LA-UR-16-24305
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Title: Aqueous Nitrate Recovery Line at Los Alamos National Laboratory

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Intended for: The ADPSM Plutonium Engineering Lecture Series is an opportunity for new hires to get an overview of work done at TA55. The presentation will be done at TA55 to LANL employees. The slides will be available to new employees via sharepoint.

Issued: 2016-06-17

Aqueous Nitrate Recovery Line at Los Alamos National Laboratory

(LA-UR-16-XXXXX)

Presented to the ADPSM
Plutonium Engineering Lecture Series

June 15, 2016

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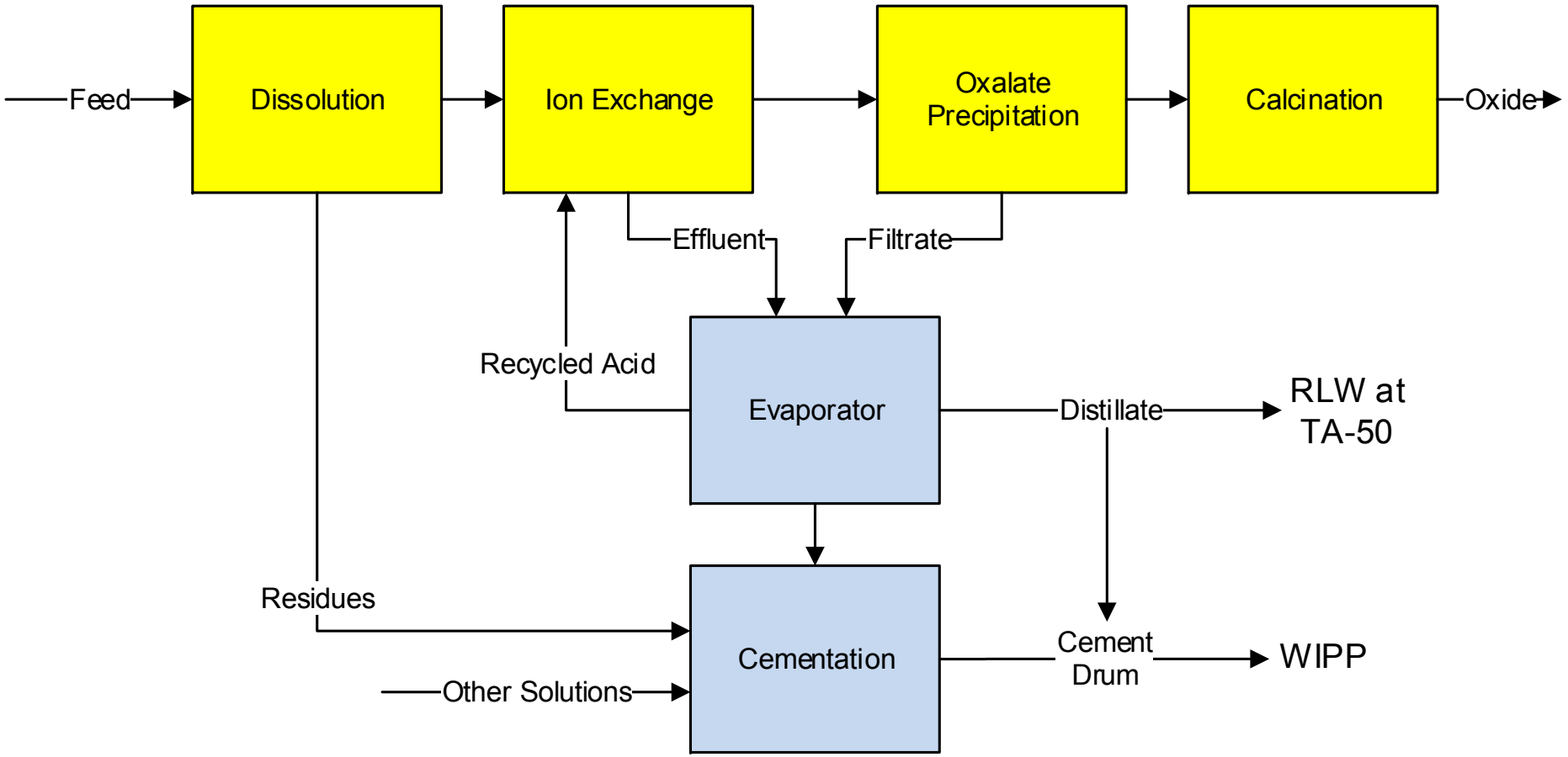
Aqueous Nitrate Flowsheet shows 4 major steps



