



Complexation Chemistry and Precipitation/Crystallization Processes

Gordon Jarvinen

Acting Director, Glenn T. Seaborg Institute
Stockpile Manufacturing & Support Directorate
Los Alamos National Laboratory

Outline

- 1) Electronic structure (orbital energies and spatial extent) of early actinides gives chemical properties resembling transition metals, but later actinides more like lanthanides
- 2) Precipitation and crystallization - generate supersaturation, e.g., by reagent addition (K_{sp}), ΔT , redox; followed by nucleation, growth (agglomeration, aging)
- 3) Batch vs continuous precipitation/crystallization operations; solid-liquid separations: filtration, centrifugation
- 4) Co-precipitation or carrier precipitation - very important tool in analytical methods for radionuclides
- 5) Plutonium first isolated as weighable compound and first production performed by multiple stages of co-precipitation using LaF_3 and bismuth phosphate, respectively
- 6) Examples of Pu and U purification and product preparation using oxalate, peroxide, fluoride, hydroxide; Cs and Sr separations at

Hanford

The Periodic Table of Elements

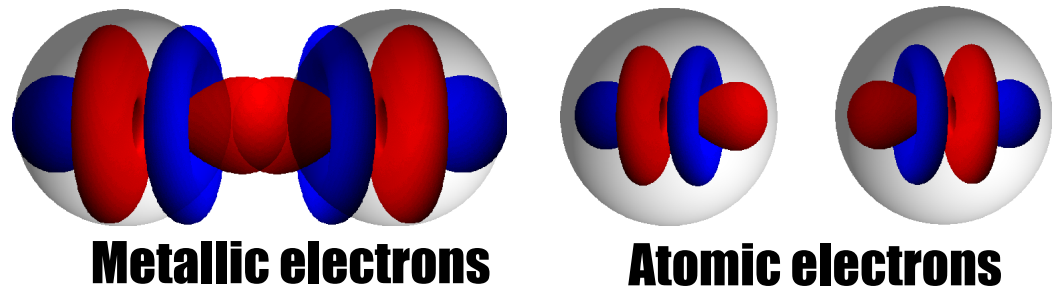
Systematic changes in chemical properties result from filling of s, p, d, and f orbitals:
lanthanides 4f, actinides 5f

| | | | | | | | | | | | | | | | | | |
|----------|----------|----------|-----------|-----------|-----------|-----------|-----------|-----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| 1 H | | | | | | | | | | | | | | | | | 2 He |
| 3 Li | 4 Be | | | | | | | | | | | 5 B | 6 C | 7 N | 8 O | 9 F | 10 Ne |
| 11 Na | 12 Mg | | | | | | | | | | | 13 Al | 14 Si | 15 P | 16 S | 17 Cl | 18 Ar |
| 19 K | 20 Ca | 21 Sc | 22 Ti | 23 V | 24 Cr | 25 Mn | 26 Fe | 27 Co | 28 Ni | 29 Cu | 30 Zn | 31 Ga | 32 Ge | 33 As | 34 Se | 35 Br | 36 Kr |
| 37 Rb | 38 Sr | 39 Y | 40 Zr | 41 Nb | 42 Mo | 43 Tc | 44 Ru | 45 Rh | 46 Pd | 47 Ag | 48 Cd | 49 In | 50 Sn | 51 Sb | 52 Te | 53 I | 54 Xe |
| 55 Cs | 56 Ba | 57 La | 72 Hf | 73 Ta | 74 W | 75 Re | 76 Os | 77 Ir | 78 Pt | 79 Au | 80 Hg | 81 Tl | 82 Pb | 83 Bi | 84 Po | 85 At | 86 Rn |
| 87 Fr | 88 Ra | 89 Ac | 104 Rf | 105 Db | 106 Sg | 107 Bh | 108 Hs | 109 Mt | 110 | 111 | 112 | | 114 | | 116 | | 118 |

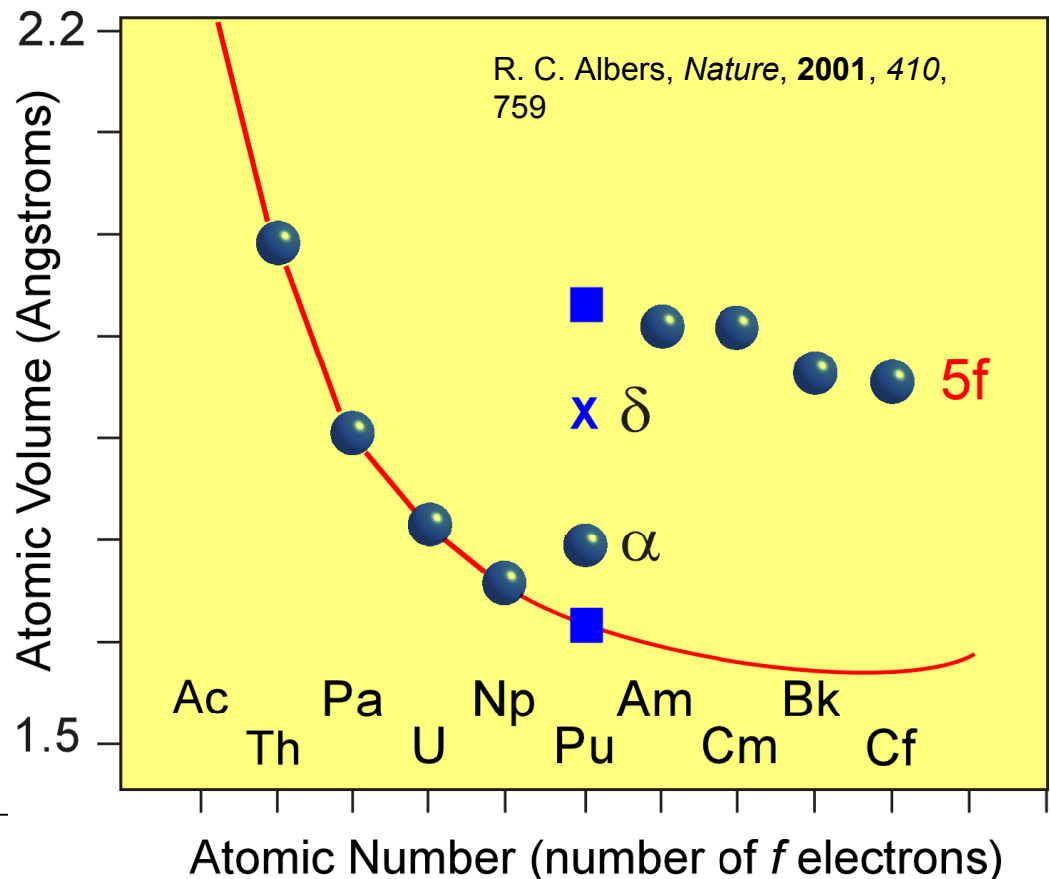
| | | | | | | | | | | | | | | |
|-------------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|-----------|-----------|-----------|-----------|
| Lanthanide series | 58 Ce | 59 Pr | 60 Nd | 61 Pm | 62 Sm | 63 Eu | 64 Gd | 65 Tb | 66 Dy | 67 Ho | 68 Er | 69 Tm | 70 Yb | 71 Lu |
| Actinide series | 90 Th | 91 Pa | 92 U | 93 Np | 94 Pu | 95 Am | 96 Cm | 97 Bk | 98 Cf | 99 Es | 100 Fm | 101 Md | 102 No | 103 Lr |

Actinide 5f electrons - itinerant versus localized

- Outer 7s and 6d electrons overlap strongly & have metallic behavior
- Light actinides have metallic-like 5f electrons
- Heavy actinides have atomic-like 5f electrons
- The transition from delocalized to localized 5f electrons takes place at Pu for the metals
- Pu appears to undergo an intermediate transition that is only partly localized!



