



# Cleanup of Uranyl Sulfate Solutions

George F. Vandegrift

Chemical Sciences and Engineering Division



## **Four Methods looked at**

- Anion Exchange of uranyl sulfate complexes
- Direct Solvent-Extraction Process for Uranyl Sulfate
- Precipitation of Uranyl Ion as Uranyl Peroxide
- Conversion to Nitrate Media Followed by UREX Processing



## Anion Exchange of Uranyl Sulfate Complexes

- Extraction of uranyl sulfate from ore-leach liquors is used successfully commercially
  - However these solutions have dilute concentrations of uranium.
  - The low capacity of anion-exchange resins (1-2meq/g) makes this method impractical for concentrated uranyl sulfate solution
    - The sorbing species are felt to be  $\text{UO}_2(\text{SO}_4)_2^{2-}$  and  $\text{O}_2(\text{SO}_4)_3^{4-}$ , which will require 2-4 mEQ/mole
      - Or for 250 L of 130 g-U/L (~150 mole—300-600 equivalents of uranyl ion)
    - The extraction column would need ~600 kg of resin (based on 1-2 mEQ/g)
- Was rejected as impractical, but does suggest solvent extraction with alkyl amines is a possibility



**Slide 3**

---

**YAJ2**

**Deleted the word hold after need**

Youker, Amanda J., 8/3/2011

# Direct Solvent-Extraction Process for Uranyl Sulfate

- The likely processing steps are:
  - Solvent extraction processing to purify uranyl sulfate from other irradiated solution components.
  - Destruction of the stripping agent in the uranyl sulfate product (likely evaporation followed by thermal decomposition).
  - Reconstituting the uranyl-sulfate/0.1 M-sulfuric-acid target solution.
  - Treatment of waste streams generated for storage and final disposal



## Direct Solvent-Extraction Process for Uranyl Sulfate

- Process is based on the extraction of uranyl-disulfate anion by a solvent composed of two-parts trioctyl ammonium sulfate (TOA) and one-part trioctyl phosphate (TOPO) diluted by either an alkane or tetrachloroethylene
- Uranium is extracted into the organic phase as  $\text{UO}_2(\text{SO}_4)_2^{2-}$  anion with two trioctyl ammonium cations and one trioctyl phosphate
- If the proper aqueous stripping solution is chosen, uranyl sulfate will be stripped and the trioctyl ammonium salt will remain in the sulfate form to be recycled directly to the extraction section.
  - Possibilities are oxalic acid or other hydrophilic complexants as a stripping agent.
  - The complexant must have three important properties
    - forms strong complexes with uranyl ion
    - will not displace sulfate in the organic-phase trioctyl ammonium sulfate salt
    - can be destroyed in the aqueous uranyl-sulfate product solution without leaving residue in the solution
- A great deal of R&D is required to design the processing facility



**Slide 5**

---

**YAJ4**

Added the word solution to the second to last bullet point

Youker, Amanda J., 8/3/2011

# Precipitation of Uranyl Ion as Uranyl Peroxide

- In principal, the precipitation should be straight forward; the solubility product ( $K_{sp} = [UO_2^{2+}] \times [O_2^{2-}]$ ) for uranyl peroxide is  $1.3 \times 10^{-36}$
- However, there are many factors that influence the concentrations of free  $UO_2^{2+}$  ion and free  $O_2^{2-}$  ion, and, therefore, the completeness of the precipitation
  - For uranyl ion, there are pH-dependent hydrolysis reactions that form the species  $UO_2OH^{1+}$ ,  $UO_2(OH)_2$ , and  $UO_2(OH)_3^{1-}$  and sulfate complexes  $UO_2SO_4$ ,  $UO_2(SO_4)_2^{2-}$ , and  $UO_2(SO_4)_3^{4-}$ .
  - The free peroxide-ion concentration is also effected by the pH, due to formation of the weak acids  $H_2O_2$  and  $HO_2^-$
  - The relative concentrations of uranyl-sulfate complexes are also related to pH through the equilibria of sulfate ion with  $HSO_4^-$  and  $H_2SO_4$
  - Further complications to the precipitation are that peroxide ion can also form complexes with uranyl ion  $UO_2(O_2)_2^{2-}$  and  $UO_2(O_2)_3^{4-}$
- Laboratory tests showed the precipitate was very fine, very difficult to filter or centrifuge, and, therefore, difficult to wash and recovery.
  - Not acceptable for in a production setting



