



Precipitation/Crystallization/Sorption Processes

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Outline

- 1) Precipitation and crystallization - generate supersaturation, e.g., by reagent addition (K_{sp}), ΔT , redox; followed by nucleation, growth (agglomeration, aging)
- 2) Batch vs continuous precipitation/crystallization operations; solid-liquid separations
- 3) Coprecipitation or carrier precipitation - very important tool in analytical methods for radionuclides
- 4) Plutonium first isolated as weighable compound and first production performed by multiple stages of coprecipitation using LaF_3 and bismuth phosphate, respectively
- 5) Examples of plutonium purification and product preparation using oxalate, peroxide, fluoride, hydroxide
- 6) Cesium and strontium separation from Hanford tank wastes
- 7) Removal of radionuclides for wastewater treatment with sorbents, coprecipitation

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
- 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 fuels and materials
- Precipitation/crystallization process design often more than separation step - designed to reduce cost of the final product

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 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 stainless steel filter wheel by vacuum, washed, partly dried, scrapped off into boat for calcining to PuO₂
- JAEA investigating partial recovery of uranyl nitrate (~60-90%) from used commercial LWR nuclear fuel dissolved in nitric acid by cooling and filtering; U, Np, Pu recovered together in subsequent coextraction

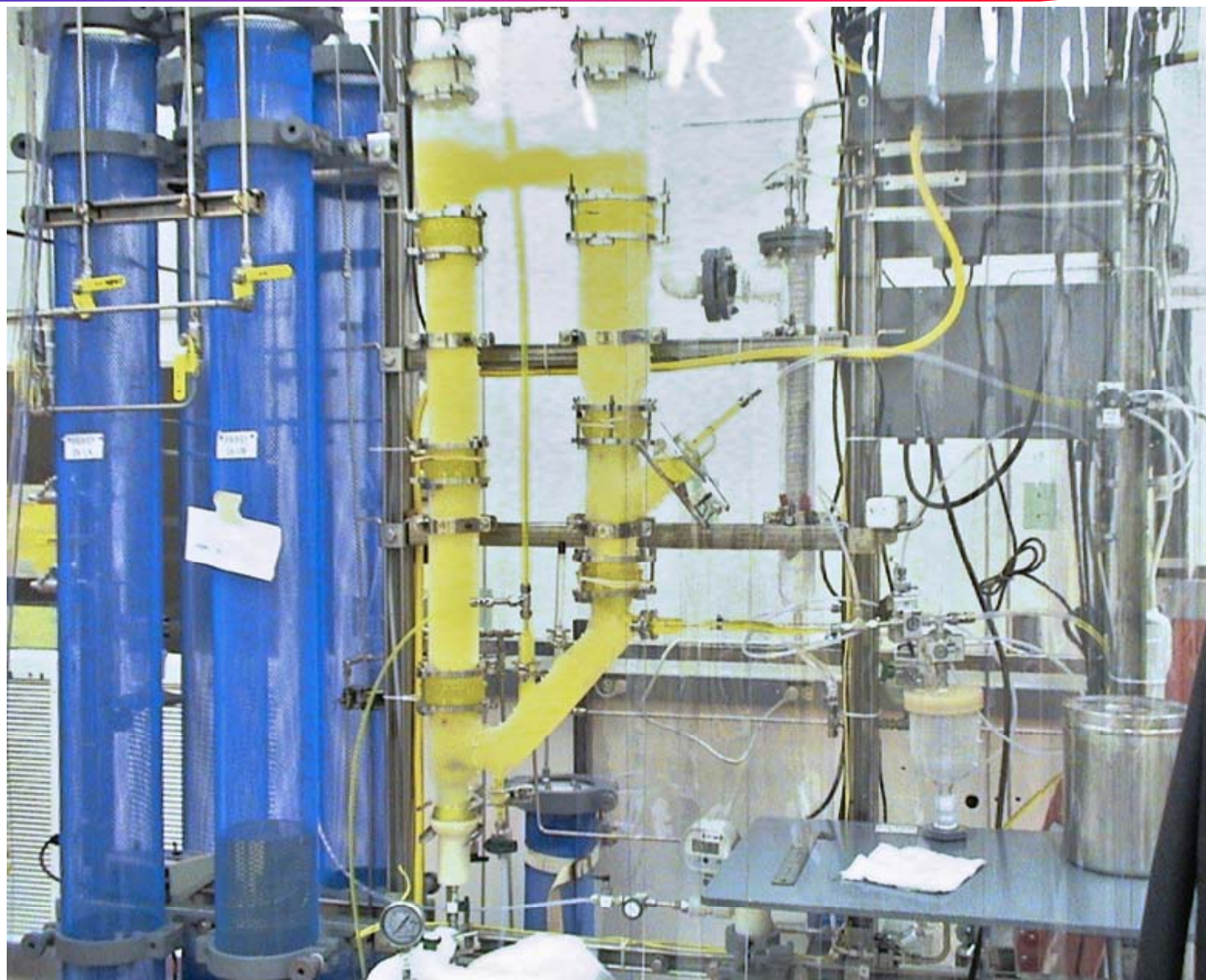
NEXT Process uses Uranyl Nitrate Crystallization

