AN ABSTRACT OF THE THESIS OF

Bernard E. Davis for the M. S. in Chemical Engineering
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Title EFFICIENCY OF THORIUM EXTRACTION BY PRIMARY

AMINES AS A FUNCTION OF PULSE FREQUENCY AND AMPLITUDE

IN A PULSED SIEVE-PLATE COLUMN

Abstract approved ████████████████
                      (Major Professor)

The amine extraction process is evaluated for pulse column operation. A 0.1 M solution of Primene JM-T (a commercial mixture of tertiary-alkyl primary amines) in a kerosene-base diluent is the extractant for thorium feed in aqueous acidic sulfate solutions.

Equilibrium isotherms at room temperature are presented at aqueous acidities of 1.0 and 0.1 N H^+ ion concentration. At the 0.1 N H^+ concentration, isotherms are presented with and without added aqueous Na_2SO_4, and the effect of insufficient sulfate ion is demonstrated.

A low-range fluorometric thorium analytical method, adapted from the literature, is presented. With a 2 ppm thorium lower limit, the method makes possible the determination of the low-thorium concentration portions of an equilibrium isotherm.

Pulse column operational data are presented showing stable and efficient extraction operation in a pulse frequency-amplitude range of 110 to 180 in./min. In this operational range, aqueous feed concentrations of 4.94 to 5.19 grams per liter were stripped to a raffinate concentration of < 2 ppm in eight 2-inch-spaced plates mounted in a 3-inch I.D. column using aqueous and organic flow rates of 123 and 250 milliliters per minute respectively. This represents a separation factor of > 2,500.

EFFICIENCY OF THORIUM EXTRACTION
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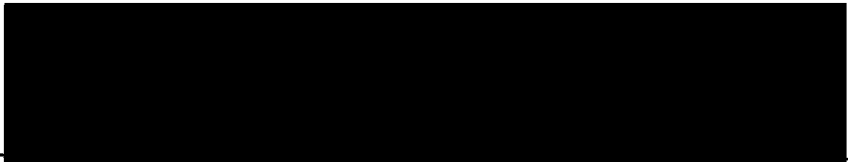BERNARD ERIC DAVIS

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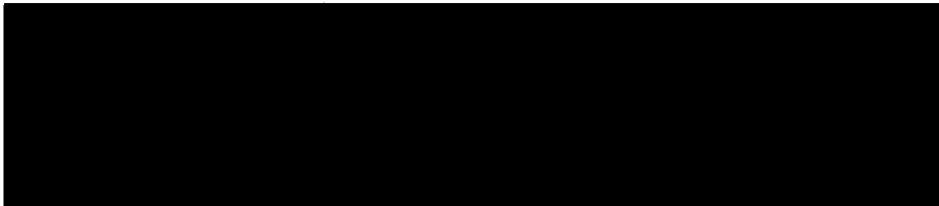the requirements for the
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APPROVED:

Assistant Professor of Chemical Engineering

In Charge of Major

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Dean of Graduate School

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INTRODUCTION

Thorium is a potentially useful fertile material for breeder

reactors. Neutrons produced by fission and slowed by a moderator

would be absorbed by thorium present with the fissionable material

in the fuel mixture to produce fissionable U^{233} by the following

reactions (5, p. 65):

$$_{90}Th^{232} + {_{0}n^{1}} \rightarrow {_{90}Th^{233}} \xrightarrow[\beta^-]{23.3 \text{ min}} {_{91}Pa^{233}} \xrightarrow[\beta^-]{27.4 \text{ days}} {_{92}U^{233}} \quad (1)$$
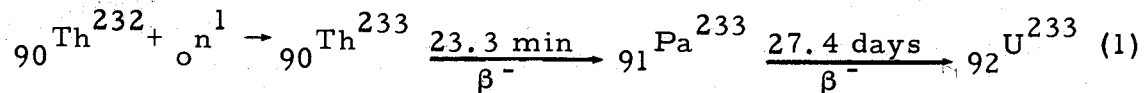
Thorium is recovered from monazite sands and from the

uranium-thorium ores of the Canadian Blind River district. Earlier

processes for separating and purifying thorium (3, p. 235-239; 2,

p. 1754-1755) were developed by Battelle Memorial Institute and the

Ames Laboratory using caustic and sulfuric acid respectively to open

up the monazite sands. In both methods the elements were partially

separated by precipitation followed by tributylphosphate (TBP) ex-

traction to purify the redissolved thorium-rich precipitate. The

amine extraction (Amex) process described by Crouse and Brown

(22, p. 1461-1464) can bring about separation of both uranium and

thorium from the rare earths usually found in thorium-uranium ores

and essentially complete recovery and separation of the thorium and uranium. The relatively pure thorium product of the Amex process is expected to eliminate the need for the TBP extraction.

Crouse and Brown (22, p. 1462) have also made detailed studies of the extraction of thorium by a branched primary amine mixture, Primene JM-T, in mixer-settler arrays. Their studies included an examination of the chemistry of the extractive and stripping systems. However the performance of this promising system had not previously been investigated in pulse columns; this thesis was initiated to make such a study.

CHEMISTRY OF THE SYSTEM

Compositions of the Phases

The compositions of the aqueous and organic feed streams used in the pulse column runs are best described by the makeup procedures summarized below. These procedures are described and explained in detail in the subsection on preparation of the phases.

The organic phase prior to sulfonation consisted of an 0.1 M Primene JM-T solution in a diluent composed of 95 volume percent kerosene and 5 percent capryl alcohol (2-octanol). The virgin aqueous solution consisted of 1.0 M Na_2SO_4 in distilled water. The pH of this solution was adjusted to approximately 1.0 with concentrated H_2SO_4. These two solutions were contacted to allow mutual saturation of the phases, sulfonation of the amines and equilibration of hydrogen ion concentrations. With the two phases thus in equilibrium, the H^+ level was adjusted by further addition of concentrated H_2SO_4 until the final equilibrated aqueous hydrogen ion concentration was 0.100 N ± 2%.

The phases were then separated and thorium added to the aqueous solution in the form of thorium nitrate tetrahydrate salt. The aqueous thorium level was adjusted to about 5 grams per liter of thorium.

After the phases were settled and separated, but prior to

aqueous thorium addition, samples were taken to determine the saturation concentration of sodium and sulfate ions in the organic phase. Using a Beckman DU spectrophotometer with a standard flame attachment, an organic sample was analyzed at 216 ppm sodium. In order to determine the sulfate concentration in the organic phase, sulfate concentrations in the aqueous phase were compared with the organic phase before and after contact. Uncontacted aqueous samples (taken immediately prior to contact with organic ingredients during makeup) and two organic-contacted, thorium-free aqueous samples were analyzed gravimetrically by barium precipitation. The uncontacted samples both yielded 1.07 M sulfate while the contacted samples were 1.00 and 1.04 M in $SO_4^=$. A third contacted aqueous sample analyzed 1.04 M in Na_2SO_4 by flame photometric sodium analysis. From these data, considering the volumetric ratios of organic and aqueous makeup, it may be concluded that the organic phase sulfate concentration was approximately 0.02 M.

Other mixtures were also studied during preliminary investigations of physical properties and thorium equilibria. These are reported in the subsection on equilibrium data.

Chemical Composition of the Extractant

The active ingredient of the organic phase was a mixture of tertiary-alkyl primary amines known by the trade name Primene

JM-T (produced by the Rohm and Haas Company). The mixture was composed of amines principally in the C_{18} to C_{22} range (34, p. 1). The principal range of chemical formulas, therefore, was $C_{18}H_{37}NH_2$ to $C_{22}H_{45}NH_2$. All of the amines included the basic structure:

$$
\begin{array}{c}
R \\
| \\
R' - C - NH_2 \\
| \\
R''
\end{array}
\qquad (2)
$$

Where R, R' and R'' represent alkyl chains. There are several possible isomers which include such a structure, even if the total number of carbon atoms is fixed. The amine mixture, Primene JM-T, contained different isomers at each carbon atom level, and each isomer consisted of highly branched alkyl chains.

Considerable chemical and physical property data for Primene JM-T are available (34, p. 3) from the supplier. These data include the specific gravity (0.840 at 25 °C) and the molecular weight, 315. This latter figure was presented by the producer as the neutral equivalent of the mixture.

Ionic Chemistry of the Extraction

The extraction of thorium with amines in an acidic sulfate system is possible because the hydrated amines have a much greater

affinity for thorium-sulfate complex ions than for sulfate or bisulfite ions.

The actual ionic species exchanging across the interface in such systems are not known with certainty but probably include some of the thorium sulfate complexes presented below. Allan, McDowell and Case (9, p. 52) have speculated on the complex association in the solvent phase. These investigators have determined that in such systems there is a series of at least four thorium sulfate complexes in the aqueous solution. The relative proportions of each complex are said to depend upon the thorium and sulfate concentrations. This series can be represented as follows:

$$\sum Th = Th^{+4} + ThSO_4^{+2} + Th(SO_4)_2 + Th(SO_4)_3^{-2}$$

$$+ Th(SO_4)_4^{-4} + \ldots + Th(SO_4)_n^{4-2n} + \ldots (?) \ldots \quad (3)$$

Upon contact of the organic and thorium-free aqueous phases during makeup, the following reactions took place:

$$NH_2R + H_2O \rightleftharpoons NH_3R^+ + OH^- \quad (4)$$

$$2NH_3R^+ + SO_4^= \rightleftharpoons (NH_3R)_2SO_4 \quad (5)$$

$$NH_3R^+ + HSO_4^- \rightleftharpoons (NH_3R)HSO_4 \quad (6)$$
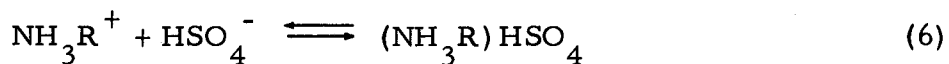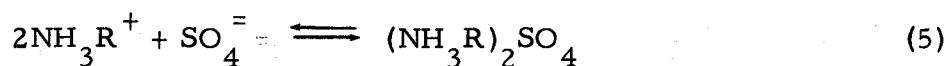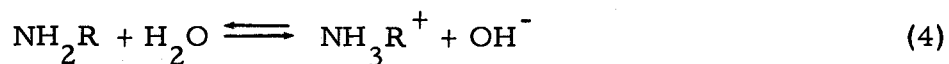
where R represents an alkyl chain. This process was considered as sulfonation of the organic phase. Water and sulfate ion were

provided by the aqueous phase to sulfonate the amines in the organic phase.

