**Fission Product decontamination factors for plutonium separated by PUREX from a low-burnup, pseudo-fast-neutron irradiated DUO2**

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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

Various literature sources provide information about overall process or cycle decontamination factors (DF) for PUREX (Gresky 1950, Arker 1954, Chandler 1954). These values are typically reported via gross gamma or beta counts with values ranging from 106 to 108. While distribution coefficients (DC) for the various process steps of PUREX have been previously reported, details about elemental DF for PUREX cycles have been largely limited to the major activity contributors, such as ruthenium and zirconium. 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. Due to recent proposals suggesting that investigation of PUREX processed plutonium for trace contaminates could give indication of material origins, DF for a broader sweep of elements were deemed necessary (Chirayath, Osborn et al. 2015).

Fission product DFs and actinide recovery as a function of coupled extraction/back-extraction PUREX steps were applied to a low-burnup (< 5000 MWd/MTU) depleted uranium dioxide (DUO2) surrogate pellet (0.28 ± 0.002 wt.% 235U) irradiated in a pseudo fast neutron spectrum. The DUO2 surrogate pellet, containing FP and weapons grade plutonium were 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 sought to develop laboratory scale methods to isolate a large percentage of plutonium, determine DC, and three step DFs as part of development of forensic radiochemical analytical capabilities at Texas A&M.

1. Background

DCs, defined as the ratio of grams per liter of solute in the organic solution over grams per liter of solute in the aqueous solution, shown in Equation 1, describe the steady state distribution of any species in the system (Benedict, Levi et al. 1982). To be expected, DCs are different from element to element, and vary widely with concentrations, and temperatures of 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).

Equation Distribution coefficient.

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

For PUREX, the mass deposition in the TBP phase, assuming equal contact volumes is derived by assuming that mass is conserved, and is shown in 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 decontamination factor (DF), which are fundamentally determined by DCs and measures the effectiveness with which a contaminant is removed from a product. With plutonium shown as the product, this is shown in Equation 3, where represents concentration, represents plutonium, and represents the contaminant. It should be noted that as long as the concentrations are of the same kind, then it does not matter whether they are reported in mass or atomic units.

Equation Decontamination factor for a single contaminate.

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

DFs are also characteristic of different process cycles, and will have much greater numerical values in industrial systems. Most industrial processes report DFs on the order of 107 for an *overall* DF. An overall DF (), by definition, would be described with Equation 4, where j is summed over all contaminants. Therefore industrial processes are more inclined to report DF with regard to total gamma or total beta activity, where an overall concentration is more easily determined. Otherwise, to be precise, each particular contaminant, or fission product, should be measured and quantified. Typically blanket DF values, with no reference towards specific contaminants or method are listed. This is a problem, because is a strong function of the pool of contaminants used for the calculation.

Equation Over-all decontamination factor.

|  |  |  |
| --- | --- | --- |
|  |  | 4 |

To show this, Equation 4 is rewritten in Equation 5 and Equation 6. The relation between individual DFs and is depicted in Equation 5, where loops over all contaminants. It is important to realize two things, first, that DFs are additive, and second, that the parenthetical statement of Equation 5 represents a percentage, where if were removed from the equation, then the summation would be precisely 1.

Equation 6 utilized Equation 2 and Equation 3 and shows for an equal volume liquid-liquid separation between nitric acid and TBP. The numerator inside the large summation for Equation 6 is constant across all contaminants and the largest initial concentrations are shown to contribute the most towards the overall DF

Equation Over-all DF in terms of indicidual DFs.

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

Equation Decontamination factor for a single contact of TBP.

|  |  |  |
| --- | --- | --- |
|  |  | 6 |

These equations highlight the fact that the contaminants used for the calculation have a large influence on what the value of is. Noting that is driven mostly by contaminants with the largest *initial* concentration followed by contaminants with large DCs. The above statements seem obvious, but their impact can be substantial. For example, if Equation 6 were used to calculate for 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.

To stress other factors that affect DFs and give context for the DF values provided in this paper, Figure 1 was produced. Figure 1 shows calculated decontamination factors for one and two contacts of TBP with the same volume ratio between both contacts with the assumptions of constant 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. Different elements have different DC, which is why several values are shown on the graph. The lower line in each case is the second contact.

Although different volume ratios will affect how close uranium is to the solubility limit, and affects the DC for various elements, two concept effects are emphasized with Figure 1. The first is that volume plays a significant role in DF - notice how extremely large DF can be achieved with minimal TBP solution, this is supported by (McHenry, Posey et al. 1963). The second is that each contact of TBP reduces DFs by a large fraction at larger volumes of TBP. The experiment utilized four contacts at a volume ratio 1.4.



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

1. Literature Review

Descriptions for various PUREX variations are provided in many sources (Reas 1957, Stoller and Richards 1961, Benedict, Levi et al. 1982) with explanations of chemistry, flow sheets, and process. These sources report overall gamma DFs of ~108 with plutonium recoveries of 99.7 % for industrial scale reprocessing facilities. Further, DC values for TBP and nitric acid are provided for U, Pu, Zr, Nb, Ru, and the rare earth elements. DCs are disclosed in numerical and graphical format and 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.

