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DEPARTMENT OF ENGINEERING RESEARCH

NORTH CAROLINA STATE COLLEGE

RALEIGH, NORTH CAROLINA

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Progress Report No. 4

covering the specific topic of

THE FLOODING CAPACITY OF A PULSE COLUMN
on the
BENZENE-WATER SYSTEM

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Contract No. AT-(40-1)-1320

"The Performance of Contactors for Liquid-Liquid Extraction"

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THE FLOODING CAPACITY OF A PULSE COLUMN
on the
BENZENE-WATER SYSTEM

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SUMMARY

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The work reported here is an extension,to the system of benzene and water, of a previous program of study of pulse column flooding behavior. This report is, therefore, closely related to Progress Report No. 3, which covered the flooding studies on the system of trichloroethylene-water, and which described the statistical guidance and analysis then employed.

The previous work was characterized by an unexpectedly large experimental error which was tentatively ascribed to the effects of grease contamination. Therefore, for this study, a strenuous effort was made to eliminate all possible contamination. While not entirely successful, grease contamination was very greatly reduced. As a result the experimental reproducibility improved tremendously, the standard deviation dropping from the previous 33 units of capacity (the sum of the input flows) to 6.1 units of capacity. Other interesting evidence in this regard was revealed.

In general, this work confirms the previous conclusion of Progress Report No. 3 that trace contamination with interfacially active agents is a factor of major importance to pulse column flooding studies, and presumably to many other phases of pulse column work as well.

A new technique, partly statistical, has been devised, and briefly tested, for the purpose of revealing the proper definitions and functional relationships with which to express the pulse column flooding behavior. The success of the new technique hinges upon the availability of an adequate body of data

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of proved precision, such as the benzene-water data are presumed to be. The technique consists of three steps, (1) the formulation of various assumptions concerning the relationships in question, (2) the derivation by the methods of least-squares of best-fitting equations relating the experimental data to equations expressing the assumed relationships in terms of the experimental conditions, (3) an analysis of variance for the derived best-fitting equations, leading to statistical measures of the lack of fit of the equations to the data, and (4) the selection of the better assumptions on the basis that the better the assumption, the better the degree of fit obtainable through its use (for a given complexity of equation).

Using this new technique, it was demonstrated that it is better, for correlating purposes, to express the flooding capacity of a pulse column as

$$C = \frac{V_D}{FA} = \frac{\text{actual discontinuous flow rate}}{\text{pulse pumping rate}}$$

than to employ the customary definition

$$C = V_D + V_C = \text{sum of the two input flows.}$$

The nomenclature is defined in the report.

A disadvantage of the new technique is the excessive amount of computational work involved, not only in the statistical calculations, but also in the first step where pertinent relationships are formulated for testing. The use of high speed computors is indicated.

INTRODUCTION

The work covered in this report is a continuation of the efforts and approach recorded in Progress Report No. 3. Both that work, and this one, were flooding studies on a pulse column, wherein the work was guided by statistical considerations, and an effort was made to find generalizations in the flooding behavior.

The work covered in Progress Report No. 3 was on the system trichloroethylene-water, and the results were on the whole gratifying. However, the efforts to duplicate the runs revealed an unexpectedly large random error, the cause for which was traced, with reasonable but not certain assurance, to contamination of the system by traces of the greases used to lubricate the pumps. Some of the runs were discarded as being unduly influenced by grease contamination, and the remaining runs were subjected to statistical analysis. Even with this rejection of the most discordant values, the standard deviation remaining was large, about 30 units of capacity (ft/hr), when it was expected that it would be at least as small as 10 units. Using a typical capacity value of about 200 units, this standard deviation was 15%, compared to the 5% or less expected.

In spite of the large experimental error, the statistical treatment of the trichloroethylene-water results was of considerable value. It was possible to show that, in the role of controlling variables, V_D, the flow rate of the discontinuous phase, and V_C, the flow rate of the continuous phase, acted not as two variables but rather as one variable, which was their ratio V_D/V_C. This behavior had been expected through analogy with packed and spray column work but now it was reasonably proved for pulse column operation.

A consequence of this demonstration of the applicability, for flooding work, of the ratio V_D/V_C, was the fact it created the possibility that all pulse column flooding correlations could be specified with one less variable than otherwise. For pulse column behavior, which tends to be overrun with variables, this was an important simplification. Indeed, there was strong motivation to proceed further, to seek other simplifications in form, and to test statistically other definitions of capacity than the one conventionally employed, which was $C = V_D + V_C$ = capacity. It was planned that the testing would be carried out by assuming a suitable relationship, then measuring statistically the ability of that assumed relationship to fit the experimental results. Presumably a choice could be made between two different assumed relationships on the basis of the closeness of the fit obtained. Unfortunately, the trichloroethylene-water data were not suitable for these further steps, because the magnitude of the experimental error tended to obscure the distinctions sought. In this manner, a real need for a better set of flooding data arose.

Based upon the considerations just expressed, a new set of flooding capacity experiments were planned for the following specific purposes:

1. The cause for the unexpectedly large experimental error encountered with the previous trichloroethylene-water runs was to be sought, and eliminated insofar as possible. It appeared probably that the cause was grease contamination.
2. With the experimental error substantially reduced, a new set of flooding capacity data was to be obtained, to form a basis for further study and statistical analysis.
3. Preferably the new set of flooding data was to be obtained on the system benzene-water, since for other phases of the pulse column program, information on this system would be needed.
4. To make the most of the opportunity, a slight modification (as explained later) of the previous statistical design was to be employed.

5. Assuming that the new data would be adequate for the purpose, the results were to be studied in an effort to find more general relationships connecting the variables. It is almost axiomatic that those relationships are the most general that are the most completely formulated into dimensionless groups, thus pointing to early tests of the value of various dimensionless formulations.

It was presumed that the better the manner of formulating the relationships, the better the degree of fit between the experimental data and the consequent correlating equation derived by the method of least squares. This being so, an analysis of the variance for each assumed relationship would provide a criterion sufficient to point to the better assumptions. It was recognized that this procedure might require more computing time than reasonable, but a decision on that point awaited the trial.

THE GREASE CONTAMINATION PROBLEM

The first step in this particular program was to inquire closely into the problem of grease contamination, since all of the evidence pointed to it as the cause of the large experimental error encountered during the previous flooding study. The results of that inquiry are as follows.

