

Precipitation and Crystallization Processes

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Introduction

Precipitation and crystallization refer to unit operations that generate a solid from a supersaturated solution. The non-equilibrium supersaturated condition can be induced in a variety of ways such as removal of solvent by evaporation, addition of another solvent, changes of temperature or pressure, addition of other solutes, oxidation-reduction reactions, or even combinations of these.

The distinction between precipitation and crystallization is quite often based on the speed of the process and the size of the solid particles produced. The term precipitation commonly refers to a process which results in rapid solid formation that can give small crystals that may not appear crystalline to the eye, but still may give very distinct x-ray diffraction peaks. Amorphous solids (at least as indicated by x-ray diffraction) may also be produced. The term precipitation also tends to be applied to a relatively irreversible reaction between an added reagent and other species in solution whereas crystallization products can usually be redissolved using simple means such as heating or dilution. Precipitation processes usually begin at high supersaturation where rapid nucleation and growth of solid phases occur. In both precipitation and crystallization processes the same basic steps occur: supersaturation, nucleation and growth. Nucleation does not necessarily begin immediately on reaching a supersaturated condition, except at very high supersaturation, and there may be an induction period before detection of the first crystals or solid particles. Nucleation can occur by both homogeneous and heterogeneous processes. In general, homogeneous nucleation is difficult to achieve because of the presence of heteronuclei from colloids, dust, or other foreign material in the solution. This is especially true in industrial practice. The walls of the solution container may also be a source of nucleation sites. After nucleation the growth phase begins and agglomeration and aging are terms used to describe features of the changes in the solid particles.

Agglomeration describes the tendency of small particles in a liquid suspension to coalesce into larger aggregates. Other terms used in the literature include aggregation, coagulation, and flocculation. The term aging refers to a variety of other processes that change a precipitate after it forms. For example, Ostwald ripening refers to the tendency of larger crystals to grow at the expense of smaller crystals when the crystals formed after nucleation are smaller than ~1 micron. Another important process is initial nucleation of a metastable solid phase that transforms with aging, e.g., amorphous solid particles that crystallize with time or a hydrated crystalline solid that converts to a more stable material. Agglomeration and crystal growth can also be influenced substantially by the presence of impurities in the solution.

The details of performing the precipitation or crystallization process can be very important to produce a pure product and one that separates well from the liquid phase. Thus, the degree of supersaturation, the order and speed of reagent addition, the temperature, and the aging time before filtration or centrifugation are used to recover the solid, and the presence of “active” impurities can all be important parameters in a precipitation or crystallization process. Usually aging results in larger particle sizes and may be referred to with terms such as digestion or ripening of the precipitate.

The references “Crystallization, 4th Edition” [Mullin, 2001] and “Handbook of Industrial Crystallization, 2nd Edition [Myerson, 2002] provide extensive information on the theory and practice of industrial precipitation and crystallization processes. This includes the great variety of applications from crystallizing drugs and proteins for medical applications, to preparing silicon materials for electronics, to waste water treatment with metal hydroxide precipitates. These

references also describe some of the vast array of equipment used to perform industrial precipitation and crystallization processes including batch and continuous operation.

Many industrial precipitations of metal species are batch processes that involve the rapid mixing of two aqueous solutions to generate supersaturation and after subsequent nucleation and growth of the solid; the solid is collected by filtration or centrifugation. This is certainly a common method for precipitating actinide metal ions from aqueous solutions. For precipitating plutonium and other fissile actinides, there is an advantage to using batch processing to simplify criticality safety operations. One can use a batch size well below the level of criticality concern and clean and inspect the solution containment vessels between batches to prevent build-up of fissile solids.

Mullin briefly summarizes (p. 323-324) some guidelines for using the strong influence of supersaturation to determine the mean particle size of a precipitate based on the Weimarn "laws" of precipitation:

1. As the concentration of reacting substances in solution is increased, i.e., as the initial supersaturation is increased, the mean size of the precipitate particles (measured at a given time after mixing the reactants) increases to a maximum and then decreases. As the time at which the measurement is made is increased, the maximum is displaced toward lower initial supersaturation and higher mean sizes.
2. For a completed precipitation, the precipitate mean size decreases as the initial supersaturation is increased.

