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Names of the authors: Tarun Bhardwaj1,Paul Mendoza1, Jarrod Allred1, Mathew Swinney1, Sunil Chirayath1, Charles M. Folden III2

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Affiliation and address of the authors: 1Nuclear Security Science & Policy Institute, Department of Nuclear Engineering, 2Cyclotron Institute, Texas A&M University, College Station, TX 77843, USA

E-mail address of the corresponding author: Folden@comp.tamu.edu

**Nuclear Forensics Measurement of Fission Products in Weapon Grade Plutonium for Fast Spectrum Reactors**

Tarun Bhardwaj+,Paul Mendoza+, Jarrod Allred+, Mathew Swinney+, Sunil Chirayath+, Charles M. Folden III\*

1Nuclear Security Science & Policy Institute, Department of Nuclear Engineering, 2Cyclotron Institute, Texas A&M University, College Station, TX 77843, USA

Abstract

The future nuclear threat posed by the plutonium puduced in fast spectrum reactors requires the development of more advanced and accurate nuclear forensics techniques. This project used the experimental methods to determine a unique intrinsic physical signature of weapon grade plutonium, which can be produced in fast spectrum reactors of foreign nuclear fuel cycles. Six small depleted uranium dioxide pellets with 0.3% enrichment and weighing about 13 mg were irradiated in the High Flux Isotope Reactor of Oak Ridge National Laboratory to 3000 MWd/t under a fast neutron flux spectrum, over the course of three months. The irradiated pellet was cooled down for………and a thorough gamma spectroscopic analysis was performed before its dissolution. The irradiated pellet was dissolved in 5 ml of 16M HNO3 for two hours at 50°C temperature. The fission product gases, 3H, 14C, 85Kr, 131-136Xe, 129I, 81Br and the oxides of nitrogen such as N2O, NO, N2O3, N2O4, and N2O5 were capture in a liquid nitrogen cold trap. The dissolved DUO2 pellet was carried through a laboratory scale Plutonium URanium Extraction (PUREX) process to recover the plutonium and analyze cesium, europium, rhodium, antimony and zirconium fission products by gamma and inductively coupled plasma mass spectroscopy (ICP-MS) at every stage of plutonium extraction. The decontamination factors for isotopes, 95Zr, 106Rh, 125Sb, 134Cs, 137Cs, 144Ce, and 154Eu were determined to be …………. Simultaneously, the distribution coefficients and ratios of separation for these radioisotopes were determined and the trace level isotopic ratio signatures, existed as a result of naturally occurring contamination, were examined. Detailed understanding of these unique characteristics such as plutonium isotopic content, concentration of uranium and other fission products aided nuclear forensics activities aimed at source attribution. These signatures, when coupled with reactor burnup data, were used to determine plutonium origin. Based on these results, the origin of fuel sample was determined and the results were in agreement with computational studies.

Keywords

Nuclear Forensics, Weapon Grade Plutonium, Fast Spectrum Reactor, PUREX, Fission Products

Introduction

One of the most crucial issues to the national security in the United States is the ability to safeguard the country against nuclear terrorism. The smuggling or detonation of a nuclear weapon in the United States will need immediate information on the nature of the device such as its design, the materials used to build it, and the materials’ source and also the identification of the perpetrators. Nuclear forensics will serve as the technical component of nation’s capability to attribute these types of nuclear events by identify the source of nuclear material. This work is part of an ongoing effort to improve nuclear deterrence by developing a methodology to attribute weapons-grade plutonium to a source fast breeder reactor using an intrinsic physical signature. Former concerns about the limit of worldwide uranium resources motivated initial interest in thorium fuel. As Gen IV concept, Fast Breeder Reactors (FBR) were found attractive because of the thorium's greater abundance, better fuel economy, burnup, reprocessing, waste reduction and also due to the improved resistance to nuclear weapons proliferation. It was expected that the proliferation risk of fast breeder reactors could be managed by closed fuel cycle. However, since plutonium is produced from depleted uranium in breeding cycle, fast breeder reactors now even pose a higher proliferation risk.