(a) Review of the Evidence

Suspicion was directed at the factor of grease contamination for the following reasons:

1. In view of the extraordinary efforts made in the design and construction of the pulse column unit, for the purpose of minimizing contamination, the only logical explanation for the appearance of precipitated material at the liquid interface was that of grease extraction from the pumps, followed by precipitation within the column by some unknown mechanism. Incidentally, the precipitation in in question is a well-recognized phenomenon in extraction work.
2. Both unusually great precipitation and unusually large experimental error in flooding capacity determinations seemed to come after instances of pump greasing. It was unfortunate that the periods of greasing were not recorded, and it was necessary to rely upon recollections a few weeks old.
3. When pump lubrication was minimized, the rate of precipitation within the column decreased and the experimental error became decidedly less.
4. The effect of grease contamination apparently was to <u>increase</u> the flooding capacity. This behavior was in agreement with two previous experiences with other systems. One experience was that the flooding capacity for benzene-water dropped abruptly after the benzene phase

had been distilled to increase its already-high purity. The other experience was that for the system benzene-phenol-water, the flooding capacity increased sharply with increase of phenol content, even in trace amounts.

(b) The Pump Situation

The pumps seemed to be the only possible point of entry of grease, or any other, contamination into the system. As it turned out, some of the pump details were quite important in regard to this problem, such as the typical details indicated in Figure 1 for the feed and discharge pumps. Note that the liquid end of the pumps is separated from the motor end, and that at the liquid end the piston functions through a set of about 5 Teflon packing rings. Backing up the packing is a packing gland nut that should be just tight enough to prevent leakage. A lantern ring permits lubrication of the piston between sections of the packing, if needed.

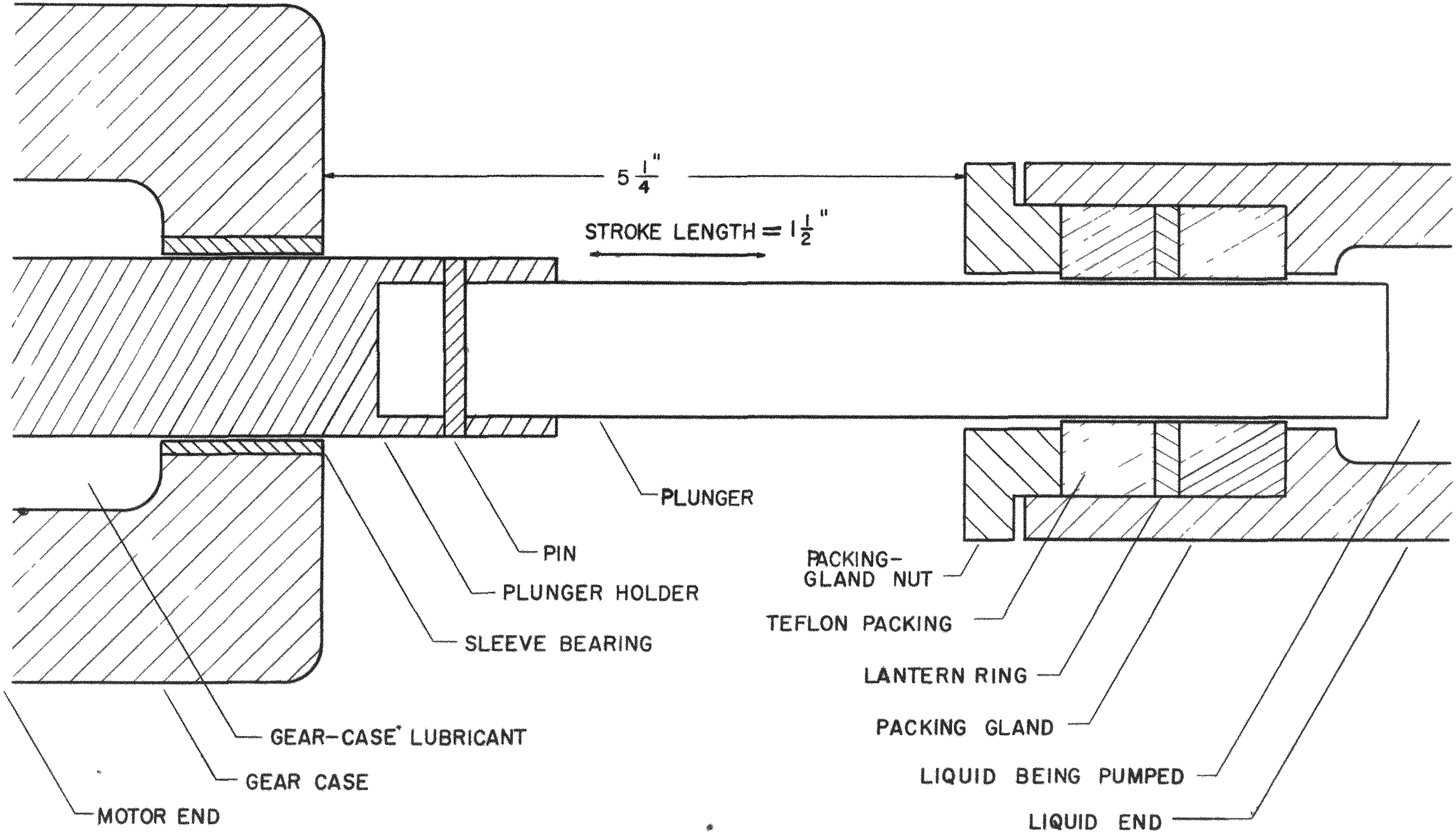
The gears of the feed and discharge pumps are immersed in gear-case lubricant. At the level of the piston, the lubricant is under a slight hydrostatic head and tends to seep along the piston holder through the sleeve bearing, thus reaching the piston itself. The pulse pump arrangement was slightly different. The sleeve bearing there was lubricated with a grease that did not have a tendency to flow along the piston. As will be seen later, these details were important.

The pumps had been purchased with the assurance that they could operate on benzene and water quite satisfactorily without the need for lubrication. To this end, the pistons had been specified to have a highly polished finish, and the packing consisted of inert Teflon rings (identified as PP201 and consisting of shredded Teflon, mica and a binder).

In practice, the pumps required lubrication of the packing glands of the liquid ends. Without lubrication, the pistons and motors overheated, the pistons chattered at low speeds and the motors frequently stalled. Finally, the

FIGURE 1

TYPICAL PLUNGER ARRANGEMENT FOR PUMPS



pumping parts were dismantled and examined closely, whereupon it was found that the pistons were badly scored and the Teflon packings damaged. During an attempt to machine the pistons smooth, it was discovered that the various pistons were neither round nor straight. Indeed, from a machinist's point of view, they were quite egg-shaped and decidedly bowed. Apparently this was a major cause of the trouble.

The pistons were replaced with new, smooth ones from the factory. No measurements were made of these pistons when there was a ready opportunity, but since they functioned satisfactorily, and since the manufacturer by then was well aware of the complaints, presumably the new pistons were as they should be. The Teflon rings (with Teflon spacers) were replaced with similar, but somewhat different ones, identified as U. S. Gasket Company No. 711-0, shredded Teflon containing no filler but a little binder material. The pump manufacturer claimed that this new packing was a decided improvement over the old packing.

