

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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AIEN 304



**TEXAS A&M ENGINEERING
EXPERIMENT STATION**

**NUCLEAR SECURITY
SCIENCE & POLICY INSTITUTE**

Outline

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- Motivation

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- Background

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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

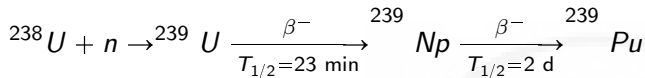
“The United States has developed a nuclear forensics capability that has been demonstrated in real-world incidents of **interdicted materials** and in exercises of actions required after a nuclear detonation. The committee, however, has concerns about the program and finds that without strong leadership,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

Major areas of concern include:

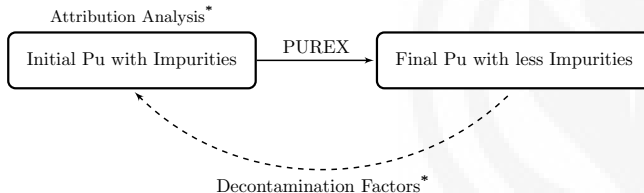
- ❖ Organization
- ❖ Sustainability
- ❖ **Workforce and Infrastructure**
- ❖ **Procedures and Tools**

Forensic Context

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

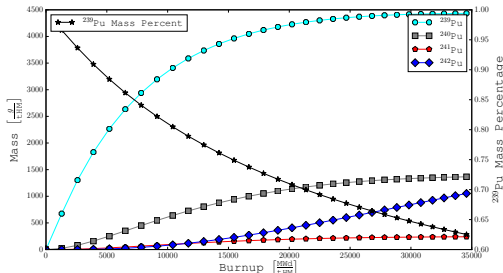


- ❖ Attribution for unpurified Pu has been previously studied [5, 6, 7]



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)

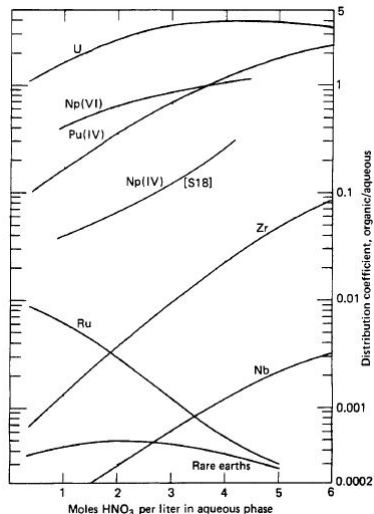
$$D = \frac{c_o}{c_{aq}}$$

- 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:

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

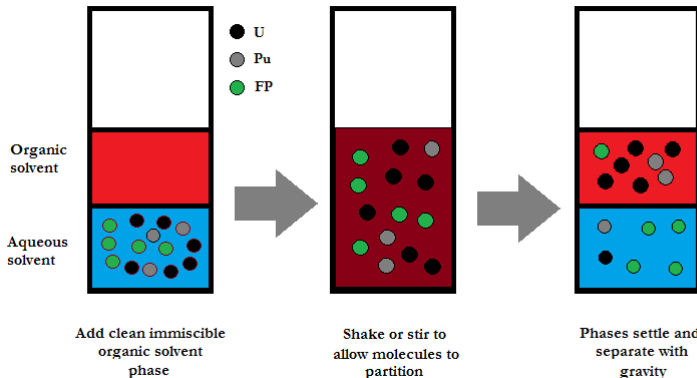
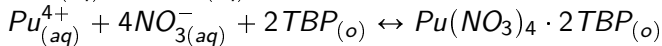
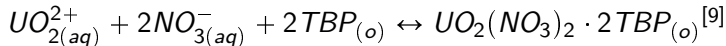
Chemical Context

