EXTRACTION OF COBALTOUS CHLORIDE
IN A TWO INCH SPRAY COLUMN

By

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ABSTRACT

A spray column two inches in diameter and 73-3/8 inches long was used to determine flooding velocities and mass transfer coefficients for the extraction of cobaltous chloride from aqueous hydrochloric acid solution with capryl alcohol and also in the reverse direction. The aqueous phase was dispersed in all cases. Tubes were installed at various points in the column so that continuous phase samples could be withdrawn along the entire column length. The disperser consisted of thirty 0.1 inch diameter nozzles.

Flooding was found to occur in a manner different from that described by previous investigators. Flooding velocities were 35% higher than those previously found for the same system but with the aqueous phase dispersed.

For the entire column, the overall height of a transfer unit based on the alcohol phase, $(HTU)_{OA}$, was relatively constant for various aqueous phase rates and for a particular alcohol phase rate. It was unaffected by the alcohol phase rate for extraction from the alcohol phase, but increased with increasing alcohol phase rate for extraction from the aqueous phase. The $(HTU)_{OW}$ increased with increasing aqueous phase rate. It increased with increasing alcohol phase rate for extraction from the aqueous phase, but decreased with increasing alcohol phase rate for extraction from the alcohol phase. The $(HTU)_{OA}$ varied from 2.5 to 6 feet and the $(HTU)_{OW}$ from 6 to 26 feet for the range of flow rates employed.

An end effect was found at the coalescence point, but none was detected for drop formation. The end effect is considerable at the lower alcohol phase rates and it is only slightly affected by the direction of extraction. It was found to be equivalent to from 0.3 to 3.6 feet of straight column.

For the straight section of the column, $(HTU)_{OA}$ varied from 3 to 6 feet. Comparison of the values of Ka and HTU obtained here with those of Kylander[9] for the extraction of cobaltous chloride from the aqueous phase with the alcohol phase dispersed indicate agreement to about 35%.

INTRODUCTION

Nickel and cobalt are very difficult to separate industrially because of their similar properties. At present one of the most widely used processes involves precipitation of the cobalt in the form of the hydrated cobaltic oxide ($Co_2O_3.3H_2O$) by addition of an alkaline solution of an oxidizing agent to an acid solution of the divalent salts. Suitable oxidizing agents include bleaching powder, sodium and potassium hypochlorite and hypobromite, and solid carbonates in conjunction with chlorine gas[2, 7, 11, 13, 15]. In a recently patented process an aqueous solution of the chlorides is treated with gaseous chlorine in the presence of sufficient calcium carbonate to keep the solution alkaline. Chlorination is continued until most of the more soluble nickelous hydroxide is dissolved, after which cobaltic hydroxide is filtered off[14].

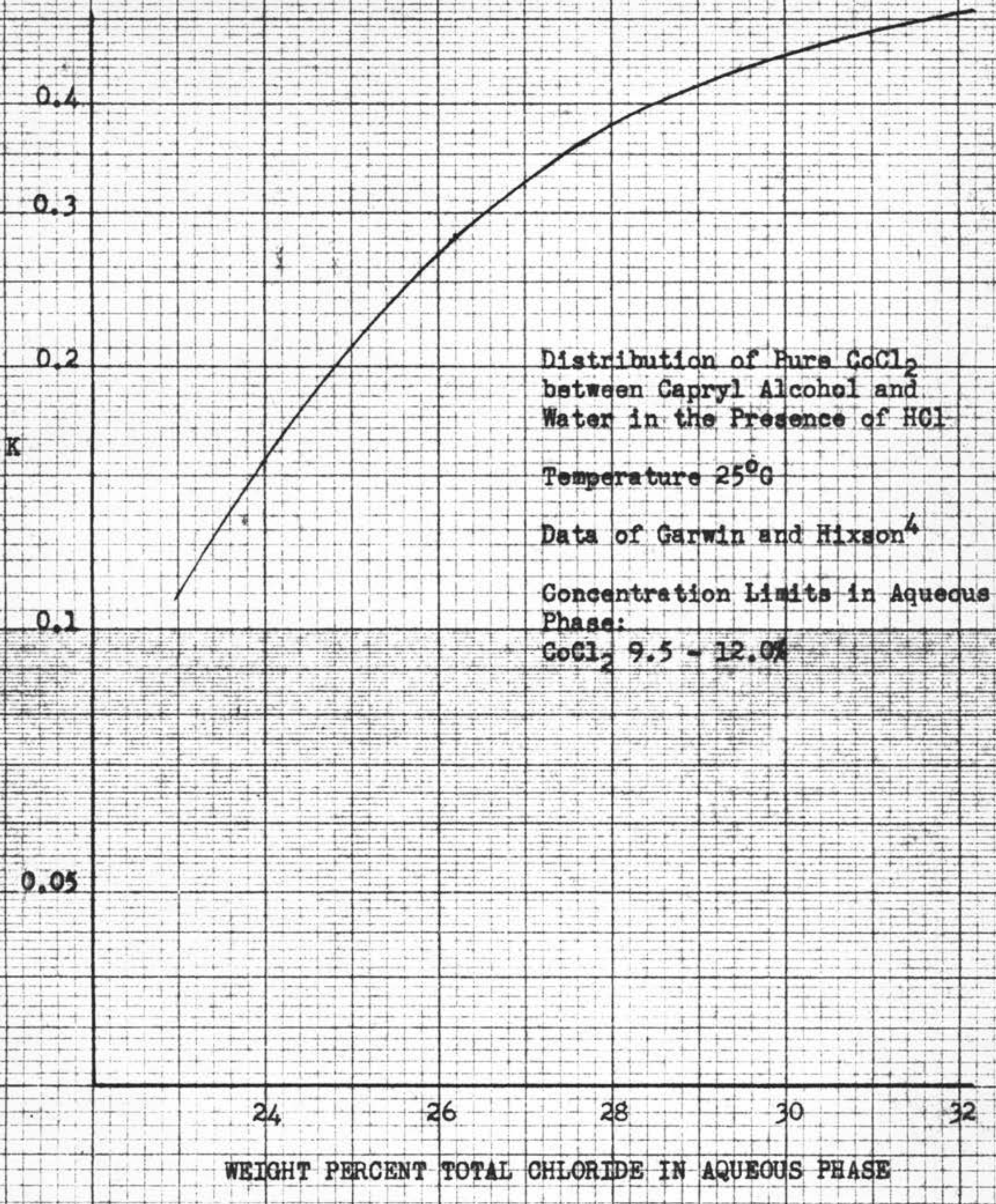
Many potential solvents were investigated by Garwin and Hixson[3, 4] for the separation of nickelous and cobaltous chlorides from aqueous solution. Capryl alcohol was selected by these investigators for study because the anhydrous cobaltous chloride solubility is much greater than the nickelous chloride solubility in the solvent (the cobaltous chloride being quite soluble), because the solvent has a low mutual solubility with water, because it is stable, and because it is available at low cost. Very little cobaltous chloride is extracted from the simple aqueous solution. The addition of certain electrolytes such as calcium chloride and hydrochloric acid results in a marked improvement in the distribution coefficient of the cobalt. In all cases the extraction of nickel is low. The distribution coefficient (K) for cobaltous chloride between aqueous hydrochloric acid and capryl alcohol at 25°C. is shown in Figure 1 as a function of total chloride concentration in the aqueous phase.

Kylander[9] studied the extraction of cobaltous chloride from an aqueous hydrochloric acid solution of cobaltous chloride and from an aqueous hydrochloric acid solution of cobaltous and nickelous chlorides in a spray column, 1 1/4 inches in diameter and 68 inches long, with the alcohol phase dispersed. The $(HTU)_{OA}$ was nearly constant at 5 to 6 feet and the $(HTU)_{OW}$ decreased very rapidly with increasing alcohol phase rate and slightly with increasing aqueous phase rate. The values were found to be independent of the relative amounts of nickel and cobalt in the aqueous phase. Flooding rates were determined with no dissolved solutes in the system.

The only other system for which mass transfer data have been determined for the extraction of an inorganic salt by an organic solvent is the system ferric chloride--hydrochloric acid--water--isopropyl ether. Geankoplis and Hixson[5] studied this system in a 1.45 inch diameter by 2.57 foot long spray column with the ether phase dispersed. Studies of mass transfer were made throughout the column with a movable sampler. The horizontal position of the sampler had no effect on the concentrations obtained. A large inlet effect, equivalent on an average to 0.5 feet of column, was obtained at the continuous phase inlet (coalescence point), and there was no end effect at the dispersed phase inlet. The additional extraction produced by the inlet effect was increased by increased dispersed phase rate and increased inlet concentration. Adding ferric chloride to the ether phase reduced the effect. As the inlet concentration of ferric chloride in the aqueous phase was increased the average $(HTU)_{OW}$ increased. At first $(HTU)_{OW}$ decreased rapidly with increased dispersed phase rate but tended to approach a constant value of 0.7 feet at higher dispersed phase rates.

Licht and Conway[10], by the use of a column of standard design and one in which the interface (coalescence point) was eliminated, and by using several column heights, determined end effects of appreciable magnitude at both ends of a spray column. Studied was the extraction of acetic acid from water using isopropyl ether, methyl isobutyl ketone, and ethyl acetate. The water phase was dispersed.

FIGURE 1



Distribution of Pure $CoCl_2$ between Capryl Alcohol and Water in the Presence of HCl

Temperature 25°C

Data of Garwin and Hixson[4]

Concentration Limits in Aqueous Phase:
$CoCl_2$ 9.5 - 12.0%

APPARATUS

A 2 inch diameter column 73-3/8 inches long, made up of eight sections of 2 inch by 1 inch Pyrex glass tees, was used for all experimental work. The sections of Pyrex glass were connected by aluminum flange sets with rubberized asbestos gaskets between the glass sections. Glass sampling tubes, 3 millimeters in outside diameter, were inserted through neoprene rubber stoppers in the side outlets of the glass tees. The sampling tubes extended 3/8 inch from the wall of the column and were bent down so that they were vertical for 1/4 inch to sample the continuous phase rising through the column. Each tee was rotated 120° clockwise from the tees adjacent to it (looking down).

The vertical locations of the sampling tubes are shown in the table below:

Point Number	Distance from Ends of Disperser Nozzles, Inches	Distance from Overflow Weir, Inches
Overflow Weir (Bottom)	73.4	0.0
1	64.5	8.9
2	56.4	16.9
3	48.4	25.0
4	40.3	33.1
5	32.2	41.2
6	24.1	49.3
7	15.9	57.4
8	7.8	65.6
Disperser (Top)	0.0	73.4

The top section of the column consisted of a 4 inch by 2 inch Pyrex glass reducer with a 1/4 inch thick Plexiglas plate at the top end. A disperser of the type suggested by Johnson and Bliss[8], consisting of thirty 0.1 inch inside diameter nozzles, was constructed of Plexiglas and placed at the large end of the conical section.

The bottom settling section was similar to that recommended by Blanding and Elgin[1]. It consisted of a 4 inch by 2 inch Pyrex glass reducer and a 4 inch diameter by 6 inch length of Plexiglas pipe. A 1/4 inch thick Plexiglas plate formed the bottom of the column. A Plexiglas weir was constructed to distribute the continuous phase. The weir was held in place by compressing sections of neoprene stoppers between the wall of the column and the weir.

For details of the column construction, see Figures 2 and 3.

AUXILIARIES

The column was supported at the bottom by a metal stand placed on the floor, and, slightly above the middle, by a bracket fastened to the wall.

Storage vessels for the aqueous phase feed, alcohol phase feed, extract, and raffinate were twelve-gallon Pyrex glass bottles.

Pressure for moving the aqueous phase feed and the alcohol phase feed was placed over the solutions by means of compressed nitrogen from a standard cylinder. The pressure supplied to the feed bottles was reduced from the cylinder pressure to 8 or 9 pounds per square inch gauge by means of a regulator commonly used in oxygen service. A section of pipe between the pressure regulator and the storage bottles was filled with ascarite to protect the regulator from hydrochloric acid vapor.

Flow rates of the continuous and dispersed phase feeds were indicated by the pressure drop across orifices made by reducing the cross-section of a piece of glass tubing. The pressure drops across the orifices were measured by inclined tube manometers. The flow rates were regulated by adjusting screw clamps on sections of rubber tubing, which gave a type of diaphragm valve.

A 300 watt light bulb was placed behind the settling section to permit the observation of the interface. A sight glass was installed between the bottom tee and the aqueous phase outlet line to aid in detecting the interface position.

Adjustment of the height of the loop in the aqueous phase exit line controlled the interface level in the column at the desired point.

All transfer lines were 7/16 inch outside diameter Saran tubing, with plastic, rubber, and glass fittings.

A shematic diagram of the extraction equipment and auxiliaries is shown in Figure 4. Figure 5 is a photograph of the equipment.

