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Design of the Laboratory-Scale Plutonium Oxide Processing Unit in the Radiochemical Processing Laboratory

March 2015

GJ Lumetta
DE Meier
JM Tingey
AJ Casella
CH Delegard
MK Edwards
RD Orton
BM Rapko
JE Smart

U.S. DEPARTMENT OF ENERGY

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Pacific Northwest National Laboratory
Richland, Washington 99352

Abstract

This report describes a design for a laboratory-scale capability to produce plutonium oxide (PuO_2) for use in identifying and validating nuclear forensics signatures associated with plutonium production, as well as for use as exercise and reference materials. This capability will be located in the Radiochemical Processing Laboratory at the Pacific Northwest National Laboratory. The key unit operations are described, including PuO_2 dissolution, purification of the Pu by ion exchange, precipitation, and re-conversion to PuO_2 by calcination.

Summary

The National Technical Nuclear Forensics Center (NTNFC) within the Domestic Nuclear Detection Office (DNDO) of the Department of Homeland Security (DHS) has funded Pacific Northwest National Laboratory (PNNL) to establish a laboratory-scale (up to 200 g Pu per batch) capability to produce plutonium oxide (PuO_2) for use in identifying and validating nuclear forensics signatures associated with plutonium production, as well as for use as exercise and reference materials. This capability is being installed in Room 604 in the Radiochemical Processing Laboratory (RPL).

The key unit operations for producing PuO_2 are as follows. The feed plutonium material is received in the RPL in oxide form. The as-received oxide is dissolved in nitric acid media (with fluoride added as needed). The resulting solution is subjected to ion exchange to remove impurities from the plutonium stream, and then the plutonium is precipitated in the form of a salt (e.g., oxalate, peroxide, or hydroxide). Finally, this Pu salt is converted back to PuO_2 by heating (calcining). In order to make this capability a useful tool for identifying and validating nuclear forensics signatures, the system is designed to be flexible, allowing variations in the different process parameters (e.g., temperature, manner of reagent addition, or type of precipitating agent).

This report describes the laboratory-scale PuO_2 production capability being established at PNNL. The key features include:

- Plutonium oxide is received at the RPL and 200 g aliquots are transferred to a glovebox in RPL Room 604 for processing.
- The PuO_2 is dissolved in nitric acid media. If necessary, fluoride (in the form of calcium fluoride or hydrofluoric acid) is added to aid in dissolving the PuO_2.
- The plutonium solution is clarified by filtration and then purified by anion exchange using Reillex HPQ® anion-exchange resin, or another suitable anion-exchange resin.
- Although the design allows for a variety of plutonium precipitation steps, the design is based primarily on Pu(III) oxalate [$Pu_2(C_2O_4)_3 \cdot 10H_2O$] precipitation. The purified Pu solution is adjusted to the +3 oxidation state with ascorbic acid, then is treated with oxalic acid to precipitate $Pu_2(C_2O_4)_3 \cdot 10H_2O$.
- The $Pu_2(C_2O_4)_3 \cdot 10H_2O$ is calcined in a muffle furnace to convert it to PuO_2.
- The PuO_2 product is packaged and distributed as directed by the NTNFC.

Functional descriptions are provided for each unit operation, and the various requirements for these operations are identified in this report. The specific equipment and their layout in the gloveboxes are also described.

This report is being issued to fulfill milestone PNNL.14.008.B.

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Acronyms and Abbreviations

Am	americium
°C	degree(s) Celsius
Ci	curie(s)
cm	centimeter(s)
DHS	U.S. Department of Homeland Security
DI	deionized
DNDO	Domestic Nuclear Detection Office
DOE	U.S. Department of Energy
DOT	U.S. Department of Transportation
ft	foot/feet
g	gram(s)
GEA	gamma energy analysis
h	hour(s)
HDPE	high-density polyethylene
HF	hydrofluoric acid
HNO_3	nitric acid
H_2O_2	hydrogen peroxide
in.	inch(es)
kg	kilogram(s)
L	liter(s)
LANL	Los Alamos National Laboratory
M	molar (moles per liter)
meq	milliequivalent(s)
mg	milligram(s)
mL	milliliter(s)
mol	mole(s)
$NaNO_3$	sodium nitrate
NTNFC	National Technical Nuclear Forensics Center
O_2	oxygen
PNNL	Pacific Northwest National Laboratory
PP	polypropylene
Pt	platinum
PTFE	polytetrafluoroethylene (Teflon®)
Pu	plutonium
$Pu_2(C_2O_4)_3\cdot10H_2O$	plutonium(III) oxalate decahydrate

PuO_2	plutonium dioxide
Rh	rhodium
RPL	Radiochemical Processing Laboratory
SRS	Savannah River Site
SS	stainless steel
UV/vis	ultraviolet/visible
vis/NIR	visible/near-infrared

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1.0 Project Description

1.1 Background

Under the auspices of the Department of Homeland Security (DHS)/Domestic Nuclear Detection Office (DNDO)/National Technical Nuclear Forensics Center (NTNFC), Pacific Northwest National Laboratory (PNNL) is establishing a laboratory-scale capability to produce plutonium oxide (PuO_2) for use in identifying and validating nuclear forensics signatures associated with plutonium (Pu) production, as well as for use as exercise and reference materials. In this context, "laboratory-scale" is defined as up to 227 g PuO_2 (200 g Pu) per batch produced. This capability will be established in Room 604 in the Radiochemical Processing Laboratory (RPL) (Figure 1.1). The key unit operations will be dissolution of the as-received PuO_2, purification of the Pu by ion exchange, precipitation, and conversion to PuO_2 by calcination. To make this capability a useful tool for identifying and validating nuclear forensics signatures, the system will be designed to be flexible, allowing variations in the different process parameters (e.g., temperature, manner of reagent addition, or type of precipitating agent).

To support the project, a comprehensive suite of analytical capabilities will be available, including both inorganic and radiochemical analyses. A thorough analysis will be performed on the feed and process materials in order to determine or develop the nuclear and chemical forensic signatures associated with PuO_2 production flowsheets. State-of-the-art elemental and isotopic analytical support is available on-site, as are advanced microscopy (optical, scanning electron, and transmission electron), spectroscopy [e.g., micro Raman and fluorescence, as well as solid ultraviolet/visible (UV-Vis), and Fourier transform infrared], and X-ray diffraction instruments. These methods will be applied as appropriate to fully characterize the feed materials, the process streams, and the PuO_2 product. Additionally, to improve the efficiency of operations and to reduce personnel radiation exposure due to transferring samples out of the glovebox, installation of on-line instrumentation will be considered as part of the design of the laboratory-scale PuO_2 processing capability. Previous research at PNNL has shown that key process parameters, such as the Pu oxidation state and nitric acid (HNO_3) concentration, can be determined rapidly and nondestructively, by using on-line spectroscopic monitoring tools.[1-3]

Figure 1.1. Gloveboxes to be Used to House the Laboratory-Scale Plutonium Oxide Processing Capability

1.2 Assumptions

The following assumptions are made regarding the design and installation of the laboratory-scale PuO_2 processing capability.

1. The capability will be established in existing gloveboxes in Room 604 of the RPL.
2. Up to 1 kg of Pu (as PuO_2) may be received in a given shipment, with the batch being separated into $\leq$ 200 g aliquots.
3. The as-received PuO_2 will have been previously processed to meet the Department of Energy (DOE) 3013 standard for long-term storage of PuO_2.
4. Each process run will be performed on 200 g lots of Pu.
5. The feed to the ion exchange column will contain approximately 40 g Pu/L and 7 mol/L HNO_3.
6. The feed to the precipitator will be adjusted to between 30 and 100 g Pu/L, depending on the specific test objectives.
   a. If the defined experimental parameters require the feed to the precipitator to be $\leq$ 30 g Pu/L, then the 200 g batch will be subdivided into smaller manageable amounts for the precipitation step.
7. The dissolver will require a heating capability.
8. The ion exchange column will require a heating capability.
9. The precipitator will require a temperature control capability.
10. Calcining will be a batch unit operation.
11. Based on a 200 g batch of Pu, 386 g Pu(III) oxalate decahydrate $[Pu_2(C_2O_4)_3 \cdot 10H_2O]$ is the batch size for the muffle furnace, which has a wet bed volume of 250 to 330 cm^3.[4] The calcining furnace is designed to accommodate more than twice this volume to allow for operational flexibility.
12. Any PuO_2 product material that is not shipped out for analysis, or archived, will be recycled to the dissolver and processed as part of the subsequent batch.

2.0 Process Description

2.1 Process Overview

The basic process for producing PuO_2 is shown schematically in Figure 2.1. Plutonium will be received in the RPL in oxide form. The as-received oxide will be dissolved in HNO_3 media. The resulting solution will be subjected to ion exchange to remove impurities from the Pu stream, and then the Pu will be precipitated in the form of a salt (e.g., oxalate, peroxide, hydroxide, or fluoride). This Pu salt will be converted to PuO_2 by heating (calcining).

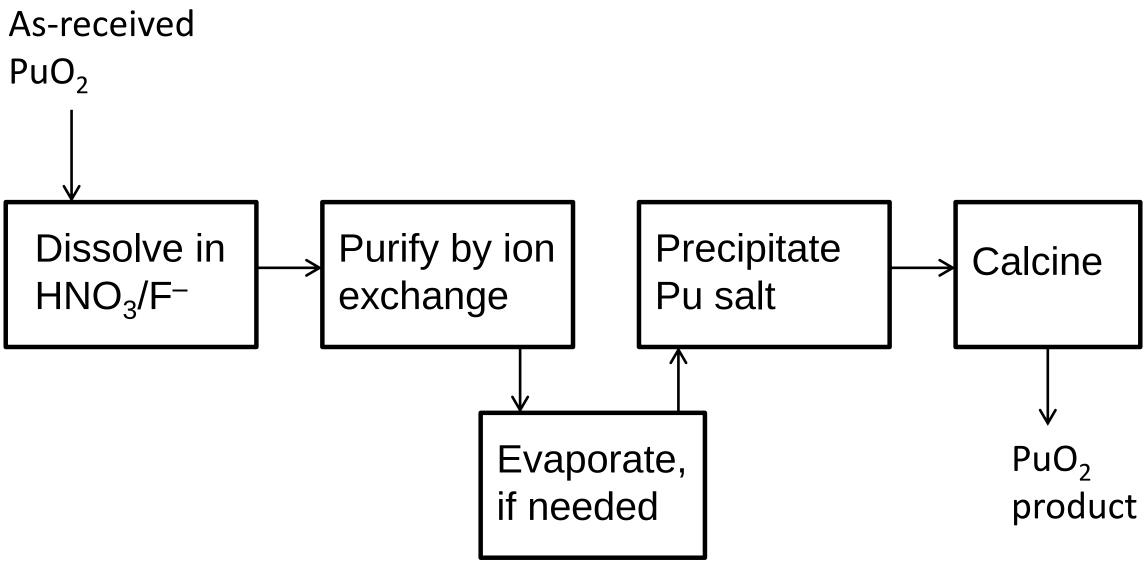


Figure 2.1. Basic Process Steps for Preparing PuO_2 in the Laboratory-Scale Plutonium Oxide Processing Capability

The feed to the process will be PuO_2 shipped to PNNL from other U.S. DOE sites, such as the Savannah River Site (SRS) or Los Alamos National Laboratory (LANL). Quantities up to 1 kg Pu as oxide may be received in a single shipment (in aliquots of 200 g Pu or less). Portions of the as-received PuO_2 (containing approximately 200 g Pu) will be transferred into a glovebox in Room 604 of the RPL, where it will be dissolved, purified, and converted back to oxide. The following sections contain detailed descriptions of the process steps to be performed.

2.2 Dissolution

The function of the dissolution stage of the process is to dissolve the as-received PuO_2 feed material into an aqueous HNO_3 solution that is suitable for the ion exchange purification step.

2.2.1 Dissolution Chemistry

Plutonium oxide can be dissolved slowly in boiling mineral acids. The most common method involves refluxing the PuO_2 in concentrated HNO_3 containing fluoride ion for an extended time. The following mechanism has been proposed for this reaction:[5]

$$HNO_3 + HF + PuO_2 \rightarrow PuF_x \rightarrow H_{z-4}Pu(NO_3)_z \rightarrow Pu(NO_3)_6^{2-} \quad (3.1)$$

Dissolution by this method is initially rapid, but slows as the reaction progresses. The rate is controlled by a chemical reaction at the PuO_2 surface, and is first order with respect to the PuO_2 surface area and the concentration of the free hydrofluoric acid (HF) in solution.[6] Dissolution rates with varying HF concentrations have been studied, and it was found that the dissolution rate increases with increasing HF concentration up to 0.2 M and then decreases at higher concentrations.[7] At HF concentrations above 0.2 M, insoluble plutonium fluoride (PuF_4) is precipitated, and the dissolution rate decreases. In an effort to boost the dissolution rates, different oxidants in combination with HF have been explored. While some of the oxidants performed well, none was adequate to produce a dissolution rate faster than that obtained with 15.6 M HNO_3/0.2 M HF.

Nitric and hydrofluoric acid addition methods have been evaluated to determine an optimal dissolution strategy.[8] The preferred method consisted of adding HNO_3 and half the required amount of the HF, heating the mixture at 110°C for 2 h, and then adding the remaining required amount of HF. By proceeding in this manner, the dissolution efficiency improved to 95% after only two passes. In this work, to avoid the hazards associated with handling aqueous HF, calcium fluoride (CaF_2) will generally be used as the fluoride source for the dissolution step.

