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Coordinated Safeguards for Materials Management in a Nitrate-to-Oxide Conversion Facility

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COORDINATED SAFEGUARDS
for
MATERIALS MANAGEMENT
in a
NITRATE-TO-OXIDE CONVERSION FACILITY

by

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ABSTRACT

The conceptual design of a materials management system for safeguarding special nuclear materials in a plutonium nitrate-to-oxide conversion facility is developed and evaluated. Dynamic material balances are drawn from information provided by nondestructive-analysis techniques, process-control instrumentation, and conventional chemical analyses augmented by process-monitoring devices. Powerful statistical methods, cast in the framework of decision analysis and applied to unit-process accounting areas, ensure adequate spatial and temporal quantification of possible diversion with minimal process disruption. Modeling and simulation techniques assist in evaluating the sensitivity of the system to various diversion schemes and in comparing safeguards strategies. Features that would improve the safeguardability of the conversion process are discussed.

EXECUTIVE SUMMARY

This report describes the third in a series of conceptual designs for advanced nuclear materials management systems for future fuel-cycle facilities. These conceptual designs are based on measurement and control technology that has been demonstrated or can be projected for the early 1980s. Their purpose is to define systems concepts, to develop methods for evaluating safeguards systems and the data they produce, and to stimulate further development of the facilities, processes, systems, and instrumentation needed to implement these concepts. When combined with the advanced physical protection elements identified in the companion Sandia Laboratories report, the concepts described here will provide a guide to effective safeguards for future industrial-scale plutonium nitrate-to-oxide conversion facilities.

The facility studied here could receive the product from the 5 tonne-per-day (TPD) nuclear fuel-reprocessing plant described in LA-6881 (Ref. 1) and convert it to plutonium-oxide feed material for the mixed-oxide fuel fabrication plant described in LA-6536 (Ref. 50). Under steady-state conditions, the conversion process effectively couples the chemical separations and fuel fabrication facilities previously studied and has enough overcapacity to make up for production transients and periods of decoupled operation. The materials management systems in all three facilities considered to date are compatible; they reinforce each other and could be readily combined to share the safeguards responsibilities in a reprocessing complex where the individual facility components would be collocated.

The pivotal role of the conversion process in safeguarding the whole nuclear fuel cycle against subnational diversion or as part of a national nuclear nonproliferation policy is

underscored by the results of this study. The conversion process is essential to large-scale commercial or military use of plutonium. It is the keystone of any fuel cycle that converts the plutonium-nitrate product of a Purex separations plant to plutonium-oxide feed material necessary for either power reactor fuel fabrication or weapons metal production. The conversion facility is unique in the civilian power economy because it invariably handles large amounts of concentrated, highly purified plutonium in a form that could be an attractive target for diversion or national misappropriation.

The utility and attractiveness of the material handled in conversion facilities have nominated them for special nonproliferation considerations in the so-called Bonded Crucial Facility (BCF) concept. In this concept, the crucial facility (the conversion plant) is expanded to include storage of the product and feed inventory for the adjacent chemical separations and fuel fabrication plants, respectively. The expanded complex can then provide continuous monitoring of the production and use of plutonium on an industry-wide or national scale. Depending on the particular application, the BCF could be operated under an umbrella of enhanced safeguards that could be extended to include multinational control.

Many of the features that make the conversion process attractive for diversion also make it more amenable to materials management using the concepts of unit process accounting and dynamic materials balancing previously developed for dynamic accountability systems. Low radiation levels and improved accessibility to the process facilitate the improved measurements necessary to implement these concepts.

The conversion process selected is based on a reference design provided by the Savannah River Laboratory. It involves the semicontinuous precipitation of plutonium (III) oxalate in four parallel process lines before drying and calcining the precipitate to a plutonium-oxide product that has the desired chemical and physical properties. The process is based on demonstrated technology, developed early in the weapons program at Los Alamos, and was selected for maximum ease of process control, product flexibility, and production scaling.

At maximum capacity (116 kg of plutonium/day) the design-basis conversion plant can accommodate the normal output of a 10-TPD Purex plant. Throughput is reduced by changing the shift structure and/or reducing the number of parallel precipitators without affecting the materials management structure.

The materials management and accounting system is designed to use demonstrated technology and is compatible with the two facilities previously studied. Optimization of the process for safeguards purposes was not undertaken; however, process modifications are suggested that would generally facilitate materials management in nitrate conversion facilities based on this process. The reference design favors production rather than safeguards and is not amenable to coprecipitation of uranium and plutonium. Studies of materials management for coseparation processes are under way in another joint Savannah River and Los Alamos study.

Two accounting strategies were devised for the materials management system described here; they involve treating each process line as a single unit or as two contiguous unit processes. In both strategies, dynamic material balances are drawn around the processing of each batch (∿2 kg of plutonium), and both strategies incorporate the <u>same</u> set of accountability measurements. Key measurement points are located at the feed solution receipt tanks (conventional volume measurement and on-line concentration measurement by absorption-edge densitometry) and at the product canister loading area (measurement by neutron counter or calorimeter). Concentration measurements require a companion determination of isotopic composition by gamma-ray or mass spectrometry. The strategies differ in that measurements of wet plutonium-oxalate precipitate in filter boats are treated as material transfers in the two-unit-process strategy and as part of the in-process inventory in the one-unit-process strategy. Pending development and demonstration of an improved measurement technique for wet plutonium precipitate, modeling and simulation studies using projected production data and realistic measurement parameters clearly showed that the single-unit-process strategy provides better sensitivity to both short-term and long-term, low-level diversion.

The two strategies are, in fact, complementary in that the same measurement data are combined to form dynamic material balances in two ways. Diversion can be better localized using the first accounting strategy because it contains two unit processes. In the second strategy the wet boat measurements are combined into the in-process inventory (the boats constitute the furnace in-process inventory); therefore, the inaccuracy of the wet boat measurements tends to cancel resulting in an improved diversion sensitivity.

The diversion sensitivity of the one-unit-process accounting strategy is as follows.

DIVERSION SENSITIVITY[a] IN THE CONVERSION PROCESS

Detection Time	Average Diversion per Batch (kg Pu)	Total at Time of Detection (kg Pu)
1 batch (1.35 h)	0.13	0.13
1 day	0.03	0.63
1 week	0.01	1.24
1 month	0.005	2.65

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[a] As determined for a single process line in the second accounting strategy in accordance with ERDAM Appendix 7401-C, "Nuclear Materials Management and Safeguards System Handbook." See Sec. IV-C.1 for the measurement strategies for selected cases.

These sensitivities were determined from a series of computer-generated process histories using decision-analysis algorithms developed to handle large quantities of materials measurement data in near-real-time. They should be compared to the value required for conventional inventory-based systems, which is a 33-kg limit of error for material balances (LEMUF) determined every two months for the entire process area.

The sensitivities reported are for the materials accountability part of a stand-alone safeguards system for the conversion process. Total installed cost is estimated to be less than $6 million and the annual operating cost is expected to be somewhat less than half that. Mean time between failure of the system should be more than three months, and mean time to repair (or replace) a vital component is estimated to be approximately 5 h. Costs would be significantly less if the conversion process dynamic accountability system were incorporated into the overall safeguards system of a larger collocated nuclear complex of the type that has been suggested for both domestic and international commercial reprocessing facilities.

Safeguards effectiveness evaluations of complex fuel-cycle facilities require intimate knowledge of the facility, its processes, and its operational details. Superimposed on these requirements are the unique characteristics of a dynamic materials management system, which subdivides the process both in time and space into individual unit process accounting areas. These considerations make it necessary to analyze large quantities of process and materials balance data efficiently in a manner amenable only to computerized data handling. Such an analysis has been done in this study both by modeling and simulating plant operations and materials flows and by computerizing the routine aspects of the decision process. In this way, the safeguards officer is protected from a literal deluge of data from normal plant operations, which an informed divertor might use to obscure abnormal operations. The development and standardization of methods for decision analysis as well as effectiveness evaluation are increasingly important components of these studies and have helped immensely in defining areas where process and measurement improvements are needed.

The importance of the nitrate conversion process in closing the nuclear fuel cycle and as a nonproliferation aid is discussed in Chap. I. The advantages of the selected process and its competitors are reviewed and compared. Other processes amenable to coprecipitation and coseparation are identified for future work.

Chapter II contains a detailed description of the reference process developed by the Savannah River Laboratory. Physical features, materials flows, and process flow sheets are provided along with a description of the normal operating procedures, the chemistry, and the reagents required.

The safeguards system design presented in Chap. III includes a brief description of the key design concepts of real-time materials control, unit process accounting, dynamic material balances, and graded safeguards. Near-real-time instrumentation for the process is identified, and the reliability, cost, and staffing requirements for the reference safeguards system are estimated.

Chapter IV treats the general problem of evaluating the effectiveness of any proposed safeguards system. It describes the nitrate-to-oxide conversion process simulation NOCSIM, the measurement simulation MEASIM, and the dynamic materials accounting strategies. It describes the safeguards decision process and the values of decision-analysis tools such as the Shewhart chart, the cusum chart, the Kalman filter, and the Wilcoxon rank-sum test. A versatile decision-analysis methodology, based on the DECANAL computer code and an innovative alarm-sequence chart, is described. Examples of all these approaches using process data from the conversion facility are presented, and their relative effectiveness is discussed.

Results, recommendations, and conclusions are summarized in Chap. V. Methodology, key measurement points, and measurement and process features are reviewed, and suggestions are made for their improvement.

Appendix A is a detailed description of the dynamic model used to simulate the conversion process. Appendix B reviews the status of measurement instrumentation and techniques for safeguarding the conversion process; both conventional and nondestructive assay (NDA) techniques are discussed. Appendix C describes the materials accounting equations used to model, simulate, and evaluate the dynamic accountability system.

The main conclusions and recommendations are as follows.

- Strategic quantities of SNM can be safeguarded in a high-throughput nitrate-to-oxide conversion facility at reasonable cost with minimal process disruption. Field testing and evaluation of safeguards system components are required to validate and refine the system design.
- The conversion process is the keystone to safeguarding the back end of the fuel cycle. Studies of these and other processes must continue to permit selecting the most safeguardable and proliferation-resistant process.
- Further studies must investigate the interaction of dynamic materials accounting, process control, and materials containment and surveillance.
- Instruments for use at key measurement points must be well characterized and field tested. Testing of absorption-edge densitometers, neutron well counters, gamma spectrometers, and calorimeters is required.
- Techniques for measuring plutonium-oxalate slurry in precipitators and filter boats should be demonstrated and evaluated.
- For each type of conversion process, arrangements of unit processes, process equipment, and operating procedures must be evaluated to exploit any inherent safeguards advantages.

I. REVIEW OF NITRATE-TO-OXIDE CONVERSION PROCESSES

A. An Introduction to Plutonium Conversion

Nitrate conversion processes are essential to commercial or military use of plutonium, either pure or coprocessed with a uranium diluent. The normal product of any spent-fuel separations plant based on the Purex process or any of its variants[1] is a concentrated aqueous solution of plutonium nitrate, $Pu(NO_3)_4$. Industrial-scale use of plutonium is invariably restricted to the metal or oxide, so efficient large-scale processes are necessary for converting the nitrate solution to the oxide form, either for direct use or as an intermediate to metal production.

Traditionally, the conversion (or reconversion) process has been treated as the initial step of a fuel-fabrication or metal-reduction sequence, starting with the stored nitrate product of the separations plant. Various end uses require properties that differ greatly and in fact may conflict, leading to a profusion of conversion processes intended to optimize the properties required of the final product. Regulatory changes effective in early 1978,[2] prohibit transportation of plutonium-nitrate solutions and require that conversion become the final step in the separations process, rather than the initial step in fabrication.

This change introduces important changes in the objectives of the conversion process and the properties desired of the oxide product. Although high purity, including freedom from decay products, remains a goal in the oxide product, the decoupling of the conversion process from the end use of the product makes it impossible to provide the required purity, oxide powder morphology, ceramic activity, and chemical reactivity simultaneously with a single product-finishing step, unless the separations plant is coupled directly and immediately to a specific fabrication sequence.

Important reasons for storing and shipping plutonium-nitrate solutions were for convenience in handling, blending, and analysis. This mode of operation also facilitated selection of a conversion process most amenable to the end use and kept the plutonium in a convenient form for purification from trace contaminations due to storage and decay immediately before, or during, conversion.

Future major suppliers of plutonium or plutonium-uranium blends may have to convert, redissolve, and reconvert their product to meet both transportation requirements and product specifications. The consequence of delays between purification and use, and the conflicting requirements of stability for shipping versus the necessary chemical and ceramic reactivity of the fabrication feed material, are likely to require redissolution and reblending of the oxide product at its destination. This step might be coupled with repurification of the nitrate solution before its reconversion to a customized fabrication feed material.

This consideration has had an important effect on our study of a safeguarded conversion process. First we have chosen to treat the conversion process separately, as a unit module, to permit maximum flexibility and to allow the results to be applied either to the product of a Purex separations plant or as part of a wet head end for a fuel-fabrication facility. Second, we have reviewed a number of candidate conversion processes and have selected one that most flexibly provides a purified, custom oxide product, consistent with demonstrated industrial feasibility and operational tractability.

The process chosen, plutonium (III)-oxalate precipitation, reliably produces a high yield of purified, tractable precipitate, over a wide range of process variables. Powder morphology and chemical and ceramic reactivity can be controlled readily by combinations of precipitation, digestion, and calcining conditions to produce a customized oxide powder suitable for further reaction, transportation, blending, or sintering to a final ceramic product.

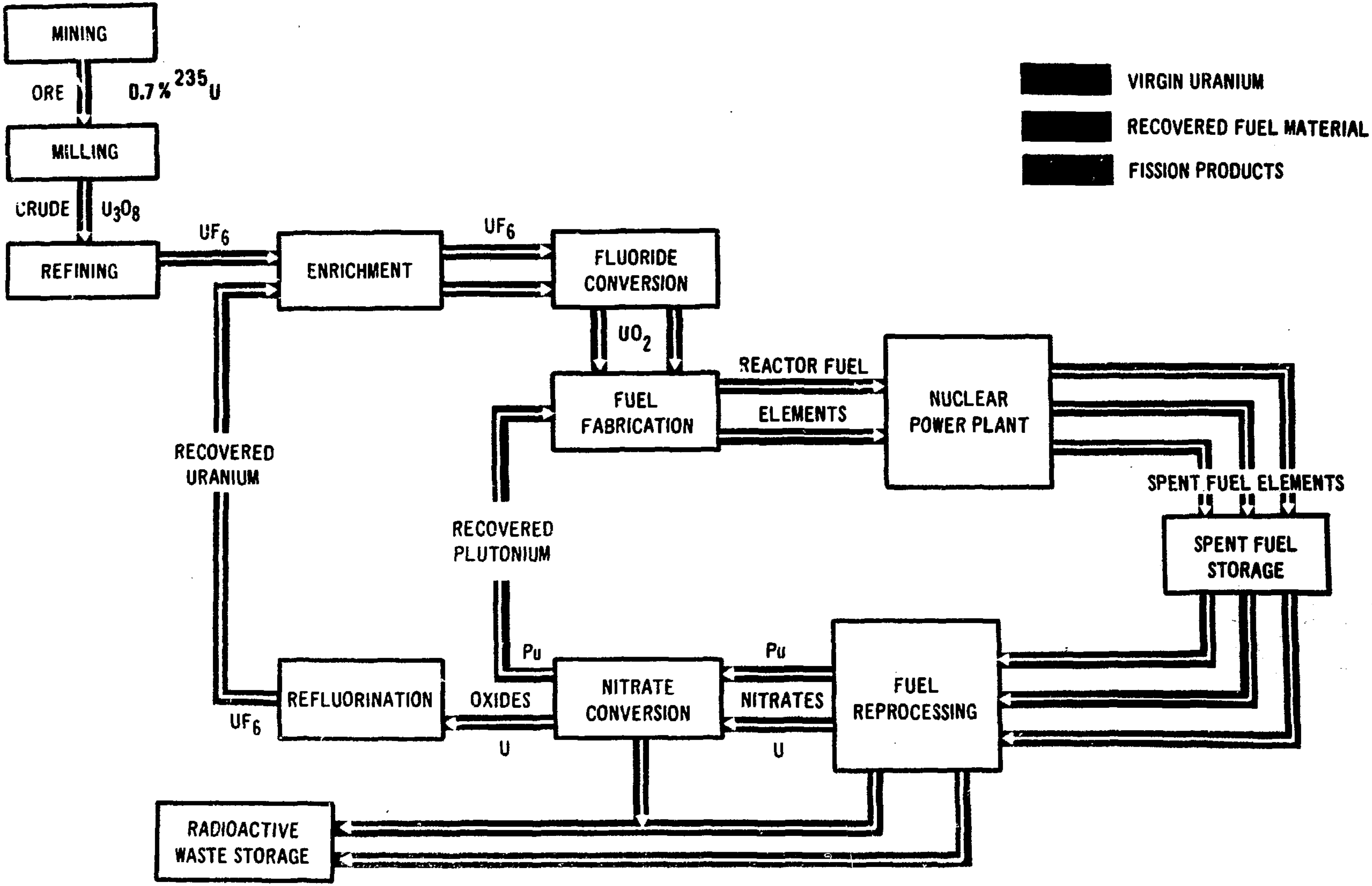
The basic process has been demonstrated and improved[3] at the LASL plutonium-recovery facility over the past two decades. Early concerns with corrosion in large-scale conversions have been eliminated by changing the reductant from hydriodic acid (HI) to hydroxylamine nitrate ($NH_2OH\ HNO_3$).

B. Safeguarding the Conversion Process

Conventional conversion processes provide a unique safeguards challenge. Unlike the situation that exists in other elements of the fuel cycle; input, in-process, and product materials are all attractive, high-purity, concentrated targets for diversion, unhampered by high-level radiation, heavy shielding barriers, or impractically low concentration levels. Also, the conversion process naturally tends to become the process buffer between the loosely coupled functions of plutonium separation (chemical reprocessing) and plutonium use (fuel fabrication) that characterize the commercial fuel cycle (see Fig. I-1). Its buffer function causes the conversion process to be bracketed physically by significant inventories of extremely attractive feed and product materials that represent the greatest diversion potential in any domestic fuel cycle and a serious nuclear proliferation risk in the nuclear fuel cycle of any nonweapons state.

The pivotal role of the conversion facility in a safeguarded fuel cycle suggests that any enhanced safeguards or nonproliferation strategy first be applied directly to the conversion plant and then expanded to include the adjacent functions of separation (or coseparation) and fuel fabrication, starting with the critical areas of product and feed storage and inventory control. This could be done best in future facilities by expanding the conversion facility to include product storage for the separations plant, solution blending or early dilution if plutonium partitioning is used, custom blending of mixed-oxide powders, coconversion, and feed storage for the fuel-fabrication plant. Colocation of these crucial functions under a single controlling

Fig. I-1. Power reactor nuclear-fuel cycle.



authority in a facility inside or contiguous to the separations plant has been suggested in the "Bonded Crucial Facility" (BCF) concept proposed as a nonproliferation strategy for foreign fuel-cycle facilities[4] (Fig. I-2). In this way, the safeguards controlling authority could monitor and verify production and consumption rates and could maintain cognizance of the disposition of all fissile products produced by the complex, thus ensuring that no significant quantities of undiluted plutonium could leave the complex undetected.

The conversion process selected for this study is intended to be compatible with the reference facility chosen for the companion study[1] of a fuel-reprocessing plant that produces pure plutonium-nitrate. Therefore, the study is not applicable to conversion of a mixed uranium-plutonium or coprocessed product. Any plutonium dilution in the process described must be by powder blending or subsequent reconversion using one of the appropriate processes described in the following section. Of these, only the Coprecal and the sol-gel processes, and possibly direct denitration, have been demonstrated to a degree comparable to the process chosen. The methodology and concepts developed here should be extended to the coprocesses as well, if they are to be considered credible safeguards alternatives.

C. Conversion Processes

A conversion process must meet several stringent technical requirements. The product must have such purity, particle size, and morphology that it can be blended with UO_2 and sintered to provide a homogeneous mixture that can be pelletized as a reactor fuel. The pellet density for reactor fuel is critical because it determines the thermal conductivity. Thermal conductivity, in turn, controls such parameters as fuel melting, fission product migration, plutonium and uranium redistribution, and reactor kinetics.

Peroxide precipitation, plutonium (III) and (IV) oxalate precipitation, direct denitration, the sol-gel process, and the Coprecal process all have been considered as possible methods

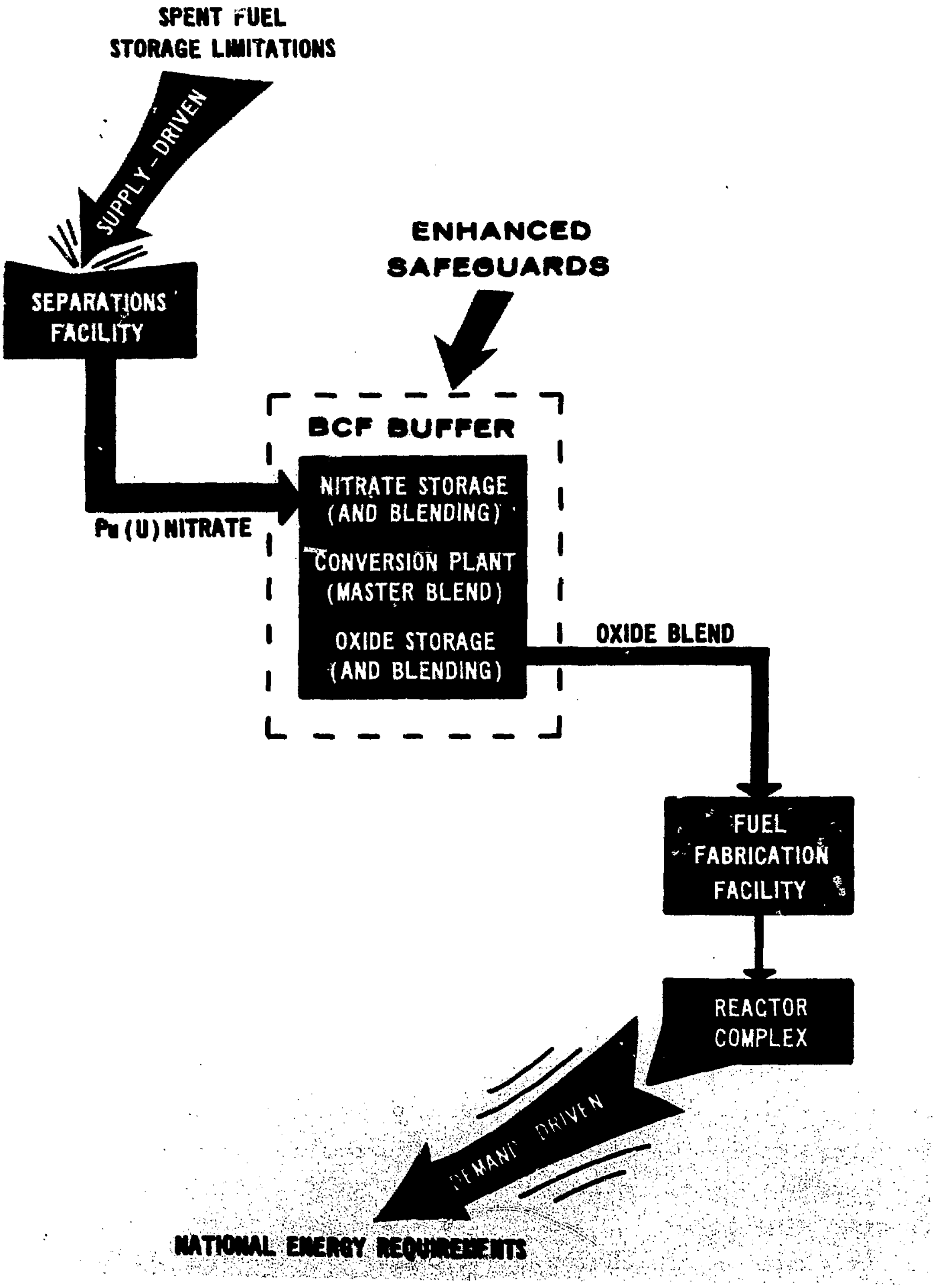


Fig. I-2. The bonded crucial facility concept.

for preparation of reactor-grade PuO_2 or $(U,Pu)O_2$. Most of these methods were developed originally for PuO_2 separation and subsequent fluorination before reduction to the metal; however, fuel-product requirements may differ from those where the oxide is only an intermediary in metal preparation. Each of these processes, studied in detail for both weapons and reactor applications, is described below.

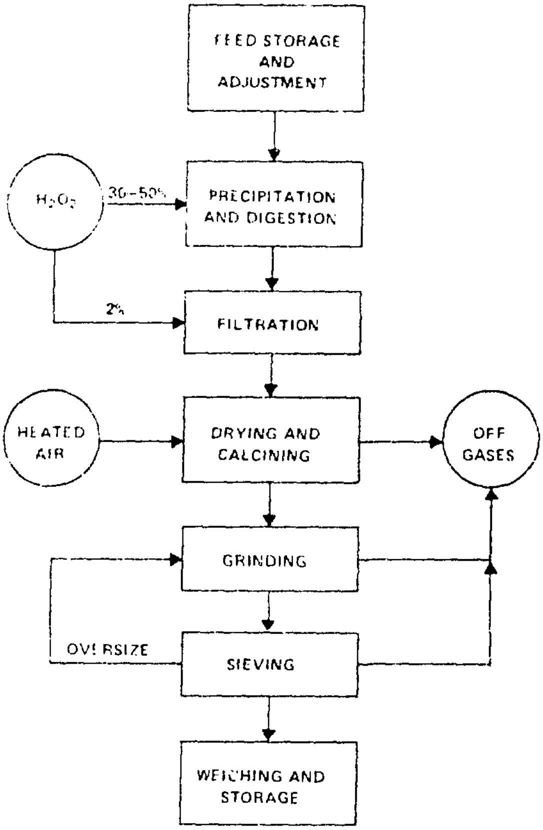


Fig. I-3. Process flowsheet for peroxide precipitation.

1. Peroxide Precipitation. Plutonium peroxide can be precipitated from feed solutions containing 10-100 g/L of plutonium and 1.5 to 6 M in nitric acid (HNO_3), but the optimum acidity appears to be 3-5 M.[5] The peroxide precipitation process is described in Fig. I-3. The process equations are

$$Pu^{4+} + 2H_2O_2 \rightarrow PuO_4(s) + 4H^+ \qquad (I-1)$$

$$PuO_4(s) \xrightarrow{500^\circ C} PuO_2(s) + O_2(g) \quad . \qquad (I-2)$$

Valence adjustment before precipitation is unnecessary because Pu^{3+} and Pu^{6+} both are converted to Pu^{4+} in the presence of peroxide. However, Pu^{6+} reduction is slow, and if concentrations of hexavalent plutonium are high the digestion time must be increased to prevent excessive plutonium loss in the filtrate. High concentrations of elements such as iron that catalyze peroxide decomposition must be avoided. These not only lead to incomplete plutonium precipitation but could cause explosive peroxide decomposition. The precipitation rate can be increased, and the particle size improved, by adding small amounts of sulfuric acid to the solution.

Acidity and temperature must be adjusted before adding peroxide (H_2O_2) to form a filterable precipitate.[5] The acidity should be >2 M to prevent colloid formation and <6 M to prevent precipitate dissolution. The temperature should be <15°C to suppress peroxide decomposition. Addition rate, stirring, and temperature must be controlled. After precipitation, excess peroxide can be destroyed by heating.

The precipitate composition can vary fairly widely, depending on precipitation conditions. The precipitate can be hexagonal or cubic, again depending on precipitation conditions. The hexagonal form is desired to give a filterable product. The cubic form, which precipitates at acid concentrations <2 M, tends to form as a colloid, causing excessive product losses on filtration.

A plutonium-peroxide precipitation process, developed at LASL for plutonium metal production, is used in recycle operations and as a purification step in producing high-quality PuO_2.[6] The peroxide is redissolved, however, and is not converted directly to oxide. Peroxide precipitation has been used at Rocky Flats as both a batch and a continuous process to recover plutonium from recycle lines.[7] Rocky Flats plans to use peroxide precipitation and filtration in its new recovery facilities, in which filter boats form the bottom of the precipitation vessels. Plutonium-peroxide precipitation also was used in producing plutonium metal at the Savannah River Plant (SRP) from 1954 to 1959.[8] Plutonium losses in the filtrate there averaged 0.3%. Higher losses, 2-8%, were reported at Rocky Flats. The filtrate, however, can be recycled to minimize losses.

The bulk density of PuO_2 formed by calcining the peroxide filter cake at 240°C was 3.5 g/cm^3.[8] After calcining at

1000°C, the density increased to 4.9 g/cm^3, which is still low. Sintering the oxide for 30 min at 600°C produced a low specific surface area of 9 m^2/g.

Peroxide precipitation is the most effective of the three precipitation processes for decontaminating plutonium from other cations. However, the initial feed for the conversion plant may be pure enough so that this additional purification is unnecessary. Also, recycling is simplified because H_2O_2 is the only reagent added, and it is readily destroyed by heating.

The major disadvantage of the peroxide method is the potential damage from sudden, explosive decomposition of peroxides, which releases large amounts of energy and produces large quantities of steam and oxygen. The heat produced can trigger further decomposition. Elements such as iron and copper catalyze the reaction. Large vent lines leading to catch tanks were used at SRP to handle these occasional explosive decompositions.

Although use of peroxide precipitation with sufficient precautions has been effective in past nuclear reprocessing, there are no proposals for its use in a commercial conversion facility. This is undoubtedly due to the potential consequences of an explosion during processing.

2. <u>Plutonium (IV) Oxalate</u>. Plutonium (IV) oxalate, $Pu(C_2O_4)_2 \cdot 6H_2O$, can be precipitated at plutonium concentrations of 1-300 g/L.

Conversion by the plutonium (IV) oxalate method using hydroxylamine as the reductant is shown in Fig. I-4. The reactions are

$$2PuO_2^{2+} + 4H^+ + 2NH_2OH \cdot HNO_3 \rightarrow 2Pu^{4+} + 5H_2O + 2HNO_3 + 2NO_x(g) \quad , \qquad (I-3)$$

$$Pu^{4+} + 2C_2O_4^{2-} + 6H_2O \rightarrow Pu(C_2O_4)_2 \cdot 6H_2O(s) \quad , \qquad (I-4)$$

$$Pu(C_2O_4)_2\cdot 6H_2O(s) \xrightarrow[\text{air}]{500°C} PuO_2(s)$$

$$+\ 2CO(g) + 2CO_2(g) + 6H_2O(g) \quad . \qquad (I\text{-}5)$$

The plutonium feed solution is contacted with enough hydroxylamine nitrate to ensure that all plutonium is in the Pu^{4+} state, and the acidity is adjusted to ∿3 M. Filterable oxalates are produced from solutions kept at 50-60°C. At acidities <2 M or temperatures <50°C, the precipitate generally is too fine to filter. At acidities >4 M or temperatures >60°C, it tends to be gelatinous and hard to handle, and the solubility increases. However, in the Allied-General Nuclear Services (AGNS) design, a rotating drum filter promotes efficient filtering of fines produced by room-temperature precipitation.[9,10]

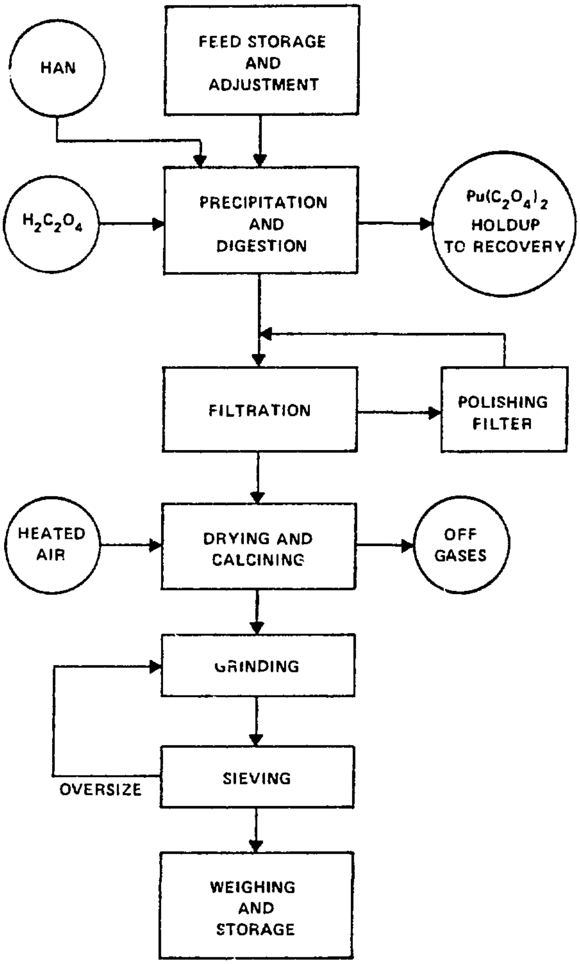


Fig. I-4. Process flowsheet for Pu(IV) oxalate precipitation.

Plutonium valence also can be adjusted using H_2O_2.[11] The peroxide is added before or during addition of oxalic acid, the rate being governed by the extent of foaming.

Advantages of the plutonium (IV) oxalate method include the stability of the solids and solutions and the relatively high decontamination levels. Plutonium (IV) oxalate precipitation has been well developed for both batch and continuous plutonium metal processing at Hanford.[11,12] Plutonium losses to the filtrate, which are relatively large, can be minimized by recycling and recovery.

Disadvantages include the need for careful control of processing parameters. Successful precipitation and subsequent filtration of plutonium (IV) oxalate at LASL required stringent control of the mixing rate, temperature, and acid concentration.[13] The number of reagents and the recycle streams, as with Pu^{3+}, are large. If calcination is incomplete, carbon impurity remains in the product.

The plutonium (IV) oxalate method was chosen for the AGNS facility primarily because of experience at Hanford and Idaho Falls and the data available on PuO_2 formed by calcining the plutonium (IV) oxalate.[9] The AGNS design is flexible, and a reduction step could be added before precipitation to convert to the plutonium (III) method.

3. <u>Plutonium (III) Oxalate</u>. Plutonium (III) oxalate, $Pu_2(C_2O_4)_3 \cdot 10H_2O$, can be precipitated from solutions containing >1 g/L of plutonium and <4 $\underline{M}$ in HNO_3.

The plutonium (III) oxalate process using ascorbic acid as a reductant is shown in Fig. I-5. The reactions are

$$2Pu^{4+} + C_6H_8O_6 \rightarrow 2Pu^{3+} + C_6H_6O_6 + 2H^+ \quad , \qquad (I-6)$$

$$10H_2O(l) + 2Pu^{3+} + 3C_2O_4^{2-} \rightarrow Pu_2(C_2O_4)_3 \cdot 10H_2O(s) \quad , \qquad (I-7)$$

$$Pu_2(C_2O_4)_3 \cdot 10H_2O(s) \xrightarrow{125°C} Pu_2(C_2O_4)_3 \cdot 2H_2O(s) + 8H_2O(g) \quad , \qquad (I-8)$$

$$Pu_2(C_2O_4)_3 \cdot 2H_2O(s) + 2O_2 \xrightarrow[air]{650°C} 2PuO_2(s) + 6CO_2(g) + 2H_2O(g) \quad . \qquad (I-9)$$

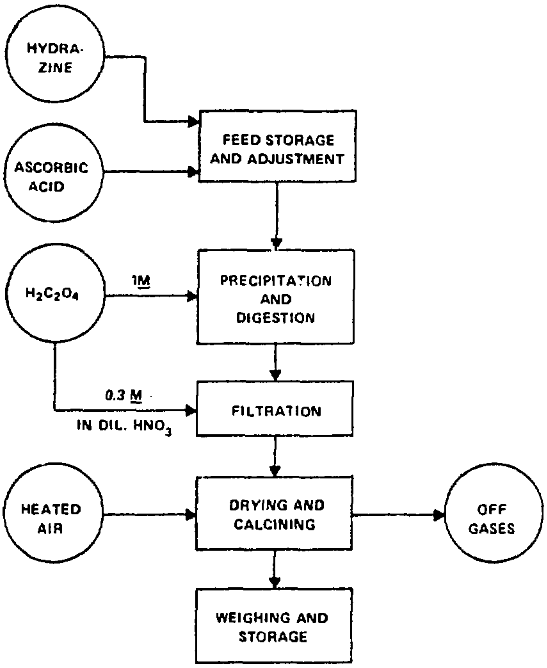


Fig. I-5. Process flowsheet for Pu(III) oxallate precipitation

Initial studies on precipitation of trivalent plutonium with oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) used HI as a reductant, leading to severe equipment corrosion. More recent work has used ascorbic acid with hydrazine and hydroxylamine with sulfamic acid as reductants, and interest in the process has revived. After plutonium reduction, oxalic acid is added to produce a precipitate that settles rapidly and can be filtered easily. Precipitation conditions such as the rate of oxalate addition and temperature are not critical for the Pu^{3+} process. Plutonium losses to the filtrate are low, and most impurities are removed. The precipitate can be washed, heated in a flow of dry air to remove most of the water, and then calcined in air to form oxide. The precipitate thus formed is coarser and settles and filters faster than that from the Pu^{4+} process.

Plutonium (III) oxalate precipitation, followed by calcination and dissolution, has been used to concentrate solvent-extraction product solutions.[14] At LASL, plutonium is dissolved, then precipitated as plutonium (III) oxalate in converting plutonium metal to oxide for fast-reactor fuel studies.[15] The oxide formed by calcining this precipitate has been used in test mixed-oxide fuel elements without further calcining or sintering. The SRP reports successful plant-scale use of the plutonium (III) oxalate process in both batch and semicontinuous modes.[16] The sizes of individual particles and agglomerates of the product PuO_2 are changed by changing the rate of precipitant mixing with the feed solution, altering concentrations, and regulating the temperature.

SRL and SRP chose the plutonium (III) oxalate process for conceptual design studies (see Chap. II).[16] It involves relatively simple, easy to maintain equipment similar to that used in producing plutonium metal. The precipitate is filterable, and particle size can be varied.

4. Direct Denitration. In direct denitration, the feed solution is evaporated to dryness. No reagents are added, and only gases are formed during drying and calcining. The general process is shown in Fig. I-6. The reactions are

$$Pu^{4+} + 4NO_3^- + H_2O(l) \rightarrow Pu(NO_3)_4(s) + H_2O(g) \quad , \qquad (I\text{-}10)$$

$$Pu(NO_3)_4(s) \xrightarrow{400^\circ C} PuO_2(s) + 0.7\ NO(g)$$

$$+ 3.3\ NO_2(g) + 1.3\ O_2(g) \quad . \qquad (I\text{-}11)$$

The equipment is simple and should be relatively easy to operate and maintain remotely. Fluidized-bed calcination, continuous calcination in a screw calciner, and batch processing all have been proposed. Denitration of $Pu(NO_3)_4$ or mixtures of uranyl nitrate and plutonium nitrate in a fluidized bed at 375°C yielded a product that could be processed into fuel elements,[17-19] although particle growth was a problem unless a jet grinder was used. The uranium-plutonium mixtures were homogeneous for both 2 and 20% PuO_2 products. Later work indicates difficulty with nozzle plugging and in obtaining a reactive oxide.[18] Production experience in denitrating to UO_3 indicates that particle size could be affected by temperature, thermal shocking, sulfate content, and jet grinding.[19]

Rocky Flats has recommended fluidized-bed direct denitration as the primary process for converting $Pu(NO_3)_4$ to oxide.[20,21] The selection was based on ratings and weighting factors assigned to a series of criteria for the processes studied.[20,21] The study indicated that direct denitration processes for conversion are best, precipitation methods are second, and the sol-gel process is third. However, differences between ratings were not large, and rating values and weighting factors were subjective.

In the Rocky Flats denitration process, feed solution is pumped to an evaporator for volume reduction, then transferred to a reactor for calcination in a fluidized column at 375°C. The product is screened and packaged. The Rocky Flats proposal will be tested during the next several years with an experimental denitrator.[22]

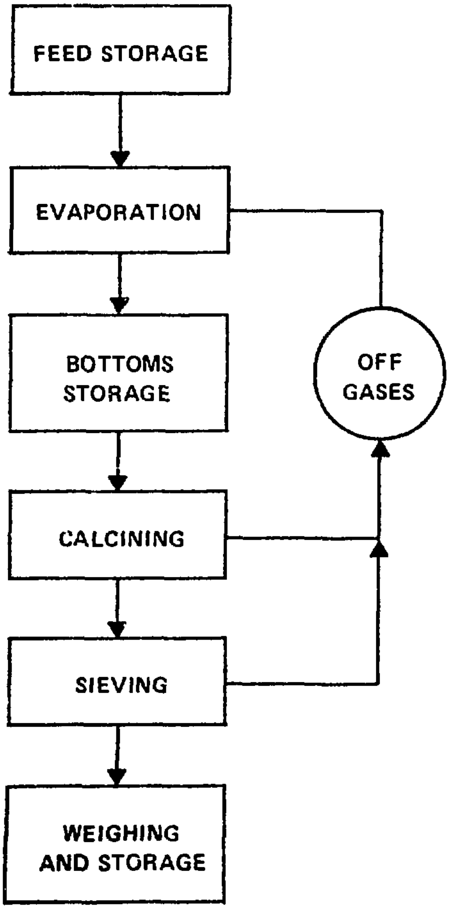


Fig. I-6. Process flowsheet for direct denitration.

A horizontal screw calciner operated at 400-450°C has been designed to convert plutonium nitrate to oxide.[23] It was found to be superior to an agitated bed or a vertical calciner in both operating reliability and oxide product characteristics.

Although the process has not been proved by actual production experience, it shows enough promise that EXXON Nuclear Company has proposed using it for conversion.[24] Their system is designed to convert 320 kg of plutonium per day to PuO_2 in four horizontal-trough screw calciners. Calcination temperature would be kept at 400-450°C. The oxide product, containing ~0.1 wt% moisture, would be blended, stored, and shipped to the fuel fabrication facility. Off-specification product, sweepings, etc., would be dissolved in HNO_3 containing ceric ion as a catalyst and recycled to the plutonium-purification cycle.

5. <u>The Sol-Gel Process</u>. The sol-gel process, designed to produce dense microspheres of oxide for reactor fuel fabrication, consists of three steps. The sol step produces a colloidal polymer of tetravalent plutonium that can be kept in suspension for extended periods. The gel step produces beads by removing water from the sol, generally using an organic liquid such as 2-ethyl-1-hexanol. In the third step, the beads are calcined to produce a high-density, uniform product.

Figure I-7 shows the process. The polymer is evaporated and resuspended as a sol solution, then dried at 300°C to form PuO_2 microspheres.[25] The reactions are

$$3Pu(NO_3)_4 + 2H_2O \xrightarrow{\text{n-hexanol}} 2Pu(NO_3)_3 + PuO_3(NO_3)_2 + 4HNO_3 \ , \qquad \text{(I-12)}$$

$$2Pu(NO_3)_3 + PuO_2(NO_3)_2 \xrightarrow[4H_2]{\text{n-hexanol}} + 3PuO_2 \cdot H_2O \text{ (polymer)} + 8HNO_3 \ , \qquad \text{(I-13)}$$

$$\text{Polymer} + \text{Heat} \rightarrow PuO_2 \text{ (Sol)} \ , \qquad \text{(I-14)}$$

$$PuO_2 \text{ (Sol)} \xrightarrow{\text{2-ethyl-1-hexanol}} PuO_2 \text{ (gel)} \ , \qquad \text{(I-15)}$$

$$PuO_2 \cdot H_2O(s) \xrightarrow{300°C} PuO_2(s) + H_2O(g) \ . \qquad \text{(I-16)}$$

Final calcining is at 1000-1200°C.

The operations produce few sidestreams, and these can be rerouted to the main process line. The process has been developed and used at Oak Ridge as well as at several foreign laboratories, but the product has not been characterized well enough for use as feed in a fuel fabrication facility. The process is fairly complex, has elaborate equipment needs, and requires testing in a pilot-scale plant before being considered seriously for full-scale production.

Three basic means of sol production have been investigated. In a method developed at the Oak Ridge National Laboratory (ORNL)[25,26] and shown in Fig. I-7, the sol is prepared by extracting HNO_3 into n-hexanol.[26] In another procedure, also developed at Oak Ridge, the sol is prepared by neutralizing HNO_3 with NH_4OH.[27] A third procedure uses long chain aliphatic amines as ion-exchange extractors for HNO_3.[28] In all three methods, process parameters must be controlled to reduce the NO_3^-/Pu ratio to near-unity. The procedure that uses aliphatic amines probably is adaptable most readily to coprocessing because UO_2^{2+} is reduced to U^{4+} during denitration without addition of a reductant. However, for preparing PuO_2 the n-hexanol procedure provides for better aqueous-organic

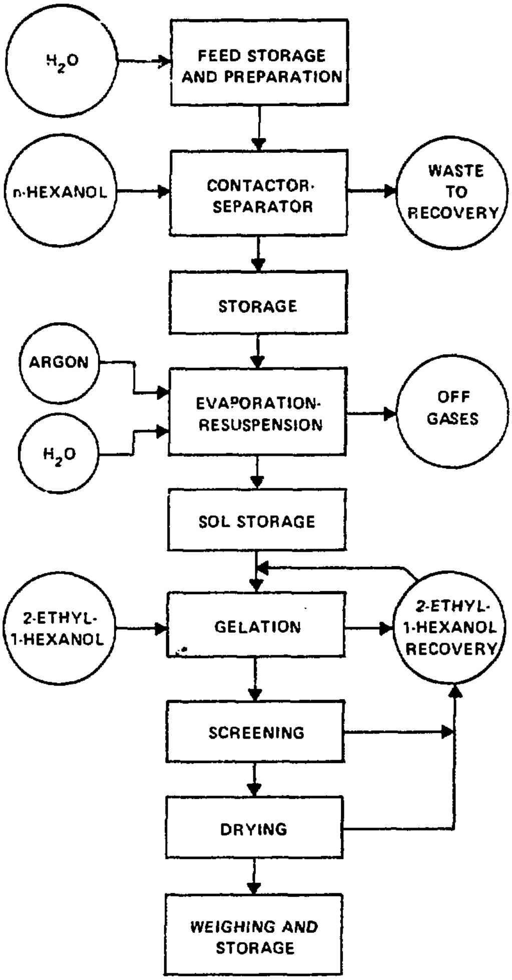


Fig. I-7. Process flowsheet for sol-gel precipitation.

phase separation and minimizes problems in recovering plutonium coextracted with the HNO_3 into the organic phase.

One major advantage claimed for the sol-gel process is that high-density beads can be remotely fabricated into mixed-oxide fuel quite readily. This would be advantageous in the uranium-thorium cycle where high gamma levels from ^{232}U necessitate remote processing.