A compilation of distribution data for PUREX extraction process provide DC information for uranium thorium, and plutonium in a variety of concentrations (Prout 1957). DC for Zr, rare earth metals, plutonium, and thorium, have been provided in the “Tri-n-butyl phosphate as an extracting solvent for inorganic nitrates” series (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). This information will be extremely useful for verifying trends between the different DF produced in this experiment.

An experiment was conducted at Oak Ridge National Laboratory for uranium process decontamination. (McHenry, Posey et al. 1963). This experiment sought to decontaminate irradiated uranium from fission products using a simple two-stage differential extraction scheme. Where differential refers to the use of minute volumes. This experiment utilized TBP and the sulfate ion for the extraction. The sulfate ion enhanced the separation between the uranium and the fission products. Distribution coefficients were reported as well as decontamination factors for zirconium, europium, and ruthenium.

Understandably, DC for elements of the alkali and alkaline earth metals have not been extensively reported, because these elements are not appreciably extracted into organic solvents. DF for these elements are important to know because Cs and Ba concentrations are useful for determining reactor parameters. Conversely, gallium has been studied for separation (Collins, Campbell et al. 2000) because it is a common contaminate in weapons grade plutonium.

Over cycle DF for PUREX has been reported for Ru, Zr, and Nb, but literature review has failed to produce DFs for the vast majority of elements.

(if you can find DC for alkali earth metals somewhere, I should add them here)

(Further studies have been done about recovering fission products from the waste stream – should I mention that?). (Swift 1961, Weaver 1963, Gupta, Singh et al. 2009)

1. Experiment

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

12.9 mg of irradiated depleted uranium dioxide was dissolved in 15.43 M HNO3, about 10% of the aliquot was further diluted to 3.95 M HNO3 and PUREX ensued with 1/100th of the pellet in 0.5 ml aliquots. This was known as the stock solution. U(VI) and Pu(IV) were extracted and decontaminated by contacting the stock solution with a solution of 30 vol.% tri-n-butyl phosphate with a kerosene diluent. Plutonium was then reduced to Pu(III) and extracted and separated from uranium by contacting the tri-n-butyl phosphate solution with dilute HNO3 acid in a 0.024 M ferrous sulfamate solution via oxidation of Fe(II). Pu(III) was converted to Pu(IV) via the addition of sodium nitrite and further decontamination/extraction ensued by repeating the process.

The pellet, both prior to dissolution and after, was counted on a standard Canberra electrode coaxial Ge detector model number CC4018 which was controlled by a Canberra Lynx MCA. 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 with use of the University of Missouri’s PerkinElmer NexION 300X quadrupole ICP-MS. A Canberra Passivated Implanted Planar Silicon (PIPS) detector coupled with an alpha spectrometer a MCA and a vacuum pump were also used qualitatively to verify plutonium separation of co-precipitated plutonium. Quantitative measurement for this method proved difficult due to smearing of alpha energies by filter paper.

Detailed three dimensional models of Oak Ridge National Laboratories’ (ORNL) High Flux Isotope Reactor (HFIR) were developed using the Monte Carlo transport computer code, MCNP, coupled with the burn-up/depletion computer code, CINDER90. These were used to model the irradiation of a DUO2 surrogate pellet so that expected activities and concentrations could be determined. A measured 12.9 ± 0.05 mg of DUO2 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 137Cs activity and through the MCNP calculation. This produced 0.237 ± 0.001 mg of Pu.

After the short lived radioisotopes had opportunity to decay, the irradiated DUO2 pellet was weighed in a weighing boat on an electronic balance and transferred to a round bottom flask. 5 ml of 8 M HNO3 was added to the round bottom flask and the flask was heated at 50°C with constant 100 rpm stirring for two hours. The dissolution apparatus is shown in Figure 2.

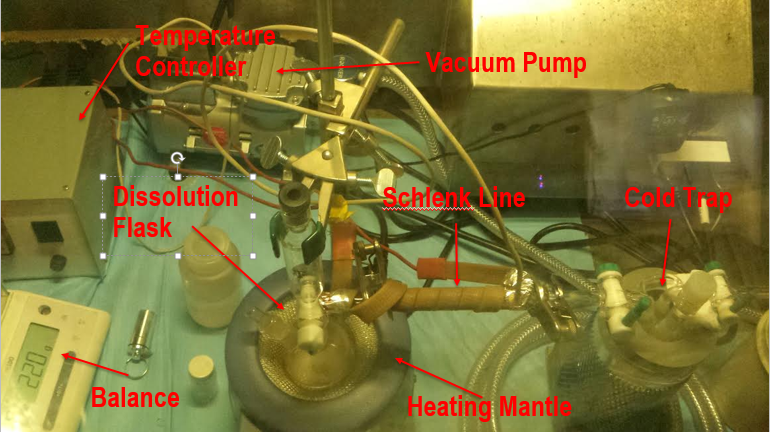


Figure Dissolution of the irradiated DUO2 pellet.