During extraction, the sulfonated organic phase and the thorium-rich aqueous phases were placed in intimate contact. The following types of reaction appear to have taken place:

$$(\frac{2n-4}{2})(NH_3R)_2SO_4 + Th(SO_4)_n^{4-2n} \rightleftharpoons (NH_3R)_{2n-4}Th(SO_4)_n$$
$$+ (\frac{2n-4}{2})SO_4^{=} \tag{7}$$

$$(2n-4)(NH_3R)HSO_4 + Th(SO_4)_n^{4-2n} \rightleftharpoons (NH_3R)_{2n-4}Th(SO_4)_n$$
$$+ (2n-4)HSO_4^{-} \tag{8}$$
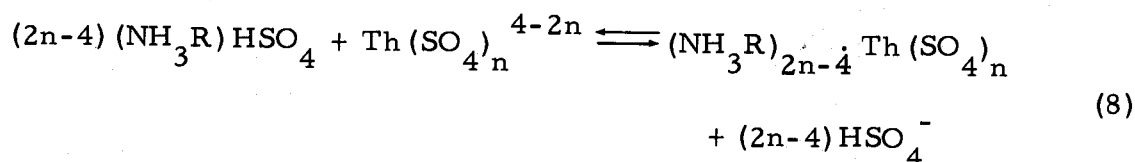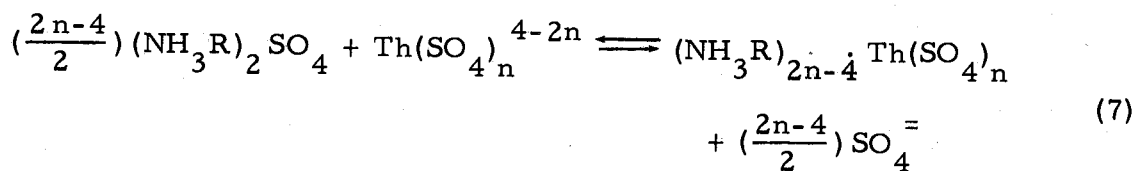
By this process, the thorium sulfate complexes were exchanged between the phases with sulfate and bisulfate ions, the latter returning to the aqueous phase.

Effect of Thorium Nitrate Upon Emulsification

Preliminary investigation disclosed a marked "salting-out" effect due to thorium nitrate. The behavior of system No. 2 (Figure 1) without thorium present was observed in a preliminary pulse column operation, and a severe emulsification problem was encountered. The slightest agitation quickly led to emulsion flooding of the column. However when the aqueous solution was loaded with thorium nitrate to 5.04 grams of thorium per liter, the

operating characteristics showed a dramatic change. With thorium present, there was no longer an emulsion problem but, instead, the problem became the opposite one of inadequate contact between the phases. For this reason it was decided to use 5 percent capryl alcohol in the kerosene diluent in the recorded pulse column runs in order to promote better contact between the aqueous and organic phases.

Preparation of the Phases

Because the makeup procedure was complex and time-consuming, and to help insure feed stream uniformity among runs, large batches, each sufficient for several runs, were prepared in 100-gallon stainless steel tanks. The nine data points presented in Figure 4 represent only two such large batches and one relatively small preliminary batch. Runs 2 through 4 were made with material from the first large batch and runs 5 through 9 from batch No. 2. The batch makeup quantity was 32 gallons of aqueous solution and 58 gallons of organic solution, the ratio being chosen in view of the relative flow rates for the two phases (see page 37).

Preparation of phases was initiated by weighing 266 lbs. of distilled water into tank A (Figure 3). Then 37-7/8 lbs. of anhydrous purified Na_2SO_4 powder was added gradually with constant agitation provided by a one-half H.P. mixer. Into this 1.00 M Na_2SO_4

solution was mixed a quantity of concentrated H_2SO_4 estimated to provide slightly less than the desired 0.100 N H^+ ion concentration after organic contact.

To this aqueous solution the organic phase ingredients were added: 363 lbs. of kerosene were added followed by 19-5/8 lbs. of 2-octanol and 8220 ml. of Primene JM-T. The entire mass, aqueous and organic, was then vigorously agitated for one hour and allowed to settle for several hours. Aqueous samples, drawn from a tap in the bottom of the tank, were titrated against 0.1000 N KOH to a phenol-phthalein endpoint. Based on the results of this titration, further concentrated H_2SO_4 was added to the mix which was again agitated, settled, sampled and the sample titrated. A second slight addition of concentrated H_2SO_4 or reagent grade NaOH pellets was usually sufficient to bring the final acidity to within the arbitrary specification of 0.100 ± 2% H^+ ion normality. In batch No. 1, for example, a total of 970 ml. of concentrated H_2SO_4 plus 19.4 grams of NaOH pellets were used in achieving a contacted aqueous H^+ ion concentration of 0.1012 N.

With the two phases thus prepared and adjusted to the proper equilibrated acidity level, it remained to separate them and to load the aqueous phase with thorium. The aqueous phase was drawn from the bottom of tank A and discharged into tank B, the organic phase being left in tank A. Approximately 1500 grams (1590 g. in batch No. 1;

1489 in batch No. 2) of thorium nitrate tetrahydrate salt was gradually stirred into tank B with the help of a mixer to yield the desired thorium concentration of about 5.0 grams per liter as thorium. This concentration is similar to that used by Crouse and Brown (22, p. 1462). The actual thorium levels of the final aqueous makeup mixtures, given in Table VI, were determined after thorough mixing by the EDTA titrimetric method.

Explanation of Phase Components and Makeup Procedures

The purpose of the addition of 1.0 M Na_2SO_4 to the uncontacted aqueous phase was to provide sufficient sulfate ion for the proper thorium extraction performance of the system. As explained on page 15 and demonstrated in Figures 1 and 2, optimum extraction performance was found to require a certain minimum sulfate ion concentration. At the 0.100 N H^+ ion (sulfuric acid) level it was found necessary to provide additional sulfate ion, while at the 1.00 N H^+ ion level (sulfuric acid) no additional sulfate was required. The lower acidity level, however, was chosen to reduce the corrosive attack upon the equipment.

In the organic phase, the arbitrary 0.1 M concentration of the active agent (Primene JM-T) in the diluent followed the precedent set by Crouse and Brown (22, p. 1462). Capryl alcohol was also added to the organic phase. Preliminary column runs with pure

kerosene diluent showed poor contact between the phases. In order

to create better mixing conditions, 5 volume percent capryl alcohol

was added to the diluent. Capryl alcohol was one of two long-chain

alcohols used at Oak Ridge (20, p. 22-23; 21, p. 12-14) for this

purpose.

The two thorium-free phases were placed in intimate contact

to provide pH and sulfate equilibrium between the phases prior to

pulse column operation since an operating situation was desired in

which the only reaction was thorium ion exchange between the phases.

This condition was attained by allowing hydrogen ions and sulfate ions

to equilibrate between the phases before the thorium ion transfer took

place.

The acidity specification of 0.100 N H^+ ion concentration was

based upon the contacted aqueous solution rather than virgin aqueous

phase because this was felt to be the more realistic approach. This

procedure also compensated for any possible variations in the alka-

linity of the as-received Primene JM-T. Since the thorium extrac-

tion may have been somewhat dependent on pH (24, p. 11), the

arbitrary specification of less than 0.002 N variation of the final

hydrogen ion level was rigidly adhered to.

Equilibrium Data

Although a few thorium distribution isotherms were presented by Crouse, Brown and Arnold (21, p. 10; 24, p. 11) for certain specific systems, such equilibrium data were very limited. Therefore, prior to pulse column operation, it was necessary to experimentally determine the appropriate equilibria.

Experimental Method

To evaluate the equilibrium thorium distribution, thorium-free aqueous and organic solutions were made up and intimately contacted and the acidity level adjusted in a manner similar to that described on page 8. Two gallons of each phase were thus prepared and separated. Samples of aqueous were removed and loaded to various thorium concentration levels by addition of thorium nitrate tetrahydrate salt. The approximate thorium level was established by adding estimated amounts of the salt. The exact thorium concentrations of these samples were determined by EDTA titration. The thorium-laden aqueous samples were shaken with equal volumes (200 ml of each phase) of virgin organic samples in separatory funnels. After thorough contact and settling, samples of aqueous solution were removed and analyzed for thorium either by EDTA titration or by fluorometry, depending upon the final aqueous concentration.

Knowing the initial and final aqueous thorium concentrations, it was

then possible to determine the equilibrium organic concentration by

difference.

Presentation of Data

Equilibrium data for the system used in the pulse column runs

are presented in Figure 5 and Table I. The general shape of the

curve and the approximate height of the plateau are in agreement

with data determined from other systems (Figure 1) and with the

findings of Crouse and Brown (21, p. 11). The step-function nature

of the curve is, of course, very interesting and the determination of

the low-thorium concentration range for this system is original with

this work. In the sharply ascending portion of the curve, all equilib-

rium aqueous thorium concentrations were determined by the fluoro-

metric method to be less than 2 ppm.