6. The Coprecal Process. The Coprecal process, outlined in Fig. I-8, consists of injecting a blended plutonium and uranyl nitrate solution into a strong ammonium hydroxide solution.[29] The precipitate is then calcined in a fluidized bed to obtain blended $(U,Pu)O_2$ for fabrication into mixed-oxide fuel. The reactions are

$$UO_2^{2+} + NH_3 + 2OH^- + 4H_2O \rightarrow UO_3 \cdot NH_3 \cdot 5H_2O(s) \ , \qquad (I\text{-}17)$$

$$Pu^{4+} + 4OH^- \rightarrow Pu(OH)_4(s) \ , \qquad (I\text{-}18)$$

$$3UO_3 \cdot NH_3 \cdot 5H_2O(s) \rightarrow 3UO_3(s) + NH_3(g) + 5H_2O(g) \ , \qquad (I\text{-}19)$$

$$Pu(OH)_4(s) \rightarrow PuO_2(s) + 2H_2O(g) \ , \qquad (I\text{-}20)$$

$$PuO_2(s) + UO_3(s) + H_2(g) \xrightarrow{6\%\ H_2+N_2} PuO_2(s)$$

$$+ UO_2(s) + H_2O(g) \ , \qquad (I\text{-}21)$$

$$UO_2(s) + 0.07\ CO_2 \rightarrow UO_{2.07} + 0.07\ CO \ . \qquad (I\text{-}22)$$

The method cannot be applied to preparing oxide containing > ~40% PuO_2. The uranium dilution prevents diversion of practically pure plutonium as nitrate solution or oxide. The liquid blending and homogeneous precipitation eliminate powder blending during fuel fabrication. All recycle material would be dissolved

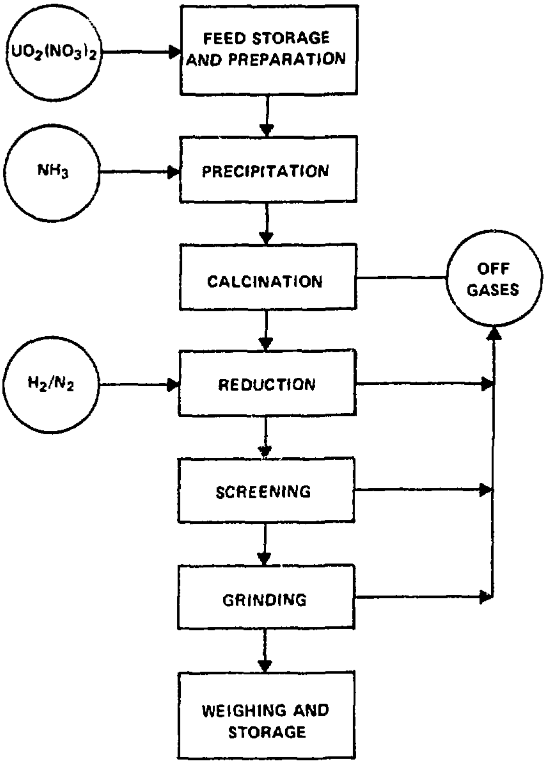


Fig. I-8. Process flowsheet for Coprecal precipitation.

relatively simply. However, the method provides no decontamination.

The Coprecal process is being tested in a pilot-plant operation at the General Electric Vallecitos Nuclear Center at Pleasanton, California. More data will be needed to prove its feasibility. The method is interesting because it involves no reprocessing of pure plutonium solutions and compounds and allows for continued study of the uranium-plutonium fuel cycle. Varying process parameters can produce a wide range of product characteristics.

D. Oxide Formation

In all conversion processes, the final desired product is plutonium oxide (PuO_2) that can be, or already is, blended with uranium oxide (UO_2 or UO_3) to form a dense homogeneous mixture useful for LWR (2-5% PuO_2) or FBR (10-25% PuO_2) fuel, or a mixed master blend of uranium and plutonium oxide. Typical PuO_2 product specifications are summarized in Table I-I.

Oxide reactivity, necessary for oxide conversion to metal, has been an important criterion in previous evaluations of conversion processes. It does not seem to be a significant factor in fuel element production unless redissolution is involved. Oxide density, sintering behavior, and stoichiometry are more important. Conditions necessary to convert various plutonium compounds quantitatively to PuO_2 have been studied thermogravimetrically and are discussed below. Note that PuO_2 is

TABLE I-I

PLUTONIUM OXIDE SPECIFICATIONS[30]

Property	Concentration			
Plutonium content (dry base)	87.2 wt % minimum			
Uranium	5000	ppm	plutonium	maximum
Americium[a]	2800	"	"	"
Water	3000	"	"	"
Carbon	500	"	"	"
Nitrogen	200	"	"	"
Chlorine + fluorine	125	"	"	"
Iron + nickel + chromium	1000	"	"	"
Sulfur	300	"	"	"
Total other impurities[b]	5000	"	"	"
Equivalent boron content	10	"	"	"
Fission products				
Gamma emitting[c]	4.0	c/g of	plutonium	maximum
Zirconium-niobium 95	5	"	"	"
Bulk Density	1.0 g/cm^3 minimum			

(All material is to be passed through a 200-mesh US standard sieve.)

---

[a] As determined within 120 days after separation by solvent extraction.

[b] Includes carbon, nitrogen, chlorine, fluorine, iron, nickel, and chromium.

[c] Gamma-emitting fission products whose parent isotopes have a half-life of 30 days or greater.

hygroscopic. The amount of water adsorbed, a function of particle size and calcining temperature, may be as high as 3% in dry oxides and 5% in incompletely calcined product.[31] This is an important consideration for safeguards accountability.

1. Plutonium Peroxide. The composition of the precipitate formed with Pu^{4+} and H_2O_2 varies with precipitation conditions. Three types of decomposition were observed.[32] Using thermogravimetric and gas analysis, weight loss at 25-135 °C was attributed to water loss, weight loss at 135-170 °C, to peroxide decomposition; and weight loss at 210-290 °C, to nitrate decomposition. A small weight loss above 300 °C was probably due to loss of excess oxygen. Although the peroxide is essentially converted quantitatively to oxide at slightly above 300 °C, if the precipitation was carried out in the presence of sulfate, heating to >600 °C will be required to decompose any entrained sulfates.

2. Plutonium (IV) Oxalate. Thermal decomposition of the plutonium (IV) oxalate, as either hexa- or nona-hydrate, has been studied extensively both in air and in an inert atmosphere.[33-38] In all cases, an initial weight loss in air was related to formation of $Pu(C_2O_4)_2 \cdot H_2O$ and $Pu(C_2O_4)_2$. After prolonged standing, some oxalate decomposition to form CO can occur from alpha radiolysis. At >175 °C, further rapid decomposition occurs, the intermediate products being variously attributed to mixed plutonium (III) or (IV) oxalates, carbonates, and oxides. Decomposition to PuO_2 is almost complete above 400 °C, but heating to 1250 °C is reported necessary to obtain stoichiometric $PuO_{2.00}$.[35] Heating the oxalate in an inert or oxygen-deficient atmosphere can contaminate the sample with free carbon.[37]

3. Plutonium (III) Oxalate. Results of studies on the thermal decomposition of $Pu_2(C_2O_4)_3 \cdot 10H_2O$, like those on the tetravalent oxalate, are inconsistent. The temperature for complete dehydration has been reported as 140 °C[34] to 350 °C.[36] Temperatures as low as 270 °C[34] and as high as 800 °C[36] have been reported to be required for quantitative conversion to $PuO_{2.00}$. The temperature required for quantitative conversion

is important if weight is to be used for accountability at the product end of the process.

4. Direct Conversion. Thermogravimetric conversion of $Pu(NO_3)_4$ in H_2O to PuO_2 is essentially complete at 250 °C.[39] However, stoichiometric $PuO_{2.00}$ was produced only at 675-805°C, depending on sample size.[35] Further weight loss on heating to 1250°C was attributed to decrepitation during heating or nitride formation during nitrate decomposition.

5. Sol-Gel Process. No thermogravimetric studies of plutonium sol conversion to PuO_2 have been reported. However, calcining temperatures >1000°C should be sufficient quantitatively to form stoichiometric PuO_2.

6. Coprecal Process. No thermogravimetric studies on the Coprecal process have been reported, but a study has shown that the oxygen-to-metal ratio of mixed $(U,Pu)O_2$ can be controlled to any desired value by measurement and control of furnace temperature and the oxygen potential in the furnace.[40]

E. Summary

Each of these conversion processes has advantages as well as disadvantages, and no clearcut decision can be made from the present information. More product characterization and process scale-up to large facilities will be required for definitive choices. Some parameters that must be evaluated are as follows.

1. Impurity Decontamination. Peroxide and oxalate precipitation provide potential decontamination from cationic impurities that form soluble peroxides or oxalates. Peroxide precipitation is most effective for cation decontamination because most elements do not form insoluble peroxides; some decontamination factors are shown in Table I-II. Decontamination factors of the two oxalate precipitation procedures are essentially equivalent; those reported for plutonium (IV) oxalate are shown in Table I-III.

Note that if sulfate is added to enhance peroxide precipitation, it may not be removed completely at temperatures normally

TABLE I-II

DECONTAMINATION FACTORS OBTAINED BY PLUTONIUM PEROXIDE PRECIPITATION[5]

Element	Decontamination Factor
Na	7
Cu	30
Ag	10
Be	25
Mg	200
Cu	3
B	25
Al	100
In	25
Si	120
Zr	3.4
Sn	7.5
Pb	10
Cr	700
Mo	140
Mn	15
Fe	60
Co	31
Ni	3000
Ru	16
Ce	60
Th	1.06

TABLE I-III

DECONTAMINATION FACTORS OBTAINED BY PLUTONIUM (IV) OXALATE PRECIPITATION[11]

Element	Decontamination Factor
Zr-Nb	3-6
Ru	12
Am	1
Th	1
Al	100
Cr	100
Ni	100
U	60

used for calcining the pure peroxide, so a higher temperature may be required.

The conversion procedures that have no precipitation step not only fail to provide decontamination from impurity elements, but actually may increase impurity concentrations through equipment corrosion by HNO_3 fumes.

2. Loss of Plutonium. Plutonium loss because of precipitate solubility or incomplete precipitation is possible in the three precipitation procedures. Generally, the plutonium (III) oxalate is least soluble and provides the most easily filterable precipitate. Plutonium (IV) oxalate solubility increases if acid and oxalate concentrations are much greater than those required quantitatively to form the precipitate, and the solubility observed under process conditions is significantly greater than that at equilibrium.[41] Plutonium (III) oxalate solubility increases with increasing acid concentration and decreasing oxalate concentration. As noted, peroxide solubility can be lowered by adding sulfate. Representative solubilities as functions of acid concentration are shown in Table I-IV. In all cases, solubility problems can be minimized by recycling the filtrate and wash solutions.

3. Conversion Temperature. The temperature required for conversion to oxide has important energy considerations for process engineering. It could have more serious implications in the future if oxide redissolution is required in the fuel fabrication plant, because PuO_2 calcined at much above 600°C becomes increasingly difficult to dissolve in HNO_3. Generally, added HF or Ce^{4+} is required to dissolve high-fired PuO_2. These additives, in turn, could increase process upsets. HF seriously increases equipment corrosion, and both fluoride and cerium are hard to remove. The peroxide process that uses H_2SO_4 probably requires the highest conversion temperature if purity of PuO_2 product is important.

As noted, PuO_2 is hygroscopic, the rate of water adsorption being related inversely to the conversion temperature. Shipper-receiver differences can become a safeguards accountability

TABLE I-IV

SOLUBILITIES OF PEROXIDE AND OXALATES OF PLUTONIUM

HNO_3 M	Pu Solubility (g/L)		
	PuO_4[a]	$Pu_2(C_2O_4)_3 \cdot H_2O$[b]	$Pu(C_2O_4)_2 \cdot H_2O$[c]
0.5	--	0.005	0.027
1.0	--	0.013	0.013
1.2	0.007	--	--
1.5	--	0.034	--
2.0	--	0.08	0.010
2.2	0.01	--	--
2.52	--	--	0.017
2.6	--	0.17	--
3.1	--	0.30	--
3.2	0.016	--	--
3.52	--	--	0.018
4.2	0.040	--	--
5.2	1.19	--	--

---

[a] 3 M H_2O_2. (See Ref. 42.)

[b] 0.19 M $H_2C_2O_4$. (See Ref. 43.)

[c] 0.02 to 0.05 M $H_2C_2O_4$. (See Ref. 44.)

problem if the product is stored for extended periods in areas of relatively high humidity.

4. Adaptability to Coprocessing. The conversion processes, except Coprecal, were studied solely on the basis that the feed material is purified $Pu(NO_3)_4$. If coprocessing is selected for the fuel reprocessing plant, the conversion processes must be re-evaluated. The peroxide and both oxalate precipitation processes probably will not be readily adaptable to conversion of coprocessed fuel. Direct denitration has been studied on a pilot-plant scale for coprocessing of uranium and plutonium nitrates at LWR (2% plutonium) and FBR (25% plutonium)

concentrations,[19] but the product quality has not been evaluated for fuel fabrication. Variations of the sol-gel process have been developed at ORNL,[27] and at several foreign laboratories,[28,45] for production of mixed UO_2-PuO_2 spheres and FBR mixed-carbide fuels.[46,47] The product generally is homogeneous and of high density. The method may have some safeguards advantage in that uranium-plutonium mixtures can be stored as the sol or gel, which are harder to separate than the nitrate solutions.

Coprecal has been developed primarily for production of mixed uranium-plutonium oxides for fast breeder reactor fuels, and it should be ideally suited for coprocessing applications.

5. Additional Considerations. Direct denitration appeals to chemical engineers because of the simple equipment and absence of reagents and sidestreams. Peroxide precipitation does not require a separate reducing agent as do the oxalate methods. The plutonium (IV) oxalate method requires less reductant than does the plutonium (III) process, but this advantage may be offset by its greater product solubility and smaller tolerance to variations in process parameters.

For safety, the peroxide process is least attractive because of possible peroxide explosions from introduction of impurities such as iron.

Finally, plutonium safeguardability should be a major consideration in selecting a conversion process for any new plant.

II. THE REFERENCE PROCESS

A. General Description

The reference nitrate-to-oxide conversion process for this study is based on a conceptual design developed by SRL and SRP.[30,48] The design is based on precipitation and calcination of plutonium (III) oxalate. LASL and SRP have extensive experience with the process; it consistently produces a readily filterable precipitate with low losses, and it is controlled easily at room temperature.

Block diagrams of the conversion line are shown in Figs. II-1 and II-2. Material transfers, concentrations, and transfer frequencies are summarized in Table II-I. The design basis throughput is 116 kg of plutonium product per day. In normal operation, a throughput of 106 kg of plutonium per day is expected.

Feed solutions containing 30 g/L of Pu^{4+} in 3 $\underline{M}$ HNO_3 are transferred to a receipt tank in the conversion facility. The feed is analyzed and then transferred to valence adjustment tanks where hydrazine and ascorbic acid are added to reduce the plutonium to the trivalent state.

The adjusted solution is transferred to a two-stage precipitator and oxalic acid is added to form a dense, easily filtered slurry of plutonium oxalate, $Pu_2(C_2O_4)_3$. This slurry is vacuum-filtered, washed, and aspirated to partial dryness in boats containing sintered-metal filters.

The filter boat is transferred through a tunnel furnace for drying and calcining. The calcined product is cooled, then unloaded into a container for assay, storage, and shipping.

Unloaded filter boats and precipitator tanks are flushed periodically, and the flush solutions are transferred to the recycle line. Filtrates, wash solutions, powder sweepings, spills, and rejected product also go to the recycle line, which is shown in Fig. II-3.

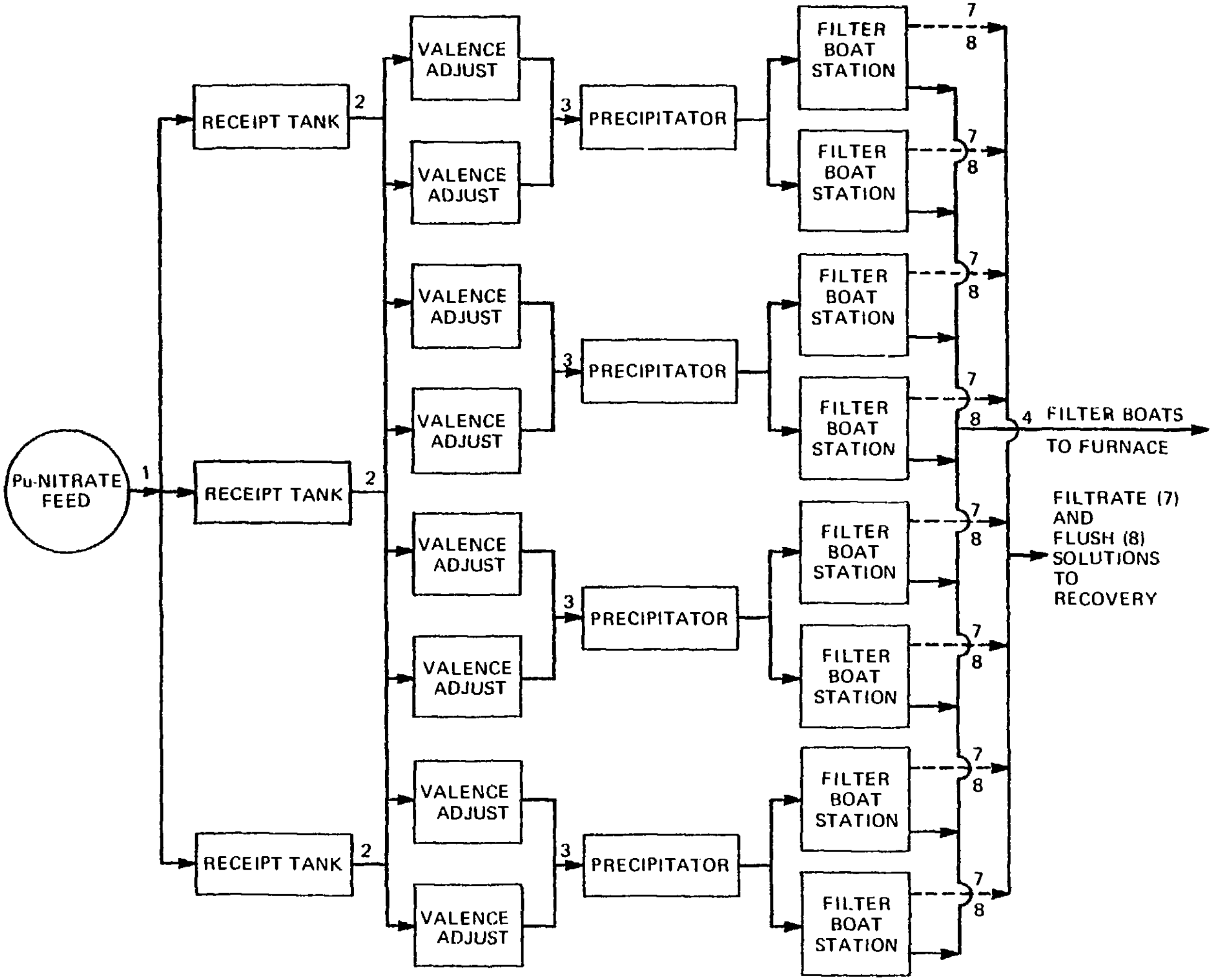


Fig. II-1. Conversion process, liquid handling.

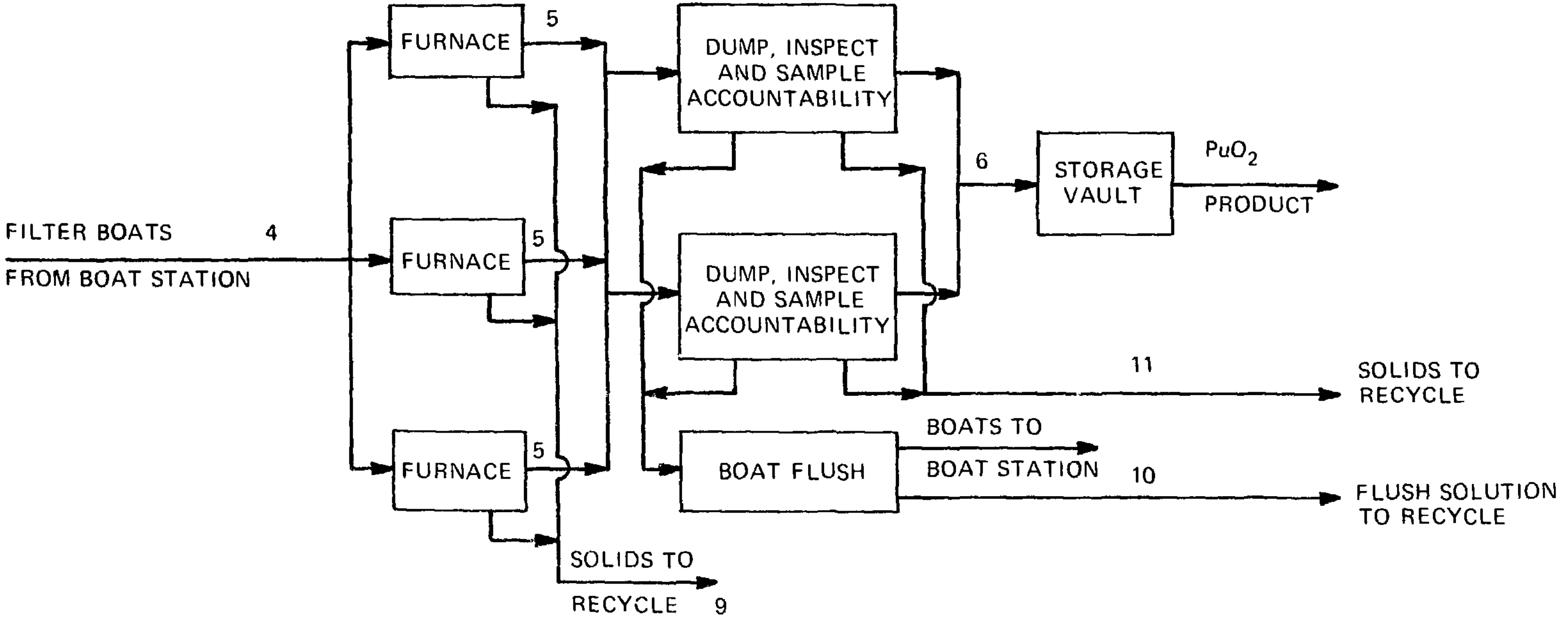


Fig. II-2. Conversion process, solids handling.

TABLE II-I

CONVERSION PROCESS DESIGN PARAMETERS

Stream	Function	Volume or Weight per Batch	Concentration	Frequency
1	Receipt tank feed	200.0 L	30.0 g/L	1/1.23 h
2	Valence adjust feed	66.67 L	30.0 g/L	1/0.41 h
3	Precipitator feed	75.44 L	26.5 g/L	1/0.41 h
4	Pu oxalate boat to furnace	4.65 kg	0.422 kg/kg	1/0.41 h
5	Pu oxide to accountability	2.21 kg	0.882 kg/kg	1/0.41 h
6	Pu product to storage	2.18 kg	0.882 kg/kg	1/0.41 h
7	Filtrate	154.9 L	66.4 mg/L	1/0.41 h
8	Precipitator flush	109.2 L	4.6 g/L	∿ 3/day
9	Furnace sweeping	0.85 kg	0.882 kg/kg	∿ 1/week
10	Boat flush	34.4 L	2.9 g/L	∿ 10/day
11a	Dump station sweep	0.85 kg	0.882 kg/kg	∿ 2/day
11b	Reject product	2.18 kg	0.882 kg/kg	∿ 1/4 days
12	Evaporator product	15.49 L	0.31 g/L	1/0.41 h
	Digester product			
13a	Precipitator flush	109.1 L	4.6 g/L	∿ 3/day
13b	Boat flush	172.1 L	2.9 g/L	∿ 2/day
14	Dissolver product	2.0 L	250.0 g/L	∿ 5/day
14a	Ion-exchange waste	202.0 L	2.2 mg/L	∿ 11/day
15	Ion-exchange product	73.0 L	6.8 g/L	∿ 11/day

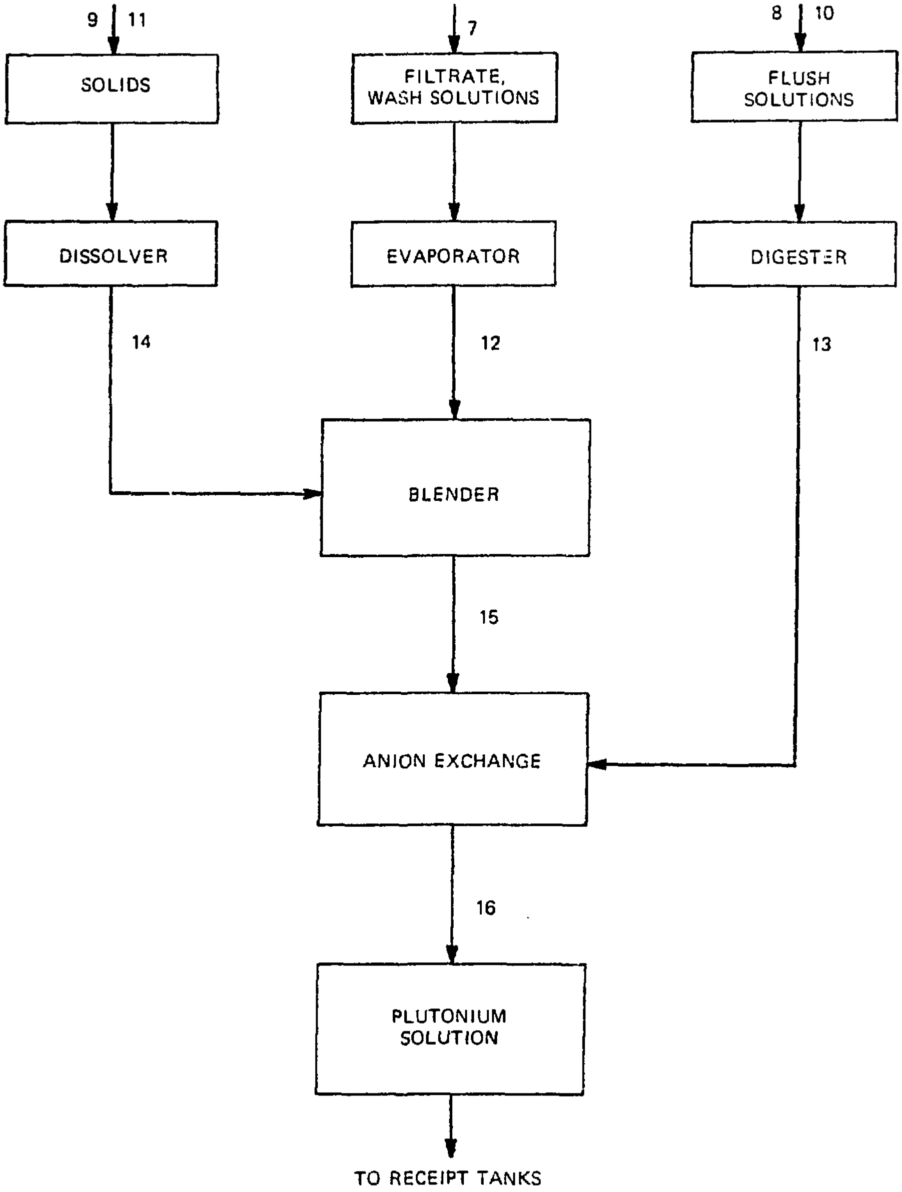


Fig. II-3. Internal recycle line.

The combined filtrate and wash solution is treated to destroy hydrazine, ascorbic acid, and oxalic acid, and then concentrated by evaporation. The sweepings and rejected product are batched (500 g Pu) and then dissolved in nitric acid that contains fluoride ion. The dissolver solution is blended with the evaporator solution to provide sufficient volume for efficient use of the plutonium capacity of the anion-exchange columns. Flush solutions are combined, and any oxalic acid is destroyed by digestion. The exchange-column plutonium product is eluted and transferred to the main process line. All waste solutions are transferred to waste management.

B. Conversion Area

The conversion area can be divided conveniently into six process steps: receipt; valence adjustment; precipitation and filtration; calcination; product dumping, inspection, and sampling; and product storage. Each step is described in the following sections.

1. Receipt Tanks. Plutonium nitrate, $Pu(NO_3)_4$, feed solution, 30 g of Pu/L in 3 $\underline{M}$ HNO_3, from the reprocessing plant is transferred to one of three receipt tanks (Fig. II-1). The solution is air-sparged briefly to eliminate the nitrogen oxides, mechanically agitated to assure uniformity, and a sample is taken for accountability. Three consecutive batches of ~67 L each are dispensed to three valence adjustment tanks, associated with three active precipitator lines. The last batch dispensed completely empties the receipt tank.

Three receipt tanks are required to maintain a normal throughput of 53 batches a day or one batch every 27 minutes. The receipt tanks are operated so that one is receiving feed, one is awaiting analysis, and one is feeding material to the process.

Operating parameters for the receipt tank area are summarized in Table II-II.

2. Valence Adjustment. The contents of the receipt tanks are transferred in 66.7-L batches (2 kg of Pu) to one of two

TABLE II-II

RECEIPT TANK AREA OPERATING PARAMETERS

Pu concentration (g/L)	30.0
Number of tanks	3
Tank capacity (L)	260
Normal receipt volume (L)	200
Normal receipt Pu (g)	6000
No. of receipts per day	17.7
Time per receipt (min)	84
Analytical sample frequency	1 per receipt

valence adjustment tanks associated with each precipitator line. A solution of 3.5 M hydrazine ($N_2H_4 \cdot HNO_3$) is added to the valence adjustment tank to destroy nitrites, and 1.04 M ascorbic acid ($C_6H_8O_6$) is added to reduce plutonium to the trivalent state. The oxidation product is dehydroascorbic acid ($C_6H_6O_6$). The reactions in the valence adjustment tank are:

$$HNO_2 + N_2H_4 \rightarrow HN_3 + 2H_2O \quad , \qquad \text{(II-1)}$$

$$HN_3 + HNO_2 \rightarrow N_2O(g) + N_2(g) + H_2O \quad , \qquad \text{(II-2)}$$

$$2Pu(NO_3)_4 + C_6H_8O_6 \rightarrow 2Pu(NO_3)_3 + C_6H_6O_6 + 2HNO_3 \quad . \qquad \text{(II-3)}$$

Two valence adjustment tanks are connected to the first stage of each precipitator so that solution can be adjusted in one tank while the other is feeding the precipitator. Process parameters for the tanks are summarized in Table II-III.

3. Precipitation and Filtration. Precipitation takes place in two stages (Fig. II-4). Primary precipitation occurs when the adjusted feed solution is mixed stoichiometrically with oxalic acid in the first-stage precipitator. A slurry of $Pu_2(C_2O_4)_3$ in HNO_3 forms in the first-stage precipitator and overflows to the second-stage precipitator at a rate controlled by the rate at which feed and oxalic acid are added to the first-stage precipitator. The slurry in the second-stage precipitator is agitated

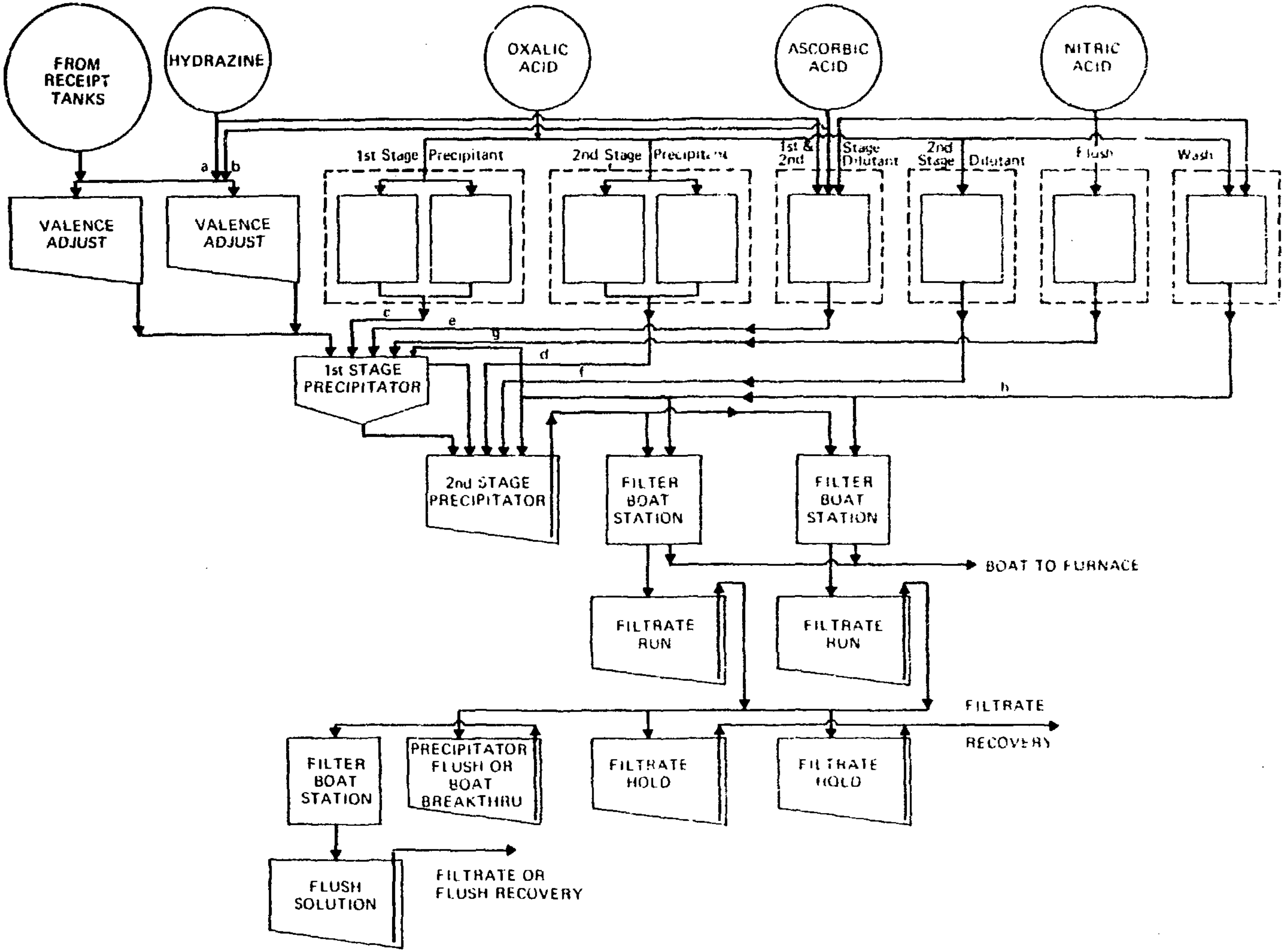


Fig. II-4. Precipitator line.

TABLE II-III

PROCESS PARAMETERS FOR VALENCE ADJUSTMENT TANKS

Pu concentration (g/L)	
Feed	30.0
Product	26.4
Number of tanks	8
Tank capacity (L)	130
Normal receipt volume (L)	
$Pu(NO_3)_4$	66.67
Hydrazine	1.08
Ascorbic acid	7.69
Pu per batch (kg)	2.0
Batches per day	53

for at least 15 min by maintaining the slurry level between 72-100 L to ensure complete precipitation. The concentration of dissolved plutonium should be <0.04 g/L.

There are two filter stations in each precipitator line to permit continuous operation. Hydraulic lifts connect and disconnect the filter boats to and from the system. The filter boats are 25-cm-diam by 15-cm-high cylinders whose bottoms are a 10-µm, type 316, stainless steel frit.

The slurry from the second stage precipitator is vacuum-transferred to filter boats positioned in a filter station. After filtration, the filter cake is washed with three 4-L solutions of 0.3 $\underline{M}$ $H_2C_2O_4$ and 0.5 $\underline{M}$ HNO_3. Outlet lines direct filtrate and wash to the filtrate run tanks.

After one filter boat has received a full batch of precipitate (∿2 kg of Pu), the slurry flow is directed to the second filter station. Thus, although the precipitators operate continuously, filtration is on a batch basis. In this semicontinuous operation the washed cake is aspirated to remove most of the adhering wash solution, and the filter boat is then moved to the drying and calcining furnaces in the solids-handling area. A clean filter boat is positioned in the filter station, and the cycle is repeated.

The eight filtrate run tanks (one for each filter station) receive about 160 L of filtrate and wash solution from each 2-kg batch of plutonium. This solution is tested to ensure that there has been no filter break. If the filtrate contains <0.04 g/L of plutonium and no solids, it is transferred to the filtrate hold tank and then to the evaporator receipt tank in the plutonium recovery area.

If a filter break is detected and precipitate is observed in the filtrate run tank, the solution is refiltered through a second filter boat to another filtrate run tank (Fig. II-4). The filter boat with the broken filter and any filter cake remaining in it is sent through the drying and calcining furnace like a normal boat. However, if the hole in the filter is large, the boat is placed in a secondary container to prevent loss of solids during solids-handling. The process parameters for a precipitator and a filter boat station are given in Tables II-IV and II-V, respectively.

Each precipitator tank is flushed once daily with 14 $\underline{M}$ HNO_3 to remove oxalate precipitate from its walls. The flush solution, 109 L containing ∿500 g of plutonium, is transferred first to the filtrate run tank, then to the hold tank, and finally to the precipitator flush run tank in the internal recycle area.

4. Calcination. The filter boat containing the aspirated filter cake is transported to the solids-handling area shown in Fig. II-2. The oxalate is dried and then calcined in one of three furnaces operating in parallel. Each furnace has drying, calcining, and cooling regions. A conveyor system indexes the boats through the furnaces on a programmed cycle of 2-h drying, 2- to 3-h calcining, and 1-h cooling. Each furnace has a six-boat capacity. In the drying region, air is heated to 100-200°C and drawn through the cake by vacuum. Adhering H_2O and HNO_3 evaporate, and removal of water of hydration begins. The oxalate decomposes, and the oxide is calcined in the second zone where a

TABLE II-IV

PROCESS PARAMETERS FOR PRECIPITATOR TANKS

Feed Pu concentration (g/L)	26.4
Number of precipitator lines	4
Tank capacity (L)	
1st stage	4
2nd stage	125
Normal receipt volume (L)	
$Pu(NO_3)_3$	75.44
Diluent (precipitator startup)	10.25
Oxalic acid	
1st stage	15.63
2nd stage	53.88
Flow rate (L/min)	
Feed	2.5
1st-stage oxalic acid	0.5
2nd-stage oxalic acid	1.8

TABLE II-V

PROCESS PARAMETERS FOR FILTER BOAT STATION

Boat dimensions (cm)	
diameter	25
height	15
Pu batch (kg)	2
Filtrate and wash (L)	160
Number of filter boats	30
Number of filter boat stations	8

temperature gradient from 450 to 650°C is maintained. Excess oxygen, provided by a flow rate of 30 m^3/min (1050 CFM) of hot air, is required for the decomposition. The calcined PuO_2 product is cooled in the cool-down section of the furnace before discharge. After cooling, the filter boats are moved to the dump-weigh station.

The reactions in the furnace are

drying,

$$Pu_2(C_2O_4)_3 \cdot 9H_2O \rightarrow Pu_2(C_2O_4)_3 + 9H_2O(g) \quad , \tag{II-4}$$

and

calcining,

$$Pu_2(C_2O_4)_3 + 2O_2(g) \rightarrow 2PuO_2 + 6CO_2(g) \quad . \tag{II-5}$$

Furnace process parameters are given in Table II-VI.

5. Product Dumping, Inspection, and Sampling. The solid PuO_2 product is dumped from the filter boats into storage and shipping cans at one of two dump-weigh stations. The empty filter boats are flushed with 10 M HNO_3, rinsed with water to remove any adhering PuO_2, and returned to the filter stations. Three filter-boat flushing stations are used, and one flush solution head tank serves all three. Approximately 300 L of 10 M HNO_3 will be required daily.

Table II-VI

FURNACE PROCESS PARAMETERS

Number of furnaces	3
Boat residence time (h)	∿6-7
Condensate (kg)	
H_2O	1.4
HNO_3	0.025
Furnace temperature (°C)	
Drying	100-200
Calcining	450-650

The PuO_2 product is sampled for accountability and quality control. Cans containing acceptable product are sealed and transferred to the storage vault. Reject product is transferred to solids recovery.

A batch of product remains in a single filter boat throughout the solids-handling operations from filtration to dumping. These boats will be numbered, and their movement will be monitored by a computerized accountability program to allow some degree of material tracing in case of a discrepancy. The boat movements are shown in Fig. II-5. The accountability computer will also monitor and control the movement and location of product storage containers in the storage vault.

6. Storage. Sealed cans containing ∿2 kg of plutonium as PuO_2 are stored in the vault until transferred to the fuel fabrication plant.

C. Recycle and Recovery Area

Filtrates and flush and wash solutions from the precipitator, solids from sweepings, filter boat flush solutions, and reject product from the conversion line are treated to recover and recycle plutonium. The recycle line is shown in Fig. II-6. A fourth minor sidestream is included to recover plutonium from waste material. Recycling and recovery through the ion-exchange blend tank is shown in more detail in Fig. II-7. The ion exchange system is shown in Fig. II-8.

The four areas of the recycle line (solids, filtrate, flush solutions, and waste) are described below.

1. Solids. The solids dissolver consists of two dissolver vessels each with a filter station and a filtrate run tank. Batches of 500 g of recycle PuO_2, which may contain both rejected product and sweepings, are dissolved by refluxing in 14 $\underline{M}$ HNO_3-0.05 $\underline{M}$ KF. The fluoride is added as solid $KF \cdot 2H_2O$. The reaction is

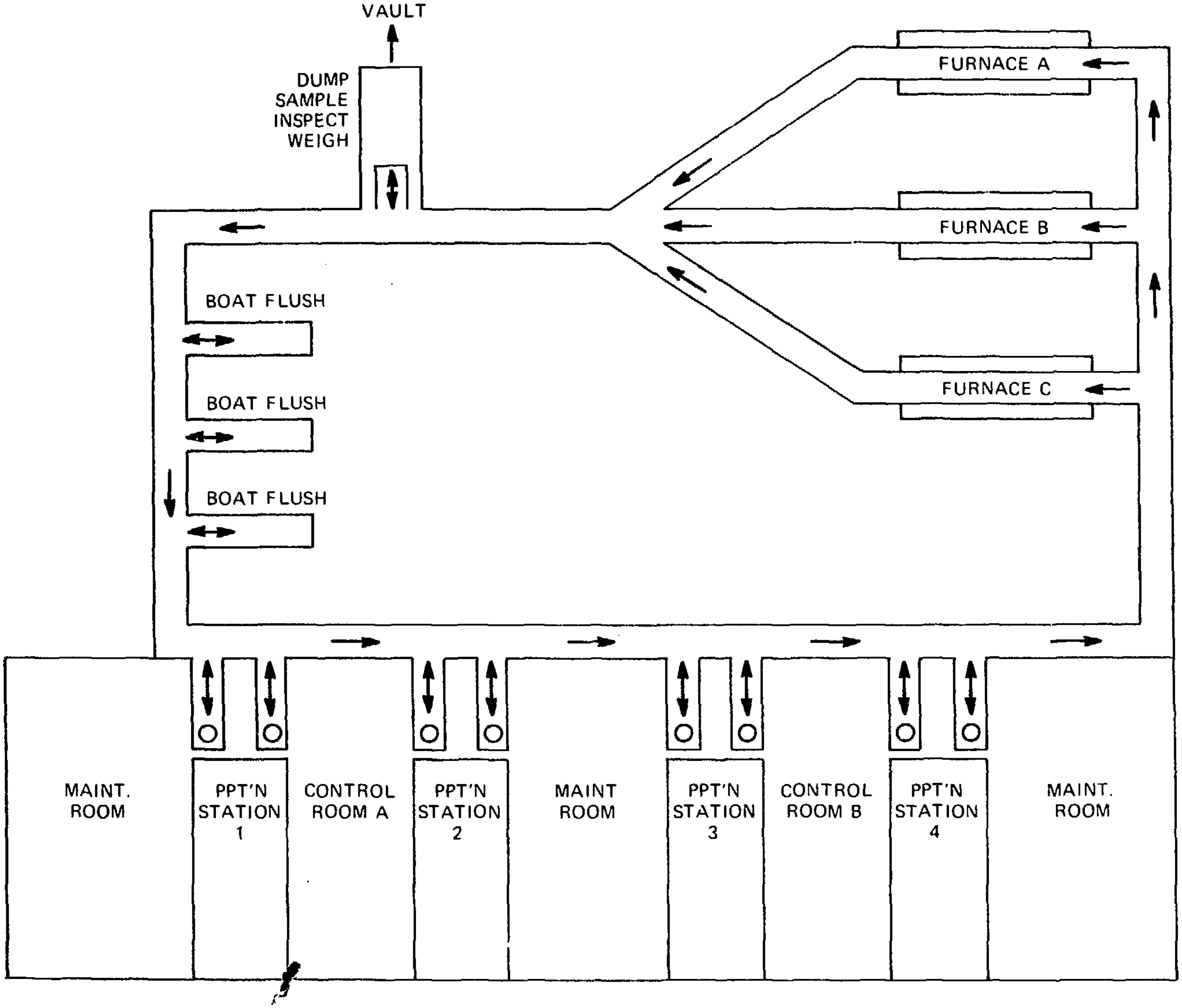


Fig. II-5. Boat movement.

