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DATE: March 18, 1957

SUBJECT: TBP Stripping in Bubble-Cap Column
and Concomitant Product Evaporation

TO: F. L. Culler

FROM: J. T. Long

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1.0 SUMMARY

An experimental demonstration of the intercycle stripping and evaporation steps was carried out on a simulated I-BP process stream using a 15-plate 8-in. dia bubble cap stripping column and a jacketed kettle reboiler. The required seven-fold volume reduction was achieved and control of the equipment was satisfactory. With 12 to 14 plates in the stripping section and 1 to 3 plates in the deentraining section, uranium losses by entrainment were much less than 0.001%. Difficulty with TBP analyses made quantitative conclusions regarding stripping impossible, but it was evident that most of the TBP was being removed in the stripping column. Flooding was encountered in the column at a boil-up rate of 400 lb/sq ft-hr, which is about three times the required boil-up rate.

It is suggested that an external reflux be used to provide a liquid seal on the plates above the feed point and to wash any entrained uranium back down the column. It was also suggested that the laboratory set-up be improved by the use of larger feed tanks and a feed pump having a constant delivery rate.

2.0 INTRODUCTION

The recovery of uranium in a Purex-type process was designed on the basis of two extraction cycles in which uranyl nitrate was to be extracted from an aqueous phase into a 6% solution of tributyl phosphate (TBP) in Amsco solvent and subsequently stripped back into an aqueous phase. The product from the first cycle was to be 0.109 molar in uranium and the feed to the second cycle was to be 0.757 molar in uranium; therefore, an evaporation of the aqueous stream was necessary. It was also desired to concentrate the product stream by evaporation.

The evaporation step is straightforward with one exception: the product of the stripping operation contains small amounts of dissolved TBP. Under certain conditions the TBP may decompose to produce an explosive "red oil". Also, dissolved TBP may complex uranium, and so cause losses in the second cycle. For these reasons TBP is stripped out before the aqueous stream is evaporated. The proposed method for carrying out this stripping is to introduce the solvent-bearing aqueous stream into a column. As the feed stream flows down the column, TBP is stripped out by steam rising up the column. The steam is formed by evaporation of the aqueous stream.

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The purpose for the present study was to demonstrate the stripping and evaporation steps and to ascertain the operating characteristics of the equipment over a range of conditions. The factors to be considered were effectiveness and reliability of equipment, method of control of equipment, capacity, and optimum feed point.

A bubble-cap column of the required size (8-in. dia) was available in the Unit Operations Section and so was used in this study. Plans originally called for a packed column as the contacting device because packed columns are cheaper and because it was thought, mistakenly, that bubble-cap columns were not available in a small enough size. Bubble-cap columns, on the other hand, have the significant advantage of sustained efficiency over a much broader range of throughput.

3.0 APPARATUS AND PROCEDURE

The equipment used in this study consisted of a modified bubble-cap column distillation apparatus (Figs. 3.1, 3.2 and 3.3). The column was a standard laboratory fractionating column fabricated by the Badger Manufacturing Company of type 347 stainless steel. It had an inside diameter of 8-1/8 in., and had 15 plates spaced seven inches apart. Each plate had two bubble caps, 1-in. (inside dimension) square downcomers leading to and from the plate, a 1/8-in. D weep-hole, and weirs to channel the liquid flow past the bubble caps. Vapors were supplied to the column from a 24-in. D jacketed kettle of type 304 ELC stainless steel. A sparging nozzle permitted introduction of live steam directly into the kettle. Vapors leaving the column were condensed in a single-pass shell-and-tube heat exchanger of type 304 stainless steel having a heat transfer area (inside tubes) of 34 sq ft.

Two feed tanks were provided. Piping was arranged so that liquid could be pumped to the top of either tank from the bottom of either tank, from the product receivers, or from a surge tank receiving concentrated solution from the reboiler. A separate pump supplied feed to the column, so that it was possible to supply the column from one of the feed tanks while new feed was being made up or recirculated (for mixing purposes) in the other. A complete description of the piping layout and instrumentation is given in the flow sheet, Fig. 3.4.

3.1 Column Operation

A synthetic I-BP solution was made up in the feed tanks. A layer of pure TBP was placed on top of the aqueous phase, and the aqueous phase was saturated with solvent at room temperature by pumping it out the bottom of the drum and back in the top above the solvent layer. After at least a half hour, the recirculation was stopped and the two layers allowed to separate.

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Fig. 3.1

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Fig. 3.2

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Fig. 3.3

MATERIALS LIST					
ITEM NO.	QTY.	NAME	SIZE	MATERIAL

FIG. 3.4

NO.	REVISIONS	DATE	APPR.	APPR.
DRAWING NO. D-				
DESIGNED	DATE	CHECKED	DATE	APPROVED
DATE	DATE	DATE	DATE	DATE
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3.2 Start Up

At the start of operations, a charge was placed in the reboiler kettle having a composition approximating that which was expected to result from the evaporation. For subsequent runs, the residue in the kettle from each previous run was used.