The round bottom flask was connected to a cold trap with the help of a Schlenk line. The fission product gases such as H2, CO2, Kr, Br, I and N2O were captured in the cold trap inside the molecular sieves which were chilled by liquid nitrogen. The 5 ml concentrated 8 M HNO3 solution was transferred from the round bottom flask to a 20 ml glass scintillation vial and kept heavily shielded. This solution is referred to as the “dissolution solution”.

In order to reduce the amount of activity per sample, 500 μl from the dissolution solution was diluted to 5 ml and the concentration was changed to 4 M HNO3 with the addition of deionized water. This was subsequently called, “stock solution”. The activity concentration of the stock solution was about 80 μCi/ml. The stock solution was stored in its own 20 ml glass scintillation vial in a lead pig inside a glovebox. Each PUREX process used 0.5 ml aliquots from this stock solution.

The flow chart for a PUREX cycle for the experiments is shown in Figure 3 below. The step titled, “Diluted to 5 ml with 4 M HNO3” has been previously described in this section. The flow chart has boxed numbers to help make the steps clearer. Each experiment started with transferring a 500 μl aliquot of stock solution along with 0.5 mg of NaNO2 with subsequent stirring, and covering in a 15 ml centrifuge tube. This produces NO2 gas. The solution was left overnight so that NO2 gas completely oxidized Pu(III) to Pu(IV).

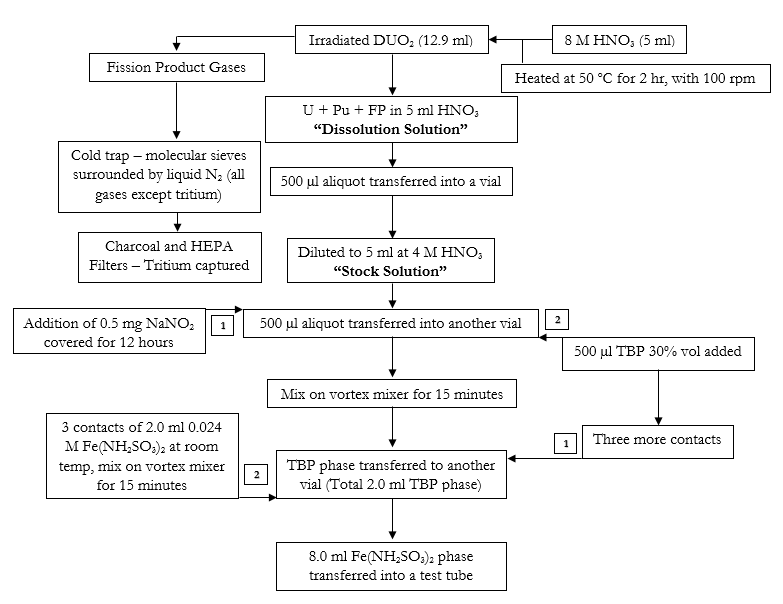


Figure Flow chart for experiment.

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 minutes 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 stock solution multiple times to ensure the quantitative recovery of heavy metal from the stock solution with the TBP collected in a single vial.

Two concentrations of HNO3 were used in the ferrous sulfamate solution. The first was 0.75 M and the second 4 M. These two concentrations were used to determine differences in uranium separation, which occurs because NO3- concentrations affect the distribution ratio for uranium.

After the back extraction of Pu(III) the solution was prepped for another cycle of Pu decontamination with the addition of NaNO2. Dry runs of the above described experiment were conducted with natural uranium to ensure that uranium is removed from the “stock solution” and does not make its way to the product solution. Each of the above steps were analyzed with gamma spectroscopy for fission products. The aqueous phases were additionally quantified by ICP-MS analysis.

1. Results and Discussion

The decontamination factor calculations utilized concentration ratios between contaminants and plutonium so that volume changes due to processing were negated. Both the single and multiple contact DF values are shown in Table 1. The elements were grouped based on location on the periodic table.

Table Decontamination factors for single and multiple contact PUREX.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| 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 | | | | |
| 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 heavy metal decontamination factors give indication of uranium separation. For reference, the plutonium recovery for the two experiments is 76% and 94%. Which correspond to a 75% and 93% uranium separation, respectfully. The DC for U and Pu were 37.5 and 16.2, which indicate that large portion 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).

A second and third plutonium extraction/back-extraction was carried out in the same manner as the 4 contact experiment described above, their purpose 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 ion(II) catalytically oxidizing to iron (III) with nitrite (Stoller and Richards 1961).

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

The transition metals filling the 4d orbital have a general decreasing extractability. The reason molybdenum has the worst of this row is because it can form a 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.% tri-n-butyl phosphate in a kerosene diluent with low uranium concentrations in 4 M nitric acid were determined. Trends among the different groups in the periodic table give indication that higher charge densities 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 neglible 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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