UCRL-13696

MASTER

SCIENCE
Applications
INCORPORATED

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

SAI-76-747-LJ

MATERIAL CONTROL
FOR A
REPROCESSING PLANT

August 15, 1976

Submitted to:

Lawrence Livermore Laboratory
Final Report on Contract 2483403

by

D. Rundquist
G. Bray
S. Donelson
J. Glancy
T. Gozani
L. Harris
R. McNamera
D. Pence
M. Ringham

SCIENCE APPLICATIONS, LA JOLLA, CALIFORNIA
ALBUQUERQUE • ANN ARBOR • ARLINGTON • ATLANTA • BOSTON • CHICAGO • HUNTSVILLE
LOS ANGELES • McLEAN • PALO ALTO • SANTA BARBARA • SUNNYVALE • TUCSON

P.O. Box 2351, 100 Prospect Street, La Jolla, California 92037

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

TABLE OF CONTENTS

1. INTRODUCTION

The maturing nuclear power industry is requiring an expanding fuel cycle to meet its power generation needs. Fuel cycle facilities are processing higher and higher throughputs of nuclear fuel material. And if the nuclear power industry continues to evolve toward a more efficient utilization of the energy available in uranium fuel, then the construction and operation of high throughput reprocessing and fuel fabrication plants handling large quantities of plutonium will be required. This places a new exposure dimension on this strategic special nuclear material.

Adequate control of special nuclear material (SNM) implies a basic knowledge of the quantities of SNM processed through or contained within a fuels processing facility with sufficient accuracy that diversion of the SNM for deleterious purposes can be detected in a timely manner. The effectiveness of an SNM inventory system to satisfy this objective must be assessed in relation to the operational constraints imposed by the technology available for use in large-scale commercial plants. A thorough understanding of the basic unit operations and the physical characteristics of the materials processed within the facilities is necessary for establishing criteria for an effective control system.

This report to the Lawrence Livermore Laboratory (LLL) describes the primary process streams containing plutonium that are handled routinely within a spent fuel reprocessing plant and conversion facility. These streams and measurement systems have been described in sufficient detail to permit a preliminary assessment of the capability of measurement systems to determine the inventory status within the facilities. As an aid in implementing the objectives of the accountability system in a realistic situation, the Allied General Nuclear Services (AGNS) reprocessing plant now under construction near Barnwell, South Carolina, was chosen as the study model.

In Section 2, the AGNS plant processes are discussed in detail emphasizing those portions of the process that contain significant quantities of plutonium. The unit processes within the separations plant, nitrate storage, plutonium product facility and the analytical laboratory are described with regard to the SNM control system currently planned for use in the facilities. Suggestions for possible SNM procedure improvements are also discussed in a general manner. Flow sheets presenting primary process equipment volumes, process stream flow rates, and plutonium concentrations are included as a guide for evaluating nuclear material control system effectiveness. The process portion of Section 2 is concluded with a brief discussion of alternative process components that might in the future be designed into a Purex separations and oxalate precipitation conversion facility. To complete the description of the AGNS report a listing of the in-process and analytical instrumentation used for process control and SNM accountability control is given.

A general discussion of laboratory techniques, nondestructive assay and process instrumentation for plutonium process and product material from a reprocessing plant is included in Section 3. An initial selection of laboratory, nondestructive assay, and process instrumentation is presented.

Section 4 contains a comprehensive discussion of holdup measurements in plutonium recycle facilities. The relative impact of holdup on SNM material accountability in a Pu recycle facility is assessed to develop the proper prospective. A review of holdup measurement techniques along with some recently reported results are presented.

Section 5 contains a brief preliminary overview of alternative processing strategies for LWR fuel. Included is a discussion on alternatives to the oxalate precipitation process for converting $Pu(NO_3)_4$ to PuO_2.

An extensive review and summary of modeling efforts for liquid-liquid extraction cycles is included in Section 6. A comprehensive bibliography of previous modeling efforts is covered.

2 BARNWELL MODEL PLANT

The Barnwell Nuclear Fuels Plant (BNFP) operated by Allied-General Nuclear Services (AGNS) was selected as the model plant for this study as it represents the latest technology in commercial use for reprocessing spent light water reactor (LWR) fuels. The BNFP separations facility has a design capacity for recovering 1500 tonnes of uranium and 15,000 kg of Pu from irradiated fuel elements annually.(1) As the BNFP is constructed, the recovered Pu will be in the form of plutonium nitrate solutions, however, a 1972 NRC ruling that all commercial shipments of Pu must be in solid form necessitates that a solidification process be added to the plant. In view of this restriction AGNS has proposed an addition to the separations facility to permit conversion of liquid $Pu(NO_3)_4$ to solid PuO_2 at a maximum rate of 100 kg of PuO_2 per day. A Preliminary Safety Analysis Report (PSAR) has been prepared by AGNS describing the conversion methods and processing equipment that would be used in the Plutonium Product Facility (PPF).(2) Further design work on the plant addition has been deferred until the technical and regulatory questions set forth in USAEC Report WASH-1327, Generic Environmental Statement--Mixed Oxide Fuel (GESMO) have been resolved.(3) The PSAR submitted does provide an adequate description of a facility designed to satisfy the safeguards requirements as they are understood today.

There are two other existing commercial reprocessing facilities in the United States that were considered as the plant model. The Nuclear Fuel Services Plant at West Valley New York was put into operation in 1966. This plant is currently shut down for modification to increase its capacity to 750 tonnes of heavy metal per year. It is unlikely that the plant will resume operations before 1980(4).

A LWR fuel reprocessing plant was constructed by the General Electric Company at Morris, Illinois. GE has concluded that the plant, as designed, cannot be operated effectively without major modifications and has postponed plant startup indefinitely. Neither the Morris plant nor the NFS plant were considered representative of large scale commercial plants of the future.

A fourth commercial reprocessing plant has been proposed. This plant to be operated by Exxon Nuclear Company at Oak Ridge, Tennessee, will be designed to reprocess spent fuel elements at a rate of 2100 tonnes of heavy metal (uranium plus plutonium) per year and is scheduled to start operation in 1984-1986. A PSAR describing the plant has been submitted for acceptance review(5). As the plant will not be in actual operation for about 10 years, it was not considered applicable for the basis of this study.

The BNFP is located on a site adjacent to the Savannah River Plant operated by ERDA near Barnwell, South Carolina. The plant will consist of four major facilities when construction is complete(6).

1. The Separations Facility. This portion of the plant will be used to receive spent fuel elements discharged from power reactors, provide storage prior to processing, prepare fuels for recovery using the shear-leach process and recover uranium and plutonium as purified concentrated nitrate solutions utilizing a modified form of the Purex process.

2. Plutonium Product Facility (PPF). Recovered plutonium nitrate solutions will be converted to plutonium oxide using the oxalate precipitation process. Plutonium oxide will be stored pending shipment to a mixed oxide (MOX) facility for fabrication into fuel elements for recycle into light water reactors or into breeder reactor fuels.

3. Uranium Hexafluroide Facility (UHF). Recovered uranyl nitrate solution will be converted to uranium hexafluoride by the fluid bed reactor technique used at Metropolis for converting yellowcake to UF_6.

4. Waste Handling Area (WHA). Radioactive wastes generated in the separations facility and the uranium hexafluoride facility will be handled, solidified, packaged and stored prior to shipment to a Federal Repository for disposal. Scrap generated in the plutonium facility will be processed and stored temporarily within the plutonium facility.

The overall process flow chart for the combined separations facility and the plutonium product facility is presented in Fig. 1.

2.1 GENERAL PROCESS DESCRIPTION - SEPARATIONS PLANT

The overall flow sheet for reprocessing spent fuel using the shear-leach feed preparation method and a modified Purex process utilizing an electrocell for plutonium valence control is given in Fig. 2(7). Further details of the dissolution and feed preparation steps are given in Fig. 3. Fig. 4 shows the coextraction and uranium and plutonium partitioning cycles, and Fig. 5 presents the plutonium extract purification and concentration processes. The uranium and plutonium concentrations given for the process streams shown on Figs. 3, 4 and 5 are average-equilibrium values based on recycling mixed oxide fuels from a LWR. The plutonium content of recycled MOX fuel is on the order of 3% of the contained heavy metal. Spent fuel from a LWR operated on a fresh fuel cycle normally has a plutonium content of 0.8 to 1.0%.

Spent fuel elements contained in shielded transport casks are received at the cask unloading facility. The fuel elements are transferred to the storage pool for interim storage prior to processing. The spent fuel elements are transferred to the

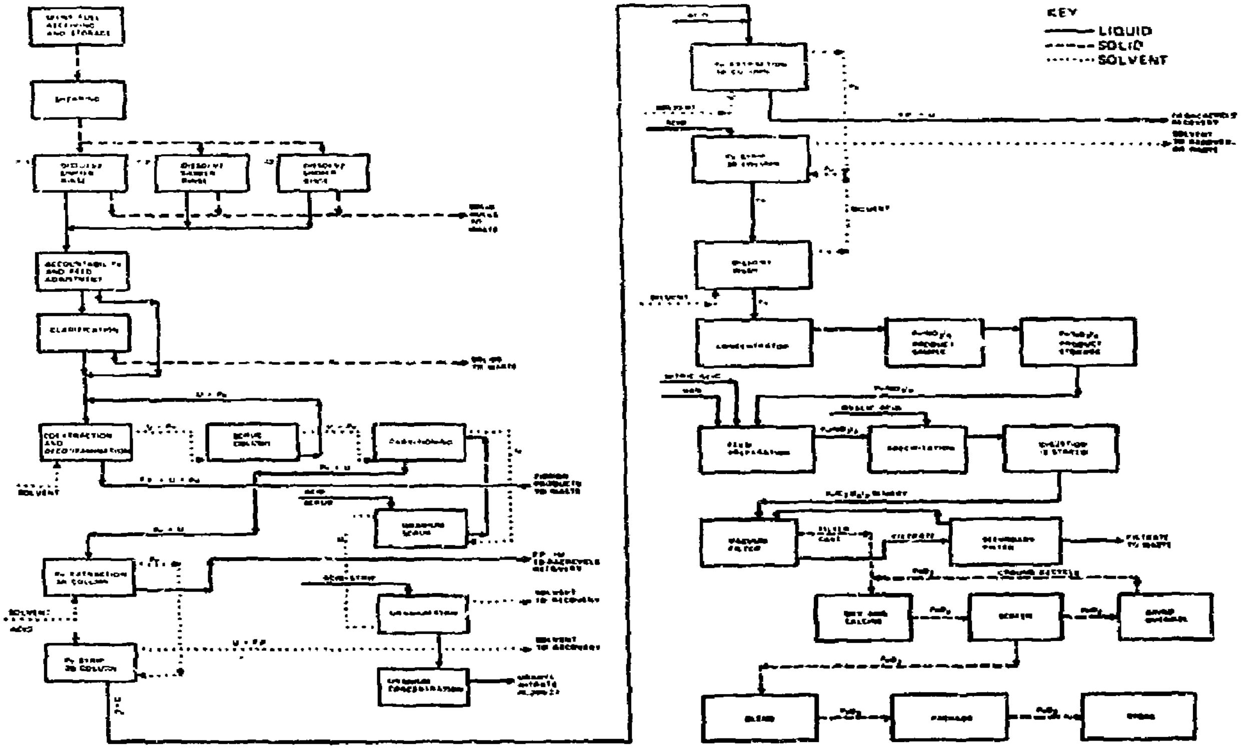
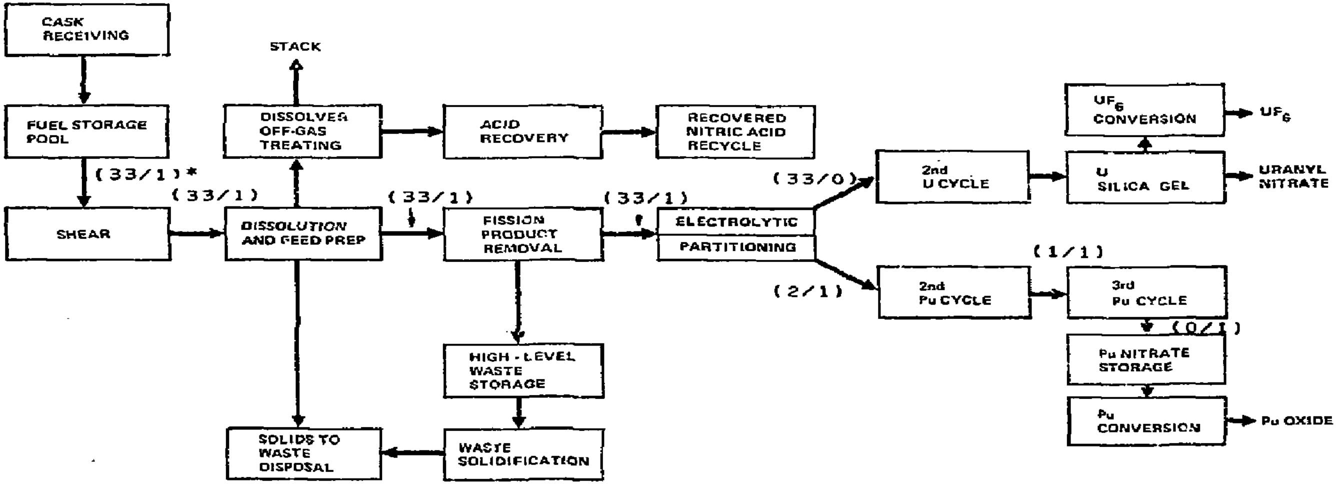


Figure 1. BNFP Flow Diagram - Combined Separations Plant and Plutonium Product Facility



*INDICATES (U/PU) METAL RATIO FOR RECYCLED MOX FUEL

Figure 2. Overall Barnwell Reprocessing Plant Schematic

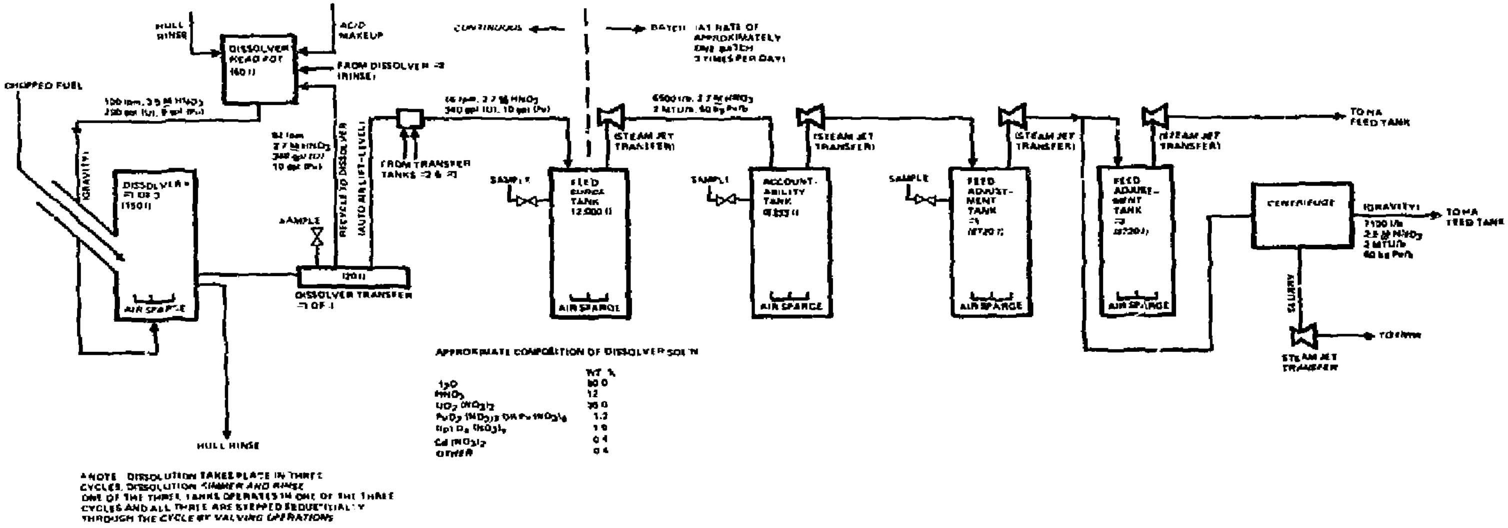


Figure 3. Dissolution and Feed Preparation

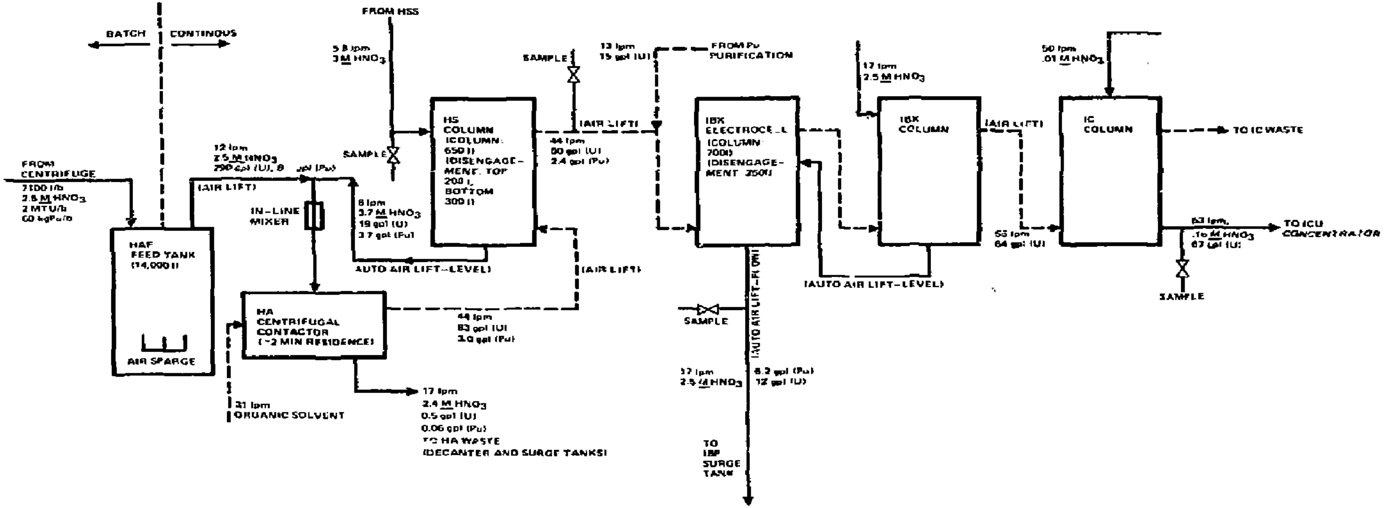


Figure 4. Co-Decontamination, Partitioning and Uranium Purification

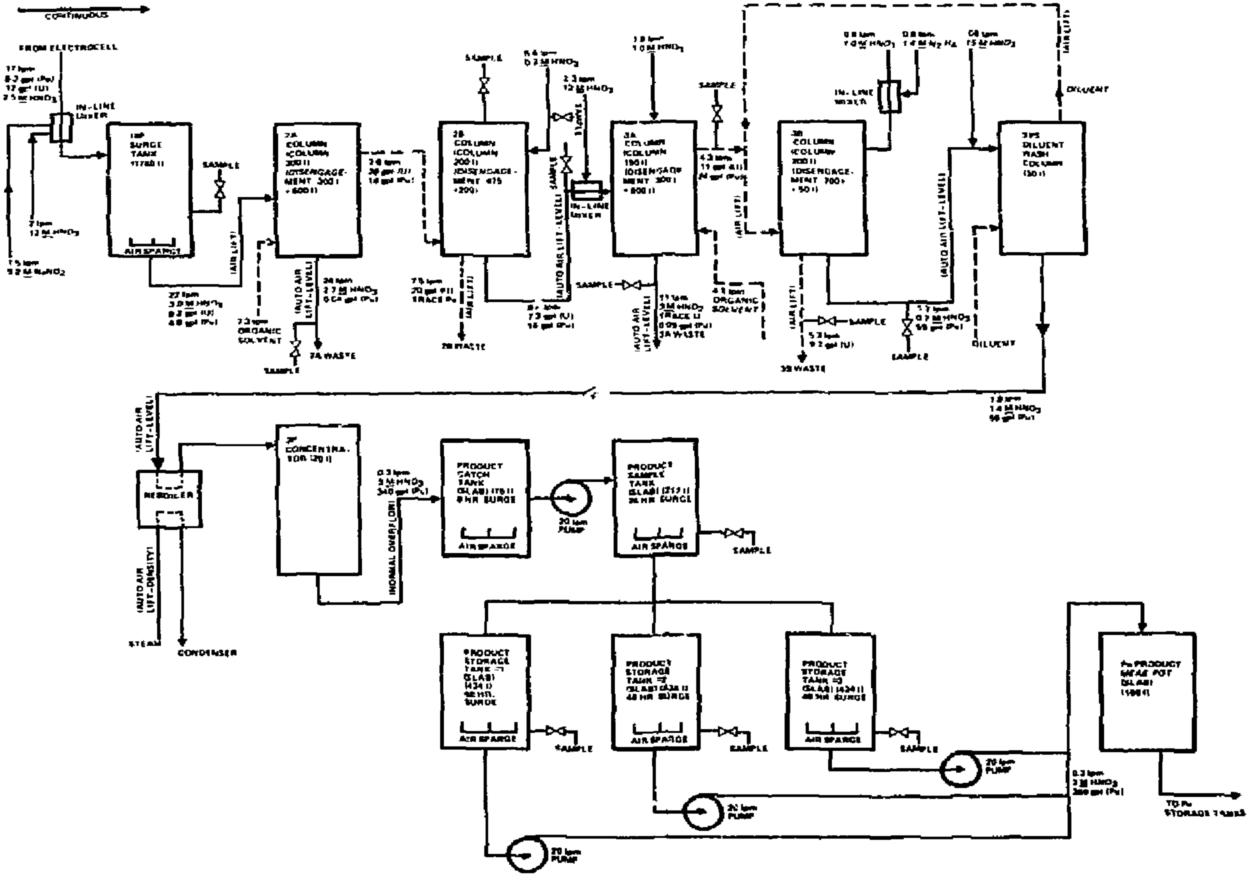


Figure 5. Plutonium Extraction and Purification

shearing cell where the elements are sheared mechanically into pieces. The pieces are gravity discharged directly to one of three dissolvers which are operated on a semi-continuous basis. Dissolution occurs in three cycles consisting of primary dissolution, simmer and rinse. One of three dissolver vessels operates in one of the three cycles, and all three are stepped sequentially through the entire cycle by valving operations.

In the dissolver, the chopped fuel is contacted by a liquor prepared from fresh nitric acid makeup, recycled dissolver solution, hull rinse liquor and rinse liquor from one of the other dissolvers. The dissolution stream is typically 3.5 molar nitric acid and contains U and Pu from the dissolver recycle streams.

The solid hulls, consisting primarily of zircalloy fuel element hardware and tubing remnants, are transferred to the solid waste treatment process. These hulls contain undissolved U and Pu. The product stream is transferred from the dissolver and mixed continuously with the product streams from each of the other two dissolvers. The mixed streams are held in a feed surge tank until a batch containing about 2000 Kg U is accumulated. The entire batch is then transferred to the accounting tank.

The fuel elements received from a given reactor reload will be processed as a lot through the accountability tank. A lot will vary from approximately 15 to 30 MT of U requiring from 3 to 6 days for processing. Prior to starting the next lot, the shear, dissolver, surge tank, and waste transfer facility are drained down and cleaned out. The materials recovered in the accountability tank are accurately sampled and assayed. The amounts of Pu and U measured in the accountability tank are used as the basis for the plant inputs for mass balance, SNM accountability and customer settlement. Further processing in the separations plant is done on a continuous basis without an attempt to segregate one customer's SNM from that of another.

The hulls are analyzed for U and Pu using counting techniques primarily as a process control measure to monitor the effectiveness of the dissolution, simmer and rinse cycles. Any Pu or U associated with the hulls is not entered into the accountability system as the hulls are packaged for disposal and the contained SNM is eliminated from the plant.

The solution in the accountability tank is transferred to either of two feed adjustment tanks to reduce the nitric acid concentration from approximately 2.7 molar to 2.5 molar in order to maintain a constant feed in the separations area. The adjusted feed stream is fed to a centrifuge by drawing from one adjustment tank while the second is being prepared. Approximately three feed-adjusted batches are processed in a 24-hour period.

A slurry containing any particulates removed from the separations plant feed stream is withdrawn from the centrifuge and transferred to high level waste for processing.

A solvent extraction system feed tank (HAF) with 14,000-liter capacity is used to convert from batch operation to continuous operation. This tank can accommodate essentially two full batches of adjusted and centrifuged feed solution.

Up to this point, the feed solution contains essentially all of the Pu, U and fission products entering the plant as spent fuel elements. A relatively small portion of these constituents have been discharged to waste with the hulls.

To avoid a criticality accident in the dissolver or other vessels of unfavorable geometry in the event that safe plutonium concentrations are exceeded, gadolinium nitrate is added to the dissolver feed solution. A positive indication of the presence of gadolinium is provided by neutron detectors installed in the dissolver acid surge tank. The gadolinium is discharged with the majority of the fission products in the waste stream from the centrifugal contactor. Criticality control through the remainder of the separations facility is maintained by solution concentration control or by geometry control.

The primary plant feed stream is mixed continuously with a recycle stream from the scrub column (HS) in the approximate proportions of two parts primary feed to one part HS column recycle. The mixed stream is fed to a centrifugal contactor in which the U and Pu are co-extracted into a solvent stream consisting of a mixture of tributyl phosphate (TBP) in n-dodecane. The bulk of the fission products remain in the aqueous phase and are processed to the high level liquid waste system via a decanter and surge tanks.

The solvent stream containing Pu, U and a portion of the fission products enters the scrub (HS) pulsed column where the solvent is contacted by a three molar nitric acid aqueous stream to achieve additional decontamination of fission products. The scrub also removes a portion of the U (∿ 3%) and Pu (∿ 20%). The aqueous stream is then routed to the mixer in the feed stream to the centrifugal contactor for recycle.

The solvent is introduced into the electrocell, a pulsed solvent extraction column in which electrolysis is employed to reduce the valence state of Pu from Pu^{+4} to Pu^{+3}. At the same time, the solvent stream is contacted with a 2.5 molar nitric acid stream. Since the Pu^{+3} species is not complexed by the solvent, the Pu^{+3} is extracted into the aqueous stream. This action effectively partitions the Pu and U components. The U-bearing solvent stream contains very little Pu (< 10,000 ppm), however the Pu-bearing aqueous stream contains a relatively large portion of the U with the U/Pu ratio at approximately 2:1.

The U-bearing solvent stream is scrubbed by a 2.5 molar nitric acid aqueous stream in the 1BX pulsed solvent extraction column to remove additional fission products. The aqueous stream is recycled to the electrocell. The solvent stream is contacted with a .01 molar nitric acid aqueous stream in which the U is extracted to the aqueous phase with a further decontamination of fission products. The dilute uranyl nitrate aqueous stream is then concentrated to form the final separations plant uranium product.

The Pu-bearing aqueous stream from the electrocell is mixed continuously with a 12 molar nitric acid stream and a 5.2 molar $NaNO_2$ stream. The combined streams are fed into an air-sparged surge tank (1BP). This procedure reoxidizes the Pu^{+3} to Pu^{+4}.

The aqueous stream is contacted by a fresh solvent stream in the first cycle Pu purification extraction column (2A) and both the Pu and U are extracted into the solvent. The aqueous stream containing about 0.04g of Pu per liter and most of the remaining fission products is routed to waste. The solvent stream overflows the 2A column and is contacted with a 0.3 molar nitric acid strip stream in the 2B column. The Pu is extracted into the aqueous stream along with about 30% of the available U. At this point the U/Pu ratio is approximately 0.5:1.

A second Pu purification cycle of solvent extraction and acid strip occurs in the 3A and 3B columns. After a diluent wash in the 3PS column, the Pu aqueous stream has been effectively decontaminated and contains less than 10,000 ppm U. A concentrator of critically safe geometry is used to increase the plutonium concentration from 0.25 molar to 1.5 molar and the product $Pu(NO_3)_4$ is collected in a series of 5 critically safe slab surge, sample and interim storage tanks. The plutonium product is transferred to a product measuring tank where accurate concentration and volume measurements are performed. The plutonium nitrate is then transferred to critically safe slab tanks for storage.

2.2 GENERAL PROCESS DESCRIPTION - PLUTONIUM PRODUCT FACILITY

The feed material for the plutonium product facility will be the plutonium nitrate solution from the storage product tanks in the separations plant with typical characteristics as given in Table 1. The gamma emissions and radioactive decay heat generation characteristics as well as criticality control for concentrated plutonium solutions and products are the cause for severe design constraints for the processing equipment within the PPF. The overall plutonium nitrate to oxide conversion system using the oxalate precipitation and calcining process is described in Fig. 6. The details of the feed preparation steps are given in Fig. 7, and the oxalate precipitation and filtering operations are described in Fig. 8. Fig. 9 provides a schematic of drying, calcining and screening operations, and in Fig. 10 the filtrate treatment system

TABLE 1. PLUTONIUM NITRATE FEED CHARACTERISTICS

Characteristic	Value
Plutonium Concentration	100-360 g/1(1)
Nitric Acid Concentration	2-10 molar
Uranium	<10,000 ppm Pu
Radioactive Decay Heat	<60 Btu/hr kg Pu
Radioactive Hydrogen Generation	$<5 \times 10^{-4}$ scfh/kg Pu
Gamma Emission	80 μCi/g Pu

Plutonium Isotopic Composition	WT %
Pu-238	2.5
Pu-239	50.0
Pu-240	25.0
Pu-241	15.0
Pu-242	7.5

---

(1) Plutonium concentrations in excess of 250 g Pu/1 may be processed if the heat generation rate is less than 60 Btu/hr g Pu.