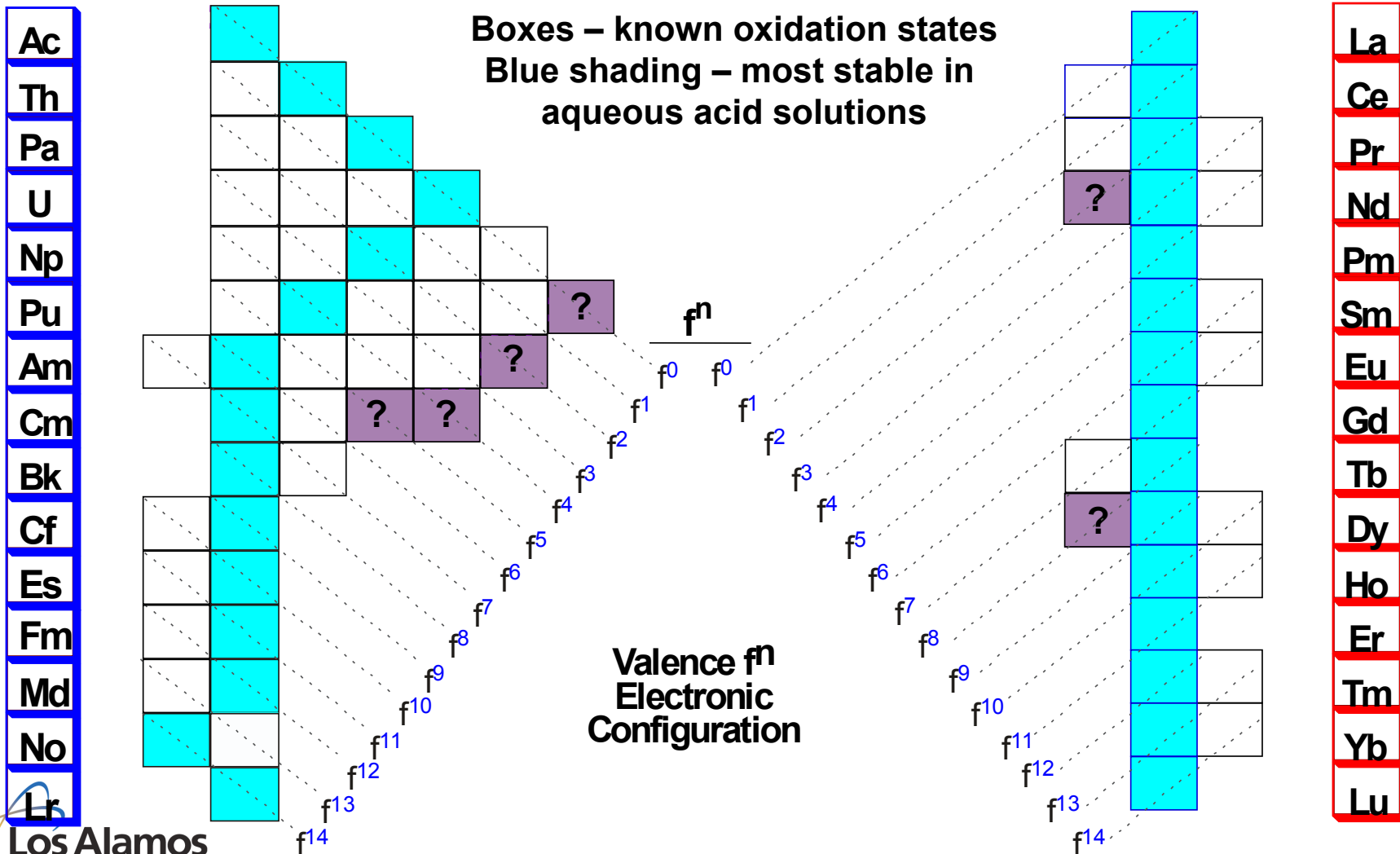
Savrasov, Kotliar, Abrahams, *Nature*, **2001**, 410, 759
 Wills, Eriksson, **2000**, *Los Alamos Science*, 26, 128



Oxidation States & Valence Electronic Configurations

| | | | | | | | | |
|---|---|----|-----|----|---|----|-----|------|
| 0 | I | II | III | IV | V | VI | VII | VIII |
|---|---|----|-----|----|---|----|-----|------|

| | | | | | | | | |
|------|-----|----|---|----|-----|----|---|---|
| VIII | VII | VI | V | IV | III | II | I | 0 |
|------|-----|----|---|----|-----|----|---|---|



Oxidation State Characteristics of the Actinides

- In acidic solution, there are four types of cations, linear O=An=O cations found in aqueous solution for V and VI oxidation states:



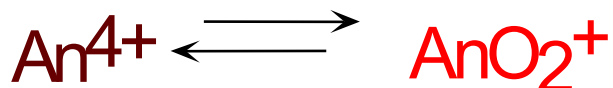
- Metal ion affinity to form complexes with “hard” donor ligands:



- Redox reactions are rapid & reversible when there is no making/breaking of An=O bonds



- Redox reactions are slow & irreversible when making/breaking An=O bonds



Chemical Bonding in f-element Compounds

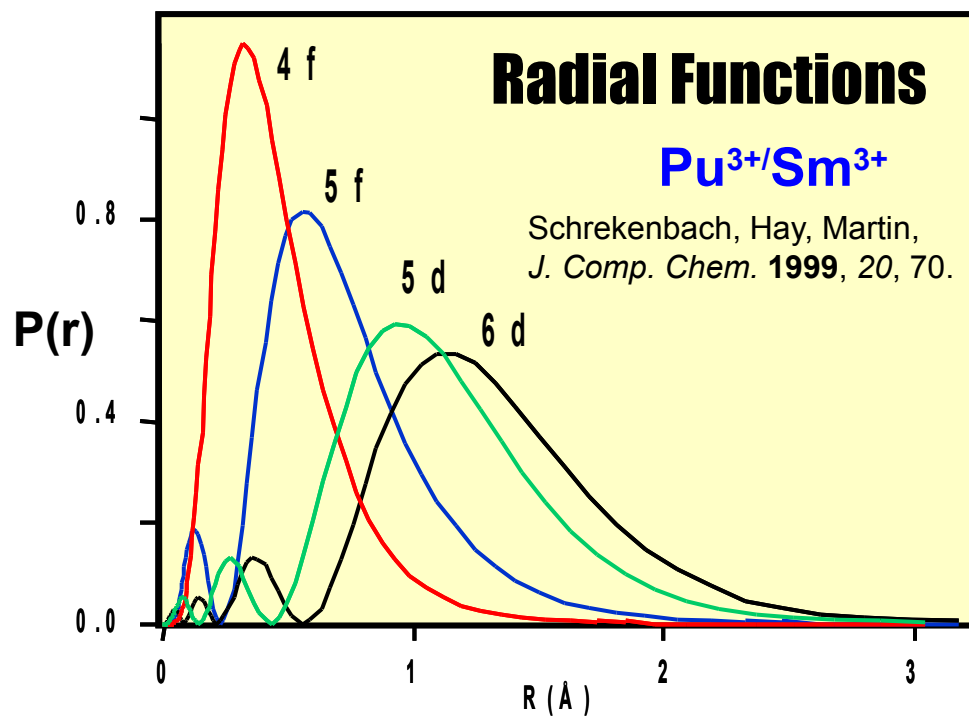
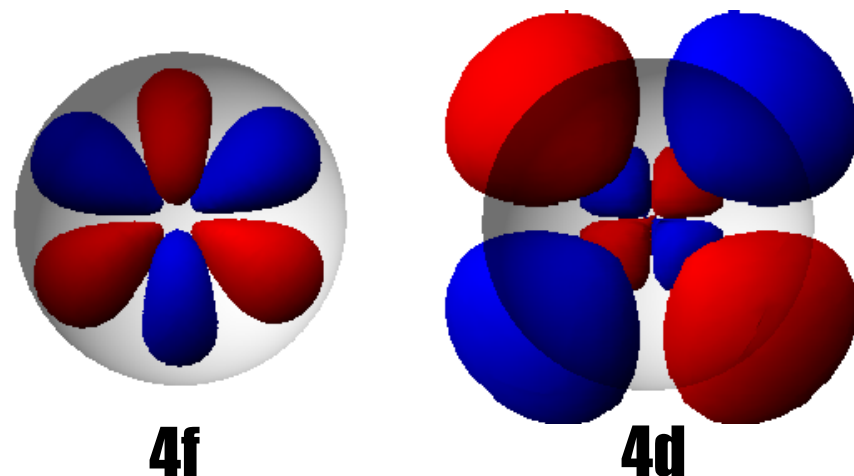
- Bonding in 4f elements often regarded as ionic or “hard” Lewis acids
- Core-like nature of f orbitals limits overlap to form bonds
- Extent of involvement of 5f electrons of actinides in bonding has been widely debated since 1950s
- Examination of covalency in 5f complexes has indicated involvement of s, p, d, and f orbitals, UO_2^{2+} contains U-O triple bonds
- Trivalent actinides can be separated from Ln(III) using ligands with “soft” donor sites, e.g. N or S vs O or F, suggesting stronger covalency in the actinides

