ĀĪM | 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
Chair:	Dr. Sunil Chirayath
Committee Members:	Dr. Sean McDeavitt
	Dr. Craig Marianno
	Dr. Cody Folden III.

Monday, February 27, 2017, 10:00 am
AIEN 304

TEES | TEXAS A&M ENGINEERING
EXPERIMENT STATION

NUCLEAR SECURITY
SCIENCE & POLICY INSTITUTE

NSSPI
NUCLEAR SECURITY
SCIENCE & POLICY INSTITUTE

$\overline{A}\underline{T}M$ | **NUCLEAR ENGINEERING**
TEXAS A&M UNIVERSITY

Outline

Motivation

- ❖ Current Events
  - ➢ Joint Comprehensive Plan of Action
  - ➢ Non-safeguarded reactors
  - ➢ Islamic State of Iraq and Syria
- ❖ Past Events
  - ➢ September 11, 2001
- ❖ Limited scope of IAEA safeguards
- ❖ "the awful arithmetic of the atomic bomb" [1]
- ❖ Need for improved forensic capabilities [2, 3, 4]

Can talk a lot on this slide: North Korea, detonating a nuclear device October 2006

Introduction
Background
Previous Work
Future Work

NUCLEAR ENGINEERING
TEXAS A&M UNIVERSITY

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- Skilled personnel in these areas are few, and key facilities are in need of replacement because they are old, outdated, or do not met modern environmental, health, or safety standards.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, mentioned here because this proposed project will help, in a small way, with two areas of concern.

Motivation

- ❖ 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:
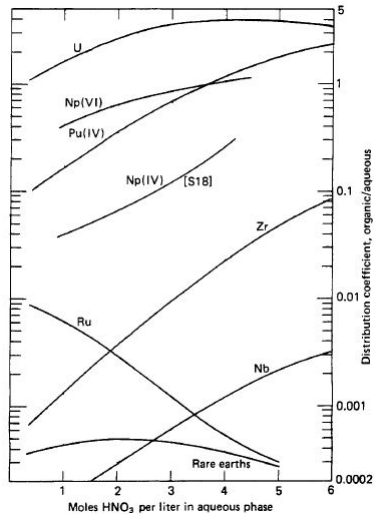 - ➢ Fast Breeder Reactor
  - ➢ CANDU Reactor

1. Madras Atomic Power Station Kalpakkam, India
2. Expected criticality in Jan 2017
3. Cost from 450 million euros to 750 euros
4. Sodium-cooled reactor design - U238 for breeding
5. 100 GWd/t for core, 40 year life, 1750 tonnes of sodium about 75% of olympic sized swimming pool.
6. liquid sodium has a density a little less than water
7. MOX fuel (UO2 and PuO2) fuel
8. Fuel discharged at 100GWd/t, but I just mentioned that we are worried about 1GWd/t, mistake?

Introduction
Background
Previous Work
Future Work

NSSPI
NUCLEAR SECURITY
SCIENCE & POLICY INSTITUTE

ĀĪM | NUCLEAR ENGINEERING
TEXAS A&M UNIVERSITY

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)
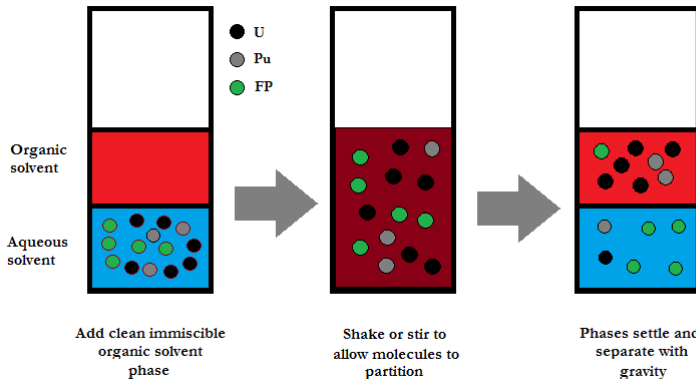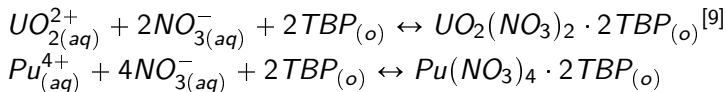

Adapted from Stoller[8]

Background

Introduction
Background
Previous Work
Future Work

NSSPI
NUCLEAR SECURITY
SCIENCE & POLICY INSTITUTE

Ā&M | NUCLEAR ENGINEERING
TEXAS A&M UNIVERSITY

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[*]
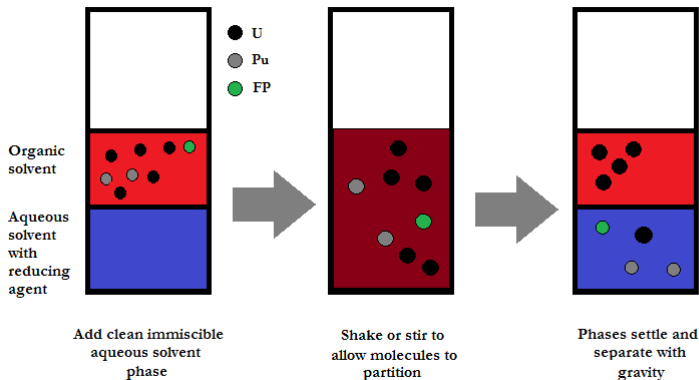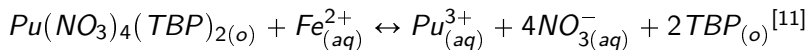   7. Plutonium Purification

[*] - Discussing Next

NUCLEAR ENGINEERING
TEXAS A&M UNIVERSITY

Extraction

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

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

Organic solvent

Aqueous solvent

U
Pu
FP

Add clean immiscible organic solvent phase

Shake or stir to allow molecules to partition

Phases settle and separate with gravity

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

Introduction
Background
Previous Work
Future Work

NUCLEAR ENGINEERING
TEXAS A&M UNIVERSITY

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.