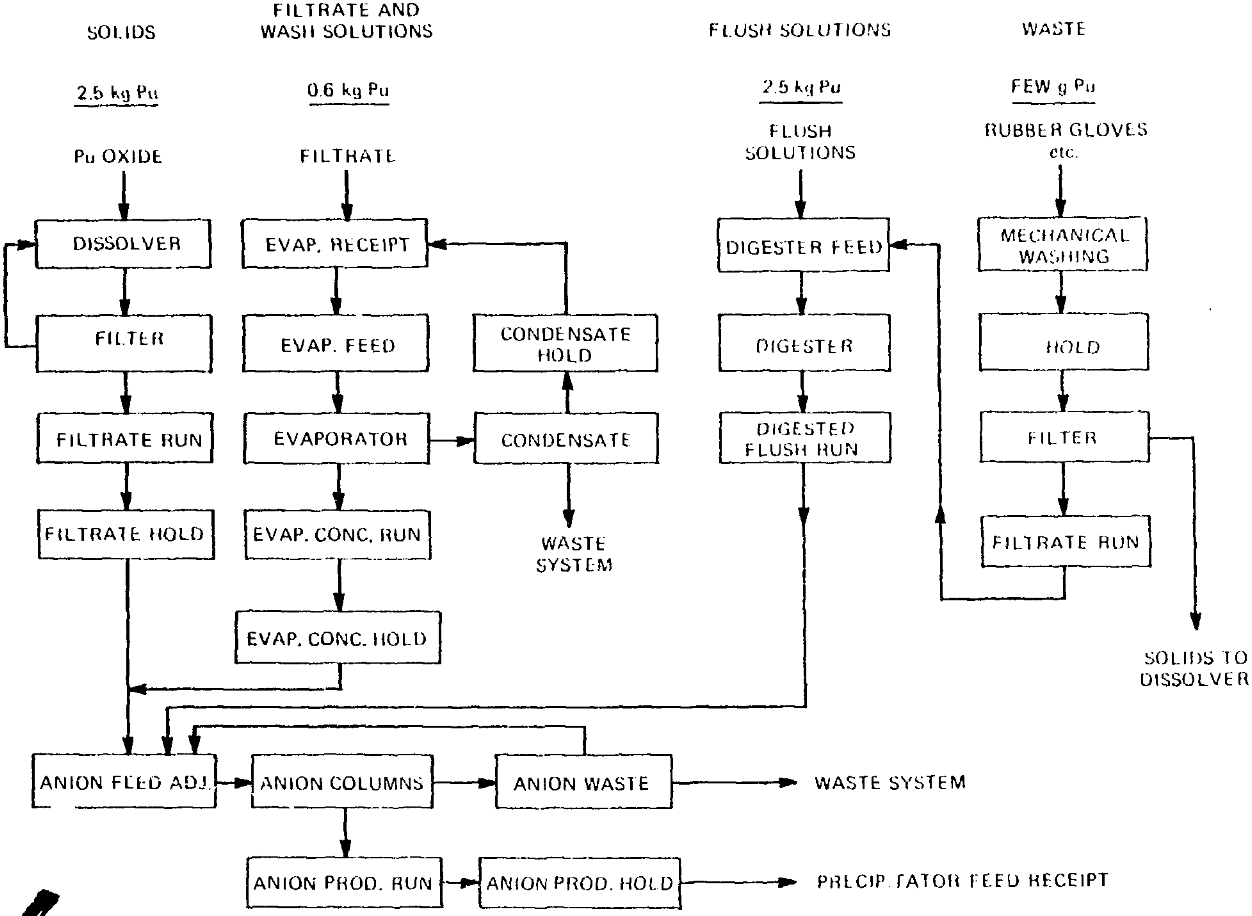


Fig. II-6. Plutonium recovery.

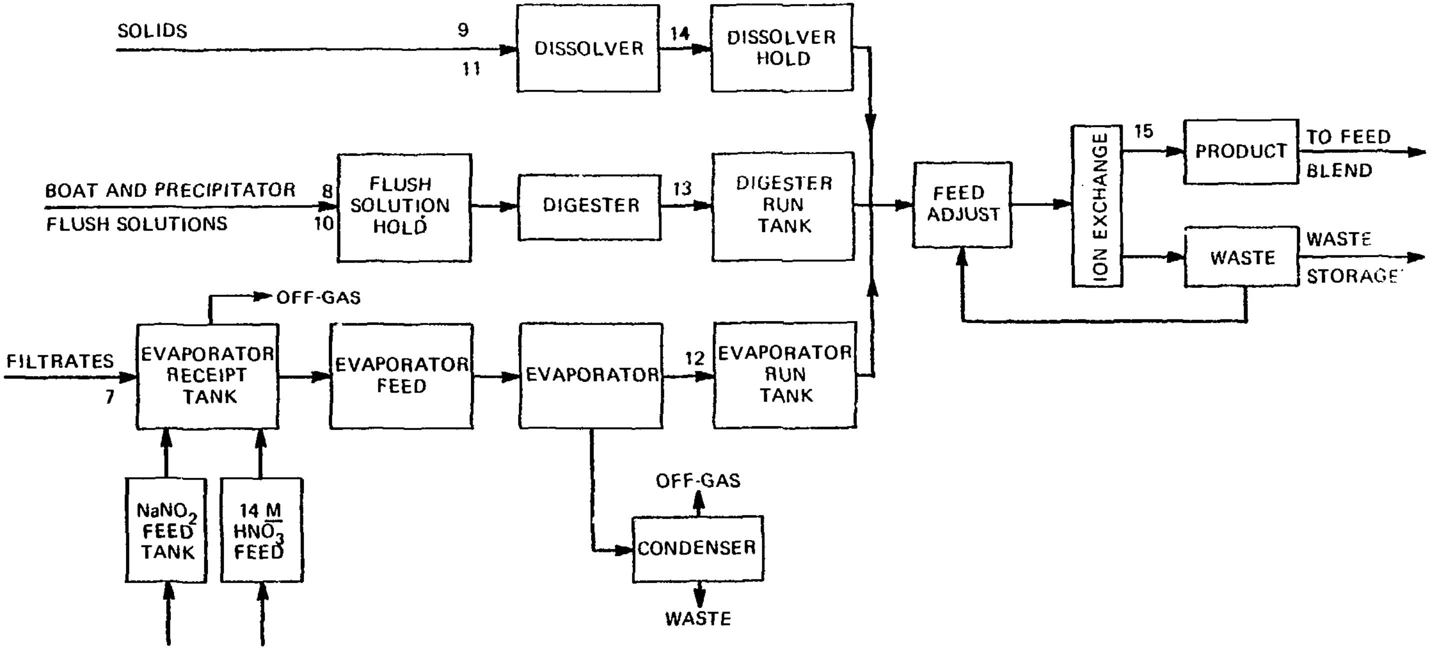


Fig. II-7. Recycle recovery (part 1).

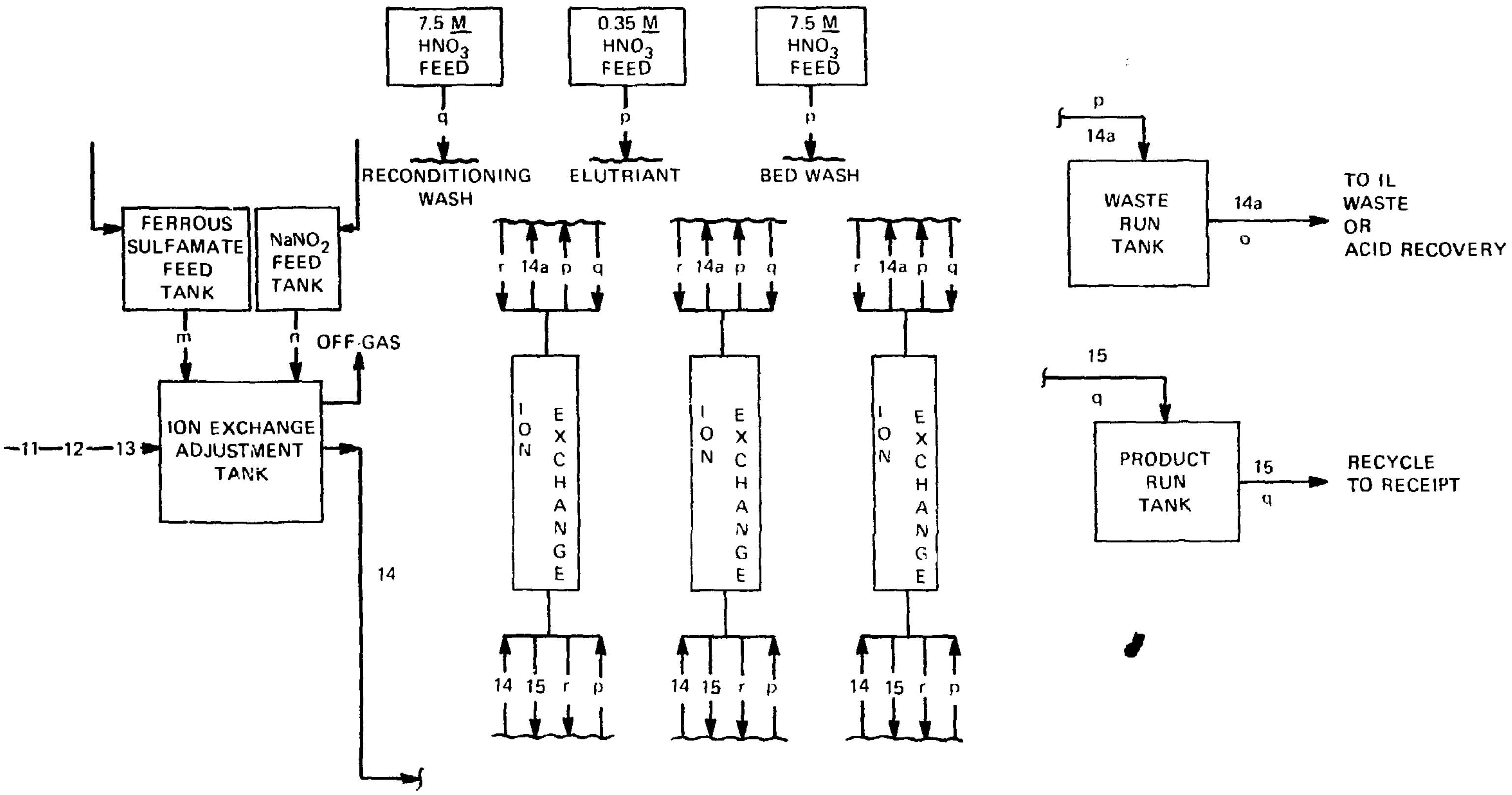


Fig. II-8. Recycle recovery (part 2).

$$PuO_2(s) + 4HNO_3 \xrightarrow{F^-} Pu(NO_3)_4 + 2H_2O \quad . \qquad \text{(II-6)}$$

Five batches (∿2500 g of plutonium) are dissolved daily. About 0.2 L of 60% $Al(NO_3)_3$ solution per batch is added to complex the F^-, and the solution is filtered to remove any undissolved particulates. The solution is transferred to the anion feed adjust tank for blending with other recycle streams.

2. Filtrates. Filtrate and wash solutions from the eight filtrate hold tanks are transferred into one of three 226-L evaporator receipt tanks. A solution of 5.3 M $NaNO_2$ is added to the solutions to destroy hydrazine. Excess nitrite is then consumed by HNO_3. The process reactions are

$$N_2H_4\ HNO_3 + HNO_3 + 2NaNO_2 \rightarrow N_2O(g) + N_2(g) + 3H_2O + 2NaNO_3 \quad , \qquad \text{(II-7)}$$

$$NaNO_2 + 2HNO_3 \rightarrow NaNO_3 + 2NO_2(g) + H_2O \quad . \qquad \text{(II-8)}$$

Gases generated during these reactions are vented to the facility off-gas system. Hydrazine oxidation prevents formation of explosive hydrazoic acid during the subsequent evaporation.

Chemical concentrations of the evaporator receipt tank feed are summarized in Table II-VII. The evaporator feed is adjusted with HNO_3 to yield 10 M in the evaporator bottoms after evaporation of the overheads and the HNO_3-consuming oxidations. The actual nitric acidity of the adjusted evaporator feed is ∿1.79 M. This evaporator operates continuously and the 10 M HNO_3 in the pot should be sufficient to oxidize oxalic and ascorbic acids.

The evaporator reduces the solution to 0.1 of its delivery volume. The evaporator product consists of 10 M HNO_3 and 0.86 M $NaNO_3$ containing ∿6 g/L of plutonium. The evaporator bottoms are transferred through the evaporator concentrate run tank to the ion-exchange blend tank. Demisters inside the

TABLE II-VII

CHEMICAL CONCENTRATIONS IN EVAPORATOR RECEIPT TANK FEED

Chemical	Concentration (M)
$H_2C_2O_4$	0.3
HNO_3	0.65
$C_6H_8O_6$	0.02
$C_6H_6O_6$	0.02
$NaNO_3$	0.08

evaporator minimize plutonium entrainment in the vapor stream, and they must be cleaned periodically.

Nitric acid concentrations are ∿0.2% in the overhead condensate and 10 M in the reboiler and take-off stream. Handling such concentrations will require a fractionating column with the equivalent of five ideal plates operating under vacuum at 2000-3300 dyne/cm^2 where the water-acid separation is enhanced. The oxalic acid-nitric acid decomposition is autocatalyzed by NO_2 in solution, and the lower pressure also allows the reboiler to operate at the lower temperatures, which is necessary to keep enough NO_x in solution for oxalic acid destruction.

The H_2O and HNO_3 from the evaporator vapor stream will be condensed in a primary condenser before the noncondensible CO, CO_2, and NO_x are vented to the off-gas system. The condensate will be discharged to intermediate level waste streams.

3. Flush Solutions. The precipitator flushing operations generate ∿330 L/day of 10 M HNO_3 solutions containing ∿5 g/L of plutonium. This solution is transferred through the filtrate run and hold tanks to a precipitator flush run tank and then to a flush solution hold tank (Fig. II-7).

Approximately 300 L/day of 10 M HNO_3 flush solution containing ∿3 g/L of plutonium is transferred from the filter boat cleaning operations to a boat flush run tank. This solution is blended twice daily with the precipitator flush solution and transferred to a flush solution digester where $H_2C_2O_4$ is destroyed through the reaction

$$2H_2C_2O_4 + 2HNO_3 \rightarrow 4CO_2(g) + 3H_2O + NO(g) + NO_2(g) \quad . \qquad (II\text{-}9)$$

The solution from the digester is blended with the other recycle streams in the ion-exchange blend tank.

4. Waste. Solid waste, such as rubber gloves, that may contain significant amounts of plutonium is mechanically washed with HNO_3. The material is filtered, and dissolved plutonium is transferred through a filtrate run tank to the flush solution digester feed tank (Sec. 3). Solids are transferred to the solids dissolver.

5. Ion-Exchange System. (Refer to Fig. II-8.) The filtered PuO_2 dissolver solution and filtrate wash solutions are blended in the ion-exchange blend tank and transferred to one of two ion-exchange adjustment tanks. The adjusted flush solutions are fed alone.

The plutonium, primarily as Pu^{4+} but with some Pu^{6+}, is reduced to the trivalent state by using a 2.2 M solution of ferrous sulfamate, $Fe(SO_3NH_2)_2$. The reactions are

$$Pu(NO_3)_4 + Fe(SO_3NH_2)_2 \rightarrow Pu(NO_3)_3 + Fe(SO_3NH_2)_2 \cdot NO_3 \; , \qquad (II\text{-}10)$$

$$PuO_2(NO_3)_2 + 3Fe(SO_3NH_2)_2 + 4HNO_3 \rightarrow Pu(NO_3)_3$$
$$+ 3Fe(SO_2NH_2)_2 \cdot NO_3 + 2H_2O \quad . \qquad (II\text{-}11)$$

The sulfamate is then reacted with $NaNO_2$ to oxidize plutonium to Pu^{4+} and iron to Fe^{3+}. Excess nitrite is destroyed by air sparging.

The adjusted stream passes to one of four anion-exchange columns having a resin volume of 12.6 L. The plutonium is adsorbed on the columns from 7.2 M HNO_3 solution, and a relatively plutonium-free stream is discharged to intermediate-level waste. The column is washed with 7.5 M HNO_3. The plutonium is then eluted from the column with 54 L of 0.35 M HNO_3 at a rate of 0.4 L/min to provide a purified product suitable for recycle to the conversion line. The ion-exchange reactions are

loading,

$$Pu(NO_3)_4 + 2HNO_3 \rightarrow Pu(NO_3)_6^{2-} + 2H^+ \quad , \qquad (II-12)$$

$$Pu(NO_3)_6^{2-} + Resin \cdot (NO_3)_2 \rightarrow Resin \cdot Pu(NO_3)_6 + 2NO_3^- \quad , \qquad (II-13)$$

elution,

$$Resin \cdot Pu(NO_3)_6 \rightarrow Resin \cdot (NO_3)_2 + Pu(NO_3)_4 \quad . \qquad (II-14)$$

The nitrate product is transferred to one of four anion product run tanks. Approximately 815 L of solution containing 6.8 g/L of plutonium or a total of 5.6 kg of plutonium in approximately eleven 73-L batches will be transferred daily to the conversion line.

D. Cold Chemical Preparation

The cold chemical preparation area in the upper level of the conversion facility is diagrammed in Fig. II-9. Solutions required in the conversion and recycle areas are transferred through head tanks to process vessels by gravity feed through head pots. Cold chemical requirements of the various streams in the conversion and recovery lines are summarized in Table II-VIII.

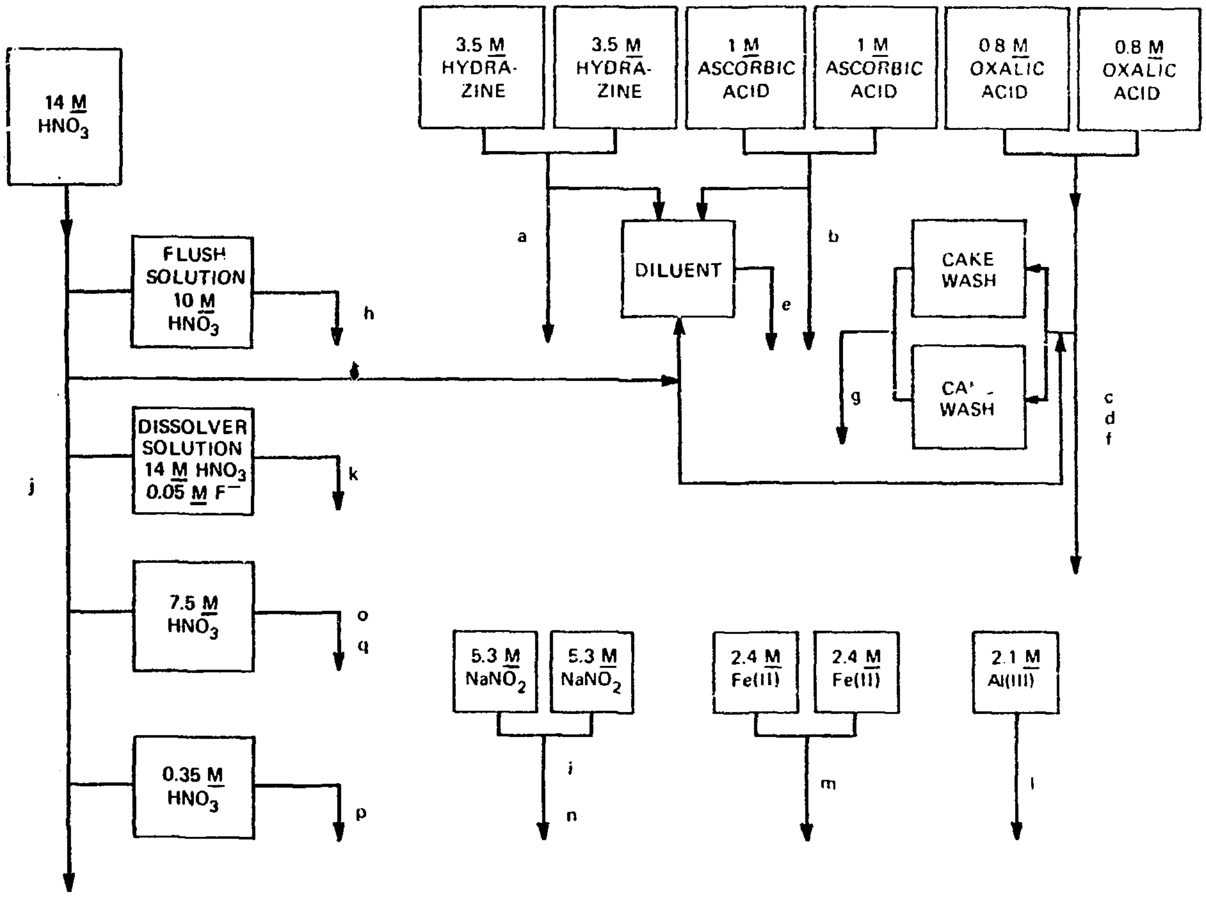


Fig. II-9. Cold chemical preparation.

TABLE II-VIII

COLD CHEMICAL REQUIREMENTS

Stream[a]	Function	Composition/Batch
a	Valence adjustment	1.1 L of 3.5 M $N_2H_4 \cdot HNO_3$
b	Valence adjustment	7.7 L of 1.0 M $C_6H_8O_6$
c	1st stage precipitant	15.6 L of 0.8 M $H_2C_2O_4 \cdot 2H_2O$
d	2nd stage precipitant	53.9 L of 0.8 M $H_2C_2O_4 \cdot 2H_2O$
e	Diluent (1 and 2)	0.9 L of 14 M HNO_3 + 0.1 L of 1 M $N_2H_2 \cdot HNO_3$ + 0.1 L of 1 M $C_6H_8O_6$ + 9.8 L of H_2O
f	2nd stage diluent	3.8 L of 0.8 M $H_2C_2O_4 \cdot 2H_2O$
g	Cake washing	0.4 L of 14 M HNO_3 + 4.5 L of 0.8 M $H_2C_2O_4 \cdot 2H_2O$
h	Precipitator flushing	100 L of 14 M HNO_3
i	Hydrazine reduction	2.5 L of 30% $NaNO_2$
j	Oxalic acid destruction	18.5 L of 14 M HNO_3
k	Solids dissolution	2 L of 14 M HNO_3 + 94 g $KF \cdot 2H_2O$
l	Fluoride complexing	0.23 L of 60% $Al(NO_3)_3$
m	Reduction to Pu(III) state	
	Evaporator bottom and oxide solution	4.04 L of 2.2 M $Fe(SO_3NH_2)_2$
	Boat flush solution	5.57 L of 2.2 M $Fe(SO_3NH_2)_2$
	Precipitator flush solution	3.81 L [illegible] 2.2 M $Fe(SO_3NH_2)_2$
n	Pu(III) oxidation to Pu(IV)	
	Evaporator bottom and oxide solution	7.25 L of 5.3 M $NaNO_2$
	Boat flush solution	9.96 L of 5.3 M $NaNO_2$
	Precipitator flush solution	6.85 L of 5.3 M $NaNO_2$
p	Bed washing	4.3 L of 7.5 M HNO_3
q	Elutriant	53.9 L of 0.35 M HNO_3
r	Reconditioning Wash	19.0 L of 7.5 M HNO

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[a] See Figs. II-1 through II-4 and Figs. II-7 through II-9.

III. THE SAFEGUARDS SYSTEM

For safeguards and nonproliferation, the plutonium nitrate-to-oxide conversion facility is one of the most important components of the LWR and fast breeder reactor nuclear fuel cycles. It is the pivotal step between the spent-fuel reprocessing and fuel fabrication facilities, and therefore processes large quantities of plutonium in both liquid and solid forms that are attractive for diversion. It is also essential for obtaining the metal required to make a reliable nuclear weapon.

From a practical standpoint, the conversion facility is usually designed to be either the last stage of reprocessing or the first stage of fuel fabrication. Because of the recent NRC regulations prohibiting shipment of liquid plutonium nitrate, the trend in the US has of necessity been toward incorporating the conversion process into the spent-fuel reprocessing facility. However, nonproliferation considerations may make a separate conversion facility desirable in implementing the nuclear fuel cycle in nonweapons states.[4] For this report and to specify the architecture of the safeguards system, we consider the conversion facility to be a separate entity, although we recognize that the resulting safeguards system may be an extension of a larger, more comprehensive system that serves a combined facility.

A. Safeguards System Architecture

The basic architecture of the safeguards system has been described in previous reports,[1,49-53] and is equally applicable to the conversion process. For convenience the description of the architecture is repeated here; more detail can be found in the references.

The general block diagram of the facility and safeguards system is shown in Fig. III-1. Functions directly related to the process are heavily outlined. Process control is distributed along the process and item-operations lines in the form of local controllers, one for each part of the process. The actions of the process controllers are supervised by the process-control coordination unit (PCCU). This hierarchical control usually is implemented through setpoint commands in which the PCCU specifies the operating point of each part of the process on the basis of operational authorizations, process-operation considerations, and safety. Many parts of the process may be self-regulating and require only monitoring for limit conditions. The PCCU does not require or imply that all process functions are under computer control, but only that operational changes are monitored through automated data acquisition.

The PCCU also implements safeguards-related recommendations that affect process operations. This implementation is necessary to ensure effective compliance from both the safeguards and process-control viewpoints. The materials measurement and accounting system (MMAS) and the PCCU also exchange process-related information to improve process operation and safeguards effectiveness.

The safeguards coordination unit (SCU), described in more detail in Ref. 50, supervises SNM safeguarding in the facility. As the focal point for safeguards decisions, the unit interacts with management and process-control coordination to ensure effective safeguards. Safeguards coordination must be as simple and reliable as possible, and its decision-making function must be balanced to avoid frequent false alarms that cause unnecessary process disruptions, while maintaining a high probability of effective response to any credible safeguards violation.

The SCU would normally rely on automated decision and control augmented by human supervision in abnormal situations. Although it is the heart of the safeguards system, the SCU must be designed carefully to minimize single-point vulnerability and

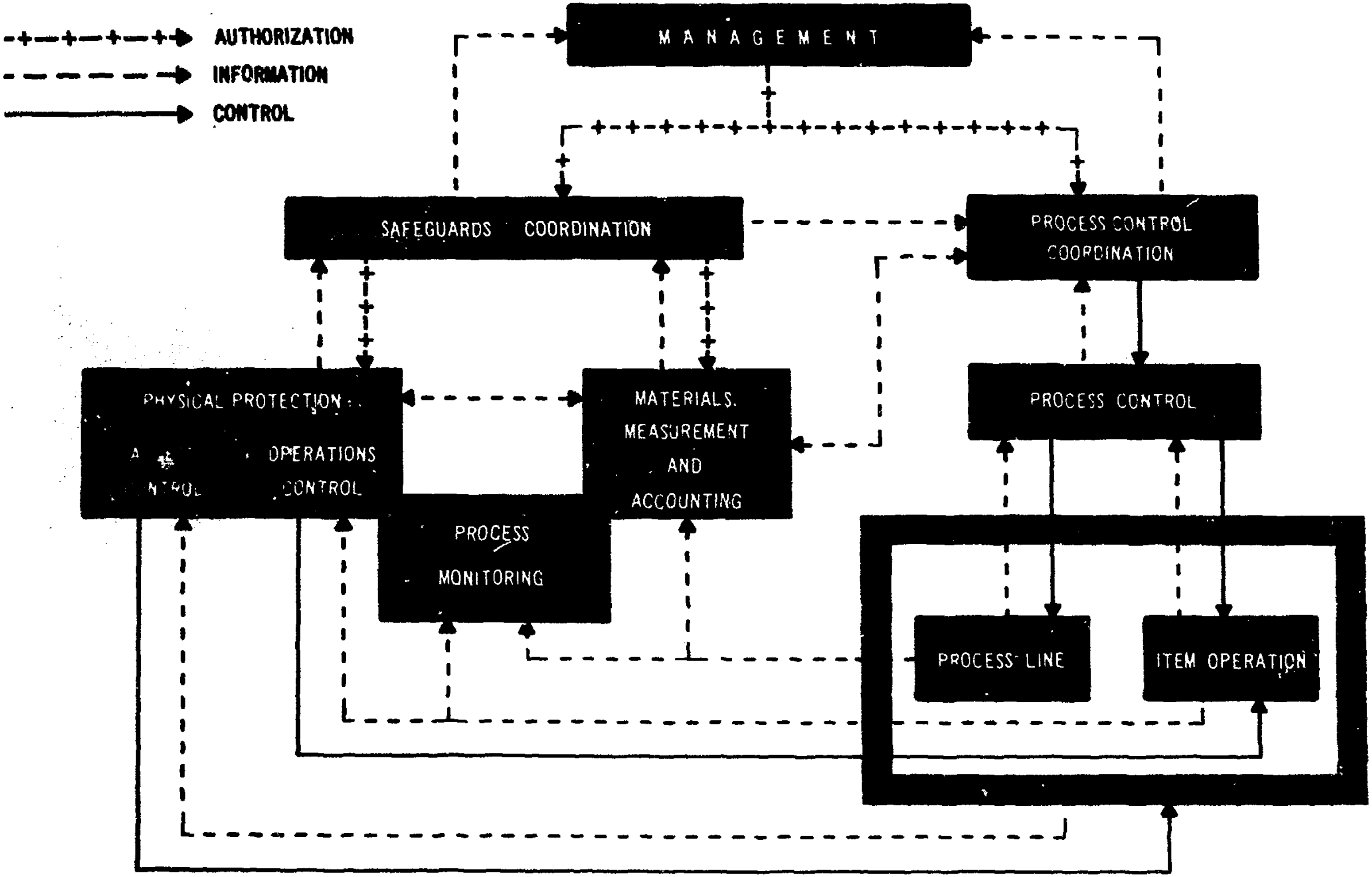

Fig. III-1. Structure of the safeguards system.

reduce the response time required to meet rapidly developing threats.

The physical protection system (PPS) controls personnel entry to and exit from the facility and movement in restricted areas inside. It includes automated equipment and enough guard forces for effective emergency response. It expands the conventional security functions, such as personnel control, to include control of item-handling operations. This arrangement provides better protection through remote, overriding control of discrete material items in handling and storage. The concept is applied only to parts of the facility outside the closely coupled process line, where material flow is not critical to smooth process operations.

The PPS provides appropriate information to the safeguards system and

- excludes all unauthorized persons and contraband from the facility,
- admits only essential persons to selected areas, and
- precludes unauthorized activities involving nuclear material and vital equipment.

Important objectives in PPS design are to automate its functions whenever possible and to harden the system against subversion. These objectives are consistent with the stated goal of reducing dependence on personnel reliability.

In the current concept of domestic safeguards, the physical-protection and materials-accounting functions complement and reinforce each other. In particular, the PPS protects not just nuclear material, but the integrity of the MMAS as well. Conversely, the MMAS confirms the effectiveness of the PPS. This approach requires high technological sophistication in the system design and operation, supplemented by thorough and frequent plant and safeguards inspections by a knowledgeable, independent safeguards staff.

Design and evaluation of the PPS for these facilities, the responsibility of Sandia Laboratories, is discussed in detail in Refs. 51-53.

The MMAS is an implementation of the DYMAC concept,[54-56] and is similar in principle to that described for a mixed-oxide fuel fabrication facility.[50] It combines conventional chemical analysis, weighing, and volume measurements with the near-real-time measurement and surveillance capabilities provided by NDA instrumentation to enhance rapid, accurate assessment of the location and amount of SNM in a facility.

The process-monitoring function combines elements of both the PPS and MMAS and gives each supplementary information on compliance of actual process operating modes with approved procedures. The concept may be regarded as an extension of physical-protection monitoring and surveillance functions into the process line, and as an upgrading of the monitoring devices (or their appropriate placement) to allow gross materials accounting (see Sec. III-C).

The safeguards computer system plays an essential role in implementing effective safeguards by collecting safeguards-related data and maintaining and controlling the safeguards information system. A major part of this role is protection of SNM; equally important is the operational effect of the computer system on the processing of nuclear material. This effect occurs because information provided through the computer system forms the basis for all safeguards decisions, which may affect the process to varying degrees. Erroneous or unavailable information can degrade decision quality and disrupt the process unnecessarily. Thus, computer system reliability and integrity directly affect economical operation of the process. Several of the many possible computer and information system implementations are discussed in Refs. 50 and 51.

B. The Materials Measurement and Accounting System

1. General Approach. The MMAS has three major tasks in SNM accounting:

- Data collection (including measurements),
- Data analysis (for diversion detection), and
- Data dissemination or reporting.

As now performed by conventional safeguards inventory control, these tasks rely heavily on material balance accounting following periodic shutdown, cleanout, and physical inventory. The classical material balance is drawn around the entire plant or a major part of the process, and is formed by adding all measured receipts to the initial measured inventory and subtracting all measured removals from the final measured inventory. During routine production, material control is vested largely in administrative and process controls, augmented by secure storage for discrete items.

Although conventional material balance accounting is essential to safeguards control of nuclear material, it has inherent sensitivity and timeliness limitations. The first limitation results from measurement uncertainties that desensitize the system to losses of trigger quantities of SNM in large-throughput plants. The timeliness of traditional materials accounting is limited by the frequency of physical inventories. There are practical limits on how often a facility can shut down its process and still be productive.

Recently developed NDA technology, state-of-the-art conventional measurement methods, special in-plant sensors, plant instrumentation signals, and the most effective statistical data-analysis techniques combined with supportive computer and data-base-management technology make several more effective methods feasible. For example, conventional methods can be augmented by unit-process accounting,[1,50,55,56] for which the facility is partitioned into discrete accounting envelopes called unit-process accounting are[redacted]AAs). A unit process can be one or more chemical or physical processes, and it is chosen on the basis of process logic and whether a suitable material balance can be drawn around it. By dividing a facility into unit processes and measuring all significant material transfers, quantities of material much smaller than the total plant inventory can be controlled. Furthermore, any discrepancies are localized to that part of the process contained in the UPAA.

Compared to the reprocessing plant, the conversion facility is small enough to require only a few UPAAs. Chapter IV will show that two or three are enough to give the desired timeliness and sensitivity.

Material balances drawn around such unit processes during plant operation are called *dynamic material balances* to distinguish them from balances drawn after a cleanout and physical inventory. Ideally, the dynamic material balances would all be zero unless nuclear material had been diverted. In practice they never are, for two reasons. First, measured values are never exact because of the errors inherent in any measuring procedure. Second, constraints on cost or effects on materials processing operations may dictate that not all components of a material balance be measured equally often; therefore, even if the measurements were exact, the material-balance values would not be zero until closed by additional measurements. In the interim, it is sometimes possible to use historical data to estimate unmeasured material, and then update the estimates when more measurements become available.

A consequence of unit-process accounting, the concept of *overlapping unit-process accounting areas* derives from the fact that two adjacent UPAAs can be combined to form a larger one, eliminating the intervening transfer measurement. This combination may be useful for cross-checking, and it allows continued materials accounting (at reduced effectiveness) in case of instrument malfunction.

The various forms and concentrations of SNM in the facility dictate that these ideas be applied flexibly. The concept of *graded safeguards* implies that material that is more attractive and accessible for diversion is more stringently safeguarded. For example, in the conversion facility, plutonium oxide at the boat dump station would probably be more desirable to a potential divertor than the relatively dilute ($\sim$30-g/L) plutonium-nitrate solution in the receipt tanks, and both would be more desirable than the oxalate slurry inside the precipitators.

The notion of graded safeguards leads naturally to possible tradeoffs among the physical-protection, process-monitoring, and materials measurement and accounting systems. The issue has no clearcut solution because of the necessarily subjective nature of the benefits derived from each system and the current lack of judgmental criteria. Certainly, increased capability in one system can be partially compensated for by less required capability in another, but the relationship is not simple, nor does a given level of safeguards have a corresponding unique system configuration. The current approach investigates various system concepts to determine the characteristics (cost, sensitivity to diversion, and so forth) of each, performs a preliminary screening of the alternatives, and leaves the final decision until later.

2. Effect of the Reference Process Design on Safeguards.

The reference conversion process is described in Chap. II. The variety of chemical and physical forms in which plutonium is present is less than that in the reprocessing plant, primarily because of the absence of fission products, but somewhat greater than that in the mixed-oxide fuel fabrication facility, as a result of the wet front end of the conversion process.

Consequently, graded safeguards are an important part of the safeguards system. For example, consider the amount and form of material required to divert 2 kg of plutonium. Plutonium concentration in the receipt tank is $\sim$30 g/L so that $\sim$67 L ($\sim$17 gal) would be necessary to obtain 2 kg of plutonium. On the other hand, one product can holds $\sim$2 kg of plutonium oxide in a volume $<$2 L ($\sim$0.5 gal), which is much more attractive for diversion; also, conversion to the oxide is a necessary step in formation of plutonium metal, a step that the divertor does not have to perform if he steals from the filter boats coming out of the furnaces or the product dump and assay station. Thus, in-process material (the relatively dilute solutions) can be measured less precisely, consistent with the ability to draw material balances effectively.

The reference conversion process is semicontinuous; the precipitators run continuously, except during flushout, but the receipt tanks and filter boats are batched. However, the parallel processing lines and the continuous precipitation operation make it so difficult to relate input batches to output batches that batch accounting throughout the process is probably not feasible.

Timeliness and sensitivity to diversion can be improved significantly by drawing dynamic material balances, based on dynamic estimates of in-process inventory, around the conversion process or parts thereof. Because the process normally is operated semicontinuously, dynamic inventory estimates from upgraded process-control measurements, historical data, computer models, etc., will be crude compared with conventional physical-inventory measurements. However, significant advantages and improvements for both safeguards and process control are provided by dynamic accountability in near-real time. Moreover, dynamic accountability is absolutely necessary for adequate safeguards in high-throughput facilities, where even the best measurement accuracies available translate into large total uncertainties.

The frequency of dynamic balancing is essentially limited by the frequency of inventory estimates. A number of on-line measurements are already included for process control in the reference process design. For example, many tanks are instrumented for sampling and for level and density measurements; recycle streams have crude monitors to check for over-concentration of material as control indicators. These process-control measurements, perhaps with some upgrading, can be used to estimate in-process inventory.

Additional instrumentation required for dynamic balancing must be selected with care. Instrument reliability is a major concern, and recalibration of instruments must be considered. Load cells (for tank-weighing measurements) to supplement or replace level indicators have been suggested by some investigators because check weights can be installed with the load cells.

However, there is no reason why "one-point" calibration checks cannot be engineered into most instrumentation.

3. System Characteristics. In conventional safeguards systems, the filling out and transmitting of large numbers of materials accounting forms requires much time and effort. These forms include records of receipts, shipments, internal transfers, and accounting measurement data. The possibilities for human error, either unintentional or malicious, are rife, and inefficiency in data management is unavoidable.

Such problems can be greatly alleviated by implementing the MMAS through computerized data acquisition and data-base management, while retaining the conventional system as a backup in case of malfunction. Under this scheme, most instruments are interfaced directly to the computer system, and use of computer terminals for data input is minimized. Security problems are eased, and a self-verification capability is easily available if the instrumentation is designed for periodic on-line recalibration under computer control. Data from sources not connected to the computer system still may be entered through a minimal number of terminals.

The computer system acts as the central data manager for materials measurement and accounting and is a powerful tool in analyzing accounting data for possible SNM diversion. It generates all permanent records of materials quantities, locations, and movements, and on demand can provide reports required for effectiveness assessment, to determine the current status of the safeguards system, and so on. In addition, the computer system interacts with the other safeguards elements to ensure most efficient use of all safeguards data. Furthermore, data may be exchanged with the PCCU as required to improve both safeguards and process control.

4. Materials Measurement Subsystem. Most process tanks are instrumented for level and density measurements that are useful for both process control and nuclear materials accounting. In addition, we recommend inclusion of NDA devices for measuring solution concentrations, for crude measurements of in-process

inventory, and for quantification of nuclear material in recycle and waste streams. Table III-I lists the instruments necessary for materials accounting in the main conversion process line. Those for a possible recycle and recovery line are not included because it is not clear that such a recycle line will be required if the conversion process is eventually incorporated into a larger fuel reprocessing complex.

Estimates of measurement errors have been grouped in two categories. Instrument precision represents the estimated scatter in a set of individual raw measurements (for example, the uncertainty caused by counting statistics in NDA measurements). Calibration error represents the uncertainty in converting raw, measured values to the quantity of interest, for example, converting raw counts to plutonium mass for NDA measurements. Calibration errors are the most difficult to estimate because they include uncertainties in standards, calibration parameters, instrument environment, techniques, etc. No calibration errors are quoted for precipitator in-process inventory measurements because these errors approximately cancel in the error models for material balances and cumulative summations of material balances (cusums) (see Sec. IV-B).

One of the most important NDA techniques for safeguarding the conversion process is absorption-edge densitometry (see Appendix A of Ref. 1, and Appendix B of this report), which is an element-specific analytical method that can be applied on-line or in-line in most areas amenable to gross absorption measurements. Although gross gamma-ray and x-ray densitometry may be suitable for process control, they are susceptible to errors caused by the presence of elements of medium or high atomic numbers, which would be included in the total plutonium analysis. With proper choice of cell path length and either K- or L_{III}-absorption edges, plutonium concentrations between $\sim$5 and 400 g/L can be measured to a precision of better than 1% (1 σ) in the presence of impurities. Furthermore, the technique could be applied to simultaneous measurement of both plutonium and

TABLE III-I

MEASUREMENTS FOR DYNAMIC ACCOUNTABILITY IN THE CONVERSION PROCESS[a]

Measurement Point	Material Description	Measurement Type	Instrument Precision (1 σ, %)	Calibration Error (1 σ, %)	Measurement Frequency
Receipt tank	Pu in HNO_3, ∿30 g/L	Volume[b]	0.2	0.1	1/batch
		Concentration (by L-edge densitometry[c])	1	0.3	
Wet boat (precipitator output)	Plutonium oxalate	Mass (by neutron well counter[d])	2	5	1/boat
Precipitator holdup	Plutonium slurry	Mass (by He-3 neutron counter[e])	2	--	1/batch
Filtrate	Pu in HNO_3, ∿30 mg/L	Volume	0.2	0.1	1/batch
		Concentration (by alpha monitor[f])	10	2	
Precipitator flush	Pu in HNO_3, ∿5 g/L	Volume	0.2	0.1	3/day
		Concentration (by L-edge densitometry)	1	0.3	
Boat flush	Pu in HNO_3, ∿1.5 g/L	Volume	0.2	0.1	2/day
		Concentration (by x-ray fluorescence)	1	0.3	
Furnace sweep	Plutonium oxide	Mass (by neutron well counter)	2	0.5	1/week
Dump station sweep	Plutonium oxide	Mass (by neutron well counter)	2	0.5	1/day
Product cans	Plutonium oxide	Mass (by neutron well counter, calorimeter, or gamma spectrometer)	1	0.5	1/can

[a] Chap. II and Appendix A.

[b] Appendix B of Ref. 1.

[c] Appendix A of Ref. 1.

[d] Appendix B.

[e] Appendix B.

[f] Appendix F of Ref. 1.

uranium in a coprocessing mode of operation or to conversion of uranium-thorium fuels.

Accurate measurements of plutonium slurry in the precipitators and plutonium oxalate in the wet filter boats are difficult because of the material form and geometry. The methods chosen require that the chemical and isotopic compositions be available from analysis of samples taken from the process. These measurements contribute most of the uncertainty in material balance calculations for the conversion process. Although the devices and techniques are well developed, further field testing and evaluation for this particular application will be necessary.

Although it is not yet part of the conversion process design, there will almost certainly be some solid, low-level waste to be packaged in 200-L (55-gal) drums for disposal. These drums should be analyzed to prevent their use for illicit removal or concealment of materials. A drum scanner measuring the 414-keV gamma ray from ^{239}Pu can detect as little as 1 g of ^{239}Pu in a 5-min scan time.[57] The accuracy for measuring ~10 g of ^{239}Pu can be as good as ±10% for matrices of low-atomic-number combustible waste, and it ranges to ±50% for unknown matrices. The instrument is in an advanced stage of development, and only additional field testing and evaluation are required.

Some additional instrumentation is required for physical inventory, mainly at the dump and assay station and in the furnaces to measure holdup. Furnace holdup can be measured with a polyethylene-moderated ^{3}He detector shielded from external material. Accuracy is at least as good as 15% at a cost of $15 thousand. A similar device is suitable for the dump and assay stations. Other portable instrumentation for measuring holdup may be required, but at small cost.

5. Diversion Detection. Analysis of materials accounting data for possible SNM diversion is one of the major functions of the MMAS. Diversion may occur in two basic patterns: short-term (the single theft of a relatively large amount of SNM), and long-term (repeated thefts of SNM on a scale too small to be

detected in a single material balance because of measurement uncertainties).

Use of unit-process accounting and dynamic material balances enhances the ability to detect such diversions, but it also means that the safeguards system operator will be inundated with materials accounting data. Furthermore, although these data contain much potentially useful information about both safeguards and process control, the significance of any isolated (set of) measurements seldom is readily apparent and may change from day to day depending on plant operating conditions. Thus, the safeguards system operator is presented with an overwhelmingly complex body of information from which he must repeatedly determine the safeguards status of the plant. Clearly, it is imperative that he be assisted by a coherent, logical framework of tools that address these problems.

Decision analysis (see Appendix E of Ref. 1, and Ref. 58), which combines techniques from estimation theory, decision theory, and systems analysis, is such a framework, and it is well suited for statistical treatment of the imperfect dynamic material-balance data that become available sequentially in time. Its primary goals are (1) detection of the event(s) that SNM has been diverted, (2) estimation of the amount(s) diverted, and (3) determination of the significance of the estimates. Figure III-2 illustrates the decision-analysis process.

The detection function is based on acceptance of the hypothesis that some (initially unknown) amount of SNM has been diverted, versus the hypothesis that no diversion has occurred. One useful kind of decision test compares a likelihood ratio to a threshold, the likelihood ratio being defined roughly as the ratio of the probability that SNM has been diverted to the probability that it has not, and the threshold being determined by the desired false-alarm and detection probabilities.

The estimation function can take several forms, including that of the Kalman filter applied to the material-balance equation.[59-63] Additional information, such as detailed process

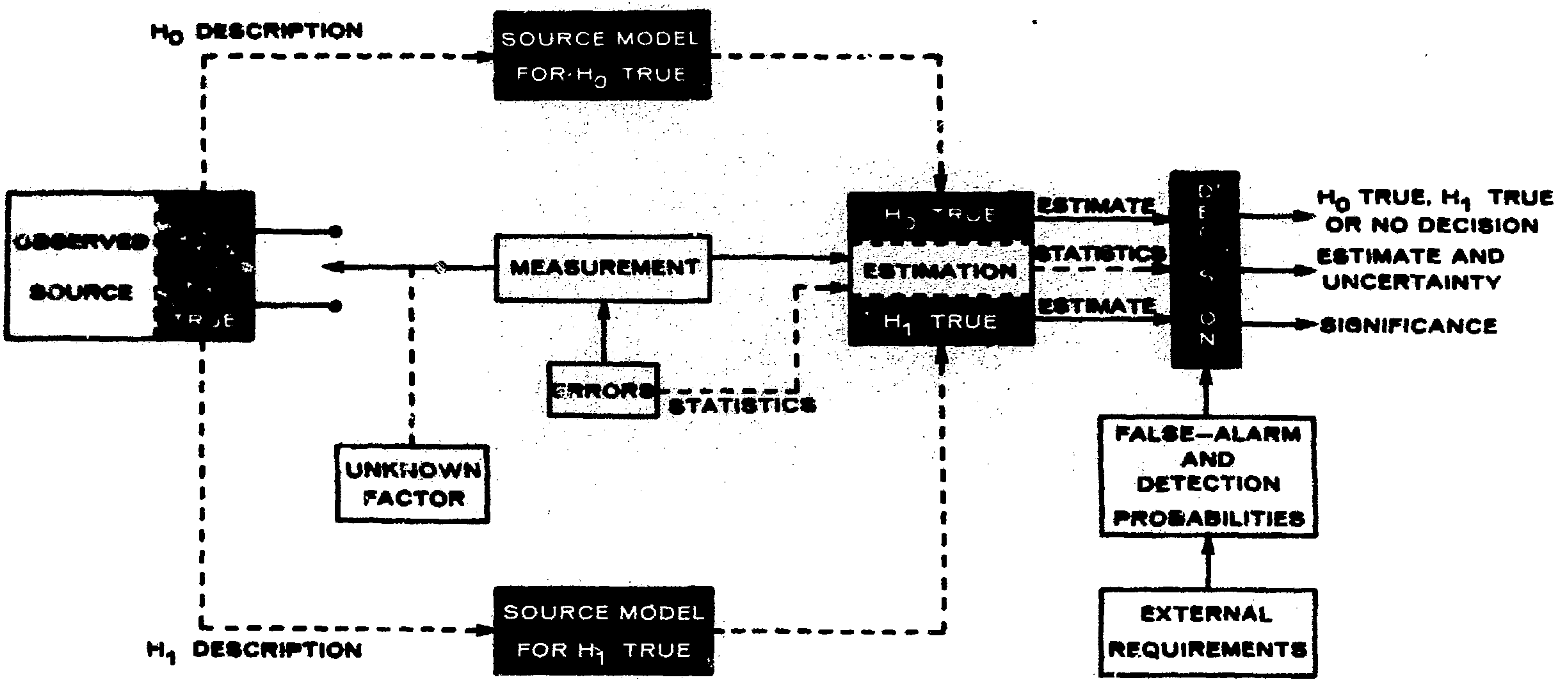

Fig. III-2. The decision-analysis process.

flow models, may be incorporated as desired. Effective estimation algorithms can greatly improve the detection function.

