Title
MECHANICAL CHARACTERISTICS AND PERFORMANCE OF LIQUID-LIQUID EXTRACTION COLUMNS

Author
Lehman, Hugh Roberts.

Publication Date
1951-11-01

~~SECRET~~
~~SECURITY INFORMATION~~

UCRL- 1558

DECLASSIFIED

UNIVERSITY OF CALIFORNIA – BERKELEY

RADIATION LABORATORY

~~SECRET~~
~~SECURITY INFORMATION~~

UNIVERSITY OF CALIFORNIA
Radiation Laboratory

Cover Sheet
Do not remove

INDEX NO. UCRL 1558
This document contains 89 pages
This is copy 69 of 87 series A

DECLASSIFIED

Issued to Information Division

~~SECRET~~
Classification

Each person who receives this document must sign the cover sheet in the space below.

Route to	Noted by	Date	Route to	Noted by	Date
	RW Hughey	1/7/52			
	B. Cughman	1-31-52			
	S. J. H[illegible]	2/16/53			
T Vermeulen T.V.					
T Vermeulen 111 Bldg 70					

~~SECRET~~
~~SECURITY INFORMATION~~

UCRL-1558
Chemistry-Separation Processes
for Plutonium and Uranium

DECLASSIFIED

UNIVERSITY OF CALIFORNIA

Radiation Laboratory

Contract No. W-7405 eng-48

CLASSIFICATION CANCELLED
BY AUTHORITY OF THE DECLASSIFICATION
BRANCH USAEC
BY B Forkett 1-11-56
SIGNATURE OF THE PERSON MAKING THE CHANGE
DATE

MECHANICAL CHARACTERISTICS AND PERFORMANCE OF LIQUID-LIQUID EXTRACTION COLUMNS

Hugh Roberts Lehman
(Thesis)

November, 1951

~~RESTRICTED DATA~~

~~This document contains restricted data as defined in the Atomic Energy Act of 1946. Its transmittal or disclosure of its contents in any manner to an unauthorized person is prohibited.~~

Berkeley, California

~~SECRET~~
~~SECURITY INFORMATION~~

DECLASSIFIED

UCRL-1558
Chemistry-Separation Processes
for Plutonium and Uranium

Standard Distribution: Series A	Copy Numbers
Argonne National Laboratory	1 - 7
Armed Forces Special Weapons Project (Sandia)	8
Armed Forces Special Weapons Project (Washington)	9
Atomic Energy Commission, Washington	10 - 16
Brookhaven National Laboratory	17 - 19
Carbide and Carbon Chemicals Company (C-31 Plant)	20
Carbide and Carbon Chemicals Company (K-25 Plant)	21 - 22
Carbide and Carbon Chemicals Company (ORNL)	23 - 30
Carbide and Carbon Chemicals Company (Y-12 Area)	31 - 32
Chicago Patent Group	33
duPont Company	34 - 39
General Electric Company, Richland	40 - 43
Hanford Operations Office	44
Idaho Operations Office	45 - 48
Iowa State College	49
Knolls Atomic Power Laboratory	50 - 53
Los Alamos	54 - 56
Mound Laboratory	57 - 59
Naval Research Laboratory	60
New York Operations Office	61 - 64
Patent Branch, Washington	65
Savannah River Operations Office	66
University of California Radiation Laboratory	67 - 70
Vitro Corporation of America	71 - 72
Technical Information Service, Oak Ridge	73 - 87

Information Division
Radiation Laboratory
Univ. of California
Berkeley, California

TABLE OF CONTENTS

Page

I. ABSTRACT . . . 3
II. INTRODUCTION . . . 4
III. PURPOSES OF THE INVESTIGATION . . . 7
IV. MATERIALS USED . . . 8
  A. Solvents . . . 8
  B. Thenoyltrifluoroacetone (TTA) . . . 10
  C. Plutonium . . . 10
V. ANALYTICAL METHODS USED . . . 12
  A. Plutonium . . . 12
  B. Determination of Distribution Coefficient . 13
  C. Miscellaneous Analyses. . . . 16
VI. APPARATUS . . . 16
  A. Packed Column. . . . 16
  B. Pulsed Column. . . . 17
  C. Layout . . . 23
  D. Pumps and Metering . . . 24
  E. Overflow Control. . . . 25
  F. Piping . . . 26
  G. Sampling System . . . 27
VII. EXPERIMENTAL PROCEDURE. . . . 28
  A. Feed Preparation. . . . 28
  B. Starting Procedure . . . 30
  C. Operation . . . 30
  D. Shutdown Procedure . . . 31
  E. Treatment of Data . . . 31
VIII. DESIGN OF THE EXPERIMENTS. . . . 34
IX. EXPERIMENTS WITH THE PACKED COLUMN. . . . 37
  A. Effect of Flow Rate. . . . 39
  B. Calculation of Film HTU's. . . . 42
  C. Effect of Continuous Phase . . . 43
  D. Effect of Solvent . . . 48
  E. Flooding . . . 51
X. EXPERIMENTS WITH THE PULSED COLUMN. . . . 53
  A. Effect of Flow Rate. . . . 54
  B. Calculation of Film HTU's. . . . 58
  C. Effect of Pulse Frequency and Amplitude . . 60
  D. Effect of Continuous Phase . . . 61
XI. COMPARISON OF PACKED AND PULSED COLUMNS . . . 63
  A. Efficiency of Transfer. . . . 63
  B. Throughput. . . . 63
XII. HOLDUP FOR THE PULSED COLUMN. . . . 65
XIII. SUMMARY AND CONCLUSIONS . . . 67
XIV. APPENDIX . . . 70
  A. Tables of Experimental Data
  B. Figures of Column Construction
XV. NOMENCLATURE . . . 87
XVI. BIBLIOGRAPHY . . . 88

Mechanical Characteristics and Performance of Liquid-Liquid Extraction Columns

Hugh Roberts Lehman
Department of Chemistry and Chemical Engineering, and Radiation Laboratory
University of California, Berkeley, California

I. ABSTRACT

Representative mass transfer data for extraction of plutonium(IV)-TTA chelate has been obtained in one inch diameter pulsed and packed columns. The use of TTA for plutonium extraction appears feasible in this type of equipment. Pulse columns exhibit greater efficiency than packed columns under similar operating conditions with respect to both mass transfer and throughput.

True film HTU's have been obtained for the first time with a solute transferring between two immiscible liquid phases. The unique ability to change the distribution coefficient at will makes the TTA system extremely useful for mass transfer studies.

Mechanical Characteristics and Performance of Liquid-Liquid Extraction Columns

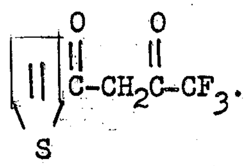
Hugh Roberts Lehman
Department of Chemistry and Chemical Engineering, and Radiation Laboratory
University of California, Berkeley, California

II. INTRODUCTION

Liquid-liquid extraction, although of increasing importance, is one of the least studied unit operations of chemical engineering. This is especially true in regard to the limited amount of performance data for certain types of extraction equipment and for systems in which chemical reaction kinetics rather than diffusional effects might be controlling.

In the present work, the performance of perforated plate pulsed columns was investigated and compared with the performance of the more conventional packed column. In these experiments, plutonium at trace concentrations was transferred between aqueous nitric acid and TTA-organic solvent solutions.

The use of beta diketones in order to form metallic chelates soluble in organic solvents was suggested by Calvin,[1] and, of a large number studied, TTA appears to be the most satisfactory.[2] TTA is an abbreviation for thenoyltrifluoroacetone,



The basic chemistry of the reactions of TTA with plutonium has been extensively investigated,[2,3] and several steps have been taken toward developing a large scale continuous process that will utilize this reaction.

Thomas and Crandall[2,4] suggested and demonstrated a batch liquid-liquid extraction pilot plant in which a practical separation of plutonium from "dissolver" solutions was achieved by the use of organic TTA solutions and by changes in the oxidation state of plutonium. Hicks and Rubin[5] suggested the desirability of altering the extraction coefficient rather than the oxidation state of plutonium and demonstrated this process in a continuous mixer-settler.[6] The present work represents the first application of column equipment to the problem of extracting plutonium as the TTA complex between aqueous and organic phases.

Although the various reactions of plutonium with TTA have been extensively reported previously, a few salient features will be reviewed here. The over-all heterogeneous reaction between plutonium(IV) and TTA may be represented by the equation

$$\mathrm{Pu}^{+4}_{(aq)} + 4\mathrm{HK}_{(org)} = \mathrm{PuK}_{4(org)} + 4\mathrm{H}^{+}{}_{(aq)} \qquad (1)$$

where HK represents TTA, PuK_4 represents the chelate of plutonium and the subscripts "aq" and "org" refer to the aqueous and organic phases containing the species indicated. The equilibrium constant for this reaction may be written as

$$K = \frac{(\mathrm{PuK}_4)_{(org)}\ (\mathrm{H}^+)^4{}_{(aq)}}{(\mathrm{Pu}^{+4})_{(aq)}\ (\mathrm{HK})^4{}_{(org)}} \qquad (2)$$

where K is of the order of $5 \times 10^{+5}$ depending upon the activities of the various species and depending slightly upon the organic solvent used.

The distribution ratio of plutonium between the organic and aqueous phases may be written as

$$E_a^o = \frac{(PuK_4)_{(org)}}{(Pu^{+4})_{(aq)}} = K\left(\frac{HK}{H^+}\right)^4 \qquad (3)$$

Because of the dependence of the distribution coefficient E_a^o on the fourth power of the ratio of the TTA to the hydrogen ion concentration, the utility of such a liquid-liquid extraction system is immediately apparent; E_a^o can be varied over wide limits by relatively small changes in the TTA or the hydrogen ion concentration.

As shown in the kinetic studies of Rubin and Hicks,[5] a noteworthy characteristic of reaction (1) is its apparent slowness in batch laboratory extractions under certain conditions, especially when E_a^o approaches unity. The slowness of this reaction led to some hesitation is using any type of continuous extraction equipment for the system. At the present time it is recognized that mixer-settlers can be used for this extraction,[6] and the present study has demonstrated also the feasibility of utilizing columns under certain conditions. Whether the rate steps in the over-all reaction as written are controlled by chemical kinetics, physical mass transfer across an interface, or combinations of these cannot yet be considered to be definitely established. It is possible that mass transfer across an interface may be limited by rates of solvation or desolvation, and from this broader viewpoint, it may be that chemical kinetics always determine the ultimate rate of transfer. This is an area of continuing investigation in this laboratory.

Insofar as mass transfer theory is concerned, the Pu^{+4} - PuK_4 system furnishes an opportunity to study variations in the distribution coefficient with a minimum effect upon other physical properties. It furnishes a system which can be operated conveniently at essentially infinite dilution with respect to the transferring species. Although the fact is frequently overlooked, only at infinite dilution is the usual simplifying assumption of constant distribution ratio in the field of mass transfer valid.

III. PURPOSES OF THE INVESTIGATION

The several purposes of this study of the mass transfer of plutonium were as follows:

1. To investigate the feasibility of employing continuous-flow packed or perforated-plate pulsed extraction columns for transferring plutonium(IV) between aqueous nitric acid and organic TTA solutions.
2. To obtain representative mass transfer data for the system for comparison of the two types of columns employed.
3. To investigate the efficiency of extraction as a function of flow rates at constant values of the distribution coefficient.
4. To investigate the efficiency of extraction as a function of the distribution coefficient and to explore the effect of operating variables for the pulsed column.
5. To investigate the problems which would probably be encountered in full-scale operation of such a system; viz. solvent and TTA life in typical recycle operations, procedures for preparing and stabilizing process solutions, and maintenance of plutonium in the +4 state in aqueous nitric acid.

IV. MATERIALS USED

A. Solvents

1. Carbon tetrachloride. Technical grade carbon tetrachloride was used for those packed column runs in which this solvent was employed. The solvent was selected because of its nonflammability, stability to radiation, stability to decomposition by strong nitric acid, insolubility in water, and availability. Its high density is a distinct advantage, in that high column throughputs are obtainable when a large density difference between the aqueous and organic phases exists. The major disadvantage of this solvent is the relatively low solubility (2×10^{-4} $\underline{M}$) of plutonium chelate in it, which increases the volume of extracting equipment required for a given plutonium capacity. This technical grade solvent did not appear to disturb the oxidation-reduction balance of the aqueous phase.

2. Ortho-dichlorobenzene. Ortho-dichlorobenzene was used as the organic solvent phase for all of the pulsed column and part of the packed column experiments. Prior work with the TTA system has been carried out with benzene, secondary butylbenzene, and carbon tetrachloride. Ortho-dichlorobenzene was selected here because of its satisfactory nonflammability combined with superior stability, low mutual solubility with nitric acid, and higher solubility of the plutonium chelate. In comparison with carbon tetrachloride, it suffers a disadvantage because of its lower density when used with aqueous uranium nitrate solutions of high density, as discussed by Davis, Hicks, and Vermeulen.[7] Because of the general similarity of ortho-dichlorobenzene to the above solvents,

no basic difference in the behavior of plutonium chelate in this solvent was anticipated, and none was found.

The ortho-dichlorobenzene used was the practical grade as supplied by Eastman Kodak Company which is labeled to be 96 percent pure. The infrared spectrum of the material indicated that it was of somewhat higher purity (97 - 98 percent) with the major impurities being other isomers. These were considered to be noninterferring for the purposes of this investigation.

It became apparent, however, after encountering difficulties in preparing PuK_4 stock solutions and observing unexpected variations in the distribution coefficients for plutonium, that the solvent as supplied possibly contained a reducing agent. It was found that the solvent was capable of reducing $KMnO_4$ solutions to the extent of having 3.4×10^{-3} meq/ml reducing power. However, this reaction is not quantitative in that ortho-dichlorobenzene itself is capable of slowly reducing $KMnO_4$.

The solvent did not appear capable of reducing potassium dichromate solutions of comparable strength. The method adopted for titrating dichromate could not detect variations in concentration of the order of the trace plutonium concentrations.

Distillation of the solvent and subsequent infrared spectrum analyses of the various fractions showed the possible presence of small quantities of organic compounds other than the isomers of ortho-dichlorobenzene. One of these absorption bands lay in the region of oxygenated organic compounds which would account for any reducing power of the solvent.

The distillation or repeated contact with $KMnO_4$ solutions or caustic washes did not appear to improve the behavior of the solvent. The initial use of fresh solvent in the extraction columns does not ordinarily reduce the plutonium, at least within the usual time of contact. Only after considerable reuse of the solvent, saturated with aqueous 1.0 M nitric acid, was reduction of plutonium(IV) in low concentrations to plutonium(III) found to occur to the extent of up to 50 percent during one half-hour contact. Investigation of this problem is being continued.

B. TTA

The TTA used in all of the runs was taken from one batch made at this laboratory approximately two years earlier.[8] This TTA had been recrystallized from hexane, and at the time of preparation was at least 98 percent pure and had a light straw color. It was used without further recrystallization, although it was somewhat darker in color than when originally prepared, due possibly to photochemical action. Some TTA from the same batch was recrystallized from pentane and this material was used in the various oxidation state determinations for plutonium and also for some of the later column runs.

C. Plutonium

1. Stabilization of trace plutonium(IV). Stable aqueous solutions of plutonium(IV) in nitric acid were prepared in batches of approximately 16 liters each. Since it was found that diluted 70 percent nitric acid would reduce +4 plutonium to the +3 state, a low concentration of

potassium dichromate (approximately 5 x 10^{-5} M) was kept in all diluted acid solutions. The dichromate concentration was followed with time, and was found to drop to zero in about a week, although the actual rate appeared to vary with the batch of nitric acid used. When the dichromate had disappeared it was raised again to approximately 10^{-4} M.

Details of feed solution preparation and addition of plutonium tracer may be found under EXPERIMENTAL PROCEDURE, Section VII.

2. PuK_4 stock solution. Concentrated plutonium chelate stock solutions were added to organic solutions to raise the plutonium chelate concentrations in the organic feed for those runs in which plutonium was extracted from the organic to the aqueous phase. Essentially saturated solutions of the chelate in benzene solutions were used for this purpose so that the hot charge to the feed tank could be conveniently handled in small volumes.

To prepare such stock solutions a 100 microliter aliquot of the aqueous plutonium(IV) stock solution (15 M in nitric acid) was diluted with 10^{-4} M potassium dichromate, usually in the ratio of one to ten by volume. This was done in a ground-glass-stoppered two milliliter volumetric flask. One molar TTA in benzene was then added, the flask was shaken for a few seconds, and the aqueous phase carefully examined to insure that the green color of plutonium(IV) was still visible. If so, the flask was placed in a secondary container, (removed from the glove box) and shaken mechanically for ten minutes. After centrifuging, the organic layer containing plutonium chelate was removed (as completely as possible) and placed in the chelate stock bottle. The remaining aqueous layer was again contacted with small amounts of the same one molar TTA solution to extract residual plutonium(IV). Ten microliters of the aqueous phase remaining was counted to determine the amount of plutonium lost in other oxidation states.

From the standpoint of solvent purity, it would have been preferable to have made up the plutonium chelate stock solution using ortho-dichlorobenzene as the solvent. This was not successfully accomplished due to the presence of reducing agents in the solvent.

V. ANALYTICAL METHODS USED

A. Plutonium

1. Organic solutions. Plutonium chelate concentrations were determined by mounting aliquots of the organic phase on glass microscope slide cover glasses, drying on a hot plate, and counting in 50 percent geometry argon or scintillation alpha counters. All samples were mounted at least in duplicate and counted for sufficient time to reduce the probable counting error below the estimated error of sampling. All results have been reported as counts per minute per 100 microliters.

2. Aqueous solutions. The total aqueous phase concentration was determined in the same manner as for the organic phase. To determine the amount of plutonium(IV) in a given aqueous sample, equal volumes of the aqueous phase and of a benzene solution 0.3 $\underline{M}$ in TTA (in order to give a very large distribution coefficient) were equilibrated in the same manner as described below for determination of the distribution coefficient. After centrifuging, both phases were counted for their plutonium content.

All plutonium in the organic phase was taken to be plutonium(IV), inasmuch as the other oxidation states are known not to extract to any significant extent under these conditions. The alpha count of the residual aqueous phase was attributed to plutonium in (III) and (VI) states.

In order to determine the oxidation states remaining, a small quantity of potassium dichromate was added to the initial aqueous phase to raise its aqueous dichromate concentration to approximately 10^{-3} M. Re-equilibration of the phases affects a redistribution of plutonium. The organic phase counts were then ascribed to the sum of the original (III) and (IV) oxidation states present, inasmuch as the oxidation of the (IV) to the (VI) state by dichromate is reported to be slow under these conditions.[9] The remaining alpha count of the aqueous phase, after correction for the amount of dilution due to addition of the dichromate solution, was considered to represent the amount of plutonium(VI) originally present. Reduction of plutonium(IV) chelate in ortho-dichlorobenzene does not appear to occur.

B. Determination of the Distribution Coefficient

In order to obtain the performance data for a liquid-liquid extraction column accurate to within 10 percent, the distribution coefficient must be known well within this limit. For most systems the distribution coefficient is not variable to any great extent. In the case of plutonium-TTA, the distribution coefficient may be set to any desired value, although the establishment, maintenance, and determination of the value to within ten percent is a relatively difficult task because of its fourth-power dependence on the TTA/H^+ ratio which magnifies any small uncertainties in concentration.

