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**Materials Measurement and Accounting
in an Operating Plutonium Conversion
and Purification Process.
Phase I: Process Modeling and Simulation**

University of California



LOS ALAMOS SCIENTIFIC LABORATORY

Post Office Box 1663 Los Alamos, New Mexico 87545

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C. C. Thomas, Jr.
C. A. Ostenak
R. G. Gutmacher
H. A. Dayem
E. A. Kern





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GLOSSARY

ACF	advanced carbide fuels
HAN	hydroxylamine nitrate
ICA	item control area
LAO	plutonium-oxalate cake
LOI	loss on ignition
MBA	materials balance area
MIP	material-in-process
MOX	mixed oxide
NDA	nondestructive assay
PF/LASS	Plutonium Facility, Los Alamos Safeguards System
POT	oxide container
ppmv	parts-per-million by volume
PUCSIM	<u>Pu Conversion Simulation</u>
ROT	insoluble oxide
RSD	relative standard deviation
SAI	solution assay instrument
SGS	segmented gamma-ray scanners
SNM	special nuclear material
SOX	scraped oxide
TNC	thermal neutron coincidence counter
UPAA	unit process accounting area

MATERIALS MEASUREMENT AND ACCOUNTING IN AN
OPERATING PLUTONIUM CONVERSION AND PURIFICATION PROCESS.
PHASE I: PROCESS MODELING AND SIMULATION

by

C. C. Thomas, Jr., C. A. Ostenak, R. G. Gutmacher
H. A. Dayem, and E. A. Kern

ABSTRACT

A model of an operating conversion and purification process for the production of reactor-grade plutonium dioxide was developed as the first component in the design and evaluation of a nuclear materials measurement and accountability system. The model accurately simulates process operation and can be used to identify process problems and to predict the effect of process modifications.

I. INTRODUCTION

Design studies of advanced nuclear materials accounting techniques for nitrate-to-oxide conversion and mixed-oxide (MOX) fuel fabrication processes have been performed as part of the Los Alamos National Laboratory safeguards programs.¹⁻⁵ These studies dealt with high-throughput facilities that were in the design and equipment development stages. This present study is the first in a series to examine a low-throughput operating facility:

- that has extensive in-line instrumentation,
- that is representative of conversion and, possibly, fuel fabrication facilities in operation or being planned, and
- that provides real process and accountability data that could be used for validation of the modeling and simulation results.

The plutonium metal-to-oxide conversion and purification process and the advanced carbide fuels (ACF) process at

the Los Alamos Plutonium Facility were considered as candidate processes for this study. Process descriptions were developed and data for the processes were collected. These were reviewed to determine their applicability to a production operation. The conversion and purification process data base was deemed to be representative of a production process. The process produces plutonium dioxide for the Fast Flux Test Facility,* and it is anticipated that it will produce feed material for the Fuels and Materials Evaluation Facility.* The ACF process is still experimental, and the resulting data base was not considered representative of a production operation. Therefore, this study is limited to the conversion and purification process, and to

- development and evaluation of a model of the process,
- review of measurement techniques and measurement control programs used in the process, and

*Facilities located at Richland, Washington.

- discussion of possible accounting strategies.

The conversion and purification process uses in-line or at-line instrumentation to provide near-real-time measurements. Near-real-time book inventory data are obtained from the facility data processing system (Plutonium Facility/Los Alamos Safeguards System--PF/LASS). Materials balances are closed semiannually following shutdown and cleanout.

The process description is presented in Sec. II and is based on information obtained from facility personnel and the process procedure manual. The dynamic model of the process is based on operating data that were adjusted to minimize or eliminate the effects of identified measurement problems and is described in Sec. III. The results of process simulation runs are also presented in Sec. III. The measurement methods and measurement control programs in use in the process are discussed in Sec. IV.A, and possible accounting strategies are considered in Sec. IV.B. The information presented in Sec. IV is essential to the design and evaluation of materials accounting strategies that we will consider in a follow-on study. Our results, conclusions, and recommendations are summarized in Sec. V.

The process model is a good representation of the Los Alamos process and can be modified readily to reflect process changes. The model can be used to identify process bottlenecks, to predict the effects of process modifications, and to match the throughput of process steps.

Modeling and simulation of the process is the first step in design and evaluation of a materials measurement and accounting system. Future work should be directed toward development of a computer model of the measurement system, simulation of accountability measurements applied to the simulated nuclear materials flows and inventories, evaluation of materials accounting strategies from simulated materials

balance data, evaluation of possible process modifications by process model simulations, and comparison of simulated materials balance data with actual plant data.

II. PROCESS DESCRIPTION

The process produces pure ceramic-grade plutonium dioxide from impure plutonium metal buttons. This process is in operation at the Los Alamos Plutonium Facility. The plutonium oxide product is used in the production of fuel rods for the Fast Flux Test Facility at Richland, Washington. The current production rate of plutonium dioxide is ~120 kg/yr, but 600 kg/yr could be produced with the present process and facilities.

The production of ceramic-grade plutonium dioxide from impure plutonium metal involves the following steps:

- (1) Oxidation of the plutonium metal button to impure oxide.
- (2) Dissolution of the impure plutonium oxide.
- (3) Primary purification by precipitation of plutonium peroxide, followed by redissolution of the precipitate.
- (4) Secondary purification by precipitation of plutonium(III) oxalate.
- (5) Conversion of the oxalate to plutonium dioxide by calcination and final purification by hydrocalcination.
- (6) Screening, blending, and canning. Samples are taken from the blend for chemical analysis and physical tests to verify that the product meets specifications.
- (7) Final canning.

Each step is described in detail below.

All operations are conducted in gloveboxes. For the gloveboxes in which the plutonium-dioxide product is screened, blended, and canned, the atmosphere is controlled so that the water vapor concentration does not exceed 100 ppmv (parts-per-million by volume).

A. Detailed Description

The process flow sheet (Fig. 1) shows the major process steps, the chemicals used, and the scrap and waste materials generated. The principal chemical reactions are summarized in Table I. Descriptions of at-line instruments and methods of analysis are in Sec. IV.

1. Plutonium Metal Oxidation. The feed material for this process step is impure plutonium metal from which fission products have been removed at other sites. The metal ingots or buttons weigh 2-2.5 kg. Plutonium buttons in their containers are transferred from the vault to the button-oxidation area. This area has two glove-boxes--one used for plutonium handling and the other containing two resistance furnaces for button oxidation. In the plutonium handling box, a button is removed from its packaging, cleaned with a steel brush, and weighed. The original weight of plutonium and oxide is calculated from the

TABLE I

SUMMARY OF PRINCIPAL CHEMICAL REACTIONS

1. Button oxidation

$$\text{Pu}_{\text{metal}} + \text{O}_2 (\text{air}) \xrightarrow{\text{heat}} \text{PuO}_2$$
2. Oxide dissolution

$$\text{PuO}_2 + 4\text{HNO}_3 \xrightarrow{\text{HF}} \text{Pu}(\text{NO}_3)_4 + 2\text{H}_2\text{O}$$

Complexing of fluoride

$$6\text{HF} + \text{Al}(\text{NO}_3)_3 + \text{AlF}_6^{3-} + 3\text{HNO}_3 + 3\text{H}^+$$
3. Peroxide precipitation

$$4\text{Pu}(\text{NO}_3)_4 + 8\text{H}_2\text{O}_2 + 2\text{Pu}_2\text{O}_7 + 16\text{HNO}_3 + \text{O}_2$$

Dissolution

$$2\text{Pu}_2\text{O}_7 + 16\text{HNO}_3 + 4\text{Pu}(\text{NO}_3)_4 + 8\text{H}_2\text{O} + 3\text{O}_2$$
4. Reduction

$$4\text{Pu}(\text{NO}_3)_4 + 2\text{NH}_2\text{OH} + 4\text{Pu}(\text{NO}_3)_3 + \text{N}_2\text{O} + \text{H}_2\text{O} + 4\text{HNO}_3$$

Oxalate precipitation

$$2\text{Pu}(\text{NO}_3)_3 + 3\text{H}_2\text{C}_2\text{O}_4 + 10\text{H}_2\text{O} + \text{Pu}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O} + 6\text{HNO}_3$$
5. Drying

$$\text{Pu}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O} \xrightarrow{\text{heat}} \text{Pu}_2(\text{C}_2\text{O}_4)_3 \cdot 2\text{H}_2\text{O} + 8\text{H}_2\text{O}$$

Calcination

$$\text{Pu}_2(\text{C}_2\text{O}_4)_3 \cdot 2\text{H}_2\text{O} + 2\text{O}_2 (\text{air}) \xrightarrow{\text{heat}} 2\text{PuO}_2 + 6\text{CO}_2 + 2\text{H}_2\text{O}$$

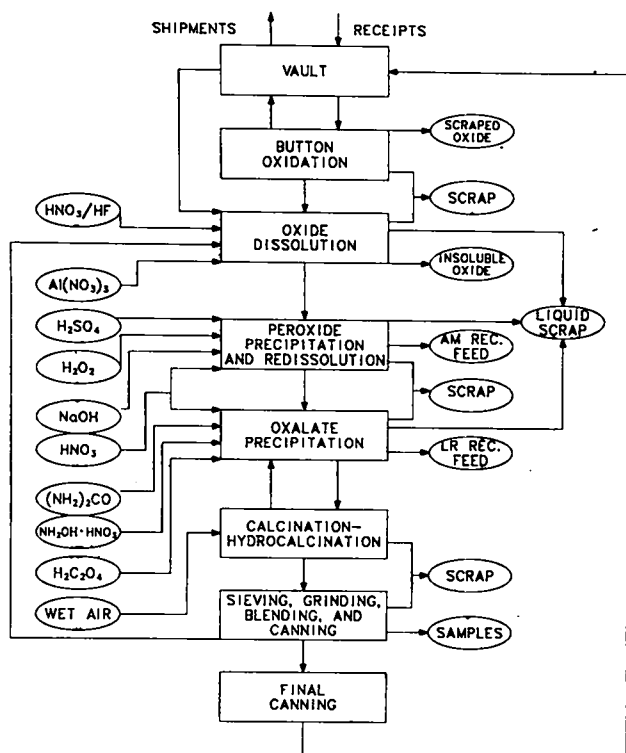


Fig. 1. Process block diagram.

gross and tare weights of the containers. The oxide scraped from the button is combined with any loose oxide found in the inner container (the total representing ~3 g of plutonium), weighed, and transferred to recovery operations. The cleaned packaging materials are placed in a stainless-steel can and are assayed for plutonium in a thermal neutron coincidence counter (TNC).

Each cleaned button is put into an alumina furnace boat and transferred to one of the two resistance furnaces for air oxidation. The 14-h heating cycle of the furnace is controlled by a microprocessor and includes heating (2 h), cooling (6 h), and 6 h at the oxidation temperature. A temperature >500°C is required to initiate oxidation of plutonium metal. However, the reaction of plutonium with oxygen is exothermic, so that some of the resulting

impure plutonium oxide may have been exposed to a much higher temperature and later may be difficult to dissolve.

At the conclusion of the oxidation step, the oxide is removed from the furnace boat and inspected for unburned metal. The oxide is weighed and transferred to an oxide container (POT). The oxide from two buttons of differing isotopic compositions may be blended, if required to meet product specifications.

Criticality considerations limit the amount of material in the oxide dissolution and subsequent precipitation steps to 1040 g of plutonium (1180 g of plutonium oxide). Accordingly, quantities of plutonium oxide not exceeding 1180 g are taken from the POT and weighed into tared stainless-steel containers. The containers are transferred either to oxide dissolution or to the vault, according to demand. A given material remains in the button handling and oxidation area for 24 h.

