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**Dissertation Title:** Experimental Characterization of Pu Separation by PUREX Process on a Low-Burnup, Pseudo-Fast-Neutron Irradiated DUO2 for Product Decontamination Factors and Nuclear Forensics

1. **Introduction**

In the wake of the Joint Comprehensive Plan of Action (JCPOA-Iran deal), North Korea’s pursuit of nuclear weapons, non-safeguarded reactors, and the onset of the Islamic State of Iraq and Syria, nuclear proliferation concerns are receiving utmost importance and attention. A nonproliferation focal point is the control and accounting of weapons usable special nuclear material (SNM), which has been the responsibility of the International Atomic Energy Agency (IAEA) with the goal of promoting the safe and peaceful use of atomic energy and nuclear technologies1. The IAEA’s efforts to meet this goal, backed by a U.S. “atoms for peace”2 program and the treaty on the non-proliferation of nuclear weapons (NPT)3, have hindered the development of weapons to a large extent4. However, efforts beyond nuclear material safeguards are necessary due to “the awful arithmetic of the atomic bomb”5. An effort outside of nuclear material safeguards for pre-detonation SNM, is to develop the nuclear forensics capability with a source attribution objective in the event of SNM interdiction.

SNM origin attribution, in this context, applies to deducing history of nuclear material, including its production process. The importance and time sensitivity of which varies widely in different circumstances, but is fundamentally an inverse problem, which are difficult to solve. For example, if purified plutonium were interdicted at a State border, information from a wide variety of sources will be used to arrive at a likely hypothesis for where the material came from. This hypothesis, is an informed, studied, and tested conclusion, but is only one possible explanation for the history of the material.

The point is not to say the exercise is meaningless, but difficult and multi-layered. Multi-layered because there are many different sources of information and a large number of possible hypotheses. This study proposes a nuclear forensics characterization procedure for separated plutonium material. Which will aid an informed hypothesis for source attribution.

Previously, computational studies have indicated that analysis of contaminants in Plutonium Uranium Recovery by Extraction (PUREX) processed plutonium could give indications of material origins6. Unlike enrichment of 235U, 239Pu “enrichment” involves neutron irradiation, which introduces radioactive fission products and hence, purification by some means. Purification by PUREX is most common for low enriched uranium fuel7 - important because 238U converts to 239Pu upon neutron capture and subsequent β- decay. Material attribution for separated plutonium is complicated because the separation process has a substantial amount of variability stemming from the changes in elemental decontamination factors (DFs, a measure of purification) that could be obtained in a PUREX process.

The measured effectiveness of a PUREX cycle is described by the DF, and measures the effectiveness with which the concentration,, of a contaminant, , is removed from a product. The product of interest in this work is plutonium, and the DF is defined by Equation 1.

Equation Decontamination Factor

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| --- | --- | --- |
|  |  | (1) |

The problem of attribution for unpurified material has been previously studied6, 8, 9, ideally, if elemental DFs for interdicted plutonium were determined, then these previous methodologies could be used to narrow material origins by applying these correction factors, assuming DFs for different isotopes of the same element are equal. This is visually represented in Figure 1, where the initial plutonium impurity levels are estimated through DFs with attribution analysis ensuing.

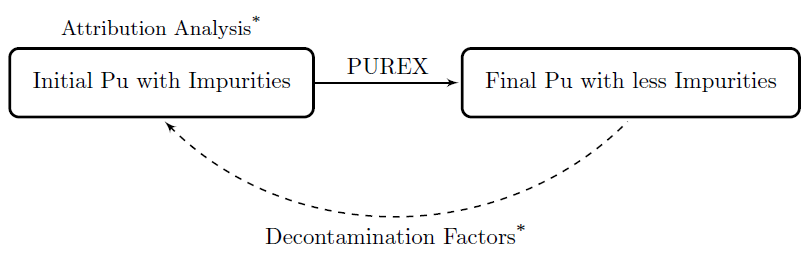


Figure Proposed research areas for irradiated fuel.

This work will start with the assumption that the specifics of the PUREX process used for plutonium separation are known, so that DFs are applied appropriately. In real world applications, this information would not be readily available, and this same analysis would have to ensue with best estimate PUREX processes and experimentally measured distribution coefficients (DCs, the ratio of concentrations between organic and aqueous phases).

1. **Objectives**

The objective of this research is to determine DFs and DCs for a benchtop scale PUREX process for important attribution elements noted in previous research (Cs, Eu, Rb, Sr, Nd, Pm, Sm, U, and Pu)6. Both DCs and DFs will be determined for this process so that the two parameters will be experimentally connected to the specific PUREX process utilized. This establishment is important because the nuances for a particular PUREX process vary widely and result in different DFs from process to process10. Mathematically, DC values, coupled with process information, can be used to calculate a reasonable estimate of a DF11-14, leading to original concentrations of impurities in purified plutonium. Which in turn allows for use of more traditional forensic analysis.

