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Plutonium Flowsheet Development in Miniature Mixer-Settlers

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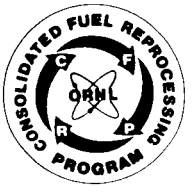

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the Department of Energy
Technical Information Center
P.O. Box 62, Oak Ridge, Tennessee 37830

ORNL/TM-7408
Dist. Category UC-86
~~(Applied)~~

Contract No. W-7405-eng-26

Consolidated Fuel Reprocessing Program

PLUTONIUM FLOWSHEET DEVELOPMENT IN MINIATURE MIXER-SETTLERS

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Chemical Technology Division

Date Published: May 1981

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ABSTRACT

Initial runs were completed in a new solvent extraction facility that has been built for testing coprocessing flowsheets with simulated LWR and FBR fuel solutions. The equipment, which is assembled in glove boxes, includes three 16-stage miniature mixer-settler banks with associated in-line monitors, pumping equipment, and sampling apparatus.

Following shakedown runs with solutions containing uranium only, two flowsheet test runs were made with a simulated LWR fuel solution (U/Pu = 100). The solution was fed to an extraction-scrub bank, where 30% tributyl phosphate in normal paraffin hydrocarbon diluent was used to coextract uranium and plutonium. The extract was fed to a second mixer-settler bank, where all of the plutonium was stripped into an aqueous product stream using hydroxylamine nitrate for plutonium reduction; a controlled fraction of the uranium was simultaneously stripped to produce a U/Pu ratio of ~2. The amount of the uranium stripped with the plutonium was regulated by careful control of an organic backscrub stream. Finally, the residual uranium in the solvent was stripped in the third mixer-settler bank.

The success of the experiments depended on precise control of very low liquid flow rates, and on in-line monitors which indicated the uranium or total heavy-metal concentrations. The most useful in-line device was the Mettler/Paar density meter, from which metal concentrations could be determined to within ~1 g/L. A miniature spectrophotometer also gave promising results for uranium analysis.

Preliminary use of a Hewlett-Packard data acquisition system was satisfactory; recorded variables were temperature, solution density, liquid flow rates, and liquid levels. Application of the system is being expanded to include control of solution concentrations from an in-line density meter. Work was completed on feed solutions of LWR composition, and preparations were begun for flowsheet experiments with feed streams of FBR composition (~10% plutonium).

1. INTRODUCTION

A new solvent extraction system with mini-mixer-settler contactors has been assembled in connecting alpha glove boxes in Building 3503. This system is being used to test uranium-plutonium flowsheets and evaluate new process options with simulated feeds prior to testing of the flowsheets with irradiated fuel solutions in the ORNL Solvent Extraction Test Facility. It also provides a test bed for in-line instrumentation which will be used to control the solvent extraction process.

Principal emphasis in the test program is on development of coprocessing flowsheets for LWR and FBR fuel types. In the coprocessing concept, the plutonium is not separated completely from the uranium as has been traditional in the Purex process. Instead, it is maintained as the minor component of the uranium-plutonium mixture throughout the processing steps, including preparation of mixed oxides for recycle. This report describes the facility and the results of both the shakedown runs (with uranium only) and the first two plutonium runs.

2. DESCRIPTION OF FACILITY

The solvent extraction contactors consist of three 16-stage mini-mixer-settler banks that are installed in alpha glove boxes in Building 3508 (Fig. 1). Also within the glove boxes are transfer pumps, in-line process monitors, the uranium-plutonium feed tank, and solution receivers. All feed streams not containing plutonium or uranium are metered from facilities outside (Fig. 2).

The three banks of mini-mixer-settlers are installed in a 1.8-m (6-ft)-long glove box. Flexible connections of 3.2-mm (1/8-in.)-diam and 1.6-mm (1/16-in.)-diam Teflon tubing were used to introduce aqueous and organic streams to any chosen mixing chamber (Fig. 3). The organic phase generally flows from right to left, with transfer pumps providing a means for automatically controlling and recording the flow between mixer-settler banks A (extraction) and B (partitioning), and between B and C (stripping). The aqueous phase flows from left to right through

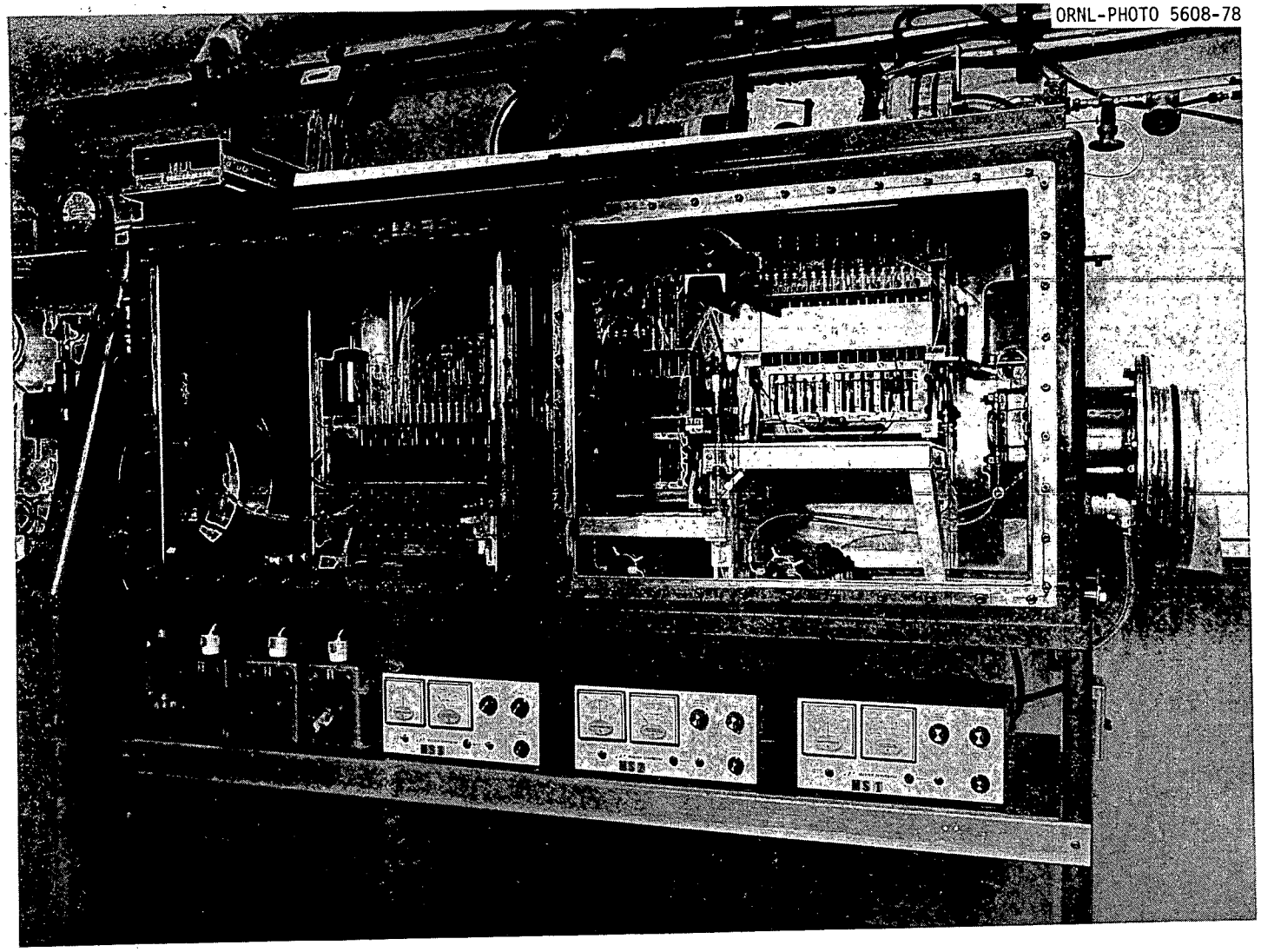

Fig. 1. Installation of three mini-mixer-settlers in an open glove box. Heater controls and agitator drive controls are located below the glove box.

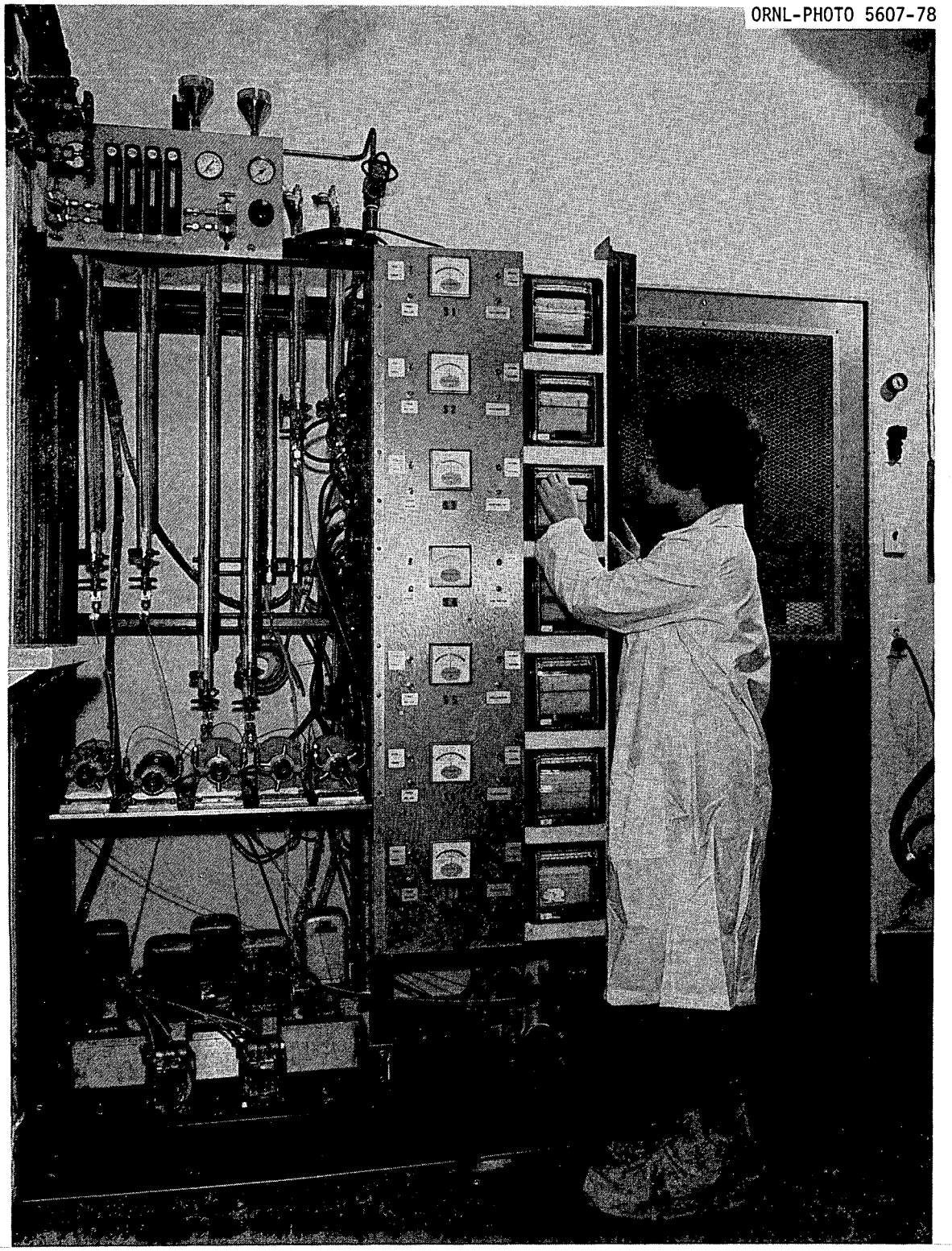

Fig. 2. Liquid metering system. Flow-measuring capillaries, 1.07 mm ID and 1.2 to 4.6 m long (0.042 in. ID and 4 to 15 ft long), permit automatic control and recording of flow rates.

