LIQUID - LIQUID EXTRACTION IN A PULSED COLUMN

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This is to certify that the

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LIQUID-LIQUID EXTRACTION IN A PULSED COLUMN

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CLAYTON DALE CALLIHAN

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of the requirements for

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Major professor

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LIQUID-LIQUID EXTRACTION IN A PULSED COLUMN

BY

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ABSTRACT

The performance of a packed liquid-liquid extraction column may be improved if a pulsating motion is imparted to the liquid in the column. The height equivalent to a transfer stage (HETS) is reduced when either the pulse amplitude or pulse frequency are increased. At low pulse rates the amplitude-frequency product seems to be the determining factor, but at high rates frequency is more beneficial than amplitude. The equivalent number of transfer stages in a given height was 1/14 as many in an unpulsed column as in a pulsed column when an amplitude of 5 mm and a frequency of 215 cycles per minute were used.

HETS was found to be more useful than HTU in evaluating the performance of these columns, since the latter varied strongly with flow ratio. HETS is largely a function of packing characteristics, pulsation rate, and superficial throughput velocity. Increasing the cross-section of the packed column by a factor of 2.43 (from 2.127-inch to 3.32-inch ID) did not significantly change the HETS if the superficial velocity, pulse amplitude, and pulse frequency were held constant. Settling and reorientation of the packing as a result of pulsation had an appreciable effect on HETS for both pulsed and unpulsed operation.

In studying the influence of operating variables on the maximum throughput velocity (flooding velocity), one variable was found unexpectedly to dominate the results. This was the rate of mass transfer of the solute from one phase to the other. In a section

31 inches high packed with 8-mm Raschig rings and using carbon tetrachloride and water as solvents, the flooding velocity was twice as high when the entering CCl_4 contained 1% acetone than it was when no acetone was present in either phase or when the acetone concentration in both phases was in equilibrium. Increasing the column height to 101 inches reduced the mass transfer per unit height and therefore reduced the flooding velocities. Increasing the ratio of water to CCl_4 from 0.4 to 4.0 caused a composition "pinch" at the bottom of the column, and the lack of mass transfer at this point reduced the flooding velocity 50%. The effect of pulsing was to increase the average mass transfer per unit of height, although at some flow ratios the pinching effect also became more severe. Pulsing increased the flooding velocity in some cases and decreased it in others. Experimentally this large effect of mass transfer on flooding rate made it difficult to measure the much smaller influence of other variables. From a design viewpoint, it casts doubt on the practical usefulness of the correlations of Hoffing and Lockhart, Breckenfield and Wilke, and other who obtained all their data in the absence of a solute.

Approved Carl Cooper

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APPRECIATION

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INTRODUCTION

Continuous liquid-liquid extraction has been used industrially to great advantage as a unit operation in the separation and purification of chemicals. This is primarily due to certain basic features inherent to the liquid-liquid extraction process itself.

One point in favor of extraction is that no heat or steam is required for the extraction step. Some heat may, however, be required to separate the product from the solvent. In several processes, such as the separation of acetic acid from water solutions, liquid-liquid extraction has contributed greatly to the economics of the process.

In the separation of high molecular weight compounds or heat sensitive materials, distillation is sometimes impractical because the materials cannot be vaporized without the use of very high vacuum and extraction is the only reasonable separation method.

Although similar in principle to fractional distillation, liquid-liquid extraction has an advantage in that the solvents can be chosen from thousands of compounds available commercially to give a great preference for one or more of the components. About the only restrictions placed on the solvents are that they must be relatively insoluble in each other. It is readily apparent, therefore, that the selectivity of the two liquids can often be made greater than in distillation where the vapor phase is substantially ideal and the activity of each component in the vapor is very nearly proportional to its concentration. Liquid-liquid extraction can, therefore, be made to give a greater degree of separation in a single equilibrium contact than is obtainable in fractional distillation.

Unfortunately, the height equivalent to an equilibrium contact in an extraction column is generally much greater than the height equivalent to a theoretical contact in a distillation column, and this has often limited the use of extraction. Thus if liquid-liquid contactors could be confidently designed with nearly the same stage height as a distillation column, a contribution would be made to the chemical industry.

The present investigation is one contribution toward solving this inefficiency problem, and presents data on extraction columns which in some tests showed even better stage efficiencies than distillation columns.

Classification of Extractors

Liquid-liquid extractors have been classified in an exhaustive study made by Morello and Poffenberger (1). The two main classifications differ depending on whether gravity or centrifugal force is used to separate the phases. Most extractors used industrially are of the gravity type, and they can be further subdivided by whether the contact is made through extended films of the two phases or through dispersed droplets of at least one of the phases. Those extractors which depend on droplet formation for operation may be further subdivided into those using power to maintain drop dispersion, and those that do not. Morello and Poffenberger pointed out that a preference was shown in industrial designs for those extractors which do not use power. Extractors that use power result in added costs, not only for the power consumed but also for the cost of maintenance of shafts, stuffing boxes, and other moving parts. Nearly all of the extractors which used an outside source of power were essentially mixer and

settler contactors employing a variety of flow patterns and arrangements.

Some of the main objections in industrial application to those extractors which use an outside source of power have been:

1. Inefficient use of the power being supplied to the extractor.
2. Too little knowledge of reliable design methods for this equipment.
3. Lack of a necessary motive for changing the design of equipment which is now performing quite well its intended function.
4. Extra cost involved when columns are shut down for repair of the mechanical parts. Pulse columns do not have this handicap because the pulsator is situated externally.

Despite these apparent disadvantages, it is recognized by a great many authors that extractors that use an outside source of power often require less space and less investment to make the same separations than their non-agitated counterparts.

It should furthermore be pointed out that 1950, the year the Morello-Poffenberger article was published, also marked the acceleration of emphasis on contactors with an outside power source. This was primarily because of the rapid interest developed by the United States government in columns that could give a great many stages in a short height in order to reduce the cost of shielding for columns extracting radio-active materials.

In view of this increased interest in extraction columns employing power, and particularly in those employing pulsation, power columns will be classified in this thesis as follows:

1. Pulsed columns.
2. Mixer-settler types of apparatus.
3. Miscellaneous power driven extractors.

Miscellaneous Types The miscellaneous classification includes only a few special types which cannot be considered as falling in the first two categories. The most important of these is the Podbelniak spiral extractor which employs centrifugal force to cause the liquid films to flow countercurrently in contact with each other. Its cost has been justified only for special applications where low holdup time is particularly important.

Mixer-Settler Types A typical mixer-settler extractor consists of a multiplicity of chambers with alternate chambers equipped with mechanical agitators and the others arranged for settling and decantation. A countercurrent flow pattern is used. Since true equilibrium is approached closely in each stage, such extractors may be calculated and designed with complete assurance. On the other hand, they are often expensive, complex, and bulky, requiring a large amount of floor space. Special designs have been introduced in an effort to minimize these undesirable features. Modified mixer-settler types represent compromises, and sacrifice efficiency per stage for a more convenient and compact arrangement. The Scheibel column is one such compromise.

In the Scheibel column a series of small mixers are connected to a central rotating shaft running vertically through the column. Between the mixing blades are non-agitated sections of the column packed with fine wire mesh. These sections act as settling chambers or calming regions where the finely divided droplets formed in the agitated sections have a chance to coalesce. Scheibel columns sometimes give more than one theoretical stage for each pair of agitators and separation sections because of countercurrent action in the wire mesh. However, the efficiency depends on the system being extracted

and the column diameter. Data reported in the literature show that a minimum theoretical stage height of one foot can be expected on a 12-inch column with a maximum throughput rate of about half that of an ordinary packed column.

Even pulsed columns sometimes include a sort of mixing-settling action. A pulsed sieve-plate column, for example, operating at low speeds, certainly has an area for dispersion, and the dispersed liquid is moved to another region for coalesence. However, all pulsed columns do not have these features and it is customary to classify them as a separate group.

Pulsed Columns If an up-and-down motion is superimposed on the net countercurrent flow of the two phases going through an extraction column, the result is a pulsed column. Although such columns were first described in the literature in 1937, very little interest actually developed until about 1950.

Almost any type of construction can be used inside the pulse column for performing the necessary dispersing and coalescing operations. For example, a series of sieve-plates could be used, in which the liquids are dispersed as they are forced through small perforations and allowed to coalesce in the region between the plates. Packing could also be used, in which the drops are dispersed on rapid contact with the stationary packing and allowed to coalesce in the spaces between. Spray columns have been tried as pulse columns, in which the dispersion is obtained by introducing a fine mist or spray. It has recently been pointed out to the author that baffle plate towers have been tried as pulsed columns, although these efforts have met with very little success.

Previous Work on Pulsed Columns

Most pulsed columns have been designed from standard unpulsed columns except that a pulsing feature has been added. This makes it impossible to discuss columns using an outside source of power without at the same time discussing the original column from which it was derived. This report will make no attempt in the following discussion to separate pulsed and unpulsed columns but will describe them together as the occasion arises.

Sieve-Plate Columns The first mention of pulsed columns in the literature was a patent issued to W. J. D. van Dijck (2) in 1937. In this patent, van Dijck described two different types of pulsed columns. One of them consisted of a series of perforated plates, commonly called sieve-plates, placed one above the other in a vertical column. Unlike the usual perforated plate column, they contained no downcomers for the heavy phase. The sieve-plates were connected to each other and the top plate was fastened by a shaft to a motor-driven eccentric. The reciprocating motion of the eccentric caused all of the plates in the column to move up and down. To the writer's knowledge, few, if any, except experimental columns were ever built of this design.

Another column mentioned in the van Dijck patent has found considerable popularity. This, the pulsed sieve-plate column is widely used in the atomic energy program in a variety of sizes. The sieve-plates remain stationary while an up-and-down motion is superimposed on the countercurrent flow of the two liquid phases by a pulsator which forces liquid in and out of the bottom of the column. If the holes in the plates are sufficiently small so that a high degree

of dispersion is obtained, then liquid cannot flow countercurrently through the column unless the pulse is operating. This fact offers certain advantages, since during a temporary shut down of the pulsator, unextracted liquid cannot get through the column.

Numerous articles on pulsed sieve-plate columns have appeared in recent literature. Foremost among these is the report by Sege and Woodfield (3), who worked on the separation of uranyl nitrate. These men, operating both a three-inch and an eight-inch diameter column, investigated a great number of the variables involved in the operation of sieve-plate columns. Many of the results that seem typical of this type of contactor are recorded in Table I.

Of possible interest in special applications is a subsequent report (4) on a 23.5-inch column. This shows that where channeling is due to the liquid at the top of the column being heavier than that at the bottom, channeling may be prevented by means of a louver-plate redistributor.

An excellent article prepared by Wiegandt and von Berg (5), presents some of the particular problems involved in the operation of both packed and sieve-plate pulsed columns. While this report does not present any actual data, a later report prepared by Chantry (6), for a doctoral thesis under the direction of these two men gives the results of runs on a 1.57-inch diameter pulsed sieve-plate column. Typical data from their report are tabulated in Table II.

Cohen and Beyer (7), give results obtained on the performance of a one-inch diameter sieve-plate column, extracting boric acid from isoamyl alcohol into water. They obtained values of a contact stage as low as 9.9 inches under certain pulse conditions. Some of these runs are tabulated in Table III.

TABLE I

PERFORMANCE OF A 3" COLUMN WITH 54 SIEVE-PLATES 2" APART AND .125" HOLES HAVING 23% FREE AREA, USING 30 VOL % TRIBUTYL PHOSPHATE AND 70 VOL % CARBONTETRACHLORIDE WITH URANYL NITRATE AS THE SOLUTE AND WATER. HEIGHT OF PLATE SECTION 108".
DATA FROM G. SEGE AND F. W. WOODFIELD

Run No	Phase Dispersed	Total Inches Pulse	Cycles per Minute	Volumetric Flow Rate Cu Ft/Hr/Sq Ft Light Phase	Volumetric Flow Rate Cu Ft/Hr/Sq Ft Heavy Phase	Solute Conc Lb Moles/Cu Ft Light In	Solute Conc Lb Moles/Cu Ft Light Phase Out	Solute Conc Lb Moles/Cu Ft Heavy In	Solute Conc Lb Moles/Cu Ft Heavy Phase Out	HTU Feet	Plate Type
1	Organic	.5	90.0	26.73	53.46	.04990	--	0	--	0.8 a	st.steel
2	"	.9	63.3	26.73	53.46	.04990	--	0	--	0.6 "	"
3	"	1.5	40.0	26.73	53.46	.04990	--	0	--	0.7 "	"
4	"	.5	90.0	53.50	107.0	.04990	--	0	--	0.9 "	"
5	"	.9	63.3	53.50	107.0	.04990	--	0	--	0.8 "	"
6	"	1.5	33.3	53.50	107.0	.04990	--	0	--	0.7 "	"
7	"	.5	100.0	127.60	72.9	--	--	.02495	--	1.1 o	"
8	"	1.0	50.0	127.60	72.9	--	--	.02495	--	1.3 "	"
9	"	1.0	80.0	127.60	72.9	--	--	.02495	--	1.2 "	"
10	Aqueous	.5	80.0	42.54	24.3	--	--	.02495	--	1.2 "	fluorothene
11	"	1.0	50.0	42.54	24.3	--	--	.02495	--	0.9 "	"
12	"	--	--	53.50	107.0	.04990	--	0	--	1.4 a	st. steel
13	Organic	--	--	89.10	178.2	.04990	--	-	--	0.6 "	"
14	Aqueous	--	--	53.50	107.0	.04990	--	-	--	0.7 "	fluorothene
15	Organic	--	--	49.50	89.1	.04990	--	-	--	0.8 "	"
16	Aqueous	--	--	127.60	72.9	0		.02495	--	1.0 o	st. steel
17	Organic	--	--	255.20	145.8	--	--	.02495	--	1.0 "	"
18	Aqueous	--	--	110.60	63.2	--	--	.02495	--	0.9 "	fluorothene
19	Organic	--	--	170.10	97.2	--	--	.02495	--	1.8 "	"
20	Aqueous	--	--	170.10	97.2	--	--	.02495	--	0.9 "	dual
21	Organic	--	--	170.10	97.2	--	--	.02495	--	1.1 "	"
22	--	--	--	59.40	118.8	.04990	--	0	--	0.7 a	st. steel

TABLE I (Continued)

Run No	Phase Dispersed	Total Inches Pulse	Cycles per Minute	Volumetric Flow Rate Cu Ft/Hr/Sq Ft Light Phase	Volumetric Flow Rate Cu Ft/Hr/Sq Ft Heavy Phase	Solute Conc Lb Moles/Cu Ft Light Phase In	Solute Conc Lb Moles/Cu Ft Light Phase Out	Solute Conc Lb Moles/Cu Ft Heavy Phase In	Solute Conc Lb Moles/Cu Ft Heavy Phase Out	HTU Feet	Plate Type
23A	--	--	--	33.00	59.4	.04990	--	0	--	0.7 a	st. steel
24	--	--	--	170.10	97.2	0	--	.02495	--	1.0 o	"
25A	--	--	--	96.40	55.1	0	--	.02495	--	0.8 "	"
26	--	--	--	124.00	27.5	.00006	--	0	--	-- a	"
27A	--	--	--	87.50	19.5	.00006	--	0	--	-- "	"
28	--	--	--	53.50	107.0	0	--	.00031	--	2.5 o	"
29A	--	--	--	29.70	59.4	0	--	.00031	--	1.0 "	"
*30b	Aqueous	--	--	99.1	79.1	.00686	--	0	--	1.7 "	"
*31	"	--	--	98.8	79.1	.00686	--	0	--	1.5 "	"
*32c	"	--	--	128.0	76.9	0	--	.01123	--	1.1 a	"
*33	"	--	--	167.1	100.3	0	--	.01123	--	1.1 "	"
*34d	"	--	--	206.1	123.7	0	--	.01123	--	-- "	"
*35c	"	--	--	69.3	55.5	.00686	--	0	--	1.5 o	"
*36	"	--	--	99.0	79.2	.00686	--	0	--	1.5 "	"
*37d	"	--	--	99.0	79.2	.00686	--	0	--	-- "	"
38	Organic	--	--	170.1	97.2	0	--	.02495	--	1.0 "	"
39	"	--	--	113.4	64.8	0	--	.02495	--	1.7 "	"
*40	Aqueous	--	--	211.7	127.0	0	--	.01123	--	1.8 a	"
*41	"	--	--	167.1	100.3	0	--	.01123	--	-- "	"
*42	"	--	--	167.1	100.3	0	--	.01123	--	1.1 "	"
*43	"	--	--	69.3	55.5	.00686	--	0	--	1.8 o	"
*44	"	--	--	69.3	55.5	.00686	--	0	--	1.9 "	"
*45	"	--	--	99.0	79.2	.00686	--	0	--	1.5 "	"

Run No	Phase Dispersed	Total Inches Pulse	Cycles per Minute	Volumetric Flow Rate Cu Ft/Hr/Sq Ft Light Phase	Heavy Phase	Solute Conc. Lb Moles/Cu Ft Light In	Phase Out	Heavy In	Phase Out	HTU Feet	Plate Type
46	Organic	.5	120	126.3	74.3	0	--	.02495	--	1.4 o	st. steel
47	"	.5	120	126.3	74.3	0	--	.02495	--	2.5 "	"
48	"	1.0	70	126.3	74.3	0	--	.02495	--	1.0 "	"
49	"	1.0	70	126.3	74.3	0	--	.02495	--	2.0 "	"
50	"	1.0	80	133.6	66.8	0	--	.02495	--	1.2 "	"
51	"	1.0	80	126.3	74.3	0	--	.02495	--	1.6 "	"
52	"	1.0	55	49.0	98.0	.04990	--	0	--	0.8 a	"
53	"	.9- 1.0	55	49.0	98.0	.04990	--	0	--	0.8 "	"
54	"	.9- 1.0	70	127.6	72.9	0	--	.02495	--	1.0 o	"
55	"	.9- 1.0	70	127.6	72.9	0	--	.02495	--	1.5 "	"
*56	"	.9- 1.0	55	125.4	75.2	0	--	.01123	--	1.0 a	"
*57	"	.9- 1.0	55	125.4	75.2	0	--	.01123	--	1.9 "	"
*58	"	.9- 1.0	55	167.0	100.2	0	--	.01123	--	1.6 a	"
*59	"	.9- 1.0	55	167.0	100.2	0	--	.01123	--	2.0 "	"
*60	"	.9- 1.0	45	59.4	47.5	.00686	--	0	--	1.2 o	"
*61	"	.9- 1.0	45	59.4	47.5	.00686	--	0	--	1.5 "	"

A -- .06" holes 21% free area.
a -- HTU values are based on aqueous phase.
o -- HTU values are based on organic phase.
b -- .1875" holes 23% free area.
c -- .1250" holes 10% free area.
d -- .1250" holes 40% free area.
* -- system refined keroscene - uranyl nitrate - water.

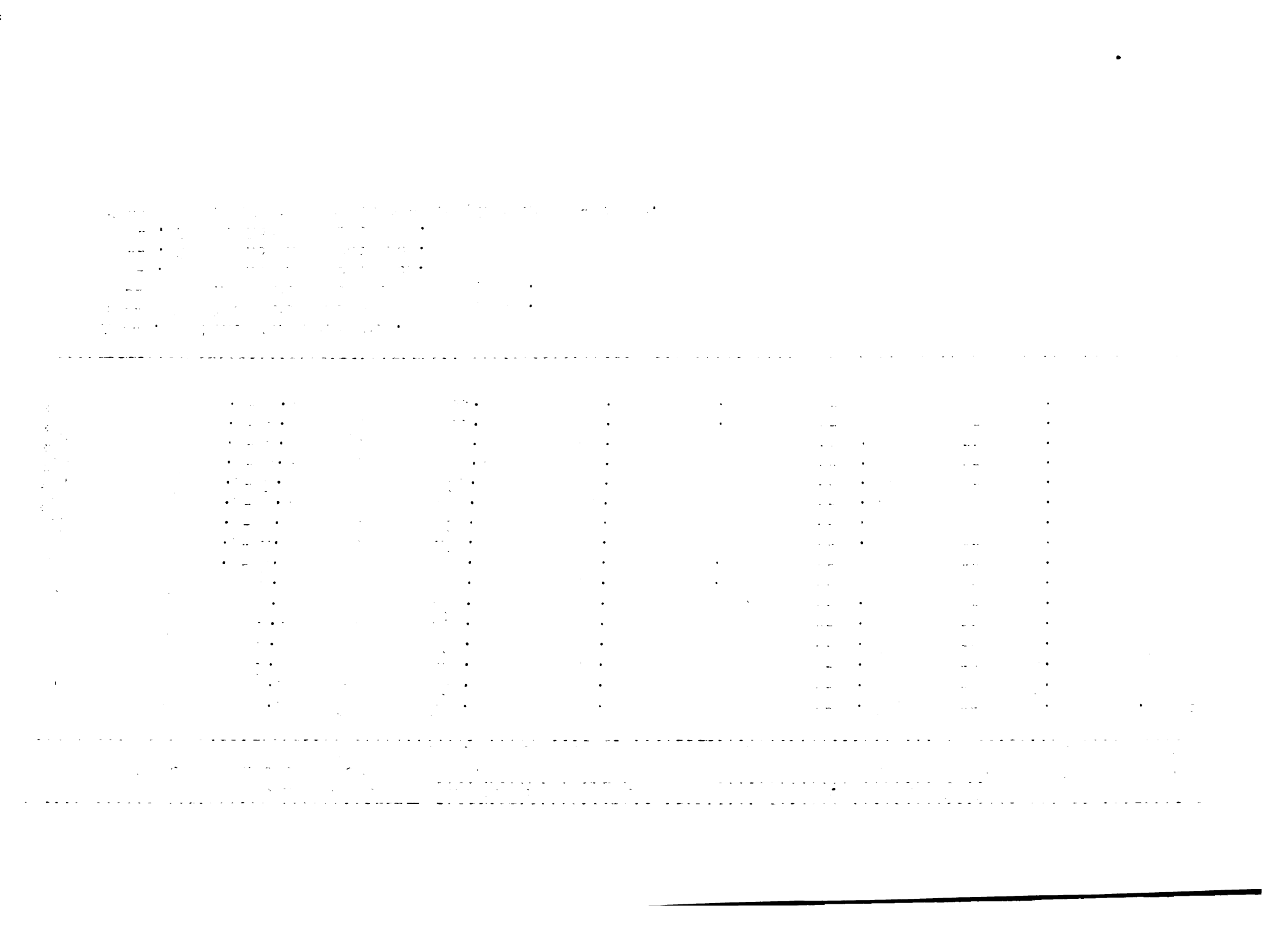

TABLE II

PERFORMANCE OF A 1.575" COLUMN WITH 11 SIEVE-PLATES - 3" APART AND 24 - 0.0469" HOLES EXTRACTING ACETIC ACID FROM WATER WITH METHYL ISOBUTYL KETONE. HEIGHT OF PLATE SECTION 33". DATA FROM W. A. CHANTRY, R. L. von BERG, AND H. F. WIEGANDT

Run No	Phase Dispersed	Total Inches Pulse	Cycles per Minute	Volumetric Flow Rate Cu Ft/Hr/Sq Ft Light Phase	Volumetric Flow Rate Cu Ft/Hr/Sq Ft Heavy Phase	Solute Conc Lb Moles/Cu Ft Light Phase In	Solute Conc Lb Moles/Cu Ft Light Phase Out	Solute Conc Lb Moles/Cu Ft Heavy Phase In	Solute Conc Lb Moles/Cu Ft Heavy Phase Out	HTU Feet	HETS Feet
20	Organic	0.0787	47	8.67	8.35	0.00500	0.1092	0.1914	0.06448	--	0.555
21	Organic	0.0787	47	14.73	8.21	0.00250	0.0900	0.2101	0.01872	--	0.518
22	Organic	0.0787	47	11.68	7.55	0.00250	0.1167	0.2111	0.02808	--	0.360
*23	Organic	0.0787	54	8.52	8.65	0.00333	0.1092	0.2122	0.08320	--	0.979
*24	Organic	0.1181	29	13.90	8.30	0.00250	0.0750	0.2028	0.03848	--	1.038
*25	Organic	0.1181	29	7.27	15.99	0.00250	0.1100	0.2028	0.13416	--	1.015
*26	Organic	0.1575	29	16.67	18.92	0.00167	0.1134	0.2038	0.08944	--	0.844
*27	Organic	0.2362	29	7.20	8.74	0.00333	0.1034	0.2018	0.10608	--	1.322

* -- 24 holes 0.0781-inch diameter.

TABLE III

PERFORMANCE OF A 1" COLUMN WITH TEN LUCOFLEX SIEVE-PLATES 2" APART AND .040" HOLES
9% FREE AREA, EXTRACTING BORIC ACID FROM ISOAMYL ALCOHOL WITH WATER.
DATA FROM R. M. COHEN AND G. H. BEYER

Run No	Phase Dispersed	Total Inches Pulse	Cycles per Minute	Volumetric Flow Rate Cu Ft/Hr/Sq Ft		Solute Conc Lb Moles/Cu Ft				HTU Feet	HETS Feet
				Light Phase	Heavy Phase	Light Phase In	Light Phase Out	Heavy Phase In	Heavy Phase Out		
1	Organic	.35	17	3.89	3.89	.00807	--	0	--	1.02 o	1.77
2	"	"	"	15.54	"	"	--	"	--	1.91 "	1.79
3	"	"	"	46.62	"	"	--	"	--	2.72 "	1.35
4	"	"	"	5.83	9.71	"	--	"	--	.82 "	1.75
5	"	"	"	29.14	"	"	--	"	--	2.18 "	2.37
6	"	"	"	5.83	19.43	"	--	"	--	4.93 "	12.83
7	"	"	"	16.39	"	"	--	"	--	1.48 "	2.74
8	"	.20	72	9.71	3.89	"	--	"	--	.98 "	1.08
9	"	"	"	29.14	"	"	--	"	--	1.55 "	.98
10	"	"	"	58.28	"	"	--	"	--	2.18 "	.93
11	"	"	"	9.71	9.71	"	--	"	--	.65 "	1.09
12	"	"	"	29.14	"	"	--	"	--	1.09 "	1.13
13	"	"	"	58.28	"	"	--	"	--	1.42 "	1.01
14	"	.15	"	19.43	3.89	"	--	"	--	1.90 "	1.53
15	"	.40	"	19.43	"	"	--	"	--	1.13 "	.96
16	"	.15	35.5	"	"	"	--	"	--	2.27 "	1.85
17	"	.45	"	"	"	"	--	"	--	1.21 "	1.03
18	"	.20	72	29.14	9.71	"	--	"	--	--	1.13
19	Aqueous	"	72	"	"	"	--	"	--	--	2.42
20	Organic	.45	35.5	"	"	"	--	"	--	--	.83
21	Aqueous	"	35.5	"	"	"	--	"	--	--	2.06

o -- HTU values based on organic phase.

Griffith, Jasny, and Tupper (8), used a two-inch diameter sieve-plate column, 140 inches long, in a region of high-amplitude frequency range, separating cobalt salts from nickel salts for the Atomic Energy Commission. Their data were somewhat erratic, and the points which they plotted showed large deviations from the expected curves. This was probably due to the rather complicated multicomponent system with which they had to work.

Belaga and Bigelow (9), reported data obtained from a sieve-plate column 45 inches long and 1.5 inches in diameter with one-inch spacings. For this work, acetic acid was extracted from the dispersed aqueous phase using methyl isobutyl ketone as the extractant. Graphs were presented showing the variation in HTU_{OE} (Height of a transfer unit*) with frequency at constant pulse, and the variation in HTU with pulse amplitude at constant frequency. The data, although certainly indicative of trends, showed considerable variation within a family of curves. HTU values were found to range from 2.63 to 6.25 inches.

Spray Columns Spray columns are another type of mixer-settler extractor which use only the energy imparted to the incoming streams and the density difference of the two phases for providing interfacial contact area. The dispersed phase is introduced into the column through one or more spray nozzles. This phase then travels through the length of column, remaining broken up into droplets. Essentially all of the mass transfer takes place near the spray nozzle, and increasing the length does not give appreciably greater mass transfer. Some spray towers are filled with packing such as Raschig rings or

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* Subscript "OE" refers to over-all transfer units based on the extract phase.

Berl saddles; these give more interfacial area, probably because of the extension of one of the phases into a film over the packing surfaces. Although spray columns containing packing are more efficient than those without, the number of stages is increased only by about one theoretical plate for six or more feet of packing height.