A method which is rapid and reasonably reliable consists of equilibrating, in a small glass stoppered volumetric flask, equal volumes of the two phases for which the distribution coefficient is desired and then mounting and counting aliquots of the two phases. Considerable attention must be paid to insuring that all equipment is scrupulously clean for these determinations, since it was found that improperly cleaned or dried glassware could lead to wild values of the distribution coefficients.

The specific reasons for these erroneous values are unknown, but probably include the following:

1. Acidic or basic impurities on the glassware leads to a false value of E for the nominal H^+ concentration. Residual traces of cleaning solution from cleaning the flasks or pipets may be a major cause of such errors.

2. Silicone grease for sealing ground glass stoppers is not sufficiently inert to be permitted to come into contact with the system. It is apparently slightly soluble in ortho-dichlorobenzene and for unknown reason its use leads to low and erratic E values.

3. In order to obtain the correct E, the aqueous phase in contact with the organic must contain 10^{-5} to 10^{-4} M dichromate. If the dichromate concentration falls to low values the E obtained will be considerably low, presumably due to partial reduction of the plutonium to the (III) state. Ordinarily, raising the dichromate concentration will result in the correct E value as evidenced by the following typical results

from duplicate distribution coefficient determinations upon the same phase.

Without dichromate

Aqueous phase count = 926 counts/minute/100 microliters

Organic phase count = 176 counts/minute/100 microliters

$E_a^o = 176/926 = 0.19$

After adding 50 microliters of 10^{-3} M potassium dichromate to 500 microliters of the aqueous phase

Aqueous phase count = 470 counts/minute/100 microliters

Organic phase count = 610 counts/minute/100 microliters

$E_a^o = 610/470 = 1.3$ (uncorrected for dilution of aqueous phase).

4. Stirred flasks, while offering some advantages for kinetic studies are not desirable unless thorough cleaning and drying procedures can be used.

5. In order to obtain maximum uniformity, plating of the samples of each of the equilibrated phases should be rapid and without interruption. In general the E values have a tendency to change slowly with time. This can be due to the slow oxidation or reduction of plutonium or possibly slight evaporation of either phase.

6. It is considered to be good practice to centrifuge the equilibrated phases between sampling to insure that sampling of suspended droplets does not occur.

Although a slight increase in accuracy would have been obtained by rinsing the "hot" pipets with a "cold" solution similar to the previous "hot" one, this was not considered justified, inasmuch as the plating time would have been roughly doubled. In addition, the extra steps required could also have led to other manipulative errors. The number of counts retained by the unrinsed pipets were of the order of three percent for both the aqueous and organic phases.

The possibility of errors from surface effects, length of time of shaking, and leakage of the volumetric flask into the secondary container were explored with negative results.

C. Miscellaneous Analyses

Additional analyses were carried out from time to time to check solution make-up accuracy. The hydrogen ion concentration of the aqueous phase was determined, whether radioactive or not, by titration of duplicate samples with 0.1 normal sodium hydroxide using a Beckman pH meter. The nitric acid concentration was determined from the break in the curve of pH versus volume of added base.

TTA concentration was determined by the ultraviolet absorption, using a Beckman spectrophotometer.[10] This was carried out by diluting the sample a hundredfold with benzene and employing the TTA-in-benzene extinction coefficient at 330 Angstroms.

VI. APPARATUS

A. Packed Column

The packed column used in these experiments consisted of a five-foot section of one inch Pyrex industrial pipe. Both top and bottom ends of the column were flared to two inch industrial pipe according to a suggestion by Blanding and Elgin.[11] This flared section was found to be required in order to obtain satisfactory high flow rates without flooding the column. Both ends were flared so that either phase could be run as the continuous phase. The column was packed with 1/4 inch Pyrex Raschig rings which extended through both flared sections. This packing was supported at the bottom with coarse stainless steel wire mesh and fixed at the top with the same type of mesh. The feed nozzles at the two ends of the column consisted of 1/4 inch x 0.035 inch stainless steel tubing, buried in the packing as recommended by Elgin. All parts of the packed column were of glass, stainless steel, or teflon. Column details are shown in photographs in the appendix.

B. Pulsed Columns

A perforated plate column in which either the plates are moved vertically in a reciprocating manner or in which the plates are fixed and the entire liquid column in pulsated has been described in a patent by van Dijck.[12] This type of column has been designated as a pulsed column.[13] In such pulsed columns the two phases are reputed to separate between pulses into separate layers which are alternately injected through the holes of the plates into one another without either phase being truly continuous for the column. While this type of action may occur in columns operated at very low pulse frequencies, more or less incomplete recoalescence appears to be the rule in columns pulsated at moderate frequencies (25 - 100 pulses/minute) and thus one phase or the other is discontinuous throughout the column. At higher frequencies the entire column becomes more opaque and apparently is filled with a coarse emulsion, the discontinuous phase of which is probably determined by the interface control which regulates the takeoff rates.

Since the energy required to mix the two phases is supplied by an external source, the droplets obtainable can be made quite small, and fresh surface is created with each pulse. It is therefore reasonable to assume that the rate of mass transfer for a pulsed column will be greater than that for a similar packed column, and in fact this is observed. In addition, the pulsating motion of the column of liquid in the column increases the permissible throughput over that obtainable with a packed column.

The pulsed columns employed in this investigation were of the type in which the plates are fixed and the liquid in the column is pulsated by means of an external pulse pump. Prior work[14] upon the system, uranyl nitrate - hexone - nitric acid - water has indicated that as a class of extraction columns, they are quite efficient. Work in this laboratory[15] with a half-inch pulsed column indicated that relatively high efficiencies and throughputs were possible with the system uranyl nitrate - pentaether - nitric acid - water.

The pulsed columns used for plutonium extraction were constructed of two foot lengths of one inch "precision bore" Pyrex industrial flanged glass pipe bolted together with metal flanges. At each flanged joint a stainless steel plate between teflon gaskets was inserted which would permit both feeding and sampling the column at that point. Perforated teflon plates were fixed at two inch intervals in the columns by means of an 1/8 inch central stainless steel rod over which were slipped spacers of 3/16 inch stainless tubing. The plates consisted of tightly fitted 1/16 inch teflon sheet with 60 evenly spaced holes, 0.050 inch in diameter.

Both top and bottom of the pulsed columns terminated in flared sections identical to those used for the packed column. The ends of the columns were capped with a flat stainless steel plate which had provisions for the central support rod, exiting stream takeoff, feed lines, sample lines and an electric probe used for control of the column interface level.

The pulsed column used for the re-extraction runs (i.e., transfer from organic to aqueous phase) was pulsed at the base of the column through the inactive aqueous feed line. During the entire run the pulse pump was thus continuously flushed with the aqueous feed and the pulse pump remained free from contamination. The top of this column was open to the atmosphere and the aqueous overhead flowed out of the top of the column by gravity. This type of column setup is shown in Figure 16 in the appendix.

The pulsed column used for the extraction runs (transfer from aqueous to organic phase) was unconventional in that it was a top-pulsed column. This construction was adopted in order to take advantage of the fact that the top feed was a "cold" organic extracting solution, the bottom feed being the "hot" aqueous feed.

In constructing and operating a top-pulsed column, the following considerations must be met: (1) air must be automatically expelled during start-up so that the pulse is not expended at the top of the column, (2) the pulse must travel down the column rather than out the column overhead line, and (3) it must "work against" an elastic section at the base of the column where it is finally expended. If the column interface is to be maintained at the top of the column, provisions must be made to avoid any disturbance of this interface by pulses returning from the overhead line; or conversely, if the interface is to be maintained at the bottom, similar provisions must be made at this end to avoid disturbance of the settling zone.

In order to solve these problems, a number of unusual features were required. To expel air from the column, a slotted overhead line consisting of a short length of capped 1/8 inch perforated stainless steel pipe was inserted into the top of the column. The slot in this pipe was made flush with the bottom face of the top plate. With this construction the pulse returning from the overhead line was directed parallel to the interface and expended itself against the column walls. The purpose of the slot was to bleed air from the top of the column. In order to afford additional interface protection, the pulse line entering the top of the column was led through the settling section into the column proper so that the entering pulse was directed toward the plates. To avoid loss of pulse through the column overhead line, a square coil of three turns approximately one foot across was placed in the line between the column and a liquid-retaining bottle; this consisted of a short length of one inch glass pipe installed in this line prior to the receiver tank. The function of this bottle was to provide a small volume of liquid to serve as an air trap in the event that a large amount of liquid is suddenly drained from the column. Surge chambers at the bottom of the column to absorb the pulse consisted of a pair of six inch vertical lengths of one inch Pyrex pipe, each connected to the column and sealed at the top to entrap air. Air pressure over the pulsating column liquid in these surge chambers could be varied remotely to adjust the pulse length in the column. The location and arrangement of these surge chambers as well as the entire column setup can be seen in Figure 17 in the appendix.

In addition to the advantage of pulsing a "cold" stream, the top-pulsed columns offers an advantage over the bottom-pulsed column in that the effective column pulse amplitude can be directly measured at any time during the course of a run. The top-pulsed column as described above operated as easily as the bottom-pulsed column and did not require a different starting procedure.

The pulse pumps used for the pulsed columns consisted of diaphragm hydraulic pumps similar in principle to the feed pumps (described later) but considerably larger and without inlet or outlet check valves. They were constructed in such a manner that the liquid pulsated was in contact with resistant materials only. In these pumps the hydraulic pulsating bellows were connected to the end of a lever, the fulcrum of which could be adjusted by means of a vernier screw in order to vary the pulse length in the column. The pulse frequency was varied by controlling the voltage to a direct current motor which actuated the lever by means of a cam.

A large Kel-F diaphragm driven by the variation in oil pressure then pulsated one of the feeds to the column. These pulse pumps were located in a nonradioactive feed line between the metering pump and the column. No activity was observed to return from the column to these pulse pumps.

The pulse frequency in both pulsed columns was measured by timing visually the pulses observed in the columns.

The pulse amplitude in the bottom-pulsed column was measured by observing the amplitude of the liquid in the highest portion of the one inch pipe section at a condition of zero flow to the column, the manual drain valve closed, the manual bottom valve open but the Hammel-Dahl micro control valve closed. The effective pulse amplitude in the column was considered to be the amplitude observed under these conditions and was about two-thirds of the amplitude observed when the manual bottom valve was closed, the difference being due to the presence of a small air chamber over the metering needle in the Hammel-Dahl pneumatic control valve. The pulse amplitude in the bottom-pulsed column was observed before and after each day's series of runs but could not be measured during the course of a run. The pulse amplitudes so measured did not appear to change over a period of several months.

The pulse amplitude of the top-pulsed column was visible at all times and was occasionally measured during the course of each run. The effective column pulse amplitude for this column was taken as the sum of the observed amplitudes in the two surge chambers at the base of the column while the column was in operation.

C. Layout

The columns described are located in a 4 foot wide x 20 foot long x 10 foot high "cave" at this laboratory. This "cave" consists of an enclosure with two inch lead walls six feet high with a number of four inch thick lead-glass windows which permit observation of the cave's interior. The cave was maintained at slight negative pressure with respect to the laboratory proper by blowers capable of handling 400 cubic feet of air per minute in order to prevent radioactive contamination from spreading into the laboratory. The columns and their related equipment were constructed in such a manner as to permit remote operation with the crew remaining outside the "cave." Due to ceiling limitations, all equipment was restricted to a height of approximately nine feet.

All of the tankage used for the columns consisted of thirty liter war-surplus aircraft stainless steel low pressure oxygen tanks coated with drum liner lacquer on the outside. Tanks containing radioactive solutions were located within the "cave," others containing "cold" solutions outside were assembled into a "tank farm." The tanks located within the cave were for two purposes: receivers and feed tanks. The receivers were identical to the feed tanks outside of the cave. The "hot" feed tanks were constructed by cutting a thirty liter tank in half and welding a flat stainless steel plate over the open end. These tanks were equipped with sealed-in electric mixers, connections for pressure or vacuum, sampling lines, sight gages, and a charging funnel. This funnel was of stainless steel with a stainless steel screw cap provided with a teflon sealing ring.

All feeds to the columns from the tanks were pumped and metered by small diaphragm pumps. For cold solutions these pumps consisted of a cam driven oil-filled bellows which actuated a flat diaphragm of Kel-F. This diaphragm pulsated the liquid in a stainless steel chamber which was provided with stainless steel intake and output check valves. The outlet valve opening pressure was so set that pulsations in the liquid caused by a pulse pump in series with the line could not operate the valve. Variation in flow rate was attained by rotation of a knurled vernier ring which controlled the length of pump stroke. Coarse adjustments could also be made by changing the type of cam used with the pump. Flow rates from 5 to 150 milliliters/minute were attained with accuracies of about 5 percent over periods of several hours. Considerable attention was required, however, to insure that the pumping rate did not drift too far from the required value. Photographs of these pumps are shown in the appendix.

Pumps used for radioactive solutions were constructed from the same parts except that provisions were made for the oil pulsing head to be located outside of the "cave" while the pumping head was located at the "hot" feed tank.

Inasmuch as it was found that small particles of dirt or metal would disturb the metering accuracy of these pumps, each pump was protected by the installation of a porous stainless steel filter in its intake line.

Due to the pulsating flow characteristics of the pumps used, a volume-consumed method of rate measurement was used. It consisted of a small calibrated sight glass installed in the pump feed line. Valves were installed in such a manner that the feed to the pump could be switched to this sight glass. The rate of flow was determined by measuring the time required to pump the known volume of solution.

E. Overflow Control

The interface level for all of the columns was controlled by varying the flow rate of the exiting bottom stream. This was done automatically by an impedance bridge system which actuated a pneumatic valve installed in the bottom overflow line. In detail, the system consisted of platinum wires sealed into glass probes which were installed in the column with the bare wire section at the desired interface level; the metal column parts being grounded. This interface probe was in turn connected to an impedance bridge and amplifying circuit. The voltage across the solution was of the order of a tenth of a volt at either 60 or 1,000 cycles per second so that electrolysis was avoided. Whether or not the bridge was in balance depended upon the phase the interface probe contacted. This information was amplified and allowed to control, in the case of the pulsed columns, a pair of alternately connected solenoid valves. One solenoid valve controlled the flow of air to, the other from, a Hammel-Dahl micropneumatic control valve. Small needle valves in both air lines permitted "floating" this bottom control valve except at the lower flow rates employed where the action tended to be cyclic. For the packed column, one solenoid valve was employed which controlled the air fed to an on-off type of pneumatic valve. This set up appeared to be satisfactory for these columns and excluding startup difficulties, was quite stable when in operation.

After leaving the automatic control valves, the bottom streams passed to small calibrated rate measuring bottles wherein the rate of column overflow could be measured remotely. This was done by opening electric solenoid valves which controlled air to stainless steel pneumatic liquid valves mounted under each calibrated rate measuring bottle and simultaneously starting an electric clock. When the measured volume of liquid had been obtained, the clock was automatically stopped by another impedance bridge and relay system.

The column overheads left the top of the column by overflowing weirs. The overhead streams flowed by gravity to rate measuring bottles similar to those described above and then to the overflow tanks.

F. Piping

Most lines whether "hot" or "cold" were of 1/4 inch x 0.035 inch stainless steel tubing, and a few were of 1/8 inch standard stainless steel pipe. Stainless steel tubing connections were made with pressure-type fittings manufactured by Weatherhead Company which consist of an internal pressure sleeve compressed by an outer cap. Connections to equipment were made with 1/4 inch tubing to 1/8 inch pipe connectors, which were found to be satisfactory with active lines. All leaks observed were traceable to improper assembly or to wear through continued reuse.

One-eighth inch stainless steel pipe was used for pulse pump to column lines, and those lines in which solutions flowed with only gravity head. These were the column overhead lines, lines from overflow rate bottles to receiver tanks, sight gages and the entire column drain system. Stainless steel pipe fittings were used but the bends in most lines were made in smooth, large radii curves in order to reduce the head loss. This was especially true in the case of lines between the pulse pumps and the columns.

In order to provide the maximum in flexibility while at the same time avoiding the possibility of cross contamination, all lines from the "cold" pumps outside the cave and the lines to the various column feed locations were brought to a terminal manifold. In order to use any equipment in a given flow pattern, the various pumps were connected to the desired feed location by means of jumpers. These jumpers consisted of short lengths of flexible polyethylene tubing terminating in the usual stainless steel compression fitting. Special provisions for the changing of hot lines were provided on the terminal manifold.

G. Sampling System

Samples from the feed tanks and columns and from the various overflow rate measuring bottles were withdrawn through 0.020 inch I.D. stainless steel tubing. This tubing led from below the surface of the liquid to be sampled, through a leak proof fitting and terminated with a sharp point at a high position in the cave. The sample bottles consisted of ten cubic centimeter pharmaceutical type serum bottles capped with retractable flap rubber stoppers. These were evacuated through a hypodermic needle connected by hose to the laboratory vacuum system. After evacuation, the needle was removed and the bottles were placed on the sharpened sampling lines by the use of long-handled tongs. The liquid being sampled rose through the sample line and into the evacuated serum bottle; when the serum bottle was removed from sample line, the liquid in the tubing returned to its normal level. This method of sampling has the advantage that the serum bottle cannot be filled to overflowing since the liquid will not continue to flow after the vacuum has been decreased by the filling of the bottle; also, the gum rubber cap wipes the sample line clean on removal of the bottle and thus prevents dripping. Sample bottles on the sample lines are shown in Figures 9 and 10.

VII. EXPERIMENTAL PROCEDURE

A. Feed Preparation

In this investigation, plutonium was transferred in the columns in both directions, that is, from the aqueous to the organic phase and then from the organic back into a fresh aqueous feed. This process required the make-up of two types of feeds.

Active aqueous feeds were made up by mixing C.P. nitric acid with distilled water to the desired acid strength and then destroying any reducing properties by making it approximately 5×10^{-6} $\underline{M}$ in potassium dichromate. This acid was then charged to the "hot" feed tank. A strong plutonium(IV) stock solution 15 $\underline{M}$ in nitric acid solution was then flushed into the aspirating funnel with the same acid in such a manner that the plutonium(IV) solution was discharged from the micro pipet under the flowing acid without contacting the atmosphere. Before the pipet was removed from the funnel, it was rinsed several times with the acid flush. After removal of the pipet, the funnel again was thoroughly flushed. During this operation and for a period thereafter, the feed solution was stirred. A sample of the aqueous feed was then removed from the tank after a small portion was permitted to flush the sampling line. The total feed count, the extractable count, the distribution coefficient and occasionally the hydrogen ion and oxidation state of this sample were determined.

Active organic feeds were prepared in two ways. The first and most frequent manner consisted merely of returning to the feed tank the organic bottoms from a series of previous runs. In the event that the total organic feed plutonium count was too low for satisfactory operation it was raised by adding a portion of saturated plutonium chelate stock solution into the feed tank using some previously retained "flushing" organic feed. The tank was sampled, and the plutonium chelate count and the distribution coefficient with the proposed aqueous feed were determined. On occasion the TTA concentration was checked. Fresh organic feeds were made up by carefully weighing out TTA and dissolving in a measured volume of the solvent used. This solution was then shaken and allowed to stand, generally over night, with a small volume of distilled water in order to achieve the equilibrium TTA hydrate concentration in the feed. This solution was charged to the feed tank, retaining a sufficient amount of "flushing" solution for several runs, and the plutonium chelate added in the manner described above.