2. Oxide Dissolution. The impure oxide is dissolved and converted to plutonium nitrate solution prior to the purification steps. For the dissolution, 4 L of concentrated nitric acid and 16 mL of concentrated hydrofluoric acid are placed in one of six dissolvers, and the contents of one can of impure oxide are carefully added. The mixture is heated under reflux for at least 4 h and sparged with argon to suspend the solids. At the end of the heating period, ~200 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ crystals are added and dissolved to complex the remaining fluoride. The solution is filtered through a medium-porosity frit.

The insoluble oxide (ROT), when more than 200 g, is returned to a dissolver flask containing 2 L of concentrated nitric acid and 8 mL of concentrated hydrofluoric acid for another period of refluxing. At the end of the heating period, 50 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ crystals are added. If the solid residue from the second dissolution is still 200 g or more, a third dissolution is performed under the same conditions.

Two dissolutions are always required; a third dissolution is required for 25% of the process batches. The final residue, typically 10-15% of the impure oxide batch, is filtered, dried, weighed, and transferred to the insoluble oxide storage container, in which residues from all six dissolvers are accumulated. When insoluble material containing 500-520 g of plutonium has been accumulated, it is weighed and transferred to the rich-residue recovery process and subsequently returned to the process as recycle feed.

Solid scrap (e.g., gloves and rags) and sweepings are placed in containers and analyzed for plutonium in a TNC. Liquids (such as the water used to moisten and rinse rags used in cleaning the glovebox) are analyzed for plutonium with a solution-assay instrument (SAI). The SAI is an at-line passive gamma-ray spectroscopy system, incorporating transmission correction. The materials are transferred to a recovery process.

The filtrates from the dissolutions of a particular batch are combined and distilled to a volume <4 L (generally 3-3.5 L). The resulting solution must then be thoroughly mixed. A 25-mL sample is taken, weighed, and analyzed for plutonium with an SAI. After the analysis, the sample is added to a subsequent batch. The solution is transferred into tared bottles and weighed.

3. Peroxide Precipitation and Dissolution. The first purification step consists of the precipitation of plutonium peroxide. Plutonium is separated from americium and many other impurities, such as aluminum, calcium, cerium, chromium, cobalt, and magnesium. Iron and copper will catalyze the decomposition of hydrogen peroxide and, if present in sufficient concentration, may lead to violent reactions. The addition of a small amount of concentrated sulfuric acid prior to the precipitation aids in the formation of large,

easily filtered particles of plutonium peroxide.

The concentrated filtrate from the dissolution of a batch of oxide is placed in one of four glass precipitation vessels (61-cm long x 23-cm diam). The vessels are equipped with cooling coils and have provisions for sparging, stirring of the solution, and temperature measurement. A 0.5-mL sample of the filtrate is titrated to determine its acidity and then returned to the original solution. The acidity of the solution is adjusted to 4 M by additions of the proper amount of nitric acid or water. The solution is stirred and cooled to below 17°C, and 35 mL of concentrated sulfuric acid are added. Next, 8 L of 30% hydrogen peroxide that have been cooled to 10°C are added, at first dropwise, with stirring. When foaming subsides completely upon continued addition of hydrogen peroxide and the pea-green precipitate of Pu_2O_7 appears, the remainder of the hydrogen peroxide is added more rapidly. The precipitate is allowed to digest without stirring for ~30 min.

The slurry is filtered through a stainless-steel boat that has a 25- μm -porosity Kynar frit. The filtrate contains the americium and other impurities. The volume of filtrate is determined. A 25-mL sample is analyzed for americium and plutonium with an SAI. The hydrogen peroxide in the filtrate is destroyed within 30 min of filtration by slowly adding the filtrate to 8 L of 9 M sodium hydroxide during air sparging. The precipitate is washed five times with 100 mL portions of 5% hydrogen peroxide-0.5 M nitric acid, and the washings are added to the sodium hydroxide. The filtrate and washings, in which hydrogen peroxide has been destroyed, are acidified with nitric acid and transferred to americium recovery.

The plutonium peroxide filter cake is dried under suction in the filter boat for 15 min. The precipitate is dissolved by adding it in small portions to concentrated

nitric acid in one of two dissolvers. The filter boat is washed under suction with some of the resulting solution and finally with several 25-30 mL portions of 1.0 M nitric acid. The solution and washings are combined and cooled to room temperature, either by standing overnight or by the use of cooling coils. The combined liquids are thoroughly mixed by air sparging, placed in tared 2-L bottles, and weighed. A 25-mL sample is weighed and analyzed for plutonium concentration with an SAI. This sample is added to a subsequent batch.

Solid scrap and sweepings are placed in containers and analyzed for plutonium in a TNC. Liquids are analyzed with an SAI. The materials are transferred to recovery operations.

4. Oxalate Precipitation. The second purification step consists of precipitation of plutonium(III) oxalate. The precipitation not only serves to remove additional impurities but also helps to regulate the particle size and surface area of the oxide product obtained by calcination of the oxalate. Hydroxylamine nitrate (HAN) reduces plutonium from the tetravalent to the trivalent state. The acidity of the plutonium solution must be reduced to ≤ 3 M before addition of HAN to prevent autocatalytic decomposition of the latter. Urea is added to react with any nitrite present because nitrite would otherwise react with HAN.

The equipment for oxalate precipitation is similar to that used for peroxide precipitation. A batch of solution from the peroxide dissolution is transferred to one of four oxalate precipitation vessels. The solution is stirred and cooled to ~22°C. A 0.5-mL sample of the solution is titrated to determine its acidity and then returned to the original solution. The acidity of the solution is adjusted to 3 M by addition of the proper amount of water or nitric acid. Urea crystals (3 g/L of solution) are added to the cooled, stirred solution and allowed to react for 30 min with any nitrite present. With

constant stirring, 500 mL of 1.9 M HAN solution are added. If no unusual reaction is observed, 4.5 L of additional HAN solution are added gradually. After all HAN has been added, the solution is allowed to stand for 1 h. The solution should be a deep blue color.

The solution is stirred and maintained at 22°C during the addition of 1100-1200 g of crystalline oxalic acid. Stirring is continued for 10-15 min, and the plutonium oxalate precipitate is allowed to settle for 15 min. The precipitate is filtered in a stainless-steel boat that has a Kynar frit. The filter cake is washed with 50-mL portions of 0.5 M nitric acid until the washings are clear. Suction is applied overnight or until the blue-green plutonium oxalate cake is sufficiently dry. The water content of the oxalate cake must be <60 wt% to permit plutonium assay with the double-ring TNC. One-fourth of the batches require additional drying time. In the filter unloading area, the oxalate filter cake is scraped from the filter boat with a porcelain spatula into a transfer container. The plutonium content of the container is determined with a double-ring TNC.

The filtrate and washings are combined, and the total volume is determined. The liquid is thoroughly mixed by sparging. A 25-mL sample is analyzed for plutonium with an SAI. The mixture is sparged and transferred to lean-residue recovery. Other solid and liquid scrap is analyzed for plutonium as before and transferred to recovery operations.

5. Calcination and Hydrocalcination.

The contents of two cans of wet oxalate cake (~2 kg of plutonium) are combined in a cylindrical Inconel vessel having a platinum frit. The vessel is placed in a resistance furnace whose heating cycle is controlled by a microprocessor. The wet plutonium oxalate is dried by heating at 125°C and then converted to plutonium

dioxide by heating at temperatures gradually increasing to 450°C while passing a current of dry air through the filter boat frit. The furnace is held at 450°C for at least 3 h. The final purification step consists of hydrocalcination (pyrohydrolysis) to remove fluoride and chloride from the product oxide. The furnace temperature is raised to 750°C, and moist air is passed through the filter boat. It is important that moist air be in contact with all of the plutonium oxide. The final ignition is at 750°C in dry air (moisture content ~0.4%). A complete heating cycle may take 24-30 h, including drying, calcination, hydrocalcination, and cooling.

When the furnace has cooled, the furnace boat is removed. The plutonium dioxide (containing ~1800 g of plutonium) is placed in a tared, stainless-steel surgical dressing jar and weighed in preparation for transfer to screening. This operation and subsequent screening, blending, and canning are performed in gloveboxes in which the moisture content is kept at 100 ppmv or less. Glovebox sweepings are weighed, assayed with a TNC, and transferred to recovery.

6. Screening, Blending, and Canning.

Specifications for ceramic-grade plutonium dioxide require that all of the material shall pass a 170-mesh (88- μ m) US standard sieve. Accordingly, all of the product is screened with a vibratory separator having a 170-mesh screen. A 30-min screening is followed by a 5-min settling period. Material that does not pass the screen is ground in a motorized mortar and pestle and re-introduced to the screen. Coarse material that cannot be ground to pass the screen is weighed and stored until 1180 g of plutonium dioxide have been accumulated. The material is then recycled through oxide dissolution. Glovebox sweepings are weighed and combined with the coarse material in a stainless-steel dressing jar.

Screening of a 2-kg batch of plutonium oxide requires less than an 8-h day.

Five batches of screened material (containing ~8 kg of plutonium) are blended in a rotating electric "V" blender to prepare an ~10-kg lot of product oxide. Each batch is weighed before blending for 5 min.

Several weighed samples of the blend are taken to verify that the product meets the specifications. The weights and purposes of the samples are:

110 g PuO ₂	Physical characterization
13 g PuO ₂	Chemical analysis
1 g PuO ₂	Shipper/receiver plutonium assay
50 g PuO ₂	Archive sample (historical), retained at least 1 yr
50 g PuO ₂	Referee sample (used only if analysis is questioned), retained at least 4 months.

Physical tests and chemical analyses are briefly described in Table II.

Plutonium-oxide powder is transferred into tared No. 2 foodpack cans with lids. Each can contains not more than 1 kg of oxide. The cans are cleaned and transported to the canning hood, where the cans are cleaned, labeled, and mechanically sealed. They are then transported to the final canning area.

7. Final Canning. The No. 2 cans are cleaned by wiping with a rag moistened with distilled water and then with a rag moistened with sodium citrate. The can is placed inside a tared plastic bag that is then sealed with tape. Each plastic bag and contents is placed in a separate tared and labeled No. 3 can, which is mechanically sealed, weighed, fitted with tamper-indicating seals, and transferred to the pure-oxide product area of the vault.

B. Comments on the Reference Process

Oxidation of the plutonium metal buttons in air leads to oxide that is difficult to dissolve. Even after two or three periods of refluxing in concentrated nitric acid containing some hydrofluoric acid, an insoluble residue remains. This residue

is oxide that has been exposed to much higher temperatures (perhaps in excess of 1000°C) than required. Plutonium dioxide ignited at temperatures no higher than 600°C should readily dissolve. We recommend investigating oxidation of plutonium metal in controlled atmospheres to keep the ignition temperature below 600°C. An argon atmosphere containing a controlled amount of oxygen--just enough to support combustion--is one possibility.

The comments regarding plutonium metal oxidation may be unnecessary for a commercial process, where impure plutonium oxide is the feed. The operations of such a process would consist of oxide dissolution, the purification steps (peroxide precipitation and dissolution, oxalate precipitation), and calcination.

The optimum concentration of excess oxalic acid in the slurry after precipitation of plutonium(III) oxalate is 0.25 M. A larger excess of oxalic acid leads to the formation of soluble plutonium oxalate complexes and greatly complicates the operations of the lean-residue recovery process to which the filtrate from the oxalate precipitation is transferred. We recommend that the quantity of oxalic acid crystals used for the precipitation be adjusted to the amount of plutonium present in the solution. The correct amount (the stoichiometric amount plus required excess) of oxalic acid should be weighed out on a balance.

C. Bibliography

Additional detailed information on the operations described may be found in the following publications.

1. E. L. Christensen and W. J. Maraman, "Plutonium Processing at the Los Alamos Scientific Laboratory," Los Alamos National Laboratory report LA-3542 (April 1969).
2. J. M. Cleveland, The Chemistry of Plutonium (Gordon and Breach Science Publishers, New York, 1970).

