Characterizaiton of Pu Separation by PUREX

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TEXAS A&M ENGINEERING EXPERIMENT STATION
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Outline

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Big Picture

- Pu isotopes produced in irradiated fuel can vary depending on
  - Burnup (irradiation history)
  - Reactor neutron spectrum (core design)
- Weapons-grade Pu can be extracted from reactor discharged fuel with a burnup of about 1 (GWD/tU)
- Two examples of non-safeguarded reactors which can intentionally discharge low burned fuel for extracting weapon-grade Pu are:
  - Indian Prototype Fast Breeder Reactor (PFBR-500MWe)
  - Indian Pressureized Heavy Water Reactor (PHWR-CANDU type 220 MWe)
- In accord with the Indo-US 123 agreement, these reactors were not required to be kept under IAEA safeguards

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Smaller Picture

- Attribution for unpurified Pu has been previously studied [2, 6, 3]
- Intercepted Pu would likely have been processed via PUREX
- Due to a lack of literature on decontamination factors and distribution coefficients for useful forensic elements (Cs, Sb, Eu, Rb, Sr, Nd, Pm, and Sm) this research was pursued.

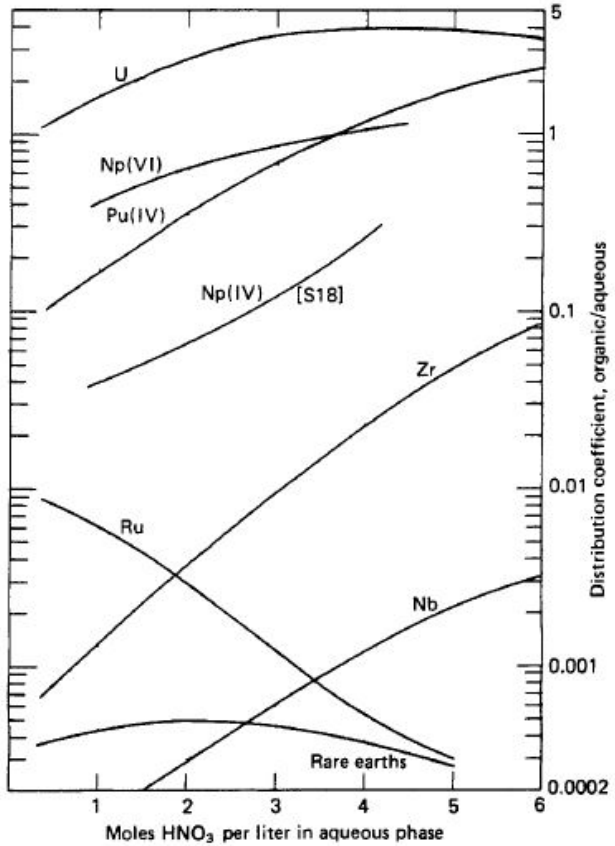

Figure 1: Effect of nitric acid concentration on distribution coefficients [7]

Background

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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