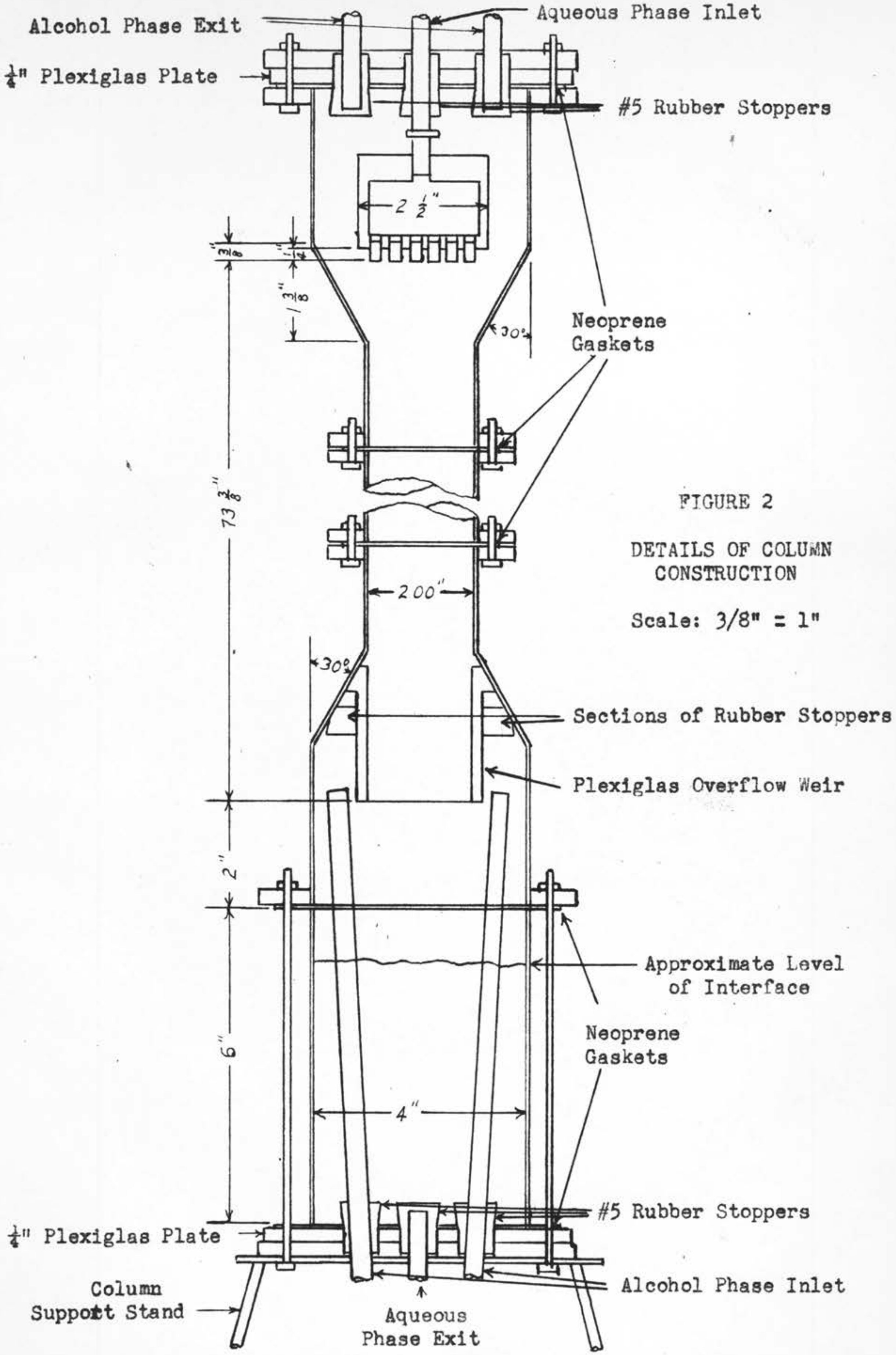


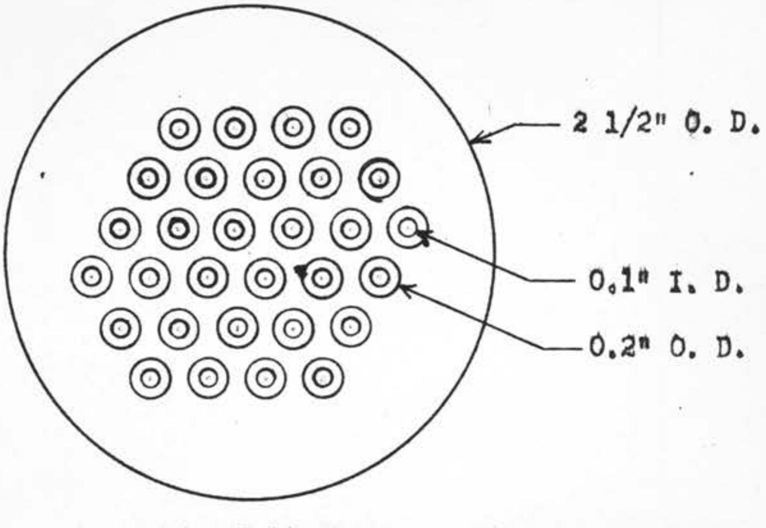
FIGURE 2

DETAILS OF COLUMN CONSTRUCTION

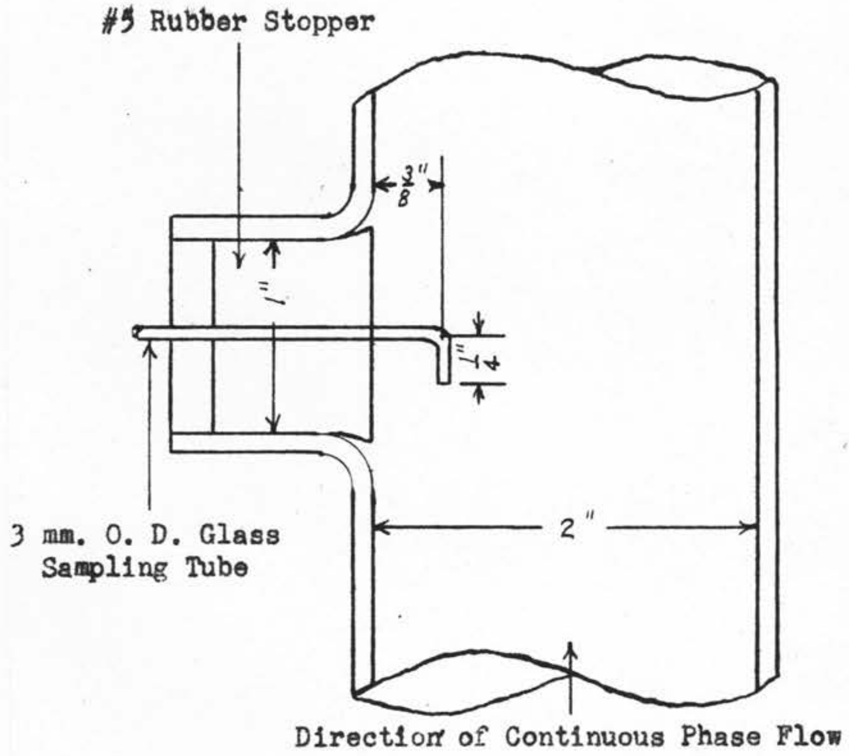
Scale: 3/8" = 1"

Figure 3

DETAILS OF DISPERSER AND SAMPLING TUBE



End View of Disperser
(Actual Size)



Glass Tee with Sampling Tube
(Actual Size)

FIGURE 4

SCHEMATIC DIAGRAM
OF EXTRACTION COLUMN AND AUXILIARIES

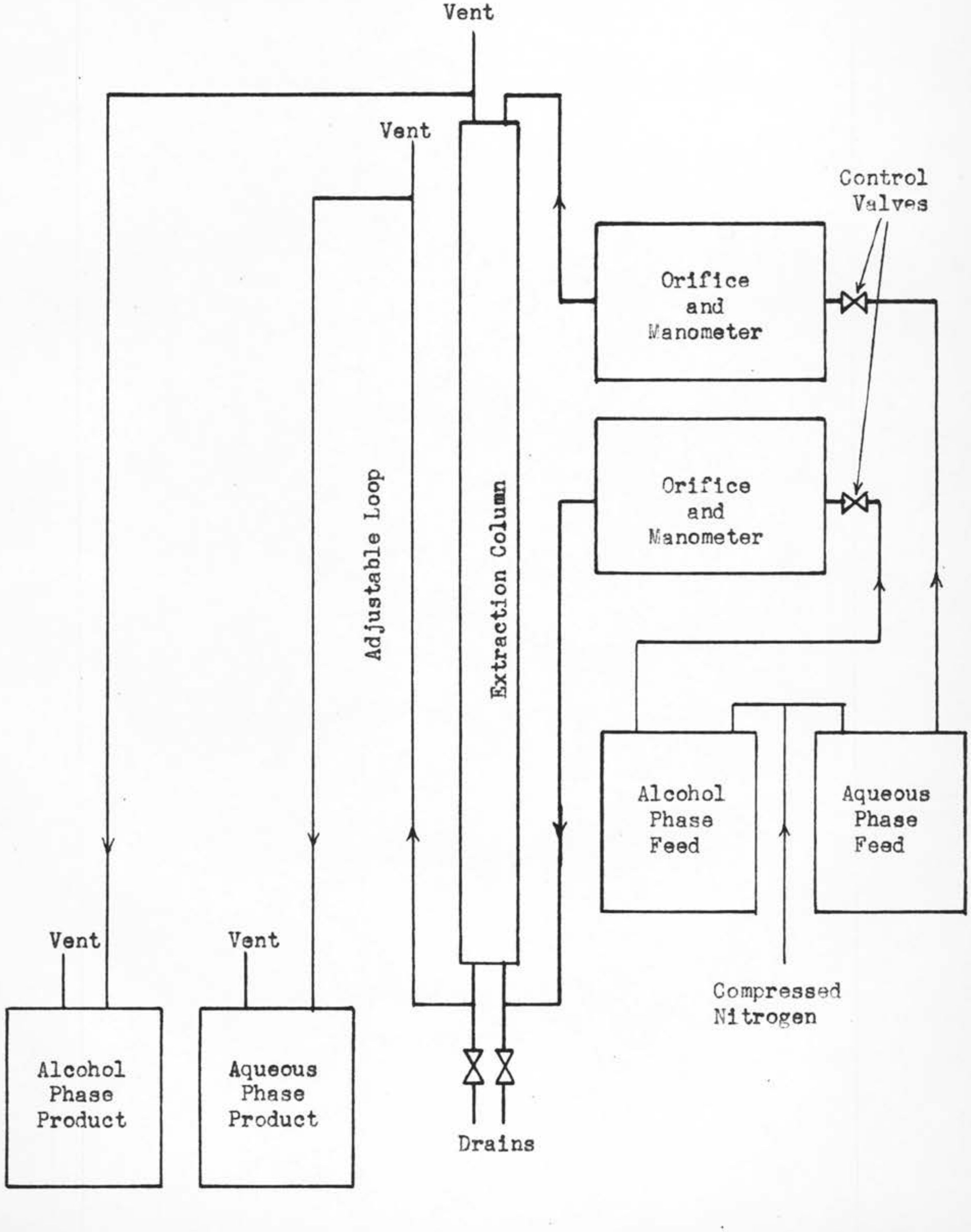
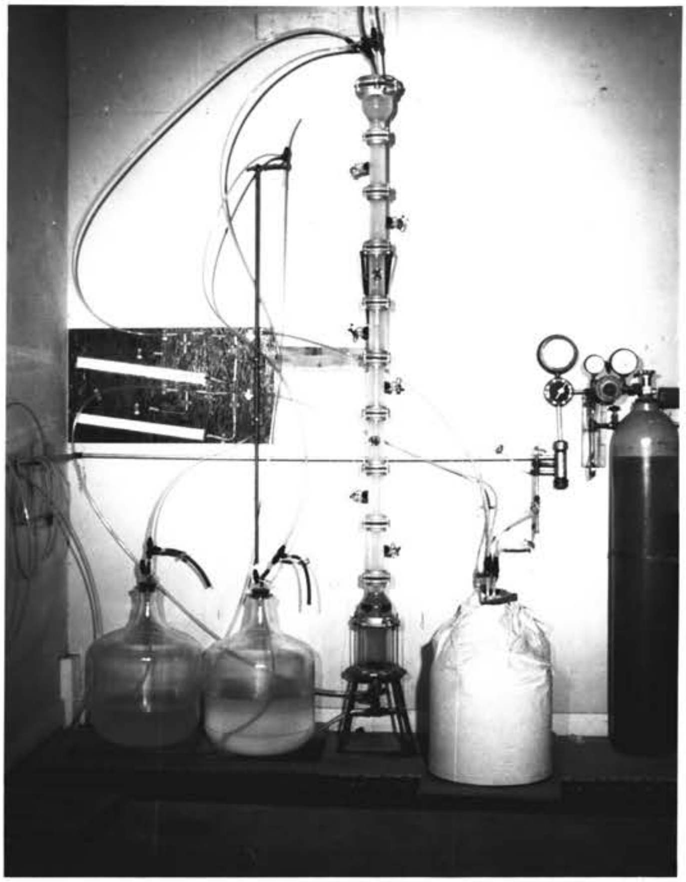


Figure 5

Photograph of Experimental Equipment



MATERIALS USED

Three series of runs were made. Series I consisted of flooding velocities for capryl alcohol and water with no dissolved salts in the system. In Series II runs cobaltous chloride was extracted from an aqueous hydrochloric acid solution of cobaltous chloride by capryl alcohol. In Series III runs 25% hydrochloric acid solution was employed to extract cobaltous chloride from capryl alcohol.

For the flooding determinations of Series I, refined grade capryl alcohol, manufactured by the Hardesty Chemical Company, Inc., and containing less than 8% methyl hexyl ketone, was used.

Chemical grade capryl alcohol (2-octanol) was used in the extraction runs of Series II and Series III. It, too, was obtained from the Hardesty Chemical Company. The material contained a maximum of 2.0% metyl hexyl ketone as the major impurity.

Baker and Adamson's concentrated hydrochloric acid and cobaltous chloride hexahydrate ($CoCl_2 \cdot 6H_2O$) of tested purity (A. C. S. specifications) were used. The concentrated hydrochloric acid was used to bring both the aqueous and alcohol phases to the desired acid concentrations, and the cobaltous chloride hexahydrate was used to make up the aqueous phase feed solutions for Series II.

Distilled water was used in the aqueous phase.

All reagents employed in the analytical work met A. C. S. specifications for purity.

PROCEDURE FOR SERIES I

Flooding Velocities

Calibration curves were made for the orifice and manometer combinations for distilled water by measuring the time required to collect 1000 ml. of water for various pressure drops across the orifices. The manometer reading was plotted versus flow rate expressed as superficial velocity through the column in feet per hour (see Figure 6). These calibration curves were used only as a guide in setting the proper flow rates in all runs. The continuous phase was capryl alcohol with a specific gravity of 0.819. The dispersed phase was distilled water. Kylander[9] found the interfacial tension for this system to be 10.5 dynes per cm.

The column was nearly filled with continuous phase by applying nitrogen pressure to the alcohol phase storage bottle and then pressure was applied to the aqueous phase storage bottle to produce flow of the dispersed phase.

The continuous phase rate was maintained constant and the dispersed phase rate set at a value considerably below flooding. The adjustable loop was adjusted to maintain the interface at the proper level. After steady operating conditions were reached, the dispersed phase rate was increased, and the interface again adjusted (the adjustable loop was raised to compensate for the increased average density of the fluid in the column). This process was repeated until a limiting pair of flow rates was reached in which the operation of the column was no longer satisfactory. This limiting pair of flow rates, defined as the flooding point, was the point at which globules of continuous phase detached themselves from the main body of the continuous phase and rose rapidly up the column for a short distance before again becoming part of the continuous phase. This phenomenon is described more completely in the discussion of the results of Series I. This was the practical limit of operation, and flooding of the type described by Blanding and Elgin[1] was not experienced. The flow rates at the flooding points were determined by measuring the time required to collect 1000 ml. of each phase.

This procedure was repeated for other continuous phase flow rates. The limiting pairs of flow rates are plotted in Figure 7.

