461
6-9-80

LA-8042, Vol. III

DR. 1291

MASTER

Materials Management in an Internationally Safeguarded Fuels Reprocessing Plant

University of California

LOS ALAMOS SCIENTIFIC LABORATORY
Post Office Box 1663 Los Alamos, New Mexico 87545

LA-8042, Vol. III
UC-15 and UC-83
Issued: April 1980

Materials Management in an Internationally Safeguarded Fuels Reprocessing Plant

E. A. Hakkila
A. L. Baker
D. D. Cobb
H. A. Dayem
R. J. Dietz
J. E. Foley
R. G. Gutmacher
J. T. Markin
H. O. Menlove
C. A. Ostenak
J. R. Phillips
T. D. Reilly
J. P. Shipley
D. B. Smith
C. C. Thomas, Jr.
W. J. Whitty
J. W. Barnes
J. E. Bennett*
A. L. Beyerlein*
L. E. Burkhart**
A. F. Cermak***
D. R. Engler****

*LASL Consultant. College of Engineering, Clemson University, Clemson, SC 29631.
**LASL Consultant. Program Director, Materials Chemistry, Iowa State University, 109 Metal Development, Ames, IA 50011.
***LASL Consultant. Allied-General Nuclear Services, P.O. Box 847, Barnwell, SC 29812.
****LASL Consultant. General Atomic Company, P.O. Box 81608, San Diego, CA 92138.

CONTENTS

APPENDIX A. AQUEOUS REPROCESSING AND CONVERSION TECHNOLOGY

APPENDIX B. THE REFERENCE FACILITIES

APPENDIX F. MODELING AND SIMULATION APPROACH

APPENDIX G. OPTIMIZATION OF MEASUREMENT CONTROL

APPENDIX H. ASPECTS OF THE INTERNATIONAL VERIFICATION PROBLEM

CONTENTS (cont)

CONTENTS (cont)

APPENDIX L. NEAR-REAL-TIME MEASUREMENT TECHNIQUES

APPENDIX M. ISOTOPIC CORRELATION TECHNIQUES

APPENDIX N. INSTRUMENTATION AVAILABLE TO IAEA INSPECTORS

APPENDIX O. INTEGRATION OF MATERIALS ACCOUNTING AND CONTAINMENT AND SURVEILLANCE

TABLES

TABLES (cont)

FIGURES

FIGURES (cont)

FIGURES (cont)

GLOSSARY

ACDA	Arms Control and Disarmament Agency
AGNS	Allied-General Nuclear Services
APAS	automated plutonium assay system
ASF	analytical services facility
BCF	Bonded Crucial Facility
BNFP	Barnwell Nuclear Fuels Plant
BWR	boiling water reactor
CPP	codecontamination-partitioning processes
CTBT	Comprehensive Test Ban Treaty
DES	Data Encryption Standard
DP	detection probability
d/p cells	differential pressure transmitters
DTY	downtime per year
FAP	false-alarm probability
FBR	fast breeder reactor
GA	General Atomic Company
HAF	high-activity feed
HAW	high-activity waste
HEU	high-enriched uranium
HLNCC	high-level neutron coincidence counter
HNO_3	nitric acid
ICPP	Idaho Chemical Processing Plant
ICT	isotopic correlation technique
IMLEs	inspector's maximum-likelihood estimates
ISS	inspector's sufficient statistic
JPDR-1	Japan Power Demonstration Reactor 1
KMP	key measurement point
LASL	Los Alamos Scientific Laboratory
LAW	low-activity waste
LLL	Lawrence Livermore Laboratory
LWR	light-water reactor
MBA	materials balance area
MMAS	materials measurement and accounting system
MOX	mixed oxide
MP	miss probability
MTBF	mean time before failure
MTTR	mean time to repair
MUF	material unaccounted for
MWd/MTHM	megawatt days per metric tonne of heavy metal
NBL	New Brunswick Laboratory
NBS	National Bureau of Standards
NDA	nondestructive assay
NM	nuclear material
NOCSIM	nitrate to oxide conversion simulation
OMLEs	operator's maximum-likelihood estimates
ORNL	Oak Ridge National Laboratory
PCCU	process-control coordination unit
PMS	process monitoring system

PNSL	plutonium nitrate storage and loadout
PPP	plutonium purification process
PPS	physical protection system
PWR	pressurized water reactor
RI	resonance integral
RSD	relative standard deviation
SAL	Safeguards Analytical Laboratory
SCS	safeguards computer system
SCU	safeguards coordination unit
SEPHIS	solvent extraction processes having interacting solutes
SGS	segmented gamma scanners
SLA	Sandia Laboratories, Albuquerque
S/R	shipper/receiver
SRL	Savannah River Laboratory
SRMs	standard reference materials
SRP	Savannah River Plant
TBP	tributyl phosphate
TCA	tricaprylamine
TCPP	Tokai codecontamination-partitioning processes
TDR	time-domain reflectometer
TN	thermal neutron
TPPP	Tokai plutonium purification process
TUPP	Tokai uranium purification process
UPAA	unit process accounting area
UPC	unit process controller
UPP	uranium purification process
USAEC	United States Atomic Energy Commission

Purex Process Identifiers

Contactors

A	extraction-scrub for U-Pu or Pu alone
B	U-Pu partition or Pu strip
C	U-Pu strip
D	extraction-scrub for Pu alone
H	preparation columns or streams

Stream

A	aqueous
F	feed
IS	intermediate scrub
O	organic
P	product containing Pu or Pu + U
R	raffinate (no appreciable U or Pu)
S	scrub
U	product containing only U
W	waste (no appreciable U or Pu)
X	extractant

MATERIALS MANAGEMENT IN AN INTERNATIONALLY SAFEGUARDED FUELS REPROCESSING PLANT

Volume III

by

E. A. Hakkila, A. L. Baker, D. D. Cobb, H. A. Dayem, R. J. Dietz,
J. E. Foley, R. G. Gutmacher, J. T. Markin, H. O. Menlove,
C. A. Ostenak, J. R. Phillips, T. D. Reilly, J. P. Shipley,
D. B. Smith, C. C. Thomas, Jr., and W. J. Whitty
LASL Safeguards Systems Staff

J. W. Barnes
LASL Engineering Staff (WX-4)

J. E. Bennett and A. L. Beyerlein
Clemson University

L. E. Burkhart
Iowa State University/DOE-Ames Laboratory

A. F. Cermak
Allied-General Nuclear Services

D. R. Engler
General Atomic Company

ABSTRACT

Supporting information required for the design, evaluation, and implementation of an improved materials accounting system for reprocessing-conversion facilities is included in the third volume (the Appendices) of this report. Appendices A, B, and C include the basic process chemistry, descriptions of the reference facilities, and recommendations for possible process and facility modifications for improved materials accounting. The operator's safeguards system structure is reviewed in App. D. Appendices E-I review the tools used in the design and effectiveness evaluation studies, including the mathematical basis for international verification of the system. Measurement methodologies are reviewed in App. J-N. Appendix O considers the problem of integrating materials accounting and containment and surveillance measures.

APPENDIX A

AQUEOUS REPROCESSING AND CONVERSION TECHNOLOGY

R. J. Dietz
LASL National Security Programs Office (DAD/SS)
E. A. Hakkila
LASL Safeguards Staff (Q-4)

The technical bases for recovering plutonium from uranium and fission products and converting the plutonium nitrate product to oxide were developed originally in connection with the weapons program. Reprocessing technology both for weapons and the peaceful nuclear reactor fuel cycle evolved to the Purex process, driven by economic considerations and the desire to minimize the volume of generated wastes. Transfer of conversion technology from weapons needs to the reactor fuel cycle is not necessarily straightforward because the properties desired for the final product differ.

The basic philosophy and historical evolution of reprocessing and conversion technology are reviewed briefly to show which process changes must be considered in safeguards systems design.

A. Evolution of Aqueous Reprocessing Technology

Nuclear fuel processing began in the US in the wartime atmosphere of the early 1940s when a laboratory separation process based on the coprecipitation of plutonium with bismuth phosphate and lanthanum fluoride was simply scaled up several orders of magnitude at the (then) Hanford Engineering Works. The inefficient and extravagant bismuth-phosphate process was superseded at Hanford in 1951 by the Redox process, based on the extractability of the higher oxidation states of plutonium and uranium in methyl-isobutyl-ketone (hexone) from concentrated aqueous-nitrate solutions. The advantage of Redox over the bismuth phosphate process was that both uranium and plutonium were recovered in a continuous industrial process rather than in a scaled-up, laboratory batch operation. The process produced large volumes of radioactive waste, caused largely by high nitrate concentrations required to drive the extraction. Aluminum nitrate was the salting agent. The solvent was also volatile and extremely flammable, and was degraded rapidly by radiation effects and the high nitrate concentrations necessary for extraction.

The Purex process corrected these deficiencies. The extractability of uranium and plutonium into tributyl phosphate (TBP) had been investigated since 1945 by the United

States Atomic Energy Commission (USAEC) and its contractors, and Purex plants at Savannah River and Hanford began operation in the mid-1950s. The designs were based on the extensive laboratory and pilot-plant studies of the previous decade and on the design, maintenance, and operating experience gained with predecessor radiochemical processes at Hanford. The Purex plants were extremely successful, and the process has been internationally pre-eminent ever since. The remote-maintenance philosophy originally developed at Hanford was extended to the Savannah River design. Purex technology also was used in the reprocessing plants at Windscale, which started operation in 1952 to recover plutonium for the British weapons program,[1] and at Marcoule, which started reprocessing plutonium for the French weapons program in 1958.

A modified Purex process is also used at the US government-owned Idaho Chemical Processing Plant (ICPP) at Idaho Falls to reprocess high-enriched uranium (HEU) fuels, even though the facility has no plutonium-handling capability. This rather unusual application illustrates both the flexibility and the dominant role of Purex in US processing philosophy. Here the process has been changed to direct the trace quantities of plutonium formed in highly enriched fuels to the high-level waste stream (first-cycle raffinate). The plant differs from the other government facilities in that direct (contact) rather than remote maintenance is used after suitable decontamination of the process equipment.

The primary reasons for considering deviations from classical Purex technology are a desire to (1) reduce liquid waste volumes and (2) minimize the degradation of the TBP by the fission-product radioactivity that results in poor efficiency in fission-product decontamination and increased discharge of uranium and plutonium to high-level wastes. The former reason was a consideration in the Morris design (see below); the latter reason becomes of increasing importance for reprocessing fuels with higher burnup such as fast breeder reactor (FBR), HEU, and (possibly) extended burnup light-water reactor (LWR). The Eurex plant at Saluggia, Italy, has investigated a flow sheet in which tricaprylamine (TCA) is used in place of TBP to reprocess enriched uranium fuel. Fission-product removal (excepting ruthenium) improved with the TCA flow sheet, but uranium recovery and plutonium removal decreased.[3]

The General Electric Morris plant was designed originally to use solvent extraction only for initial fission-product decontamination. Solvent extraction was replaced by anion exchange for purification of plutonium and by a fluoride volatility process for recovery of uranium.[2] Technical problems associated with radioactive waste handling prohibited operation of the plant. Fluoride volatility is being considered by the French for reprocessing fast breeder fuels.[4]

Plant maintenance philosophy is extremely important in the design of a safeguards system. It directly affects not only the accessibility of the nuclear material (NM) to diversion but also the measurement strategy and the access to instrumentation for calibration, repair, and replacement. Chemical separations plants have been operated under the entire spectrum of maintenance capability, ranging from no maintenance (British Windscale Plant) to remote maintenance (US production plants) to direct maintenance (Eurex plant at Saluggia). Most commercial plants have used a graded-maintenance approach based on the last two of these philosophies, with remote maintenance limited to the mechanically complex, highly radioactive, first stages of the process, as in the Allied-General Nuclear Services (AGNS) plant. Subsequent purification stages can be designed for no maintenance or for limited direct maintenance under extraordinary conditions of plant malfunction. With continued emphasis on lowered exposures for personnel, remote maintenance will receive increased attention in the design of facilities.

The type of contactor used in the Purex process is also of safeguards importance in that it influences the materials flow, the degree of recycle and backcycle, and the holdup of fissile material in the plant. In the interest of increased throughput and decreased solvent irradiation, mechanically driven contactors replaced convective or gravity-fed extraction columns rather early in the evolution of reprocessing plants. Pulsed columns were used at Hanford and Idaho Falls to enhance mixing of the aqueous and organic phases, while the Savannah River Plant (SRP), the French plant at LaHague, the Japanese pilot plant at Tokai (designed by the French), the early Windscale plant, and the German WAK plant were designed around the pump-mix mixer-settler that combines centrifugal mixing with convective disengagement.

More recently, SRP replaced first-stage mixer-settlers with centrifugal contactors that provide centrifugal phase separation, eliminating the large disengagement volumes previously required and thereby reducing both the holdup and the solvent damage. The duPont Company and Savannah River Laboratory (SRL) have developed a design integration study for a 3000-MT/yr reprocessing plant that uses multistage centrifugal contactors for the decontamination and the plutonium purification operations.[5] The contactor holdup volume is significantly less than for either pulsed columns or mixer-settlers, and it is estimated that a drain-down physical inventory could be performed in one 8-h shift.[6] These are important safeguards considerations.

A recent innovation in commercial plants is the French-designed Robatel multiple-stage centrifugal contactor. The contactor is characterized by small volumes and extremely short contact times, and combines multistage operation with forced mixing and separation in a single axial-flow device. A ten-stage Robatel is used as the first-cycle contactor in the AGNS plant. Subsequent AGNS contactors are pulsed columns, including the so-called Electropulse column in which partition is effected by reduction of plutonium (IV) to the trivalent state by electrically generated uranium (IV).

B. An Introduction to Plutonium Conversion

Nitrate conversion processes are essential for the commercial use of plutonium, either pure or coprocessed with a uranium diluent. The normal product of any spent-fuel separations plant based on the Purex process is a concentrated aqueous solution of plutonium nitrate, $Pu(NO_3)_4$. Industrial-scale use of plutonium is invariably restricted to the metal or oxide; therefore, efficient large-scale processes are necessary for converting the nitrate solution to oxide.

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

Traditionally, the conversion (or reconversion) process has been treated as the initial step of a fuel-fabrication or metal-reduction sequence, starting with the stored nitrate product of the separations plant. Various end uses require properties that differ greatly and in fact may conflict, leading to a profusion of conversion processes intended to optimize the properties required of the final product. Regulatory changes effective in the US in early 1978 and in Great Britain in 1979 prohibit the transportation of plutonium nitrate solutions; consequently, conversion became the final step in the separations process. This change introduces important changes in the objectives of the conversion process and the properties desired of the oxide product. Although high purity, including freedom from decay products, remains a goal in the oxide product, the decoupling of the conversion process from the end use of the product makes it impossible to provide the required purity, oxide powder morphology, ceramic activity, and chemical reactivity simultaneously with a single product-finishing step unless the separations plant is coupled directly and immediately to a specific fabrication sequence.

Peroxide precipitation, plutonium (III) and (IV) oxalate precipitation, direct denitration, the sol-gel process, and the Coprecal process all have been considered as methods for preparation of reactor-grade PuO_2 or $(U,Pu)O_2$. The precipitation and direct denitration methods were developed originally for PuO_2 separation and subsequent fluorination before reduction to the metal for weapons use; however, fuel-product requirements may differ from those where the oxide is only an intermediary in metal preparation. The process chemistry is reviewed in Ref. 2, and in more detail in the referenced reports.

1. The Coprecal Process. In the Coprecal process a blended plutonium and uranyl nitrate solution is injected into a strong ammonium hydroxide solution.[7] The precipitate is then calcined in a fluidized bed to obtain blended $(U,Pu)O_2$ for fabrication into mixed oxide (MOX) fuel.

The method cannot be applied to preparing oxide containing >40% PuO_2 and is interesting because it involves no reprocessing of pure plutonium solutions and compounds. The uranium dilution prevents diversion of practically pure plutonium as nitrate solution or oxide. The liquid blending and homogeneous precipitation eliminate powder blending during fuel fabrication. All recycle material would be dissolved relatively simply. However, the method provides no decontamination.

The Coprecal process is being tested in a pilot-plant operation at the General Electric Vallecitos Nuclear Center at Pleasanton, California. Varying process parameters can produce a wide range of product characteristics. More data will be needed to prove the feasibility of the Coprecal process.

2. The Sol-Gel Process. The sol-gel process,[8-11] designed to produce dense microspheres of oxide for reactor fuel fabrication, consists of three steps. The sol step produces a colloidal polymer of tetravalent plutonium that can be kept in suspension for extended periods. The gel step produces beads by removing water from the sol. In the third step, the beads are calcined at 1000-1200°C to produce a high-density, uniform product. Processing can be terminated at any of the three stages; thus, the gel beads can be transported and then can be redissolved readily if additional processing or blending is required at the fuel fabrication facility. One major advantage claimed for the sol-gel process is that high-density beads can be fabricated remotely into MOX fuel.

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

3. Direct Denitration. In direct denitration, the feed solution is evaporated to drive off residual nitric acid (HNO_3) and water and to decompose the nitrate salt, producing an oxide. No reagents are added, and only gases are formed during drying and calcining. The equipment is simple and should be relatively easy to operate and maintain remotely. Fluidized-bed calcination,[12] continuous calcination in a screw calciner,[13] and batch processing[14] all have been proposed. Nozzle-plugging and difficulties in obtaining a reactive oxide could be problems for fluidized-bed calcination.[15] Production experience in denitrating to UO_3 indicates that particle size could be affected by temperature, thermal shocking, sulfate content, and jet grinding.[16]

Although direct denitration has not been proved by actual production experience, it shows enough promise for EXXON Nuclear Company to propose its use for conversion.[17] Their system is designed to convert 320 kg of plutonium per day to PuO_2 in four horizontal-trough screw calciners. The process also is being considered by the Japanese.

4. Peroxide Precipitation. Peroxide precipitation[18,19] is the most effective of the three precipitation processes for decontaminating plutonium from other cations. However, the initial feed for the conversion plant may be pure enough so that this additional purification is unnecessary. Also, recycling is simplified because H_2O_2 is the only reagent added and it is readily destroyed by heating.

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

With sufficient precautions the use of peroxide precipitation has been effective in past nuclear reprocessing and was selected as the conversion process for the Hot Experimental Facility being designed by the ORNL.[20]

5. Plutonium (IV) Oxalate Precipitation. Advantages of the plutonium (IV) oxalate method[21-24] include the stability of the solids and solutions and the relatively high decontamination levels. Plutonium (IV) oxalate precipitation has been well developed for both batch and continuous plutonium metal processing at Hanford.[22,24] The relatively large plutonium losses to the filtrate can be minimized by recycling and recovery.

Disadvantages include the need for careful control of processing parameters. Successful precipitation and subsequent filtration of plutonium (IV) oxalate at Los Alamos Scientific Laboratory (LASL) required stringent control of the mixing rate, temperature, and acid concentration.[25] The number of reagents and the recycle streams, as with plutonium (III), is large. If calcination is incomplete, carbon impurity remains in the product.

The plutonium (IV) oxalate method was chosen for the AGNS facility primarily because of experience at Hanford and Rocky Flats and the data available on PuO_2 formed by calcining the plutonium (IV) oxalate.[21] The AGNS design is flexible, and a reduction step could be added before precipitation to convert to the plutonium (III) method. The method also is being considered for the large Japanese reprocessing plants.

6. Plutonium (III) Oxalate Precipitation. Plutonium (III) oxalate precipitation in some respects is similar to plutonium (IV) oxalate precipitation with the major exception that the former requires a reduction step preceding precipitation. The precipitate is coarser and settles and filters faster than the precipitate obtained from the plutonium (IV) process; hence, the process is easier to control.

In initial studies on precipitation of trivalent plutonium with oxalic acid, HI was used as a reductant and led to severe equipment corrosion. In more recent work, ascorbic acid with hydrazine or hydroxylamine with sulfamic acid was used as a reductant, and interest in the process has revived. After plutonium reduction, oxalic acid is added to produce a precipitate that settles rapidly and can be filtered easily. Precipitation conditions such as the rate of oxalate addition and temperature are not critical for the plutonium (III) process. Plutonium losses to the filtrate are low, and most impurities are removed. The precipitate can be washed, heated in a flow of dry air to remove most of the water, and then calcined in air to form oxide.

Plutonium (III) oxalate precipitation, followed by calcination and dissolution, has been used to concentrate solvent-extraction product solutions. At LASL, plutonium is dissolved, then precipitated as plutonium (III) oxalate in converting plutonium metal to oxide for fast-reactor fuel studies.[26] The oxide formed by calcining this precipitate has been used in test MOX fuel elements without further calcining or sintering. Successful plant-scale use of the plutonium (III) oxalate process in both batch and semicontinuous modes has been reported.[27] The sizes of individual particles and agglomerates of the product PuO_2 are changed by changing the rate of precipitant mixing with the feed solution, altering concentrations, and regulating the temperature.

SRL and SRP chose the plutonium (III) oxalate process for conceptual design studies[28,29] and their design was selected as the reference for this study. It involves relatively simple, easy to maintain equipment similar to that used previously for the large-scale precipitation of plutonium solutions. The precipitate is filterable, and particle size can be varied to accommodate a variety of product requirements.

REFERENCES

1. Hon. Mr. Justice Parker, "The Windscale Inquiry," report presented to the Secretary of State for the Environment, Her Majesty's Stationery Office, London (January 26, 1978).

2. W. P. Bebbington, "The Processing of Nuclear Fuels," Sci. Am. 235, 30-41 (1976).

3. S. Cao, H. Dworschak, G. Rolandi, and R. Simonetta, "Italian Experience with Pilot Reprocessing Plants," in Nuclear Power and Its Fuel Cycle (International Atomic Energy Agency, Vienna, 1977), Vol. 3, pp. 547-559.

4. J. Sauteron, M. Bourgeois, J. Couture, and P. Roblin, "Technologie du Retraitement des Combustibles des Reacteurs Rapides," in Nuclear Power and Its Fuel Cycle (International Atomic Energy Agency, Vienna, 1977), Vol. 3, pp. 633-646.

5. J. Ergel, Savannah River Laboratory, personal communication, November 1978.

6. J. Ergel, Savannah River Laboratory, personal communication, March 1979.

7. Savannah River Plant document DPSTD-AFCT-77-10-TL (November 1977).

8. M. H. Lloyd and O. K. Tallent, "A New Solvent Extraction Process for Preparing PuO_2 Sols," Nucl. Technol. 18, 205-215 (1973).

9. M. H. Lloyd and R. G. Haire, "A Sol-Gel Process for Preparing Dense Forms of PuO_2," Nucl. Appl. 5, 114-122 (1968).

10. W. E. Sperry, "Sol-Gel Process for Plutonium Nitrate to Oxide Conversion," Rocky Flats Plant report RFP-2605 (May 1979).

11. M. Zifferero, "Sol-Gel Research and Development in Italy," Comitato Nazionale per l'Energia Nucleare report RT/CHI-(68)28 (May 1968).

12. K. R. Souply and D. H. Neal, "Fluid Bed Direct Denitration Process for Plutonium Nitrate to Oxide Conversion," Rocky Flats Plant report RFP-2600 (June 1977).

13. K. R. Souply and W. E. Sperry, "Screw Calciner Mechanical Direct Denitration Process for Plutonium Nitrate to Oxide Conversion," Rocky Flats Plant report RFP-2601 (October 1977).

14. K. R. Souply and W. E. Sperry, "Batch Direct Denitration Process for Plutonium Nitrate to Oxide Conversion," Rocky Flats Plant report RFP-2604 (July 1978).

15. W. J. Bjorklund and G. F. Offutt, "Fluidized Bed Denitration of Uranyl Nitrate," AICHE Symp. Series 123, 129 (1973).

16. N. M. Levitz, D. E. Grosvenor, S. Vogler, F. G. Teats, and N. Quattropani, "Continuous Conversion of Uranium/Plutonium Nitrates to Oxides," Nucl. Technol. 20, 60-63 (October 1973).

17. "Nuclear Fuel Recovery and Recycling Center, Preliminary Safety Analysis Report," Docket 50-564, EXXON Nuclear Company.

18. J. A. Leary, A. N. Morgan, and W. J. Maraman, "Plutonium Peroxide Precipitation," Ind. Eng. Chem. 51, 27-31 (1959).

19. K. R. Souply and W. E. Sperry, "Peroxide Precipitation and Calcination Process for Plutonium Nitrate to Oxide Conversion," Rocky Flats Plant report RFP-2606 (in press).

20. "Hot Experimental Facility Interim Design Report," Oak Ridge National Laboratory and Bechtel National Incorporated report ORNL/AFRP-78/6 (October 1978).

21. "Barnwell Nuclear Fuel Plant--Plutonium Product Facility Preliminary Safety Analysis Report," Docket 50-332, Allied General Nuclear Fuel Services, Barnwell, South Carolina (July 1974).

22. K. M. Harmon and W. H. Reas, "Conversion Chemistry of Plutonium Nitrate," Hanford Works report HW-49597A (April 1957).

23. R. M. Greinetz and D. H. Neal, "Plutonium (IV) Oxalate Precipitation and Calcination Process for Plutonium Nitrate to Oxide Conversion," Rocky Flats Plant report RFP-2602 (July 1978).

24. H. W. Crocker and H. H. Hopkins, Jr., "Conversion of Plutonium Nitrate to Plutonium Tetrafluoride via the Continuous Oxalate-Fluoride Method," Hanford Works report HW-SA-2880 (January 1963).

25. R. L. Nance, Los Alamos Scientific Laboratory, personal communication, December 1976.

26. W. J. Maraman, A. J. Beaumont, R. L. Nance, J. C. Roybal, and R. S. Winchester, "Purification and Concentration of Solvent Extracted Plutonium by Oxalate Precipitation," Los Alamos Scientific Laboratory report LA-1991 (January 1955).

27. Savannah River Laboratory Monthly Reports for the ^{238}Fuel Form Process (1972-1976).

28. Savannah River Laboratory document DPSTP-LWR-76-5 (November 1976).

29. Savannah River Plant document DPSP-LWR-77-29 (March 1977).

APPENDIX B

THE REFERENCE FACILITIES

E. A. Hakkila
LASL Safeguards Staff (Q-4)
J. W. Barnes
LASL Engineering Staff (WX-4)

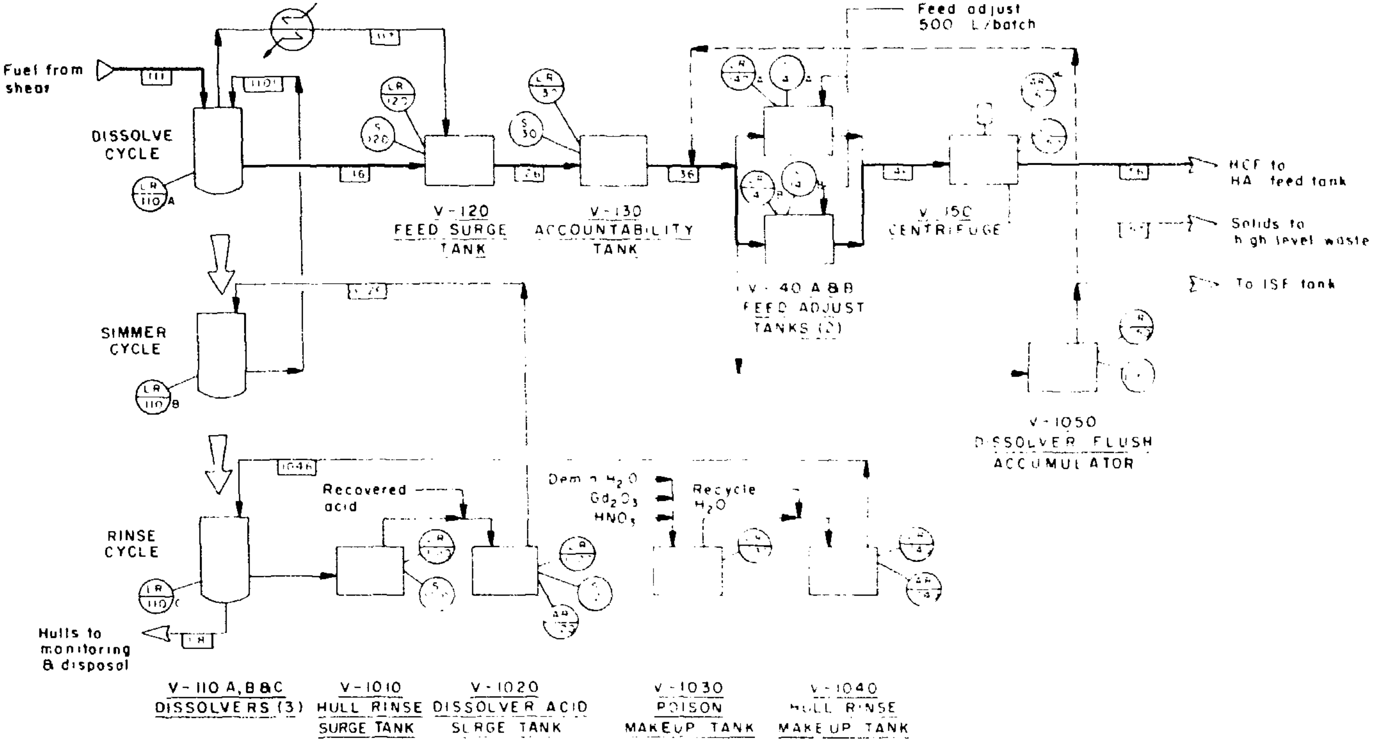
The AGNS 1500-MTHM/yr nuclear fuel reprocessing plant at Barnwell and a 30-MT/yr plutonium nitrate conversion plant (3000-MTHM equivalent) designed by SRP (but not built) were the reference facilities selected for the major portion of this study. They are typical of plants that will be required in 1990 to support a mature nuclear industry. In addition, the 210-MT/yr Tokai plant operated by the Japanese was studied to test advanced accountability concepts on a plant more typical of those in operation today. These facilities are described in more detail in this section.

A. Fuel Reprocessing

The reference fuel-reprocessing plant for this study is based on the AGNS chemical separations facility, and much of the description in the following section was obtained from the AGNS Final Safety Analysis Report.[1] Additional details on the process design are available in Ref. 2. The plant is designed to receive and process irradiated power-reactor fuel originally containing UO_2, or UO_2 and PuO_2, at 3.5% ^{235}U enrichment or 29 kg of fissile plutonium per tonne (or the equivalent) before irradiation. Fuel batches having an average burnup not exceeding 40 000 MWd/MTHM (megawatt days per metric tonne of heavy metal) are processed at rates up to 5 MTHM/day after a decay period of at least 160 days. Fuel with a greater fissile content (up to 5% ^{235}U or the equivalent in fissile-plutonium content) may be processed by decreasing the plant throughput.

The Barnwell Nuclear Fuels Plant (BNFP) uses the Purex recovery process, which has been in large-scale use for >25 yr and is used, with minor variations, by most of the reprocessing plants now operating or planned throughout the world, including the 1500-MT/yr plant to be built in Japan, the 1200-MT/yr add-on at Windscale, and the 1400-MT/yr plant planned for Gorleben, FRG.

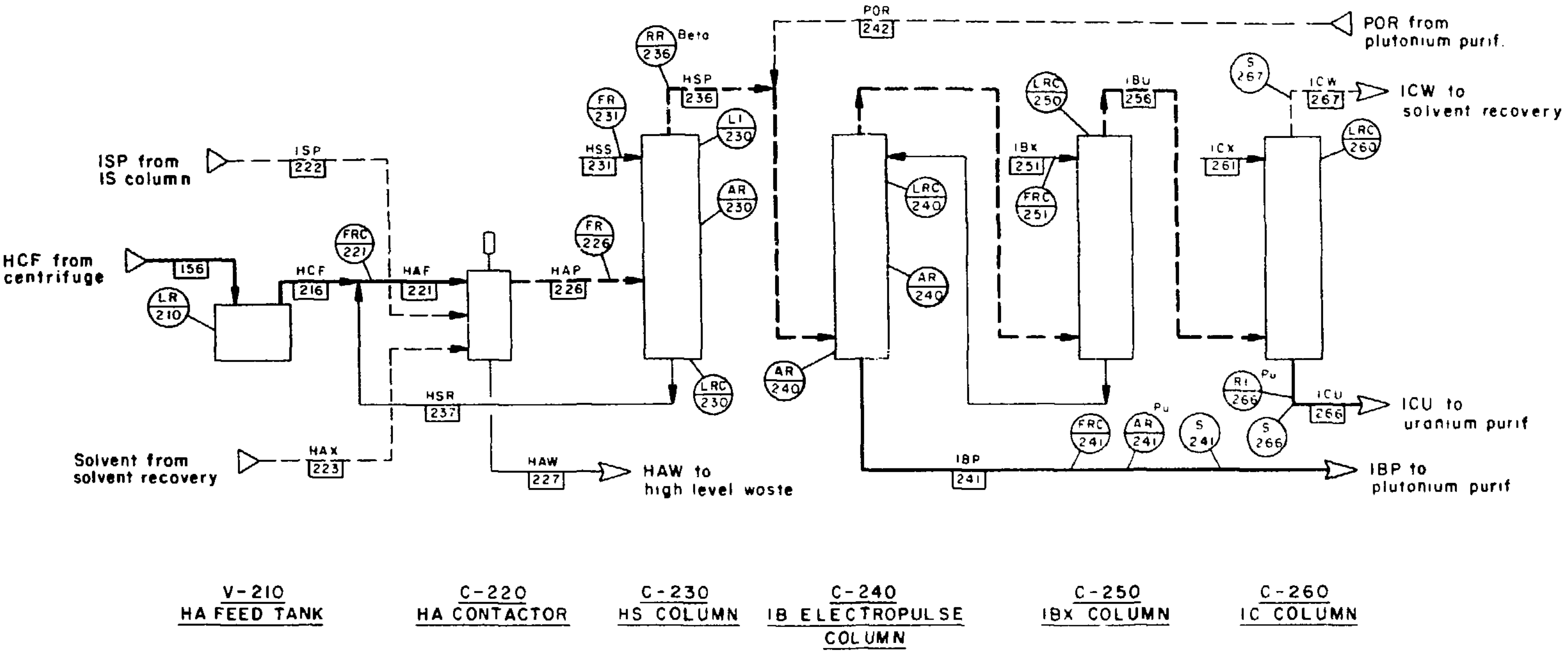
Process flows through the reference plant are shown in Figs. B-1 to B-7, and the basic process functions and chemistry involved are summarized in Table B-I. The spent-fuel assemblies arrive at the reprocessing facility by rail or truck and are held in a



Material balance

Stream no	111	116	117	118	126	136	146	156	157		1101	1026	1046
Service	Sheared Fuel	Dissolver Soln	[illegible]	[illegible]	[illegible]		HA Feed		[illegible]		[illegible]	[illegible]	[illegible]
Liters/batch		3000	250		3250	6500	7000	7000			2800	2800	1000
Kilograms/batch	1400			300									
Uranium, G/L	(1000 KG)	335			310	310	285	285					
Plutonium, G/L	(10 KG)	3.4		(<10G)	3.1	3.1	2.9	2.9	(<10G)				
Gadolinum, G/L		4.0			3.7	3.7	3.4	3.4			4.3	4.3	12
Fission prod, G/L		16			15	15	14						
HNO_3, M					3.0	3.0	2.5	2.5			8.0	8.0	0.5

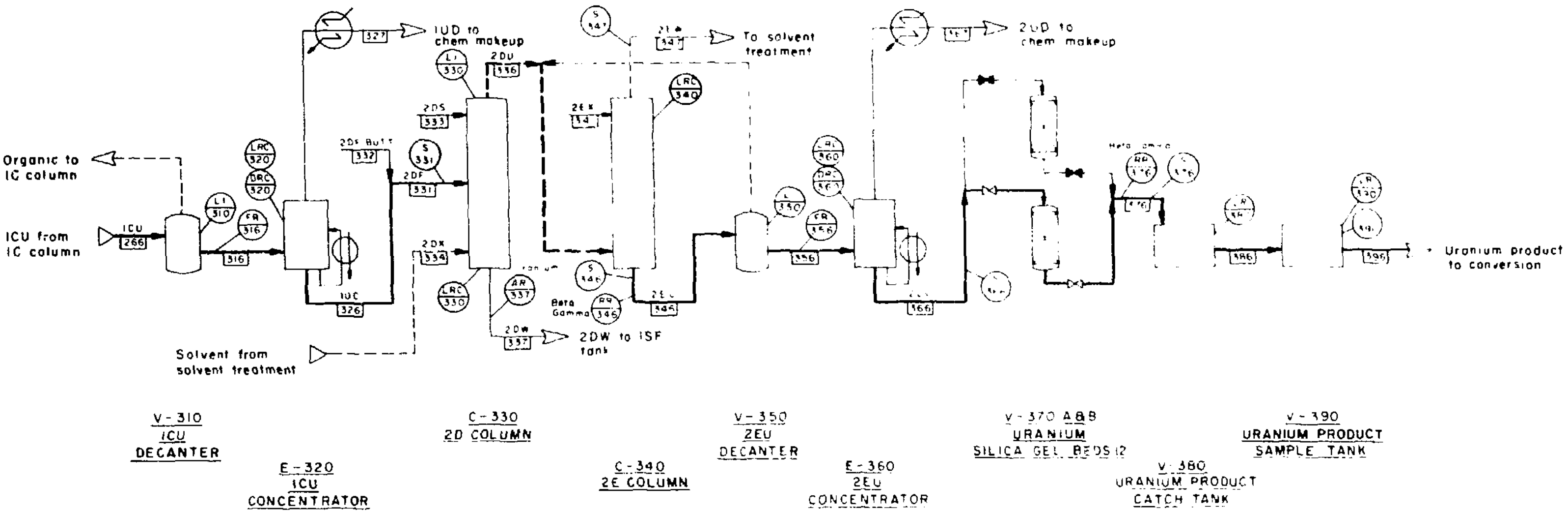
Fig. B-1. Fuel dissolution and feed preparation, 1500-MT/yr plant. (These values are not flow-sheet values of any existing reprocessing facility but represent typical values within reasonable ranges of a workable flow sheet.)



Material balance

Stream no.	216	221	222	223	226	227	231	236	237	241	242	251	256	261	266	267
Service	HCF	HAF	ISP	HAX	HAP	HAW	HSS	HSP	HSR	IBP	POR	IBX	IBU	ICX	ICU	ICW
Liters/h	730	1100	620	1835	2625	1030	350	2630	370	435	255	420	2865	3085	3195	2805
Kilograms/h	1150	1565	520	1505	2430	1160	380	2395	415	485	210	460	2605	3035	3420	2220
Uranium, G/L	285	195	~7		80	<1		80	~20	~10	~15		73		65	<0.1
Plutonium, G/L	2.9	2.2	0.1		0.8	$<10^{-1}$		0.8	~1	4.8						
Fission prod, G/L	14	10				1.0										
HNO_3, M	2.5	3.0	0.1		0.3		3.0		~4	2.6	0.06	2.9	0.2	0.01	0.2	

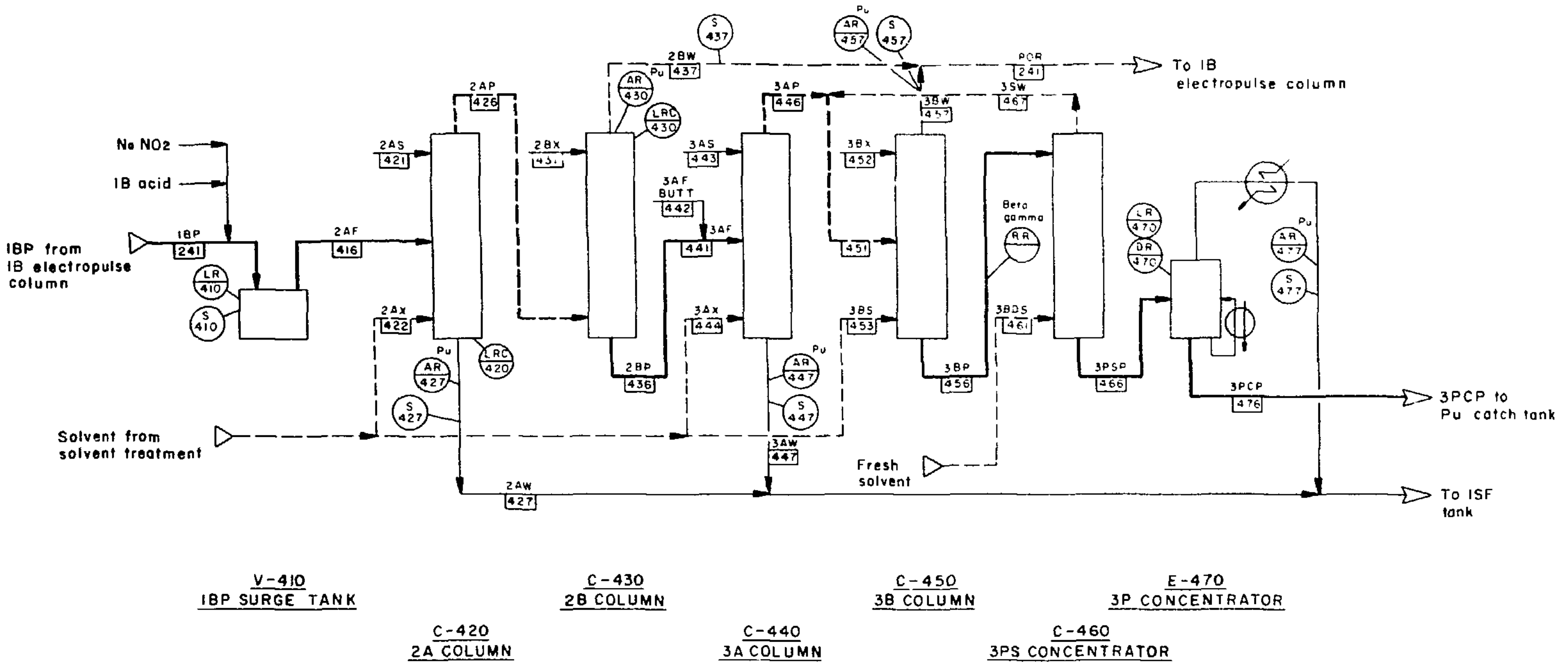
Fig. B-2. Uranium-plutonium codecontamination and partitioning, 1500-MT/yr plant. (These values are not flow-sheet values of any existing reprocessing facility but represent typical values within reasonable ranges of a workable flow sheet.)



Material balance

Stream no	316	326	327	331	332	333	334	336	337	341	346	347	366	367	386	396
Service	ICU	IUC	IUD	2DF	2DF BUTT	2DS	2DX	2DU	2DW	2EX	2EU	2EW	2UC	2UD	U PROD	U PROD
Liters/h	3195	625	2540	735	110	340	2205	2305	1000	2225	2330	2275	580	1710	560	560
Kilogram/h	3420	900	2520	140	340	340	1800	2145	1035	2190	2335	1800	940	1690	845	845
Uranium, G/L	65	335			285			90	5		90	0 1	360		370	370
Plutonium, G/L																
HNO_3, M	0 2	0 9	0 01	1 8	12 0	0 01			1 8		0 01		0 04	0 01	0 04	0 04

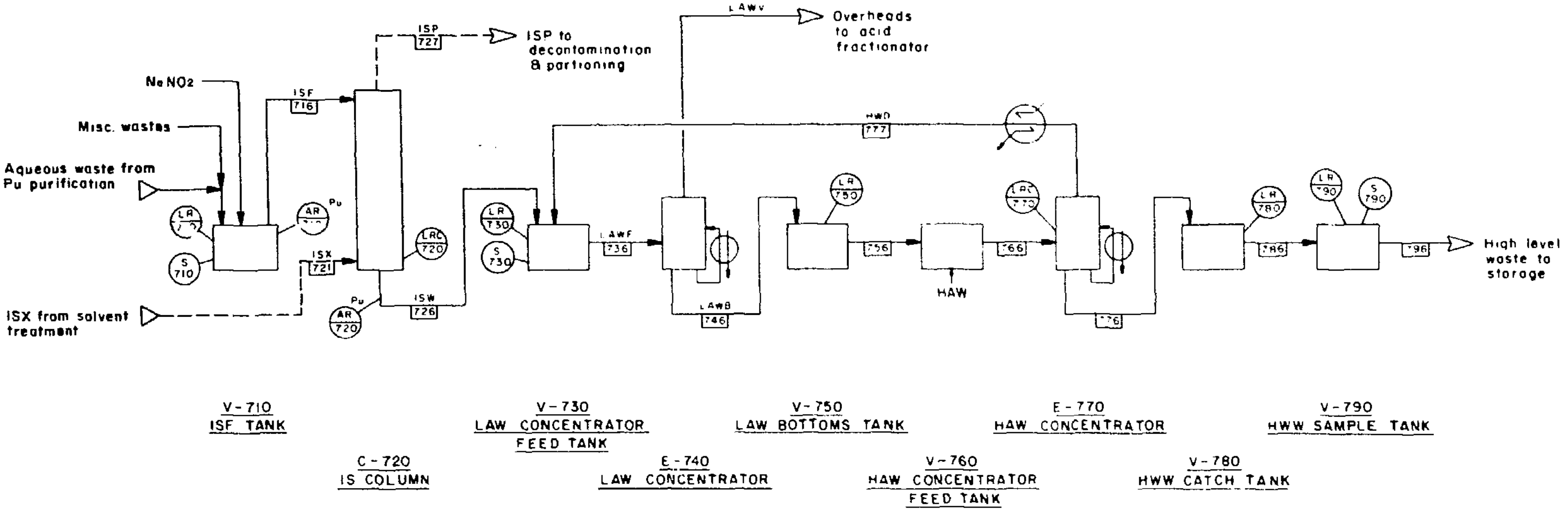
Fig. B-3. Uranium purification, 1500-MT/yr plant. (These values are not flow-sheet values of any existing reprocessing facility but represent typical values within reasonable ranges of a workable flow sheet.)



Material balance

Stream no.	416	421	422	426	427	431	436	437	441	442	443	444	446	447	451	452	453	456	457	461	466	467	476
Service	2AF	2AS	2AX	2AP	2AW	2BX	2BP	2BW	3AF	3AF BUTT	3AS	3AX	3AP	3AW	3BF	3BX	3BS	3BP	3BW	3BDS	3PSP	3SW	3PCP
Liters /h	435	60	145	150	500	130	135	150	180	45	35	85	85	215	86	35	20	35	105	1	35	1	8
Kilograms /h	490	60	120	130	540	130	140	125	200	60	35	70	75	230	76	35	15	40	90	1	40	1	10
Uranium, G/L	~10			~30			~30		~25				~50		~50				~40				
Plutonium, G/L	5			14	0.05		15	Tr	12				25	0.1	25			60			60		250
HNO_3, M	3.2	1.0		0.05	3.0	0.3	0.3	0.05	4.0	12.0	1.0		0.1	3.0	0.1	0.2		0.5	0.1		1.4		

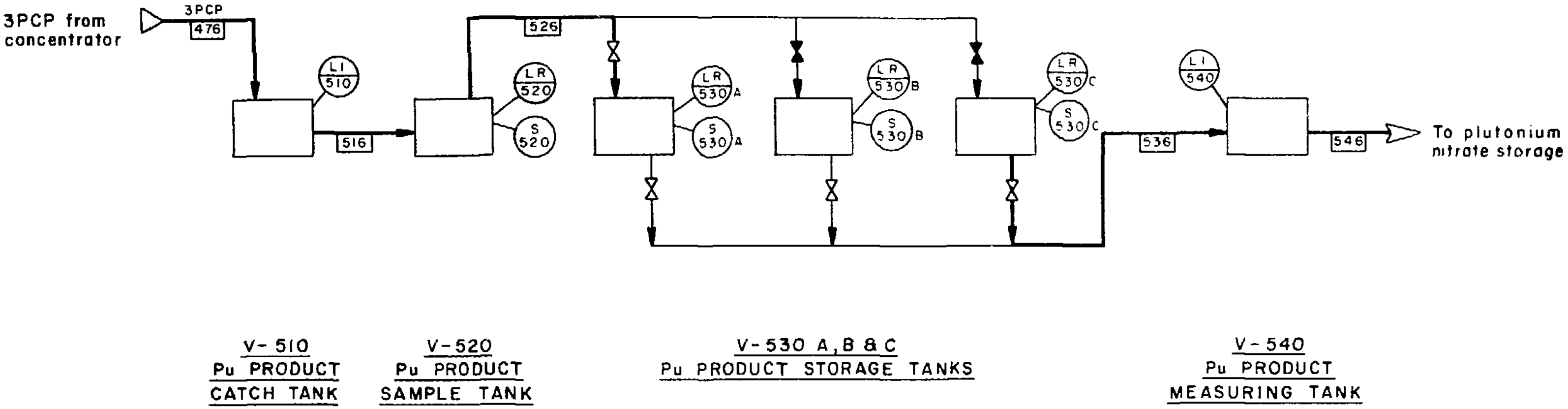
Fig. B-4. Plutonium purification, 1500-MT/yr plant. (These values are not flow-sheet values of any existing reprocessing facility but represent typical values within reasonable ranges of a workable flow sheet.)



Material balance

Stream no.	716	721	726	727	736	746	756	766	776	777	786	796
Stream name	ISF	ISX	ISW	ISP	LAWF	LAWB			HWW			HWW
Liters/h	1745	620	1730	620	4030	145			105			2700L/BA
Kilograms/h	1845	510	1835	520	4230	170			130			
Uranium, G/L	~ 2			~ 7					~ 5			~4
Plutonium, G/L	~ 0.02			0 1					~ 0 2			~ 0 1
Fission prod, G/L												63
HNO_3, M	2 2		2 2	0 1	1 8	7 6			6 7			4 3

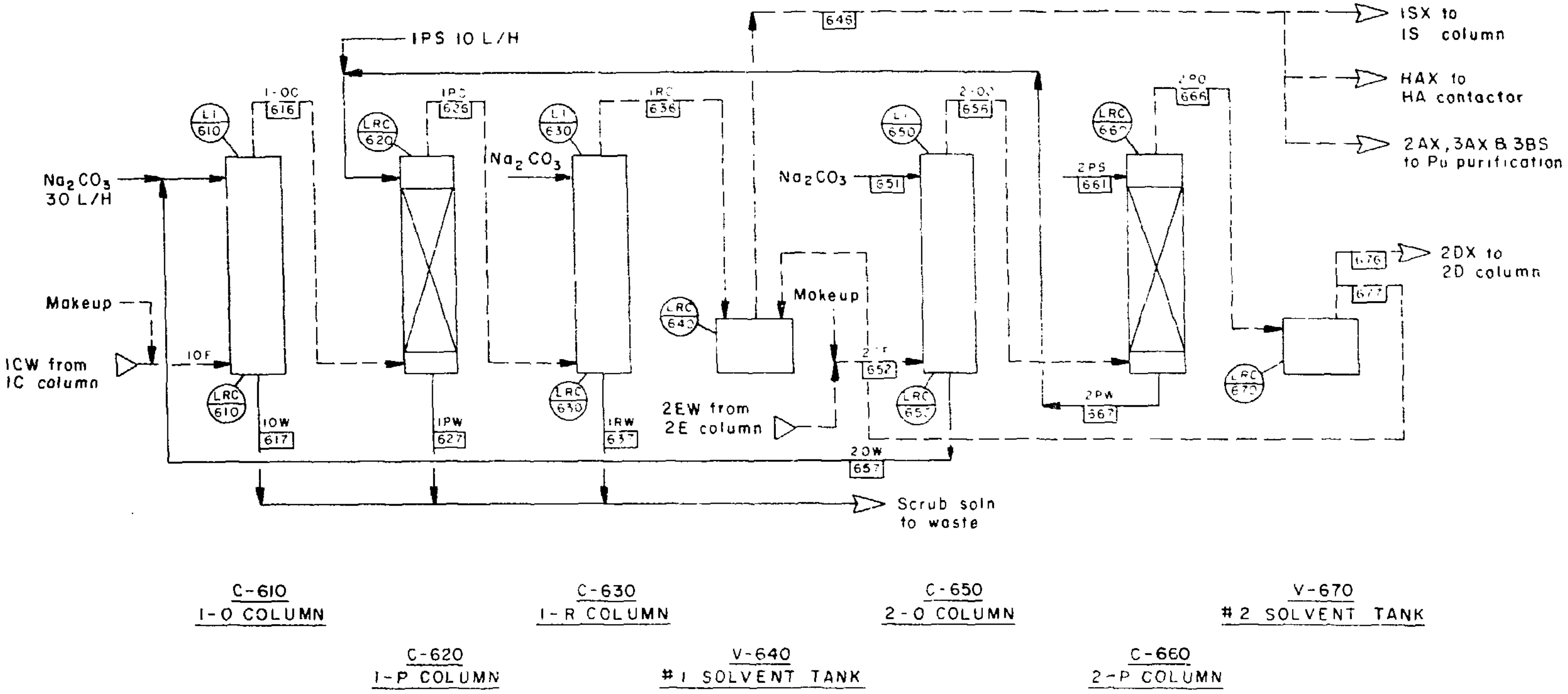
Fig. B-5. Aqueous waste treatment, 1500-MT/yr plant. (These values are not flow-sheet values of any existing reprocessing facility but represent typical values within reasonable ranges of a workable flow sheet.)



Material balance

Stream no.	476	516 – 546
Service	3PCP	Pu product
Liters/h	8	
Kilograms/h	10	
Plutonium, G/L	250	250
HNO_3, M		

Fig. B-6. Plutonium nitrate storage, 1500-MT/yr plant. (These values are not flow-sheet values of any existing reprocessing facility but represent typical values within reasonable ranges of a workable flow sheet.)



Material balance

Stream no.			616	617	626	627	631	636	637	646	651	652	656	657	661	666	667	676	677
Service	IOF	Na_2CO_3	1-00	IOW	IPO	IPW	Na_2CO_3	IRO	IRW		Na_2CO_3	2OF	2-00	2OW	2PS	2PO	2PW	2DX	Solvent Tk
Liters/h	2805	30	2805	50	2725	40	45	2745	45		20	2280	2280	20	35	2210	35	2205	5
Kilograms/h	2220	30	2220	50	2220	40	45	2220	45		20	1805	1805	20	35	1805	35	1800	5
Uranium, G/L	<0.1			~10								<0.1		~10					
Plutoniun, G/L																			
HNO_3, M					10^{-3}	0.05									0.15	10^{-3}	0.05		

Fig. B-7. Solvent treatment, 1500-MT/yr plant. (These values are not flow-sheet values of any existing reprocessing facility but represent typical values within reasonable ranges of a workable flow sheet.)

TABLE B-I

SUMMARY OF PROCESS FUNCTIONS AND CHEMICAL REACTIONS

Process Step	Function and Principal Chemical Reactions
Cask receiving and handling	Receipt and preparation of shipping cask for unloading.
Fuel storage and transfer	Storage of fuel elements until dissolution.
Shear	Preparation of fuel for dissolution.
Dissolution and feed preparation	Conversion of the fuel to a liquid solution. $3UO_2 + 8HNO_3 \xrightarrow{<8\ \underline{M}} 3UO_2(NO_3)_2 + 4H_2O + 2NO$ $UO_2 + 4HNO_3 \xrightarrow{>8\ \underline{M}} UO_2(NO_3)_2 + 2H_2O + 2NO_2$ Fission-product oxides + $HNO_3 \rightarrow FP(NO_3) + H_2O$ $PuO_2 + 4HNO_3 \rightarrow Pu(NO_3)_4 + 2H_2O$ $NO + 2HNO_3 \xrightarrow{>8\ \underline{M}} 3NO_2 + H_2O$
Solid-waste handling and storage	Disposal of undissolved cladding hulls
Codecontamination and partition cycle:	
Extraction	Separation of the plutonium and uranium from the bulk of the fission products into the organic-solvent phase $UO^{++}_{2(aq)} + 2NO^{-}_{3(aq)} + 2TBP_{(o)} \rightarrow [UO_2(NO_3)_2 \cdot 2TBP]_{(o)}$ $Pu^{+4}_{(aq)} + 4NO^{-}_{3(aq)} + 2TBP_{(o)} \rightarrow [Pu(NO_3)_4 \cdot 2TBP]_{(o)}$

TABLE B-I (cont)

SUMMARY OF PROCESS FUNCTIONS AND CHEMICAL REACTIONS

Process Step	Function and Principal Chemical Reactions
Partitioning (reduction of plutonium)	Separation of plutonium from uranium. (Plutonium is stripped into an aqueous solution of HNO_3 and hydrazine. Plutonium is electrochemically reduced to drive equilibrium to the aqueous phase. Hydrazine stabilizes the trivalent plutonium by scavenging nitrous acid. A small fraction of the uranium is also stripped into the aqueous solution and reduced to U(IV), which reduces the plutonium.) $[Pu(NO_3)_4 \cdot 2TBP]_{(o)} \rightarrow Pu^{+4}_{(aq)} + 4NO^-_{3(aq)} + 2TBP_{(o)}$ $[UO_2(NO_3)_2 \cdot 2TBP]_{(o)} \rightarrow UO^{++}_{2(aq)} + 2NO^-_{3(aq)} + 2TBP_{(o)}$ $Pu^{+4}_{(aq)} + 1e^- \rightarrow Pu^{+3}_{(aq)}$ $UO^{++}_{2(aq)} + 2e^- + 4H^+ \rightarrow U^{+4}_{(aq)} + 2H_2O$ $U^{+4}_{(aq)} + 2Pu^{+4}_{(aq)} + 2H_2O \rightarrow UO_2^{++}\ 2Pu^{+3} + 4H^+$ $N_2H_4 + 2HNO_2 \rightarrow N_2 + N_2O + 3H_2O$
Uranium stripping	Uranium is stripped into a very dilute solution of HNO_3. $[UO_2(NO_3)_2 \cdot 2TBP]_{(o)} \rightarrow UO^{++}_{2(aq)} + 2NO^-_{3(aq)} + 2TBP_{(o)}$
Second uranium cycle	Further decontamination of uranium from fission products. Repeat of uranium reactions for extracting and stripping.
Uranium silica gel, product storage	Final decontamination and disposition of uranium. $(\text{Fission product})_{(aq)} \rightarrow (\text{fission product})_{(\text{silica gel})}$
Second and third plutonium cycle, storage, and shipping:	Final decontamination and disposition of plutonium
Absorption	$N_2O_4\ (g) + H_2O \rightarrow HNO_3 + HNO_2$ Nitrite formation for U and Pu adjustment and hydrazine kill
Oxidation	$Pu^{+3} + NO_2^- + 2H^+ \rightarrow Pu^{+4} + H_2O + NO$ $U^{+4} + 2NO_2^- \rightarrow UO_2^{+2} + 2NO$

TABLE B-I (cont)

SUMMARY OF PROCESS FUNCTIONS AND CHEMICAL REACTIONS

Process Step	Function and Principal Chemical Reactions
Extraction	$Pu^{+4}_{(aq)} + 4NO^-_{3(aq)} + 2TBP_{(o)} \rightarrow [Pu(NO_3)_4 \cdot 2TBP]_{(o)}$
Reduction and stripping	$N_2H_4 + 2HNO_2 \rightarrow N_2 + N_2O + 3\ H_2O$
	$2Pu^{+4} + 8NO_3^- + NH_2OH \cdot HNO_3 \rightarrow 2Pu^{+3} + \frac{1}{2}N_2O + \frac{1}{2}H_2O + 3H^+ + 9NO_3^-$
	$Pu^{+4} + 4NO_3^- + NH_2OH \cdot HNO_3 \rightarrow Pu^{+3} + \frac{1}{2}N_2 + H_2O + 2H^+ + 5NO_3^-$
Uranium extraction	$UO^{++}_{2(aq)} + 2NO^-_{3(aq)} + 2TBP_{(o)} \rightarrow [UO_2(NO_3)_2 \cdot 2TBP]_{(o)}$
Concentration	$3Pu^{+3}_{(60\ g/L)} + 4H^+ + NO_3^- \rightarrow 3Pu^{+4}_{(250\ g/L)} + NO + 2H_2O$
	$2N_2H_4 + 2HNO_3 \rightarrow N_2 + 5H_2O + N_2O$
No. 1 and No. 2 solvent systems:	Removal of degradation products and/or fission products from solvent.
Carbonate wash	$Na_2CO_3 + 2(C_4H_9)_2HPO_4 \rightarrow 2(C_4H_9)_2NaPO_4 + H_2CO_3$
	$2Na_2CO_3 + Zr(HPO_4)_2 \rightarrow 2Na_2(HPO_4) + Zr(CO_3)_2$
Liquid-waste treatment and storage:	
High-activity waste concentration	Reduction of high-activity waste volume for storage.
	1300 gal/MTU → 150 gal MTU
	$2\cdot4\ \underline{M}\ HNO_3 \rightarrow 6\ \underline{M}\ HNO_3$
	Sugar addition to form nitrite and suppress ruthenium volatility
	$C_{12}H_{22}O_{11} + 48HNO_3 \rightarrow 48NO_2 + 12CO_2 + 35H_2O$
Low-activity waste concentration	Decontamination of feed to acid recovery. Sugar addition to form nitrite and suppress ruthenium volatility.
	$C_{12}H_{22}O_{11} + 48HNO_3 \rightarrow 48NO_2 + 12CO_2 + 35H_2O$

TABLE B-I (cont)

SUMMARY OF PROCESS FUNCTIONS AND CHEMICAL REACTIONS

Process Step	Function and Principal Chemical Reactions
General purpose waste treatment and concentration	Oxalate destruction in the general purpose waste-concentrator feed tank
	$H_2C_2O_4 + H_2O_2 \rightarrow 2CO_2 + 2H_2O$
	$2KMnO_4 + 5H_2C_2O_4 + 6HNO_3 \rightarrow 2Mn(NO_3)_2 + 2KNO_3 + 10CO_2 + 8H_2O$
	$2KMnO_4 + 5H_2O_2 + 6HNO_3 \rightarrow 2Mn(NO_3)_2 + 5O_2 + 8H_2O + 2KNO_3$
	Reduction of intermediate-activity waste volume for storage
	1800 gal/MTU → 40 gal/MTU
Nitric-acid recovery and storage	Concentration and recycle of HNO_3
	2.2 $\underline{M}$ $HNO_3 \rightarrow$ 12 $\underline{M}$ HNO_3
Off-gas treatment:	
Iodine scrubbing	Removal of radioiodine from gaseous effluents
	$CH_3I_{(g)} \rightarrow CH_3I_{(aq)}$
	$CH_3I_{(aq)} + Hg(NO_3)_2 \rightarrow HgI^+_{(aq)} + CH_3NO_3 + NO_3^-$
	$H_2O + I_2 + 5HNO_3 \rightarrow 2IO_3^- + 5HNO_2 + 2H^+$
	$Hg^{++} + 2IO_3^- \rightarrow Hg(IO_3)_2$
	$2HNO_3 + I_2 + 2Hg(NO_3)_2 \rightarrow HgI^+ + Hg(IO_3)^+ + H_2O + 4NO_2 + 2NO_3^-$
Silver-zeolite adsorption	$I_2 + 2Ag \rightarrow 2AgI$
	$2CH_3I + 2Ag \rightarrow 2AgI + C_2H_6$
NO_x absorption	$NO + \frac{1}{2}O_2 \rightarrow NO_2$
	$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$

fuel-storage pool while awaiting processing. The fuel elements are mechanically sheared into small pieces and the fuel is dissolved with a concentrated HNO_3 solution. Following dissolution, the solution is contacted with TBP in a normal paraffin hydrocarbon solvent (dodecane) to separate most of the fission products from the plutonium and uranium. The solvent stream containing the plutonium and uranium enters the partitioning step where the bulk of the uranium is separated from the plutonium. The uranium stream is further decontaminated with a solvent-extraction, aqueous-strip cycle and is then concentrated. The concentrated uranyl nitrate passes through silica-gel beds to remove traces of zirconium and niobium and is stored as the nitrate before conversion to UO_2 and UF_6 in a separate plant. The plutonium stream from the partitioning cycle is further purified in two separate solvent-extraction and acid-strip process steps. The plutonium nitrate solution is concentrated and stored awaiting conversion to plutonium oxide. Solvents used in the purification process are treated to remove fission products and degraded organics and are recycled to the plant. The wastes from the processes are treated in either liquid- or solid-waste processing systems. Off-gases are treated before being vented to the atmosphere. Each of the process steps is described in more detail below.

1. Fuel Receiving and Storage. The spent-fuel assemblies arrive in shielded casks via rail or truck. These massive casks, which may weigh up to 100 tonnes, provide radiation shielding to prevent excessive exposure to operations personnel, prevent release of hazardous materials should an accident occur during transit, and provide the means for dissipating the heat generated by the spent fuel. The massive casks and the specialized equipment necessary for transport and handling also provide incidental physical containment for their contents. The cask and vehicle are monitored for external contamination and are washed to remove surface dirt. The cask is removed from the vehicle to a test and decontamination pit to determine the fuel and cask coolant condition. A cask cool-down facility is used to reduce the cask and fuel temperature.

The cask is moved to the cask-unloading pool and is lowered to the bottom of the pool where the cask is opened and the fuel is removed. The fuel is moved to the fuel-storage pool and is stored until it is scheduled for reprocessing. An assembly may remain in the storage pool for 120 days or more for additional decay and cooling. The design capacity of the pool is 360 MTHM, or ∿3 months of plant throughput. The storage pool design allows for ∿25% of capacity for boiling water reactor (BWR) fuel and ∿75% for pressurized water reactor (PWR) fuel.

2. Dissolution and Feed Preparation. The fuel assemblies are transferred remotely from the fuel storage pool to the feed mechanism of the mechanical shear after a full batch or a lot belonging to a single customer has been accumulated. The fuel assemblies are chopped into small segments (~5 to 8 cm long) to expose the fuel to the acid solvent. The fuel segments fall into the dissolver containing a gadolinium nitrate neutron poison and hot 3 M to 8 M HNO_3, which dissolves the solid UO_2-PuO_2-fission-product matrix (Fig. B-1). The dissolver solution is transferred to the accountability tank before recovery and purification. The dissolver liquor is prepared by adding fresh HNO_3 to the hull-rinse liquor.

The solid hulls, consisting primarily of stainless steel or Zircaloy fuel-element hardware and tubing remnants, are rinsed and transferred to the solid-waste treatment process. These hulls may contain up to 0.1% of the total incoming uranium and plutonium. The cladding hulls are monitored for fissile material, packaged, and transferred to the solid-waste storage area.

Gases generated during dissolution are directed to the off-gas treatment system, which removes particulates, radioiodine, and nitrogen oxides. The dissolver solution is transferred to tanks for accountability sampling and final acid adjustment (2 M to 3 M HNO_3) before feeding to the solvent-extraction process.

3. Uranium-Plutonium Codecontamination and Partitioning. After acid adjustment the feed is clarified by a centrifuge, and the acid solution is contacted countercurrently in a multistage centrifugal contactor with an organic phase consisting of 30% TBP in dodecane (Fig. B-2). The organic solution preferentially extracts the tetravalent plutonium and hexavalent uranium, leaving ~95% of the fission products in the aqueous raffinate. The organic solution from the centrifugal contactor passes through a pulsed scrub column (HS column), where a 3 M aqueous HNO_3 solution removes fission products extracted in the centrifugal contactor. The scrub solution is recycled back to the centrifugal contactor. The aqueous solution leaving the centrifugal contactor contains 99.8% of the fission products and is sent to a high-level waste concentrator.

The organic solution from the HS column is joined by organic raffinates from the plutonium purification process (PPP) and passes through a partitioning column (1B electropulse column), where tetravalent plutonium is reduced to the less extractable trivalent state by electrochemically generated uranium (IV). This allows the plutonium to be reduced and simultaneously stripped into an aqueous HNO_3 solution containing hydrazine as a holding reductant within a single column. The organic solution passes through the 1BX scrub column to remove residual plutonium and then to the 1C column where the uranium is stripped into acidified water (∿0.01 M HNO_3).

4. Uranium Purification. The aqueous strip solution containing the uranium is concentrated from 0.3 M to 1.5 M uranium, adjusted with HNO_3 to ∿2.0 M, and is again preferentially extracted by 30% TBP-organic solution in a pulsed extraction column (2D column) (Fig. B-3). Before leaving the column, the organic solution is scrubbed with 0.01 M HNO_3 solution, which removes ruthenium and zirconium-niobium. Hydroxylamine nitrate and hydrazine are also added to the scrub solution to remove residual plutonium by chemical reduction to the less extractable trivalent state. Uranium is stripped from the organic solution in the 2E pulsed column using 0.01 M HNO_3. This aqueous solution is concentrated by evaporation from 0.4 M to 1.5 M uranium. Finally, the concentrated uranium solution is passed through one of two parallel silica-gel beds to remove residual traces of zirconium-niobium. Uranyl nitrate product solution is analyzed and transferred to the UF_6 facility for subsequent shipment as a nitrate solution or for conversion to UF_6.

5. Plutonium Purification. Plutonium in the aqueous stream leaving the 1B partitioning column is reoxidized to the extractable tetravalent state with dinitrogen tetroxide and is preferentially extracted into the TBP-organic solution in the pulsed extraction column (2A) of the second plutonium cycle (Fig. B-4). In the top portion of the column, the organic stream is scrubbed with 1.0 M HNO_3 solution to remove extracted ruthenium and zirconium-niobium. The organic stream passes through a strip column (2B), where tetravalent plutonium is transferred to an aqueous stream of dilute (0.3 M) HNO_3. The extraction-scrubbing sequence is repeated in a third plutonium cycle (3A and 3B columns) for further decontamination from fission products. To effect a higher plutonium product concentration, the plutonium is reduced in the third strip column (3B) by hydroxylamine nitrate to the strippable trivalent state. A TBP-organic scrub solution is added to remove residual uranium from the plutonium aqueous stream as it leaves the third strip column. The plutonium nitrate solution is washed with organic diluent to remove traces of TBP. Plutonium is concentrated from 60 to 250 g/L in a titanium concentrator. The plutonium nitrate product solution is sampled and analyzed and then is stored in geometrically favorable tanks for criticality safety in the plutonium nitrate storage and loadout (PNSL) area.

6. Liquid Wastes. The radioactive aqueous-waste streams from all the solvent extraction cycles are concentrated in the high-level or low-level waste concentrators (Fig. B-5). The acidic, high-level, concentrated bottoms are stored in cooled stainless-steel waste tanks, and the overheads are fed to the low-activity waste (LAW) concentrator. The overheads from the LAW concentrator are fed through a distillation column to recover most of the HNO_3 as a 12 $\underline{M}$ solution. The distillation column overheads (primarily water) are recycled as process water, or are sampled and released to the stack through a vaporizer. The 12 $\underline{M}$ recovered acid is used in process steps where the residual radioactivity can be tolerated. The bottoms from the LAW concentrator are fed to the high-activity waste concentrator. Two 300 000-gal high-level, liquid-waste, storage tanks provide sufficient capacity to store wastes for ~3 yr of normal plant operation.

Miscellaneous process waste streams containing salts and fission products (<1 Ci/L and no appreciable uranium or plutonium) are acidified and concentrated to ~50 Ci/L in a general-purpose concentrator. Concentrated wastes are stored as intermediate-level liquid waste in an uncooled, stainless-steel, intermediate-level waste tank. Each silica-gel bed is flushed once a week with oxalic acid and water, and the flush solution is transferred to the general-purpose concentrator. The condensed overheads from the general-purpose concentrator are vaporized to the stack.

Other miscellaneous low-level liquid-waste streams such as waste water from fuel storage, plant floor sumps, and cold chemicals are sent to a service concentrator where the water is evaporated and discharged to the stack. The concentrated solution is stored with the intermediate-level liquid waste.

7. Gaseous Wastes. Off-gases from the dissolver are scrubbed with circulating mercuric nitrate-HNO_3 solution to remove radioactive iodine, then are treated in an absorber to convert nitrogen oxides to HNO_3 suitable for recycling. The dissolver off-gas and vessel off-gas streams are combined and passed through a second iodine scrubber containing mercuric nitrate, then through iodine adsorption beds, and finally through high-efficiency filters before being released to the stack.