G. Seaborg, *J. Am. Chem. Soc.* **1954**, 76, 1461

H. Taube, *J. Chem. Phys.* **1962**, 76, 1461

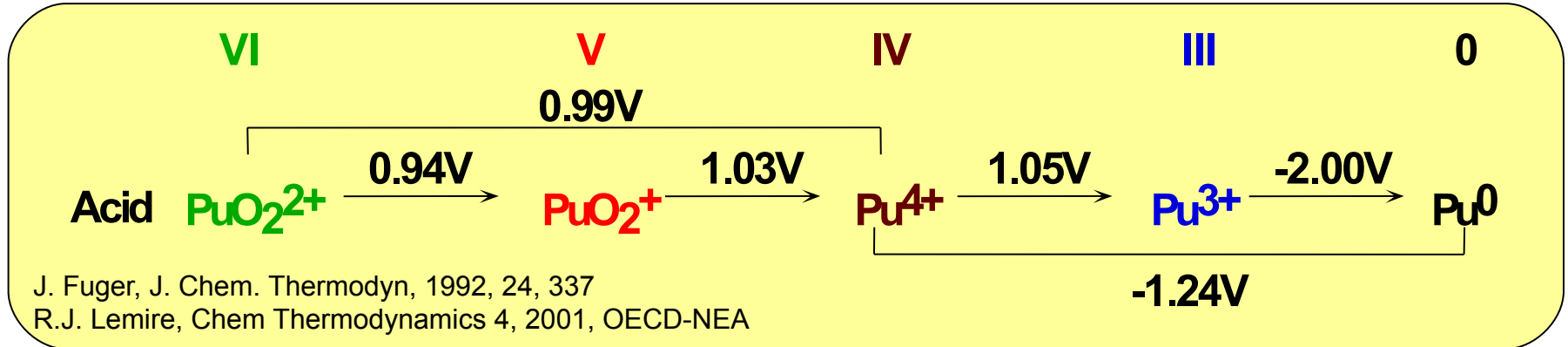
R. Hoffman, *Inorg. Chem.* **1980**, 19, 2656

R. Denning, *Struct. Bonding*, **1992**, 79, 215



Oxidation-reduction properties of plutonium

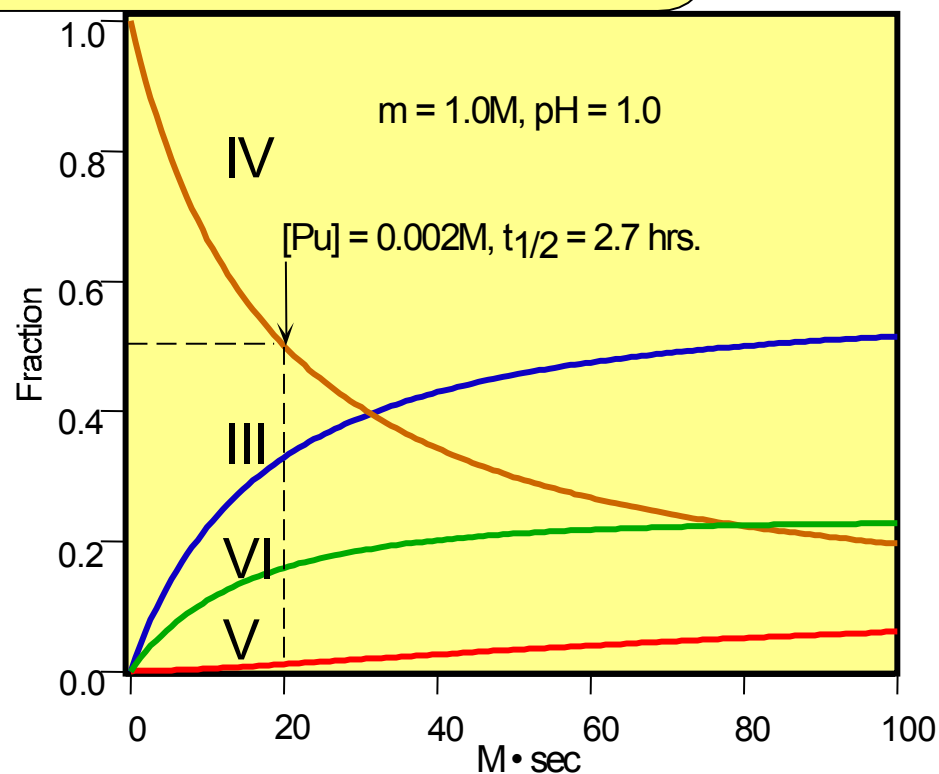
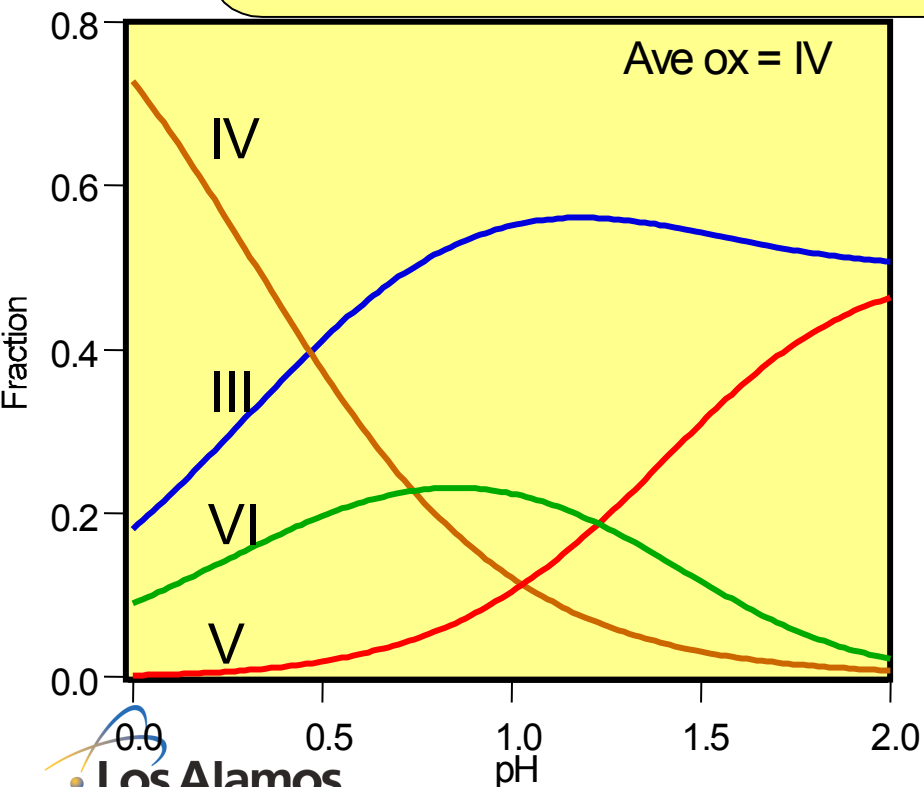
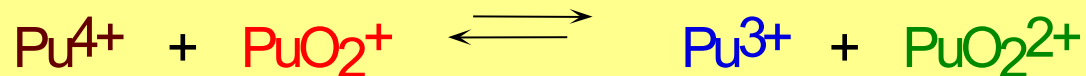
Among the most intricate in the periodic table



