

Experimental Characterization of Pu Separation by PUREX Process on a Low-Burnup, Pseudo-Fast-Neutron Irradiated DUO_2 for Product Decontamination Factors and Nuclear Forensics

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**TEXAS A&M ENGINEERING
EXPERIMENT STATION**

**NUCLEAR SECURITY
SCIENCE & POLICY INSTITUTE**

Outline

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- Motivation

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Procedure

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- Mass Spectrometry

- Gamma Spectroscopy Results

- Gamma Spectroscopy Results

- Future Work



Motivation

❖ Current Events

- Joint Comprehensive Plan of Action
- Non-safeguarded reactors
- Islamic State of Iraq and Syria

❖ Past Events

- Septemer 11, 2001

❖ Limited scope of IAEA safeguards

❖ “the awful arithmetic of the atomic bomb”^[1]

❖ Need for improved forensic capabilities^[2, 3, 4]

Definitions

- ❖ Special Nuclear Material (SNM)
 - Plutonium, ^{233}U , or ^{235}U
- ❖ Nuclear Forensics
 - The investigative activity that surrounds the search for attributes of undetermined radioactive specimens for the purpose of attribution.
- ❖ SNM origin attributes/indicators
 - Indicators or clues for SNM origin attribution. Examples include burnup, fluence rate, initial fuel enrichment, fuel age, and fast-to-thermal irradiation ratios
- ❖ Decontamination Factors (DF)
 - A measure of the effectiveness with which a product is decontaminated from a contaminant

$$DF_j = \frac{\frac{c_j}{c_{Pu}}|_{\text{initial}}}{\frac{c_j}{c_{Pu}}|_{\text{final}}}$$

National Context

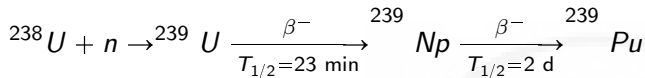
“The United States has developed a nuclear forensics capability that has been demonstrated in real-world incidents of **interdicted materials** and in exercises of actions required after a nuclear detonation. The committee, however, has concerns about the program and finds that without strong leadership, careful planning, and additional funds, these capabilities will decline” [2]

Major areas of concern include:

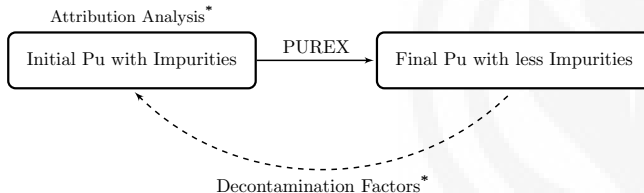
- ❖ Organization
- ❖ Sustainability
- ❖ **Workforce and Infrastructure**
- ❖ **Procedures and Tools**

Forensic Context

- ❖ Nature of inverse problems
- ❖ Plutonium purification necessary for weapons production

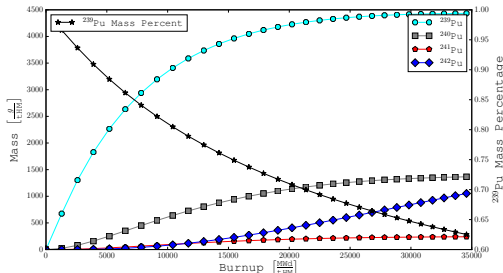


- ❖ Attribution for unpurified Pu has been previously studied [5, 6, 7]



Nuclear Context

- ❖ Weapons-grade Pu can be extracted from reactor discharged fuel with a burnup of about 1 (GWD/tU)
- ❖ Pu isotopes produced in irradiated fuel can vary
- ❖ Two examples of reactors which can intentionally discharge low burned fuel for extracting weapon-grade Pu are:
 - Fast Breeder Reactor, CANDU Reactor



Chemical Context

- ❖ Plutonium Uranium Redox EXtraction (PUREX)
 - Liquid-liquid solvent extraction
 - Many stages:
- ❖ Distribution Coefficient (D): The ratio between the organic and aqueous phases (aka: D-values)

