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Chemistry - Separation Processes
for Plutonium and Uranium
(M-3679, 18th ed)

KNOLLS ATOMIC POWER LABORATORY

SCHENECTADY, NEW YORK

A LOW WASTE VOLUME, FIRST CYCLE, 1A PUREX FLOW SHEET

J. K. Davidson
W. O. Haas, Jr.

July 15, 1956

OPERATED FOR THE

U.S. ATOMIC ENERGY COMMISSION

BY THE

GENERAL ELECTRIC COMPANY

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ABSTRACT

The KAPL No. 6, first-cycle Purex 1A flow sheet is presented as an example of waste volume reduction through optimum solvent-extraction flow sheet design. Calculated on the basis of previous flow sheets, a 54 to 69% reduction of first-cycle waste storage volume is achieved by taking advantage of the extractibility and reflux of nitric acid in TBP systems to provide adequate salting while minimizing the amount of acid going to waste.

Although this report is concerned only with the first Purex cycle, the calculations are equally valid for the second uranium cycle, and the principles presented are applicable to similar nitric acid - salted TBP systems.

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A LOW-WASTE-VOLUME, FIRST-CYCLE, 1A PUREX FLOW SHEET

J. K. Davidson and W. O. Haas, Jr.

I. INTRODUCTION

One of the advantages of TBP - nitric acid solvent-extraction systems is the possibility of recovering the nitric acid salting agent from aqueous waste by fractional distillation. Since radioactive process waste is stored as neutralized concentrate, the volume of hot waste can be significantly reduced by removing acid prior to neutralization.

A more fundamental step in the reduction of waste volume is the use of a flow sheet designed to give the minimum amount of waste compatible with other requirements. With such a flow sheet the economic advantage of subsequent treatment to reduce waste volume may become marginal.

The KAPL low-acid first-cycle 1A Purex flow sheet is designed to give the minimum amount of waste compatible with low product loss and adequate decontamination. The extractibility of nitric acid in TBP systems was used to promote acid reflux in the 1A extraction section by adjustment of flow-sheet parameters. With suitably chosen parameters a stable system is obtained in which the acid concentration remains constant and high through the bulk of the extraction section but drops sharply in the last few stages leading to the waste stream. Adequate salting for good recovery is maintained by the extraction of acid in these last stages despite the relatively low acid concentration of the waste stream.

Calculated on the basis of the ORNL-846 high-acid flow sheet[1] the KAPL No. 6 flow sheet represents a 54 to 69% reduction in storage volume of first-cycle aqueous waste. This reduction is obtained without appreciably affecting decontamination, recovery, or stability and without increasing the complexity or cost of operation. In contrast, distillation of nitric acid from first-cycle aqueous waste has the disadvantage of requiring an additional operating step, with the corrosion problems and more serious hazards inherent in distilling highly radioactive nitric acid which may contain organic residues.

II. SUMMARY OF HIGH- AND LOW-ACID FLOW-SHEET COMPARISON

Storage volumes of waste from the KAPL No. 6 low-acid, and the ORNL-846, high-acid, first-cycle 1A Purex flow sheets are compared in Table 1 to illustrate the savings which can be achieved by flow-sheet design.(1)

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(1)Flow-sheet conditions are given in Table 3 and Figure 1.

[redacted]

TABLE 1. First-Cycle Waste Storage Volumes - Flow-Sheet Comparison

Flow sheet	KAPL No. 6	ORNL-846
Without acid recovery		
Volume, gal./metric ton U*	174	555
With 90% acid recovery		
Volume, gal./metric ton U*	32	70
Overhead from acid recovery		
Nitric acid, lb/metric ton U	392	1336

*Based on storage of neutralized concentrate, 35% solids.

In the absence of acid recovery steps the storage volume of aqueous waste from the low-acid flow sheet is 69% less than that from the high-acid flowsheet. If 90% of the nitric acid is recovered from the wastes before neutralization, the storage volume of waste from the low-acid flow sheet is 54% less than that from the high-acid flow sheet, with the low-acid flow sheet placing a significantly smaller load on the distillation equipment. Substitution of the low-acid flow sheet for the high-acid flow sheet accomplishes 79% of the volume reduction obtained by recovering acid from high-acid waste.

The reduction of first-cycle waste volume much beyond the 32 gal. of 35% solids per metric ton of uranium obtained on recovering acid from low-acid waste depends upon eliminating added process reagents. Of these 32 gal., $NaNO_2$ from the valence adjustment step is responsible for 11 and KNO_3 from the $KMnO_4$-MnO_2, head-end step is responsible for 5. Nitrogen dioxide may be substituted for $NaNO_2$ but, beyond this point, investigation of concentrated residues from other cycles is more profitable in the over-all waste picture.

First-cycle decontamination characteristics of the high and low-acid flow sheets are similar. The only significant difference in decontamination noted in a series of four pairs of high-level, first-cycle pilot plant runs (common feed was used for each high-acid, low-acid pair) was the somewhat better ruthenium decontamination with the high-acid flow sheet and the better zirconium + niobium decontamination of plutonium product with the low-acid flow sheet.

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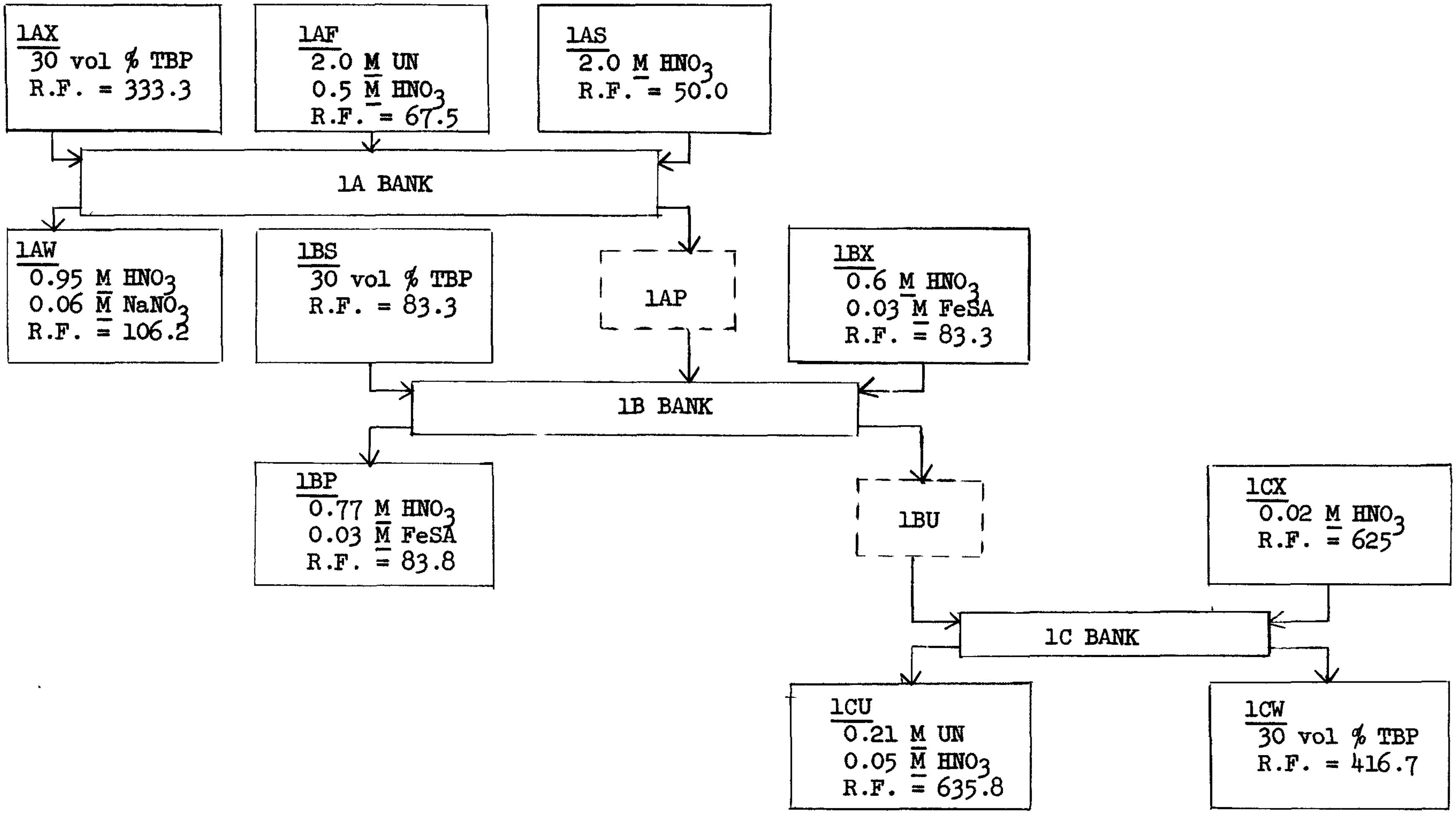

FIGURE 1. KAPL No. 6, Low-Acid First-Cycle Purex Flow Sheet

TABLE 2. First-Cycle Log Decontamination - Flow Sheet Comparison

Specification-Limiting F.P.	High-Acid Flow Sheet		Low-Acid Flow Sheet	
	Uranium	Plutonium	Uranium	Plutonium
Ruthenium	3.0	3.2	2.8	2.9
Zirconium + Niobium	4.0	3.0	4.0	3.7

Purex 1A flow sheets are designed for operation at close to maximum capacity to obtain optimum decontamination and economy. To avoid unstable operation in terms of excessive product loss, flow-sheet design must make allowances for the limits of analytical and flow-rate control, and for the probable range of operating temperatures. With other parameters at their nominal values, the KAPL No. 6 and ORNL-846 1A flow sheets become unstable if the solvent flow is reduced by more than 6% and 4%, respectively. The effects on flow-sheet stability of variations in other important parameters have been determined for both flow sheets; these effects are given in Tables 4 and 5. As instability would normally be corrected by changing the extractant flow rate, they are given in terms of per cent variation in solvent flow giving an equivalent effect.

Column 4 of these tables gives the expected maximum deviation of each parameter under operating conditions. If each of the parameters varied from their nominal value the maximum expected amount in the direction of instability, the resulting systems would lack uranium capacity by 1.4% for the low-acid flow sheet and 3.4% for the high-acid flow sheet.* Odds against such an occurrence are very large, and the maximum total effect of parameter variation expected is well within the safety factors of the two flow sheets. In addition, under actual operating conditions both the high- and low-acid systems can tolerate reasonably long periods of instability before incurring appreciable product loss. This reservoir capacity of the flow sheets permits operation at close to maximum capacity with normal operating corrective measures even if uranium capacity is exceeded at times.

The two flow sheets are similar with respect to product loss and partition. Other than appreciably lowering the amount of acid in the first-cycle plutonium product, operation of the 1A system under low-acid conditions did not affect the 1B and 1C systems.

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*Temperature variation was not included.

TABLE 3. Comparison of First-Cycle 1A Flow Sheets

	KAPL No. 6	ORNL-846
1AF		
Relative flow rate	67.5	100.0
$UO_2(NO_3)_2$, M	2.00	1.35
HNO_3, M	0.50	2.00
$NaNO_2$, M	0.10	0.10
KNO_3, M	0.04	0.03
1AS		
Relative flow rate	50.0	66.7
HNO_3, M	2.00	3.00
1AX		
Relative flow rate	333.3	333.3
TBP, vol %	30.0	30.0
1AP		
Relative flow rate	346.4	347.5
$UO_2(NO_3)_2$, M	0.390	0.387
HNO_3, M	0.10	0.16
1AW		
Relative flow rate	106.2	154.7
HNO_3, M	0.95	2.22
$NaNO_2$, M	0.06	0.06
KNO_3, M	0.03	0.02
Volume, gal./metric ton U	873	1272
HNO_3, lb/metric ton U	436	1485

TABLE 4. Factors Affecting Stability of the KAPL No. 6 1A Purex Flow Sheet

(Uranium capacity is exceeded if extractant (1AX) flow is reduced by more than 6%, with other parameters remaining at their nominal values. Variations in other parameters affect uranium capacity as the sum of their equivalent effects in terms of per cent 1AX flow-rate variation.)

			Effect of Parameter Variation on Flow-Sheet Capacity in Terms of % 1AX Flow-Rate Variation	
1A Stream	Parameter	Nominal Value	Expected Maximum Parameter* Variation under Operating Conditions	Equivalent 1AX Flow Variation, %
Extractant (1AX)	Flow rate	333.3	± 1.5%	± 1.5
	% TBP	30.0	± 0.8%**	± 2.6***
Feed (1AF)	Flow rate	67.5	± 1.5%	∓ 1.4
	UN	2.00 M	± 0.03 M	∓ 1.6
	HNO_3	0.50 M	± 0.15 M	†
Scrub (1AS)	Flow rate	50.0	± 1.5%	∓ 0.15
	HNO_3	2.00 M	± 0.03 M	± 0.15
	Temperature, °C	25	††	- 0.2

*Combination of operating tolerances, instrument errors, and analytical confidence levels.

**30.0 ± 0.8%

***30.0 ± 2.6%

†Minor variations of 1AF acidity have an insignificant effect on the scrub system.

††No estimate of expected variation made. Equivalent 1AX flow-rate variation is for a 1°C rise in temperature.

TABLE 5. Factors Affecting Stability of the ORNL-846 1A Purex Flow Sheet

(Uranium capacity is exceeded if extractant (1AX) flow is reduced by more than 4%,* with other parameters remaining at their nominal values. Variations in other parameters affect uranium capacity as the sum of their equivalent effects in terms of per cent 1AX flow-rate variation.)

1A Stream	Parameter	Nominal Value	Effect of Parameter Variation on Flow-Sheet Capacity in terms of % 1AX Flow-Rate Variation: Expected Maximum Parameter** Variations under Operating Conditions	Equivalent 1AX Flow Variation, %
Extractant (1AX)	Flow rate	333.3	± 1.5%	± 1.5
	% TBP	30.0	± 0.8%***	± 2.6†
Feed (1AF)	Flow rate	100.0	± 1.5%	∓ 1.4
	UN	1.35 M	± 0.03 M	∓ 2.0
	HNO_3	2.00 M	± 0.15 M	††
Scrub (1AS)	Flow rate	66.7	± 1.5%	∓ 0.15
	HNO_3	3.00 M	± 0.03 M	± 0.15
	Temperature	25°C	†††	- 0.2

*Can be raised to 8% by reducing the scrub: extractant ratio to that of the KAPL No. 6 flow sheet.
**Combination of operating tolerances, instrument errors, and analytical confidence levels.
***30.0 ± 0.8%
†30.0 ± 2.6%
††Minor variations of 1AF acidity have an insignificant effect on the scrub section.
+++No estimate of expected variation made. Equivalent 1AX flow-rate variation is for a 1°C rise in temperature.

III. DESIGN OF THE KAPL NO. 6, LOW-ACID 1A PUREX FLOW SHEET

First-cycle Purex waste volumes and product decontamination depend almost entirely on the 1A flow sheet. For that reason little attention is given to the 1B and 1C flow sheets in this report beyond determining that changes in 1A design do not affect their operation adversely.

For clarity the following discussion of low-acid 1A flow sheet development is given in logical rather than historical sequence. A more qualitative discussion of 1A flow-sheet design principles is given in the Appendix to help interpret a complicated but not inherently difficult situation.