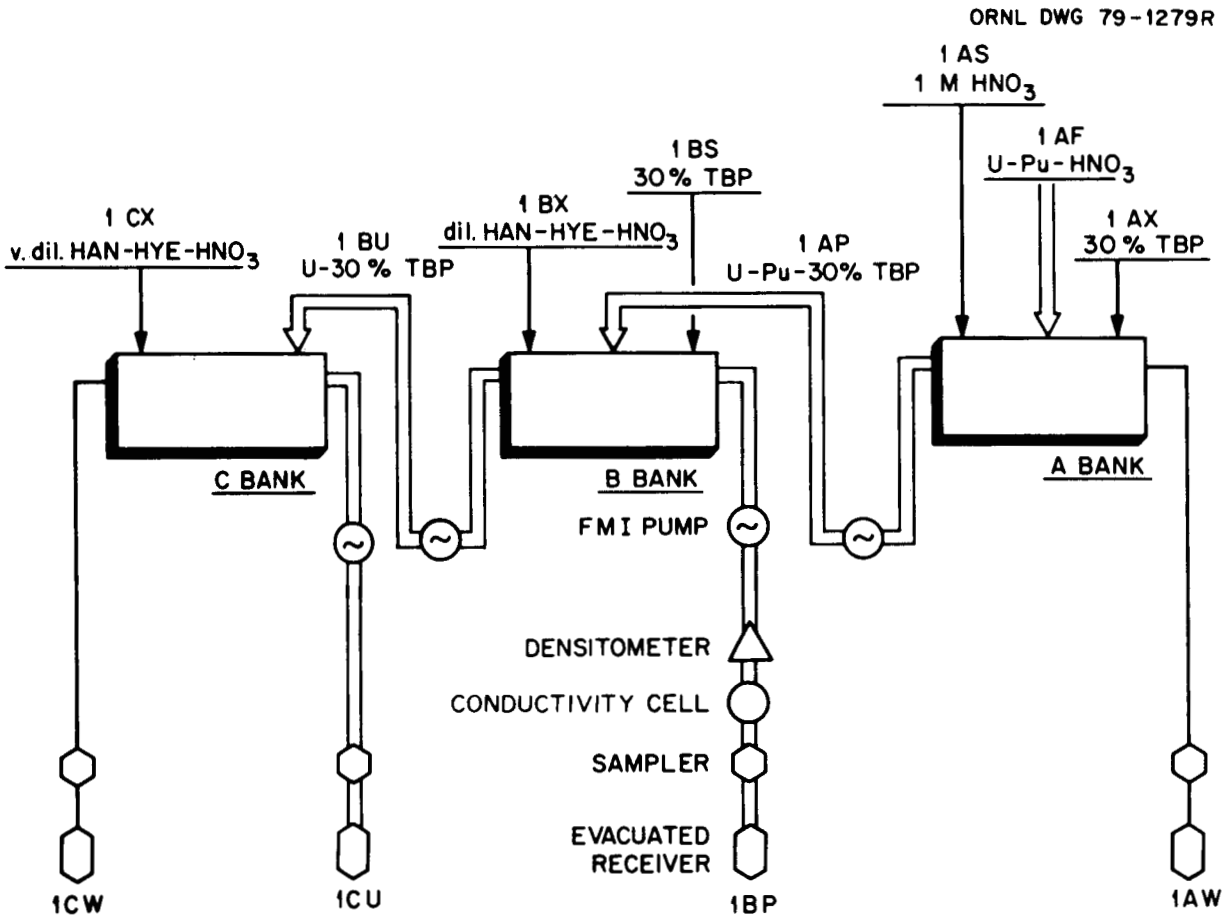

Fig. 3. Equipment flowsheet for plutonium-uranium partitioning experiment PX-3. HAN = hydroxylamine nitrate; HYE = hydrazine nitrate.

the individual mixer-settler banks and leaves each bank by overflowing a a weir. The aqueous streams are collected by vacuum transfer in glass receivers located in the connecting glove box. In-line process monitors were most frequently located in the 1BP product stream. The facility is described in more detail in the subsections that follow.

2.1 Mixer-Settlers

Three identical banks of mixer-settlers were fabricated according to drawings provided by the Savannah River Laboratory. Machined from stainless steel and faced front and back with Pyrex cover plates, each mixer-settler bank is made up of alternating mixing chambers and settling chambers on each side, similar to the original KAPL* design. Liquid holdup volumes are ~3.5 mL for each mixing chamber and ~11.2 mL for each settling chamber, for a total solution volume of ~235 mL for an individual bank.

Agitation of the 16 mixing chambers in each contactor was provided by square-edged, four-paddle, 6.4-mm (0.25-in.)-diam agitators, which were driven by a single 0-3000 rpm servomotor through an array of gears. The agitator speed was controlled by manually setting the desired value for the front mixers (the rear mixers operated at a 10% higher rate because of the gearing) and verifying the actual value with a photo-tachometer. The submergence of the agitators also affected the degree of agitation, the pumping rate between stages, and the position of the organic-aqueous interface. Therefore, suitable agitator settings were determined by some trial-and-error experiments performed at a fixed rotational speed, using reference flowsheet conditions. Following this, the agitator speed was increased in ~50-rpm increments in order to establish a value just short of producing organic-phase underflow. The resulting speeds were ~1550, ~1550, and ~1600 rpm for banks A, B, and C respectively.

Sampling was required to document the steady-state compositions. The volume of each sample had to be limited to about 1 mL because of the

*KAPL = Knolls Atomic Power Laboratory.

small volume available in the settlers. For this purpose, a permanent array of 32 Vacutainer* holders was mounted above the gear box on each mixer-settler with 1.6-mm (1/16-in.)-diam stainless steel tubes projecting into the organic or aqueous phase of all settling chambers. The Vacutainers were adjusted to the vacuum required to withdraw the desired volume, in the 1- to 3-mL range, by pumping them down in a device designed and built for that purpose (Fig. 4).

2.2 Control of Liquid Flow Rate

The required liquid feed rates to the mixer-settlers fall in the range 0.1 to 4 mL/min, and the desired precision is approximately ±5% or better. In order to provide maximum flexibility in the metering systems, they were designed around a valveless pump head with wetted parts of alumina and Teflon (Model RH1CKC, Fluid Metering, Inc., Oyster Bay, N.Y.) having variable displacements of 10 to 100 μL per revolution. Gear-head servomotors (0 to 100 rpm) were coupled to the pump heads. Modifications to the servomotor controllers (586 BV, Electrocraft Corp.) and interfacing with Foxboro pneumatic recorder-controllers were specified by J. M. Madison and D. R. Miller, of the ORNL Instrumentation and Controls Division.

The completed metering system (Fig. 5) included a small calibration tube for the purpose of periodically verifying the flow rates indicated by the capillary pressure drop. In addition to the automatic control mode of operation, manual control was possible with either the Foxboro or the Electrodyne controller. The same basic system was also used for two transfer pumps (1AP and 1BU streams) located within the glove box; these were automatically controlled from a level signal from an 8-mm-ID by 150-mm-high "surge tank" on the suction of each pump.

The flow rates reported here are not based on the capillary pressure drop data, but on the more direct measures provided by calibration tank pump-down rate and the feed-tank depletion rate (linear regression of level vs time). However, experience with the system demonstrated that

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*Vacutainer is a registered trademark of Becton-Dickinson and Co., Paramus, N.J.

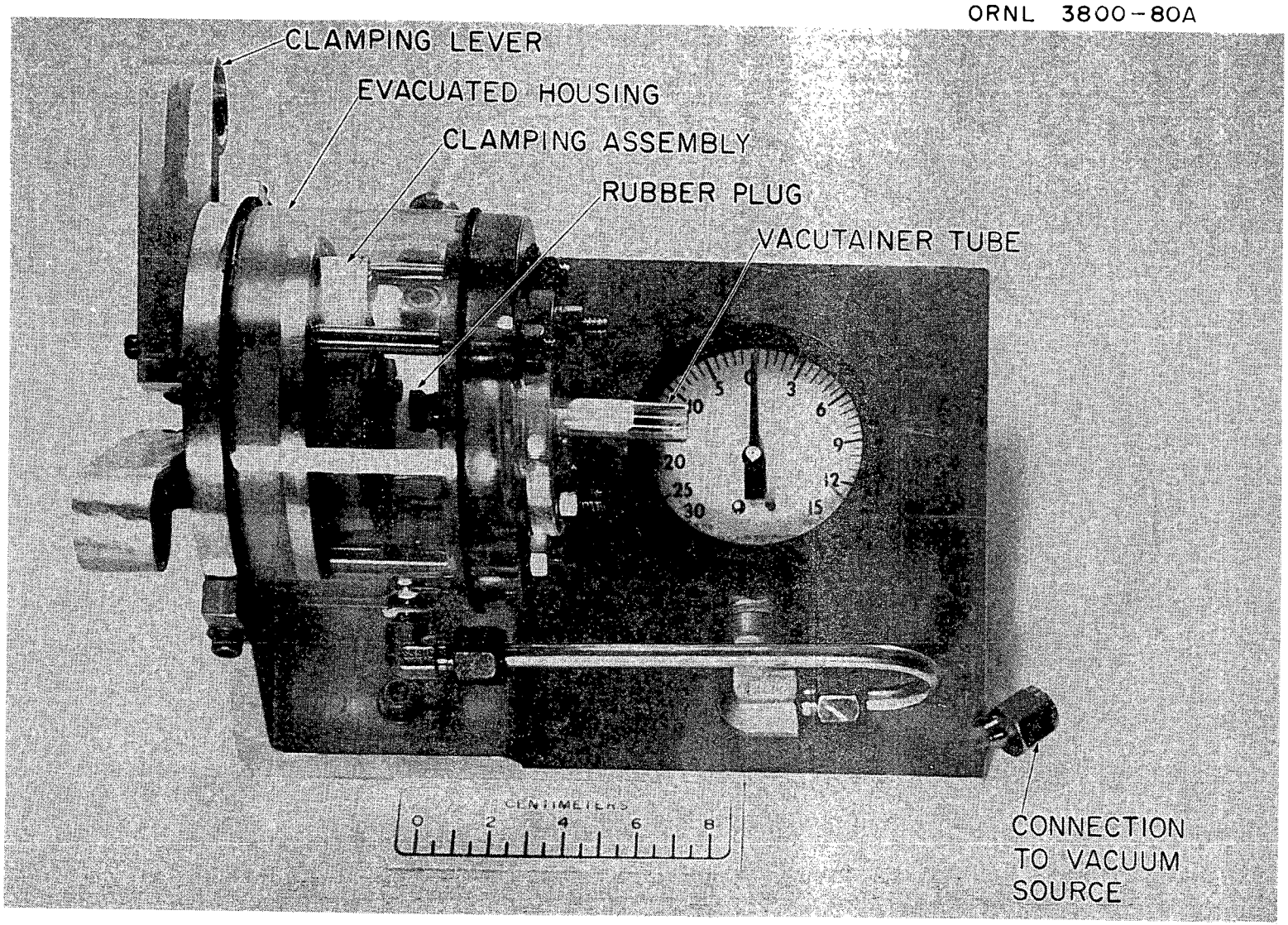

Fig. 4. Vacuum-adjusting device for Vacutainer tubes.