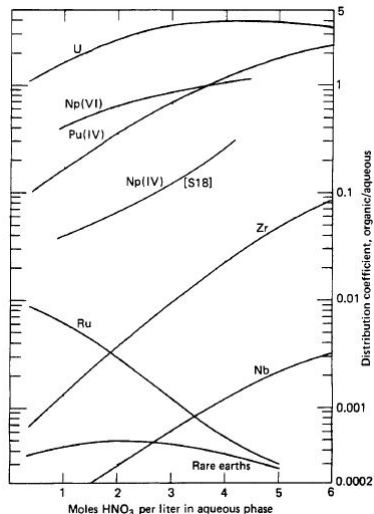
$$D = \frac{c_o}{c_{aq}}$$

- Specific element to element
- Vary widely^[8]
- The fraction of mass, f_o deposited in the organic phase, assuming a volume ratio between the aqueous and organic phases, V_R , is:

$$f_o = (1 + D^{-1}V_R^{-1})^{-1}$$

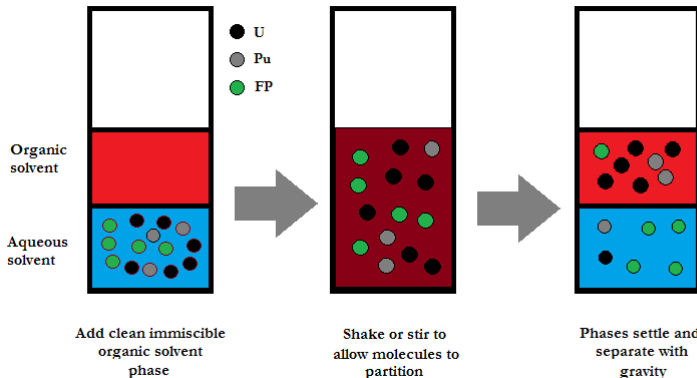
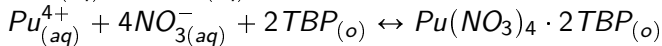
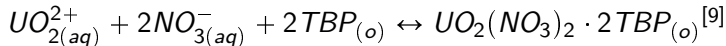
Chemical Context

- ❖ Lack of literature on decontamination factors and distribution coefficients for useful forensic elements (Cs, Sb, Eu, Rb, Sr, Nd, Pm, and Sm)
- ❖ With a known process and D-values, DF values for individual elements can be determined

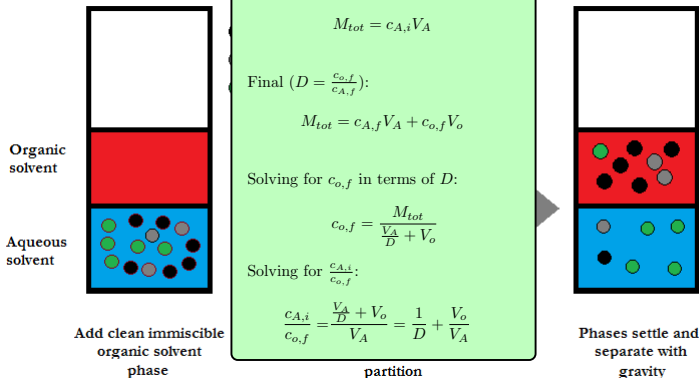
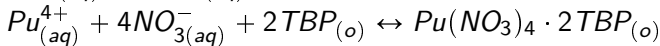
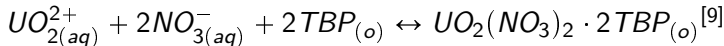


Adapted from Stoller^[8]

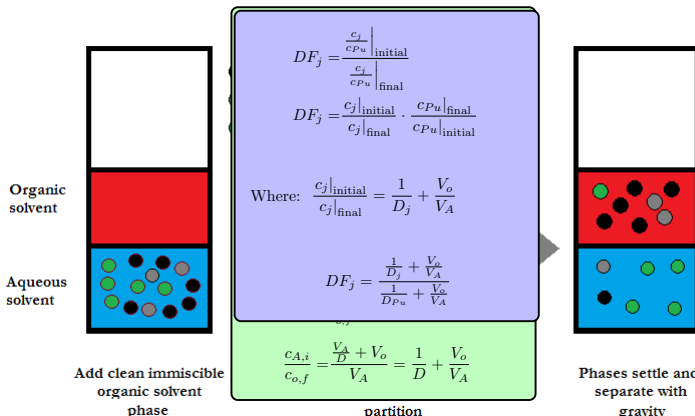
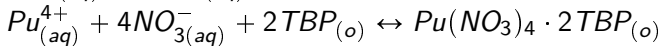
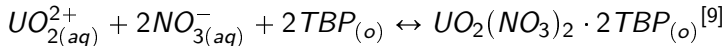
Extraction



