Hot Test Evaluation of the Reverse TALSPEAK Process

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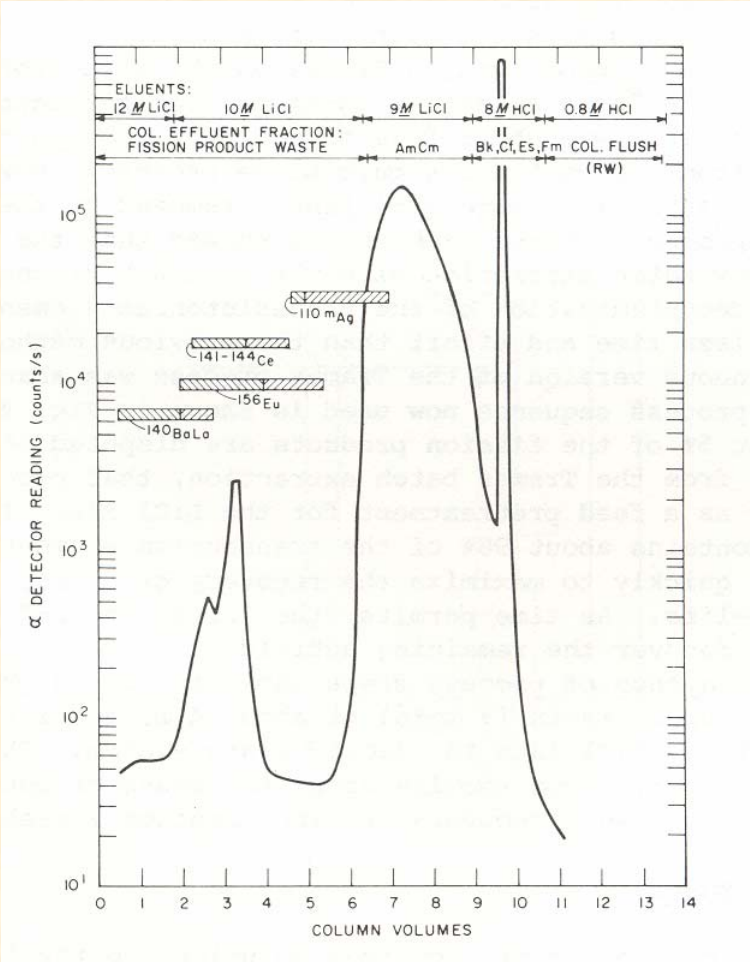
Experience with Transuranium Element Processing Is the Basis for Development of Advanced Fuel Cycle Processes

- **Transuranium elements are produced in the High Flux Isotope Reactor (HFIR) and the Radiochemical Engineering Development Center (REDC) at Oak Ridge National Laboratory**
- **Plutonium-242, americium-243, and curium mixed isotopes are irradiated to produce berkelium, californium, einsteinium, and fermium isotopes**
- **New separations and target fabrication processes were developed for shielded, remote operations**
- **Relatively high level emissions of heat, neutrons, and alpha particles are present in these operations**

Actinide/Lanthanide Separation For Transuranic Element Processing



Column effluent composition

- **LiCl-based chromatographic anion exchange process is used**
- **Basis of separation is difference in distribution coefficients of anionic chloride complexes of actinides and lanthanides**
- **A 2-L resin column is used. Batch size is limited to 35 g of actinides or 20 g of ^{244}Cm. Resin is replaced after ~3 loadings and elutions**
- **Process is too expensive and would introduce unacceptable complications if used for commercial-scale advanced fuel cycles**

Several Batch Solvent Extraction Processes Are Used at REDC

- **All use di-2-ethylhexyl phosphoric acid (HDEHP), a cationic exchanger, as the extractant**
- **The PUBEX process is used to recover plutonium and other tetravalent elements from ~6 *M* HNO_3 solution**
- **The CLEANEX process is used to recover actinide and lanthanide elements from other fission products, activation products, and corrosion products. Feed solutions are ~0.03 *M* acid**
- **The TALSPEAK process was developed to partition actinides from lanthanides using polyacetic acid complexing at pH 3–4 in a lactic, glycolic, or citric acid buffer**

Availability of Corrosion-Resistant Equipment Enables Use of Nitric Acid and Hydrochloric Acid

