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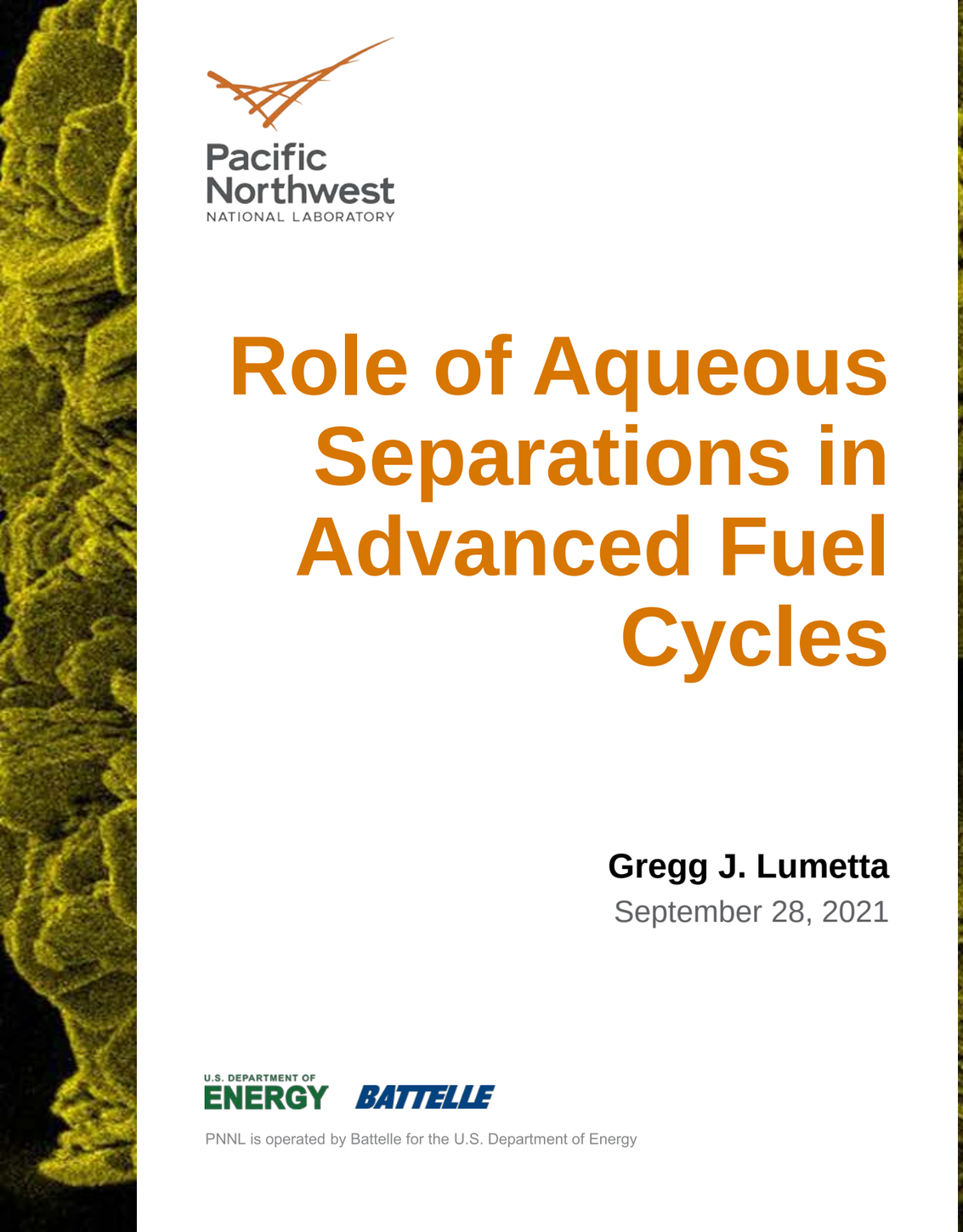
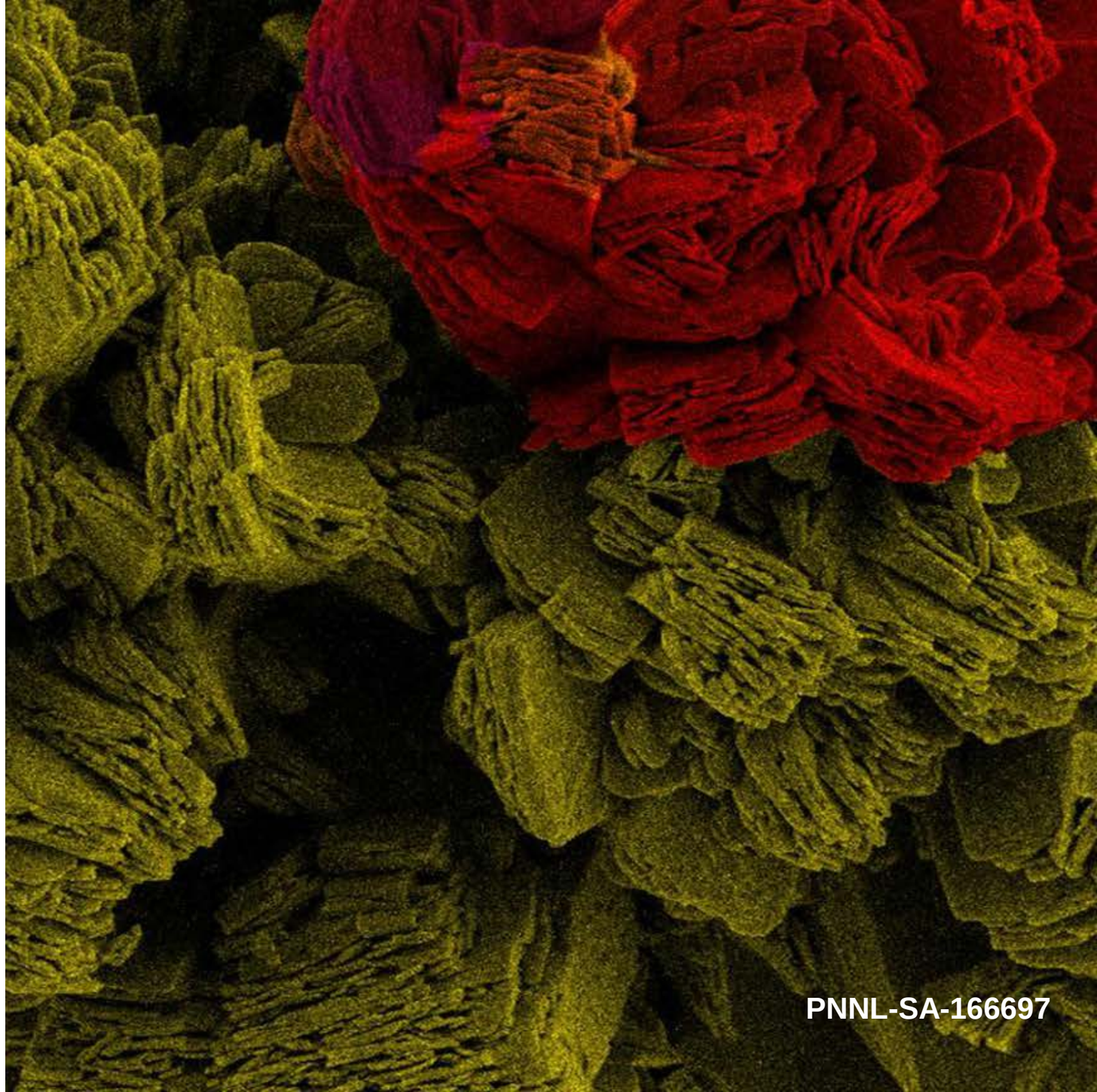
Role of Aqueous Separations in Advanced Fuel Cycles

Gregg J. Lumetta

September 28, 2021





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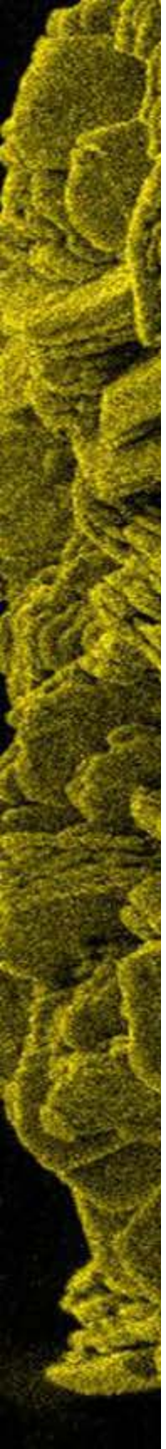
PNNL-SA-166697

Why recycle used nuclear fuel?