TABLE II

REQUIREMENTS^a AND TESTS FOR CERAMIC-GRADE
PLUTONIUM DIOXIDE FOR THE FAST FLUX TEST FACILITY

Physical Properties

1. Sieve Analysis

a. Requirement:

<u>US Standard Sieve</u>	<u>% of PuO₂ Powder Passed</u>
170 mesh (88 μm)	100
200 mesh (74 μm)	99 min
325 mesh (44 μm)	95 min

b. Test: A weighed sample of powder is passed through the three sieves stacked on a shaker. The weight of powder retained by each sieve is measured, as well as the weight of powder that passes through the finest sieve.

2. Particle Size Distribution

a. Requirement: 50% of the particles shall be <20 μm.

b. Test: The Particle Size Analyzer measures sedimentation rates of particles in suspension by measuring the concentration of particles remaining in suspension as a function of time. The data are automatically converted to particle size distribution.

3. Surface Area

a. Requirement: Surface area of the powder shall be ≥ 2.5 m²/g.

b. Test: The amount of gas required to cover the surface of the tested sample with a monomolecular layer of close-packed molecules is determined with a Surface Area Analyzer. Nitrogen gas at liquid nitrogen temperature is the adsorbate.

4. Sinterability

a. Requirement: The product shall be sinterable to an average density equal to at least 90% of the theoretical density of PuO₂ (11.46 g/cm³).

b. Test: Ten pellets are pressed and sintered at 1550 ± 50°C. The density of each pellet is obtained by weighing it on an analytical balance and measuring its length and diameter with a precision micrometer.

Chemical Properties

5. Loss on Ignition (LOI)

a. Requirement: LOI $\leq 2.5\%$ by weight.

b. Test: A weighed sample is ignited at 950°C for 2 h, allowed to cool in a desiccator, and reweighed.

6. Plutonium Content

a. Requirement: The minimum plutonium content of a representative sample at the time of packaging shall be 85% by weight. The minimum plutonium content of a sample after ignition to 950°C shall be 87.5% by weight.

b. Test:^b Weighed samples are dissolved and analyzed for plutonium by controlled-potential coulometry.

7. Isotopic Composition of Plutonium

a. Requirement

<u>Isotope</u>	<u>Wt%, Based on Total Pu Wt</u>
239Pu + 241Pu	88.0 ± 0.5
241Pu	2.5 maximum
238Pu	0.15 maximum
All others, excluding 240Pu	0.35 maximum
240Pu	Balance

TABLE II (cont)

- b. Test:^b The isotopic composition is determined by surface-ionization mass spectrometry.
8. Americium content
- a. Requirement: Americium - 0.25 wt% maximum.
- b. Test:^b Americium is determined by measuring the gamma activity of the dissolved sample in a well-type NaI(Tl) crystal coupled to a photomultiplier tube. A correction for plutonium gamma activity is made.
9. Oxygen-to-Plutonium Ratio
- a. Requirement: O/Pu = 1.95 to 2.00.
- b. Test:^b The ratio is determined by thermogravimetry.
10. Impurities
- a. Requirement: Total impurities, exclusive of U and Am, shall not exceed 5000 µg/g. Uranium shall not exceed 2000 µg/g. There are also maximum values for 29 metallic impurities and six non-metals:

Al	250 µg/g
B	10
Be	20
Ca	500
Cd	20
Co	20
Cr	200
Fe	350
K	200
Li	10
Mg	100
Na	300
Ni	300
Ta	400
V	200
W	100
Sum of Cu, Si, Ti, Zn	800
Sum of Ag, Mn, Mo, Pb, Sn	200
Sum of Dy, Eu, Gd, Sm	100
Carbon	200 µg/g
Chlorine	50
Fluorine	25
Nitrogen (as nitride)	200
Phosphorus	200
Sulfur	300

- b. Tests: Details of the tests will be found in Los Alamos National Laboratory report LA-4622 (see footnote b).

^aRequirements taken from RDT Standard E13-1T, "Fast Flux Test Facility Ceramic Grade Plutonium Dioxide."

^bFor details of chemical analysis methods, see J. E. Rein, G. M. Matlack, G. R. Waterbury, R. T. Phelps, and C. F. Metz, Eds., "Methods of Chemical Analysis for FBR Uranium-Plutonium Oxide Fuel and Source Materials," Los Alamos National Laboratory report LA-4622 (March 1971). All chemical analyses are performed on material that has been ignited to constant weight at 950°C. In addition, plutonium concentration, fluorine, and chlorine are determined on an unignited sample.

3. R. M. Greinetz and W. E. Sperry, "Plutonium Peroxide Precipitation and Calcination Process for Plutonium Nitrate to Oxide Conversion," Rockwell International, Rocky Flats Plant report RFP-2606 (February 1980).
4. R. M. Greinetz and D. H. Neal, "Plutonium (III) Oxalate Precipitation and Calcination Process for Plutonium Nitrate to Oxide Conversion," Rockwell International, Rocky Flats Plant report RFP-2603 (February 1980).
5. P. G. Hagan and F. J. Miner, "Plutonium Peroxide Precipitation: Review and Current Research," in Actinide Separations, J. D. Navratil and W. W. Schulz, Eds. (American Chemical Society, Washington, DC, 1980), pp. 51-67.
6. K. M. Harmon, B. F. Judson, W. L. Lyon, R. A. Pugh, and R. C. Smith, "Plutonium Reconversions," in Reactor Handbook, Vol. II, Fuel Reprocessing, 2nd Ed., S. M. Stoller and R. B. Richards, Eds. (Interscience Publishers, Inc., New York, 1961), Chap. 11.
7. L. W. Reese, G. L. Taylor, and M. Haas, "Preparation of Ceramic Grade Plutonium Dioxide for the Fast Flux Test Facility," presented at the 24th National Symp. for Chemical Technicians/179th National Meeting of the American Chemical Society, Houston, Texas, March 24-25, 1980.

III. DYNAMIC MODEL OF THE PROCESS

Modeling and simulation of the process can aid in the design and evaluation of alternative process operations and accounting strategies. Simulation techniques may be used to predict the behavior of materials flows and materials measurements over a wide range of operating conditions and to accumulate rapidly data representative of relatively long operating periods. In addition, the use of simulation techniques for generating process data is less time-consuming and less expensive than obtaining the necessary data from experiments on test loops and mockups of plant operation. This section describes briefly the computer code PUCSIM (Pu Conversion Simulation), the process model that was developed to simulate process operation, and presents selected process simulation results.

A. The PUCSIM Computer Code

The computer code PUCSIM was developed specifically to simulate operation of the process model. PUCSIM is written in FORTRAN and constitutes the user-supplied portion of the more general MODEL code; both PUCSIM and MODEL were developed by the Los Alamos Safeguards Systems Group. Through the MODEL code, PUCSIM employs a modified version of the GASP IV simulation package⁶ to schedule discrete events (unit-process transfers and in-process operations) and provide other process dynamics. PUCSIM was developed and tested using a PRIME 750 computer and consists of ~2500 FORTRAN statements. A simulation of 1000 h of process operation requires ~200 000 16-bit words of storage. Operating periods of up to 10 000 h were simulated requiring ~300 s of computer time.

The PUCSIM code is structured with much of the process-specific information in the input data to minimize the FORTRAN coding changes required for evaluating alternative process operations. Input data include initial values for all process variables and the range for each independent process variable. The independent variables and their respective ranges used in the PUCSIM process model are given in Tables III and IV.

A block diagram of the process model is given in Figs. 2a and 2b. Each unit process type is modeled separately in PUCSIM as an individual subroutine. Parallel unit processes are modeled within the same subroutine. When an event takes place in a particular unit process, values of the independent process variables are sampled from their respective probability density functions, and the dependent process variables are calculated by conservation-of-mass equations. All process variables then are stored in a data vector. The data vectors for each unit process are stored sequentially in a separate data file. This

TABLE III
INDEPENDENT PROCESS VARIABLES FOR THE PROCESS

UPAA Description and Designation Symbol ^a	UPAA Number	UPAA Component/Stream	Nominal Pu Content (g) ^b	Range (%)	Residence Time (h)	Inventory (kg)	
Button oxidation (BU)	1	--	--	--	24		
		NX (feed)	1994	4	24		
		POT					5
		Scraped oxide (SOX)	3	66	24		
		Scrap	0.25	100	24		
		Holdup	1	100			
		OF-1, OF-2 (product)	1034	0			
Oxide dissolution (OD)	2a	--	--	--	48-72		
		ROT-1	250	10	24		
		ROT-2	125	50	48		
		ROT-3	160	10	72		
		ROT storage	--	--	~96	0.52	
		ROT #	520	0	~96		
		Solid scrap	<0.5	--	Variable		
		Liquid Scrap	<0.5	--	Variable		
		Holdup	9	100			
		Peroxide precipitation and redissolution (PR)	2b	--	--	--	24
Am recovery feed (FAM)	2			100	24		
Solid scrap	<0.5			--	Variable		
Liquid scrap	<0.5			--	Variable		
Holdup	20			100	--		
Oxalate precipitation (OY)	2c	--	--	--	24-48		
		LR recovery feed (OXF)	6	100			
		Oxalate transfer (CAN)	2.5	0			
		Solid scrap	<0.5	--	Variable		
		Liquid scrap	<0.5	--	Variable		
		Holdup	20	100			
Calcination-hydrocalcination (HC)	2d	--	--	--	24-30		
		Oxalate transfer (2 CANS)	2.5 ea	0			
		Handling	1	100			
		Holdup	2	100			
Sieving, grinding, blending, and canning (BL)	3	--	--	--	1 wk		
		Sweepings	530	50			
		Solid scrap	<0.5	--			
		Samples ^c	195	1			
		Coarse oxide	5	100			
		Holdup	5	100			

^aSee Fig. 2.

^bThese quantities are independent, stochastic variables in the computer simulation.

^cSee Table IV.

TABLE IV
ANALYTICAL SAMPLES OF PuO₂ PRODUCT

Sample Description	Item ID	Nominal Pu Content (g)	Range (g)
Chemical and isotopic analysis	LAO-CS	9	0
Certification tests	LAO-CC	97	+0,-9
Archive (1-yr retention)	LAO-CA	44	0
Referee (4-month retention)	LAO-CB	44	0
Special contractor Pu analysis	LAO-SR	1	0

data-storage format is useful for further processing and for input to measurement simulation programs.

The dynamics for the unit processes are defined in eight attribute files of the modified GASP IV simulation package. The purpose of each of these files is given in Table V. The first file is used to schedule discrete events and the other seven are queue files that simulate possible delays in the process (material may be ready for transfer from one unit process to another that is not yet ready to receive it). For example, when a batch of plutonium peroxide has been dissolved, the full dissolver is placed into queue file 5

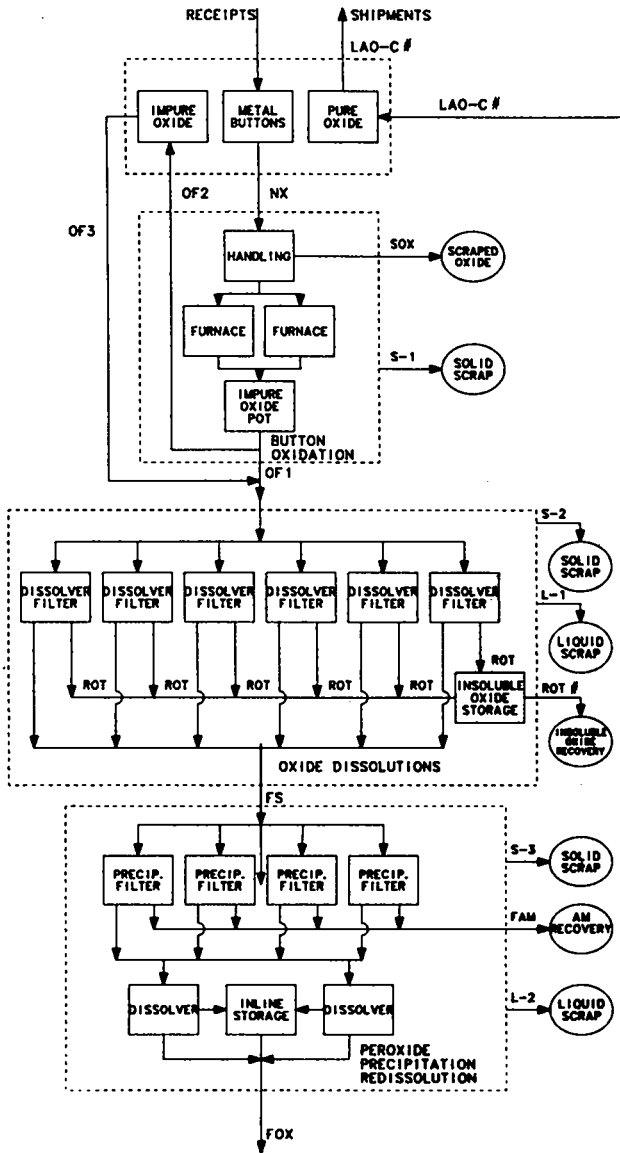


Fig. 2a. Process model schematic.