8. Solid Wastes. Waste solidification will be required in the future. Liquid wastes will be stored pending completion of a solid-waste conversion facility.

9. Plutonium Nitrate Storage. The $Pu(NO_3)_4$ product from the separations area is sampled, analyzed, and then transferred to a bank of forty-eight 880-L

criticality-safe $Pu(NO_3)_4$ slab tanks, where it will remain until conversion to PuO_2 (Fig. B-6). The plutonium nitrate storage area capacity is 8000 kg of plutonium, or ∿6 months normal plant throughput.

10. Uranium Product Storage. Uranyl nitrate solution from the separations plant is sampled and stored temporarily in the separations facility before transfer to longer term storage tanks at the UF_6 facility, where the nitrate is converted to UF_6 for enrichment feed. The storage capacity of the uranium product catch tank and uranium product sample tank is ∿1 day of plant throughput.

11. Solvent Treatment. Radioactive impurities and solvent degradation products are removed continuously from the organic solvent streams in two independent systems (Fig. B-7). Solvent treatment system No. 1 processes the solvent streams that have been exposed to high levels of radiation during the codecontamination and the plutonium recovery cycles. Segregating the solvent in this manner reduces cross-contamination of the final product uranium. Solvent treatment system No. 2 processes solvent that is subjected to low radiation exposure from the second uranium cycle. The feed for the 1-O column of the No. 1 solvent treatment system is received from the 1C column via the 1CW stream. The scrub stream to the 1-O column (the 1OS stream) is 0.2 $\underline{M}$ sodium carbonate, with a flow of ∿44 L/min. If process losses of uranium and plutonium in the 1OF are too high and the aqueous carbonate waste 1OW has a high uranium or plutonium content, the 1OW stream can be diverted to the carbonate diversion tank for recycle to the system. The solvent is further purified in the 1-P column (0.17 $\underline{M}$ HNO_3 wash) and the 1-R column (0.2 $\underline{M}$ sodium carbonate wash). The purified solvent is stored in the No. 1 solvent system feed tank for use in the 1S column, the HA contactor, and the 2A and 3A columns of the PPP.

The feed stream for the No. 2 solvent treatment system is received from the 2E column via the 2EW stream. The 2-O column scrub stream (2OS) is 0.2 $\underline{M}$ sodium carbonate. If the process losses of uranium in the 2OF are too high and the aqueous carbonate waste 2OW has a high uranium content, the 2OW can be diverted to the carbonate diversion tank for recycle to the system. The solvent is further purified in the 2P column by scrubbing with 0.16 $\underline{M}$ HNO_3. The purified solvent is stored in the No. 2 solvent system feed tank for use in the 2D column or for transfer to the No. 1 solvent system feed tank.

Fresh TBP can be added to both solvent system feed tanks to maintain its concentration at 30%. Aqueous wastes generated by the solvent treatment systems are sent to the general purpose concentrator feed tank where they are sampled before being concentrated. Following concentration, the waste is sent to the intermediate-level liquid waste storage facilities. Organic liquid wastes are incinerated.

12. Acid Recovery. Nitric acid used or produced in the process is purified and concentrated by multiple distillation for recycle to the process. Little, if any, uranium or plutonium should be contained in the recovered acid.

13. Heavy-Metal Recovery from Acid Streams. Uranium and plutonium in the aqueous streams from the 2D, 2A, and 3A columns and the 3P concentrator overheads are recovered in the 1S column. The solutions are collected in the 1SF tank and N_2O_4 is added to ensure that plutonium is in the tetravalent state. The solution is extracted in the 1S column with TBP from the No. 1 solvent system feed tank, and the organic stream containing uranium and plutonium is cycled to the HA contactor. The aqueous stream is transferred to the LAW concentrator feed tank.

B. Nitrate-to-Oxide Conversion

The reference nitrate-to-oxide conversion process for this study is based on a conceptual design developed by SRL and SRP.[3,4] Additional information on the process is available in Ref. 5. The design is based on precipitation and calcination of plutonium (III) oxalate. LASL and SRP have extensive experience with the process; it consistently produces a readily filterable precipitate with low losses, and it is controlled easily at room temperature.

The plant is designed to convert 100 kg/day of plutonium as the nitrate to plutonium oxide or, with a 50% availability factor, ~50 kg/day to match the output of the reprocessing plant. Conversion is performed in three parallel process lines, with a fourth line serving as a spare. Each line processes 2 kg of plutonium per batch, with a residence process time of ~6-7 h. Block diagrams of the conversion line are shown in Figs. B-8 and B-9. Material transfers, concentrations, and transfer frequencies are summarized in Table B-II.

Plutonium nitrate at a concentration of 250 g/L is transferred from the plutonium nitrate storage area to three 200-L receipt tanks. The plutonium is diluted to 30 g/L with ~3 $\underline{M}$ HNO_3. The feed is analyzed and then transferred in ~67-L batches to three valence adjustment tanks where hydrazine and ascorbic acid are added to reduce the plutonium to the trivalent state.

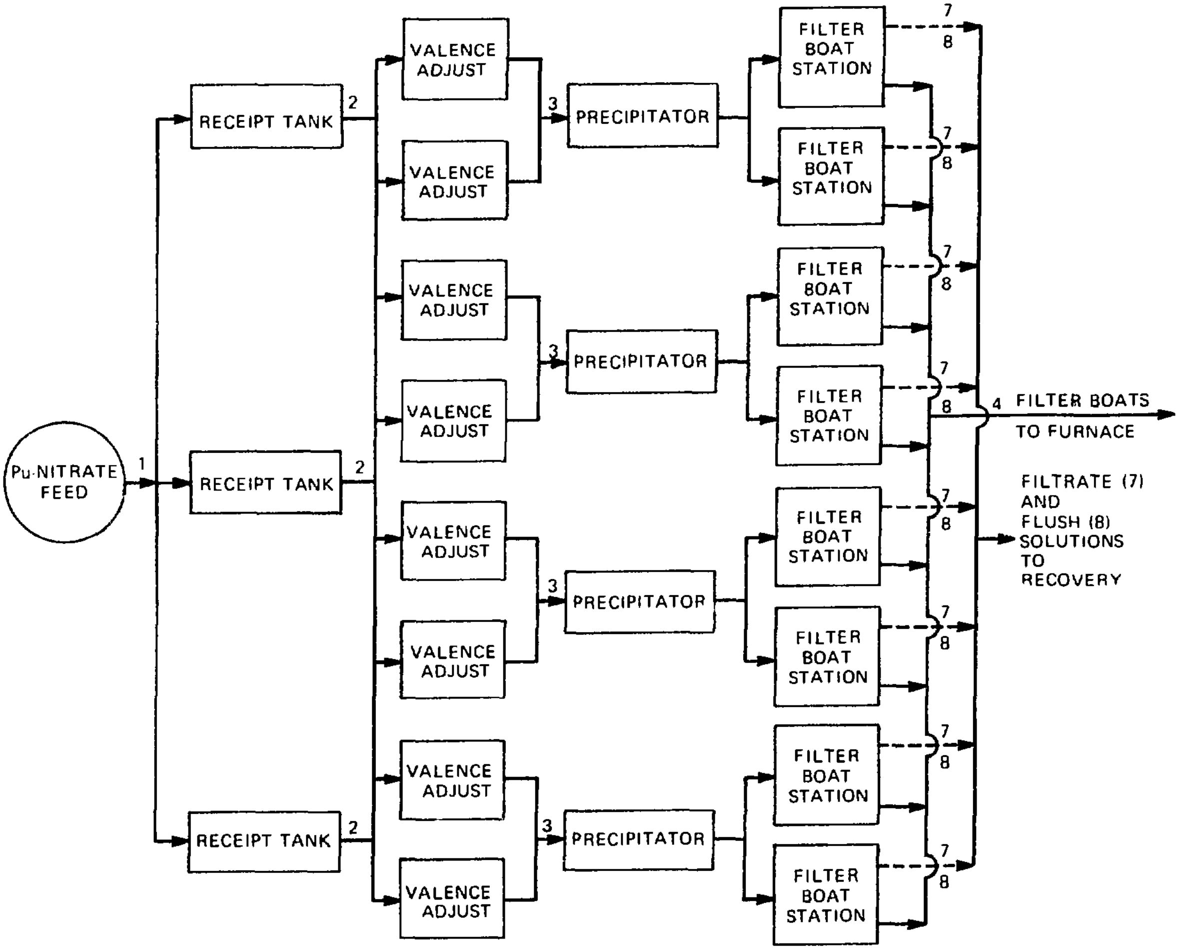


Fig. B-8. Conversion process, liquid handling.

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

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

Unloaded filter boats and precipitator tanks are flushed periodically, and the flush solutions are transferred to the recycle line. Filtrates, wash solutions, powder sweepings, spills, and rejected product also go to the recycle line, which is shown in Fig. B-10.

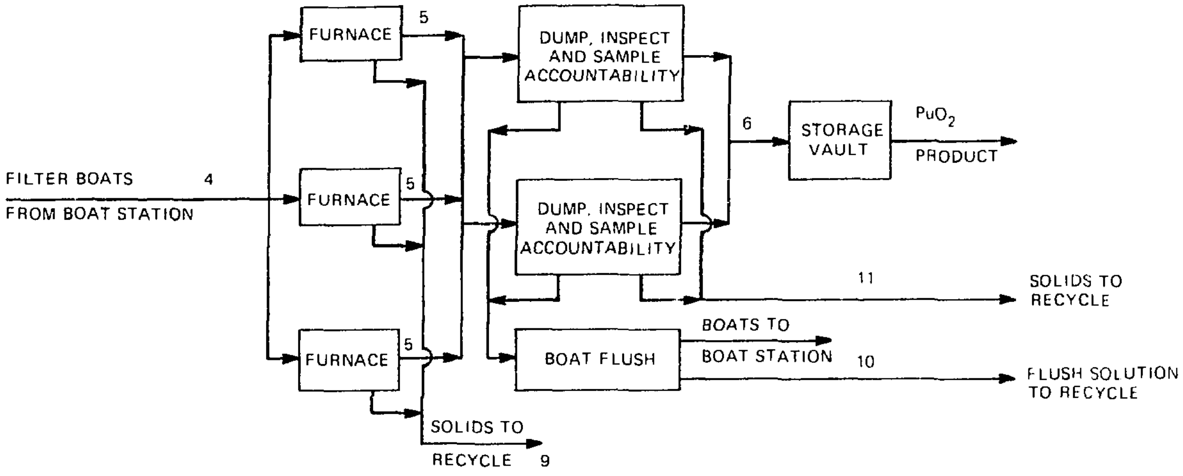


Fig. B-9. Conversion process, solids handling.

TABLE B-II

CONVERSION PROCESS DESIGN PARAMETERS[a]

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

---

[a] Design basis throughput of 106 kg/day.

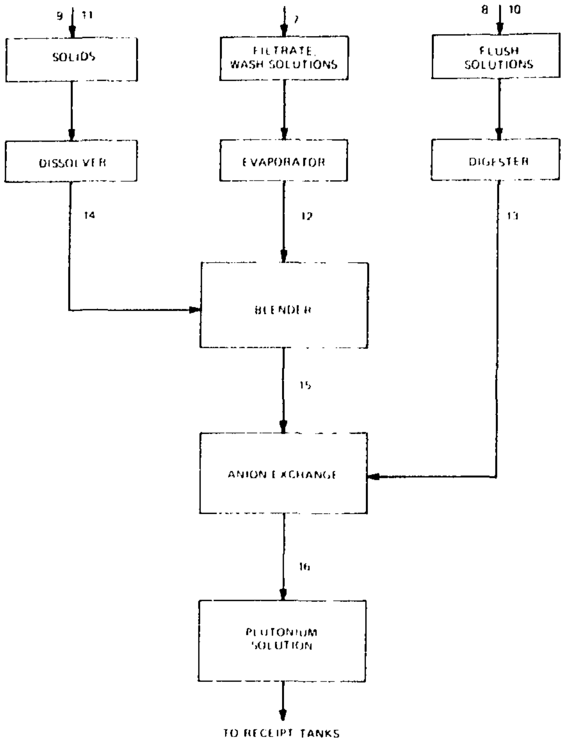


Fig. B-10. Internal recycle line.

The combined filtrate and wash solution is treated to destroy hydrazine, ascorbic acid, and oxalic acid, and then is concentrated by evaporation. The sweepings and rejected product are batched (500 g Pu) and then dissolved in HNO_3 that contains fluoride ion. The dissolver solution is blended with the evaporator solution to provide sufficient volume for efficient use of the plutonium capacity of the anion-exchange columns. Flush solutions are combined, and any oxalic acid is destroyed by digestion. The exchange-column plutonium product is eluted and transferred to the main process line. All waste solutions are transferred to waste management.

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

1. Receipt Tanks. The conversion process is linked to the reprocessing plant by receiving the plutonium nitrate solution at a concentration of 250 g/L from the nitrate storage area and diluting to ∿30 g/L in the receipt tanks with 3 $\underline{M}$ HNO_3 (Fig. B-9). The solution is air-sparged briefly to eliminate the nitrogen oxides, mechanically agitated to assure uniformity, and a sample is taken for accountability. Three consecutive batches of ∿67 L each are dispensed to three valence adjustment tanks, associated with three active precipitator lines. The last batch dispensed completely empties the receipt tank.

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

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

2. Valence Adjustment. The contents of the receipt tanks are transferred in 66.7-L batches (2 kg Pu) to one of two valence adjustment tanks associated with each precipitator line. A solution of 3.5 M hydrazine (N_2H_4) is added to the valence adjustment tank to destroy nitrites, and 1.04 M ascorbic acid ($C_6H_8O_6$) is added to reduce plutonium to the trivalent state. The oxidation product is dehydroascorbic acid ($C_6H_6O_6$). The reactions in the valence adjustment tank are:

$$HNO_2 + N_2H_4 \rightarrow HN_3 + 2H_2O \ ,$$

$$HN_3 + HNO_2 \rightarrow N_2O(g) + N_2(g) + H_2O \ ,$$

$$2Pu(NO_3)_4 + C_6H_8O_6 \rightarrow 2Pu(NO_3)_3 + C_6H_6O_6 + 2HNO_3 \ .$$

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

3. Precipitation and Filtration. Precipitation takes place in two stages (Fig. B-11). Primary precipitation occurs when the adjusted feed solution is mixed stoichiometrically with oxalic acid in the first-stage precipitator. A slurry of $Pu_2(C_2O_4)_3$ in

TABLE B-III

RECEIPT TANK AREA OPERATING PARAMETERS

Plutonium concentration (g/L)	30.0
Number of tanks	3
Tank capacity (L)	260
Normal receipt volume (L)	24
Normal receipt plutonium (g)	8-9
Number of receipts per day	11.8
Time per receipt (h)	3
Analytical sample frequency	1/receipt

TABLE B-IV

PROCESS PARAMETERS FOR VALENCE ADJUSTMENT TANKS

Plutonium concentration (g/L)	
Feed	30.0
Product	26.4
Number of tanks	8
Tank capacity (L)	130
Normal receipt volume (L)	
$Pu(NO_3)_4$	66.67
Hydrazine	1.08
Ascorbic acid	7.69
Plutonium per batch (kg)	2.0
Batches per day	25

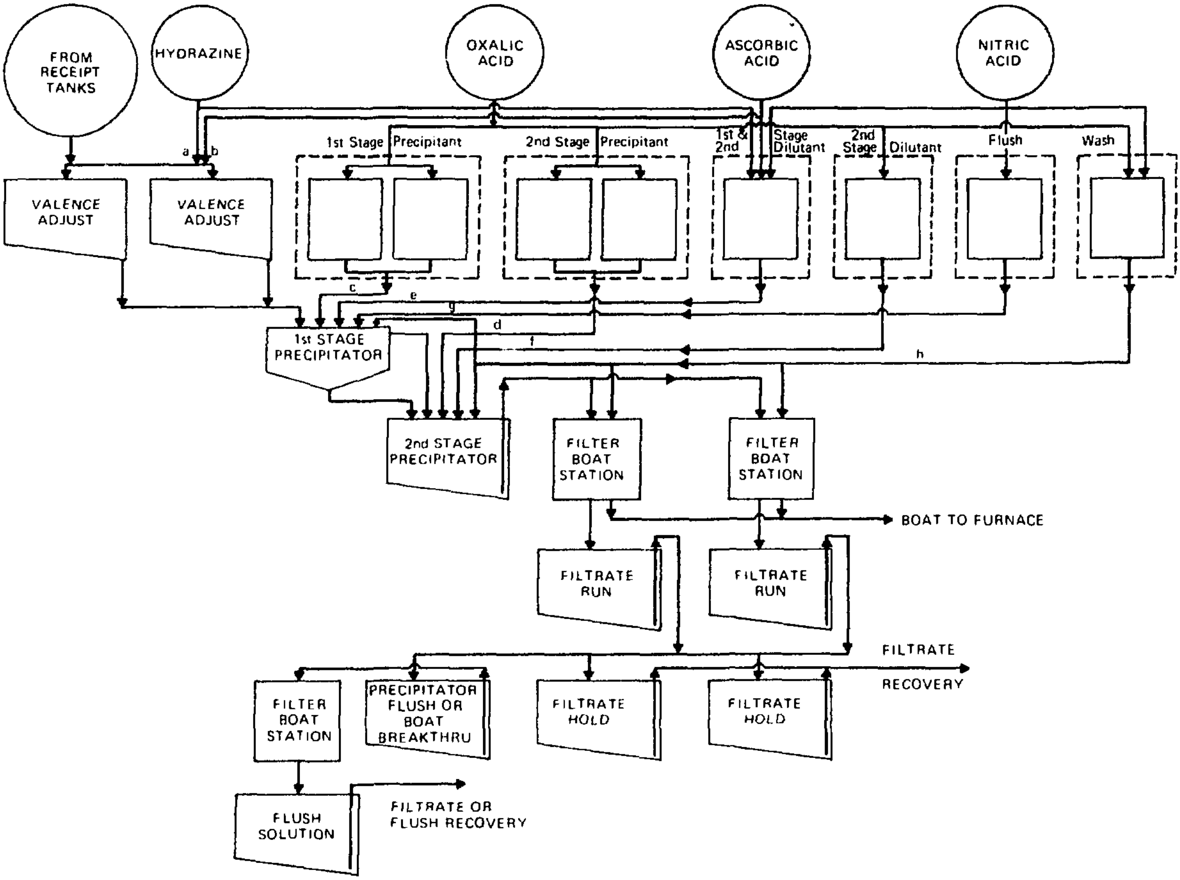


Fig. B-11. Precipitator line.

HNO_3 forms in the first-stage precipitator and overflows to the second-stage precipitator at a rate controlled by the rate at which feed and oxalic acid are added to the first-stage precipitator. The slurry in the second-stage precipitator is agitated for at least 15 min by maintaining the slurry level between 72-100 L to ensure complete precipitation. The concentration of dissolved plutonium should be <0.04 g/L.

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

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

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

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

If a filter break is detected and precipitate is observed in the filtrate run tank, the solution is refiltered through a second filter boat to another filtrate run tank (Fig. B-11). The filter boat with the broken filter and any filter cake remaining in it is sent through the drying and calcining furnace like a normal boat. However, if the hole in the filter is large, the boat is placed in a secondary container to prevent loss of solids during solids-handling. The process parameters for a precipitator and a filter boat station are given in Tables B-V and B-VI, respectively.

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

4. Calcination. The filter boat containing the aspirated filter cake is transported to the solids-handling area (Fig. B-9). The oxalate is dried and then calcined in one of two furnaces operating in parallel. Each furnace has drying, calcining, and cooling regions. A conveyor system indexes the boats through the furnaces on a programmed cycle of 2 h of drying, 2 to 3 h of calcining, and 1 h of cooling. Each furnace has a six-boat capacity. In the drying region, air is heated to 100-200°C and drawn through the cake by vacuum. Adhering H_2O and HNO_3 evaporate, and removal of water of hydration begins. The oxalate decomposes, and the oxide is calcined in the second zone where a temperature gradient from 450 to 650°C is maintained. Excess oxygen, provided by a flow rate of 30 m^3/min (1050 CFM) of hot air, is required for the decomposition. The calcined

TABLE B-V

PROCESS PARAMETERS FOR PRECIPITATOR TANKS

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

TABLE B-VI

PROCESS PARAMETERS FOR FILTER BOAT STATION

Boat dimensions (cm)	
Diameter	25
Height	15
Plutonium batch (kg)	2
Filtrate and wash (L)	160
Number of filter boats	15
Number of filter boat stations	4

PuO_2 product is cooled in the cool-down section of the furnace before discharge. After cooling, the filter boats are moved to the dump-weigh station.

The reactions in the furnace are drying,

$$Pu_2(C_2O_4)_3 \cdot 9H_2O \rightarrow Pu_2(C_2O_4)_3 + 9H_2O(g) \ ,$$

and calcining,

$$Pu_2(C_2O_4)_3 + 2O_2(g) \rightarrow 2PuO_2 + 6CO_2(g) \ .$$

Furnace process parameters are given in Table B-VII.

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

TABLE B-VII

FURNACE PROCESS PARAMETERS

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

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

A batch of product remains in a single filter boat throughout the solids-handling operations from filtration to dumping. The boats will be numbered, and their movement will be monitored by a computerized accountability program to allow some degree of material traceability in case of a discrepancy. The boat movements are shown in Fig. B-12. The accountability computer will also monitor and control the movement and location of product storage containers in the storage vault.

6. Storage. Sealed cans containing ∿2 kg of plutonium as PuO_2 are stored in the vault until they are transferred to the fuel fabrication plant. Storage is provided for ∿4000 kg of plutonium (2000 cans).

7. Recycle and Recovery Area. Filtrates and flush and wash solutions from the precipitator, solids from sweepings, filter boat flush solutions, and reject product from the conversion line are treated to recover and recycle plutonium. The recycle line is shown in Fig. B-13. A fourth minor sidestream is included to recover plutonium from waste material. Recycling and recovery through the ion-exchange blend tank is shown in more detail in Fig. B-14. The ion exchange system is shown in Fig. B-15.

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

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

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

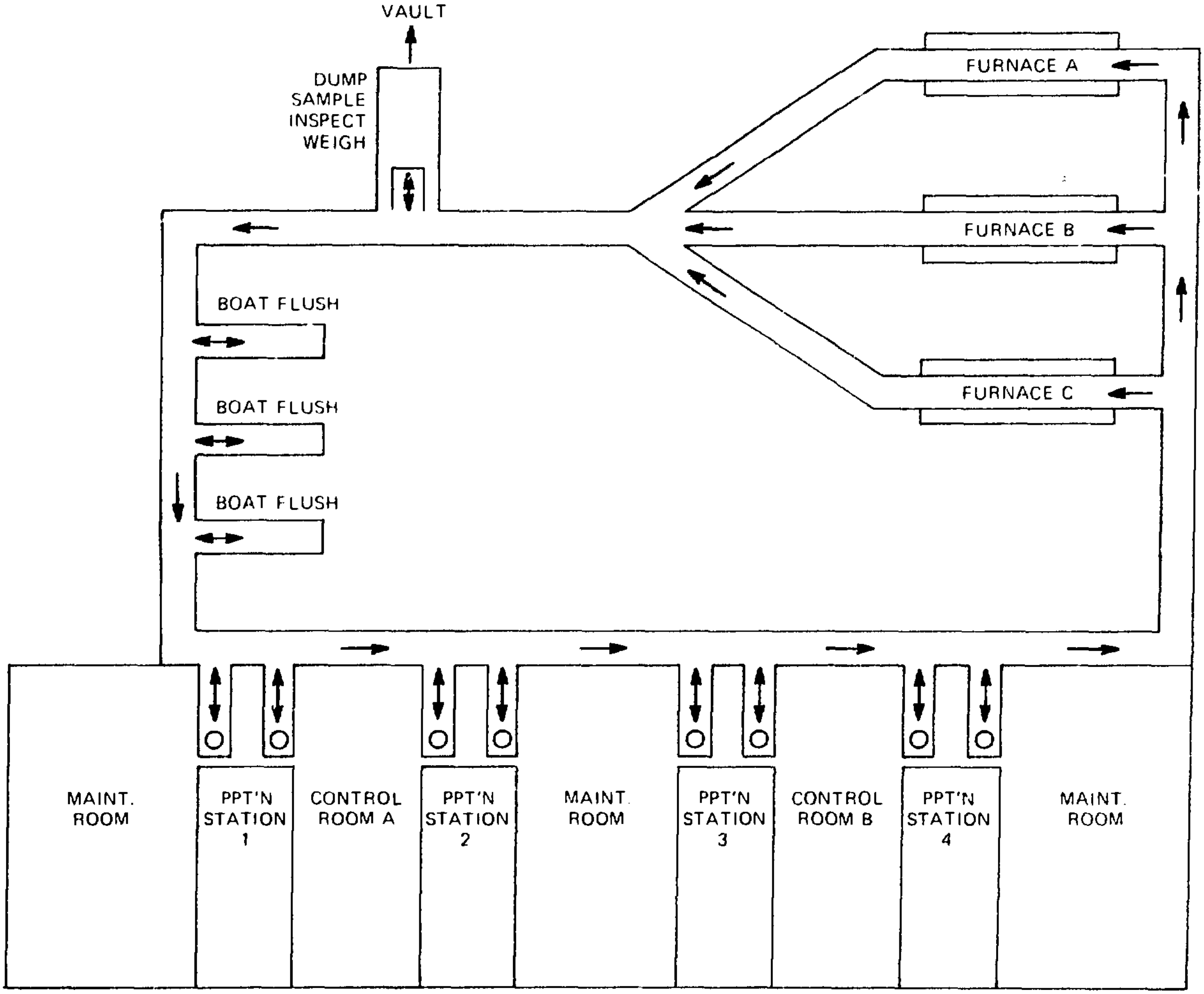


Fig. B-12. Boat movement.

Two to three batches (∿1000-1500 g Pu) are dissolved daily. About 0.2 L of 60% $Al(NO_3)_3$ solution per batch is added to complex the fluoride, and the solution is filtered to remove any undissolved particulates. The solution is transferred to the feed-adjust tank for blending with other recycle streams.

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

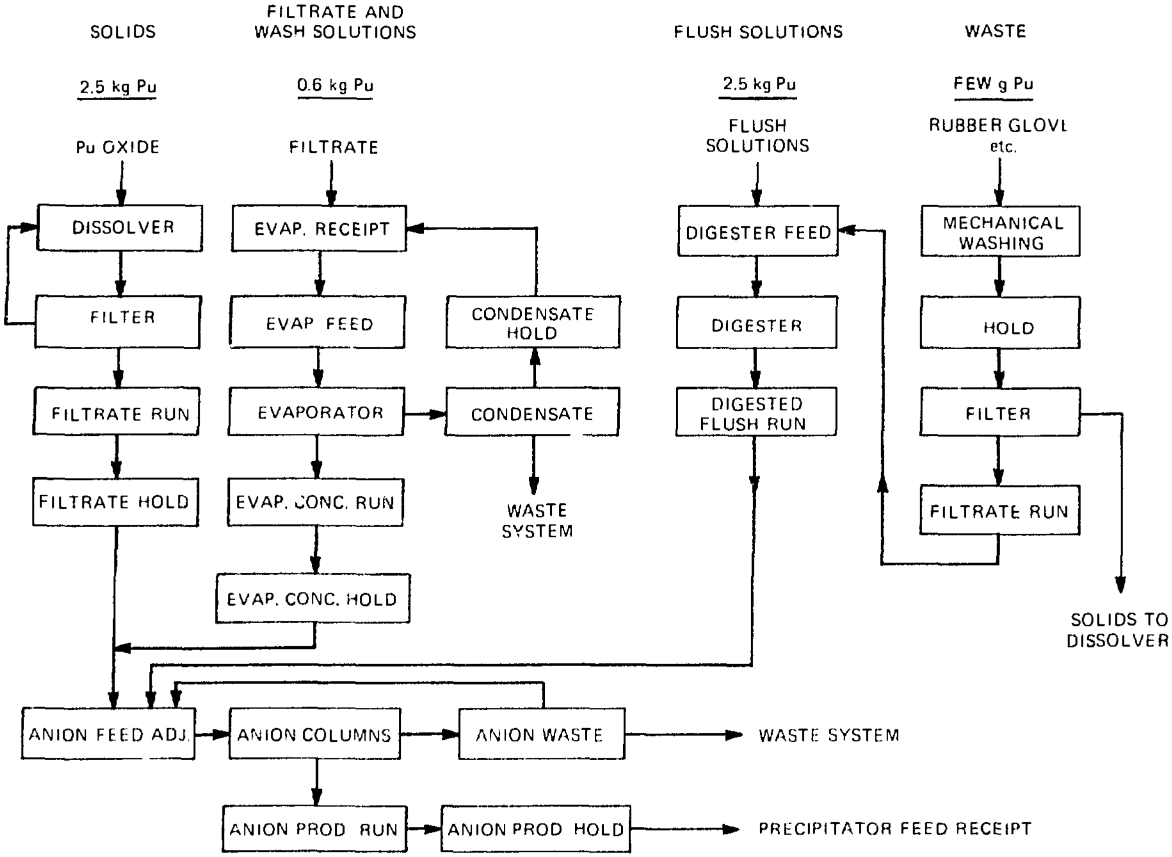


Fig. B-13. Plutonium recovery.

$$N_2H_4 \cdot HNO_3 + HNO_3 + 2NaNO_2 \rightarrow N_2O(g)$$

$$+ N_2(g) + 3H_2O + 2NaNO_3 \ ,$$

$$NaNO_2 + 2HNO_3 \rightarrow NaNO_3 + 2NO_2(g) + H_2O \ .$$

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

Chemical concentrations of the evaporator receipt tank feed are summarized in Table B-VIII. The evaporator feed is adjusted with HNO_3 to yield 10 M in the

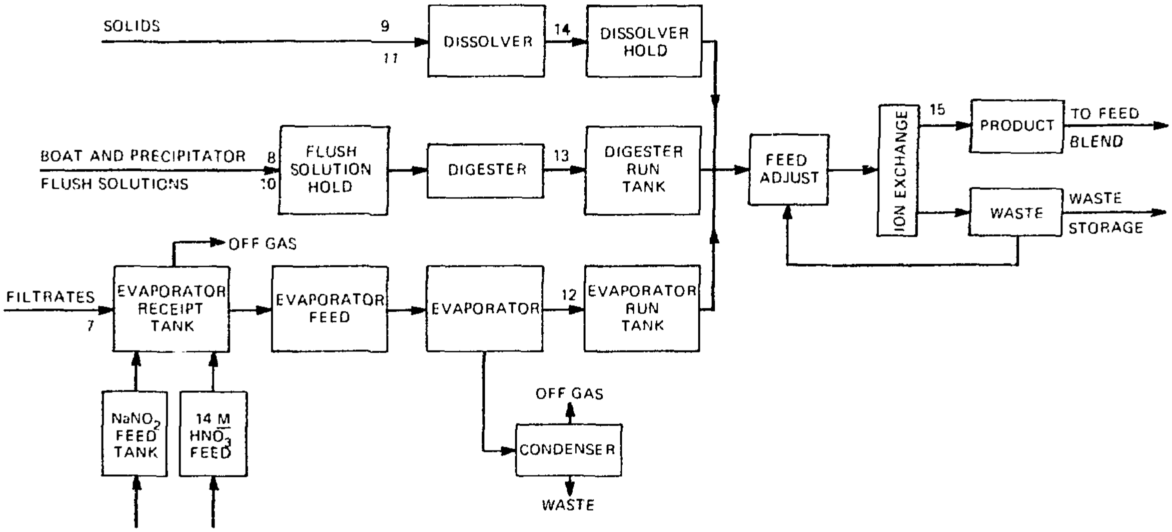


Fig. B-14. Recycle recovery (part 1).

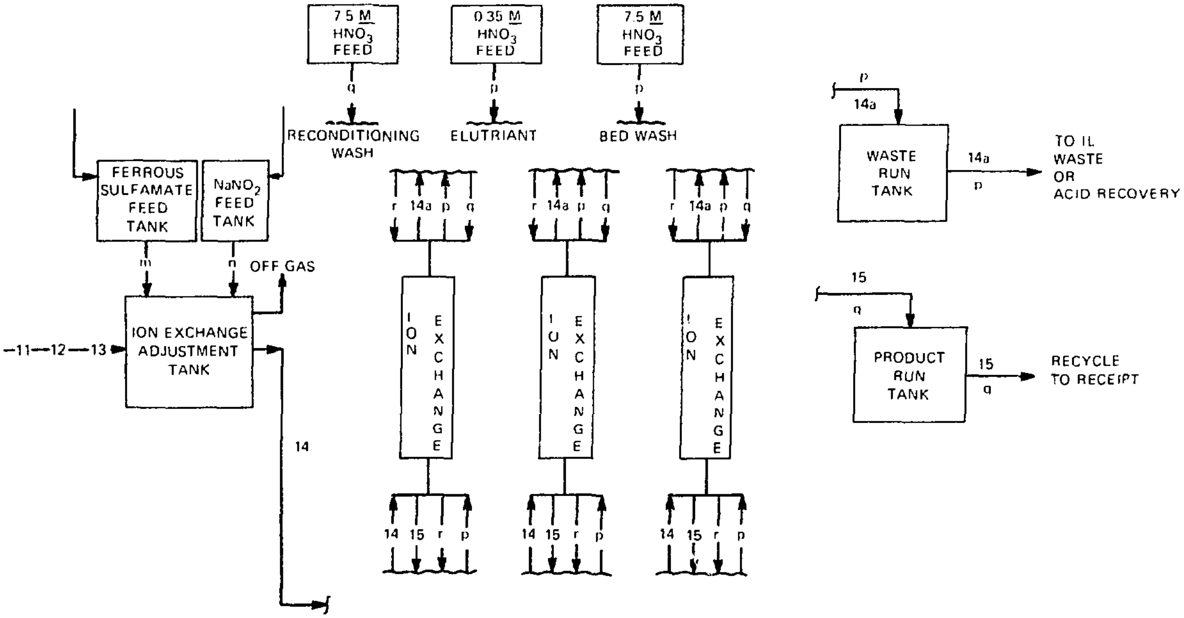


Fig. B-15. Recycle recovery (part 2).

TABLE B-VIII

CHEMICAL CONCENTRATIONS IN EVAPORATOR RECEIPT TANK FEED

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

evaporator bottoms after evaporation of the overheads and the HNO_3-consuming oxidants. The actual nitric acidity of the adjusted evaporator feed is ∿1.79 M. This evaporator operates continuously, and the 10 M HNO_3 in the pot should be sufficient to oxidize oxalic and ascorbic acids.

The evaporator reduces the solution to 10% of its delivery volume. The evaporator product consists of 10 M HNO_3 and 0.86 M $NaNO_3$ containing 6 g/L of plutonium. The evaporator bottoms are transferred through the evaporator concentrate run tank to the ion-exchange blend tank. Demisters, which are inside the evaporator to minimize plutonium entrainment in the vapor stream, must be cleaned periodically.

Nitric acid concentrations are ∿0.2% in the overhead condensate and 10 M in the reboiler and takeoff stream. Handling such concentrations will require a fractionating column with the equivalent of five ideal plates operating under vacuum at 2000-3300 dyn/cm^2 to enhance the water-acid separation. The oxalic acid-HNO_3 decomposition is autocatalyzed by NO_2 in solution, and the lower pressure also allows the reboiler to operate at the lower temperatures necessary to keep enough NO_x in solution for oxalic acid destruction.

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

c. Flush Solutions. The precipitator flushing operations generate ∿75 L/day of 10 M HNO_3 solutions containing ∿5 g/L of plutonium. This solution is transferred through the filtrate run and hold tanks to a precipitator flush run tank and then to a flush solution hold tank (Fig. B-14).

Approximately 75 L/day of 10 M HNO_3 flush solution containing ∿3 g/L of plutonium is transferred from the filter boat cleaning operations to a boat flush run tank. This solution is blended twice daily with the precipitator flush solution and transferred to a flush solution digester where $H_2C_2O_4$ is destroyed through the reaction

$$2H_2C_2O_4 + 2HNO_3 \rightarrow 4CO_2(g) + 3H_2O + NO(g) + NO_2(g) \ .$$

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

d. Waste. Solid wastes, such as rubber gloves, that may contain significant amounts of plutonium are scrubbed with HNO_3. The material is filtered, and dissolved plutonium is transferred through a filtrate run tank to the flush solution digester feed tank. Solids are transferred to the solids dissolver.

e. Ion-Exchange System. (Refer to Fig. B-15.) The filtered PuO_2 dissolver solution and filtrate wash solutions, are blended in the ion-exchange blend tank and transferred to one of two ion-exchange adjustment tanks. The adjusted flush solutions are fed separately.

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

$$Pu(NO_3)_4 + Fe(SO_3NH_2)_2 \rightarrow Pu(NO_3)_3 + Fe(SO_3NH_2)_2NO_3 \ ,$$

$$PuO_2(NO_3)_2 + 3Fe(SO_3NH_2)_2 + 4HNO_3 \rightarrow Pu(NO_3)_3$$

$$+ 3Fe(SO_3NH_2)_2\ NO_3 + 2H_2O \ .$$

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

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

loading,

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

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

elution,

$$Resin \cdot Pu(NO_3)_6 \rightarrow Resin \cdot (NO_3)_2 + Pu(NO_3)_4 \ .$$

The nitrate product is transferred to one of four anion product run tanks. Approximately 200 L of solution containing 6.8 g/L of plutonium or a total of 1.4 kg of plutonium in approximately three 67-L batches will be transferred daily to the conversion line.

8. Cold Chemical Preparation. The cold chemical preparation area in the upper level of the conversion facility is diagrammed in Fig. B-16. Solutions required in the conversion and recycle areas are transferred through head tanks to process vessels by gravity feed through head pots. Cold chemical requirements of the various streams in the conversion and recovery lines are summarized in Table B-IX.

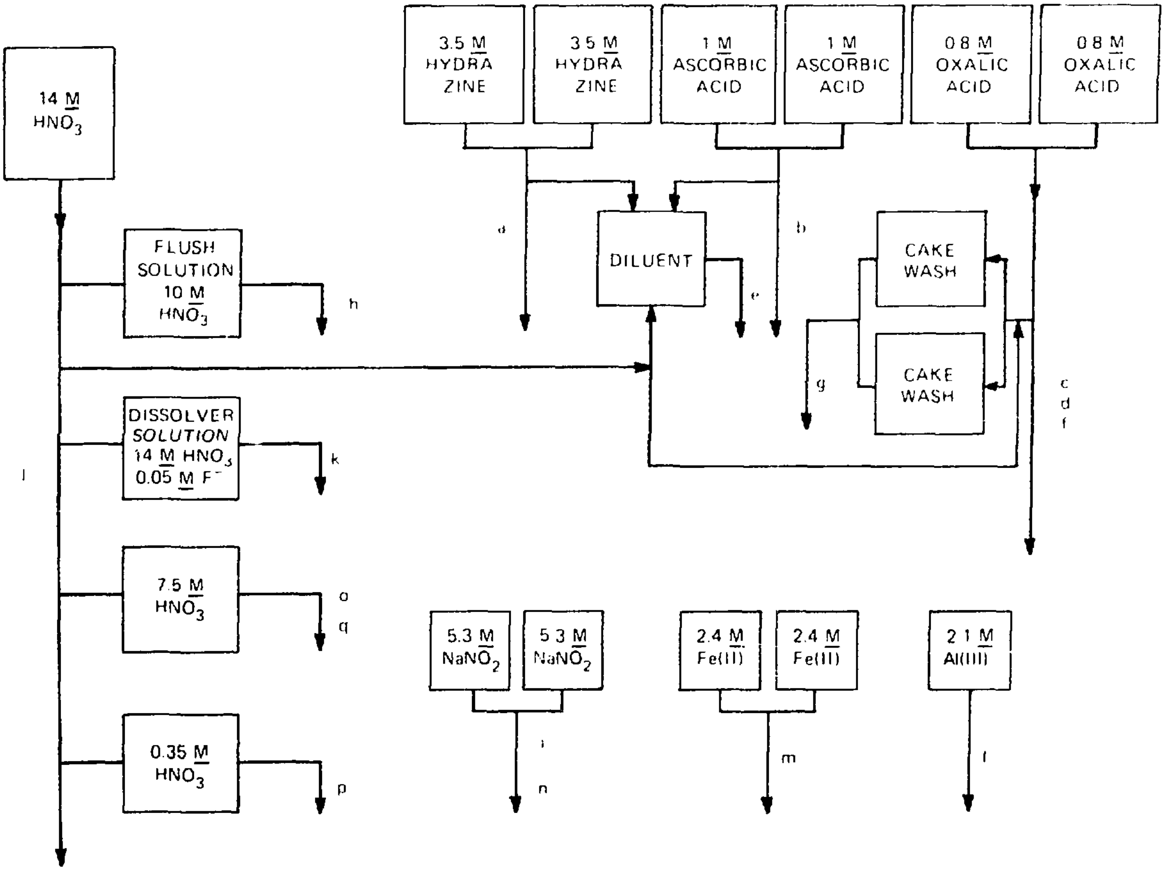


Fig. B-16. Cold chemical preparation.

TABLE B-IX

COLD CHEMICAL REQUIREMENTS

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

---

[a] See Figs. B-8 through B-11 and Figs. B-14 through B-16.

C. Small Reprocessing Plant

The reference facility for the small reprocessing plant is the 1-MT/day Tokai plant. The plant is designed to reprocess 1 MT/day of LWR fuel, but the nominal plant throughput is 0.7 MT/day. Plutonium reduction in the partition cycle is performed by addition of uranium (IV) rather than by electrical reduction. Because the first cycle contains two codecontamination steps and a solvent scrub to provide improved fission-product decontamination in the partition extractor, only one purification cycle is required. Silica-gel beds are not used for final uranium cleanup. The process is shown schematically in Figs. B-17 to B-20. This plant was selected because reprocessing data (plant description, flow sheets, throughputs) are available.[6-9]

The Tokai plant uses a chop-leach headend and conventional Purex technology as does the BNFP, but with significant differences that include the exclusive use of mixer-settlers rather than a centrifugal contactor and pulsed columns. In addition, buffer tanks are located before the second extraction cycle (extractor 3, Fig. B-18), and before the plutonium purification cycle (preceding the oxidation columns, Fig. B-20). The presence of these tanks, with associated samplers and volume measurement devices, facilitates dividing the process into additional unit process accounting areas (UPAAs) for near-real-time accounting.

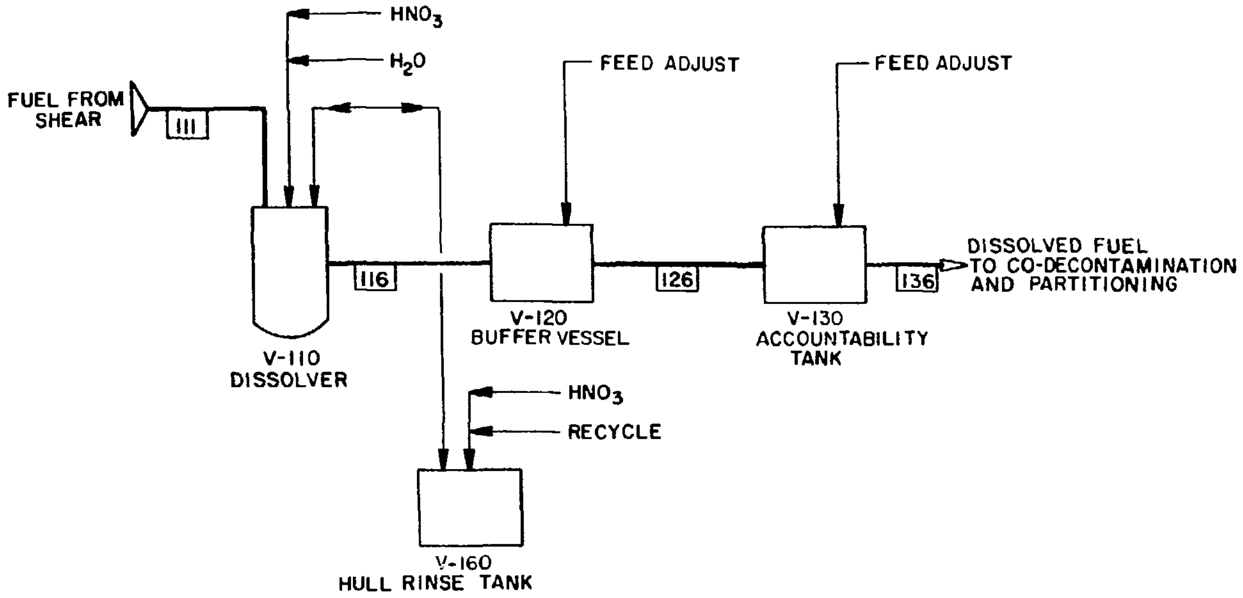
1. Fuel Receiving and Storage.

Feed is received to the plant in casks weighing up to 90 tonnes. Because the plant is designed to process natural uranium fuels as well as enriched LWR uranium fuels, two storage pools are provided. The natural uranium pool has an 84-tonne capacity; the enriched uranium pool has a 64-tonne capacity. Fuel is transferred to the appropriate storage pool from the unloading cell.

2. Fuel Dissolution and Feed Preparation.

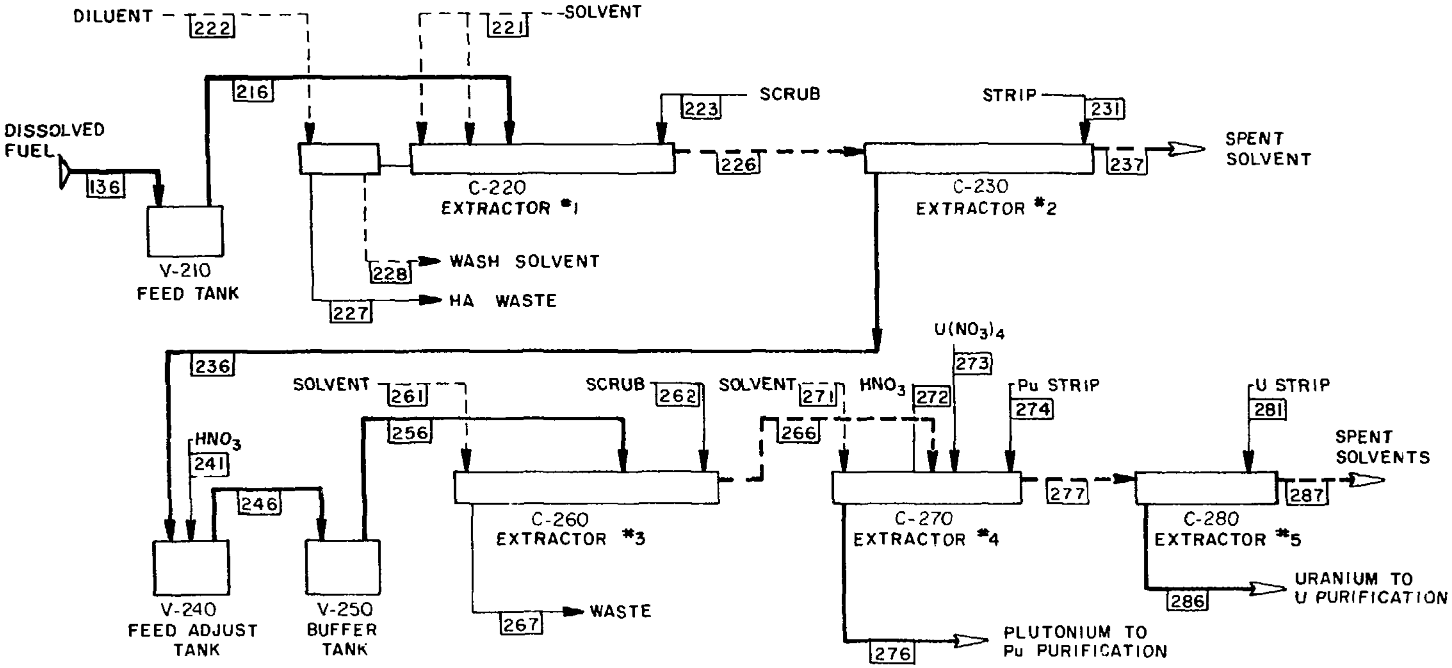
Natural uranium fuel elements are declad mechanically under water. Light-water-reactor fuels are mechanically chopped into lengths of 3-4 cm. The chopped pieces are fed directly to one of three dissolvers (Fig. B-17). Each dissolver has a normal capacity of 350 kg of fuel and a maximum capacity of 480 kg. Two fuel assemblies make up one dissolver batch for BWR fuels, and one fuel assembly constitutes a dissolver batch for PWR fuels. Two dissolver batches are processed daily. Leached hulls are removed to the highly radioactive solid waste storage area.

After dissolution the solution is adjusted to $\sim 3\ \underline{N}$ in HNO_3 and 180 g/L of heavy metal. The adjusted feed is centrifuged, then transferred to the accountability tank.



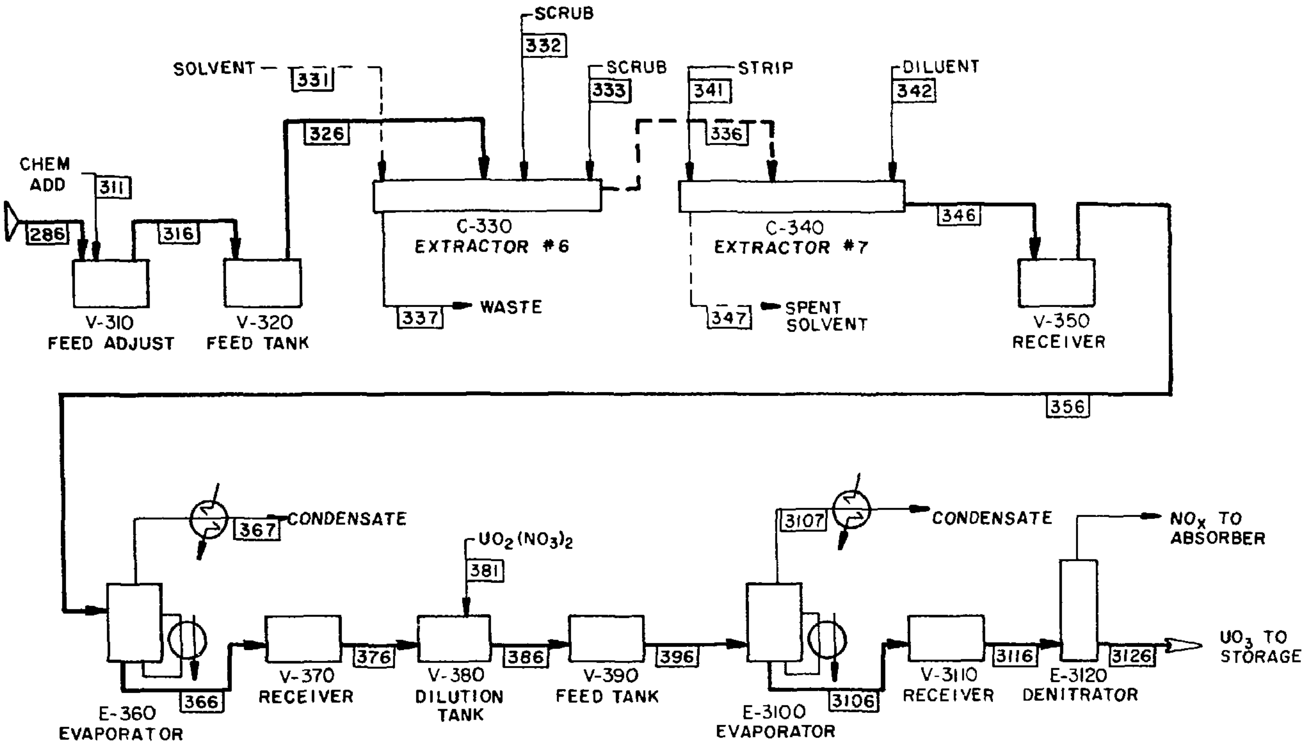
STREAM NO.	111	116	126	146
SERVICE				
LITERS/ba			1750	
Kg/ba	320			
U, g/L			180	
Pu, g/L			2	
HNO_3, mol				
OTHER				

Fig. B-17. Fuel dissolution and feed preparation, 210-MT/yr plant. (These values are not flow-sheet values of any existing reprocessing facility but represent typical values within reasonable ranges of a workable flow sheet.)



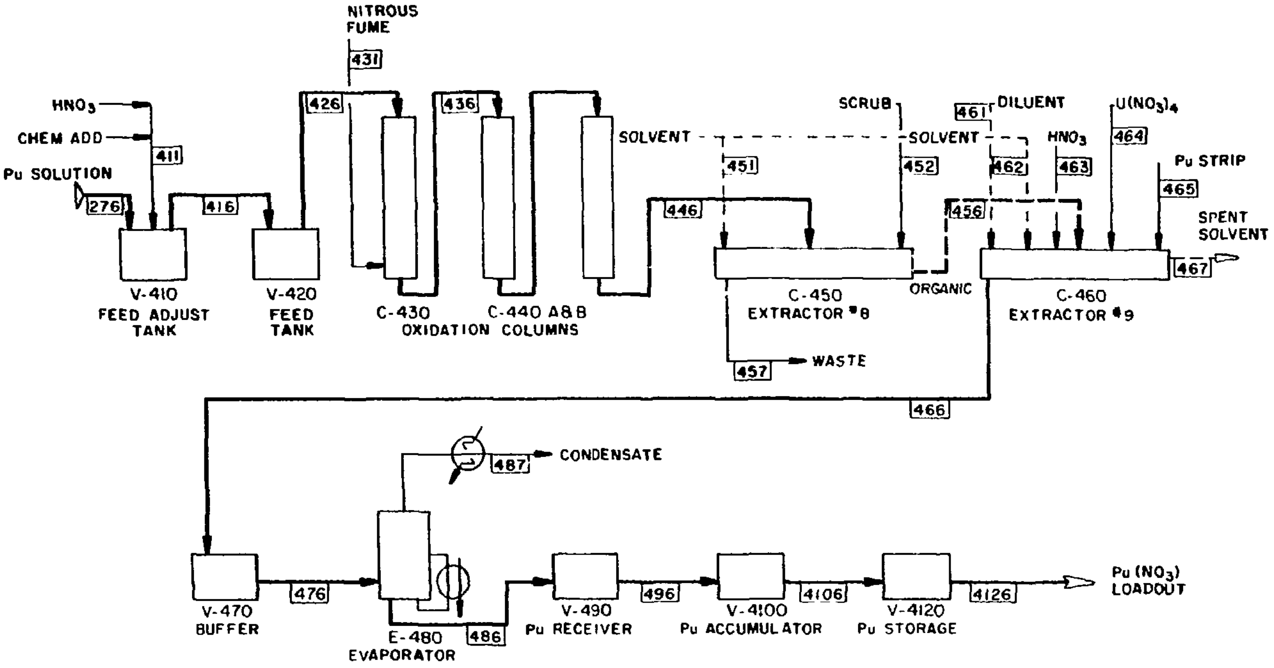
STREAM NO.	136	221	222	223	226	227	228	231	236	237	241	256	261	262	266	267	271	272	273	274	276	277	281	286	287
SERVICE	1F	1X	1X'	1S	2F	1W	1X'W	2S	2P	2W	ACID ADD	3F	3X	3S	4F	4W	4X	HNO_3	U^{+4}	4S	4Pu	4U	5S	5UP	5W
LITERS/ba																									
Kg/ba																									
U, g/L	180				90				75			57			77				200			65		59	
Pu, g/L	2				1				0.8			0.6			0.8						2.25	$<10^{-6}$		$<10^{-6}$	
HNO_3, mol				3	0.17	2.9		0.02	0.25		11.0	3.0		3.0		2.9		11.0	1.5	0.02	1.7	0.01	0.02		
N_2H_4																		5g/L							

Fig. B-18. Uranium-plutonium codecontamination and partitioning, 210-MT/yr plant. (These values are not flow-sheet values of any existing reprocessing facility but represent typical values within reasonable ranges of a workable flow sheet.)



STREAM NO.	286	311	316	331	332	333	336	337	341	342	346	347	366	381	386	3126	3127
SERVICE	5UP	CHEM ADD	6F	6X	3S'	3S	7F	6W	7X	DIL	7UP	7W					
LITERS/ba																	
Kg/ba																	
U, g/L	56		50				80				70						
Pu, g/L	0.002		0.001														
HNO_3, mol	0.03	11.0	1.5		11.5	1.5	0.1	1.5	0.02		0.1						

Fig. B-19. Uranium purification, 210-MT/yr plant. (These values are not flow-sheet values of any existing reprocessing facility but represent typical values within reasonable ranges of a workable flow sheet.)



STREAM NO.	276	411	416	446	451	452	456	457	461	462	463	464	465	466	467	486
SERVICE	4P	CHEM ADD		8F	8X	8S	9F	8W	9S'	9S	HNO$_3$	9X	9X'	9P	9W	Pu PROD
LITERS/ba																
Kg/L																
U, g/L	<0.002		1	1			3					200				
Pu, g/L	2.25		2	2			6							15		250
HNO$_3$, mol	1.7			3.5		1.0	0 2	3				1.5	0.2	1.5		
N$_2$H$_4$												5 g/L	5 g/L			

Fig. B-20. Plutonium purification, 210-MT/yr plant. (These values are not flow-sheet values of any existing reprocessing facility but represent typical values within reasonable ranges of a workable flow sheet.)

3. Uranium-Plutonium Codecontamination and Partitioning. Uranium and plutonium are separated from the bulk of the fission products in the first extraction cycle by extracting with TBP in dodecane from HNO_3 (Fig. B-18). In the partition cycle, uranium and plutonium are extracted from HNO_3 in a bank of 17 mixer-settlers. Then plutonium is reduced to the trivalent state with tetravalent uranium and is stripped from the organic phase in a bank of twelve mixer-settlers.

4. Uranium Purification. After the stripping from the organic phase with 0.02 $\underline{N}$ HNO_3, uranium is purified in a single purification cycle (Fig. B-19). This cycle consists of extractions of uranium into the organic phase from 1.5 $\underline{N}$ HNO_3 and stripping with 0.02 $\underline{N}$ HNO_3 to provide a product stream containing 70 g/L of uranium. This product is concentrated and can be converted to UO_3 by fluidized-bed direct denitration for storage.

5. Plutonium Purification. After oxidation to plutonium (IV), plutonium is purified in a single purification cycle (Fig. B-20). The tetravalent plutonium at a concentration of 2 g/L and containing ∿2 mg/L of uranium is extracted into the organic phase from 3.5 $\underline{N}$ HNO_3. The plutonium is stripped by using uranium (IV) as a reductant. The aqueous pure plutonium product stream containing 15 g/L of plutonium in 1.5 $\underline{N}$ HNO_3 is concentrated to 250 g/L for storage.

6. Liquid Wastes. High-level liquid wastes will be stored pending development of acceptable waste disposal plans.

7. Gaseous Wastes. Gaseous wastes will be purified to remove fission products before being disposed through the ventilation stack.

8. Solid Wastes. The leached hulls and other solid wastes will be removed to the highly radioactive solid waste storage after monitoring.

9. Plutonium Nitrate Storage. The plutonium nitrate is stored in criticality-safe tanks at a concentration of 250 g/L.

10. Uranium Product Storage. Uranium is stored as UO_3 after fluidized-bed denitration.

11. Solvent Treatment. Solvent from the first cycle is regenerated for use in this cycle. Solvent from the remaining cycles is regenerated for use in these cycles.

12. Acid Recovery. The acid from the bottom parts of all columns will be recovered by means of evaporators preceded by diluent scrubbers.

REFERENCES

1. "Barnwell Nuclear Fuels Plant Separations Facility--Final Safety Analysis Report," Docket 50-332, Allied-General Nuclear Services, Barnwell, South Carolina (October 10, 1973).
2. E. A. Hakkila, D. D. Cobb, H. A. Dayem, R. J. Dietz, E. A. Kern, E. P. Schelonka, J. P. Shipley, D. B. Smith, R. H. Augustson, and J. W. Barnes, "Coordinated Safeguards for Materials Management in a Fuel Reprocessing Plant," Los Alamos Scientific Laboratory report LA-6881 (September 1977).
3. Savannah River Laboratory document DPSTP-LWR-76-5 (November 1976).
4. Savannah River Plant document DPSP-LWR-77-29 (March 1977).
5. H. A. Dayem, D. D. Cobb, R. J. Dietz, E. A. Hakkila, E. A. Kern, J. P. Shipley, D. B. Smith, and D. F. Bowersox, "Coordinated Safeguards for Materials Management in a Nitrate to Oxide Conversion Facility," Los Alamos Scientific Laboratory report LA-7011 (April 1978).
6. K. Ikawa, H. Ihara, H. Sakuragi, H. Nishimura, and M. Hirata, "Study of the Application of Dymac Principles to Safeguarding Fuel Reprocessing Plants," Japan Atomic Energy Research Institute report JAERI-Memo-8241 (April 1979).
7. K. Nakajima, "Development of Safeguards Procedures for a Reprocessing Plant with Mechanical Head-End and Mixer-Settler Contactors Using a Purex Flow Sheet," International Atomic Energy Agency report IAEA/R-796-F (February 1971).
8. R. Curillon and J. Viennot, "Japanese Fuel-Reprocessing Plant Described," Energ. Nucl., 10, 160-168 (May 1968).
9. G. Lefort, P. Miguel, and M. DeRubercy, "Investigation and Testing of the Extraction Procedure Used in the Japanese Plant," Energ. Nucl. 10, 169-180 (May 1968).

APPENDIX C

PROCESS DESIGN AND OPERATING FEATURES RELEVANT TO MATERIALS ACCOUNTING

E. A. Hakkila, D. D. Cobb, and D. B. Smith
LASL Safeguards Staff (Q-4)

Features of process design and operation strongly affect the application to high-throughput reprocessing and conversion facilities[1,2,3] of both conventional and dynamic materials accounting methods. Traditionally, little consideration is given to safeguards effectiveness before the establishment of a plant and process design. The safeguards system designer typically is presented either with an existing facility or with a relatively complete and fixed plant design. We have accepted this prevailing philosophy in our current safeguards studies; that is, the base-line facility designs are assumed to be fixed. However, with the increased recognition of the importance of safeguards, the situation may be changing, and, in future plant designs, safeguards criteria should be regarded as equivalent in importance with health, safety, and economic considerations.

A. Guiding Principles

Certain guiding principles govern effective materials control and accounting in any NM process. These are discussed further in App. E. Each measurement is important for its impact on the sensitivity of loss detection. Thus, the necessity for each measurement point and the desired quality of each measurement should be judged by systematically analyzing the anticipated effects on materials-accounting sensitivity.

In high-throughput processes, the relative accuracy between feed and product measurements limits the long-term detection sensitivity.[4,5] Consequently, a significant effort should be directed at controlling long-term relative biases between feed and product measurements. Theoretically, the limiting factor is the uncertainty in the relative bias between the physical standards used for these measurements, which may be <0.1%. To approach this limit, sources of long-term measurement bias other than standards must be controlled by careful design of the sampling, measurement, and calibration hardware and procedures (Ref. 6, Part F; Refs. 7-10). Feed and product accountability vessels must be designed for accurate calibration and should be accessible for frequent calibration checks and periodic recalibrations. The best available sampling and assay methods must be used, and analysts must be carefully trained in the use of calibration and analysis procedures.

In dynamic materials accounting, the precision of the in-process inventory measurements and the variability of any unmeasured holdup are the limiting uncertainties in short-term detection.[5] The majority of the inventory should be in tanks and vessels that are instrumented for on-line measurements. These measurements need not be of high quality, precisions of 1 to 5% being generally adequate. However, even with very precise measurements, large buffer-storage tanks may introduce large absolute errors that will seriously degrade the short-term detection sensitivity. On the other hand, relatively minor holdups and sidestreams will have little effect on detection sensitivity, and estimates based on historical data can be used until these components are measured, for example, during a physical inventory.

If all major in-process-inventory and process-stream components are measured, dynamic materials balances can be drawn around transfers between tanks and across vessels. Such balances may not require the precision and accuracy of conventional accountability, but they will be both sensitive and timely in absolute terms. Thus, process-design criteria for materials accounting should specify measurements for all the major inventory and flow components, and these criteria should be integrated early in the plant design.

Process operating modes also affect materials-accounting sensitivity. Well-defined input and output batches facilitate accounting; if the process is operated continuously, batch definition requires continuous stream measurements. If there are significant recycle streams, input-output correlations will be of limited value. Operating the process in relatively small batch-fed campaigns with a flushout between campaigns helps alleviate these problems.

The effect of in-process inventory on short-term detection sensitivity is minimized by operating the process near steady state, which is the normal mode of operation for high-throughput processes. In case of a severe upset, the ability to drain the in-process material into instrumented tanks and then to recover normal operation aids materials accounting and control and may extend the time required between physical inventories. During nonroutine operations, such as startup and shutdown, well-characterized "reference states" of the process can be established as fiducials for materials accounting.

B. Base-Line Large Chemical Separations Process

Design features of the base-line large chemical separations process constrain the application of advanced materials measurement and accounting techniques.[1] The following aspects are discussed:

- Inaccessibility,
- Continuous flow,
- Large process vessels,
- Contactor design,
- Recycle streams.

1. Inaccessibility. Plant maintenance philosophy is extremely important in the design of a safeguards system. It affects not only the accessibility of NM to diversion but also the measurement strategy and the access to instrumentation for calibration, repair, and replacement. The design of the reference facility (as a commercial venture) for maximum throughput and economic recovery, along with the extremely high radiation levels characteristic of process solutions throughout most of the process, result in minimum provisions for accessibility and maintenance. Most process equipment is located in congested, heavily shielded process cells. Provision is made for remote maintenance of the mechanically complex, highly radioactive first stages of the process. Subsequent purification stages are designed for no maintenance or for limited direct maintenance after process flushout and decontamination under extraordinary conditions of plant malfunction.

Thus, there is virtually no possibility in the reference facility for introducing additional instrumentation into process cells to facilitate materials accounting. Most data obtained directly from the main process streams and tanks come from process-control instruments provided to monitor liquid densities and levels, flow rates, and temperatures. Process-monitoring devices that are intended to detect gross changes or upset conditions in the process may require upgrading to produce data suitable for materials accounting. However, the upgraded instruments must be equally rugged, reliable, radiation-resistant, maintenance-free, and subject to remote calibration.

2. Continuous Flow. From the input accountability tank to the plutonium-product catch tank, the flow of solution through the process is essentially continuous and there are no identifiable batches around which materials balances can be drawn. Materials balances, therefore, must be closed by integrating, over time, measured flow rates in all process streams entering and leaving any given portion of the process. The uncertainties associated with such measurements may be considerably larger than those realized in the measurement of discrete quantities of the same material unless high quality flow and concentration measurements are incorporated in major process and recycle streams.

3. Large Process Vessels. Because of the desired high throughput of the reference facility, most of the process tanks and vessels are large (up to 15 000 L). While many of these tanks have been provided with density and liquid-level measuring devices, air sparges for mixing, and pneumatic transfer lines for remote sampling, small uncertainties in the measured liquid level or plutonium concentration or incomplete mixing of the tank contents can cause large absolute errors in the plutonium inventory. Proper mixing and sampling of tank contents should be considered during facility design and construction.

4. Contactor Design. In the Purex process, plutonium and uranium are coextracted from the dissolver solution into an organic phase that is then contacted with a reducing aqueous phase into which the plutonium is selectively back-extracted, leaving the uranium in the organic phase. These essential processes are performed in solvent-extraction contactors. In a contactor, the solvent phases are mixed mechanically. In the reference facility, a ten-stage centrifugal contactor is used for initial codecontamination, and a series of pulsed-columns are used for uranium-plutonium partitioning and final plutonium product purification.

An important property of pulsed-column contactors, with respect to materials accountability, is their relatively large plutonium inventory. That is also true of the mixer-settler contactors used in the base-line small chemical separations process. The total plutonium inventory of the contactors in the large reference facility is ∿25 kg. Much of this in-process inventory is not accessible for direct measurement and can vary substantially under normal operating conditions. The feasibility of estimating a contactor inventory for dynamic accounting by combining theoretical-model predictions with process-control measurements is being investigated (see App. J and Ref. 11).

The in-process inventory in contactors can be reduced by at least an order of magnitude for the same throughput by using centrifugal contactors in place of pulsed columns or mixer-settlers. Centrifugal contactors also have the advantages of rapid drain-down, with negligible drain-down volume, and rapid startup after shutdown may be effected in an 8-h shift[12] rather than over a period that may be as long as a week, as may be required for pulsed columns.

5. Recycle Streams. The design philosophy for the reference reprocessing plant incorporates as much flexibility as possible to permit economical plant operation and the reworking of off-specification materials. As a result, there are numerous recycle loops to facilitate intraplant transfers of material. In effect, material can be piped from almost any point in the process to almost any earlier stage. The recycle routes significantly

complicate the partitioning of the process into unit process accounting areas and the establishment of correlations based on feed and product measurements. For example, the measurement of plutonium in the accountability tank is accomplished by isotope-dilution mass spectrometry and is sensitive to the presence of any residual plutonium from previous campaigns. Ideally, the dissolver would be designed to receive only fresh or regenerated HNO_3; recycled acid should be introduced only downstream of the accountability tank. Recycle streams in other areas of the plant should include measurements of flow and concentration.

C. Base-Line Conversion Process

The conversion facility has special safeguards implications because it invariably handles plutonium in large quantities as a concentrated, highly purified material free from lethal penetrating radiation. It is therefore extremely attractive as a target for diversion. However, many of the features that make the conversion process attractive for diversion also make it more amenable to dynamic materials accounting.[2] Low radiation levels and improved accessibility to the process facilitate the necessary measurements. The parallel process lines are ideally suited to the application of unit process accounting. The reduced throughput and inventory for each line result in improved accounting sensitivity relative to the total plant, and each line can be treated as a separate UPAA.

The batch-fed and semicontinuous operation of the reference process also simplifies application of dynamic materials accounting. The precipitators run continuously, except at times of flushout, but the feed tanks and filter boats are batched. Furthermore, there is no exchange of material between the parallel lines.

The major problem arises in accounting for the plutonium oxalate slurry in the precipitators. Uncertainties in measuring the precipitator in-process inventory limit the short-term detection sensitivity.[2] Measurement of mixed-phase material is a generic safeguards problem for any conversion process.

The conversion process for the small reference facility has not yet been selected. Because the conversion process potentially can address special international safeguards technical and institutional needs, safeguards features should be extremely influential in the selection of a conversion process and the design of its process features.

D. Design Criteria for Future Reprocessing Facilities

Future reprocessing facilities should incorporate safeguards criteria in the original designs. Specific design trade offs require a detailed analysis in each case. The following items illustrate possibilities that should be considered.

1. NDA on Spent Fuel. At present, spent fuel received to the storage pool is verified by examination of the final identification number. Actual analytical verification is not obtained until the fuel is dissolved and isotope dilution mass spectrometric analysis is performed. Nondestructive measurements are being developed to confirm fuel burnup and to verify directly the fissile contents of irradiated fuels.[13,14] These methods, reviewed in App. N, require further development and field testing; however, they should be considered in design of the fuel receiving and storage area.

2. Input Accountability. The feed and product accountability tanks should be designed for highly precise and accurate measurements, with provision for periodic calibration checks and recalibration.

The input measurement is especially important to fuel-cycle safeguards because it presents the first opportunity to make a high-quality measurement of the plutonium produced in reactors and is the basis for closing the shipper/receiver (S/R) balances on spent fuel shipped for reprocessing. Input batch identity should be maintained at the accountability tank by limiting as much as possible the mixing and recycle in the dissolver area and by facilitating efficient flushing of the dissolver and the accountability tank heels after each batch. To prevent contamination of accountability tank heels, it may be advantageous to obtain accountability samples from the dissolver.

One source of sampling error at the input accountability tank is the suspended particulates in the dissolver solution. Solids could account for as much as 0.3% of the accountability-tank volume and ∿0.8 kW of heat per tonne of dissolved fuel. The feed-clarifying centrifuge should be located between the dissolver and the accountability tank to remove suspended solids.