- JAEA scaling up annular continuous crystallizer with slowly rotating internal spiral blades to dislodge crystals growing on wall and move them to filter for washing and recovery; centrifugal basket filter to recover and wash crystals



Photos from presentation at Plutonium Futures
- The Science 2003 in Albuquerque, NM

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

Table 1. Precipitation reactions characteristic of various actinide oxidation states (aqueous solution 1 M H⁺).^a

<i>Anion</i>	<i>M³⁺</i>	<i>M⁴⁺</i>	<i>MO₂⁺</i>	<i>MO₂²⁺</i>
OH ⁻	I	I	I	I
F ⁻	I	I	I ^b	S
IO ₃ ⁻	I	I	S	S
O ₂ ²⁻	-	I	-	I ^h
C ₂ O ₄ ²⁻	I	I	I	I
CO ₃ ²⁻	(I) ^c	I ^c	I ^d	S
CH ₃ CO ₂ ⁻	S	S	S	I ^e
PO ₄ ³⁻	I	I	I ^f	I ^g
Fe(CN) ₆ ⁴⁻	I	I	S	I

I=insoluble, S=soluble.

^a The OH⁻ and CO₃²⁻ precipitations occur in alkaline solution.

^b At pH=6, RbPuO₂F₂ and NH₄PuO₂F₂ may be precipitated by addition of RbF or NH₄F, respectively.

^c Complex carbonates are formed.

^d Solid KPuO₂CO₃ precipitates on addition of K₂CO₃ to Pu(V) solution.

^e From solution of Pu(VI) in CH₃CO₂H, NaPuO₂(CH₃CO₂)₃ precipitates on addition of Na⁺.

^f Addition of (NH₄)₂HPO₄ to Pu(V) solution yields (NH₄)HPuO₂PO₄ with Pu(V).

^g On addition of H₃PO₄, HPuO₂PO₄ · xH₂O precipitates.

^h At higher pH (2-4), UO₄ · 2H₂O precipitates; Np(V), Pu(V), Np(VI), Pu(VI) reduced by H₂O₂.

An(III, IV) precipitations from nitric acid solution of irradiated plutonium

Table 2. Decontamination factors for plutonium precipitated from an irradiated plutonium alloy dissolved in nitric acid

<i>Element</i>	<i>Pu(III) oxalate</i>	<i>Pu(IV) oxalate</i>	<i>Pu(IV) peroxide</i>	<i>Pu(III) fluoride</i>
Fe	33	10	50	1.4
Co	47	> 95	30	8.6
Zr	3.5	> 44	1	1.1
Mo	> 13	> 15	> 140	1.1
Ru	> 38	33	> 14	36
Ce	1	1	6	1.1

An(III, IV) precipitations did not give large decontamination factors from fission products and corrosion products; $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ crystallization from ~ 1M HNO_3 decontamination factors ~200 for many fission products

Coprecipitation or Carrier Precipitation

- In general, an actinide metal ion will coprecipitate if the anion contained in the bulk precipitate forms an insoluble salt with the actinide metal ion in that oxidation state.
- Coprecipitation 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 coprecipitations 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.