The nonactive feed solutions were made up in a manner identical to that described for the active solutions except for the addition of plutonium.

These solutions were charged by vacuum to the appropriate tank in the "tank rack" after prior tank cleaning and flushing.

B. Starting Procedure

To begin operations, the pump feeding the phase intended to be the continuous one, was started and set at a high rate in order to fill the column. When the column was almost filled, the pump rate was lowered to the desired value. In the case of the pulsed columns, the pulse amplitude was checked at the condition of no flow. With the continuous flow rate established at approximately the correct value, the discontinuous phase liquid pump was started and the pumping rate set to the desired value. At this time the interface controller was turned on and the amplifier adjusted by visual observation of the column interface level. An oscilloscope pattern which indicated bridge balance aided in achieving proper control settings. After establishment of the interface level, the manual valve in series with the pneumatic control valve was opened. From this time onward the column was operated without further attention to the location of the interface.

C. Operation

At frequent intervals during all runs the feed rates were checked as described above. Flow rates were adjusted throughout the runs. The measured rates were plotted as functions of time in order to assist in maintining constant flow rates.

The column used was operated for about five throughputs of each phase as related to its estimated column holdup. This was considered to be a sufficient period of time for the column to achieve steady-state. The course of the run's approach to steady-state was followed by sampling the column at frequent intervals. In many cases this time allowed was not sufficient for the column to have reached steady-state as evidenced by plots of these analyses as function of time. In such cases the data were not utilized for calculation.

D. Shutdown Procedure

After the completion of each run, the flow rates were either immediately changed to some other value to begin another run, or the column was dumped through the manual drain valve after rechecking the pulse amplitude in the case of the pulsed columns.

E. Treatment of Data

Upon the completion of a run or a short series of runs, the various data collected were treated as described below.

The average steady-state flow rates were estimated from the plots of the measured flow rates versus time, more weight being given to the flow rates toward the time of final column sampling. From these averaged rates, the slopes of the operating lines were calculated from the relation

$$R = L/G \tag{4}$$

where R is the slope of the operating line (immiscible solvents being assumed) and L and G were the flow rates to the column in (cu. ft.)/(hr.)(sq.ft.) for the polar and nonpolar phases respectively.

A material balance was then written over the column by combining the averaged flow rates and the various averaged stream alpha counts. The percent material balance error was calculated, considering the error as positive for apparent mass gained. From the ratio of the alpha counts, the slope of the operating line was recalculated according to the expression

$$R' = \frac{\text{Difference in organic streams alpha counts}}{\text{Difference in aqueous streams alpha counts}}$$

over the column as operated. The material balance error and the difference between R and R' is partially indicative of the relative accuracy of any particular run.

The operating and equilibrium lines for the runs were plotted on an x-y diagram. The coordinates used were the number of plus four plutonium alpha counts per minute per hundred microliters of solution. These units are proportional to concentrations. The number of theoretical stages and the heights equivalent to a theoretical stage were then calculated.

For those runs in which the data were considered to be of sufficient accuracy, the over-all HTU of the organic phase was calculated. For dilute solutions this H_{OG}, where G refers to the organic phase, is related to the H_{OL} by the ratio of the flow rates times the distribution coefficient, E_a^o (or m) according to the expression

$$H_{OG} = m\ G/L\ H_{OL} \tag{5}$$

and consequently was not ordinarily calculated.

The HTU calculated was that proposed by Colburn[16] and is defined as

$$Z = (N_{OG})\ (H_{OG}) \tag{6}$$

where Z is the column height in feet, N_{OG} is the number of "G" phase transfer units which are defined as

$$N_{OG} = \int_{y_1}^{y_2} \frac{dy}{\Delta y} \tag{7}$$

in the present case. Equation (7) readily can be integrated for extraction from the aqueous to the organic phase, for example, by recalling that

$$y^* = m\ x \tag{8}$$

$$y = R(x - x_1) \tag{9}$$

$$\Delta y = y^* - y \tag{10}$$

where y^* and y are organic phase alpha counts on the equilibrium and operating lines respectively and x and x_1 are the aqueous phase alpha counts for any point and for the exiting stream respectively. Substitution into equation (7) and integration results in the expression

$$N_{OG} = \frac{1}{m/R - 1} \ln \frac{(m - R)x + Rx_1}{mx_1} \tag{11}$$

For the opposite case, i.e., re-extraction from the organic to a "cold" aqueous phase, a similar integration results in the expression

$$N_{OG} = \frac{1}{1 - m/R} \ln \frac{(R - m)x + y_1}{y_1} \tag{12}$$

Both equations (11) and (12) lead to values for N_{OG}. From this value, H_{OG}'s were calculated from equation (6).

In the cases where the operating and equilibrium lines are closely parallel, equations (11) and (12) become indeterminate. In such cases the number of transfer units were calculated by averaging the Δy's over the column, assuming this average value to be constant over the column and removing it from the integral sign of equation (7) and solving directly.

The data obtained from the operation of the column and the quantities derived from them are shown in Tables VIII to XII at the end of this report.

VIII. DESIGN OF THE EXPERIMENTS

The method of attack adhered to throughout these experiments was to utilize the HTU surface concept developed empirically by Rubin and Lehman.[15] A brief review of this method is thus in order.

The basic assumption of this correlational method is that the film HTU's are functions of the column flow rates <u>independently</u> and not functions of their ratio as postulated by Colburn and Welsh[17] and Laddha and Smith.[18] Upon this basis, a surface may be utilized to described the variation of the continuous phase film HTU. It was found by Rubin and Lehman that these surfaces appear to be described by the equations:

$$H_L = a + bL + d/G + e\,L/G \qquad (13)$$

when the L phase is continuous and

$$H_G = a' + b'G + d'/L + e'G/L \qquad (14)$$

when the G phase is continuous.

As the film HTU for the discontinuous phase has been shown to be essentially constant by Colburn and Welsh and by Laddha and Smith, the over-all HTU equations can be derived by substitution of either of the above relations (depending upon which phase is the continuous one) into

$$H_{OG} = H_G + m\, G/L\, H_L \tag{15}$$

or

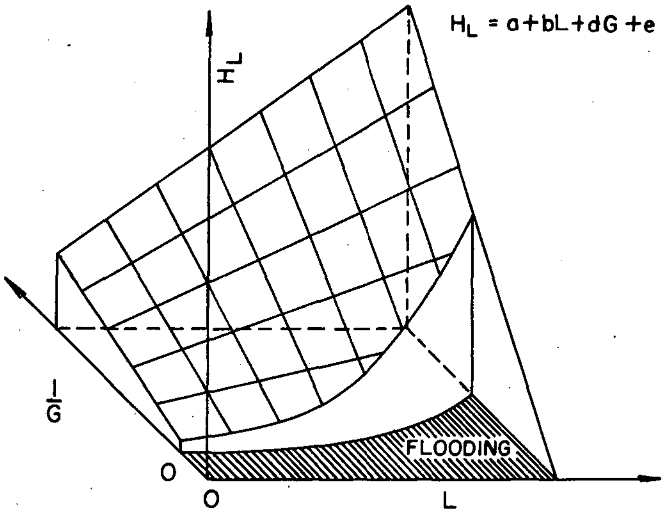
$$H_{OL} = H_L + L/mG\, H_G \tag{16}$$

The resulting equations show that the over-all HTU's also may be represented by a surface of the type shown in Figure 1.

By the use of the HTU surface concept, a qualitative picture with a minimum of data can be gained by the "mind's eye" of what otherwise might be disconnected and unintelligible data.

To illustrate the power of the method, consider the recent data of Hou and Franke[19] who studied liquid-liquid extraction in columns filled with fine packing. In these experiments, over-all HTU's were measured with the purpose of determining the practicality of using various 1/8 inch helices as tower packings and the effects of changing tower length, continuous phase, and flow rate. They used the system, acetic acid - isopropyl ether - water. A series of HTU determinations were made at constant L flow rate while the G flow rates were varied, and conversely. In another series the authors held the flow ratio constant and varied the total column throughput. These data are plotted in their paper and show the effect of these variables but not concisely enough for the over-all situation to be visualized.

CONTINUOUS FILM HTU FOR G AS DISPERSED PHASE



DISCONTINUOUS FILM HTU FOR G AS DISPERSED PHASE

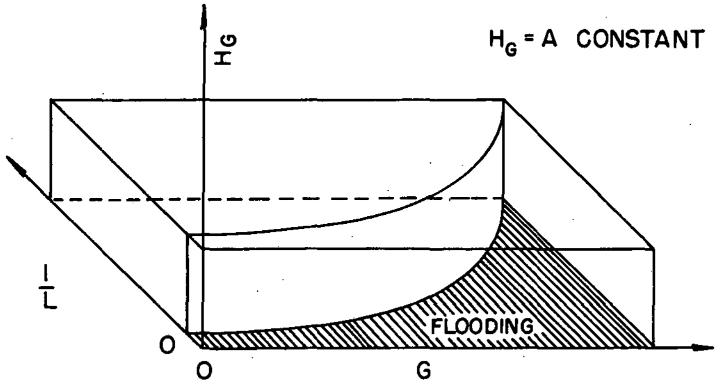


FIG. 1

MU 2761

By treating their data for the eighteen inch column according to the method outlined, the mass transfer picture can be readily grasped as shown in Figure 2. It will be noted that despite tower length and other packing variations, the general skeleton of the HTU surface is quite evident. It is also interesting to note in how many ways such data should check within itself. The typical H_{OL} versus L/mG plot used by many authors is unsuccessful in correlating all the data in their investigation.

The ultimate goal in the field of mass transfer is the development of a correlational method by which column performance can be predicted from first principles. To date this has been unattainable, although the path to this end clearly lies through determining the variables which comprise the film values (i.e., either film mass transfer coefficients or film HTU's).

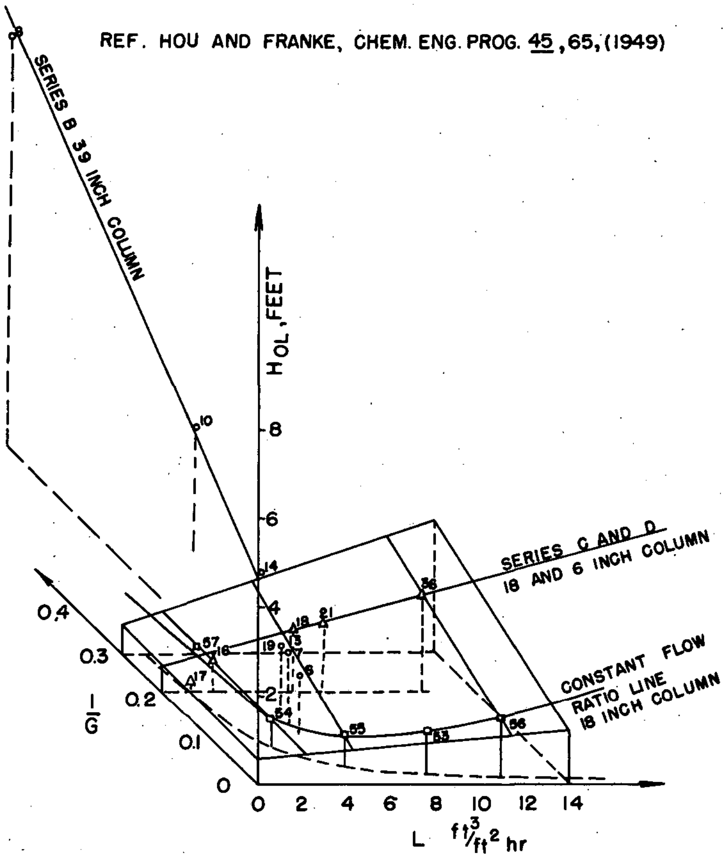
Unfortunately the literature of mass transfer contains many articles reporting film values which were obtained by fallacious methods. This has been commented upon by Treybal and Work[20] and by Colburn in the discussion section of the papers by Allerton, Strom and Treybal[21] and Row, Koffolt, and Withrow.[22] Rubin and Lehman[15] have demonstrated mathematically the nature of the fallacy and discussed the apparent impossibility of obtaining film from over-all values.

Up to the present, the only valid film values in the field of liquid-liquid extraction are those reported by Colburn and Welsh[17] and by Laddha and Smith.[18] The method used by these investigators was to operate columns with pairs of solvents with only slight mutual solubilities and to calculate HTU's on the basis of the degree of approach to saturation

OVERALL HTU SURFACE FOR 18 INCH PACKED COLUMN

PACKING: 1/8" GLASS HELICES

SYSTEM: ACETIC ACID - ISOPROPYL ETHER - WATER
ISOPROPYL ETHER DISPERSED



REF. HOU AND FRANKE, CHEM. ENG. PROG. 45, 65, (1949)

FIG. 2

MU 2762

of each solvent with the other. Unfortunately this method cannot be applied to systems with a solute transferring between two phases. Therefore, the only data until this investigation are for the systems; isobutanol - water, 3-pentanol - water, and isobutyraldehyde - water. It is interesting to note that the film HTU's obtained are of essentially the same value; presumable this can be attributed to the similarity of the systems used. Another interesting feature of their results is the remarkable constancy of the film HTU for the discontinuous phase regardless of variations in either flow rate.

Because equations (15) and (16) are not independent, it is ordinarily impossible to utilize them to obtain film from over-all values. However, if m can be varied with a mimimum effect upon other physical factors, then pairs of simultaneous equations result which can be solved for the film HTU's (or mass transfer coefficients if the interfacial area is known). The plutonium-plutonium chelate system employed in this investigation thus presents a unique opportunity to obtain experimental film HTU's. With the exception of some film HTU's obtained upon the basis of doubtful approximations, the film HTU's reported herein represent the first obtained for the transfer of a solute between two phases in liquid-liquid extraction.

IX. EXPERIMENTS WITH THE PACKED COLUMNS

A. Effect of Flow Rate

Experiments were carried out in the packed column in which a TTA-carbon tetrachloride solution was maintained as the continuous phase and the distribution coefficient for plutonium was 0.0610. Transfer was from the organic to the aqueous phase throughout this series. Holding the G flow rate constant, L was varied over a factor of five. These data are shown in Table I.

Table I

Packed Column with Carbon Tetrachloride Continuous

Run No.	E^o_a	L	G	H_{OG}
140-P2-Pu-17	0.061	11.7	8.0	1.88
142-P2-Pu-18	0.061	16.8	8.2	1.61
142-P2-Pu-19	0.061	8.5	8.3	3.06
144-P2-Pu-20	0.061	3.4	8.2	6.93
146-P2-Pu-21	0.061	21.6	8.2	1.18
150-P2-Pu-24	0.061	17.0	20.6	flooded

The resultant plot of H_{OG} versus 1/L is shown in Figure 3. It can be seen that a straight line plot was obtained which has an intercept very close to zero. It is therefore apparent that for the 1/L coordinate the HTU surface correlation method described above is valid for this series of experiments. An equation describing these results is

$$H_{OG} = 0.15 + 23.3\ (1/L) \tag{17}$$

It will be noted that the above equation should correlate the data for the column used with carbon tetrachloride as the continuous phase at an m of 0.061 and a G of 8.2.

HTU_{OG} vs. $1/L$ AT CONSTANT G

PACKED COLUMN, CARBON TETRACHLORIDE CONTINUOUS

SYSTEM: Pu - HNO_3-TTA - CARBON TETRACHLORIDE

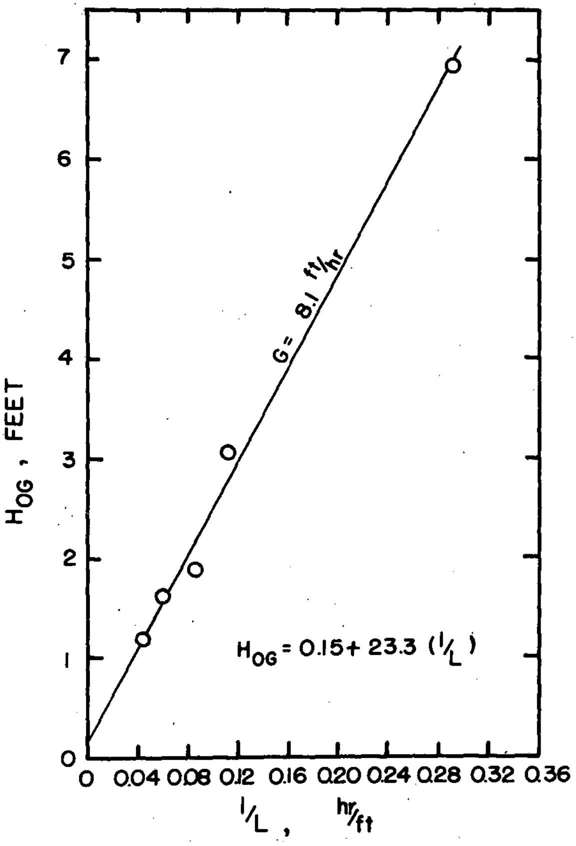


FIG. 3

MU 2763

Other experiments were carried out under the same conditions except that the L rate was held constant and G varied in order to determine the shape of the surface in this direction. Unfortunately due to poor material balances, mechanical difficulties and flooding, only two points in addition to one obtainable from Figure 3 were obtained. These two points are considered to be somewhat doubtful as to accuracy, although they are indicative of the direction of the surface in the G direction.

B. Calculation of Film HTU's

In order to predict over-all H TU's at other values of the distribution coefficients, the film HTU's must be known. These can be obtained by using the results of Run No. 137-P2-Pu-15 which was operated under the same conditions as those described above with the exception that the distribution coefficient was equal to 0.100. If the G flow rate of 7.73 for this run can be assumed to be sufficiently close to those making up Figure 3, then a value of the H_{OG} can be read from the graph and two simultaneous equations can be written by substitution into equation (15) which are

$$3.33 = H_G + (0.100)(7.73/8.30)H_L$$

$$2.87 = H_G + (0.061)(8.20/8.30)H_L$$

from the run and the graph respectively. Solution of this pair of equations leads to the film HTU's which are

$$H_G = 2.37 \text{ ft and } H_L = 10.3 \text{ ft.}$$

The discontinuous value, i.e. H_L, is expected to remain constant regardless of low rate while H_G should vary. It is interesting to note the large value of the aqueous film HTU. The H_G is of the same order of magnitude as the results of Colburn and Welsh, and Laddha and Smith.

C. Effect of Continuous Phase

In order to investigate the effect of which phase was continuous, a pair of runs was made with essentially the same flow rates but with alternate continuous phase. This pair of runs yielded the following results.

Run No.	Phase Cont.	E_a^o	L	G	H_{OG}
135-P2-Pu-14	Aq	0.10	8.21	8.09	2.38
137-P2-Pu-16	Org	0.10	8.30	7.73	3.33

From this preliminary data, it must be concluded that there is some advantage to operating the packed column with the aqueous as the continuous phase, although column performance is better judged by comparison of the film HTU values.