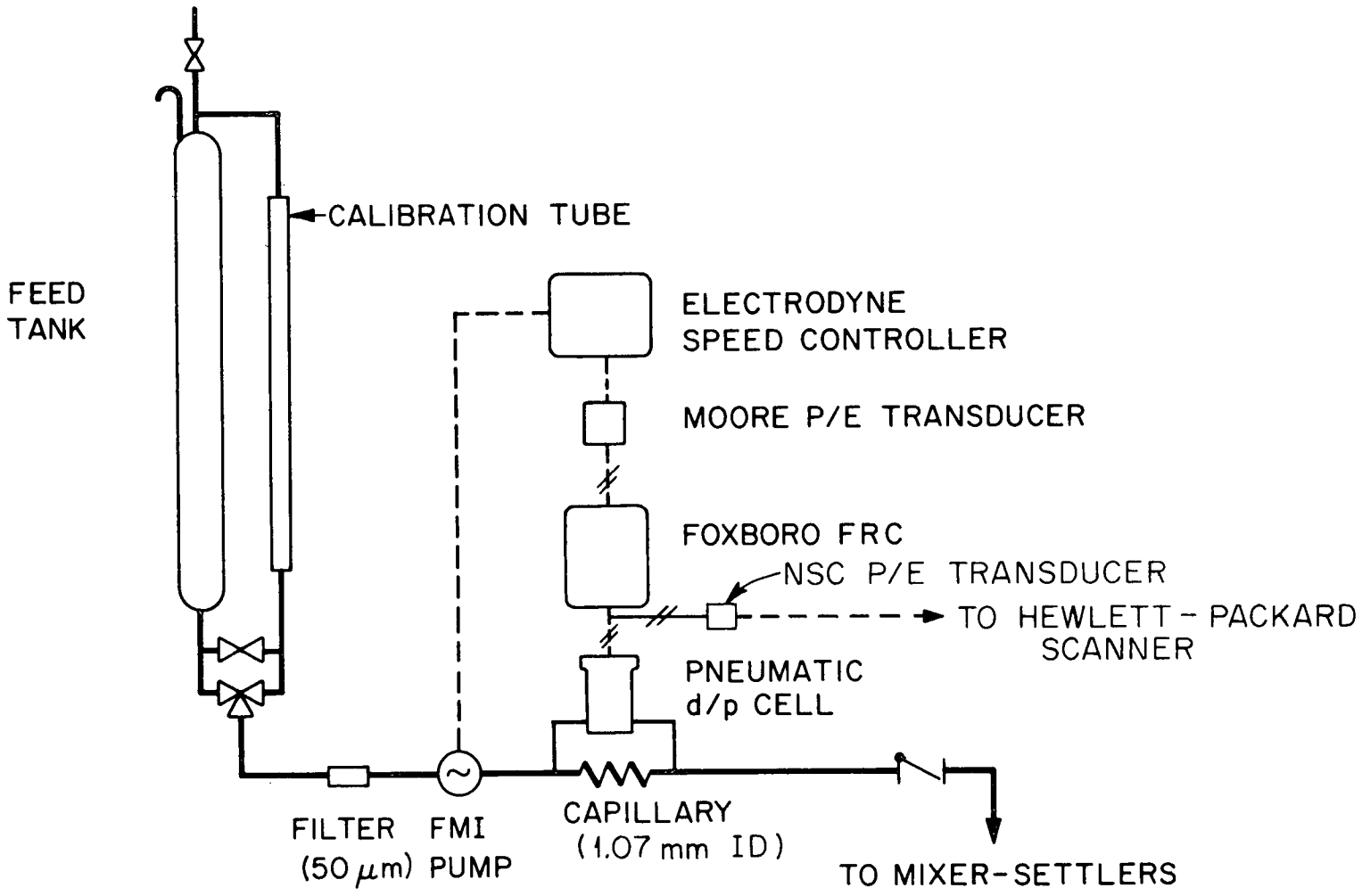

Fig. 5. Metering system for feed solutions, typical of six circuits. The capillary is housed in a thermostated air bath.

the frequency of flow-rate errors due to capillary plugging was almost nil; therefore, the capillary pressure drop signals will be used in future experiments. These will be recorded, and flow rates will be calculated by a Hewlett-Packard data acquisition system (see Sect. 2.4). The results of capillary calibrations against the precision voltmeter of the Hewlett-Packard system are summarized in Table 1. In the vicinity of the flow rates to be used in an FBR flowsheet experiment, the actual rates will be within ~3% of the values calculated from the full-range equations. Constants for these equations (not shown) were determined by multiple linear regression of flow rate vs transducer voltage and capillary temperature. The correlation coefficient was typically 0.98.

2.3 In-line Process Monitors

Real-time measurements of solute concentrations are indispensable if feedback control is to be employed in the mixer-settler system. Examples of this application are (1) a heavy-metal monitor in the extraction bank which would modulate the 1AX flow rate so as to maintain the metal concentration in the organic phase as high as possible, consistent with achieving high metal recoveries; and (2) a uranium monitor in the 1BP stream of the partitioning bank which would control the 1BS backscrub rate in order to regulate the amount of uranium that accompanies plutonium in the 1BP stream. To date, several monitors have been tested in the latter application. Calculations of metal and acid concentrations have been based on measurements of solution density and temperature, spectral response, and electrical conductivity.

2.3.1 Density meters

Of all the devices tested, the Mettler/Paar density meters Models DMA45 and DMA46 provided the most precise measures of uranium and heavy-metal concentrations over the widest range. Each meter was served by a remote cell consisting of a thermostated oscillating tube located within the glove box. The temperature of each cell was controlled to within 0.1°C. Solution holdup within the cell (~3 mL) and the 1.6-mm (1/16-in.) connecting tubing typically totaled ~10 mL, entailing a lag time of ~4 min. This was later reduced to $\leq$ 2 min when 0.8-mm-ID connecting tubing was used.

Table 1. Results of capillary calibrations near reference flow rate values

Dimensions of capillaries: 1.07 mm ID by 1.2 to 4.6 m long
Form of the full-range equations: $C = K_1 + K_2V + K_3t$

Capillary No.	Temp. (°C)	Test solution	Flow rate (mL/min) Ref.	Flow rate (mL/min) Test	P/E transducer voltage ($\bar{V} \pm 1\sigma$)	C^a/C_{test}	C^b/C_{test}	C^c/C_{test}
2	29.6	3 M HNO_3	0.11	0.099	5.441 ± 0.051	1.040	0.910	0.975
3	32.7	30% TBP–NDD	1.71	1.70	7.437 ± 0.006	1.031	1.022	1.026
4	29.4	3 M HNO_3	0.17	0.153	7.256 ± 0.001	1.021	1.013	1.017
5	31.2	H_2O	1.67	1.69	6.743 ± 0.001	1.007	1.000	1.004
6	32.8	90 g/L HM[d]–30% TBP	1.76	1.70	9.035 ± 0.013	1.025	1.016	1.021
8	29.5	0.3 M HNO_3	0.22	0.19	4.986 ± 0.002	0.999	0.982	0.990

[a]Flow rate calculated at $(\bar{V} + 1\sigma)$ and (T + 0.1°C).
[b]Flow rate calculated at $(\bar{V} - 1\sigma)$ and (T - 0.1°C).
[c]Flow rate calculated at $\bar{V}$,T.
[d]HM = heavy metal.

The analytical results for 1-mL samples taken from the 1AP and 1BU streams (experiment UX-2) showed excellent agreement with uranium concentrations calculated from the in-line density measurements provided by the Mettler/Parr density meters. Uranium concentrations for 17 density readings of the 1BU stream were calculated for the organic phase by using the appropriate equation developed by D. R. Johnson of the Savannah River Laboratory:[1]

$$\begin{aligned} U(g/L) = {} & 736.43(d_T) - 617.54 - 0.125(T) - 28.57\,[H^+] \\ & + 0.83(d_T)(T) + 2.21(T)[H^+] + 7.26(d_T)[H^+] \\ & - 2.55(d_T)[H^+](T), \end{aligned} \qquad (1)$$

where d_T = measured density at temperature T (°C).

The calculated average (and standard deviation) was 71.4 ± 0.3 g/L (based on an assumed 0.02 M H^+), as compared with 71.7 ± 0.3 g/L by the Davies-Gray titrimetry procedure. The corresponding concentrations for the 1AP stream were 89.1 ± 0.3 g/L and 90.5 ± 1.4 g/L. The effect of acid concentration on the calculated uranium concentration was small for the expected range of acid concentration for the organic phase; this concentration was closely estimated by computer calculations using the SEPHIS[2] code.

Much wider ranges of nitric acid concentration are possible in the aqueous phase, depending on flowsheet conditions. Therefore, a measurement of nitric acid concentration is required as input for the calculation of metal concentration. For the 1BP aqueous product stream, a flow-type electrical conductivity cell was placed in series with the Mettler/Paar density meter. The conductivity cell, designed by J. E. Strain of the ORNL Analytical Chemistry Division, provided an excellent measure of acid concentration. Since no direct determination of plutonium concentration could be made during experiment PX-3, the calculated heavy-metal concentrations in the 1BP product stream were biased on the high side by ~1 to 2 g/L (Fig. 6), which was not a significant error for control purposes. Post-run calculations of uranium concentrations were made from analytical measurements of plutonium and acid concentration in conjunction with density measurements using the following equation (origin detailed in Appendix C):

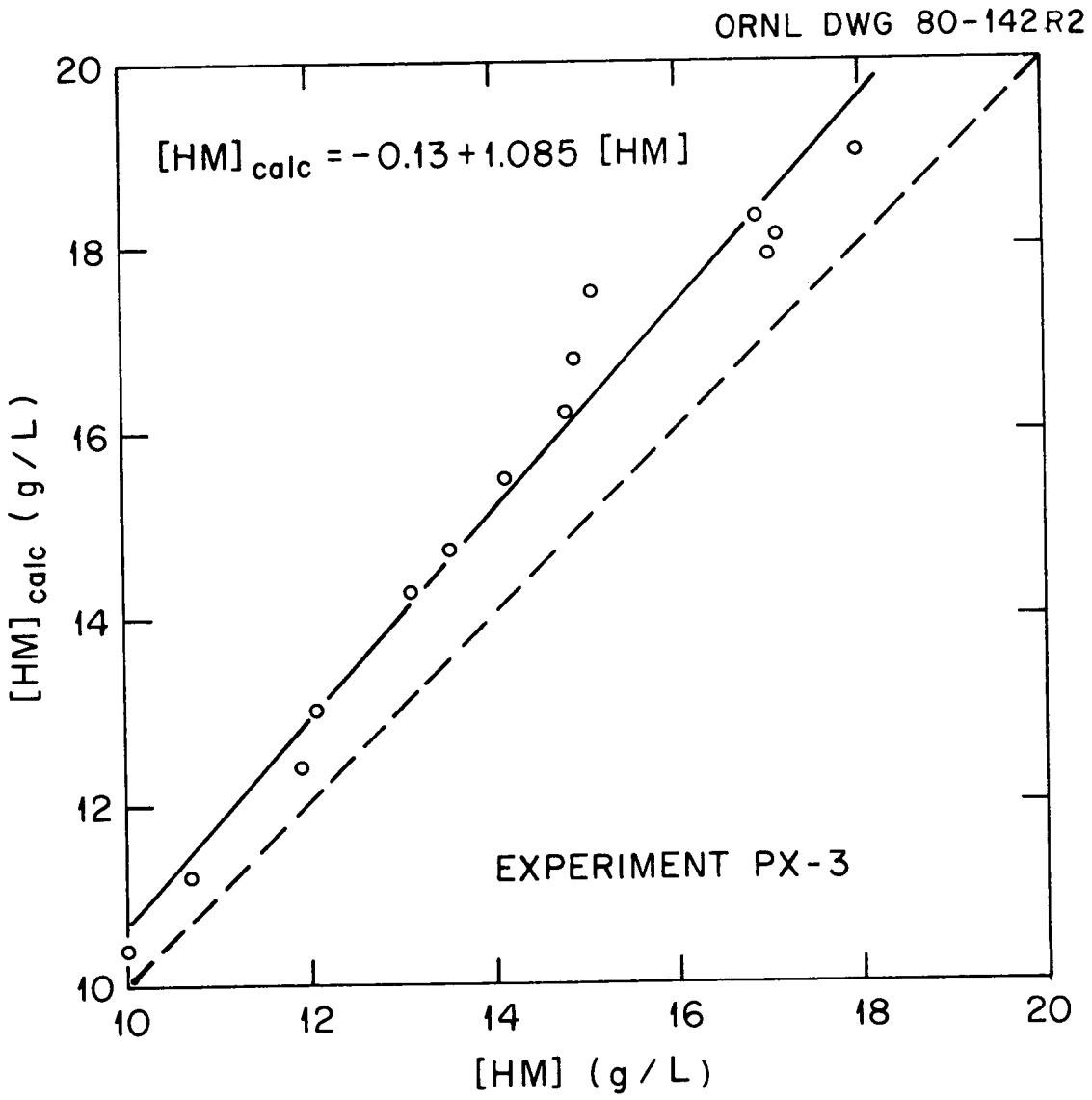

Fig. 6. Heavy-metal concentration calculated as f(ρ, T, $[H^+]$) vs heavy-metal concentration by wet analysis. [Pu] = 4.50 ± 0.2 g/L; $[H^+]$ = 0.48 to 0.52 M; T = 39.8 to 40°C.

$$[U](g/L) = 739.69\left[\left(\frac{d_T - 0.000286T + 0.00573}{1.020 - 0.000773T}\right) - 0.99707 - 0.001516\ [Pu]\ g/L - 0.032191\ [H^+]_M\right]. \quad (2)$$

The resulting heavy-metal concentrations were biased on the high side by 2 g/L — not significantly different from the results obtained by using Eq. (1). Normally, either the uranium or the plutonium concentration will be known from an in-line measurement, and a density determination will permit the calculation of the second metal from a relationship similar to Eq. (2).