A. Equilibria

In previous Purex flow sheets adequate salting for plutonium recovery was apparently based on raffinate acidity,(1) with flow rates and concentrations being chosen to have this acidity correspond to the extraction factor [(extractant flow rate/aqueous flow rate). E(o/a)] calculated to give adequate recovery in the number of extraction stages available. Because the reflux and build-up of HNO_3 concentration in the extraction section were not being used to advantage, precise acid equilibrium data were not necessary. Design of stable 1A flow sheets which utilize acid reflux to obtain adequate salting with minimum waste acid requires more exact knowledge of the relation between the distribution of $UO_2(NO_3)_2$ and HNO_3 in the system.

In the Appendix the discussion of 1A flow-sheet design is based on the assumption that aqueous acid concentrations remain constant within each section. The situation actually existing is not that simple. In the scrub section some acid will be extracted from the scrub stream as it enters the 1A bank, and acid concentrations will change as the uranium concentration changes. Even larger variations in acid concentration will occur in the extraction section where uranium concentrations cover a much wider range. As a result, an acid as well as a uranium X-Y diagram will be required for precise calculation and, to complicate the situation further, the uranium and acid distributions will have to be calculated simultaneously as they are not independent. The distribution data used are given in Figures 19 and 20 (pp. 61 and 63).

The solid curves of Figure 19 represent equilibrium distributions of $UO_2(NO_3)_2$ at conditions of constant aqueous acidity; the broken curves represent equilibrium distributions of uranium at conditions of constant organic

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(1) Since the extraction coefficients (E o/a) of $UO_2(NO_3)_2$ are appreciably higher than those of plutonium (IV) nitrate, and the concentrations of the latter are insignificant in comparison with those of the other components, first-cycle Purex flow sheets are designed to recover plutonium nitrate while allowing capacity for $UO_2(NO_3)_2$.

acidity. These are useful for complete solution of flow-sheet problems since points on the uranium and the corresponding acid equilibrium diagrams have a one-to-one correspondence. Any point on either diagram defines four equilibrium concentrations; an equilibrium point on the uranium diagram is also an acid equilibrium point.

To emphasize the relation of the uranium and acid distribution diagrams, the two can be considered as distortions of each other. In converting the acid diagram of Figure 20 to the uranium diagram of Figure 19, the following steps would be made: (1) the vertical coordinates representing constant aqueous acidity would become solid curves; (2) the horizontal coordinates representing constant organic acidity would become broken curves; (3) the origin representing zero acid concentrations in the two phases would expand into the distribution curve for uranium in the absence of acid; (4) the curve for acid distribution in the absence of uranium would disappear into the origin; (5) the solid curves representing constant aqueous uranium would become vertical coordinates; and (6) the broken curves representing acid distribution at constant organic uranium concentrations would become horizontal coordinates in transfer.

The fact that this conversion can be made is important since it makes possible the transfer of acid operating lines from the acid plot to the uranium plot. In transfer these straight lines become curved. The vertical and horizontal tie-lines connecting the operating and equilibrium lines in the McCabe-Thiele-type diagram for HNO_3 also become curved in transfer but like the transposed acid operating lines retain their original relationship to the distorted acid coordinates as they still represent constant acid concentrations in the organic and aqueous phases. Since acid and uranium equilibrium conditions for each state will be represented by a single point on the uranium plot, the uranium and acid McCabe-Thiele-type stage-to-stage steps will appear on the uranium diagram in double sawtooth fashion with common equilibrium points as shown in Figure 2.

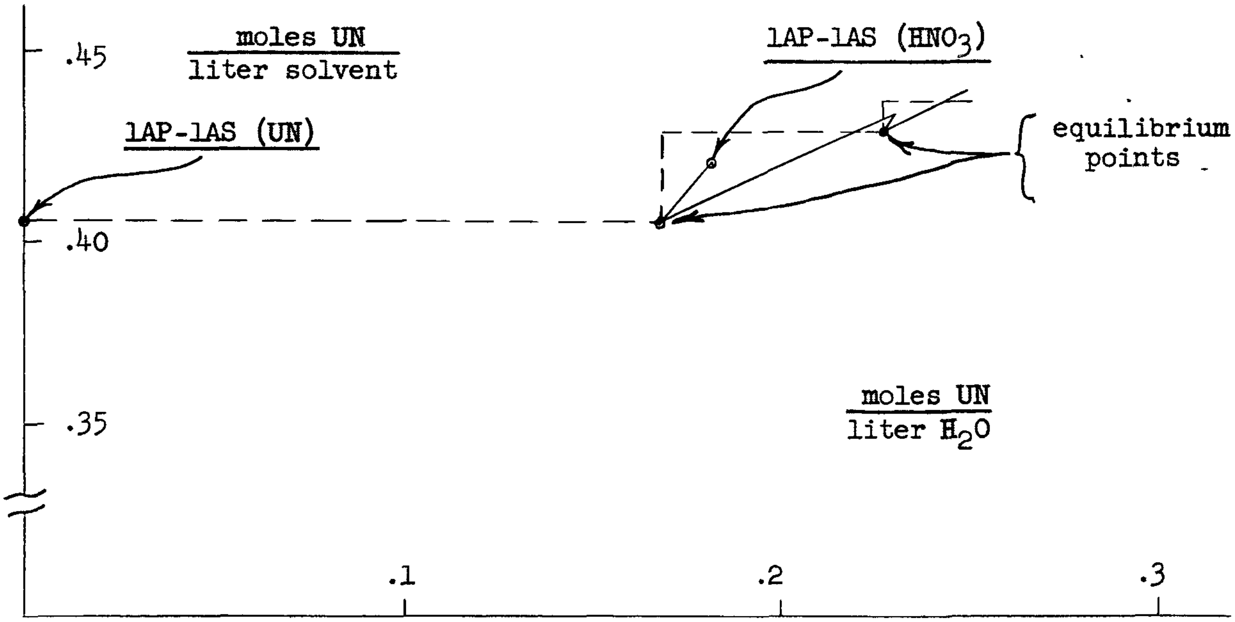

FIGURE 2. Combined Uranyl Nitrate - Nitric Acid X-Y Diagram

Although more complicated, the actual concepts and reasoning are the same as those employed in simple McCabe-Thiele-type construction. Use of the diagrams is illustrated below in calculating the minimum salting requirements for the Purex 1A scrub section.

B. Scrub Section

Design of the scrub section for the low-acid flow sheet was based on the uranium product concentration of 0.405 mole/liter solvent obtained with the ORNL-846 1A flow sheet. To minimize salting requirements and enhance acid reflux, the 1AS to 1AX solvent-free flow ratio was chosen to be 0.141. This was thought to be a practical lower limit with regard to decontamination and hydraulic stability.

The other important scrub section parameter remaining is the scrub stream (1AS) acidity since the acid contribution from the extraction section can be ignored in calculations near the product end of the system as a result of efficient acid stripping at the feed stage and adjacent scrub stages. To determine the minimum concentration required for uranium recovery it is necessary to use the curves in Figures 19 and 20 in constructing X-Y diagrams. The slope and intercept of the uranium operating line being fixed, an arbitrary choice of 1AP acidity is made and an acid operating line of slope 0.141 placed on the acid diagram intersecting the vertical coordinate of the chosen 1AS acidity at a point corresponding to an estimate of the product stream acidity. This point falls below the intersection of the 1AS acidity and the broken curve representing an organic uranium concentration of 0.405 mole/liter solvent.

This acid operating line is then transferred to the uranium diagram, and both uranium and acid stages are stepped off. To do this a horizontal line is drawn from the intercept of the uranium operating line and the ordinate, and a curved line of constant organic acidity is drawn from the intersection of the transposed acid operating line and the solid curve representing the chosen 1AS acidity. If the chosen 1AP acid is correct, the intersection of the straight and the curved tie-lines corresponds to the equilibrium point of the first stage. A vertical line and a curve, representing constant aqueous concentrations of uranium and acid, are then projected from the equilibrium point to their respective operating lines. These two points represent the uranium and acid concentrations between the first and second stages. By repeating the first step of constructing horizontal and curved tie-lines representing constant organic concentrations of uranium and acid from the two material balance points, an intersection defining the equilibrium conditions of the second stage is obtained.

This procedure is continued as long as it is apparent that the choice of 1AP acid is correct as judged by convergence of succeeding points.* If the points diverge, a new value of 1AP acidity is chosen and the process repeated. In practice it will be found possible to determine the correct product acidity within a short time as the criterion is very sensitive to small changes in acidity. Usually only a few stage points need to be constructed to determine the correct 1AP acidity within limits of analytical accuracy.

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*Divergence after a few stages could also be caused by an insufficient concentration of acid in the 1AS.

Once the uranium equilibrium curve for a given 1AS acidity is determined, its effect on uranium capacity may be examined. As mentioned in the Appendix, the capacity requirements of the scrub section will be satisfied if the operating and equilibrium lines touch. If the operating line is tangent to the equilibrium curve, the 1AS acidity is at a practical minimum. For reasons of stability, discussed in a later section, a 1AS stream of slightly higher acidity is chosen (2.0 M for the KAPL No. 6 flow sheet). When the amount of acid leaving the system in the product (1AP) stream is determined for a suitably low 1AS acidity, the amount of acid available from the scrub section for extraction section salting will be known and both uranium capacity and plutonium recovery in the extraction section of the low acid flow sheet may be calculated for various choices of feed concentrations and flow rates.

C. Extraction Section

To obtain maximum salting with the minimum amount of acid, the 1AF was made as concentrated as freezing point and operational convenience would permit. To prevent hydrolysis of plutonium (IV) and maintain optimum conditions for the $KMnO_4$ - MnO_2 head-end process and plutonium valence adjustment step it is desirable to keep the feed slightly acidic at all times. For the KAPL flow sheet 0.5 M HNO_3 was chosen as the minimum concentration assuring an acid feed under plant operating conditions. Since the maximum uranium concentration considered feasible in 0.5 M HNO_3 is approximately 2 M, the relative flow rate required to deliver product 0.405 mole/liter solvent was calculated on that basis. The acid concentration in the 1AW stream is calculated by adding the amounts coming into the extraction section from the 1AF and from the scrub section and dividing by the solute-free 1AW flow rate. The acid operating line of slope (1AS + 1AF)/(1AX) = 0.308 is then constructed on the acid diagram from the point representing the calculated 1AW aqueous acidity and the absence of acid in the incoming extractant stream.

Working backward it is assumed that excess capacity for uranium is available and that, therefore, the effect of uranium on acid distribution can be ignored in a McCabe-Thiele-type acid construction at the raffinate end of the system. Results of doing this, shown in Figure 3, illustrate the degree of acid reflux taking place in these systems.

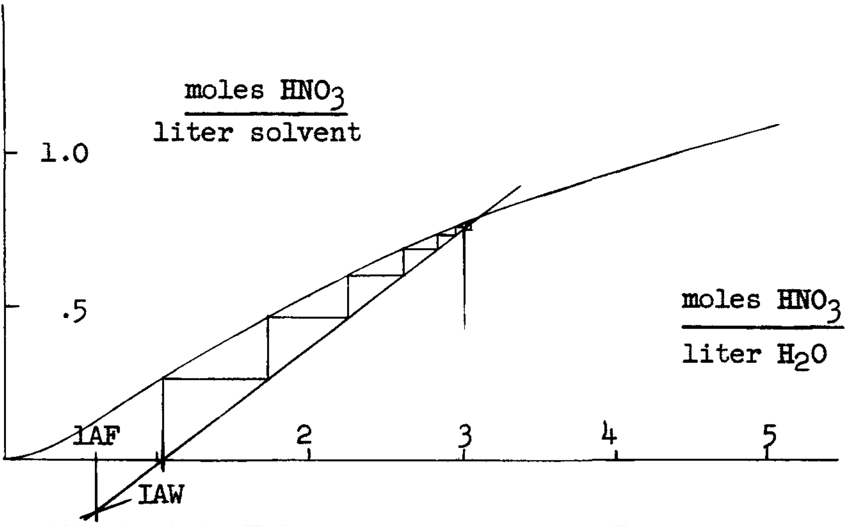

FIGURE 3. Nitric Acid X-Y Diagram for the 1A Extraction Section

Obviously at some point in going from the raffinate end of the system to the feed stage, the uranium concentration will become large enough to influence acid distribution. Examination of the uranium X-Y diagram for the system indicates, however, that even at the calculated 1AW acidity, with no acid reflux assumed, the uranium concentration in the second stage below the feed stage will be too small to influence acid distribution appreciably. The stepping-off of acid stages can then be carried out for n-2 stages, where "n" is the number of extraction stages. If "n" is nine, the convergence of the acid operating and equilibrium lines limits the maximum acid concentration to approximately 3.0 $\underline{M}$ in the aqueous phase. As the uranium concentration increases in the next two stages, the steps will take a path similar to that in Figure 3. Not until the feed stage is reached does the organic acid concentration decrease appreciably; the aqueous acid concentration still remains high since the aqueous at this point contains the acid displaced from the organic phase by uranium. The McCabe-Thiele acid construction for the scrub section can now be transferred from the uranium diagram to the acid diagram (Figure 4). If conditions for excess uranium capacity in the extraction section exist, stage acid concentrations for all but the few intermediate stages near the feed stage will be known accurately.

