PNL-SA-9360

CONF-810706--37

CALCULATING THE INVENTORY OF SOLVENT EXTRACTION COLUMNS FOR MATERIAL BALANCES WITHOUT SHUTDOWN

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PNL-SA--9360

DE82 006885

JULY 1981

FOR PRESENTATION AT THE
22ND ANNUAL MEETING OF THE
INSTITUTE OF NUCLEAR MATERIALS MANAGEMENT
SAN FRANCISCO, CALIFORNIA
JULY 13-16-1981

WORK PERFORMED FOR THE
OFFICE OF NUCLEAR REGULATORY RESEARCH
U.S. NUCLEAR REGULATORY COMMISSION
FIN NO. B-2134

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CALCULATING THE INVENTORY OF SOLVENT EXTRACTION COLUMNS FOR MATERIAL BALANCES WITHOUT SHUTDOWN*

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ABSTRACT

This study demonstrates a feasible way to determine the nuclear material inventory of solvent extraction columns for calculating material balances without process shutdowns. An existing computer code, SEPHIS, was used to calculate the inventories in the solvent extraction cycles of a uranium recovery process. The applicability of the method was tested using published data on the uranium concentration profiles of solvent extraction pulse columns. The application of this method to the extraction cycles of the uranium recovery process is presented for daily uranium loss monitoring over those process units.

INTRODUCTION

Special nuclear material (SNM) loss detection capabilities can be improved by focusing on small segments of the process over short time intervals rather than on entire material balance areas over time periods of 60 days or more. One approach to upgrading the timeliness and sensitivity of SNM loss detection may be the use of process, production. and quality control data to monitor for losses over small segments of the process and over short time intervals. Loss monitoring in this manner generally requires a means of determining the in-process inventories of SNM. For continuous processes, the inventory determinations should be accomplished without shutdown. This presents a measurement problem not encountered in the batch or campaign processing modes of operation of several recent studies of methods of prompt loss detection (Miles et al. 1979; Brouns et al. 1980; Hawkins et al. 1980; Glancy et al. 1980).

A study was conducted for the Nuclear Regulatory Commission by the Pacific Northwest Laboratory to determine if loss detection timeliness of about one day plus improved localization and sensitivity are feasible. As part of that study, material accounting over individual processing operations was tested on several examples of classical process models. One model was a high-enriched uranium recovery process involving continuous solvent extraction operations. This paper presents an example of daily SNM monitoring in the solvent extraction cycle in which the column inventories are calculated using a computer code. An existing program, called SEPHIS (Richardson 1973), for calculating the concentrations in Purex process solvent extraction contactors was used to calculate the equilibrium uranium profiles in the extraction columns of this process. From these data, the column inventories were calculated and the variance of each column inventory was estimated. The process flow and composition data, uranium profiles of the columns, and inventory values are presented in this paper.

THE MATERIAL ACCOUNTING SYSTEM

The uranium scrap recovery process was modeled for a feed rate of 9.6 kg of high enriched uranium per day and a five-day-per-week continuous operation. The scrap feed. consisting of rejected Zircaloy clad fuel elements, laboratory and metallurgical residues, cleanup powders, concentrates from liquid waste evaporation, and incinerator ash, is dissolved in HNO_3 and HF with aluminum ion complexing for corrosion control. The dissolver solution is centrifuged and made into feed batches for processing. Two cycles of Purex solvent extraction in pulse columns are used with intervening concentration to ~100 g/ℓ uranyl ion. After the second cycle, the product is concentrated and converted to U_3O_8 by a diuranate batch precipitation process.

An example of a material accounting control unit in this process is shown in Figure 1. The first Purex extraction cycle is shown with the process control and accountability measurement points indicated by circled numbers. Most of the process data used for uranium accounting in this model are hourly flow rates and ^{235}U assays of solution samples using a gamma well counter. The nominal flows and concentrations of this solvent extraction cycle are given in Table 1.