2.3.2 Spectrophotometers

The spectrophotometric determination of uranium concentration in the presence of nitric acid was demonstrated by a dual-wavelength method[3] for aqueous solutions. However, the application of this method to glove-box use was not immediately practicable because of the lack of space for a suitable spectrophotometer. However, open glove-box experiments were carried out (before plutonium was used) to demonstrate the principle. A very small spectrophotometer for measurements at a single wavelength was successfully tested for later use within the glove box.

Preliminary measurements of uranium concentration with a laboratory spectrophotometer gave encouraging results. A Perkin-Elmer Model 570 spectrophotometer (located outside the glove box) with a 5-mm flow cell was provided with a continuous sample of the 1CU stream (uranium concentration, ~70 g/L) during open glove-box tests with uranium only. Aside from a minor problem with deposition of carbon on the cell windows (from the carbon liner of the sample transfer pump), this type of in-line monitor appeared promising.

For a more accurate evaluation of the technique, three solutions were prepared by dilution of a stock solution, and an all-ceramic-and-Teflon FMI pump was used for continuous solution transfer. The following equation, developed by D. T. Bostick,[4] was employed in the calculations:

$$[U],\ g/L = 6.83 \times 10^2\ A_{416} - 5.00 \times 10^2\ A_{426} - 0.973,$$

where absorbance values are for a 1-mm pathlength.

The results are shown in Table 2. A Beckman DB-G spectrophotometer was used successfully to measure uranium concentrations in the range of 5 to 10 g/L in the aqueous phase (Sect. 3.1.3).

The dual-wavelength technique was judged to be sufficiently promising that penetrations were built into the glove box to accommodate the light pipes which would be required to connect an internal cell with an external spectrophotometer, in the event that a prototype instrument should become available as a result of developmental work in the Instrumentation and Controls Division. The use of such an instrument would be directed primarily toward the determination of plutonium.

A miniature spectrophotometer (Bausch & Lomb Spectronic Mini-20) was obtained for permanent use inside the glove box. A 10-mm quartz flow cell was fabricated, and the spectrophotometer was calibrated with aqueous uranium solutions in the 3- to 30-g/L range. Response was linear at 416 nm over a nitric acid concentration range of 0.03 to 0.25 M. Suggested settings for plutonium measurements[5] were 476 nm for Pu^{4+} (below 0.5 M H^+) and 565 nm for Pu^{3+}.

2.4 Automatic Data Acquisition System

The objectives of the plutonium flowsheet work require the accurate measurement and recording of very small flow rates in order for the experimental results to be confidently scaled to larger systems. A Hewlett-Packard data acquisition system was purchased to meet that goal, as well as to record and reduce the data from in-line monitors and to print and plot the experimental results.

Hewlett-Packard components already in place include the calculator (Model 9825S), the scanner (Model 3495A), the digital voltmeter (Model 3455A), and the printer (Model 9866B). Programming work, by J. T. Hutton of the Instrumentation and Controls Division, has been completed for the following tasks:

Table 2. Spectrophotometric determination of uranium concentrations

Solution	Nominal concentration[a] [U] (g/L)	Nominal concentration[a] $[H^+]$ (M)	Reported concentration[b] [U] (g/L)	Reported concentration[b] $[H^+]$ (M)	Calculated concentration[c] [U] (g/L)
1	31.9	0.26	30.6	0.29	32.1
2	63.8	0.53	61.4	0.55	60.7
3	95.7	0.79	94.0	0.83	86.8

[a]By dilution.

[b]By ORNL Analytical Chemistry Division.

[c]By using Eq. (1).

1. pre-experiment entries to identify all streams (up to 17), their source, destination, and capillary flowmeter, if any;

2. scanning routines for 19 thermocouples, 8 capillary flow meters, 2 liquid level probes, and 2 density meters;

3. calculation of flow rates based on capillary flowmeters and by linear regression on the volumes of the feed tanks and receivers;

4. calculation of volumetric balances for aqueous and organic phases, for each bank;

5. the calculation of heavy-metal concentrations from in-line density meters.

The plotter (Model 9872A) and the multiprogrammer (Model 6940B) have not yet been connected. The first task assigned to the multiprogrammer is process automation to control the solution loading in a selected stage of the extraction bank. An in-line density meter or spectrophotometer will provide the measure of metal concentration to the control loop. The controller output will vary the pumping rate of, for example, the 1AX extractant feed.

3. EXPERIMENTAL RESULTS - PARTIAL PARTITIONING OF URANIUM-PLUTONIUM

Experimental work for this initial phase of the flowsheet development program was carried out in two stages: (1) shakedown runs in open glove boxes with uranium, and (2) closed glove-box runs with plutonium and uranium.

3.1 Shakedown Experiments

The open glove-box work included tests to verify flow rate control for all feed streams, tests of the sampling system, and experiments to establish a range of flow rates, flow rate ratios, and stirrer speeds

which produced acceptable hydraulic performances with reference solution compositions. Uranium-plutonium partitioning performance in the B bank was judged on the basis of the observed concentration of uranium and the hypothetical concentration of plutonium in the 1BP product stream. The desired range for the Pu/(Pu + U) ratio in the 1BP stream was 0.25 to 0.40.

3.1.1 Experiment UX-1

Preliminary operation of the mixer-settlers was carried out at nominal flow rates and concentrations based on flowsheet conditions shown in Fig. 7 and Table 3 in order to select suitable agitator settings (depth and speed) for the initial flowsheet experiment (UX-1).

Following initial operation of about 8 h, the system was shut down and samples were taken from one-fourth of the settling compartments; at this point, uranium concentrations were at 50 to 80% of the final steady-state values. After an overnight shutdown, the experiment was resumed; approximately steady-state concentrations in the 1BP and 1CU streams were reached in ~350 min (Fig. 8). Over the final 200 min of the experiment, uranium analyses of the two streams showed a rate of concentration increase of only 0.02% per minute. Continuous in-line measurements of 1AP solution density indicated an average value of 0.9125 with a standard deviation of 0.0006, equivalent to 77.9 ± 0.5 g/L. The uranium concentration in the 1BP stream would have been equivalent to a Pu/HM* ratio of 0.35 if plutonium had been present in the 1AF feed. For the B bank and much of the C bank, measured post-run uranium stage concentrations were in good agreement with values calculated by the SEPHIS program. The measured/calculated concentration ratio was generally 80 to 90%.

3.1.2 Experiment UX-2

The agitator depth settings for experiment UX-1 covered a range of values. Small changes were made, while operating at reference feed rates, in order to arrive at a limited number of depth settings for

*HM = heavy metal.

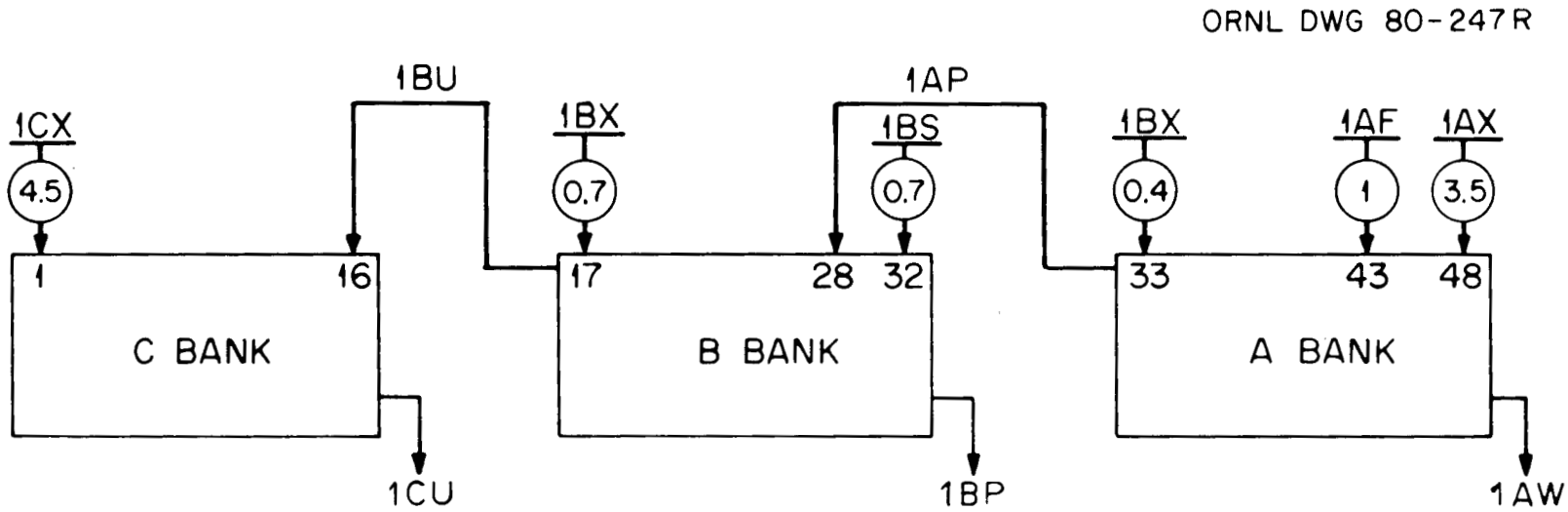

Fig. 7. Reference conditions for uranium-plutonium partial partitioning flowsheet experiments. Relative flow rates (circled) are approximate; actual flow rates are tabulated in Appendix A.

Table 3. Composition of feed solutions for partitioning experiments

Stream	Component	Experiment				
		UX-1	UX-2	UX-3	PX-2	PX-3
1AF	U, g/L	280.8	275.2	275.6	277.6	259.6
	Pu, g/L	-	-	-	2.97	2.98
	H^+, M	30.9	3.02	3.03	2.99	3.23
1AS	H^+, M	0.5	<0.01	0.54	0.5	0.77
1BX	HAN,[a] M	0.06	0.06	0.05	0.06	0.06
	HYE,[b] M	0.1	0.09	0.08	0.11	0.10
	H^+, M	0.14	0.23	0.16	0.21	0.18
1CX	HAN, M	0.02	0.02	0.008	0.01	0.04
	HYE, M	0.01	0.01	0.015	0.02	0.05
	H^+, M	0.01	0.02	0.004	0.02	0.03
1AX	H^+, M		0.01	0.01		
1BS	H^+, M		0.01	0.01		

[a]HAN = hydroxylamine nitrate.

[b]HYE = hydrazine nitrate.