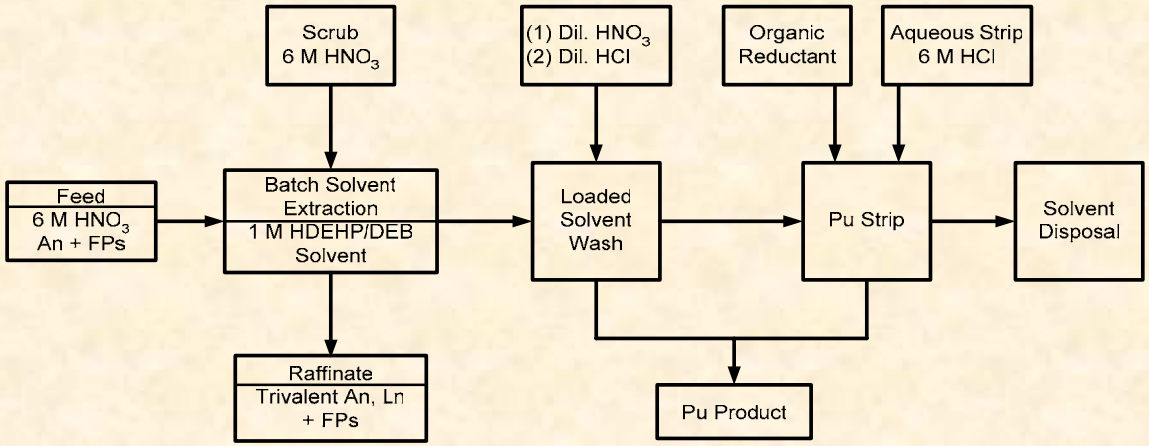


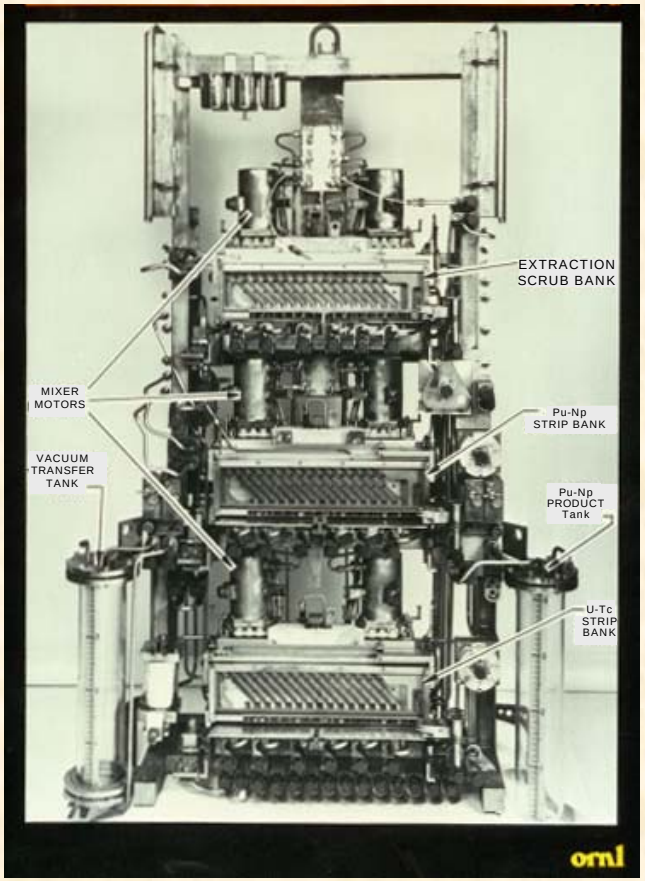
Diagram of PUBEX Process

- **PUBEX process strongly extracts tetravalent plutonium**
- **Organic-soluble reductant, 2, 5-Di-*tert*-butyl hydroquinone (DBHQ), used to reduce Pu^{+4} to Pu^{+3}**
- **DBHQ is unstable in nitric acid**
- **Loaded solvent is stripped with hydrochloric acid**

Challenges for Separation of Actinides in Spent Nuclear Fuels

- **Prevention of interferences due to the hydrolyzable solid-forming characteristics of plutonium and the fission products, zirconium and molybdenum, at low nitric acid acidities**
- **Interferences from other extractable fission products (palladium)**
- **Management of the multiple valance states of Pu, Np, Tc, and Am**

