NUCLEAR ENGINEERING
TEXAS A&M UNIVERSITY

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

A PhD. Prelims Defense by: Paul Mendoza

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Dr. Craig Marianno
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AIEN 304

TEES | TEXAS A&M ENGINEERING EXPERIMENT STATION

NUCLEAR SECURITY SCIENCE & POLICY INSTITUTE

Outline

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 investiative 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

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

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:

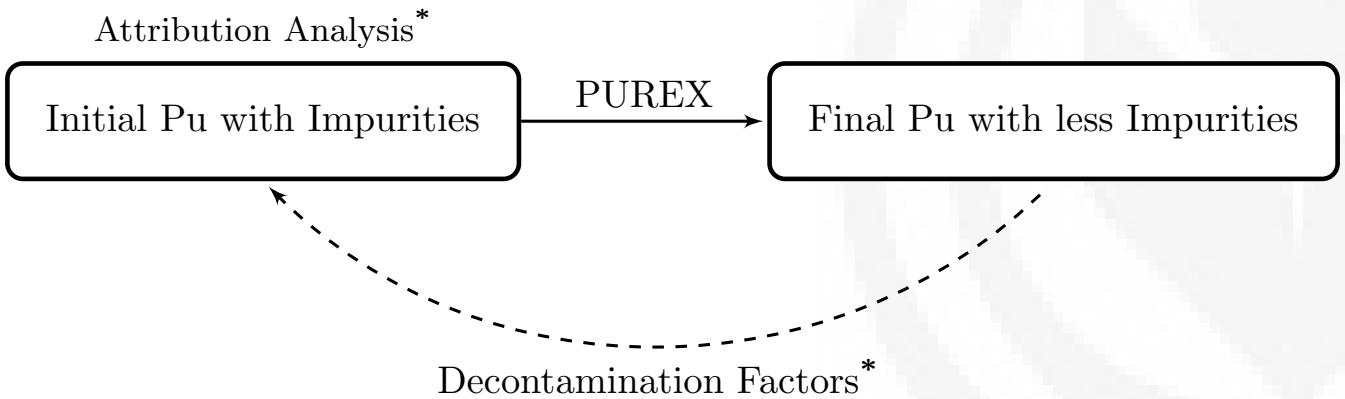
- Organization
- Sustainability
- **Workforce and Infrastructure**
- **Procedures and Tools**

Forensic Context

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

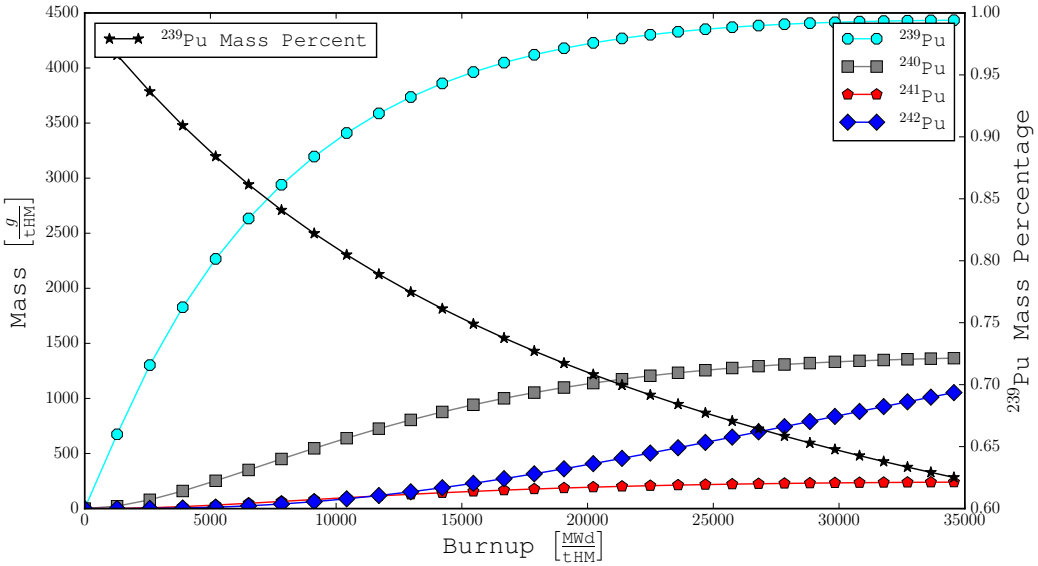
$$^{238}U + n \rightarrow ^{239}U \xrightarrow[T_{1/2}=23\text{ min}]{\beta^-} ^{239}Np \xrightarrow[T_{1/2}=2\text{ d}]{\beta^-} ^{239}Pu$$

- 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)