Pattern recognition techniques can be very useful for determining the significance of the estimates. One such tool is the alarm-sequence chart, which indicates (1) those material-balance sequences for which the possibility of diversion has been detected, (2) the false-alarm probability for that level of diversion, and (3) the length of the sequence. This chart has been most useful in separating material-balance sequences that have both normal unmeasured sidestreams and diversion from sequences without diversion.[50,64]

Decision analysis based on mathematically derived decision functions is appealing because it can quantify intuitive feelings and condense large collections of data to a smaller set of more easily understood descriptors (statistics). It can also eliminate personal biases and other errors caused by subjective evaluation of data while providing a degree of consistency for the decision process.

During actual operation the safeguards system operator will need a readily available battery of such techniques. One test or another often will yield inconclusive results, so that additional tests may provide further evidence to support his decisions. However, informed reason must govern interpretation of the test results. The fact that two different tests applied to the same data give similar (or at least consistent) results may or may not be significant, depending on the degree of independence of the tests; completely independent tests are clearly most desirable.

The safeguards system operator must be able to apply the decision analysis test quickly and easily in whatever fashion seems most appropriate at the moment, within the limit of good statistical-analysis practice, with reasonable assurance that he can understand the meaning of the results. It is unrealistic to expect all users to be equally proficient in test application and interpretation. Careful design of the human-engineering aspects of the tests minimizes these difficulties and enhances diversion detection.

6. Diversion Deterrence Factors. Besides its diversion detection and quantification functions, the MMAS also contributes to a potential divertor's perception of the probability that he will fail in his attempt. Therefore, it is important that safeguards capabilities be continuously demonstrated and advertised in general terms without disclosing information that would allow a divertor to take advantage of reduced safeguards effectiveness during, for example, periods of instrument malfunction. This means that whereas the general capabilities of the safeguards system should be widely known, the actual safeguards status at any time should be available only to those with a definite need to know.

Similarly, it is possible to conceal the true effectiveness of safeguards by random inspections of the facility, nonperiodic use of additional instrumentation, and even emplacement of dummy instrumentation. The last idea is widely practiced in commercial businesses in the form of fake TV cameras for surveillance. All these techniques combine to make a divertor think he is more likely to be caught, so he becomes more hesitant to make the attempt. However, these concepts, being based on subterfuge, are vulnerable to the knowledgeable insider.

C. Process-Monitoring System

The chemically hostile environment of a conversion plant requires that instrumentation be designed for physical ruggedness and reliability, which often significantly compromises measurement ability. Thus, there is a need for a limited set of on-line, plant-grade measurement equipment and other simple, reliable, process-monitoring devices specifically designed to detect an abnormal situation, with less regard for materials accounting. This represents an extension of some of the types of instrumentation used for physical protection into the process area for monitoring purposes.

To illustrate, consider a typical process tank that has an inlet, an outlet controlled by a valve and transfer jet, a liquid-level probe, a specific-gravity probe, a sampler, and an air-sparge line.[65] All valve positions are monitored, pressures in all transfer lines are measured, and each line has an SNM sensor (a simple go-no-go device). The process-monitoring system checks to see that all these variables are behaving in accordance with approved procedures. For example, a drop in tank level when all valves are closed, or a negative pressure in a probe line, would indicate an attempt to remove SNM from the tank.

Such a process-monitoring system can provide nearly immediate detection of diversion attempts by continuously comparing actual operating conditions with those expected. However, it must always be supplemented by materials accounting to indicate how well it has been working during the last accounting period. This is especially true if there has been some malfunction or if some part of the process-monitoring system could have been subverted.

D. Safeguards Systems Reliability

As previously discussed here and elsewhere,[1,50,51,66-68] safeguards system reliability is extremely important because it affects both safeguards effectiveness and process operations. Safeguards system reliability has two important aspects: <u>how often</u> can a safeguards failure be expected, and <u>how long</u> can a failure be expected to last. The first aspect is described by the mean time between failures (MTBF); the second, by the mean time to repair (MTTR). Equivalently, the probability of survival to a time t since the last failure is

$$P_s(t) = \exp(-t/\mathrm{MTBF}) \quad ,$$

and the fraction of time the system can be expected to operate, called the availability, is

$$A = \frac{MTBF}{MTBF + MTTR} \quad .$$

Both MTBF and MTTR (or P_s and A) must be known in assessing the impact of safeguards-related failures, particularly upon the process. Because of the relatively long transient response of the process, especially during startup and shutdown, the differential effect between one comparatively long-lasting failure and several shorter-lived ones of the same total duration can be large. Thus, one must guard against building into the system good availability (through low MTTR) at the expense of decreasing MTBF.

We believe the reliability of the safeguards system for the conversion plant should not differ greatly from that calculated for the mixed-oxide fuel fabrication facility.[50] Therefore, an MTBF of at least 3 months and an MTTR of less than 5 h seem achievable. Whether or not these figures are acceptable depends on the plant management's assessment of operational effectiveness and on safeguards considerations.

E. Safeguards Staffing

Table III-II lists the staff required for the conversion plant safeguards system, excluding the security force (discussed in the companion Sandia Laboratories report[53]). The required safeguards staff is smaller when the automated system is used. Furthermore, many support functions for the reference plant (for example, those for process control) also can support the safeguards system with only a small increase in personnel, especially if standard equipment is used throughout. These numbers do not reflect the possibility that the conversion process may be part of a larger facility. In that case, the safeguards staffing burden on the conversion process would be much smaller because the levels shown in Table III-II are sufficient to handle a combination reprocessing and conversion complex.

TABLE III-II

SAFEGUARDS STAFFING FOR THE CONVERSION PLANT

Supervisory Personnel	
Materials management manager	1
Data evaluation specialist	1
Senior level professionals	4

Shift Personnel (Total for four shifts)	
Safeguards officer	4
Safeguards assistant	4
Data analyst	4
Computer staff	12
Instrumentation technician	4
Safeguards line inspector	8
TOTAL	42

F. Safeguards Costs

The safeguards costs given in Table III-III are estimates of the costs of additional instrumentation required to draw dynamic material balances and perform the physical inventories. Costs of volume-measuring and other devices necessary for process control are not included, nor are data on the physical-protection or process-monitoring systems. Allowances are made for floor space, engineering planning (architectural engineering), installation, equipment engineering design and procurement, and contingency.

The costs and numbers of instruments shown in the table are conservative, and no credit is taken for instrumentation of this type that may be required for process control. In some cases,

TABLE III-III

SAFEGUARDS COSTS

Item	Unit Cost ($ thousand)	Number	Extension ($ thousand)
Safeguards computer and information system hardware	400	1	400
Spare parts (at 25%)	--	--	100
Software development (at 300%)	--	--	1500
Absorption-edge densitometer (plus two spares)	100	7	700
Neutron counter[a] (plus three spares)	40	17	680
Alpha monitor (plus two spares)	15	14	210
X-ray fluorescence device (plus one spare)	15	2	30
Portable neutron counter for furnace holdup and dump and assay station (plus one spare)	15	2	30
Miscellaneous portable instrumentation			100
SUBTOTAL			3740
Equipment engineering design and procurement (at 15%)			560
Contingency (at 30%)			1290
TOTAL			5590

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[a] In some cases, e.g. for product cans, calorimeters or gamma spectrometers could be substituted at similar cost.

it may be possible to use the same instrument in several locations but separate instruments are specified. The projected costs of many of these devices (e.g., the absorption-edge densitometer) may decrease as development proceeds.

Safeguards staffing costs are assumed to be $20 thousand/man-yr with 150% overhead, for a total (see Table III-II) of $2.1 million. Yearly software maintenance and modification are taken to be 10% of the original software cost, or about $150 thousand. Hardware maintenance and supplies, at 10% of the original hardware cost, consume about $200 thousand/yr. Thus, the operating cost for this part of the safeguards system should be about $2.5 million/yr.

IV. SAFEGUARDS EFFECTIVENESS EVALUATION

A. Evaluation Methodology

The main conversion process line from receipt of the nitrate feed to loadout of the oxide product is an especially important part of the fuel cycle from the standpoint of safeguards, because fissile material is processed in relatively pure and concentrated forms. The reference conversion process and the conceptual safeguards system are described in Chaps. II and III, respectively. The results presented in this chapter are derived from a detailed evaluation of concepts proposed for dynamic accountability in the main process line. Promising strategies, both for instrumentation and accounting procedures, are evaluated and compared. Evaluation methodologies developed during previous safeguards studies[1,50,69] provide reliable, quantitative estimates of detection sensitivity, and these quantitative results are the basis for credible recommendations.

Operating histories of modern, commercial conversion facilities are not yet available. However, a dynamic model of the conversion process has been developed and is described in Appendix A. This model, called NOCSIM, is used for computer simulation of process operation. The simulated data from NOCSIM represent the materials flows and inventories under normal conditions, when the process is operating near equilibrium. These simulated data are consistent with current best estimates of the expected performance of the process. Validating this process model and modeling related processes such as coconversion are important steps in follow-on safeguards design studies which should be taken at the earliest opportunity.

Models of ac surements and associated measurement errors a next section. Equations for dynamic material balances and cusums of dynamic balances are given (see also Appendix C), along with models for the uncertainties caused by measurement errors. The model measurements are applied to the simulated process-flow data using a computer code, MEASIM, developed for that purpose. The measured values are combined to form dynamic material balances given various strategies for dynamic materials accounting. Key measurement points include the receipt tanks and the product-dumping stations. The plutonium concentration in the nitrate feed solution is measured using absorption-edge densitometry. The plutonium content of product canisters is measured using calorimetry and/or NDA gamma and neutron techniques (Chap. III and Appendix B). These on-line measurement methods are element or isotope specific; this feature would be equally important for application to coconversion processes. In most cases, the measurement models are based on the performance of similar instrumentation characterized in both laboratory and field applications with similar materials.

The most promising measurement and accounting strategies are combined with powerful statistical data analysis and sequential decision techniques in comparative studies of diversion sensitivity. A general framework of data analysis and decision methods has been developed, and is described in detail in Ref. 1, Vol. II, Appendix E. Within this framework, the cusum, Kalman filter, and other data analysis techniques are combined naturally with techniques from decision theory such as the V-mask and the sequential probability ratio tests. This approach is called decision analysis (Chap. III). A versatile computer code, DECANAL, has been developed to apply the decision-analysis algorithms to simulated accounting data. These algorithms are relatively simple to implement on a modest-sized computer. Interpretation of the results is aided by computerized display and pattern recognition tools such as the alarm-sequence chart.[63] This package is an important first step in software development of dynamic accountability systems.

The effectiveness of the materials measurement and accounting system is evaluated by applying the decision-analysis algorithms to the simulated accounting data. Sensitivity to diversion and effective false-alarm and detection probabilities are estimated by examining test results from many sets of materials-accounting data derived from the process and measurement models.

The decision tests include the Shewhart (material balance) chart, the cusum with alarm-sequence chart, the Kalman filter with alarm-sequence chart, and the nonparametric Wilcoxon rank sum test with alarm-sequence chart.

The Shewhart chart is the oldest graphical-display tool widely used by industry for process control.[70,71] In its standard form, measured data are plotted sequentially on a chart with warning and action limits. These limits are usually set at the 2-σ and 3-σ levels, respectively. In safeguards applications, the Shewhart chart is a sequential plot of the material balance data with 1-σ error bars.

The cusum chart, developed in England, was first used during the early 1950s for improved process control.[71] It and its near relative, the Wald test, developed in the United States during World War II, have found wide acceptance in industry because, unlike the Shewhart chart, they are sensitive to small shifts in process parameters. The cusum is very easy to calculate; it is simply the unweighted cumulative summation of the raw data. The cusum chart is a sequential plot of the cusum values. We have applied it to safeguards by sequentially plotting the cusum of dynamic balances and its standard deviation, which are calculated from the raw material balance data.[1,50,64]

The Kalman filter has found wide application to communications and control systems for signal processing in stochastic environments. It is a powerful tool for extracting weak signals embedded in noise. Its application to safeguards is relatively new,[1,61-63] and has arisen because dynamic accountability systems will rapidly generate large quantities of data that may contain "weak signals" caused by repeated, small diversions.

A new application of the nonparametric Wilcoxon test and the associated rank-sum chart to safeguards data is described in Ref. 1. This test has been used in other fields to analyze data for which the underlying distribution of the measurement uncertainty is unknown. Like the cusum, the Wilcoxon test is very easy to implement; it calculates a weighted sum of the number of positive values in sets of material balance data.

The algorithms for the Shewhart chart, cusum, and Kalman filter are structured to account for correlated data so that correct variances are computed for the associated decision tests. The actual false alarm and detection probabilities for the Wilcoxon test depend on the degree of data correlation. If correlations are large, the Wilcoxon test performance will suffer unless corrective measures are taken.

The Shewhart chart is included in the examples (Sec. C) to illustrate the improved detection of long-term diversion that is possible with more sophisticated data analysis techniques. Although useful for detection of single, large thefts, the Shewhart chart tends to obscure trends in the material balance data, such as those caused by long-term diversion.

The cusum and the Kalman filter are complementary in several respects. The cusum estimates the total amount of missing SNM at the current time, and its standard deviation is taken as the 1-σ error in the estimate of the total. The Kalman filter, on the other hand, estimates the average amount of SNM missing from each material balance, and its standard deviation estimate is taken as the 1-σ error in the estimate of the average. Thus, both the cusum and Kalman filter search for a persistent, positive shift of the material balance data, the cusum by estimating the total, the Kalman filter by estimating the average.

However, the Kalman filter has two advantages over the cusum. First, it provides a better indication of missing SNM because it makes more efficient use of available information; tests based on Kalman filter estimates are more discriminating. Second, certain forms of the Kalman filter provide improved estimates of in-process inventory, useful for both process control and safeguards. Disadvantages of the Kalman filter are its relative complexity and the fact that its application requires considerable care.

The decision tests must examine all possible, contiguous subsequences of the available material balance data because, in practice, the time at which a sequence of diversions begins is never known _a priori_.[1,50,64] Furthermore, to ensure uniform application and interpretation, each test should be performed at several levels of significance. Thus, a graphical display that indicates those sequences that cause alarms, specifying each by its length, time of occurrence, and significance, is essential. One such tool is the alarm-sequence chart,[64] a type of pattern recognition device that has proven very useful for summarizing the results of the various tests and for identifying trends.

To generate the alarm-sequence chart, each sequence that causes an alarm is assigned a descriptor that classifies the alarm according to its significance (false-alarm probability), and a pair of integers (r_1,r_2) that are, respectively, the indexes of the initial and final material balances in the sequence. The alarm-sequence chart is a point plot of r_1 vs r_2 for each sequence that caused an alarm, with the significance range of each point indicated by the plotting symbol. The correspondence of plotting symbol to significance is given in Table IV-I. The symbol T denotes sequences of such low significance that it would be fruitless to examine extensions of those sequences; the position of the symbol T on the chart indicates the termination point.

For example, consider a sequence of material balance data beginning at balance number 12, and suppose that one of the tests gives an alarm with a false alarm probability of 2×10^{-4} at balance number 19. Then on the alarm sequence chart for that test, the letter D would appear at the point (12,19). This procedure continues for all possible subsequences of the available material balances. Clearly, it is always true that $r_1 \leq r_2$

TABLE IV-I

ALARM CLASSIFICATION FOR THE ALARM-SEQUENCE CHART

Classification (Plotting Symbol)	False-Alarm Probability
A	10^{-2} to 2×10^{-3}
B	2×10^{-3} to 10^{-3}
C	10^{-3} to 5×10^{-4}
D	5×10^{-4} to 10^{-4}
E	10^{-4} to 10^{-5}
F	10^{-5} to 10^{-8}
G	$< 10^{-8}$
T	~ 0.5

so that all symbols lie to the right of a 45° line through the origin. Persistent data trends (repeated diversion) cause long alarm sequences ($r_1 << r_2$), *and the associated symbols on the* alarm chart extend far to the right of the 45° line.

Measurement and measurement error models are described in the following section. Sample results from sensitivity studies made using the decision-analysis techniques are given in Sec. C.

B. Measurement and Error Models

1. Measurements. Operation of the materials measurement and accounting system is simulated using the Monte Carlo computer code MEASIM (Measurement Simulation). This code simulates measurement of the true material flow data generated by NOCSIM (see Appendix A) and transmits appropriate measured values to DECANAL, the safeguards data-analysis code.

MEASIM incorporates both additive and multiplicative measurement-error models,[70] although for this study only the multiplicative model is required. In this model, the measured value M of a true quantity μ is given by

$$M = \mu(1 + \varepsilon + \eta) , \tag{IV-1}$$

where ε is the relative error caused by instrument imprecision, and η is the relative error produced by uncertainty in the instrument calibration. Both errors are assumed to be independent and to be normally distributed with mean zero and variances σ_ε^2 and σ_η^2, respectively. The variance σ_M^2 of M is given by

$$\sigma_M^2 = \mu^2 \left(\sigma_\varepsilon^2 + \sigma_\eta^2\right) . \tag{IV-2}$$

All measurement results obtained from a given instrument using the same set of values for the calibration parameters are correlated through the calibration error η. The covariance σ_{ij} between the i^th and j^th measured values is given by

$$\sigma_{ij} = \mu_i \, \mu_j \, \sigma_\eta^2 . \tag{IV-3}$$

In the simulation, a value for η is periodically sampled from the appropriate distribution to coincide with the frequency of instrument recalibration. A value of ε is sampled for each measurement. Variance and covariance terms are estimated by replacing the true quantities μ in Eqs. (IV-2) and (IV-3) by the appropriate measured quantities.

The precisions assigned to the measurements are based on estimates for similar instrumentation obtained from the literature (see Sec. III-B, and Appendix B). A table of specific instrument applications and their associated uncertainties (Table III-I) is given in Sec. III-B.

2. Material Balances. Each material balance is a linear combination of measured quantities P_i of plutonium:

$$MB = \sum_{i=1}^{n} c_i P_i , \tag{IV-4}$$

where $c_i = +1$ (-1) if P_i is an input (output) quantity for the accounting area. Often, the measured mass of plutonium is given by the product of two different measured quantities:

$$P = xy, \tag{IV-5}$$

where x is either liquid volume or mass, and y is the plutonium concentration or mass fraction. The measurement error model for both x and y is similar to that given in Eq. (IV-1), namely

$$x = X(1 + \varepsilon + \eta)$$

$$y = Y(1 + \gamma + \delta), \tag{IV-6}$$

where X and Y are true values, and the error components are defined as in Eq. (IV-1).

The variance σ_{MB}^2 in the computed value of a material balance is a combination of the uncertainties in the contributing measured values. Ordinarily, a number of measurements will be made using a given instrument before it is recalibrated, and appropriate correlation terms must be included in the computation of the material-balance variance. The general form of the equation used to compute the approximate variance of each material balance is

$$\sigma_{MB}^2 = \sum_{i=1}^{n} X_i^2 Y_i^2 \left(\sigma_\varepsilon^2 + \sigma_\gamma^2\right)$$

$$+ \sum_{i=1}^{n} \sum_{j=1}^{n} c_i c_j \, X_i X_j \, Y_i Y_j \left(q_{ij}\sigma_\eta^2 + p_{ij}\sigma_\delta^2\right) . \tag{IV-7}$$

The quantity q_{ij} is +1 if X_i and X_j have been measured with a common value of η (that is, using the same instrument calibration) and is zero otherwise. Similarly, p_{ij} is +1 or 0, depending on whether a common value of δ was used in the measurements of Y_i and Y_j. Each i=j term in the double sum in Eq. (IV-7) is the component of variance due to calibration uncertainty for a single measurement; these terms are present even if all measurements of X or Y are uncorrelated.

Measured values of net material transfers and initial and final in-process inventories, along with appropriate components of variance and covariance, are passed to the safeguards data analysis code for each material balance period. These quantities are sufficient for computation of material balances, cusums, and the other test statistics described in Appendix E of Ref. 1.

In terms of the net transfer T, initial inventory I_i, and final inventory I_f, the material balance equation becomes

$$MB = T + I_i - I_f \quad . \qquad \text{(IV-8)}$$

Because two inventory measurements appear with opposite signs in each material balance equation, the terms in the computation of the material balance variance, Eq. (IV-7), that arise from calibration errors in the inventory measurements approximately cancel. The magnitude of these terms is $(I_i - I_f)^2 \sigma_\eta^2$. If the model process is operated near equilibrium, so that $I_i \cong I_f$, the contribution to σ_{MB}^2 is relatively small; i.e., calibration errors in the inventory measurements partially cancel. In the error model, perfect cancellation is assumed and σ_η is set to zero for all in-process inventory measurements.

3. Cusums. A cusum is computed after each material balance period. It is the sum of all material balances for the unit process since the beginning of the accounting period. The cusum variance is a complex combination of the variances of individual material balances, as these balances usually are not independent. There are two principal sources of correlation between material balances. The first is the correlation, discussed previously, between measurement results obtained using a common instrument calibration . The magnitudes of the associated covariance terms depend on the magnitude of the calibration error and the

frequency of each instrument recalibration; omission of these terms can cause gross underestimation of the cusum variance. The second source of correlation between material balances is the occurrence, with opposite signs, of each measured value of in-process inventory in two adjacent material balances. As a result, only the first and last measurements of in-process inventory appear in the cusum, and only the corresponding variances appear in the cusum variance. The cusum variance is computed using an equation that has the same form as Eq. (IV-7). Detailed equations for material balances, cusums, and their associated variances are given in Appendix C.

C. Accounting Strategies and Effectiveness Evaluation

1. Accounting Strategies. The conversion process (Figs. II-1 and II-2) has four identical precipitation lines operated in parallel. These lines are instrumented identically. Therefore, dynamic accountability was simulated for a single representative line, which produces one product batch (∿2 kg of PuO_2) every 1.35 h on the average.

Two basic strategies for dynamic materials accounting were investigated. Both use the same measurements and measurement points (Table III-I). In each, dynamic material balances are formed from periodic measurements of transfers and in-process inventories. For each batch, (1) receipt tank in-process inventory, (2) precipitator in-process inventory, (3) precipitator product (wet cake in filter boats), (4) filtrate and wash solutions, and (5) product cans are measured. Approximately once a day, (1) precipitator flush solution, (2) boat flush solution, and (3) loose powders recovered from the dumping station are measured. The loose powders recovered from the furnace are measured approximately once a week.

All instruments, except those that measure volume, are recalibrated once a day while the precipitator line is being drained and flushed, a period of about 8 h. Volume measuring instruments are not recalibrated during the accounting periods.

a. First Accounting Strategy. The first accounting strategy consists of two unit process accounting areas. The first unit process boundaries are at the receipt tanks and the filter boat loading stations. The second area boundaries are the filter boat loading stations and the oxide product dumping station. The residence time of the material is a little more than 1 h in the first unit process and ~6 h in the second, most of which is required for calcining.

As Table III-I shows, the large calibration uncertainty estimated for wet boat measurement strongly affects this accounting strategy because each wet boat is the output from the first unit process and the input for the second. Thus, large uncertainties and correlations in the wet-boat measurements affect both unit processes. Two cases are compared to illustrate this effect. The first uses the 5% calibration error estimated for wet-boat measurements in Chap. III (Table III-I). In the second, a significantly improved calibration that uses better standards to characterize the oxalate slurry is assumed, and the calibration error is reduced to 1%.

These two cases are compared in Figs. IV-1 through IV-4 and in Table IV-II. In the figures, material balance and cusum data are plotted for a typical week of simulated operation. One-sigma error bars are plotted with each data point. These errors include correlations between material transfer measurements, and correlations that are introduced because an ending inventory of one balance period is the beginning inventory of the next period (see Sec. IV-B and Appendix C).

The following conclusions are drawn from an examination of Figs. IV-1 through IV-4 and Table IV-II.

- Errors in measurement of net transfers of material and material balances are dominated by errors in calibration of the wet-boat measurements. The large calibration uncertainty introduces a bias that persists during each daily calibration period.

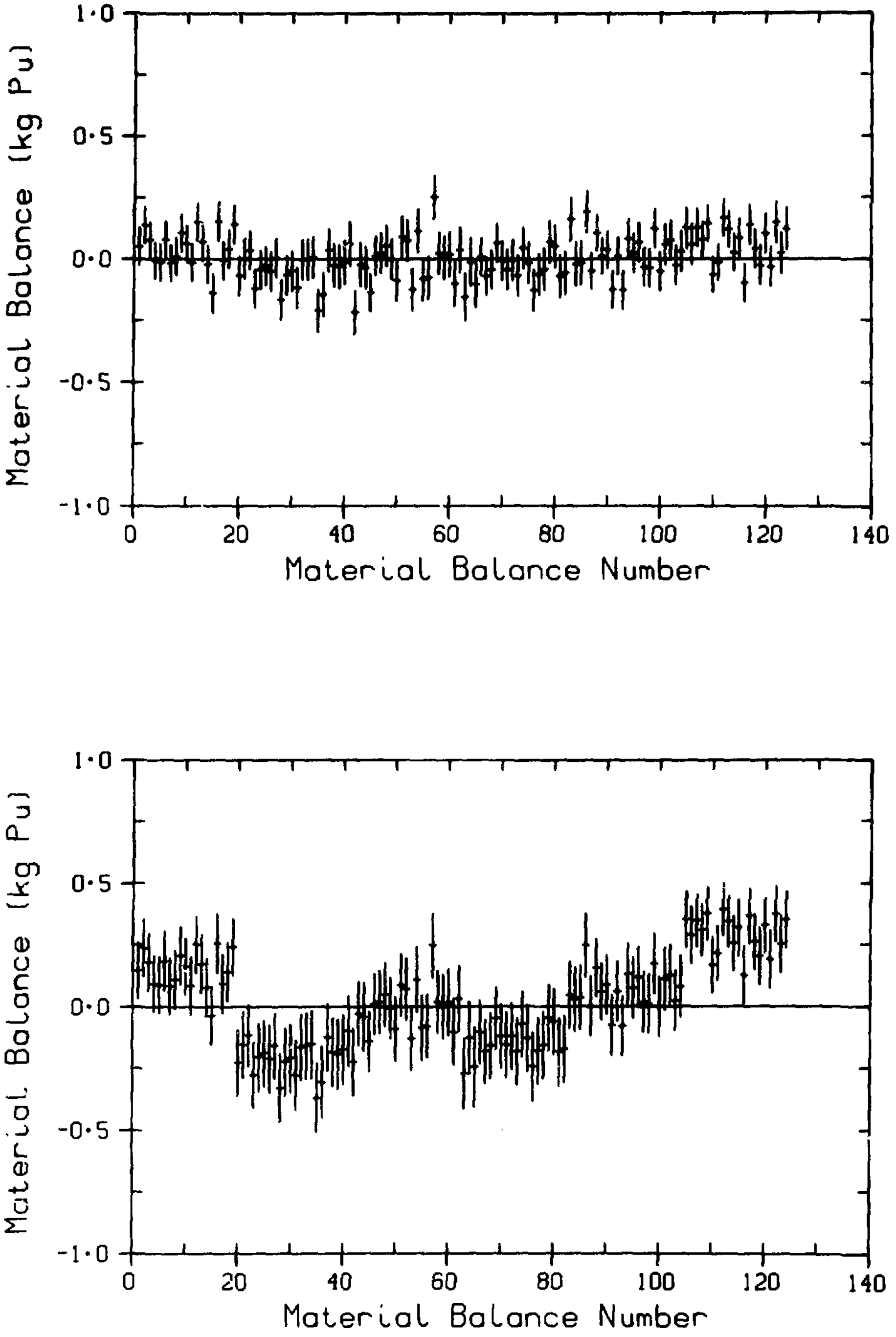
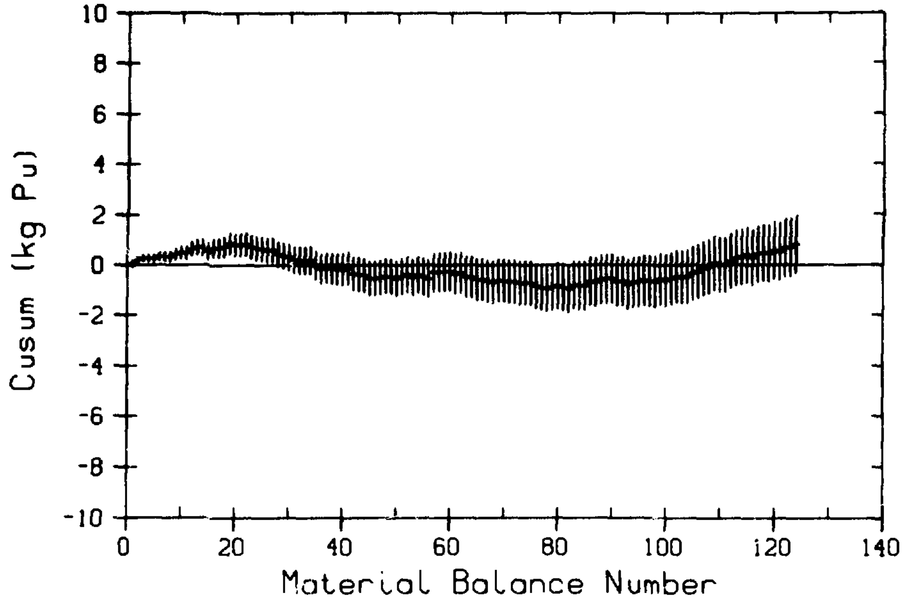


Fig. IV-1. Material balance charts for strategy one, accounting area one: calibration error = 1% (upper), 5% (lower).



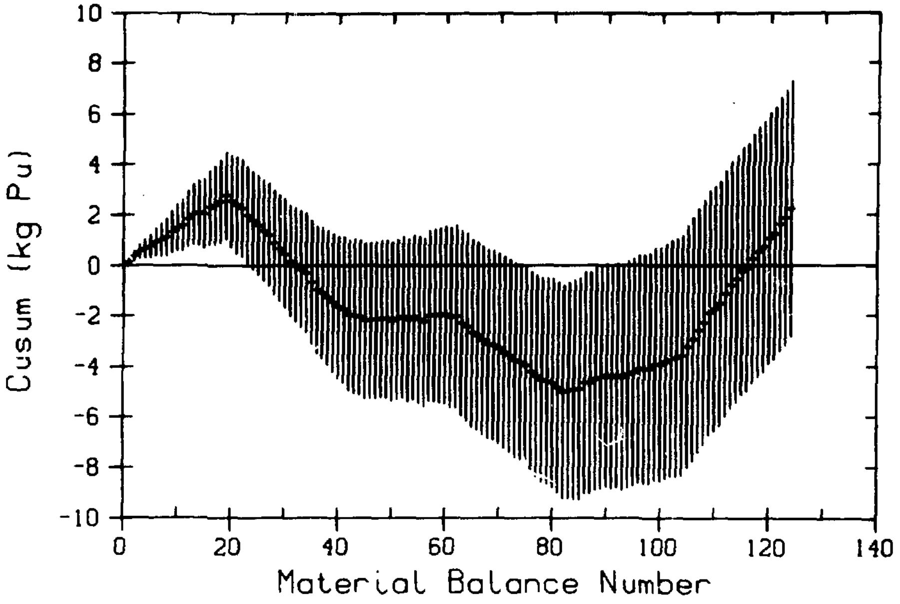


Fig. IV-2. Cusum charts for strategy one, accounting area one: calibration error = 1% (upper); 5% (lower).

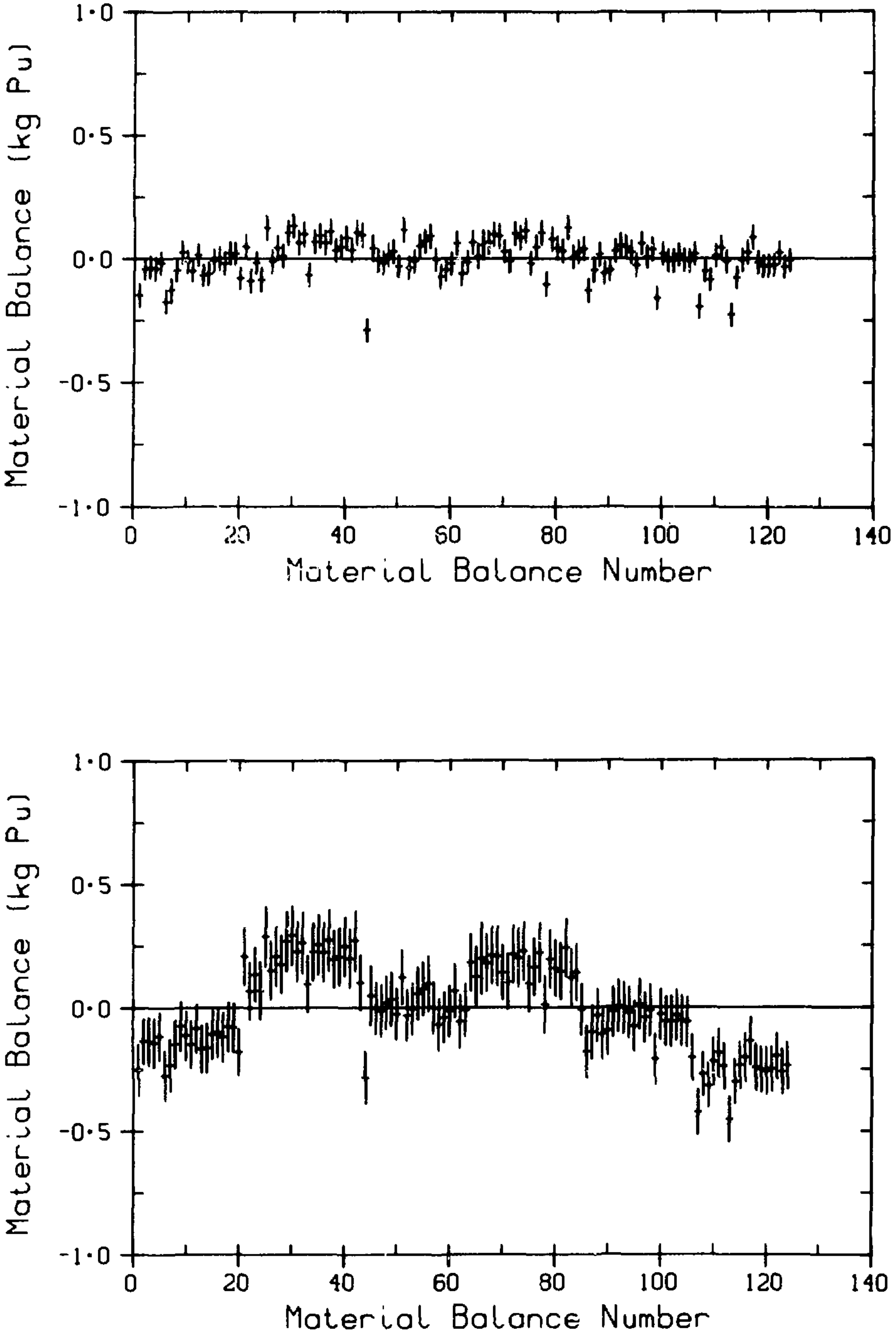
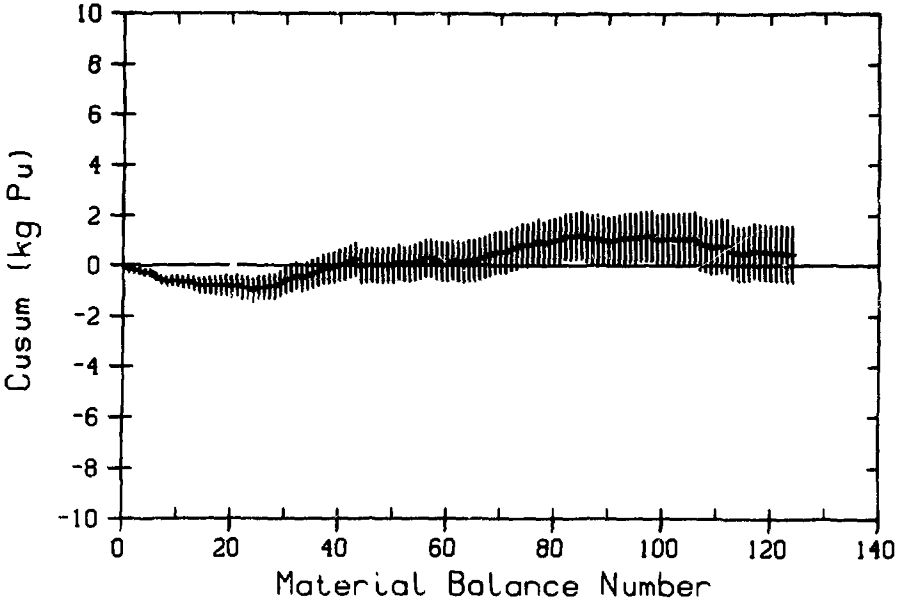


Fig. IV-3. Material balance charts for strategy one, accounting area two: calibration error = 1% (upper); 5% lower.



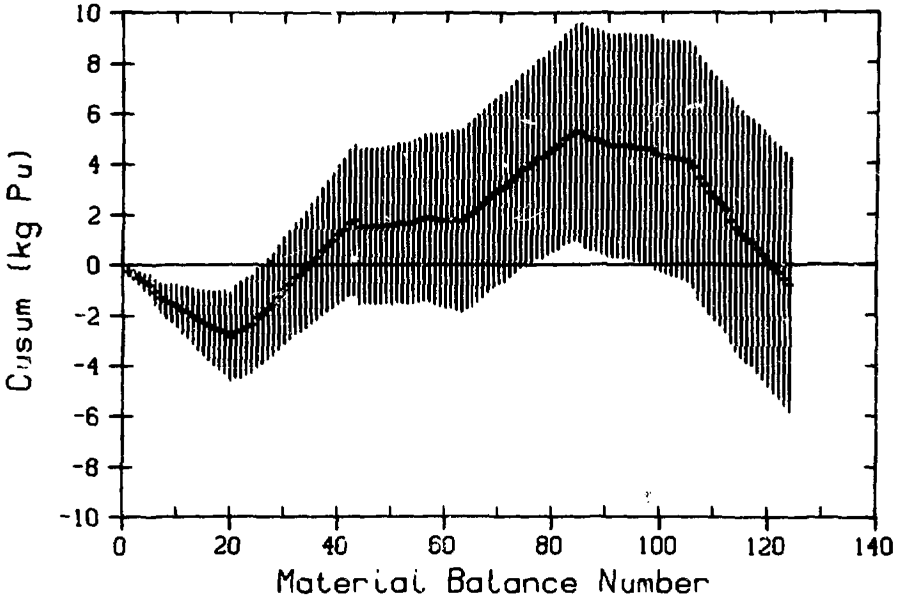


Fig. IV-4. Cusum charts for strategy one, accounting area two: calibration error = 1% (upper); 5% (lower).

TABLE IV-II

MEASUREMENT ERRORS IN THE FIRST ACCOUNTING STRATEGY

	Variance, kg^2 Pu (Standard deviation, kg Pu)			
	Calib. Error = 5%		Calib. Error = 1%	
	Area 1	Area 2	Area 1	Area 2
Net transfers[a]	0.013 (0.11)	0.012 (0.11)	0.0027 (0.052)	0.0026 (0.051)
In-process inventory[a]	0.0019 (0.043)	--	0.0019 (0.043)	--
Material balance[a]	0.017 (0.13)	0.012 (0.11)	0.0065 (0.079)	0.0026 (0.051)
Cusum[b]	24.9 (5.0)	24.7 (5.0)	1.3 (1.1)	1.3 (1.1)

---

[a] A one-week average.

[b] At the end of a week.

- Correlated wet-boat measurements contribute most to the uncertainty in the cusum.
- The size of the cusum uncertainty by the end of one week is almost linearly proportional to the size of the wet-boat calibration error.
- The biases associated with the large wet-boat calibration error introduce observable trends into the cusum.
- Material balance and cusum data on the first and second unit processes are nearly "mirror images" because the bias associated with the wet-boat calibration error appears with opposite signs in the material balances of the two accounting areas.

b. Second Accounting Strategy. If a calibration error of ∿5% is the best available for wet-boat measurements, a different accounting strategy that uses the same set of measurements, but in which the wet boats become part of the in-process inventory, improves the detection sensitivity. This is because the beginning and ending inventories for each balance period are approximately the same size and appear in the material balance with opposite signs. Under these conditions, calibration errors associated with measurements of in-process inventory tend to cancel (see Sec. IV-B).

A second accounting strategy combines the two unit processes of the first strategy into one accounting area. The boundaries are the receipt tanks and the product dumping station; i.e., each main process line is a single unit process. The receipt tank feed and dump station product transfers are identical to those of the first strategy. However, the in-process inventory includes the contents of wet boats in the furnace as well as the precipitator contents. The furnace inventory is composed of the contents of four boats. The in-process inventory is much greater in this strategy, ∿10 kg of plutonium compared with 2 kg in the first strategy.

Calibration errors that affect the in-process inventory measurements of the precipitator and of the wet boats entering the furnace are assumed to cancel completely. However, measurement errors due to instrument precision (Table III-I) significantly affect the in-process inventory measurements because the inventory is large.

The effect of changing the relative precision of in-process inventory measurements from 2 to 5%, for both the precipitator and wet boat measurements, is shown in Table IV-III. This factor of 2.5 change in precision produced the following results:

- The net transfer measurement errors are unchanged, as expected.
- The in-process inventory measurement error increases by a factor of 2.5.
- In both cases, the in-process inventory error dominates the material balance error, and the material balance error increases by a factor of 2.5.

TABLE IV-III

MEASUREMENT ERRORS IN THE SECOND ACCOUNTING STRATEGY

	Variance, kg^2 Pu (Standard deviation, kg Pu)	
	Instrument Precision = 5%	Instrument Precision = 2%
Net transfers[a]	0.0011 (0.033)	0.0011 (0.033)
In-process inventory[a]	0.050 (0.22)	0.0081 (0.090)
Material balance[a]	0.10 (0.32)	0.016 (0.13)
Cusum[b]	0.53 (0.73)	0.45 (0.67)

---

[a] A one-week average.

[b] At the end of a week.

- Correlated material transfer measurements contribute most to the cusum error by the end of a week, so the cusum error at the end of a week changes only ∿10%.

c. <u>Comparison of the Two Accounting Strategies</u>. The first and second accounting strategies, using the measurement error parameters given in Table III-I, are compared in Table IV-IV. The following conclusions are drawn.

- The net transfer measurement error in strategy two is less than in strategy one because it does not include a wet-boat transfer.
- The in-process inventory error in strategy two is larger because it includes the furnace inventory of wet boats.
- Material balance errors are approximately the same in both strategies.

TABLE IV-IV

MEASUREMENT ERRORS IN THE TWO STRATEGIES

	Variance, kg^2 Pu (Standard deviation, kg Pu)		
	First Strategy		
	Area 1	Area 2	Second Strategy
Net transfers[a]	0.013 (0.11)	0.012 (0.11)	0.0011 (0.033)
In-process inventory[a]	0.0019 (0.043)	-- --	0.0081 (0.090)
Material balance[a]	0.017 (0.13)	0.012 (0.11)	0.016 (0.13)
Cusum[b]	24.9 (5.0)	24.7 (5.0)	0.45 (0.67)

---

[a] A one-week average.

[b] At the end of a week.

- At the end of a week, the cusum error in strategy one is significantly larger because of the contribution of correlations in the wet-boat transfer measurements associated with the large calibration error.

If calibration of the wet-boat measurements can be improved, to say 1%, comparisions of detection sensitivies of the two accounting strategies become much closer than Table IV-IV indicates. Strategy one has two accounting areas, so a potential diversion can be better localized in one of them. Strategy one, with improved wet-boat measurement calibrations, provides greater sensitivity to single thefts; i.e., errors in the material balances would become smaller in strategy one than in strategy two. Strategy two, however, is more sensitive to long-term, low-level diversion in all cases considered.

These two accounting strategies complement each other. The same measurements and measurement points are used in both. The same data are analyzed in different ways. This flexibility provides safeguards advantages that should be exploited using analysis software constructed for this purpose.

The same principle applies to the accounting data collected from each main process line. The total data base can be examined using appropriate analysis software designed to counter strategies based on manipulation and eventual diversion of material from all process lines. This concept of overlapping unit processes provides additional safeguards assurance.

2. Effectiveness Evaluation. The ability of the materials measurement and accounting system to detect diversion from the conversion process has been evaluated by applying the methodology outlined in Sec. IV-A to the second accounting strategy in which each process line is considered as a separate unit process accounting area. The estimated detection sensitivity levels are given in Table IV-V for periods of one material balance (one batch), one day (about 20 batches), one week (about 125 batches), and one month (about 530 batches). The number of batches per day is not constant because the schedule for daily flushing of precipitators can vary.

Sample results of sensitivity studies are given in Figs. IV-5 through IV-28. Eight figures each are presented for operating periods of one day (the nominal time between precipitator flushouts), one week, and one month. In each figure, the upper plot shows accounting data from typical operation of the model process, and the lower gives data from the same operating period, but with a uniform diversion pattern. The diversion levels are the estimated sensitivity levels given in Table IV-V, i.e., 30 g of plutonium per material balance period for 1 day, 10 g per balance for 1 week, and 5 g per balance for 1 month. Examination of many sets of such data indicates that these sensitivity levels are conservative. The probability of false alarms estimated for each period is ∿5%.

The figures in each set contain the following information (see Sec. IV-A).