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Extraction

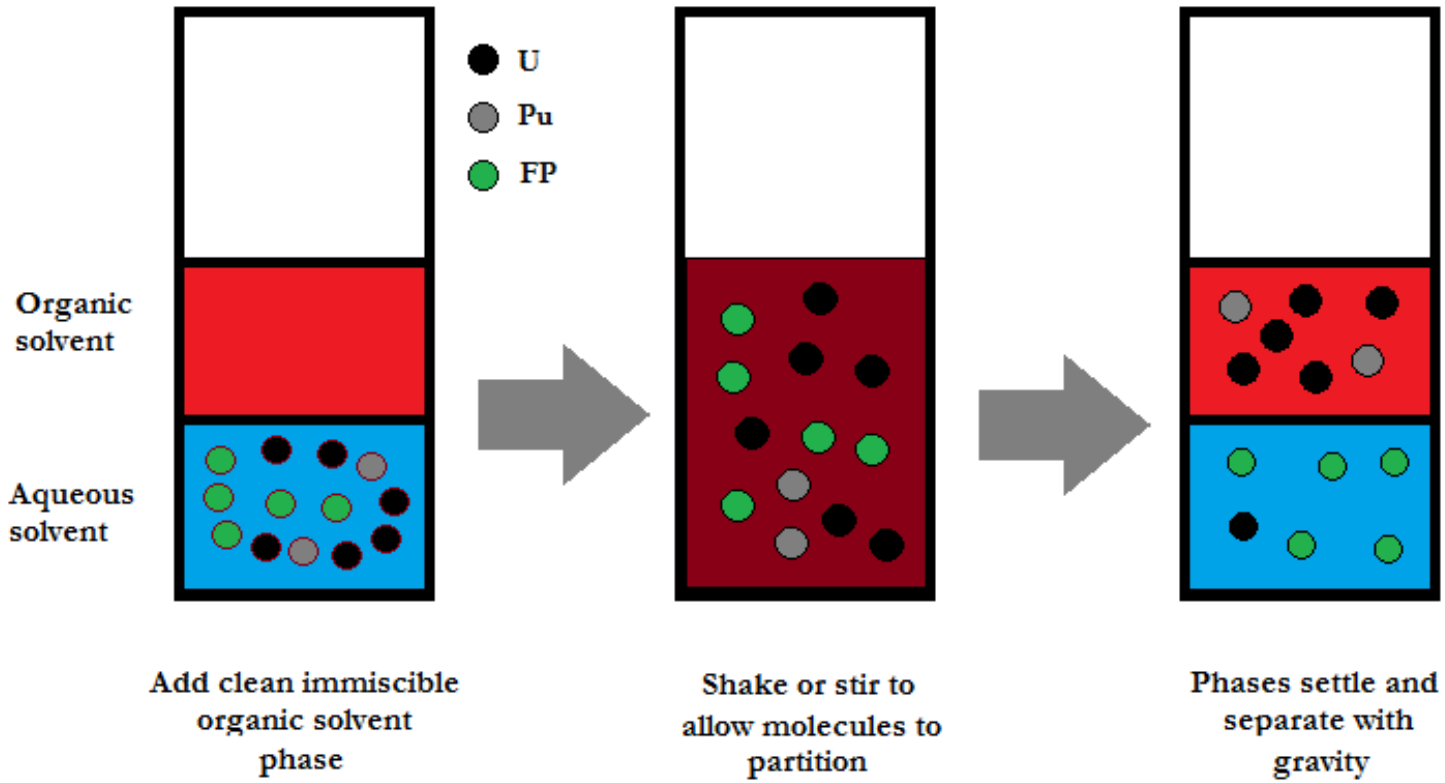

Figure 2: Extraction graphic

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Back-Extraction

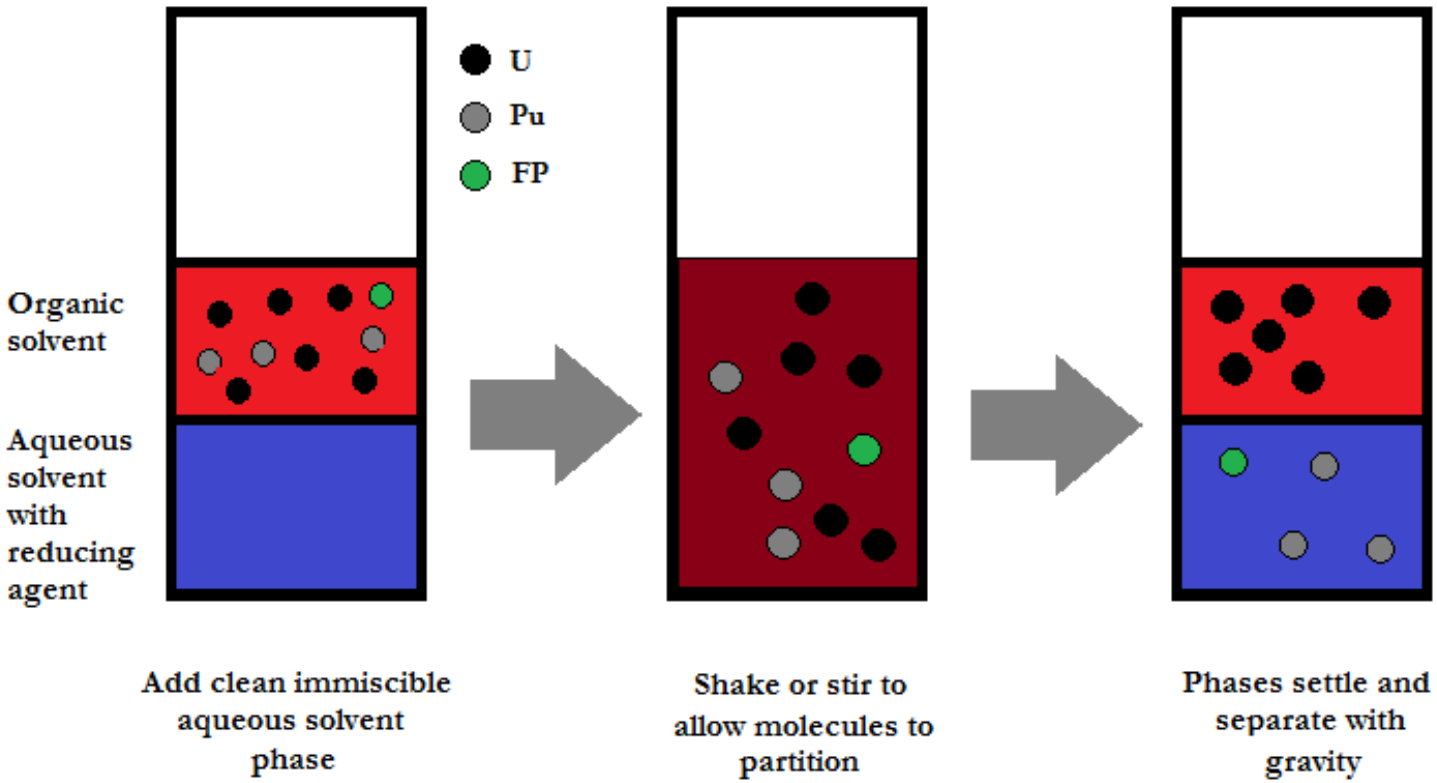

Figure 3: Back-extraction graphic

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Extraction and Back-extraction

- Extraction

$$UO_2^{2+}(aq) + 2NO_3^-(aq) + 2TBP(o) \leftrightarrow UO_2(NO_3)_2 \cdot 2TBP(o)$$ [1]

$$Pu^{4+}(aq) + 4NO_3^-(aq) + 2TBP(o) \leftrightarrow Pu(NO_3)_4 \cdot 2TBP(o)$$

Most of the fission products are left in the aqueous solution at valence III and V states[4]

- Back-extraction

$$Pu(NO_3)_4(TBP)_{2_o} + Fe_{aq}^{2+} \leftrightarrow Pu_{aq}^{3+} + 4NO_{3_{aq}}^- + 2TBP_o$$ [5]

