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TITLE: REQUIREMENTS FOR NEAR-REAL-TIME ACCOUNTING OF STRATEGIC NUCLEAR MATERIALS IN NUCLEAR FUEL REPROCESSING

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Requirements for Near-Real-Time Accounting of Strategic
Nuclear Materials in Nuclear Fuel Reprocessing

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ABSTRACT

A Purex-based nuclear fuel reprocessing plant has been studied for possible incorporation of near-real-time accounting to supplement conventional accounting procedures. Near-real-time accounting of special nuclear materials relies on in-line or at-line flow measurements and plutonium assay of product and waste streams, complemented by conventional analytical chemistry for daily instrument calibrations. In-line alpha monitors could be used for waste stream measurements of plutonium, even in the presence of high beta-gamma fluxes from fission products. X-ray absorption edge densitometry using either K- or L-absorption edges could be used for plutonium concentration measurements in main product streams. Some problem areas identified in waste stream measurements include measurements of leached hulls and of centrifuge sludge. Conventional analytical chemical methods for measuring plutonium in weapons grade material can be modified for reprocessed plutonium. Analytical techniques requiring special precautions will be reviewed.

Some suggested areas for improvements in process design to facilitate materia ͻ accountability in future plants will be discussed.

KEYWORDS: Nuclear safeguards, dynamic materials accounting, in-line analysis, nuclear fuel reprocessing.

INTRODUCTION

Safeguards has become an increasingly important consideration in the public acceptance of nuclear energy. This is particularly true in the back end of the nuclear fuel cycle where large amounts of fissile material are available in a relatively pure, concentrated form. The Safeguards Systems Group at the Los Alamos Scientific Laboratory has been tasked by ERDA and DOE to design integrated materials accounting systems for various plants in the back end of the fuel cycle. To date, studies have been completed for plutonium handling in a LWR fuel fabrication plant, a nitrate-to-oxide conversion plant, and a LWR fuel reprocessing plant. Each system is based on a specific facility -- for the fuel reprocessing plant the AGNS plant at Barnwell, South Carolina (BNFP) was selected. This plant is one of the most modern reprocessing plants in the world. It was designed to reprocess 1500 MT of irradiated fuel per year, producing approximately 15 tonnes of plutonium, or on the basis of 300 operating days per year, approximately 50 kg per day of plutonium.

Design concepts and evaluation methods were developed for advanced nuclear materials management systems to safeguard in-process materials in current and future fuel reprocessing facilities. The concepts are based on a thorough evaluation of the Barnwell plant and represent minor extrapolations of existing fuel-reprocessing technology, conventional analysis, state-of-the-art nondestructive assay (NDA), and data-processing and analysis systems. Concepts applicable to domestic and foreign commercial or government-owned facilities to be built in the next decade were evaluated with simulated production data.

THE PUREX RECOVERY PROCESS

All present and currently proposed aqueous separations facilities including the BNFP are based on the Purex solvent-extraction process, developed by the US Atomic Energy Commission (AEC) in the late 1940s to satisfy military needs for weapons-grade plutonium. In the Purex process both uranium and plutonium are recovered, and the radioactive waste volumes are reduced by minimal use of nonvolatile salting agents and reactants.

Purex and its subsequent variants are based on dissolution of the irradiated fuel in nitric acid, oxidation of the contained plutonium and uranium, and coextraction of the oxidized species into an organic phase consisting of a hydrocarbon diluent containing tributyl phosphate (TBP), which forms extractable complexes with the oxidized species. The organic phase is scrubbed to remove most of the nonextractable fission products and transuranics from the coextracted fissile materials; then it is contacted with an aqueous phase that selectively reduces the plutonium, stripping it from the organic phase. The partitioned phases, the organic uranium and the aqueous plutonium, are then individually subjected to additional extraction, ion exchange, and other purification steps that eventually produce two pure product streams containing uranyl nitrate and plutonium nitrate. The scrubbing and stripping solutions from the purification and "polishing" steps are recycled along with the spent solvent streams to give a total recovery of uranium and plutonium product that can be approximately 99.9% with a net fission-product decontamination factor of more than one million.

Solvent damage from radiation exposure in the first extraction (co-decontamination) stage has always been an important problem in the operation of a Purex process. This solvent degradation poses problems for analytical chemistry as well as for the process engineer because the dibutyl and monobutyl phosphate plutonium complexes do not behave in extraction or chemical analysis schemes as does the normal TBP complex. After most of the fission products have been removed, contact time in subsequent extraction, partition, and purification steps is not nearly so important, and less vigorous means of attaining equilibrium are used in the interest of reduced mechanical complexity.