Plutonium isotopes, 238Pu, 239Pu, 240Pu, 241Pu and 242Pu, are produced in various amounts in depleted UO2 blanket of FBRs. Plutonium isotopic characteristics essentially depend on the amount of fuel burn-up, the nature of the neutron energy spectrum to which the fuel was exposed and the amount of time since the irradiation occurred. However, the plutonium isotopic characteristics can be significantly different depending on the fast neutron energy spectrum and depleted uranium used in the fast breeder radial blankets. The weapon grade plutonium produced in FBR blanket can readily be distinguished from other types of reactors based on their isotopic composition. In general, the design aspects of typical FBRs require that the main core fuel elements be replenished about every six months. During this six month period of normal FBR operation, depleted uranium in the blanket region will experience a burnup of about 1 GWd/t. Consequently, any country operating FBR will typically be generating significant amount of high quality weapon grade plutonium.

When developmental FBRs begin operating in the near future, it will be very useful for the Domestic Nuclear Detection Office’s global nuclear detection architecture to understand the details of a potentially unique fingerprint associated with plutonium produced in depleted uranium blanket of FBRs. Detailed understanding of these unique characteristics such as plutonium, uranium and other fission product isotopes will contribute to the nuclear forensics activities targeted at the origin source of interdicted smuggled plutonium (pre-detonation material) as well as to some extent for post-detonation analysis. In a situation like this, experimental radiochemistry will eventually provide the most accurate analysis of interdicted smuggled or post-detonation plutonium. For higher quality application of nuclear forensics, destructive analysis on plutonium will be required to produce more accurate and precise results as compared to the non-destructive analytical techniques. Therefore, the main goal of this project was to separate the plutonium from depleted uranium dioxide (DUO2) fuel pellet, irradiated under the FBR environment, and measure the isotopic content of 238Pu, 239Pu, 240Pu, 241Pu and 242Pu, 95Zr, 106Rh, 125Sb, 134Cs, 137Cs, 144Ce, and 154Eu fission products at different stages of chemical processing.

Most of the work on technical nuclear forensics has been the computational studies which demonstrate the ability of isotopic data to retain information about the source of the produced special nuclear material. An application of using isotopic composition and ratios in spent nuclear fuel utilized measurement of isotopic ratios of stable noble fission product gases during reprocessing in order to verify burnup. Although, the isotopic ratios and database developed by this technique are not useful for analyzing the post-processed materials. Others have studied the spent nuclear fuel to determine the burnup, enrichment and the age of the fuel.[[5](#_ENREF_5)] This combined data was then subsequently used for reactor attribution purpos. This study looked at fission products in the matrix of fuel without any consideration of chemical anlaysis and deduced reactor type and information about the history of the fuel. Analysis of plutonium isotopes alone has also been studied to help identify the fast nuclear reactors.[[11](#_ENREF_11)] Although, this technique was able to distinguish plutonium produced in fast reactor from the thermal reactor, it was difficult to distinct it from other types of reactors. Besides, this study did nto consider the other isotopes and was limited in precisely determining the type and burnup of the reactor.

Previous experimental work in the area of attribution has also been carried out but with varied implementation and scope.[[1-7](#_ENREF_1)] In one study, 239Pu production from 238U was investigated on the basis of experimental data. 238U samples were irradiated in the experimental fast reactor of Joyo, Japan under various irradiation conditions. Then, the isotopic composition of U, Pu and Nd was measured by chemical analysis. Based on these experimental studies, 239Pu production ratio (239Pu atoms to initial 238U atoms) and burnup of the reactor were determined for different irradiation areas.[[1]](#endnote-1)

