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CONVERSION CHEMISTRY OF PLUTONIUM NITRATE

by

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and

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INTRODUCTION

The steps taken in the conversion of plutonium from plutonium nitrate - nitric acid solutions to plutonium metal are as follows:

1. Preparation of a plutonium solution having a composition suitable for further processing;
2. Precipitation of a plutonium halide (e.g., PuF_3) or of a compound which can be converted to a halide by dry chemical treatment;
3. The drying of the precipitated halide or dry-chemical conversion to a halide;
4. The reduction of the plutonium halide by a more electropositive metal in a hermetically sealed bomb.

It is the purpose of this paper to present data and information which are pertinent to these processes.

PLUTONIUM CHEMISTRY

The oxidation-reduction potentials of plutonium ions in aqueous solution(1) are presented in Figure 1. It can be seen from Figure 1 that plutonium is a very electropositive metal, similar to uranium and zirconium, and that very powerful reducing agents are required to produce plutonium metal from its salts or compounds. It is also noted that the plus five oxidation state of plutonium is unstable with respect to the $+4$ and $+6$ ion and, therefore, the $+5$ ion can frequently be neglected when considering the aqueous chemistry of plutonium. Further, the Pu^{+4} ion can also disporportionate according to the equilibrium

$$3\,Pu^{+4} + 2\,H_2O \rightleftharpoons 2\,Pu^{+3} + PuO_2^{++} + 4\,H^{+} \qquad K = 1 \times 10^{-3}.$$

Although the equilibrium constant(2) for this reaction is small, measurable concentrations of Pu^{+3} and PuO_2^{++} are frequently found in Pu(IV) solutions.

Although times does not permit a detailed discussion of the chemistry of the various plutonium species, it is advantageous at this point to mention the similarity of the chemistry of Pu^{+3} with the $+3$ rare earth ions; Pu^{+4} with U^{+4}, Zr^{+4}, and Ce^{+4}; and PuO_2^{++} with UO_2^{++}. Differences in the chemistry of a specific plutonium ion and the analogous ion mentioned above are, of course, to be expected and are frequently observed.

PROCESS - AQUEOUS

For purposes of discussion it will be assumed that the starting plutonium solution from which plutonium metal is to be produced is derived from a Redox or Purex type solvent extraction process. In such a case as this, the final product bearing stream is a dilute plutonium nitrate-nitric acid solution.

[redacted]

Figure 1

OXIDATION AND REDUCTION POTENTIALS OF PLUTONIUM

Acid Solution

$$\begin{tikzcd}
\mathrm{Pu} \arrow[r, "+2.03\ v"] & \mathrm{Pu^{+3}} \arrow[r, "-0.97\ v"] & \mathrm{Pu^{+4}} \arrow[r, "-1.15\ v"] \arrow[rr, bend right, "-1.04\ v"'] & \mathrm{PuO_2^{+}} \arrow[r, "-0.93\ v"] & \mathrm{PuO_2^{++}}
\end{tikzcd}$$

Basic Solution

$$\begin{tikzcd}
\mathrm{Pu} \arrow[r, "+2.42\ v"] & \mathrm{Pu(OH)_3} \arrow[r, "+0.95\ v"] & \mathrm{Pu(OH)_4} \arrow[r, "-0.76\ v"] \arrow[rr, bend right, "-0.51\ v"'] & \mathrm{PuO_2OH} \arrow[r, "-0.26\ v"] & \mathrm{PuO_2(OH)_2}
\end{tikzcd}$$

[redacted]

The first step in the metal reduction process is to concentrate the plutonium nitrate in the starting solution to 10 to 100 grams of plutonium per liter. This is done to avoid significant precipitation losses in subsequent steps and to minimize the size of the processing equipment. Several alternate concentration procedures can be employed, and for example, plutonium solutions have been concentrated satisfactorily by evaporation, by the use of ion exchange resins, and by solvent extraction cycles.

Once the plutonium has been concentrated, a variety of plutonium compounds can be precipitated which are suitable for direct reduction to the metal or which can subsequently be converted to a satisfactory material for reduction. Figure 2 is a schematic diagram showing selected precipitates which may be prepared and the subsequent steps necessary for metal production. Table I shows some of the more important chemical and physical properties of the plutonium compounds of interest.

The final selection of the process for metal preparation may best be made upon consideration of the purity of the starting solution, the ease of which the plutonium can be recovered from the waste streams, and the type and size of process equipment which is available or must be procured. A description of the preparation of the compounds shown in Figure 2 and the merits and boundary conditions for each of the processes are presented in the subsequent portions of this paper.

Plutonium Peroxide Precipitation

A flowsheet for the precipitation of plutonium peroxide from a typical feed is shown in Figure 3.

Plutonium peroxide may be precipitated satisfactorily from feed solutions containing 10 to 100 grams of plutonium per liter, 1.5 to 6 M nitric acid, and in the presence of large concentrations of other metallic ions. A separate valence adjustment step is unnecessary as both hexavalent and trivalent plutonium are converted to the tetravalent state by hydrogen peroxide.

The composition of the compound varies widely with precipitation conditions, but it usually contains about three peroxide oxygen atoms per plutonium atom and small but variable amounts of nitrate, sulfate, hydroxide, oxide and water.

The solid may precipitate in large easily filtered particles if it is formed in the presence of sulfate, a strike temperature above 30 C is used, or if enough acid is present to give a slurry acidity of 2.5 molar or more. Generally, since hydrogen peroxide is unstable and the use of a low temperature is desirable to reduce its decomposition rate, sulfate is added to give the desired crystal form.