The film HTU's can be calculated by combining the above Run. No. 135-P2-Pu-14 with averaged results of a number of runs at the same flow rates in which m was 3.0 if the assumption is made that the direction of transfer does not alter the HTU's. This is reasonable from the standpoint of the two film theory of mass transfer and should be true especially at trace concentrations. The pair of simultaneous equations which result are

$$2.38 = H_G + 0.10(8.09/8.21)H_L$$

$$26 = H_G + 3.0(8.09/8.20)H_L$$

for Run No. 135-P2-Pu-14 and the averaged results respectively.

Solution of this pair of equations leads to

$$H_G = 1.5 \text{ ft and } H_L = 8.2 \text{ ft}$$

which applies to the case of continuous aqueous phase.

It is interesting to note that the film HTU for the organic phase is again considerably smaller than that of the aqueous phase, despite the fact that the role of the two phases in their passage through the column is reversed. In view of the values of the film HTU's it is not surprising that the efficiency of transfer is higher for the case when the column was operated with the organic phase dispersed since both film HTU's are lower in this case under otherwise similar operating conditions.

A number of runs were made in the packed columns using 0.05 M TTA-carbon tetrachloride as the discontinuous phase and 1 M aqueous nitric acid as the continuous phase. In these experiments the plutonium was transferred from the aqueous to the organic phase at a relatively constant value of the distribution coefficient. The flow ratio was also held approximately constant while the total column throughput was varied. These runs yielded the results shown in Table II.

Table II

Run No.	E_a^o	L	G	HETS	H_{OG}
119-Pl-Pu-8	3.22	3.66	3.60	6.5	18.3
103-Pl-Pu-3	3.0	4.12	4.05	6.6	14.2
107-Pl-Pu-7	3.22	8.00	8.17	8.8	26.0
103-Pl-Pu-1	3.0	8.29	8.70	10.3	29.6
111-Pl-Pu-4	3.0	8.50	8.50	8.5	19.6
121-Pl-Pu-9	3.22	18.6	18.3	8.5	24.6
105-Pl-Pu-2	3.0	19.0	19.2	9.75	22.1

Examination of the duplicate runs within the above series shows the typical accuracy that was obtained for the transfer of plutonium from the aqueous to the organic phase. This accuracy is considerably lower than that obtainable for transfer in the opposite direction because of the difficulty of checking the oxidation state of the plutonium in the aqueous phase. Upon the accuracy of these determinations depends not only the slope of the equilibrium line but also the location of the column operating line. If comparatively complete extraction of the available plutonium(IV) is permitted to occur (by alteration of the column flow ratios), the resulting HTU accuracy is quite low.

The results of the above data are plotted in Figure 4 and while not conclusive, they indicate that the efficiency of transfer in this case is not markedly affected by the total column throughput except at very low column throughputs and that a maximum exists at G equal to about 20. Considering these data from the viewpoint of the HTU surface correlational method, the surface for transfer from the aqueous to the organic phase with nitric acid continuous is probably of the type as shown in Figure 5 provided the curve of Figure 4 is real.

Calculation of the film HTU's for this series of runs was made previously by combination of equation (15) with the results of Run No. 135-P2-Pu-14. The resulting film HTU's are

$$H_G = 1.5 \text{ ft and } H_L = 8.2 \text{ ft}$$

as stated before. From these values and the curve of Figure 4 can be obtained an equation describing the data for this column with nitric acid as the continuous phase. This has not been done due to the scatter of the

HTU_{OG} AS A FUNCTION OF TOTAL THROUGHPUT FOR THE PACKED COLUMN

SYSTEM: Pu - HNO_3 - TTA - CARBON TETRACHLORIDE

AQUEOUS PHASE CONTINUOUS

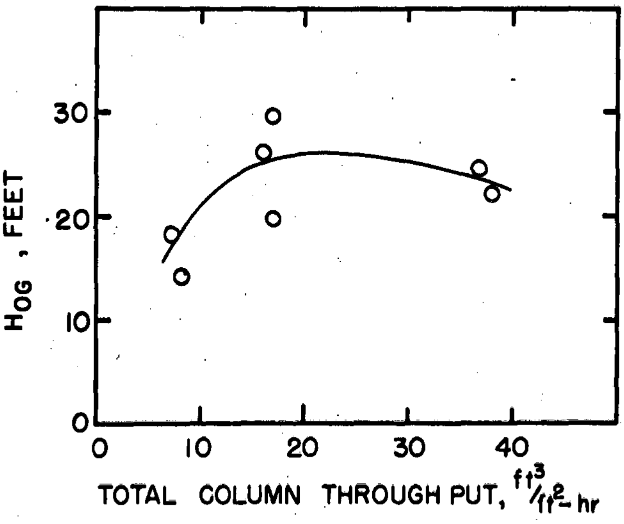


FIG. 4

MU 2764

POSSIBLE HTU SURFACE FOR PACKED COLUMN
WITH AQUEOUS CONTINUOUS

SYSTEM: Pu - HNO_3 - TTA - CARBON TETRACHLORIDE

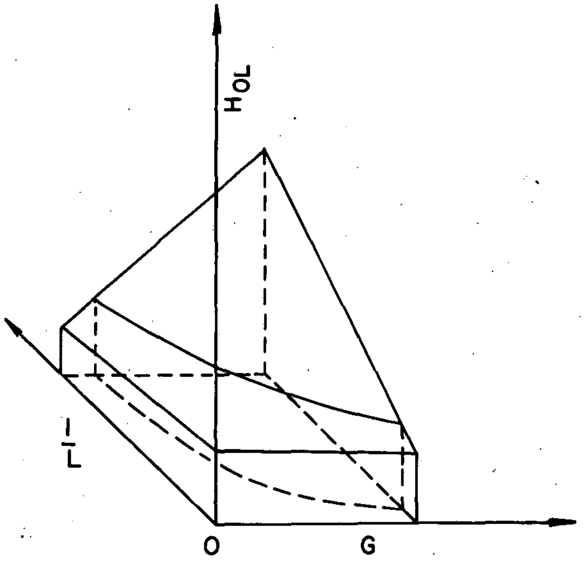


FIG. 5

MU 2765

data in Figure 4.

D. Effect of Solvent

Extraction runs in the packed column were made with ortho-dichlorobenzene as the solvent with the direction of transfer from organic to aqueous. In these runs the aqueous phase was continuous. The runs were carried out at an E of 1.12 and at varying flow rates; the data are summarized in Table III.

Table III

Summary of Runs with Ortho-Dichlorobenzene

Transfer from Organic to Aqueous Phase

Run No.	E_a^o	L	G	R	R'	Mat. Bal. % Error	HETS	H_{OL}
304-P2-Pu-25	1.12	3.4	8.2	0.42	0.42	-3.0	11.9	10.1
306-P2-Pu-26	1.12	11.5	8.2	--	--	flooded	--	--
306-P2-Pu-21	1.12	8.2	8.2	1.04	1.12	-2.0	14.2	13.2
308-P2-Pu-28	1.12	5.5	8.2	0.67	0.71	-1.0	18.8	12.0
311-P2-Pu-31	1.12	5.4	11.5	--	--	flooded	--	--
311-P2-Pu-32	1.12	11.6	3.4	3.34	3.29	0	8.3	19.4
313-P2-Pu-33	1.12	8.6	3.4	2.49	2.49	0	8.9	16.5

The above H_{OL} values are plotted versus L in Figure 6 and are represented by

$$H_{OL} = 3.18 + 0.47L + 59.6/G + 1.63L/G \quad (18)$$

The HTU surface for the system has been sketched in Figure 7.

H_{OL} vs. L AT CONSTANT G
IN THE PACKED COLUMN
ORTHO-DICHLOROBENZENE DISPERSED
SYSTEM: Pu-HNO_3-TTA-ORTHODICHLOROBENZENE

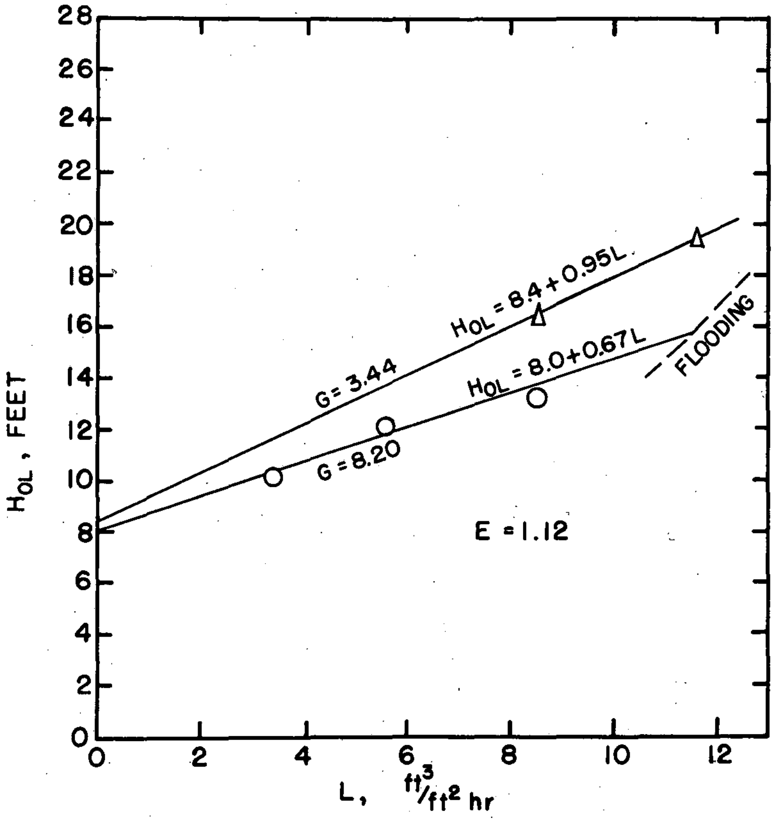


FIG. 6

MU2766

HTU SURFACE FOR TRANSFER OF PLUTONIUM
IN A ONE INCH COLUMN PACKED WITH 1/4 INCH RINGS
SYSTEM: Pu - HNO_3 - TTA - ORTHODICHLOROBENZENE
ORTHODICHLOROBENZENE DISPERSED

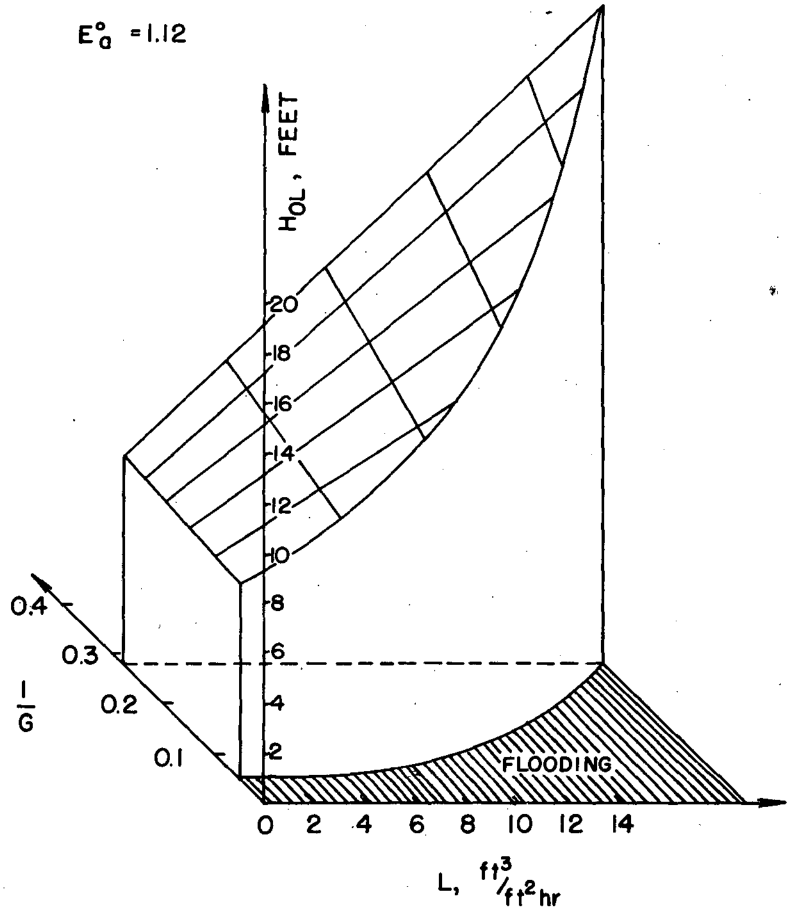


FIG. 7

MU 2767

Unfortunately, film values cannot be determined from these data since runs were not made with varying E.

It is of interest to compare the efficiency of transfer of plutonium in the packed column as a function of the solvent employed. From Figure 6 at flow rates of L and G each equal to 8.1 $ft^3/hr\ ft^2$ it may be calculated that H_{OL} is 13.5 feet. A direct comparison with data for carbon tetrachloride cannot be made since no runs were performed with that solvent at an E of 1.12. However, utilizing the film values previously determined for continuous carbon tetrachloride at flow rate of 8.1, H_{OG} may be calculated:

$$H_{OG} = 1.5 + 1.12(8.1/8.1)8.2$$
$$= 10.7 \text{ ft}$$

Multiplying by L/mG gives

$$H_{OL} = 9.6 \text{ ft}$$

Similar results can be calculated for other flow rates in the same manner.

It is evident that insofar as the solvents are concerned, the use of carbon tetrachloride offers an advantage from the standpoint of efficiency of transfer.

E. Flooding

Comparison of the data for flooding shows that the same column is capable of handling considerably more carbon tetrachloride than orthodichlorobenzene. For example, Table IV lists flooding data as obtained in the packed column.

Table IV

Comparison of Flows at Flooding
With Different Organic Solvents

Run No.	Phase Cont.	Solvent Used	L	G	$\sqrt{U_T}$
304-P2-Pu-26	Aq	o-dichlorobenzene	11.5	8.2	6.3
un-numbered	Aq	o-dichlorobenzene	11.2	8.2	6.2
311-P2-Pu-31	Aq	o-dichlorobenzene	5.4	11.5	5.7
135-P2-Pu-15	Aq	carbon tetrachloride	21.0	21.0	9.2
150-P2-Pu-24	Org	carbon tetrachloride	17.0	206.0	8.7

$\sqrt{U_T}$ is a constant defined by

$$\sqrt{U_T} = \sqrt{L} + \sqrt{G}, \tag{19}$$

as used by previous investigators[23] for the calculation of flooding in liquid-liquid extraction towers. It will be noted that the data of Table IV approximately meets this condition.

It is evident that the packed column employed can handle almost twice as much carbon tetrachloride as ortho-dichlorobenzene when the aqueous phase is continuous. It is considered very probable that the greater density difference between carbon tetrachloride and the aqueous phase over that of ortho-dichlorobenzene is not only the cause of the higher throughput but also of the lower HTU's obtained when using carbon tetrachloride. The basis for this "informed guess" is the thought that the higher velocity of the carbon tetrachloride relative to the aqueous phase increases the mass transfer coefficient more than the higher density difference reduces the column hold-up, viz, interfacial area in the relation

$$HTU_{OG} = G/K_{OG})(\Delta C_{av}) \qquad (20)$$

X. EXPERIMENTS WITH THE PULSED COLUMN

Due to the greater practical interest in orthodichlorobenzene as a solvent for the plutonium-plutonium chelate extraction system, this solvent was exclusively employed for the pulsed column runs. Operations with this solvent were considerably more difficult than when carbon tetrachloride was used because of the difficulties experienced with the apparent reducing properties of the ortho-dichlorobenzene. Thus, in the case of the pulsed column runs, the major error in the experiments to be reported is the uncertainty in the distribution coefficient, E.

For the majority of the experiments carried out in the pulsed columns, the pulse frequency, pulse amplitude and the distribution coefficient were maintained constant. Also the aqueous phase was maintained continuous in most of the runs inasmuch as prior work indicated this might represent an optimum operating condition. This has been confirmed for the pulsed column in experiments to be described later. In the present series of runs, the column flow rates were varied to investigate the effect of this variable upon the transfer height.

A complete summary of all pulsed column runs may be found in Tables VIII and IX in the appendix.

A. Effect of Flow Rate

Runs were carried out with the aqueous phase continuous and the distribution coefficient set to approximately 1.05 at constant amplitude and frequency. The data of two series of runs in which G was varied while L was maintained constant are shown in Figure 8. An unusual feature of these data is the constancy of the H_{OL} for runs at L equal to approximately 8.5 ft^3/ft^2/hour. From the viewpoint of the HTU surface concept, this means that the "contour" at L = 8.5 is very close to a region in which there is a horizontal line on the surface.

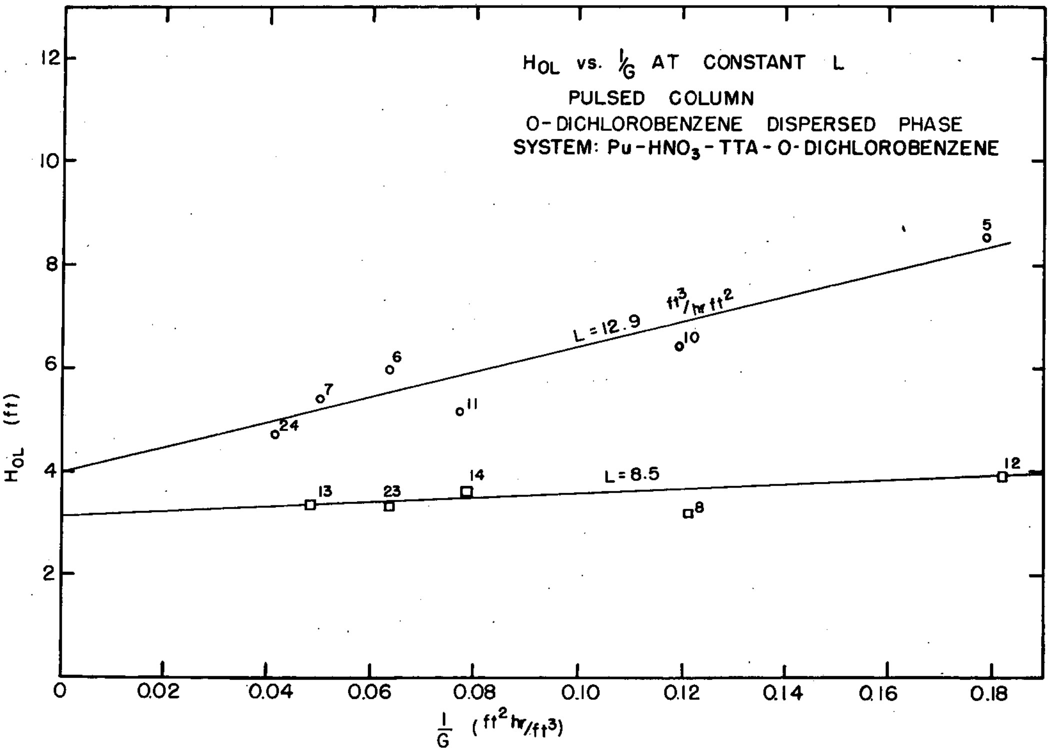
H_{OL} data are plotted versus L at constant G values in Figure 9. While there are considerable scatter in these data, the general pattern can be seen. It is evident that lines fan out at the higher L values; those at the lower G's being higher, while a common point (which is the projection of a horizontal line parallel to the 1/G axis) appears to exist at a L value of about eight. Figure 10 was constructed from the curves of Figure 8 in order to obtain the smoothed variation of H_{OL} with L.