To determine whether excess extraction capacity for uranium does exist, a horizontal line is drawn through the scrub operating point adjacent to the feed stage in the uranium X-Y diagram. The aqueous coordinate of the intersection of this line with the uranium equilibrium curve for the estimated feed stage acidity corresponds to the feed stage aqueous uranium concentration. A vertical line is dropped from this point to the extraction operating line, and the McCabe-Thiele-type construction is continued with the use of uranium equilibrium lines for the predetermined aqueous acid concentrations of the

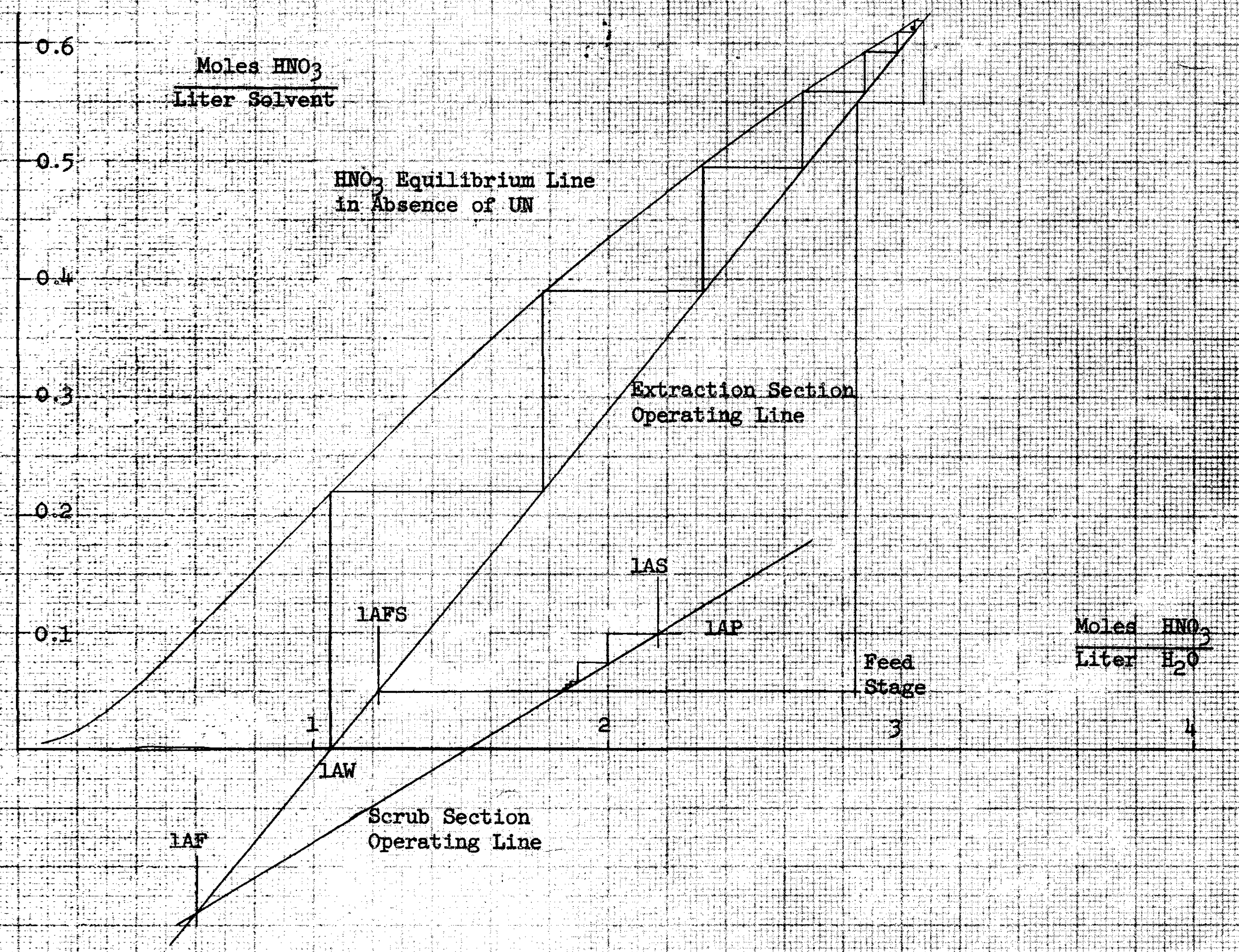

FIGURE 4. Nitric Acid X-Y Diagram for the KAPL No. 6 1A Flow Sheet

succeeding stages. It is evident from Figure 5 that the assumption of marked decrease of uranium concentration within a few stages of the feed stage was correct even for a low estimate of feed stage acidity. More exact uranium and acid concentrations for the stages adjacent to the feed stage can be determined by following the procedure outlined for calculating the 1AP acidity.

D. Plutonium Recovery

Calculation of plutonium recovery is now necessary. The flow sheet as designed to this point is adequate with respect to uranium scrub and extraction capacity, and the relative aqueous flow rates are at a practical optimum for plutonium recovery. The adequacy of the salting for plutonium recovery must be established to determine whether the 1AF and 1AS acid concentrations should be increased.

Figures 21 and 22 (pp.65 and67) and the acid and uranium X-Y diagrams of Figures 4 and 5 were used to determine the plutonium (IV) extraction coefficients in the individual stages. Since the concentrations of plutonium are too low to affect its own extraction coefficients or those of the other components, concentrations can be put on an arbitrary basis. To cover the range of relative plutonium concentrations accurately, plutonium X-Y diagrams were constructed on log-log paper. With an arbitrary loss of unity assumed, the extraction section operating line is plotted as in Figure 6, using the equation:

$$Y = \frac{\text{aqueous flow rate}}{\text{solvent flow rate}} \cdot (X - 1)$$

Starting at the aqueous concentration of unity a vertical line is drawn to the point representing the extraction coefficient in the stage nearest the raffinate as calculated from Figures 4 and 21. From this point a horizontal line representing constant organic concentration is drawn to the operating line. Another vertical line of constant aqueous acidity is extended up to a point coinciding with the extraction coefficient of the second stage above the raffinate, and a horizontal line is again drawn from this point to the operating line. This geometrical construction is continued until the horizontal line constructed corresponds to the relative concentration of plutonium in solvent leaving the feed stage. Care should be taken to calculate plutonium coefficients from Figures 5 and 22 rather than Figures 4 and 21 when appreciable concentrations of uranium are present.

A separate log-log X-Y diagram is made for plutonium (IV) distribution in the scrub section. Using log-log paper having a similar scale, the product concentration is arbitrarily assumed to be unity and the operating line

$$Y = \frac{\text{aqueous flow rate}}{\text{organic flow rate}} \cdot X + 1$$

as drawn in Figure 7. Construction of the McCabe-Thiele-type steps proceeds in a manner similar to that used in the extraction section but starts with

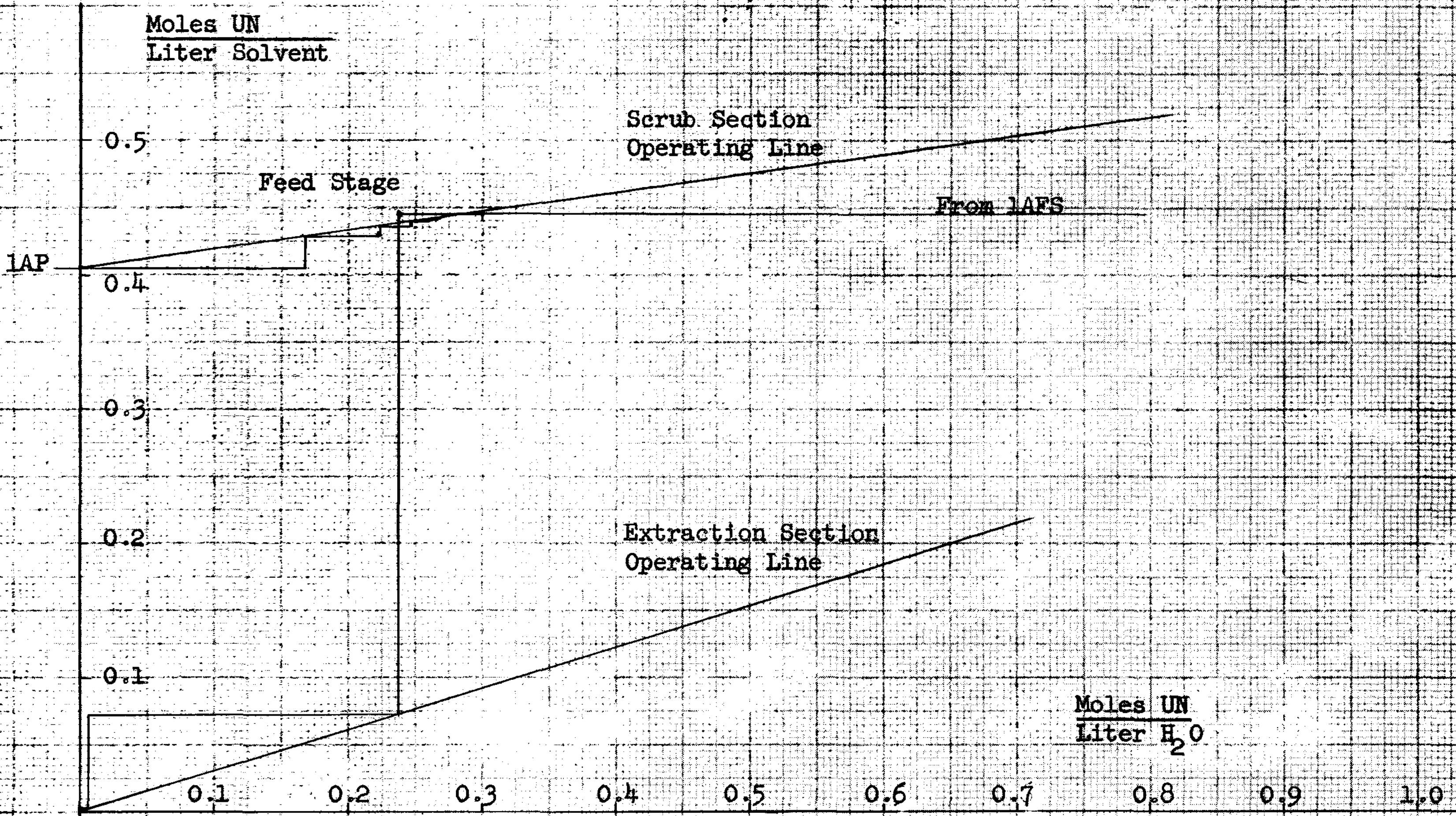

FIGURE 5. Uranyl Nitrate X-Y Diagram for the KAPL No. 6 1A Flow Sheet

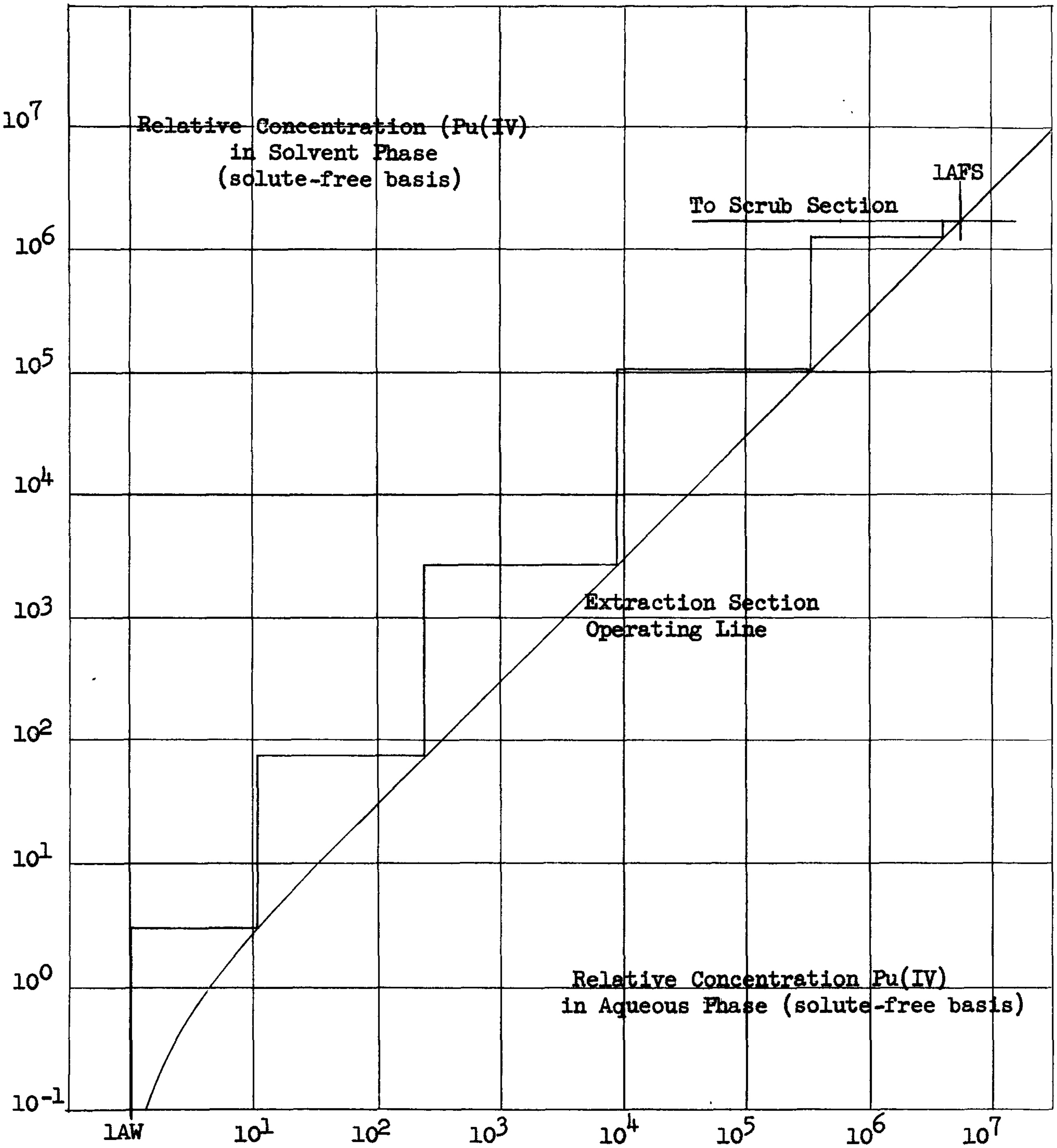

FIGURE 6. Relative Plutonium Distribution in Six-Stage Extraction Section - KAPL No. 6, 1A Flow Sheet

extension of a horizontal line representing an arbitrary product concentration of unit. The final step in preparing the scrub section X-Y diagram is the extension of the line representing the concentration of Pu (IV) in solvent coming from the extraction section and entering the scrub section.

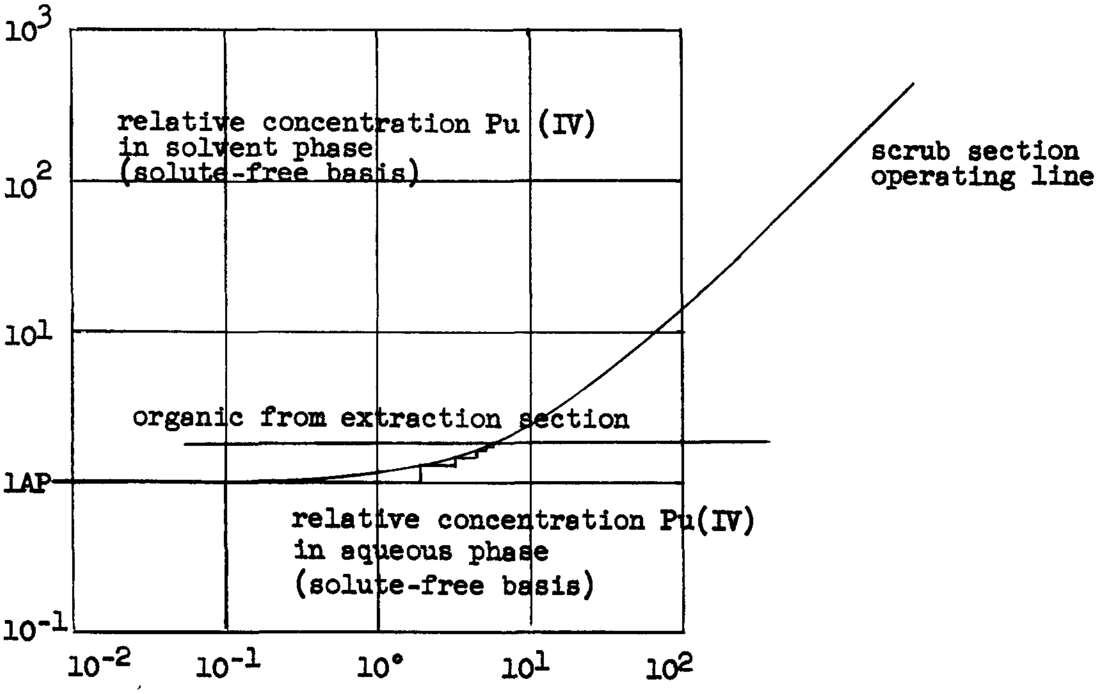

FIGURE 7. Relative Plutonium Distribution in Five Stage Scrub Section - KAPL No. 6, 1A Flow Sheet

Since the concentration of plutonium (IV) in the solvent stream joining the extraction and scrub sections can have only one value under steady-state operation, the X-Y diagram for one section can be transferred to the diagram for the other section. In addition to coincidence of the solvent concentration common to both sections, equivalent extraction coefficients, as represented by straight lines with a slope of unity, must coincide. With transfer, the diagram of Figure 8 is obtained. The relative feed concentration of plutonium (IV) is represented by the intersection of the two operating lines. Taking into account the relative flow rates of the 1AF and 1AW streams, a theoretical loss can now be calculated. For plant design, stages are added to allow for less than 100% stage efficiency and minor flow variations.(1)

---

(1)Stage efficiencies in mixer-settlers drop off as extraction factors depart markedly from unity because of the exaggerated effect of back-mixing and bypassing as well as non-attainment of equilibrium. The stage calculations are much more exact for such units, however, than for columns where the effectiveness of very large or very small extraction factors is limited.