A precipitation yielding easily filterable crystals is made by the slow addition (one-half hour or longer) of enough 30 to 50 percent hydrogen peroxide to yield a final slurry concentration of 8 to 12 percent. For feeds containing more than one gram per liter of iron, which catalyzes hydrogen peroxide decomposition, a strike temperature below room temperature is desirable.

Figure 2

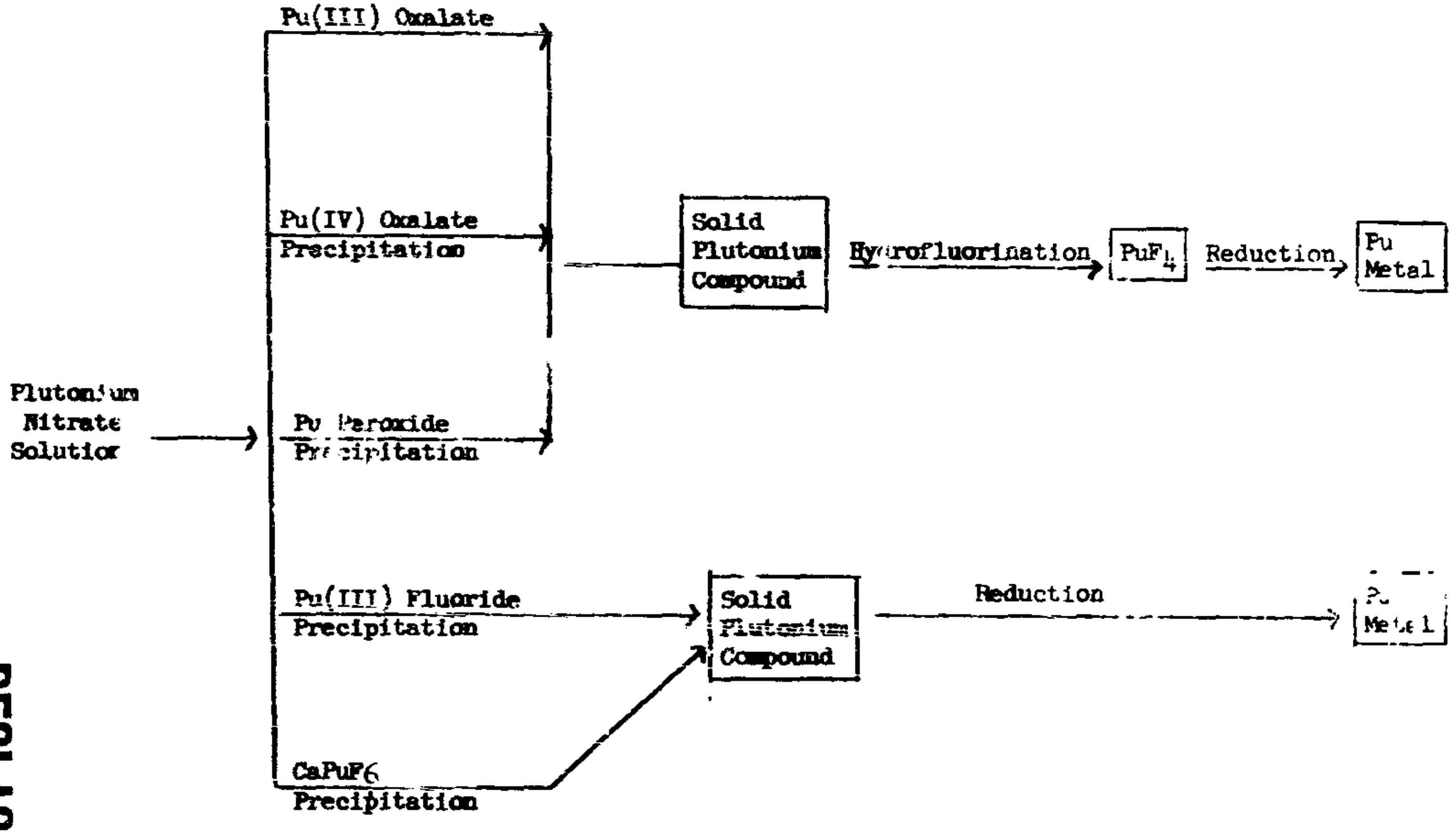

Plutonium Nitrate Solution
Pu(III) Oxalate
Pu(IV) Oxalate Precipitation
Pu Peroxide Precipitation
Pu(III) Fluoride Precipitation
CaPuF6 Precipitation
Solid Plutonium Compound
Hydrofluorination
PuF4
Reduction
Pu Metal
Solid Plutonium Compound
Reduction
Pu Metal