FIGURE 6

CALIBRATION CURVES FOR ORIFICE - MANOMETER COMBINATIONS FOR WATER

(Used only as a guide)

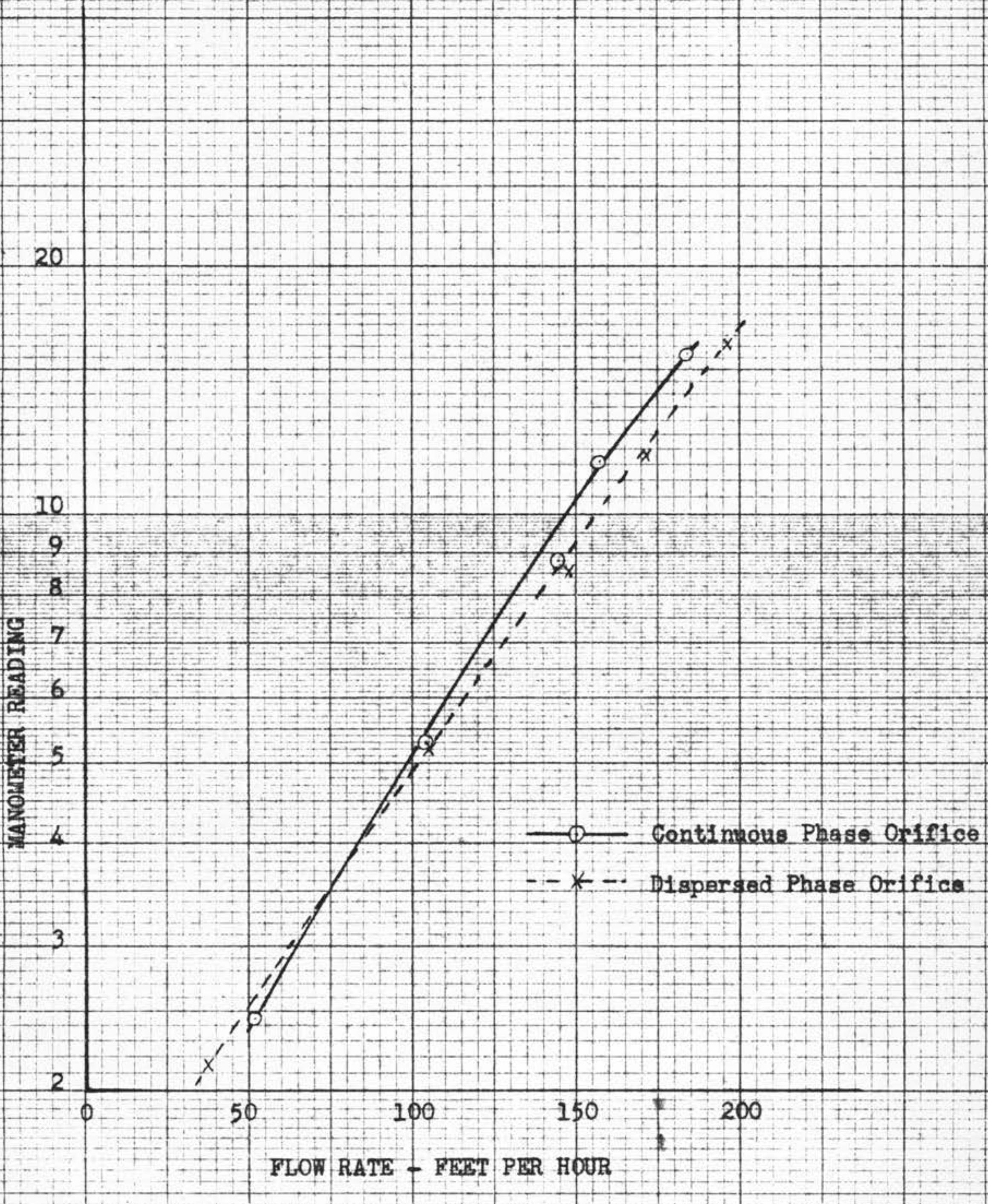
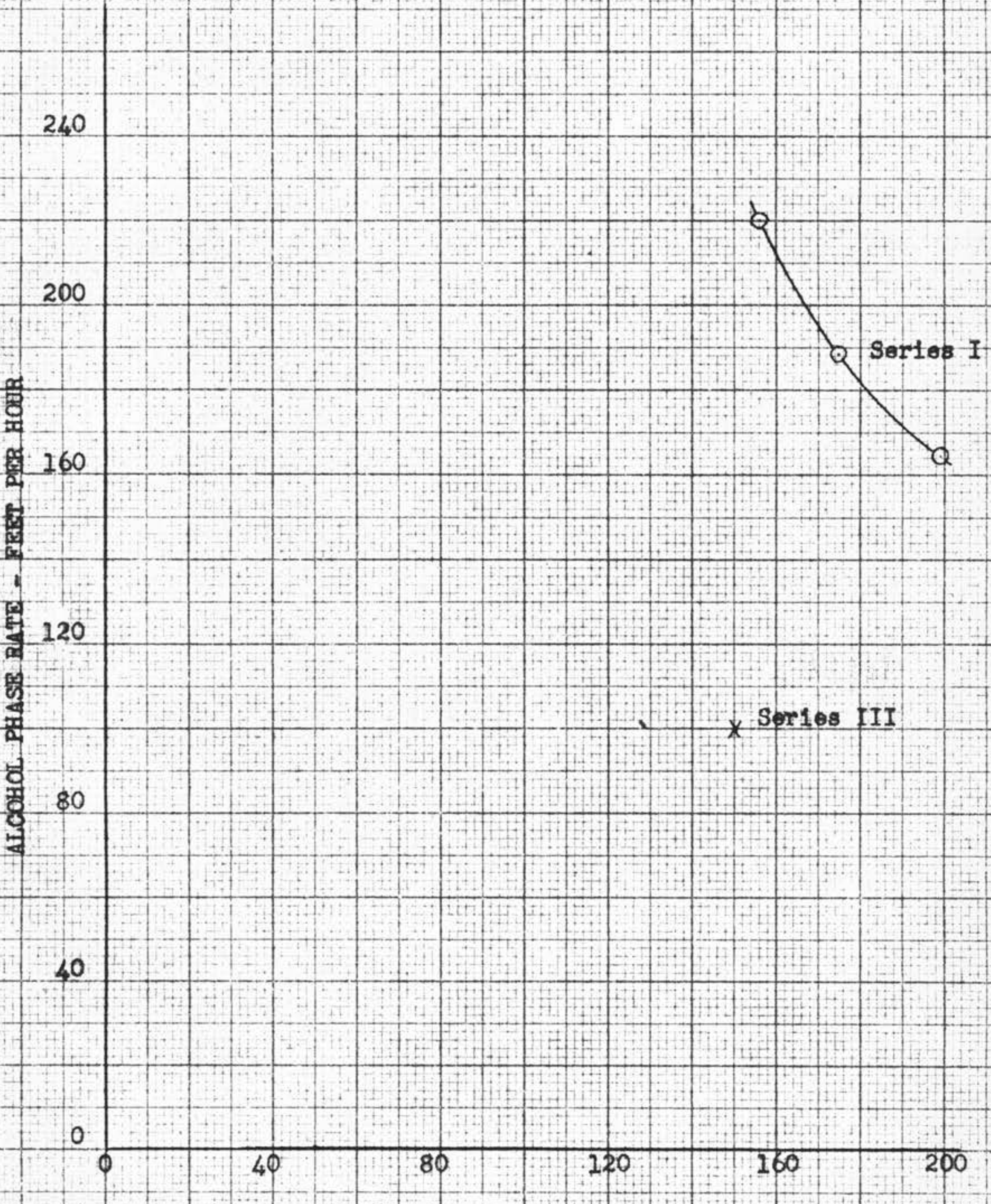


FIGURE 7

FLOODING VELOCITIES
IN THE SPRAY COLUMN
(AQUEOUS PHASE DISPERSED)



PROCEDURE FOR SERIES II AND III

Cobaltous Chloride Extraction

Before the first Series II run was made, an aqueous solution to which the desired quantity of concentrated hydrochloric acid solution had been added was run through the spray column countercurrent to the alcohol phase several times in order that the HCl concentration in both phases would be nearly in equilibrium and so that very little HCl would be transferred in an actual run. Sufficient cobaltous chloride hexahydrate was then added to the aqueous phase to bring the salt concentration to the desired value.

The column was nearly filled with continuous phase and then flow of the dispersed phase was started as in Series I. The interface was set at the proper point by positioning the adjustable loop and when the interface was steady, the flow rates of both phases were measured by determining the time required to collect 1000 ml. of each phase. Adjustments were made to obtain the flow rates desired. The manometer readings were used only as indicating devices for maintaining constant flow rates throughout the run.

In the early runs, samples of the exit streams were taken at intervals and analyzed. Steady state conditions appeared to be reached after two complete changes of continuous phase as shown in the following table for run 3 of Series II:

Number of Changes of Continuous Phase	$CoCl_2$ Concentration in Alcohol Phase Leaving Column, Percent
2	0.80
3	0.81
4	0.81

In subsequent runs sampling of the exit streams and intermediate points was begun after 2 1/2 or 3 changes of continuous phase. Intermediate samples were drawn off at a rate of 3 to 5 ml. per minute. Samples of both aqueous and alcohol phase feeds were taken from the storage bottles immediately before the run was started.

For the first Series III run the aqueous phase feed was 25% hydrochloric acid solution and the alcohol phase feed consisted of the extract from the first Series II run. Operation of the equipment and sampling procedure was the same as for Series II.

After a Series III run was terminated the aqueous product phase was distilled to separate the hydrochloric acid and the cobaltous chloride for the reuse of each. The distilled hydrochloric acid was collected in a receiver containing 25% HCl. When the distillation was started HCl vapor came over first; this was followed by an azeotrope containing approximately 20% HCl. The overall composition of the distillate was thus about 25% HCl. The cobaltous chloride residue was added to the raffinate of the previous Series II run and this was then used as the aqueous phase feed for the next Series II run. The alcohol phase from which most of the cobaltous chloride had been removed in the previous Series III run was used as alcohol phase feed for the next Series II run. The hydrochloric acid distilled over was employed as aqueous phase feed for the next Series III run. For a Series II run the aqueous phase feed contained approximately 25% HCl and 8-10% cobaltous chloride. The HCl concentration in the alcohol phase was 9-10%.

ANALYTICAL METHODS

A. Aqueous Phase. A 5 ml sample of the aqueous phase was diluted to 100 ml.

1. Total chloride. Determination of the total chloride concentration of the aqueous phase was necessary since the distribution coefficient for cobaltous chloride is known as a function of total chloride concentration. The Volhard method was chosen for the total chloride determination because it is much more rapid than gravimetric methods, because the cobalt ion does not interfere with the end point, and because the titration is carried out in acid solution. A 5 ml aliquot of the diluted aqueous phase sample was pipetted into a 250 ml glass stoppered Erlenmeyer flask and diluted with distilled water. Four ml of concentrated nitric acid were added. Sufficient standard silver nitrate solution was added from a burette to completely precipitate the chloride and provide a small excess. Two or 3 ml of nitrobenzene and 2 ml of saturated ferric ammonium sulfate were added and the flask was then stoppered and shaken well to completely coagulate the silver chloride precipitate. The excess silver nitrate was then determined by back-titrating with standard potassium thiocyanate until a brownish tinge appeared, marking the formation of an iron complex with the thiocyanate radical, and indicating the end point. Duplicate determinations were made. These agreed to 0.05 ml.

2. Cobaltous chloride. A 10 ml aliquot of the diluted aqueous phase sample was pipetted into a 125 ml Erlenmeyer flask, and the flask then placed in the oven at 95-100°C overnight to evaporate the sample to dryness. The sample was then redissolved in distilled water and the chloride content determined by the Volhard method in the same way the total chloride

determinations were made. Duplicate determinations were made. These usually agreed to 0.05 ml. From the amount of chloride in the sample the cobaltous chloride content could be readily calculated.

3. Specific gravity. Specific gravities were determined at room temperature relative to water at 4°C, using a Westphal balance.

B. Alcohol phase. A 10 ml sample of the alcohol phase was added to approximately 150 ml of distilled water in a 250 ml volumetric flask. At low chloride concentrations, the cobaltous chloride and hydrochloric acid greatly favor the aqueous phase. The mixture was shaken well in the flask and the two phases allowed to separate. Further additions of water were made, with shaking and settling until the water-alcohol interface was at the 250 ml mark. In this way essentially all of the solutes were transferred to the water. The alcohol was then decanted and the water phase, which contained the solutes, was used for the analyses. The methods used were the same as for the aqueous phase except for the sizes of the samples which are indicated below.

1. Total chloride. Ten ml aliquots of the above aqueous extract were taken for analysis. These determinations were not needed for calculation of mass transfer coefficients. They showed, however, that the HCl concentration in the alcohol phase was relatively constant throughout the column. Duplicate determinations were made. These usually agreed to 0.05 ml.

2. Cobaltous chloride. Twenty-five ml aliquots of the aqueous extract were evaporated to dryness and analyzed in the same manner as the aqueous phase samples. Duplicate determinations were made. These usually agreed to 0.05 ml.

3. Specific gravity. Specific gravities of the alcohol phase were determined in the same manner as for the aqueous phase.

RESULTS

The flooding data of Series I are plotted as the alcohol phase flow rate versus the corresponding aqueous phase flow rate in Figure 7. Also included is a flood point determined for Run No. 3 of Series III.

The values of Ka and HTU for runs of Series II and Series III were obtained by using the following equations:

When steady-state conditions are maintained in an extraction column, the rate at which material is being transferred at any point is represented by the following equations for Series II:

$$dN = K_A(C_A^* - C_A)dA \qquad (1)$$

$$dN = K_W(C_W - C_W^*)dA \qquad (2)$$

If the driving force for mass transfer is assumed to be linear with mass transfer, and if adV is substituted for dA, equation (1) may be integrated to give:

$$N = K_Aa(\Delta C)_{lm}V \qquad (3)$$

or

$$K_Aa = \frac{N}{V(\Delta C)_{lm}} \qquad (4)$$

where N is defined as:

$$N = S(L_{AT}C_{AT} - L_{AB}C_{AB}) \qquad (5)$$

If it is assumed that the volume change of the phase under consideration is negligible as solute is transferred, equation (5) reduces to:

$$N = SL_A(C_{AT} - C_{AB}) \qquad (6)$$

The overall height of a transfer unit based on the alcohol phase is:

$$(HTU)_{OA} = \frac{L_A}{K_Aa} \qquad (7)$$

Similar equations may be derived for the aqueous phase by substituting the subscript W for the subscript A in equations (3) through (7).