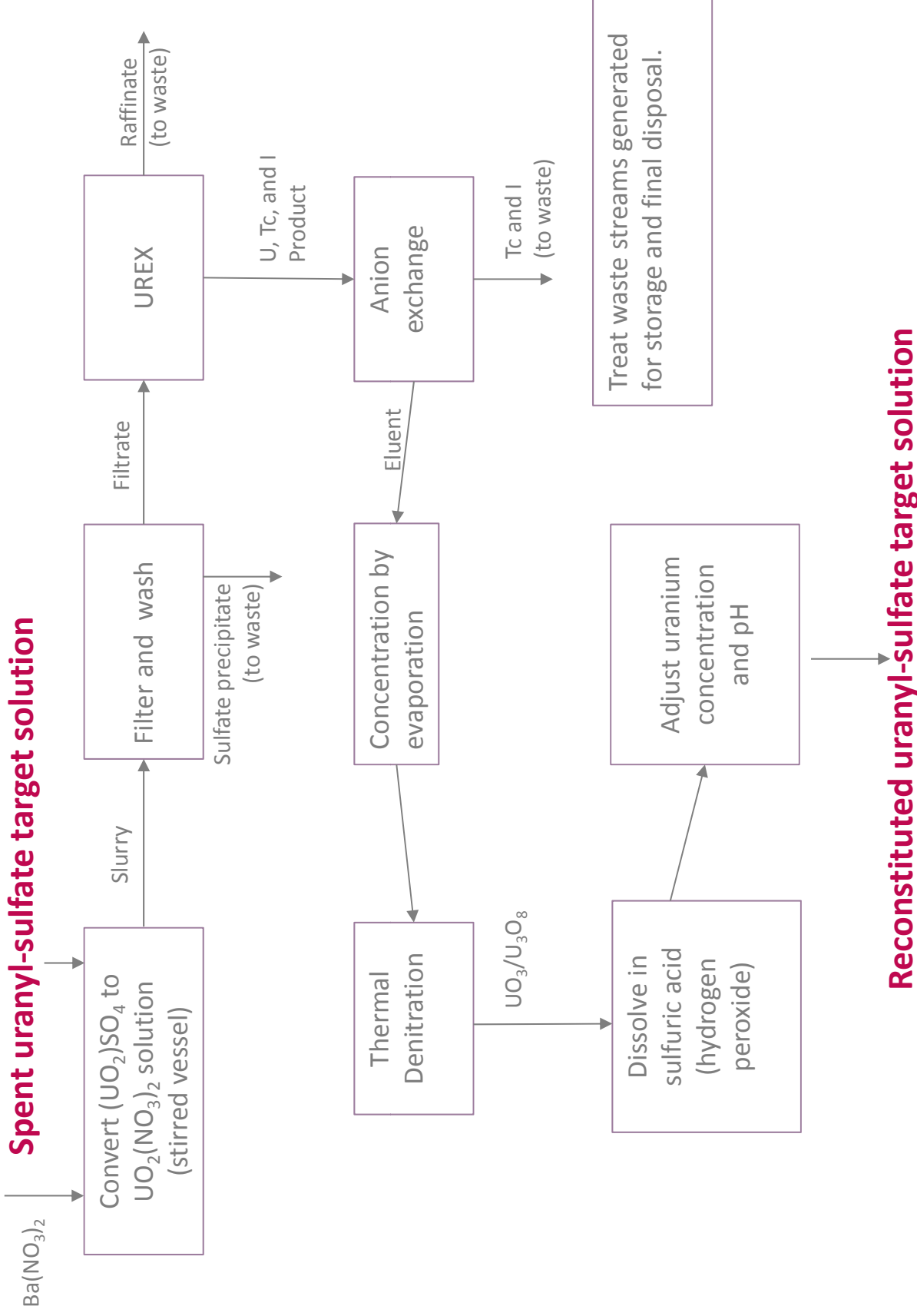


# Conversion to Nitrate Media followed by UREX and Reconversion to Sulfate Media

- Steps
  - Addition of solid  $\text{Ba}(\text{NO}_3)_2$  to the irradiated uranyl-sulfate solution in a stirred vessel; addition rate, stirring speed, and temperature must be set to optimize the morphology and size of the crystals formed to allow facile filtration.
  - Passing the slurry into a filtration system to collect and wash the precipitate (minimize uranium losses).
  - UREX processing of the filtrate.
  - Run U-product solution through an anion-exchange column to remove pertechnetate and iodide.
  - Concentration and denitration of the solution to form  $\text{UO}_3$ .
  - Dissolution of  $\text{UO}_3$  in sulfuric acid ( some hydrogen peroxide may be required if all uranium is not in the VI oxidation state).
  - Reconstituting the uranyl-sulfate/0.1 M-sulfuric-acid target solution.
  - Treatment of waste streams generated for storage and final disposal
- All process steps are used commercially and well understood
  - Minimum R&D is required to design processing facility

