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

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Monday, February 27, 2017, 10:00 am
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]

Wanted to take some time to talk about the motivation behind this project. There are a lot of stuff going on in the world. Here I've listed a few that pertain to nuclear weapons.

- Iran limiting capabilities for 8 years
- non-safeguarded reactors, in India for example
- North Korea, detonating a nuclear device October 2006
- ISIS, if they could, would probably want nuclear weapons, and they would use them on us

As 911 indicated, we have enemies, who don't like us. To quote William Perry, "Our greatest threat is a terrorist nuclear strike". Lukily, aquiring nuclear weapons is no easy task. And thanks to organizations like the international atomic energy agency, or the treaty on the non proliferation of nuclear weapons, the international community is generally on board with nonproliferation. Nontheless, all sources of special nuclear material are not safeguarded, and the "awful arithmetic of the atomic bomb", to quote Eisenhower, doesn't leave much room for calculational errors.

- Forensic capabilities need to improve, which we will talk about in a minute, but first, some definitions

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

At this point I wanted to take a moment to define some terms. To help narrow our nonproliferation scope. First,

- Special nuclear material, this is the material that is traditionally safeguarded. One of three building blocks for nuclear weapons, which are the material, design information, and manufacturing skills
- Nuclear forensics - investigative activity, determing attributes of SNM. This could include composition, material form, or date since processing. Involves a broad range of scientific destructive and nondestructive techniques. The time scale for full nuclear forensic analysis for samples can vary widely, depending on the prepardness of whatever laboratory is receiving the sample. In Moody's book, nuclear forensic analysis, he cites several examples that took a couple of months to analyze
- For my project I will be determining several attributes or indicators for a sample. I wanted to note that these indicators are clues or evidence towards a conclusion. And the examples listed are indicators that I would like to determine.

Forensic 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**

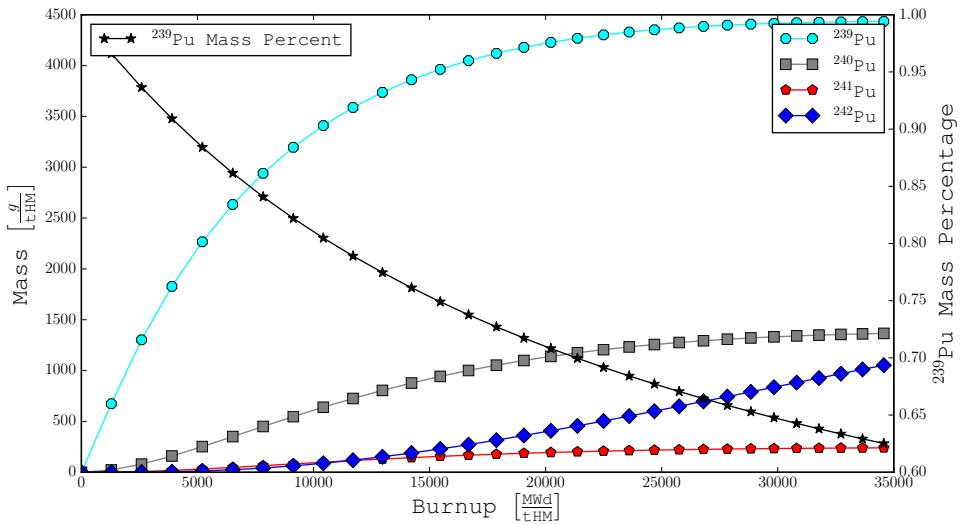
According to a report from the committee on nuclear forensics released in 2010, the United States forensic capability has been demonstrated in real world scenarios, but is at risk unless certain developmental requirements are met. The committee listed 4 areas of concern, where improvment is needed.

- In terms of organization, nuclear forensics responsibility is shared by several agencies without central authority and with no consensus on strateic requirements to guide the program.
- For sustainability, our current capabilities are the fruit of the nuclear weapons program and our laboratory infrastructure, funding for both have been decling
- Skilled personnel in these areas are few, and key facilities are in need of replacement because they are old, outdated, or do not met modern environmental, health, or safety standards.
- In recent years, nuclear forensic techniques methodologies have been on the rise, some from presented from our own department, but according to this source, a large fraction of techniques are remnants of the cold war era, with less restrictions. Also, forensic excersises usually take months to complete, a time scale which is too long

Problem must be met on an administrative level, but this project will help with two of these important goals. Developing the workforce, by example of yours truly, and the procedures we'll talk about in a moment.

