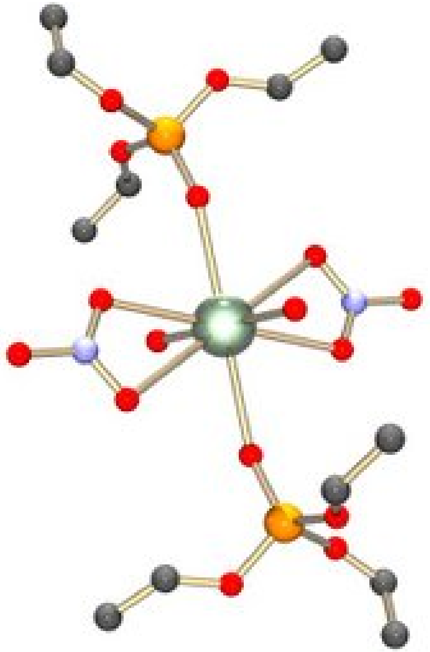
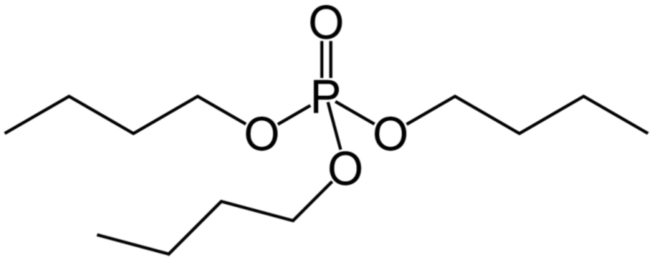
RDCH 702: Lecture 9 Separations

- Separation methods
    - Solvent extraction
        → PUREX
    - Ion exchange
    - Volatility
    - Electrochemistry
- Specific actinide separations

- Basic concept of separations
    - Oxidation state
    - Ionic radius
- Development of advanced separations
    - Trivalent actinides
- Necessary for fuel cycle due to formation of mixtures due to fission
    - Actinides
        → Transuranics
    - Fission products
        → Se (Z=34) to Dy (Z=66)

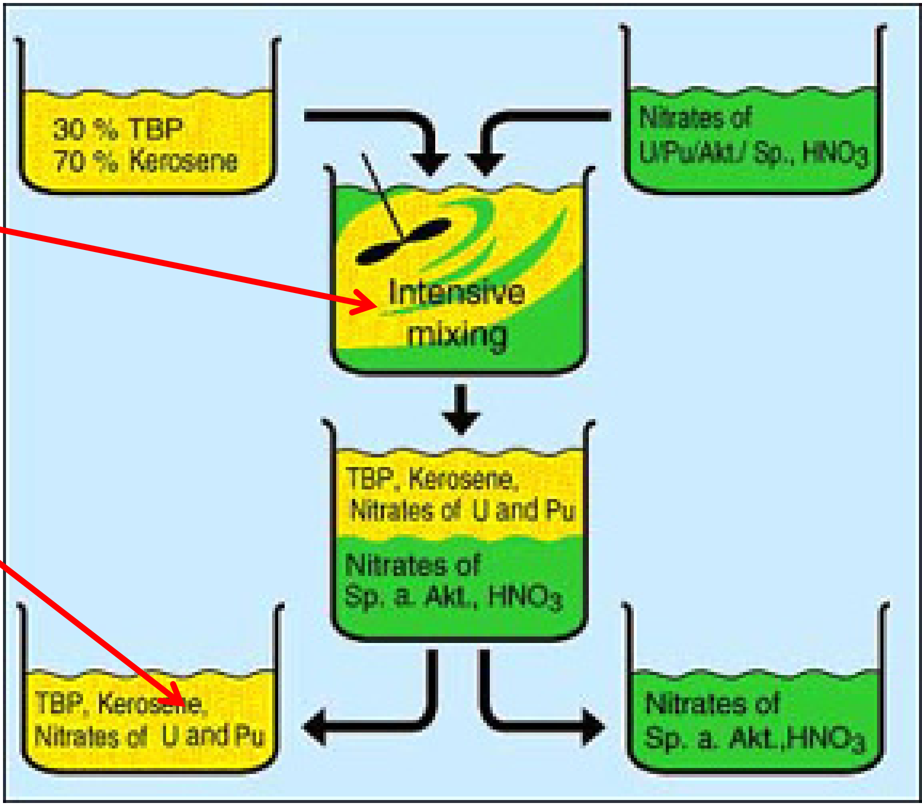




Tributyl phosphate (TBP)

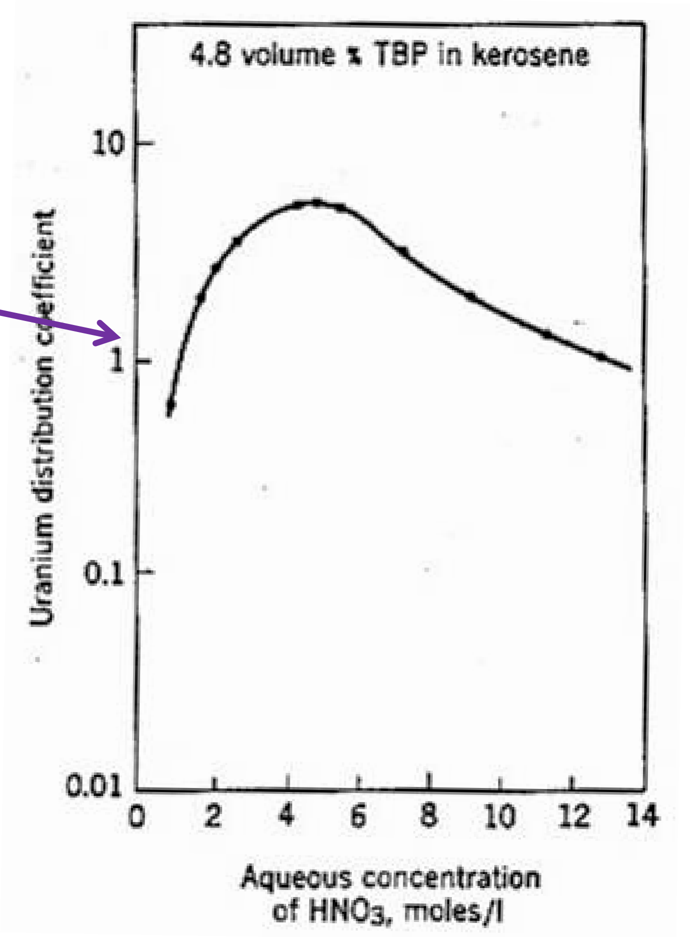
Solvent Extraction

- Two phase system for separation
  - Sample dissolved in aqueous phase
    - → Normally acidic phase
- Aqueous phase contacted with organic containing ligand
  - Formation of neutral metal-ligand species drives solubility in organic phase
- Organic phase contains target radionuclide
  - May have other metal ions, further separation needed
    - → Variation of redox state, contact with different aqueous phase
- Back extraction of target radionuclide into aqueous phase
  - Reduction of Pu to trivalent
- Distribution between organic and aqueous phase measured to evaluate chemical behavior



Solvent extraction

- Influence of chemical conditions
  - Solvent
  - Metal ion and acid concentration
    - → Phase splitting
- Distribution coefficient
  - $K_d = \frac{[M]_{org}}{[M]_{aq}}$
  - Used to determine separation factors for a given metal ion
    - → Ratio of K_d for different metal ions
      - * May be represented by K_d or D
    - → $K_d = 1$
      - * 50 % of metal in organic phase
    - → $K_d = 10$
      - * 90.9 % of metal in organic phase
    - → $K_d = 100$
      - * 99.01 % of metal in organic phase
  - Distribution can be used to evaluate stoichiometry
    - → Evaluation distribution against change in solution parameter
      - * Plot log K_d versus log [X], slope is stoichiometry
- Extraction can be explained by complexation
  - Used to determine complexation constants



Distribution coefficient and stoichiometry

- Plot log K_d versus log [X]
  - slope is stoichiometry of evaluated parameter
- Consider reaction
  - $xM + yL \leftrightarrow M_xL_y$
    - → Want to determine value for y
    - → Plot log K_d against log [L]
- Use complexation constant and distribution coefficient
- $K = \frac{[M_xL_y]}{[M]^x[L]^y}, K_d = \frac{[M]_{org}}{[M]_{aq}} = \frac{[M_xL_y]}{[M]}$
- Substitute K_d into K equation, x=1
  - $K = \frac{K_d}{[L]^y}$
- Log of equation
  - Log K = log K_d – y log [L]; rearrange equation
  - Log K_d = Log K + y log [L]
    - → Log K is constant
    - → Slope of log K_d versus log L gives y, the L stoichiometry

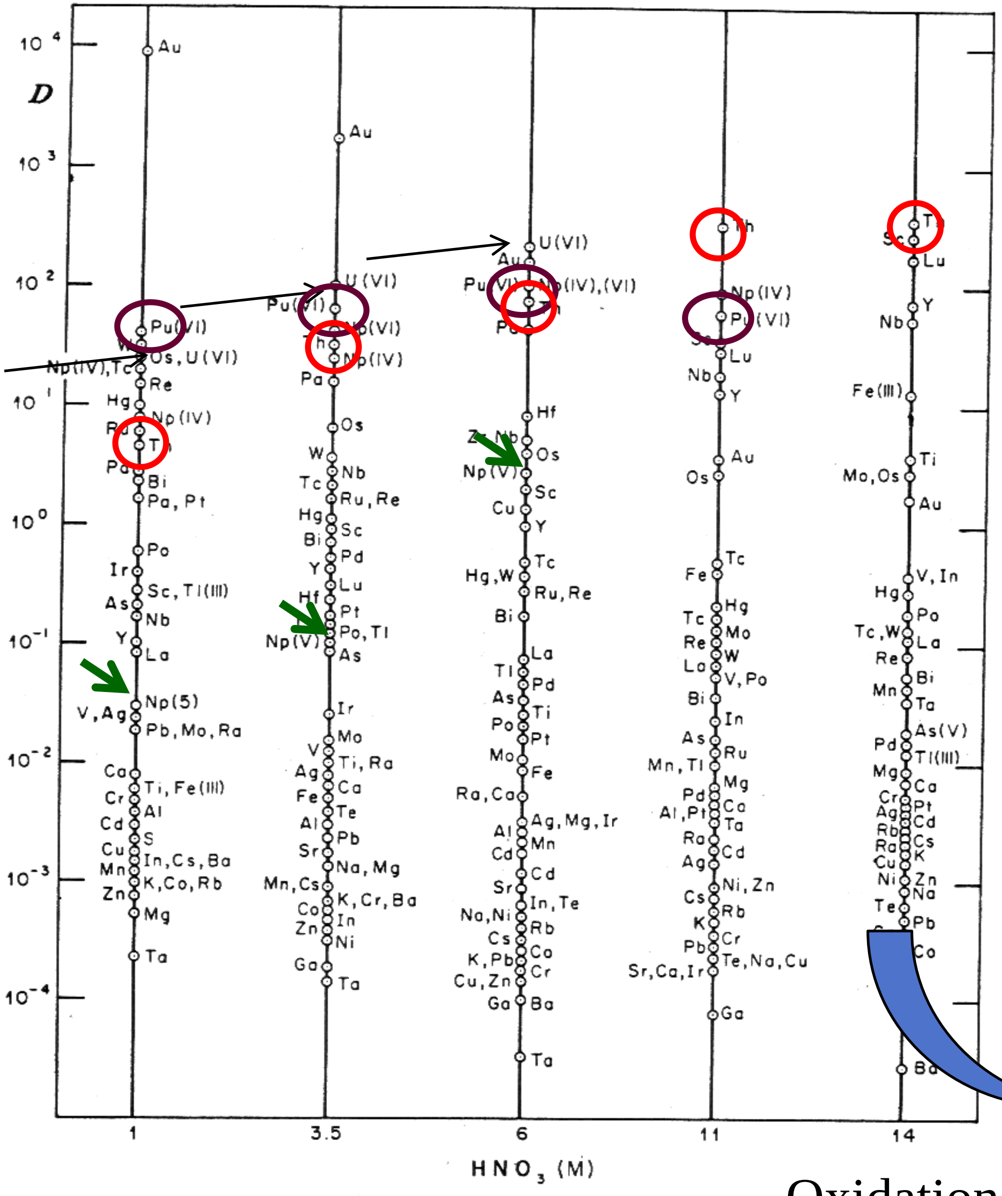


Chart Fd 2 Undiluted tributyl phosphate

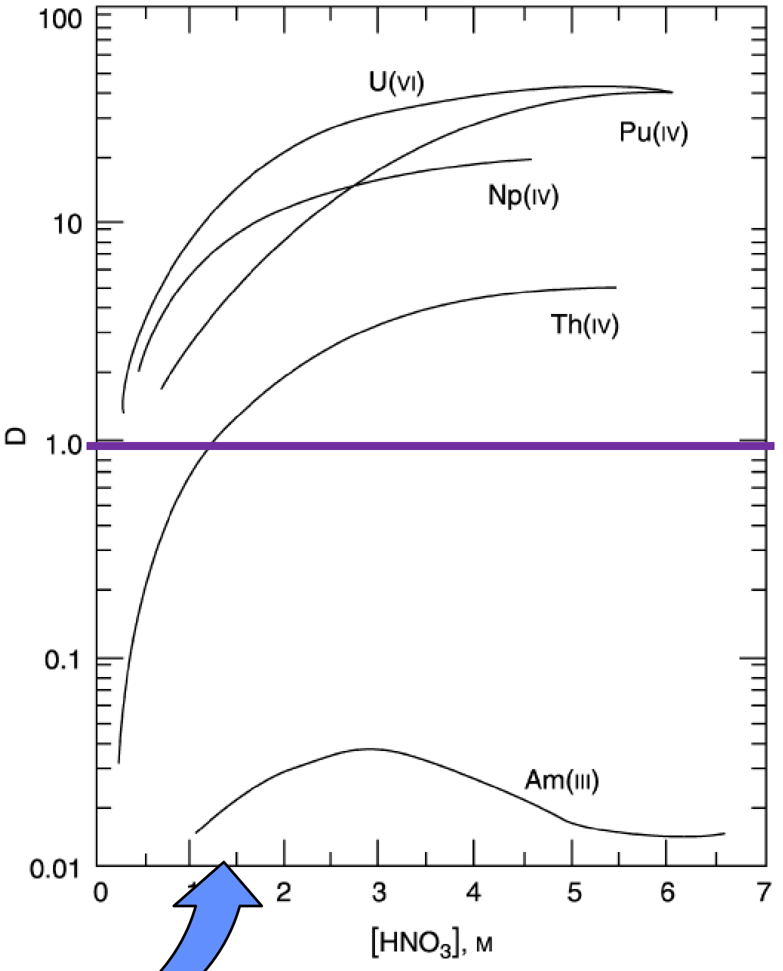


Fig. 24.6 D[illegible]action of actinides into tri(n-butyl)phosphate/dodecane as a function of nitric acid concentration.

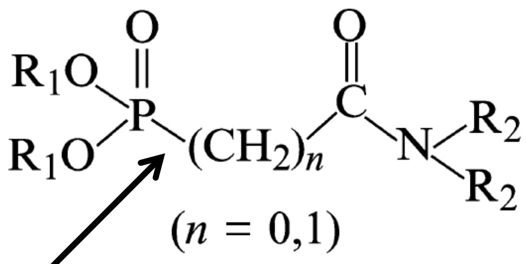
Oxidation state importance

D variation with acid concentration

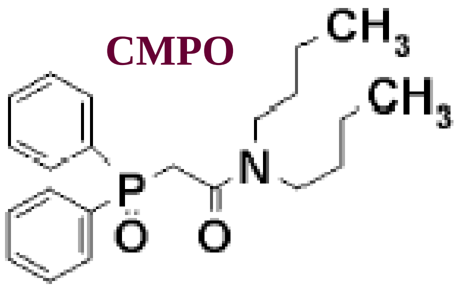
Solvation Extraction Mechanism

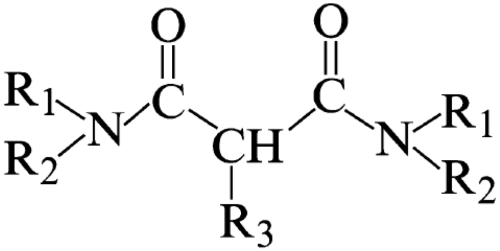
$$An^{z+} + zL^{-} + \overline{nS} \Leftrightarrow \overline{AcL_zS}$$

- Extraction of neutral complex
  - $UO_2(NO_3)_2$ forms with TBP (P=O functional group)
    - → Equilibrium shifts with nitrate, back extraction into aqueous at low nitric acid
- Other extractants include bifunctional ligands
  - Carbamoyl phosphate compounds
    - → 2 to 4 CMP per extracted molecule
  - Carbamoylphosphine oxide (CMPO)
    - → 2 CMPO for U and Pu, 3 for trivalents
      - * Basis of TRUEX separation for Ln/An
  - Malonamide extracts can replace CMPO
    - → CHON principle
    - → DIAMEX process



CMPO





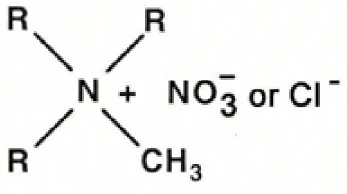
Malonamide

Ion Pair Formation

$$An^{z+} + zL^{-} + \overline{AL} \Leftrightarrow \overline{AnL_{z+1}A}$$

Figures 2 & 3

- Charged metal complex with extractant of opposite charge
  - Quaternary ammonium salt with anionic actinide nitrate
    - → R_4N^+
    - → Aliquat 336
  - Tertiary amines
    - → $R_3HN^+AnX_n^{-(n-z)}$ for monovalent X with An with Z charge
      - * Require equilibration with acid
- Can be sorbed to resins for separations
  - TEVA resins

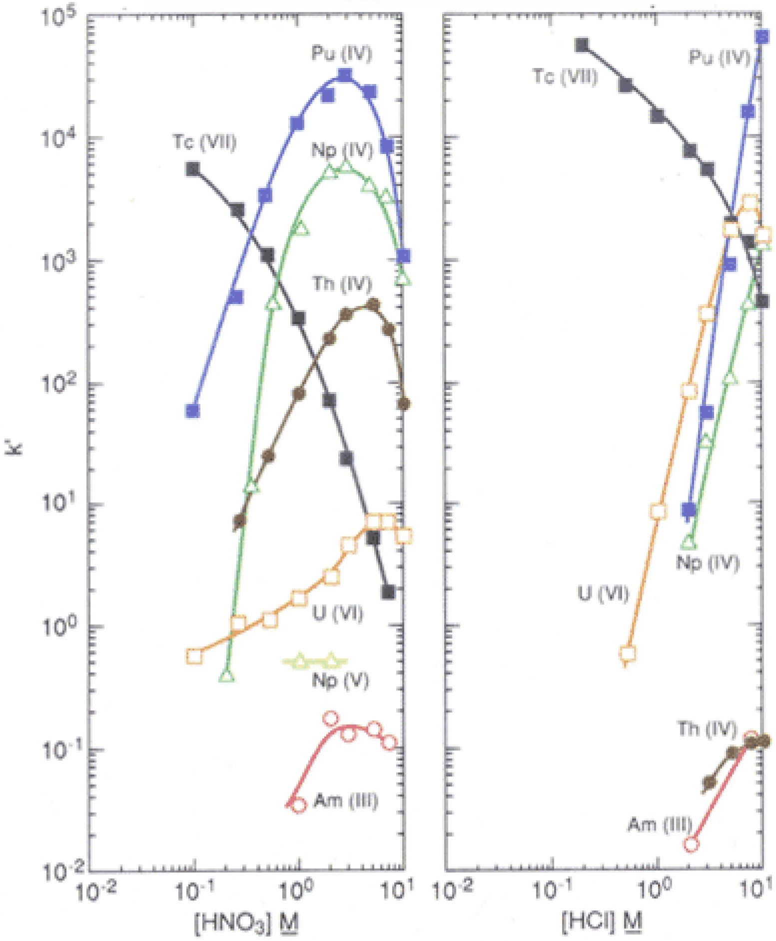


Trialkyl, methylammonium nitrate (or chloride)

R = C_8H_{17} and $C_{10}H_{21}$

Acid dependency of k' for various ions at 23°C.

TEVA Resin

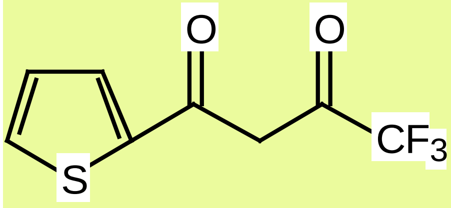


Horwitz, et al. (HP195)

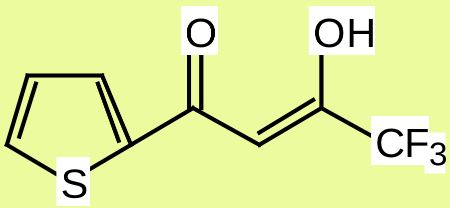
Liquid cation exchanger and chelating agents

$$An^{z+} + \overline{zHL} \Leftrightarrow \overline{AnL_z} + zH^{+}$$

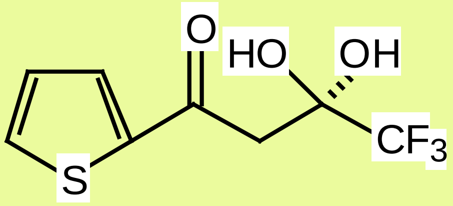
- Metal ion exchanged into organic phase, ion transfer in aqueous phase
- Use of organic soluble acid
  - i.e., alkyl phosphinic acid (R_2PO_2H)
- Can be controlled by acidity
- May form aggregates or micelles
- Thenoyltrifluoroacetone (TTA)
  - $M^{z+}_{(aq)} + zHTTA_{(org)} \longleftrightarrow M(TTA)_{z(org)} + H^{+}_{(aq)}$
  - What is the equilibrium constant?