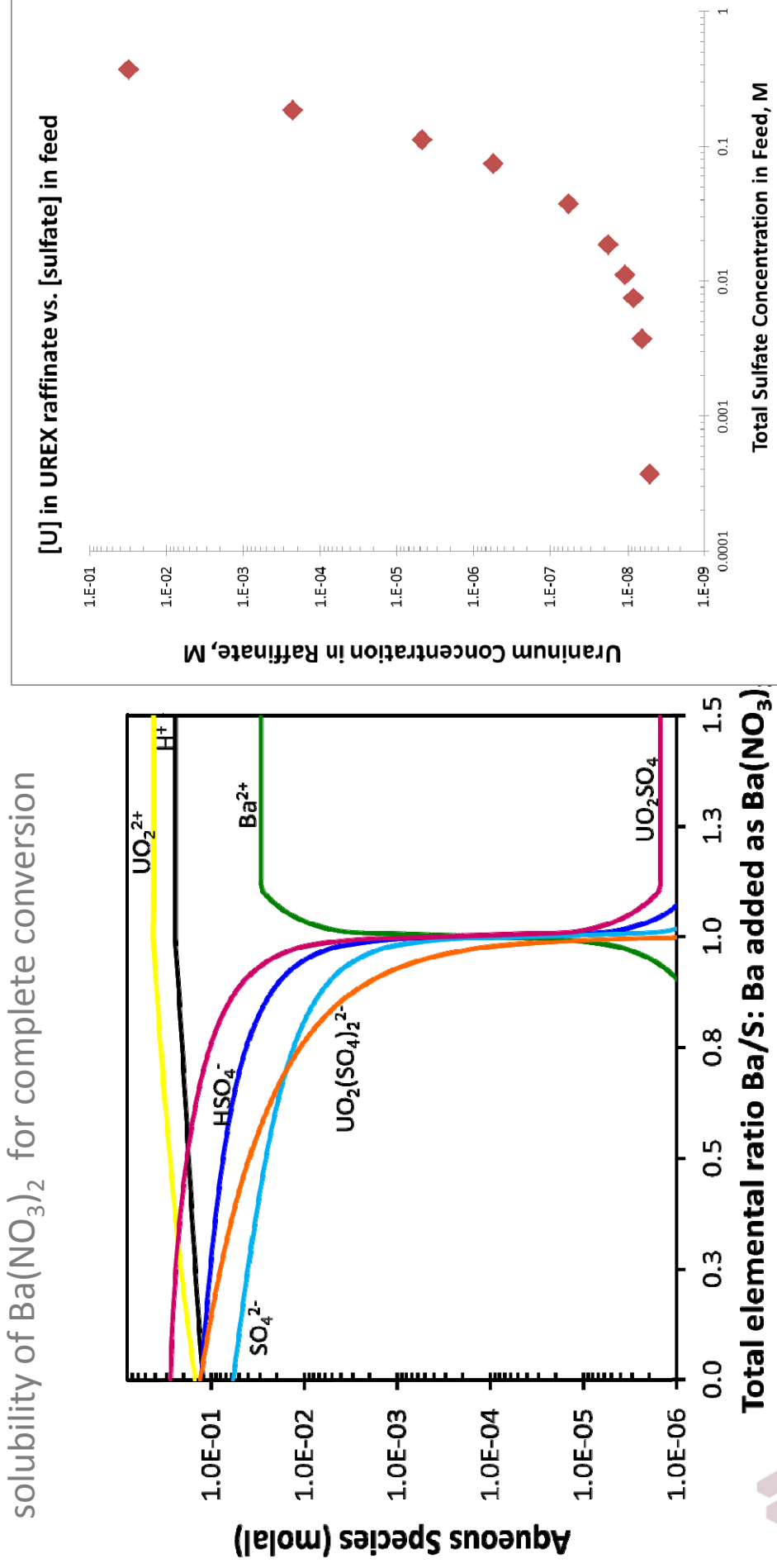


# Target-Solution-Cleanup Flowsheet



# Conversion from Sulfate to Nitrate Media

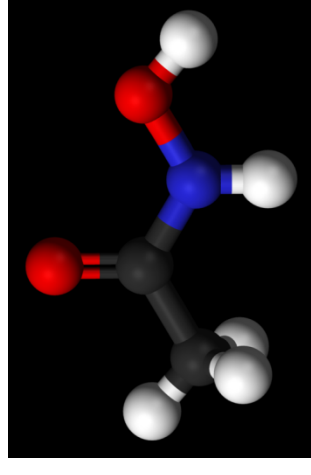
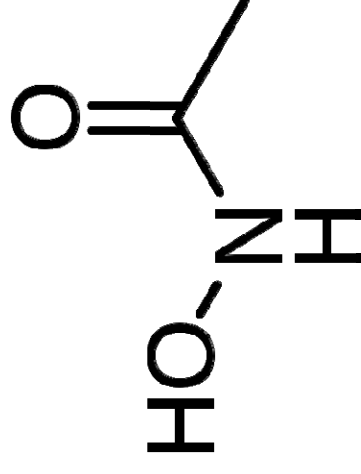
- The addition of solid  $\text{Ba}(\text{NO}_3)_2$  to the spent SHINE Target solution will drop sulfate concentration to levels below of concern to UREX processing
- Total sulfate in the feed can be  $\leq 0.01\text{M}$  with no significant effect
- Experimental results verify models prediction, but the solution must be heated to increase solubility of  $\text{Ba}(\text{NO}_3)_2$  for complete conversion



# UREX Process

- The UREX solvent extraction process is a modification of the commercial PUREX process
  - Modified by the addition of acetohydroxamic acid (AHA) to the scrub feed
  - AHA is a commercially available chemical which provides several advantages UREX process
    - Pu and Np do not extract due to a combination of complexation and reduction by AHA
    - Fission products that are troublesome to PUREX (Zr, Ru, Mo) are also complexed by AHA and, therefore, not extractable
    - Because of these features, UREX needs only one cycle compared to three for PUREX for producing high purity uranium in high yield
    - On standing (especially with heat) in nitric acid solutions, AHA will decompose to acetic acid and nitrous acid

- The UREX process was developed at Argonne National Laboratory under the DOE NE AFCI/GNEP program.
- It has been demonstrated at the pilot-scale at Argonne and Savannah River National Laboratories using dissolved high-burn-up spent fuel