TABLE IV-V

DIVERSION SENSITIVITY[a] OF THE CONVERSION PROCESS

Detection Period	Average Diversion per Balance (kg Pu)	Total at Time of Detection (kg Pu)
One batch	0.13	0.13
One day	0.03	0.63
One week	0.01	1.24
One month	0.005	2.65

---

[a] As determined for a single process line in the second accounting strategy according to ERDAM Appendix 7401-C, "Nuclear Materials Management and Safeguards System Handbook."

(1) Material balance (or Shewhart) charts--The dynamic material balances are plotted sequentially with one-sigma error bars.

(2) Cusum charts--Cumulative summations of dynamic balances are plotted sequentially with one-sigma error bars.

(3) Alarm-sequence charts for the cusum data--Symbols indicate the length and significance of each sequence of dynamic material balances that generated an alarm.

(4) Estimates of in-process inventory--Kalman filter estimates of in-process inventories are plotted sequentially with one-sigma error bars.

(5) Estimates of missing material--Kalman filter estimates of average amounts of missing material per balance period are plotted sequentially with one-sigma error bars.

(6) Alarm-sequence charts for the Kalman filter estimates--Same as (3) but derived from the Kalman filter estimates of missing material.

(7) Wilcoxon rank-sum charts--Ranking data obtained by applying the Wilcoxon nonparametric test to the dynamic material balance data are plotted sequentially with one-sigma error bars.

(8) Alarm-sequence charts for the Wilcoxon data--Same as (3) but derived from the Wilcoxon test.

D. Summary

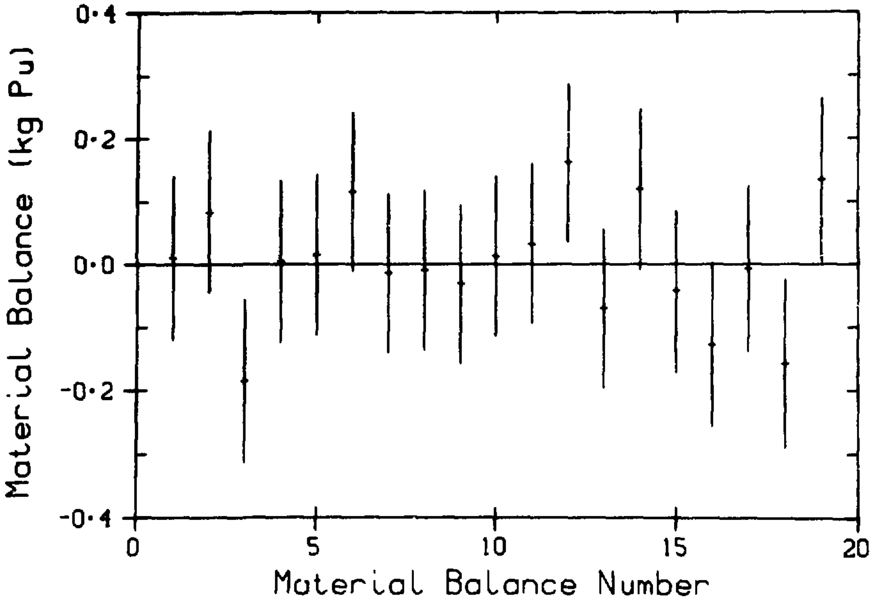
The conceptual dynamic accountability system for the conversion process (Chap. III) is close-coupled to the process line. As such, it combines enhanced, real-time process monitoring with quantitative, element-specific measurements for accounting purposes. Detection sensitivities of the dynamic system estimated during various operating periods are given in Table IV-V. Sample results from application of the data analysis techniques to simulated operating data are given in the figures.

In comparison, current regulations[72] require that conventional periodic material balancing in conversion plants be performed on a two-month inventory cycle. The material balance uncertainty (2 σ) must be less than 0.5% of the facility throughput for each two-month accounting period. This limit of error corresponds to 33 kg of plutonium for the reference conversion process, which has a design throughput of 6600 kg of plutonium in two months. A recent estimate[73] of the 2-σ limit of error that should be achievable by periodic, two-month material balancing in conversion plants is 0.38%, which corresponds to about 25 kg of plutonium for the reference process.

The dynamic system is sensitive to changes in process operation. For example, the Kalman filter estimates of in-process inventory (Fig. IV-16) clearly show the daily precipitator flushouts. Not so readily apparent in the data are small sidestreams of unmeasured material, mostly small oxide powder losses in the furnace and at the boat-dumping station. These losses introduce a small, persistent bias in the dynamic material balances, which is detectable upon close scrutiny of the data. Periodically, part of this material is recovered and measured. The recovered portions are subtracted from the cusum. Analogous situations were encountered in previous safeguards studies of large mixed-oxide fuel fabrication and reprocessing plants.[1,50]

Large, unexpected process losses or gains would be detected almost immediately and would be localized by the dynamic accountability system. For example, a boat dumped in the furnace, or even an unexpectedly fast buildup of holdup in the furnace, would be readily apparent, especially if the cusum and Kalman filter control charts and their associated alarm-sequence charts are used. Such changes in the process or process errors pose difficult problems for traditional accounting procedures[74] because their effects often show up only long after the fact when the accountability data are evaluated. Our studies[1,50,69] have shown that the sensitivity of dynamic systems to process conditions is the basis for enhanced safeguards assurance through application of facility-specific concepts for dynamic accountability. Process changes are detected and localized rapidly. Their effects can be analyzed and removed from the accounting data to unmask attempted diversion.

Two strategies for dynamic accounting in the conversion process have been compared. The first separates each process line into two unit-process accounting areas, essentially separating the precipitation and calcining operations. The second considers each process line from receipt of the nitrate feed to loadout of the oxide product as a single accounting area. Two important results of this comparison should be emphasized. First, application of NDA measurement techniques to plutonium-oxalate slurries in different geometries such as precipitator tanks and filter boats should be demonstrated. Gross neutron and/or neutron coincidence counting, both candidate measurement methods, should be experimentally characterized for this application. An important, related point is that development of appropriate standards for such measurements should be considered. A second important result is that the dynamic accountability data can be combined in various ways and tested for diversion. The two accounting strategies compared for the conversion process are good examples of the flexibility and redundancy of information in the measurement data. Another example, not explicitly considered, is that data from each process line can be combined to counter diversion strategies that cross process-line boundaries. Redundant accounting information, available because the unit process boundaries overlap, provides added assurance and decreases vulnerability.



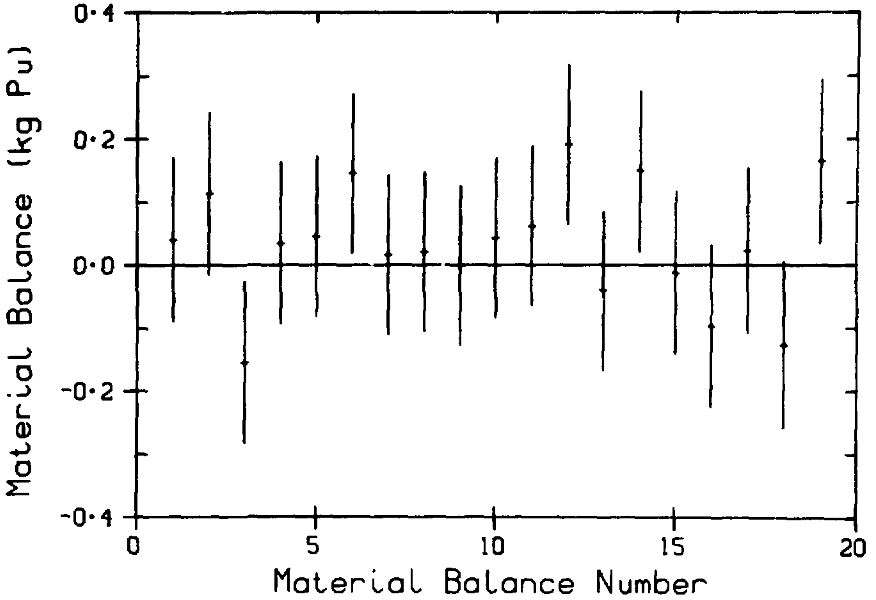


Fig. IV-5. Material balance charts for one day without diversion (upper), with diversion (lower).

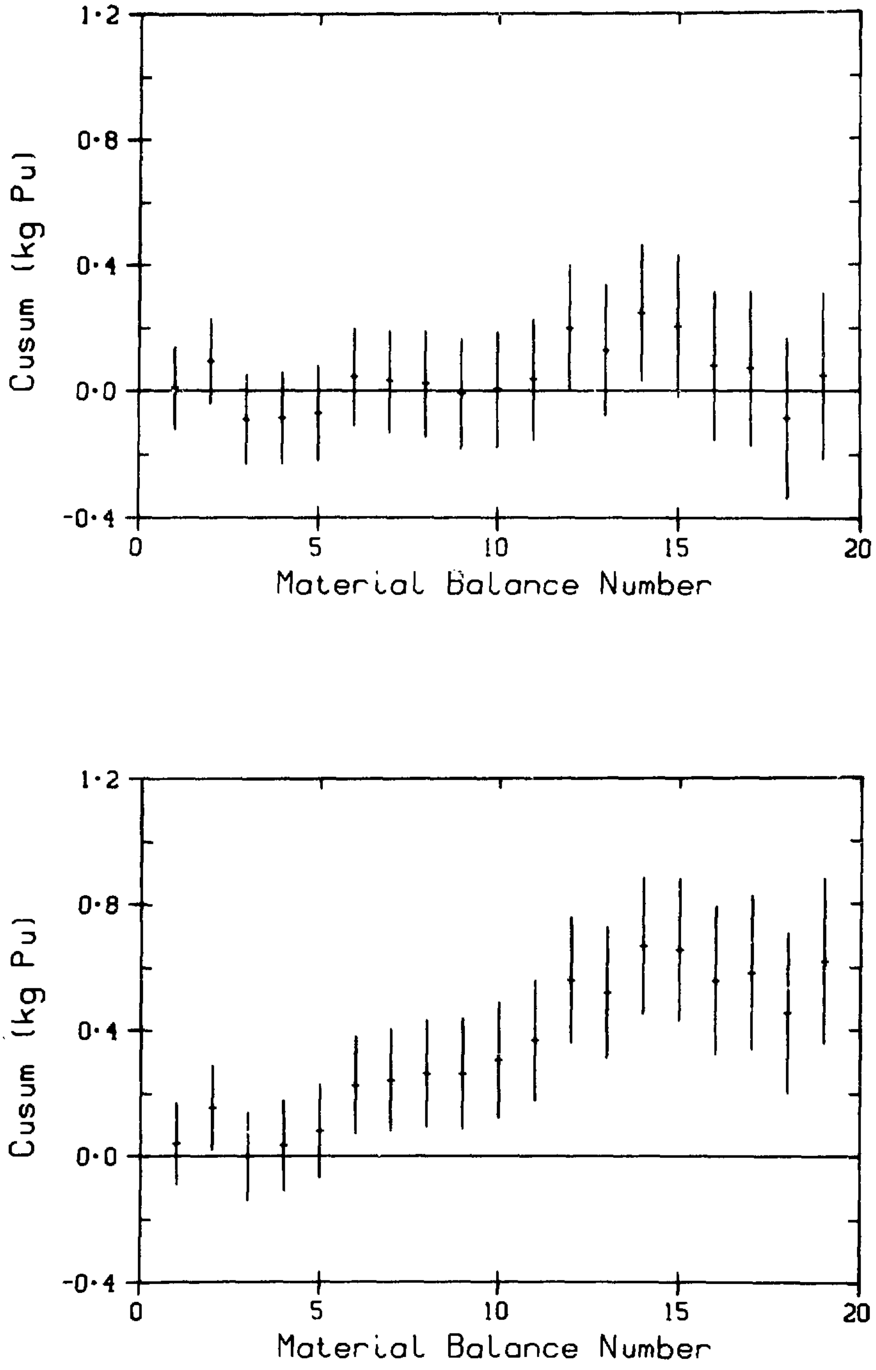


Fig. IV-6. Cusum charts for one day without diversion (upper), with diversion (lower).

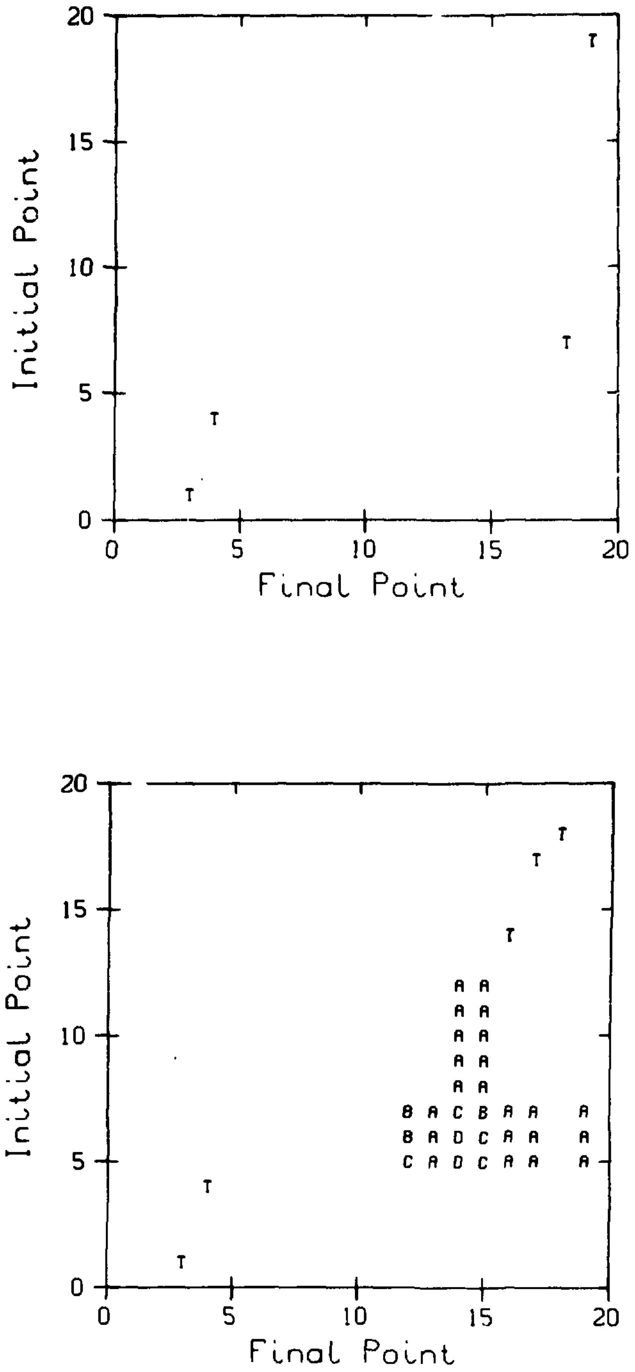


Fig. IV-7. Alarm-sequence charts for one-day cusums without diversion (upper), with diversion (lower).

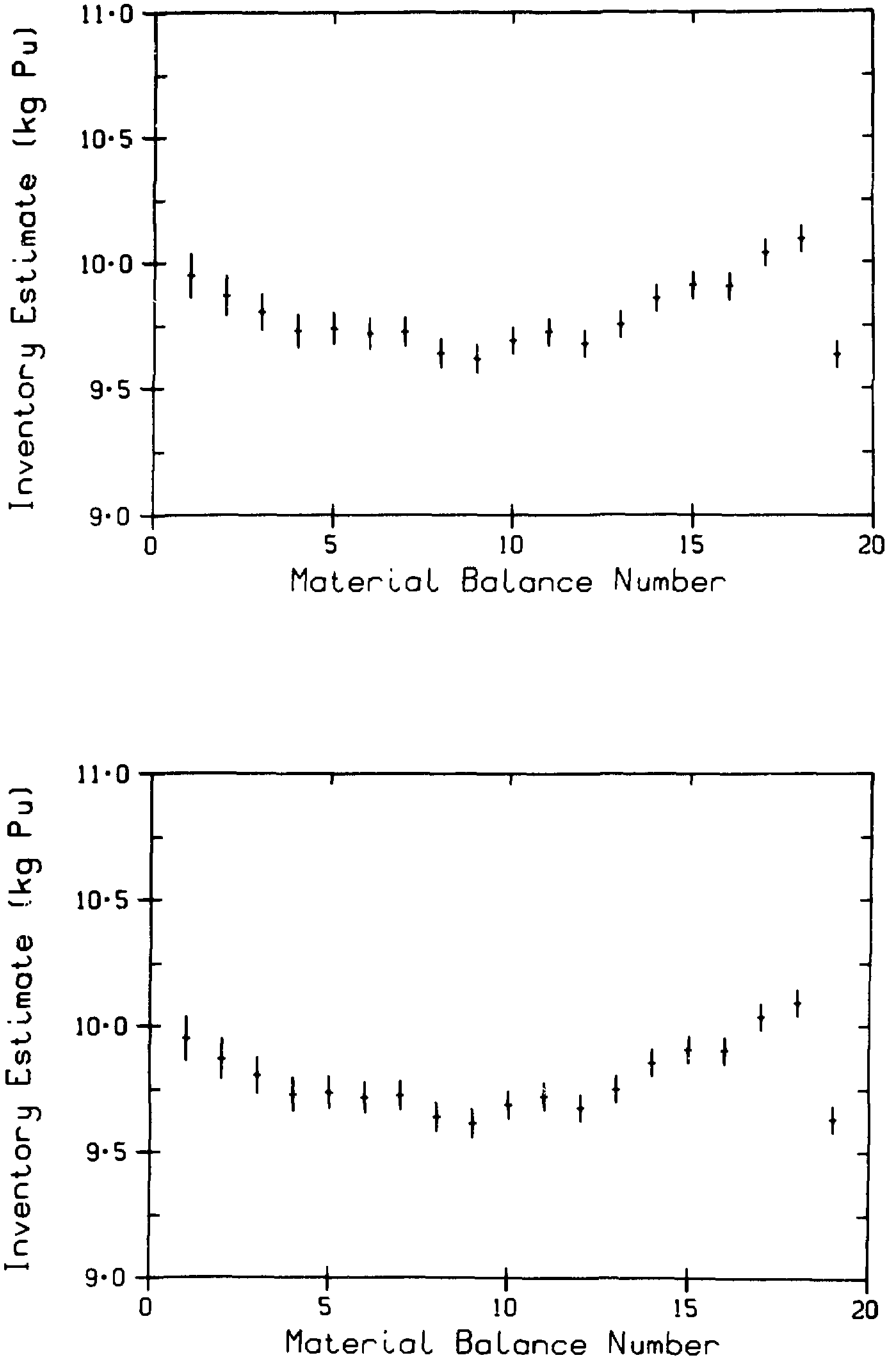


Fig. IV-8. Kalman filter inventory estimates for one day without diversion (upper), with diversion (lower).

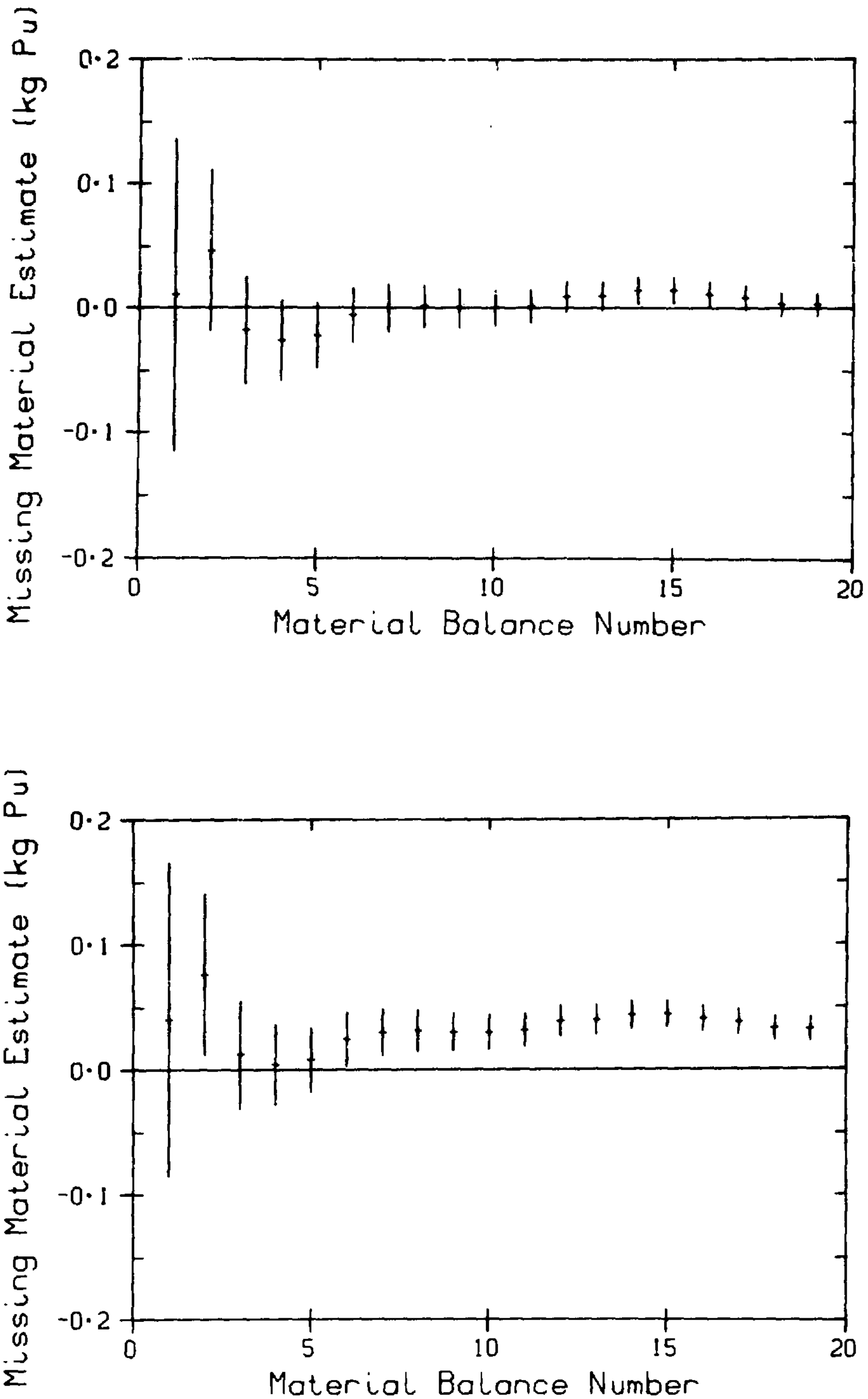


Fig. IV-9. Kalman filter estimates of average missing material for one day without diversion (upper), with diversion (lower).

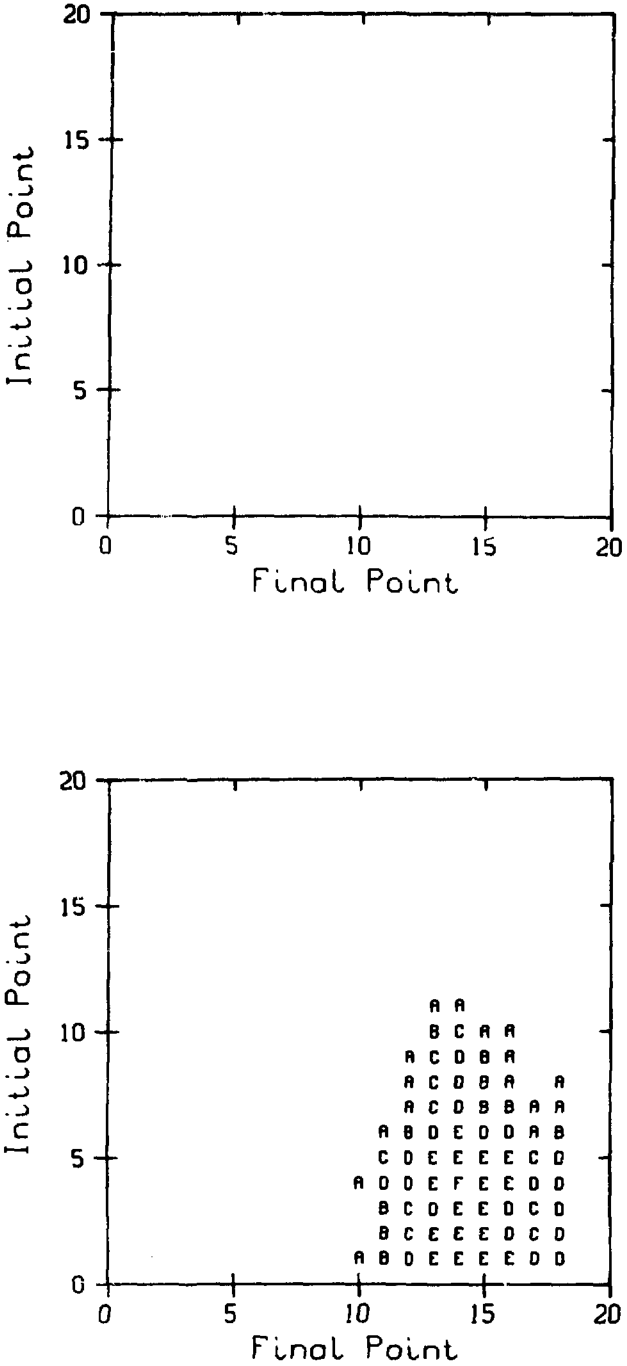
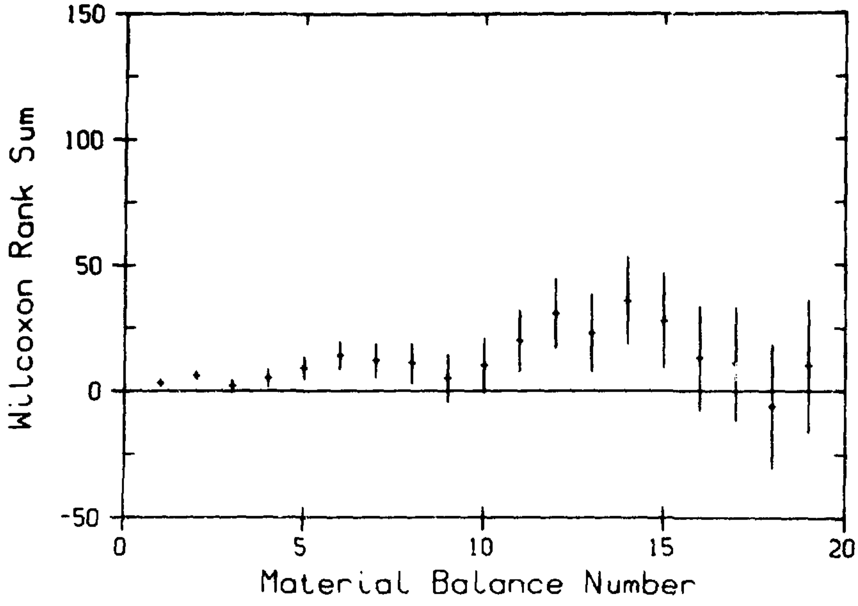


Fig. IV-10. Alarm-sequence charts for Kalman filter estimates for one day without diversion (upper), with diversion (lower).



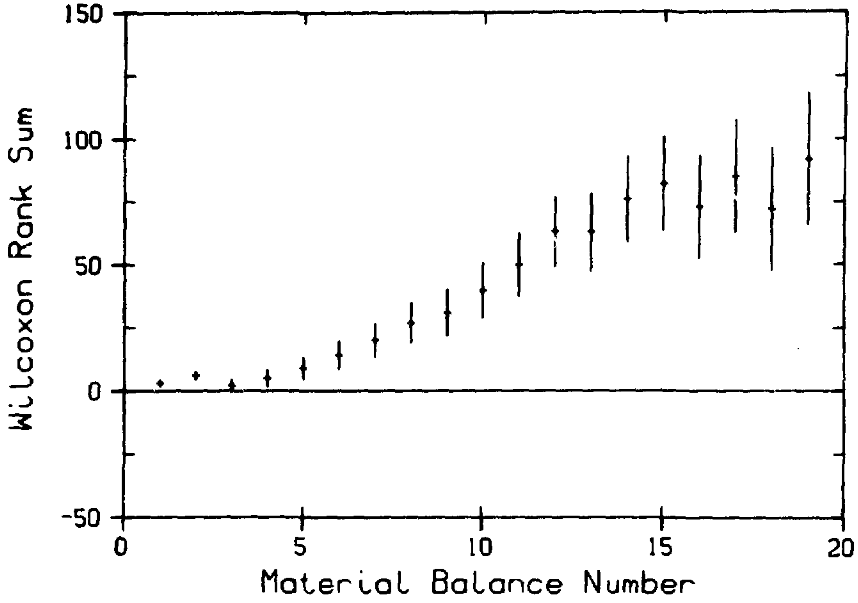


Fig. IV-11. Wilcoxon rank-sum charts for one day without diversion (upper), with diversion (lower).

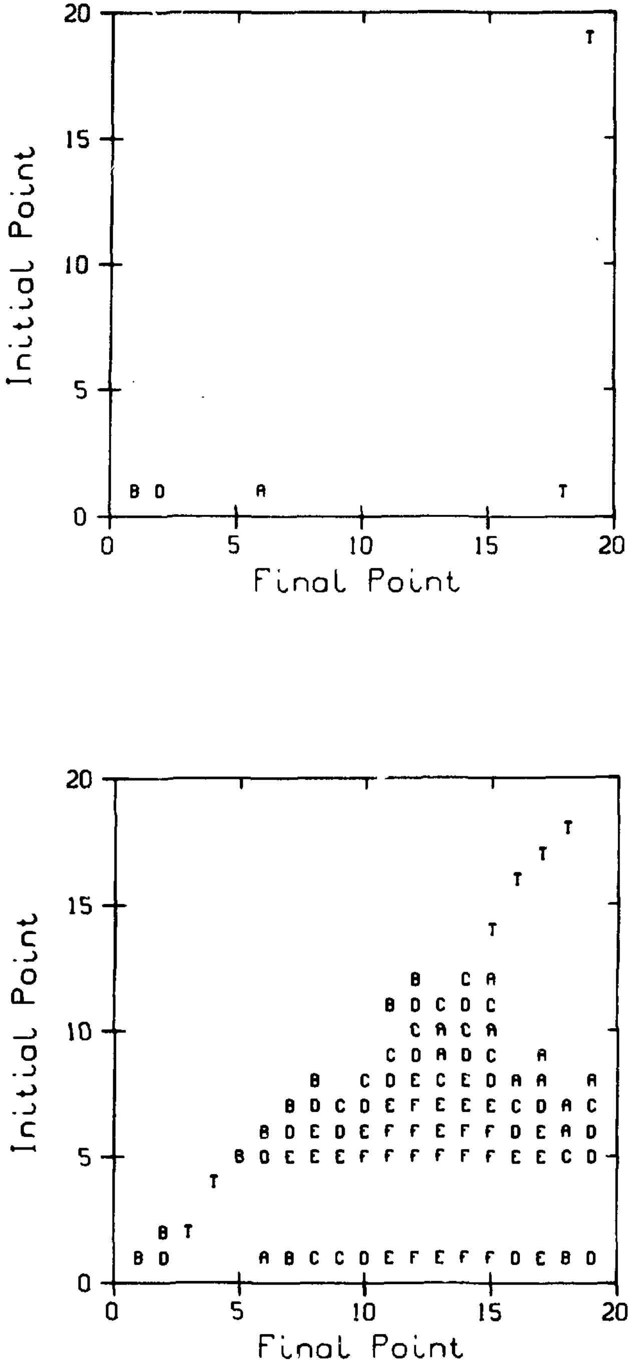


Fig. IV-12. Alarm-sequence charts for the Wilcoxon rank sums for one day without diversion (upper), with diversion (lower).

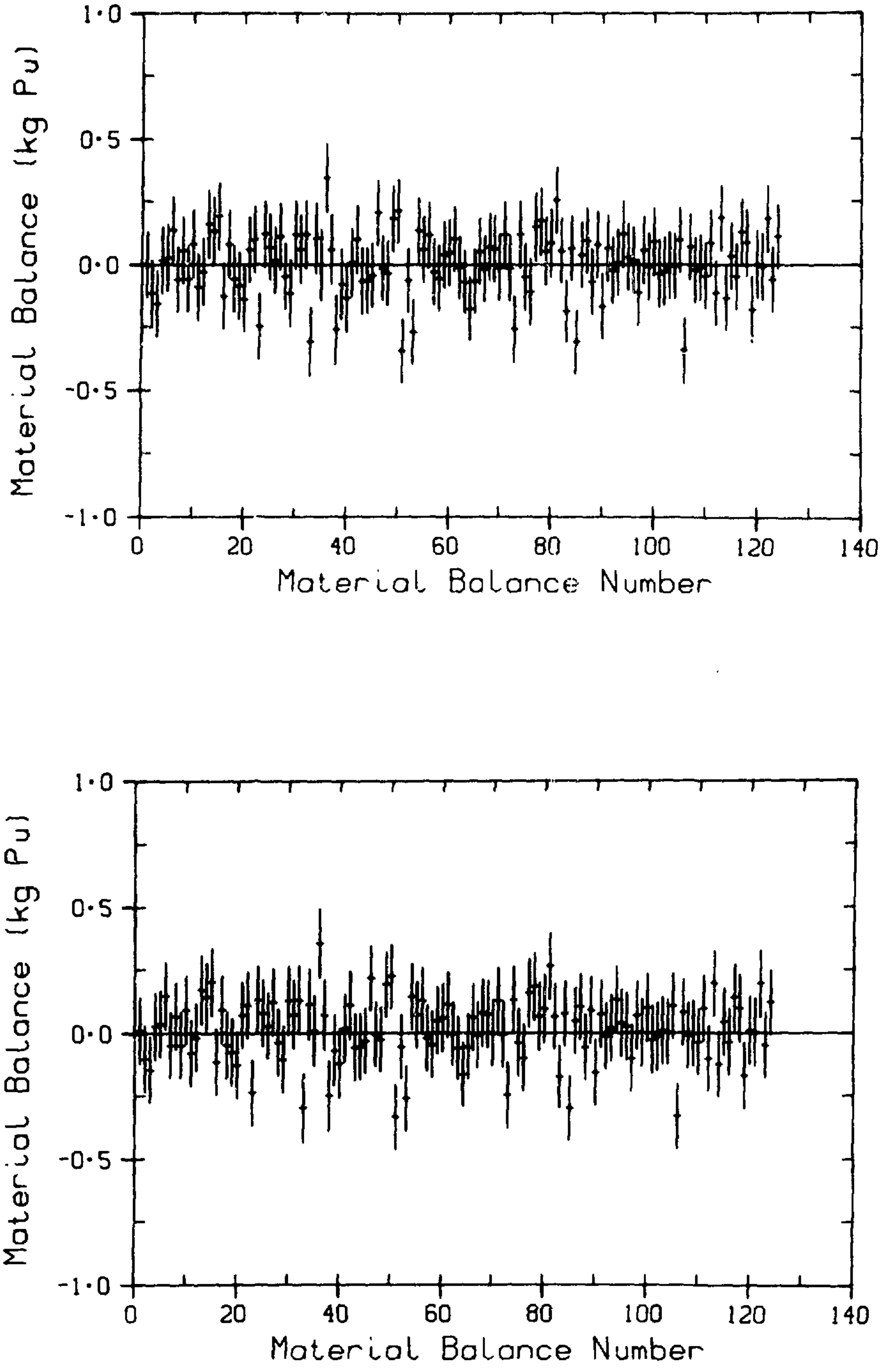
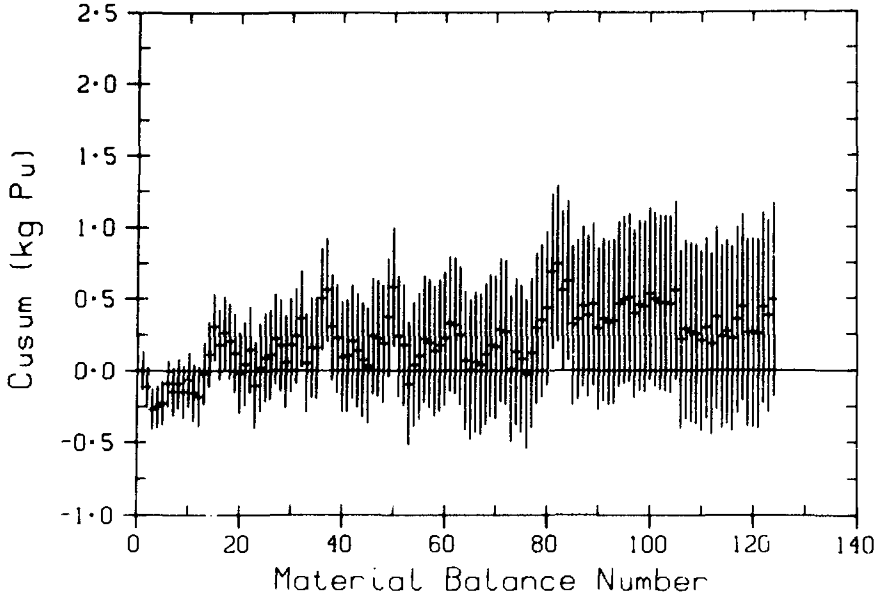


Fig. IV-13. Material balance charts for one week without diversion (upper), with diversion (lower).



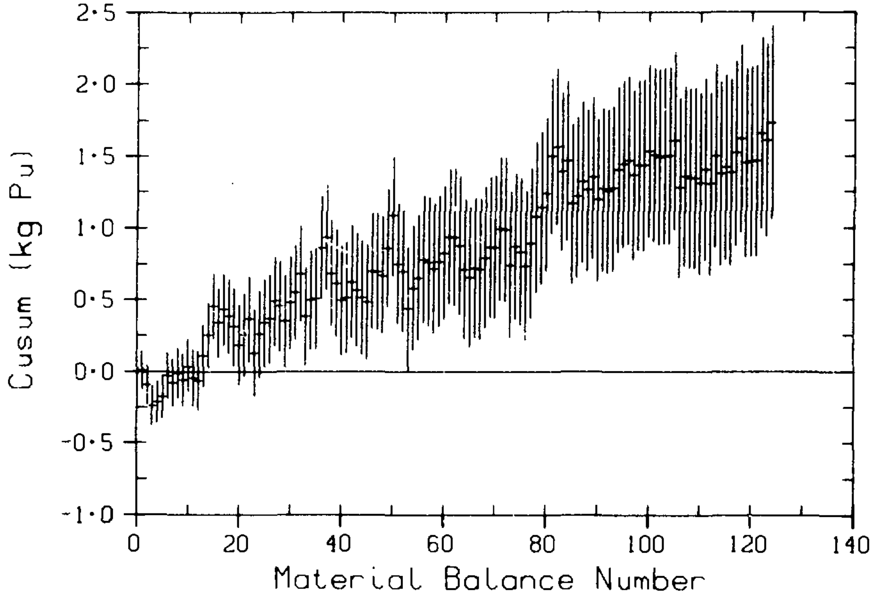


Fig. IV-14. Cusum charts for one week without diversion (upper), with diversion (lower).

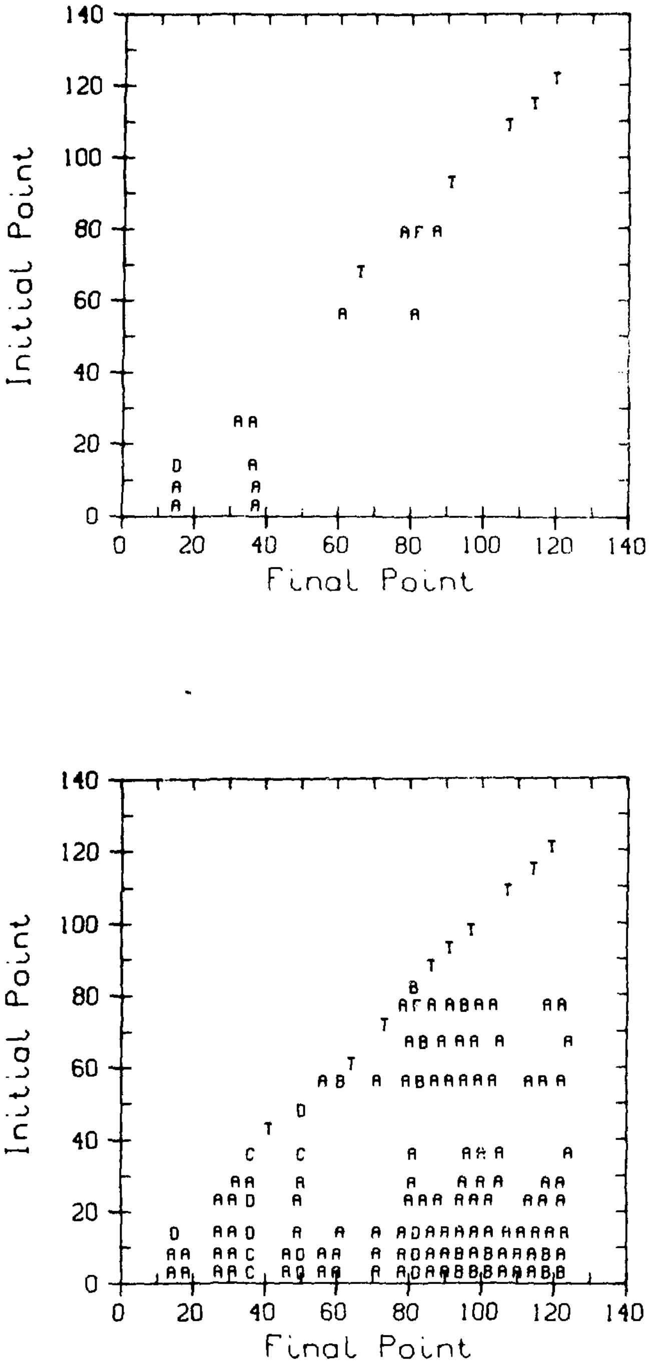
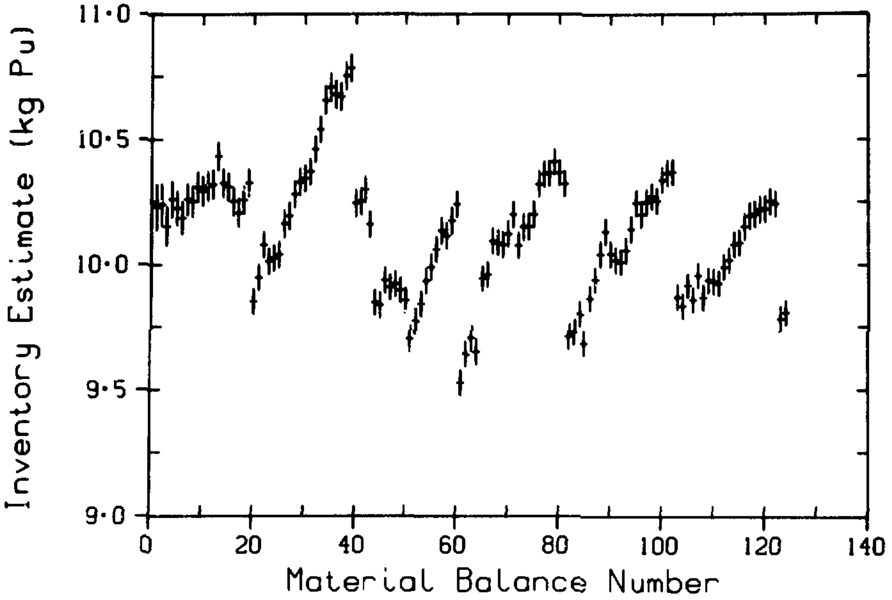


Fig. IV-15. Alarm-sequence charts for one-week cusums without diversion (upper), with diversion (lower).



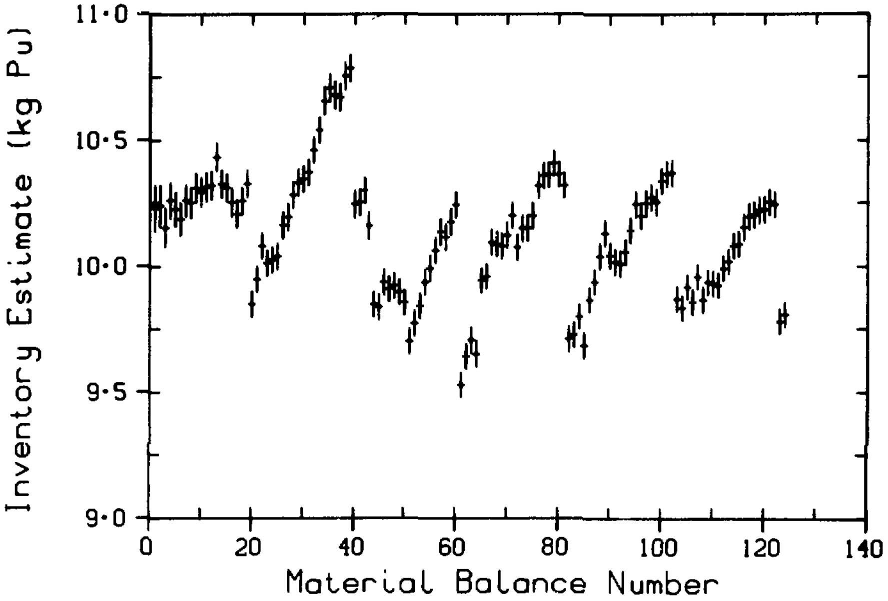
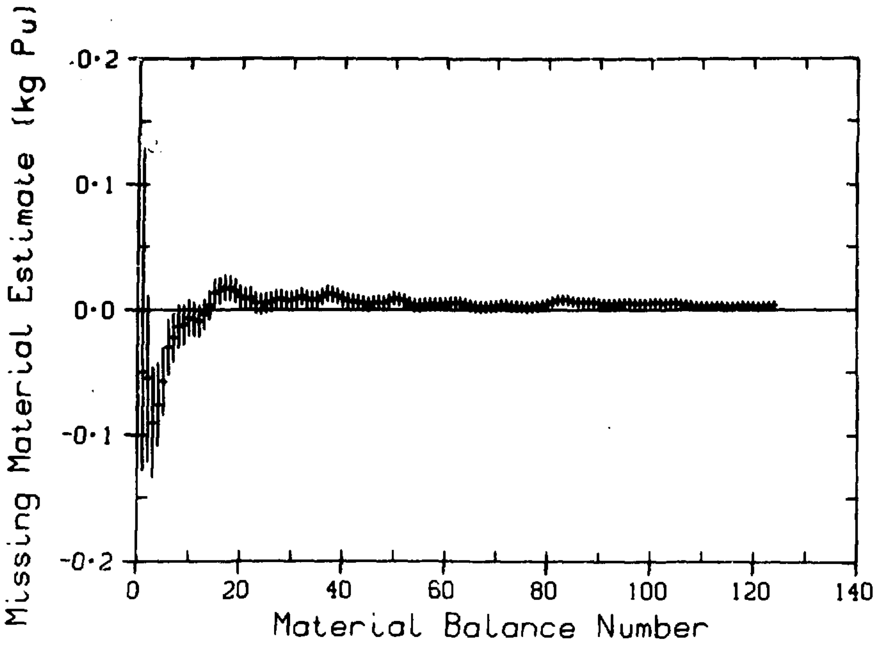


Fig. IV-16. Kalman filter inventory estimates for one week without diversion (upper), with diversion (lower).