In Figure 1 the equilibrium curve described above is presented

as curve No. 1. It will be noted that curve No. 2 is nearly identical

to it. The systems described by the two curves were also nearly

identical, the only difference being that in the system of curve No. 2

the diluent was pure kerosene. (No capryl alcohol was used.) The

slight organic extractive superiority of curve No. 1 over curve No. 2

may be explained by the superior inter-phase contact in the presence

of the capryl alcohol. At higher thorium concentration the difference

Figure 1   Equilibria in Various Systems

Curve No. 1: 0.1 N H^+, with 2-octanol, with Na_2SO_4

Curve No. 2: 0.1 N H^+, without 2-octanol, with Na_2SO_4

Curve No. 3: 1.0 N H^+, without 2-octanol, without Na_2SO_4

Curve No. 4: 0.1 N H^+, without 2-octanol, without Na_2SO_4
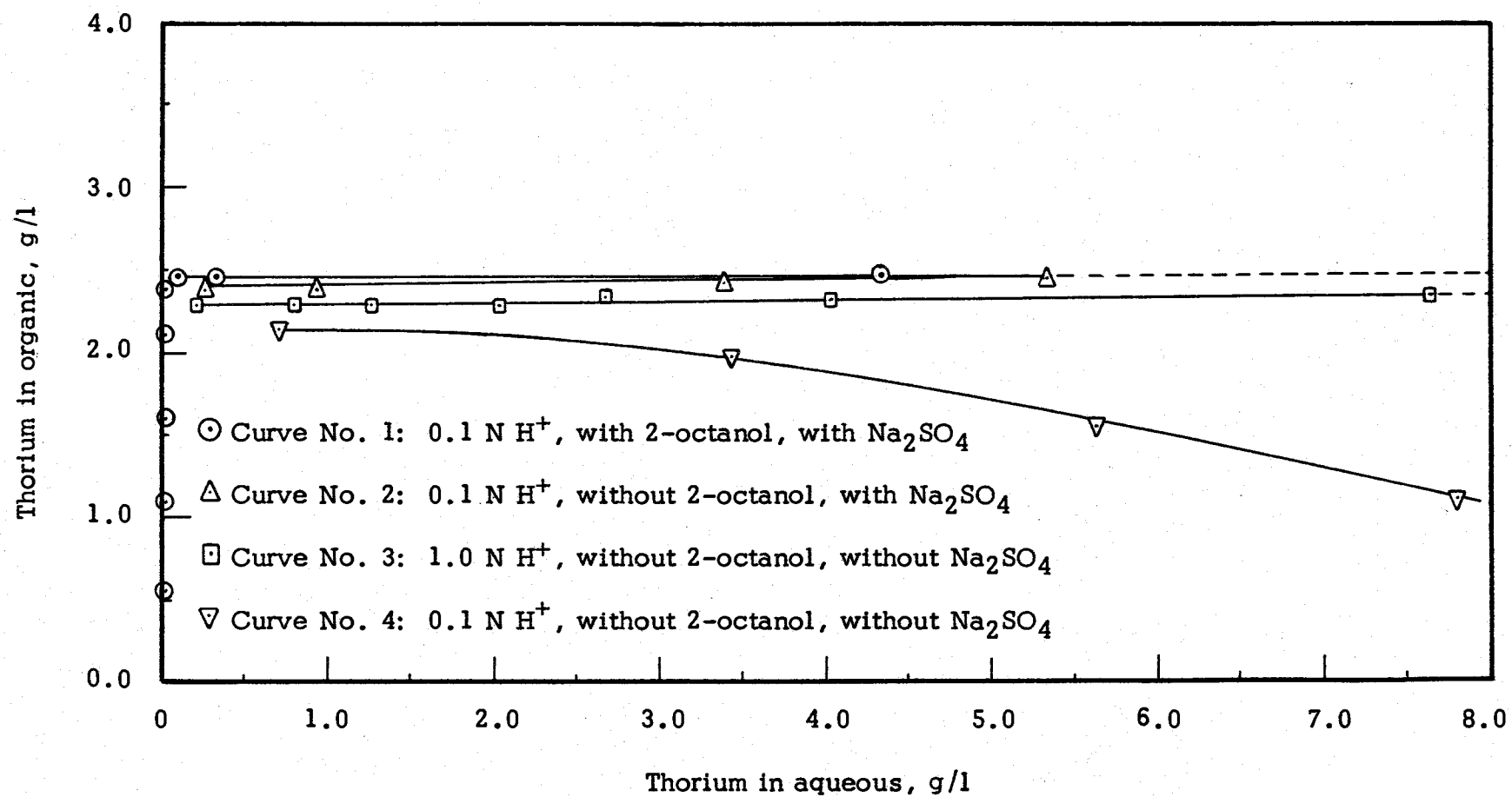
is less noticeable; perhaps the relatively greater ionic driving forces render the diffusional resistances less significant.

The aqueous phase acidity after organic contact of the system represented by curve No. 3 of Figure 1 was adjusted to the $1.00 \; N \; H^+$ level with sulfuric acid. (Acidity control to $\pm 2\%$ was achieved by phenolphthalein titration.) Neither sodium sulfate nor capryl alcohol was added to this system. The curve is of the same general shape as curves 1 and 2 but it has a lower saturation plateau.

Curve No. 4 of Figure 1 is unusual since it shows a decrease in organic thorium concentration with increasing aqueous concentration. It is also to be noted that the highest portion of the curve is considerably lower than the corresponding portion of curve No. 2. The systems represented by the two curves are identical except for the sodium sulfate addition to the system represented by curve No. 2. No sodium sulfate was added to system No. 4. It was concluded that the amount of sulfate ion added to the system as H_2SO_4 was insufficient to bring the thorium into the organic phase at high thorium concentrations. It is apparent that as increasing thorium levels were reached, more of the limited sulfate ions were required to form the first two complexes of equation 1, leaving fewer for formation of the anion complexes necessary for ion exchange. Thus, with increasing thorium, the level of exchanged thorium necessarily decreased.

Table I. Equilibrium Date for the System 0.1 N H^+, with 2-Octanol and Na_2SO_4

Thorium Concentrations, g/l

Uncontacted Aqueous	Equilibrium Aqueous	Equilibrium Organic
0.561	< 0.002	0.560
1.08	< 0.002	1.08
1.59	< 0.002	1.59
2.11	< 0.002	2.11
2.38	< 0.002	2.37
2.54	0.093	2.45
2.77	0.315	2.45
6.79	4.32	2.47

Notes: (1) This is the system used in the pulse column runs.

(2) The equilibrium aqueous samples for the first five samples were analyzed by the fluorometric method; the remainder by the EDTA method.

Table II. Equilibrium Data for the System 0.1 N H^+, without 2-Octanol, but with Na_2SO_4

Equilibrium Thorium Concentration, g/l

Aqueous	Organic
0.270	2.40
0.936	2.39
3.39	2.44
5.32	2.46

Note: All data above were obtained using the EDTA analytical method.

Table III. Equilibrium Data for the System 1.0 N H^+, without 2-Octanol and Na_2SO_4

Equilibrium Thorium Concentration, g/l

Aqueous	Organic
0.213	2.29
0.812	2.29
1.27	2.28
2.03	2.27
2.67	2.33
4.03	2.32
7.64	2.35

Note: All data above were determined using the EDTA analytical method.

Table IV. Equilibrium Data for the System 0.1 N H^+, without 2-Octanol and Na_2SO_4

Equilibrium Thorium Concentration, g/l

Aqueous	Organic
0.710	2.14
3.43	1.98
5.64	1.55
7.81	1.13

Note: All data above were obtained using the EDTA analytical method.

The effect of sulfate concentration upon thorium extraction is also shown by Figure 2. Acidity-adjusted but thorium-free aqueous and organic solutions of the system represented by curve No. 4 of Figure 1 were set aside, and the aqueous solution was loaded to 7.18 grams per liter with thorium. Samples of this aqueous solution were then loaded with Na_2SO_4 to the concentrations recorded in Table V. These sulfonated aqueous thorium solutions were each contacted with equal volumes of organic phase, and the equilibrium thorium concentrations were determined by the usual method. Figure 2 shows that the extractive power of the organic phase increases with increasing sulfate concentration in the 0.1 N H^+ system up to a plateau which occurs at an aqueous Na_2SO_4 molarity of about 1.0. This curve was the basis for using a 1.0 sodium sulfate molarity in the aqueous phase for the pulse column runs. These data were collected using non-standardized EDTA in the analyses and, therefore, are valid only in showing the qualitative effect of sulfate concentration upon extractive performance.

Figure 2   Thorium in Organic Phase Vs.
            Na_2SO_4 Molarity of Virgin Aqueous

System exclusive of Na_2SO_4:

0.1 N H^+, without 2-octanol.

The fixed thorium concentration of the

uncontacted aqueous was 7.18 g/l.

This aqueous was contacted with equal

volumes of thorium-free organic.

*Aqueous saturated with Na_2SO_4, actual

molarity unknown but less than 2.0.

Thorium in organic, g/l

Molarity of Na_2SO_4 in virgin aqueous
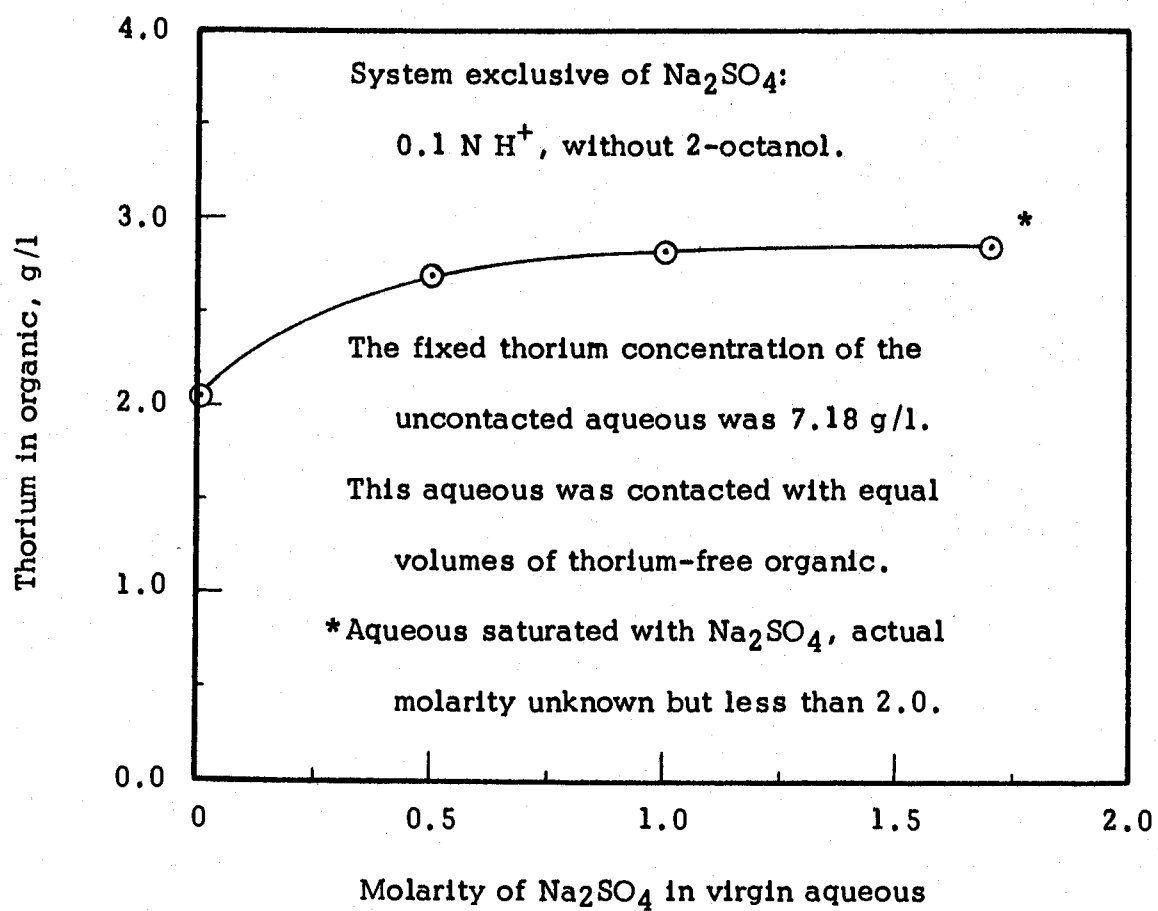
Table V. Effect of Na_2SO_4 upon Thorium Extraction at 0.1 N H^+