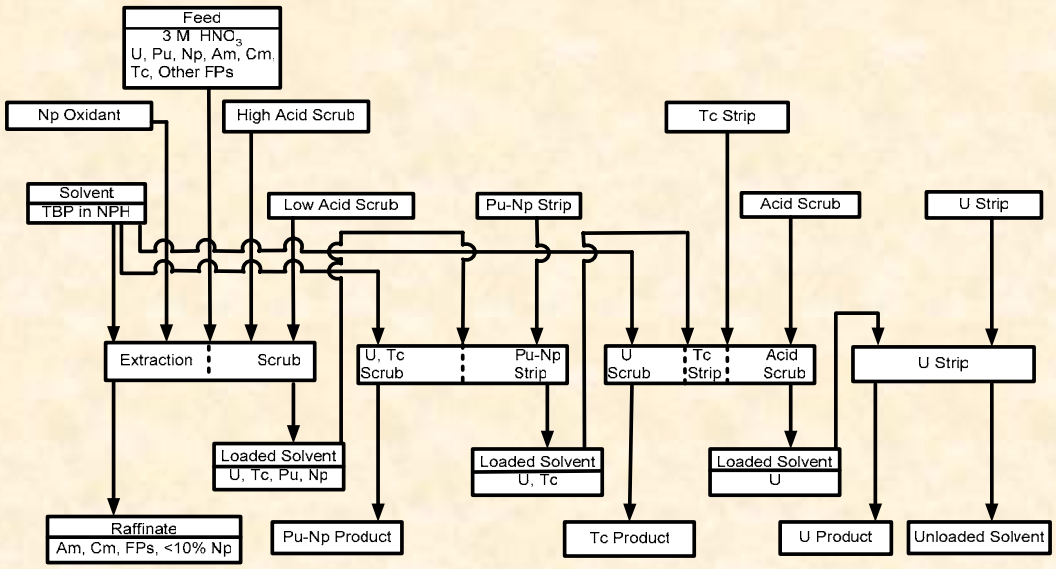
Continuous Solvent Extraction Test Facility at REDC



SETF Mixer-Settler

- **Spent fuel dissolver with perforated basket for leaching sheared hulls—2 kg HM capacity**
- **Feed adjustment evaporator and clarification by high-efficiency filtration**
- **Continuous, countercurrent solvent extraction in three 16-stage mixer settlers**
- **Reagent tanks and flow controllers**
- **Effluent collection tanks**

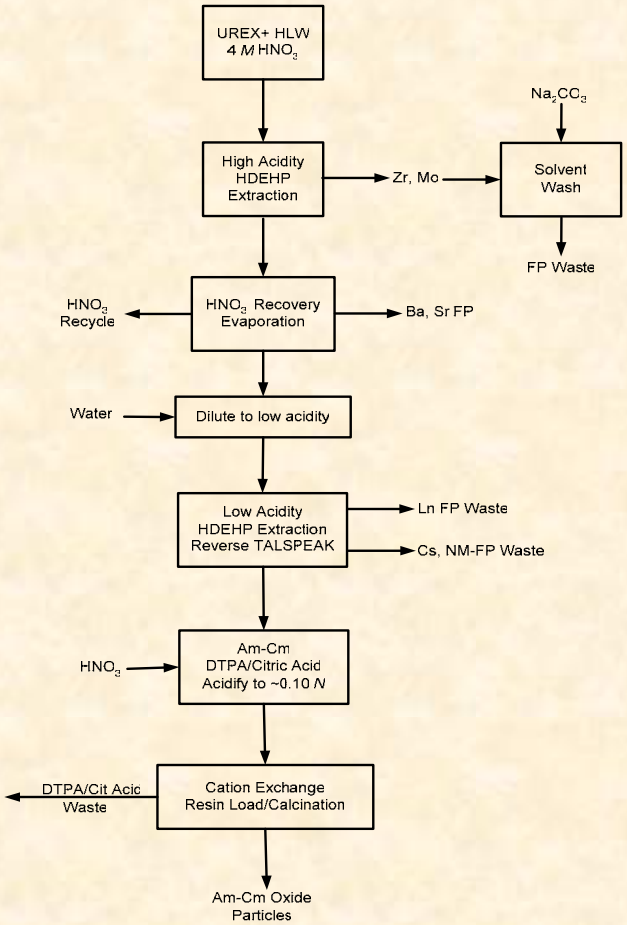
UREX+2 Co-decontamination Solvent Extraction Flowsheet



UREX+2 Co-decontamination

- **Co-extraction of U, Np, Pu, and Tc**
- **Partitioning of neptunium-plutonium using hydroxylamine nitrate (HAN) as reductant**
- **Individual steps to strip technetium and uranium, or**
  - **Co-stripping of uranium and technetium**
  - **Recovery of technetium by anion exchange**

