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PRODUCTION OF PLUTONIUM METAL FROM AQUEOUS SOLUTIONS

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DATA RECORD – WORKS TECHNICAL DEPARTMENT

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SAVANNAH RIVER PLANT

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Cation Exchange Concentration

Introduction

The primary separation of plutonium from irradiated uranium by the Purex solvent extraction process at the Savannah River Plant produces a dilute plutonium solution containing residual fission products and uranium. A cation exchange process is used for concentration and further decontamination of the plutonium, as the first step in the final preparation of metal. Requirements for this primary isolation step are:

- Additional decontamination.
- Low waste losses.
- A suitable product (concentration and chemical composition) for subsequent precipitation.
- Ability to process dilute feed (as weak as waste).

Cation exchange originally was installed as a potential improvement on evaporative concentration, which poses safety and corrosion problems. Ion exchange has operated well; no evaporators ever have been installed for the final plutonium concentration.

The exchange units are small fixed-bed columns of Dowex 50W resin, with their dimensions fixed by requirements of nuclear safety. The process was developed at Oak Ridge National Laboratory and is still essentially as outlined by Tober.[7]

Process Description and Chemistry

The columns are operated on a batch basis with counterflow absorption and elution (see figure 1). The solvent extraction product solution flows down through the column, until a desired load of plutonium has been absorbed. Then, a wash of dilute sulfuric acid down the column removes some of the residual uranium and fission-product zirconium and niobium that were absorbed with the plutonium.

Next, an eluting solution (5.7M nitric acid - 0.3M sulfamic acid) flows up through the column and the bulk of the plutonium is removed, leaving a heel. The eluting solution is followed by an upflow reconditioning wash which restores the low acid condition so the column is ready for the next cycle of absorption. The solution from the top of the column is divided into fractions according to plutonium content; a rich portion is taken for the product fraction while fore and tailing fractions are recycled. Additionally there are certain nonroutine column operations, including an extended product elution for heel removal, a refrigerated wash for degassing or reduction purposes, and a fission product elution if the column accumulates excessive radiation.

The basic equilibrium involved is:

$$Pu^{+3} + 3H\ (Resin) = Pu\ (Resin)_3 + 3H^+$$

Plutonium is absorbed from the dilute nitric acid feed solution produced by the solvent extraction process and is eluted by the strong acid. In this Plant, the Pu(III) system is favored over Pu(IV) for absorption for several reasons:

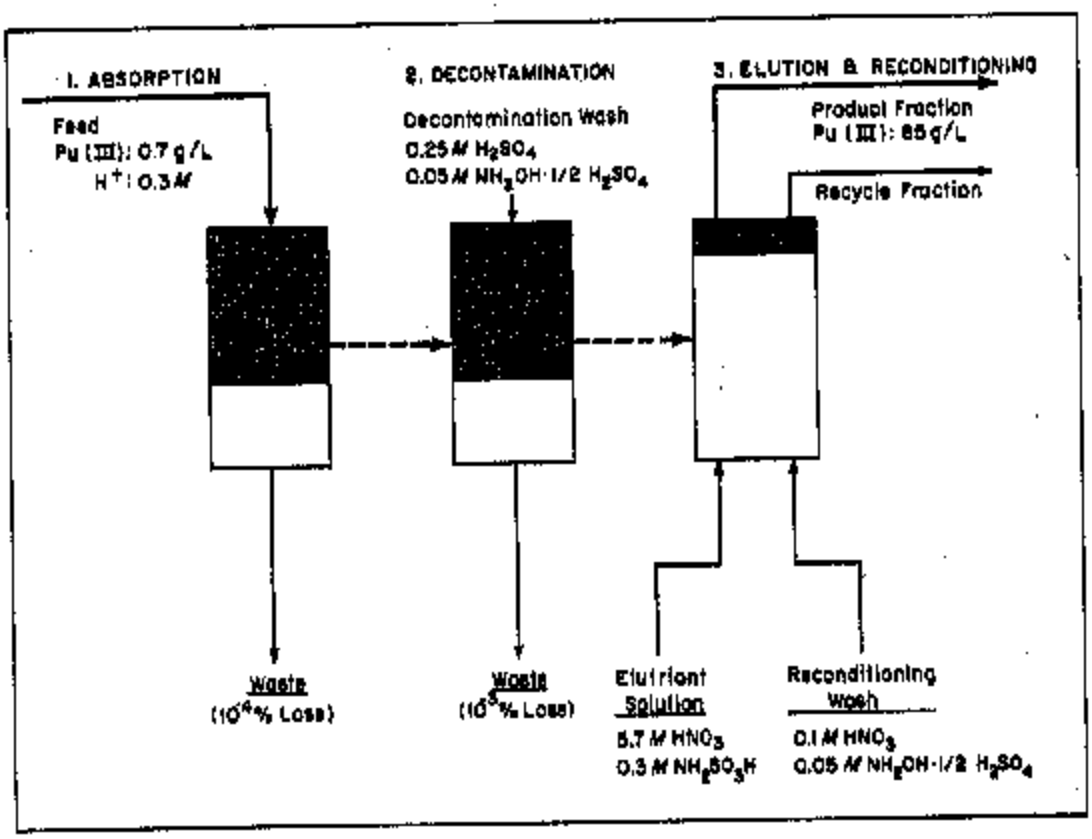


FIGURE 1. CATION EXCHANGE COLUMN CYCLE

- Hydroxylamine sulfate has already been added to the solvent strip solution in the canyon to aid in the back extraction of plutonium as Pu(III), so no further feed adjustment is required for ion exchange.

- The sulfate in the decontamination wash would complex Pu(IV) and cause high losses if the absorbed Pu were in that form.

- The capacity of the resin (hence the column batch size) is larger with Pu(III).

- The elution characteristics of Pu(III) are better.

The Pu(III) state is stabilized by hydroxylamine in dilute nitric acid solutions and by sulfamic acid in strong acid. In addition, this oxidation state is very favorable for subsequent precipitation processes and appears to have unique advantages in the peroxide precipitation process, as discussed later.

One potential problem with Pu(III) is the instability with respect to oxidation in strong nitric acid; the reaction can become autocatalytic with vigorous evolution of nitrogen oxide gases. However, the rate of oxidation is dependent on concentration and, by experience, there is little chance of rapid oxidation if sulfamic acid stabilizer is present and if the peak concentration of plutonium in the strong-acid eluting solution is less than 130 g/ℓ. With proper control so that concentrations above this level are avoided, many months of operation have been maintained without appreciable oxidation.

Separation of impurities from plutonium by the resin can occur by several mechanisms:

- Anionic or un-ionized impurities, or weakly absorbed cations, can pass through the resin unabsorbed.
- Materials that are absorbed, but less strongly than plutonium, are displaced downward by plutonium during absorption.
- Materials that are held more strongly than plutonium in the elutriant solution may be left on the resin during plutonium elution.
- Materials complexed preferentially by sulfate may be removed from the resin selectively with the decontamination wash.

All of these effects are important in the separation from specific impurities, as discussed later.

Gas on the resin interferes with fluid flow and with the solution-resin exchange; it may be formed in the oxidation of plutonium, or by radiolysis of solution when a loaded column remains idle, or by reactions of the reducing agents (hydroxylamine and sulfamic acid). This gas can be removed [and any Pu(IV) in the column reduced to Pu(III)] with a refrigerated wash of dilute nitric acid and hydroxylamine.

Equipment

The ion exchange columns are packed beds. The resin retainer at the bottom of the column is fixed; the top resin retainer is movable and spring-loaded to maintain a compressed bed as the resin expands

and contracts in different solutions during the process cycle. Any fluidization of the bed markedly decreases the efficiency of the operation. Two diameters of columns have been used, 7 inches and 10 inches (see figure 2). The length of the resin bed in the 7-inch unit has been 13 inches or 15.5 inches in two modifications. To maintain nuclear safety, the internal height of the 10-inch unit is limited further and the length of the resulting resin bed is 5 inches; two such columns, separated adequately to reduce interaction, are operated in series as a single unit with an effective bed depth of 10 inches. Both the 7-inch and 10-inch diameters are considerably larger than the safe diameter of a reflected, infinitely long cylinder, which frequently is used for design purposes; the larger diameters are based on the "limited safety" concept, with the limitations on the height of the column, interaction, reflection, and possible concentrations considered adequate for safe operation.

As the permissible diameter is increased, the column time cycle is decreased; processing rates are based on flow per unit area, so increasing column area increases the total flow. For sharp separation of various fractions, the column design has the minimum dead space or mixing volume at the ends of the bed that is consistent with good distribution of solution.