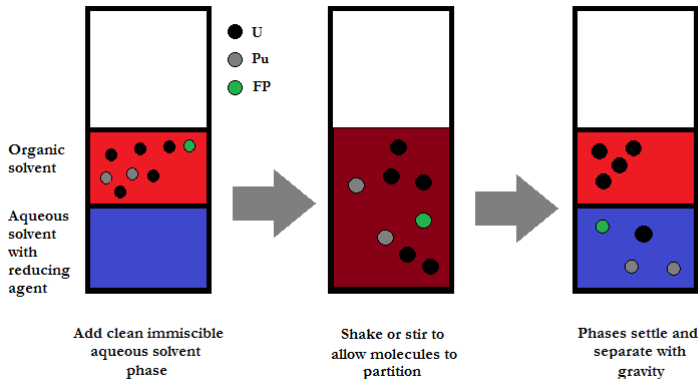
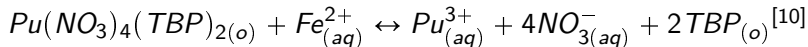
Extraction



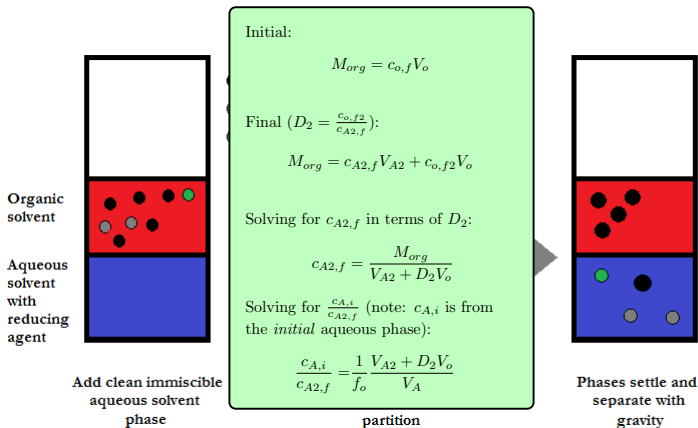
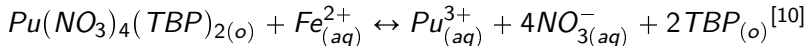
Extraction



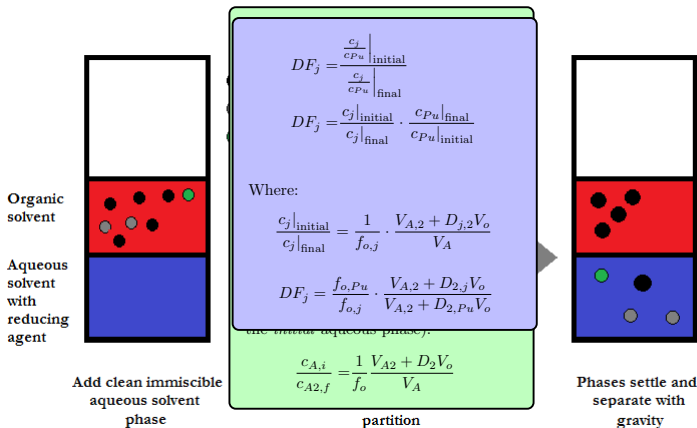
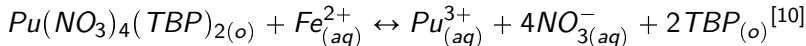
Back-Extraction



Back-Extraction

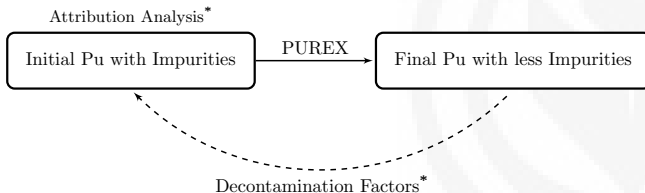


Back-Extraction



Decontamination Factors and their use

- ❖ After several cycles of Pu extraction/scrubbing/back-extraction are completed, the effectiveness of a PUREX cycle is described by the decontamination factor (DF):
- ❖ DFs are characteristic of different process cycles
- ❖ Larger values (10^7) for industrial scale PUREX (compared to benchtop)^[8, 9]