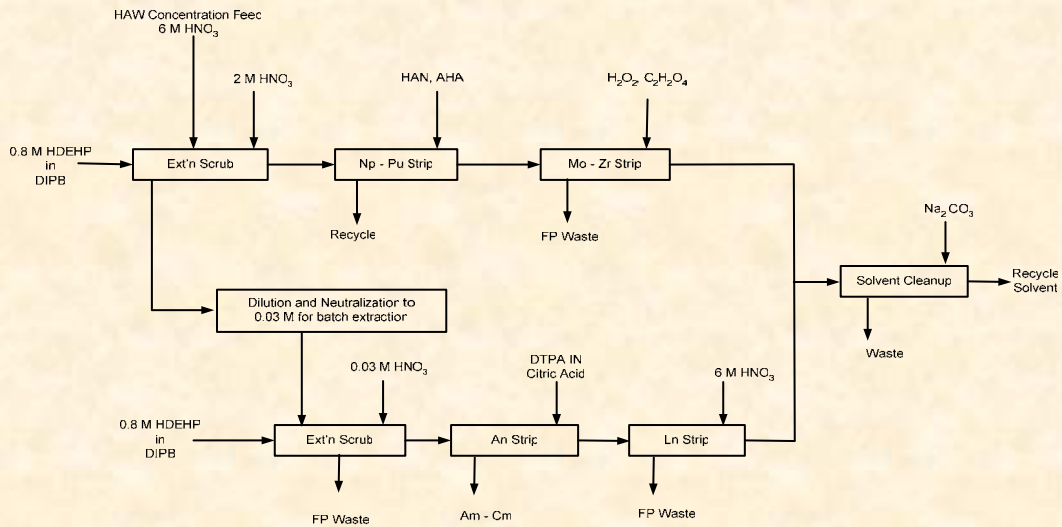
Current Reverse TALSPEAK Process Flowsheet



Current Reverse TALSPEAK Flowsheet

- **Intended to recover minor actinides, americium and curium, from fission products in UREX+2 co-decontamination process raffinate stream**
- **Uses a single solvent system (HDEHP in appropriate diluent)**
- **Uses multiple extraction steps to avoid hydrolytic problems with fission products, zirconium and molybdenum**