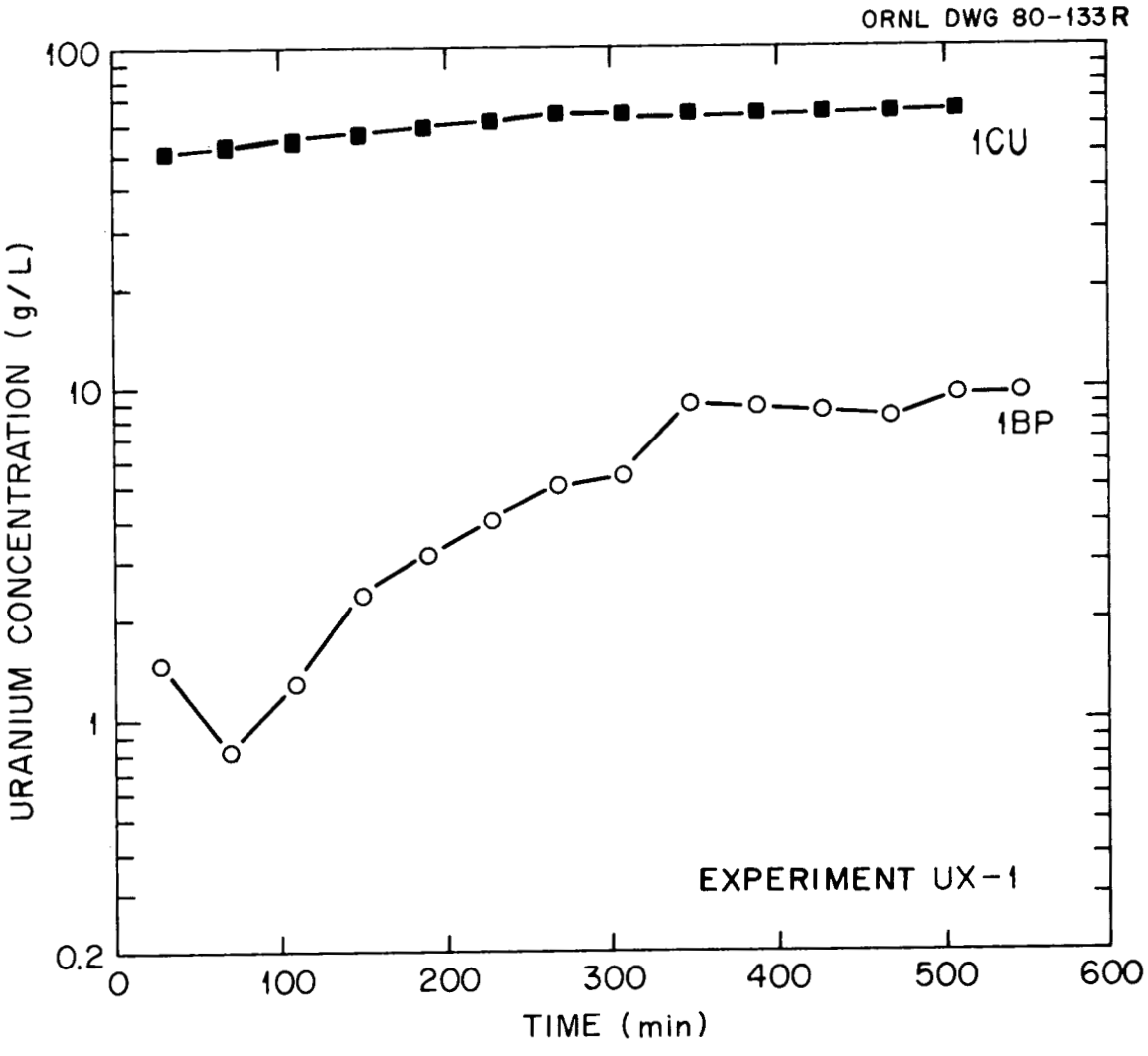

Fig. 8. Uranium concentration vs time for uranium product stream 1CU and product stream 1BP (normally containing uranium and plutonium).

experiment UX-2. These are summarized in Appendix B. The agitator speed was increased in 50-rpm increments to establish a value just short of producing organic-phase underflow.

The glove boxes were enclosed, and experiment UX-2 with uranium was carried out to demonstrate that the necessary manipulations could be performed through the gloves. Prior to the experiment, the feed solution (uranium concentration, 280 g/L) was filtered through an uncoated Vacco etched-disc filter (pore size, ~1 μm) at the rate of ~1 mL min^{-1} cm^{-2} and a pressure difference of ~85 kPa (~0.85 atm) in order to establish a reference rate for a clean solution.

A total liquid feed rate to the system of 4 mL/min, which was ~25% lower than that for experiment UX-1, resulted in improved hydraulic behavior. Flow rate control was very precise, as confirmed by pressure drop recordings for all metering capillaries (see also Table 1).

Analytical results showed that the uranium concentrations in the 1AW and 1CW streams continued to decrease during the 500-min run (Fig. 9), although the streams monitored by the density meters, 1AP and 1BU, were at steady state for >300 min (Fig. 10). This illustrated that the 1AP and 1BU monitors provided a useful measure of the approach to steady state for certain stages. Not surprisingly, however, the approach to steady state in streams 1AW and 1CW could not be sensed by this indirect measurement. Uranium concentration in the 1BP stream initially leveled off at a satisfactory value of ~13 g/L but later exceeded 36 g/L as the low acid concentration in the 1AS took effect. The high uranium concentration would have been equivalent to an unacceptably low value of ~12% plutonium in the uranium-plutonium product, if plutonium had been present in the 1AF stream.

3.1.3 Experiment UX-3

A final uranium experiment, UX-3, was performed to demonstrate that the required uranium concentration of 6 to 12 g/L could be maintained in the 1BP stream, where the plutonium concentration will be ~4 g/L. The 1BP stream was continuously monitored by two in-line instruments: a

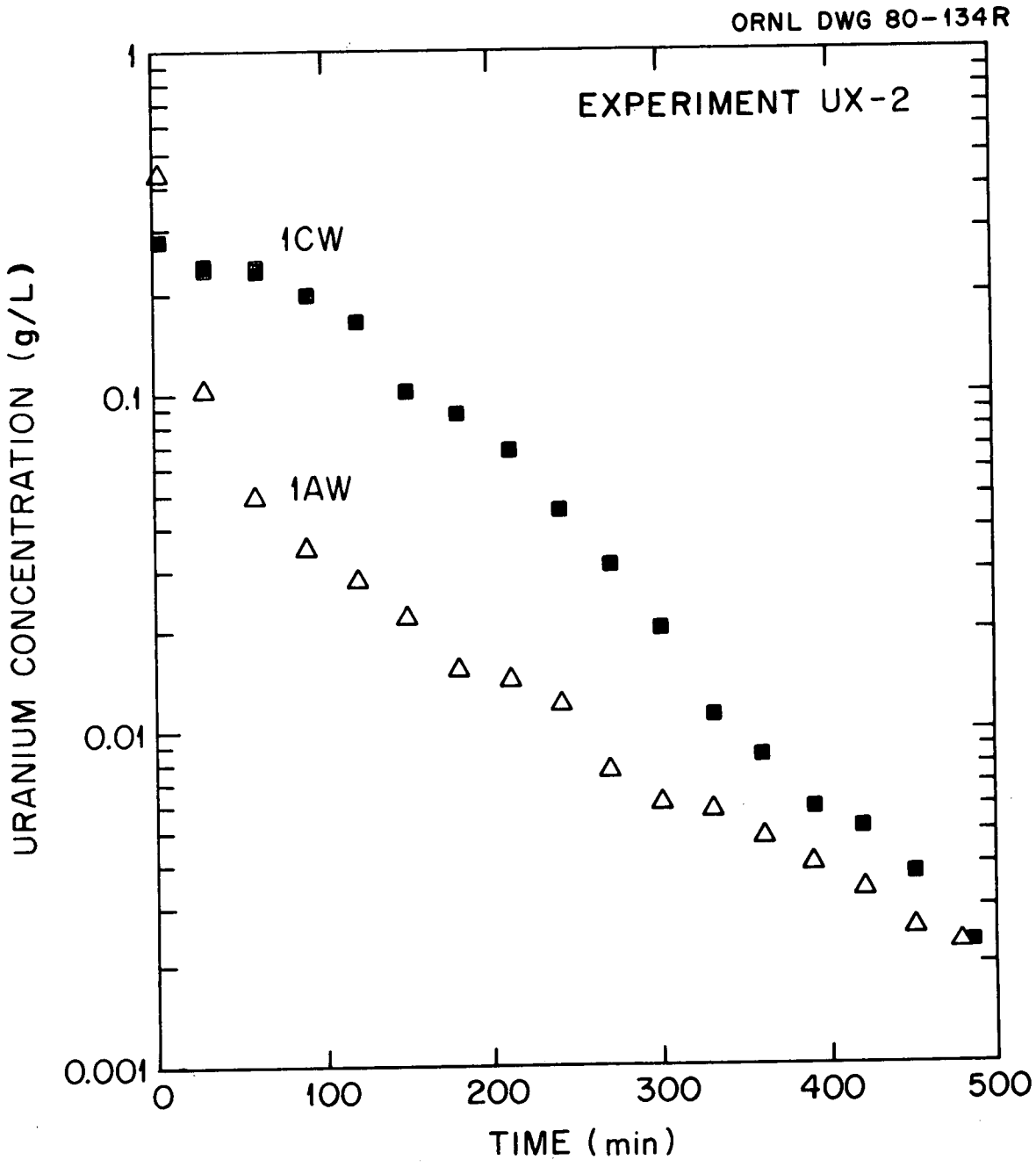

Fig. 9. Uranium concentration vs time for aqueous waste stream 1AW and stripped organic stream 1CW.

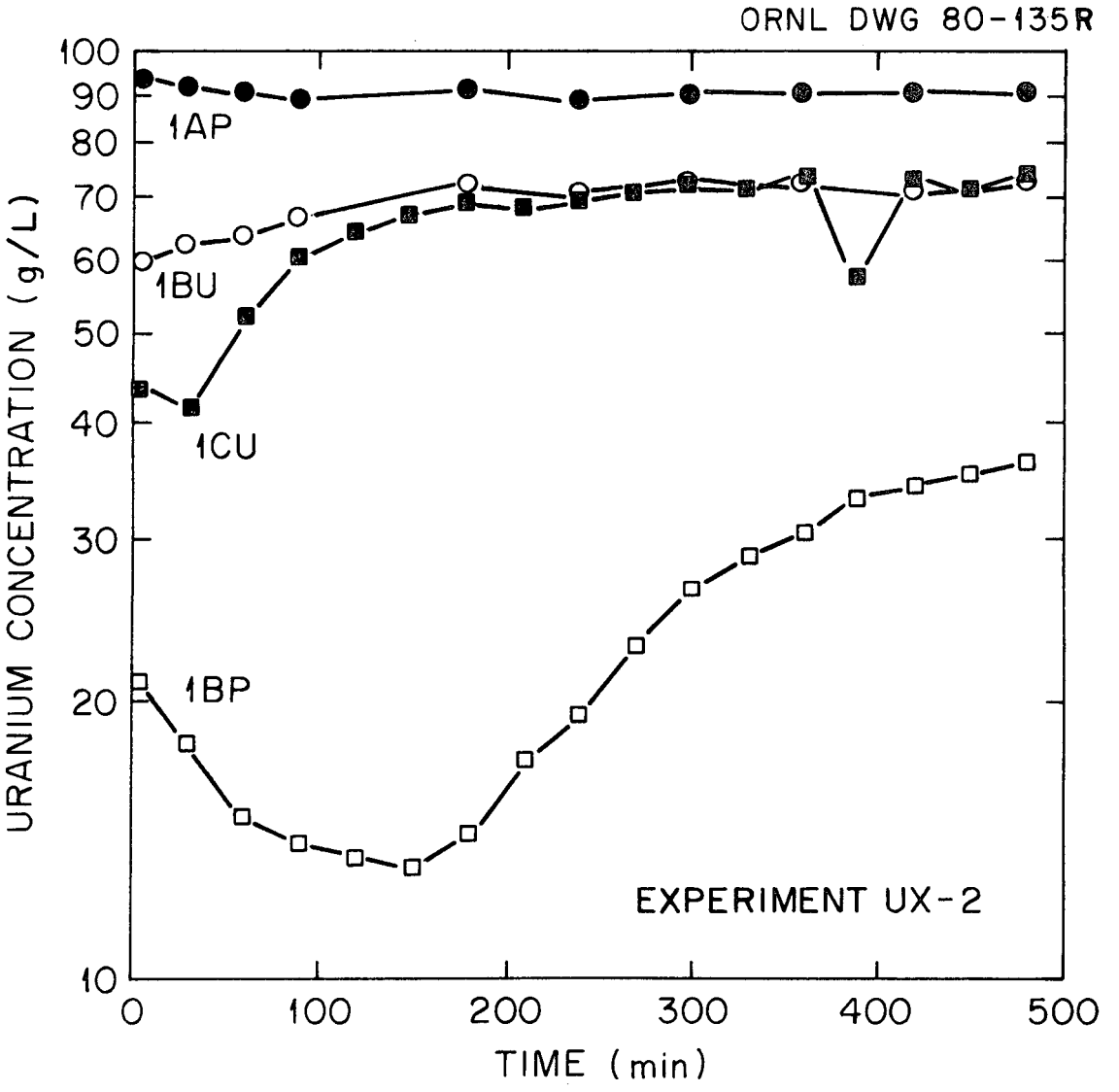

Fig. 10. Uranium concentration vs time for high-concentration streams. Analyses by Davies-Gray titrimetry.