In a real case study, two UO2,134Cs and 137Cs contaminated metal pieces were found in Karlsruhe, Germany in 1997, with 235U enrichment varying up to 89.1%. The analysis of the metal pieces showed that they were stainless steel. Later, the elemental composition and dimensions of steel revealed its origin of material to be the BR-10 fast spectrum reactor in Obninsk, Russia.[[2]](#endnote-2) Although successful, the source attribution was actually based on the fuel rod analysis and there was little contribution of fuel characteristic. Another paper described the determination of trace-level activation products, 232U, 236U, 239Pu, 240Pu and 241Pu, by different analytical methods such as alpha spectrometry and ICP-SFMS using solution based nebulization and laser ablation. This technique only identiﬁed the raw material used for fuel fabrication and the irradiation conditions to reveal the provenance of the illicit material and that was also with the comparison of suitable databases.[[3]](#endnote-3)

Recently, analytical techniques for age determination of plutonium have also been studied in the field of nuclear forensics [1]. Wallenius et al. determined the age of plutonium, after the separation, in solutions based on 238Pu/234U, 239Pu/235U and 240Pu/236U ratios by isotope dilution thermal ionization mass spectrometry (TIMS) [2]. Chen et al. used TEVA and TRU resins to separate plutonium, americium and uranium in plutonium solutions for subsequent isotope dilution analysis with inductively coupled plasma mass spectrometry (ICP-MS) [3]. The age of plutonium was determined based on the 241Pu/241Am and 240Pu/236U ratios. Again, this study lacked the foundation of a link between plutonium and its source of origin.[[4]](#endnote-4) One study looked at PUREX co-processing of spent LWR fuels.[[7](#_ENREF_7)] A couple of decontamination factors and production yields for uranium and plutonium were determined, however, this study was limited in determining decontamination factors for a wide array of isotopes that could be used for the nuclear forensics purpose of FBR generated weapon grade plutonium. Besides, there have been several books and papers that have studied the PUREX process. Variations in solvent concentrations and flow rates coupled with uranium saturation have been studied extensively. Although, the distribution coefficients between organic and aqueous phases in 30% TBP have been reported for several isotopes under different circumstances, in reality they contribute very little to the nuclear forensics for the fast spectrum reactor source attribution.[[12](#_ENREF_12)]

While these computational studies were never supported by experimental results, the experimental studies in themselves are conducted by the analysis of sequestered one, two or more radioisotopes mixed together exaggeratedly. There has been no study in literature that creates the real world senario of weapon grade plutonium production and separation from fast spectrum reactor. Furthermore, these studies attribute nuclear material to a source reactor based on age determination, fuel rod analysis, spent nuclear fuel composition and irradiation typically to an average burn-up level, where the composition of plutonium is not weapons-grade.

Therefore, we developed a new computational model by using trace fission product to plutonium ratios for nuclear forensics attribution of plutonium to fast breeder reactors, used for its production. This model was then tested experimentally for quantifying the confidence and predictive accuracy. Experimental validation determined the degree to which this model is an accurate representation of the real world from the perspective of the intended use. Unlike previous studies, this model verification and validation was important to provide the quantified level of agreement between experimental data and model prediction, as well as the predictive accuracy of the model. This study provides a comprehensive list of distribution coefficients of plutonium and other fission products not only in TBP in contact with nitric acid but in contact with ferrous sulphamate as well. Applying radiochemical technique for the determination of plutonium and other fission products isotopic ratios provided an accurate and precise information about the origin of weapon grade plutonium in a fast breeder reactor.

Theory

Selection of Isotopic Ratios

The Pu-239 is produced in major quantity by the neutron capture of 238U in depleted UO2 in a fast neutron environment by the following reaction.