Keto



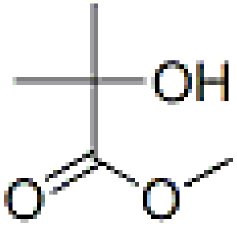
Enol



Hydrate

Extractant Ligands

- α-hydroxyisobutyric acid
  - Used in lanthanide separations



- Di-(2-ethylhexyl) phosphoric acid (HDEHP)
  - Exploited in solvent and solid systems
  - TALSPEAK (Am)

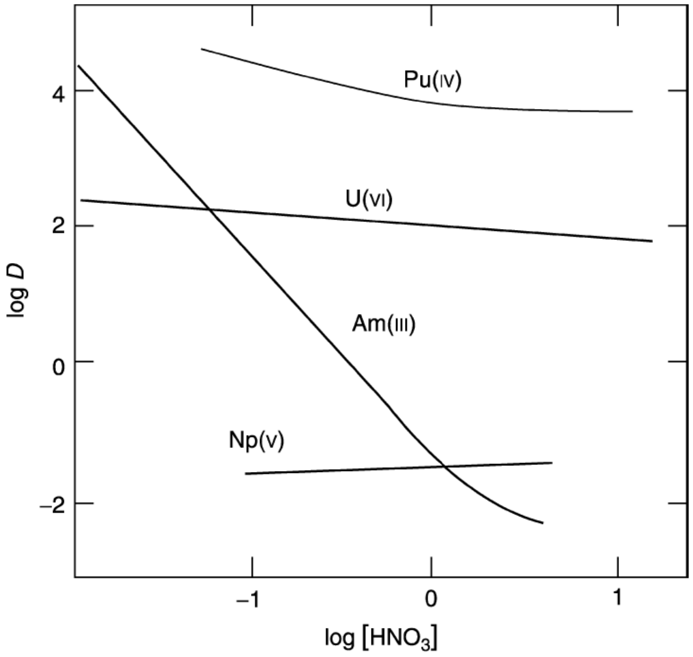
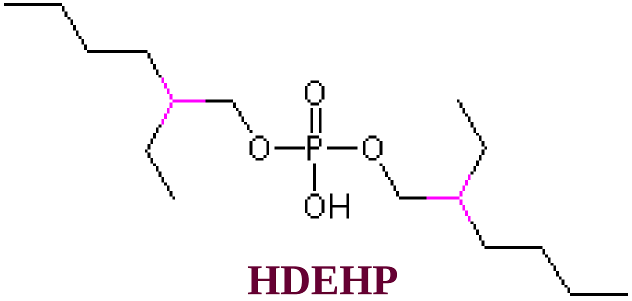
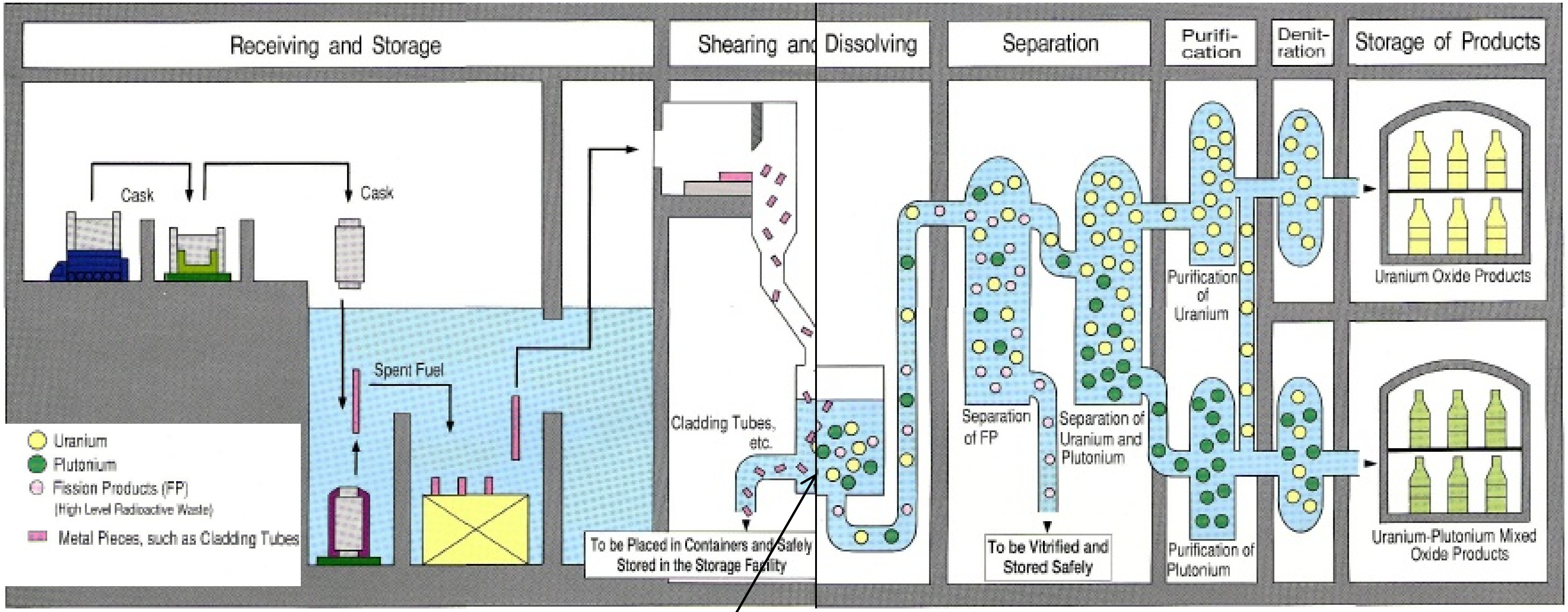


Fig. 24.8 *Dependence of extraction of Pu(IV), U(VI), Am(III), and Np(V) into* 0.5 M *HDEHP/iso-octane on nitric acid concentration* (*Myasoedov* et al., 1974).



HDEHP

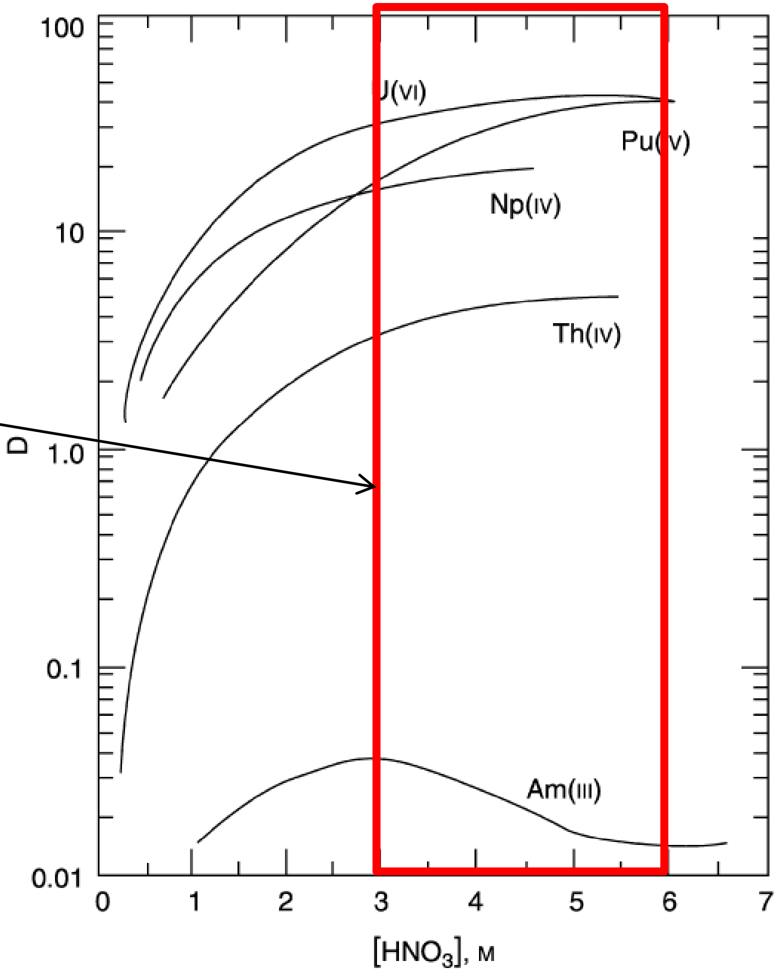
PUREX overview



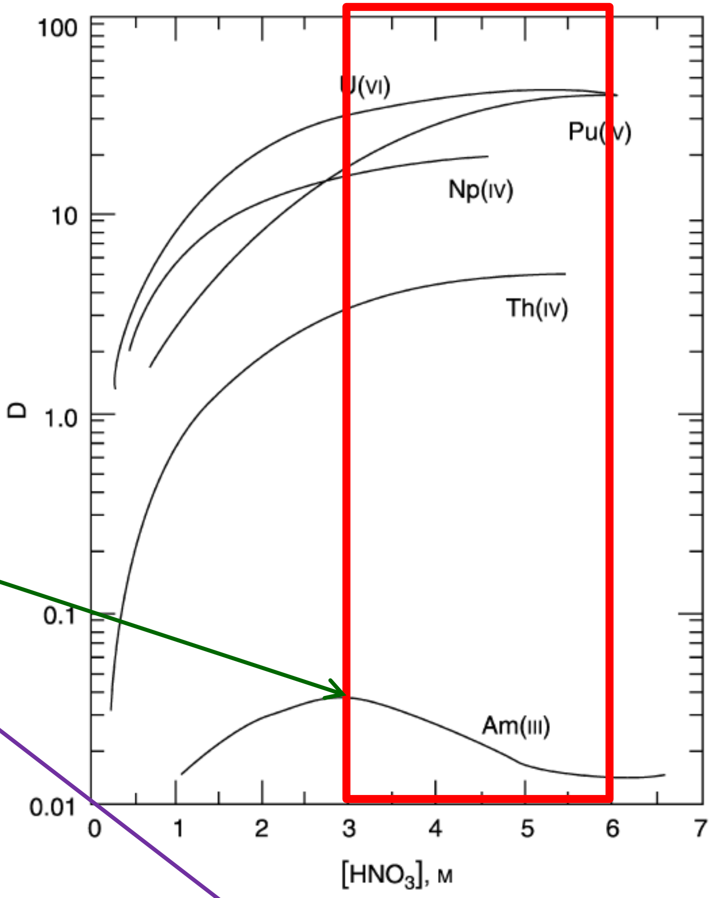
- PUREX (Pu-U Reduction EXtraction) liquid-liquid extraction process developed to recover Pu for weapons production
  - Developed during Manhattan Project
    - → Patented 1947. deployment at Savannah River 1954 and Hanford 1956
  - U and Pu extracted from aqueous to organic phase
  - Pu reduced, goes to aqueous phase while U remains in organic phase
- Decladding – mechanical, chemical
- Nitric acid dissolution – e.g., rotary wheel
- Solvent extraction and product preparation
  - Includes purification step
- Waste treatment and disposal – off-gases; acid, water, and solvent recycle

PUREX Process

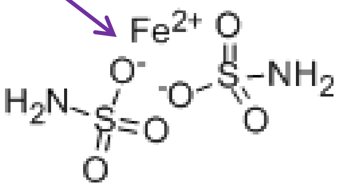
- Irradiated uranium fuel dissolved in nitric acid
  - contacted with a solution of TBP in kerosene
    - 30 % TBP in kerosene
- Hexavalent and tetravalent ion extraction
- $UO_2^{2+}{}_{(aq)} + 2NO_3^-{}_{(aq)} + 2TBP_{(org)} \Leftrightarrow UO_2(NO_3)_2(TBP)_{2\ (org)}$
- $Pu^{4+}(aq) + 4NO_3^-(aq) + 2TBP(org) \Leftrightarrow Pu(NO_3)_4(TBP)_2\ (org)$
- UO_2^{2+} and Pu^{4+} extracted in 3 M HNO_3 to 6 M HNO_3
  - High K_d range for UO_2^{2+} and Pu^{4+}
- Metal ions with other oxidation states extract poorly
  - Np oxidation state drives behavior in PUREX
    - Np^{4+} and NpO_2^{2+} extracts over entire range
    - NpO_2^+ begins to extract at high acid end of range
  - Mono-, di-, and trivalent limited extraction
- Reduction of Pu drives separation from U
  - Trivalent Pu separates from hexavalent U by backextraction from organic



PUREX Process

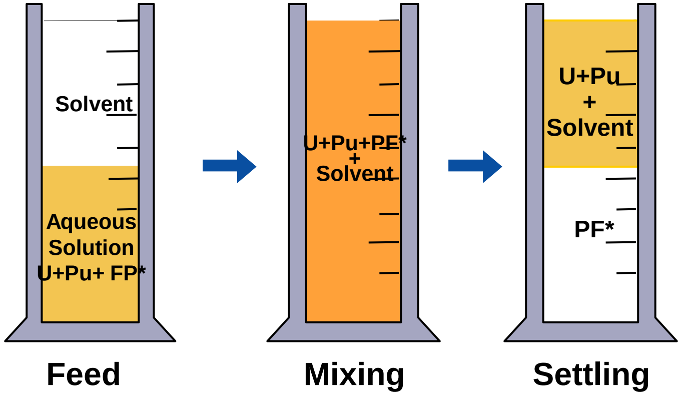


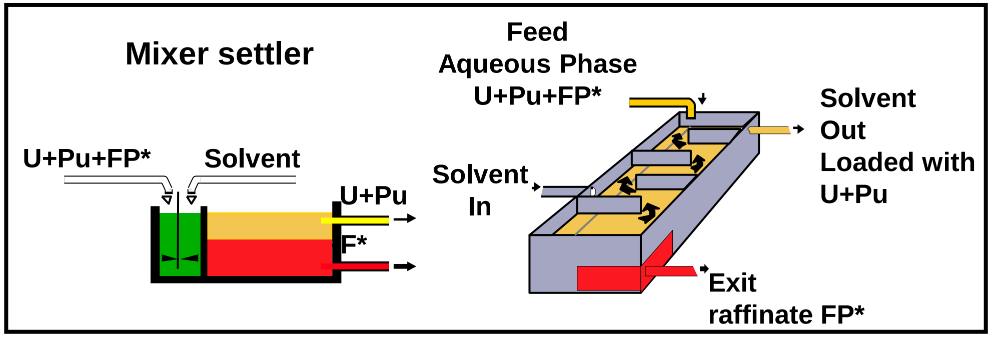
- Pu reduction drives separation from U
  - Trivalent Pu separates from hexavalent U by backextraction from organic
- Pu reducing agents form Pu(III) which backextracts to aqueous phase
- Ferrous sulfamate: Fe $^{2+}$: $Fe(H_2NO_3S)_2$
  - $Pu^{4+} + Fe^{2+} \leftrightarrow Pu^{3+} + Fe^{3+}$
- Uranium (IV)
  - $2Pu^{4+} + U^{4+} + 2H_2O \leftrightarrow 2Pu^{3+} + UO_2^{2+} + 4H^+$
- Hydroxylamine nitrate ($NH_3OH^+NO_3^-$)

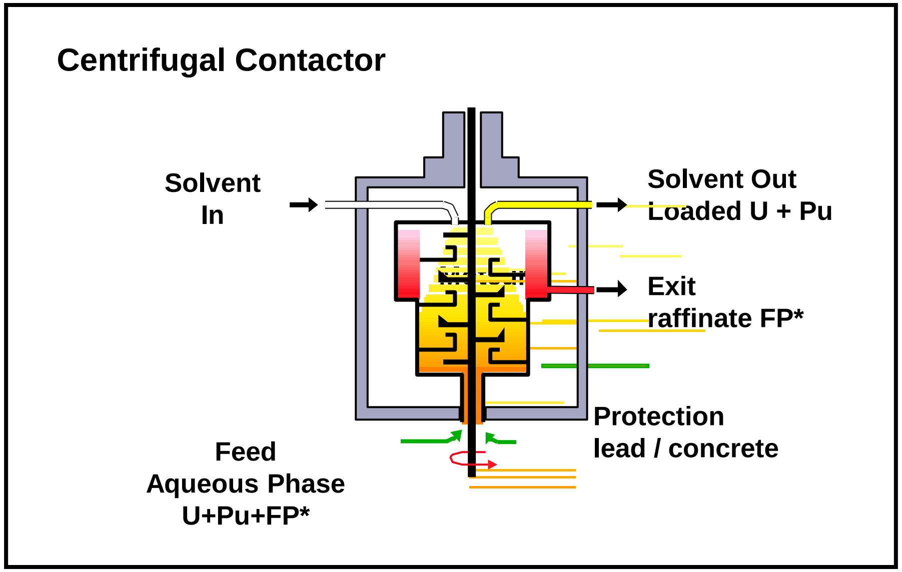


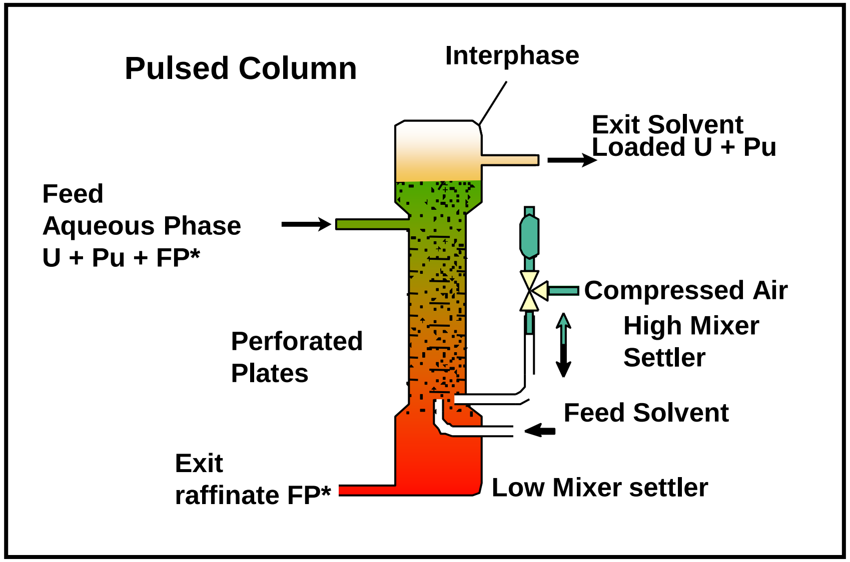
$$2Pu^{4+} + 8NO_3^- + NH_3OH^+NO_3^- \longleftrightarrow 2Pu^{3+} + \frac{1}{2}N_2O + \frac{1}{2}H_2O + 3H^+ + 9NO_3^-$$

Solvent Extraction in PUREX









**** FP : Fission Products***

PUREX process

- Plant-scale performance of a two-cycle PUREX process:
  - Separation of Pu from U: 10^6
  - Separation of fission products from Pu: 10^8
  - Separation of fission products from U: 10^7
  - Pu and U recovery
- How to achieve high separation with K_d on the order of 10^2
  - Multiple stages