Other areas receiving attention in modified Purex processes have been the selection of suitable reductants for the partitioning step and the postpartition purification and polishing operations. The desire for reductants having minimal effect on product purity and waste volumes has resulted in the use of organic reductants that decompose to volatile products, of uranium-IV reductants that add no new material to the product, and, ultimately, of electrolytic reduction, which adds nothing to the process stream, as in the proprietary AGNS Electropulse System.[1]

BNFP is pure state-of-the-art Purex: chop-leach head end with continuous dissolution, centrifugal extraction, and electrolytic partitioning. There are two uranium-extraction cycles plus a silica-gel polishing column and two plutonium-extraction cycles. First-stage extraction is performed with the Robatel centrifugal contactor; subsequent co-decontamination, partition, and purification contactors are pulsed columns, including a proprietary Electropulse partitioning column. In this system, partition is effected by electrolytic reduction of uranium-VI to uranium-IV, which subsequently reduces plutonium-IV to plutonium-III. Considerable uranium is stripped along with the plutonium, necessitating an additional plutonium-purification step and significant back cycle. The plant uses remote maintenance at the head end and through the first cycle, and anticipates no maintenance in other areas of the plant except those in which the products have been decontaminated to the level where direct maintenance is feasible.

Because details of the AGNS design and materials flows are available and because the plant itself is in an advanced state of completion, it was selected for our safeguards modeling and design purposes.

CONVENTIONAL MATERIALS ACCOUNTING AT BNFP

The conventional materials accounting system at BNFP is based on daily analysis of the accountability tank, waste streams, and plutonium nitrate product tanks. The measurement points and precisions of analytical methods are summarized in Table 1. NRC regulations

TABLE I

CONVENTIONAL MATERIALS ACCOUNTABILITY AT BNFP

Tank	Frequency	Method	Measurement Error, 1σ
Accountability	3/day	Mass spectrometry	0.2 to 0.5%
Leached hulls	1/batch	^{144}Pr	?
HAW surge	6/day	Mass spectrometry	5 to 3%
Pu nitrate	each batch	Coulometry, amperometry	0.3 to 0.1%

specify 1% error in measuring plant throughput. Throughput is verified semiannually by flushout-cleanout and measurement of in-process holdup. Based upon a plutonium throughput of 50 kg per day, the allowable material-unaccounted-for between cleanouts is 75 kg.

Thus, one is faced with the problem that a divertor could hide sufficient plutonium for several weapons in the measurement uncertainty, and it could take up to six months before one could detect missing material. Clearly, this is an uncomfortable situation for the nuclear materials manager.

DYNAMIC MATERIALS ACCOUNTING

The basic philosophy behind dynamic materials accounting is to provide sufficient instrumentation that one can obtain near-real-time measurements of material flow rates and concentrations in all streams leading into the process area. Furthermore, the process could be divided into as many materials accounting areas as one can successfully instrument. Thus, timely material balances can be drawn about relatively small amounts of SNM. For a plant such as BNFP, the most desirable areas to instrument would be those containing the largest amounts of plutonium in a form most attractive to the divertor. The plutonium at the head end of the process is not attractive because it contains lethal concentrations of fission products and is diluted approximately 100-fold with uranium. However, after the 1B column, the bulk of the fission products have been removed and the uranium/plutonium ratio has been reduced to 2/1. From this point the plutonium becomes increasingly attractive as it proceeds through the process to the plutonium nitrate storage tanks. Hence, this area was selected for design of a dynamic materials accounting system.[2]

System Design

A schematic of the BNFP is shown in Figures 1 and 2. To isolate the plutonium purification process (PPP) (Figure 2) as a unit process requires flow and concentration measurements at the 1BP tank (input) and 3P concentrator (output). In addition, acid recycles (2AW, 3AW, 3PD) and organic recycle (2BW, 3BW) must be monitored for flow and concentration. The nominal flow rates and plutonium concentrations for these streams are summarized in Table II.

TABLE II

CONCENTRATIONS AND FLOW RATES IN THE PPP

Stream	Flow (L/h)	Plutonium Concentration (g/L)
1BP	400	5
3PCP	8	250
2AW	500	trace
3AW	215	0.1
3PD	32	trace
2BW	150	trace
3BW	105	trace

Flow Measurement

The precisions for flow measurement in the input and output streams should be 1% (1σ) or better. For the 1BF stream this can be attained with a calibrated orifice meter in the 1BP surge tank or with in-line ultrasonic or magnetic flowmeters. The flow measurement precisions for the recycle streams are less stringent; possibly air lifts could be calibrated to the order of 5-10%.