Process Feed

- **Vault**
  - Oxides (LZB, PMB), residues, sweepings (VTB)
- **Casting Skulls, Anode Heels, “rejects”**
  - Suspect chloride oxide
- **PuBe**
  - High purity mixed metal oxides

Pot Dissolution

- **15.6 M nitric acid**
- **Fluorine catalyst (HF or CaF_2)**
- **Ar sparge**
- **Slowly add feed**
- **4 hrs at 96˚C, under reflux**

$$PuO_2 + 6HNO_3 \rightarrow Pu(NO_3)_6^{-2} + 2H_2O + 2H^+$$
$$Pu + 6HNO_3 \rightarrow Pu(NO_3)_6^{-2} + 2H_2 + 2H^+$$

Pot Dissolution - Filtration

- **Add aluminum nitrate**

$$Al(NO_3)_3 + 6HF \rightarrow AlF_6^{-3} + 3H^+ + 3HNO_3$$

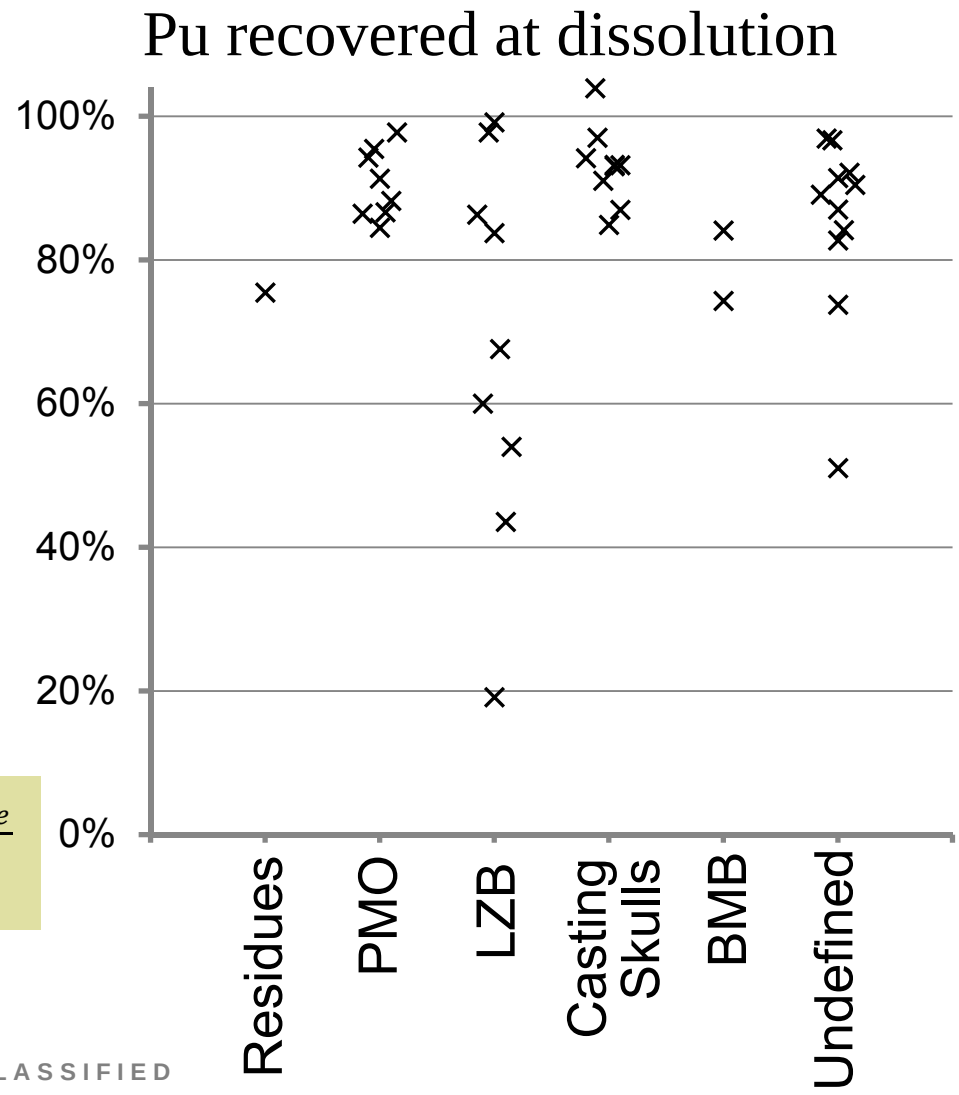
- **Filter solution**
- **Rinse residue**
- **May perform multiple passes with residues**
- **Cl^- concentration measurement**