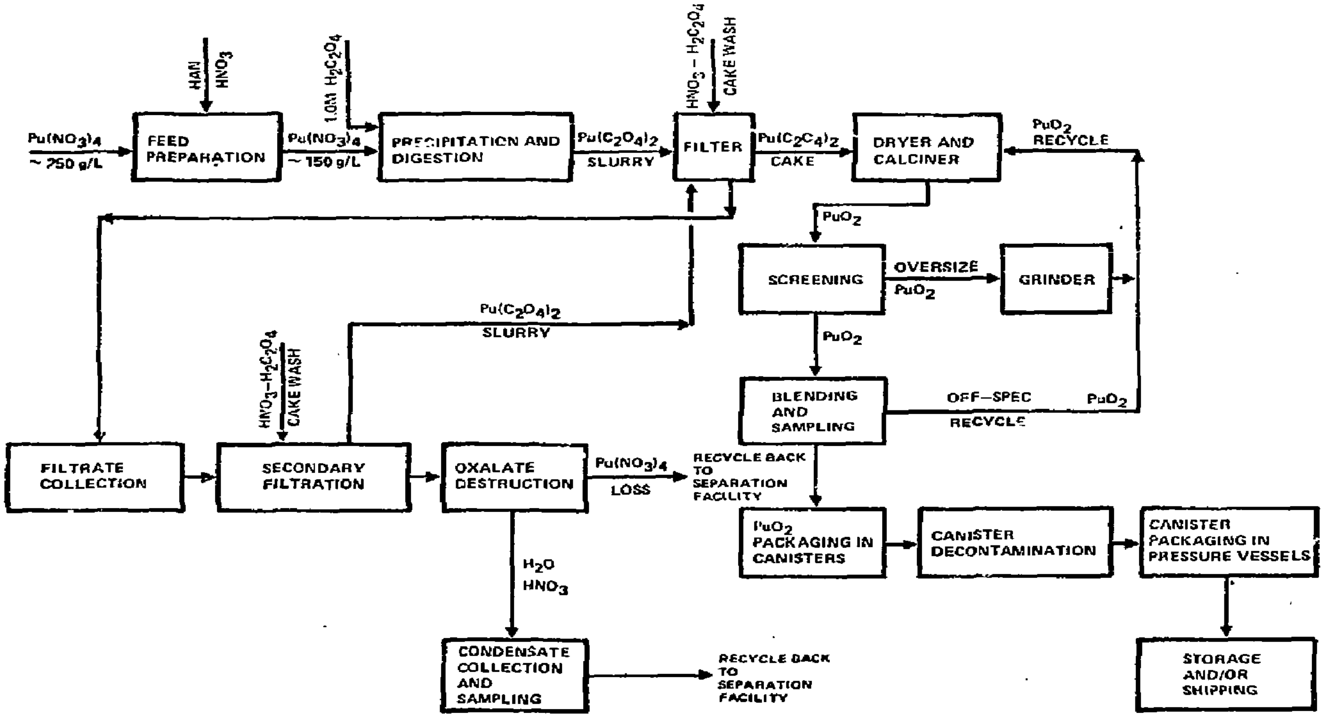


Figure 6. Overall Plutonium Nitrate to Plutonium Oxide Conversion Facility Schematic

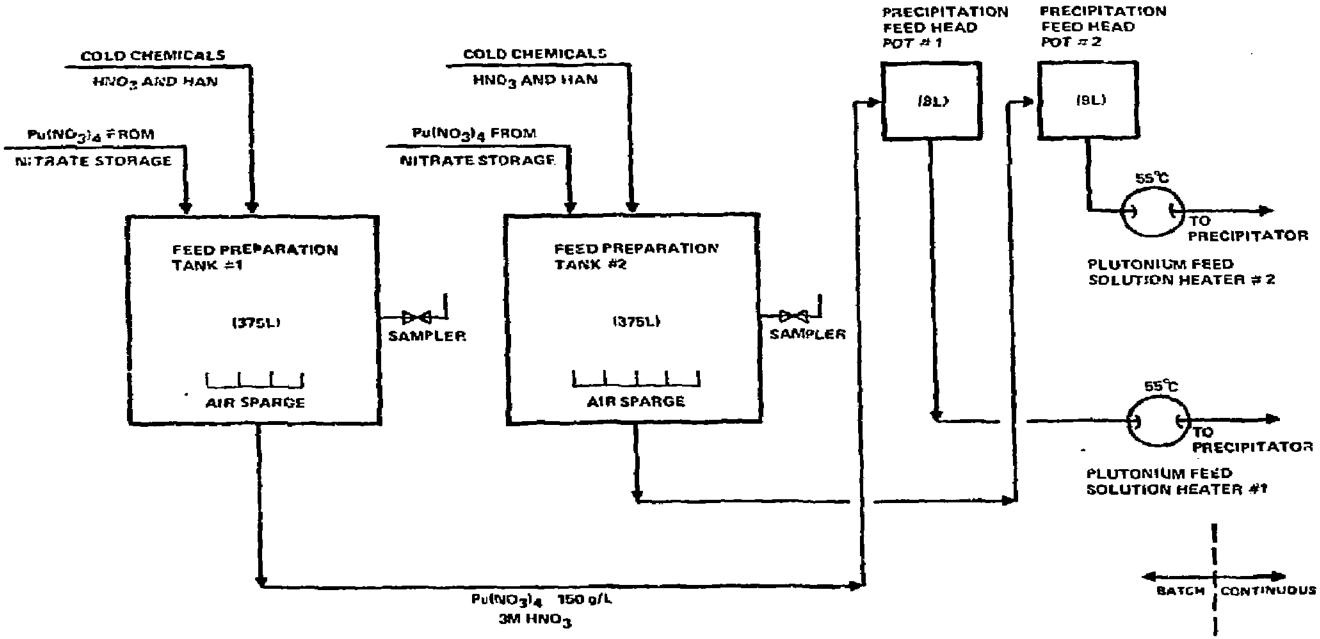


Figure 7. Feed Preparation

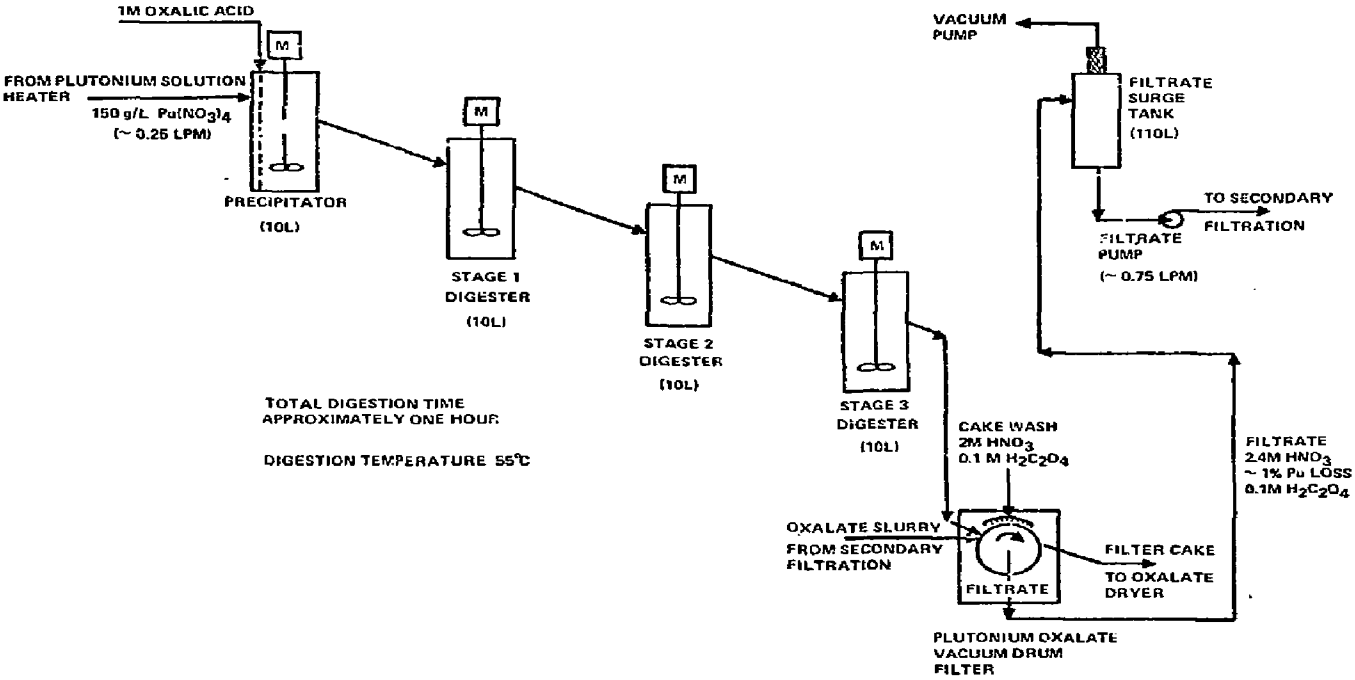


Figure 8. Precipitation and Filtration

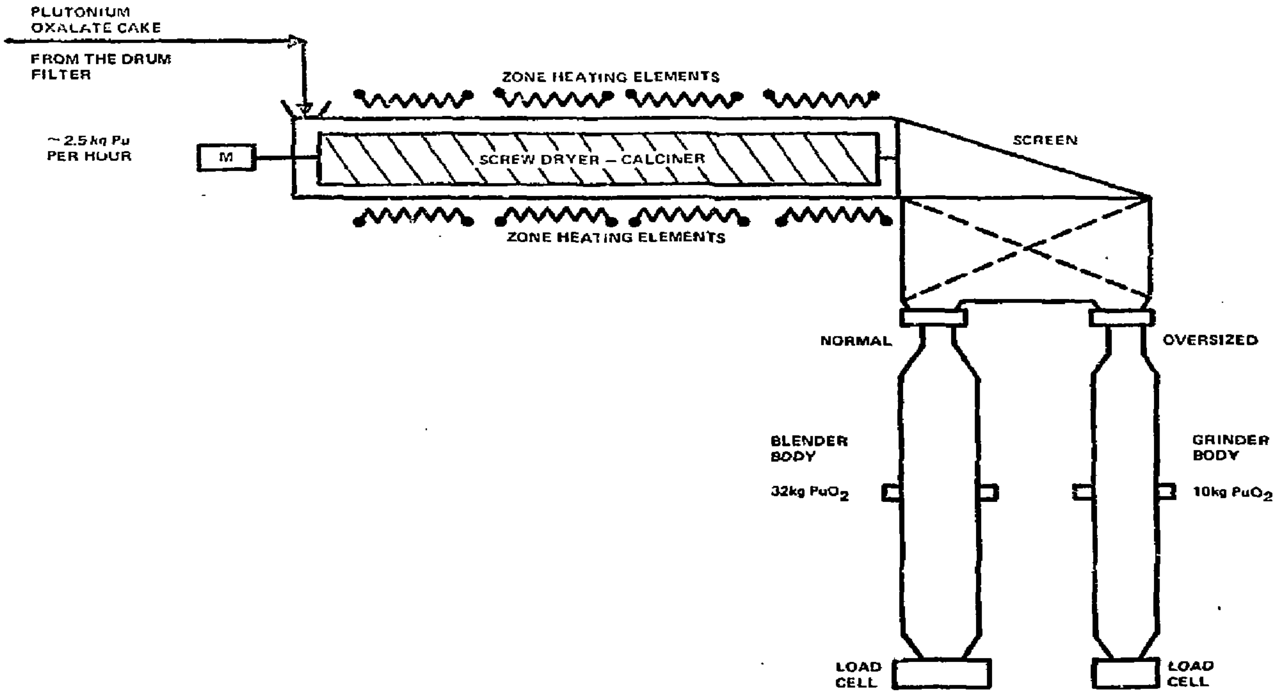


Figure 9. Drying, Calcining and Screening

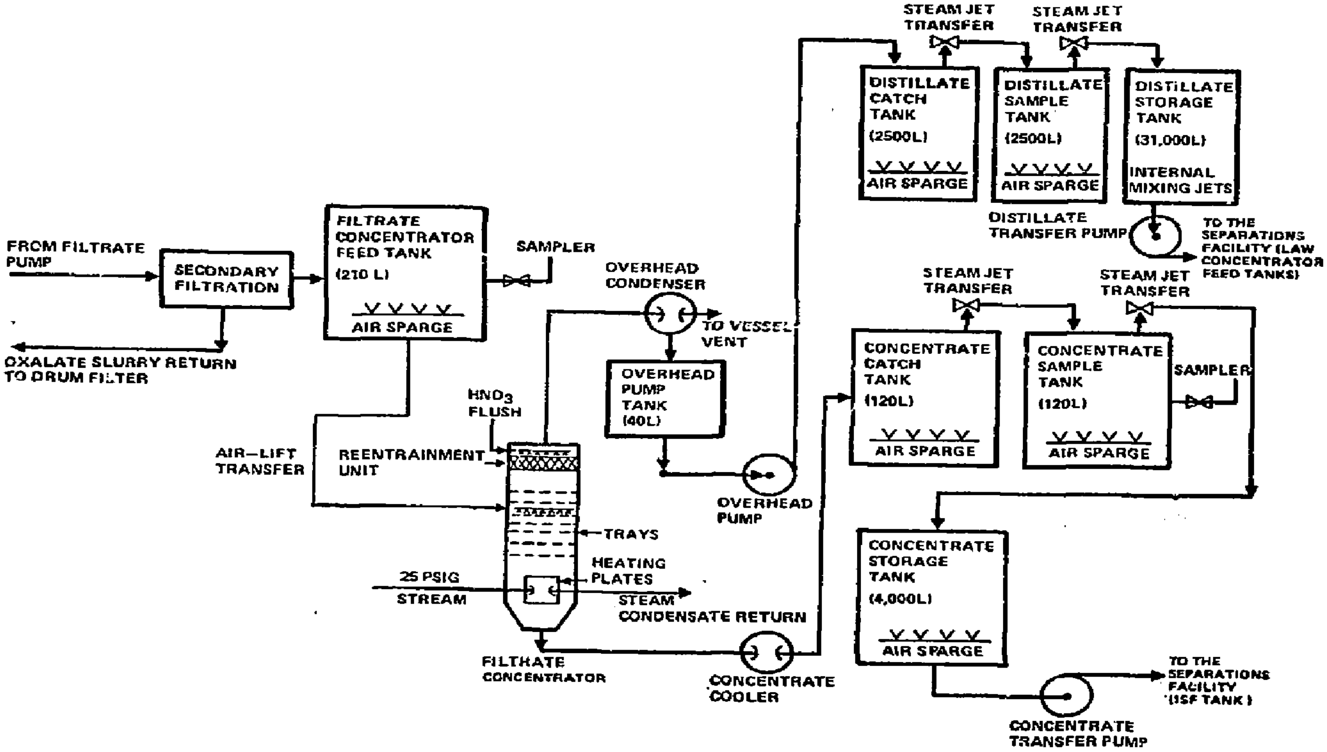


Figure 10. Filtrate Treatment System

is presented. The PPF has a design capacity of 100 kg PuO_2 per day with the production divided into two process lines each capable of processing 50 kg Pu daily.

The plutonium nitrate solution is transferred from the storage tanks to one of two feed preparation tanks on a batch basis. The nitric acid concentration is adjusted to 3 molar to provide a constant feed for the conversion process. It is essential that the nitric acid molarity be maintained at more than 2 molar as Pu emulsions may form at acid concentrations below 1.5 molar. Hydroxylamine (HAN) is also added at the feed adjustment tank to reduce any Pu^{+6} to Pu^{+4} prior to the precipitation step. After the feed adjustment step is complete, the nitrate solution is heated to 55°C in an in-line heater and fed continuously into a precipitator equipped with a mechanical stirrer. A solution of oxalic acid is added to the precipitator and the slurry produced is allowed to overflow to the digester. The digester consists of three, in-line mechanically stirred vessels that are arranged to permit the overflow of one unit to cascade into the next. The oxalate slurry flow rate is adjusted such that the digestion time is approximately one hour.

The slurry is fed into a rotary drum vacuum filter for primary filtration. The oxalate cake is rinsed on the filter drum and scraped off with a doctor blade. The filtrate is transferred to a filtrate surge pump prior to further processing.

The plutonium oxalate $Pu(C_2O_4)_2$ cake from the drum filter is discharged into a rotary screw dryer-calciner. The $Pu(C_2O_4)_2$ is destroyed by heating in air to form the desired product PuO_2. The oxalate cake feed rate, screw speed, heating rate and final calcining temperature are all critical to the production of PuO_2 with the proper characteristics for compacting into satisfactory fuel pellets during subsequent fabrication operations.

The calciner discharges directly to a screen through which the product is collected in a container with 32-kg Pu capacity and the oversize PuO_2 is collected in a separate container while also serves as a recycle grinder. When the oversize collector vessel is full (10 kg PuO_2) as indicated by a load cell, the collector is transferred to a twin roll horizontal grinder. The collector is rotated for several hours to allow the oversize PuO_2 to self-grind to the proper mesh size. When grinding is complete, the collector is transferred to the inlet of the dryer calciner, and the ground PuO_2 fed to the dryer through a separate feed screw as an additive to the normal feed stream.

The PuO_2 product powder is discharged from the screen into the blender container. When the blender contains 32 kg of PuO_2 as indicated by a load cell, the blender is automatically valved off and the blender transferred to the blending stand. The container is rotated about its radial mid-place until blending is completed. Homogeneity is determined by gamma scanning the outer surface of the container and comparing counts received from various powder volumes. The powder is also sampled to assure product purity and physical characteristics satisfy the specifications. The blender container is transferred to the powder load-out stand, where the content of the blender is discharged into four product cannisters each holding 8 kg of PuO_2. The cannister covers are installed, each cannister sealed and the outer surfaces decontaminated.

Four product cannisters are loaded into a storage pressure vessel that is in turn lidded, sealed and decontaminated. The loaded pressure vessels are transferred to plutonium storage.

2.3 MATERIAL ACCOUNTABILITY IN THE BNFP

The BNFP is to be operated as an integrated plant with several interacting operating facilities as described in Sections 2.1 and 2.2. Each of these facilities is further subdivided into Material Control Areas (MCA) that are identifiable physical areas such that the quantity of SNM moving into or out of the MCA is measured. Some MCA's are identifiable physical areas that have transfer control based on item identification and piece-count of the items. These MCA'a are identified as item control areas (ICA). All other MCA's are referred to as material balance areas (MBA's). The BNFP is divided into eleven MCA's as shown in Table 2.

In theory, if the plant could be operated in a manner such that on any given day, the quantity of SNM in each storage location, in each process vessel or container, and in each scrap, waste and sample stream could be measured with sufficient accuracy, diversion of significant quantities of Pu would be unlikely without detection by the material control system. Inherently, as the plant throughput is increased, the accuracy of the determination of the quantities of SNM in inventory or in process at any given time expressed as a percentage of plant throughput must be improved as the amount of Pu that could be diverted without detection to just remain at some fixed level relative to the critical mass of plutonium(8).

In the case of a combination spent fuel reprocessing and plutonium conversion facility based on the BNFP design, it is apparent that the characteristics of the feed and product materials are the dominant factor in facility design. Because

TABLE 2. BNFP MATERIAL CONTROL AREAS

MCA	Description	Type of Control
1.	Fuel Receiving and Storage	ICA
2.	Separations Process area	MBA
3.	Plutonium Nitrate Storage Area	MBA
4.	UF_6 Process Area	MBA
5.	UF_6 Product Storage Area	ICA
6.	UF_6 Scrap and Waste Storage Area	ICA
7.	Analytical Services Laboratories	MBA
8.	Plutonium Conversion (PuO_2) Process Area	MBA
9.	Plutonium Oxide (PuO_2) Storage Area	ICA
10.	Plutonium Scrap and Waste Storage Area	ICA
11.	Central Waste Handling Area	ICA

of the high radiation levels of the incoming spent fuel elements and the toxicity of the product Pu, the major portion of the SNM within the plant must be confined behind shielding walls or process containers such as glove boxes. These necessary protective barriers are in themselves effective deterrents to diversion. Small quantities of materials in the form of samples, scrap and waste are routinely handled outside the major process. Although the concentration of SNM in these materials is generally low, in a complex facility there are a large number of streams extraneous to the main process that can at various times contain several kg of SNM in aggregate. These streams contribute disproportionately to the difficulty of achieving the objectives of the material accountability systems for a variety of reasons:

- It is difficult to identify every possible form of scrap, waste and plant effluent stream in sufficient detail to provide monitoring systems that can accurately measure the SNM content over the concentration ranges that occur in the actual streams.
- The SNM is often associated with large quantities of materials that by sheer bulk and physical geometry prevent accurate measurement of the SNM.
- The SNM is often present in an non-homogeneous array, i.e. undissolved U and Pu solids are located at discrete points on the surfaces of solid hulls discharged from the separations plant dissolvers.
- The SNM is associated with highly radioactive wastes that preclude accurate measurement of SNM, i.e. Pu or U discharged in the waste stream from the coextraction cycles.
- Intermittent plant operating upsets permitting unmeasured flow of SNM for short periods, e.g. a process filter failure permitting SNM to enter the plant waste or ventilation systems.

- Equipment failure requiring discharge of SNM in an abnormal form precluding accurate measurment of the SNM content, i.e. failure of the plutonium oxalate filter-dryer resulting in a non-homogeneous mixture of wet, dry and partially converted plutonium oxalates that require extensive preparation before an accurate determination of the Pu content can be made.

Typically at any given time the amount of SNM in a specific waste scrap or sample stream is small; however, the aggregate amount of SNM contained in all of the extraneous process streams typically represents 10% or more of the plant in-process inventory. The uncertainty of the measurements of the SNM content of these materials and the extraordinary length of time required to obtain the analytical results using techniques commonly in use presents a formidable obstacle in detecting diversion of small quantities of SNM.

As an aid to evaluating the effectiveness of improved process control information, the primary process streams for the BNFP have been characterized in Table 3. Considering the size of a unit containing 200 g Pu, the minimum size of a shielded container with 200 g Pu needed to protect the diverter from serious injury, the form of material diverted, and the usefulness of the diverted materials to the diverter were used for characterization. The last column in Table 3 is obviously subjective as the capability of a diverter for converting the diverted Pu to forms suitable for his purposes can not be readily assessed. The various streams have been characterized as follows:

- Very Poor - The Pu is associated with large quantities of highly radioactive fission products such that 3-5 feet of concrete or other shielding material is necessary to prevent serious injury to the diverter.

Table 3. BNFP Process Streams - Diversion Characteristics

Process Area	Process Stream Description	Form	Approximal Process Unit Containing 200 g Pu	Container to Hold 200 g Pu Without Serious Injury to the Diverter	Usefulness to Diverter For Weapon or Criticality
Fuel Receiving and Storage	Receive Spent Fuel Element	Fuel Element	<1 element	Spent fuel shipping cask - 50,000 lb	Very poor
	Store Spent Fuel Elements	Fuel	<1 element		
Separation Facility	Chopped Fuel	2" long pieces	Several hundred		
	Dissolver Solution	Liquid	20 liters		
	Hull Rinse Solution	Liquid	200 liters		
	Rinsed Hulls	Solid	20 kg		
	Accountability Tank	Liquid	20 liters		
	Centrifuge Feed	Liquid	22 liters		
	Centrifuge Slurry	Liquid	500 liters		
	Centrifugal Contractor Fuel	Liquid	22 liters		
	Centrifugal Contractor Waste	Liquid	3000 liters		
	Scrub Column Feed	Liquid	60 liters	Heavily shielded container	Poor
	Scrub Column Aqueous Discharge	Liquid	55 liters		
	Electrocell Solvent Feed	Liquid	80 liters		
	Electrocell Aqueous Discharge	Liquid	16 liters		
	Plutonium Purification Column Feed	Liquid	40 liters		
	Plutonium Purification Column Waste	Liquid	5000 liters		
Separations	Plutonium Purification Solvent Stream	Liquid	15 liters	5 gal. container	Good
	Plutonium Purification Aqueous Stream	Liquid	12 liters	5 gal. container	Good
	Plutonium Purification Solvent Stream	Liquid	8 liters	2 gal. container	Very Good
	Plutonium Purification Aqueous Stream	Liquid	4 liters	1 gal. container	
	Concentrator Product - $Pu(NO_3)_4$	Liquid	0.75 liters	12 oz. container	
$Pu(NO_3)_4$ Storage	Plutonium Product Storage $Pu(NO_3)_4$	Liquid	0.75 liters	12 oz. container	
Plutonium Conversion Area	Plutonium Nitrate $Pu(NO_3)_4$ Feed	Liquid	0.75 liters	12 oz. container	
	Plutonium Nitrate Prepared Feed	Liquid	1.25 liters	20 oz. container	
	Plutonium Nitrate Precipitator Feed	Liquid	1.25 liters	20 oz. container	
	Plutonium Oxalate Slurry Feed to Vacuum Filter	Slurry	4 liters	1 gal. container	
Filter	Vacuum Filter Filtrate	Liquid	400 liters	2-55 gal. drums	
	Vacuum Filter Cake - $Pu(C_2O_4)_2$	Semi-solid	2 liters	1/2 gal. container	
	Calciner Product PuO_2	Solid	0.1 liters	2 oz. container	Excellent

- Poor - The Pu is associated with a moderate amount of fission products such that 8" of concrete or 2" of lead shielding is required to avoid serious injury to the diverter.
- Good - The Pu is associated with only small quantities of fission products such that minimal shielding is required. Also the Pu is in a chemical form that would not require a high degree of sophistication to convert the Pu to a form useful to the diverter.
- Very Good - The Pu is in a concentrated liquid form and free of radioactive fission products.
- Excellent - The Pu is in a concentrated solid form.

From the description of the main process streams given in Table 3 it is apparent that only the decontaminated $Pu(NO_3)_4$, $Pu(C_2O_4)_2$ and PuO_2 streams are of practical use to any but extremely capable and sophisticated groups of diverters. This does not mean that the other streams can be neglected in a materials control system, as the overall material balance for the area cannot be assured if the waste streams are neglected. Direct flow process stream data is not essential as the SNM input will eventually be collected and measured in the product receivers. In-process material control may be useful to reduce the time interval between the input and product measurements, thus reducing the time that a diversion may go undetected. The basic questions to be answered are:

1. Where in the plant can improved in-process measurements and controls be useful in detecting diversions?
2. Can the in-process material control systems be implemented with current state-of-the-art technology?
3. Will the in-process material control systems improve the plant production capabilities?

2.4 PROCESS CONTROL IMPROVEMENTS FOR ACCOUNTABILITY

In this section, descriptions of possible improvements to the process control system that could enhance the capabilities of the SNM accountability system for detecting diversions are discussed. The possible effects on plant operation are also outlined with each major portion of the plant described in some detail.

2.4.1 Receiving and Storage Area Transfer Control

SNM material control is accomplished in the spent fuel element receiving and storage areas by piece-count control of the individual fuel element assemblies. The BNFP relies on shipping documents and operator observation to assure that the proper fuel elements have been received, unloaded and stored. Fuel element locations in the storage racks are maintained using manual input for the inventory records.

Possible Improvement. The storage area crane would be programmed to deliver or retrieve an element assembly automatically at a definite storage location. Each storage location could be equipped with a positive device indicating the physical presence of an element in the location. By combining the information from the storage crane movements and the element locators, the actual physical location of any fuel element could be determined at any time (effectively real-time piece count inventory).

Available Technology. Positive motion stacker-retreiver systems including hardware and software are commercially available that can store and retrieve from programmed locations. The available systems are generally designed specifically for a given set of storage requirements. The system for an automated transfer crane operations would require allowances for the radioactive environment for this particular operation. Various types of positive locators (mechanical, sonic, optical) are available for detecting the presence of a fuel element. These detectors would again require modifications for the particular application. Applicable hardware can be purchased on special order for both operations.

Material Accountability Improvement. From a plant operational viewpoint, definite knowledge of the location of each fuel element would be an advantage in assuring that all of the elements in a given customer's account were in fact processed in the planned production lot and that no intermixing of lots occurred by accident or operator error. These same requirements can be achieved by carefully performed, inspected and audited manual operations.

From a SNM materials control viewpoint, the knowledge that the spent fuel element is within the storage area (not necessarily its actual location) is the important criteria. As a spent fuel element can not be diverted from the plant without the use of spent fuel element shipping cask or similar device, diversion can be readily detected by means other than direct inventory observations. The SNM content of the element is not of vital concern as the SNM will not be inputed to the accountability records (except as an item entry with calculated values) until the SNM content is measured in the accountability tank. Normal visual inspection, and inventory records can be used effectively to assure the presence of the elements in the facility.

Automated storage and retrieval systems with positive identification of storage locations would not appreciably improve the ability of the SNM accountability system to detect or prevent diversions.

2.4.2 Spent Fuel Shearing

SNM material control at the spent fuel element shear is accomplished by piece-count control. The chopped pieces are discharged directly to the dissolver. As the materials at this station are highly radioactive and are handled remotely behind heavilly shielded walls, diversion at this point verges on the incredible. The normal plant operating procedures can be considered sufficient for SNM control.

2.4.3 Dissolution, Simmer and Rinse

At the dissolver, there are several main process streams that have similar characteristics in regard to fission product activity. These are the dissolver recycle stream, dissolver rinse stream and the hull rinse stream. These streams are generated at all three dissolver stations and are mixed continuously in the dissolver head pot. At this point in the process the SNM has not been entered on a quantitative basis into the accountability records, therefore detailed knowledge of the SNM content of these streams is unnecessary from an accountability viewpoint. From a plant operations position, the uranium concentration in the three streams provides a measure of the efficiency of the dissolver operations.

The chopped fuel solid hulls are discharged from the dissolvers to solid waste. These hulls are monitored for U and Pu concentration by counting the ^{144}Pr and calculating the uranium and plutonium concentrations in equilibrium with the ^{144}Pr.

The SNM content of the hulls is important to the overall SNM accountability system of the separations plant. Although the solid hulls can not be diverted directly because of their extreme radioactivity, it is possible that the chemical plant operators could surreptiously re-rinse the hulls to remove additional SNM after accountability measurements of the dissolver product have been made in the accountability tanks By adding this additional rinse liquor to the feed adjustment tank, it is possible to generate a small but significant "off balance sheet" source of SNM for possible diversion at downstream points.

Re-rinsing capabilities within the plant are essential for effective plant operations in the event of improper dissolver operation. Positive plant interlocks at the feed surge tank and the accountability tank transfer jets to prevent passage of unassayed dissolver or rinse liquor may be of interest.

Possible Improvement. The steam jet transfer from the accountability tank to the feed adjustment tank could be programmed to permit transfer of the known volume of feed liquor previously measured in the accountability tank. The steam jet transfer is normally accomplished by controlling the flow rate of steam to the transfer jet. By adding a mass flow recording controller to the steam system, it would be possible to have an independent record of the volume transferred from the accountability tank. The added instrumentation would not be of direct benefit to plant operations.

The off-gas ventilation systems for the dissolvers, the dissolver head-pot, the dissolver transfer station and the feed surge tanks are possible sources for "off balance sheet" SNM. During dissolution, simmer and rinse cycles in the dissolvers, air sparging is used as aid in mixing the dissolver contents. Excessive sparging can entrain droplets of dissolver solution containing SNM that are carried into the process vessel off-gas system (PVOG). Since these operations are carried out upstream of the SNM accountability tanks, it is possible that the SNM contained in these off-gas streams can be recovered surreptitiously during plant clean-up operations.

Possible Improvement. The PVOG system knockout pots and drain sumps in the plant upstream of the accountability tanks could be equipped with level recorder controllers interlocked with the accountability tank transfer jets to prevent passage of unassayed SNM from the ventilation system drains. This additional instrumentation would be of no benefit to plant operations.

2.4.4 Separations Plant Head End

The SNM content of each customer's batch of incoming spent fuel elements is determined by draining down and flushing out the process units upstream of the accountability tank. The wash liquors are collected, sampled and analyzed for the SNM content. The SNM measured during the cleanup is added to the known amount of SNM processed through the accountability tank during the the particular campaign. The total amount of SNM determined is used as the basis for financial settlement with the customer for the SNM to be recovered and for the total amount of SNM considered as input at the plant for SNM accountability purposes.

The SNM measured at the accountability tank and recovered during the head-end drain down and flush-out operations is compared with the amount of SNM estimated to be present from burnup calculations. This comparison provides a base for the customer to determine if the amount of SNM determined at the accountability tank is reasonable for the lot of elements processed. The accountability tank measurements are considered final in the event of a descrepancy.

Drain down and cleanout of the front end of the separations plant occurs every 3 to 6 days depending on the number of fuel elements contained in a single customer's batch. The head-end cleanup and SNM sampling procedures require 8 to 16 hours to complete. Shutdown of the remainder of the plant downstream of the accountability tanks is prevented by the surge volume of the feed adjustment tanks and the separations plant feed tank. As a consequence a complete head-end in-process is taken every 5 days on the average. Additional in-process controls in the head-end of the plant could not be expected to improve the SNM control system efficiency.

2.4.5. Solvent Extraction and Product Concentration

The balance of the separations plant from the accountability tank through the U and Pu concentrated product tanks is treated as a single operational unit and a single MBA. The operations performed in the separations portion of the plant include feed adjustment, feed clarification, U and Pu co-extraction and primary fission product decontamination, U and Pu partitioning, separate cycles for U and Pu purification and separate U and Pu product concentration.

In general, in-process flow measurements for the solvent extraction systems are made indirectly by monitoring the flow of air or steam to the transfer jets. Thus flow rates for the individual process streams at various columns are known to within 5-10% when using steam jet transfers and to 3% when air jets are employed. The relative inaccuracy of the steam jets is caused by the entrainment of steam into the process liquor during transfer causing a 3 to 5% dilution of the process stream and because of the necessity to blow down and drain the steam line when the transfer is completed to avoid siphoning radioactive liquids into the cold portions of the plant.