Preliminary Batch Tests

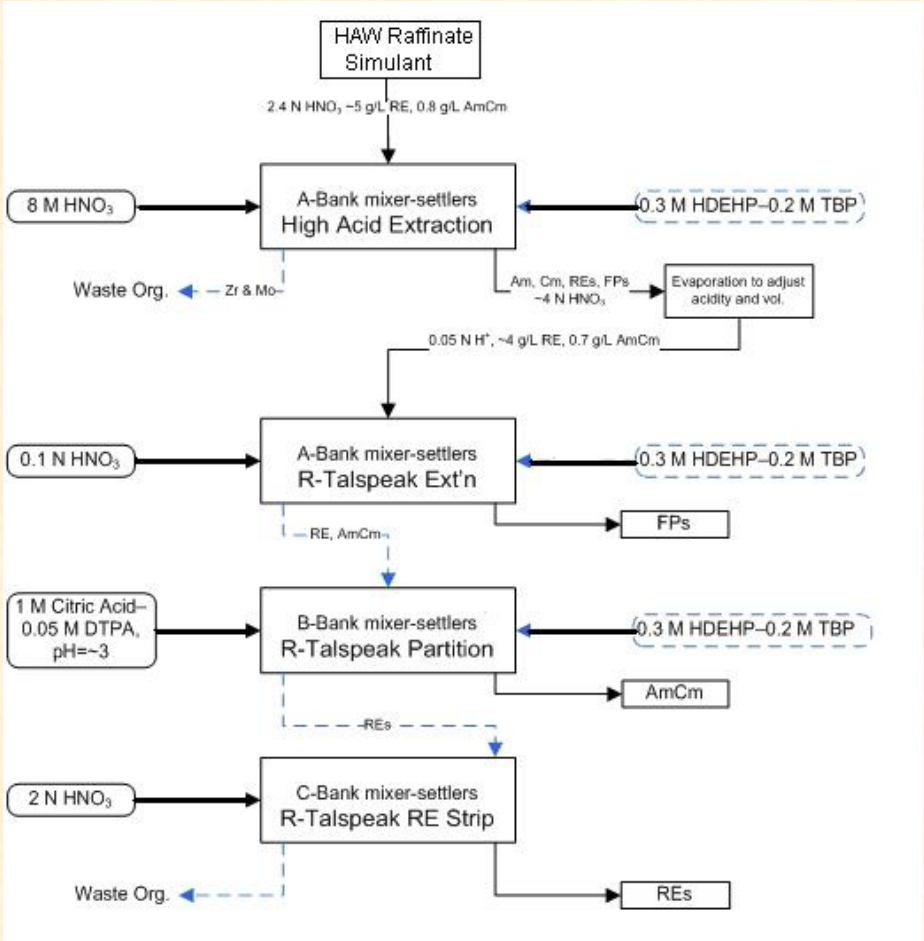


Results from Batch Tests

	Distribution Coefficients					Separation Factors		
	Nd	Ce	^{154}Eu	^{241}Am	^{244}Cm	Nd/Am	Ce/Am	Eu/Am
Extraction								
Raffinate	8.0	3.7	150	4.4	6.0	1.8	0.70	34
Actinide Stripping								
1st DTPA	7.3	4.9	22	0.30	0.25	25	17	65
2nd DTPA	7.1	18	19	0.29	0.26	25	63	65
3RD DTPA	14.1	31	21	0.49	0.22	29	64	44
Lanthanide Stripping								
6*M* HNO_3	0.01	0.01	0.03	0.09	0.04			

- **Initial plans were to concentrate the HAW stream from the UREX+2 co-decontamination**
- **Solids (Ba, Sr, etc.) encountered during evaporation but removed easily by filtration**
- **Solvent used was 0.8 *M* HDEHP in di-isopropyl benzene**
- **Viscous emulsions were encountered and phase separations were difficult**
- **Distribution coefficients were high for zirconium and molybdenum. Residual U, Pu, and Np extracted**
- **Various stripping agents tested. Only sodium carbonate was effective for all metals**

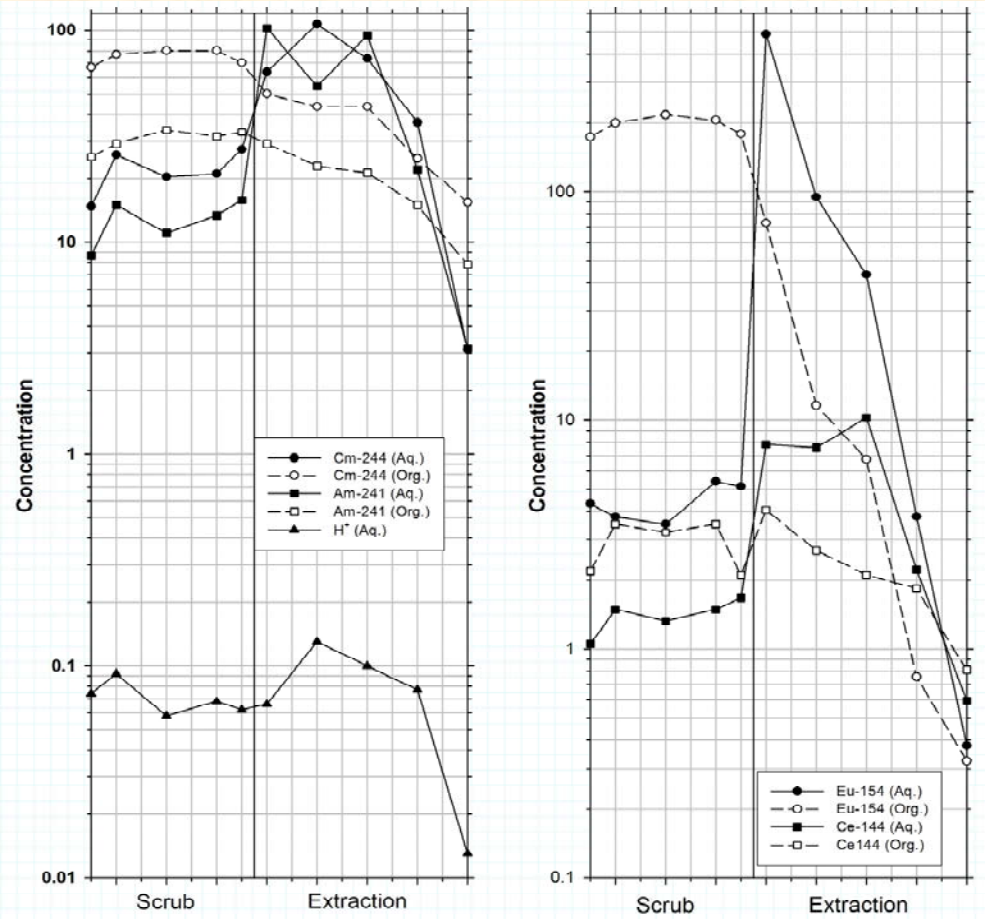
Continuous Hot Test of Reverse TALSPEAK Process