The negative intercepts in this figure cannot have any physical reality and are shown merely for purposes of illustrating the trend of the lines with flow rate. Such negative intercepts have been obtained by other investigators[22,24] in liquid extraction towers and as yet have not been explained.

Figures 9 and 10 are fitted by

$$H_{OL} = 1.3 + 0.21\ L - 31.5/G + 4.22(L/G) \qquad (21)$$

which describes essentially all of the data for m = 1.0, a frequency of about 37.5 cycles per minute and a pulse amplitude of seven tenths of an inch.



H_{OL} vs. $1/G$ AT CONSTANT L
PULSED COLUMN
O-DICHLOROBENZENE DISPERSED PHASE
SYSTEM: Pu-HNO_3-TTA-O-DICHLOROBENZENE
L = 12.9 $ft^3/hr\ ft^2$
L = 8.5
5
10
6
7
11
24
13
23
14
12
8
H_{OL} (ft)
12
10
8
6
4
2
0
0.02
0.04
0.06
0.08
0.10
0.12
0.14
0.16
0.18
$\frac{1}{G}$ ($ft^2\ hr/ft^3$)

FIG. 8

MU 2768

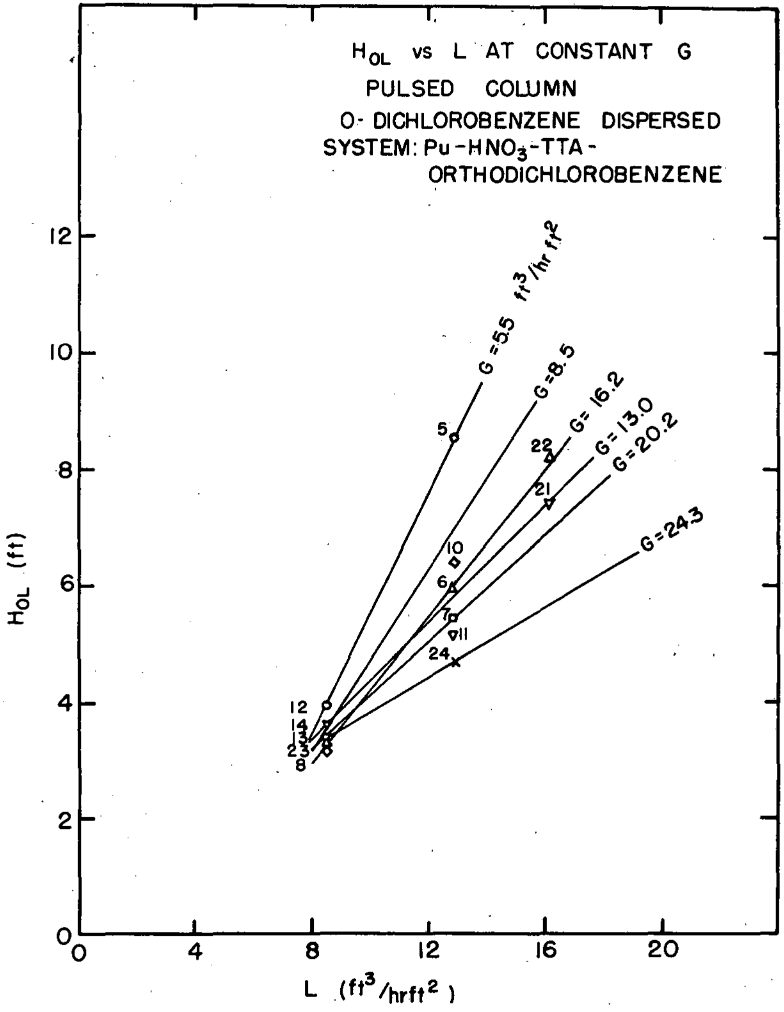

H_{OL} vs L AT CONSTANT G
PULSED COLUMN
O- DICHLOROBENZENE DISPERSED
SYSTEM: Pu-HNO_3-TTA-ORTHODICHLOROBENZENE
G = 5.5 $ft^3/hr\,ft^2$
G=8.5
G= 16.2
G= 13.0
G=20.2
G=24.3
5
22
21
10
6
7
11
24
12
14
13
23
8
H_{OL} (ft)
L ($ft^3/hrft^2$)
0
2
4
6
8
10
12
0
4
8
12
16
20

FIG. 9

MU 2769

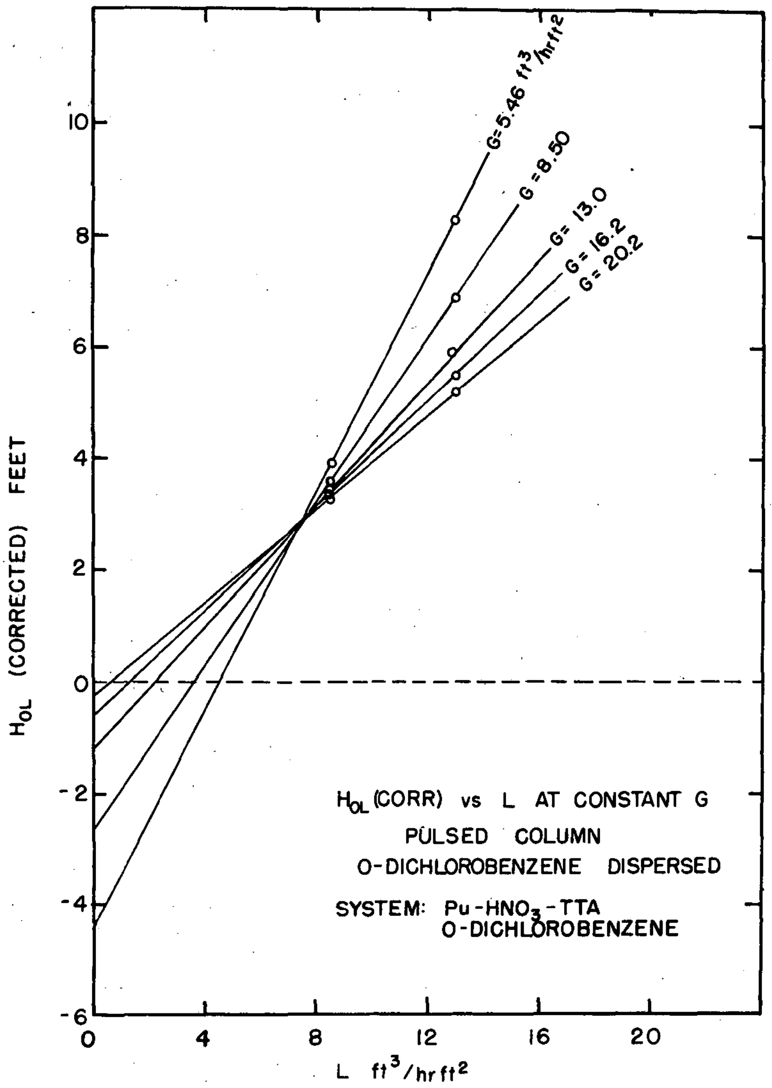


FIG. 10

MU 2770

B. Calculation of Film HTU's

As stated previously, values of the film HTU's are required in order to calculate over-all HTU's at different distribution coefficients.

It is considered that the distinction between continuous and discontinuous phases is not as sharply defined in a pulsed column as in a packed column. For this reason it is felt that both film values may vary with flow rate, although each should be constant over the tower length for any particular flow rates, and for this reason correlation of film values with flow rate has not been attempted.

In order to illustrate the usefulness of the concept a sample calculation will be given.

From Runs 165-II-Pu-2 and 176-II-Pu-3 at different m but otherwise similar conditions:

$$.94 = H_G + (0.035/1.03)(H_L)$$

$$5.04 = H_G + (1.04/1.03)(H_L)$$

Solving,

$$H_L = 4.25 \text{ ft and } H_G = 0.80 \text{ ft}$$

Therefore, for G and L each equal to 8.2 $ft^3/hr\ ft^2$,

$$H_{OG} = 0.80 + 4.25\ m$$

For m = 0.87

$$H_{OG} = 4.54 \text{ ft.}$$

Experimentally, from Figure 11, at an amplitude of 0.68 inches, $H_{OG} = 4.8$ ft.

This agreement shows the usefulness of the film values for transposing data to different values of the distribution coefficient, even for

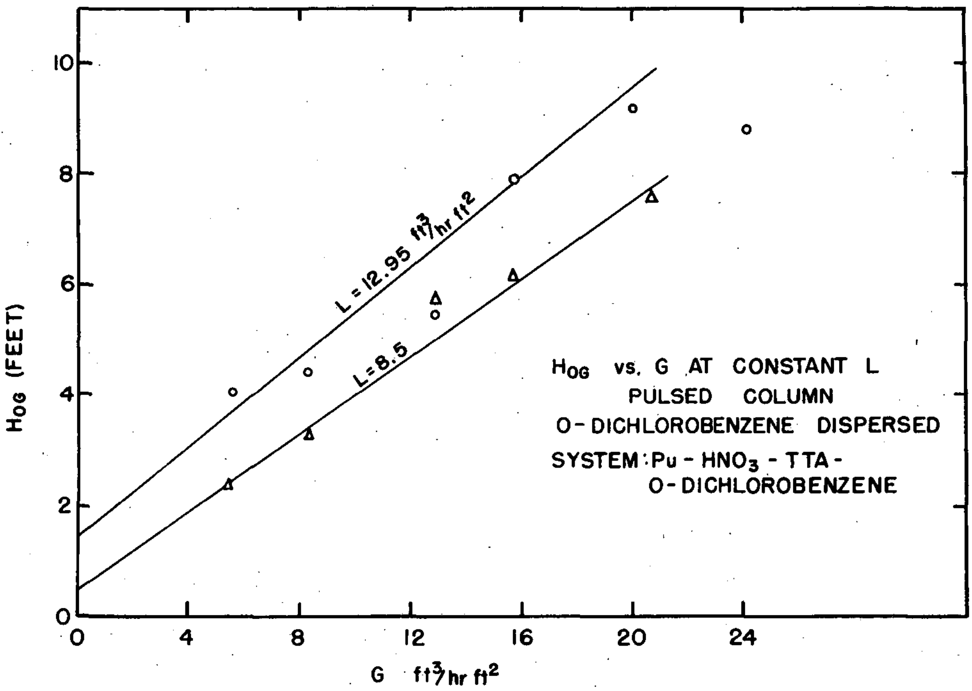


FIG. 11

MU 2771

a factor of 30 for m as in the above example.

C. Effect of Pulse Amplitude and Frequency

Runs in which pulse amplitude or frequency were varied under otherwise constant conditions are listed in Table V.

Table V

Effect of Varying Pulse Frequency and Amplitude at Constant Flow Rate

2" plate spacing 60-0.050" holes per plate

Run No.	E	Cont. Phase	L	G	Amplitude Inches	Freq. Cycles/min	H_{OG}
169-I-Pu-3	0.96	Aq	12.5	12.8	2.0	37.5	1.03
188-I-Pu-8	0.87	Aq	12.6	12.7	1.2	37.4	3.96
189-I-Pu-9	0.87	Aq	12.5	12.6	1.1	37.5	2.73
189-I-Pu-10	0.87	Aq	12.7	12.5	0.6	37.5	5.56
192-I-Pu-11	0.87	Aq	12.6	12.6	1.1	37.5	2.94
193-I-Pu-12	0.87	Aq	12.5	12.6	0.6	37.5	5.22
183-I-Pu-6	0.92	Aq	12.5	13.0	1.8	47.0	5.42
184-I-Pu-7	0.92	Aq	12.5	12.5	1.1	46.9	2.25
219-II-Pu-14	1.027	Aq	8.4	12.8	0.7	38.7	5.72
220-II-Pu-15	1.027	Aq	8.5	12.8	0.3	38.4	6.65

These data are shown in Figure 12 and serve to indicate that for a pulse frequency of 37.5 cycles/minute, pulse amplitudes which approach the plate spacing in magnitude tend to increase the efficiency of transfer.

This conclusion must be tempered by the results of Runs 183-I-Pu-6 and 184-I-Pu-7 which have a pulse frequency of 47. These apparently conflicting results are possibly indicative that there exists some minimum HTU condition for the system similar to that reported in other investigations of pulsed column behavior.[13]

It is apparent from Figure 12 that increased pulse amplitude leads to greater efficiency of transfer.

D. Effect of Continuous Phase

The effect of continuous phase in the pulsed column is shown in Table VI by comparison of pairs of runs under similar conditions.

Table VI

Effect of Continuous Phase

Run No.	E	Cont. Phase	L	G	Amplitude Inches	Freq. Cycles/min	H_{OG}
169-I-Pu-3	0.960	Aq	12.5	12.8	2.00	37.5	1.0
172-I-Pu-4	0.960	Org	12.6	12.7	2.00	41.2	1.2
165-II-Pu-2	0.035	Aq	12.8	12.4	1.00	37.0	0.9
162-II-Pu-1	0.035	Org	12.6	12.3	1.00	38.4	2.8
286-II-Pu-30	1.504	Aq	5.5	15.7	0.68	38.7	19.6
294-II-Pu-33	1.499	Org	5.5	15.7	0.68	39.2	80.3
288-II-Pu-31	1.504	Aq	16.2	15.7	0.68	38.7	8.8
296-II-Pu-34	1.499	Org	16.1	15.8	0.68	38.5	40.0
290-II-Pu-32	1.504	Aq	32.2	15.7	0.68	38.7	7.0
298-II-Pu-35	1.499	Org	22.2	15.8	0.68	38.5	31.0

THE EFFECT OF PULSE AMPLITUDE
UPON HTU_{OG} AT A CONSTANT FREQUENCY

SYSTEM: Pu - NITRIC ACID - TTA -
ORTHO - DICHLOROBENZENE

ORTHO - DICHLOROBENZENE DISPERSED

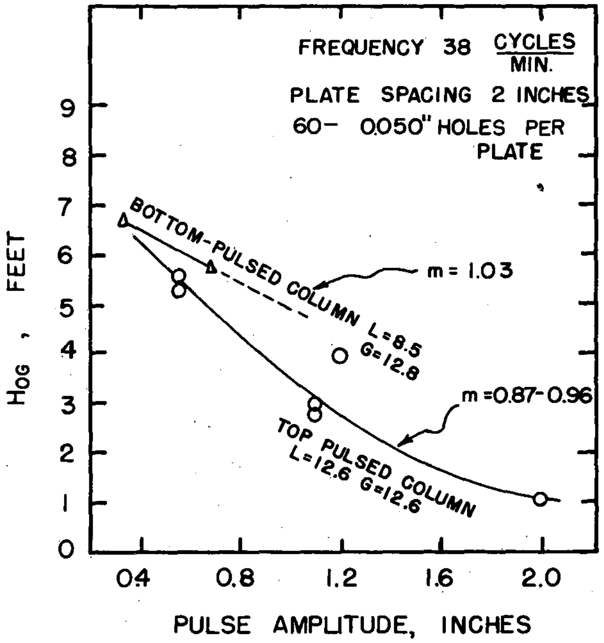


FIG. 12

MU 2772

Transfer of plutonium is much more efficient in the pulse column when the aqueous phase is continuous. This result is in agreement with data found previously for the packed column.

XI. COMPARISON OF PACKED AND PULSED COLUMNS

A. Efficiency of Transfer

It is of interest to compare the relative efficiencies for mass transfer of plutonium in the packed and pulsed column. This can be done for the case when ortho-dichlorobenzene is the dispersed solvent phase as shown in Figure 13.

The efficiency of the pulse column is considerably higher than for the packed column under similar conditions. HTU's for the packed column are approximately three times those for a pulsed column.

B. Throughput

The pulsed column is capable of handling considerably more total flow than the packed column when ortho-dichlorobenzene is the dispersed phase. In fact, it was difficult to obtain packed column data for comparison purposes because operation was so frequently limited by flooding. The constant in equation (19) for the packed column was approximately six. Neither pulsed column approached flooding under the conditions reported here. Experience indicates that the pulsed column will carry at least twice the throughput of the packed column.

COMPARISON OF PACKED AND PULSED COLUMNS UNDER SIMILAR CONDITIONS

SYSTEM: Pu-HNO_3-TTA-ORTHODICHLOROBENZENE
ORTHO-DICHLOROBENZENE DISPERSED
E APPROXIMATELY 1.1

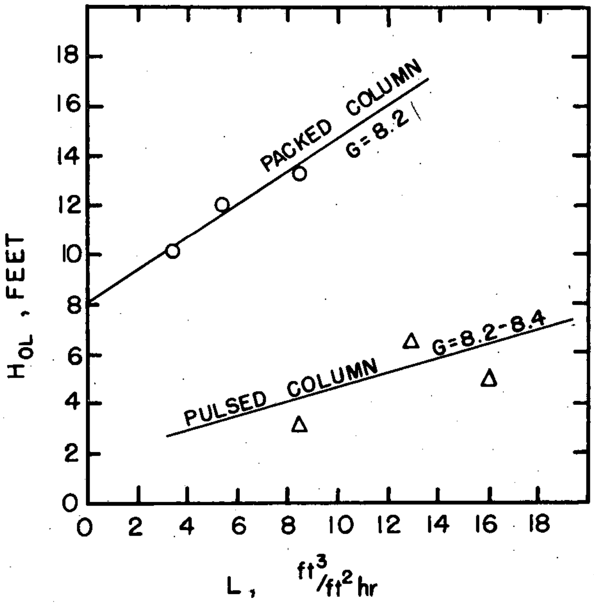


FIG. 13

MU 2773

XII. HOLDUP DATA FOR THE PULSED COLUMN

The fractional organic holdup of the seven foot bottom-pulsed column was studied at a frequency of 38.5 cycles/minute and at a pulse amplitude of 0.68 inches with ortho-dichlorobenzene as the dispersed phase. The holdup was measured by operating the column until steady-state was achieved, then shutting off all flows and measuring the amount of organic phase that settled out of the active length of the column. This volume was measured in the bottoms rate-measuring bottle.

The volumes obtained were divided by the difference between the total column volume and the measured organic volume, i.e., by the aqueous holdup. The resulting data are reported as volumetric holdup ratio in Table VII and are shown in Figure 14.

Table VII

Holdup Ratio in the Pulsed Column

Frequency - 38.5 cycles/minute. Amplitude - 0.68 inches.

System: Aqueous 1 M HNO_3 - ortho-dichlorobenzene.
(Ortho-dichlorobenzene dispersed.)