Pulsed Spray Columns An interesting report describing a pulsed spray column has been published by C. J. Billerbeck et al (10). These investigators used a 1.5-inch column to extract acetic acid from water with methyl isobutyl ketone. The results of several of their runs are tabulated in Table IV.

Packed Columns The packed column extractor has a complex mechanism of mass transfer. In these units mass transfer takes place not only by extended films on the packing surfaces but also through direct interfacial contact of droplets of the two phases. Efforts to increase the packing surface by using finer packing usually results in greater investment, because the capacity is reduced and the packing weight is more per cubic foot. Actually an optimum size occurs in any given column; packing smaller than the optimum is uneconomical because of high capital investment, and larger packing provides too little surface area for mass transfer. Packed columns are simple to build and easy to operate. The packing can be of almost any material and shape such as Raschig rings, Berl saddles, Lessing rings, spheres, Intalox saddles, spiral rings, or even gravel or cinders. About the only restriction is that the packing should be chemically inert to the liquids being contacted. It may further be pointed out that, as an approximation, the amount of flow varies inversely with the surface area of the packing. Besides the packing

TABLE IV

PERFORMANCE OF A 1.5" PULSED SPRAY COLUMN EXTRACTING ACETIC ACID FROM WATER WITH METHYL ISOBUTYL KETONE.
DATA FROM C. J. BILLERBECK, J. FARQUHAR III, R. C. REID, J. C. BRESEE and A.S. HOFFMAN.

Run No	Phase Dispersed	Total Inches Pulse	Cycles per Minute	Volumetric Flow Rate Cu Ft/Hr/Sq Ft Light Phase	Volumetric Flow Rate Cu Ft/Hr/Sq Ft Heavy Phase	Solute Conc Lb Moles/Cu Ft Light In	Solute Conc Lb Moles/Cu Ft Light Phase Out	Solute Conc Lb Moles/Cu Ft Heavy In	Solute Conc Lb Moles/Cu Ft Heavy Phase Out	HTU Feet	HETS Feet
1	Organic	0	0	67.08	26.49	.0025	.0575	.1664	.0187	2.12 o	1.585
2	"	0	0	67.74	40.37	"	--	"	--	1.38 o	--
3	"	0	0	64.71	60.00	"	--	"	--	1.36 o	--
4	"	.4375	200	65.27	57.70	"	--	"	--	1.02 o	--
5	"	"	300	65.59	57.73	"	--	"	--	.26 o	--
6	"	"	200	64.75	38.27	"	--	"	--	1.34 o	--
7	"	"	300	65.05	37.37	"	--	"	--	1.01 o	--
8	"	"	400	65.29	37.52	"	--	"	--	.88 o	--
9	"	"	500	62.17	37.64	"	--	"	--	.96 o	--

o -- HTU values based on aqueous phase.

and a long vertical tube, only packing supports and distributors are needed for the construction of these columns.

A great many studies have been made on packed columns to determine the effect of which phase wets the packing, how the choice of continuous phase affects the efficiency, etc. Many of the packed columns reported have heights of a transfer stage from 5.0 to 20 feet. Smaller heights of a transfer stage are sometimes encountered in systems with good transfer characteristics, particularly when fine packing and small column diameters are used. Large packed columns are noted for channeling. Murch (11), claims that the height of a contact stage is approximately proportional to the column diameter.

Pulsed-Packed Columns Because of the inherent deficiencies of packed columns, it seemed like a natural step to go from packed columns to pulsed-packed columns. The packing could then act as an inmovable stirrer and the liquids, as they move up the column on the upstroke of the pulse, could smash against the packing and break up into fine droplets causing a large increase in interfacial area. This should in no way affect the continuous countercurrent flow of the two phases. Furthermore, the pulse could be supplied by a piston or bellows external to the column, for easy access. It is readily apparent that this up-and-down motion of the liquid should at least markedly decrease channeling, if not eliminate it altogether. Because the stroke of the piston must normally follow a sine wave, there are periods during the cycle when coalescence may take place. Coalescence followed by redistribution into drops with new surfaces plays an important part in efficient mass transfer.

Among the first unclassified investigations made on pulsed-packed columns was that of Feick and Anderson (12), who used a 1-1/2-inch column with 3/8-inch ceramic Raschig rings and 1/2-inch McMahon saddles to investigate two different systems. The systems they studied were the extraction of benzoic acid from toluene with water, and the extraction of acetic acid from toluene with water. According to the authors the efficiency of the columns was increased in some runs so the height of a theoretical contact was improved from nearly 12 feet down to about 7 inches. The authors attributed this improvement to an increased area of contact between the two phases under agitation rather than to an increase in mass transfer coefficient. They concluded this from experiments in which they replaced one solute whose major diffusional resistance lies in one phase with a solute whose resistance lies in the other; if the same improvement in extraction was found in both cases, it must be due to increased area. The results of several of these runs have been tabulated in Table V.

Wiegandt and von Berg (5), published a summary of the work done on pulsed-packed columns up until 1954. In this article they reviewed the work done by two engineering students at Cornell University, P. C. Goundry and V. M. Romero. The authors tried to correlate data obtained by these men with that obtained by Feick and Anderson. They were able to draw some general conclusions and to offer a comprehensive explanation of what actually occurs inside pulse columns. Their conclusions will be given later on in this report where they can be compared with the conclusions drawn by this investigator.

TABLE V:

PERFORMANCE OF A 1.4375" COLUMN PACKED WITH 0.5" MCMAHON SADDLES EXTRACTING BENZOIC ACID FROM TOLUENE WITH WATER. PACKING HEIGHT 36.25". TEMP 28.9°C.
DATA FROM G. FEICK AND H. M. ANDERSON

Run No	Phase Dispersed	Total Inches Pulse	Cycles per Minute	Volumetric Flow Rate Cu Ft/Hr/Sq Ft Light Phase	Volumetric Flow Rate Cu Ft/Hr/Sq Ft Heavy Phase	Solute Conc Lb Moles/Cu Ft Light Phase In	Solute Conc Lb Moles/Cu Ft Light Phase Out	Solute Conc Lb Moles/Cu Ft Heavy Phase In	Solute Conc Lb Moles/Cu Ft Heavy Phase Out	HTU Feet	HETS Feet
1	Toluene	0	0	81.3	76.2	.00943	.00913	0.0	.000281	7.50 a	--
2	"	.1875	750	33.8	35.7	.00954	.00875	"	.000815	.93 a	.64
3	"	"	500	61.8	51.6	.00954	.00870	"	.000834	.78 a	--
4	"	"	250	33.2	41.2	.00954	.00868	"	.000748	1.44 a	--
5	"	.0937	1000	31.0	34.7	.01131	.01035	"	.000890	.92 a	--
*6	"	"	1000	57.6	55.3	.01131	.01040	"	.000770	1.63 a	--
*7	"	0	0	19.1	23.6	.01085	.01032	"	.000530	3.16 a	--
*8	"	0	0	14.1	14.3	.01085	.01027	"	.000587	10.20 a	--
*9	"	.1875	200	17.4	19.8	.01088	.00998	"	.000801	.673a	--
*10	"	"	300	13.8	13.0	.01088	.00993	"	.000801	.659a	--
*11	"	"	400	8.58	7.87	.01088	.00990	"	.000806	.558a	--
*12	"	0	0	1.72	23.50	.01095	.00849	"	.000155	13.40 a	12.08
*13	"	.1875	400	1.78	22.90	.01095	.00951	"	.000752	.592a	.636
*14	"	"	300	4.23	19.50	.01095	.00763	"	.000784	.837a	--
15b	"	0	0	21.20	28.20	.07540	.00628	"	.05470	1.14 o	1.316
16b	"	.1875	250	23.20	28.20	.07540	.00017	"	.0623	.484o	--
17b	"	.3750	250	23.40	29.70	.07540	.00004	"	.0625	.371o	--
18b	"	"	400	24.60	28.50	.07540	.00003	"	.0677	.354o	--
19b	"	0	0	51.80	8.50	.0660	.00966	"	.320	1.090o	--
20b	"	.3750	200	53.20	8.90	.0660	.00194	"	.374	.572o	--
21b	"	.1875	400	52.10	8.70	.0660	.00068	"	.374	.422o	--
22b	"	.1875	600	52.10	8.40	.0660	.00002	"	.407	.185o	--

a -- HTU values are based on the aqueous phase.
o -- HTU values are based on the organic phase.
* -- .374" Raschig rings.
b -- Solute changed to acetic acid.

D. M. Schuler (13), working on a master's program at Michigan State University under the direction of Dr. C. M. Cooper, investigated the effect of pulsation on a two-inch packed column. This work was begun in 1952 and finished in 1953, at which time the present author began his investigations. Schuler, working with the system carbon tetrachloride, acetone, and water, concluded that the height of a theoretical contact was reduced by pulsation from 23.6 inches to 6.3 inches. Some of his experimental data are listed in Table VI.

A report on pulse columns was published by J. D. Thornton (14), working for the Atomic Energy Research Establishment at Harwell, England. Using a 3-inch packed column, as well as a 3-inch sieve-plate column, he investigated the system water-toluene with acetone as the solute. He presented only a generalized graphical correlation of his results. Because this work was of unusual interest, it was hoped that the actual data could be made available and be included in the present correlation. Efforts to obtain these data have been unsuccessful.

In a report of the doctoral dissertation by Chantry, mentioned previously, data were also presented on the performance of a pulsed-packed column. Chantry claimed that, for a 1.57-inch column using the system methyl isobutyl ketone-acetic acid-water, the height of a theoretical contact can be lowered from 10.0 inches to 3.6 inches. Representative experimental runs appear in Table VII.

Table VIII lists the physical properties of the liquids used in the tabulations contained on the preceding pages.

TABLE VI

PERFORMANCE DATA OF A 2.062" COLUMN PACKED WITH .307" GLASS RASCHIG RINGS EXTRACTING ACETONE FROM CARBONTETRACHLORIDE WITH WATER. PACKING HEIGHT 32". DATA FROM D. M. SCHULER.

Run No	Phase Dispersed	Total Inches Pulse	Cycles per Minute	Volumetric Flow Rate Cu Ft/Hr/Sq Ft Light Phase	Heavy Phase	Solute Conc Lb Moles/Cu Ft Light Phase In	Light Phase Our	Heavy Phase In	Heavy Phase Out	HTU Feet	HETS Feet
1	Organic	.11	125	20.34	29.12	0	.01503	.01375	.00332	--	1.50
2	"	0	"	"	"	"	.01453	.01484	.00473	--	2.00
3	"	.17	"	"	"	"	.01721	.01488	.00294	--	1.25
4	"	.24	"	"	"	"	.01572	.01297	.00209	--	1.06
5	"	.32	"	"	"	"	.01509	.01154	.00106	--	.735
6	"	.51	"	"	"	"	.01918	.01400	.00071	--	.538
7	"	.35	"	5.04	27.74	"	.02015	.01129	.00762	--	1.76
8	"	"	"	18.31	16.07	"	.01397	.01653	.00064	--	.866
9	"	"	"	20.54	4.93	"	.00419	.01759	.00043	--	1.59
10	"	0	0	20.34	20.34	"	.01184	.01559	.00377	--	2.06
11	"	0	0	19.42	4.67	"	.00146	.01131	.00128	--	2.71
12	"	0	0	6.95	27.74	"	.01728	.00911	.00569	--	2.25

TABLE VII

PERFORMANCE OF 1.575" COLUMN PACKED WITH 0.25" PORCELAIN RASCHIG RINGS EXTRACTING ACETIC ACID FROM WATER WITH METHYL ISOBUTYL KETONE. PACKING HEIGHT 27.2".
DATA FROM W. A. CHANTRY, R. L. von BERG, and H. F. WIEGANDT

Run No	Phase Dispersed	Total Inches Pulse	Cycles per Minute	Volumetric Flow Rate Cu Ft/Hr/Sq Ft		Solute Conc Lb Moles/Cu Ft				HTU Feet	HETS Feet
				Light Phase	Heavy Phase	Light In	Phase Out	Heavy In	Phase Out		
1	Organic	.276	17	6.84	7.54	.00083	.1042	.2038	.10400	--	.750
2	"	.118	29	8.26	8.65	.00333	.1150	.1976	.07488	--	.545
3	"	.236	29	6.41	8.20	.00083	.1150	.1976	.09776	--	.692
4	"	.374	29	8.45	8.15	.00167	.1109	.2090	.05720	--	.542
5	"	.059	47	9.84	8.00	.00333	.1517	.1893	.07072	--	.703
6	"	.197	47	9.55	8.69	.00083	.1542	.1924	.06032	--	.567
7	"	.394	47	8.37	8.20	.00167	.1659	.2070	.06240	--	.683
8	"	.079	55	9.19	8.64	.00083	.1117	.2059	.05928	--	.547
9	"	.157	55	9.15	8.71	.00167	.1167	.2038	.05408	--	.378
10	"	.118	78	8.30	8.35	.00083	.1300	.2309	.06240	--	.500
11	"	.335	78	7.66	8.60	.00167	.1134	.2090	.08008	--	.692
12	"	.059	88	8.29	7.75	.00250	.1175	.1997	.05824	--	.369
13	"	.217	88	9.42	7.93	.00167	.1159	.2111	.05512	--	.492
14	"	.059	147	8.34	8.27	.00333	.1150	.1997	.04576	--	.343
15	"	.098	147	8.53	8.89	.00250	.1100	.1914	.05408	--	.380
16	"	.039	252	8.29	7.37	.00167	.1250	.2163	.04576	--	.275
17	"	0	0	14.17	14.40	.00167	.1025	.1882	.07072	--	.616
18	"	.236	47	14.17	13.90	.00333	.1134	.1997	.04680	--	.354
19	"	.236	47	12.60	14.15	.00333	.1084	.2018	.04992	--	.474

Table VIII is a list of the physical properties of the systems shown in Tables I, II, III, IV, V, VI, and VII. They are listed as nearly as possible at the temperature at which they were used in the investigations.

TABLE VIII

Liquid	Viscosity Centipoises	Surface Tension Dynes/cm	Temp °C	Specific Gravity	Interfacial Tension With Water Dynes/cm
Toluene	0.526	27.4	30	0.855	36.1
Toluene	0.590	28.5	20	0.866	36.1
Water	0.800	71.18	30	1.0	--
Methyl Isobutyl Ketone	0.546	25.40	25	0.8017	10.7
30 vol % tributyl phosphate 70 vol % carbon-tetrachloride	--	--	--	1.4	--
Refined Keroscene	--	--	--	0.85	--
Refined Keroscene	--	--	--	0.81	--
Isoamyl Alcohol	8.0	23.8	20	0.81	5.0
Carbontetrachloride	9.58	26.95	20	1.595	45.0

Purpose

It was the over-all purpose of this investigation to determine a basis for designing pulsed-packed columns from a minimum of experimental data. To do this, methods should be found to predict HETS and limiting capacities, possibly from experimental data on small laboratory columns. A number of experimental investigations were proposed either at the start or during the course of the investigation. These include the effect of the following factors on flooding velocity:

1. column diameter
2. packing density
3. flow ratio
4. column height
5. pulse amplitude
6. pulse frequency
7. interface level
8. direction and rate of mass transfer

They also include the effect on HETS of the factors listed below:

1. column diameter
2. packing density
3. throughput rate
4. flow ratio
5. pulse amplitude
6. pulse frequency
7. liquid inlets

Limitations and Scope This report confines itselt to those variables most important to the design and operation of a pulse column. It makes no attempt to go into many details which may

in turn be calculated from present-day knowledge.

A list of the most important variables that would normally be encountered in a pulsed column investigation are given below:

1. column diameter
2. column height
3. packing shape and size
4. ratio of packing diameter to tower diameter
5. material of construction of packing
6. solvent-solute system
7. flow ratio of the two phases
8. end construction, and its accompanying end effects
9. fraction of the total volumetric throughput
10. pulse amplitude
11. pulse frequency
12. which phase, if either is continuous
13. wetting characteristics of packing
14. packing density
15. packing support and fraction of free area
16. direction of mass transfer
17. concentration of solute in the two phases
18. form of the pulse wave

Using only 3 values of each variable and investigating all possible combinations would require 3^{18} or 130,000,000 individual experiments. Since an average time of three hours is required for each experiment, this would require 390,000,000 hours, or at a normal working year of 2,080 hours, this is 187,600 years. Fortunately such a number of experiments is not necessary to be able to establish

with a high degree of certainty how some of these variables change the column operation. On the other hand, it is not difficult to understand why this investigation makes no attempt to claim completeness.

The experimental work here has been limited to:

a. one type and diameter of packing

b. one solvent-solute system

c. one kind of tube construction

d. one pulse wave form

e. one type of packing support

Furthermore, all of the possible combinations of the rest of the variables were not investigated but only those combinations which seemed most significant toward accomplishing the purpose of this work. All of these separate variables were investigated to some extent, but in a few cases only qualitative or limited quantitative data were obtained.

APPARATUS AND PROCEDURE

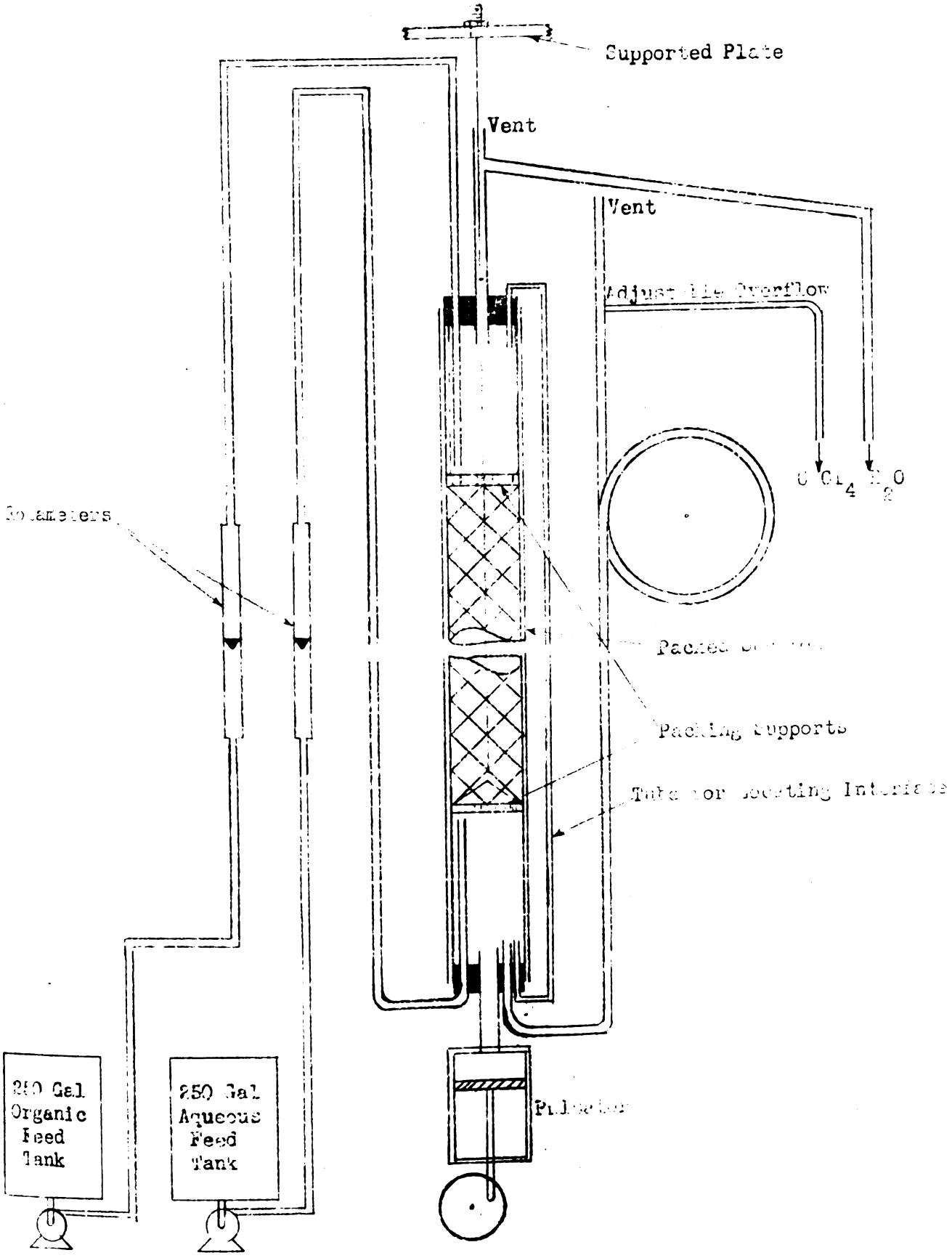
A schematic representation of the experimental pulse columns is given in Figure 1. This represents essentially the three different columns built, with the exception that the 3.32-inch diameter column has expanded chambers at both ends of the column so that an area is provided for the superficial velocity of the outgoing phase to decrease (see Figure 3). This decrease in velocity is reported as necessary by Blanding and Elgin (15), to prevent entrainment of the entering phase in the outgoing stream. Figure 2 is a photograph of the 2.127-inch column, and Figure 3 shows the 3.32-inch column.

In this investigation, 8-mm lime-glass Raschig rings were used as packing for all of the experiments. The characteristics of these are given in Appendix I. The 2.127-inch column held about 3 pounds of packing when filled to a height of 30 inches. The 3.32-inch column held about 25 pounds of packing when filled to a height of 105 inches. The exact height and weight of packing varied with the procedure used for settling the packing.

The packing supports were 1/4-inch high stainless steel rings cut from tubes with 1/4-inch wall thickness. Strands of No. 16 B & S gage nichrome wire were silver soldered across the rings at intervals of 0.30 inches. This made a wire grid for the packing to rest on which had 50% free area. A packing "support" was also placed on top of the packing to keep it from moving up with the pulse stroke. This was held in place by four rods extending to the top of the column. A wire passed through the center of the packing and fastened to the bottom support. A threaded bolt fastened to the end of the

Fig. 9 A

SCHEMATIC DRAWING OF PULSED PACKED COLUMN



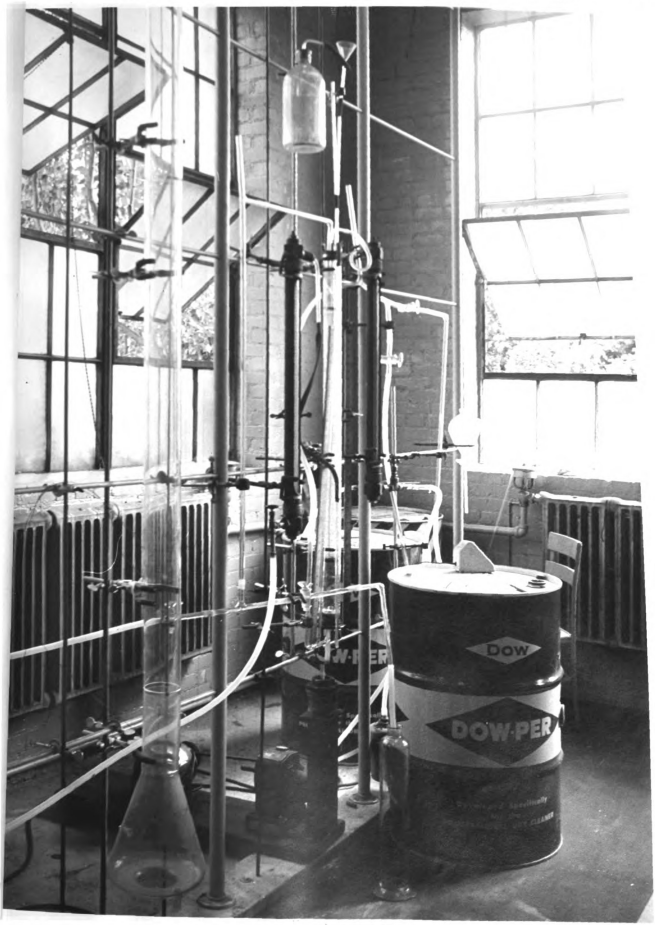
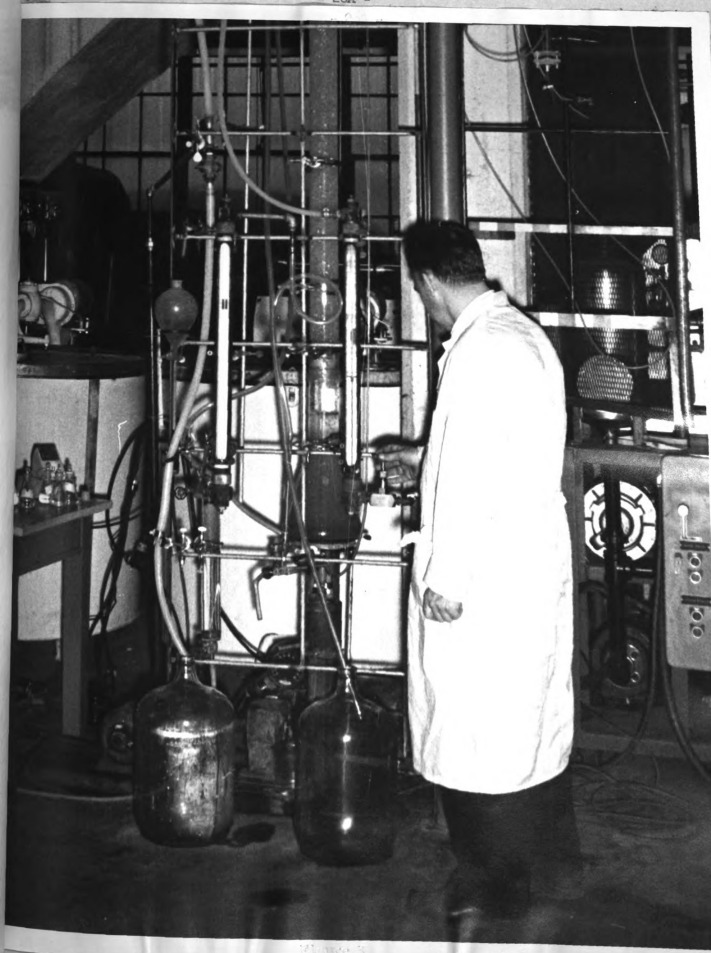


Figure 2



wire allowed the bottom support to be pulled upward in the column as the packing settled. This decreased the relative distance between the two supports and kept the packing from moving appreciably when the supports were fastened into place. The 3.32-inch column also had two packing supports constructed in the same way. These, however, had 61.7% free area.

The expanded end sections on the large column were designed with a tapered Venturi-like approach to the packed section and tapered from 3.32 inches in diameter to 9.5 inches in a height of 12 inches.

The water overflow was provided with a vent so no siphon action could occur to put a reduced pressure on the column. The water flowed from the top of the large column through 18-mm ID glass tubing to the drain. The small column used 14-mm ID glass tubing for the water exit. In each column the exit water line was made sufficiently large that little friction loss occurred to put back pressure on the column. The exit lines in both columns were designed for a superficial water velocity of less than one foot per second at maximum throughput.

The CCl_4 overflow in each column was provided with a vent to avoid siphoning action, and in addition was designed to permit variation of its height so that the interface level of the CCl_4 phase could be positioned at any desirable place in the column. The adjustable overflow leg discharged to a 250-gallon glass lined storage tank. The 3.32-inch column used 1/2-inch ID Tygon tubing and connected at the column to 12-mm glass tubing. The small column used 3/8-inch ID Tygon tubing and 8-mm ID glass tubing connections. The adjustable leg had to be repositioned each time the CCl_4 rate

was changed. In both columns the vents were large enough to handle the extra volume of liquid brought in by the upward pulse stroke, so it was not necessary to put in an expansion chamber at the top of the column.

The CCl_4 was pumped into the column by means of a stainless steel centrifugal pump* from a 250-gallon glass-lined tank. The CCl_4 flowed through 1/2-inch polyethylene tubing to filters that contained cheese cloth as a filtering media. From the filter, the CCl_4 passed through 1/2-inch stainless steel needle valves to rotameters. These rotameters were 3/4-inch size with three specially constructed floats to measure extremely small changes in volumetric throughputs. From the rotameters the CCl_4 entered the top of the column through 12-mm ID glass tubing for the large column, and 8-mm ID glass tubing for the small column. In both columns the CCl_4 was allowed to discharge directly onto the top packing support from the glass lines without using any type of special sparger or distributing weir.

The water was pumped into the bottom of the column through the same size pumps, rotameters, and tubing. The water was stored in a 250-gallon stainless steel tank and a 1/4-inch valve was used in the line leading to the column. Two D-11 stainless steel pumps were connected in series to both the CCl_4 and water feed lines when large flow rates of these feeds were required.