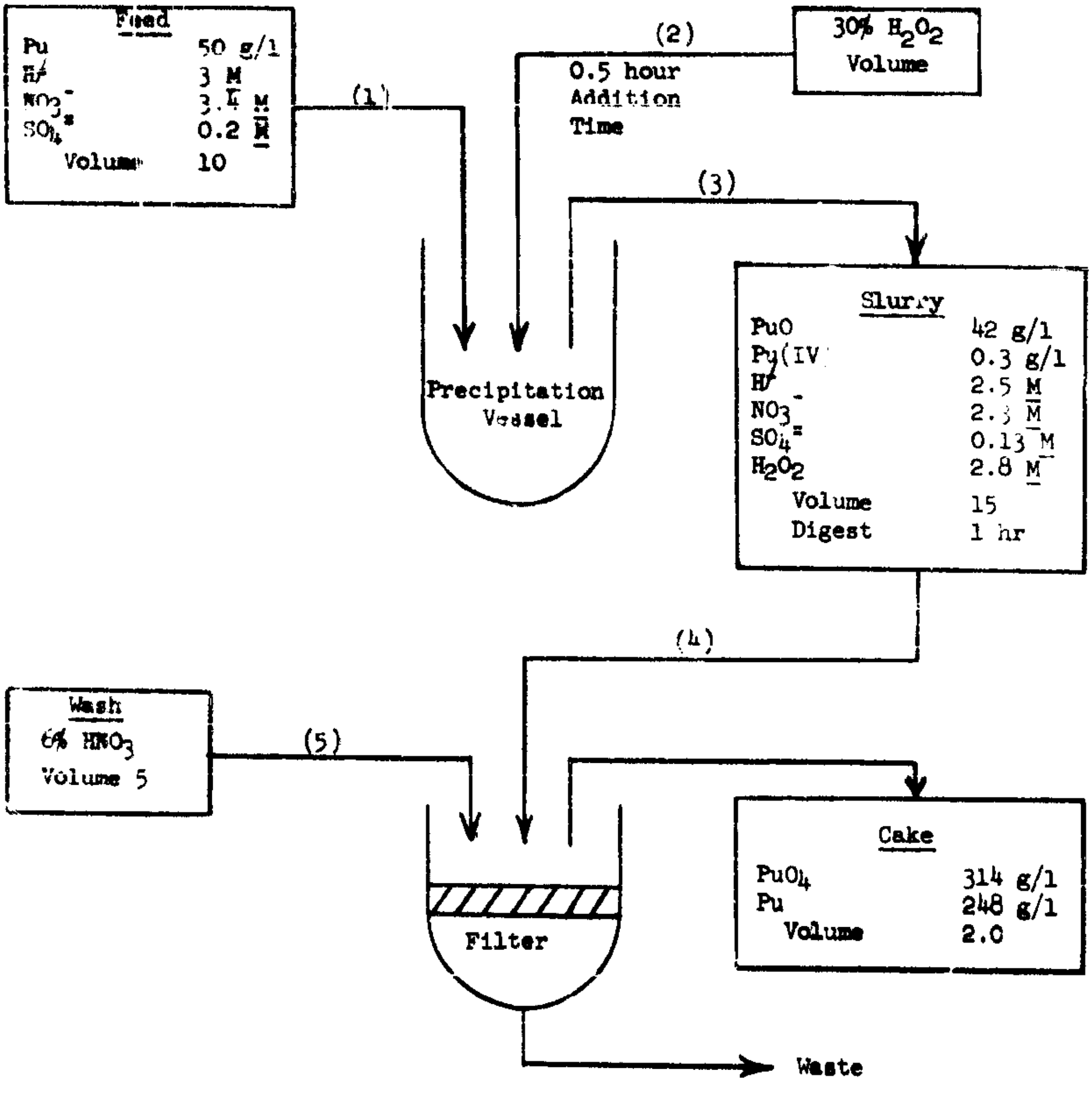
TABLE I

PROPERTIES OF SELECTED PRECIPITATES AND COMPOUNDS

Name	Measured Solubility Medium	 Grams Pu/Liter	Bulk Density grams Pu/cc Filter Cake	 Dry Compound
Pu(III) Oxalate	0.5 $\underline{M}$ $H_2C_2O_4$ - 3 $\underline{M}$ HNO_3	0.01	0.6 - 0.8	--
Pu(IV) Oxalate	0.1 $\underline{M}$ $H_2C_2O_4$ - 4 $\underline{M}$ HNO_3	0.003	0.5 - 0.6	0.6
Pu(IV) Peroxide	3 $\underline{M}$ H_2O_2 - 1 $\underline{M}$ HNO_3	0.10	0.1 - 0.6	--
Pu(III) Fluoride	1 $\underline{M}$ HF - 1 $\underline{M}$ HCl	0.037	--	1 - 2.5
CaPu(IV) Fluoride	2 $\underline{M}$ HF - 4 $\underline{M}$ HNO_3	0.06	0.9	1
Pu(IV) Fluoride	2 $\underline{M}$ HF - 2 $\underline{M}$ HNO_3	0.70	0.6 - 1.0	0.5 - 2
Pu(IV) Oxide	--	--	--	1.8 - 2.2

Figure 3

TYPICAL FLOWSHEET FOR PRECIPITATION OF PLUTONIUM PEROXIDE



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Final slurry acidities between one and three molar are optimum. At lower acidities the precipitate particle size tends to be small, and separation of certain elements such as vanadium, uranium, thorium, and zirconium is less efficient. At higher acidities, the solubility of plutonium peroxide increases rapidly and is more or less incomplete above 6 molar.

Most common cationic impurities, excluding uranium, have little effect on plutonium peroxide precipitations up to mole ratios of impurities to plutonium of about five; however, an ionic impurity which forms strong plutonium complexes, such as fluoride, phosphate, and oxalate (except sulfate) increase solubilities and give poorly formed precipitates.

The bulk density of plutonium peroxide filter cakes when freshly precipitated varies from 0.1 to 0.6 grams of plutonium per cubic centimeter. The coarser precipitates can be retained by sintered filtered media of 60 micron average pore size, while 30 micron pore size media are necessary for the finely divided precipitates.

Plutonium(IV) Oxalate

A typical flowsheet for the precipitation of plutonium(IV) oxalate is shown in Figure 4.

The compound may be precipitated satisfactorily from solutions containing from 1 to 300 grams per liter plutonium and enough acid to make the final slurry 1.5 to 4.5 M nitric acid. At acidities below 1.5 molar, co-precipitation of impurities is favored, and the precipitate is too finely divided for rapid settling or filtration. At slurry acidities above 4.5 molar, the plutonium(IV) oxalate solubility is high, and the precipitate is thixotropic.