In addition to confirming the well-known beneficial effect of using reasonably dilute reactants to produce coarse precipitates, the laws demonstrate that excessive dilution can be detrimental, a fact that is not always fully appreciated. Experimental evidence for the Weimarn laws has been provided by Mullin and Ang (1977) for the precipitation of nickel ammonium sulfate.

Some measure of control over nucleation and growth, and hence of precipitation, may also be exercised by the addition of substances, such as surfactants and polyelectrolytes. Impurities in the system, whether deliberately added or already present, can have a powerful influence on the morphology of the final precipitated particles.

For the actinide metal ion precipitations to be reviewed briefly below, limiting the amount of added precipitating agent such as oxalic acid (e.g., to form $\text{Pu}_2(\text{oxalate})_3$) is used to both control the initial supersaturation to get larger particle sizes that are readily filtered and to limit the formation of soluble anionic complexes of the actinide that reduce the yield of the product. The optimal "recipes" for accomplishing this balance were generally developed empirically with knowledge of the solubility of the limiting metal ion compound (K_{sp}), guidance from general principles such as the Weimarn laws for precipitation, and, in some cases, knowledge of the stability constants for the metal species in solution.

Coprecipitation refers to the variety of ways that other solutes in a multicomponent solution or impurities may associate with a precipitate or crystal. This includes surface adsorption, incorporation of other anions or cations in the lattice of a growing crystal as part of a stable solid solution or by entrapment, and even physical inclusion of pockets of mother liquor. Coprecipitation is a very important method for recovering small amounts of a solute that may be

far below its solubility limit in the precipitate of a major component (sometimes referred to as the carrier). Coprecipitation has been a crucial separation process to isolate traces of radionuclides and investigate their chemical behavior since the discovery of radioactivity.

Precipitation, Coprecipitation, and Crystallization Methods for Actinide Processing

The different oxidation states of the early actinide ions (particularly U, Np, and Pu) in aqueous solution show large differences in coordination chemistry that facilitate separation by a variety of methods. Table 1 lists the qualitative solubility behavior of the actinides in oxidation states III-VI with some common anions. These precipitations are very useful for separating mixtures of the actinides and for recovery of solid products from an aqueous stream usually after using another separation process such as ion exchange or solvent extraction. They are generally not selective enough to be used as the primary process for separation of plutonium or other actinides from all the fission products in irradiated fuel or targets. This is illustrated by a study (Winchester and Maraman, 1958) that used precipitation of Pu(III) oxalate, Pu(IV) oxalate, Pu(III) fluoride and Pu(IV) peroxide to recover plutonium directly from an irradiated plutonium-rich alloy dissolved in nitric acid. The decontamination factors reported in Table 2 indicate that none of the precipitation processes used achieved high enough fission product or corrosion product (Fe and Co) removal for use as a primary separation process. However, as will be described below, a series of coprecipitations with other metal ion species such as bismuth phosphate were used in the first large-scale separations of plutonium from irradiated uranium. These processes were replaced in time by more efficient solvent extraction processes.

The examples of actinide precipitations and coprecipitations discussed below are excerpted from the chapter on plutonium from the *Chemistry of the Actinide and Transactinide Elements* 3rd Edition, 2006. The behavior of other actinide metal ions in the same oxidation state is similar. The choice of plutonium examples was made because they illustrate many of the important features that go into choosing a particular separation approach. In addition, plutonium is a crucial component of nuclear fuel recycle and has been separated on a larger scale than any other synthetic element.

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

Anion	M ³⁺	M ⁴⁺	MO ₂ ⁺	MO ₂ ²⁺
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.

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

Element	Pu(III) oxalate	Pu(IV) oxalate	Pu(IV) peroxide	Pu(III) fluoride
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

Coprecipitation methods

Coprecipitation processes were the first to be used for the recovery of plutonium and to examine its chemical properties. The tiny amounts of plutonium present in the first preparations were too small to be precipitated directly, so coprecipitation or “carrier” precipitations were used to purify, and deduce the chemical properties of plutonium and many other radioactive elements. Coprecipitation separation methods are a common feature of many analytical procedures for radionuclides. 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 the same oxidation state or states present in the solution. Coprecipitation methods have been used to purify plutonium in microgram amounts and for recovery on a production scale. Useful precipitation methods for uranium and plutonium have been reviewed (Sorantin, 1975). A very large and useful set of separation procedures compiled by element for most of the periodic table are contained in the Nuclear Science Series: Monographs on Radiochemistry and Radiochemical Techniques published by the National Academy of Science – National Research Council from 1959 to 1977. This series is out of print, but can be found online (<http://lib-www.lanl.gov/radiochemistry/elements.htm>). A useful collection of radioanalytical procedures that use many coprecipitation steps is found in the report: Collected Radiochemical and Geochemical Procedures 5th Edition, LA-1721, May 1990, compiled and edited by J. Kleinberg.