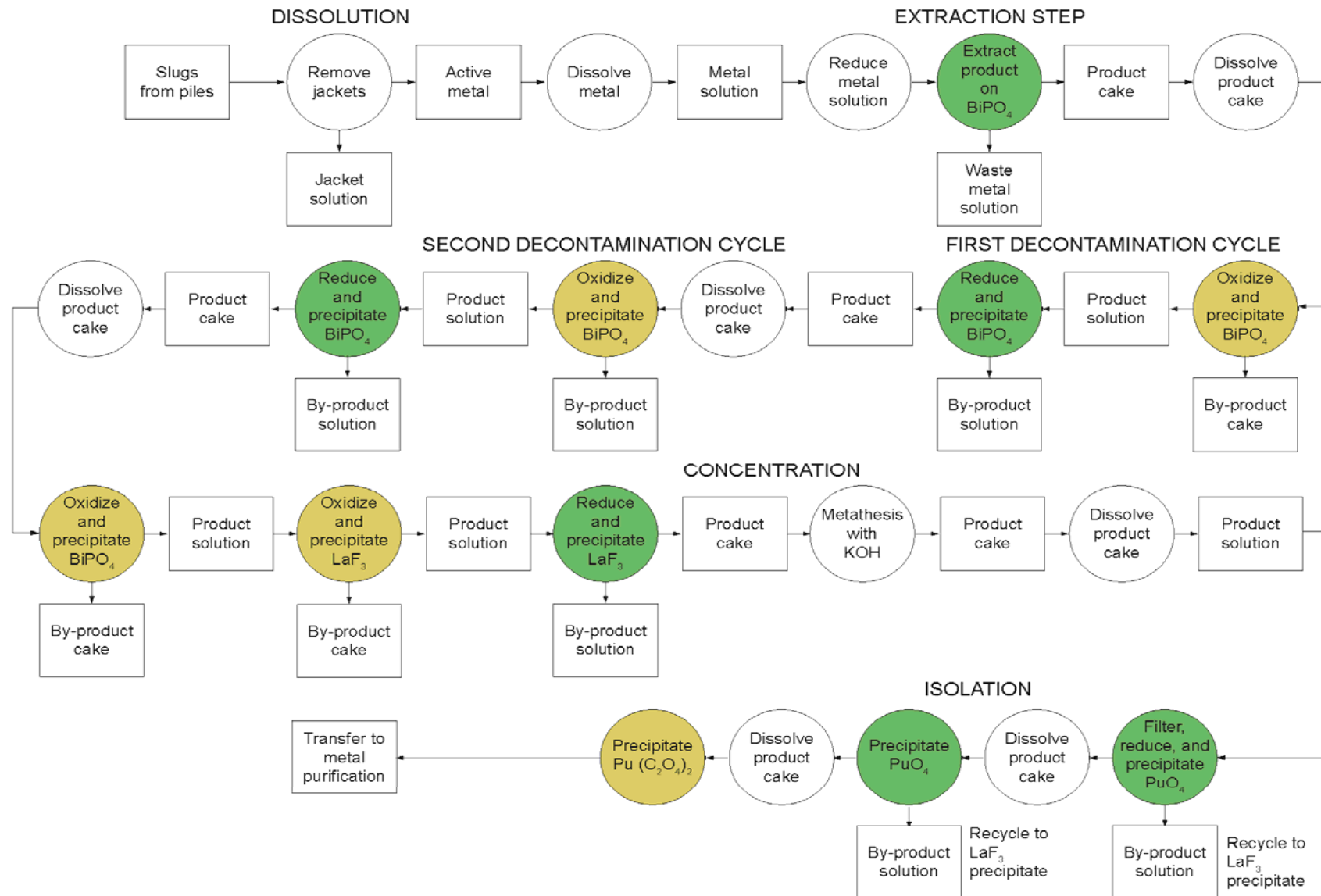
First Isolation of Weighable Plutonium Compound

- 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 coprecipitation, 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.

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, coprecipitations, and redissolutions was used that resembles the LaF_3 process (some cycles of LaF_3 coprecipitation 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. Replaced by solvent extraction processes.