- Same reasons people recycle other stuff
  - Maximize utilization of materials extracted from the earth
    - ✓Uranium
  - Conserve landfill space
    - ✓Geological repository



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But it’s not economical

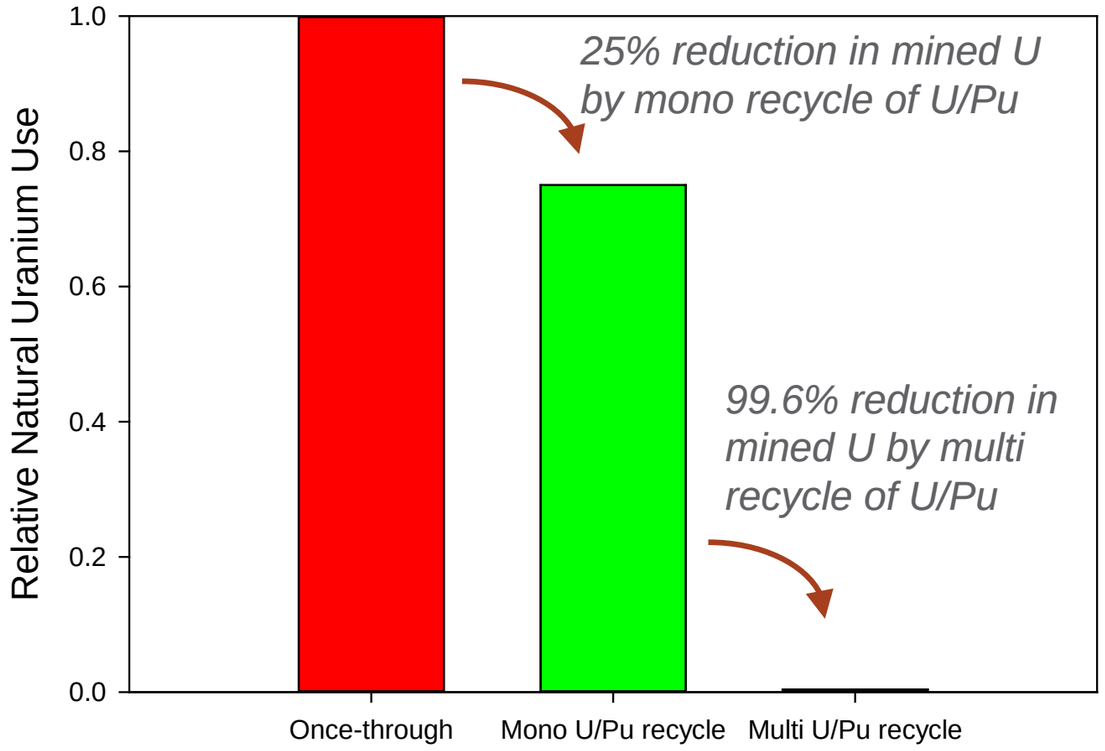
In (the) current market, it can be more expensive to … process recycled (uranium) than it would be to make new (uranium).

In Washington’s current market, it can be more expensive to transport, clean, and process recycled glass than it would be to make new glass.

Washington's "Glass“ Half Full or Half Empty? An Examination of Glass Recycling in Washington State.
Washington State Department of Commerce, October 31, 2020

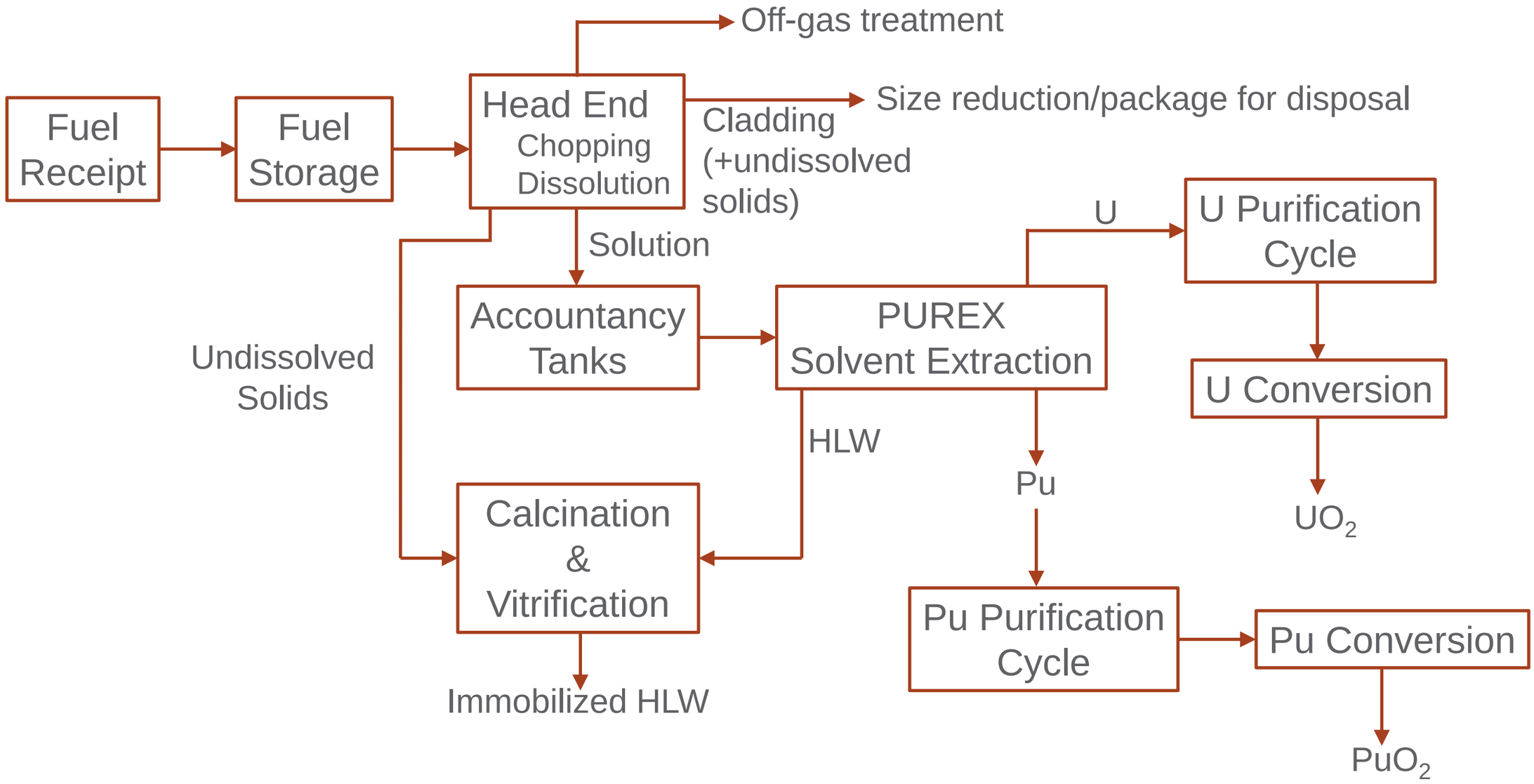
Blue Sky Vision

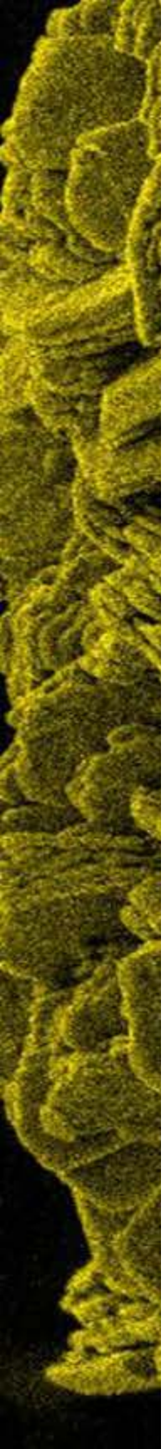
- Sustainable nuclear power *system*
  - Fleet of thermal and fast reactors
  - Multi-recycle of U and Pu
  - Separation and transmutation of minor actinides
  - Only fission products geologically disposed



Adapted from *Strategies and Considerations for the Back End of the Fuel Cycle*, NEA No. 7469, Nuclear Energy Agency, Organisation for Economic Co-Operation and Development (2021)

Key features of a late 20th Century reprocessing facility (typically located adjacent an ocean)





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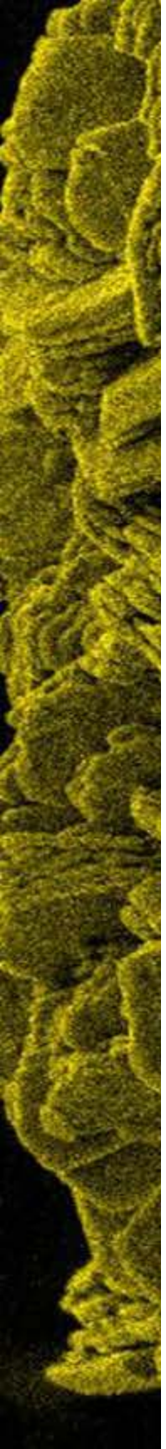
Disadvantages of current reprocessing facilities

- Substantial mechanical handling to expose fuel for dissolution
- Fuel dissolution is a batch process
- Tank space requirements substantially drive facility size (and cost)
  - Accountancy tanks, feed tanks, product tanks, surge tanks, solvent holding tanks, etc.
- Nitric acid and NOx management
  - Evaporators, calciners
  - Recycling and management of contaminated HNO_3 within the facility
- Tritium management
  - Current technology results in widespread distribution of ^{3}H throughout the plant
  - Tritiated water discharged to the environment
- Large amount of secondary waste from solvent washing
- Krypton capture
  - Might or might not be a problem depending on the scenario
    - ✓ Short cooled fuel



Aqueous processing has advantages for a 21st century reprocessing plant

- Engineering principles extremely well understood
  - Scalable
  - Industrially applied in the nuclear industry for over 60 years
- Separations amenable to continuous operation with minimal mechanical handling and ‘moving parts’ requiring maintenance
- Highly selective separations possible
  - Very high decontamination factors can be achieved
- The same generic liquid-liquid extraction process technology and equipment can be used to separate multiple target constituents
- Waste streams are understood with TRL 9 technologies available for immobilization

Opportunities for improvement

- Process simplification

  To paraphrase Andreas Geist...We must reduce the number of boxes.