Lanthanum fluoride

Precipitation of lanthanum fluoride or other lanthanide fluorides from acid solutions carries trivalent and tetravalent actinides, but not the pentavalent and hexavalent ions. The lanthanide and yttrium fission products coprecipitate, but most of the other fission products remain in solution. The behavior of neptunium and plutonium in the lanthanum fluoride precipitation was used to establish the existence of two oxidation states of these elements before weighable quantities were available (Seaborg and Wahl, 1948). The lanthanum fluoride carrier precipitation was also a key step in the first isolation of a weighable quantity of plutonium compound described briefly below.

Cunningham and Werner isolated PuO₂ and weighed 2.77 micrograms, the first weighable quantity of any synthetic element, on September 10, 1942 at the Metallurgical Laboratory of the University of Chicago (Cunningham and Werner, 1949). The plutonium had been separated from about 90 kilograms of uranyl nitrate hexahydrate that had been irradiated for one to two months with neutrons produced by bombarding a beryllium target with deuterons at the cyclotron facility at Washington University in St. Louis. The separation of plutonium was accomplished through oxidation state adjustments and a series of LaF₃ precipitations that carried Pu(IV) and Np(IV) but not Pu(VI) or Np(VI). The brief overview that follows provides an example of a coprecipitation separation method and also illustrates the painstaking effort required in these first explorations of plutonium chemistry.

The 90 kg of irradiated UO₂(NO₃)₂•6H₂O was mixed with 100 liters of diethyl ether to yield about 120 liters of ether solution containing uranyl nitrate solvate, UO₂(NO₃)₂[O(CH₂CH₃)₂]₂, and a small amount of fission products and 8 liters of an aqueous phase that consisted of about 50 wt% uranyl nitrate hydrate with most of the fission products and transuranic elements, principally neptunium and plutonium. This was essentially a solvent extraction step that partitioned most of the U(VI) to the ether phase along with a small amount of the fission products.

The aqueous phase was diluted to 20 liters and made 2 M in nitric acid and 0.014 M in La(III) and then HF was added to give a solution 4 M in HF. The 40 g of LaF₃ precipitate contained the transuranium elements and about 25% of the original fission product activity (mostly the lanthanide and yttrium fission products). The separated LaF₃ precipitate was heated in concentrated sulfuric acid to distill HF and then dissolved in and diluted to 5 liters with 2 M nitric acid. The Pu(IV) was oxidized to Pu(VI) by using K₂S₂O₈ and Ag(I) as a catalyst. The solution was then made 4 M in HF and the LaF₃ precipitate separated by filtration. The ~40 g of LaF₃ contained most of the remaining fission product activity, while the solution contained the Pu(VI) and Np(VI). The addition of a 6% SO₂ solution to the filtrate and washings reduced the Pu and Np and the excess peroxydisulfate. Addition of 2 g of La(NO₃)₃ in solution, precipitated LaF₃ that carried the tetravalent Pu and Np. Repeated cycles of precipitation with progressively smaller amounts of LaF₃ were used to further decontaminate the Pu and Np. For two of the LaF₃ precipitation cycles, KBrO₃ was employed as the oxidizer to selectively oxidize Np, but not Pu. This allowed the separation of the Np into the filtrate solutions while Pu was carried with the LaF₃. These additional cycles of smaller precipitations eventually yielded a 120 microliter solution of 1.7 M HNO₃ and 5 M HF that was fumed in a platinum crucible and treated with 10 M ammonium hydroxide. The washed precipitate of plutonium hydroxide contained about 40 micrograms of Pu. The microliter-scale solution manipulations were performed in a specially designed glass apparatus viewed with a microscope. Additional purification steps yielded a 50 microliter solution of Pu in nitric acid. Ten microliters of this solution were placed on a platinum weighing pan, dried, and heated to give the oxide. This sample provided the first weighable quantity of plutonium that is now displayed in the Seaborg Museum at the University of California, Berkeley.