Background

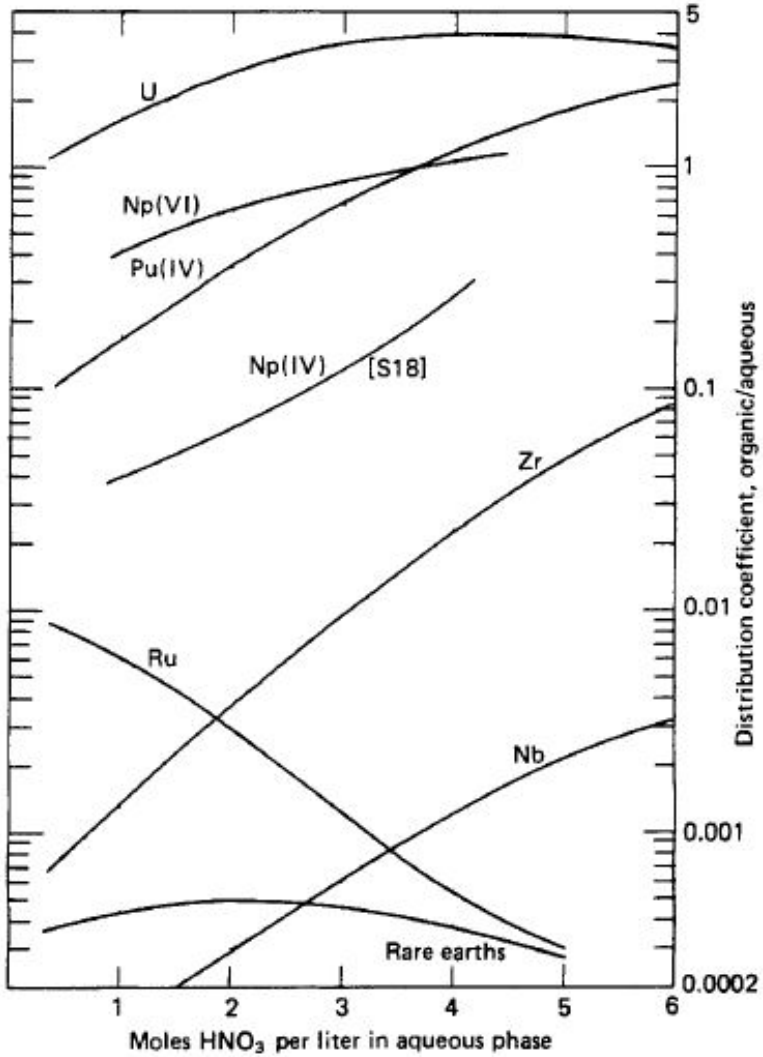
- Weapons-grade Pu can be extracted from reactor discharged fuel with a burnup of about 1 (GWD/tU)
- Pu isotopes produced in irradiated fuel can vary
- Two examples of reactors which can intentionally discharge low burned fuel for extracting weapon-grade Pu are:
  - Fast Breeder Reactor
  - CANDU Reactor



- Lower burnup fuel produces weapons
- Plutonium isotopics depend on
  - Burnup (irradiation history)
  - Reactor neutron spectrum (core design)
- Fast Breeder Reactor
  - Madras Atomic Power Station Kalpakkam, India
  - Expected criticality in Jan 2017
  - Cost from 450 million euros to 750 euros
  - Sodium-cooled reactor design - U238 for breeding
  - 100 GWd/t for core, 40 year life, 1750 tonnes of sodium about 75% of olympic sized swimming pool.
  - liquid sodium has a density a little less than water
  - MOX fuel (UO2 and PuO2) fuel
  - Fuel discharged at 100GWd/t, but I just mentioned that we are worried about 1GWd/t, mistake?

Smaller Picture

- Attribution for unpurified Pu has been previously studied [5, 6, 7]
- Interdicted Pu would likely have been processed
- Lack of literature on decontamination factors and distribution coefficients for useful forensic elements (Cs, Sb, Eu, Rb, Sr, Nd, Pm, and Sm)



Adapted from Stoller[8]

Background

What is PUREX - A type of laundry detergent?