Hydrogen peroxide is added for valence adjustment, either before or during the oxalic acid addition, and at a rate governed by the extent to which foaming occurs. The valence adjustment, which may produce plutonium(III) as an intermediate, is rapid at 50 C, but at lower temperatures it may be prohibitively slow for solutions which contain less than 30 grams per liter plutonium and are devoid of impurities which catalyze the decomposition of hydrogen peroxide.

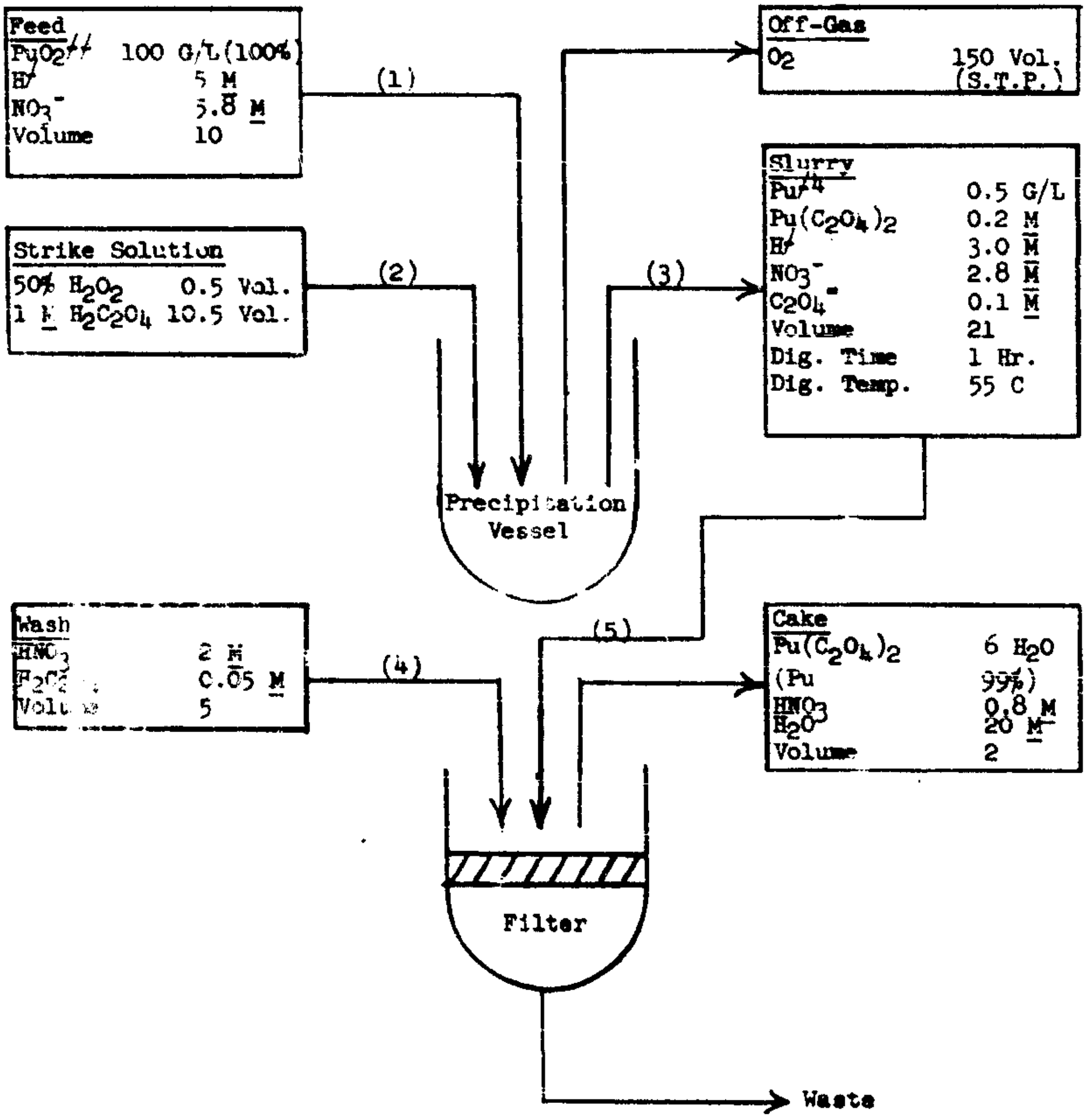
Equilibrium solubilities of plutonium(IV) oxalate are much lower than those obtained in the usual quick precipitation. The solubility of plutonium(IV) oxalate in 0.75 M nitric acid - oxalic acid solutions have been reported(3) and may be expressed by the following equation

$$\text{Solubility } (\underline{M}) = \frac{3.11 \times 10^{-5}(H^{+})^{2}}{(H_2C_2O_4)} + 3.0 \times 10^{-5} + \frac{7.54 \times 10^{-4}(H_2C_2O_2)}{(H^{+})^{2}}$$

From a practical point of view the best range for the free oxalic acid concentration is between 0.05 to 0.15 molar, depending upon the purity of the solution. The solubility is also a function of the slurry temperature; the best precipitations appear to occur at a temperature of 50 to 60 C, with the oxalic acid addition

Figure 4

TYPICAL PLUTONIUM(IV) OXALATE FLOWSHEET



spread over a time of 10 to 60 minutes, depending upon the agitation and slurry volume. Too rapid an addition or too low a temperature may produce a finely divided, hard-to-filter precipitate. Temperatures above 60 C have been found to produce thixotropic precipitates.