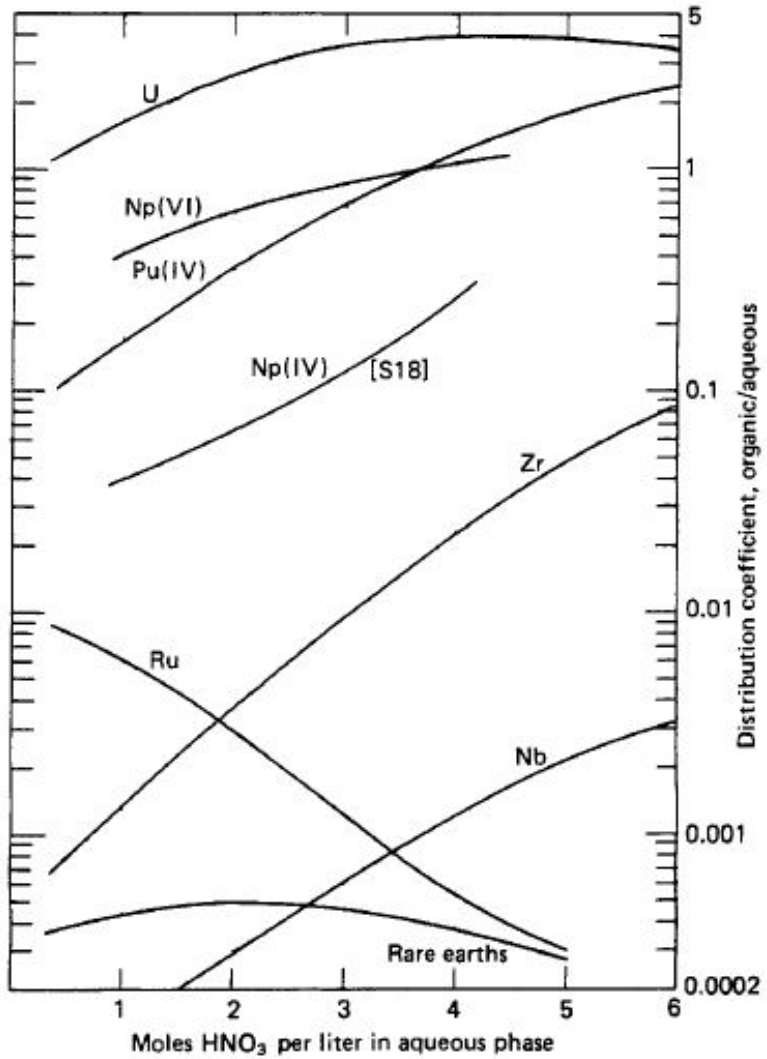
$$D = \frac{c_o}{c_{aq}}$$

  - 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

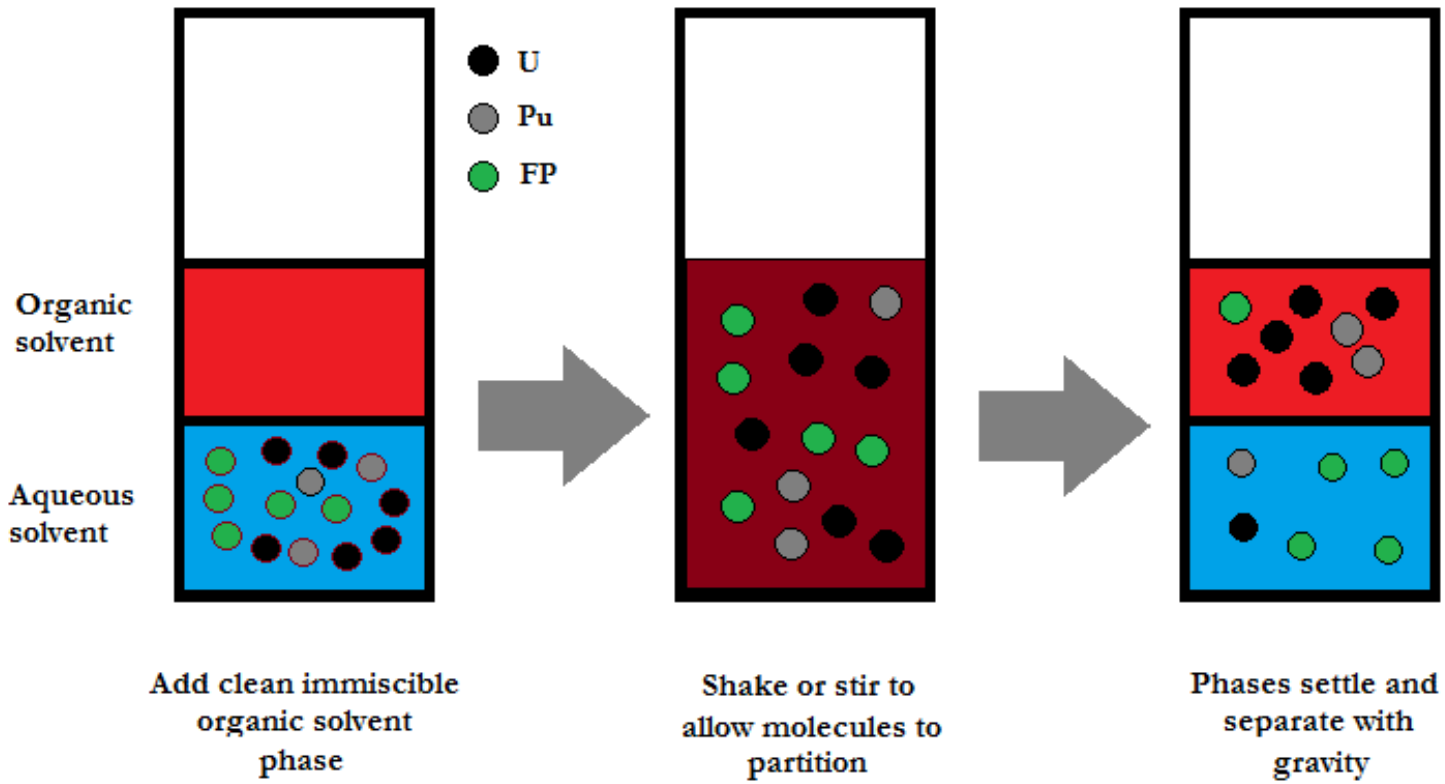


Adapted from Stoller[8]

Extraction

$$UO_{2(aq)}^{2+} + 2NO_{3(aq)}^{-} + 2TBP_{(o)} \leftrightarrow UO_2(NO_3)_2 \cdot 2TBP_{(o)}$$ [9]

$$Pu_{(aq)}^{4+} + 4NO_{3(aq)}^{-} + 2TBP_{(o)} \leftrightarrow Pu(NO_3)_4 \cdot 2TBP_{(o)}$$



