ORNL-3045
UC-10 - Chemistry-Separation Processes
for Plutonium and Uranium

McCABE-THIELE GRAPHICAL SOLUTION OF URANIUM-THORIUM PARTITIONING FROM 30% TBP-AMSCO SOLVENT

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OAK RIDGE NATIONAL LABORATORY

operated by

UNION CARBIDE CORPORATION

for the

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ABSTRACT*

McCabe-Thiele diagrams showed uranium and thorium losses of <0.05% and 0.3%, respectively, with five stages each in the stripping and scrubbing steps in partitioning of uranium and thorium. The results were confirmed experimentally in a batch countercurrent test. The procedure considered was stripping of thorium from a 30% TBP—Amsco 125-82 solution by dilute nitric acid and scrubbing the uranium from the thorium strip with fresh solvent.

* Essentially the same report was originally issued as an ORNL internal memo, CF 60-6-1.

CONTENTS

1.0 INTRODUCTION

A solvent extraction procedure was investigated for separating small quantities of uranium from macroquantities of thorium. This is required for the recovery of uranium and thorium from spent nuclear reactor fuels such as the CETR. Thorium is stripped, in a two-section cascade, from the solvent (BF) with 0.01 M HNO_3 (BX) and uranium is scrubbed from the aqueous thorium stream (BT) with fresh solvent (BS)(Fig. 1). The operating flow rates and number of stages required for satisfactory partitioning, i.e., <0.1% uranium loss and <1.0% thorium loss, were determined from McCabe-Thiele diagrams, and results were confirmed experimentally in a batch countercurrent test.

The use of McCabe-Thiele diagrams has been explained in a number of texts on solvent extraction and in ORNL-2477.[1] From equilibrium curves the number of stages can be calculated for particular operating flow ratios. In a compound cascade such as the partitioning case, one additional fact must be known: either the number of stages in one section or sufficient stages to result in a "pinch" of one solute in one of the sections. In simple cases the equilibrium distributions of solutes are assumed to be independent of each other. However, in this case uranium distribution is strongly affected by the salting strength of thorium nitrate in the aqueous phase. Consequently the graphical solution was made by first constructing the thorium diagram and then using the thorium concentration in the aqueous phase in each stage to determine the uranium equilibrium curve for the corresponding stage. By trial and error several operable flow ratios were determined, and the number of stages was calculated for each section of the partitioning column.

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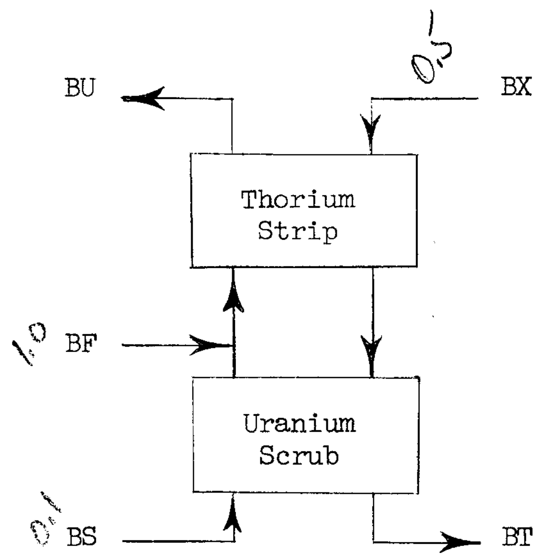

Fig. 1. Uranium-thorium partitioning scheme

2.0 McCABE-THIELE DIAGRAMS

The graphical method is illustrated in Figs. 2, 3, and 4 for a BF/BS/BX flow ratio of 1.0/0.1/0.5. First the thorium diagram (Fig. 2) was constructed with a composite equilibrium curve, the lower end being at 0.0 M nitric acid and the upper at 0.1 M HNO_3, based on data from Siddall.[2] It was assumed and later verified experimentally, that most of the nitric acid in the BF stream would transfer to the aqueous phase and consequently the appropriate equilibrium curve would be for 0.0 M nitric acid in the strip section and for 0.1 M nitric acid in the scrub section. From an over-all thorium material balance the concentrations of thorium in the thorium (BT) and uranium (BU) product streams were calculated. The scrub operating line (O.L.) was constructed through the point BT at a flow ratio (A/O) or slope of 5/1. The scrub stages were stepped off, starting at BT, and a pinch point between the operating line and equilibrium curve was obtained, showing that the maximum concentration of thorium could be obtained in less than three stages.