Decontamination factors have been measured for plutonium(IV) oxalate precipitations as follows; 3 to 6 for zirconium-niobium, 12 for ruthenium, 1 for americium, 1 for UX_1 (thorium). Separation factors for bulk contaminants (100,000 parts impurity per million parts plutonium) average about 100 for aluminum, chromium, and nickel, and about 60 for uranium.

Plutonium(III) Oxalate Precipitation

Plutonium(III) oxalate is a blue-green solid with a low solubility and the desirable property that it settles rapidly and is easy to filter. The solubility of plutonium(III) oxalate may be expressed by the following equation:

$$\text{mg/l Pu} = 3.24\,(H^{+})^{3}\,(H_2C_2O_4)^{-3/2}$$

The compound may be precipitated at room temperature from any acid plutonium(III) solution containing one or more grams of plutonium per liter and not more than four molar acid. Oxalic acid may be added as either a solution or a solid, as rapidly as desired and with a digestion period of about one-half hour. Reducing agents which may be used for the preparation of plutonium(III) include hydriodic acid and hydroxylammonium ion.

Precipitation of Calcium Plutonium Fluorides

A typical flowsheet for the precipitation of calcium plutonium(IV) fluoride is shown in Figure 5. The resulting solid after drying in argon or nitrogen can be reduced satisfactorily to plutonium metal.

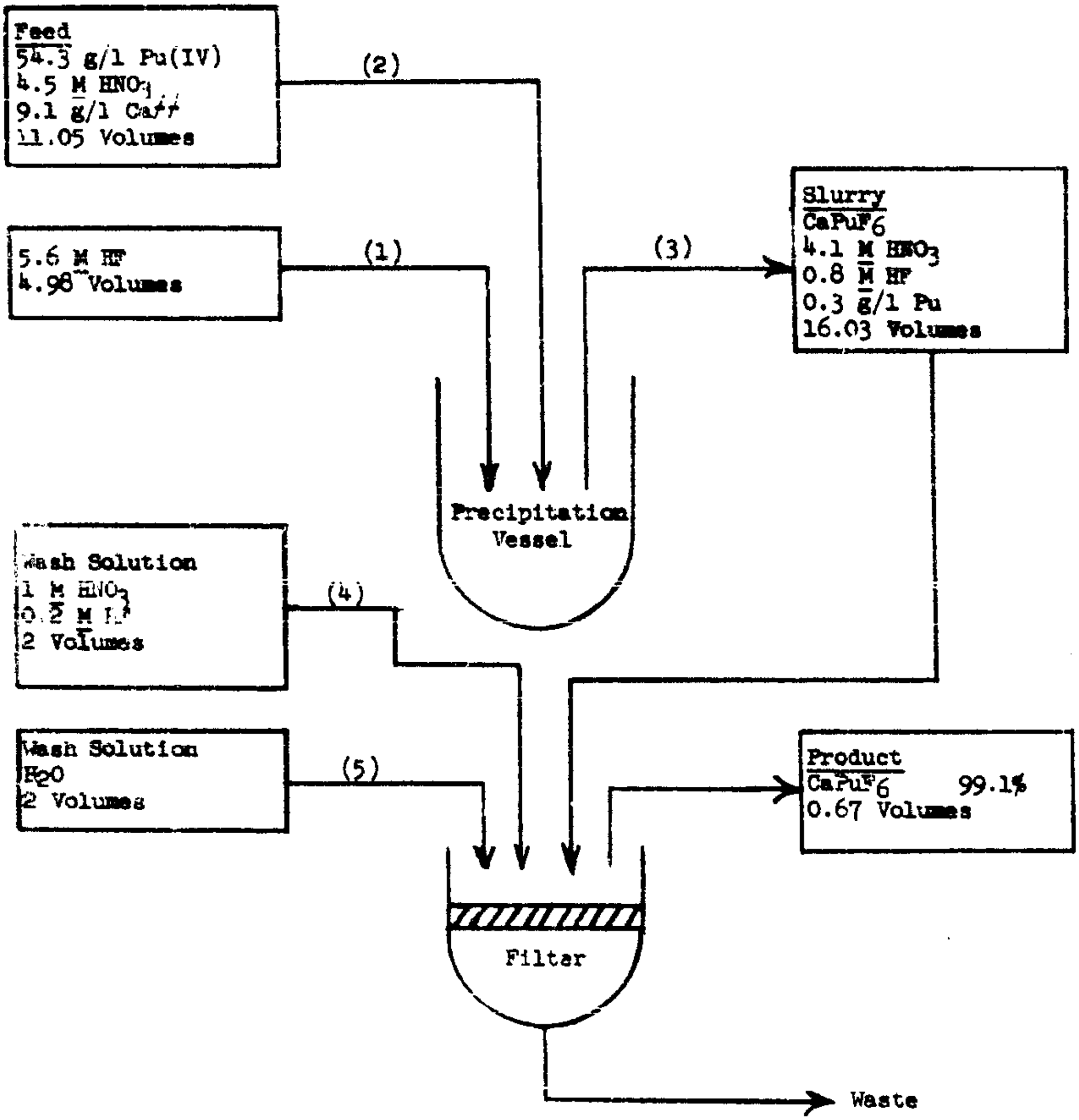
Research and development studies have indicated the following steps should be employed to insure control of the precipitate composition and ease of filterability: 1) the feed should contain equal mole concentrations of plutonium and calcium, and 2) the feed should be added slowly to hydrofluoric acid which is 6 molar or less. The precipitation is found to give little or no separation from aluminum, iron, chromium, nickel, or lanthanum; however, separation factors of 80 to 200 have been observed for zirconium-niobium.