The objective will be pursued by performing mass, gamma, and alpha spectroscopies on solutions/samples obtained from various PUREX process steps and analyzing the results. The PUREX process followed for this study will have four extraction and three back extraction steps for obtaining purified plutonium. These steps are chosen because they are the main steps for the separation of heavy metal from fission products, and uranium from plutonium12. Each step in the process will be analyzed for DC values, and the overall process will be analyzed so that the DFs can be determined through initial and final solutions and through using individual DCs concurrently.

Further, several forensic analyses will be pursued for the case of plutonium. The analyses performed will include fuel burnup which produced plutonium, fluence rate (assuming constant), initial enrichment, fuel age, and fast-to-thermal ratio calculations. These attributes are important for source attribution. These analyses will be first undertaken for unprocessed plutonium material. Then the experimentally and mathematically determined DFs for the PUREX process performed will be applied to determine the attributes of separated plutonium. The second step emulates a scenario where useful information is derived from experimentally processed plutonium using PUREX. These two determinations will then be compared to calculation results from the general purpose Monte Carlo N-Particle (MCNP) radiation transport code modeling the reactor fuel burnup operations which produced the plutonium in question.

The above points are summarized in the list below:

1. Complete four extraction three back-extraction PUREX process in triplicate
   1. Collect DCs for each step
   2. Determine from DCs and the initial and final product the DFs
2. Determine attribution indicators of burnup, fluence rate, initial enrichment, fuel age, and fast-to-thermal ratios with data from:
   1. Unprocessed plutonium
   2. PUREX processed plutonium
   3. MCNP based reactor modeling and fuel burnup analysis
3. **Present Status of the Question**

There is a reasonably large body of literature on the work done in the area of using isotopic compositions in order to determine or verify the origin of plutonium and also the information on the process used to separate plutonium from reactor fuel. These works are varied in implementation and scope.

Isotopic compositions and ratios in spent reactor fuel have been used for burnup verification. One study utilized measurement of isotopic ratios of stable noble fission gases during reprocessing in order to verify burnup15. They used data analysis methods to determine specific fuel parameters and then compared them with the measured values of stable noble gases. Fuel burnup is important because low burned uranium fuel (<5000 MWD/tU) yields weapons useable plutonium material. If a fuel assembly were burned to a lower level than reported, then further investigation is necessary to either alleviate or confirm suspicions of nefarious activities.

Others have analyzed later stages of processing used nuclear fuel. Given the spent fuel from a reactor that is used for a radiological dispersal device (RDD), a study sought to determine the burnup, enrichment, and age for the fuel 8. These combined data would then be subsequently used for reactor attribution purposes. This study is similar to our scenario in that it looks at FP in the matrix of the fuel itself and deduces reactor type and information about the history of the fuel, but this method does not consider any chemical processing.

Analysis of plutonium isotopes alone have been suggested to help identify reactor type at the same processing step as for the proposed project 9. The reactors considered were of the fast and thermal neutron spectrum type. This study concluded that while it is possible to identify with a high level of confidence differences in plutonium composition between fast and thermal reactors, it is difficult to make this same distinction in “dedicated production reactors fueled with natural uranium.” This should be contrasted with our study with depleted uranium in a fast neutron spectrum and specifically for low-burnup neutron irradiations.

PUREX co-processing, where uranium and plutonium are not separated during reprocessing, of spent LWR fuels has also been studied 10. Several decontamination factors and production yields for uranium and plutonium were determined. The specific goal of this paper was to demonstrate that uranium and plutonium could be co-extracted for reprocessing. This study was also limited in determining decontamination factors for a wide array of isotopes, which may not be important in terms of reprocessing, because higher levels of contamination are acceptable for fuel, but it is important in nuclear forensic analysis, because trace isotopes, whether radioactive or not, could give an indication of the origin of plutonium.

Descriptions of various PUREX processes are provided in many sources with explanation of chemistry including flow sheets and DFs7, 16-20. These sources generally report overall beta or gamma radiation DFs of up to 108 with Pu recoveries of 99.7% for industrial scale reprocessing facilities. While DCs 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 95Zr20. A compilation of distribution data for PUREX extraction processes provides data for U, Th, and Pu in a variety of concentrations21. DCs for Zr, rare earth metals, Pu, and Th are also available 22-27. Additionally, Ga has been studied for separation28 because it is a common contaminant in weapons-grade plutonium.

This work is unique in that elemental DFs will be determined and used on a PUREX processed plutonium with an attribution analysis ensuing.