2.2.2 Dissolution Protocol

This section describes the assumed dissolution protocol that is adapted from Martinez et al.[8] Before beginning the bulk dissolution process, the dissolution protocol will be tested at a small scale (1 to 10 g PuO_2). Adjustments will be made (e.g., HNO_3 concentration, fluoride addition rate) as necessary to achieve adequate dissolution of the as-received PuO_2 material.

The PuO_2 feed is placed in a polytetrafluoroethylene (PTFE) reflux apparatus. The vessel is constructed of PTFE to minimize the introduction of impurities into the Pu solution. For a 227 g batch of PuO_2 (200 g Pu), a two-strike dissolution process is assumed.(a) Each strike uses 1 L of 15.7 M HNO_3 containing 0.1 M CaF_2 (giving a total fluoride concentration of 0.2 M). The solution from the first strike will be removed from the undissolved solids before implementing the second strike. A typical dissolution procedure would be as follows. First, 1 L of 15.7 M HNO_3 and 3.9 g of CaF_2 (0.1 mole fluoride) is added to the vessel containing the PuO_2 feed material. The dissolution vessel is fitted with a PTFE reflux condenser and then placed in either a heating block or heating mantle, and digested at 110°C for 2 h with stirring. After 2 h, an additional 3.9 g of CaF_2 (0.1 mole fluoride) is added to bring the total F^- concentration to approximately 0.2 M; the solution is digested at 110°C for an additional 2 h with stirring. Typical dissolution efficiencies after the first-pass dissolution are assumed to be between 70 and 90%. At this point, the Pu solution is removed, leaving the undissolved PuO_2 heels in the reaction chamber for a second pass through the dissolution process. The second dissolution strike is identical to the first. A two-pass dissolution will result in ~2 L of 13.2 M HNO_3/0.2 M F^-/0.1 M Ca^{2+}/0.4 M $H_2[Pu(NO_3)_6]$ (neglecting any complexation of Pu by the fluoride ion). At any point in the process, samples can be removed through a sample port to assess Pu solution concentrations or analyze the undissolved residue.

(a) Multiple smaller-volume strikes could also be used if this were found to be more effective.

2.2.3 Solution Clarification

Before introduction to the ion exchange column, any undissolved solids must be removed from the dissolved Pu solution. Commercial off-the-shelf filtration units will be used for this purpose. The filtration equipment will be made of plastic (e.g., polypropylene [PP] or high-density polyethylene [HDPE]) to minimize metal-ion contamination of the dissolved Pu solution. After filtration, the clarified Pu nitrate solution will be transferred to a tank and adjusted for the purification step as described in the next section.

2.3 Purification by Ion Exchange

The function of the ion exchange step is to remove impurities from the dissolved Pu stream. The primary impurities of concern are the ingrown daughter products (e.g., ^{241}Am), but depending on the processing history of the feed PuO_2, other impurities might be present as well. The requirements for the purified Pu stream will be defined by the specific needs of the DNDO/NTNFC signature development program.

Various well-established methods are available for purifying Pu in HNO_3 solutions. These methods include precipitation, solvent extraction, and ion exchange. Anion exchange is the method of choice for this project, but the system will be designed with sufficient flexibility that cation exchange or extraction chromatography methods could be considered in the future. Anion exchange has been shown to be very effective for Pu purification, and indeed is the method selected at SRS for both Pu and neptunium purification in the HB-Line, Phase II.[9-11]

The following approach will be taken to purify the Pu solution by anion exchange. The HNO_3 concentration of the Pu feed solution will be adjusted to approximately 7 M HNO_3. The nitrous acid typically present in such relatively concentrated HNO_3 solutions serves to adjust the Pu oxidation state to the desired +4, but hydrogen peroxide (H_2O_2) will be added as required to achieve complete conversion to Pu(IV). At this high nitrate concentration, Pu(IV) has been shown to strongly sorb onto strongly basic anion-exchange resins as the hexanitrate dianion $[Pu(NO_3)_6]^{2-}$.[12] The anion-exchange resin will be contained in a jacketed column made from quartz. The jacketed column will allow for processing at non-ambient temperatures, if desired. The circulating fluid for the jacketed column will be heated using a circulating bath.

For the initial stages of this project, the proposed resin for this system is Reillex HPQ®, now sold by Vertellus Specialties. Reillex HPQ is a macroporous, strongly basic anion-exchange resin containing mostly (~70%) methylated poly(4-vinylpyridine) cross-linked with di-vinylbenzene.[13] This resin has been used for decades at both SRS and at LANL for Pu purification.[14] The superior chemical and radiation stability of this material over other strongly basic, commercial anion-exchange resins makes it the material of choice for actinide separations in high radiation environments. In the event that Reillex HPQ is not available, Lewatit® Monoplus MP 800 KR is a potential alternative resin. The Lewatit resin is also a macroporous, strongly basic, anion-exchange resin (quarternary amine type I) based on cross-linked polystyrene.

Prior to loading into the anion-exchange column, the resin will be converted from the as-received chloride form to the nitrate form by washing with excess 1 M sodium nitrate ($NaNO_3$), contacting with 8 M HNO_3 at 85°C for 45 minutes, and then rinsing with deionized (DI) water.[9] The hot HNO_3

treatment has been shown to prevent an otherwise exothermic event observed for the as-received resin in contact with 8 M HNO_3, and also improves the kinetic properties of the resin.[15] Immediately before use, one bed volume of 7 M HNO_3 will be passed into the column to condition it so that Pu hydrolysis does not occur upon initial loading of the column.

Based on the dissolution process described in Section 2.2, it is assumed that the following adjustments will be made to the ion exchange feed solution. First, 2.55 L of 3.4 M HNO_3 will be added to adjust the HNO_3 concentration to ~7 M. Second, assuming fluoride was added to aid in dissolving the PuO_2, aluminum nitrate [$Al(NO)_3$] will also be added to complex the fluoride ion present in the ion-exchange feed solution. One mole of aluminum will be added per mole of fluoride. Again, based on the description in Section 2.2, 0.25 L of 1.6 M aluminum nitrate will be added (0.4 moles of Al). Third, H_2O_2 will be used to adjust the Pu valence to the +4 oxidation state.[16] Based on the procedure described by Ryan,(a) 0.2 L of 30% H_2O_2 will be added (1 mL 30% H_2O_2 per gram of Pu). The 30% H_2O_2 will be added in three nearly equal increments.

The adjusted feed solution will be pumped through the column, with the effluent collected in an appropriate receiving tank. The resin will then be rinsed with nominally six bed volumes of 7 M HNO_3. This rinsing solution will also be directed to the receiving tank containing the effluent. The loading and column washing steps will be performed in an up-flow configuration. The column-loaded Pu will then be eluted with low concentration (e.g., 0.35 M) HNO_3 solution.[9, 17] The elution will be conducted in a down-flow configuration. This Pu-containing eluate will be captured in a receiving tank for storage and delivery to the precipitation area of the glovebox.

2.4 Evaporation

If required by the testing objectives, the purified Pu solution will be concentrated by distilling off excess liquid until the desired Pu concentration is achieved. The condensate will be collected in a graduated cylinder in order to monitor the progress of the evaporation process. The Pu concentration in the adjusted Pu solution will be verified by spectrophotometry (either within the glovebox or with a sample removed from the glovebox).

2.5 Precipitation

Following purification, the Pu will be precipitated from solution in the form of a salt, and then converted to the PuO_2 by heating. For the purposes of this design report, it is assumed that the Pu will be precipitated as Pu(III) oxalate; however, the system will be designed to accommodate various precipitation approaches. The Pu(III) oxalate precipitation step functions to convert the Pu(IV) nitrate solution product from the anion-exchange purification step to a washed and damp Pu(III) oxalate product, by valence and acid adjustment and by chemical precipitation. Plutonium(III) oxalate has the formula $Pu_2(C_2O_4)_3{\bullet}10H_2O$. The precipitation process may follow the chemical conditions given in an existing RPL procedure(a) based on SRS experience,[18] but other conditions may be used as outlined in a review of Pu(III) oxalate precipitation chemistry.[19] The optimum batch conditions for more concentrated Pu feed solutions involve slowly adding 1 M $H_2C_2O_4$ (oxalic acid) solution (in direct-strike fashion) to the Pu(III)

(a) Ryan, J. L. *Purification of Plutonium Using Lewatit UMP-950 Ion Exchange Resin*; Procedure 325-PU-Purify-1; Pacific Northwest National Laboratory: Richland, WA, 1998.

solution at room temperature with a target slurry solution composition of 1 M HNO_3 with 0.25 M excess $H_2C_2O_4$.[19] The precipitation system is designed to accommodate Pu concentrations in the range 30 to 100 g Pu/L in a single batch. If the experimental parameters require the Pu concentration to be ≤ 30g/L, the 200 g Pu batch will be divided into two or three precipitation batches.

The precipitation reactor will be designed so that it can function either in a batch mode or in a continuous mode in which the $H_2C_2O_4$ and Pu solutions are added simultaneously to the reactor vessel. The apparatus will be designed also to accommodate potential future Pu(IV) oxalate [$Pu(C_2O_4)_2 \bullet 6H_2O$] and other potential Pu precipitation schemes. Although Pu throughput is unlimited in the continuous mode, the batch size will depend on the Pu solution concentration and the maximum target production of 200 g of contained Pu.

To prepare Pu(III) oxalate from Pu(IV) nitrate solution, the following sub-steps must be completed:

1. Adjust ~80 g Pu(IV)/L anion-exchange eluate in ~0.35 M HNO_3 to the target Pu and HNO_3 concentrations by dilution or evaporation. Target acid concentrations will be reached using concentrated (~15.7 M) or dilute (≥ 0.35 M) HNO_3.
2. Adjust the Pu valence to the +3 state. Both a chemical reductant (e.g., ascorbic acid, hydroxylamine) and a nitrous acid (HNO_2) scavenger (e.g., hydrazine (N_2H_4), sulfamic acid, urea) are needed to prepare and stabilize the Pu(III) nitrate from the Pu(IV) feed solution. In the absence of a HNO_2 scavenger, Pu(III) reoxidizes to Pu(IV).
3. Adjust the precipitation temperature. The precipitation temperature will be controlled using a circulating water bath to the value specified in the test protocol.
4. Precipitate Pu(III) oxalate: batch or continuous precipitation of Pu(III) oxalate will be performed by mixing the freshly prepared Pu(III) nitrate solution with the $H_2C_2O_4$. The $H_2C_2O_4$ may be introduced as its solution, which is effectively limited to ≤ 1 M, or as solid crystals of $H_2C_2O_4 \bullet 2H_2O$. The precipitating mixtures will be stirred using an overhead stirrer at controlled stirrer speed, or by air sparging. If elevated digestion temperatures are needed, a heated circulating bath will be employed.
5. Digest Pu(III) oxalate: the appropriate digestion/residence time will be monitored before the solution and the Pu(III) oxalate solids are separated.
6. Separate and wash Pu(III) oxalate: the Pu(III) oxalate solids will be filtered from the slurry, and the filter cake will be washed on the filter using a ~0.5 M HNO_3/0.2 M $H_2C_2O_4$ solution.
7. Deliver damp Pu(III) oxalate: the washed damp $Pu_2(C_2O_4)_3 \cdot 10H_2O$ solids will be delivered to the next functional step in the process, drying and calcination.

2.6 Calcination

In air, the thermal decomposition of both Pu(IV) and Pu(III) oxalate to PuO_2 is mostly complete at 450°C,[20] although higher temperatures, approximately 800°C,[18, 21] are often used to drive off residual carbon by air oxidation. The highest published temperature range used was 1,200–1,250°C for complete conversion to PuO_2.[20] Calcination in argon requires higher temperatures for conversion (~ 600°C), with carbon-containing impurities remaining due to lack of oxidation. To minimize carbon-containing impurities, 100% O_2 environments have been used.[20]

The prescribed standard method for conversion of $Pu_2(C_2O_4)_3 \cdot 10H_2O$ by Porter and Symonds recommends heating $Pu_2(C_2O_4)_3 \bullet 10H_2O$ in a stream of air from room temperature to 125°C at a rate of about 1.5°C/min (over approximately 1 h), and holding for 1 h at 125°C to convert to the anhydrous form $Pu_2(C_2O_4)_3$.[18] After the 1 h holding period, the temperature is increased at a rate of 3–5°C/min until the final calcination temperature is reached (most often between 450°C and 750°C), which is maintained for 1 to 2 h. The resulting PuO_2 is then cooled to room temperature under the air stream. Samples can be taken and analyzed both before and after calcination to verify complete conversion to the oxide. If the conversion is incomplete, the material can be manually stirred and fired again.

The PuO_2 product will be sampled and characterized to determine product quality. At a minimum, this characterization will include determining elemental purity and radiochemical purity. As directed by the client, samples of the product material will shipped for further analysis, both within PNNL and to other laboratories participating in the DNDO/NTNFC program. A portion of the PuO_2 product will be archived, and then the remainder will be re-dissolved to serve as feed to the next processing batch.

3.0 Design Features and Equipment Lists

This section provides descriptions of the equipment to be used to perform the functions described in Section 2.0, including lists of the specific equipment items to be procured. The information is organized according to the primary unit operations (e.g., dissolution, ion exchange, etc.). The tanks associated with the entire process are discussed separately in Section 0.

