four-contact DF values are shown in Table 1. The heavy metal decontamination factors give an indication of U separation. For reference, the plutonium recovery for the two experiments is 76% and 94%, respectively, which correspond to a 75% and 93% uranium separation, respectively. The DCs for U and Pu were 37.5 and 16.2, respectively, which indicate that large fractions of the U and Pu were removed from stock solution. The reason for the lower than expected extractions is due to the TBP holdup volume left in the organic phase (Long 1967).

Table Decontamination factors for single and multiple contact PUREX. Elements are grouped based on their location on the periodic table.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Element | 1 Contact TBP/ 1 Contact Fe | ± | 4 Contact TBP/ 3 Contact Fe | ± |
| Heavy Metal | | | | |
| U | 6.85 | 0.46 | 15.08 | 0.60 |
| Alkali Metals | | | | |
| Rb | 32 | 1.55 | 1.84 | 0.26 |
| Cs | 146 | 7.58 | 11.92 | 0.96 |
| Alkaline Earth Metals | | | | |
| Sr | 233.5 | 12.74 | 38.26 | 2.23 |
| Ba | 344.4 | 200 | 0.39 | 50 |
| Transition Metals/Post Transition Metals | | | | |
| Mo | 20.67 | 2.03 | 1.19 | 0.25 |
| Ru | 49 | 1.9 | 2.84 | 0.111 |
| Pd | 65 | 14.3 | 3.62 | 0.94 |
| Cd | 61 | 6.6 | 3.5 | 0.98 |
| Sn | 7.45 | 0.43 | 13.85 | 1.29 |
| Lanthanides | | | | |
| Ce | 35.24 | 1.68 | 3.2 | 0.67 |
| Nd | 15.2 | 1.429 | 8.6 | 3.4 |
| Pm | 10.7 | 0.66 | 3.3 | 0.5 |
| Sm | 9.94 | 0.25 | 2.5 | 0.19 |
| Eu | 8.4 | 0.49 | 2.6 | 0.23 |

The alkali and alkaline earth metals both have very high decontamination factors. It should be noted that the Ba calculation utilized 138Ba with background barium subtracted; the background was determined with 134Ba, and is subject to very high errors due to the low amounts of 134Ba in the system. Ba and Sr form divalent cations and are not readily extractible in TBP. Cs and Rb have a large difference in DF (Still working on figuring that out).

The transition metals have a general decreasing extractability. The reason Mo has a lower DF than Ru, Pd, and Cd is because it can form 4+ and 6+ oxidation states in aqueous solutions (Czack, Czack et al. 1987), which are more extractable in organic solutions.

The lanthanides are known to have an increasing extractability with increasing atomic number (Scargill, Alcock et al. 1957), which is reflected in a decreasing DF. (Is this due to lanthanide contraction? Where as the atoms get smaller, with a higher charge density, they are more easily extracted? – Does this explain why Cs is better than Rb, and why Ba is better than Sr?)

1. Conclusions

Decontamination factors for U, Mo, Ru, Ce, Sm, Sr, Pm, Eu, Nd, Pd, Cd and Sn for a two-step PUREX cycle using 30 vol.% TBP in a kerosene diluent with low U concentrations in 4 M HNO3 were determined. Trends among the different groups in the periodic table give indication that the higher charge densities of the heavier lanthanides are more extractable in TBP. Overall gamma decontamination factors for a single contact procedure were determined to be ~20 and 5 for a four-contact procedure, indicating that multiple contacts increases plutonium recovery, but decreases decontamination factors. Plutonium extraction was 93% and 90% for the first two cycles and negligible for the third cycle due to Fe(II) oxidation.

Do I include trends for Cs and Rb (and Sr and Ba) – if what I said above is correct

Can I talk about lanthanide trends being potentially useful for forensic analysis?

Future work of characterizing Cs, Nd, and other isotopes of interest for interdicted Pu?

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