Plutonium(III) Fluoride Precipitation

Most attempts to precipitate the simple plutonium fluorides (PuF_3 and PuF_4) have given precipitates which were difficult to wash without peptizing and which were difficult to separate from the supernates. It has been shown, however, that plutonium(III) fluorides can be precipitated in an easily filtered crystal form from relatively pure plutonium solutions. Precipitation of the trifluoride has two attractive advantages: 1) it can be readily dried and reduced to the metal without a high temperature fluorination step; and 2) under

Figure 5

TYPICAL FLOWSHEET FOR PRECIPITATION OF $CaPuF_6$



the right conditions, the solubility is very low. On the other hand, the precipitation does not give very good separation from some impurities, such as aluminum.

Two procedures have been developed for precipitating plutonium trifluoride from pure plutonium nitrate solution. In one case, 2.7 M HF is added over a 30 minute period to an equal volume of plutonium solution at a temperature of 40 C or higher. In the second method, equal volumes of 2.7 M HF and plutonium solution at 25 C are added simultaneously over a 30 minute period to one-half volume of 0.1 M HNO_3. Vigorous agitation is quite important. Both methods are followed by a 30 minute digestion and yield readily filterable precipitates, although the second method results in larger crystal size. After filtration, the precipitate is washed with 0.8 M HF to prevent plutonium oxidation, and two alcohol washes (optional) and aspiration at room temperature are employed to dry the cake. The precipitate can be made anhydrous by passing helium at 200 C over the cake for several hours or drying at 600 C for one-half hour. The later procedure results in a material with less than 0.2 percent water.

PROCESS - DRY CHEMICAL

In the foregoing portions of this paper we have considered the steps necessary to produce: 1) plutonium halides which can be reduced directly to the metal, and 2) plutonium compounds which can be converted readily to a halide for the subsequent reduction step. In the latter case, plutonium(III) oxalate, plutonium(IV) oxalate, and plutonium peroxide cannot be reduced to the metal and, therefore, must be treated by dry chemical methods to produce an anhydrous plutonium halide. Although for purposes of discussion we will consider only the conversion of these three compounds to plutonium fluoride, other halides can and have been used for metal preparation. Since plutonium oxide may appear as an intermediate compound in each of these processes, the conversion of plutonium oxide to plutonium fluoride will also be included in the discussions. An abbreviated flowsheet for the conversion of the above compounds to plutonium(IV) fluoride is presented in Figure 6.

Plutonium(IV) fluoride can be prepared by treating plutonium(III) or (IV) oxalate, plutonium peroxide, or plutonium oxide with a mixture of anhydrous hydrofluoric acid and oxygen. Oxygen is used to prevent the formation of plutonium(III) fluoride which might otherwise result from the hydrogen which is frequently found in commercial hydrogen fluoride. Plutonium trifluoride can, of course, be reduced to plutonium metal, but the reduction conditions are somewhat more stringent. If plutonium(III) fluoride is formed, it may be converted to the tetrafluoride upon treatment with hydrogen fluoride and oxygen at a temperature at least equal to the original hydrofluorination temperature.

The hydrofluorination reaction is exothermic, and with some compounds, plutonium peroxide, for example, the reaction will start at ambient temperatures. However, to obtain an anhydrous product, the reaction temperature should be at least 400 C - temperatures of 400 to 600 C are commonly used.

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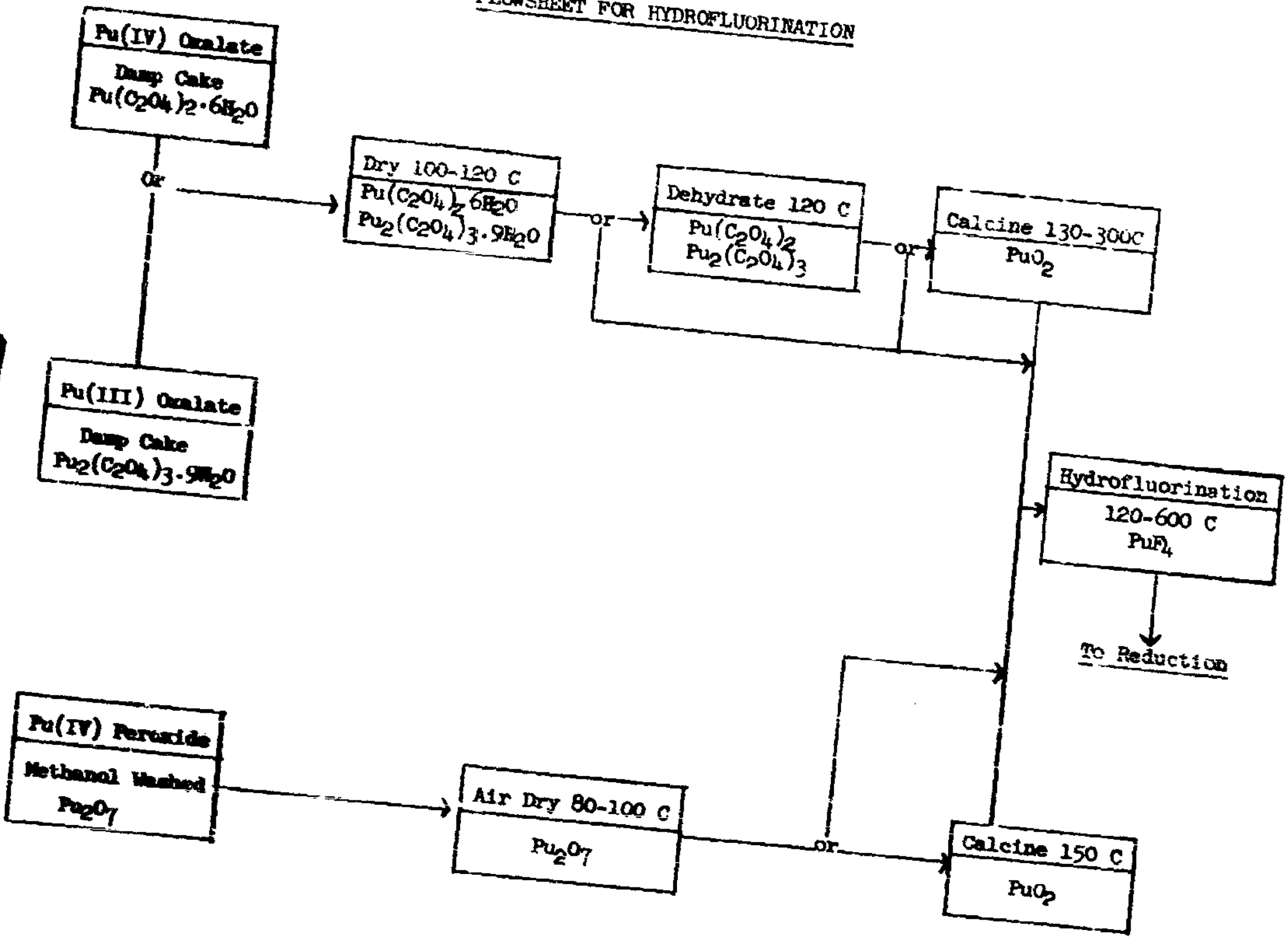
Figure 6