3.1 Dissolver

Table 3.1 lists the specific equipment to be procured for the dissolver system. The dissolver consists of a 2 L PTFE reaction vessel with a flat flange on the top. A multi-port lid is attached to the flanged top of the reaction vessel along with a gasket for sealing the interface between the vessel and the lid. The lid is fitted with a reflux condenser, also constructed of PTFE. The lid can also be fitted with a PTFE dropping funnel, if needed, for reagent (e.g., HNO_3) addition. The other ports on the lid can be sealed during digestion of the PuO_2 feed material, but can be used for reagent (e.g., CaF_2) addition or for withdrawal of the dissolved Pu solution. The dissolution vessel is heated with a heating mantel that is controlled using a J-Kem Model 270 temperature controller. This temperature controller has two independent circuits—one for primary temperature control of the heating mantel and one to serve as an over-temperature shut off. The mixture can be stirred using a magnetic stirrer placed beneath the heating mantel. The condenser is cooled using a water-circulating bath located external to the glovebox; the water will be circulated through a closed loop to prevent contamination of the circulating bath.

The following is a list of the requirements for the dissolver system.

Equipment

- A balance with a capacity of 400 g and a sensitivity of 0.01 mg or better
- 1500 mL capacity PTFE dissolution vessel, equipped with a PTFE reflux condenser and a port for solids addition
- heating mantle
- vacuum filtration apparatus with filter paper or PTFE filter membrane
- 3 L capacity tank for receipt of clarified Pu solution.

Reagents

- DI water
- reagent-grade concentrated (~16 M) HNO_3
- reagent-grade CaF_2 or other fluoride sources.

Test Materials

- Pu oxide
- coupons for corrosion doping (e.g., 325 L stainless steel, Hastelloy®, Pyrex®, etc.) (if required for the experimental objectives).

Analytical Services

- Pu solution concentrations by absorption spectrophotometry or gamma energy analysis (GEA)
- Pu isotopic analysis by inductively coupled plasma mass spectrometry
- Pu residue analyses by X-ray diffraction and fusion digestion followed by alpha energy analysis (AEA).

Table 3.1. Equipment List for Dissolver System, Including Post-Dissolution Filtration

Item Description	Vendor	Item number	quantity
Heating Mantle for 2000-ml beaker, 550 watts, 115 VAC	Cole Parmer	EW-36227-16	1
MegaMag Genie, Large-Capacity Analog Magnetic Stirrer; 120V	Cole Parmer	EW-86575-10	1
Mono-Mold Standard Stir Bar with Spinning Ring, 3"L x 1/2" dia	Cole Parmer	SC-04612-30	5
PolyScience 5260 Recirculating Chiller, -10 to 70C, Centrifugal, 120V	Cole Parmer	EW-12910-13	1
Fittings to connect SS tubing with chiller and condenser	Grainger	NA	4
Tubing, Seamless, 1/2 In, 6 ft, 316 SS	Grainger	3ACH7	4
BOLA Reaction Vessel, Flat Flange, 2000 mL	Finemech Precision Mechanical Components	B281-09	1
BOLA Gaskets, Flat Flange	Finemech Precision Mechanical Components	B282-02	1
BOLA Lids, Flat Flange	Finemech Precision Mechanical Components	B283-02	1
BOLA Joining Pieces, Flat Flange	Finemech Precision Mechanical Components	B284-02	1
BOLA Dropping Funnel, 125 mL	Finemech Precision Mechanical Components	B285-01	1
BOLA Vertical Liebig Condenser, 450 mm	Finemech Precision Mechanical Components	B301-04	1
BOLA Standard Ground Joint Tube Fitting,NS 29/32; Ø 6 x 8 mm	Finemech Precision Mechanical Components	B304-22	2
BOLA Plug, aØ 8 mm	Finemech Precision Mechanical Components	D648-08	1
Model 270 · Thermocouple type K · Complete system	J-Kem Scientific	Catalog# 270-K-S	1
Wire, Thermocouple Lead, K, 100 feet	Grainger	5ZY36	1
Jack, Thermocouple, K	Grainger	5ZY34	10
Plug, Thermocouple, K	Grainger	5ZY32	10
Extension power cord	Grainger	3EB10	1
Vacuum/pressure diaphragm pumps, PTFE-coated wetted parts	Cole Parmer	UX-79200-30	1
1/8" NPT/barbed fitting	Grainger	6AFP4	2
Tubing, 1/8 In ID, 1/4 In OD, 50 Ft, PTFE	Grainger	2TXE8	1
Advantec PTFE Hydrophobic Membranes with Support	Cole Parmer	WU-02916-52	1
Advantec Polypropylene Filter Holder for 25-mm membranes	Cole Parmer	WU-06623-32	5
Female Luer X 1/8" Hose Barb Adapter, PVDF	Cole Parmer	WU-41507-28	1
Male Luer With Lock Ring X 1/8" Hose Barb, PVDF	Cole Parmer	WU-41507-25	1

3.2 Ion Exchange System

The ion exchange system consists of a jacketed quartz column along with the associated pumps and transfer lines. The circulating fluid for the jacketed column is heated using a circulating bath. The circulating-bath reservoir is located outside of the glovebox, with self-contained lines running the heat transfer fluid to and from the jacketed column. Using quartz as the column material minimizes the introduction of impurities caused by leaching of the column material, provides relatively good radiation resistance, and allows for ready viewing of the resin. Viewing of the resin is important to determine whether the resin bed remains properly packed and check that no channeling occurs, which would alter the ability of the resin to selectivity load and purify Pu. The column contains screens at both ends to prevent resin particles from leaving the column. These screens are adjustable to fit various amounts of resin as needed, and are designed to accommodate potential shrinking and swelling of the resin. The inner diameter of the column is 5.0 cm (2.0 inches) with a length of 1.0 m (39.4 inches). These dimensions are chosen so that a commercial off-the-shelf jacket can be attached to the column. The 5.0-cm diameter provides a safe geometry to help mitigate criticality concerns, yet still will provide sufficient column capacity to readily achieve the target loading of 200 g (0.84 moles) of Pu.

Data from Sigma-Aldrich Co. indicates that the capacity of Reillex HPQ is 3.4 meq/g dry weight and that the as-received resin is 55% water, thus giving an as-received capacity of 1.53 meq/g as-received resin. This information indicates that approximately 1,110 g of resin would be required to process 200 g of Pu. The bulk density has been reported as 0.89 g/mL,[14] which indicates that at least 1,240 mL of bed volume is needed to process 200 g of Pu. The 5.0 cm diameter by 100 cm high column provides a volume of 7.9 L, six times the volume needed for the Reillex HPQ resin bed. However, this design allows for the possibility of using other resins with somewhat lower exchange capacity.

The system will contain pressure relief valves or rupture disks in each area that might be isolated in the process to mitigate the consequences of any violent gas release that might occur as the result of an exothermic or gas-releasing decomposition either from the nitrate solution or from resin decomposition. Fluid transfers with this system are controlled with pumps placed in-line with each system tank.

Table 3.2 lists the specific equipment to be procured for the ion exchange system. The following is a list of the requirements for the ion exchange system.

Equipment

- peristaltic pumps for solution transport
- flow meters for monitoring solution flow from and to the tanks and at the column entrance and exit
- one Raman spectrometer with two detectors for monitoring HNO_3 concentrations at the column entrance and exit (optional)
- one vis/NIR spectrophotometer and two flow-through cells for Am and Pu monitoring at the column entrance and exit (optional)
- multiplexer for Raman and vis/NIR spectrometers (optional)
- one computer for analysis of spectroscopic and flow data (optional)
- 6 L capacity ion-exchange feed tank (see Section 0)
- 15 L capacity ion-exchange effluent receipt tank, shielded to reduce worker exposure to the 59.5 keV ^{241}Am gamma emission (see Section 0)
- 3.5 L capacity purified Pu receipt tank (see Section 0)
- three-way valves
- two-way valves
- variable-pressure relief valves
- 5.0 cm (2.0 inches) diameter, 1.0 m (39.4 inches) high, jacketed quartz ion exchange column, including variable-height screens.

Reagents

- High-purity 3.5 M HNO_3
- 30% H_2O_2
- ion exchange resin (Reillex HPQ or Lewatit® Monoplus MP 800 KR).

Analytical Services

- Pu and Am solution concentrations by on-line spectrophotometry; supplemented by GEA and/or AEA
- HNO_3 concentration by on-line Raman spectroscopy; supplemented by potentiometric titration with standard sodium hydroxide
- inductively coupled plasma optical emission spectrometry for metal analysis.

Table 3.2. Equipment List for Ion Exchange System

Equipment Item #	Item Description	Vendor	Item number	quantity
1	Customized 5 cm dia, 100 cm ht quartz column	Allen Scientific Glass, Inc.	N/A	1
2	stand for 5 cm column	Spectrum Chromatography	Part # 123322	1
3	Support rods for 5 cm column	Spectrum Chromatography	Part # 123321	2
4	Support rings for 5 cm column	Spectrum Chromatography	Part # 123340	2
5	PTFE cloth 10 micron bed support - 10 cm by 10 cm	Spectrum Chromatography	Part # 124090	2
6	Polypropylene cloth 50 micron flow dispeser - 1 sq yard	Spectrum Chromatography	Part # 124092	1
7	Borosilicated jacket for 5 cm dia column ht 100 cm (3.5 ft)	Spectrum Chromatography	Part # 124332	1
8	Masterflex L/S PTFE tubing pump system - 3 to 300 rpm, 9 to 260 VAC	Cole-Parmer	77912-10	2
9	PTFE tubing for non-pump Masterflex pump, 4.48 by 6 mm, 25 ft	Cole-Parmer	06605-54	50 ft
10	PTFE tubing for Masterflex pump use, 6 mm OD, two 15' lenghts	Cole-Parmer	T-77390-60	30 ft
11	Cap (83B) with two 1/4" ID tubing connectors	Nalgene	2158-0021	2

It is highly desirable to equip the ion exchange and associated equipment with spectroscopic tools for real-time monitoring of solution conditions. During installation of the laboratory-scale capability, appropriate glovebox penetrations will be established for potential installation of optional spectroscopic monitoring equipment. Visible/near-infrared (vis/NIR) spectrophotometry and Raman spectroscopy could be installed to monitor key attributes of the adjusted ion-exchange feed solution. Specifically, the vis/NIR can be used to verify that the Pu oxidation state is +4, and the Raman spectrometer can be used to verify that the HNO_3 concentration is 7 mol/L before the solution is fed to the ion exchange column. Figure 3.1 illustrates the location where such measurements can take place. Both of these techniques can be performed remotely with in-line cells or probes being coupled by fiber optic cables to the spectrometers located outside the glovebox.[1] These spectroscopic tools would be inserted between the ion exchange feed tank and the ion exchange column. The system could be valved such that the solution can flow through the spectroscopy equipment and back into the feed tank during the feed adjustment steps. Once the Pu oxidation state and HNO_3 concentrations have been verified, the solution can be routed to the ion exchange column. The outlet of the ion exchange column could also be equipped with in-line vis/NIR (Figure 3.1). At this point, the column eluent could be monitored for Pu content so that only those fractions containing significant Pu are collected into the Pu product receipt tank. It should be noted that if specific test objectives require the process to be operated at non-optimal conditions, the spectroscopic monitoring tools can also be used to verify that the non-optimal conditions are met.