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*Work performed for the Office of Standards Development, U.S. Nuclear Regulatory Commission Under Contract DE-AC06-76RLO 1830 FIN No. B21341

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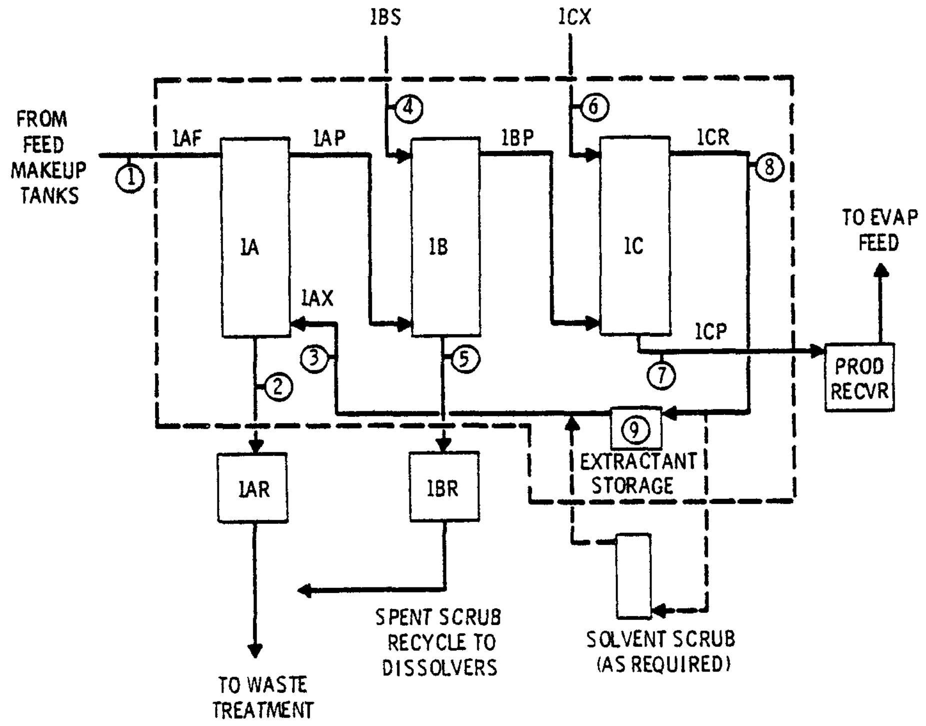

MEASUREMENT POINT	DATA COLLECTED
1	HOURLY FLOW RATE; ^{235}U CONCENTRATION KNOWN FROM ANALYSIS OF FEED BATCHES
2, 5, 7	HOURLY FLOW RATES AND ^{235}U CONCENTRATIONS
9	^{235}U INVENTORY AT END OF EACH CONTROL PERIOD
2, 3, 4, 6, 8	OTHER PROCESS CONTROL DATA (FLOW CONTROLS AT ALL POINTS AND ^{235}U MONITORING BY IN-LINE GAMMA COUNTER AT POINTS 2 AND 8)

FIGURE 1. Example Control Unit - First Cycle Extraction

TABLE 1. Flows and Concentrations in First Cycle Extraction

	1AF(a)	1AX	1AR(a)	1AP	1BS	1BR	1BP	1CX	1CP	1CR
Flow, ℓ/hr	143.0	140.0	143.0	140.0	28.0	28.0	140.0	70.0	70.0	140.0
U, g/ℓ	3.07	0.006	<0.005	3.13	0	0.02	3.12	0	6.23	0.005
H, M	1.5	0	1.3	0.2	0	0.5	0.1	0.01	0.2	<0.01
F, M	3.8	0	3.8	(t)	0	(t)	0	0	0	0
Al, M	0.7	0	0.7	0	1.3	1.3	0	0	0	0
Zr, M	0.6	0	0.6	(t)	0	(t)	0	0	0	0
TBP, %	-	10	-	10	-	-	10	-	-	10

(a) Several minor constituents omitted.
(t) = trace.