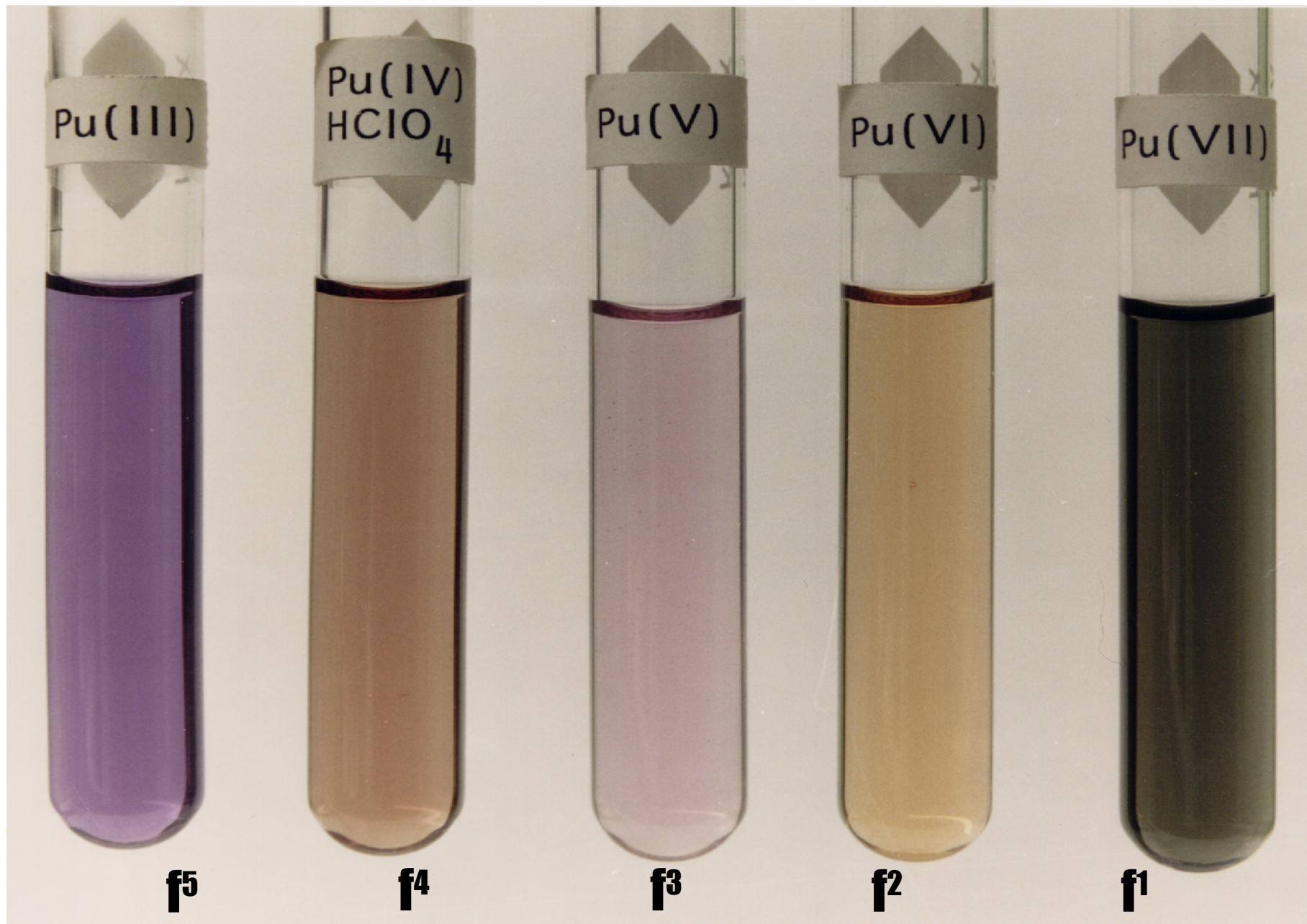
- Redox potentials that couple the four common oxidation states in acid solution are all remarkably similar, ca. 1.0 Volt
- Appreciable concentrations of 3 or 4 oxidation states can exist together at equilibrium
- The equilibria depend on H^+ concentration, and are quite complicated
- Complexation can stabilize a given oxidation state against redox

- e.g., Pu(IV) is very stable in HCl (Cl^- complexation)

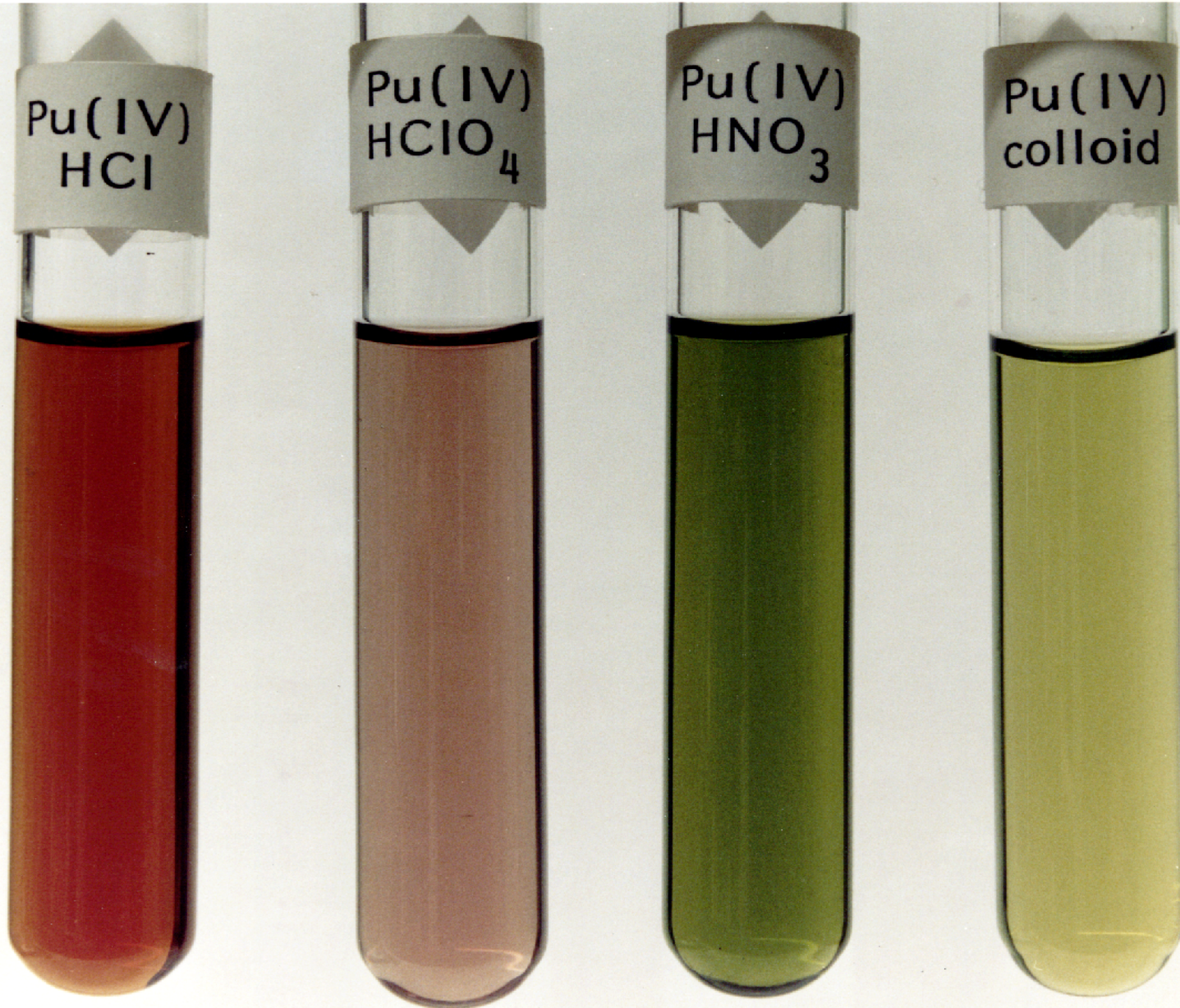
Redox Stability and Equilibrium Concentrations