  - Eliminate purification cycles
    - ✓One cycle to give
      - Pure U
      - U/Pu or U/Np/Pu
    - ✓Reduced solvent inventory and secondary liquid effluent volumes
  - Group actinide separation
    - ✓Why not just let the Pu go with the U, and recycle the lot into new fuel?
      - What advanced reactors could use such a fuel directly?
      - For LWRs the U enrichment would be too low and not enough Pu to make up for it
        - Could recycle U from used HALEU fuel to boost up the U enrichment
        - Could tap into existing excess Pu stocks
    - ✓Co-recovery of Z 92 – 95
      - Similar questions to above

Opportunities for improvement (2)

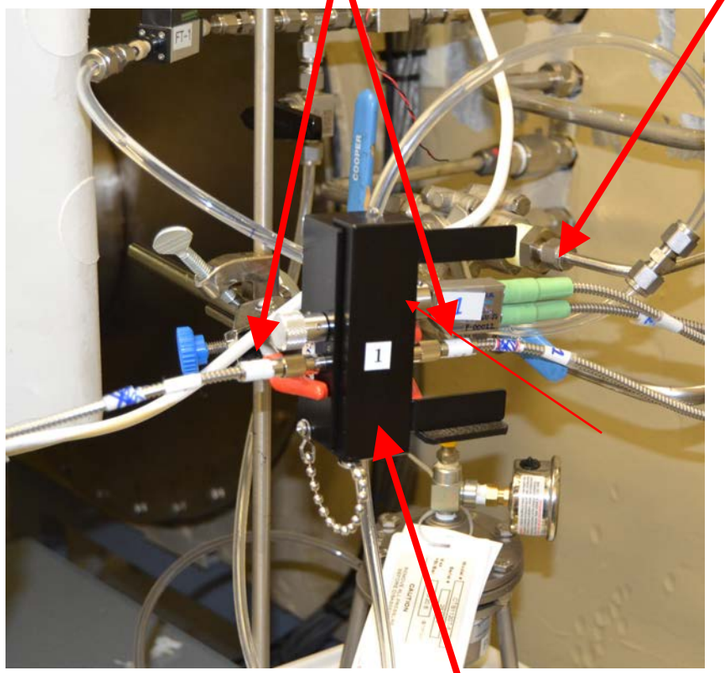
- Real-time monitoring of process streams
  - Can the need for accountancy tanks be eliminated, along with the delay caused by safeguards driven analyses?
  - Can the need for surge tanks be reduced, or even eliminated, by real-time process feedback and control?
  - Can process monitoring and automated control be used to produce products within particular characteristics (e.g., a specifically targeted U/Pu product)?
- Development of highly selective ligands
  - Eliminate co-extraction of traditionally problematic elements
    - ✓ Zr, Tc
    - ✓ Selective extractants
    - ✓ Selective holdback reagents
  - Liquid extraction systems with high capacity for metals (reduce plant size)

Opportunities for improvement (3)

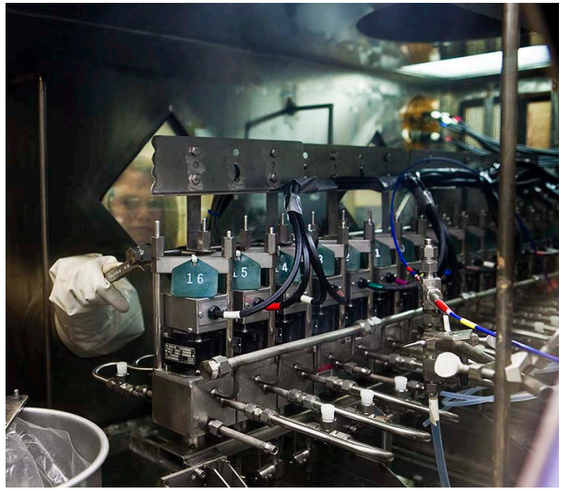
- Environmental Impact
  - Capture and isolate tritium, iodine and noble gas fission products
  - Capture and transmute high heat-producing minor actinides to improve geologic repository utilization
  - Alternative CHON-based extractants
  - Reduce number of secondary liquid effluent streams

Real-time monitoring to maintain a specific U/Pu ratio: The CoDCon Project

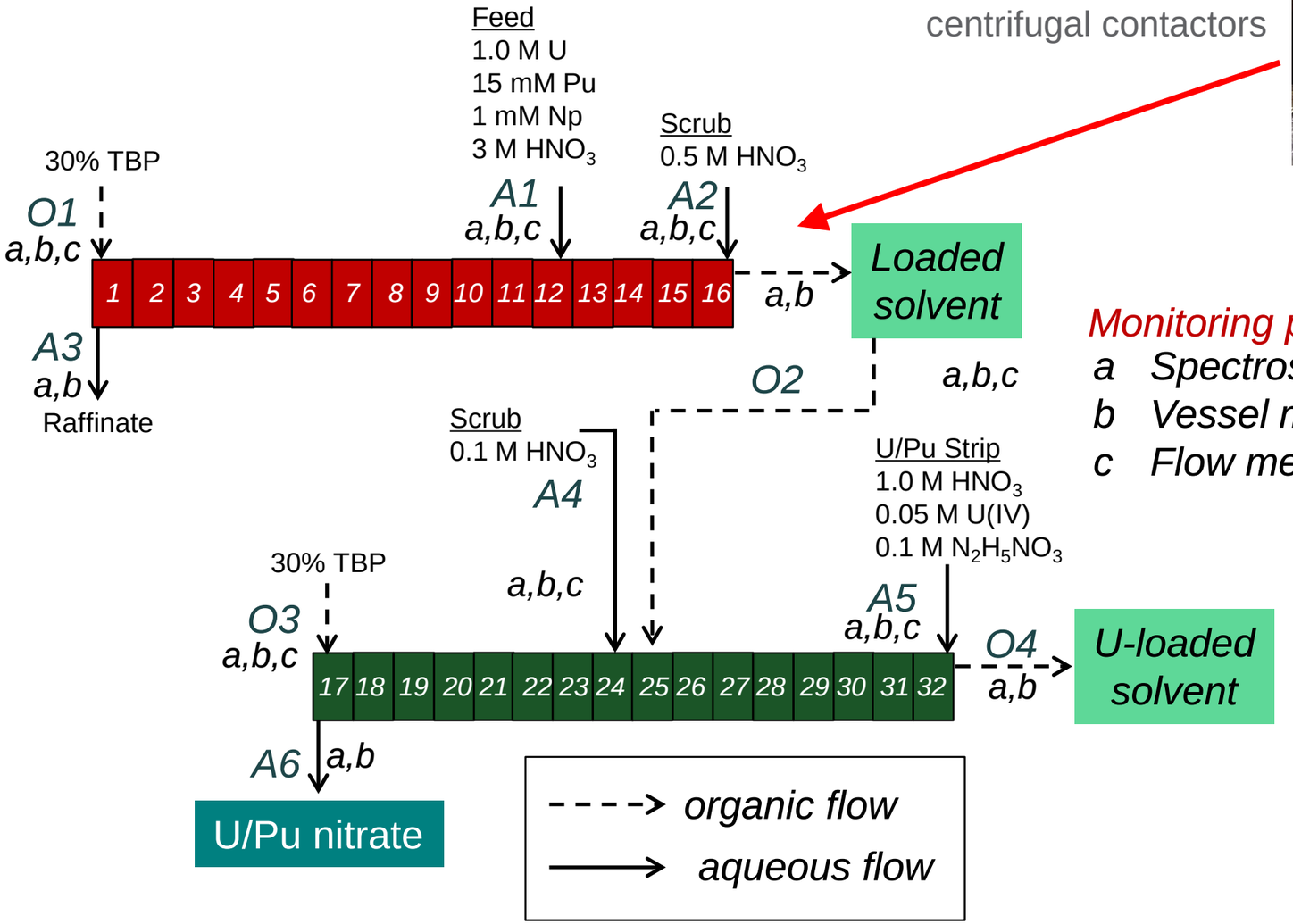
- No separated Pu
  - Flowsheet designed to produce product with 70% U and 30% Pu
- How well can the U/Pu ratio be maintained under processing conditions?
- Real-time optical spectroscopy coupled with chemometric model allowed control of the U/Pu ratio in the product