Dissolution efficiency

Depends on

- Feed Type
- Number of passes

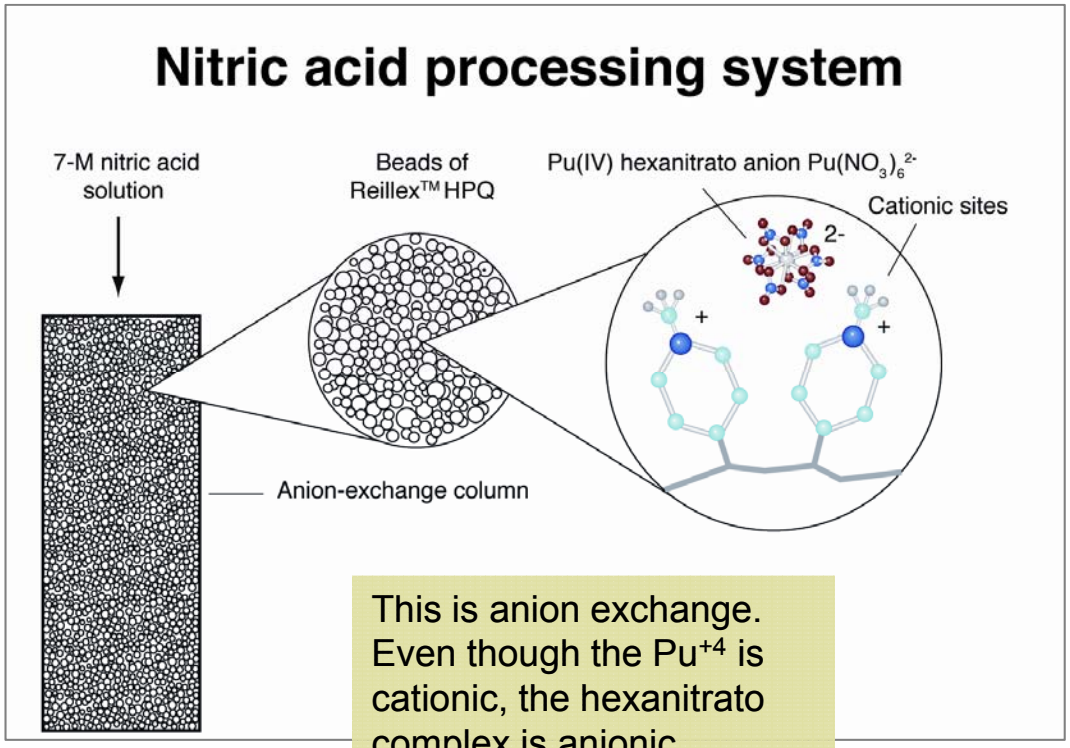
$$\% \, Recovered = 1 - \frac{Mass_{Pu,initial} - Mass_{Pu,Filtrate}}{Mass_{Pu,initial}}$$