L_{ft^3/ft^2hr}	G_{ft^3/ft^2hr}	Holdup Ratio
4.28	8.50	0.210
4.28	15.78	0.347
4.28	20.40	0.500
4.28	20.60	0.390
8.26	8.50	0.226
8.26	10.84	0.262
8.26	12.78	0.310
8.26	15.78	0.371
8.26	17.50	0.408
12.87	7.40	0.242
12.87	12.53	0.380
12.87	17.40	0.568
16.13	5.55	0.185
16.13	8.22	0.250
16.13	7.21	0.310
16.13	10.36	0.399
16.13	13.10	0.500
16.13	15.60	0.533
16.13	19.60	0.545

HOLD-UP RATIO IN THE PULSED COLUMN
AS FUNCTION OF FLOW RATES

FREQUENCY - 38.5 CYCLES/MIN.
AMPLITUDE - 0.68 INCHES

SYSTEM: 1 M. NITRIC ACID - ORTHODICHLOROBENZENE
ORTHO - DICHLOROBENZENE DISPERSED

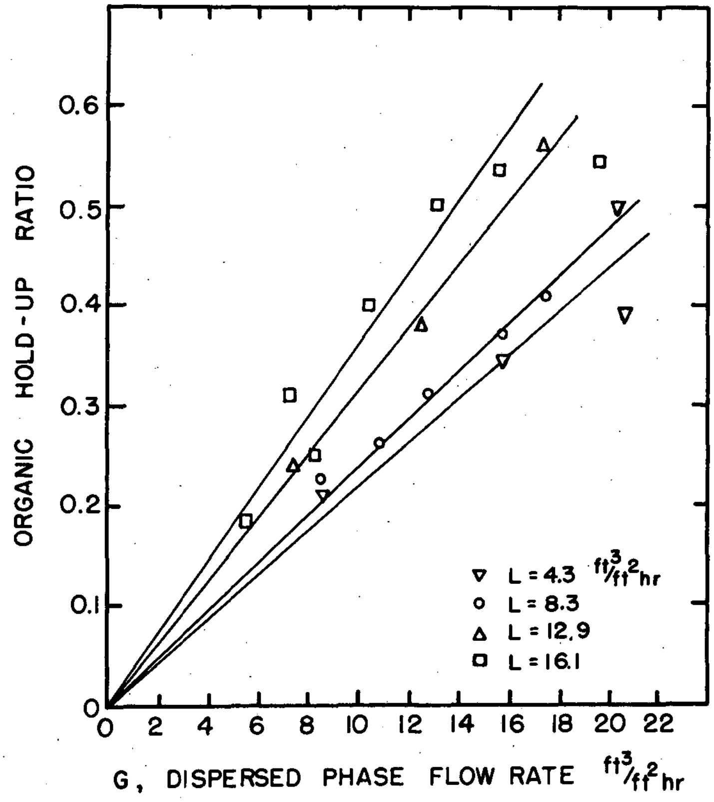


FIG. 14

MU 2774

Empirically, the plot of the data shows the holdup ratio to be a function of the ratio G/L. A theoretical holdup mechanism has not been developed.

XIII. SUMMARY AND CONCLUSIONS

Upon the basis of the information gained from the runs described it may be concluded that it is entirely feasible to transfer plutonium(IV) in either direction between aqueous nitric acid and TTA-organic solvent solutions in both packed and pulsed columns at practical flow rates. Thus in the flow sheet for the extraction of plutonium from "dissolver solutions" as proposed by Rubin and Hicks,[5] the contacting equipment possibly could be packed or pulsed columns of suitable design.

Representative mass transfer data for the system have been presented for both types of extraction column. The efficiency of transfer, while not as high as for some widely differing systems, (i.e., with polar organic solvents) is of the same order of magnitude as much of the data of liquid extraction (where nonpolar solvents were involved) reported in the literature despite the apparent slowness of batch reactions of the Pu(IV)-PuK_4 system. It is of interest to note that the over-all HTU's for the packed column reported here are very similar in value to those reported by Chu, Taylor, and Levy[25] for an almost identical packed column using the system, benzoic acid - benzene - water.

In regard to the relative performance of the packed and pulsed columns, the pulsed column is distinctly superior from both the standpoint of efficiency of mass transfer and throughput. Although the packed column does offer the advantages of simplicity of construction, maintenance and operation; it is considered that the higher efficiency and throughput obtainable with a pulsed column would warrant its choice in preference to the packed column. Either type of column is conveniently operated with radioactive streams.

It has been demonstrated that in all cases investigated, the efficiency of transfer is higher with the aqueous phase maintained as the continuous one. The reason for this effect is presumably due to the finer droplets obtained (and hence greater interfacial area) when the solvent is dispersed in the nitric acid phase.

In recycle operations, the TTA-solvent solution appears to be stable in stainless steel equipment over long periods of time. Some difficulties were encountered with the oxidation state of plutonium tracer in the aqueous phase because of the reducing properties of the ortho-dichlorobenzene employed. Trace plutonium(IV) appears to be stable in nitric acid solutions for long periods of time.

The over-all HTU's for the system studied were observed to vary as functions of flow rates for both packed and pulsed columns. The HTU surface correlational method appears to be applicable to the system and it thus appears to behave as do most of the previously reported liquid-liquid extraction systems.

Because of the opportunity to vary the distribution coefficient for the aqueous plutonium-plutonium chelate system with a minimum effect upon other variables, a number of film HTU's for the system in packed and pulsed columns have been determined. These film HTU's represent the first experimentally determined values for the case of the transfer of a solute between two immiscible phases. The values so obtained have been compared and found similar in magnitude to the film HTU's reported by Colburn and Welsh and by Laddha and Smith.

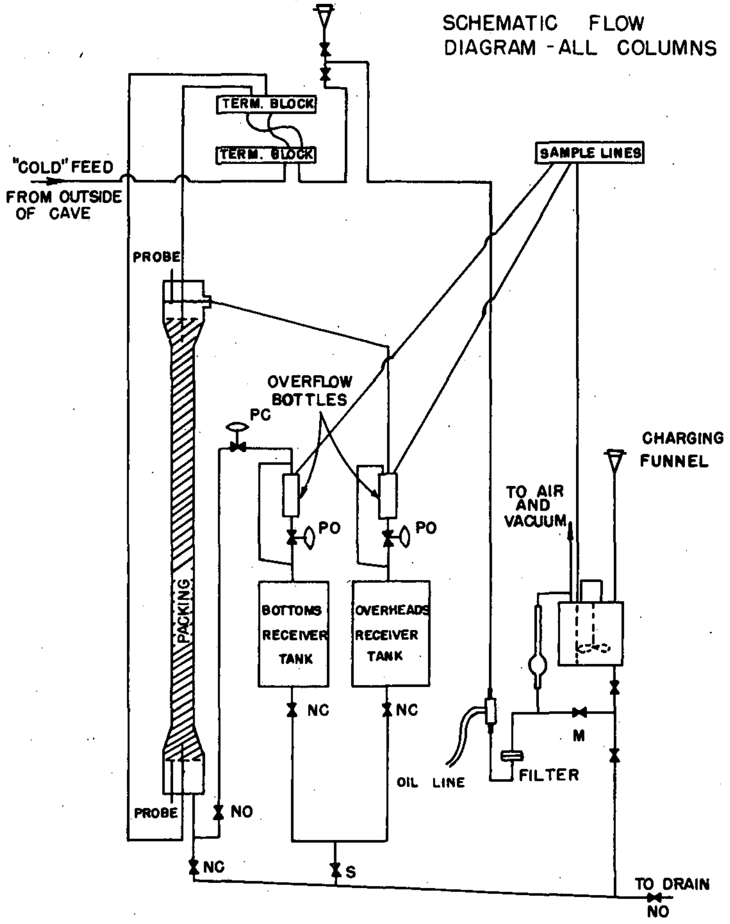
The effects of amplitude and frequency in the pulsed column have been briefly investigated. At the pulse frequency employed for the majority of the runs, a pulse length of the order of the plate spacing appeared to be the more efficient although there were indications that at a higher frequency, a condition exists with the maximum efficiency amplitude less than the plate spacing.

The holdup of the pulsed column as a function of the continuous and discontinuous flow rates has been investigated.

APPENDIX

A. Tables of Experimental Data.

B. Figures of Column Construction.



SCHEMATIC FLOW DIAGRAM - ALL COLUMNS

FIG. 15

VALVE LEGEND

NO	MANUAL, NORMALLY OPEN
NC	MANUAL, NORMALLY CLOSED
S	ELECTRIC SOLENOID, NORMALLY CLOSED
PO	PNEUMATIC, NORMALLY OPEN, QUICK CLOSING
PC	PNEUMATIC CONTROL
M	METERING MANUAL