The strip section of the diagram was constructed with an operating line through the point BU at an A/O flow ratio of 5/11. The concentration of thorium in the solvent entering the strip section is automatically located by proceeding at constant aqueous composition from the pinch point in the scrub section up to the intersection with the strip operating line. The strip stages were then stepped off down to the point BU. Here the pinch occurred in the dilute end of the diagram, showing that additional thorium can be stripped with additional stages.

For the uranium diagram a series of "floating" equilibrium curves was used, based on the thorium concentrations in corresponding stages in the thorium diagram. Because of lack of equilibrium data for uranium in the presence of thorium, the curves were constructed by assuming that the salting effect of thorium was equivalent to nitric acid based on nitrate concentration (data for nitric acid salting from Codding[3]). This assumption has been confirmed for nitrate concentrations up to 1.0 M.[4]

The uranium diagram for the strip section (Fig. 3) was constructed for two cases, one for four stages, the same number used for the thorium diagram in Fig. 2, and the other for five stages. The uranium concentration in the aqueous phase leaving the bottom of the strip section is virtually the same for the two cases. The obvious effect of using more stages in the strip section than are necessary to obtain thorium stripping is that uranium refluxing occurs. In the limiting case where a sufficient excess of stages is available to cause a pinch between the operating line and the uranium equilibrium curve at zero thorium concentration, the uranium concentration in the aqueous phase would build up to about 0.08 M, which is 10 times the BU concentration.

In the case for four stages the operating line was constructed through point BU, which was obtained by an over-all uranium material balance, with the same slope as used in the thorium strip diagram (A/O = 5/11). The stages were stepped off, starting at BU, the appropriate equilibrium curve being used for each stage. For example, for stage 4 the uranium equilibrium curve is at 0.045 M thorium in the aqueous as read from stage 4 in the thorium strip diagram (Fig. 2). Construction of the uranium diagram was continued