Steam was admitted to the kettle jacket and cooling water was turned on in the condenser. As soon as the column had come to temperature (10 or 15 min), feed was pumped onto the selected feed plate at a selected constant rate. Steam pressure in the kettle jacket was adjusted to maintain a constant level in the reboiler.

When the first feed tank was nearly empty, feed was pumped from the second feed tank while the first tank was being refilled by combining the accumulated overheads and bottoms. Unfortunately, the recombined feed was not of exactly the same composition as the original feed. This discrepancy could not be avoided, since analytical results could not be returned from the laboratory in time for feed adjustment. Most runs were continued for 12 hr.

4.0 EXPERIMENTAL

The objective of this program was the finding of answers to four questions:

1. Will the equipment completely remove TBP from the process stream and at the same time reduce the volume of the stream seven-fold without losing uranium by entrainment?
2. What is the best method of control of the equipment?
3. What is the flooding rate of the column?
4. What is the optimum feed point location on the column?

Because the program was curtailed, complete answers were not obtained. However, useful information was obtained and appears below.

4.1 Satisfaction of Flow Sheet Requirements

The ability of an eight-inch bubble cap column to carry out the inter-cycle stripping and evaporation functions prescribed by the flow sheet is discussed below in three parts: (1) TBP stripping, (2) process stream volume reduction, and (3) uranium losses.

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4.1.1 TBP Stripping

Qualitatively, a considerable amount of organic solvent was removed from the feed stream, appearing as a separate phase in the overhead stream. Quantitatively, the completeness of TBP removal could not be demonstrated because of difficulties in chemical analysis. Analyses were made for total phosphorus, so that no distinction was made between phosphorus in the form of TBP and phosphorus appearing in decomposition products which certainly were formed during the course of operation.

It is known that tributyl phosphate will decompose to form species such as $\text{UO}_2 [(\text{C}_4\text{H}_9\text{O})_2 \text{OPO}]_2$, $\text{UO}_2 [(\text{C}_4\text{H}_9\text{O}) \text{O}_2\text{PO}]$, or $(\text{UO}_2)_3 (\text{PO}_4)_2$. That some of these species are water-soluble is not unlikely and cannot be ruled out. During the course of the present investigation, an insoluble phase heavier than the aqueous phase was obtained in relatively large amounts. The "interfacial crud" encountered in liquid extraction is another example of these decomposition products. Undoubtedly, the large amounts of decomposition products encountered in this study were generated by the extended digestion in the kettle, probably aided by the free nitric acid present.

It is probable that the TBP stripped from the feed stream would pass up and out of the column with very little decomposition because of short exposure to high temperature and high acid concentration. But any TBP finding its way to the reboiler, either through misoperation of the equipment or less than 100% efficiency of the stripping column, would then to a great extent remain in the kettle until it was beaten to pieces by the rigorous conditions there present. And once decomposition products were formed, they would be recycled to the next feed and thus mask all subsequent results.

Unfortunately, insurmountable difficulties in analyzing for small amounts of phosphorus made it impossible to demonstrate any of these phenomena. Therefore, quantitative demonstration of the efficacy of the column in stripping tributyl phosphate from the aqueous feed is lacking at this time.

4.1.2 Process Stream Volume Reduction

The 25 Process flow sheet calls for a seven-fold volume reduction. A volume reduction approximating this amount was achieved fairly consistently except in those runs in which sparging took place (Table 4.1).

The extent of volume reduction was calculated by two methods: (1) the ratio of feed rate to bottoms rate was calculated; (2) the ratio of uranium concentration in the bottoms to uranium concentration in the feed was calculated. A disadvantage of the first method was the difficulty in measuring rates accurately, and a disadvantage of the second method was the lag in any

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Table 4.1

PROCESS STREAM VOLUME REDUCTION

Run No.	Jacket Steam Pressure, psig	Feed Rate, gph	Volume Reduction	
			<u>Feed Rate</u> Bottoms Rate	<u>Conc U in Bottoms</u> Conc U in Feed
4	14.2	8.65	9.1	4.8
5	16	8.54	6.5	4.7
6	17	8.20	6.0	5.7
7	18	8.13	7.3	(missing)
8	18	8.25	7.7	7.2
9	18	8.37	6.6	6.2
10	18	8.27	6.6	6.4
11	18	8.10	6.4	6.2
12	18	8.62	6.6	7.4
13	23	10.87	7.1	5.9

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change in kettle concentration (more than 17 hours of operation was required to withdraw a volume of bottoms equal to the charge in the kettle).