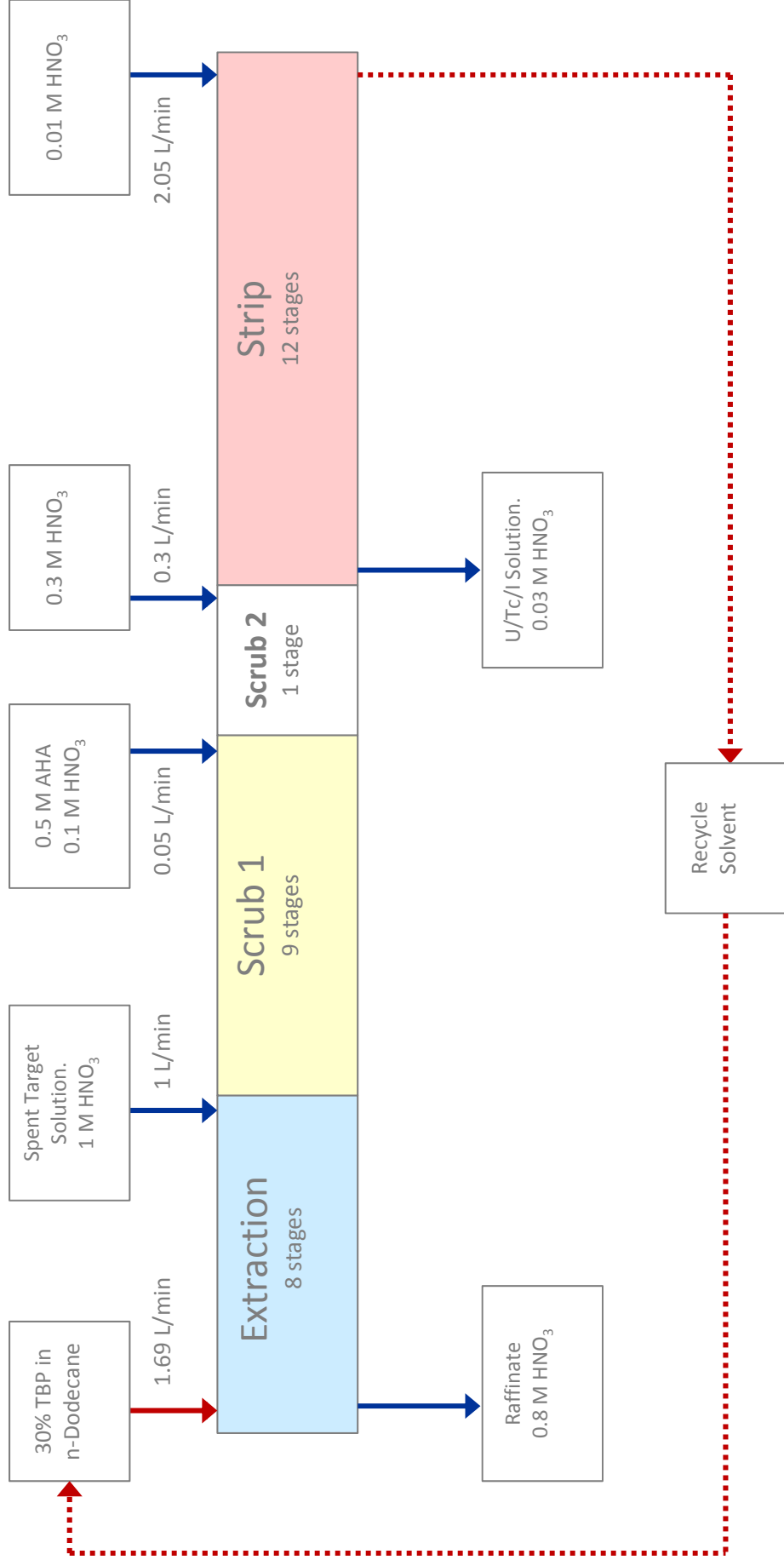


# AMUSE

- The AMUSE (Argonne Model for Universal Solvent Extraction) code, also developed under AFCI/GNEP, has a module for designing UREX flowsheet
  - Code has been validated
  - Code predictions were verified with UREX pilot-scale demonstration results
  - Is used throughout the DOE complex for flowsheet design/development
- AMUSE has two main modules
  - SASPE (Spreadsheet Algorithm for Speciation and Partitioning Equilibria)--chemistry module that calculates distribution ratios based on chemically correct equations and thermodynamic activities
  - SASSE (Spreadsheet Algorithm for Stagewise Solvent Extraction)--mass balance module that calculates the partitioning of species between the organic and aqueous phases in every stage based on the distribution ratio calculations
- A 30-stage flowsheet was developed for treating a 130 g-U/L uranyl nitrate solution
- The flowsheet predicts:
  - 99.999999% of the uranium will report to the U-product stream
  - All impurities will be reduced by  $\geq 10^7$  (except I and Tc, which will be removed in the anion-exchange process)