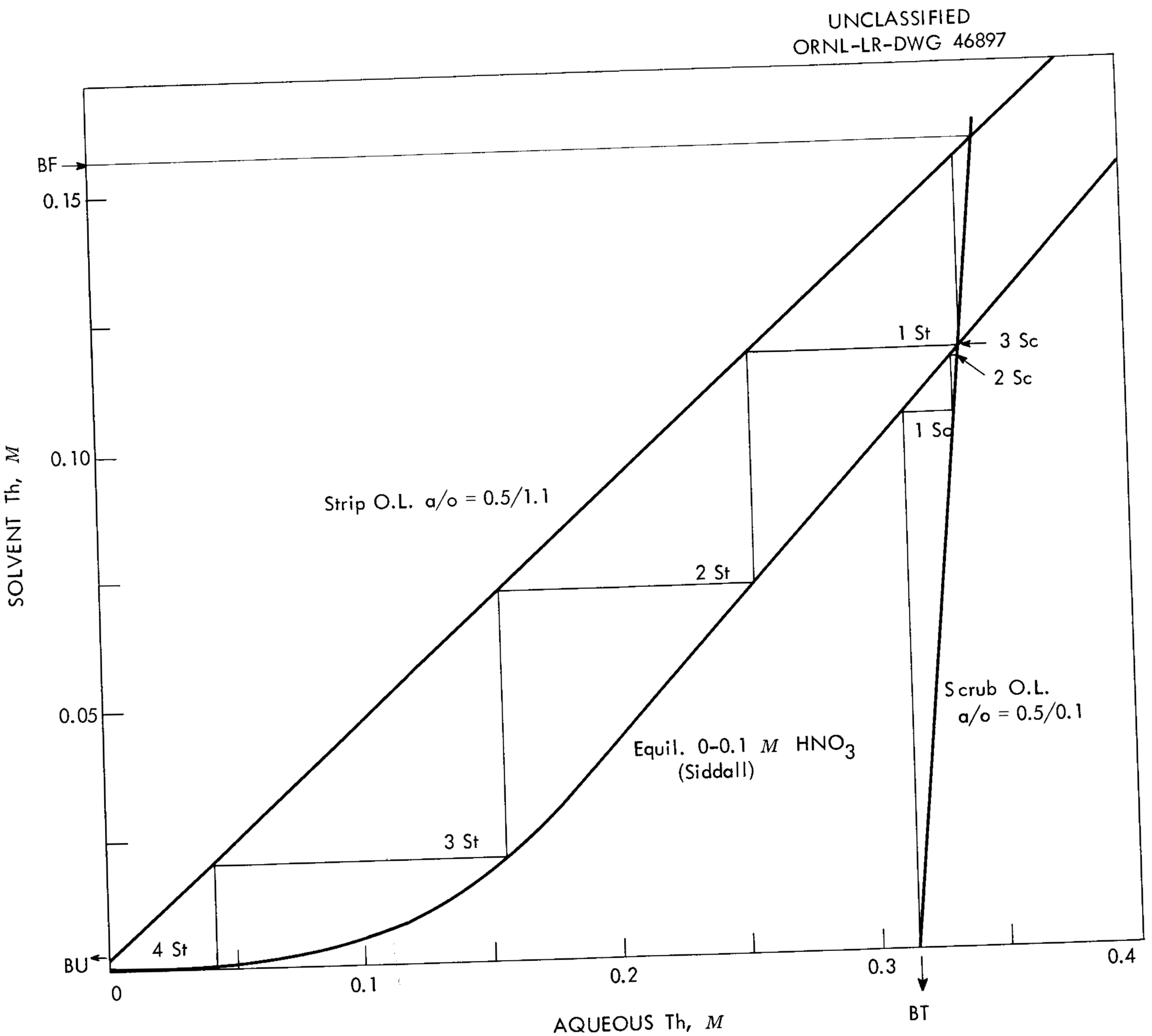

Fig. 2. Thorium diagram for 1% loss of thorium.