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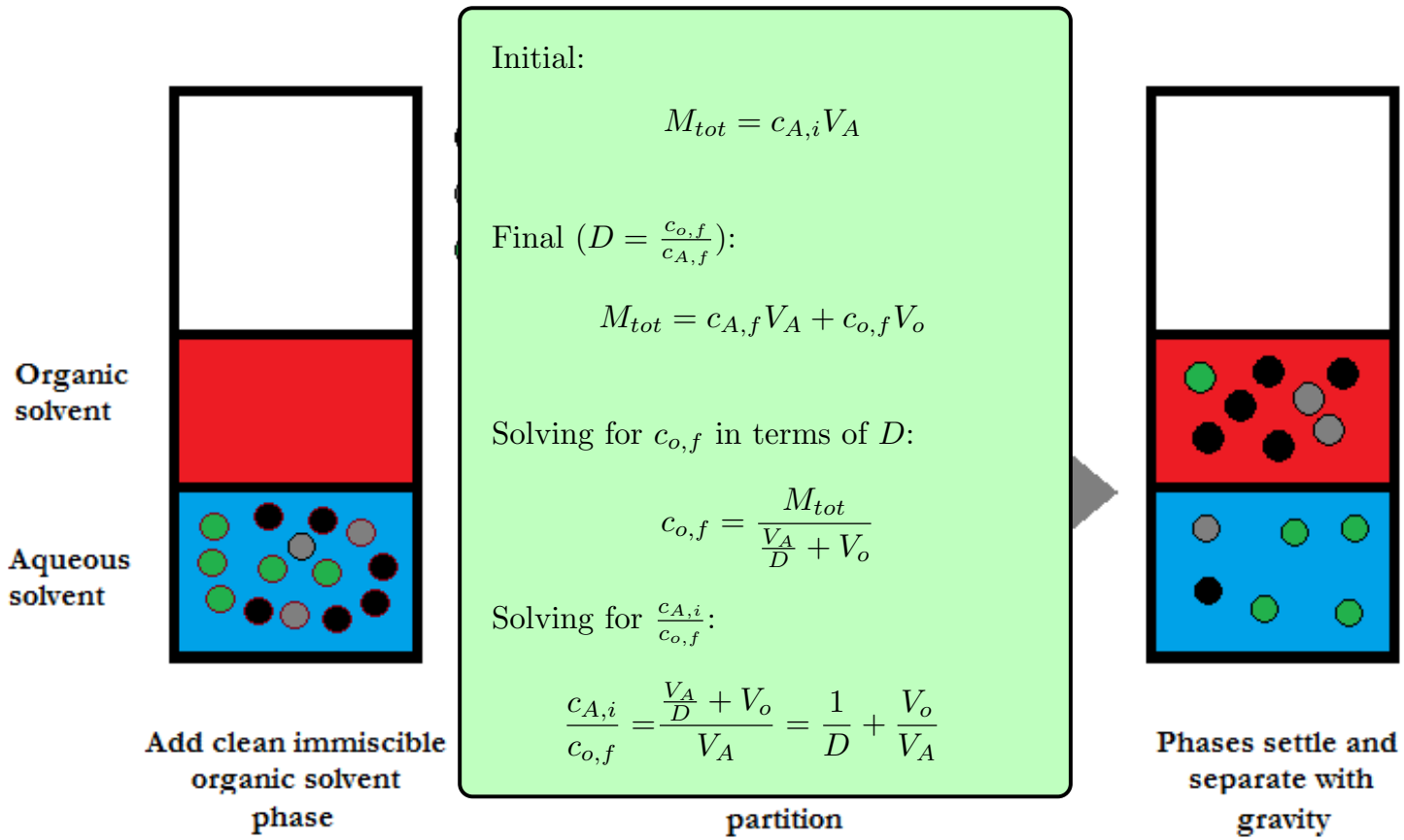

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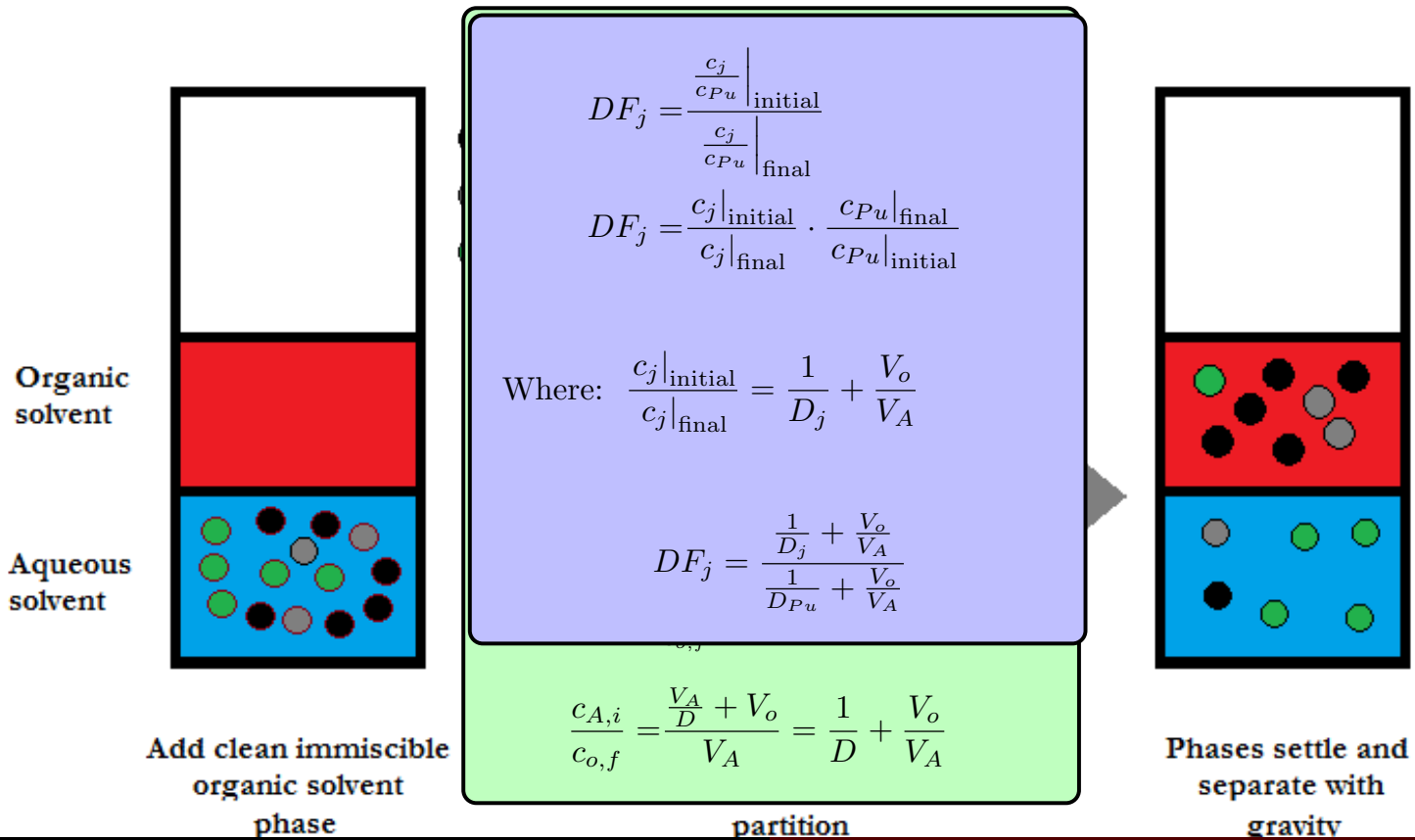
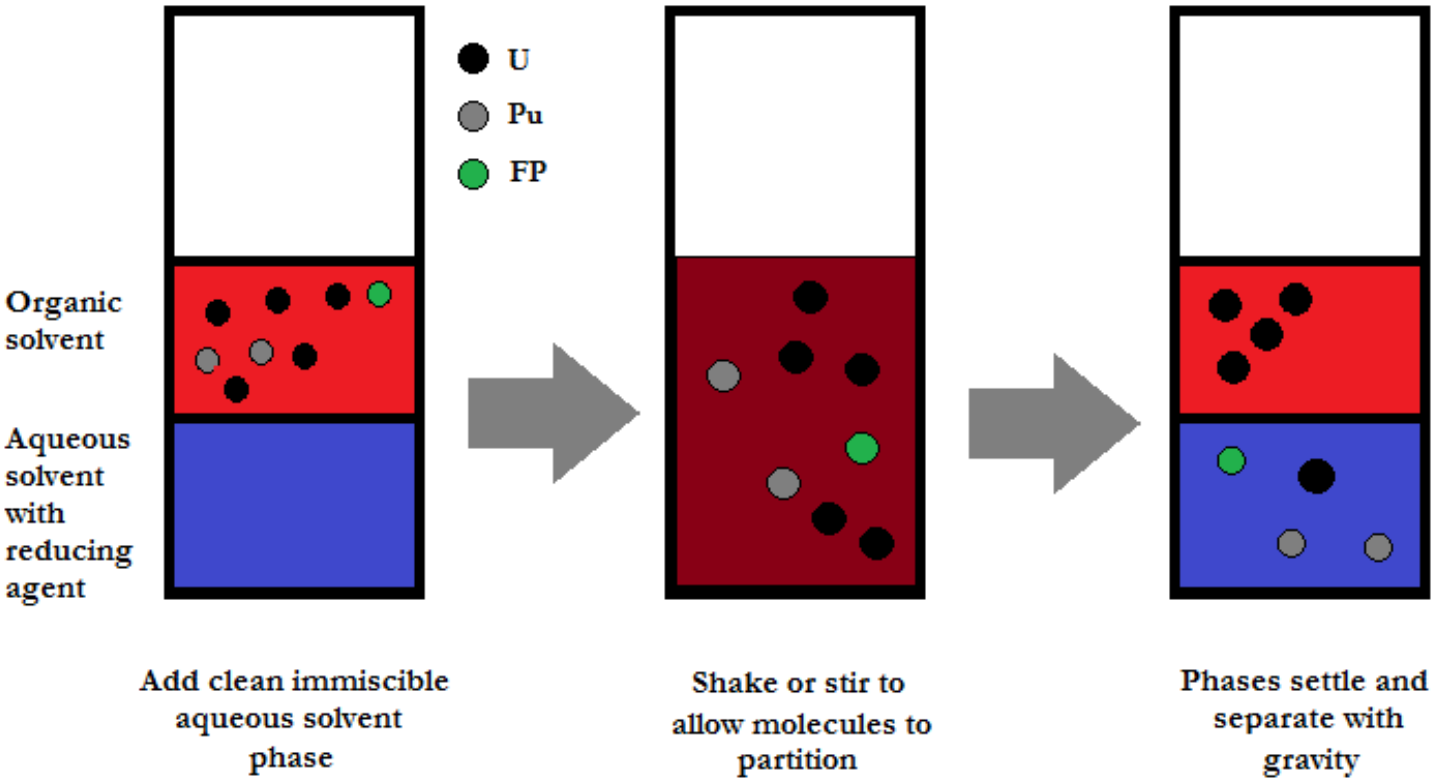