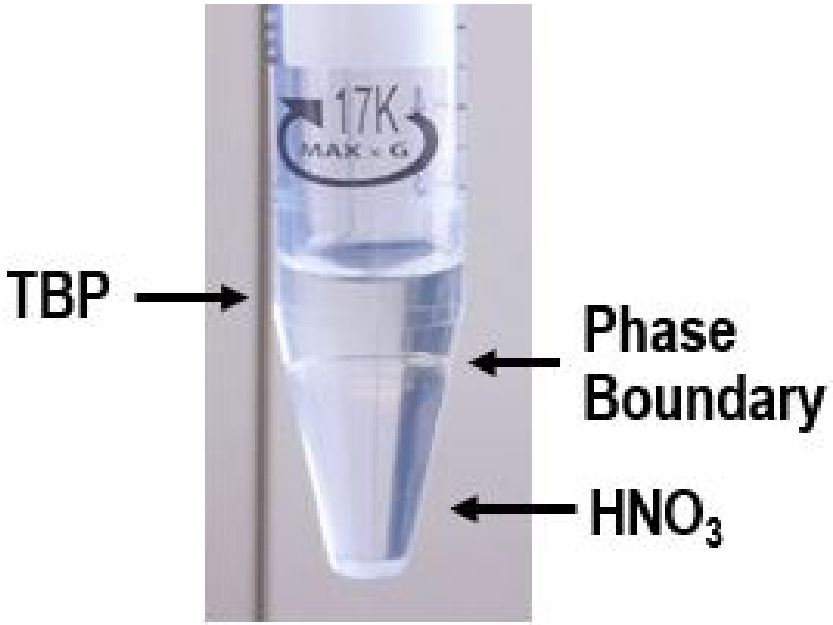

Figure 4: TBP and HNO_3

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Distribution Coefficients - The Missing link

- Distribution Coefficient (DC): The ratio between the organic and aqueous phases

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

- Specific element to element
- Vary widely with:[7]
  - Concentrations of solutions
  - Saturation of U and Pu in the system
  - Temperature of the solvents
- The fraction of mass, f_o deposited in the organic phase, assuming a volume ratio between the aqueous and organic phases, V_R, is:

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

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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)[7, 1]

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Complexity of reprocessing schemes

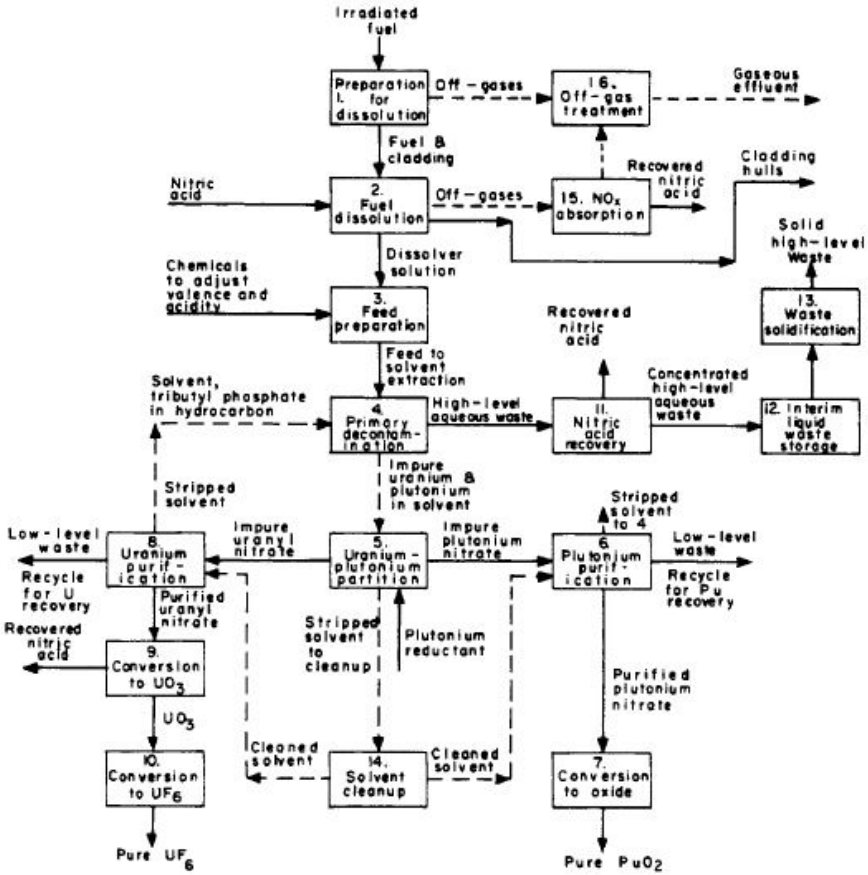

Figure 5: Principal steps in PUREX[1]