Steam and air jets are used for the transfer of highly radioactive liquids within the BNFP because of the simplicity of operation. No moving parts are required within the shielded process areas, and the steam or air control valves can be located within the operating galleries. Because of the relatively small flows of the transfer motive fluid (air or steam), conventional electronic and pneumatic rotometers are used effectively to control flow to the transfer jets.

2.4.6 Feed Adjustment and Clarification

At the feed adjustment tanks, the nitric acid concentration is adjusted from 2.7 molar to 2.5 molar to provide a constant feed for the extraction operations. A centrifuge is provided for clarifying the extraction column feed stream if a high concentration of solids is detected in the adjusted feed, otherwise the feed can be passed directly to the extraction system feed tank. The slurry from the centrifuge will be discharged to the high level waste system.

The clarified feed is discharged to the extraction system feed tank (HAF). The surge capacity of this tank is sufficient to permit the batch operations conducted in the plant head-in to be converted to continuous operations for the balance of the separations plant.

The centrifuge will not be required for every transfer made between the feed adjustment tanks and the HAF. Consequently it can be drained down and flushed out periodically to reduce the holdup inventory for this portion of the plant.

Improved SNM accountability can be determined in this portion of the plant as the draw-down liquid volume of the feed adjustment tank could be compared on a real-time basis with the change in volume at the HAF tank allowing for the known volume of any waste discharged from the centrifuge and the known flow rate (accurate to about 3%) of the centrifugal contactor makeup feed stream. This system could be used to provide additional assurance of the complete transfer of an adjusted feed batch to the extraction system.

2.4.7. Co-extraction and Decontamination

The clarified feed stream is mixed with the aqueous stream from the scrub column (HS) on a continuous basis. Prior to entering the centrifugal contactor, the streams are normally combined with a ratio of 2 parts fresh feed to 1 part recycle feed. The mixed feed stream is contacted with an organic solvent stream in essentially counter-current flow in a centrifugal contactor (HA). The U and Pu are selectively extracted from the aqueous phase to the solvent phase. The major portion of the metallic fission products remain in the aqueous phase and are processed to waste treatment, together with approximately 0.2% of the U and [redacted] ≤1% of the Pu that entered the centrifugal contactor.

In the scrub column (HS), the organic solvent stream containing the U and Pu together with a small portion of the fission products is contacted with 3 molar nitric acid. This process provides additional decontamination of fission products but alo re-extracts approximately 20% of the U and Pu back into the aqueous phase. The aqueous stream from the HS column is recycled back to the centrifugal contactor as part of the contactor feed stream.

During plant startup, a minimum of eight hours operation is necessary to establish equilibrium conditions with the centrifugal contactor and the HS column. When the process is first initiated, the HS column is filled with fresh nitric acid and the U, Pu-bearing solvent phase is added to the column. The U-Pu concentrations in the aqueous phase continue to increase as the counter-current extraction process progresses within the column. As the aqueous stream from the HS column constitutes about 30% of the feed to centrifugal contactor, and the contactor in turn feeds the HS column, equilibrium conditions are achieved only after the concentrations in both process units become stabilized.

The primary uncertainty in determining the inventory of SNM within the combination of the contactor and HS column is associated with the SNM content of the aqueous waste stream discharged from the centrifugal contactor. This stream contains the bulk of the radioactive fission products and also has a Pu concentration of 0.06 g Pu per liter. With an average flow rate of 17 liters per minute, 1.5 kg Pu are discharged to waste treatment daily. The wastes are collected and analyzed for U and Pu content. If the U or Pu concentration is sufficiently high, the waste streams are recycled to the electrocell for recovery of additional SNM.

2.4.8. Uranium and Plutonium Partitioning Purification and Concentration

The U and Pu partitioning purification and concentration systems are considered as a single operational unit. Referring to Fig. 4 and 5, it can be seen that recycle streams from subsequent purification solvent extraction cycles for both U and Pu make up a major portion of the aqueous and organic feed streams to the partitioning electrocell. Equilibrium concentrations of Pu and U in these units are achieved only after several hours of operation because of the interaction of the recycle streams with the primary feed streams.

The electrocell is operated as described in Section 2.1, with the Pu being stripped from the solvent by a nitric acid stream after the Pu^{+4} is reduced to Pu^{+3} by the electrolysis within the specially designed pulsed partitioning column. The U and Pu purification cycles consist of repeated interchange of the SNM from the aqueous to solvent phase with the partial elimination of radioactive fission products with each interchange.

The purified aqueous stream from the final purification extraction column (3PS) is fed directly to the Pu concentrator. The concentrator bottoms are drawn off continuously into the product surge tank. The concentrator feed stream has a Pu concentration of about 56 g Pu per liter. The concentrator bottoms typically contain 340 g of Pu per liter.

Again, as in the case of the coextraction cycle, the primary difficulty in maintaining an accurate plutonium inventory within these portions of the plant is the uncertainty in measuring the plutonium concentration and volumes of the streams discarded to waste. There are 4 separate waste streams generated on a continuous basis. The two aqueous streams are from the strip columns (streams 2A and 3A waste). These streams have a total flow rate of 35 liters per minute and a Pu concentration of approximately 0.06 g of Pu per liter. About 2 Kg of Pu are directed to backcycle treatment daily in the two aqueous streams. The uncertainty in the measurement of the Pu concentration of 15% and the volume measurement of 3% results in an overall uncertainty of about 390 g Pu/day.

The two organic solvent waste streams (2B and 3B) have a total flow rate of 13 liters per minute and contain trace quantities of Pu. The limit of detectability for Pu in these streams is about .001g of Pu per liter (1 ppm). If the waste streams are assumed to be at the limit of detection, then 20 g of Pu would be assumed to be discarded daily. If the waste streams are assumed to contain 50% of the detectable limit, then 10 g of Pu would be assumed to be discarded daily.

2.4.9 Plutonium Nitrate Sampling and Product Storage

The plutonium nitrate is transferred from the product surge tank to the product sample tank on a batch basis. Each batch transferred is air sparged for about 8 hours to assure adequate mixing before being sampled. This extensive mixing cycle is necessary because the plutonium nitrate product sampling tank is constructed with slab geometry with only a 2.25-in. space between the tank sides.

2.4.10 Plutonium Nitrate Storage

The plutonium nitrate is transferred from the plutonium measurement pot to the plutonium nitrate storage facility. The storage facility consists of two shielded cells each containing 24 slab tanks. The slab tanks are arranged in units of six utilizing common transfer pumps, sample mainfolds, and plutonium rework manifolds. Each slab tank can be air-spared for thorough mixing of the tank contents and flushed with nitric acid.

For material control purposes, each plutonium nitrate slab tank that is filled will be sealed using tamper-proof seals after it is verified that the transfer from the plutonium measurement pot has been completed. The tank seals remain in place until the solution is transferred to the plutonium conversion process. Periodic inspections are made to assure that the seals have not been disturbed.

Possible Improvement

The individual storage slab tanks could be mounted on load cells. As the liquid is drawn down in the plutonium product measuring tank during a transfer, the corresponding weight increase would be noted in storage tank. Periodic checks of the storage tank. Periodic checks of the storage tank weights would provide additional assurance that plutonium had not been withdrawn between inventories.

2.5 PROCESS CONTROL IMPROVEMENTS (PPF)

The plutonium product facility (PPF) is to be constructed immediately adjacent to the spent fuel processing separations facility. The PPF is designed to process 100 kg of PuO_2 daily in two process lines each capable of producing 50 kg of PuO_2 daily. A general description of the plutonium nitrate to plutonium oxide conversion process has been given in Section 2.2. The process flow diagrams for the overall process are given in Fig. 6 and the details of the individual process operations are given in Figs. 7, 8, 9 and 10.

2.5.1 Feed Preparation, Precipitation and Digestion

The plutonium nitrate solution is withdrawn from a selected slab storage tank in the separations facility and charged into one of the two feed preparation tanks at the beginning of each process line. Nitric acid is added to reduce the Pu concentration from 350 g Pu per liter to 150 g Pu per liter. Hydroxylamine (HAN) is added to the solution to reduce the Pu^{+6} that may be present to Pu^{+4}. The prepared feed is then transferred on a continuous basis to the preciptiation tank. Oxalic acid is added to the solution at a controlled rate forming a plutonium oxalate ($Pu(C_2O_4)_2$) slurry. The slurry is permitted to overflow to a set of three digestion tanks arranged to permit the slurry to cascade from one digestor to the next. Excess oxalic acid is added to the solution to assure complete formation of plutonium oxalate. The flow rates to the precipitator and the digestors are controlled to provide a residence time for the plutonium compounds of at least one hour within the process units.

2.5.2 Filtration, Drying, Calcining, Grinding and Blending

The plutonium oxalate slurry is discharged continually from the overflow of the final stage digester directly into a rotary vacuum drum filter. The filter cake is removed from the drum by a doctor blade and is fed directly into the electrically heated dryer-calciner. The filtrate is withdrawn through the axis of the drum filter and is transferred to a polishing filter for removal of additional $Pu(C_2O_4)_2$. The filter cake from the polishing filter is recycled to the rotary drum filter for plutonium recovery. The clean oxalate solution is concentrated and the oxalate destroyed by heating the solution in the presnce of nitric acid. The overheads are condensed, sampled for possible plutonium content and transferred to the low level waste system in the separations plant for treatment and discard.

The tank bottoms are cooled and sampled for possible Pu content. The solution is transferred to the separations plant for nitric acid recovery.

The $Pu(C_2O_4)_2$ is converted to PuO_2 in the dryer-calciner by heating the oxalate to temperatures up to 750°C in air. The carbon in the oxalate is converted to CO_2.

The characteristics of the PuO_2 formed depend on the size of crystallites formed during the precipitation and digestion cycles, the feed rate of the oxalate cake to the dryer-calciner, the rate of heating of the cake in the dryer, the depth of cake in the dryer-calciner and the final temperature reached by the PuO_2 in the calciner. Proper control of the PuO_2 physical characteristics, particularly crystallite size and form, is essential for producing PuO_2 that can readily be compressed and sintered into fuel pellets suitable for reactor loading(9).

The calcined PuO_2 is discharged from the dryer-calciner into a continuous screen in which any oversize PuO_2 is routed to an oversize collector and the PuO_2 product is collected separately.

When the oversize collector is full as determined by a load cell, the collector is transferred to a grinding station.

The collector rotated for several hours. The rolling action is sufficient for the oversize plutonium oxide powder to be self-ground to size. The collector containing the ground PuO_2 is transferred to the feed point of the dryer-calciner and the ground material is recycled through the calciner.

The screened product is discharged into a separate container until a load cell indicates that the desired weight of 32 kg of PuO_2 has been reached. At this point, the container is disconnected from the screening station by proper action of isolation valves and the container is transferred to the blending station. The container is rotated for several hours to assure homogeneity of the PuO_2. Homogeneity is checked by counting the gamma activity at various points along the container and compairing the counts obtained at corresponding locations.

The container is transferred to the loading station where the PuO_2 is loaded into four storage containers each containing 8 kg of PuO_2. The individual storage containers are lidded, sealed and the outer surfaces are decontaminated.

Four of the decontaminated storage cans are packed into a single pressure vessel for storage. The pressure vessel containing 32 kg of PuO_2 is in turn lidded, sealed and decontaminated. The pressure vessel is transferred to the storage area.

During the conversion process from oxalate precipitation through PuO_2 screening, the plutonium undergoes chemical and physical changes that preclude accurate determination of the plutonium concentration within the various process units. SNM control is maintained by measuring the amount of plutonium charged into the process and the plutonium recovered as PuO_2. The plutonium discarded to waste from the oxalate filter in the filtrate is also measured accurately. Periodically, the process equipment is flushed out and drained down in order to measure the amount of plutonium contained within the process equipment.

Process shutdowns for inventory purposes cause severe process upsets resulting in relatively large amounts of off-specification materials. The conversion process is normally run on a continuous basis and the flush out process alters plutonium concentrations and solution volumes. These in turn affect the residence time of the oxalate cake in the dryer-calciner which in turn affects the size of the calcined PuO_2 product. Off-size product must then be ground and recycled.

Possible Improvements

The concentration of plutonium within the precipitation and the digestors could be monitored on a continuous basis by gamma counting several regions of each tank continuously. When equilibrium conditions are established after several hours of operation the gamma activity at fixed points should remain relatively stable. Variations outside normal ranges would provide an indication of process upsets or possible attempts to divert materials from the process.

Similar counting devices could be installed on the dryer-calciner with similar results. It may be possible to determine the actual plutonium inventory within the process units by comparing the count data with pluontium content measured after drain down and flush out procedures carried out in conjunction with several normal inventories.

By proper correlation of the data obtained from the load cells within the screening, blending and container loading operational areas, positive verification can be obtained on the completeness of each transfer of PuO_2. Real-time inventory within these areas could be achieved by using positive locators to indicate the presence of a container at each operating or storage location. By combining this information with knowledge of authorized material or container transfers the in-process inventory could be determined at any time.

2.6 *ANALYTICAL SAMPLING*

The separations facility and the plutonium product facility have upwards of 150 remote sampling stations located in sampling galleries near the unit operation to be sampled and controlled. Most of the in-process samples taken are radioactive and are withdrawn from the process vessel or process line by means of air lifts arranged as shown in Fig. 11.

In order to draw a sample, the air lift is activated manually by a chemical plant operator working from an operating station adjacent to the sampler. Typically, the sample stream is allowed to flow through the sample bottle and back to the process vessel for several minutes before the actual sample is taken. This precaution is necessary to ensure that all traces of the previous sample have been flushed from the sampling system.

The sample bottles are sealed, placed in shielded containers, and properly labeled for transfer to the analytical laboratory. In some parts of the plant, sample transfers are made using pneumatic transfer mechanisms, from sections where transfers are made infrequently, the samples are delivered manually.

When the samples are received at the analytical laboratory, the sample identification is recorded. The samples are weighted to determine the approximate SNM content, the proper entries made in the SNM accounts for the laboratory MBA, and the samples are distributed to the proper work stations within the laboratory for the proper analysis.

Sample sizes vary from milligrams to several gram quantities depending on the type and number of analyses needed. During an average day, more than 500 in-process and product samples are processed, with the amount of contained plutonium exceeding 1000 grams. About 2000 grams of plutonium are expected to be in inventory or in-process within the laboratory at any time. About 5000 grams of plutonium will be held continuously in the laboratory

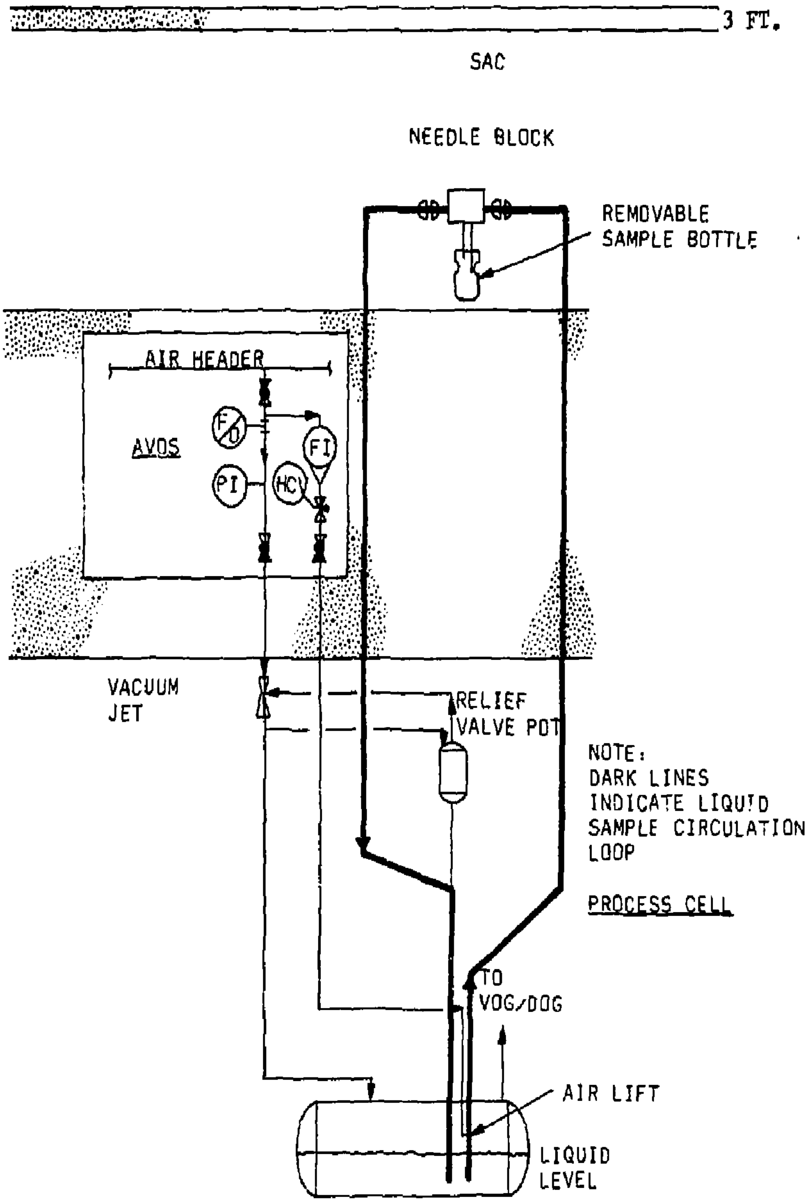


Figure 11. Remote Sampler Schematic

as nondestructive test samples, standards and reserve samples. The laboratory total inventory will be on the order of 8 kilograms.

The samples processed within the laboratory result in fairly large volumes of solid and liquid high level wastes. These wastes are analyzed for plutonium and transferred to the proper waste system for processing.

2.7 PROCESS COMPONENT ALTERNATIVES

There are several alternatives to the process equipment selected for the reference plant. The general impact of the alternatives on the safeguards system have been considered and a summary of these conditions is given in Table 4.

Tritium and krypton are two radioactive substances that are released from the reprocessing plant in a gaseous form. One method that has been proposed for removing these contaminants is to heat the pieces of the sheared fuel elements to 700°C in a rotary kiln or other suitable device prior to charging the dissolver. If the spent fuel is heated in the absence of a large gas stream, the tritium and krypton driven off will be in a relatively concentrated form, thereby simplifying later immobilization or recovery steps. Existing reprocessing facilities were not designed considering this process operation and no provisions have been made for installing the necessary equipment. The process has not yet been demonstrated to operate reliably in a radioactive environment limiting possible application to future plants.

TABLE 4. PROCESS ALTERNATIVES

PROCESS ALTERNATIVE	PURPOSE	EQUIPMENT DESCRIPTION	LOCATION	SAFEGUARDS IMPLICATION	TECHNICAL CONSIDERATIONS
Install Voloxidation Process Equipment	Permit partial recovery of tritium and krypton	High temperature continously operated rotary kiln (700 C)	Between shear & dissolver	Installation would create a large in-process inventory of SSNM between the shear item control station & the accountability tank. Traces of Pu & U in kiln off-gas	Process has not been demonstrated for reliability in radioactive environment
Substitute a Pulse Column for the Centrifugal Contactor	Use pulse column for primary fission product decontamination device	Pulse column may be more reliable than a centrifugal contactor as a unit operation	Between dissolver & partitioning column	Larger in-process inventory at primary decontamination station	Increased contact time between solvent & high activity fission product stream causes additional solvent degradation
Eliminate Centrifuge	Eliminate need for a mechanical device in highly radioactive environment	Solids clarification is a requirement between the dissolver & the centrifugal contactor. May not be necessary ahead of a pulse column used for primary fission product decontamination		Eliminate the separate waste stream from the centrifuge	Pulse columns have been operated with a heavy solids content in the aqueous stream but not in the extremely radioactive environment of the fluid stage contactor
Substitute a Conventional Pulse Column for the Electric Cell Partitioning Unit	Use chemicals for the Pu^{+} & to Pu^{+3} reduction rather than electrolysis	Pulse columns may be more reliable for partitioning than a electrocell	Between primary fission product decontamination & U and Pu purification systems	Additional chemicals in the high level waste streams	Electrocell cell eliminates the need for Pu^{+4} to Pu^{+3} chemical reductants
Substitute another dewatering device for the Oxalate Rotary Drum Filter	Develop a more reliable means for oxalate drying	Exxon Nuclear has proposed a *proprietary unit* for this operation	Between the oxalate digester and the *calcine*	May reduce in-process inventory *at drying operation*	Rotary drum filters are the only devices *that have been used* for dewatering on a pilot basis for $Pu(C_2O_4)_2$

The installation of the process as presently contemplated would significantly increase the quantity of SSNM between the item control receiving station and the accountability tank.

If a pulse column is substituted for the centrifugal contactor as the unit for primary fission product decontamination, it may be possible to eliminate the centrifuge as a means for removing solids from the feed stream to the column. Pulse columns in the Fernald plant have operated successfully with aqueous feed streams containing up to 1% solids. Operations of this type have not been demonstrated in a highly radioactive environment or when solvent degradation by radiation effects is a serious problem. By using a centrifuge and a centrifugal contactor, the SSNM in-process inventory at the decontamination operations is less than would be the case if a pulse column were used for this purpose. An additional waste stream is created, however, in the form of the slurry from the centrifuge. The effect of this waste stream on the total volume of waste is offset by the smaller quantity of degraded solvent that results from the use of the high speed, small contact time centrifugal contactor.

The reference process flow sheet is based on using electrolysis for reducing the valence of Pu^{+4} to Pu^{+3}. This unit operation can also be accomplished by the addition of a chemical reductant such as ferrous sulfamate, the technique used in the Purex plant at Hanford. The elimination of a chemical reductant by the electrocell process reduces the volume of the aqueous streams discharged to waste.

In the conversion plant, a rotary drum filter has been selected as the primary unit for dewatering the plutonium oxalate slurry from the digesters. Exxon Nuclear has proposed another form of dewatering unit that, at this time, is considered proprietary. It is expected that the proposed unit will be more reliable than the drum filter that has been the conventional equipment selection for this operation. If another process unit can be operated successfully, then the rework stream volume created by equipment malfunctions at this station may be decreased.

2.8 MEASUREMENTS AND INSTRUMENTATION

The measurements that are to be performed in the Barnwell plant of Allied-General Nuclear Services can be grossly characterized as predominantly contributing to process control and to the operational safety of the process. Only a relatively small number of instruments/measurements are designed primarily to provide special nuclear material accountability data points. The actual concentrations of Pu or U for example, are measured off-line via destructive analytical techniques. Measurements that could contribute to a determination of inprocess inventories or in-process flow rates of Pu are in general indirect measurements -- that may measure, for example, the air flow rate that is used to lift the Pu-containing stream from one tank to another. There are measurements, on-line, that directly depend on some physical property of Pu; however, they are qualitative in nature since the detector may respond to other nonfissile material sources or the system may not be calibratable in terms of grams of Pu per liter of solution.

Certain portions of the process are controlled automatically, i.e., sensors are used to control valves without the intervention of an operator. However, in most places in the separations area, for example, the operator can intervene in the normal flow of material. A gross characterization of the process is that it is remotely controlled but not automatic.

The description of the measurements and instruments that follow are limited to measurements of Pu or to material that may contain Pu. The order of presentation is dependent on the process flow from the head end of the separations area to the final load out of the PuO_2 at the end of the conversion area.

2.8.1 SEPARATIONS AREA

In-line measurements on process tanks in the separations area are listed in Table 5. The table is ordered according to the process operation, the measurements that are made at the specific tanks, the indicator location (local, panel, or control room), the type of indication that is made, and finally whether the measurement actuates an automatic control mechanism.

As the table clearly indicates the minimum instrumentation for most tanks (that are not pulse columns) is a level/density indicator and temperature indicators. Level and density are monitored by use of an air bubble system. A schematic illustration is shown in Fig. 12. The U-tube manometer for accountability points has a readout capability of 0.01 inches with a ±0.75% precision for all recorders. The tank volume is calibrated by use of the weight tank calibration method where accurately weighted increments of water are added to the vessel to be calibrated. Liquid depth is recorded for each increment. Temperature corrections for both the water and manometer fluid are made. The precision and the basis of a calibration and of subsequent volume measurements depend on the techniques and the instruments used. A volume of solution in a 5,000-gal process tank can be measured to within ±0.22% from a single calibration(10). Additional calibrations made over the operating lifetime of the tank can improve upon this considerably, possibly by a factor of 10 or more.

TABLE 5.

IN-LINE MEASUREMENTS FOR REPROCESSING PLANT

Process Operation	Measurement	Sensor Location	Indicator Location	Indication	Control
1. Dissolution	Level	Dissolver Tank	Panel	Recording	No
	Density				No
	Pressure (gas)				No
	Temperature				Steam on poison H_2O heater
	Level	Dissolver Transfer Tank	Panel	Recording	Air lift to feed surge tank
	Density				Steam jet transfer from dissolver recycle
	Temperature				No
2. Feed Preparation	Level	Feed Surge Tank	Panel	Recording	No
	Density				No
	Temperature				No
	Level	Accountability Tank	Panel	Recording	No
	Density				No
	Temperature				No
	Level		Local	Indicating	No
	Density				No
	Level	Feed Adjustment Tanks	Panel	Recording	No
	Density				No
	Temperature				No
	Level	Centrifuge	Panel	Indicating	No
	Radiation (γ)			Recording	No

TABLE 5 (Cont)

IN-LINE MEASUREMENTS FOR REPROCESSING PLANT

Process Operation	Measurement	Sensor Location	Indicator Location	Indication	Control
3. Co-Decontamination	Level	HA Feed Tank	Panel	Recording	No
	Density				No
	Temperature				No
	Temperature	Centrifugal Contactor Input and Output Lines	Panel	Recording	No
	Temperature	Organic Feed Line to HS Column	Panel	Recording	Steam to in-line heat exchanger
	Weight (level)	HS Column	Panel	Recording	No
	Neutron	HS Column	Control Room	Recording	No
	Level	HS Column (top)	Panel	Indicator	No
	Density			Recording	No
	Level	HS Column (bottom)		Recording	Aqueous recycle to centrifugal contactor
4. Partitioning	Radiation (βγ)	Organic Line from HS Column to Electrocell	Panel	Recording	No
	Temperature				No
	Level	IBX Electrocell		Indicator	No
	Density			Recording	No
	Weight (level)				No
	Level				Aqueous recycle from IB(x) column to electrocell
	Temperature	Organic and Aqueous Output Lines from Electrocell		Recording	No

TABLE 5 (Cont)

IN-LINE MEASUREMENTS FOR REPROCESSING PLANT

Process Operation	Measurement	Sensor Location	Indicator Location	Indication	Control
4. Partitioning (Continued)	Analytical (Pu γ)	Pu Stream from Electrocell	Panel	Recording	No
	Flow				Aqueous Pu stream from electrocell
	Density	IBX Column (top)	Panel	Recording	No
	Level			Indicator	No
	Level			Recording	Aqueous feed
	Analytical (neutron)	IBX Column		Recording	No
	Weight				No
5. Plutonium Purification	Temperature	IBP Surge Tank Feedline	Panel	Indicator	Steam to in-line heater for feed to surge tank
	Analytical (NO_2)	IBP Surge Tank	Panel	Recording	No
	Density				No
	Level				No
	Temperature	Line from Surge Tank to 2A Column			No
	Density	2A Column (top)	Panel	Recording	No
	Weight (level)	2A Column			No
	Level	2A Column	Panel	Recording	Aqueous waste flow
	Analytical (Puγ)	2A Waste Stream			No

TABLE 5 (Cont)

IN-LINE MEASUREMENTS FOR REPROCESSING PLANT

Process Operation	Measurement	Sensor Location	Indicator Location	Indication	Control
5. Plutonium Purification (Continued)	Level	2B Column (top)	Panel	Indicator	No
	Density			Recording	No
	Analytical (Puγ)				No
	Level				Aqueous flow to 3A column
	Weight	2B Column (bottom)			
	Temperature	Line from 2B to 3A	Panel	Indicator	Steam to heat exchanger for aqueous flow 2B to 3A
	Level	3A Column (top)	Panel	Indicator	No
	Density			Recording	No
	Temperature				No
	Weight (level)	3A Column (bottom)			Aqueous 3A waste stream
	Analytical (Puγ)	3A Waste Line			No
	Density	3B Column (top)	Panel	Recording	No
	Level			Indicator	No
	Analytical (Puγ)			Recording	No
	Level				Aqueous flow from 3B to diluent wash column
	Weight	3B Column (bottom)			No
	Radiation (βγ)	Aqueous Line from 3B	Panel		No

TABLE 5 (Cont)

IN-LINE MEASUREMENTS FOR REPROCESSING PLANT

Process Operation	Measurement	Sensor Location	Indicator Location	Indication	Control
5. Plutonium Purification (Continued)	Density	Diluent Wash Column (top)	Panel	Recording	No
	Level			Indicator	No
	Weight	Diluent Wash Column (bottom)		Recording	No
	Level				Aqueous flow to concentrator
	Pressure (gas)	Pu Concentrator	Panel	Recording	No
	Level				No
	Temperature				No
	Density				Steam to reboiler
	Level	Pu Product Catch Tank	Panel	Recording	No
	Density				No
	Temperature				No
	Level	Pu Product Sample Tank	Panel	Recording	No
	Density				No
	Temperature				No
	Level	Pu Product Storage Tank	Panel	Recording	No
	Density				No
	Temperature				No

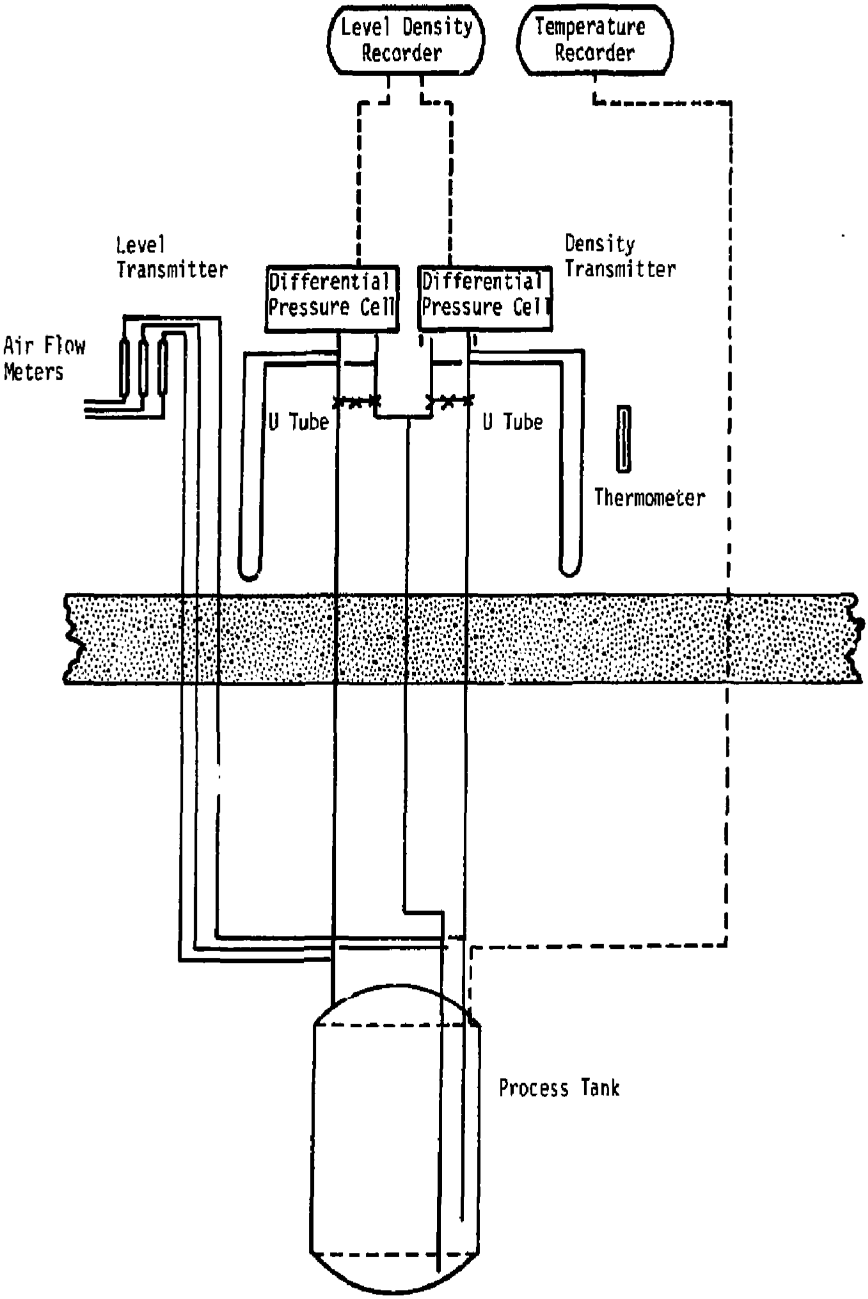


Figure 12. Level/Density and Temperature Schematic

Thermocouples to measure process temperatures are made of chromel-alumel because of its long-term stability and resistance to corrosion. The thermocouples will be calibrated against a platinum, platinum-rhodium thermocouple or a precision thermometer using a stirred heated oil bath. A precision of $\pm 1.5^{\circ}C$ can be obtained.