3. Contactors. The short-term sensitivity of materials accounting probably will be limited by the ability to estimate in-process inventories in the solvent-extraction contactors.[1,15] Sufficiently accurate models and instruments should be available for on-line estimation of contactor inventories to at least 10% (preferably 5%) under normal operating conditions.

Contactor inventories are reduced by more than an order of magnitude if centrifugal contactors are used in place of pulsed columns or mixer-settlers. In addition to low hold-up, centrifugal contactors provide the added advantages of rapid shutdown and return to steady state after startup.

One study[16] indicates that centrifugal contactors can be substituted for pulsed columns or mixer-settlers throughout the codecontamination-separation and plutonium-purification cycles with the exception of the codecontamination stripping stage. There a larger contact time is dictated by the kinetics of ruthenium extraction. Questions have been raised over the use of centrifugal contactors for the third plutonium cycle in the reference facility, where kinetic effects associated with plutonium (III) reduction/oxidation may limit the use of centrifugal contactors. Additional research and development is required in that area.

4. First-Cycle Decontamination. Improved decontamination is possible at the front end of the separations process by providing a second decontamination cycle before partitioning, as has been done in the reference small plant. The reduced radioactivity in the uranium-plutonium product stream might permit inclusion of an additional flow accountability point before partitioning. That is especially desirable, both for process control and for safeguards, in the event that a coprocessing mode of operation is selected.

5. Process Tanks. All process tanks should be instrumented for liquid level, density, and temperature measurements and should be equipped with air spargers and sampler lines. Detectors for near-real-time accounting should be installed in the sample galleries to provide rapid concentration measurements that are backed up by wet chemistry.

Intermediate buffer-storage and process-run tanks should be batch operated. Two or more tanks of relatively small capacities operated in parallel are much better for accounting than a single, large tank operated continuously.[17]

6. Process Buffer Tanks. Installation of buffer tanks to decouple the codecontamination and partitioning and the partitioning and plutonium purification operations helps to define unit process accounting areas. Buffer tanks have been installed in the small reference facility and are proposed as a safeguards feature for a designed high-throughput facility.[16] The decoupling permits a drain-down inventory in the PPP without disrupting head-end operations.

7. Product Concentration. Concentration of the final $Pu(NO_3)_4$ to ∿250 g/L is primarily for convenience in storing and transferring between reprocessing and conversion facilities. Collocation of those facilities would require that the concentration of the final plutonium-product solution from the reprocessing plant be maintained below ∿50 g/L or that an intermediate blending step be performed. Without concentration, the product

stream could be used directly as feed for the conversion plant, and the product concentrator and associated heater and feed tanks could be eliminated. From a safeguards viewpoint, the volume of product solution required to divert a significant quantity of plutonium would increase by a factor of 4 to 8 and would decrease the plant hold-up by the amount in the concentrator (normally ∿15 kg of plutonium in the base-line large plant).

8. Process Stream Measurements. Flow meters capable of periodic recalibration should be installed in major process streams; a measurement precision of 1% or better is required. A 5-10% measurement precision is acceptable for flow meters in waste streams. In-line or at-line detectors should be incorporated to measure plutonium concentrations in major process streams with a measurement precision of 1% or better and in waste streams with a precision of 5 to 20%.

Product tank construction should consist either of vertical slab tanks or harp tanks.[18] Operation of tanks at a fixed volume may improve precision of volume measurements.

9. Instrument Accessibility. All in-line or at-line instruments, including flow meters and concentration sensors, should be installed in a manner that permits accessibility for recalibration and maintenance by plant personnel or inspection by the national or international safeguards staff. All sensors should be interfaced directly to the safeguards computer system and, within practical considerations, should be tamper-safed or tamper-indicating.

10. Redundant Measurements. Redundant volume, flow, and concentration measurements should be considered for key measurement points (KMPs). Volume measurements for the accountability tank may include acoustic[19] or radio-frequency[20] instruments or magnesium addition[21] to back up the manometric measurement.

Concentration measurements may be based on periodic laboratory checks to verify in-line instruments.

11. Computer Data Handling. All data handling should be performed by computer to minimize human access and consequent errors. All in-line and laboratory instruments should be linked directly to the data-base computer. The computer system is described in more detail in App. D.

E. Collocation and International Plutonium Management

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

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

Increased interest in international plutonium management and collocation will tend to influence process and storage considerations in future multinational or internationally safeguarded facilities. The role of the conversion facility in providing a base for these special arrangements will be extremely important for all the reasons stated: large storages of attractive material, freedom from lethal penetrating radiation, and most of all, the superior safeguardability of both the material and the facility. Safeguards considerations must be incorporated in the earliest design stages and in the selection of conversion process features for facilities not yet completed.

REFERENCES

1. E. A. Hakkila, D. D. Cobb, H. A. Dayem, R. J. Dietz, E. A. Kern, E. P. Schelonka, J. P. Shipley, D. B. Smith, R. H. Augustson, and J. W. Barnes, "Coordinated Safeguards for Materials Management in a Fuel Reprocessing Plant," Los Alamos Scientific Laboratory report LA-6881 (September 1977).

2. H. A. Dayem, D. D. Cobb, R. J. Dietz, E. A. Hakkila, E. A. Kern, J. P. Shipley, D. B. Smith, and D. F. Bowersox, "Coordinated Safeguards for Materials Management in a Nitrate to Oxide Conversion Facility," Los Alamos Scientific Laboratory report LA-7011 (April 1978).

3. D. B. Smith, "Importance of Process Design on Safeguards Systems," in US DOE Safeguards Technology Training Program - Measurement and Accounting Systems for Safeguarding Nuclear Materials (Los Alamos Scientific Laboratory, March 1979).

4. T. I. McSweeney, J. W. Johnston, R. A. Schneider, and D. P. Granquist, "Improved Material Accounting for Plutonium Processing Facilities and a 235-U-HTGR Fuel Fabrication Facility," Battelle-Pacific Northwest Laboratories report BNWL-2098 (October 1975).

5. H. A. Dayem, D. D. Cobb, R. J. Dietz, E. A. Hakkila, J. P. Shipley, and D. B. Smith, "Dynamic Materials Accounting in the Back End of the LWR Fuel Cycle," Nucl. Technol. 43, 222-243 (1979).

6. IAEA Safeguards Technical Manual, International Atomic Energy Agency Technical Document IAEA-174 (Vienna, 1976).

7. J. L. Jaech, "Statistical Methods in Nuclear Material Control," TID-26298, Technical Information Center, Oak Ridge, Tennessee (1973).

8. R. Avenhaus, Material Accountability: Theory Verification and Applications (John Wiley & Sons, New York, 1977).

9. J. E. Lovett, Nuclear Materials: Accountability, Management, Safeguards (American Nuclear Society, 1974).

10. D. B. Smith, "Physical Standards and Valid Calibration," Proc. Safeguards Symp., Vienna, 1975 (International Atomic Energy Agency, Vienna, 1976), Vol. II, pp. 63-70.

11. D. D. Cobb and C. A. Ostenak, "Dynamic Materials Accounting for Solvent-Extraction Systems," paper presented at ANS Topic. Conf. Meas. Tech. for Safeguards and Mater. Control, Kiawah Island, South Carolina, November 26-29, 1979.

12. J. Ergel, Savannah River Laboratory, personal communication, March 1979.

13. D. D. Cobb and H. A. Dayem, "Preliminary Concepts: Safeguards for Spent Light-Water Reactor Fuels," Los Alamos Scientific Laboratory report LA-7730-MS (June 1979).

14. S. T. Hsue, T. W. Crane, W. L. Talbert, Jr., and J. C. Lee, "Nondestructive Assay Methods for Irradiated Nuclear Fuels," Los Alamos Scientific Laboratory report LA-6923 (January 1978).

15. K. Ikawa, H. Ihara, H. Sakuragi, H. Nishimura, and M. Hirata, "Study of the Application of DYMAC Principles to Safeguarding Spent Fuel Reprocessing Plants (TASTEX Task F)," Power Reactor and Nuclear Fuel Development Corporation, Japan (April 1979).

16. J. Ergel, Savannah River Laboratory, personal communication, November 1978.

17. H. A. Dayem, "Coprecal: Process Modification for Safeguards Improvement: Addition of Aliquot Tanks (Preliminary Analysis)," Los Alamos Scientific Laboratory report LA-7746-MS (June 1979).

18. W. Davies, P. T. Good, and A. G. Hamlin, "A Statistical Examination of the Practical Problems of Measurement in Accountancy Tanks," in Nuclear Safeguards Technology 1978 (International Atomic Energy Agency, Vienna, 1979), IAEA-SM-231-57, Vol. II, pp. 593-619.

19. J. Watson and T. L. Jones, "An Acoustic Technique for the Determination of Liquor Levels in Tanks," presented at First Meeting-Coordinated Research Program, the Use of Installed Instrumentation in Irradiated Fuel Reprocessing Facilities for Safeguards Purposes (International Atomic Energy Agency, Vienna, March 12-16, 1979).

20. J. M. Crawford, M. H. Ehinger, C. Joseph, and M. L. Madeen, "Studies and Research Concerning BNFP, Nuclear Materials Control and Accounting System Evaluation Report--FY 1978 Integrated Uranium Run," Allied-General Nuclear Services report AGNS-1040-2.2-50 (October 1978), App. H.

21. C. K. Mathews, H. C. Jain, V. D. Kavimandan, and S. K. Aggarwal, "Tracer Techniques for the Input Accountability of Plutonium in Reprocessing Plants: Magtrap and Leadtrap," Nucl. Technol. 42, 297-303 (1979).

APPENDIX D

OPERATOR'S SAFEGUARDS SYSTEM STRUCTURE

J. P. Shipley
LASL Safeguards Staff (Q-4)

A comprehensive operator's in-plant safeguards strategy includes four functions:

- Exclusion of all unauthorized persons from the facility and selective exclusion of others from sensitive areas within the plant;
- Monitoring of all activities involving NM to determine whether each activity is consistent with safeguards requirements and with normal, expected facility operation;
- Accounting for all NM in the facility to determine whether correct amounts of all materials are present in their proper locations; and
- Response to and reporting of the facility's safeguards status.

At the same time, the safeguards system is bounded by the following constraints:

- It must be economical;
- It must be based on demonstrated technology;
- It must not disrupt process operations unnecessarily; and
- It must not compromise public health, safety, and environmental requirements or unnecessarily infringe upon employee rights and working conditions.

These constraints support the principle that the fundamental purpose of any nuclear fuel-cycle facility is to process NM. Safeguards are vitally important, but relationships among sometimes conflicting objectives must be kept in perspective.

A basic management, control, and coordination structure of operator's safeguards systems for domestic nuclear fuel-cycle facilities was proposed in earlier reports.[1-4] A block diagram of a facility and its safeguards system is shown in Fig. D-1. The safeguards system (1) provides timely, accurate reports on the safeguards status of the facility; (2) implements safeguards requirements imposed by the regulatory authorities; and (3) initiates and coordinates external responses to possible safeguards breaches. The system comprises several subsystems, including (1) the safeguards coordination unit (SCU), (2) the physical protection system (PPS), (3) the materials measurement and accounting system (MMAS), (4) the process monitoring system (PMS), and (5) the safeguards computer system (SCS), which is not shown on the diagram. These subsystems and the related functions of process control and plant management are discussed below.

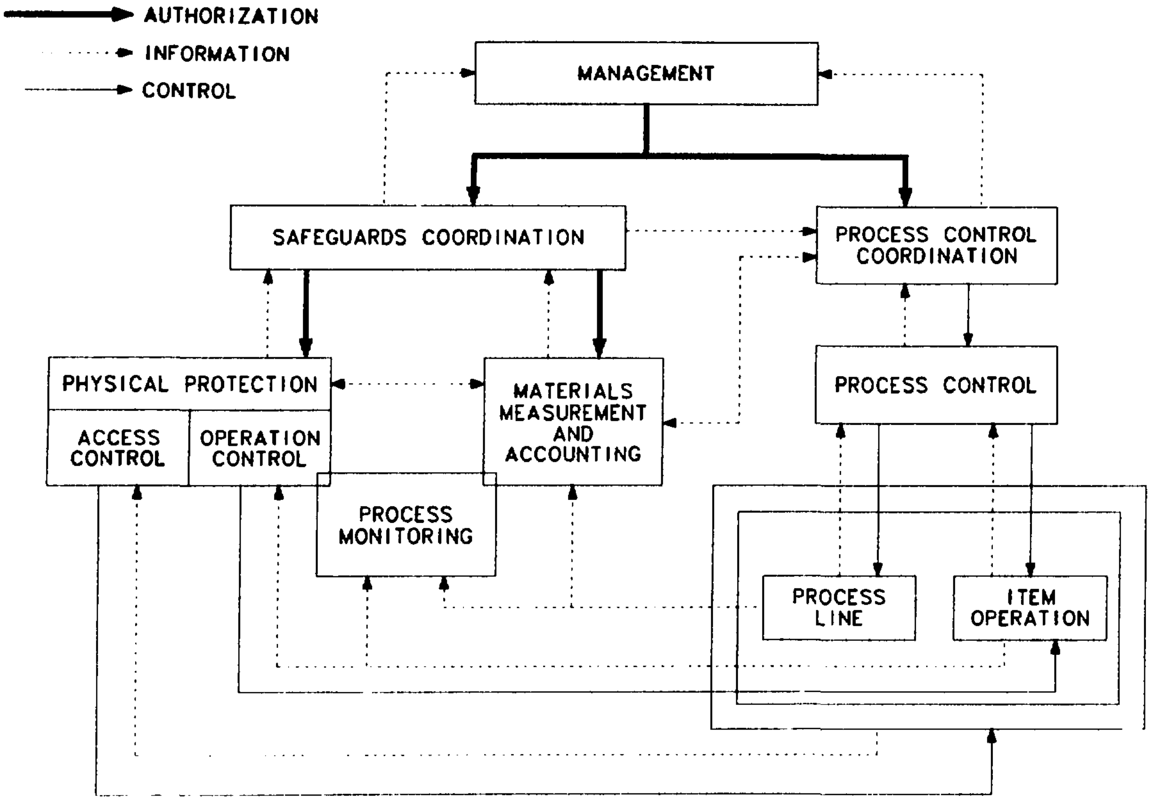


Fig. D-1. Structure of the safeguards system.

A. Safeguards Coordination Unit

The SCU supervises NM safeguarding in the facility. As the focal point for safeguards decisions, the unit interacts with management and the process-control coordination unit (PCCU) to ensure effective safeguards while minimizing process disruptions. The SCU has three primary functions: (1) data collection and processing, which are required for (2) safeguards condition assessment, which in turn is the basis for (3) the response determination decision. A structural diagram of the SCU is shown in Fig. D-2.

The Safeguards Officer uses the processed data to assess the plant condition. The result of the condition assessment is the plant's status with respect to safeguards requirements. All identified status/response situations are standardized in a manual of operating procedures. This manual (or appropriate portions thereof) is available to plant personnel on a need-to-know basis. The safeguards officer has the responsibility to react

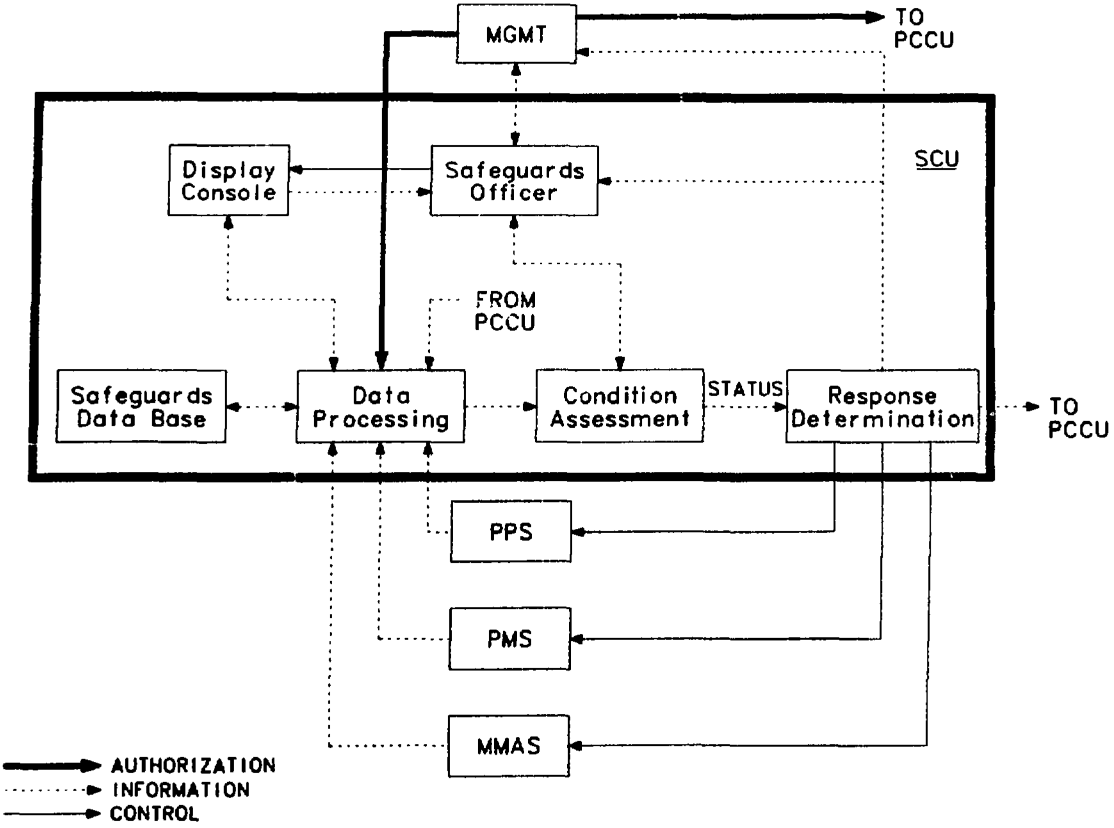


Fig. D-2. SCU structure.

to situations where standard procedures have not been written. This scheme combines the efficiency of a machine in data-handling with the adaptability of a human supervisor in decision-making.

In assessing the plant's condition, the Safeguards Officer uses reports from various parts of the plant. Taken together, these reports constitute the plant's status, details of which are stored in the safeguards and process information systems. However, the information normally displayed to the Safeguards Officer is condensed for quick assessment, with nonstandard situations flagged to indicate areas that should be investigated. The Safeguards Officer can ask for more detail, either in response to a flag or of his own volition.

The SCU recommendations range from no recommendation to the extremes of process shutdown and plant evacuation. If the safeguards system is successful, usually there will be no recommendation at all. In abnormal safeguards situations, the course of action is chosen by agreement among the Safeguards Officer, plant management, and PCCU, although some responses may be dictated by regulation. In emergency situations, the PCCU must respond quickly to prevent safety problems and must inform plant management and the SCU of the action taken.

B. Physical Protection System

The PPS controls personnel entry and exit for the facility and for restricted areas inside. The system includes automated equipment and enough guards to provide effective response in an emergency. It expands the conventional security functions, such as access control, to include control of item-handling operations (operations control). This arrangement provides more effective protection through remote, overriding control of discrete material items in handling and storage. The concept is applied only to those portions of the facility that are outside the closely coupled process line, such as the product loadout area, where materials flow is not critical to smooth process operations. Important objectives in the PPS design are to automate its functions whenever possible and to harden the system against subversion--objectives consistent with the stated goal of reducing dependence on personnel reliability. The PPS provides appropriate information to the safeguards system through the SCU, and it

- Excludes all unauthorized persons and contraband from the facility,
- Admits only essential persons to selected areas, and
- Precludes unauthorized activities involving NM and vital equipment.

In the current concept of domestic safeguards, physical protection and materials accounting complement and reinforce each other. In particular, the PPS protects not just NM, but the integrity of the MMAS as well. Conversely, the MMAS confirms the effectiveness of the PPS. For international safeguards, the PPS might be considered part of the hostile environment to be used actively to subvert the materials accounting and containment/surveillance measures that form the backbone of IAEA safeguards.

Design and evaluation of the PPS are the responsibility of Sandia Laboratories, Albuquerque (SLA) and are discussed in detail in Refs. 5-7, for example.

C. Materials Measurement and Accounting System

Three major MMAS functions in NM accounting are

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

As currently performed by conventional inventory control methods, these functions rely heavily on materials balance accounting following periodic shutdown, cleanout, and physical inventory. The classical materials balance associated with the MMAS is drawn around a materials balance area (MBA), which may be as large as the entire plant. The balance is formed by adding all measured receipts to the initial measured inventory and subtracting from that sum all measured removals and the final measured inventory. During routine production, materials control is vested largely in administrative and process controls, augmented by secure storage for discrete items.

Although conventional materials balance accounting is essential to safeguards control of NM, it has inherent limitations in sensitivity and timeliness. Sensitivity is limited by measurement uncertainties that desensitize the system to losses of safeguards-significant quantities of NM for high-throughput plants. Timeliness is limited by the frequency of physical inventories, which is constrained by the practical limits of how often a facility can shut down its process and still be productive.

The reference MMAS is an implementation of the dynamic materials accounting concept[8,9] incorporating recently developed nondestructive assay (NDA) technology, state-of-the-art conventional measurement methods, special in-plant sensors, plant instrumentation signals, and the most effective statistical data-analysis techniques combined with supportive computer and data-base-management technology. Conventional MBA accounting methods are augmented by unit process accounting, where the MBAs are partitioned into discrete accounting envelopes called UPAAs. A UPAA is one or more chemical or physical processes chosen on the basis of process logic and the ease in drawing frequent materials balances during process operation. When an MBA is divided into unit processes and all significant materials flows and in-process inventories are measured, quantities of material much smaller than the total plant inventory can be controlled. Any discrepancies are localized to that portion of the process contained in the UPAA. Periodic physical inventories, including process shutdown and cleanout, may be necessary to establish reference points for a dynamic accountability system.

Materials balances drawn around UPAAs during plant operation are called dynamic materials balances to distinguish them from balances drawn after a cleanout and physical inventory. Ideally, all dynamic materials balances would be zero unless NM had been diverted. In practice, they never are. First, measured values are inexact because of the errors inherent in any measuring procedure. Second, constraints on cost or effects on materials processing operations may dictate that not all components of a materials balance be measured equally often; therefore, even if the measurements were exact, the dynamic materials balances would not be zero until closed by additional measurements. In the interim, historical data might be used to estimate unmeasured material, and the estimates could be updated when additional measurements become available.

A consequence of unit process accounting, the concept of overlapping UPAAs, derives from the fact that adjacent UPAAs can be combined to form larger UPAAs by eliminating the intervening transfer measurements. Such combinations are useful for cross checking and for system redundancy, which allows continued materials accounting if analyses fail or samples are not available.

These ideas are applied flexibly throughout the facility. Their application is graded according to the safeguards strategic value and vulnerability of the material, hence, the concept of graded safeguards. For example, in the chemical separations plant, the separated plutonium nitrate is a much more attractive material to a potential divertor than is the highly radioactive dissolver solution. To escape detection by the MMAS, a potential divertor would have to remove small amounts of material over a long period, possibly from several process locations, thereby increasing his risk of detection by the other elements of the safeguards system.

D. Process-Monitoring System

The chemically and radioactively hostile environment of a reprocessing plant requires that instrumentation be designed for physical ruggedness and reliability, often at the expense of measurement ability. Thus, there may be need for a limited set of on-line, plant-grade measurement equipment and other simple, reliable, process-monitoring devices specifically designed to detect an abnormal situation, with less regard for the measurement precision and accuracy traditionally required for materials accounting.

The PMS combines elements of the PPS and MMAS and provides each with supplementary information regarding compliance of actual process operating modes with approved procedures. It extends physical protection monitoring and surveillance functions into the process line, and with upgrading or appropriate placement of the monitoring devices could allow gross materials accounting.

The PMS collects timely information to detect a theft in progress. Wherever possible, plant instrumentation is used to assess bulk materials balances on transfers between tanks and across vessels. The balances are crude by accounting standards but have the advantage of near-real-time availability.

Consider a typical process tank that has an inlet, an outlet controlled by a valve and transfer jet, a liquid-level probe, a specific-gravity probe, a sampler, and an air-sparge line. All valve positions are monitored, pressures in all transfer-lines are measured, and each line has a radiation sensor. The PMS checks to see that all these variables are behaving normally. For example, a drop in tank level when all valves are closed, or a negative pressure in a probe line, would indicate an attempt to remove NM from the tank. Such systems can provide nearly immediate detection of diversion attempts by continuously comparing actual operating conditions with those expected.

E. Safeguards Computer System

The SCS plays an essential role in effective safeguards by collecting safeguards-related data and maintaining and controlling the safeguards information system. A major part of this role is the protection of NM. Equally important is the effect of the computer system on NM processing: information provided through the computer system forms the basis for most safeguards decisions, which may have varying degrees of effect on the process. Erroneous or unavailable information can degrade decision quality and disrupt the process. Thus, the reliability and integrity of the computer system directly affect economical operation of the process.

In conventional safeguards systems, filling out and transmitting many materials accounting forms (records of receipts, shipments, internal transfers, and accounting measurement data) requires much time and effort. Many possibilities exist for human error, either unintentional or malicious, and inefficient data management is unavoidable.

Such problems can be alleviated by implementing the MMAS through computerized data acquisition and data-base management, with the conventional system retained as a back-up in case of malfunction. In this scheme, most instruments are interfaced directly to the SCS, and the use of computer terminals for data input is minimized. Security problems are eased somewhat, and a self-verification capability is provided easily by designing instrumentation for periodic on-line recalibration under computer control.

The SCS acts as the central data manager for the MMAS and is a powerful tool in analyzing accounting data for possible NM diversion. It generates all permanent records of materials quantities, locations, and movements and, on demand, can provide reports required for assessment of effectiveness and current status of the safeguards system, and other relevant information. Furthermore, data can be exchanged with the PCCU to improve both safeguards and process control.

Possible configurations of the SCS are discussed in Ref. 1. References 10 and 11 report recent work in this area by TRW Defense and Space Systems Group. Implementation in a large reprocessing facility is discussed in Ref. 12-14.

F. Process Control

The primary goal of process control is efficient operation of the process line. This goal has three important aspects: (1) economical operation, (2) health and safety considerations, and (3) effective safeguarding of NM.

Economy of operation in a commercial facility is accomplished by designing the process control to maximize throughput while consuming a minimum amount of resources. The process must be operated at the design rate with as few interruptions as possible. However, the process-control function must be able to interact with the health and safety and safeguards functions so that all three operational aspects are satisfied.

The process line is divided into several unit processes, each having its own unit process controller (UPC) reporting to one of the control subsystems of the PCCU (Fig. D-3). The PCCU is responsible for the coherent operation of the entire process line, that is, it performs a supervisory function. It determines operating levels and sequences for each UPC so that they all work together. This form of hierarchical control, called set-point control, is the traditional method of controlling complex systems. The PCCU is also responsible for implementing safeguards-related recommendations that affect

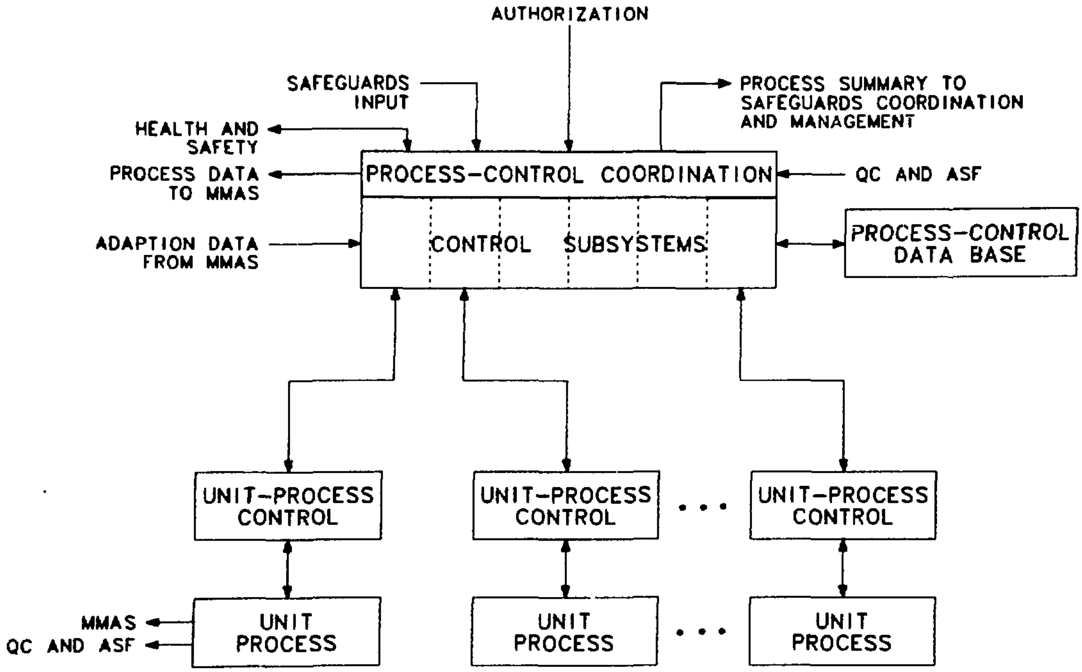


Fig. D-3. Process-control hierarchy.

process operations. This implementation is necessary to ensure effective compliance with both safeguards and process control. The MMAS and the PCCU also exchange process-related information to improve both process operation and safeguards effectiveness.

G. Plant Management

The plant management structure (Fig. D-4) is straightforward and similar to traditional configurations in nuclear plants. Management operations consist of the following steps.

(1) The general manager decides on a fuel contract and authorizes processing.

(2) The general manager's fuel projects staff defines the scope and issues a work order to the plant manager.

(3) The plant manager and his staff, using the process information system, plan and schedule the work load.

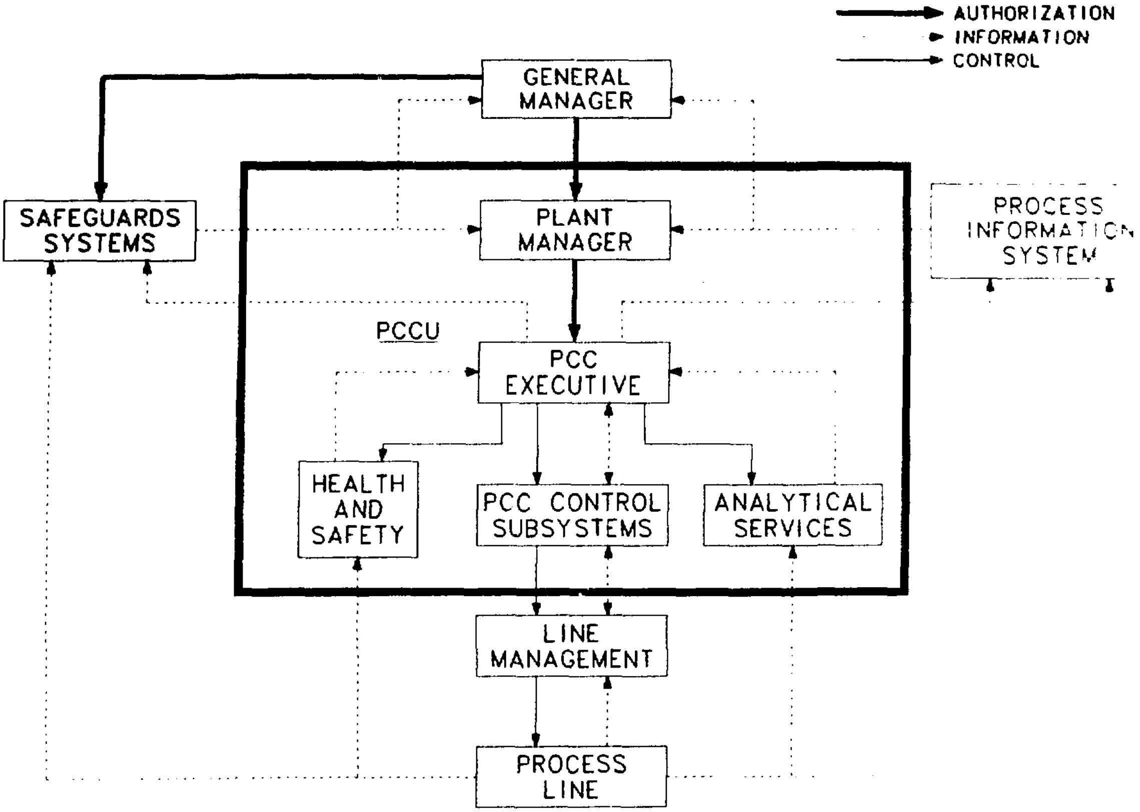


Fig. D-4. Plant management structure.

(4) The plant manager combines the work plan with any safeguards constraints and authorizes the start of work. A shop order describes the technical requirements and scheduling. This same information is transmitted to the safeguards system.

(5) The plant manager continually reviews the shop order status and safeguards system input and initiates any necessary action.

(6) Line management, with the help of the PCCU, organizes the work load and executes process operations on the basis of feedback from the process line, quality control, analytical laboratory, and health and safety, and on the basis of data from the process information system.

(7) Quality control maintains surveillance of product quality, analytical instrumentation calibration and inspections, and analytical data.

(8) Health and safety continually monitors all plant safety requirements, including criticality-related materials transfers.

(9) The safeguards system continually assesses the plant status and makes action recommendations to the general manager and plant manager in case of possible safeguards breaches.

REFERENCES

1. J. P. Shipley, D. D. Cobb, R. J. Dietz, M. L. Evans, E. P. Schelonka, D. B. Smith, and R. B. Walton, "Coordinated Safeguards for Materials Management in a Mixed-Oxide Fuel Facility," Los Alamos Scientific Laboratory report LA-6536 (February 1977).

2. E. A. Hakkila, D. D. Cobb, H. A. Dayem, R. J. Dietz, E. A. Kern, E. P. Schelonka, J. P. Shipley, D. B. Smith, R. H. Augustson, and J. W. Barnes, "Coordinated Safeguards for Materials Management in a Fuel Reprocessing Plant," Los Alamos Scientific Laboratory report LA-6881 (September 1977).

3. H. A. Dayem, D. D. Cobb, R. J. Dietz, E. A. Hakkila, E. A. Kern, J. P. Shipley, D. B. Smith, and D. F. Bowersox, "Coordinated Safeguards for Materials Management in a Nitrate-to-Oxide Conversion Facility," Los Alamos Scientific Laboratory report LA-7011 (April 1978).

4. H. A. Dayem, D. D. Cobb, R. J. Dietz, E. A. Hakkila, E. A. Kern, E. P. Schelonka, J. P. Shipley, and D. B. Smith, "Coordinated Safeguards for Materials Management in a Uranium-Plutonium Nitrate-to-Oxide Coconversion Facility: Coprecal," Los Alamos Scientific Laboratory report LA-7521 (February 1979).

5. L. D. Chapman, J. M. de Montmollin, J. E. Deveney, W. C. Fienning, J. W. Hickman, L. D. Watkins, and A. E. Winblad, "Development of an Engineered Safeguards System Concept for a Mixed-Oxide Fuel Fabrication Facility," Sandia Laboratories report SAND76-0180 (August 1976).

6. W. C. Fienning, A. E. Winblad, and J. P. Shipley, "A Preliminary Concept Definition of a Combined Safeguards System for a Mixed-Oxide Fuel Fabrication Facility," Sandia Laboratories report SAND77-0224 (October 1977).

7. W. D. Chadwick, G. E. Rochau, W. C. Fienning, R. B. McKnight, and A. E. Winblad, "A Concept Definition of an Engineered Safeguards System for a Spent Fuel Reprocessing Facility," Sandia Laboratories report SAND77-1539 (March 1979).

8. G. R. Keepin and W. J. Maraman, "Nondestructive Assay Technology and In-Plant Dynamic Materials Control--DYMAC," in Safeguarding Nuclear Materials, Proc. Symp., Vienna, October 1975 (International Atomic Energy Agency, Vienna, 1976) Paper IAEA-SM-201/32, Vol. I, pp. 304-320.

9. R. H. Augustson, N. Baron, R. F. Ford, W. Ford, J. Hagen, T. K. Li, R. S. Marshall, V. S. Reams, W. R. Severe, and D. G. Shirk, "A Development, Test and Evaluation Programme for Dynamic Nuclear Materials Control," in Nuclear Safeguards Technology 1978, Proc. Symp., Vienna, October 2-6, 1978 (International Atomic Energy Agency, Vienna, 1979), IAEA-SM-231/101, Vol. II, pp. 445-462.

10. J. H. Fuchs, D. M. Kisner, R. K. McClean, H. R. Milder, K. Mizuba, and G. E. Short, "Unified Safeguards Information System Concept," TRW Defense and Space Systems Group report 32076-6001-RU-00 (May 20, 1977).

11. D. M. Kisner, H. R. Milder, and K. Mizuba, "Preliminary Hardware Configuration Recommendations for Safeguards Information System," TRW Defense and Space Systems Group report 31134-6001-RU-00 (May 24, 1977).

12. J. M. Crawford, M. H. Ehinger, C. Joseph, and M. L. Madeen, "Development of a Computerized Nuclear Materials Control and Accounting System for a Fuel Reprocessing Plant," Nucl. Mater. Manage. VIII, 405-415 (1979).

13. J. M. Crawford, M. H. Ehinger, C. Joseph, and M. L. Madeen, "Nuclear Materials Control and Accounting System Test Program--FY 1977 Cold Uranium Run," Allied General Nuclear Services report AGNS-1040-2.2-2.5 (April 1978).

14. J. M. Crawford, M. H. Ehinger, C. Joseph, and M. L. Madeen, "Nuclear Materials Control and Accounting System Test Program--FY 1978," Allied General Nuclear Services report AGNS-1040-2.2-2.6 (August 1978).

APPENDIX E

DYNAMIC MATERIALS ACCOUNTING SYSTEMS: SOME DESIGN PRINCIPLES

D. D. Cobb
LASL Safeguards Staff (Q-4)

A. Introduction

This appendix presents principles that can serve as guidelines for designing an effective NM accounting system. These guiding principles should be of particular value to the design of nuclear processing facilities for which safeguards are important design criteria. It is not possible to give generic guidance for every application, because the relevance and the relative importance of the basic principles always will depend on the specific application.

Dynamic materials accounting systems are intended to provide timely assessments of the locations and amounts of NM.[1] To implement dynamic materials accounting, the facility may be partitioned into discrete accounting envelopes called UPAAs for which all significant transfers and in-process inventories of NM are measured. Quantities of material much smaller than the total plant inventory are controlled, and any unmeasured losses are localized both in space and time to that portion of the process contained in the UPAA. Thus, a potential divertor is forced to consider removing small amounts of material from several process locations over a relatively long time to avoid detection.

B. Measurement Models

Because the sensitivity of any accounting system is limited by measurement errors, measurement models and error estimates for various types of instrumentation are required to predict system performance.[1-3] One rather general measurement model is

$$m = M(1 + \varepsilon + \eta) \quad , \qquad \text{(E-1)}$$

where m is the measured value of a true quantity M. The measurement errors, ε and η, are discussed below. This model applies when error standard deviations are expressed on a relative basis and is appropriate for measurement situations in which the associated error tends to be proportional to the quantity being measured. Other models are available to describe the situation when the measurement errors tend to be additive and constant in magnitude.

The measurement errors in Eq. (E-1) have been grouped in two categories, instrument precision (ε) and calibration error (η). Both ε and η are regarded as observations on random variables. Instrument precision represents the deviation of the measured value from the true quantity caused by the dispersion in a set of individual measurement results (for example, the uncertainty caused by counting statistics in NDA measurements). The calibration error represents those errors that persist, unchanged, throughout a limited set of measurements as a result of the uncertainty in converting raw measurement results into the quantity of interest (for example, converting counts to plutonium mass for NDA measurements). The latter errors are the most difficult to estimate because they include uncertainties in standards, calibration parameters, and instrument environment.

The error random variables (ε and η) have means zero and variances σ_ε^2 and σ_η^2, respectively. The variance, σ_m^2, of the measured value m is given by

$$\sigma_m^2 = M^2\left(\sigma_\varepsilon^2 + \sigma_\eta^2\right) \quad . \tag{E-2}$$

To simulate a series of measurements from a given instrument, one value of ε is sampled from the appropriate ε-error distribution for each measurement, whereas a new value of η is sampled from the appropriate η-error distribution only when the instrument is recalibrated. All measurements from the same instrument having the same η error are correlated. These correlations become important and may dominate the materials balance error if the measurement method cannot be recalibrated frequently or if the source of the η error is not susceptible to calibration. The covariance between the i^{th} and j^{th} measurements is given by

$$\sigma_{ij} = M_i M_j \sigma_\eta^2 \quad . \tag{E-3}$$

C. An Example

1. Ideal Process. An example will serve to illustrate dynamic materials accounting concepts and principles. Figure E-1 represents an ideal process having a daily throughput of 50 kg of NM consisting of twenty-five 2-kg batches and no process losses. The in-process inventory of NM is 25 kg, and the residual holdup is 5 kg after shutdown and cleanout, which are postulated to occur once each month. The entire process is contained in a single MBA (Fig. E-1a), whereas storage areas for feed and product are in separate MBAs and are not shown.

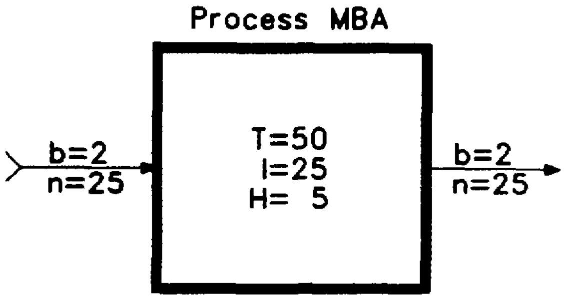
Figures E-1b and E-1c show two possible divisions of the process MBA into UPAAs for dynamic accounting purposes. In Fig. E-1b the MBA is divided into a series of five UPAAs. To accomplish this division, transfers of NM between adjacent UPAAs and the in-process inventory in each UPAA are measured. In Fig. E-1c, the MBA is divided into five parallel UPAAs. In this case the input, output, and inventory of each UPAA are measured. Note that each UPAA in the series arrangement has reduced inventory but the same throughput compared to the entire MBA, whereas each UPAA in the parallel arrangement has both reduced inventory and reduced throughput. In practice, the division of the MBA into UPAAs depends on the process configuration.

The uncertainty in measured materials balances for the ideal process can be calculated with the measurement model described in Sec. E-B. For a given accounting period during which N batches are processed, the dynamic materials balance, MB_N, for any single UPAA is given by

$$MB_N = \Delta I_N + T_N \quad , \qquad \text{(E-4)}$$

where ΔI_N is the net change in NM inventory and T_N is the net transfer of NM (inputs minus outputs) across the UPAA during the accounting period. If there were no measurement errors, MB_N would be exactly zero and, if the process were operated at steady state, ΔI_N and T_N would also be zero.

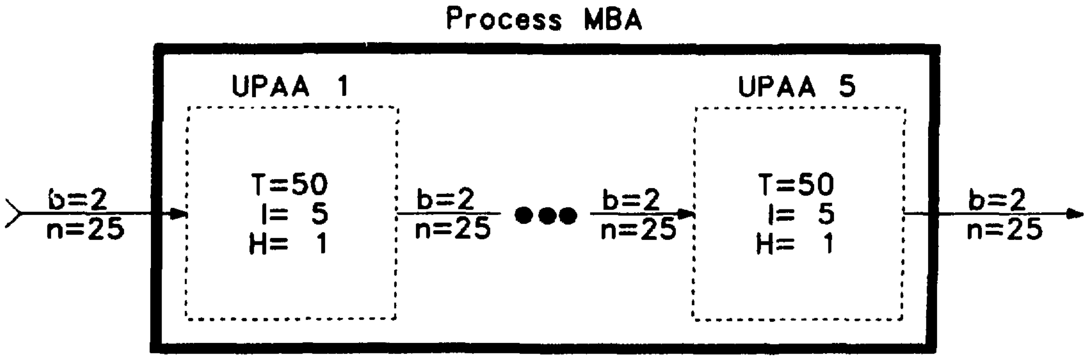
2. Materials Balance Variance. Measurement errors produce an uncertainty in MB_N having a variance σ^2_{MB} (assuming no correlation between transfer and inventory measurements) given by



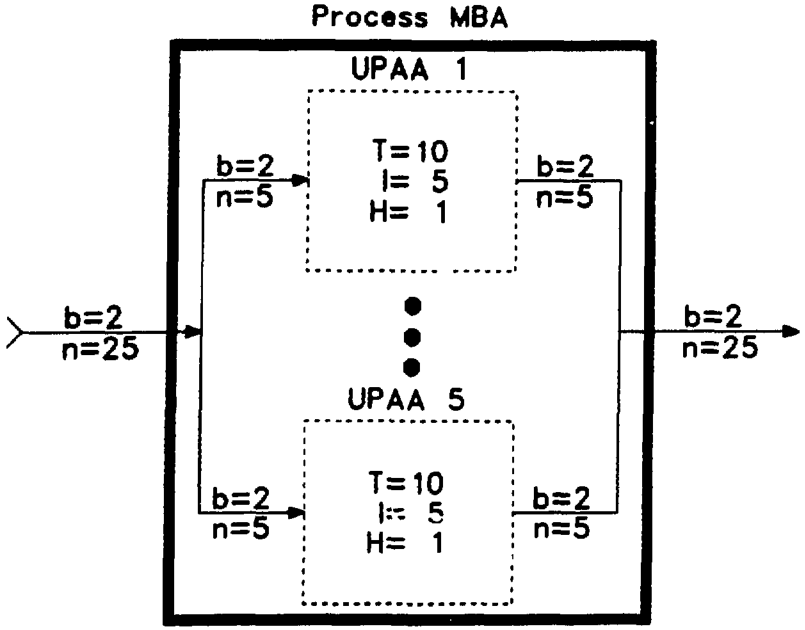
Legend

b=batch size(kg)
n=no. of batches/day
T=throughput(kg/day)
I=in-process inventory(kg)
H=holdup after cleanout(kg)

a. Ideal process MBA.



b. MBA divided into a series of five UPAAs.



c. MBA divided into five parallel UPAAs.

Fig. E-1. Ideal process block diagram.

$$\sigma^2_{MB} = \sigma^2_{\Delta I} + \sigma^2_{T} \quad . \tag{E-5}$$

An understanding of the behavior of the inventory-change and net-transfer variances, $\sigma^2_{\Delta I}$ and σ^2_{T}, is basic to the design of effective accounting systems.

3. Inventory Variance. With the measurement model of Sec. E-B, if the initial and final inventories, I_0 and I_N, are measured during the same calibration period (i.e., have the same ϵ error), the variance, $\sigma^2_{\Delta I}$, of the net inventory change, ΔI, is

$$\sigma^2_{\Delta I} = \left(I_0^2 + I_N^2\right)\sigma^2_{\epsilon I} + \left(I_0 - I_N\right)^2 \sigma^2_{\eta I} \quad , \tag{E-6}$$

where $\sigma^2_{\epsilon I}$ and $\sigma^2_{\eta I}$ are the ϵ- and η-error variances of the inventory measurements. Note that if the initial and final inventories are equal, $I_0 = I_N$, then $\sigma^2_{\Delta I}$ has the minimum value

$$\sigma^2_{\Delta I} = 2I_0^2\sigma^2_{\epsilon I} \quad . \tag{E-7}$$

For a large class of process equipment, efficiency and economy dictate that the in-process inventory be held nearly constant during normal operation. Such near-steady-state operation benefits materials accounting by reducing the contribution of inventory measurement errors to the materials-balance uncertainty. Furthermore, the condition $I_0 \simeq I_N$ implies that the dependence of σ_{MB} on $\sigma_{\eta I}$ is weak [Eq. (E-6)]; hence, a well-known value for $\sigma_{\eta I}$ is not required. This result is important because standardization of in-process inventory measurements may be difficult, especially for process equipment located in high radiation fields behind heavy shielding. The ideal process is assumed to satisfy the steady-state condition so that Eq. (E-7) holds. It is shown in Sec. E-C.4 that uncertainties in the measured inventories limit the accounting sensitivity over sufficiently short accounting periods.

b. Net Transfer Variance. The variance σ_T^2 of the net transfer T of material during the accounting period is

$$\sigma_T^2 = 2NB^2\sigma_{\varepsilon B}^2 + 2N^2B^2\sigma_{\eta B}^2 \quad , \tag{E-8}$$

where B is the input and output batch size (in this example, they are equal), and $\sigma_{\varepsilon B}^2$ and $\sigma_{\eta B}^2$ are the ε- and η-error variances of the input and output measurements. For simplicity of presentation, the error variances of the input and output measurements have been set equal, but the two measurement methods are uncorrelated (hence, the factor of 2).

The first term in Eq. (E-8) occurs whenever N input and N output batches are measured during the accounting period. The second term in Eq. (E-8) accounts for pair-wise correlations among those input or output measurements having a common calibration. The transfer measurements are correlated because the measurement methods are not recalibrated during the processing of N batches. Note that the number of pair-wise correlations increases as N^2: if N is sufficiently large, correlation terms make the dominant contribution to σ_T^2. The second term in Eq. (E-8) is equal to the first term after N_0 batches have been processed, where N_0 is

$$N_0 = \frac{\sigma_{\varepsilon B}^2}{\sigma_{\eta B}^2} \quad . \tag{E-9}$$

It is shown in Sec. E-C.4 that input-output measurement correlations limit the accounting sensitivity over sufficiently long accounting periods.

3. Recalibration. If the η-error sources are susceptible to calibration, the effect of transfer-measurement correlations is reduced by recalibrating the measurement methods. If the methods are calibrated K times during the accounting period, and if n_k is the number of batches processed between the kth and (k + 1)th calibrations, then σ_T^2 is given by

$$\sigma_T^2 = 2NB^2\sigma_{\varepsilon B}^2 + 2B^2\sigma_{\eta B}^2 \sum_{k=1}^{K} n_k^2 \quad , \tag{E-10}$$

where

$$N = \sum_{k=1}^{K} n_k \quad .$$

The number of correlation terms increases as Σn_k^2 with recalibration rather than as N^2 without recalibration. If the input-output measurements are calibrated K times during the processing of N batches and the period between calibrations is uniform, say, n batches are processed between any two calibrations, then N = Kn and the total number of correlation terms in Eq. (E-10) is Kn^2. This number can be substantially less than N^2 depending on the values chosen for K and n, that is, depending on the frequency of recalibration.

4. Results and Conclusions. Table E-I shows calculated values of the standard deviation, σ_{MB}, of dynamic materials balances for the ideal process. Results are given for four accounting periods: 1 batch, 1 day, 1 wk, and 1 month (30 days), and for two input-output calibration periods: 1 day and 1 month. The inventory-change [Eq. (E-6)] and the net-transfer [Eq. (E-10)] components of σ_{MB} are given separately. Calculated values are shown for one UPAA in a series arrangement, one UPAA in a parallel arrangement, and for the entire process MBA (see Fig. E-1).

The particular values of the measurement-error relative standard deviations (RSDs) used in the calculations are: $\sigma_{\varepsilon I}$ = 10%, $\sigma_{\varepsilon B}$ = 2%, and $\sigma_{\eta B}$ = 0.5%. The value of N_o [Eq. (E-9)] corresponding to these choices is 16, so that the η-terms are equal to the ε-terms in Eq. (E-10) after 16 batches have been processed. A 1-day calibration period corresponds to processing 25 batches through a single UPAA in series, 5 batches through a single UPAA in parallel, and 25 batches through the entire MBA between input-output calibrations.

TABLE E-I

DYNAMIC ACCOUNTING IN AN IDEAL PROCESS

	Standard Deviation (kg)					
	Monthly Recalibration			Daily Recalibration		
Accounting Period	Series UPAA	Parallel UPAA	Process MBA	Series UPAA	Parallel UPAA	Process MBA
Batch						
Inventory change	0.71	0.71	1.58	0.71	0.71	1.58
Net transfer	0.06	0.06	0.06	0.06	0.06	0.06
Material balance	0.71	0.71	1.58	0.71	0.71	1.58
Day						
Inventory change	0.71	0.71	1.58	0.71	0.71	1.58
Net transfer	0.45	0.14	0.45	0.45	0.14	0.45
Material balance	0.84	0.72	1.64	0.84	0.72	1.64
Week						
Inventory change	0.71	0.71	1.58	0.71	0.71	1.58
Net transfer	2.59	0.60	2.59	1.20	0.38	1.20
Material balance	2.68	0.93	3.03	1.39	0.80	1.98
Month						
Inventory change	0.14	0.14	0.32	0.14	0.14	0.32
Net transfer	10.72	2.23	10.72	2.48	0.79	2.48
Material balance	10.72	2.24	10.72	2.48	0.81	2.50

Examination of the data in Table E-I supports the following conclusions. For relatively short accounting periods (<1 wk in this example), the materials-balance standard deviation (σ_{MB}) is determined primarily by the size of the inventory (I) and the inventory instrument-precision RSD ($\sigma_{\varepsilon I}$). For longer accounting periods (1 wk or longer), σ_{MB} is determined primarily by the sizes of the transfers (B), the transfer calibration-error RSD ($\sigma_{\eta B}$), and the number (K) of transfer-measurement recalibrations. Similar conclusions have been noted previously,[1-4] and they apply generally to materials accounting in high-throughput processes.

Note that the results for the process MBA are a synthesis of the UPAA results. The particular synthesis used to calculate the process MBA values in Table E-I is very simple and represents only one possibility; namely, all the independent input and output measurements for the UPAAs are discarded, leaving only one input, one output, and five inventory measurement points for the entire MBA. If the inventories were measured only after a cleanout (at the end of each month in this example), then only one materials balance would be available per month. That situation corresponds to the process-MBA entries in the last row of Table E-I and represents the current practice of NM accounting. The other entries in Table E-I represent the additional information that becomes available for analysis if conventional accounting methods are augmented by dynamic materials accounting methods.

A more efficient synthesis of the UPAA data for the entire MBA is available. For example, the independent, parallel UPAA results in Table E-I can be combined in quadrature to yield results for the entire MBA. Consider the 1-month accounting data with no recalibration: the materials-balance standard deviation for one parallel UPAA is 2.24 kg; the standard deviation for all five parallel UPAAs (i.e., the MBA) is $2.24\sqrt{5} = 5$ kg, versus 10.7 kg obtained by discarding the independent UPAA input-output measurements. The corresponding values for 1 month with daily recalibration are 0.81 kg for one parallel UPAA and $0.81\sqrt{5} = 1.8$ kg for the MBA, versus 2.5 kg in Table E-I. A more efficient synthesis of the data from UPAAs in a series arrangement is also possible. The calculation is more complex and is not presented here; however, the advantage is similar to that shown for the parallel UPAA case.

D. Summary

The sensitivity, timeliness, and localization features of materials accounting systems are enhanced by dividing the process into UPAAs and measuring the transfers and in-process inventories of NM. The sensitivity over sufficiently short accounting periods is limited by uncertainties in the measured inventories. The sensitivity over sufficiently long accounting periods is limited by correlations between transfer measurements. Thus, the accessibility of process equipment and associated input-output streams for inventory and transfer measurements is an important consideration in designing high-throughput nuclear processes. Adequate measurement control should include well-characterized standards for input-output measurements and provision for frequent recalibration.

The UPAA data can be synthesized in space and time in a variety of ways to counter possible diversion strategies. This flexibility also enhances the overall system reliability. For example, if data from the measured intermediate transfers between two adjacent UPAAs in series are lost or compromised for some reason, the two UPAAs can be combined into a single UPAA and dynamic accounting can continue, although perhaps with some reduction in sensitivity. If all the measurements are available, the UPAAs are independent accounting envelopes providing maximum localization and overall system sensitivity. Furthermore, any combination of the UPAA data may be examined for diversion using appropriate data-analysis software. Techniques have been developed for computer-based analysis of dynamic materials accounting data. These techniques, referred to as decision analysis, are described elsewhere.

The materials accounting sensitivity achievable by applying the design principles depends on the process. Every process is unique, and a significant difference in process or measurement parameters will alter the relative importance of these principles. Clearly, a detailed analysis is required in every case to reach quantitative conclusions. The analysis should include detailed descriptions (models) of the process, the proposed measurements, and the proposed data-analysis procedures. It should be kept in mind that, ultimately, the sensitivity will be limited by measurement correlations and biases. The extent to which those effects are identified and included in the analysis will determine how faithfully the analysis predicts the actual system performance. The most efficient and cost-effective procedure is to incorporate the design of the materials accounting system into the design of the process at an early stage.

REFERENCES

1. H. A. Dayem, D. D. Cobb, R. J. Dietz, E. A. Hakkila, J. P. Shipley, and D. B. Smith, "Dynamic Materials Accounting in the Back End of the LWR Fuel Cycle," Nucl. Technol. 43(2), 222-243 (1979).
2. D. D. Cobb and J. P. Shipley, "Performance Analysis of Nuclear Materials Accounting Systems," Nucl. Mater. Manage. VIII(2), 81-92 (Summer 1979).
3. J. L. Jaech, "Statistical Methods in Nuclear Material Control," TID-26298, Technical Information Center, Oak Ridge, Tennessee (1973).
4. T. I. McSweeney, J. W. Johnston, R. A. Schneider, and D. P. Granquist, "Improved Material Accounting for Plutonium Processing Facilities and a 235-U-HTGR Fuel Fabrication Facility," Battelle-Pacific Northwest Laboratories report BNWL-2098 (October 1975).

APPENDIX F

MODELING AND SIMULATION APPROACH

H. A. Dayem
LASL Safeguards Staff (Q-4)

A. Introduction

Modeling and simulation of a facility and its MMAS are an essential part of the design and evaluation of safeguards systems. Materials accounting operating data from nuclear fuel-cycle facilities are generally not available because the facilities either have not been used in production or have not been built. Even if facilities with advanced accounting systems were operating, their use in the design and evaluation of alternative operating and accounting strategies would be time-consuming, expensive, and impractical. Therefore, the necessary operating and measurement environment must be simulated by models that are based on and are consistent with current best estimates of the expected performance of the process and the measurement system. Modeling and simulation techniques permit the prediction of the behavior of materials flows and materials measurements under a wide range of operating parameters and quickly accumulate data representative of relatively long operating periods.

The modeling and simulation approach requires:[1]

(1) A dynamic model of the process based on design data;
(2) Simulation of the model process on a computer:
(3) A dynamic model for each measurement system;
(4) Simulation of accountability measurements on NM flow and in-process inventory data from the model process; and
(5) Evaluation of simulated data from various materials accounting strategies.

B. Process Model

A detailed reference process design is required for making quantitative estimates of MMAS sensitivity because process variability, particularly in the levels of in-process inventory and material sidestreams (scrap, waste, and recycle), can significantly affect materials control. Operation of a model process is simulated by standard Monte Carlo techniques developed for dynamic systems.[2,3] The dynamics of each process step are described by the continuity equation written for the flows of bulk material and NM:

$$\dot{V} = \sum_i F_i \quad ,$$

$$\dot{H} = \sum_i C_i F_i \quad , \qquad (F\text{-}1)$$

where

i = i^{th} material flow,

F = volumetric or mass flow rate of bulk material (inputs positive, outputs negative),

C = NM concentration,

V = bulk volume or weight,

H = in-process inventory of NM,

$(\dot{})$ = time derivative, and

Σ = summation over all materials flows.

The solution of the complete set of coupled differential equations for all process steps, subject to initial conditions and subsidiary constraints, describes the process dynamics. Random variation in the process is determined by the statistics selected for the independent process variables. The independent variables are selected after a detailed examination of the process and the operating procedures.

A computer code is developed to simulate the operation of the model process. The GASP IV simulation package[4] is used to schedule process events and to provide other routine services. GASP IV can execute both discrete-event and continuous-time simulations.

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

1. Large Chemical Separations Facility. The large chemical separations facility model is based on a Purex flow sheet using the AGNS's BNFP as a reference design.[5] The process descriptions and data in Ref. 5 have been clarified, supplemented, and updated in discussions with AGNS personnel. The chemical separations facility is conveniently divided into three modules: codecontamination-partitioning processes (CPP), plutonium purification process (PPP), and uranium purification process (UPP). The following is a brief description of process operation (see App. B and Ref. 5 for details).

Figure F-1 is a block diagram of the CPP. On the average, two and one-half dissolver batches are transferred to the accountability tank every day. After the accountability tank level is measured and samples are taken for chemical analysis, the solution is transferred to one of two parallel feed-adjustment tanks for final acid adjustment before being fed to the centrifuge.

The dissolution and feed preparation are batchwise operations. The rest of the process, from the high activity feed (HAF) tank to the product catch tanks, operates continuously. The HAF tank continuously feeds a codecontamination and a partitioning stage in which aqueous and organic phases are contacted in a centrifugal contactor (the HA contactor) and then in a sequence of three pulse columns (the HS, 1B, and 1BX columns). Solids from the centrifuge are periodically flushed into the high-activity waste (HAW) sample tank. High-level waste from the HA contactor is concentrated and collected in the HAW sample tank. The volume of the HAW sample tank is measured and a sample is taken for chemical analysis approximately every 16 h before the batch is transferred to high-level waste storage. Table F-I lists the amounts of material transferred per batch for the batch portion of the model CPP. Table F-II lists typical uranium and plutonium concentrations and volumetric flow rates in the model CSP streams. Nominal in-process inventory values are given in Table F-III.

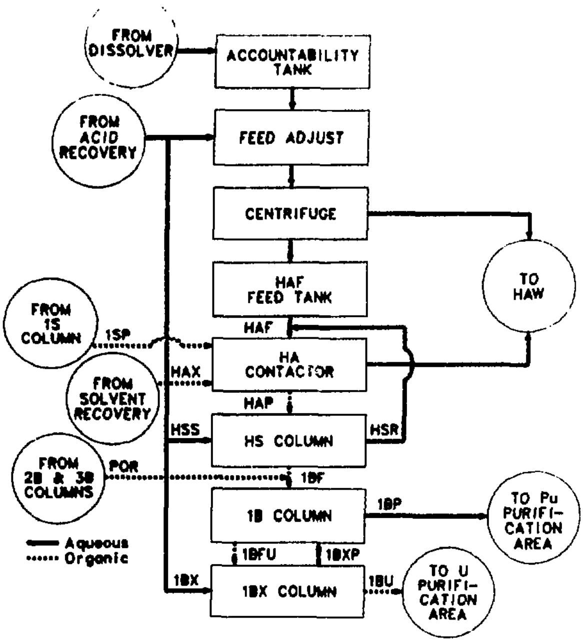


Fig. F-1. Codecontamination-partitioning process block diagram.

TABLE F-I

MODEL CPP BATCH TRANSFERS[a]

Batch Identification	Volume (L/batch)	U Concentration (g/L)	Pu Concentration (g/L)
Accountability tank[b]	6700	297	2.97
Feed-adjust chemicals[b]	500	--	--
Feed adjust[b]	7200	276	2.76
HAW sample tank[c]	2358	3.57	0.141

---

[a] These values are not flow-sheet values for any existing reprocessing facility but represent typical values within reasonable ranges of a workable flow sheet.

[b] A batch is processed every 9.6 h.

[c] A batch is processed every 16 h.

Figure F-2 is a block diagram of the PPP. After the first stage of fission-product extraction and uranium-plutonium solvent-extraction cycles, the 1BP stream from the 1B electropulse column enters the 1BP surge tank. The 1BP stream is a solution of plutonium nitrate (∿5 g Pu/L), and approximately twice as much uranyl nitrate, in 2.5 M HNO_3. The 1BP surge tank continuously feeds two additional solvent extraction cycles in which aqueous and organic phases are contacted in a sequence of four pulse columns--the 2A, 2B and the 3A, 3B columns. The aqueous and organic waste streams (raffinates) from the pulse columns contain virtually all the residual uranium and fission products. The product stream (3BP) from the 3B column passes through the 3PS diluent-wash column, and then is concentrated in the 3P concentrator to produce an essentially pure solution of plutonium nitrate (∿250 g Pu/L) in 2.8 M HNO_3. The concentrator product (3PCP) is collected in the plutonium catch tank, which has an 8-h surge capacity. At this point, the PPP is converted to a batch process. After the catch tank is filled, the contents are pumped rapidly to the plutonium sample tank, which has a 24-h surge capacity. The contents of the sample tank, in turn, are pumped to one of three interim product storage tanks, each with a surge capacity of ∿48 h, to await transfer to the plutonium product loadout (storage) area.

TABLE F-II

MODEL CPP CONTINUOUS FLOW STREAMS [a]

Stream[b] Identification	Flow Rate[c] (L/h)	Uranium[c] Concentration (g/L)	Plutonium[c] Concentration (g/L)
HSR	350	20	1
HAF	1100	194.8	2.2
HAW	1100	0.5	0.02
1SP	800	6.3	0.09
HAX	1800	--	--
HAP	2600	84.1	1.0
HSS	350	--	--
POR	250	15	0.01
1BF	2850	75.6	0.7
1BP	425	8.82	5.0
1BFU	2850	75	0.006
1BXP	425	4.4	0.04
1BX	425	--	--
1BU	2850	74.3	--

---

[a] These values are not flow-sheet values for any existing reprocessing facility but represent typical values within reasonable ranges of a workable flow sheet.

[b] See Fig. F-1 for stream identification.

[c] Materials flow rates may not balance exactly because of round-off error.

TABLE F-III

MODEL CPP IN-PROCESS INVENTORIES[a]

Identification[b]	Volume (L)	Uranium[c] Concentration (g/L)	Plutonium[c] Concentration (g/L)
Centrifuge	80	276	2.76
HAF feed tank	13 000	276	2.76
HA contactor	100	100	1
HS column	1 500	100	1
1B column	800	200	2
1BX column	2 400	62	0.4

---

[a] These values are not flow-sheet values for any existing reprocessing facility but represent typical values within reasonable ranges of a workable flow sheet.

[b] See Fig. F-1.

[c] Average concentration, a model of the concentration profiles and the holdup in pulse columns is described in App. J.

The PPP is designed to recover 50 kg of plutonium per day from spent fuel containing ∿1 wt% plutonium. Table F-IV lists typical plutonium concentrations and volumetric flow rates in the model PPP streams. Nominal in-process holdup values given in Table F-V are based on typical Purex process inventories. Note that the total in-process holdup is ∿41 kg of plutonium in the continuous part of the model PPP, i.e., in that portion of the process preceding the catch tank. Therefore, the residence time of plutonium in the continuous portion of the process is 20 h. The continuous nature of the process and the long residence time are important design considerations for the safeguards system.

Figure F-3 is a block diagram of the UPP. After fission product extraction and uranium-plutonium partition, the 1BU stream passes from the 1BX column to the 1C column. The 1BU stream contains essentially no plutonium. The rest of the UPP

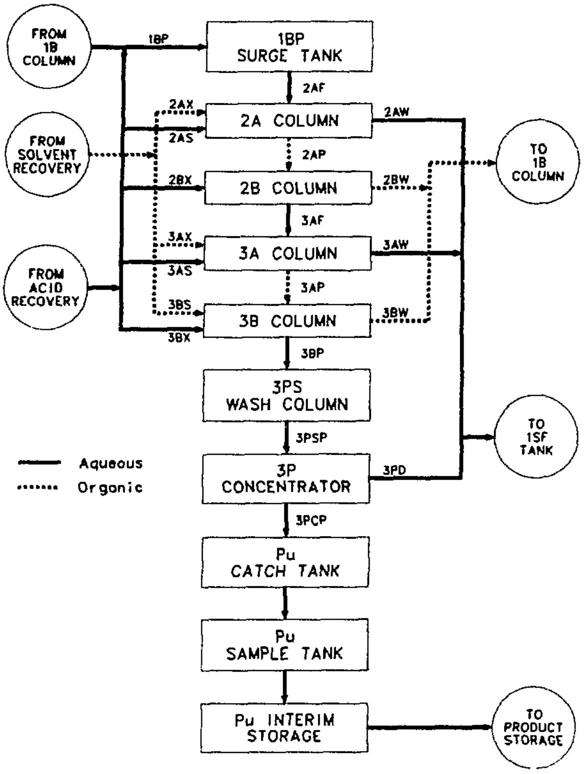


Fig. F-2. Plutonium purification process block diagram.

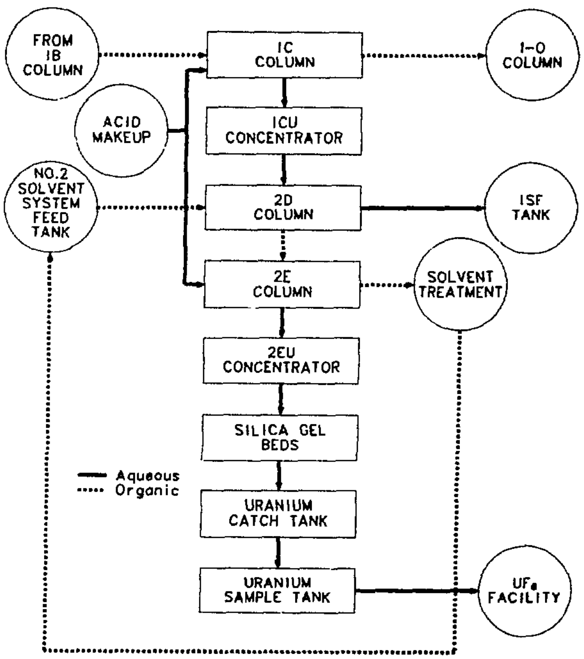


Fig. F-3. Uranium purification process block diagram.

comprises a concentrator to adjust the uranium concentration; an extraction cycle to remove ruthenium, zirconium-niobium, and residual plutonium; another concentrator; and silica-gel beds to remove residual traces of zirconium-niobium. The UPP produces a 4460-L batch containing 373.66 g U/L approximately every 8 h.

2. Conversion Process. The conversion process model is based on a preliminary SRL-SRP design.[6,7] This process converts plutonium nitrate solution, $Pu(NO_3)_4$, from a chemical separations facility to plutonium oxide powder, PuO_2, suitable for MOX fuel fabrication. Conversion is by the plutonium (III) oxalate precipitation process with a nominal throughput of 59 kg of plutonium per day (see App. B).

Figure F-4 shows the model conversion process. Plutonium nitrate solution from the chemical separations facility is fed to a receipt tank (∿200 L, ∿30 g Pu/L). The receipt tank is air-sparged and mechanically agitated, and an accountability sample is taken

TABLE F-IV

PLUTONIUM CONCENTRATIONS AND VOLUMETRIC FLOW RATES IN STREAMS OF THE MODEL PPP[a]

Stream Identification[b]	Flow Rate (L/h)	Plutonium Concentration (g/L)	Plutonium Flow Rate (g/h)
1BP	425.0[c]	5.0[c]	2125.0
1B Acid, $NaNO_2$	5.0	--	--
2AF	430.0[c]	4.942	2125.0
2AS	60.0[c]	--	--
2AX	150.0[c]	--	--
2AW	490.0	0.10	49.0
2AP(2BF)	150.0	13.84	2076.0
2BX	130.0[c]	--	--
2BW	150.0	0.010	1.50
2BP(3AF)	130.0	15.96	2074.5
3AS	60.0[c]	--	--
3AX	80.0[c]	--	--
3AW	190.0	0.10	19.0
3AP(3BF)	80.0	25.69	2055.5
3BS	20.0[c]	--	--
3BX	35.0[c]	--	--
3BW	100.0	0.010	1.0
3BP(3PSF)	35.0	58.70	2054.5
3PSP(3PCF)	35.0[c]	58.70	2054.5
3PD	26.79	0.10	2.679
3PCP	8.207[c]	250.0	2051.8

---

[a] These values are not flow-sheet values for any existing reprocessing facility but represent typical values within reasonable ranges of a workable flow sheet.

[b] See Fig. F-2.

[c] These quantities are independent, stochastic variables in the computer simulation (Sec. F-B).