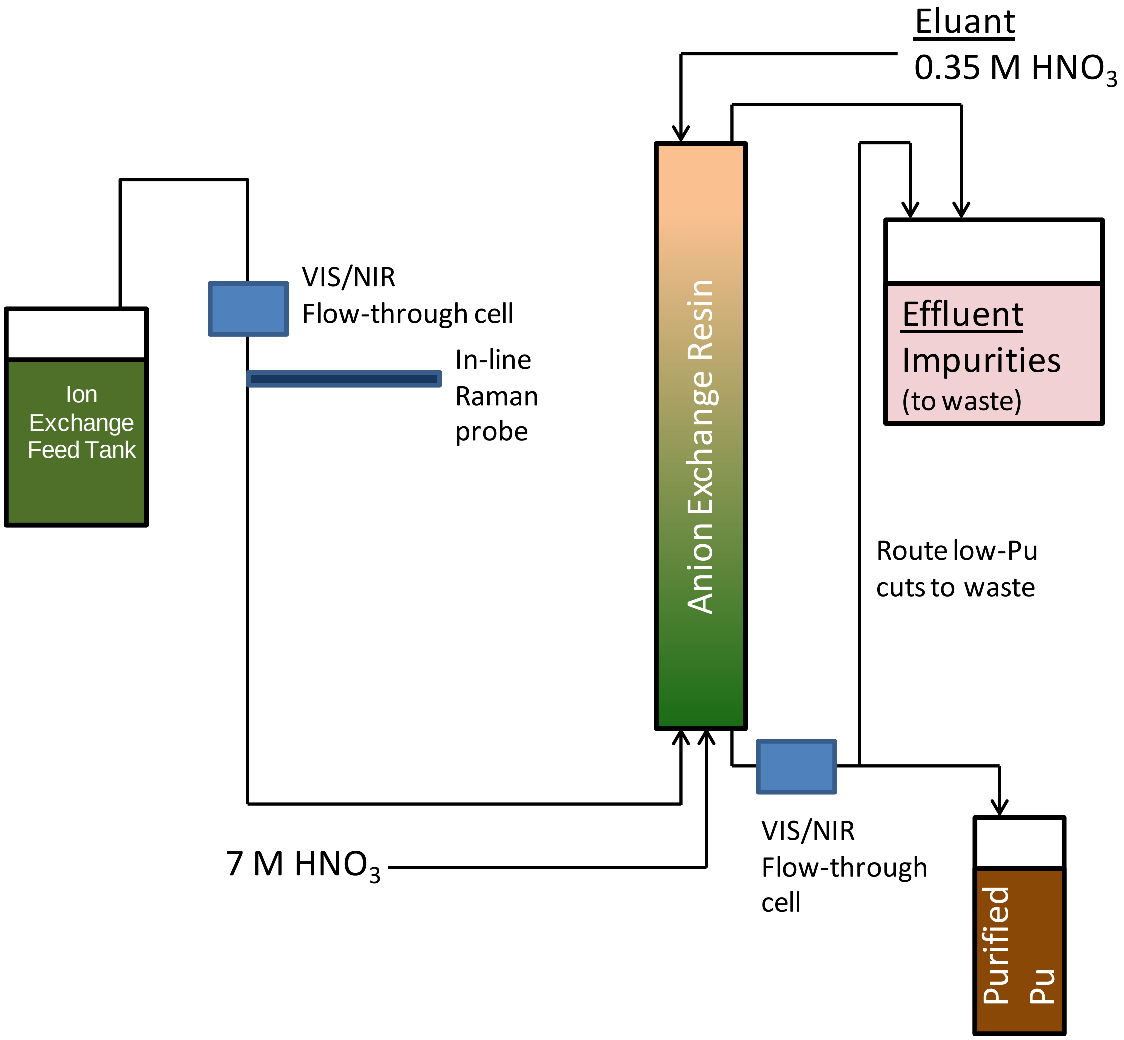


Figure 3.1. Proposed Locations for Installation of On-Line Spectroscopic Tools

3.3 Evaporator

The evaporator is constructed from quartz to avoid the introduction of impurities into the purified Pu nitrate solution. It consists of a relatively simple distillation apparatus with a 2 L capacity. Heating of the apparatus is achieved by means of a heating mantel. The condenser is cooled with a circulating chiller that is located outside of the glovebox.

Table 3.3 lists the specific equipment to be procured for the evaporator. The following is a list of the requirements for the evaporator.

<u>Equipment</u>

- 2 L capacity quartz still with critically safe geometry
- chilled circulating bath for cooling the condenser

- graduated condensate collection vessel (e.g., graduated cylinder) for monitoring the degree of evaporation.

Table 3.3 presents a list of the components required to construct the evaporator. The evaporator consists of an ambient-pressure distillation apparatus, consisting of a 2 L quartz flask fitted with a 2-port reaction flask head. One port will be available for the addition of solution to the flask, while the other port will be fitted with a sidearm adaptor for connection to a condenser.

Table 3.3. Equipment List for Evaporator System

Item Description	Vendor	Item Number	Quantity
2-L quartz reaction flask, flat bottom, 168-mm flat flange	Ace Glass, Inc.	D151235	1
2-L 470-Watt aluminum-housed heating mantle	Ace Glass, Inc.	12058-16	1
Quartz reaction head, 2-ports, 34/45 center neck, 24/40 side neck, vertical 168-mm flat flange	Ace Glass, Inc.	D151234	1
Quartz sidearm adapter, 24/40 top outer joint, 24/40 lower inner joint, 24/40 inner joint sidearm	Ace Glass, Inc.	D151236	1
Graham style condenser with reinforced 24/40 standard taper outer joint at the top	Ace Glass, Inc.	5979-14	1
Reaction flask clamp, two-piece, anodized, 143-mm	Ace Glass, Inc.	6508-11	1
34/45 quartz stopper	Ace Glass, Inc.		1
24/40 quartz stopper	Ace Glass, Inc.		1
PolyScience 5260 Recirculating Chiller, -10 to 70C, Centrifugal, 120V	Cole Parmer	EW-12910-13	1
Fittings to connect stainless steel (SS) tubing with chiller and condenser	Grainger	N/A	4
Tubing, Seamless, 1/2 In, 6 ft, 316 SS	Grainger	3ACH7	4

3.4 Precipitator and Filter

The precipitator is a custom-built apparatus. For maximum flexibility, the precipitation vessel is based on the mixed-suspension, mixed-product removal designs used in the Hanford Site Plutonium Finishing Plant Remote Mechanical A (RMA) and Remote Mechanical C (RMC) Lines, the Plutonium-Uranium Extraction Plant N Cell Pu(IV) oxalate continuous process vessels, and the test vessel used to develop Pu(IV) oxalate process parameters in the 1980s.[22] The vessel is designed to operate either in continuous mode with oxalic acid added as an aqueous solution, or in batch mode with the oxalic acid added as a solid or an aqueous solution in either direct- or reverse-strike mode. When operated in batch mode, the vessel can accommodate 10 L of the reaction mixture (7 L of 30 g Pu/L feed solution plus an additional 3 L of headspace).

The vessel and all wetted surfaces will be constructed of PP to avoid the introduction of metallic impurities into the Pu(III) oxalate. Figure 3.2 illustrates various aspects of the precipitator design. For convenience in fabrication, the precipitator is constructed in two pieces. The top straight cylindrical section is attached to the lower rounded section by a threaded design (Figure 3.2). This design also allows removal of the bottom part for thorough cleaning, if necessary. The inner diameter of the primary vessel chamber is 11.7 cm (4.6 in.) and the outer diameter is 14.0 cm (5.5 in.). To be consistent with Hanford Site continuous processing practice, the precipitation vessel is cylindrical with a rounded bottom that has a rounded cone rising from the center of the bottom (Figure 3.2).

The vessel is furnished with a central cylindrical draft tube (Figure 3.2) and has a variable-speed overhead impeller running at the center bottom of the draft tube to provide a downward flow. The draft tube is 55.9 cm (22 in.) long, with an inner diameter of 7.9 cm (3.1 in.) and an outer diameter of 8.9 cm (3.5 in.). There is a 2.54 cm (1 in.) vertical gap between the bottom of the draft tube and the lowest point of the radius of the bottom. The outer diameter of the draft tube is 3.5 in. The inner diameter of the draft tube is 3.1 in. The draft tube fins provide a space of about 1.5 cm (0.59 in.) between the outer diameter of the draft tube and the inner diameter of the vessel. These four fins function as baffles to improve mixing and solids suspension. The downward central flow and the rounded vessel bottom features also promote the suspension of slurry solids.

When operated in continuous mode, the metered Pu(III) nitrate and oxalic acid input solutions are added to the draft tube just above the impeller so that intimate mixing occurs rapidly. When operated in batch mode, solid oxalic acid or aqueous oxalic acid solution is added through a funnel/tube arrangement in the lid to the precipitation vessel. The digestion temperature can be adjusted using a heating bath circulating through a jacket on the outside of the vessel. The plutonium oxalate slurry is removed by suction through PP (or equivalent) tubing, and the slurry is directed to a suction filter to separate the solids from the mother solution. The same apparatus can also be used in the simpler batch precipitation mode. In batch mode, oxalic acid solution or solid is generally added directly to the Pu solution already present in the precipitation vessel; this is referred to as *direct-strike* mode. *Reverse-strike* addition can also be performed in which the Pu solution is added to an oxalic acid solution contained in the vessel.

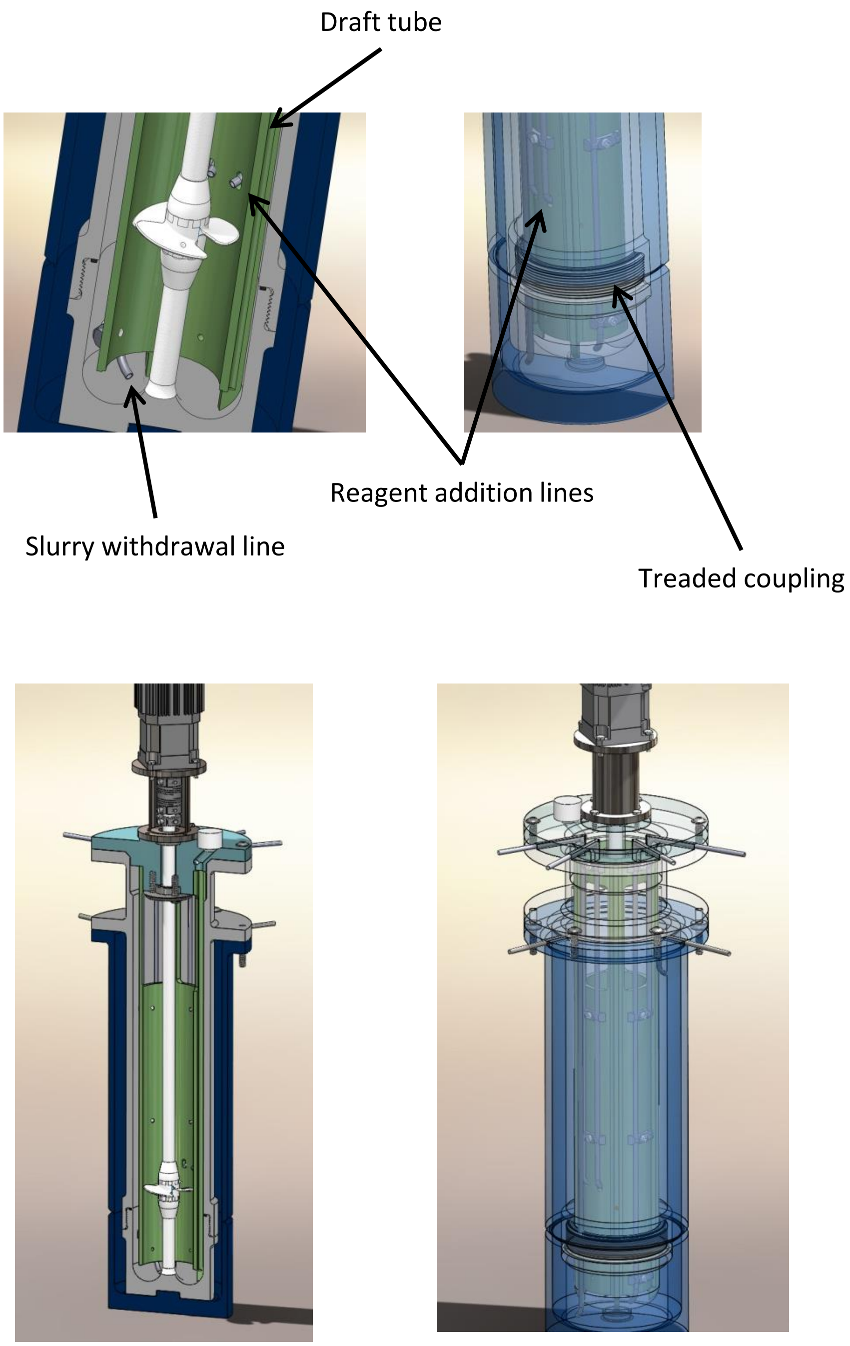


Figure 3.2. Various Views of the Plutonium Oxalate Precipitation Apparatus

Following precipitation, the Pu oxalate solid is collected by vacuum filtration. A commercially available funnel unit will be used (Figure 3.3), but this will likely need to be modified (e.g., the top end of it cut off) to provide a critically safe geometry. The Pu oxalate solid will be collected onto a double-glazed PP felt cloth, which is also commercially available. The Pu oxalate will also be washed with ~0.5 M HNO_3/0.2 M $H_2C_2O_4$ solution in this filter apparatus. The solids will then be transferred to an appropriate container for transfer to the glovebox containing the calcination furnace.

Figure 3.3. Illustration of Tabletop Buchner Funnel to be Used to Collect the Pu Oxalate Solids

The following is a list of the requirements for the Pu oxalate precipitation and filtration system. Table 3.4 lists the filtration equipment required.

Equipment

- 12 L capacity precipitation vessel, equipped with overhead mechanical stirrer and jacketed for temperature control
- circulating bath for temperature control
- PP tabletop Buchner funnel with 26 cm inner diameter
- double-glazed PP felt filter cloth
- 7.5 L oxalate feed adjustment tank
- 12 L oxalate filtrate receipt tank
- two variable-rate metering pumps (maximum 1 L/h)
- one peristaltic pump
- PP, or equivalent, tubing.

Reagents

- Reagent-grade ascorbic acid, crystal
- reagent-grade 85% hydrazine, solution
- high-purity concentrated ~15.7 M HNO_3, solution
- high-purity concentrated 0.35 M HNO_3, solution
- reagent-grade oxalic acid, crystal.

Test Materials

- Coupons for corrosion doping, if required by the testing objectives (e.g., 316 L stainless steel, Hastelloy, Pyrex, etc.)
- Pu nitrate eluate solution from ion exchange purification.