To test for uranium losses from this control unit, a material balance is calculated at 24-hour intervals as follows:

$$\Delta = \Sigma(U_iF_iT_i)_1 - \Sigma(U_iF_iT_i)_2 - \Sigma(U_iF_iT_i)_5 - \Sigma(U_iF_iT_i)_7 + (U_9V_9)_B - (U_9V_9)_E + U_{inv}(1A + 1B + 1C)_B - U_{inv}(1A + 1B + 1C)_E$$

where

Δ = inventory difference

$\Sigma(U_iF_iT_i)_j$ = the sum for the 24-hour period of the product of uranium concentration, flow rate, and time interval for each reading at measurement point j

V_9 = volume in the extractant storage tank; the B and E subscripts signify beginning and ending inventory measurements

$U_{inv}(1A + 1B + 1C)$ = sum of the inventories of the three pulse columns.

The inventory difference would be tested for significance with respect to a multiple of the standard deviation of Δ, e.g., $2\sigma_\Delta$.

DETERMINING THE EXTRACTION SYSTEM INVENTORIES

The principal computational problem in this example was the determination of column inventories and the associated variance. The uranium in a solvent extraction column is distributed between the organic and aqueous phases and the concentrations vary throughout the column. Direct measurement of the uranium inventory in an operating column has not been demonstrated although a method using NDA instruments suggested by Morrison and Blakeman (1979) may be feasible. However, the inventory can be calculated if the profiles of uranium concentration and volumes of the phases in each contactor stage are known. Computer codes have been developed for calculating uranium profiles in solvent extraction contactors of dilute Purex process systems. Reviews of the status and capabilities of these codes have been published recently (Cobb et al. 1980a; Cobb et al. 1980b).

A computer code entitled SEPHIS, developed at ORNL (Groenier 1972), was available in a version modified by G. L. Richardson (1973 and 1975) for estimating the extraction column profiles of Purex pulse columns. However, the code does not provide for the presence of interacting cationic and anionic species such as zirconium, aluminum, and fluoride ions that are present at moderately high concentrations in the feed to the first extraction cycle of this scrap recovery process. To handle this situation, an empirical equation was developed for a salt strength term to be inputted to the code as the "inextractable salt" in the feed composition. The equation was derived and tested using published data for zirconium and aluminum containing feeds in the Purex process at the Idaho Chemical Processing Plant (Offutt et al. 1968; Henry et al. 1971; Henry et al. 1973). The results of the tests of the SEPHIS calculations using the salt equation are given in Table 2.

The data in Table 2 show comparisons of the flowsheet (measured) uranium and acid concentrations in the principal streams with the SEPHIS calculated values. The agreement is generally good considering the high concentrations of Al, F, and Zr ions in the feed streams. For the five cases shown, these ion concentrations in the 1AF had the following range of values:

Al^{+3}	0.52 to 0.66 M
F^-	3.3 to 4.29 M
Zr^{+4}	0.5 to 0.68 M

The uranium inventories of the columns calculated from the SEPHIS-generated uranium profiles would probably be in good agreement with actual inventories because the calculated concentrations of uranium in the high-concentration stages of the columns, i.e., the 1AP, 1BP, and 1CP values, are usually within a few percent of the flowsheet values. The 1BR is not well predicted by SEPHIS but it has a low flow rate and consists of only about a 2% recycle of uranium back to the 1A column feed point.

APPLICATION TO THE URANIUM SCRAP RECOVERY PROCESS

Using the unextractable salt equation, the SEPHIS code was used to calculate the uranium profiles and inventories of each column of the first extraction cycle of the uranium scrap process operating under equilibrium conditions. The stream compositions and flow rates for that process were shown in Table 1. The column dimensions, stage volumes, number of stages, and phase volume ratios assumed are given in Table 3.

The calculated average uranium concentrations and inventories for each stage in the columns are given in Table 4 and a plot of the uranium profiles is shown in Figure 2. The total uranium inventories of the columns for the given flowsheet conditions (Table 1) are 38.7, 49.1 and 199.2 grams for the extraction, scrub and strip columns, respectively. These results are obtained from the data in Table 4 by adding the inventories of the disengaging sections to the within-stage inventories given.