CoDCon Run 3

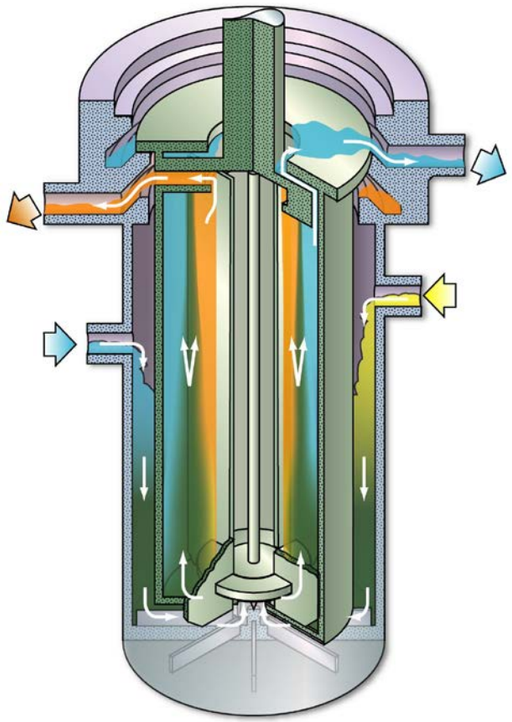


Bank of sixteen 2-cm centrifugal contactors



Monitoring points

- *a Spectroscopy*
- *b Vessel mass*
- *c Flow meter*

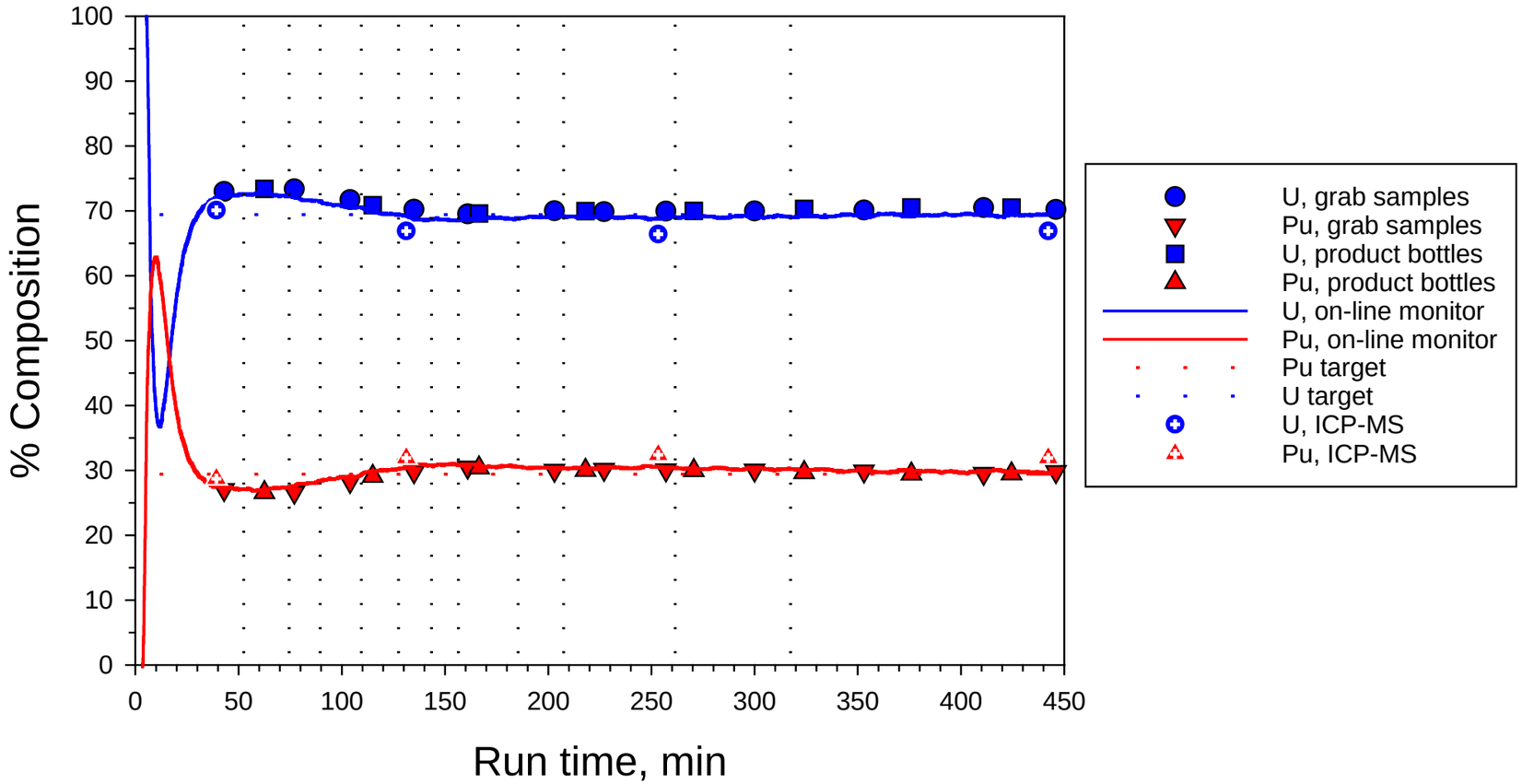


CoDCon Run 3 result

- Very stable operation
- Tweaks made to the fresh TBP flowrate mainly were attempts at fine tuning
- Off-line spectrophotometric analysis of bottles collected at t > 90 min

  U: 70.3 ± 0.4 %
  Pu: 29.7 ± 0.4 %

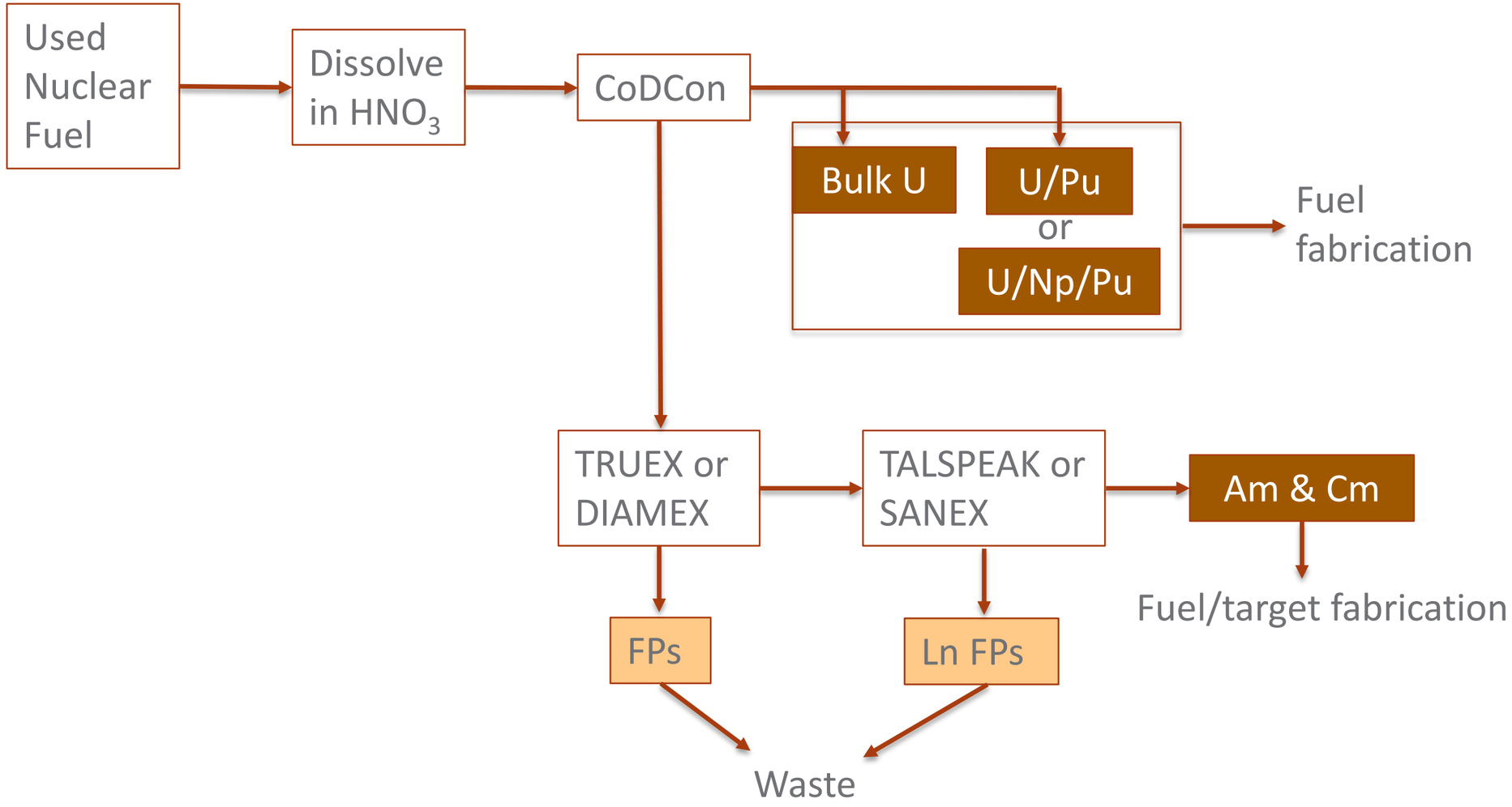
- But ICP-MS indicated 66.1% U and 33.9% Pu



Uncertainties in the analytical measurements dominate the uncertainty in the U/Pu product.