TABLE F-V

IN-PROCESS HOLDUP IN TANKS AND VESSELS OF THE MODEL PPP [a]

Identification[b]	Volume (L)	Plutonium Concentration (g/L)	Plutonium Holdup (g)
1BP Tank	1500	4.942	7413
2A Column	700	c	4595
2B Column	500	c	2804
3A Column	600	c	5422
3B Column	440	c	4800
3PS Wash Column	20	58.70	1174
3P Concentrator	60	250.	15000
Pu Catch Tank (8-h surge)	65.66	250.	16415
Pu Sample Tank (24-h surge)	196.98	250.	49244
Pu Interim Storage Tank (48-h surge)	393.95	250.	98487

---

[a] These values are not flow-sheet values for any existing reprocessing facility but represent typical values within reasonable ranges of a workable flow sheet.

[b] See Fig. F-2.

[c] A model of the concentration profiles and the holdup in the pulse columns is described in App. J.

before three ∿67-L batches are metered to three different valence adjustment tanks. The last batch completely empties the receipt tank. Hydrazine and ascorbic acid are added to the valence adjustment tank to reduce the plutonium to the trivalent state. The adjusted solution (∿26.5 g of Pu/L) is transferred to a precipitator and digested with oxalic acid to produce an oxalate slurry, which is vacuum-filtered through sintered-metal filter boats. The wet cake (∿2 kg Pu) is washed with ∿12 L of 0.5 $\underline{M}$ HNO_3 and 0.3 $\underline{M}$ oxalic acid.

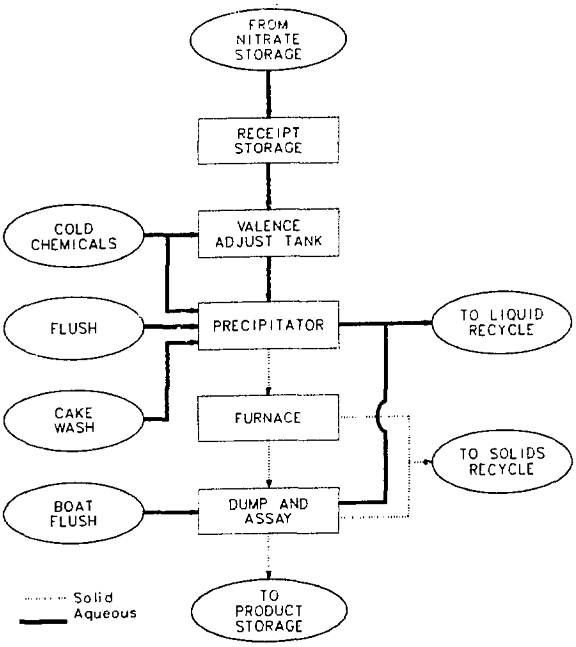


Fig. F-4. Conversion process block diagram.

The filtrate and cake wash solution (∿30 mg Pu/L) is transferred to recovery operations. The boat is fed into a furnace for drying and calcining, which take ∿6 h. The calcined product in each boat is transferred to a container for sampling and storage. The filter boat is flushed with ∿5 L of HNO_3 and rinsed with ∿1 L of water before being returned to a filter station. The flush and rinse solutions are transferred to recovery.

The model process has a throughput of 50 kg of plutonium per day; on the average a 2-kg batch is processed every 58 min. Table F-VI lists typical batch sizes and concentrations in the model process.

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

3. The Model Small Chemical Separations Facility. The small chemical separations facility model is based on a Purex flow sheet that uses the Tokai-mura plant as the reference design.[8] The process description in Ref. 8 is not sufficiently detailed to develop a dynamic model of the process. However, a static model of the main process streams was developed. Assumptions that are consistent with the plant throughput were made in cases where necessary information was not available. As in the large chemical separations facility, the Tokai facility can be divided into three modules: codecontamination-partitioning processes (TCPP), plutonium purification process (TPPP), and uranium purification process (TUPP).

Figures F-5 through F-7, respectively, are block diagrams of the TCPP, TPPP, and TUPP. Table F-VII lists the in-process inventories of the major process vessels. The inventories are based on data in Ref. 8 for reprocessing PWR fuel with a burnup of

TABLE F-VI

BATCH SIZES AND CONCENTRATIONS IN STREAMS OF THE MODEL CONVERSION PROCESS

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

---

[a] See Fig. F-4.

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

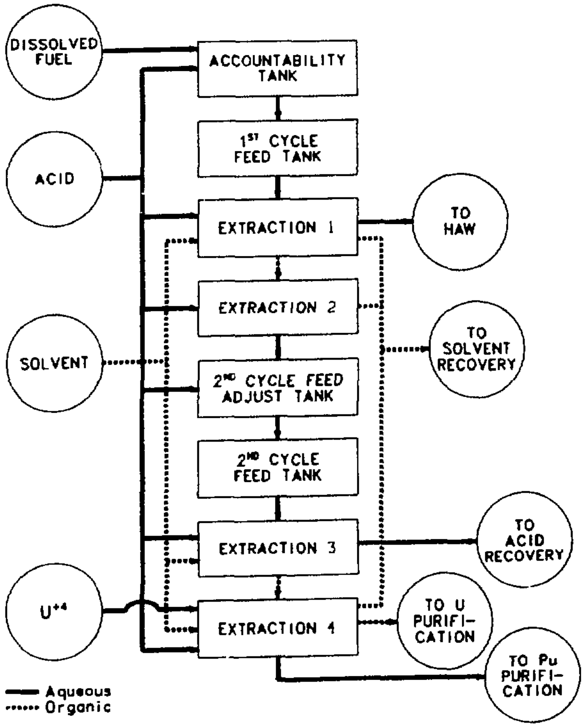


Fig. F-5. Tokai codecontamination-partitioning process block diagram.

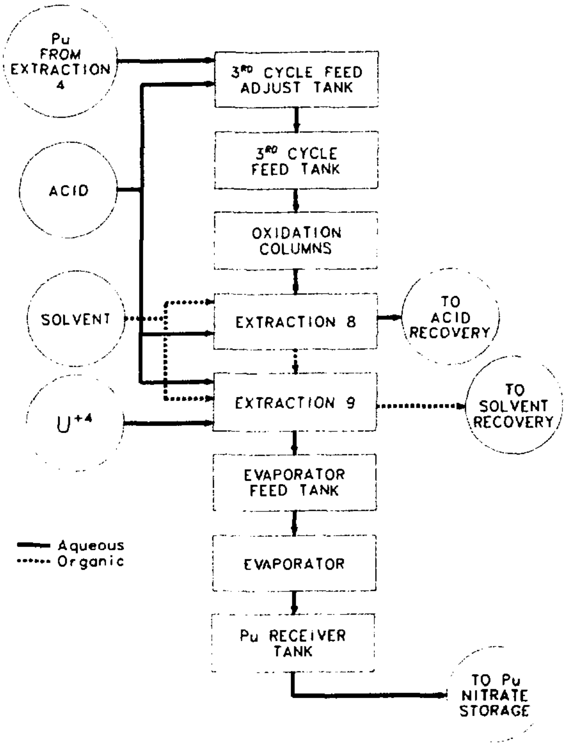


Fig. F-6. Tokai plutonium purification process block diagram.

27 500 MWD/T. It is assumed that two 1750-L accountability batches containing 180 g U/L and 2 g Pu/L, a single 28-L plutonium nitrate product batch containing 250 g Pu/L, and four 630-L uranyl nitrate batches containing 250 g U/L are processed every day.

4. Example. Figures F-8 through F-10 show sample data generated by the conversion model process NOCSIM (nitrate to oxide conversion simulation) from a typical day of process operation. Values of NM variables are plotted at event times.

The concentration and mass of precipitator feed batches are given in Figs. F-8 and F-9, respectively. The input concentration varies uniformly over the range 24-25 g Pu/kg and the input mass over the range 79-84 kg. Figure F-10 shows the in-process inventory in a precipitator. The abrupt change in holdup near 13 h is caused by runout of the precipitator line followed by feed transfer to a clean standby line. Note that the materials transfers and holdup quantities are calculated in terms of total mass (kg) and

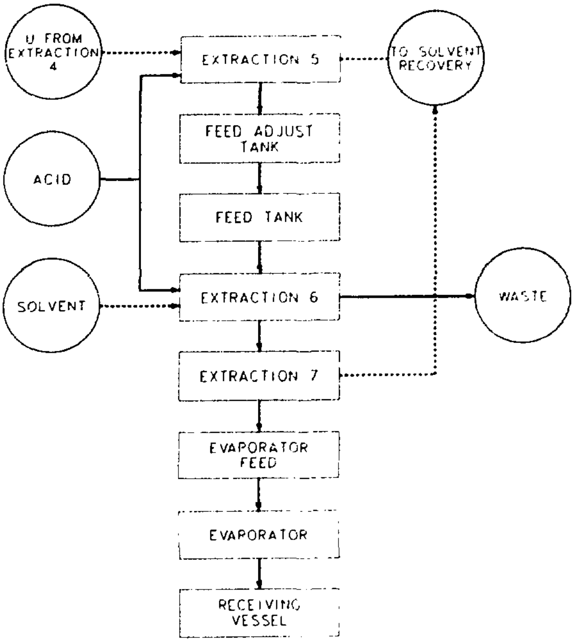


Fig. F-7. Tokai uranium purification block diagram.

TABLE F-VII

IN-PROCESS INVENTORIES IN THE MODEL TOKAI FACILITY

Identification	Inventory (kg)
1st cycle feed tank	2.5
Extraction 1	0.7
Extraction 2	0.1
2nd cycle adjust tank	0.04
2nd cycle feed tank	1.3
Extraction 3	0.5
Extraction 4	0.4
3rd cycle adjust tank	0.1
3rd cycle feed tank	1
Oxidation columns	0.2
Extraction 8	0.5
Extraction 9	0.3
Evaporator feed tank	1.1

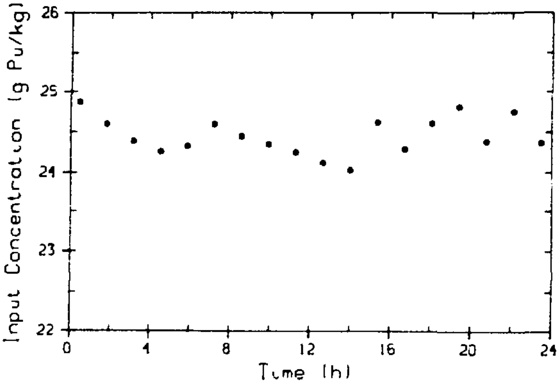


Fig. F-8. Precipitator feed concentration.

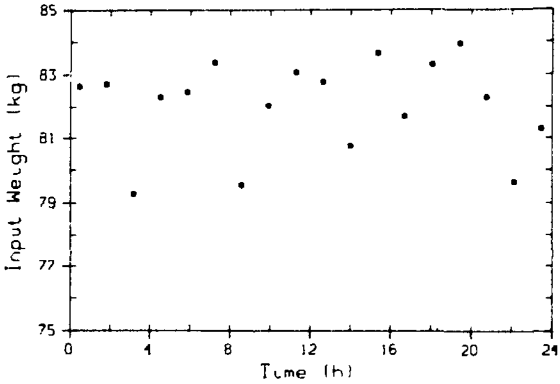


Fig. F-9. Precipitator feed weight.

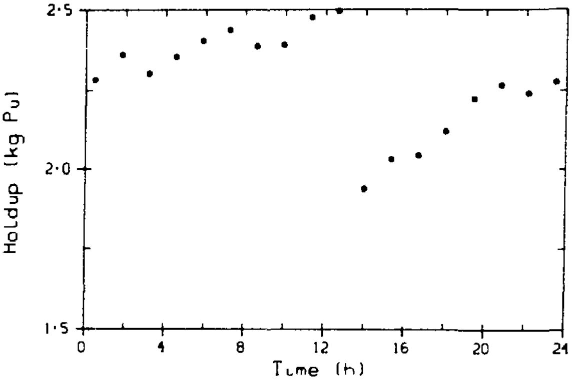


Fig. F-10. Precipitator in-process inventory.

plutonium mass fraction (kg Pu/kg) because the material changes form in the precipitator (liquid to slurry) and volumes are not conserved.

C. Measurement Models

Operation of the materials measurement and accounting system is simulated by another Monte Carlo computer code. The code simulates measurements of the "true" materials flow data generated by the model process and calculates appropriate components of variance and covariance.[9]

The measurements simulation code incorporates both additive and multiplicative measurement-error models.[10] The model chosen for a particular measurement depends on the characteristics of the types of instruments available.

1. Additive Model. In the additive model, the measured value m of a true quantity M is given by

$$m = M + \varepsilon + \eta \quad , \tag{F-2}$$

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

$$\sigma_m^2 = \sigma_\varepsilon^2 + \sigma_\eta^2 \quad . \tag{F-3}$$

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

$$\sigma_{ij} = \sigma_\eta^2 \quad . \tag{F-4}$$

2. Multiplicative Model. In this model, the measured value m of a true quantity M is given by

$$m = M(1 + \varepsilon + \eta) \quad , \tag{F-5}$$

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

$$\sigma_m^2 = M^2\left(\sigma_\varepsilon^2 + \sigma_\eta^2\right) \quad . \tag{F-6}$$

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

$$\sigma_{ij} = M_i M_j \sigma_\eta^2 \quad . \tag{F-7}$$

3. Measurement Simulation. In the measurement simulation, a value for η is sampled periodically from the appropriate distribution to coincide with the frequency of instrument recalibration. A value of ε is sampled for each measurement. Variance and covariance terms are estimated by replacing the true quantities M by the appropriate measured quantities. The precisions and accuracies assigned to the measurements are based on estimates for similar instrumentation.

D. Materials Balances

Each materials balance MB is a linear combination of measured quantities P_i of plutonium.

$$MB = \sum_{i=1}^{n} c_i P_i \quad , \qquad (F-8)$$

where c_i is +1 if P_i is an input or an initial in-process inventory and -1 if P_i is an output or final in-process inventory quantity for the accounting area. Often, the measured mass of plutonium is given by the product P of two different measured quantities.

$$P = xy \quad , \qquad (F-9)$$

where x is either liquid volume or mass, and y is either plutonium concentration or mass fraction. The measurement-error model for both x and y is similar to that given in Eq. (F-2) or Eq. (F-5).

$$x = X + \varepsilon_x + \eta_x \quad \text{and} \quad y = Y + \varepsilon_y + \eta_y$$

for the additive model, or

$$x = X(1 + \varepsilon_x + \eta_x) \quad \text{and} \quad y = Y(1 + \varepsilon_y + \eta_y)$$

for the multiplicative model, where X and Y are true values, and the error components are defined as in Eq. (F-2) or Eq. (F-5). In some cases, the additive model may be appropriate for one of the measured quantities (X or Y), whereas the multiplicative model is appropriate for the other. In such cases, a combined model is used.

The variance σ^2_{MB} in the computed value of a materials balance is a combination of the variances of the contributing measured values. Ordinarily, several measurements will be made with a given instrument before it is recalibrated, and appropriate correlation terms must be included in the computation of the materials balance variance. The general form of the equation used to estimate the variance of each materials balance is

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

$$+ \sum_{i=1}^{n} \sum_{j=1}^{n} a_i a_j X_i X_j Y_i Y_j \tag{F-10}$$

$$\cdot \left(q_{ij}\sigma_{\eta_x}^2 + p_{ij}\sigma_{\eta_y}^2\right) \ .$$

The quantity q_{ij} is +1 if X_i and X_j have been measured with a common value of $\sigma_{\eta x}$ (that is, using the same instrument calibration) and is zero otherwise. Similarly, p_{ij} is +1 or 0, depending on whether a common value of $\sigma_{\eta y}$ was used in the measurements of Y_i and Y_j. Each i = j term in the double sum in Eq. (F-10) is the component of variance caused by calibration uncertainty for a single measurement; these terms are present even if all measurements of X or Y are uncorrelated.

Equation (F-10) is written for the case where the multiplicative model is appropriate for the measurement of both X and Y. If the additive model applies to either measurement, the corresponding quantity (X or Y) is set to unity.

Measured values of net materials transfers and initial and final in-process inventories, along with appropriate components of variance and covariance, are computed by the measurement simulation code for each materials balance period. These quantities are sufficient for computation of materials balances, Cusums, and the other test statistics described in Ref. 5.

In terms of the net transfer T (inputs positive, outputs negative), initial inventory I_i, and final inventory I_f, the materials balance equation becomes

$$MB = T + I_i - I_f \quad . \tag{F-11}$$

In some of the proposed accounting strategies, the terms in the computation of the materials balance variance, Eq. (F-10), arising from calibration errors in the inventory measurements approximately cancel because two inventory measurements appear with opposite signs in each materials balance equation. The magnitude of these terms is $(I_i - I_f)^2 \sigma_\eta^2$. In such cases, if the model process is operated near steady state so that $I_i \approx I_f$, the contribution to σ^2_{MB} is relatively small; that is, calibration errors in the inventory measurements nearly cancel. In the error model, perfect cancellation is assumed for those in-process inventories in which $I_i \approx I_f$, and σ_η is set to zero for the associated in-process inventory measurements.

REFERENCES

1. D. D. Cobb and D. B. Smith, "Modeling and Simulation in the Design and Evaluation of Conceptual Safeguards Systems," Nucl. Mater. Manage. VI(III), 171-184 (1977).
2. T. Naylor, J. L. Balintfy, D. S. Burdick, and K. Chu, Computer Simulation Techniques (John Wiley and Sons, New York, 1966).
3. J. Kleijnen, Statistical Techniques in Simulation (Marcel Dekker, New York, 1974).
4. A. Pritsker, The GASP IV Simulation Language (Wiley-Interscience, New York, 1976).
5. "Barnwell Nuclear Fuels Plant Separations Facility--Final Safety Analysis Report," Docket 50-332, Allied-General Nuclear Services, Barnwell, South Carolina (October 10, 1973).
6. Savannah River Laboratory document DPSTP-LWR-76-5 (November 1976).
7. Savannah River Plant document DPSP-LWR-77-29 (March 1977).
8. K. Ikawa, H. Ihara, H. Sakuragi, H. Nishimura, and M. Hirata, "Study of the Application of Dynamic Principles to Safeguarding Spent Fuel Reprocessing Plants," Japan Atomic Energy Research Institute report JAERI-memo-8241 (April 1979).
9. J. P. Shipley, "Data Analysis for Nuclear Materials Accounting," Proc. Symp. Safeguards and Nucl. Mater. Manage., 1st, Brussels, Belgium, 1979 (Commission of European Communities, Ispra, 1979), pp. 391-395.
10. J. L. Jaech, "Statistical Methods in Nuclear Material Control," TID-26298, Technical Information Center, Oak Ridge, Tennessee (1973).

APPENDIX G

OPTIMIZATION OF MEASUREMENT CONTROL

J. T. Markin
LASL Safeguards Staff (Q-4)

A. Introduction

Keeping materials balance variances within acceptable limits requires some form of measurement control. For processes operating near steady state and having small fluctuations in inventory (the desired case in high-throughput commercial facilities), the net transfer measurement errors soon become the dominant component of the materials balance variance.[1] Control of the net transfer measurement error so that major systematic errors do not propagate over long times is possible, for example, through judicious recalibration of the transfer measurement instruments. However, if the process contains many such instruments, with a variety of error variances and calibration costs, then the best allocation of limited recalibration resources may be uncertain. In this appendix we propose a simple method for allocating resources that is optimal in the sense of achieving the minimum net transfer variance within a resource constraint. Use of the method requires only a common measure of recalibration costs and a knowledge of error structure for each instrument.

The method allows a proposed process to be analyzed for the minimum net transfer variance attainable at any level of recalibration resource investment, allows an existing process to be analyzed for the impact on the net transfer variance of proposed instrumentation changes, and permits specific instrument recalibration schedules to be developed for use in process simulations. The utility of the method is illustrated in the sequel by an example drawn from a commercial reprocessing plant in which reductions in the net transfer variance attained with an optimal recalibration strategy are compared with some other intuitively reasonable strategies.

B. Net Transfer Variance Propagation

Measurement error models for a single instrument include both additive and multiplicative forms.[2] Although the measurement control methods developed in this appendix apply equally to either model, we assumed for this purpose the multiplicative form

$$M = M^a(1 + \varepsilon + \eta) \quad , \qquad \text{(G-1)}$$

where M is the measured value, M^a is the actual value, ε is the random error component, and η is the calibration error component. With this model, the variance of the sum of N batch-transfer measurements made with the instrument is[1]

$$\sigma_T^2 = Nb^2\left(\sigma_\varepsilon^2 + \sigma_\eta^2\right) + b^2\sigma_\eta^2 \sum_{k=1}^{K} n_k\left(n_k - 1\right) \quad , \qquad \text{(G-2)}$$

where K is the number of recalibrations, n_k is the number of batches between the k and $(k+1)^{st}$ recalibrations, and b is the batch size (here assumed constant).

The second term in Eq. (G-2) represents the contribution to the transfer variance made by correlations between measurements that were made with the same unrecalibrated instrument. This is the component of Eq. (G-2) that can be reduced by more frequent recalibrations; the first term remains unchanged. If there is more than one materials transfer stream to be measured, then σ_T^2 is the sum of terms of the form Eq. (G-2), one term for each instrument used in a transfer measurement, assuming that each instrument is dedicated to one materials transfer stream. Efficient recalibration allocations are obtained by minimizing the sum of these terms and choosing an appropriate number of recalibrations K for each instrument.

C. Recalibration Strategies

A recalibration strategy is an assignment of a specified number of recalibrations to each instrument over some time interval. Such a strategy is said to be optimal if it minimizes σ_T^2 under a given resource constraint. By modification of Eq. (G-2), some standard mathematical methods can be applied to solve for an optimal strategy. We show later in this appendix that, for a fixed number of recalibrations K, the net transfer variance in Eq. (G-2) is minimized by choosing a uniform spacing between recalibrations, i.e., the n_k of Eq. (G-2) should be chosen as nearly equal as possible. It follows (see discussion below) that a good approximation to the transfer correlation term in Eq. (G-2) is

$$b^2\sigma_\eta^2 N\left(\frac{N}{K} - 1\right) \quad . \qquad \text{(G-3)}$$

Clearly, increasing K, the number of recalibrations, will reduce σ_T^2.

If two instruments have systematic error variances σ_1^2, σ_2^2 and costs per recalibration C_1, C_2, the expression in Eq. (G-3) allows the problem of finding an optimal strategy to be formulated as

$$\text{minimize } b^2\sigma_1^2 N\left(\frac{N}{K_1} - 1\right) + b^2\sigma_2^2 N\left(\frac{N}{K_2} - 1\right) \qquad \text{(G-4)}$$

subject to the constraint

$$K_1 \times C_1 + K_2 \times C_2 \leq C \quad . \qquad \text{(G-5)}$$

Here K_1 and K_2 are the number of recalibrations for each instrument that are to be determined, and C is an upper limit on recalibration costs. The problem in Eq. (G-4) is solved by standard optimization methods. A program, RECAL, that incorporates a dynamic programming algorithm was written to solve problems of the form of Eq. (G-4) and was applied to data from a commercial reprocessing plant.

D. Optimal Recalibration Interval

To show that the expression

$$\sum_{k=1}^{K} n_k(n_k - 1) \qquad \text{(G-6)}$$

constrained by

$$\sum_{k=1}^{K} n_k = N \qquad \text{(G-7)}$$

is minimized by choosing the n_k equal, use the method of Lagrange multipliers. Define the relation

$$L = \sum_{k=1}^{K} n_k (n_k - 1) + \lambda \left(\sum_{k=1}^{K} n_k - N \right) \quad , \tag{G-8}$$

where λ is an undetermined multiplier, K is fixed and known, and n_k are the problem unknowns. Then a necessary condition for n_1, n_2, ..., n_k to solve the problem of minimizing Eq. (G-6) subject to Eq. (G-7) is that the n_k be a solution of the equations

$$\frac{\partial L}{\partial n_k} = 0 \qquad k = 1, 2, \ldots, K \tag{G-9}$$

and

$$\sum_{k=1}^{K} n_k = N \quad . \tag{G-10}$$

For each k,

$$\frac{\partial L}{\partial n_k} = 2n_k + \lambda - 1 = 0 \quad , \tag{G-11}$$

it follows that $\lambda = 1 - 2n_k$, and therefore that $n_1 = n_2 = \ldots = n_K$, so the best strategy is to recalibrate at regular intervals.

Equality of the n_k and the constraint [Eq. (G-7)] imply that $n_k = N/K$, $k = 1, 2, \ldots, K$, so that the expression in Eq. (G-6) becomes

$$N\left(\frac{N}{K} - 1\right) \quad . \tag{G-12}$$

In practice, only natural number solutions for the n_k are useful. While Eq. (G-12) is not exact under this condition, it has been found to be a good approximation to Eq. (G-6) when N is greater than about 2 × K.

E. Example Process

The process used for illustrating selection of optimal strategies is the AGNS reprocessing plant, which processes irradiated power-reactor fuel by the Purex recovery process to produce nitrate solutions of plutonium and uranium. This process is discussed in detail in App. B, and process flows are described in App. F.

To calculate the net transfer variance of the plutonium measurements, consider only the material input to the accountability tank and material output through the 1BP stream; although other output sidestreams exist, they are of significantly lower magnitude and are therefore neglected. The average batch size of the plutonium is ∿20 kg processed over a period of 9.6 h.

The amount of material in the accountability tank is estimated by a volume measurement and a wet-chemistry concentration measurement. Material output through the 1BP stream is estimated by a flow rate measurement and a densitometer concentration measurement. Instrument precision for these measurements is summarized in Table G-I.

Recalibration costs for each instrument are referenced to the cost of recalibrating one NDA instrument. In the absence of precise cost estimates, values of 100 units for the volume instrument, 10 units for the wet-chemistry instrument, 5 units for the flow meter, and 1 unit for the densitometer are assumed.

TABLE G-I

INSTRUMENT PRECISION

Measurement Point	Measurement Type	Relative Standard Deviation	
		Random	Systematic
Accountability Tank	Volume	3.0 (-3)	1.0 (-3)
	Concentration	1.0 (-2)	3.0 (-3)
1BP Stream	Flow Rate	1.0 (-2)	5.0 (-3)
	Concentration	1.0 (-2)	3.0 (-3)

Optimal strategies generated by RECAL using the above cost and precision data were compared with two other strategies that seem reasonable. These strategies are:

A. Allocate recalibration of the wet-chemistry instrument, the flow meter, and the densitometer in inverse proportion to their recalibration cost.

B. Same strategy as A, except make allocation proportional to instrument precision.

Assuming a recalibration resource of 1 unit per batch, Fig. G-1 compares the net transfer relative standard deviation attainable with strategies A, B, and the optimal strategy over a period of 100 batches. As expected, the optimal strategy performs better than A and B, reaching an improvement of about 15% at 100 batches. The effect of varying the resource amount when using an optimal strategy is shown in Fig. G-2. For this example, the optimal strategy over 100 balance periods is 6 recalibrations of the wet-chemistry instrument, 4 recalibrations of the flow meter, and 20 recalibrations of the densitometer.

F. Worth of Instrument Improvements

In the reprocessing example, the optimal strategy did not select any recalibrations of the volume measuring instrument because of its high 100 unit cost per recalibration. Indeed, under the assumption of 1 recalibration unit per batch and 100 batches, no volume recalibration is selected in an optimal strategy until the volume cost is reduced to 20

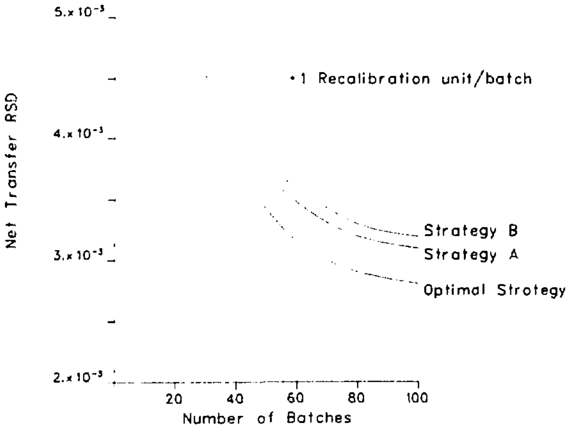


Fig. G-1. Comparison of recalibration strategies.

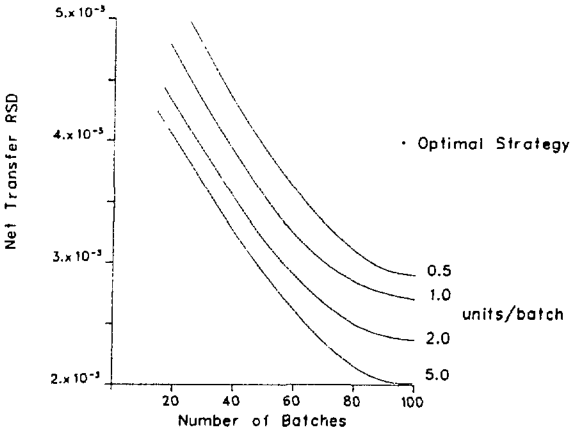


Fig. G-2. Variation of recalibration resource.

units per recalibration. Thus a reduction in volume recalibration cost is not useful unless the lower threshold is reached. This example illustrates another use of this method in examining the sensitivity of σ_T^2 to changes in either the recalibration cost or precision of an instrument. Using σ_T^2 as a measure of effectiveness, one can rank proposed instrumentation improvements according to their efficacy in improving the sensitivity of the materials accounting system.

REFERENCES

1. H. A. Dayem, D. D. Cobb, R. J. Dietz, E. A. Hakkila, J. P. Shipley, and D. B. Smith, "Dynamic Materials Accounting in the Back End of the LWR Fuel Cycle," Nucl. Technol. 43, 222-243 (1979).

2. J. L. Jaech, "Statistical Methods in Nuclear Material Control," TID-26298, Technical Information Center, Oak Ridge, Tennessee (1973).

APPENDIX H

ASPECTS OF THE INTERNATIONAL VERIFICATION PROBLEM

J. P. Shipley, R. J. Dietz, and D. B. Smith
LASL Safeguards Staff (Q-4)

A. Introduction

The central problem of international safeguards is the development of techniques for IAEA inspectors to verify the results of the State's materials accounting system. The IAEA provides that "the technical conclusion of the Agency's verification activities should be a statement, in respect of each material balance area, of the amount of material unaccounted for over a specific period, giving the accuracy of the amounts stated" (Ref. 1, para. 30). At the same time Ref. 1, para. 31, provides that the Agency "shall make full use of the State's system of accounting for and control of all nuclear material subject to safeguards under the Agreement, and shall avoid unnecessary duplication of the State's accounting and control activities." Thus, the inspector's verification activities are based on materials accounting and depend fundamentally on the detailed structure of the State's accounting system.

With the advent of stringent IAEA guidelines for timely detection in sensitive nuclear facilities, and the development of near-real-time accounting, new inspectors' procedures must be developed to take advantage of the increased materials accounting capability. In particular, verification of on-line measurements must be implemented. This appendix discusses some of the problems associated with verification and considers some technical solutions to these problems.

B. Diversion Sensitivity for the IAEA

The IAEA provides the basis for negotiating safeguards agreements between the IAEA and States party to the Non-Proliferation Treaty,[1] but does not define safeguards system effectiveness. The IAEA Safeguards Technical Manual[2] discusses only briefly the concepts of "degree of certitude of detection and degree of certitude of not concluding that a diversion has taken place when it has not." Ninety-five percent is given as the value ordinarily used for the associated probabilities.

These two concepts are related to the detection and false-alarm probabilities that must be specified whenever the "effectiveness" or "sensitivity" of a NM accounting system is quantified. These probabilities and the related notions of alarm level and detection sensitivity in the context of international safeguards are examined.

The detection function is based on acceptance of the hypothesis (H_1) that some (initially unknown) amount of NM is missing versus the hypothesis (H_0) that all NM is present. The detection probability (DP) is the probability of detecting a diversion of given magnitude with an alarm level established at a value AL. The magnitude of the diversion that can be observed with probability DP is called the detection sensitivity of the materials accounting system. The false-alarm probability (FAP) is the probability that the test statistic of interest (e.g., the materials balance, MB, or the materials unaccounted for, MUF) will exceed AL when no diversion has occurred. Likewise, the miss probability (MP) is the probability of concluding that no NM is missing when, in fact, diversion has occurred.

Figure H-1 illustrates the relationship between DP, FAP, AL, and the diversion sensitivity. The materials balance (or other test statistic) is assumed to be a random variable that is distributed normally with variance σ^2. The left-hand probability distribution curve represents the case of no diversion. The area under this curve for values of MB $\geq$ AL is the FAP. The AL is set at a value $n\sigma$, where n depends on the desired (or tolerable) false-alarm rate. The right-hand curve corresponds to a diversion of magnitude $N\sigma$, the diversion sensitivity. The area under this curve for values of MB $\geq$ AL is the DP.

The value of n to be used in fixing AL for a specified FAP has not been clearly established. In practice, AL often is set at 1.96σ (or 2σ, which is considered "close enough"). If the FAP is defined as above, which is consistent with the "degree of certitude" quoted from the IAEA Safeguards Manual, AL = 1.96σ corresponds to a FAP of 0.025.[3]

The facility operator, however, might be concerned with a large negative value of MB as well as with a large positive value. A positive deviation from zero would indicate a possible diversion (or other loss) of material; a negative MB could result from biased measurements. Thus, the operator might define the FAP to be the probability that the absolute value of the measured MB exceeds AL when the materials balance is zero. In this case, AL = 1.96σ corresponds to a FAP of 0.05.

The IAEA inspector, on the other hand, may be interested primarily in the diversion of material, and a FAP of 0.05 is associated with AL = 1.65σ. Thus, the alarm level depends not only on the desired FAP, but also on the interpretation or definition of the FAP.

The diversion sensitivity, in turn, depends on AL and on the desired detection probability, and both of these quantities must be specified, if a stated value of the diversion sensitivity is to have any meaning. Table H-I gives the diversion sensitivity for 95% detection probability corresponding to several values of AL.

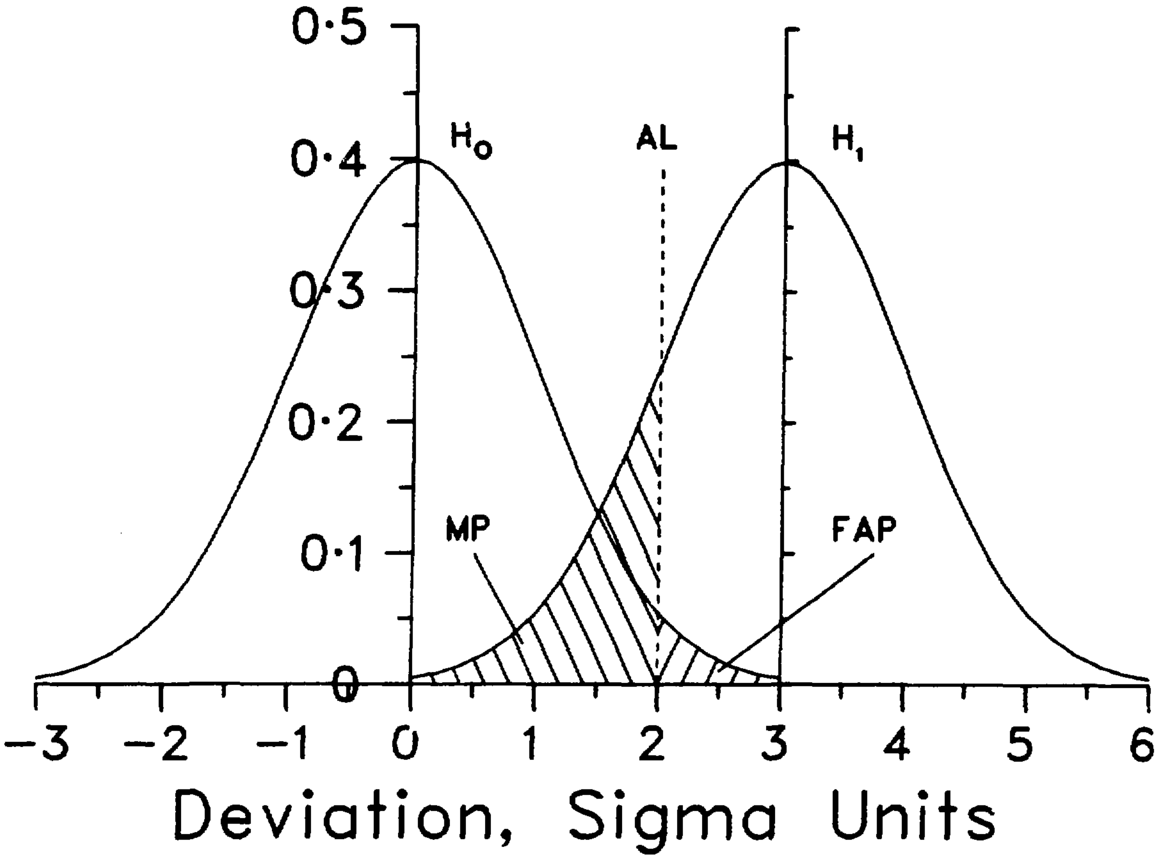


Fig. H-1. Probability density function representing no missing and missing nuclear material.

Alternative ways of stating the diversion sensitivity are:

- The diversion sensitivity is X kg of plutonium with 95% detection probability and the alarm level at Y (or $n\sigma$).
- The diversion sensitivity is X kg of plutonium with 95% detection probability and a FAP of 5%.
- The diversion sensitivity is X kg of plutonium with 95% detection probability at the 5% level of significance.

The last two statements can be ambiguous if the FAP is not carefully defined.

C. The Instrument Verification Problem

Consider an on-line instrument measuring NM transfers at a key measurement point and assume that the instrument is owned and operated by the operator and that the measurement results are available in real time to the inspector and to the operator. For

TABLE H-I

DIVERSION SENSITIVITY AT 95% DETECTION PROBABILITY

AL[a]	FAP[b]	Diversion Sensitivity[a]
1.65	.05	3.29
1.96	.025	3.60
2.00	.023	3.64

---

[a] Multiples of σ, the materials balance standard deviation.

[b] Defined as the probability that a diversion will be indicated when none has occurred.

example, such a device might measure flow or concentration at the input to the 1BP tank between the partitioning and plutonium purification processes in a reprocessing plant.

It is likely that for an on-line instrument the operator will have a computerized data acquisition system, although it is not fundamental to the arguments below. Digitized signal output is assumed. The inspector need not have a real-time computerized analysis capability, but he must have some means for at least acquiring and storing the digital data.

It is further assumed that the instrument will have an on-line calibration capability. This will be especially important for the operator if the instruments are accessible for calibration and maintenance only at physical inventories. As part of this capability, it is assumed that the inspector can insert standards of his own, and furthermore, he can request calibration measurements at random at a reasonable frequency. An example of such a device is the LASL/Q-1-built absorption-edge densitometer placed at the Tokai reprocessing facility under one of the TASTEX tasks.

For the inspector to believe the measurement results, three methods of subverting the instrument must be addressed:

- Materials tampering; is the instrument measuring the material as claimed by the operator?
- Instrument tampering; has the instrument been miscalibrated or degraded?
- Data tampering; has the operator falsified data output from the instrument?

Following are some suggestions for addressing these problems.

1. Materials Tampering. The materials tampering problem is one of the hardest to treat from the inspector's point of view, but is also one of the hardest to implement from the operator's point of view. If the instrument is relatively inaccessible, one effective strategy for the inspector would be to observe the initial installation and any follow-on maintenance and calibration activities requiring access to the instrument. It may be possible to place seals on the instrument between maintenance or recalibration operations.

Materials tampering can be made much more difficult by correlating the instrument measurement results with the operation of the process. However, this technique requires a very sophisticated inspector's safeguards system. Furthermore, the method is somewhat intrusive in that it requires access to process operating variables, which operators may be reluctant to release for proprietary reasons.

Probably the best means of augmenting the inspector's presence is the analysis of materials accounting data for instrument failure and tampering. This method would be based on the concept of overlapping unit process accounting areas[4,5] to eliminate the effects of selected instruments from the redundant materials accounting data. For example, a transfer measurement could be eliminated from the analysis by combining two adjacent unit process accounting areas into one. The resultant materials accounting data, while perhaps of poorer quality, are not dependent on that transfer measurement and can therefore be used as an indicator of a possible inconsistency in the data.

This technique is even more powerful if the inspector has sufficient data to analyze the aggregation of his own and the operator's accounting measurements. Methods for doing this analysis in the simplest case are described in Sec. H-D.

2. Instrument Tampering. Tampering with the instrument electronics can take two forms: miscalibration or introduction of a bias, and degradation of instrument performance by increasing the noise. The first difficulty is minimized by the ability of the inspector to perform on-line recalibration checks of the instrument. Ideally, the recalibration checks should be invisible to the operator. However, because the instrument belongs to the operator, the ideal is probably neither possible nor necessary.

If the occurrence of an inspector's recalibration check is known to the operator, and if the inspector is checking only his own standards that have been measured elsewhere, then it is possible for the operator to restore the instrument to normal operation (e.g., take out the bias he has been inserting for actual measurements) during the period of the inspector's recalibration check. The inspector can defeat this strategy by means of "running standards." The basic idea is for the inspector to use as one of his standards a replicate sample previously measured by the operator. The identity of the standard must be unknown to the operator. Thus, if the operator added a bias in the original measurement, the subsequent measurement will not contain that bias because the operator thought he was measuring an inspector's standard.

Increasing the measurement noise of the instrument could provide evidence that the measurement error statistics gathered in the measurement control program were too good. However, the results of that program should be monitored closely by both the operator and the inspector, and it would seem to be hard for the operator to do significant damage without alerting the inspector. Increasing the measurement noise on the average does not aid the operator in hiding diversion of NM. Furthermore, the inspector's data analysis algorithms would indicate a malfunctioning instrument.

3. Data Tampering. Presuming that the data at the output of the instrument are secure, the next problem is to transmit them to the inspector. The operator will have the same data, and if he wishes to subvert the system, he may try either to change the measurement results before they are transmitted to the inspector or to insert false measurement results. Thus, the inspector's problem is to authenticate both the originator of the data, that is, the instrument, and the data. He is not concerned with secrecy of the data.

Cryptographic techniques can treat the authentication problem for this specialized situation. The general problem of cryptography has been discussed in Refs. 6-8. The evaluation in Ref. 8 concluded that public-key encryption is preferred for safeguards applications. For those unfamiliar with cryptographic techniques, Refs. 6 and 7 outline the concepts of secret-key and public-key cryptosystems, respectively. The following arguments are based on those principles.

As shown in Fig. H-2, assume that the inspector can place at the instrument output software and hardware capabilities sufficient for data encryption and decryption, and that he has a corresponding capability at the data reception point. The procedure is as follows. The inspector generates a mated pair of keys, K_D and K_E. K_D is kept by the inspector and security measures must be taken to keep it secret. The instrument is provided with the corresponding public key, K_E. Because the security of the system will not depend on keeping K_E secret, there is no serious problem in distributing it to the instrument.

Next, the cryptographic unit at the instrument composes a random number, R, from the random pulse train obtained from the instrument. The random number R is the secret key to be used for encrypting and decrypting the subsequent materials accounting data.

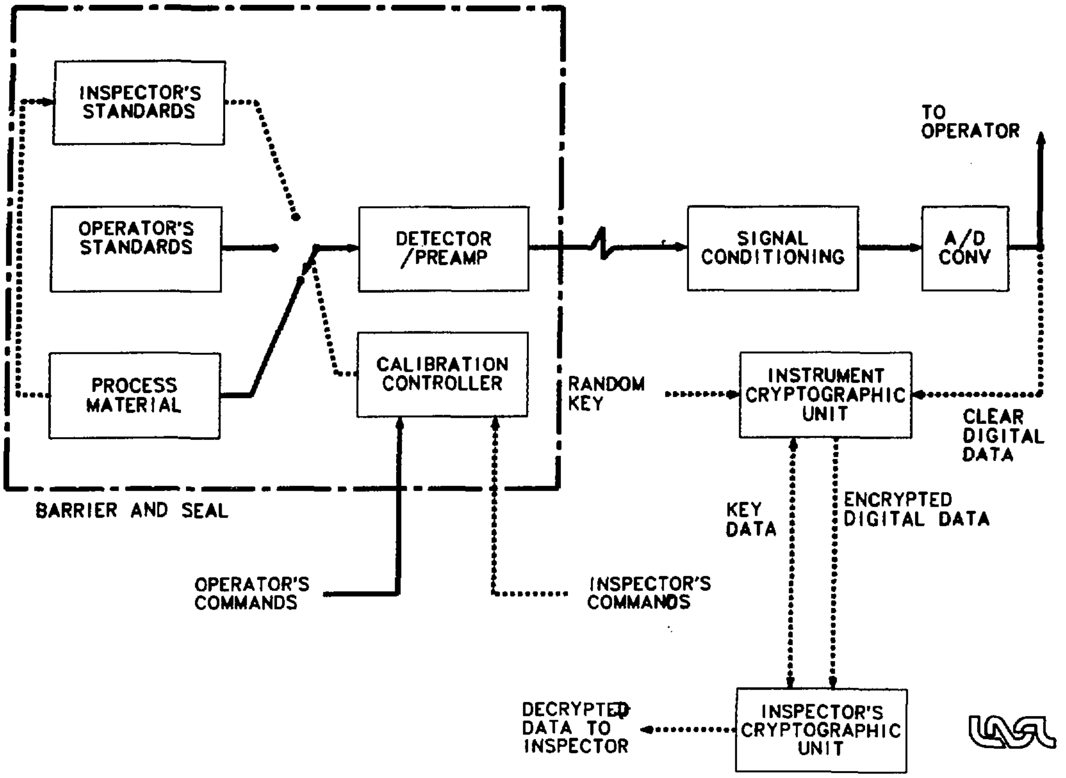


Fig. H-2. A block diagram of an instrument verification system.

Having stored R, the cryptographic unit at the instrument encrypts the message "This is instrument X. The current secret key is R." using the key K_E and sends the resulting ciphertext to the inspector. The inspector decrypts the ciphertext using key K_D and stores R. R is then used as a key in a secret-key cryptosystem for all further communications between the inspector and the instrument until the inspector requests the instrument to generate a new secret key.

Two rules govern the use of the key: (a) The inspector ignores all messages he receives that are encrypted using K_E, except those of the form "This is instrument ___. The current secret key is _____." (b) The instrument cryptographic unit ignores all messages it receives except those encrypted under the current R.

Using this system the operator can neither modify data nor insert false data because for the inspector to receive the data, they must be encrypted using the key R. However, R is unknown to the operator; R truly is a random number, having been generated by some random process, and was sent to the inspector from the cryptographic unit at the instrument in ciphertext form and encrypted with the public key, K_E. The operator cannot decipher the ciphertext version of R because he does not have the decryption key, K_D.

By rule (a) above, the operator can communicate with the inspector only by using K_E in just one way, to send the inspector an encrypted message "This is instrument X, the current secret key is R'." for some R' of his choice. This will cause the inspector to begin communicating with the instrument using R' instead of R, but by rule (b) the instrument will steadfastly ignore all messages encrypted under R' and will therefore not properly perform the recalibration checks mentioned above. The secret key R may be changed as frequently as desired, either by the inspector or by the cryptographic unit at the instrument.

Implementation of such a system is relatively straightforward and inexpensive. For the level of authentication required, a small microprocessor with simple software is probably sufficient for the cryptographic units. In addition, this scheme needs no modification of the operator's instrument. Only the outputs from the instrument are required. The operator's ability to use the instrument and acquire data is not compromised.

D. Statistical Aspects of the International Verification Problem

The statistical methods currently available for developing and evaluating inspection strategies for process MBAs are based on two statistics, commonly referred to as D and (MUF-D).[9-10] These statistics are combinations of both the operator's and inspector's measurements and are designed to counter the basic diversion strategies of diversion into MUF and data falsification. The D-statistic incorporates paired differences of operator's and inspector's measurements to detect operator bias (inadvertent or deliberate) in MUF; (MUF-D) is the inspector's estimate of MUF, independent of operator measurement bias.

While these statistics are reasonable, it may be that a more fundamental analysis of the verification problem will give insight into more optimum inspection and evaluation methods. This section considers a very simple verification problem, but performs a logical, thorough analysis of it to create the basis for treatment of more realistic problems.

1. The Simplest Statistical Verification Problem.

For purposes of illustration, consider a portion of a NM process for which one materials balance is drawn, as in Fig. H-3. This process has initial inventory I(0), final inventory I(1), input transfer during the period T(0), and output transfers T(1) and d during the same period. Output d

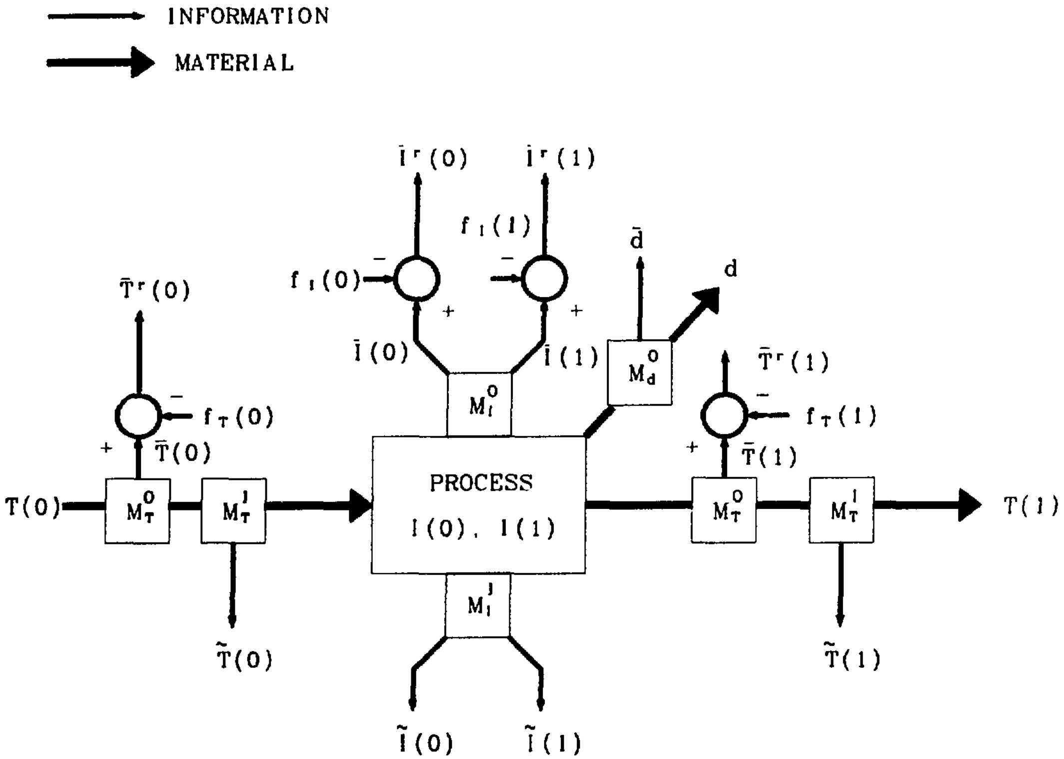


Fig. H-3. A simple statistical verification example.

represents a diversion, which may be zero, by the operator. These are all true values of the materials quantities for the process. Note that each inventory or transfer may be a composite of many pieces; that is, there may be more than one batch in an inventory or transfer, for example, and the total is the sum of the batches.

The operator obtains measured values of the transfers using the three instruments labeled M_T^O and M_d^O. The measured values are labeled $\bar{T}(0)$, $\bar{T}(1)$, and $\bar{d}$ for inputs, outputs, and diversion, respectively.

Presumably, the operator knows how much material he would like to take, that is, he wants to choose d. However, he only has an estimate of d, $\bar{d}$, obtained from instrument M_d^O. The designation of $\bar{d}$ as the result of using M_d^O is not meant to restrict the practical realization of M_d^O, which can range from an analytical device to an eyeballing, hand-hefting exercise. The point is that the operator does not know how much material he took, except insofar as the output of M_d^O provides an estimate, and that uncertainty is included in this analysis.

Similarly, the operator uses M_I^O to measure the inventories, obtaining $\overline{I}(0)$ and $\overline{I}(1)$. In all cases, a bar over a materials quantity denotes a value generated by an operator's measuring instrument.

The reported values the operator sends to the inspector, denoted with a superscript r as in $\overline{T}^r(0)$, are (possibly) falsified versions of the operator's measured values. Thus, the operator may subtract a falsification value (which may be positive or negative) from each of his measured values before reporting them to the inspector. For example, the input transfer reported value is (Fig. H-3)

$$\overline{T}^r(0) = \overline{T}(0) - \underline{f}_T(0) \quad .$$

As for diversion, the inspector is assumed to have no a priori knowledge of the extent to which the operator performs falsification.

The inspector also measures the same materials quantities, except for diversion, with instruments labeled M_T^I and M_I^I, obtaining measured values $\tilde{T}(0)$, $\tilde{T}(1)$, $\tilde{I}(0)$, and $\tilde{I}(1)$. These inspector's measurements are assumed not to have been tampered with by the operator.

To summarize our assumptions,

- The operator specifies the desired value of diversion, d, before any measurements are made. The inspector does not know d.
- The operator has all his measurements available, but none of the inspector's, to use in determining his reported values. That is, the operator falsifies on the basis of his own measurements and his selection of d.
- The inspector has no tamper-indicating features built into the operator's instruments.
- Probabilistic descriptions of the operator's (unfalsified) and inspector's measurement errors are common knowledge.
- The inspector's measurements are secure from operator tampering.
- The inspector has both his own measurement results and the operator's reported values for use in his analysis.

Normally, the fourth assumption implies that the operator and inspector cooperate in a well-developed measurement control program. Other statistical techniques are available for checking the results of that program to protect against artificially manipulated descriptions of the measurement errors. It is also possible for the inspector to couch his analysis in nonparametric terms, at some expense in sensitivity to diversion and falsification. This aspect is beyond the scope of the current work.

Given the measurement data and governed by these assumptions, the inspector's task is to decide whether or not the operator has diverted material and/or falsified his measurement results and to quantify the amounts of diversion and falsification. In the sequel, we shall formulate this problem in more explicit mathematical form and lay out the procedures followed by the operator and inspector in striving for their goals.

2. Mathematical Formulation. Let us first choose some new notation that will simplify the analysis. Define the following vectors:

$$\begin{aligned} Z &= [I(0)\ \ I(1)\ \ T(0)\ \ T(1)]^t \ , \\ \bar{Z} &= [\bar{I}(0)\ \ \bar{I}(1)\ \ \bar{T}(0)\ \ \bar{T}(1)]^t \ , \\ \bar{Z}^r &= [\bar{I}^r(0)\ \ \bar{I}^r(1)\ \ \bar{T}^r(0)\ \ \bar{T}^r(1)]^t \ , \\ \tilde{Z} &= [\tilde{I}(0)\ \ \tilde{I}(1)\ \ \tilde{T}(0)\ \ \tilde{T}(1)]^t \ , \\ F &= [f_I(0)\ \ f_I(1)\ \ f_T(0)\ \ f_T(1)]^t \ , \end{aligned} \tag{H-1}$$

which are column vectors of true materials quantities, operator's measured results, operator's reported results, inspector's measured results, and operator's falsification values, respectively. The superscript t denotes vector or matrix transpose. Remember that each term in a vector may be a composite of many values, so that the vector may be of high dimension. On the other hand, if each term is composed of only one value, then the vector is of dimension four. Because of its special character, the diversion, d, and its operator-measured value, $\bar{d}$, are treated separately and not included as part of Z and $\bar{Z}$.

Given these definitions, the materials balance equation can be written simply as

$$\begin{aligned} \ell^t Z &\triangleq [1\ -1\ \ 1\ -1][I(0)\ \ I(1)\ \ T(0)\ \ T(1)]^t \\ &= I(0) - I(1) + T(0) - T(1) = d \ . \end{aligned} \tag{H-2}$$

Again, if the terms in Z are composite, then the elements in the vector ℓ are vectors of the same dimensions as the number of components in the corresponding terms of Z. Also, the operator's reported values are

$$\bar{Z}^r = \bar{Z} - F \quad .$$

a. The Inspector's Problem. When the inspector begins his analysis, he has available the aggregation, Z_A, of the operator's reported and his own measurement data:

$$Z_A \triangleq \begin{bmatrix} \bar{Z}^r \\ \tilde{Z} \end{bmatrix} , \tag{H-3}$$

and he has probabilistic descriptions of these quantities in terms of their conditional probability density functions (see Sec. H-D.3.a below), which depend on parameters unknown to him. On the basis of this information, the inspector must decide whether or not the operator has diverted and/or falsified his data. In mathematical terms, the inspector must choose between the two hypotheses*

$$\begin{aligned} H_0 &: d = 0 \ \underline{\text{and}} \ F = 0 \quad , \\ H_1 &: d \neq 0 \ \underline{\text{and/or}} \ F \neq 0 \quad . \end{aligned} \tag{H-4}$$

The inspector will also want to estimate the diversion and falsification levels and their significances, and those estimates will be available in the course of the analysis.

Note that we have constructed the H_1 hypothesis so that the inspector looks for diversion and falsification of either sign: the inspector considers either occurrence as an anomaly. It is equally possible to look only for positive diversion and falsification that would hide it, but that development is left for later work.

---

*For background material on hypothesis testing, estimation, and related concepts, see Refs. 11-14.

b. The Inspector's Decision Rule. At this point, the inspector has two candidate density functions to describe the aggregated data, one if H_0 is true and another if H_1 is true, denoted by

$$p(z_A|H_0) \text{ and } p(z_A|H_1) \quad ,$$

respectively.* Note that the second density function, for H_1 true, implies that d and F may not be zero. In general, the density function will depend on specific values for d and F, which the inspector will have to obtain by methods to be outlined below. Formally, these dependences can be written as

$$p(z_A|H_0) = p(z_A|H_0;Z,0) = p(\bar{z}^r,\tilde{z}|H_0;Z,0)$$

$$p(z_A|H_1) = p(z_A|H_1;Z,F) = p(\bar{z}^r,\tilde{z}|H_1;Z,F) \quad .$$

Note that $p(z_A|H_1)$ is an implicit function of the diversion d through the materials balance constraint, Eq. (H-2), on Z.

Denote the inspector's decision rule by the pair of variables $\delta(H_0|Z_A)$ and $\delta(H_1|Z_A)$, where

$$\delta(H_0|Z_A) = \begin{cases} 0 \text{ if the inspector accepts } H_1 & , \\ 1 \text{ if the inspector accepts } H_0 & , \end{cases}$$
$$\delta(H_1|Z_A) = \begin{cases} 0 \text{ if the inspector accepts } H_0 & , \\ 1 \text{ if the inspector accepts } H_1 & . \end{cases} \qquad \text{(H-5)}$$

---

*Lower-case stochastic quantities are variables; upper case indicates observed or realized values of those variables.

We require that the inspector make a decision, so that

$$\delta(H_0 | Z_A) + \delta(H_1 | Z_A) = 1 \text{ for all } Z_A \quad . \tag{H-6}$$

These variables can be thought of as the conditional probability of the inspector's accepting H_0 or H_1, respectively, given the aggregated measurement data.

Now, the inspector's decision can have four <u>outcomes</u>:

1. He can accept H_0 when H_0 is true;
2. He can accept H_0 when H_1 is true;
3. He can accept H_1 when H_0 is true;
4. He can accept H_1 when H_1 is true.

The second outcome is a miss, the third outcome is a false alarm, and the first and last outcomes are correct decisions. The probability that the inspector misses diversion and/or falsification (outcome 2) is

$$P_M(\delta, Z, F) = \int_{\{Z_A\}} p(\bar{z}^r, \tilde{z} | H_1; Z, F)\, \delta(H_0 | \bar{z}^r, \tilde{z}) \; d\bar{z}^r \; d\tilde{z} \quad , \tag{H-7}$$

where the integration is performed over the space of possible Z_A values and depends on the decision rule. The probability of outcome 4 is $1 - P_M$. Likewise, the probability of a false alarm (outcome 3) is

$$P_F(\delta, Z, F) = \int_{\{Z_A\}} p(\bar{z}^r, \tilde{z} | H_0; Z, 0)\, \delta(H_1 | \bar{z}^r, \tilde{z}) \; d\bar{z}^r \; d\tilde{z} \quad , \tag{H-8}$$

and the probability of outcome 1 is $1 - P_F$. Refer to Fig. H-1 for a graphical representation of these quantities.

The inspector would like to choose his decision rule to achieve satisfactory values of P_M and P_F. There are many ways to do this, but the following approach is one of the most common and is known to be effective. We use the Neyman-Pearson criterion[15] in which the decision rule is chosen to minimize P_M for a fixed value of P_F. To proceed, we define the risk function

$$R(\delta, Z, F) = P_M(\delta, Z, F) + \lambda[P_F(\delta, Z, F) - \alpha] \quad , \tag{H-9}$$

where λ is a Lagrange multiplier, and α is the desired FAP. We can expand the risk function using Eqs. (H-6) through (H-9):

$$R(\delta, Z, F) = 1 - \lambda\alpha - \int_{\{Z_A\}} [p(z|H_1; Z, F) - \lambda p(z|H_0; Z, 0)]\, \delta(H_1|z)\; dz \quad . \tag{H-10}$$

Thus, to minimize the risk, the inspector should set $\delta(H_1|z) = 1$ (diversion and/or falsification) for all values of $z = Z_A$ that yield a positive integrand, and zero otherwise. From Eq. (H-10), the test that the inspector would like to perform and that would implement his decision rule is

$$\text{If } L(Z_A, Z, F) \triangleq \frac{p(Z_A|H_1; Z, F)}{p(Z_A|H_0; Z, 0)} \overset{H_0}{\underset{H_1}{\lessgtr}} \lambda \quad . \tag{H-11}$$

That is, if the likelihood ratio is less than λ, accept H_0; otherwise accept H_1. The value of the Lagrange multiplier, λ, also called the test threshold, is determined by satisfying the constraint $P_F = \alpha$. The two density functions in Eq. (H-11) are also called likelihood functions, and their relative values at Z_A are indicative of whether Z_A is more likely to have been generated under H_0 true or H_1 true.[11-15]

Equation (H-11) is the standard likelihood ratio test that has been known for many years. This form of test, a likelihood ratio compared to a threshold, always results whenever a risk function that is a linear combination of P_M and P_F is minimized.

As indicated in Eq. (H-11), the likelihood ratio the inspector would like to use depends on Z and F (and implicitly on d), which the inspector does not know. So, to perform his test the inspector must obtain values for these quantities. There are several ways of doing this, but the following approach is most common.

The inspector knows that there are two possible sets of values for Z: one that corresponds to H_0 true, which implies that $p(z_A|H_0;Z,0)$ describes Z_A and that the materials balance is zero ($\ell^t Z = 0$); and one that corresponds to H_1 true, which implies that $p(z_A|H_1;Z,F)$ describes Z_A and that the materials balance is d($\ell^t Z = d$). Therefore, he constructs two estimates of Z, one for H_0 true and one for H_1 true, by choosing those values of Z that are most likely to have been the causes, under each of the two hypotheses, of the observed Z_A. These two estimates are found by maximizing the two density functions (separately) in Eq. (H-11) with respect to Z, and they are called inspector's maximum-likelihood estimates (IMLEs).

Similarly, the inspector selects estimates for F and d by choosing those values that are most likely to have been the cause of the observed Z_A, assuming that H_1 is true. Because of our definition of the null hypothesis, the inspector assumes that F and d are zero for H_0 true.

Now, to summarize: for H_0 true, the IMLE of Z, denoted by $\hat{Z}_0$, is the solution to the maximization problem

$$\begin{aligned}\tilde{J}_0 &= \max_{Z} p(Z_A|H_0;Z,0) , \text{ subject to } \ell^t Z = 0 \quad , \\ &= p(Z_A|H_0;\hat{Z}_0,0) \quad . \end{aligned} \tag{H-12}$$

For H_1 true, the IMLEs of Z, F, and d, denoted by $\hat{Z}_1$, $\hat{F}$, and $\hat{d}$, respectively, are the solutions to

$$\begin{aligned}\tilde{J}_1 &= \max_{Z,F,d} p(Z_A|H_1;Z,F) , \text{ subject to } \ell^t Z = d \quad , \\ &= p(Z_A|H_1;\hat{Z}_1,\hat{F}) \quad . \end{aligned} \tag{H-13}$$

The inspector's decision rule, in the form of a test, is

$$\text{If } L(Z_A) \triangleq \frac{p(Z_A|H_1;\hat{Z}_1,\hat{F})}{p(Z_A|H_0;\hat{Z}_0,0)} \overset{H_0}{\underset{H_1}{\lessgtr}} \lambda \quad . \tag{H-14}$$

c. The Operator's Problem. The operator's goal is to have the inspector decide that H_0 is true, especially when it is not. The operator also would generally like for the inspector's false-alarm rate to be low* because any alarm is likely to be disruptive and arouse suspicions; that is, the operator might like to falsify without having diverted to help ensure that the inspector would decide H_0 true. Because the inspector estimates the diversion and falsification, Eq. (H-13), his test in Eq. (H-14) is effective against falsification whether or not the operator has diverted. It is also possible to construct tests for the inspector that are sensitive only to falsification.

Assuming that the operator knows the inspector's test and, therefore, his risk function, Eq. (H-10), the operator will select his falsification F to yield reported values $\overline{Z}^T$ that are most likely to cause the inspector to decide H_0 is true based on the inspector's risk function. However, the operator has less information than the inspector in that he does not know the inspector's measured values. Thus, the operator desires to minimize the value of the likelihood ratio in Eq. (H-14) that the inspector is likely, in some sense, to obtain. This is equivalent to maximizing the risk function in Eq. (H-10) with respect to the falsification.

Now, the operator knows that the inspector will estimate two possible sets of values for the true quantities Z: one set for H_0 true and one for H_1 true. The operator, then, must put himself in the inspector's place and determine similar estimates against which to work his falsification problem.

In addition, the operator must estimate the values of the inspector's measurements, $\tilde{Z}$. Although he does not know $\tilde{Z}$, he does know that they will approximate the true values, Z, in the sense that the expected value of $\tilde{Z}$ is Z. Thus, one operator's estimate of $\tilde{Z}$ is his own estimate of Z under whichever hypothesis the operator knows to be true, H_1 in the current analysis. (Remember that the inspector's measurements cannot be falsified by the operator.) In estimating Z, the operator has one additional piece of information not available to the inspector: he has his own measured value of diversion, $\overline{d}$. The totality of the operator's knowledge is contained in the following density function evaluated at the operator's observed values:

---

*Scenarios are possible in which the operator deliberately causes many false alarms to discredit the inspector's system. That is a different problem than the one treated here, but it is suited to the same methods.

$$p(\bar{Z},\tilde{z},\bar{d}\,|\,Z,d) \quad .$$

In analogy with the inspector's problem, the operator's maximum-likelihood estimates (OMLEs) of Z and d assuming H_1 is true, denoted by Z_1^* and d^*, respectively, are the solutions to

$$\begin{aligned} \bar{J}_1 &= \max_{Z,\tilde{z},d} p(\bar{Z},\tilde{z},\bar{d}\,|\,Z,d), \text{ subject to } \ell^t Z = d \quad , \\ &= p\left(\bar{Z},Z_1^*,\bar{d}\,|\,Z_1^*,d^*\right) \quad , \\ &= p\left(\bar{Z}^r,Z_1^*,\bar{d}\,|\,Z_1^*,d^*,F\right) \quad , \end{aligned} \tag{H-15}$$

where we have used the fact that the OMLE of the inspector's values is also the OMLE of the true values, Z_1^*. The last equality in Eq. (H-15) holds because $\bar{Z}^r$ is deterministically related to $\bar{Z}$ through the falsification.

Similarly, the OMLE of the IMLE of the true values under the assumption of H_0 true, denoted by Z_0^*, is the solution to

$$\begin{aligned} \bar{J}_0 &= \max_{Z} p\left(\bar{Z},Z_1^*,d\,|\,Z,d = 0\right), \text{ subject to } \ell^t Z = 0 \quad , \\ &= p\left(\bar{Z},Z_1^*,\bar{d}\,|\,Z_0^*,d = 0\right) \quad , \\ &= p\left(\bar{Z}^r,Z_1^*,\bar{d}\,|\,Z_0^*,d = 0,F\right) \quad . \end{aligned} \tag{H-16}$$

Again, we have used Z_1^*, the OMLE of the true values for H_1 true (which the operator knows to be the case), as the OMLE of the inspector's measurements. Note that Z_0^* generally will be an implicit function of F, which we have not yet determined. That is the next step.

Having the OMLEs of the true values, of the operator's measurements, and of the IMLEs of the true values, the operator determines his optimal falsification values, F^*, as the solution to

$$J^* = \min_F \frac{p\left(\overline{Z}^r, Z_1^* | H_1 ; Z_1^*, F\right)}{p\left(\overline{Z}^r, Z_1^* | H_0 ; Z_0^*, 0\right)} \quad , \tag{H-17}$$

$$\text{with } \overline{Z}^r = \overline{Z} - F \quad .$$

Some interesting points about Eq. (H-17) can be made. Although the numerator of J^* is formally dependent on F, it is functionally independent of F. This is true because $\overline{Z}^r$ results from a deterministic transformation of $\overline{Z}$, which is independent of F. On the other hand, the denominator of J^* is dependent on F through the definition of $\overline{Z}^r$. Thus, the operator's selection of F^* can be thought of as maximizing the likelihood function for H_0 true, the decision the operator hopes the inspector will make. The details of these ideas will be more apparent in the development below.

d. Summary of Inspector's and Operator's Procedures. Given his own measurements and having diverted amount d, the operator:

- Obtains OMLEs of Z, $\tilde{Z}$, and d for H_1 true, denoted by Z_1^*, Z_1^*, and d^*, respectively, from Eq. (H-15);
- Obtains, as functions of F, OMLEs of the IMLE of the true materials quantities for H_0 true, denoted by Z_0^*, from Eq. (H-16);
- Determines his falsification values F^* and reported values $\overline{Z}^r$ from Eq. (H-17).

Given both the operator's reported values and his own measurements, the inspector:

- Obtains the IMLE of Z assuming H_0 true, $\hat{Z}_0$, from Eq. (H-12);
- Obtains the IMLEs of Z, F, and d assuming H_1 true, denoted by $\hat{Z}_1$, $\hat{F}$, and $\hat{d}$, respectively, from Eq. (H-13);
- Performs the likelihood-ratio test in Eq. (H-14).

It should be clear that the inspector's and operator's procedures may be thought of as a game[11] having the payoff function R(δ,Z,F) defined by Eq. (H-10). The game can be written in standard form as finding the solutions to

$$J = \min_{\delta} \max_{F} R(\delta, Z, F) \quad ,$$

$$\text{subject to } \ell^t Z = d \quad ,$$

where the operator chooses F, having $\bar{Z}$ and $\bar{d}$, and the inspector chooses δ, having both $\bar{Z}^r$ and $\tilde{Z}$. The true values Z are estimated by both the operator and inspector on the bases of the information they possess.

3. Development for Gaussian Errors. To carry the analysis further, we require information concerning the probabilistic properties of the measurement errors. The usual assumption is that the measurement errors are sufficiently well-characterized by Gaussian distributions. (See Ref. 16 for probabilistic background.) Under this condition, the inspector's and operator's procedures outlined above can be shown to reduce to especially simple and logical forms. We obtain those results in this section.

a. Probabilistic Descriptions. We assume that all measurement errors are additive and have Gaussian distributions. (These assumptions can be relaxed, but they are convenient for this analysis.) Thus, the vectors in Eq. (H-1) can be written

$$\begin{aligned} \bar{Z} &= Z + \bar{\varepsilon} + \bar{\eta} \quad , \\ \bar{Z}^r &= Z - F + \bar{\varepsilon} + \bar{\eta} \quad , \qquad \text{(H-18)} \\ \tilde{Z} &= Z + \tilde{\varepsilon} + \tilde{\eta} \quad , \end{aligned}$$

where the ε- and η-error terms are the so-called random and systematic measurement errors, respectively. The ε errors are those that change randomly with each measurement; each component of ε is statistically independent of all other errors. The η-error components are also random but may be correlated from measurement to measurement because they arise from such sources as instrument calibration errors, measurement standards errors, sampling errors, etc. In fact, each η-error term may be a composite of several such errors, each caused by a different source.