Anion Exchange

- **Dissolution in HNO_3 makes Pu^{+4}**
- **Pu^{+4} in 7 M HNO_3 forms hexanitrato complex**
  - $Pu(NO_3)_6^{2-}$
  - Adsorbs to cationic sites on resin
- **Pu^{+4} in 3 M HNO_3 forms dinitrato complex**
  - $Pu(NO_3)_2^{+2}$
  - Desorbs from cationic sites on resin
- **Elution with 0.45 M HNO_3**

Pu^{+4}
NO_3^{-1}



This is anion exchange. Even though the Pu^{+4} is cationic, the hexanitrato complex is anionic.

Anion Exchange: Column and feed preparation

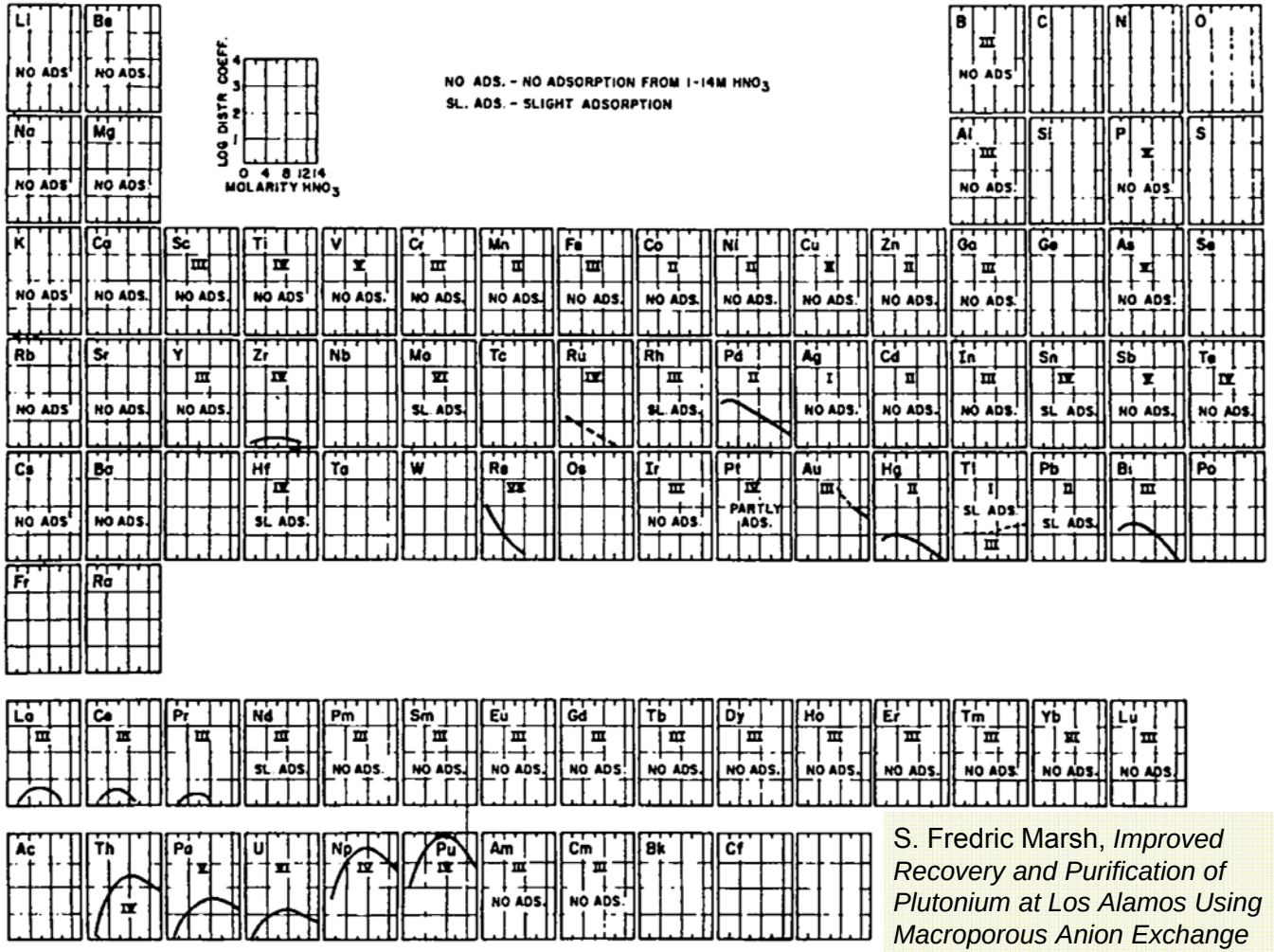
- **Feed Treatment**
  - Mass of Pu per run determined by resin capacity (2 kg Pu)
  - Adjust acid molarity to ~7M
  - Optional Peroxide Treatment
    - Pu^{+6} -> Pu^{+4}
- **Condition column**
  - 15 liters of ~7M nitric acid