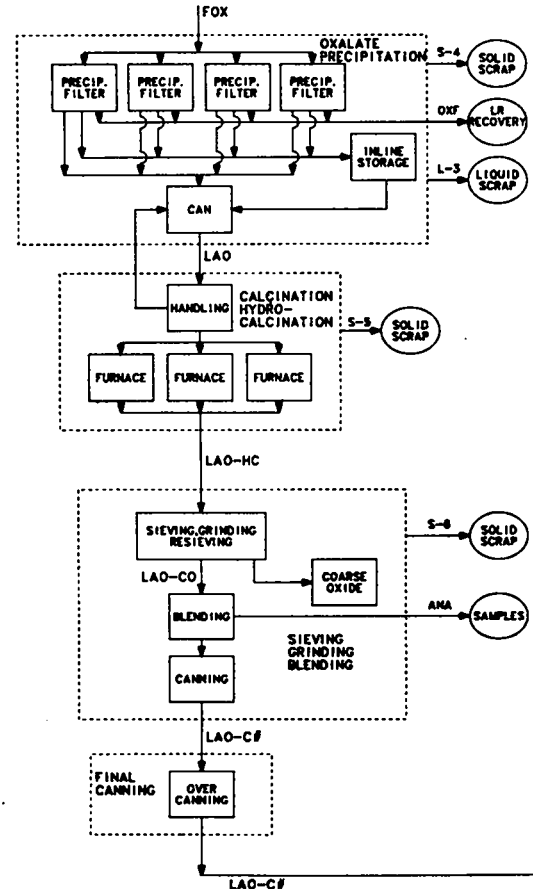


Fig. 2b. Process model schematic.

TABLE V
SUMMARY OF GASP-IV FILES USED BY PUCSIM

File No.	Purpose
1	Event scheduling
2	Empty button-furnace queue
3	Full oxide-dissolver queue
4	Empty peroxide-dissolver queue
5	Full peroxide-dissolver queue
6	Empty oxalate-precipitator queue
7	Empty oxalate-furnace queue
8	Full oxalate-furnace queue

rather than unloaded if all oxalate precipitators are in use. When an oxalate precipitator is unloaded, the program checks whether a full plutonium peroxide dissolver is in the queue. If yes, it is removed from the queue and unloaded. If not, the empty oxalate precipitator is placed into queue file 6 until there is a full peroxide dissolver.

In addition to scheduling process events, the modified GASP IV simulation package provides a statistical analysis of each process variable and of each attribute file. Statistical data on each attribute file are generated, and at the end of a run the mean number of entries (e.g., dissolvers, precipitators, and furnaces) in each file and the mean residence time of an entry in each queue file are computed for an average 8-h workday (Table VI). Mean load factors for each process area also are calculated (Table VII). The data in Tables VI and VII give, respectively, the average number of pieces of specific process equipment, either full or empty, that remain idle during an 8-h workday because of process delays (Table VI); the average number of hours that an item of process equipment remains idle during an 8-h workday (Table VI); and the fraction of a 24-h day during which time special nuclear material (SNM) is present in a given process area (Table VII).

Table VI indicates that for an average 8-h workday ~ 1.65 fully loaded peroxide dissolvers must wait ~ 3.45 h each for an empty oxalate precipitator, and Table VII indicates that SNM is present in the oxalate precipitation process area for a greater fraction of time (~ 0.83) than it is in the peroxide precipitation and redissolution process area (~ 0.67). Together, such statistics can aid in the design and evaluation of alternative process operations and accounting strategies. For example, data on the effects of adding, deleting, or altering equipment in specific process areas could be generated from simulated process operation rather than from expensive and time-consuming experimental mockups.

Development of the process model required an analysis and evaluation of historical data for each of 28 unit processes. The data base for the model was collected for the period October 1979 through January 1980. Although three furnaces were available for burning metal buttons during this period, the process model comprises only two to reflect current practice. Also, in the process model, four batches of screened material are blended rather than five (current practice). Finally, PUCSIM was written to simulate a 1-shift/day, 7-days/wk schedule rather than the actual 5-days/wk

TABLE VI
STATISTICS ON GASP IV QUEUE FILES USED BY PUCSIM^a

File No. ^b	Mean Number of Entries ^c	Mean Residence Time (h) of an Entry ^c
2	0.67	4.42
3	0.08	1.76
4	1.18	4.40
5	1.65	3.45
6	0.12	4.31
7	1.58	7.40
8	0.02	1.68

^aBased on 10 000 h of simulated steady-state process operation.

^bSee Table VII for description of each file.

^cFor an average 8-h workday.

TABLE VII
MEAN LOAD FACTORS FOR REFERENCE PROCESS AREAS^a

Process Area	Mean Load Factor ^b
Button oxidation	
Pu handling	0.06
Furnaces (2)	0.66
POT	0.05
Oxide dissolution	
Dissolvers (6)	0.98
Insoluble-oxide storage	0.73
Peroxide precipitation and redissolution	
Precipitators/dissolvers (4)	0.67
Oxalate precipitation	
Precipitators (4)	0.83
Calcination-hydrocalcination	
Oxalate handling	0.52
Furnaces (3)	0.48
Sieving, blending, and canning	
Sieving	0.77
Blending and canning	0.30
Final canning	
Overcanning	0.08

^aBased on 10 000 h of simulated steady-state process operation.

^bDefined here as the fraction of a 24-h day during which time SNM is present in a given process area.

operation, so that a continual 1-shift/day annual throughput potential could be determined. PUCSIM is structured to permit straightforward incorporation of any process modifications.

B. Simulation Results

Selected simulation results are presented in this section. Figures 3-7 are examples of SNM transfers and in-process inventories from a 2.5-wk period (8-h workday, 7 days/wk) of simulated steady-state process operation (>1000 events). In each graph, the process variable is plotted at the event time (events can be simultaneous or up to ~100 h apart depending on the process step). Except as noted in the text, the graphics represent single-valued functions.

Plutonium metal buttons (~2 kg each) are received and stored in the vault metal-button area. From there either one or two buttons are transferred to the plutonium handling glovebox; two buttons are transferred simultaneously when there are <10 cans of impure PuO₂ in the vault. A

buffer of ~10 cans of impure PuO₂ was maintained in the process model vault to allow the oxide dissolution process to be demand-driven rather than supply-driven. Figure 3 shows the plutonium content of the impure metal buttons transferred from the vault to the plutonium handling glovebox.

Each cleaned metal button is transferred to a furnace boat and placed in one of two resistance furnaces for air oxidation, which takes ~14 h. Residence time in a furnace is ~23 h. Some plutonium oxide remains in each furnace boat.

Impure PuO₂ is transferred from either one or two furnaces to the oxide container (POT), in which the PuO₂ is accumulated before it is canned in 1.034-kg plutonium batches. Figure 4 shows the plutonium content of the mass transfers and in-process inventories for POT. Batches are transferred from POT, on demand, to one of six oxide dissolvers (batch transfers to dissolvers may be simultaneous). At 3:30 p.m. on each operating day, any cans of impure PuO₂ remaining in the button oxidation area are transferred to the canned impure-oxide area of the vault for storage. The transfer from POT of ~3.1 kg of plutonium (3 cans of impure PuO₂) at 367.5 h (Fig. 4) is an example of this type of transfer.

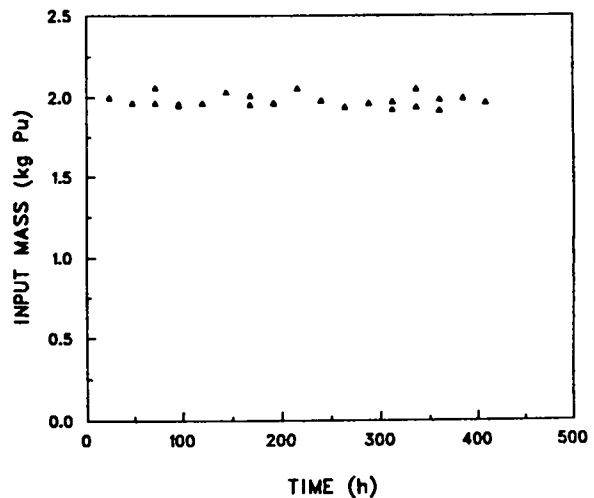


Fig. 3. Plutonium handling: metal button(s) input.