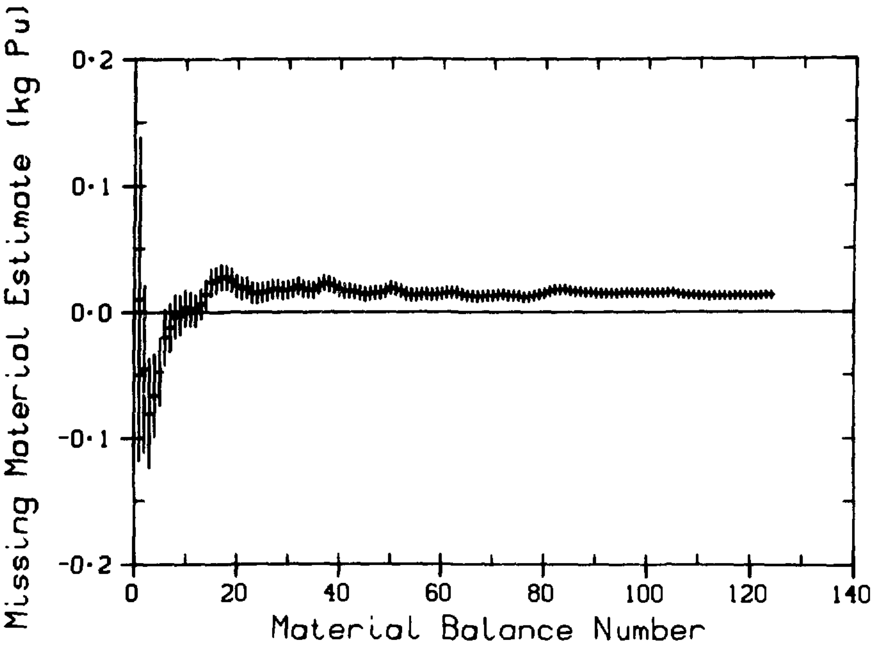


Fig. IV-17. Kalman filter estimates of average missing material for one week without diversion (upper), with diversion (lower).

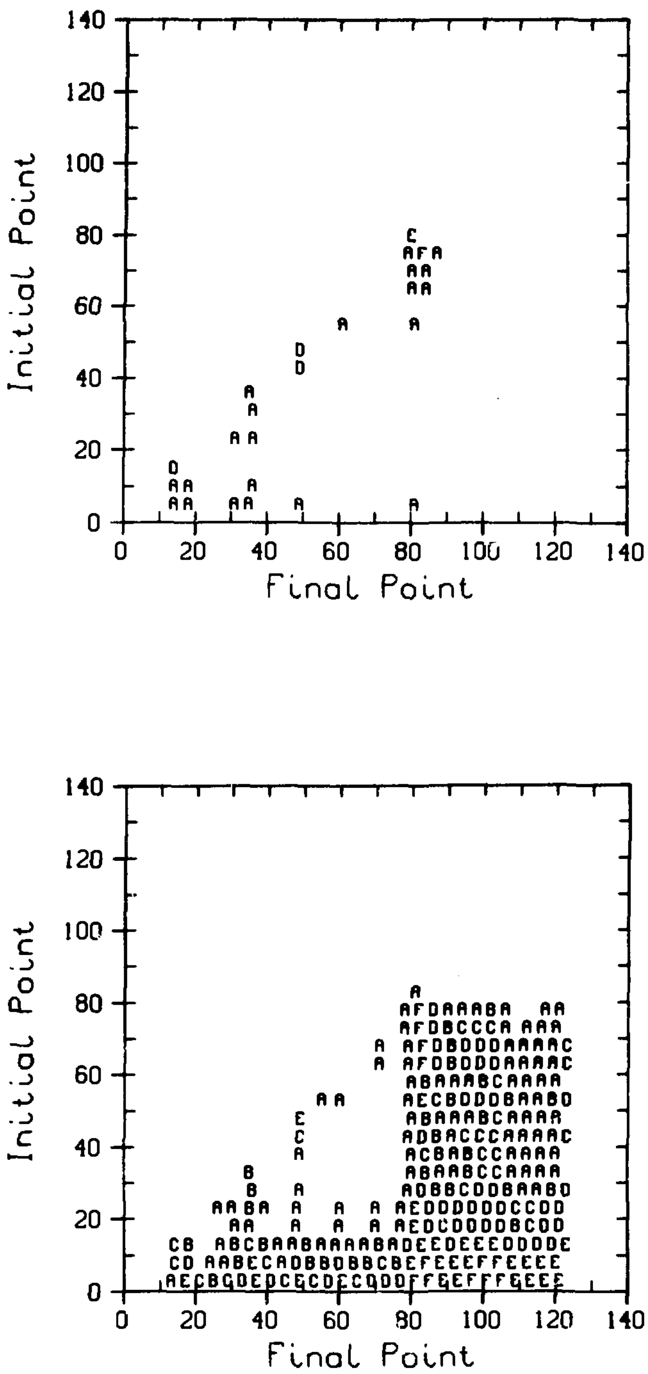


Fig. IV-18. Alarm-sequence charts for one-week Kalman filter estimates without diversion (upper), with diversion (lower).

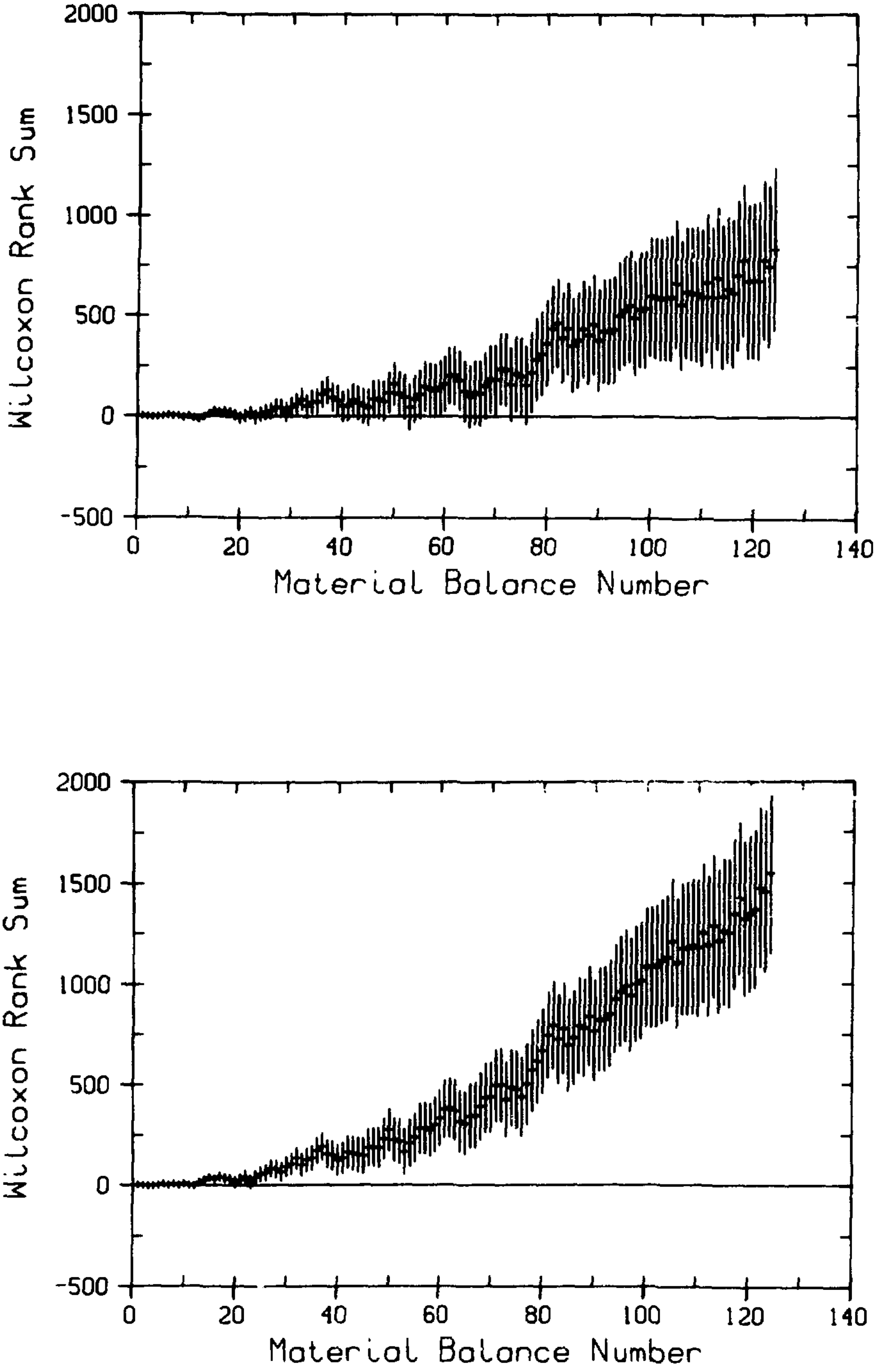


Fig. IV-19. Wilcoxon rank-sum charts for one week without diversion (upper), with diversion (lower).

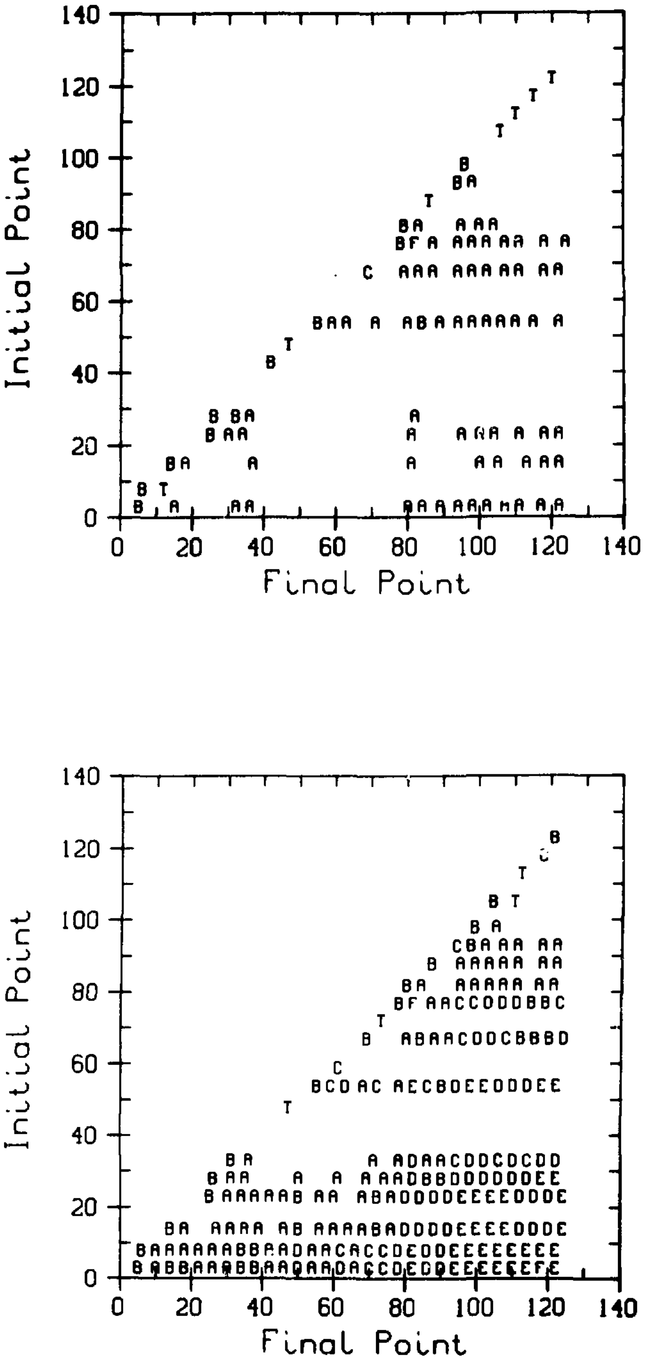


Fig. IV-20. Alarm-sequence charts for one-week Wilcoxon rank sums without diversion (upper), with diversion (lower).

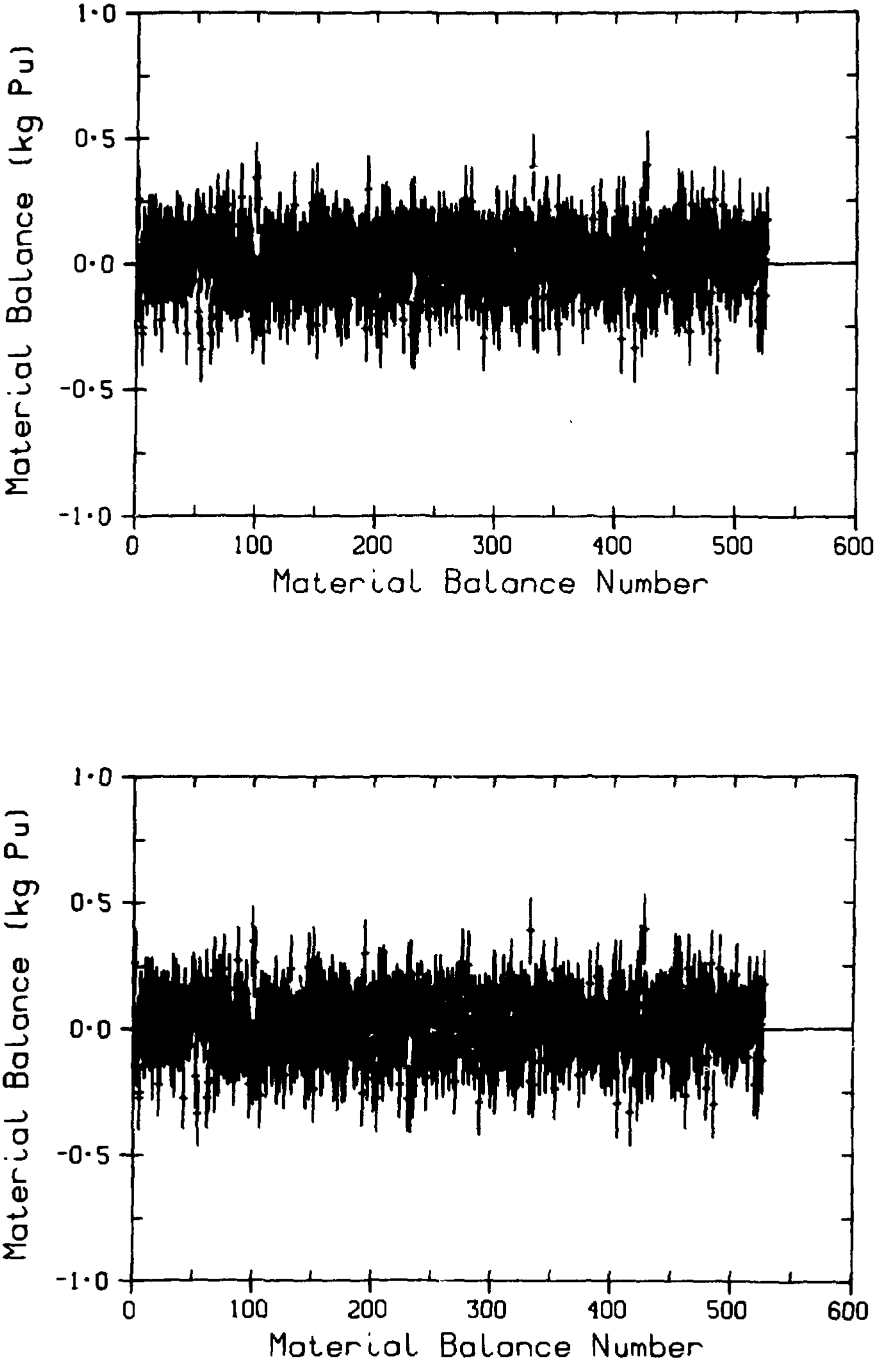


Fig. IV-21. Material balance charts for one month without diversion (upper), with diversion (lower).

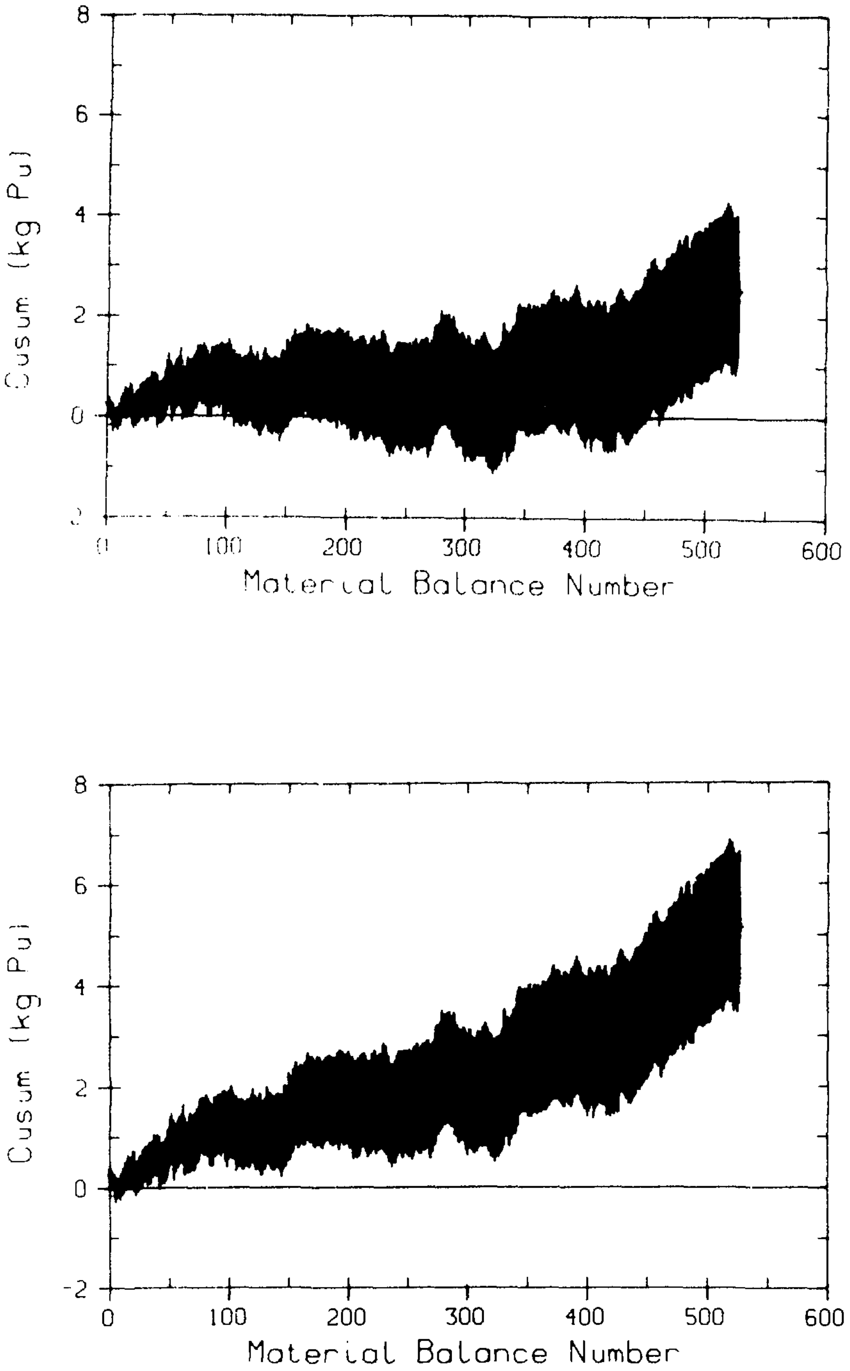


Fig. IV-22. Cusum charts for one month without diversion (upper), with diversion (lower).

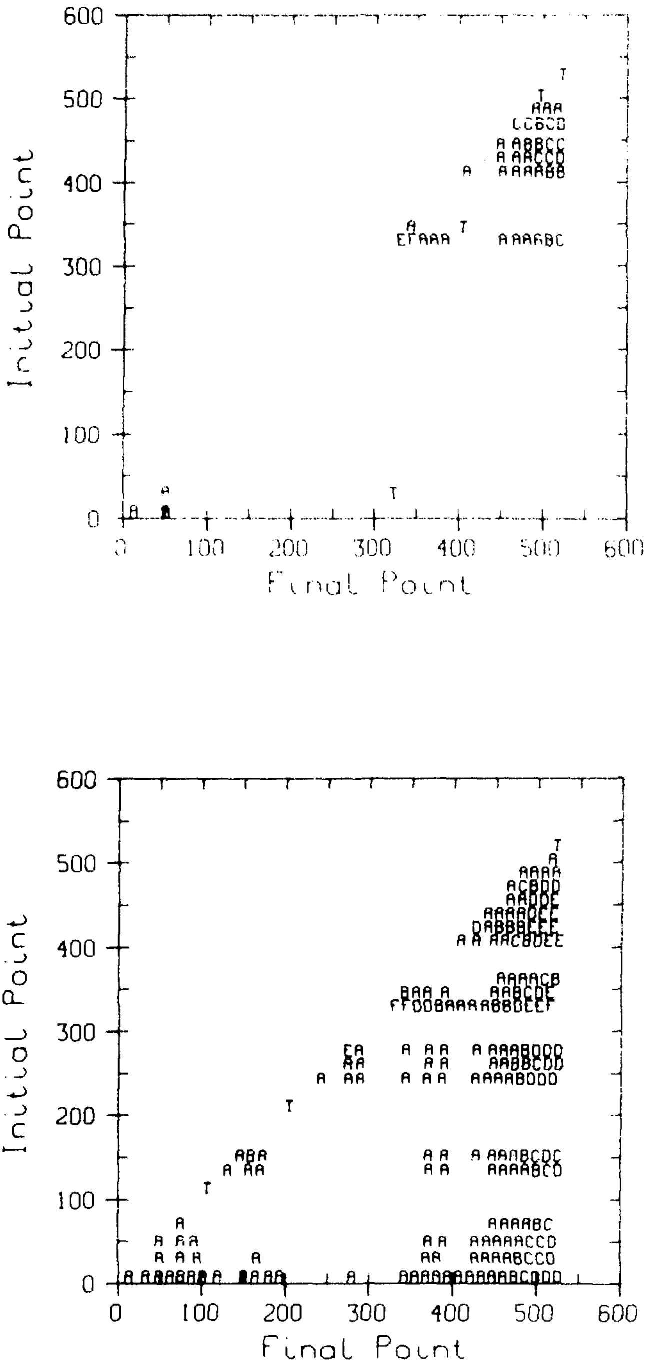
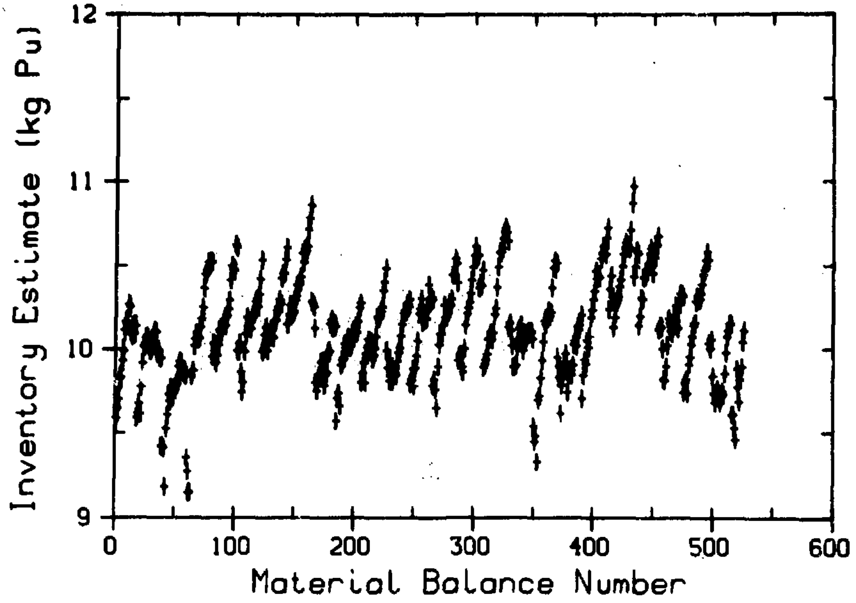


Fig. IV-23. Alarm-sequence charts for one-month cusums without diversion (upper), with diversion (lower).



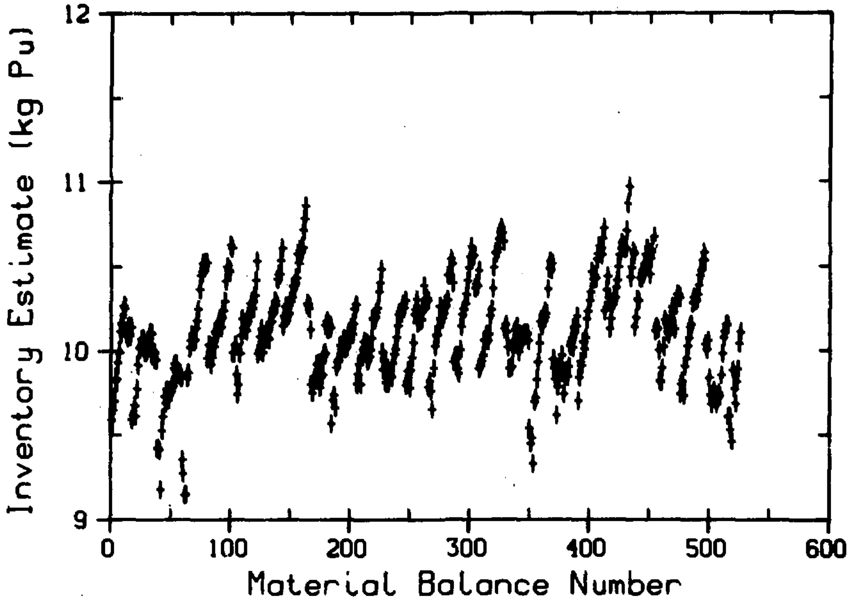
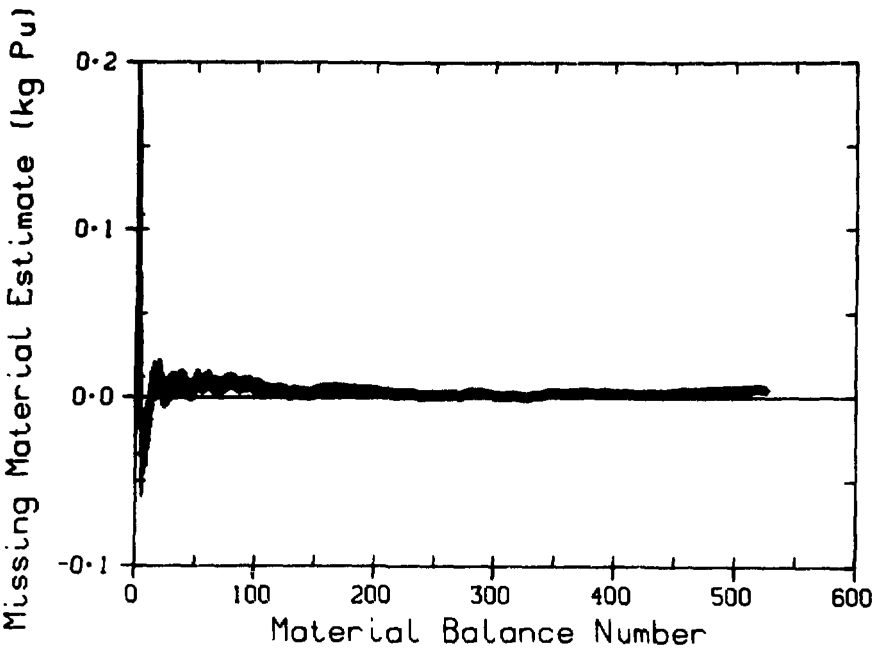


Fig. IV-24. Kalman filter inventory estimates for one month without diversion (upper), with diversion (lower).



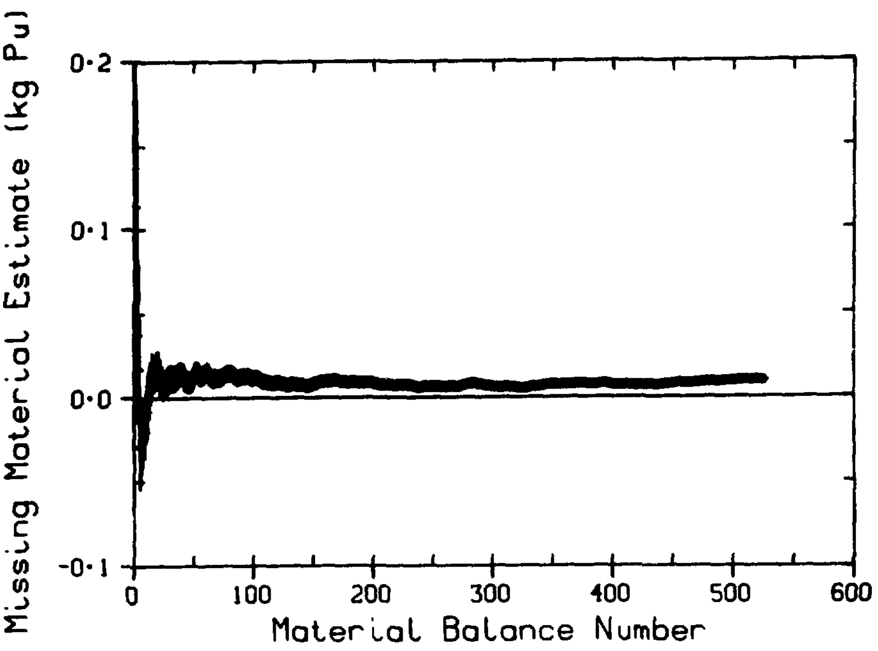
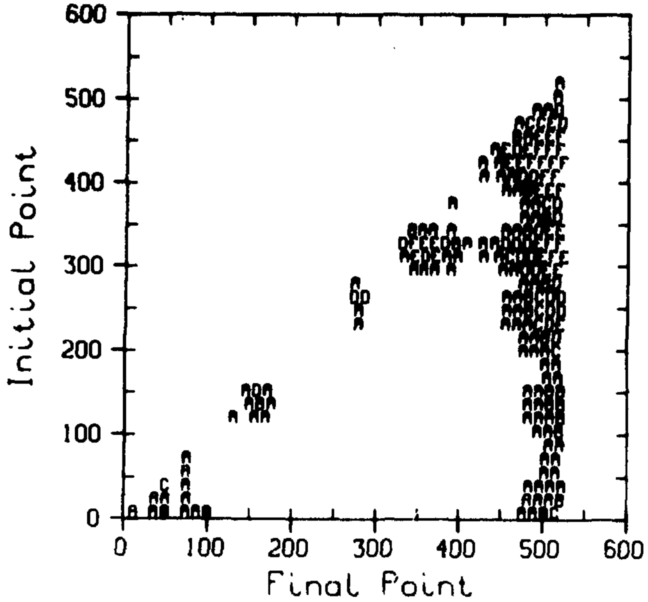


Fig. IV-25. Kalman filter estimates of average missing material for one month without diversion (upper), with diversion (lower).



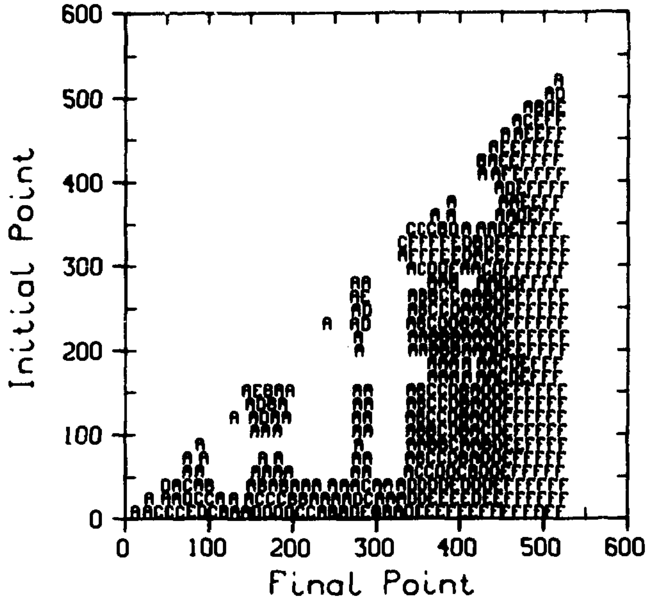
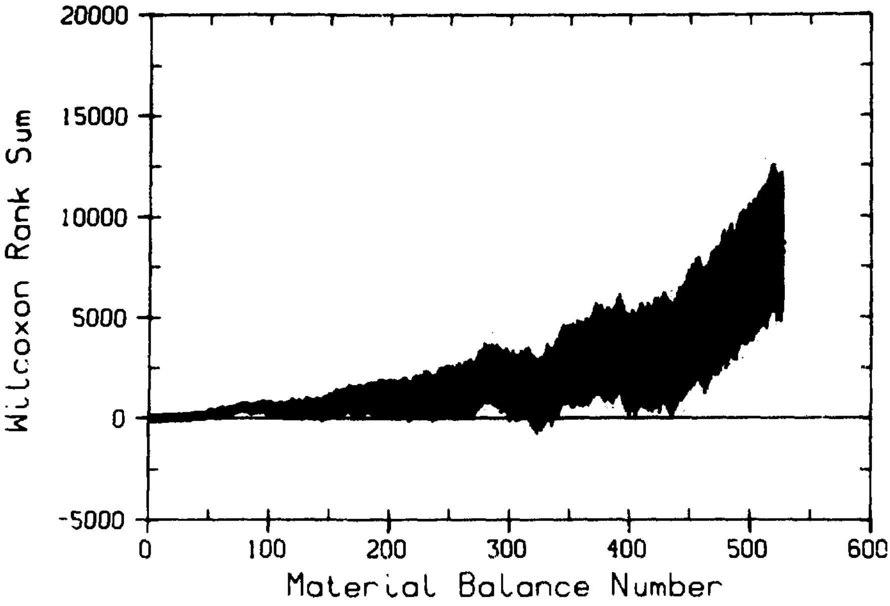


Fig. IV-26. Alarm-sequence charts for one-month Kalman filter estimates without diversion (upper), with diversion (lower).



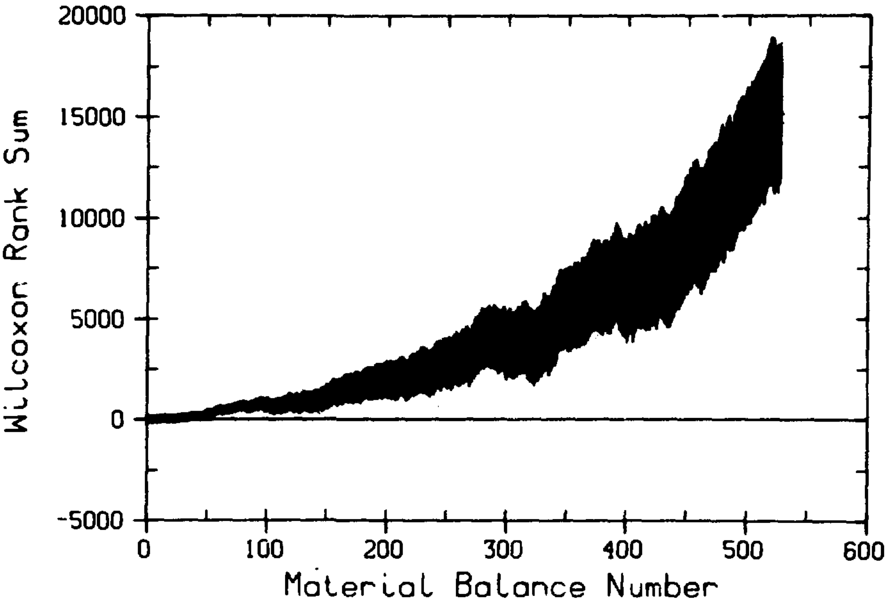


Fig. IV-27. Wilcoxon rank-sum charts for one month without diversion (upper), with diversion (lower).

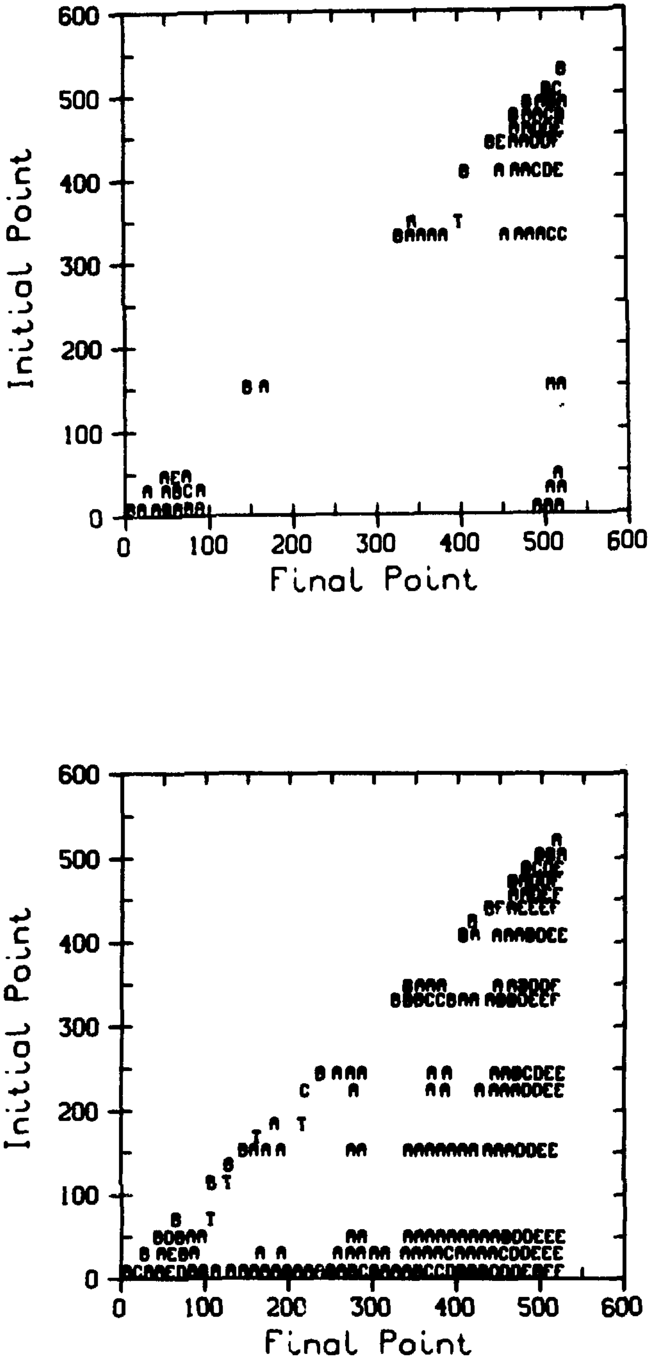


Fig. IV-28. Alarm-sequence charts for one-month Wilcoxon rank sums without diversion (upper), with diversion (lower).

V. RESULTS, RECOMMENDATIONS, AND CONCLUSIONS

A. Results

Conceptual design of an effective safeguards materials management system for a plutonium nitrate-to-oxide conversion process is complete. Its details are given in Chaps. III and IV. Other accomplishments include development of control logic, management strategy, system architecture, data-evaluation procedures, and potential process modifications for improved safeguards.

1. Features of the Materials Measurement and Accounting System.

Recently developed NDA technology, state-of-the-art conventional measurement methods, special in-plant sensors, process instrumentation, and powerful data analysis techniques, supported by computer and data base management technology, combine to form an effective, timely safeguards materials management system.

Conventional materials accounting methods are supplemented by dynamic materials accounting in which the facility is partitioned into discrete accounting envelopes called unit-process accounting areas (UPAAs). Dynamic material balances drawn around such unit processes during the course of normal plant operation permit more timely materials accounting and facilitate detection of repeated small thefts of SNM. The related concept of overlapping UPAAs may be useful for cross-checking, and it allows continued materials accounting, with less sensitivity and timeliness, in case of instrument malfunction.

The notion of graded safeguards is based on the observation that the strategic value and safeguards vulnerability of the material depend on its location and form within the process and within the fuel cycle. For example, in the conversion plant, plutonium nitrate at the receipt tank is somewhat less attractive to a potential divertor than the plutonium oxide at the output of the process. Moreover, because all the SNM is processed in a relatively pure and concentrated form, the conversion facility is the most attractive diversion target among the facilities that make up the power reactor nuclear fuel cycle (Fig. I-1).

The *key measurement points* in the conversion process are the receipt tank (volume and concentration) and the product cans (plutonium content). Absorption-edge densitometry is used to measure the plutonium concentration in the receipt tank solution. A neutron well counter or calorimeter is used to measure the plutonium content in a product can. Each measurement assumes that a companion measurement of the plutonium isotopic composition by gamma or mass spectroscopy is available. These on-line measurements are amenable to near-real time accountability.

Two materials accounting strategies have been identified. Both use the *same* measurement instruments and points. The first treats each process line as two unit process accounting areas (UPAAs). The first UPAA includes the receipt tanks and a precipitator; the second, a furnace and a product dump and assay station. The second accounting strategy involves a single UPAA that includes the receipt tanks, a precipitator, a furnace, and a dump and assay station.

Nuclear material diversion can be localized better using the first strategy because of its two accounting areas. The sensitivity of this strategy depends very much on ability to calibrate the wet-boat measurement instruments. If improved ($\sim$1% RSD) calibration of the wet-boat measurement instruments is possible, this strategy is more sensitive to a single theft. Even with better wet-boat measurement instrument calibration, the second strategy remains more sensitive to long-term, low-level diversion. The ability to use the same data for two different strategies provides safeguards advantages that can be exploited by using the appropriate analysis software.

2. Performance Evaluation Tools. Because the reference process is not yet in use, evaluation of the safeguards system depends on process and measurement simulation models. Three computer codes have been developed for this purpose. NOCSIM is a computerized, dynamic model of normal conversion plant operation (Appendix A). MEASIM applies simulated accountability measurements to process-flow data generated by NOCSIM, and computes measurement errors, including correlations for all transfer- and inventory-measurement points (Sec. IV-B and Appendix C). DECANAL produces dynamic material balances and cusums from the measurement data and applies powerful decision-analysis tools to the study of diversion-detection sensitivity (Chaps. III, IV, and Appendix E of Ref. 1). Separation of the materials flow, materials measurement, and data analysis functions provides flexibility in investigating a variety of process-operating modes, measurement techniques, and diversion schemes. These techniques can be used to evaluate the effectiveness of dynamic materials accounting concepts for any facility.

3. Diversion Detection Algorithms. DECANAL is an important first step in software development for dynamic accountability systems in actual facilities. The tests used to make decisions in DECANAL are complementary. The Shewhart chart of material balances is the easiest and fastest analysis to apply, but it is sensitive only to comparatively large single thefts of nuclear material. The cusum (V-mask) test, Kalman filter, and Wilcoxon test are most useful in detecting repeated small thefts.

The nonparametric Wilcoxon test is easy to apply, but it is also less sensitive to diversion because it does not use (or require) detailed *a priori* knowledge of measurement errors. However, it is useful as a backup to the other tests, especially when incomplete descriptions of measurement errors must be used (which will often be the case). Application of this test to safeguards data is under study.

The cusum test is relatively easy to apply and is related to the unweighted, moving-average test. The only prerequisite is the ability to estimate the cusum variance on the basis of measurement system errors (including all significant correlations).

Tests based on the use of the Kalman filter are intrinsically more sensitive than the cusum (V-mask) or Wilcoxon tests. The Kalman filter provides a framework in which process-model descriptions can be incorporated to improve accounting estimates. For example, it gives improved estimates of in-process inventory. However, the Kalman filter is also more difficult to apply properly than the cusum test, especially where measurement correlations are important.

The alarm-sequence chart is an especially useful pattern-recognition tool. It is important from the point of view of human engineering because it gives the safeguards analyst a quick look at a continually updated summary of results from the dynamic accountability system. The cusum chart and plots of the Kalman-filter estimates of in-process inventory and missing material are also good graphical-display tools. They should be useful for process control as well as safeguards.

4. Diversion Sensitivity. Table V-I lists thresholds for diversion sensitivity of a single process line in the conversion process. These results are discussed fully in Chap. IV. Sensitivities range from 0.13 kg of plutonium in one batch to 2.65 kg of plutonium in one month. These results, which we believe are achievable at reasonable cost and with only minor extrapolations of present technology, are a significant improvement over current regulatory requirements and industry practice, a limit of error of 0.5% of the entire plant throughput for 60-days, equivalent to 33 kg of plutonium. This is true even without the substantial additional benefits that should be derived from improved physical security and materials containment and surveillance.

5. Features of the Process-Monitoring System. Process-monitoring combines elements of both the physical-protection system and the materials measurement and accounting system, and gives each supplementary information on compliance of actual process-operating modes with approved procedures. The concept may be regarded as an extension of physical-protection monitoring

TABLE V-I

DIVERSION SENSITIVITY[a] OF THE CONVERSION PROCESS

Detection Time	Average Diversion per Batch (kg Pu)	Total at Time of Detection (kg Pu)
1 batch (1.35 h)	0.13	0.13
1 day	0.03	0.63
1 week	0.01	1.24
1 month	0.005	2.65

---

[a] As determined for a single process line in the second accounting strategy in accordance with ERDAM Appendix 7401-C, "Nuclear Materials Management and Safeguards System Handbook." See Sec. IV-C.1 for descriptions of the measurement strategies for selected cases.

and surveillance into the process line, and as an upgrading of the monitoring devices (or their appropriate placement) to allow gross materials accounting (see Sec. III-C). The process-monitoring system, using plant instrumentation wherever possible, collects timely information of the type intended to detect a theft in progress from a limited set of on-line measurement equipment, plant-grade instrumentation, and other simple, reliable, process-monitoring devices.

6. Reliability. Although no detailed reliability calculations have been performed for this safeguards system, we believe that an overall MTBF of 3 months and an MTTR of <5 h are reasonable, readily achievable goals. Detailed reliability calculations are not appropriate at the conceptual design stage because they depend so much on details of the advanced engineering design.

7. Cost. The capital cost of the safeguards system (not including a large part of the physical-protection system) is estimated to be about $5.6 million; annual operating costs are approximately $2.5 million.

B. Identified Problem Areas

1. Plutonium Oxalate Slurry Measurement. The geometry of the precipitator and the form of the material combine to make measurement of precipitator in-process inventory difficult. In fact, this measurement and that of the precipitate in the wet boats are primary limiting factors in reducing the uncertainties in the dynamic material balances computed for the conversion process. The proposed ^{3}He neutron counter measurements require knowledge of the chemical and isotopic compositions of the material. Also, instrument calibration standards must be developed. The methods and instruments are available, but further field testing and evaluation are required for this particular application.

