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Partitioning from 30% TBP-Amsco Solvent
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ABSTRACT

A graphical method based on the McCabe-Thiele diagram was utilized to define operable flow ratios and to calculate the number of theoretical stages required for partition of uranium and thorium from 30% TBP-Amsco 125-82 solvent.

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SUMMARY

McCabe-Thiele diagrams were used to define the operable flow ratios and to calculate the number of theoretical stages required for partition of uranium and thorium from 30% TBP-Amsco 125-82 solvent in a typical flowsheet for processing thorium-uranium power reactor fuels.

Partition is achieved in a two-section cascade consisting of thorium stripping by dilute nitric acid and uranium scrubbing from the thorium by fresh solvent. The key point in the method is that uranium distribution is dependent on the salting effect of thorium in the aqueous phase which can be adjusted by selection of flow ratios to give satisfactory partition. The limits of operable flow ratios are represented by cases where an infinite number of stages are required in either section.

A sample calculation, confirmed experimentally in a batch counter-current test, showed that five stages in each section resulted in less than 0.05% uranium loss and 0.3% thorium loss.

McCabe-Thiele Graphical Solution of Uranium-Thorium Partitioning from 30% TBP-Amsco Solvent

One of the flowsheets proposed for processing U-Th fuels (typically Consolidated Edison) involves separation of small quantities of uranium from macroquantities of thorium in the extract from 1st cycle extraction. The flowsheet involves a two-section cascade in which thorium is stripped 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 problem is to determine the operating flow rates and number of stages required for satisfactory partitioning, i.e., <0.1% uranium loss and <1.0% thorium loss. Graphical solution of the problem using McCabe-Thiele diagrams was made and confirmed experimentally in a batch counter-current test.

The use of McCabe-Thiele diagrams is explained in a number of texts on solvent extraction and by M. E. Whatley (ORNL-2477). From equilibrium curves the number of stages can be calculated for particular operating flow ratios. In a compound cascade such as the partition 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 distribution of solutes is 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 were calculated for each section of the partition column.

The graphical method is illustrated in Figs. 2, 3, and 4 for one flow ratio ($BF/BS/BX = 1.0/0.1/0.5$). First the thorium diagram (Fig. 2) was constructed using a composite equilibrium curve, the lower end being at 0.0 M HNO_3 and the upper end at 0.1 M HNO_3 , based on data from Siddall (DP-181). Here an assumption, which later was experimentally verified, was made that most of the HNO_3 in the BF stream would transfer to the aqueous phase and consequently the appropriate equilibrium curve would be for 0.0 M HNO_3 in the strip section and for 0.1 M HNO_3 in the scrub section. From an over-all thorium material balance the concentrations of thorium in the thorium product stream (BT) and the uranium product stream (BU) were calculated. The scrub operating line was constructed through the point BT at the flow ratio or slope (A/O) 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 using an operating line drawn through the point BU at the flow ratio A/O 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 strip operating line. The strip stages were then stepped off down to the point BU. Here the pinch occurs in the dilute end of the diagram showing that further stripping of thorium can be obtained with additional stages.

For the uranium diagram a series of "floating" equilibrium curves were 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 by Coddington, Ind. and Eng. Chem, 50, 145, 1958). This assumption has been confirmed for nitrate concentration up to 1.0 M (ORNL Status and Progress Report, p. 12, ORNL-2945, April 1960).

The uranium diagram for the strip section (Fig. 3) was constructed for two cases, one being four stages (the same number used for the thorium diagram in Fig. 2) and the other for five stages. In the case using four stages (shown as Arabic numbers) the operating line is constructed through point BU (obtained by over-all uranium material balance) with the same slope as used in the thorium strip diagram ($A/O = 5/11$). The stages are stepped off, starting at BU, using the appropriate equilibrium curve for each stage. For example for stage No. 4 the uranium equilibrium curve is at 0.045 M thorium in the aqueous as read from stage No. 4 in the thorium strip diagram (Fig. 2). Construction of the uranium

diagram is continued until four stages are constructed to obtain the uranium concentration in the aqueous stream leaving the bottom of the thorium strip section.

In the case for five stages (shown with Roman numerals in Fig. 3), the uranium diagram is started at point BU and stage No. 5 is constructed using 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 are stepped off using the same uranium equilibrium curves for each stage number as was used in the case of four stages.

The two cases show that the uranium concentration in the aqueous phase leaving the bottom of the strip section is virtually the same. 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 ten times the BU concentration.

The uranium diagram for the scrub section (Fig. 4) 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. Since the diagram pinches in the dilute end the uranium loss could be reduced by additional stages.

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 are 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 are required for thorium stripping and $BF/BS/BX = 1.0/0.2/1.0$, where an infinite number of stages are required for uranium scrubbing. Between these limits the flowsheet is operable to give the desired partition of uranium and thorium. The minimum stage requirements (3^+ for thorium strip and 5 for uranium scrub) are at a flow ratio of $BF/BS/BX = 1.0/0.2/0.6$.

Experimental confirmation¹ of the graphical calculation of number of stages was made by the Chemical Development Section B of Chemical Technology

¹Monthly Report of Chemical Development Section B for May 1960, ORNL CF-60-6-108.

Division in batch countercurrent equipment (Table 2). 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 was 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 based on 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 which 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 data on operating lines based on phase ratios and compositions of BU and BT. The data also agree with equilibrium curves at various thorium nitrate concentrations as calculated from data for nitric acid salting (Coddington) using nitrate equivalency for thorium nitrate salting.

Fig. 1. Partition Flowsheet

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

Based on feed (BF) composition of 0.0084 M U, 0.158 M Th and 0.05 M HNO₃; allowing 1% loss of thorium and 0.1% loss of uranium.

Flow Ratio			No. Stages Required		Concentration, M			
BF	BS	EX	U Scrub	Th Strip	BU		BT	
					U	Th	U	Th
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. Partition Data - Countercurrent Run X-950

Solvent Feed: 0.18 M Th, 0.011 M U, 0.11 M HNO₃
 Aqueous Strip: 0.01 M Al (NO₃)₃
 Flow Ratio: BF/BS/EX = 1/0.2/0.6

Stage No.	Stagewise 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

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

Fig. 3. Uranium diagram for strip section.

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

Fig. 5. Thorium diagram for run X 950

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

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