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Complexity of reprocessing schemes

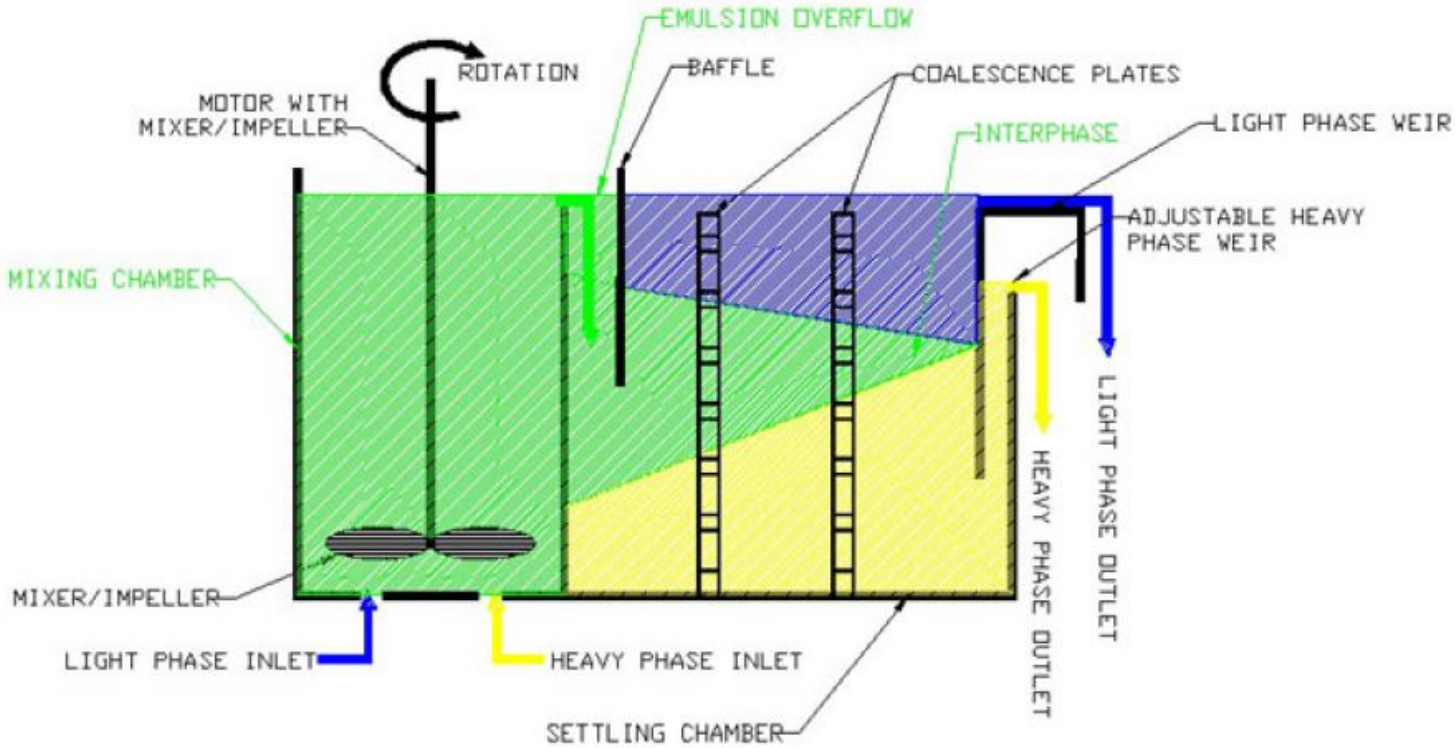

Figure 6: Mixer-Settler Diagram

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