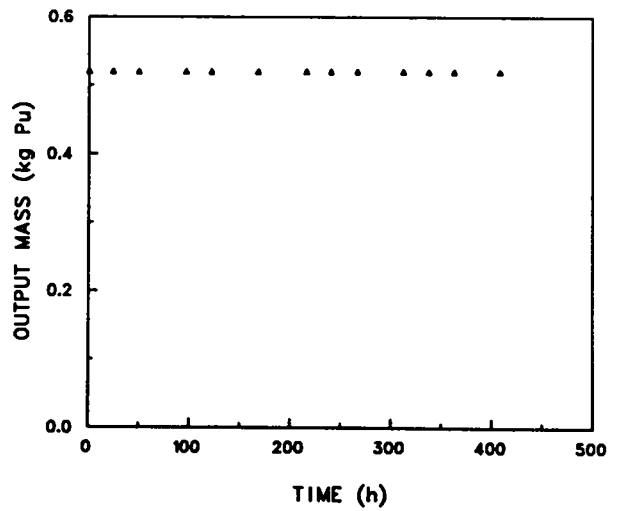
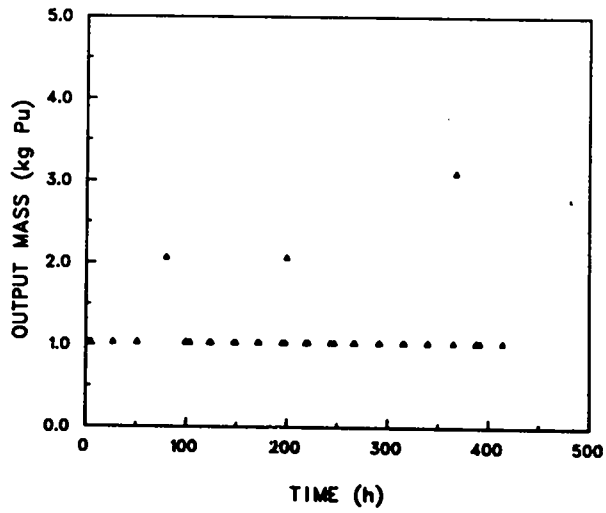
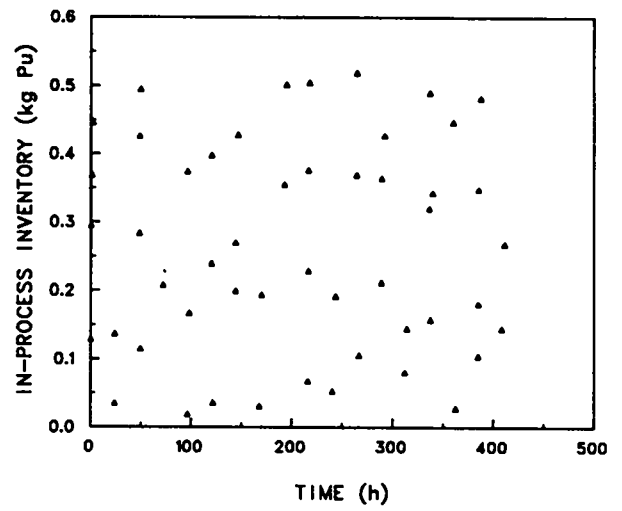
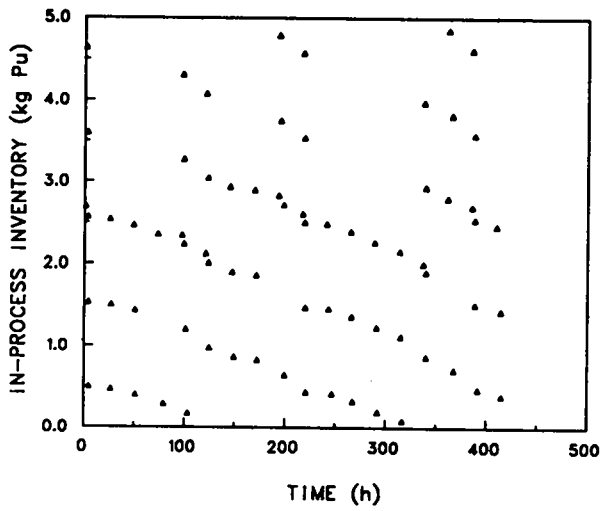
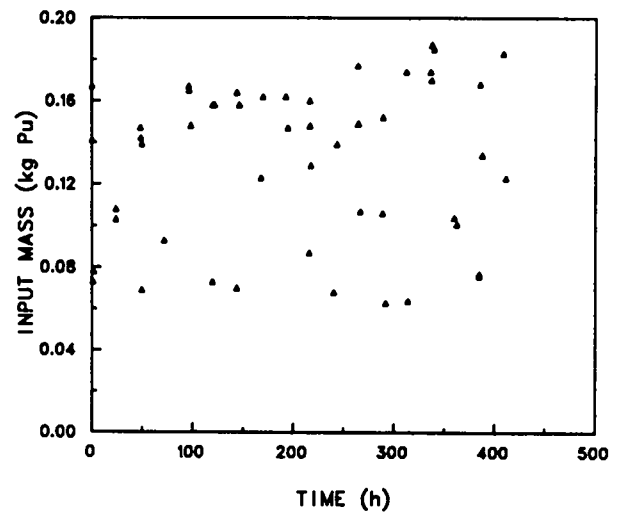
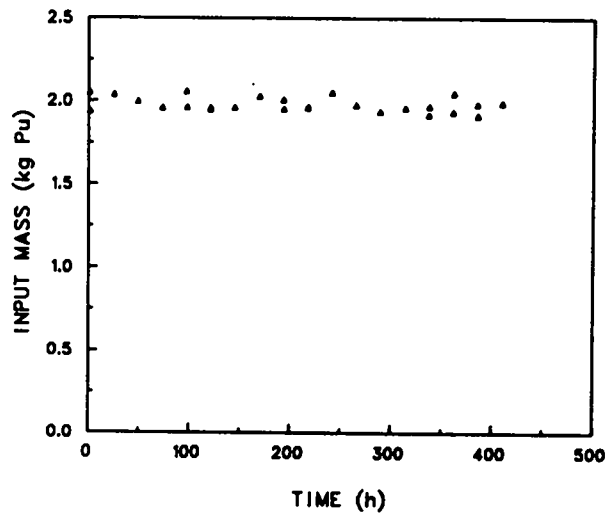


Fig. 4. Oxide container (POT): input (upper), in-process inventory (middle), output (lower).

Fig. 5. Insoluble-oxide storage container: input (upper), in-process inventory (middle), output (lower).

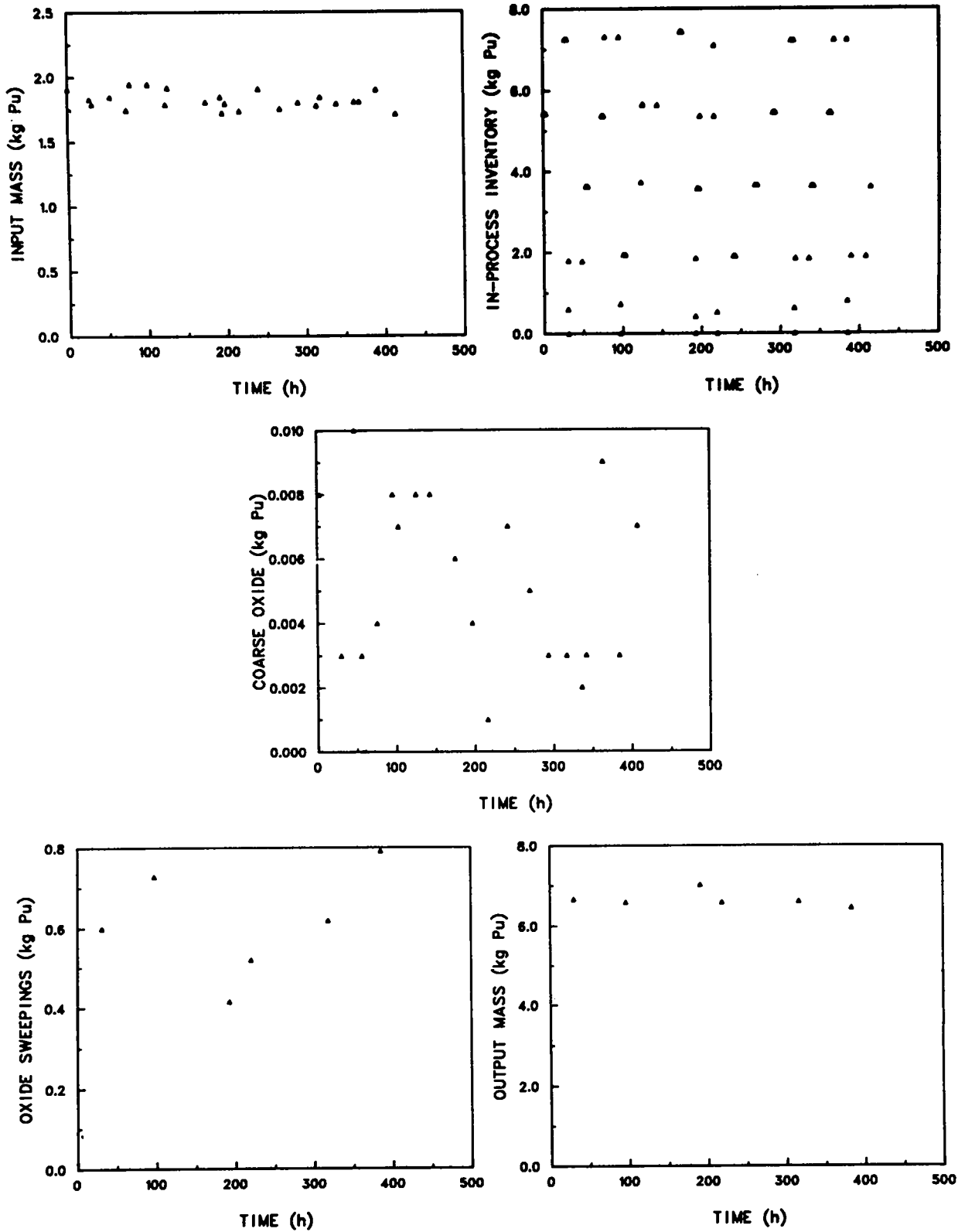


Fig. 6. Screening: input (upper left), in-process inventory (upper right), coarse oxide (middle), oxide sweepings (lower left), output (lower right).

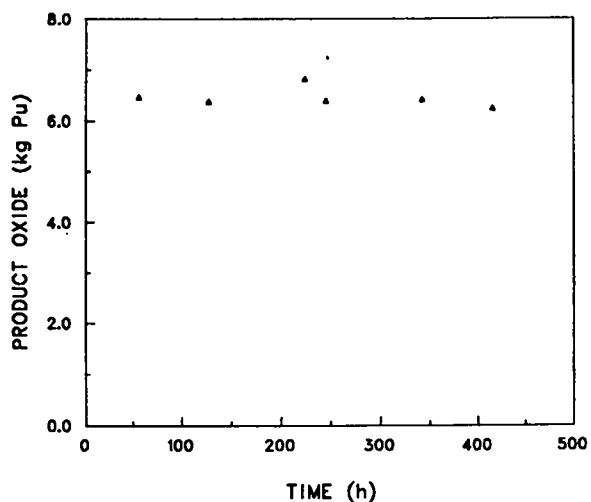


Fig. 7. Final canning: product PuO_2 output.

In the oxide dissolution area, one can of impure PuO_2 is received, on demand, at each dissolver location from either the button-oxidation area, when a canned batch is available, or from the vault. Each batch may require up to three dissolutions, and each dissolution requires one 8-h workday. Plutonium is held up on each dissolver filter.

Figure 5 shows the plutonium content of the mass transfers and in-process inventories for the insoluble-oxide storage container, in which the solid residue from all six dissolvers is accumulated. As soon as the accumulated material contains ≥ 520 g of plutonium, a ROT batch containing 520 g of plutonium is transferred to the insoluble-oxide recovery and recycle operations.

In the peroxide precipitation and redissolution process area, an individual batch of plutonium nitrate solution is received from oxide dissolution when a precipitation vessel becomes available. The resultant plutonium-peroxide filter cake is transferred to one of four dissolvers. Two dissolver locations, each containing two dissolvers, are shown in Fig. 2a. Plutonium is held up in each precipitator and filter.

After oxalate precipitation, the slurry is filtered, and the wet plutonium oxalate filter cake is dried for ~ 1 day. A second day is required to dry $\sim 25\%$ of the process batches. The plutonium-oxalate cake (LAO) is stored in-line until transferred to a can for routing to the plutonium calcining glovebox. Plutonium is held up in each precipitator and filter and in the emptied oxalate cans that are returned from the plutonium calcining glovebox in the calcination-hydrocalcination process area.

The calcination-hydrocalcination process requires ~ 24 -30 h. Some plutonium is held up in the plutonium calcining glovebox and in each furnace boat.

Plutonium dioxide is transferred from one of three furnaces to screening, where it is separated into coarse and fine fractions. The coarse fraction is then ground and rescreened, and the coarse PuO_2 remaining after rescreening is accumulated for recycle through the oxide-dissolution process. Following daily operations, the screening glovebox is swept, and the oxide sweepings also are accumulated for recycle through the oxide-dissolution process. After four furnace batches have been screened, the fines are combined and transferred to the blending glovebox before final canning. The composite PuO_2 batch (< 8 kg of plutonium) is then weighed, blended, and sampled. Some plutonium is held up in the blending glovebox. Figure 6 gives the plutonium content of the mass transfers and in-process inventories for the screening process.

Figure 7 shows the plutonium content of the product oxide transferred from the final canning process area to the pure-oxide product area of the vault. The product oxide (< 8 kg of plutonium) is transferred to the vault in cans containing ~ 1 kg PuO_2 .

IV. MATERIALS MEASUREMENT AND ACCOUNTING SYSTEM

The existing materials measurement and accounting system is examined in this section. Measurement methods used in the process are basically nondestructive assay (NDA) techniques augmented by chemical methods. These measurement methods and the measurement control programs were described previously⁷⁻¹² and are summarized in Sec. IV.A. Possible accounting strategies are presented in Sec. IV.B.