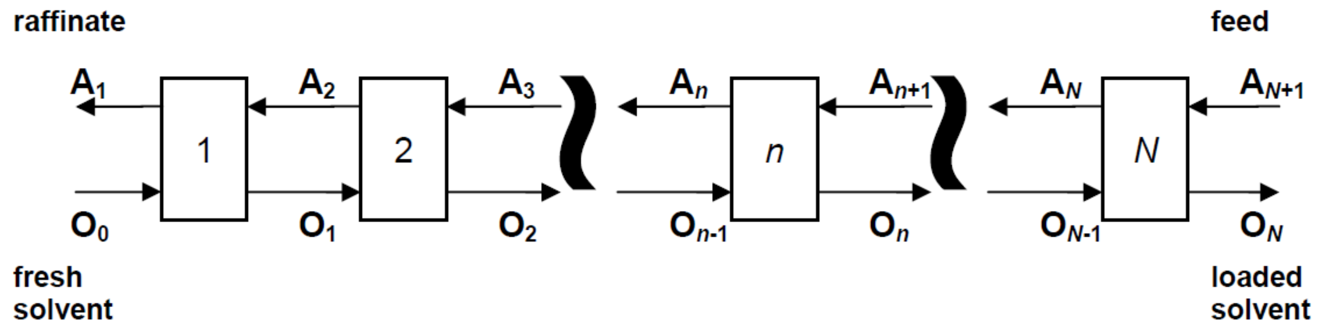
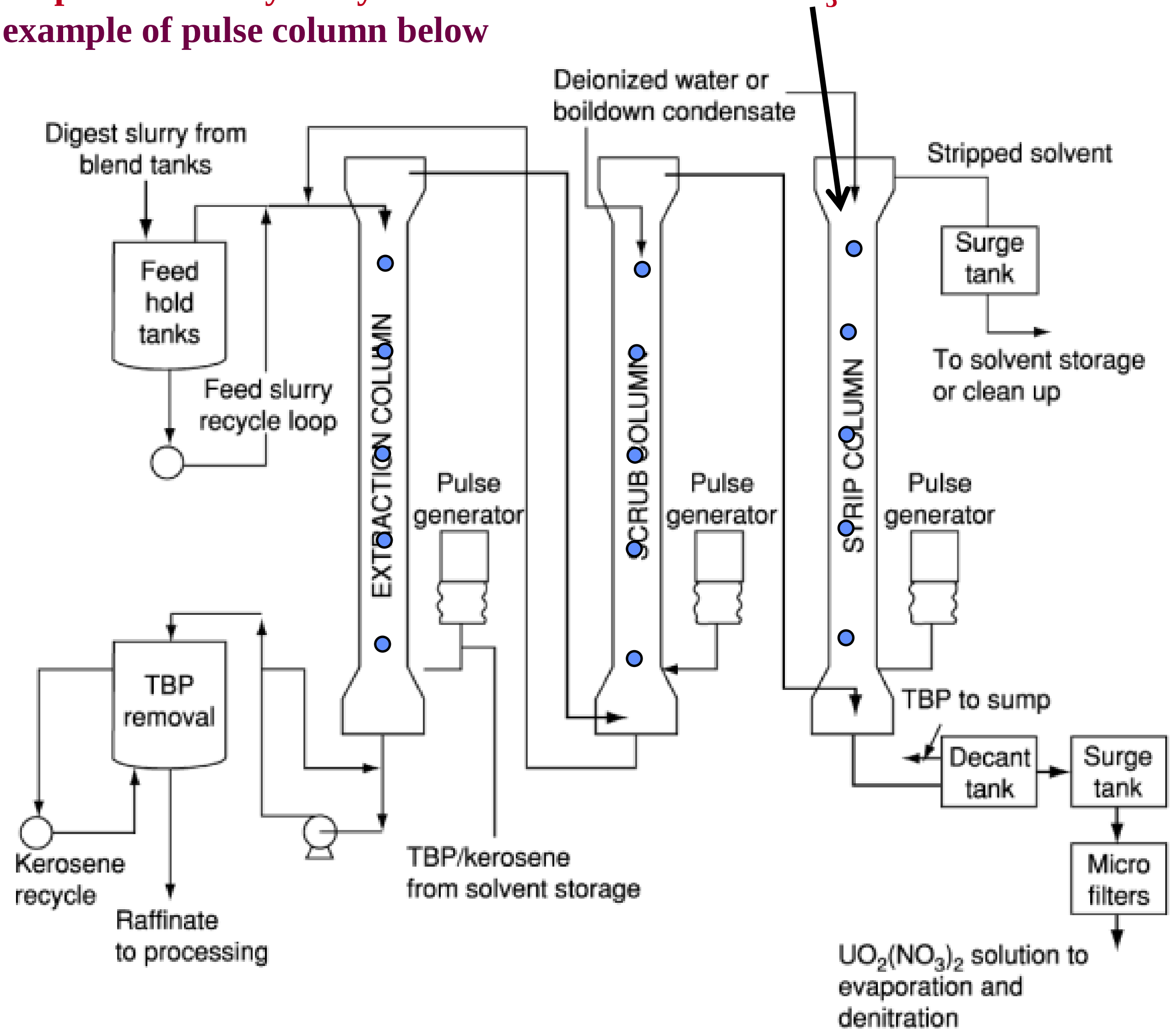


Figure 1. Countercurrent – multistage extraction process flow diagram

http://www.cresp.org/NuclearChemCourse/monographs/11_Law_Liquid-liquid%20extraction%20equipment%20jdl_3_2_09.pdf

U-Pu separation in PUREX

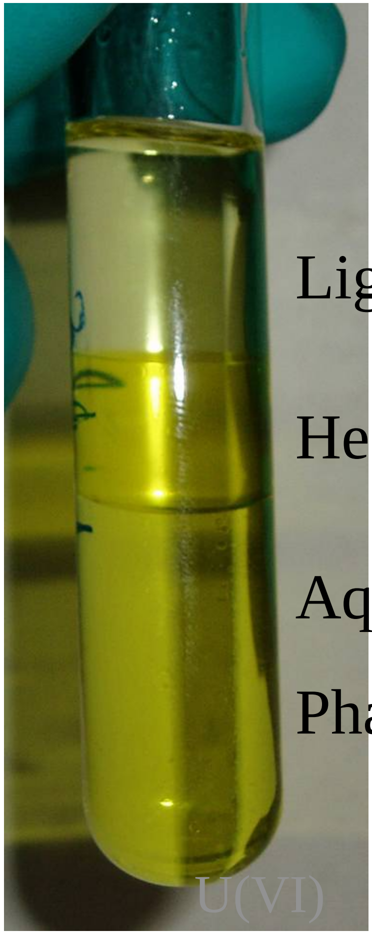
- Based on formation of nitrate species
    - 30 % TBP in kerosene
    - 3.5 M NHO_3
    - Strip has 0.1 M hydroxylamine nitrate in 3.5 M HNO_3
- Process example of pulse column below



Third Phase Formation

- In liquid-liquid solvent extraction certain conditions cause the organic phase to split
  - PUREX separations TBP
  - Possible with advanced separations
- Limiting Organic Concentration (LOC) – highest metal content in phase prior to split
  - Light phase – mostly diluent
  - Heavy phase – extractant and metal rich
- Safety issues, relate to criticality
- Can be exploited for synthesis

Actinide Third Phases



Light Phase

Heavy Phase

Aqueous

Phase

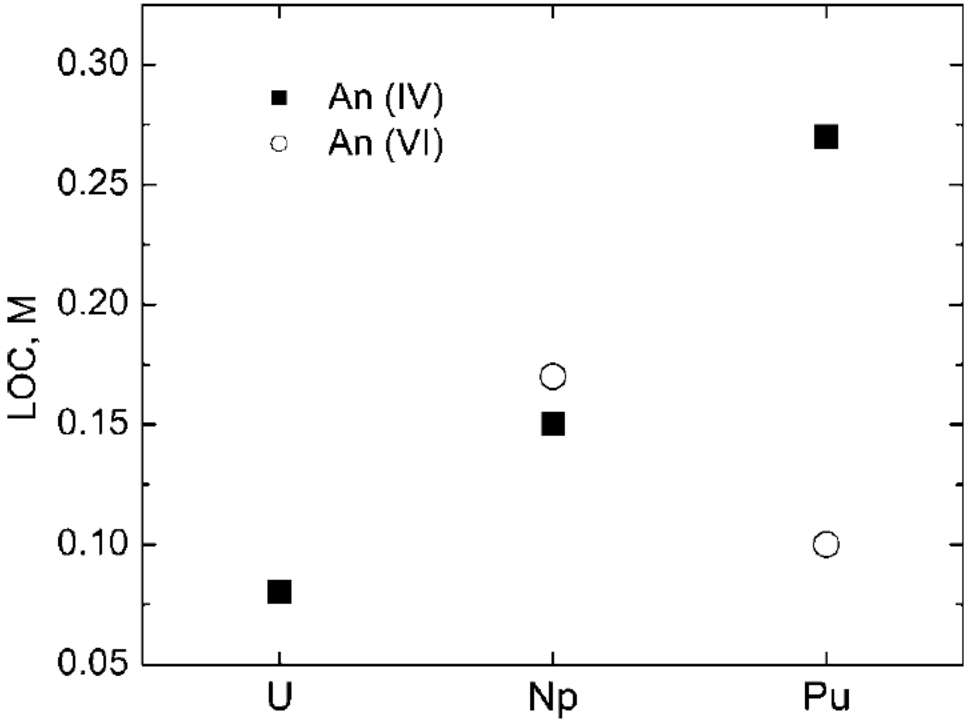


Figure 1. Actinide LOC values in 7M HNO_3/1.1 M TBP/dodecane, M at T = 20–25°C (Data reproduced from Reference 12).

Table 1. Concentrations at the LOC boundary for neptunium, M

$[HNO_3]_{aq}$	Np(IV)	$[H^+]_{org}$	Error	Np(VI)	$[H^+]_{org}$	Error
4	0.10	1.39	0.03	0.27	1.01	0.01
6	0.12	1.49	0.02	0.23	1.20	0.02
7	0.15	1.51	0.01	0.17	1.51	0.17
8	0.10	1.62	0.02	0.14	1.46	0.02
10	0.10	1.52	0.06	0.08	1.72	0.02

RDCH 702: Lecture 9 Separations

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- Basic concept of separations
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- Development of advanced separations
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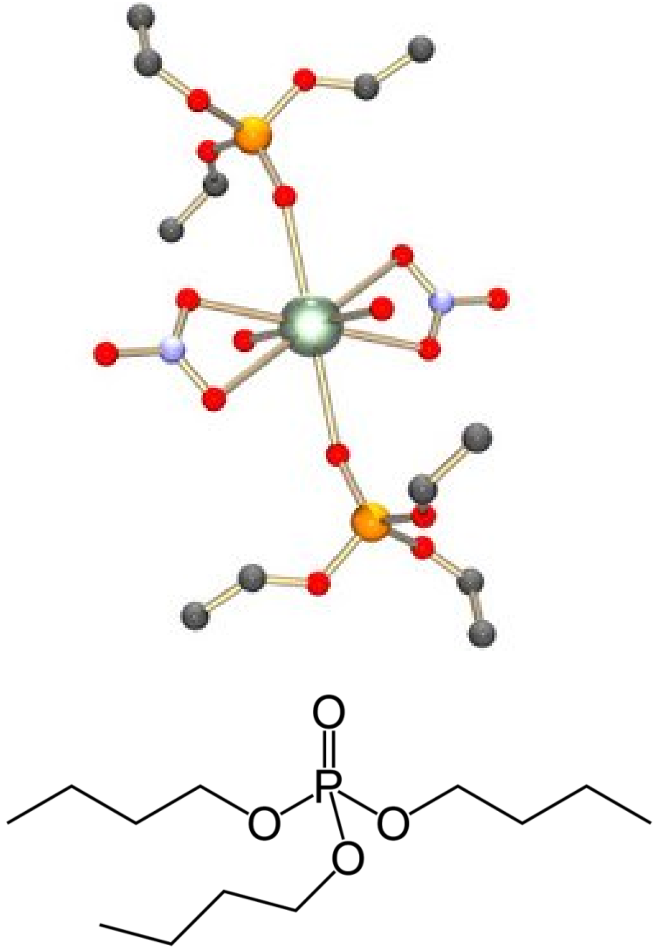
- Necessary for fuel cycle due to formation of mixtures due to fission
  - Actinides
    - → Transuranics
  - Fission products
    - → Se (Z=34) to Dy (Z=66)



Tributyl phosphate (TBP)

RDCH 702: Lecture 9 Separations Part 2

- **Separation methods**
  - **Solvent extraction**
    - → **PUREX**
  - **Ion exchange**
  - **Volatility**
  - **Electrochemistry**
- **Specific actinide separations**

- **Basic concept of separations**
  - **Oxidation state**
  - **Ionic radius**
- **Development of advanced separations**
  - **Trivalent actinides**
- **Necessary for fuel cycle due to formation of mixtures due to fission**
  - **Actinides**
    - → **Transuranics**
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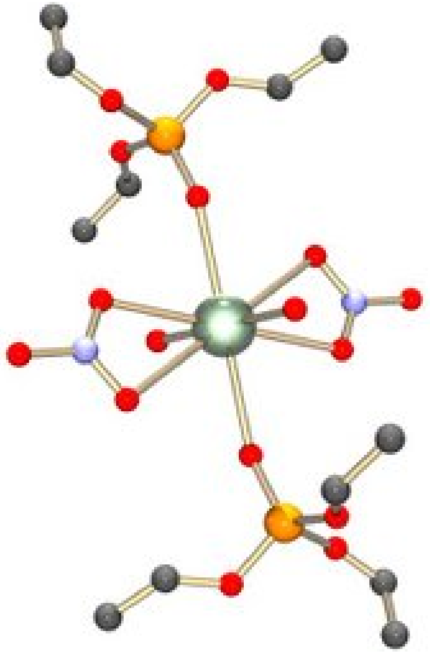
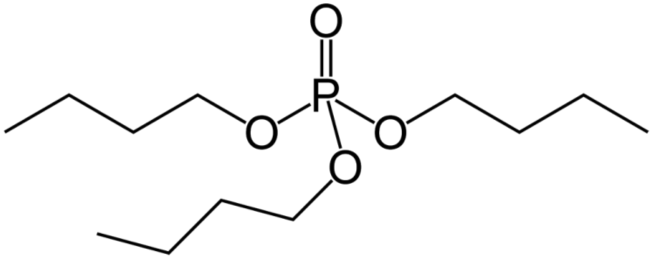
    - → **Se (Z=34) to Dy (Z=66)**

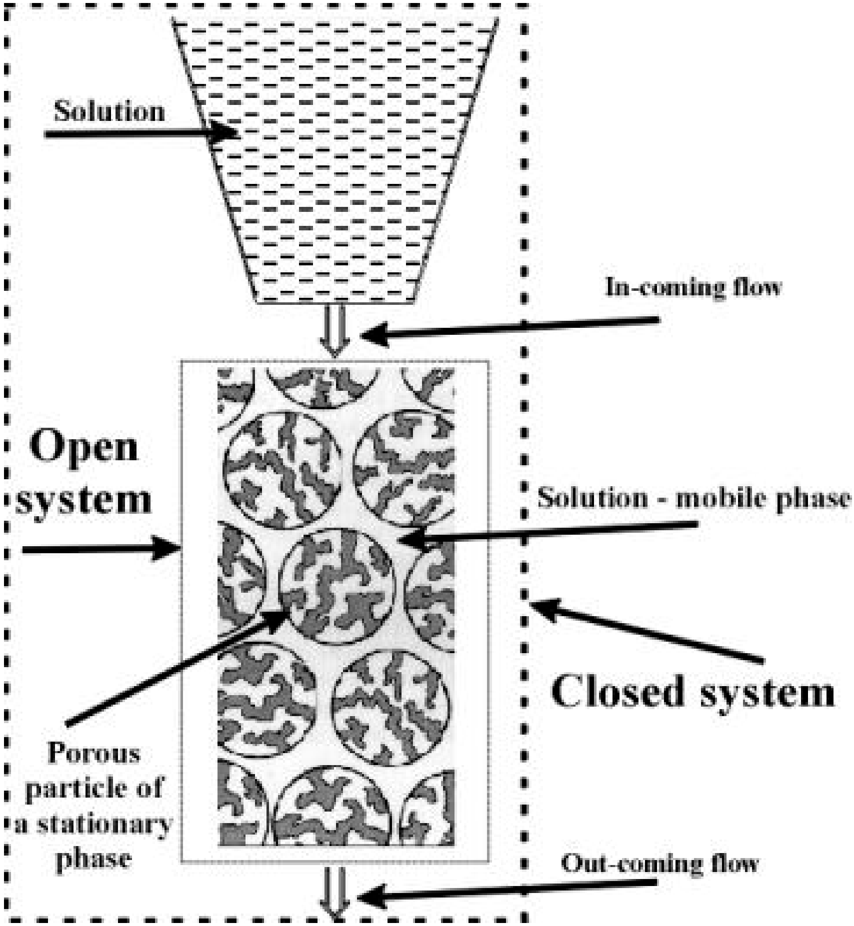




Tributyl phosphate (TBP)

Ion Exchange/Chromatography Separations

- Dissolved sample, solid exchanger
- Adjustment of solution matrix
  - Based on column chemistry and other elements in solution
- Retention of target radionuclide on column
  - Removal of other elements
- Solution adjustment
  - Acid concentration, counter ion variation
  - Addition of redox agent
- Elute target radionuclide
- Can include addition of isotopic tracer to determine yield
- Chemical behavior measured by distribution
  - Similar to K_d
    - → (mg metal/g resin)/(mg metal/mL solution)
    - → mL/g



Ion Exchange Resins

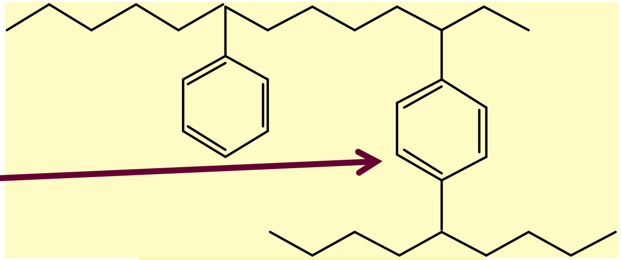
- Resins
    - Organic or inorganic polymer used to exchange cations or anions from a solution phase
- General Structure
    - Polymer backbone not involved in bonding
    - Functional group for complexing anion or cation
- Properties
    - Capacity
        - → Amount of exchangeable ions per unit quantity of material
            - * Proton exchange capacity (PEC), meq/g
    - Selectivity
        - → Cation or anion exchange
            - * Cations are positive ions
            - * Anions are negative ions
        - → Some selectivities within group
            - * Distribution of metal ion can vary with solution

Organic Resins

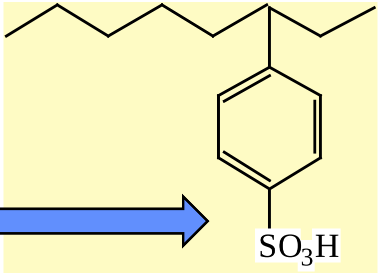
- Backbone
  - Cross linked polymer chain
    - → Divinylbenzene, polystyrene
    - → Cross linking limits swelling, restricts cavity size
- Functional group
  - Functionalize benzene
    - → Sulfonated to produce cation exchanger
    - → Chlorinated to produce anion exchanger
- Structure
  - Randomness in crosslinking produces disordered structure
    - → Range of distances between sites
    - → Environments
      - * Near organic backbone or mainly interacting with solution

<u>Sorption based resins</u>

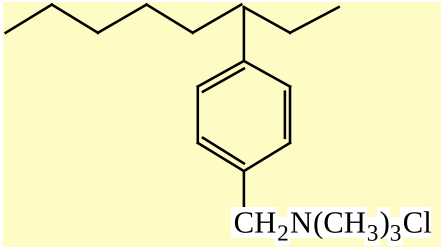
- Organic with long carbon chains (XAD resins)
  - Sorbs organics from aqueous solutions
  - Can be used to make functionalized exchangers



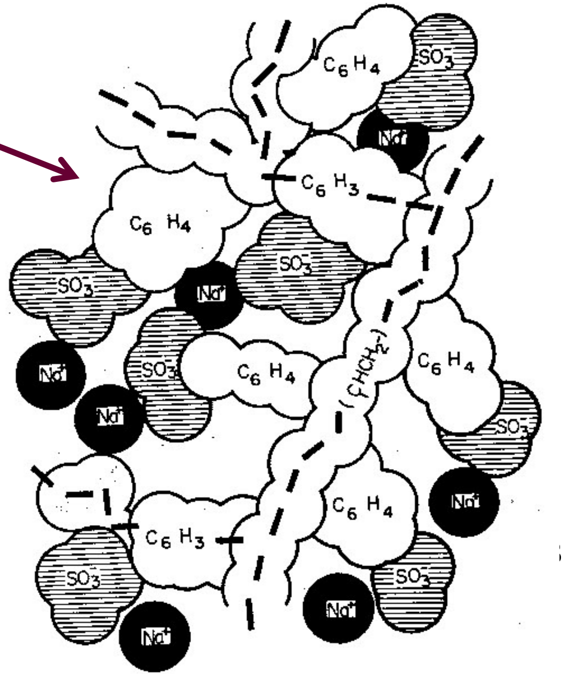
Linkage group



Cation exchange

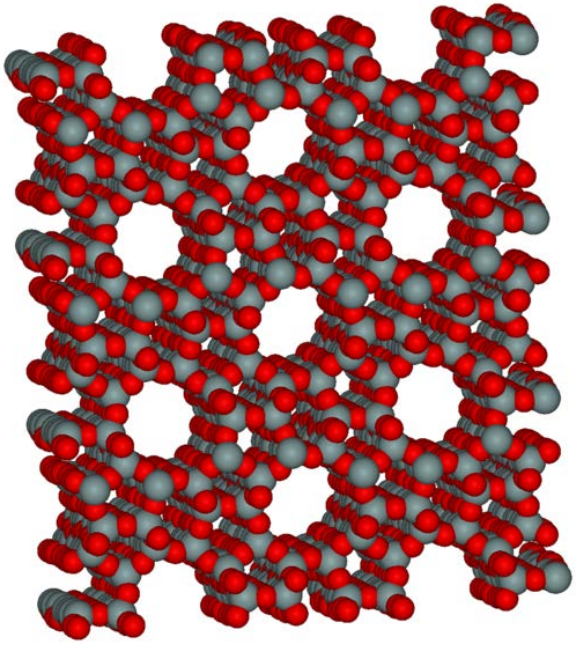


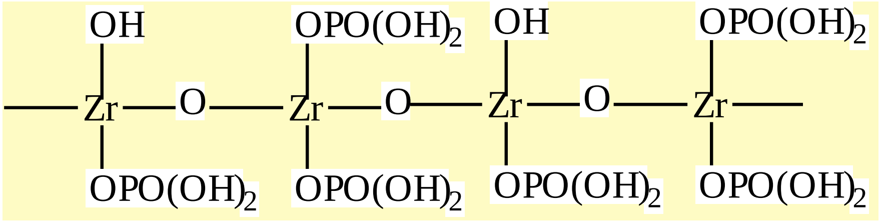
Anion exchange



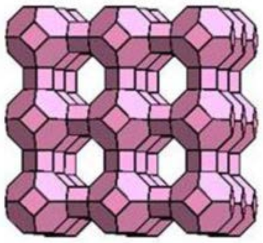
Inorganic Resins

- More formalized structures
  - Less disorder
- Silicates (SiO_4)
- Alumina (AlO_4)
  - Both tetrahedral
  - Can be combined
    - → $(Ca,Na)(Si_4Al_2O_{12}).6H_2O$
  - Aluminosilicates
    - → zeolite, montmorillonites
    - → Cation exchangers
    - → Can be synthesized
- Zirconium, Tin- phosphate
  - Easy to synthesis
    - → Metal salt with phosphate
    - → Precipitate forms
      - * Grind and sieve
  - Zr can be replaced by other tetravalent metals
    - → Sn, Th, U
- Zeolites
  - Microporous, aluminosilicate minerals
  - Used as sorbants