FLOWSHEET FOR HYDROFLUORINATION



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If a distinct calcination step is carried out (see Figure 6), the maximum temperature should be kept below 480 C, and the hydrofluorination temperature should at least equal the calcination temperature. Plutonium oxides which are prepared at high temperatures become refractory and are difficult to hydrofluorinate.

The hydrofluorination process is best carried out in two steps, a low temperature hydrofluorination period at about 180 C and a high temperature period at 500 to 600 C. Hydrofluorination is nearly complete during the low temperature operation. In the case of plutonium peroxide, it is important that the peroxide not be allowed to decompose appreciably prior to hydrofluorination because the decomposition product is not readily converted to the fluoride.

METAL REDUCTION

Plutonium metal may be prepared in the massive state by reducing any of the several plutonium halides with an appropriate alkali or alkali earth metal. Table II shows a selected listing of plutonium reduction reactions, the heat of reaction at 291K, and the melting points of the reaction slag. The choice of the system to be employed for metal reduction can only be made upon consideration of many factors. For example, it is desirable that the plutonium halide and reductant be relatively stable with respect to humid air for ease of handling, that heat of reaction be sufficiently great to raise the temperature of the reacting materials to above the melting point of the slag, and that the melting point of the slag be low such that it stays molten for a sufficiently long period of time to permit metal coalescence.

It can be seen from Table 2 that the first two reactions produce high melting slags, and, in fact, successful reductions of plutonium oxide have not been made for this reason. Reduction of plutonium(IV) fluoride with lithium is possible, but the reductant is difficult to handle safely. Plutonium chloride, bromide, and iodide are very hydroscopic, and care must be exercised to ensure the absence of moisture prior to or during preparation for the bomb reduction operation.

Plutonium(IV) fluoride is often used, principally because it is nonhydroscopic. The reduction of plutonium tetrafluoride is generally carried out in a refractory-lined, sealed container built to withstand pressures of 50 to 400 psig and temperatures up to 1600 C. A schematic flowsheet for the metal reduction process is presented in Figure 7.

Calcium metal, about 125 percent of the stoichiometric requirement, is used as the reductant, giving the reaction