A. Measurements

1. Weight. When the composition of a material is well known, the amount of nuclear material can be determined from the bulk weight and an assay factor. The bulk weight is determined with a balance, and the assay factor is based on chemical analysis or historical experience. Much of the solid material handled in the reference plutonium conversion and purification process is well-characterized and, therefore, amenable to such measurements. In addition, solution measurements are based on NDA of weighed sample aliquots and the bulk solution weight.

The majority of the balances used to obtain bulk weights are commercially available, digital-readout electronic balances.⁷ These units have been modified to minimize the amount of electronics within the glovebox. Only the weighing pan and force-restoring mechanism are located within the glovebox. The weight cell components are housed in a stainless-steel compartment and are resistant to chemical corrosion and radiological damage. The electronics package is located outside the glovebox in a position convenient for the operator. The electronics and electromechanical sections of the balance are connected by a cable terminated with standard connectors. The cable penetrates the glovebox with a through-bulkhead, hermetically sealed receptacle. This remoting technique has some limitations. The electronic signal

is weak so that cable length is limited to 20 feet. Also, because of the weak signal, movement of the connecting cable causes capacitance changes in the cabling sufficient to produce changes in the balance calibration.

An alternative remoting method results in improved signal transmission but less corrosion resistance. For this method, the transducer board is placed inside the electromechanical weight cell housing, producing a stronger, more stable signal to the external electronics package. If, in addition, a strain-relieved direct connection of the cable to the weight cell and electronics packages is made, movement of the cable no longer affects balance calibration. These techniques have been used where corrosion resistance was not a significant factor.

Three types of electronic balances are in use: 5.5-kg capacity readable to 0.1 g, 5.5-kg capacity readable to 0.01 g, and 15-kg capacity readable to 0.1 g. The performance characteristics of the two 5.5-kg balance models are identical.⁷

It has been shown that the random error for an electronic balance is proportional to mass. The random error variance can be described as the sum of an absolute error variance and a proportional error variance. A set of random errors for a typical 5.5-kg balance is 0.055 g at the 1-kg level and 0.085 g at the 4-kg level. For a typical 15-kg balance, the random errors are 0.050 g at the 1-kg level and 0.083 g at the 4-kg level. Long-term bias ranges from 0.02 g to 0.12 g per determination and is a function of mass.

The electronic balances are used for most weight measurements. However, product bulk weights are determined with an electromechanical balance. The balance is located within the blending and canning glovebox where it is not subject to chemical corrosion. The balance has a 7-kg capacity and is readable to 0.1 g. The

performance of this balance is similar to that of the comparable 5.5-kg electronic balances.

2. Gamma-Ray Techniques

a. Solution Assay. Solutions containing plutonium are generated in several of the processing steps. These solutions include waste streams, precipitation filtrates, and concentrated plutonium nitrate solutions. Plutonium concentrations range from <1 g/L to 200-300 g/L. A solution may contain daughter isotopes such as ^{241}Am and ^{237}U . Concentrations of ^{241}Am can be as high as several g/L.

An SAI is used for the measurement of plutonium in these solutions.⁹ The SAI currently in use is optimized for the determination of plutonium concentrations in the 1- to 500-g/L range. Solutions containing <1 g/L are assayed with the SAIs with a somewhat lower precision and accuracy. An SAI designed to measure these lower-concentration solutions is being developed.

The SAI uses a transmission-corrected gamma-ray counting method for the plutonium measurement. The observed counting rate of the 414-keV gamma-ray emitted by the ^{239}Pu in the sample is corrected for sample self-absorption. Self-absorption is measured with a plutonium transmission source. A calibration factor converts the transmission-corrected counting rate to grams of plutonium in the weighed sample aliquot. The isotopic composition of the plutonium must be known because the SAI measures only the ^{239}Pu isotope. The sample aliquots are taken with a 25-mL syringe sampler and weighed. The sample volume is sufficiently accurate to permit calculation of concentration on a volume basis for plutonium solutions that are not transferred on a bulk weight basis (e.g., filtrates and liquid wastes).

The SAI and the measurement procedure are described in detail in Ref. 9. The main hardware components of the system are

(1) a germanium detector and sample holder, (2) electronics, (3) a minicomputer, (4) an operator console, and (5) a mobile maintenance-and-graphics cart. One of the 5.5-kg electronic balances is located in the glovebox with the sample holder, and a key on the operator console automatically transfers the balance reading to the SAI minicomputer.

The sample holder contains the plutonium transmission source that is fixed on a rotating tungsten shutter located above the sample vial position. Four measurements are required to determine the ^{239}Pu content of the sample aliquot: (1) the transmission source alone, (2) the background, (3) the sample alone, and (4) the transmission source plus the sample. The first two measurements are made once or twice a day. The last two measurements are made on each sample and are initiated by a single command.

For plutonium concentrations between 1.0 and 500 g/L, relative standard deviations (RSDs) of 1 to 5% are reported for assay times of 1 to 2000 s. A bias of +0.24% relative to isotopic-dilution mass spectrometry and of -0.7% relative to electrochrometric titration with a photometric endpoint detection was observed.⁹

For plutonium concentrations between 0.1 and 0.7 g/L, a RSD of 13% can be expected for counting times of 2000 s. The RSD will increase to 25% or more for concentrations in the range of 0.01 to 0.09 g/L. These values are based on assay data from a variety of process solutions.*

b. Solid Scrap Assay. Most solid scrap generated in the process is in a form suitable for measurement by neutron techniques. However, if such scrap contains water or other hydrogenous materials, the plutonium content based on neutron emission data may be in error because of neutron

*Unpublished data were supplied by Faye Hsue, Los Alamos National Laboratory, June 1980.

multiplication. Measurements using gamma-ray counting techniques may be more appropriate for such materials and could be used to verify questionable neutron measurement results.

Segmented gamma-ray scanners (SGSs) are used routinely elsewhere in the facility for the assay of plutonium-bearing waste and scrap in drums or cans and could be used for measurement of process scrap that is not suitable for neutron counting. These scanners are computer controlled and use lithium-drifted germanium detectors. The drum scanner can detect ~ 1 g of ^{239}Pu in a 5-min scan.¹³ The relative inaccuracy for measuring >10 g of ^{239}Pu may be as low as 10% in matrices of low atomic number and may increase to 50% in unknown matrices. For scrap materials encountered in the process, the measurement is estimated to have an accuracy of 10-20%.

3. Neutron Techniques. Neutron techniques for the determination of plutonium can be classified as passive or active. The passive technique depends upon the natural emission of neutrons, while the active technique induces neutron emission by external means. Coincidence counting techniques are used to differentiate fission neutrons from background neutrons and those arising from (α, n) reactions. Passive TNCs are used in the process measurement system for the determination of plutonium in solid scrap and waste and in wet oxalate filter cake.

The TNC measurement is isotope dependent. Only the even-numbered isotopes of plutonium-- ^{238}Pu , ^{240}Pu , and ^{242}Pu --have high enough spontaneous fission rates to contribute to the passive neutron measurement. Thus, the isotopic composition must be known to convert the neutron counting data to total plutonium content. Because the spontaneous fission rates of the isotopes are different, an effective mass of ^{240}Pu is used and is defined as

$$\begin{aligned} \text{mass } ^{240}\text{Pu effective} &= 2.49 (\text{mass } ^{238}\text{Pu}) \\ &+ \text{mass } ^{240}\text{Pu} \\ &+ 1.57 (\text{mass } ^{242}\text{Pu}). \end{aligned}$$

Mass spectrometry and alpha spectrometry are usually used to determine the isotopic composition. Alternatively, gamma-ray techniques could be used, but the ^{242}Pu content must be estimated by isotopic correlation techniques or by difference.

a. Solid Scrap and Waste. The typical TNC used for the assay of solid scrap and waste consists of a sample-counting cavity surrounded by a ring of ^3He detectors in cadmium-lined polyethylene moderators.¹⁰ These counters have a "well" configuration and are mounted either above or below the glovebox with one end of the well opening into the glovebox. The shielding, moderator, detectors, and electronics controls and measurement package are located outside the glovebox.¹¹

The electronics for the TNC incorporate a microprocessor-based control module with a hand-held terminal.¹¹ The microprocessor is programmed through operator-selected options to direct the counter system to (1) measure dead time, (2) determine background, (3) calibrate from a series of standards, (4) assay a sample, or (5) perform a precision or accuracy check. All calculations appropriate to a given option are performed by the microprocessor.

The following precisions and accuracies for thermal neutron measurements of scrap and waste are reported.¹⁴

<u>Material Category</u>	<u>Precision (%, 1σ)</u>	<u>Accuracy (%, 1σ)</u>
Scrap	2-8	2
Waste	10-15	5-10

If the isotopic composition of the material is not well known, the uncertainties can

be considerably greater than those listed above. This problem can arise in the process when scrap or waste has been accumulated over a period during which feed batches of different isotopic compositions were processed. The isotopic composition of the accumulated material will not be well known, and the TNC measurements could have a substantial uncertainty. Similar problems can be encountered when materials of different isotopic composition are blended.

b. Wet Oxalate Filter Cake. The filter cake from the oxalate precipitation process can contain 30 wt% or more of water. As indicated previously, the TNC measurement is based on spontaneous fission of the even-numbered plutonium isotopes. When a significant quantity of water is present, the spontaneous fission and (α, n) neutron energies are reduced by proton-neutron elastic scattering. Consequently, ^{239}Pu fission becomes a source of coincidence neutrons whose count rate is a function of the water present in the oxalate filter cake.

The special TNC developed in response to this problem¹² consists of two rings of ^3He detectors in polyethylene. The ratio of the neutron counts between the inner ring and outer ring of detectors is sensitive to the average neutron energy and, therefore, to the water content of the oxalate filter cake. The ring ratio provides a correction method that compensates for the effect of water on the neutron coincidence count rate of the filter cake.

The method has been demonstrated¹² for filter cakes containing 30 to 60 wt% water and total plutonium masses from 750 to 1000 g. Data from 26 batches of plutonium oxalate showed a negative bias of 0.8% and a RSD of 2.2%.

4. Chemical Techniques. On a routine basis, product oxide samples are assayed for adherence to specification (see Sec. II). The methods for determination of total plutonium and isotopic composition are discussed in the following sections.

a. Total Plutonium. Total plutonium is determined by controlled-potential coulometry. This method may be regarded as a special kind of redox titration in which electric current is used as the titrant. A 0.5 M sulfuric acid solution is used as supporting electrolyte because Pu(VI) can be quantitatively reduced to Pu(III) in that medium. Optimum accuracy requires an iron correction and chemical calibration of the coulometer. Iron interferes quantitatively with the plutonium determination in H_2SO_4 . It is thus necessary to determine iron spectrophotometrically in a separate aliquot of the solution and to apply a correction to the plutonium results.

A RSD of 0.1% is obtained routinely in the coulometric determination of plutonium in sulfuric acid medium. A detailed discussion and procedure may be found in Ref. 15, Chap. 4.3.

b. Isotopic Composition. Mass spectrometry is applicable to the isotopic analysis of plutonium in a variety of forms and in mixtures with uranium. The sample must be dissolved in a suitable acid medium and chemically treated to obtain a purified plutonium fraction. The separation of uranium and americium from plutonium is especially important because ^{238}U and ^{241}Am are mass interferences. The purified plutonium fraction (after dilution, if necessary) is used for mass spectrometry. The separation should be used on plutonium standards, as well as samples, to remove americium and other decay products. A detailed procedure for the separation and mass-spectrometric measurement is given in Ref. 15.