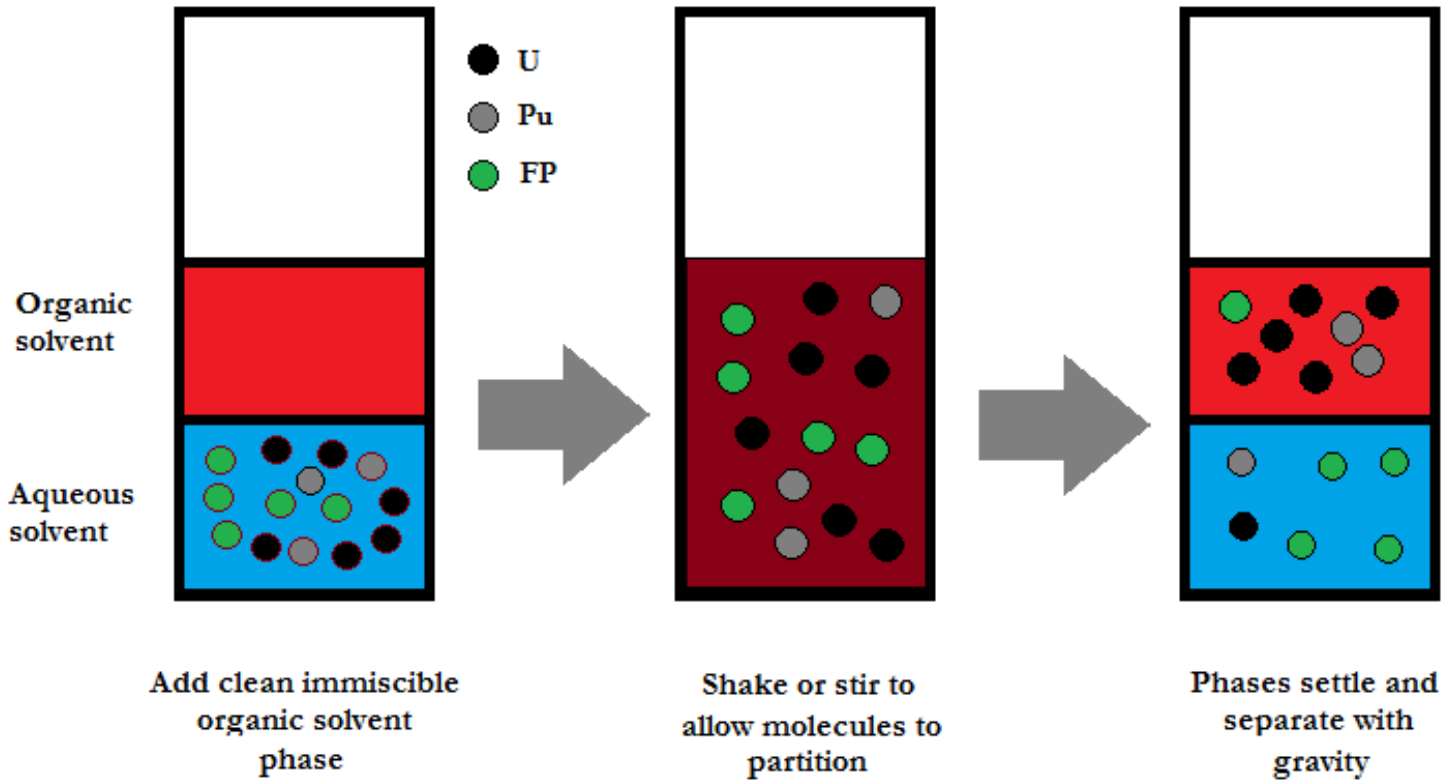
- Plutonium Uranium Redox EXtraction
  - Liquid-liquid solvent extraction
  - Many stages:
    1. Preparation for Dissolution
    2. Dissolution
    3. Preparation of Dissolved Feed
    4. Primary Decontamination - Extraction to organic*
    5. Scrubbing
    6. Plutonium Partition - Back-Extraction to aqueous*
    7. Plutonium Purification