Besides 239Pu, other isotopes of plutonium such as 238Pu, 240Pu, 241Pu and 242Pu are also formed in various amount. These isotopes, all combined together, make the basis of weapon grade Pu vector that is directly correlated to the burn-up and type of a reactor. More specifically, the weapon grade Pu vector depends on the neutron energy spectrum, the amount of time passed after the irradiation and the type of uranium used in the fast breeder radial blanket, i.e. 99.75% 238U. The detailed characterization of weapons-grade plutonium also includes the various fission product contaminants originated from the chemical processing of the irradiated fuel such as 95Zr, 106Rh, 125Sb, 134Cs, 137Cs, 144Ce, and 154Eu. These specific fission products were selected based on the amount of their production, detection by gamma and mass spectroscopy, relatively longer half-life and high radioactivity, dependence of fast neutron spectrum on the production and the decontamination factor of the isotope during the chemical separation process of plutonium. Even after going through several separation and purification cycles, final weapon grade plutonium product contains these fissoin products as impurity. These fission products are produced in different amount in different reactors and make their own way to the finally separated weapon grade plutonium in different quantity based on their specific chemistry while going through the chemical processing. Therefore, besides the isotopes of plutonium, the quantitative and qualitative information of these fission product radioisotopes also is necessary to determine the source of weapon grade of plutonium.

The radioisotope 137Cs was selected for its high individual fission yield of about 6 percent, long half-life of over 30 years and the easily measurable gamma radiation. 137Cs is a direct fission product with a fission yield that is constant regardless of fissile isotope or neutron energy. The 134Cs, 125Sb and 154Eu were again basically selected based on their prompt analysis by gamma spectroscopy. However, the radioactivity concentrations for these gamma emitting isotopes are orders-of magnitude less than the 137Cs and 144Ce. The concentration of 144Ce is relatively high in weapon grade plutonium and it undergoes beta radiation decay followed by gamma emissions of 134 keV, for the prompt gamma spectroscopic measurements. 148Nd, on the other hand, was chosen because making it is a good burn-up indicator due to its small cross section and relatively large total fission yield, while the fission yields of the main fissile isotopes 235U, 239Pu and 241Pu are almost the same. 150Sm was chosen on the fact that plutonium produced in a fast spectrum reactor will have two orders-of-magnitude more 150Sm contamination than plutonium produced in thermal neutron spectrum because of the radiative capture cross section of neutron poison fission product 149Sm.

To aid the forte, multiple and diverse routs were added to this nuclear forensics analysis method. Not only the individual isotopes, this method also took the other fission products to 239Pu ratio in account. The fission products to 239Pu ratio provides the exact statistics about the source FBRs because these reactors produce relatively a large amount of plutonium. Besides, the different isotopes of individual elements were taken in account in this study. Different isotopes of individual elements are produced in different amount in FBRs. However, during the chemical processing, they behave as sole element and proportionally present in separated plutonium. The presence of these specific isotopes further attribute to the accuracy of statistics regardless the differed chemical process used to separete plutonium. For example, 137Cs and 134Cs are produced and will be present in plutonium in significantly different amount. On the other hand, 150Sm to 154Sm and 242Pu to 239Pu ratios are more than an order-of-magnitude different in case of FBR.

Experimental

**Fabrication of DUO2 Fuel Pellets**

The fuel pellets were fabricated using commercially available DUO2 powder supplied by AREVA. The powder charge of ~0.5 g was poured into a 12.70 mm diameter cylindrical die and pressed to 30.35 kN (238.8 MPa) to produce a DUO2 wafer approximately 0.065 cm thick. The wafers were sintered at 1800°C for 4 hours using a Nb-1Zr crucible in a graphite furnace under flowing argon. The ramp from room temperature to the sintering temperature and the ramp from sintering temperature to room temperature was 5°C/min. A 3.00 mm precision diamond coring bit was used to core out 3-4 disks from each wafer. The disks were then mounted to an aluminum disk and polished to a target thickness of ~ 0.023 cm using a Struers Allegro disk with 9 μm diamond suspension.