(c) Installation of the new Teflon packing

The new packing fit so tightly that it was impossible to install it without some lubrication. Accordingly, the inner and outer circumferences were lightly greased and about 5 rings (with spacers) installed on the pistons in the packing glands. The packing gland nut was tightened to what is called "hand-tight", then loosened slightly. The pumps were then put into operation for about a day, at the end of which the packing nut was gradually tightened just until all leakage stopped.

For the light greasing, the water pump packings were lubricated with Nordcoseal 357, which is soluble in water. Similarly, the benzene pump packing was touched with Nordcoseal 147, which is soluble in benzene. In this manner, both greases should be removed as quickly as possible during operation. However, it was recognized that some of the grease was deeply buried and would only leach out slowly. At most, only about 0.1 gram of grease was employed per piston.

EQUIPMENT, MATERIALS AND PROCEDURE

(a) Equipment

The equipment was the same as that described in Progress Report No. 3. For convenience, three descriptive figures of the previous report are reproduced here as Figures 2, 3 and 4. In addition, the pulse column itself is briefly described as follows. The column was a precision bore tube of chemical pyrex, 1.92 inches in internal diameter, and 48 inches long. It contained 23 perforated plates of 20 gage stainless steel spaced 2.00 inches apart, each perforated with 1/8 inch holes in a 60° triangular pattern providing 21% free space. Attached to each end of the plate section were enlargements which served as settling zones, and to which the feed and exit lines were attached.

(b) Materials

The water employed was a good grade of distilled water. The benzene was the best obtainable commercial grade, purchased under the designation of nitration grade, thiophene-free 1° benzene from the Barrett Division of Allied Chemical and Dye Corporation.

(c) Clean-up Procedure

To avoid as much as possible the effects of grease contamination, the entire apparatus was subjected to a thorough cleaning before the flooding studies were started.

When the unit was opened, it became apparent that there was need of cleaning, particularly in the feed tanks. On virtually all walls, there were deposits that were extensive although quite light and of little body. Presumably they were precipitated grease residues. However, the sum total of all the deposits could hardly total one gram.

Before cleaning the equipment generally, the pumps were cleaned and re-

FIGURE 2
EQUIPMENT LAYOUT

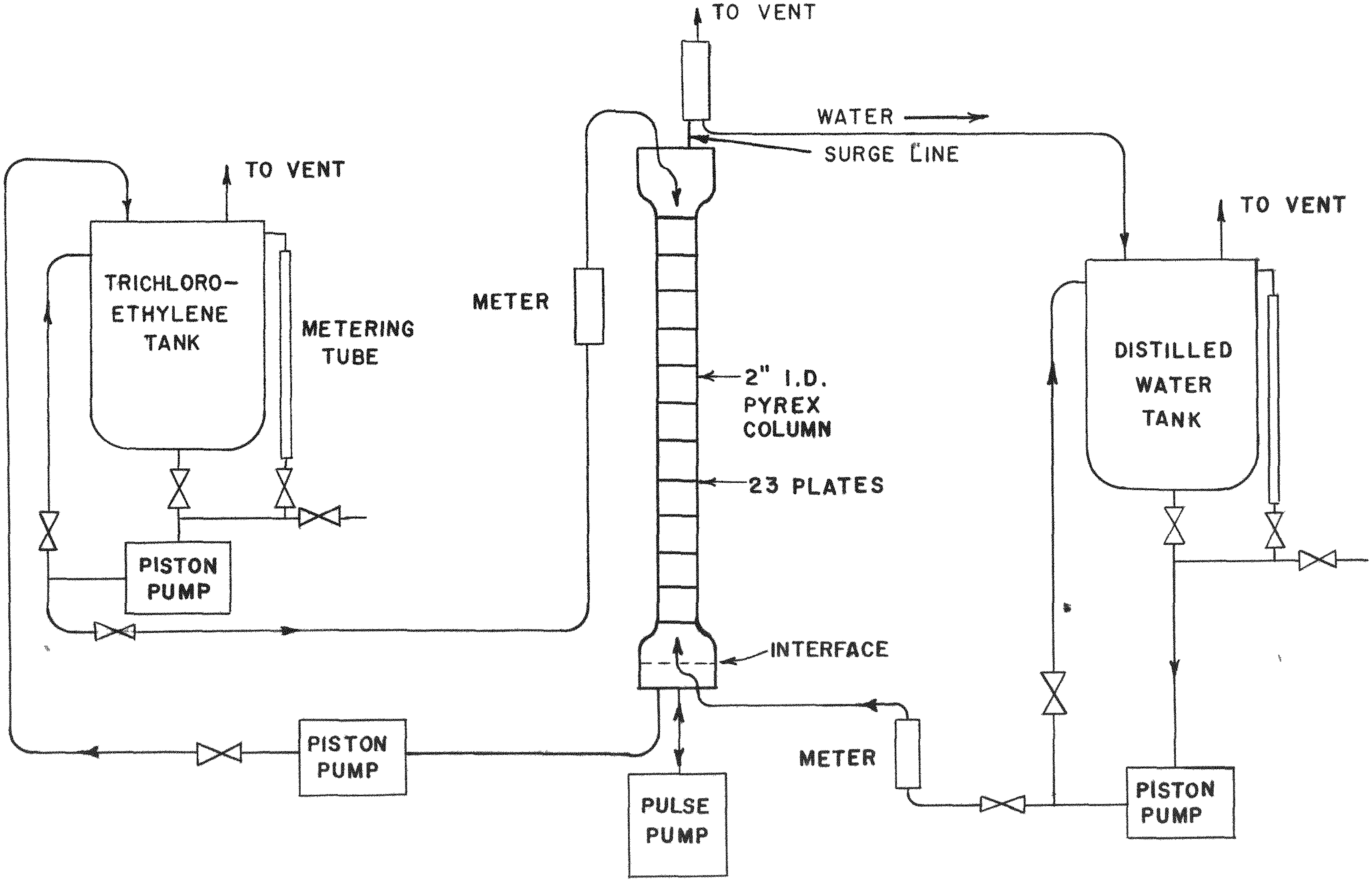
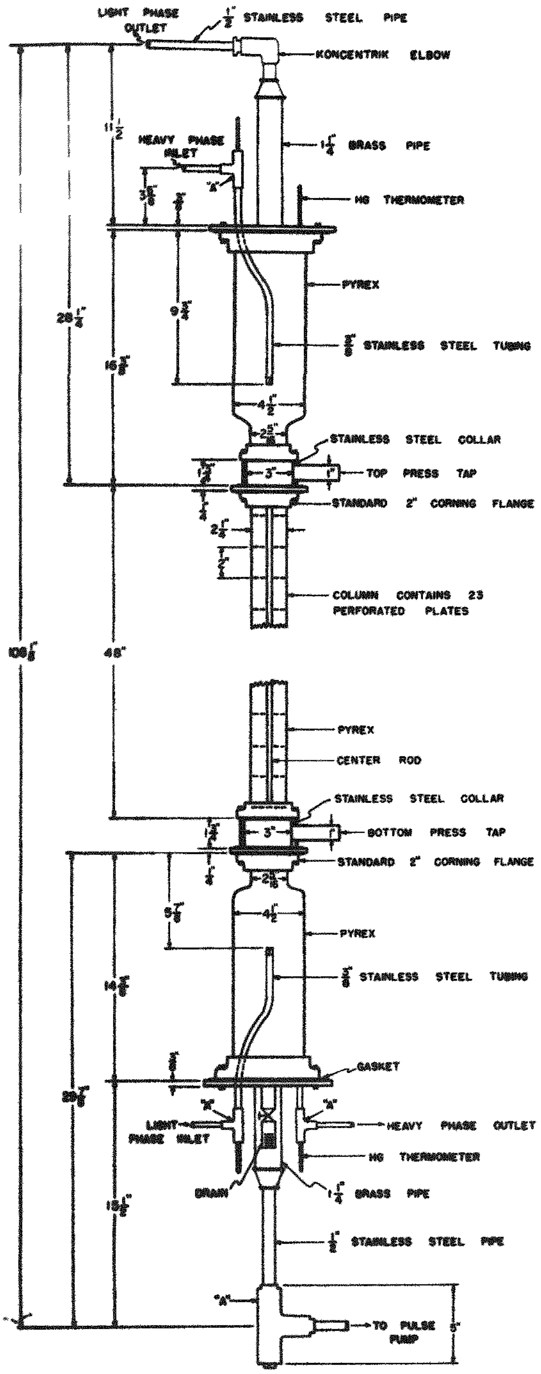