In Series III, cobaltous chloride was being transferred from the alcohol phase to the aqueous phase so all the equations become valid if the signs of the concentrations are changed in equations (1), (2), (5), and (6).

The use of the logarithmic mean concentration difference is justified since the equilibrium line deviates negligibly from a straight line for the concentrations employed, and the change in volume, calculated for each phase was found to be less than 1% in every run.

Table I in the Appendix contains the data and intermediate calculations for both Series II and Series III necessary to obtain values of Ka and HTU for the entire column, and various sections of the column, and the magnitude of the end effect at the coalescence point. The results are plotted as Ka and HTU for the entire column (including end effect) in Figures 8-13 and with the end effect eliminated in Figure 15. The abscissa in each case is the aqueous phase flow rate, the alcohol phase flow rate being constant. The end effect in terms of the height of a column to which it is equivalent is plotted against aqueous phase flow rate at constant alcohol phase flow rate in Figure 14.

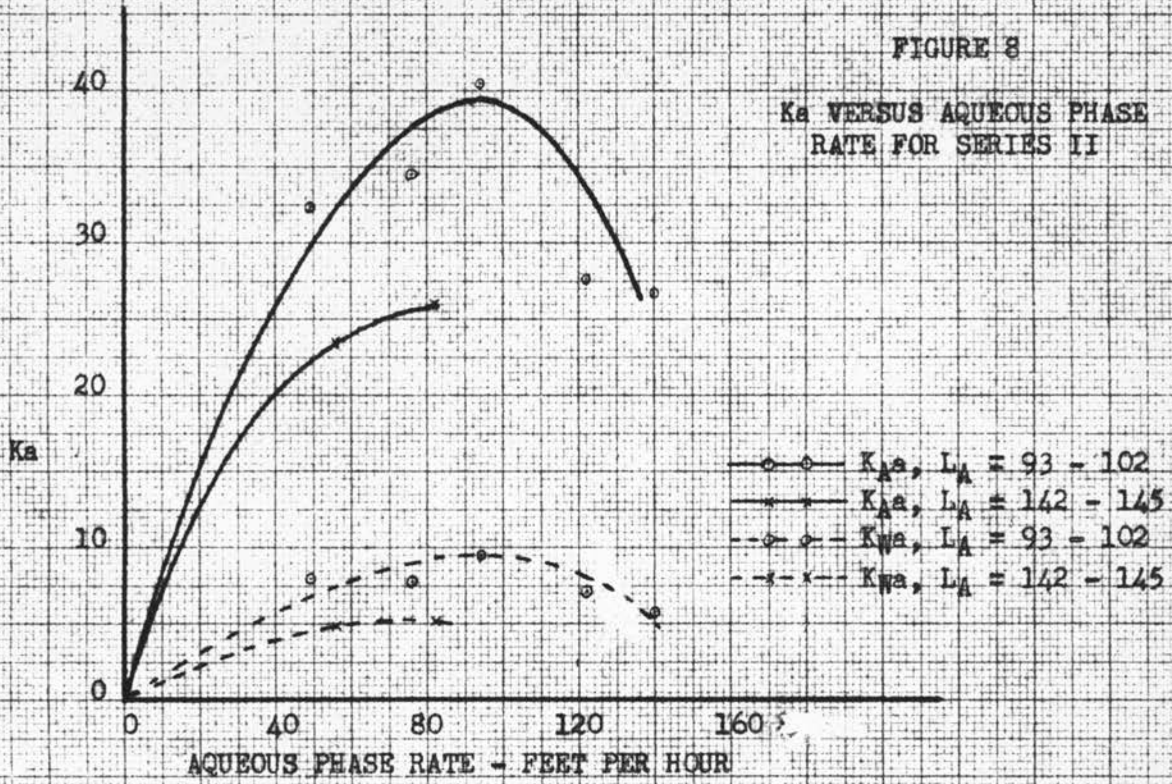


FIGURE 8

Ka VERSUS AQUEOUS PHASE RATE FOR SERIES II

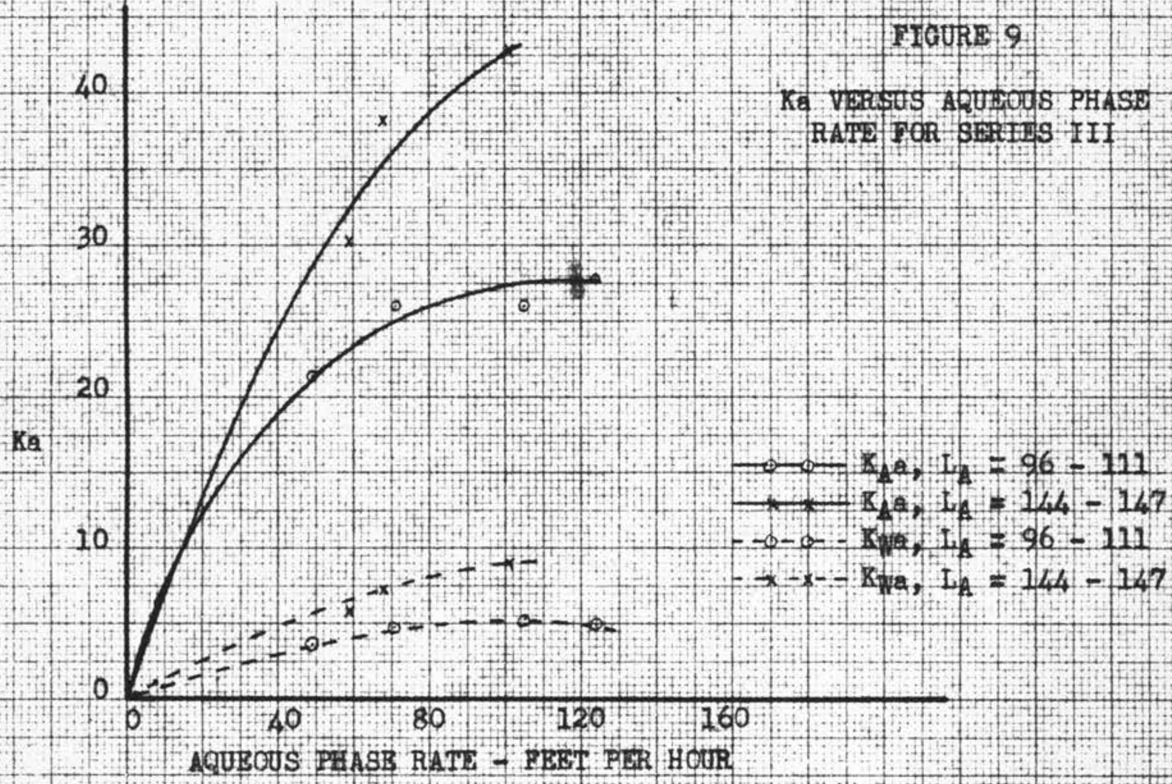


FIGURE 9

Ka VERSUS AQUEOUS PHASE RATE FOR SERIES III

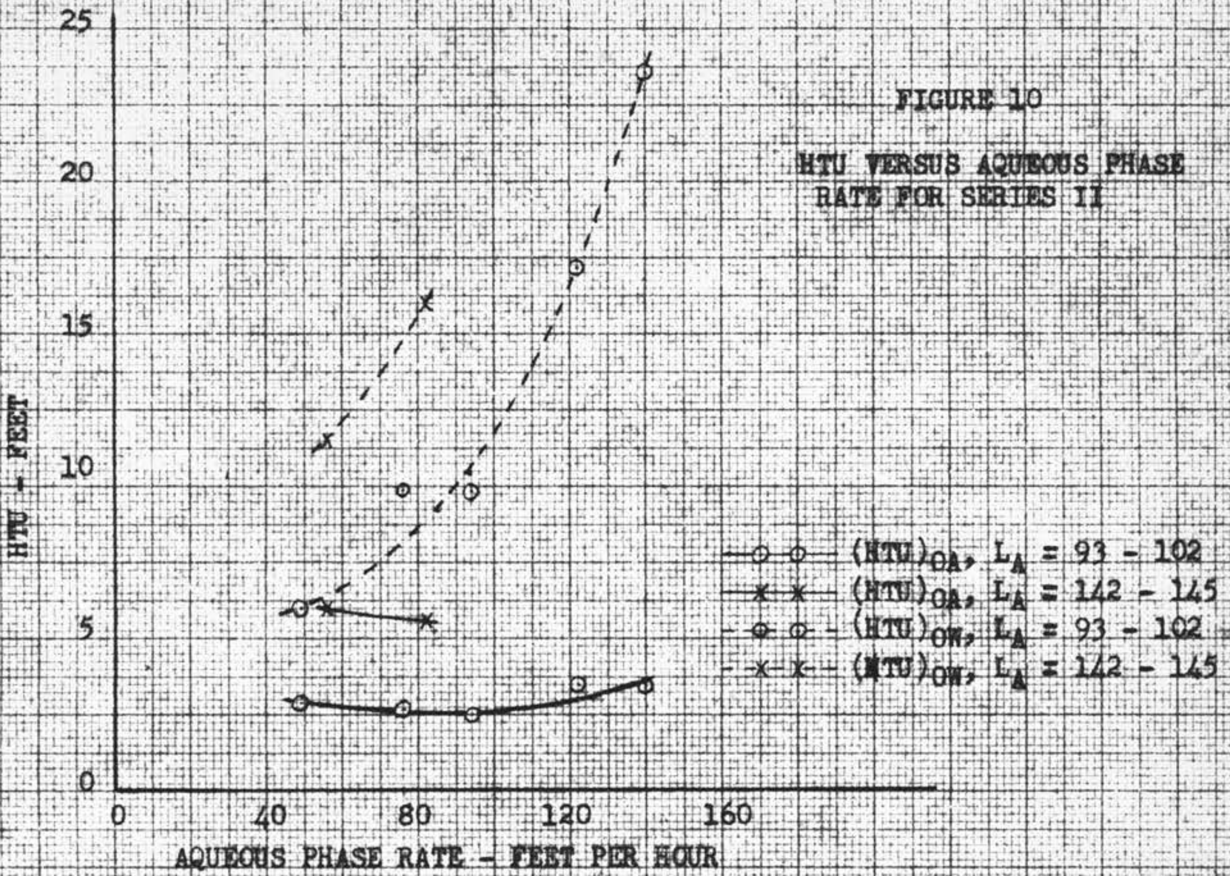


FIGURE 10

HTU VERSUS AQUEOUS PHASE RATE FOR SERIES II

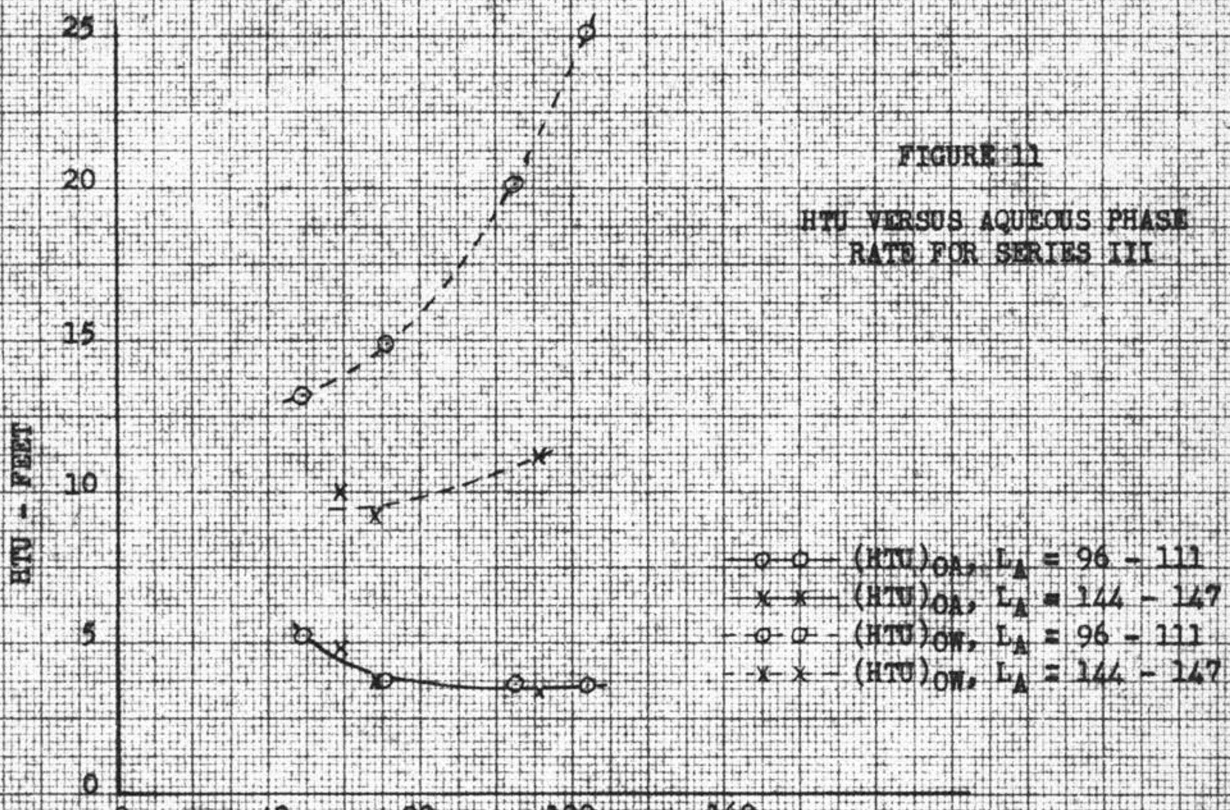


FIGURE 11

HTU VERSUS AQUEOUS PHASE RATE FOR SERIES III

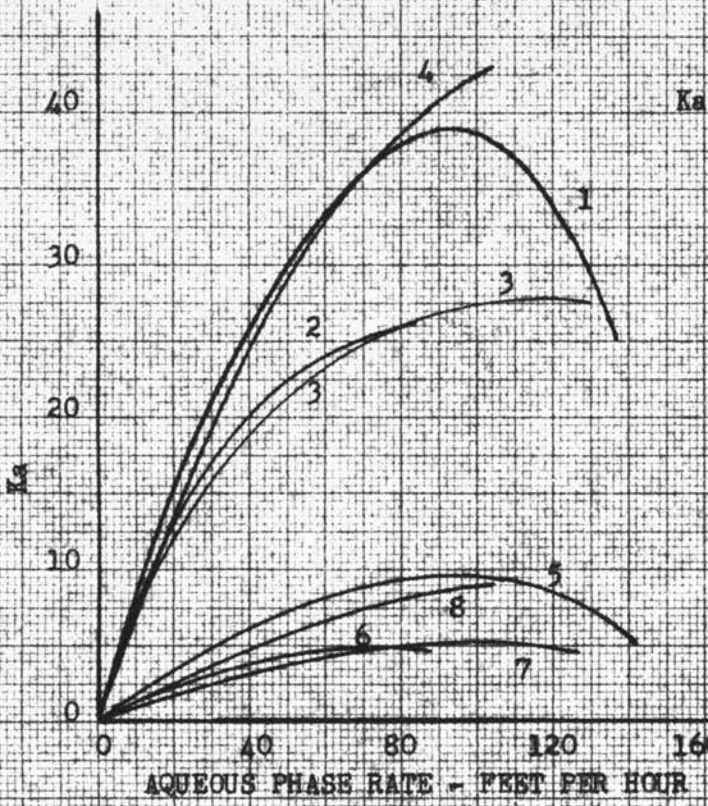


FIGURE 12

Ka VERSUS AQUEOUS PHASE RATE FOR SERIES II AND SERIES III

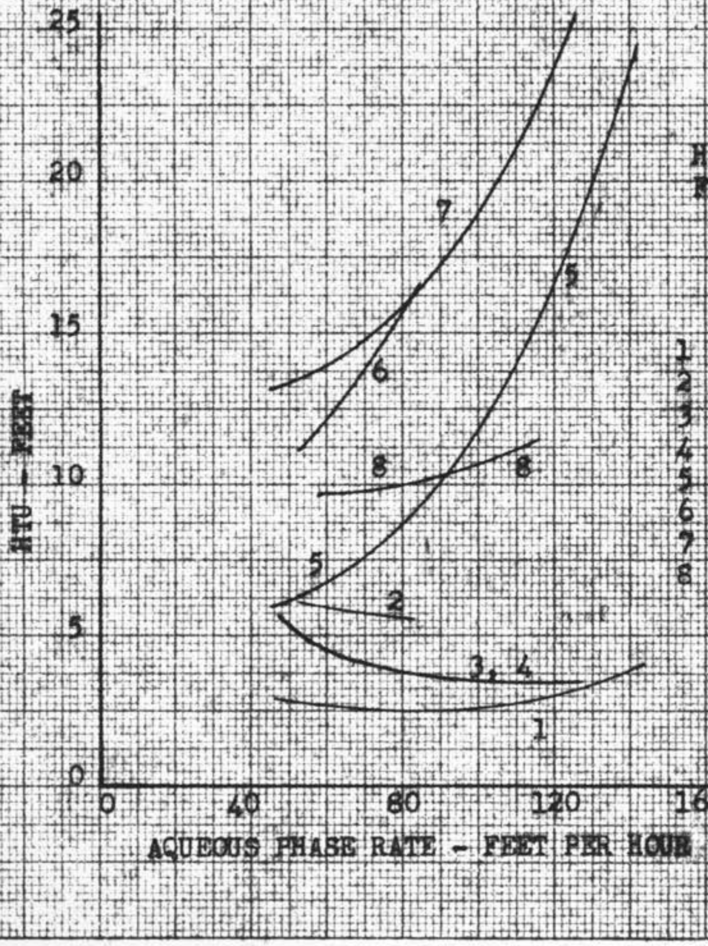


FIGURE 13

HTU VERSUS AQUEOUS PHASE RATE FOR SERIES II AND SERIES III

FIGURE 14

END EFFECT VERSUS AQUEOUS PHASE RATE

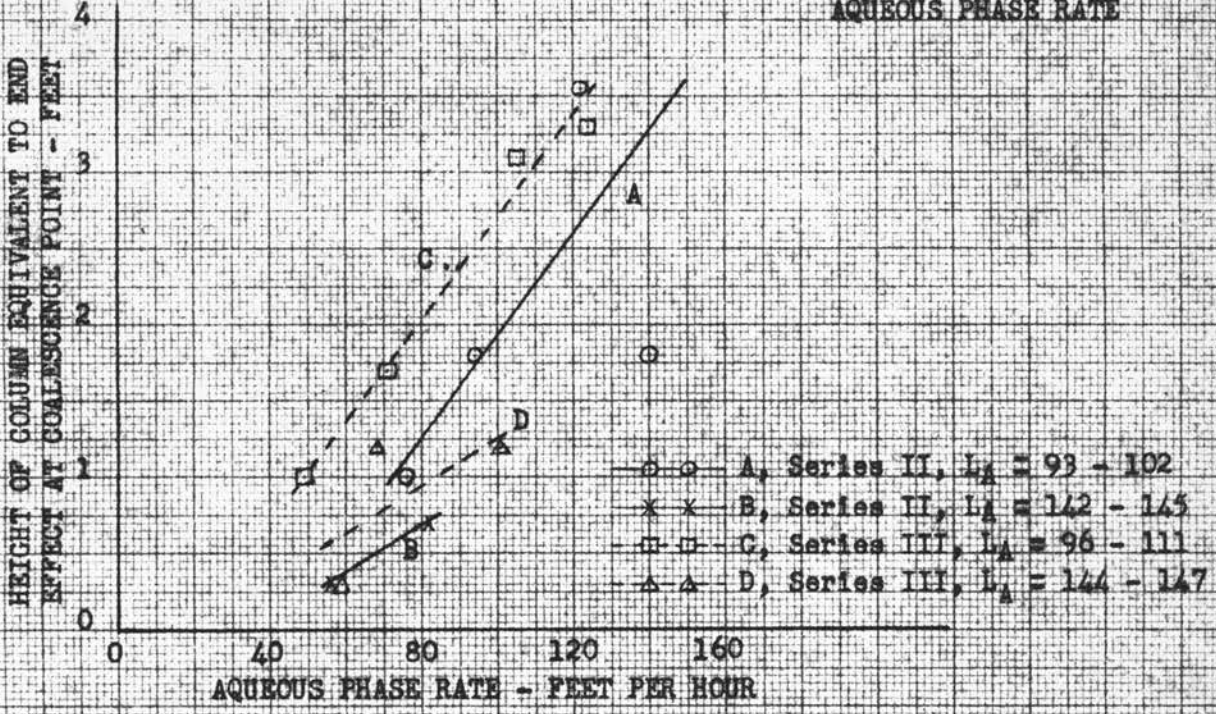
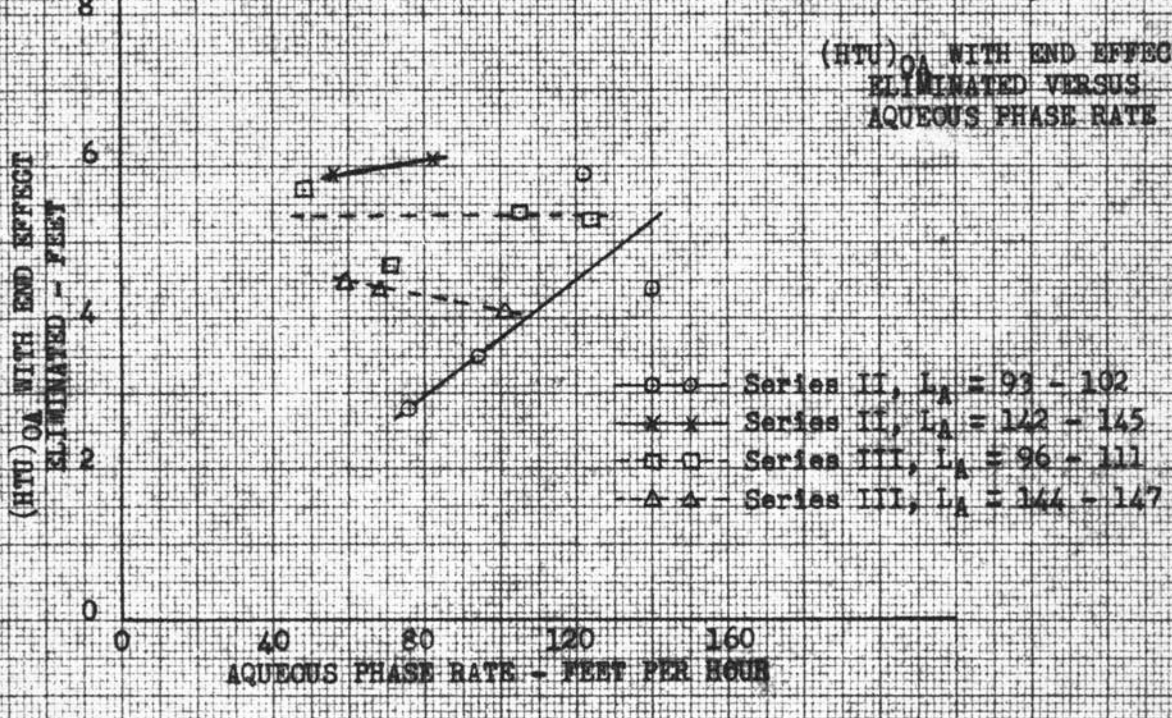


FIGURE 15

$(HTU)_{OA}$ WITH END EFFECT ELIMINATED VERSUS AQUEOUS PHASE RATE



DISCUSSION OF RESULTS - CONCLUSIONS

Series I. Flooding velocities were determined in order to find the limiting rates which could be employed in the operation of the column and also to compare the results with those of Kylander[9] in which the alcohol phase was dispersed.

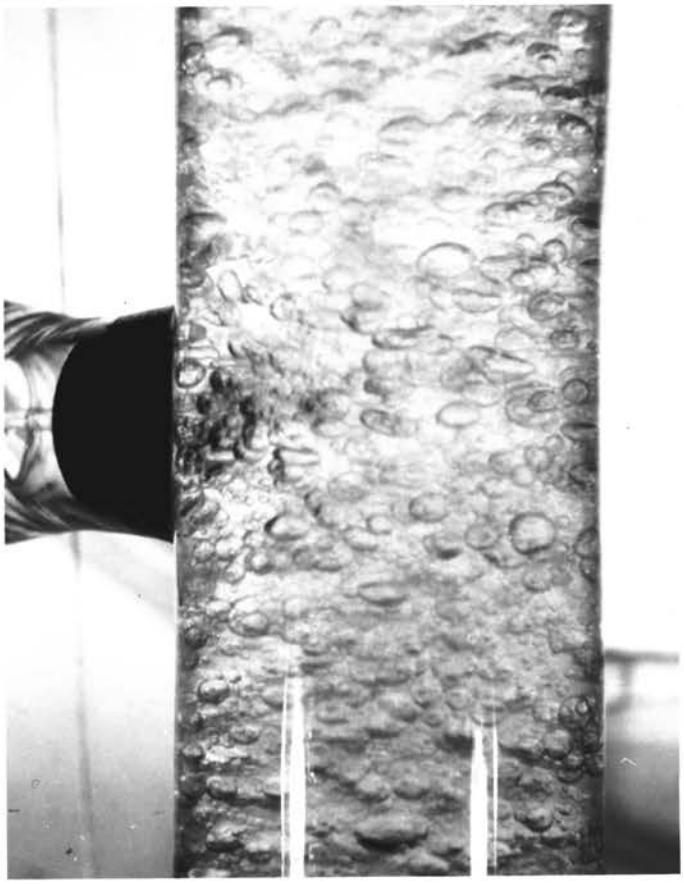