Two 250-gallon glass-lined tanks were used for the CCl_4. One tank was used as a collector for the CCl_4 discharged from the column, while the other was used as a feed tank. Both tanks contained built-in

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* Eastern Industries, Model D-11.

agitators with stainless steel blades. They were also jacketed for constant temperature control. However, it was felt that the room stayed at a temperature close enough to 25°C that temperature regulation was not necessary.

Tap water could not be fed to the column directly from the water main, because the water in the lines was under a pressure of 60 lb/sq.in. and contained a great deal of dissolved air. When the pressure was reduced, much of the air was released; this collected in the rotameters and made then inoperable. Therefore, the water was stored in a 250-gallon stainless steel tank where it was allowed to lose its dissolved air and also to come to room temperature.

The pulsator used at the beginning of these experiments was a brass bellows of approximately 2-1/4-inch ID and contained six corrugations. The pulsation was produced by an adjustable motor-driven eccentric. The bellows was compressed on the upstroke of the eccentric causing liquid to flow into the column. On the downstroke of the eccentric the bellows would open due to the weight of the liquid resting on it. The bellows was sealed at the top by a No. 11 rubber stopper. It was found that after several hours this rubber stopper would soften because it was in contact with CCl_4. When the rubber was softened it would move up with the upward stroke of the eccentric and down with the downstroke. This would markedly change the amount of pulse volume which the eccentric was originally set for. It was therefore decided to replace this unit with a reciprocating piston in a 4-inch ID nickel-plated cylinder.

The leather seal used for the new pulsator was a standard replacement part for a reciprocating water pump. Inside the cylinder and below the piston a small drain was installed through which the small amount of CCl_4 that leaked past the leather plunger was drained. The outlet at the top of the cylinder, leading into the large column, was 5/8-inch ID x 3/4-inch OD stainless steel tubing. The entire inner surface of the cylinder, where CCl_4 came in contact with the metal, was nickel plated to prevent corrosion. The amplitude on this type of pulsator was very reproducable and the measurements which were made at the beginning and end of each run were always found to be the same. The stainless steel tube leading out of the top of the pulsator was connected to another stainless steel tube of exactly the same size. The latter went through the rubber stopper into the bottom of the column and projected two inches into the column. The two stainless steel nipples were fastened together with a short section of 3/4-inch ID polyethylene tubing. The rubber stopper in the bottom of the column was covered with a 1/16-inch layer of mercury to prevent corrosion by the CCl_4. The entrance from the pulsator into the small column was glass tubing 12-mm ID x 15-mm OD x 5-inches length.

The form of the pulse wave supplied by the piston was essentially a sine wave, since the eccentric covered the 360° cycle in a uniform manner. A three-speed pulley was attached to the shaft of a 1/4-HP motor that had a speed of 1750 RPM. The 3-speed pulley on the motor shaft was in turn fastened to another 3-speed pulley by a V-belt. The second pulley drove the shaft of a speed reducer that had a speed reduction ratio of 10.4. This allowed the speed of the eccentric

to be varied from 65 to 215 RPM.

All of the materials of construction for these columns had to be corrosion resistant because CCl_4 saturated with water is extremely active and attacks the less resistant metals. Iron, steel, and galvanized surfaces are quite poor in this respect. Polyethylene becomes brittle after contact with CCl_4 for three to six months. Tygon appears to be slightly more resistant to CCl_4 but becomes brittle after approximately six-month exposure.

Solvent-Solute System The system carbon tetrachloride - water - acetone was selected primarily because at solute concentrations up to one percent the distribution coefficient is essentially constant. The components are also easily obtained and offer little fire hazard.

The experiments were always started with a mixture of carbon tetrachloride* containing approximately 1% by weight acetone**. The acetone was extracted from the carbon tetrachloride with tap water that had been allowed to lose its dissolved air and come to room temperature. The extract, after sampling to determine its acetone concentration, was discarded to the sewer. The raffinate, which was saturated with water, was sampled and discharged to a 250-gallon storage tank. When all of the feed solution had been used, the agitator in the storage tank was turned on for 30 minutes. At the end of this time the carbon tetrachloride solution was analyzed for acetone content and enough more acetone was added to bring the concentration back to approximately 1% for another run.

Analytical Procedures Several methods were tried for the quantitative analysis of acetone in water and in CCl_4. These methods all used the same basic step of titrating the HCl released when

* Dow technical grade.

** Merck C.P. grade

acetone reacts with hydroxylamine hydrochloride.

$$\begin{matrix} CH_3 \\ \diagdown \\ \quad C = O \\ \diagup \\ CH_3 \end{matrix} + HONH_2 \cdot HCl \qquad \begin{matrix} CH_3 \\ \diagdown \\ \quad C = NOH \\ \diagup \\ CH_3 \end{matrix} + HCl + H_2O$$

The method was first proposed by Hoepner (16), and later investigated more thoroughly by Marasco (17), who found that certain conditions had to be carefully controlled in order to obtain good results. Bennett and Donovan (18), did further work on this analysis. Bryant and Smith (19), proposed a method of analysis using a pyridine solution with bromophenol blue indicator to determine the HCL liberated. All of these methods were tried by this author and the one selected was essentially the one proposed by Bennett and Donovan.

In this method, 12 g. of hydroxylamine hydrochloride are added to 6000 ml of tap water. Sufficient methyl orange indicator (about 5 ml of saturated water solution) is added to give it a golden yellow color. Either acid or base is added to this solution to bring it to the neutral point. For the tap water at Michigan State University, 31 ml of 1.0 N HCl is required. Approximately 600 ml of this solution is then poured into each of two 1000-ml beakers. One of these beakers is considered the standard color, and to the other is added 20 ml of the solution to be analyzed. The HCl liberated by the acetone is titrated with 0.2 N alkali. Either NaOH or KOH can be used. The amount of alkali needed to bring the color back to that of the standard solution in the other beaker measures the amount of HCl liberated. This, of course, is directly proportional to the acetone present in the 20 ml sample.

Since the reaction only takes place in the water phase, it is necessary to supply vigorous agitation to the solution when CCl_4 is

being analyzed. Even in analyzing the water phase, this method takes several minutes because, even though the solution is initially titrated to the neutral point, the release of HCl is slow and more is usually given off after a few minutes standing. The time necessary for this analysis depends on the quantity of acetone originally present; about 10 minutes is required for the average determination.

A refinement of this procedure was brought about by the introduction of an electrometric titration apparatus. In this technique, the pH of the standard liquid is determined by a potentiometer. The liquid is constantly stirred by an electric stirrer provided with the apparatus. The standard solution is then removed and replaced with the solution to be analyzed. Alkali is added slowly and with constant agitation while the pH instrument indicates the acidity. Enough alkali is added to bring the pH back to that originally determined for the standard solution.

One note of caution should be mentioned when using this procedure. The 600 ml of hydroxylamine hydrochloride is intended to provide at least 50% in excess of the amount required for the acetone. However, if more concentrated acetone solutions are used or larger samples taken, then correspondingly larger amounts of the amine hydrochloride solution should to used.

The analytical procedure was tested over the entire range for which it was expected to be used in this investigation. These results were reproducible and checks for known acetone concentrations were satisfactory.

The following is typical of these checks: Four 10-ml samples of 0.174-normal aqueous solution of acetone were analyzed; two in

the presence of 20 ml of carbon tetrachloride and two in water. The samples were placed individually on the electrometric titration apparatus. The samples in carbon tetrachloride used 38.5 ml and 38.8 ml of 0.0454 N sodium hydroxide, while those in water used 38.4 and 38.6 ml. These values gave a maximum error of 1.15% for the 1.74 millimols present in the original 10-ml samples. This agreement was considered to be excellent for the proposed investigation.

Operating Procedure To begin a series of extraction runs, the column was first filled with water, then Raschig rings were poured into the top of the column and allowed to fall down through the water and settle on the bottom packing support. When the rings had filled the column to the predetermined height, the top packing support was put in place and the top rubber stopper was fastened in to prevent the upper packing support from moving. Only unpulsed runs could be made using this procedure. If it were desired to make pulsed runs, the upper packing support was left off and the water in the column was replaced with CCl_4. Then the pulse was turned on and allowed to run for a period of time depending on the degree of settling or packing density desired. The reason for filling the column with CCl_4 for settling the packing can easily be seen if one recalls that CCl_4 has a density of 1.59 g/ml and lime glass has a density of 2.2 g/ml. Because the density difference is much less between glass and CCl_4 than it is between glass and water, the rings are more mobile and free to rise and fall with the pulse stroke when immersed in CCl_4. When the packing had reached the desired density, which could be determined by weighing the amount

of rings that were added and knowing the volume they occupy, the top packing support could be put in place and fastened with the rubber stopper.

A long wire, fastened to the bottom packing support and running up through the column to a stationary plate above, was tightened by turning a nut on a threaded bolt fastened to the end of the wire. This had the effect of raising the bottom packing support and clamping the packing in a non-movable position.

A typical settling cycle for the 3.32-inch column involved the pulsator being set at 10-mm amplitude and 65 RPM and allowed to run for 12 hours. At the end of this time the frequency was turned up to 125 RPM and the pulsator was allowed to run for an additional three hours. The packing density changed from 44.5 to 49.8 lb/cu ft during this period.

The pulse amplitude referred to in this report is the total millimeters of travel, or the sum of the up and down stroke measured in an empty cross-section of the column. The piston pulsator was capable of 50 mm of amplitude, but it was never set for more than 10.5 mm because it was feared that the glass column was not of sufficient strength to withstand this much pulsed volume. In fact, four end sections were broken during this investigation.

The CCl_4, which contained approximately 1 weight percent acetone, was pumped from the 250-gallon mixing tank through the rotameters and into the top of the column. The CCl_4 was previously saturated with water so there was no gain in volume of the CCl_4 flowing through the column. On the other hand, the water was not saturated with CCl_4 in the feed tank, but the curvature caused in the operating line due to the increase in volume of the water phase was insignificant.

It should be pointed out that the rotameters, although calibrated for throughput, were never used for measuring the flow through the column but were only used to indicate any change in the volume of flow that occurred during a run. Rates were measured by collecting the two outgoing phases in 5-gallon bottles for an interval of time that was measured with a stop watch. The two phases, after weighing, were then blended thoroughly and small samples were taken from each for analysis.

In most of the runs the column was operated at its maximum throughput capacity. To reach this maximum capacity the flow rate of one of the streams was raised in small increments until an interface appeared above the top packing support, below the bottom packing support, or in both regions. Such interfaces occur because all of the stream entering the column at that end cannot flow through the packing under the conditions of operation. If the adjustable CCl_4 overflow leg is kept in a high position, an interface will ordinarily appear only at the top, and if it is kept in a low position the interface will ordinarily appear only at the bottom. In the runs reported in this thesis, the overflow leg was adjusted to an intermediate point such that interfaces occurred at both ends simultaneously. Capacities obtained in this way were greater than those which would have been obtained if either the top or the bottom interface alone was allowed to limit the operation. The column was always run at such balanced flooding conditions except in a very few tests where the rate was decreased intentionally to see what effect this might have on HETS. The flooding runs are identified by the letter F and those below flooding by R.

The column was started by first turning on the pumps leading from the water and CCl_4 feed tanks. The needle valves in the two lines were used to adjust the volume of the flow of each phase through the apparatus. It was usually easier to set the CCl_4 rate at some given throughput on the rotameter in that line. The water rate was then gradually increased until the appearance of an interface at the top or bottom of the column. When this interface appeared, the height of the adjustable CCl_4 overflow leg was either raised or lowered until the interface disappeared and the water rate increased again. When interfaces appeared at both top and bottom the leg was readjusted; the lower interface was positioned by simultaneously increasing or decreasing the water rate. A time of 30 minutes to one hour was usually required for adjusting the interfaces to their necessary positions.

One of our requirements of column operation was that the interfaces should all remain immovable for at least one hour of constant operation before the readings and samples were taken. That is, if one of the interfaces started to move into or away from the packing, making it necessary to change the rate of flow of one of the phases, then the time had to be restarted. This was done to be sure that all of the contents of the column were in a steady state condition. Because of the expanded end sections on the 3.32 inch column, more time was required for it to reach steady state than was required for the small column.

If the run was to be pulsed, the pulsator, which had been previously adjusted for amplitude and frequency, was turned on after the appearance of the two interfaces. Because pulsing usually changed the throughput rates, it was almost always necessary to make more adjust-

ments in the rates of the two phases as well as changes in the height of the CCl_4 overflow leg. The pulsed column was again brought into balance by the method mentioned previously and operated for one hour before recording rates and taking samples.

The exit water and CCl_4 lines were each equipped with two 1/2-inch brass cocks. When the column had run the necessary time, the valve in the water line leading to the drain was closed and the valve leading to the 5-gallon weighing bottle was opened. The time to fill the bottle was measured by stopwatch, and after the quantity in the bottles was weighed, the rate was calculated. At the same time that the water sample was taken, a sample was also taken of the CCl_4. A 250-ml sample of each of these two phases was placed in a glass stoppered bottle to prevent the acetone from evaporating.

At the beginning of the sampling procedure, readings were taken on each of the rotameters, the height of the CCl_4 outlet leg was measured, and the height of the interface in the 6-mm glass level gage on the side of the column was read.

The small samples of each of the two phases were analyzed and the amount of acetone present recorded in millimoles/liter. Knowing the flow rates of the two phases and the amount of acetone in the incoming and outgoing streams made it possible to make a material balance around the column. If this material balance did not check within 5%, the results were discarded and the run repeated.

Accuracy and Reproducibility An attempt was made to determine what kind of accuracy could be expected from these experiments. This would, of course, be reflected in the answers obtained from a series of experiments which might be expected to give the same

answer. As an example, the HETS (height equivalent to a theoretical stage) appeared to be independent of the flow ratio when the column was operated at flooding in the manner of operation described in the preceding pages. When the HETS values found for a series of 10 runs on the small column, which were identical except for the flow ratios, were compared, they were found to have a maximum deviation from the mean of 16.21% and an average deviation of 8.11%. If the arithmetic mean of 58.72 inches can be considered as the correct answer, then the standard deviation is 5.57 inches.

A similar comparison was made of the HETS values obtained on the 3.32-inch column for 10 identical runs with varying flow ratios. Here the maximum deviation was found to be 20% and the average deviation 14.0%. If the arithmetic mean of 62.97 inches is the correct answer, the standard deviation is 8.25 inches.

The results quoted above are the most erratic results obtained, because they were made on unoriented packing. The packing appears to have a tendency to orient during the first series of experiments that are made after the packing density has been changed. This phenomenon will be discussed later under Experimental Results. It will be sufficient here to point out that after these initial trials had been made and the packing had become oriented, the results stabilized and were much more reproducible. Illustrative of this last point is a series of five trials made on the 3.32-inch column after the packing had become oriented. On these five experiments the maximum error was 0.138% while the average was 0.076%. The standard deviation calculated in the same manner as the others is 0.482 inches when the mean is 57.9 inches.

One of the reasons for the choice of the system water-acetone-carbon tetrachloride for use in these experiments is the fact that the equilibrium line is essentially straight in the dilute region. The line does, however, have some slight curvature. Assuming a straight line makes little if any difference where only a few theoretical plates are obtained, because in this case the operating and equilibrium lines are far apart.

With a large number of plates, the operating and equilibrium lines are close together. If they are straight and parallel they do not have to be as close at any one point as they would if considerable difference in shape or curvature existed. Small errors in positioning of the operating line, therefore, lead to much greater errors in the HETS when the NTS in the column is large, and this effect becomes even more important when the operating and equilibrium lines are not straight and parallel.

These factors were recognized and taken into account before beginning experimental work. The columns under pulse turned out to be much more efficient than had been originally anticipated, thereby giving a great many stages in the column. This necessitated making the operating line and equilibrium line essentially parallel. Actually, conditions were chosen to make the operating line somewhat closer to the equilibrium line at the dilute end, where small percentage errors in analysis would not have as much effect on the distance between the two lines. This was also convenient, because operating in this manner made it not so important to correct for curvature at the concentrated end.

Several runs were selected where the H_2O/CCl_4 flow ratio multiplied by the distribution coefficient had a value of 1.0 to 1.1. These values are tabulated below in Table IX.

TABLE IX

Dependence of Stages on Exit Raffinate Concentrations

Run No	Flow Ratio	Final Conc	Stages
F144	1.1	121.0	1.37
F146	1.1	28.3	7.30
F152	1.04	21.7	9.9
F152P	1.05	18.2	11.35
F153P	1.007	15.0	17.6
F152P	1.005	16.5	16.35
F137	1.02	113.0	1.77

Packing height, 101 inches, in 3.32-inch column
Packing density, 50.4 lb/cu ft
CCl_4/H_2O Flow Ratio, appoximately 2.1

When these values are presented graphically in Figure 4, it becomes evident that, when many stages are present, a very slight error in analysis of the raffinate stream would be greatly magnified in the number of plates.

Method of Calculation The data representing the efficiency of column operation can be expressed in either transfer units or theoretical stages. The latter has been used for the calculations in this thesis; however, many of the experimental results have been calculated using both concepts. The arguments for and against this choice have been left for presentation under the heading, Discussion of Results.

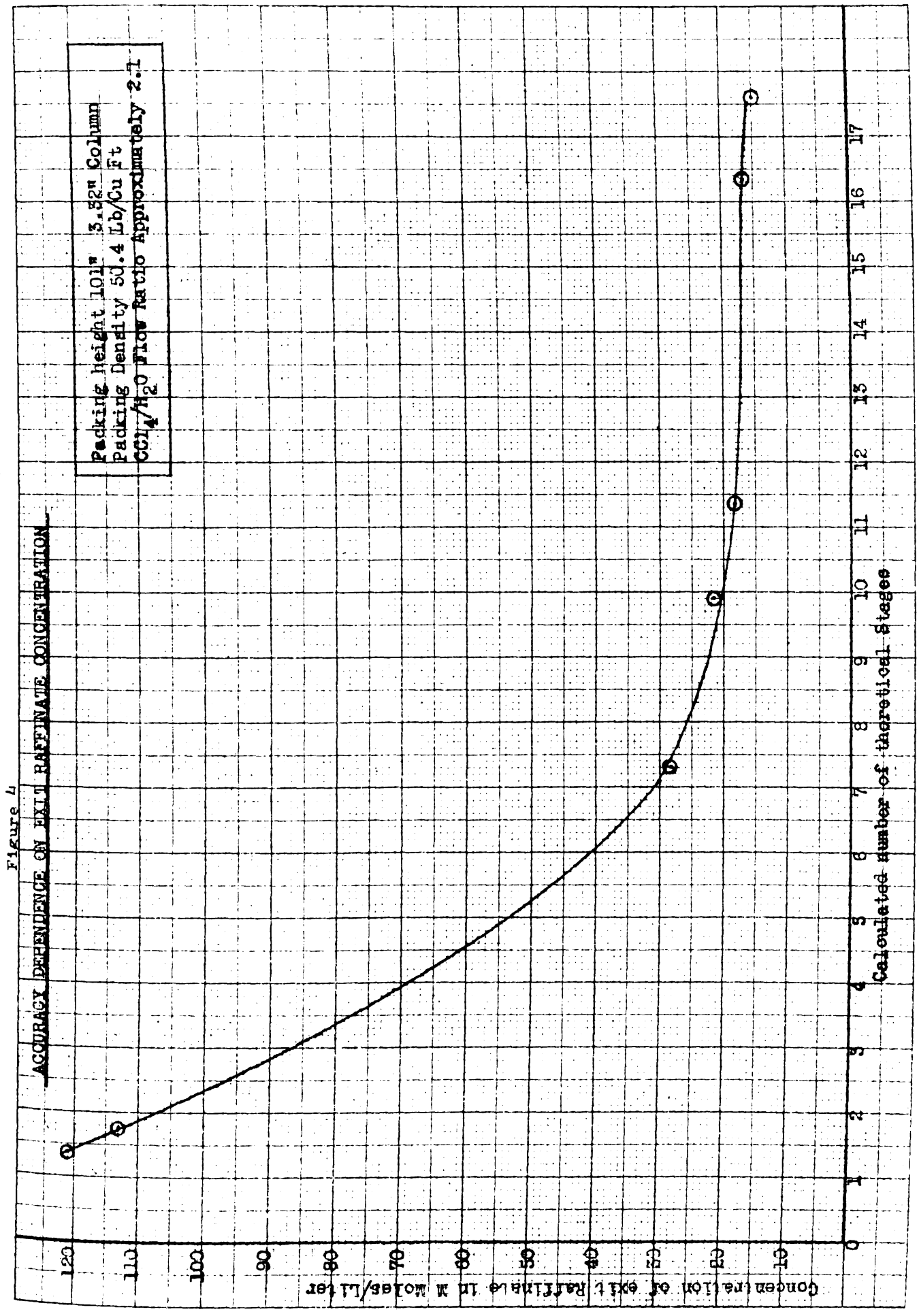

ACCURACY DEPENDENCE ON EXIT RAFFINATE CONCENTRATION
Packing Height 101" 3.82" Column
Packing Density 50.4 Lb/Cu Ft
CCl_4/H_2O Flow Ratio Approximately 2.7
Concentration of exit Raffinate in M Moles/Liter
Calculated Number of theoretical Stages
120
110
100
90
80
70
60
50
40
30
20
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17

Figure 4

The theoretical stage concept considers the column as consisting of a number of equilibrium contacts or theoretical plates, called the number of theoretical stages and commonly abbreviated NTS. When the NTS is divided into the height of the column, the height equivalent to a theoretical stage, or HETS is obtained.

In all of the runs made in this investigation where HETS values were calculated, the inlet solvent (water) had a zero concentration of the solute (acetone) when it entered the column. In the calculations when only a few plates were obtained, the equilibrium line was considered to be straight and to have a slope equivalent to 2.135 parts of acetone in water to one part of acetone in carbon tetrachloride.

In runs of low NTS, the number of theoretical stages may be calculated analytically using a method originally derived by Kremser (20) for gas absorption. This method was reviewed and expanded later by Sounder and Brown (21). In the derivation, two hypothetical plates, in addition to those in the column, are considered to exist; one above the column and the other below. The top hypothetical plate has the gas leaving the column in equilibrium with the entering liquid, while the bottom plate has the leaving liquid in equilibrium with the incoming gas. A material balance is first made around the top of the column, followed by an equilibrium step. This stepwise procedure is continued going down the column until a general expression is obtained for any plate. The general term is then combined with a material balance around the whole column, and when the assumption is made that the entering absorbent contains none of the solute, the resulting equation can be simplified and rearranged to give:

$$(NTS + 1) \ln m/R = \ln \left[1 + (m/R - 1) Y_{1/Y_2}\right]$$

In this equation, NTS represents the number of theoretical stages; Y_1 and Y_2 are the concentrations of the solute in the solution being extracted (carbon tetrachloride) at the inlet and outlet respectively. The extraction factor m/R, is the ratio of the slope of the equilibrium line to the slope of the operating line. The slope of the equilibrium line, m, is the distribution coefficient and the slope of the operating line, R, is the ratio of the flow of carbon tetrachloride to the flow of water.

When the equilibrium line cannot be considered straight, the number of plates may be counted on a McCabe-Thiele diagram as shown in Figure 5. The only inaccuracy in this method is that a proper numerical value for fractional plates cannot be obtained.

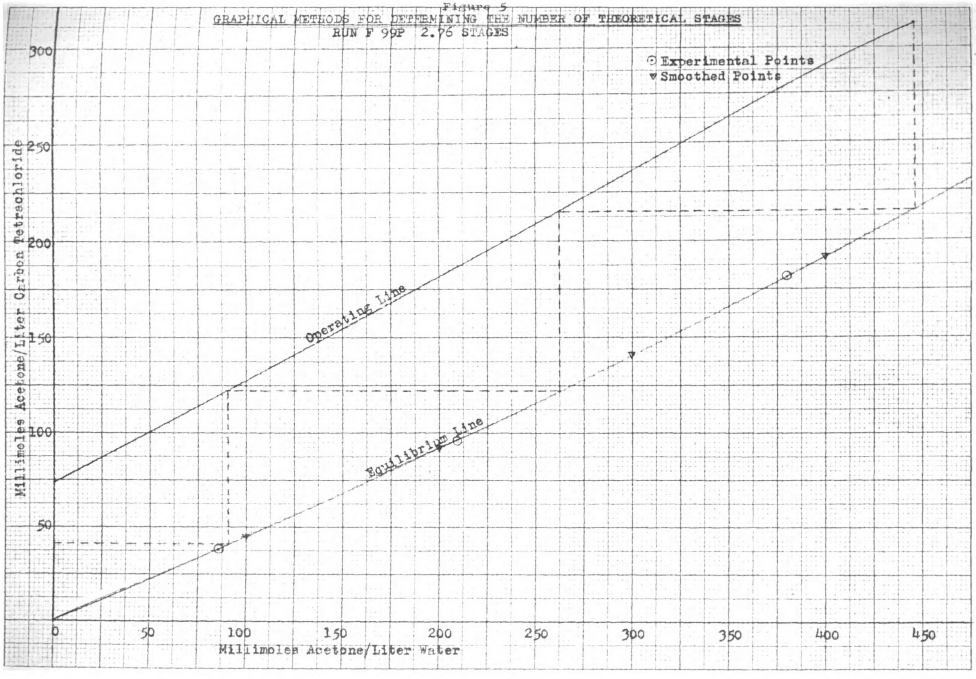


Figure 5
GRAPHICAL METHODS FOR DETERMINING THE NUMBER OF THEORETICAL STAGES
RUN F 99F 2.76 STAGES
Experimental Points
Smoothed Points
Operating Line
Equilibrium Line
Millimoles Acetone/Liter Carbon Tetrachloride
Millimoles Acetone/Liter Water
0
50
100
150
200
250
300
350
400
450

EXPERIMENTAL RESULTS

Distribution of Acetone in Water and Carbon Tetrachloride In order to obtain distribution data corresponding as nearly as possible that occurring in the column, equilibrium determinations were made on carbon tetrachloride samples containing acetone which were taken from the CCl_4 feed tank. Measured volumes of these were added to glass-stoppered bottles containing water and carbon tetrachloride in known proportions. A few Raschig rings were added to each bottle and then the bottles were sealed and placed on electric shakers. After shaking for two hours, the bottles were removed and a potentiometric titration was made for the acetone content in each phase. Knowing the volumes of both phases and the amount of acetone added, it was possible to obtain a material balance as a check of the analysis. These data are given in Table X. The tests were all run at room temperature.

TABLE X

Distribution of Acetone in Water and Carbon Tetrachloride

Acetone in Water	Acetone in CCl_4	Distribution Coefficient
85.5	38.2	2.24
209.0	96.6	2.16
380.0	181.7	2.09
529.0	260.5	2.03
680.0	340.0	2.00

The acetone concentration is expressed as millimoles/liter of solution. The experimental points are shown on Figure 5, as well as the smoothed

curve through the points. Coordinates for the smoothed curve were analyzed by Newton's method of differences and are shown in Table XI.

TABLE XI

Distribution of Acetone in Water and Carbon Tetrachloride

Acetone in Water	Acetone in CCl_4	ΔY_1	ΔY_2	Distribution Coefficient
0	0	--	--	0
100	45	- 45	--	2.222
200	92	- 47	2	2.174
300	141	- 49	2	2.128
400	192	- 51	2	2.083
500	245	- 53	2	2.041
600	297.5	- 55	2	2.017
650	326.0	--	--	1.994

The acetone concentration is expressed in millimoles/liter of solution.

Seidell (22), reports a value of m equal to 2.233 at 186 millimoles per liter of acetone in water and 2.205 at 322 millimoles per liter of acetone in water, determined by Herz and Rathmann in 1913. The corresponding values from Figure 5 of this thesis are 2.228 and 2.133.

As a further check of the distribution coefficient, several values were calculated from runs which were known to pinch at the concentrated end of the column, assuming equilibrium existed at this end. These values checked very closely with the ones obtained in Table X. The average value of m in the range of concentration used in this investigation is 2.135. This is the value used for all calculations where the distribution curve could be considered a straight line without noticeably affecting the accuracy.

Small Column Operation

Runs on the 2.127-inch diameter column may be divided into three types: unpulsed runs on loosely settled packing, unpulsed runs on settled packing, and pulsed runs on settled packing.

Unpulsed Runs on Loosely Settled Packing Runs F56 through F63A appearing in Table XII, were unpulsed runs on loosely settled packing. These runs were made at flooding to determine the throughput rate and HETS as a function of flow ratio.