* - Discussing Next

Extraction

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

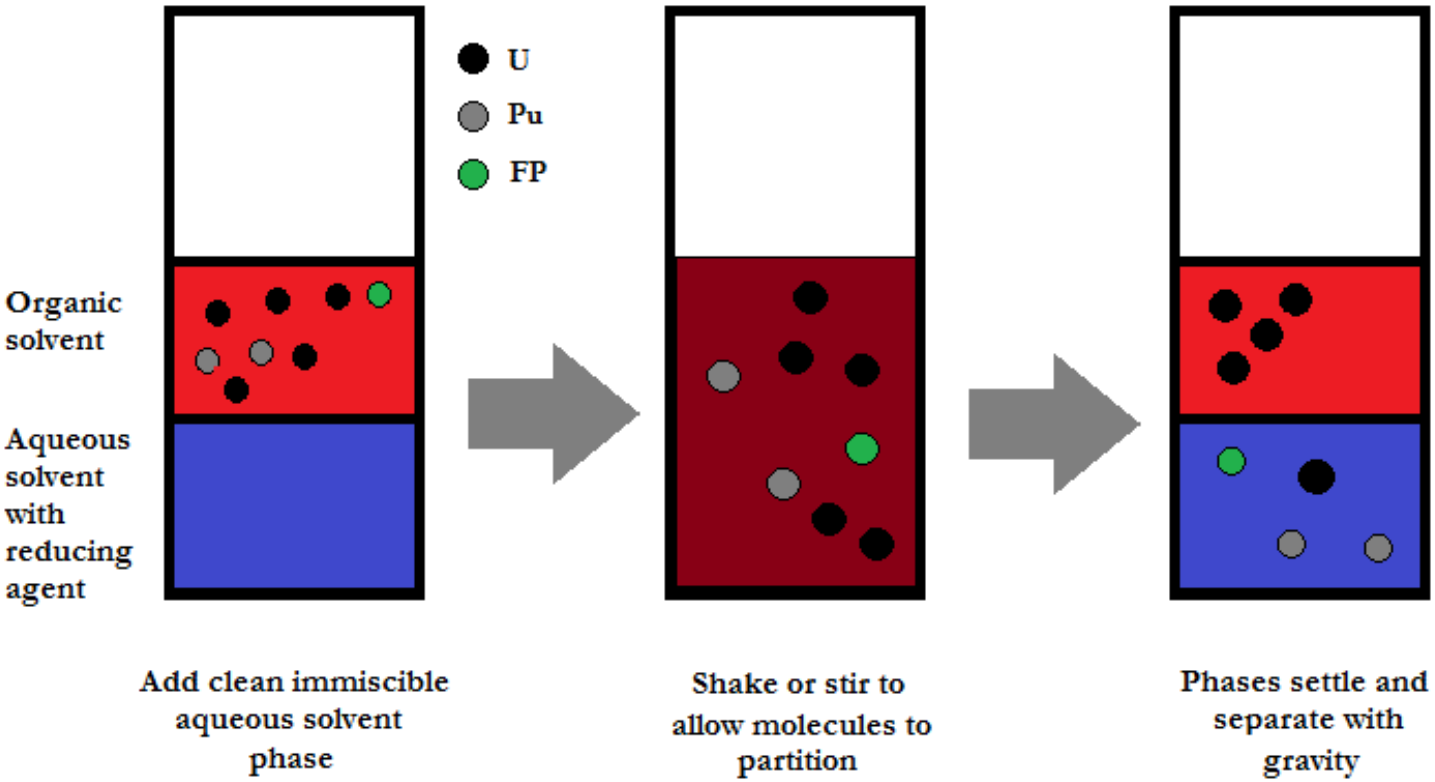
$$Pu_{(aq)}^{4+} + 4NO_{3(aq)}^{-} + 2TBP_{(o)} \leftrightarrow Pu(NO_3)_4 \cdot 2TBP_{(o)}$$



1. Most of the fission products are left in the aqueous solution at valence III and V states[10]

Back-Extraction

$$Pu(NO_3)_4(TBP)_{2(o)} + Fe^{2+}_{(aq)} \leftrightarrow Pu^{3+}_{(aq)} + 4NO^{-}_{3(aq)} + 2TBP_{(o)}$$ [11]



1. The fission products that contribute mostly to the radioactive contamination of product in PUREX are zirconium, niobium, and ruthenium - with multiple oxidation states.