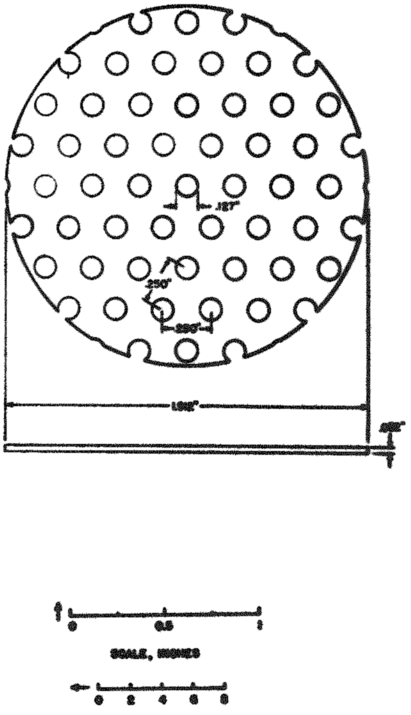
Fig. 3 - Pulse Column Unit



NOTES "A" – KONCENTRIK TEE
GASKETS ARE AMERIPOL RUBBER
ALL DIAMETERS SHOWN ARE O D

FIG. 4

COLUMN AND PLATE DETAILS



packed with new Teflon rings, assembled with about 0.1 gm or less of soluble grease per piston. Refer to the previous section for details. The pumps were then run for about 1/2 hour, presumably dissolving off the most exposed films of grease.

Then the entire apparatus was drained and charged with 3% aqueous NaOH. This solution was circulated through the apparatus for several hours. Then the weak alkali was discarded and the various pieces of apparatus opened. The tanks, gage glasses and column were hand-cleaned with detergent, followed by weak alkali, followed by water. After reassembling, the unit was flushed with tap water until the slippery feeling of NaOH was gone, then flushed with distilled water until free of NaOH (by test with phenolphthalein). Next, the tanks were charged with a small quantity of benzene and water, and the unit operated for awhile, discarding and not recycling the outlet streams from the column.

At this stage it was considered that the pulse unit itself was clean, but that residual traces of the small amounts of grease (0.1 gm per piston) employed to facilitate the repacking of the pumps might slowly emerge to cause trouble later on. This was because some of that grease no doubt became sandwiched between the various packing rings, hence buried rather deeply.

Presumably it would become available only as fast as it diffused out of its comfined layers, excepting for the occasions when the packing rings might be momentarily squeezed enough to eject material into the stream.

To cover this situation, the pulse unit was charged with benzene and water, and put into operation, recycling the phases. Soon a light-grey precipitate started forming at the interface although at a rate quite a bit slower than previously (during the trichloroethylene-water runs). For several days the precipitation continued, but at a decreasing rate. At intervals, the unit was shut down and the inside walls of the glass column were wiped clean of adhering precipitate (which looked but did not feel greasy). Then fresh benzene and water were charged and the unit again set to recycling for a running period of 8 days. During this time, the rate of precipitate formation continually decreased to an almost negligible rate. At times, the slight precipitate collection was flushed out of the system. At the end of this clean-up period, it was thought that the source of contamination has been suppressed to the point of negligible effect. At least no further effort seemed warranted.

(d) Operating Procedure

The operating procedure, including the manner of determining the flooding capacities, was essentially that described in Progress Report No. 3. The benzene was made the discontinuous phase, flowing upward and generating the interface at the top of the column. As before, the outlet streams from the column were recycled to the feed tanks.

There was one added feature to the procedure. To counteract the slight rate of precipitate formation still existing, at regular intervals the feed materials were exchanged for fresh charges. Of the 54 flooding capacity runs later made on this system, approximately each fourth was made on different batches of feed stocks.

In the determination of the flooding capacity, the capacity was approached from both sides, and taken finally as that operating capacity just on the verge of visual flooding.

THE STATISTICAL DESIGN

The statistical design employed was very similar to the third order composite design described in Progress Report No. 3. The differences consisted of a somewhat different positioning of the statistical points, in an effort to improve the precision of the estimates for the coefficients of the best-fitting equations subsequently derived. The design can be described by saying that each statistical unit took on values of 0, ± 0.86, ± 1.00 and ± 1.19. The actual combinations employed are presented in Table 2, along with other information.

The programming called for a random sequence in 27 runs, followed by a duplication of the runs in another random sequence.

Preliminary runs on the pulse column were employed to establish reasonable operating limits for the benzene-water system and the pumps. Based upon the information obtained, the relationships between the statistical units and the operating units were defined as indicated in Table 1.

TABLE 1

Correspondence Between Standardized and Operating Units

Amplitude		Frequency		V_D/V_C Ratio	
x_1	A-inches	x_2	F-cpm*	x_3	Ratio
-1.19	0.202	-1.19	20.0	-1.19	0.336
-1.00	0.242	-1.00	24.8	-1.00	0.400
-0.86	0.277	-0.86	28.3	-0.86	0.455
0.00	0.633	0.00	50.0	0.00	1.000
0.86	1.444	+0.86	71.7	+0.86	2.20
+1.00	1.651	+1.00	75.2	+1.00	2.50
+1.19	1.982	+1.19	80.0	+1.19	2.98

* cpm = cycles per minute

The functional relationships are as follows:

$$\lg A = (1/2.40)(x_1 - 0.4775)$$

$$F = 25.2x_2 + 50$$

$$V_D/V_C = 3^{0.834x_3}$$

RESULTS AND OBSERVATIONS

Runs 10 through 20 were made on one charge of benzene and water, runs 22 through 35 on the second charge, runs 36 through 50 on the third and runs 51 through 69 on the fourth and last charge (not every number from 10 through 69 represented a run).