Ion Exchange: Column Loading

- **Pu solution pumped through the three serial 10-liter columns**
  - 30 liters, total column volume
- **Loading Rate varies with Pu concentration**
  - 50-90 liters/hr

Ion Exchange: Column Washing

- 5-7 M acid
- 5-7 column volumes
- 50-70 liters/hr
- Effluent sent to evaporator



S. Fredric Marsh, *Improved Recovery and Purification of Plutonium at Los Alamos Using Macroporous Anion Exchange Resin*, LA-10906

Fig. 1. Distribution of elements from nitric acid onto strong-base anion exchange resin.

Ion Exchange: Elution

- **Column out-flow redirected**
- **Elute column**
  - 0.45 M acid
  - 40-50 liters/hr
  - ~3 column volumes

Ion Exchange:
Technical Safety Requirements and Resin Lifetime

- **Polyvinyl Pyridine Resin can degrade**
  - Only <8 M HNO_3
  - Resin kept wet
  - ≤65˚C
  - Max. 500 Mrad exposure
- **How many times can resin be used?**
  - 1500 g/run, 4 runs/yr = 39 runs, 10 yr
  - 1500 g/run, 1 run/day, 20 days/month = 740 runs, 37 months

In 1976, a Hanford anion exchange column used for Am recovery deflagrated. The operator received multiple cuts, first- and second-degree burns, and gross internal and external Am contamination. (Dowex resin)

Seven additional accidents involving actinides prior to 1968, at Oak Ridge, Rocky Flats, Hanford, Brookhaven, Savannah River, and Kerr-McGee's Cimarron fuel fabrication facility.

Oxalate Precipitation

- **Reduce Pu^{+4} to Pu^{+3} (Hydroxylamine nitrate)**

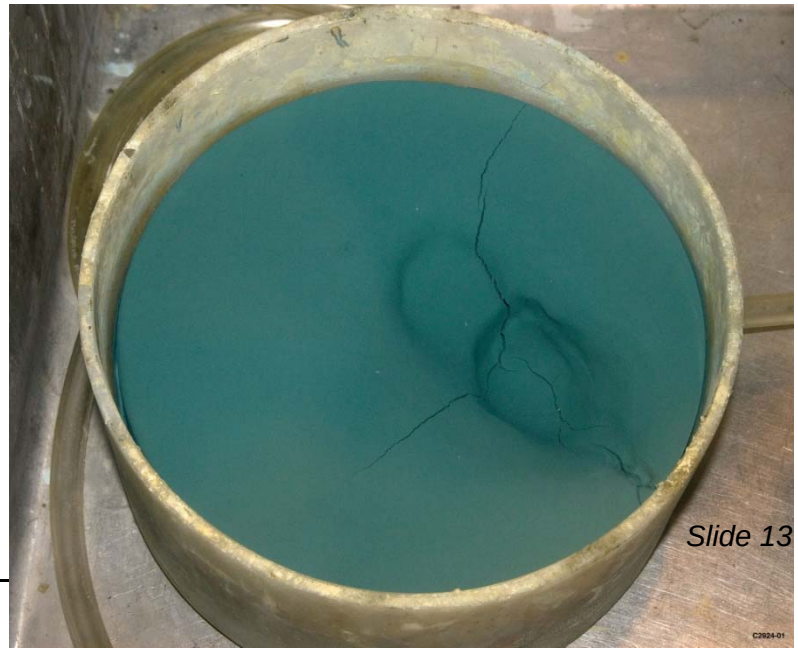
  $2Pu(NO_3)_4 + 2NH_2OH{\cdot}HNO_3 \rightarrow 2Pu(NO_3)_3 + 2H_2O + N_2 + 4HNO_3$