$-\mathrm{Zr}(\mathrm{OH})(\mathrm{OPO(OH)_2})-\mathrm{O}-\mathrm{Zr}(\mathrm{OPO(OH)_2})_2-\mathrm{O}-\mathrm{Zr}(\mathrm{OH})(\mathrm{OPO(OH)_2})-\mathrm{O}-\mathrm{Zr}(\mathrm{OPO(OH)_2})_2-$

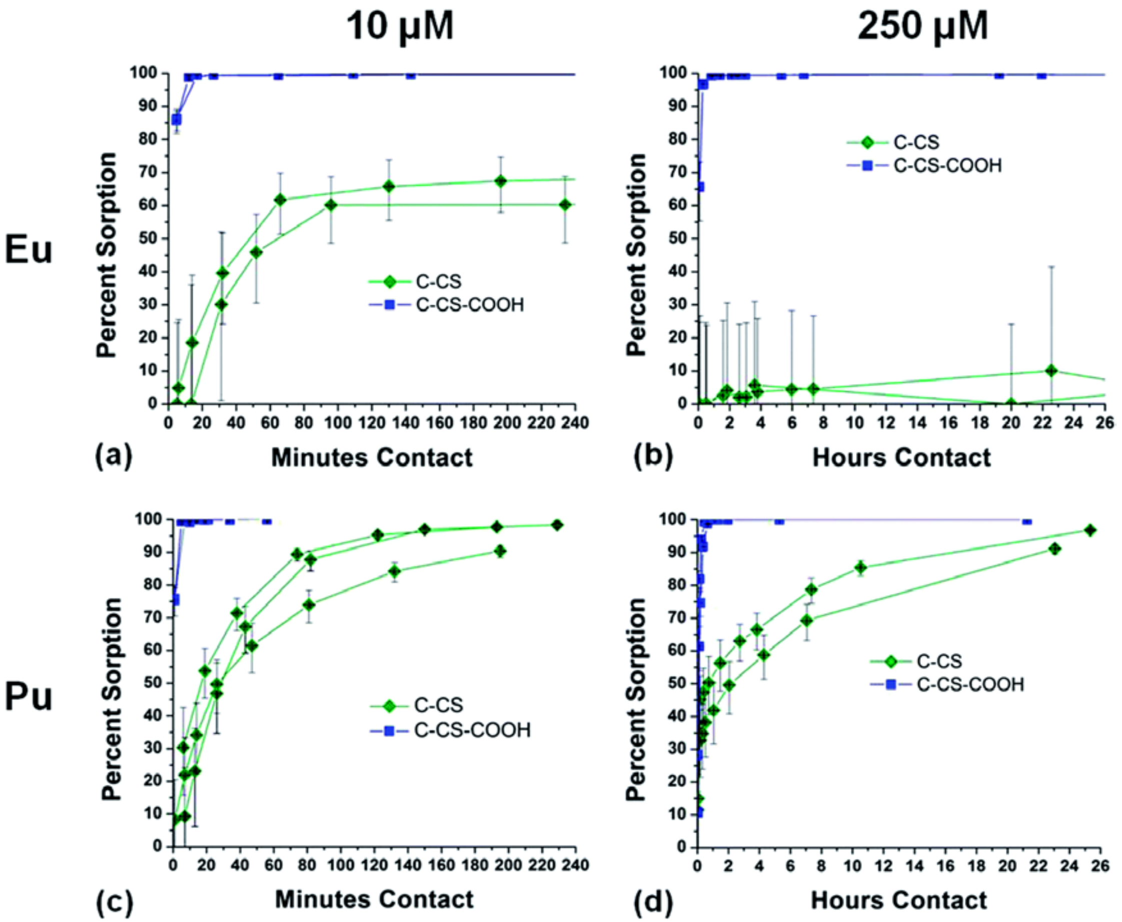


Kinetics

- **Diffusion controlled**
  - **Film diffusion**
    - → **On surface of resin**
  - **Particle diffusion**
    - → **Movement into resin**
- **Rate is generally fast**
- **Increase in crosslinking decrease rate**
- **Theoretical plates used to estimate reactions**

Swelling

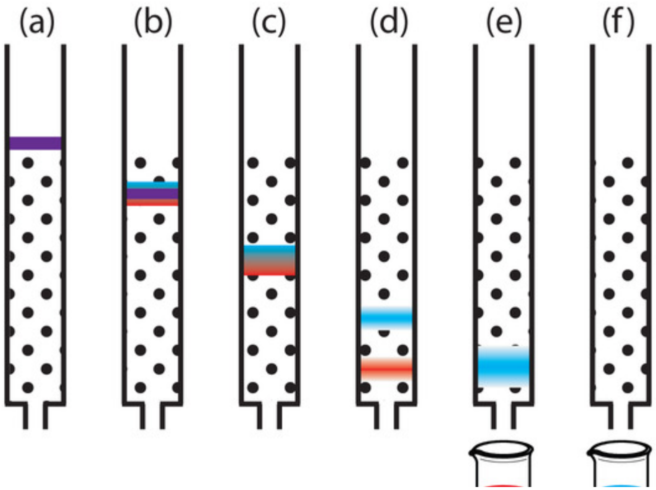
- **Solvation increases exchange**
- **Greater swelling decreases selectivity**

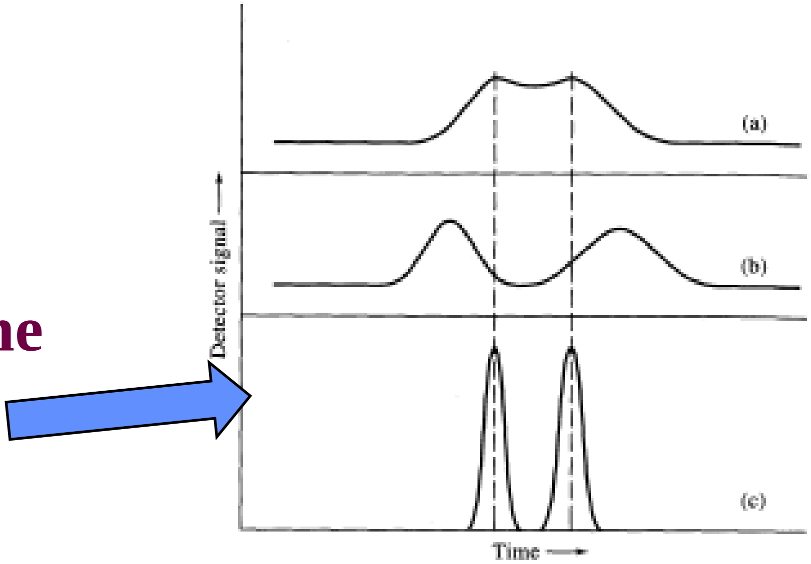


Sorption interactions of plutonium and europium with ordered mesoporous carbon

Column Chromatography Ion Exchange

- **Chromatogram**
  - **concentration versus elution time**
- **Strongly retained species elutes last**
  - **elution order**
- **Analyte is diluted during elution**
  - **dispersion**
- **Zone broadening proportional to elution time**
- **Separations enhanced by varying experimental conditions**





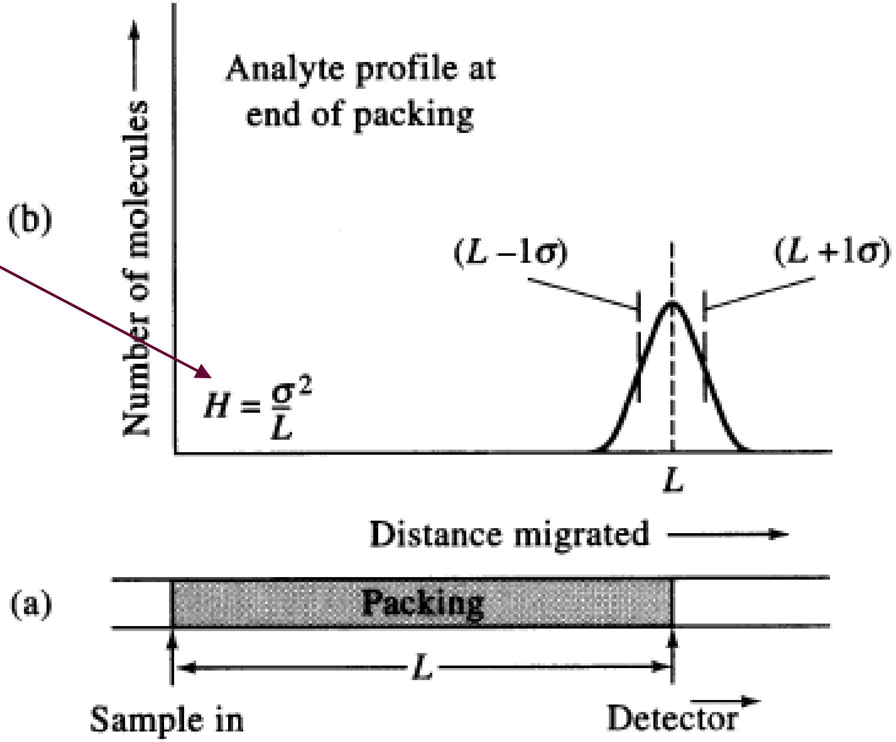
Broadening

- Individual molecule undergoes "random walk"
- Many thousands of adsorption/desorption processes
- Average time for each step with some variations
  - Gaussian peak

    →like random errors
- Breadth of band increases down column because more time
- Efficient separations have minimal broadening

Theoretical plates

- **Column efficiency increases with number of plates**
  - **N=L/H**
    - → **N= number of plates, L = column length, H= plate height**
  - **Assume equilibrium occurs at each plate**
  - **Movement down column modeled**
- **Plate number can be found experimentally**
- **Other factors that impact efficiency**
  - **Mobile Phase Velocity**
  - **Higher mobile phase velocity**
    - → **less time on column**
    - → **less zone broadening**



K_d = mL/g

= (mg metal/g resin)/(mg metal/mL solution)

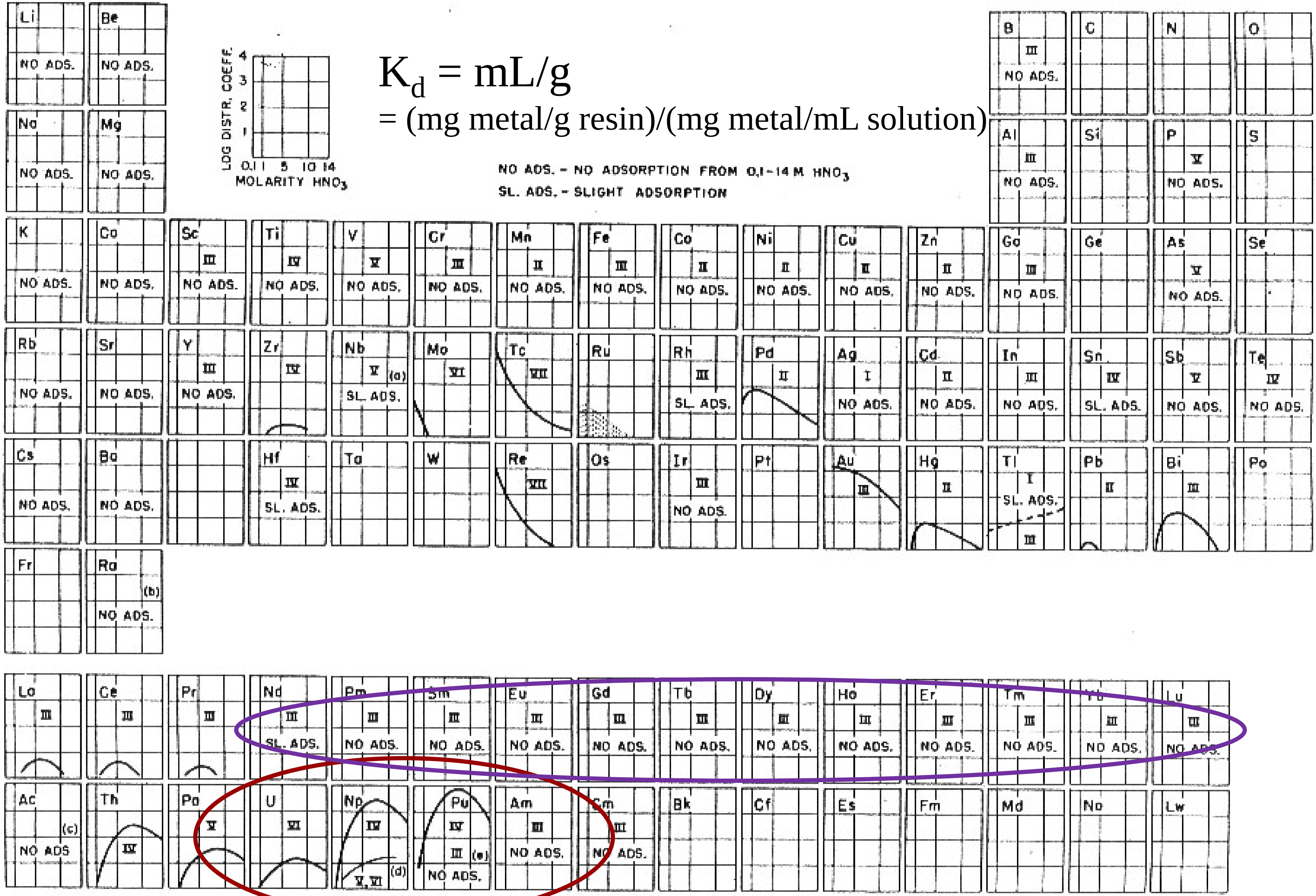


Fig. 8. Adsorption of the elements from HNO_3 solutions by a strong-base anion-exchange resin, Dowex-1, as a function of HNO_3 molarity. [From Faris and Buchanan (*138*); reproduced with permission of *Analytical Chemistry*.]

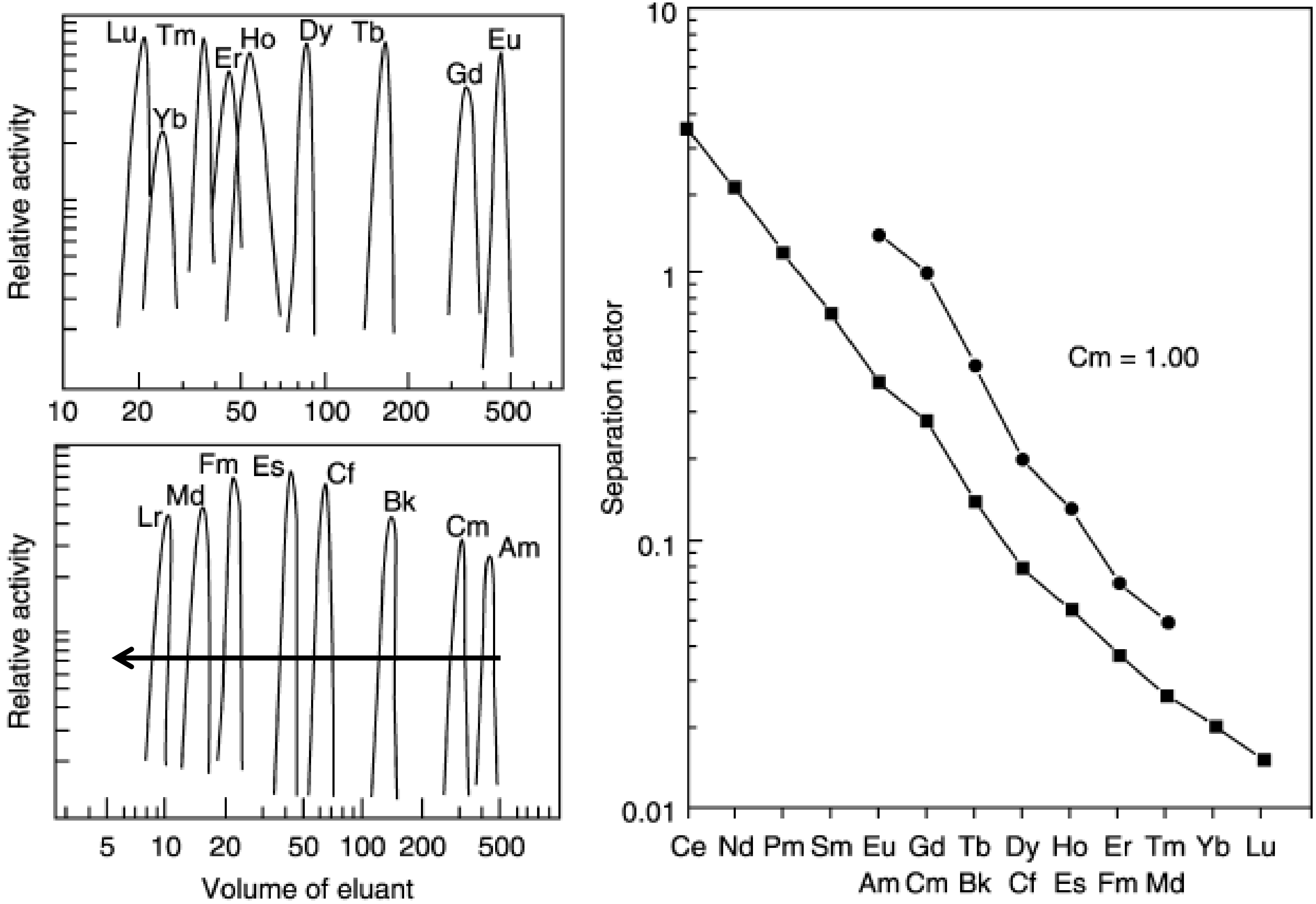


Fig. 24.4 *Elution profiles for trivalent lanthanide and actinide ions and separation factors (relative to Cm = 1.0) for α-hydroxyisobutyrate elution from Dowex 50 cation exchange resin (Choppin and Silva, 1956).*

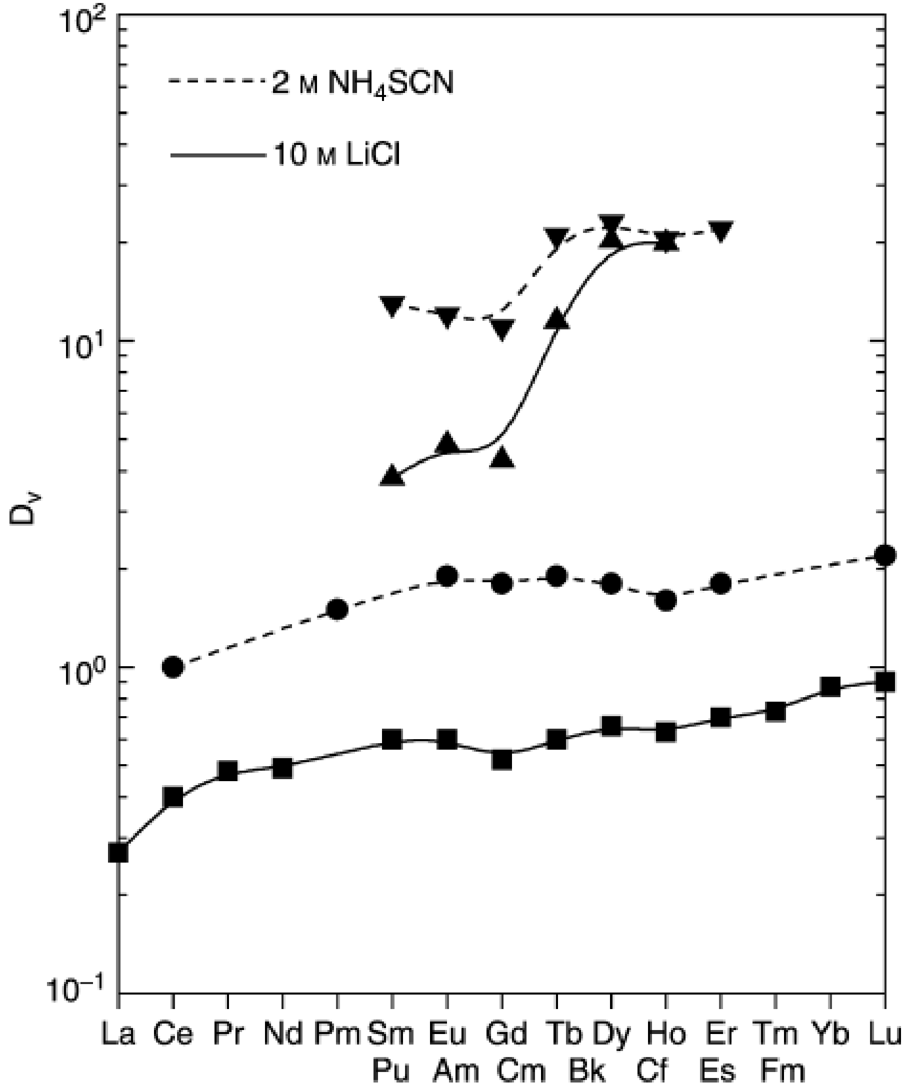


Fig. 24.2 *Partitioning of trivalent actinides and lanthanides onto Dowex* 1 *anion exchange resin from* 10 M *lithium chloride* (*Hulet* et al., 1961) *and* 2 M *ammonium thiocyanate* (*Surls and Choppin*, 1957) *solutions* (▼, ▲, *actinides*, ●, ■, *lanthanides*).