1. **Procedure**

The objectives for this project were split into two distinct parts, chemical reprocessing, and forensic analysis. The procedure will also be broken up along these same lines. Although both parts require some element of experimental procedure, the first requires more and will be discussed in greater detail below under the heading of experimental, while the other will be more analytical in nature.

***Analytical Procedure****:* This experiment will utilize an irradiated 12.9 ± 0.1 mg of DUO2 irradiated to a lower burnup in a particular fast neutron environment. The specifics of this information is known to some, but not to the author, and working through the procedures for the forensic analysis will give some grounding for the history of the sample. Working from this “blind” perspective will help by removing bias towards particular results or conclusions.

Attribution indicators such as burnup or fluence rate each capitalize on certain information of how nuclides are produced or consumed in a nuclear reactor and on the rate of their production or consumption, which depends on the neutron spectra, fluence rate and accurate neutron interaction cross section data. The specific information that will be used for each of the indicators are discussed below.

Burnup is an operational parameter for the amount of energy produced from a mass of fissionable material, and is calculated with Equation 2, where refers to the mass of heavy metal in the irradiated fuel in metric tons. This is useful for reactor designers and operators, whose goal is to produce electricity efficiently. From an operational standpoint this term is relatively straightforward to determine. Knowing the amount of fuel put into a system, the amount of energy produced can be calculated with a specific heat calculation on the working fluid in the reactor system and the operation time. To precisely determine this parameter from a reactor physics point of view the total number fissions from each fissionable isotope should be known along with respective recoverable energy. This information is more difficult to acquire because the concentrations of fissionable material in a fissioning system (nuclear reactor) is constantly changing. Burnup will thus be determined with a fission product that builds into the fuel matrix linearly as a function of burnup such as 137Cs or 148Nd29.

Equation Burnup equation

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| --- | --- | --- |
|  |  | (2) |

The rest of the indicators are dependent on the neutron flux (fluence rate) spectrum the uranium sample was irradiated in. An issue with this dependency is the great complexity surrounding the shape of the neutron flux spectrum. It varies with temperature, geometry, fuel composition, and density of the materials in the system. It also has a spatial dependency, and derives itself from the cross sections of the materials themselves. These complexities cannot be ignored or simplified for precise answers, and various transport codes like MCNP30 or WIMS31 can be used to resolve the flux spectra, but in the case at hand, detailed descriptions of irradiated contexts are assumed to be unavailable for the sake of the forensic exercise, and the ensuing calculations will have a degree of error mostly due to the following assumptions.

The reason the neutron flux spectrum is important for the following calculations is because the calculations use one group cross sections, which is an assumption in itself. In order to calculate a single group cross section to determine estimates on the attribution indicators, a fast-to-thermal ratio will be assumed. This fast-to-thermal ratio is assumed to be constant, when in reality it may not be. This assumption is necessary for the calculations, but also may be valid because lower burnups are more common for weapons grade plutonium. Then the indicators of flux magnitude, initial enrichment, and fuel age will be determined. Then, another fast-to-thermal ratio will be assumed with the same calculation ensuing. This will be done for a wide range of fast-to-thermal ratios and the most internally consistent set of results will then be compared to results from MCNP and hopefully this methodology will provide a similar answer. This methodology should also provide a fast-to-thermal ratio which would give an indication to what type of reactor the fuel was irradiated in.

The flux magnitude calculation will be completed with the typical burnup monitor 148Nd29, 32. These monitors are known to build into the fuel matrix linearly as a function of burnup, and typically a fission yield is used in order to calculate an actual value. In the case of 148Nd there is a potential for a sizeable amount of contribution from the 147 mass chain, and therefore, an effective yield value would be necessary for this calculation, especially in thermal systems33. If burnup for the system were already known, say with 137Cs, then the effective yield could be used to solve for fluence rate from a balance equation of 148Nd. This is how this calculation will be performed.

Given that only a single isotope undergoes fission in a system, the initial enrichment of a sample would increase linearly with burn-up. Most systems have fissile material transmuted into the system through capture reactions. Due to this, multiple isotopes fission, and more complicated analysis is required. Even so, a series of conservation equations may be solved iteratively with the assumption that burnup, heavy metal compositions, and single group cross sections are known. This methodology was presented by Doyle34, and will be used for this calculation.

The fuel age will be determined with a simple decay calculation, but requires information from all of the above analyses as well as a Bateman solver with readily changeable one group cross sections. These are needed to estimate the expected value of a radioactive species in a fissioning system at a particular burnup with particular cross sections. The radioactive species should have some level of independence for its yield for different fission isotopes and be readily found in the fuel matrix.