  80-100% stoichiometric excess

- **Add oxalic acid** 10% stoichiometric excess

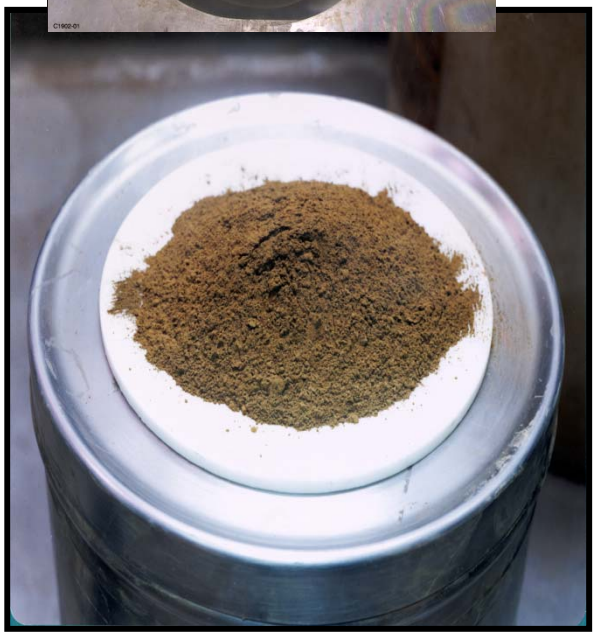
  $2Pu(NO_3)_3 + 3\,H_2C_2O_4 \rightarrow Pu_2(C_2O_4)_3 + 6HNO_3$

- **Settle, Filter and Wash**
  - Oxalate Filtrate to Evaporator
- Pu^{+4} Oxalate can be obtained if required



Calcination

- **Air dry cake on filter boat**
- **Transfer to furnace can**
- **6 hours at 600˚C in glovebox atmosphere**
- **40 mesh sieve**



$$Pu_2(C_2O_4)_3 + 2O_2 \rightarrow 2PuO_2 + 6CO_2$$

RFX Process Time

Dissolution	2-3 days per pass
Prepare solution and load column	1/2 day
Wash column	1 day
Elute	1/2 day
Precipitation	2 days*
Calcination	2 days
Sampling	0 days*