Na_2SO_4 In Virgin Aqueous	Equilibrium Thorium Concentrations, g/l	
	Aqueous	Organic
0	7.18*	--
0	5.14	2.04
0.5	4.51	2.67
1.0	4.35	2.83
**	4.31	2.87

* Uncontacted aqueous concentration.

** Saturated, exact molarity unknown but less than 2.0.

Notes: (1) All data above were obtained by EDTA analyses.

(2) System: 0.1 N H^+, without 2-octanol.

(3) These data were collected using non-standardized EDTA and, therefore, are valid only in showing the qualitative effect of sulfate concentration upon extractive performance.

ANALYTICAL PROCEDURES

Two analytical methods were adapted and employed for determining thorium in aqueous solutions. The first was a rapid, high-range, titrimetric EDTA method suitable down to about 100 ppm thorium. The second was a more complex fluorometric method for analyzing low-range samples down to 2 ppm thorium. No thorium analyses of the organic phase were necessary since it was always possible to determine thorium content in the organic phase from the difference between initial and final aqueous concentrations.

EDTA Method

The applicable portion of the EDTA method of Apple and White (1, p. 43) with minor modifications was checked against gravimetrically-determined thorium knowns and found reliable in the range described above. This method is rapid and is unaffected by acidity or sulfate level. The EDTA used was Hellige Certified Reagent Versene Hardness Titrating Solution. The concentration of this solution is adjusted so that 1.00 milliliter equals 1.00 milligram of $CaCO_3$. This represents a versene molarity of 0.009991. Xylenol orange solution, used as indicator, gave a satisfactory endpoint for 0.01 M versene titration and was found to be superior to Alizarin Red S. indicator proposed in the earlier method of Fritz and Ford (26, p. 1640).

The procedure for the EDTA titrimetric method was as follows:
Five milliliters of aqueous thorium unknown sample were pipeted into
a 100 ml. beaker. A Beckman Model H glass electrode pH meter was
used in adjusting the pH of the sample to 3.0 ± 0.2 by dropwise addi-
tion of an acetate buffer solution whose composition is given in the
appendix. This represents a slight modification of the method of
Apple and White (1, p. 43). Starting at a lower pH they added 3.0
ml. of acetate buffer followed by dropwise addition of 20% NaOH to
the above pH. Four to six drops of xylenol orange indicator solution
(see Appendix A) were added, and the sample was titrated to the
pink-to-yellow endpoint with a 10 milliliter microburet. The thorium
concentration was calculated as

$$\text{Mg. of Th} = 232.1 \ VM \tag{9}$$

where V and M represent the milliliters and molarity respectively
of the EDTA titre. For a versene molarity of 0.009991 and a 5.00
ml. sample, this formula was converted to:

$$\text{Grams Th per liter} = (0.46378) \ V \tag{10}$$

Obstacles to Achieving a Low-Range Method

Operation of the pulse column quickly showed that an analytical
method applicable in the range below 100 ppm thorium was required.

A rapid method was desired to permit analysis during pulse column operation; such on-stream analysis was possible with the EDTA titrimetric method. Several methods of thorium analysis applicable in the low concentration range are noted in the literature. However these methods are not applicable in the presence of high concentrations of sulfate ion.

Apple and White (1, p. 43) suggest that the EDTA method is applicable in the low concentration range if back-titration with 0.002 M copper solution to a 0.001 M EDTA endpoint is carried out; however this method failed to produce a distinct endpoint. The popular Thoron (36, p. 844-849) colorimetric method is not applicable in the presence of sulfate and separation of thorium and sulfate was not feasible with such relatively high sulfate concentrations as used in this study. Other colorimetric methods listed in the literature (36, p. 850) involving such coloring agents as carmine red, quinalizarin and napthazarin were likewise not applicable in the presence of sulfate. A nephelometric method based on thorium iodate precipitation also was impractical at high sulfate concentrations.

Spectographic and X-ray methods were also useless at low concentrations since thorium has no suitable diffraction lines. Practical mass spectrography equipment was unavailable.

The possibility of analyses based on the natural alpha radiation of thorium was discounted. Daughter elements of the thorium decay

chain which were present in the aqueous feed would have remained in the raffinate and made it impossible to determine the thorium concentration accurately by simple radiation counting. However the more complicated radiotracer method of Sill (41, p. 675-676) may be worthy of consideration. The tracer method was avoided in this study as offering more potential problems and fewer advantages than the fluorometric method finally selected for use.

Fluorometric Method

The fluorometric method of Sill and Willis (43, p. 954-964) was based on a thorium complex with morin (2',3,4',5,7-pentahydroxyflavone). It was a time-consuming method which could not be performed while operating the pulse column. However the method did provide reproducible results down to 2 ppm and was not affected by the high sulfate concentration.

Analytical Chemistry

The fluorometric reagents and samples were prepared strictly according to the authors' recommended procedures (43, p. 955). A detailed outline of the sample preparation procedures is presented in Appendix B. The basic chemistry of the method is as follows:

Organic materials were removed by oxidizing agents. Diethylenetriaminepentaacetic acid (DTPA) and triethanol amine

(TEA) were added to the acidic thorium solution to prevent hydrolysis during subsequent pH adjustment. Without these reagents, some thorium would have been precipitated as the hydroxide. The TEA prevented precipitation in more alkaline regions where the DTPA complex was unstable. Quinine Sulfate was used as a fluorescent indicator in establishing a pH of approximately 11, and piperidine buffer was added. Finally, the addition of morin created the desired fluorescent complex.

The time between addition of morin and measurement of fluorescence was critical and, whenever possible, was kept within two minutes. Since temperature was also critical, the samples were kept in a constant temperature bath between the time of addition of morin and fluorescence measurement. The sample holder for fluorescence measurement was cooled with water from this same constant temperature bath. Fluorescence readings were taken quickly to avoid heating the sample which might have occurred during measurement in spite of the cooling coils. It was noted that fluorescence sensitivity increased with decreasing temperature.

With each set of sample runs, blank and known standard samples covering the concentration range of the unknowns were run also. Since the unknowns were measured by curves established from knowns each time, effects of differences in time and temperature from one sample set to another were cancelled.

Fluorometric Equipment

Fluorescence was measured by using a Beckman DU spectro-photometer with a stock RCA 1P28 photomultiplier and a modified 73500 Beckman DU/DK fluorescence attachment. The fluorescence attachment was changed in several ways for this method. The stock mercury lamp was replaced with a 6 volt, 10 watt Volkswagen tung-sten filament bulb with a stabilized D.C. source. The tungsten fila-ment bulb provided more light energy, but it also produced more heat. Since the stock plastic sample holder could not conduct away the heat, the lamp tended to heat the sample as well as damage the holder. The plastic holder was replaced by a copy fabricated from copper tubing. The metallic holder was coiled with 3/32-inch copper cooling coils soldered to the holder and connected in series with the cooling coils in the walls of the fluorescence attachment. A Gorman Rupp rubber pump was installed at the inlet to these coils. This water-cooled, metallic sample holder was designed and constructed by Mr. Richard Van Santen and Mr. James Riehl of Wah Chang Corporation.

A 465 mμ narrow pass primary filter was used between the light source and the sample. Fluorescent light passed to the photo-multiplier via the Beckman DU adjusted to a slit width setting of 1.0

and a secondary wave length setting of 535 mµ.

In this method the choice of filters was most critical. Dr. Sill's work (43, p. 955-956) showed that the excitation spectra peak for the thorium-morin complex occurred at 461 mµ and the emission spectra peak for thorium-morin occurred at 534 mµ. Therefore these are the ideal wave lengths respectively for primary and secondary filtration. However the emission spectra peak for the morin is 551 mµ. This close proximity illustrates the necessity for primary and secondary filtration at wave lengths very close to the ideal conditions.

Cylindrical sample tubes were used, the same tube being used for each sample of a set. The tubes were held in an identical position in the sample holder by a sample positioner.

PULSE COLUMN LITERATURE

A wealth of information about pulse columns has been published from Van Dijck's patent (50) in 1935 through the recent longitudinal mixing study by Sehemel and Babb (38, p. 210-214). Much of this literature is listed in the bibliography section and a good review of many of these studies was presented by Welch (52, p. 4-17). Available in the literature are extensive evaluations of the various operating variables (54, p. 187; 15, p. 282; 45, p. 1008), design factors (46, p. 12; 37, p. 401; 47, p. 39-52) and operating characteristics (37, p. 397; 54, p. 186; 30, p. 58-62).

Several of these studies (37, p. 399; 52, p. 39) have verified the validity of the pulse frequency-amplitude product as an operating parameter and have demonstrated that there is an optimum value of f x a in terms of H.T.U. The theory (37, p. 398) is that efficiency improves with increasing agitation until the onset of unstable operation (usually the point of incipient emulsion formation).

A particularly comprehensive study of the effect of pulse column variables is that of Sege and Woodfield (37, p. 396-402). This work was consulted in establishing the plate design and spacing and the flow rates in the present study (pages 32 and 36).