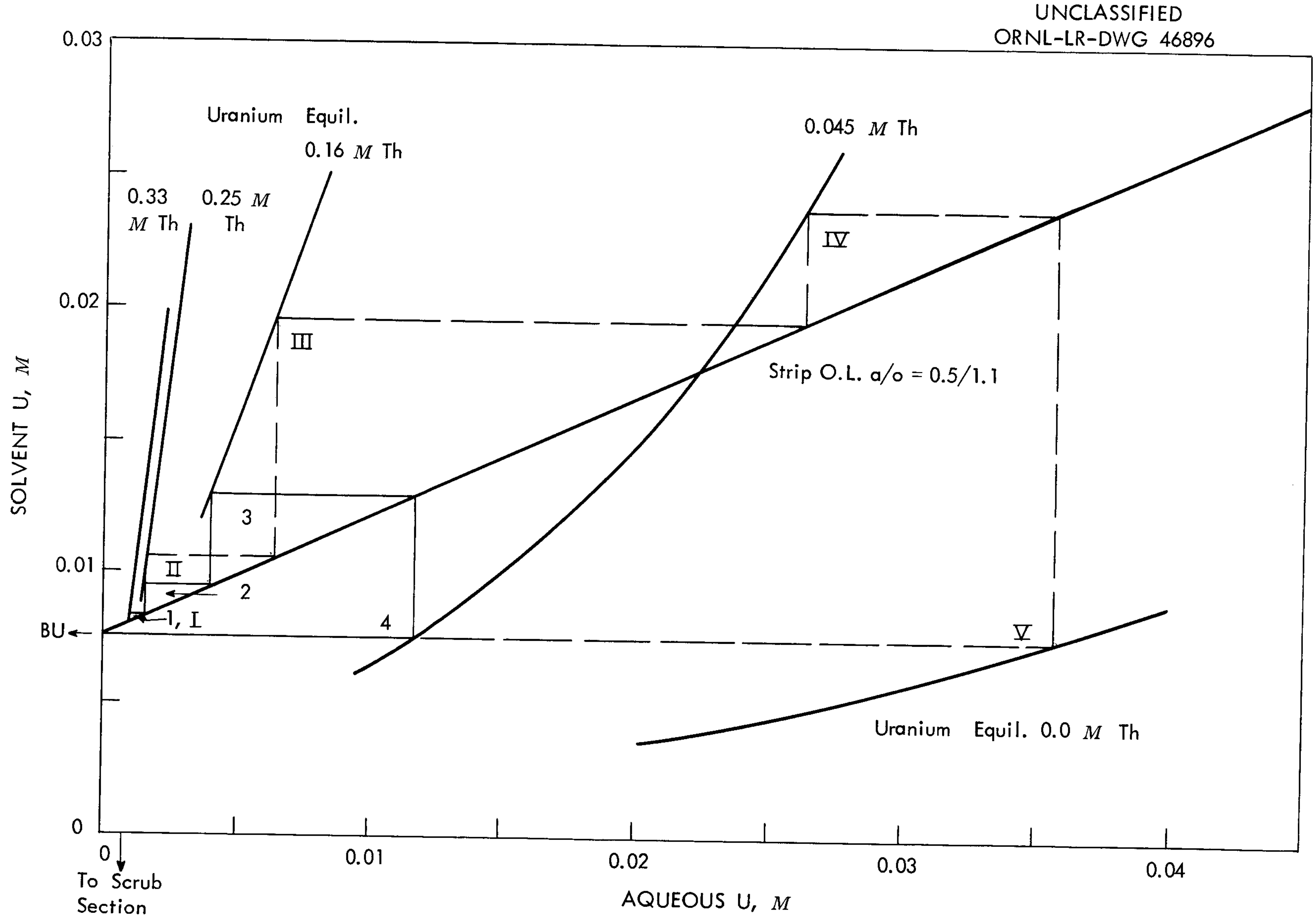

Fig. 3. Uranium diagram for strip section case for four stages shown by Arabic numerals; for five stages, by Roman numerals.