D_v =([M]/mL resin)/([M]/mL solution)

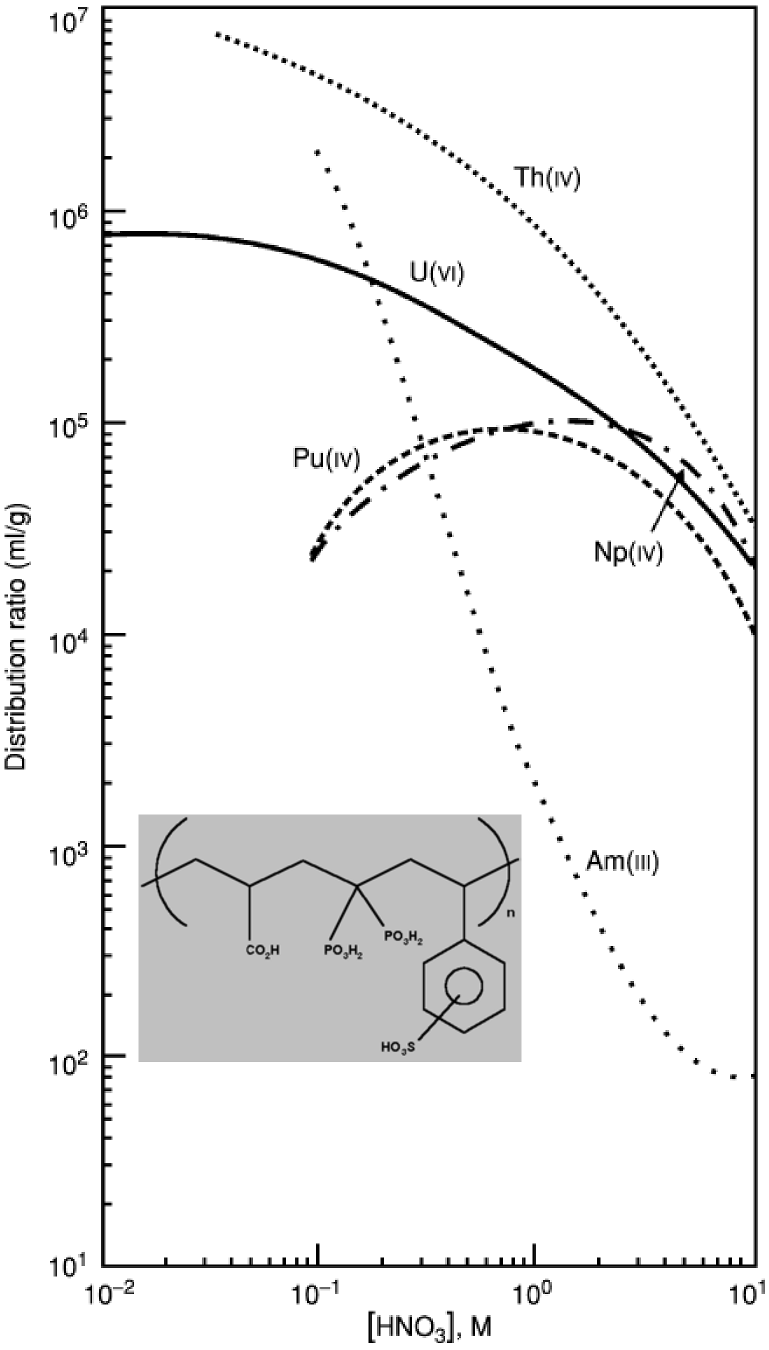


Fig. 24.5 *Distribution of selected actinide ions onto Diphonix resin from nitric acid solutions* (*Chiarizia* et al., 1997).

Volatility: AIROX

- **For treatment of oxide fuel**
- **UO_2 oxidized to U_3O_8**
  - **Heating to 400-600 °C in O_2 containing atmosphere**
  - **Around 30% volume increase**
- **U_3O_8 reduction by addition of H_2**
- **Kr, Xe, I removed**
  - **Some discrepancies**

Element	**Ref. 1**	**Ref. 2**	**Ref. 3**	**Ref. 4**
Ag	80	0	0	0
Cd	0	75	75	80
Cs	99	90	100	99
In	0	75	0	75
Ir	0	0	75	0
Mo	80	0	0	80
Pd	80	0	0	0
Rh	80	0	0	0
Ru	80	90	100	80
Se	80	0	0	99
Tc	80	---	0	0
Te	99	75	75	99

1. AECL Technologies, Inc. “Plutonium Consumption Program-CANDU Reactor Projects,” Final Report, July 1994.
2. SCIENTECH, Inc., Gamma Engineering Corp., “Conceptual Design and Cost Evaluation for the DUPIC Fuel Fabrication Facility,” Final Report, SCIE-COM-219-96, May 1996.
3. Recycling of Nuclear Spent Fuel with AIROX Processing, D. Majumdar Editor, DOE/ID-10423, December 1992.
4. Bollmann, C.A., Driscoll, M.J., and Kazimi, M.S.: Environmental and Economic Performance of Direct Use of PWR Spent Fuel in CANDU Reactors. MIT-NFC-TR-014, 44-45, June 1998.

Element Volatility

- Melting points correlate with vapor pressure
  - Zone refining can have applications
- Data for elements
  - Need to consider solid solutions and intermetallics in fuel

Melting Points

Element	°C
He	-272
Kr	-157
Xe	-111
Cs	29
Rb	39
I	114
Te	450
Pu	640
Ba	725
Sr	764
Ce	795
Eu	822

Element	°C
La	920
Pr	935
Nd	1010
Pm	1042
Sm	1072
U	1132
Y	1523
Pd	1552
Zr	1852
Rh	1966
Tc	2200
Ru	2250
Mo	2617

Volatility: CO_2

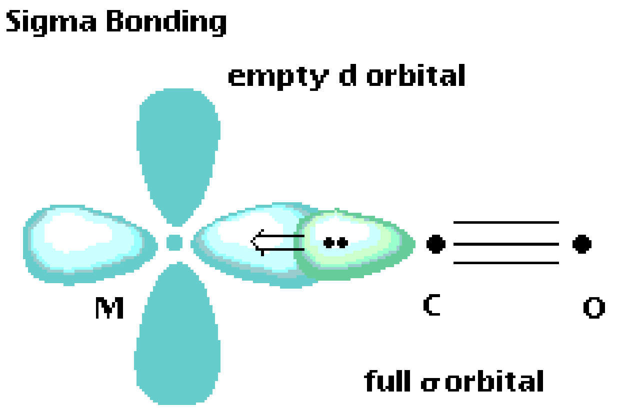
- **Nearly 70 % of Eu, Gd, Nd, and Sm by oxidation under CO_2 at 1000 °C**
  - **Attributed to Rh as catalyst in matrix**
  - **Volatile species not identified**
- **Near complete removal for Ag, Cs, and Mo**

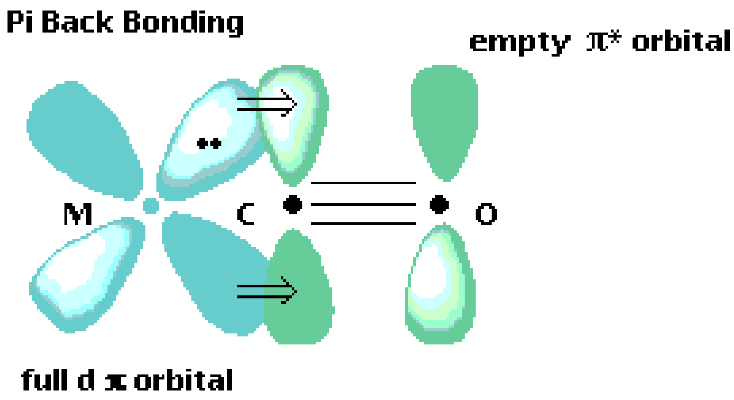
Evaluated rate constants (min^{-1}) for the CO_2 volatilization of Cs, Ag, Rh, Eu, Sm, and Nd in UO_2

Element	750 °C	1000 °C	1250 °C
Cs	7.84+0.96E-03	4.82±0.42E-02	1.72±0.59E-01
Ag	1.09±0.22E-02	1.74±0.62E-01	5.25±0.38E-01
Rh	9.22±0.40E-02	2.24±0.41E-01	4.94±0.54E-01
Eu	3.28±0.34E-02	1.11±0.66E-01	2.84±0.29E-01
Sm	3.85±0.54E-02	9.23±1.01E-02	2.15±0.29E-01
Nd	3.99±0.94E-02	7.85±1.95E-02	1.96±0.20E-01

Carbonyl (CO)

- Metals form a range of complexes with CO
  - Range of oxidation states
    →0 to cations
- Tends to form volatile species
- Mond process
  - Ni treated with CO at 60-80 °C
  - Decomposes at 180 °C to form pure Ni and CO

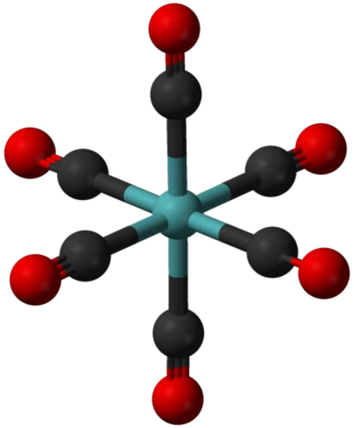




Carbonyl

- No evidence of U or Pu carbonyl from direct reaction of CO with metal
- Group 1 and 2
  - Form true carbonyls with metals at very low temperature
- No evidence of simple Zr carbonyls
  - Laser ablation experiments
- Lanthanides: Ln from laser ablation studies
  - Volatile species observed
- Noble metal: neutral binary carbonyls: $Mo(CO)_6$, Tc, Ru, Rh
  - Mo and Pd from the chloride
  - Pd forms mixed halide carbonyl
  - $Ru(CO)_5$ volatile species at 25° has been observed
    - → Ru was on Al_2O_3 catalysts (mixed reactions)

$Mo(CO)_6$



Halides (F, Cl, Br, I)

- **Can be produced from direct metal reaction**
  - **Compounds often unstable, mixed oxygen species common**
- **Van Arkel process for obtaining pure Zr**
  - **Zr with I_2 at 200 °C forms ZrI_4**
  - **Zr tetrahalide critical temperatures (sublimation, triple point):**

    → F (600 °C), Cl (437 °C), Br (450 °C), I (499 °C)
- **metal is converted into a volatile halide compound**
- **volatile compound is decomposed**
  - **Can be used as plating method (i.e., Zr layer on metal fuel)**

Halides

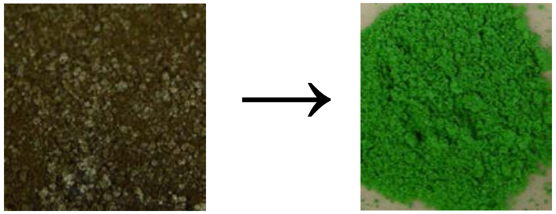
- **Fluorination of simulated thermal reactor fuel containing UO_2, PuO_2, and fission product oxides has been studied**
  - **U selectively fluorinated to UF_6 with BrF_5 at 200 to 400 °C.**
  - **PuF_4 converted to PuF_6.**
  - **Most fission products form fluorides that volatilize at high temperatures than the actinides**

    → Preferential distillation
- **Chlorination also examined, similar to fluoride behavior**

Anatasia, L.J., Alfredson, P.G., and Steindler, M.J.: Fluidized-Bed Fluorination of UO_2-PuO_2-Fission Product Pellets with BrF_5 and Fluorine. Part I: The Fluorination of Uranium, Neptunium, and Plutonium. Nuclear Applications and Technology, **7**, 425-432, 1969.
Anatasia, L.J., Alfredson, P.G., and Steindler, M.J.: Fluidized-Bed Fluorination of UO_2-PuO_2-Fission Product Pellets with BrF_5 and Fluorine. Part II: Process Considerations. Nuclear Applications and Technology, **7**, 433-442, 1969.
Selvaduray, G., Goldstein, M.K., and Anderson, R.N.: Separation Technologies Reviewed. Nuclear Engineering International, **23**, 35-40, 1978.

Halides

- **Actinide halides**
  - **Formed from other fluorides or dioxide in halide-organic solvents**
    - →$2AlCl_3 + UF_6$ ←→$2AlF_3 + UCl_6$
    - →UF_4 can be prepared from $UO_2 + NH_4HF_2$
    - →Heating metal with I_2 can form AnI_3
  - **Melting points**
    - →AnF_6: U= 64 °C, Np=55 °C, Pu = 52 °C
    - →AnF_4: U=1036 °C, Pu= 1027 °C
    - →UCl_6 (177 °C)
    - →$AnCl_4$: U = 590 °C, Np = 517 °C
    - →AnI_3: U=766 °C, Np = 760 °C, Pu = 777 °C

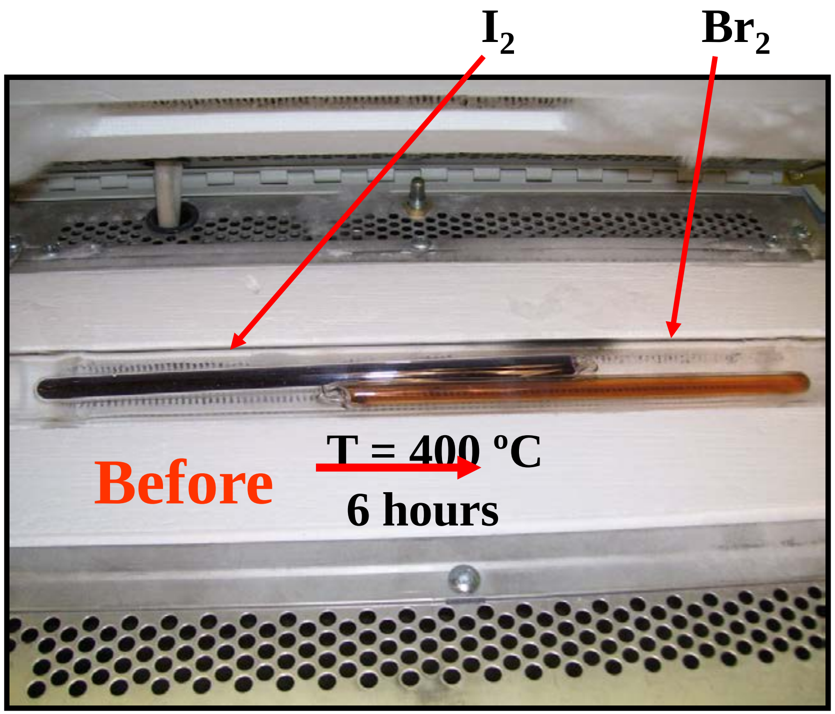


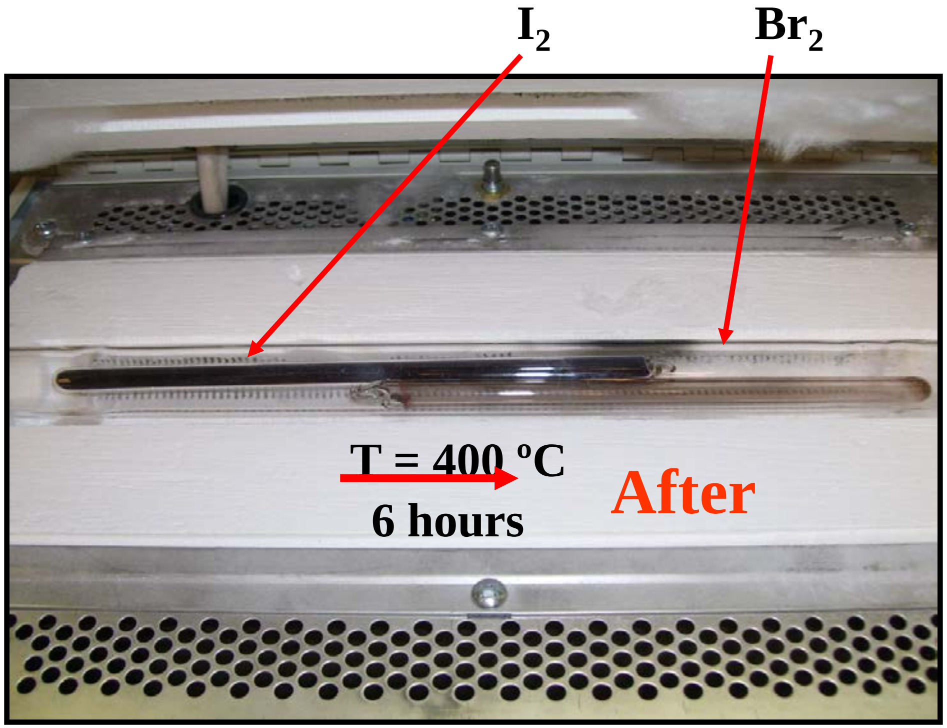
Halides

- Group 1
  - Produced from the carbonate or hydroxide and HX (halide acid)
  - Can be made by metal reaction
  - Melting points
    - → Trends: F>Cl>Br>I
      - * Rb: 642 °C to 823 °C; Cs: 621 °C to 703 °C
- Group 2
  - Can be formed from direct metal reaction
  - Trend as Group 1
  - melting points (538 °C [SrI_2] to 1477 °C [SrF_2]
- Lanthanides
  - Metal reactions
  - Melting point
    - → Over 1200 °C for fluorides, 600 °C to 800 °C for other halides

Halides: Example with Tc

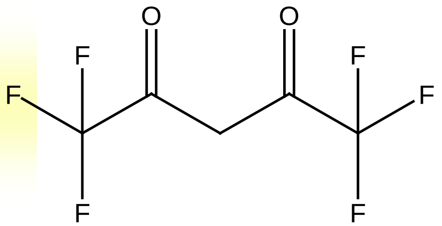
Direct reaction of the elements:





Formation of volatile Tc-Br species

Hexafluoroacetylacetonate (hfac)

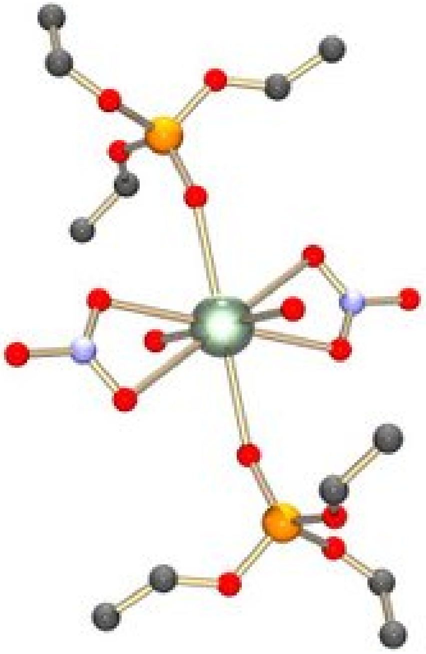


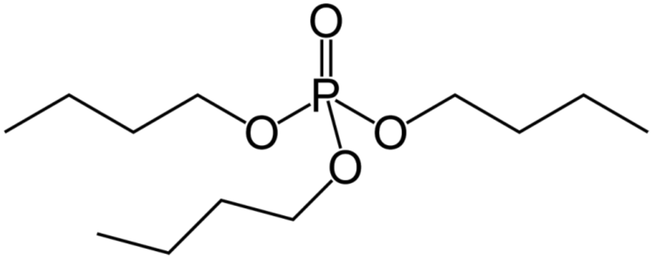
- Complexes known for high volatility and ease of synthesis
- Can be used to effect separation directly from a mixture of metal oxides with solvent free reactions
  - Solvent free: mixing of solids
- U from Pb demonstrated in solvent
  - Selective species formation
- hfac used for vapor deposition of metal
  - Possible route to separation and metal formation in single step
- Initial studies performed with actinides, lanthanides and fission elements

RDCH 702: Lecture 9 Separations Part 2

- Separation methods
  - Solvent extraction
    - → PUREX
  - Ion exchange
  - Volatility
  - Electrochemistry
- Specific actinide separations

- Basic concept of separations
  - Oxidation state
  - Ionic radius
- Development of advanced separations
  - Trivalent actinides
- Necessary for fuel cycle due to formation of mixtures due to fission
  - Actinides
    - → Transuranics
  - Fission products
    - → Se (Z=34) to Dy (Z=66)



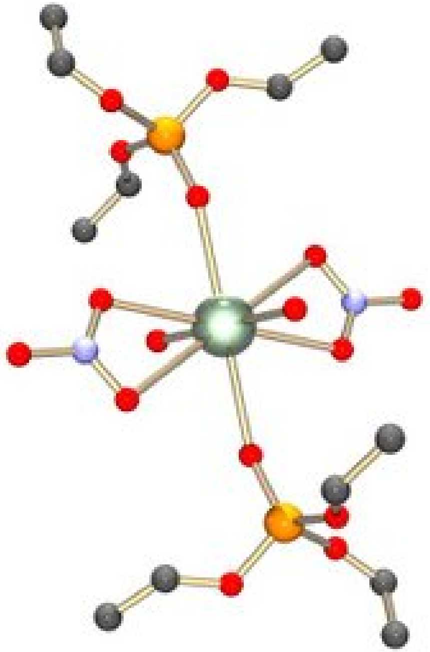


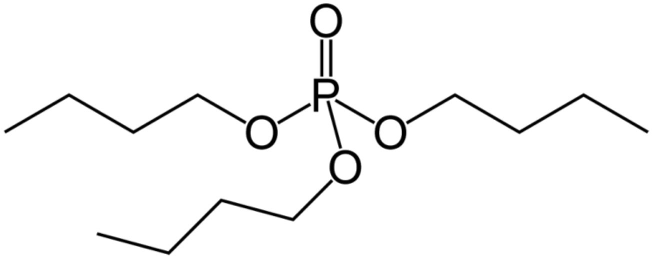
Tributyl phosphate (TBP)

RDCH 702: Lecture 9 Separations Part 3

- Separation methods
  - Solvent extraction
    - → PUREX
  - Ion exchange
  - Volatility
  - Electrochemistry
- Specific actinide separations

- Basic concept of separations
  - Oxidation state
  - Ionic radius
- Development of advanced separations
  - Trivalent actinides
- Necessary for fuel cycle due to formation of mixtures due to fission
  - Actinides
    - → Transuranics
  - Fission products
    - → Se (Z=34) to Dy (Z=66)