2. Furnace and Dump Station Holdup Measurement. The uneven distribution of loose powders at the dumping stations and the furnaces, as well as the large furnace geometry, make accurate holdup measurements in these process steps difficult. Residual holdup can be measured using portable instrumentation or area monitors. LASL experience in making such measurements indicates that an accuracy of 50% or better is achievable for small quantities of residual powders.[75].

3. Process Design Considerations for Materials Containment and Surveillance. Materials containment and surveillance is enhanced if mixing between parallel process lines is prohibited. That is, once material is dispensed from a receipt tank it should remain within a single process line until it is loaded into a product can or sent to recycle and recovery. The conceptual design presently contains four precipitator lines, three furnaces, and two dump and assay stations. Process line integrity can be achieved by adding one more furnace and two dump and assay stations.

4. Accountability in the Recycle and Recovery Area. Materials accounting in the recycle and recovery area has not been investigated quantitatively because these functions may not be necessary if the conversion process is part of a larger fuel reprocessing complex. The solids recovery line is by far the

most attractive target for diversion within the recycle and recovery area. Reject product and sweepings from the furnaces and the product dump and assay stations are recycled through solids recovery, and they account for approximately half the total capacity of the recycle and recovery area. The currently proposed use of fluoride to help redissolve recovered powders complicates accountability in this area because neutronic measurements are difficult in the presence of fluorine. Use of ceric ion to aid redissolution should be investigated. Materials accounting in the recycle and recovery area, if there is to be one, needs further study.

C. Recommendations

The following recommendations should facilitate materials measurement and accounting in the conversion process.

- Instruments used at key measurement points must be well characterized and field tested. Extensive testing of absorption-edge densitometers, neutron well counters, gamma spectrometers, and calorimeters is required.
- Techniques for measuring plutonium oxalate slurry in precipitators and filter boats should be demonstrated and evaluated.
- Techniques for recalibrating volume measurements on-line should be developed.
- Techniques for product boat-dumping should be improved to minimize losses.
- Plutonium oxide redissolution without fluorine should be investigated.
- Computerized models of the process and dynamic accountability system should be validated by field test and evaluation of system components.
- Conversion processes that yield a product usable only as reactor fuel should be evaluated for their safeguards value.

D. Conclusions

Strategic quantities of SNM can be safeguarded in a high-throughput nitrate-to-oxide conversion facility at reasonable cost and with minimal disruption of production. The safeguards measurement system provides better information than that now available to enhance process control. The system design is facility specific, and it must be implemented from the conceptual design stage to ensure compatibility with the process. Only one of several candidate processes has been evaluated.

The study identifies several points in the process where more precise and accurate measurements will reduce materials accounting errors and improve diversion detection sensitivity.

There should be a continuing effort to refine and validate computerized models of processes and measurements. Development of decision-analysis and graphical-display tools for dynamic accountability in conversion processes is essential if the mass of data generated by the materials measurement and accounting system is to be interpreted correctly and quickly.

The interaction among dynamic materials accounting, process control, and materials containment and surveillance should be studied. Substantial benefits, for both safeguards and process control, probably will result.

The conversion process presents a challenging safeguards problem. It is small compared to a chemical separations plant, but it has a high throughput of material that is very attractive for diversion. This situation lends itself well to the "bonded crucial facility" (BCF) concept (see Chap. I) in which the conversion process is expanded to include the product and feed storage functions for the most attractive materials in the fuel cycle. Furthermore, because the material being processed is relatively pure, and radiation levels are negligible, the conversion process is amenable to real-time instrumentation. Stringent safeguards for the conversion process are necessary because its smallness, its high throughput, and the purity of the material being processed make it the most likely target for diversion in the power reactor fuel cycle. Fortunately, these attributes also make the conversion process potentially the most safeguardable of the fuel cycle facilities studied to date.

APPENDIX A

DYNAMIC MODEL OF THE NITRATE-TO-OXIDE CONVERSION PROCESS

I. INTRODUCTION

This study provides design concepts for near real-time accounting of SNM in nitrate-to-oxide conversion facilities. The conversion process is particularly important because the SNM from feed through product is in a relatively pure, concentrated form attractive for diversion. In the absence of operating histories from modern facilities, simulated process data are required to evaluate concepts developed for control of in-process material. The control capability is especially sensitive to in-process holdup of SNM in piping, vessels, and tanks. The simulated data are developed accurately to represent the dynamic behavior of this in-process holdup as well as the flow of material through the process.

The modeling and simulation approach is described in recent studies of coordinated safeguards for both a mixed-oxide fuel fabrication facility (see Chap. IV and Appendix D of Ref. 50) and for a fuel reprocessing plant (see Chap. VI and Appendixes E and G of Ref. 50). This approach includes[69] (1) construction of a detailed process model based on the design of a reference facility; (2) simulation of the model process operation on a digital computer by treating the flows of SNM as stochastic variables; (3) application of accountability measurements to the simulated SNM flow and holdup data; and (4) evaluation of selected materials control strategies. This Appendix describes a computer model (NOCSIM) that simulates the dynamic behavior of the conversion process in anticipated normal operating conditions.

II. THE MODEL PROCESS

The conversion process model is based on a preliminary SRL-SRP design.[30,48] This process converts plutonium nitrate solution, $Pu(NO_3)_4$, from a chemical separations facility to plutonium oxide powder, PuO_2, suitable for mixed-oxide fuel fabrication. Conversion is by the plutonium (III) oxalate precipitation process with a nominal throughput of 106 kg of plutonium per day (Chap. II).

Figure A-1 shows the model conversion process. Plutonium-nitrate solution from the chemical separations facility is fed to a receipt tank (∿200 L, ∿30 g of Pu/L). The receipt tank is air-sparged and mechanically agitated, and an accountability sample is taken before three ∿67-L batches are metered to three different valence adjustment tanks. The last batch dispensed completely empties the receipt tank. Hydrazine and ascorbic acid are added to the valence adjustment tank to reduce the plutonium to the trivalent state. The adjusted solution (∿26.5 g of Pu/L) is transferred to a precipitator and digested with oxalic acid to produce an oxalate slurry, which is vacuum-filtered through sintered-metal filter boats. The wet cake (∿2 kg of plutonium) is washed with ∿12 L of 0.5 *M* nitric acid and 0.3 *M* oxalic acid. The filtrate and cake wash solution (∿30 mg of Pu/L) is transferred to recovery operations. The boat is fed into a furnace for drying and calcining, which takes ∿6 h. The calcined product in each boat is transferred to a container for sampling and storage. The filter boat is flushed with ∿5 L of nitric acid and rinsed with ∿1 L of water before being returned to a filter station. The flush and rinse solution are transferred to recovery.

The model process has a throughput of 106 kg of plutonium per day; on the average a 2-kg batch is processed every 27 min. Three precipitator lines are operated in parallel to achieve this throughput while providing sufficient residence time for efficient precipitation. Each precipitator line operates semi-continuously by alternating batches from two valence adjustment

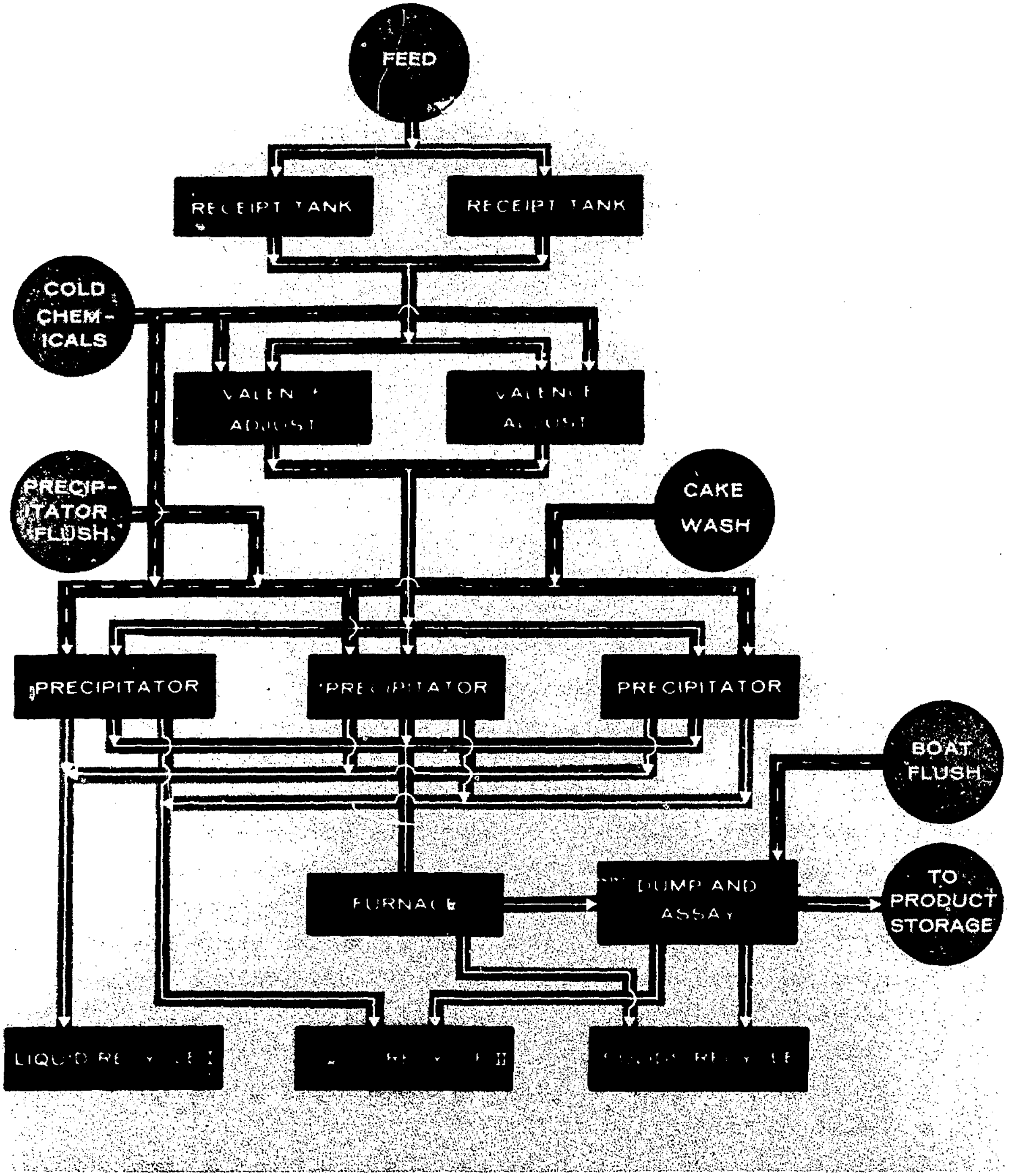


Fig. A-1. Conversion-process block diagram.

tanks to each precipitator. Table A-I lists typical batch sizes and concentrations in the model process.

A precipitator line is removed from the process line for flushing and is replaced by a spare line approximately every 8 h. The furnace is swept once a week, and the dumping station is swept once a day to recover loose plutonium oxide. Flush solutions, sweepings, and reject powders are transferred to recovery and recycle operations.

III. THE NOCSIM COMPUTER CODE

A computer code, NOCSIM, has been written using standard Monte Carlo techniques developed for dynamic systems[76,77] to simulate operation of the model nitrate-to-oxide conversion process. NOCSIM is run on a CDC 6600 computer at the LASL Central Computing Facility and requires approximately 50 000 words of core memory storage. The source code contains approximately 2000 FORTRAN statements maintained in UPDATE format. In addition, the code uses the executive function of the GASP IV Simulation Package,[78] which schedules events and provides other routine services. GASP IV can execute both discrete-event and continuous simulations.

Input data include initial values for all process variables and values of the statistical parameters that describe each independent, stochastic variable. Each process step (Fig. A-1) is modeled separately. When an event is scheduled in a particular process step, the values of all concentrations, material transfers, and in-process holdups associated with that step are computed and stored in a data matrix with 10 rows and 2 columns. Simulated data from each process step are saved in separate data files. These data are available for further processing and as input to computer codes that simulate accountability measurements and material balances.

Typically, a 72-h period of process operation is simulated in a single NOCSIM run. With an average time of 0.45 h between events, 1653 events occur during the 72-h period, and 33 060

TABLE A-I

BATCH SIZES AND CONCENTRATIONS IN STREAMS OF THE MODEL CONVERSION PROCESS

Stream Identification[a]	Batch Size[b]	Concentration[b]
Receipt tank feed	200 L	30.0 g Pu/L
Valence adjust feed	66.67 L	30.0 g Pu/L
Precipitator feed	75.44 L	26.5 g Pu/L
Furnace feed	4.65 kg	0.423 kg Pu/kg
Product	2.21 kg	0.882 kg Pu/kg
Filtrate and cake wash	154.8 L	0.03 g Pu/L
Precipitator flush	109.0 L	4.6 g Pu/L
Boat flush	7.9 L	1.1 g Pu/L
Furnace sweep	0.57 kg	0.882 kg Pu/kg
Dump station sweep	0.57 kg	0.882 kg Pu/kg
Valence adjust cold chemicals	8.8 L	--
Precipitants	69.5 L	--
Precipitator flush	109.0 L	--
Cake wash	12.0 L	--

---

[a] See Fig. A-1.

[b] These quantities are independent, stochastic variables in the computer simulation.

words of data are saved. NOCSIM is designed for ease of sequential running so that continuous process operation over any specified period can be simulated.

IV. EXAMPLES

Figures A-2 through A-7 show SNM concentrations, transfers, and holdups from a typical day of simulated operation. Values of the SNM variables are plotted at event times (either 0.45- or 1.35-h intervals).

A receipt tank is filled with ∿200 L of plutonium-nitrate solution from the chemical separations facility. The concentration ranges from 29.5 to 30.5 g of Pu/L. Figure A-2 shows the plutonium concentration and total volumes in a receipt tank for a typical 24-h period of operation. After it is filled, the tank is air sparged and sampled for accountability. Three 62- to 70-L batches of equal concentration are dispensed in three consecutive events. The third batch dispensed completely empties the receipt tank.

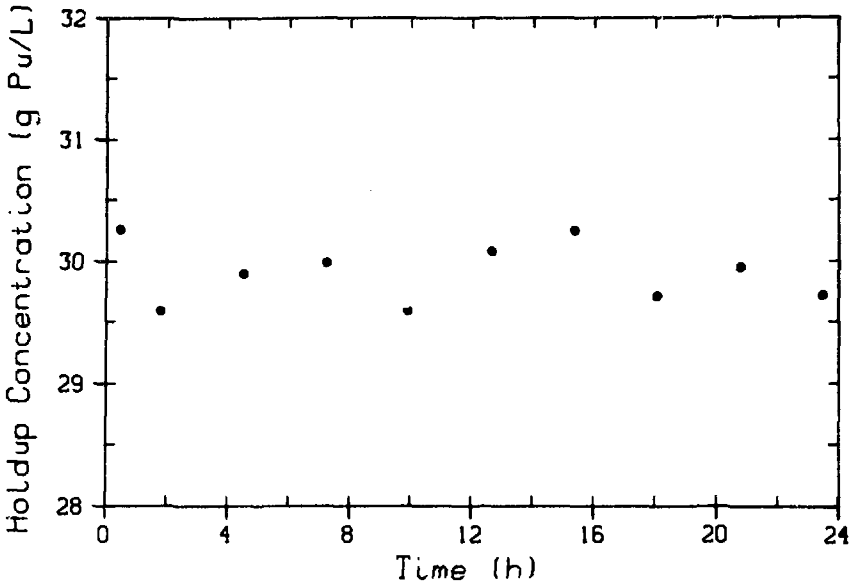
The concentration and mass of precipitator feed batches are given in Fig. A-3. In the precipitator, the physical form of the SNM is changed from liquid to solid (slurry). The materials transfers and holdup quantities of solid materials are calculated in terms of total mass (kg) and plutonium mass fraction (kg of Pu/kg of material).

In-process holdup in a precipitator and batches of oxalate in a sequence of filter boats are shown in Fig. A-4. The abrupt change in holdup near 13 h is caused by runout of the precipitator line followed by feed transfer to a clean standby line. The precipitators are drained and flushed periodically to control solids buildup.

In-process inventory in a furnace and recycle solids are shown in Fig. A-5. Each furnace has a capacity of six boats but will normally have an in-process inventory of four boats. Residence time in the furnace is 6 h. During this particular 24-h period of operation, a product batch of 1.90 kg of plutonium was found to be out of specification and was rejected at 4 h. At 11.3 h, a sweep of the dump stations yielded 0.49 kg of plutonium-oxide powder.

The concentration and volume of the combined filtrate and cake wash batches are given in Fig. A-6 (liquid recycle I). The concentration ranges from 15 to 55 mg of Pu/L. The normal volume is 147-163 L/batch. Two points (3.2 h, 167 L and 13.1 h, 170 L) exceed this range. These volumes resulted from runouts of precipitators that contained more than the normal batch volume.

Figure A-7 shows the concentration and volume of combined precipitator and boat flush solutions (liquid recycle II). Precipitators were flushed at 3.2, 10.8, and 13.1 h.



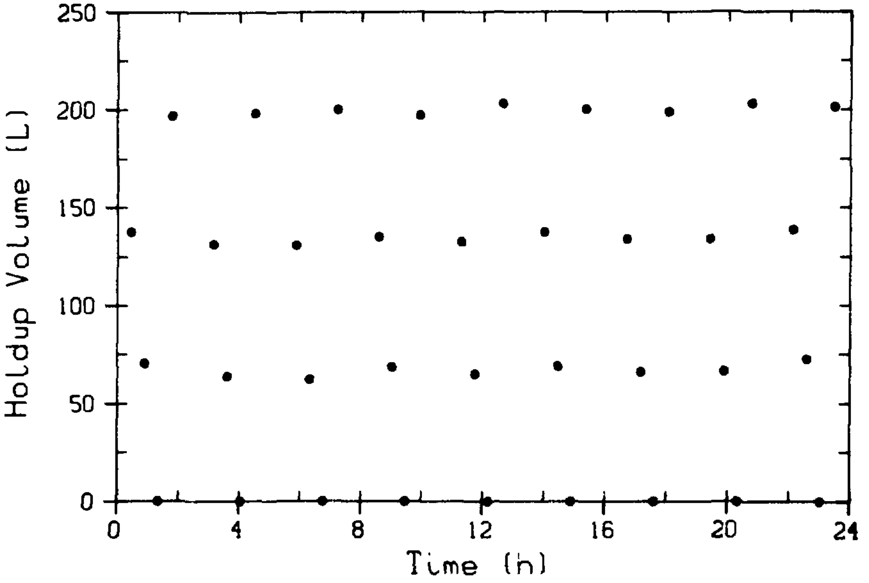


Fig. A-2. Receipt tank in-process inventory: concentration (upper), volume (lower).

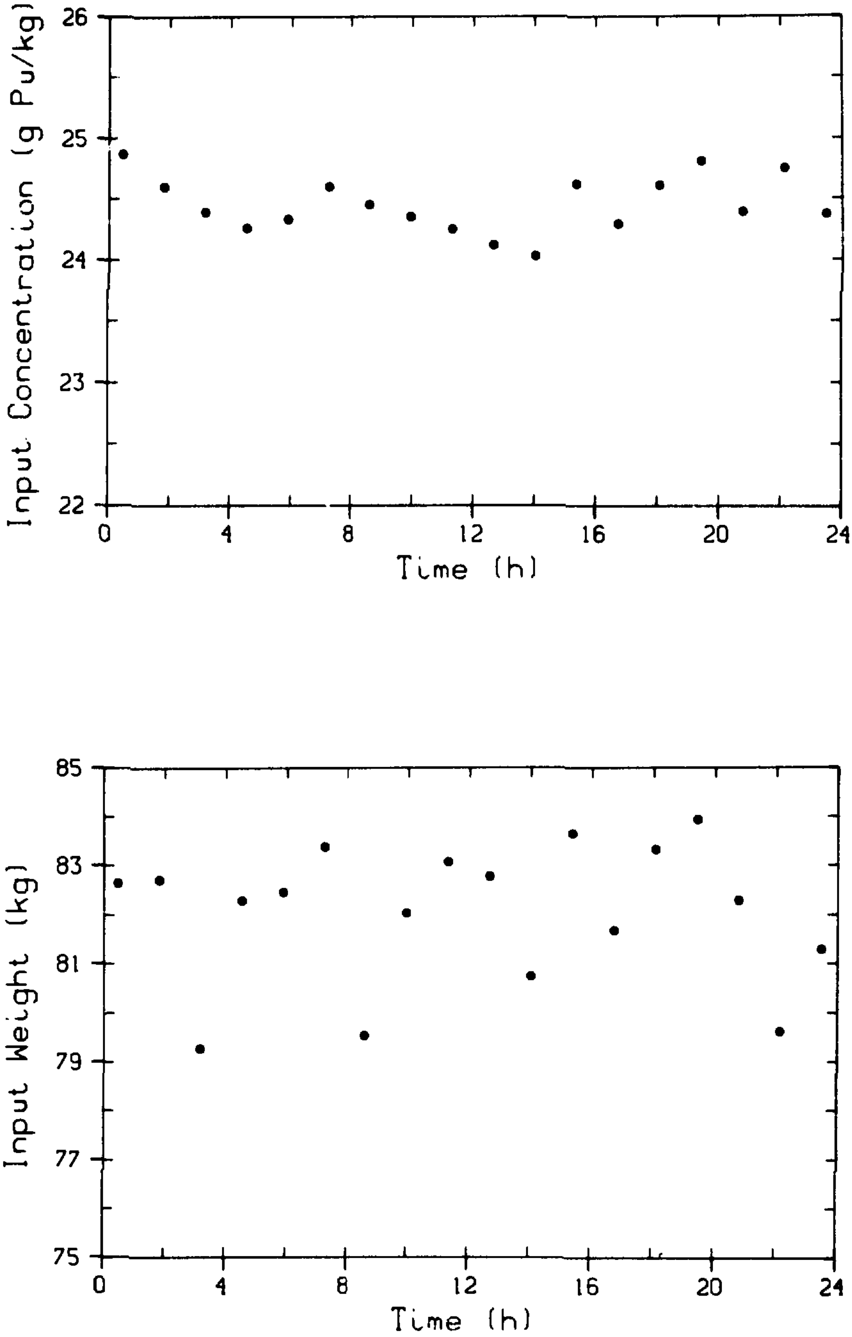


Fig. A-3. Precipitator feed: concentration (upper), weight (lower).

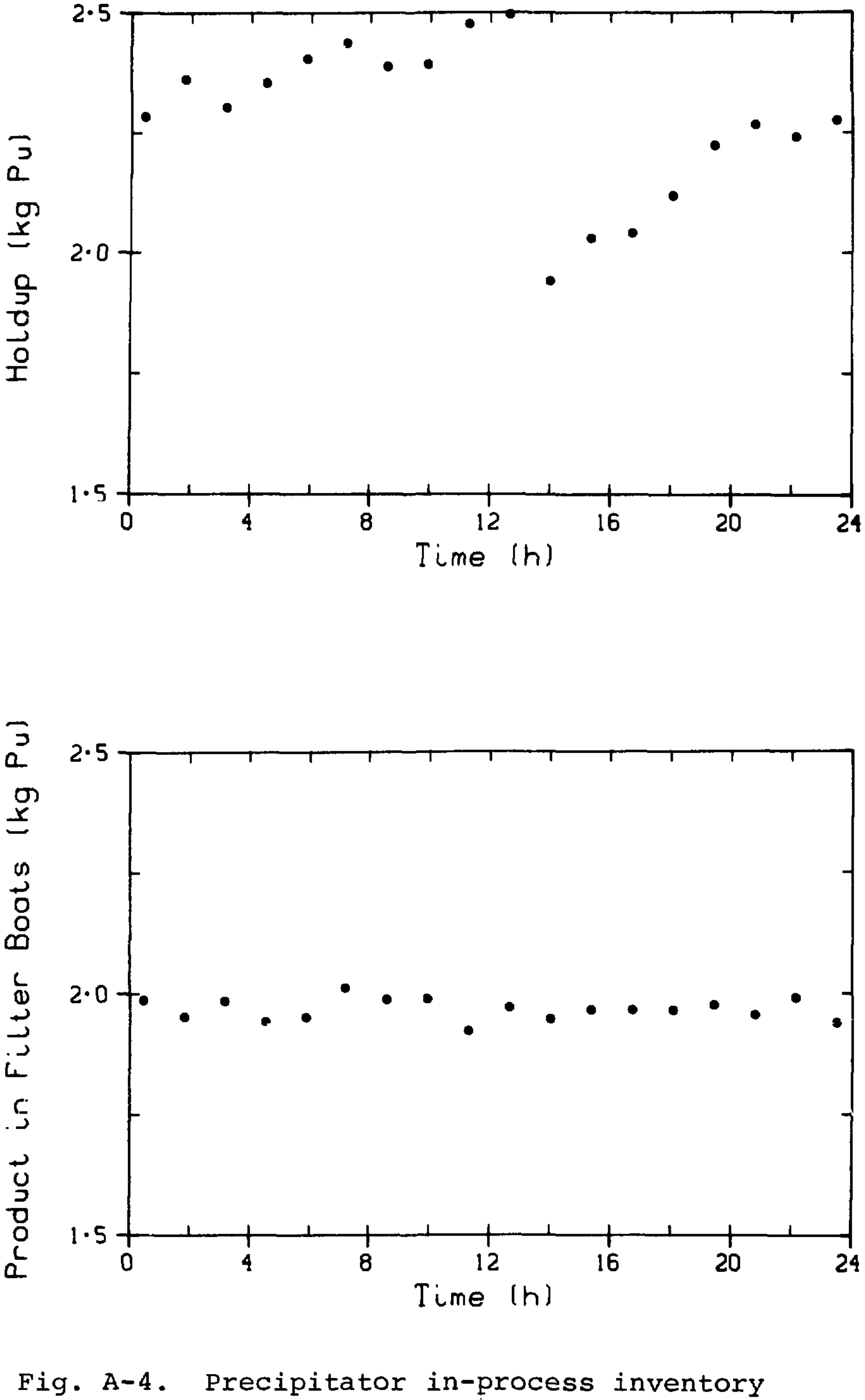


Fig. A-4. Precipitator in-process inventory (upper), product (lower).

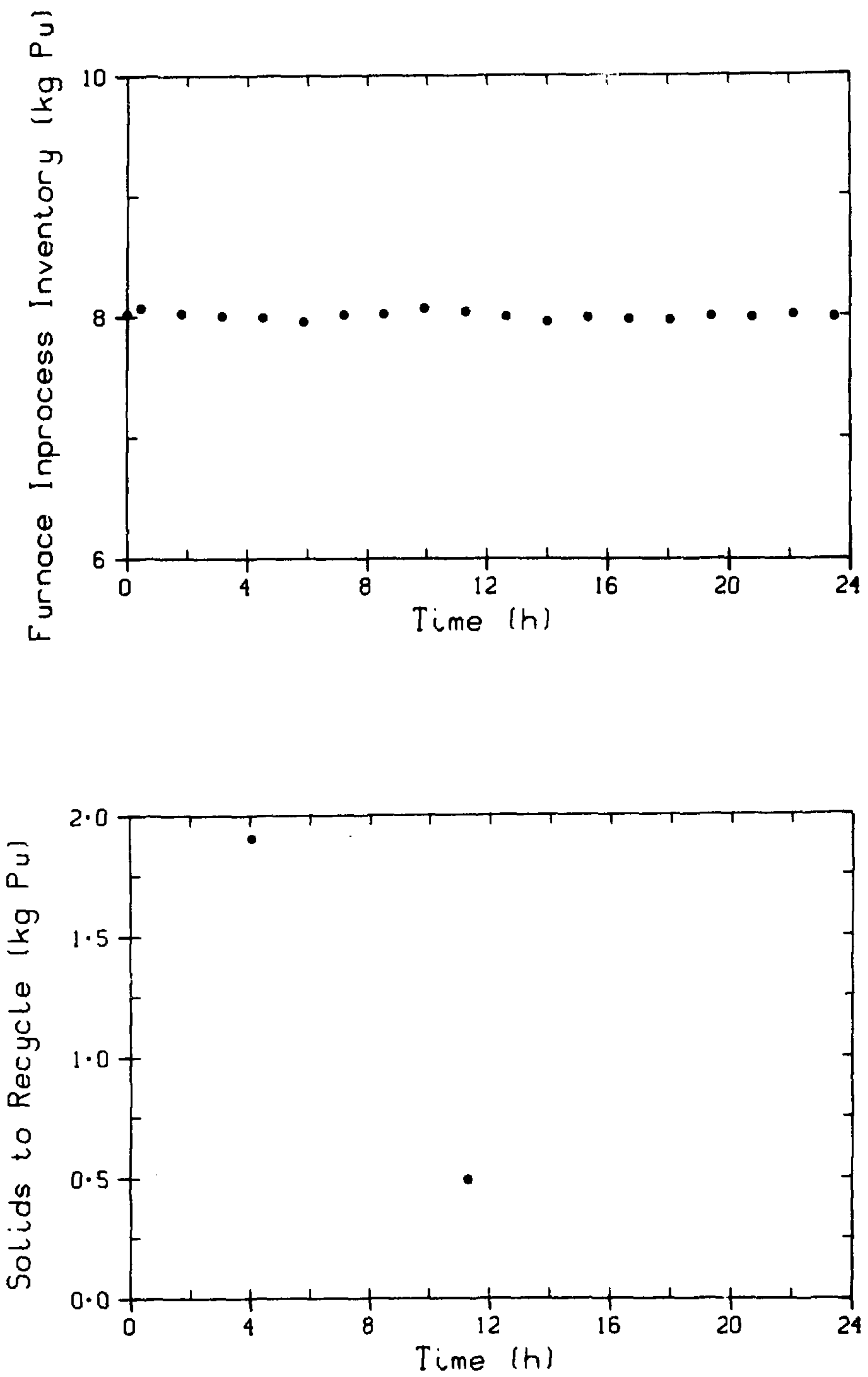


Fig. A-5. Furnace in-process inventory (upper), solids recycle feed (lower).

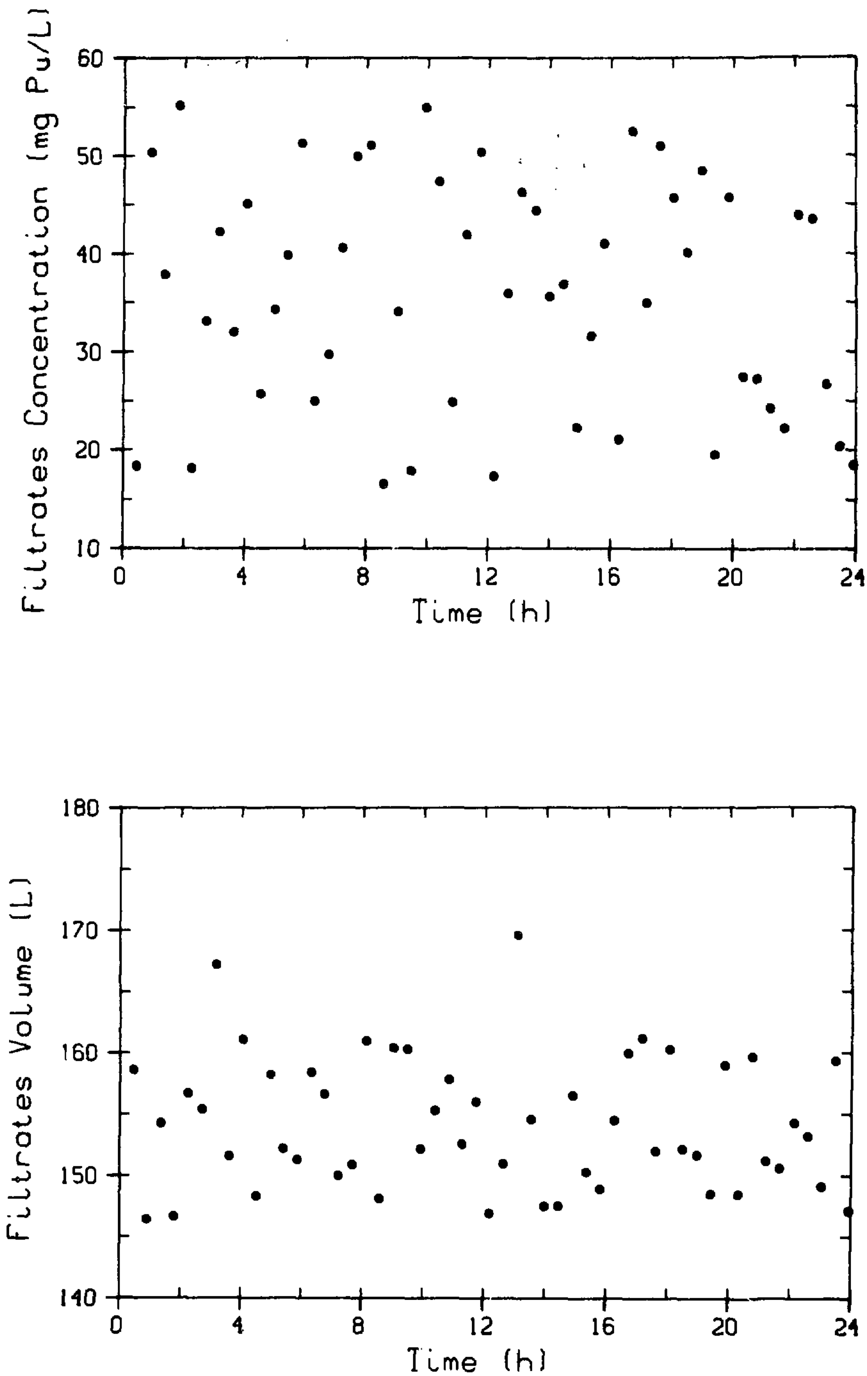


Fig. A-6. Filtrates and cake wash: concentration (upper), volume (lower).

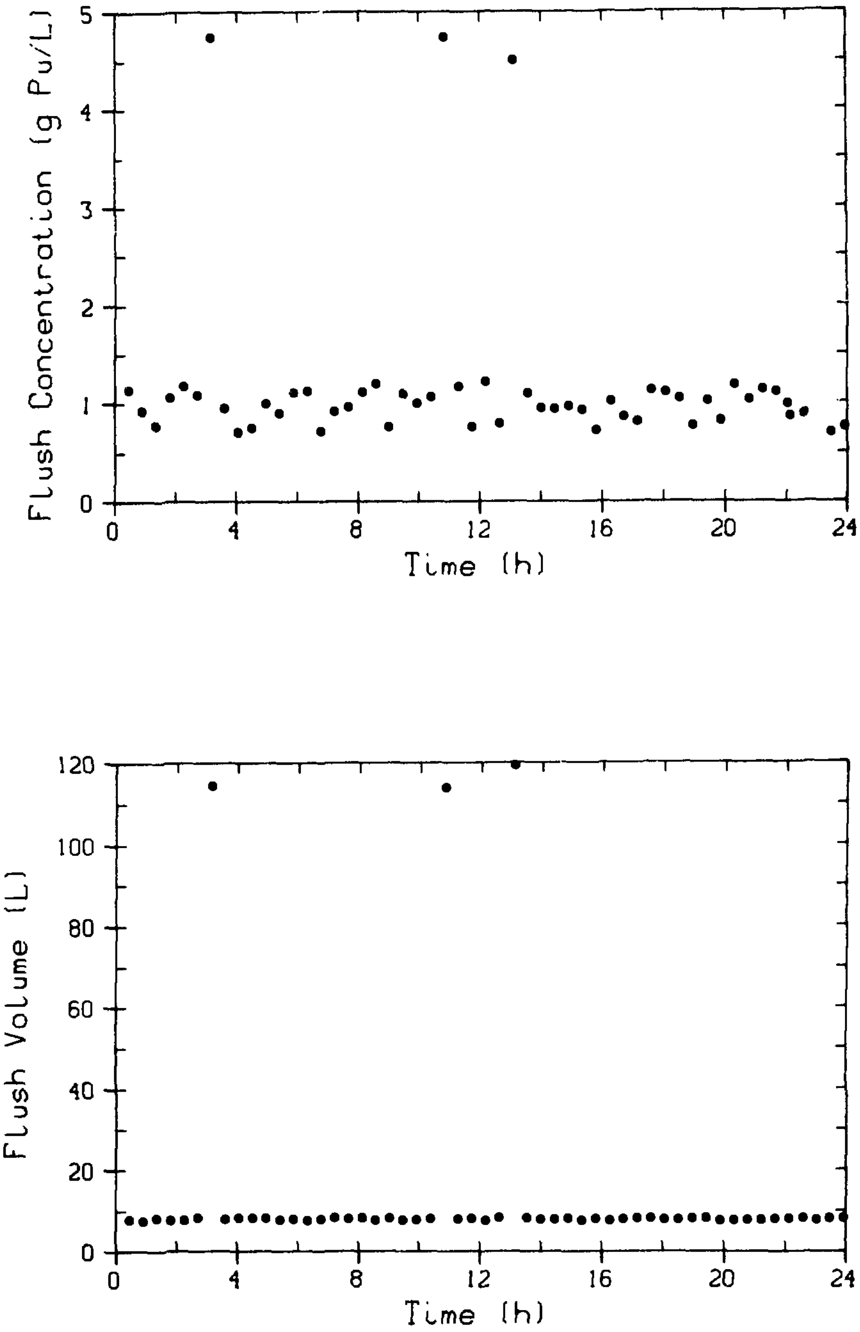


Fig. A-7. Flush solutions: concentration (upper), volume (lower).

APPENDIX B

ASSAY METHODS FOR THE PLUTONIUM CONVERSION PROCESS

I. INTRODUCTION

A variety of conventional analytical and NDA measurement techniques are available for characterizing feed, process, and product streams in the plutonium nitrate-to-oxide conversion plant. These methods have been described in detail elsewhere; therefore, only the more important features that affect their application in the conversion plant are reviewed here.

The plutonium material in the nitrate-to-oxide conversion plant generally is better characterized and purer than that in a fuel-reprocessing plant. Table B-I summarizes the characteristics of typical process streams.

II. STANDARDS

All analytical methods, whether conventional chemical analyses or NDA techniques, require calibration standards representative of the sample being analyzed. Both calibration methods and the standards used, must be traceable to the National Bureau of Standards (NBS), as prescribed in Ref. 2, pp. 368-371. The use and availability of standard reference materials (SRMs) in analytical chemistry is discussed by Rodden,[79] and the plutonium-containing SRMs available from the NBS are summarized in Table B-II.[80] The preparation of working standards from NBS metal, from production metal, or from plant nitrate solution is treated by Rein et al.,[81] and the use of PuO_2 as a reference standard is described by Swinburn and McGowan.[82]

TABLE B-I

CHARACTERISTICS OF SOME PLUTONIUM CONVERSION PLANT PROCESS STREAMS

Area	Plutonium Concentration	Comments
Feed	30 g/L	3 M HNO_3
Precipitator product	0.518 g/g	oxalate; hydrated and adsorbed H_2O; adsorbed HNO_3
Product	0.882 g/g	oxide
Precipitator flush	5 g/L	14 M HNO_3
Boat flush	1.5-3 g/L	14 M HNO_3
Filtrates	14-50 mg/L	0.8 M HNO_3

The use of PuO_2 as a standard is of particular interest in the conversion plant.

The preparation of standards for NDA analysis is not as straightforward because samples often are not homogeneous or well-characterized. The preparation and use of standards for NDA analysis has been reviewed,[83] and methods for calibrating NDA systems have been described.[84]

The lack of suitable standards or standardized procedures for NDA analysis has been recognized in the field and by the NBS.[85] As a result, the NBS has proposed a program to study NDA calibration methods, and to provide standard measurement procedures for NDA gamma ray, active and passive neutron, calorimetry, and x-ray fluorescence and absorption-edge techniques.[86,87]

A program to prepare test materials for NDA interlaboratory comparisons also is under way at the New Brunswick Laboratory.[88] The first phase of this program consists of studying suitable matrix materials for obtaining stable homogeneous standards.[89]

TABLE B-II

WORKING STANDARDS FOR PLUTONIUM ANALYSIS

Plutonium Assay Standards

SRM	Type	Certified For	Wt/Units (g)	Purity (%)
944	Plutonium sulfate tetrahydrate	Plutonium content	0.5	47.50[a]
945	Plutonium metal, standard matrix	Impurities	5	(99.9)[b]
949d	Plutonium metal assay	Plutonium content	0.5[c]	99.99

Plutonium Isotopic Standards

SRM	Type	Wt/Units (g)	Atomic Percent				
			^{232}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu
946	Plutonium sulfate tetrahydrate	0.25	0.247	83.128	12.069	3.991	0.565
947	Plutonium sulfate tetrahydrate	0.25	0.296	75.696	18.288	4.540	1.180
948	Plutonium sulfate tetrahydrate	0.25	0.011	91.574	7.914	0.468	0.033

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[a] Stoichiometric.

[b] Values in parentheses are not certified and are given for information only.

[c] Nominal weight.

III. WEIGHING AND VOLUMETRIC METHODS

A. Weighing Methods

Load-cell weighing systems are particularly well suited for measuring bulk quantities of material in nuclear facilities. The weighing platform can be separated physically from the associated electronics and readout mechanism. Only the platform need be exposed to the environment of a glovebox or process area, and the electronics can be located elsewhere to provide ready access for calibration and maintenance.

Load cells having 10-, 100-, and 1000-kg capacities are available commercially, and they should be large enough for all anticipated applications in the conversion facility. These units have the following measurement errors (per cent of full scale) (see Ref. 50, p. C-23):

Zero balance	1%
Hysteresis	0.02-0.05%
Repeatability	0.01-0.03%
Linearity	0.05-0.25% .

Determination by weighing the mass of solution in large process tanks and vessels would be the most direct method of obtaining this information, but successful use of load cells for such measurements has not yet been demonstrated. Idaho Chemical Processing Plant has evaluated the in-plant performance of a load-cell weighing system on an existing input accountability tank.[90] Because of large thermal forces generated in the tank and attached piping, it was impossible to attain the measurement accuracy for which the weighing system was designed. The study showed that to obtain useful accuracy, tanks installed on weighing systems must be specially designed for the application.

B. Volume Measurements

Materials accountability in the nitrate-to-oxide conversion facility will require frequent measurements of the plutonium content of feed, filtrate, and flush tanks. It is anticipated that these measurements will be based on measurement of the liquid volume in the tank combined with liquid-density and plutonium-concentration measurements to yield the required inventory. Volume-measurement technology for large process vessels has been reviewed recently.[91] The results are as follows.

Volume determinations usually are inferred from the measured liquid level in a calibrated tank. At present, the best developed liquid-level measuring system for use in nuclear facilities is the dip-tube manometer, or pneumatic bubbler. When combined with a commercially available electromanometer, such systems can have a detection sensitivity of 0.25 mm of water. Furthermore, the instrument output is directly computer-compatible. With careful calibration and an effective measurement-control program, calibration errors approaching 0.1% RSD and single volume-measurement errors of 0.5% or less should be attainable.

IV. CHEMICAL METHODS OF ANALYSIS

The applications and limitations of various conventional chemical methods for measuring plutonium in the process and waste stream of a reprocessing plant have been discussed recently,[92] and they are generally relevant to a conversion plant.

A. Gravimetric Methods

Gravimetric methods can be used for highly precise measurements of plutonium concentration in small samples. The method relies on obtaining a compound of the element to be determined and igniting it to a constant-weight stoichiometric composition. The method is applicable only to relatively pure materials; impurities must be determined using spectrographic or other procedures, and appropriate corrections must be applied to the final weight. Under carefully controlled conditions, a relative precision of 0.02% (RSD) in the mass determination can be obtained. Two types of weighing measurements can be used. The first involves only a determination of gross weight in which the uncertainty includes errors in zero balance, hysteresis, linearity, and repeatability. The second involves a determination of both tare and gross weights in which the net weight is found by subtraction. This second method minimizes, if not eliminates, errors due to zero balance (the largest error) and hysteresis, providing more accurate net weight values. Regardless of the method, calibration and check-weighing programs must be implemented to ensure that measurement results are both accurate and reliable.

B. Mass-Spectrometric Methods

Mass spectrometry is potentially the most accurate method for determining the plutonium isotopic composition and, in turn, the effective atomic weight for analytical measurements in nuclear fuel plants. For major isotopes, RSDs of 0.01 to 0.02% can be obtained.[93] Isotope-dilution mass spectrometry can be used to measure plutonium concentration in vessels with a RSD of 0.1 to 0.5%.[94] Mass spectrometry can be used to measure isotopic compositions for NDA instrument calibration.

C. Electrometric Methods

Potentiometric, amperometric, and coulometric methods probably provide the most precise measurements of total plutonium concentration. All three methods have demonstrated RSDs of 0.02 to 0.1% for routine analysis of weapons grade plutonium.[92] They would be valuable for calibration checks of NDA instruments in the feed and product streams of a conversion plant.

D. Spectrophotometric Methods

Spectrophotometry can provide rapid calibration checks of NDA techniques for measuring plutonium in waste streams. RSDs of 1-10% are typical, depending on the plutonium concentration and impurities. An automated spectrophotometer may be adapted for at-line measurement of plutonium in waste streams.[95]

V. NDA METHODS

NDA techniques fall into two major categories, active and passive. Active assay involves irradiation with neutrons or photons to induce nuclear or electron interactions in the sample. The resulting neutron, gamma-ray, or x-ray "signatures" are interpreted to determine quantitatively the amount of the designated element present.

Passive assay uses naturally occurring gamma-ray and/or neutron radiations as direct elemental or isotopic signatures.

A. Neutron Techniques

Application of neutron techniques to plutonium assay has been discussed elsewhere (for example see Ref. 96), so only details important to measurements in a conversion facility are reviewed here.

Neutrons from plutonium samples arise from either (α,n) reactions or fission. The (α,n) neutrons result from reactions of alpha particles from the radioactive decay of plutonium with light elements in the matrix material. The neutron yield is a function of alpha-particle energy, the (α,n) cross sections of the matrix elements, and the matrix configuration. Furthermore, the alpha-particle intensity depends on the isotopic composition and is particularly sensitive to the ^{238}Pu content. As a consequence, (α,n) neutrons ordinarily are not useful as a quantitative signature for plutonium, and, in fact, they usually constitute a large background that must be eliminated from most measurements.

Fission neutrons can result from spontaneous fission or from fissions induced by an external neutron source such as ^{252}Cf. Because the fission process produces more than one neutron per fission, fission neutrons can be differentiated from (α,n) neutrons using coincidence-counting techniques. Indeed, coincidence counting of fission neutrons will be a requisite feature of any neutron-based NDA system intended for quantitative assay of plutonium in the conversion facility. Only the even isotopes of plutonium, ^{238}Pu, ^{240}Pu, and ^{242}Pu, have high enough spontaneous fission rates to contribute to a passive neutron measurement. Hence, the isotopic composition must be known in order to infer total plutonium content.