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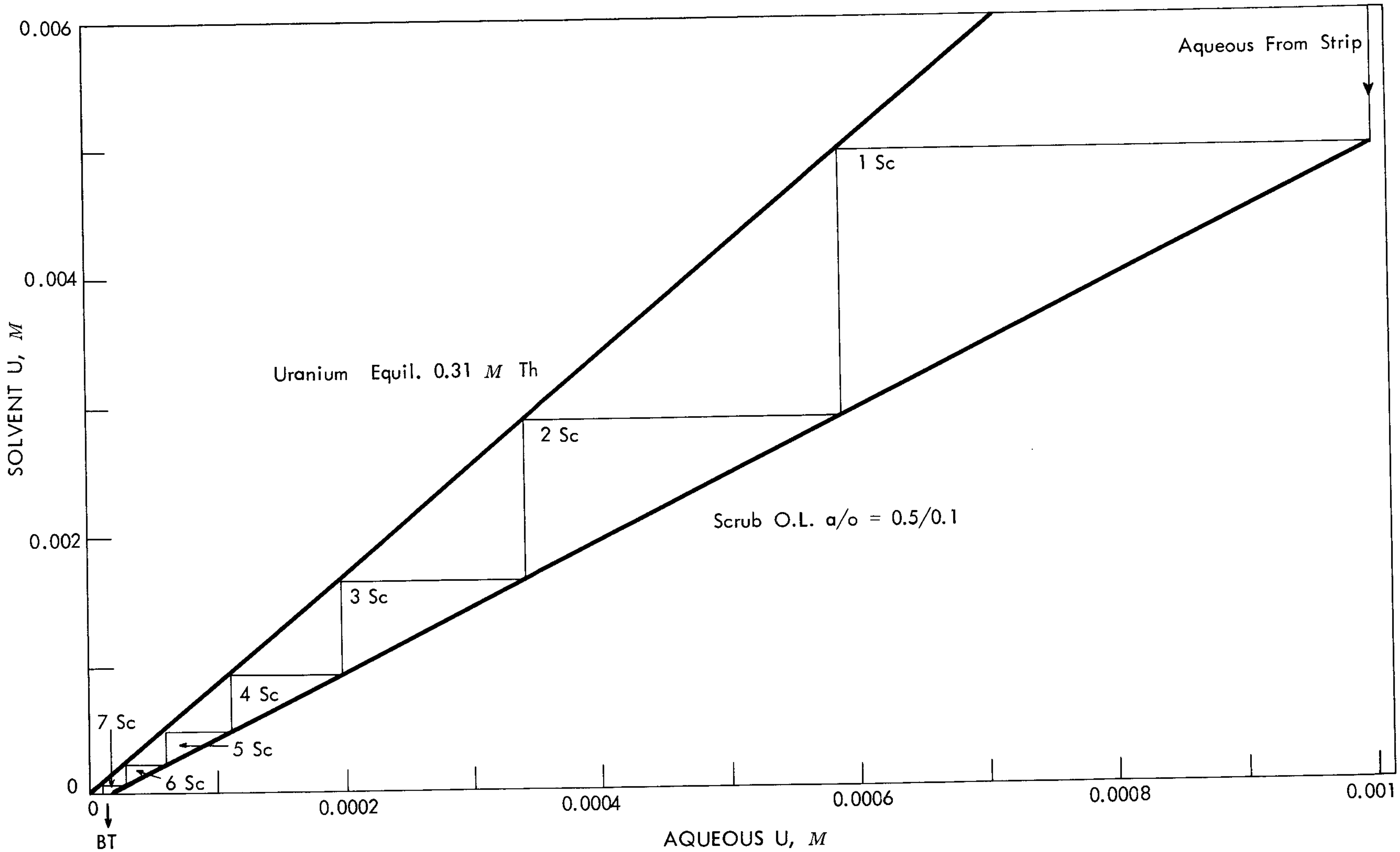

Fig. 4. Uranium diagram for scrub section (0.1% loss).

until four stages were constructed to obtain the uranium concentration in the aqueous stream leaving the bottom of the thorium strip section.

In the case for five stages, the uranium diagram was also started at point BU and stage 5 was constructed from a uranium equilibrium curve at 0.0 M thorium in the aqueous phase corresponding to the concentration that would be obtained with five stages in the thorium strip diagram (Fig. 2). The remaining stages in the uranium diagram were stepped off by use of the same uranium equilibrium curves for each stage number as was used in the four-stage case.

The uranium diagram for the scrub section (Fig. 4) is pinched in the dilute end, showing that the uranium loss could be reduced by additional stages. It was constructed on a different graph merely because an expanded scale was needed to show sufficient detail. The diagram uses an equilibrium curve at constant thorium salting strength because the thorium aqueous concentration is virtually constant in the scrub section (Fig. 2). The operating line of slope, A/O, of 5/1 was constructed through point BT, representing 0.1% loss. The stages were stepped off starting at the aqueous composition leaving the bottom of the strip section to the point BT.

The calculated number of stages required for 0.1% uranium loss and 1.0% thorium loss using constant feed (BF) composition and a range of flow ratios is shown in Table 1. The number of stages is determined by the requirements for thorium in the strip section and for uranium in the scrub section. The limits of operable flow ratios lie between BF/BS/BX = 1.0/0.1/0.4, where an infinite number of stages is required for thorium stripping, and BF/BS/BX = 1.0/0.2/1.0, where an infinite number of stages is required for uranium scrubbing. Between these limits the flowsheet is operable to give the desired partitioning of uranium and thorium. The minimum stage requirements (3 for thorium stripping and 5 for uranium scrubbing) are at a flow ratio of BF/BS/BX = 1.0/0.2/0.6.