- ❖ 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

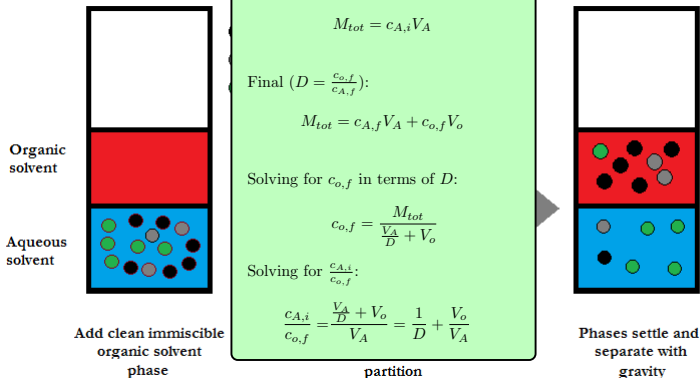
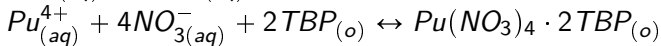
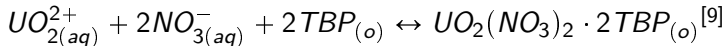


Adapted from Stoller^[8]

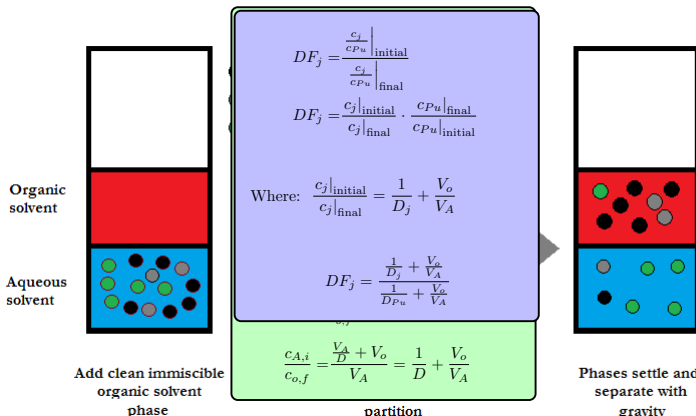
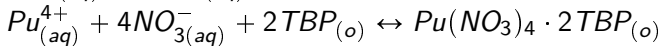
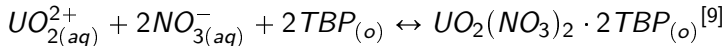
Extraction



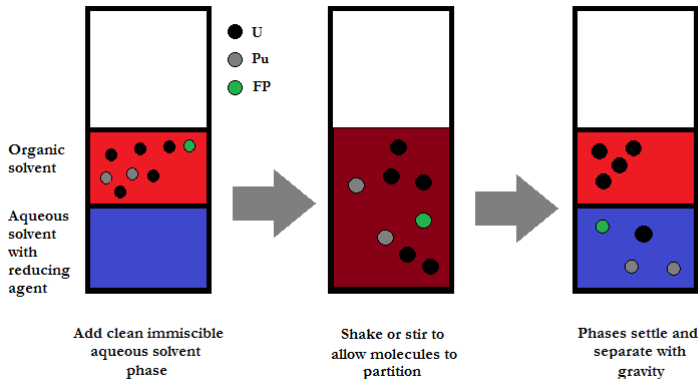
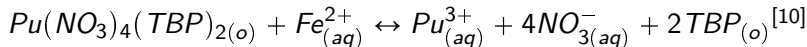
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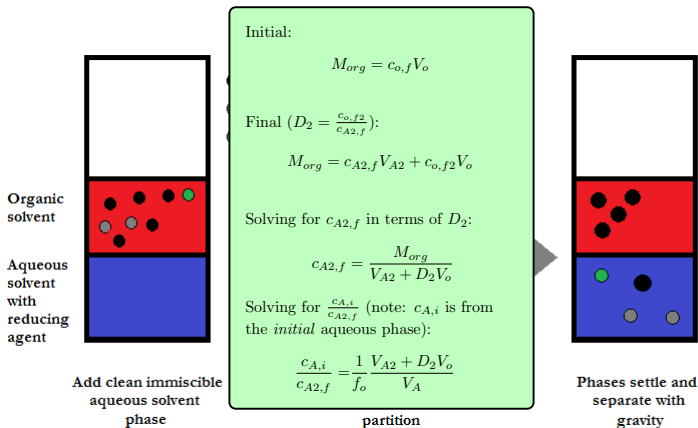
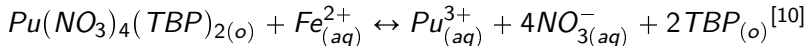
Extraction