Oxidation States of Plutonium in Aqueous Solutions



Ligand Effects on Spectra of Pu Oxidation States



Precipitation/Crystallization Processes

- Precipitation and crystallization refer to processes that generate a solid from a supersaturated solution
- Generate supersaturation in solution through a variety of mechanisms - solvent removal by evaporation or dialysis, addition of another solvent, T or P changes, addition of reagent to form solid phase, change pH, or redox state
- Solid-liquid separation step - filtration, centrifugation, etc.
- Great variety of equipment for precipitation and crystallization and subsequent solid-liquid separation
- Vast array of industrial processes use precipitation and crystallization operations from pharmaceuticals, to electronics (silicon), to nuclear materials
- Precipitation/crystallization process design often more than separation step - engineered to reduce cost of the final product, e.g. $(\text{NH}_4)_4\text{UO}_2(\text{CO}_3)_3$ crystal size for UO_2 fuel pellets

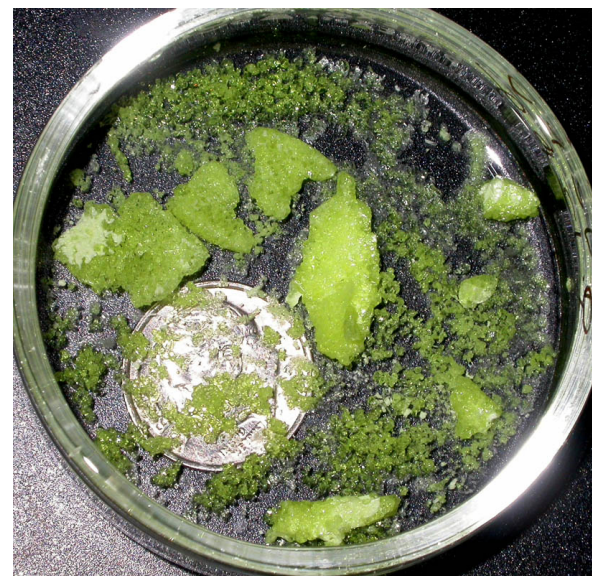
Precipitation and Crystallization

- Precipitation often just fast crystallization, but precipitation tends to give more irreversible product
- Many ways to generate supersaturation, solid in upper photo oxalate addition to Pu(III) solution; lower photo cooling of uranyl nitrate solution
- $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ low supersaturation and slow crystal growth - too slow! inclusions of mother liquor carry impurities into product, nucleation and growth occurred on vessel walls



Precipitation and Crystallization

- $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ crystals grown at two different temperatures in unstirred vessels
- Smaller crystals that can be more effectively washed result at lower T (upper photo)
- Weimarn's "laws" of precipitation, higher initial supersaturation tends to give smaller average particle size
- Nucleation and growth on vessel walls tends to encourage aggregation into clusters
- Agitation of solutions tends to give smaller and more uniform crystals



Batch and Continuous Processes

- For actinide operations where criticality is possible, batch operations can have the advantage of allowing clean out and inspection between batches to avoid build-up of fissile solids; usually makes materials accountability easier
- Many types of equipment for batch and continuous precipitation-crystallization, some actinide examples:

Continuous rotating stainless steel filter wheel used in French design for Pu(IV) oxalate precipitation, rapid mixing of solutions, precipitate recovered on vacuum filter wheel, washed, partly dried, scrapped off into boat for calcining

JAEA investigating recovery of uranyl nitrate from used commercial nuclear fuel dissolved in nitric acid using external cooling of cylindrical vessel with slowly rotating internal spiral blades to move crystals to filter for washing and recovery

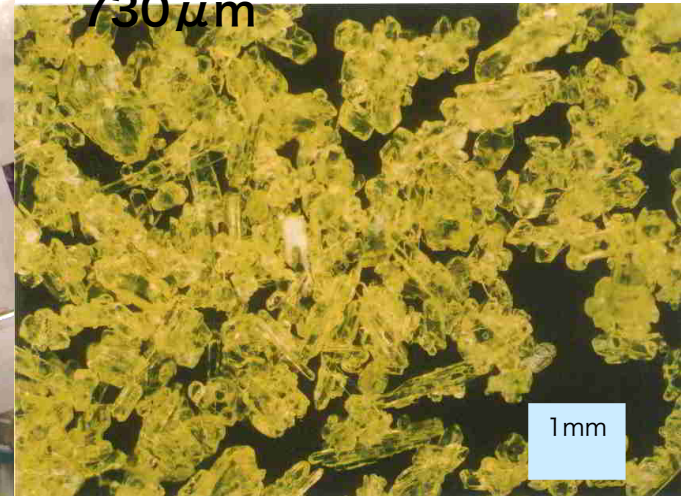
LANL project to develop adiabatic evaporative loop crystallizer for uranyl nitrate recovery from nuclear fuel dissolved in nitric acid

NEXT Process uses Uranyl Nitrate Crystallization

- JAEA scaling up annular continuous crystallizer; feed solution at $\sim 45\text{ }^{\circ}\text{C}$ external wall cooled to $0\text{ }^{\circ}\text{C}$; slowly rotating internal spiral blades to move crystals to filter for recovery; centrifugal basket filter to recover and wash crystals, Pu(VI) and U(VI) can be recovered with U(VI)