Gas must be excluded as much as possible from the resin beds for efficient exchange and the units are designed specifically from this viewpoint. An ever-open vent provides a means of escape for gas introduced in the feed so it will not enter the resin bed. The vent also insures relief of excessive pressurization from any source.

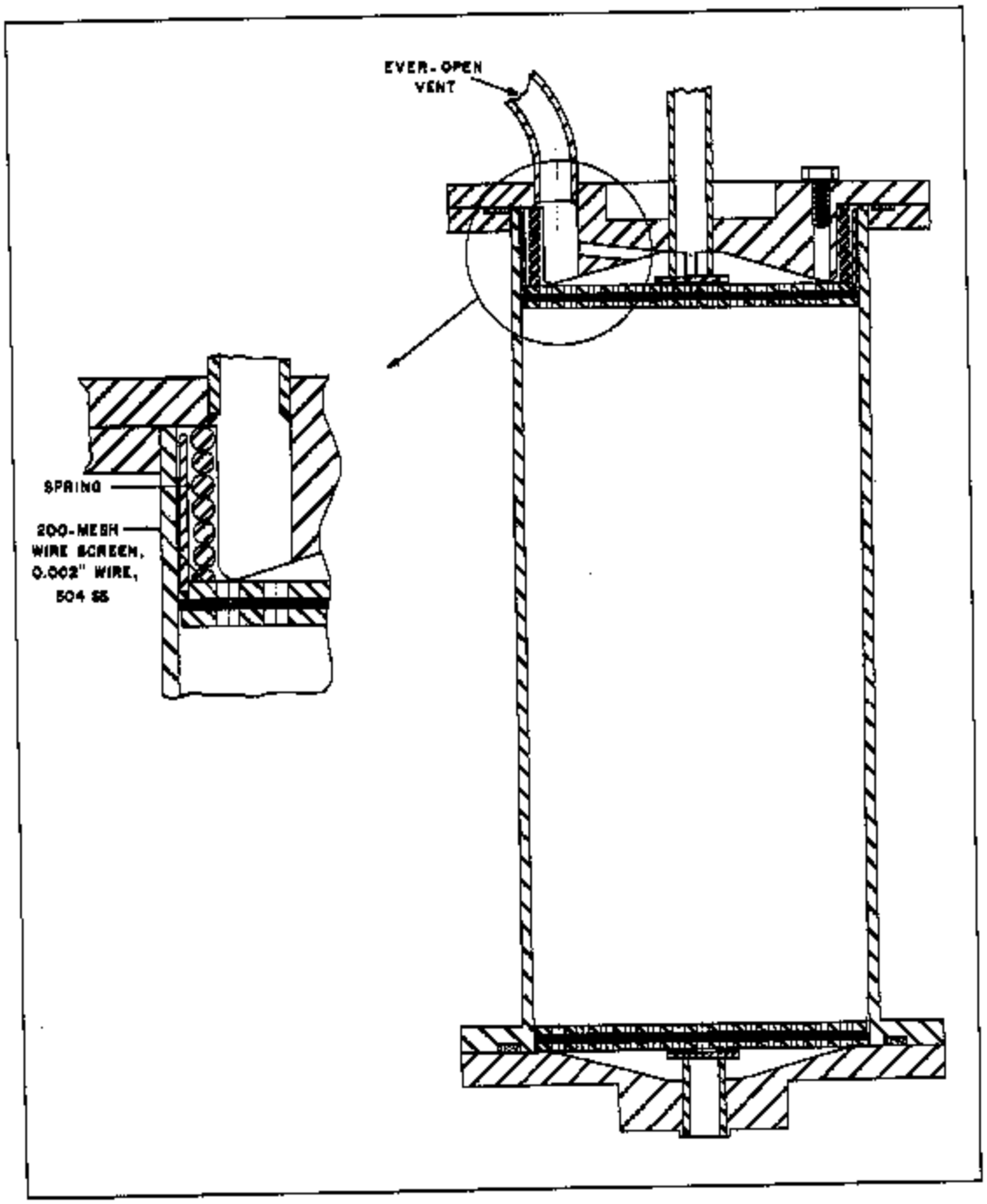
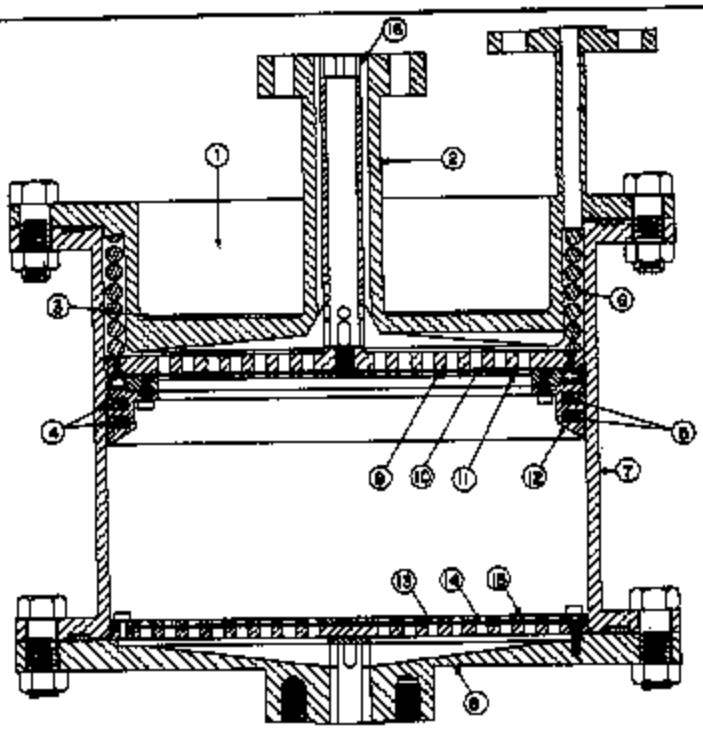


FIGURE 2A. 7-INCH ION EXCHANGE COLUMN



Item	Description
1	Expanded Polyethylene Foam
2	Column Top
3	Polyethylene Coated Cadmium Plate
4	"Teflon" Wiper Rings (Glass Reinforced)
5	Metal Wiper Springs
6	Stainless Steel Follower Plate Spring
7	Column Body
8	Column Bottom
9	Top Screen
10	Top Support Plate
11	Screen Support Plate (Top)
12	Wiper Holder
13	Bottom Support Plate
14	Bottom Screen
15	Screen Support Plate (Bottom)
16	Guide Tube

FIGURE 28. 10-INCH ION EXCHANGE COLUMN

The column feed and effluent lines are arranged and vented in such a manner that the columns always will be full of solution, and cannot drain accidentally.

The resin used is Dowex 50W, 10 to 12% cross-linked, 50 to 100 mesh. The particle size provides a compromise between rapid exchange and high flow rate. The resin is graded hydraulically before use and the pressure drop of the graded resin is in the range of 9 to 15 psi/ft of length at standard flow (15 to 20 ml/min/cm^2); the grading is important because even a few percent fines increases the pressure drop greatly. The feed also is prefiltered to prevent solids from raising the pressure drop by accumulating in the resin beds, which act as excellent filters themselves.

A properly installed column generally will give at least one year of service; the limit is set by slower flow and increasing losses. The pressure drop increases from fractured beads; the exchange capacity decreases as a result of plutonium alpha radiation. About the only failure that can occur in these simple units is a jammed follower plate, which may result from improper assembly. The failure is apparent quickly. If the plate jams with the bed in the expanded position, the bed fluidizes during elution and gives low product concentrations and increasing losses; if the plate jams with the bed in the contracted position, resin is forced past the retainer when it expands.

A well-designed, packed bed has a "volume change" of 50% of the bulk volume of the resin bed; the unit represents the volume required for a change in composition of the feed to begin to appear

in the effluent. This "volume change" is a useful unit for design work since it can be used to standardize flowsheets on columns of different sizes, as long as the length of the columns is the same. The performance characteristics of packed beds of fine resin are a function only of length, within a wide range of diameters, and laboratory runs have been scaled up successfully by a factor of 500. For example, performance of the two 10-inch-diameter, 5-inch-deep beds in series corresponds to the laboratory performance of a single 10-inch-long column of 1 sq cm area.

Steady-State Batch Operation

Countercurrent operation of a fixed bed of resin is a simple concentration method that frequently is overlooked in favor of more sophisticated, but less efficient, methods. Flow direction is the key to satisfactory performance with this plutonium cation exchange system; traditional cocurrent operation with downflow absorption and elution is not feasible for operation requiring large throughput. The following discussion of the effect of variables on the plutonium system will illustrate the general application.