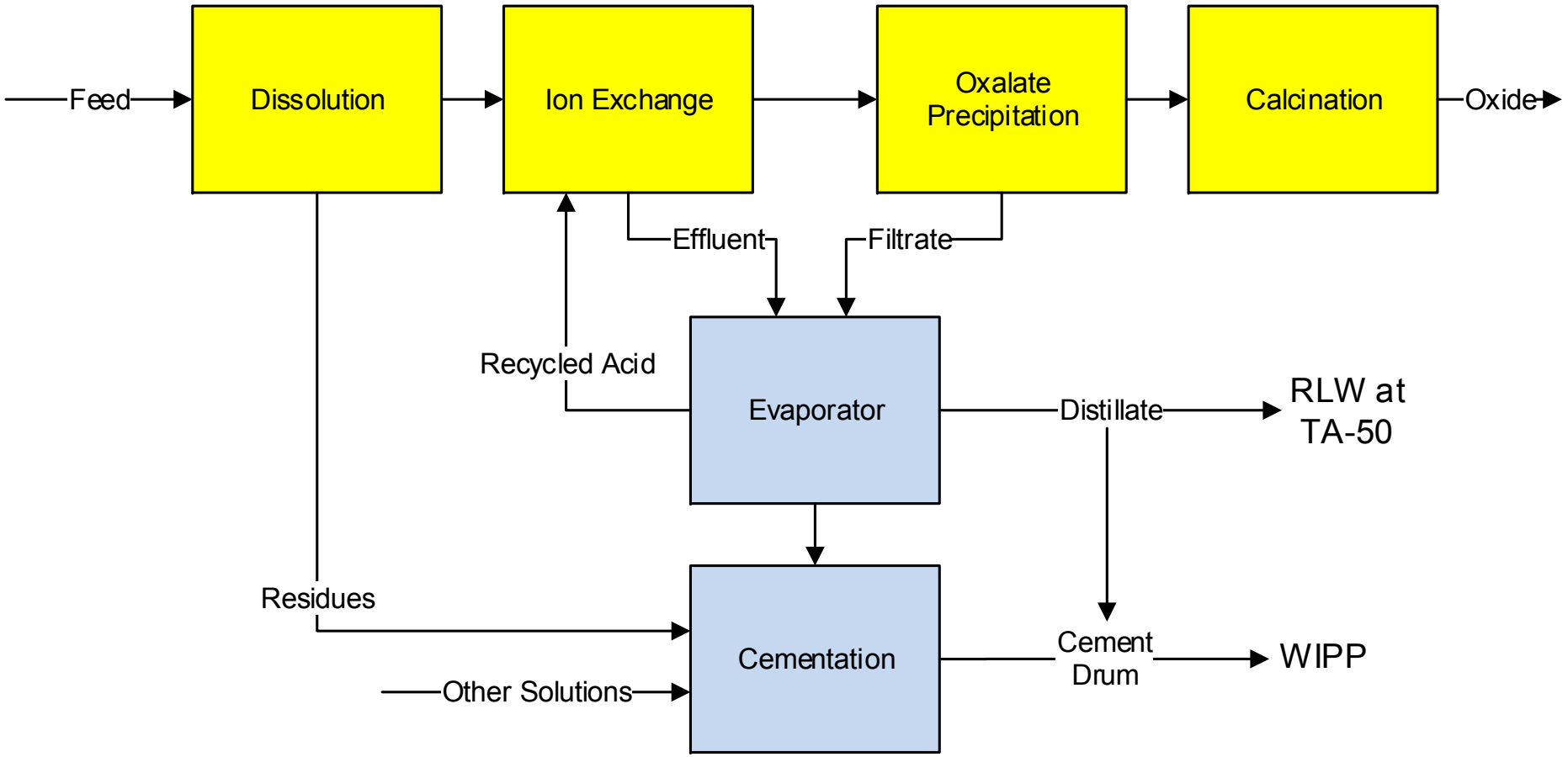
- **Lack of personnel**
- **Some operations cannot be unattended**
- **Two-man rule**

Waste Treatment:
Evaporator (Volume Reduction)

Products

- **'Cold' distillate**
  - Molarity preserved
  - Recycled Acid or Radioactive Liquid Waste
- **Bottoms**
  - Salts, Liquid
  - Sent for Cement Fixation