Most of the pulse column efficiency data in the literature are reported in terms of H.T.U. or overall height of a transfer unit

(48, p. 345-346) which is calculated from the N.T.U. (overall number of transfer units) and the active pulse column height. Other measures of efficiency used (52, p. 10) include the overall mass transfer coefficient, K, and the height equivalent to a theoretical stage, H.E.T.S. (49, p. 427). This latter efficiency measurement, which is not very useful, is determined by merely stepping off stages and dividing the result into the active height. Typical values of H.T.U. for pulse columns range from zero to two feet. Increasing efficiency is represented by decreasing values of H.T.U. and H.E.T.S. and by increasing N.T.U. and K values.

PULSE COLUMN APPARATUS

A flow diagram of the equipment is presented in Figure 3.

This equipment was originally designed and constructed by Dr. Walter Meyer, but modifications beneficial to the present study were made by the author. Major changes include the installation of an organic feed distributor ring and the addition of 100 gallon aqueous and organic makeup and storage tanks with associated feed lines and pumps. Only corrosion-resistant materials were used in contact with the experimental solutions. Tanks, piping and column plates and spacers were of stainless steel. Other materials with which the streams came in contact included polyethylene and tygon tubing, nylon fittings, rubber pump blades and housings and the glass column with Teflon pulsation bellows.

The column proper consisted of a 36-inch length of 3-inch I.D. Pyrex Double Tough glass pipe. Both ends of the column were fitted with identical 10-inch pyrex tees. A 6-inch length of glass pipe was attached to the top tee and open to the atmosphere--an aid in preventing column overflow. The bottom tee anchored the column to the base. Through the horizontal portion of the two tees passed the column feed and outlet lines. All joints were sealed with Teflon gaskets.

Eight standard sieve plates were centered within the height of

Figure 3   Diagram of Pulse Column Apparatus
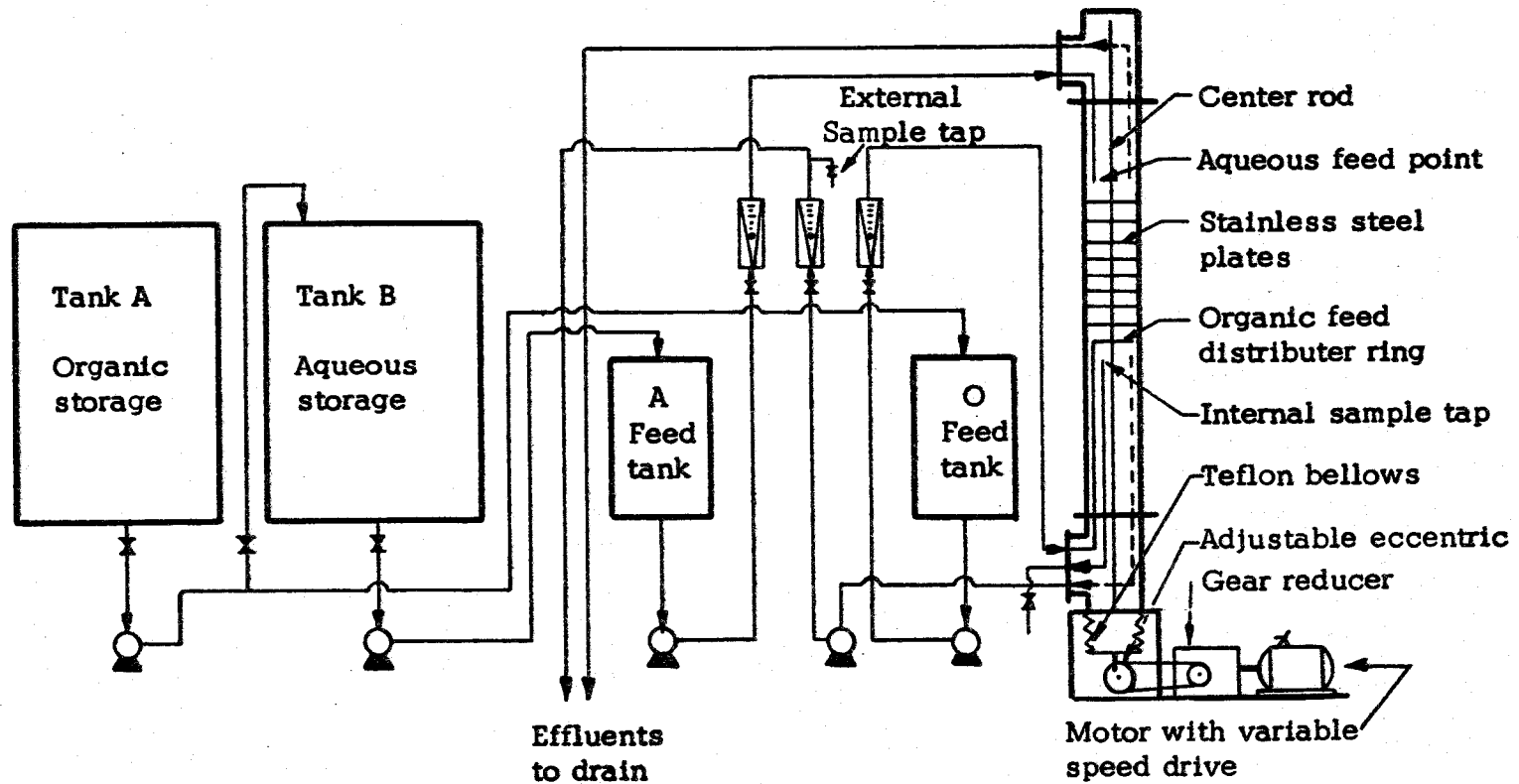
the column at a spacing of two inches. Eight was considered to be the minimum number of plates consistent with representative pulse column operation; a minimum number of plates was desired to reduce the time necessary to achieve equilibrium. Each plate contained 114 one-eighth-inch diameter holes arranged such that the centers formed a pattern of equilateral triangles. The plates contained 22.6 percent free area. This geometry and the two-inch plate spacing are recommended by Sege and Woodfield (37, p. 396) as a "standard cartridge" affording a useful compromise between high throughout capacity and near-optimum extractive effectiveness. The plates had been cut from 0.064 gauge, type 310 stainless steel sheet and the spacers from 5/8-inch, type 304 stainless steel tubing. A 3/8-inch, type 316 stainless steel center rod, threaded into a fixture in the base of the column, was used for centering and mounting the plates. The edges of the plates were fitted with Teflon gaskets to prevent flow between the column wall and the plates.

Organic feed was introduced two inches below the bottom plate by means of a perforated polyethylene ring. The external organic feed pipe connected to an internal 1/4-inch polyethylene tube leading through a nylon tee fitted to the distributor loop. The 2-3/4-inch O.D. loop of 3/16-inch tube, perforated on its inside surfaces slightly below the top with ten 3/64-inch holes, provided uniform distribution of the dispersed phase around the cross section of the

column. Without such a distributor, it was found that the organic bubbles would proceed up the column directly above the input point and would cover only about half the plate area of the bottom plates. The aqueous feed was introduced two inches above the top plate by a similar internal 1/4-inch polyethylene extension of the external feed pipe. A distributor ring was not necessary for the aqueous feed since it was discharged into the continuous phase. However moderate distribution was provided by sealing the end of the tube and drilling a ring of 3/64-inch perforations around the circumference of the tube near the sealed end. These extended aqueous and organic feed lines provided an effectively shortened column commensurate with an actual plate section height of 14.3 inches. The shortened effective column prevented contact between the phases above and below the plate section.

A raffinate sample tap was available down stream from the raffinate rotameter. However, at the slow feed rates used, considerable run time would have been required to transfer the pure raffinate from the bottom plate through the column and lines to the tap. Run time was reduced by using an internal sample tap, a 1/8-inch I.D. polyethylene tube which sampled the aqueous phase two inches below the organic feed distributor.

The extract was allowed to overflow through a line connecting the upper column tee and leading to the drain. No pumping,

sampling or flow measurement of the extract stream was necessary, and gravity overflow provided a fairly constant, self-adjusting level in the column. Raffinate was pumped from the bottom tee of the column through a rotameter to the drain.

Pulsation was produced by a three-inch I.D. Teflon bellows connected to an adjustable eccentric drive. The eccentric was driven by a $\frac{1}{2}$ H. P. electric motor through a Boston 40:1 gear reducer and a Reeves Flexi-Speed Drive. Pulse amplitudes from zero to three inches were possible. By adjustment of the flexi-speed drive and choice of pulleys, one could achieve a pulse rate range from 20 to 150 pulses per minute.

Both feed streams and the raffinate stream were pumped by individual Eastern Industry pumps through $\frac{1}{4}$ -inch, type 304 stainless steel pipe. Flow in each of the lines was measured by a Manostat Predictability Flowmeter, model FM1048T using stock ground glass floats. The flows were adjusted by $\frac{1}{4}$ -inch stainless steel needle valves.

All controls and meters were mounted on a schematic flow diagram control panel which aided column operation.

PULSE COLUMN OPERATING PROCEDURES

Before starting each run, aqueous and organic feed solutions were pumped from the storage tanks to fill feed tanks A and O respectively and provide an ample volume of feed for the run.

The desired pulse amplitude was set by means of the adjustable eccentric. The amplitude was measured by determing the high and low points of the phase interface during slow pulsation. Pulse amplitudes of from 1.20 to 2.43 inches were used. Pulse frequencies were set with the variable speed drive. The range of pulse frequencies used was 50 to 116 cycles per minute. Both adjustments, amplitude and frequency, were checked for consistency after each run.

At the start of a run the column usually contained some aqueous phase and organic phase from the previous run. If not, aqueous feed was pumped in to fill the plate section. Runs were initiated by starting the pulse unit. The organic feed pump was started and the flow rate set at 250 ml./min. The organic extract simply overflowed from the top of the column. The aqueous feed pump and the raffinate pump were started, and both flow rates were adjusted to 123 ml./min. These start-up adjustments were made rather rapidly, only about a minute being required. Slight adjustments were made in the aqueous feed and effluent flow rates in order to establish and maintain the aqueous-organic interface level. The median interface level was

kept about 2 inches above the top plate or even with the aqueous input

point. Aqueous feed and effluent flow rate controls were quite stable,

but the organic feed stream required frequent adjustment during the

duration of runs (normally $1\frac{1}{2}$ to 2 hours). At the end of the run,

pulsation and flows were stopped and all tanks sealed with paper and

tape to curtail evaporation between runs.