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

Working with Plutonium



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 with reducing agent, e.g., H_3NOH^+
- 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

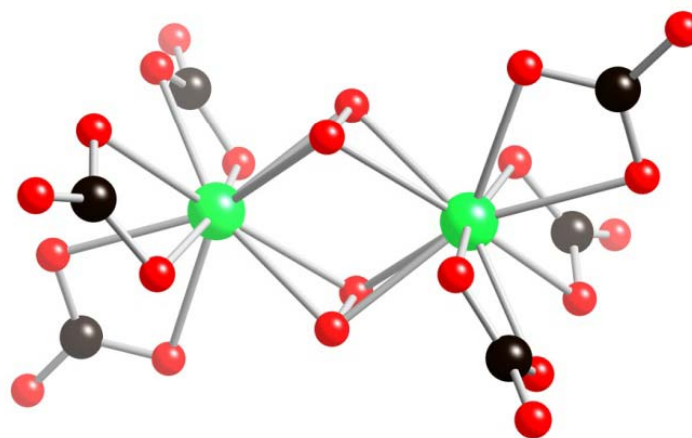
Pu(IV) oxalate precipitation

- $\text{Pu}(\text{C}_2\text{O}_4)_4 \cdot 6\text{H}_2\text{O}$ 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 coprecipitation of U(IV) and Pu(III) for MOX fuels



Pu(IV) peroxide precipitation

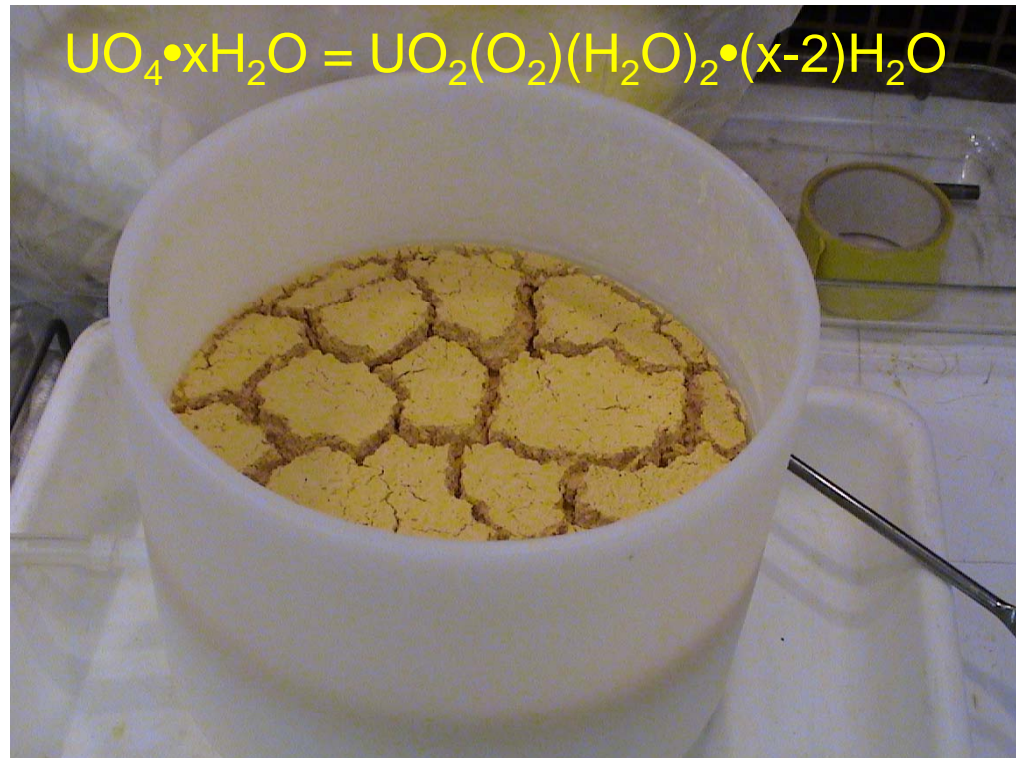
- Pu(IV) precipitates from acid solutions upon addition of H_2O_2
- Typically $[\text{Pu(IV)}] > \sim 1 \text{ g/L}$ and $[\text{H}^+] \sim 2.5\text{-}5.5 \text{ M}$
- Nonstoichiometric solid, $\text{O}_2^{2-}/\text{Pu}$ ratio may approach 1.7 (expect 2.0 for $\text{Pu}(\text{O}_2)_2$, incorporates other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