Under the assumption of Gaussian errors, we need only the means (expected values) and variances of the measurement errors for their complete probabilistic description. The errors are taken to have mean zero: available bias estimates have been incorporated, and the associated uncertainties are included in the variances of the systematic errors.

With errors of the form shown in Eq. (H-18), the variance of a single measurement, say that for $\overline{T}(0)$, is

$$\begin{aligned}
\text{var}\ [\overline{T}(0)] &\triangleq E\{[\overline{T}(0) - T(0)]^2\} \\
&= E\left[\bar{\varepsilon}_T^2(0) + 2\bar{\varepsilon}_T(0)\bar{\eta}_T(0) + \bar{\eta}_T^2(0)\right] \\
&= E\left[\bar{\varepsilon}_T^2(0) + \bar{\eta}_T^2(0)\right] \\
&= \bar{\sigma}^2_{\varepsilon T}(0) + \bar{\sigma}^2_{\eta T}(0) = \bar{\sigma}^2_T(0) \quad ,
\end{aligned}$$

where E denotes the expected value operator, and similarly for the other measurements.* Thus the variance matrix for the collection of operator's measurements, $\overline{Z}$, is

$$\overline{\Sigma} \triangleq \text{var}\ (\overline{Z}) = E[(\overline{Z} - Z)(\overline{Z} - Z)^t]$$

$$= \begin{bmatrix}
\bar{\sigma}^2_I(0) & \bar{\sigma}_I(0,1) & \bar{\sigma}_{IT}(0,0) & \bar{\sigma}_{IT}(0,1) \\
\bar{\sigma}_I(1,0) & \bar{\sigma}^2_I(1) & \bar{\sigma}_{IT}(1,0) & \bar{\sigma}_{IT}(1,1) \\
\bar{\sigma}_{TI}(0,0) & \bar{\sigma}_{TI}(0,1) & \bar{\sigma}^2_T(0) & \bar{\sigma}_T(0,1) \\
\bar{\sigma}_{TI}(1,0) & \bar{\sigma}_{TI}(1,1) & \bar{\sigma}_T(1,0) & \bar{\sigma}^2_T(1)
\end{bmatrix} \quad , \qquad \text{(H-19)}$$

---

*Remember that $\sigma^2_{\varepsilon T}(0)$ and $\sigma^2_{\eta T}(0)$ are n × n matrices if $\overline{T}(0)$ is a vector having n components.

where the off-diagonal terms account for correlations among measurement errors for the components of $\bar{Z}$.

Variance matrices are always symmetric and, in practice, are nonsingular.[16] Clearly, $\tilde{\Sigma}$, the variance matrix for the inspector's measurements, has the same form as $\bar{\Sigma}$, and

$$\bar{\Sigma}^r = \bar{\Sigma} \quad .$$

For the purposes of this analysis, we do not yet need explicit definitions for the off-diagonal terms. They are straightforward to calculate once the individual measurement characteristics are specified.

Similarly, the variance matrix for the aggregation of the operator's and the inspector's measurements is

$$\begin{aligned} \mathrm{var}\ (Z_A) &\triangleq \mathrm{var} \begin{bmatrix} \bar{Z}^r \\ \tilde{Z} \end{bmatrix} = \begin{bmatrix} \mathrm{var}\ (\bar{Z}^r) & \mathrm{cov}\ (\bar{Z}^r, \tilde{Z}) \\ \mathrm{cov}\ (\tilde{Z}, \bar{Z}^r) & \mathrm{var}\ (\tilde{Z}) \end{bmatrix} = \begin{bmatrix} \bar{\Sigma} & 0 \\ 0 & \tilde{\Sigma} \end{bmatrix} \\ &= \mathrm{var} \begin{bmatrix} \bar{Z} \\ \tilde{Z} \end{bmatrix} \triangleq \Sigma_A \quad . \end{aligned} \tag{H-20}$$

We assume that the inspector indeed makes measurements independent of those of the operator, which implies that

$$\mathrm{cov}\ (\bar{Z}^r, \tilde{Z}) \triangleq E[(\bar{Z}^r - Z)(\tilde{Z} - Z)^t] = 0 \quad .$$

This assumption can also be removed, at some cost in complexity, to allow for the possibility that the inspector might use some of the operator's measurements or standards, for example. Note that Σ_A has dimension equal to the sum of the dimensions of $\bar{\Sigma}$ and $\tilde{\Sigma}$.

Given the means and variances of the measurement data, the conditional probability density functions of $\bar{Z}$, $\bar{Z}^r$, $\tilde{Z}$, and Z_A can be written as

$$p(\bar{Z}|Z) = \bar{A} \exp\left[-\frac{1}{2}(\bar{Z} - Z)^t\bar{\Sigma}^{-1}(\bar{Z} - Z)\right] \quad , \tag{H-21}$$

$$p(\bar{Z}^r|Z,F) = \bar{A} \exp\left[-\frac{1}{2}(\bar{Z}^r - Z + F)^t\bar{\Sigma}^{-1}(\bar{Z}^r - Z + F)\right]$$

$$= p(\bar{Z}|Z) \quad , \tag{H-22}$$

$$p(\tilde{Z}|Z) = \tilde{A} \exp\left[-\frac{1}{2}(\tilde{Z} - Z)^t\tilde{\Sigma}^{-1}(\tilde{Z} - Z)\right] \quad , \tag{H-23}$$

$$p(Z_A|Z) = p(\bar{Z}|Z)p(\tilde{Z}|Z) \quad . \tag{H-24}$$

Equation (H-24) holds because we have assumed that the operator's measurements are independent of those of the inspector. The normalization coefficients $\bar{A}$ and $\tilde{A}$ depend on the numbers of components in $\bar{Z}$ and $\tilde{Z}$ and their variances.[16] They will be unimportant in the sequel.

Note that the density functions in Eqs. (H-21) through (H-24) are conditioned on the value of Z, which is unknown. We have seen that the operator and inspector will be required to obtain values for Z to insert into their analyses. The density function for $\bar{Z}^r$ is also conditioned on F, the operator's falsification vector. The operator is allowed to determine F, but the inspector will have to estimate F on the basis of the measurements.

The operator's own measurement $\bar{d}$ of his diversion d has density function

$$p(\bar{d}|d) = A_d \exp\left[-\frac{(\bar{d} - d)^2}{2\sigma_d^2}\right] \quad , \tag{H-25}$$

which the operator knows, but the inspector does not. We assume that the operator's measurement of d is independent of all his other measurements and those of the inspector. Thus, the joint conditional density function of <u>all</u> the measurements, given Z and d, is

$$p(\bar{Z},\tilde{Z},\bar{d}|Z,d) = p(\bar{Z},\tilde{Z}|Z)p(\bar{d}|d) \quad .$$

All these density functions can be conditioned on which hypothesis is true. However, the forms of the functions do not change; the ranges of the conditioning parameters (Z,F,d) are restricted.

b. Solution to the Operator's Problem. Following the development given in Sec. H-D.2 above, the operator first forms the joint conditional density function to be used in Eq. (H-15):

$$p(\bar{z},\tilde{z},\bar{d}|Z,d) = \bar{A} \exp\left[-\frac{1}{2}(\bar{z} - Z)^t\bar{\Sigma}^{-1}(\bar{z} - Z)\right]$$

$$\cdot \tilde{A} \exp\left[-\frac{1}{2}(\tilde{z} - Z)^t\tilde{\Sigma}^{-1}(\tilde{z} - Z)\right]$$

$$\cdot A_d \exp\left[-\frac{(\bar{d} - d)^2}{2\sigma_d^2}\right] , \qquad \text{(H-26)}$$

using Eqs. (H-22) through (H-25). We can make an immediate simplification because the inspector's measured values, $\tilde{z}$, are unknown. In this case, as discussed earlier, the operator's best prediction of $\tilde{z}$ is his own estimate of Z, Z_1^*, for H_1 true. Thus, the second factor in the density function is just $\tilde{A}$. If any inspector's values should be known to the operator, then the operator would also make use of those values by incorporating them in the density function.

In performing the maximization called for in Eq. (H-15), we will find it more convenient to work with the logarithm of the density function. This is possible because the logarithm is a monotonic function. Using the method of Lagrange, the function to be maximized with respect to Z and d is

$$\bar{G}_1(Z,d) = \ln p(\bar{z},\tilde{z},\bar{d}|Z,\tilde{z} = Z,d) + \bar{\mu}_1(\ell^t Z - d)$$

$$= \ln(\bar{A}\tilde{A}A_d) - \frac{1}{2}(\bar{z} - Z)^t\bar{\Sigma}^{-1}(\bar{z} - Z) - \frac{(\bar{d} - d)^2}{2\sigma_d^2}$$

$$+ \bar{\mu}_1(\ell^t Z - d) ,$$

where $\bar{\mu}_1$ is a Lagrange multiplier. A necessary condition for $\bar{G}_1(Z,d)$ to be a maximum is that its partial derivatives with respect to Z and d, evaluated at the optimum values, be zero:

$$\left.\frac{\partial \bar{G}_1}{\partial Z}\right|_{Z_1^*} = \left(\bar{Z} - Z_1^*\right)^t \bar{\Sigma}^{-1} + \bar{\mu}_1 \ell^t = 0$$

$$\left.\frac{\partial \bar{G}_1}{\partial d}\right|_{d^*} = \frac{\bar{d} - d^*}{\sigma_d^2} - \bar{\mu}_1 = 0 \quad .$$

Solving these equations for Z_1^* and d^*,

$$Z_1^* = \bar{Z} + \bar{\mu}_1 \bar{\Sigma} \ell$$

$$d^* = \bar{d} - \bar{\mu}_1 \sigma_d^2 \quad .$$

The Lagrange multiplier is found by forcing Z_1^* and d^* to satisfy the constraint $\ell^t Z_1^* = d^*$:

$$\ell^t Z_1^* = \ell^t \bar{Z} + \bar{\mu}_1 \ell^t \bar{\Sigma} \ell = \bar{d} - \bar{\mu}_1 \sigma_d^2 = d^* \quad ,$$

which results in

$$\bar{\mu}_1 = - \frac{\ell^t \bar{Z} - \bar{d}}{\ell^t \bar{\Sigma} \ell + \sigma_d^2} \quad .$$

We may think of $\ell^t\bar{Z}$ as the operator's materials balance, $\bar{M}$, which would be analogous to the inspector's materials balance based only on the inspector's measurements. The variance of $\bar{M}$ is $\ell^t\bar{\Sigma}\ell$.

Substituting in the equations for Z_1^* and d^*, the operator's estimates for the true materials quantities and the diversion, respectively, are

$$z_1^* = \bar{z} - \frac{\bar{\Sigma}\ell}{\ell^t\bar{\Sigma}\ell + \sigma_d^2}(\ell^t\bar{z} - \bar{d})$$

$$d^* = \bar{d} + \frac{\sigma_d^2}{\ell^t\bar{\Sigma}\ell + \sigma_d^2}(\ell^t\bar{z} - \bar{d}) \quad . \tag{H-27}$$

Next, the operator must estimate what the inspector will estimate as the true materials quantities assuming that H_0 is true. That is, the operator must find Z_0^* from Eq. (H-16). Proceeding as before, the function to be maximized with respect to Z is

$$\begin{aligned}\bar{G}_0(z) &= \ln p\left(\bar{z}^r, \tilde{z}, \bar{d} \,|\, z, \tilde{z} = z_1^*, 0\right) + \bar{\mu}_0\ell^t z \\ &= \ln(\bar{A}\tilde{A}A_d) - \frac{1}{2}(\bar{z}^r - z)^t\bar{\Sigma}^{-1}(\bar{z}^r - z) \\ &\quad - \frac{1}{2}\left(z_1^* - z\right)^t\tilde{\Sigma}^{-1}\left(z_1^* - z\right) - \frac{\bar{d}^2}{2\sigma_d^2} + \bar{\mu}_0\ell^t z \quad ,\end{aligned}$$

where $\bar{\mu}_0$ is another Lagrange multiplier. A necessary condition for $\bar{G}_0(z)$ to be a maximum is that its partial derivatives with respect to Z, evaluated at the optimum values, be zero:

$$\left.\frac{\partial\bar{G}_0}{\partial Z}\right|_{z_0^*} = \left(\bar{z}^r - z_0^*\right)^t\bar{\Sigma}^{-1} + \left(z_1^* - z_0^*\right)^t\tilde{\Sigma}^{-1} + \bar{\mu}_0\ell^t = 0 \quad .$$

Solving for Z_0^*,

$$Z_0^* = \left(\bar{\Sigma}^{-1} + \tilde{\Sigma}^{-1}\right)^{-1}\left(\bar{\Sigma}^{-1}\bar{Z}^r + \tilde{\Sigma}^{-1}Z_1^*\right) + \bar{\mu}_0 \ell \quad .$$

To simplify the notation, let us define

$$\underline{\Sigma} = \left(\bar{\Sigma}^{-1} + \tilde{\Sigma}^{-1}\right)^{-1} \quad ,$$

$$\underline{Z} = \underline{\Sigma}\left(\bar{\Sigma}^{-1}\bar{Z}^r + \tilde{\Sigma}^{-1}Z_1^*\right) \quad . \qquad \text{(H-28)}$$

Then we can write Z_0^* as

$$Z_0^* = \underline{Z} + \bar{\mu}_0 \underline{\Sigma} \ell$$

similar to the equation for Z_1^*. We find the Lagrange multiplier by forcing the constraint $\ell^t Z_0^* = 0$ to hold:

$$\ell^t Z_0^* = \ell^t \underline{Z} + \bar{\mu}_0 \ell^t \underline{\Sigma} \ell = 0 \quad ,$$

which results in

$$\bar{\mu}_0 = -\frac{\ell^t \underline{Z}}{\ell^t \underline{\Sigma} \ell} \quad .$$

We may think of $\ell^t \underline{Z}$ as the operator's estimate of the inspector's estimate of the materials balance, $\underline{M}$, when the inspector pools all the data and assumes the operator's data have not been falsified. The variance of $\underline{M}$ is $\ell^t \underline{\Sigma} \ell$. Thus, the value of Z_0^* is

$$Z_0^* = \underline{Z} - \frac{\underline{\Sigma}\ell}{\ell^t\underline{\Sigma}\ell}\,\ell^t\underline{Z} \quad . \tag{H-29}$$

Note that Z_0^* depends on the falsification F because $\underline{Z}$ is a function of $\overline{Z}^r$, Eq. (H-28).

The next step is for the operator to select his falsification values, F^*, from Eq. (H-17). From Eqs. (H-21) through (H-24), the numerator of the likelihood ratio is

$$\begin{aligned} p\left(\overline{Z}^r, Z_1^* \middle| H_1; Z_1^*, F\right) &= \overline{A}\exp\left[-\frac{1}{2}\left(\overline{Z}^r - Z_1^* + F\right)^t \overline{\Sigma}^{\,-1}\left(\overline{Z}^r - Z_1^* + F\right)\right] \\ &= \overline{A}\exp\left[-\frac{1}{2}\left(\overline{Z} - Z_1^*\right)^t \overline{\Sigma}^{\,-1}\left(\overline{Z} - Z_1^*\right)\right] \quad , \end{aligned}$$

and the denominator is

$$\begin{aligned} p\left(\overline{Z}^r, Z_1^* \middle| H_0; Z_0^*, 0\right) &= \overline{A}\exp\left[-\frac{1}{2}\left(\overline{Z}^r - Z_0^*\right)^t \overline{\Sigma}^{\,-1}\left(\overline{Z}^r - Z_0^*\right)\right] \\ &\quad \cdot \tilde{A}\exp\left[-\frac{1}{2}\left(Z_1^* - Z_0^*\right)^t \tilde{\Sigma}^{\,-1}\left(Z_1^* - Z_0^*\right)\right] \quad , \\ &= \overline{A}\exp\left[-\frac{1}{2}\left(\overline{Z} - Z_0^* - F\right)^t \overline{\Sigma}^{\,-1}\left(\overline{Z} - Z_0^* - F\right)\right] \\ &\quad \cdot \tilde{A}\exp\left[-\frac{1}{2}\left(Z_1^* - Z_0^*\right)^t \tilde{\Sigma}^{\,-1}\left(Z_1^* - Z_0^*\right)\right] . \end{aligned} \tag{H-30}$$

As indicated earlier, the numerator of the likelihood ratio is functionally independent of F, whereas the denominator is not. Therefore, the operator should choose $F = F^*$ to maximize the density function, or its logarithm, in Eq. (H-30). A necessary condition for that to occur is that the partial derivatives of the log likelihood function with respect to F, evaluated at F^*, be zero, which implies that

$$\left(\overline{Z} - Z_0^* - F^*\right)^t \overline{\Sigma}^{\,-1}\left(I + \frac{\partial Z_0^*}{\partial F}\right) + \left(Z_1^* - Z_0^*\right)^t \tilde{\Sigma}^{\,-1}\left(\frac{\partial Z_0^*}{\partial F}\right) = 0 \quad ,$$

where I is the unit matrix of proper dimension, and

$$\frac{\partial z_0^*}{\partial F} = -\left(I - \frac{\underline{\Sigma}\ell\ell^t}{\ell^t\underline{\Sigma}\ell}\right)\underline{\Sigma}\,\overline{\Sigma}^{\;-1} = -\frac{\partial z_0^*}{\partial \overline{z}^r} \quad .$$

Using Eqs. (H-27) through (H-29), and after much rearranging, the operator's optimum value of falsification, F^*, is*

$$\begin{aligned} F^* &= \overline{z} - \overline{\Sigma}\left(\overline{\Sigma} + \tilde{\Sigma}C_1^t\right)^{-1}\left(I - C_1\right)z_1^* \\ &= \overline{z} - \overline{\Sigma}\left(\overline{\Sigma} + \tilde{\Sigma}C_1^t\right)^{-1}\left(I - C_1\right)\left[\left(I - C_2\ell^t\right)\overline{z} + C_2\overline{d}\right] \quad , \qquad \text{(H-31)} \end{aligned}$$

where the matrices C_1 and C_2 are not functions of the data and are given by

$$C_1 = (\ell^t\underline{\Sigma}\ell)^{-1}\underline{\Sigma}\ell\ell^t \qquad C_2 = \left(\ell^t\overline{\Sigma} \quad + \sigma_d^2\right)\overline{\Sigma}\ell \quad . \qquad \text{(H-32)}$$

The operator's reported values, then, are

$$\overline{z}^r \triangleq \overline{z} - F = \overline{\Sigma}\left(\overline{\Sigma} + \tilde{\Sigma}C_1^t\right)^{-1}\left(I - C_1\right)z_1^* \quad . \qquad \text{(H-33)}$$

From these results, we see that the operator never need calculate Z_0^*, Eq. (H-29), explicitly. His procedure in practice is a two-step one: (1) calculate Z_1^* from Eq. (H-27); this allows him to compute his own materials balance, $\ell^t Z_1^*$, to protect against the subnational threat, for example; (2) calculate his reported values from Eq. (H-33).

---

*It can be shown that the required matrix inverse exists whenever $\overline{\Sigma}$, the operator's variance matrix, is nonsingular.

It is interesting that Eq. (H-31) generally calls for falsification even though the operator may have diverted nothing. This is a consequence of our decision to allow the operator to pursue the more general goal of minimizing the inspector's likelihood of rejecting H_0, rather than just concealing the operator's diversion activities if and when they occur. This is an important point: the operator has more reason to falsify than solely to hide diversion. He may have no intention of diverting NM, but he would very much like to keep the inspector's false-alarm rate low. Equation (H-31), with $\bar{d} = 0$, is his prescription for doing that.

In this analysis, we have not considered the possibility that the inspector might examine the sample statistics of the operator's reported data. For example, if the $\bar{Z}^r$ were composite, the inspector could calculate the sample variances of the $\bar{Z}^r$ and compare them with $\bar{\Sigma}$ to see if they were consistent. As another example, the inspector would be highly suspicious if the materials balance based on the operator's reported values, $\ell^t\bar{Z}^r$, were "too near" zero. Equation (H-31) will not cause this to happen, in general, but we have not allowed the operator to protect himself against this possibility explicitly, nor is the inspector permitted to take advantage of that fact in this development. These are problems to be pursued later.

c. Solution to the Inspector's Problem. Again following the development in Sec. H-D.2, the inspector first forms the conditional density function in Eq. (H-12) pursuant to finding $\hat{Z}_0$, his estimate (IMLE) of the true materials quantities assuming H_0 is true:

$$p(Z_A|H_0;Z,0) = \bar{A}\exp\left[-\frac{1}{2}(\bar{Z}^r - Z)^t\bar{\Sigma}^{-1}(\bar{Z}^r - Z)\right] \cdot \tilde{A}\exp\left[-\frac{1}{2}(\tilde{Z} - Z)^t\tilde{\Sigma}^{-1}(\tilde{Z} - Z)\right] \quad , \qquad \text{(H-34)}$$

from Eqs. (H-12) and (H-21) through (H-24). Analogous to the operator's method, the function to be maximized by finding $\hat{Z}_0$ is

$$\tilde{G}_0(Z) = \ln(\bar{A}\tilde{A}) - \frac{1}{2}(\bar{Z}^r - Z)^t\bar{\Sigma}^{-1}(\bar{Z}^r - Z) - \frac{1}{2}(\tilde{Z} - Z)^t\tilde{\Sigma}^{-1}(\tilde{Z} - Z) + \tilde{\mu}_0\ell^t Z \quad ,$$

where $\tilde{\mu}_0$ is a Lagrange multiplier. A necessary condition for a maximum is that the partial derivative of $\tilde{G}_0$ with respect to Z, evaluated at $\hat{Z}_0$, be zero:

$$\left.\frac{\partial G_0}{\partial Z}\right|_{\hat{Z}_0} = (\bar{Z}^r - \hat{Z}_0)^t \bar{\Sigma}^{-1} + (\tilde{Z} - \hat{Z}_0)^t \tilde{\Sigma}^{-1} + \tilde{\mu}_0 \ell^t = 0 \quad .$$

Solving for $\hat{Z}_0$,

$$\hat{Z}_0 = (\bar{\Sigma}^{-1} + \tilde{\Sigma}^{-1})^{-1}(\bar{\Sigma}^{-1}\bar{Z}^r + \tilde{\Sigma}^{-1}\tilde{Z} + \tilde{\mu}_0 \ell) \quad .$$

Using the notation of Eq. (H-28) and defining

$$\underset{\sim}{Z} = (\bar{\Sigma}^{-1} + \tilde{\Sigma}^{-1})^{-1}(\bar{\Sigma}^{-1}\bar{Z}^r + \tilde{\Sigma}^{-1}\tilde{Z}) \quad , \tag{H-35}$$

we can write $\hat{Z}_0$ as

$$\hat{Z}_0 = \underset{\sim}{Z} + \tilde{\mu}_0 \underline{\Sigma} \ell \quad .$$

The value of the Lagrange multiplier is found by forcing the materials balance constraint to be satisfied:

$$\ell^t \hat{Z}_0 = \ell^t \underset{\sim}{Z} + \tilde{\mu}_0 \ell^t \underline{\Sigma} \ell = 0 \quad .$$

Rearranging,

$$\tilde{\mu}_0 = -(\ell^t \underline{\Sigma} \ell)^{-1} \ell^t \underset{\sim}{Z} \quad ,$$

and $\hat{Z}_0$ is given by

$$\hat{Z}_0 = \underset{\sim}{Z} - (\ell^t \underline{\Sigma} \ell)^{-1} \underline{\Sigma} \ell \ell^t \underset{\sim}{Z} \quad . \tag{H-36}$$

In a similar fashion, the inspector must calculate his estimate of the true materials quantities assuming H_1 is true, $\hat{Z}_1$, and his estimates of the diversion and falsification, $\hat{d}$ and $\hat{F}$, respectively, from Eq. (H-13). The density function in that equation is

$$p(Z_A | H_1 ; Z, F) = \bar{A} \exp \left[-\frac{1}{2} (\bar{Z}^r - Z + F)^t \bar{\Sigma}^{-1} (\bar{Z}^r - Z + F) \right] \cdot \tilde{A} \exp \left[-\frac{1}{2} (\tilde{Z} - Z)^t \tilde{\Sigma}^{-1} (\tilde{Z} - Z) \right] \quad .$$

The function to be maximized in finding $\hat{Z}_1$, $\hat{d}$, and $\hat{F}$ is

$$\tilde{G}_1(Z, d, F) = \ln (\bar{A}\tilde{A}) - \frac{1}{2} (\bar{Z}^r - Z + F)^t \bar{\Sigma}^{-1} (\bar{Z}^r - Z + F) - \frac{1}{2} (\tilde{Z} - Z)^t \tilde{\Sigma}^{-1} (\tilde{Z} - Z) + \tilde{\mu}_1 (\ell^t Z - d) \quad ,$$

where $\tilde{\mu}_1$ is another Lagrange multiplier. As usual, the necessary condition for a maximum is that the partial derivatives of $\tilde{G}_1$ with respect to Z, d, and F, evaluated at $\hat{Z}_1$, $\hat{d}$, and $\hat{F}$, be zero:

$$\left. \frac{\partial \tilde{G}_1}{\partial Z} \right|_{\hat{Z}_1, \hat{d}, \hat{F}} = (\bar{Z}^r - \hat{Z}_1 + \hat{F})^t \bar{\Sigma}^{-1} + (\tilde{Z} - \hat{Z}_1)^t \tilde{\Sigma}^{-1} + \tilde{\mu}_1 \ell^t = 0 \quad ,$$

$$\left. \frac{\partial \tilde{G}_1}{\partial d} \right|_{\hat{Z}_1, \hat{d}, \hat{F}} = -\tilde{\mu}_1 = 0 \quad ,$$

$$\left.\frac{\partial \tilde{G}_1}{\partial F}\right|_{\hat{Z}_1,\hat{d},\hat{F}} = (\bar{Z}^r - \hat{Z}_1 + \hat{F})^t \bar{\Sigma}^{-1} = 0 \quad .$$

Solving these equations for $\hat{Z}_1$, $\hat{d}$, and $\hat{F}$ yields

$$\begin{aligned} \hat{Z}_1 &= \tilde{Z} \quad , \\ \hat{d} &= \ell^t \tilde{Z} \quad , \\ \hat{F} &= \tilde{Z} - \bar{Z}^r \quad . \end{aligned} \tag{H-37}$$

That is, the IMLEs of the true materials quantities and the diversion, if falsification may have occurred (i.e., H_1 true), are based solely on the inspector's data. Furthermore, the inspector's best estimate of the falsification is just the difference between his measured values and the operator's, taken on an individual basis.

The next step is for the inspector to calculate the likelihood ratio in Eq. (H-14) in preparation for performing his test. From Eq. (H-37), the numerator density function in Eq. (H-14) is just $\bar{A}\tilde{A}$ by construction. The denominator density function is

$$\begin{aligned} p(Z_A|H_0;Z_0,0) = \bar{A} \exp & \left[- \frac{1}{2}(\bar{Z}^r - \hat{Z}_0)^t \bar{\Sigma}^{-1} (\bar{Z}^r - \hat{Z}_0)\right] \\ & \cdot \tilde{A} \exp \left[- \frac{1}{2}(\tilde{Z} - \hat{Z}_0)^t \tilde{\Sigma}^{-1} (\tilde{Z} - \hat{Z}_0)\right] \quad , \end{aligned}$$

and, using the properties of the logarithm function, we can write the inspector's test as

$$\text{If } \frac{1}{2}(\bar{Z}^r - \hat{Z}_0)^t \bar{\Sigma}^{-1} (\bar{Z}^r - \hat{Z}_0) + \frac{1}{2}(\tilde{Z} - \hat{Z}_0)^t \tilde{\Sigma}^{-1} (\tilde{Z} - \hat{Z}_0) \underset{H_1}{\overset{H_0}{\lessgtr}} \ln \lambda \ .$$

The inspector's test statistic can be expressed in terms of measured values only by substituting for $\hat{Z}_0$ from Eq. (H-36). When this is done, after a great deal of algebraic manipulation, the result is

$$\text{If } \frac{1}{2}(\bar{Z}^r - \tilde{Z})^t \underset{\sim}{\Sigma}^{-1}(\bar{Z}^r - \tilde{Z}) + \frac{M_p^2}{2\sigma_p^2} \overset{H_0}{\underset{H_1}{\lessgtr}} \ln \lambda \quad , \tag{H-38}$$

where

$$\begin{aligned} \underset{\sim}{\Sigma} &= \bar{\Sigma} + \tilde{\Sigma} \quad , \\ \underline{\Sigma} &= (\bar{\Sigma}^{-1} + \tilde{\Sigma}^{-1})^{-1} \quad , \\ M_p &= \ell^t \underset{\sim}{Z} = \ell^t \underline{\Sigma}(\bar{\Sigma}^{-1}\bar{Z}^r + \tilde{\Sigma}^{-1}\tilde{Z}) \quad , \\ \sigma_p^2 &= \ell^t \underline{\Sigma} \ell = \text{var } (M_p) \quad . \end{aligned} \tag{H-39}$$

Equation (H-38) can be written in more illustrative form as

$$\text{If } \frac{1}{2}(\hat{F}^t \underset{\sim}{\Sigma}^{-1}\hat{F}) + \frac{M_p^2}{2\sigma_p^2} \overset{H_0}{\underset{H_1}{\lessgtr}} \ln \lambda \quad , \tag{H-40}$$

using Eq. (H-37). The quantity on the left of Eqs. (H-38) and (H-40) is called the inspector's sufficient statistic (ISS).

Clearly, the ISS has two components: one sensitive to falsification and the other sensitive to diversion meant to be hidden within the measurement uncertainties. Furthermore, these two pieces are statistically independent as evidenced by the form of the ISS, a fact that may be easily verified by direct computation of the covariance between them.

The falsification component of the ISS is intuitively obvious, in retrospect. It depends on a measurement-by-measurement comparison of the operator's and inspector's values, and <u>not</u> only on a comparison of the operator's and the inspector's materials balances, $\ell^t\bar{Z}^r$ and $\ell^t\tilde{Z}$. If all measurement error variances were equal, the two approaches would be equivalent; for unequal variances, the latter approach would allow the operator to falsify in any manner he chooses, as long as his resulting balance is statistically consistent with that of the inspector. It is also clear that the inspector's sensitivity to falsification depends on the goodness of both his own and the operator's measurements, that is, $\underset{\sim}{\Sigma}$, which is larger than either the inspector's or operator's measurement error variance by Eq. (H-39).

If there has been no falsification, which the inspector can decide by examining the falsification component of the ISS, then his best estimate of any diversion is M_p, the pooled materials balance based on a weighted linear combination of <u>all</u> the data. The variance of M_p is $\sigma_p^2 = \ell^t\underline{\Sigma}\ell$, which is smaller than the variance of the materials balance calculated using either the operator's or inspector's data alone, as shown in Eq. (H-39). Thus, if the operator is not falsifying, the inspector always has a better materials balance than the operator, although in practice the improvement may be slight. In any case, the definitions of σ_p^2 and $\underline{\Sigma}$ indicate to the inspector those measurements for which upgrading would provide the most benefit.

The threshold for the test, λ, can be found by standard methods. At the threshold, let the value of the inspector's sufficient statistic be ISS = ISS_T. Then, for a specified FAP, α, ISS_T is the solution to

$$\alpha = \int_{\mathrm{ISS}_T}^{\infty} p(\mathrm{ISS}\,|\,H_0)\; d(\mathrm{ISS}) \quad ,$$

where ISS has a chi-square distribution by Eq. (H-40). The test threshold is

$$\ln \lambda = \mathrm{ISS}_T \quad . \tag{H-41}$$

<u>4. Further Developments.</u> As specified at the beginning of this section, we have considered the simplest, in most respects, statistical verification problem. Addressing the following areas would provide a more general treatment of the problem:

- The operator may have knowledge of some of the inspector's measurement results before the operator falsifies. The inspector may or may not know the extent of the operator's knowledge.
- The inspector can look for positive diversion only, and falsification of the appropriate sign.
- The inspector's and operator's measurements may not be statistically independent for any of several reasons, including common standards, for example.
- If the inspector's and operator's measurements are composites of many values, the measurement results may be obtained on a random sampling basis.
- If the inspector has incomplete knowledge of the probabilistic descriptions of the measurement errors, or if he wishes to protect against a misstatement of them, he may want to perform a nonparametric analysis.
- The inspector may wish to examine the sample statistics of the operator's data to make sure they are consistent with the measurement error descriptions.

All these modifications would be straightforward, albeit tedious, to incorporate. However, there are two additional areas of development that need to be pursued, particularly in view of the advent of high-throughput nuclear facilities and the concomitant consideration of near-real-time accounting in which data from several related materials balance areas and periods will be available. They are:

- Development of inspector procedures for time sequences of correlated materials balances, and
- Development of inspector procedures for spatially related materials balance areas.

These two developments are also interesting because, unlike the problem treated in this work, the possibility exists for the inspector to trade off measurement effort in time and location.

REFERENCES

1. "The Structure and Content of Agreements Between the Agency and States Required in Connection with the Treaty on the Non-Proliferation of Nuclear Weapons," International Atomic Energy Agency document INFCIRC/153 (June 1972).

2. IAEA Safeguards Technical Manual, Part A, "Safeguards Objectives, Criteria, and Requirements," (International Atomic Energy Agency, Vienna, 1976), para 5.1.3.

3. A. Hald, Statistical Tables and Formulas (John Wiley & Sons, Inc., New York, 1952), pp. 34-35.

4. E. A. Hakkila, D. D. Cobb, H. A. Dayem, R. J. Dietz, E. A. Kern, E. P. Schelonka, J.P. Shipley, D. B. Smith, R. H. Augustson, and J. W. Barnes, "Coordinated Safeguards for Materials Management in a Fuel Reprocessing Plant," Los Alamos Scientific Laboratory report LA-6881 (September 1977).

5. H. A. Dayem, D. D. Cobb, R. J. Dietz, E. A. Hakkila, E. A. Kern, J. P. Shipley, D. B. Smith, and D. F. Bowersox, "Coordinated Safeguards for Materials Management in a Nitrate-to-Oxide Conversion Facility," Los Alamos Scientific Laboratory report LA-7011 (April 1978).

6. L. M. Adleman and R. L. Rivest, "The Use of Public Key Cryptography in Communication System Design," IEEE Comm. Soc. Mag. 16(6), 20-23 (1978).

7. W. Diffie and M. E. Hellman, "Privacy and Authentication: An Introduction to Cryptography," Proc. IEEE 67, 397-427 (1979).

8. R. A. Lederer, Sandia Laboratories, Albuquerque, "Securing Data in International Safeguards Systems: Transmission, Storage, and Management," personal communication to D. B. Smith (April 1979).

9. C. G. Hough, R. A. Schneider, K. B. Stewart, J. L. Jaech, and C. A. Bennett, "Example of Verification and Acceptance of Operator Data-Low-Enriched Uranium Fabrication," Battelle Pacific Northwest Laboratories report BNWL-1852 (August 1974).

10. IAEA Safeguards Technical Manual, Part E, International Atomic Energy Agency Technical Document IAEA-174 (Vienna, 1976).

11. D. Blackwell and M. A. Girshick, Theory of Games and Statistical Decisions (John Wiley & Sons, Inc., New York, 1954).

12. E. L. Lehmann, Testing Statistical Hypotheses (John Wiley & Sons, Inc., New York, 1959).

13. A. P. Sage and J. L. Melsa, Estimation Theory with Applications to Communications and Control (McGraw Hill Book Co., New York, 1971).

14. C. R. Rao, Linear Statistical Inference and Its Applications, 2nd Ed. (John Wiley & Sons, Inc., New York, 1973).

15. J. Neyman and E. S. Pearson, "On the Problem of the Most Efficient Tests of Statistical Hypotheses," Phil. Trans. Roy. Soc., Ser. A, 231, pp. 289-337 (1933).

16. W. Feller, An Introduction to Probability Theory and Its Applications, Vol. I (John Wiley & Sons, Inc., New York, 1973).

APPENDIX I

OPERATOR'S SAFEGUARDS SYSTEM: SECURITY AND RELIABILITY OF THE MATERIALS MEASUREMENT AND ACCOUNTING SYSTEM

J. T. Markin and A. L. Baker
LASL Safeguards System (Q-4)

A. Safeguards Security Overview

More and more Nuclear Facility Information Systems are being upgraded by computerizing older facilities and by installing computers and computer information systems in new facilities (see Ref. 1, Sec. III). This trend is a result of the desire for increased speed in data processing and improved timeliness and accuracy of the data base and the output documents. Computerized information systems also offer greater flexibility in manipulating data to detect meaningful trends.

Current technology can assure valid security controls for safeguarding information from computerized systems. This technology can enable the safeguards system to detect in a timely manner safeguards violations at the national and subnational levels with a high degree of confidence. Computerized data-acquisition systems operated in known hostile environments provide levels of protection far in excess of the level required for international safeguards, whereas relatively simple tamper-indicating systems could provide adequate verification of integrity and sufficient indication of national diversion.[2]

Information-system action usually begins at the source by the direct transfer of digital data from interfaced instruments. Human interactions, such as data entry or gathering through computer terminals, must be kept to the absolute minimum. Subnational fraud is controlled by interactive personnel authentication techniques and the use of two-person or shipper and receiver concurrence on NM transactions. To control national or facility-wide subversion, the system is programmed to provide entry error detection through reasonableness bounds and comparisons. Data-base integrity is maintained by establishing and tracing manually verifiable audit trails available for internal facility and external IAEA Inspector audits and by providing secure input for random interrogation and independent verification of the data base by the inspectorate.

Recent developments in encryption and data-authentication techniques are applicable to securing information transmission to a safeguards information center or data bank. The National Bureau of Standards (NBS) Encryption Standard is now functioning in the commercial sector as an easily implemented data security measure. A system known as TRUST, developed in 1968 by SLA for the Arms Control and Disarmament Agency (ACDA) and the IAEA, provided complete authentication, integrity verification, and fraud detection in data from operating CANDU reactors during normal and refueling operations.[3] TRUST is extremely difficult to break even though the adversary has total knowledge of the data being transmitted. Its primary limitations are the amount and rate of data transmission. More compact and sophisticated derivatives of TRUST are being proposed for international use in unattended sensor stations for the proposed Comprehensive Test Ban Treaty (CTBT).[4] The current ACDA-sponsored program, RECOVER, is being designed to provide secure data transmission from nuclear facilities to IAEA headquarters.

Personnel identification tests at system sign-on and file-access points protect data-base integrity from unauthorized disclosure. Covert data collection is inhibited through the use of metallic room and component shields designed to attenuate both near-field and far-field electromagnetic emanations from terminals, printers, and computer main frames as is currently done in secure communications centers. Time-domain reflectometry for detecting taps or more complex tap-resistant, dual-channel fiber-optics communication links can be used. In addition to data authentication and encryption, random character stuffing in the data stream is used to inhibit signal-pattern recognition.

Data are transmitted from computers to off-site data repositories by the message-formatting, error-detection, and error-correction methods of ARPANET for communicating through noisy land-line or satellite channels.[5] An encryption interface incorporated into ARPANET allows computers to intercommunicate at US defense security levels at least as high as SECRET. Classified data packets travel through the network simultaneously with unclassified data packets. The proposed RECOVER system sponsored by ACDA is intended for remote read-out of nuclear facility information system computer data and will use the simpler NBS Encryption Standard.

A safeguards control system encompassing a broad range of sensors, displays, alarms, and enable/disable functions may use any or all of the previously described authentication, encryption, and encoding techniques. Essential control signals within the facility are routed through protected wire lines sealed in conduit. Secure computer operating systems that inhibit penetration are being developed for large main-frame computers[6] and medium-scale minicomputers.[7]

The most credible threat to the security system is a computer operator who could exercise essentially unlimited privileges with the machine and its resources. The computer operator must be severely restricted in his functions and closely supervised and/or employed by the appropriate safeguards authority.

The extent to which data- and computer-security countermeasures need be incorporated in the overall system depends upon the specific installation, the type of fuel cycle, and the threat environment. The computer-security simulation code SECSIM provides methods and measurement criteria for determining security effectiveness.[8] Graded technological, administrative, and physical-security strategies are modeled and evaluated, allowing successive designs to converge toward a systems architecture having an acceptable level of security effectiveness.

B. Data Protection and Authentication

International aspects of safeguards system security will emphasize the protection of measurement data. The IAEA specification[9] that the inspector make use of the State's system of accounting requires that the input data generated by measurement instruments be verifiable. The inspector must verify not only that the instrument is in correct calibration but also that it is measuring the material purported to be measured and that the data received by the inspector was actually sent by the instrument.

Each of these possible operator methods for subverting the accounting system--miscalibration, materials substitution, or data-tampering--has an appropriate inspector response (Sec. VI). The inspector checks for possible miscalibration of an instrument by on-line calibration using standards previously measured by the operator but unknown to him. Materials substitution is prevented either by correlating the expected process sequence with the instrument measurements or by using overlapping UPAAs to remove a selected instrument's input to the materials balance. Tampering with instrument data is countered by encoding methods that may, for example, use recently developed public-key cryptography. These responses to potential subversion by the operator are discussed in detail in App. H. Implementation of these inspector procedures will guarantee reliable measurement data.

Candidate encryption systems that could be used in a safeguards security system are the Data Encryption Standard (DES) and the public-key system.[10] The DES algorithm, developed by IBM, defines a set of operations to be performed on a 64-bit block of information to encipher it into a 64-bit block of ciphertext. To use DES for data distribution, the encipher key is secured by the sender. Data are enciphered with this secret key and transmitted over unsecure transmission lines to their destination, where the recipient decrypts the data by using the decipher key. This approach does not allow authentication if an unauthorized person has knowledge of the encipher key.

A more promising solution to ensuring data security is the use of public-key cryptography, where the sender and receiver generate two keys--an enciphering key E and a deciphering key D. The keys are related in that they implement inverse operations; operating on a plaintext message first with E and then D reproduces the message. The advantage of this system is that it is not feasible to derive D from E, so the enciphering key is not secret. To send a secure message, encipher with the public key E, send the ciphertext over a (possibly insecure) channel, and decipher with the secret key D. Details of implementing public-key cryptography in the international safeguards environment are discussed in App. H and Ref. 10.

C. Safeguards System Reliability

Reliable instrument data form the basis of dependable safeguards operation. Reliability is important because process disruption must be minimized and accurate and timely materials accounting must be ensured. The likelihood that a measurement instrument will be operational when required is specified by the mean time before failure (MTBF) (a measure of the frequency of failure occurrence) and the mean time to repair (MTTR) (a measure of the time an instrument is unavailable after a failure). Two useful descriptions of instrument reliability, survival probability P and availability AV, are calculated from the MTBF and MTTR. The survival probability P that an instrument functions for some length of time T before failure is

$$P = \exp(-T/MTBF) \quad ,$$

and the availability or fraction of the time that an instrument is operational out of its total demand time is

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

Another commonly used measure of instrument performance is the downtime per year (DTY)

$$DTY = (1 - AV)8760 \text{ h/yr} \quad .$$

Reliability of the process measurements is enhanced through redundant instrumentation. The computer code RELSIM was developed to evaluate instrumentation redundancy strategies in complex networks that include nonidentically redundant components and that have survivability criteria involving M of N instruments. RELSIM is useful in simulating systems in which incremental upgrading of instrument reliability is taking place, especially through the use of nonidentical redundancies introduced to avoid common-mode failures that can lead to simultaneous failures of instruments. The RELSIM code has been applied to the reference process to evaluate the reliability attainable under differing instrumentation redundancy strategies.

Reliability calculations for the instrumentation in each UPAA are based on a categorization of the measurement points into a set of KMPs representing a minimum set of measurements that might be used to estimate a materials balance, and an extended set of measurement points, including the KMPs plus some additional points, that allow a more accurate materials balance estimate. The key and extended sets of points are summarized in Table I-I and availability estimates for the instruments used at these points are summarized in Table I-II. A complete description of the instrumentation at all process measurement points is given in Sec. IV.

Minimum availability requirements for the key or major flow measurement points were chosen to avoid interference of instrument failure with normal process flow and to take into consideration those process characteristics allowing flexibility in scheduling a measurement, such as batch frequency or parallel tanks that allow the process to continue although only M of N tank instruments are functional. Required measurement point availabilities compatible with uninterrupted process flow are given in Table I-III.

The RELSIM computer program was used to find the availability of measurements in each UPAA, assuming either nonredundant instrumentation or redundant instrumentation that uses one back-up instrument. For reliability calculations the UPAA measurement capability is said to be available when there is at least one functioning set of instrumentation at each measurement point. The UPAA availabilities are shown in Table I-IV in terms of downtime; estimated UPAA availabilities are based on the instrument reliabilities of Table I-II, and required UPAA availabilities are based on the KMP reliabilities of Table I-III.

Considering only the KMPs, the required availability is attained in UPAA 1 and UPAA 3 with nonredundant instrumentation and in UPAA 2 with singly redundant instrumentation. However, the significant reductions in downtime attainable with redundant instrumentation suggest a redundant instrumentation plan for all UPAAs.

TABLE I-I

MEASUREMENT POINTS FOR RELIABILITY ANALYSIS

UPAA 1

Accountability tank[a]
Feed adjust tank
HAW stream
1BP surge tank[a]

UPAA 2

1BP surge tank[a]
2AW stream
2BW stream
3AW stream
3BW stream
3PD stream
3PCP stream
Pu nitrate sample tank[a]

UPAA 3

Receipt tank[a]
Precipitator
Furnace sweep
Boat flush
Dump station sweep
Pu product[a]

---

[a] Key measurement points.

TABLE I-II

ESTIMATED INSTRUMENTATION DOWNTIME

Instrument	Downtime (%)
Electromanometer	2
Chemical analysis	2
Flow meter	1
Densitometer	1/2
Neutron well counter	1/2
Balance	1/2
Mass spectrometer	3

TABLE I-III

KEY MEASUREMENT POINT REQUIRED AVAILABILITIES

Measurement Point	Availability
Accountability tank	0.8621
1BP surge tank	0.9993
Sample tank	0.9993
Receipt tank	0.9708
Product canister	0.9615

TABLE I-IV

UPAA DOWNTIME SUMMARY

UPAA	Key Measurement Points Required h/yr	Key Measurement Points Estimated Nonredundant h/yr	Key Measurement Points Estimated Redundant h/yr	Extended Measurement Points Estimated Nonredundant h/yr	Extended Measurement Points Estimated Redundant h/yr
1	1212.5	745.0	17.5	1499.1	39.1
2	12.2	667.1	13.5	1397.2	21.4
3	582.0	102.3	0.5	481.1	5.0

Under this strategy the maximum expected downtime in any UPAA is ∿18 h/yr for key points and ∿40 h/yr for the extended set of points. These downtimes are so small that virtually no process interference would be expected.

REFERENCES

1. E. A. Hakkila, D. D. Cobb, H. A. Dayem, R. J. Dietz, E. A. Kern, E. P. Schelonka, J. P. Shipley, D. B. Smith, R. H. Augustson, and J. W. Barnes, "Coordinated Safeguards for Materials Management in a Fuel Reprocessing Plant," Los Alamos Scientific Laboratory report LA-6881 (September 1977).

2. L. J. Hoffman, Modern Methods for Computer Security and Privacy (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1977), p. 3.

3. J. Campbell, Sandia Laboratories, personal communication to E. P. Schelonka, August 1978.

4. A. M. Fine, R. S. Reynolds, R. E. D. Stewart, and P. A. Stokes, "Feasibility Study of an Advanced Unattended Seismic Observatory", Sandia Laboratories report SLA-73-0008 (March 1973).

5. L. G. Roberts and B. D. Wessler, "Computer Network Development to Achieve Resource Sharing", AFIPS Conf. Proc., Spring Joint Computer Conference (1970).

6. G. E. Reynolds, "Multics Security Evaluation: Exemplary Performance Under Demanding Workload", ESD-TR-74-193, Vol. IV, Electronics Systems Division, Hanscom Air Force Base, Massachusetts, (November 1976).

7. M. Kert, "Advances in Minicomputer and Front-End Security", Proc. Computer Security and Privacy Symp., Scottsdale, Arizona, April 19-20, 1977.

8. E. P. Schelonka, "Event and Effectiveness Models for Simulating Computer Security", presented at the IEEE Computer Conference COMPCON FALL, Washington, DC, September 5-8, 1978.

9. "The Structure and Content of Agreements Between the Agency and States Required in Connection with the Treaty on the Non-Proliferation of Nuclear Weapons," IAEA INFCIRC/153 (June 1972).

10. R. A. Lederer, "Securing Data in International Safeguards Systems: Transmission, Storage, and Management," personal communication to D. B. Smith (April 1979).

APPENDIX J

ESTIMATION OF IN-PROCESS INVENTORY IN SOLVENT-EXTRACTION CONTACTORS

D. D. Cobb and C. A. Ostenak
LASL Safeguards Staff (Q-4)

J. E. Bennett and A. L. Beyerlein
Clemson University

L. E. Burkhart
Iowa State University/DOE-Ames Laboratory

D. R. Engler
General Atomic Company

A. F. Cermak
Allied-General Nuclear Services

A. Introduction

All commercial nuclear fuels reprocessing plants use the Purex process for the separation and purification of uranium and plutonium from spent nuclear fuels. Separation and purification are achieved with a series of solvent-extraction contactors in which uranium and plutonium are selectively transferred between relatively immiscible countercurrent aqueous and organic streams. To optimize the sensitivity of near-real-time accounting for NM in reprocessing plants, estimates of the in-process inventories in the solvent-extraction contactors are required.

The LASL Safeguards Systems Group (Q-4) has initiated a modest effort within the existing US Department of Energy-Safeguards and Security research and development program to develop techniques for estimating contactor inventories. Under LASL sponsorship, researchers at Clemson University are studying the effects of mass-transfer dynamics and chemical kinetics on contactor behavior and of modern systems identification techniques that can be used for real-time estimation of contactor inventory. In addition, researchers at Iowa State University and the DOE-Ames Laboratory are developing state-of-the-art theoretical models of pulsed-column behavior.

The General Atomic Company (GA) is providing experimental data on pulsed-column uranium inventories from process development work at their Solvent-Extraction Pilot Plant. This pilot plant is a valuable resource for obtaining essential operating data to compare with pulsed-column models. In addition, AGNS is supplying pulsed-column data from their Engineering Laboratory. Such data, virtually nonexistent in the open literature, are essential for model verification.

The importance of contactor in-process inventory to dynamic accounting systems for reprocessing plants is highlighted in recent safeguards systems studies.[1-3] Tables J-I and J-II show the inventory of in-process plutonium for the model 1500-MTHM/yr reference separations plant (pulsed-column contactors) and the model 210-MTHM/yr small separations plant (mixer-settler contactors), respectively.

For the reference large plant, Table J-III shows the effect of uncertainties in pulsed-column inventory estimates on dynamic materials accounting in the PPP, (see App. B for a description of this process). The calculated standard deviation of near-real-time materials balances is given as a function of the relative uncertainty in estimating the inventory in each column contactor for accounting periods of 8 h to 7 days. The contactor-inventory uncertainty has a significant effect over relatively short accounting periods, but has a much smaller effect over longer periods as throughput-measurement

TABLE J-I

MODEL 1500-MTHM/YR REFERENCE PLANT IN-PROCESS INVENTORY

Process Equipment	Inventory (kg Pu)
Decon/Partition	
Feed-Adjust Tanks (2)	19.9 ea
Centrifuge	<<1
HA Feed Tank	35.9
HA Contactor	<<1
HS Column	1.5
1B Column	1.6
Total: ≤80 kg	Contactors: ∿3-4 kg
Plutonium Purification	
1BP Tank	7.4
2A Column	4.6
2B Column	2.8
3A Column	5.4
3B Column	4.8
3PS Wash Column	1.2
3P Concentrator	15.0
Total: ∿41 kg	Contactors: ∿19 kg

TABLE J-II

MODEL 210-MTHM/YR SMALL PLANT IN-PROCESS INVENTORY

Process Equipment	Inventory (kg Pu)
Feed Tank 1	2.5
Mixer-Settler 1	0.7
Mixer-Settler 2	0.1
Feed Tank 2	1.3
Mixer-Settler 3	0.5
Mixer-Settler 4	0.4
Feed Tank 3	1.0
Oxidation Columns	0.2
Mixer-Settler 5	0.5
Mixer-Settler 6	0.3
Feed Tank 4	1.1

Total: ∿8.6 kg　　Contactors: ∿2.5 kg

TABLE J-III

EFFECT OF COLUMN-INVENTORY-ESTIMATION UNCERTAINTY ON MATERIALS ACCOUNTING IN THE REFERENCE PPP

	Materials-Balance Standard Deviation (kg Pu)			
	Column-Inventory-Estimation Uncertainty			
Accounting Period	2%	5%	10%	20%
8 h	0.63	0.86	1.41	2.64
1 day	0.76	0.96	1.47	2.67
2 days	1.06	1.22	1.65	2.77
3 days	1.42	1.54	1.90	2.93
5 days	2.20	2.28	2.54	3.38
7 days	3.01	3.06	3.26	3.95

errors dominate (see App. E). Thus, good estimates of the contactor inventory are essential for detecting short-term losses of in-process materials. The goal of the current program is to develop techniques for estimating contactor inventories to 5-10%. The safeguards systems studies indicate that such estimates should be adequate for effective near-real-time accounting.

B. Techniques for Contactor In-Process Inventory Estimation

The following techniques for estimating contactor in-process inventory have been identified: (1) direct inventory measurements; (2) isotope tracer methods; (3) dynamic state estimation; and (4) "reduced-order" dynamic state estimation. None of these techniques has been fully developed for contactor-inventory estimation. Elements of each technique, separately or in combination, may be applicable to any particular contactor system.

1. Direct Inventory Measurements. A variety of process control instrumentation is installed in a nuclear reprocessing plant. Much of this plant-grade instrumentation is used to monitor and control the operation of solvent-extraction contactors. For example, the acid concentrations, flow rates, and temperatures of inlet and outlet streams, the aqueous-organic interface levels, and the pulse amplitudes and frequencies are all monitored and controlled.

Process control measurements are typically made on input-output streams of the contactors. Stream flow-rate measurements may be obtained from the steam-jet or air-lift transfer systems. Rough calibration of those liquid-transfer systems could result in flow-rate measurements having accuracies of 5-10%. Orifice meters in headpots also could be calibrated in terms of flow rate. If alpha monitors are placed on raffinate and recycle streams, they can be calibrated to provide plutonium concentration measurements that should be adequate (10% or better) for the small concentrations (<0.1 g Pu/L) in those streams.[1]

Neutron detectors can be used to monitor the contactors for plutonium concentration "bulges" indicative of process upsets and possible criticality excursions. Whereas these neutron sensors are adequate for criticality control, they normally would not be calibrated or shielded for quantitative inventory measurements.

Sample lines may be available from selected mixer-settler stages or from outlet lines of pulsed-column disengagement sections. Where present, such sample lines could provide useful data for estimating contactor inventories.

Of particular interest for contactor-inventory estimation is the availability of high-quality flow and concentration measurements for contactor feed and product streams. If the separations process is designed so that the contactors are separated by buffer tanks, as in the case of the model small plant, then the feed and product flows and concentrations can be obtained by combining volume measurements with chemical analyses of samples of the tank contents.

A number of additional samples may be required for contactor-inventory estimation, perhaps dictating the use of rapid NDA techniques. Continuous measurements of plutonium concentration in process streams may be possible with appropriate NDA techniques and sample loops. (Measurement techniques for process streams are discussed in App. L.)

If the contactors are closely coupled, as in the reference process, it may be necessary to estimate the combined in-process inventory of a series of contactors bounded by the available input-output accounting measurements, thereby complicating the inventory-estimation algorithm and probably degrading the materials accounting sensitivity.

In summary, high-quality techniques for the direct measurement of contactor inventory are not available, and their development probably would result in substantial instrumentation costs and could require costly process design modifications. At this time, the development of methods for estimating contactor inventory by indirect measurements is more promising.

2. Isotope Tracer Methods. Isotope tracer methods for inventory determination fall into two categories, the step-displacement and the tracer-pulse techniques. Both have been proposed as possible methods for estimating the in-process inventory in an entire chemical separations process without first having to drain and flush the process line.

a. The isotope step-displacement method is discussed in Ref. 1, Vol. II, App. D and in the references therein. This method is proposed for relatively small, batch-operated chemical separations processes having little batch-mixing, that is, having small heels between batches. When the in-process inventory is to be determined, a special feed batch is prepared that has a different plutonium isotopic composition from the normal feed batches. Small output batches are collected, sampled, and isotopically analyzed from all product and recycle streams until the analyses indicate that all normal in-process materials initially present have been displaced by the special batch.

The sensitivity of the method depends primarily on the number and size of the small output batches and the maintenance of input-batch integrity throughout the process. For a large reprocessing plant, the technique may not be applicable because of (1) the large number of small batches that must be collected and analyzed, (2) the desirability of maintaining isotopically uniform product, and (3) the loss of batch integrity during normal, continuous operation.

The feasibility of the step-displacement method has been demonstrated at the small, batch-operated Eurochemic and Nuclear Fuel Services reprocessing plants.[4-5] Although difficulties were encountered in applying the method, the two plants conducted a few successful experiments resulting in plutonium and uranium inventory estimates to 5% or better.

b. The <u>isotope tracer-pulse method</u> is described in Ref. 6. The method is based on linear systems theory, in which the impulse response function of a linear, stationary system can be derived solely from input-output observations.

Rigorous application of this theory requires that two assumptions be satisfied: (1) the process is linear and is maintained at steady state during the input-output observations; and (2) the process and measurement statistics are all stationary during the observations. If these assumptions are satisfied, the in-process inventory can be estimated by first adding a series of trace quantities (pulses) of isotopically identifiable material to the input stream and then sampling and isotopically analyzing the output streams.

To apply this method successfully probably would require careful conditioning of the input stream by using well-characterized pulses of the tracer isotope and frequent, perhaps continuous, flow-rate and isotopic-assay measurements of the output streams. Because a chemical separations process will disperse the input pulses significantly in time, the output measurements must extend over a period that is significantly longer than the residence time. For example, the plutonium residence time in the reference PPP is about 1 day, and may be as long as 3 h in a single contactor.[1] The resulting inventory estimate would be averaged over an extended period, and steady-state operation would have to be maintained for good results.

3. <u>Contactor Models.</u> The most widely used computer model for solvent-extraction process development is SEPHIS (solvent extraction processes having interacting solutes).[7-10] SEPHIS was originally developed to predict the transient and steady-state

behavior of solvent-extraction contactors operating with a dilute Purex (15% TBP) LMFBR flow sheet.[7] SEPHIS has since been modified for standard Purex (30% TBP) flow sheets, incorporating changes in the computer-program structure and in the mathematical modeling of the system.[8-10]

In addition to SEPHIS, other computer models for different contactor types are being developed to simulate the solvent extraction portions of the Purex process. These computer models are discussed below.

a. Mixer-Settler Models. SEPHIS performs a stage-wise, iterative calculation of the approach to steady state of the uranium, plutonium, and HNO_3 concentrations in a multistage contactor. The contactor is modeled as a series of ideal mixer-settler stages operating at mass-transfer equilibrium; therefore, it appears that SEPHIS more nearly describes the operation of mixer-settlers than of continuous differential contactors (columns). The required number of ideal stages is a function of the phase flow ratios, the feed concentrations, and the specific equilibrium data.

Early modifications of SEPHIS included[8,9]: (1) the salting effect from nonextractable nitrate salts; (2) provisions for estimating the partitioning of plutonium from uranium; (3) the relationship between solute-free concentrations and molarities for aqueous and organic solutions; (4) the variation of temperature profile with the time interval; (5) the amount of water extracted by TBP; (6) the criterion for convergence of stage calculations; and (7) upgrading of distribution coefficients in an attempt to extend the code to higher temperatures and TBP concentrations.

The fourth and most recent modification,[10] SEPHIS-MOD4, incorporates (1) a revised convergence criterion that provides better steady-state results for flow-sheet testing, (2) program mechanics that better simulate actual run conditions during transient periods, and (3) a more representative model of mixer-settler operation.

Starting with initial uranium, plutonium, and HNO_3 concentrations and feed stream compositions, the SEPHIS program calculates the concentrations in each ideal stage at the end of each time step. Thus, calculations of transient behavior as well as of steady-state conditions can be made. However, though SEPHIS-MOD4 does include kinetics subroutines for the reduction of plutonium and allows for the insertion of other integrated chemical rate equations, it does not account for deviations from mass-transfer equilibrium, which may be important, particularly during transients. Finally, there is little experimental validation of SEPHIS in the published literature, even for steady-state operation.

Researchers at Clemson University are developing an improved chemical model, PUBG, for estimating the in-process inventories of mixer-settlers.[11] Unlike SEPHIS-MOD4, PUBG uses total flow, neglects volume of mixing effects in the flows, and calculates distribution coefficients on the basis of molarity; SEPHIS-MOD4 uses solute-free flows and bases distribution coefficients on molality. More important, whereas SEPHIS-MOD4 assumes mass-transfer equilibrium, PUBG simulates the effects of departures from equilibrium by allowing the user to specify the effective mass-transfer area (A).

For mass-transfer areas between A → ∞ (the SEPHIS equilibrium limit) and A = 10 (a large departure from equilibrium), corresponding in-process plutonium inventories can increase by 40% (Table J-IV). An increase in the inventory of 10% or more (A ≤ 40) over the equilibrium value might be expected. In practice, it may be possible to "calibrate" the model predictions for each mixer-settler bank by choosing an appropriate value for the A parameter for each set of run conditions. Furthermore, calculations indicate that the value of A, hence the departure from mass-transfer equilibrium, is very sensitive to the plutonium concentration in the waste stream (Table J-V). This concentration is commonly measured for process control, and the A parameter might be determined from measurements of the aqueous waste stream concentrations.

A comparison of the inventories of uranium and plutonium determined by experiment[8] and calculated by SEPHIS-MOD4 and PUBG (at the SEPHIS equilibrium

TABLE J-IV

PLUTONIUM AND URANIUM INVENTORIES CALCULATED FOR
DIFFERENT MASS-TRANSFER AREAS
(15-STAGE EXTRACTION/SCRUB MIXER-SETTLER)

	Plutonium Inventory (g)			Uranium Inventory (g)		
Model	Aqueous	Organic	Total	Aqueous	Organic	Total
SEPHIS-MOD4	95	521	616	13	200	213
PUBG: A → ∞	89	524	613	12	202	214
A = 100	96	531	627	13	204	217
A = 40	114	549	663	16	206	222
A = 20	151	586	737	22	212	234
A = 10	215	648	863	33	224	257

TABLE J-V

TOTAL PLUTONIUM INVENTORIES AND AQUEOUS WASTE STREAM CONCENTRATIONS CALCULATED FOR DIFFERENT MASS-TRANSFER AREAS (15-STAGE EXTRACTION/SCRUB MIXER-SETTLER)

Model	Plutonium Inventory (g) Total	Plutonium Concentration (g/L) Aqueous Waste Stream
SEPHIS-MOD4	616	5.3×10^{-6}
PUBG: $A \rightarrow \infty$	613	4.4×10^{-6}
$A = 100$	627	3.5×10^{-5}
$A = 40$	663	2.6×10^{-4}
$A = 20$	737	1.4×10^{-3}
$A = 10$	863	5.6×10^{-3}

limit) is given in Table J-VI. The experimental values shown are for a laboratory-scale batch extraction process using an 11-stage mixer-settler operating with a dilute (15.3% TBP) Purex flow sheet. Although SEPHIS-MOD4 and PUBG are capable of simulating various Purex process flow sheets, validation of the computer models with LWR (30% TBP) Purex flow sheets is not yet possible because of the lack of corresponding experimental data.

A few comparisons of calculated and experimental stage profiles and inventories have been published by SRL for their miniature mixer-settlers.[12] They modified the SRL contactor model TRANSIENTS[13] to calculate the total in-process uranium inventory in each mixer-settler bank; modifications were necessary to accommodate their 7.5% TBP-in-kerosene flow sheet that consists of two cycles to recover and purify uranium.

In Table J-VII, SRL's calculated and experimental uranium inventories for their 12-stage stripping mixer-settler are compared with PUBG and SEPHIS-MOD4 calculations. The TRANSIENTS calculation agrees with the experimental data nearly as well as PUBG (A = 4.8) because an efficiency factor of 70% is used in TRANSIENTS to account for departures from mass-transfer equilibrium.

TABLE J-VI

EXPERIMENTAL PLUTONIUM AND URANIUM INVENTORIES VERSUS SEPHIS-MOD4 AND PUBG (11-STAGE EXTRACTION/SCRUB MIXER-SETTLER)

	Plutonium Inventory		Uranium Inventory	
	Aqueous	Organic	Aqueous	Organic
Experiment[8]	18.9	14.9	81.0	183.5
SEPHIS-MOD4	23.3	16.6	88.5	173.3
PUBG A → ∞	20.0	15.7	78.9	173.3

Using the data generated by the modified TRANSIENTS code, SRL also derived power-law correlations[12] for calculating the total uranium inventory in the mixer-settler banks under various operating conditions. In all cases, the dependence of uranium inventory on uranium concentration in the feed stream was nearly linear.

b. Pulsed Columns. A set of SEPHIS-MOD3 calculations of plutonium inventory in the 2A pulsed column (second-cycle extraction) was provided by AGNS.[1,14] In a total of 87 SEPHIS runs the feed, scrub, and extractant flow rates and the plutonium

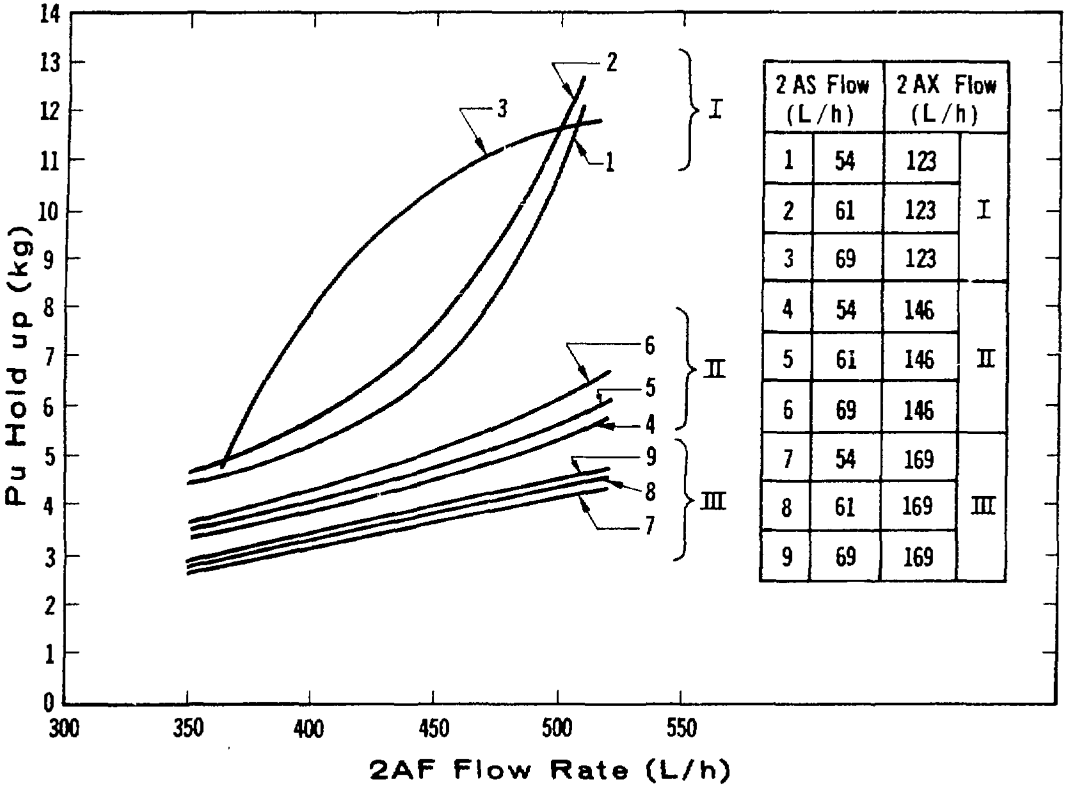
TABLE J-VII

EXPERIMENTAL URANIUM INVENTORIES VERSUS SEPHIS-MOD4, PUBG AND TRANSIENTS (12-STAGE STRIPPING MINIATURE MIXER-SETTLER)

	Uranium Inventory (g/L)		
	Aqueous	Organic	Total
Experiment[12]	3327	206	3533
SEPHIS-MOD4	2865	49	2914
PUBG A → ∞	2917	53	2970
A = 4.8	3318	224	3542
TRANSIENTS[12] (Eff. = 0.7)	3207	262	3469

concentration in the feed stream (1BP) were varied over typical operating ranges. The small amount of uranium in the feed stream had a negligible effect on the plutonium distribution in the column, as did the HNO_3 concentration in the scrub stream which can be controlled within a narrow range. The effect of varying the HNO_3 concentration in the feed stream (0.9-1.1 $\underline{M}$) was also negligible. Temperature variations were not considered.

A summary of the SEPHIS calculations of plutonium inventory versus feed (2AF) flow rate in the 2A column is shown in Fig. J-1. The calculated inventory includes the total plutonium in the scrub, extraction, and disengagement sections of the column. The inventory value corresponding to nominal flow-sheet values is 4.5 kg Pu. We estimate that ∿90% of this inventory resides in the scrub and product disengagement sections (Ref. 1, App. G).



	2 AS Flow (L/h)	2 AX Flow (L/h)	
1	54	123	I
2	61	123	
3	69	123	
4	54	146	II
5	61	146	
6	69	146	
7	54	169	III
8	61	169	
9	69	169	

Fig. J-1. Plutonium inventory vs 2AF flow rate.

Burkhart and coworkers at Iowa State University are developing a state-of-the-art computer model for simulating pulsed-column operation that incorporates several improvements over SEPHIS.[15] The model is based on a critical review of about 160 papers and an extensive survey of design and operating features of full-scale pulsed columns throughout the world. Calculations are performed stage-wise, using finite-difference equations that include the effects of reaction kinetics, nonequilibrium mass transfer, back-mixing, and new correlations of phase volumes with phase flow rates.

In Ref. 15, three versions of the Burkhart model, ranging from a SEPHIS-type version to the most comprehensive version (one "real stage" per plate), are compared with input-output data (presumably steady-state) from a Hanford partitioning column. Interestingly, even though all three versions of the model used the same input-output data, the plutonium inventory calculated by the most sophisticated version is more than double that given by the SEPHIS-type version. Corresponding plutonium concentration profiles calculated by the comprehensive "real-stage" model versus the SEPHIS-type model are compared in Fig. J-2. These comparisons contradict the belief that SEPHIS inventory predictions are on the high side, and therefore could have important consequences for both criticality control and safeguards accountability.

Further comparisons of the Burkhart model, now being made, are based on experimental data provided by GA and AGNS. Data from these two independent sources are being used for the development of theoretical correlations relating in-process inventory to observable process parameters.

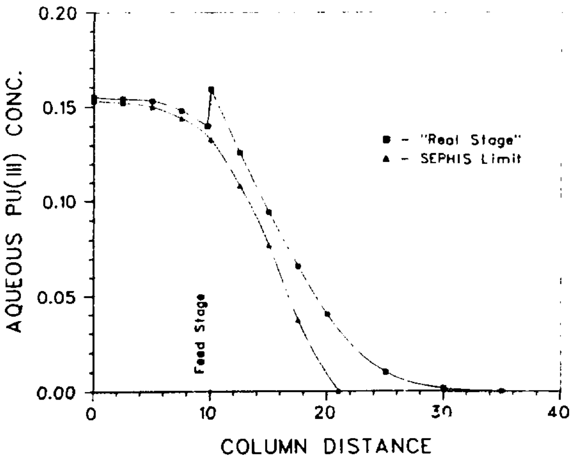


Fig. J-2. Plutonium concentration profiles: "real stage" vs SEPHIS-limit models.