Analytical Services

- Pu solution concentrations by absorption spectrophotometry or GEA
- Pu valence by spectrophotometry

- HNO_3 concentration by Raman spectroscopy; supplemented with titration in ammonium oxalate complexing buffer.[23]

Table 3.4. Equipment List for Oxalate Filter

Item Description	Vendor	Item Number	Quantity
Tabletop Buchner funnel; 10.25 in. inner diameter, with removable perforated plate	VWR	47750-812	1
Double-glazed PP felt filter cloth	Lamports Filter Media	7406	Multiple (consumable item)

3.5 Calcination Furnace

Although variations exist on the exact ramp rates, isotherms, and environments, there are common variables necessary for calcination of Pu(III) oxalate. The equipment requirements for the calcination operation are listed below.

<u>Equipment</u>

- A furnace meeting the following criteria:
    - a multiple-step programmable ramp rate for controlled heating
    - compatible with flowing environments of air and oxygen (O_2); filtration should not be necessary on the exit gas lines from the furnace
    - capable of a maximum temperature of 1,000°C, although 1,200°C is more desirable
    - it must fit through the 14 15/16 in. (37.9 cm) diameter bag-out port and fit within the footprint of Glovebox #1 in RPL/604 [approximately 29 in. by 29 in. (73.7 cm by 73.7 cm)] with enough room to spare for opening and closing of the furnace door and ventilation on the sides
    - capacity to hold a batch of 200 g Pu [386 g Pu2(C2O4)3•10H2O]; the Pu oxalate bed should not be greater than one-half inch deep, because otherwise incomplete calcination might result.
- Auxiliary items:
    - platinum/rhodium (Pt/Rh) or Pt-plated stainless steel liner
    - Pt/Rh or Pt-plated crucibles, tongs
    - heat resistant gloves (optional)
    - a stainless steel guard to place over the top of the crucible to prevent contamination of the PuO_2 product by material falling from the furnace
    - shelf in the furnace to allow space for two crucibles.

- Disperse Reflectance Spectroscopy to assess the degree of conversion to the oxide (optional).
- Glovebox penetration:
    - Purge gas line
    - communication/power line to the furnace
    - fiber optic port.

Chemicals

- Compressed air or O_2.

The wet-bed density of $Pu_2(C_2O_4)_3{\cdot}10H_2O$ is reported to be in the range 0.6 – 0.8 g Pu/cm^3,[4] which translates to 250 – 330 cm^3 of material to be calcined. However, other PuO_2 precursors have a much lower density [e.g., down to 0.1 g Pu/cm^3 for Pu(IV) peroxide]. In order to maintain flexibility in the system, the furnace is designed to accommodate up to 750 cm^3, at a bed depth of $\leq$ 1.3 cm (0.5 inch). Due to space limitations in the glovebox, such a batch must be split between two crucibles, which can be calcined simultaneously through the use of a shelf in the furnace.

A custom designed muffle furnace is to be used to meet these requirements (Figure 3.4). The furnace is constructed in two pieces to allow installation through the 14 $^{15}/_{16}$ in. (37.9 cm) diameter bag-out port. Once in the glovebox, the two halves are joined together to complete construction of the furnace. The internal dimensions of the furnace are 5 in. H × 7 in. W × 12 in. D (12.7 cm × 17.8 cm × 30.5 cm). Gas inlets are supplied to the furnace for introducing air or O_2. The oven requires 208 V, single phase, power and draws 14.5 A; these electrical requirements are to be added to the laboratory. The furnace is capable of achieving a maximum temperature of 1,200°C. Operation of this furnace requires crucibles to remain 1 in. (2.54 cm) away from the wall for proper heating; resulting in a maximum crucible size of 1 in. H × 5 in. W × 10 in. D (2.5 cm × 12.7 cm × 25.4 cm). Double the capacity can be gained through implementation of a shelf. The crucibles will be constructed of Pt, Pt/Rh, or Pt-plated stainless steel; other materials of construction may be used, as directed by DNDO/NTNFC.

Table 3.5 lists the specifications for the custom muffle furnace, along with the specifications for the associated controllers. Included are a primary controller, and an independent secondary controller that will stop power to the furnace in case of malfunction in the primary power controller and/or thermocouple.

Table 3.5. Specification for the Calcination Furnace and Associated Controllers

Item	***Specification***
Muffle Furnace	
Internal chamber dimensions	5 in. H × 7 in. W × 12 in. D
External dimensions (approximate)	12.5 in. H × 14 in. W × 21 in. D
Connected load	3 kW, 208V, 1 phase, 50/60 Hz
Current (calculated)	14.5 A
Maximum temperature	1,200°C
Heating mechanism	Iron-chrome-aluminum alloy wire helically wound and imbedded in the ceramic refractory forms
Location of heaters	Top, bottom, and side walls in heating chamber
Door	Manually opening side hinged, with locking latch
Insulation	Light weigh ceramic fiber
Shell construction	Fabricated/welded stainless steel
Controller	
Controller	Eurotherm 2404 programmable controller with four programs, each with 16 segments
Power controller	Solid state relay
Thermocouple	Type K
Configuration	Single zone
Power requirements	20 A, 208 V, 1 phase, 60 Hz
Independent Over-Temperature Controller	
Controller	Eurotherm 3216HL digital
Power controller	Mechanical contactor
Thermocouple	Type K

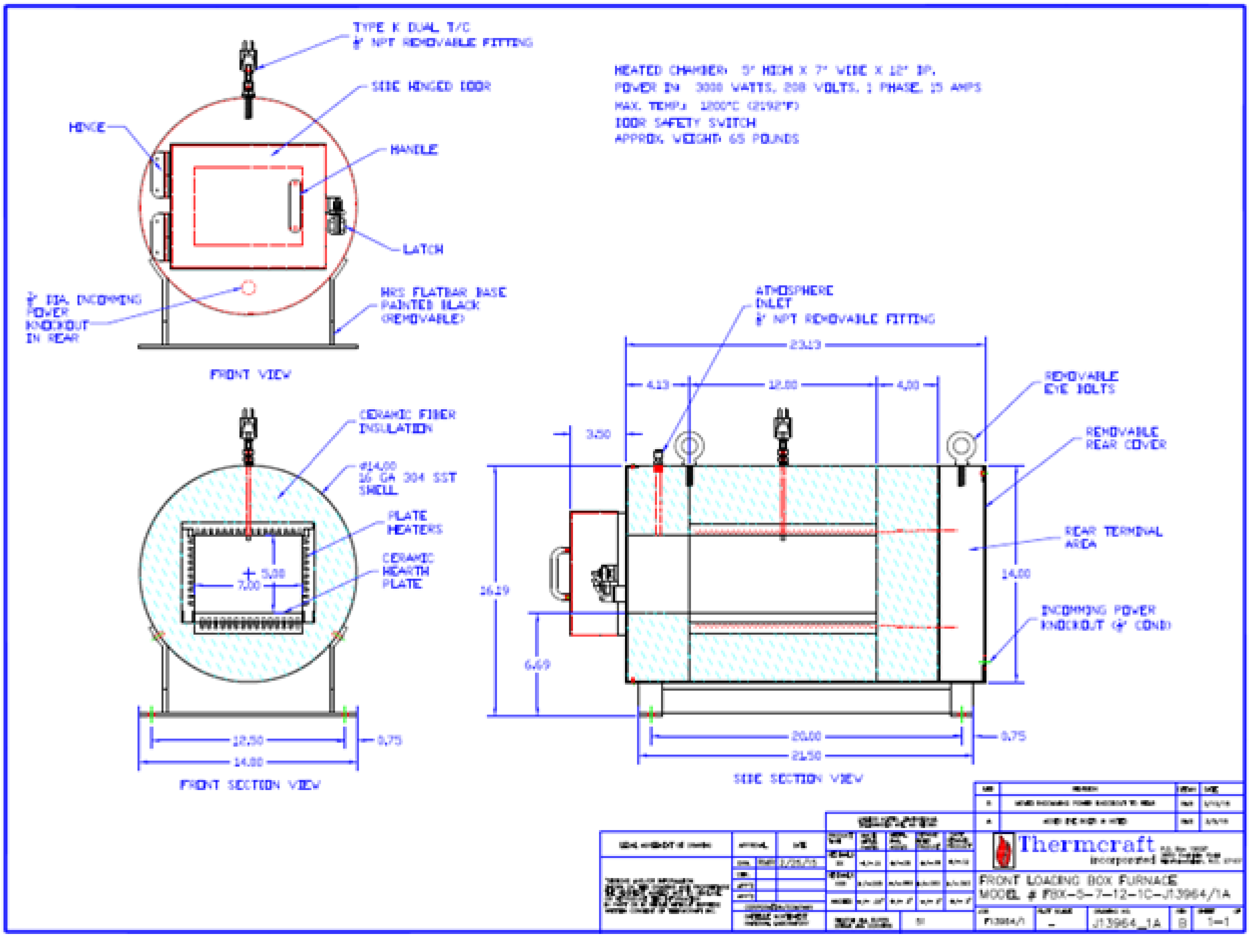


Figure 3.4. Schematics of the calcination furnace from Thermcraft Incorporated.

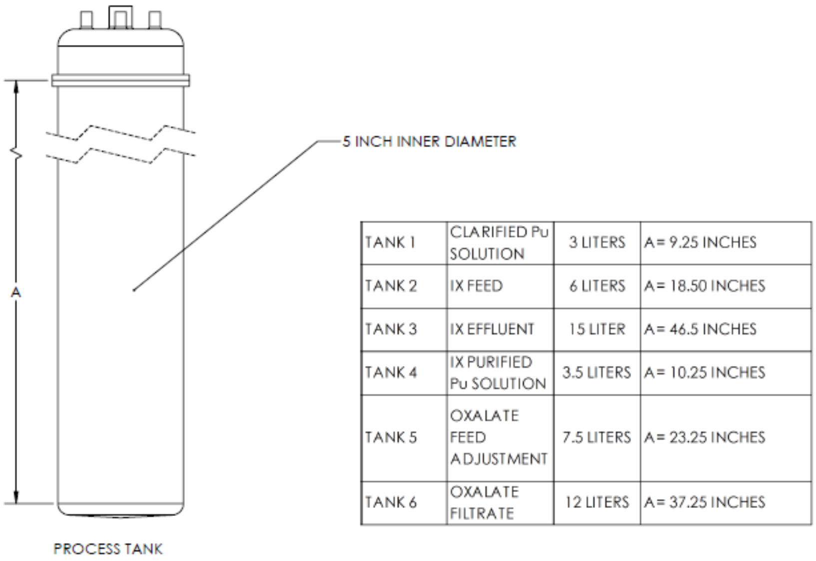
3.6 Process Tanks

This section describes the process tanks installed in Glovebox #3 in RPL Room 604 to support the 200 g scale PuO_2 production process. A total of twelve tanks are required, which includes the six primary tanks serving each function, along with six back-up tanks that are identical to the six primary tanks.

Figure 3.5 schematically illustrates the process tanks used to support the laboratory-scale PuO_2 production system, including the tank dimensions. Table 3.6 summarizes the material of construction and capacity of each tank. The tanks are of custom design and fabrication. None of the tanks is constructed of stainless steel because it is desirable to be able to visually observe the liquid levels in the tanks. Using stainless steel would require adding instrumentation to monitor the tank fluid levels, complicating the system. Furthermore, stainless steel is avoided for Tanks 4 and 5 (purified Pu solution and oxalate feed) to avoid contamination by metallic impurities. Tanks 1, 2, and 3 (clarified Pu solution, ion exchange feed, and ion exchange effluent, respectively) are constructed from borosilicate glass. This material offers excellent stability towards the high concentrations of HNO_3 that will be encountered with these process solutions. Leaching of impurities (e.g., boron and silicon) from the glass can be expected, but these will be removed from the Pu stream by the ion exchange process. The oxalate filtrate tank (Tank 6) is also constructed from borosilicate glass since leaching of impurities from the glass does not matter in this case (i.e., the solution stored in Tank 6 is process waste material).

The tank for the purified Pu solution (Tank 4) and the oxalate feed tank (Tank 5) are constructed from HDPE. This material is transparent enough to visually monitor the fluid level, but is also reasonably stable towards the relatively low HNO_3 concentrations encountered with these process solutions. Use of HDPE avoids potential contamination of the Pu solutions by metallic impurities at this point in the process.

To aid in monitoring the fluid levels in the various process tanks, penetrations for video feeds will be installed in Glovebox #3. These penetrations will allow for optional installation of video cameras so that personnel can more clearly see the liquid levels in the tanks. Trays will be placed on the floor of the glovebox under the tanks to serve as secondary containment in the event of a tank failure.



TANK 1	CLARIFIED Pu SOLUTION	3 LITERS	A= 9.25 INCHES
TANK 2	IX FEED	6 LITERS	A= 18.50 INCHES
TANK 3	IX EFFLUENT	15 LITER	A= 46.5 INCHES
TANK 4	IX PURIFIED Pu SOLUTION	3.5 LITERS	A= 10.25 INCHES
TANK 5	OXALATE FEED ADJUSTMENT	7.5 LITERS	A= 23.25 INCHES
TANK 6	OXALATE FILTRATE	12 LITERS	A= 37.25 INCHES

Figure 3.5. Schematic Illustration of the Process Tanks

Table 3.6. Process Tanks for the Laboratory-Scale PuO_2 Production Capability

Tank #$^{(a)}$	***Description***	***Capacity, L***	***Material of Construction***
1	Clarified Pu Solution	3	Borosilicate glass
2	IX Feed$^{(b)}$	6	Borosilicate glass
3	IX Effluent	15	Borosilicate glass
4	IX Purified Pu Solution	3.5	HDPE
5	Oxalate Feed Adjustment	7.5	HDPE
6	Oxalate Filtrate	12	Borosilicate glass

4.0 System Layout

This section describes how the various system components and unit operations are arranged in the RPL Room 604 gloveboxes. Utility requirements for the gloveboxes are also described.