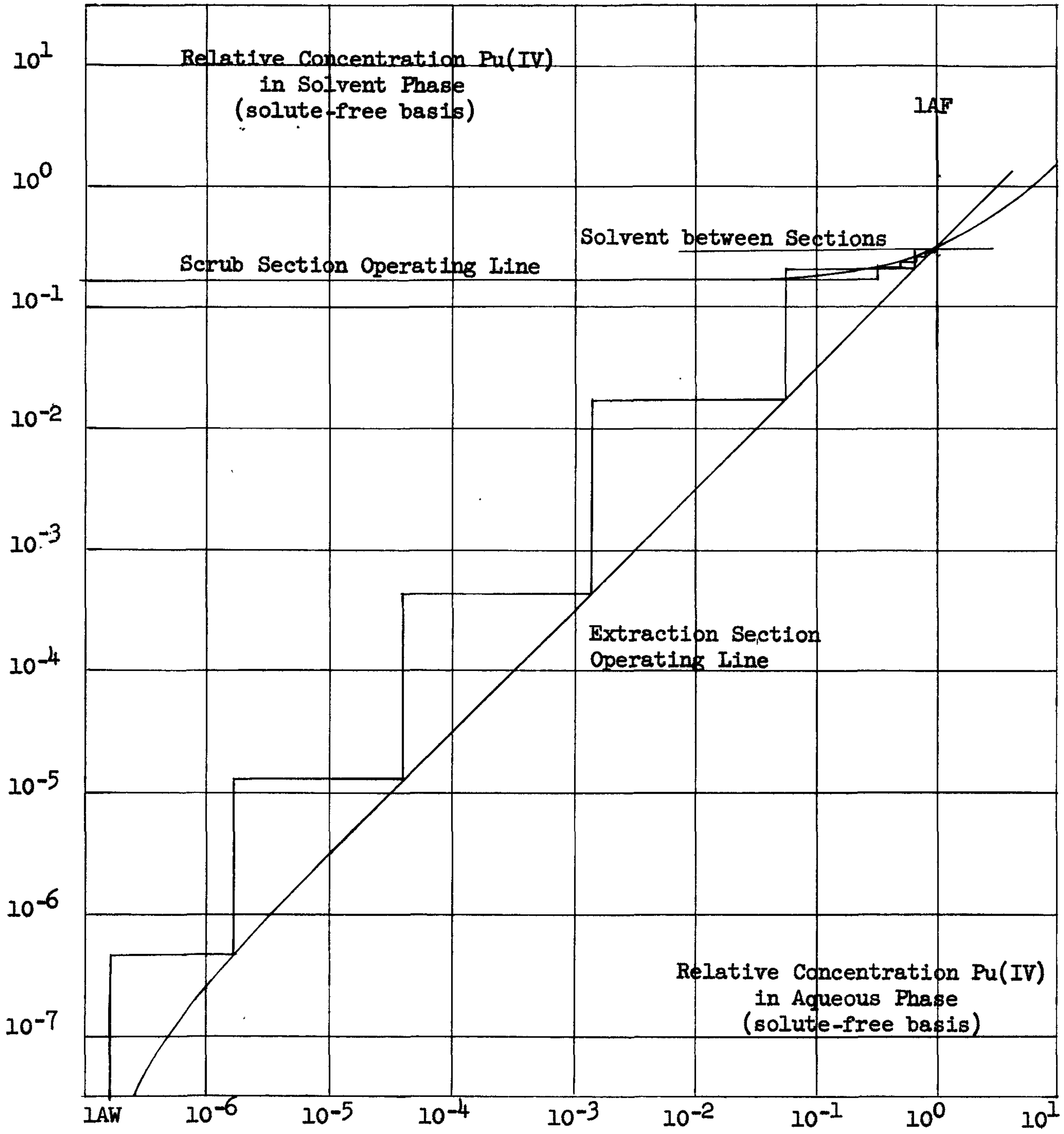

FIGURE 8. Relative Plutonium Distribution in the KAPL No. 6, 1A Flow Sheet

Essentially these additional stages are added to the center of the extraction section, where they are most effective in providing a safety factor against plutonium (IV) losses.

E. Flow-Sheet Stability

In designing 1A Purex flow sheets for optimum uranium capacity, allowance must be made for the limits of analytical accuracy and flow-rate control and for the probable range of operating temperatures. It is desirable to operate close to maximum capacity for efficiency and the improved decontamination obtained with high solvent saturation. Exceeding capacity, however, should be avoided, not primarily because of small uranium losses, but because of the high plutonium reflux and loss that accompanies such a condition.

Under conditions of either the KAPL No. 6 and ORNL-846 1A flow sheets the scrub section is the only part of the system that is critical with respect to minor variations in parameters. With flow-sheet parameters at their nominal values, the extraction section possesses an approximately 20% reserve capacity for uranium recovery. In addition, the capacity of the extraction section is only moderately affected by changes in parameters other than the 1AX flow rate since the maximum concentration of uranium available in solvent from the extraction section is nearly invariant with flow ratio and acidity.

The excess capacity of the extraction section, however, is inadequate to cope with excessive reflux in the scrub section. Relatively minor variations in flow-sheet parameters will cause the scrub section to return more uranium to the 1AFS than can be recovered by the extraction section. In such a case the solvent going from the feed stage into the scrub section is in equilibrium with 1AFS. Loss of uranium will occur if the 1AFS delivers more uranium to the extraction section than can be returned to the scrub section by solvent in equilibrium with it. Under such conditions acid reflux will be repressed by the high uranium concentrations in solvent. Coupled with the lower uranium extraction coefficients existing throughout the bank this will have a disproportionately large effect on plutonium reflux and losses.

In calculating the stability of the KAPL No. 6 and ORNL-846 flow sheets the criterion previously mentioned was used. The flow sheet was said to be in a condition of incipient instability, in terms of the X-Y diagram, when the scrub section operating line was tangent to the scrub section equilibrium line. Taking into account the effect of changed 1AX flow rate on product concentration and other parameters, the percentage difference between the nominal 1AX flow rate and reduced 1AX flow rate at incipient instability was termed the degree of safety. This was found to be 6% for the KAPL No. 6 1A flow sheet and 4% for the ORNL-846 flow sheet, although the latter could be raised to 8% by decreasing the 1AS to 1AX flow ratio of the ORNL flow sheet to that of the KAPL flow sheet.

With the uranium diagram first adjusted to a condition of incipient instability by reduction of the 1AX flow rate, other flow-sheet parameters were then varied and their effect on stability judged by the per cent variation in 1AX flow rate required to bring the scrub operating line back to tangency with the equilibrium curve. This equivalency was used because solvent flow rate is most readily adjusted to remedy unstable operation or correct for off-specification feed.

For small variations in TBP concentration the equilibrium curves were shifted using the following equations:

$$\frac{\Delta u_o}{u_o} = \frac{2\Delta T_o}{1.095 + 2.19\ u_o + 0.369\ h_o}$$

$$\frac{\Delta h_o}{h_o} = 0.652 \times \frac{\Delta u_o}{u_o}$$

T_o = molar concentration of TBP in solvent

u_o = moles uranium/liter solvent

h_o = moles HNO_3/liter solvent

aqueous acid and uranium concentrations are the same for T_o and $T_o + \Delta T_o$.

In the absence of extensive equilibrium data for temperatures other than 25°C, the effect of temperature variation on flow-sheet capacity was determined in a series of solvent extraction runs in "Mini" mixer-settlers. This was feasible despite analytical limits and flow-rate variation since only the equivalency of temperature variation and relative extractant flow rate was desired. Use of the same feeds through a run-series eliminated variation in concentrations, and a common drive to the syringe-displacement feed system eliminated variation in flow ratios. Equivalency was determined by bracketing points of approach and departure from incipient stability as judged by uranium analyses of extraction stage samples. When such a point was bracketed by varying relative solvent flow rates at one temperature, the process was repeated at other temperatures. An example of the type of data obtained is shown in Figure 9. Although the method is not a substitute for equilibrium data, it represents a considerable short-cut over the conventional equilibrations and calculations that otherwise would have been required. The equivalencies obtained were found to be reproducible and self-consistent. The effect of temperature on plutonium extraction is not of concern since the extraction coefficients (o/a) for plutonium (IV) in the absence of uranium increase with increased temperatures. Operation much below 25°C is not likely.

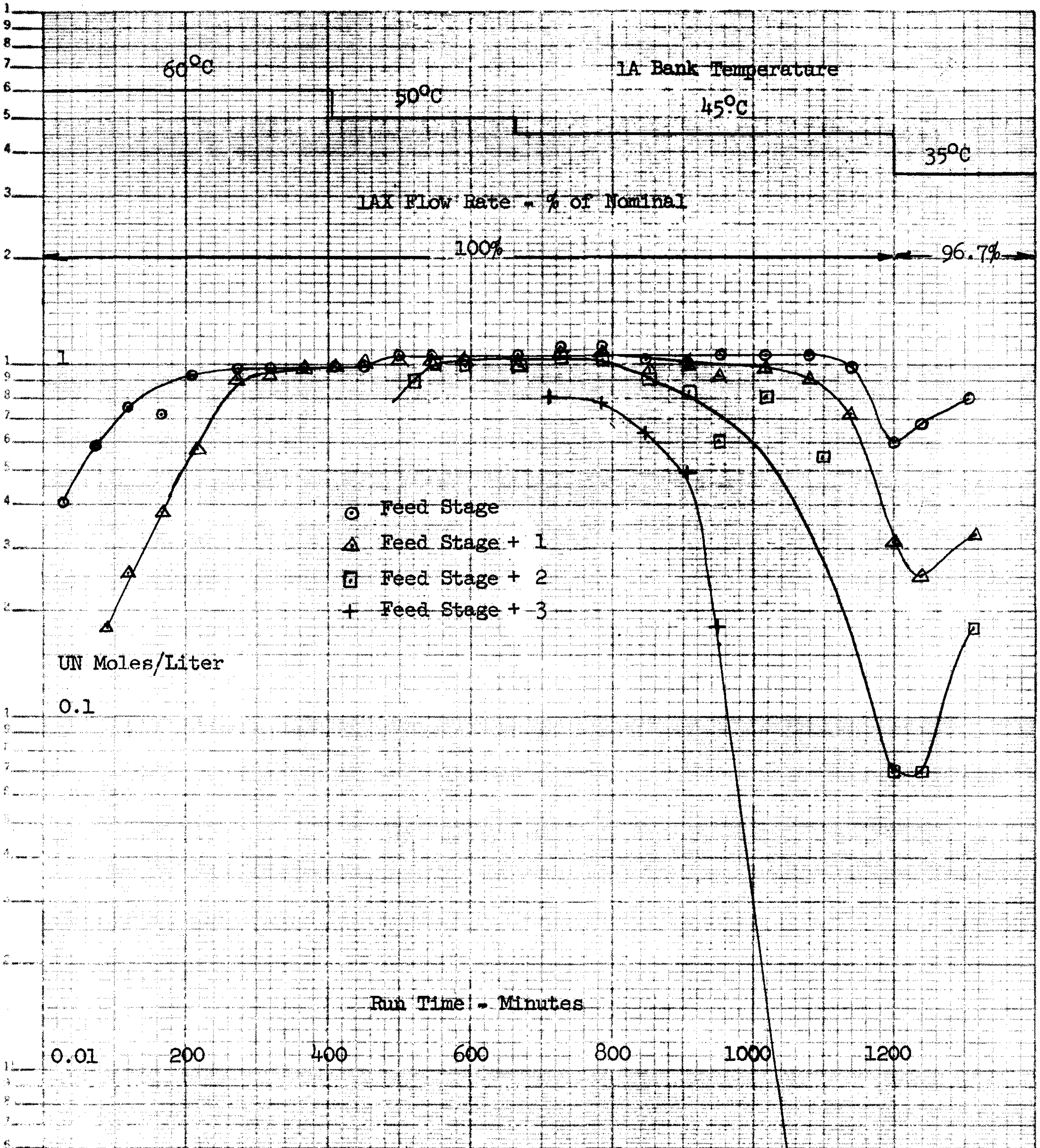

FIGURE 9. Effect of Temperature on Uranium Distribution in the IA Extraction Section - ORNL-846 Flow Sheet

Tables 4 and 5 give the estimated variation of each parameter under normal operating and analytical conditions and their equivalency in per cent extractant flow rate. Since the variations are as likely to be on the safe side as on the side of instability, and since the extraction equipment acts as a reservoir to damp out short-term fluctuations, designing for ever-safe operation is not necessary or desirable. The amount of operating margin used will depend on circumstances but normally would decrease with increased experience.

IV. EFFECT OF THE LOW-ACID 1A FLOW SHEET ON THE 1B AND 1C SYSTEMS

Since the 1B and 1C systems produce no aqueous waste directly, they are mentioned in this study only as their operation is affected by changes in the 1A flow sheet. The reduction in second-cycle plutonium waste obtained indirectly as a result of changing from high- to low-acid first-cycle operation is insignificant.

Organic product (1AP) from the low-acid 1A system was designed to contain the same concentration of $UO_2(NO_3)_2$ as the product of the ORNL-846 high-acid 1A system. The only change of any magnitude in feed to the 1B system is the acid concentration. With no other 1B parameter changes the change in 1B feed acidity is reflected in a reduction of acid concentration in the 1B scrub section and the plutonium product stream. This affects the partition of uranium from plutonium to a slight but not serious extent and will have no effect on the partition of plutonium from uranium or the behavior of the 1C system. The capacity of the 1B system for uranium remains more than adequate following the first-cycle low-acid flow sheet and presents no serious problem with regard to stability. Uranium and acid X-Y diagrams of the low-acid first-cycle 1B flow sheets are given in Figures 10 and 11.

V. PILOT PLANT RUN RESULTS

Eleven full activity-level pilot plant runs were made with the KAPL low-acid first-cycle flow sheet. The first four were paired with high-acid runs using common feed for each pair. The last seven were run consecutively with individual dissolvings and $KMnO_4$ - MnO_2 head-end steps.

As can be seen from results of the paired runs reported in Table 6, the high- and low-acid flow sheets are quite similar with respect to decontamination. The only significant differences appear to be the somewhat better ruthenium decontaminations obtained with the high-acid flow sheet and the definitely better zirconium + niobium decontamination of the first-cycle plutonium product obtained with the low-acid flow sheet. With either flow sheet first-cycle decontaminations are adequate for a two-cycle process.

The partitions of plutonium from first-cycle uranium product given in Tables 8 and 9 were considered satisfactory since the loss of plutonium was insignificant and only a small amount of additional partition is required of the second uranium cycle.