For a constant continuous phase flow rate and a low dispersed phase flow rate the holdup in the column was relatively low and the drops of dispersed phase fell uniformly through the continuous phase. A photograph of the operation under these conditions is shown in Figure 16. As the dispersed phase rate was increased, the holdup became greater, some coalescence of the dispersed phase drops occurred in the column, and there was some recirculation of the dispersed phase drops. This condition of relatively high holdup, slightly below the flooding point, is shown in Figure 17. As the dispersed phase rate was increased further globules of alcohol detached themselves from the main portion of the continuous phase and rose rapidly up the column for a short distance before they again became part of the continuous phase. When this took place, coalescence of dispersed phase particles increased markedly, and local recirculation of the dispersed phase drops became much greater in magnitude. This change in operating conditions occurred at the same time throughout the entire length of the column proper. When the column was operating under flooded conditions the interface between the two phases in the bottom settling section, instead of staying at the same location, rose and fell rapidly, indicating surges of first one phase and then the other. Figure 18 is a photograph of the column operating under flooding conditions.

The flooding point obtained in this work was different from that experienced by Kylander[9] and Blanding and Elgin[1]. Kylander[9] defined flooding as the point at which dispersed phase (alcohol) drops collected in the conical section above the disperser to such an extent as to interfere with drop formation from the jets leaving the disperser. Blanding and Elgin[1] found that at a certain pair of flow rates, a condition of high drop holdup would start at the top of the column and proceed uncontrolled downward until the entire column was filled with closely packed drops. This was considered to represent flooding although the column would operate satisfactorily at these rates.

The limiting linear velocities of both phases through the column used in this investigation were found to be approximately 35% higher than those obtained by Kylander[9] in a 1 1/4 inch diameter column for the same ratio of dispersed phase flow to continuous phase flow. Blanding and Elgin[1] also found differences in flooding velocities for the same pair of fluids when the continuous and dispersed phases were reversed. With 1/8 inch diameter nozzles for the system naphtha--water, flooding velocities were higher with the water dispersed and for the system methyl-isobutyl ketone--water, flooding velocities were higher with the ketone dispersed.