4.1 Glovebox Utility Requirements

All of the unit operations require installation in a negative-pressure glovebox equipped with an airlock and bag-out ports. The gloveboxes must be certified to handle up to 200 g of Pu as oxide. The three existing gloveboxes in RPL Room 604 meet these requirements. However, specific utilities must be added to these gloveboxes to perform the functions of the laboratory-scale PuO_2 production unit. Table 4.1 lists the minimum required utilities that must be supplied to the gloveboxes in RPL Room 604. In many cases, duplicate or triplicate of the indicated services will be incorporated to allow maximum flexibility of the system.

Table 4.1. Minimum Utility Requirements for the Laboratory-Scale PuO_2 Production Unit

Description	Power Requirements	Inside or Outside Glovebox?
Dissolution Unit (GB #3)		
Balance	110 V	Inside
Heating mantle	110 V	Pass-through to outside
Temperature controller	110 V	Outside
Thermocouples (2)	N/A	Pass-through to outside
Magnetic stirrer	110 V	Inside
Ion Exchange Unit (GB #3)		
Peristaltic pump #1 (single head)	110 V	Inside
Peristaltic pump #2 (dual head)	110 V	Outside
Evaporator (GB #3)		
Heating mantle	110 V	Pass-through to outside
Temperature controller	110 V	Outside
Thermocouples (2)	N/A	Pass-through to outside
Precipitation Unit (GB #3)		
Pump #3 (metering)	110 V	Inside
Pump #4 (metering)	110 V	Outside
Pump controller	110 V	Outside
Pump #5 (peristaltic)	110 V	Inside
Overhead stirrer	110 V	Pass-through to outside
Stirrer controller	110 V	Outside
Calcination Unit (GB #1)		
Furnace	208V, 1 phase, 50/60 Hz	Outside
Gas line (air or O_2)	N/A	Inside with penetration to hook up to external compressed air or oxygen

Description	Power Requirements	Inside or Outside Glovebox?
Sample Packaging and Handling (GB #2)		
Balance	110 V	Inside
Crosscutting Utility Needs		
Circulating bath	110 V	Outside
Distribution manifold for circulating fluid	N/A	Inside
Lines from circulating manifold to glovebox wall (2)	N/A	Inside with penetration to hook up to external circulating bath
Vacuum pump	110 V	Inbox
Penetrations for fiber optics (1 for GB#1, 8 for GB#3)	N/A	Glovebox wall
Generic instrument connectors (16)	N/A	Glovebox wall
Compressed nitrogen	N/A	Outside
Nitrogen sparge manifold	N/A	Inside with penetration to hook up to external compressed nitrogen
Video connections (16)	N/A	Glovebox wall
Video cameras (16)	110 V	Inside
Video monitoring equipment	110 V	Outside

4.2 Process Flow

Figure 4.1 and Figure 4.2 schematically illustrate the process flow for the laboratory-scale PuO_2 production operation. The process is initiated by adding a weighed quantity of the as-received PuO_2 material into the PTFE dissolution vessel. Nitric acid and CaF_2 (or HF) are added manually into the dissolution vessel as described in Section 2.2.2. Following the dissolution process, the dissolved Pu solution is pulled via vacuum transfer through an in-line filter, and the clarified Pu solution is collected into Tank #1 (Table 3.6).(a) The solution is moved forward to one of the ion exchange feed tanks (Tank #2 in Table 3.6) and the acidity is adjusted to 7 M HNO_3. Aluminum nitrate and H_2O_2 are manually added per the description in Section 2.3. The solution in the ion exchange feed tank can be mixed by either sparging with nitrogen, or by pumping in a closed loop configuration (or both). If pumped through the closed loop, optional real-time monitoring of the solution could be employed to verify the HNO_3 concentration (7 M) and the Pu oxidation state (+4). If real-time monitoring is not available, grab samples will be taken to verify these parameters.

Once the composition of the ion exchange feed solution is verified, the solution is pumped through the ion exchange column in an up-flow direction. The column effluent is collected into Tank #3 (Table 3.6). After loading the Pu(IV) nitrate solution into the column, the column is washed with 7 M HNO_3. The 7 M HNO_3 solution is pumped into the glovebox from a carboy located external to the glovebox. The column wash solution is collected into the column effluent tank. Following column washing, 0.35 M HNO_3 is introduced to the column in a down-flow direction. The 0.35 M HNO_3 solution is also pumped into the glovebox from an external carboy. The solution exiting the column will be monitored either visually (looking for the coloration in the eluent) or (preferably) using real-time spectroscopic monitoring

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(a) In this discussion, single specific tanks are referenced, but it is implied that the identical redundant tanks could also be used.

to determine the point at which the Pu begins to elute from the column. The initial Pu-deficient fraction will be routed to the column effluent tank. Once the Pu begins to elute from the column, the eluent will be routed to the purified Pu tank (Tank #4 in Table 3.6).

Depending on the test objectives, the purified Pu solution is either moved directly forward to the oxalate feed adjustment tank (Tank #5 in Table 3.6), or is first concentrated by evaporation and then moved forward to the oxalate feed adjustment tank. In the feed adjustment tank, manual additions are made to adjust the acidity and introduce the ascorbic acid reducing agent and hydrazine nitrate stabilizer. As with the ion exchange feed tank, the solution in the oxalate feed tank can be mixed by either sparging with nitrogen, or by pumping in a closed loop configuration. Again, optional real-time monitoring of the solution could be employed to verify the HNO_3 concentration and the Pu oxidation state (+3) if it is pumped through the closed loop. If real-time monitoring is not available, grab samples will be taken to verify these parameters. The adjusted feed solution is transferred to the oxalate precipitation vessel; the manner and order in which this is done will be dependent upon the specific testing parameters.

The slurry containing the plutonium oxalate will be pumped using a peristaltic pump to the tabletop Buchner funnel, and the filtrate solution will be pulled by vacuum to the filtrate collection tank (Tank #6 in Table 3.6). After washing with dilute nitric/oxalic acid solution, the wet plutonium oxalate will be transferred into a plastic container, transferred out of Glovebox #3, and moved to Glovebox #1 (through Glovebox #2). The plutonium oxalate material is transferred into boats for calcination in the furnace. The product is then transferred to Glovebox #2 and distributed as directed by DNDO/NTNFC.