Objectives I

Characterize a 4 extraction 3 back-extraction PUREX process

- Collect D-values for each step
 - ✓ □ $^{144}\text{Ce}, ^{155}\text{Eu}^*, ^{154}\text{Eu}^*, ^{125}\text{Sb}, ^{106}\text{Ru}, ^{134}\text{Cs}, ^{137}\text{Cs}$ (Measured Gamma in triplicate)
 - ✓ □ Convert Gamma Spectrum to D-values
 - ✓ □ $^{85}\text{Rb}^*, ^{90}\text{Sr}^*, ^{97,98,100}\text{Mo}, ^{101,102,104}\text{Ru}, ^{110}\text{Pd}, ^{112}\text{Cd}, ^{133}\text{Cs}^*, ^{140,142}\text{Ce}, ^{143}\text{Nd}^*, ^{147}\text{Pm}^*, ^{151}\text{Sm}^*, ^{154}\text{Eu}^*, \text{U}^*, \text{Pu}^*$ (Mass Spec)
 - Convert all mass spec data to D-values
- Collect DF-values for the process
 - ✓ □ Prepare alpha samples for each step (triplicate)
 - Analyze alpha samples for each step
 - Convert alpha spec + gamma spec data to DF values
 - ✓ □ Convert Mass spec data to DF values (published)
- Mathematically connect D-values to DFs
 - Derive equations with uncertainty propagation
 - Analyze connection with uncertainty

Objectives II

Determine attribution indicators:

- Mathematically derive equations for above indicators with respect to one of the isotopes determined above
 - ✓
□ Burnup
 - ✓
□ Fluence Rate
 - ✓
□ Initial Enrichment
 - ✓
□ Fuel Age
 - Fast-to-thermal ratios (requires iteration)
- Program a system to iteratively solve for these parameters given heavy metal concentration ratios
 - Make a program that can read ENDF files for x-sections
 - ✓
□ Create/Use a bateman solver with automated x-section modifications
 - ✓
□ Create program to calculate single group x-sections from ENDF data and an assumed fast-to-thermal ratio
 - Couple all programs together in a single program
- Use above information to determine indicators for three sets of data

Present Status of the Question

Forensic Status



D-values and DF values



Procedure

Analytical Procedure - Burnup



Analytical Procedure - Fluence Rate



Analytical Procedure - Initial Enrichment



Analytical Procedure - Fuel Age



Analytical Procedure - Fast-to-thermal ratio



Experimental Procedure - Chemistry Procedure



Experimental Procedure - Mass Spectrometry



Experimental Procedure - Gamma Spectrometry



Experimental Procedure - Alpha Spectrometry



Current and Expected Results

Irradiation

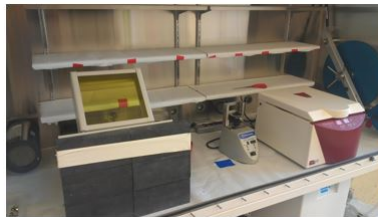
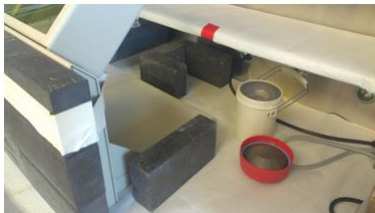
- ❖ 12.9 ± 0.1 mg of DUO_2 was irradiated
 - High Flux Isotope Reactor at Oak Ridge National Laboratory
- ❖ Burnup was 4.43 ± 0.31 GWd/tHM^[11] from ^{137}Cs
- ❖ $0.196 \pm$ mg of total Pu was produced as measured by ICP-MS



Dissolution of the spent fuel pellet



Glovebox



Experiments

❖ Single stage extraction and back-extraction

- Purpose: quantify product recovery, D-values and DF values for single stage extraction and back extraction
- Conditions:

Starting Solution	Extraction Solution	Back extraction solution
4 M nitric acid	30% vol.% TBP, 70 vol.% kerosene	0.024 M ferrous sulfamate in 0.75 M nitric acid

❖ Multi-contact extraction and back-extraction

- Purpose: Quantify DF for a process with 4 extractions, 3 back extractions
- Conditions:

Starting Solution	Extraction Solution	Back extraction solution
4 M nitric acid	30% vol.% TBP, 70 vol.% kerosene	0.024 M ferrous sulfamate in 4 M nitric acid

Mass spectrometry Results

Recoveries of U and Pu

	Pu Recovery	U Recovery
Single stage	$(83.4 \pm 9.5)\%$	$(11.2 \pm 1.3)\%$
Multi-contact Cycle 1	$(99.7 \pm 4.2)\%$	$(6.8 \pm 0.3)\%$
Multi-contact Cycle 2	$(93.0 \pm 4.6)\%$	$(6.6 \pm 0.3)\%$
Overall Experiment 2	$(92.7 \pm 6.0)\%$	$(0.45 \pm 0.03)\%$