The preferred and most widely used technique for the determination of the isotopic composition of plutonium is surface-ionization mass spectrometry. If the abundance of ^{238}Pu is less than 0.7%, alpha spectrometry is frequently used for the determination of that isotope. The amount of plutonium required for an analysis is 10^{-9} to 10^{-6} g, depending on the sensitivity of the mass spectrometer.

The precision attainable varies with the relative abundances of each isotope. The following approximate RSDs may be expected¹⁶ in the isotopic analysis of plutonium.

<u>Relative Abundance</u> (wt %)	<u>Relative Standard</u> <u>Deviation (%)</u>
0.01-0.1	2.5-5
0.1-1	0.3-1.5
1-10	0.1-0.3
10-100	0.03-0.1

The accuracy is estimated to be 0.15% relative for abundances of 5-100%. Outside of this range, poorer accuracy must be expected.

5. Measurement Control Program. The measurement control program uses two types of checks to assure proper instrument performance.⁸ An accuracy check is made at least four times a week to verify that no changes have occurred in instrument response to working standards. Precision checks are made weekly for changes in instrument reproducibility and to detect nonrandom fluctuations in counting instruments that might indicate electronics problems. The data generated by these performance checks are transmitted directly to the main computer for checks against control limits. The control limits used are the 95% confidence-interval warning limit and the 99% confidence-interval action limit. If an instrument check exceeds either the

action limit or the warning limit, the computer does not allow the instrument to be used for accountability measurements until appropriate corrective action has been taken.

The type of performance check used depends on the instrument being tested. The accuracy check for balances requires measurement of two standard weights that fall within the normal operating range of the balance. A t-test compares the difference between the measured and standard values to ensure that the response is consistent with previous observations. Precision checks consist of replicate measurements of the standard weights used to estimate standard deviations for each weight level. These standard deviations are then compared with historical values based on prior data, using an F-test to monitor changes in balance reproducibility.

A t-test is also used to check counting instrument accuracy. The expected response of a plutonium standard is compared with the measured response. Precision checks consist of two different tests that use the same set of replicate measurements of a plutonium standard. The reduced chi-squared test is used to determine whether the counting instrument is behaving properly. The replicate data are tested for randomness using a mean-square successive-difference test that can detect long-term trends or rapid oscillations that might otherwise go unnoticed.

B. Accounting Strategies

In conventional materials accounting strategies, materials balance closure is obtained once each physical inventory from the algebraic sum of the measured inputs (positive) and outputs (negative) of the process during the balance period and the measured process inventories obtained from process shutdown and cleanout at the beginning and end of the balance period. The materials loss-detection sensitivity will

be related to process throughput and physical inventory frequency. Timely detection of nuclear materials loss is limited by the physical inventory frequency.

Materials accounting and control can be improved substantially if conventional materials balance accounting measures are augmented by dynamic materials accounting methods. Dynamic materials accounting allows frequent materials balance closures (hours to days) by combining measurements of all significant transfers and in-process inventory.* The frequency of materials measurement is governed by process logic and measurement capabilities.

Under dynamic materials accounting, a process materials balance area (MBA) is partitioned into discrete accounting envelopes or unit process accounting areas (UPAAs). A UPAA can include the entire MBA or portions of the MBA. The distinguishing feature of a UPAA is that materials balances are closed in near-real-time by measuring all inputs and outputs and by measuring or estimating in-process inventories.

In this study, the process operates on a one-shift basis. A product batch containing nominally 8 kg of plutonium oxide is produced every 5 working days. The amount of product is derived from the data base collected for the process simulation and may actually be as much as 10 kg. In practice, the period between product batches can be more than 5 days and is a function of demand. The process simulation assumes maximum demand.

In the identification of possible accounting strategies, the process is divided into three components: (1) the conversion process, (2) the final canning operation, and (3) the storage vault. Final canning and the vault are item control areas (ICAs), where control is by piece count and materials control measures.

*Defined here as all material in the process, including holdup.

The conversion process is a single MBA that can be partitioned into one or more UPAAs.

Three possible accounting strategies that could be applied to the process (Fig. 1) and the corresponding NDA and conventional measurements (Fig. 8) are described below. The UPAA structure for each accounting strategy is shown in Table VIII. The strategies are shown schematically in Figs. 9-11. The transfer measurements for each type of material encountered in the process are summarized in Table IX.

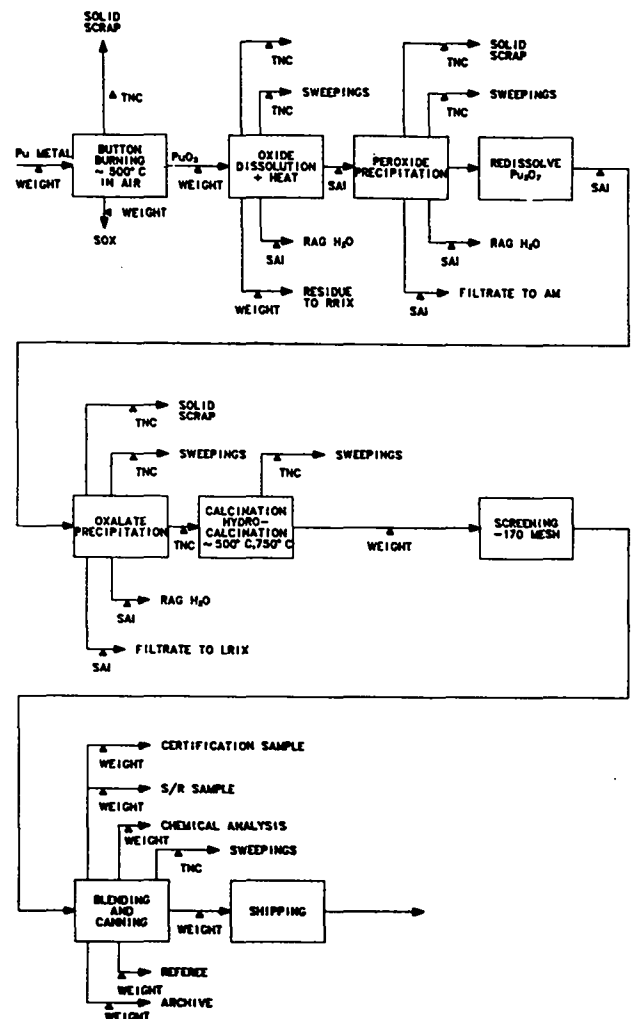


Fig. 8. Process measurement points. (Figure provided by Milton Haas).

TABLE VIII
ACCOUNTING STRATEGIES

Accounting Strategy	Button Oxidation	Oxide Dissolution	Peroxide Precipitation & Redissolution	Oxalate Precipitation	Calcination/ Hydrocalcination	Sieving, Gringing Blending & Canning
1	UPAA-123					
2	UPAA-1	UPAA-2				UPAA-3
3	UPAA-1	UPAA-2a	UPAA-2b	UPAA-2c	UPAA-2d	UPAA-3

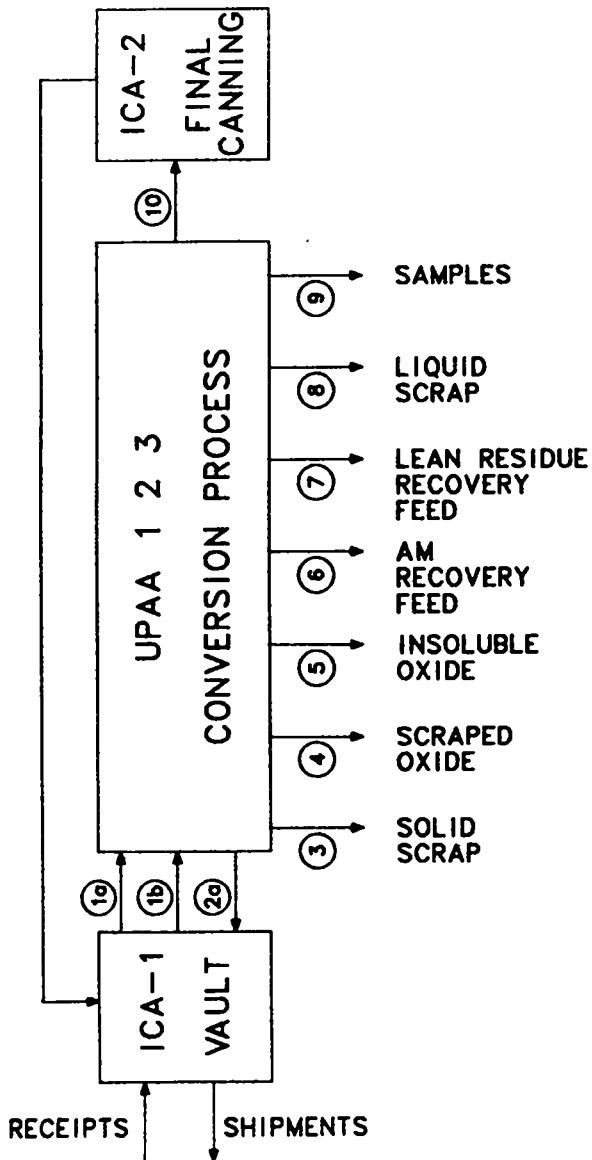


Fig. 9. Accounting strategy 1.

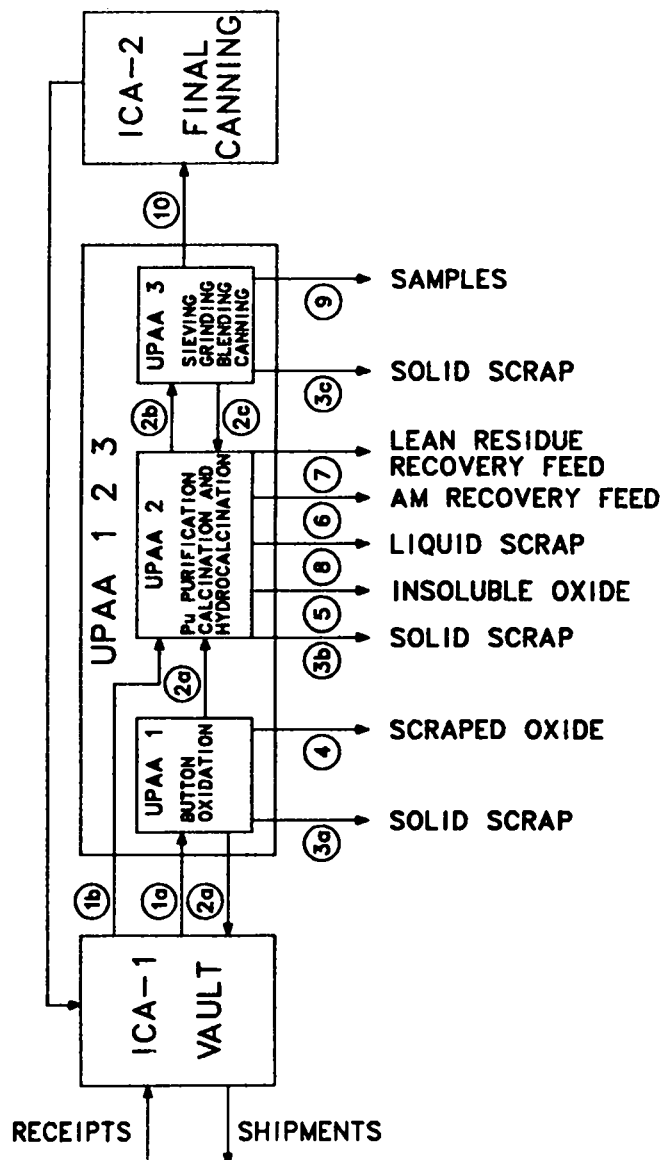


Fig. 10. Accounting strategy 2.