Back-Extraction

$$Pu(NO_3)_4(TBP)_{2(o)} + Fe^{2+}_{(aq)} \leftrightarrow Pu^{3+}_{(aq)} + 4NO^{-}_{3(aq)} + 2TBP_{(o)}$$ [10]



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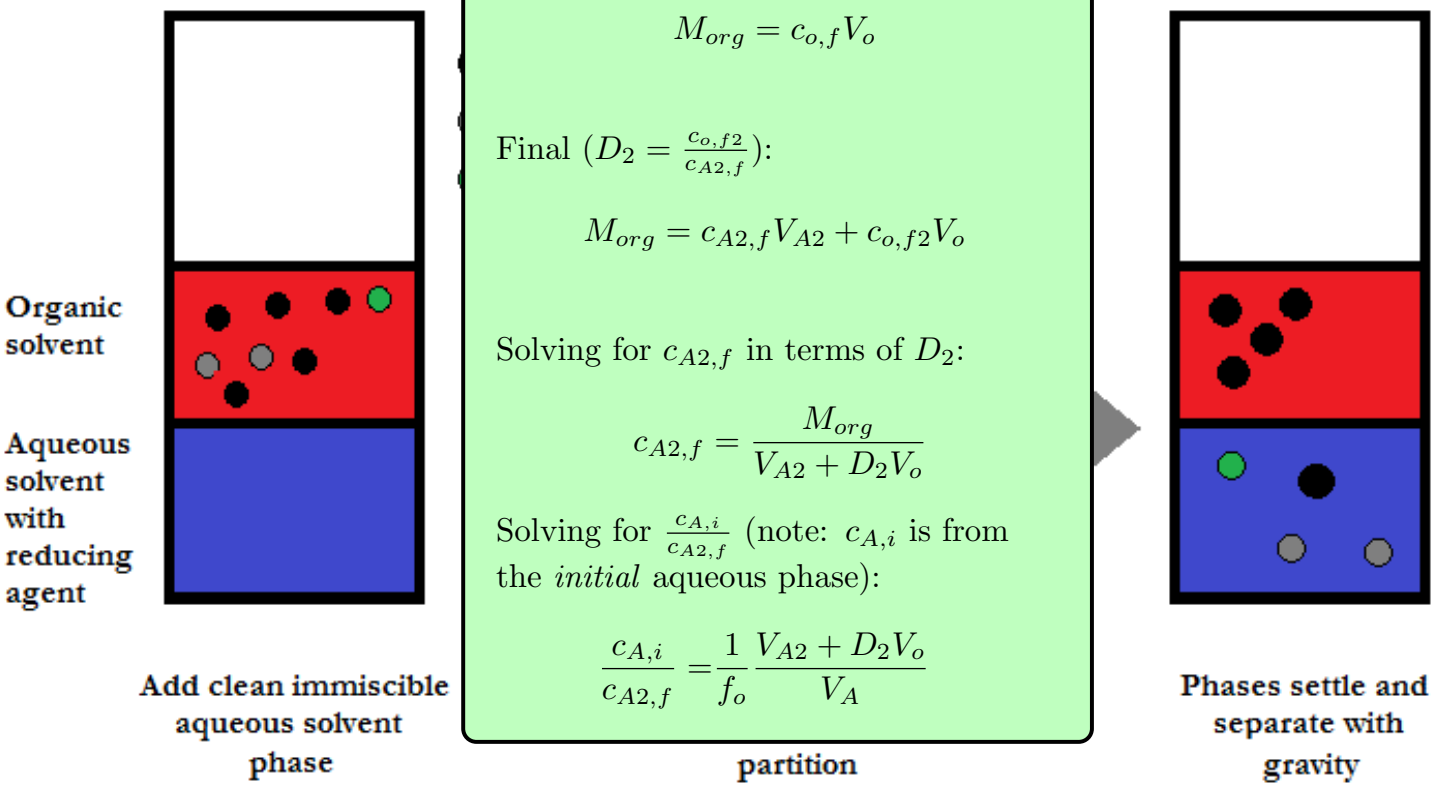