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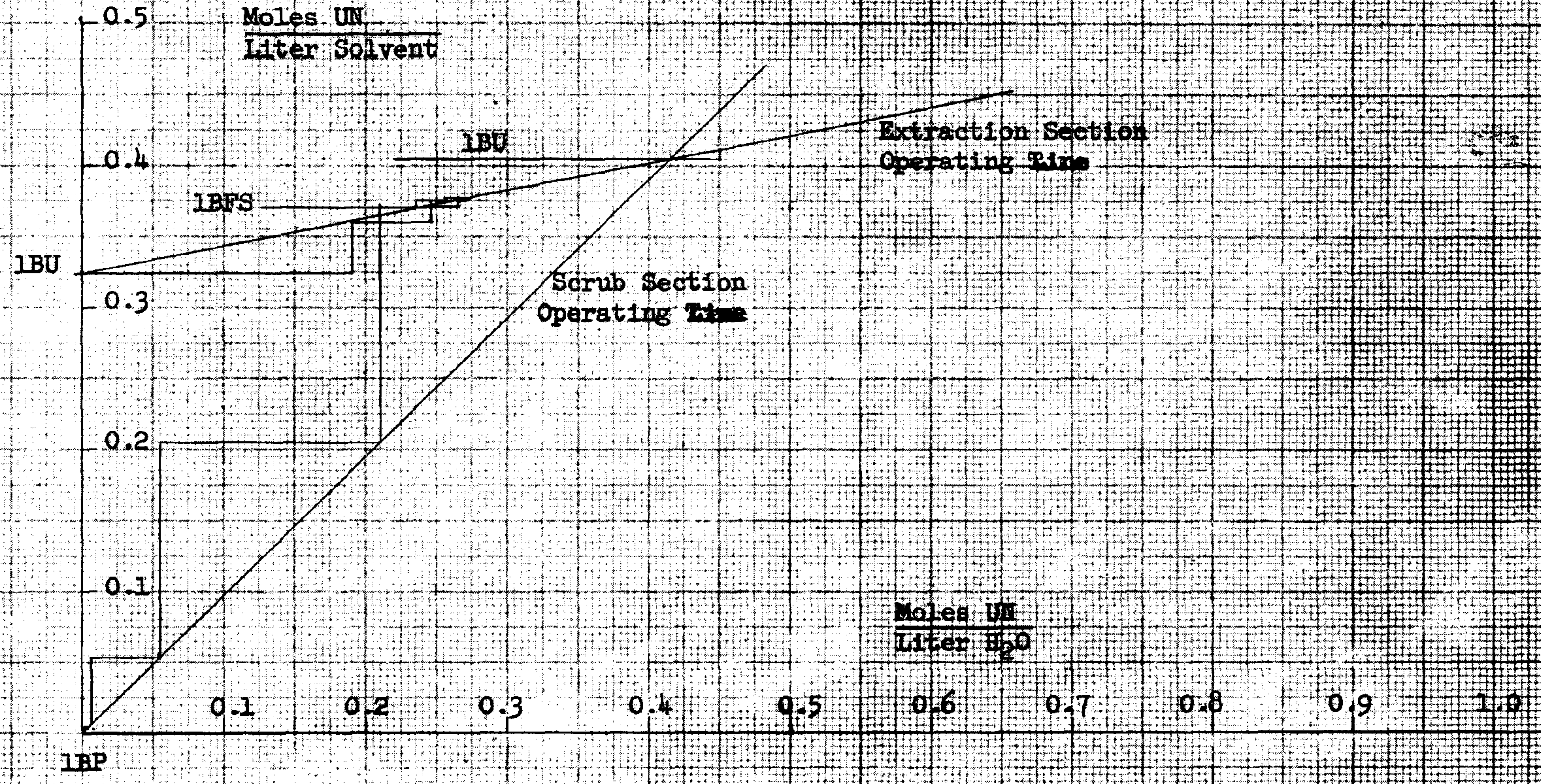

FIGURE 10. Uranyl Nitrate X-Y Diagram for the 1B Flow Sheet

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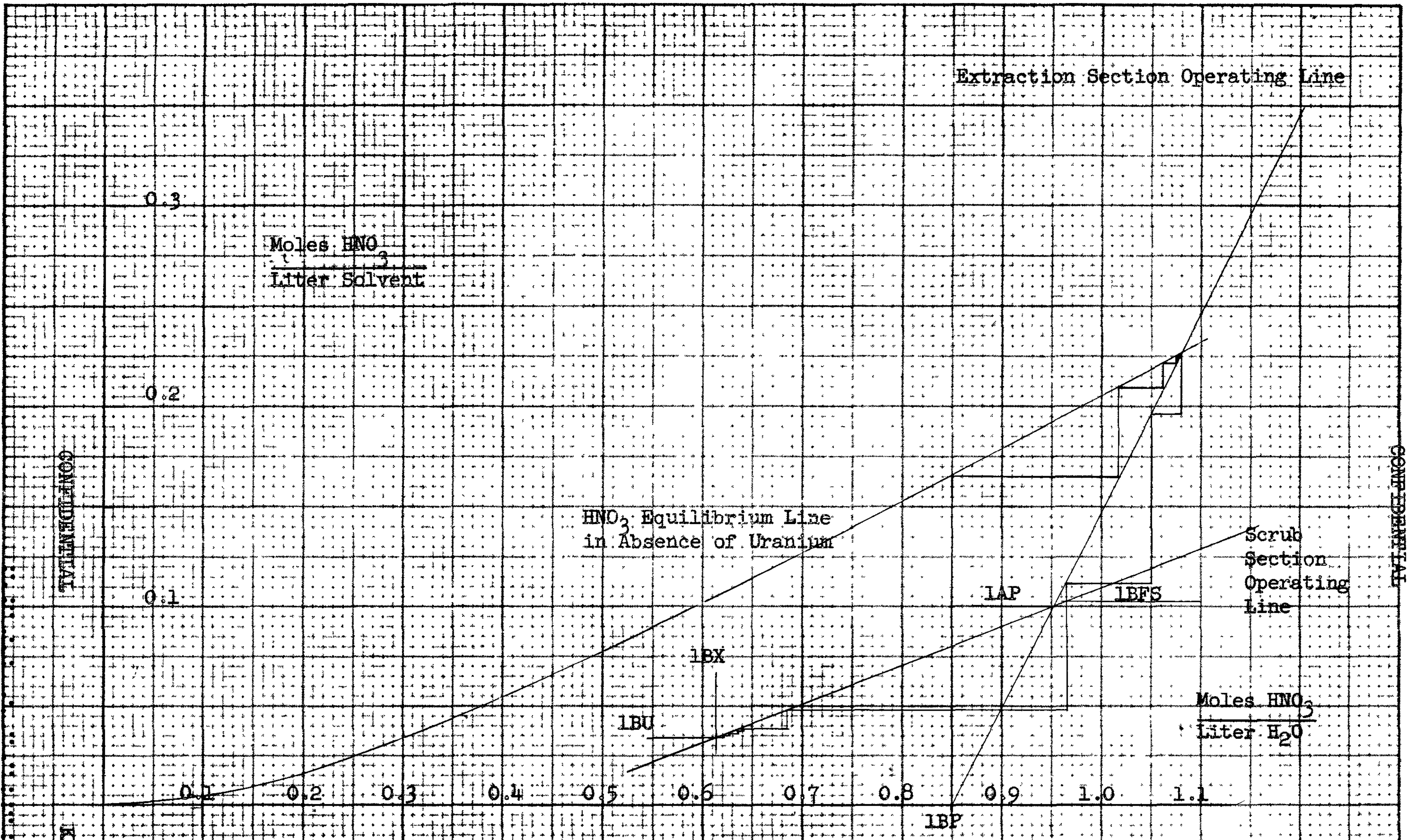

FIGURE 11. Nitric Acid X-Y Diagram for the 1B Flow Sheet

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Partitions of uranium from plutonium product were adequate in about half of the runs with both the high- and low-acid flow sheet. Although no additional partition is obtained in the second plutonium cycle all present post-solvent-extraction coupling steps provide sufficient additional partition to provide satisfactory product. Like the decontaminations reported in Tables 6 and 7, the partitions given in Tables 8 and 9 are for run composites and reflect the effects of temporary maloperation. Under continuous plant processing it is believed that such occurrences will diminish in frequency with increasing experience.

With few exceptions the losses of uranium and plutonium were satisfactorily low. The values reported in Tables 8 and 9 are for steady-state conditions and do not represent run composites.

TABLE 6. Pilot Plant Run Results*

Decontamination - Comparison of High-and Low-Acid Flow Sheets**

Run No.	10	11	12	13	14	15	16	17
1A flow sheet	LA	HA	LA	HA	LA	HA	LA	HA
Log decontaminations								
Across 1A bank (1AF to 1AP)								
Beta	3.9	3.9	4.0	3.9	4.3	4.4	4.1	4.1
Gamma	3.3	3.0	3.0	2.7	3.7	3.7	3.2	3.1
To uranium product (1AF to 1CU)								
Beta	4.9	4.9	5.0	5.0	5.1	5.5	5.6	5.6
Gamma	4.1	4.0	4.1	4.0	4.4	4.4	3.8	4.2
Ruthenium	2.5	2.7	2.7	2.9	2.9	3.2	3.8	3.9
Zirconium + niobium	4.1	3.9	4.3	4.0	4.3	4.2	3.6	4.1
To plutonium product (1AF to 1BP)								
Beta	4.6	4.6	4.6	3.9	4.9	4.8	5.1	5.1
Gamma	3.8	2.9	3.4	2.9	4.4	3.7	4.0	3.9
Ruthenium	2.7	3.4	2.7	2.8	3.2	3.5	3.7	3.8
Zirconium + niobium	3.6	2.7	3.5	2.7	4.3	3.6	4.0	3.6

*KAPL-809, "Pilot Plant Progress Report," August, September, October 1952, F. C. Steiner and J. F. LaBonte, December 10, 1952.

KAPL-860, "Pilot Plant Progress Report," November, December 1952, January 1953, F. C. Steiner, April 8, 1953.

**The 1A flow sheets used were similar to those of Table 3 with the exception of a 10% reduction in feed uranium concentration to ensure stability with the most adverse combination of normal operational and analytical variations. Decontaminations reported are for run composites and may reflect the effect of temporary upsets.

TABLE 7. Pilot Plant Run Results*

Decontamination - KAPL No. 6 Flow Sheet**

Run No.	18	19	20	21	22	23	24
Log decontaminations							
Across 1A bank (1AF to 1AP)							
Beta	3.5	3.7	3.9	3.9	3.5	3.3	3.9
Gamma	2.4	2.8	3.1	3.1	2.9	2.7	2.6
To uranium product (1AF to 1CU)							
Beta	4.6	4.7	5.8	5.6	4.7	5.0	4.5
Gamma***	2.6	3.1	4.0	4.3	3.5	3.9	3.3
Ruthenium	2.9	3.1	3.2	3.4	3.1	3.3	3.5
Zirconium + niobium***	2.5	3.1	3.7	4.0	3.3	3.7	3.2
To plutonium product (1AF to 1BP)							
Beta	4.4	4.2	4.8	5.0	4.5	4.7	4.5
Gamma	3.4	3.6	3.9	4.3	3.7	3.8	3.4
Ruthenium	2.7	3.1	2.9	3.3	3.5	3.4	3.3
Zirconium + niobium	3.4	3.3	3.7	4.1	3.6	3.8	3.3

*KAPL-913, "Pilot Plant Progress Report," February through June 1953, A. J. Arker and C. M. Wilson, November 2, 1953.

**The 1A flow sheet used was that of Table 3. Decontaminations reported are for run composites and may reflect the effect of temporary upsets.

***Siliceous material carried zirconium-niobium into the uranium product in run 18 as a result of addition of mechanically dejacketed slugs to the dissolver following complete dissolution of the heel. The effect of this material was still apparent in run 19.

TABLE 8. Pilot Plant Run Results*

Losses and Partitions

Comparison of High-and Low-Acid Flow Sheets**

Run No.	10	11	12	13	14	15	16	17
1A flow sheet	LA	HA	LA	HA	LA	HA	LA	HA
Per cent loss								
Aqueous raffinate (1AW)								
Uranium	0.01	0.002	0.006	<0.001	0.002	0.002	0.002	-
Plutonium	0.008	0.03	0.05	0.2	0.003	0.007	1.2	-
Organic raffinate (1CW)								
Uranium	0.05	0.008	0.08	0.01	0.002	0.07	0.01	0.003
Log partition								
To uranium product (1CU)	4.3	4.1	3.7	4.9	4.0	4.6	4.0	3.7
To plutonium product (1BP)	5.3	6.1	5.4	6.1	4.7	5.1	6.1	-

*KAPL-809, "Pilot Plant Progress Report," August, September, October 1952, F. C. Steiner and J. F. LaBonte, December 10, 1952.

KAPL-860, "Pilot Plant Progress Report," November, December 1952, January 1953, F. C. Steiner, April 8, 1953.

**The 1A flow sheets used were similar to those of Table 3 with the exception of a 10% reduction in feed uranium concentration to ensure stability with the most adverse combination of normal operational and analytical variations. Partitions reported are for run composites and may reflect the effect of temporary upsets. Losses reported are steady-state values.

TABLE 9. Pilot Plant Run Results*

Losses and Partitions - KAPL No. 6 Flow Sheet**

Run No.	18	19	20	21	22	23	24
Per cent loss							
Aqueous raffinate (1AW)							
Uranium	0.003	0.05	0.002	0.009	0.003	0.001	0.003
Plutonium	0.02	0.3	0.6	0.009	0.01	0.02	0.02
Organic raffinate (1CW)							
Uranium	0.001	0.06	0.002	0.08	0.004	0.02	0.007
Log partition							
To uranium product (1CU)	4.0	3.2	4.6	4.9	4.5	3.7	3.6
To plutonium product (1BP)	5.8	5.9	6.1	4.0	4.2	4.6	4.6

*KAPL-913, "Pilot Plant Progress Report," February through June 1953, A. J. Arker and C. M. Wilson, November 2, 1953.

**The 1A flow sheet used was that of Table 3. Partitions reported are for run composites and may reflect the effect of temporary upsets. Losses reported are steady-state values.

APPENDIX

APPENDIX. PRINCIPLES OF 1A FLOW-SHEET DESIGN

Purex 1A flow sheets for the extraction and decontamination of $UO_2(NO_3)_2$ and $Pu(NO_3)_4$ can be designed on the assumption that the concentration of the HNO_3 salting agent remains constant within each section of the system. HNO_3, however, is also extractable, competing with $UO_2(NO_3)_2$ and plutonium nitrate for TBP. While it is necessary to consider the interrelation of all three extracting components and TBP to design an efficient flow sheet, discussion of some of the more important design factors is aided by making simplifying assumptions. Following a discussion of the equilibria and reflux of HNO_3 in the system, the capacity of 1A Purex scrub and extraction sections for $UO_2(NO_3)_2$ will be considered, with constant aqueous acid concentrations assumed.