Low aqueous and organic flow rates were chosen to conserve the

feed liquids which were expensive and laborious to prepare. Low feed

rates were desirable since the runs were necessarily of long duration.

The ratio of the flow rates was established from a consideration of the

equilibrium curve (Figure 5) and the anticipated input thorium concen-

trations of the two phases. The ideal operating line would be one con-

necting the origin with the tie line at the input aqueous concentration.

(This is very nearly what was achieved.) The slope of such a line

(2.48/5.00 = 0.496) is also the ideal slope of the operating line. Since

the slope of the operating line equals aqueous flow rate divided by

organic flow rate or $\frac{Ra}{E}$ (49, p. 411), the desired ratio of flows was

established. To set the magnitude of the flow rates, the data of Sege

and Woodfield (37, p. 400) were consulted. These data indicate that

H.T.U. values for pulse column operation are essentially indepen-

dent of combined superficial volume velocity. It was, therefore,

possible to arbitrarily set the flow rates consistent with material

conservation and normal operating characteristics. The actual flow

rates used (123 ml./min. aqueous and 250 ml./min. organic; ratio = 0.492) were also chosen to coincide with even decimals (8.0 and 10.6 respectively) on the rotameters.

Aqueous samples were taken at regular intervals, usually every 15 minutes, during runs. In all but one run they were drawn from the internal tap in order to save run time that would have been involved in purging extracted material through the piping to the external sample tap. In run No. 9, alone, samples were drawn from the external tap because froth was present at the internal tap, as explained in the section on results of pulse column runs. In sampling from the internal tap, about 30 ml. was drawn and discarded to purge the sample tap tubing. This was followed by the drawing of about 20 ml. of sample. The samples were drawn slowly to avoid undue interference with the interface level. In the first four runs samples were analyzed by the EDTA method while the run was in progress. In runs 5 through 9 samples were set aside for the more time-consuming fluorometric analyses which were carried out after the run was completed.

Samples were drawn at different times over an operating period sufficiently long for the system to reach steady state. The raffinate thorium concentration decreased with time until an asymptotic steady state level was reached. With the EDTA analytical method, by analyzing during the run, it was possible to tell

when steady state was reached and end the run at that point, saving

time and feed liquids. With the fluorometric method it was necessary

to allow sufficient time to assure the attainment of steady state and

verify that equilibrium had been achieved by analyses performed

after the run was completed. The time necessary to achieve steady

state operation was much less if the run followed closely the previous

run.

RESULTS OF PULSE COLUMN RUNS

The results of the pulse column runs, presented in Table VI
and Figure 4, indicate that nearly perfect extraction was attained in
the pulse-amplitude product range of 110 to 180 in./min.

Method of Presentation

The results were plotted as equilibrium raffinate thorium con-
centration in ppm versus the frequency-amplitude product. The
accepted measure of pulse column extraction efficiency, the over-all
height of a transfer unit (H.T.U.)(52, p. 9), was avoided because of
the unusual nature of the equilibrium curve. With the unusual
"step function" equilibrium curve (Figure 5), accurate determina-
tion of H.T.U. by Treybal's method (49, p. 428-429) would have been
impossible (see page 48) primarily because of the possible "pinch
point" below the analytical limit. The accurate determination of
H.T.U. would have been further limited by the experimental error
in the location of the operating line (see page 46). The gross inac-
curacy due to the combination of these factors would render any
H.T.U. determinations of no consequence. Since the aqueous feed
concentrations were relatively uniform (about 5% variation) and the
reduction ratios for the aqueous thorium concentration were large
(20:1 to greater than 2,500:1), it was considered appropriate to take

the aqueous input concentration as essentially constant and to plot

the raffinate thorium concentration as the measure of extraction

efficiency.

Referring to Figure 4 the shaded portion of the curve below the

2 ppm thorium level indicates the lower limit of the fluorometric

analytical method. Samples analyzing < 2 ppm were plotted in this

shaded area.

Results

As can be seen from Figure 4, a sharp improvement in extrac-

tion performance was found with increasing f x a product in the four

runs made in the pulse frequency-amplitude range of 60 to 96 in./min.

In the four runs made in the 109 to 140 in./min. range it was neces-

sary to switch to the fluorometric analytical method since raffinate

samples contained less than 2 ppm thorium. To check the validity

of the assumption that frequency-amplitude is an operating parameter,

run No. 7 was made at a relatively lower frequency and higher ampli-

tude than runs 5, 6 and 8. Table VI verifies that with a comparable

f x a product, the result fell within the range established by the

other runs.

In all of the above runs (1 through 8), stable operation was

demonstrated, and there was no emulsion problem. The interface

between the phases at the aqueous feed point was sharp and distinct.

Figure 4   Raffinate Thorium Concentration
Vs. f x a
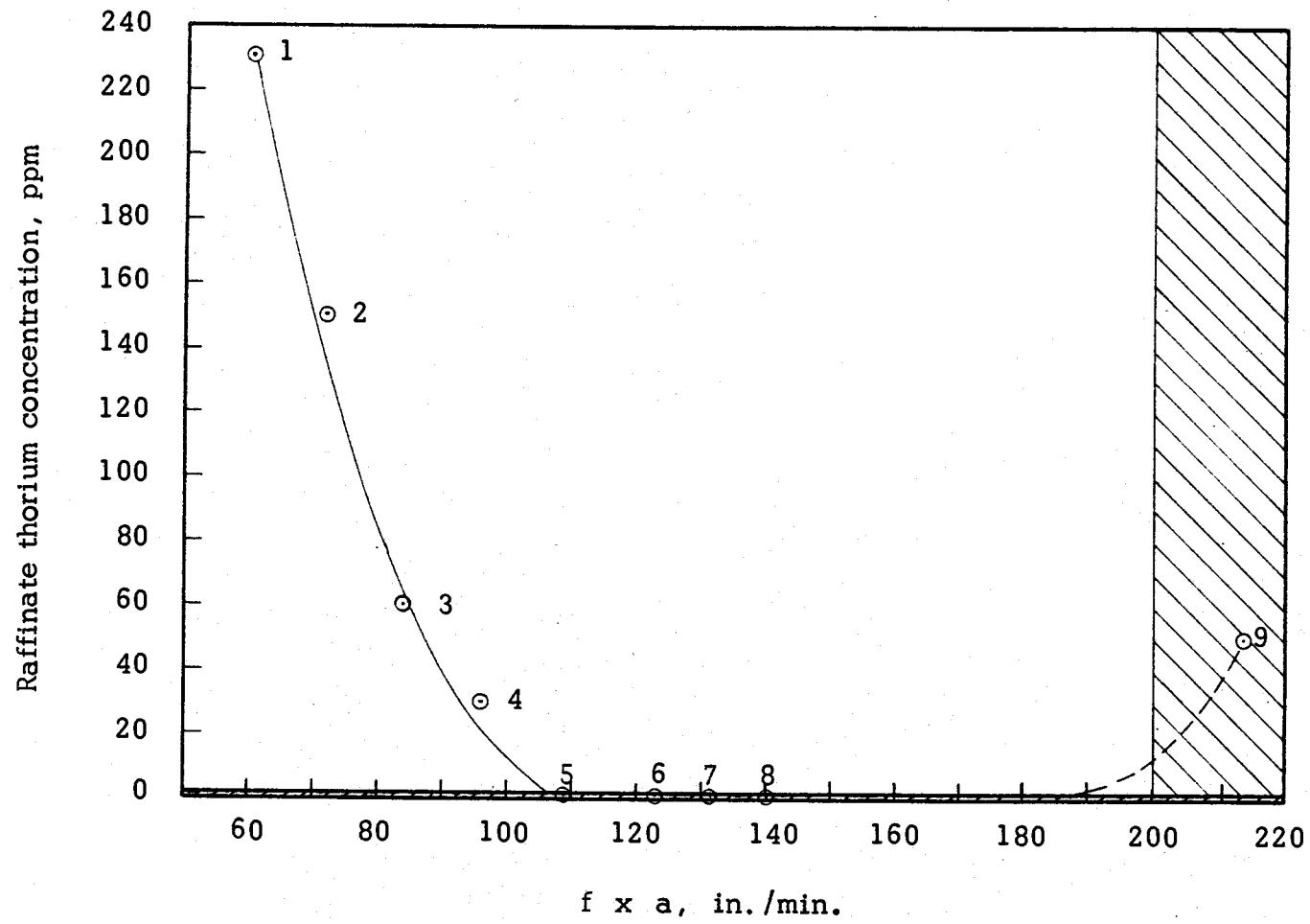
f x a, in./min.

Table VI. Experimental Data from Pulse Column Runs

Run No.	Th in Aqu. Feed, g/l	f cycles/min.	a in.	f x a in./min.	Th in Raff., ppm
1	4.94	50	1.20	60	230
2	5.19	60	1.20	72	150
3	5.19	70	1.20	84	60
4	5.19	80	1.20	96	30
5	5.09	78	1.40	109	< 2
6	5.09	70	1.75	123	< 2
7	5.09	54	2.43	131	< 2
8	5.09	80	1.75	140	< 2
9	5.09	116	1.85	214	50

Note: The EDTA analytical method was used in runs 1 through 4; the fluorometric method was used in runs 5 through 9.

All samples were drawn from the internal sample tap and after setting

had only an oily film of organic layer present on top of the aqueous

solution. Some tiny droplets of organic were present in the column

in the region of the sample tap, but the bulk of the organic feed was

buoyed up through the plates in a desirable manner.

Run No. 9 was made to establish the upper frequency-amplitude

operating limit. At an f x a product of 214, the performance was

marginal. The "interface" at the feed input point became very

indistinct, the entire plate section became frothy and there was a

yellow emulsion in the area of organic input and froth below this

point which extended to the edge of the neck of the lower column T.

Although the internal sample tap drew a froth which proved to be about

80% organic, it was possible to maintain the operation. The aqueous

in the raffinate rotameter and at the external sample tap remained

clear. After 135 minutes of operation, equilibrium was verified by

two external tap samples separated by a fifteen-minute interval and

both analyzing 50 ppm thorium.