VARIANCE OF THE INVENTORY ESTIMATES

The SEPHIS program was also used to generate data from which the variance of each column inventory was estimated. This was done by determining the effect on the inventory of variations of the input parameters, such as feed solution concentrations and flow ratios. Each parameter

TABLE 2. Comparison of Calculated and Published Flowsheet Data for the First Extraction Cycle

	Flowsheet Reference(a)									
	IN-1091 Fig. 2		IN-1091 Fig. 14		IN-1091 Fig. D-1		IN-1471 Fig. 1		IN-1471 Fig. 3	
Percent TBP	5		10		10		5		5	
Constituent	M U	M H+	M U	M H+	M U	M H+	M U	M H+	M U	M H+
1AF	3.48-3(b)	2.07	4.53-3	1.66	3.95-3	1.88	4.07-3	2.06	3.45-3	1.80
1AR-Flowsheet(c)	1.7-5	2.02	3.4-6	1.51	1.68-5	1.74	4.6-6	1.95	2.1-6	1.69
-Calculated	1.8-5	2.02	9.4-7	1.53	2.7-6	1.75	1.1-5	2.0	6.0-6	1.75
1AP-Flowsheet	5.6-3	0.08	4.7-3	0.15	3.66-3	0.15	6.05-3	0.16	5.08-3	0.16
-Calculated	5.5-3	0.09	4.7-3	0.14	4.2-3	0.14	6.0-3	0.092	5.08-3	0.087
1BR-Flowsheet	0.84-3	0.55	2.5-3	2.1	0	0	1.51-3	0.91	4.2-4	0.44
-Calculated	0.52-3	0.54	1.6-4	0.61	3.8-5	0.34	6.2-4	0.44	5.2-4	0.42
1BP-Flowsheet	5.4-3	0.001	4.6-3	0.01	3.66-3	0	5.9-3	0	5.0-3	0
-Calculated	5.4-3	0.011	4.7-3	0.03	4.2-3	0	5.9-3	0	5.0-3	0
1CP-Flowsheet	11.2-3	0.007	8.4-3	0.02	9.41-3	0.005	9.16-3	0.005	8.5-3	0.005
-Calculated	11.3-3	0.028	8.5-3	0.06	9.4-3	0.005	9.2-3	0.005	8.5-3	0.005
1CR-Flowsheet	4.2-7	0	3.4-6	-	3.36-6	-	4.2-7	0	2.1-6	-
-Calculated	1.2-8	0	2.1-7	5.5-6	3.2-8	4.0-6	2.0-9	1.4-6	1.8-9	1.4-6

(a) Reports IN-1091 (Offutt, G. F. et al. 1968) and IN-1471 (Henry, R. N. et al. 1971).

(b) 3.48 x 10^{-3} M.

(c) The IAR and ICR are low level raffinates routed to waste processing but 1BR is recycled to the 1A feed and blended with the 1AF.

TABLE 3. First Cycle Extraction Columns (12.7-cm^2 Diameter, 126.68-cm^2 Cross Sectional Area)

	Extraction	Scrub	Strip
Number of Stages	4	2	2
Average Stage Height (cm)	156	152	213
Stage Volume (ℓ)	19.7	19.5	27.2
Disengaging Sections (ℓ)	5.75	5.75	5.75
Aqueous to Organic Phase Ratios in the Dispersion Region	3	3	3

was varied by an amount approximately equal to the standard deviation of its measurement. The resulting variations of the column inventories are assumed to be the effect of expected random variations around nominal values.

A summary of the parameter variation tests and their effect on column inventories is given in Table 5. The percentage variation of the parameters is referred to as the parameter "error." Since the parameter errors are expected to be independent, the overall effect on the inventories was estimated by a simple sum of squares. The square root of this sum is given for each column in the bottom row of the table.