A. Equilibria and Nitric Acid Reflux

The extraction of $UO_2(NO_3)_2$ and HNO_3 from aqueous solutions into organic solvents containing TBP is governed by the following equilibria:[2]

$$UO_{2\,aq}^{+2} + 2NO^{-}_{3\,aq} + 2TBP_{org} \overset{K_U}{\rightleftharpoons} UO_2(NO_3)_2 \cdot 2TBP_{org}$$

$$E_U\ (o/a) = \frac{(UO_2(NO_3)_2 \cdot 2TBP)_{org}}{(UO_2^{+2})_{aq}} \approx K_U \cdot [NO_3^-]^2_{aq} \cdot [TBP]^2_{org}$$

$$H^+_{aq} + NO^-_{3\,aq} + TBP_{org} \overset{K_H}{\rightleftharpoons} HNO_3 \cdot TBP_{org}$$

$$E_H\ (o/a) = \frac{(HNO_3 TBP)_{org}}{(H^+)_{aq}} \approx K_H \cdot [NO_3^-]_{aq} \cdot [TBP]_{org}$$

where K_U and K_H are equilibrium constants

E_U and E_H are extraction coefficients,

organic over aqueous

$[TBP]_{org}$ is the activity of uncomplexed TBP in the organic phase.

The dependent relations between the above equilibria are shown in Figures 19 and 20. The equilibria indicate that uranium extraction is limited by the complex $UO_2(NO_3)_2 \cdot 2TBP$. For the 30 vol % TBP solvent used in these Purex flow sheets, this means that the maximum concentration of uranium in solvent is 0.548 mole/liter of solvent.

In addition to the two macrocomponents whose extractions are interdependent, there is plutonium (IV) nitrate present in concentrations too small to affect the extraction of uranium and HNO_3 but whose extraction is affected by them. The probable equilibria involved in the extraction of plutonium is:[3]

$$Pu(NO_3)_{m_{aq}}^{+(4-m)} + (4-m)NO_{3_{aq}}^{-} + 2TBP_{org} \xrightleftharpoons{K_{Pu(IV)}} Pu(NO_3)_4 \cdot 2TBP$$

$$E_{Pu(IV)}\ (o/a) = \frac{(Pu(NO_3)_4 \cdot 2TBP)_{org}}{(Pu(NO_3)_4^{+(4-m)})_{aq}} \approx K_{Pu(IV)} \cdot [NO_3^-]_{aq}^{(4-m)} \cdot [TBP]_{org}^{2}$$

where $K_{Pu(IV)}$ is an equilibrium constant

$[TBP]_{org}$ is the activity of uncomplexed TBP in the organic phase.

The distribution of plutonium (IV) nitrate between 30% TBP in hydrocarbon diluent and aqueous HNO_3 is given in Figure 21, and the experimental data on the derived relation

$$E_{Pu(IV)}/E_U = K\ (NO_3)^{(2-\frac{m}{2})}$$

is given in Figure 22.

As a result of competition between $UO_2(NO_3)_2$ and HNO_3 for TBP, acid extraction coefficients (E_H o/a) are much higher at the raffinate end of the 1A extraction section where uranium concentrations are low, than at the feed stage and in the scrub section where uranium concentrations are relatively high. Combined with the relative flow rates required for product recovery and decontamination, the resulting extraction factors

$$\frac{\text{solvent flow rate}}{\text{aqueous flow rate}} \cdot E_H\ o/a$$

are in the range favorable to acid extraction at the raffinate end of the 1A system and acid stripping near the feed stage and in the scrub section.

Such conditions result in acid reflux in the 1A system. By adjusting relative flow rates and concentrations the amount of reflux can be appreciably increased before capacity, recovery, and decontamination are affected. Under conditions of the KAPL No. 6 flow sheet, acid concentrations through the larger part of the extraction section are more than three times as great as that in the raffinate. As a result, the last few stages of low acidity can be largely ignored as a factor in plutonium recovery.

B. 1A Scrub Section Capacity for Uranyl Nitrate

Satisfactory capacity(1) for uranium is the first consideration in designing a 1A flow sheet. For the KAPL No. 6 1A flow sheet this was arbitrarily defined as the capacity yielding a product with the uranium to solvent ratio of the ORNL-846 flow sheet. The resultant product (1AP) concentration of 0.405 mole/liter solvent is then the first fixed reference point. (Moles/liter solvent and moles/liter H_2O rather than moles/liter solution are used to obtain straight operating lines and simplify construction of McCabe-Thiele-type diagrams. See Table 10 for conversion equations.)

Material balance and the above choice of product concentration require that the difference between the amount of uranium in the organic phase leaving, and the aqueous phase entering each scrub stage remain at the value solvent flow/aqueous flow · 0.405 under steady-state operation. The locus of concentrations obeying this condition is the scrub operating line which has a slope equal to the scrub to extractant (1AS to 1AX) flow ratio and intersects the ordinate at 0.405 mole/liter of solvent. Stage equilibrium requires that the concentrations of acid and uranium in the aqueous and organic streams leaving each stage correspond to single points on the distribution diagrams of Figures 19 and 20. For the purpose of illustration, and as a first approximation, the aqueous acid concentration in the scrub section will be assumed constant and equal to its concentration in the 1AS stream.

Working backward from the product concentration of 0.405, it is obvious that the higher the scrub flow rate is with respect to the extractant flow rate, the greater will be the stripping of uranium from the organic phase; the subsequent increase in organic uranium concentration from stage-to-stage will have to be correspondingly large to maintain the difference required by material balance considerations. If material balance requires postulating an

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(1) Capacity is used to denote limits of the flow sheet without regard to equipment. In calculating recovery capacity of the extraction section, e.g., an infinite number of theoretical stages are postulated.

organic stream with a uranium concentration above 0.548 mole/liter solvent, it is evident that a 1AP concentration of 0.405 is not possible with the 1AS to 1AX ratio chosen. This situation is illustrated in the McCabe-Thiele-type diagram of Figure 12.(1)

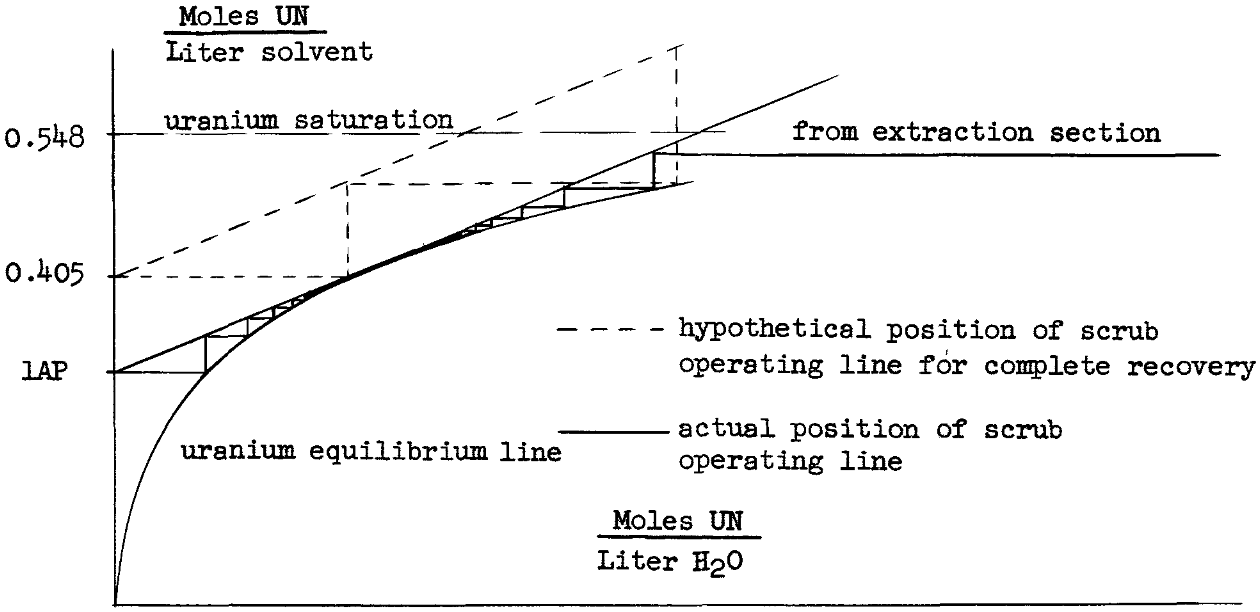

FIGURE 12. Uranyl Nitrate X-Y Diagram of the 1A Scrub Section with Insufficient Capacity

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(1) In such plots the horizontal and vertical tie lines intersecting on the operating and equilibrium lines denote constancy of concentration between stages and express the relationship between the two requirements of material balance and equilibrium for steady-state operation. Actual concentrations at any point in truly counter-current equipment, such as a packed column, remain on the operating line. Equilibrium points on the plot have no counterpart in the column but represent aqueous and organic concentrations in diverging phases which are separated by a distance corresponding to the height of a theoretical stage. For mixer-settler operation, where the flow is counter-current between stages and co-current in each stage, the equilibrium points on the plot essentially correspond to concentrations in the settling sections, and operating points on the diagram correspond to concentrations in the two phases passing between adjacent stages.[4]

Under more favorable conditions, i.e., a lower scrub-extractant flow ratio or a higher acid concentration in the scrub stream, or both, the stage-to-stage increase in uranium concentration will not be as great and the scrub operating line and scrub equilibrium line will intersect. In this case the concentrations of uranium in the organic and aqueous phases rapidly converge toward the point of intersection in going from the product stream toward the feed stage forming a so-called "pinch", as shown in Figure 13.

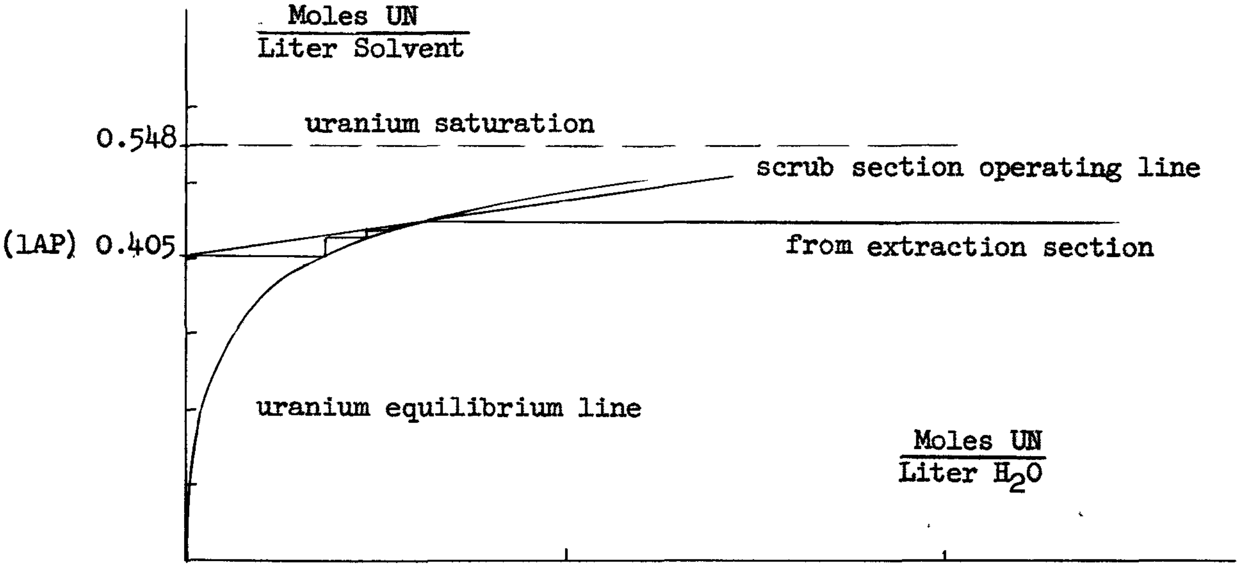

FIGURE 13. Uranyl Nitrate X-Y Diagram of 1A Scrub Section with Sufficient Capacity

There is no question of an impossible situation arising in the scrub section under these latter conditions. There is, however, the new problem of designing an extraction section to recover both the uranium stripped from solvent in the scrub section and that introduced in the feed.

C. 1A Extraction Section Capacity for Uranyl Nitrate

With complete recovery assumed, the amount of uranium entering the extraction section in the feed stream is fixed by the product concentration of 0.405 mole UN/liter solvent and the 1AX flow rate. The amount of uranium returned to the extraction section by the scrub stream is determined by the degree of reflux occuring in the scrub section. The concentration of uranium in the combined aqueous feed to the extraction section is represented geometrically by the aqueous coordinate at the intersection of the extraction section operating line and a horizontal line from the scrub operating point adjacent to the feed stage. This aqueous coordinate is termed 1AFS as it results from a combination of scrub (1AS) and feed (1AF). The feed (1AF) concentration at steady-state operation is represented geometrically by the aqueous coordinate at the intersection of the scrub and extraction operating lines. These relations are shown in Figure 14.

Again, by making the simplifying assumption that the equilibrium curve is that represented by a single aqueous acid concentration, the situation in the extraction section illustrated in Figure 15 occurs.

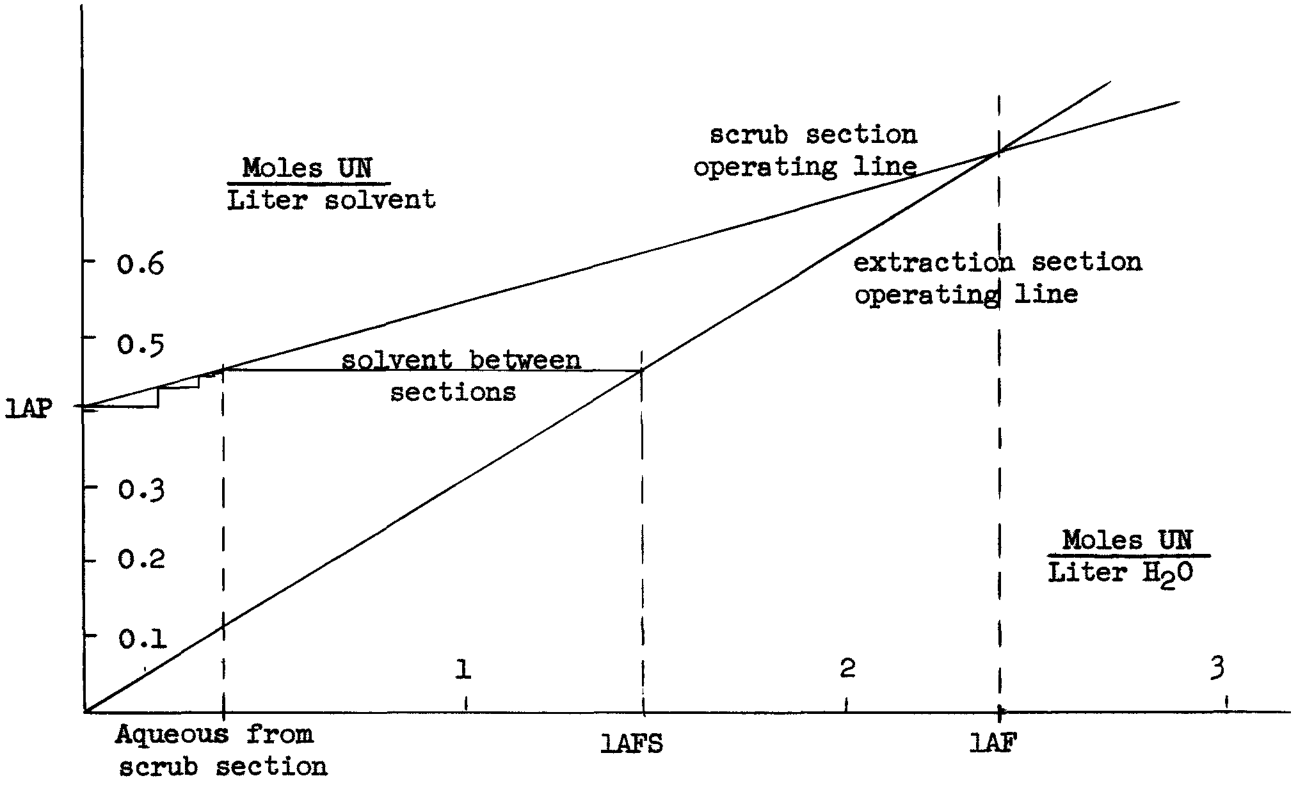

FIGURE 14. Relation of Uranyl Nitrate Operating Lines in 1A Purex Systems

Since complete recovery is assumed, the operating or material balance line is drawn from the origin. This indicates that no uranium is leaving or entering the system at the raffinate end.