The in-line density measurements as shown in Fig. 12 are measured by the pneumatic "bubbler" system. This density measurement is dependent on the probe separation distance which is known to ±1/64 inch. In addition, the in-line density measurements can be cross-calibrated with the more accurate off-line density measurements that are made on samples sent to the analytical laboratory.

In addition to the in-line instrumentation on the process vessels there are a number of in-line process monitors that are used to supplement the laboratory analysis and facilitate a timely process control. The in-line monitors are calibrated routinely by adjusting instrument readings to correspond with analyzed laboratory samples. There are six types of in-line radiation monitors and two types of nonradiation in-line monitors. All of these monitors are briefly discussed below for completeness even though their location may be outside the main plutonium process or waste streams.

Recycle Water Monitors

Function:	Measures radioactive contamination in process condensate from concentrators
Detector:	3x3 inch NaI with single channel analyzer

Process Location	Stream Composition	Expected Activity (photons/sec-cm^3)
Acid Fractionator Accumulator	Water and Trace HNO_3	121
General Purpose Distillate Receiver	Water and Trace HNO_3	77
Service Concentration Feed Tank	Waste Water	$4x10^{-2}$
IUD/2UD Surge Tank	Water and Trace HNO_3	29

In-Line Gamma Monitors

Function:	Indicates total or specific fission product activity in process lines
Detector:	NaI with single channel analyzer, recorder and alarm
General Location:	In small analyzer cell in sample analytical cells

Process Location	Activity Monitored	Expected Activity (photons/sec-cm^3)
2 EU Line	Low Gamma in Uranyl Nitrate	166
3 BP Line	Low Gamma in Pu Nitrate	7.5
Uranium Product	Low Gamma in Uranyl Nitrate	75
No. 1 Solvent Feed	Low Gamma in Solvent	$2.14x10^3$
HSP Line	Medium Gamma in Solvent	$1.28x10^6$

In-Line Alpha Monitor

Function:	Measures total alpha activity in process streams
Detector:	Thin cerium-activated Vycor glass scintallators with electronics for $\beta\gamma$ suppression
General Location:	In sample analytical cells

Process Location	Stream Composition	Expected Pu Concentration (g/liter)	Other Activity (Photons/sec-cm^3)
1 CU Line	Pu (in U and Solvent)	1×10^{-4}	2.6×10^{5}
1 BP Line	Pu (in HNO_3)	1	1.7×10^{6}
2 AW Line	Pu (in HNO_3)	4×10^{-3}	1.1×10^{6}
3 BW Line	Pu (in Solvent)	1×10^{-3}	.16
1 SW Line	Pu (in HNO_3)	2×10^{-4}	2.85×10^{6}
1 SF Tank	Pu (in HNO_3)	5×10^{-3}	2.85×10^{6}
POR Line	Pu (in Solvent)	1.7×10^{-2}	95
2 BW Line	Pu (in Solvent)	1.4×10^{-2}	173
3 AW Line	Pu (in HNO_3)	1.5×10^{-2}	1.08×10^{3}
3 PD KC Pot	Pu (in weak HNO_3)	7×10^{-3}	.05

Neutron Monitors

Function:	Measures total neutrons from spontaneous fissions and (α,n) reactions
Detector:	^{10}B proportional counters with detection sensitivity of 30 counts/sec per unit neutron flux
General Location:	Removable mount on pulse column

Process Location	Activity Monitored	Remarks
1B Electropulse Column	Neutrons with medium gamma activity	Shielded from gamma
HS Column	Neutrons with medium gamma activity	Shielded from gamma

Nuclear Poison Concentration Monitors

Function:	Monitors $Gd(NO_3)_3$ concentration in dissolver feed solution
Detectors:	Neutron detector with Pu-Be neutron source mounted for transmission measurements
General Location:	In tanks

Process Location	Activity Monitored	Detector	Gamma Background (γ/cm^2-sec)
Seal Solution Makeup Tank	$Gd(NO_3)_3$ Concentration	^{10}B	121
Dissolver Acid	$Gd(NO_3)_3$ Concentration	U Fission Chamber	5.5×10^7

Leached Hull Monitor

Function:	Determines completeness of fuel dissolution by monitoring ^{144}Pr content remaining in fuel hulls
Detector:	4"x5" NaI with Pb filer (15 cm)
General Location:	Leached hull area in RMSC

Nitrate Monitor

Function:	Determines if surplus of sodium nitrite to insure oxidation of Pu^{+3}
Detector:	Calorimeter which measures amount of NO_2 in air stream after passing through process liquid
Locations:	1BP and 1SF streams

Uranium Colorimetric Analyzer

Function: Measures color of uranyl nitrate

Detector: Same as Nitrate monitor

2.8.2 Analytical Measurements

The accountability of the input and output streams is analytically determined from samples brought to the laboratory. The quality of processing and decontamination and percentage loss to waste is also determined by laboratory analysis of samples and supplemented by in-line measurements.

A remote sampler schematic is shown in Fig. 11. The schematic illustrates the use of indirect indicators for flow measurements. FI is a rotometer on the air that is used to transport the solution to the needle block through the sample bottle and back to the process vessel. Typically, a vessel will be air sparged and the solution will be circulated through the system for a statistically determined period of time. Although it is very difficult to determine a quantitative systematic bias in sampling there are known sources of error due to:

1. concentration or dilution by the air lift used to transport the sample to the sample port,
2. incomplete mixing in the tank,
3. dirty sample lines,
4. presence of solids.

Before samples are analytically processed, replicate samples are checked for density and compared with tank density. For liquid wastes roughly 5 to 10% of the Pu could be in a solid form.

DENSITY (ANTON-PAAR DMA 10 DENSIMETER)

Using this Densimeter the density of a homogeneous liquid sample can be measured to a precision of ± 0.0003 mg/l. The densimeter measures the change in resonant frequency of a hollow mechanical oscillator (volume 0.6 ml) when filled with substances of different mass. The density of the material in the oscillator is determined by the following equation

$$\rho_{\text{sample}} = \rho_{H_2O} + A\,(T^2_{\text{sample}} + T^2_{H_2O})$$

when

ρ = density

A = instrument constant

T = period of oscillation

INPUT PLUTONIUM CONCENTRATION

The input Pu concentration and isotopes are measured by an Isotopic Dilution Mass Spectrometry Technique$^{(10)}$. Measurement is based on spiking an aliquot of a sample with a known amount of ^{242}Pu. The spiked and unspiked samples are analyzed by a mass spectrometer. The Pu accuracy for LWR fuel is expected to be between 0.5 and 1%. Other techniques are more accurate however, they require more handling which make them unfeasible in a production plant reprocessing high burnup LWR fuel.

PRODUCT PLUTONIUM ANALYSIS

Output plutonium produce is measured via an oxidation-reduction amperometric end-point detection method. The Pu in 0.5 $(NH_2)_2\ SO_4$ solution is oxidized to the hexavalent state with

Ag(II) oxide. Excess oxidant is destroyed by heating. The solution is made 5 N in H_2SO_4 and the Pu(VI) is titrated with standard ferrous ammonium sulfate solution. The end point is detected amperometrically by measuring the current generated by excess titrant at a rotating platinum microelectrode vs. a saturated mercurous sulfate electrode.

HIGH LEVEL LIQUID WASTE

High level liquid waste will be sampled and measured via Isotopic Dilution Mass Spectrometry. Low Pu concentration levels of waste will be measured via alpha counting techniques. Generally, this will require a pretreatment step to separate the Pu from the other alpha emitters. In addition, the total solid content of the sample must be limited to (less than 30 mg/cm^2) to prevent excessive self absorption.

2.8.3 Plutonium Nitrate Storage Area

The slab storage tanks have the usual vessel instrumentation of level/density and temperature. In addition, each tank may be sampled for analytical analysis. Since no processing is involved in this area outside of wet blending, no other instrumentation is necessary besides flow monitors.

2.8.4 Plutonium Conversion Area

The detailed design of the Allied-General Nuclear Services Plutonium Conversion Facility at Barnwell, South Carolina, has not been completed. A preliminary safety analysis report has been submitted and has been accepted by the NRC for review; however, a construction permit has not been issued. Because of the incompleteness in design, a discussion of instrumentation is somewhat speculative.

Since the oxalate precipitation conversion process is relatively simple with stable reactants and products, the required process control instrumentation is minimal. The Pu nitrate feed is adjusted to the proper concentration (preliminary design was 150g Pu/liter, more recent Hanford results suggest a concentration of 200g Pu/liter) and the nitric acid is 3 molar. Hydroxylamine nitrate is added for Pu valence control. The feed preparation vessels have the usual level/density and temperature instrumentation.

The adjusted feed is fed continuously from the wet cell to the precipitation vessel where 1 molar oxalic acid is introduced. The remaining precipitation-digester, filter, and calcining is continuous with temperature control and flow rate the important process control variables. Provisions are included on all the precipitator-digestor vessels for adding oxalic acid if needed.

The oxalate filtrate feed line to the concentrator will have in-line alpha monitors (see Fig. 10 on Filtrate Treatment System). The return lines of the acid cooling and heating system will also have either in-line alpha monitors or adjacent-to-line radiation monitors. Controls, recorder, and alarms will be located in the conversion control room area.

The output of the calciner goes into a blender body or for oversized particles into a grinder body. Both of these containers are on load cells as shown in Fig. 9. These containers also may be sampled for laboratory analysis.

After blending the PuO_2 is loaded into 8kg containers, decontaminated and weighted and then loaded into the storage vessel. This thick walled vessel holds 4 PuO_2 containers which are sealed inside for storage and subsequent shipment in an overpeak.

2.3.5 Solid Waste Assay System

The present intent at AGNS is to place solid general process trash that is generated throughout the Barnwell Facility in 55 gallon drums and process these drums through a central drum assay facility. Each drum is to be scanned for total and fissile U and Pu content. To accommodate the expected high throughput (6000 drums per year from the separations and Pu product facility) coupled with an unknown matrix material and potentially relatively high background activity, a variety of detection approaches will be used. These include passive gamma measurements for ^{235}U, ^{238}U, and ^{239}Pu, passive neutron measurements for ^{240}Pu and active neutron measurements using a ^{252}Cf neutron source to determine the total fissile content in the drum. Preliminary tests indicate that approximately 0.25g total fissile, 0.26g ^{239}Pu, 0.05g ^{240}Pu and 100g ^{238}U can be measured under various detection conditions with a precision of 50% relative standard deviation. The complete assay system will be computerized so that drum movement, data-taking, attenuation-correction and final output are automatic.

3. MEASUREMENTS AND INSTRUMENTATION FOR REPROCESSING PLANTS

This section is divided into four parts with the first three describing general techniques that have been utilized or may be utilized in a separations and conversion facility. These techniques and instrumentations are classified under Laboratory Techniques, Nondestructive Assay and Process Instrumentation. Obviously, there is some overlap in the classifications. Weighing, for example, is certainly used in the laboratory as well as part of the process instrumentation. We have arbitrarily included all of the weighing discussion in the Process Instrumentation Section (3.3). The last part of this section is an initial set of techniques and/or instruments that might be used in a Purex separation, oxalate precipitation conversion facility. Basically, this initial set includes techniques or instruments that are planned for the AGNS facility at Barnwell with some additional instrumentation that primarily serves only Safeguards interests.

3.1 LABORATORY TECHNIQUES

The methods described in this section as "Laboratory Techniques" are defined to be those techniques or measurements that are conducted on samples drawn from the process lines or storage areas and removed to a centralized laboratory area for analysis. Obviously, some of the techniques utilized in the laboratory area are also amenable to on-line or process area operation and are nondestructive in application. Consequently, there are overlaps in the employment of a generic method so that an ambiguity often exists between the terms analytic method and nondestructive assay (NDA) or destructive assay versus NDA. We discuss here those techniques that satisfy the above sampling and removal definition. In practice the laboratory techniques often utilize different hardware or procedures compared to that utilized for the same method applied at a process line or area. Typically, the laboratory techniques yield more accurate results since the measurement is likely to be conducted in a more controlled environment.

Laboratory techniques incorporates those techniques that may require a pretreatment before transporting to the laboratory area. This includes radioactivity hot process samples that have to be separated from the fission products prior to the laboratory analysis and unstable material such as PuO_2 from the conversion line that should be weighed and possibly stabilized before further handling.

The discussion will be limited to the techniques that directly measure, or can be related to the plutonium content. Any required pretreatment steps or other supportive chemistry, are assumed to be part of the technique, but will not be discussed explicitly in detail. This includes such steps as an anion-exchange clean-up before assay(11). If however, this specific treatment is required before the laboratory analysis, the time required to effect a separation is relatively lengthy (approximately 16 hours for a complete procedure) and must be included in any consideration of the timeliness of the laboratory analysis.

3.1.1 Measurement Control Program

An assessment of the accuracy of plutonium measurements naturally involves a detailed analysis of the technique and hardware utilized. However, an equally important part of any assessment is an evaluation of the laboratory measurement control program.

An effective measurement control program includes a formalized procedure for qualifying laboratory analysts(12) and for providing a continuing quality assurance of the various laboratory techniques utilized and the analysts performing them. For example, every technique has a written procedure that must be followed. In addition, a non-negligible fraction of the laboratory workload (≈5%) includes the analysis of standard solutions(13). Another fraction of the workload includes the analysis of referee samples by different analysts on different shifts. In addition, replicate samples may be recycled into the laboratory at later time periods. These checks and others are vital to maintain, and if possible, improve the precision and accuracy of the laboratory measurement program. Without an effective measurement control program, the most accurate laboratory technique is practically worthless.

3.1.2 Standards

All laboratory techniques have a calibration based on or traceable to National Bureau of Standards Certified Reference Material. The primary metal standard CRM949 has a certified Pu assay to within an uncertainty of ±0.06% at the 95 percent confidence level. The Certified Reference Material sets the limit for the ultimate absolute accuracy claimed for any laboratory technique. Table 6 lists the available NBS Plutonium Certified Reference Material. We have listed the certified istopic content of CRM948 as an example. These values must be corrected for the 14.8 year half-life of ^{241}Pu.

CRM949 is a well characterized Pu metal material that is widely used to calibrate assay methods(14). CRM944 is a stoichmatic material suitable for preparation of low concentration working assay solutions. CRM945 is a Pu metal that was prepared primarily for emission spectrochemical impurity standards. CRM's 946, 947, and 948 are isotopic standards that should be chosen to be nearest to the fuel cycle material being measured.

TABLE 6 NBS PLUTONIUM CERTIFIED REFERENCE MATERIAL

NBS CRM	Type	Certified For	Value		Comments		
949	Pu Metal	Pu Content	99.99% Pu		$\sim$3% ^{240}Pu		
944	$PuSO_4 \cdot 4H_2O$	Pu Content	47.50% Pu		$\sim$6% ^{240}Pu		
945	Pu Metal	Impurities, Pu Content	99.9 % Pu		$\sim$6% ^{240}Pu		
946	$PuSO_4 \cdot 4H_2O$	Isotopic Abundance	$\sim$12% ^{240}Pu		$\sim$4% ^{241}Pu		
947	$PuSO_4 \cdot 4H_2O$	Isotopic Abundance	$\sim$18% ^{240}Pu		$\sim$4.5% ^{241}Pu		
948	$PuSO_4 \cdot 4H_2O$	Isotopic Abundance	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu*	^{242}Pu
			0.011	91.477	7.910	0.569	0.0330
			±.001	±0.010	±0.010	±.002	±.0003
			Atomic percent uncertainty at 95% confidence lvel				

*must correct for decay

3.1.3 Sampling

Accurate analysis by a laboratory technique requires that a sample be representative of the material from which it was drawn. In the separations area of a reprocessing plant where Pu is in solution, recirculation samples are primarily employed. In most cases, the samplers are connected to vessels that contain air sparging units to mix the vessel contents prior to sampling or transfer. For sampling, it is important for the air sparging to be on long enough to insure homogeneity. This is particularly true in critically safe slab tanks where the vessel width is only 2½ inches wide. Stratification of solutions is one problem that can be overcome by thorough mixing; another problem with obtaining a representative sample may be the presence of polymers or precipitates. Polymers will not form in solutions where nitric acid concentration is greater than 4M. If the acid concentration is less than 4M the solution should be checked for polymers. Precipitates, if found, should be redissolved into solution. The uncertainty, at one standard deviation, for sampling of input solutions is thought to range from 0.1 to 0.3%(15).

Sampling PuO_2 powder and subsequent handling of the sample requires somewhat more care than for $Pu(NO_3)_4$ samples. PuO_2, when calcined at temperatures lower than approximately 1200°C, is hygroscopic and must be handled in a controlled atmosphere. U.S. NRC Regulatory Guide 5.6 recommends the atmosphere contain less than 10 ppm of H_2O. Besides the hygroscopic problem it is difficult to grab a truly random sample of solid material. When the capability for blending or homogenizing the material exists along with a controlled atmosphere the sampling error (1σ) should be less than .3%. If this is not the case, the sampling may range much higher. Reference 15 gives a range between .5 and 1%.

3.1.4 Techniques

In Table 7 a comprehensive list of laboratory techniques employed on Pu bearing material is given. All of these techniques have been utilized in the U.S. or foreign laboratories to analyze Pu materials. Some techniques are, of course, more popular than others. The specific techniques used at a given laboratory may depend on the plant facility, its capabilities and available hardware.

As mentioned above, laboratory techniques are primarily employed in a controlled environment to achieve a maximum accuracy. However, the sampling and analysis techniques often require significant amounts of time. Since most material accountability systems rely on laboratory techniques the timeliness of the laboratory technique can be important.

For example, if a sample requires an anion-exchange cleanup prior to assay, this procedure could take up to 16 hours. The mass spectrometry operation is expected to take 1-2 hour sample preparation ½ hour for transfer and 2 hours for analysis of U and Pu. Reference 11 estimates that a complete controlled potential coulometry or amperometric titration procedure including measuring replicate samples and standards requires 4 to 6 hours. These times all assume no backlog of samples that might require a waiting period for an analyst and/or hardware.

3.1.5 Automation of Laboratory Techniques

Because of the time problem and because of economic considerations, the trend in recent years has been to automate laboratory techniques. This has safeguards implications beyond any increase in timeliness due to the lessening of manual operations and hopefully, lowering the material assessability.

TABLE 7. LABORATORY TECHNIQUES

METHOD	MEASUREMENT PRINCIPLE	APPLICABILITY	INTERFERENCES OR LIMITATIONS	CALIBRATION		SENSITIVITY RANGE (mg Pu)	LABORATORY RELIABILITY (1σ)	PRODUCTION ACCURACY (1σ)	COMMENTS
				TYPE	FREQUENCY				
1. Isotope Dilution Mass Spectrometry	Sample aliquot spiked with known amount of ^{242}Pu or ^{244}Pu. Spiked and unspiked samples analyzed by mass spectrometry.	Pu bearing solutions and substances	Ions of same m/e ^{238}Pu and ^{238}U ^{241}Pu and ^{241}Am	NBS certified reference material	Each Day	Min 0.05	0.20-0.40% isotopic estimate at 2σ ^{239}Pu ± 0.1 ^{240}Pu ± 0.5% ^{241}Pu ± 1-5% ^{242}Pu ± 1-10%	0.7% (0.2-3%)	Method of choice for input accountability solutions Suitable commercial spectrometer Nuclide (State College, Pa) Model 12-90-SU or 12-90-35
2. Controlled Potential Coulometry	Pu (IV) reduced to Pu (III) in an electrolyte at a Pt electrode maintained at constant potential versus a saturated calomel electrode (SCE). Pu(III) then oxidized to Pu(IV) at a different constant potential versus the SCE. Quantity of Pu calculated from number of coulombs required for oxidation.	Pu metal, oxide, mixed oxide and nitrate solutions	If Pu(VI) is likely to be present then electrolyte of choice is .5 M H_2SO_4 Fe < 100 ppm of Pu. Corrections can be made for 100 < Fe < 1000 ppm of Pu No free fluoride	Chemical Electrical	Beginning, middle and end of each shift At least every 6 mos	5-10	0.05-0.1%	0.25% (.1 to .5%)	Could be used for dissolver solutions or for product solutions if Fe impurities <1000 ppm Commercial equipment available MT Electronics Co.
3. Amperometric Titration with Fe(II)	Pu oxidized to Pu(VI) with AgO in sulfuric acid solution. Excess oxidant is destroyed by heating. Titrant (FE II) added until endpoint exceeded. The current flow observed between two electrodes at constant potential is proportional to excess titrant added.	Pu metal, solutions oxide, carbide mixed oxide and mixed carbide	Interference caused by ions oxidized by AgO and later reduced by ferrous sulfate in sulfuric acid. Ce, Cr, Mn, V corrections possible if x < 200 ppm Americium may cause on interference	Chemical Electrical	Beginning, middle and end of each shift At least every 6 mos.	5-20	0.05-0.1%	0.2% (0.06-.5%)	Other titrametric methods available. Most require larger amounts of Pu. Some utilize potentiometric end-point determination. Parts available commercially such as precision micrometer, rotating Pt microelectrode. Titrant must be checked frequently for air oxidation of Fe(II)
4. Density	The change in the resonant frequence of a hollow mechanical oscillation (V tube) is measured.	homogeneous liquid samples	No precipitated solids		To manufacturers specifications	--	[illegible] g/ml	--	Air and water used as standards Available commercially Arcon-Paar DMA 10 Densimeter
5. Alpha-Spectrometry	Alpha particles are counted by a detector such as a silicon surface barrier detector. Usually used for ^{238}Pu determination when ^{239}Pu and ^{240}Pu are known.	All samples of Pu	Any alpha emitting isotope with a energy in the 5 to 6 MeV region ^{241}Am must be removed from sample	Pu standard	daily	^{238}Pu range from 0.01 to .7 tot.	depends on peak statistics	1-2%	Method of choice for ^{238}Pu when weight percentage low or when ^{238}Pu is present. Precise ^{238}Pu measurement important for calorimetry Technique also used on low concentration waste streams. Pretreatment step most likely required

TABLE 7. (cont.)

METHOD	MEASUREMENT PRINCIPLE	APPLICABILITY	INTERFERENCES OR LIMITATIONS	CALIBRATION		SENSITIVITY RANGE (mg Pu)	LABORATORY RELIABILITY (1σ)	PRODUCTION ACCURACY (1σ)	COMMENTS
				TYPE	FREQUENCY				
6. *X-Ray* Fluorescence	*Deexcitation of Pu through* the L x ray lines is measured by a high resolution spectrometer	*Pu solutions includ*ing input solutions, mixed oxides	*Sample preparation* critical because of L x-ray attenuation	*Pu standard*	*Each shift*	*Depends on* exciting source and concentration	.4%	.7% (0.1 to 1.0%)	Isotopic sources and machine exciting sources have been used.
7. Gravimetry	PuO_2 ignited at 1100 to 1250°C and weighed	Pure samples only	Non-volatile impurities must be *determined* separately	Scale	Each measurement	Scale Sensitivity		.1% (0.05 to .2%)	Technique not used in U.S. much because of difficulty in producing a stoichomatic form and handling difficulty for Pu powders.
8. Spectral Photometry	a) Measure the characteristic color of Pu in *solution. Differential* spectrophotometry	Pure Pu solutions	Spectrum of Pu solution a func*tion of species* present	--	--	Works best for high concentration solutions		.1% (0.05 to .2%)	Must have tightly controlled conditions. Used infrequently in *U.S.*
	b) Measure color of organic color complexes of Pu (IV)	Pu in waste solutions after chemical separation	Spectrum of Pu solution a function of species present			Very sensitive covers wide range		3 to 10%	Numerous organic color complexing agents some rather nonspecific
9. Other Methods									
Activation Analysis	Sample irradiated by a neutron source. Measure decay radiation such as delayed neutrons or gamma-rays	All Pu	Detect Neutrons-depends on irradiating neutron energy spectrum and background Gammas-fission product λ_0 or impurities may interfere	Standard for type of sample	Each measurement	Potentially most sensitive method available			Need a powerful neutron source such as a reactor or large ^{252}Cf source.
Gamma-Spectrometry	Detect spontaneously emitted gamma-rays following alpha decay of Pu	All Pu	Fission product γ's or other impurities	Standard for each type	Each shift	Depends on sample and setup			Requires complex equipment and analysis -- can do isotopics
Gamma-Absorptometry	Measure transmission of gamma or x-rays through a solution	Pu solutions	Other high-Z material in the solution	Standard Solution	Each shift				

References

1. American Society for Testing and Materials, "Standard Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear Grade Mixed Oxides ((U, Pu) O_2)" C 698
2. Darryl D. Jackson, James E. Rein, and Glenn R. Waterbury "Chemical Assay of Plutonium for Safeguards" Nuclear Technology, Vol. 23, 132-141
3. Clement J. Rodden, Editor, "Selected Measurement Methods for Plutonium and Uranium in the Nuclear Fuel Cycle" Second Edition TID-7029 National Technical Information Service
4. R. G. Gutmacher, F. Stephens, K. Ernst, J. E. Harrar, J. Magistad, T. E. Shen, S. P. Turel, "Methods for the Accountability of Plutonium Dioxide", WASH-1335 Superintendent of Documents
5. R. G. Gutmacher, F. Stephens, K. Ernst, S. P. Turel, T. E. Shea, "Methods for the Accountability of Plutonium Dioxide" WASH-1335 Superintendent of Documents.
6. Adolf von Baeckmann, "Destructive Analysis of Nuclear Materials for Safeguards" from Symposium of the Practical Application of Research and Development in the Field of Safeguards sponsored by The European Safeguards Research and Development Association. March 7 and 8, 1974.

Moreover, automation often means the direct interconnection of the laboratory technique hardware with a computer. This should reduce transcription erros that often plague a totally manual operation.

Table 8 presents a list of laboratory techniques that have been automated. In many cases experience is now being developed on the production accuracy and reliability of such instruments. It is likely that more automated laboratory instruments will be developed since they clearly meet a safeguards and economic need.

3.2 NONDESTRUCTIVE ASSAY

Nondestructive assay (NDA) implictly means that no chemical change in the material is required to perform the measurement. Consequently, samples are not a priori required and the measurement can be conducted on large quantities of process material, scrap, or waste. In general, if bulk measurements are made, they are conducted on or near the process operation. Here, the environment such as the radiation background, temperatures, humidity, etc., is likely to be more difficult to control. It follows that NDA's are often less accurate than laboratory techniques and provide more of a qualitative trend indication.

In this section we present an overview of NDA applied to a reprocessing facility. Since in recent years there has been a proliferation of NDA instruments -- particularly to measure scrap and waste -- we have described the general measurement methods instead of describing every specific NDA instrument. This makes it difficult to pinpoint the expected precision and accuracy since these quantities are measurement/instrument specific. Table 9 lists the NDA methods along with or some specific NDA instruments that have been designed into reprocessing plants.

TABLE 8. AUTOMATED OR PARTLY AUTOMATIC LABORATORY TECHNIQUES FOR Pu

Method	Measurement Principle	Time Per Assay	Precision (1σ)	References
1. *Automated* Spectrophotometer	*Measures optical* absorbance on tetrapropylammonium plutonyl	5 *min*	Roughly .5% over most of sensitivity range .5 to 15 mg	D.D. Jackson, D.J. Hodgkins, R.M. Hollen, J.E. Rein, "Automated Spectrophotometer for Plutonium and Uranium Determination", Los Alamos Scientific Laboratory, LA-6091, Feb. 1976.
2. Electrochemical Determination of Pu	Controlled-potential and controlled-current can be performed under control of a calculator	--	.1 to .2%	Under development at LASL, see IAEA Vienna Symposium paper (Oct. 1975), by D.D. Jackson, S.T. Marsh, J.E. Rein, G.R. Waterbury, LA-UR-75-1607.
3. Amperometere Titration (partly automated)	Automatic titration	14 min.	-	Pel, Bartscher, Z. Analytische Chemie, in press in 1974.
4. Controlled Potential Coulometry	Several prototypes in operation at AERE Harwell	--	--	Phillips and Milner, Analyst 94, 833 (1969)
5. X-Ray Fluorescence Analysis	Automation of sampling, sample preparation, measurement and data processing--available commercially	--	--	Von Baeckmann, Neuber, Wilhelmi and Koch, IAEA STI/PUB/291 (1972), 329.
6. Mass Spectrometry	Automated sample input, filament heating, focussing, scanning, and data evaluation.	-	-	Von Baeckmann, Neuber, Wilhelmi, and Koch, *IAEA STI/PUB/291* (1972), 329 and private communication with AGNS personnel (1976)
7. Separation of Uranium and Pu	Automated anion exchange method in 8n HNO_3	--	--	Bol, Brandalise, Bier, De Rossi, and Koch, EUR 4927 d (1973)

Automated units should approach *best manual precision and accuracy.*

TABLE 9. NONDESTRUCTIVE ASSAY

METHOD	MEASUREMENT PRINCIPLE	APPLICABILITY	INTERFERENCES OR LIMITATIONS	CALIBRATION		SENSITIVITY RANGE (mg Pu)	LABORATORY RELIABILITY (±%)	PRODUCTION ACCURACY (±%)	COMMENTS
				TYPE	FREQUENCY				
1. Calorimetry	A calorimeter is an instrument for measuring heat. The calorimetric method is essentially the measurement of the amount of electrical energy necessary to duplicate the thermal effect accompanying a physical or chemical change.	Plutonium containing product and scrap	Isotopic composition of Pu must be known along with other radionuclide impurities that have short half lives (^{241}Am)	Electrical	daily	Depends on calorimetry design and Pu isotopics technique can cover a wide range.	~ 0.1% (well specified Pu isotopics	~ .5 (well specified isotopics)	Accuracy dependent on knowledge of isotopic composition, particularly ^{238}Pu and ^{241}Am.
2. Scrap and Waste Assay	Passive Neutron. Neutrons resulting from the spontaneous fission and (α,n) reactions of Pu isotopes are detected.	All Pu forms	Plutonium isotopic content (particularly ^{240}Pu) along with chemical form must be known	Standard containers approximating Pu isotopic and chemical form.	Beginning and end of each shift	Depends on equipment design, sample geometry, and neutron background	<5	≤10%	Best for highly controlled Pu substances with few impurities and known Pu isotopics.
	Passive Gamma Ray. Gamma-rays following the alpha decay of Pu isotopes are detected.	All Pu forms	Fission products or other gamma emitting isotopes may directly interfere or cause instrument dead time losses. Attenuation of gammas must be accounted for.	Standard containers approximating Pu chemical form and geometrical distribution.	Beginning and end of each shift	Depends on equipment design, geometry, and gamma background.	<2	≤10%	Method capable of accurate isotopic determinations for well characterized samples, i.e., ≤1%
	Fission Multiplicity Detectors. Spontaneous radiations (γ's and/or neutrons) are detected in a coincidence mode. Method based on the multiplicity of radiations from spontaneous fission (i.e., averaging 2.5 neutrons and 7 photons)	All Pu forms	Method dominated by ^{240}Pu content (and ^{238}Pu) so isotopic content must be known. Attenuation and moderation characteristics of samples must be controlled.	Standard containers approximating Pu isotopics and geometry	Beginning and end of each shift	Depends on equipment design, Pu isotopics and radiation background.	<3	≤10%	Method capable of 1% accuracy for small, well characterized samples. Capable of ±5% measurements for large containers (≤55 gallons) with low density matricies and low radiation background.
	Active Neutron Interrogation. Samples are irradiated by a neutron source inducing fission. Prompt and/or delayed gamma-rays or neutrons are detected. Can use fission multiplicity principle in conjunction with neutron source.	All Pu forms	Interrogating neutron energy spectrum should be controlled. Self shielding of Pu may be important	Standard containers approximating Pu densities and geometry	Beginning and end of each shift	Depends on equipment design, sample size, and neutron energy spectrum	<2	<10.	By utilizing a low energy neutron source method determines the ^{239}Pu and ^{241}Pu content. Capable of 1% accuracy for small well characterized samples. Isotopic neutron sources include spontaneous fission sources (^{252}Cf)(α,n), sources (Pu-Be, AmLi), and (γ,n) sources (Sb-Be) A variety of commercial equipment is available from the IRT Corp. and National Nuclear Corp.