Beckman spectrophotometer (Model DB-G) and a Mettler/Parr density meter (Model DMA45). A nearly steady-state uranium concentration of 8 g/L (equivalent to ~33% plutonium) was obtained after 300 min. The 1BS organic backscrub rate was then increased from 0.25 to 0.26 mL/min in order to reduce the uranium concentration (Fig. 11). The uranium concentration subsequently reached the desired value of 6 g/L, where it was held for the remainder of the run. Results for five flowing stream samples and ten in-line determinations from this time interval were as follows:

Analytical results	5.87 ± 0.072 g/L
Spectrophotometer	4.76 ± 0.19 g/L
Density meter	4.28 ± 0.15 g/L

Post-run acid analyses were used to calculate uranium concentrations from the density meter measurements.

3.2 Plutonium-Uranium Partitioning Experiments

Changes made to the system in preparation for the experiments with plutonium included the following: (1) the flow path of 1BP solution to the densitometer was made once-through in order to reduce the effective time lag from >1 h to a few minutes, and (2) the spectrophotometer cell was removed from the 1BP stream since no means was yet available for carrying the light beam to a spectrophotometer outside the glove box.

3.2.1 Experiment PX-2

Following several hours of operation with plutonium, the experiment was interrupted in order to investigate the low HM concentration in the 1BP stream, as indicated by the density meter. The cause was traced to the differential pressure transmitter used to control the 1AF feed rate. The presence of a small volume of air in the high-pressure chamber permitted the chamber to act as a pneumatic accumulator, as follows: during the pump discharge stroke, solution from the pump was forced into

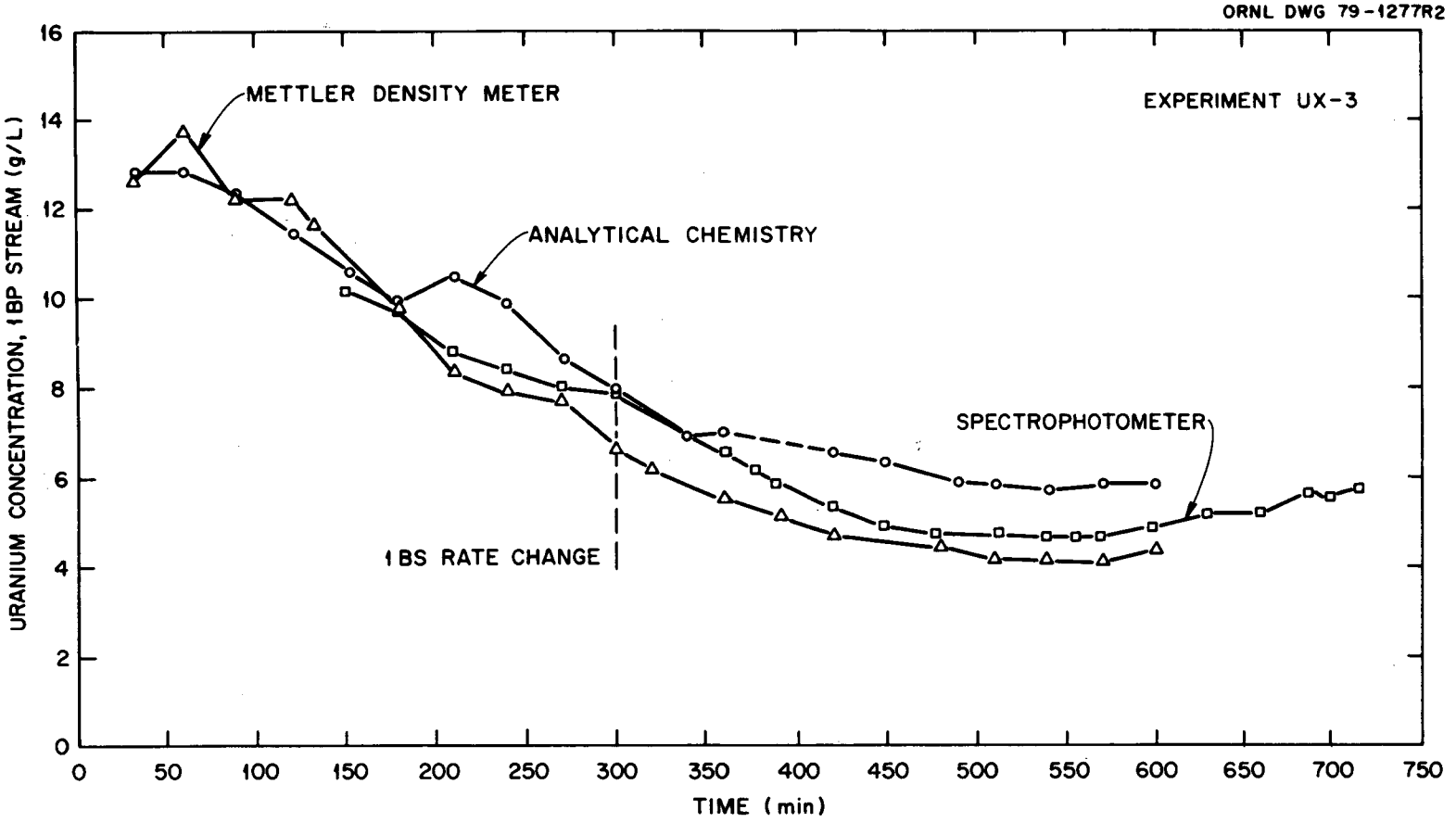

Fig. 11. Uranium concentration in the 1BP stream vs time. The spectrophotometric measurements are shifted 100 min to the right in order to reflect the measured lead time of 100 min for 80% response to a step change in concentration.

the chamber (due to back pressure from the restricting capillary), where it was mixed with a large volume of solution which initially contained no plutonium. During the suction stroke of the pump, the compressed air volume in the chamber expanded slightly, delivering a now-diluted solution to the capillary. In order to proceed with the experiment, it was necessary to remove the transmitter and metering capillary from the solution circuit and shift the flow control to manual selection of the required speed for the servomotor.

The mixer-settlers were emptied and the experiment was resumed. After ~6 h of operation and overnight shutdown, the flows were restarted, and sampling was begun. The analytical results (Fig. 12) showed a decline in uranium concentration from its peak, following an increase in the organic backscrub rate at 215 min. Throughout the final 90 min of the run, the average plutonium concentration of 4.2 g/L was in excellent agreement with the expected value (Fig. 13, stage No. 32).

The average uranium concentration, 8.6 g/L (Fig. 11), was substantially higher than 2.5 g/L, the concentration predicted by the SEPHIS program for the run conditions. This discrepancy was due, at least in part, to the organic-phase underflow observed in the second backscrub stage.

The Pu/HM ratio was well within the desired range throughout the final 400 min of the experiment (Fig. 14). This observation confirmed that control of the ratio by the organic backscrub rate is feasible in cases where an in-line monitor provides a measure of the ratio. During the experiment, the ratio was inferred from the measurement of total HM concentration.

Both the plutonium and the uranium losses to the 1AW stream were <0.001% of the total metal in the feed. The downward trend for uranium losses to the 1AW with time (Fig. 15) was similar to that observed in earlier experiments. The plutonium losses, although characterized by wide variations in concentration, roughly paralleled the trend for uranium losses. The amount of plutonium lost to the 1CW recycle solvent was <0.0001%.

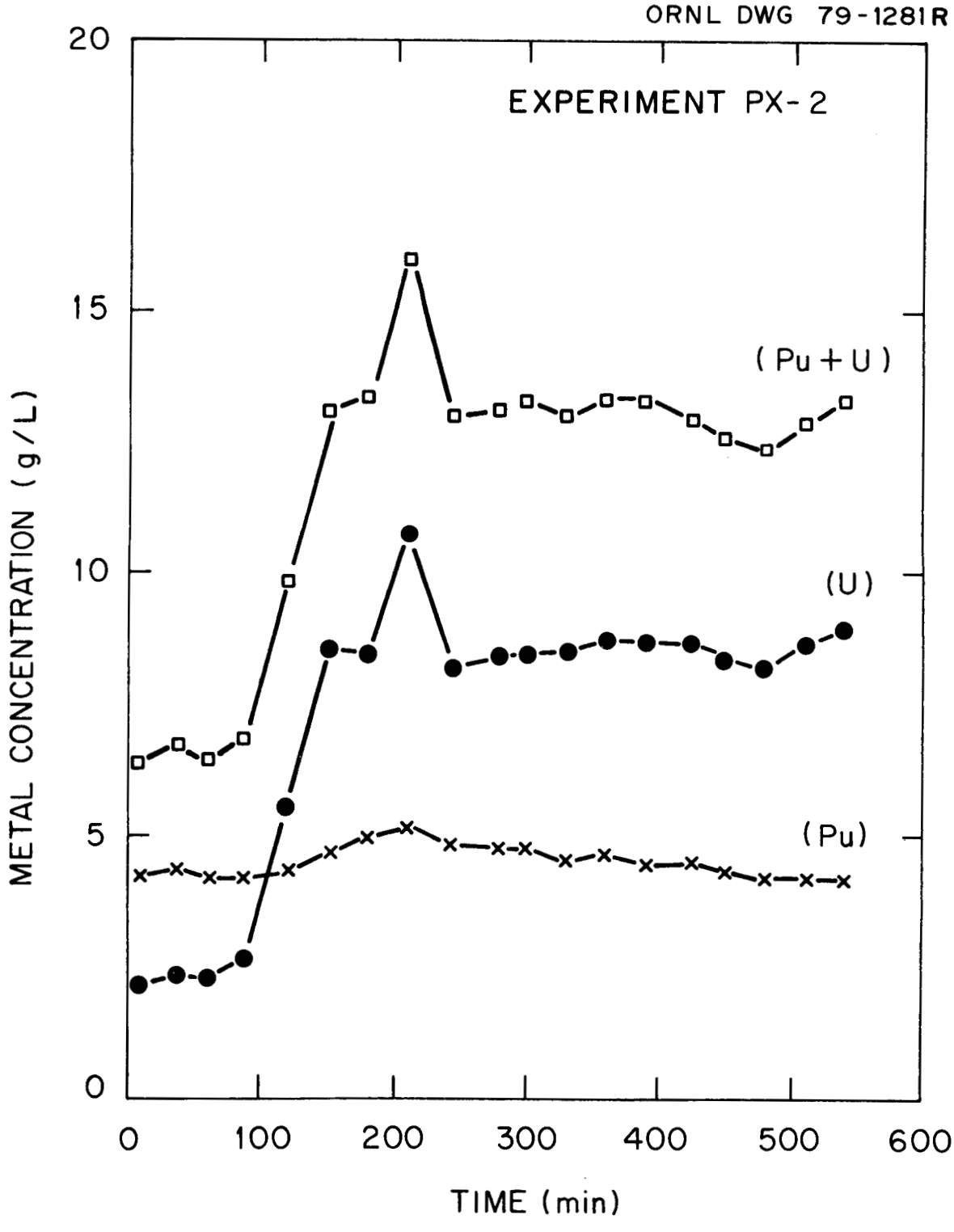

Fig. 12. Metal concentration in the 1BP product stream vs time. Organic backscrub, 1BS, was increased from 4.17 to 4.67 μL/s (0.25 to 0.28 mL/min) at 215 min. Temperature of mixer-settler, 42-44°C.