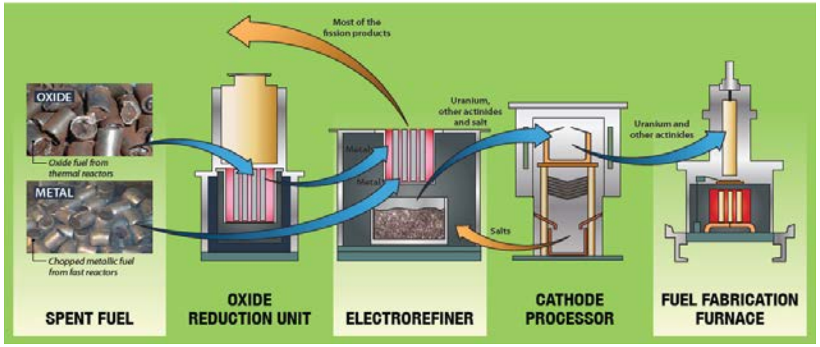


Tributyl phosphate (TBP)

Pyroprocesses

- Electrorefining/Electrochemistry
- Uses molten salt as solvent
  - KCl-NaCl
  - Avoids problems associated with aqueous chemistry

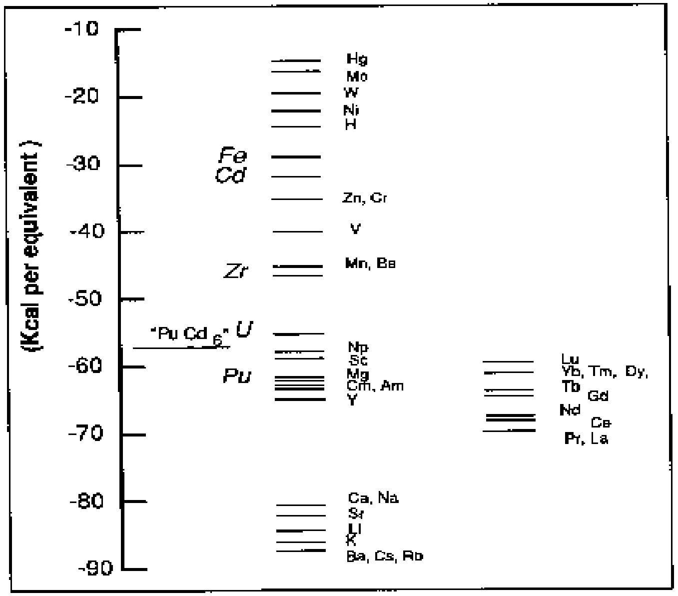
    →Hydrolysis and chemical instability
- Reduction of metal ions to metallic state
- Differences in free energy between metal ions and salt
- Thermodynamic data at hand or easy to obtain
- Sequential oxidation/reduction
  - Cations transported through salt and deposited on cathode
  - Deposition of ions depends upon redox potential



Electrochemical Separations

- Selection of redox potential allows separations
    - Can use variety of electrodes for separation
- Free energies
    - noble metals
    - iron to zirconium
    - actinides and rare earths
    - Group 1 and 2
- Solubility of chlorides in cadmium
- Explored at part of Integral Fast Reactor (IFR) program

Free Energies for Metal Chlorides



...e et al. PARTITIONING AND TRANSMUTATION OF LONG-LIVED NUCLIDES

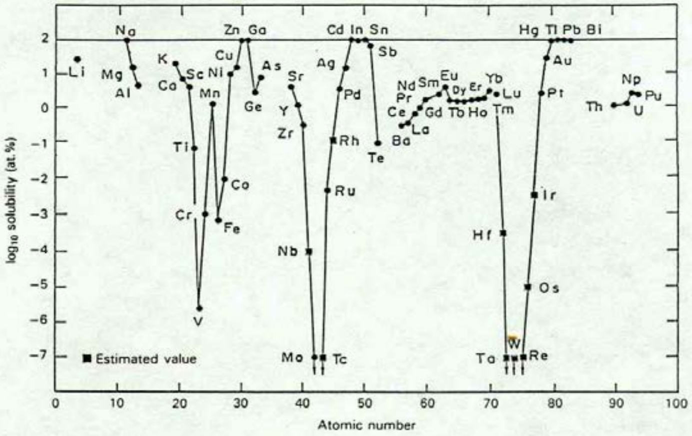


Fig. 5. Solubility of elements in cadmium at 500°C (Ref. 27).

Molten Salt

- **Volatility of chlorides as separation basis**
  - **Gaps between groups**
  - **High vapor pressures achievable at low temperature**

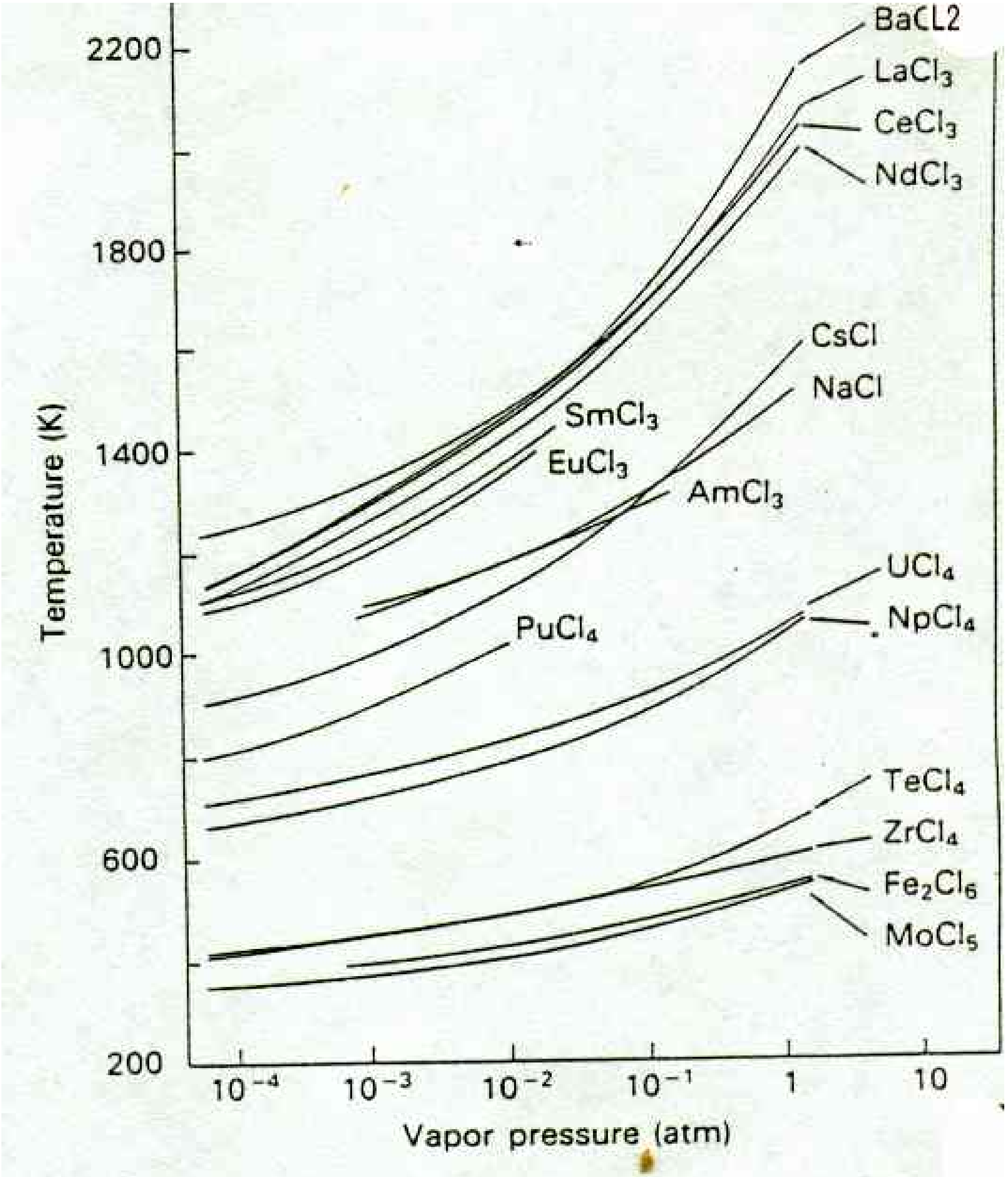


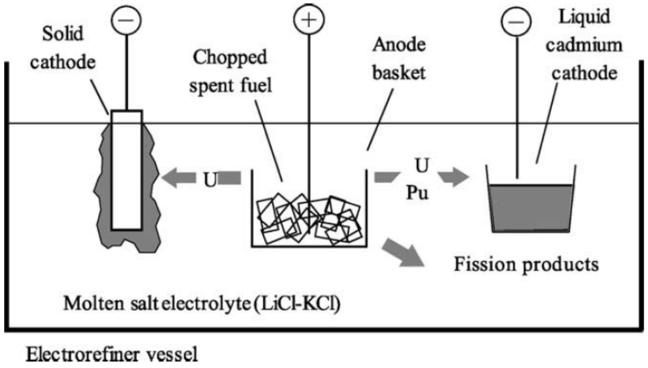
Fig. 4. Vapor pressure of chlorides as a function of temp ature.[15,22,23]

Molten Salt Example

- Oxide fuel dispersed in $CaCl_2$ /CaF_2 at 800 °C
    - Inclusion of Ca metal reduces U salt to a metal
- Reduced metals dissolved in receiver alloy
    - Example Cu - 40% Mg - Ca
    - Uranium exceeds solubility limits receiver alloy and precipitates
- Pu, other actinides, rare-earths, and noble metal fission products accumulate in receiver alloy
    - Separated by distillation
- Alkali metals (Rb and Cs), alkali-earths (Sr and Ba),and remaining iodine and bromine accumulate in the $CaCl_2$/CaF_2 salt.
- Salt contains CaO from the reduction process
    - CaO is electrolytically reduced to metal for reuse

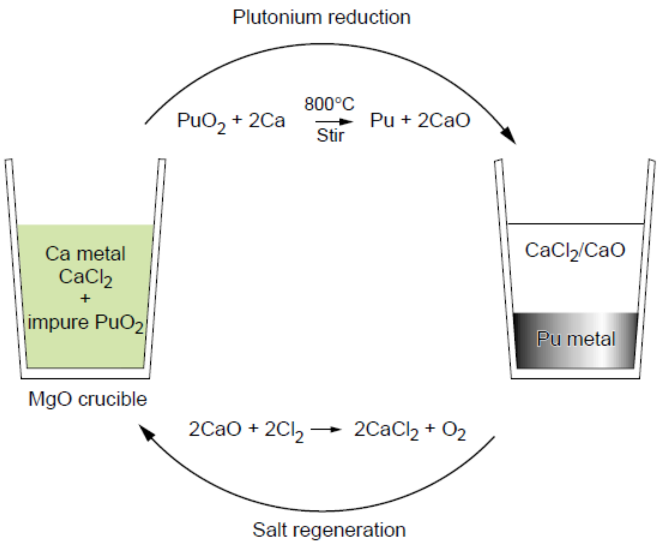
Molten Salt

- LiCl-KCl-UCl_3 at 450-500 °C
- Chopped metallic fuel added to anode baskets
  - U oxidized at anode to U(III)
  - Reduced back to metal at cathode
- Transuranics and fission products oxidized
  - Co-deposition of actinides with cadmium cathode

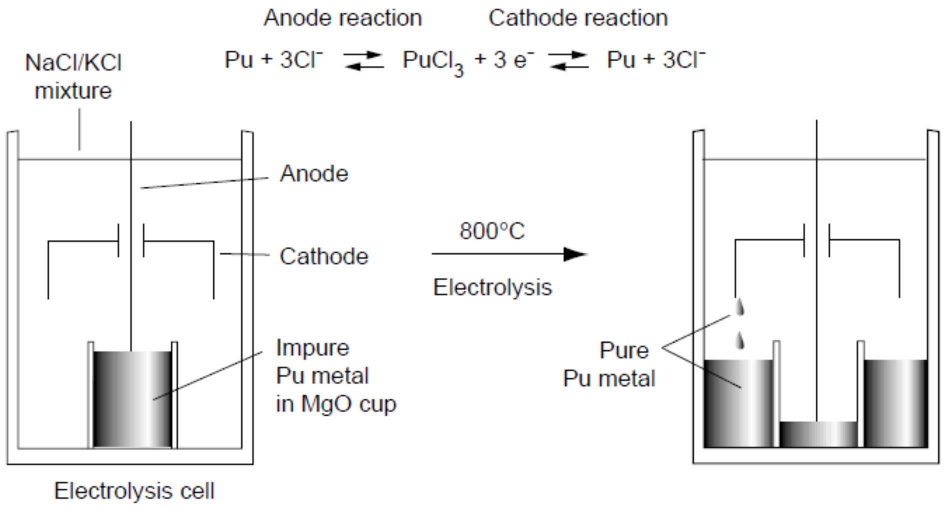


Pu Processing

(a) Direct Oxide Reduction (DOR)



(b) Electrorefining (ER)



- **DOR reduces plutonium dioxide to metal**
  - **PuO_2 and $Ca/CaCl_2$**
  - **Formation of Pu metal and CaO**
  - **CaO treated with Cl_2**

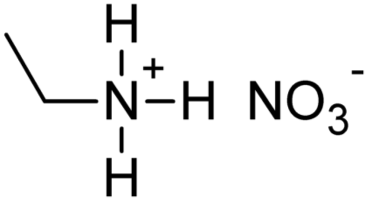
- **Pu metal purified by electrorefining**
- **Pu metal melted in NaCl/KCl at 800°C**
- **Pu oxidized to $PuCl_3$,**
  - **dissolves in molten salt**
- **$PuCl_3$ migrates to cathode and reduced**
- **Pu metal drips from cathode and collects in annular region outside cup**
  - **ring of pure Pu produced**

Ionic liquids

- **Room temperature ionic liquid (ILs) composed of ions that are liquid below 373 K**
- **Composed of a bulky, unsymmetrical organic cation and an organic or inorganic anion**
  - **Range of possible pairs, can be task specific**
    - **Low vapor pressure**
    - **Ability to dissolve organic and inorganic compounds**
    - **Conductive**
    - **Wide electrochemical window**
- **Ionic liquids are tunable to obtain properties needed for particular application**
  - **Solubility**
  - **Reaction Rate**
  - **Electrochemical window**
  - **Specific metal ion interaction**

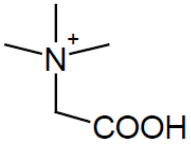
Introduction: Ionic liquids

- Ethylammonium nitrate electrochemistry in 1914

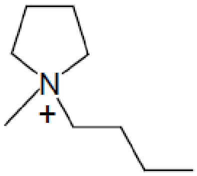


- Initial efforts focused on chloroaluminate anion ($AlCl_4^-$)
  - Electroplate aluminum
    - J. Electrochem. Soc. 98, 203 (1951)
  - Detailed studies, identification of limitations with chloroaluminate
    - Moisture sensitivity
    - Requires non-ambient conditions
      - Inorg. Chem. 17, 2728 (1978)
- Newer ionic liquids have non-hydrolyzing or stable anions
  - Moisture stable ionic liquids developed
    - JACS, 965 (1992)

Examples of IL cations and anions



carboxy-N,N,N-trimethylmethanaminium



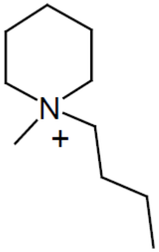
1-butyl-1-methylpyrrolidinium

Cl^-

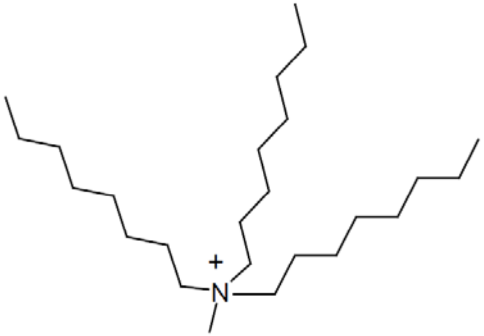
chloride

$-SO_2CF_3$

trifluoromethylsulfonate



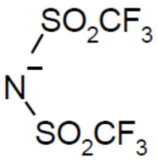
1-butyl-3-methylpiperidinium



tri-n-ocylmethylammonium

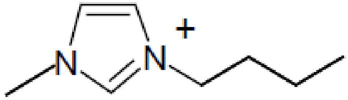
NO_3^-

nitrate



$N^-(SO_2CF_3)_2$

bis(trifluoromethanesulfonyl)imide



1-butyl-3-methylimidazolium

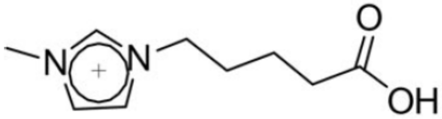
BF_4^-

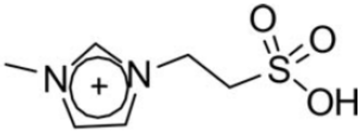
tetrafluroborate

PF_6^-

hexafluorophosphate

Can functionalize ILs

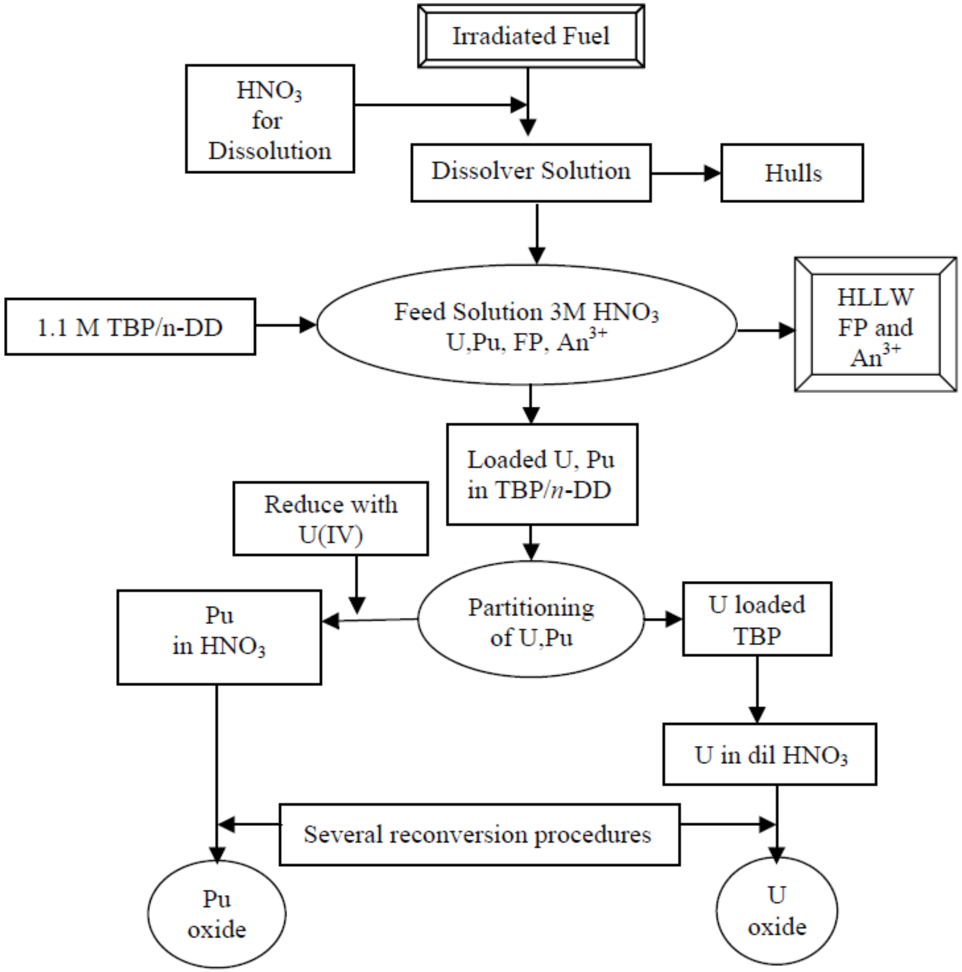




- 10^{18} possible combinations
- Route for task specific properties
  - Group actinide separation

Ionic liquids in separations

- **Ionic liquids can replace traditional solvents in the PUREX**
  - **Studies showed favorable extraction when ILs used in conjunction with extractants**
  - **Chem. Commun. 1765 (1998)**
- **Possible recovery of metals through electrodeposition**
  - **direct from the organic phase following solvent extraction**



From J. Nucl. Radiochem. Sci., 10(1), 1-6 (2009)

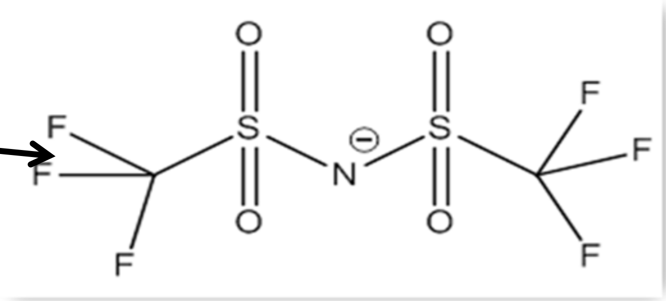
f-element reduction in ionic liquids

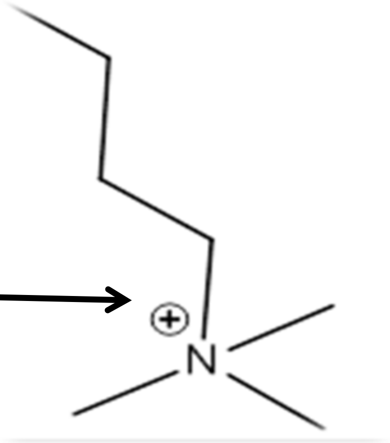
- Haloaluminates not stable to reduction of An(III) or Ln(III) to metal state
- Development of moisture-stable ILs
  - good cathodic stability
  - large ~6V electrochemical windows
- Application based upon the molten salt system (450 - 800°C)
  - Ionic liquids eliminate
    - Specialized corrosion resistant cell
    - Operation at elevated temperatures
    - Production of caustic side reactions
- Electrochemistry of Sm^{3+}, La^{3+}, Eu^{3+} and Th^{4+} in $[Me_3NBu][TFSI]$
  - Reported reduction of Sm, La, and Eu to the metallic state
  - Th was reported to reduce to Th^0 but subsequently was converted to ThO_2 by moisture in ionic liquid
    - Dalton Trans, 24, 4532-4534 (2002)