Bismuth phosphate process

The bismuth phosphate process was used for the first large-scale purification of plutonium from neutron-irradiated uranium at the Hanford site during the Manhattan Project and after the war until the 1950's when it was displaced by solvent extraction processes. The precipitation of BiPO₄ from acid solutions carries the trivalent tetravalent actinides and especially Pu(IV), but not the pentavalent and hexavalent ions. Bismuth phosphate is quite insoluble in moderately concentrated nitric and sulfuric acids. This is an important property because addition of sulfuric acid to a nitric acid solution of neutron-irradiated uranium could be used to keep the relatively large quantity of U(VI) in solution as a sulfate complex while bismuth phosphate was precipitated and carried the plutonium. The BiPO₄ solid carried only small amounts of the fission products. The BiPO₄ could be redissolved in concentrated nitric acid; this simplified the process relative to using a lanthanum fluoride carrier that is difficult to redissolve. A series of oxidation state adjustments and precipitations of BiPO₄ from solutions of neutron-irradiated uranium in nitric acid separated the plutonium from the uranium, neptunium and fission products in a scheme that resembles the lanthanum fluoride process described above. In fact, cycles of lanthanum fluoride precipitation from nitric acid were incorporated into the bismuth phosphate process to concentrate and further purify the plutonium.

Thompson and Seaborg first developed the bismuth phosphate process (Thompson and Seaborg, 1956). The scale-up of the process from the laboratory to an operating plant by a factor of 10⁸ in a short time is a remarkable story (Hill and Cooper, 1958). An overall decontamination factor from the fission products of 10⁷ was obtained at Hanford for the plutonium product. The disadvantages of the process included discarding the uranium with the fission products, generation of large volumes of high salt wastes, and batch operation. Continuous solvent extraction processes based on extraction of uranium and plutonium from nitric acid solutions of dissolved fuel displaced the bismuth phosphate process.

Precipitation and crystallization methods for conversion chemistry of plutonium

Solvent extraction processes have displaced the original bismuth phosphate co-precipitation method for production scale plutonium separation from neutron-irradiated uranium fuels and targets, but precipitation and crystallization from aqueous solutions have always been important for preparing and purifying solid compounds for the various applications of plutonium. The major products are plutonium metal for irradiation targets and fuels, weapons components, or storage and PuO₂ for mixed oxide fuels, heat sources (when the ²³⁸Pu content is high), and storage.

The bulk of the aqueous processing of plutonium takes place in nitric or hydrochloric acid solutions and most plutonium solids are precipitated from these solutions (Cleveland, 1980; Christensen, Bowersox *et al.*, 1988). The most common precipitations are oxalate, peroxide, hydroxide, and fluoride. The typical reasons for using these precipitations are:

- Good recovery of the plutonium can be obtained in the solid in a form suitable for preparing metal or oxide.
- Relatively concentrated plutonium nitrate or chloride solutions can be largely or partially purified from many cationic impurities.
- Precipitation from relatively dilute solutions provides a very quick and convenient method for concentrating plutonium.
- Calcination at 500-800 °C readily converts properly precipitated Pu(III) and Pu(IV) oxalates to PuO₂ which is suitable for direct oxide reduction with calcium to the metal or hydrofluorination to PuF₄ that is then reduced to metal.
- Precipitation of plutonium or americium hydroxides from waste solutions such as oxalate or peroxide filtrates generally provides an effective method to recycle the plutonium and americium in the separated precipitate and to disposition the alkaline filtrate to low-level waste treatment operations.

This group of common precipitation methods will be briefly reviewed. The detailed procedures used at different facilities have varied quite widely because of the many facility-specific factors that enter into the process design. Both batch and continuous processes have been developed for these precipitations.