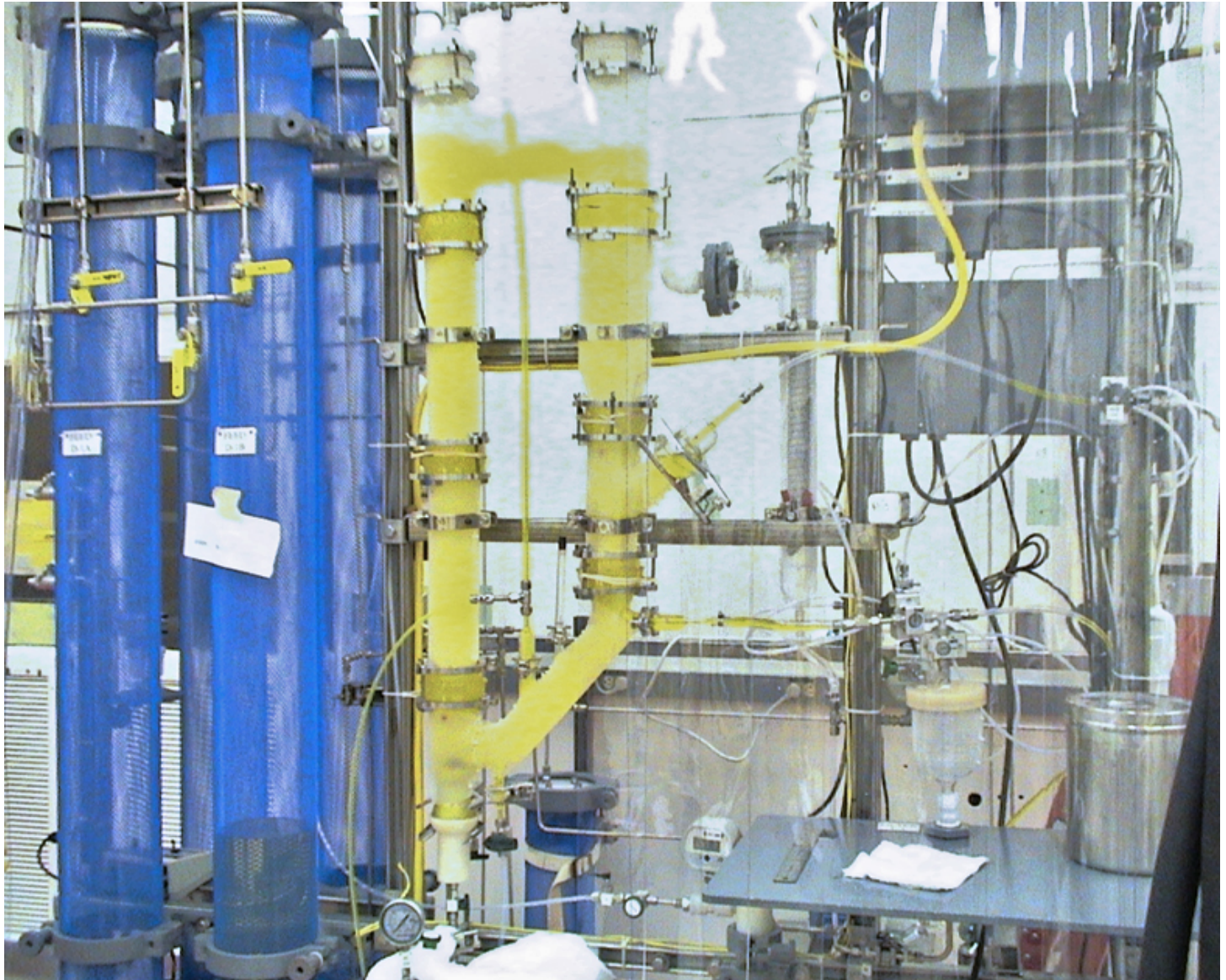


Average crystal size :
 $730\text{ }\mu\text{m}$



A. Shibata, et al. *J. Nucl. Sci. & Tech.* 2009, **46**, 204-209.
J. Nucl. Sci. & Tech. 2007, **44**, 344-348..

Continuous Loop Crystallizer Design for $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$



General Precipitation Behavior of Actinide Oxidation States

Precipitation reactions characteristic of various actinide oxidation states (aqueous solution, 1 M H^+ , except OH^- and CO_3^{2-} at higher pH).

| Anion | M^{3+} | M^{4+} | MO_2^+ | MO_2^{2+} |
|-----------------|-----------------------|---------------------|---------------------|---------------------|
| OH^- | Insol. | Insol. | Insol. | Insol. |
| F^- | Insol. | Insol. | Insol. ^a | Sol. |
| IO_3^- | Insol. | Insol. | Sol. | Sol. |
| O_2^{2-} | - | Insol. | - | - |
| $C_2O_4^{2-}$ | Insol. | Insol. | Insol. | Insol. |
| CO_3^{2-} | (Insol.) ^c | Insol. ^c | Insol. ^c | Sol. |
| $CH_3CO_2^-$ | Sol. | Sol. | Sol. | Insol. ^d |
| PO_4^{3-} | Insol. | Insol. | Insol. ^e | Insol. ^f |
| $Fe(CN)_6^{4-}$ | Insol. | Insol. | Sol. | Insol. |

^a At pH=6, $RbPuO_2F_2$ and $NH_4PuO_2F_2$ may be precipitated by addition of RbF or NH_4F , respectively.

^b **Complex carbonates $Ln(CO_3)_4^-$ and $Ln(CO_3)_5^{2-}$ increase solubility at higher CO_3^{2-} concentrations.**

^c Solid $KPuO_2CO_3$ precipitates on addition of K_2CO_3 to $Pu(V)$ solution.

^d From solution of $Pu(VI)$ in CH_3CO_2H , $NaPuO_2(CH_3CO_2)_3$ precipitates on addition of Na^+ .

^e Addition of $(NH_4)_2HPO_4$ to $Pu(V)$ solution yields $(NH_4)HPuO_2PO_4$ with $Pu(V)$.

^f On addition of H_3PO_4 , $HPuO_2PO_4 \cdot xH_2O$ precipitates.

Co-precipitation or Carrier Precipitation

- In general, an actinide metal ion will co-precipitate if the anion contained in the bulk precipitate forms an insoluble salt with the actinide metal ion in that oxidation state.
- Co-precipitation methods are very common features of radioanalytical procedures - NAS-NRC Nuclear Science Series: Monographs on Radiochemistry and Radiochemical Techniques and Collected Radiochemical and Geochemical Procedures, 5th edition, good sources of information.
- The tiny quantities of plutonium in the first preparations were too small to precipitate directly, so co-precipitations were used to deduce the chemical properties of plutonium and other new actinides using techniques developed in the early 1900s for the study of radioisotopes.

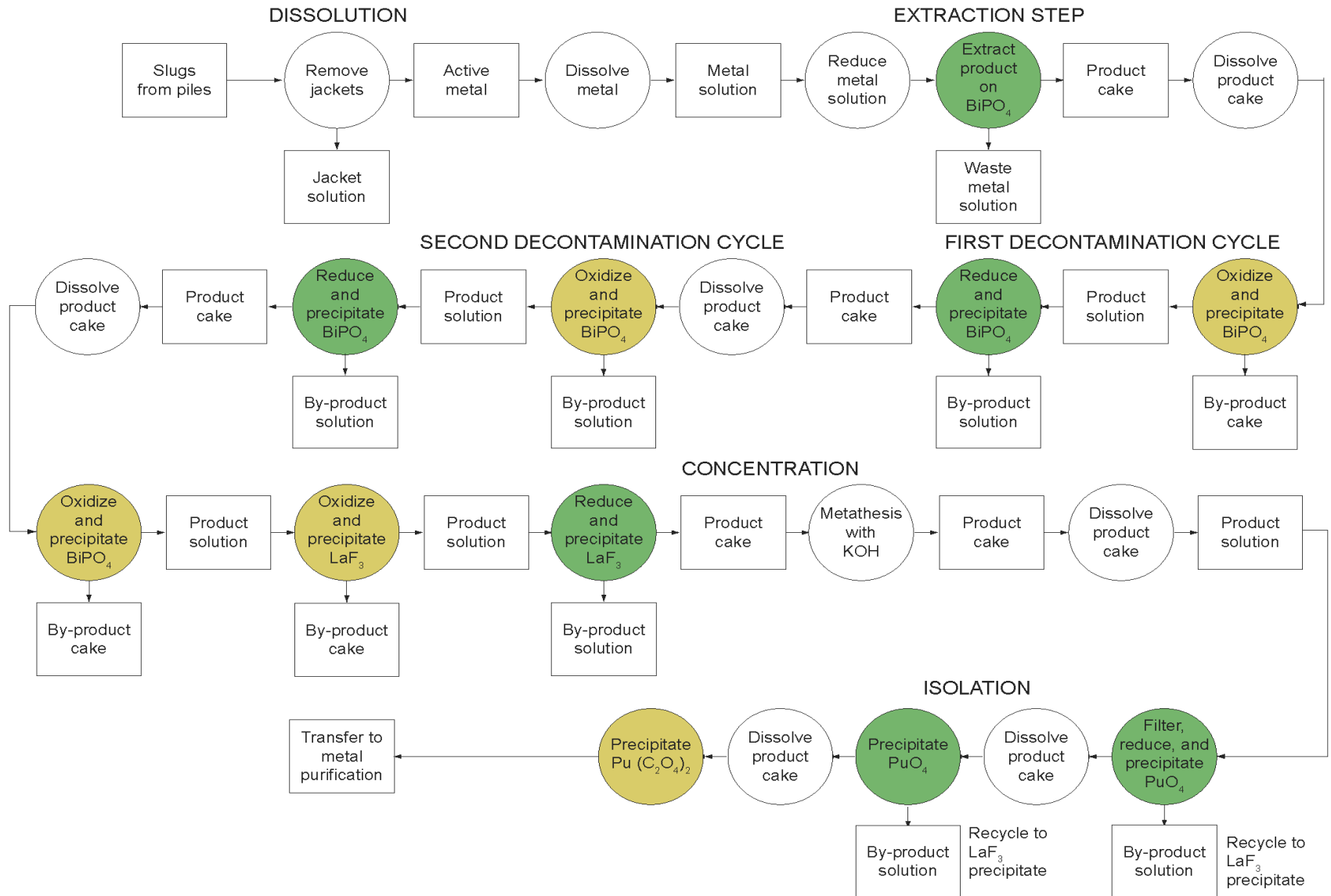
First Isolation of Weighable Plutonium Compound