- Role of water central, useful in dissolution by problematic in full reduction

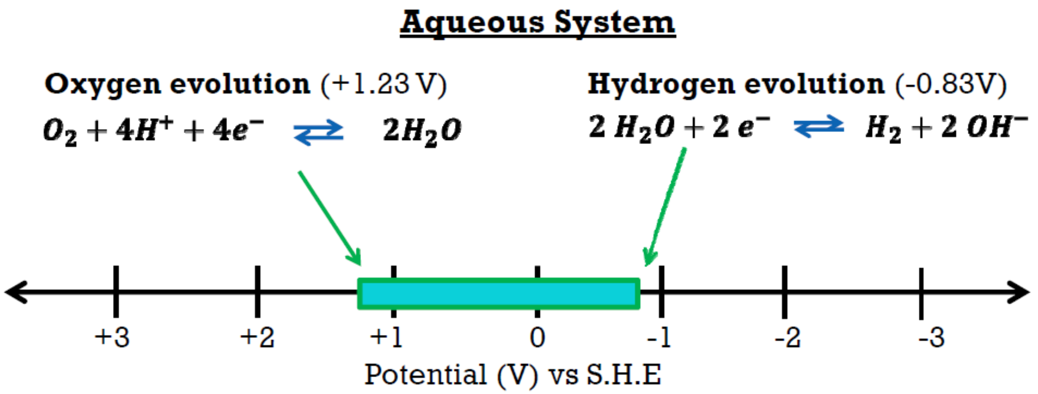
Choice of Ionic Liquid

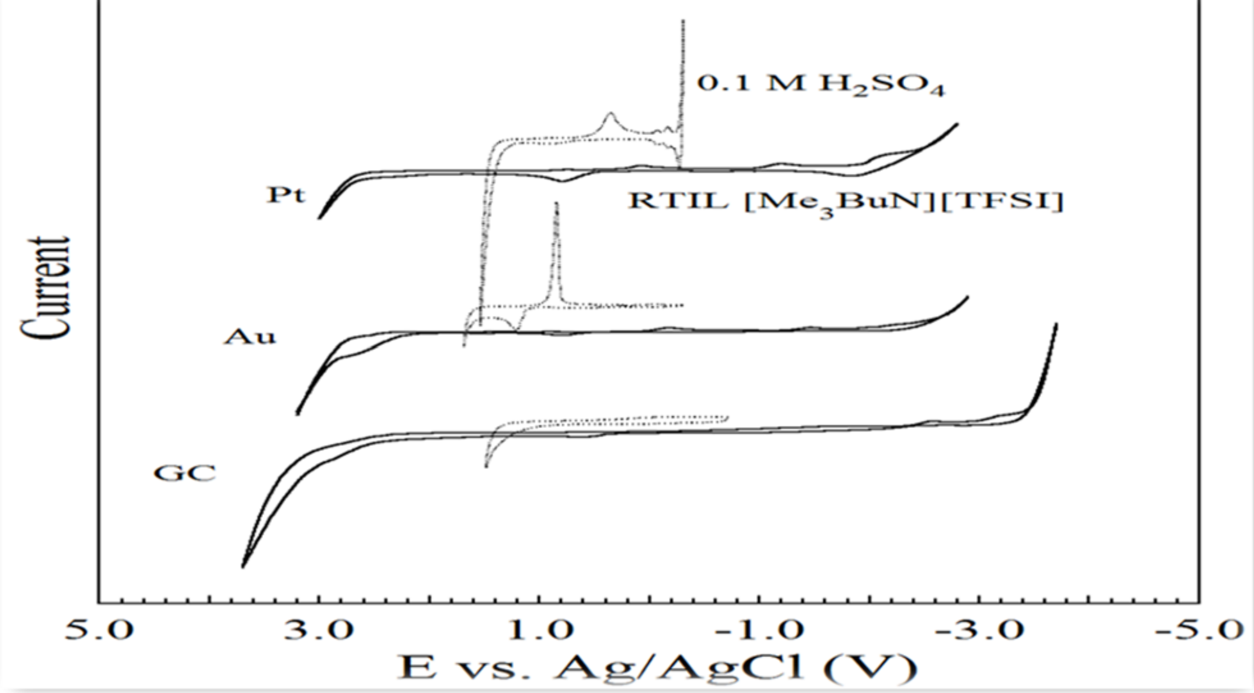
- A number of ionic liquids initially investigated
- bis(trifluoromethanesulfonyl)imide (TFSI) anion selected for study at UNLV
  - Functionalized TFSI evaluated
    - propyl and imidazolium
  - large potential window with Au, Pt, and Glassy carbon electrodes
    - Suitable for reduction of lanthanides and actinides
- Ionic liquid
  - N-trimethyl-N-butylammonium bis(trifluoromethanesulfonyl)imide
    - Used with actinides
  - Written as $[Me_3NBu][TFSI]$





Electrochemistry in ionic liquids



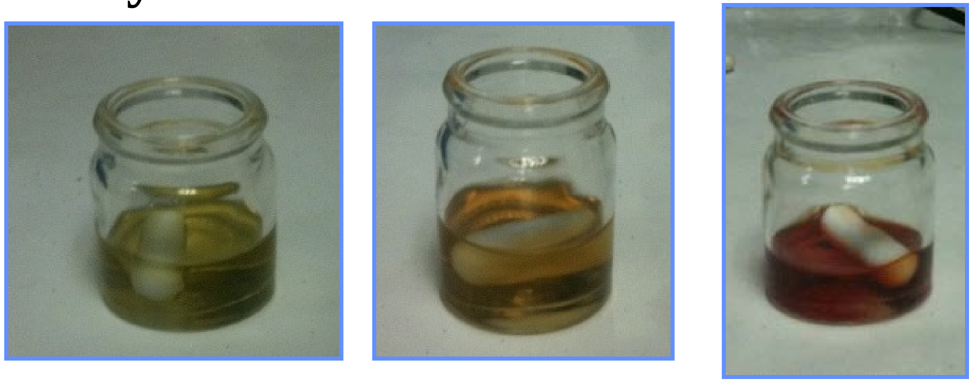


- **ILs have wider potential window**
  - **Actinide electrochemistry possible**
  - **Must limit water in the system**
- **TFSI is a poor ligand**
  - **Moves deposition to favorable potential**
- **Electrode can influence window**
  - **Glassy Carbon (GC) widest potential window**

U TFSI compound synthesis

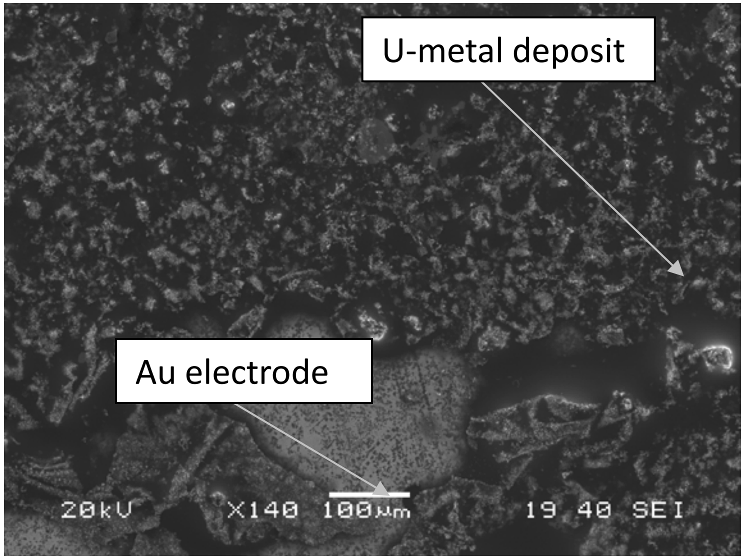
$$UI_3(THF)_4 + 3KTFSI \xrightarrow{THF} U(TFSI)_3 + 3KI_s$$

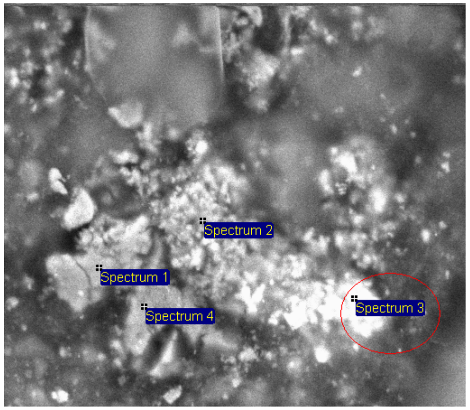
- **All reactions were performed in an argon filled glove box**
- **K(TFSI)(s) synthesized by adding H(TFSI) and KH THF solution**
  - **K(TFSI) separated by decanting excess THF**
    - **→ 90% yield**
- **K(TFSI) and $UI_3(THF)_4$ dissolved in THF**
  - **Excess of K(TFSI) added to ensure reaction completion**
  - **Clear pale yellow solution was stirred for 24 hours**
  - **Final orange red solution**
    - **→ Contained off white KI solid precipitate**
    - **→ THF solution contained product $U(TFSI)_3$**
    - **→ Solid was isolated by evaporating excess THF**
      - *** 74% yield**

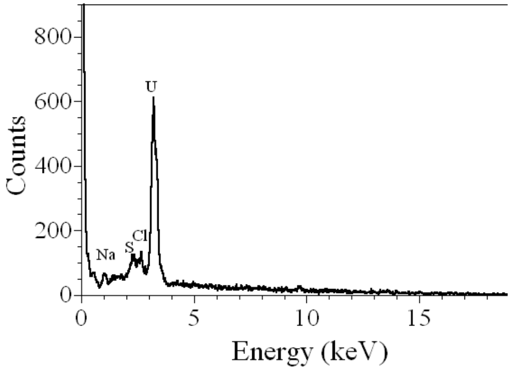


Formation of Uranium Deposits

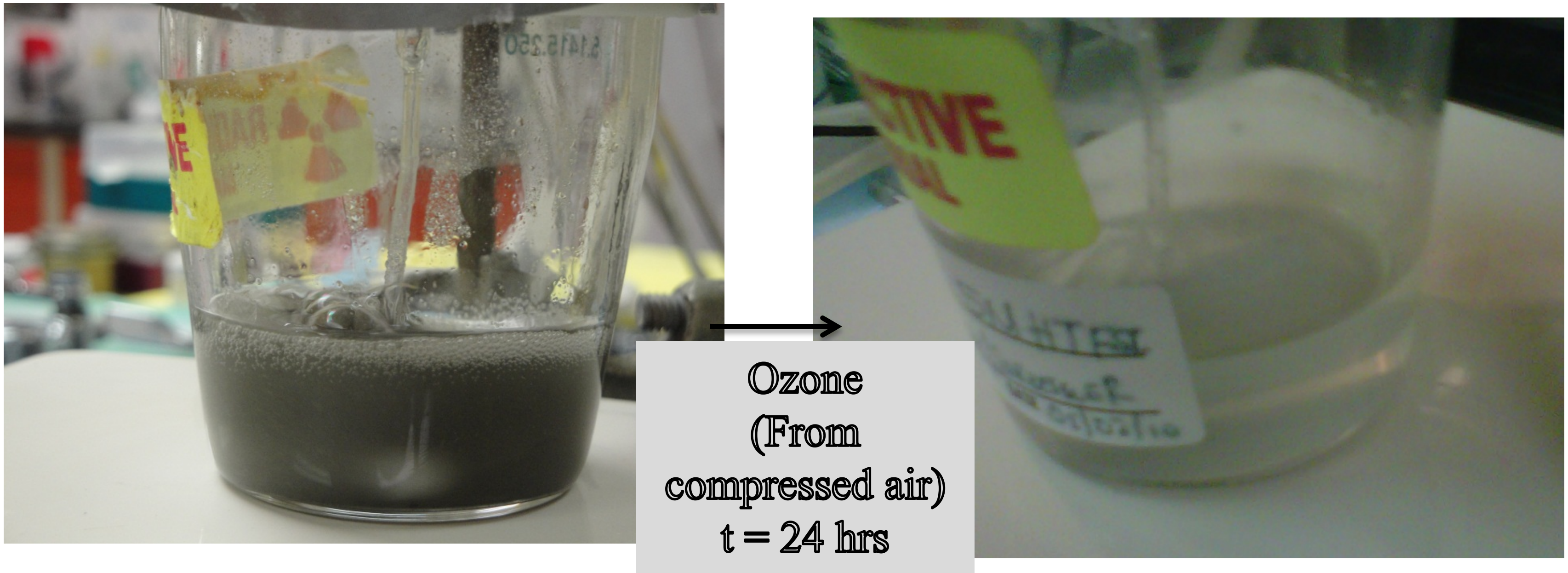
- **Constant potential of -1.5 V versus NHE**
- **SEM, EDS, and XRD analysis performed**
- **SEM of U deposited on Au foil**
- **XRD evaluation of sample**
    - **Alpha U metal**
- **SEM EDS**
    - **No oxygen at 5.5 keV**







Direct dissolution of U_3O_8 into ionic liquid



Ozone
(From
compressed air)
t = 24 hrs

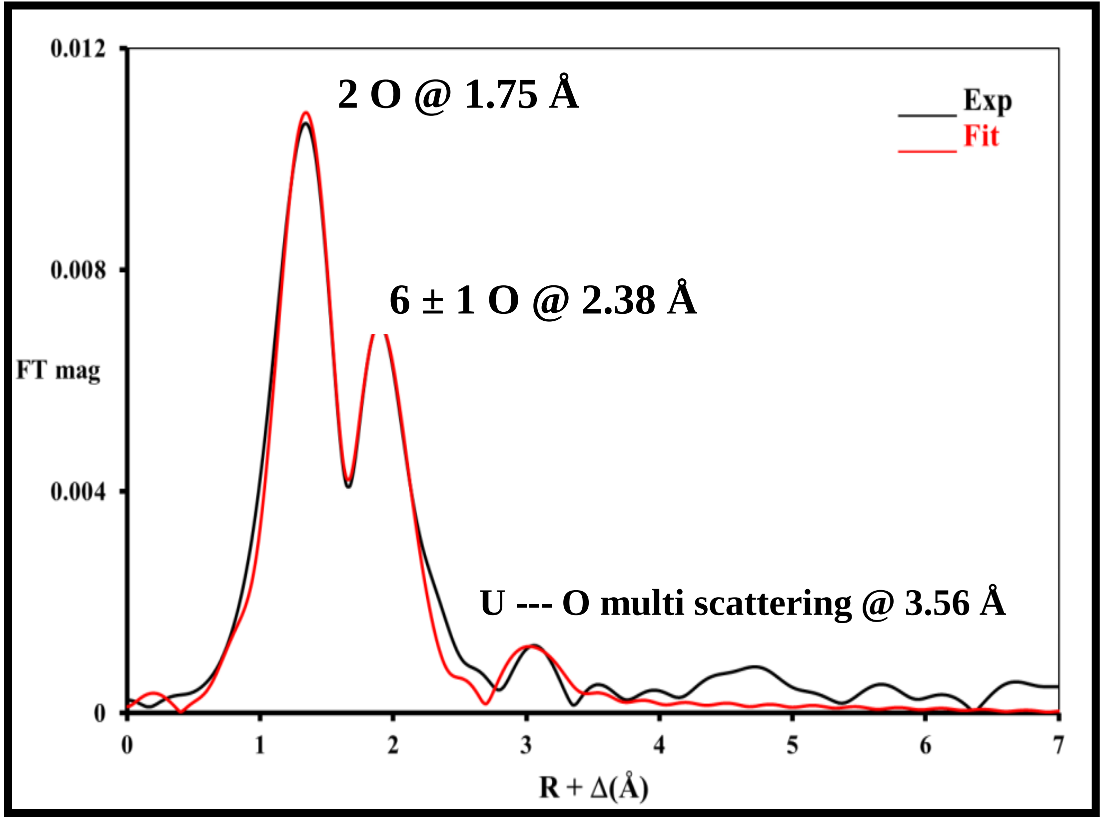
- **Original dissolution conditions:**
- **45 mg U_3O_8 with 3.27 M HTFSI in $Me_3NBuTFSI$ Stirred for <u>weeks</u> with no change**

- **RESULT: dissolution of material**
- **oxidizing gas used**
  - **O_3, NO_2**
- **Addition of HTFSI**
  - **Promote formation of uranium-TFSI complex**

Direct dissolution of U_3O_8 into RTIL

Proposed dissolution mechanism:

$$U_3O_8 + 6\ HTFSI + O_3 \rightleftharpoons 3\ UO_2^{2+} + 6\ TFSI^- + 3\ H_2O + O_2$$

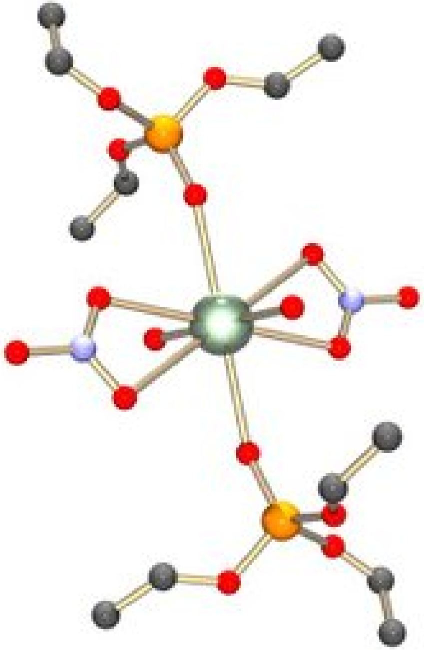


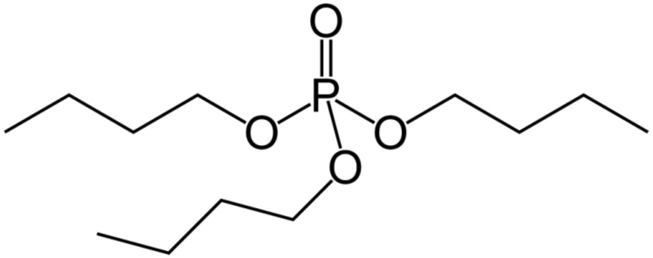
- Supporting EXAFS data of the original dissolution solution
- confirmed presence of UO_2^{2+}
- coordinated with five to six equatorial oxygens.