Coincidence counting of ^{240}Pu and ^{242}Pu spontaneous-fission neutrons is accomplished with assemblies of ^{3}He (or BF_3) counters embedded in polyethylene moderators.[97-101] Table B-III lists estimates of the isotopic composition and neutron yields from spontaneous fission and (α,n) reactions of PuO_2 recycle fuel.[102] High (α,n) rates can complicate the coincidence method through accidental (random) coincidences and by fissions induced in the fissile components of the material, i.e., the multiplication effect.

If the coincidence-counting method is to be used to analyze large amounts of PuO_2 or scrap containing light elements that have high (α,n) yields, such as boron and fluorine, coincidence detectors with short die-away times are required to enhance the contribution of real coincidence events relative to accidental events, thereby reducing statistical uncertainties. This requirement has led to the concept of varying the physical die-away time of a neutron coincidence detector by changing the number and geometrical configuration of polyethylene moderators and cadmium (or boron) neutron absorbers.[103]

Table B-IV shows typical precisions and accuracies of neutron coincidence counters for the general categories of product, scrap, and waste[93] in the process environment. The data demonstrate the loss of precision and accuracy possible when the material composition (both elemental and isotopic) is poorly characterized and/or nonuniform.

In the conversion facility, neutron NDA methods will be used to measure PuO_2 product, precipitator in-process inventory, and wet-boat contents.

B. Gamma-Ray Techniques

Only the passive gamma-ray techniques appear applicable for measuring plutonium in the conversion facility. Use of passive

TABLE B-III

EMISSION RATE FROM ONE GRAM OF PLUTONIUM[a]

Isotope	Wt%	Spontaneous Fission		Spontaneous Fission Prompt Neutrons		(α,η) Neutrons from PuO_2	
		(sf/s)	(%)	(n/s)	(%)	(n/s)	(%)
^{238}Pu	1.9	20.9	14.8	47.2	15.3	266.0	76.1
^{239}Pu	63.0	0	0	0	0	28.4	8.1
^{240}Pu	19.0	89.5	63.6	194.2	63.2	32.3	9.2
^{241}Pu	12.0	0	0	0	0	1.2	0.3
^{242}Pu	3.8	30.4	21.6	65.7	21.4	0.4	0.1
^{241}Am	0.6	0	0	0	0	21.4	6.1
Total		140.8	100.0	307.1	100.0	349.7	100.0

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[a] LWR fuel with 35 000-MWD/MTU burnup.

TABLE B-IV

TYPICAL NEUTRON COINCIDENCE COUNTER UNCERTAINTIES

Material Category	Precision (%)	Accuracy (%)
Feed and product	1	1
Scrap	2-8	2
Waste	10-15	5-10

gamma-ray spectroscopy in assaying plutonium-bearing solutions is evaluated in Refs. 83, 104, and 105. The useful gamma-ray signatures from the plutonium isotopes and ^{241}Am are summarized in Table B-V. The ^{242}Pu isotope does not have a useful gamma ray, so it cannot be measured by this method.

Sodium iodide, lithium-drifted germanium [Ge(Li)] and intrinsic germanium detectors generally are used for gamma-ray measurments. The Ge(Li) and intrinsic germanium detectors provide much better energy resolution for adjacent peaks, but they require liquid N_2 cooling. Nevertheless, one or the other is required if good quantitative data on isotopic abundances are to be obtained. For rugged on-line instruments, the NaI detector is preferred if overlapping spectra are not a problem. More recently, CdTe detectors, which have an energy resolution of 8% at 122 keV and are usable at room temperature, have been investigated as a substitute for NaI.[106] This detector shows promise, but further development is required in matching detector and preamplifier and in reducing charge collection problems.

Gamma-ray spectroscopy can be used to measure the relative isotopic abundances of the plutonium isotopes, and to measure total plutonium concentration. The relative isotopic ratios are required for interpretation of calorimetric measurements or of neutron coincidence measurements of spontaneous fission of ^{240}Pu and ^{242}Pu. Relative isotopic measurements generally are obtained by using gamma-ray energies in a narrow energy

TABLE B-V

MAJOR GAMMA-RAY SIGNATURES OF PLUTONIUM AND AMERICIUM

Isotope	Energy (keV)	Intensity $(g\text{-}s)^{-1}$	Comments
^{238}Pu	766.40 152.77	1.5×10^5 6.5×10^6	Most useful for quantitative assay. Ge(Li) or NaI. Useful for isotopic determinations with Ge(Li).
^{239}Pu	413.69	3.4×10^4	The 413.69 usually provides the basis for Ge(Li) assays. The 413.69 plus the 375.02 and its weak neighbors form a complex upon which NaI assays are based.
^{239}Pu	129.28	1.4×10^5	Useful for isotopic determinations with Ge(Li). Plutonium-239 has over 100 gamma rays, some of which are useful for careful work with Ge(Li).
^{240}Pu	--	--	Several weak gamma rays but all suffer bad interference from gammas of other isotopes. Requires very careful work with high-resolution detector to make use of any of them.
^{241}Pu	207.98	2.0×10^7	Actually from ^{237}U daughter and requires about 25 days after chemical separation to come into equilibrium at stated value. May also have a few per cent interference from ^{241}Am which emits same gamma. Nevertheless a good clean strong gamma useful with both NaI and Ge(Li).
	164.59	1.8×10^6	Useful with Ge(Li). Also from ^{237}U.
	148.60	7.5×10^6	Useful with Ge(Li). Direct from ^{241}Pu.
^{241}Am	59.54	4.6×10^{10}	Very strong gamma but attenuation problems. Useful with Ge(Li) or NaI. Has several other much less intense gammas sometimes useful for Ge(Li) work.
^{242}Pu	--	--	No useful gamma rays at all. Nature failed us at this point.

region to minimize self-absorption effects, and by applying peak-stripping and background subtraction corrections with a computer. The relative precision of this measurement can be better than 0.5% (see Sec. VI-C of this Appendix). Total plutonium concentrations between 0.1 and 400 g/L can be determined in a 30-min counting period with a RSD better than 1% and an accuracy of 0.5% by measuring the ^{239}Pu isotope.[105]

The solid low-level waste from the conversion plant may be packaged in 55-gal drums for disposal, and it should be analyzed for plutonium. A drum scanner that uses a NaI detector to measure the 414-keV gamma ray from ^{239}Pu can detect as little as 1 g of ^{239}Pu in a 5-min scan.[57] The relative accuracy for measuring >10 g of ^{239}Pu can be as good as 10% in matrices of low atomic number and ranges to 50% in unknown matrices. Hence, the measurement accuracy will depend largely on the administrative control exercised in sorting waste. This instrument is in advanced development and requires only additional field testing and evaluation.

Active gamma-absorption methods have been proposed for plutonium solution assay. These methods depend on absorption of a monoenergetic gamma ray by the plutonium in the sample. Use of either ^{241}Am (60 keV)[107,108] or ^{57}Co (122 keV) (see Ref. 105, p. 18) has been proposed. A RSD and relative accuracy of ∿1% are obtainable, but any variations in matrix composition, including solvent, are measured as plutonium. Use of a dual-energy absorptiometer, where the second energy is ∿500 keV, can minimize solvent and light element interferences.[109] However, any heavy element contaminants such as uranium, neptunium, and americium will be measured with the plutonium, and even medium atomic number elements such as iron will interfere.

C. X-Ray Techniques

Two forms of active x-ray techniques (x-ray emission and x-ray absorption) are applicable to plutonium assay.[105] X-ray emission can be used to measure plutonium concentrations of one to several grams per liter with a 1% RSD. The K-, L-, and

M-series x-ray lines have been used for this analysis, but the L-series lines generally are preferred for solution assay. Wide variations in matrix composition may require an internal standard such as yttrium or thorium. The procedure is rapid and amenable to automation;[110,111] however, it is not an on-line method, and samples must be removed from the process stream.

X-ray absorption has been applied both in gross absorption and in absorption-edge densitometry. Gross absorption using either polychromatic[112] or monochromatic x-rays[113] suffers from the same lack of specificity as do gamma absorption methods. Hence, any variations in impurity element concentrations will be measured as changes in plutonium concentration.

Absorption-edge densitometry[105] is an element-specific analytical method that can be applied in-line or on-line to most measurement situations that are amenable to gross-absorption techniques. With proper choice of cell path length and K- or L_{III}-absorption edges, plutonium (or uranium) concentrations between 5 and 400 g/L can be measured with a relative standard deviation of better than 1%. For example, plutonium concentrations of 10-25 g/L were measured using the L_{III} edge with a 0.6% RSD,[114] and concentrations of 140-400 g/L were measured using the K edge with a 0.3% RSD.[115] For in-line safeguards accounting measurements, absorption-edge densitometry, rather than gross absorptiometry, should be used.

Absorption-edge densitometry offers an added advantage in that if both uranium and plutonium are present, as they would be in coprocessing, both can be measured simultaneously.

VI. CALORIMETRY

A. General

Plutonium calorimetry[116,117] is a nondestructive assay technique based on measuring heat generated by the radioactive decay of plutonium and americium. All but a negligible part of the decay energy is transformed into heat when the decay particles (alpha, beta, and low-energy gamma) are absorbed by the sample and calorimeter walls. In plutonium from processed reactor fuels, the energy from α-decay predominates and the energy release from ^{238}Pu, the plutonium isotope that has the highest specific α activity, is dominant.

The calorimetric method consists essentially of measuring the electrical energy needed to duplicate or balance the rate of heat emission (power) from the sample. The heat source (standard or unknown sample) in the calorimeter chamber is separated from a constant-temperature environment (heat sink) by a thermal resistance. In steady-state operation, equilibrium is determined by establishing a constant temperature difference between the calorimeter chamber and the surrounding environment; it is attained when thermal energy transfer to the environment equals that generated in the calorimeter chamber.

Calorimetry is applicable to assay of materials such as oxide powder or fuel pellets that have high plutonium concentrations. The total power of a sample can be determined without subsampling or aliquotting, permitting assay of sealed containers of material. Furthermore, calorimetry is relatively insensitive to the geometry and matrix effects that are a major concern when using many other NDA methods.

Calorimetry is both precise and accurate. In spite of potential sources of error discussed below, the precision (RSD) of a plutonium assay by calorimetry typically is 0.5% or better. However, because the design and construction of a calorimeter depend on the magnitude of the sample power, the physical size of the sample, and the types of radiation emitted, the concept of a "universal calorimeter" for all measurements is neither practical nor economical.

The lower limit of detectability of heat-flow calorimeters is 0.1 $\mu W/cm^2$ of sample-chamber surface area.[117] For ^{239}Pu, this corresponds to roughly 0.2 g in a 4-L container or 0.1 g in a 1-L container.

Calorimetric assay of plutonium is treated in USAEC Regulatory Guide 5.35,[118] and recommended calibration procedures for steady-state operation of heat-flow calorimeters are given in ANSI standard N15.22-1975.[117]

B. Measurement Time

Calorimetry is a relatively slow method because the sample and calorimeter must come to equilibrium before the power determination can be made. For PuO_2 feed or scrap samples, as long as 10 h may be required. Given well-controlled geometry and small samples, the equilibration time can be less than 1 h. The time required depends on the calorimeter design and operation and on the volume and packaging of the unknown sample.

Plutonium assay calorimeters are generally either single- or twin-chambered units with chamber(s) located in a constant-temperature (isothermal) heat sink. Three modes of steady-state operation are commonly used: replacement, differential, and servocontrolled or isothermal.

In the replacement method, the unknown sample is placed in the calorimeter chamber and, when equilibrium is reached, the corresponding temperature rise is recorded. The calorimeter is then calibrated by replacing the sample with a known power source of approximately the same magnitude and repeating the measurement. The replacement mode of operation, although perhaps the simplest and most straightforward, is the most time-consuming.

In the differential method, electrical heat in the reference side of a twin-chambered calorimeter is compared directly to the sample heat. Measurement times can be approximately half those required in the replacement method because sample and calibration runs are made simultaneously. However, such time reductions require relatively precise ($\sim$1%) prior knowledge of the unknown sample power. Therefore, the differential method is most useful for assaying nearly identical product materials.

In the isothermal mode of operation, the calorimeter is kept at a constant temperature above ambient by a servocontroller. When an unknown power source (the sample) is introduced, the power required to maintain the constant temperature is reduced. The sample power is the difference between the original control power and the new value. This mode of operation permits the fastest measurement, as the time to reach equilibrium depends only on the time constant of the sample and the magnitude of the temperature perturbation due to its introduction into the calorimeter. The time required to make the power measurement can be reduced further by pre-equilibrating the sample to near-operating temperature. Factors of 2-3 reductions in the time required to attain equilibrium within 0.01% have been reported[116] for a pre-equilibrating, servocontrolled calorimeter. However, where high measurement throughput is required, not all of this time is saved, because the time required for pre-equilibration must be included.

Nonsteady-state operation of plutonium calorimeters is possible and can also reduce measurement times. A method developed at Mound Laboratory to predict calorimeter equilibrium within 0.1% or better[119-122] is based on the fact that when a source of constant power is placed in a calorimeter the approach to equilibrium is an exponential function of time. Although the first part of the equilibrium curve consists of several exponential terms, it rapidly conforms to a single exponential function. Calorimeter output data collected at equally spaced time intervals are used to evaluate the system time constant, the equilibrium values, and the point at which the prediction process can be terminated. Assay times in calorimeters have been reduced 40-60% for samples 2.5-cm in diameter by 7.6 cm long to 17.2-cm in diameter by 28 cm long. This technique for predicting equilibrium cannot be used yet with servocontrolled calorimeters because of the fluctuations in the exponential equilibrium curve introduced by the analog servocontrol systems now in use. Experiments are under way to develop a digital control system that will permit simultaneous application of both of these time-saving methods.[123]

Mound Laboratory is developing as an in-line glovebox assay system for mixed-oxide fuels an automated plutonium assay system (APAS)[124,125] that uses mutiple servocontrolled calorimeters for plutonium measurement. A minicomputer controls container movement through an XYZ transporter, acquires and analyzes data, and prepares reports. After pre-equilibration, samples ranging from 100 g of mixed oxide to 1 kg of PuO_2 require less than 1 hour for power measurement. The sample container is a reusable stainless-steel can, ~6 cm in diameter by 15 cm long. The APAS also has a gamma-ray spectrometer for rapid measurement of the isotopic composition.

As indicated above, sample geometry, especially diameter, is a determining factor both in calorimeter design and in the time required to reach equilibrium. A portable calorimeter has been developed and used routinely to assay, within 30 min, short, mixed-oxide fuel rods whose plutonium and americium isotopic compositions are similar to those of FFTF-type fuel.[126-128] This calorimeter is a servocontrolled, preheated type with a sample chamber ~1 cm in diameter. The measurement capacity is 15-90 cm of fuel column length that contains 1-100 g of plutonium. The 13- to 23-min measurement times required do not include the 10- to 15-min preheating period; however, the next rod to be measured can be preheated while its predecessor is being measured.

C. Measurement Errors

Reilly and Evans[93] give an excellent summary of the precision and accuracy attained in using calorimeters for plutonium assay. The thermal power of a plutonium sample can be determined very precisely and accurately in a calorimeter because the measurement is traceable to well-characterized, primary NBS electrical standards. Thermal-power measurement RSDs of ~0.02 to 0.04% have been reported,[116,127] and a series of measurements of an electrical heat standard indicated a relative bias of 0.01% with respect to its accurately known value. Although thermal power values might be used directly in shipper-receiver situations with expected relative differences of 0.1% or less, most materials control applications of calorimetry require conversion of power to plutonium mass.

Conversion of thermal power to plutonium mass requires determination of the effective specific power of the sample. If the disintegration energy and half-life of each heat-contributing isotope are known, the isotopic specific power can be computed. Or, the specific power of each isotope can be measured directly if pure samples are available. In either case, the plutonium isotopic composition and ^{241}Am content must be known or determined if the amount of plutonium is to be inferred from the measured power. Assigned values of nuclear constants for radionuclides in plutonium-bearing solids are given in Ref. 117; the recommended values for half-lives and specific powers are reproduced in Table B-VI.

Generally, the precision of the plutonium-mass determination is limited by the uncertainty associated with measurement of the isotopic composition. Figure B-1 shows the precision obtainable in mass spectrometry of different plutonium isotopes.[129] For major isotopes, RSDs of 0.01 to 0.02% can be attained. The precisions for well-characterized material (a solution of NBS SRM) are significantly better than those for process and product solutions, particulary at isotopic concentrations <1%. The figures also shows that ^{238}Pu measurement by alpha spectrometry

TABLE B-VI

SPECIFIC POWERS OF PLUTONIUM AND AMERICIUM

Isotope	Half-Life (yr)	Specific Power (W/g)	Uncertainty in Specific Power (%, 1σ)
^{238}Pu	87.79	5.6716×10^{-1}	0.10
^{239}Pu	24 082	1.9293×10^{-3}	0.27
^{240}Pu	6 537	7.098×10^{-3}	0.2
^{241}Pu	14.35	3.390×10^{-3}	0.06
^{242}Pu	379 000	1.146×10^{-4}	--
^{241}Am	434.1	1.1423×10^{-1}	0.14

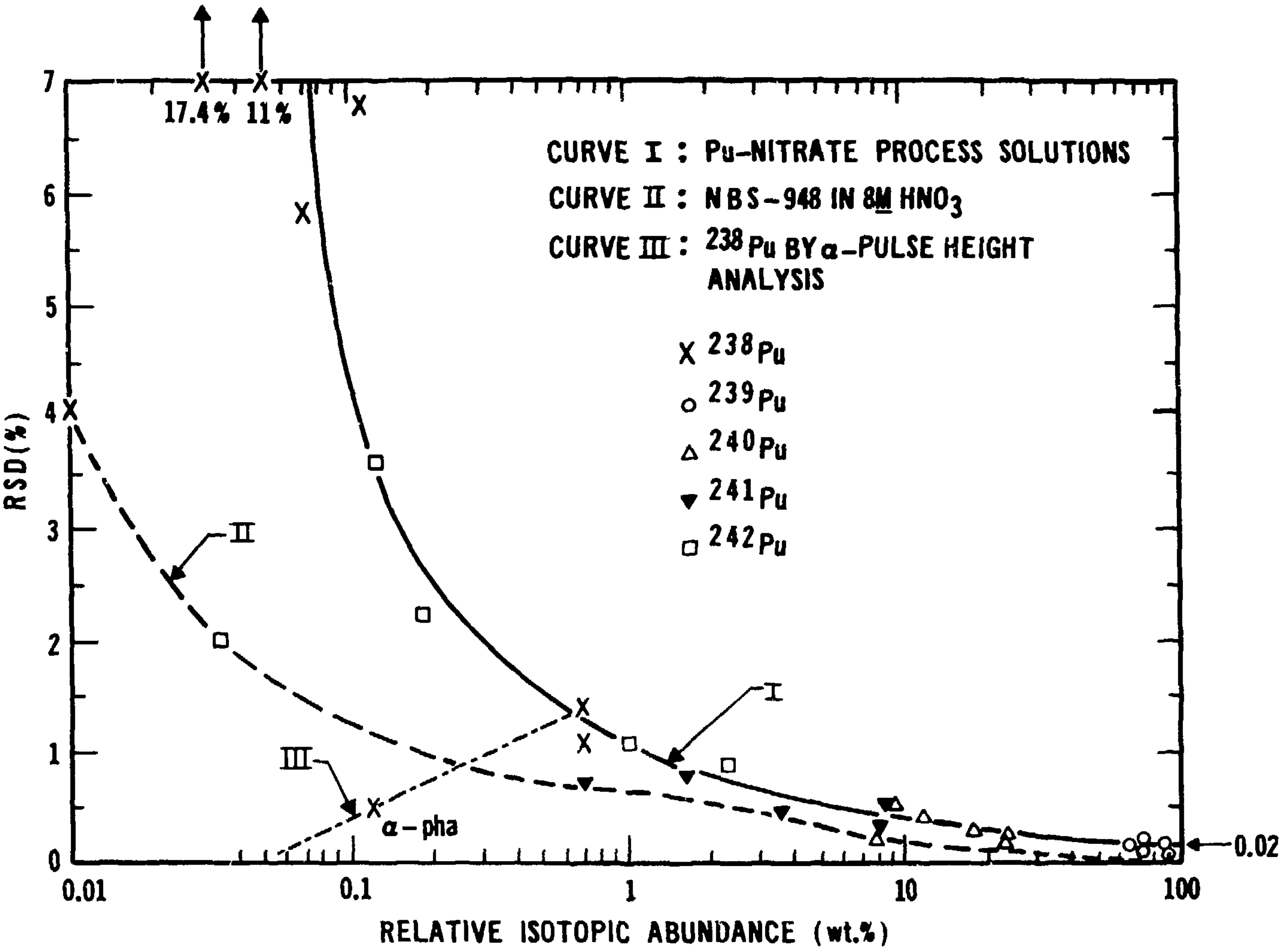

Fig. B-1. Precision of plutonium isotopic measurement.

is more precise than mass spectrometry at concentrations <0.7%. More recent studies have shown that precision and accuracy can be improved by taking proper care to minimize instrumental and operating errors. An interlaboratory exchange program should an overall RSD of 0.1% for measuring total plutonium in four well-characterized samples of different isotopic compositions.[94]

Of particular concern are ^{238}Pu and ^{241}Am, which usually have small relative abundances but may contribute significantly to the thermal power. Furthermore, because of americium ingrowth, the thermal power of reactor-fuel samples increases in time. Tables B-VII to B-IX list the composition about 1 yr after reprocessing of recycle plutonium for three different burnups, along with the fraction of the total heat produced by each isotope, and the uncertainties in the determination of plutonium mass due to the uncertainty in the specific power and relative abundance of each isotope. The relative precision of the plutonium mass measurement is computed for three different precisions of the abundance measurements,[93] high- and low-precision mass spectrometry and gamma-ray spectroscopy. Although the gamma-ray spectroscopy errors in the ^{239}Pu and ^{240}Pu abundances are considerably greater than the high-precision mass-spectrometry errors, they are compensated for by the relatively small errors in the high specific-power isotopes ^{238}Pu and ^{241}Am. Thus, the same precision can be achieved in a plutonium mass measurement using either method to measure the isotopic composition.

In freshly processed plutonium, such as might be encountered if the conversion plant is tied to the reprocessing plant, the americium content should be lower. In any case, the americium fraction at the time of the calorimetric assay must be known accurately or inferred from the known age of the sample.

The accuracy of calorimetric assay for plutonium depends on the accuracy of the known isotopic compositions, measured calorimetric heat values, and specific power values of the radionuclides in the sample. The specific power values listed in Table B-VI are those adopted by ANSI N15.22-1975,[117] which

TABLE B-VII

PRECISION OF CALORIMETRIC MEASUREMENT OF 18 000-MWD/MTU BURNUP

Isotope	Isotopic Abundance, A (%)	Fractional Specific Power	Isotopic Uncertainty $^{\sigma}A_i/A_i$ (%) Mass Spectrometry High Precision	Mass Spectrometry Low Precision	Gamma Spectroscopy
^{238}Pu	0.25	0.3124	0.75	2.20	0.5
^{239}Pu	75.0	0.3188	0.04	0.1	0.75
^{240}Pu	18.0	0.2815	0.16	0.3	0.85
^{241}Pu	4.5	0.0336	0.3	0.53	0.1
^{242}Pu	1.0	0.0003	--	--	--
^{241}Am	0.212	0.0534	2	10	0.8

Total specific power, P_{eff} = 4.538×10^{-3} W/g.

High plutonium precision = 0.28% RSD.

Low plutonium precision = 0.88% RSD.

Gamma plutonium precision = 0.39% RSD.

TABLE B-VIII

PRECISION OF CALORIMETRIC MEASUREMENT OF SPENT LWR

			Isotopic Uncertainty σ_{A_i}/A_i (%)		
			Mass Spectrometry		
Isotope	Isotopic Abundance, A (%)	Fractional Specific Power	High Precision	Low Precision	Gamma Spectroscopy
^{238}Pu	1.1	0.6225	0.5	1.0	0.32
^{239}Pu	61.6	0.1186	0.05	0.12	2.2
^{240}Pu	20.9	0.1480	0.16	0.28	1.0
^{241}Pu	12.6	0.0426	0.2	0.35	0.08
^{242}Pu	3.8	0.0004	--	--	--
^{241}Am	0.595	0.0678	2	10	0.8

Total specific power, $P_{eff} = 1.002 \times 10^{-2}$ W/g.

High plutonium precision = 0.35% RSD.

Low plutonium precision = 0.92% RSD.

Gamma plutonium precision = 0.37% RSD.

TABLE B-IX

PRECISION OF CALORIMETRIC MEASUREMENT OF SATURATED LWR RECYCLE MATERIAL

			Isotopic Uncertainty σ_{A_i}/A_i (%)		
			Mass Spectrometry		
Isotope	Isotopic Abundance, A (%)	Fractional Specific Power	High Precision	Low Precision	Gamma Spectroscopy
^{238}Pu	3.3	0.8128	0.35	0.6	0.17
^{239}Pu	41.1	0.0344	0.1	0.18	6.2
^{240}Pu	27.6	0.0851	0.14	0.22	1.2
^{241}Pu	17.6	0.0259	0.18	0.3	0.085
^{242}Pu	10.4	0.0005	--	--	--
^{241}Am	0.831	0.0412	2	10	0.75

Total specific power, $P_{eff} = 2.303 \times 10^{-2}$ W/g.

High plutonium precision = 0.31% RSD.

Low plutonium precision = 0.64% RSD.

Gamma plutonium precision = 0.29% RSD.

were determined as weighted means of all available experimental data. Mound Laboratory calorimeter measurements of well-characterized metal exchange plutonium samples have indicated a possible bias in the specific heat value of ^{239}Pu.[130] The value obtained agrees with the ANSI mean value within the stated standard deviation, but the error was sufficient to cause a 0.2% bias in the plutonium assay.

To resolve apparent discrepancies in published values of nuclear constants for the plutonium isotopes, a multilaboratory committee was formed early in 1974 to administer a half-life measurement program.[131] The program calls for measurements of aliquots from a single metal sample of high isotopic and chemical purity by three different techniques (calorimetry, alpha counting, and mass spectrometry). Each technique is used by at least two laboratories. Further, all samples are to be characterized for plutonium concentration and isotopic abundances by more than one laboratory.

Plutonium-239 was the first isotope considered. All the participating laboratories have completed their half-life measurements of ^{239}Pu, and, when statistical analyses are finished, the committee will recommend a composite half-life value. The committee also has reviewed two recent independent measurements[132,133] of the half-life of ^{238}Pu. Because the two results agree closely, the committee has accepted the average, 87.74 ± 0.04 yr, as the best half-life value of ^{238}Pu.[134] The participating laboratories are now measuring the half-life of ^{241}Pu; measurements on ^{240}Pu will follow.[135]

D. Application

In the conversion facility, calorimetry can be considered for measuring the PuO_2 product. Each package containing ∿2 kg of plutonium as PuO_2 can be assayed in ∿2 h in a servo-controlled calorimeter with sample preheating. If a digital controller is successfully developed so that equilibrium also can be predicted, this time will be further reduced. It should be possible to design, at a reasonable cost, an automatic, computer-controlled system with enough calorimeter chambers to keep up with the PuO_2 powder production rate (one 2-kg container every ∿20 min).[123] Measurement precisions (RSD) <1% should be attainable from either high-precision mass spectrometry or gamma-ray spectroscopy determination of isotopic abundance.

Calorimetry can at least characterize calibration standards accurately for other NDA methods.[118,136] It will establish traceability of these standards to NBS plutonium standards and can be used as part of the measurement control program to monitor the accuracy of other NDA measurement techniques periodically.

VII. MOISTURE DETERMINATION IN PLUTONIUM OXALATE

A possible measurement point for safeguards accountability in the conversion process is at the calciner entrance. During conversion, 2-kg batches of plutonium (III) oxalate are precipitated, filtered, and air-dried using an air aspirator. At this point, the oxalate should be a decahydrate containing ∿0.78 kg of adsorbed H_2O (in addition to the water of hydration), 21 g of adsorbed free $H_2C_2O_4$, and 25 g of HNO_3. The filter boats are passed into a three-stage calcining furnace. They stay in the first stage, at 100-200°C, for ∿2 h. At this temperature, adsorbed H_2O and HNO_3 evaporate, excess oxalic acid sublimes, and the plutonium oxalate decahydrate decomposes to the dihydrate.

The filter boats could be weighed before they enter the first furnace stage, and the amount of plutonium could be determined if a method for rapid H_2O determination were available. Methods that can be considered for in-line measurement of water include (1) radio frequency (rf) methods, (2) neutron scattering, and (3) x-ray scattering.

A. Radio Frequency Methods

Moisture meters have been developed for rf measurement of the H_2O content of various materials including cotton, timber, and cereals.[137] However, part of the sample probably would have to be transferred to a special sample cell, thereby reducing the effectiveness of this technique for rapid on-line measurement.

B. Neutron Methods

Neutron scattering is a standard technique for determining H_2O in such materials as soils, coking materials, and ceramics.[138,139] A depth probe inserted into the sample, or a surface probe, which operates in almost direct contact with the sample surface, can be used. Fast neutrons from an external source strike the sample, and those that are thermalized are measured. When used to measure plutonium oxalate, the system would have to be calibrated with dry oxalate to subtract out effects of spontaneous fission, (α,n) neutrons, and neutron thermalization by carbon and oxygen atoms in the oxalate. For measuring the H_2O content of soil or coke, the method is reported[139] to have a sensitivity of ~ 0.01 g/cm^3. For plutonium oxalate with a density of about 3 g/cm^3, this is equivalent to a concentration of $\sim 0.3\%$.

LASL has developed a system for determining hydrogen in fissile materials.[140,141] This instrument uses a ^{252}Cf source, and the sample is inserted into a well drilled into a steel block. It was developed specifically for small samples, but possibly could be modified for bulk samples by using a surface probe.

C. X-Ray Scattering

The H_2O content of solid samples can be determined by measuring the ratio of Compton to Rayleigh x-ray scattering. Rayleigh (coherent) scattering is basically a cubic function of the atomic number and weight of the scattering atom. Compton (incoherent) scattering is a function of incident energy (wavelength), scattering angle, and atomic number. The wavelength of the Compton radiation, λ_c, is given by

$$\lambda_c = \lambda - 0.2427 \text{ Cos } \phi \ ,$$

where λ is the wavelength of the primary radiation and ϕ is the scattering angle. The wavelength (energy) separation thus increases with increasing scattering angle and can be controlled by instrument design.

The intensity of the Compton radiation is greatest from light elements (hydrogen) and increases as primary radiation energy increases. Thus, the Compton/Rayleigh ratio from hydrogen also should increase when the primary energy is increased. Total x-ray scattering, however, decreases with increasing energy. A practical limit to the primary energy should be a compromise between the desired ratio of Compton to Rayleigh peak intensities and the total scattering intensity, and it appears to lie in the energy region between 50 and 100 keV. An ^{241}Am source has an energetic gamma ray at 60 keV, and may be useful. The ratio of the two scattered peaks is difficult to calculate theoretically, and the technique should be evaluated with actual samples to determine whether the sensitivity and precision needed for measuring hydrogen in plutonium oxalate (or PuO_2 product) could be attained. Possibly U_3O_8 containing known, added amounts of water could be used for the evaluation.

D. Conclusions

Radio frequency methods probably are not readily adaptable to in-line measurement, but they could be applied on-line or at-line.

Sample integrity may pose problems for both the neutron and x-ray scattering methods. The total sample volume is only about 1.28 L, and the sample may not be thick enough for the neutron measurements. The x-ray scattering method is primarily a surface measurement tool, and we do not know whether the surface moisture after air aspiration is representative of that throughout the sample.

Either the neutron or the x-ray scattering method might be combined with a neutron measurement of plutonium content to provide a more precise measurement of the boat contents.

VIII. SUMMARY

Conventional analytical methods will be required for the NDA measurement control program. For very precise analysis of high-purity nitrate feed solution and PuO_2 product, gravimetry or electrometric titrations may be used. Mass spectrometry can be used to measure isotopic ratios.

For in-line NDA analysis of the feed stream, absorption-edge densitometry can provide the required precision (∿1% RSD) in near-real time. With suitable calibration, alpha monitors may be used for waste streams, or the automated spectrophotometer could be used if higher precision is required.

APPENDIX C

MATERIALS ACCOUNTING EQUATIONS FOR THE CONVERSION PROCESS

I. INTRODUCTION

Equations for the material balances and cusums and their associated variance equations for the conversion process are presented here. The accounting strategies for the process are discussed in Sec. IV-C. In the first accounting strategy, one process line is divided into two unit process accounting areas. In the second, one complete line of the process is treated as a single UPAA.

II. ACCOUNTING STRATEGY ONE

A. Unit Process Accounting Area One

The first UPAA consists of the receipt tanks and one precipitator.

1. Material Balance. A dynamic material balance is drawn after a boat is filled (∿ every 1.35 h). The material balance equation after the nth batch of material has been transferred is

$$\begin{aligned} MB1_n = {} & C_n(V_{n-1} - V_n) - WB_n + HU_{n-1} - HU_n \\ & - FC_n\, FV_n - \delta_{PF_n}\, PFC_n\, PFV_n \quad , \end{aligned} \tag{C-1}$$

where

C = plutonium concentration in receipt tank solution,

V = volume of receipt tank solution,

WB = plutonium content of precipitator product (wet boat),

HU = plutonium in-process inventory in precipitator,

FC = plutonium concentration in filtrate solution,

FV = volume of filtrate solution,

$$\delta_{PF_n} = \begin{cases} 1 & \text{if a precipitator flush occurred,} \\ 0 & \text{otherwise,} \end{cases}$$

PFC = plutonium concentration in precipitator flush solution,

PFV = volume of precipitator flush solution.

The material balance equation can be rewritten as

$$MB1_n = T1_n + HU_{n-1} - HU_n \quad , \tag{C-2}$$

where $T1_n$ is the nth net material transfer in this unit process, given by

$$T1_n = C_n(V_{n-1} - V_n) - WB_n - FC_n\ FV_n - \delta_{PF_n}\ PFC_n\ PFV_n \quad .$$

2. Material Balance Variance. The variance of the nth material balance is the sum of the variance of the nth net transfer and those of the nth and (n-1)st in-process inventories; i.e.,

$$\sigma^2_{MB1_n} = \sigma^2_{T1_n} + \sigma^2_{HU_n} + \sigma^2_{HU_{n-1}} \quad . \tag{C-3}$$

Following the form of Eq. (IV-2), the total variance of the nth net transfer is estimated by

$$\sigma^2_{T1_n} = C_n^2 \Bigg[\left(V_{n-1}^2 + V_n^2\right)\left(\sigma^2_{\varepsilon_c} + \sigma^2_{\eta_c} + \sigma^2_{\varepsilon_v} + \sigma^2_{\eta_v}\right)$$

$$- 2V_{n-1} V_n \left(\sigma^2_{\varepsilon_c} + \sigma^2_{\eta_c} + \sigma^2_{\varepsilon_v}\right)\Bigg] \qquad \text{(C-4)}$$

$$+ WB_n^2 \left(\sigma^2_{\varepsilon_{WB}} + \sigma^2_{\eta_{WB}}\right)$$

$$+ FC_n^2 \; FV_n^2 \left(\sigma^2_{\varepsilon_{FC}} + \sigma^2_{\eta_{FC}} + \sigma^2_{\varepsilon_{FV}} + \sigma^2_{\eta_{FV}}\right)$$

$$+ \delta_{PF_n} \; PFC_n^2 \; PFV_n^2 \left(\sigma^2_{\varepsilon_{PFC}} + \sigma^2_{\eta_{PFC}} + \sigma^2_{\varepsilon_{PFV}} + \sigma^2_{\eta_{PFV}}\right) ,$$

where σ^2_ε and σ^2_η are the variances of the instrument and calibration errors (see Sec. IV-B).

The variance of the nth change in in-process inventory is

$$\sigma^2_{HU_n} = HU_n^2 \; \sigma^2_{\varepsilon_{HU}} \quad . \qquad \text{(C-5)}$$

3. Cusum. The cumulative sum (cusum) of material balances can be taken over sequences of any length. The cusum from the mth through nth (n>m) material balances is given by

$$CS1_n = \sum_{i=m}^{n} T_i + HU_m - HU_n \quad . \qquad \text{(C-6)}$$

4. Cusum Variance. The total variance of the cusum is a linear combination of the net transfer variances, the initial and final in-process inventory variances, and the correlation terms between the transfers. The correlation between any two

in-process inventory measurements is zero in this model. Following the form of Eq. (IV-7), the cusum variance is given by

$$\sigma^2_{CS1_n} = \sum_{i=m}^{n} \sigma^2_{T1_i} + \sigma^2_{HU_m} + \sigma^2_{HU_n} \qquad \text{(C-7)}$$

$$\begin{aligned} &+ 2 \sum_{\substack{i=m \\ i > j}}^{n} \sum_{j=m}^{n} \\ &\left[C_i \, C_j \left(V_{i-1} - V_i\right)\left(V_{j-1} - V_j\right)\left(\delta_{C_{ij}} \, \sigma^2_{\eta_C} + \sigma^2_{\eta_V}\right) \right. \\ &+ WB_i \, WB_j \, \sigma^2_{\eta_{WB}} + FC_i \, FC_j \, FV_i \, FV_j \left(\delta_{FC_{ij}} \, \sigma^2_{\eta_{FC}} + \sigma^2_{\eta_{FV}}\right) \\ &\left. + \delta_{PF_{ij}} \, PFC_i \, PFC_j \, PFV_i \, PFV_j \left(\delta_{PFC_{ij}} \, \sigma^2_{\eta_{PFC}} + \sigma^2_{\eta_{PFV}}\right)\right], \end{aligned}$$

where

$$\delta_{PF_{ij}} = \begin{cases} 1 & \text{if the precipitator flushes occur at events } i \text{ and } j \\ 0 & \text{otherwise.} \end{cases}$$

$$\delta_{C_{ij}}, \ \delta_{FC_{ij}}, \ \delta_{PFC_{ij}} = \begin{cases} 1 & \text{if measurements } i \text{ and } j \text{ occur in the same calibration period,} \\ 0 & \text{otherwise.} \end{cases}$$

Volume measurements are not recalibrated. Therefore, the double sum extends over all measurements made within the sequence (m,n).

B. Unit Process Accounting Area Two

The second UPAA in the first strategy consists of a furnace and a product dump and assay station. The equations for the material balance and cusum and their associated variances are similar to those for area one. A material balance is drawn for each batch (∿ every 1.35 h).

1. Material Balance.

$$MB2_n = WB_n - P_n - \delta_{BF_n} BFC_n BFV_n - \delta_{FS_n} FS_n - \delta_{DS_n} DS_n , \quad (C-8)$$

where

P = plutonium content of product,

$$\delta_{BF} = \begin{cases} 1 & \text{if the contents of the boat flush solution tank is measured,} \\ 0 & \text{otherwise,} \end{cases}$$

BFC = plutonium concentration in boat flush solution,

BFV = volume of boat flush solution,

$$\delta_{FS} = \begin{cases} 1 & \text{if a furnace sweep is done,} \\ 0 & \text{otherwise,} \end{cases}$$

FS = plutonium recovered from furnace sweep,

$$\delta_{DS} = \begin{cases} 1 & \text{if a dump station is swept,} \\ 0 & \text{otherwise,} \end{cases}$$

DS = plutonium recovered from a dump station sweep.

2. Material Balance Variance.

$$\sigma^2_{MB2_n} = WB_n^2 \left(\sigma^2_{\varepsilon_{WB}} + \sigma^2_{\eta_{WB}}\right) + P_n^2 \left(\sigma^2_{\varepsilon_p} + \sigma^2_{\eta_p}\right) \quad (C-9)$$

$$+ \delta_{BF_n} BFC_n^2 BFV_n^2 \left(\sigma^2_{\varepsilon_{BFC}} + \sigma^2_{\eta_{BFC}} + \sigma^2_{\varepsilon_{BFV}} + \sigma^2_{\eta_{BFV}}\right)$$

$$+ \delta_{FS_n} FS_n^2 \left(\sigma^2_{\varepsilon_{FS}} + \sigma^2_{\eta_{FS}}\right) + \delta_{DS_n} DS_n^2 \left(\sigma^2_{\varepsilon_{DS}} + \sigma^2_{\eta_{DS}}\right) .$$

3. Cusum.

$$CS2_n = \sum_{i=m}^{n} MB2_i \quad . \quad (C-10)$$

4. Cusum Variance.

$$\begin{aligned}\sigma^2_{CS2_n} = \sum_{i=m}^{n} \sigma^2_{MB2_i} + 2 \sum_{\substack{i=m \\ i > j}}^{n} \sum_{j=m}^{n} \Bigg[& WB_i \; WB_j \; \sigma^2_{\eta_{WB}} + P_i \; P_j \; \sigma^2_{\eta_P} \\ & + \delta_{BF_{ij}} \; BFC_i \; BFC_j \; BFV_i \; BFV_j \left(\delta_{BFC_{ij}} \; \sigma^2_{\eta_{BFC}} + \sigma^2_{\eta_{BFV}} \right) \\ & + \delta_{FS_{ij}} \; FS_i \; FS_j \; \sigma^2_{\eta_{FS}} + \delta_{DS_{ij}} \; DS_i \; DS_j \; \sigma^2_{\eta_{DS}} \Bigg] , \qquad (C\text{-}11)\end{aligned}$$

where

$$\delta_{BFC_{ij}} = \begin{cases} 1 & \text{if measurements } i \text{ and } j \text{ occur in the same calibration period,} \\ 0 & \end{cases}$$

III. ACCOUNTING STRATEGY TWO

Accounting strategy two consists of a single UPAA that contains the receipt tanks, a precipitator, a furnace, and a product dump and assay station. A material balance is drawn when a product can is filled. The equations are similar to those for strategy one.

A. Material Balance

$$MB_n = T_n + \Delta HU'_n \quad , \qquad (C\text{-}12)$$

where

$$T_n = C_n (V_{n-1} - V_n) - P_n - FC_n\ FV_n - \delta_{PF_n}\ PFC_n\ PFV_n$$

$$- \delta_{BF_n} BFC_n\ BFV_n - \delta_{FS_n}\ FS_n - \delta_{DS_n}\ DS_n \quad ,$$

$$\Delta HU'_n = HU'_{n-1} - HU'_n \quad ,$$

and

$$HU'_n = HU_n + \sum_{i=0}^{3} WB_{n-i} \quad .$$

Therefore,

$$\Delta HU'_n = HU_{n-1} - HU_n + WB_n - WB_{n-4} \quad .$$

Note that the net transfer can also be written as

$$T_n = T1_n + MB2_n \quad . \tag{C-13}$$

B. Material Balance Variance

$$\sigma^2_{MB_n} = \sigma^2_{T_n} + \sigma^2_{\Delta HU'_n} \quad , \tag{C-14}$$

where

$$
\begin{aligned}
\sigma^2_{T_n} = C_n^2 \Bigl[& \left(V^2_{n-1} + V^2_n\right)\left(\sigma^2_{\varepsilon_c} + \sigma^2_{\eta_c} + \sigma^2_{\varepsilon_v} + \sigma^2_{\eta_v}\right) \\
& - 2\, V_{n-1}\, V_n \left(\sigma^2_{\varepsilon_c} + \sigma^2_{\eta_c} + \sigma^2_{\eta_v}\right)\Bigr] \\
& + P_n^2 \left(\sigma^2_{\varepsilon_p} + \sigma^2_{\eta_p}\right) \\
& + FC_n^2\, FV_n^2 \left(\sigma^2_{\varepsilon_{FC}} + \sigma^2_{\eta_{FC}} + \sigma^2_{\varepsilon_{FV}} + \sigma^2_{\eta_{FV}}\right) \\
& + \delta_{PF_n}\, PFC_n^2\, PFV_n^2 \left(\sigma^2_{\varepsilon_{PFC}} + \sigma^2_{\eta_{PFC}} + \sigma^2_{\varepsilon_{PFV}} + \sigma^2_{\eta_{PFV}}\right) \\
& + \delta_{BF_n}\, BFC_n^2\, BFV_n^2 \left(\sigma^2_{\varepsilon_{BFC}} + \sigma^2_{\eta_{BFC}} + \sigma^2_{\varepsilon_{BFV}} + \sigma^2_{\eta_{BFV}}\right) \\
& + \delta_{FS_n}\, FS_n^2 \left(\sigma^2_{\varepsilon_{FS}} + \sigma^2_{\eta_{FS}}\right) + \delta_{DS_n}\, DS_n^2 \left(\sigma^2_{\varepsilon_{DS}} + \sigma^2_{\eta_{DS}}\right) \quad ,
\end{aligned}
$$

and

$$
\sigma^2_{\Delta HU'_n} = \left(HU^2_{n-1} + HU^2_n\right) \sigma^2_{\varepsilon_{HU}} + \left(WB^2_n + WB^2_{n-4}\right) \sigma^2_{\varepsilon_{WB}} \quad .
$$

C. Cusum

$$
CS_n = \sum_{i=m}^{n} MB_i \quad . \tag{C-15}
$$

D. Cusum Variance

$$\begin{aligned}
\sigma^2_{CS_n} = {} & \sum_{i=m}^{n} \sigma^2_{T_i} + \left(HU^2_m + HU^2_n\right) \sigma^2_{\varepsilon_{HU}} \\
& + \sum_{i=0}^{3} \left(WB^2_{m+i} + WB^2_{n-i}\right) \sigma^2_{\varepsilon_{WB}} \qquad \text{(C-16)} \\
& + 2 \sum_{\substack{i=m \\ i > j}}^{n} \sum_{j=m}^{n} \\
& \Big[C_i \; C_j \left(V_{i-1} - V_i\right)\left(V_{j-1} - V_j\right)\left(\delta_{C_{ij}} \; \sigma^2_{\eta_C} + \sigma^2_{\eta_V}\right) \\
& + P_i \; P_j \; \sigma^2_{\eta_P} + FC_i \; FC_j \; FV_i \; FV_j \left(\delta_{FC_{ij}} \; \sigma^2_{\eta_{FC}} + \sigma^2_{\eta_{FV}}\right) \\
& + \delta_{BF_{ij}} \; BFC_i \; BFC_j \; BFV_i \; BFV_j \left(\delta_{BFC_{ij}} \; \sigma^2_{\eta_{BFC}} + \sigma^2_{\eta_{BFV}}\right) \\
& + \delta_{PF_{ij}} \; PFC_{ij} \; PFC_i \; PFC_j \; PFV_i \; PFV_j \\
& \quad \left(\delta_{PFC_{ij}} \; \sigma^2_{\eta_{PFC}} + \sigma^2_{\eta_{PFV}}\right) \\
& + \delta_{FS_{ij}} \; FS_i \; FS_j \; \sigma^2_{\eta_{FS}} + \delta_{DS_{ij}} \; DS_i \; DS_j \; \sigma^2_{\eta_{DS}} \Big] \quad .
\end{aligned}$$

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