Generally speaking, the rate of precipitation that collected at the interface was very greatly reduced (to less than 1/10) compared to the trichloroethylene-water runs. However, it was not entirely eliminated.

A very unusual situation occurred in regard to the interfacial precipitation, that was most enlightening. Starting with run 38 a yellow-orange (later yellow-brown, then brown) film made its appearance inside the column, coating out on the walls and collecting at the interface. Heretofore, the precipitate had been grey. It was finally determined that this contamination consisted of gear-case lubricant from at least one feed pump. This gear-case lubricant could only enter the system after an admirable feat of gymnastics. Refer to Figure 1. The gear-case lubricant only directly contacted one end of a piston, hence seemingly had no opportunity to cross the space necessary to make contact with the wiping action at the liquid end. But close inspection left no doubt that contact was being made. Examination revealed that the gear-case lubricant was able to, and did in fact, creep along the stainless steel piston surface. Presumably this would be called a type of wetting action, or capillary action. It crept along a piston until a continuous film was established between the gear-case and the liquid end. Then, as material was removed by leaching at the liquid end, more gear-case lubricant was drawn along the piston surface by the wick-like action.

As soon as the situation was realized (run 51), the pistons of all pumps were wiped clean and lightly washed with solvent. Immediately, the brownish precipitation started to decline, and by the time run 52 was started, it had ceased. The relation of cause and effect seemed clearly established. For all subsequent runs, the pistons were wiped clean each run.

With the yellow-brown precipitate gone, there remained only a very small amount of the customary greyish precipitation, until run 67. That run was made at a high feed rate, requiring fast pump action. The feed pumps began to leak a little, so the packing gland was tightened slightly. A result was a recurrence of noticeable amounts of grey precipitate. It seemed logical to attribute this re-appearance to traces of old lubricant being squeezed out of the pump packing by the more stringent conditions.

The data obtained on the flooding behavior of the benzene-water system at room temperature are presented in Tables 2 and 3.

TABLE 2

Operating Conditions for Flooding Studies

Set Number	B-W Run Number	Statistical Units			Operating Units			
		x_1 (A)	x_2 (F)	x_3 (V_D/V_C)	A Inches	F cpm	V_D/V_C ratio	FA ft/hr.
1	32	-1	-1	-1	0.24	24.8	0.407	29.8
	51*				0.24	25.0	0.403	30.0
2	34	+1	-1	-1	1.65	24.5	0.399	202.2
	67				1.65	24.8	0.400	204.6
3	36	-1	+1	-1	0.24	75.3	0.400	90.4
	47*				0.24	75.4	0.404	90.5
4	41*	+1	+1	-1	1.65	75.2	0.401	620.5
	52				1.65	76.3	0.402	629.5
5	26	-1	-1	+1	0.24	24.5	2.43	29.4
	48*				0.24	25.1	2.52	30.1
6	35	+1	-1	+1	1.65	24.8	2.56	204.6
	61				1.65	24.7	2.48	203.8
7	30	-1	+1	+1	0.24	75.2	2.50	90.2
	64				0.24	75.4	2.51	90.5
8	40*	+1	+1	+1	1.65	74.3	2.61	613.0
	62				1.65	75.2	2.38	620.5
9	33	0	0	0	0.63	50.7	0.996	159.8
	57				0.63	50.2	0.995	158.1
10	29	-0.86	0	0	0.28	50.0	1.000	70.0
	54				0.28	50.2	1.000	70.3
11	25	+0.86	0	0	1.44	50.0	1.001	360.
	43*				1.44	50.0	0.997	360.
12	28	0	-0.86	0	0.63	28.1	0.992	88.5
	59				0.63	28.5	1.003	89.8
13	37	0	+0.86	0	0.63	71.6	1.005	225.6
	44*				0.63	72.0	0.992	226.8
14	27	0	0	-0.86	0.63	50.5	0.456	159.1
	68				0.63	50.0	0.455	157.5
15	24	0	0	+0.86	0.63	50.0	2.17	157.5
	60				0.63	50.8	2.16	160.0
16	20	-1.19	-1.19	0	0.20	20.0	0.982	20.0
	58				0.20	20.6	1.000	20.6
17	17	-1.19	+1.19	0	0.20	80.0	1.01	80.0
	55				0.20	80.0	1.00	80.0
18	13	-1.19	0	-1.19	0.20	49.5	0.335	49.5
	45*				0.20	50.0	0.341	50.0
19	19	-1.19	0	+1.19	0.20	50.0	3.02	50.0
	63				0.20	50.0	3.02	50.0
20	15	+1.19	-1.19	0	1.98	20.0	0.99	198.0
	56				1.98	19.9	1.00	197.0
21	42*	+1.19	+1.19	0	1.98	79.9	0.986	792.
	50*				1.98	80.3	0.975	795.
22	12	+1.19	0	-1.19	1.98	50.2	0.342	497.
	49*				1.98	49.9	0.336	494.
23	38*	+1.19	0	+1.19	1.98	50.0	3.00	495.
	65				1.98	50.0	2.89	495.

TABLE 2

Operating Conditions for Flooding Studies (continued)

		Statistical Units			Operating Units			
Set Number	B-W Run Number	x_1 (A)	x_2 (F)	x_3 V_D/V_C	A Inches	F cpm	V_D/V_C ratio	FA ft/hr.
24	10	0	-1.19	-1.19	0.63	20.0	0.334	63.3
	53				0.63	20.0	0.339	63.3
25	14	0	-1.19	+1.19	0.63	19.9	3.02	63.0
	66				0.63	20.3	2.98	63.8
26	11	0	+1.19	-1.19	0.63	80.0	0.337	253.2
	69				0.63	80.0	0.337	253.2
27	16	0	+1.19	+1.19	0.63	80.0	3.00	253.2
	46				0.63	80.1	3.01	253.6

* During these runs there was slight contamination with gear-case lubricant. See text.