Distribution Coefficients - The Missing link

- 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 with:[8]
  - Composition of phases
  - Solution saturation
  - Temperature of the solvent
- The fraction of mass, f_o deposited in the organic phase, assuming a volume ratio between the aqueous and organic phases, V_R, is:

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

1. Distribution coefficients can be reported in terms of volume basis (weight per unit volume), or a mass basis (mass of solute per unit mass of solute free solvent)- usually reported on volume basis
2. Note not a function of density, even though the two solutions have different densities, when solving for this value it cancels out
3. Solved this way to show, volume matters, and to give me a more intuitive sense of where things are going

Decontamination Factors - The Pot of gold

- After several cycles of Pu extraction/scrubbing/back-extraction are completed, the effectiveness of a PUREX cycle is described by the decontamination factor (DF):

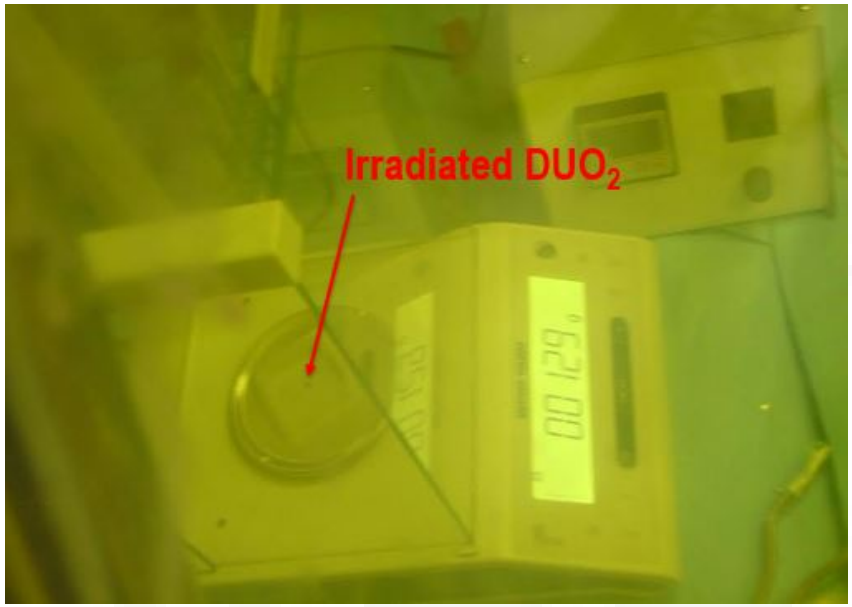
$$DF_j = \frac{\left|\frac{c_j}{c_{Pu}}\right|_{initial}}{\left|\frac{c_j}{c_{Pu}}\right|_{final}}$$

- DFs are characteristic of different process cycles
- Larger values (10^7) for industrial scale PUREX (compared to benchtop)[8, 9]