# The UREX Flowsheet for Periodic Cleanup of SHINE Target Solutions

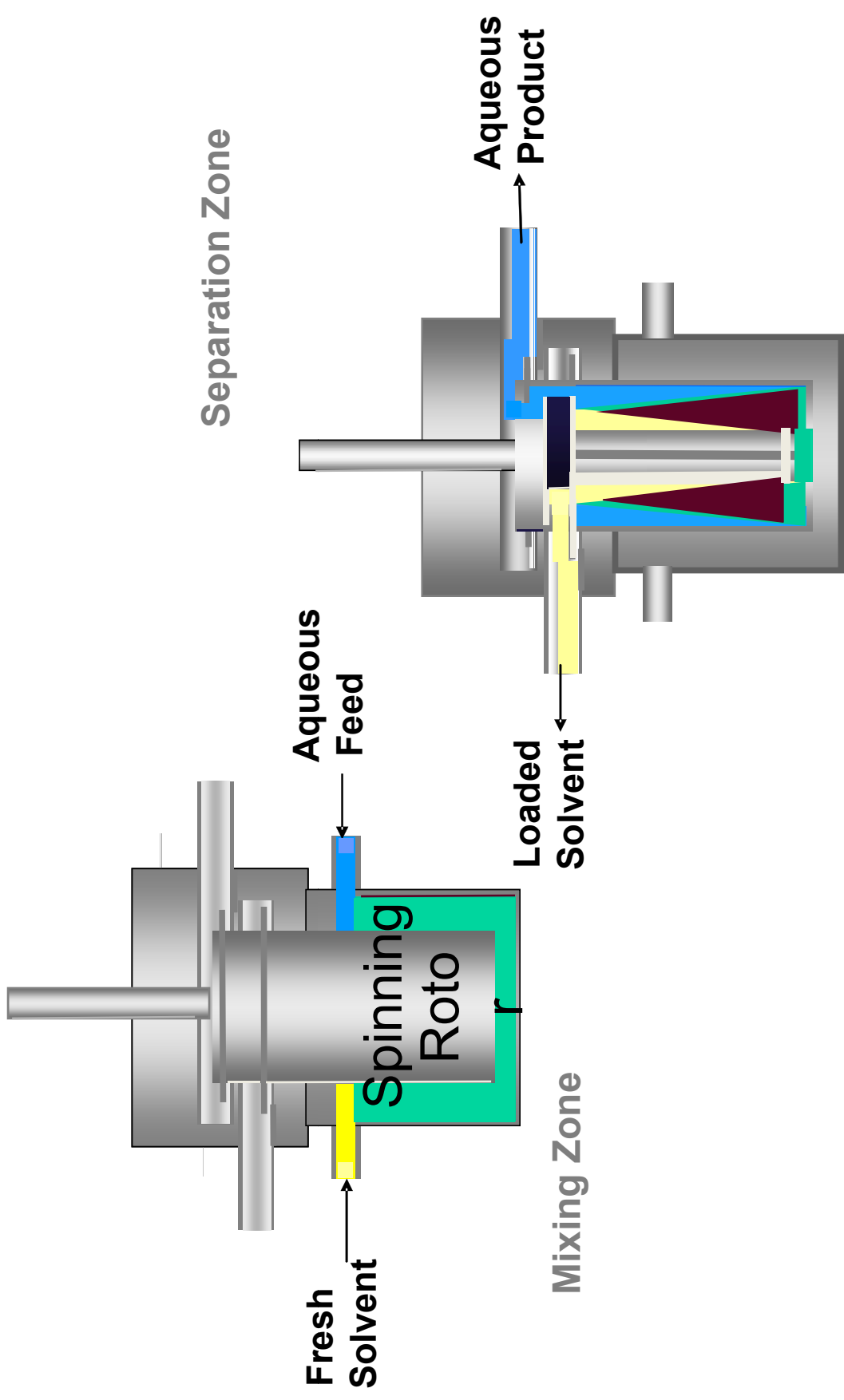


# The Argonne-Design Annular Centrifugal Contactor

- Invented at the Savannah River Site
- Developed at Argonne National Laboratory and later at Oak Ridge National Laboratory
- Commercial units sold by CINC (USA) and Rousselet Robatel (France)
  - Argonne can also produce units for sale
- Major advantages
  - High throughput
  - Small hold-up volume
  - Small footprint
  - High efficiency
  - A stage is a stage
    - Easily scalable to/from any size unit
    - Highly predictable behavior (easily modeled)
  - High throughput and small hold-up leads to minimum radiolytic and hydrolytic damage to solvent
- Used for production/waste cleanup at La Hague, Savannah River Site, and LANL
- Pilot facilities at Argonne, PNNL, SRNL, ORNL, INL, Y-12, and the Hanford site



# Centrifugal contactors are fast and efficient







## Bottom Line

- Out of the four options, conversion to nitrate followed by UREX is the surest means for cleanup
  - A process flowsheet was designed using the AMUSE code
- All equipment and process steps for the cleanup are mature/well-characterized
  - Development needs are only for optimization for a specific feed, facility, and process goals