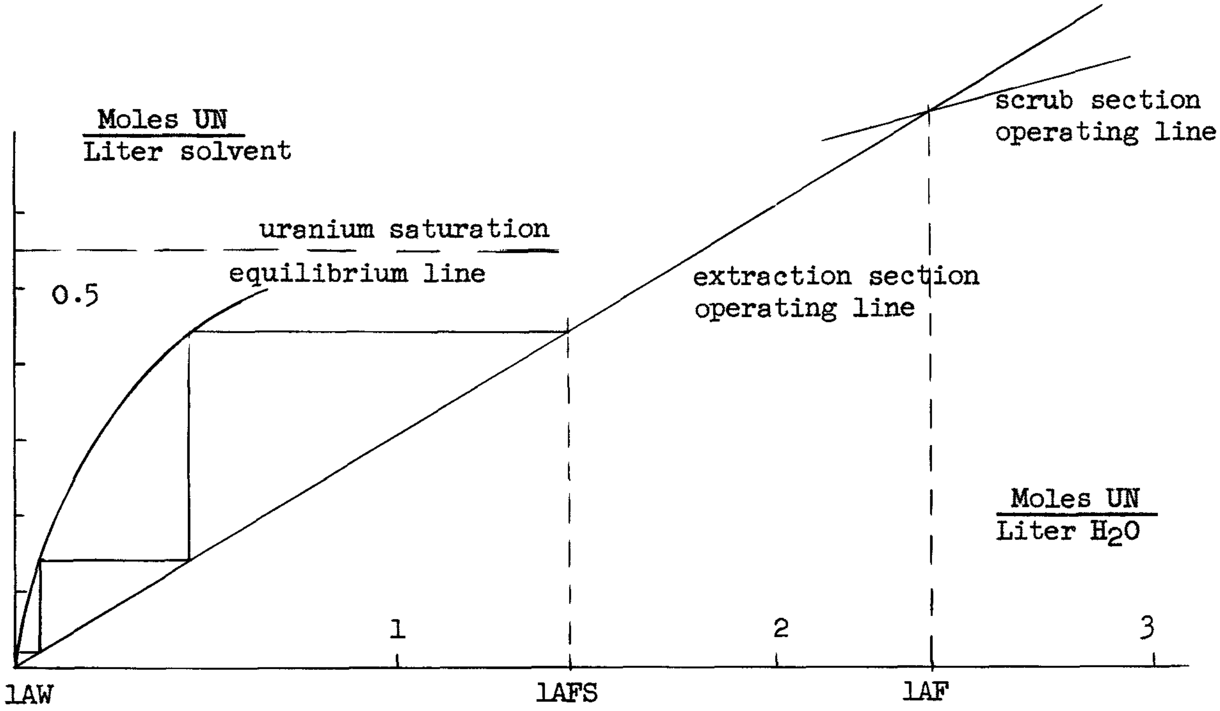

FIGURE 15. Uranyl Nitrate X-Y Diagram of 1A Extraction Section with Sufficient Capacity

If the relative aqueous flow rate is too high, as in the case of Figure 16, the system will be incapable of extracting all of the 1AFS uranium and construction of a McCabe-Thiele-type diagram will reveal that loss of uranium will occur.

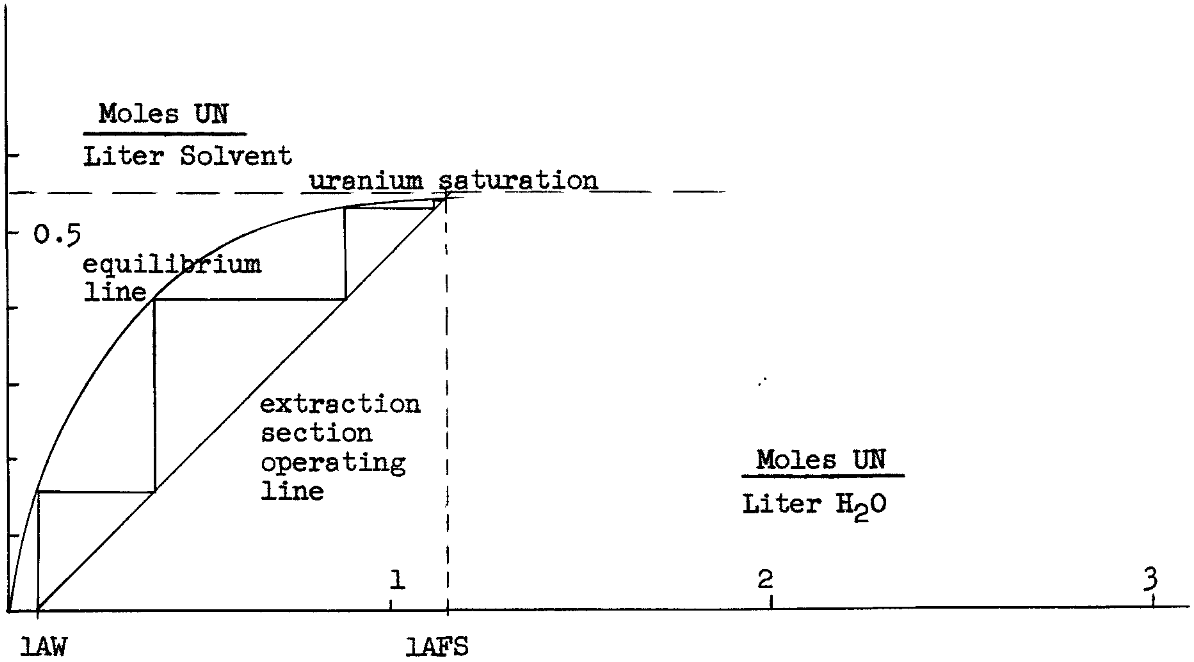

FIGURE 16. Uranyl Nitrate X-Y Diagram of 1A Extraction Section with Insufficient Capacity

If the aqueous flow rate is reduced by increasing the 1AF uranium concentration and proportionately reducing the flow, as in Figure 15, uranium recovery will no longer be limited by the flow sheet. Other alternatives improving recovery but previously ruled out to simplify discussion are: (1) reduction of the relative scrub flow rate, and (2) increase of aqueous HNO_3 concentrations in the 1AS, 1AF, or both.

Under conditions of the KAPL No. 6 and ORNL-846 flow sheets the extraction section can, if necessary, deliver to the scrub section solvent which is nearly saturated with uranium. As shown in Figure 17, the relation between the extraction section operating line and the uranium equilibrium curves is such that this property of the extraction section will remain fairly constant with reasonably large flow-sheet variations.

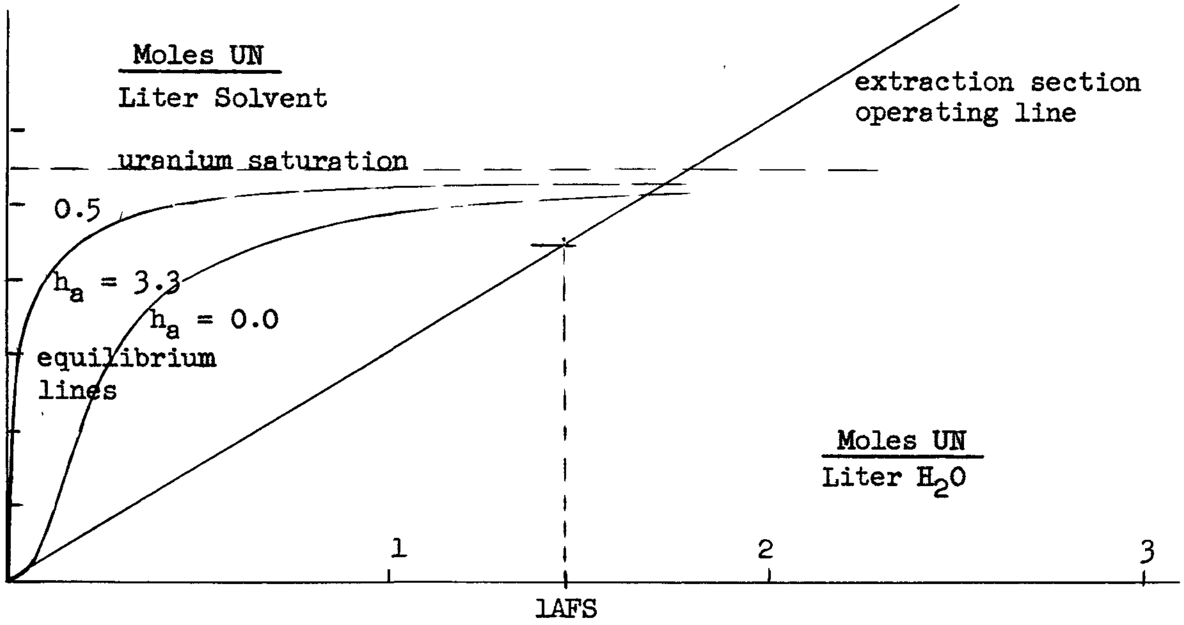

FIGURE 17. Relation of Uranyl Nitrate Operating and Equilibrium Lines in 1A Purex Systems

If the concentration of uranium in 1AFS exceeds the aqueous concentration defined by the intersection of the uranium equilibrium line and the extraction section operating line drawn from the origin, the latter will shift to the right to accommodate the new situation. In this case the aqueous intercept of the operating line will indicate the concentration of uranium in the waste stream. Figure 18 illustrates how this situation can result from excessive uranium reflux in the scrub section. The scrub section can be considered as limiting capacity for uranium recovery in both flow sheets as reflux in this section is relatively sensitive to parameter variations and little can be done to increase the uranium capacity of the extraction section.

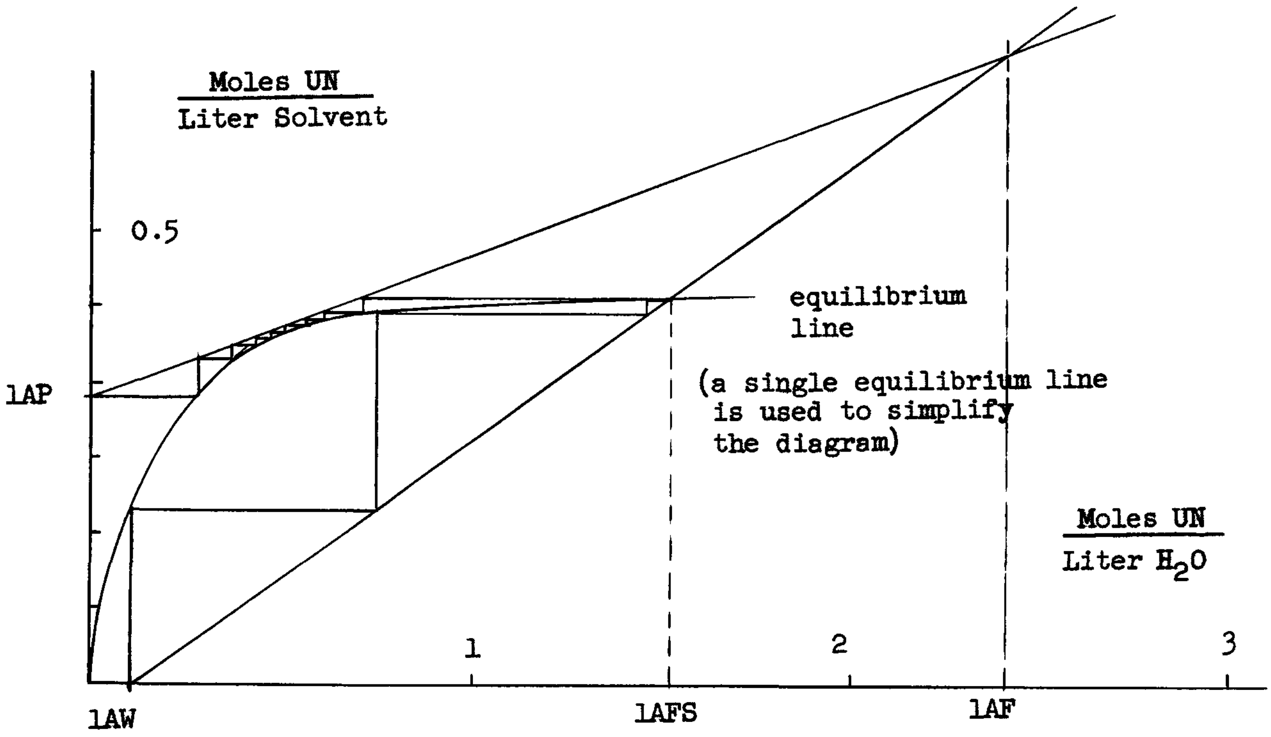

FIGURE 18. Uranyl Nitrate X-Y Diagram of 1A System - Effect of Insufficient Scrub Section Capacity