The data of Table 5 indicate that the inventories of all three columns are affected most by the concentration of uranium in the 1AF stream and by the 1AF and 1AX flow rates. The 1A column inventory is also moderately affected by the 1AF salting strength, TBP concentration in the 1AX stream, and column temperature. The 1C column inventory is also affected by the TBP concentration, the acidity of the 1AF stream, the 1BS salt strength, and column temperature. From these data the standard deviation of the calculated

TABLE 4. Uranium Concentration Profiles and Column Inventories in First Cycle Extraction

	Stage Average Uranium Concentrations					
Section	Aqueous Phase		Organic Phase		U Inventories	
& Stage	M-U	g/ℓ	M U	g/ℓ	Moles	Grams
Extraction						
1	1.886-6	0.00044	2.508-5	0.00589	1.508-4	0.0354
2	7.002-6	0.00165	9.827-5	0.0231	5.852-4	0.137
3	7.921-5	0.0186	1.107-3	0.260	6.595-3	1.55
4	1.074-3	0.252	1.328-2	3.121	8.094-2	19.02
Scrub:						
1	7.288-5	0.0171	1.329-2	3.123	6.619-2	15.55
2	5.890-5	0.0138	1.330-2	3.126	6.603-2	15.52
Strip:						
1	2.644-2	6.213	3.300-3	0.776	5.619-1	132.05
2	6.526-3	1.534	3.183-5	0.0075	1.333-1	31.33

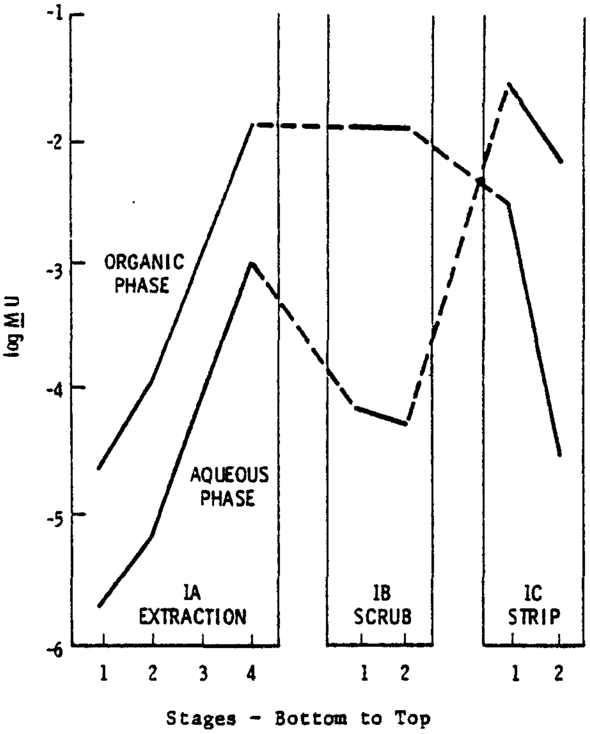

FIGURE 2. Uranium Concentration Profiles -1st Cycle Extraction Columns

column inventories is estimated to be in the range of 10-15% for this processing model under steady-state operation.

The calculated inventories are also subject to bias because of the approximations that are inherent in the structure of the code. Consequently, the predicted column profiles often differ from experimentally determined values (Cobb et al. 1980a; Groenier 1972). However, an inventory bias will cancel in the equation for a material balance if the magnitude of the bias remains constant over the range of operation of the extraction system.

CONCLUSIONS

The use of computer calculated extraction column inventories is proposed as a way to estimate inventories for loss monitoring in an accounting control unit of a continuous extraction process. A recalculation of each inventory of an accounting period, such as every 24 hours, would be rapid and inexpensive. The accuracies and variances of the calculated inventories should be verified by experimental measurements of the extraction column profiles for the specific process conditions used.

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*All of these documents, except Morrison, 1979 and Cobb, 1980b, are available from the National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161.

TABLE 5. Effect on Uranium Inventories of Errors in SEPHIS Input Terms

Parameter	Relative Error, %	Relative U Inventory Error, %			
		1A	1B	1C	Total of Three Columns
TBP Concentration	5	1	~0	3	2
1AF Flow Rate	5	5.3	5.4	5	5.2
1AX Flow Rate	5	5.3	5	2	~0
1AF U Concentration	10	10	10	10	10
1AF Acidity	10	1	~0	2	1
1AF Salting Strength	10	3	~0	1	~0
1BS Salting Strength	10	~0	~0	2	1.5
Operating Temperature, °C	5°C	2	~0	2.5	2
Extimated Standard Deviation	-	13	12.4	12.4	12

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