TABLE 3

Responses Obtained during Flooding Studies

Set Number	B-W Run Number	Capacities in ft/hr. V_C	V_D	$V_D + V_C$	Dimensionless Responses $\frac{V_D}{FA}$	$\frac{V_D + V_C}{FA}$
1	32	35.6	14.5	50.1	0.487	1.684
	51*	37.3	15.1	52.4	0.503	1.749
2	34	111.5	44.5	156.0	0.220	0.772
	67	112.5	45.1	157.6	0.220	0.771
3	36	85.3	34.1	119.4	0.377	1.320
	47*	83.0	33.6	116.6	0.371	1.290
4	41*	19.9	8.0	27.9	0.0129	0.0450
	52	19.7	8.0	27.7	0.0127	0.0440
5	26	13.1	31.9	45.0	1.085	1.531
	48*	12.2	30.6	42.8	1.016	1.421
6	35	28.0	69.1	97.1	0.338	0.475
	61	27.6	68.6	96.2	0.337	0.472
7	30	24.8	62.0	86.8	0.688	0.963
	64	24.4	61.2	85.6	0.676	0.946
8	40*	7.2	18.9	26.1	0.0308	0.0426
	62	5.9	14.2	20.1	0.0229	0.0324
9	33	63.6	63.4	127.0	0.397	0.795
	57	63.6	63.4	127.0	0.401	0.804
10	29	45.1	45.0	90.1	0.643	1.286
	54	47.1	47.0	94.1	0.669	1.339
11	25	32.1	32.2	64.3	0.0894	1.785
	43*	33.6	33.5	67.1	0.0930	1.865
12	28	56.1	55.7	111.8	0.630	1.264
	59	56.1	56.5	112.6	0.629	1.254
13	37	50.1	50.3	100.4	0.223	0.445
	44*	56.8	56.4	113.2	0.249	0.500
14	27	110.7	50.4	161.1	0.317	1.014
	68	114.2	51.9	166.1	0.330	1.055
15	24	34.7	75.2	109.9	0.478	0.698
	60	34.6	74.6	109.2	0.466	0.683
16	20	16.2	15.9	32.1	0.795	1.605
	58	17.1	17.1	34.2	0.830	1.660
17	17	46.2	46.8	93.0	0.585	1.163
	55	46.3	46.4	92.7	0.580	1.159
18	13	62.5	20.9	83.4	0.422	1.685
	45*	60.0	20.5	80.5	0.410	1.610
19	19	16.1	48.6	64.7	0.972	1.294
	63	16.3	49.0	65.3	0.980	1.306
20	15	64.3	63.7	128.0	0.322	0.646
	56	56.9	57.0	113.9	0.289	0.578
21	42*	8.2	8.1	16.3	0.01024	0.0206
	50*	8.4	8.1	16.5	0.01019	0.0208
22	12	39.4	13.5	52.9	0.0272	0.1064
	49*	32.7	11.0	43.7	0.0223	0.0885
23	38*	8.2	24.6	32.8	0.0497	0.0662
	65	6.5	18.7	25.2	0.0378	0.0509

TABLE 3

Responses Obtained during Flooding Studies (continued)

Set Number	B-W Run Number	Capacities in ft./hr.			Dimensionless Responses	
		V_C	V_D	$V_D + V_C$	$\frac{V_D}{FA}$	$\frac{V_D + V_C}{FA}$
24	10	85.6	28.6	114.2	0.452	1.805
	53	85.1	28.9	114.0	0.456	1.800
25	14	22.6	67.3	89.9	1.068	1.426
	66	20.4	60.6	81.0	0.950	1.270
26	11	127.3	43.0	170.3	0.170	0.672
	69	100.1	33.7	133.8	0.133	0.528
27	16	20.4	60.9	81.3	0.241	0.321
	46*	20.2	61.1	81.3	0.241	0.321

* During these runs there was slight contamination with gear-case lubricant. See text.

TREATMENT AND DISCUSSION OF RESULTS

(a) Alternate Definitions for Column Capacity

Customarily, the column capacity is defined as

$$C = V_D \div V_C$$

In Progress Report No. 3, covering a flooding capacity study of the system trichloroethylene-water, that particular definition had been employed and found to be not unsatisfactory. By that, it is meant that no inconsistencies were disclosed, and it was possible to adequately fit the data with a (second order) equation employing the capacity so defined. It should be noted, however, that the precision of the data was poor, thereby obscuring somewhat the conclusions.

However, the definition of $C = V_D \div V_C$ is purely an arbitrary one, not dimensionless, and without any theoretical background. In its place, experience suggests that some dimensionless formulation would be better.

The product of frequency times amplitude has the dimensions of a flow rate. In fact, this product has at times been spoken of as a pulse pumping rate.

$$F \times A = \frac{\text{cycles}}{\text{hr}} \times \frac{\text{ft}}{\text{cycles}} = \frac{\text{ft}}{\text{hr}}$$

Some ideas on pulse column behavior suggested the use of this FA product to formulate the following dimensionless ratios.

$$C = \frac{V_D}{FA}$$

$$C = \frac{V_D \div V_C}{FA}$$

These dimensionless groups are alternates, and competitors, to the previous definition, $C = V_D \div V_C$. To permit their testing, these new formulations were calculated for each run. The resultant values are included in Table 3 along with other information.

(b) Best-fitting Equations

To test the relative worth of the three capacity definitions, it was first necessary to obtain best-fitting equations employing each definition.

Accordingly, the capacity by each definition was assumed to be expressable as a Taylor's Series in terms of the three operating variables, each written in statistical units. For each capacity definition, two Taylor's Series were assumed. One included only terms through the second order. The other included in addition the third order terms.

By the methods of least-squares, the six best-fitting equations defined above were derived. These equations are presented in Tables 4 and 5 in the form of the coefficients of the pertinent Taylor's Series.

(c) Analysis of Variance for the Equations

The analyses of the variance for the six best-fitting equations are presented in Tables 6, 7, and 8. Each table treats both the second order and the third order equations for the pertinent capacity definition.

(d) Comparison among Definitions of Capacity

There is no rigorous criterion for deciding which of the three alternate definitions of capacity is the better.

However, it seemed reasonable to argue in the manner that follows. The arguments are intuitive, but they will suffice until better ones are devised.

The difficulty in comparison lies in the fact that the measured response in each case is on a scale different from that of each other case. Therefore, the sums of squares and mean squares in the three tables, Tables 6, 7 and 8, are not expressed on a common basis. However, exactly the same set of experiments are involved each time. And since the experimental error is physically and conceptually the same for each case, the fact that the recorded measures of experimental error differ for each case means only that the

TABLE 4

Estimated Values for Coefficients of Second Order Equations

Coefficients	$C = \frac{V_D}{FA}$	$C = V_D + V_C$	$C = \frac{V_D + V_C}{FA}$
b_0	+0.3999	+121.046	+1.0912
b_1	-0.2577	- 4.190	-0.4613
b_2	-0.1563	- 5.371	-0.3222
b_3	+0.1242	- 15.026	-0.1216
b_{11}	-0.0289	- 40.123	-0.0823
b_{22}	+0.0426	- 2.456	-0.0465
b_{33}	-0.0023	- 4.120	-0.0975
b_{12}	-0.0076	- 34.128	-0.0251
b_{13}	-0.0939	- 1.825	+0.0453
b_{23}	-0.0632	- 1.769	+0.0269

$$C = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{11}x_1^2 + b_{22}x_2^2 + b_{33}x_3^2 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3$$