Plutonium(III) oxalate precipitation

Since the time of the Manhattan project, workers have found it useful to precipitate the easily filterable turquoise-blue Pu₂(C₂O₄)₃•10H₂O by reducing plutonium to the trivalent state in low acid solution and carefully adding an oxalic acid solution. Directly adding solid oxalic acid will produce a crystalline precipitate with a smaller average particle size (Christensen, Bowersox *et al.*, 1988). The solubility of Pu₂(C₂O₄)₃•10H₂O can be approximated by the expression [Pu (mg L⁻¹)] = 3.24[H⁺]³[H₂C₂O₄]^{-3/2} (Harmon and Reas, 1957). However, the typical filtrate from a production run will have somewhat higher concentrations of plutonium (0.1-0.5 g L⁻¹) left in solution than that calculated from this equation. The precipitation is useful over a wide range of conditions when the Pu(III) concentration is more than 1 g L⁻¹ and with less than 4 M acid. The Pu(III) oxalate precipitation gives good decontamination factors from such impurities as Al(III), Fe(III), and U(VI). There is less decontamination from sodium, potassium and calcium and none from Am(III). Plutonium(III and IV) can be scavenged from very dilute solutions using Ca(II) or Pb(II) oxalates as carriers (Maraman, Beaumont *et al.*, 1954; Akatsu, 1982; Akatsu, Moriyama *et al.*, 1983).

Plutonium(IV) oxalate precipitation

Plutonium(IV) precipitates as the tan solid $\text{Pu}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$ from low acid solutions upon addition of oxalic acid, but is usually a very fine solid and tacky at room temperature (Christensen, Bowersox *et al.*, 1988). Precipitation at elevated temperatures can greatly improve the filterability of the solid. Typical losses of plutonium to the filtrate in practical operations are 0.2-0.5 g L⁻¹. The precipitation is used over a wide range of conditions with Pu(IV) concentrations greater than 1 g L⁻¹ and acid concentrations between 1-5 M. The decontamination factors for impurities such as Al(III), Fe(III) and U(VI) are typically higher than for the Pu(III) oxalate method. There is no decontamination from Am(III).

The French process used to make MOX fuel in the MELOX plant uses a PuO_2 powder derived from carefully controlled precipitation of Pu(IV). The Pu(IV) oxalate provides a crystal morphology that gives the required characteristics in the oxide powder for mixing and grinding with uranium oxide to prepare the MOX pellets. However, the MOX material does not have U and Pu oxides in a true solid solution and the Pu oxide domains can be difficult to dissolve in nitric acid at higher burn-ups. Recently the CEA has been studying the coprecipitation of U(IV) and Pu(III) with oxalic acid. Pu/(U+Pu) ratios as high as 29% and 45% were used and the mixed solution of U(IV) and Pu(III) in nitric acid was mixed with a concentrated solution of oxalic acid. The solid was converted into oxide at 700 °C under Ar flow. X-ray diffraction and SEM analysis demonstrated the formation of a solid solution of $(\text{U,Pu})\text{O}_2$ with a controlled oxygen stoichiometry and well-defined particle morphology that resembles that of the oxalate precursor solid (Arab-Chapelet *et al.* 2008).

Plutonium(IV) peroxide precipitation

Plutonium peroxide is an olive-green solid formed by the addition of hydrogen peroxide solutions to acid solutions of Pu(IV). The typical range of acid concentration is 2.5-5.5 M. The solutions are often cooled to 10-15 °C to reduce the decomposition of hydrogen peroxide. High levels of iron, copper, manganese or nickel catalyze the decomposition of the H_2O_2 and interfere with the precipitation. At higher acid concentrations and with careful H_2O_2 addition, a very filterable hexagonal form of plutonium peroxide precipitates. At lower acidities a gelatinous cubic form precipitates that is difficult to filter. Plutonium peroxide is not a stoichiometric compound and its O:Pu ratio may approach 3.5 (Cleveland, 1979; Cleveland, 1980), but does not reach 4.0 as is suggested by the formula $\text{Pu}(\text{O}_2)_2$. Anions such as nitrate, chloride and sulfate, if present in the solution, are incorporated into the solid. Indeed, sulfate is added in some processes at a concentration of 0.1-0.3 M to nitric acid solutions to improve the filterability of the peroxide precipitate.

The Pu(IV) peroxide precipitation is a powerful method for purification of plutonium from many impurity elements except those such as Th, Np, and U that form similar peroxides under these conditions. Unlike the oxalate precipitations, Am(III) is removed to a high degree. The excellent decontamination factors obtained for many elements and the use of one reagent that is easily decomposed to water and oxygen in subsequent operations are the major advantages of using this process. The disadvantages are greater losses of plutonium in the filtrate (typically 0.1 to 0.5%) and violent decomposition that can occur during precipitations in the presence of high concentrations of iron and other metal ion catalysts for the decomposition reaction.