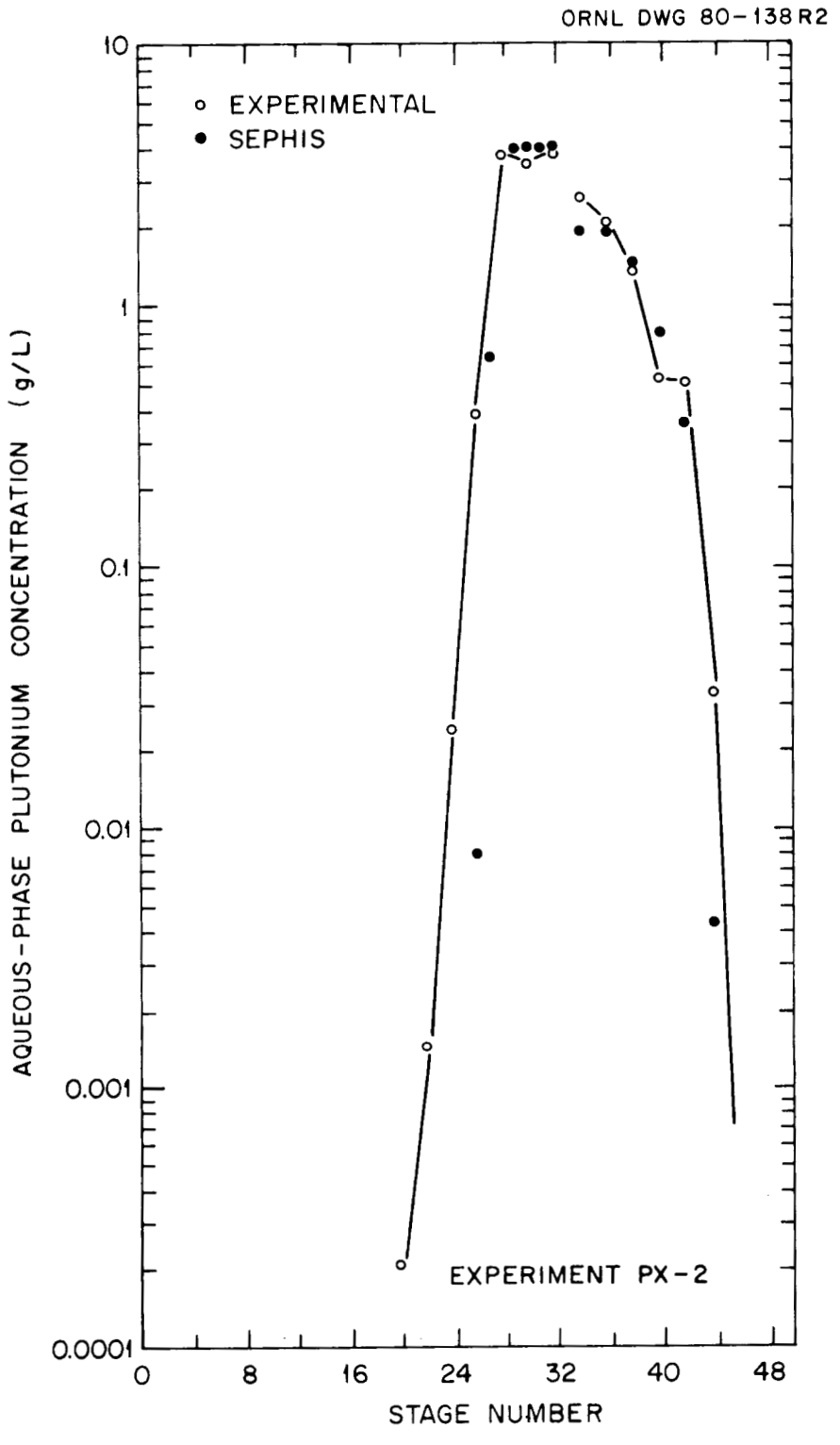

Fig. 13. Plutonium concentration in aqueous phase vs stage number. Comparison of experimental measurements (post-run sampling) with concentration calculated by the SEPHIS program.

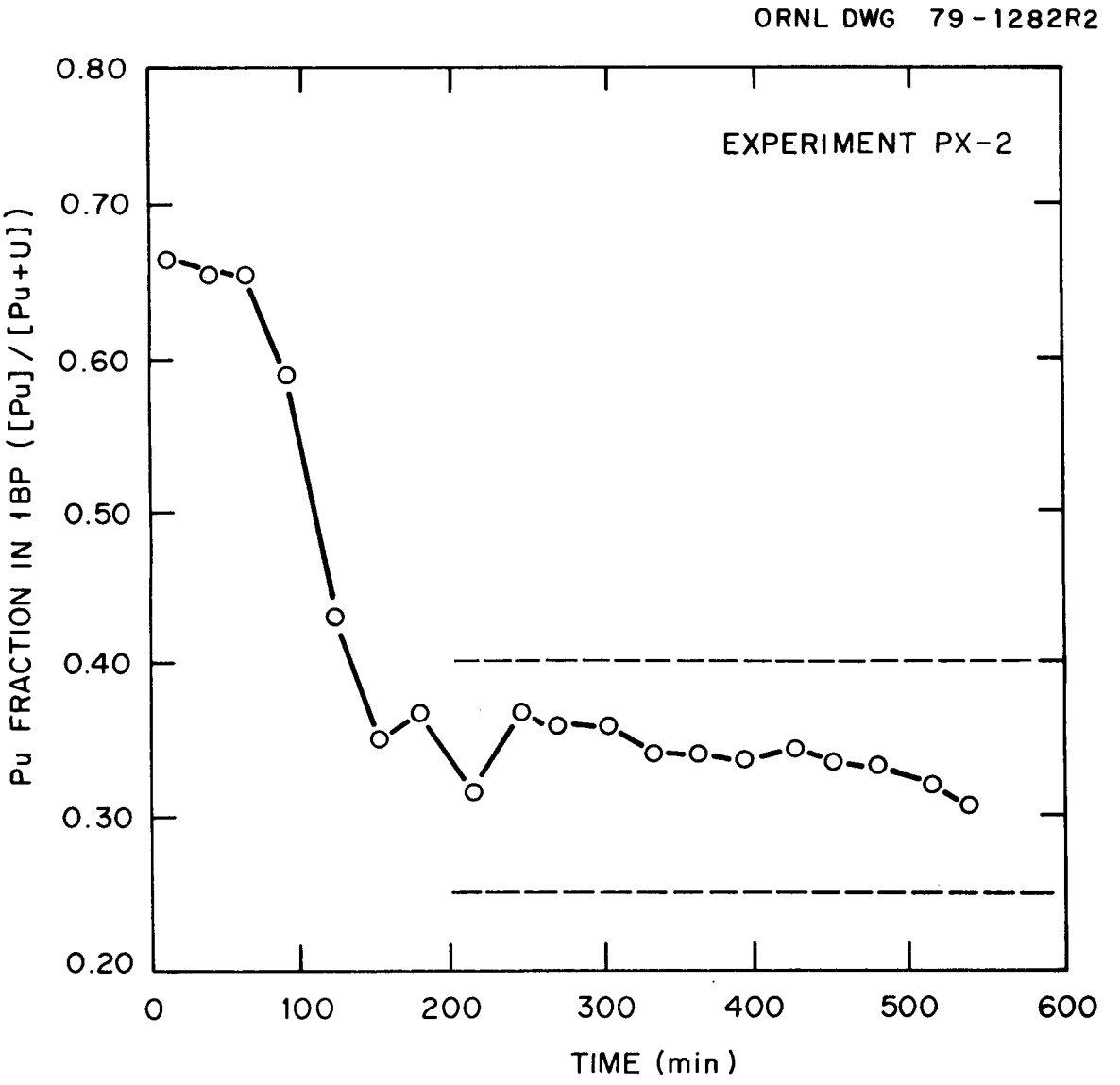

Fig. 14. Plutonium/heavy metal ratio of 1BP product stream vs time. Horizontal dashed lines define the desired range: 0.25 to 0.40 plutonium fraction.

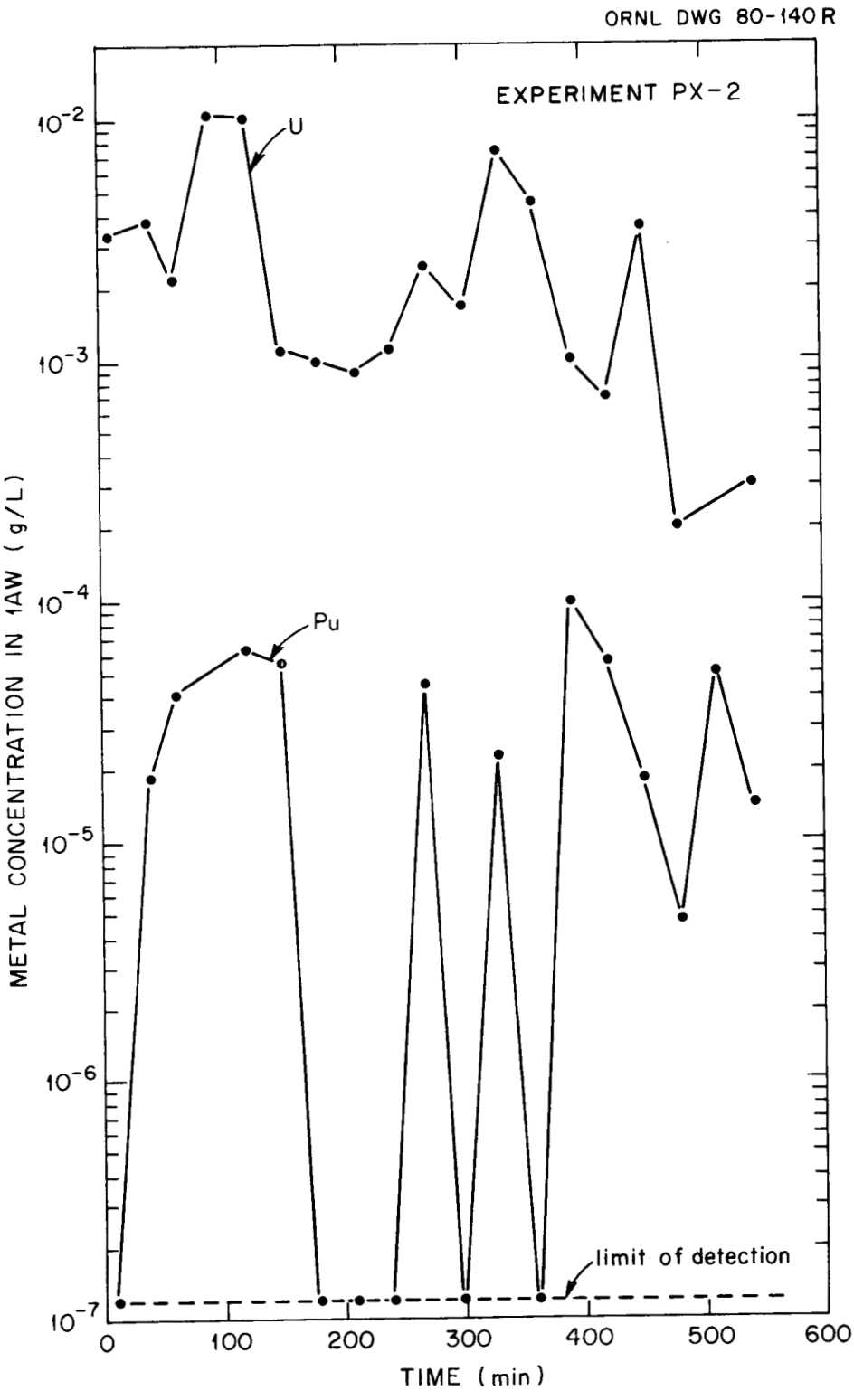

Fig. 15. Uranium and plutonium concentrations in the 1AW waste stream vs time.