Figure 16

Appearance of Column at Low Holdup

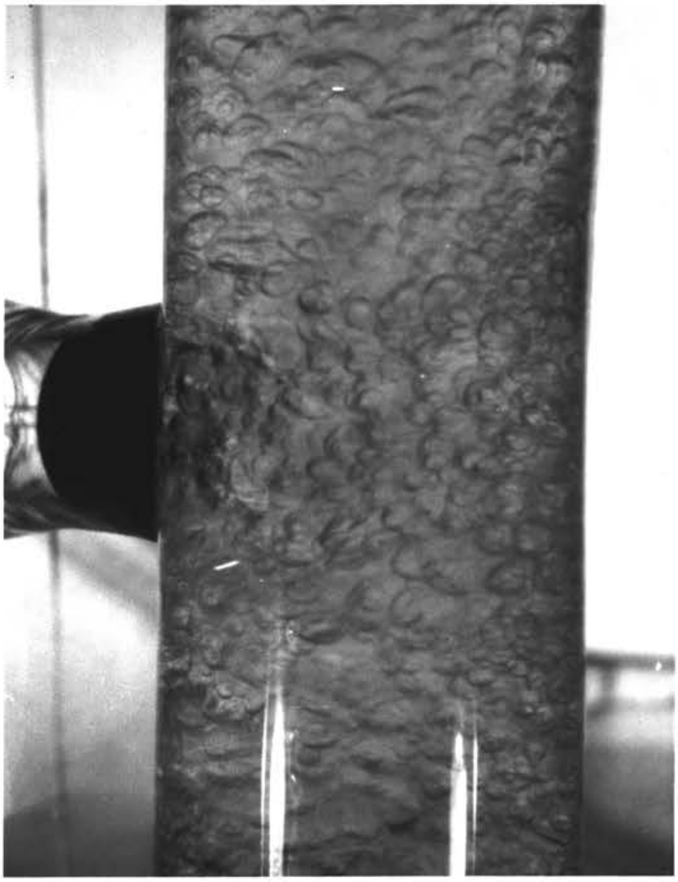


Aqueous (Dispersed) Phase Rate = 100 feet per hour

Alcohol (Continuous) Phase Rate = 200 feet per hour

Figure 17

Appearance of Column at High Holdup

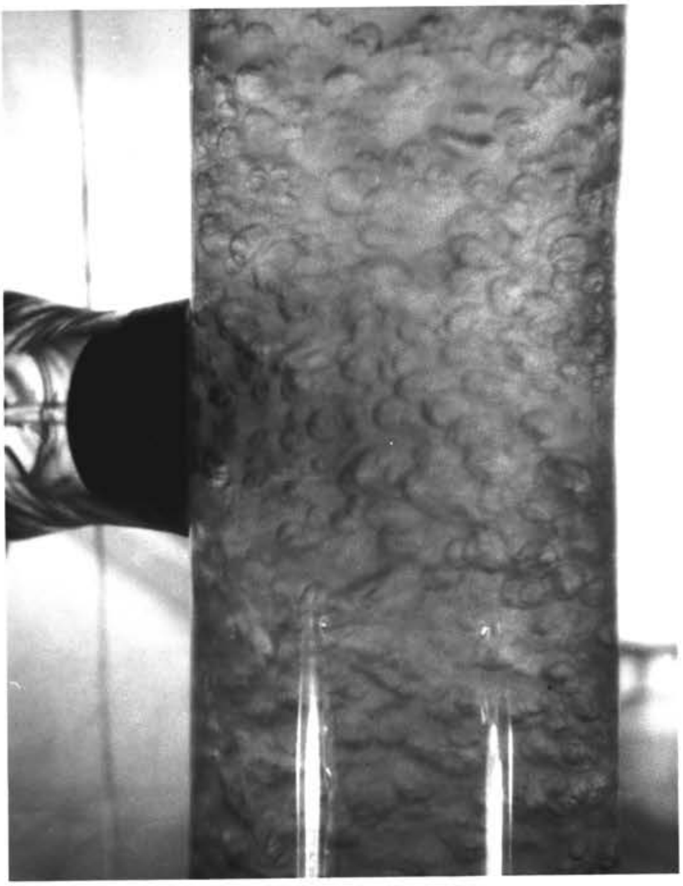


Aqueous (Dispersed) Phase Rate = 150 feet per hour

Alcohol (Continuous) Phase Rate = 200 feet per hour

Figure 18

Appearance of Column Under Flooded Conditions



Aqueous (Dispersed) Phase Rate = 200 feet per hour

Alcohol (Continuous) Phase Rate = 200 feet per hour

Series II and Series III. For the runs of Series II the data show, at an alcohol phase flow rate of about 100 feet per hour, that as the aqueous phase rate is increased, the Ka goes through a maximum and then falls off. The general slope of the curve is the same at an alcohol phase rate of 145 feet per hour. This would indicate that as more aqueous phase enters the system, more drops are formed, increasing the interfacial area, but as the aqueous phase rate is increased further, coalescence of the drops occurs until a point is reached at which the interfacial area begins to decrease. The values of Ka for the same aqueous phase rate are higher for the lower alcohol phase rate.

For Series III Ka again increases as the aqueous phase rate is increased, but no maximum is apparently approached. Ka is higher at the higher alcohol phase rate for the same aqueous phase rate, in contrast to the opposite trend in Series II.

The $(HTU)_{OA}$ for Series II and III (see Figure 13) was relatively constant for various aqueous phase rates at a particular alcohol phase rate. The values of (HTU)OA ranged from 2.5 to 6 feet, increasing with increasing alcohol phase rate in Series II but being independent of this factor in Series III. The $(HTU)_{OW}$ shows a consistent increase with increasing aqueous phase rate. It increases with increasing alcohol rate is Series II but with decreasing alcohol rate is Series III. The values of $(HTU)_{OW}$ ranged from 6 to 26 feet for the flow rates investigated.

Kylander[9] investigated the extraction of cobaltous chloride from aqueous hydrochloric acid solution with capryl alcohol with the alcohol phase dispersed. For the range where the alcohol and aqueous phase flow rates are the same as those employed in Series II of this investigation, the following data, taken from the smoothed curves, are tabulated:

Investigator	Alcohol Phase Rate ft./hr.	Aqueous Phase Rate ft./hr.	K_Aa	K_Wa	$(HTU)_{OA}$	$(HTU)_{OW}$
Kylander	95	48	22	6.1	4.3	7.1
Present Work	95	49	30	7.0	2.9	6.1
Kylander	142	48	37	9.2	4.3	4.9
Present Work	142	56	23	4.8	6.0	11.5

The values of $(HTU)_{OA}$ obtained in the two studies differ by approximately 35% in each case; at the lower alcohol phase rate the $(HTU)_{OA}$ in this work was higher than that obtained by Kylander[9], but at the higher alcohol phase rate the reverse was true.

In the taking of intermediate samples from the column through the sampling tubes, less than one percent of the material withdrawn was dispersed phase in most cases. At higher dispersed phase rates, however, as much as ten percent dispersed phase was entrained, but it was readily separated by allowing it to settle out in a vertical tube as the sample was withdrawn. Samples taken at intermediate points close together showed so little change in cobaltous chloride concentration that values of HTU calculated over very short sections were meaningless due to limitations in the accuracy of the analyses. No trend could be detected in the straight section of the column, however, and there was no evidence of an end effect at the top of the column where the drops of dispersed phase were formed.

The points plotted for the entire column length are based on the average of the material transferred as indicated by analysis of both the aqueous and alcohol phases. An average deviation of ten percent was obtained. Calculations for portions of the column, however, are based on the alcohol phase analyses only (since intermediate samples are involved). For comparison, values of Ka and HTU for the entire column length, based on the alcohol phase analyses only, are included in Table I. Discrepancies in the overall material balances are believed due to small concentration differences obtained between inlet and outlet samples, particularly at the lower total throughputs. At high throughputs some difficulty was encountered in maintaining the interface at a constant position in the column. This would cause slight errors in flow measurements and possibly mean a slight deviation from steady-state conditions.

An appreciable end effect was found at the coalescence point (bottom of the column). By assuming a constant $K_A a$ in the straight section of the column (and analyses throughout the column indicate that this is the case, as shown for run 4 of Series III in the following table:)

Section	$K_A a$ (Estimated Error = ± 30%)
1-3	32
3-6	9
6-8	16
8-Top	17

the end effect was isolated and plotted as the number of feet of straight column to which it is equivalent (see sample calculations). The end effect is appreciably higher for the lower alcohol rate, being apparently little affected by the direction of extraction. The end effect varies from 0.3 to 3.6 feet.

In order to facilitate design calculations the end effect was isolated from the straight section of the column and values of $(HTU)_{OA}$ with the end effect eliminated are plotted against aqueous phase rate in Figure 15. With the exception of the 100 feet per hour alcohol phase rate curve for Series II, the $(HTU)_{OA}$ corrected for end effect seems to be quite constant for a particular alcohol phase rate and direction of extraction. It ranges from 3 to 6 feet for all conditions studied.

Geankoplis and Hixson[5] found an appreciable end effect at the coalescence point, averaging the equivalent of 0.5 foot of column height, and no end effect for drop formation. This work substantiates their findings. Licht and Conway[10] found appreciable end effects at both ends of the column in the extraction of acetic acid from water with several organic solvents and with the water phase dispersed. By using several column heights and one column which was designed to eliminate the formation of an interface, end effects at both ends were determined. However, this author doubts that the coalescence point was completely eliminated. It is possible that the end effect indicated for drop formation is not justified and should be added to the end effect obtained for coalescence.

Hardy[6] and Nandi and Viswanathan[12] used several column lengths and detected end effects which they ascribed to drop formation without actually determining to which end of the column the added extraction could be attributed.

The flooding point obtained for run 3 of Series III was considerably below the curve obtained in Series I, the total flow being about 2/3 the flow in Series I. This appears to be due primarily to smaller drops caused by the lower interfacial tension. For Series III an interfacial tension of 3.8 dynes per cm. was found, compared to 10.5 dynes per cm. for Series I. Kylander[9] also found the flooding point lowered to about the same extent with salts in the system relative to the system capryl alcohol--water.

SUMMARY

All experimental work was done in a spray column two inches in diameter and 73-3/8 inches long.

Flooding velocities were determined for the system capryl alcohol--water. These were found to be 35% higher than those previously found for the same system but with the aqueous phase dispersed. The type of flooding occurring in this system was different from that found by others in that it consisted of globules of continuous phase detaching themselves from the main body of the continuous phase and rising rapidly up the column for a short distance before again becoming part of the continuous phase.

For the extraction of cobaltous chloride from both the alcohol phase and aqueous phase, Ka was found to increase with increasing aqueous phase rate. A maximum was found for the extraction from the aqueous phase, indicating coalescence of dispersed phase drops, but not for extraction in the reverse direction. The effect of alcohol phase rate on Ka was found to be a function of the direction of extraction.

For the entire column, the $(HTU)_{OA}$ was relatively constant for various aqueous phase rates and for a particular alcohol phase rate. It was unaffected by the alcohol phase rate for extraction from the alcohol phase, but increased with increasing alcohol phase rate for extraction from the aqueous phase. The $(HTU)_{OW}$ increased with increasing aqueous phase rate, and it increased with increasing alcohol phase rate for extraction from the aqueous phase, but decreased with increasing alcohol phase rate for extraction from the alcohol phase. The $(HTU)_{OA}$ varied from 2.5 to 6 feet and the $(HTU)_{OW}$ from 6 to 26 feet for the range of flow rates employed. The values of Ka and HTU deviate by approximately 35% from those found for the same linear flow rates in a previous investigation with the alcohol phase dispersed.

Samples of the alcohol phase were taken at intermediate points in the column and an appreciable end effect was found at the coalescence point, but none was detected for drop formation. The end effect is considerable at the lower alcohol phase rates and is only slightly affected by the direction of extraction.

For convenience in design calculations the end effect was isolated from the straight section of the column and the column considered as two sections. The $(HTU)_{OA}$ for the straight section varied from 3 to 6 feet and the end effect in terms of length of straight column was found to vary from 0.3 to 3.6 feet.

RECOMMENDATIONS

Recommendations for further work on the separation of nickel and cobalt by liquid-liquid extraction are as follows:

1. Determination of end effects with the alcohol phase dispersed.
2. Determination of extraction capacities for the recovery of cobalt from the alcohol phase with the alcohol phase dispersed.
3. Investigation of the use of other solvents, particularly higher alcohols.

APPENDIX

TABLE I

RUN	FLOW RATE				SPECIFIC GRAVITY				WEIGHT PERCENT $CoCl_2$								
	Cu. ft./hr.		Ft./hr.		Alcohol		Aqueous		Alcohol							Aqueous	
	Alcohol	Aqueous	Alcohol	Aqueous	In	Out	In	Out	In	1	2	3	6	8	Out	In	Out
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)
1	2.08	1.06	95	49	0.898	0.900	1.185	1.176	1.44	----	----	----	----	----	2.25	7.21	6.15
5	2.04	1.66	94	76	0.884	0.898	1.200	1.187	0.63	1.43	----	1.95	2.49	2.57	2.61	9.69	8.23
2	2.21	2.04	102	94	0.888	0.904	1.201	1.187	0.76	1.65	----	----	----	2.54	2.70	9.30	7.54
4	2.13	2.65	99	122	0.885	0.901	1.204	1.192	0.51	1.86	----	2.48	2.70	2.75	2.78	9.90	8.51
3	2.02	3.04	93	140	0.887	0.896	1.194	1.188	0.66	1.40	----	1.75	2.07	2.22	2.26	8.69	7.99
6	3.09	1.22	142	56	0.885	0.890	1.192	1.179	0.72	0.95	----	----	----	1.79	1.82	9.05	7.39
7	3.16	1.80	145	82	0.889	0.895	1.211	1.196	0.57	1.02	----	----	----	2.08	2.15	11.39	9.64
1	2.41	1.06	111	49	0.900	0.891	1.121	1.143	2.24	1.78	1.53	1.27	----	----	0.81	0.16	2.35
5	2.11	1.54	97	71	0.896	0.885	1.124	1.141	2.56	1.71	----	1.12	0.78	0.65	0.63	0.03	2.09
2	2.10	2.28	96	105	0.901	0.892	1.130	1.140	2.63	1.43	----	0.83	----	0.61	0.56	0.00	1.39
4	2.16	2.69	99	124	0.899	0.886	1.125	1.135	2.41	1.23	----	0.72	0.60	0.50	0.47	0.00	1.13
3			Approx. 100	150 Approx.	FLOODED												
6	3.14	1.28	144	59	0.893	0.888	1.130	1.143	1.82	1.54	----	----	----	0.66	0.58	0.06	1.99
7	3.14	1.49	144	68	0.890	0.885	1.128	1.137	1.64	1.19	----	----	----	0.47	0.43	0.06	1.91
8	3.20	2.20	147	101	0.894	0.891	1.132	1.141	1.95	1.29	----	0.90	0.58	0.47	0.43	0.06	1.77