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



Mixed Oxide (MOX) Fuel Fabrication

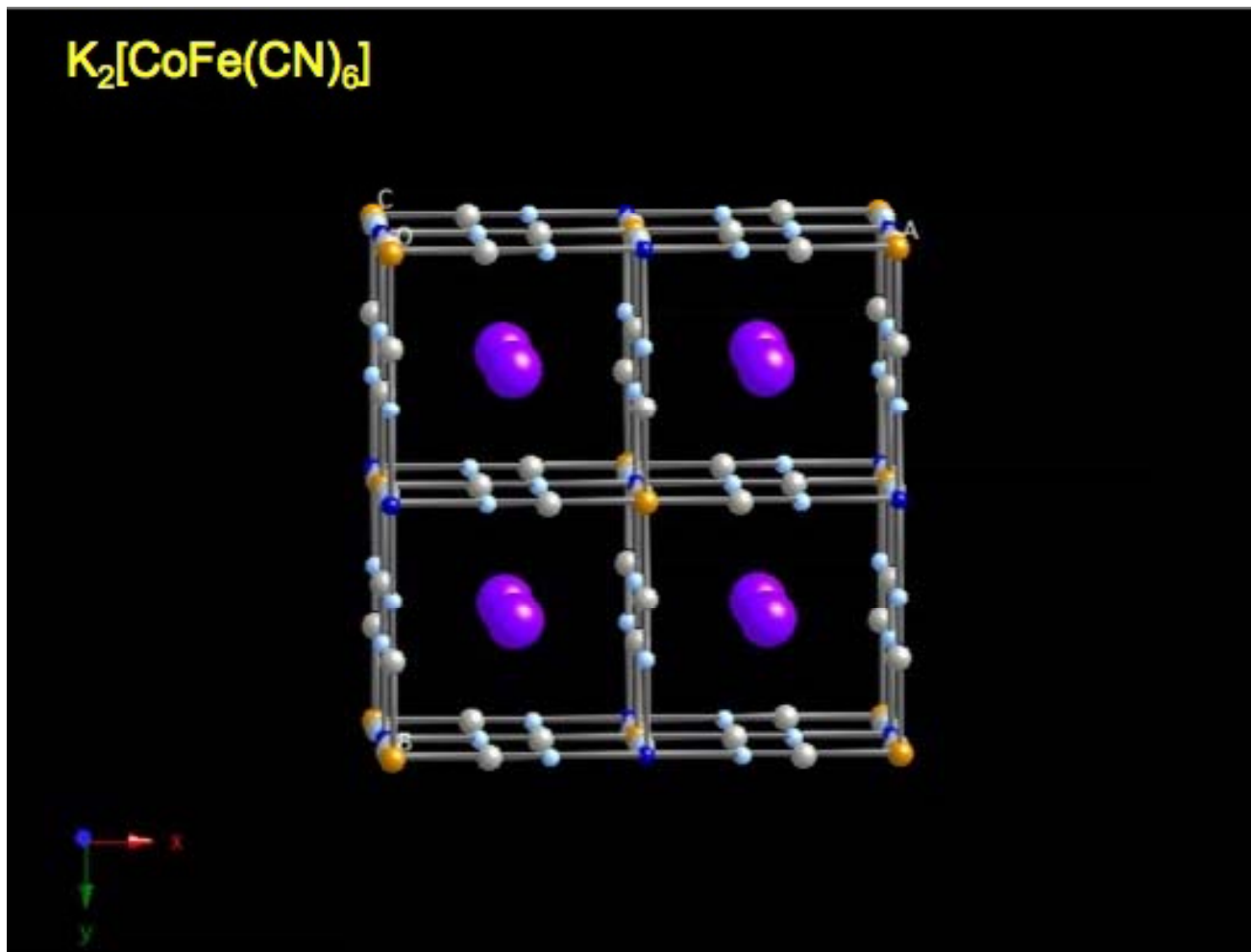
- Two major routes to MOX fuel developed: comilling and coprecipitation
- Micronized master blend (MIMAS) process ball mills UO_2 and PuO_2 (~30 wt%) and then blends with additional UO_2 to prepare final composition for making pellets
- Coprecipitation adds CO_2 and NH_3 to nitric acid solution of U(VI) and Pu(VI) to generate $[\text{NH}_4]_4[(\text{U},\text{Pu})\text{O}_2(\text{CO}_3)_3]$
- Heat mixed carbonate under N_2/H_2 atmosphere to generate $(\text{U},\text{Pu})\text{O}_2$
- Coprecipitation of U(IV) and Pu(III) oxalate also under development



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 metathesized with Ag₂CO₃ to yield Cs₂CO₃. The Cs recovery was >99%. Ferrocyanide precipitation replaced by phosphotungstic acid precipitation of Cs directly from acid feed.