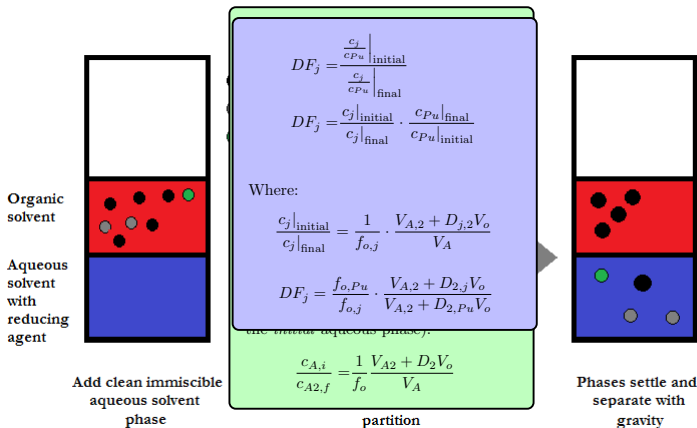
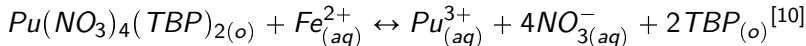
Back-Extraction



Back-Extraction

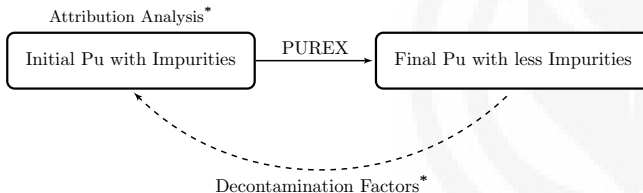


Back-Extraction



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)^[5]
 - ✓ □ 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

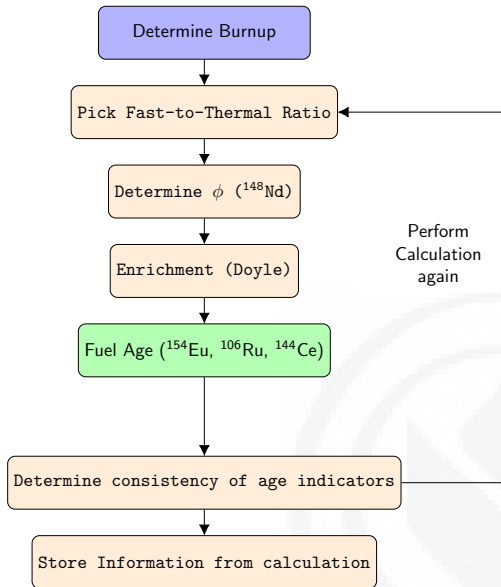
Determine attribution indicators:

- 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

- ❖ Stable noble fission gases as burnup verification^[11]
- ❖ Determine burnup, enrichment, and fuel age from used fuel in a RDD^[12]
- ❖ Analysis of purified plutonium isotopics for reactor type^[13]
- ❖ PUREX co-processing DF values for U and Pu^[14]
- ❖ PUREX D-values and DF values under numerous circumstances^[9, 15, 16, 17, 18, 8]
 - DF values for ¹⁰⁶Ru and ⁹⁵Zr^[8]
 - Compilation of D-values for U, Th, and Pu^[19]
 - D-values for rare earths, Pu, Th^[17, 20, 21, 22, 23, 24, 25, 26, 27, 28]
 - Ga D-values^[28]

Procedure



Analytical Procedure

❖ 12.9 ± 0.1 mg of DUO_2 irradiated at HFIR

$$\frac{dn_i}{dt} = -\lambda_i^{\text{eff}} n_i + \sum_{j=1}^N b_{j \rightarrow i}^{\text{eff}} n_j$$

$$\lambda_i^{\text{eff}} = \lambda_i + \phi \sum_{j=1}^N \sigma_{i \rightarrow j}$$

$$b_{j \rightarrow i}^{\text{eff}} = b_{j \rightarrow i} \lambda_j + \sigma_{j \rightarrow i} \phi + \gamma_{j \rightarrow i} \sigma_{j, f} \phi$$

$$\frac{d\vec{n}}{dt} = \mathbf{A}\vec{n}(t) \rightarrow \vec{n} = e^{\mathbf{A}t} \vec{n}_0$$