Process stability is achieved and low losses are maintained if the movement of plutonium down the column during absorption and decontamination is balanced by movement upward during elution. During absorption, a band of saturated resin grows down the column to a point governed by the plutonium capacity of the resin in the feed solution. Below the loaded band and short exchange zone, the clean resin serves as a stripping section and reduces the losses to a

negligible level in the space of only a few inches. The decontamination wash of dilute sulfuric acid causes a further downward movement of the loaded band. During upflow elution, the elutriant solution moves the plutonium back up the stripping section, then is enriched progressively as it flows through the loaded band. At every stage of elution, the product solution leaves the column after contact with the most saturated resin left, so that maximum product concentration is reached. Very high product concentrations can be reached this way with long loaded bands; the band length for Pu(III) is limited deliberately to avoid high concentrations and possible oxidation. The total time cycle can be short since the elution can be stopped, leaving a heel on the column, when the desired amount of plutonium has been collected as product.

For general design work, possible stable cycles can be calculated from resin saturation data and distribution coefficients. For any flowsheet, the maximum load of plutonium is fixed by the volume of resin in the column and the grams of plutonium held per liter of resin at given feed acidities and plutonium concentrations, with allowance for a stripping section of resin. The limiting volumes of absorption flow and decontamination wash down, and minimum volume of elutriant up, are functions of the relative movement of the dilute plutonium in the stripping section. The distance moved by the plutonium in the stripping section is directly proportional to the volume of a given solution put through and inversely proportional to the distribution coefficient of plutonium between the resin and that solution. This relation between downward and upward movement is at equilibrium conditions. Comparatively rapid flow rates

actually are used to achieve minimum time cycles and the net effect of greater spread during absorption and reduced efficiency during elution requires increased elutriant volume to maintain stability.

The actual plant operating conditions are a matter of economy and compromise; many combinations of losses, decontaminations, product concentrations, and recycle fractions can be set, with some limits set by the required throughput. Typical operating ranges are summarized below. The values do not represent extremes, but are nominal figures that represent extended periods of operation. It must be understood that the various conditions represent the experience over years of operation, and do not represent run-by-run changes or uncertainties. In practice, individual flowsheets have been maintained for months at a time.

Process Experience

Absorption. Typical values for some of the variables are shown in table I. The ranges on the feed plutonium and the acidity have been set by various solvent extraction flowsheets.

Table I. Absorption

Feed Composition	
Plutonium, g/ℓ	0.2 - 1.2
HNO_3, M	0.2 - 0.6
$NH_2OH \cdot 1/2\ H_2SO_4$, M	0.025 - 0.05
Column Absorption Batch,* g Pu	
7 in. dia	350 - 775
10 in. dia	750 - 850
Column Heel, % of absorption batch	5 - 15
Flow Rate, ml/min/cm^2	10 - 20
Losses (Absorption and Decontamination Wash), %	10^{-4} - 10^{-1}

* Amount loaded in addition to the heel.

The wide range in absorption batch size represents the extremes from conservative startup conditions, with dilute feed and high acid, to strong plutonium and low acid. The nominal load on the 7-inch-diameter column is 700 grams. Much more dilute feed (1×10^{-2} g/ℓ) has been processed during startup and flushing operations. In another specialized application, feed up to 6 g Pu/ℓ has been standard. The absorption batch size is limited primarily to prevent excessively high plutonium concentrations (oxidizing conditions) during elution, as well as for control of losses. The performance of the subsequent peroxide precipitation step is sensitive to the concentration of sulfate, and a byproduct of oxidation of plutonium during elution is the oxidation of sulfamic acid to sulfuric acid. On the 7-inch columns, for example, there was no outward manifestation of oxidation as the batch size was raised from 750 to 775 grams,

but the small increment was sufficient so that sulfate in the eluate, which had been below detectable limits, reached 0.02M and interfered with further processing.

Absorption at 20 ml/min/cm^2 gives fairly sharp absorption bands and reasonable time cycles. The limit here is determined primarily by pressure drop in the system and the available gravity head; it has been considered undesirable to pump-feed the columns and risk excessive pressurization. Higher rates would decrease the absorption part of the time cycle but would affect the losses and other characteristics adversely and no great effort has been made to increase the rate.

The losses, as measured, include the total column waste from absorption and from the decontamination wash. The loss can be set to almost any desired value by adjustment of the operating conditions. Losses as low as 1×10^{-4}% have been maintained for extended periods of time, but the low level requires more elutriant, with resultant longer cycles and larger recycles, for any given set of other conditions. For minimum cycle time, the elutriant volume may be reduced until the losses reach whatever is deemed acceptable (generally 1×10^{-2}%).

Decontamination Wash. The volume of the sulfuric acid wash under the conditions specified in table II is set on a sliding scale, according to the amount of uranium and Zr-Nb in the feed and the required decontamination. Concentration of the sulfate wash is a matter of choice; the 0.19M solution gives slightly poorer decontamination than the 0.25M solution but the losses are considerably

lower. Below a concentration of 0.19M there is an increasing loss in decontamination power. Standard wash volumes used have been 6 to 24 volume changes.

Approximate ranges in decontamination factors which have been obtained are shown. Decontamination, even with no wash, is due to several mechanisms as explained previously. Ru apparently exists in the feed in two forms, one of which does not absorb when the column is being loaded. The other form is eluted with the plutonium; the range in decontamination represents the split between the species. None of the absorbed form is removed with sulfate so there is no change in decontamination as a function of wash volume.

Table II. Decontamination Factors

		Uranium		
Volume Changes of Wash	Ru	U/Pu <0.1	U/Pu >0.5	Zr-Nb
0	2 - 4	4 - 20	>20	1 - 10
24	2 - 4	30 - 80	>100	10 - 70

Wash Composition

H_2SO_4, M	0.19 or 0.25
$NH_2OH \cdot 1/2\ H_2SO_4$, M	0.05
Volume, volume changes*	6, 12, 18, or 24
Flow Rate, ml/min/cm^2	2 - 3

* Volume change is 50% of the physical volume of the bed.

Decontamination from uranium is obtained by several mechanisms, including breakthrough and sulfate complexing. It is absorbed more weakly than plutonium. At low concentrations it is displaced down the column, while at high concentrations it will actually break through and appear in the absorption waste. Actual displacement and breakthrough points are functions of the uranium, plutonium, and acid in the feed and account for the spread in decontamination values at no wash. Complexing of uranium by sulfate increases the decontamination considerably with the maximum wash volume; smaller washes give intermediate factors.

Decontamination from fission product Zr-Nb with no wash is a case of preferential elution of the plutonium which leaves the Zr-Nb behind, while sulfate complexing increases the decontamination when the wash is used. The range in decontamination apparently is a function of the history of the feed. The two fission products, Zr-95 and Nb-95 are analyzed together and treated as one; they have similar but not identical behavior on the cation exchange resin so variations in their ratio which result from changes in solvent extraction flowsheets also give variations in decontamination. Also, off-standard solvent extraction operations apparently can form some abnormal species of Zr-Nb which does not decontaminate readily and can reduce the decontamination below the normal lower limit. The species has not been identified, but the circumstances under which it is encountered indicate that it is formed by association with degraded organic material from the solvent.

Other decontamination agents have not been tested widely as a replacement for sulfate because of various specific objections such

as potential precipitation of plutonium, interference with normal waste handling, and corrosion. Dilute fluoride ion has been tested, but it interfered with operation considerably. Erratic column performance was credited to the complexing power of fluoride for Pu(IV) and possible precipitation of both PuF_3 and PuF_4. In addition, traces of fluoride ion that spread through the system dissolved fission product activity that had deposited on the walls of the equipment and gross amounts of activity appeared in streams that normally were inactive.

Elution. The composition of the elutriant has not been varied deliberately since startup. It represents about the maximum nitric acid concentration that is compatible with a Pu(III) flowsheet, and the sulfamic acid is near the solubility limit. The volume of the elutriant required is a function of all other operations and is based primarily on the waste losses, which are a function of the absorption conditions, column load, volume of decontamination wash, and the flow rates in these steps. The volumes shown in table III cover the range from the best to the worst combinations of these variables. The elutriant flow rate is a compromise between efficiency and time cycle. With the 50 to 100-mesh resin, there is little difference in elution characteristics at rates slower than 0.2 $ml/min/cm^2$. As the rate is increased to obtain shorter time cycles, the elution curve for plutonium begins to spread, the average concentration of a given volume of product solution decreases, the column heel increases (for a given elutriant volume), and losses increase. The effect on losses rapidly becomes greater at rates higher than 0.5 $ml/min/cm^2$ although the product concentration is

only slightly affected. In one series of experiments, the average concentration of a certain sized product fraction was successively 66.5, 66, and 64.5 g/ℓ at rates of 0.4, 0.5, and 0.6 ml/min/cm^2.