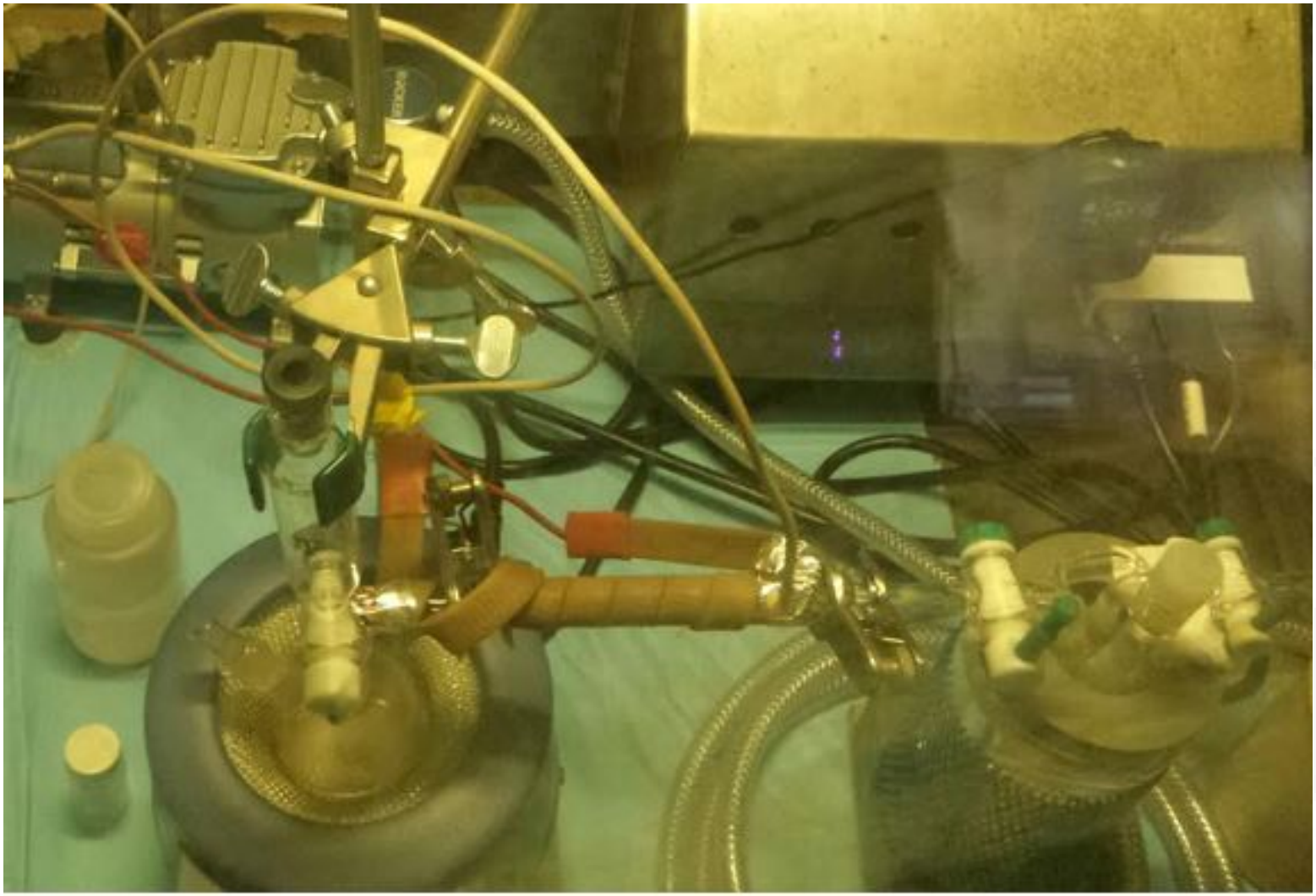
Previous Work

Irradiation

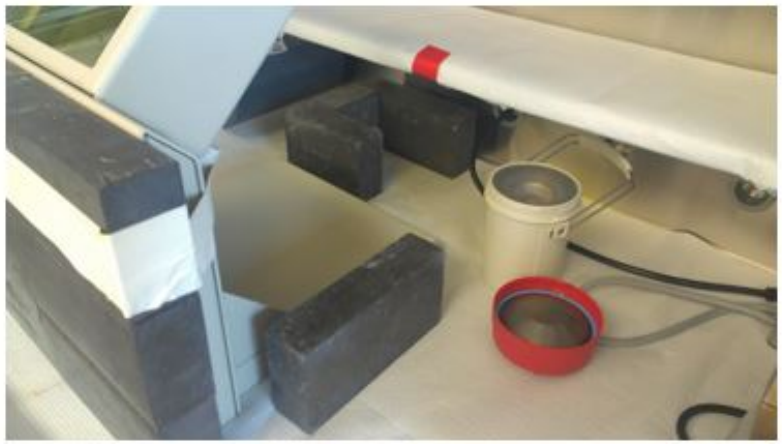
- 12.9 $\pm$ 0.1 mg of DUO_2 was irradiated
  - High Flux Isotope Reactor at Oak Ridge National Laboratory
- Burnup was 4.43 $\pm$ 0.31 GWd/tHM[12]
- 0.196 $\pm$ mg of total Pu was produced as measured by ICP-MS

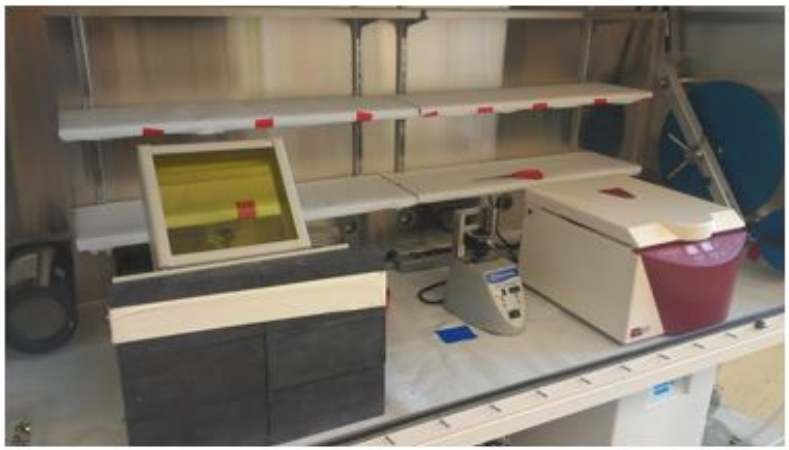


Dissolution of the spent fuel pellet



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: Maximize recovery of Pu 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

Previous Experiment 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)%

Previous Experiment 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

Conclusions

- Two PUREX experiments were conducted
  - Single stage: Determined DC values for Pu, U and several FP
  - Multi-contact: Utilized Experiment 1 to recover over 92% of Pu while leaving less than 1% of the U
- DF values were measured for 12 FP elements
- DF values were lower than those typically found in industrial scale PUREX plants due to multiple extraction and back-extraction steps without an intermittent scrubbing step.
- This work provide DF data that will be built upon for nuclear forensic investigations of interdicted Pu.