It can be seen in Table XII that the sum of the square roots of the velocities of the two phases gradually decreased after the first few runs. This was attributed to contamination collecting on the surfaces of the packing, in the form of a dark brown stain. When the packing was washed with concentrated hydrochloric acid, the color disappeared and the rates measured after this were found to be in accord with the original values. For the rest of the investigation the packing was acid treated after approximately every two days of continuous operation.

The remaining runs in Table XII are proceeded by an R, indicating that they were not made at flooding but at reduced throughput. These runs, utilizing only part of the column capacity, were made to determine what effect reduced throughputs might have on HETS.

Pulsed and Unpulsed Runs on Settled Packing Table XIII lists both pulsed and unpulsed runs on settled packing for the 2.127-inch column. To settle the packing, the amplitude of the pulsator was set at 8 millimeters and the frequency at 125 RPM. The top packing support was removed and the carbon tetrachloride in the column was

TABLE XII

PERFORMANCE OF THE 2.0625" COLUMN WITH UNSETTLED PACKING. PACKING DENSITY 47.1 lb/cu ft
PACKING HEIGHT 30.5". UNPULSED

Run No	Volumetric Flow Rates ml/min Water	CCl_4	Flow Ratio CCl_4/H_2O	Solute Conc M Moles/Liter Water Out	CCl_4 In	CCl_4 Out	Sum of Sq. Roots Flow Rates	NTS	HETS Inches
F56	650	1360	2.10	118.5	186.7	128	62.4	.495	61.7
F57	489	1554	3.18	148.3	186.7	139	61.5	.460	66.3
F58	347	1840	5.30	203.0	186.7	148.5	61.5	.530	57.6
F59	276	2055	7.45	284.0	186.7	156	61.9	.545	56.0
F60	880	975	1.10	111.0	230.0	143	61.0	.473	64.5
*F61	660	1055	1.60	151.0	242.0	140	58.2	.587	52.0
F61A	872	1045	1.20	118.0	235.0	131	61.8	.517	59.0
F62	1313	633	.48	58.0	235.0	103	61.4	.463	65.9
*F63	1710	354	.21	40.0	265.0	58	60.2	.620	49.2
F63A	1854	330	.18	34.0	258.0	60	61.3	.561	54.4
R64	281	285	1.01	156.0	256.0	98	--	.828	36.5
R65	330	254	.77	129.0	256.0	89	--	.775	39.0
R66	839	245	.29	50.0	256.0	72	--	.576	52.6
R67	1470	248	.17	26.0	256.0	77	--	.452	67.0
R68	538	242	.46	72.0	256.0	77.5	--	.666	45.4
R69	1004	240	.24	40.0	256.0	73	--	.535	56.6

F -- run at flooding.
R -- regular runs with interface held at the middle of the packing.
* -- the packing was dirty on this run, after flushing the column with concentrated HCl, the run was repeated.

TABLE XIII

PULSED AND UNPULSED FLOODING RUNS ON THE 2.127" COLUMN WITH SETTLED-UNORIENTED PACKING
PACKING DENSITY 51.7 lb/cu ft PACKING HEIGHT 30.75 COPPER BELLOWS USED FOR THE PULSATOR

Run No	Volumetric Flow Rates ml/min Water	CCl_4	Total Pulse mm	Cycles per Minute	Solute Conc M Moles/Liter Water Out	CCl_4 In	CCl_4 Out	NTS	HETS Inches
F70	250	1620	0	0	379	266	210	.673	45.7
F70P	250	2500	5	125	303	153.5	126	1.038	29.7
*F71	169	1566	0	0	-	153.5	137.5	.34	90.5
F71P	332	2240	5	125	274.5	153.5	113.2	1.20	25.5
F72	433	1280	0	0	110.7	153.5	116	.41	75.0
F72P	540	1654	5	125	230.0	153.5	78.5	1.50	20.5
F73	770	794	0	0	69	155.0	88.2	.454	67.8
F73P	866	1100	5	125	156.5	155.0	32.0	1.79	17.2
F74	891	740	0	0	60	155.0	83.0	.451	68.2
*F75	1435	267	0	0	43	296	62.5	.610	50.5
F75A	1501	363	0	0	-	--	--	--	--
F76	1730	160	0	0	24	296	36.0	.66	46.7
F76P	1240	120	2	125	25	296	24.0	.793	38.8

* -- after this run the column was cleaned with HCl.

pulsed for 10 hours. At the end of this time, when an attempt was made to replace the top packing support, the column broke and another column of exactly 2.062-inches in diameter could not be located. This made it necessary to perform the remaining small column experiments in a column of 2.127-inch inside diameter.

The same settling cycle was repeated on the new column. The packing density was found to be 51.7 lb/cu ft, while the height of the packing was 30.75-inches.

Those runs which use a pulse have a P after the experimental number. The pulse amplitude in these runs was measured before and after the series and it was found that the amplitude had decreased from 5 millimeters to 2 millimeters. This was due to the rubber stopper in the top of the pulse bellows gradually being softened by the carbon tetrachloride and moving up and down with the pulse stroke. The data obtained from these pulsed runs have been disregarded in the general correlations and conclusions, because the amplitude was not known with sufficient accuracy. The unpulsed data in Table XIII are, however, entirely satisfactory.

A new pulsator was made to replace the old one. This was a reciprocating piston type with a leather cup to prevent the carbon tetrachloride from going past the piston and out the bottom of the pulsator. This pulsator worked very well; even though the amplitude was always measured before and after a series of runs from then on, it was never found to have changed.

Waring Blender Tests When the new pulsator was installed, the two liquid phases in the column began to take on a different appearance as they were pulsed. The liquids appeared to be broken

up in very fine droplets and the individual phases after separation gave a milky or hazy appearance. Because many articles in the literature mention emulsification as occurring in columns when the two phases are highly agitated, it was suspected that this was emulsification.

It was also speculated that this emulsification might be a result of some impurities in the system that were acting as surface active agents. In order to test this theory, a Waring Blender was obtained and a standard procedure set up to see if the cause of the trouble could be located.

The procedure used was to mix together 100 ml of water and 400 ml of carbon tetrachloride to which 1% of acetone had been added. This mixture was then placed in the Waring Blender and allowed to stir at high speed for exactly two minutes. At the end of this time, 100 ml of the blended materials was poured into a 100-ml graduated cylinder. A stop watch was started as soon as the necessary amount had been poured into the cylinder. A notation was made of the time it took for the suspension to clear to the five milliliter mark and then also to the ten milliliter mark. The results of these tests are given in Table XIV.

Because these experiments showed that distilled carbon tetrachloride was much better than the regular carbon tetrachloride, it was decided to steam distill all of the 300 gallons of carbon tetrachloride that was being used as feed to the column. This was done, and all runs made after that point used steam-distilled carbon tetrachloride.

Pulsed and Unpulsed Runs Containing No Acetone Because the Waring Blender tests showed that the presence of acetone greatly increased the tendency toward fine dispersions or emulsification,

TABLE XIV

WARING BLENDER TESTS FOR EMULSIFICATION

Run No	Materials	Time in Seconds to Reach 5 ml	Time in Seconds to Reach 10 ml
1	regular *CCl_4 + tap water	600	1080
2	regular CCl_4 + distilled water	300	1080
3	reagent grade CCl_4 + distilled water	no emulsion	
4	reagent grade CCl_4 + tap water	no emulsion	
5	reagent grade CCl_4 + 1% acetone + tap water	120	180
6	new CCl_4 + 1% acetone + tap water	90	124
7	regular CCl_4 + 1% acetone + tap water	1680	--
8	reagent grade CCl_4 + 1% acetone soaked 12 hours in polyethylene + tap water	420	660
9	reagent grade CCl_4 + 1% acetone soaked 12 hours in Tygon + tap water	720	--
10	reagent grade CCl_4 + 1% acetone soaked 12 hours in rubber from stoppers + tap water	150	360
11	regular CCl_4 + 1% acetone + tap water	360	510
12	distilled CCl_4 + 1% acetone + tap water	195	250
13	reagent grade CCl_4 + 1% acetone + tap water	205	290
14	regular CCl_4 + 1% acetone + tap water + activated charcoal	300	540

* regular CCl_4 refers to the Dow technical grade used as feed for the column.

TABLE XIV (Continued)

Run No	Materials	Time in Seconds to Reach 5 ml	Time in Seconds to Reach 10 ml
15	regular CCl_4 + 1% acetone + tap water + Fe_2O_3	300	480
16	distilled CCl_4 + 1% acetone + tap water	220	330
17	reagent grade CCl_4 + 1% acetone + tap water	190	260
18	steam-distilled CCl_4 + 1% acetone + tap water	300	410
19	steam-distilled CCl_4 (using a glass condenser) + 1% acetone + tap water	185	230
20	steam-distilled CCl_4 (using a glass condenser) + 1% acetone + tap water	240	350
21	steam-distilled CCl_4 (collected in glass) + 1% acetone + tap water	187	278
22	reagent grade CCl_4 + 1% acetone + 0.04% H_2SO_4 + tap water	225	300

a series of runs were made where acetone was left out of the system. These runs appearing in Table XV were made on well settled packing on the 2.127-inch column at various flow ratios. In part of the runs, a small amount of acetone was present in the carbon tetrachloride. Those runs made after F80 contained no acetone in either phase.

Pulsed and Unpulsed Runs Containing Acetone Once again acetone was added to the carbon tetrachloride feed and runs were made on the 2.127-inch column at a packing density of 51.7 lb/cu ft. These runs, appearing in Table XVI, show a decided increase in throughput rates, apparently due to the presence of acetone or to its transfer from one phase to the other.

In Table XVI are also runs showing the effect of frequency on throughput rate and HETS at constant amplitude. Appearing on the same table are results which show the effect of amplitude on throughput rate and on HETS at constant frequency.

Pulsed Runs Utilizing Only Part of the Column Capacity Previously, runs were made showing the effect of reduced throughput when the column was unpulsed. Table XVII lists trials made showing the effect of reduced throughputs when the column was pulsed. For these runs, the carbon tetrachloride-to-water flow ratio was held essentially constant at 2.1.

It will be recalled that the amount of possible throughput was greatly decreased when acetone was not present in the organic phase. In order to determine whether this effect was due to the presence of acetone or to its rate of transfer, several runs were made in which two times as much acetone was present in the water phase as in the carbon tetrachloride. In other words, as much acetone was present in

TABLE XV

PULSED AND UNPULSED FLOODING RUNS ON THE 2.127" COLUMN WITH SETTLED PACKING PACKING HEIGHT 30.75" PACKING DENSITY 51.7 lb/cu ft SMALL AMOUNTS OF ACETONE IN THE ORGANIC FEED

Run No	Volumetric Flow Rates ml/min Water	CCl_4	Flow Ratio CCl_4/H_2O	Sum of Sq Roots
F77	840	406	0.483	49.14
F77P	406	440	1.083	41.14
F78	366	954	2.60	50.02
F78P	182	562	3.08	37.20
F79	995	139	0.14	43.35
F79P	1360	128	0.093	48.45
F77A	780	446	0.572	49.02
F77AP	373	444	1.19	40.38
F78A	560	882	1.57	53.36
F79A	945	133	0.141	42.28
F79AP	1250	166	0.133	48.23
*F80	650	746	1.146	52.82
F80 - 1	650	343	0.528	44.02
F80P - 1	675	288	0.427	43.00
F80A	670	173	0.258	39.05
F80AP	672	282	0.420	42.70
F80B	685	193	0.282	40.08
F80C	610	463	0.760	46.22
F80CP	630	310	0.492	42.70
F80E	660	150	0.227	37.95
F80EP	650	300	0.462	42.82
F81P	985	213	0.216	46.00
F82	278	780	2.80	44.60
F82P	271	450	1.66	37.67
F80F	640	143	0.224	37.25
F80FP	636	307	0.482	42.73
F80G	640	193	0.302	39.20
F80GP	636	308	0.485	42.76

* -- after this run, the carbon tetrachloride feed contained no acetone.
P -- pulsed at 65 RPM and 5 MM amplitude

TABLE XVI

PULSED AND UNPULSED FLOODING RUNS ON THE 2.127" COLUMN WITH WELL SETTLED PACKING
PACKING HEIGHT 30.75" PACKING DENSITY 51.7 lb/cu ft

Run No	Volumetric Flow Rates ml/min Water	CCl_4	Total Pulse mm	Cycles per Minute	Solute Conc M Moles/Liter Water Out	CCl_4 In	CCl_4 Out	NTS	HETS Inches
F80h	667	916	0	0	261	359.0	169.0	0.77	40.0
F80hP	653	1240	5	65	152.5	359.0	148.5	1.25	24.6
F81	1842	164.7	0	0	27.3	348.5	43.0	0.65	47.4
F81P	1530	126	5	65	22.0	348.5	7.0	1.18	26.1
*F81AP	1186	134	5	125	28.5	348.5	1.6	1.81	17.0
**F81BP	965	112.5	5	215	40.6	348.5	1.0	--	--
F81CP	1460	130	5	125	--	348.5	--	--	--
F81DP	1540	126	5	65	--	348.5	--	--	--
F81A	1940	130	0	0	--	348.5	--	--	--
F81EP	860	130	5	215	--	348.5	--	--	--
F81FP	1400	130	5	125	--	348.5	--	--	--
F81GP	1380	130	5	125	--	348.5	--	--	--
F82	350	1590	0	0	--	348.5	--	--	--
F83P	350	1820	5	125	--	348.5	--	--	--
F84P	350	1750	5	65	--	348.5	--	--	--
F85	570	1190	0	0	296	343.5	189.0	0.82	37.6
F86P	610	1260	5	65	383	343.5	158.0	1.18	26.1
F87P	610	1220	5	125	480	343.5	110.0	1.90	16.2
F88P	600	1133	5	215	574	343.5	40.0	5.13	6.0
F89	340	1564	0	0	492	371.0	265.0	0.81	38.0

* -- slightly below flooding.
** -- this reached a pinch point in the column.

TABLE XVI (Continued)

PULSED AND UNPULSED FLOODING RUNS ON THE 2.127" COLUMN WITH WELL SETTLED PACKING
PACKING HEIGHT 30.75" PACKING DENSITY 51.7 lb/cu ft

Run No	Volumetric Flow Rates ml/min Water	CCl_4	Total Pulse mm	Cycles per Minute	Solute Conc M Moles/Liter Water Out	CCl_4 In	CCl_4 Out	NTS	HETS Inches
***F90P	345	1570	2	65	548	371.0	247.5	1.11	27.7
F91P	560	1240	2	65	387	371.0	193.0	0.948	32.5
F92P	1680	142	2	65	26	371.0	21.0	0.878	35.0
F93	1930	111	0	0	19.6	371.0	30.0	0.690	44.6
***F94P	215	1900	10.5	65	711	366.2	288.0	1.365	22.5
F95P	720	1290	10.5	65	427	366.2	130.7	1.460	21.1
F96P	1610	120	10.5	65	27	366.2	3.2	1.40	22.0
F97P	910	968	10.5	65	295	366.2	89.0	1.36	22.6
F97	778	1138	0	0	256.3	366.2	191.0	0.692	45.8
F98P	1140	625	10.5	65	184.5	366.2	28.6	1.670	18.4
F80IP	355	2010	5	215	--	366.2	--	--	--

*** -- NTS questionable because of a pinch point at concentrated end of the column.

TABLE XVII

PULSED AND UNPULSED FLOODING RUNS ON THE 2.127-INCH COLUMN WITH WELL SETTLED PACKING
Packing Height, 30.75-inches Packing Density, 51.7 lb/cu ft

Run No	Volumetric Flow Rates ml/min Water	Volumetric Flow Rates ml/min CCl_4	Total Pulse mm	Cycles per Minute	Solute Conc M Moles/Liter Water In	Water Out	CCl_4 In	CCl_4 Out	NTS	HETS Inches
F99P	706	1375	10.5	125	0	471	316	74.0	2.76	11.15
R100P	640	1220	10.5	125	0	480	316	62.0	3.20	9.62
R101P	351	660	10.5	125	0	495	316	53.0	3.63	8.48
R101AP	318	641	10.5	125	0	543	316	46.5	4.92	6.26
R102P	250	343	10.5	125	0	414	316	12.0	5.21	5.91
R102AP	235	343	10.5	125	0	440	316	14.5	5.35	5.76
R103P	583	1096	10.5	125	0	482	313	58.0	3.34	9.22
R104P	449	833	10.5	125	0	489	313	50.6	3.71	8.30
R105P	515	887	10.5	125	0	461	313	46.2	3.49	8.82
R105AP	515	887	10.5	125	0	464	313	46.0	3.50	8.80
R106P	440	768	10.5	125	0	475.5	313	40.3	4.0	7.70
R107P	91	221	5.0	125	0	568	308.5	53.7	8.32	3.70
R108P	311	616	5.0	125	0	477	308.5	68.0	3.04	10.12
F109P	657	1254	5.0	125	0	408	308.5	94.6	1.89	16.23
F81HP	621	800	5.0	215	0	416	307	13.3	5.18	5.94
F110a	328	597	0	0	630	--	316	--	--	--
F111a	941	125	0	0	630	--	316	--	--	--
F112a	442	339	0	0	630	--	316	--	--	--
F113a	200	848	0	0	630	--	316	--	--	--
*R114	574	1247	0	0	0	574	292	25.4	.151	--
*R115P	548	1264	5.0	125	0	548	292	25.6	.148	--

R -- below flooding velocity.
* -- column contains no packing.
a -- no mass transfer occurring.

the CCl_4 as in the previous runs but no mass transfer could take place because the two phases were in equilibrium. The results, also listed in Table XVII, show that the throughput rates are very low; apparently mass transfer has to occur to obtain high throughput rates.

A great deal has been written about end-effects in liquid-liquid extraction columns. Scheibel and Frey (23), say in the Encyclopedia of Chemical Technology that considerable transfer takes place at the top and the bottom of the column, and that if the height of the column is doubled, the number of theoretical stages may not double. Spargers or entrance nozzles apparently play an important part in the efficiency of some columns. To determine if the were true for the apparatus used in this thesis, a short column of the same diameter was set up without packing so the ends of the inlet tubes were five inches apart. Two runs were then made, one unpulsed and the other with a pulse amplitude of five millimeters and a frequency of 125 RPM. The results of these experiments appear in Table XVII and show that simple inlet tubes, such as were used in these experiments, are the equivalent of only a small fraction of a transfer stage.

Large Column Operation

One of the main purposes of this investigation was to determine what factors affect scale-up. With this in mind, a 3.32-inch diameter column was designed and built in order to compare its operation with that of the 2.127-inch column. The 8-millimeter packing was added to the large column in exactly the same manner as used for the small columns. The height of the unsettled packing was 107.75 inches.

Expanded End Sections The large column differed from those which preceded it, not only in height and diameter, but also in that it was constructed with special end sections. These end sections should in no way affect the efficiency of the column, since the inlet tubes still terminated at the packing supports and the two liquids did not remain in contact any longer because of the end sections. The end sections were added to give more settling time at the outlets and, if necessary, to eliminate the effects described by Blanding and Elgin.

One of the disadvantages of expanded end sections for experimental work became apparent after the first few runs. As noted earlier in this report, the interfaces were maintained two inches below the bottom packing support and two inches above the top packing support; however, it made very little difference in HETS values or throughputs whether this was two inches or four inches. With expanded end sections present, this two inches brought the interfaces down into a section with a large cross sectional area. If the interface levels were changing slightly while samples were being taken, the rates measured would not be a correct measure of the flow through the packing. In order to overcome this, great care had to be taken to be sure the interfaces did not move during the sampling.

Since the end sections were made of light glass they were very fragile. Several were broken during the course of this investigation.

Probably the most important disadvantage of these expanded end sections for experimental work was that they held a large volume of slow moving liquid. Because of this, the column had to be operated much longer at steady state conditions to be sure that all of the

liquid in these sections represented exactly the liquid coming out of the packing.

Unpulsed Runs on Loosely Settled Packing Table XVIII lists the results of unpulsed runs using loosely settled packing on the 3.32-inch column. All of these experiments used carbon tetrachloride feed containing 1% acetone. In the initial runs, F118 through F123, the interfaces were regulated in the expanded end sections, and the rates may therefore be somewhat questionable. This was confirmed by poor material balances in these runs. For all runs made later, the interfaces were maintained in the narrow section of the column.

Unpulsed Runs on Well Settled Packing The packing was settled by pulsing the carbon tetrachloride in the column for 12 hours with the pulse amplitude set at 10 millimeters and the frequency at 65 RPM. At the end of this time the packing height had decreased 9.75 inches from the original 107.75 inches. Since the packing should have settled more than this, the frequency was turned up to 125 RPM and the pulsator allowed to run for two more hours. The packing settled 3.5 inches more, and again the frequency was turned down to 65 RPM for two hours. The overall change in height was 13.75 inches.

The results of unpulsed runs on the 3.32-inch column, using settled packing and having a packing height of 108.25 inches, are listed in Table XIX.

It should be pointed out that, at the beginning of this series, the entrance tube for the carbon tetrachloride broke off just above the bottom rubber stopper. Since it was felt that this should make little difference in the results, it was not repaired until the next series of runs, the results of which are reported in Table XX.

TABLE XVIII

UNPULSED FLOODING RUNS ON 3.32" COLUMN WITH UNSETTLED PACKING
PACKING HEIGHT 107.75" PACKING DENSITY 44.5 lb/cu ft

Run No	Volumetric Flow Rates ml/min Water	CCl_4	Solute Conc M Moles/Liter Water Out	CCl_4 In	CCl_4 Out	Sum of Sq Roots	NTS	HETS Inches
F118	2255	431	60	317.0	2.0	73.70	2.06	52.3
F118A	1882	794	65	317.0	2.8	71.60	--	--
F118B	2700	1328	134	299.2	27.0	87.25	1.477	73.0
F119	1472	3490	418	299.2	117.0	97.50	1.717	62.75
F120	1960	424	64	299.2	3.5	66.90	1.893	57.0
F121	2655	1875	184	307.0	47.5	94.80	1.392	77.4
F122	2190	2410	261	307.0	70.0	92.90	1.467	73.5
F F123	1720	3100	348	307.0	80.0	97.20	1.78	60.6
F124	2290	1106	130	283.5	14.0	81.06	1.86	57.8
F125	2380	411	45	283.5	--	69.10	--	--
F126	3690	146	5.7	283.5	--	72.80	--	--
F127	3200	267	14	283.5	--	72.89	--	--
F128	1370	3285	511	337.0	126.0	94.30	1.99	54.2
F129	1965	2490	336.3	337.0	72.0	94.20	1.76	61.2

F - for runs made after this one, the interface was regulated in the narrow section rather than in the expanded end sections. Flooding rate data preceeding this may be wrong due to hold up in the end sections.

TABLE XIX

UNPULSED FLOODING RUNS ON 3.32" COLUMN WITH SETTLED PACKING PACKING HEIGHT 108.25"
PACKING DENSITY 49.8 lb/cu ft ENTERING WATER SPARGER JUST ABOVE RUBBER STOPPER

	Volumetric Flow Rates ml/min		Solute Conc M Moles/Liter					
			Water	CCl_4				
Run No	Water	CCl_4	Out	In	Out	Sum of Sq Roots	NTS	HETS Inches
F130	1210	2160	370	308.0	106.3	81.3	1.510	71.8
F131	972	2490	443	308.0	135.5	81.08	1.605	67.5
F132	1640	1468	239	333.5	70.0	78.80	1.337	81.0
F133	1388	1720	296	333.5	89.0	78.70	1.416	76.6
F133A	1391	1700	306	333.5	85.5	78.50	1.448	74.8
F134	1361	131	32	333.5	0	48.35	--	--
F135	1385	900	462	333.5	0	67.20	--	--

TABLE XX

PULSED AND UNPULSED FLOODING RUNS ON 3.32" COLUMN WITH SETTLED PACKING
PACKING HEIGHT 101.0" PACKING DENSITY 50.4 lb/cu ft

Run No	Volumetric Flow Rates ml/min Water	CCl_4	Total Pulse mm	Cycles per Minute	Solute Conc M Moles/Liter Water Out	CCl_4 In	CCl_4 Out	HTS	HETS Inches
F136	601	2800	0	0	531.0	294.5	181	1.735	58.2
F137	997	2083	0	0	427.5	319.0	113	1.77	57.1
F138	280	2842	0	0	--	319.0	--	--	--
F138A	280	3250	0	0	--	319.0	--	--	--
F139	1446	1433	0	0	--	305.0	74.5	--	--
F140	1127	433	0	0	--	305.0	6.8	--	--
F141	1585	1215	0	0	179.0	305.0	58.0	1.753	57.6
F142	1721	995	0	0	174.5	304.0	52.0	1.729	58.4
F142A	1777	1038	0	0	179.0	304.0	48.0	1.735	58.2
F143	1435	457	0	0	--	304.0	--	--	--
F144	1000	2112	0	0	363.0	308.0	121.0	--	--
F145P	924	2075	2.0	65	475.0	308.0	95.5	2.43	41.6
F146P	470	919	2.0	125	592.0	331.0	28.3	7.30	13.8
F147P	1083	848	2.0	65	172.0	331.0	--	--	--
F148P	322	1042	2.0	65	595.0	331.0	147.2	2.47	41.0
F149P	481	1042	5.75	65	578.0	294.0	27.2	10.65	9.5
F150P	347	866	5.75	125	589.0	294.0	58.0	--	--
*F151P	411	967	9.50	65	607.0	302.5	44.0	17.1	5.9
*F151P(1)	403	962	9.50	65	605.0	302.5	46.0	17.3	5.85
F152P	480	991	9.50	65	580.0	300.0	21.7	11.4	7.90

* -- HTS determined graphically.

TABLE XX (Continued)

PULSED AND UNPULSED FLOODING RUNS ON 3.32" COLUMN WITH SETTLED PACKING
PACKING HEIGHT 101.0" PACKING DENSITY 30.4 lb/cu ft

Run No	Volumetric Flow Rates ml/min Water	CCl_4	Total Pulse mm	Cycles per Minute	Solute Conc M Moles/Liter Water Out	CCl_4 In	CCl_4 Out	NTS	HETS Inches
F13UP(1)	510	1038	5.50	65	574.0	300.0	10.2	11.3	7.30
F13UP	421	892	5.50	125	602.5	300.0	15.0	17.6	5.74
F13UP(1)	414	879	5.50	125	602.0	300.0	16.3	16.4	6.16
F13UP	559	1057	5.50	65	579.0	326.5	10.4	12.1	8.34
*F13UP	427	958	9.5	65	582.0	316.5	34.2	17.2	5.87
*F13UP(1)	417	953	9.5	65	627.5	316.5	42.9	17.2	5.87
F13UP	487	897	9.5	65	594.0	324.0	2.55	18.2	5.55
F13UP(1)	481	891	9.5	65	595.0	324.0	2.45	18.2	5.56

* -- NTS determined graphically.

Pulsed Runs on Well Settled Packing At this point in the investigation the glass column broke in such a manner that it necessitated removal of the packing. When the packing was replaced, an attempt was made to settle it to about the same density as before, but at a more rapid rate. The carbon tetrachloride was pulsed at 10 millimeters amplitude and 125 RPM for three hours. The packing at the end of this time was slightly more dense than it had been before the column was broken. The results of both pulsed and unpulsed runs with a packing height of 101 inches appear in Table XX.

A curious phenomenon was noticed on the 3.32-inch column with its large packing height. When an effort was made to obtain flooding rates using a large volume of water and a small volume of carbon tetrachloride, a great deal of difficulty was encountered in operating the column. If, for example, the water rates were increased slowly until interfaces appeared at the ends of the column, these interfaces moved rapidly away from the packing, indicating flow rates considerably in excess of flooding. A large decrease in rate was then necessary to retard the movement of the interfaces, and this decrease, after a while, would cause the interfaces to move rapidly back toward the packing. Because of this sensitivity, an unusually large amount of time was necessary to bring the column into balance. It should also be pointed out that such a balance could be obtained only if the carbon tetrachloride rate was held constant and the water flow used for the adjustments.

DISCUSSION OF RESULTS

Factors Which Influence Flooding Rates

Height of Adjustable Overflow Leg Flooding, as referred to in this report, corresponds to the maximum throughput obtainable in the column. To obtain this maximum throughput, it was necessary to position the adjustable overflow leg until the corresponding interface indicated in the side tube was near the center of the column. Under these conditions, both inlet streams were simultaneously tending to overflow into the outlet tubes of the opposite phases. It also became difficult to distinguish a continuous from a discontinuous phase in the column.