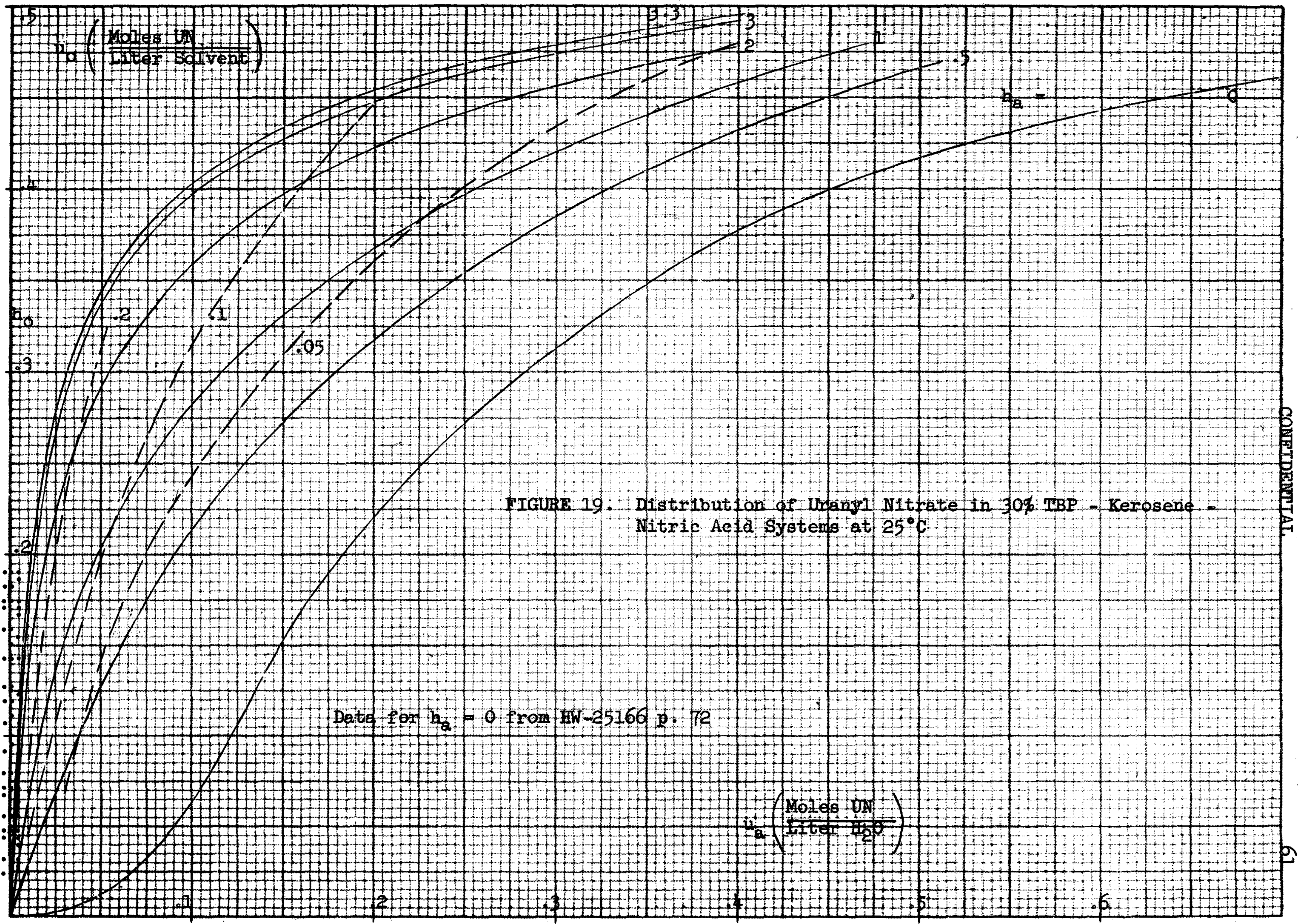

FIGURE 19. Distribution of Uranyl Nitrate in 30% TBP - Kerosene - Nitric Acid Systems at 25°C

Data for h_a = 0 from HW-25166 p. 72

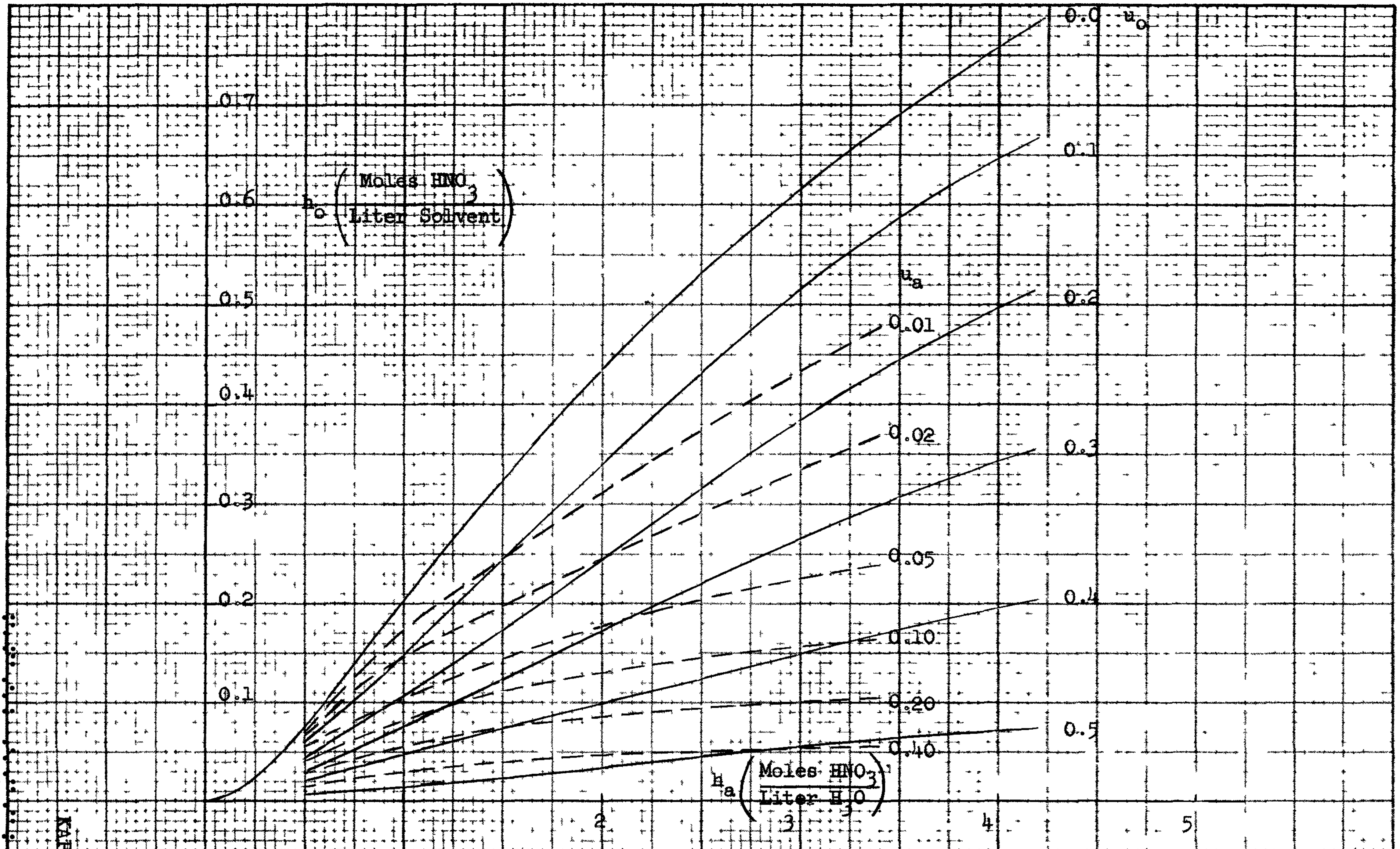

FIGURE 20. Distribution of Nitric Acid between 30% TBP - Kerosene in the Presence of Uranyl Nitrate at 25°C

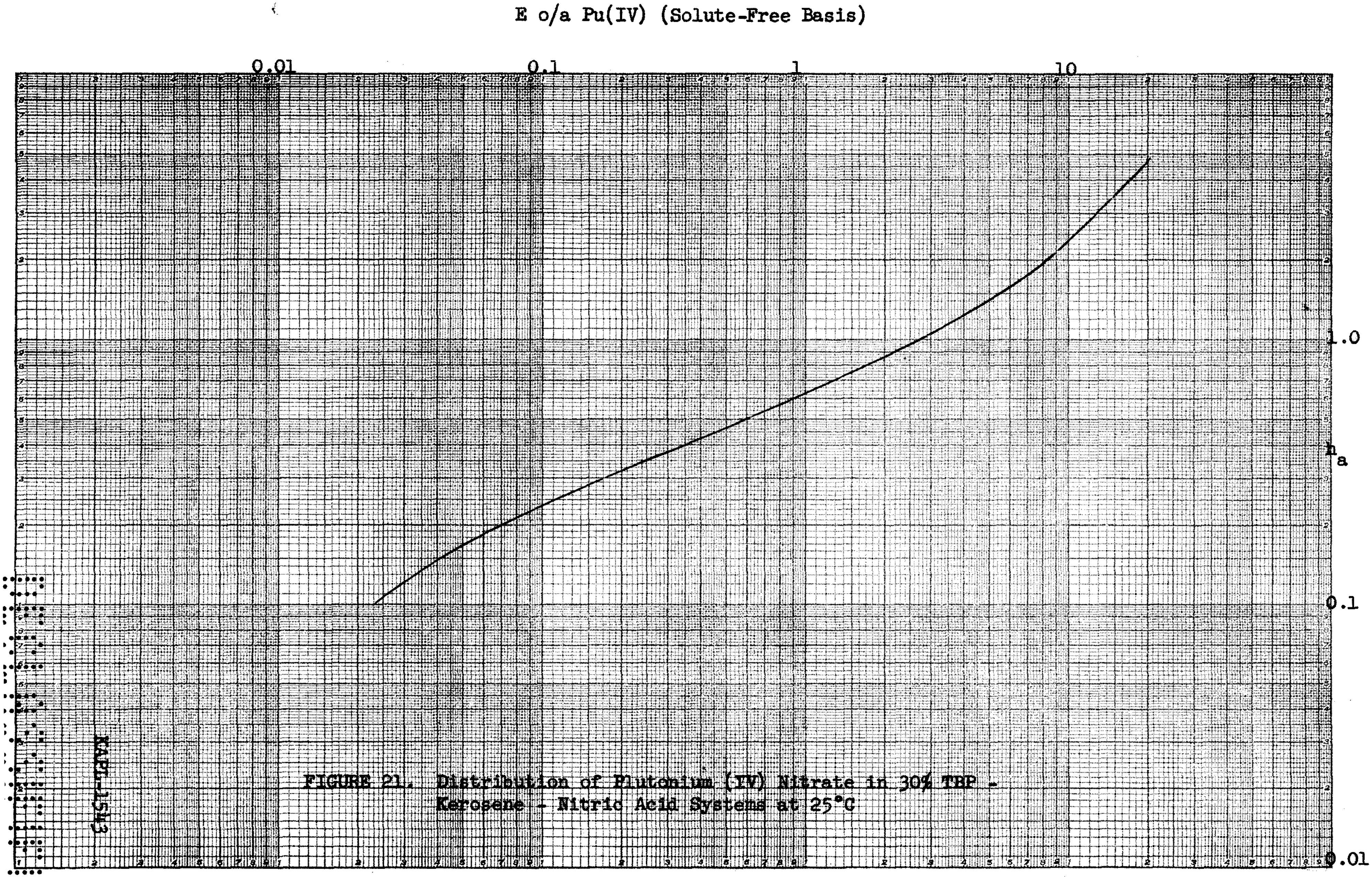

FIGURE 21. Distribution of Plutonium (IV) Nitrate in 30% TBP - Kerosene - Nitric Acid Systems at 25°C

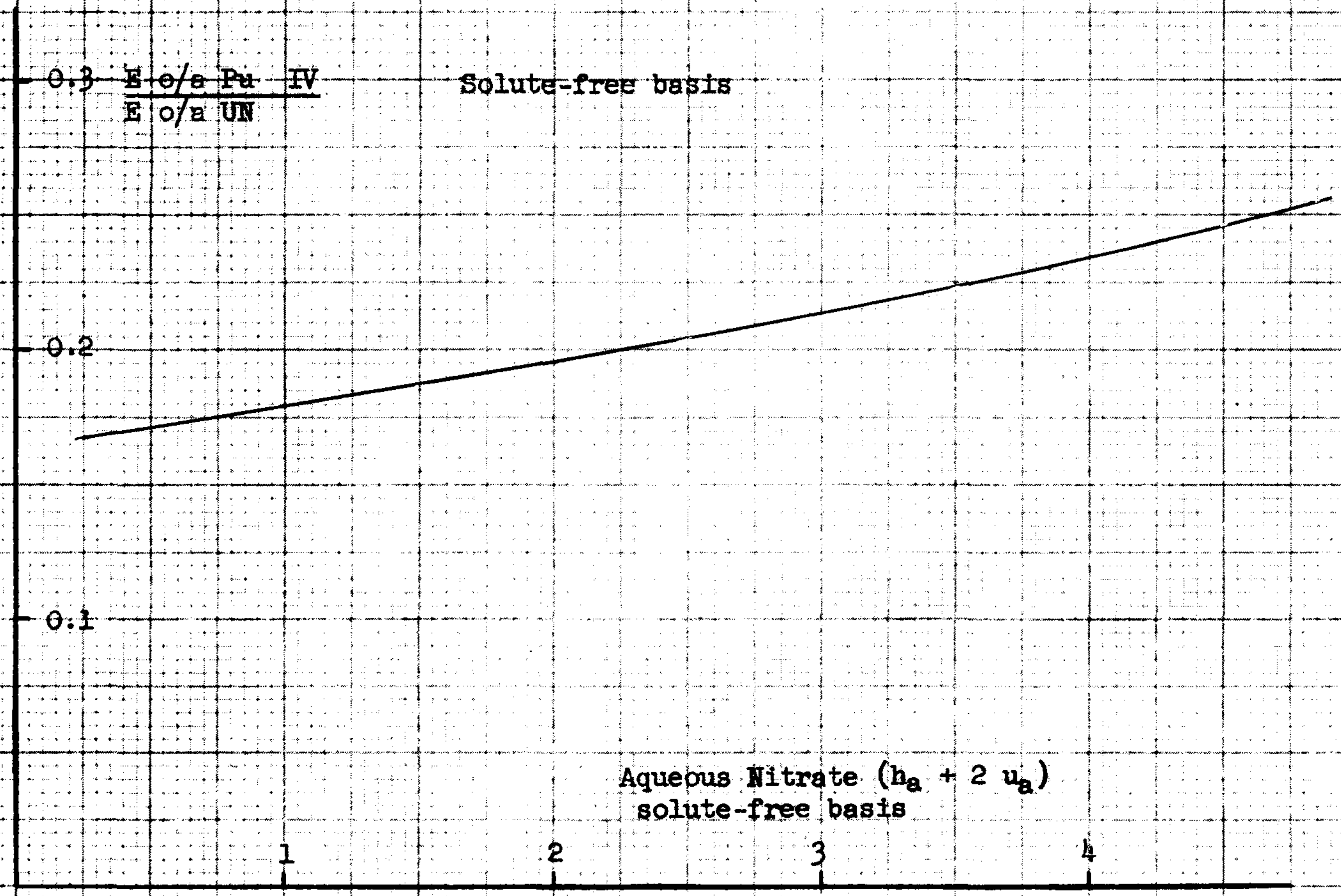

FIGURE 22. Distribution of Tracer Plutonium (IV) Nitrate in the Presence of Macro Uranyl Nitrate - 30% TBP - Kerosene - Nitric Acid Systems at 25°C

[redacted]

TABLE 10. Conversion Equations for 30% TBP and Aqueous Solutions Containing Uranyl Nitrate and Nitric Acid - 25°C

$$\frac{\text{volume solute-free solvent}}{\text{volume solvent solution}} = 1 - 0.086\ U_o - 0.046\ H_o = \frac{1}{1 + 0.086\ u_o + 0.046\ h_o}$$

$$\frac{\text{volume solute-free aqueous}}{\text{volume aqueous solution}} = 1 - 0.076\ U_a - 0.031\ H_a = \frac{1}{1 + 0.076\ u_a + 0.031\ h_a}$$

$$\frac{u_o}{U_o} = \frac{h_o}{H_o} = \frac{1}{1 - 0.086\ U_o - 0.046\ H_o} = 1 + 0.086\ u_o + 0.046\ h_o$$

$$\frac{u_a}{U_a} = \frac{h_a}{H_a} = \frac{1}{1 - 0.076\ U_a - 0.031\ H_a} = 1 + 0.076\ u_a + 0.031\ h_a$$

U_o = uranium molarity in solvent

H_o = HNO_3 molarity in solvent

U_a = uranium molarity in aqueous solution

H_a = HNO_3 molarity in aqueous solution

u_o = moles uranium/liter solvent

h_o = moles HNO_3/liter solvent

u_a = moles uranium/liter H_2O

h_a = moles HNO_3/liter H_2O

[redacted]

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