10% analytical uncertainty translates to 4% uncertainty in the U/Pu ratio

Recovery of minor actinides (Am and Cm)



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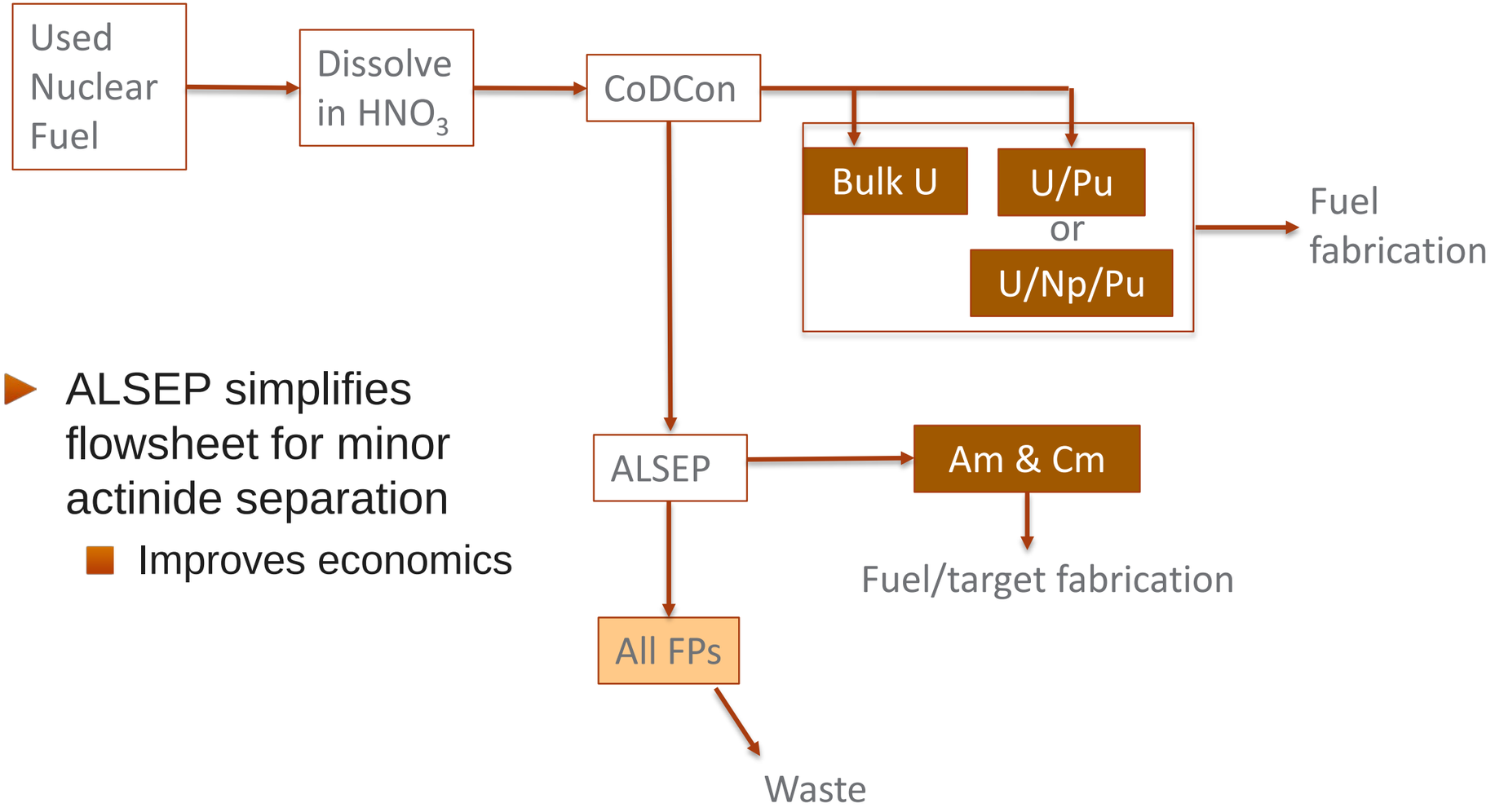
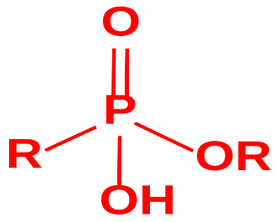


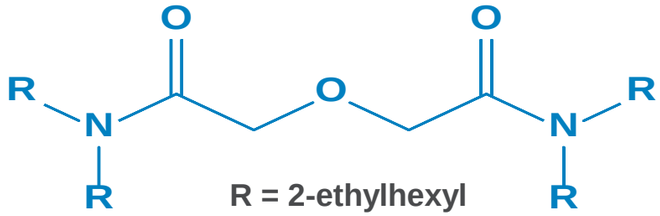
- ALSEP simplifies flowsheet for minor actinide separation
  - Improves economics

ALSEP: Actinide Lanthanide SEParation

Acidic Extractant: HEH[EHP]
2-ethylhexyl phosphonic acid
mono-2-ethyl-hexyl ester



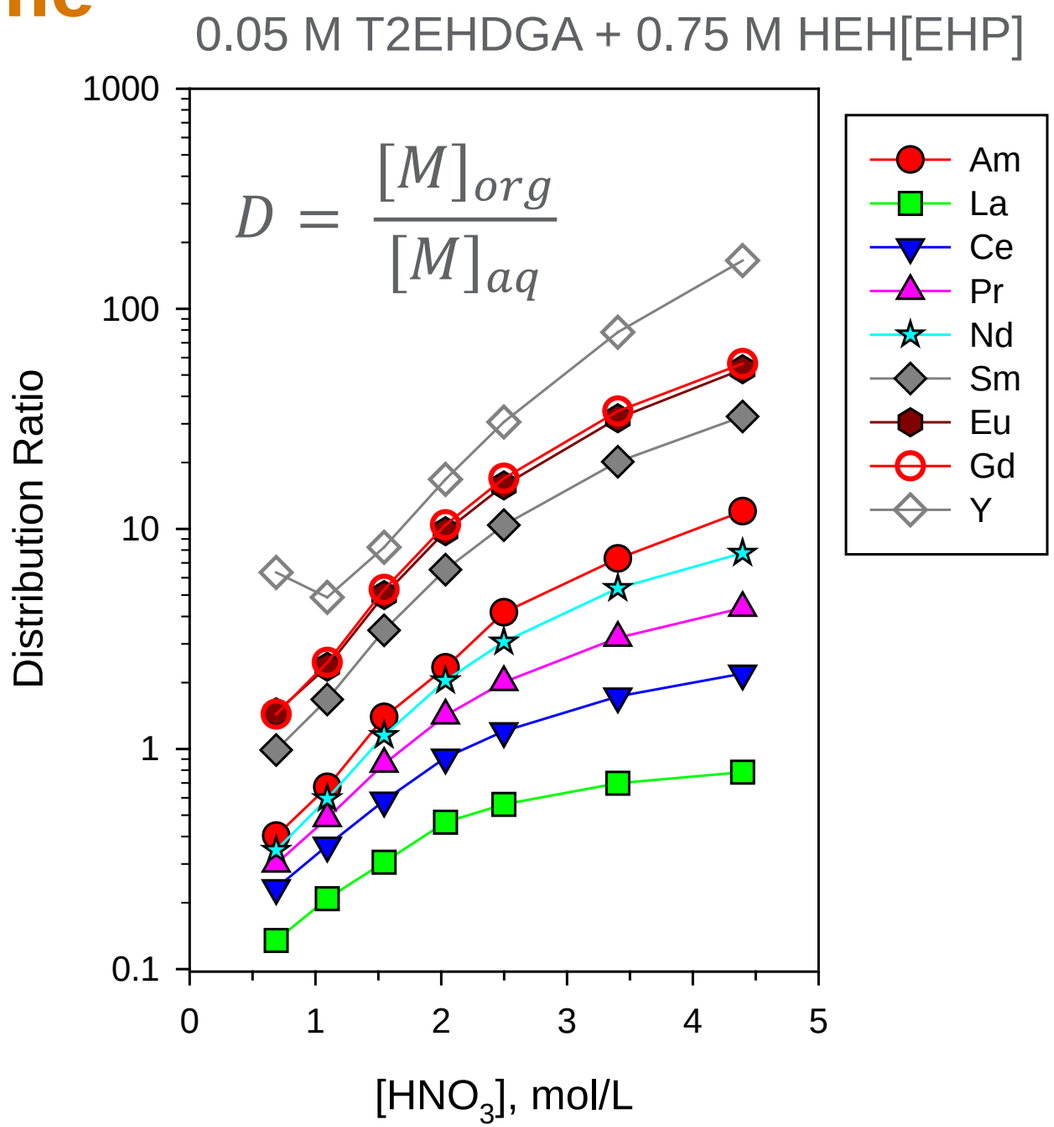
Neutral Diglycolamide: T2EHDGA
tetra-2-ethylhexyl diglycolamide



- Simpler overall process flowsheet than provided by alternative separations
- Ln/MA separation from post-PUREX (or CoDCon) raffinate
  - Co-extract MA & Ln from 3-5 M HNO_3; **DGA extracts MA & Ln**
  - Selectively strip MA from loaded ALSEP solvent using polyaminocarboxylate ligand in aqueous phase; **HEH[EHP] retains Ln in organic phase**
  - Strip Ln using aqueous complexant, e.g., TEDGA (DGA, R = ethyl)