Table III. Elution and Reconditioning

Compositions	
Elutriant, M	
HNO_3	5.7
NH_2SO_3H	0.3
Reconditioning, M	
HNO_3	0.1
$NH_2OH \cdot 1/2\ H_2SO_4$, or	0.05
NH_2SO_3H	0.1
Volumes, volume changes	
Elutriant	1.6 - 4.0
Reconditioning	2
Flow Rates, ml/min/cm^2	
Elutriant	0.2 - 0.5
Reconditioning	0.2 - 0.8
Product Fraction	
Pu Concentration, g/ℓ	50 - 70

The exact composition of the reconditioning wash is not important and is a matter of convenience in make-up. Use of the same solution for reconditioning and the refrigerated degassing wash simplifies feed preparation. The volume of the reconditioning solution has not been varied because it is independent of practically all other conditions and represents the volume necessary to remove

strong acid. The initial part of the reconditioning is made at the same flow rate as the elution because it is still moving elutriant ahead of it. Once the acidity of the solution leaving the column starts to decrease, the rate can be raised as shown in the table. This reduces the time cycle without affecting the reconditioning appreciably.

Concentration of the product fraction and amount of plutonium in the recycle stream are largely a matter of choice. The 50 to 70 g/ℓ concentrations represent solutions that were compatible with the subsequent precipitation step. Higher concentrations can be obtained if smaller volumes of the product solution are taken from the peak of the elution curve, but the recycle increases. The amount of recycle also is increased when large volumes of elutriant are required to counteract large decontamination washes or other unfavorable conditions; the various combinations of cases give the wide variation in recycle.

Miscellaneous Operations. The conditions for the refrigerated wash and fission product removal steps are shown in table IV. The primary use for the refrigerated wash is for delays between process steps (such as overnight or weekend shutdowns) or for known presence of Pu(IV); it causes essentially no loss. Occasionally, accumulated fission products on the column must be removed to reduce the radiation so the unit can be replaced or maintained without shielding. Oxalic acid solution has been very effective for this purpose; ammonium citrate also has been used. These agents also complex plutonium so the plutonium heel on the column must be removed first

with an extended product elution step to prevent loss (10 volume changes of product elutriant is standard for this purpose). The volume of oxalic acid solution that is required for decontamination depends on the total activity and form of the fission products. In typical cases, the indicated volume has reduced the radiation from the column by factors of 20.

Table IV. Refrigerated Wash and Fission Product Removal

Refrigerated Wash	
Composition, M	
HNO_3	0.1
$NH_2OH \cdot 1/2\ H_2SO_4$	0.05
Flow Rate, ml/min/cm^2	5 - 15
Volume, volume changes	10
Fission Product Wash	
Oxalic Acid Concentration, M	0.5
Flow Rate, ml/min/cm^2	0.2
Volume, volume changes	5

Precipitation of Plutonium Peroxide

Introduction

The precipitation of plutonium peroxide is a standard method of isolating from solution a solid plutonium compound which can be fluorinated and subsequently reduced to plutonium metal. The peroxide system is desirable because it provides excellent decontamination from cationic impurities and because the only foreign material introduced (hydrogen peroxide) is destroyed easily in the heated filtrate. This simplifies the subsequent recycle of the residual unprecipitated plutonium. A disadvantage of the method lies in the handling of dissolved and solid peroxides, which can be violently unstable under certain conditions.

On the basis of prior experience, this precipitation method was selected for plutonium isolation at the Savannah River Plant, with feed to be supplied by the cation exchange system. Considerable development work was necessary to establish the best precipitation conditions, but ultimately precipitates could be produced routinely which filtered and dried rapidly, were dense and even visibly crystalline, and were so reactive and free from impurities that the subsequent fluorination step could be shortened drastically.

Process Description and Chemistry

A process block diagram is presented in figure 3. Hydrogen peroxide solution is added to batches of plutonium concentrate from the cation exchange step and the resulting precipitate of plutonium peroxide

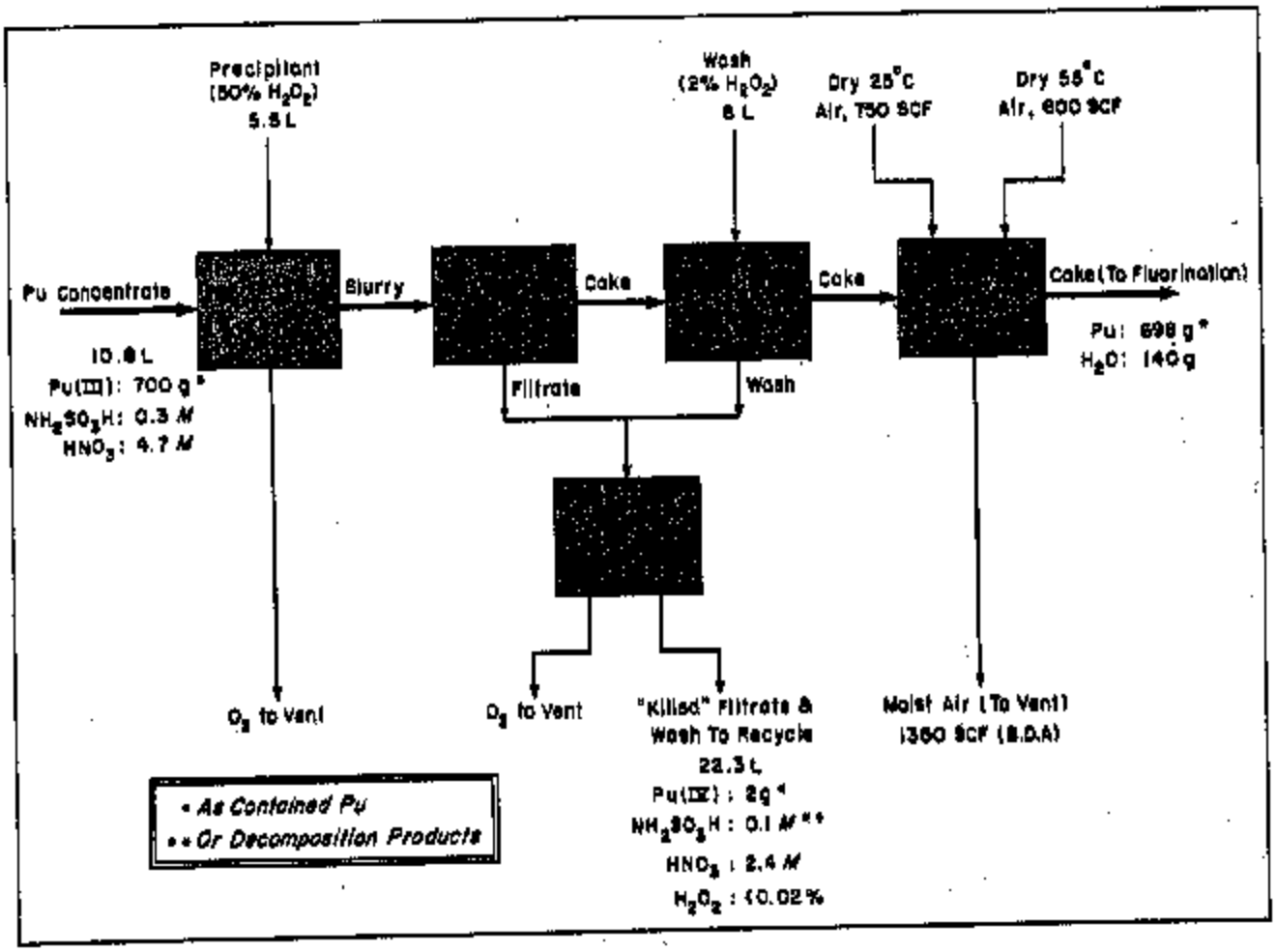


FIGURE 3. PRECIPITATION BLOCK DIAGRAM

is filtered, washed, and dried to a state suitable for fluorination.