Based upon these results, it was estimated that emulsion diffi-

culties would occur in any operation above 200 in./min. This area

is accordingly cross-hatched to indicate unsatisfactory operation.

Also based upon run No. 9, the dotted portion of the curve (Figure 4)

was drawn to show the probable approximate performance curve in

the upper f x a region.

Separation Factor

When expressed as a "separation factor", the results of the

pulse column runs in the f x a range of 110 to 180 in./min. are

quite remarkable for a short 8-plate column. If such a factor is

defined as the ratio of the input aqueous thorium concentration to the

raffinate thorium concentration (5.09/ < 0.002), the values obtained

are greater than 2,500.

Operating Line

The results of pulse column runs are also represented by the

operating line in Figure 5. This particular operating line represents

runs performed using materials from the second large makeup batch

and, accordingly, shows aqueous feed entering the top of the column

at 5.09 grams of thorium per liter. The lower end of the operating

line is shown to intersect the origin. Actually, the line intersects

the abscissa at the 0.002 g/l (2 ppm) thorium concentration of the

raffinate, but this minute variance from the origin cannot be dis-

tinguished on the scale used. The organic feed entered the column

at zero thorium concentration, as shown, but the extract concentra-

tion could only be determined by material balance around the column.

Using the aqueous and organic flow rates of 123 and 250 ml./min.

respectively, the extract thorium concentration was determined to

Figure 5   Equilibrium Curve and Operating Line

System: 0.1 N H^+, with 2-octanol, with Na_2SO_4

Slope = 0.476

Thorium in organic, g/l

Thorium in aqueous, g/l
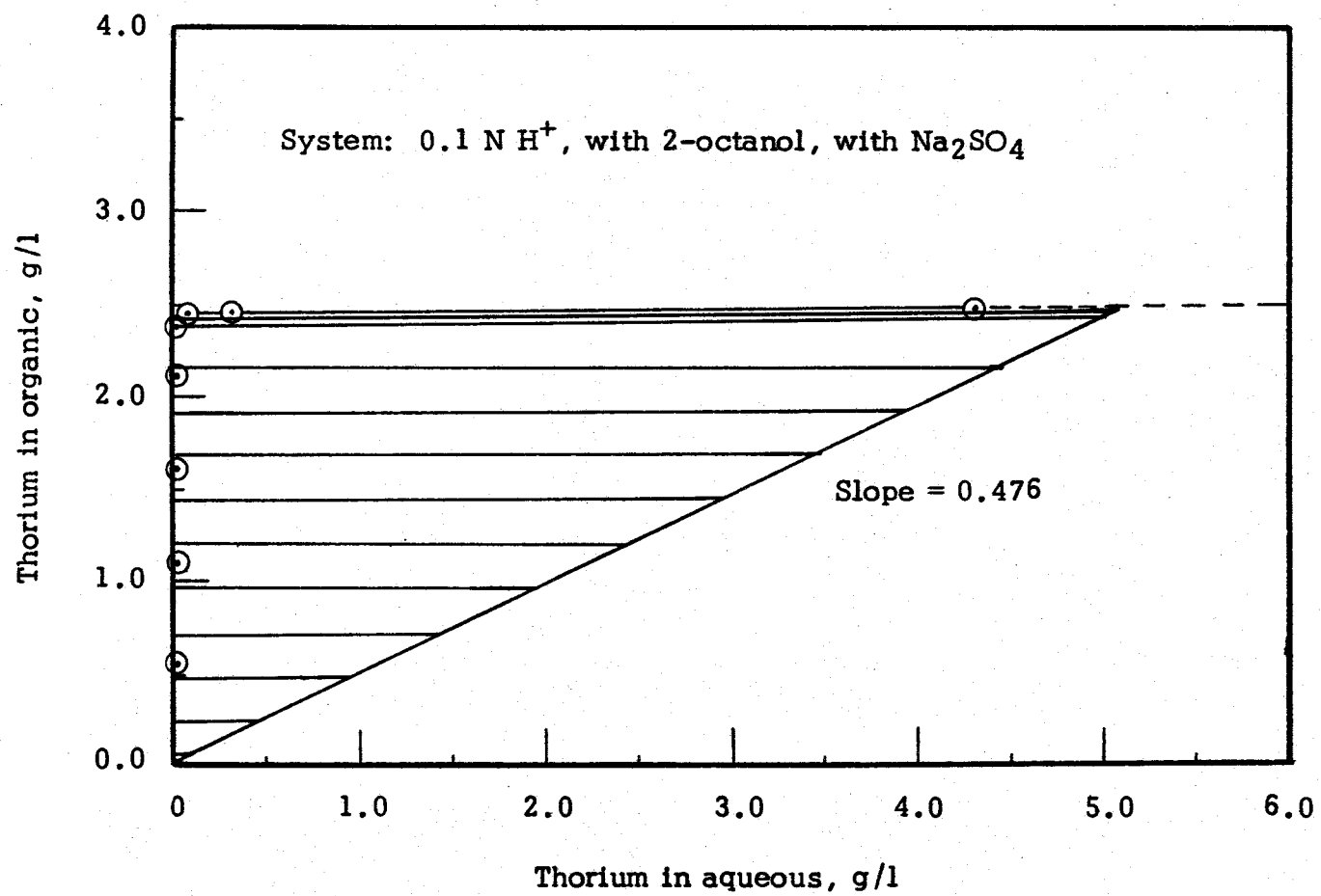
be 2.55 grams per liter. However this value is not possible because

the equilibrium plateau level is only 2.45 g/l. Since the EDTA and

fluorometric analyses were very reliable, the error is apparently in

the flow rates. The flows were difficult to control; the organic feed,

especially, required continual adjustment. If overall errors of

5 ml./min. and 10 ml./min. for the aqueous and organic flow rates

respectively are assumed, the calculated extract thorium concentra-

tion will vary from 2.36 to 2.66 g/l. On this basis and because of

the highly efficient nature of the extraction, a representative extract

concentration of 2.42 g/l, slightly below the saturation plateau, was

chosen to represent the upper end of the operating line.

Comparison with Oak Ridge Mixer-Settler Results

Although a direct comparison is not possible because the sys-

tems used are somewhat different, the results of the pulse column

operation compare favorably with mixer-settler experience at Oak

Ridge. Crouse and Brown (22, p. 1462) report a four-stage extrac-

tion of monazite liquor which produced a raffinate thorium concen-

tration of < 10 ppm from an input liquor concentration of 5 to 7 g/l.

The extractant was 0.1 M Primene JM in 97% kerosene--3% tri-

decanol and the organic and aqueous flow rates were 80 ml./min.

and 43 ml./min. respectively.

EVALUATION OF N_{tOR}, H_{tOR}, AND $K_R a$

The most accepted measure of pulse column performance (52, p. 9) is the overall height of a transfer unit; H.T.U. Treyball (49, p. 428-429) presents a derivation of the overall height of a transfer unit based upon the raffinate. His derivation led to the definition

$$H_{tOR} = \frac{Ra}{K_R a(1 - x)_M} \qquad (9)$$

where the subscript, M, indicates a logarithmic average. The value of H_{tOR} throughout a column is known experimentally to be approximately constant. Since x is very nearly zero at the lower end of the column, $(1 - x)_M$ can be taken as unity at x_2 and equation 9 at this point becomes

$$H_{tOR} = \frac{Ra}{K_R a} \qquad (10)$$

The derivation, for this point, then simplifies to

$$R\, dx = K_R a\, (x - x^*)\, dZ \qquad (11)$$

or

$$dZ = \left(\frac{Ra}{K_R a}\right) \frac{dx}{x - x^*} \qquad (12)$$

Since, at x_2,

$$\frac{Ra}{K_R a} = H_{tOR} = a\ constant \qquad (13)$$

equation 12 can be integrated to yield

$$Z = \frac{Ra}{K_R a} \int_{x_2}^{x_1} \frac{dx}{x - x^*} \tag{14}$$

Upon substitution, this becomes the expression for the overall number of transfer units

$$N_{tOR} = \frac{Z}{H_{tOR}} = \int_{x_2}^{x_1} \frac{dx}{x - x^*} \tag{15}$$

which can be integrated graphically (see Figures 6 and 7).

Since the height of the active section, Z, and the raffinate flow rate, Ra, are both known (1.50 ft. and 0.362 $\frac{liter}{hr. \, sq. \, ft.}$ respectively), it is possible to calculate N_{tOR} and H_{tOR} for the column and $K_R a$ at x_2 (the bottom of the column). However the accuracy of such determinations is limited, in the present case, by the nature of the equilibrium curve and by the experimental error in locating the upper end of the operating line. Accuracy is further limited by a "pinch" effect at the lower end of the operating line. In this region $\frac{1}{x - x^*}$ approaches infinity and its exact value is unknown since the concentrations of both x and x^* are below the analytical limit. Therefore the standard measures of efficiency were not used to compare the pulse column runs, but an illustrative set of calculations is presented to determine the order of magnitude of these values.

In the calculation of N_{tOR} for the operating line of Figure 5, arbitrary values of x were selected between x_1 and x_2 upon the operating line and the corresponding values of x^* were determined by drawing horizontal lines from the operating line to the equilibrium curve. Corresponding values of $\frac{1}{x - x^*}$ (Appendix D) were plotted for graphical integration (Figure 6). The integration yielded an approximate N_{tOR} value of 5.4; substitution into equation 13 resulted in an H_{tOR} of 0.28 ft. It was then possible to calculate a $K_R a$ value of $1.3 \frac{liters}{hr.cu.ft.}$ for the bottom point on the operating line. The high value of N_{tOR} is due to the magnitude of $\frac{1}{x - x^*}$ in the low concentration regions. This result is in qualitative agreement with the excellent performance achieved in the pulse column runs.

SUMMARY AND CONCLUSIONS

The amine extraction process, developed and evaluated in

mixer-settler arrays by the U. S. Atomic Energy Commission at

Oak Ridge for the recovery and purification of thorium, a potential

breeder reactor fuel, was evaluated for pulse column operation.

Primene JM-T, a commercially-available mixture of tertiary-alkyl

primary amines, was used as the active ingredient of the organic

extracting phase.