Mass Spectrometry Results

Decontamination Factors

Element (Z)	SS	Error	MC Cycle 1	Error	Isotopes Used
Rb(37)	39.0	5.9	11.8	0.8	⁸⁵ Rb
Sr(38)	283	43	84.6	5.9	⁹⁰ Sr
Mo(42)	5.7	0.8	1.9	0.2	^{97,98,100} Mo
Ru(44)	59.2	6.4	16.6	2.5	^{101,102,104} Ru
Pd(46)	65	14	8.9	1.2	¹¹⁰ Pd
Cd(48)	74	17	22.1	2.5	¹¹² Cd
Cs(55)	177	28	52.9	3.9	¹³³ Cs
Ce(58)	43	16	11.5	4.9	^{140,142} Ce
Nd(60)	19.2	2.1	5.9	0.4	¹⁴³ Nd
Pm(61)	12.8	1.9	3.9	0.3	¹⁴⁷ Pm
Sm(62)	11.5	1.5	3.6	0.3	¹⁵¹ Sm
Eu(63)	10.0	1.4	3.6	0.3	¹⁵⁴ Eu
U(92)	7.4	1.2	14.7	0.9	²³⁸ U

Gamma Spectroscopy Results



Initial vs Final solutions



Subsection 5

Future Work

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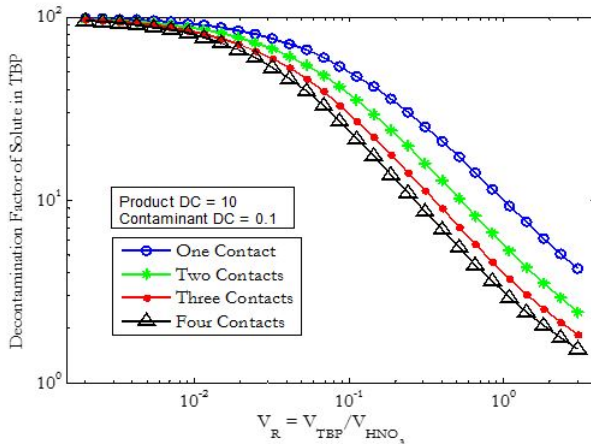
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Questions?

Previous Experiment Results



Decontamination Factors for multi-contact extraction.

References I

- [1] Dwight D Eisenhower. Atoms for peace speech. *Voices of Democracy*, 1953.
- [2] *Nuclear Forensics: A Capability at Risk (Abbreviated Version)*. The National Academies Press, Washington, DC, 2010.
- [3] AAAS/APS. Nuclear forensics: Role, state of the art and program needs. Report, AAAS/APS, 2008.
- [4] Kenton J Moody, Ian D Hutcheon, and Patrick M Grant. *Nuclear forensic analysis*. CRC Press, 2014.
- [5] Sunil S Chirayath, Jeremy M Osborn, and Taylor M Coles. Trace fission product ratios for nuclear forensics attribution of weapons-grade plutonium from fast and thermal reactors. *Science & Global Security*, 23(1):48–67, 2015.
- [6] Mark Robert Scott. *Nuclear forensics: attributing the source of spent fuel used in an RDD event*. PhD thesis, Texas A&M University, 2005.
- [7] Alexander Glaser. Isotopic signatures of weapon-grade plutonium from dedicated natural uranium-fueled production reactors and their relevance for nuclear forensic analysis. *Nuclear Science and Engineering*, 163(1):26–33, 2009.

References II

- [8] Sidney M Stoller, Walter Henry Zinn, Stuart MacLain, and Atomic Energy Commission USA. *Reactor handbook. 2. Fuel reprocessing*. Interscience Publ., 1961.
- [9] M Benedict, H Levi, and T Pigford. Nuclear chemical engineering. *Nucl. Sci. Eng.:(United States)*, 82(4), 1982.
- [10] RJM Konings, LR Morss, J Fuger, LR Morss, NM Edelstein, and J Fuger. The chemistry of the actinide and transactinide elements. *Springer, Dordrecht*, 4:2113–224, 2006.
- [11] Mathew Wayne Swinney. *Experimental and Computational Assessment of Trace Nuclide Ratios in Weapons Grade Plutonium for Nuclear Forensics Analysis*. PhD thesis, 2015.
- [12] Kenneth D Kok. *Nuclear engineering handbook*, volume 60. CRC Press, 2009.
- [13] Sunil S. Chirayath, Jeremy M. Osborn, and Taylor M. Coles. Trace fission product ratios for nuclear forensics attribution of weapons-grade plutonium from fast and thermal reactors. *Science and Global Security*, 23(1):48–67, 2015.

Mass Spec