Crystal Structure of Hexacyanoferrate $K_2[CoFe(CN)_6]$



Ammonium Ferric Hexacyanoferrate

- $\text{NH}_4[\text{FeFe}(\text{CN})_6]$
- Added to animal fodder after Chernobyl to decrease milk contamination by increasing elimination of ^{137}Cs
- 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,
Journal of Nuclear Science and Technology, Vol. 6 (1968), pp. 309-312
- $(\text{NH}_4)_4\text{Fe}^{2+}(\text{CN})_6 + \text{Fe}^{3+}\text{Cl}_3 \rightarrow \text{NH}_4\text{Fe}^{3+}[\text{Fe}^{2+}(\text{CN})_6] + 3 \text{NH}_4\text{Cl}$



Cs Precipitants, Ion Exchangers, and Extractants

1. Crystalline Silicotitanate (CST)	High affinity for Cs in highly alkaline solutions containing high Na concentrations
2. Zeolites	Used in clean-up efforts after accident at Three Mile Island; dissolve in highly alkaline solutions
3. Ammonium molybdophosphate (AMP)	Highly selective for Cs in acidic tank waste at INL, but dissolves in alkaline solutions > pH 5
4. Potassium cobalt (II) ferrocyanide (KCFC)	Highly selective for cesium in alkaline waste solutions
5. Ammonium ferric hexacyanoferrate (AFCF)	Added to animal fodder after Chernobyl to reduce milk and meat contamination by increasing elimination of ¹³⁷Cs
6. Sodium Tetrphenylborate	Used at SRS to precipitate Cs from high level tank waste (but decomposition observed to give benzene in actual processing solution apparently catalyzed by metal ions in tank waste)
7. BobCalixC6	Used in the caustic-side solvent extraction (CSSX) process designed at ORNL to remove Cs from alkaline (high sodium) tank waste solutions

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.

Sorbents for Radionuclides

- Many solid materials have been used as “sorbents” for radionuclides including activated charcoal, silica, alumina, hydrated titanium oxide, iron hydroxides, manganese dioxide, zirconium phosphates, zeolites, and clays - a combination of surface adsorption and ion exchange mechanisms are observed.
- These materials overlap with the very large area of inorganic ion exchangers that should be discussed under ion exchange processes.
- Metal cations binding to oxide surfaces can exhibit selectivity much like oxygen donor ligands, i.e., An(IV) bind most strongly, An(VI) less strongly, An(III) and An(V) very weakly. However, there are certainly interesting examples of selectivity observed, e.g, a radioanalytical method for sodium, takes advantage of the sorption properties of $\text{Sb}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ in concentrated HCl that only retains Na and Ta among 60 elements tested.
- The use of surface sorbents often requires careful preparation of the surface, e.g., large literature on preparation of alumina, silica for chromatographic separations of metal ions or organic compounds.
- Sorbents can be deployed as finely divided solids dispersed in solution or in a column mode.

Sorbents for Radionuclides

- Removal of radionuclides from low-level process or waste solutions is a common application of sorbents.
- Iron oxides and hydroxides used as solid sorbents, but the larger industrial application is as a coprecipitant to remove many contaminants from process or waste waters. Iron hydroxide acts as a coagulant or flocculant for many colloidal species including silica and acts as carrier for metal ions, including actinide metal ions.
- The low-level radioactive liquid waste treatment facility at LANL long used $\text{Fe}(\text{OH})_3$ precipitation and large settling tanks to obtain the low levels of Pu and Am alpha activity required by DOE regulations before discharge to canyon. In recent years the $\text{Fe}(\text{OH})_3$ coprecipitations have been replaced with ultrafiltration and reverse osmosis processes to reduce overall low-level solid waste volumes for disposal. Future operations plan to have no liquid discharge.

Conclusion

- Precipitation, coprecipitation, crystallization and sorption 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.