3.0 EXPERIMENTAL VERIFICATION

The graphical calculation of the number of stages was confirmed experimentally in batch countercurrent equipment (Table 2).[5] The flow ratio was BF/BS/BX = 1.0/0.2/0.6 and five physical stages were used in each section. The loss of thorium was 0.3% and uranium, 0.045%. The thorium diagram (Fig. 5) shows an excellent fit of the experimental data. The operating lines were constructed, with the slopes equal to the phase ratios, through the exit stream compositions BU and BT. The stages were stepped off by use of the composition of the phases at each mechanical stage of the countercurrent equipment. The steps fit very well on the operating lines, showing good material balance. The fit of the data to the equilibrium curve from Siddall shows a discrepancy that may have been caused by diluent (Amsco 125-82 vs Ultrasene), temperature, or TBP concentration. This shift in the equilibrium curve accounts for the fact that one extra stage over the calculated value in Table 1 was required for thorium stripping. The uranium diagram (Fig. 6) for the experimental test shows a good fit of the stagewise analyses on operating lines constructed with slopes equal to the phase ratios and through the exit stream compositions BU and BT. The data also agree with equilibrium curves at various thorium nitrate concentrations as calculated from data for nitric acid salting (Codding), using nitrate equivalency for thorium nitrate salting.

Table 1. Calculated Stage Requirements for Partitioning of Uranium and Thorium

Based on feed (BF) composition of 0.0084 M U, 0.158 M Th and 0.05 M HNO_3; allowing 1% loss of thorium and 0.1% loss of uranium

Flow Ratio			No. Stages Required		Exit Stream Compositions for Specified Losses			
					BU		BT	
BF	BS	BX	U Scrub	Th Strip	U, M	Th, M	U, M	Th, M
1.0	0.1	0.4	-	∞	0.0076	0.0014	0.000020	0.39
1.0	0.1	0.5	7	4	0.0076	0.0014	0.000016	0.31
1.0	0.1	0.6	18	3	0.0076	0.0014	0.000013	0.26
1.0	0.2	0.5	4	5	0.0070	0.0013	0.000016	0.31
1.0	0.2	0.6	5	3	0.0070	0.0013	0.000013	0.26
1.0	0.2	1.0	∞	2	0.0070	0.0013	0.000008	0.16

Table 2. Partitioning Data*

Solvent feed: 0.18 M Th, 0.011 M U, 0.11 M HNO_3
Aqueous strip: 0.01 M Al $(NO_3)_3$
Flow ratio: BF/BS/BX = 1/0.2/0.6

Stage No.	Concentration, M			
	Thorium		Uranium	
	Aq	Org	Aq	Org
5 St	0.032	0.00045	0.014	0.0095
4 St	0.13	0.016	0.0055	0.018
3 St	0.22	0.064	0.0021	0.012
2 St	0.30	0.11	0.0015	0.0095
1 St	0.35	0.15	0.0012	0.0095
1 Sc	0.35	0.16	0.00046	0.0041
2 Sc	0.35	0.15	0.00021	0.0016
3 Sc	0.35	0.15	0.000088	0.00060
4 Sc	0.34	0.15	0.000029	0.00021
5 Sc	0.30	0.13	0.0000084	0.000063

* Countercurrent run X-950.