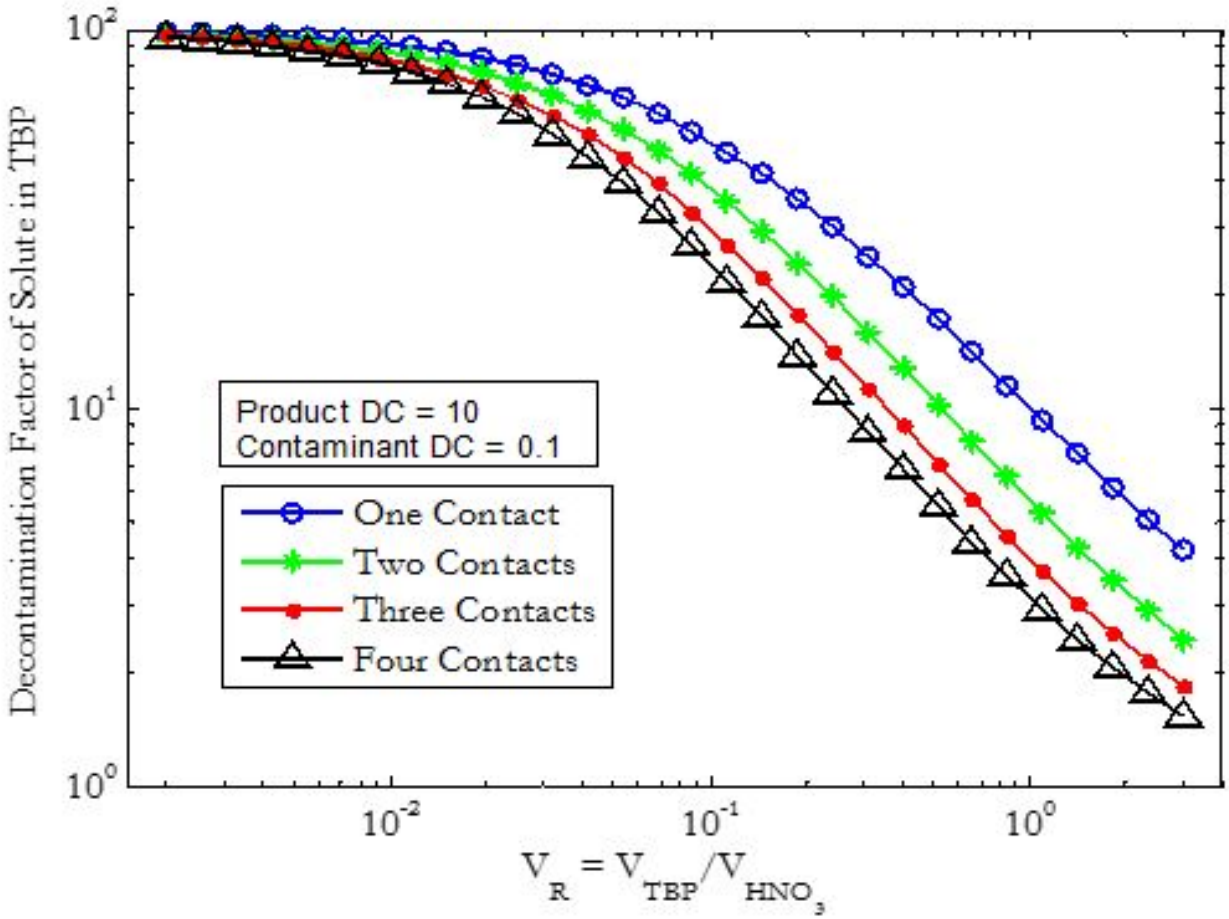
Future Work

Future Work

- Modify Multi-contact extraction, to recover a larger fraction of Pu
- Investigation of how D-values for (Cs, Sb, Eu, Rb, Sr, Nd, Pm, and Sm) change as a function of nitric acid concentration
- Determine statistical uncertainty of D and DF values.
  - Repeat above experiments 3-5 times
- Connect D-values with process information to DF values

Questions?