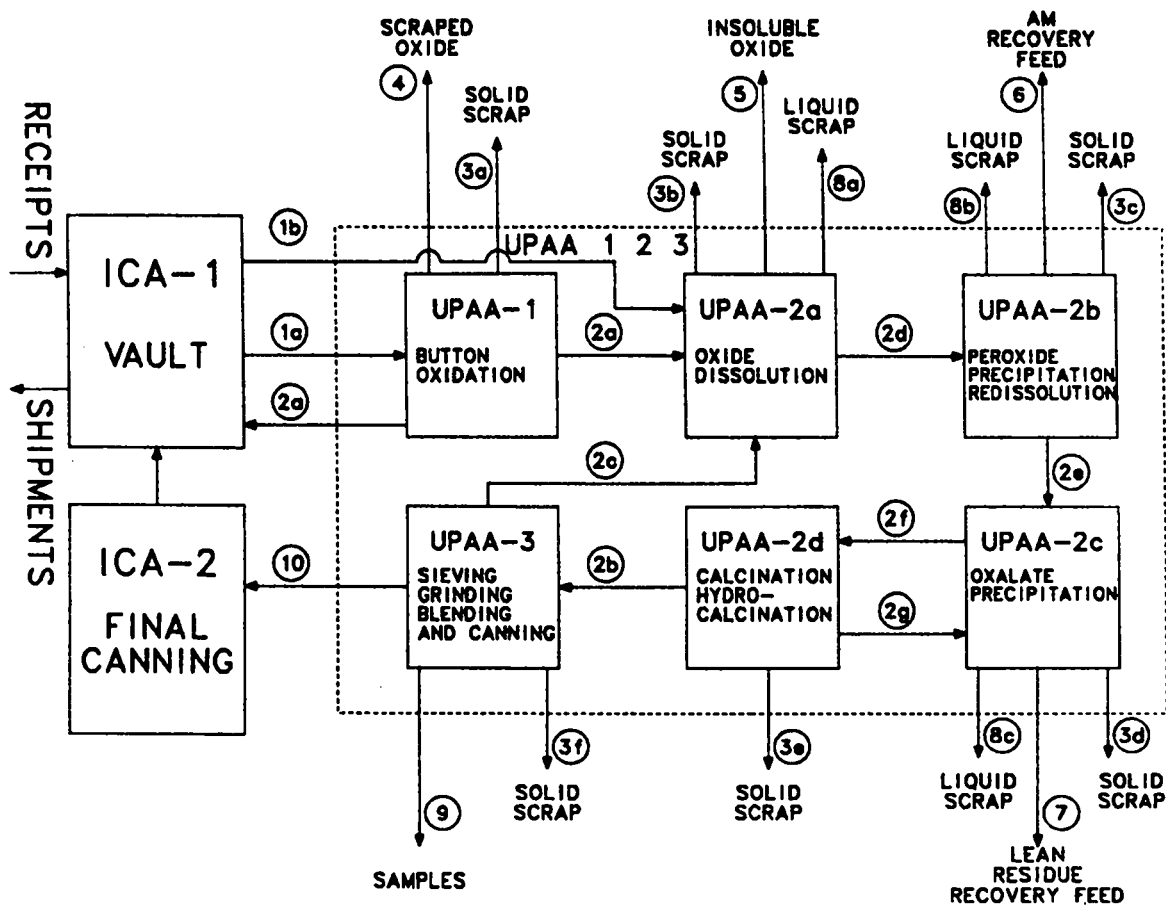


Fig. 11. Accounting strategy 3.

The three accounting strategies differ in their degree of complexity and the number of measurements required for accounting. Strategy 1 is the simplest, and strategy 3 is the most complex.

In accounting strategy 1, input into UPAA 123 from the vault, product output from the UPAA to final canning, and all the sidestreams leaving the UPAA are measured for accounting purposes. Batch residence time in UPAA 123 ranges from 8-13.25 days.

Strategy 2 adds transfer measurements between UPAA 1 and 2 and UPAA 2 and 3. In this strategy some of the sidestreams are individually identified and measured (e.g., streams 3a, 3b, and 3c). Approximate residence times are 1 day in UPAA 1,

5-7.25 days in UPAA 2, and 2-5 days in UPAA 3.

Strategy 3 divides UPAA 2 into four separate UPAA's. Transfers between all UPAA's are measured and all sidestreams are individually identified and measured. Approximate residence times are 2-3 days in UPAA 2a, 1 day in UPAA 2b, 1-2 days in UPAA 2c, and 1-1.25 days in UPAA 2d. Batch residence times for UPAA 1 and 3 are the same as in Strategy 2. The ranges of residence time in UPAA 2a, 2c, and 2d result from process variations (e.g., ROT dissolution time). In the case of UPAA 3, 4-5 batches from the calcination and hydrocalcination step are blended every fifth day prior to canning. One day for screening and grinding, 3 days in storage, and 1 day

TABLE IX
MATERIALS TRANSFER MEASUREMENTS

<u>Material Type</u>	<u>Stream No.</u>	<u>Measurement Technique</u>	<u>Technique</u>	<u>Uncertainty</u>
			<u>Random</u> (%, 1σ)	<u>Systematic</u> (%, 1σ)
Metal buttons	1a	Weight Assay factor	0.2-0.6 0.1	0.2-0.6 0.05
Solutions				
Low concentration liquid wastes	8(8a-8c)	SAI	25%	---
Am and LR recovery feeds	6 & 7	SAI	13%	---
Peroxide and oxalate precipitation feeds	2d & 2e	SAI Weight	1-5 0.2	0.24-0.7 0.6
Impure oxide				
Oxide dissolution feed	1b & 2a	Weight Assay factor	0.6 0.1	0.2 0.05
Scraped oxide	4	Weight Factor	0.6 0.6	0.2 ---
Insoluble oxide	5	Weight Factor	0.6 0.6	0.2 ---
Oxalate filter cake	2f	Double ring TNC	2.2	0.8
Pure oxide				
Coarse material and solid scrap	2c & 3f	TNC	2	2
Product	9 & 10	Weight Assay factor	0.6 0.1	0.2 0.05
Solid scrap & waste				
Scrap	3(3a-3e)	TNC	2-8	2
Waste		TNC	10-15	5-10

^aStream numbers as shown in Figs. 9-11.

for blending and canning yields a 5-day residence time. Similarly, the last batch will have a residence time of ~2 days. The screening and grinding step can be accomplished in <1 day, thus providing the ability to process 5 batches in 5 days.

Although the accounting strategies were discussed above in the context of a dynamic materials accounting system, they can be used in conjunction with shutdown and cleanout (physical inventory) as conventional accounting strategies, which is the practice of the Los Alamos Plutonium

Facility. The following discussion is concerned with the current practice at the Los Alamos Plutonium Facility.

Materials balances are closed semi-annually after shutdown and cleanout (physical inventory). More frequent physical inventories may be conducted if process data indicate a potential criticality problem. Strategy 2 was used prior to the availability of the SAI and double-ring TNC instruments. Strategy 3 is in use at the present time.

Accounting strategy 3 with its near-real-time measurements and the data processing and data base management capabilities of the PF/LASS provides the process operator and the responsible nuclear materials accountability officer with considerable timely information. For example, the accounting system provides near-real-time information on the book inventory for any UPAA, material in transit, and instrument status. The process supervisor can obtain, on demand, the book inventory for a particular UPAA essentially instantaneously.

The PF/LASS accounting system generates a book-inventory difference when material is transferred out of a UPAA. The difference is derived from the incoming material minus the related outgoing material, measured scrap, and waste removals. The inventory difference thus includes the contribution of the particular batch (or batches where blending is involved) to the UPAA holdup and unmeasured sidestreams. This book-inventory difference is referred to as material-in-process (MIP) at the Los Alamos Plutonium Facility. When an unmeasured sidestream such as accumulated scrap is measured, the accounting system generates a negative inventory difference that is algebraically added to the MIP for the UPAA. The cumulative sum* of the MIPs, therefore, can provide the process supervisor with an estimate of the holdup in the UPAA and can be used to indicate that cleanout may be necessary. Unusually large, single MIPs can suggest process and/or measurement problems.

Large cumulative sum MIPs or unusually large single MIPs can also suggest diversion. However, diversion can only be confirmed by verification of the MIPs, either by estimation of the in-process inventory by means that are independent of the data

*This cumulative sum is not currently provided automatically by PF/LASS but could be programmed into it.

used to generate the MIPs or by measurement (physical inventory) of the nuclear materials content of the UPAA. Physical inventory of a UPAA might require shutdown and cleanout. Currently, MIP data can only be evaluated by physical inventory.

Active memory storage capacity in PF/LASS is somewhat limited, and, therefore, the amount of historical data retained in readily accessible form is limited. Tracing of the course of a batch through a process (audit trail) on the PF/LASS computer would be impossible if processing of the batch started at some time prior to the earliest time in the current PF/LASS data base. However, the Los Alamos Safeguards System primary data base computer does not have this active storage capacity limit. A data base containing all the Plutonium Facility materials transfer data is available, and an automated audit trail procedure has been developed and demonstrated.¹⁷ This capability was of considerable value to this study.

Accounting strategy 3 as used at the Los Alamos Plutonium Facility possesses many of the features of a dynamic materials accounting system including near-real-time accounting. In essence, the accounting system is a dynamic book accounting system, but it cannot be considered a true dynamic materials accounting system in terms of the definition given previously because it does not have the capacity to measure or estimate the in-process inventory independently without shutdown and cleanout. Addition of such a capacity to the present system would obviously convert it to a dynamic materials accounting system and might lead to elimination of the semiannual process shutdown and cleanout or, at least, to a reduction of the frequency.

The information presented in this section could be used to develop a model of the measurement system and the measurement control system. This model could

then be used in conjunction with the process model to evaluate the proposed accounting strategies. This latter effort should compare the diversion-detection sensitivity of the current periodic physical dynamic book inventory system to that of the same system with in-process inventory verification.

V. RESULTS, CONCLUSIONS, AND FUTURE WORK

This study has resulted in the development of a process model that was used to evaluate process performance. The data used in the simulation were collected for the period October 1979 through January 1980. Simulation runs mimic the process within the data base and the model assumptions (e.g., 1 shift/day, 7 days/wk operation and maximum throughput). Provisions were made for a variety of scrap and waste streams that were maintained at zero or low nuclear materials levels in the simulation in keeping with the data base. The model structure is flexible and can be altered readily to include process and procedural modifications such as alternative final calcination steps, button-oxidation conditions, and equipment distribution (numbers of dissolvers, precipitators, etc.).

Conclusions based on the results of the process modeling and simulation are:

- The process model throughput is limited by the oxalate-precipitation step because of the additional 24-h filter-cake drying time that is modeled to occur for ~25% of the batches. Additional processing capacity or an alternative drying procedure would eliminate this limitation.
 - If the residence time in the oxalate-precipitation step were reduced to a maximum of 24 h, the model process throughput would be limited by the dissolver residence time of 2 to 3 days.
- The process operating on a 1-shift, 7 days/wk schedule has a throughput potential of ~815 kg plutonium/yr, barring equipment breakdown and assuming elimination of the semiannual physical inventories.
 - The production loss because of physical inventories is ~95 kg of plutonium/yr.
 - The process operating on a 1-shift, 5 day/wk basis has an annual throughput of 586 kg, which is in reasonable agreement with the design throughput of 600 kg/yr.

We recommend that future effort should include:

- investigation of the potential effects of process modifications using simulation techniques and the process model;
 - modeling of the existing measurement system;
 - examination of methods for measurement or estimation of in-process inventory that do not require shutdown and cleanout;
 - simulation of accountability measurements applied to simulated nuclear materials flows and inventories; and
 - evaluation of alternative measurement and accounting strategies from simulated materials balance data and, when possible, comparison of simulated data with actual process data.
- The results from the recommended work would provide:
- a basis for design of near-real-time accountability systems for both future and existing conversion and purification facilities, and
 - a verification of the modeling and simulation approach to the design and evaluation of dynamic accounting strategies with actual process data.

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