Currently, empirical values for both the uranium mass-transfer and back-mixing coefficients are being derived from comparisons of experimental and theoretical uranium concentration profiles. Experimental data were supplied by AGNS for one of their laboratory-scale pulsed columns operating with a 30% TBP uranium-extraction flow sheet. Comparisons of experimental uranium concentration profiles with profiles calculated by SEPHIS and the Burkhart model are shown in Table J-VIII and Figs. J-3 and J-4. In contrast

TABLE J-VIII

EXPERIMENTAL URANIUM CONCENTRATIONS VERSUS SEPHIS AND THE BURKHART MODEL (2-IN.-I.D. EXTRACTION/SCRUB PULSED COLUMN)

Distance (ft) from Column Bottom	Uranium Concentration (g/L)					
	SEPHIS		Experiment		Burkhart Model	
	Aq	Org	Aq	Org	Aq	Org
24 (scrub)	0	52.5	0	54.0	0	54.0
21	17.2	65.0	15.0	62.7	15.0	62.7
18	25.0	71.0	19.7	67.5	19.8	67.5
15 (feed)	25.0	71.0	20.0	68.5	21.4	69.0
12.8	10.0	32.5	9.0	38.0	9.1	39.2
12.2	1.5	6.2	1.5	20.1	1.5	17.6
11.2	0.4	1.0	0.4	8.0	0.4	7.0
9	0	0	0	1.0	0	1.0
7	0	0	0	0	0	0

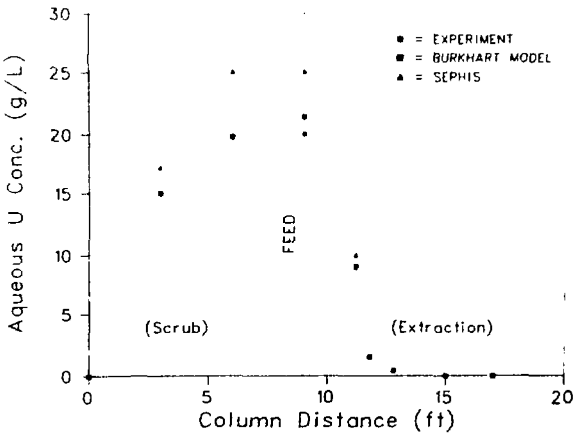


Fig. J-3. Experimental and calculated aqueous uranium concentrations for a pulsed column.

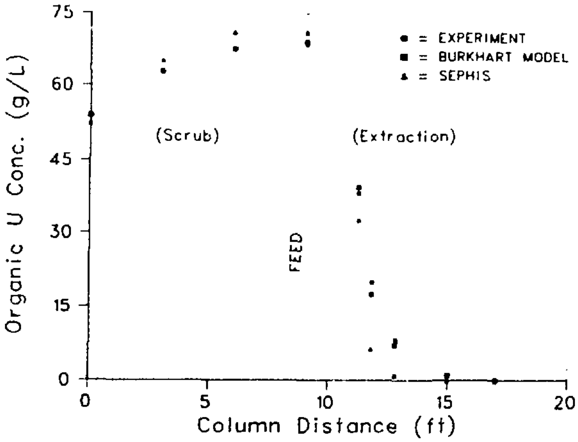


Fig. J-4. Experimental and calculated organic uranium concentrations for a pulsed column.

with SEPHIS, the aqueous and organic uranium concentrations for the Burkhart model closely fit the experimental data, apparently because back-mixing and finite mass transfer are taken into account. Similar comparisons of experimental and theoretical plutonium concentration profiles also are needed if empirical values for the plutonium mass-transfer rate and back-mixing coefficient are to be determined.

c. Centrifugal Contactors. Centrifugal contactors minimize the accountability problem in the Purex process because their in-process inventory is much smaller than that of mixer-settlers or pulsed columns having the same throughput. We are unaware of any published literature on theoretical modeling work for centrifugal contactors. Presumably, one could make stage-wise, SEPHIS-type calculations by matching desired end-point conditions, but the standard modeling assumptions made in SEPHIS might be less applicable to centrifugal contactors than to mixer-settlers.

One recommendation (Ref. 1 and App. C) for improved materials accountability is to use centrifugal contactors wherever possible to reduce the in-process inventory. For example, AGNS is using a 10-stage centrifugal contactor in their codecontamination cycle. The total centrifugal contactor volume may be ~100 L, which corresponds to a liquid residence time of ~100 s. The plutonium inventory therefore should be <100 g and would be a negligible contributor to near-real-time materials balances.

4. Dynamic State Estimation. Modern systems identification and state estimation techniques potentially can provide the best possible estimates of contactor inventory. A framework, such as the Kalman filter, could be used to combine the following elements: (1) a dynamic contactor model that is valid for a wide range of operating conditions, ideally including startup, shutdown, and upset transients; (2) a sufficient set of process observables and corresponding measurements, probably including real-time measurements of contactor inputs and outputs; and (3) the statistics of both the process and the measurements.

Clemson University has initiated studies[11] of modern system identification techniques that may be useful for real-time estimation of both transient and steady-state contactor behavior. Initially, Kalman filtering techniques were applied first to estimate (identify) the system parameters of a linear model from feed-stream data, and then to estimate the plutonium inventory by using the "identified" model. Recently, this model was extended to incorporate the time delay between feed and product streams, so that both input and output data can be used to estimate the plutonium inventory. In Fig. J-5, sample results of this time-delay model for a third-order linear system are compared with PUBG calculations.

Candy and coworkers[16] have considered an example of state estimation in which an idealized contactor model served as the basis of an extended-Kalman-filter estimation-detection scheme. A three-stage contactor model was developed using 27 "states," and all 27 states were assumed to be directly observable, that is, measurable. A set of real-time measurements having errors of 1% or less was invoked. With these assumptions, the detection algorithm was sensitive to unmeasured losses of plutonium from the contactor system.

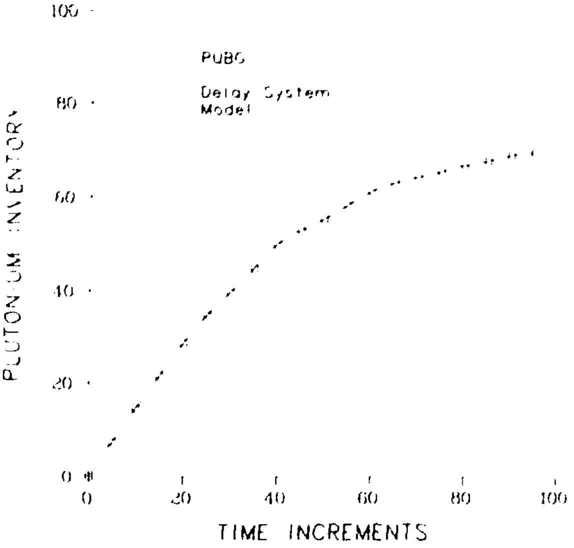


Fig. J-5. Plutonium inventory for PUBG model and delay system model.

Although probably not feasible today, the development of dynamic state estimation techniques could significantly enhance materials accountability in future large-scale reprocessing plants, and further development of these techniques is being pursued.

5. <u>"Reduced-Order" Dynamic State Estimation</u>. Because full dynamic state estimation of contactor inventory is not yet feasible, a restricted approach is being considered for near-term applicability. We refer to this restricted state estimation scheme as "reduced-order" dynamic state estimation because, although the same three elements (models, measurements, and statistics) are required for its implementation, the scope of the required input information can be restricted to a currently practicable level.

As an example of "reduced-order" dynamic state estimation, consider a mass balance drawn about one or more contactors in series,

$$I(t_2) = I(t_1) + T(t_1,t_2) \quad , \qquad \text{(J-1)}$$

where I is the in-process inventory and T is the net transfer of NM across the contactor(s) during the accounting period t_1 to t_2. Then, if the flows and concentrations are measured and the process is operated near steady state, at least at the end points of the accounting period, a steady-state contactor model could provide the required inventory estimates at the end points to close the mass balance. If transient (upset) conditions were encountered near the end of the accounting period, closure of the balance would have to be delayed until a steady-state condition was restored.

Depending on the valid operating range of the contactor model, a series of well-characterized "reference states" of the contactors might be established that would be used for in-process inventory estimation. Such reference states also would be used as materials accounting fiducials during periods of startup, shutdown, or recovery from upsets.

C. Conclusion

To optimize the benefits of near-real-time (dynamic) materials accounting in reprocessing plants, it will be necessary to estimate the in-process inventory of solvent-extraction contactors. Contactor-inventory-estimation techniques are now being developed because direct measurements of the quantities of uranium and plutonium in contactors are not practicable during process operations. Modern state estimation techniques potentially can provide the most accurate inventory estimates. As a first step toward the development of a comprehensive dynamic-state estimation technique, a reduced-order estimation technique based on near-steady-state contactor models and process measurements appears promising. However, any inventory-estimation technique probably will require experimental validation (or calibration) for each contactor system.

The following list summarizes the conclusions of this study to date.

- Contactor-inventory estimates to 5-10% will be useful for near-real-time accounting in reprocessing plants.
- Contactor-inventory estimation, based on model predictions and process measurements, appears to be the most promising technique; however, more theoretical and experimental work is necessary to develop this technique for plutonium recovery processes.
- SEPHIS-type modeling assumptions may not be suitable for quantitative estimation of in-process inventories.
- Some adaptation and validation of models will be required for each contactor system.
- Improved experimental plutonium distribution coefficients over a range corresponding to commerical fuels reprocessing flow-sheet conditions are needed.

- More experimental solvent-extraction data are needed under commercial reprocessing conditions.

REFERENCES

1. F. A. Hakkila, D. D. Cobb, H. A. Dayem, R. J. Dietz, F. A. Kern, E. P. Schelonka, J. P. Shipley, D. B. Smith, R. H. Augustson, and J. W. Barnes, "Coordinated Safeguards for Materials Management in a Fuel Reprocessing Plant," Los Alamos Scientific Laboratory report LA-6881 (September 1977).

2. D. D. Cobb and C. A. Ostenak, "Dynamic Materials Accounting for Solvent-Extraction Contactors," to be published in ANS Proc. Topical Conference on Measurement Technology for Safeguards and Materials Control, Kiawah Island, South Carolina, November 26-29, 1979.

3. K. Ikawa, H. Ihara, H. Sakuragi, H. Nishimura, and M. Hirata, "Study of the Application of Dymac Principles to Safeguarding Spent Fuel Reprocessing Plants," Japan Atomic Energy Research Institute report JAERI-memo-8241 (April 1979).

4. D. E. Christensen, R. A. Ewing, E. P. Gaines, R. Kraemer, R. A. Schneider, L. R. Stieff, and H. Winter, "A Summary of Results Obtained from the First MIST Experiment at Nuclear Fuel Services, West Valley, New York," in Safeguards Techniques, Proc. Symp., Karlsruhe, July 6-10, 1970 (International Atomic Energy Agency, Vienna, 1970), Paper IAEA-SM-133/54, Vol. I, pp. 563-582.

5. R. Kraemer and A. Rota, "Experimental Demonstration of a New Physical Inventory Technique by Means of Isotope Analysis," EUR-4576e, KFK-1100, Joint Integral Safeguards Experiment (JEX-70) at the EUROCHEMIC Reprocessing Plant, Mol, Belgium (January 1970-July 1971).

6. S. M. Zivi and W. B. Seefeldt, "Temporal Response Methods for Dynamic Measurement of In-Process Inventory of Dissolved Nuclear Materials," US Nuclear Regulatory Commission report NUREG-0249 (September 1977).

7. W. S. Groenier, "Calculation of the Transient Behavior of a Dilute-Purex Solvent Extraction Process Having Application to the Reprocessing of LMFBR Fuels," Oak Ridge National Laboratory report ORNL-4746 (April 1972).

8. S. B. Watson and R. H. Rainey, "Modifications of the SEPHIS Computer Code for Calculating the Purex Solvent Extraction System," Oak Ridge National Laboratory report ORNL-TM-5123 (December 1975).

9. G. L. Richardson, "Effect of High Solvent Irradiation on TBP Processing of Spent LMFBR Fuels," Hanford Engineering Development Laboratory report HEDL-TME-73-51 (June 1973).

10. A. D. Mitchell, "A Comparison Between SEPHIS-MOD4 and Previous Models of the Purex Solvent Extraction System," Oak Ridge National Laboratory report ORNL/TM-6565 (February 1979).

11. A. L. Beyerlein, J. E. Bennett, J. F. Geldard, and H. F. Chung, "Deviations from Mass Transfer Equilibrium and Mathematical Modeling of Mixer-Settler Contactors," to be published in ANS Proc. Topical Conference on Measurement Technology for Safeguards and Materials Control, Kiawah Island, South Carolina, November 26-29, 1979.

12. M. C. Thompson and R. L. Shankle, "Calculation of Uranium Inventories in Mixer-Settlers During Solvent Extraction with 7.5% TBP," Savannah River Laboratory report DP-1357 (August 1974).

13. J. T. Lowe, "Calculation of the Transient Behavior of Solvent Extraction Processes," Ind. Eng. Chem. Proc. Des. and Dev. 7, 362-366 (1968).

14. B. M. Legler, Allied-General Nuclear Services, to E. P. Schelonka, Los Alamos Scientific Laboratory, personal communication, May 4, 1977.

15. S. M. Yih and L. Burkhart, "State-of-the-Art Simulation of a U-Pu Partitioning Column for Nuclear Fuel Reprocessing," ANS Proc. Winter Meeting, TANSAO 30, 328 (November 1978).

16. J. V. Candy, R. A. Emmert, and G. K. Patterson, "Process Monitor Design for an Extraction Column: An Application of Estimation/Detection," Lawrence Livermore Laboratory report UCID-18128 (March 1979).

APPENDIX K

CONVENTIONAL MEASUREMENT TECHNIQUES

E. A. Hakkila, C. C. Thomas, Jr., D. B. Smith,
C. A. Ostenak, and R. G. Gutmacher
LASL Safeguards Staff (Q-4)

Various chemical and nondestructive analytical techniques are required to implement either a conventional or a near-real-time materials accountability system in a fuel reprocessing and conversion facility. Overall system efficacy depends on such factors as standards, sampling, assay time, and the applicability of the analytical methods to the desired measurement points; methods applicable to uranium and plutonium measurements are discussed extensively in previous LASL reports.[1-5] The techniques appropriate to conventional materials accounting in the fuel reprocessing and conversion facility are reviewed here.

A. Standards and Sampling Techniques

1. Standards. All procedures and instruments used for NM accountability should be calibrated with approved reference standards. All weight and volume measurements should be traceable to the appropriate National Measurement System standards. Approved or certified standards are available from the NBS,[6] the New Brunswick Laboratory (NBL),[7] and international sources such as the IAEA.

Secondary (bench or working) standards may be primary standards obtained from any of the sources noted above.[8] Alternatively, they may be prepared from process solutions by characterization against NBS standard reference materials (SRMs). The preparation and evaluation of secondary plutonium nitrate standards have been described[9] and should be incorporated into the analytical-laboratory standard operating procedure. The same techniques are applicable to the preparation of uranium working standards from uranium process materials. These standards should be analyzed daily or by each shift to ensure that the method is under control. Process samples should not be analyzed until satisfactory values are obtained on bench standards.

Primary standards for chemical analysis can also be used for NDA applications, but generally must be incorporated into a matrix to simulate process samples. Because this can introduce errors, these secondary standards must be evaluated for homogeneity, etc.

The NBL has initiated a program to develop low- and medium-density NDA standards for uranium scrap analyses[10] and plans to develop similar NDA standards for plutonium scrap analysis.[11]

2. Sampling Techniques. Measurements of product and waste streams will require analysis of solids as well as solutions and, in some cases, heterogeneous mixtures. Because of the radiation levels associated with many process materials, remote sampling techniques will be required. The crucial analytical points will be the accountability and product storage tanks. The waste streams will be of lesser importance but must be monitored, not only to measure the amounts of uranium and plutonium going to waste but to ensure that uranium and plutonium are not returned to process vessels for subsequent diversion and that waste discard values are not overstated to conceal this action.

The air-lift sampling system should be designed to allow for extensive recirculation of solutions through the sample lines and sample bottle during the sampling operation.[12-14] Vessel sparging, mixing time, and sample-circulation time should be considered in establishing proper sampling procedures for replicate samples. Solids must be dissolved after sampling and included in the total analysis. For highly radioactive samples the possibility of bubble formation must be considered in volume measurements, and temperature corrections should be applied.

The main sources of sampling error for solutions are expected to be (1) concentration or dilution of the sample by the air-lift system, (2) incomplete mixing of the solution in the tank, (3) contamination of the sample in the sample lines, (4) sample heterogeneity caused by suspended solids and (5) nonrepresentative samples as a result of inadequate circulation. Where analytical precision, expressed as RSD, of better than 0.5% is required, all sampling should be done on a weight basis rather than a volume basis. Remote volume samplers seldom can provide routine precision better than 0.5%, and even volumetric measurements generally are no better than 0.2% on a routine basis.

A sampling apparatus capable of providing pipetting accuracy of <0.1% under hot-cell conditions has been described.[15] All steps, including pipette rinsing, are performed remotely, and the Teflon piston surface does not touch the solution being pipetted.

B. Weight and Volume Measurements

Mass and volume calibration techniques are the subject of American National Standards N15.18 and N15.19, respectively.[16,17]

1. Weight Measurements. Load-cell weighing systems are potentially well suited for measuring bulk quantities of materials in nuclear reprocessing plants and may be used for accountability and product tank measurements. The weighing platform can be separated physically from its associated electronics and read-out mechanism. Only the platform need be exposed to the environment of a glovebox or process area, and the electronics can be located elsewhere to provide ready access for calibration and maintenance.

Load cells having 10-, 100-, and 1000-kg capacities are available commercially. These units have the following measurement errors (per cent of full scale):[18]

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

Use of load cells on the accountability tank or product tank is potentially the most accurate measure of the amount of solution in a tank. However, in practice it is difficult to isolate the tank effectively from the remainder of the process, and vibrations transmitted through connecting pipes impair measurement accuracy. The ICPP has evaluated the in-plant performance of a load-cell weighing system on an existing input accountability tank.[19] Because of large thermal forces generated in the tank and attached piping, it was impossible to attain the measurement accuracy for which the weighing system was designed. Although weighing accuracies of 0.2% could be obtained at stable temperatures, normal operating errors as large as 2% were observed.[19] The ICPP study showed that to obtain useful accuracy, tanks installed on weighing systems must be specially designed for the application. Currently, this method is being evaluated jointly by the US and Japan as Task D of the TASTEX program.

2. Volume Measurements. Determinations of the amount of uranium and plutonium in the process tanks of the fuel reprocessing and conversion facility rely on the measurement of solution concentrations and tank volumes. Volume can be measured gravimetrically by weight methods (see previous section) or volumetrically by measuring liquid level and density in the tanks. Volume-measurement technology for large process vessels has been reviewed recently.[20] The results are as follows.

a. Pneumatic Bubbler. The dip-tube manometer or pneumatic bubbler has been the acceptable method for measuring the liquid level of radioactive solutions in process tanks and was used at the Nuclear Fuel Services plant at West Valley, New York. Differential pressure can be measured with a liquid manometer, an electromanometer, or a precision pressure transducer having digital output, with the latter two providing direct computer-compatible output. The electromanometer is being evaluated for accountability tank and plutonium nitrate storage tank measurements jointly by Japan and the US as Task E of the TASTEX program. With careful calibration and an effective measurement-control program, calibration errors approaching 0.1% RSD and single volume-measurement errors of 0.5% or less should be attainable.

Comparison of a RUSKA XR-38 pressure counter, a RUSKA DDR-6000 digital pressure gauge, and a Bell and Howell electromanometer showed equivalent precision for the three instruments. The range of calibration error (1σ) was 0.3-0.5 mm of water.[21] A pressure transducer with an expected accuracy of 0.015% and a volume accuracy of 0.1% is being evaluated at the ICPP.[22]

Problems associated with pneumatic bubbler measurements include gradual plugging of instrument probes, variations in bubbler air flow, and leaks or restrictions in pressure-sensing lines.

b. Time-Domain Reflectometer. A time-domain reflectometer (TDR) is a coaxial probe suspended from the top of the tank. Liquid level is inferred from the time delay after an electrical pulse has been initiated in the probe until the reflected electrical signal has been received from the impedance mismatch at the liquid surface. The instrument accuracy is claimed to be comparable to that of pressure probes. Currently, the instrument is being evaluated at the BNFP under process operating conditions but with nonradioactive solutions.[23] A TDR instrument is undergoing further evaluation at the EUREX pilot reprocessing plant at Saluggia, Italy, in a joint US-EURATOM program. Preliminary data indicate a measurement error of 0.1% for liquid heights of 2 m. The BNFP preliminary data show a standard deviation of 2.1 cm but do not specify liquid height.

Advantages of the technique include: solids accumulation in the tank does not affect gauge operation; an air supply is not needed; high precision is theoretically possible; and the instrument can be adapted to continuous computer-recording of data.

c. Acoustic Techniques. Liquid level can be measured with an acoustic pulse that is directed to the liquid surface via a constraining tube.[24] A prototype instrument tested at Dounreay provided an accuracy of better than 1 mm in locating the liquid-air interface.

d. Tracer Techniques. The volume of solution in a process vessel can be determined by the so-called isotopic dilution technique, which involves (1) introducing a measured amount of chemical tracer (spike) into the tank, (2) adding measured increments of diluent, and (3) sampling and analyzing the tank solution for the concentration of the tracer introduced. Laboratory experiments with a simulated dissolver solution have shown the feasibility of the technique using the isotopes of lithium;[25] however, results of a plant test to trace several batches of dissolved high- and low-enriched fuel with ^{7}Li showed a large (>20%) and unexplained positive bias on all measurements.[26] Isotopes of magnesium and lead have been used successfully in experiments in the reprocessing plant at Tarapur, India, to measure the volume of solution in the accountability tank; an accuracy of better than 0.5% was reported.[27]

Perrin[28] recently proposed a modification of the lead tracer technique that adds two separated isotopes of lead to the accountability tank. He estimates total uncertainties ranging from 0.69 to 0.32% relative for the uranium and 0.65 to 0.28% relative (dependent on the mass spectrometric error) for the plutonium.

The cost and effectiveness of tracer techniques for accountability tank measurements have not been adequately assessed and require further work.

e. Tank Calibration. Tank calibration is the establishment of a mathematical relationship between the observed liquid level in the tank and the contained volume of solution. The objective is to construct a calibration curve or relationship such that error components associated with volume measurements based on the curve can be estimated. In a volume measurement made after tank calibration, the error component caused by imprecise tank calibration is identical for all measurements made at the same liquid level; therefore, it is important that the calibration error be both well-characterized and as small as practicable.

Methods for calibrating process tanks in the nuclear industry are limited because of the hostile radioactive environment in which these tanks usually are located. Except for a period before hot operation, access to the tanks is usually limited to the installed instrumentation and pipelines. Thus, considerable reliance must be placed on the initial calibration effort; later calibrations primarily monitor the condition of the tanks and the validity of the original calibration.

The most widely used calibration methods in the nuclear industry are in accordance with, or adaptations of, the methods described by R. J. Jones[29] and later by C. J. Rodden (Ref. 14, pp. 61-65). Known increments of liquid (usually water) are added to the tank and the associated liquid levels are measured. The calibration curve is obtained by least-squares fitting techniques.

There are two practical methods in use by which known increments of water are added to a tank undergoing calibration. The gravimetric method involves careful weighing of each increment transferred to the tank from a test measure and subsequent inference of the associated volume. The volumetric transfer method requires previously calibrated vessels or provers, and the tank volume is determined from the number of "dumps" required to fill the tank to a measured level. Recent experiments as part of an NBS program to support measurements of large process tanks show the two methods to have equivalent precisions.[30,31] The volumetric transfer method, however, is more convenient and is specifically recommended.[30]

Industry-accepted procedures for the volume calibration of straight-walled process vessels are given in American National Standard N15.19,[17] which also describes measurement-system requirements for the in-tank determination of solutions containing NM and provides approved statistical methods for the treatment of calibration data. Calibration procedures appropriate for process vessels in the nuclear industry are also given in the IAEA Safeguards Technical Manual.[32]

The precision to which large process vessels can be calibrated has been investigated for more than a decade in nuclear facilities throughout the world.[33,34] Schneider and Granquist,[35] and McSweeney et al.[36] have presented composite summaries of tank calibration data based on the best performance that has been reported or observed. Reported values consistently lie in the range of 0.1 to 0.2% RSD and represent the best performance for careful calibration under controlled conditions using what are thought to be the most accurate measurement methods, namely, either gravimetric or volumetric provers and dip-tube bubblers with precision manometer or electromanometer liquid-level instrumentation.

The NBS Mass and Volume Section has engaged in a program to investigate the accuracy of volumetric calibrations of nuclear fuel reprocessing tanks. Intended, in part, to generate data for testing ANSI Standard N15.19,[17] the experiments have sought to determine the ultimate capability of the transfer method of calibrating large process vessels and the calibration effort required to achieve such performance. The results, to date, of these investigations are described in a series of reports[30,31,37-39] and indicate that if proper care is exercised, an overall tank calibration uncertainty of 3 parts in 10^4 is obtainable. NBS defines uncertainty as three times the standard deviation.

To demonstrate the capability of the transfer method of calibrating large vessels in a nuclear facility, NBS, with the cooperation and support of the management and staff of

AGNS, conducted several calibrations on one of the tanks in the BNFP.[40] The study showed that, with transfer calibration methods, pneumatic bubblers, and commercially available differential pressure instrumentation, calibration precisions on the order of a "few parts in 10 000" can be achieved. Application of the technique to an input accountability tank at the Savannah River Plant has been reported by Jones.[41]

The calibration uncertainty of the liquid-level/volume relationship for a large process tank depends both on the calibration methods and on the actual tank geometry. The capability of the more accurate calibration techniques is such that significant obstructions in the tank and deviations from straight-walled geometry can be clearly identified. Thus, the limiting factor in the calibration error of a tank at any given liquid level may well depend on tank imperfections and nonuniformities at that level. While it may be expedient to assume a linear calibration curve over the range of tank operation, that is, to assume the tank is well-characterized as having constant cross-sectional area, the consequence is an unnecessarily large calibration error.

The problem of tank nonuniformity can be treated in several ways. ANSI Standard N15.19[17] recommends segmented calibration equations, that is, a sequence of linear calibration equations, for tanks that resemble a series of straight-walled tanks. Alternatively, appropriate volume corrections can be applied for deviations caused by tank imperfections at liquid levels identified during calibration.[39,40] Jones[42] proposed an additional approach that treats the effective cross section of the tank as a function of level and fits a polynomial equation to the calibration data. The degree of the polynomial depends on the number of deviations of the calibration data from the linear model. If the departure from linearity of the true tank geometry does not add significantly to the calibration error, the linear calibration model should be used.

Careful consideration in the original design of process tanks can minimize the effect of tank geometry on calibration error. The design should preclude deformation of the tank wall caused by internal pressure, but any necessary structural bracing should be external to the tank. Tanks with straight walls and a minimum of internal plumbing are recommended.

Measurement errors associated with volume determinations made during routine operation depend critically on the conditions at the time of measurement. Strictly speaking, the calibration relationship applies only to the operational procedures and parameter conditions that were obtained at the time of calibration. Changes in operational procedure (for example, drain time after air-sparging, valve positions, etc.) can introduce significant measurement errors that are difficult to evaluate. Measurement parameters such as temperature, humidity, and density can be corrected to the same reference values used in the calibration procedure;[17,39,40] however, corrections for large changes in parameters (particularly temperature) may be unreliable[17,21] and should be avoided. Measurement errors introduced by unrecognized or ignored effects can be significantly larger than the errors from calibration or those of the level-measuring instrumentation. Obviously, a well-designed measurement control program is mandatory.

Values for the overall precision of single volume measurements reported in the literature[19,33-36,43,44] lie between 0.2 and 0.7% RSD. These numbers undoubtedly represent best performance values. With careful calibration and under well-controlled measurement conditions, the content of a large process vessel can be measured to an RSD of 0.3% or better;[32,45] however, RSDs of 1 to 2% are not unusual for routine plant measurements.

C. Chemical Analytical Methods

Several methods of chemical analysis capable of providing better than 0.1% (1σ) precision with high accuracy and high sensitivity (<1 mg) have been developed and evaluated for uranium and plutonium. Most analytical methods for determining plutonium have been developed using weapons-grade plutonium, which is predominantly ^{239}Pu. When these methods are applied to reactor-grade plutonium, which contains significant concentrations of ^{238}Pu (an intense alpha-emitter) and ^{241}Pu (an intense beta-emitter), some problems may be encountered.

Irradiation may decompose organic reagents used for extraction of plutonium and may decrease the extraction efficiency.[46] Plutonium oxalate is susceptible to decomposition by alpha radiation (Ref. 46, p. 407). Scientists working with ^{238}Pu have pointed out the need for special techniques.[47] Because a higher probability exists for radiation-induced reduction of Pu (VI) to Pu (IV) and oxidation of Pu (III) to Pu (IV), greater care must be exercised to minimize these reactions during analysis. Precision and accuracy for analysis of reactor-grade material may well be poorer than literature values obtained for weapons-grade material.

Chemical methods for uranium and plutonium analysis at the fuel reprocessing and conversion facility include mass spectrometry, gravimetry, electrometric titrations, spectrophotometry, alpha spectrometry, fluorimetry, and x-ray fluorescence. These methods can be used to determine (1) major constituents in the dissolver solution and product tanks and (2) minor constituents in recycle streams and wastes. The applications and limitations of these analytical techniques as they are used for safeguards are discussed briefly.

1. Mass Spectrometry. Although instrumentation for mass spectrometry is complex and expensive and elaborate sample preparation is required (Refs. 14, pp. 335-368; Refs. 48-55), most Purex reprocessing plants use thermal-ionization mass spectrometry to determine the isotopic compositions for uranium and plutonium in samples taken from various process tanks and subsequently to determine the effective atomic weights for calculating the total uranium and plutonium present. Isotope-dilution mass spectrometry can also be used to measure concentrations in process tanks.[50,51,55]

In isotope-dilution mass spectrometry, accurately known amounts of ^{233}U, or ^{242}Pu or ^{244}Pu, respectively, are used as spikants for chemically analyzing aliquots of fractionated uranium and plutonium solutions. For plutonium determination, either ^{242}Pu or ^{244}Pu can be used as the spike, with the latter preferred if available, because it is not present in significant quantities in irradiated LWR fuel. For uranium, ^{233}U is used as the spike for analyzing conventional uranium-based LWR spent fuels.

For determination of major isotopes, RSDs of 0.01-0.02% (1σ) can be attained. The precision for well-characterized materials such as NBS SRMs generally is significantly better than for process and product samples, probably reflecting problems in sampling and sample preparation. Overall precision for measuring dissolver samples has been 0.3-1%, but may be improved to 0.3% with more stringent quality control.[28]

2. Gravimetry. Gravimetry requires that a compound of the element to be determined be ignited to a constant-weight stoichiometric compound. The method is applicable only to relatively pure materials; impurities must be determined by spectrographic or other procedures, and appropriate corrections must be applied to the final weight. Where quantitative separations from impurities can be achieved, precisions of better than 0.1% are possible.

Gravimetric methods can be used to assay both uranium and plutonium product streams. Uranium content can be determined with an RSD of 0.02 to 0.5% for nitrate solutions, oxides, and UF_6 following sample preparation and ignition at 850-900°C to U_3O_8 (Ref. 14, pp. 70-74). However, for plutonium, it is difficult to obtain a stoichiometric PuO_2 product for weighing, and this fact plus the hygroscopic nature of PuO_2 make gravimetry a less-than-ideal method for quantifying plutonium content.

3. Electrometric Titrations. Amperometry, potentiometry, and coulometry have been applied to the determination of uranium and weapons-grade plutonium with <0.1% RSDs and probably provide the most accurate and precise methods for determining these

elements in high-purity materials.[52-55] The attainment of similar precision with reactor-grade plutonium must be demonstrated.

Electrometric methods for high-precision measurements of uranium and plutonium have been summarized (Ref. 2, App. F). The electrometric methods for determining uranium rely on the reaction $U^{4+} \rightarrow U^{6+}$ after quantitative reduction of the uranium to the tetravalent state (Ref. 14, pp. 74-88, 254-268, 299-306; Refs. 56-61). Differences between methods result from the reductants and oxidants used. Reducing agents used to obtain U^{4+} include zinc amalgam, the Jones reductor, Ti^{3+}, the lead reductor, Fe^{2+} in phosphoric acid, and electrical reduction. The Jones reductor generates a mixture of U^{3+} and U^{4+}, and the trivalent uranium must be air-oxidized to the tetravalent state before titration. The reduction with an excess of ferrous ion in concentrated phosphoric acid followed by titration with dichromate can be performed in the presence of Pu^{4+} without interference. Some of the standard electrometric techniques for determination of uranium are summarized in Ref. 2, Table XII. Of these methods for determining uranium, the Davies and Gray/New Brunswick Laboratory method is the most versatile and has been automated for rapid analysis of process samples.[61]

For the electrometric determination of plutonium, the plutonium may be oxidized quantitatively to Pu^{6+}, then titrated to Pu^{4+} (Ref. 14, pp. 254-268, 299-306; Ref. 48, pp. 257-261, 304-307, 420-422; Refs. 62-67). This couple generally is preferred if uranium or iron is present. Oxidants for the first step include AgO and $HClO_4$. If AgO is used, the excess is destroyed by gentle heating. The oxidation capability of $HClO_4$ is destroyed by diluting the sample after the plutonium has been oxidized. Errors can be introduced into the plutonium measurement if conditions for the dilution are not followed properly. The reduction to Pu^{4+} usually is carried out with Fe^{2+}, and can be performed directly or, by using a potentiometric end point, can be sharpened by adding a measured excess of Fe^{2+} with the excess titrated with Ce^{4+}.

Alternatively, plutonium can be determined by quantitative reduction to Pu^{3+} and subsequent titration to Pu^{4+} (Ref. 14, pp. 268-299, 385-388; Ref. 48, pp. 256-257; Refs. 68-73). Common reducing agents are liquid zinc amalgam, the Jones reductor, the lead reductor, Ti^{3+}, Cr^{2+}, and electrical methods. The liquid zinc-amalgam method suffers in that an extra transfer is required to remove the amalgam before titration. Small amounts of titratable material can be leached from the Jones reductor. Fewer elements are reduced with $TiCl_3$ than with the Jones or lead reductors; therefore, fewer interferences may occur.[69] However, Ti^{3+} is destroyed readily by contact with air.

The oxidation titration to Pu^{4+} usually is performed electrolytically or with Ce^{4+} or $K_2Cr_2O_7$. Dichromate has the advantage of being available as a primary standard and being more stable than Ce^{4+} over extended storage periods. Uranium and iron interfere with methods involving the Pu^{3+}-Pu^{4+} couple. An exception is the controlled-potential coulometric technique, which in the presence of uranium can be used to measure successively both elements in the same sample.

4. Spectrophotometry. Spectrophotometric methods rely on the principle that the quantity of monochromatic light absorbed by a compound or complex in solution is proportional to the concentration of the measured species. Generally, the concentration-absorbance function is expressed by Beer's law, but variations from Beer's law may result at high concentrations or if other competing reactions occur. The RSD attainable by direct spectrophotometry generally is 0.5% or greater and seldom is <0.2%. However, differential techniques that compare the absorbance of the unknown solution to a precisely known reference solution can improve the method to provide an RSD of <0.05%.

Specificity in absorptiometry is a complex function of many factors such as sharpness of absorption bands, specificity of reagents, other elements or compounds present, and the quality of monochromators used. Specificity often can be improved by using preliminary separations, masking agents, and pH control. Because of the nonspecificity of reagents for plutonium and uranium (when both are present) and their nuclear reaction products (americium, neptunium, fission products), time-consuming separations often are involved. These additional separations may limit the precision that can be obtained for major-element analysis. For these reasons, spectrophotometric methods find only limited use in a fuel reprocessing plant, usually for process control and analysis of waste streams. It should be noted, however, that the uranyl nitrate method,[74,75] which is used for in-line process control, lacks the precision generally required for safeguards applications, and browning of the optics can occur in process streams containing fission products. Some reagents of interest for analytical applications in nuclear fuel reprocessing plants summarized in Ref. 2, App. F; Ref. 14, pp. 222-225; and Ref. 76-86.

The spectrophotometric methods for trace concentrations of uranium are of interest for determining uranium in waste streams and possibly in the final plutonium product. The determination of uranium with Z-(2-pyridylazo)-5-diethylaminophenol has been modified specifically for determining uranium in reprocessing plant waste streams[77] and in plutonium nitrate and oxide products.[78]

For plutonium, the differential spectrophotometric method[85] can be used to make measurements in product storage tanks; a precision equivalent to that obtainable by the best electrometric methods, 0.05% (1σ), is possible. In addition, spectrophotometry can provide rapid calibration checks of NDA techniques for measuring plutonium in waste streams. Precisions of 1-10% are typical, depending on the plutonium concentration and impurities. An automated spectrophotometer may be adapted for at-line measurement of plutonium in waste streams.[83]

Both uranium and plutonium can be measured by using an automated spectrophotometer developed at LASL for the analysis of scrap materials.[86] The elements are determined sequentially with an analysis time of 5 min and 1% RSD for milligram amounts of uranium and plutonium by a tetrapropylammonium nitrate extraction method. The instrument has not been evaluated for use on reprocessing samples.

5. Alpha Spectrometry. Alpha spectrometry is an isotope- rather than element-specific analytical method, and is most suitable for determining ^{238}Pu; uranium also can be determined, but low concentrations of plutonium can interfere seriously. With appropriate sample preparation, alpha spectrometry has been applied to measuring plutonium in process samples of known isotopic compositions with an RSD of 3-5% (1σ).[55,87] The technique is particularly well-suited to measuring low plutonium concentrations in waste streams. The method also has been applied to the determination of plutonium in dissolver solutions following solvent-extraction separation of the plutonium (Ref. 14, pp. 392-398; Refs. 55, 88).

Quantitative alpha-particle spectrometry is based on measuring the alpha-radiation intensity of the sample. The alpha particles are ejected with discrete energies, and, for uranium, neptunium, plutonium, and americium isotopes characteristic of the nuclear fuel cycle, these energies range from 4 to 5.5 MeV. Alpha-particle energies are rapidly degraded by interactions with electrons, and complete attenuation is effected by ∿5 cm of air. Absorption by water and self-absorption by the sample are even more rapid, and normal quantitative alpha spectrometry is limited to analysis of thin, dry films.

Detectors used for alpha spectrometry include the standard radiation instruments such as proportional, scintillation, and solid-state devices.

6. Fluorimetry. The fluorimetric determination of low concentrations of uranium is based on the fact that uranium fluoresces when excited by ultraviolet light; the method is not applicable for determining plutonium. The fluorescent spectrum for uranium consists

of four bands in the visible region, with the most intense band at 554.6 nm. If 365-nm excitation from a high-intensity mercury lamp is used, few other elements will interfere by fluorescence.

Samples generally are evaporated and fused in a carbonate flux containing ∿10% NaF (Ref. 89) or a NaF flux, sometimes containing LiF (Ref. 90) or some carbonate. Carbonate fluxes are preferred for ease of handling the fusion mass and for providing better analytical precision. Fluoride fluxes provide better sensitivity but are more sensitive to variations in flux temperature and cooling conditions.

Although few elements or compounds interfere with the method by overlapping fluorescent spectra, a number of elements interfere through quenching or enhancement. Quenching can result from absorption of the incident light, absorption of the fluorescent light, interference with the energy transfer paths at phosphor centers, or precipitation of uranium.[91]

Most of the transition elements interfere by quenching to some degree. With a flux of 98% NaF-2% LiF, serious quenching is observed in the presence of small amounts of cadmium, chromium, cobalt, copper, iron, magnesium, manganese, nickel, lead, platinum, silicon, thorium, and zinc. Many of the interferences can be removed by a combination of precipitation and solvent extraction of the uranium into methyl isobutyl ketone containing tetrapropylammonium nitrate[14] or into ethyl acetate (Ref. 48, pp. 232-237). Alternatively, quenching interference can be minimized by measuring the fluorescence from a fused button of the sample and a similar button containing a known added amount of uranium (spiking).

Fluorimetry has evolved as a standard method for determining small amounts (1-100 ng) of uranium. High-throughput, off-line measurements of uranium in waste streams can be made by processing samples in the analytical laboratory. The RSD for measuring uranium in simulated reprocessing plant waste streams is reported to be 13%.[92] In addition, an automated fluorimeter capable of processing sixteen samples per 1.5 h has been designed and tested at ORNL;[93] sensitivity is 0.2 µg/L and precision is 6% at the 10-µg/L level.

7. X-Ray Fluorescence. X-ray fluorescence techniques have been applied to the analysis of actinide solutions for over 25 yr. They are sensitive and accurate and are capable of measuring microgram quantities of material to relative accuracies of 1% or less. Typical analysis times are short (0.5 h or less). Currently, x-ray fluorescence is used primarily to measure solutions from the reprocessing of spent fuels. However, the technique has been applied to solutions at all stages of the fuel cycle.

The fundamentals of x-ray fluorescence analysis are reviewed in detail in the literature.[94-97] The analyst has considerable latitude in selecting a technique, including choices of excitation source, x-ray line, and detector.

For uranium and plutonium measurements, lines in the K, L, or M series can be used; the more intense lines in these series are summarized in Table A-III of Ref. 2. The main considerations in the choice of a line to use in an x-ray fluorescence measurement are line intensity above background and interferences from adjacent lines. The most common choice is one or more of the L lines. They provide good intensities in an air path for solution or solid analyses, and can be used with any type of excitation or detection system.

The most commonly used excitation source is the x-ray generator, although the use of radioisotopes is becoming more common because solid-state detectors are readily available. Both wavelength- and energy-dispersive detection systems have been used to measure uranium and plutonium in solution. Wavelength dispersion offers high resolution but at low efficiencies. Energy dispersion is generally more efficient but has poorer resolution at energies <20 keV. At energies >20-25 keV, a Si(Li) energy-dispersive spectrometer provides better resolution as well as efficiency.

Although x-ray fluorescence measurements of NM solutions have had wide exposure in the literature, current safeguards applications are limited because of competition from other less complex and less matrix-dependent methods. To reduce the matrix sensitivity, samples are often evaporated as thin films. That technique reduces the scattered background compared to the sample signal, thus increasing sensitivity and reducing counting times.[98] Measurements of thin films are linear with the concentration of NM over a small range, above which saturation effects become important.

Several systems have been developed to assay highly radioactive spent-fuel solutions. One of these systems[99-101] uses a wavelength-dispersive spectrometer to assay solutions having uranium-plutonium ratios of 50:1 to 300:1 with accuracies of $\sim 1\%(1\sigma)$ in 2-5 min. Solutions having activities of <1 Ci/mL are handled routinely by evaporating small samples onto a filter paper. Samples having low beta-gamma activities can be analyzed directly in solution after addition of an internal standard. The fission products cause no serious line interference. An automatic sample-preparation system is being developed to allow on-line analysis.

Uranium and plutonium solutions that have beta-gamma activities to 1 Ci/L have been measured directly through a Plexiglas window.[102] The system used is as close to in-line analysis as one can devise. An automatic sampler removes solutions from the sample line and yttrium is added to serve as an internal standard. Solution transfers are made by pneumatic tube. A minicomputer performs data reduction, and overall precision and accuracy of better than 1% are claimed for the technique.

In another system,[103] hot dissolver solutions containing uranium and plutonium at ratios up to 400:1 and uranium concentrations of ∿50 g/L are measured with an x-ray tube in combination with a Si(Li) detector. Preliminary tests indicate that accuracies of 1-2% are possible with 10-min analysis times. However, accuracies of only 3% are obtained because of problems in sample preparation. A new preparation method now being evaluated should improve measurement accuracy.

A proposed wavelength-dispersive system can measure uranium and plutonium concentrations in irradiated samples to a precision of better than 1%.[104] The instrument should be adaptable to off-line analysis of dissolver-type samples (as slurries or solution) with an analysis time of 4-8 h. For samples of lower activity, analysis time is significantly shorter.

A system also has been developed for automatic sampling and sample preparation of dissolver solutions from the reprocessing of thorium-uranium fuels[98] and could be applied to uranium-plutonium fuels. For solutions emitting up to 2000 Ci/L, samples containing 1.0 mL of solution are automatically aliquoted and mixed with an internal standard. The aliquots are evaporated onto a filter paper, which is transferred to a shielded x-ray spectrograph. All operations are performed remotely under computer control.

The high sample throughput for analytical laboratories at large reprocessing plants may dictate automated analytical methods such as x-ray fluorescence to provide timely, accurate information for both process control and safeguards.

D. Nondestructive Analytical Methods

NDA techniques generally rely on measurements of phenomena associated with nuclear properties of the element, hence are generally isotope rather than element specific. These phenomena may include emission of neutrons, gamma-rays, and heat. Other NDA techniques used are x-ray and gamma-ray absorptiometry, which rely on atomic, rather than nuclear, processes and hence are element sensitive. NDA techniques are either passive or active. Passive assay uses naturally occurring neutron and gamma-ray emissions as direct elemental or isotopic signatures. Active assay involves irradiation with neutrons or photons to induce nuclear or electron interactions in the sample. The resulting neutron, gamma-ray, or x-ray "signatures" are interpreted to determine quantitatively the amount of the designated element present.

1. Neutron Techniques. Both passive and active neutron techniques are discussed elsewhere,[105] and only methods relevant to conventional materials accounting in the fuel reprocessing and conversion facility are reviewed here. Passive neutron methods are used to measure PuO_2 product, precipitator in-process inventory, wet-boat contents, and leached hulls. In addition, passive neutron methods are used to detect both uranium and plutonium in low-level wastes, with the sensitivity a factor of 10^5 to 10^6 greater for the even-numbered plutonium isotopes than for uranium.[106] Curium or californium can interfere with the plutonium measurement.

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

Fission neutrons result from spontaneous fission or from fissions induced by an external neutron source such as ^{252}Cf. Because the fission process produces more than one neutron per fission, fission neutrons can be differentiated from (α,n) neutrons by coincidence counting.

Neutron measurements of leached hulls can be performed with passive or active methods. With passive neutron methods, both spontaneous fission and (α,n) neutrons can be measured. The (α,n) neutron yield is sensitive to the light-element content of the hulls, particularly fluoride. The method can be made specific for spontaneous fission neutrons by using coincidence counting techniques, but there will be some loss in sensitivity. The passive neutron techniques are sensitive to curium content of the fuel, and the ^{242}Cm and ^{244}Cm concentration relative to plutonium must be known. A prototype passive neutron system for measurement of plutonium in leached hulls is being developed and evaluated at Hanford.[107]

An active neutron method based on the LASL-designed ^{252}Cf Shuffler is being developed for measuring uranium in fluorinel sludge,[108] and the technique has been proposed for measuring fissile materials in hulls. This system also can be operated in the passive mode.

Further work on development of neutron methods for leached-hull assay is required.

Both passive and active neutron assay are also being investigated at LASL for measurement of plutonium and uranium in low-level wastes.[106,109,110] With suitable calibration, accuracy is of the order of 10-20%. In addition, an active neutron interrogation system has been built at LASL for assay of ^{235}U and fissile plutonium in solid high-level wastes. A sensitivity of 1 g fissile plutonium per 55-gal drum can be achieved in the presence of 1000 R/h of fission products.[111] Also, high-level solid wastes such as centrifuge sludge can be measured by active neutron interrogation. A prototype system designed and built at LASL will be tested at ICPP for determining ^{235}U in sludge.[112] Precision, accuracy, and sensitivity will be measured.

2. Gamma-Ray Techniques. Passive gamma-ray techniques also benefit conventional materials accounting of uranium and plutonium in the fuel reprocessing and conversion facility. These emission techniques can be used to quantify any ^{235}U and ^{239}Pu contained in the solid low-level waste generated by fuel reprocessing and conversion operations. In addition, gamma-ray methods have been proposed for measuring the fissile content of leached hulls.

For assay of ^{235}U and ^{239}Pu contained in 55-gal drums of low-level waste, the 186-keV and 414-keV lines, respectively, are measured.[113] A drum scanner that uses a sodium iodide (NaI) or lithium-drifted germanium [Ge(Li)] detector to measure the 414-keV gamma ray from ^{239}Pu can detect ∿1 g of ^{239}Pu in a 5-min scan;[114] the Ge(Li) detector can provide much higher resolution. The relative accuracy for measuring >10 g of ^{239}Pu can be as good as 10% in matrices of low atomic number and ranges to 50% in unknown matrices. Hence, the measurement accuracy depends largely on the administrative control exercised in sorting waste to ensure reproducible matrices. The drum scanner is commercially available.

In addition to NaI and Ge(Li) detectors, intrinsic germanium detectors are used for gamma-ray measurements. The Ge(Li) and intrinsic germanium detectors provide much better energy resolution for adjacent peaks, but they require liquid-nitrogen cooling. Nevertheless, one or the other is required if good quantitative data on isotopic abundances are to be obtained. For rugged on-line instruments, the NaI detector is preferred if overlapping spectra are not a problem. More recently, CdTe detectors, which have an energy resolution of 8% at 122 keV and are usable at room temperature, have been investigated as a substitute for NaI.[115] The CdTe detector shows promise, but further development is required to match detectors and preamplifiers and to reduce charge-collection problems.

The status of leached-hull measurements made by a gamma-ray method has also been reviewed at LASL.[116] The gamma-ray method relies on correlating the measurement of the 2.186-MeV gamma ray of ^{144}Ce(^{144}Pr) remaining in the hulls to the undissolved uranium (or plutonium). The ratio of ^{144}Ce/U in the dissolver solution determined by laboratory analysis is used to calculate the amount of undissolved fuel remaining in the leached hulls. The method is being evaluated at AGNS.[117] The method is not applicable to analysis of aged fuel elements because of the decay of 284-day half-life ^{144}Ce. Serious interference from ^{60}Co in the stainless steel end fittings of fuel rods is a potential problem.

3. Calorimetry. Plutonium calorimetry[118,119] is an NDA technique based on measuring heat generated by the radioactive decay of plutonium and americium. All but a negligible part of the decay energy is transformed into heat when the decay particles (alpha, beta, and low-energy gamma) are absorbed by the sample and calorimeter walls. In plutonium from processed reactor fuels, the energy from alpha-decay predominates and the energy release from ^{238}Pu, the plutonium isotope that has the highest specific activity, is dominant.

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

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

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

High-precision calorimetry depends on an accurate knowledge of the sample's effective specific power, which can be obtained from the isotopic composition of the material. The mass ratios are used to calculate a weighted-average specific power. The isotopic analysis can be performed either by mass spectrometry or gamma spectrometry. The total assay can be nondestructive by combining gamma-spectrometric analysis with calorimetry. Gunnink[120] indicates that a 100-min gamma analysis with a gamma-stripping program designed for the analysis of plutonium gives the specific power with a precision of better than 1% for a sample containing 1-2 g of plutonium.

Calorimetry probably will not have any safeguards applications in the reprocessing plant because most samples are liquids; however, in the conversion facility, calorimetry can be considered for measuring the PuO_2 product. Each package containing ∿2 kg of plutonium as PuO_2 can be assayed in ∿2 h in a servo-controlled calorimeter with sample preheating. The use of real-time prediction of calorimeter equilibrium will reduce the assay time to <60 min.[121] The equilibrium prediction method has been tested on samples ranging from 2.54 cm by 7.62 cm to 12.70 cm by 27.94 cm. The differences between the actual and predicted equilibrium values were always <0.3% relative and generally <0.1% relative and were within the uncertainty of the predicted value of the 95% confidence level.

"Portable"[122] and "transportable"[123] calorimeters have been described in the literature. The portable device measures samples in a 1.6-cm-diam, 5-cm-long aluminum cylinder and is therefore limited in sample capacity. A measurement precision of 0.1% with an equilibration time of 15 min has been obtained. Tests with a PuAl alloy source in sand to simulate PuO_2 were made by using a 4-min measurement following a 15-min equilibration. The isotopic composition was determined from a 30-min gamma assay. A mass-determination uncertainty of <1% was obtained in almost all cases.[122] The device weighs ∿18 kg and is totally self-contained, incorporating a microprocessor-controlled data-acquisition system.

The transportable unit[123] uses a Mound twin-resistance calorimeter that was redesigned to permit operation outside a temperature-controlled water bath. The unit was retrofitted with two additional water jackets through which water was transferred from an external reservoir. The modification did not degrade the unit's performance. The modified calorimeter accepted samples 6.86 cm by 16.26 cm. Precisions of ∿0.5% (RSD) can be obtained. Currently, a device capable of handling sample containers as large as 12.7 cm in diameter is being evaluated.[124]

Calorimetry also can be used to characterize calibration standards for other NDA methods.[125,126] It can establish traceability of these standards to NBS plutonium standards and can be used as part of the measurement control program to monitor periodically the accuracy of other NDA measurement techniques.

REFERENCES

1. J. P. Shipley, D. D. Cobb, R. J. Dietz, M. L. Evans, E. P. Schelonka, D. B. Smith, and R. B. Walton, "Coordinated Safeguards for Materials Management in a Mixed-Oxide Fuel Facility," Los Alamos Scientific Laboratory report LA-6536 (February 1977).

2. E. A. Hakkila, D. D. Cobb, H. A. Dayem, R. J. Dietz, E. A. Kern, E. P. Schelonka, J. P. Shipley, D. B. Smith, R. H. Augustson, and J. W. Barnes, "Coordinated Safeguards for Materials Management in a Fuel Reprocessing Plant," Los Alamos Scientific Laboratory report LA-6881 (September 1977), Vol. II.

3. H. A. Dayem, D. D. Cobb, R. J. Dietz, E. A. Hakkila, E. A. Kern, J. P. Shipley, D. B. Smith, and D. F. Bowersox, "Coordinated Safeguards for Materials Management in a Nitrate-to-Oxide Conversion Facility," Los Alamos Scientific Laboratory report LA-7011 (April 1978).

4. E. A. Hakkila, "A Critical Review of Analytical Techniques for Safeguarding the Thorium-Uranium Fuel Cycle," Los Alamos Scientific Laboratory report LA-7372 (October 1978).

5. H. A. Dayem, D. D. Cobb, R. J. Dietz, E. A. Hakkila, E. A. Kern, E. P. Schelonka, J. P. Shipley, and D. B. Smith, "Coordinated Safeguards for Materials Management in a Uranium-Plutonium Nitrate-to-Oxide Coconversion Facility: Coprecal," Los Alamos Scientific Laboratory report LA-7521 (February 1979).

6. "Catalog of NBS Standard Reference Materials," National Bureau of Standards Special Publ. 260 (April 1979).

7. "NBL Reference Materials, 1978-1979 Price List," New Brunswick Laboratory (US Government Printing Office, 1978).

8. K. F. Lauer and Y. LeDuigou, "Proper Use of Reference Materials for the Accurate Determination of Uranium, Plutonium, and Thorium in the Nuclear Fuel Cycle," in Analytical Methods in the Nuclear Fuel Cycle, Proc. Symp., Vienna, November 29-December 3, 1971 (International Atomic Energy Agency, Vienna, 1972), pp. 145-152.

9. J. E. Rein, S. F. Marsh, G. C. Swanson, G. R. Waterbury, G. L. Tietjen, and R. K. Zieqler, "Preparation of Working Calibration and Test Materials: Plutonium Nitrate Solution," Los Alamos Scientific Laboratory and US Nuclear Regulatory Commission report LA-NUREG-6348 (January 1977).

10. A. M. Voeks, N. M. Trahey, and J. M. Scarborough, "Preparation of Test Materials for an Interlaboratory Comparison Program on NDA Physical Standards," in Analytical Chemistry in Nuclear Fuel Reprocessing, W. S. Lyon, Ed. (Science Press, Princeton, 1978) pp. 338-344.

11. N. M. Trahey, New Brunswick Laboratory, personal communication, June 1979.

12. H. G. Duggan and J. W. Landry, "Remote Liquid Sampling: A Completely Automated Air-Lift System," Nucleonics 12, 67 (November 1954).

13. W. E. Foster, "Liquid Samplers for Safeguards Use," WCAP-6025, Westinghouse Atomic Power Department, Pittsburgh, Pennsylvania (October 1959).

14. C. J. Rodden, Ed., "Selected Measurement Methods for Plutonium and Uranium in the Nuclear Fuel Cycle," US Atomic Energy Commission report TID-7029 (1972), pp. 25-56.

15. V. Wenzel and H. J. Riedel, "Actinide Composition Studies on Thorium/Uranium Fuel Elements with Known Irradiation Data," in Analytical Methods in the Nuclear Fuel Cycle, Proc. Symp., Vienna, November 29-December 3, 1971 (International Atomic Energy Agency, Vienna, 1972), pp. 549-562.

16. "Mass Calibration Techniques for Nuclear Material Control," American National Standard document ANSI N15.18-1975 (American National Standards Institute, NY, 1975).

17. "Volume Calibration Techniques for Nuclear Materials Control," American National Standard document ANSI N15.19-1975 (American National Standards Institute, NY, 1975).

18. For definitions of the measurement errors as well as their numerical values, see Bulletin 72A of Transducers, Inc., 12140 E. Rivera Rd., Whittier, California 90606.

19. F. M. Groth and F. O. Cartan, "Evaluation of Instrumentation for Nuclear Fuels Reprocessing Plant Input Weight Measurements," Allied Chemical Corp. report ICP-1014 (July 1972).

20. D. B. Smith, "A Critical Review of Volume Measurement Technology," in "Coordinated Safeguards for Materials Management in a Fuel Reprocessing Plant," Los Alamos Scientific Laboratory report LA-6881 (September 1977), Vol. II, Appendix C.

21. S. C. Suda, "Instruments and Data Analysis Methods for Volume Measurements," in Safeguarding Nuclear Materials, Proc. Symp., Vienna, October 20-24, 1975, (International Atomic Energy Agency, Vienna, 1976), Paper IAEA-SM-201/25, Vol. II, pp. 187-196.

22. C. M. Slansky, Ed., "Technical Division Quarterly Progress Report Oct. 1-Dec. 31, 1976," Allied Chemical Corporation report ICP-1111 (March 1977), pp. 41-42.

23. J. M. Crawford, M. H. Ehinger, C. Joseph, and M. L. Madeen, "Studies and Research Concerning BNFP, Nuclear Materials Control and Accounting System Evaluation Report--FY 1978 Integrated Uranium Run," Allied-General Nuclear Services report AGNS-1040-2.2-50 (October 1978), App. H.

24. J. Watson and T. L. Jones, "An Acoustic Technique for the Determination of Liquor Levels in Tanks," presented at First Meeting-Coordinated Research Program, the Use of Installed Instrumentation in Irradiated Fuel Reprocessing Facilities for Safeguards Purposes (International Atomic Energy Agency, Vienna, March 12-16, 1979).

25. H. Bokelund, "Investigation of Reprocessing Input Measurement Using Tracer Techniques," IAEA Contract 876/RB.

26. R. Berg, "Verification of Reprocessing Input Measurements," IAEA Contract 988 (1971).

27. C. K. Mathews, H. C. Jain, V. D. Karmandan, and S. K. Aggarwal, "Tracer Techniques for the Input Accountability of Plutonium in Reprocessing Plants: Magtrap and Leadtrap," Nucl. Technol. 42, 297-303 (1979).

28. R. E. Perrin, "New Measurement Capabilities of Mass Spectrometry in the Nuclear Fuel Cycle," Nucl. Mater. Manage. VIII, 601-619 (1979).

29. R. J. Jones, Ed., "Selected Measurement Methods for Plutonium and Uranium in the Nuclear Fuel Cycle," U.S. Atomic Energy Commission report TID-7029 (1963), Chap. 4, pp. 54-58.

30. R. M. Schoonover and J. F. Houser, "Pressure Type Liquid Level Gages," National Bureau of Standards report 10-396 (1971).

31. R. M. Schoonover, "The Equivalence of Gravimetric and Volumetric Test Measure Calibration," National Bureau of Standards report NBSIR 74-454 (February 1974).

32. IAEA Safeguards Technical Manual, International Atomic Energy Agency Technical Document IAEA-174, Part E, Methods and Techniques, Chap. 3 (1975), pp. 27-38.

33. C. G. Hough, "Statistical Analysis-Accuracy of Volume Measurements in a Large Process Vessel," Hanford Laboratories report HW-62177 (October 1959).

34. C. Beets, "Role of Measurements of Nuclear Materials in Safeguards," in Practical Applications of R&D in the Field of Safeguards, Proc. European Safeguards Research and Development Association (ESARDA) Symp., Rome, Italy, March 7-8, 1974, pp. 229-261.

35. R. A. Schneider and D. P. Granquist, "Capability of a Typical Material Balance Accounting System for a Chemical Processing Plant," Battelle Pacific Northwest Laboratories report BNWL-1384 (May 1970).

36. T. I. McSweeney, J. W. Johnston, R. A. Schneider, and D. P. Granquist, "Improved Material Accounting for Plutonium Processing Facilities and a 235-U-HTGR Fuel Fabrication Facility," Battelle-Pacific Northwest Laboratories report BNWL-2098 (October 1975).

37. R. M. Schoonover and J. F. Houser, "Uncertainties in the Calibration of Large Vessels," National Bureau of Standards report 10-081 (1969).

38. J. F. Houser, "Procedures for the Calibration of Volumetric Test Measures," National Bureau of Standards report NBSIR 73-287 (August 1973).

39. R. M. Schoonover, H. H. Ku, J. R. Whetstone, and J. F. Houser, "Liquid Level Instrumentation in Volume Calibration," National Bureau of Standards report NBSIR 75-900 (October 1975).

40. P. E. Pontius and J. R. Whetstone, "The Calibration of an Industrial Process Tank by Transfer Methods," National Bureau of Standards report, to be published.

41. F. E. Jones, "Application of an Improved Volume Calibration System to the Calibration of Accountability Tanks," in Nuclear Safeguards Technology, Proc. Symp., Vienna, October 2-6, 1978 (International Atomic Energy Agency, Vienna, 1979), IAEA-SM-231/95, Vol. II, pp. 653-659.

42. F. Jones, "An Alternative to Linear Least Squares Treatment of Process Tank Calibration Data," 18th Annual INMM Meeting, Washington, DC, June 29-July 1, 1977.

43. C. L. Pleasance, "Accurate Volume Measurement of Large Tanks," ISA Journal 8, No. 5, 56-59 (May 1961).

44. W. Gmelin and P. Siwy, "Contribution to the Statistical Analysis of Input Measurements at a Reprocessing Plant," International Atomic Energy Agency report IAEA/STR-9 (1970).

45. W. Davies, P. T. Good, and A. G. Hamlin, "A Statistical Examination of the Practical Problems of Measurement in Accountancy Tanks," in Nuclear Safeguards Technology, Proc. Symp., Vienna, October 2-6, 1978 (International Atomic Energy Agency, Vienna, 1979), IAEA-SM-231/57, Vol. II, pp. 593-619.

46. J. M. Cleveland, The Chemistry of Plutonium (Gordon and Breach Science Publishers, New York, 1970) p. 434.

47. C. S. MacDougall and G. R. Waterbury, "Controlled-Potential Coulometric Determination of Plutonium-238 Dioxide Fuels," Anal. Chem. 45, 976-978 (1973).

48. 1978 Annual Book of ASTM Standards, Part 45, Nuclear Standards (American Society for Testing Materials, Philadelphia, 1978), pp. 252-342.

49. L. Koch, "Determination of Isotopic Concentrations of Uranium and Plutonium," Radiochim. Acta 12, 160-162 (1969) (in German; English abstract).

50. J. E. Rein and C. F. Metz, "The Application of Isotope Dilution Mass Spectrometry to the Determination of Uranium and Plutonium in Nuclear Fuels," in Analytical Chemistry of Nuclear Fuels, Proc. Panel, Vienna, 1970 (International Atomic Energy Agency, Vienna, 1972), pp. 47-109.

51. H. Bokelund, "Determination of Plutonium by Isotope Dilution Mass Spectrometry Following TTA-Extraction," J. Radioanal. Chem. 2, 191-196 (1969).

52. F. B. Stephens, R. G. Gutmacher, K. Ernst, J. E. Harrar, and S. P. Turel, "Methods for the Accountability of Uranium Dioxide," US Nuclear Regulatory Commission report NUREG 75/010 (June 1975).

53. F. B. Stephens, R. G. Gutmacher, K. Ernst, and J. E. Harrar, "Methods for the Accountability of Mixed Oxides," US Nuclear Regulatory Commission report NUREG-0256 (April 1977).

54. R. G. Gutmacher, F. Stephens, K. Ernst, S. P. Turel, and T. E. Shea, "Methods for the Accountability of Plutonium Dioxide," US Atomic Energy Commission report WASH-1335 (December 1974).

55. F. B. Stephens, R. G. Gutmacher, K. Ernst, J. E. Harrar, and S. P. Turel, "Methods for the Accountability of Reprocessing Plant Dissolver and Waste Solutions," US Nuclear Regulatory Commission report NUREG/CR-0515 (December 1978).

56. G. Phillips and D. Crossley, "The Determination of Plutonium/Uranium Ratios by Controlled-Potential Coulometry at a Solid Electrode," United Kingdom Atomic Energy Authority report AERE-R-8794 (May 1977).

57. W. Davies and W. Gray, "A Rapid and Specific Titrimetric Method for the Precise Determination of Uranium Using Iron (II) Sulphate as Reductant," Talanta 11, 1203-1211 (1964).

58. A. R. Eberle, M. W. Lerner, C. G. Goldbeck, and C. J. Rodden, "Titrimetric Determination of Uranium in Product, Fuel, and Scrap Materials After Ferrous Ion Reduction in Phosphoric Acid," New Brunswick Laboratory report NBL-252 (July 1970).

59. G. C. Goode, J. Herrington, and G. Hall, "The Determination of Uranium in the Presence of Plutonium by Controlled Potential Coulometry, Application to the Analysis of Fuel Element Processing Solutions," Anal. Chim. Acta 30, 109-113 (1964).

60. J. T. Byrne, M. K. Larsen, and J. L. Pflug, "Accurate Determination of Uranium in the Presence of Small Amounts of Molybdenum," Anal. Chem. 31, 942-945 (1959).

61. J. E. Harrar, W. G. Boyle, J. D. Breshears, C. L. Pomernacki, H. R. Brand, A. M. Kray, R. J. Sherry, and J. A. Pastrone, "An Automated Sample-Processing and Titration System for the Determination of Uranium," Nucl. Mater. Manage. 5, 199-210 (1976).

62. W. D. Shults, "Applications of Controlled-Potential Coulometry to the Determination of Plutonium," Talanta 10, 833-849 (1963).

63. C. A. Seils, R. J. Meyer, and R. P. Larsen, "Amperometric Titration of Plutonium (VI) with Iron (II)," Anal. Chem. 35, 1673-1675 (1963).

64. K. S. Bergstresser and G. R. Waterbury, "An Evaluation of the Amperometric Titration of Plutonium," Los Alamos Scientific Laboratory report LA-3091 (May 1964).

65. J. L. Drummond and R. A. Grant, "Potentiometric Determination of Plutonium by Argentic Oxidation, Ferrous Reduction, and Dichromate Titration," Talanta 13, 477-488 (1966).

66. G. R. Waterbury and C. F. Metz, "Precise Determination of Plutonium by Potentiometric Titration," Anal. Chem. 31, 1144-1148 (1959).

67. W. N. Carson, Jr., J. W. Vanderwater, and H. S. Gile, "Coulometric Determination of Plutonium," Anal. Chem. 29, 1417-1422 (1957).

68. C. E. Pietri and J. A. Baglio, "The Determination of Plutonium Based on National Bureau of Standards Potassium Dichromate," Talanta 6, 159-166 (1960).

69. R. J. Kofoed, Jr., "Plutonium Oxidation-Reduction Titrations," Hanford Atomic Products Operation report HW-53368 Suppl. (December 1963).

70. Technical Manager Chemical Services, "The Titrimetric Determination of Plutonium, Chromous Reduction-Ceric Sulphate Titration," United Kingdom Atomic Energy Authority report PG309(w) (1962).

71. D. D. Jackson, R. M. Hollen, F. R. Roensch, and J. E. Rein, "Highly Selective Coulometric Method and Equipment for the Automated Determination of Plutonium," in Analytical Chemistry in Nuclear Fuel Reprocessing, W. S. Lyon, Ed., (Science Press, Princeton, 1978) pp. 151-158.

72. G. S. Barney, "Coulometric Determination of Plutonium in Solutions of Dissolved Reactor Fuel Elements," Atlantic Richfield Hanford Co. report ARH-SA-55 (January 1970).

73. F. A. Scott and R. M. Peekema, "Analysis for Plutonium by Controlled-Potential Coulometry," in Proc. U.N. International Conf. on Peaceful Uses of Atomic Energy, 2nd, Geneva (United Nations, New York, 1958), Vol. 28, 573-578.

74. C. A. Prohaska, "A Flow Colorimeter for Measuring Uranium Concentration in Process Streams," US Atomic Energy Comm. report DP-229 (1957).

75. F. A. Scott and R. D. Dierks, "Photometer for Continuous Determination of Uranium in Radioactive Process Streams," Anal. Chem. 32, 268-272 (1960).

76. K. L. Cheng and P. F. Lott, "Reaction of Hydrogen Peroxide with Complexes of (Ethylenedinitrilo) Tetraacetic Acid," Anal. Chem. 28, 462-465 (1956).

77. W. I. Winters, "Spectrophotometric Determination of Uranium in Nuclear Waste," Atlantic Richfield Co. report ARH-SA-250 (1976).

78. W. I. Winters, "Spectrophotometric Determination of Trace Uranium in Plutonium Nitrate and Oxides with 2-(2-Pyridylazo)-5-Diethylaminophenol," Atlantic Richfield Hanford Co. report ARH-ST-116 (1975).

79. L. Sommer, V. M. Ivanov, and H. Novotna, "The Reaction of Uranyl Ions with 4-(2-Pyridylazo) resorcinol," Talanta 14, 329-343 (1967).

80. S. Shibota, M. Furukawa, and Y. Ishiguro, "Spectrophotometric Determination of Uranium with 1-(5-Methyl-2-Pyridyl)azo-2-Napthol," Microchim. Acta 1974, 129-133.

81. D. A. Johnson and T. M. Florence, "Spectrophotometric Determination of Uranium (VI) with 2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol," Anal. Chim. Acta 53, 73-79 (1971).

82. W. J. Maeck, G. L. Booman, M. C. Elliott, and J. E. Rein, "Spectrophotometric Extraction Methods Specific for Uranium," Anal. Chem. 31, 1130-1134 (1959).

83. D. D. Jackson, D. J. Hodgkins, R. M. Hollen, and J. E. Rein, "Automated Spectrophotometer for Plutonium and Uranium Determination," Los Alamos Scientific Laboratory report LA-6091 (1976).

84. W. J. Maeck, G. L. Booman, M. C. Elliott, and J. E. Rein, "Spectrophotometric Extraction Method Specific for Plutonium," Anal. Chem. 33, 998-1001 (1961).

85. W. I. Winters, "The Differential Spectrophotometric Determination of Plutonium Using the Cary Model 16 Spectrophotometer," Atlantic Richfield Hanford Co. report ARH-2745 (1973).

86. D. D. Jackson, R. M. Hollen, S. F. Marsh, M. R. Ortiz, and J. E. Rein, "Determination of Submilligram Amounts of Uranium with the LASL Automated Spectrophotometer," in Analytical Chemistry in Nuclear Fuel Reprocessing, W. S. Lyon, Ed. (Science Press, Princeton, 1978), pp. 126-133.

87. R. A. Schneider and K. M. Harmon, "Analytical Technical Manual," Hanford Atomic Products Operation report HW-53368 (February 1961).

88. F. L. Moore and J. E. Hudgens, Jr., "Separation and Determination of Plutonium by Liquid-Liquid Extraction," Anal. Chem. 29, 1767-1770 (1957).

89. M. H. Campbell, "Fluorimetric Uranium Analysis with a High Carbonate Flux," Hanford Atomic Products Operation report HW-53455 (November 1957).