3.2.2 Experiment PX-3

The results obtained for experiment PX-3 demonstrated that the desired Pu/HM ratio of 0.25 to 0.40 could be attained in the 1BP product stream despite a relatively high acid concentration (1 M HNO_3) in the 1AS stream. Otherwise, the feed solutions (Table 3) and flow rates (Appendix A) were almost identical to those for experiment PX-2.

Following preliminary operation during which the product composition ranged from 37 to 45% plutonium, the 1BX feed composition was found to be too concentrated in hydroxylamine nitrate (HAN). Therefore, a new feed solution was prepared before run PX-3 was resumed. The composition of the product was controlled by variations in the flow rate of the 1BX partitioning solution since an experimental test of SEPHIS calculations at nominal run conditions had shown this to be a more effective means of control than varying the 1BS organic backscrub rate. However, the experimental response of uranium concentration in the product stream appeared to be only weakly coupled to the 1BX rate. The largest change in rate (~6% reduction) did not produce a clearly identifiable response in the 1BP composition over the final 250 min of the run. The Pu/HM ratio at the end of the run was near steady state at a value of 0.25 (Fig. 16), with the uranium concentration increasing only 0.8 g/L over the final 90 min.

4. CONCLUSIONS

The miniature mixer-settler facility has proved to be a flexible system for examining prospective uranium-plutonium flowsheets. The tests were performed without fission products. Control of the Pu/(Pu+U) ratio in the product stream was successfully demonstrated for a flowsheet in which the ratio was regulated by variation of the organic backscrub (1BS) rate.

Liquid flow rates were accurately measured and controlled at very low values, using capillary flow elements, despite the pulsating output from the piston-type metering pumps.

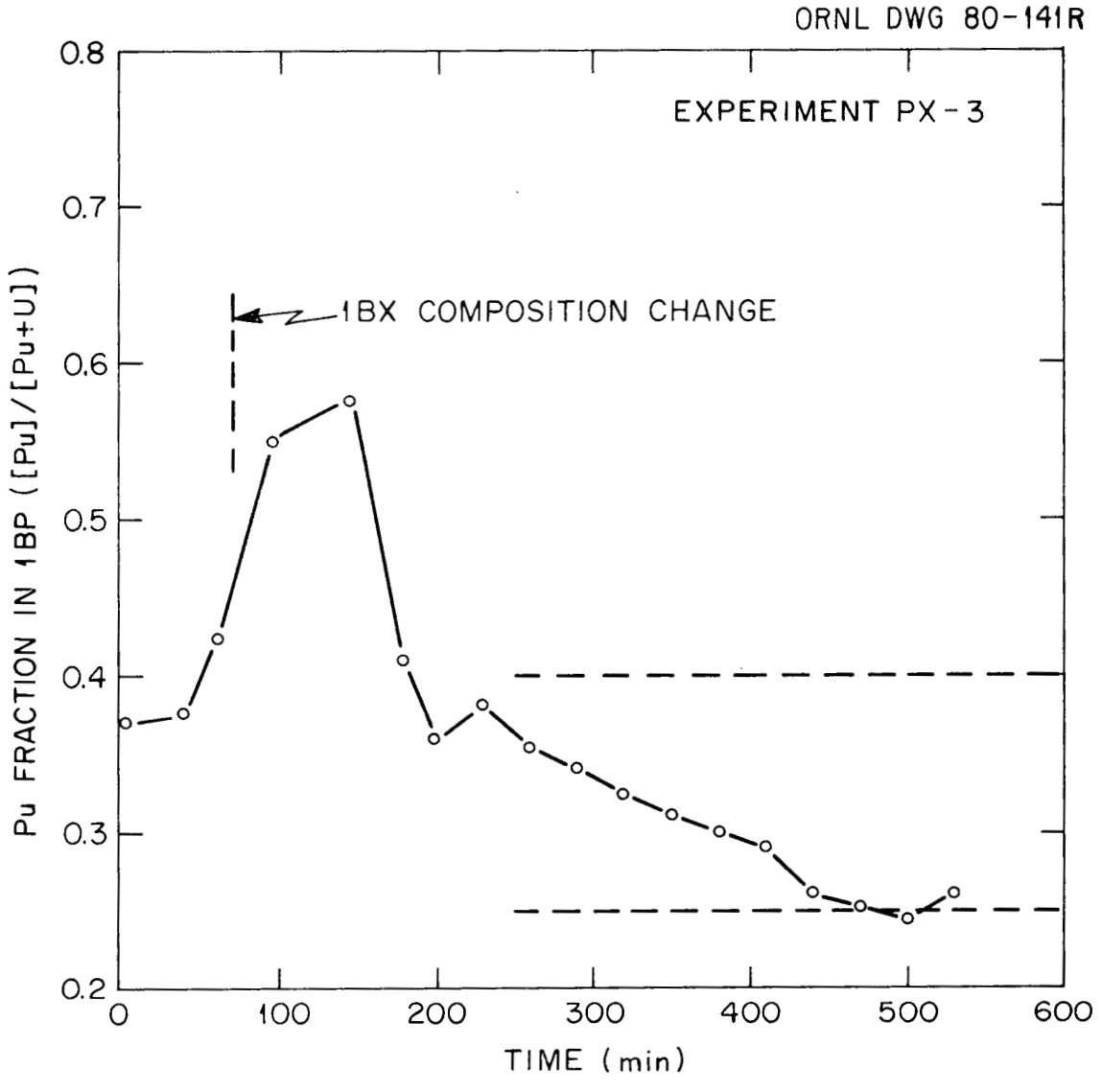

Fig. 16. Plutonium fraction in the 1BP stream vs time. Horizontal dashed lines define the desired range: 0.25 to 0.40 plutonium fraction.

In-line Mettler/Paar density monitors were very valuable for control purposes. For uranium concentration, excellent agreement was obtained between wet-chemical analyses and values calculated from Savannah River Laboratory equations using measured densities and temperatures. For the uranium-plutonium systems, the concentration of one of the heavy metals must either be estimated or determined by an independent means (e.g., spectrophotometrically) in order to calculate the concentration of the second metal from the density measurements.

The in-line spectrophotometer proved to be an excellent monitor of uranium concentration in the aqueous phase based on absorbance measurements at 416 and 426 nm. A miniature spectrophotometer for glove-box operation displayed linear response over a concentration range of 3 to 30 g/L at 416 nm. The miniature spectrophotometer also appeared to be useful for Pu^{4+} measurements at 476 nm.

5. ACKNOWLEDGMENTS

The authors wish to thank D. F. Green, R. L. Hickey, and G. C. Young for their assistance in carrying out the experiments. Gratitude is also expressed to W. D. Bond, D. J. Crouse, and A. D. Mitchell for their consultations on experimental design. Special appreciation is due D. J. Crouse and V. C. A. Vaughen for their helpful suggestions as technical reviewers of this report.

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7. APPENDIXES

Appendix A: Summary of Flow Rates and Flow Ratios for Uranium-Plutonium Partitioning Experiments

Feed rate (mL/min)	Experiment				
	UX-1	UX-2	UX-3	PX-2	PX-3
1AF	0.540	0.428	0.423	0.420	0.432
1AS	0.222	0.158	0.170	0.169	0.166
1AX	1.899	1.409	1.467	1.455	1.470
1BX	0.368	0.283	0.282	0.299	0.311
1BS	0.311	0.225	0.251	0.287	0.293
1CX	2.11	1.568	1.888	1.912	2.017
Total	5.45	4.07	4.48	4.54	4.69
Relative feed rate					
1AF	1	1	1	1	1
1AS	0.41	0.37	0.40	0.40	0.38
1AX	3.5	3.3	3.5	3.5	3.4
1BX	0.68	0.66	0.67	0.71	0.72
1BS	0.58	0.53	0.59	0.68	0.68
1CX	3.9	3.7	4.5	4.6	4.7
Total flow rate[a]					
Extraction	2.661	1.995	2.06	2.044	2.068
Scrub	2.121	1.567	1.637	1.624	1.636
Backscrub	0.679	0.508	0.533	0.586	0.604
Partition	2.267	1.917	2.000	2.041	2.074
Strip	4.009	2.977	3.355	3.367	3.487
Organic/aqueous flow ratio					
Extraction	2.34	2.40	2.47	2.48	2.46
Scrub	8.55	8.92	8.63	8.77	8.86
Backscrub	0.85	0.795	0.89	0.85	0.94
Partition	6.00	5.77	6.09	5.85	5.67
Strip	1.05	1.042	0.910	0.910	0.874

[a]Total flow rate = summation of countercurrent aqueous and organic flows.

Appendix B: Agitator Depth Settings and Rotational Speed for Experiments UX-2 through PX-3

	C Bank[a]															
Stage	1	2	3	4	5	6	7[b]	8	9[b]	10	11	12	13	14	15	16
Submergence[c]	10.8	6.1	5	7.5	6.3	6.5	6.5	7.3	6.5	6.8	7.3	7.3	7.4	7.3	7.3	7.2
	B Bank[d]															
Stage	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32
Submergence[c]	9	9	9	9	9	9	9	9	9	9	9	12.5	12.5	13.5	13.2	12.5
	A Bank[d]															
Stage	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48
Submergence[c]	8.8	5	6	5	8.6	5	9	11.4	10.8	5	10	6.8	7	7	7	7.2

[a]1600 rpm.

[b]Underflow of organic phase.

[c]Submergence is distance from the elevation of the settler overflow weir to the upper end of the impeller (±0.5 mm).

[d]1550 rpm.

Appendix C: Uranium Concentration in Aqueous Solution as a Function of Density, Plutonium Concentration, and Nitric Acid Concentration

The following equation defines solution density in terms of the usual solution components:

$$d_{25}* = (1000 - 72.4\ [U]_{\underline{M}} - 130\ [Pu]_{\underline{M}} - 30.9\ [H^+]_{\underline{M}} - 31\ [NO_3^-]_{\underline{M}})\left(\frac{0.99707}{1000}\right)$$
$$+ 0.39404\ [U]_{\underline{M}} + 0.49202\ [Pu]_{\underline{M}} + 0.063\ [H^+]_{\underline{M}} + 0.213\ [NO_3^-]_{\underline{M}}$$

In the absence of fission product nitrates, this reduces to

$$d_{25} = 0.99707 + 0.321852\ [U]_{\underline{M}} + 0.362401\ [Pu]_{\underline{M}} + 0.032191\ [H^+]_{\underline{M}}$$

Substituting into Johnson's equation** for temperature dependency for aqueous solutions containing uranium and H^+ (between 20 and 55°C),

$$d_T = 1.020\ d_{25} + 0.000286(T) - 0.000773\ d_{25}T - 0.00573,$$

results in

$$d_T = [0.99707 + 0.321852\ [U]_{\underline{M}} + 0.362401\ [Pu]_{\underline{M}} + 0.032191\ [H^+]_{\underline{M}}]]$$
$$\times\ (1.020 - 0.000773T) + 0.000286T - 0.00573.$$

From this, we obtain

$$d_T = [0.99707 + 0.001352\ [U],\ g/L + 0.001516\ [Pu],\ g/L$$
$$+ 0.032191 \times [H^+]_{\underline{M}}]\ (1.020 - 0.000773T) + 0.000286T - 0.00573,$$

and

$$[Pu],\ g/L = 659.628\left[\left(\frac{d_T - 0.000286T + 0.00573}{1.020 - 0.000773T}\right) - 0.99707\right.$$
$$\left. - 0.001352\ [U],\ g/L - 0.032191\ [H^+]_{\underline{M}}\right]$$

and

$$[U],\ g/L = 739.688\left[\left(\frac{d_T - 0.000286T + 0.00573}{1.020 - 0.000773T}\right) - 0.99707\right.$$
$$\left. - 0.001516\ [Pu],\ g/L - 0.032191\ [H^+]_{\underline{M}}\right].$$

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*Purex Manual.

**W. D. Burch et al., Consolidated Fuel Reprocessing Program Progress Report for Period January 1 to March 31, 1979, ORNL/TM-6836 (June 1979), pp. 2-29.

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