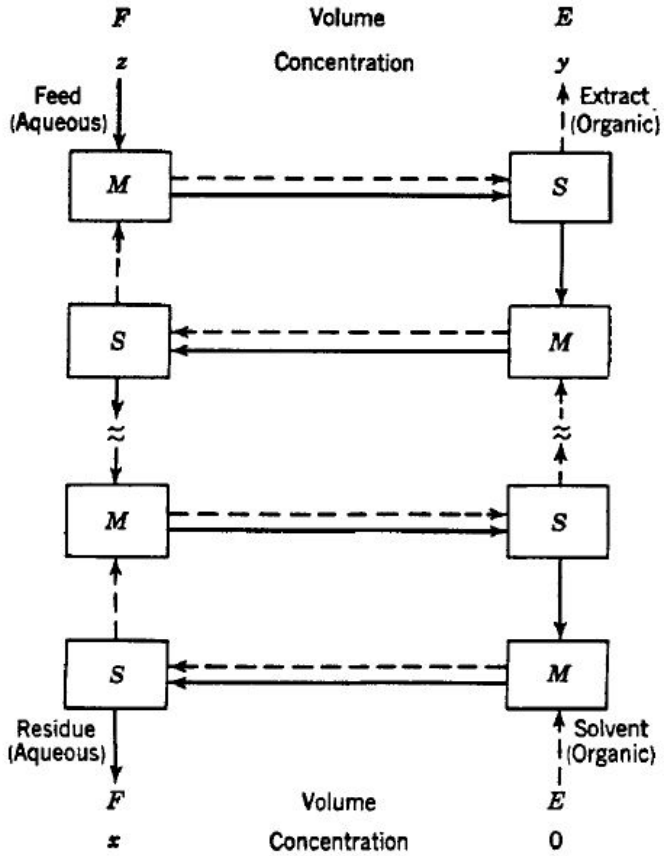

Figure 7: Multistage countercurrent solvent extraction. M, mixer; S, settler.[1]

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Complexity of reprocessing schemes