RUN	$\#CoCl_2$/cu. ft.						$\#CoCl_2$ TRANSFERRED PER HOUR						% DEVIATION FROM AVERAGE
	Alcohol				Aqeous		Aqueous	Alcohol				Average of (24) and (25)	$\frac{(24)-(25)}{(29)} \times 100$
	In	1	8	Out	In	Out		Bottom-top	Bottom-1	1-8	1-Top		
	(18)	(19)	(20)	(21)	(22)	(23)	(24)	(25)	(26)	(27)	(28)	(29)	(30)
1	0.81	----	----	1.26	5.33	4.51	0.89	0.96	----	----	----	0.925	- 8
5	0.35	0.79	1.44	1.46	7.25	6.09	1.98	2.27	0.90	1.33	1.38	2.13	- 14
2	0.42	0.92	1.43	1.52	6.98	5.58	2.92	2.45	1.11	1.13	1.34	2.68	+ 18
4	0.28	1.04	1.55	1.56	7.43	6.33	3.04	2.74	1.62	1.09	1.13	2.89	+ 10
3	0.37	0.78	1.24	1.26	6.47	5.92	1.73	1.83	0.84	0.93	0.99	1.78	- 5
6	0.40	0.52	0.99	1.01	6.73	5.44	1.63	1.91	0.39	1.46	1.52	1.77	- 16
7	0.31	0.57	1.16	1.20	8.61	7.19	2.64	2.82	0.80	1.90	2.02	2.73	- 7
1	1.26	1.00	----	0.45	0.11	1.67	1.67	1.97	0.64	----	1.33	1.82	- 17
5	1.43	0.95	0.36	0.35	0.02	1.49	2.26	2.30	1.02	1.25	1.28	2.28	- 2
2	1.48	0.80	0.33	0.31	0.00	0.99	2.26	2.47	1.45	0.88	1.02	2.37	- 9
4	1.35	0.68	0.27	0.26	0.00	0.80	2.16	2.36	1.45	0.89	0.91	2.26	- 9
3			FLOODED										
6	1.01	0.86	0.37	0.32	0.04	1.42	1.78	2.19	0.50	1.55	1.69	1.98	- 21
7	0.91	0.66	0.26	0.24	0.04	1.35	1.96	2.12	0.80	1.26	1.32	2.04	- 8
8	1.12	0.72	0.26	0.24	0.04	1.26	2.69	2.74	1.20	1.47	1.54	2.72	- 2

RUN	% Cl IN AQUEOUS PHASE AND CORRESPONDING K								EQUILIBRIUM $CoCl_2$ CONCENTRATION IN ALCOHOL PHASE (SEE NOTE)							
	Bottom		1		8		Top		Weight %				#/cu. ft.			
	% Cl	K	% Cl	K	% Cl	K	% Cl	K	Bottom	1	8	Top	Bottom	1	8	Top
	(31)	(32)	(33)	(34)	(35)	(36)	(37)	(38)	(39)	(40)	(41)	(42)	(43)	(44)	(45)	(46)
					SERIES II											
1	26.57	0.300	-----	-----	-----	-----	27.75	0.361	1.84	----	----	2.60	1.04	----	----	1.46
5	26.12	0.275	26.32	0.285	26.62	0.302	26.63	0.302	2.26	2.51	2.92	2.93	1.25	1.39	1.64	1.64
2	26.61	0.302	26.92	0.318	27.25	0.334	27.31	0.339	2.28	2.65	3.06	3.15	1.26	1.48	1.72	1.79
4	27.32	0.339	27.52	0.350	27.66	0.356	27.66	0.356	2.88	3.27	3.52	3.52	1.59	1.82	1.98	1.98
3	26.55	0.298	26.61	0.301	26.68	0.305	26.68	0.305	2.38	2.55	2.64	2.65	1.32	1.42	1.48	1.48
6	26.17	0.276	26.20	0.278	26.34	0.286	26.34	0.286	2.04	2.15	2.58	2.59	1.13	1.19	1.43	1.44
7	25.95	0.264	26.01	0.268	26.15	0.274	26.16	0.274	2.54	2.72	3.10	3.12	1.41	1.51	1.73	1.74
					SERIES III											
1	25.77	0.253	25.51	0.239	-----	-----	24.98	0.210	0.59	0.39	----	0.03	0.33	0.22	----	0.02
5	25.91	0.262	25.62	0.245	25.26	0.225	25.25	0.224	0.55	0.29	0.01	0.01	0.31	0.16	0.01	0.00
2	26.04	0.270	25.92	0.263	25.84	0.258	25.84	0.258	0.37	0.15	0.01	0.00	0.21	0.09	0.00	0.00
4	25.83	0.257	25.47	0.236	25.25	0.224	25.24	0.223	0.29	0.10	0.00	0.00	0.16	0.06	0.00	0.00
3				FLOODED												
6	25.91	0.262	25.85	0.258	25.68	0.251	25.66	0.250	0.52	0.40	0.04	0.02	0.29	0.22	0.02	0.01
7	25.89	0.261	25.77	0.253	25.58	0.242	25.57	0.242	0.50	0.31	0.03	0.01	0.28	0.17	0.02	0.01
8	26.05	0.270	26.11	0.273	26.19	0.276	26.18	0.276	0.48	0.28	0.03	0.02	0.27	0.15	0.02	0.01

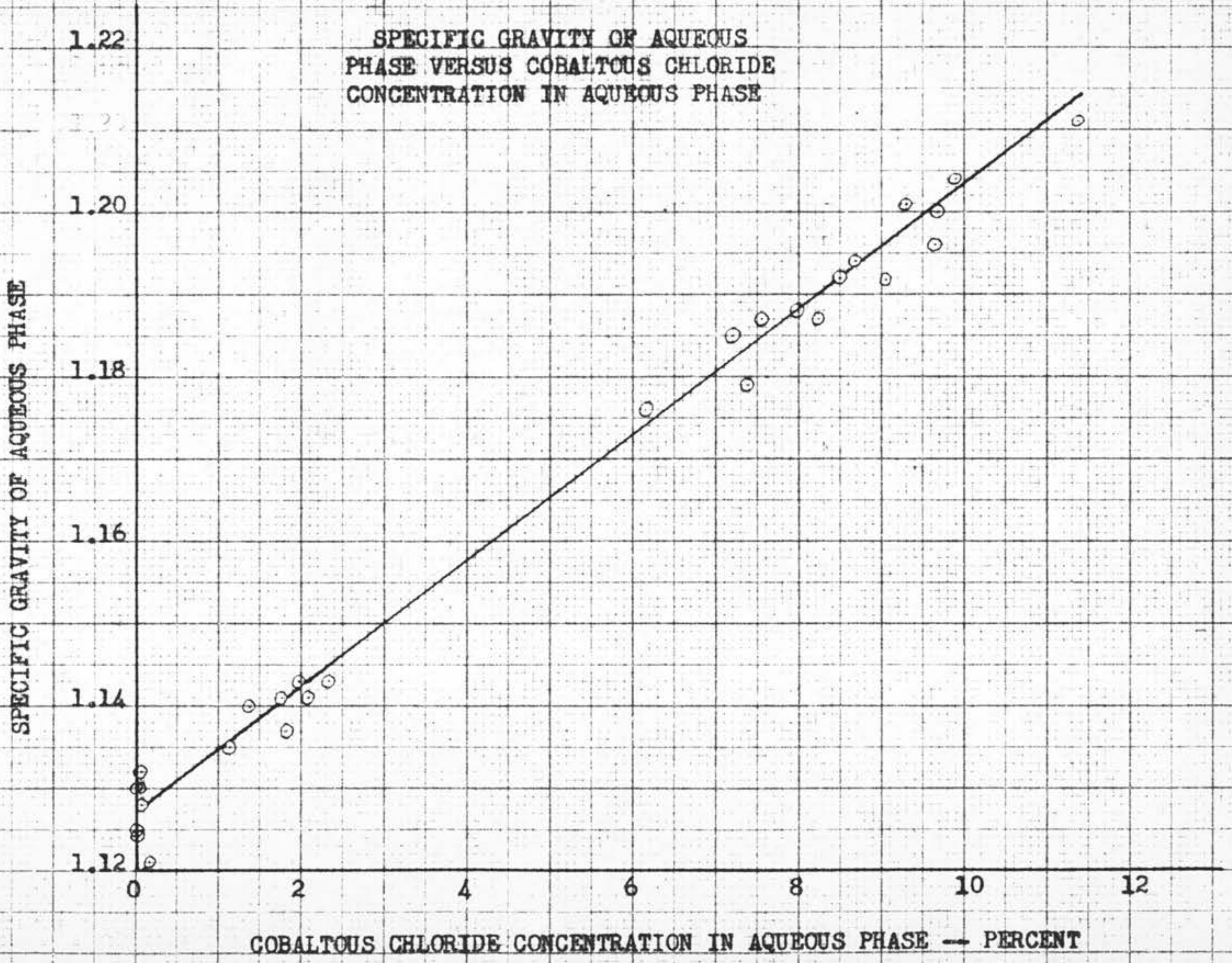
RUN	ΔC--# $CoCl_2$/cu. ft. BASED ON ALCOHOL PHASE CONCENTRATION								K_Aa #/hr.---cu. ft.--#/cu. ft.				
					Log Mean				Bottom-Top		Bottom-1	1-8	1-Top
	Bottom	1	8	Top	Bottom-Top	Bottom-1	1-8	1-Top	Based on (29)	Based on (25)			
	(47)	(48)	(49)	(50)	(51)	(52)	(53)	(54)	(55)	(56)	(57)	(58)	(59)
1	0.23	----	----	0.19	0.21	----	----	----	32.9	34.3	----	----	----
5	0.89	0.60	0.21	0.20	0.46	0.74	0.36	0.36	34.5	37.0	75.8	35.8	32.3
2	0.83	0.56	0.29	0.27	0.50	0.69	0.50	0.49	40.5	36.8	99.5	26.8	28.9
4	1.31	0.78	0.43	0.42	0.78	1.03	0.59	0.58	27.7	26.3	97.5	17.9	16.5
3	0.95	0.61	0.24	0.22	0.50	0.77	0.40	0.38	26.8	27.4	67.3	22.6	21.2
6	0.73	0.66	0.44	0.43	0.56	0.69	0.54	0.54	23.5	25.6	34.7	26.2	24.1
7	1.10	0.94	0.57	0.54	0.79	1.02	0.74	0.72	26.0	26.8	48.7	25.0	23.9
1	0.92	0.78	----	0.43	0.65	0.85	----	0.59	21.1	22.7	46.6	----	19.3
5	1.12	0.79	0.35	0.34	0.66	0.95	0.54	0.53	26.0	26.1	66.8	22.4	20.5
2	1.27	0.71	0.32	0.31	0.68	0.97	0.50	0.49	26.0	27.2	92.7	19.1	17.9
4	1.19	0.63	0.27	0.26	0.61	0.88	0.42	0.42	27.8	29.0	102	20.2	18.7
3					FLOODED								
6	0.72	0.63	0.34	0.31	0.49	0.68	0.47	0.45	30.3	33.5	45.6	32.0	31.6
7	0.63	0.49	0.24	0.23	0.40	0.56	0.35	0.34	38.4	39.7	88.5	34.6	32.9
8	0.85	0.56	0.24	0.23	0.47	0.70	0.38	0.37	42.9	43.7	107	37.5	35.4

RUN	$(HTU)_{OA}$ feet					END EFFECT AT COALESCENCE POINT	EQUILIBRIUM $CoCl_2$ CONCENTRATION IN AQUEOUS PHASE (SEE FIGURE 19)				ΔC--# $CoCl_2$/cu. ft. BASED ON AQUEOUS PHASE CONCENTRATIONS			K_Wa #/hr.--cu. ft.--#/cu. ft.	$(HTU)_{OW}$ feet
	Bottom-Top		Bottom-1	1-8	1-Top		Weight %		#/cu. ft.						
	Based on (55)	Based on (56)				Feet of Column	Bottom	Top	Bottom	Top	Bottom	Top	Log Mean		
	(60)	(61)	(62)	(63)	(64)	(65)	(66)	(67)	(68)	(69)	(70)	(71)	(72)	(73)	(74)
1	2.90	2.8	---	---	---	---	4.80	6.23	3.50	4.60	1.01	0.73	0.86	8.07	6.0
5	2.72	2.5	1.2	2.6	2.8	1.0	2.34	8.64	1.67	6.50	4.43	0.75	2.07	7.71	9.9
2	2.51	2.8	1.0	3.8	3.5	1.8	2.51	7.96	1.79	5.96	3.79	1.02	2.11	9.54	9.8
4	3.54	3.8	1.0	5.5	5.9	3.6	1.51	7.81	1.07	5.84	5.26	1.59	3.07	7.07	17.2
3	3.46	3.4	1.4	4.1	4.4	1.8	2.22	7.41	1.58	5.52	4.34	0.95	2.25	5.92	23.6
6	6.04	5.6	4.1	5.4	5.9	0.3	2.61	6.36	1.87	4.70	3.57	2.03	2.73	4.86	11.5
7	5.57	5.4	3.0	5.8	6.1	0.7	2.15	7.85	1.57	5.88	5.62	2.73	4.00	5.12	16.1
1	5.25	4.9	2.4	---	5.7	1.0	8.85	3.85	6.67	2.82	4.88	2.70	3.69	3.69	13.2
5	3.73	3.7	1.4	4.3	4.7	1.7	9.77	2.80	7.43	2.01	5.94	1.99	3.61	4.74	14.9
2	3.70	3.5	1.0	5.0	5.4	3.1	9.74	2.18	7.39	1.55	6.40	1.55	3.42	5.19	20.2
4	3.57	3.5	1.0	4.9	5.3	3.3	9.38	2.12	7.12	1.51	6.31	1.51	3.41	4.91	25.2
3			FLOODED												
6	4.76	4.3	3.2	4.5	4.5	0.3	6.94	2.33	5.15	1.66	3.73	1.62	2.53	5.88	10.0
7	3.75	3.6	1.6	4.2	4.4	1.2	6.28	1.79	4.64	1.27	3.28	1.22	2.09	7.34	9.3
8	3.43	3.4	1.4	3.9	4.1	1.2	7.22	1.58	5.37	1.12	4.11	1.07	2.26	9.01	11.2

Note: Specific gravity of an alcohol phase which would be in equilibrium with an aqueous phase is assumed to be equal to the measured specific gravity at that point in the column during steady state operation. Specific gravities at intermediate points were determined by interpolation.

FIGURE 19

SPECIFIC GRAVITY OF AQUEOUS PHASE VERSUS COBALTOUS CHLORIDE CONCENTRATION IN AQUEOUS PHASE



SAMPLE CALCULATIONS

Run number 7 of Series II.