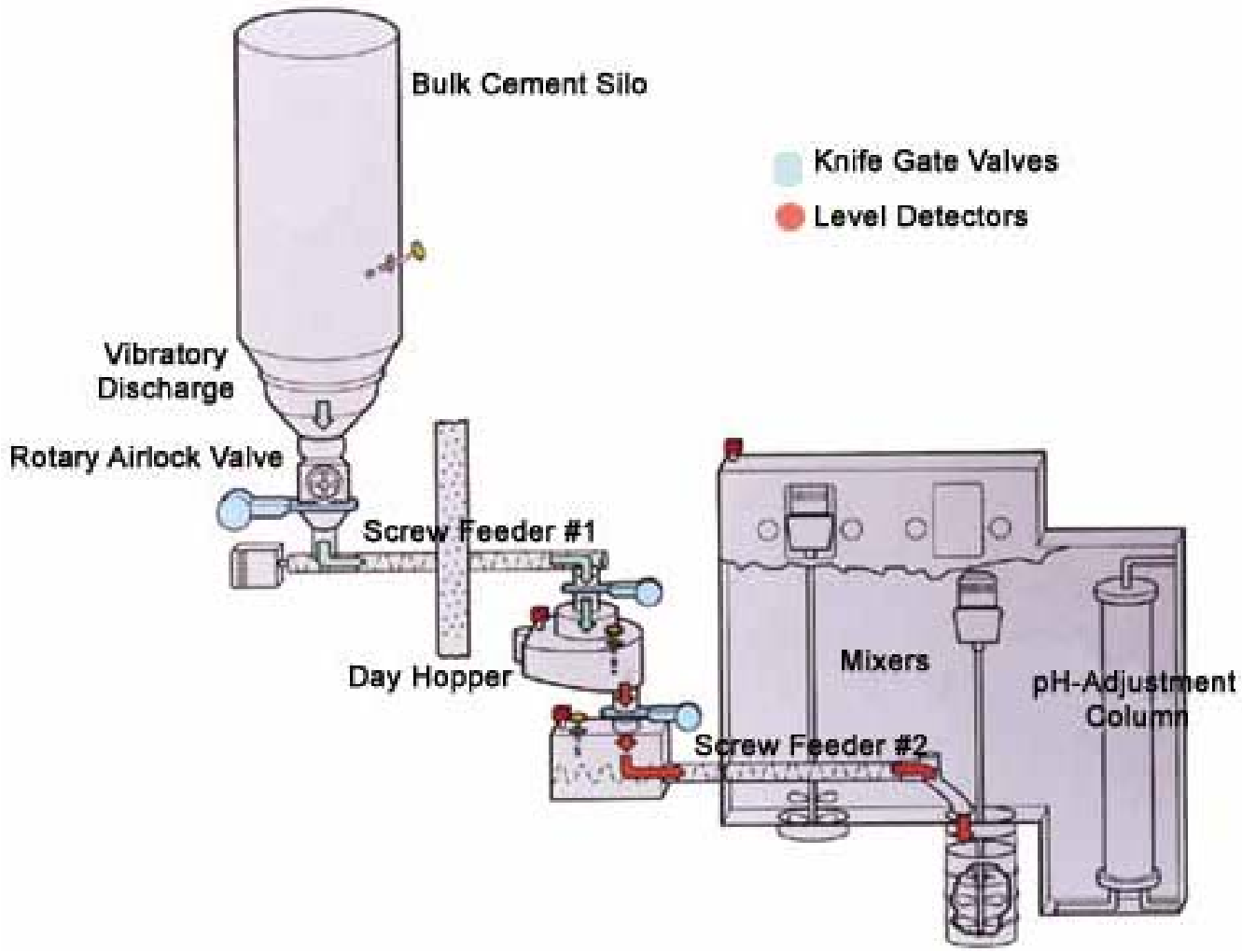
Aqueous Nitrate Flowsheet shows 4 major steps



Waste Treatment: Cement Fixation

- **Stabilizes salt residue waste for disposal**
- **Immobilize RCRA waste constituents**
  - No longer ‘Mixed Waste’
- **TRU waste sent to WIPP**

Waste Treatment: Cement Fixation



Challenges

- **Criticality Safety**
  - 21 of the 22 known process facility criticality accidents have involved solutions
  - Nitrate processing equipment allows solutions to be transferred “from anywhere to anywhere”
  - Not all vessels are inherently safe
- **Experience**

Tanks

Summary

- PuO_2 residues
- Dissolved, purified by ion exchange, precipitated, oxidized
- Waste acid recycled, to Rad Liquid Waste, or Cement Fixation