Analytical Procedure - Burnup

- ❖ Operational Parameter
- ❖ Calculated:
 - Specific heat calculation on working fluid
 - Number and isotopes that fission in the system
 - **burnup isotope indicator**

$$\begin{aligned}
 BU &= \frac{\text{Power}[\text{MW}] \cdot \text{days}}{m[HM]} \\
 &= \left[\frac{N^B}{N_0^{HM}} \right] \frac{N_A E_R}{\gamma_B} \cdot \frac{1}{M_0^{HM}}
 \end{aligned}$$

Back-Extraction

$(n, \gamma) {}^{137}_{55}\text{Cs} \quad \beta^{-1} \rightarrow {}^{136}_{56}\text{Ba}$ ${}^{136}_{55}\text{Cs}$ 13 days 0.025 eV: 11 Epi: 57	$(n, \gamma) {}^{138}_{55}\text{Cs} \quad \beta^{-1} \rightarrow {}^{147}_{56}\text{Ba}$ ${}^{137}_{55}\text{Cs}$ 0.025 eV: 0.2 Epi: 0.3
	$(n, \gamma) {}^{137}_{54}\text{Xe} \quad \text{Stable 8.9\%} \quad \beta^{-1} \rightarrow {}^{137}_{55}\text{Cs}$ ${}^{136}_{54}\text{Xe}$ 0.025 eV: 0.2 Epi: 0.1
	${}^{137}_{54}\text{Xe}$ 3.8 min

Back-Extraction

$(n, \gamma) {}^{148}_{60}\text{Nd} \rightarrow \beta^{-1} \rightarrow {}^{147}_{61}\text{Pm}$ ${}^{147}_{60}\text{Nd}$ 11 days 0.025 eV: 380 Epi: 630	$(n, \gamma) {}^{149}_{60}\text{Nd}$ Stable - 5.8% ${}^{148}_{60}\text{Nd}$ 0.025 eV: 2.2 Epi: 14
	$\beta^{-1} \rightarrow {}^{147}_{60}\text{Nd}$ ${}^{147}_{59}\text{Pr}$ 13.4 min
	$\beta^{-1} \rightarrow {}^{148}_{60}\text{Nd}$ ${}^{148}_{59}\text{Pr}$ 2.29 min

Analytical Procedure - Fluence Rate

❖ Burnup Indicator assumptions

- Short lived precursors of same mass bin with small cross sections
- **Small contributions from other mass bins**
- *Stable*

$$\phi \approx \frac{\lambda_7}{\sigma_7 \left(\frac{\gamma_7}{\gamma_8^* - \gamma_8} - 1 \right)}$$

❖ Assumptions:

- Build in can be described by constant ϕ , single group x-sections
- Constant fissionable material, σ_a for $^{148}\text{Nd} \approx 0$
- Cumulative yeild instantly arrives at ^{147}Nd
- Utilizes a taylor series expansion

Analytical Procedure - Initial Enrichment and Fuel Age

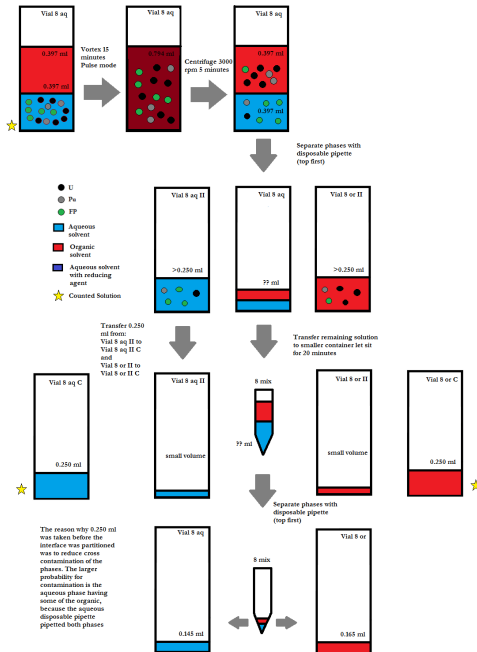
Initial Enrichment

- ❖ Heavy metal converts to heavier metal and to Fission products
- ❖ Account for in Burnup, and mass in heavy metals
- ❖ Solution assumes all higher actinides are built into the system from capture in ^{238}U

$$\epsilon_0 = \frac{N^{U238}(T)}{N_0^U} \left[\frac{N^{U235}(T)}{N^{U238}(T)} + \frac{N^{U236}(T)}{N^{U238}(T)} \right] + \frac{M_0^U}{N_A E_R} BU(T) - G^{238} - G^{239} - G^{240} - G^{241}$$