90. F. A. Centanni, A. M. Ross, and M. A. DeSesa, "Fluorometric Determination of Uranium," Anal. Chem. 28, 1651-1657 (1956).

91. G. L. Booman and J. E. Rein, "Uranium," in Treatise on Analytical Chemistry, I. M. Kolthoff and P. J. Elving, Eds. (Interscience Publishers, New York, 1961), Part II, Vol. 9, pp. 1-188.

92. M. W. Lerner, "Evaluation of the Methods in TID-7029, Selected Measurement Methods for Plutonium and Uranium in the Nuclear Fuel Cycle," New Brunswick Laboratory report NBL-231 (February 1966).

93. J. D. Caylor, S. H. Cole, T. L. Futrell, R. J. McElhaney, and V. M. Giles, "An Automated Fluorometer for Uranium Analysis," in Analytical Chemistry in Nuclear Fuel Reprocessing, W. S. Lyon, Ed. (Science Press, Princeton, 1978), pp. 167-175.

94. E. P. Bertin, "Recent Advances in Quantitative X-Ray Spectrometric Analysis by Solution Techniques," Adv. X-Ray Anal. 11, 1-22 (1968).

95. E. P. Bertin, Principles and Practice of X-Ray Spectrometric Analysis (Plenum Press, New York, 1970).

96. L. S. Birks and J. V. Gilfrich, "X-Ray Spectrometry," Anal. Chem. 48, 273R-281R (1976).

97. R. Woldseth, All You Ever Wanted to Know About X-Ray Energy Spectrometry (Kevex Corp., Burlingame, California, 1973).

98. B. G. Brodda, H. Lammertz, H. Maselter, and J. Vieth, "Remotely Controlled Computer-Guided Preparation Facility for X-Ray Fluorescence Measurement Samples at a Fuel Reprocessing Plant," Kerntechnik 19, 433-444 (1977).

99. A. von Baeckmann, D. Ertel, and J. Neuber, "Determination of Actinide Elements in Nuclear Fuels by X-Ray Analysis," Adv. X-Ray Anal. 18, 62-75 (1975).

100. D. Ertel, "Simultaneous Determination of Uranium and Plutonium in Inactive Purex Process Solutions by X-Ray Fluorescence," J. Radioanal. Chem. 2, 205-209 (1969).

101. P. A. Pella and A. von Baeckmann, "The X-Ray Spectrometric Determination of Uranium and Plutonium in Solutions of Spent Nuclear Fuels," Anal. Chim. Acta. 47, 431-438 (1969).

102. G. Malet and G. Charpentier, "Simultaneous Determination of Uranium and Plutonium by X-Ray Fluorescence in the Reprocessing of Rhapsodie Fuel," in Analytical Methods in the Nuclear Fuel Cycle, Proc. Symp., Vienna, November 29-December 3, 1971 (International Atomic Energy Agency, Vienna, 1972), pp. 343-352.

103. W. L. Pickles and J. L. Cate, Jr., "Quantitative Nondispersive X-Ray Fluorescence Analysis of Highly Radioactive Samples for Uranium and Plutonium Concentration," University of California Radiation Laboratory report UCRL-74717 (August 1973).

104. C. R. Hudgens and B. D. Craft, "Feasibility Study of the Proposed Use of Automated X-Ray Fluorescence Analysis for Measurement of U and Pu in Dissolver Tanks," Monsanto Research Corporation report MLM-2533 (September 1978).

105. R. H. Augustson and T. D. Reilly, "Fundamentals of Passive Nondestructive Assay of Fissionable Material," Los Alamos Scientific Laboratory report LA-5651-M (September 1974).

106. T. D. Reilly and M. L. Evans, "Measurement Reliability for Nuclear Material Assay," Los Alamos Scientific Laboratory report LA-6574 (January 1977).

107. N. A. Wogman, R. L. Brodzinski, and D. P. Brown, "An Instrument for Monitoring the Transuranic Content of Chopped Leached Hulls from Spent Nuclear Fuel Elements," Battelle Pacific Northwest Laboratories report PNL-SA-6652 (March 1978).

108. G. W. Eccleston and H. O. Menlove, "A Measurement System Using High Resolution Spent Fuel Assemblies and Waste Solids," Nucl. Mater. Manage. VIII, 344-355 (1979).

109. J. L. Parker, T. D. Reilly, and R. B. Walton, "Gamma-Ray and Passive Neutron Assay of Waste Drums," in "Nuclear Analysis Research and Development Status Report Sept.-Dec. 1974," Los Alamos Scientific Laboratory report LA-5880-PR (April 1975), p. 14.

110. T. W. Crane, J. L. Parker, and C. A. Spirio, "Comparison of Gamma and Neutron NDA Techniques for 30-gal Waste Barrels," in "Nuclear Analysis Research and Development Status Report September-December 1977," Los Alamos Scientific Laboratory report LA-7211-PR (July 1978), pp. 52-54.

111. T. W. Crane, D. A. Close, M. S. Krick, and H. O. Menlove, "Neutron Methods for Assay of Fissionable Material in the Presence of Fission Products," in Analytical Chemistry in Nuclear Fuel Reprocessing, W. S. Lyon, Ed. (Science Press, Princeton, 1978) pp. 285-291.

112. G. W. Eccleston, "Fluorinel and Storage (FAST) Facility Delayed Neutron Interrogator," in "Nuclear Analysis Research and Development Program Status Report Sept.-Dec. 1978," Los Alamos Scientific Laboratory report LA-7706-PR (May 1979).

113. E. D. Blakeman, E. J. Allen, and J. D. Jenkins, "An Evaluation of NDA Techniques and Instruments for Assay of Nuclear Waste at a Waste Terminal Storage Facility," Oak Ridge National Laboratory report ORNL/TM-6163 (May 1978).

114. T. D. Reilly and J. L. Parker, "A Guide to Gamma-Ray Assay for Nuclear Material Accountability," Los Alamos Scientific Laboratory report LA-5794-M (March 1975).

115. J. W. Tape, "CdTe Gamma-Ray Detector Investigations," in "Nuclear Safeguards Research and Development Program Status Report January-April 1977," Los Alamos Scientific Laboratory report LA-6849-PR (August 1977), p. 27-28.

116. T. D. Reilly, "The Measurement of Leached Hulls," Los Alamos Scientific Laboratory report LA-7784-MS (July 1979).

117. K. J. Hofstetter, B. C. Henderson, J. H. Gray, and G. A. Huff, "Non-Destructive Assay of Leached Hulls in a Nuclear Fuel Reprocessing Plant," in Analytical Methods for Safeguards and Accountability Measurements of Special Nuclear Material, H. T. Yolken and J. E. Bullard, Eds., NBS Special Publication 528 (November 1978), pp. 71-77.

118. F. A. O'Hara, J. D. Nutter, W. W. Rodenburg, and M. L. Dinsmore, "Calorimetry for Safeguards Purposes," Mound Laboratory report MLM-1798 (January 1972).

119. "Calibration Techniques for the Calorimetric Assay of Plutonium-Bearing Solids Applied to Nuclear Materials Control," American National Standard document ANSI N15.22-1975 (American National Standards Institute, NY, 1975).

120. R. Gunnink, J. B. Niday, and P. D. Siemens, "A System for Plutonium Analysis by Gamma Ray Spectrometry. Part I: Techniques for Analysis of Solutions," University of California Radiation Laboratory report UCRL-51577, Pt 1 (April 1974).

121. C. L. Fellers and P. W. Seabaugh, "Real-Time Prediction of Calorimeter Equilibrium," Nucl. Instrum. Methods 163, 499-505 (July 15, 1979).

122. C. T. Roche, R. B. Perry, R. N. Lewis, E. A. Jung, and J. R. Haumann, "A Portable Calorimeter System for Nondestructive Assay of Mixed-Oxide Fuels," in Nuclear Safeguards Analysis, E. A. Hakkila, Ed. (American Chemical Society, Washington, DC, 1978), pp. 158-178.

123. M. F. Duff and C. L. Fellers, "Feasibility of a Mound-Designed Transportable Calorimeter," Mound Facility, Miamisburg, Ohio report MLM-2603 (April 16, 1979).

124. W. W. Strohm, Mound Facility, personal communication, August 13, 1979.

125. US AEC Regulatory Guide 5.35: Calorimetric Assay of Plutonium (June 1974).

126. W. W. Strohm and J. F. Lemming, "Traceability of the Nondestructive Assay of Plutonium Using Calorimetry for Measurement Control," Nucl. Mater. Manage. VI(3), 663-673 (1977).

APPENDIX L

NEAR-REAL-TIME MEASUREMENT TECHNIQUES

E. A. Hakkila, C. A. Ostenak, and C. C. Thomas, Jr.
LASL Safeguards Staff (Q-4)

Dynamic materials accountability supplements conventional accountability by obtaining additional measurements in near-real-time to permit materials balances to be closed more frequently. In some areas conventional methods, as reviewed in App. K of this report, may be appropriate if NM concentrations are low or if measurements are performed only infrequently. In areas where measurement turn-around of the order of hours is required, it is often necessary to use in-line or at-line techniques requiring minimal sample manipulation. For static components such as tanks, volume and concentration measurements are required; for dynamic process areas, flow and concentration measurements are needed.

For the reprocessing-conversion facility, measurements may be required from the fuel receiving pool through the PuO_2 loadout area. A discussion of techniques for the measurement of irradiated fuel assemblies is presented in App. I of this report. Volume measurements are reviewed in App. K.

A. Flow Measurement

Flow measurement instruments in reprocessing plants are used primarily for process control where high precision is not a requirement. Monitoring of process streams is held to a minimum and generally only those instruments essential for plant operation are provided. Flow measurement instruments have not been designed for use in accountability systems.

Systems and equipment in a reprocessing plant are subject to severe radiation and corrosion environments. Instruments must be simple and reliable with minimum potential for mechanical failure or degradation from radiation or from solvents. Meters without moving parts are preferred.

The most accurate means of measuring flow is to follow the progress of batch transfers. Batch volumes can be measured to high accuracies (∿0.025 cm or 0.1% of scale, depending upon the system). Measurement of the rate of change in tank inventory can give a highly accurate indication of flow rate and is the best technique available. Where materials accounting is handled by batch accumulation and analysis, this method is the most convenient and accurate for handling the accountability. Continuous rather than batch transfer is used in the reprocessing area, and other means of flow measurement are required.

Fluid transfers in reprocessing facilities are effected by airlifts to headpots to provide gravity feed to the various separation units. Flow rates generally are monitored to within 5-10%, although orifice meters in headpots can measure flow to <1%.

Various types of flow meters have been considered for flow measurement in reprocessing plants and are summarized. (Flow meter applications are reviewed in Ref. 1, App. B, Table B-1.) Present applications and R&D efforts in the US on use of flow meters for materials accountability are summarized below.

1. Orifice Meters. Orifice meters are rugged and require little maintenance, hence can be used in radioactive reprocessing plant environments where access is difficult. Orifice meters are used for process control in US Government reprocessing plants and are incorporated in several areas of the AGNS plant at Barnwell, SC, including the 1BP metering headpot.[2] Additionally, AGNS has developed a V-notch weir-type metering headpot.

Accuracy in the range 0.5-10% can be expected, depending on variations in flow rate and calibration procedures. For accuracy of 1% or better, periodic recalibration is required to correct for corrosion and erosion of the orifice.

2. Bubble-Transit Meter. The bubble-transit flow meter is based on use of ultrasonic sensors to measure the passage of injected or random bubbles in the flowing fluid.[3] The ultrasonic detectors are mounted exterior to process lines and are designed primarily for low flow rates, such as are encountered in the concentration output line in the plutonium purification area. The flow meter is being developed and evaluated at the ICPP.

Periodic recalibration is not required except to reduce systematic errors, and the instrument is not susceptible to plugging or corrosion. Accuracy of 0.5% has been demonstrated in some laboratory tests.

3. Gyroscopic-Coriolis Mass Flow Meter. The gyroscopic-coriolis mass flow meter is a patented device manufactured by Micro Motion, Inc.[4] The angular deflection of a U-shaped pipe is measured optically as the pipe is subjected to oscillation. Four sizes of meter are available, covering mass flow rates from 2 to 230 kg/min. Continuous computer-operated data recording is possible.

The instrument has been evaluated at AGNS to provide an accuracy of 0.5% in measuring mass flow of process streams (Ref. 5, App. G). Cost is $1500-4000, depending on size and type of output (analog and/or digital). The meter has not yet been evaluated in radioactive environments, but such an evaluation will be made at ICPP.

4. Vortex-Shedding Flow Meter. In vortex-shedding flow meters, localized vortices or eddies are created by an obstruction placed in the fluid stream.[6] The rate of vortex formation is a function of the flow velocity. A vortex-shedding meter that measures the rate of vortex formation by using a heated thermistor will be evaluated at LASL during FY 79-80 and at ORNL. An accuracy of 0.5% is claimed for the meter, but this claim has not been evaluated under reprocessing plant conditions. Cost is reported to be comparable to the orifice meter, approximately $1000 per installation.[7]

A vortex-shedding flow meter that uses a piezoelectric sensor to monitor liquids or gases, including superheated steam, will be marketed in the US.[8] In this flow meter, vortex-induced deformations of a stainless steel bar placed in a fluid stream are detected by a piezoelectric sensor within the bar. The flow-meter electronics translate these deformations into frequency, which is directly proportional to flow rate. Advantages of the sensor used in this flow meter include (1) no fluid contact, (2) higher temperature limits, (3) reduced corrosion problems, and (4) no moving parts.

5. Ultrasonic Flow Meter. The ultrasonic flow meter is based on the change in velocity of an ultrasonic beam transmitted through a flowing liquid. Transducers generally are mounted in the pipe, but they may be placed exterior to the pipe wall to avoid intrusion into the pipe.

Application in pipes having a diameter <4 cm (1.5 in.) generally is not recommended. The instrument has not been tested in a radioactive environment.

The ultrasonic flow meter can measure flow with an accuracy of 0.5%.[9] Interference by entrained air can be eliminated by transducer and detector circuit design. The use of ultrasonic flow meters and extrinsic factors affecting measurement accuracy have been reviewed by Managan.[10]

6. Electromagnetic Flow Meter. The electromagnetic flow meter operates on the principle that a conductor moving at right angles through a magnetic field induces a voltage. The magnitude of the potential is proportional to the magnetic field intensity and the flow rate of the conducting fluid. The meter can be operated in a radioactive environment and has been used at US Government reprocessing plants for several years.

Precision and accuracy of 1% or better are possible. The meter can be used in pipes as small as 0.25 cm, at a cost proportional to pipe diameter. For 10-cm-diam pipes, the estimated cost is $2500-$3000.[6]

7. Correlation Flow Meter. This instrument uses the normal solid particles, bubbles, and other discontinuities present in most flowing liquids to make a nonintrusive flow measurement.[3] The discontinuities are detected by ultrasonic detectors mounted on the outside of the pipe, and transit time is measured by computer correlation of detector output. Accuracies of 1% or better are anticipated. The technique is being evaluated at ICPP.

B. Concentration Measurement

Concentration measurements for near-real-time accounting can be made on-line, off-line, or in the laboratory, with on-line generally preferred for speed and freedom from potential sample-tampering. Calibration checks are made by conventional analytical methods. Methods of interest that have been proposed or are being considered for continuous monitoring in a reprocessing plant are summarized.

1. Input. The measurement of NM in the accountability tank solution is one of the most challenging problems in nuclear materials accountability, whether for conventional or continuous measurement. The measurement conventionally is performed by isotope-dilution mass spectrometry (App. K, Sec. C.1), a method that may be appropriate for near-real-time accounting where material balances are performed batchwise.

X-ray fluorescence is being investigated for verification of mass spectrographic methods, using both wavelength- and energy-dispersive techniques. X-ray fluorescence requires minimal sample preparation. Addition of an internal standard may be required to minimize effects from variation in sample composition and power supply fluctuation, although an external standard may be used.

A wavelength-dispersive x-ray fluorescence method is being investigated at Mound Laboratory.[11] The instrument is in the design stage; expected cost for a prototype is in excess of $0.5 million, with a significant fraction of the cost attributable to the power supply. It is estimated that both uranium and plutonium can be measured with a RSD of 0.5% or better if a specially designed high-voltage generator and high-precision goniometer are used.

Wavelength-dispersive x-ray fluorescence also is being investigated at Lawrence Livermore Laboratory (LLL), but design information is not available.

An energy-dispersive system, designed at LLL, is being investigated at the SRP for reprocessing samples.[12] Precisions for measuring uranium and plutonium are approximately 1 and 3%, respectivelv, and the accuracy is 2%.

A *feasibility study using inductively-coupled plasma emission spectroscopy to* analyze dissolver solutions has been proposed by the DOE Ames Laboratory of Iowa State University.

For rapid verification of accountability tank samples, ICPP is evaluating a lightweight (100-150 kg) mass spectrometer[3] that can be taken into a nuclear facility in a light truck or van and used for rapid measurement of uranium or plutonium isotope ratios in plant samples. Two commercially purchased quadrupole mass spectrometers and a specially designed magnetic mass spectrometer are being evaluated.

An analysis time of 10-15 min is anticipated, with an RSD of 1% for measuring relative isotopic concentrations.

2. Process and Product Streams. Concentration of uranium and plutonium in process streams can be measured by several x-ray or gamma-ray techniques. X-ray fluorescence is described in the previous section and in App. F.

a. Absorption-Edge Densitometry. After fission-product decontamination, process streams can be analyzed in-line or off-line by absorption-edge techniques involving either L_{III} or K edges. In those techniques the transmitted intensity is measured for two x rays or gamma rays selected immediately above and below an absorption edge for the element determined. The method is element specific. The L_{III} edge is useful for uranium and plutonium concentrations below ∿30 g/L;[13,14] the K-edge method is useful for concentrations greater than ∿20 g/L.[15] With proper choice of cell path length and K- or L_{III}-absorption edges, plutonium (or uranium) concentrations between ∿5 and 500 g/L can be measured with <1% RSD.

The input to the plutonium purification area can be measured by using the L_{III}-absorption edge. Plutonium concentrations between 10 and 25 g/L in samples without fission products have been measured with an RSD of 0.6%.[15] A commercial x-ray spectrograph costing $60,000 was adapted for the measurement. Application to reprocessing samples containing fission products has not been investigated, but a technique using an x-ray tube source and a curved-crystal spectrometer as a filter has been proposed.[16]

Uranium input to the uranium purification area and both plutonium and uranium outputs from their respective purification areas can be measured by K-edge absorption. An RSD of 0.2-0.5% was measured for plutonium concentration in the range 150-500 g/L.[17] The work was performed at AGNS using an instrument designed at LLL.[17,18] Similar precision should be obtainable for uranium. An added advantage of absorption-edge densitometry is that if both uranium and plutonium are present in solution, as they would be in coprocessing, they can be measured simultaneously. Finally, for in-line safeguards accounting measurements, absorption-edge densitometry, rather than gross absorptiometry, should be used.

A LASL-designed and -built K-edge densitometer will be evaluated at Tokai for measurement of plutonium in reprocessing product samples as Task G of the TASTEX program.[19]

b. Gamma-Ray Spectrometry. In gamma-ray methods the intensities of gamma rays emitted by isotopes of the element to be determined are measured and compared to standards. Ideally, gamma rays for all isotopes should be measured. The ^{242}Pu isotope does not emit usable gamma rays, and its concentration must be inferred from burnup or mass spectrometry data. Gamma-ray spectrometry is being investigated for measurement of plutonium in product solutions. The instrument is being designed at LLL and will be tested at Tokai as Task H of the TASTEX program.[18,19] Instrument evaluation also is being performed at AGNS.[17] If ^{242}Pu is estimated from input accountability tank data, an RSD of better than 0.5% is anticipated.

A gamma-ray plutonium assay system also has been developed at LASL and has been used routinely for assay of reprocessed unirradiated plutonium solutions.[20,21] For plutonium concentration between 0.5 and 500 g/L an RSD of ∿1% is reported in an assay time of <45 min. Accuracy of 0.5% relative to mass spectrometry was observed.

c. Dual Gamma-Ray Absorptiometer. Two gamma rays (60-keV ^{241}Am and 662-keV ^{137}Cs) are transmitted through the solution, and uranium concentration in product lines is measured by comparing the ratio to ratios measured for known standards. The useful concentration range is 20-350 g/L with an expected accuracy of 0.5%.[3] The method is not element specific, and other high- or medium-Z elements can interfere. This instrument is undergoing laboratory testing in preparation for testing at ICPP. A similar instrument was installed and is being tested at Saluggia, Italy, in cooperation with Euratom.

d. X-Ray Fluorescence. The K-series x-rays for plutonium are excited by a ^{57}Co source, and the intensities are measured with an energy-dispersive detector.[22] An instrument incorporating these functions was designed at LLL and tested at the SRL. The useful concentration range is 1-500 g/L, with an analysis time of 100 to >1000 s, depending on concentration. The technique is nondestructive and nonintrusive. It can be applied on-line to solutions flowing in pipes. An RSD of 1% is anticipated, but has not been demonstrated for process samples.

e. Calorimetry. In-line calorimetry can be used to measure the PuO_2 product in the conversion facility. Mound Laboratory is developing an in-line automated plutonium assay system (APAS)[23,24] that uses multiple servo-controlled calorimeters for plutonium measurement in MOX fuels. A minicomputer controls container movement by an XYZ transporter, acquires and analyzes data, and prepares reports. After pre-equilibration, samples ranging from 100 g of MOX to 1 kg of PuO_2 require ∿1 h for power measurement. The sample container is a reusable stainless steel can, ∿6 cm in diameter by 15 cm long. The APAS also has a gamma-ray spectrometer for rapid measurement of the isotopic composition.

f. Density. Density measurements are required on a number of streams in the reprocessing plant to convert solution weight data obtained with dip-tube pneumatic bubbler systems to solution volume. The density is determined either in the laboratory on representative samples or in-line with a dip-tube system. Laboratory measurements usually are made on samples from tanks such as the input accountability tank, uranyl nitrate accountability tank, and the plutonium precipitator feed preparation tank.

The laboratory densimeters should be capable of remote measurement and should have a precision of ±0.0003 g/mL or better.[25] The densimeters operate on the principle of measuring the change in resonant frequency at a glass U-tube mechanical oscillator when the U-tube is filled with fluids of different mass. The instruments are available in various configurations, including remote sensing heads, built-in thermostats, and microcomputer calculators to provide direct digital readout of the density. The usual hot cell or glovebox installation consists of a remote oscillator sensing head mounted within the cell or box, with the instrument chassis located on the outside.[25]

The dip-tube pneumatic bubbler density measurement system is similar to the dip-tube liquid level system discussed in App. K. The essential difference is that the second leg of the system is not at atmospheric pressure but is a second dip-tube separated from the first dip-tube by a known distance. The solution level must be above the end of both dip-tubes for the system to work. The density of the solution can be calculated from the known dip-tube separation and the measured pressure difference.

Errors in level and density measurements made with dip-tubes have been discussed.[26,27] The systems considered in those studies were differential pressure transmitters (d/p cells). Bradley and his coworkers report that the measurement error is dominated by the d/p cell accuracy and is ∿0.5% of span and ∿0.25% of span for pneumatic and electronic output units, respectively.

An early safeguards program investigation[28] of the two dip-tube density system using a pneumatic d/p cell found the system to have a "conservatively" estimated 2-σ precision of 0.009 specific gravity units for a range of 1.0-1.6 specific gravity units. A pneumatic d/p cell was used. The estimated 2-σ precision is consistent with the ±0.5% of span instrument accuracy.

An NBS study of in-tank solution density instrumentation showed that a precision of 2.2 parts in 10^4 could be obtained with a probe separation of 25 cm. The calibrating fluid was water, and temperature was carefully measured during measurements.[29]

Density measurement has been used in reprocessing plants for measuring in-process inventory, primarily for process control, and has been proposed in this study as a means of determining in-process inventory for near-real-time accounting. The method is sensitive to HNO_3 concentration and temperature, and the effects have been measured for uranium product solutions having uranium concentrations in the range 0.05-0.60 $\underline{M}$ (12-143 g/L).[30] Errors in determining uranium concentration are in the range 0.0017-0.0043 $\underline{M}$, equivalent to RSD (1σ) in the range 0.8-3.9%. In measurements of LWR dissolver solutions, RSD of 0.8-1.2% were reported.[31] The RSD for uranyl nitrate product was <0.2%, and for plutonium nitrate the RSD was in the range 1.2-2%. The larger errors for plutonium may be caused by a larger variation in HNO_3 concentration.

g. Spectrophotometry. A rapid off-line spectrophotometric method has been described[32] for determining plutonium in dissolver and other reprocessing samples. Plutonium is oxidized to the hexavalent state using AgO, neodymium is added as an internal standard, and plutonium and neodymium absorbances are measured in the near infrared region. Fission-product activity to 500 Ci/L and uranium concentration to 400 g/L do not interfere for determining 1-5 g/L of plutonium. Precision of better than 1.5% (1σ) and an accuracy of 0.5% is claimed for an analysis time of 1 h.

h. Neutron Techniques. Neutron techniques can be applied to the determination of uranium and plutonium. Neutron yields from uranium are too low to enable uranium determination in the presence of plutonium.

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

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

Coincidence counting of ^{240}Pu and ^{242}Pu spontaneous-fission neutrons is accomplished with assemblies of ^{3}He (or BF$_3$) counters embedded in polyethylene moderators.[33-37] Table L-I lists estimates of the isotopic composition and the neutron yields from spontaneous fission and (α,n) reactions of PuO$_2$ recycle fuel.[38] High (α,n) rates can complicate the coincidence method through accidental (random) coincidences and by fissions induced in the fissile components of the material, that is, the multiplication effect.

If coincidence counting is to be used to analyze large amounts of PuO$_2$ or scrap containing light elements, such as boron and fluorine, that have high (α,n) yields, coincidence detectors with short die-away times are required to enhance the contribution of real coincidence events relative to accidental events, thereby reducing statistical uncertainties. This requirement has led to the concept of varying the physical die-away time of a neutron coincidence detector by changing the number and geometrical configuration of polyethylene moderators and cadmium (or boron) neutron absorbers.[39]

TABLE L-I

EMISSION RATE FROM 1 g OF PLUTONIUM[a]

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

---

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

Table L-II shows typical precisions and accuracies of neutron coincidence counters for the general categories of product, scrap, and waste[40] in the process environment. The data demonstrate the loss of precision and accuracy possible when the elemental and isotopic material composition is poorly characterized or nonuniform.

In the conversion facility, neutron NDA methods will be used to measure PuO_2 product and in-process inventories.

3. Liquid Waste Streams. Concentration of uranium and plutonium in waste streams must be measured to close a materials balance around a unit process on a measured basis. In the plutonium purification area, plutonium must be measured in the aqueous and organic streams.

Solid waste measurements are described in App. K and App. N.

a. In-Line Alpha Monitors. In-line alpha monitors are used in reprocessing plants for process control to verify that excess plutonium is not discharged from columns to waste or recycle. Alpha monitors measure total alpha intensity, which for reprocessing solutions arises primarily from ^{238}Pu. Hence, isotopic composition must be known. Commercially available alpha monitors have been evaluated at AGNS for continuous quantitative determination of plutonium in the concentration range from 10^{-3} to

TABLE L-II

TYPICAL NEUTRON COINCIDENCE COUNTER UNCERTAINTIES

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

0.1 g/L with an RSD of 12%.[41] Interference from beta activity to a 10^4 ratio relative to alpha activity, and to gamma radiation to 0.5 mCi/L, is eliminated by electronic discrimination.

In-line alpha counters in use in the solvent phase from the first-cycle extraction bank, the aqueous phase from the first-cycle partition bank, and the aqueous phase of the first-cycle partition bank feed stage have been described by Chabert[42] and are used routinely in France. The unit uses a scintillation (ZnS) probe and a rotating drum to present the sample to the probe. The drum rotates inside a tank containing the process fluid. The RSD is 3.1-3.2% for counters used in the aqueous phase and 4.6% for those used in the solvent phase. The rate of failure of the units over a period of ∿4 yr was ∿1% and the immobilization rate, including routine maintenance, was ∿2%.

b. In-Line Polarography. In polarographic analysis the voltage between two electrodes immersed in the solution is monitored across a range that includes a redox reaction for the element to be measured. No titrant is required, and measurement can be made after addition of a suitable supporting electrolyte. Polarography has been investigated both in the US and abroad for in-line measurement of uranium in waste streams. Polarography has been used at Hanford[43] to measure uranium in reprocessing plant waste streams in the concentration range ∿0.1 to 10 g/L with 7.5-min analysis times. Although the RSD for synthetic solutions was 2% (1σ), an RSD of 10% was obtained for process samples.

A cell using two synchronized dropping mercury electrodes was constructed at SRP[44] for measuring 10^{-4} to 10^{-5} $\underline{M}$ uranium in flowing streams. Concentrations of 10^{-2} $\underline{M}$ Fe^{3+} or nitrite, or dissolved TBP, did not interfere. The maximum period of continuous operation was 8 h. The instrument was not installed in-line after the evaluation.

In-line polarography is not now being pursued in the US as a safeguards measure. The technique has been investigated in West Germany[45] and Japan.[46,47]

C. Moisture Determination in Plutonium Oxalate

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

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

1. Radio-Frequency Methods. Moisture meters have been developed for radio-frequency measurement of the H_2O content of various materials, including cotton, timber, and cereals.[48] However, part of the sample probably would have to be transferred to a special sample cell, thereby reducing the effectiveness of this technique for rapid on-line measurement.

2. Neutron Methods. Neutron scattering is a standard technique for determining H_2O in such materials as soils, coking materials, and ceramics.[49,50] A depth probe inserted into the sample, or a surface probe that operates in almost direct contact with the sample surface, can be used. Fast neutrons from an external source strike the sample, and those that are thermalized are measured. When used to measure plutonium oxalate, the system would have to be calibrated with dry oxalate to subtract out effects of spontaneous fission, (α,n) neutrons, and neutron thermalization by carbon and oxygen atoms in the oxalate. For measuring the H_2O content of soil or coke, the method is

reported[50] to have a sensitivity of ~ 0.01 g/cm^3. For plutonium oxalate with a density of ~ 3 g/cm^3, this is equivalent to a water concentration of $\sim 0.3\%$.

LASL has developed a system for determining hydrogen in fissile materials.[51,52] The instrument involved uses a ^{252}Cf source, and the sample is inserted into a well drilled into a steel block. It was developed specifically for small samples, but might be modified for bulk samples by using a surface probe.

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

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

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

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

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

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

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

An alternative approach that provides a more or less direct measurement of the plutonium content of wet plutonium oxalate is being investigated at LASL.[53] The method is a passive neutron assay using a double-ring thermal neutron coincidence counter. The inner-to-outer ring neutron-counting data provide an indication of water content, thereby providing a correction for neutron multiplication. Data collected to date indicate a potential precision of the order of 4% relative.

REFERENCES

1. E. A. Hakkila, D. D. Cobb, H. A. Dayem, R. J. Dietz, E. A. Kern, E. P. Schelonka, J. P. Shipley, D. B. Smith, R. H. Augustson, and J. W. Barnes, "Coordinated Safeguards for Materials Management in a Fuel Reprocessing Plant," Los Alamos Scientific Laboratory report LA-6881 (September 1977).

2. "Barnwell Nuclear Fuels Plant Separations Facility--Final Safety Analysis Report," Docket 50-332, Allied-General Nuclear Services, Barnwell, South Carolina (October 10, 1973).

3. C. M. Slansky, Ed., "Technical Division Quarterly Progress Report Oct. 1-Dec. 31, 1976," Allied Chemical Corporation report ICP-1111 (March 1977), pp. 41-42.

4. J. E. Smith, "Gyroscopic/Coriolis Mass Flow Meter," Meas. Control (July-August 1977), pp. 53-57.

5. J. M. Crawford, M. H. Ehinger, C. Joseph, and M. L. Madeen, "Studies and Research Concerning BNFP, Nuclear Materials Control and Accounting System Evaluation Report--FY 1978 Integrated Uranium Run," Allied-General Nuclear Services report AGNS-1040-2.2-50 (October 1978).

6. C. L. Smith, "Liquid Measurement Technology," Chemical Engineering Deskbook (April 1978), pp. 155-164.

7. "New Flowmeters Put Squeeze on Orifice Plate," Chem. Eng. News (December 19, 1977), pp. 20-21.

8. "Piezoelectric Sensors Improve Flowmeters," Chem. Eng. News (July 9, 1979), p. 23.

9. Joseph Segall, "Clamp-On Flowmeters," Meas. Control (November-December 1977), pp. 87-89.

10. W. W. Managan, "Extrinsic Factors Affecting Accuracy of Ultrasonic Flowmeters for LMFBRs," Argonne National Laboratory report ANL-CT-76-40 (1976).

11. C. R. Hudgens and B. D. Craft, "Feasibility Study of the Proposed Use of Automated X-Ray Fluorescence Analysis for Measurement of U and Pu in Dissolver Tanks," Monsanto Research Corporation report MLM-2533 (September 1978).

12. W. L. Pickles and J. L. Cate, Jr., "Quantitative Nondispersive X-Ray Fluorescence Analysis of Highly Radioactive Samples for Uranium and Plutonium Concentration," Adv. in X-Ray Anal. 17, 337-347 (1973).

13. E. A. Hakkila, "X-Ray Absorption Edge Determination of Uranium in Complex Mixtures," Anal. Chem. 33, 1012-1015 (1961).

14. E. A. Hakkila, R. G. Hurley, and G. R. Waterbury, "Three-Wavelength X-Ray Absorption Edge Method for Determination of Plutonium in Nitrate Media," Anal. Chem. 38, 425-427 (1966).

15. T. R. Canada, D. G. Langner, J. L. Parker, and E. A. Hakkila, "Gamma- and X-Ray Techniques for the Nondestructive Assay of Special Nuclear Material in Solution," in "Coordinated Safeguards for Materials Management in a Fuel Reprocessing Plant," Los Alamos Scientific Laboratory report LA-6881 (September 1977), Vol. II, App. A.

16. J. W. Tape, T. R. Canada, and E. A. Hakkila, "Application of Dispersive X-Ray Filtering Techniques to Absorption-Edge Densitometry," in "Nuclear Safeguards Research and Development Program Status Report January-April 1977," Los Alamos Scientific Laboratory report LA-6849-PR (August 1977), pp. 10-11.

17. K. J. Hofstetter, G. A. Huff, R. Gunnink, J. E. Evans, and A. L. Prindle, "On-Line Measurement of Total and Isotopic Plutonium Concentrations by Gamma-Ray Spectrometry," in Analytical Chemistry in Nuclear Fuel Reprocessing, W. S. Lyon, Ed., (Science Press, Princeton, 1978), pp. 266-274.

18. R. Gunnink and J. E. Evans, "In-Line Measurement of Total and Isotopic Plutonium Concentrations by Gamma Ray Spectrometry," Lawrence Livermore Laboratory report UCRL-52220 (February 1977).

19. DOE-OSS, "Tokai Advanced Safeguards Technology Exercise," December 28, 1977; revised January 15, 1979.

20. T. D. Reilly and J. L. Parker, "A Guide to Gamma-Ray Assay for Nuclear Material Accountability," Los Alamos Scientific Laboratory report LA-5794-M (March 1975).

21. J. L. Parker, "A Plutonium Solution Assay System Based on High Resolution Gamma Ray Spectrometry," American Society for Metals, Salt Lake City, Utah, February 1978.

22. D. C. Camp, W. D. Ruhter, and S. Benjamin, "Nondestructive, Energy-Dispersive X-Ray Fluorescence Analysis of Product-Stream Concentrations from Processed LWR Fuels," Lawrence Livermore Laboratory report UCRL-52616 (January 1979).

23. J. F. Lemming, J. H. Birden, and R. A. Neff, "An In-Line Automated Plutonium Assay System," Nucl. Mater. Manage. V(3), 156-163 (1976).

24. J. F. Lemming, J. H. Birden, F. X. Haas, A. R. Campbell, and W. W. Rodenburg, "An Automated Nondestructive Assay System," IEEE Trans. Nucl. Sci. V.NS-24(1), 621-623 (February 1977).

25. F. B. Stephens, R. G. Gutmacher, and K. Ernst, "Methods for the Accountability of Reprocessing Plant Dissolver and Waste Solution," US Nuclear Regulatory Commission report NUREG/CR-0515 (December 1978).

26. M. J. Kelly, "Get Maximum Accuracy from Your Dip-Tube Level and Density Systems," Control Eng. (August 1958), pp. 79-80.

27. N. C. Bradley, W. P. Murray, and J. M Googe, "Errors in Measuring Level and Density with Purged Dip Tubes," Oak Ridge National Laboratory report ORNL/TM-5995 (November 1977).

28. W. E. Foster and E. R. Rosal, "Specific Gravity Instruments for a Nuclear Reprocessing Plant," Westinghouse Electric Corporation report WCAP-6033 (December 1, 1959).

29. F. E. Jones, A. M. Schoonover, and J. F. Houser, "In-Tank Measurement of Solution Density," presented at Conf. on Measurement Technology for Safeguards and Materials Control, Kiawah Island, South Carolina, November 27-30, 1979. To be published in proceedings.

30. B. G. Brodda, "Establishing the Calibration Functions for In-Line Determinations of Uranium and Thorium in Various Process Flows of the Experimental Jupiter Reprocessing Plant," Julich Nuclear Research Institute report JUL-968-CT (June 1963).

31. R. Berg, "Verification of Reprocessing Plant Input and Output Analyses," in Nuclear Safeguards Technology 1978, Proc. Symp. Vienna, October 2-6, 1978 (International Atomic Energy Agency, Vienna, 1979), Vol. II, pp. 661-668.

32. M. C. Bouzou and A. A. Brutus, "Spectrophotometric Determination of Plutonium in Irradiated Fuel Solutions--Procedures and Shielding Facilities," Abstract in Am. Nucl. Soc. Trans. 33, Supp. No. 1, 37-38 (1979).

33. R. Berg, R. Swennen, G. Birkhoff, L. Bondar, J. Ley, and G. Busca, "Determination of the Pu-240 in Solid Waste Containers by Spontaneous Fission Neutron Measurements. Application to Reprocessing Plant Waste," EUR 5158e (1974).

34. K. Bohnel, "Die Plutoniumbestimmung in Kernbrennstoffen mit der Neutronenkoinzenmethode," Kernforschungszentrum Karlsruhe report KFK 2203 (1975).

35. K. P. Lambert and J. W. Leake, "A Comparison of the Ispra and Harwell V.D.C. Systems for the Assay of Pu-240 by Spontaneous Fission Neutron Measurements," United Kingdom Atomic Energy Authority report AERE-R 8300 (April 1976).

36. M. M. Stephens, L. V. East, T. L. Atwell, and T. D. Reilly, "Automated Neutron Assay for Richland Operations Office," in Los Alamos Scientific Laboratory report LA-6142-PR (May-August 1975), p. 13.

37. J. E. Foley, "Neutron Coincidence Counters for Nuclear Safeguards Applications," IEEE Trans. Nucl. Sci. NS-19, No. 3, p. 453 (1972).

38. E. V. Weinstock, "The LMFBR Fuel Cycle: Part I, Description and Schedules," report prepared by BNL-TSO for the Division of Nuclear Materials Security of the AEC (November 15, 1973), p. 39.

39. J. E. Foley, "Analytical Study on Design of Neutron Coincidence Counters," in "Nuclear Safeguards Research and Development Program Status Report, September-December, 1970," Los Alamos Scientific Laboratory report LA-4605-MS (January 1971).

40. T. D. Reilly and M. L. Evans, "Measurement Reliability for Nuclear Material Assay," Los Alamos Scientific Laboratory report LA-6574 (January 1977).

41. K. J. Hofstetter, G. M. Tucker, R. P. Kemmerlin, J. H. Gray, and G. A. Huff, "Application of On-Line Alpha Monitors to Process Streams in a Nuclear Fuel Reprocessing Plant," in Nuclear Safeguards Analysis, Nondestructive and Analytical Chemical Techniques, E. A. Hakkila, Ed., (American Chemical Society, Washington, DC, 1978), pp. 124-143.

42. J. Chabert, "In-Line Alpha Counters," Nucl. Appl. 6, 56-62 (1969).

43. C. E. Michelson and K. Koyama, "Process Polarography: Some Problems in the Automatic Determination of Uranium in Nitric Acid," Hanford Atomic Products Operation report HW-42637 (April 1956).

44. R. C. Propst, "In-Line Polarography of Uranium in Process Waste," E. I. duPont de Nemours and Co. report DP-572 (June 1961).

45. B. G. Brodda, P. Filss, H. Kirchner, and U. Wenzel, "Analysis and Material Balance in the Reprocessing of HTGR Fuels," Kernforschungsanlage Julich report JUL-1033-CT (December 1973).

46. K. Motojima and K. Katsuyama, "Polarographic Determination of Uranium in the Reprocessing of Nuclear Fuel," Japan Analyst 12, 358-363 (1963).

47. K. Motojima, H. Okashita, and T. Sakamoto, "Polarographic Determination of Uranium in the Waste Solution of Nuclear Fuel Reprocessing," Japan Analyst 13, 1097-1100 (1964).

48. G. G. Blake, Conductimetric Analysis at Radio Frequency (Chemical Publishing Co., New York, 1952), pp. 69-77.

49. C. H. M. van Bavel, "Neutron Measurement of Surface Soil Moisture," J. Geophys. Res. 66, 4193-4198 (1961).

50. K. Miyagawa, I. Mishima, T. Takeda, and Y. Tanabiki, "Application of Neutron Moisture-Gauge in the Steel Industry," Trans. ISIJ 9, 285-296 (1969).

51. H. O. Menlove and D. A. Close, "^{252}Cf-Based Hydrogen Monitor," in "Nuclear Analysis Research and Development Program Status Report January-April 1975," Los Alamos Scientific Laboratory report LA-6040-PR (August 1975), p. 14.

52. D. A. Close, R. C. Bearse, H. O. Menlove, and A. E. Evans, "Cf-252 Based Hydrogen Monitor," in "Nuclear Analysis Research and Development Program Status Report May-August 1975," Los Alamos Scientific Laboratory report LA-6142-PR (December 1975), pp. 23-25.

53. R. S. Marshall and B. H. Erkkila, "The Measurement of Plutonium Oxalate in Thermal Neutron Coincidence Counters," Proc. of Oak Ridge National Laboratory Conf. on Analytical Chemistry in Energy Technology, Gatlinburg, Tennessee, October 9-11, 1979,

APPENDIX M

ISOTOPIC CORRELATION TECHNIQUES*

C. C. Thomas, Jr. and R. G. Gutmacher
LASL Safeguards Staff (Q-4)

A. Introduction

The elemental and isotopic compositions of the fuel change during operation of a nuclear reactor. Uranium isotopes are consumed (burned) and plutonium isotopes are produced. The process, controlled by natural laws, leads to simple relationships between the initial and final elemental and isotopic compositions of the nuclear fuel. The plutonium produced is related to the uranium remaining; similarly, there are simple relationships between many of the isotopes of plutonium and uranium. Relationships also exist between the heavy-metal isotopes and fission-product isotopes. These relationships, referred to as isotopic functions, are important in the development of a technique to certify measurements of the quantity and isotopic composition of the plutonium entering a fuel reprocessing plant.

The amount of plutonium in spent fuel must be certified because no accountability measurement is made on the fuel from the time it leaves the fabrication plant until it is dissolved in the reprocessing plant. As a result, the measurements performed on the dissolver solution in the accountability tank are vulnerable to understatement of the plutonium content.[1] This situation is illustrated in Fig. M-1. The greatest asset of the isotopic correlation technique (ICT) is the possibility of its use to fill the safeguards gap between the fuel fabricator and the reprocessor by certifying the spent-fuel content at the input of a reprocessing plant.

The ICT is a method of correlating the changes in the fuel composition with fuel burnup. The technique has been reviewed by a number of authors.[1-5] The correlations can be divided into three categories:[2]

(1) Correlations based on isotopes of heavy metals,
(2) Correlations based on isotopes of stable fission products, and
(3) Correlations based on isotopes of radioactive fission products.

---

*Workers at Battelle Pacific Northwest Laboratories have adopted the term Isotopic Safeguards Techniques since they feel the statistical meaning of "correlation" is not always descriptive of the technique. Correlation will be used in this appendix because it is used internationally.

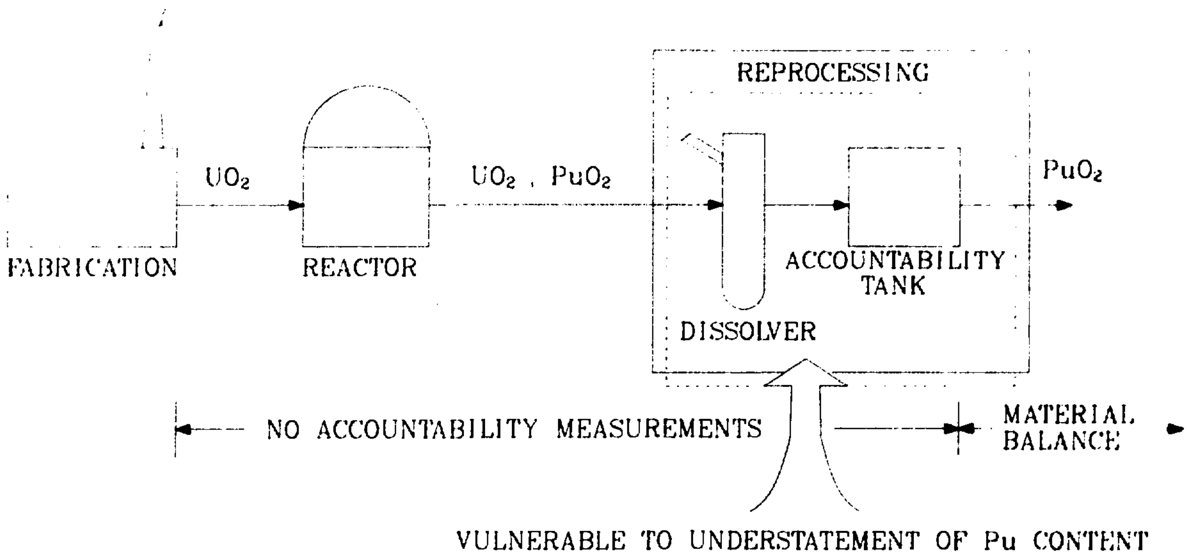


Fig. M-1. Why isotopic safeguards are important (Ref. 1).

At present, only the first category can be considered to be in a satisfactory state of development, because the data base is sufficient to permit an evaluation of various isotopic functions and the effect of varying reactor parameters on the correlations. The remaining two correlation categories lack an extensive historical data base and require further development. However, potential applications of these correlations are sufficiently promising to warrant collection of the required data base. The emphasis in the balance of this appendix is on correlations based on isotopes of heavy metals.

The simple relationships or isotopic functions that are the basis of ICT have been observed in measurements of isotopic compositions in batches of dissolved spent fuel at reprocessing plants. These measurements represent random samples of large amounts of irradiated fuel in batches as large as 1 tonne. Functional relationships noted under these circumstances provide the highest degree of confidence because they represent measurements on actual spent fuel coupled with predictions from burnup calculations.[1,5,6]

An isotopic function can be defined as the functional relationship between any given sets of isotopic concentrations or fuel parameters. Examples include Pu/U vs $\Delta^{235}U$, $\Delta^{236}U$ vs $\Delta^{235}U$, $(^{239}Pu)^2$ vs ^{235}U, burnup vs $^{132}Xe/^{134}Xe$, and burnup vs $^{134}Cs/^{137}Cs$.[1,2,5-7] The symbol Δ refers to changes in concentration during fuel burnup.

The slope of an isotopic function is referred to as the isotopic ratio. For example,

$$\text{Isotopic Ratio} = \frac{(^{236}\text{U irradiated}) - (^{236}\text{U initial})}{(^{235}\text{U irradiated}) - (^{235}\text{U initial})} \;.$$

The most useful functions will be those having a constant isotopic ratio; that is, functions that are linear. It is desirable that the isotopic ratios be independent of factors such as reactor operating conditions, burnup, and cladding. To date, no single ratio has been discovered that possesses all the desired characteristics and is applicable to all reactor types. However, a number of ratios appear to be satisfactory within specific limitations. These form the basis of the current applications of the ICT to safeguards.

Isotopic ratios can be used for certification in three ways, depending on the extent of the data base.[1,2,5-8]

(1) Internal consistency checks among batches in a campaign, because the ratios formed from the measurement data should be relatively constant for the same fuel lot. Outliers that require remeasurement can be identified. No data base is required for these checks.

(2) Comparison of measured ratios in the current campaigns with values for spent fuel from the same or a similar reactor processed in previous campaigns. Consistency of the isotopic ratios from the different campaigns serves to certify the data from the current campaign.

(3) Independent calculation of the Pu/U ratio from verified measurement of the initial and final ^{235}U concentrations.[5] An extensive data base is required for this application.

Berg et al.[2] have discussed four methods of assessing reprocessing plant input: volume-concentration measurement, Pu/U ratio measurement, heavy-isotope correlations, and fission-gas correlations. Their summary of the operations and measurements required at the reprocessing plant for each of the four methods is reproduced here as Table M-I. A fifth method, based on radioactive fission-product isotope correlations, has been added by us. In our opinion, isotopic correlation techniques at present are useful only for certification and are not a substitute for independent analytical measurements.

TABLE M-I

OPERATIONS AND MEASUREMENTS INVOLVED IN EACH METHOD OF ANALYSIS OF THE REPROCESSING PLANT INPUT[a]

Operations and Measurements Methods		Volume Measurement	Density Measurement	Aliquoting of Sample	Isotope Dilution Analysis	Mass Spectrometer Measurement	Analysis of Recycled Material	Gamma-Ray Spectrometry Destructive or NDA	Initial Weight of Fresh Fuel	Isotope Correlation by Historical Data
I.	Volume-Concentration Method	*	*	*	*	*	*			
II.	Pu/U Ratio Method				*	*	*		*	
III.	Heavy-Isotope Correlation					*	*		*	*
IV.	Fission-Gas Isotopes Correlation					*			*	*
V.	Radioactive Fission-Product Isotope Correlation							*	*	*

---

[a] After Ref. 2, Fig. 17.

If the Pu/U ratio measurement method is used, the plutonium input to a reprocessing plant can be calculated from the following:[9]

$$\text{Plutonium at input} = \text{Final } \frac{\text{Pu}}{\text{U}} \text{ ratio} \times (\text{Initial Uranium} - \text{Burnup})$$

Use of the relationship requires measurements from three separate sources.

(1) The measured amount of uranium at fabrication (initial uranium). This is based on bulk weight and chemical analysis and is reported to have[1] a 0.15% relative precision and a 0.05% relative bias.

(2) The burnup, which can be calculated from the heat produced during irradiation or from the neodymium isotopic data. The heat calculation has an accuracy of the order of 5% for a single fuel assembly.[1] The error is not very significant, because only 2-5% of the initial uranium is burned. The

neodymium method is more accurate, but, because the measurement must be made on the dissolved fuel, its use removes one of the data sources that is independent of the reprocessing plant.

(3) The Pu/U ratio obtained from isotope-dilution mass-spectrometric analysis of dissolver batches in the reprocessing plant. This is the value that the safeguards inspector must verify. The ratio can be verified by independent sampling and analysis or certified by isotopic correlation techniques.

Addition of recycled nuclear material to the accountability tank before the measurements are made must be taken into consideration. Measurement of recycled material, however, is required for any verification procedure and is not unique to ICT. The amount of recycled material might be determined using fission-gas correlations because the isotopic composition of krypton and xenon is not affected by the recycling procedure.[2]

Three sources of data have been used to derive and evaluate isotopic functions: burnup codes, measured data from burnup samples, and measured data from reprocessing plant input accountability tanks. The last source of data is most useful for safeguards purposes.

B. Heavy-Metal Isotopic Functions

The largest and most satisfactory data base is that for isotopic functions based on heavy-metal isotopes. Eleven of these functions are presented in Ref. 8 and have been critically reviewed.[7] All isotopic ratios studied to date have important characteristics in common. Although each ratio may have similar characteristics for all reactors of a given type, its numerical values are unique to each reactor within the type. In addition, each of the isotopic ratios is a function of initial enrichment in ^{235}U for each reactor.

Heavy-metal isotopic correlations have been studied for a limited number of reactors. The Battelle data base has a significant amount of data on four PWRs and three BWRs. Very limited data are available on two additional BWRs, two heavy-water reactors and two graphite-moderated reactors.

The burnup range at any given initial enrichment is quite small for most of those reactors. The best data are from the Yankee-Rowe PWR, with a burnup range of 9700-25 600 MWd/MTU. The burnup variation for other PWRs at any one enrichment is, at best, 10%. The Yankee-Rowe data are indicative of the best that can be obtained by this technique. No other set of data has shown the same degree of consistency.

Four of the eleven ratios considered in Ref. 8 are of primary interest. These and two other ratios that may be useful in conjunction with the primary four are discussed in the following sections. The six ratios and their applications are given in Table M-II.

The effects of various parameters on the ratios are given in Table M-III. The parameters that have been considered are defined as follows:[8]

Enrichment Averaging - combining irradiated fuels of more than one initial enrichment in a reprocessing batch.

Exposure Averaging - combining fuels of varying exposures (burnups) in a reprocessing batch.

Fringe Effects - differences arising from fuel being irradiated only in the outer extremity of the core.

Unirradiated Assembly - effects resulting from an unirradiated assembly being dissolved in a reprocessing batch.

Cladding Effects - effects caused by a difference in cladding type (Zircaloy compared to stainless steel).

Moderator Void Fraction - differences resulting from a change in the void fraction (fraction of volume occupied by vapor) in BWRs.

1. Pu/U Vs ^{235}D*. This is one of the most important functions because it has the potential of certifying the Pu/U ratio. For PWRs, the isotopic ratio is apparently linear over the entire burnup range. The isotopic ratio apparently is not sensitive to fringe or averaging effects. Yankee-Rowe ratio data exhibit an excellent linear relationship with initial enrichment, with the exception of data for Zircaloy-clad fuel, which scatter badly.[7] The exception suggests a cladding effect that is contrary to the summary table in Ref. 8 but that is in agreement with earlier reports from the Battelle group.[10]

In the case of BWRs, it is more difficult to draw conclusions. Much of the available data was taken on single batches, and the data from several reactors were obtained on batches of mixed enrichments and cladding. Isotopic ratio data from Dresden I appear to correlate well with initial enrichment except for one batch having stainless steel cladding, the exception again suggesting a possible cladding effect. The Dresden I data also show a rapid increase in the ratio with decreasing initial enrichment, for enrichments less than ∿1.6%.

---

*$^{235}D = \Delta^{235}U$ = Initial ^{235}U - Final ^{235}U.

TABLE M-II

SUMMARY OF SELECTED ISOTOPIC FUNCTIONS[a] APPLICATIONS

Function	Application	Remarks
	PRESSURIZED WATER REACTORS	
Pu/U versus ^{235}D	Internal consistency check; Pu/U ratio certification	
Pu/U versus (100-^{239}Pu)	Substitution detection; backup for Pu/U ratio certification	Some question about linearity
^{236}U versus ^{235}U	Internal consistency check; certification of ^{235}U and ^{236}U content; initial enrichment check	
(^{239}Pu)^2 versus ^{235}U	Substitution detection	Some question about linearity
^{240}Pu versus (^{239}Pu)(100-^{239}Pu)	Certification of ^{240}Pu if ^{239}Pu well known	Insensitive to total Pu and minor ^{239}Pu variations
(^{240}Pu)(^{241}Pu) versus (^{235}U)(^{242}Pu)	Backup for substitution detection; certification of ^{241}Pu and ^{242}Pu content	
	BOILING WATER REACTORS	
Pu/U versus ^{235}D	Internal consistency check; Pu/U ratio certification	Question about linearity
Pu/U versus (100-^{239}Pu)	Substitution detection; backup for Pu/U ratio certification	Question about linearity
^{236}U versus ^{235}U	Internal consistency check; certification of ^{236}U and ^{235}U content; possible initial enrichment check	
(^{239}Pu)^2 versus ^{235}U	Substitution detection	Pu/U versus (^{239}Pu)(^{242}Pu)/(^{240}Pu)^2 useful backup for this function
^{240}Pu versus (^{239}Pu)(100-^{239}Pu)	Certification of ^{240}Pu if ^{239}Pu well known	Insensitive to total Pu and minor ^{239}Pu variations
(^{240}Pu)(^{241}Pu) versus (^{235}U)(^{242}Pu)	Substitution detection backup if usable	Data for BWRs correlates poorly--may not be usable

---

[a] From Refs. 7 and 8.

TABLE M-III

SUMMARY OF SELECTED ISOTOPIC FUNCTIONS[a] EFFECTS OF VARIOUS PARAMETERS

Function	Enrichment Averaging	Exposure Averaging	Fringe Effects	Unirradiated Assembly	Cladding Effects	Moderator Void Fraction
			PRESSURIZED WATER REACTORS			
Pu/U versus ^{235}D	Slight effect See text	No effect	No effect	See text	Possible See text	NA
Pu/U versus (100-^{239}Pu)	No Effect	Slight IR increase	5-10% IR reduction	30% IR reduction	5% lower IR for Zr over SS	NA NA
^{236}U versus ^{235}U	Some Effect See Text	No Effect	5% increase in IR	See text	Possible See text	NA
$(^{239}\text{Pu})^2$ versus ^{235}U	Slight IR increase	Slight IR increase	5-10% increase in IR	10-30% strong increase	No Effect	NA
^{240}Pu versus (^{239}Pu) (100-^{239}Pu)	No effect	No effect	No effect	No effect	IR slightly higher for Zr	NA
(^{240}Pu) (^{241}Pu) versus (^{235}U) (^{242}Pu)	No effect	No effect	5% increase in IR	20% reduction in IR	Zr reduces IR slightly	NA
			BOILING WATER REACTORS			
Pu/U versus ^{235}D	See text	No effect	5-10% reduction in IR	See text	Possible See Text	IR fluctuates with increasing void
Pu/U versus (100-^{239}Pu)	No effect	Slight IR increase	5-10% reduction in IR	40% IR reduction	5% lower IR for Zr over SS	6% IR decrease for 25% void increase
^{236}U versus ^{235}U	Slight IR increase	Slight IR increase	5% IR increase	See text	IR slightly higher to SS	IR decreases slightly with increase
$(^{239}\text{Pu})^2$ versus ^{235}U	Slight IR increase	Slight IR increase	5% IR increase	10-30% IR increase	5-10% increase for SS	Possible See text
^{240}Pu versus (^{239}Pu) (100-^{239}Pu)	No effect	No effect	No effect	No effect	IR slightly higher for Zr	No effect
(^{240}Pu) (^{241}Pu) versus (^{235}U) (^{242}Pu)	No effect	5-20% reduction in IR	No effect	20% reduction in IR	Slight decrease in IR for Zr	12% reduction for 25% void increase

---

[a] From Refs. 7 and 8.

Key to Abbreviations

IR = Isotopic ratio

NA = Not applicable

SS = Stainless steel

Zr = Zircaloy

Katz[7] shows that the isotopic ratio does have a slight but significant response to enrichment averaging. Enrichment averaging should be avoided to minimize errors when applying ICT.

Substitution of an unirradiated fuel assembly of the same enrichment as the initial enrichment of the irradiated assemblies cannot be detected by this ratio.[7] However, if the unirradiated assembly has a different enrichment, the substitution can be detected.

2. Pu/U Vs (100-^{239}Pu).* This function has been recommended[8] as a good backup for certification of the Pu/U ratio. It can also be used to detect substitution. There is some question with respect to its linearity. Yankee-Rowe Core V data show a small but systematic increase in the function with increasing burnup.[7] The function is also reported[8] to have a slight increase with exposure averaging and a small (5-10%) reduction caused by fringe effects and cladding effects for both PWRs and BWRs. It exhibits a decrease with increasing void fractions in BWRs.

3. ^{236}U Vs ^{235}U. This function has been recommended for certifying the ^{236}U and ^{235}U content of LWR fuel. Data from two PWRs, Yankee-Rowe and Indian Point, correlate well, again with the exception of the Yankee-Rowe Zircaloy-clad fuel. It appears that the data from both PWRs and BWRs may lie on a single curve when the isotopic ratios are plotted against the initial enrichment. This is not true for plots of ^{236}U content as a function of ^{235}U content. However, the function appears to be somewhat sensitive to moderator void fraction. The function's sensitivity to enrichment averaging is less than for the (Pu/U)/^{235}D ratio, because it is less sensitive to initial enrichment. The effects of substitution are the same as for the (Pu/U)/^{235}D ratio.[7]

Extrapolation of the function has been suggested as a method of confirming the initial enrichment. Yankee-Rowe data have been extrapolated with reasonably good results.[7]

4. ^{239}Pu^2 Vs ^{235}U. This function is recommended for detection of substitution of unirradiated uranium. The function is reported to be fairly linear even at low burnup but showed exposure-averaging effects.[8] Such effects would suggest some nonlinearity.[7] If the function were truly linear, it could be extrapolated back to the initial enrichment.

---

*The 100 represents the initial 100 wt% of ^{239}Pu because the first atom of Pu formed is ^{239}Pu.

Results obtained with Yankee-Rowe fuels were unacceptably high, suggesting that the function is nonlinear at low burnups.

The ratio is reported to be sensitive to enrichment and exposure averaging and to fringe effects for both PWRs and BWRs. It also is reported to be somewhat affected by moderator void fraction.[8] The ratio is normally calculated[8] as

$$\text{Isotopic Ratio} = \frac{(100)^2 - (^{239}\text{Pu})^2}{\text{Initial } ^{235}\text{U} - \text{Final } ^{235}\text{U}} = \frac{10\ 000 - (^{239}\text{Pu})^2}{^{235}\text{D}} .$$

Katz[7] indicates that if the function were completely linear the ratio could also be calculated as

$$\text{Isotopic Ratio} = \frac{(^{239}\text{Pu})^2}{\text{Final } ^{235}\text{U}}$$

and recommends this formulation in view of the nonlinearity. He has applied the formulation to the Humboldt Bay (BWR) data and notes that the isotopic ratio is apparently independent of void-fraction and averaging effects. Katz also has plotted the isotopic ratio versus initial enrichment for a number of BWRs. The data points appear to fall on a single curve. Recalculation of all available data by using both formulations of the ratio seems warranted.

5. Other Functions. The function ^{240}Pu vs (^{239}Pu)(100-^{239}Pu) seems to be linear over the entire range of burnups and is useful for certifying the ^{240}Pu. However, it is insensitive to the total quantity of plutonium and to small variations in ^{239}Pu. It is reported to be insensitive to moderator void fraction. The function is less generally useful than (^{239}Pu)^2 vs ^{235}D.

The function (^{240}Pu)(^{241}Pu) vs (^{235}U)(^{242}Pu), again, appears to be linear, but in the case of BWRs is reported to exhibit exposure averaging and possible moderator void fraction effects. The isotopic ratio correlates well with initial enrichment for Yankee-Rowe and Indian Point data with the exception of the Yankee-Rowe Zircaloy-clad fuel. BWR ratio data correlate very poorly with initial enrichment.

The function Pu/U vs $(^{239}Pu)(^{242}Pu)/(^{240}Pu)^2$ is reported to be independent of moderator void fraction.[7,10] It is, however, more sensitive to exposure averaging than the $(^{239}Pu)^2/^{235}U$ ratio and should be used in conjunction with this ratio. Its application should be limited to BWRs at present.

C. Fission-Product Correlations

Two types of fission-product correlations are being investigated: those involving stable fission products and those involving radioactive fission products. At present, the data base is insufficient for the type of evaluation that has been performed on heavy-metal isotopic correlations. However, the potential for the fission-product correlations warrants a brief discussion of their current status. Fission-product correlations have been reviewed by several authors.[2,3,11] Recent work of interest has been reported in Refs. 12-17. Fission-product correlations that have been suggested as useful are presented in Table M-IV.

Experimental data for the application of fission-gas correlations can be obtained on the dissolver off-gas, thereby involving a minimum of interference with facility operations. Data for application of radioactive fission-product correlations could, in theory, be obtained by NDA. The major problem is fabrication of suitable calibration standards. The fission-product ratios can be obtained by measurements on samples taken from the dissolver solution. An advantage of all fission-product correlations is their insensitivity to the presence of recycle material.

Several investigators note that the $^{134}Cs/^{137}Cs$ ratio is sensitive to irradiation history[13,16] and that corrections are required for burnup correlations.[16] Maeck et al.[17] point to a problem involved in the correlation of $^{132}Xe/^{131}Xe$ with burnup. The correlation was first reported by Koch and Bresesti[18] for six different reactor fuels, representing both pressurized and boiling water reactors. The burnup indicated by their data for a given $^{132}Xe/^{131}Xe$ ratio varies as much as 35%. The problems noted with the correlations of burnup and either $^{134}Cs/^{137}Cs$ or $^{132}Xe/^{131}Xe$ also were observed by Maeck and his coworkers[17] for the highly enriched uranium fuel used in the Advanced Test Reactor and Engineering Test Reactor. They conclude that differences in neutron spectra have a significant effect, especially when the neutron-capturing nuclide has a resonance integral (RI) cross section that is much larger than the thermal neutron (TN) cross section.* As a result, they suggest that use of $^{132}Xe/^{131}Xe$ to estimate burnup be re-evaluated and that caution must be exercised in using ^{134}Cs for isotope correlation studies.

---

*For ^{131}Xe:RI = 870 b, TN = 90 b; for ^{133}Cs:RI = 415 b, TN = 29 b.

TABLE M-IV

FISSION-PRODUCT CORRELATIONS

Correlation Fission-Product Ratio	^{235}D	Burnup[a]	^{240}Pu[b]	^{241}Pu[b]	^{242}Pu[b]	$\frac{Pu}{U}$	$\frac{U}{Uo}$[c]	Neutron Flux
STABLE FISSION PRODUCTS								
^{84}Kr/^{86}Kr	*							
^{83}Kr/^{86}Kr		*						
^{84}Kr/^{83}Kr		*						
^{132}Xe/^{131}Xe		*	*	*	*			
^{134}Xe/^{136}Xe		*						*
^{132}Xe/^{134}Xe		*						
^{143}Nd/$^{145+146}$Nd[d]		*						
^{148}Nd/$^{145+146}$Nd								*
RADIOACTIVE FISSION PRODUCTS								
^{134}Cs/^{137}Cs[e]		*	*			*	*	
^{154}Eu/^{137}Cs		*				*	*	
^{135}Cs/^{137}Cs								*

---

[a] Burnup has been variously expressed in fissions/initial total heavy-metal atoms (FIMA%, F_T%), atom percent fission (a/oF), or heat generation (MWD/tonne U).

[b] Expressed as ^{240}Pu IMA, ^{241}Pu IMA, or ^{242}Pu IMA = atoms/initial total heavy-metal atoms.

[c] U/Uo = Final Uranium/Initial Uranium.

[d] Can be used with ^{145}Nd/^{146}Nd to estimate capture-to-fission ratio for ^{235}U (see Ref. 17).

[e] Correlations between ^{137}Cs and Pu/U have also been suggested.

Maeck et al.[17] point out that the use of ^{148}Nd as a fission monitor can lead to high, biased values in the measurement of the number of fissions and burnup, especially when the sample has been exposed to a high thermal neutron flux. As cause of the bias, they cite the large thermal neutron capture cross section (440 b) associated with ^{147}Nd. Presumably, similar problems may exist with low-enrichment high-burnup fuels. Maeck et al. suggest use of the sum of ^{145}Nd and ^{146}Nd as the preferred monitor for fissions in highly enriched fuels.

Investigations of fission-product correlations to date suggest a number of functions that may be of value and have identified some problem areas. The data base now available does not permit conclusions to be drawn on the ultimate usefulness of any of these correlations.

D. Applications of Isotopic Functions to Safeguards

The principal use of the ICT probably is the certification of the Pu/U ratio in the dissolver or accountability tank of the reprocessing plant. Independent calculation of the Pu/U ratio by the ICT is not possible at present except perhaps for spent fuel from the Yankee-Rowe reactor. In this section, examples of ICT applications are given to demonstrate use of the technique. These examples are drawn from Refs. 7, 8, and 19.

1. Internal Consistency Checks. An example of an internal consistency check on data for Yankee-Rowe Core V fuel is shown in Table M-V. Numerical values of four isotopic ratios and their means and standard deviations are tabulated. No outliers were found in any of the ratios when a two standard deviation (2-σ) criterion for their identification was applied. The (Pu/U)/(100-^{239}Pu) ratio clearly is increasing with increasing burnup. (Data from Yankee-Rowe Core VIII, which had a smaller burnup range, did not exhibit this characteristic.) However, on the basis of the agreement between the (Pu/U)/^{235}D and the (^{239}Pu)^2/^{235}U ratios, an inspector would conclude that the measurements had been confirmed.

Timmerman et al.[8] illustrate the use of ICT to detect an analytical result that requires remeasurement. The data were obtained from 24 small-burnup samples from the Japan Power Demonstration Reactor I (JPDR-1). On the basis of the 2-σ criterion, one sample was identified as an outlier. The outlier was confirmed by performing a regression analysis on the data. The need for the inspector to remeasure each batch in a campaign can be eliminated by identifying the questionable batches and remeasuring those batches and other randomly selected batches. However, the inspector should sample all batches to prevent the plant operator from knowing which batches will be subject to confirmatory analytical measurements.

Timmerman et al.[8] also discuss use of an external analysis as a backup to an internal consistency check. First, the internal analysis was performed as usual, in this case on data from the reprocessing of Indian Point I fuel. Two isotopic functions were used: Pu/U vs ^{235}D and Pu/U vs (100-^{239}Pu). An outlier was identified, and the data were reanalyzed with the outlier eliminated. It was then found that three batches had at least one ratio with a deviation from the mean >1.5σ. For corroboration of these results

TABLE M-V

EXAMPLE OF Pu/U AND ISOTOPIC CONSISTENCY
YANKEE-ROWE CORE V DATA[a]

Batch No.	Exposure MWD/MTU	$\frac{Pu/U}{^{235}D}$	%[b] Dev.	$\frac{Pu/U}{100-^{239}Pu}$	% Dev.	$\frac{^{239}Pu^2}{^{235}U}$ [c]	% Dev.	$(\frac{^{240}Pu}{^{235}U})(\frac{^{241}Pu}{^{242}Pu})$ [d]	% Dev.
1	9 700	5 371	-0.52	332.3	-5.38	2 278	-0.34	36.09	-0.07
20	13 900	5 448	+0.91	334.0	-2.05	2 252	-0.94	38.21	+1.76
10	15 800	5 417	+0.33	353.5	+0.65	2 249	-1.00	35.68	-0.42
22	19 700	5 441	+0.78	356.5	+1.51	2 285	-0.18	36.40	+0.20
18	21 400	5 306	-1.72	358.6	+2.11	2 344	+1.17	35.98	-0.16
16	25 600	5 413	+0.26	363.3	+3.16	2 348	+1.26	34.66	-1.30
		$\bar{X}$=5,399		$\bar{X}$=351.2		$\bar{X}$=2 293		$\bar{X}$=36.17	
		σ=0.98%		σ=3.17%		σ=1.90%		σ=3.22%	
		2σ bounds upper 5503 lower 5295		2σ bounds upper 373.0 lower 329.4		2σ bounds upper 2278 lower 2208		2σ bounds upper 38.45 lower 33.89	

---

[a] From Refs. 7 and 19 - Raw data presented in Ref. 19.

[b] Percent deviation of ratio value from mean ratio value.

[c] Calculated as per Katz,[7] $(^{239}Pu)^2$/Final ^{235}U.

[d] Calculated from final values in weight percent.

by an external analysis, data from the reprocessing of spent fuel from the Yankee-Rowe reactor (the same type of reactor as Indian Point I) with a similar irradiation history and initial enrichment were used. The slope/intercept equations for the two isotopic functions derived from the Yankee-Rowe data were used to predict Pu/U ratios for each batch. The predicted values were compared with the measured values for Indian Point I. The outlier was confirmed and the values recalculated after its elimination. The external analysis now served to confirm the magnitude of the deviations of the three questionable batches. In the opinion of Timmerman et al., remeasurement was not required.