$$PuF_4 + 2\ Ca \rightarrow Pu + 2\ CaF_2 \qquad \Delta H = -157.6\ Kcal$$

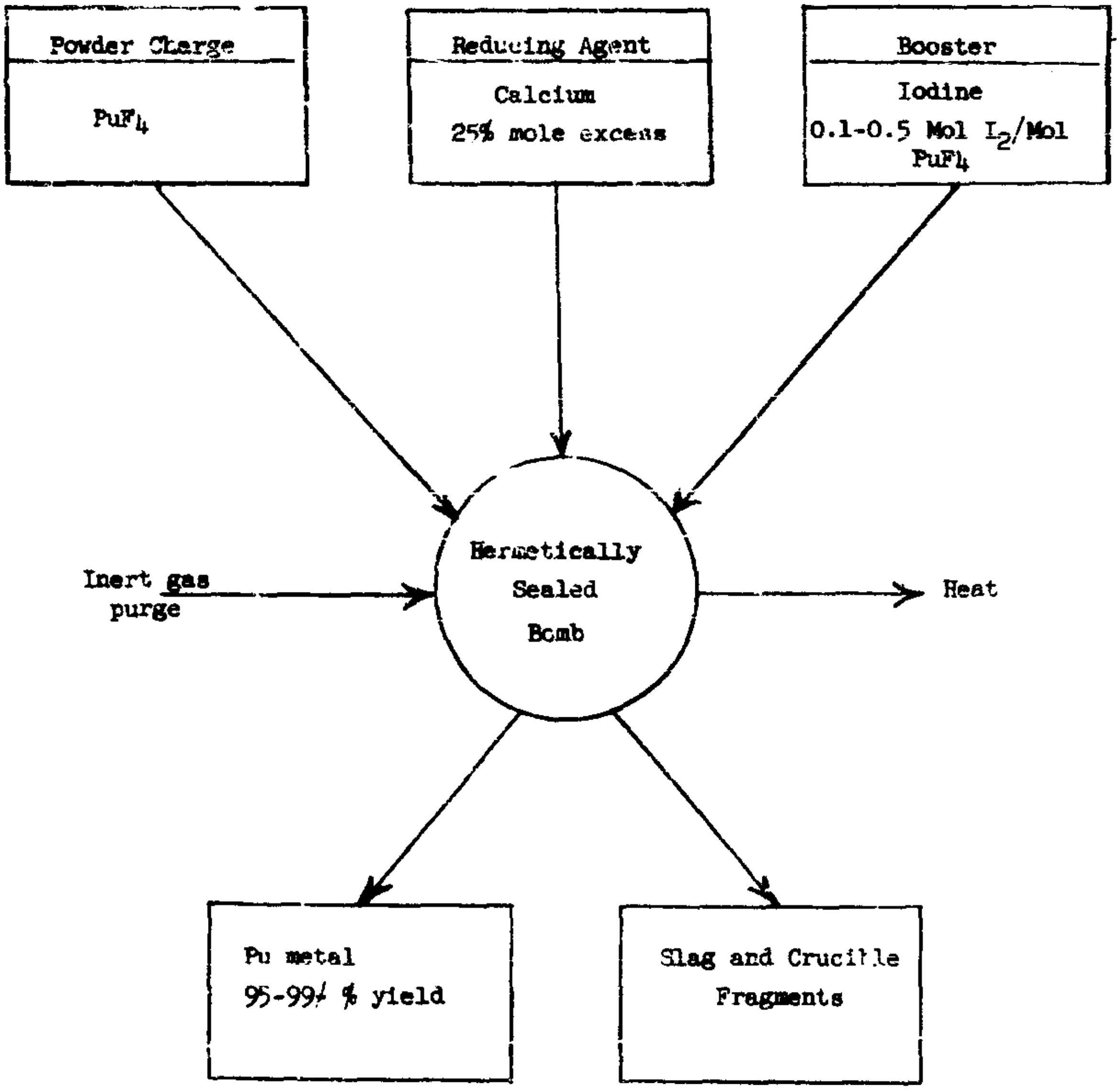
Iodine, along with an equivalent amount of calcium, may be added to provide additional heat and to favorably alter the properties of the slag.

The "booster ratio" (moles I_2/mole PuF_4) required to give high yields of plutonium metal depends upon the size of the reduction charge. Small scale reductions require

TABLE II

POSSIBLE REACTIONS FOR THE PREPARATION OF PLUTONIUM METAL

Reaction	ΔH at 291° K Kcal/mol Pu	Melting Point of Slag, °C
$PuO_2 + 2\ Ca \longrightarrow Pu + 2\ CaO$	-52.4	2572
$PuO_2 + 2\ Mg \longrightarrow Pu + 2\ MgO$	-40.5	2500 - 2800
$PuF_4 + 4\ Li \longrightarrow Pu + 4\ LiF$	-159.7	870
$PuF_4 + 2\ Ca \longrightarrow Pu + 2\ CaF_2$	-149.5	1330
$PuF_3 + 3/2\ Ca \longrightarrow Pu + 3/2\ CaF_2$	-54.8	1330
$PuCl_3 + 3/2\ Ca \longrightarrow Pu + 3/2\ CaCl_2$	-56.0	772
$PuBr_3 + 3/2\ Ca \longrightarrow Pu + 3/2\ CaBr_2$	-55.5	765
$PuI_3 + 3/2\ Ca \longrightarrow Pu + 3/2\ CaI_2$	-59.9	575


Powder Charge
PuF_4
Reducing Agent
Calcium
25% mole excess
Booster
Iodine
0.1-0.5 Mol I_2/Mol PuF_4
Inert gas purge
Hermetically Sealed Bomb
Heat
Pu metal
95-99+ % yield
Slag and Crucible Fragments

a greater "booster ratio" to compensate for relatively larger heat losses. The optimum ratio of iodine to plutonium tetrafluoride as a function of charge size is given in Table III. For reductions of about one kilogram or more of plutonium, the supplemental heat provided by a "booster" is less significant. However, the use of as little as 0.05 moles of iodine per mole of plutonium has been found to slightly improve reduction yields and to facilitate the separation of metal regulus from the slag and refractory.

Metal reduction yields of 97 to 99 percent may be obtained in this process. Oxygen has a deleterious effect on the metal yield; however, reasonably good yields may be obtained from plutonium(IV) fluoride containing up to ten percent plutonium oxide.

The pressure vessel may be heated either by induction or by a resistance furnace. The "booster reaction" starts at about 400 C, while a temperature of over 600 C is necessary to initiate the calcium-plutonium fluoride reaction.

After the reduction reaction has taken place and the pressure vessel cooled to near ambient temperature, the plutonium regulus may be separated from the reduction slag. The regulus is frequently washed with concentrated nitric acid to remove any adhering slag or calcium metal. The resulting product is generally free of inclusions and voids.

TABLE III

OPTIMUM RATIO OF IODINE TO PLUTONIUM TETRAFLUORIDE IN VARIOUS NOMINAL CHARGE SIZES FOR REDUCTION BY CALCIUM

Scale (Grams of Pu)	"Booster Ratio" (Moles I_2/mole PuF_4)
5	0.50
50	0.35
500	0.30
1000	0.15
1500	0.10

KM Harmon:WH Reas:rd

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