Experimentally determined equilibrium isotherms at room

temperature were evaluated for four aqueous-organic systems. In

each case the organic phase consisted of 0.1 M Primene JM-T dis-

solved in a kerosene diluent. The kerosene was diluted in one case

with 5% capryl alcohol because the addition of the long-chain alcohol

improved interphase contact in the pulse column. In all cases,

before thorium was added to the aqueous phase, the two phases were

equilibrated with respect to sulfate and H^+ ion concentrations. The

phases were then separated and thorium dissolved in the aqueous

solution by addition of $Th(NO_3)_4 \cdot 4H_2O$ salt. An equilibrium curve

was determined for an organic-contacted aqueous phase hydrogen ion

concentration of 1.0 N. The H^+ concentration was established by

adding sulfuric acid to the system. Another isotherm at 0.1 N H^+

ion concentration in the organic-contacted aqueous solution was also

determined; this curve showed a declining organic thorium loading with increasing total thorium. That this effect was due to a lack of sulfate ion was demonstrated by a further isotherm at the same acidity but with 1.0 M Na_2SO_4 added to the aqueous phase.

The typical isotherm for this system was found to be essentially a step function in which all points on the rapidly ascending portion vary from the ordinate by no more than the 2 ppm analytical limit, whereas the saturated portion of the curve is a nearly horizontal line. A low-range fluorometric analytical method for thorium, adapted for use with the aqueous samples, made it possible to determine thorium concentration down to a 2 ppm limit in the presence of high sulfate ion concentrations. The method made possible the accurate determination of isotherms in the low-range area as well as the accurate measurement of pulse column extraction performance.

Nine pulse column runs were performed with the organic as the dispersed phase at countercurrent aqueous and organic flow rates of 123 and 250 ml./min. respectively. The thorium-barren aqueous phase after contact with the barren organic phase was 0.1 N in H^+ ion and 1.0 M in Na_2SO_4. Thorium concentrations in the aqueous feed streams varied from 4.94 to 5.19 grams per liter. The organic phase consisted of 0.1 M Primene JM-T dissolved in a 95% kerosene-5% capryl alcohol diluent. All batches of organic feed prior to use were contacted with the thorium-free aqueous to equilibrate the

phases with respect to H^+ and $SO_4^=$. The 3-inch I.D. glass column contained 8 plates on a 2-inch spacing with each plate containing 114 one-eighth inch diameter holes or 22.6% free area. Pulse amplitudes were varied from 1.20 to 2.43 inches and frequencies ranged from 50 to 116 cycles per minute.

In the pulse frequency-amplitude product range of 110 to 180 inches per minute the operation was stable and the raffinate analyzed < 2 ppm thorium, this representing a separation factor (aqueous input to raffinate thorium concentration ratio) of > 2,500. At greater agitation rates performance declined due to increased emulsification of the phases. In the pulse-amplitude product range below 110 in./min. the operation was stable and the performance showed rapid improvement with increased agitation.

It is concluded that thorium purification and separation by liquid ion exchange pulse column treatment is certainly possible. Excellent extraction is obtained under stable operating conditions over a wide pulse frequency-amplitude range. However, in the thorium raffinate concentration range between 5,000 and 2 ppm, a pulse column would probably not be justified. Adequate separation could more simply be obtained using only a limited number of mixer-settler units in series.

NOMENCLATURE

A	=	aqueous phase
a	=	pulse amplitude, in.
β^-	=	a beta particle
DTPA	=	diethylenetriaminepentaacetic acid
E	=	organic phase superficial flow rate, $\dfrac{\text{liters}}{\text{hr.sq.ft.}}$
EDTA	=	ethylenediaminetetraacetic acid (versene)
g/l	=	grams per liter
g.	=	grams
f	=	pulse frequency, cycles/min.
f x a	=	pulse frequency-amplitude product, in./min.
H.E.T.S.	=	height equivalent to a theoretical stage
H.P.	=	horse power
H_{tOR}	=	overall height of a transfer unit, raffinate phase, ft.
H.T.U.	=	overall height of a transfer unit, ft.
I.D.	=	inside diameter, in.
K	=	mass transfer coefficient
$K_R a$	=	overall raffinate mass transfer coefficient, $\dfrac{\text{liters}}{\text{hr.cu.ft.}}$
M	=	molarity
mg.	=	milligrams
$m\mu$	=	wave length, millimicrons
N	=	normality

N_{tOr} = overall number of transfer units, raffinate phase, dimensionless

N. T. U. = overall number of transfer units, dimensionless

n = an integer

$_o n'$ = a neutron

O = organic phase

O. D. = outside diameter, in.

ppm = parts per million

R, R', R'' = alkyl chains

Ra = raffinate solution superficial flow rate, $\dfrac{liters}{hr. sq. ft.}$

TBP = tributylphosphate

TEA = triethanolamine

V = volume, milliliters

x = raffinate phase thorium concentration, grams of thorium per liter

Z = active pulse column height, ft.

Superscripts and Subscripts

Av = average

M = logarithmic average

* = equilibrium concentration

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APPENDICES

APPENDIX A

COMPOSITION OF REAGENTS FOR THE TITRIMETRIC METHOD

The acetate buffer was prepared by dissolving 136 grams of sodium acetate trihydrate in 200 ml. of water, adding 57 ml. of glacial acetic acid, and diluting to 1000 ml. with water.

The xylenol orange indicator consisted of 100 mg. of the orange dye dissolved in 10 ml. ethanol and diluted to 100 ml. with water.

APPENDIX B

FLUOROMETRIC METHOD FOR THORIUM--PROCEDURE

These instructions were adapted from the procedure of Sill and Willis (43, p. 955).

Note: A blank and known standards covering the concentration range of the samples are to be run with each set of samples.

Step

1. Place the sample in a 100-ml. beaker.

   1. Use 1.00 ml. for the 0 to 100 ppm range and 0.10 ml. for the 0 to 10 ppm range.

2. Add 2 drops of 72% $HClO_4$, 3 drops of concentrated HNO_3 and 1 ml. of concentrated H_2SO_4 - Na_2SO_4 solution.

3. Evaporate the solution carefully to dryness on an asbestos-covered hot plate.

   3. Heat until all H_2SO_4 condensed on the beaker walls has been volatilized and fuming has ceased. Avoid heating longer or hotter than necessary.

4. Cool the sodium acid sulfate residue; add 2 ml. of water and one drop of 25% $NaHSO_3$.

5. Cover the beaker with a wash glass; boil the solution down to about 0.5 ml.

   5. All of the residue must be dissolved to insure that trace quantities of anhydrous sulfates are dissolved.

6. Remove cover glass; rinse with a few drops of water.

   6. Be sure that all material dissolves.

7. Add 3 drops of 0.01% quinine sulfate and 10.00 ml of 1 to 1 mixture of $NaClO_4$-DTPA-TEA and Na_2SO_4 solutions.

8. Transfer the solution quantitatively to a 25-ml volumetric flask, being careful that the total volume does not exceed 17 ml.

9. Add 1 additional drop of 25% $NaHSO_3$.

10. While swirling flask near a long-wave ultraviolet lamp, add 1.0 M NaOH dropwise until the bright blue fluorescense disappears.

11. Add 5.00 ml of the piperidine buffer, swirl and rinse the sides of the flask with a few drops of water.

12. Add 1.00 ml. of morin, mix and dilute to volume carefully to minimize drainage from the neck of the flask. Mix thoroughly.

13. Allow to stand for 20 minutes at room temperature (away from hot plates or cold windows).

14. Measure fluorescence on Beckman DU.

8. Rinse the beaker 3 consecutive times, adding single drops of water systematically around the sides of the beaker.

10. A mounted graduated burette is suggested.

13. Temperature and time are critical. The time after morin addition to measurement should be kept within 1 or 2 minutes of the recommended 20 minutes.

14. a) Take the reading quickly and in a standard manner.

   b) Use the same tube for each sample; rinse once with new solution each time. Wipe outside of tube before each reading. Wash tube inside and out before each set. Use tube positioner.

c) Set instrument to read
0% transmittance on
blank, 100% on high
standard; check these
settings.

15. Determine unknowns from
curve based on knowns run
with each set.

APPENDIX C

SOURCES OF CHEMICALS USED IN FEED STREAMS

Chemical	Producer	Grade, Description
Na_2SO_4	Baker and Adamson	Purified, Code 2321, Anhydrous Powder
$Th(NO_3)_4 \cdot 4H_2O$	Lindsay Chemical Div. American Potash and Chemical Corp.	Reagent, Code 103, 99.9% Pure, Granules
2-Octanol (Capryl Alcohol)	J. T. Baker Co.	Purified, Code 9332
Primene JM-T	Rohm and Haas Co. Special Products Dept.	
Kerosene	Tidewater Oil Co.	"Burnright Kerosene"
Con. H_2SO_4	Baker and Adamson	Reagent, Code 1180

APPENDIX D

GRAPHICAL INTEGRATION TO DETERMINE N_{tOR}

Part 1

x	x*	x-x*	$\dfrac{1}{x-x^*}$
5.09	0.02	5.07	0.197
5.00	0.01	4.99	0.200
4.50	< 0.002	4.50	0.222
4.00	< 0.002	4.00	0.250
3.50	< 0.002	3.50	0.286
3.00	< 0.002	3.00	0.333
2.50	< 0.002	2.50	0.400
2.00	< 0.002	2.00	0.500
1.50	< 0.002	1.50	0.666
1.00	< 0.002	1.00	1.000
0.50	< 0.002	0.50	2.000
0.10	< 0.002	0.009	11.1

Part 2

Δx	$\left(\dfrac{1}{x-x^*}\right)_{Av}$	$\left(\dfrac{\Delta x}{x-x^*}\right)_{Av}$
0.09	0.20	0.018
0.50	0.21	0.105
0.50	0.23	0.115
0.50	0.27	0.135
0.50	0.31	0.155
0.50	0.35	0.175
0.50	0.43	0.215
0.50	0.55	0.275
0.50	0.78	0.39
0.50	1.32	0.66
0.30	3.8	1.14
0.20	10	2
	Total	5.383

Approximate value of N_{tOR}: 5.4

Figure 6   Graphical Integration to
Determine N_{tOR}