The chemistry of the precipitation of the Pu(IV) peroxide from nitric acid solutions is complex, involving the oxidation-reduction behavior of H_2O_2 and Pu,[1] formation of at least two soluble peroxy-complexes of Pu,[1] formation of $(Pu\text{-}O\text{-}Pu)^{+6}$ hydrolysis dimers (in the weaker acid solutions),[4] and the formation of two different crystalline phases of the solid peroxide[5] (both of which contain coprecipitated anions).[2] Conditions for producing each of the crystalline phases were established by Leary et al,[4] who found that an undesirable (colloidal) face-centered-cubic form would precipitate from nitric acid solutions below 2M in acidity, but that at higher acidities a desirable hexagonal structure would form. They explained these observations on the basis of the larger proportion of hydrolyzed Pu(IV) in low-acid solutions. These results also tended to clarify the function of the coprecipitated sulfate ion, which had been added to the feed for many years for the purpose of "improving" the precipitate. Sulfate is an effective coagulant for positively-charged colloids, such as the peroxide precipitate formed in low acid.[3] These results also indicated that sulfate had little effect on which phase would form in precipitation.

It was found in Plant operation that if the desired (hexagonal) phase could be formed in the first place through proper choice of precipitation conditions, there was no need for sulfate addition. The elimination of the use of sulfate proved to be of extreme importance, as cakes formed under satisfactory conditions of mixing without sulfate were about six times as dense and filtered six

times as fast as those formed under conditions of poor mixing with sulfate present to aid coagulation. In addition, the subsequent fluorination furnace cycle was shortened greatly when it was no longer necessary to remove the added sulfate from the cake by prolonged high-temperature roasting. The increased density of the peroxide was reflected in increased density of the tetrafluoride; the great benefit here was an increase in batch size and productivity in the fluorination and reduction equipment, in which the volume was limited.

The variables of importance in producing this satisfactory precipitate were identified and optimized. They were (1) rate of addition of H_2O_2 solution, (2) degree of agitation, (3) amount of H_2O_2 added under controlled rate, and (4) total amount of H_2O_2 added in the precipitation step.

The fact that the Pu in the feed solution is present initially as Pu(III) in this process is thought to aid the precipitation, since the oxidation to Pu(IV) by H_2O_2 is not instantaneous; the lower Pu(IV) concentration is conducive to the formation of larger crystals. Actually, precipitates from solutions which initially contained Pu(IV) (and no sulfamic acid), while still satisfactory, were not quite as good as those made from normal cation exchange concentrate.

Further experimental laboratory work would be rewarding in clarifying the precipitation mechanisms and the complex equilibria. The distinct change in precipitate properties when a certain minimum volume is added at a certain maximum rate during

precipitation suggests that there are both competitive and rate determining steps. Spectrophotometric methods appear to be particularly applicable to this study.

Equipment

A precipitator is shown in figure 4. It is made of glass, and cooled with stainless steel tubes containing "Freon" refrigerant. The agitator has a series of flat paddles or marine propellers on a central shaft.

A "boat" which is used for filtering, washing, and drying the cake is shown in figure 5. It is made of stainless steel and contains a 7-inch-diameter frit (porosity F sintered stainless steel 3/16-inch thick).

The peroxide destruction step indicated on the process block diagram (figure 3) is performed on the filtrate in stainless steel tanks heated electrically or with steam. Cooling water is also provided for these vessels.

Reagents are fed to the precipitators by gravity. Filtration, washing, and drying are all accomplished by the application of vacuum to the underside of the boat.

Process Experience

Precipitation. Conditions of precipitation are presented in Table V. A batch of concentrate is cooled, and H_2O_2 solution is added through a rate-controlling orifice until a predetermined

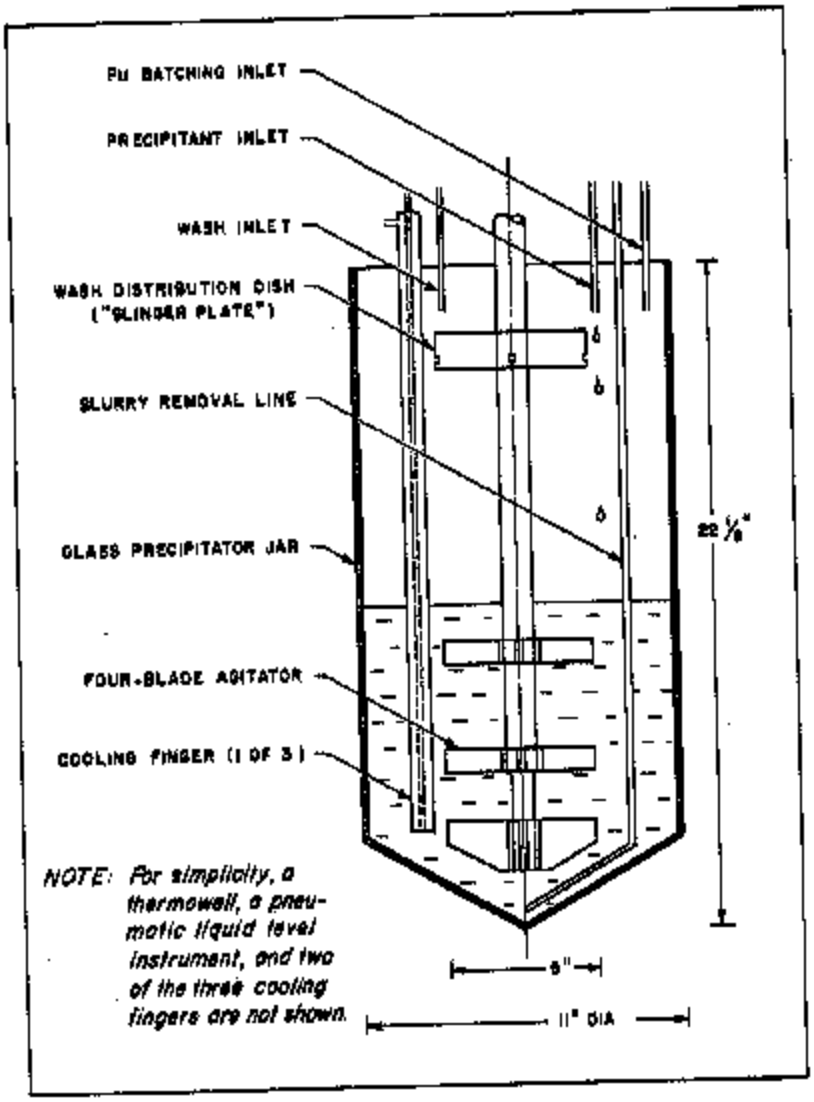


FIGURE 4. PEROXIDE PRECIPITATOR

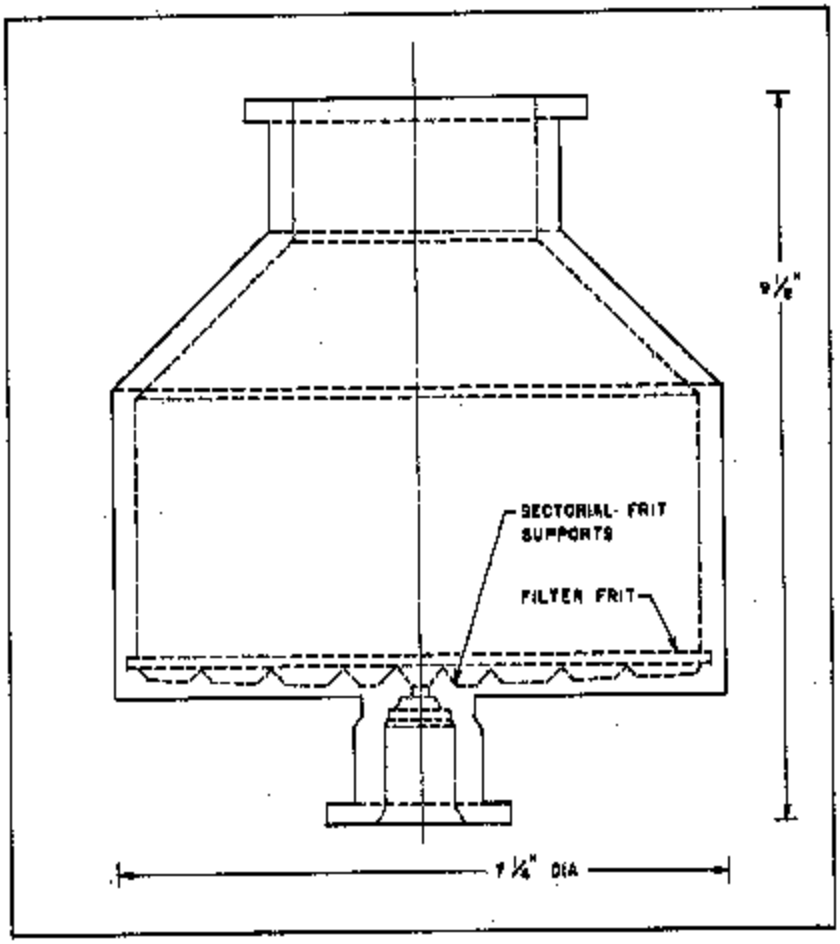


FIGURE 5. STAINLESS STEEL FILTER BOAT

volume has been added (enough to raise the total peroxide concentration to at least 2M. Under these conditions, in an acidity of about 4M, all traces of the red peroxy-complex[1] are gone and the slurry is tan colored). At this point, the remaining volume of H_2O_2 is added rapidly, to reduce the solubility of the precipitate by raising the total peroxide concentration to about 6M H_2O_2. (Note that the total volume of precipitant added is about eight times the stoichiometric amount required for oxidation and precipitation of the Pu.) The temperature is then lowered while the precipitate is digested, and the filtration is then performed.