Most of the literature articles read refer to one phase as being continuous and the other phase as being dispersed, indicating that the interface in the side tube was held either at the top or the bottom of the column during operation at rates below flooding. Most authors used some mechanism to balance the outlet streams as the rates were increased toward flooding, so two distinct interfaces were visible at the flooding point. In effect, the conditions obtained at flooding by these authors were the same as those obtained in this thesis. Ballard and Piret (24), report that the capacity of the column depends on which phase is held continuous as the rates are increased toward flooding; however, Hoffing and Lockhart (25), indicate that these conclusions may be in error. No attempt was made here to study this factor, but it would appear logical from observations and reasoning that Hoffing and Lockhart are correct

since the two phases are indistinguishable at flooding.

Flow Ratio Nearly all of the Tables presented in the experimental section list examples showing how flow ratio affects the flooding rate. For convenience, a series of runs from Table XII are repeated below in Table XXI.

TABLE XXI

UNPULSED FLOODING RATES ON THE 2.0625-INCH COLUMN
Packing Density, 47.1 lb/cu ft Packing Height, 30.5-in

Run No	Volumetric Flow Rates ml/min		Sum of the Square Roots
	Water	CCl_4	
F56	650	1360	62.4
F57	489	1554	61.5
F58	347	1840	61.5
F59	276	2055	61.9
F60	880	975	61.0
F61A	872	1045	61.8
F62	1313	633	61.4
F63A	1854	330	61.3
		Avg.	61.60

It may be observed that the flooding rates expressed as the sum of the square roots of the two phases is nearly a constant. The use of this function, suggested by Elgin and Browning (26), has proven to be useful for analyzing results of the present tests. Although a fairly constant value is sometimes obtained for the unpulsed runs where a short packed section was used, this appears to be an exception. For example, Table XIX in the experimental section lists seven runs which show quite clearly that the proposed relationship does not hold where the packing height is high. Most of the flooding runs in this investigation show deviations from a constant value for the

sum of the square roots but these deviations are generally explainable on the basis of special phenomena occurring within a given series.

For those cases where the suggested relationship holds, it is mathematically obvious that the x and y intercepts given at zero flow of one of the phases must be equal to the constant squared. That is,

$$U_a^{1/2} + U_b^{1/2} = C$$

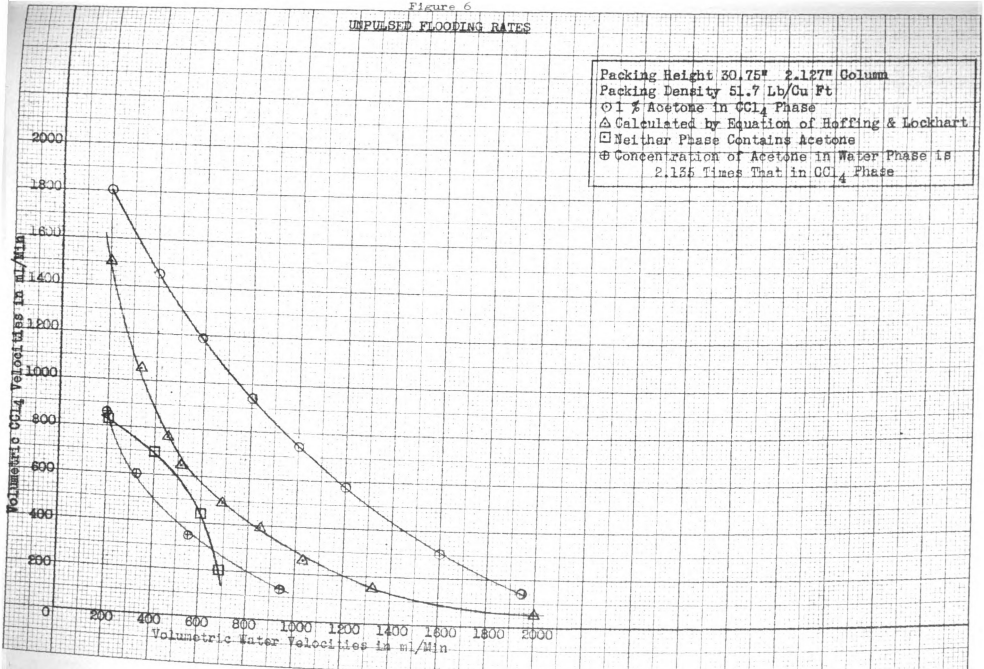
where U_a is the volumetric flow of liquid a and U_b is the volumetric flow of liquid b, therefore when $U_a = 0$, U_b must equal C^2. This is extremely difficult to prove experimentally because phsyical limitations in the system do not allow zero countercurrent flow of one of the streams. On the other hand, tests at very high and very low flow ratios show that the relationship still holds approximately for the extremes that can be measured.

Figure 6 presents graphically the results of several series where the flow ratios were varied over a wide range. These results have been transferred from other graphs, hence the actual experimental points are not shown. It is obvious from the shape of the curves that some of them follow the proposed parabolic function, while others do not. Other examples will be pointed out later in this section where the deviation is even greater than that shown here.

Effect of Solute Transfer Figure 6 may also be used to show how the flooding curves are affected by mass transfer. The curve connecting the circular points represent data on the 2.127-inch column, taken from Tables XIII and XVI, in which the carbon tetrachloride feed contained 1% acetone. The curve through the rectangular points also appearing in Figure 6 represent data taken

Figure 6

UNPULSED FLOODING RATES



from Table XV, in which no acetone was present in either of the two streams. It is readily apparent from these two curves that the presence of a small amount of acetone in the entering organic feed greatly increases the allowable throughputs.

In an effort to explore the cause of the increased throughputs when 1% acetone was present in the organic phase, several flooding runs were made in which the carbon tetrachloride feed contained 1% acetone but the water feed contained sufficient amounts of acetone so that no appreciable mass transfer could take place. These data also appear in Figure 6 and show that if mass transfer does not occur, then the allowable throughput rates are only about half the rates obtained for those runs where mass transfer does occur.

A series of both pulsed and unpulsed runs was also made where the acetone concentration in the entering organic phase was very low. These data are tabulated in Table XV and presented graphically by the circular points in Figure 7. The runs in which no acetone was present in either of the streams are also replotted on this figure for comparison. The same quantitative trend that was found in Figure 6 can be observed here; that is, if acetone was present in the organic feed, the allowable throughput rates were much higher than they were for those runs which contained no acetone in the carbon tetrachloride feed or for those which contained acetone in both streams.

Thornton (14), has shown that if a solute is present in the aqueous phase but not in the organic phase, low flooding velocities are obtained compared to the opposite situation. This observation, combined with the results obtained here, show that the mass transfer

Figure 7

FLOODING RATES WITH BOTH NO SOLUTE PRESENT AND SLIGHT AMOUNTS IN THE ORGANIC PHASE PULSED AND UNPULSED

Packing Height 30.75" 2.1272 Column
Packing Density 51.7 Lb/Cu Ft
⊙ Using Slight Amounts of Acetone in the CCl_4 Unpulsed
⊕ " " " " " " " " *Pulsed
⊡ Using no Acetone in Either Phase Unpulsed
⊞ " " " " " " *Pulsed
* Pulsed at 5mm Amplitude and 65 RPM

Volumetric CCl_4 Velocity ml/Min

1000
800
600
400
200
0

200 400 600 800 1000 1200 1400

Volumetric Water Velocity ml/Min

process has a decided influence on flooding rates and that even the direction of mass transfer has a large effect.

When these phenomena were first observed, it was felt that they must be due to surface active effects of acetone, in which the acetone greatly lowered the interfacial tension between the two phases. If this were true, however, those runs which contained acetone in both phases should have had even higher throughput rates, because in these runs more acetone was available for lowering the interfacial tension. This was not the case. One explanation may be that if acetone is present in the carbon tetrachloride, and since the equilibrium distribution favors a shift in the direction of the water phase (much more so than for the reverse situation), then acetone is diffusing more rapidly to the interfaces being formed in the dispersion process and these interfaces act as localized areas of extremely low interfacial tension.

Physical Properties of the Liquids Several investigators have derived empirical formulae for predicting the flooding rates of packed columns from the physical properties of the two liquids. Among these authors are Breckenfeld and Wilke (27), Crawford and Wilke (28), and Hoffing and Lockhart (25). All of the equations proposed are similar in that they use the same physical properties as a basis for deriving relationships for the flooding rates. Using the following equation proposed by Hoffing and Lockhart, the coordinate were obtained for the curve connecting the triangular points in Figure 6.

$$U_w = \left[\frac{f(R)\,\Delta\rho^{.50}}{3.33 \times 10^{-5}\ \rho_s^{.22}\ \rho_w^{.10}\ \mu_s^{.08}\ \mu_w^{.10} \left(\frac{\sigma_{w-s}}{\sigma_{w-s}}\right)^{.5} \left(a/F^{1.2}\right)^{.6}} \right]^{1.25} R^{.2}$$

F = cu ft of void volume/cu ft packed volume, = 0.711;

a = sq ft of packing surface/cu ft of packed volume, = 184.5;

$f(R)$ = ordinate of a graph which plots the reciprocal of the above equation vs U_s/U_w on log log paper and represents a summary of all pertinent data obtained to date by various authors;

$\Delta\rho$ = density difference of the two phases in g/cc, = 0.580;

ρ_s = density of the solvent phase in g/cc, = 1.58;

ρ_w = density of the aqueous phase in g/cc, = 1.00;

μ_s = viscosity of the organic phase in centipoises, = 0.975;

μ_w = viscosity of the aqueous phase in centipoises, = 1.00;

σ = interfacial tension in dynes/cm;

U = velocity of either phase through the tower, cu ft/hr/sq ft of column cross section (converted to ml/min).

On the same figure, the flooding curves are plotted for data obtained in this investigation on the 2.127-inch column. When the curve obtained by using the equation of Hoffing and Lockhart is compared to the one in which 1% acetone was used in the feed, it becomes apparent that the empirical equation does not consider the effect of a solute in the organic phase. A similar comparison with the curve in which acetone was present in both phases shows that the proposed equation also does not consider a solute present in both phases. In all fairness to the proponents of these equations, it should be pointed out that, if the effect of the solute on the physical properties at non-equilibrium conditions were actually known or could be measured, the predicted flooding rates might be closer. Still it must be remembered that any practical extraction system will contain a solute that must be transferred across inter-

facial boundaries; under this condition, these equations may be of limited practical value.

Packing Height For a sufficiently tall column, packing height can have a pronounced affect on the maximum allowable throughput rates, if acetone is present in the entering organic phase. Although it is rather difficult to distinquish between the effects of packing height and packing density, for the purpose of this thesis an effort is made to treat them separately.

Figure 8 and 9 plot flooding rates obtained on the 3.32-inch column at various packing densities when the entering organic phase contains 1% acetone. The effect of packing height on flooding rates can be seen in Figure 8 where the packing density is 44.5 lb/cu ft. Here it can be seen that, if the concentration of acetone in the exit organic phase falls below 47.5 millimoles/liter, the flooding rates decrease sharply. Below this critical value, the water rates no longer appear to be a function of flow ratio, but appear to be directly dependent on the amount of acetone left in the carbon tetrachloride phase.

The same phenomenon can be observed in Figure 9, but here it is also shown that the packing density and, in turn, the column efficiency greatly affect the amount of acetone left in the organic phase. That is, if the packing has a higher density, the acetone is more quickly washed out of the organic phase because more area per unit volume of packing is available for mass transfer. When the packing density is 50.4 lb/cu ft, approximately the same break-off concentration is found for the acetone in the effluent organic phase as when the packing density is 44.5 lb/cu ft. The net results

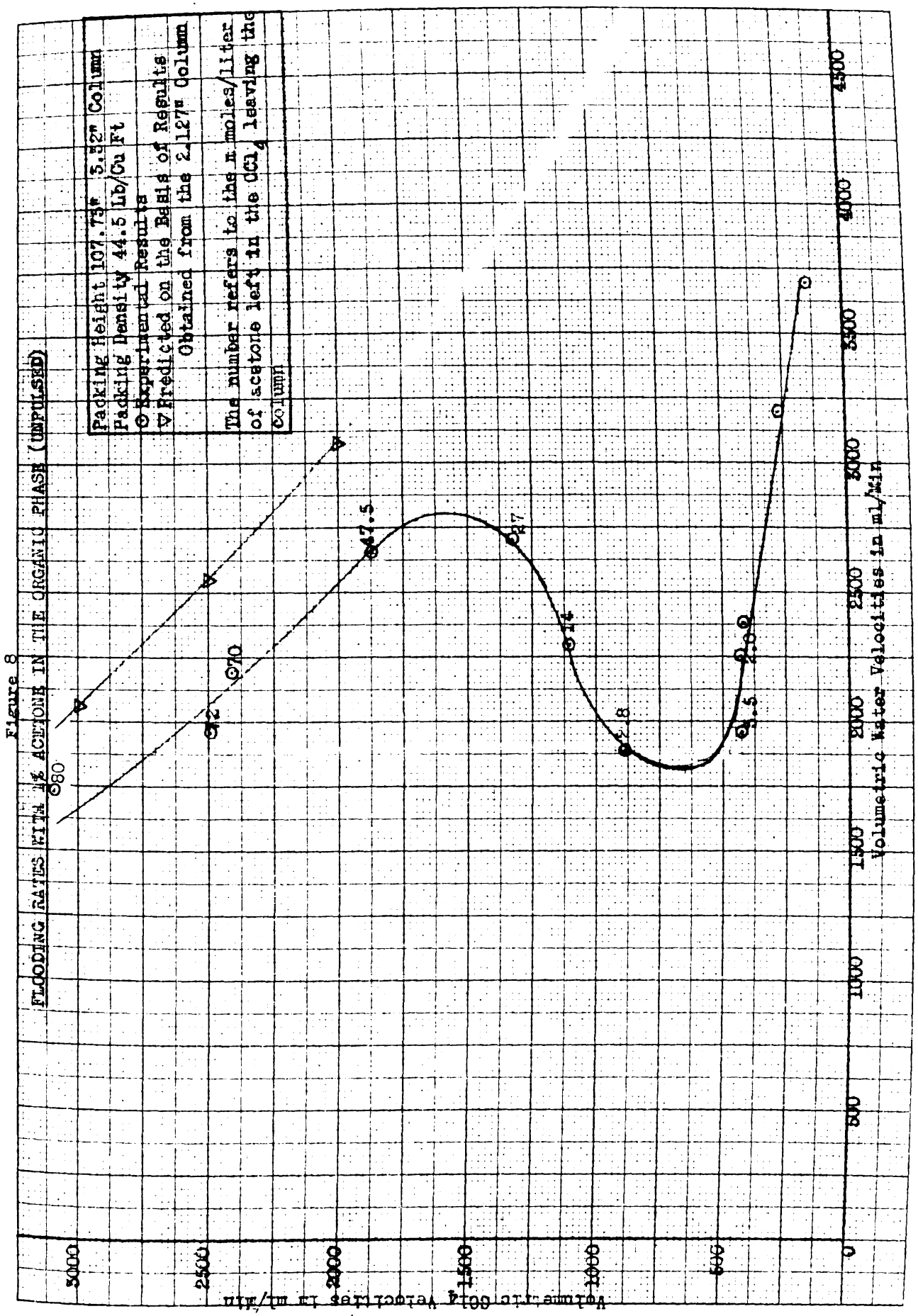

FLOODING RATES FIT 1% ACETONE IN THE ORGANIC PHASE (UNPULSED)
Packing Height 107.75" 5.82" Column
Packing Density 44.5 Lb/Cu Ft
Experimental Results
Predicted on the Basis of Results Obtained from the 2.127" Column
The number refers to the n moles/liter of acetone left in the CCl_4 leaving the column
Volumetric Water Velocities in ml/Min
Volumetric Solid Velocities in ml/Min
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
600
1500
2000
2500
80
70
47.5
27
14
7.8
3.5
2.0

Figure 8

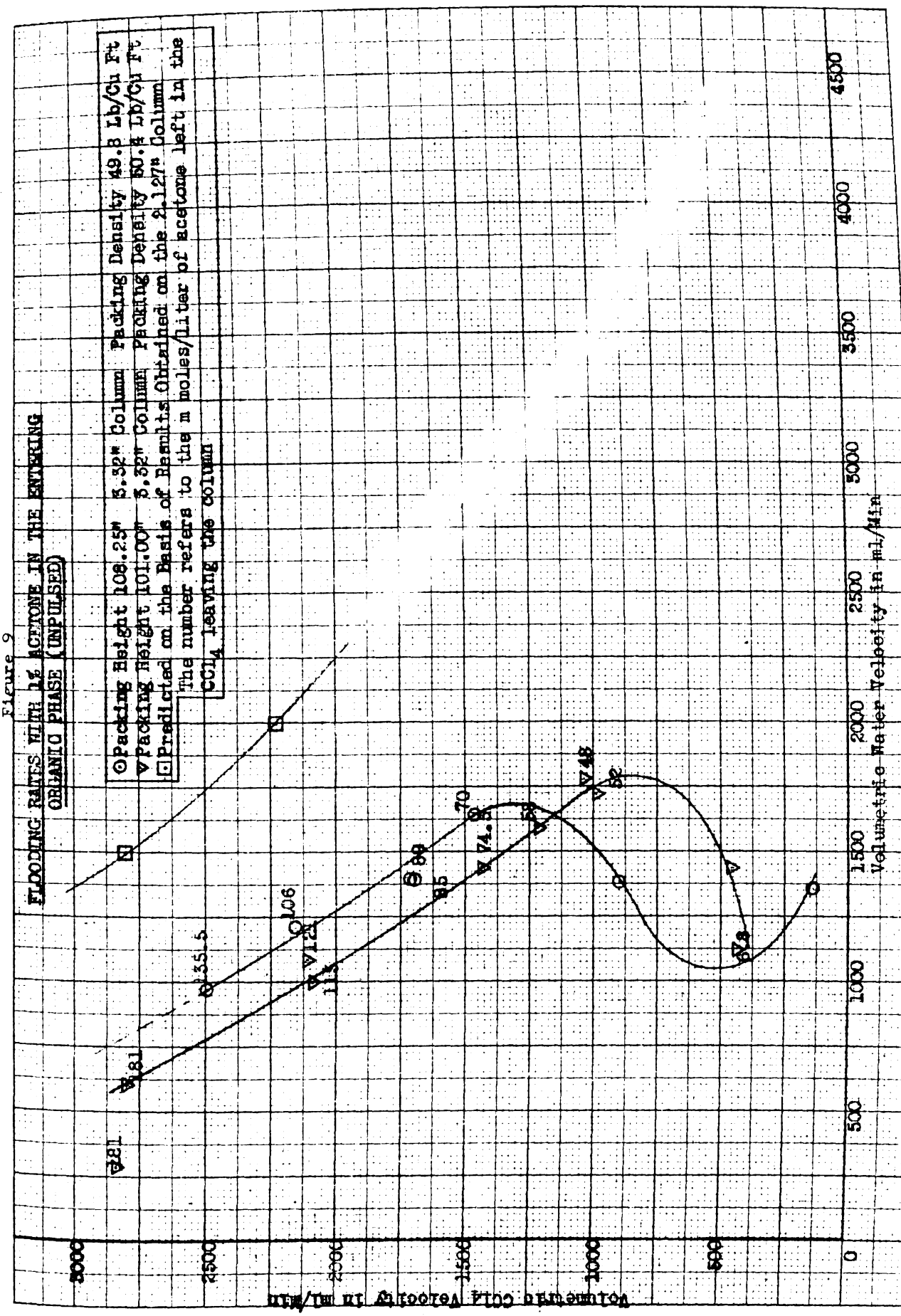

FLOODING RATES WITH 1% ACETONE IN THE ENTERING ORGANIC PHASE (UNPULSED)
⊙Packing Height 108.25" 5.32" Column Packing Density 49.8 Lb/Cu Ft
▽Packing Height 101.00" 5.32" Column Packing Density 50.4 Lb/Cu Ft
⊡Predicted on the Basis of Results Obtained on the 2.127" Column
The number refers to the m moles/liter of acetone left in the CCl_4 leaving the column
Volumetric Water Velocity in ml/Min
Volumetric Coal Velocity in ml/Min
0
500
1000
1500
2000
2500
3000
3500
4000
4500

Figure 9

of these observations are that the packing density has little effect on the break-off concentration where the flooding rates start to decrease sharply; however, an increase in packing density does cause a decrease in total throughput at any flow ratio. It should be pointed out that, for the small column with its short packing height, this phenomenon of sharp flooding rate decrease was not observed, because the concentration of acetone in the effluent organic phase did not decrease to the break-off concentration for any of the unpulsed runs.

Although the reductions in throughput rates can be correlated quite nicely with acetone concentration in the effluent organic phase, the concentrations at any point in the column are determined by packing height, packing density, and column efficiency. These factors, in turn, determine the rate of mass transfer. Therefore, it can be concluded that the throughput rates are actually dependent on the direction and amount of mass transfer.

From these data it can also be concluded that the sum of the square roots of the velocities of the two phases is not always a constant, but happens to be nearly a constant only if sufficient amounts of solute are transferred.

Packing Density Flooding rates have been obtained and plotted at three different packing densities on the 3.32-inch column and at two different densities on the 2.127-inch column. Values obtained where the acetone concentration in the effluent organic phase was above the break-off concentration were averaged, and were converted to a constant representing the volumetric sum of the square roots of the two phases. These runs in turn were converted to the sum of

the square roots of the superficial velocities, and are plotted as the abscissa in Figure 10, against packing density as the ordinate. These data represent averages of many individual measurements.

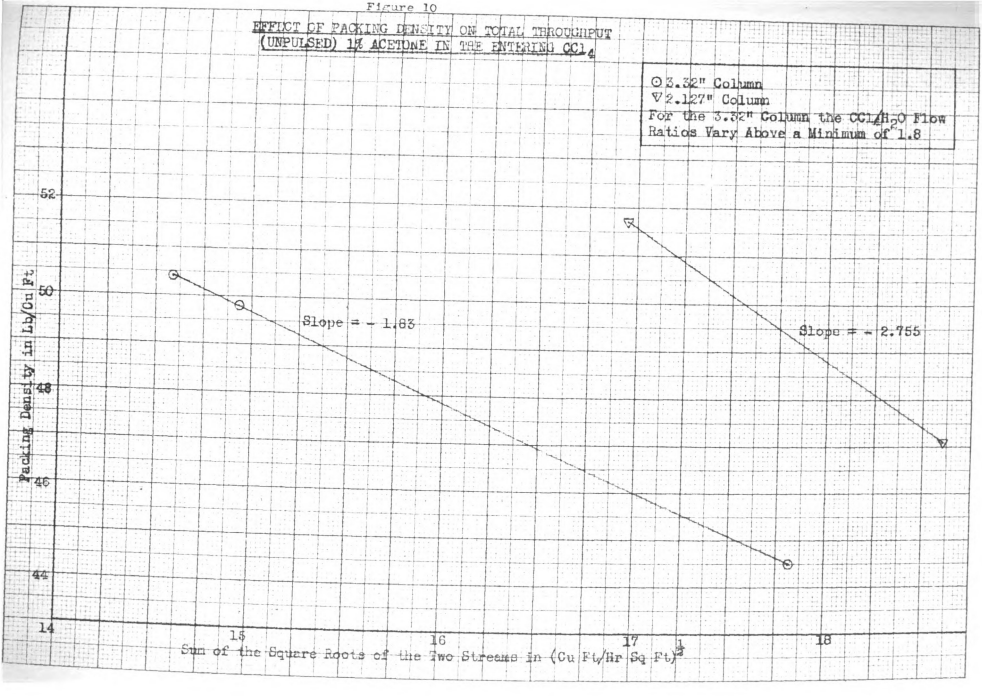
From this graph it might be concluded that flooding rates on the 3.32-inch column are decreased a great deal more, than on the 2.127-inch column, for the same increase in packing density. It should also be pointed out that packing orientation, which will be discussed in detail later in this report, has little effect on flooding rates.

The data presented in Figure 10 must be regarded with a great deal of caution because these graphs are affected by three entirely different phenomena. First, the packing height in the two columns was different; that in the 3.32-inch column was approximately 100 inches while the 2.127-inch column had a packing height of approximately 30 inches. This could cause a large difference in the throughput rates of the two columns due to the total amount of mass transfer occurring. Furthermore, the increased packing density, which might be expected to decrease the rates in both columns by approximately the same amount, may decrease the rates in the larger column more because of a greater proportionate decrease in mass transfer. Secondly, the ratio of column diameter to packing diameter was different in the two cases, permitting different degrees of channeling in the two columns. A third possibility may also occur; that is, if the packing support should happen to be limiting, the packing density just above the bottom packing support or just below the top packing support may be the primary factor in determining throughput rates. This could cause a different effect of packing density in the two columns.

Figure 10

EFFECT OF PACKING DENSITY ON TOTAL THROUGHPUT
(UNPULSED) 1% ACETONE IN THE ENTERING CCl_4

⊙ 3.32" Column
▽ 2.127" Column
For the 3.32" Column the CCl_4:H_2O Flow Ratios Vary Above a Minimum of 1.8



An interesting comparison can be made if a hypothetical packing density of 48 lb/cu ft is assumed in both columns and new constants are taken from the graph of packing density versus the sum of the square roots of the superficial velocities (Figure 10). This constant can then be used to plot a new flooding curve for each column. Table XXII lists the coordinates for Figure 11.

TABLE XXII

COMPARISON OF FLOODING RATES OF THE TWO COLUMNS
Unpulsed; 1% Acetone in the Entering CCl_4
Values are Calculated from a Hypothetical
Packing Density of 48.0 lb/cu ft

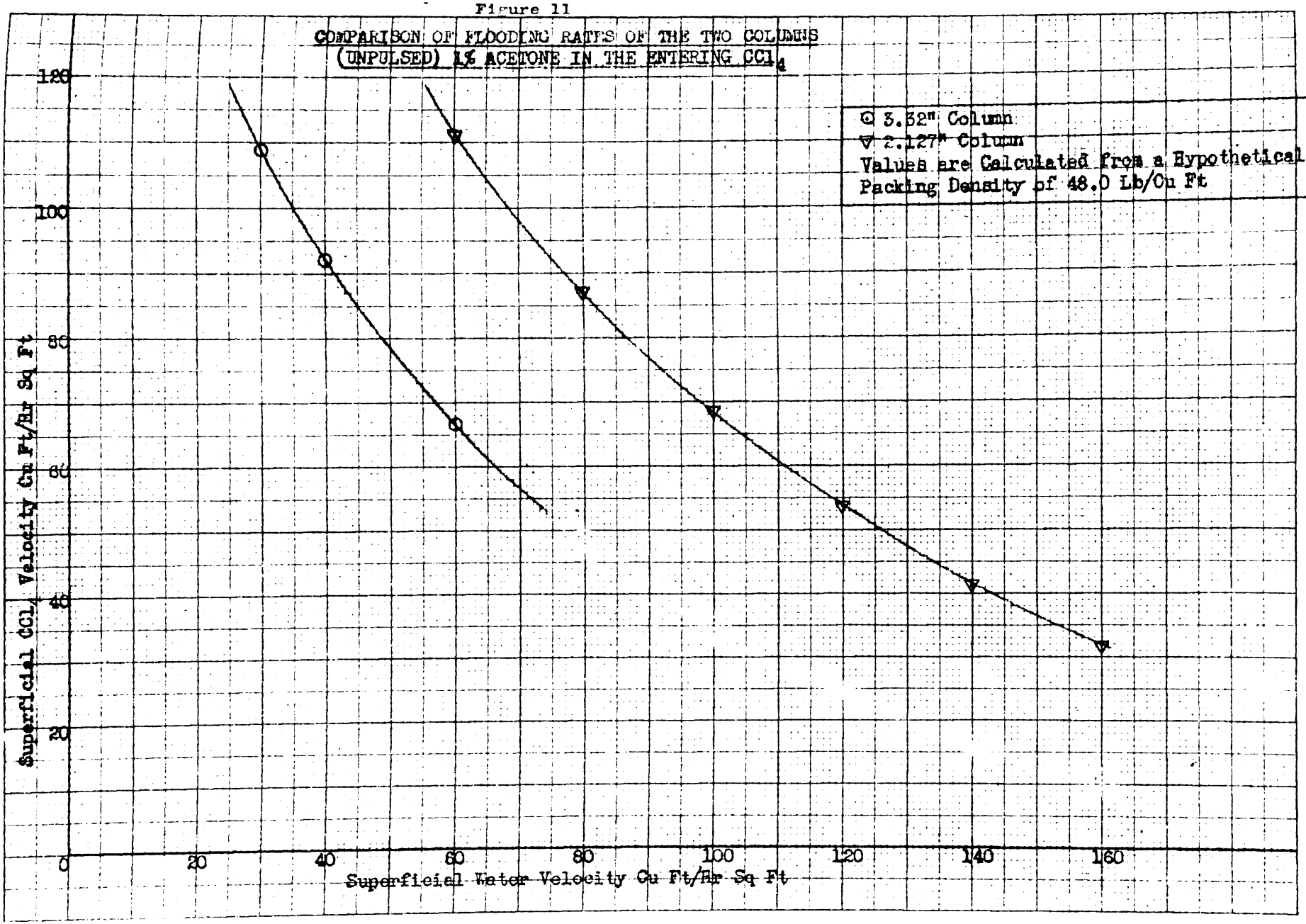
Superficial Velocity cu ft/hr/sq ft			
3.32-inch Column		2.127-inch Column	
Water	CCl_4	Water	CCl_4
160	10.6	160	31.7
140	16.7	140	41.6
120	24.6	120	53.8
100	34.9	100	68.6
80	48.5	80	87.2
		60	111.2
		40	143.0
		20	190.8

From these data it is possible to conclude that for two columns of different diameters, both using the same size of packing, the superficial velocity will be higher for the smaller column than for the large. Unfortunately, these results are strongly influenced by the three factors mentioned above, so the conclusion will probably be wrong at least in magnitude, if not in direction.