4.1.3 Uranium Losses

With an assumed permissible uranium loss of 0.0027 mg/ml (0.01% of the uranium in the feed stream), the actual losses encountered were far below the permissible loss for all runs in which the vapor rate was not significantly greater than the design rate of 1.2 ft/sec (Table 4.2). Except for very high vapor velocities and feed introduced at the top of the column, uranium losses were 0.0001 mg/ml or less.

4.2 Control of Equipment

The laboratory equipment had three control points: (1) the feed rate to the column was maintained constant by a positive displacement pump; (2) steam pressure to the kettle jacket was maintained constant by a pressure control valve; and (3) the liquid level was maintained fairly constant by a liquid level controller actuated by dip tube sensing elements.

Unfortunately, the feed concentration could not be maintained constant. The effect of varying feed concentrations is shown in Fig. 4.1. From this figure it can be seen that (1) from six to ten hours is required to reach equilibrium in the exit stream after a change in the feed stream, and (2) fluctuations in the exit stream are not so large in magnitude as are the fluctuations in the feed stream. This indicates that, given a feed of unvarying composition, the equipment would have maintained very good control as it was set up.

4.3 Column Flooding Rate

The flooding rate, as defined by the point at which excessive uranium entrainment occurs, is at a vapor velocity of about 3 ft/sec, or 400 lb/sq ft-hr. In Run 14D, excessive entrainment occurred with a vapor rate of only 2.5 ft/sec, with the feed introduced on the next to the top plate. However, in Run 14B (in which the feed was introduced on the middle plate) entrainment was tolerable with a vapor rate of 3.1 ft/sec. This apparent discrepancy is believed attributable to the fact that the plates above the feed plate were essentially dry; this condition could be corrected by a small stream of demineralized water reflux.

4.4 Optimum Feed Point

Introduction of the feed on or above the twelfth plate is indicated by this study. The difficulty of completely stripping out the TBP indicates the

Fig. 4.1. Variation in Bottoms Stream With Time

Table 4.2

ENTRAINMENT OF URANIUM IN OVERHEAD STREAM

Run No.	Feed Plate	Vapor Rate, Ft/Sec	Uranium Concentration in Overhead, mg/ml
4	8	1.08	0.00005
5	8	0.90	0.00008*
7	8	0.97	0.00012
9	8	0.94	0.0001
11	8	0.96	0.00005
13	8	1.31	0.00006
14A	8	3.76	0.107
14B	8	3.10	0.00041
14C	8	2.62	0.00034
6	12	0.90	0.00057
8	12	0.95	0.00007
10	12	0.95	(missing)
12	14	0.98	0.00004*
14D	14	2.51	0.0096
15	14	3.10	0.480

*But one sample contained 0.180 mg/ml.

necessity of feeding as high on the column as possible. Feeding on the twelfth plate was proven satisfactory, and feeding on the fourteenth plate was satisfactory except at very high boil-up rates. Perchance the washing of the top (fifteenth) plate with a water reflux would have removed this difficulty.

5.0 RECOMMENDATIONS FOR EQUIPMENT MODIFICATION

During the course of the current investigation, certain modifications of the equipment suggested themselves. These modifications and the expected improvement follow.

5.1 Use of Reflux

It is suggested that a small stream of demineralized water be introduced on the top plate of the column as a sort of reflux. It had been hoped that heat loss from the uninsulated column would be sufficient to provide internal reflux, but this was not the case. Observation through the sight glasses showed that the plates above the feed plate were running dry, and so were of limited use. The use of a water "wash", or external reflux, should reduce uranium entrainment up the column and may also increase the TBP stripping efficiency. Of course, it will be necessary to increase the boil-up rate to remove the additional water, but the column will permit a 100% increase in boil-up rate before flooding and will probably evidence increased efficiency at higher boil-up rates.

5.2 Feed Make-up

The long time (six to ten hr) required to reach equilibrium in the reboiler kettle dictates fairly long runs, requiring large quantities of feed. Accordingly, it is advisable to increase the feed tank capacity to an amount sufficient to satisfy the requirements for a run of at least 12 hr duration. Under the present flow sheet, this would be 116 gal of feed.

5.3 Feed Pump

In the original installation, feed was pumped to the column with a Zenith gear pump. This pump was frequently stalled by very fine particles of grit in the gears, even after a Cuno filter was installed ahead of the pump. The Zenith pump also was not quite able to deliver feed at the required rate. After some time, the Zenith pump was replaced by an Eco gear pump. This pump had sufficient capacity and was not stopped by grit. However, the feed rate varied from time to time and had to be adjusted continually.

Accordingly, it is suggested that a Lapp Pulsafeeder be installed to pump feed to the column.

6.0 APPENDIX

The experimental work here reported was performed between June 18 and July 9, 1954, and recorded in Secret Notebook No. 3509, pages 1-37. Work was done by J. T. Long, R. J. McNamee, R. D. Arthur, and F. L. Rogers. The report was written in August 1954.