TABLE 9. (cont.)

METHOD	MEASUREMENT PRINCIPLE	APPLICABILITY	INTERFERENCES OR LIMITATIONS	CALIBRATION		SENSITIVITY RANGE (mg Pu)	LABORATORY RELIABILITY (1σ)	PRODUCTION ACCURACY (1σ)	COMMENTS
				TYPE	FREQUENCY				
3. On-Line Alpha Monitor	A thin Ce activated glass scintillator is utilized to preferentially detect alpha emitting isotopes in a flowing stream	Homogeneous waste or product streams	Detects all alphas without any energy discrimination. High beta activity (10 mCi/cc) could cause some pulse pile up	Could utilize standard solutions	Each shift	Maximum sensitivity 150 cps/μCi/cc) (see Fig.)	≤5% of system carefully rinsed and stabilizing circuits used	--	Can directly relate to Pu concentration of stream if free of other alpha emitting contaminants and Pu isotopics and ^{241}Am content known. No extensive operating data on present design available as yet.
4. Leached Hull Monitor	Undissolved fuel remaining in sheared cladding hulls contains quantities of fission products. The gamma activity from a fission product daughter is detected (i.e., ^{144}Pr) and when correlated with laboratory data indicates the amount of undissolved fuel	Leached fuel hulls	Because of intensity of activation products and other lower energy fission products, pulse pile-up is a problem. ^{60}Co is expected to be the most important background contribution	Remotely positioned ^{144}Ce source	Each shift	Depends on background activity from ^{144}Ce in hulls and activation product activity	40	--	No U. S. operating data available
5. Neutron Monitors (on line)	Neutron proportional counter mounted near column to monitor Pu concentration	Any column	Pu isotopics change effect the response	--	--	.7 g/liter range 0-10g/liter	--	--	A qualitative trend indicator of Pu concentration.
6. Sample Stream γ-Ray Spectroscopy	High resolution Ge(Li) detector scans product sample stream. Flow meter determines flow rate past detector	Any Pu $(NO_3)_4$ product stream	Residual fission product activity interferes with intensity determinations	Standard sources or standard solution	Each shift	Depends on design	≤ 1%	--	No on-line experience with high burnup power reactor fuel.
7. Dual Energy Gamma Absorptimeter	Two energy gamma transmission measurement made to determine heavy metal content in solutions	Any Pu $(NO_3)_4$ product stream	Residual fission product activity could interfere along with undissolved solids	Standard [illegible] source	--	--	--	--	A qualitative indicator of Pu concentration. Single energy absorptimeter has been routinely used at Windscale for years.

References

1. L. A. Kull "Catalogue of Nuclear Material Safeguards Instruments", Brookhaven National Laboratory Report 17165 August 1972.

2. R. H. Augustson and T. D. Reilly, "Fundamentals of Passive Non-destructive Assay of Fissionable Material" Los Alamos Scientific Laboratory, Manual LA-5651-15, Sept. 1974.

3. Raymond Gunnink, "Status of Plutonium Isotopic Measurements by Gamma-Ray Spectroscopy" Lawrence Livermore Laboratory, UCRL 76418

4. IAEA Safeguards Technical Manual Part E Methods and Techniques IAEA-174 (1975)

5. American National Standard Guide to Calibrating Non-destructive Assay Systems N15.20-1975

6. F. A. O'Hara, J. D. Nutter, W. W. Rodenburg, M. L. Dinsmore, "Calorimetry for Safeguards Purposes" Mound Laboratory MLM-1798

7. T. Gozani, "On-Line Plutonium Alpha Monitor" to be published.

8. T. Gozani, "Leached Hull Monitor for Detection of Undissolved Irradiated Fuel", Proceedings 15th Annual Meeting (1974) Institute of Nuclear Materials Managers, p. 203.

3.3 PROCESS INSTRUMENTATION

The reprocessing plant operating environment has an overriding effect on the choice of instruments and measurement devices that can be used reliably for control of normal chemical processing functions. The high levels of penetrating radiation in the plant head end through the first stage of product purification require that metals or carefully selected ceramics be substituted for organic materials commonly used for sealing devices and insulating materials. The fact that entry to the highly radioactive cells for maintenance, repair, or replacement can only be accomplished when the plant is drained down, flushed out and thoroughly decontaminated makes it mandatory that devices of all types be kept to the absolute minimum within the cells.

The operational difficulties are typified by the unusual methods used for extraction column flow control. In an ordinary processing plant handling nonradioactive materials, a flow meter could be placed directly in the line between the feed adjustment tank and the centrifugal contractor. By proper choice of the primary device and the sensing element, flow measurements of 0.5% of the instrument span could be achieved with careful calibration of the system. The measured feed flow could then be used to control flow in the feed stream to within ±1% by adjusting the air flow to the transfer jet. The feed stream flow measurement could also be used to establish an aqueous-to-organic flow ratio to the contactor. With sensitive flow measurements on the organic stream, a control loop could be devised the would have the capability of maintaining column flow ratios well within ±1%.

In contrast, the aqueous feed flow to the centrifugal contactor in a typical reprocessing plant is controlled by inference. The flow meters are mounted outside the process cells to measure the motive air flow to the transfer jets used to transport the feed solution to the contactor rather than the actual feed stream. By careful study of the air jet transfer characteristics, the feed stream flow rate can be controlled to within ±3% by proper adjustments of the motive air flow. Organic flow rates are controlled in a similar manner. By careful design of the contactor and choice of process flow sheet characteristics, this degree of control has been used successfully for plant operation.

As a further consideration, air jets for liquid transfer within the radioactive environment have the great advantage that no moving parts are needed within the cells. In ordinary chemical plant practice, many of the liquid transfers would be made by electro-mechanical pumps. Flow control could then be maintained either through variable speed control of the pump, recycle of a portion of the flow to the pump inlet or one of several other control methods.

Within the reprocessing plant, liquid levels within the process vessels are normally controlled by the use of air purged dip tubes. By measuring the air pressure necessary to maintain a controlled air flow rate through a tube discharging near the bottom of the vessel and comparing the pressure with that of a similar air flow to the free space above the liquid in the vessel, the pressure differential between the two tube discharge points can be obtained. If the density of the liquid is known, then the liquid level in the tank can be calculated.

Liquid density measurements are normally made by a variation of the pressure differential dip tube method used for measuring liquid levels. The differential pressure between air flows through two submerged tubes that are separated vertically by an accurately known distance is a direct measure of the liquid density within the process vessel.

In practice, the liquid density measured within the vessel is correlated to the density determined on liquid samples withdrawn periodically from the process vessels with proper correction for temperature effects.

The purged dip tube differential pressure method for liquid level and density measurement has the advantage that the measurement sensors are external to the cell. Measurement errors can be introduced by corrosion products adhering to the probes or by partial plugging of the submerged tubes by solids.

Interface control in the disengagement sections of the extraction columns is maintained by using purged dip tubes locacted at the proper elevations with known distances between pairs of submerged tube discharge points. Changes in liquid density can be sensed and corresponding changes can be made in flow rates to adjust the aqueous organic interface within the proper range.

Process vessels within the reprocessing plant are normally operated slightly below atmospheric pressure to avoid the potential hazards that could result from pressurization of vessels containing radioactive materials. Most of the pressure measurements made are associated with the pressures within the vessel off-gas systems and the cell ventilation system using Pitot tube devices. Again, the choice of pressure transducer is influenced primarily by the need for reliability and maintenance free operation within the radioactive environment.

Temperatures within the process cells are measured using thermocouples as these instruments in their normal configuration.

are resistant to radiation-induced effects. Resistance thermometers and liquid-filled thermometers can be used effectively in the nonradioactive portions of the plant.

Instrumentation systems most often consist of several components in addition to the sensing and readout devices. Generally, a signal convertor is required and if the measurement data are to be used or displayed at a distant location, a transmitter is also needed. Each of these links must be considered in the design of the overall system in order to preserve the accuracy, precision and reliability inherent in the sensing element. Several factors influence the choice of instruments for chemical plant operations including accuracy, precision, need for calibration, reliability, false alarm rate, response time, resistance to environmental effects and cost. In many cases, the most accurate instrument is not the best choice because of the overriding influences from other design considerations.

Table 10 presents those process control instruments that are commonly used in chemical processing plants. Those instruments that can conveniently be used in a reprocessing plant are noted.

3.4 REPROCESSING PLANT MEASUREMENT UPGRADE FOR SAFEGUARDS

Any detailed system studies on the material accountability of a reprocessing plant requires a set of measurements and uncertainties. In this section we present an initial measurement set that might be used for accountability purposes and some additional measurements that serve mainly a safeguard function. This initial set is appropriate for a Barnwell type facility. Any significant changes in the processes described in Section 2 may require a measurement change. The measurements listed in Section 2 are assumed to be incorporated

TABLE 10. PROCESS CONTROL INSTRUMENTATION

MEASUREMENT VARIABLE	SENSING MEANS	MEASUREMENT PRINCIPLE	RANGE	CALIBRATION		USES	ACCURACY	SENSITIVITY	LOCATION	COMMENTS
				Type	Frequency					
Temperature	Liquid Filled	Temperature sensitive bulb containing a liquid only, a liquid & its vapor or a gas connected by capillary tubing to a helical expandable element	-200 to +350°C	uniform	occasional	liquid & gas measurements	0.5% of span	0.1% of span	used only in nonradioactive portions of plant	Moderately affected by radiation
	Vapor Pressure		-270 to +350°C	nonuniform	frequent	liquid & gas measurements				Moderately affected by radiation
	Gas Pressure		-300 to +800°C	uniform	occasional	liquid & gas measurements				Radiation resistant with proper choice of gas
	Resistance	Resistance of winding in temperature sensitive tip varies with temperature change	-100 to +350°C	uniform	occasional	liquid & gas measurements	0.3%	0.1% of	used only in nonradioactive portions of plant	Seriously affected by radiation
	Thermocouple	Emf generated by difference in thermal characteristics of dissimilar metals in contact	-200 to 1550°C	nonuniform	frequent	liquids, gas & molten metals	0.5% of span	0.2% of span	used in radioactive environments on dissolver, process lines	Moderately affected by radiation
	Optical Pyrometer	Color of light from incandescent object is compared to light of known standard temperature	650 - 4000°C	nonuniform	frequent	solids, molten metals	0.3% of span	0.2% of span	calciner control	Useful only in visible color range
Flow	Differential Pressure	Flow through a suitable device-orifice nozzle or venturi results in a differential pressure inferential of flow rate sensed by a manometer or mechanical device	all flow rates with static pressures up to 5000 psi			liquids, gases & vapors	design dependent	design dependent	used only in nonradioactive portions of plant	Requires inline device as primary sensor
		orifice type	size dependent	uniform	occasional	accurate, high line pressure drop	design dependent	design dependent	used only in nonradioactive portions of plant	Clean fluids only. Narrow flow range
		nozzle type	special design	nonuniform	frequent	steam flow, moderate line pressure drop	design dependent	design dependent		Moderate solids using purge systems
		venturi type	special design	nonuniform	frequent	low line pressure drop	design dependent	design dependent		Large amount of solids can be handled
	Magnetic	liquid acting as a moving conductor as it flows through in a flow tube, cuts magnetic lines of flux from AC-powered coils external to tube	0.3 to 400,000 liters per min	uniform	occasional	suitable for dirty, viscous, corrosive or flowing liquids	0.5 of scale	0.25% of scale		Liquids with electrical conductivity of 2 microinches/cm or greater. Seriously affected by radiation
	Turbine	Fluid impacts a force on a multiblade rotor casuing rotation at a velocity proportional to flow rate. As each blade passes the face of the magnetic coil, a pulse of AC voltage is induced	0.3 to 200,000 liters per min.	uniform over selected ranges	occasional	inline measurement of liquid flow	0.2% of actual flow	0.2% within linear range		Clean fluids only. Seriously affected by radiation
Pressure	Pressures & changes in pressure cause deformations of sensing elements that are proportional to pressure or pressure change	elements of various shapes convert pressure changes to mechanical motion. Elements include diaphragms, bellows, special coil, helical coils, double bellows & double coils	pressure sensors are available from 0.01 in. of water pressure to 80,000 psi	instruments have both linear & nonlinear ranges	moderate	some portion of pressure sensor is exposed to process streams. The primary sensor can be partially protected using pressure seals	design dependent	design dependent	used for nonradioactive process streams; not used within cells	Not used in high radiation fields because of difficulty of periodic maintenance and calibration

TABLE 10 (cont.)

MEASUREMENT VARIABLE	SENSING MEANS	MEASUREMENT PRINCIPLE	RANGE	CALIBRATION		USES	ACCURACY	SENSITIVITY	LOCATION	COMMENTS
				Type	Frequency					
Pressure	Force Balance	Primary sensor deflection caused by presence is partially compensated by applying an opposing force to sensing element	from 0.01 in. of water to 80,000 psi	wide linear	moderate	Some portion of the pressure sensor is exposed to process streams. Primary sensor can be partially protected using pressure seals	design dependent	design dependent	used for non-radioactive process streams. Not used within cells	Not used in high radiation fields because of difficulty of periodic maintenance & calibration
pH	Electrodes	Variations in hydrogen ion activity are sensed by changes in electrical potential generated by the pH electrode	full pH range	unifrom	frequent	primary sensor must be in contact with process liquid. Electrode cleaners are required for many applications	0.5% of scale	0.3% of scale	used for non-radioactive process streams. Not used within cells	Seriously affected by radiation
Position Indicators	Mechanical	Movement of mechanical sensor indicates presence or position of an object				Devices can be completely mechanical, mechanical-electrical, or mechanical-electronic	generally on-off		used to indicate position of dissolver diverter	Devices can be designed to withstand penetrating radiation
	Optical	Photoelectric cell senses presence, absence or change in light beam intensity with object motions				Can be used for fill level of powder hoppers, cans	generally on-off		used for non-radioactive streams	Seriously affected by radiation
	Ultrasonic	Sound is interrupted or alternated by presence of an object				Detect fill level of powder hoppers or trays				Seriously affected by radiation
Liquid Level	Continuous Purge	Air-purge through tubing below liquid level with back pressure in bubble tube equal to the hydrostatic head at reference level	0-250 ft H_2O	uniform	seldom	liquids in open or vented tanks	design dependent	design dependent	primary sensing means in radioactive environment	Liquids of constant density Purge gas compatible with process
	Diaphram	Sealed chambers with diaphgram exposed to process liquid. Hydrostatic pressure on the flexible diaphragm compresses gas in closed system equal to hydrostatic head at diaphragm level	0-250 ft H_2O	uniform	occasional	liquids in open or vented tanks	design dependent	design dependent	used in non-radioactive portions of plant	Useful for level measurement of constant density liquids
	Differential Pressure Cell	Sensing element deflected by change in hydrostatic head at element level	0-800 in. of water	uniform	occasional	liquids in open, vented or closed tanks	design dependent	design dependent	used in non-radioactive portions of plant	Process-wetted sensing element
Liquid Level *or Density*	Buoyancy	Sense the buoyant force exerted *by a displacer element. Level* measurements are made as are surface liquid varies over length of element	level--up to *several feet* of level change	uniform	occasional	liquids in *open, vented* or closed tanks	0.5% *of span*	0.1% *of span*	used in non-radioactive portions of plant	Process-wetted sensing element

TABLE 10 (cont.)

MEASUREMENT VARIABLE	SENSING MEANS	MEASUREMENT PRINCIPLE	RANGE	CALIBRATION		USES	ACCURACY	SENSITIVITY	LOCATION	COMMENTS
				Type	Frequency					
Liquid Level or Density	Ultrasonic	Density measurements are made with the element completely submerged. Ultrasonic sound waves are attenuated or reflected by changes in level across sensor or by changes in density		nonuniform	frequent	liquids or solids in open, vented or closed tanks, or process piping	design dependent	design dependent		Seriously affected by radiation
	Continuous Purge	Difference in each pressure of air purge flowing through two submerged bubble tubes with an accurately known vertical difference provides measurement of liquid density		uniform	seldom	liquids in open, vented or closed vessels	design dependent	design dependent	Primary means in radioactive environment	Used for liquid density measurements and interface control
Weight	Balance	Weight measured is compared directly to a known weight	0 to 1000 lb	uniform	moderate	precision weighing of small quantities	0.001% of scale	0.001% of scale	Laboratory	Generally not used for industrial weighing
	Balance Beam	Weight measured is compared with weight on lever arm	0 to 200,000 lb	uniform	moderate	direct weighing of objects	0.01% of scale	0.01% of scale	Nonradioactive portion of plant	
	Load Cell	Weight increases pressure on a hydraulic non-compressible fluid	0 to 10^6 lb	uniform	moderate	general industrial weighing	0.01% of scale	0.01% of scale	Weighing process vessels, bins fuel assemblies	Can be made resistant to penetrating radiation
	Strain Guage	Pressure changes electrical resistivity of embedded electrical conductor	0 to 10^6 lb	uniform	frequent	general industrial weighing	0.01% of scale	0.01% of scale	Weighing process vessels, bins, fuel assemblies	Can be made resistant to penetrating radiation

in this initial set. Additional details, including the expected accuracies, are given below. The accuracies quoted are the expected production accuracies derived from the references listed in subsections 3.1, 3.2, or 3.3.

3.4.1 Laboratory Measurements

Laboratory techniques supply the basic accountability measurements for the input and output of the separation and conversion facilities. We shall assume for this initial set that the laboratory techniques are not automated (except for the mass spectrograph which is interfaced to a computer). When more data becomes availble on the accuracies to be expected over long periods of time, along with the measurement times, reliability, tamperproofness, etc., it would be apropros to include these newly developed automated laboratory techniques in an ideal measurement set.

In Table 11 we list the selected laboratory techniques by method, where in the process lines they may be applied, the estimated total assay time (which includes sampling, running of standards, etc) and the estimated random and systematic accuracy. Because most of these laboratory techniques require significant manual efforts, the estimated times may only be an optimistic guess. Significantly longer time periods could be possible before an assay is complete.

3.4.2 Nondestructive Assay

In nuc r fuel cycle material accountability systems NDA plays a porting role for SNM accountability except for waste and ibly scrap assays. This is true for the present measurement stem. However, in addition, NDA may provide qualitative support (such as the on line alpha monitor) or direct confirmatory measurement support for more accurate measurements (e.g., the samples sent to the laboratory are

TABLE 11. SELECTED LABORATORY TECHNIQUES

Method	Applications	Estimated Assay Time	(1σ) Uncertainty (%)		Comments
			Random	Systematic	
1. Isotope Dilution Mass Spectrometry	Input accountability tank	4 hrs	.7	.1	1.5 hr sample preparation, 1/2 hr transfer, 2 hr analysis
	All isotopes	"	^{239}Pu .05 ^{240}Pu .2 ^{241}Pu 2 ^{242}Pu 3	.01 .1 .3 .9	Isopotic compositions (and relative accuracies) depend on burnup of fuel being proces processed
	High concentration Pu liquid waste	"	5	.1	Sampling a problem since waste solution may contain 5-10% solids
2. Amperometric Titration	Product nitrate and oxide	5 hrs	.2	.1	
3. Alpha Spectrometry	Pu solutions	40 min	2	.5	Determines ^{238}Pu
4. Densimeters	All homogeneous solutions				No precipitates in sample
	organic	20 min*	.04	.01	*Time assumes no pretreatment required
	aqueous	20 min*	.03	.01	

normally weighed in and out -- NDA would provide a direct check that the samples do indeed contain Pu).

In Table 12 we have listed the NDA systems that might be used in a Reprocessing Facility. The random and systematic uncertainties are based on projected results. In most cases there are not significant production assay data to support the estimates in Table 12. However, there has been some testing of NDA devices to lend credance to these numbers. For example, Figure 13 illustrates the sensitivity of an on-line alpha monitor to alpha and beta radiations. From the figure it is clear that biasing above the relative pulse height of 40 essentially removes the beta ray sensitivity of the detector (unless the beta activity is relatively much higher than the alpha activity). Clearly more comprehensive experimental efforts would be required to project the actual operational sensitivity on the process waste streams.

3.4.3 Process Measurements

The primary factors for the design of the process instrumentation systems for control of necessary operating parameters for the reprocessing plant is the need for extremely high reliability of those portions of the system within the cell radiation barriers. Sensors within the cells must be resistant to the effects of penetrating radiation, require infrequent calibration and maintenance, and isolate the radioactive process streams from the plant operating spaces. Those portions of the overall instrument system external to the cell including signal converters, transmitters, and display units can be chosen on the basis of normal chemical engineering practices.

Several of the typical instrumentation systems combining sensors, converters, and transmitters are listed in Table 13 together with the overall system effectiveness. In all cases, the system signal can be converted to an electrical signal that can be used for computer data logging or, ultimately, for automatic control of the plant operations.

TABLE 12. SELECTED NONDESTRUCTIVE ASSAY

Method	Applications	Estimated Assay Time	(1σ) Uncertainty (%) Random	(1σ) Uncertainty (%) Systematic	Comments
1. Calorimetry	PuO_2 product 8 kg cans	1.5 hrs	.2	≤.1	Establishes a signature for each primary container. Isotopics known.
2. On-line Alpha Monitor	Various waste streams. See Section 2.	variable	3	10	Normal operating sensitivity ∼ 100 cps/μCi/cm
3. Leached Hull Monitor	Sheared hulls in head in area	variable	--	40	Random uncertainty dependent on unknown amount of ^{144}Ce imbedded in cladding
4. On-line Neutron Monitors	1 BX column HS column	variable	--	--	A qualitative indicator
5. Small Sample Assays	Input to laboratory small solid or liquid samples (low radioactivity)	5-10 min	1-5	1-2	Passive assay for ^{239}Pu content
6. Laboratory Waste	Solid waste in 5 gallon cans Liquid waste in 1 gallon cans	5 min	--	5	Passive system using fission multiphasty detector and NaI detector. Ramdon uncertainty cepends on Pu quantity
7. Waste barrel Scanner (55 Gallons)	Conversion area solid waste; low background radioactivity	5 min	--	5	Passive system using a fission multipharty detection and NaI detector. Fission efficiency of ∼ 16%. (Need isotopics for total Pu.)
8. Waste Barrel Scanner	All areas possibly with high radiation backgrounds	depends on material	Low Density 10 Medium Density 15	 20 25	Active and passive system using ^{252}Cf neutrons.

TABLE 13. SELECTED PROCESS CONTROL SYSTEMS

	Primary Sensor			Signal Converter			Transmitter			System	
Parameter	**Type**	**Accuracy**	**Precision**	**Type**	**Accuracy**	**Precision**	**Type**	**Accuracy**	**Precision**	**Accuracy**	**Precision**
Temperature	Thermocouple	±1.0°C	±0.5°C	EMF to Current	±1.0°C	±0.5°C	Electrical	±0.1°C	±0.1°C	±2°C	±1°C
				EMF to Pneumatic	±1.0°C	±0.5°C	Pneumatic	±0.1°C	±0.5°C	±2°C	±1°C
Level	Purged Dip Tubes	±0.3%	±0.1%	Back Pressure			Pneumatic	±0.1%	±0.05%	±0.75%	±0.5%
				Manometer	0.01" of water						
Density	Purged Dip Tubes	±0.3%	±0.1%	Back Pressure			Pneumatic	±0.1%	±0.05%	±0.75%	±0.5%
				Manometer	0.01" of water						
Flow	Air Jet	±2%	±1%	Rotometer on Motive Air Streams	0.3% of scale	0.1% of scale	Electrical	0.1% of scale	0.05% of scale	±3.0%	1.0%
Weight	Load Cell	±0.05%	±0.02%	Liquid Pressure to Air Pressure	±0.03%	±0.02%	Pneumatic	±0.03%	±0.02%	0.1% of scale	0.05% of scale
	Laboratory Balance				Not Applicable			Not Applicable		0.005% of scale	0.002% of scale

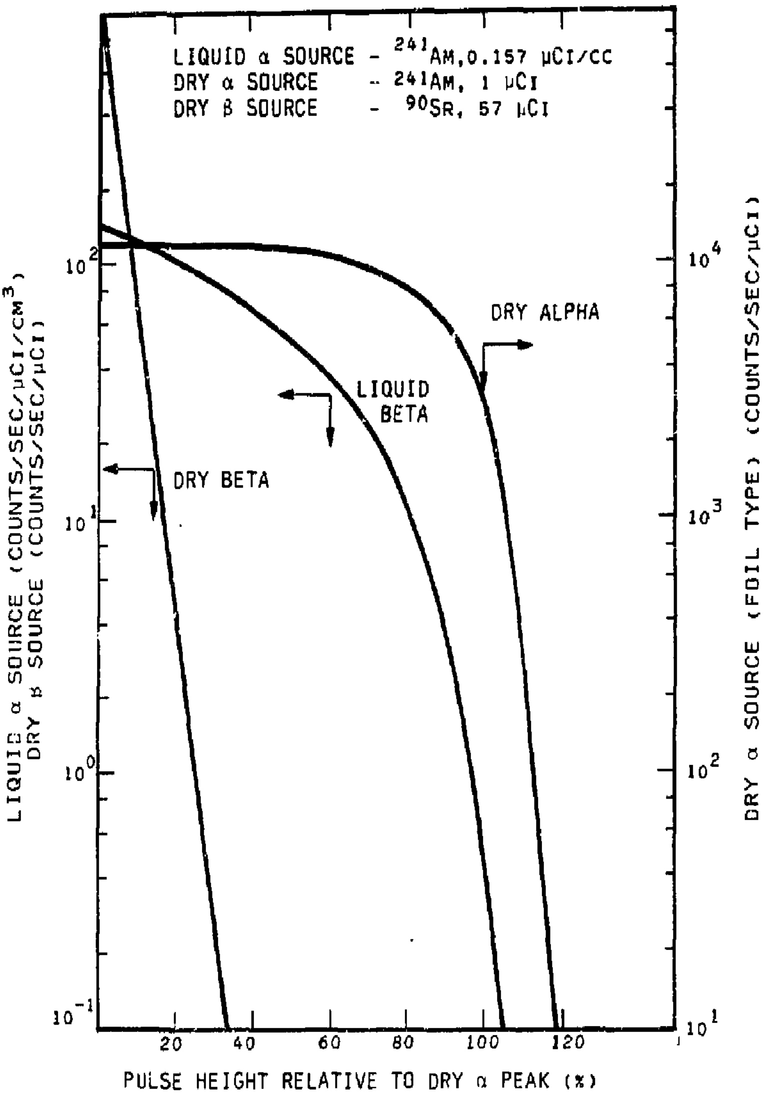


Figure 13. Discrimination Curves for Sensor

4. HOLDUP IN PLUTONIUM RECYCLE FACILITIES

The purpose of this section is to discuss the significance of holdup determinations in the nuclear fuel cycle facilities and review the present status of holdup measurements.

Plutonium residual holdup is defined as the plutonium inventory component remaining in and about process equipment and handling areas after those collection areas have been prepared for inventory. One may subdivide the holdup into two parts pertaining to runout, where all the material in a system or subsystem is processed without adding new material, and cleanout where following runout the residual material is flushed out by a proper dissolver.

a. Holdup residue after cleanout, which is fixed (approximately constant) material that normally remains with processing equipment after it is cleaned or flushed out.

b. Holdup residue after runout, which is the sum of fixed holdup residue plus the residual in-process material that remains with the processing equipment after it is runout or drained out.

Plutonium accumulates in cracks, pores and zones of poor circulation within process equipment. The walls of process vessels and associated plumbing often become coated with plutonium during solution processing. Surfaces internal and adjacent to process equipment, especially glove-box walls and floors, accumulate deposits of plutonium which can become appreciable. Pu also accumulates in air filters and associated duct work.

The absolute amounts of Pu holdup must be small for efficient processing and proper hazard control. However, the total amount of plutonium holdup may be significant in the context of the tolerable facility MUF. Facilities processing or using special nuclear material are usually designed to minimize the holdup of the material by avoiding as much as possible sharp bends, pores, crevices, etc. The accumulation of the SNM, or for that matter any material, will result from dust or liquid precipitation (and evaporation in the latter case) in zones of poor circulation, and from surface adsorption in the process vessels and plumbing walls. While good and careful design of the processing facility can reduce the amount of the holdup material, there is no feasible way of eliminating it short of complete dismantling of the equipment.

The physical principles of holdup measurements are relatively simple. They are based on the controlled observation of gamma rays emitted by the decay of ^{239}Pu (the "385" keV complex) and the neutrons emitted by the (α,n) reactions. and by spontaneous fissions. The neutron signatures require the knowledge of the isotopic and the chemical composition of the plutonium bearing material. The poor accuracy and the difficulties normally associated with holdup measurements result from the geometrical complexity of the measurement configuration, variable background, lack of isolation between investigated areas, possibility for significant and unknown amounts of self shielding for the measured gamma rays and lack of accurate knowledge of the isotopic and chemical composition of the plutonium. The existing plants which handle Pu were built with little or no consideration for holdup measurements.

The importance of the hold-up determinations and the significance of their uncertainty in the context of an overall accounting system is discussed in this section. We review, first, holdup in a model mixed oxide facility since system studies and experimental results are available. Next, the significance of holdup in a reprocessing plant are discussed. Following this the nuclear signatures utilized in the present measuring techniques and possible future signatures are discussed. Recent holdup measurements establishing the present state-of-the-art including the presently achievable measurement accuracy are described. The section is concluded by summarizing the fundings and recommendations.

4.1 SIGNIFICANCE OF HOLDUP IN MIXED OXIDE FACILITIES

The significance of the holdup measurements and their uncertainties within the context of the determination of MUF in a fuel cycle facility can be demonstrated by the analysis of material balance uncertainties and their origin in fuel cycle facilities. Such analyses can provide proper prospective of the holdup measurements in relation to a facility material accounting system.