Plutonium(III) fluoride precipitation

Addition of aqueous HF to a solution of Pu(III) in nitric or hydrochloric acid precipitates blue-violet $\text{PuF}_3 \cdot x\text{H}_2\text{O}$ ($x \sim 0.75$) (Christensen, Bowersox *et al.*, 1988). The Pu(IV) concentration should be kept low because the hydrated PuF_4 precipitate is very gelatinous and much more soluble than the trifluoride. Significant Pu(IV) content will thus increase filtering time and plutonium losses to the filtrate. Reducing agents such as hydroxylamine, sulfamic acid or ascorbic acid are commonly used. With careful oxidation state control losses of plutonium to the filtrate are very low (0.05-0.1%). A disadvantage of preparing any fluorine-containing compound of plutonium is increased production of neutrons from alpha-n reactions relative to the oxygen, carbon, and nitrogen-based precipitants. The trifluoride precipitation does not give decontamination factors from cationic impurities that are as high as the oxalate or especially the peroxide precipitations. It gives moderate decontamination from many impurities including iron, but not from aluminum, zirconium, and uranium. Dried PuF_3 can be roasted in oxygen to produce a mixture of PuF_4 and PuO_2 that can be directly reduced with calcium metal to give 95-97% yields of plutonium metal.

Plutonium hydroxide precipitation

Hydroxide precipitation is quite useful to produce a filtrate with very low levels of plutonium. Sodium or potassium hydroxide solutions are commonly added to precipitate the gelatinous green Pu(IV) hydroxide (Christensen, Bowersox *et al.*, 1988). If Pu(III) is present, it will slowly oxidize to Pu(IV). Many other metal ions will precipitate as hydroxides as well or be carried by the plutonium hydroxide so that this is not a useful purification procedure. The hydroxide is generally difficult to filter. If large amounts of magnesium or calcium are present, the voluminous hydroxide precipitates of these metal ions make filtration especially difficult, unless they are avoided by carefully controlling the pH. The dried hydroxide cake can be recycled for plutonium recovery by dissolving it in acid. The formation of the Pu(IV) oxy-hydroxide polymer should be avoided because this material behaves quite differently from the hydroxide precipitate and can be quite difficult to redissolve in acid.

Miscellaneous precipitations

Other precipitations have been tested for plutonium processing operations, but have not been deployed or as widely used as those reviewed above. These include CaPuF_6 and Cs_2PuCl_6 from acid solutions for metal production operations (Christensen, Bowersox *et al.*, 1988; Muscatello and Killion, 1990) and $(\text{NH}_4)_4\text{PuO}_2(\text{CO}_3)_3$ or mixed $(\text{NH}_4)_4(\text{Pu,U})\text{O}_2(\text{CO}_3)_3$ from alkaline solution for the preparation of mixed oxide fuels (Roepenack, Schneider *et al.*, 1984).

Examples of Precipitation, Coprecipitation, and Sorption Separation Methods for Fission Products or Other Metal Species

Cesium and strontium recovery at Hanford

A variety of precipitation and coprecipitation processes were used at various stages to recover Cs and Sr from the waste tanks at Hanford. The Cs-137 and Sr-90 were recovered for use as irradiation sources and thermoelectric generators, to reduce heat load in the waste tanks, and to explore methods for removal of Cs and Sr in advanced nuclear power cycles. Some selected examples are briefly outlined, but much more detail is available on the operation of the processes (Gasper, www.if.uidaho.edu/~beitgeor/hlwfiles/Cs%20and%20Sr%20Recovery%20and%20Encapsulation.pdf).

The first 30,000 curies of Cs-137 was recovered from the tank wastes using a nickel ferrocyanide precipitation process. The feed was the acid raffinate from PUREX operations that was concentrated by evaporation and partially denitrated (CAW for Current Acid Waste). The CAW feed was neutralized with NaOH and ammonia gas to precipitate the bulk of the fission products and Fe, Al, Cr, and Ni. The filtered supernatant containing the Cs was acidified, boiled to remove CO₂ and the pH adjusted to 4. Soluble nickel and ferrocyanide salt solutions were added simultaneously to precipitate Ni₂Fe(CN)₆ which ion exchanges some of the Ni for Cs. The loaded nickel ferrocyanide was metastasized with Ag₂CO₃ to generate Cs₂CO₂ and silver loaded nickel ferrocyanide. The Cs recovery was greater than 99%. The ferrocyanide precipitation process was eventually replaced by a phosphotungstic acid (PTA) precipitation of Cs directly from the CAW feed. The PTA precipitation process was used to recover over 18 megacuries of Cs-137.