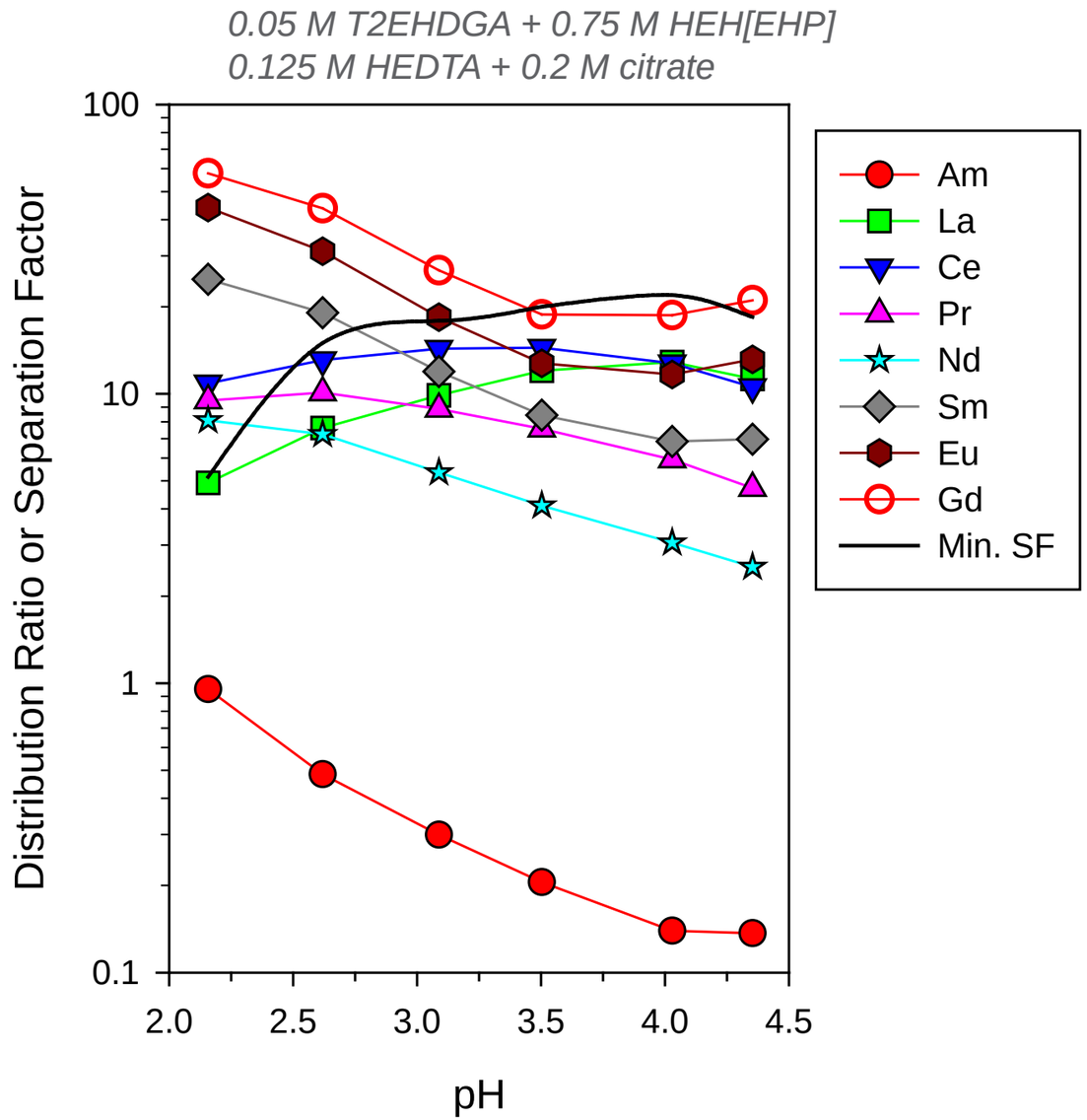
ALSEP extraction regime

- Am extracted at ≥ 2 M HNO_3
- Lanthanide distribution ratio (D) values increase with increasing Z, up to Eu and Gd
- La D values are < 1
  - Can separate La from the MA in the extraction stages



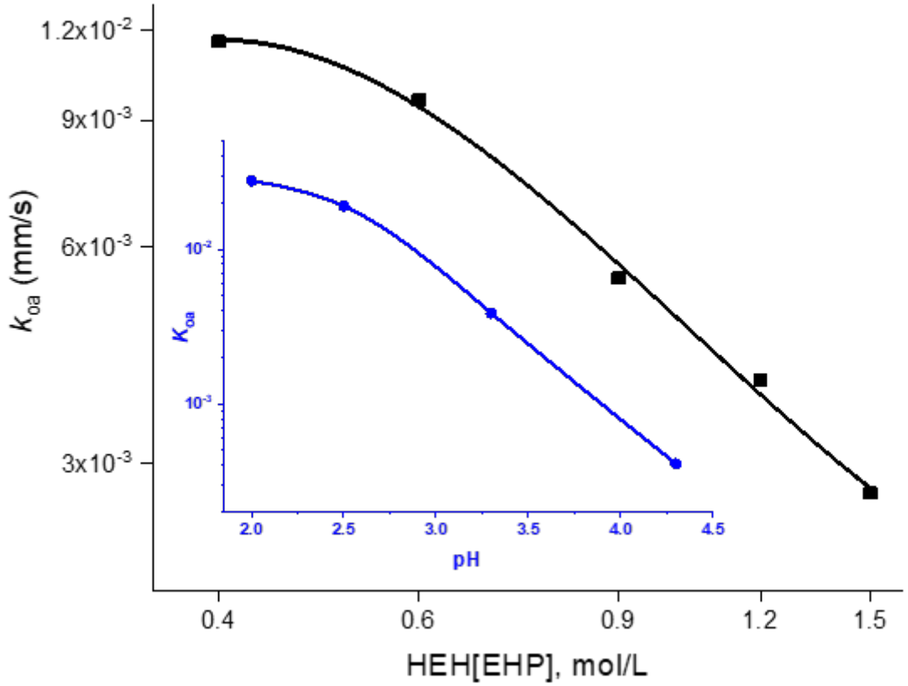
ALSEP minor actinide stripping regime

- pH dependence much less than for traditional TALSPEAK
  - e.g., logD_{Am} vs pH slope is about -0.3 versus -2 for TALSPEAK
- Above pH 2.9, the minimum separation factor depends little on pH
  - ✓ SF ~ 21 to 25
  - ✓ Defined by Nd/Am couple
- But stripping kinetics slow for this formulation



ALSEP minor actinide stripping regime revised

- To overcome slow MA stripping kinetics
  - Decreased the HEH[EHP] concentration from 0.75 to 0.5 M
  - Switched from HEDTA to DTPA, and lowered the pH
    - ✓ 0.015 M DTPA and 0.2 M ammonium citrate
    - ✓ pH 2.0

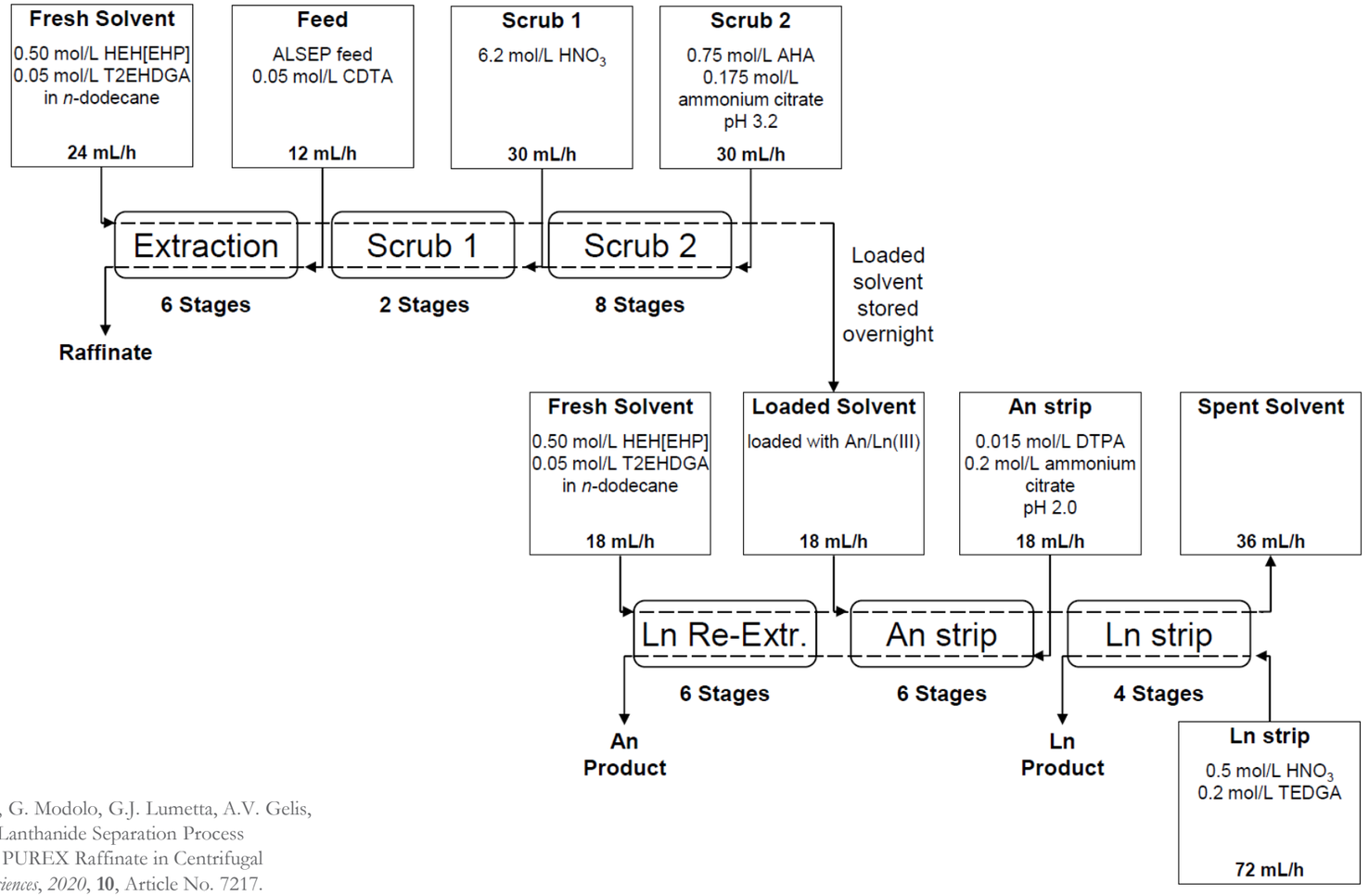


Am backward-extraction rate constant as a function of the HEH[EHP] concentration and the pH of the DTPA buffered solution (inset). Aqueous phase 0.015 mol/L DTPA.0.2 mol/L $(H/NH_4)_3$Citrate, pH 2.0, variable HEH[EHP] conc.; Inset: 0.75 mol/L HEH[EHP]/n-ddn, Aqueous phase: 25 mmol/L DTPA, 0.5 mol/L $(H/NH_4)_3$ Citrate, variable pH.