***Experimental procedure:***The experimental part of this project will focus on developing a benchtop scale PUREX process, and analyzing this process. The PUREX process extracts cations of U and Pu from nitric acid by forming complex compounds with TBP and subsequently partitions uranium and plutonium by reducing plutonium (in this case with Fe[II]). First experiments will be conducted to verify that these two process step (extraction and back-extraction) for PUREX are performing as expected for the heavy metals, and subsequent experiments will be conducted for the determination of DCs for the two steps as well as DFs for a four extraction/three back-extraction process.

The irradiated DUO2 pellet, containing fission products and Pu, will be dissolved in HNO3 for the experiments. The two main solutions used in this process are HNO3 and 30 vol.% tri-n-butyl phosphate (TBP) in a kerosene diluent. Quantification of material in these two respective solutions at various process steps will be done with a standard Canberra electrode coaxial High Purity Ge (HPGe) detector. The HPGe is a semiconductor detector which has the advantage of distinguishing gamma ray peaks at resolutions of 10 keV, which is important because the fuel matrix has several gamma emitters. The data collected will be in the form of count rates in a gamma spectrum, and calibration sources will be used to convert these values to mass. Due to the large number of gamma spectrums that need to be collected and analyzed, a program will be written to automate analysis for a number of radionuclides.

Aqueous samples will additionally be analyzed for plutonium content through mass spectroscopy and alpha analysis. Due to cost constraints, mass spectrometry will only be applied to a single process, while alpha analysis will ensue for the others. The NexION 300X quadrupole ICP-MS will be utilized for gathering mass spectrometric data. This machine works by drying, atomizing, and ionizing liquid samples. These samples are then passed through cone filters, curved in a quadrupole ion deflector, purified in a universal cell, refined in another quadrupole with a final mass to charge filtration and focused on a dual mode detector. The detector registers counts per second for particular isotopes masses and calibration with seven different standards will be used to determine isotopic concentrations for a range of isotopes and elements.

Alpha analysis on will occur with a passivated implanted planar silicon (PIPS) detector produced under the auspices of Canberra. The spectrometer model 7401, multichannel analyzer, and NimBin model 2100, were also made by Canberra. Calibration will utilize a 4-peak Pu, Am, Gd, and Cm source from Eckert and Ziegler. Samples from aqueous solutions will first be diluted and then 10-20 μl volume samples will be dried on an aluminum surface.

Each extraction or back-extraction removes a certain percentage of dissolved material based on DCs. This is here defined as the ratio of grams per liter of solute in organic solution over grams per liter of solute in the aqueous solution, shown in Equation 3, describes the steady state location of any species in the system7. DCs are specific to an element and vary widely with the concentration and temperature of the solvents. DCs will be determined with the above analytical tools.

Equation Distribution Coefficient

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

1. **Expected Results**

***Completed Analytical*:** Equations for burnup, flux magnitude, initial enrichment, and fuel age have been settled upon. A program was written to set up and solve an ORIGEN235 type system with options for tweaking cross section information, something that ORIGEN2 does not allow simply. The solver uses a best rational approximation, which reduces calculation time for each solution, which also presents an option for quantifying uncertainty in these calculations. Additionally programs have been set up for calculation of single group cross sections given a flux spectra. These pieces of code still need to be linked together in a single package so that a fast-to-thermal ratio can be determined iteratively and final results for the forensic analysis presented. These results will include pre and post processed plutonium with the expectation that preprocessed plutonium will produce more accurate results. “Accuracy”, in this instance, will be determined by the closeness of these determined values to what MCNP predicts.

***Completed Experimental*:** The experimental procedure for separating uranium and plutonium from fission products (extraction) as well as Pu and U from each other (back-extraction) has been experimentally verified. Experiments with natural uranium analyzed with mass spectrometry were conducted to ensure that uranium does not proceed to the product solution. Initially a low nitric acid concentration in the back-extraction solution caused the uranium to proceed to the product, but increasing the concentration remedied this problem because the aqueous phase already had nitrate ions. Also a single extraction and back-extraction was conducted to ensure that plutonium separates from uranium in the final aqueous solution.

A process, containing four extractions and three back-extractions, has been completed and analyzed with mass spectrometry. The results, containing DCs and DFs for several elements, for this and the previous experiment were published36. This process was improved, and completed three full times, with several other partial experiments. All of the process steps have been analyzed with gamma spectroscopy and several still need alpha spectrums collected. The DF results for the second round of experiments are expected to be better in the sense that purer plutonium is being produced by this process.

***Unexpected Results*:** If results for either part of the proposed research do not come out as expected, results will still be presented so that future generations can learn from this experience. For example, if plutonium were not extracted for a series of experiments, then the results would still be valid for the described process.

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