MU 2775

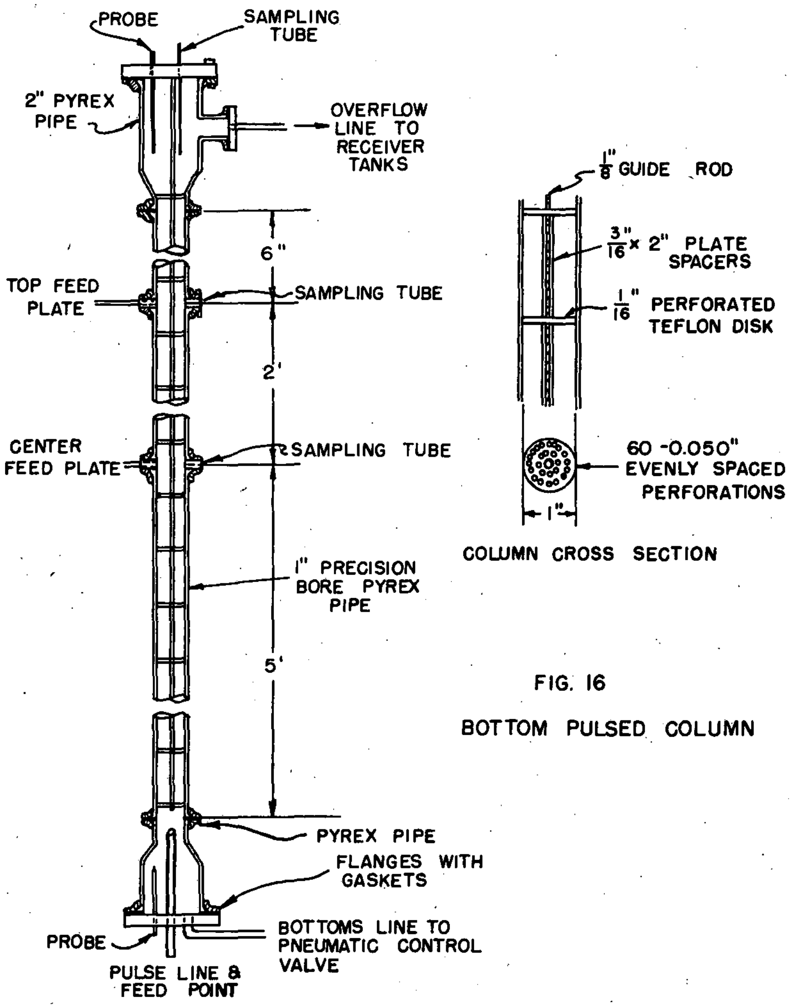


FIG. 16

BOTTOM PULSED COLUMN

MU 2776

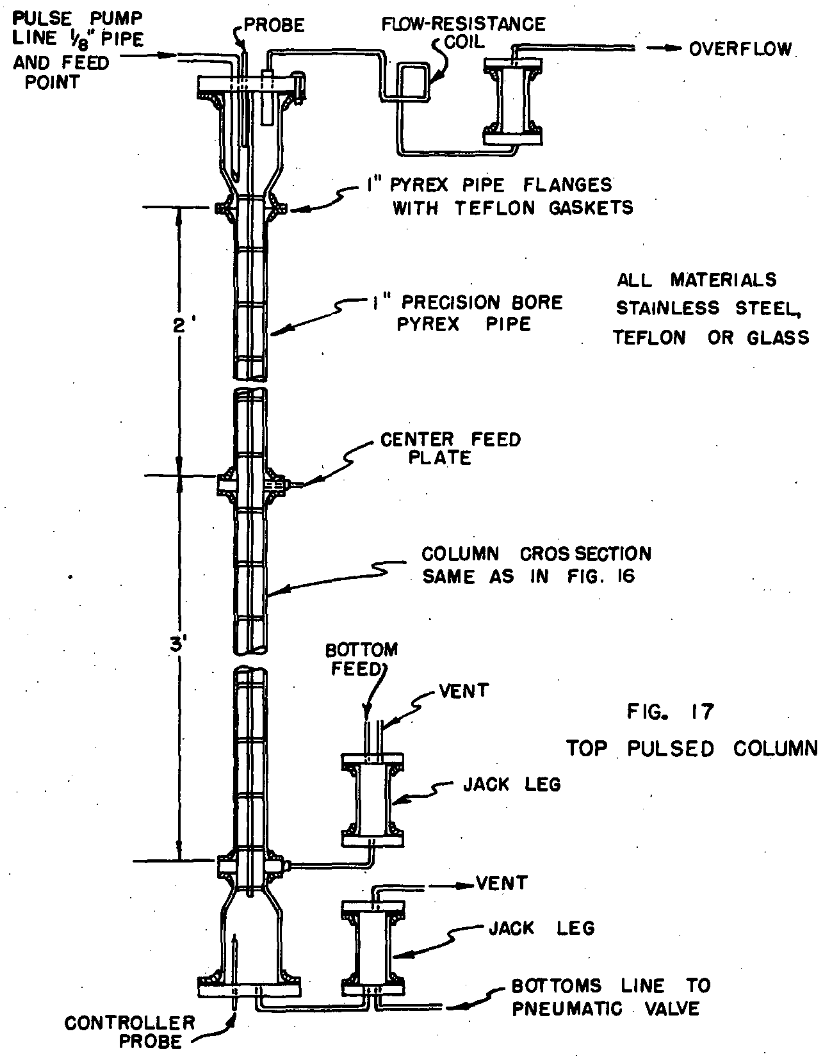


FIG. 17
TOP PULSED COLUMN

MU 2777

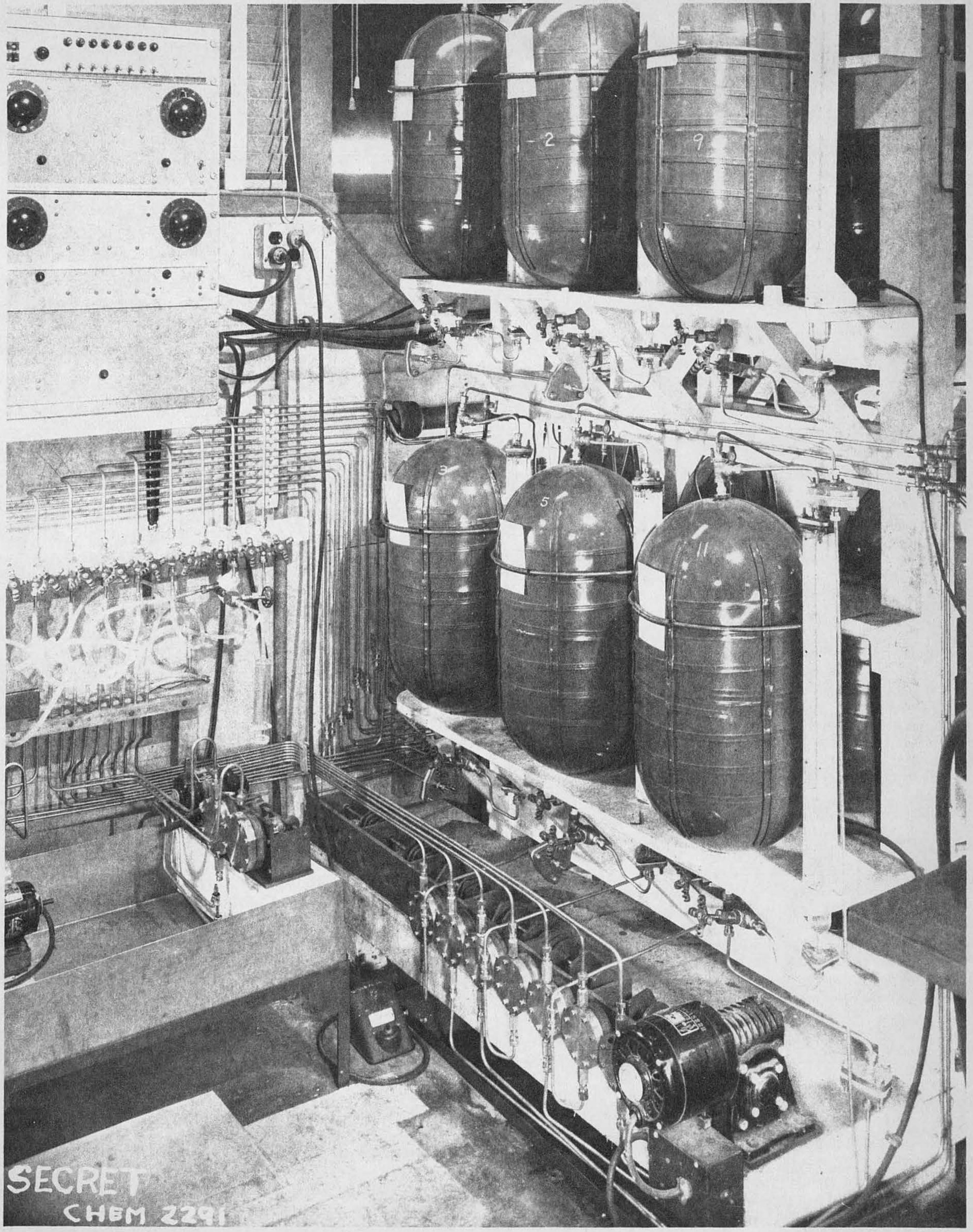


FIG. 18
FEED TANKS AND PUMPS

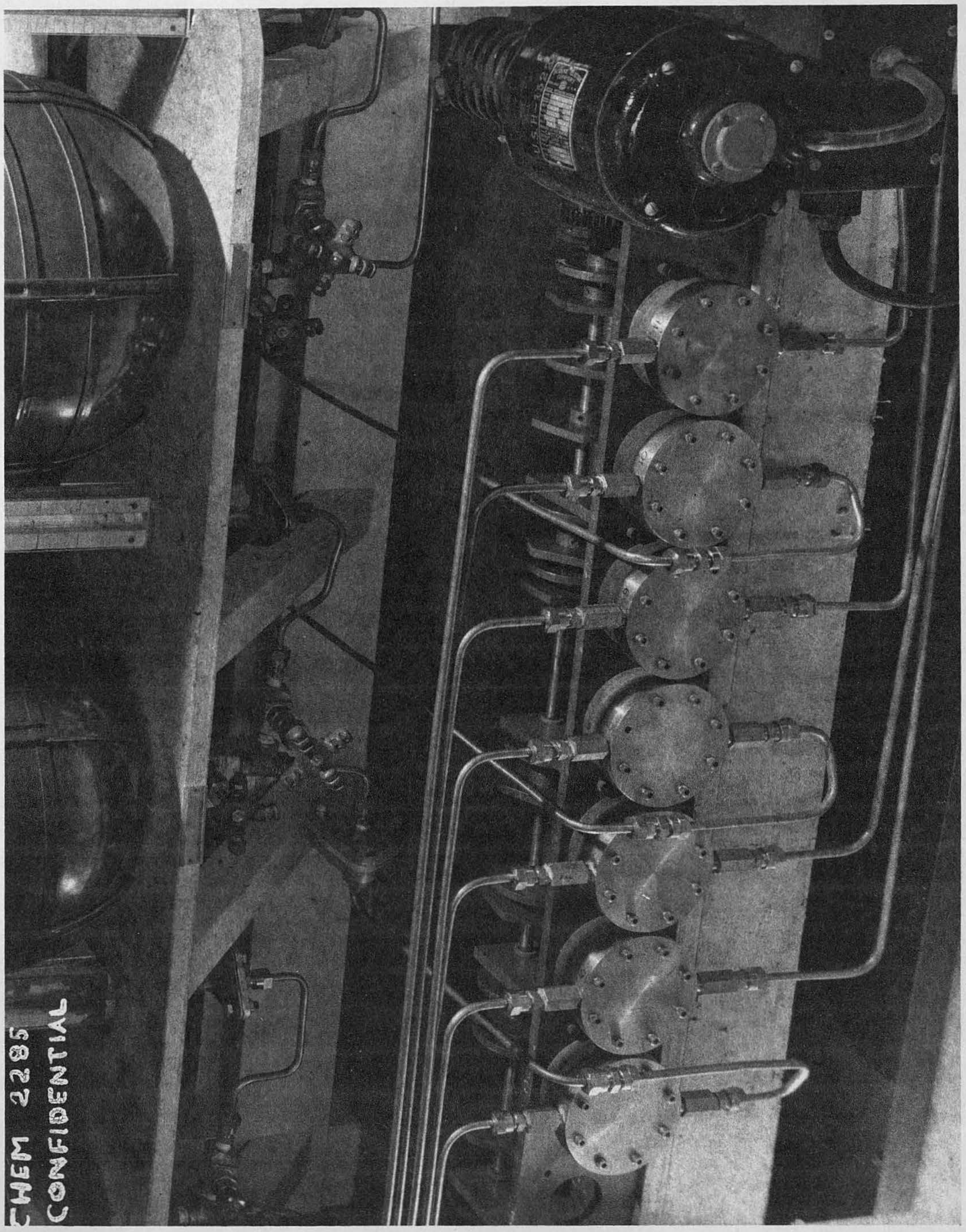


FIG. 19
FEED PUMPS

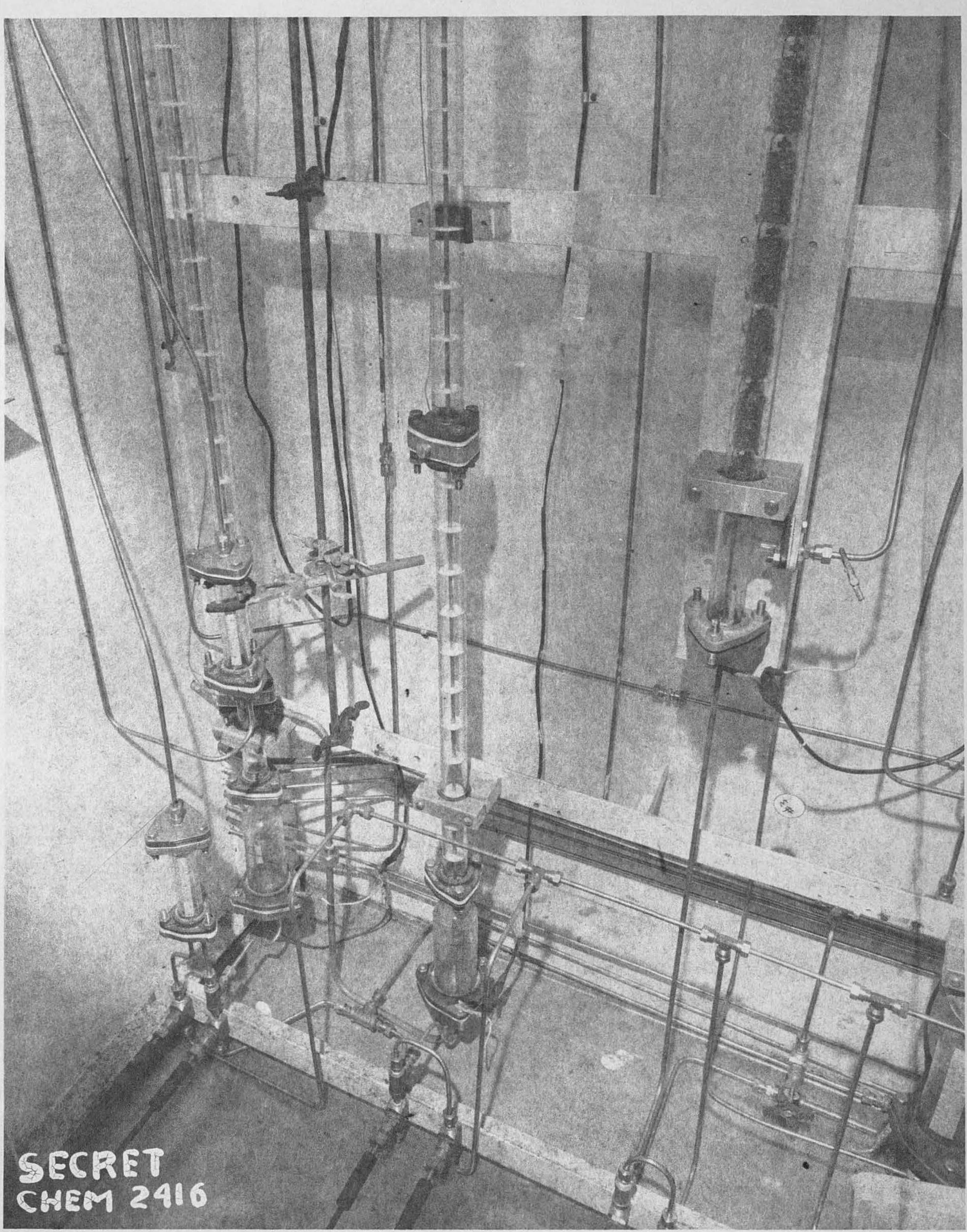
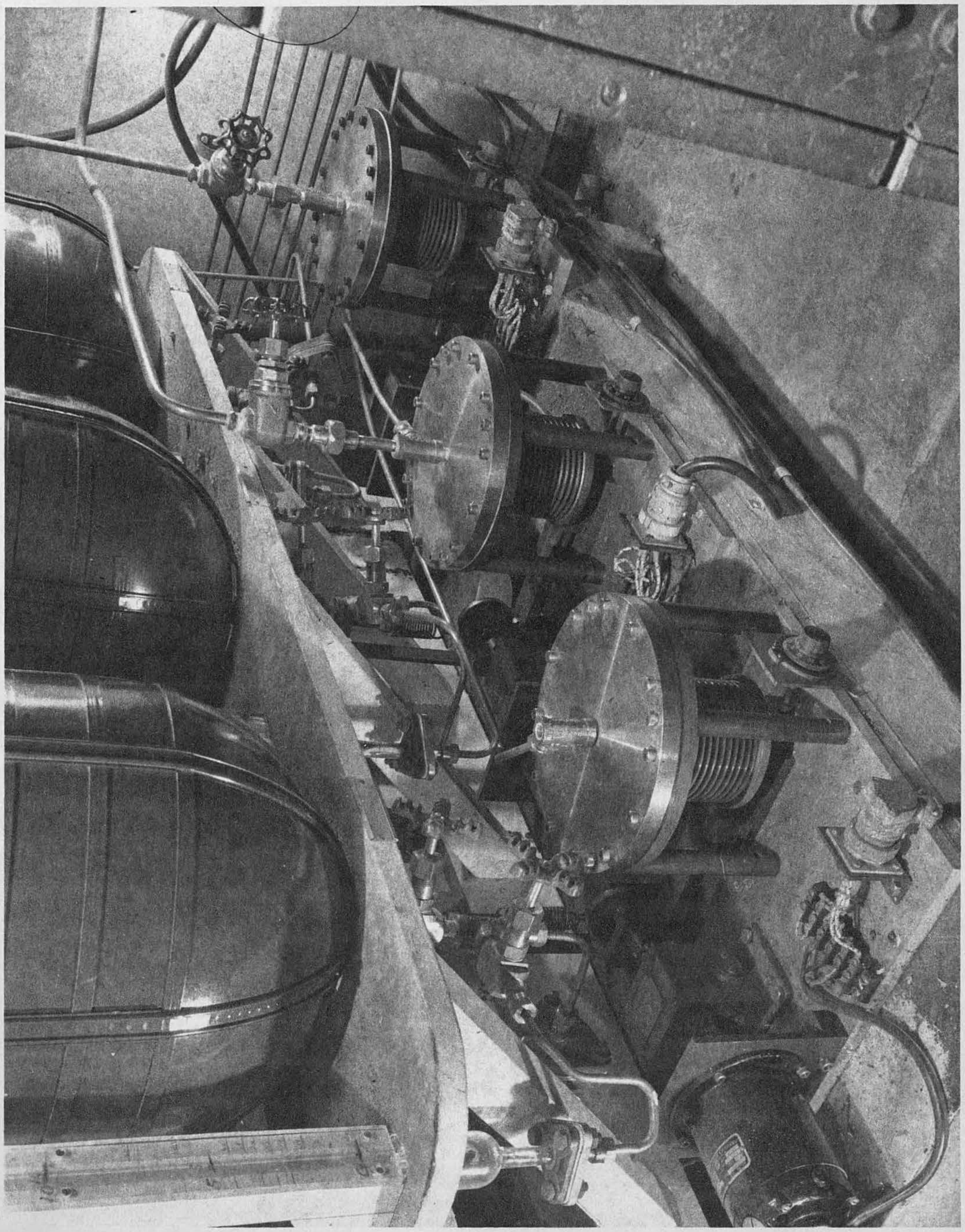