The first example is based on the study of a Model 200 MT Mixed Oxide Fuel Rod Fabrication Plant(16). The material balance uncertainties are calculated for that facility assuming accurate weight measurements and accurate laboratory analysis of samples for the feed (PuO_2) and the product material (mixed oxide fuel rods). The dirty scrap and waste are assumed to be measured with the "best" nondestructive assay system. The various measurements uncertainties and related quantities are listed in Table 14, for an 8 week (2 months) inventory case. The definition of the symbols' appearing in this Table are given in Appendix 1. The material balance uncertainties for the various components of the MOX model plant is given in Table 15. The calculational method of the variances is summarized

TABLE 14 BASIC MEASUREMENT UNCERTAINTIES USED TO COMPUTE MATERIAL BALANCE UNCERTAINTIES FOR MODEL MIXED OXIDE FUEL FABRICATION PLANT

8 WEEK LOW HOLDUP CASE

MATERIAL	HM	HS	HA	PM	PS	PA	OM	OS	OA	NM	NS	NA
FLOW STREAM MEASUREMENT DATA												
PUO2 FEED	0.100	0.500	0.200	0.030	0.000	0.100	0.020	0.020	0.020	1.000	5.000	1.000
MO2 FUEL ROD PRODUCT	0.100	0.500	0.200	0.030	0.000	0.100	0.020	0.020	0.020	1.000	5.000	1.000
DIRTY SCRAP (1-LITER CANS)	2.500	0.000	0.000	0.000	0.000	0.000	5.000	0.000	0.000	1.000	1.000	1.000
WASTE (55-GALLON DRUMS)	5.000	0.000	0.000	0.000	0.000	0.000	10.000	0.000	0.000	1.000	1.000	1.000
CONSTANT-CONTENT INVENTORY MEASUREMENT DATA												
2A PUO2 STORAGE	0.100	0.500	0.200	0.030	0.000	0.100	0.020	0.020	0.020	1.000	5.000	1.000
1S MO2 FUEL ROD STORAGE	0.100	0.500	0.200	0.030	0.000	0.100	0.020	0.020	0.020	1.000	5.000	1.000
DIRTY SCRAP STORAGE	2.500	0.000	0.000	0.000	0.000	0.000	5.000	0.000	0.000	1.000	1.000	1.000
WASTE STORAGE	5.000	0.000	0.000	0.000	0.000	0.000	10.000	0.000	0.000	1.000	1.000	1.000
VARIABLE-CONTENT INVENTORY MEASUREMENT DATA												
4A PUO2 BULK STORAGE NO 1	0.100	0.500	0.200	0.030	0.000	0.100	0.020	0.020	0.020	4.000	5.000	1.000
4A PUO2 BULK STORAGE NO 2	0.100	0.500	0.200	0.030	0.000	0.100	0.020	0.020	0.020	4.000	5.000	1.000
4A PUO2 BULK STORAGE NO 3	0.100	0.500	0.200	0.030	0.000	0.100	0.020	0.020	0.020	4.000	5.000	1.000
4C RECYCLED MO2 STORAGE NO 1	0.100	0.500	0.200	0.030	0.000	0.100	0.020	0.020	0.020	4.000	5.000	1.000
4C RECYCLED MO2 STORAGE NO 2	0.100	0.500	0.200	0.030	0.000	0.100	0.020	0.020	0.020	4.000	5.000	1.000
4C RECYCLED MO2 STORAGE NO 3	0.100	0.500	0.200	0.030	0.000	0.100	0.020	0.020	0.020	4.000	5.000	1.000
6 MO2 POWDER STORAGE (4 SILOS)	0.100	0.500	0.200	0.030	0.000	0.100	0.020	0.020	0.020	1.000	5.000	1.000
HOLDUP RESIDUE AFTER CLEANOUT	5.000	0.000	0.000	0.000	0.000	0.000	30.000	0.000	0.000	1.000	1.000	1.000

See Appendix 1 for the definition of the symbols.

TABLE 15 MATERIAL BALANCE UNCERTAINTIES FOR MODEL 200 MT MIXED OXIDE FUEL ROD FABRICATION PLANTS (2 Month Inventory)

	Measurement of	Throughput (Kg Pu) Per Shift	Throughput (Kg Pu) Per Accounting Period	Variance	% of σ^2 (Total)
Flow Stream Data	PuO_2 Feed	7.125	1140	0.919	22.01
	MO_2 Fuel Rod Product	7.04	1126	0.898	21.48
	Dirty Scrap (1-liter cans)	0.10	6.80	0.116	2.78
	Waste (55-gallon drums)	0.2	6.80	0.466	11.15
Constant Content Inventory Data	2A PuO_2 Storage	7.125	174.56	0.045	1.08
	15 MO_2 Fuel Rod Storage	7.04	309.76	0.131	3.13
	Dirty Scrap Storage	0.10	6.80	0.116	2.78
	Waste Storage	0.2	6.80	0.466	11.15
Variable Content Inventory Data	4A PuO_2 Bulk Storage #1	--	144	0.150	3.60
	4A PuO_2 Bulk Storage #2	--	144 (x2)	0.276	6.61
	4A PuO_2 Bulk Storage #3	--	144	0.150	3.60
	4C Recycled MO_2 Storage #1	--	24.7	0.004	0.11
	4C Recycled MO_2 Storage #2	--	24.7	0.008	0.19
	4C Recycled MO_2 Storage #3	--	24.7	0.004	0.11
	6 MO_2 Powder Storage (9 silos)	--	1.8	0.0	0.0
	Holdup Residue After Cleanout	--	6	0.428	10.23
	σ^2 (Total = 4.178 Kg^2)	LEMUF = 4.1 Kg Pu		LEMUF/FEED = 0.36%	

in Appendix 1. The last column of Table 15 points to the main contributors to the total variance σ^2(total), and hence also to the LEMUF (=2σ). The individual contribution to σ^2(total) is high when the material throughput is high; as is the case of PuO_2 Feed and MO_2 Fuel Rod Product even though the measurement uncertainties are quite small. The contribution is also high when the measurement uncertainties are large, like the cases of Waste (55-gallon drums and storage) and Holdup Residue, even though their total throughputs are small. The effect of varying the total holdup amount over a reasonable range of 4 to 8 KgPu using the same measurement uncertainties (listed in Table 14) is shown in Table 16. This table shows that for the model plant a change of a factor of 2 in holdup residue increases its contribution to the variance by more than a factor of 3. The effect of varying the dominant holdup measurement error, namely the long term systematic error (QW), (which is mainly due to calibration difficulties) is shown in Table 17. The error is varied over a range covering a highly optimistic region of 0 to 10%, a realistic domain for a future plant, 20 to 40% and ending with measurement errors of 40 to 60% (all, at 1 sigma level) which are achieved in today's plants. Table 17 shows that for a 2 month inventory with flush out no significant benefit will result from reducing holdup measurements errors below 30%. However, for a runout inventory where the holdup residue is 3 times larger reducing the error below 20% will have an important impact on the LEMUF.

The previous discussion and Tables indicate that if one wants to reduce the error in the holdup measurement, or for that matter, any measurement error the relative contribution to the total

TABLE 16 THE EFFECT OF HOLDUP RESIDUE ON MATERIAL BALANCE VARIANCES
(2 Month Inventory)

Measurements	% of σ^2 (Total) for Holdup of		
	4 Kg Pu	6 Kg Pu	8 Kg Pu
PuO_2 Feed	23	22	20
Mo_2 Fuel Rod Product	23	21	20
Dirty Scrap (1-liter cans)	3	3	3
Waste (55-gallon drums)	12	11	10
2A PuO_2 Storage	1	1	1
15 MO_2 Fuel Rod Storage	3	3	3
Dirty Scrap Storage	3	3	3
Waste Storage	12	11	10
4A PuO_2 Bulk Storage #1	4	4	3
4A PuO_2 Bulk Storage #2	7	7	6
4A PuO_2 Bulk Storage #3	4	4	3
4C Recycled MO_2 Storage #1	0	0	0
4C Recycled MO_2 Storage #2	0	0	0
4C Recycled MO_2 Storage #3	0	0	0
6 MO_2 Powder Storage (9 silos)	0	0	0
Holdup Residue After Cleanout	5	10	17
σ^2 (Total) Kg^2	3.94	4.18	4.51
(LEMUF/FEED)%	0.35	0.36	0.37

TABLE 17 THE EFFECT OF HOLDUP MAJOR MEASUREMENT UNCERTAINTY ON MATERIAL BALANCE VARIANCES AND LEMUF (2 Month Inventory MOX Fuel Fabrication Plant)

	QW*%	σ^2 (Total) (Kg Pu)	$\frac{\sigma^2\text{(Holdup)}}{\sigma^2\text{(Total)}}$ %	LEMUF (KG Pu)
Cleanup Residue 6 Kg Pu	0	3.773	0.60	3.88
	10	3.818	1.77	3.92
	20	3.953	5.14	3.98
	30	4.178	10.23	4.09
	40	4.493	16.54	4.24
	50	4.898	23.43	4.43
	60	5.393	30.46	4.64
Cleanup Residue 8 Kg Pu	0	3.795	1.19	3.90
	10	3.885	3.47	3.94
	20	4.155	9.75	4.08
	30	4.605	18.57	4.29
	40	5.235	28.37	4.58
	50	6.045	37.97	4.92
	60	7.035	46.70	5.31
Runout Inventory 18 Kg Pu	0	3.953	5.12	3.98
	10	4.356	13.91	4.17
	20	5.573	32.71	4.72
	30	8.597	50.64	5.51
	40	10.433	64.06	6.46
	50	14.078	73.36	7.50
	60	18.536	79.77	8.61

*The long term systematic measurement uncertainty of holdup residue. This is the dominant source of error for holdup determination. The random error RW is assumed to be 5% in these calculations.

variance and the eventual effect on the LEMUF should be an important criteria for this assessment*. For example, in the situation depicted in Table 16, it does not make sense to reduce the holdup measurements as long as the errors in the measurements of PuO_2 Feed and Product rods are not reduced. However, this may indeed be required in the future if the LEMUF is to approach the 2 Kg Pu level. Table 18 shows cases where the reduction in the holdup measurement uncertainties is highly desirable because of their dominance. In cases where the throughput is substantially lowered, e.g., by more frequent inventories, the contribution of the holdup residue, which is assumed to be independent of the throughput (6 Kg Pu and 18 Kg Pu for the cleanout and runout inventories respectively) is greatly enhanced. This is demonstrated in the measurement variance to the total variance for cleanout and runout inventories when given as a function of the accounting period. The measurement uncertainties used in this computation are the same as those used for the base case (see Table14). The significance of the holdup measurement and the desirability of improvement for short accounting periods is quite obvious from Table 18.

4.2 SIGNIFICANCE OF HOLDUP MEASUREMENT IN A MODEL REPROCESSING PLANT

In the previous section, the effect of holdup and its measurement uncertainties were assessed for different accounting periods in a model mixed oxide fuel fabrication plant. It was shown under what conditions a reduction in holdup

---

*Different considerations will prevail when a plant or part of a plant is de-commissioned. Usually in these situations the holdup residue must be determined as accurately as possible.

TABLE 18. LEMUF AND RELATIVE CONTRIBUTION OF HOLDUP MEASUREMENTS TO THE MATERIAL BALANCE UNCERTAINTIES VS. INVENTORY TIME (For MOX Fuel Fabrication Plant)

Accounting Period	Cleanout Inventory		Runout Inventory	
	LEMUF (Kg Pu)	$\frac{\sigma^2\text{ (Holdup)}}{\sigma^2\text{(Total)}}$ %	LEMUF (Kg Pu)	$\frac{\sigma^2\text{ (Holdup)}}{\sigma^2\text{(Total)}}$ %
1 week	2.2	35	4.3	83
1 month	3.0	18	4.8	67
2 months	4.1	10	5.5	51
3 months	5.2	6	6.4	38
6 months	8.7	2	9.5	17
1 year	15.9	0.7	16.3	6

measurement uncertainty will have a significant impact on the LEMUF of the facility. In this section, the impact of the uncertainties in the holdup measurements on the LEMUF of a model reprocessing plant will be discussed. The model plant for reprocessing 1500 MT heavy metal/year is described in (17). The material balance uncertainties for the basic four material accounting areas were calculated for different accounting periods. The assumed measurement uncertainties and the resultant material balance uncertainties for the cleanout inventory of the conversion (Pu-nitrate to Pu-oxide) area are given in Tables 19 and 20 respectively. Table 20 reveals that the impact of holdup measurement uncertainties on the "LEMUF" determined in a cleanout inventory at the conversion plant is negligible even if the accounting period were further reduced. The material balance uncertainties in this facility are dominated by the large quantities of Pu-nitrate input and Pu-oxide output and the large measurement uncertainties in the general process trash and dirty scrap. A similar situation prevails in the material balance accounting of the separations plant. This is shown in Table 21 which is based on the measurement uncertainties listed in Table 22. Here also, the contribution of the holdup measurement uncertainty to the total material balance variance is practically insignificant regardless of inventory frequency.

When runout inventories are conducted, the holdup material is substantially higher than in the case of cleanout inventory and the weight of the holdup measurement uncertainty correspondingly increases. In the case of the conversion area the holdup residue amounts to 4.5 Kg Pu. Nonetheless, the contribution of the holdup measurement error to the total measurement variance does not exceed 1.5% for a one month inventory period. For the separation area, the assumed holdup residue for runout inventory amounts to 15 Kg Pu. Here, the contribution of the holdup measurement uncertainty to the overall variance is about 18% for 1 month inventory time, 10% for 2

TABLE 19 MEASUREMENT UNCERTAINTIES USED TO COMPUTE MATERIAL BALANCE UNCERTAINTIES FOR THE CONVERSION AREA IN A MODEL SPENT FUEL REPROCESSING PLANT

CONVERSION AREA-CLEANOUT INVENTORY(H-MONTH ACCOUNTING PERIOD) BASELINE NDA

MATERIAL	RM	RS	RA	PM	PS	PA	QM	QS	QA	NM	NS	NA
FLOW STREAM MEASURMENT DATA												
PU NITRATE INPUT	0.300	0.100	0.200	0.100	0.100	0.100	0.020	0.020	0.020	1.000	1.000	1.000
DIRTY SCRAP(ANAL.LAB)	5.000	0.000	0.000	0.000	0.000	0.000	2.000	0.000	0.000	1.000	1.000	1.000
PU OXIDE OUTPUT	0.100	0.300	0.200	0.050	0.000	0.100	0.020	0.020	0.020	6.000	6.000	1.000
CLEAN SCRAP(PU NITRATE)	0.300	0.100	0.200	0.100	0.100	0.100	0.020	0.020	0.020	1.000	1.000	1.000
GENERAL PROCESS TRASH	15.000	0.000	0.000	15.000	0.000	0.000	15.000	0.000	0.000	20.000	1.000	1.000
ANALYTICAL SAMPLES	5.000	0.000	0.000	0.000	0.000	0.000	2.000	0.000	0.000	10.000	1.000	1.000
DIRTY SCRAP(PU OXIDE)	2.500	0.000	0.000	0.000	0.000	0.000	5.000	0.000	0.000	1.000	1.000	1.000
CONSTANT-CONTENT INVENTORY MEASURMENT DATA												
VARIABLE-CONTENT INVENTORY MEASURMENT DATA												
HOLDUP RESIDUE AFTER CLEANOUT	10.000	0.000	0.000	0.000	0.000	0.000	40.000	0.000	0.000	1.000	1.000	1.000

TABLE 20 MATERIAL BALANCE UNCERTAINTIES FOR THE CONVERSION AREA OF 1500 MT/Y MODEL REPROCESSING PLANT (2 Months Cleanout Inventory)

Measurement of	Throughput (Kg Pu)		Variance	% of
	Per Shift	Per Accounting Period	σ^2 (Kg^2)	σ^2 (Total)
Pu-Nitrate Input	49.7	2486	11.745	26.9
Dirty Scrap (Anal-Lab)	0.05	2.5	0.003	0
Pu-Oxide Output	47.7	2384	4.423	10.1
Clean Scrap (Pu-Nitrate)	0.5	25	0.001	0
General Process Trash	0.5	25	21.108	48.4
Analytical Samples	0.1	5	0.010	0
Dirty Scrap (Pu-Oxide)	1.0	50	6.281	14.4
Holdup Residue After Cleanout	--	1.5	0.003	0.006

σ^2 (Total) = 43.598 Kg^2, "LEMUF" = 2σ = 13.206 Kg, LEMUF/FEED = 0.531%

TABLE 21 MATERIAL BALANCE UNCERTAINTIES FOR THE SEPARATION AREA OF 1500 MT/Y MODEL REPROCESSING PLANT (2 Months Cleanout Inventory)

Measurement of	Throughput (Kg Pu) Per Shift	Throughput (Kg Pu) Per Accounting Period	Variance σ^2 (Kg^2)	% of σ^2 (Total)
Pu-Nitrate Input	49.9	2494	41.915	72.9
Liquid Waste (Anal. Lab)	0.03	1.5	0	0
Clean Scrap (Anal-Lab)	0.03	1.5	0	0
Clean Scrap (Conversion)	0.5	25	0	0
Pu-Nitrate Output	49.8	2488	10.936	19.0
General Process Trash	0.13	6.3	1.319	2.3
Intermed. Level Liquid Waste	0.25	12.5	1.309	2.3
High-Level Liquid Waste	0.25	12.5	1.309	2.3
Analytical Samples	0.05	2.5	0	0
Holdup Residue After Cleanout	--	5	0.050	1.2

σ^2 (Total = 57.467, LEMUF = 15.161 Kg Pu, LEMUF/FEED = 0.608%

TABLE 22 MEASUREMENT UNCERTAINTIES USED TO COMPUTE MATERIAL BALANCE UNCERTAINTIES FOR THE SEPARATION AREA IN A MODEL SPENT FUEL REPROCESSING PLANT

SEPARATIONS AREA (6-MONTH ACCOUNTING PERIOD)

MATERIAL	RH	RS	RA	PH	PS	PA	OH	OS	OA	NH	NS	NA
FLOW STREAM MEASURMENT DATA												
PU NITRATE INPUT	0.500	0.300	1.000	0.200	0.100	0.200	0.020	0.020	0.020	5.000	3.000	1.000
LIQUID WASTE (ANAL. LAB)	5.000	0.000	0.000	0.000	0.000	0.000	2.000	0.000	0.000	1.000	1.000	1.000
CLEAN SCRAP (ANAL. LAB)	0.300	0.100	0.200	0.100	0.100	0.100	0.020	0.020	0.020	1.000	1.000	1.000
CLEAN SCRAP (CONVERSION)	0.300	0.100	0.200	0.100	0.100	0.100	0.020	0.020	0.020	1.000	1.000	1.000
PU NITRATE OUTPUT	0.300	0.100	0.200	0.100	0.100	0.100	0.020	0.020	0.020	3.000	3.000	1.000
GENERAL PROCESS TRASH	15.000	0.000	0.000	15.000	0.000	0.000	15.000	0.000	0.000	20.000	1.000	1.000
INTERMED-LEVEL LIQUID WASTE	2.000	6.000	20.000	3.000	6.000	10.000	1.000	1.000	1.000	3.000	3.000	1.000
HIGH-LEVEL LIQUID WASTE	2.000	6.000	20.000	3.000	6.000	10.000	1.000	1.000	1.000	3.000	3.000	1.000
ANALYTICAL SAMPLES	5.000	0.000	0.000	0.000	0.000	0.000	2.000	0.000	0.000	20.000	1.000	1.000
CONSTANT-CONTENT INVENTORY MEASURMENT DATA												
VARIABLE-CONTENT INVENTORY MEASURMENT DATA												
HOLDUP RESIDUE AFTER CLEANOUT	10.000	0.000	0.000	0.000	0.000	0.000	50.000	0.000	0.000	1.000	1.000	1.000

month inventory times and 3% for a 6 month inventory time. Thus, if the measurement uncertainty in the Pu-nitrate input, which constitutes more than 60% of the total measurement variance, is substantially reduced and/or if the inventory period is further shortened, then the incentive to greatly reduce the holdup measurement error would be more evident. This error was realistically assumed to be 40% (at 1σ) for the long term systematic error and 10% for the random error.

4.3 NUCLEAR SIGNATURES FOR HOLDUP MEASUREMENTS

The measurement of holdup of nuclear material is inherently difficulty. Primarily, this is because of the nature of the geometry involved, namely, a complex arrangement of plumbing and ducts, large glove boxes, large thick-walled storage containers, etc. Other difficulties can arise due to the high radiation background, the varying thicknesses of the various objects, the irregular geometry all coupled with the unknown distribution of holdup material. These facts limit the possible nuclear material signatures and techniques one can employ in quantitative measurements of holdup residues.

The requirement of penetrability dictates the usage of gamma and neutron radiations emitted by the nuclear material or by their daughter product. Inducing secondary radiation in the nuclear material by using, for example thermal neutrons and measuring the induced neutron and gamma radiations, is hardly practical because of the low concentration of the fissile material and the complex geometry. Thus, the holdup measurements are limited, for all practical purposes, to the passive detection of gamma and neutron radiations emitted spontaneously by the nuclear material.

4.3.1 Gamma Ray Signatures

The characteristic gamma rays and their emission intensities of important isotopes is tabulated in Table A2-1 of Appendix 2.

The obvious advantage of the detection of gamma rays is that they are copiously abundant and are characteristic to specific isotopes. The degree of specificity depends on the energy resolution of the detector employed. The specificity of the gamma radiation and the fact that the most important fissile isotopes ^{235}U and ^{239}Pu emit such a radiation, allow in principle, a direct quantitative measurement of these isotopes without prior knowledge of the isotopic composition of the material processed in the plant. As will be mentioned later, this constitutes an important source of error for the other gamma and neutron based measurement schemes. The main disadvantage of the gamma radiation from ^{235}U and ^{239}Pu is their strong attenuation in the structural material. The gamme-ray mass absorption coefficients for different materials as a function of energy is shown in Figure A2-1 of Appendix 2. The important gamma lines are indicated on this figure. An indication of the γ attenuation is provided by the length of the mean free path (MFP) in various substances. Table 23 gives the MFP (in cm) for a few γ and neutron energies in four important substances. 1.4 cm of steel will reduce the gamma radiation by about a factor of e (2.72), while a plastic material of the same thickness will reduce the intensity by only 14%. It is obvious that ^{235}U holdup measurements can be perfomed only if the measured containers are made of low Z materials (e.g., plastic) or of relatively thin metal sheet-like plumbing ducts. Since there is no other passive signature, such as neutron emission, from ^{235}U, it is obvious that holdup measurement of ^{235}U is severely limited. The penetrability of the radiation from ^{239}Pu is higher (see Fig. A2-1 and Table 23) but still causes measurement difficulties, limits the attainable accuracy, and requires a careful calibration(18).

TABLE 23. MEAN FREE PATH (1/Σ(TOTAL, cm) FOR PHOTONS AND NEUTRONS

Material	Density g/cm^2	Gamma			Neutrons	
		400 keV	1 MeV	2 MeV	Thermal	Fast
H_2O	1	9.5	14.3	20.0	0.34	2.2
Fe	7.86	1.4	2.9	3.0	0.86	3.6
Pb	11.35	0.4	1.2	2.0	2.7	5.6
UO_2	10.30	0.4	1.2	2.1	1.3	2.8

The gamma attenuation through walls of varying thicknesses in the complex geometries constitutes a significant source of error in the holdup measurements.

Penetrating radiation which is emitted by traces of fission products in the reprocessed plutonium may also provide a useful signature. It is expected that the amount of ^{95}Zr - ^{95}Nb and ^{106}Rh - ^{106}Ru fission products in the plutonium separated from high burnup spent fuel will be in excess of 2μCi per gram Pu. The intensities of the different gamma lines for low, medium and high concentration of fission product traces in Pu are given in Table 24. The substantially higher penetrability of these gamma rays and the high intensity can lead to a high detection sensitivity for Pu holdup in process equipment. The main drawback of using these fission product traces to measure holdup plutonium is the need to correlate this activity with the plutonium concentration. How good these correlations are, is difficult to assess at this time. It is plausible, however, that in process equipment, espcially for a MO_2 fuel fabrication plant, the measurements of the fission product activities will improve the accuracy of the Pu holdup measurements.

Another potential source of more penetrating gamma radiation is the 766 keV line associated with the α decay of ^{238}Pu. This relatively intense line can be of use for Pu originating in high burnup fuel where the amount of ^{238}Pu exceeds about 0.5%, yielding approximately 750 photons/sec/gram Pu (see also Table 25). The utilization of this line to determine quantitatively the total mount of Pu will require a knowledge of the isotopic composition of the plutonium along with the assumption of constancy of this composition. The ^{238}Pu line will be useful by itself if the fission product traces in Pu are low. Otherwise, its contribution will be lumped together with the ^{95}Zr - ^{95}Nb activity.

TABLE 24. APPROXIMATE GAMMA RAY EMISSION RATES (SEC^{-1}) FROM TRACES OF FISSION PRUDCTS* PER GRAM Pu

Radioactive Isotope	Half-Life	γ-Energy (MeV)	Emission rates per gm Pu*		
			Low	Medium	High
^{95}Zr	65 days	.724	$3x10^4$	$5x10^5$	$2x10^6$
		.756	$5x10^5$	$5x10^5$	$2x10^6$
^{95}Nb	35 days	.765	$7x10^4$	$1x10^6$	$3x10^6$
^{106}Ru**	363 days	.513	$7x10^4$	$1x10^6$	$3x10^6$
		.624	$4x10^4$	$5x10^5$	$2x10^6$
		> 1 MeV	$7x10^3$	$1x10^5$	$3x10^5$

---

*Three levels of fission product traces in the recovered Pu are assumed. Low -2μCi/gm Pu. Medium - 30 μCi/gm Pu. High - 80 μCi/gm Pu.

**$^{106}Rh \xrightarrow{\beta^-\ (368\ days)} {}^{106}Ru \xrightarrow{30\ sec} {}^{106}Pd$

4.4 NEUTRON SIGNATURES

Neutrons are emitted in the spontaneous fission of ^{238}Pu, ^{240}Pu and ^{242}Pu and through the interaction of emitted α particles with certain light nuclei. The neutron emission rates from spontaneous fission and (α,n) reactions in oxides and fluorides are given in Tables A2-2 and A2-3 respectively of Appendix 2. The emitted neutrons suffer little absorption in passing through most structural and containment materials. This is the main advantage the neutron signatures offers over the gamma signature. To be useful for the assay of plutonium holdup, the neutron production rate per gram of Pu must be known. This requires the knowledge of the isotopic composition for the spontaneous fission contribution and, in addition, a knowledge of the chemical form of Pu and the amount and distribution of certain high (α,n) yield target material (e.g., aluminum). Neutron and gamma yields from Pu with three different isotopic compositions are given in Table 25. It is seen that the neutron emission rate, with about equal contributions from spontaneous fission and (α,n) reaction in the oxygen in PuO_2, is substantially lower than the gamma emission rate but still has useful intensities.

4.5 HOLDUP MEASUREMENT TECHNIQUES AND RESULTS

The difficulty in measuring finely dispersed plutonium in large work boxes, tanks or other objects with complex geometries and containing different types of equipment has been emphasized throughout this section. The available nuclear signatures and measurement techniques were shown to be limited to the detection of the characteristic gamma rays from the fissile isotopes, ^{239}Pu and ^{235}U with the possibility of using the specific fission product traces as added information on the ^{239}Pu concentration. When the geometrical and structural configuration makes the gamma measurements unreliable because of excessive attenuation, the measurement of fast neutrons emitted in spontaneous fissions and (α,n) reactions becomes the main tool for Pu holdup determination.

The suggested experimental procedures and tools for in-situ assay of plutonium residual holdup, is described generically in Regulatory Guide 5.23(18). This Regulatory Guide discusses the available measuring tools namely, NaI(Tl) for the gamma detectors and semidirectional and non-directional neutron detectors. The possibility of using the newly available CdTe detector which could measure, because of its small size, the gamma activity in situations where other detectors have proven to be cumbersome has been recently suggested(19). The CdTe detector can be used to measure the holdup inside (and obviously outside) pipes and other difficult configurations and more use of it may be seen in the future. The present and future use of the high resolution Ge(Li) and intrinsic Ge gamma spectrometers for the purpose of holdup measurements seems to be very limited. This is because these detectors are inconvenient for applicaion in the difficult geometries which are typical in such situations. Also, their use will be time consuming rendering the holdup measurements prohibitively long. Regulatory Guide No. 5.23 describes in detail, the generic measurement procedures including calibration and sources of errors. The latter consists of a

1. counting statistics
2. instrument instabilities
3. geometric uncertainties

TABLE 25-A. EMISSION RATE FOR 1 GRAM Pu FROM YANKEE FUEL WITH 35,000 MWD/TU BURN-UP

Isotope	Weight%	Gamma Emission		Spontaneous Fission Prompt Neutron		(α,n) Neutron From PuO_2	
		γ/sec	Energy (keV)	Neut/Sec	%	Neut/Sec	%
^{238}Pu	1.9	3×10^3	766	47.2	15.3	266.0	76.1
^{239}Pu	63.0	8×10^4	320-430	0	0	28.4	8.1
^{240}Pu	19.0	--	--	194.2	63.2	32.3	9.2
^{241}Pu	12.0	2×10^6	208	0	0	1.2	0.3
^{242}Pu	3.8	--	--	65.7	21.4	0.4	0.1
^{241}Am	0.6	3×10^8	60	0	0	21.4	6.1
	Total			307.1	100.0	349.7	100.0
Total Neutron Emission Rate				657 Neut/sec/gram			

TABLE 25-B. EMISSION RATE FOR 1 GRAM Pu OF AN AVERAGE COMPOSITION (INCLUDING RECYCLE IN 1990)

Isotope	Weight%	Gamma Emission		Spontaneous Fission Prompt Neutron		(α,n) Neutron From PuO_2	
		γ/sec	Energy (keV)	Neut/Sec	%	Neut/Sec	%
^{238}Pu	1.2	2×10^3	766	30.0	7.5	168.0	63.6
^{239}Pu	53.0	7×10^4	320-430	0	0	23.9	9.0
^{240}Pu	25.8	--	--	264.0	66.4	43.9	16.6
^{241}Pu	13.5	2×10^6	208	0	0	1.4	0.5
^{242}Pu	6.0	--	--	103.7	26.1	0.6	0.2
^{241}Am	0.7	3×10^8	60	0	0	26.3	10.0
	Total	182.7	100.0	397.7	100.0	264.1	100.0
Total Neutron Emission Rate				662 neut/sec/gram			

TABLE 25-C. EMISSION RATE FOR 1 GRAM Pu (WITH ISOTOPIC COMPOSITION OF EQUILIBRIUM RECYCLE)

Isotope	Weight%	Gamma Emission		Spontaneous Fission Prompt Neutron		(α,n) Neutron From PuO_2	
		γ/sec	Energy (keV)	Neut/Sec	%	Neut/Sec	%
^{238}Pu	3.4	5×10^3	766	84.5	15.0	476.0	83.7
^{239}Pu	41.7	5×10^4	320-430	0	0	18.8	3.3
^{240}Pu	27.1	--	--	276.9	49.1	46.1	8.1
^{241}Pu	15.4	3×10^6	208	0	0	1.5	0.3
^{242}Pu	11.7	--	--	202.2	35.9	1.2	0.2
^{241}Am	0.7	3×10^8	60	0	0	25.0	4.4
	Total	258.6	100	563.6	100	568.6	100
Total Neutron Emission Rate				1132 neut/sec/gram			

    3.1 isolation of measured collection zones
    3.2 overlapping collection zones
4. attenuation uncertainties
5. interpretation uncertainties
    5.1 interferring radiations
        5.1.1 background and background variation in the gamma energy window
        5.1.2 a change in the high (α,n) yield impurities in the case of neutron counting
6. isotopic uncertainties

The contribution of total counting statistics to the overall error is usually insignificant. Instrument instabilities can be greatly reduced by proper equipment stabilization and frequent calibration. Hence, the contribution of this error will normally be small. The geometric and attenuation uncertainties can be rather significant. The magnitude of these uncertainties are determined during the calibration by moving the calibration source over the volume of observation measuring the additional signal due to the source ("add a source" technique). The interferring radiation in the case of gamma measurements normally will not be high. This situation may change, however, if the trace amounts of fission products, especially ^{95}Zr, ^{95}Nb and ^{106}Ru discussed in Section 4.1, are high. The variation in the (α,n) yield impurities has to be estimated using the permissible concentrations of these materials in the process. If the process equipment is cleaned each time the isotopic composition of the plutonium feed is varied, the holdup will consist primarily of the current material. When mixing occurs, the stream-averaged isotopic composition for preparation of the standard is probably the best estimate. The isotopic uncertainties are then determined by estimating the range of the process variation. As was mentioned before, the isotopic uncertainty significantly affects the neutron measurements.