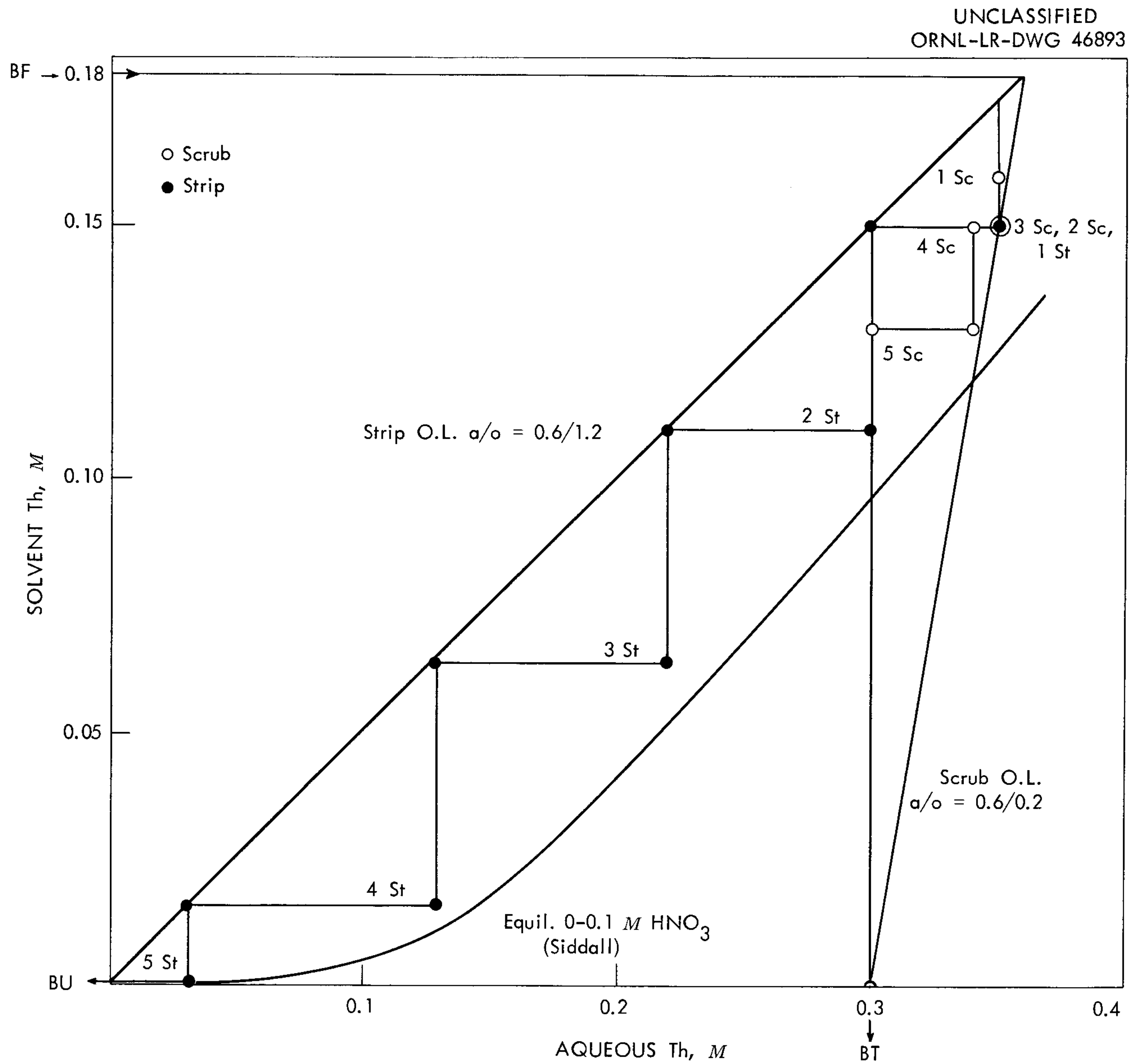

Fig. 5. Thorium diagram for run X 950.