Introduction
Background
Previous Work
Future Work

ĀM | NUCLEAR ENGINEERING
TEXAS A&M UNIVERSITY

NSSPI
NUCLEAR SECURITY
SCIENCE & POLICY INSTITUTE

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

Introduction
Background
Previous Work
Future Work

NUCLEAR ENGINEERING
TEXAS A&M UNIVERSITY

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]

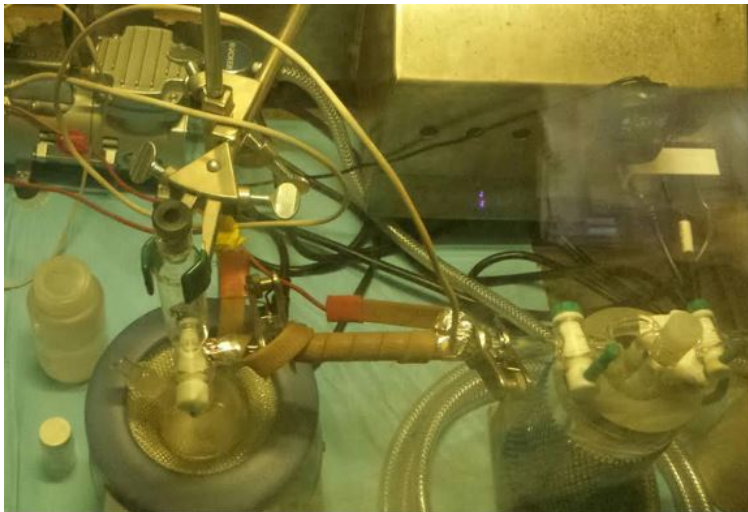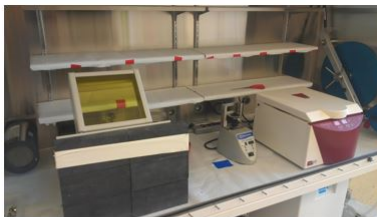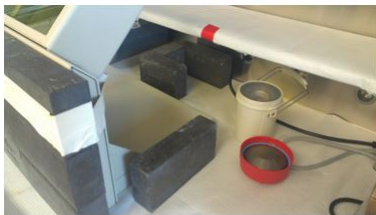# Previous Work

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

Irradiated DUO$_2$

NSSPI
NUCLEAR SECURITY
SCIENCE & POLICY INSTITUTE

A̲T̲M̲ | **NUCLEAR ENGINEERING**
TEXAS A&M UNIVERSITY

Dissolution of the spent fuel pellet

Glovebox

Introduction
Background
Previous Work
Future Work

NUCLEAR ENGINEERING
TEXAS A&M UNIVERSITY

NSSPI
NUCLEAR SECURITY
SCIENCE & POLICY INSTITUTE

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

NSSPI
NUCLEAR SECURITY
SCIENCE & POLICY INSTITUTE

Introduction
Background
Previous Work
Future Work

ĀĪM | NUCLEAR ENGINEERING
TEXAS A&M UNIVERSITY

Previous Experiment 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	$(92.7 \pm 6.0)\%$	$(0.45 \pm 0.03)\%$

Introduction
Background
Previous Work
Future Work

NSSPI
NUCLEAR SECURITY
SCIENCE & POLICY INSTITUTE

ĀĪM | NUCLEAR ENGINEERING
TEXAS A&M UNIVERSITY

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

NSSPI
NUCLEAR SECURITY
SCIENCE & POLICY INSTITUTE

Ā|M | NUCLEAR ENGINEERING
TEXAS A&M UNIVERSITY

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.
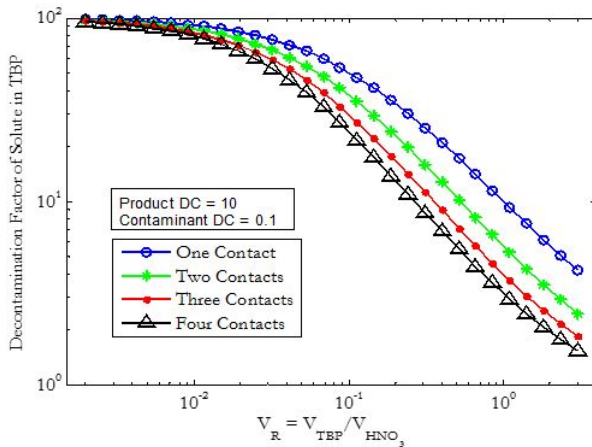
Future Work

Introduction
Background
Previous Work
Future Work

A&M | NUCLEAR ENGINEERING
TEXAS A&M UNIVERSITY

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?

NSSPI
NUCLEAR SECURITY
SCIENCE & POLICY INSTITUTE

Questions?
References

ĀĬM | NUCLEAR ENGINEERING
TEXAS A&M UNIVERSITY

Previous Experiment Results

Decontamination Factors for multi-contact extraction.

Questions?
References

NSSPI
NUCLEAR SECURITY
SCIENCE & POLICY INSTITUTE

ĀĪM | NUCLEAR ENGINEERING
TEXAS A&M UNIVERSITY

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] Kenneth D Kok. *Nuclear engineering handbook*, volume 60. CRC Press, 2009.

[11] 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.

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

NUCLEAR ENGINEERING
TEXAS A&M UNIVERSITY

NSSPI
NUCLEAR SECURITY
SCIENCE & POLICY INSTITUTE

Mass Spec