A.V. Gelis, P. Kozak, A. Breshears, M.A. Brown, C. Launiere, E.L. Campbell, G.B. Hall, T.G. Levitskaia, V.E. Holfeltz, G.J. Lumetta, "Closing The Nuclear Fuel Cycle With A Simplified Minor Actinide Lanthanide Separation Process (ALSEP) And Additive Manufacturing," *Scientific Reports, 2019,* **9:**12842.

ALSEP flowsheet test

- Counter-current flowsheet test conducted at FZ-Jülich (Germany)
- Simulate PUREX raffinate
  - Spiked with Am and Cm



A. Wilden, F. Kreft, D. Schneider, Z. Paparigas, G. Modolo, G.J. Lumetta, A.V. Gelis, J.D. Law, A. Geist, "Counter Current Actinide Lanthanide Separation Process (ALSEP) Demonstration Test with a Simulated PUREX Raffinate in Centrifugal Contactors on the Laboratory Scale," *Applied Sciences*, *2020*, **10**, Article No. 7217.

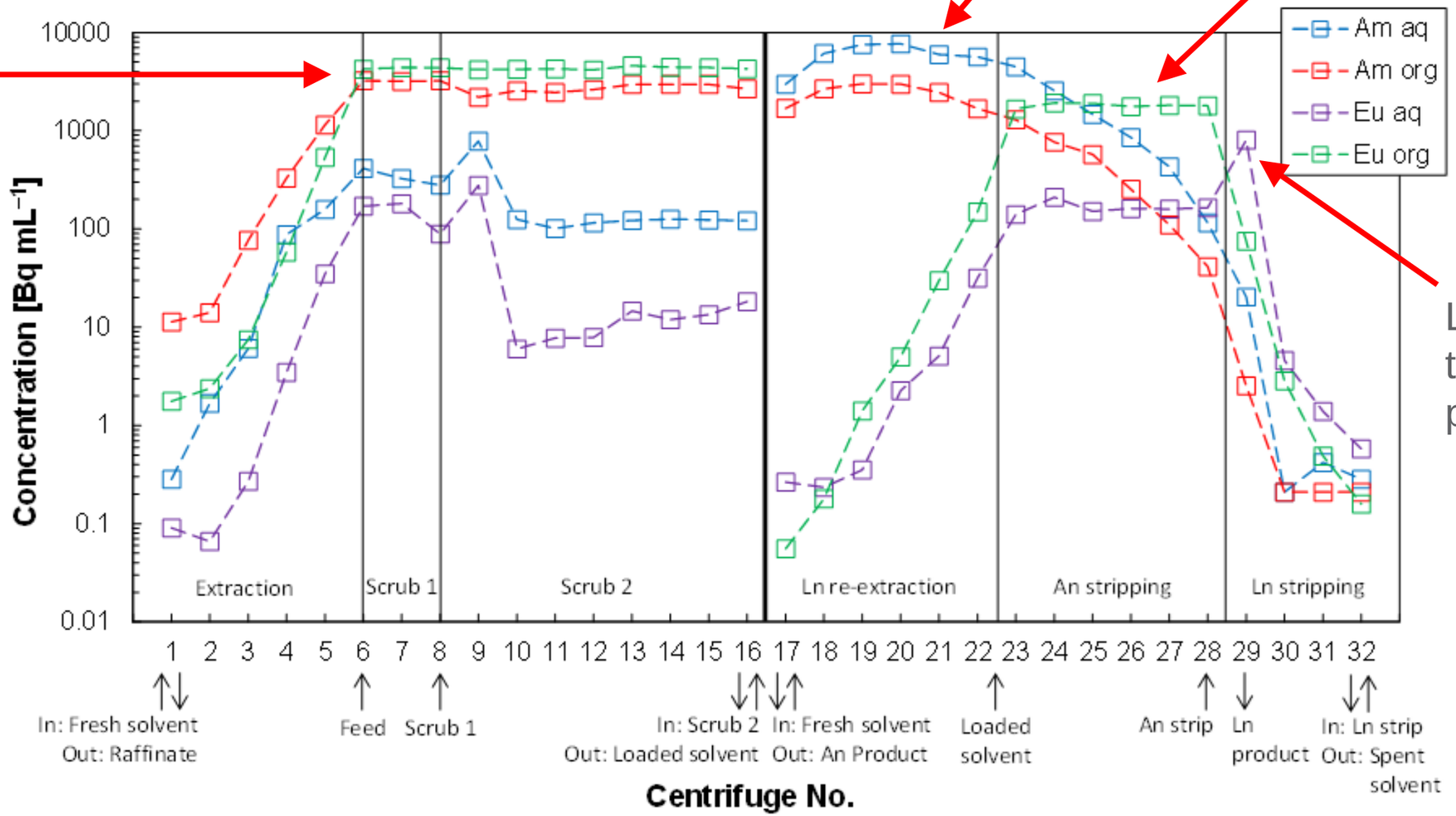
Am and Eu stage profiles

MA and Ln extracted into organic phase

MA transferred to aqueous phase

Ln remain in organic phase

Ln transferred to aqueous phase



Batch ALSEP test with dissolved irradiated fuel

- High burnup ATM 109 fuel dissolved in HNO_3
- Uranium, Np, and Pu removed by extraction with TBP
- CDTA added to suppress Zr extraction
- Three successive extraction contacts with 0.05 M T2EHDGA/0.5 M HEH[EHP]
- ALSEP organic phases combined and
  - Scrubbed with 3 M HNO_3
  - Scrubbed with 1 M acetohydroxamic acid (AHA) plus 0.175 M ammonium citrate at pH 3.3
- Scrubbed ALSEP solvent split into two portions
  - One portion stripped with 0.015 M DTPA plus 0.175 mol/L ammonium citrate at pH = 2.0
  - One portion was stripped with 0.125 M HEDTA plus 0.2 mol/L ammonium citrate at pH = 3.0
  - Both stripped with 0.5 M TEDGA in 1.0 mol/L HNO_3

A.V. Gelis, P. Kozak, A. Breshears, M.A. Brown, C. Launiere, E.L. Campbell, G.B. Hall, T.G. Levitskaia, V.E. Holfeltz, G.J. Lumetta, "Closing The Nuclear Fuel Cycle With A Simplified Minor Actinide Lanthanide Separation Process (ALSEP) And Additive Manufacturing," *Scientific Reports, 2019,* **9:**12842.

Results of test with irradiated fuel

Distribution ratios:

Contact	^{154}Eu	^{241}Am
Extraction 1	13.9	3.3
Extraction 2	(a)	(a)
Extraction 3	(a)	(a)
3 M HNO_3 scrub	59.3	10.5
AHA scrub 1	315	20.3
AHA scrub 2	(a)	31.2

Contact	^{154}Eu	^{241}Am
HEDTA MA strip 1	10.4	0.1
HEDTA MA strip 2	10.9	0.2
Post-HEDTA Ln strip	(b)	(b)
DTPA MA strip 1	9.9	0.1
DTPA MA strip 2	8.7	0.1
Post-DTPA Ln strip	(b)	(b)

(a) ***Counts in aqueous phase below detection.***

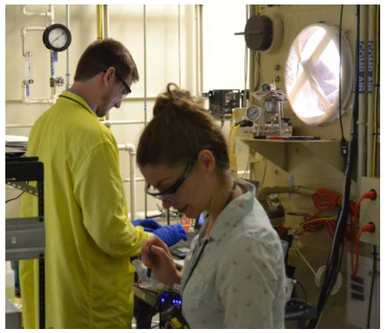
(b) ***Counts in organic phase below detection.***

Key takeaways

- Solvent extraction is still the gold standard for recycling of fissile material from spent nuclear fuel
- Opportunities for improvement
  - Process simplification
    - ✓ALSEP provides example
      - Condensing two processes into one
  - Robust, real-time, process monitoring and control
    - ✓CoDCon provides examples
      - Rigorous control of U/Pu product
  - Secondary waste minimization

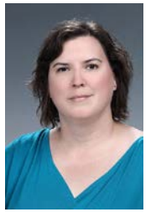
Acknowledgements

- This work was sponsored by the U.S. Department of Energy Office of Nuclear Energy through the Nuclear Fuel Cycle and Supply Chain office.
- The author thanks Stuart Arm for his helpful suggestions regarding industrial implementation of reprocessing technology.
- The author also thanks the small army of people that have supported these efforts over the years.
- Pacific Northwest National Laboratory is operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract No. DE-AC05-76RL01830.