where x_1 = amplitude in statistical units

x_2 = frequency in statistical units

$x_3 = V_D/V_C$ in statistical units

TABLE 5

Estimated Values for Coefficients of Third Order Equations

Coefficients	$C = \frac{V_D}{FA}$	$C = V_D + V_C$	$C = \frac{V_D + V_C}{FA}$
b_0	+0.3999	+121.046	+1.0912
b_1	-0.3599	- 12.285	+0.6795
b_2	-0.2111	- 15.347	-0.4164
b_3	+0.0620	- 37.863	-0.2310
b_{11}	-0.0289	- 40.123	-0.0823
b_{22}	+0.0426	- 2.456	-0.0465
b_{33}	-0.0023	- 4.120	-0.0975
b_{12}	-0.0076	- 34.128	-0.0251
b_{13}	-0.0939	- 1.825	+0.0453
b_{23}	-0.0632	- 1.769	+0.0269
b_{111}	+0.0422	- 4.174	-0.5166
b_{222}	-0.0243	+ 16.539	-0.0560
b_{333}	+0.0332	+ 8.681	+0.0417
b_{112}	+0.0957	- 12.348	+0.1929
b_{122}	+0.0519	+ 14.627	-0.2919
b_{113}	+0.0097	+ 12.836	+0.0647
b_{133}	+0.0152	+ 2.458	-0.3866
b_{223}	+0.0196	+ 3.348	+0.0126
b_{233}	+0.0138	- 0.532	+0.0176
b_{123}	+0.0180	+ 9.987	+0.0501

$$\begin{aligned} C = {} & b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{11}x_1^2 + b_{22}x_2^2 + b_{33}x_3^2 + b_{12}x_1x_2 \\ & + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{111}x_1^3 + b_{222}x_2^3 + b_{333}x_3^3 + b_{112}x_1^2x_2 \\ & + b_{122}x_1x_2^2 + b_{113}x_1^2x_3 + b_{133}x_1x_3^2 + b_{223}x_2^2x_3 + b_{233}x_2x_3^2 + b_{123}x_1x_2x_3 \end{aligned}$$

where x_1 = amplitude in statistical units

x_2 = frequency in statistical units

x_3 = V_D/V_C in statistical units

TABLE 6

Analysis of Variance for $C = V_D/FA$

Source of Variation	Degrees of Freedom	Sums of Squares	Mean Squares	F Statistic
Total	54	14.053069		
Due to mean	1	9.016086		
Due to linear terms	3	4.401202	1.467067	
Due to second order terms	6	0.456494	0.076082	
Due to third order terms	10	0.150024	0.015002	32.47
Lack of fit	7	0.016786	0.002398	5.19
Residual (experimental error)	27	0.012477	0.000462	

Estimated standard deviation = 0.0215

Pooled estimate of std. dev. = 0.0294
(obtained by pooling lack of
fit and residual terms)

Coefficient of variation = 0.0526

TABLE 7

Analysis of Variance for $C = V_D \div V_C$

Source of Variation	Degrees of Freedom	Sums of Squares	Mean Squares	F Statistic
Total	54	484,245.87		
Due to mean	1	392,243.80		
Due to linear terms	3	11,273.04	3,757.68	
Due to second order terms	6	66,539.95	11,089.99	
Due to third order terms	10	8,530.22	853.22	22.60
Lack of fit	7	4,639.54	662.79	17.56
Residual (experimental error)	27	1,019.32	37.75	

Estimated standard deviation = 6.14

Pooled estimate of std. dev. = 12.9
(obtained by pooling lack of
fit and residual terms)

Coefficient of Variation = 0.0720

TABLE 8

Analysis of Variance for $C = \frac{V_D + V_C}{FA}$

Source of Variation	Degrees of Freedom	Sums of Squares	Mean Squares	F Statistic
Total	54	63.933367		
Due to mean	1	45.461850		
Due to linear terms	3	13.726690	4.575563	
Due to second order terms	6	0.439758	0.073293	
Due to third order terms	10	2.490322	0.249032	147.7
Lack of fit	7	1.769212	0.252745	149.9
Residual (experimental error)	27	0.045535	0.001686	

Estimated standard deviation = 0.0410

Pooled estimate of std. dev. = 0.231
(obtained by pooling lack of
fit and residual terms)

Coefficient of variation = 0.0447

scales of measurement are different.

By ratioing, for each method of analysis, the mean squares to the experimental error on the same scale, sets of numbers are obtained which are all on the same basis, hence suitable for intercomparison. Incidentally, the results of this ratioing are already well known to statisticians as values of the F statistic. The ratios are presented in Table 9.

TABLE 9

Values of the F Statistic for the Three Definitions of Capacity

Source of Variation	$C = \frac{V_D}{FA}$	$C = V_D + V_C$	$C = \frac{V_D + V_C}{FA}$
Due to linear terms	3,175.47	99.54	2,713.86
Due to second order terms	164.68	293.77	43.47
Due to third order terms	32.47	22.60	147.71
Lack of fit	5.19	17.56	149.91
Experimental error	1.00	1.00	1.00

There are two arguments that can be made, as follows:

1. To each value of the F statistic, can be assigned a specific probability. For instance, the probability of obtaining an F value of 5.19 (with the degrees of freedom involved) is only 6 in 10,000. That is to say, if there were actually no lack of fit, and 10,000 sets of experiments like these were run, in only 6 cases would there be an F value this large or larger. Consequently, it is highly probably that there is a lack of fit, and the F value is an (inverse) measure of that probability. The probability of getting an F value of 17.56 is only 1 in 10 million, and of 149.9, far less than even that.

We conclude that it is likely that the definition of $C = V_D/FA$ permits a significantly better fit to the data than do the other definitions, because of the smaller F value obtained for the lack of fit (using third order equations each time).

2. We take extra confidence in the fact that for the definition of $C = V_D/FA$, the progression of F values becomes progressively smaller as more and more terms are employed in the Taylor's Series. One would naturally expect the degree of fit to improve asymptotically as more and more terms are employed. In contrast, the erratic behavior of the F values for the other trials seems unnatural, and of a nature to give rise to suspicion.

(e) The Selected Definition, $C = \frac{V_D}{FA}$

The representation of the experimental data permitted by the definition of $C = V_D/FA$ was considered excellent. Expressed in terms of the representative V_D/FA value of 0.80, the experimental error (std. dev.) was only 2.7%, and the experimental error plus lack of fit (by the third order equation) was only 3.7%.

An attempt was made to take the best-fitting equation using V_D/FA, and to somehow make the information contained therein readily available. However, the calculation task turned out to be overwhelming, when only desk calculating machines were available.

An alternate procedure was to use the best-fitting second order equation as an approximation for the best-fitting third order equation. There were derived several V_D/FA contours of the space model in statistical units. A representation of the contours is presented in Figure 5.

It appears from Figure 5 that the contour surfaces are not badly approximated by planes. This situation is not as apparent from the photograph as it is from the actual model. It would be interesting to observe the shape of the contour surfaces for the third order model. If a representation by planes were possible, a simplification in the mathematical relationships would result.