Concentration

The plutonium concentrations of input and output product streams of the PPP can be measured using absorption-edge densitometry. The Pu concentrations in the 1BP stream can be measured at the L_{III} edge using either x-ray tube[3] or bremsstrahlung sources.[4] For plutonium concentrations of approximately 5 g/L a precision of 1-2% can be obtained.[3] The 1BP stream also could be measured at the K edge using longer cells. For highly radioactive solutions a curved crystal spectrometer may be used as an energy filter for an energy dispersive detector.[5] Additional research and development is required to evaluate the effect of fission products on the method and to measure the precision and accuracy under plant conditions.

The plutonium isotopic composition and concentration at concentrations representative of the 3PCP stream for reprocessing samples can be measured using a radioisotope source at the K-absorption edge. Using a ^{75}Se-^{57}Co source as suggested by Canada,[6] Hofstetter, et al.[7] obtained a precision (1σ) of 0.2 to 0.5% for plutonium concentrations between 150-500 g/L. The plutonium isotopic composition of these samples was similar to that expected for first-cycle LWR fuel.

The recycle stream concentrations generally are expected to be less than 0.1 g/L, hence poorer measurement precision can be tolerated than for the product streams. In-line alpha monitors have been installed in these streams for process control to assure that columns are operating properly. These alpha monitors are being evaluated at the BNFP for the quantitative measurement of plutonium in flowing streams. They have been shown to have a linear response to plutonium concentration in the range between 10^4 to 10^9 dpm/mL with an alpha/beta discrimination factor of 10^4.[8] A relative precision of 5-10% (1σ) for plutonium concentrations should be obtainable.

One area that presents a problem in measuring plutonium in the plutonium purification area is the determination of in-process holdup. Capacities of the tanks and columns in this area are shown in Table III.

Approximately 22 kg the 41-kg holdup is in the 1BP tank and the concentrator, and can be estimated from the in-line concentration instruments and tank volumes. However, the amount in the columns cannot be measured accurately, and can contribute significantly to the uncertainty in plutonium content of the PPP.

An alternative to actually measuring plutonium concentration is the estimation of concentrations from a knowledge of column operation.[9] The feasibility of this approach was tested by mathematical simulation of column operation for the 2A column. A schematic of the 2A column, with flow rates into and out of the column, is shown in Figure 3. The plutonium holdup as a function of 2AF, 2AS, and 2AX flow rates was modeled using the SEPHIS code,[10] and results are summarized in Figure 4.[11] The largest variations in holdup occur at low 2AX (organic) flow rates. However, the data indicate that from a knowledge of the input stream flow rates the plutonium holdup in the column can be estimated. The accuracy of the estimate has to be verified with actual column operation.

DISCUSSION AND RESULTS

The operation of the plutonium purification process was mathematically modeled using Monte Carlo techniques.[9] The measurement points and associated errors for each point are summarized in Table IV. Four different strategies were used to evaluate the diversion sensitivity, and are summarized in Table V. The measurement errors for the four cases are

TABLE III

IN-PROCESS HOLDUP IN TANKS AND VESSELS OF THE PPP

Identification[a]	Volume (L)	Plutonium Concentration (g/L)	Plutonium Holdup (kg)
1BP tank	1500	4.942	7.4
2A column	700	b	4.6
2B column	500	b	2.8
3A column	600	b	5.4
3B column	440	b	4.8
3PS wash column	20	53.70	1.2
3P concentrator	60	250.	15.

[a] See Figure 2.

[b] A model of the concentration profiles and the holdup in the pulse columns is described in Reference 9.

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

TABLE IV

MEASUREMENT ERRORS FOR DYNAMIC MATERIALS ACCOUNTABILITY IN THE PPP

		Precision (1σ), %	Calibration Error (1σ), %
1BP	Flow	1	0.5
	Concentration	1	0.3
2AW 2BW 3AW 3BW	Flow	5	1
	Concentration	10	2
3PCP	Flow	1	0.5
	Concentration	1	0.3

TABLE V

MEASUREMENT STRATEGIES

Case	Balance Period	Recalibrate Flow	In-Process Inventory Measurement Precision (1σ), %
1	8 h	--	10
2	8 h	24 h	10
3	8 h	24 h	5
4	1 h	24 h	5

Measurement of concentration and flow every 0.25 h.

summarized in Table VI, and show that in each case measurement error is dominated by uncertainties in in-process inventory. The diversion sensitivity was determined using decision analysis theory described in a preceding paper ("Decision Analysis for Dynamic Accounting of Nuclear Material" by James P. Shipley), and is shown for cases 1 and 4 in Table VII. Improvement in diversion sensitivity is obtained by increasing measurement frequency. Note that for case 4 (1-h measurement frequency) a diversion sensitivity of 4.2 kg at the end of one week is obtained. This can be compared to the conventional sensitivity of 75 kg per six-month inventory period.