RDCH 702: Lecture 9 Separations Part 3

- Separation methods
  - Solvent extraction
    - → PUREX
  - Ion exchange
  - Volatility
  - Electrochemistry
- Specific actinide separations

- Basic concept of separations
  - Oxidation state
  - Ionic radius
- Development of advanced separations
  - Trivalent actinides
- Necessary for fuel cycle due to formation of mixtures due to fission
  - Actinides
    - → Transuranics
  - Fission products
    - → Se (Z=34) to Dy (Z=66)



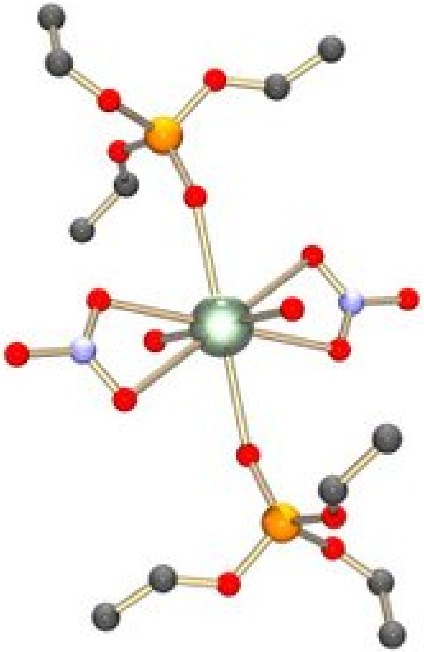


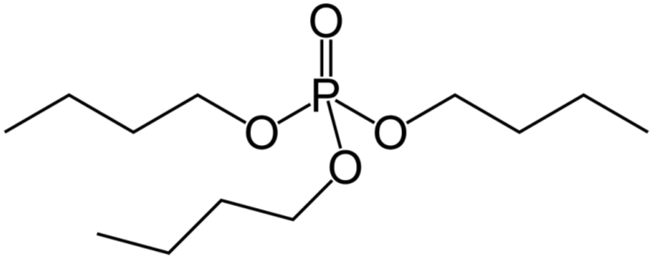
Tributyl phosphate (TBP)

RDCH 702: Lecture 9 Separations Part 4

- **Separation methods**
  - **Solvent extraction**
    - → **PUREX**
  - **Ion exchange**
  - **Volatility**
  - **Electrochemistry**
- **Specific actinide separations**

- **Basic concept of separations**
  - **Oxidation state**
  - **Ionic radius**
- **Development of advanced separations**
  - **Trivalent actinides**
- **Necessary for fuel cycle due to formation of mixtures due to fission**
  - **Actinides**
    - → **Transuranics**
  - **Fission products**
    - → **Se (Z=34) to Dy (Z=66)**





Tributyl phosphate (TBP)

Pu separations

- **1855 MT Pu produced**
  - **Current rate of 70-75 MT/years**
  - **225 MT for fuel cycle**
  - **260 MT for weapons**
- **Large scale separations based on manipulation of Pu oxidation state**
  - **Aqueous (PUREX)**
  - **Non-aqueous (Pyroprocessing)**
- **Precipitation methods**
  - **Basis of bismuth phosphate separation**
    - → **Precipitation of $BiPO_4$ in acid carries tri- and tetravalent actinides**
      - * **Bismuth nitrate and phosphoric acid**
      - * **Separation of solid, then oxidation to Pu(VI)**
    - → **Sulfuric acid forms solution U sulfate, preventing precipitation**
  - **Used after initial purification methods**
  - **LaF_3 for precipitation of trivalent and tetravalent actinides**

Pu separations

- Solvent extraction
  - TBP extraction, PUREX process
    - → Some interest in 3rd phase formation
- Extraction chromatography
  - Extractant on solid support
- Ion-exchange
  - Both cation and anion exchange
    - → Anion exchange based on formation of appropriate species in acidic solution
    - → Change of solution impact sorption to column
- Pu separation
  - Sorb Pu(IV,VI) in 6 M acid, reduce to Pu(III)
- General cation exchange trends for Pu
  - HNO_3, H_2SO_4, and $HClO_4$ show stronger influence than HCl
  - Strong increase in distribution coefficient in $HClO_4$ at high acidities exhibited for Pu(III) and Pu(VI)
- Anion exchanges in high acid, formation of charged species

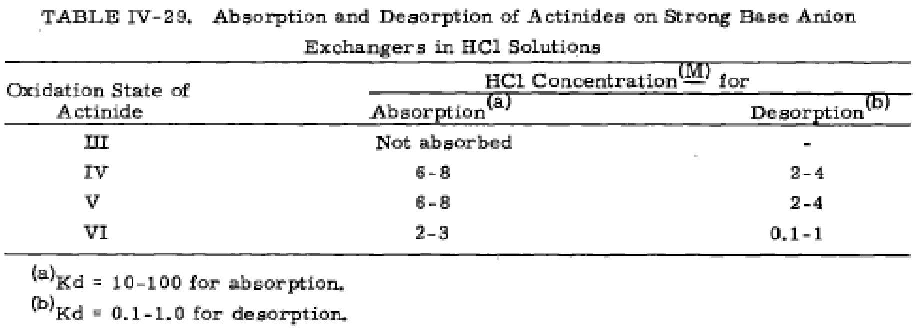


TABLE IV-29. Absorption and Desorption of Actinides on Strong Base Anion Exchangers in HCl Solutions

Oxidation State of Actinide	HCl Concentration (M) for	
	Absorption[a]	Desorption[b]
III	Not absorbed	-
IV	6-8	2-4
V	6-8	2-4
VI	2-3	0.1-1

[a] Kd = 10-100 for absorption.

[b] Kd = 0.1-1.0 for desorption.

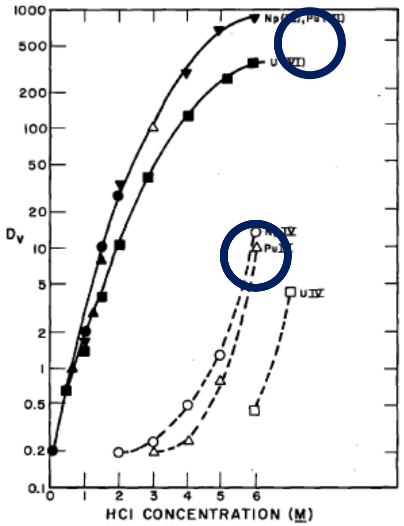


Fig. 52. Volume distribution coefficients, Dv, for tetra and hexavalent U, Np, and Pu between Dowex 1 and hydrochloric acid solutions.[266]

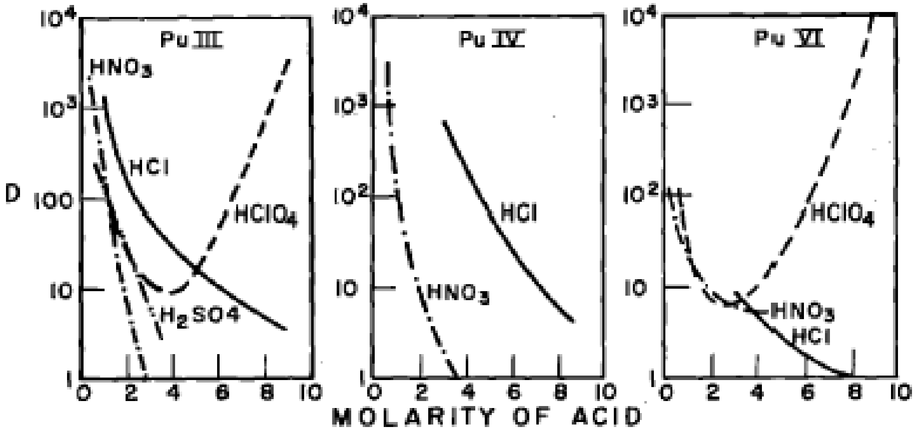


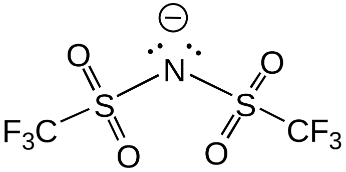
Fig. 39. Typical distribution coefficients of Pu on Dowex 50 in common acidic solutions.

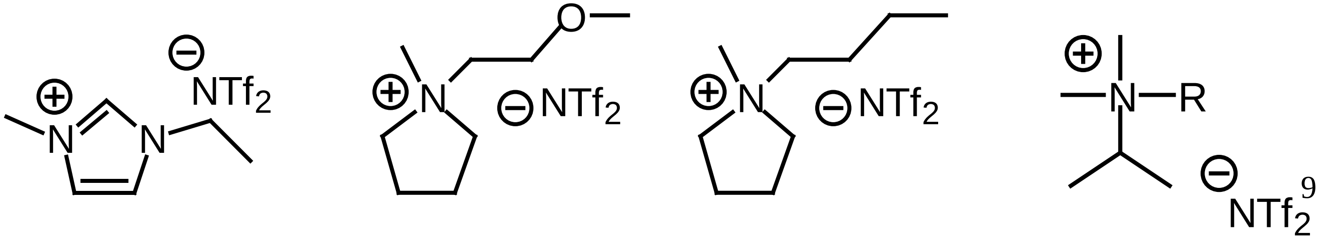
Pu separations

- **Halide volatility (PuF_6, $PuCl_6$)**
  - **PuO_2 in fluidized bed reactor with fluorine at 400° C**
    - **→ Can substitute NH_4HF_2 for some fluorination**
    - **→ Also use of O_2F_2**
  - **PuF_6 decomposes to PuF_4 and F_2 in a thermal decomposition column**
- **Supercritical fluid extraction**
  - **Most research with CO_2**
  - **Use complexants dissolved in SCF**
    - **→ $TBP \cdot HNO_3$, TTA for extraction from soil**
  - **Change of pressure to achieve separations**

Pu separations

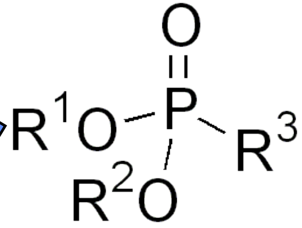
- Alkaline solutions
  - Need strong ligands that can compete with hydroxide to form different species
    - → F^-, CO_3^{2-}, H_2O_2
      - * High solubility, based on oxidation state
      - * Stabilize Pu(VII)
- Room temperature ionic liquids
  - Quaternary ammonium with anions
    - → $AlCl_4^-$, PF_6^-
  - Liquid-liquid extraction
  - Electrochemical disposition



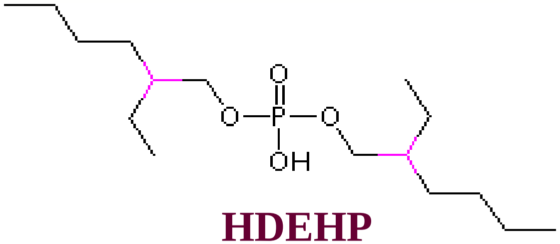


Am solvent extraction

- Tributylphosphate (TBP)
  - Am extracted from neutral or low acid solutions with high nitrate
  - Am(VI)
    - → Oxidation with $(NH_4)_{10}P_2W_{17}O_{61}$ to stabilize Am(VI)
    - → 100 % TBP from 1 M HNO_3
      - * Separation factor 50 from Nd
  - Am separation from lanthanides
    - → 1 M ammonium thiocyanate aqueous phase
- Dibutyl butylphosphonate (DBBP)
  - Phosphonate functional group
  - Similar to TBP, stronger extractant of Am
- Trialkylphophine oxide (TRPO)
  - Increase in basicity of P=O functional group from TBP to DPPB to TRPO
  - Am and Cm extraction from 1-2 M HNO_3
  - 30 % TRPO in kerosene
    - → Am, Cm, tetravalent Np and Pu, hexavalent U extracted
      - * Actinides stripped with 5.5 M HNO_3 (Am fraction)
    - → TRPO with C_6-C_8 alkyl group

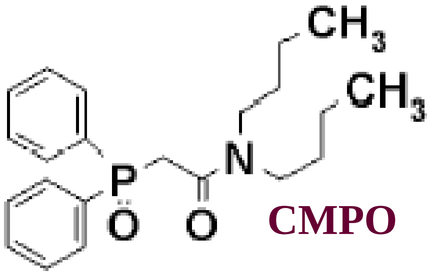


Am solvent extraction



HDEHP

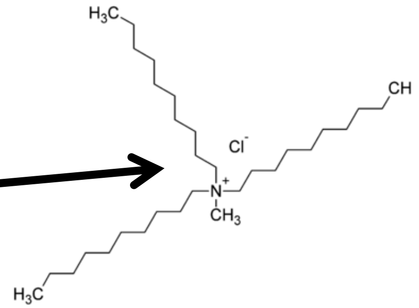
- **Bis(2-ethylhexyl)phosphoric acid (HDEHP)**
  - **Has been used to Am separation**
  - **Part of TALSPEAK**
    - → **Extracts lanthanides stronger that actinides**
    - → **TALSPEAK components**
      - * **Bis(2-ethyl-hexyl)phosphoric acid (HDEHP)**
      - * **HNO_3**
      - * **DTPA**
      - * **Lactic acid**
- **Carbamoylphosphine oxide (CMPO)**
  - **Synthesized by Horwitz**
    - → **Based on DHDECMP extractions**
      - * **Recognized functional group, simplified ligand synthesis**
      - * **Purified by cation exchange**
  - **Part of TRUEX**
    - → **TRUEX (fission products)**
      - * **0.01 to 7 M HNO_3**
      - * **1.4 M TBP**
      - * **0.2 M Diphenyl-N,N-dibutylcarbamoyl phosphine oxide (CMPO)**
      - * **0.5 M Oxalic acid**
      - * **1.5 M Lactic acid**
      - * **0.05 M DTPA**

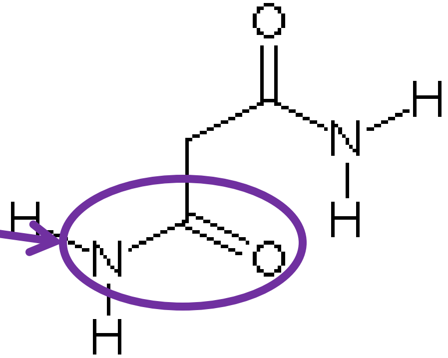


CMPO

Am solvent extraction

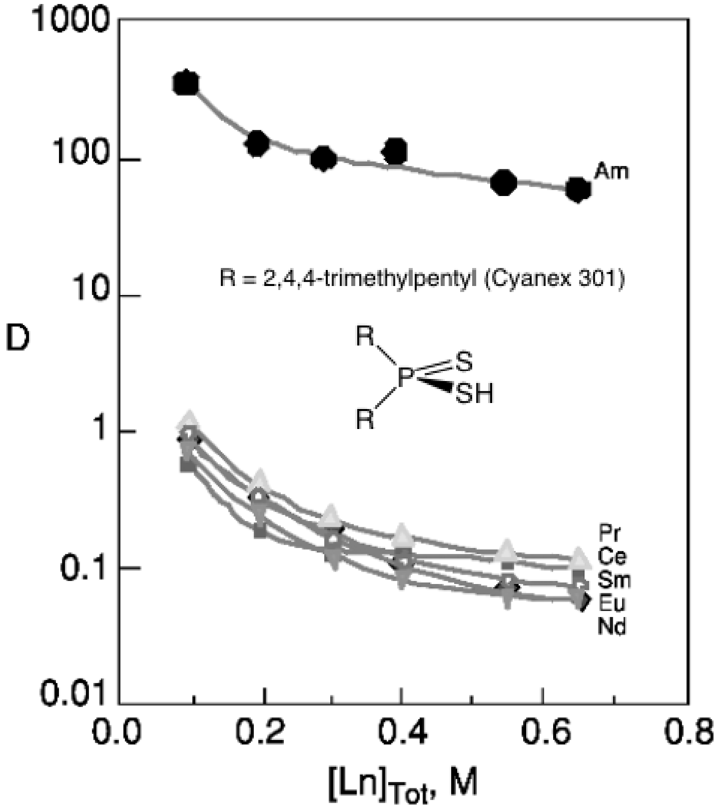
- Tertiary amine salt
  - Low acid, high nitrate or chloride solution
    - → $(R_3NH)_2Am(NO_3)_5$
- Quaternary ammonium salts (Aliquat 336)
  - Low acid, high salt solutions
    - → Extraction sequence of Cm<Cf<Am<Es
  - Studies at ANL for process separation of Am
- Amide extractants
  - $(R_1,R_2)N\text{-}C(O)\text{-}CR_3H\text{-}C(O)\text{-}N(R_1R_2)$
    - → Diamide extractant
    - → Basis of DIAMEX process
  - N,N'-dimethyl-N,N'-dibutyl-2-tetradecyl-malonamide (DMDBTDMA)
    - → DIAMEX with ligand in dodecane with 3-4 M HNO_3
      - * Selective extraction over Nd





Am/Ln solvent extraction

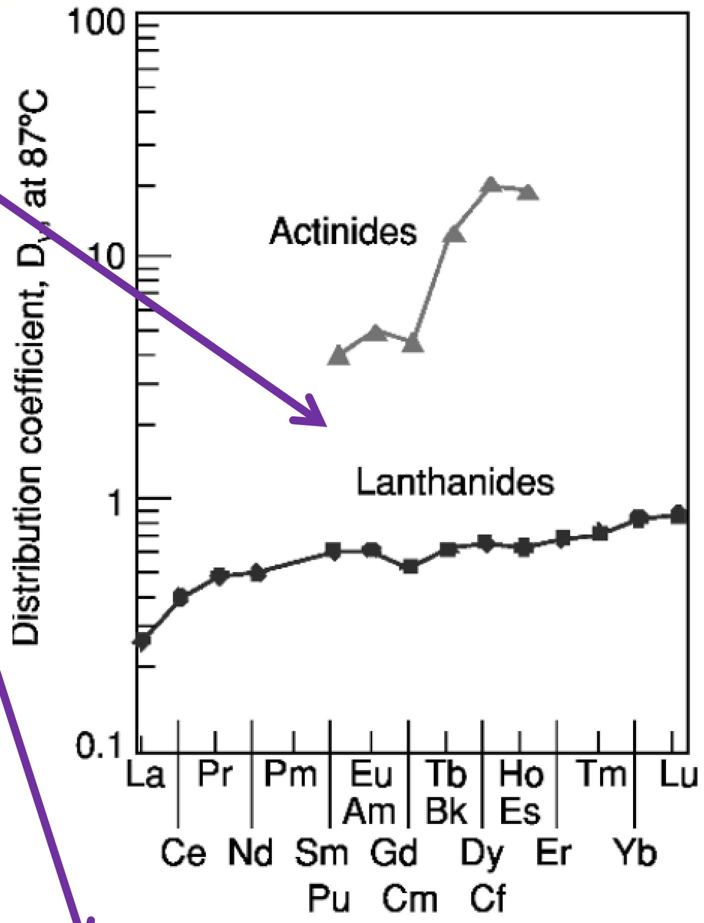
- Extraction reaction
  - $Am^{3+}+2(HA)_2 \rightarrow AmA_3HA+3H^+$
    - → Release of protons upon complexation requires pH adjustment to achieve extraction
      - * Maintain pH greater than 3
- Cyanex 301 stable in acid
  - HCl, H_2SO_4, HNO_3
    - → Below 2 M
- Irradiation produces acids and phosphorus compounds
  - Problematic extractions when dosed 10^4 to 10^5 gray
- New dithiophosphinic acid less sensitive to acid concentration
  - R_2PSSH; R=C_6H_5, ClC_6H_4, FC_6H_4, $CH_3C_6H_4$
    - → Only synergistic extractions with, TBP, TOPO, or tributylphosphine oxide
    - → Aqueous phase 0.1-1 M HNO_3
    - → Increased radiation resistance



Distribution ratios of Am(III) and Ln(III) in 1.0 M Cyanex 301-heptane (16 mol% of Cyanex 301 neutralized before extraction contacts)

Ion exchange separation Am from Cm

- LiCl with ion exchange achieves separation from lanthanide
- Separation of tracer level Am and Cm has been performed with displacement complexing chromatography
    - DTPA and nitrilotriacetic acid in presence of Cd and Zn as competing cations
    - displacement complexing chromatography method is not suitable for large scale
- Ion exchange has been used to separate trace levels of Cm from Am
    - Am, Cm, and lanthanides sorbed to a cation exchange resin at pH 2
        - Separation of Cm from Am was performed with 0.01 % ethylenediamine-tetramethylphosphonic acid at pH 3.4 in 0.1 M $NaNO_3$
        - separation factor of 1.4
- Separation of gram scale quantities of Am and Cm by cation and anion exchange
    - use of α-hydroxylisobutyrate or diethylenetriaminepentaacetic acid as an eluting agent or a variation of eluant composition by addition of methanol to nitric acid
        - best separations were achieved under high pressure conditions
            - separation factors greater than 400



Distribution coefficients of actinides and lanthanides into Dowex 1 8 resin from 10 M LiCl

Extraction chromatography

- Mobile liquid phase and stationary liquid phase
  - Apply results from solvent extraction
    - → HDEHP, Aliquat 336, CMPO
      - * Basis for Eichrom resins
      - * Limited use for solutions with fluoride, oxalate, or phosphate
    - → DIPEX resin (Eichrom)
      - * Bis-2-ethylhexylmethanediphosphonic acid on inert support
      - * Lipophilic molecule
        - ⁂ Extraction of 3+, 4+, and 6+ actinides
      - * Strongly binds metal ions
        - ⁂ Need to remove organics from support
  - Variation of support
    - → Silica for covalent bonding
    - → Functional organics on coated ferromagnetic particles
      - * Magnetic separation after sorption

Am separation and purification

- **Precipitation method**
  - **Formation of insoluble Am species**
    - **AmF_3, $K_8Am_2(SO_4)_7$, $Am_2(C_2O_4)_3$, $K_3AmO_2(CO_3)_2$**
      - **Am(V) carbonate useful for separation from Cm**
      - **Am from lanthanides by oxalate precipitation**
        - **Slow hydrolysis of dimethyloxalate**
        - **Oxalate precipitate enriched in Am**
        - **50 % lanthanide rejection, 4 % Am**
  - **Oxidation of Am(VI) by $K_2S_2O_8$ and precipitation of Cm(III)**
- **Pyrochemical process**
  - **Am from Pu**
    - **O_2 in molten salt, PuO_2 forms and precipitates**
    - **Partitioning of Am between liquid Bi or Al and molten salts**
      - **K_d of 2 for Al system**
    - **Separation of Am from PuF_4 in salt by addition of OF_2**
      - **Formation of PuF_6, volatility separation**

Cm separation and purification: Similar to Am

- Solvent extraction
  - Organic phosphates
    - → Function of ligand structure
      - * Mixed with 6 to 8 carbon chain better than TBP
  - HDEHP
    - → From HNO_3 and LiCl
  - CMPO
    - → Oxidation state based removal with different stripping agent
  - Extraction of Cm from carbonate and hydroxide solutions, need to keep metal ions in solution
    - → Organics with quaternary ammonium bases, primary amines, alkylpyrocatechols, β-diketones, phenols
- Ion exchange
  - Anion exchange with HCl, LiCl, and HNO_3
    - → Includes aqueous/alcohol mixtures
    - → Formation of $CmCl_4^-$ at 14 M LiCl
      - * From fluorescence spectroscopy
- Precipitation
  - Separation from higher valent Am
    - → 10 g/L solution in base
    - → Precipitation of $K_5AmO_2(CO_3)_3$ at 85 °C
    - → Precipitation of Cm with hydroxide, oxalate, or fluoride

Review

- **Understand the differences and techniques for**
  - **Solvent extraction**
  - **Ion exchange**
  - **Electrochemistry**
  - **Volatility**
- **Understand how oxidation state influences different separation methods**
- **Understand the different mechanisms in solvent extraction**
- **Compare and contrast specific actinide separation**
- **Describe the components of an ion exchange resin**
- **Provide a ion exchange and solvent extraction separation for Am from the other actinides.**
- **Provide the basic of electrochemical and IL separations.**
  - **What is the differences in these methods?**

Questions

- **Describe the concepts in solvent extraction?**
- **What is third phase formation in solvent extraction?**
    - **How can it be controlled?**
    - **What is third phase important to understand for actinide separations?**
    - **How can it be exploited in chemistry?**
- **Describe a volatility based separation for Pu.**

PDF Quiz

- **Respond to Lecture 9 PDF quiz**
- **Provide comment on blog**