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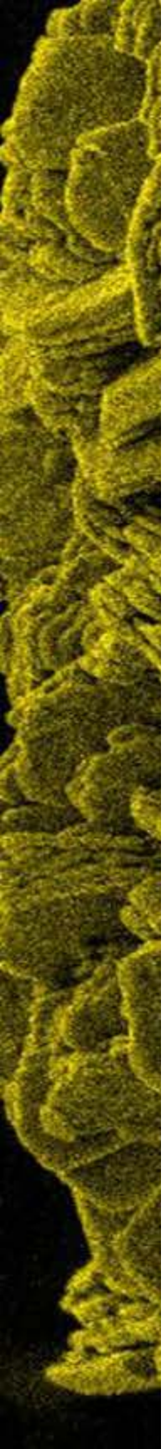
Thank you



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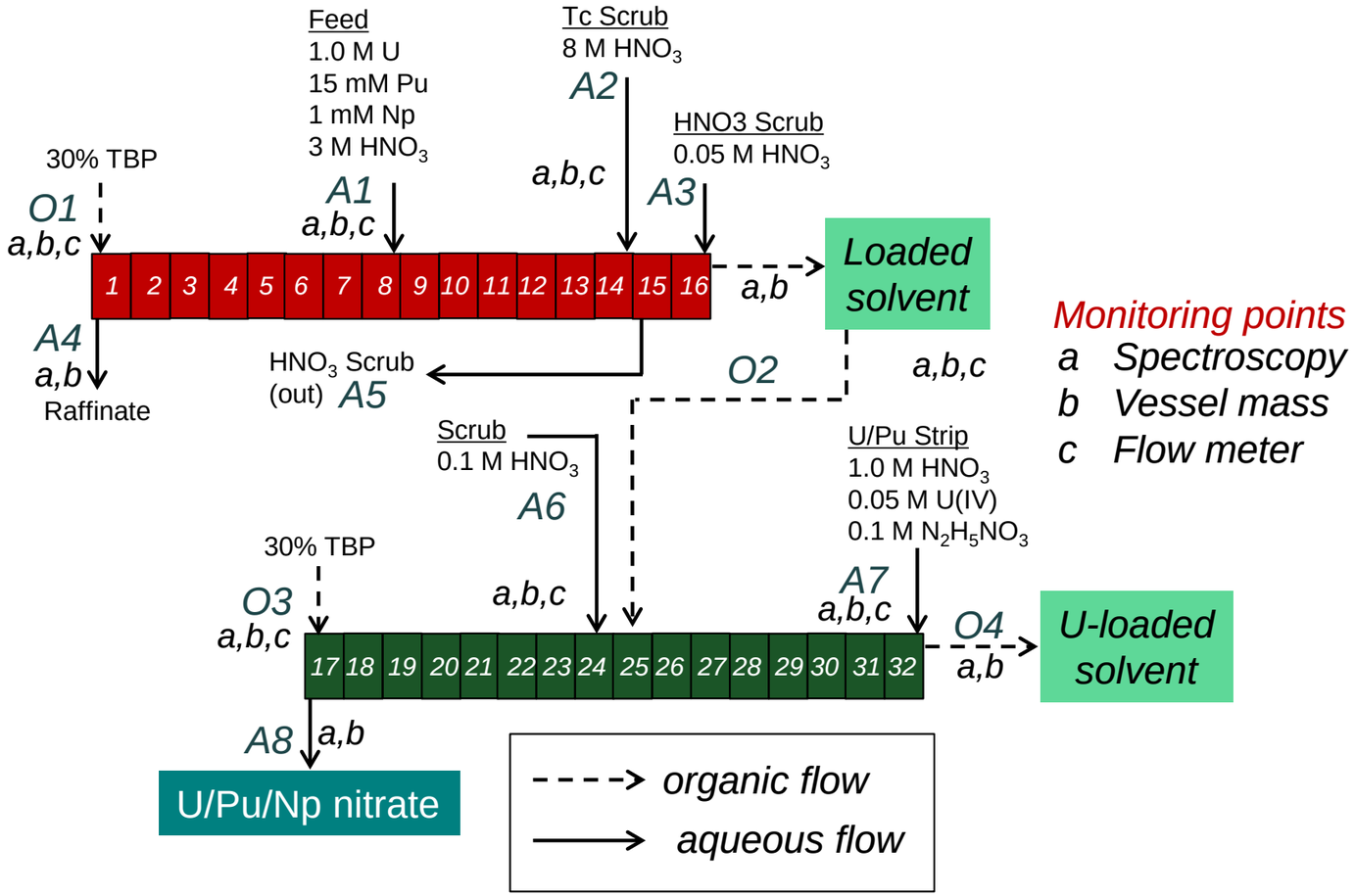
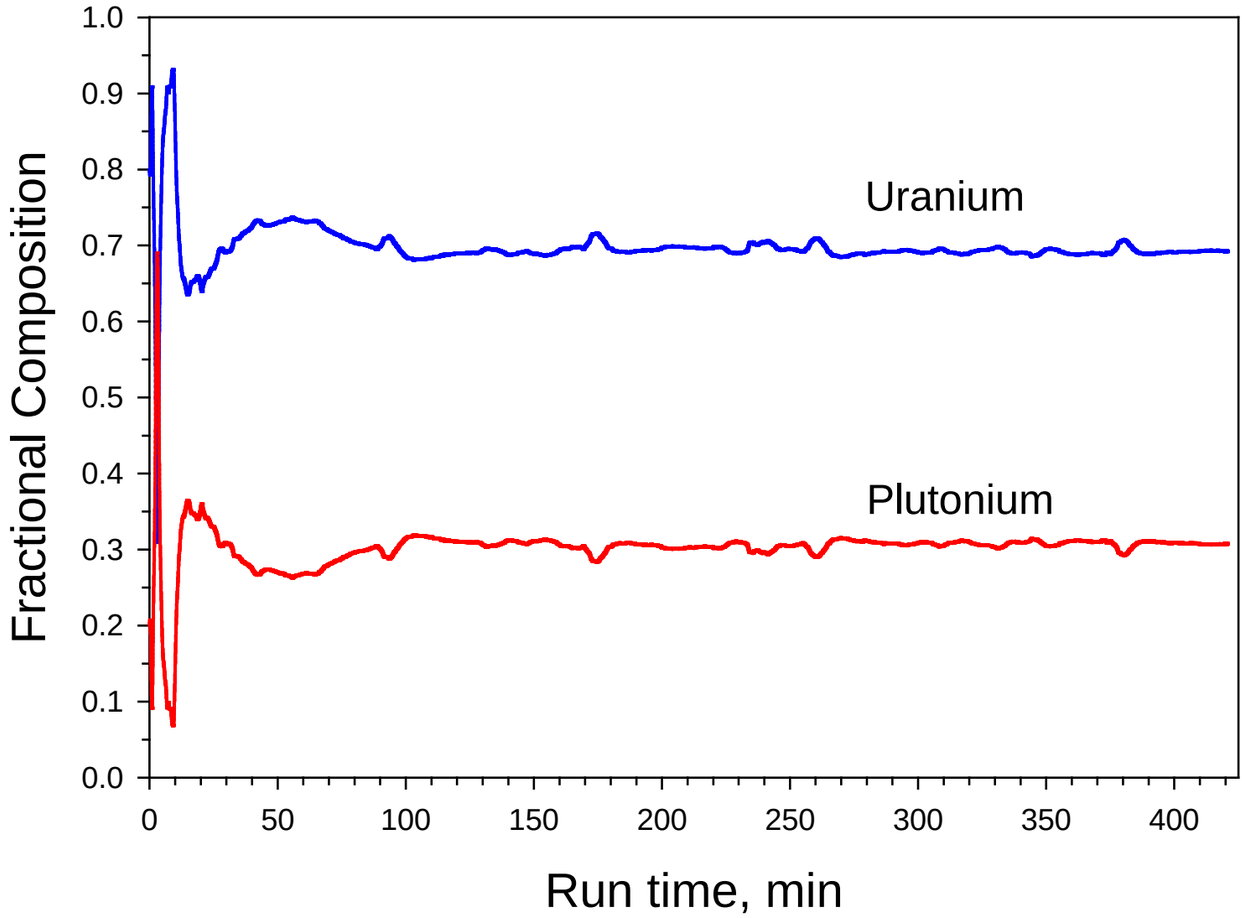
Backup slides

CoDCon Run 5

- More complicated dissolved fuel simulant
  - Non-rad fission products
  - Tc
  - Np
- Intended to route
  - Tc to raffinate
  - Np to U/Pu product
- Result indicated additional flowsheet development needed for routing of Tc and Np



CoDCon Run 5 result



ALSEP minor actinide stripping regime

- Am and heavier Ln
  - Decreasing *D* values with increasing pH for Am and the heavier Ln suggest a more pronounce role for extraction with HEH[EHP]

$$M^{3+}(aq) + 3(HA)_2(org) \rightleftarrows M(AHA)_3(org) + 3H^+(aq)$$

- Light Ln
  - Flatter pH dependence suggests less influence of HEH[EHP] and more influence of the neutral T2EHDGA

$$M^{3+}(aq) + 3NO_3^-(aq) + xDGA(org) \rightleftarrows M(NO_3)_3{\cdot}xDGA(org)$$

- pH dependence much less than for TALSPEAK
  - e.g., logD_{Am} vs pH slope is about -0.3 versus -2 for TALSPEAK
  - Above pH 2.9, the minimum separation factor depends little on pH
    - ✓ SF ~ 21 to 25
    - ✓ Defined by Nd/Am couple