Previous Experiment Results



Decontamination Factors for multi-contact extraction.

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References II

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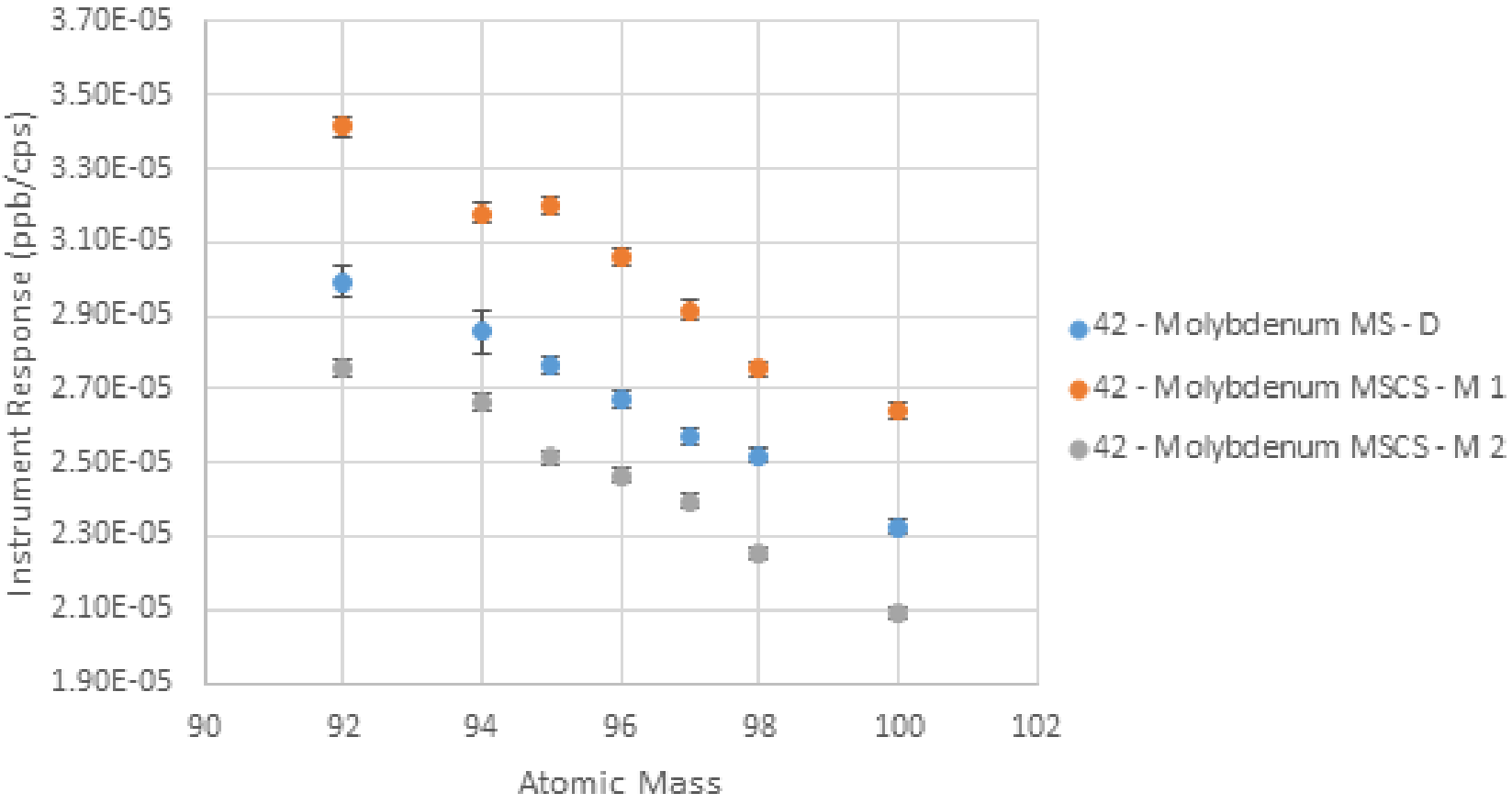
Mass Spec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Instrument Response (ppb/cps)
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Atomic Mass
42 - Molybdenum MS - D
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42 - Molybdenum MSCS - M 2