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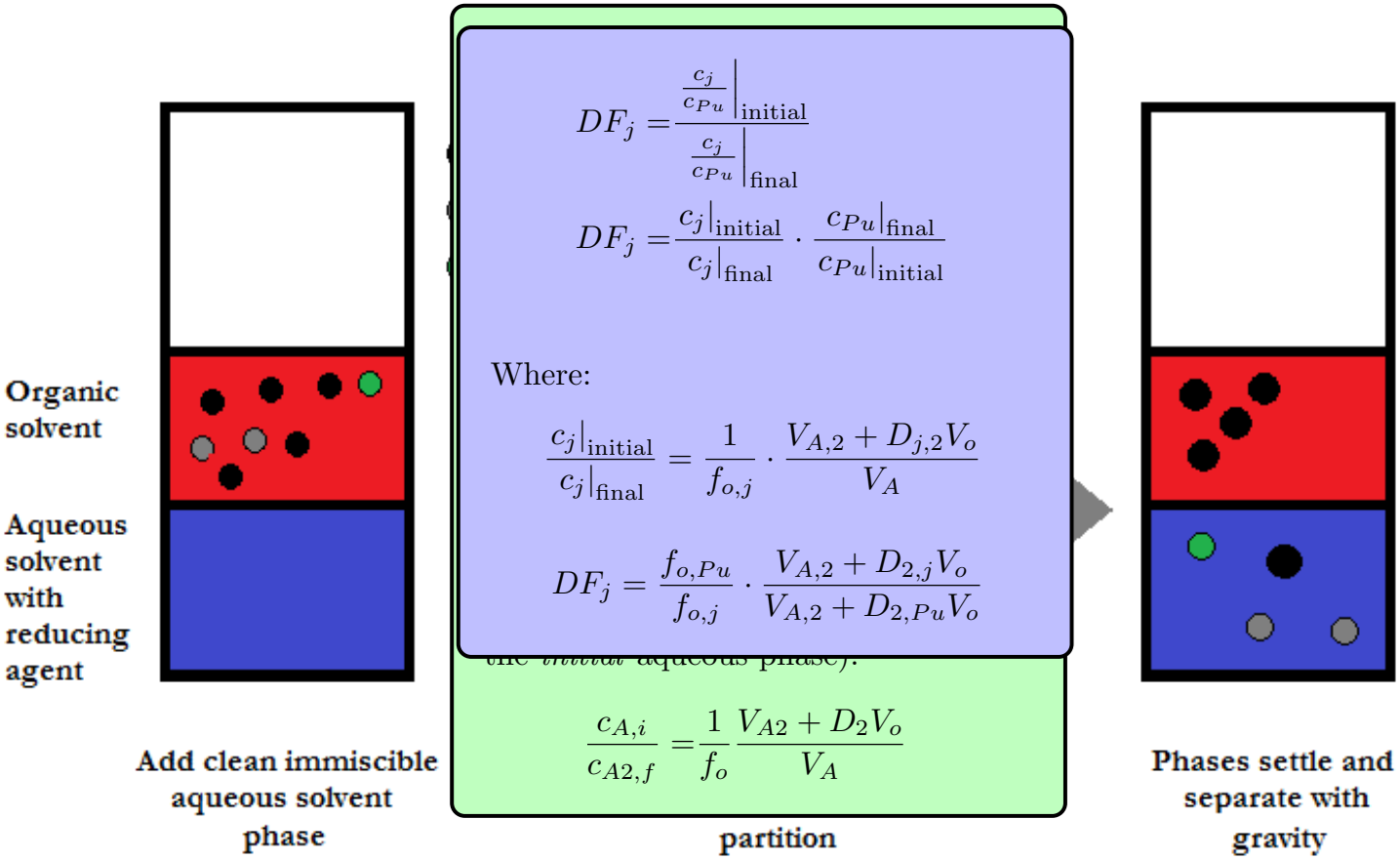


$$DF_j = \frac{\left.\frac{c_j}{c_{Pu}}\right|_{\text{initial}}}{\left.\frac{c_j}{c_{Pu}}\right|_{\text{final}}}$$

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

Where:

$$\frac{c_j|_{\text{initial}}}{c_j|_{\text{final}}} = \frac{1}{f_{o,j}} \cdot \frac{V_{A,2} + D_{j,2}V_o}{V_A}$$