TABLE VI

MEASUREMENT ERRORS IN FOUR DYNAMIC-ACCOUNTABILITY CASES

| | Variance (kg^2 Pu) (standard deviation, kg Pu) | | | |
	Case 1	Case 2	Case 3	Case 4
Net transfers One-week average	0.022 (0.15)	0.022 (0.15)	0.022 (0.15)	0.00073 (0.027)
In-process inventory One-week average	0.98 (0.99)	0.98 (0.99)	0.36 (0.60)	0.36 (0.60)
Material balance One-week average	1.99 (1.41)	1.99 (1.41)	0.74 (0.86)	0.74 (0.86)
Cusum End of day End of week	2.13 (1.46) 8.51 (2.92)	2.13 (1.46) 3.29 (1.81)	0.89 (0.95) 1.98 (1.41)	0.89 (0.95) 1.98 (1.41)

TABLE VII

DIVERSION SENSITIVITY[a] FOR THE PLUTONIUM PURIFICATION PROCESS

Measurement Case	Average Diversion per Balance (kg Pu)	Detection Time (h)	Total at Time of Detection (kg Pu)
1 (8 h)	4.2	8	4.2
1	0.30	168 (1 week)	6.3
1	0.15	672 (4 week)	12.6
4 (1 h)	2.6	1	2.6
4	0.075	24	1.8
4	0.025	168 (1 week)	4.2

[a] As determined consistently with ERDAM Appendix 7401-C, "Nuclear Materials Management and Safeguards System Handbook."

The safeguards materials accountability improvements described in this report are based on a measurement overlay for an existing reprocessing plant. Hopefully, the system could be improved if it could be incorporated into the plant design at an early stage. The following were identified as areas of safeguards concern for future facilities of this type.

Location of Centrifuge

One source of sampling error at the input accountability tank results from 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. Consideration should be given to installing the centrifuge between the dissolver and the accountability tank, as has been done for the Japanese plant at Tokai and the proposed EXXON Nuclear Company plant.

Accountability Tank

Further consideration should be given to using load cells to measure the volume of the input accountability tank. The design must, as much as possible, isolate the tank from the associated piping. If practicable, mass measurements using load cells would be particularly advantageous for processing fuels with higher burnup or shorter cooling times, which would have higher intrinsic heat-generating capacities.

Flowmeters

Flowmeters having provision for periodic recalibration should be installed in specific crucial process streams; a measurement accuracy of 1% or better is required. A 5-10% measurement accuracy is acceptable for flowmeters in waste streams.

Concentration Sensors

In-line or at-line detectors should be incorporated to measure plutonium concentrations in major process streams with a measurement accuracy of 1% or better, and in waste streams with an accuracy of 5-20%.

Instrument Accessibility

All in-line or at-line instruments, including flowmeters and concentration sensors, should be installed in a manner that permits ready accessibility for recalibration and maintenance by plant personnel or inspection by the national or international safeguards staff. Sensors should be directly interfaced to the safeguards computer system for dynamic materials accounting.

HA Contactor

An improved decontamination factor may be attainable at the front end of the separations process by increasing the number of stages in the HA contactor, or by providing a second decontamination cycle before partition, as has been done effectively in some other facilities. The reduced radioactivity in the uranium-plutonium product stream might permit inclusion of an additional accountability point before the plutonium-process area at the HS column. This would be highly desirable both for process control and for safeguards in the event that a co-processing mode of plant operation is selected.

3P Concentrator

Concentration of the final $Pu(NO_3)_4$ from 60 to 250 g/L is primarily for convenience in storing and shipping. Under current NRC regulations co-location of reprocessing and nitrate-to-oxide conversion facilities will be required. If the concentration of the final plutonium-product solution from the reprocessing plant is maintained below 50 g/L, this solution can be used directly as feed for the conversion plant, and the 3P concentrator and associated heater and feed tanks can be eliminated. From a safeguards viewpoint, this would increase the amount of solution required to divert 1 kg of plutonium by a factor of 4 to 8, and would decrease holdup by the volume of the concentrator. In order to provide a 3- to 6-month product-storage capacity, the number of nitrate-storage tanks would have to be increased proportionally unless the plutonium-product output were directly coupled to the input of a contiguous conversion plant.

Centrifugal Contactor

In general, in-process inventory can be reduced by a factor of 20 by using centrifugal contactors in place of pulsed columns in the plutonium-purification area.[12] Using a French-designed eight-stage contactor, the pulsed columns in the plutonium-purification

area could be replaced as follows:

2A column - 9 contactors
2B column - 3 contactors
3A column - 4 contactors
3B column - 2 contactors.