Fuel Age

$$t_d = -\frac{1}{\lambda} \ln \left(\frac{N_{\text{measured}}}{N_{EOI}} \right)$$



Experimental Procedure - Mass Spectrometry



Experimental Procedure - Gamma Spectrometry



Experimental Procedure - Alpha Spectrometry



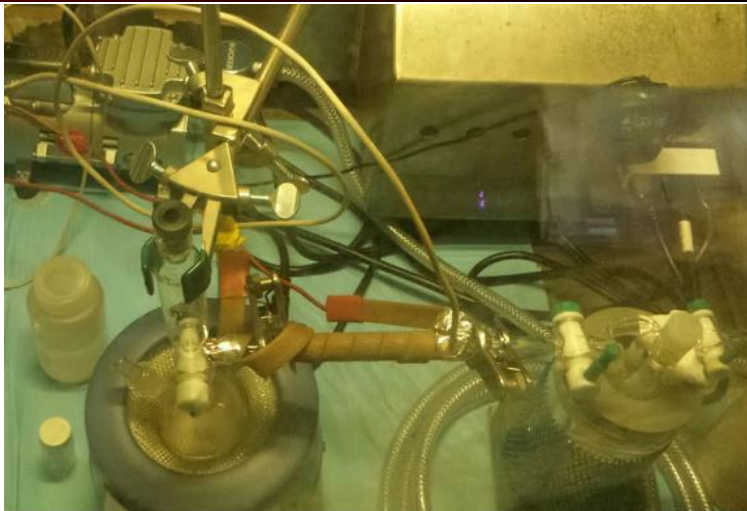
Current and Expected Results

Irradiation

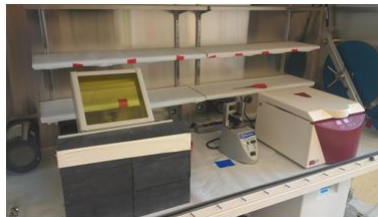
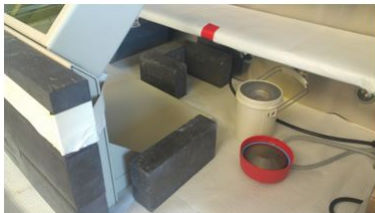
- ❖ 12.9 ± 0.1 mg of DUO_2 was irradiated
 - High Flux Isotope Reactor at Oak Ridge National Laboratory
- ❖ Burnup was 4.43 ± 0.31 GWd/tHM^[29] from ^{137}Cs
- ❖ $0.196 \pm$ mg of total Pu was produced as measured by ICP-MS



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

Objectives I

Characterize a 4 extraction 3 back-extraction PUREX process

- Collect D-values for each step
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 - ✓ ☐ Convert Gamma Spectrum to D-values
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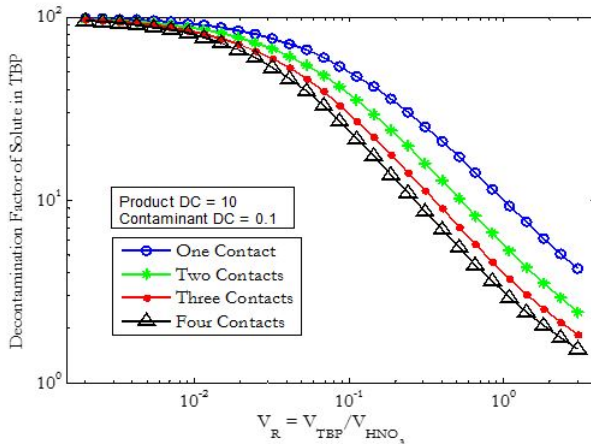
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Determine attribution indicators:

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Questions?

Previous Experiment Results



Decontamination Factors for multi-contact extraction.

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