- Cunningham and Werner isolated and weighed 2.77 micrograms of PuO_2 on September 10, 1942.
- Started with 90 kg of irradiated $\text{UO}_2(\text{NO}_3)\cdot 6\text{H}_2\text{O}$, mixed with 100 L of diethyl ether on roof of the Metallurgical Lab, produced 8 L of aqueous phase with about 50 wt% uranyl nitrate hydrate and most of the fission products and transuranic elements
- Precipitation of LaF_3 from nitric acid solution carries An(III,IV), but not An(V,VI). $\text{K}_2\text{S}_2\text{O}_8$ oxidizes Np and Pu to VI, but KBrO_3 oxidizes Np, but not Pu.
- First LaF_3 batch ~ 40 g; multiple cycles of co-precipitation, redissolution, oxidation, etc. yield 120 microliter solution containing ~ 40 micrograms of Pu. These solutions were manipulated in a specially designed glass apparatus viewed with a microscope.
- Today more than 2300 tonnes of Pu exist (mostly in used nuclear fuel) and hundreds of tonnes have been separated.

First Production of Plutonium Used Bismuth Phosphate Process

- Precipitation of BiPO_4 from moderate concentrations of nitric or sulfuric acid solution carries An(III,IV), but not An(V,VI). Addition of sulfuric acid to nitric acid solution of irradiated uranium targets keeps large amount of uranium in solution while BiPO_4 is precipitated.
- BiPO_4 could be redissolved in concentrated nitric acid to simplify the processing (LaF_3 requires heating in H_2SO_4 to distill off HF).
- A large series of redox cycles, co-precipitations, and redissolutions was used that resembles the LaF_3 process (some cycles of LaF_3 co-precipitation were used).
- Scale-up from laboratory scale to production by a factor of 10^8 in a short time is a remarkable story. Overall decontamination obtained at Hanford of 10^7 from fission products. Later replaced by solvent extraction processes that recovered both U and Pu, generated less waste, and operated continuously.

Schematic Flowsheet for Bismuth Phosphate Process



Precipitation Processes Used in Plutonium Processing

- Major products of plutonium processing are metal for fuels and weapons components and oxide for fuels and heat sources (Pu-238 application as long-term heat and power source for deep space missions).
- Most aqueous plutonium processing takes place in nitric and hydrochloric acids. The most common precipitations use oxalate, peroxide, fluoride and hydroxide. Some desirable features are:
 - High yield of plutonium in a form suitable to prepare metal or oxide
 - Remove common impurities (e.g., some iron always present in stainless steel equipment, Al added to complex fluoride in some cases)
 - Provide convenient method to concentrate plutonium from relatively dilute solutions

Pu(III) oxalate precipitation

- $\text{Pu}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ precipitates on addition of oxalic acid to Pu(III) solutions in nitric or hydrochloric acid
- Useful for Pu concentrations greater than ~ 1 g/L and less than 4 M acid concentration
- Good decontamination from Al(III), Fe(III), U(VI); moderate from Na, K and Ca; and Am(III) and Ln(III) coprecipitate
- Easily filterable, can add solution of oxalic acid or solid (gives smaller average particle size)
- Readily calcined to PuO_2



- Pu(III,IV) removed from very dilute solutions by coprecipitation with Ca(II) and Pb(II) oxalates

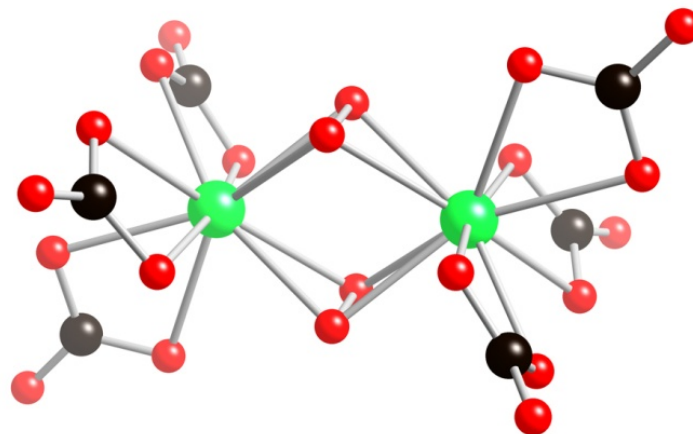
Pu(IV) oxalate precipitation

- $\text{Pu}(\text{C}_2\text{O}_4)_6 \cdot 6\text{H}_2\text{O}$ precipitates upon addition of oxalic acid to nitric and hydrochloric acid solutions of Pu(IV)
- Useful when $[\text{Pu}(\text{IV})] > \sim 1 \text{ g/L}$ and $[\text{H}^+] \sim 1\text{-}5 \text{ M}$
- Very fine solid tends to form, can be difficult to filter, elevated T improves filterability
- Good decontamination from Al(III), Fe(III), U(VI)
- Readily calcined to PuO_2 ; used in French MOX process
- Recent CEA work on co-precipitation of U(IV) and Pu(III) for MOX fuels