Flowsheet for the Reverse TALSPEAK Test

- **Flowsheet changed to begin directly with high-acidity extraction of zirconium and molybdenum**
- **Switched to less viscous solvent. Chose 0.3 *M* HDEHP—0.2 *M* TBP in normal parrafin diluent**
- **Flow ratios chosen from reference study**

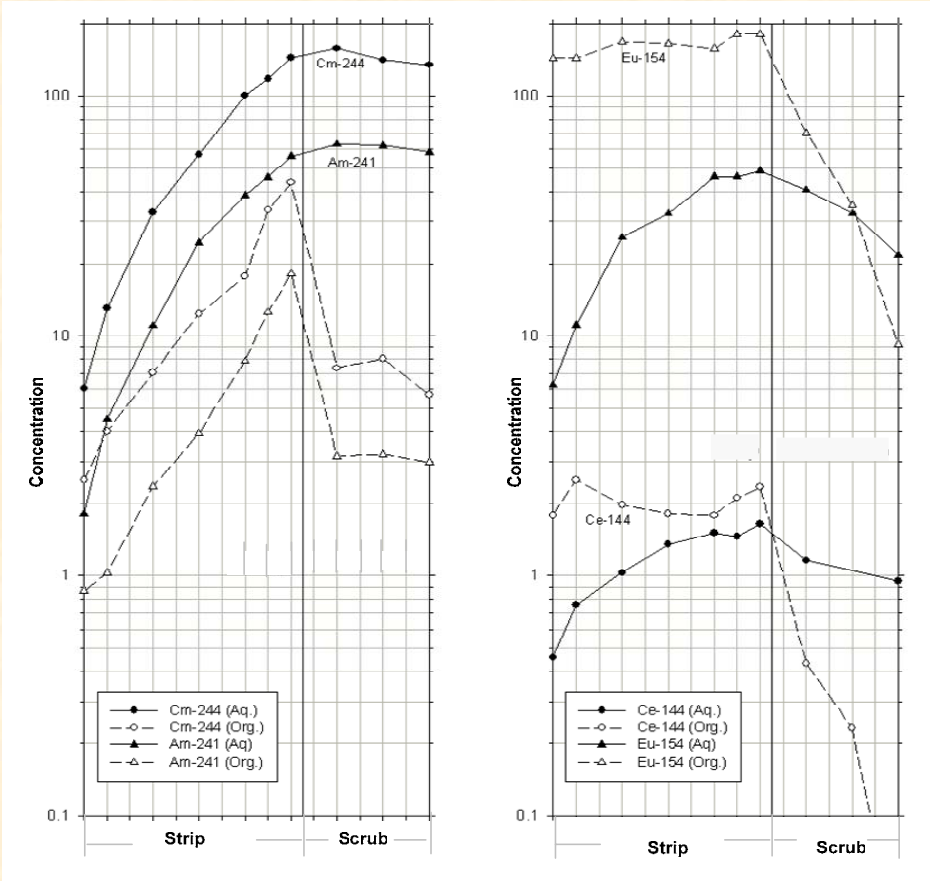
Difficulties Were Encountered in Low Acidity Extraction



Extraction Bank Profiler

- **Solids accumulation in extraction bank**
- **Filtration of feed solution was necessary**
- **Deleterious effect of increasing scrub acidity from 0.02 *M* HNO_3 to 0.1 *M* HNO_3 (increased losses to raffinate)**

Difficulties in Partitioning Step



Concentration Profile During Partitioning

- **Recoveries of curium and americium in actinide product were 83% and 90%, respectively**
- **Approximately 5% of europium was co-stripped**
- **Possible causes may include solvent quality, slow kinetics, inadequate flow ratios, or presence of impurities**
- **Follow-up lab studies are planned**
- **Development of a process model is necessary**

Conclusions

- **Initial results not satisfactory. Further studies are necessary**
- **Potential value of flowsheet is still promising because of overall simplicity**
- **Capability exists for intermediate acidity level extraction of gadolinium**
  - **Large amounts of this material may be present in spent fuel and dissolver solutions due to addition as burnable poison or criticality control**