In addition to low holdup, centrifugal contactors provide added advantages of rapid drain-down with negligible drain-down volume, and rapid startup after shutdown. Disadvantages include relatively low flow rates of 100 L/h in both aqueous and organic phases, greater accessibility of material to possible diversion, and more stringent design requirements for optimizing organic/aqueous flow ratios.

CONCLUSIONS

The primary conclusion from this study is that current technology can provide improved procedures for safeguarding strategic quantities of SNM in a nuclear-fuel reprocessing facility at a reasonable cost and with minimal disruption of production processes. The system design must be facility-specific for each reprocessing plant, taking into consideration such features as plant throughputs, side streams, materials control philosophy, and equipment maintenance features. The formation of a dynamic materials balance area around the plutonium-process area adds another level of safeguards protection of plutonium in its most concentrated and pure form, the form most attractive to a potential divertor.

The study has also identified generic features and processes in the reference facility that contribute most importantly to measurement uncertainties and that could be improved in future facility designs if they were to be optimized for their safeguardability.

REFERENCES

1. "Barnwell Nuclear Fuels Plant Separations Facility--Final Safety Analysis Report," ocket 50-332, Allied-General Nuclear Services, 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. E. A. Hakkila, R. G. Hurley, G. . . Waterbury, "Three-Wavelength X-Ray Absorption Edge Method for Determination of Plutonium in Nitrate Media," Anal. Che . 38, 425-427 (1966).

4. T. R. Canada, S. T. Hsue, D. G. Langner, E. R. Martin, J. L. Parker, T. D. Reilly, and J. W. Tape, "Applications of the Absorption-Edge Densitometry NDA Technique to Solutions and Solids," Nucl. Mater. Manage. VI, No. III, 702-710 (1977).

5. 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.

6. T. R. Canada, J. L. Parker, and T. O. Reilly, "Total Plutonium and Uranium Determination by Gamma-Ray Densitometry," ANS Trans. 22, 140-142 (1975).

7. K. .'. 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," Twenty-First Conference on Analytical Chemistry in Energy Technology, Gatlinburg, Tennessee, October 4-6, 1977.

8. K. J. Hofstetter, G. M. Tucker, J. H. Gray, and C. A. Huff, "Applications of On-Line Alpha Monitors to Process Streams at the Barnwell Nuclear Fuel Plant," 1978 Spring Meeting. American Chemical Society, Anaheim, California, March 13-17, 1978. To be published in American Chemical Society Symposium Proceedings Series.

9. D. D. Cobb, "Appendix G: Dynamic Model of the Plutonium Purification Process," in Coordinated Safeguards for Materials Management in a Fuel Reprocessing Plant, Vol. II, Los Alamos Scientific Laboratory report LA-6881 (September 1977).

10. G. W. Reddick, "Solvent Extraction in HTGR Reprocessing Interim Development Report," General Atomic report GA-A13835 (1976).