External analysis used in conjunction with an internal consistency check provides an additional basis for decisions on questionable (borderline outlier) batches. External analysis must never be used to change the status of a batch that has been determined by the internal analysis to be an outlier.

The examples of internal consistency checks cited above are for PWRs and are reasonably straightforward. A more difficult situation is illustrated by data from the Humboldt Bay BWR (Table M-VI).[7,19] Core I of that reactor (the only core reprocessed to date) included fuels of different initial enrichment, different claddings, different moderator void fractions, and different exposures. Inspection of the $(Pu/U)/^{235}D$ ratio for the 2.578% initial enrichment clearly demonstrates the effect of moderator void fraction on the ratio. The $(Pu/U)/[(^{239}Pu)(^{242}Pu)/(^{240}Pu)^2]$ and the $(^{239}Pu)^2/^{235}U$ ratio are both independent of void fraction. Both show relatively low standard deviations and no outliers. The fact that both of these ratios are constant and that remeasurement of selected batches showed no discrepancies was accepted as confirmation of the results for the 11 batches.[7]

The amount of data available for the 2.310% initial enrichment is insufficient for statistical treatment. The $[(Pu/U)/(^{239}Pu)(^{242}Pu)/(^{240}Pu)^2]$ and the $(^{239}Pu)^2/^{235}U$ ratios appear to be constant. That, coupled with the fact that two of the three batches were remeasured, was taken as confirmation of the results.[7]

The last six batches are considerably more difficult to confirm because they all contained assemblies of two or more different initial enrichments, different claddings, and differences in exposure and void fraction. The $(Pu/U)/[(^{239}Pu)(^{242}Pu)/(^{240}Pu)^2]$ ratio, which is sensitive to exposure averaging, is less useful for the last six batches because they contained fuel with a fairly wide range of burnups. Batches 5 and 12 can be compared with batch 13 because the initial enrichments are about the same. All four isotopic ratios for these batches check reasonably well. Batches 2 and 23 have similar initial enrichments, as do batches 18 and 19. The last three

TABLE M-VI

REPROCESSING PLANT INPUT DATA FOR HUMBOLDT BAY BWR REACTOR[a]

Batch No.	^{235}U, w/o Initial	Final	^{235}D w/o	Pu/U g/tonne U	$\frac{Pu/U}{^{235}D}$	$\frac{Pu/U}{(^{239}Pu)(^{242}Pu)/(^{240}Pu)^2}$	$\frac{(^{239}Pu)^2}{^{235}U}$	$\frac{Pu/U}{(100-^{239}Pu)}$
29	2.578	1.919	0.659	2756	4182[b]	1.751[c]	3642[d]	168.1
28	2.578	1.874	0.704	2820	4006	1.705	3647	162.8
25	2.578	1.860	0.718	2924	4072	1.733	3620	162.9
26	2.578	1.847	0.731	3133	4286	1.781	3619	171.8
27	2.578	1.837	0.741	3288	4437	1.724	3654	181.9
17	2.578	1.810	0.768	3455	4498	1.745	3654	185.0
4	2.578	1.764	0.814	3920	4816	1.777	3623	195.4
16	2.578	1.751	0.826	3938	4762	1.724	3648	196.2
14	2.578	1.709	0.869	4018	4624	1.737	3635	189.6
15	2.578	1.706	0.872	4079	4677	1.711	3595	188.1
13	2.578	1.683	0.895	4236	4733	1.704	3644	195.3
22	2.310	1.250	1.060	5159	4901	1.784	3997	177.2
21	2.310	1.223	1.087	5219	4801	1.803	3982	172.7
20	2.310	1.167	1.143	5398	4723	1.797	4085	174.4
5	2.557	1.706	0.851	3931	4620	1.618	3593	181.1
12	2.567	1.655	0.912	4234	4643	1.678	3636	188.8
23	2.402	1.441	0.961	4577	4673	1.602	3751	172.8
2	2.433	1.423	1.010	4796	4749	1.572	3742	177.4
19	2.276	1.108	1.168	5576	4774	1.801	4183	174.7
18	2.258	1.087	1.171	5741	4902	1.788	4197	176.9

---

[a] From Refs. 7 and 19.

[b] Low void fraction.

[c] For 2.578% initial enrichment $\overline{X}=1.736$ $\sigma=1.52\%$.

[d] For 2.578% initial enrichment $\overline{X}=3635$ $\sigma=0.51\%$.

isotopic ratios in Table M-VI, particularly $(^{239}Pu)^2/^{235}U$, agree in both cases. That is the best confirmation obtainable with limited data.

The Humboldt Bay example illustrates the importance of managing dissolver batches to prevent mixing of unlike fuels in the same batch. Such management facilitates application of the isotopic correlation technique and would benefit the plant operator as well because the ICT would provide an independent certification of his input accountability measurements.

2. Independent Calculation of the Pu/U Ratio. When sufficient historical data are available to establish a firm correlation between $(Pu/U)/^{235}D$ and the initial enrichment, the Pu/U ratio can be calculated from a knowledge of the initial and final ^{235}U values. It has been done for Yankee-Rowe fuel[19] with impressive agreement (better than 1%) for seven campaigns. An extensive data bank is required. At present, such a data bank exists only for the Yankee-Rowe reactor. Data from other reactors show considerably more scatter and, in some cases, are not linear.

3. Substitution. Two types of substitution are of concern: (1) substitution of uranium of a different initial enrichment (e.g., natural or depleted uranium) and (2) substitution of unirradiated uranium of the same initial enrichment. To detect substitution, the selected ratio is compared to historical values.

The $(Pu/U)/^{235}D$ ratio is capable of detecting the substitution of natural uranium for as little as 5% of the fuel in a 4.935% initial enrichment fuel assembly.[7] However, it cannot detect the substitution of unirradiated uranium of the same initial enrichment. The $(Pu/U)/(100-^{239}Pu)$ ratio is sensitive to substitution of unirradiated uranium of any enrichment and is therefore recommended for substitution checks.

4. Overall Materials Balances. Isotopic correlation techniques can be used in several ways to verify "across-the-plant" materials balances, to verify data for an entire campaign, or to confirm total uranium burnup. Some of these applications are described in this section.

Once the Pu/U ratio has been certified, the total plutonium input can be calculated either from (1) the measured volume of solution in the dissolver or accountability tank and the measured plutonium concentration or (2) from the measured Pu/U ratio by the expression

$$\text{Pu at input} = \frac{\text{Pu}}{\text{U}} \text{ ratio} \times \text{final U} \quad .$$

The final amount of uranium can be obtained by taking the fuel fabricator's value for initial uranium and subtracting the amount burned up, calculated from reactor operations data. Alternatively, the final amount of uranium can be measured in the reprocessing plant, in which case concentration and volume measurements are required. Corrections for headend losses (as in the chop-leach process), use of recycle acid, and use of tetravalent uranium as a reductant must be applied when appropriate.

In calculation of the plutonium input for an entire campaign consisting of many batches, the uncertainties in the volume measurements would constitute the dominant source of error. If a weighted Pu/U ratio[9] is used for a campaign:

$$\text{Weighted } \frac{\text{Pu}}{\text{U}} \text{ ratio} = \frac{\sum_{j=1}^{n} U_j (\text{Pu/U}) j}{\sum_{j=1}^{n} U_j}$$

where

U_j = (concentration of uranium in batch j)(volume of batch j),
$(\text{Pu/U})_j$ = measured Pu/U ratio for batch j,

then the weighting factors tend to cancel out errors in volume measurement.

The total uranium burnup calculated from the reactor operations data can be verified. In general, total uranium content changes at a rate of ∿0.15% per thousand MWd/tonne U_{final}. A more exact relationship[19] requires certified plant operator's data for the weighted Pu/U ratio, weighted uranium and plutonium isotopic compositions, and initial enrichment values:

$$\frac{U_{\text{initial}}}{U_{\text{final}}} = \frac{1 + (1 + 1.866W_0 + 2.085W_1 + 8.95W_2)\text{Pu/U} - 0.9081W_5}{1 - 0.9081W_5^0}$$

where W_0 = final ^{240}Pu weight fraction,
W_1 = final ^{241}Pu weight fraction,
W_2 = final ^{242}Pu weight fraction,
W_5 = final ^{235}U weight fraction,
W_5^0 = initial ^{235}U weight fraction.

Certified isotopic composition data on output material from the reprocessing plant can be used to monitor the composition of the input material. With the exception of the small effect of variable waste losses, the weighted isotopic compositions of the input and product materials for a campaign should be almost exactly equal when beginning and ending inventories are taken into account. The above statement was confirmed by historical data[19] for weighted feed and product isotopic compositions for 11 campaigns at the Nuclear Fuels Service Plant at West Valley, New York. The data, though uncorrected for waste losses or beginning and ending inventory, agree for most isotopes within a few tenths of a percent relative, a deviation that probably can be ascribed to measurement error alone. Weighted isotopic composition data on output material from a campaign can thus be used to confirm input isotopic composition and to detect any bias or falsification of input isotopic data of more than ∿1% relative.

E. Data Banks

Several data banks are of importance to isotopic correlations. These include the following:

(1) The ESARDA Data Bank of Isotopic Compositions maintained at the Commission of the European Communities Joint Research Centre, Ispra, Italy.
(2) The European Institute for Transuranium Elements Data Bank maintained at Karlsruhe, FRG.
(3) The Isotopic Safeguards Data Base maintained at Battelle Pacific Northwest Laboratory, Richland, Washington, USA.
(4) The IAEA Data Bank maintained at the International Atomic Energy Agency, Vienna, Austria.

It is anticipated that as more data become available from fuel reprocessing, these data bases will be updated and the understanding of isotopic correlations will be improved.

F. Conclusions

At present, only those correlations involving heavy-metal isotopes are reliable enough for use in certification of Pu/U ratios and heavy-metal isotopic compositions. Isotopic correlation techniques based on heavy-metal isotopes can be used to certify analytical data obtained by analysis of solution in the accountability or dissolver tank, provided recycle material is taken into consideration. The ICT can be used to identify outliers and detect substitution of unirradiated uranium. Data certified by ICT may be applied to estimation of overall plant materials balances.

Correlations based on fission-product isotopes are not sensitive to the presence of recycle material and could be a valuable tool for the safeguards inspector. However, considerable effort will be required to expand the data base to make use of fission-product isotopic functions. Development of nondestructive measurement techniques for the radioactive fission-product isotopes should be encouraged.

Currently, the independent calculation of the Pu/U ratio is not feasible for any reactor other than Yankee-Rowe. Additional data are required before this capability can be demonstrated for any other reactor. Under ideal conditions it may be possible to develop the required data base within 3-5 refuelings.

As stated previously, in our opinion, isotopic correlation techniques are currently useful only for certification and are not a substitute for independent analytical measurements.

ACKNOWLEDGEMENTS

The cooperation of S. T. Hsue (LASL Safeguards Staff Q-1), H. M. Katz (Department of Chemical Engineering, Howard University, Washington, DC) R. A. Schneider (Exxon Nuclear Company, Richland, Washington), and C. L. Timmerman (Energy Systems Department, Battelle Pacific Northwest Laboratories, Richland, Washington) in providing reference material and critically reviewing this appendix is gratefully acknowledged.

REFERENCES

1. C. L. Timmerman, "Isotopic Safeguards Techniques," Battelle Pacific Northwest Laboratories report ISPO-25 (PNL-SA-6761) (June 1978).

2. R. Berg, C. Foggi, L. Koch, R. Kraemer, and F. J. Woodman, "Value and Use of Isotopic Correlations in Irradiated Fuels," in Practical Applications of R&D in the Field of Safeguards, Proc. European Safeguards Research and Development Association (ESARDA) Symp., Rome, Italy, March 7-8, 1974, pp. 184-211.

3. D. Gupta, "Isotopic Correlation for Accounting and Control of Nuclear Materials in a Fuel Cycle - A Review Paper," Kernforschungszentrum Karlsruhe report KFK-2400 (September 1976).

4. S. Sanatani, "Applications of Isotopic Correlation Technique (ICT) to International Safeguards," ICT-19, ESARDA Symp. on Isotopic Correlation and Its Application to the Nuclear Fuel Cycle, Stresa, Italy, May 9-11, 1978.

5. D. E. Christensen and R. A. Schneider, "The Purpose of Isotopic Correlation Safeguards Techniques," Battelle Pacific Northwest Laboratories report ACDA/ST-227, Vol. II (November 14, 1974).

6. D. E. Christensen, K. B. Stewart, and C. L. Timmerman, "Continuation of the Development and Application of Isotopic Safeguards Techniques to Chemical Reprocessing Plants," Battelle Pacific Northwest Laboratories report AC6AC714 (November 29, 1974).

7. H. M. Katz, "Isotopic Safeguards Techniques--Draft," Discussion Paper for Working Meeting, Brookhaven National Laboratory, Upton, LI, New York, June 18-19, 1979.

8. C. L. Timmerman, G. P. Selby, and B. A. Napier, "Selected Isotopic Functions: A Description and Demonstration of Their Uses," Battelle Pacific Northwest Laboratories report ISPO-37 (PNL-2761) (October 1978).

9. K. B. Stewart and R. A. Schneider, "Properties of the Pu Estimates Based on Weighted Pu/U Values," in Safeguards Techniques (International Atomic Energy Agency, Vienna, Austria, July 1970), IAEA SM-133/55, Vol. I, pp. 583-606.

10. D. E. Christensen, R. A. Schneider, and K. B. Stewart, "Summary of Experience with the Use of Isotopic Correlation Safeguards Techniques," Battelle Pacific Northwest Laboratories report BNWL-SA-4273 (March 20, 1972).

11. L. Koch, H. Braun, and A. Cricchio, "Some Correlations Between Isotopes of Xe, Kr, U, and Pu and Burnup Parameters for Various Thermal and Fast Reactors," in Safeguards Techniques (International Atomic Energy Agency, Vienna, Austria, July 1970), IAEA-SM-133/25, Vol. I, pp. 539-544.

12. P. Rousset, "Isotopic Correlations of Fission Gas Applied to Light Water Reactors," ICT-16, ESARDA Symp. on Isotopic Correlation and Its Application to the Nuclear Fuel Cycle, Stresa, Italy, May 9-11, 1978.

13. C. Foggi and F. Frenquellucci, "Isotopic Correlations Based on Radioactive Fission Product Nuclides in Power Reactor Irradiated Fuels," ICT-21, ESARDA Symp. on Isotopic Correlation and Its Application to the Nuclear Fuel Cycle, Stresa, Italy, May 9-11, 1978.

14. C. Beets, "Joint Safeguards Experiment MOL-IV (1972-73) at the Eurochemic Reprocessing Plant," ICT-30, ESARDA Symp. on Isotopic Correlation and Its Application to the Nuclear Fuel Cycle, Stresa, Italy, May 9-11, 1978.

15. B. Brandalise, L. Koch, C. Rijkeboer, and D. Romkowski, "The Applications of Isotope Correlations in Verifying Automatic Analysis of Irradiated Fuels," ICT-7, ESARDA Symp. on Isotopic Correlation and Its Application to the Nuclear Fuel Cycle, Stresa, Italy, May 9-11, 1978.

16. A. Hermann and C. Mehner, "Investigation into the Possibilities of Determining the Uranium and Plutonium Content of VVER-Type Fuel for Safeguards in Connection with Isotope Correlation Techniques," in Nuclear Safeguards Techniques 1978, Proc. Symp., Vienna, October 2-6, 1978 (International Atomic Energy Agency, Vienna, 1979), IAEA-SM-231/20, Vol. II, pp. 733-745.

17. W. J. Maeck, R. L. Tromp, F. A. Duce, and W. A. Emel, "Isotope Studies Relative to High Enrichment Test Reactor Fuels," Allied Chemical Corporation report ICP-1156 (June 1978).

18. L. Koch and M. Bresesti, "Improved Method for the Verification of Reprocessing Input Analysis," Nucl. Mater. Manage. IV(3), 498-507 (1975).

19. R. A. Schneider, K. B. Stewart, and D. E. Christensen, "The Use of Isotopic Correlations in Verification (Safeguards Application)," Battelle Pacific Northwest Laboratories report BNWL-SA-4251 (February 10, 1972).

APPENDIX N

INSTRUMENTATION AVAILABLE TO IAEA INSPECTORS

J. R. Phillips, J. E. Foley, H. O. Menlove, and T. D. Reilly
LASL Safeguards Staff (Q-5)

A. Introduction

The IAEA part of its safeguards verification procedures conducts inspections to obtain independent measurements and observations for comparison with information provided by the State's materials accountability system.[1] The instrumentation available to the IAEA inspectors generally has been limited to portable instruments for the nondestructive measurement of NM. The variety of portable instrumentation available has expanded rapidly in the past few years. In-plant instrumentation is also becoming available for IAEA inspectors at selected facilities.

Here we discuss the instrumentation available to IAEA inspectors for safeguarding an LWR fuels reprocessing plant. Five measurement areas have been identified: (1) irradiated fuel assemblies, (2) leached hulls, (3) process samples, (4) solid products, and (5) waste products. Each area is discussed briefly and with emphasis on available instrumentation. Many of these instruments are just being implemented, therefore little inspection experience is available.

B. Irradiated Fuel Assemblies

The nondestructive measurement of irradiated fuel assemblies in a reprocessing facility is essential for the timely verification of the material received, as well as for the periodic verification of the material in the storage pool. Two levels of verification important to the IAEA have been identified: (1) qualitative verification and identification of the material as irradiated fissile material, and (2) quantitative verification through the measurement of parameters that can be correlated with the burnup or plutonium content of the material.

The qualitative verification of fuel assemblies in the fuel storage and receiving area of the reprocessing facility can be accomplished by using gamma-ray or neutron signatures. Stored fuel assemblies can be measured <u>in situ</u> by using gross gamma detectors such as ion chambers, scintillators, or thermoluminescent dosimeters. For these measurements, the detectors must be introduced into the cooling pool. Another approach detects the Cerenkov glow resulting from the interaction of the fission-product radiation with the cooling water.[2] This qualitative measurement can be made from above the water surface of the storage pond, thereby obviating the introduction of equipment into the pool. Although the gross-gamma and the Cerenkov techniques can indicate whether stored fuel assemblies contain irradiated material, it is difficult to correlate these measurements with burnup or fissile content. These techniques are not now used in Agency inspections, but experimental evaluations involving Agency participation are under way. Successful evaluation may lead to routine applications within the next 1-2 yr.

Various nondestructive gamma-ray and neutron techniques have been investigated to identify and to quantify parameters that can be related to the burnup of irradiated fuel assemblies.[3-8] The gamma-ray techniques usually involve isotopic ratios, ^{134}Cs/^{137}Cs and ^{154}Eu/^{137}Cs, or ^{137}Cs activities as an indirect measurement of burnup values and have a precision of about 5%.[9,10] An apparatus similar to the one represented schematically in Fig. N-1 is used. The fuel assembly is positioned in front of the collimating tube, and a complete gamma-ray spectrum is recorded with a germanium detector and a multichannel analyzer. Specific spectral information is obtained through a spectral unfolding routine and is then related to declared or calculated activity ratios or activities. Inspectors must be well trained to operate the instrumentation and interpret the data. Agency inspectors have performed these measurements successfully at reactor facilities in countries such as Sweden, Finland, Bulgaria, and Japan.

The neutrons from the spontaneous fissioning and (α,n) reactions in irradiated fuel assemblies also can be used to indicate burnup.[11] Neutron measurements have several advantages over gamma-ray techniques: (1) the higher penetrability of neutrons permits measurements of the inner layers of the assembly, and (2) neutron techniques can be significantly simpler than gamma-ray spectroscopy in instrumentation and execution.

The passive techniques mentioned above are indirect measurements and must be correctly correlated to obtain the fissile content of the irradiated fuel material. Active nondestructive techniques are the only methods that measure the fissile content directly. Active neutron interrogation can be applied to measure fissile material remaining in irradiated fuel assemblies.[12-14] Conceivably, an active interrogation system could be installed at a specific facility and operated by IAEA personnel during an inspection; however, at present, such systems are not available for verification of spent fuel assemblies.

C. Leached Hulls

Leached hulls are a major waste product from a reprocessing plant that uses a chop-leach headend process. A small amount of undissolved fuel remains after leaching

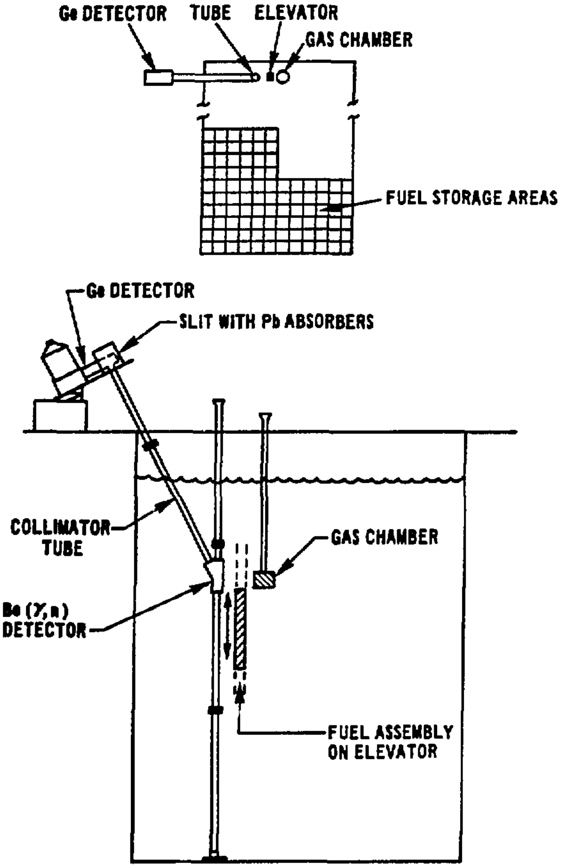


Fig. N-1. Schematic of the experimental apparatus for the measurement of gamma-ray and neutron signatures of irradiated fuel assemblies.

and is discarded along with the cladding pieces. This residue usually contains between 0.1 and 1.0% of the original fuel content.[15] These quantities are not particularly large but, if unmeasured, they could introduce a bias in the materials balance of a reprocessing facility. For safeguards, a measurement accuracy of 10-20% should be sufficient.

Most hull monitoring systems involve the measurement of fission-product activities that can be related to the quantity of fissile material remaining in the hulls. The applicability of various active interrogation techniques is being evaluated.[15] At present, IAEA inspectors have no capability to assay the quantity of fissile material remaining in leached hulls. Because of the high radiation levels, the inspector probably will use the operator's equipment for any verification measurement. In principle, the inspector could measure the specific fission-product activities in the waste disposal containers. However, to quantify these measurements he would have to accept the reactor operator's information on the irradiation history of the fuel material or obtain the ratio of the specific fission product to the fissile material.

Another safeguards problem associated with this diversion path must be addressed. The hull disposal containers could be used to divert large quantities of clean plutonium. At these extremely high radiation levels, kilogram quantities of plutonium placed in the leached-hull batch would not significantly affect the gamma-ray level. If passive neutron techniques are used, the quantity of concealable plutonium is reduced to several hundred grams. This diversion path could be verified only by using an active technique that probably will not be available to IAEA inspectors. At present, IAEA inspectors make no measurements on leached hulls.

D. Process Samples

1. Gamma-Ray and X-Ray Techniques. Liquid solutions containing NM can be assayed nondestructively by various x-ray and gamma-ray techniques. By definition, solutions satisfy the basic requirements for quantitative gamma-ray assay if (1) the mixture of NM and solvent is reasonably uniform and (2) the self-attenuation of the NM can be ignored. In addition, NM solutions can be contained in optimum configurations and accurate standards can be easily prepared.

In practice these basic requirements may not be realized. The solution may contain suspended particulate matter or different phases of varying densities and compositions. Solution standards are also difficult to maintain and stabilize. Evaporation and radiolysis of the solution as well as diffusion through the container material may change the chemical state and the mass of a standard solution.

The optimum measurement technique and the obtainable precision and accuracy for a given type of solution will depend on all the above considerations. Additional factors will also be influential, including the NM concentration, the presence of other radioisotopes, the intensity of fluorescent x-rays, and the relative isotopic concentration in the NM. No universal x-ray or gamma-ray technique exists; the proper choice can be made only after characterizing the solution to be analyzed and understanding the inherent strengths and limitations of the available assay techniques.

The characteristics of some typical reprocessing plant solutions are summarized in Table N-I. Each of these solutions will require a specific x-ray or gamma-ray assay technique to analyze the materials. Possible applications of NDA techniques for each process area are listed in Table N-II. Several methods might be adaptable to any one area, and the choice of the specific method would be dictated partly by process design considerations.

For a nondestructive method to be applicable to the measurement of NM concentration, it should have the demonstrated ability to measure the NM within a few minutes with precision and accuracy of 1% or better, and it should be free from any significant interference from extraneous materials present in the process streams. The gamma-ray and x-ray techniques listed in Table N-II have been shown to meet these requirements.

The main limitations of passive gamma-ray techniques are that they measure isotopic rather than elemental concentrations and that they generally cannot measure ^{240}Pu and ^{242}Pu.[16-18] With previous knowledge of isotopic composition (from mass-spectrometric data), appropriate corrections can be applied to yield overall

TABLE N-I

CHARACTERISTICS OF SOME REPROCESSING PLANT SOLUTIONS

Area	Concentration			Comments
	Uranium	Plutonium	Other	
Dissolver	300 g/L	3 g/L	Fission products 1500-2000 Ci/L	Analyses required for total U, Pu, and isotopics
1BP tank	10 g/L	1-5 g/L	1-5 Ci/L fission products, primarily Ru, Rh, Zr, Nb	
U product	350 g/L	---	---	High purity; negligible Pu or fission products
Pu product	1%	250 g/L	Trace Am, U	Can contain up to 1% heavy metals
Recycle acid (Pu purification area)	0.01-1 g/L	0.01-1 g/L	---	Up to 3 Ci/L FP, primarily Ru, Rh, Zr, Nb
Recycle solvent (Pu purification area)	0.01-1 g/L	0.01-1 g/L	---	Pu to 10^{-3} Ci/L FP, primarily Ru and Rh

concentrations with accuracies of better than 1%. Even where isotopic mixing in process streams has occurred, knowledge of original isotopic composition and isotopic correlations can be applied to provide acceptable accuracies.

X-ray fluorescence techniques are element- rather than isotope-sensitive and in this respect have an advantage over the passive gamma-ray methods for concentration measurements. However, they are not readily adaptable to in-line or at-line measurements, and a sample must be withdrawn from the process stream. Nevertheless, by using automated instruments and the thin-sample approach, the only sample preparation required is addition of an internal standard and possibly evaporation onto a filter paper. Samples having beta-gamma levels up to 1 or 2 Ci/L can be analyzed. For these reasons the technique is being considered seriously as an alternative to mass spectrometry for measuring uranium and plutonium in dissolver and accountability solutions.[19] For properly designed reprocessing plants, the method could be applied to measure plutonium in input and output streams for pulse columns.[20,21]

Gamma-ray absorptiometry has been applied or is being planned at several reprocessing plants for in-line measurement of uranium or plutonium concentration.[22] Of the NDA techniques discussed, gamma-ray absorptiometry is probably the most

TABLE N-II

POSSIBLE NDA APPLICATIONS FOR REPROCESSING PLANT SOLUTIONS

Area	Method
Dissolver	Gamma emission, x-ray fluorescence
1BP tank	X-ray absorption-edge densitometry Gamma emission, x-ray fluorescence
U product	X-ray absorption-edge densitometry Gamma-ray absorption
Pu product	X-ray absorption-edge densitometry
Recycle acid (Pu purification area)	Gamma emission, x-ray fluorescence
Recycle solvent (Pu purification area)	Gamma emission, x-ray fluorescence

susceptible to interference from extraneous materials and the least satisfactory for nuclear safeguards. For example, in the plutonium product solutions, heavy-metal impurities such as uranium, americium, and neptunium may be present in amounts up to 1% of the plutonium, and will be measured as plutonium. Similarly, medium-atomic-number matrix contaminants such as iron also will interfere.

Unlike gross gamma absorptiometry, absorption-edge densitometry is element-specific, and with suitable instrumentation and procedures could be applied to simultaneous in-line measurements of uranium and plutonium after the first partition cycle. Because of the high uranium-plutonium ratio, the technique is not applicable to measuring plutonium in dissolver solutions. The method is rapid and readily adaptable to in-line measurements.

Most of these techniques require installation of instrumentation that would be available for the IAEA inspectors to operate. Alternatively, Agency inspectors might verify the performance of the operator's measurement systems. Two nondestructive assay systems are being installed in the Tokai fuel reprocessing facility to demonstrate the applicability of these techniques: a K-edge densitometer for measuring plutonium product concentrations and a passive gamma-ray spectrometer for determining the isotopic composition of the plutonium. The first instrument is based upon an active-transmission technique, which determines the total concentration in samples with concentrations >100 g Pu/L. The second system measures the isotopic ratios and plutonium concentration for plutonium solution. Each of these techniques could be applied on-line or off-line to the measurement of liquid products by IAEA personnel during inspections.

2. Mass Spectrometry Using the Resin Bead. Reliable isotopic analysis of plutonium and uranium in spent fuel solutions can be performed with minimal chemistry by the anion resin-bead technique. The resin bead is allowed to equilibrate with the solution for 24-48 h, and then is analyzed by mass spectrometry. A single bead can be used to determine the isotopic composition of plutonium and uranium on samples containing as little as 10^{-9} to 10^{-10} g of each element per bead.[23] The problem of transporting plutonium samples to the Safeguards Analytical Laboratory (SAL) in Seibersdorf for analysis is greatly reduced because of the minimal quantity of radioactive material. Agency use of this technique is under study in the US, Japan, Germany, and at SAL.

3. Isotopic Correlations. Nuclear fuels subjected to irradiation undergo a number of changes in their chemical and isotopic compositions, such as burnup of part of the fuel atoms initially present and buildup of actinide nuclides and fission products. The theory of isotopic correlations and their importance to NM accountability in international reprocessing is discussed in App. M.

The isotopic correlation techniques are already being applied by some reprocessing plants and reactor operators.[24] Safeguards applications are being developed to demonstrate the applicability of the isotopic correlation technique to the safeguarding of fissile material at the input of a reprocessing facility. Cooperative experiments have been performed by Euratom Safeguards and IAEA Safeguards groups. The technique is still in the developmental stage but is emerging as an important measure for the accountability and control of NM.

4. Calorimetry. Calorimetric assay provides the IAEA inspectors with a precise nondestructive method for determining the plutonium content of samples by measuring alpha-decay heat.[25,26] Calorimetric assay is an absolute measurement of the heat generated within the sample and is independent of the chemical form of the plutonium as well as of the geometric configuration. This heat measurement can often be achieved with a precision of 0.1% or better and with negligible bias. The conversion of measured heat output to grams of plutonium requires an accurate knowledge of the isotopic composition. In particular, the minor isotopes ^{238}Pu and ^{241}Am are major heat producers and must be known accurately. The accuracy of the plutonium determination is

usually limited more by the knowledge of isotopic compositions than by the heat measurement. In the future, a gamma-ray spectrometric isotopic determination may be used in conjunction with the calorimetric heat measurement.

A portable calorimeter system for the NDA of plutonium materials has been developed for the IAEA by Argonne National Laboratory.[27,28] The agency will receive three fast-response calorimeters provided under the US technical assistance program. One calorimeter is a small, portable device for measuring samples about 2 cm in diameter by 5 cm tall. A second device will measure bulk samples up to ∿2 L in volume. The third calorimeter has an active length ∿3 m and is designed to measure MOX fuel rods. With these instruments, inspectors will be able to analyze rapidly (∿20 min) small quantities of plutonium (up to 18 g of high-burnup plutonium) such as fuel pellets and MOX powders with a measurement precision of 0.1%. The bulk calorimeter has successfully measured sealed cans holding up to 3 kg of plutonium. The most important application of calorimetry in the fuel reprocessing-conversion facility may be in analyzing PuO_2 product and in verifying the content of PuO_2 product canisters.

5. Safeguards Analytical Laboratory.[29] When satisfactory nondestructive techniques are not available, destructive techniques must be employed to verify the assay of fissile materials. The IAEA established the SAL at Seibersdorf, Austria, to perform rapid, accurate analysis of NM. The Laboratory is organized into five specialized areas: (1) analysis of uranium- or thorium-containing materials; (2) analysis of plutonium-containing materials; (3) mass spectrometry; (4) radio-chemistry; and (5) emission spectroscopy.

Two surface-ionization mass spectrometers have been in operation since November 1976. Both instruments can be used for the isotopic analysis of uranium, thorium, or plutonium. One instrument requires 0.1-1 mg of plutonium or 1-10 mg of uranium for a relative precision of the order of 0.2%. The second instrument is slightly less precise but has a sensitivity about 100 times greater; optimal precision is obtained with sample loadings of only 10-50 ng. The second instrument can be used in conjunction with the resin-bead sampling technique to provide IAEA inspectors with the capability of obtaining isotopic information from a minimal amount of radioactive material.

E. Product Material

1. Balances. Weighing devices form an important class of NDA instruments and require a set of standard or certified weights or other means for calibration. In the case

where a sample has been chemically analyzed, mass ratios often provide the relationship between the plutonium content and that of the total batch. For a metal, mass provides a direct analysis. Even for solutions, where the comparison is usually made on a volume basis, a mass ratio can be used.

Mass measuring devices available to the IAEA are listed in Table N-III.[30] Electronic balances also are available in some facilities.[31] In a plutonium facility, electronic balances typically have capacities in the 5-15 kg range and have sensitivities of 0.1 g or better. The advantage of the electronic balance is that the readout portion of the instrument can be located outside the glovebox for more convenient servicing.

Load cells are used for weighing items, such as solution tanks, that are heavier than balances can handle.[32]

2. Neutron Measurements. The passive neutron-well coincidence counter is one of the most useful NDA instruments for plutonium assay. IAEA inspectors are using the portable high-level neutron coincidence counter (HLNCC).[33]

TABLE N-III

WEIGHING DEVICES AVAILABLE TO IAEA INSPECTORS[a]

Type of Device	Standard Capacity	Deviation	Remarks
1. Equal-arm balance	0.5-25 kg	0.3 g	Time-consuming operation
2. Equal-arm scale	2 kg	0.4 g	Accuracy 0.05%
2.1. Torsion type	2 kg	0.4 g	Accuracy 0.2%
3. Top-loading scale	120 g	0.001 g	
4. Platform scales			
4.1. Platform modified	110-360 kg	0.1 kg	
4.2. Built-in warehouse	9000 kg	1 kg	
5. Railway scale	20 000-70 000 kg	5 kg	Two-section, Type S
6. Load cells			
6.1. Hydraulic	2000 kg	4-40 kg	Design accuracy 0.05% Precision was result of experimental constraints
6.2. Strain gauge	2000 kg	0.5 kg	

---

[a] Table adapted from Ref. 30.

The neutron coincidence counter assays plutonium-bearing material by detecting spontaneous fission neutrons from the plutonium in the presence of a random neutron background originating principally from (α,n) reactions in the material. The coincidence logic of the system separates the time-correlated spontaneous fission neutrons from these random neutrons. The counter is termed a high-level coincidence counter because it is designed to handle the high counting rates associated with large masses of plutonium (several kilograms).

Basically, the coincidence counter consists of a sample-counting cavity surrounded by ^{3}He proportional counters. These thermal-neutron detectors are embedded in cadmium-lined polyethylene slabs. Neutrons are absorbed by the polyethylene or cadmium of the counter, leak out the sides or ends of the counter, or are thermalized by the polyethylene and are captured by the ^{3}He proportional counters. Figure N-2 is a photograph of the counter.

The counter can be used for the assay of plutonium samples ranging from <1 g to ∿3000 g. For a can containing 1 kg of PuO_2 (20% ^{240}Pu), the expected statistical precision is ∿1% for a 5-min count. The measurement accuracy can approach this value if the standards closely resemble the unknowns. Multiplication effects are large in this plutonium mass range and thus the accuracy is degraded if the standards have different characteristics than the samples. The totals-to-coincidence ratio in the HLNCC is used as a check on this multiplication effect, and correction techniques are being developed to relate samples with different multiplication properties.

Because the ^{240}Pu dominates the coincidence counting, the IAEA combines high-resolution gamma-ray spectrometry with neutron coincidence counting to determine the plutonium isotopic ratios.

3. Item Counting and Irradiation Verification. An important part of the IAEA inspection procedure is the determination that all of the items on an inventory listing are present at the facility and that some fraction of these items actually exhibit attributes characteristic of the materials in the samples. Whereas item counting and item identification (serial numbers) require no equipment, attribute verification is done with simple NDA equipment. The IAEA currently measures qualitatively the gamma-ray signatures of plutonium and uranium to verify that inventory samples actually contain those materials. The IAEA uses the Pitman model 322 selective gamma monitor and the Eberline SAM-II to establish in a short time that samples contain plutonium or uranium.

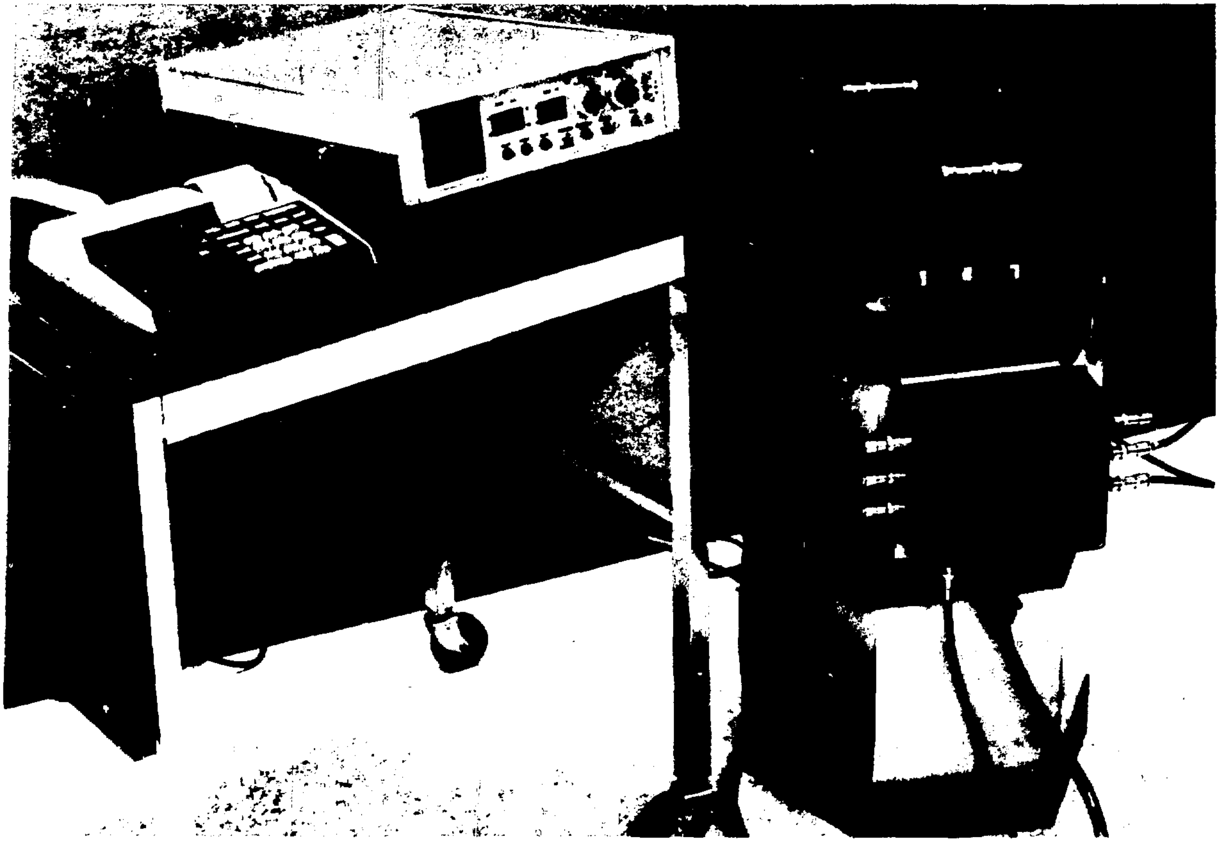


Fig. N-2. The IAEA HLNCC with its shift-register electronic unit and HP-97 programmable calculator used for data collection and determination of plutonium content.

The results of the measurements made with these instruments are qualitative; the inspector establishes the presence of plutonium and uranium in the sample, but does not establish the amount.

Qualitative measurements could also be made with high-resolution gamma-ray techniques and neutron-counting techniques. A combination of independent qualitative measurements by both techniques could add significantly to the confidence of the verification.

F. Waste Products

1. Segmented Gamma Scan. Among the techniques for nondestructively determining quantities of NM, passive gamma-ray measurements provide one of the best

quantitative methods for isotopes that have a unique gamma-ray signature. Segmented gamma scanners (SGS)[34] use a procedure for measuring fissile or fertile NM in matrices of low-Z material and quantitatively correcting for gamma-ray attenuation on a segment-by-segment basis. The procedure can be performed with a variety of equipment configurations, and is rather complex and tedious. The SGS is an instrument in which these complex procedures have been incorporated into a plant-tested automated instrument that is simple to operate.

Usually the most difficult problem in the passive gamma-ray assay of bulk samples is to correct for the self-attenuation. Unfortunately, gamma-ray attenuation is not only a function of energy but also of matrix material parameters such as density and atomic weights. For unknown or nonuniform matrix material the SGS uses a separate external transmission source, emitting gamma radiation close to the gamma-ray energy of the isotope being measured, to measure sample self-attenuation.

Inhomogeneities of the sample under measurement further complicate the measurement. If the matrix material varies in the sample container, the measurement of transmission at one point may not yield the transmission at the location of the material emitting the gamma rays. The sample is divided into collimator-defined horizontal segments, each of which is separately measured for its own attenuation, and the count rate from each individual segment is corrected for its respective attenuation. The sum of segment-by-segment results will yield a better measurement of the total sample than will a simple attenuation average over the whole sample. This vertical segmentation of the sample accommodates variations in matrix material and yields good results for a large variety of samples that otherwise are not easily measured.

The IAEA has been evaluating the feasibility of using an SGS to measure the plutonium content of waste containers. An SGS was installed at the CNEN-Casaccia Research Facility in 1978. The waste containers are $\sim$22 cm in diameter and 45 cm long with $\sim$1 g of reactor-grade plutonium dispersed in low-density waste. Preliminary analysis indicates that the system could be used by a well-trained IAEA inspector as a safeguards verification technique.

2. HLNCC. Neutron-well coincidence counters can be used for waste as well as for product material measurements. The HLNCC, which is used by the IAEA, can be modified to measure the larger containers in which waste material is typically stored. The HLNCC has six separate side sections that can separate to accommodate larger containers, but the efficiency drops because of the loss in geometric coupling.

For small containers (less than ∿5 L) that fit inside the HLNCC in its normal configuration, a 1-g PuO_2 sample (20% ^{240}Pu) gives a statistical precision of ∿3% for a 1000-s count. For larger containers, the counting efficiency will decrease as the solid angle coupling between the sample and the detector decreases. Plutonium masses of interest in waste containers are generally small and multiplication is not a problem. However, matrix effects in the waste container will normally add to the measurement error. If the matrix material is not hydrogenous, the effect is small (<1-2%). For hydrogenous matrix materials, the effect on the counting efficiency can be large and the standards should contain material similar to the assay samples.

The IAEA has six HLNCC units available for inspection activities. The HLNCC is commercially available in the US.

3. Large Coincidence Counters. The typical neutron coincidence counter consists of an annulus of polyethylene moderator containing one or more rings of ^3He- or BF_3-filled detectors surrounding the sample to be assayed. Counters for samples in barrels of <1 to 55 gal[35] have been constructed and extensively tested in the laboratory and in the field. A large coincidence counter is shown in Fig. N-3.

A large neutron coincidence counter has been used continuously since 1972 at LASL's plutonium processing facility for routine assay of plutonium-bearing scrap in 30-gal barrels. The counter is located inside a thick water shield to reduce the background from nearby plutonium storage areas to an insignificant level. The total neutron background and coincidence neutron background rate are due primarily to cosmic rays.[36]

The counter's neutron detection efficiency is nearly constant throughout its interior; thus, assays will be rather insensitive to the location of the plutonium in the barrel. Assays are relatively independent of the matrix material in the sample,[37] except for samples containing large quantities of hydrogenous material.

Typical counting times are 200 s, with assay precision better than 10%. The instrument can detect ∿5 mg of ^{240}Pu in 1000 s at the 2300-m (7200-ft) altitude of Los Alamos, or about 2 mg ^{240}Pu at sea level.

G. Summary

Portable instrumentation now is available to IAEA inspectors for the measurement of irradiated fuel assemblies, process samples, and product materials. In addition, leached hulls, other process and product materials, and waste materials can be analyzed with in-plant instrumentation.

Fig. N-3. Large 4π neutron coincidence counter used for the passive assay of plutonium content in 55-gal barrels.

Detectors and data acquisition systems are available for the measurement of irradiated fuel assemblies; however, the scanning apparatus must be uniquely designed for the specific storage pond. Prototype units of Cerenkov instrumentation are being evaluated by the Agency. Measurements of leached hulls require the use of the operator's equipment and calibration information.

Gamma-ray and x-ray systems for the analysis of process samples are specialized for each application and facility and would require an independent verification by the IAEA inspectors. Possible verification methods include the use of standards or the shipment of samples to the SAL for analysis. Segmented gamma scan systems have been used by Agency personnel to measure a variety of samples.

HLNCCs are routinely used to assay plutonium samples and are commercially available. Large 4π neutron coincidence counters generally are uniquely designed for specific application, hence are not available from commercial vendors.

A large variety of instrumentation is available to the IAEA inspectors for safeguards verification measurements--especially if in-plant instrumentation is available to them.

REFERENCES

1. "Treaty on the Nonproliferation of Nuclear Weapons," United Nations Publication OPI/372, International Atomic Energy Agency (1976).

2. E. J. Dowdy, N. Nicholson, and J. T. Caldwell, "Irradiated Fuel Monitoring by Cerenkov Glow Intensity Measurements," Los Alamos Scientific Laboratory report LA-7838-MS, ISPO report 61 (1979).

3. T. N. Dragnev, "Experimental Techniques for Measuring Burnup Nondestructive Techniques: Gamma Spectroscopy," International Atomic Energy Agency report IAEA/STR-48 (October 1974).

4. S. T. Hsue, T. W. Crane, W. L. Talbert, Jr., and J. C. Lee, "Nondestructive Assay Methods for Irradiated Fuels," Los Alamos Scientific Laboratory report LA-6923 (January 1978).

5. N. Beyer, M. de Carolis, E. Dermendjiev, A. Keddar, and D. Rundquist, "IAEA NDA Measurements as Applied to Irradiated Fuel Assemblies," in Nuclear Safeguards Technology 1978, Proc. Symp., Vienna, October 2-6, 1978 (International Atomic Energy Agency, Vienna, 1979), IAEA-SM-231/106, Vol. I, pp. 443-457.

6. K. Nakajima, T. Koizumi, T. Yamanouchi, S. Watanake, and N. Suyama, "Development and Demonstration of Safeguards Techniques in the Tokai Fuel Reprocessing Plant," in Nuclear Safeguards Technology 1978, Proc. Symp., Vienna, October 2-6, 1978 (International Atomic Energy Agency, Vienna, 1979), IAEA-SM-231/34, Vol. II, pp. 701-732.

7. H. Graber, A. Keddar, G. Hofmann, and S. Negel, "Gamma Spectrometric Determination of Burnup and Cooling Time of Irradiated ECH-l Fuel Assemblies," in Nuclear Safeguards Technology 1978, Proc. Symp., Vienna, October 2-6, 1978 (International Atomic Energy Agency, Vienna, 1979), IAEA-SM-231/129, Vol. I, pp. 353-368.

8. S. Tsujimura, "Applicability of Nondestructive Assay Techniques to Spent Fuels from BWR," in Nuclear Safeguards Technology 1978, Proc. Symp., Vienna, October 2-6, 1978 (International Atomic Energy Agency, Vienna, 1979), IAEA-SM-231/29, Vol. I, pp. 305-316.

9. J. R. Phillips, D. M. Lee, T. R. Bement, J. K. Halbig, S. T. Hsue, and K. Kaieda, "Nondestructive Examination of Irradiated LWR Fuel Assemblies," Nucl. Mater. Manage. VIII, 451-467 (1979).

10. A. J. G. Ramalho and E. Payne, "Spent Fuel Measurements Using High Resolution Gamma Systems," Proc. 20th Annual Meet. Inst. Nucl. Mater. Manage., Albuquerque, New Mexico, July 1979.

11. S. T. Hsue, J. E. Stewart, K. Kaieda, J. K. Halbig, J. R. Phillips, D. M. Lee, and C. R. Hatcher, "Passive Neutron Assay of Irradiated Nuclear Fuels," Los Alamos Scientific Laboratory report LA-7645-MS (February 1979).

12. P. Filss, "NDA Techniques for Irradiated Fissile Material in Extended Configurations," in Nuclear Safeguards Technology 1978, Proc. Symp., Vienna, October 2-6, 1978 (International Atomic Energy Agency, Vienna, 1979), IAEA-SM-231/17, Vol. II, pp. 97-111.

13. G. W. Eccleston, H. O. Menlove, and M. W. Echo, "A Measurement for High Enrichment Spent Fuel Assemblies and Waste Solids," Nucl. Mater. Manage. VIII, 344-355 (1979).

14. G. L. Ragan, M. M. Chiles, C. W. Ricker, D. T. Ingersoll, and G. G. Slaughter, "Nondestructive Assay of Subassemblies of Various Spent or Fresh Fuels by Active Neutron Interrogation," Nucl. Mater. Manage. VIII, 334-343 (1979).

15. T. D. Reilly, "The Measurement of Leached Hulls," Los Alamos Scientific Laboratory report, LA-7784-MS, ISPO-63 (1979).

16. J. L. Parker, "A Plutonium Solution Assay System Based on High-Resolution Gamma-Ray Spectroscopy," Los Alamos Scientific Laboratory report LA-8146-MS (January 1978).

17. R. Gunnink, "Gamma Spectrometric Methods for Measuring Plutonium" in Analytical Methods in Safeguards and Accountability Measurements of Special Nuclear Material, (NBS Special Publication 528, 1978), H. T. Yolken, J. E. Bullard, Eds., Proc. ANS Topical Meeting, Williamsburg, Virginia, May 15-17, 1978, pp. 49-63.

18. R. Gunnink, J. E. Evans, "In-Line Measurement of Total and Isotopic Plutonium Concentrations by Gamma-Ray Spectrometry," Lawrence Livermore Laboratory report UCRL-52220 (February 1977).

19. T. R. Canada, J. L. Parker, and T. D. Reilly, "Total Plutonium and Uranium Determination by Gamma-Ray Densitometry," ANS Trans. 22, 140 (1975).

20. A. von Baeckmann, "Determination of Uranium and Plutonium in Solutions of Spent Nuclear Fuels by X-ray Fluorescence Analysis," in Safeguards Techniques, Proc. IAEA Symp. on Safeguard Techniques, Karlsruhe, July 6-10, 1970 (International Atomic Energy Agency, Vienna, 1970) Vol. II, pp. 45-51.

21. G. Malet and G. Charpentier, "Simultaneous Determination of Uranium and Plutonium by X-ray Fluorescence in the Reprocessing of Rhapsodie Fuel," in Analytical Methods in the Nuclear Fuel Cycle, Proc. Symp., Vienna, November 29-December 3, 1971 (International Atomic Energy Agency, Vienna, 1972), pp. 343-352.

22. J. S. Stutheit, "Dual-Energy Absorptiometer," E. I. duPont de Nemours and Co. report DPSPU 68-30-9 (January 1969).

23. R. L. Walker, R. E. Eby, C. A. Pritchard, and J. A. Carter, "Simultaneous Plutonium and Uranium Isotopic Analysis From a Single Resin Bead - A Simplified Chemical Technique for Assaying Spent Reactor Fuels," Anal. Lett. 7, 563-573 (1974).

24. C. Foggi, "The ESARDA Working Group on Isotopic Correlation and Reprocessing Input Accountancy," European Safeguards Bulletin, Issue No. 2, Spring 1978.

25. American National Standard: Calibration Techniques for the Calorimetric Assay of Plutonium-Bearing Solids Applied to Nuclear Materials Control, ANSI N15.22-1975.

26. T. Dragnev, "Nondestructive Assay Techniques for Nuclear Safeguards Measurements," At. Energy Rev., Vol. II, No. 2, 341 (1973).

27. C. T. Roche, R. B. Perry, R. N. Lewis, E. A. Jung, J. R. Haumann, "Calorimetric Systems Designed for In-Field Non-Destructive Assay of Plutonium-Bearing Materials," in Nuclear Safeguards Technology 1978, Proc. Symp., Vienna, October 2-6, 1978 (International Atomic Energy Agency, Vienna, 1979), IAEA-SM-231/78, Vol. II, pp. 137-146.

28. C. T. Roche, R. B. Perry, R. N. Lewis, E. A. Jung, and J. R. Haumann, "ANL Small-Sample Calorimeter System Design and Operation," Argonne National Laboratory report ANL-NDA-1, ISPO-13 (July 1978).

29. "Nonproliferation and International Safeguards," IAEA report 575 prepared for the UN Special Sessions on Disarmament, May 23-June 28, 1978.

30. IAEA Safeguards Technical Manual, Part E, Methods and Techniques, IAEA Technical Document IAEA-174 (1975).

31. "Nuclear Safeguards Research and Development Program Status Report, May-August 1978," Los Alamos Scientific Laboratory report LA-7616-PR (April 1979), pp. 66-69.

32. R. H. Augustson, "DYMAC Demonstration Program: Phase 1 Experience," Los Alamos Scientific Laboratory report LA-7126-MS (February, 1978), pp. 16-22.

33. M. S. Krick and H. O. Menlove, "The High-Level Neutron Coincidence Counter (HLNCC) Users' Manual," Los Alamos Scientific Laboratory report LA-7779-M, ISPO-53 (June 1979).

34. E. R. Martin, D. F. Jones, and J. L. Parker, "Gamma-Ray Measurements with the Segmented Gamma Scan," Los Alamos Scientific Laboratory report LA-7059-M (December 1977).

35. "Nuclear Safeguards Research and Development Program Status Report," Los Alamos Scientific Laboratory report LA-4523-MS (1970), p. 18.

36. C. G. Montgomery and A. R. Tobey, Phys. Rev. 76, 1478 (1949).

37. "Nuclear Safeguards Research and Development Program Status Report," Los Alamos Scientific Laboratory report LA-4605-MS (1970), p. 24.

APPENDIX O

INTEGRATION OF MATERIALS ACCOUNTING AND CONTAINMENT AND SURVEILLANCE

J. P. Shipley, W. J. Whitty, and D. D. Cobb
LASL Safeguards Staff (Q-4)

A. Introduction

The basis for international safeguards for nations signatory to the Non-Proliferation Treaty (INFCIRC/153)[1] specifies that international safeguards systems make use of both materials accounting and containment and surveillance techniques. The two measures must be integrated in the most effective way to achieve satisfactory deterrence through improved timeliness and likelihood of diversion detection, while maintaining costs at reasonable levels. Effective integration requires that throughout the facility we analyze the relative merits of materials accounting and containment and surveillance, including possible trade-offs between them and areas where they should overlap and complement each other. This analysis requires some means of evaluating the performances of each component and of the composite system. Performance evaluation is a difficult problem because materials accounting and containment and surveillance are basically different and are only partially commensurable. Furthermore, they serve generally dissimilar purposes.

This appendix addresses the fundamental problem of integration by examining the bases for materials accounting and containment and surveillance and by defining the interfaces between them. We also suggest some possible techniques for partially commensurate performance evaluation. The integration problem was discussed preliminarily in Ref. 2. SLA is performing a much more detailed assessment of relevant containment and surveillance methods as a companion to this report.[3]

B. Characteristics of International Safeguards Measures

1. Materials Accounting. The underlying philosophy of materials accounting is to verify the truth of the statement "No NM has been diverted." by determining that all NM supposed to be present is, i.e., that all NM is "accounted for." This is commonly done by (1) having the facility operator draw materials balances about suitable areas of the facility and (2) having the IAEA inspector confirm (or deny) the operator's results on the basis of examining the operator's data and making some set of independent measurements.

Note that materials accounting and its verification by the inspector are based on comparing a "book inventory" to a measured physical inventory, which is an estimate of the "actual inventory." The current book inventory is obtained by algebraically adding (inputs positive, outputs negative) to the last previous physical inventory the subsequent measured transfers. This process implies a series of discrete times at which inventory estimates are made, and all such estimates are related through the continuity, or materials balance, equation. Thus, the timeliness of materials accounting is determined by the frequency at which actual inventory estimates can be made. On the other hand, actual inventory estimation only has to occur whenever a new estimate is needed. The frequency of estimation of the actual inventory should be consistent with process operating procedures, measurement instrument availability and capability, and timeliness requirements. Consequently, materials accounting has a certain degree of flexibility afforded by its dependence on the law of conservation of mass.

Another aspect of this flexibility, and a fundamental reason for the effectiveness of materials accounting, is that the physical evidence of a diversion does not disappear after the diversion has occurred. That is, any set of materials balances covering the time at which diversion occurred contains information about that diversion, although the quality of the information may not be satisfactory if the diversion level and time scale are greatly different from the measurement uncertainties and the time coverage of the materials balances. Thus, materials accounting need not provide immediate and specific indication of the diversion act to be effective.

Several factors affect the IAEA's ability to perform verification. The primary one that has implications for the materials accounting/containment and surveillance interface is the possibility of incorrect and insufficient information on NM transfers and inventories. This factor translates into several considerations relevant to containment and surveillance:

- The absence of paths unknown to the inspector for NM transfers into and out of the area for which a materials balance is drawn;
- The absence of places to conceal NM inside the area for which a materials balance is drawn; and
- The ability of the inspector to obtain sufficient unfalsified measurements to verify a materials balance within prescribed uncertainty limits.

The first two considerations result in the requirement that all NM flows and inventories be accessible for verification by the inspector at the KMPs. A transfer path not passing through a key flow measurement point would allow illicit inputs (clandestine feed) and outputs (diversion) that would be invisible to the materials accounting system, as long as the transfers balanced over each materials balance period. The addition of NM concealment places within the process could remove even that restriction on a divertor.

The third consideration bears comment. The inspector must have the stated ability; he need not actually make all the measurements, but the operator must be convinced he could, and the operator must not know in advance which ones he will make. Otherwise, the operator could select a measurement that he knows the inspector cannot or will not make, falsify his reported value of that measurement at will, and divert correspondingly without fear of detection through the inspector's verification of the the materials accounting results. Therefore, the inspector must be able to draw a materials balance, and he must be able to gather unfalsified data with which to draw that balance. The inspector must only collect sufficient data, for example, by random sampling, to achieve satisfactory and timely sensitivity to diversion if the operator has no prior knowledge of which measurements the inspector will make. If the inspector is unable to gather the data required to reach the desired diversion sensitivity, then the verification must include means other than materials accounting.

2. Containment and Surveillance. Containment and surveillance seek to verify the statement "No NM has been diverted." by determining that no NM is where it is not supposed to be, the complementary approach to materials accounting.

The basic ideas behind containment and surveillance are two-fold:

- Determine those paths by which a divertor might remove NM from the process, and
- Monitor those paths to the extent necessary to obtain reasonable sensitivity to diversion.

That is, containment and surveillance measures are generally directed at detecting the passage of NM from where it is supposed to be to where it is not, as that passage occurs. Consequently, indications from the containment and surveillance system may be more timely than those from the materials accounting system. However, a diversion not detected immediately may never be detected; a capable divertor can destroy lingering evidence of his act without violating a physical law, unlike the case for materials accounting.

Because of the immediacy requirement, a system based solely on containment and surveillance must seem to be working at all times and to cover all diversion paths the divertor might want to use. Otherwise, the divertor could select a diversion path and time for which he could be certain of having a zero detection probability. In parallel with the characteristics of materials accounting, the containment and surveillance system must appear to the operator to be able to detect diversion along any path he might choose at any time.

Determining the possible diversion paths is difficult because of the quantity and variety of diversion paths. In the usual approach, consideration is restricted to those diversion paths considered "credible." However, this is still a large number, and the question always remains whether or not some have been omitted. In addition, it is the divertor, not the designers of the system, who ultimately decides what is credible, although an intelligent designer may have significant impact on the divertor's decision.

Determination of the credible diversion paths is a dynamic process in the sense that the containment boundaries must be continuously monitored to detect the appearance of new diversion paths. The initial assessment of diversion paths can be based on examination of the facility construction details and comparison with the plans. After that, the inspector need only look for changes, but he must be certain that none escapes him.

The containment and surveillance system does not have a natural time fiducial corresponding to the materials balance period for materials accounting. This fact and the many different measurement characteristics of the spectrum of containment and surveillance devices have important implications for assessing how well the system can be expected to work. Determination of expected false-alarm rates and diversion sensitivities is difficult. The effects of systematic errors, which will be important for detecting diversion of bulk NM through quantitative surveillance devices, depend on the time structure of the diversion and the measurement processes. These effects are especially important if advantage is to be taken of the analysis of trends in the containment and surveillance data. At present, all these considerations are in various stages of being examined.

Some types of containment and surveillance devices are designed to detect the presence of NM where none would normally be, which is a relatively easy technical problem. However, many devices must detect the illicit presence of NM only at certain times, depending on the process operating procedures. This is a much more difficult task because the instrument must be coordinated with the process, and the normal occasional presence of NM may adversely affect measurement quality, for example, by increasing the background noise in a radiation-sensitive device.

Based on all these characteristics, and in keeping with the categorization of Shea and Tolchenkov,[4] the containment and surveillance system may be considered to have three possible functions:

- Monitoring the integrity of the materials accounting system,
- Monitoring the integrity of the containment, including the validity of verified inventories, and
- Detecting illicit flow of NM through the containment boundaries.

3. The Materials Accounting/Containment and Surveillance Interface. From the previous discussions, the following interfacial characteristics between materials accounting and containment and surveillance can be identified:

(1) The containment and surveillance system attempts to ensure that all NM flows and inventories are accessible for verification at the KMPs.
(2) The containment and surveillance system attempts to ensure the availability to the inspector of a sufficient set of unfalsifiable materials accounting data.
(3) Materials accounting confirms the performance of the containment and surveillance system and alleviates the need for it to function continuously.
(4) Containment and surveillance decrease the measurement load on materials accounting, for example, by sealing measured items.
(5) Both systems look for illicit movements of NM, but in complementary fashions. The relative importance attached to either depends on the diversion sensitivities and the difficulty with which a divertor can circumvent each system.

The first characteristic requires a close correspondence between containment boundaries and areas for which materials balances are drawn. It is possible for one containment boundary to envelop several MBAs or UPAAs, but an MBA or UPAA cannot extend across a containment boundary.

This correspondence between containment boundaries and MBAs or UPAAs is also important because it limits the flexibility of the divertor. The materials accounting system forces the divertor to divert from several areas and at several times. He cannot concentrate on that form of NM that is least detectable by the containment and surveillance system, and he must make several passes through the system--all of which should decrease his probability of success.

C. Performance Evaluation

1. Materials Accounting. If the underlying assumptions for materials accounting are valid, then the four basic performance measures are total NM missing, time to detection of that total, probability of detection, and false-alarm probability.[5] For

fixed false-alarm probability, these performance measures constitute a three-dimensional performance surface showing detection probability vs the total amount missing and the detection time expressed as the number of materials balances (see Vol. II, Sec. V and Ref. 5). A battery of tests, including the Cusum, assures that the performance is independent of diversion scenario.

2. Containment and Surveillance. Specification of containment and surveillance performance requires:

- A statement of diversion paths treated,
- Values for some suitable set of performance measures, such as those for materials accounting, for illicit NM movements, and
- A statement of other benefits, such as ensuring the integrity of the materials accounting system.

Note that only the second point is, perhaps, quantifiable in the same terms as for materials accounting. Some preliminary work has been done along these lines.[6-9] SLA has taken a different approach to performance evaluation[3] in which sensors are characterized by threshold rates relating the sensitivity of a device to the amount of NM that can pass the sensor per unit time without detection. For deterministic analysis the threshold for each sensor approximates a boundary where the probability of detection is assumed to change instantaneously from zero to one as the threshold is crossed in increasing units of mass per unit of time. Present SLA efforts also involve probabilistic analyses of containment and surveillance systems performance similar to the approach outlined in Refs. 6-9. Historical information on the sensors is required to determine false-alarm characteristics and the equipment thresholds. Equipment reliability and redundancy requirements also need to be determined.

The other two points of the performance specification must not be omitted, although they may provide little quantitative information for the IAEA's goal of verification. Those two points constitute important benefits and limitations that are essential to the integration of materials accounting with containment and surveillance and the evaluation of overall systems performance.

3. Application of the Performance Measures. Quantitative indicators of the expected behavior of the safeguards system, that is, performance measures, facilitate the integration of materials accounting and containment and surveillance techniques, including trade-offs among inspection options and costs. Effective integration requires detailed understanding of the characteristics and capabilities of both techniques through a

thorough analysis of the facility design and operating requirements, complemented by simulated operations for which the performance measures take on specific values.

Design concepts for materials accounting are evolved by identifying KMPs and appropriate measurement techniques, comparing possible materials accounting strategies, and using the performance measures of detection probability, detection time, and total loss at given false-alarm rates to develop performance surfaces. Then, the containment and surveillance techniques necessary to support the materials accounting system are specified according to the particular features of the proposed materials accounting system.

SLA has identified the primary and secondary containment zones and related diversion points for an AGNS-type facility.[3] Diversion paths have been analyzed by fault-tree analysis, and the related diversion points are categorized at the primary containment zone boundaries into four levels of increasing degree of modification or interference with normal plant operations necessary for diversion to occur. Major contributions to possible diversion are identified at each level. Potential surveillance devices to monitor the integrity of the containment and/or to indicate or detect the movement of NM have been identified. Because these devices have an assumed zero probability of detection below the threshold amounts and one above the thresholds, the performance surfaces for materials accounting systems will need to be compared at the threshold amounts of quantity diverted, and the curvature of the performance surfaces should be investigated. High detection probability for materials accounting systems will be necessary below the thresholds to provide an adequate level of protection. These comparisons between the materials accounting and containment and surveillance systems performance will indicate the appropriateness of the containment and surveillance systems in supporting the KMPs and will indicate needed areas of research on the different systems. The evaluation will give a qualitative and partially quantitative understanding of the safeguards systems effectiveness and the parameters and their relative importance.

D. Integration of the Systems

Once the requirements of the overall safeguards system have been established and the various subsystems designed, the system must be evaluated to determine whether it meets the design requirements. After verification that the system meets basic requirements, trade-off and sensitivity analyses can be applied to improve the overall systems performance and to investigate the effect on systems performance by variation of the parameters. Finally, costs and systems effectiveness estimates can be combined in some fashion so that the decision-maker can have a sound information base for selecting the safeguards system design for the facility. These concepts are discussed in more detail below.

1. Limited or Partial Integration. Integration generally means the systematic structuring of all components and procedures in a safeguards system to coordinate materials accounting and containment and surveillance activities. This will provide more effective safeguards than if those measures were treated separately.

The final containment and surveillance system for a facility can be specified only after examining the detailed design of the materials accounting system and normal process streams.[6] Preliminary work, however, can specify the containment boundaries inherent in an existing physical plant. In addition, evaluation of potential containment and surveillance devices and preliminary diversion path analysis for such an existing facility can be completed by network analysis techniques. These steps, identification of physical containment boundaries, identification of containment and surveillance devices, and diversion path analysis have been partially completed by SLA. Probabilistic representation of containment and surveillance systems performance, tamper-safing, and verification evaluation techniques need to be developed (see App. H). The design of the materials accounting system and various materials accounting options are described in Vol. II of this report.

2. Trade-off and Sensitivity Analyses. Trade-off analysis is applicable when there are competing or inconsistent objectives or different ways of structuring the system without degradation of overall systems performance, or it can be used to reduce the cost of a system with the performance held constant. Another application of trade-off analysis is to improve the total systems performance with costs held constant. In this study, trade-off analysis is the balancing of subsystems within technical constraints only. Furthermore, trade-offs will be investigated among alternative materials accounting systems and among containment and surveillance systems separately.

Trade-off analysis and sensitivity analysis are closely linked. Sensitivity analysis searches for changes in the value of performance measures caused by changes in systems parameters. During the initial evaluation of the safeguards system, sensitivity analysis can help to determine critical parameters, and, used again at the last phase, it can help to identify the most efficient or least sensitive alternatives to uncertainties in costs.

3. Cost Analysis and Selection of a Balanced, Partially Integrated System. Cost analysis for a safeguards system will depend on the complexity of the system, the level of development of the instruments proposed, and the degree of substitutability of various components and subsystems. If a single measure of safeguards systems effectiveness is not possible, then some multiple of effectiveness measures, when considered with costs, will provide a rational basis for choosing preferred alternative systems options.

Systems effectiveness measures provide simplified analytical representations of the real physical system under consideration. Even the best representation of the physical system is imperfect and subjective. Cost estimates also will be imperfect. The selection of the final system or a few potential systems will be aided by the technical and economic aspects of the alternatives, no matter how imperfect. The selection will be heavily influenced by the decision-maker's subjective perceptions of what can be implemented in the real world where political and other qualitative factors must be considered. However, a well-structured procedure for evaluating the alternatives and realistic cost estimates will provide a valuable framework on which to base a selection.

REFERENCES

1. "The Structure and Content of Agreements Between the Agency and States Required in Connection with the Treaty on the Non-Proliferation of Nuclear Weapons," IAEA INFCIRC/153 (June 1972).

2. J. P. Shipley, M. E. Bleck, C. P. Cameron, J. L. Darby, R. J. Dietz, and E. A. Hakkila, "Preliminary Concepts: International Safeguards for a Light-Water Reactor Fuels Reprocessing Plant," Los Alamos Scientific Laboratory report LA-7551-MS (March 1979).

3. C. P. Cameron and M. E. Bleck, "International Safeguards for a Light-Water Reactor Fuels Reprocessing Plant: Containment and Surveillance Concepts," Sandia Laboratories report (in press).

4. T. Shea and D. Tolchenkov, "The Role of Containment and Surveillance in IAEA Safeguards," in Nuclear Safeguards Technology 1978, Proc. Safeguards Symp., Vienna, October 2-6, 1978 (International Atomic Energy Agency, Vienna, 1979), IAEA-SM-231/110, Vol I., pp. 547-559.

5. D. D. Cobb and J. P. Shipley, "Performance Analysis of Nuclear Materials Accounting Systems," Nucl. Mater. Manage. VIII, 81-92 (1979).

6. H. G. Sturman, R. W. Foulkes, D. Boardman, J. M. Gregson, and M. A. Simpson, "Safeguarding a Future Industrial Reprocessing Plant," in *Proc. Symp. Safeguards and Nucl. Mater. Manage., 1st,* Brussels, Belgium, 1979 (Commission of European Communities, Ispra, 1979), pp. 25-27.

7. Y. Akimoto, T. Ishii, S. Yamagami, and T. Shibota, "A Quantitative Evaluation of the Effectiveness of Safeguards with Emphasis on Containment and Surveillance," in *Proc. Symp. Safeguards and Nucl. Mater. Manage., 1st,* Brussels, Belgium, 1979 (Commission of European Communities, Ispra, 1979), pp. 77-79.

8. J. M. Gregson and A. A. Musto, "Quantification of the Safeguards Assurance Given by Containment/Surveillance," in *Proc. Symp. Safeguards and Nucl. Mater. Manage., 1st,* Brussels, Belgium, 1979 (Commission of European Communities, Ispra, 1979), pp. 80-88.

9. F. Brown, "Quantification of the Safeguards Assurance Given by Containment/Surveillance," Inst. Nucl. Mater. Manage. *VIII* (1979, in press).

☆ U.S Government Printing Office: 1980 — 677 — 115/69