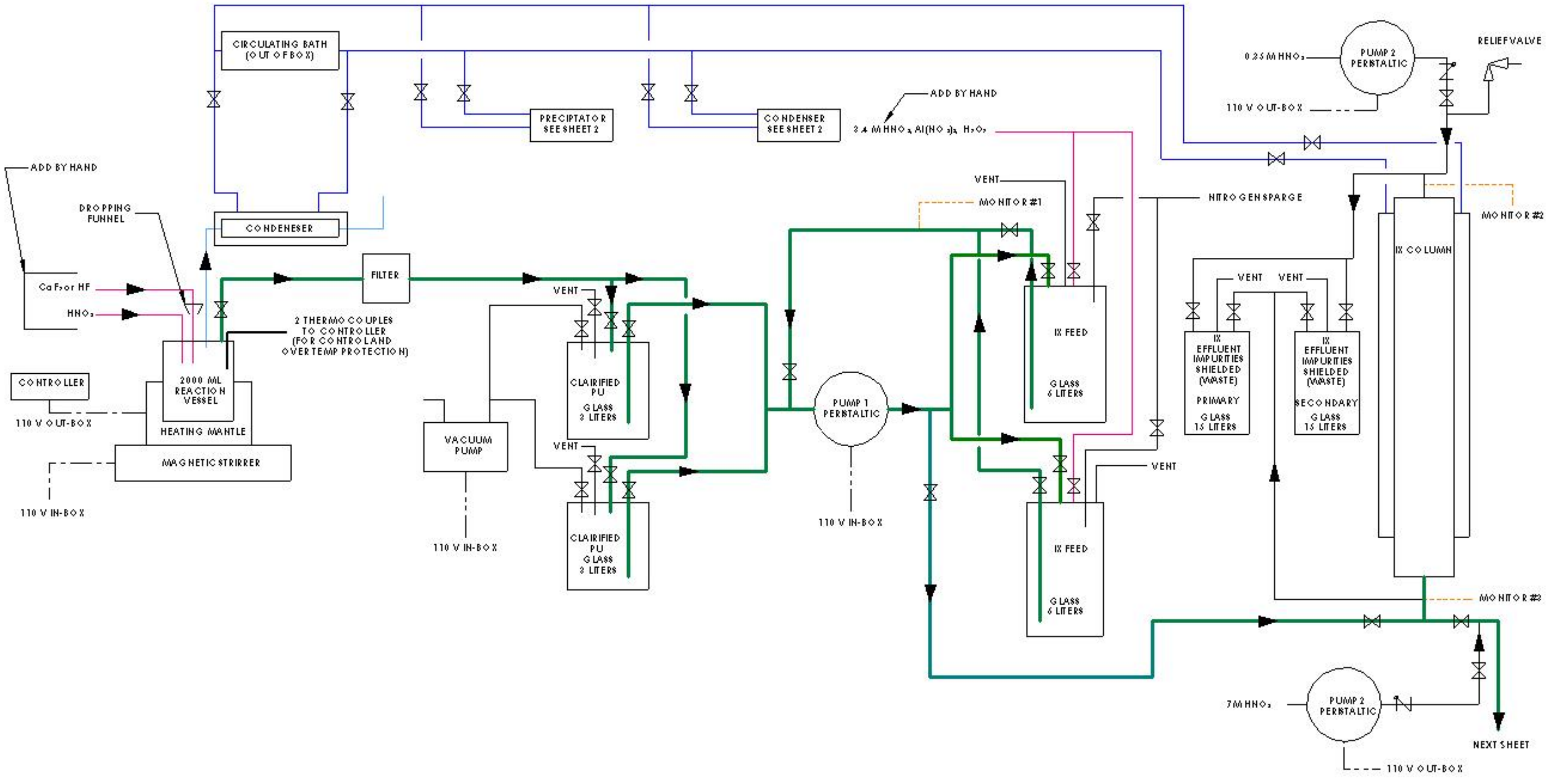

Figure 4.1. Flow Diagram for Dissolution and Ion Exchange Units

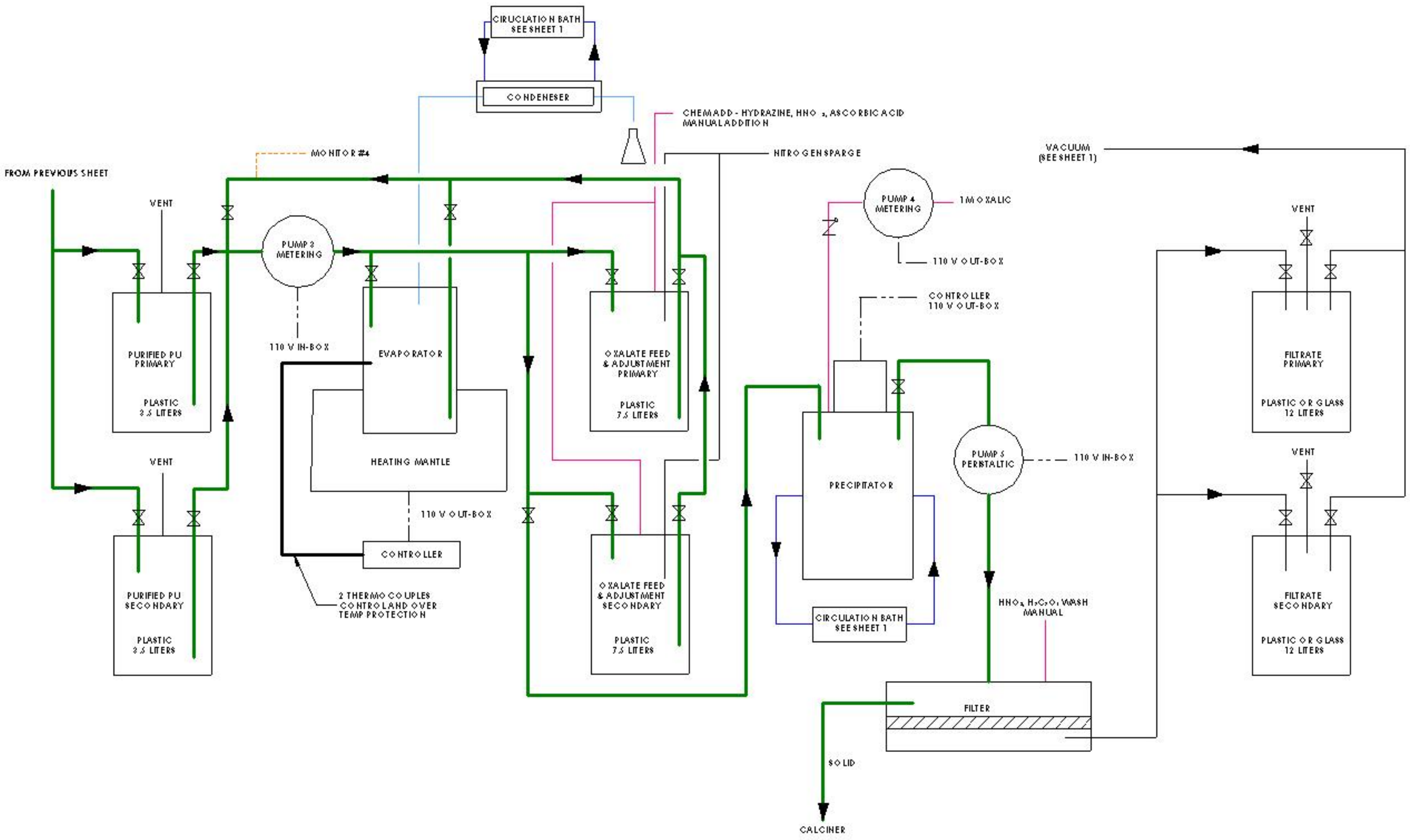

Figure 4.2. Flow Diagram for Evaporator and Precipitation Unit

4.3 Glovebox Arrangement

RPL Room 604 contains three gloveboxes. These are numbered 1 through 3, with Glovebox #1 being located at the north end of the room and Glovebox #3 at the south end (Figure 4.3). Conceptually, the PuO_2 production capability in RPL Room 604 will consist of five primary work stations. The dissolution station will be located at the north end of Glovebox #3, immediately adjacent to the airlock door. This station will consist of a balance, the dissolution vessel, and a filtration apparatus. The ion exchange station will be located in the middle part of Glovebox #3. This station will consist of the ion exchange feed vessel(s), the ion exchange column, the purified-Pu receipt vessel, and the effluent waste tank. At least two nonradioactive chemical feed tanks will also be included in the ion exchange system; these can be assumed to be located on the top of the glovebox. The Pu precipitation station will be located at the north end of Glovebox #3. This station will consist of the precipitation vessel with mixer, a circulating heating bath (located outside the glovebox), and pumps for metering in the Pu solution and the precipitant. Also associated with the precipitation station will be a filter apparatus for collecting the precipitated Pu. The calcination station will be located in Glovebox #1. This station will primarily consist of a muffle furnace. Finally, the product distribution station will be located in Glovebox #2. This station will consist mainly of a balance for measuring out aliquots of the product for shipping and archiving.

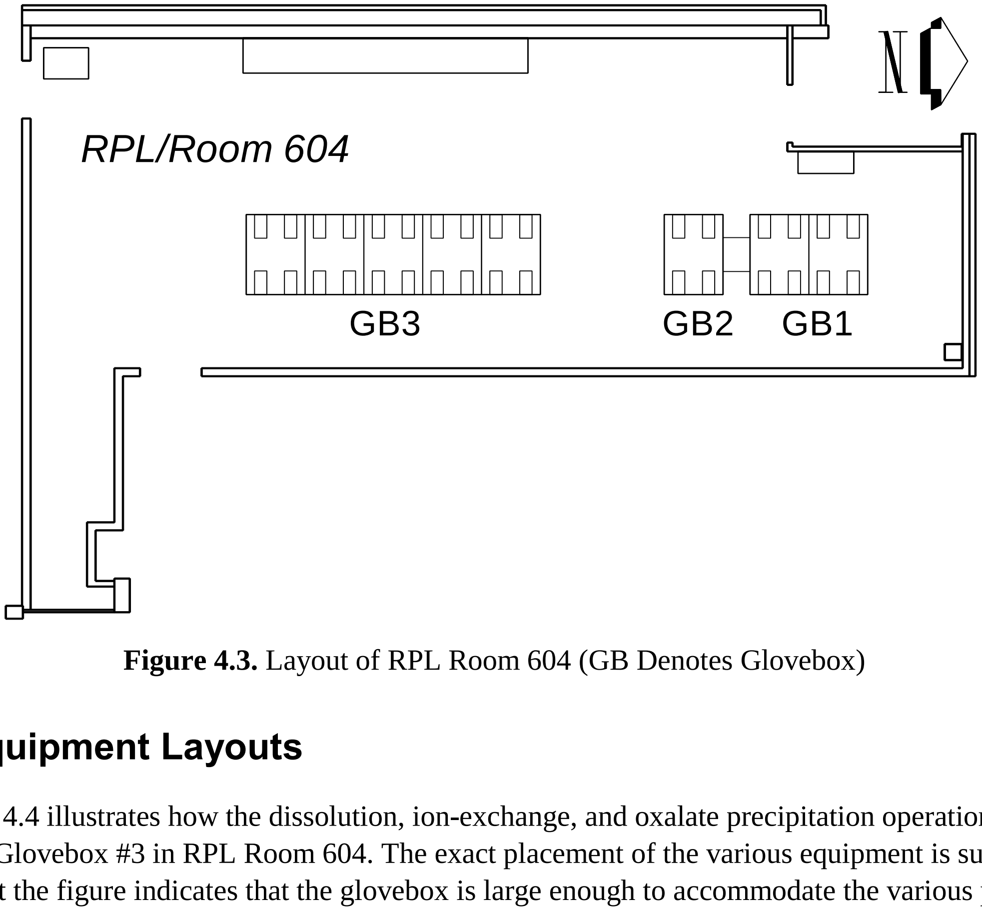

Figure 4.3. Layout of RPL Room 604 (GB Denotes Glovebox)

4.4 Equipment Layouts

Figure 4.4 illustrates how the dissolution, ion-exchange, and oxalate precipitation operations are to be located in Glovebox #3 in RPL Room 604. The exact placement of the various equipment is subject to change, but the figure indicates that the glovebox is large enough to accommodate the various process equipment. The dimensions for the various process vessels shown in the figures are based on an assessment of criticality risk.

The PuO_2 feed material is transferred into Glovebox #3 via the airlock at the south end of glovebox. The feed material is moved to the north end of the glovebox, where it is weighed and dissolved. From that point, the material flow, as described in Section 4.2, is from north to south in Glovebox #3. This movement of material results in the collection of the plutonium oxalate near the south end of the box, where it can be packaged and transferred out of the glovebox through the airlock. The plutonium oxalate is then moved into Glovebox #2 through the airlock at the south end of that glovebox, and is then passed from Glovebox #2 into Glovebox #1, where the calcination furnace is located (Figure 4.5). Other than a balance, no special equipment is expected to be installed in Glovebox #2 for the purposes of packaging the PuO_2 materials, so a layout for Glovebox #2 is not specified at this point.

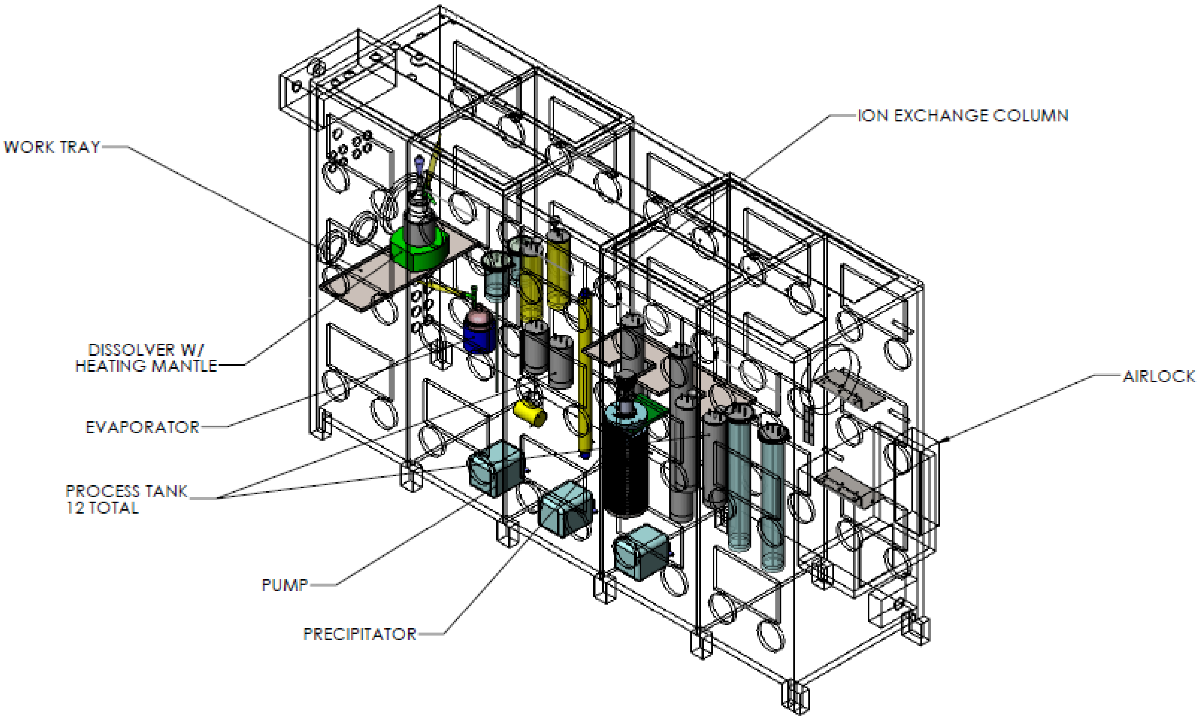

Figure 4.4. Simplified View of the Layout of Equipment in Glovebox #3

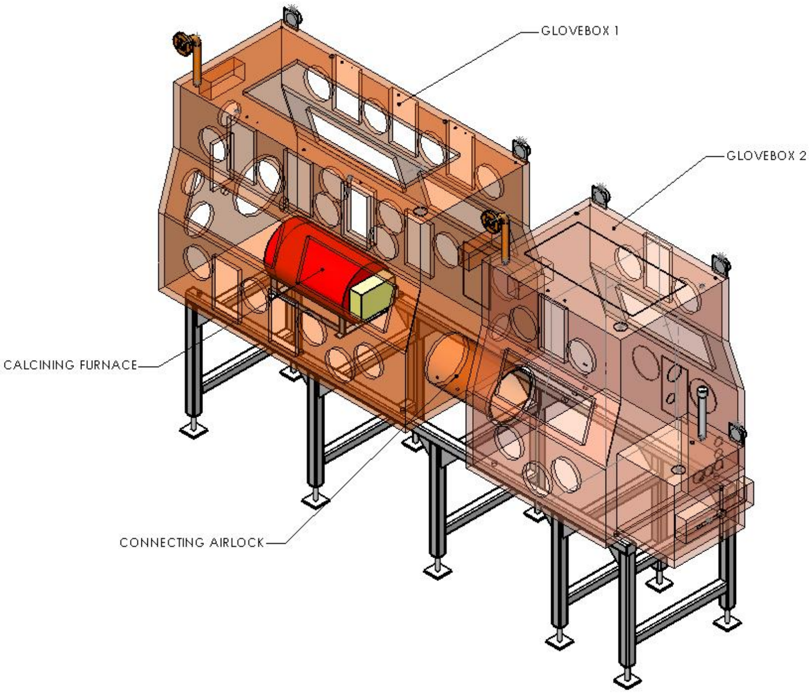

Figure 4.5. Layout of Furnace in Glovebox #1

5.0 Material Inputs and Outputs

This section provides an estimate of the flow of materials into and out of the laboratory-scale PuO_2 processing system. It should be noted that a rigorous evaluation of the flowsheet has not been performed, and thus the values reported here should be viewed as indicative, not definitive. Furthermore, actual material usage will vary depending on the specific requirements of each experimental run.

5.1 Dissolution

Figure 5.1 illustrates the flows into and out of the dissolver section of the process. The primary inputs and outputs for the dissolution portion of the flowsheet are as follows.

Inputs:

Stream 1:	226 g of as-received PuO_2
Stream 2:	2.0 L 15.7 M HNO_3
Stream 3:	15.6 g CaF_2

Outputs:

Stream 4:	the clarified impure Pu solution, estimated to contain 513 g $H_2Pu(NO_3)_6$, 1662 g HNO_3, 15.6 g CaF_2, and 892 g H_2O.

The undissolved solids could be recycled back to the dissolver or disposed. Because the amounts and identities of the undissolved solids are unknown, these materials are not accounted for in the mass flow.

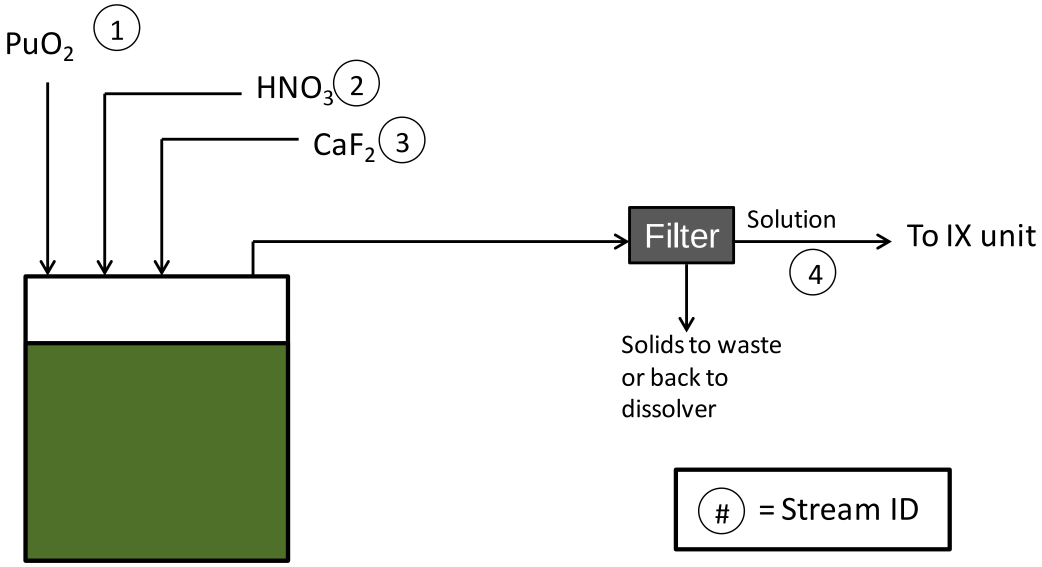

Figure 5.1. Material Flows Into and Out of the Dissolver Section (IX Denotes Ion Exchange)

5.2 Ion Exchange

The material flows into and out of the ion exchange section of the process are shown in Figure 5.2. The primary inputs and outputs for the dissolution portion of the flowsheet are as follows.