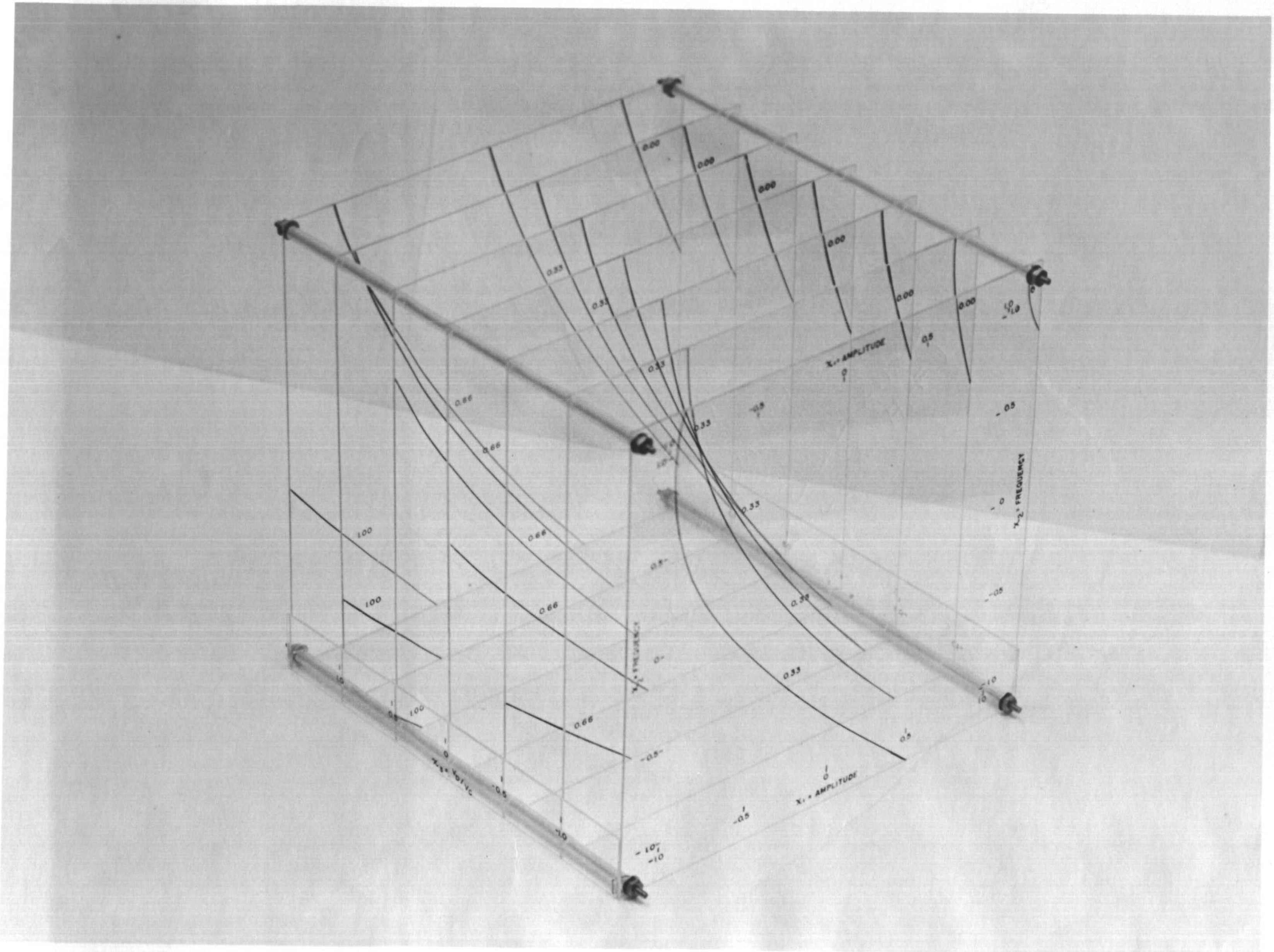


Fig. 5 - Space Model of Capacity Contours for $C = \frac{V_D}{FA}$

CONCLUSIONS

This work has led to these specific conclusions.

1. It is a point of major importance that the strenuous efforts to eliminate grease contamination did in fact result in a large reduction in the experimental error. This together with some other circumstantial evidence, is reasonable proof that trace contamination is a major factor in pulse column work, not only in regard to flooding but also in regard to mass transfer tests. It would have been most unwise to have proceeded with mass transfer experiments until this point was settled.

2. With the experimental error greatly reduced, the results on the benzene-water flooding tests demonstrated quite satisfactorily that the statistical approach employed is of great assistance in exploring response functions. Looking forward to mass transfer operations, which entail more factor dependence, it is highly gratifying to see this approach successfully demonstrated.

3. A new, and apparently powerful, research tool has been devised and tested in a preliminary fashion. It is a tool capable of selecting between alternate ways of generalizing experimental data, hence a tool capable of locating the better methods of correlation. It consists essentially of rating a given assumed relationship, in a statistical fashion, on the basis of its relative ability to permit a close fit of the data by an equation.

4. With this new analytical tool, it has been reasonably demonstrated, although not proved, that one of the dimensionless groups expressing flooding behavior in a pulse column is the group $(\frac{V_D}{FA})$. In Progress Report No. 3, we had shown that $(\frac{V_D}{V_C})$ was a controlling dimensionless group. Therefore, we now have a total of two groups reasonably well demonstrated.

5. In the benzene-water data, we now have a rather extensive body of experimental flooding data of very good precision. In addition, we have an equation which fits these data quite closely throughout the entire experimental region. Therefore, the equation can serve as a tool for generating precise experimental results (within its range of validity) under any conditions we choose. This would make it possible to test in a satisfactory way many ideas concerning the theoretical manner in which flooding data should be correlated. The one difficulty is that the calculation effort required to derive much information from the best-fitting equation is overwhelming. The need for a high speed computor is evident.

ACKNOWLEDGEMENT

In the conception, planning and guidance of this particular work, Dr. G. E. P. Box played a prominent part. Unfortunately, his return to England from the United States, and other circumstances, did not permit him to participate in the analysis of these results, nor in the preparation of this report.

TABLE OF NOMENCLATURE

A = pulse amplitude, in inches of height in the installed plate assembly

C = capacity of the pulse column, by any definition

Alternate definitions are

$$C = V_D + V_C = \text{ft/hr}$$

$$C = \frac{V_D}{FA} = \text{dimensionless}$$

$$C = \frac{V_D + V_C}{FA} = \text{dimensionless}$$

F = pulse frequency, in cycles per minute

V_C = input flow rate of the continuous phase, in ft/hr

V_D = input flow rate of the discontinuous phase, in ft/hr

V_D/V_C = dimensionless flow ratio of the input streams

X_1 = amplitude expressed in standardized units

X_2 = frequency expressed in standardized units

X_3 = flow ratio expressed in standardized units