Pu(IV) peroxide precipitation

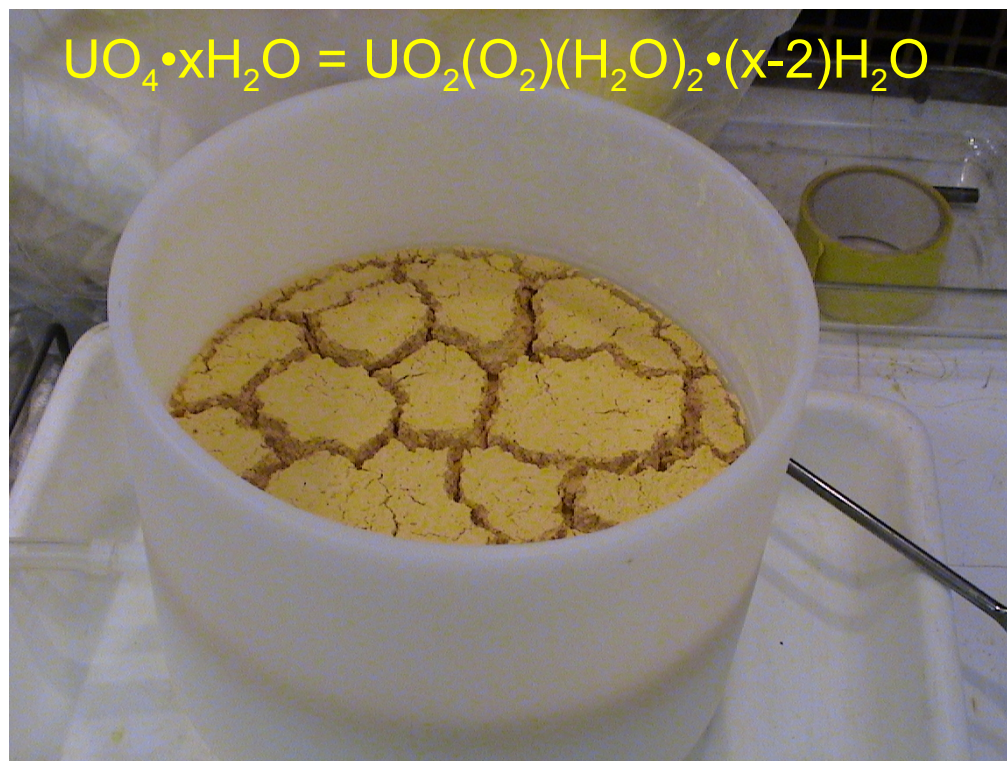
- Pu(IV) precipitates from acid solutions upon addition of H_2O_2
- Typically $[\text{Pu(IV)}] > \sim 1 \text{ g/L}$ and $[\text{H}^+] \sim 2.5\text{-}5.5 \text{ M}$
- Nonstoichiometric solid, $\text{O}_2^{2-}/\text{Pu}$ ratio may approach 1.7 (expect 2.0 for $\text{Pu}(\text{O}_2)_2$, incorporates other anions, e.g. NO_3^- , Cl^- , SO_4^{2-})
- Very filterable hexagonal form at higher acidities, gelatinous cubic form at lower acid
- Good decontamination from many elements except An(IV)
- Coordination geometry likely resembles structure of $\text{Na}_8\text{Pu}_2(\text{O}_2)_2(\text{CO}_3)_6 \cdot 12\text{H}_2\text{O}$ formed in high pH carbonate solutions



Runde, *et al. Chem. Commun.* **2007**, (17)1728-1729

U(VI) precipitation methods

- In U production, ion exchange or solvent extraction process in acid solutions typically yields an acid solution of U(VI) of mixed nitrate or chloride and sulfate
- Precipitation of U commonly done with base or peroxide
- Addition of H_2O_2 at pH 2.5-4.0 to U(VI) solutions gives $\text{UO}_4 \cdot x\text{H}_2\text{O}$
- Readily calcined to U_3O_8
- Good separation from many elements



U(VI) precipitation methods

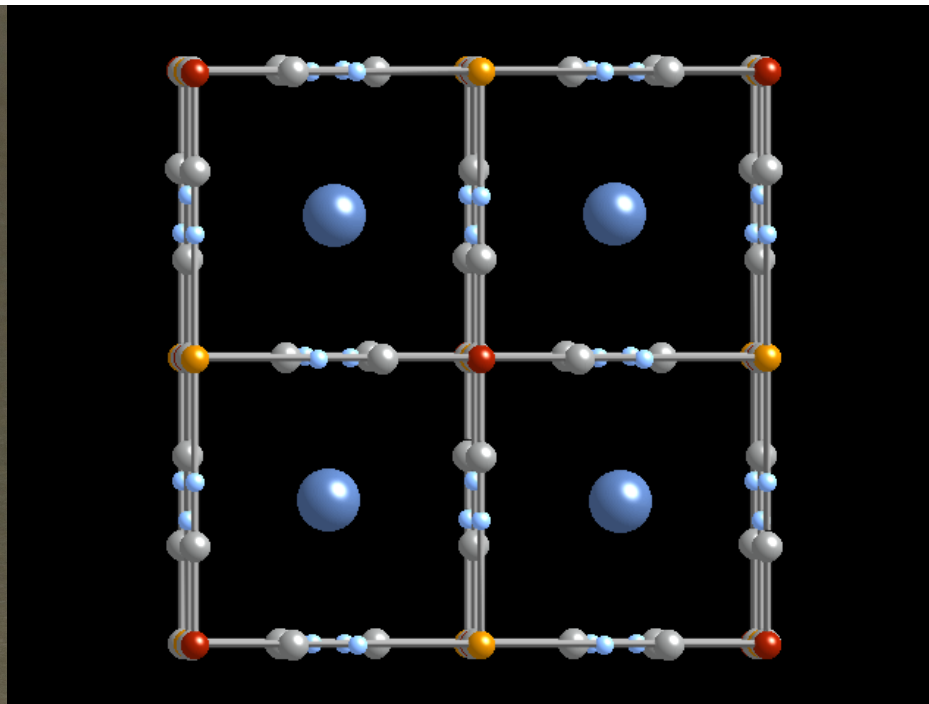
- Neutralization of U(VI) acid solutions with NaOH, NH₃ or magnesia precipitates polyuranates (yellow cake)
- Simple formulas often written such as (NH₄)₂U₂O₇, but solid phases produced are much more complicated
- Preliminary pH adjustment to 3.5-4.2 may be done to remove Fe(III)
- “(NH₄)₂U₂O₇” readily calcined to U₃O₈ or UO₃
- Hydroxides of impurities can coprecipitate



Cesium and Strontium Recovery at Hanford

- Tens of millions of curies of Cs-137 and Sr-90 were separated and purified at Hanford for use as irradiation sources and thermoelectric generators, to reduce heat load in the waste tanks, and to explore methods for advanced fuel cycle separations.
- The first 30,000 curies of Cs-137 was recovered using nickel ferrocyanide precipitation.
- The acid raffinate from PUREX operations was concentrated by evaporation and partially denitrated. This feed (CAW) was neutralized with NaOH and ammonia to precipitate the bulk of the fission and corrosion products. The filtered supernatant was acidified to pH 4 and boiled to remove CO₂.
- Ni(II) solution and ferrocyanide solution added to precipitate Ni₂Fe(CN)₆ that exchanges some nickel for cesium. Cs-loaded ferrocyanide metastasized with Ag₂CO₃ to yield Cs₂CO₃. The Cs recovery was >99%. Ferrocyanide precipitation replaced by phosphotungstic acid precipitation of Cs directly from acid feed.

Ammonium Ferric Hexacyanoferrate $\text{NH}_4[\text{FeFe}(\text{CN})_6]$



- **Approximate D values normalized to**
 $\text{Na}^+ 1 : \text{K}^+ 10 : \text{Rb}^+ 10^3 : \text{Cs}^+ 10^4$
K. Watari, K. Imai, and M. Izawa, *J. Nucl. Sci. Tech.*,
1968, 6, 309-312.
- **$(\text{NH}_4)_4\text{Fe}^{2+}(\text{CN})_6 + \text{Fe}^{3+}\text{Cl}_3 \rightarrow$**
 $\text{NH}_4\text{Fe}^{3+}[\text{Fe}^{2+}(\text{CN})_6] + 3 \text{NH}_4\text{Cl}$

Cesium and Strontium Recovery at Hanford

- The first megacurie of Sr-90 was recovered at Hanford using a PbSO_4 coprecipitation process.
- Sodium sulfate and tartaric acid (used to keep Fe(III) in solution) were added to the acidic waste feed from PUREX operations.
- $\text{Pb}(\text{NO}_3)_2$ and NaOH were then added to precipitate PbSO_4 .
- PbSO_4 was separated by centrifugation.
- NaOH and Na_2CO_3 were added to convert the sulfate to the carbonate.
- PbCO_3 solid was dissolved in nitric acid and oxalic acid added to precipitate Pb, Ce(IV) and other lanthanides leaving the Sr in solution for further purification operations.
- PbSO_4 coprecipitation was replaced by solvent extraction process using di-2-ethylhexylphosphoric acid.

Conclusion

- Precipitation, co-precipitation, and crystallization processes important part of separations “tool box” and have a great variety of applications in industrial operations.
- These operations will continue to be used and developed for future nuclear fuel cycles.