11. B. M. Legler, "Sensitivity Analysis for Plutonium Holdup in the 2A Column," personal communication, May 4, 1976.

12. A. F. Cermak, Allied-General Nuclear Services, personal communication, August 15, 1977.
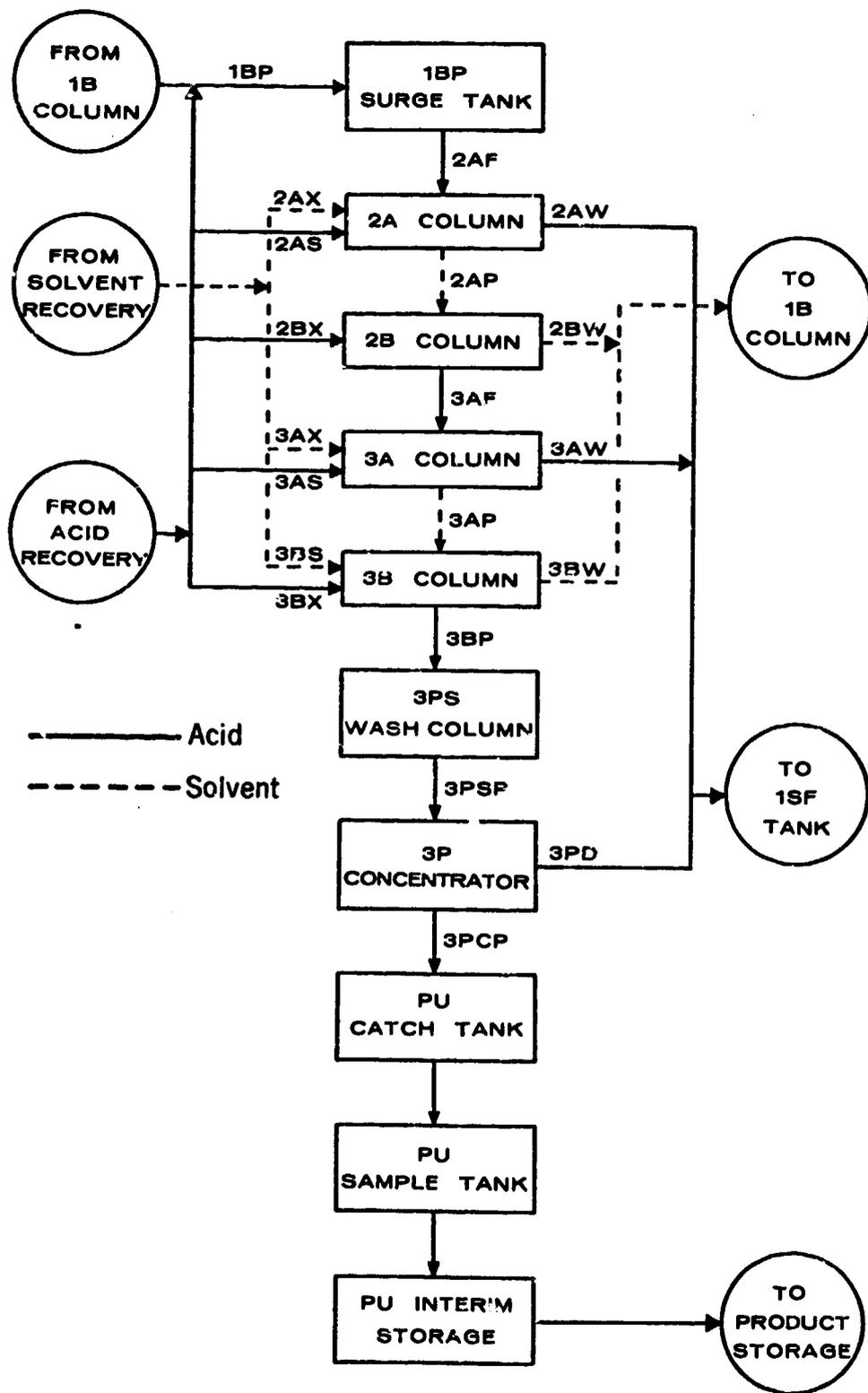
Figure 2. Plutonium purification process block diagram.
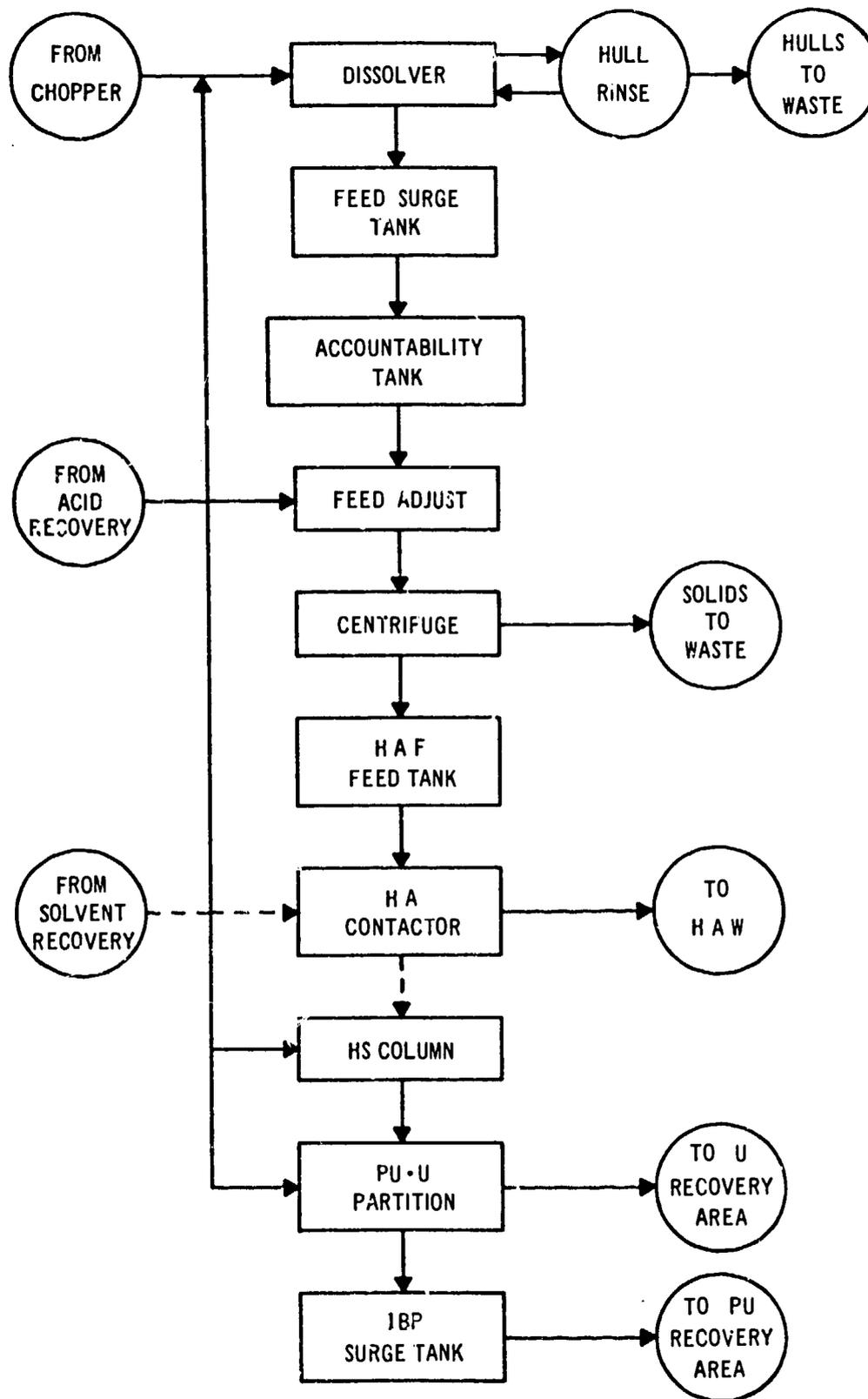
Figure 1.   Dissolver-separations process block diagram.