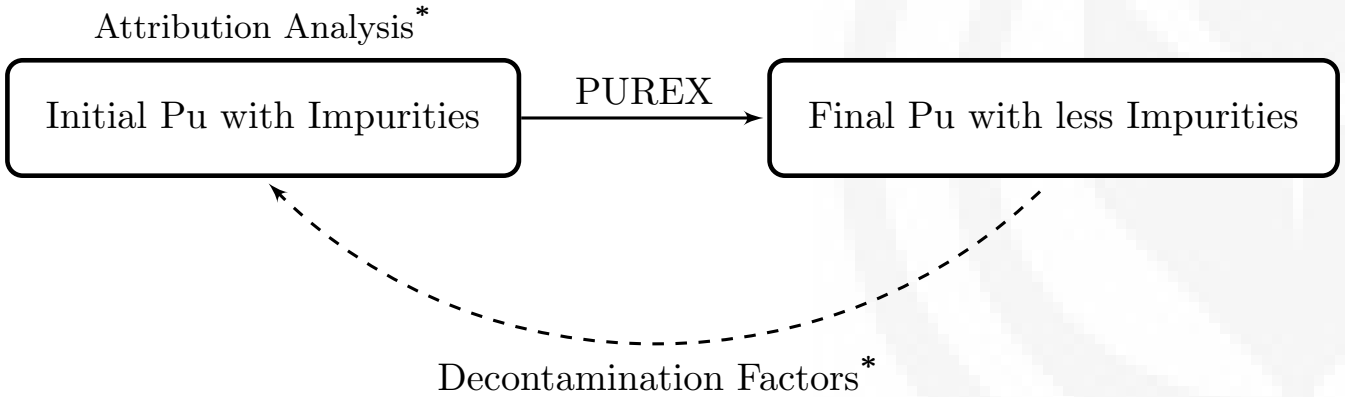
$$DF_j = \frac{f_{o,Pu}}{f_{o,j}} \cdot \frac{V_{A,2} + D_{2,j}V_o}{V_{A,2} + D_{2,Pu}V_o}$$

the initial aqueous phase):

$$\frac{c_{A,i}}{c_{A2,f}} = \frac{1}{f_o}\frac{V_{A2} + D_2V_o}{V_A}$$

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}Ce,$^{155}Eu^{*}$,$^{154}Eu^{*}$,^{125}Sb, ^{106}Ru, ^{134}Cs, ^{137}Cs (Measured Gamma in triplicate)
  - ✓ Convert Gamma Spectrum to D-values
  - ✓ $^{85}Rb^{*}$,$^{90}Sr^{*}$,$^{97,98,100}Mo$,$^{101,102,104}Ru$, ^{110}Pd,^{112}Cd,$^{133}Cs^{*}$,$^{140,142}Ce$,$^{143}Nd^{*}$, $^{147}Pm^{*}$,$^{151}Sm^{*}$,$^{154}Eu^{*}$,U^{*},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

- Stable noble fission gases as burnup verification[11]

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

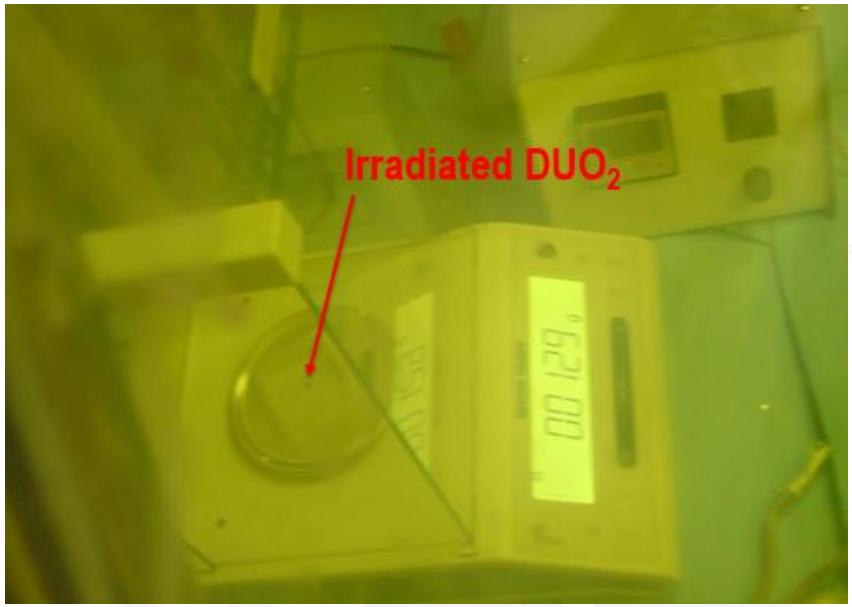
Experimental Procedure - Gamma Spectrometry