Pulse Amplitude Pulsed flooding runs were made on the 2.127-inch column at a packing density of 51.7 lb/cu ft and a frequency of 65 RPM. The pulse amplitude was varied from 0 to 10.5 millimeters. These

Figure 11

COMPARISON OF FLOODING RATES OF THE TWO COLUMNS (UNPULSED) 1% ACETONE IN THE ENTERING CCl_4



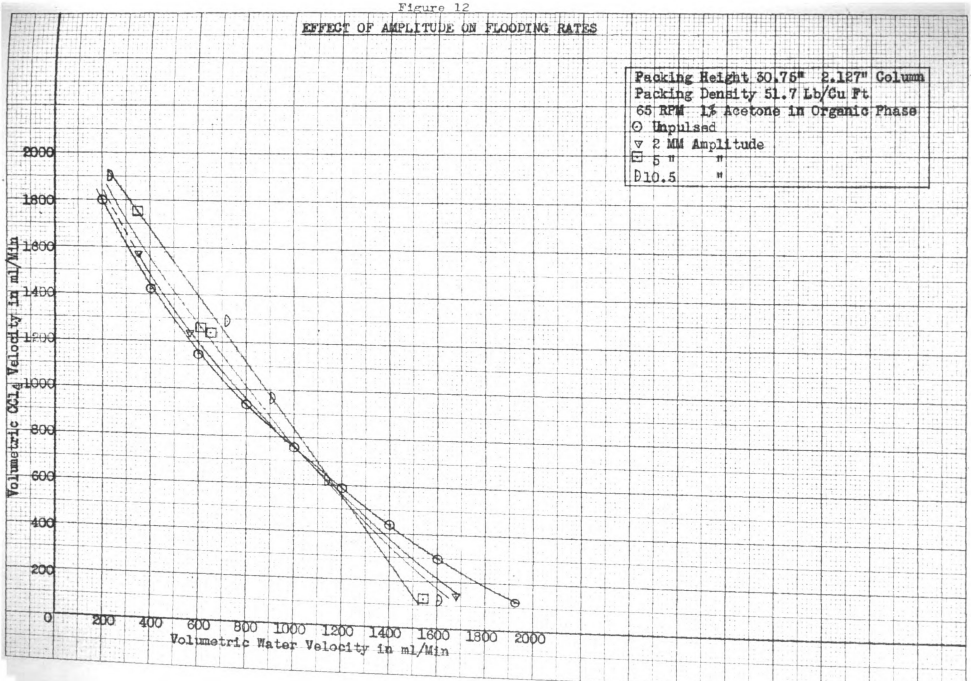
data are tabulated in Table XVI and are presented graphically in Figure 12. For the purpose of comparison, a plot was also made of unpulsed flooding runs on the same column at the same packing density. The latter may be considered as pulsed runs with zero amplitude. A comparison of the curves clearly shows that the allowable throughput rates may be increased by the application of pulse to a packed column, if the carbon tetrachloride-to-water volumetric flow ratio exceeds 0.58. The amount of increase in throughput with pulse becomes larger with increased amplitudes, and no upper limit has been found beyond which further increases in amplitude will not cause corresponding increases in throughput. Flooding velocities also increase with an increase in the carbon tetrachloride-to-water flow ratio at constant amplitude, and again no upper limit could be observed.

It is obvious from Figure 12 that a reverse situation is found below the limiting flow ratio. That is, below a ratio of 0.58 the maximum allowable throughput decreases with an increase in amplitude at constant frequency. Here again, no limit could be found for decreases up to the maximum amplitude used. If one follows a curve of constant pulse conditions over the range of flow ratios, it becomes obvious that the smaller the flow ratio the greater the decrease in throughput at constant pulse amplitude and frequency.

The effect of amplitude was also studied by making a series of runs in which the flow rate of one of the phases was held constant while the rate of the other phase was adjusted to the flooding point at various pulse amplitudes. These data are presented in Figure 13 and show that, if the water rate is held constant at 350 milliliters

Figure 12

EFFECT OF AMPLITUDE ON FLOODING RATES

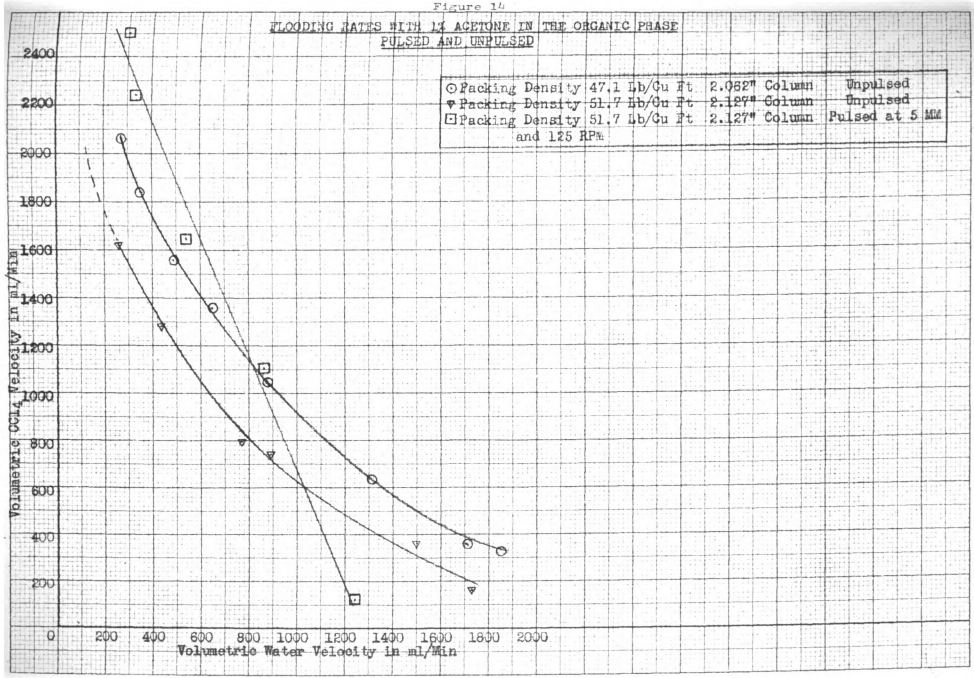


per minute, the volumetric velocity of the carbon tetrachloride increases with increasing amplitude at constant frequency. This graph also shows that, when the carbon tetrachloride rate is held constant at 160 milliliters per minute, the water rate decreases with an increase in amplitude.

As a further study of the effect of pulse on flooding velocities, several unpulsed runs were made in which the packing density was at first 47.1 lb/cu ft and was later increased to 51.7 lb/cu ft where both pulsed and unpulsed runs were made. These data are given in Tables XII and XIII and are compared graphically in Figure 14. The conclusions that can be reached regarding these runs are essentially the same as those presented above. The flooding rates are increased by pulse above a certain flow ratio and decreased by pulse below this flow ratio. The flow ratio in this case also turns out to be 0.58, the same as that obtained in Figure 12.

A few words should be said concerning the pulsed runs appearing in Figure 7. It will be recalled that the curves through the circular points represent data on a system containing very small amounts of acetone, and the rectangular and triangular points represent data on a system with no acetone present in either phase. In the latter curves, throughput capacities for pulsed and unpulsed runs are equal at a flow ratio of 0.46; when a small amount of acetone is present this value is 0.24. It will be noticed that the relative positions of the pulsed and unpulsed curves are reversed from those in which 1% acetone was present in the entering organic phase. That is, above a certain ratio of carbon tetrachloride to water, the throughput rates are decreased by pulsation instead of increased as in runs where

Figure 14


FLOODING RATES WITH 1% ACETONE IN THE ORGANIC PHASE
PULSED AND UNPULSED
⊙ Packing Density 47.1 Lb/Cu Ft 2.062" Column Unpulsed
▽ Packing Density 51.7 Lb/Cu Ft 2.127" Column Unpulsed
⊡ Packing Density 51.7 Lb/Cu Ft 2.127" Column Pulsed at 5 MM and 125 RPM
Volumetric CCl4 Velocity in ml/Min
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
200 400 600 800 1000 1200 1400 1600 1800 2000
Volumetric Water Velocity in ml/Min

acetone was present. Below this ratio the throughput rates are increased by pulse. The relative magnitude of both increase and decrease in throughput rates due to pulsation appear to be even more pronounced when no acetone is present than when 1% acetone is present in the entering organic feed.

The author has been unable to find any reference in the literature to an increase in allowable throughput when pulsation has been applied to a packed column. Feick and Anderson (12), for example, say that pulsation reduces the maximum throughput by a considerable factor, particularly if Raschig rings are used for the packing. Chantry, von Berg, and Wiegandt (6), say that throughputs are reduced somewhat by pulsation.

The original theory that was proposed to explain the increased throughputs when acetone was present in the organic feed might be extended to cover those cases where pulse is applied with acetone present. When a high rate of carbon tetrachloride is put into the column, the acetone contained in it will diffuse rapidly to the surfaces, because the equilibrium distribution favors a high concentration in the water phase. The finer dispersion of droplets obtained when pulse is applied makes more interfaces for the acetone to collect on. This in turn makes more areas of extremely low interfacial tension which is reflected in higher throughput rates. When the column is unpulsed the same phenomena occur, but there is less interfacial area so the throughput rates are lower.

The value of the flow ratio where the throughput rates of the pulsed and unpulsed runs are equal is 0.58 at low amplitudes. This value turns out to be very nearly equal to the slope of the equilibrium

curve, so at this flow ratio the equilibrium line and operating line are essentially parallel. The trend described above should gradually start reversing itself at the value of the distribution coefficient. That is, below this flow ratio the column should start pinching at the top and above this flow ratio it will pinch at the bottom. The value of the distribution coefficient is approximately 0.50. The slight lag indicated in the graph may be due to the fact that some of the curves were extrapolated in this region because runs were not made at exactly the necessary flow ratio. Slight inaccuracies in measurements may also account for some of this discrepancy. Another possible explanation of the increased flooding rates when pulse is applied is that the packing supports may be limiting. In such cases, they could be acting as sieve-plates which are known to allow more liquid to pass through when pulse is applied. On the other hand, this could hardly account for the decrease at certain flow ratios.

Pulse Frequency A series of pulsed flooding runs were made on the 2.127-inch column with a packing density of 51.7 lb/cu ft and a constant pulse amplitude to 5 mm. The results of these runs are tabulated in Table XVI and are expressed graphically in Figure 15.

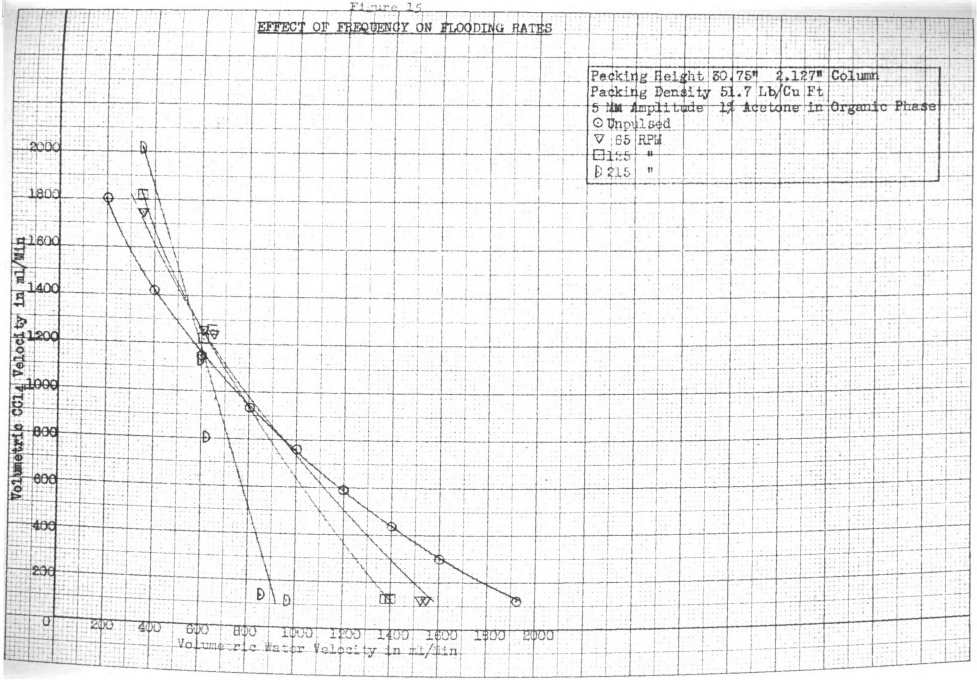
These data also show an increase in throughput above a certain value of the carbon tetrachloride-to-water flow ratio, but the ratio in this case has increased a great deal over the previous value of 0.58 obtained for the effect of amplitude. It should further be pointed out that the amount of increase in the flooding rates due to frequency is much greater than that due to amplitude.

In order to show the increased dependence of flooding rates on frequency, the data described above are plotted at constant flow rates of one of the phases. These data, which give the quantity of the

EFFECT OF EDTA ON ALGOLITHIC ACTIVITY

Figure 15

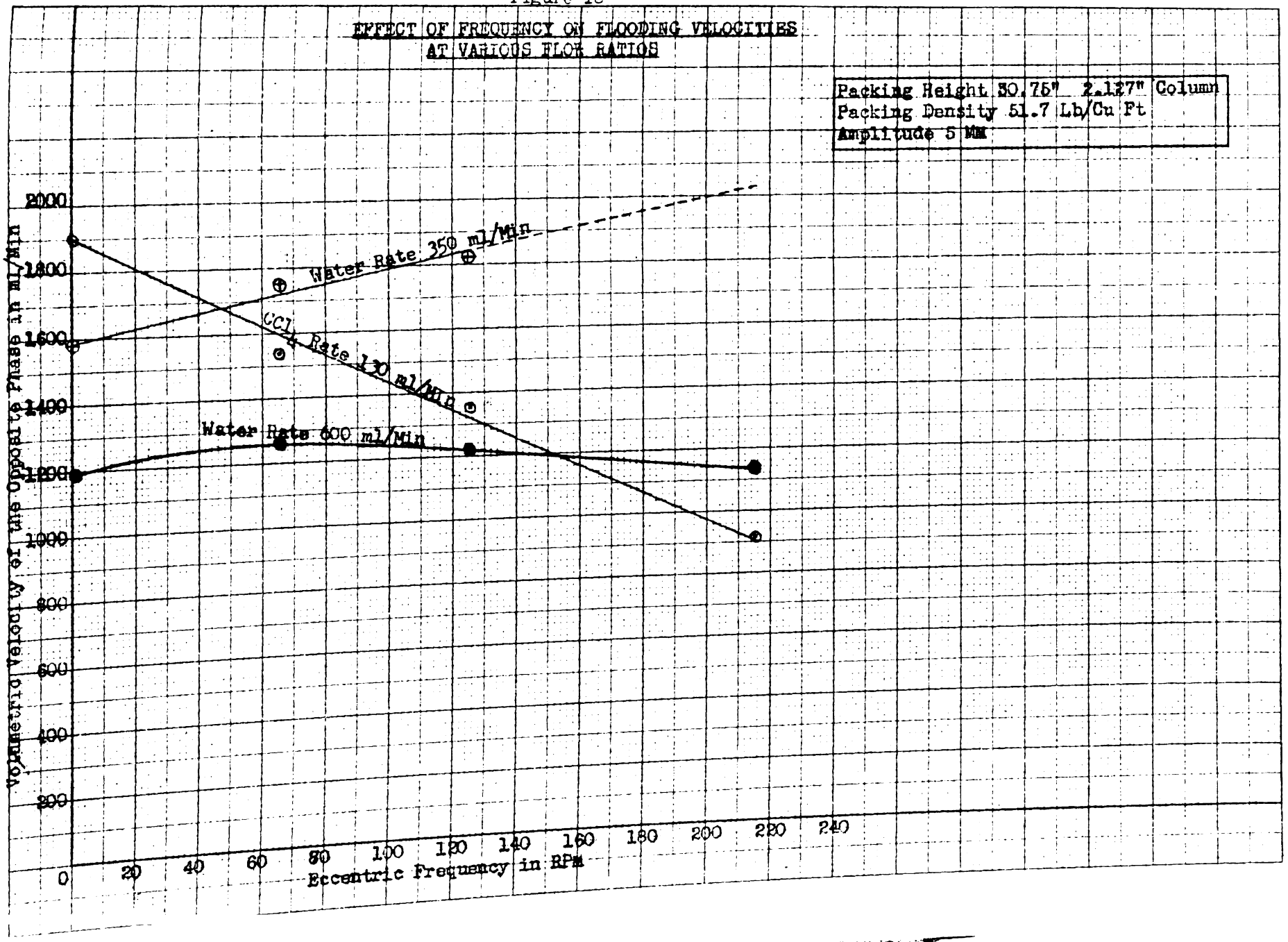
EFFECT OF FREQUENCY ON FLOODING RATES



opposite phase versus the frequency, are shown graphically in Figure 16. When the curves are compared with those appearing in Figure 13, it is apparent that flooding rates are much more strongly affected by changes in frequency.

To reconcile the increase in critical flow ratio with the theories advanced earlier in this paper, it is necessary to consider flooding curves on the large column. In these curves it is shown that, if the acetone concentration in the effluent carbon tetrachloride stream falls below a certain concentration, the flooding rates are greatly decreased, because too little acetone is present to diffuse to the surface in sufficiently high concentrations to get the described effect. The same situation exists here. When the carbon tetrachloride contains too little acetone to get the necessary high concentration at the interfaces, the throughput rates decrease. The rate at which the concentration of the acetone in the carbon tetrachloride is depleted will depend directly on the efficiency of column operation. The greater the frequency, the higher the column efficiency. Therefore, is this theory is correct, the higher the frequency the higher should be this critical flow ratio. The connection between flow ratio and acetone concentration should be readily apparent; the higher the flow ratio, the more the carbon tetrachloride rate increase and the greater the amount of acetone coming in. Furthermore, the higher the flow ratio, the less the amount of water coming in for the acetone to diffuse to. This brings out the obvious conclusion that acetone concentration at the interfaces in any portion of the column is dependent on both flow ratio and column efficiency. The curves in Figure 14 show quite plainly this anticipated result of increase

Figure 16


EFFECT OF FREQUENCY ON FLOODING VELOCITIES
AT VARIOUS FLOW RATIOS
Packing Height 30.75" 2.127" Column
Packing Density 51.7 Lb/Cu Ft
Amplitude 5 MM
Water Rate 350 ml/Min
CCl4 Rate 130 ml/Min
Water Rate 600 ml/Min
Volumetric Velocity of the Opposite Phase in ml/Min
2000
1800
1600
1400
1200
1000
800
600
400
200
0
20
40
60
80
100
120
140
160
180
200
220
240
Eccentric Frequency in RPM

in critical flow ratio with an increase in column efficiency; that is, the higher the frequency the higher the efficiency and the higher the critical flow ratio. In this series of curves the flow ratios vary from 0.843 for the minimum frequency of 65 RPM to 2.42 for the maximum frequency of 215 RPM.

Particle Dispersion When the first pulsed runs were attempted in this investigation with settled packing, the contents of the column turned white and milky. Throughput rates were greatly decreased, and difficulty was encountered in separating the two phases in the end sections before they left the column. This phenomenon was less pronounced at high throughputs than at low. It was also less pronounced at low column efficiencies than when the column had a great many theoretical stages. The investigator thought that this was emulsification because a great many references have been made in the literature to emulsification occurring in pulsed column studies.

Considerable effort was expended to eliminate this phenomenon. Experiments were made on a Waring Blender to find out what could be causing it. All of the carbon tetrachloride was steam distilled because it was thought that the trouble may have been due to contaminants in the organic feed. Even the feed water was treated to remove impurities which might be present. Nothing that was done seemed to offer any solution to the problem, so the experiments were continued with what was thought to be emulsification.

One of the convenient ways to make a column operate more efficiently at given concentrations of the solute in the entering stream is to increase the amount of mass transfer occurring within the column. A greater amount of interfacial area has to be obtained

to do this, and to get more interfacial area the liquids must be broken up into fine dispersions. The more efficiently the column operates, the finer are these dispersions.

The author has reached the conclusion that what was originally thought to be emulsification was actually only fine dispersions, and these are necessary for the efficient operation of a column, even though they result in reduced throughput.

Factors Which Influence Column Efficiencies

Throughput Rates The choice made for the method of column operation in this investigation has proved to be fortunate, not only for determining throughputs, but also for determining column efficiencies. The column was always operated at maximum throughput rates when column efficiencies were determined, except in a very few runs where throughputs were intentionally decreased to see what effect this might have on the efficiencies. In these special runs, the interface was regulated at the middle of the column.

One of the reasons that this method of column operation was fortunate is that it eliminated the necessity of making a choice of which phase to make continuous. Three interfaces were always present, one at either end of the column and one in the side tube. The interface in the side tube automatically moved up or down the column with changes in flow ratio. If a large fraction of carbon tetrachloride was being fed to the column, the middle interface moved down so that water was the discontinuous phase over a greater portion of the column, and vice versa. Actually at flooding the two phases are indistinguishable and it is probably incorrect to speak of a continuous or discontinuous phase when three interfaces are present.

The method of balanced column operation was also advantageous for obtaining column efficiencies because it eliminated the effect of decreased throughputs. A series of runs were made on the 2.062-inch column in which the carbon tetrachloride rates were kept constant while the water rates were varied from flooding down to 10.3 $(ft/hr)^{1/2}$. These runs were not pulsed. The data originally listed in Table XII have been corrected for entrance effects and are repeated in Table XXIII below. These data are also presented graphically in Figure 17.

TABLE XXIII

EFFECT OF REDUCED THROUGHPUT ON HETS (UNPULSED)
2.06-INCH DIAMETER COLUMN

Run No	Flow Rate (cu ft/hr/sq ft) Water	CCl_4	Sum $(\text{cu ft/hr sq ft})^{1/2}$	NTS	HETS (Inches) Corrected*
R64	25.65	26.1	10.28	0.828	45.0
R65	20.10	23.25	10.27	0.775	48.8
R66	76.50	22.4	13.48	0.576	71.6
R67	134.2	22.7	16.36	0.452	101.0
R68	49.1	22.15	11.72	0.666	59.1
R69	92.0	22.0	14.29	0.535	79.2
Flooding	170.0	30.2	18.52	0.525	81.3

* These values have been corrected for entrance effects.

The graphs show that HETS values are greatly affected by the total amount of the two phases through the column. In other words, if the column had been operated at any fraction of the flooding velocity, then all of the HETS values obtained would have had to be corrected for the change in efficiency due to this reduction in throughput rates.

Figure 17

EFFECT OF REDUCED THROUGHPUT ON HTPS

(Unpulsed) HTPS Corrected For End Effects

⊙ 2.0625" Column Packing Density 47.1 Lb/Cu Ft

▽ 2.0625" Column Packing Density 47.1 Lb/Cu Ft (Flooding)

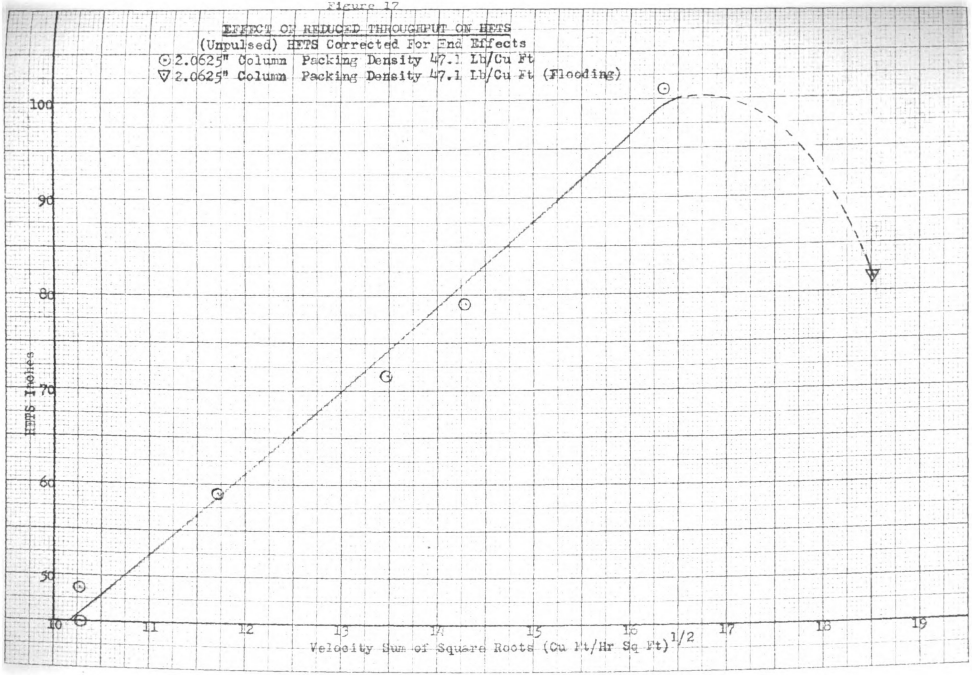


Figure 17 indicates that an unpulsed column should be operated either very close to flooding or below 75% of this value. The HETS values become sharply poorer just below flooding, reach a maximum between 85 and 90% of maximum throughput and then start gradually improving, so that at 77.5% of maximum throughput the HETS is the same as that obtained at flooding. Below 77.5% of the maximum rate the HETS values gradually keep improving without any limit that could be found in these experiments. These results should be observed with some caution, however, because a large difference in operating conditions occurs between flooding (3 interfaces) and nonflooding (1 interface).

Garner et al (29), say that unpulsed packed columns should be designed near the loading velocity where the HETS is a minimum.

A series of runs was also made on the 2.127-inch column to determine the effect of reduced throughput with pulsation. The frequency was set at 125 RPM, and two different amplitudes were used. The CCl_4/water flow ratio was kept approximately constant at 2.1. These data are given in Table XVII. The sum of the volumetric velocities of the two phases, which represents some fraction of the maximum throughput of the column, has been converted to a per cent of the total throughput in Table XXIII (a).

TABLE XXIII (a)

EFFECT OF REDUCED THROUGHPUT (PULSED AT 125 RPM)

10.5-mm amplitude

Run No	Water Flow ml/min	CCl_4 Flow ml/min	% of Maximum Throughput	HETS Inches
F99P	706	1375	100.0	11.15
F100P	640	1220	88.5	9.62
R103P	583	1096	79.8	9.22
R105P	515	887	68.7	8.82
R105P (A)	515	887	68.7	8.80
R106P	440	768	59.0	7.70
R102P	250	343	43.8	6.26
R102P (A)	235	343	28.6	5.76
		5.5-mm amplitude		
F109P	657	1254	100.0	16.23
R108P	311	616	48.2	10.12
R107P	91	221	15.7	3.70

These data are presented graphically in Figure 18. They show that the efficiency of a column is dependent on the total throughput rate. An unpulused column is much more dependent on throughput rate than a pulsed column. Pulsed columns show a maximum HETS at flooding and this gradually improves with decrease in throughput. The higher the pulse frequency and amplitude the less dependent HETS values are on throughput. From this it would appear that pulsed columns should not be designed to operate near flooding.