The first megacurie of Sr-90 was produced at Hanford using a lead sulfate coprecipitation process. Sodium sulfate and tartaric acid (used to hold iron in solution) were added to the acidic waste stream from PUREX operations. Then Pb(NO₃)₂ and sodium hydroxide were added to precipitate PbSO₄. The PbSO₄ was separated by centrifugation. Sodium hydroxide and sodium carbonate were added to convert the sulfate to the carbonate. The PbCO₃ was dissolved in nitric acid and oxalic acid added to precipitate lead, cerium, and the other rare earths leaving the Sr in solution. This method was later replaced with a solvent extraction process using di-2-ethylhexylphosphoric acid to recover strontium.

Additional examples of cesium precipitants or ion exchangers

A review by Todd et al. (2004) covers a broad range of cesium and strontium separation processes and some selected examples of cesium precipitants/ion-exchangers are noted here. The use of phosphotungstic acid to precipitate Cs from acidic solution was noted above. The compound ammonium molybdophosphate has also been used to selectively recover Cs from acidic tank wastes. It has usually been deployed as a solid powder that is added to the solution and ion exchanges Cs for ammonium, but the compound has also been bound in a polymer binder, polyacrylonitrile (PAN), and used in a column.

Many types of metal ferrocyanides have been studied for Cs removal from acidic to basic solutions. These materials are finely divided solids that are typically added to the Cs-containing solution and recovered by centrifugation or filtration. Some granular solid forms and PAN-

bound materials have been used in column mode. The removal of Cs involves both ion exchange for the metal ions, protons, or ammonium cations not bound in the cubic $\text{Fe}(\text{CN})_6\text{-M(II,III)}$ framework and more complex incorporation of cesium into new phases that form in the solid material.

Sodium tetraphenylborate has been used as a selective precipitant for Cs from alkaline solutions. It was proposed for in-tank precipitation of Cs for processing of high-level waste supernatants at the Savannah River site. Problems with rather rapid catalytic decomposition of tetraphenylborate to give benzene from metal species in the complex tank mixtures resulted in the adoption of the Caustic-Side Solvent Extraction process based on calixarene-crown type compounds as the primary method to remove Cs from the alkaline tank solutions.

Examples of Sorbents for Radionuclides

Many solid materials have been used as sorbents for radionuclides and are used in radioanalytical procedures. Activated charcoal, silica, alumina, clays, and iron hydroxides are among the many materials used to sorb ions from solutions. The negatively charged surfaces of oxide materials can sorb cations from solution sometimes with seemingly surprising selectivity. For example, in a radioanalytical procedure for sodium it is noted that in concentrated HCl only sodium and tantalum, among 60 elements tested, were retained on hydrated antimony(V) oxide, $\text{Sb}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ (Kleinberg, 1990). Careful preparation of the sorbent material is often required. For example, a large literature exists to prepare silica and alumina materials for applications in chromatographic columns. Sorbents have been deployed as finely divided solids or used in columns. The compendia of radioanalytical procedures noted above contain other examples of the use of sorbents.

Sorbents are commonly used for wastewater treatment in industry and that is also true for nuclear processing applications. Sand filters that are used for particulate removal in wastewater treatment can also function as sorbents for low-levels of some radionuclides. Silica has been used to remove radioactive zirconium-niobium from solutions of uranyl nitrate produced in PUREX operations (Karraker, 1957). Iron hydroxides are used as sorbents, but more often as a carrier in precipitations and soluble salts of both Fe(II) and Fe(III) are used in the initial precipitation reaction. Iron hydroxide precipitations have been used to remove low-level activity from plutonium and americium from actinide processing facility wastewaters at Los Alamos to very low levels before discharge to the environment. More recently ultrafiltration and reverse osmosis steps have replaced the iron hydroxide precipitation to reduce overall solid waste volumes (Moss et al., 1998).

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