The critical nature of the volume added at the slow rate cannot be overemphasized; filtration times increase sharply and density decreases if the peroxide is even a small fraction below the minimum amount indicated above. Also, the rate during slow addition appears to have a disproportionate effect, and too fast a rate gives markedly poorer performance, though it is difficult to separate the rate effect from mixing efficiency as discussed below. The total volume of peroxide added also affects the density of the precipitate, in addition to the expected effect on filtrate loss; the density decreases at the minimum total volume shown in table V.

The agitation during the addition of H_2O_2 is of great importance; too high an agitator speed will lead to the formation of fines, and too low a speed (or too fast an addition rate) allows precipitation to proceed in zones of incompletely mixed H_2O_2 (low-acid, high-peroxide conditions) which can produce the colloidal form

of the precipitate. Thus, it is of primary importance to prevent the existence of any region in the precipitator where the acidity falls below 2M, and to delay rapid additions until a proper foundation has been laid, ie, a peroxide content of at least 2M (in an acidity of about 4M). The upper limit on agitator speed, above which excessive fines are formed, corresponds to a blade tip-speed of about 5 feet per second for either turbine-type or flat-paddle agitators, both of which create considerable turbulence (this tip-speed limit holds for blades 2-1/2 inches and 5 inches in diameter). The tip-speed limit for marine propellers, which give good dispersion with little turbulence, is about 8 feet per second. In practice, the agitators are operated about 10% below the upper limit to give the best possible mixing without generating excessive fines.

The temperature conditions are not critical, but refrigeration is desirable since it minimizes catalytic decomposition of the H_2O_2 by the impurities in the feed. Feeds containing as much as 1.5 g Fe/ℓ are handled satisfactorily with the cooling available; the complexing effect of the sulfamic acid present in the feed may also tend to render the iron less harmful.

As indicated under "Process Description and Chemistry," precipitations are made in the absence of sulfate and sometimes in the absence of sulfamate. Precipitation yields are about 99.5%, and decontamination factors are comparable to those presented by Leary et al.[4]

Table V. Precipitation Variables

Variable	Nominal Value	Range Investigated
Pu Feed Solution		
Batch size, g Pu	700	350 - 700
Pu concentration, g/ℓ	65	50 - 70
H^+ concentration, M	4.7	4.5 - 5.0
NH_2SO_3H concentration, M	0.3	0 - 0.3
Precipitant		
H_2O_2 reagent strength, %	50	30 - 50
Volume 50% H_2O_2 added slowly, ℓ	2.4	1.8 - 3.0
Total volume 50% H_2O_2 added, ℓ	5.5	4.5 - 6.5
Addition rate during slow addition, ℓ/m	0.55	0.4 - 0.8
Agitator speed (5 in. flat paddles), rpm	225	150 - 350
Temperature		
During precipitation, °C	15	5 - 20
During digestion, °C	6	2 - 10

Filtration. The cold precipitator slurry is filtered through a porous stainless steel frit. Filtration times vary inversely with the degree of vacuum available on the downstream side of the filter frit; for a vacuum of 15 inches Hg, a filtration time of about 15 minutes is common. If for some reason, a filtration is excessively long, say an hour, the cake warms up and peroxide decomposition within the warm unwashed cake may become excessive; this can result in turn in the formation of a slimy, even less filterable mass. Thus filtration should be as rapid as possible in order to maintain a low cake temperature until the wash step is completed.

Washing. The wash reduces the concentration of residual H_2O_2, HNO_3, and NH_2SO_3H in the cake, measurably increasing the stability of the cake and the purity of the final metal. Four 1.5ℓ, refrigerated washes are made with 2% H_2O_2. The wash liquor is added to the filtrate and both are sent to the peroxide destruction step. Washes of 5% and 1% H_2O_2 also have been used; the residual 5% solution appeared to increase slightly the instability of the cake during further processing, while the 1% solution hydrolyzed the cake somewhat, making it difficult to dry.

Drying. Dry (room temperature) air is passed through the cake at about 5 scfm for 2-1/2 hours; this is followed by dry warm (55°C) air at about 5 scfm for two hours. This reduces the final average moisture content of the cake to about 0.20 g H_2O/g Pu, a desirable level for feed to the subsequent fluorination step. (The water content is based on an empirical formula weight of 319 for plutonium peroxide.) Constant-rate drying conditions prevail, and the air leaving the bed averages a moisture pickup of about one-half of its adiabatic saturation value at the measured air flow.

If an attempt is made to do all the drying with warm air, the cake produced is hard, lumpy, and difficult to fluorinate. This is believed caused by "bridging" between precipitate particles when plutonium peroxide which dissolves in the residual liquid in the cake reprecipitates as the solution in the cake evaporates. The effect is minimized by performing the initial drying with room temperature air (down to a moisture content below 1 g H_2O/g Pu) since cake solubility in the residual solution remains lower.

Peroxide Destruction. The large excess of H_2O_2 (about 4M) in the filtrate and wash solution must be destroyed for reasons of safety in subsequent handling of this solution. Accordingly, the peroxide is destroyed by heating the solution to 50°C, holding this temperature for 45 minutes, and then heating to 90°C briefly to destroy the last traces of peroxide. The two stages of temperature control are for safety; the raw filtrate undergoes runaway decomposition if heated directly to above 60°C. This treatment routinely leaves the filtrate with an H_2O_2 content of less than 0.02%. Low acidity and the presence of sulfate both interfere with this step, often necessitating its repetition. It is fortunate that the same conditions found desirable for producing a dense, filterable cake, ie, high acid and no sulfate, also are desirable for the peroxide destruction step.

Safety. Because of the extreme toxicity of plutonium, all lines and vessels are enclosed in ducts and plastic-paneled cabinets (these cabinets also house the fluorination and reduction equipment). The vessels are maintained at a differential of about 2 inches H_2O below the pressure in the cabinets, and the cabinets are maintained at a differential of about 0.8 inch H_2O below the pressure in the room. These conditions, maintained by the use of separate exhaust systems for the cabinets and the vessel vents, insure that all leaks will result in air flows away from operating personnel. All air from vessels, cabinets, and rooms is filtered and monitored before it is discharged to the environment from a 200-foot stack.

A primary safety consideration is the instability of H_2O_2 if it contacts impurities either before or after it enters the process. No piping is connected to the drums of 50% H_2O_2 other than a 6-inch piece of pipe with a valve. This eliminates the possibility of foreign matter accidentally entering the drum from more extensive piping. Solution is dispensed as needed into small, covered stainless steel containers which are moved to the proper additions funnels. To allow for sudden decomposition within the precipitator or the peroxide destruction vessels, 1-1/2-inch vent lines are used and reserve cooling capacity is provided.

Because the precipitators and associated equipment are larger than the "infinitely safe" diameter (about 6 inches) for plutonium, adequate control of the batch size is essential to prevent a criticality accident. This is accomplished by the use of instruments to analyze each batch of concentrate by the gamma absorption technique,[6] the use of pneumatic liquid level indicators in the batching tanks, the precipitators, and the peroxide destruction tanks; and the use of automatic pneumatic shutoff controls to prevent overfilling the precipitators.

Summary. The following were of prime importance to the production of a dense, free-filtering cake, suitable for fluorination:

- Agitation and addition rate matched to prevent zones of low acidity or excessive turbulence.
- Control of addition rate until the critical phase of the precipitation is complete.

- Addition of sufficient total peroxide for good yields.
- Prompt filtration.
- Prompt and thorough washing.
- Two-step (ie, cold and warm air) drying.