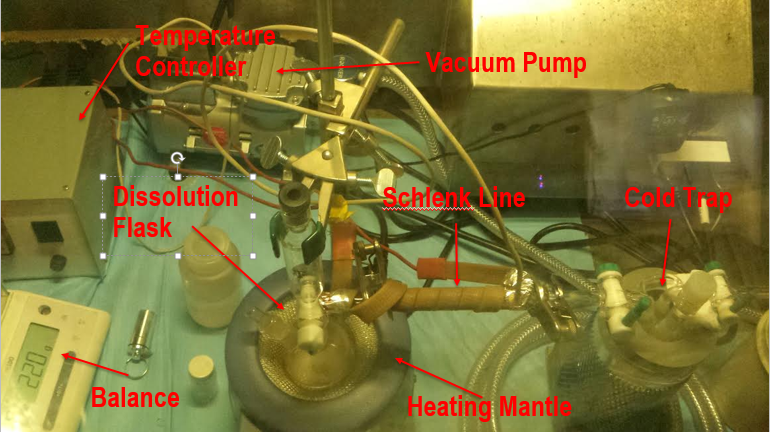
DUO2 Disk Irradiation

The six DUO2 disks were loaded into a Gd shielded rabbit capsule. The design of the shielded rabbit capsule utilized a 22.86 mm Gd thermal neutron shield (designed to maximize the fast-to-thermal flux ratio) that could contain up to six fuel pellets (~3 mm in diameter and ~200 μm thick). Since the diameter of the DUO2 pellets was less than the 3.0±0.03 mm, used in the safety basis calculations for the approved design, thermal analysis of the capsule were performed using a minimum diameter of 2.75 mm. The maximum individual pellet heat load was maintained at 5 W. The safety calculations showed that no melting could occur in the capsule under the prescribed safety condition of steady-state operation at 130% reactor power. This capsule was irradiated in the High Flux Isotope Reactor (HFIR) of Oak Ridge National Laboratory for two cycles over the course of three months.



Fig. 1 Gadolium shielded rabbit capsule for the irradiation

**Dissolution of DUO2 pellet**

After the short lived radioisotopes were decayed, the irradiated DUO2 pellet was weighed on an electronic balance and transferred to a round bottom flask. A solution of 5 ml of 16M 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. The round bottom flask was connected to a cold trap with the help of a heated schlenk line. The fission product gases such as tritium, CO2, Kr, Br, I and several other oxides of nitrogen were captured in cold trap inside the molecular sieves which were surrounded by liquid nitrogen. The dissolved DUO2 Pellet was transferred from the round bottom flask to

**Fig. 2** Dissolution of the Irradiated DUO2 Pellet

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 of dissolution solution was diluted to 5 ml and the concentration of HNO3 was adjusted to 4M. This was subsequently called the “stock solution”. The stock solution was stored in another 20 ml glass scintillation vial in a lead pig inside the glovebox. Each PUREX process used 500 μl aliquots from this stock solution.

The first experiment proceeded with transferring 500 μl aliquot into a 15 ml centrifuge tube. The Pu (III) in aliquot was converted to Pu (IV) by adding 0.5 mg of NaNO2 with subsequent stirring. The solution was left overnight so that NO2 gas completely oxidized Pu (III). This 500 μl aliquot was then contacted with 700 μl of 30% by volume Tri-Butyl Phosphate (TBP), diluted in kerosene, at room temperature. Equal volumes of TBP and stock solution were not used, and an extra 200 μl of TBP was added at contact to create a buffer layer of sorts during the separation phase. A similar procedure was used during the plutonium and uranium separation. Both the aqueous and organic phase were mixed on a vortex mixer for 15 minutes at 1500 rpm, and then separated with the help of a centrifuge. Subsequent contacts of 500 μl TBP occurred to ensure the quantitative recovery of plutonium and uranium from the aqueous phase. The total organic TBP phase was then contacted with an equal volume plus 700 μl of 0.024 M Fe(NH2SO3)2 and 0.75 M HNO3 solution to separate the plutonium from the uranium.

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