Recently, several careful and detailed results of holdup measurements in mixed-oxide fuel fabrication plants(19,20,21) and Pu-scrap recycle plant(22) were given.

The most extensive measurements (performed by two independent groups) are reported in(19), where the holdup measurements in an entire mixed-oxide fuel fabrication plant (Kerr-McGee) are described. The measurements, which follow Regulatory Guide 5.23(18) whenever possible, obtained essentially the same results for the total amount of holdup Pu. The measurement uncertainties were estimated to be about 50% (at 1 sigma) through the agreement between the two results, assuming complete independence, indicates an error of 20% to 25% (at 1 sigma). Realizing that the measured plant was not designed at all to facilitate holdup measurements and that no calibration and insertion of standards into glove boxes prior to start up of plant were made, one is led to conclude that the obtained estimated value of the measurement uncertainty should be considered as an upper limit for the uncertainty in plants which will be designed to take into account the holdup measurement prerequisites. A room integrated holdup measurement was successfully demonstrated in the Kerr-McGee exercise (20) by using a relatively large nondirectional neutron detector which was placed in the middle of a well isolated and shielded room. The holdup in that room was measured within an estimated uncertainty of 50% (at 1 sigma level). The needed calibration coefficients and the uncertainty were determined by both calculation and calibration measurements.

Very careful Pu holdup measurements, using mainly a NaI(Tl) detector, and to a lesser extent, a semi-directional neutron detector, were performed on glove boxes, conveyors and tanks in areas of varying background at ARHCO(22). The measurement procedures of(18) were applied and the agreement between the assigned values, based on the nondestructive measurements, and the determination of the recovered plutonium has been within 16 percent for quantities ranging from several grams up to the kilogram level. Preliminary results from similiar measurements on several glove boxes showed an agreement of 20%(21). Measurement uncertainties of 20% (at 1 sigma level) or below, are outstanding for this type of measurements. However, it should be recalled that the configurations studied at ARHCO(22) and England(21) are much simpler than the Kerr-McGee case.

4.6 CONCLUSIONS

The need and desirability to reduce the holdup measurement uncertainty within the context of nuclear material safeguards accountability should be determined relative to other measurement errors and their impact on the overall material balance uncertainty. In many situations, as discussed in this section, the contribution of holdup and its measurement uncertainty is quite insignificant. However, for short inventory time and especially for run-out inventory, the hold-up and its uncertainty can become quite a significant contributor to the material balance uncertainty and hence, to the LEMUF.

The nuclear material signatures available for holdup measurements are basically the decay gamma lines and spontaneous and (α,n) neutrons. The possibility of using the more penetrating gamma rays emitted by traces of difficult to separate fission products such as ^{95}Zr-^{95}Nb and ^{106}Rb-^{106}Ru as a signature is suggested.

The most recent meausrements including a very elaborate one(19) clearly provide a practical range of achievable measurement accuracy. The measurement uncertainty in a complex unoptimized configuration is about 50% at a 1 sigma level. Under more favorable conditions, achievable holdup accuracies can be as low as 15% to 20%. All holdup measurements are very time consuming and are labor intensive.

In addition to the utilization of NaI(TI) gamma spectrometers and semi- and non-directional neutron detectors, the compact CdTe gamma spectrometer may emerge as a measuring tool for otherwise inaccessible locations including inner walls, ducts and tanks. The possibility of performing an integral measurement on the holdup in an entire isolated room by using large non-directional neutron detectors has been demonstrated, achieving an accuracy of about 50% in favorable situations. Based on one study, it has been found that placing a sample of known surface area, having the same characteristics as the equipment walls, at various positions in plutonium work boxes and process areas to monitor depositions could be advantageous. It can provide a proper calibration and allow an estimate of the holdup by area extrapolation. One may extend this concept and place not only flat surfaces, but incorporate other shapes and structures in the proper location for similar purposes. The present study fully concurs with the recommendation of the Kerr-McGee study.

Regulatory Guides, 5.8, 5.25 and 5.42 discuss the design of processing equipment to minimize holdup and to facilitate cleanout. However, since such designs cannot be perfect, it will be necessary to make measurements of the holdup of high-enriched uranium and plutonium in future facilities. The

Kerr-McGee and other studies have shown that: (1) equipment should be designed to minimize holdup and to facilitate cleanout, (2) there should be a continuing plan to improve the techniques for measurement of holdup, (3) in the future, plant designs should take into account the necessity for holdup measurements (for example, locate equipment so that each significant item can be "viewed" by passive assay instruments without interference from other objects; define "geometries" and determine radiation attenuation and scattering factors; don't buy pipes, etc.) and (4) the assay procedures should be determined in advance and the system calibrated before and during start-up operations.

5. REPROCESSING ALTERNATIVES - A PRELIMINARY OVERVIEW

5.1 PROCESSING STRATEGIES

Utilization of Pu produced in the LWR fuel cycle requires the processing of spent LWR fuel to recover the Pu and using this Pu in the fabrication of fresh mixed-oxide (MOX) fuel. Although MOX fuel can be used as both LWR fuel (3 to 5 wt. % Pu) and LMFBR fuel (20 to 25 wt. % Pu), its use as LWR fuel is being considered here. Processing Pu for LWR fuel consists of the following four distinct steps:

- Separations (separation of the fission products from the U and Pu, and the partial or total separation of the U and Pu into nitrate solutions).
- Conversion (conversion of nitrate solutions containing Pu or Pu and U into oxide powder form).
- Blending (blending of nitrate solutions containing Pu and U and/or blending of oxide powders containing Pu and U).
- Fabrication (fabrication of MOX pellets and fuel rods from oxide powders containing Pu and U).

From a processing viewpoint, these four process steps can be performed in separate facilities which are large distances apart. However, production efficiency and transportation costs suggest some colocation, particularly for the blending. In addition, safety and safeguard aspects of Pu-materials transportation provide further incentives for colocation. The impact of colocating some or all of these process steps is not examined in this preliminary overview, but it may prove to be an important issue.

The alternative ways of processing Pu fuel are determined by the configurations of the four basic process steps which can be developed. These configurations can be developed for two principal variables:

- U-Pu separation which is total (or nearly so), partial or none (i.e. mixed)
- U-Pu blending which is dry, wet or both.

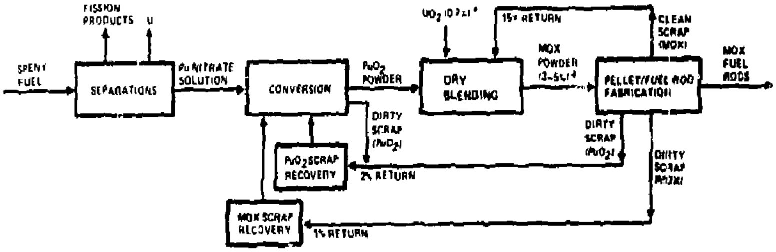
Based on these variables, nine configurations can be defined. Block diagrams of the resulting nine configurations are presented in Figs. 14 through 16. For each process step shown in the block diagrams, material form and enrichment or fissile content is given. The material form and quantity of clean and dirty scrap recycle is shown for each configuration. Waste streams are omitted, and U recycle is not addressed explicitly. Some key characteristics of the nine configurations are summarized in Table 26 This table includes the quantities of Pu product material generated by the conversion and fabrication processes, normalized to one kg of Pu recovered in the separations process.

Based on these characteristics and some general considerations, a preliminary (and incomplete) listing of the advantages and disadvantages of the nine configurations is presented in Table 27. Completion of Table 27 requires further study on the commerical feasibility of partial U-Pu separation and on the conversion of U+Pu solutions to MOX powder.

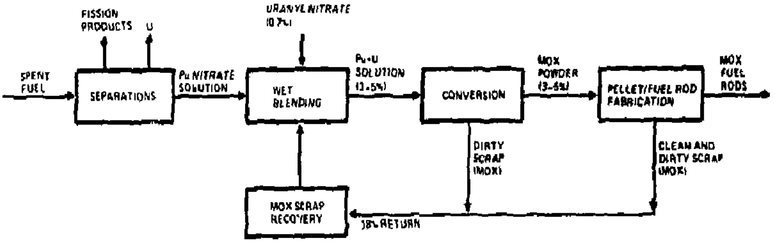
- Because of the requirements for enriched U feed material, for very high conversion throughput, for very high fabrication throughput and because they are not applicable to the LMFBR fuel cycle, the Group C configurations associated with no U-Pu separation are the least attractive.

- Depending on the commercial feasibility of partial U-Pu separation and of conversion of U+Pu solutions, the Group B configurations may be the most attractive.

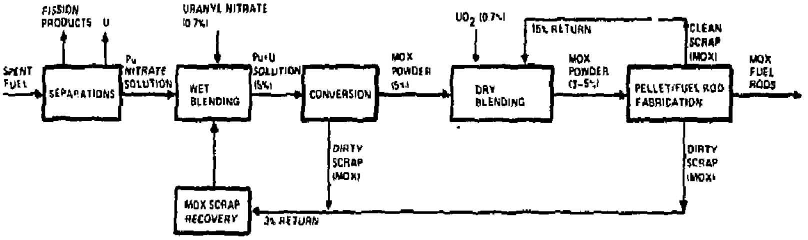
CASE 1 (TOTAL U-Pu SEPARATION + DRY CUSTOM BLENDING)-PLAN FOR BARNWELL-ANDERSON PLANTS



CASE 2 (TOTAL U-Pu SEPARATION + WET CUSTOM BLENDING)



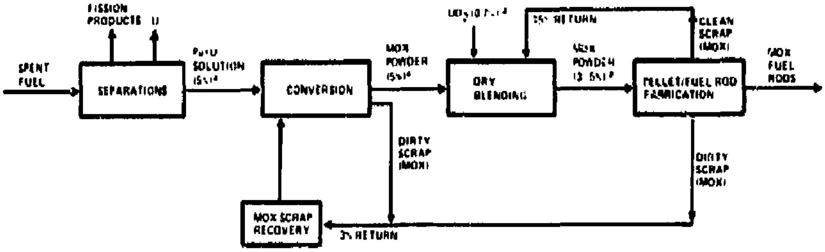
CASE 3 (TOTAL U-Pu SEPARATION + WET MASTER BLENDING + DRY CUSTOM BLENDING)



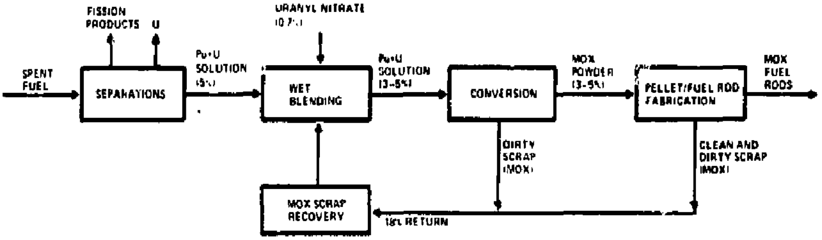
a. ENRICHMENT (Pu WT. % FOR MOX AND Pu+U SOLUTION, U-235 WT. % FOR UO_2 AND URANYL NITRATE)

Figure 14. Pu Fuel Processing Configurations for Total U-Pu Separation (Group A).

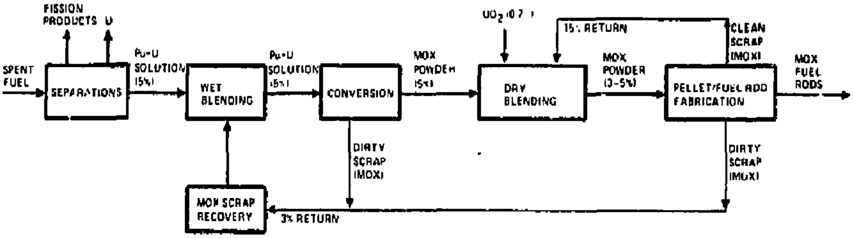
CASE 4 (PARTIAL U–Pu SEPARATION + DRY CUSTOM BLENDING)



CASE 5 (PARTIAL U–Pu SEPARATION + WET CUSTOM BLENDING)

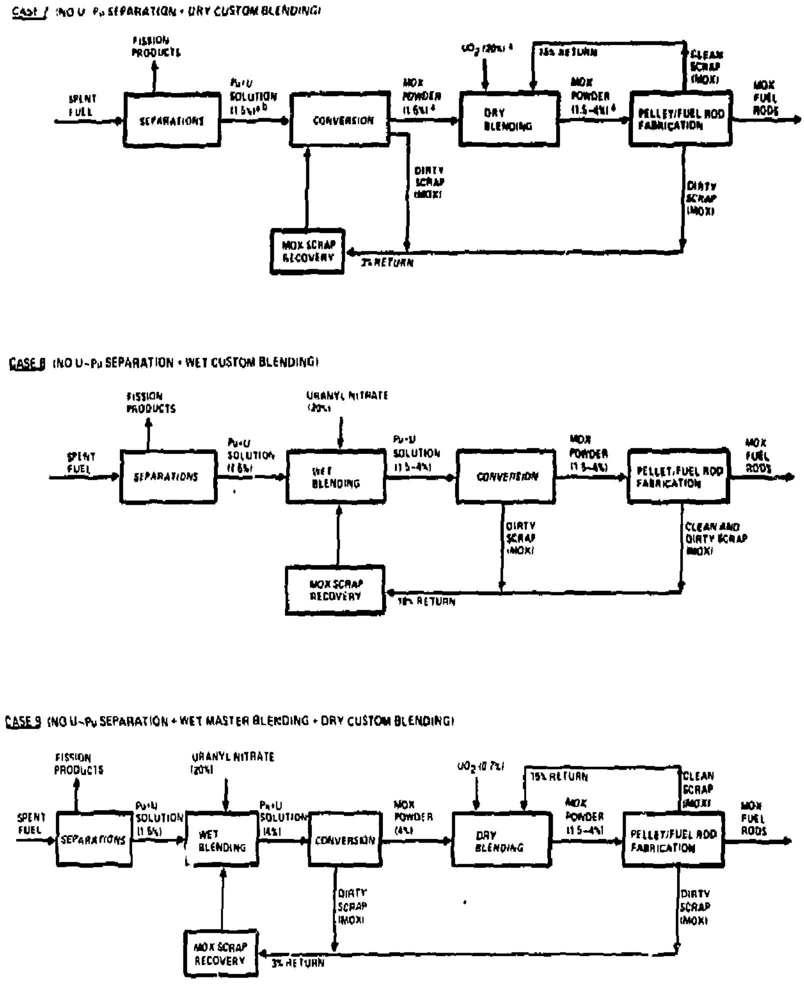


CASE 6 (PARTIAL U–Pu SEPARATION + WET MASTER BLENDING + DRY CUSTOM BLENDING)



a ENRICHMENT (Pu WT. % FOR MOX AND Pu+U SOLUTION, U–235 WT. % FOR UO_2 AND URANYL NITRATE)

Figure 15. Pu Fuel Processing Configurations for Partial U-Pu Separation (Group B).



a FISSILE CONTENT (WT % OF U-235 + Pu-239 + Pu-241)
b 0.8 WT % U-235 AND 0.7 WT % (Pu-239 + Pu-241)

Figure 16. Pu Fuel Processing Configurations for No U-Pu Separation (Group C).

TABLE 26. CHARACTERISTICS OF Pu FUEL PROCESSING CONFIGURATIONS FOR LWR FUEL CYCLE

Group	Case	U-Pu Separation	U-Pu Blending	Highest Pu-Content Material Present[a]	Type of U-Feed Material Required[b]	Scrap Recovery[c]	Conversion Requirement[d]	Fabrication Requirement[e]
A	1	Total	Dry	PuO_2 (88%)	UO_2 (0.7%)	PuO_2 (2%), MOX (1%)	1.2	20-33
	2	Total	Wet	Pu Nitrate (20%)	Uranyl Nitrate(0.7%)	MOX (18%)	24-41	20-33
	3	Total	Wet + Dry	Pu Nitrate (20%)	Uranyl Nitrate(0.7%) and UO_2 (0.7%)	MOX (3%)	21	20-33
B	4	Partial	Dry	MOX (5%)	UO_2 (0.7%)	MOX (3%)	21	20-33
	5	Partial	Wet	Pu + U Solution (5%)	Uranyl Nitrate(0.7%)	MOX (18%)	24-41	20-33
	6	Partial	Wet + Dry	MOX (5%)	UO_2 (0.7%)	MOX (3%)	21	20-33
C	7	None	Dry	MOX (0.7%)	UO_2 (20%)	MOX (3%)	147	143-165
	8	None	Wet	MOX (0.7%)	Uranyl Nitrate (20%)	MOX (18%)	174-201	143-165
	9	None	Wet + Dry	MOX (0.7%)	Uranyl Nitrate (20%) and UO_2 (0.7%)	MOX (3%)	170	165-700

a The Pu weight percentage is given in parenthesis for each Pu material.

b. The U-235 weight percentage is given in parenthesis for each U material.

c. The scrap recovery requirement, expressed as a percentage of throughput, is given in parenthesis for each case.

d. The conversion requirement is given for each case as Kg of Pu material converted from solution to powder per Kg of Pu separated.

e. The fabrication requirement is given for each case as Kg of MOX fuel fabricated per Kg of Pu separated.

TABLE 27. ADVANTAGES AND DISADVANTAGES OF Pu FUEL PROCESSING CONFIGURATIONS FOR LWR FUEL CYCLE

Group	Case	U-Pu Separation	U-Pu Blending	Advantages		Disadvantages	
				Group	Case	Group	Case
A	1	Total	Dry	A. Separation process is well defined.	1. Conversion process is well defined; conversion requirement is smallest	A. Pu content of material is highest (20-88 wt. %)	1. PuO_2 (88 wt. % Pu) is very attractive material for diversion; PuO_2 scrap recovery is required and is not well defined.
	2	Total	Wet		2. Wet blending is more uniform; coprecipitated MOX product and scrap are most easily dissolved.		2. Pu nitrate (20 wt. % Pu) is fairly attractive material for diversion; MOX scrap recovery requirement is large.
	3	Total	Wet + Dry		3. Coprecipitated MOX product and scrap are more easily dissolved		3. Pu nitrate (20 wt. % Pu) is fairly attractive material for diversion; two U feed materials are required; two blendings are required.
B	4	Partial	Dry	B. Pu content of all material is fairly low (<5 wt. %); coprecipitated MOX product and scrap are more easily dissolved.	4.	B. Partial U-Pu separation process is not well defined.	4.
	5	Partial	Wet		5. Wet blending is more uniform; coprecipitated MOX product and scrap are most easily dissolved.		5 MOX scrap recovery requirement is large.
	6	Partial	Wet + Dry		6.		6.
C	7	None	Dry	C. Pu content of all fuel material is very low (<1 wt %). separations process is simplest and hence separations facility is smallest; coprecipitated MOX product and scrap are more easily dissolved.	7.	C Enriched U feed material is required and hence SWU requirement is large; conversion and fabrication requirements are very large; not applicable to LMFBR fuel cycle.	7
	8	None	Wet		8. Wet blending is more uniform; coprecipitated MOX product and scrap are most easily dissolved.		8. MOX scrap recovery requirement is large.
	9	None	Wet + Dry		9.		9. Fabrication requirement is largest; two U feed materials are required; two blendings are required.

5.2 CONVERSION ALTERNATIVES

In addition to the oxalate precipitation technique for converting plutonium nitrate to PuO_2 described in Section 5.1, there are several alternative processes. Technology is available for either conversion of the plutonium nitrate to the oxide alone or as a mixed plutonium and uranium nitrate to the oxides.

5.2.1 Plutonium Nitrate Conversion

Methods available for plutonium nitrate solution conversion to the oxide are described as follows:

Peroxide. The plutonium is precipitated as a nonstoichiometric Pu_2O_7 using a 30% solution of H_2O_2. An advantage of this technique is that it does not require prior valence adjustment as both the hexavalent and trivalent plutonium are converted to the tetravalent state by the H_2O_2. The process is also flexible to feed concentration and flow and large concentrations of certain other metallic ions. Because iron catalyzes the decomposition of H_2O_2, the presence of iron and/or the reaction temperature must be closely controlled. Other solutions that form peroxides (U and Th) and strong peroxy complexes (Zr, Ce, Mn) and anionic impurities that form strong plutonium complexes adversely effect degree of precipitation. Along with these many disadvantages, the difficulty in converting Pu_2O_7 into a homogeneous PuO_2 product have not made this technique a competitive process for commercial application for plutonium nitrate conversion.

Plutonium Oxalate. The main advantages of this process are that a good product form and purity is easily obtained, it is flexible to feed variations, and the process has been demonstrated on a large scale. The disadvantages include the requirement for valence adjustment, a large number of process steps, and a relatively large part of the plutonium must be recycled for recovery.

Plutonium Sol Gel. In this process plutonium sols are prepared from $Pu(NO_3)_4$ solution in which the nitrate is continuously extracted with n-hexanol. A seeding technique is used to improve the sol crystallite sizes. These plutonium sols are very stable, denitrate rapidly (10-15 min.) at ∿200°C, and are insensitive to overheating. These sols can easily be used to prepare PuO_2 microspheres. Because the process is quite complicated and has not been demonstrated on an engineering scale, it has not received much attention for a commercial plutonium nitrate conversion process.

Direct Denitration. Direct conversion of plutonium nitrate solutions using fluidized-bed denitration has been successfully demonstrated with pilot-scale. The PuO_2 product is quite suitable for storage and transport. The merits of this process include its simplicity, ease in scale-up for larger systems, and does not require valence adjustment. However, the PuO_2 product from the process is dissolved with more difficulty than the products from the other processes.

5.2.2 Mixed Oxide Conversion

If mixed plutonium and uranium oxides are the desired end product, there are several important advantages to performing the conversion concurrently. The critical masses of plutonium are increased by more than a factor of 5 when the PuO_2 is diluted by 75% with depleted UO_2. Also, the total amount of scrap for recycle is generally less with the mixed processes.

The following are some candidate processes for mixed conversion.

Coprecipitation. In this process the uranium and plutonium nitrates are combined after plutonium valence adjustment and coprecipitation of uranium duirinate and plutonium hydroxide is accomplished with ammonia. The resultant precipitate is then filtered, usually on a vacuum drum filter, then washed and converted to the oxides in a continuous vibrating tube reactor. The process is somewhat continuous, is amenable to varying feed rates and compositions, and has been demonstrated on an engineering scale. The main disadvantages of the process are that it involves a large number of process steps, the scrap recycle requirements are high, and the PuO_2 product is finer than desired for shipment.

Sol Gel Conversion. In this process, UO_2 and PuO_2 sols are prepared separately, similar to that described for PuO_2 sols, and the UO_2 and PuO_2 sols are then blended and used to prepare mixed UO_2 - PuO_2 microspheres. Both the UO_2 and PuO_2 sols denitrate rapidly and form a uniform and desirable product. The process may also have some advantages with regard to shipping - handling and scrap recycle. However, the process is complicated, requires a large number of process steps, and has not been demonstrated on a large scale.

Direct Codenitration. This process is similar to that described earlier for the direct conversion of plutonium nitrate solutions using a fluidized-bed process to accomplish the denitration. The codenitration is accomplished by spraying a uranyl-plutonium nitrate solution into a heated fluidized bed of the oxide product. The product is a totally homogeneous granular mixture of UO_2-PuO_2 which is converted to UO_2-PuO_2 with hydrogen, or other gaseous reductant, also in a fluidized bed. The process has been demonstrated on a pilot-plant-scale, appears applicable over a wide range of uranium plutonium concentration, yields a homogeneous product, and is easily scaled to larger equipment. The main disadvantages of the process are the second step needed for UO_3-UO_2 conversion and close process control is needed to maintain a satisfactory product. The product from this process is generally more difficult to dissolve than the products from the other processes.

6. PROCESS MODELING AND SIMULATION

This section presents a survey of the available literature on transient characteristics of LWR Fuel reprocessing units. Included are papers presenting experimental data, process and control models, and methods of control. These papers reference other works which may also be of interest.

6.1 LITERATURE REVIEW

Papers dealing with liquid-liquid extractors are in abundance. These are reviewed in Section 6.1.1. Other process equipment such as filters, dryer-calciners, digesters, and grinders appear less frequently and are usually control oriented. They are reviewed in subsequent sections.

Several text books are of general interest in modeling chemical processes. References 23, 24, and 25 appear particularly suitable in this respect. Many of the models developed in Reference 23 were programmed as subroutines. Some of these may be directly useful, but the author's simple and practical approach to modeling is probably his main contribution.

6.1.1 Liquid-Liquid Extraction

Chemical processing to achieve separation of plutonium and uranium from each other and from waste products is an important step in fuel reprocessing. Separation is accomplished through countercurrent liquid-liquid extraction systems containing immisible liquids in environments which are both chemically harsh and radioactive. The chemical environment is selected to promote mass transfer of most of one or more constituents in the original phase. Subsequent separation of phases separates the constituents.

The degree of separation attainable depends upon the differences in distribution coefficients (defined as ratio of concentrations of a given constituent in the two phases under equilibrium conditions) of the materials to be separated. The distribution coefficient in turn may depend upon the oxidation state of the solute ions, the presence of complexing agents, or upon other elements of the chemical environment in each phase (26). Separation efficiencies seldom reach the maximum attainable due to imperfect contacting between phases. The rate of mass transfer between phases depends upon the amount of contact surface between phases, the concentrations of material in the two phases, and the mass transfer coefficient (27). In general, mass transfer rates increase with increasing contact surface and increasing concentration differences between phases but the functional dependences are not generally known.

The extraction system of interest for separation of uranium and plutonium is the pulsed perforated plate column. Pulsation not only provides the necessary mixing function but also aids phase separation. There is also evidence that it promotes back mixing of the continuous phase (28 pp. 259-263) which is undesirable since it tends to decrease the driving force (concentration gradient) for mass transfer.

A complete simulation of pulsed columns for purposes of control or material accountability requires a means of predicting concentration profiles as a function of time in response to adjustable parameters such as input phase flow rates and concentrations, and in addition, pulsing frequency and amplitude. An interesting and practical treatment of pulsed column hydrodynamics which allows prediction of the effect of pulse frequency and amplitude upon concentration profiles is given in Reference 29. It also provides a quantitative expression for estimating back flow of the continuous phase.

Reference 26 provides a detailed formulation of material balances for a pulsed column utilized in partitioning uranium and plutonium. The material balances account for reaction chemistry within each phase and expressions are given for determining distribution coefficients and reaction rate coefficients. While pulsing characterisitcs were neglected, holdup dynamics were assumed important and were calculated assuming proportionability between holdup and pseudo flow rates between model stages. The use of pseudo flow rates in this work (also described in Reference 30) is similar to the treatment in Reference 31 which deals with a mixer-settler extractor for separating the rare earths. Both Reference 26 and 30 were nonlinear control oriented simulations concerned with manipulation of aqueous flow rate as a means of controlling column behavior.

A recent article (32) presents a general review of the underlying theory of liquid-liquid extraction and also presents a survey of the equipment. The article includes an extensive bibliography. This article does not address the transient response of the processes nor model development, but is of general interest.

A computer code SEPHIS (Solvent Extraction Processes Having Interacting Solutes) developed by W. S. Groenier (33) has been widely used for simulating countercurrent liquid-liquid extraction processes. This report presents the general development and resulting computer program. The original application involved a dilute-Purex flowsheet proposed for recovery of spent LMFBR fuels. It has since been modified by S. B. Watson and R. H. Rainey (34) who indicate other users. Included in Reference 34 is a discussion of how to apply SEPHIS to practical solvent extraction processes, the updated version of the code, and a set of user input instructions.

A report, Reference 35, describes the liquid-liquid extraction pilot plant at General Atomic Company in San Diego. The report discusses the application of the Acid-Thorex process on input feeds representative of those from HTGR fuels. This report does not present models or transient responses, but illustrates a valuable location of equipment upon which experiments could be devised. These experiments could concentrate on the transient response and be used to validate models.

Reference 36 presents the results of a study simulating holdup dynamics to provide a better understanding of the operating characteristics. As a result, the investigators were able to design an online measurement and control system that improved unit capacity by 15%. The paper summarizes the material balance equations used. Comparison between the simulation and the extractor showed good agreement.

A good review of dynamic simulation of liquid-liquid extraction performed by various investigators to 1969 is presented by Pollack and Johnson (37). They review the various approaches to process modeling and conclude that since "no work on the dynamics of center feed columns with internal or external reflux has been attempted" the application of previous studies to commercial columns is difficult.

Mills and Bell (38) present results of their work to develop the transient response of a series of mixer settlers. The paper references the computer codes SIMTEX and QUANTEX. The description of their model is not presented. Some transient responses are shown to step changes in feed flowrate. This article does not discuss holdup. The intent was to develop control setpoints.

A paper by Burton and Mills (39) describes some early work in the United Kingdom dealing with computer program SIMTEX (Simulation of Tributyl Phosphate Extraction Plants). The program was adapted to evaluate flowsheets for countercurrent extraction of uranium-plutonium fuels in aqueous nitric acid with a dilute solution of tributyl phosphate in odorless kerosene. Transient response is not discussed although the paper implies development in this area is to follow. The work by Milles, et al., in the U.K. should be investigated further.

Reference 40 presents an outline of a model of a liquid-liquid extraction column. Transient results obtained with the aid of a 3-inch diameter, 20-foot high column are compared to the model. The authors state "the resulting simulations indicated that the models based on assumptions of non-equilibrium and nonuniform mixing could be used to predict steady state times quite well. The simulation results, when compared with the experimental data, showed that these models whould have definite utility in describing extraction columns in process control computer simulations of equipment systems". The models are not directly applicable to material control but again the approach is relevant.

Reference 41 presents the results of dynamic tests on a 3/4 inch diameter glass column with two or three plants. The dynamic results are expressed in terms of amplitude ratio and phase angle. The authors suggest that the work was exploratory and was intentionally limited to a few plates because a continuous method of chemical analysis was not available for studying the output. This paper is not particularly related to material control but provides background information.

Reference 42 discusses chemistry and use of hydroxylamine in plutonium extraction at La Hague. The paper indicates several factors affecting efficiencies and presents experimental data. The authors suggest two plutonium concentration and purification flow sheets. Modeling is not discussed.

A detailed listing of the continuity equation describing the mass transfer in a two-phase continuous-countercurrent extractor is given in Reference 43. The paper addresses the transient response to a prescribed set of boundary conditions.

Reference 44 presents the development of a microscopic space and time dependent hydrodynamic model of a stirred reactor. The objective was to determine the sampling location providing the best estimates of bulk properties in batch and semibatch reactors. The model was based upon distributed material balances and includes reaction kinetics. The solution for the 120 nonlinear differential equation set was obtained utilizing IBM's Continuous System Modeling Program (CSMP).

Reference 45 presents the development of a mathematical model of a multistage mixer-settler, the so-called Cadman-Hsu model. The model is developed from instantaneous overall and component mass balances and results in a set of nonlinear differential equations. The equations are linearized and summerized in matrix notation. An example is presented in which a control system is designed. Comparisons to actual extractors are not given. Reference 46 discusses the application of the Cadman-Hsu model on a copper extractor. The author suggests that a less complex model compares favorably when the chemical kinetics are fast.

Reference 47 presents the results of experimentation with a multistage mixer-settler. Models are not presented. The data presented could be useful in developing models of liquid-liquid extraction columns.