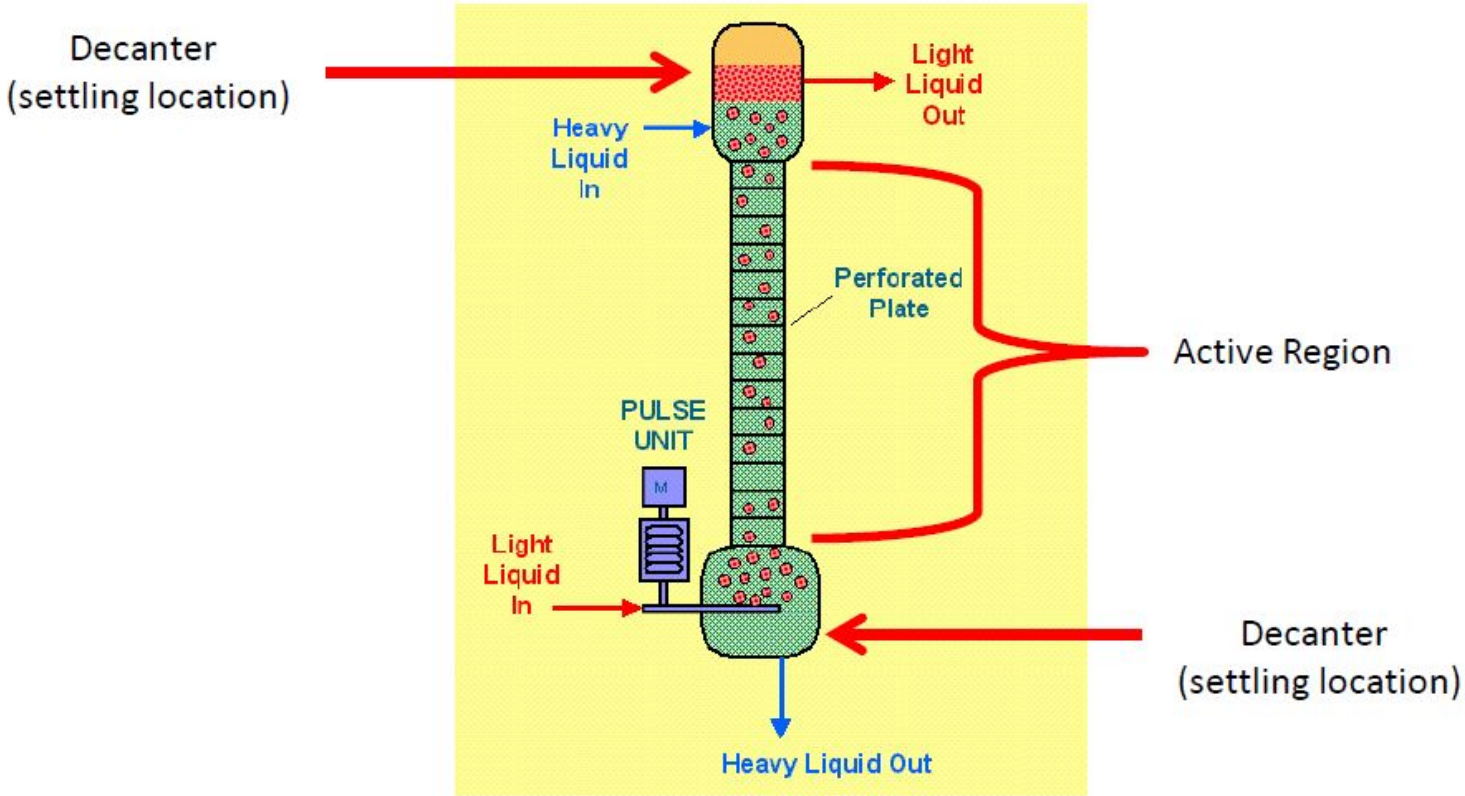

Figure 8: Pulsed Column Diagram

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Irradiation

- 12.9 $\pm$ 0.1 mg of DUO_2 was irradiated over the course of three months
  - High Flux Isotope Reactor at Oak Ridge National Laboratory
- The final burnup was 4.43 $\pm$ 0.31 GWd/tHM[8]
- 0.196 $\pm$ mg of total Pu was produced as measured by ICP-MS

Figure 9: Picture of irradiated sample

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Experiments

- Experiment 1
  - Purpose: quantify product recovery 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

- Experiment 2
  - Purpose: recover a large fraction of Pu (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

Completed Work

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Previous Experiment Results

Recoveries of U and Pu

	Pu Recovery	U Recovery
Experiment 1	(83.4±9.5)%	(11.2±1.3)%
Experiment 2 Cycle 1	(99.7±4.2)%	(6.8±0.3)%
Experiment 2 Cycle 2	(93.0±4.6)%	(6.6±0.3)%
Overall Experiment 2	(92.7±6.0)%	(0.45±0.03)%

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Previous Experiment Results

Decontamination Factors

Element (Z)	Exp.1	Error	Exp.2 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