Experimental Procedure - Alpha Spectrometry

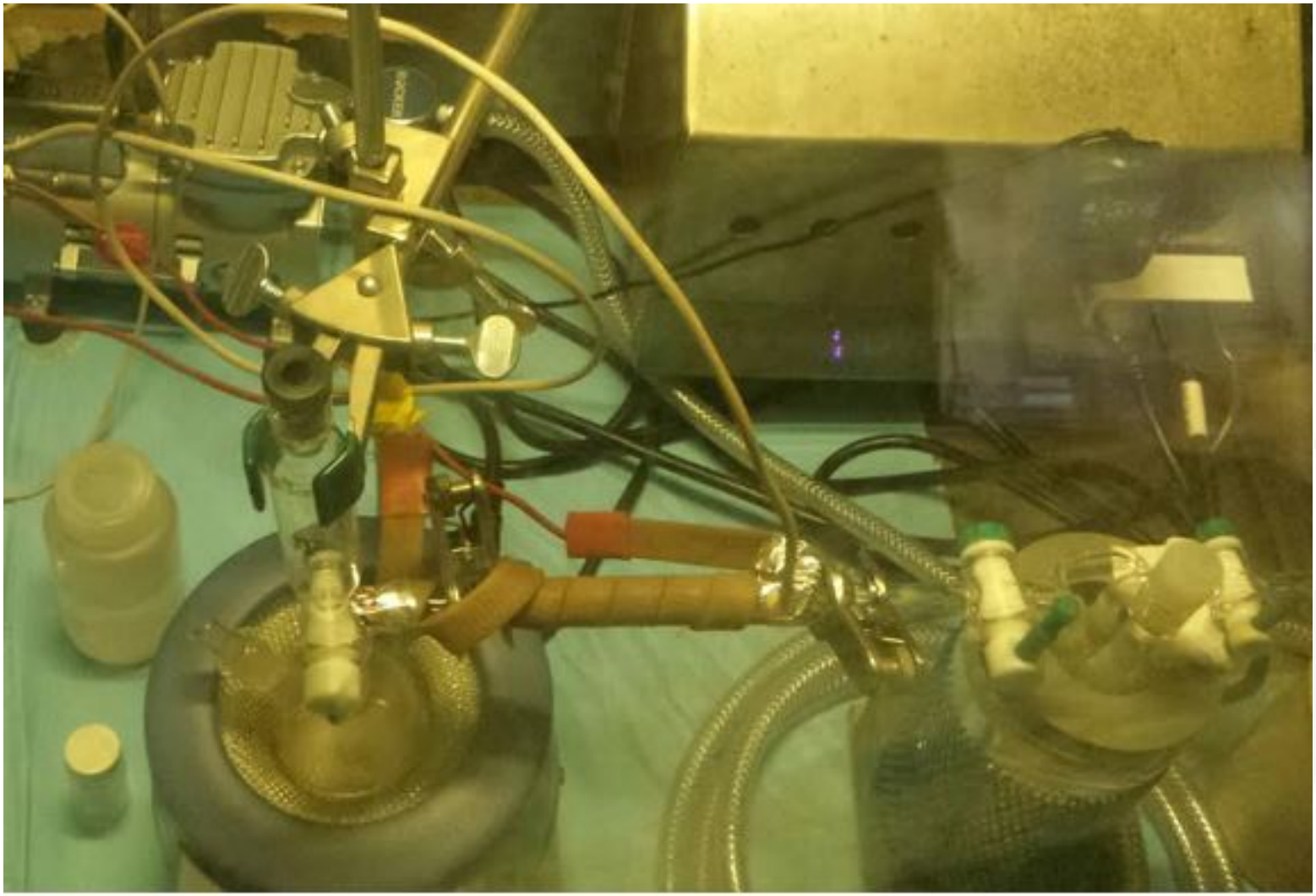
Current and Expected Results

Irradiation

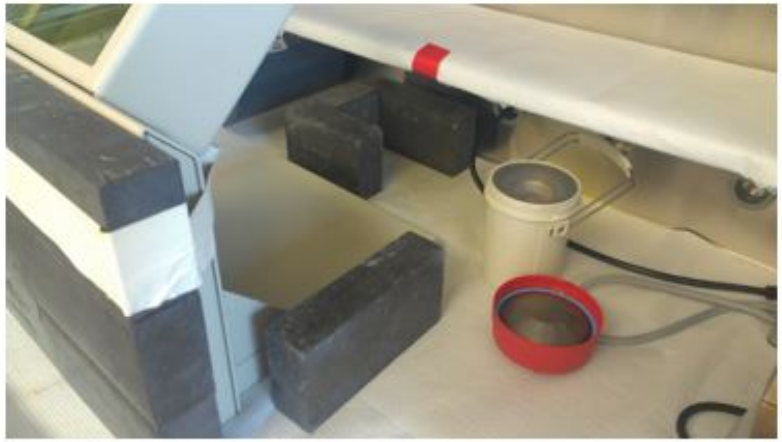
- 12.9 $\pm$ 0.1 mg of DUO_2 was irradiated
  - High Flux Isotope Reactor at Oak Ridge National Laboratory
- Burnup was 4.43 $\pm$ 0.31 GWd/tHM[12] from ^{137}Cs
- 0.196 $\pm$ mg of total Pu was produced as measured by ICP-MS

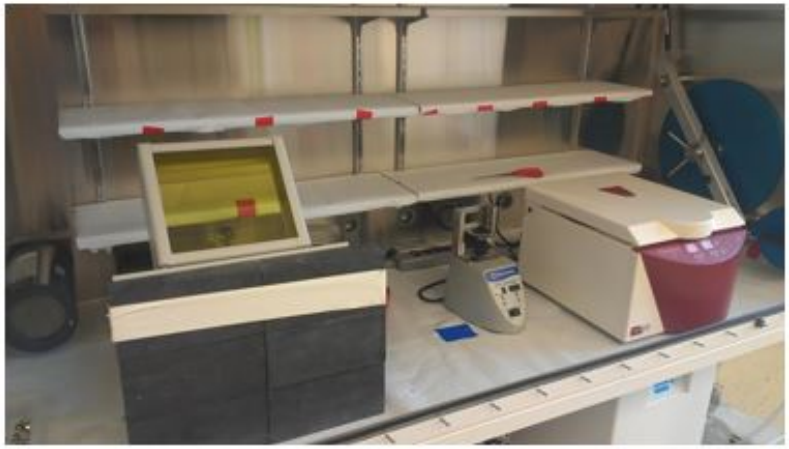


Dissolution of the spent fuel pellet



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±9.5)%	(11.2±1.3)%
Multi-contact Cycle 1	(99.7±4.2)%	(6.8±0.3)%
Multi-contact Cycle 2	(93.0±4.6)%	(6.6±0.3)%
Overall Experiment 2	(92.7±6.0)%	(0.45±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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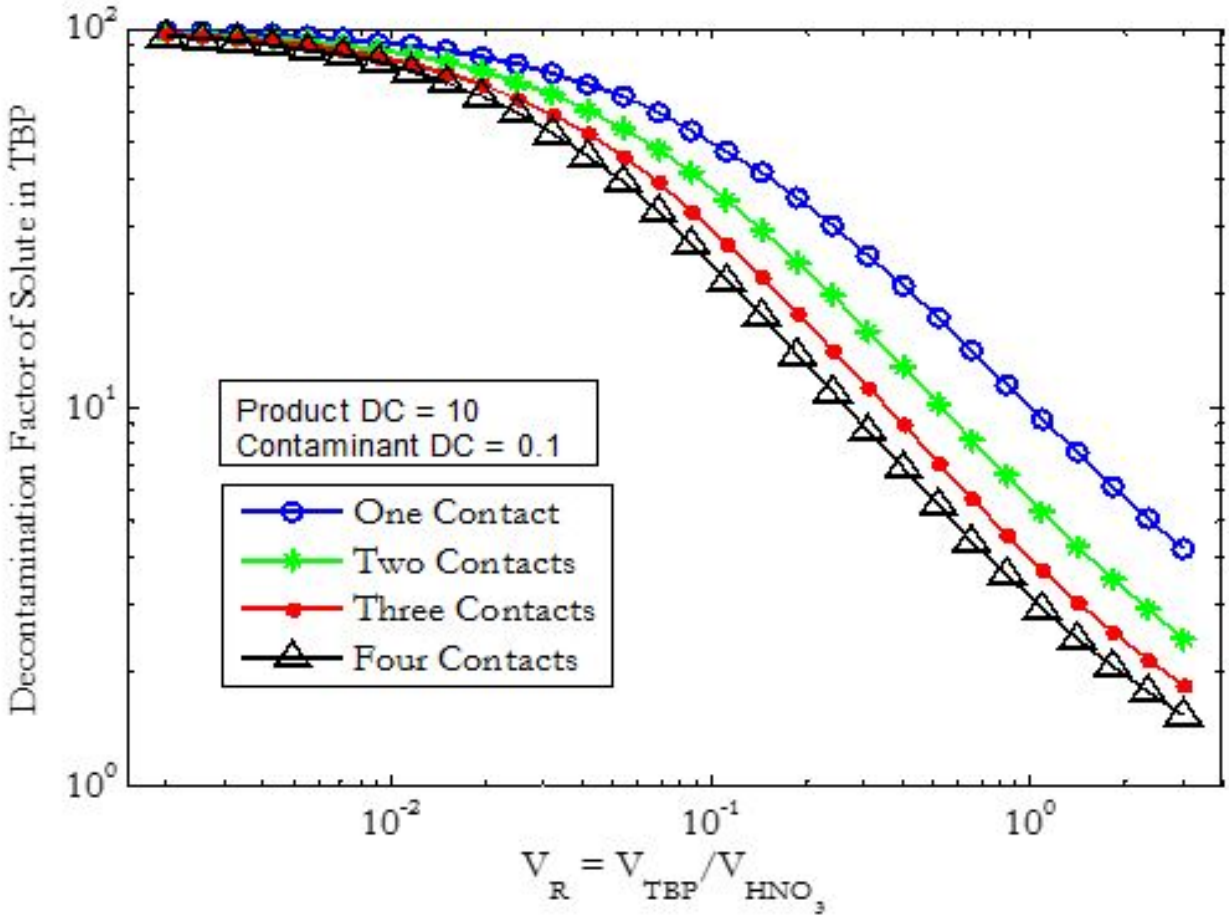
Questions?