Reference 48 presents a description of instrumentation useful as in-line monitors and capable of providing continuous indication of changing process conditions. The authors state that the concepts presented should be adaptable to commercial scale processing facilities. Models of such equipment should accompany process models, particularly for those which would be utilized for control purposes, but also to allow comparison of simulation results with measurable experimental data.

The basic chemistry of plutonium is presented in Reference 49. Much of the data necessary for modeling the process will be found in this reference.

Reference 50 discusses a simple model of the hydrodynamics of a centrifugal extractor. The modeling assumptions are delineated and the resulting equations presented. The model is linearized and the authors subsequently emphasized the control study. Comparison with experimental data is included.

Todd and Davis (51) give an interesting discussion of centrifugal extractors. Experimental data is given on a pilot size unit and the paper discusses commercial size unit scaleup. Modeling is not discussed.

Schmieder, et al.(53), present a good discussion of a laboratory scale electrolytic mixer-settler. Experimental data are presented. Models are not discussed.

6.1.2 Driers-Calciners

A few papers are reviewed that discuss the modeling of rotary kilns. None are directly applicable as they deal with different materials but the modeling approaches are relevant.

A. Marritius, et al.(53), present a detailed steady state model development of a kiln. The equations developed could be generalized to establish a dynamic model. The paper reviews other kiln models. The process involved aluminum oxide but the modeling approach is applicable to other materials. The author points out that "although rotary kilns are used in many chemical processes, the math modeling represents a difficult and incompletely solved problem."

Reference 54 discusses a microscopic dynamic model of a cement kiln. It presents a very detailed account of model techniques with comparisons to test data. The model contains at least three partial differential equations for energy balance and 12 partial differential equations for various material balances, as well as at least 15 other algebraic relationships. It contains good detailed discussion of the dynamics of a kiln.

A dynamic model of a rotary cement kiln is presented in Reference 55. A summary of the equations and data required by the model is tabulated. A good example of the equations required to model a kiln is given. The authors report good agreement with test data.

Reference 56 discusses testing performed on a cement kiln to determine how to improve the control such that product output rate is smoothed. They concluded that the kiln should be treated as a multivariable control problem with digital control and that experimental studies of the process such as those reported can provide insight needed to develop models. Detailed model development is not presented but transient data for this process is given. One conclusion is of special interest: the amoung of CO_2 released is a good measurement of the calcining rate and could be used to improve kiln operation. A similar measurement in the plutonium conversion kiln may be important.

6.1.3 Grinders and Filters

Reference 57 discusses models of various processes which include grinding, filtering and drying. The model development is difficult to follow and the models are not presented. The authors suggest some interesting measurement instruments such as radiometric concentration meter, a noncontact conductance meter for measurements of solids in suspensions, and a high frequency capacitance humidity meter.

An adaptive transfer function model of a rotary filter was implemented in a digital computer to control a rotary filter (58). The discussion of the model is sketchy. Empirical relationships were used and given. The authors report success in improving the control of the filter but indicate problems with the computer and the measurements. They were successful in controlling the thickness of the filter cake, and in producing a slurry of a specified concentration and consistency at the highest possible rate.

6.1.4 Digester

The paper by Freedman (59) presents a control scheme for a wood chip digester. The approach employed a semi-empirical model of the process. The control was implemented by direct digital control (DDC) wherein the predictor model was updated periodically to conform to the changing process. Kalman filtering techniques were applied to correct the measurement signals.

6.1.5 General Approach to Process Control with a Digital Computer

A paper by Bornard and Badgerahanian (60) describes a unique 10-year study to investigate the control of distillation processes with a digital computer. They express belief that the results obtained "would have escaped us to a great extent if we had restricted ourselves to a simulation study alone." They suggest that the experimental pilot plant was essential to success. The paper suggests that they utilized the latest control techniques such as estimation, identification, adaptive, and multivariable control. They grant that "the modeling studies provided the user with a better quantitative knowlege of the process itself." Models are not presented in the paper. Several references to articles in French are made.

6.2 RELATIONSHIP OF PAST MODELING TO MATERIAL ACCOUNTABILITY

There has been development work in mathematically characterizing chemical process equipment. This work was usually directed towards developing methods for controlling the process. The assumptions made, such as holdup varying linearly with aqueous or organic flow rate, may be insufficient for models used in material accountability. The basic fundamental approaches can be carried over. The problem will be to accurately determine the model parameters after the model is developed. Validation of the models require extensive test and experimentation. Validation need not delay model development, but rather should follow it. As the development of the model proceeds, the basic experiments can be defined and planned. Also instrumentation can be specified.

As given in several critique papers, e.g., (61, 62, 63, 64) the single most difficult problem to overcome in process control and modeling is the lack of understanding of the process. The lack of observability of the state variables increases the problem. The problem is further compounded if linear models are employed when the process is expected to vary over a large range.

There are two basic approaches to model development. One is the use of conservation theorems coupled with the chemical kinetics to develop nonlinear dynamic relations with parameters empirically determined; Reference 26 is an example of this approach The other is somewhat of a black box approach. Output observations in response to pulse inputs are made on the process at various time slices and some technique such as Weiner filtering(65), or other recursive realization algorithms(66) used to establish linear, low-order dynamic relationships. Both approaches can be used as they complement each other. The first approach yeilds a more detailed understanding of the process, but involves more detailed development work. The second is experimental in nature and can be utilized to calibrate the first approach but only at the operating point at which the empirical model was determined.

Models of the instrumentation are required. In fact, as mentioned in Reference 65, some new methods of instrumentation must be developed. Models of instrumentation may be derived by applying conservation theorems. The dynamic characteristics are observed during calibration and testing and compared to the results of the model. The dynamic characteristics are compared to the frequency contents of the dominant modes in the process. If the instrument is very fast, on the order of 10 or more, in comparison to the dominate process modes, then the instrumentation model is reduced to an algebraic relationship. Instrumentation is a source of noise which must be evaluated and characterized with correlation functions. This data is included in the final steps of modeling.

6.3 APPROACH TO MODELING PLUTONIUM EXTRACTION TO ESTABLISH A REAL TIME RUNNING INVENTORY AND MATERIAL ACCOUNTING

One possible approach to the problem of real time material accountability and safeguards is suggested. The basic features are:

1. On line digital monitoring and alarm
2. Periodic tracer pulse calibration without shutdown of the process
3. Mathematical representation of the process in the digital monitor.

4. Development of instrumentation to observe the state of the process, in particular isotopic composition

The approach is not without problems. The question of accuracy and model uncertainty must be addressed. If these answers are negative, the model will not perform in a manner to allow material accounting. The approach is:

1. Develop a math model of the physical process using fundamental conservation theorems coupled with chemical kinetics and implement this model on an online digital computer.
2. Develop instrumentation to observe variables in the process and transmit them to the digital computer using multiplex techniques.
3. Develop an estimate of the state of the process by an appropriate technique such as Kalman filtering.
4. Compare the estimate of the state to the predicted state, and alarm the operator if a deviation is apparent, otherwise log the process characteristics.
5. Calibrate the digital math model periodically via tracer pulse techniques.
6. Perform a physical inventory to establish buildup of residue in the process.

To implement this approach will require the development of several software and hardware items. First, the process must be modeled. An approach similar to that in Reference 26 is recommended. The model must be validated. This validation is critical requiring experimentation and testing. An evaluation of the holdup of the process streams is a critical parameter to be established in these tests. An evaluation of the accuracy of material accounting will be established by this experimentation.

Instrumentation must be developed and characterized. The noise inherent in this equipment must be characterized and combined with model uncertainties. The drift of the instrumentation and of the process itself must be characterized preferably by experimentation. These characteristics should be modeled and built into the digital computer monitor. The relationship of the tracer pulse and accuracy of that techniuqe must be examined.

REFERENCES

1. "Barnwell Nuclear Fuel Plant - Separation Facility Final Safety Analysis Report", Allied General Nuclear Services, Barnwell, South Carolina (October 1973).

2. "Barnwell Nuclear Fuel Plant - Plutonium Product Facility Preliminary Safety Analysis Report," Allied General Nuclear Services, Barnwell, South Carolina (July 1974).

3. "Generic Environmental Statement Mixed Oxide Fuel", USAEC Report WASH-1327, United States Atomic Energy Commission, Washington, D. C., (1974).

4. "Assessment of Nuclear Fuel Reprocessing", DPST-75-448, E. I. DuPont de Memours and Co., Savannah River Laboratory (September 1975).

5. "Nuclear Fuel Recovery and Recycling Center-Preliminary Safety Analysis Report," Exxon Nuclear Company, Richland, Washington, (January 1976).

6. A. L. Ayers, "Safeguards in Reprocessing" Presented at IAEA International Symposium on the Safeguarding of Nuclear Materials, Vienna, Austria, October 20-24, 1975.

7. S. M. Stoller and R. B. Richards, "Reactor Handbook, Second Edition, Volume II Fuel Reprocessing," Interscience Publishers, Inc., New York, New York, (1961).

8. T. I. McSweeney, *et al.*, "Improved Material Accounting for Plutonium Processing Facilities and a ^{235}U-HTGR Fuel Fabrication Facility", Report prepared for the U.S. N.R.C. Special Safeguards Study. Battelle Pacific Northwest Laboratories (October 1975).

9. J. V. Panesko, "Effect of Process Controls on Sintered Density of Oxide." ARH-CD-300, Atlantic Richfield Hanford Company, Hanford, Washington, (April 1975)

10. C. J. Rodden, "Selected Measurements Methods for Plutonium and Uranium in the Nuclear Fuel Cycle", TID-7029 2nd Edition, Office of Information Services, United States Atomic Energy Commission.

11. R. G. Gutmacher, F. Stephens, K. Ernst, J. E. Harrar, J. Magistad, T. E. Shen, S. P. Turel, "Methods for the Accountability of Plutonium Nitrate Solutions", WASH-1282 Superintendent of Documents, U. S. Government Printing Office.

12. Criteria for Laboratory Accreditation,ASTM Standardizations News, (March 1976).

13. D. J. Rochon, "Laboratory Quality Control Program Standards and Referees", Atlantic Richfield Hardford Company ARH-9, (December 1, 1967).

14. G. C. Swanson, J. E. Rein, S. F. Marsh, G. R. Waterbury, "Preparations of Working Calibrations and Test Materials for Intra- and Interlaboratory Surveillance of Nuclear Materials Measurement Methods - Plutonium Nitrate Solution", Los Alamos Scientific Laboratory, LA-5627 (presently being revised).

15. IAEA Safeguards Technical Manual Part E Methods and Techniques IAEA-174 (1975).

16. E. E. Bain, Jr., et al, "An Evaluation of Real-Time Material Control and Accountability in a Model Mixed-Oxide Fuel Plant", SAI Report # SAI-75-648-LJ (Sept. 1975)

17. G. R. Bray, et al., "Material Control and Accounting for Plutonium Recycle Facilities" SAI Report # SAI-76-539-LJ (March 1976).

18. "In Situ Assay of Plutonium Residual Holdup" Regulatory Guide 5.23, USAEC-Directorate of Regulatory Standards (May 1974).

19. "Measurement of Plutonium in Processing Equipment at Kerr-McGee Plutonium Fuels Fabrication Facility", A Draft Report to the Director of Inspection and Enforcement of the USNRC, by the Division of Safeguards and Security of the U. S. ERDA, (June 1, 1976).

20. J. W. Tape, et al., "Total Room Holdup of Plutonium Measured with a Large-Area Neutron Detector", LASL Report LA-UR-76-1287 (June 1976).

21. A. A. Anderson, et al., "Hidden Inventory and Safety Considerations", Proceedings of INMM 1976 Meeting (June 1976).

22. C. H. Kindle, "In Situ Measurement of Residual Plutonium", ARCHO Report #ARH-SA-248 (June 1976).

23. Franks, R.G.E., "Modeling and Simulation in Chemical Engineering", Wiley Interscience, 1972.

24. Himmelblau, D.M. and K.B. Bischoff," Process Analysis and Simulation", Wiley, 1967.

25. Levenspiel, O., "Chemical Reactor Engineering", Wiley, 1972.

26. McCutcheon, E.B., "Simulation and Control Synthesis for a Pulse Column Separation System for Plutonium-Uranium Recovery", Ph.D. Thesis, Iowa State University, Ames, Iowa, 1975.

27. Wilburn, N.P. and W. L. Nicholson, "Nonlinear Model Determination of Contratration Profiles in Two-Phase Countercurrent Extractors", Hanford Lab Report No. HW-SA-3484, 1964.

28. Hanson, C., "Recent Advances in Liquid-Liquid Extraction," Pargamon Press, New York, New York, 1971.

29. DilLiddo, B.A. and T. J. Walsh, "Computer Simulation of Pulse Columns', Industrial and Engineering Chemistry, Volume 53, No. 10, October 1961.

30. McCutcheon, E. B., L.E. Burkhart and R. E. Felt, "Simulation and Control Synthesis of a Pulse Column Separation System for Plutonium-Uranium Recovery", Paper Presented at 1975 ANS Winter Meeting, November 1975.

31. Seeman, R. C., "Predictive Control of a Mixer-Settler Extractor Separating the Rare-Earths", Ph.D., Thesis, Iowa State University, Ames, Iowa, 1973.

32. Bailes, P.J., C. Hanson and M. A. Hughes, "Liquid-Liquid Extraction: The Process, the Equipment", Chemical Engineering, January 19, 1976.

33. Groenier, W. S., "Calculation of the Transient Behavior of a Dilute-Purex Solvent Extraction Process Having Application to the Reprocessing of LMFBR Fuels", ARNL-4746, April 1972.

34. Watson, S. B. and R. H. Rainey, "Modifications of the SEPHIS Computer Code for Calculating the Purex Solvent Extraction System" ORNL-TM-5123, December 1975.

35. Redick, G. W, "Solvent Extraction in HTGR Reprocessing Interim Development Report" General Atomic Report No. GA-A138-35, February 1976.

36. Ochiai, S., "Measurement, Control and Simulation of an Industrial Liquid-Liquid Extractor" IFAC 1975 paper 45.4.

37. Pollock, G. G. and A. I. Johnson, "The Dynamics of Extraction Processes, Part I. Introduction and Critical Review of Previous Work" Canadian Journal of Chemical Engineering, Vol. 74, October 1969.

38. Mills, A. L. and P. G. Bell, "Automatic Control and Response Characteristics of Small Scale Solvent Extraction Equipment" Proceedings of International Solvent Extraction Conference, April 1971.

39. Burton, W. R. and A. L. Mills, "Computer Calculation of Flowsheets for Reprocessing Nuclear Fuels", Nuclear Engineering, July 1963.

40. Biery, J. C. and D. R. Boylan, "Dynamic Simulation of a Liquid-Liquid Extraction Column", I&EC Fundamentals, Volume 2, No. 1, February 1963.

41. Watjen, J. W., and R. M. Hubbard, "The Dynamic Behavior of a Pulsed-Plate Extraction Column", A.I.Ch.E. Journal, September 1963.

42. Patigny, P., et. al., "Utilization of Hydroxylamine Nitrate for the Final Concentration and Purification of Plutonium in the Irradiated Fuel Reprocessing Factory at La Hauge", ISEC 1974.

43. Wilburn, N. P. and W. L. Nicholson, "Nonlinear Model Deliniation of Two-Phase Countercurrent Extractors", Hanford Atomic Products Report HW-SA-3484, 1964.

44. Waggoner, R. C. and G. K. Patterson, "Effect of Imperfect Mixing on the Persormance and Control of Batch and Semibatch Reactors", ISA Transactions, 1975.

45. Cadman, T. W. and C. K. Hsu, "Dynamics and Control of Multistage Liquid Extraction", Transaction of the Institute of Chemical Engineers, Volume 48, 1970.

46. Aly, G. S., "Dynamic Behaviour of Mixer Settlers: IV The Cadman-Hsu Model", ISEC, 1974.

47. Burns, P. E., and C. Hanson, "Tansient Response of a Multistage Mixer-Settler", British Chemical Engineering, (January 1967).

48. Jones, H. M. and R. Y. Lyon, "Use of In-Line Monitors for Process Control of the Purex Plant", Proceedings of The 20th Conference in Remote Systems Technology, 1972.

49. Cleveland, J. M., "The Chemistry of Plutonium", Gordon and Breach Science Publishers, New York, New York, 1970.

40. Boland, J. J. and J. M. Van Der Kaa, "Transient Hydrodynamic Behavior of a Centrifugal Extractor and Choice of a Non Interactive Control Scheme", IFAC, Paper 1.4, 1972.

51. Todd, D. B. and G. R. Davies, "Performance of Centrifugal Extractors", About 1968.

52. Schmieder, H., et al., "Electrolytic Methods for Application in the Purex Process", ISEC Proceedings, 1974.

53. Manitius, A., E. Kurcyusy, and W. Kawecki, "Mathematical Model of the Aluminum Oxide Rotary Kiln", Industrial Engineering Chemistry, Process Design Development, 1974.

54. Sprang, H. A. III, "A Dynamic Model of a Cement Kiln" Automation, 1972.

55. Lyons, J.W., et al., "Experimentation with a Wet-Process Rotary Cement Kiln Via the Analog Computer", I&EC Process Design and Development, (January, 1962).

56. Gale, W. M. and C. A. Stapleton, "Experimental Verification of the Correlation Between Calcining Rate and other Cement Kiln Variables", IFAC, Paper 3.2, 1972.

57. Egorov, S. V. et al., "The Developing of a System for Computer Industrial Process Control of Operation at a Potassium Dressing Plant", IFAC, 1975, Paper 60.5.

58. Hill, P. M. and W. A. Greener, "Computer Control of a Rotary Wash Filter", UKAC, 1971.

59. Freedman, B. G., "Model Reference Control for Batch Digesters", Chemical Engineering Practice, (April 1976).

60. Bornard, C. and L. Badgerahanian, "Antomatization of Distillation Processes from the Laboratory to the Industrial Plant", ASME, Paper 75-AUT-E, 1975.

61. Nooyoung, L. and V. W. Weekman, Jr., "Advanced Control Practice in the Chemical Process Industry: A View from Industry", A. I. Ch. E. Journal (Volume 22, No. 1), (January 1976).

62. Foss, A. S., "Critique of Chemical Process Control Theory", IEEE Transactions on Automatic Control, (December 1973).

63. Lefkowitz, I. "Systems Control of Chemical and Related Process Systems", IFAC 1975, Paper 38.2.

64. Sargent, R. W. H., "Optical Process Control", IFAC, 1975, Paper 38.3.

65. Zivi, S. M. and W. B. Siefeldt, "Temporal Response Methods for Dynamic Measurement of In-Process Inventory of Dissolved Nuclear Materials", Nuclear Materials Management, (Spring 1976).

66. Jayarman, K. and L. Lapidus, "Practical Realizations in Process Modeling", A. I. Ch.E., Journal (Volume 22, No. 2), (March 1976).

APPENDIX 1

COMPUTATIONAL METHOD FOR MATERIAL BALANCE UNCERTAINTIES

In this Appendix, the key parameters used for the computation of the material balance uncertainties are defined, and the computational methods are presented.

The method used to compute material balance uncertainty is described in detail in the PNL study.(8) The following equations were used.

Material Balance Uncertainty (2 sigma) = 2σ

where

$$\sigma^2 = \sum_i \sigma_i^2 \text{ (flow)} + \sum_j \sigma_j^2 \text{ (item inventory)} + \sum_k N_k \sigma_k^2 \text{ (bulk inventory)}.$$

$$\sigma_i^2\text{(flow)} = (m_i n_i F_i)^2 \left|(r_i^2/m_i n_i) + (p_i^2/m_i) + q_i^2\right|$$

i = index for each flow stream (feed, product, clean scrap, dirty scrap, liquid waste, solid waste, analytical samples, etc.).

F_i = average quantity of plutonium per batch or unit time period in the ith flow stream.

n_i = average number of batches transferred or unit time periods elapsed for the ith flow stream per calibration period for the plutonium assay instrumentation.

m_i = average number of calibration periods for the ith flow stream per accounting period.

$(m_i n_i F_i)$ = average quantity of plutonium transferred in the i^{th} flow stream per accounting period

r_i = one-sigma relative random measurement uncertainty.

$$r_i^2 = \frac{r_{wi}^2}{N_{wi}} + \frac{r_{si}^2}{N_{si}} + \frac{r_{ai}^2}{N_{ai}}$$

r_w = one-sigma relative random uncertainty associated with weight, volume or NDA measurement.

N_w = average number of weight, volume of NDA measurements per batch or unit time period.

r_s = one-sigma relative random uncertainty associated with sampling.

N_s = average number of samples taken per batch or unit time period.

r_a = one-sigma random uncertainty associated with laboratory analyses of plutonium concentration.

N_a = average number of times each sample is analyzed for its plutonium concentration.

p_i = one-sigma relative short-term systematic measurement uncertainty.

$$p_i^2 = p_{wi}^2 + p_{si}^2 + p_{ai}^2$$

p_w = one-sigma relative short-term uncertainty associated with weight, volume or NDA measurement.

p_s = one-sigma relative short-term uncertainty associated with sampling.

p_a = one-sigma relative short-term uncertainty associated with laboratory analysis of plutonium concentration.

q_i = one-sigma relative long-term systematic measurement uncertainty

$$q_i^2 = q_{wi}^2 + q_{si}^2 + q_{ai}^2$$

q_w, q_s and q_a are defined in the same manner as p_w, p_s and p_a.

$$\sigma_j^2(\text{item inventory}) = (C_{bj} + C_{ej}) I_j^2 r_j^2 + (C_{bj}^2 + C_{ej}^2) I_j^2 (p_j^2 + q_j^2)$$

j = index for the j^{th} type of item container

C_{bj} and C_{ej} = average number of j^{th} type of item containers, each with an average plutonium content of I_j, which are counted* at the beginning and end of an accounting period, respectively.

---

*Plutonium containers which remain sealed throughout an accounting period are not counted for purposes of determining material balance uncertainty.

r_j, p_j and q_j are defined in the same manner as r_i, p_i and q_i.

$$\sigma_k^2(\text{bulk inventory}) = (I_{bk}^2 + I_{ek}^2)r_k^2 + (FD)\ (I_{bk} - I_{ek})^2(p_k^2 + q_k^2)$$
$$+ (FS)\ (I_{bk}^2 + I_{ek}^2)\ (p_k^2 + q_k^2).$$

k = index for the k$^{\text{th}}$ type of bulk storage container.

I_{bk} and I_{ek} = average plutonium content of the k$^{\text{th}}$ type of bulk storage container at the beginning and end of an accounting period, respectively.

r_k, p_k and q_k are defined in the same manner as r_i, p_i and q_i.

FD (Fraction of Difference) and FS (Fraction of Sum) are fractions which add to unity. It is appropriate to use the difference term (i.e., FD = 1.0 and FS = 0) when the plutonium content of a bulk storage container is determined in a manner which suggests that systematic uncertainties tend to cancel so that the net uncertainty is determined by the difference between two measurements. Alternatively, it is appropriate to use the sum term (i.e., FD = 0 and FS = 1.0) when the nature of the measurements indicates that the systematic uncertainties are additive. For the PNL results(1) given below, the computations were performed with FD = 1.0 and FS = 0. The SAI results reported here were computed with FD = FS = 0.5.

N_k = number of the k$^{\text{th}}$ type of bulk storage containers.

APPENDIX 2

NEUTRON AND GAMMA RAY EMISSION RATES AND GAMMA ABSORPTION COEFFICIENTS RELATED TO HOLD-UP MEASUREMENTS

TABLE A2-1. IMPORTANT GAMMA RAY LINES

Isotope	Energy (keV)	Intensity photons/sec/g
^{235}U	185.72	4.3×10^{4}
^{238}U*	1001.10	1.0×10^{2}
	766.40	3.9×10^{1}
	852-883	1.2×10^{4}
^{238}Pu	Σ(320-430)**	1.3×10^{5}
	413.69	3.4×10^{4}
	375.02	3.6×10^{4}
	129.28	1.4×10^{5}
	51.63	4.7×10^{5}
^{240}Pu	45.23	3.8×10^{6}
^{241}Pu***	332.36	1.1×10^{6}
	207.98	2.0×10^{7}
	164.59	1.8×10^{6}
	148.60	7.5×10^{6}
^{241}Am	59.54	4.5×10^{10}
^{242}Pu	None	

*Radiation from the decay of ^{238}U daughter product ^{234m}Pa. Intensity given for equilibrium condition.

**This is defined loosely as the "385" keV complex of gamma ray lines.

***Radiation from the decay of ^{237}U which results from the α decay of ^{241}Pu. Intensity given for equilibrium condition.

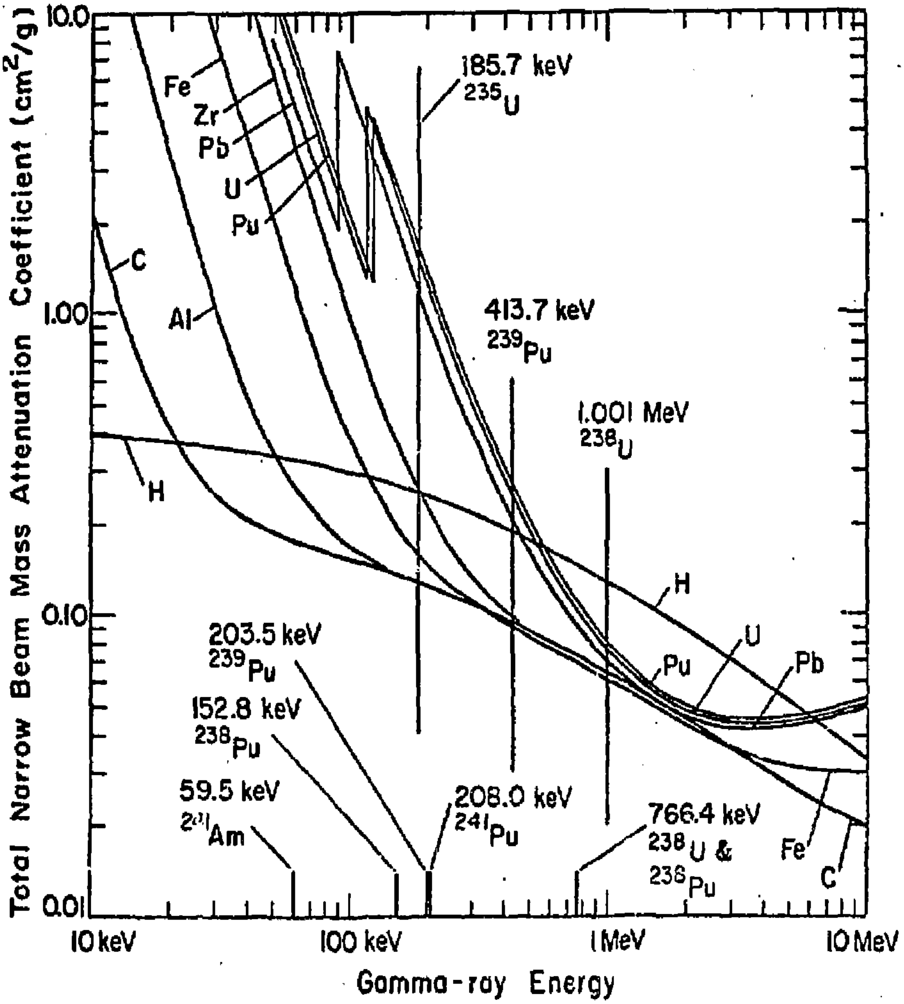


Figure A2-1. Mass Absorption Coefficients for Gamma Ray

TABLE A2-2. SPONTANEOUS FISSION OF FISSIONABLE ISOTOPES

Isotope	Sp. F. Half-Life (year)	$\bar{\nu}$	Yield Sp. F./sec/g
^{232}Th	1.4×10^{18}		4.1×10^{-5}
^{234}U	2.0×10^{16}	~2	2.8×10^{-3}
^{235}U	1.9×10^{17}	~2	2.96×10^{-4}
^{236}U	2×10^{16}	~2	2.8×10^{-3}
^{238}U	9.86×10^{15}	1.95	5.64×10^{-3}
^{238}Pu	4.9×10^{10}	2.26	1.1×10^{3}
^{239}Pu	5.5×10^{15}	2.2	1.0×10^{-2}
^{240}Pu	1.17×10^{11}	2.17	4.71×10^{2}
^{241}Pu	5.0×10^{15}	2.2	1.1×10^{-2}
^{242}Pu	6.8×10^{10}	2.16	8.0×10^{2}
^{241}Am	2×10^{14}	2.3	2.7×10^{-1}
^{252}Cf	86	3.8	6.14×10^{11}

TABLE A2-3. (α,n) YIELDS FROM OXIDES AND FLUORIDES

Material	Yield neut/sec/gram isotope
$^{234}UO_2$	~14
$^{234}UF_6$	5.8×10^{2}
$^{235}UF_6$	12.2×10^{-2}
$^{238}UF_6$	12.9×10^{-3}
$^{238}PuO_2$	1.4×10^{4}
$^{238}PuF_4$	2.1×10^{6}
$^{239}PuO_2$	45
$^{239}PuF_4$	4300
$^{240}PuC_2$	170
$^{240}PuF_4$	1.6×10^{4}
$^{241}PuO_2$	~10
$^{241}AmO_2$	3754
$^{242}PuO_2$	~10

ERRATA Sheet For
SAI-76-747-LJ
(Material Control For A Reprocessing Plant)

1. Page 38, 1st paragraph, line 11 reads

   with approximately 0.2% of the U and 4% of the Pu that entered - - -

   should read: with approximately 0.2% of the U and ≤1% of the Pu that entered - - -.

2. Page 62, 8th line from bottom of page reads

   4"x5" NaI with Pb filer (15 cm).

   should read: 4"x5" NaI with Pb filter - - -.

3. Page 64, last line reads

   0.5 $(NH_2)_2$ SO_4 solution is oxidized to the - - - - -

   should read: 0.5M H_2SO_4 solution is oxidized to the - - -.

4. Page 69, 2nd paragraph, 3rd line reads

   tory area. This includes radioactivity hot process - - - -

   should read: tory area. This includes radioactively hot process - - - - -

5. Page 73, last line reads

   operations and hopefully, lowering the material assessability

   should read: operations and hopefully, lowering the material accessibility - - -

6. Page 76, 3rd line from bottom, delete the word or

   should read: specific. Table 9 lists the NDA methods along with some

7. Page 79, 7th column, entitled Sensitivity Range, first entry should read (see Fig. 13).

8. Page 92, center callout reads

   LIQUID
   BETA

   should read LIQUID
   ALPHA

9. Page 95, 8th line down reads

   described. The section is concluded by summarizing the findings and recommendations.

   <u>should read</u>: described. The section is concluded by summarizing the fundings and recommendations.

   Page 95, last paragraph, 10th line, remove apostrophe after the work symbols.

   <u>should read</u>: The definition of the symbols appearing - - -

10. Page 101, 14th line reads

    is greatly enhanced. This is demonstrated in the measurement - - - - -

    <u>should read</u>: is greatly enhanced. This is demonstrated by the ratio of the measurement - - - - - - - -

    19th line add the word its

    <u>should read</u>: of the holdup measurement and the desirability of its improvement - - -

11. Page 110, Table title should read:

    MEAN FREE PATH ($1/\Sigma$(TOTAL), cm) FOR PHOTONS - - -

12. Page 114, 3rd line, should read:

    configuration makes the gamma measurements reliable because

    4th line from bottom of page - delete the a and add semicolon.

    <u>should read</u>: errors. The latter consists of:

13. Page 119, 3rd paragraph, 8th line reads

through the agreement between the two - - - - - - - - - - -

should read: though the agreement between the two - - - -

14. Page 122, 9th line reads

radiation attenuation and scattering factors; don't buy pipes,

should read: radiation attenuation and scattering factors; don't bury pipes,

15. Page 131, 2nd paragraph, 3rd line reads

and coprecipitation of uranium duirinate and plutonium - - - -

should read: and coprecipitation of ammonium diuranate and plutonium - - - - - - -