Preparation of Plutonium Tetrafluoride and Reduction to Metal

Introduction

The conversion of plutonium peroxide to plutonium tetrafluoride with hydrogen fluoride, followed by reduction of the tetrafluoride with calcium, long has been a standard method for the production of plutonium metal. Most of the controlling variables had been explored thoroughly before the construction of the Savannah River Plant and the existing technology was the basis for the original design of the Plant. Many improvements were made to the original operation during the following years. Most of these were matters of technique; the most significant advance was the realization of the close relationship between the entire series of isolation operations and the reduction yield. The single most important discovery was that the sulfate content of the peroxide cake regulated the ease of fluorination. When sufficient knowledge of the controlling variables was gained, it became possible to shorten the fluorination furnace cycle to a fraction of the original. Also, the density of the fluoride was increased so that batch sizes could be increased, and the increased reduction batch size allowed the elimination of the iodine booster.

Process Description and Chemistry

The basic process at this Plant was unchanged from the normal sequence (see figure 6). Dry plutonium peroxide is exposed to hydrogen fluoride in a furnace at temperatures up to 600°C. The resulting tetrafluoride is mixed with metallic calcium and packed in a magnesia crucible in a steel pressure chamber, which is heated in an induction furnace until

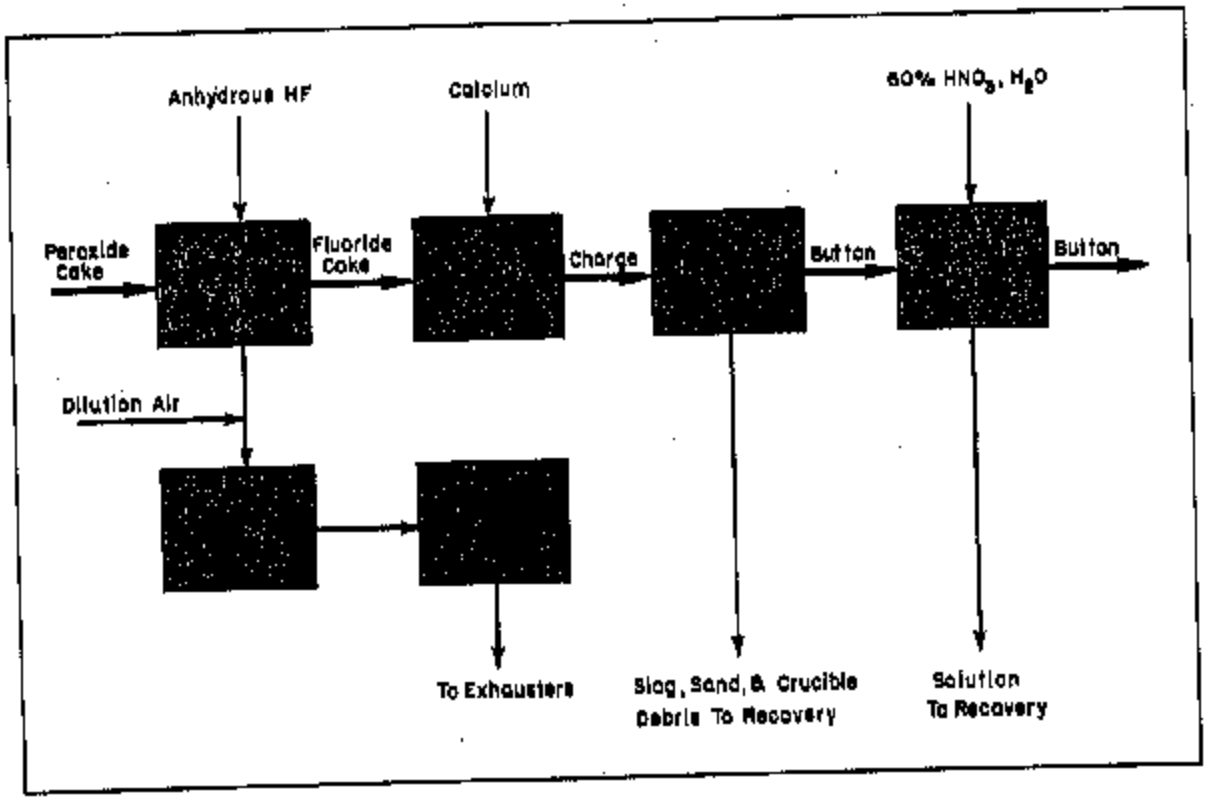


FIGURE 6. DRY CHEMISTRY BLOCK DIAGRAM

the charge fires. (Iodine booster may be added to small batches to furnish more heat by reacting with calcium.) The plutonium is reduced to molten metal, which separates from the slag and solidifies into a "button" in the bottom of the crucible. Finally, the chamber is dumped and the "button" is separated from the slag, crucible, and packing sand which ultimately are dissolved for recovery of the residual plutonium.

The reactions for fluorination and reduction are:

$$PuO_2 \cdot XA + 4HF = PuF_4 + 2H_2O + \tfrac{1}{2}O_2 + (XA)$$

$$PuF_4 + 2Ca = Pu + 2CaF_2$$

$$Ca + I_2 = CaI_2$$

In the fluorination reaction, the "X" represents the quantity of "A," the coprecipitated anion. At this Plant, "A" normally could be almost any mixture of sulfate, sulfamate, and nitrate, according to the specific feed.

The over-all efficiency of the process may be based on time cycles, batch size, reduction yield, and utilization of HF, and is determined largely by the composition of the peroxide cake. Specifically, the sulfate and moisture content are the factors that must be controlled properly. The sulfate concentration in the feed to the peroxide precipitation step determines the fluorination time that is required for good reduction yields to be obtained; very short cycles can give good yields in the absence of sulfate. (A good yield arbitrarily is defined as greater than 95%.)

After many experiments, one of several standard furnace cycles is

used according to the expected sulfate content of the feed. The exact chemical effect of sulfate has not been established but Plant experience indicates that residual sulfate (or sulfate product) not removed during fluorination interferes with reduction, as opposed to sulfate actually repressing the conversion of plutonium peroxide to tetrafluoride. For example, one indication of excess sulfate is excessive splattering of the reduction charge over the inside of the pressure chamber.

In addition to harmful effects on furnace cycle or reduction yield, sulfate in the original peroxide cake decreases the bulk density of the final tetrafluoride, and hence can decrease the permissible batch size. The degree of moisture in the peroxide cake at the beginning of fluorination also affects the density; the drier the cake, the greater is the density. However, there is a practical limit to cake drying, as detailed below.

The gross effect of sulfate on the performance may indicate something of the mechanism of decomposition of sulfamate. The peroxide cake undoubtedly contains some sulfamate ion when precipitated from the 4.7M nitric acid - 0.3M sulfamic acid feed solution. Since sulfate effects become apparent at 0.02M in the feed, either an extremely small amount coprecipitates or sulfamate does not convert to sulfate at the Plant furnace conditions.

The important variables in the reduction operation are (1) the batch size of plutonium, (2) the amount of calcium, and (3) the atmosphere in the pressure chamber. As discussed under "Process Experience", a large batch size may allow elimination of the iodine booster, the

amount of calcium influences the purity, and traces of moisture or air depress the reduction yield.

The work discussed here is not a definitive study because of limitations on the equipment and on available analytical techniques. Several items are worthy of further work, particularly as the basis for any new installations. The actual role of sulfate should be determined as should be the effect of the crystal structure of the peroxide. The actual rate of conversion of good cakes should be measured to establish a true minimum fluorination time. The minimum time is limited by the heating and cooling of the massive furnaces; fast-acting furnaces might allow even shorter cycles.

Equipment

The fluorination boats are made of Hastelloy C, with frits and liners made of platinum, to avoid corrosion and contamination of cakes by corrosion products; the shape is similar to that of the filtration boats. After being loaded, the boats are placed on hydraulically operated platforms that are raised to form the furnace bottoms. The boat rests on a gasket of soft "Armalon" ("Teflon" felt), which gives a satisfactory seal. Metal-to-metal seals were unsatisfactory; boats and stainless steel and unlined Hastelloy C noses corroded excessively (gold plating did not help). Corrosion increases greatly when cycle times above the minimum are required. The fluorination furnace enclosures are made of heavy stainless steel and lined with Hastelloy C, and provide adequate strength to withstand the vigorous reactions which sometimes occurred in early operation. However, the massive

structure lengthens the heating and cooling times.

The excess HF in the furnace off-gas is absorbed in a bed of limestone. The gas must be diluted with large volumes of air to prevent condensation of moisture generated by the reaction of HF with both the cake and the limestone. Condensed moisture promotes corrosion of the off-gas lines and collects in the limestone.