Previous Experiment Results



Decontamination Factors for multi-contact extraction.

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[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.

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[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.

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[11] William S Charlton, Bryan L Fearey, Charles W Nakhleh, Theodore A Parish, Robert T Perry, Jane Poths, John R Quagliano, William D Stanbro, and William B Wilson. Operator declaration verification technique for spent fuel at reprocessing facilities. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 168(1):98–108, 2000.

[12] Mathew Wayne Swinney. *Experimental and Computational Assessment of Trace Nuclide Ratios in Weapons Grade Plutonium for Nuclear Forensics Analysis*. PhD thesis, 2015.

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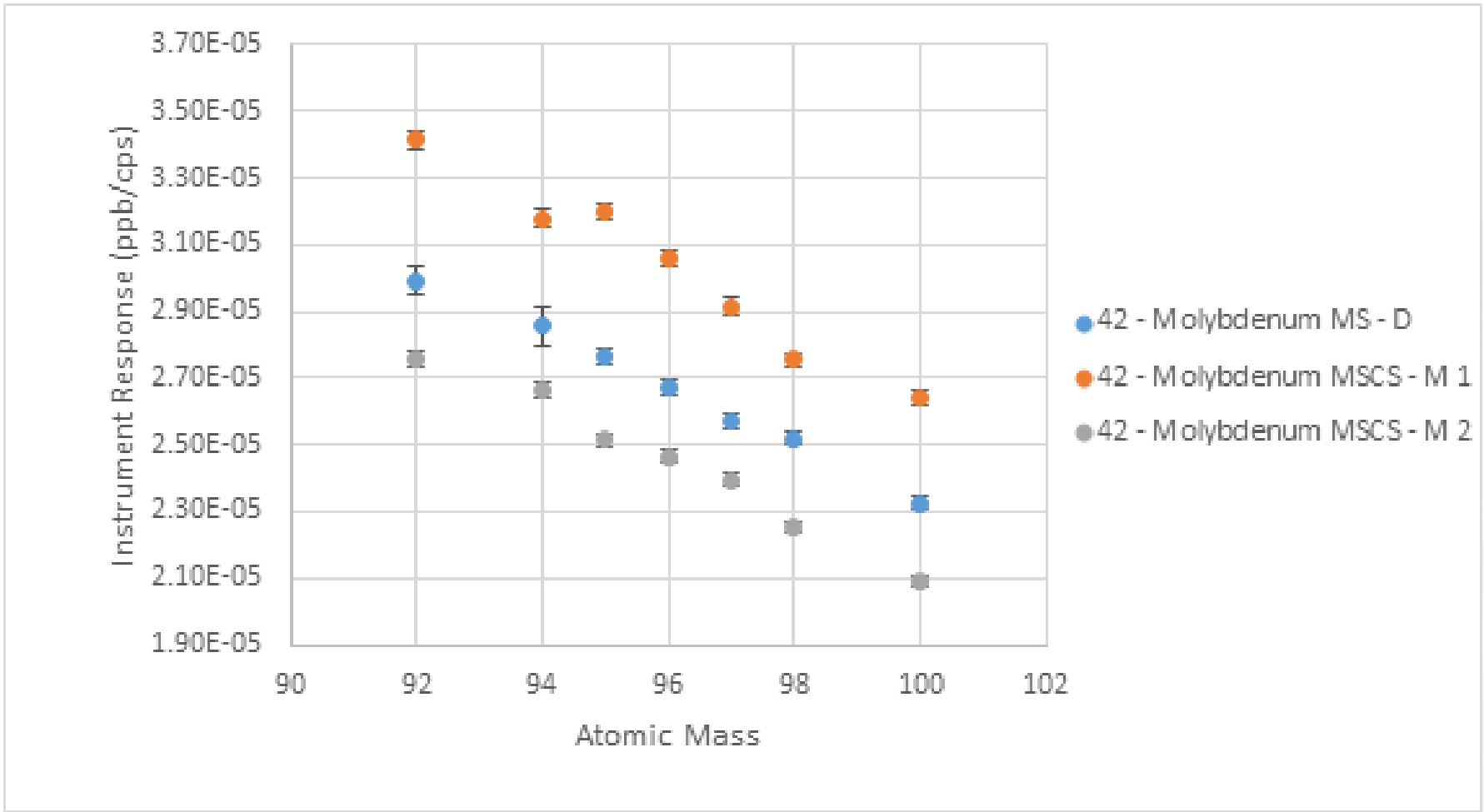
[14] Sunil S. Chirayath, Jeremy M. Osborn, and Taylor M. Coles. Trace fission product ratios for nuclear forensics attribution of weapons-grade plutonium from fast and thermal reactors. *Science and Global Security*, 23(1):48–67, 2015.

Mass Spec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2.70E-05
2.50E-05
2.30E-05
2.10E-05
1.90E-05
Instrument Response (ppb/cps)
90
92
94
96
98
100
102
Atomic Mass
42 - Molybdenum MS - D
42 - Molybdenum MSCS - M 1
42 - Molybdenum MSCS - M 2