FIG. 20

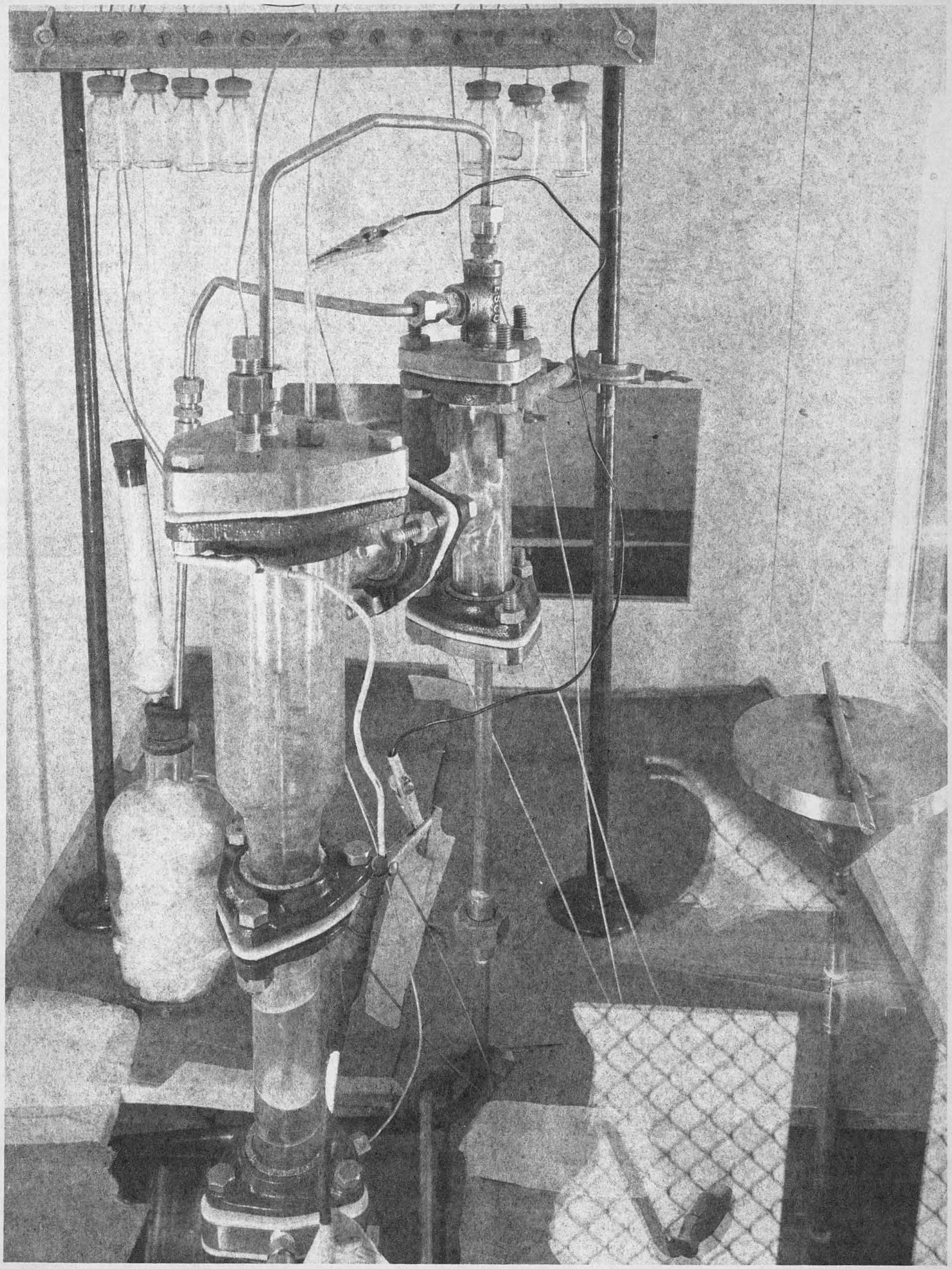
GENERAL VIEW - 1" PULSE COLUMN



CONFIDENTIAL

FIG. 21
BELLOWS–TYPE PULSE PUMPS

OZ 1174



CONFIDENTIAL

FIG. 22

HEAD OF 7' PULSE COLUMN AND SAMPLE BOTTLE RACK FOR INTERNAL SAMPLES

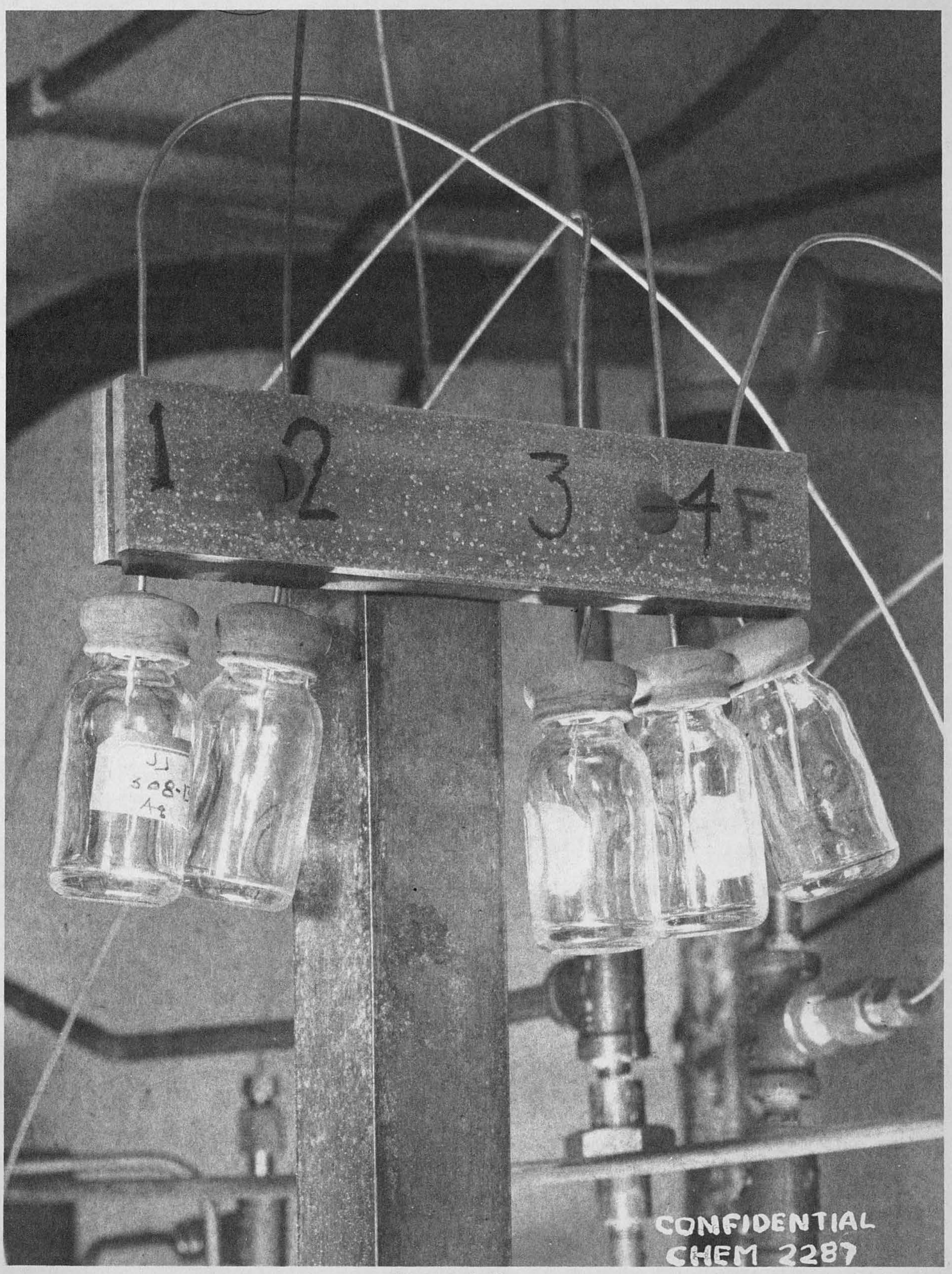


FIG. 23
CLOSE UP OF SAMPLE RACK
FOR OVERFLOW SAMPLES

OZ 1176

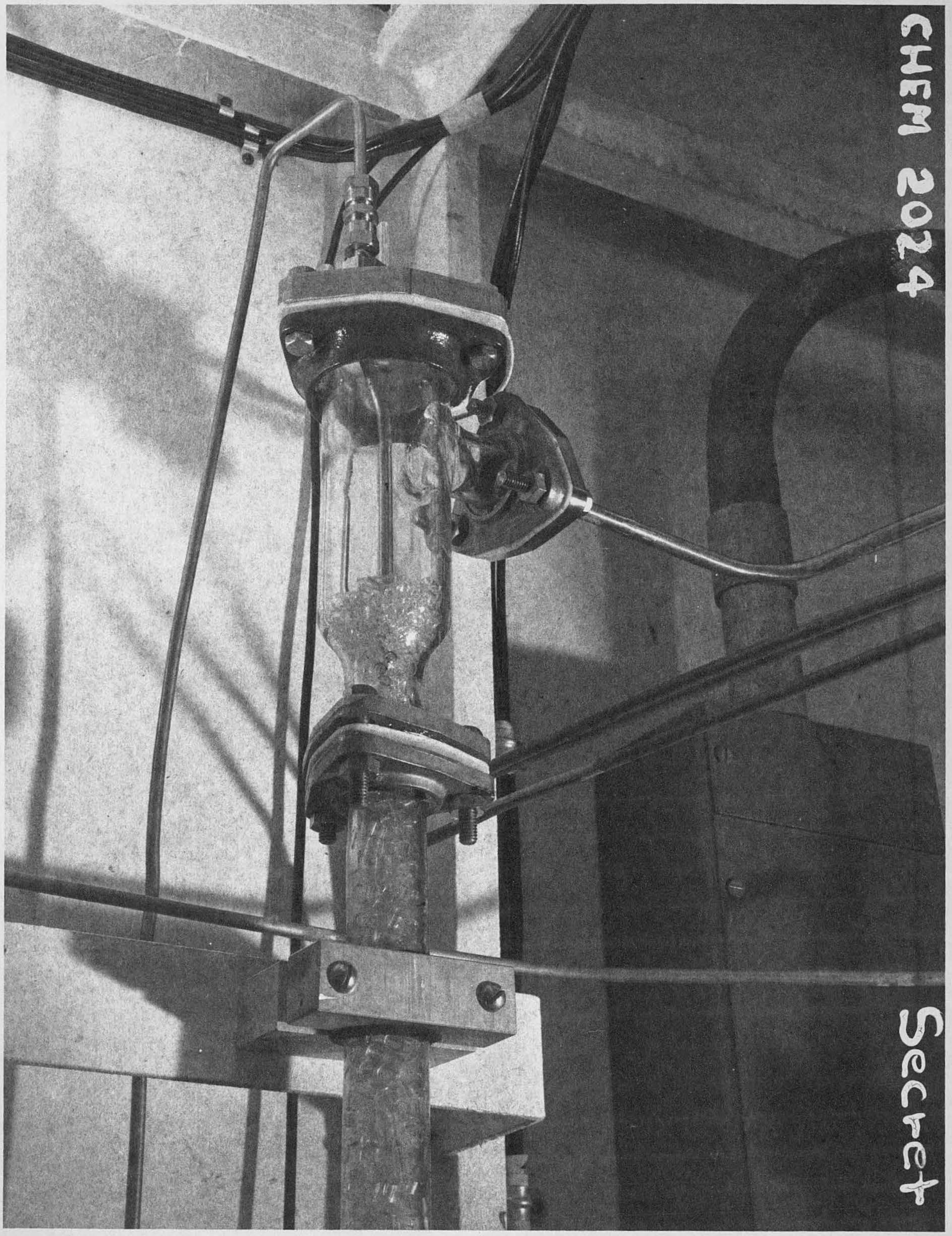


FIG. 24
HEAD OF 1" PACKED COLUMN

OZ 1177

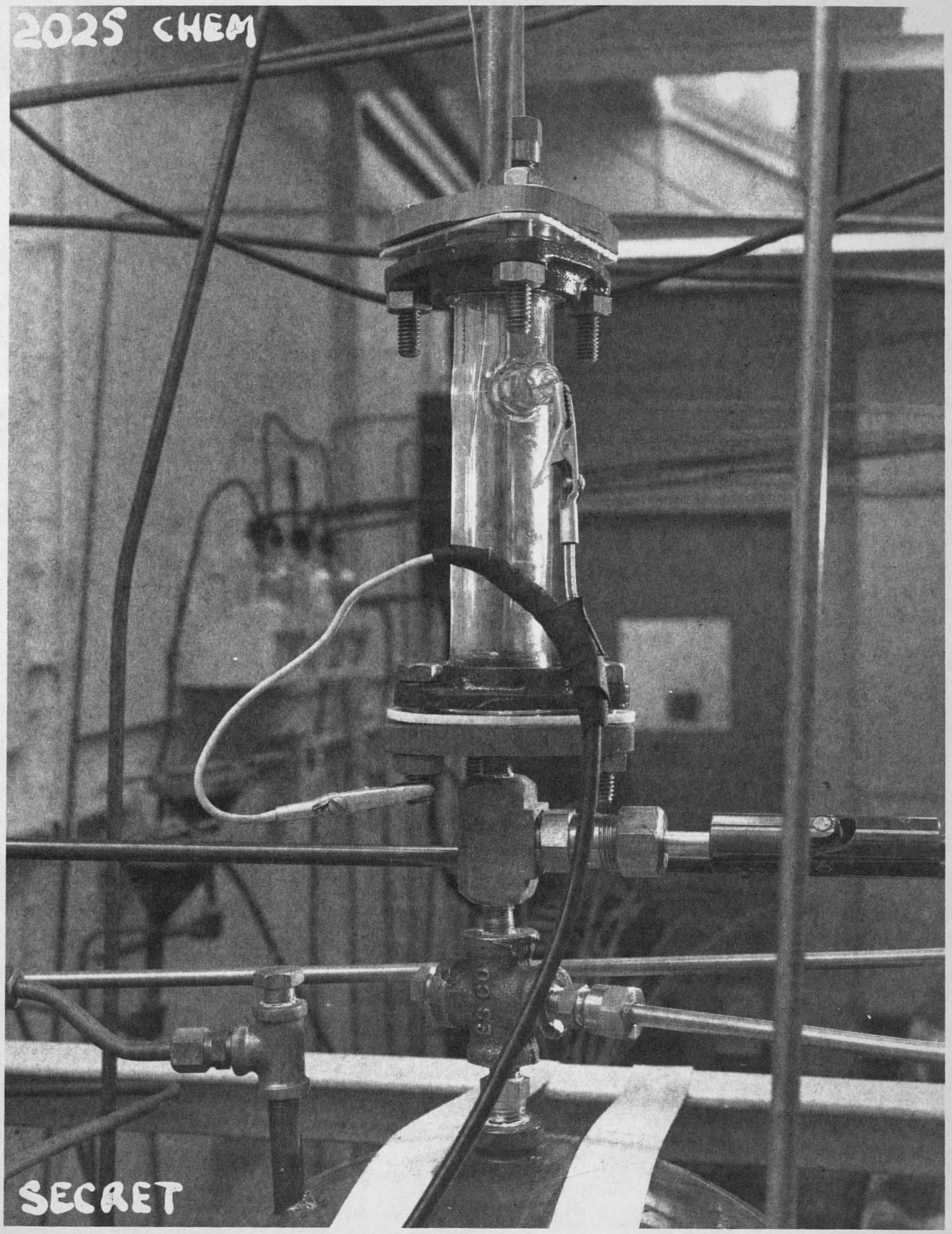


FIG. 25

OVERFLOW SAMPLE COLLECTING BOTTLE

OZ 1178

Table VIII

Pulsed Column (ortho-dichlorobenzene-TTA-nitric acid)
Transference: Aqueous to Organic Phase

Run Number	E_a^o	Cont. Phase	L ft/hr	G ft/hr	R	R'	Freq. Cycles/ minute	Ampl. in	HETS ft	H_{OG} ft	Mat'l Balance Error %
153-I-Pu-1	11.00	Aq	8.5	8.0	1.070	0.905	25.7	2.0	8.80	--	-9.5
157-I-Pu-2	11.00	Aq	8.7	8.2	1.055	0.930	48.0	1.8	6.10	36.20	-8.4
157-I-Pu-2a	11.00	Aq	8.7	8.2	1.055	1.017	90.5	0.9	5.10	21.80	-3.5
169-I-Pu-3	0.96	Aq	12.5	12.8	0.975	0.956	37.5	2.0	1.03	1.03	-1.5
172-I-Pu-4	0.96	Org	12.6	12.7	0.981	0.966	41.2	2.0	1.22	1.20	-1.0
181-I-Pu-5	0.99	Aq	8.8	8.3	1.060	1.020	47.2	1.8	7.28	7.25	-1.6
183-I-Pu-6	0.92	Aq	12.5	13.0	0.965	0.976	47.0	1.8	5.79	5.42	0.4
184-I-Pu-7	0.92	Aq	12.5	12.5	1.000	0.978	46.9	1.1	2.30	2.25	-1.3
188-I-Pu-8	0.87	Aq	12.6	12.6	0.994	0.888	37.4	1.2	3.50	3.96	-6.5
189-I-Pu-9	0.87	Aq	12.5	12.6	0.994	0.999	37.5	1.1	3.19	2.73	0.9
189-I-Pu-10	0.87	Aq	12.7	12.5	0.987	0.948	37.5	0.6	5.92	5.56	-1.6
192-I-Pu-11	0.87	Aq	12.6	12.6	0.990	0.957	37.5	1.1	3.15	2.94	-1.7
193-I-Pu-12	0.87	Aq	12.5	12.6	0.991	0.975	37.5	0.6	5.50	5.22	-0.8

Table IX

Pulsed Column (ortho-dichlorobenzene-TTA-nitric acid)   Transference: Organic to Aqueous Phase

Run Number	E_a^o	Cont. Phase	L ft/hr	G ft/hr	R	R'	Freq. cycles/ minute	Ampl. in	HETS ft	H_{OG} ft	H_{OL} ft	Mat'l Balance Error %
162-II-Pu-1	0.035	Org	12.6	12.3	1.022	1.060	38.4	1.00	9.80	2.80	--	-2.75
165-II-Pu-2	0.035	Aq	12.8	12.4	1.030	1.050	37.0	1.00	3.50	0.94	--	-1.00
176-II-Pu-3	1.040	Aq	12.9	12.5	1.030	1.020	38.5	1.00	4.95	5.04	5.00	+0.35
177-II-Pu-4	1.040	Aq	12.9	8.4	1.560	1.620	38.5	1.00	3.65	2.98	4.48	-3.50
197-II-Pu-5	1.090	Aq	12.9	5.6	2.310	2.200	38.5	0.68	5.34	4.02	8.53	+3.90
199-II-Pu-6	1.090	Aq	12.8	15.7	0.820	0.790	38.8	0.68	6.38	7.89	5.95	+1.66
199-II-Pu-7	1.090	Aq	12.8	20.0	0.642	0.710	38.8	0.68	7.31	9.18	5.40	-3.50
204-II-Pu-8	1.050	Aq	8.4	8.2	1.025	1.010	38.7	0.68	3.20	3.27	3.19	+0.85
210-II-Pu-10	1.070	Aq	12.9	8.4	1.540	1.530	38.7	0.68	3.79	4.44	6.40	+0.72
212-II-Pu-11	1.070	Aq	13.0	12.9	1.000	1.000	39.5	0.68	5.21	5.30	4.95	0.04
215-II-Pu-12	0.933	Aq	8.5	5.5	1.545	1.570	38.8	0.68	2.96	2.37	3.93	-1.56
217-II-Pu-13	0.933	Aq	8.5	20.6	0.415	0.453	38.5	0.68	5.43	7.55	3.36	-3.01
219-II-Pu-14	1.027	Aq	8.4	12.8	0.657	0.644	38.7	0.68	5.27	5.72	3.60	0.80
220-II-Pu-15	1.027	Aq	8.5	12.8	0.661	0.676	38.4	0.33	5.55	6.65	4.24	-1.14
224-II-Pu-16	1.145	Aq	16.1	5.6	2.910	2.950	38.5	0.68	3.02	2.03	5.16	-1.28
226-II-Pu-17	1.145	Aq	16.1	8.2	1.945	2.020	38.5	0.68	3.73	2.89	4.91	-1.98
230-II-Pu-18	0.780	Aq	16.1	12.9	1.250	1.205	38.6	0.68	5.29	4.45	7.14	+2.58
232-II-Pu-19	0.780	Aq	16.2	15.7	1.030	0.961	38.5	0.68	7.14	6.42	8.48	+4.05
234-II-Pu-20	0.780	Aq	16.1	20.2	0.796	0.774	38.7	0.68	9.48	9.51	9.70	1.26
238-II-Pu-21	1.084	Aq	16.1	12.8	1.255	1.216	38.5	0.68	6.70	6.31	7.31	1.74
241-II-Pu-22	1.084	Aq	16.2	15.7	1.026	0.952	38.5	0.68	8.16	8.66	8.20	3.34
245-II-Pu-23	1.000	Aq	8.5	15.8	0.539	0.520	38.6	0.68	4.56	6.14	3.31	1.28
247-II-Pu-24	1.000	Aq	12.9	24.1	0.535	0.522	39.0	0.68	6.39	8.76	4.69	0.80
257-II-Pu-25	1.838	Aq	4.2	13.0	0.328	0.311	39.3	0.68	2.61	6.55	1.17	0.94
260-II-Pu-26	1.838	Aq	4.3	15.8	0.272	0.284	38.5	0.68	5.22	13.12	1.94	0.61
268-II-Pu-28	0.970	Aq	4.3	12.9	0.332	0.319	38.6	0.68	9.50	15.80	12.00	1.05
278-II-Pu-29	2.600	Aq	4.3	5.5	0.774	0.831	38.7	0.68	9.70	17.30	8.78	-1.61
286-II-Pu-30	1.504	Aq	5.5	15.7	0.339	0.294	38.7	0.68	9.75	19.60	4.41	2.81
288-II-Pu-31	1.504	Aq	16.2	15.7	1.025	0.998	38.7	0.68	7.59	8.79	5.98	0.00
290-II-Pu-32	1.504	Aq	22.2	15.7	1.410	1.468	38.7	0.68	6.95	7.00	6.56	1.27
294-II-Pu-33	1.600	Org	5.5	15.7	0.351	0.371	39.2	0.68	69.50	80.30	17.60	-0.35
296-II-Pu-34	1.600	Org	16.1	15.8	1.015	0.974	38.5	0.68	38.20	40.00	25.40	0.74
298-II-Pu-35	1.600	Org	22.2	15.8	1.410	1.240	38.5	0.68	30.40	31.00	27.30	2.44

Table X

Packed Column (Carbon tetrachloride- TTA-nitric acid)
Transference: Aqueous to Organic Phase

Run Number	E_a^o	Cont. Phase	L ft/hr	G ft/hr	R	R'	HETS ft	H_{OG} ft	Mat'l Balance Error %
103-Pl-Pu-1	3.00	Aq	8.29	8.70	0.953		10.3	29.6	-4.0
103-Pl-Pu-2	3.00	Aq	19.00	19.20	0.990		9.8	22.1	3.8
105-Pl-Pu-3	3.00	Aq	4.12	4.05	1.020		6.6	14.2	5.1
111-Pl-Pu-4	3.00	Aq	8.50	8.50	1.000		8.5	19.6	0.8
117-Pl-Pu-7	3.22	Aq	8.00	8.17	0.980		8.8	26.0	8.8
119-Pl-Pu-8	3.22	Aq	3.66	3.60	1.015	1.098	6.5	18.2	6.5
121-Pl-Pu-9	3.22	Aq	18.6	18.30	1.017	1.010	8.5	24.6	8.5

Table XII

Packed Column (Ortho-dichlorobenzene-TTA-nitric acid)

Transference: Organic to Aqueous Phase

Run Number	E_a^o	Cont. Phase	L ft/hr	G ft/hr	R	R'	HETS ft	H_{OG} ft	Mat'l Balance Error %
304-P2-Pu-25	1.12	Aq	3.40	8.17	0.416	0.415	11.9	10.1	-3.1
304-P2-Pu-26	1.12	Aq	11.52	8.21	1.400		flood		
306-P2-Pu-27	1.12	Aq	8.53	8.21	1.040	1.120	14.2	13.2	-0.8
308-P2-Pu-28	1.12	Aq	5.54	8.17	0.672	0.714	18.8	12.0	1.4
308-P2-Pu-29	1.12	Aq	5.54	5.54	1.000	0.942		16.4	
311-P2-Pu-30	1.12	Aq			1.590			17.8	
311-P2-Pu-31	1.12	Aq	5.45	11.50	0.474		flood		
311-P2-Pu-32	1.12	Aq	11.60	3.44	3.380	3.290	8.3	19.4	0.0
313-P2-Pu-33	1.12	Aq	8.57	3.44	2.490	2.490	8.9	16.5	0.0

XV. NOMENCLATURE

E	The distribution coefficient of plutonium in the plus four oxidation state between aqueous and organic TTA solutions.
G	Flow rate of the nonpolar phase into or out of the column in (cu ft)/(hr)(sq ft).
H_{OG}	Height of the over-all transfer unit for the G phase, feet.
H_{OL}	Height of the over-all transfer unit for the L phase, feet.
H_G	Height of film transfer unit for G phase in feet.
H_L	Height of film transfer unit for L phase in feet.
K	The equilibrium constant for reaction (1) as used in equations (2) and (3).
L	Flow rate of the aqueous phase into or out of the column in (cu ft)/(hr)(sq ft).
m	The slope of the equilibrium line and identical to E.
N_{OG}	The number of over-all G phase transfer units.
R	The ratio of the flows, L/G, and equal to the slope of the operating line for the column.
R'	The ratio of the difference in the stream alpha counts over the column, defined as $R' = \frac{\text{Difference in organic stream alpha counts}}{\text{Difference in aqueous stream alpha counts}}$ Provided that the column mass balance is correct, R' = R.
x	Aqueous phase alpha counts/minute/100 microliters due to plutonium in the plus four oxidation state.
y	Organic phase alpha counts/minute/100 microliters.
*	Organic phase alpha counts/minute/100 microliters in equilibrium with an aqueous phase of composition x.
Z	Column height in feet.

BIBLIOGRAPHY

1. M. Calvin, Metallurgical Laboratory Report CN-2586 (December, 1944).
2. J. R. Thomas, H. W. Crandall, and J. C. Reid, Metallurgical Laboratory Report CN-2657 (January, 1945).
3. D. L. Heisig and T. E. Hicks, University of California Radiation Laboratory Report UCRL-1169 (to be issued).
4. J. R. Thomas and H. W. Crandall, Metallurgical Laboratory Report CB-3733 (December, 1946).
5. B. Rubin and T. E. Hicks, University of California Radiation Laboratory Report UCRL-126 (1948).
6. T. E. Hicks, B. Rubin, and T. Vermeulen, University of California Radiation Laboratory Report UCRL-400 (1949).
7. M. W. Davis, Jr., T. E. Hicks, and T. Vermeulen, University of California Radiation Laboratory Report UCRL-1013 (January, 1951).
8. M. W. Davis, Jr. and H. R. Lehman, University of California Radiation Laboratory Report UCRL-152 (1948).
9. R. E. Connick, Metallurgical Laboratory Report CN-3869 (May, 1948), p. 62.
10. W. C. Orr, University of California Radiation Laboratory Report UCRL-196 (September, 1948).
11. F. H. Blanding and J. C. Elgin, Trans. Am. Inst. Chem. Engrs. 38, 305 (1942).
12. W. J. D. Van Dijck, U. S. Patent No. 2,011,186 (1935).

13. W. A. Burns, C. Groot, and C. M. Slansky, Hanford Report HW-14728 (October, 1949).

14. W. J. Blaedel and H. H. Hyman, Metallurgical Laboratory Report CN-3525 (March, 1946).

15. B. Rubin and H. R. Lehman, University of California Radiation Laboratory Report UCRL-718 (May, 1950).

16. A. P. Colburn, Trans. Am. Inst. Chem. Engrs. 35, 211 (1939).

17. A. P. Colburn and A. P. Welsh, Trans. Am. Inst. Chem. Engrs. 38, 179 (1942).

18. G. S. Laddha and J. M. Smith, Chem. Eng. Prog. 46, 195 (1950).

19. H. L. Hou and N. W. Franke, Chem. Eng. Prog. 45, 65 (1949).

20. R. E. Treybal and L. T. Work, Trans. Am. Inst. Chem. Engrs. 38, 203 (1942).

21. J. Allerton, B. O. Strom, and R. E. Treybal, Trans. Am. Inst. Chem. Engrs. 39, 361 (1943).

22. S. B. Row, J. H. Koffolt, and J. R. Withrow, Trans. Am. Inst. Chem. Engrs. 37, 559 (1941).

23. J. C. Elgin and F. M. Browning, Trans. Am. Inst. Chem. Engrs. 31, 639 (1935).

24. O. S. Knight, Trans. Am. Inst. Chem. Engrs. 39, 439 (1943).

25. T. C. Chu, C. C. Taylor, and D. D. Levy, Ind. Eng. Chem. 42, 1157 (1950).

SECRET

DECLASSIFIED

~~SECRET~~