Inputs:

Stream 4:	as described above
Stream 5:	2.55 L 3.4 M HNO_3; added to adjust the solution to 7.0 M HNO_3
Stream 6:	0.25 L 1.6 M $Al(NO_3)_3$; added to complex fluoride ion (1 mole Al/mole F)
Stream 7:	0.2 L 30% H_2O_2; added to adjust to Pu(IV)
Stream 8:	adjusted ion exchange feed solution
Stream 9:	7.4 L 7 M HNO_3; column wash with 6 bed volumes
Stream 10:	2.5 L 0.35 M HNO_3; column elution with 2 bed volumes

Outputs:

Stream 11:	purified Pu solution; estimated to contain 513 g $H_2Pu(NO_3)_6$, 55 g HNO_3, and 2,450 g H_2O(a)
Stream 12:	effluent containing the impurities; estimated to contain 5490 g HNO_3, 15.6 g CaF_2, 85.2 g $Al(NO_3)_3$, and 9,400 g H_2O

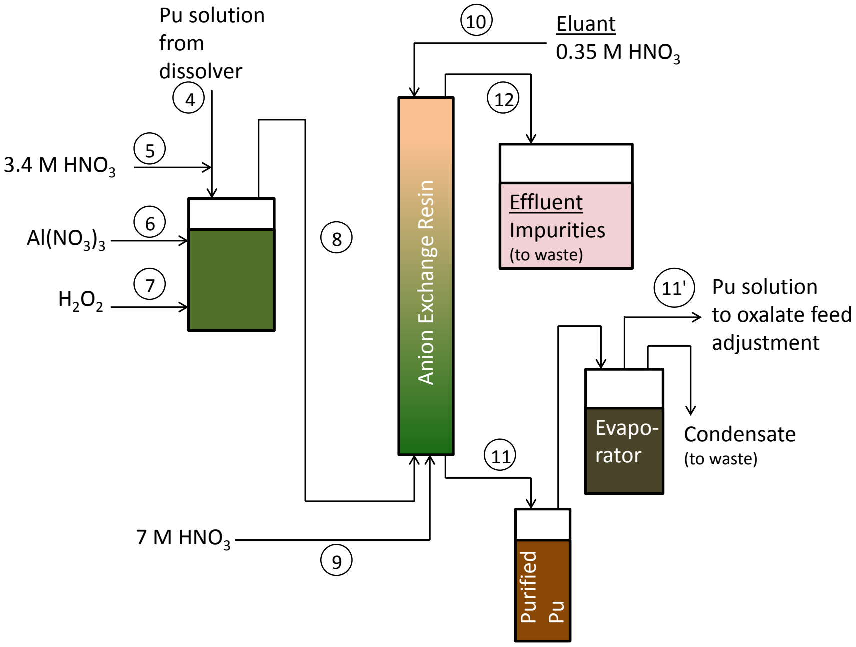

Figure 5.2. Material Flows Into and Out of the Ion Exchange Section

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(a) For the purposes of determining the material balance for this report, it is assumed that the entire ion exchange eluate would be collected and moved forward in the process. In actual operations, the elution process will be monitored visually or spectrophotometrically so that only that part of the eluate containing the main portion of the Pu is collected for further processing.

5.3 Precipitation

Figure 5.3 illustrates the material inputs and outputs from the precipitation section of the process. The primary inputs and outputs for the dissolution portion of the flowsheet are as follows.

Inputs:

Stream 11: as described above

Stream 13: 0.37 L 15.7 M HNO_3; added to adjust the solution to 1.0 M HNO_3

Stream 14: 50 mL 85% hydrazine solution adjusted with 56 mL 15.7 M HNO_3; added as HNO_2 scavenger

Stream 15: 300 g ascorbic acid; added to adjust to Pu(III)

Stream 16: 270 g $H_2C_2O_4 \cdot 2H_2O$

Stream 18: 0.7 L 0.2 M HNO_3/0.1 M $H_2C_2O_4$; oxalate product wash

Outputs:

Stream 17: 385 g $Pu_2(C_2O_4)_3 \cdot 10H_2O$ product

Stream 19: filtrate and wash; estimated to contain 485 g HNO_3, 28 g N_2H_4, 300 g ascorbic acid (or oxidized product thereof), 86 g $H_2C_2O_4$, and 7,310 g H_2O

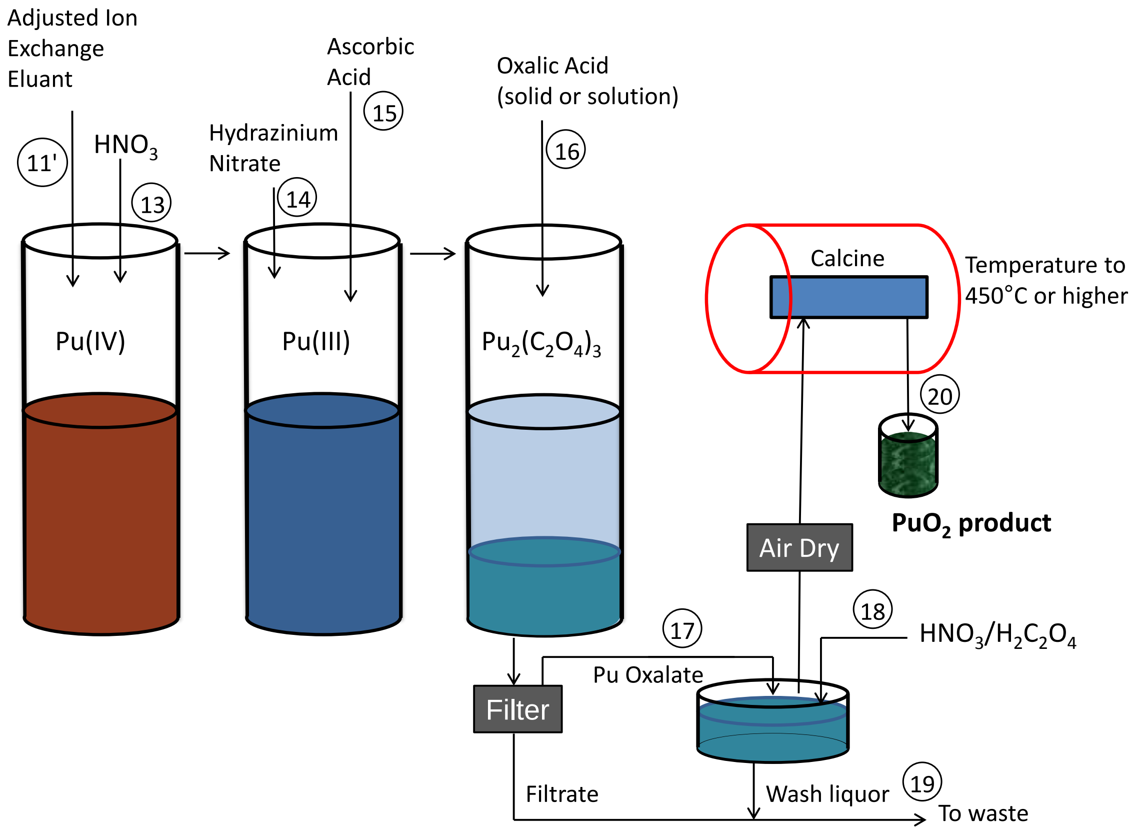

Figure 5.3. Material Flows Into and Out of the Precipitation and Calcination Sections

5.4 Calcination

Figure 5.3 also shows the material flow into and out of the calciner (excluding off-gas). The primary inputs and outputs for the dissolution portion of the flowsheet are as follows.

Inputs:

Stream 17: 385 g $Pu_2(C_2O_4)_3 \cdot 10H_2O$ product (after washing)

Outputs:

Stream 20: 226 g PuO_2 product (100% recovery assumed)

6.0 Shipping and Receiving

This section describes aspects of receiving the PuO_2 to be processed, and shipping of the PuO_2 product material to other laboratories for characterization. Successful production of pedigreed PuO_2 in the laboratory-scale system depends upon receiving Pu stock materials in the RPL and shipping samples of the PuO_2 products to other laboratories across the DOE complex. The current baseline for planning purposes is the receipt of PuO_2 in batches containing less than 200 g of Pu. Multiple batches of similar material will be received so that nominally a 1 kg inventory of Pu as PuO_2 will be maintained at PNNL for this project.

Samples of the pedigreed PuO_2 product will be shipped to other laboratories under the direction of DNDO/NTNFC. The amount of material in the samples will be on the order of gram; samples will be packaged in single-use stainless steel containers. The containers will be packaged in approved U.S. Department of Transportation (DOT) shipping containers and shipped after approval is obtained from DNDO/NTNFC and the destination laboratory.

6.1 U.S. Department of Transportation Regulations

Plutonium-bearing materials will be shipped in DOT-certified containers according to DOT Regulations. PNNL has the capability to handle several certified containers, including the 9977 drum. Trained shipping personnel at PNNL will prepare shipping documentation and label shipping containers.

Plutonium can be shipped in an arrangement of nested food-pack cans within a 9977 drum. This arrangement will be the primary method for shipping samples to other DOE sites. The certification of the 9977 drum does not expire until September 30, 2017. Eight 9977 drums are currently available at PNNL for this project.

6.2 Product and Sample Containers

There are no special container requirements for the bulk product material since it will not be stored for an extended period. It is assumed that immediately after completion of a batch, aliquots of the bulk material will be distributed to other laboratories, and an archived sample will be taken. The remaining material is assumed to be recycled back to the dissolver and used for the next process run.

Sample containers will be constructed of stainless steel and will be compatible with the 9977 shipping drum. The containers will have a threaded lid for robust closure. Figure 6.1 illustrates one potential configuration for the sample container.

Figure 6.1. An Example Configuration for the PuO_2 Sample Container

7.0 Facility Operational Issues

This section discusses specific operational constraints for implementation of this project in the RPL at PNNL. Included are discussions of safeguards, criticality safety, and the building inventory for radioactive materials.

7.1 Safeguards

The RPL is capable of handling Category III levels of special nuclear material; however, most of the inventory is maintained at Category IV levels. The limits for Category III levels are listed in Table 7.1. There is no lower limit for Category IV levels, and the value of the upper limit is equivalent to the lower limit of Category III inventories. All operations anticipated for the laboratory-scale PuO_2 processing capability can be performed at Category IV levels since the largest processing batch will be less than 200 g of Pu.

Table 7.1. Graded Safeguards at PNNL (PNL-MA-500)[1]

Item	Description of Material	Pu Category III Limits (kg) Lower (≥)	Pu Category III Limits (kg) Upper (<)
Pure Products	Pits, major components, button ingots, recastable metal, directly converted materials	0.2	0.4
High-Grade Materials	Carbides, oxides, nitrates, solutions (≥25 g/L), fuel elements and assemblies, alloys and mixtures	0.4	2
Low-Grade Materials	Solutions (1–25 g/L), process residues requiring extensive reprocessing, ^{238}Pu (except waste)	3	16

All Pu stock materials received for this project will be maintained in a Material Balance Area according to the guidance provided by the Safeguards and Security Program documents in PNL-MA-500. Transfers of samples of pedigreed PuO_2 to other laboratories will be done in compliance with the PNNL Safeguards and Security Program. If Pu metal is received at PNNL in quantities greater than Category IV limits (200 g), increased accounting and control of Pu inventories will be implemented to meet PNNL Safeguards and Security requirements.

7.2 Criticality Safety

Criticality prevention requirements dictate the application of the double contingency principle, which requires that preventative measures be in place so that at least two unlikely, independent, and concurrent changes in process conditions must occur before criticality is possible. Criticality Safety Specifications (CSSs) identify limits on mass or number; moderation; reflection; spacing between batches, arrays, controlled areas, open shipping containers, or other accumulations of fissile material; and sometimes on

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[1] *Nuclear Material Control and Accountability Plan*. PNL-MA-500, Pacific Northwest National Laboratory, Richland, WA,

volume or geometry and/or interaction. A CSS will be prepared for receiving, storage, handling, and shipping Pu-bearing material as part of the laboratory-scale PuO_2 processing operations.

7.3 Facility Inventory

A Radioactive Material Evaluation Program has been implemented in the RPL to inventory radioactive materials in the facility. The current limit for in-process radioactive material within the facility is 1350 Ci of ^{239}Pu equivalents, which is over 20 kg of ^{239}Pu. This inventory includes all of the projects in the building, but current inventories in the building allow sufficient room for receiving up to 1 kg of Pu as the oxide.

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