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Previous Experiment Results

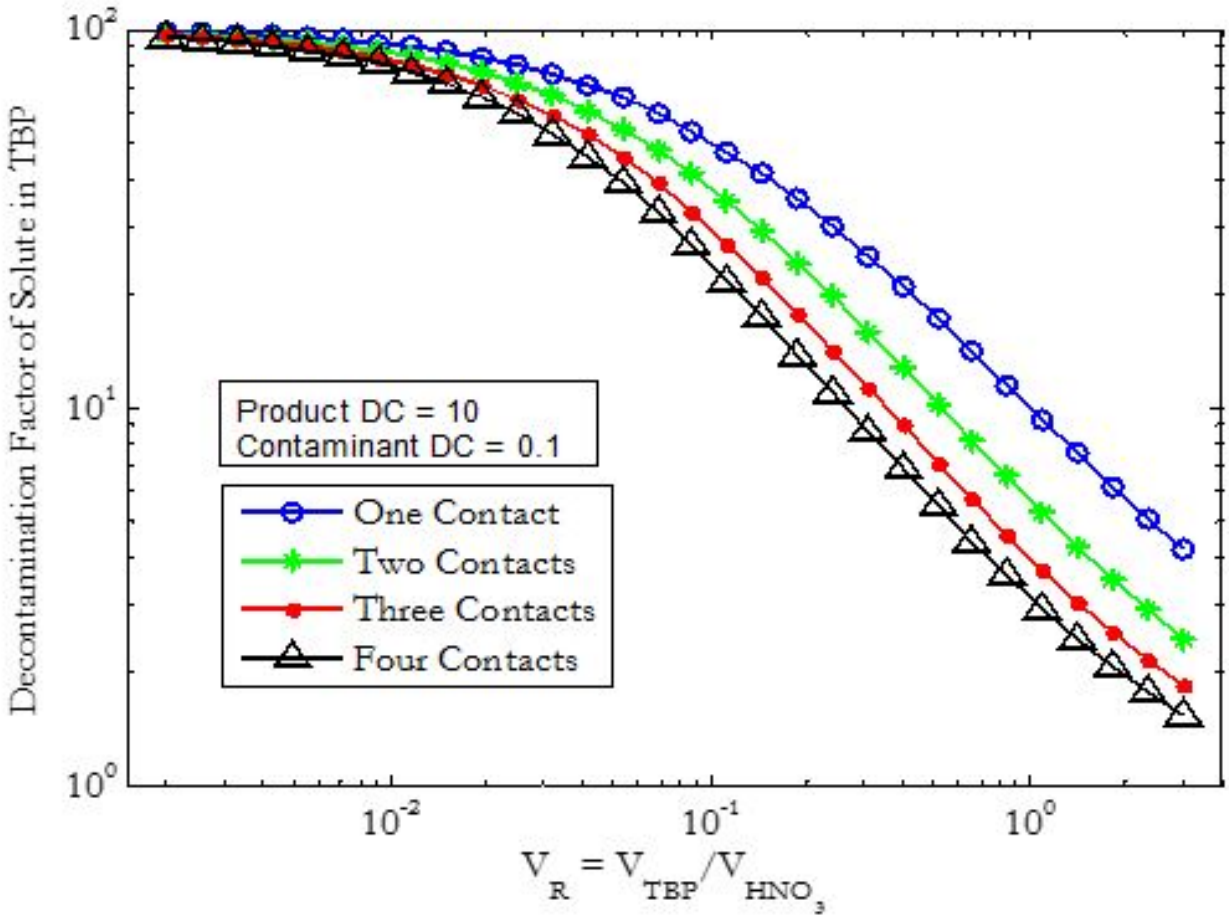

Figure 10: Decontamination Factors for multi-contact extraction.

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Conclusions

- Two PUREX experiments were conducted
  - Experiment 1: Determined DC values for Pu, U and several FP
  - Experiment 2: 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 critical DF data that will be needed for potential nuclear forensic investigations of interdicted Pu. Such a sample might have already been purified, so accurate DF data will alow for estimation of the original amounts of forensic isotopes. Regardless, additional research is needed to study the effects of additional scrubbing and stripping steps on individual DFs.

Future Work

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Future Work

- More experiments, varying concentrations
- Look into solution based iterative process determining algorithms

Questions?

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[3] 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.

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