Cohen and Beyer (7), working with a pulsed sieve-plate column, reported that HETS values are fairly insensitive to changes in flow rates at higher pulse frequency, and at lower frequency the HETS varies over somewhat wider ranges. Chantry, von Berg,and Wiegandt (6), state that lower stage heights are expected with increased rates as

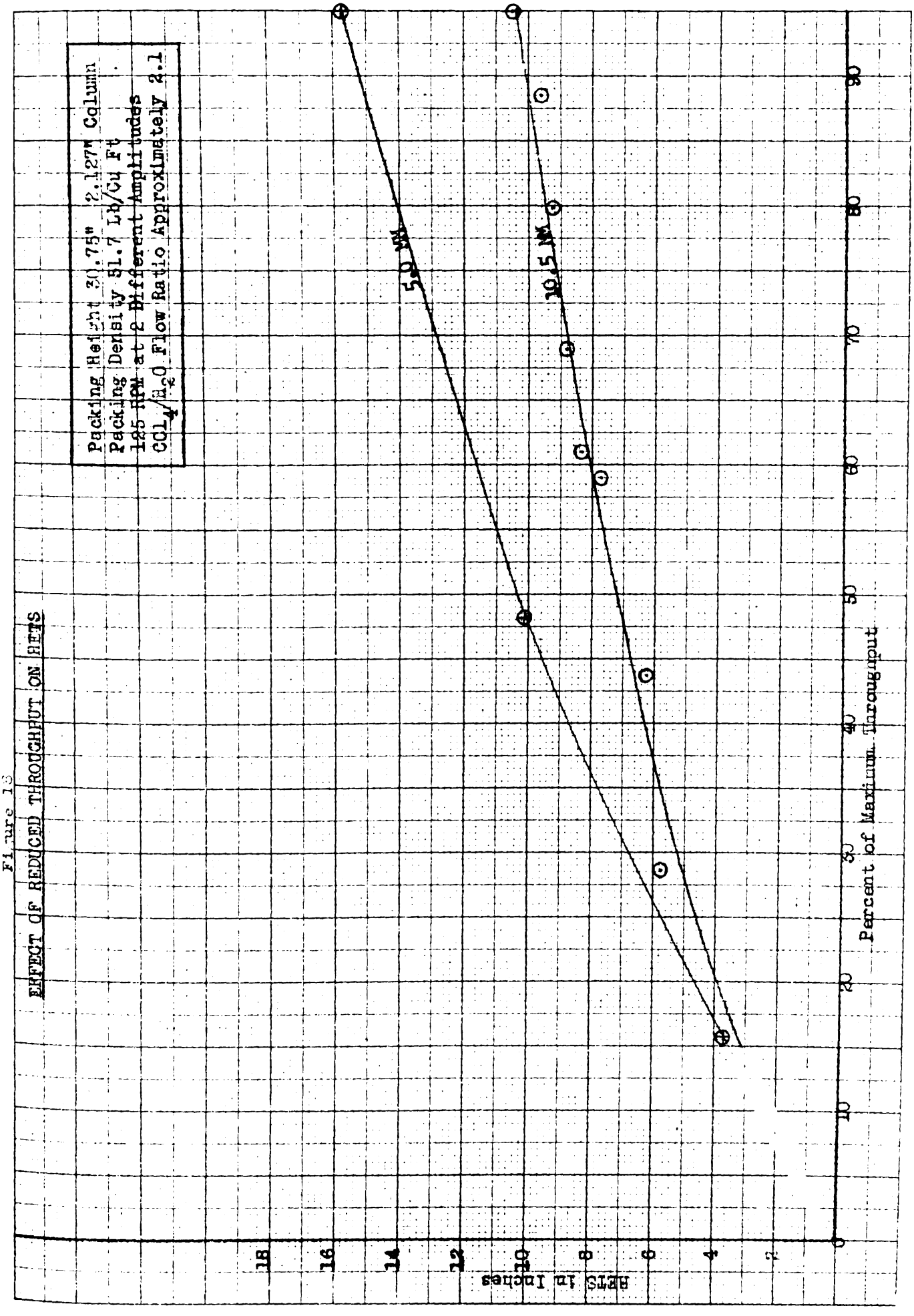


Figure 13

EFFECT OF REDUCED THROUGHPUT ON HETS

a result of great turbulence in both phases, and that this effect should be less noticable on a pulsed column because much of the turbulence is supplied from an external source. Thornton (14), working with a pulsed sieve-plate column, also agrees with the results obtained here.

Flow Ratio The concept of a theoretical stage has been used for many years as a convenient method for designing distillation columns. In this theory, the column is considered to consist of a finite number of equilibrium stages. The usual plate distillation column actually does consist of a finite number of contact stages or plates, but the plates do not represent equilibrium stages because equilibrium is rarely reached. The process is a countercurrent stagewise system but certainly not a countercurrent equilibrium stagewise system.

Objections have been raised to the use of the theoretical stage concept on packed columns, because packed columns are true countercurrent processes. A packed column does not consist of a finite number of equilibrium stages, or even a finite number of contact stages; because of this, the HETS concept is not recommended by some authors.

The HTU theory, on the other hand, has been proposed to replace the theoretical stage method. This is defined by an integral and can treat the countercurrent process as it actually exists in the column, in a differential manner.

The HTU concept assumes equilibrium at the interfaces; this is a highly complicated phenomenon which must rely on instaneous mass transfer in these areas. To find the number of transfer units, one

must assume that either one film or the other is controllin and that the remaining film contributes nothing to the resistance to mass transfer. In practice, both films contribute different amounts to the overall resistance and neither has a tendency to approach negligible proportions.

In the final analysis, any method has to be judged by the results that are obtained by using it. For example, a packed column operated in any given manner should have an equivalent of a certain number of theoretical stages. This number of stages can be thought of as some number of plates in a distillation column. The number of plates cannot change regardless of the flow ratio. That is, some of the plates are not discarded because the flow ratio changes. The same is true of the inlet concentrations of the two phases. Just because the entering phases might have different concentrations at one time than another does not mean that part of the plates will disappear. On the other hand, if the operating conditions change, the efficiency of the plates should change and the number of theoretical stages will be different.

A series of unpulsed flooding runs were made on the 2.062-inch column using non-settled packing. The carbon tetrachloride-to-water flow ratio was varied from 7.45 to 0.178. The concentration of acetone in the entering carbon tetrachloride was varied from 186.7 to 265 millimoles per liter. These data are from Table XII, and are converted to HTU values in Table XXIV. The subscript OA refers to overall mass transfer based on the aqueous phase, while the subscript OO refers to overall mass transfer based on the organic phase.

TABLE XXIV

INFLUENCE OF FLOW RATIO ON HETS AND HTU
2.062-INCH COLUMN NON-SETTLED PACKING

Run No	Flow Ratio CCl_4/H_2O	HETS (Inches)	HTU_{OA} (Inches)	HTU_{OO} (Inches)
F56	2.10	61.7	61	59.8
F57	3.18	66.3	54.6	81.5
F58	5.30	57.6	37.8	94.0
F59	7.45	56.0	31.9	111.0
F60	1.10	64.5	91.5	47.6
F62	0.481	65.9	152.0	34.4
F63A	0.178	54.4	241.0	20.1

These data are presented graphically in Figure 19 and clearly show that HTU values vary over a wide range with changes in flow ratio, while the HETS values remain essentially constant.

As further proof that HETS values are independent of flow ratio when the column is operated at balanced flooding conditions, other runs were made using settled packing, both pulsed and unpulsed. These data have been calculated in both HTU and HETS units and appear in Table XXV below.

TABLE XXV

INFLUENCE OF FLOW RATIO ON HETS, HTU_{OO}, AND HTU_{OA}
2.127-INCH COLUMN; PACKING DENSITY, 51.7 lb/cu ft; PULSED AND UNPULSED

Pulsed at 10.5 mm and 65 RPM					Unpulsed				
Run No	Flow Ratio	HETS	HTU_{OA}	HTU_{OO}	Run No	Flow Ratio	HETS	HTU_{OA}	HTU_{OO}
F94P	8.85	22.5	11.78	48.7	F80h	1.7	40	50.1	40
F95P	1.80	21.1	24.0	20.2	F93	0.0575	44.6	44.5	11.2
F96P	0.0745	22.0	182.0	6.35	F97	1.41	45.8	55.3	36.6
F97P	1.14	22.6	30.7	16.40	F76	0.081	46.7	34.6	13.1
					F70	6.24	45.7	27.3	79.6

The data above are presented graphically in Figure 20.

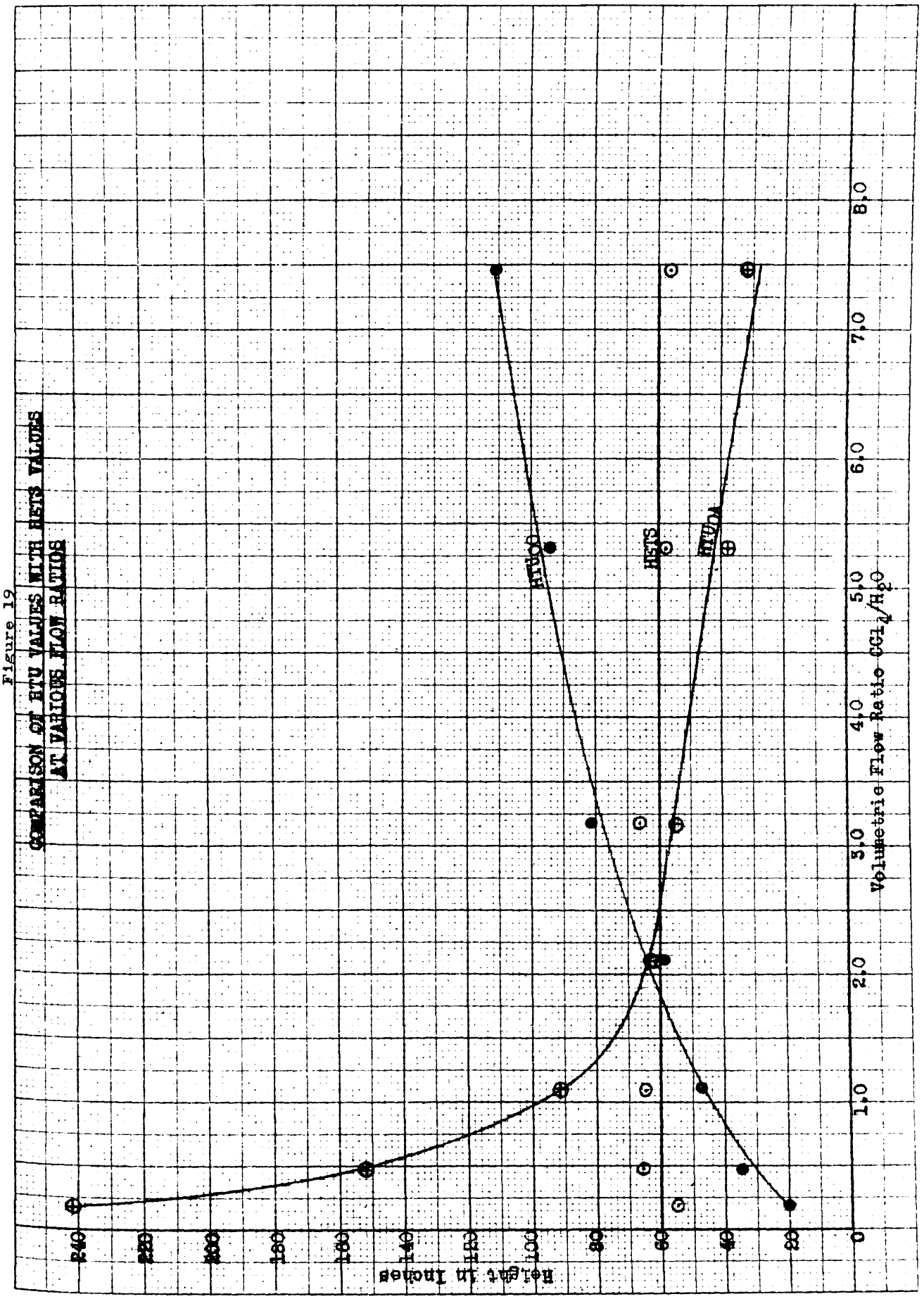
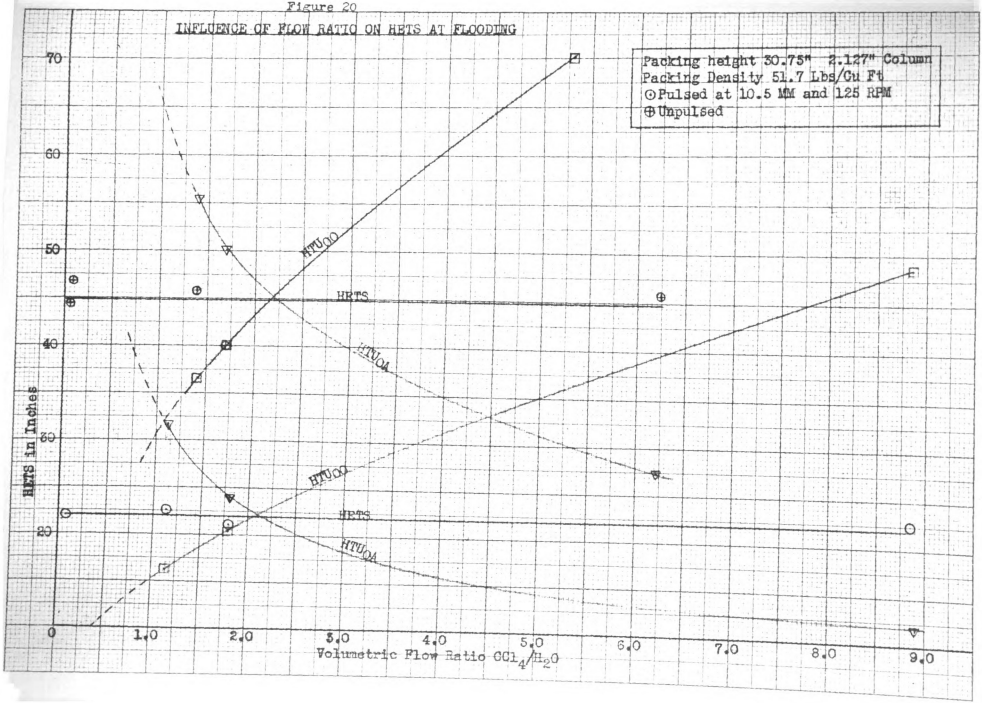


Figure 19

COMPARISON OF HTU VALUES WITH HETS VALUES AT VARIOUS FLOW RATIOS

Figure 20


INFLUENCE OF FLOW RATIO ON HETS AT FLOODING
Packing height 30.75" 2.127" Column
Packing Density 51.7 Lbs/Cu Ft
⊙Pulsed at 10.5 MM and 125 RPM
⊕Unpulsed
HTUOO
HETS
HTUOM
HTUOO
HETS
HTUOA
HETS in Inches
Volumetric Flow Ratio CCl_4/H_2O
0
10
20
30
40
50
60
70
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0

Even though HETS values are relatively insensitive to changes in flow ratios when the column is operated at balanced flooding conditions, an obvious question is whether or not the same is true of columns operating below flooding. In order to answer this question, a great many literature references containing experimental HTU values plotted against flow ratios have been examined. The HTU values based on the phase not already appearing on the graphs were added. The HETS values were also added to the same graphs. All of the plots examined showed that HETS changed much less than HTU.

Two graphs were selected at random from those observed in the literature to illustrate the point made above. These data are tabulated in Table XXVI below.

TABLE XXVI

INFLUENCE OF FLOW RATIO ON HETS, HTU_{OC}, AND HTU_{OD}

Taken from Thornton (14)				Taken from Treybal (30)			
U_C/mU_D	HTU_{OC}	HTU_{OD}	HETS	mU_D/U_C	HTU_{OC}	HTU_{OD}	HETS
0	0.8			2	30	60	41.5
1	1.6	1.6	1.60	4	17	68	31.4
2	2.32	1.17	1.62	10	8.4	84	21.5
3	3.0	1.00	1.65	20	4.9	98	15.4
4	3.8	0.95	1.76	40	3.05	122	11.7
5	4.6	0.92	1.85	60	2.2	132	9.1
				80	1.79	143	7.8
				100	1.54	154	7.25

The data from the table above are presented graphically in Figure 21.

It can further be proven mathematically that the HETS values must always lie between the values of HTU_{OA} and HTU_{OD} by the following relationships which were developed to be used with a straight equilibrium

PLOW MATRIX WITH SIGHTS AND HITO OF NOTATION

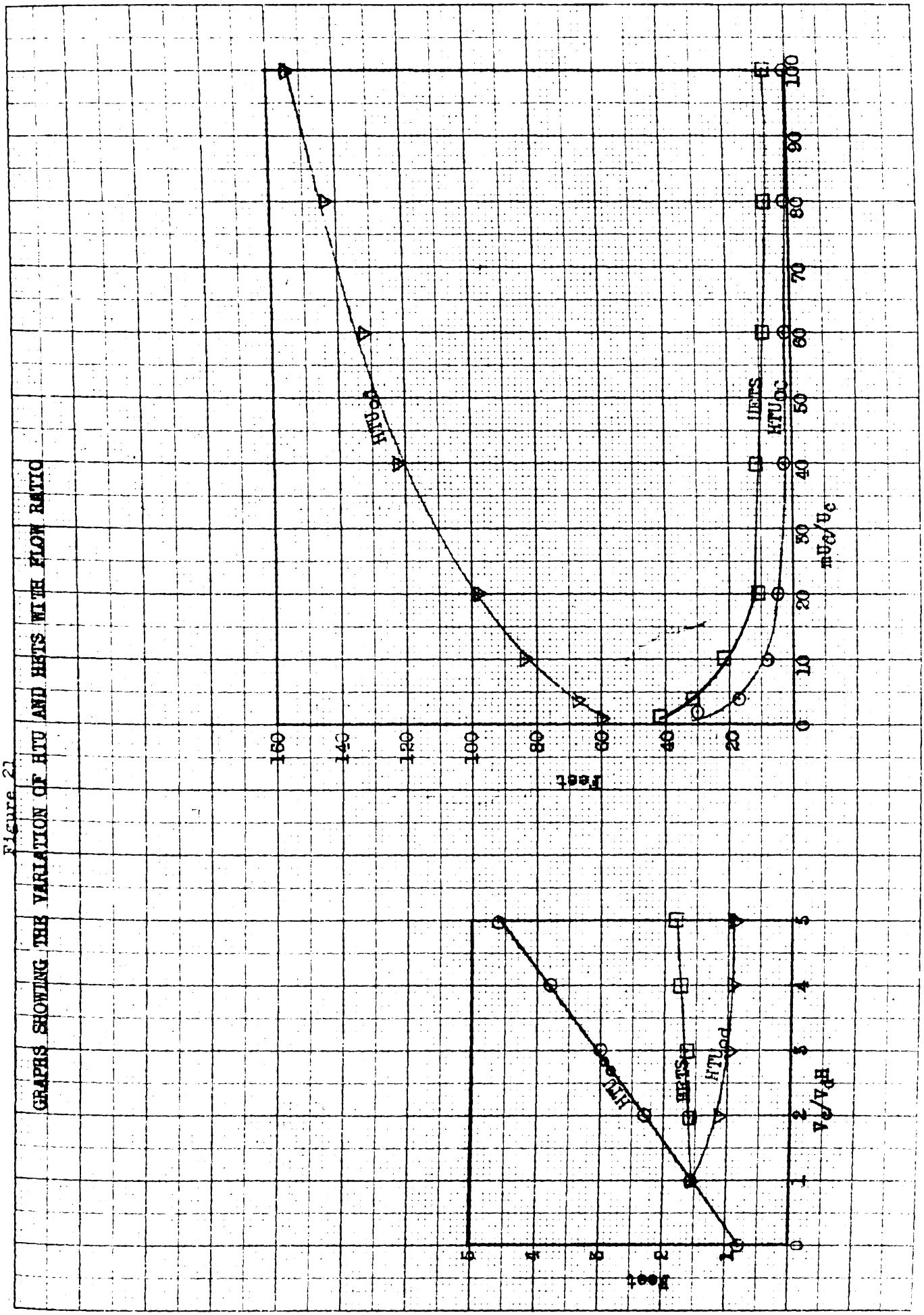


Figure 21

GRAPHS SHOWING THE VARIATION OF HTU AND HETS WITH FLOW RATIO

line and operating line.

$$HTU_{OA} = \frac{HETS\ (1 - P)}{\ln 1/P} = HTU_{OO}\ \frac{1}{P}$$

where P = m L/G

m = distribution coefficient

L/G = flow ratio

Let m, L, and G take any finite positive values, and substitute these into the equation above. The values of HETS will always be between HTU_{OA} and HTU_{OO}. By mathematical reasoning, the curve representing HETS values must have a slope less than or equal to whichever HTU curve has the maximum slope. The boundary conditions are such that the HETS line can never cross either of the other lines. Therefore the HETS values must change by an amount equal to or less than the maximum change in HTU values.

The conclusion reached by this author is that HTU values are much too erratic. They are highly dependent on flow ratio, the correct choice of which film is controlling, and other factors. Most important, HTU values are highly dependent on which phase is continuous and which is discontinuous.

End Effects Two runs were made on the 2.127-inch column to determine what fraction of the total mass transfer occurring in the column could be attributed to the entrance and exit tubes. To do this, the packing was taken out of the column so that only the lines carrying the two phases into and out of the column were left. Run R114 was made without pulse and R115P was pulsed at 125 RPM and 5-millimeter amplitude. The results which appear in Table XVII show that only 0.14 of a theoretical stage is due to the entrance and exit effects.

Sherwood and Pigford (31) say that the HTU values in some columns may vary by as much as the first power of the column height. This effect is particularly noticeable in spray columns but has also been observed in packed towers.

Murch (11) has developed an empirical formula for calculating the HETS for a distillation column. In this equation he suggests that HETS is proportional to the 1/3 power of the column height. A great many other investigators have reported similar results on studies of experimental columns.

The conclusion reached here is that end effects are not important unless special spargers or distributing weirs are used. The small amount of extraction due to end effect remains fairly constant with or without pulsation, and allowances can therefore be made for it in interpreting experimental results.

Orientation of Packing Some experiments in this investigation exhibited an effect referred to as orientation, for lack of a more precise word to describe it. This phenomenon was usually apparent in the first series of runs made after the packing had been originally placed in the column, but was also noticeable to a lesser extent for the beginning runs made after the packing density had been changed. Illustrative of this point are runs chosen from Table XIII using well settled packing on the 2.127-inch column and repeated for convenience in Table XXVII. In the same table runs are listed for the 3.32-inch column using non-settled packing. It should be pointed out that after five to 15 runs had been made on the packing, the results became reproducible and no further changes in HETS values due to this phenomenon were observed.

TABLE XXVII

EFFECT OF PACKING ORIENTATION ON HETS
FLOODING RUNS ON THE 2.127-INCH COLUMN
PACKING DENSITY 51.7 lb/ft^3
(unoriented packing)

Unpulsed			Pulsed at 5 mm, 125 RPM		
Run No	HETS	Sum of The Square Roots	Run No	HETS	Sum of The Square Roots
F71	90.5	57.93	F70P	29.7	65.80
F72	75.0	58.50	F71P	25.5	65.54
F73	67.8	56.50	F72P	20.5	64.0
F74	68.2	58.10	F73P	17.2	61.7
F75	50.5	54.20			
F76	46.7	55.19			

FLOODING RUNS ON THE 3.32-INCH COLUMN
PACKING DENSITY 44.5 lb/ft^3
(unoriented packing)

Run No	HETS	Sum of The Square Roots
F121	77.4	94.80
F122	73.5	92.90
F123	60.6	97.20
F124	57.8	---
F128	54.2	94.30

This phenomenon was not observed every time a change was made in the packing density, nor did it seem to affect flooding rates on any of the runs where it was observed.

Similar results have been reported by other investigators. Thornton (14), for example, working on a 6-inch diameter packed column, concluded that packings tend to orient, an effect which leads to a progressive increase in over-all HTU and a decrease in throughput.

This author can only agree with the first part of Thornton's statement, that packing tends to orient. However, it is obvious from Table XXVII that the efficiency of the column increases, rather than decreases, with this orientation. Furthermore, the limiting throughput does not show an increase but appears to remain essentially constant within the experimental error expected for such unstable column conditions.

Packing Density The packing was poured into the top of the column which had previously been filled with water. When this was done on the 2.026-inch column, the resulting density was 47.1 lb/cu ft, while the 3.32-inch column gave a density of 44.5 lb/cu ft using the same procedure. Apparently the speed of adding the packing had some effect on the resulting packing density. The speed of pouring the packing into the column was never uniform.

A series of flooding runs was made on the columns to see what effect the non-settled packing might have on column efficiency. The packing was then settled by pulsing and another series made to see what effect settled packing may have on HETS. The results are tabulated in Table XXVIII.

TABLE XXVIII

EFFECT OF PACKING DENSITY ON HETS AT FLOODING (UNPULSED)

2.0265-INCH COLUMN Packing Density 47.1 lb/cu ft		2.127-INCH COLUMN Packing Density 51.7 lb/cu ft		3.32-INCH COLUMN Packing Density 44.5 lb/cu ft		3.32-INCH COLUMN Packing Density 50.4 lb/cu ft	
Run No	HETS	Run No	HETS	Run No	HETS	Run No	HETS
F56	61.7	F70	45.7	F118	52.3	F136	58.2
F57	66.3	F72	75.0	F118B	73.0	F137	57.1
F58	57.6	F73	67.8	F119	62.75	F141	57.6
F59	56.0	F74	68.2	F120	57.0	F142	58.4
F60	64.5	F75	50.5	F121	77.4	F142A	58.2
F61	52.0	F76	46.7	F122	73.5		
F61A	59.0	F80h	40.0	F123	60.6		
F62	65.9	F81	47.4	F124	57.8		
F63	49.2	F85	37.6	F128	54.2		
F63A	54.4	F89	38.0	F129	61.2		
		F93	44.6				
		F97	45.8				
Average	58.66	Average	50.61	Average	62.97	Average	57.90
*Corrected	82.40	*Corrected	67.20	*Corrected	69.0	*Corrected	63.40

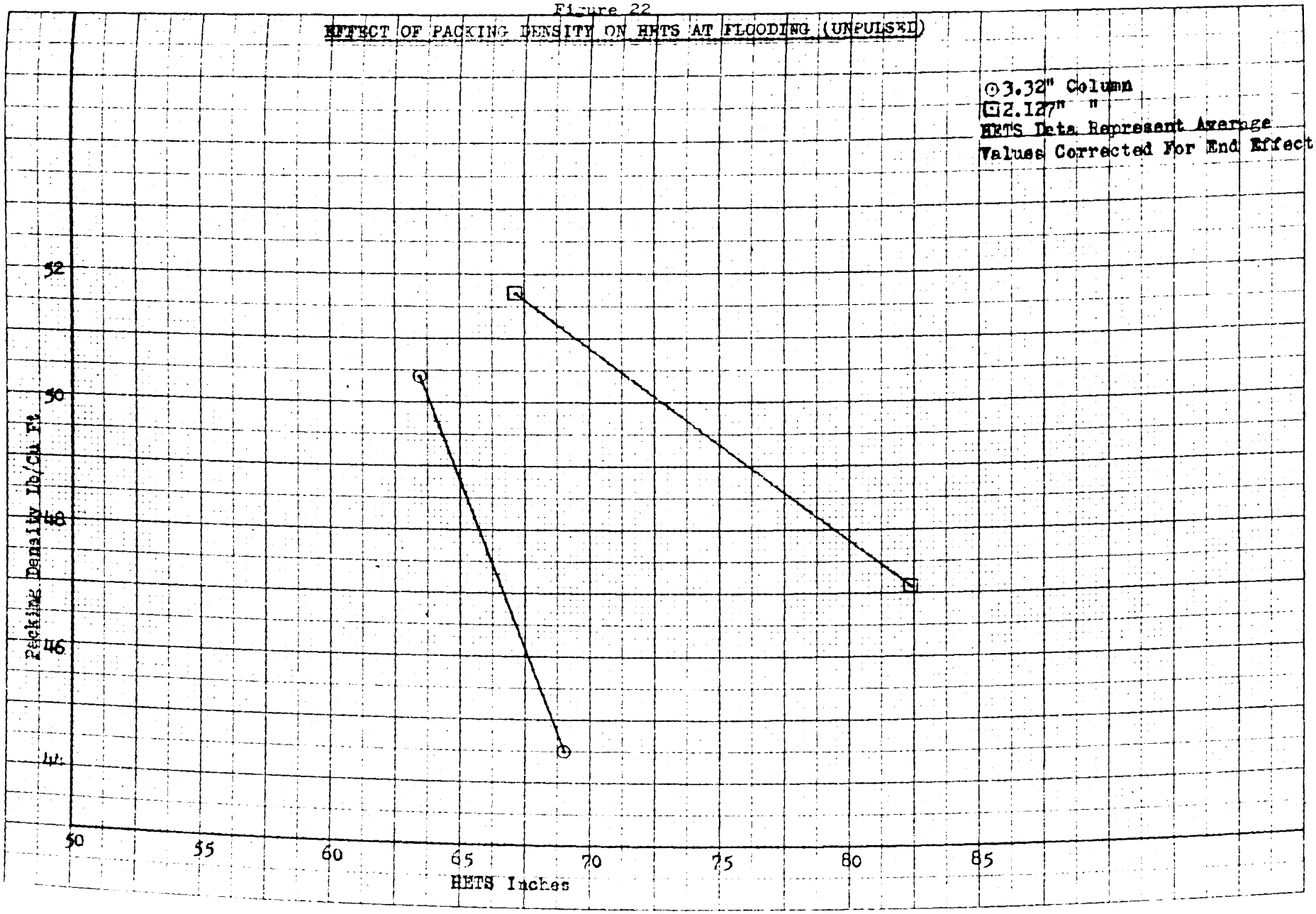
* These values are corrected for end effects.