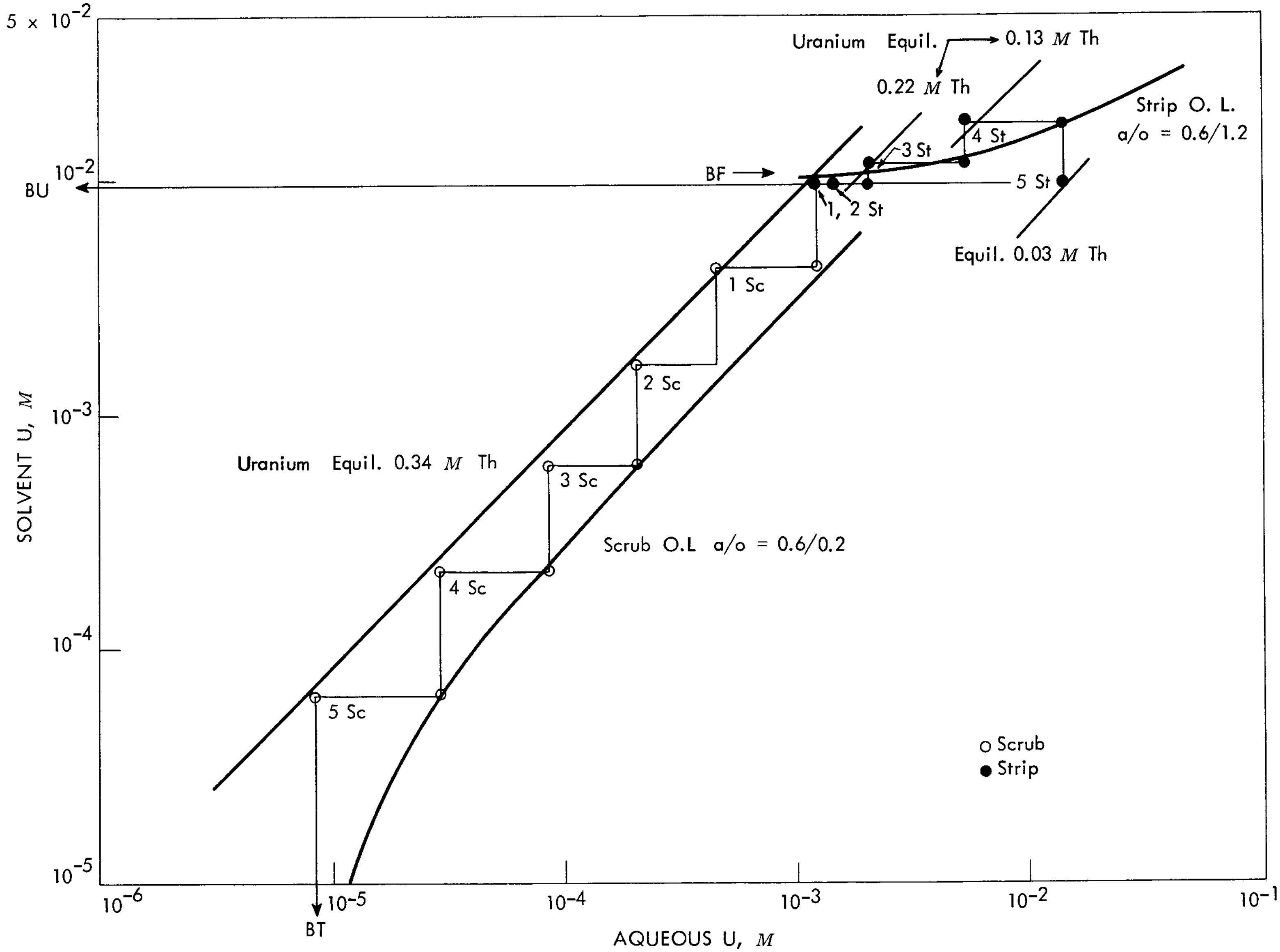

Fig. 6. Uranium diagram for run X-950.

4.0 REFERENCES

1. M. E. Whatley, "A Summary of the Separation Operations," ORNL-2477 (Apr. 11, 1958).

2. T. H. Siddall, III, "Extraction of Thorium Nitrate from Nitric Acid by TBP-'Ultrasene'," DP-181 (October 1956).

3. J. W. Codding, W. O. Haas, Jr., and F. K. Heumann, "Tributyl Phosphate-Hydrocarbon Systems: Organizing Equilibrium Data," Ind. Eng. Chem. 50: 145 (1958).

4. "ORNL Status and Progress Report for April, 1960," ORNL-2945, p. 12.

5. Monthly Report for Chemical Development Section B for May 1960, ORNL-CF 60-6-108.

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