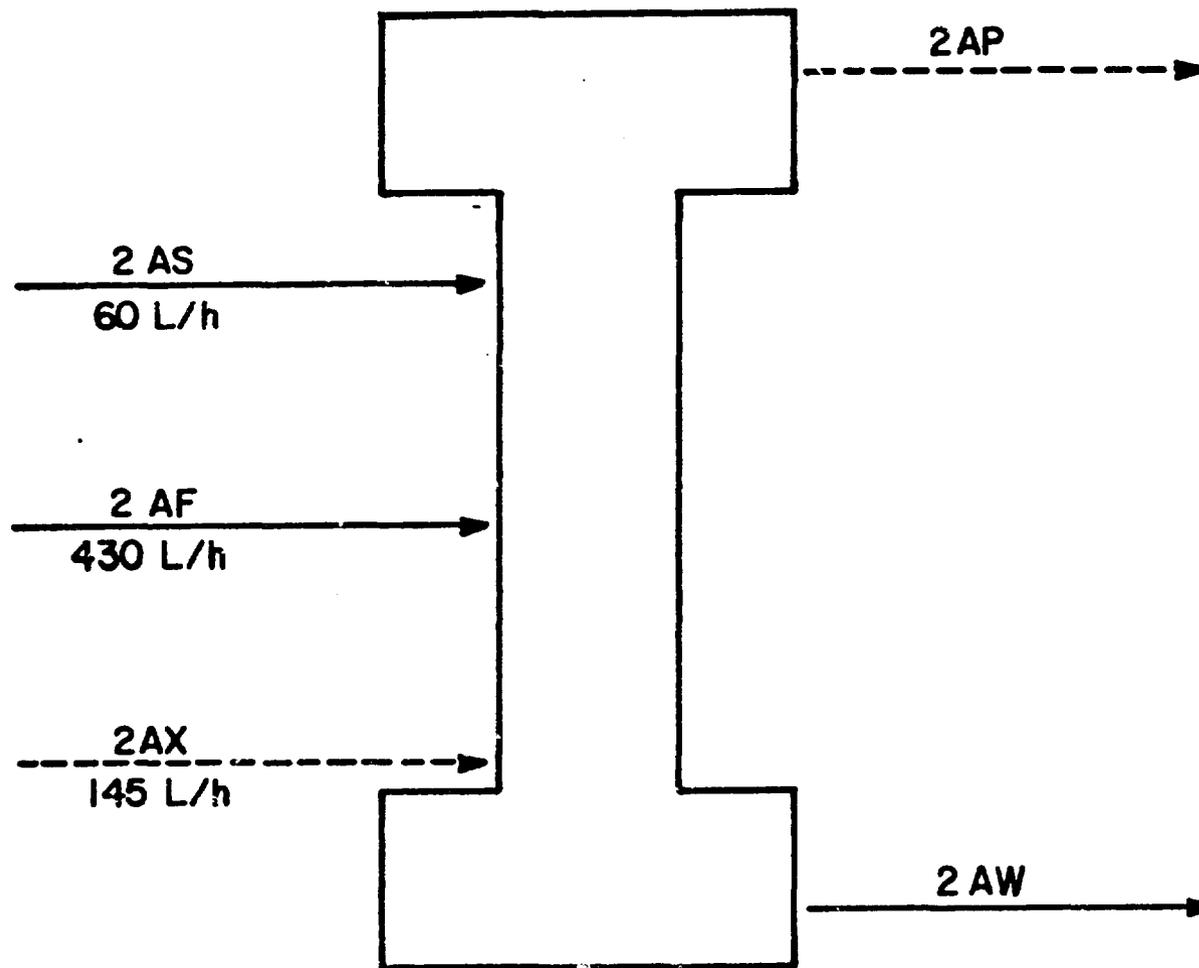
Figure 3. Schematic of 2A column.
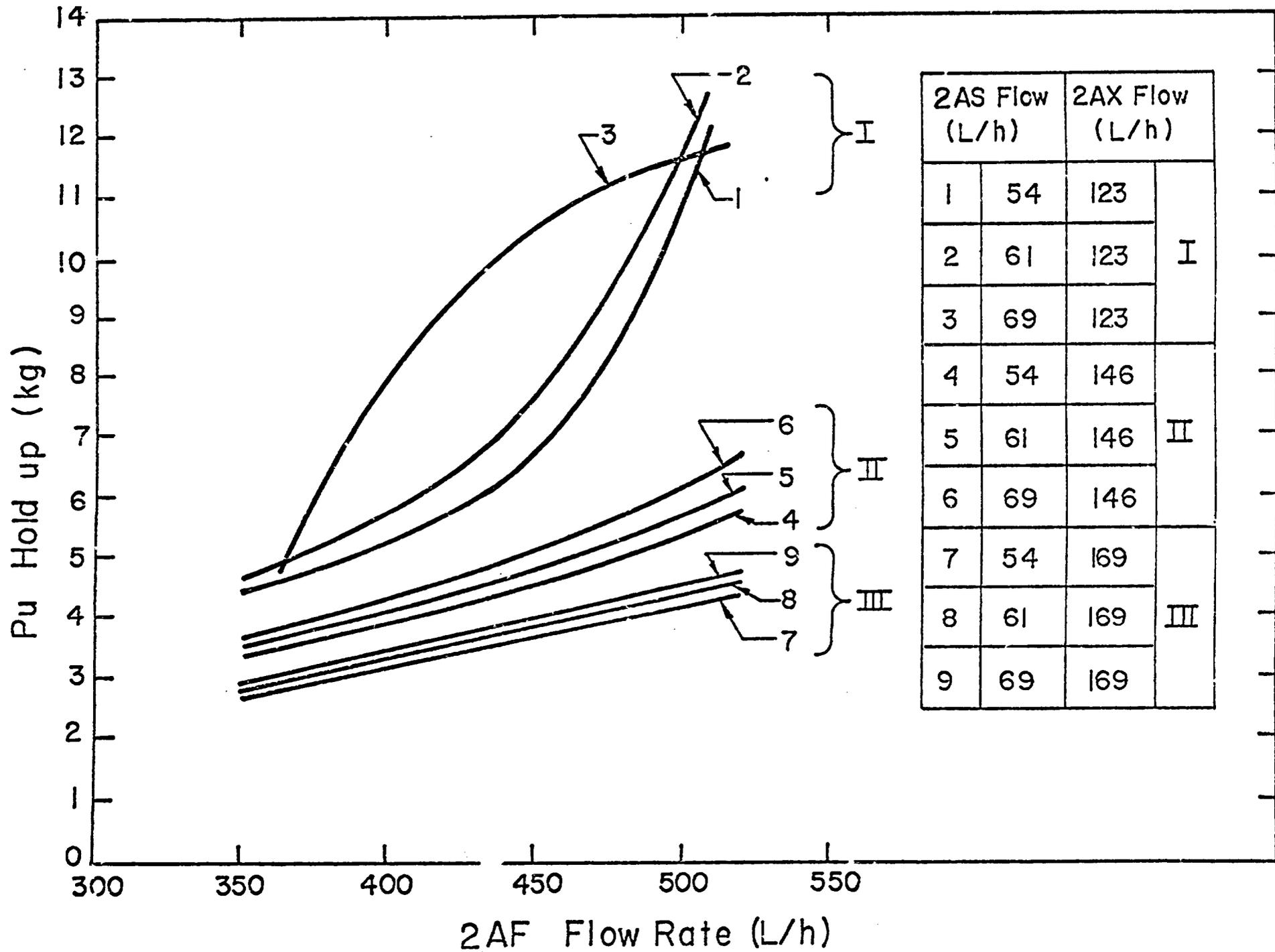
Figure 4. Pu holdup as a function of 2AF, 2AS, and 2AX flow rates.