The data in Table XXVIII are presented graphically in Figure 22. The curves show that the small column gives a much greater improvement in efficiency than the large column for the same increase in packing density. This might be accounted for by the fact that packing in the small column had a great deal more tendency to orient than packing in the large column. That is, a large portion of the packing in the small column was either vertical or horizontal, positions which are expected to give the most efficient operation. Very little of this type of packing alignment was noticed in the large column.

The author has been unable to find any reference in the literature to a qualitative study of the effect of packing density. There have been a few references to the phenomena of packing settling, or orientation, but only in a general way.

Figure 22

EFFECT OF PACKING DENSITY ON HETS AT FLOODING (UNPULSED)



Pulse Amplitude Several series of runs were made to determine what affect amplitude would have on the operating efficiency of a column. The first series was made on the 2.127-inch column with a packing density of 51.7 lb/cu ft. The frequency was held constant at 65 RPM. HETS values were determined at two different flow ratios to be certain that changes in flow ratio would not change the column efficiencies. The results of these experiments are tabulated in Table XXIX.

TABLE XXIX

EFFECT OF AMPLITUDE ON HETS AT FLOODING (PULSED)
Frequency 65 RPM Packing Density 51.7 lb/cu ft
Packing Height 30.75-in

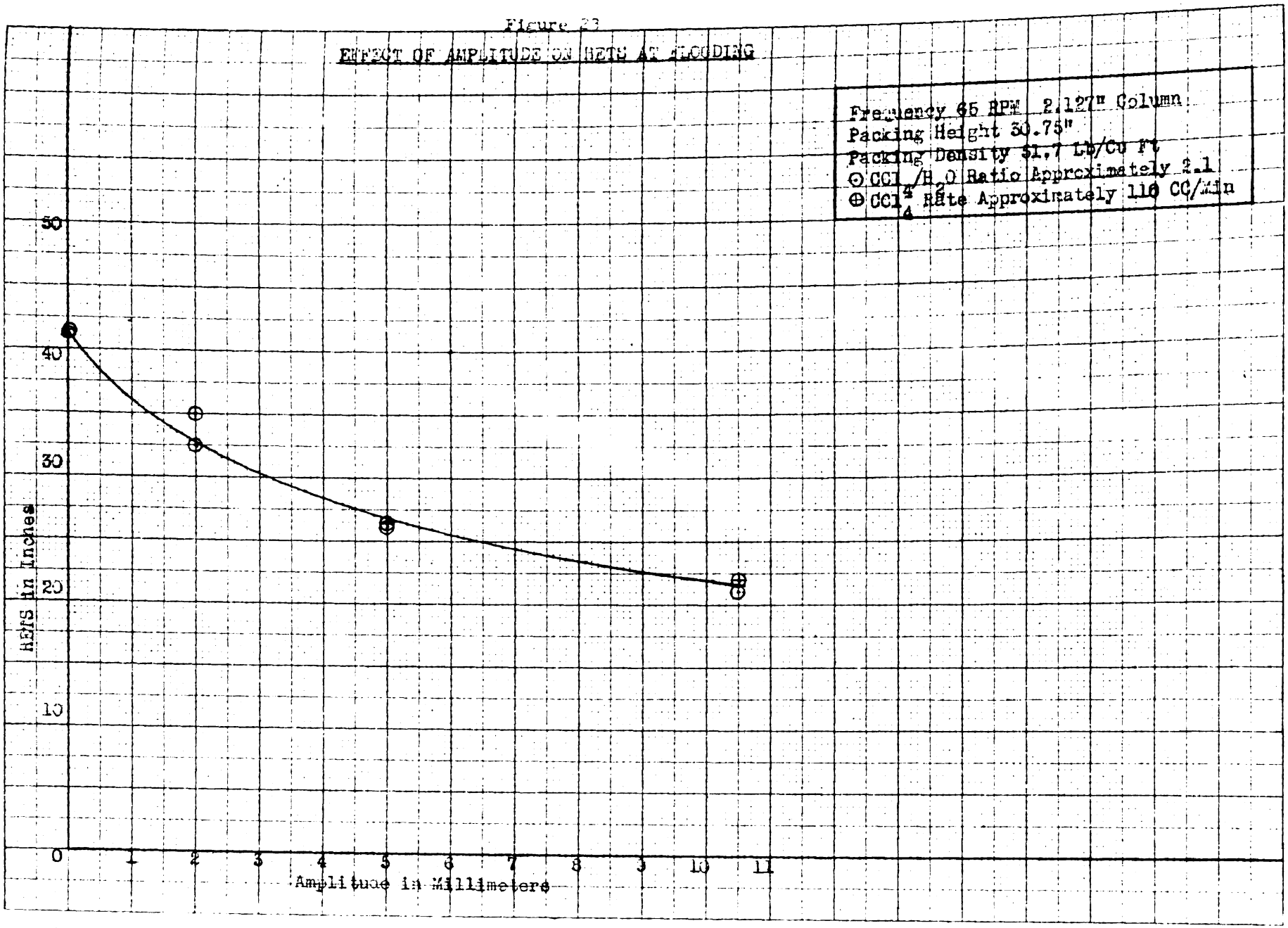
CCl_4/H_2O Flow Ratio 2.1			Constant CCl_4 Rate 110 ml/min		
Run No	Amplitude	HETS	Run No	Amplitude	HETS
--	0	41.5	--	0	41.4
F91P	2.0	32.5	F92P	2.0	35.0
F86P	5.0	26.1	F81P	5.0	26.1
F95P	10.5	21.1	F96P	10.5	22.0

These data are presented graphically in Figure 23 and once more show that HETS values are independent of flow ratios. The curves show a gradual decrease in HETS with increasing amplitude.

Another series of experiments was tried on the 3.32-inch column to determine if amplitude would cause similar decreases in HETS of this tower. The packing density was 50.4 lb/cu ft and the carbon tetrachloride-to-water flow ratio was maintained as nearly as possible at 2.0. It should be pointed out that the reason for the close adjustment in flow ratio was to try to keep the operating line and

Figure 23

EFFECT OF AMPLITUDE ON HETS AT FLOODING



equilibrium line parallel to avoid a pinch in the column. The results were not very reproducible so several runs were made at each value of the amplitude and these were averaged. These data are tabulated in Table XXX, and presented graphically in Figure 24.

TABLE XXX

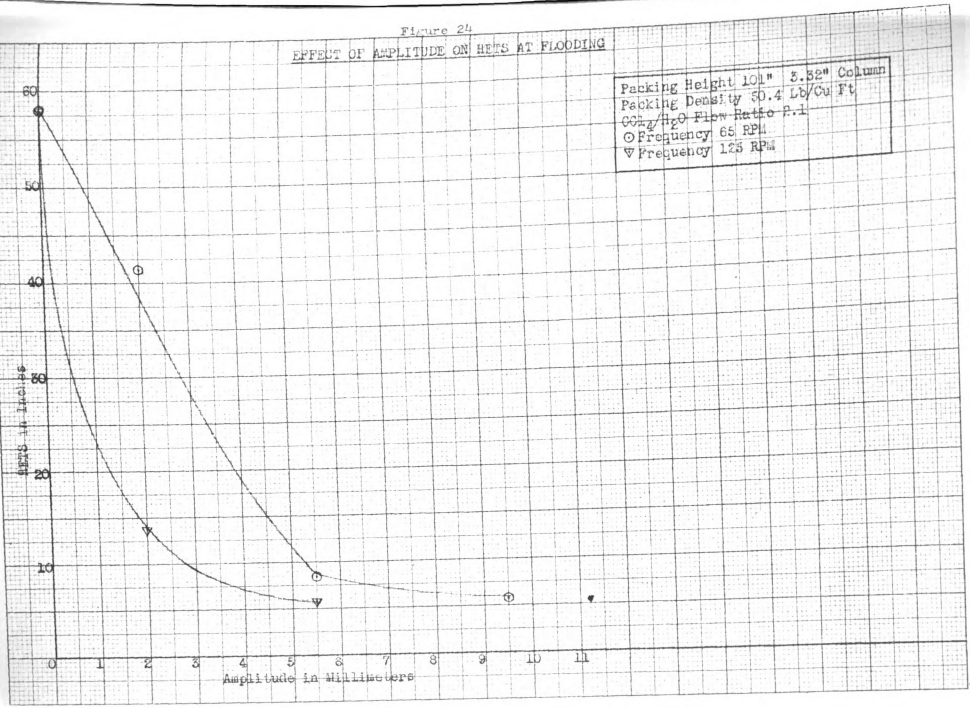
EFFECT OF AMPLITUDE ON HETS AT FLOODING
Packing Density 50.4 lb/cu ft Packing Height 101-in.
CCl_4/H_2O Flow Ratio 2.0

	65 RPM				125 RPM		
Run No	Amplitude	HETS (Inches)	Average	Run No	Amplitude	HETS	Average
5 Runs	0	57.91	57.91	5 Runs	0	57.91	57.91
F145P	2	41.6	41.3	F146P	2.0	13.8	13.8
F148P	2	41.0		F153P	5.5	5.74	5.95
F152P	5.5	7.9		F153P(1)	5.5	6.16	
F152P(1)	5.5	7.9	8.41				
F154P	5.5	8.34					
F149P	5.75	9.5					
F155P	9.5	5.87					
F155P(1)	9.5	5.87					
F156P	9.5	5.56					
F156P(1)	9.5	5.56	5.76				
F151P	9.5	5.90					
F151P(1)	9.5	5.84					

Added complications entered into the runs on the 3.32-inch column that were not noticeable in the small column. The greater height of packing in this column, with the added increase in efficiency due to pulsation, has resulted in too many theoretical stages. This has caused the acetone to be extracted from the organic phase to such an extent that the throughput rates have been decreased. (It will be recalled that flooding rates are dependent on acetone concentration). An added complication is that these runs contain an increase in efficiency due to decreased throughputs as well as an increase in

Figure 24

EFFECT OF AMPLITUDE ON HETS AT FLOODING



efficiency due to pulsation. A correction would have to be made for this decrease in throughput before Figures 23 and 24 could be compared directly.

A great many authors have plotted graphs that show the effect of amplitude on column efficiencies. For example, Chantry et al (6), using a 1.5-inch packed column, show an effect of amplitude very similar to that obtained in this investigation. Cohen and Beyer (7), using a one-inch pulsed sieve-plate column, also observed a decrease in HETS with an increase in amplitude.

Pulse Frequency Further series of runs were made on the 2.127-inch column at a constant amplitude to 5 mm to determine the effect of frequency on HETS. Two different flow ratios were used in these series as further assurance that flow ratio would have no effect on HETS values. The packing density was 51.7 lb/cu ft. These data are given in Table XXXI.

TABLE XXXI

EFFECT OF FREQUENCY ON HETS AT FLOODING
2.127-Inch Column Packing Height, 30.75-inches
Packing Density, 51.7 lb/cu ft 5-mm amplitude

CCl_4/H_2O Flow Ratio 2.1			CCl_4 Rate approx. 110 ml/min		
Run No	Frequency	HETS (Inches)	Run No	Frequency	HETS (Inches)
--	0	41.4	--	0	41.4
F86P	65	26.1	F81P	65	26.1
F87P	125	16.2	F81P(A)	125	17.0
F88P	215	6.0	F81P(H)	215	5.94

These data are presented graphically in Figure 25.

It is apparent from the graph that HETS decreases greatly with an increase in frequency. The column efficiency appears to be more dependent on frequency than on amplitude.

Similar results have been reported by Sege and Woodfield (4), working on a 3-inch pulsed sieve-plate column. They concluded that amplitude and frequency effects should be combined in a term af^n where n has a value between 1 and 2. This, of course, shows the added dependence of column efficiencies on frequency.

A more exact measure of the individual effects of amplitude and frequency might be found if these values were converted to pulsed volumes and plotted against HETS. This was done by multiplying the cross sectional area of the piston by frequency by amplitude (in inches) to obtain the cubic inches per minute of liquid displaced by the pulse piston.

These data are plotted in Figure 26 and show quite clearly that column efficiency can be increased more by increases in frequency than by comparable increases in amplitude. This would indicate that the best column operation may be at high frequency and low amplitude.

Miscellaneous The large column was equipped with expanded end chambers such as those recommended by Blanding and Elgin, while the small column had none. It is difficult to assign any real value to the presence of such chambers except perhaps for experimental purpose.

Expanded end sections could be quite necessary in a pulse column if an exceptionally high degree of agitation is imparted to the two liquids. Such agitation promotes the formation of exceedingly fine droplets of the two phases and these are sometimes difficult to separate. The end chambers can, therefore, act as settling chambers where the

superficial velocities of the two phases are slowed down a sufficient amount to allow for disengagement of the dispersed phase.

Expanded end sections may also be helpful when the interface is regulated very close to one end of the packing. Here they would act as a safty measure to prevent entrainment in case of minor changes in flow rates. The same advantage would be even more noticeable if the column were operated at flooding, where two interfaces are present to cause entrainment.

Except for those conditions stated above, the presence of expanded end sections seems to offer few advantages. Thes conclusions should be regarded with some caution, however, because special spray nozzles or spargers may alter the column operation enough to warrant their use.

The amount of free area in the packing support used in this investigation appeared to have little effect either on the allowable throughput or on the column efficiency. Apparently 50% of free area, such as that used for the small column, is sufficient to eliminate any noticeable effects of restricted flow through the packing supports.

Little effort has been made in this investigation to analyze the economics of pulse columns. Other authors have considered this aspect in greater detail. Chantry et al (6) have concluded that the power requirements, even for a column several feet in diameter, are small; more important engineering considerations are pump size and vibrational stresses at higher frequencies. Jealous and Johnson (32) have derived an equation for calculating power requirements for pulsation. They have also recommended that a flywheel be used on the pulsator because the power is negative over half of the cycle. Other investigators have

pump for one of the entering phases.

Comparison of the Two Columns

Unpulsed Packed Columns The purpose of this investigation has been to determine what factors influence design. Each of these factors has been presented and discussed individually, but a comparison of the two columns of different diameters has been reserved for the conclusion of the discussion section, after most of the data have been presented. Little need be said here to interpret the influence of various factors on design because these have already been discussed in detail. Instead, the various factors will be utilized to answer the question of what might be expected in the design of large columns.

An extrapolation was first made using Figure 22 at two different hypothetical packing densities to obtain HETS values for both the 2.127-inch and the 3.32-inch columns. These values, which have been corrected for end effects, are entered in Table XXXII below. Figure 10 was then used to obtain the expected throughput rates at these hypothetical packing densities. The values obtained for the 3.32-inch column were converted to a percent of throughput based on the 2.127-inch column. It was originally thought that Figure 17 might be used to get the expected HETS improvement due to this decreased throughput. Unfortunately the change in efficiency with reduction in throughput rates is not linear for unpulsed columns. Furthermore, the large diameter column also had a greater packing height and, since the total amount of mass transfer was greater in this column, the throughput rates were probably decreased because of mass-transfer effect even though the column was

operated at flooding. Just before flooding, more holdup of the discontinuous phases is expected; this in turn causes increased turbulence, with the result that higher efficiencies are obtained in the column. It is obvious from these remarks that it would be unwise to compare reduced throughput rates at flooding with reduced throughput rates when the column is not flooded.

Since the two columns cannot be compared directly, linear approximations may be assumed for the comparison. For example, at a packing density of 47.5 lb/cu ft the larger column has a stage efficiency showing 18.5% improvement over the small column, but this is accompanied by a 12.5% reduction in throughput. At a packing density of 50 lb/cu ft the efficiency is improved 12.5% and the throughput is reduced 15.5%.

TABLE XXXII

EFFECT OF COLUMN DIAMETER ON HETS VALUES

Column Diameter (Inches)	Packing Density (lb/cu ft)	HETS	Sum of $(ft/hr)^{1/2}$	% of Maximum Throughput
2.127	47.5	81.1	18.46	100.0
3.32	47.5	66.1	16.19	87.6
2.127	50.0	72.9	17.46	100.0
3.32	50.0	63.7	14.82	84.5

It can also be pointed out that increasing the packing density from 47.5 to 50 lb/cu ft for the small column gave HETS improvement of 10%, was accompanied by a 5% decrease in throughput. For the same increase in packing density in the large column, the HETS improved 3.6% and the throughput decreased 8.5%.

The ratio of tower diameter to packing diameter is 6.75 for the small column and 10.5 for the large column.

From the above data it is obvious that increases in packing density give increases in column efficiency, but these are accompanied by decreases in allowable throughput rates. At a ratio of tower diameter to packing diameter of 6.75, the increase in efficiency is twice as much as the decrease in throughput. On the other hand, for a ratio of tower diameter to packing diameter of 10.5, the increase in efficiency is less than half as much as the decrease in throughputs.

Although these are rather meager data, it may be concluded that channeling, if it exists, is more pronounced in the small column than it is in the large column. It can also be concluded that settling of the packing is advantageous if the ratio of tower diameter to packing diameter is less than approximately 7, although it might be deleterious to settle the packing if this ratio is 10 or more.

Pulsed Columns A table similar to Table XXXII was made up to determine if channeling and scale-up factors could be observed for pulsed columns. This problem is complicated by the extremely high efficiencies due to pulsation as well as by other factors such as reduced throughput. Both columns contained so many stages that end effects were neglected. The only amplitude considered was 5.0 mm and the only frequency was 125 RPMS.

HETS values were taken from Figure 18 which correspond to certain superficial velocities. These are tabulated in Table XXXIII. A value of HETS was taken from Table XX and corrected to 5.0-mm amplitude. These data are also added to Table XXXIII.

TABLE XXXIII

COMPARISON OF HETS VALUES (PULSED)
5-mm amplitude 125 RPM 2.1 CCl_4/H_2O Flow Ratio

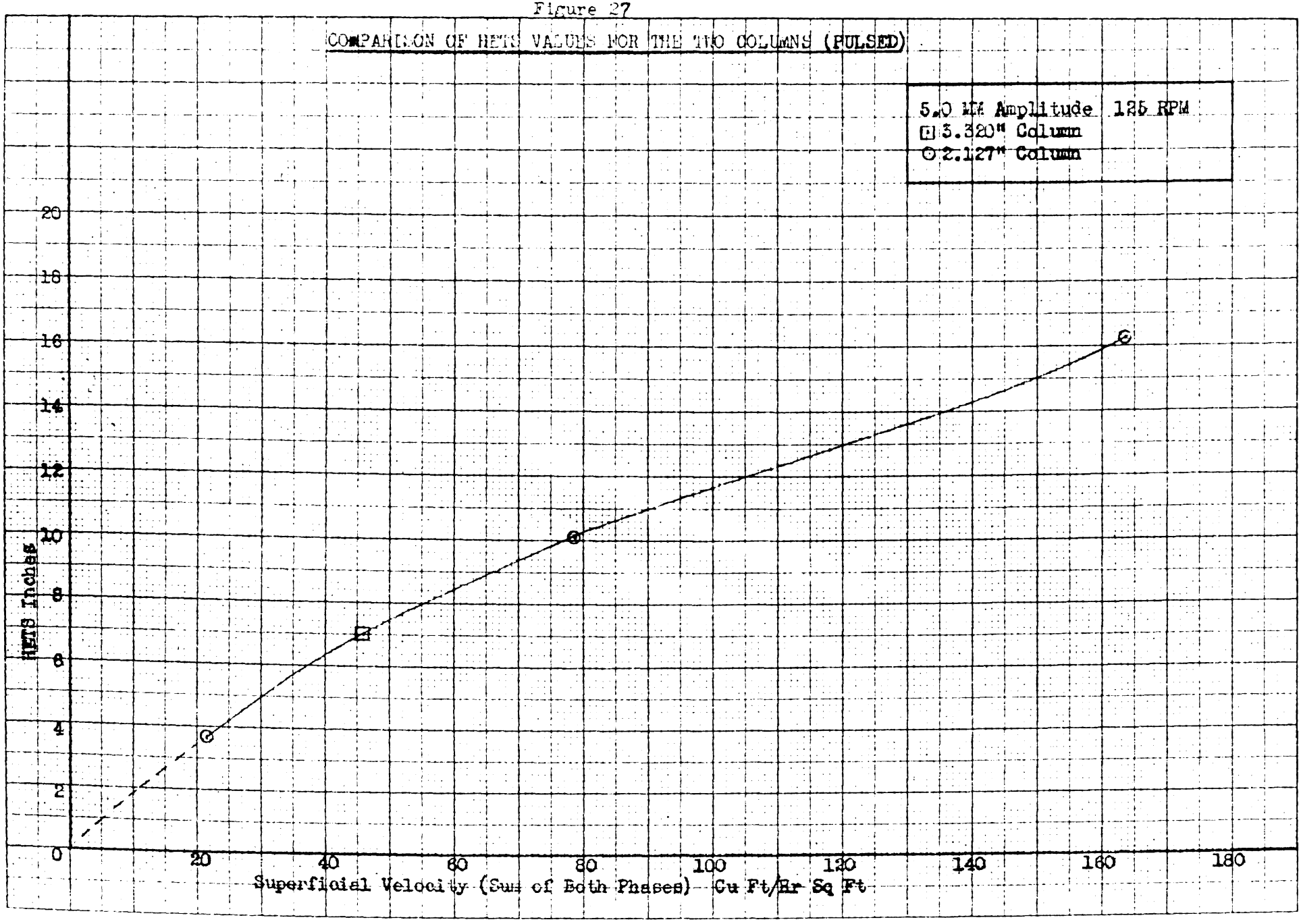
Column Diameter (Inches)	Superficial Velocity	% of Total	HETS
2.127	163.7	100.0	16.23
2.127	78.9	48.2	10.10
2.127	21.6	13.2	3.70
3.32	46.0	28.1	7.0

These data are presented graphically in Figure 27 and show that pulse columns exhibit little noticeable channeling as might be anticipated.

Comparison with Other Columns A review of the tabulation on pulse columns presented in the introduction of this report shows that, in general, pulse columns will give a minimum HETS of about six inches. That value also seems to be about the best that could be obtained in this investigation. Lower values were found, but only when the throughput rates were greatly diminished.

If a value of 6 inches for a theoretical stage could always be anticipated for pulse columns, this would make an excellent design tool.

Figure 27


COMPARISON OF HETS VALUES FOR THE TWO COLUMNS (PULSED)
5.0 MM Amplitude 125 RPM
⊡ 3.320" Column
⊙ 2.127" Column
HETS Inches
0
2
4
6
8
10
12
14
16
18
20
20
40
60
80
100
120
140
160
180
Superficial Velocity (Sum of Both Phases) Cu Ft/Hr Sq Ft

CONCLUSIONS

The following conclusions have been made as a result of this investigation:

1. The amount and direction of mass transfer has a very significant effect on the maximum allowable throughput rates. This is shown by the following:
   a. For the small column, unpulsed, when the entering carbon tetrachloride contained 1% acetone the maximum throughput rates were approximately twice those obtained when no acetone was present in either phase or when acetone was present in both phases in approximately equilibrium amounts.
   b. At a flow ratio of approximately four volumes of water to one of carbon tetrachloride, in the large column, practically no mass transfer occurs in the lower part of the column. This causes the maximum allowable throughput rates to decrease to less than half those obtained in the small column at comparable flow ratios.
   c. The large column gives about 30% less permissible throughput than the small column at flow ratio greater than 2.1 volumes of carbon tetrachloride to one volume of water.
   d. When sufficient acetone is present in the column, i.e., when the flow or carbon tetrachloride is high, the application of pulse permits increased throughput rates due to the greater amount of mass transfer.

e. When the efficiency of column operation is increased by using higher frequency or longer pulse stroke, further increases in the maximum throughput rates are observed. At the same time, the flow of carbon tetrachloride, which contains acetone, must again be increased to allow for the greater mass transfer. Almost a quantitative reversal of this effect occurs at lower flow ratios.

2. The equations of Hoffing and Lockhart, Breckenfeld and Wilke, as well as others, could not be used to predict maximum throughput rates when a solute was present. This was due to the fact that when a solute was present the physical properties of the two liquids could not be measured at the non-equilibrium conditions existing in the column.

3. Pulsing tends to gradually increase the packing density of pulsed columns; therefore, by their nature, pulsed columns cannot operate at low packing densities. High packing densities tend to decrease the maximum allowable throughput rates, but these decreases are accompanied by comparable increases in column efficiencies.

4. Pulsation can give as much as a 20-fold improvement in column efficiency. This, however, is obtained only under extreme operating conditions. At reasonable throughput rates and with vigorous pulsing, a stage height of approximately six inches (14-fold improvement) was obtained. A summary of the published data on pulsed-packed columns and pulsed sieve-plate columns contained in the beginning of this report shows that other investigators have also obtained similar stage heights.

5. Both pulsed and unpulsed packed columns show an increase in efficiency with decreased throughput rates. Pulsed columns appear to be less dependent on total throughputs than unpulsed columns. Unpulsed packed columns may exhibit an initial sharp decrease in column efficiency down to about 85% of the maximum throughput rate and from there give a gradual improvement with further decreases in throughput rates. This latter observation should be regarded with some caution, however, due to the extreme change in operating conditions at the onset of flooding.
6. Stable emulsions did not form in any of these runs. At high amplitude and frequency, fine dispersions did occur, but these settled immediately when the pulse was stopped. Finer dispersions resulted in lower permissible throughput rates and better column efficiencies.
7. New packing at first tended to change (perhaps to orient) with continued pulsing, giving a progressive improvement in column efficiency. The limiting throughputs remained essentially constant during this period. After an initial series of runs had been made, no further change could be noticed.
8. The HETS concept proved to be better than the HTU concept, because HETS was independent of flow ratio and feed concentration, whereas HTU values exhibited a pronounced dependence on flow ratio.

9. At low and moderate conditions of pulse, both amplitude and frequency gave comparable improvements in column efficiency as observed from the pulsed volumes. When more vigorous pulse conditions were used, frequency increases appeared to produce more improvement than could be obtained with increases in amplitude.

10. Mass transfer at the simple inlet tubes used in this investigation was not particularly significant (equivalent to only 0.15 NTS). This is in contrast to results reported in the literature where most of the mass transfer apparently occured at the ends of the columns.

11. Maximum allowable throughput rates were sometimes increased and sometimes decreased by the application of pulse. This was true at certain flow ratios, regardless of whether or not a solute was present.

12. Inconclusive results were obtained in this investigation on the effects of scale-up. Apparently, a change in diameter from 2.127 to 3.32 inches is not of sufficient magnitude to give a good comparison.

APPENDIX I

LIME-GLASS RASCHIG RINGS

Weight per ring, 0.503 gms
Displacement per ring, 0.1979 ml
Area per ring, 407.2 sq mm

Bulk Density lb/cu ft	Void Fraction ft^3/ft^3	Area ft^2/ft^3
44	0.7228	174
48	0.6976	190
52	0.6724	205

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