The magnesium oxide crucible is packed into the steel pressure chamber and is held in position with a thin layer of magnesium oxide sand. The crucible is fitted with a magnesia cap to prevent spattering of the slag onto the furnace head and the upper portion of the pressure chamber. The pressure chamber is placed on a hydraulic lift which raises it into the induction furnace and seals it against the furnace head by means of an annealed aluminum gasket. See figure 7 for complete assembly.

The reduction furnace has inert gas (helium or argon) and vacuum fittings so that air can be purged from the pressure chamber. The furnace head valve can be flushed with chloroform or other iodine solvent, if iodine is used in the reduction mixture. The furnace head, valves, and associated piping as well as the induction coil are mounted for convenient maintenance; replacement is necessary occasionally for each of these parts.

Process Experience

Fluorination. Fluorination and reduction data are presented in table VI. The influence of sulfate on the ease of fluorination may

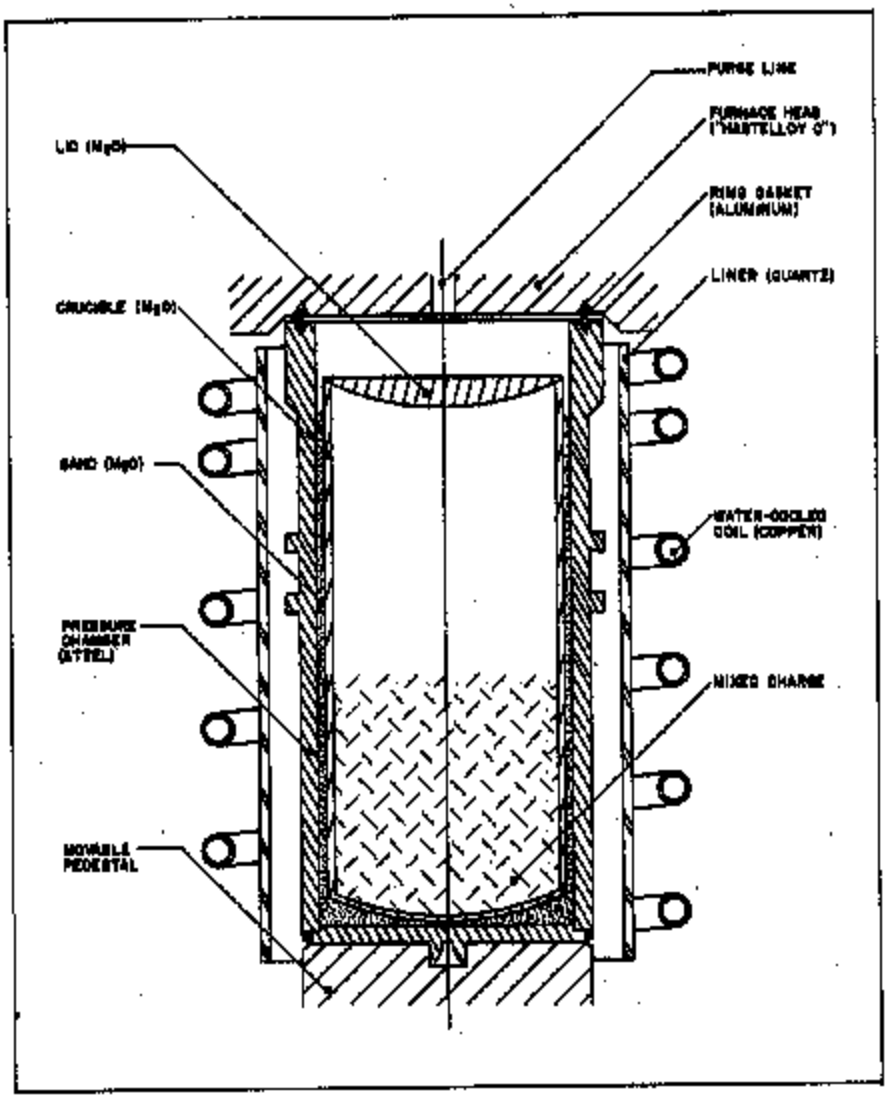


FIGURE 7. REDUCTION FURNACE

be illustrated by the required time cycles. The original standard cycle required 8 to 12 hours, and included 1.5 hours at 150°C, 3.0 hours at 600°C, and associated heating and cooling periods; this gave good performance with sulfate concentrations ranging from 0.075M to 0.15M in the precipitation feed. As the sulfate in the feed was decreased gradually to less than 0.02M, it was found that the 150°C step could be eliminated and then that the 600°C step could be shortened drastically. The minimum cycle in routine use was 3.5 hours, during which the cake was heated directly to 600°C and immediately cooled. The minimum cycle that might be attained with a furnace that heated and cooled rapidly is not known.

The minimum required cycle is quite sensitive to the limit of 0.02M sulfate. For example, this figure is reached due to slow conversion of sulfamate to sulfate when ion exchange concentrate is stored for more than a day, and a slightly longer cycle is required for concentrate stored over a weekend. Also, as discussed in the "Cation Exchange" section, the mere change in column batch size from 750 to 775 grams on the 7-inch columns gave an increase in sulfate sufficient to extend the cycle.

A high utilization of hydrogen fluoride was obtained from the enhanced reactivity and short furnace cycles obtained with well-prepared peroxide cakes. The maximum utilization of 52% was obtained with large, sulfate-free batches, which had short time cycles; the minimum utilization corresponded to small, high-sulfate batches, which required long cycles.

Oxygen aids in the removal of sulfate from the cake, and is used

in cases of known high sulfate. However, oxygen does not appear necessary in any quantity with low sulfate and actually is not fed deliberately; the only source is the air-purge on the instrument lines.

The moisture content of the air-dried peroxide cakes must be controlled between 0.20 and 0.35 gram of water per gram of plutonium (based on an assumed formula weight of 319 for plutonium peroxide) or difficulties occur in the furnace when hydrogen fluoride flow is started. Fresh cakes that are drier than this range frequently react violently and expel cake from the boat or even the furnace. Cakes with a moisture content above the limit sometimes decompose to moist, foamy masses that slowly boil out of the boat into the furnace. Aged, dry cakes lose the extreme sensitivity that characterize the fresh cakes; it is not known if this change represents a slow conversion of the structure of the peroxide or merely a loss of peroxy-oxygen. Washing with alcohol to promote drying is not recommended; alcohol was part of the original flowsheet but caused many violent reactions both in and out of the furnaces.

Table VI. Summary of Process Variables

Fluorination	
Time cycle, hr	3.5 - 12
Gas flows, g/hr	
HF	100 - 450
O_2	0 - 50
HF utilization, %	5 - 52
Batch size, g	350 - 1500

Reduction	
Time cycle	
Heating, min	8 - 13
Total (preparations, heating, and cooling), hr	3 - 5
Calcium, % excess	15 - 50
Iodine, mol I_2/mol Pu	0 - 0.3
Batch size, g	250 - 800

Reduction. The reduction of plutonium tetrafluoride to pure plutonium metal can be made with calcium alone, above some critical batch size determined by the thermal properties of the equipment. Iodine booster may be used to allow reduction of small batches or of incompletely converted tetrafluoride. However, iodine causes various complications and corrosion problems; elimination of iodine ranks with the bigger batch size as a prime reward of increased tetrafluoride density. Continual reference has been made to the increased bulk density of the tetrafluoride that resulted from

various changes. For reference, the bulk density can be defined in terms of the grams of plutonium per cc in the mixed reduction charge in the pressure chamber; this number sets the possible batch size for reduction. With a normal calcium excess of 25 to 30%, a plutonium density of 1 g/cc or better is considered good.

The reduction with calcium also serves as an auxiliary decontamination step, in accord with the liquid-metal extractions of some pyrometallurgical systems. The amount of excess calcium was varied in a series of experiments from 15 to 50% over the stoichiometric requirement for reduction and gave measurable changes in the purity of the plutonium. The actual upper limit on the amount of calcium that is convenient to use is set by the heat conservation characteristics of the system. Too much calcium represents a heat sink that can interfere with proper melting and coalescence of the charge.

The humidity of the processing line and the atmosphere in the pressure chamber also have disproportionate effects upon the reduction performance and should be mentioned. Very erratic and poor yields have been obtained when the dew point of the ventilation air exceeded -10°F in the cabinets used for operations starting with the drying of the peroxide. The exact effect of the atmospheric moisture and the part of the process that is affected never have been identified. Poor yields also have been obtained if the pressure chamber containing the reduction charge was not sealed or purged adequately with inert gas to remove air. Even small amounts of air cause excessive splattering and poor coalescence of the charge.

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