The numbers in parentheses refer to the numbers heading the columns in Table I. Columns (1) through (17), (31), and (37) are observed experimental data.

$$(18) = \frac{62.4 \times (5) \times (9)}{100} = \frac{62.4 \times 0.889 \times 0.57}{100}$$

$$= 0.31\ \#CoCl_2/\text{cu. ft.}$$

$$(19) = \frac{62.4 \times \left[(5) + \left(\frac{(15) - (10)}{(15) - (9)}\right)\left((6) - (5)\right)\right] (10)}{100}$$

$$= \frac{62.4 \left[0.889 + \left(\frac{2.15 - 1.02}{2.15 - 0.57}\right)\left(0.895 - 0.889\right)\right] 1.02}{100}$$

$$= 0.57\ \#CoCl_2/\text{cu. ft.}$$

$$(20) = \frac{62.4 \left[(5) + \left(\frac{(15) - (14)}{(15) - (9)}\right)\left((6) - (5)\right)\right] (14)}{100}$$

$$= \frac{62.4 \left[0.889 + \left(\frac{2.15 - 2.08}{2.15 - 0.57}\right)\left(0.895 - 0.889\right)\right] 2.08}{100}$$

$$= 1.16\ \#CoCl_2/\text{cu. ft.}$$

$$(21) = \frac{62.4 \times (6) \times (15)}{100} = \frac{62.4 \times 0.895 \times 2.15}{100}$$

$$= 1.20\ \#CoCl_2/\text{cu. ft.}$$

$$(22) = \frac{62.4 \times (7) \times (16)}{100} = \frac{62.4 \times 1.211 \times 11.39}{100}$$

$$= 8.61\ \#CoCl_2/\text{cu.ft.}$$

$$(23) = \frac{62.4 \times (8) \times (16)}{100} = \frac{62.4 \times 1.196 \times 9.64}{100}$$

$$= 7.19\ \#CoCl_2/\text{cu. ft.}$$

$$(24) = \left[(22) - (23)\right](2) = (8.61 - 7.19)1.796 = 2.64 \ \#CoCl_2/hr.$$

$$(25) = \left[(21) - (18)\right](1) = (1.20 - 0.31)3.164 = 2.82 \ \#CoCl_2/hr.$$

$$(26) = \left[(19) - (18)\right](1) = (0.57 - 0.31)3.164 = 0.80 \ \#CoCl_2/hr.$$

$$(27) = \left[(20) - (19)\right](1) = (1.16 - 0.57)3.164 = 1.90 \ \#CoCl_2/hr.$$

$$(28) = \left[(21) - (19)\right](1) = (1.20 - 0.57)3.164 = 2.02 \ \#CoCl_2/hr.$$

$$(29) = \frac{(24) + (25)}{2} = \frac{2.64 + 2.82}{2} = 2.73 \ \#CoCl_2/hr.$$

$$(30) = \frac{(24) - (25)}{(29)} \times 100 = \frac{2.64 - 2.82}{2.73} \times 100 = -7\%$$

$$(33) = (31) + \left[\frac{(15) - (10)}{(15) - (9)}\right]\left[(37) - (31)\right]$$

$$= 25.95 + \frac{2.15 - 1.02}{2.15 - 0.57}(26.16 - 25.95) = 26.01\% \ Cl$$

$$(35) = (31) + \left[\frac{(15) - (14)}{(15) - (9)}\right]\left[(37) - (31)\right]$$

$$= 25.95 + \frac{2.15 - 2.08}{2.15 - 0.57}(26.16 - 25.95) = 26.15\% \ Cl$$

(32), (34), (36), and (38) are the distribution coefficients (K) corresponding to the total chloride concentration in the aqueous phase (See Figure 1).

$$(39) = (32) \times (17) = 0.264 \times 9.64 = 2.54\% \ CoCl_2$$

$$(40) = (34)\left[(17) + \left(\frac{(10 - (9)}{(15) - (9)}\right)\left((16) - (17)\right)\right] =$$

$$= (0.268)\left[9.64 + \frac{1.02 - 0.57}{2.15 - 0.57}(11.39 - 9.64)\right] = 2.72\% \ CoCl_2$$

$$(41) = (36)\left[(17) + \left(\frac{(14) - (9)}{(15) - (9)}\right)\left((16) - (17)\right)\right]$$

$$= 0.274\left[9.64 + \frac{2.08 - 0.57}{2.15 - 0.57}(11.39 - 9.64)\right] = 3.10\% \ CoCl_2$$

$$(42) = (38) \times (16) = 0.274 \times 11.39 = 3.12\% \ CoCl_2$$

For the calculation of (43)-(46), the specific gravity of the alcohol phase which would be in equilibrium with the bulk of the aqueous phase was assumed to be the observed alcohol phase specific gravity at that point in the column.

$$(43) = \frac{62.4 \text{ x } (5) \text{ x } (39)}{100} = \frac{62.4 \text{ x } 0.889 \text{ x } 2.54}{100}$$

$$= 1.41 \ \#CoCl_2/\text{cu. ft.}$$

$$(44) = \frac{62.4 \left[(5) + \left(\frac{(15) - (10)}{(15) - (9)}\right) \left((6) - (5)\right)\right] (40)}{100}$$

$$= \frac{62.4 \left[0.889 + \frac{2.15 - 1.02}{2.15 - 0.57} (0.895 - 0.889)\right] 2.72}{100}$$

$$= 1.51 \ \#CoCl_2/\text{cu.ft.}$$

$$(45) = \frac{62.4 \left[(5) + \left(\frac{(15) - (14)}{(15) - (9)}\right) \left((6) - (5)\right)\right] (41)}{100}$$

$$= \frac{62.4 \left[0.889 + \frac{2.15 - 2.08}{2.15 - 0.57} (0.895 - 0.889)\right] 3.10}{100}$$

$$= 1.73 \ \#CoCl_2/\text{cu.ft.}$$

$$(46) = \frac{62.4 \text{ x } (6) \text{ x } (42)}{100} = \frac{62.4 \text{ x } 0.895 \text{ x } 3.12}{100}$$

$$= 1.74 \ \#CoCl_2/\text{cu. ft.}$$

$$(47) = (43) - (18) = 1.41 - 0.31 = 1.10 \ \#CoCl_2/\text{cu. ft.}$$

$$(48) = (44) - (19) = 1.51 - 0.57 = 0.94 \ \#CoCl_2/\text{cu. ft.}$$

$$(49) = (45) - (20) = 1.73 - 1.16 = 0.57 \ \#CoCl_2/\text{cu. ft.}$$

$$(50) = (46) - (21) = 1.74 - 1.20 = 0.54 \ \#CoCl_2/\text{cu. ft.}$$

$$(51) = \frac{(47) - (50)}{\ln \frac{(47)}{(50)}} = \frac{1.10 - 0.54}{\ln \frac{1.10}{0.94}} = 0.79 \ \#CoCl_2/\text{cu. ft.}$$

$$(52) = \frac{(47) - (48)}{\ln \frac{(47)}{(48)}} = \frac{1.10 - 0.94}{\ln \frac{1.10}{0.94}} = 1.02 \ \#CoCl_2/\text{cu. ft.}$$

$$(53) = \frac{(48) - (49)}{\ln \frac{(48)}{(49)}} = \frac{0.94 - 0.57}{\ln \frac{0.94}{0.57}} = 0.74 \ \#CoCl_2/\text{cu. ft.}$$

$$(54) = \frac{(48) - (50)}{\ln \frac{(48)}{(50)}} = \frac{0.94 - 0.54}{\ln \frac{0.94}{0.54}} = 0.72 \ \#CoCl_2/\text{cu. ft.}$$

The effective volume of the column is 0.1333 cu. ft..

Column (55) is the K_Aa calculated from the average quantity of $CoCl_2$ transferred.

$$(55) = \frac{(29)}{(51) \times 0.1333} = \frac{2.73}{0.79 \times 0.1333} = \frac{26.0 \ \#/\text{hr.}}{(\text{cu. ft.})(\#/\text{cu. ft.})}$$

Column (56) is the K_Aa calculated from the quantity of $CoCl_2$ transferred by the alcohol phase.

$$(56) = \frac{(25)}{(51) \times 0.1333} = \frac{2.80}{0.79 \times 0.1333} = \frac{26.8 \ \#/\text{hr.}}{(\text{cu. ft.})(\#/\text{cu. ft.})}$$

The effective volume of the section of the column from the bottom to point 1 is 0.01613 cu. ft.

$$(57) = \frac{(26)}{(52) \times 0.01613} = \frac{0.80}{1.02 \times 0.01613} = \frac{48.7 \ \#/\text{hr.}}{(\text{cu. ft.})(\#/\text{cu. ft.})}$$

The effective volume of the section of the column from point 1 to point 8 is 0.1030 cu. ft..

$$(58) = \frac{(27)}{(53) \times 0.1030} = \frac{1.90}{0.74 \times 0.1030} = \frac{25.0 \ \#/\text{hr.}}{(\text{cu. ft.})(\#/\text{cu. ft.})}$$

The effective volume of the section of the column from point 1 to the top is 0.1172 cu. ft.

$$(59) = \frac{(28)}{(54) \times 0.1172} = \frac{2.02}{0.72 \times 0.1172} = \frac{23.9 \ \#/\text{hr.}}{(\text{cu. ft.})(\#/\text{cu. ft.})}$$

Column (60) is the $(HTU)_{OA}$ calculated from the average quantity of $CoCl_2$ transferred.

$$(60) = \frac{(3)}{(55)} = \frac{145}{26.0} = 5.57 \text{ feet}$$

Column (61) is the $HTU)_{OA}$ calculated from the quantity of $CoCl_2$ transferred by the alcohol phase.

$$(61) = \frac{(3)}{(56)} = \frac{145}{26.8} = 5.4 \text{ feet}$$

$$(62) = \frac{(3)}{(57)} = \frac{145}{48.7} = 3.0 \text{ feet}$$

$$(63) = \frac{(3)}{(58)} = \frac{145}{25.0} = 5.8 \text{ feet}$$

$$(64) = \frac{(3)}{(59)} = \frac{145}{23.9} = 6.1 \text{ feet}$$

To calculate the end effect in terms of the number of feet of straight column to which it is equivalent, the value of K_Aa which was calculated for the section of the column from point 1 to the top was assumed to apply to the entire column except the end effect at the coalescence point. This calculation was done by trial and error by first assuming a quantity of material transferred for the entire column except the bottom end.

Assume 2.43 $\#CoCl_2$/hr. transferred in the straight section of the column.

$$\text{log mean } \Delta C = \frac{2.43}{(59) \times 0.1333} = \frac{2.43}{23.9 \times 0.1333} = 0.763 \ \#CoCl_2/\text{cu. ft.}$$

If 2.43 $\#CoCl_2$/hr. are transferred in the straight section, the concentration difference in the alcohol phase at the bottom end of the straight section must be:

$$(47) - \left[\frac{(25) - 2.43}{(25)}\right]\left[(47) - (50)\right] = 1.10 - \frac{2.82 - 2.43}{2.82} \ (1.10 - 0.54)$$

$$= 1.03 \ \#CoCl_2/\text{cu. ft.}$$

$$\text{log mean } \Delta C = \frac{1.03 - (50)}{\ln \frac{1.03}{(50)}} = \frac{1.03 - 0.54}{\ln \frac{1.03}{0.54}} = 0.762 \ \#CoCl_2/\text{cu. ft.}$$

which checks the value obtained by assuming a quantity of material transferred in the straight section. If it did not check another trial would be required.

At the coalescence point at the bottom of the column:

$$\text{log mean } \Delta C = \frac{(47) - 1.03}{\ln \frac{(47)}{1.03}} = \frac{1.10 - 1.03}{\ln \frac{1.10}{1.03}} = 1.07 \ \#CoCl_2/\text{cu. ft.}$$

From the equation:

$$K_Aa = \frac{N}{V(\Delta C)_{lm}}$$

$$V = \frac{N}{K_Aa(\Delta C)_{lm}}$$

$$V = \frac{(25) - 2.43}{(59) \times 1.07} \quad \frac{2.82 - 2.43}{23.9 \times 1.07} = 0.0154 \text{ cu. ft.}$$

The cross-sectional area of the column is 0.0218 sq. ft.

$$(65) = \frac{0.0154}{0.0218} = 0.7 \text{ ft.}$$

Another method of calculating the end effect is by means of NTU's.

$$(NTU)_{OA} = \frac{H}{(HTU)_{OA}}$$

The height of the column is 6.11 feet.

For the entire column:

$$(NTU)_{OA} = \frac{6.11}{(61)} = \frac{6.11}{5.4} = 1.12$$

For the straight section of column:

$$(NTU)_{OA} = \frac{6.11}{(64)} = \frac{6.11}{6.1} = 1.00$$

End effect = 1.12 - 1.00 = 0.12 $(NTU)_{OA}$

End effect = 0.12 x 6.1 = 0.8 feet

$$(66) = \frac{(9)}{(32)} = \frac{0.57}{0.264} = 2.15\% \ CoCl_2$$

$$(67) = \frac{(15)}{(38)} = \frac{2.15}{0.274} = 7.85\% \ CoCl_2$$

See Figure 19 for the specific gravities used in the calculation of (68) and (69).

$$(68) = \frac{62.4 \times \text{sp. gr.} \times (66)}{100} = \frac{62.4 \times 1.143 \times 2.15}{100}$$

$$= 1.57 \ \#CoCl_2/\text{cu. ft.}$$

$$(69) = \frac{62.4 \text{ x sp. gr. x } (67)}{100} = \frac{62.4 \text{ x } 1.187 \text{ x } 7.85}{100}$$

$$= 5.88 \ \#CoCl_2/\text{cu. ft.}$$

$$(70) = (23) - (68) = 7.19 - 1.57 = 5.62 \ \#CoCl_2/\text{cu. ft.}$$

$$(71) = (22) - (69) = 8.61 - 5.88 = 2.73 \ \#CoCl_2/\text{cu. ft.}$$

$$(72) = \frac{(70) - (71)}{\ln \frac{(70)}{(71)}} = \frac{5.62 - 2.73}{\ln \frac{5.62}{2.73}} = 4.00 \ \#CoCl_2/\text{cu. ft.}$$

$$(73) = \frac{(29)}{(72) \text{ x } 0.1333} = \frac{2.73}{4.00 \text{ x } 0.1333} = \frac{5.12 \ \#/\text{hr.}}{(\text{cu. ft.})(\#/\text{cu. ft.})}$$

$$(74) = \frac{(4)}{(72)} \quad \frac{82}{5.12} = 15.1 \text{ feet}$$

NOMENCLATURE

a	interfacial area per unit volume, sq. ft./cu. ft.
dA	differential area, sq. ft.
C	cobaltous chloride concentration, #/cu. ft.
ΔC	$(C - C^*)$ at any point in the column, #/cu. ft.
H	height of the column, ft.
HTU	height of a transfer unit, ft.
K	distribution coefficient, (weight percent salt in the alcohol phase at equilibrium)/(weight percent salt in the aqueous phase at equilibrium)
K_A	extraction capacity coefficient, based on alcohol phase, #/(hr.)(sq. ft. of interfacial area)(ΔC)
Ka	extraction capacity coefficient, #/(hr)(cu. ft. of column)(ΔC)
L	liquid flow rate, ft./hr.
N	rate of cobaltous chloride transfer, #/hr.
NTU	number of transfer units
S	cross-sectional area of the column, sq. ft.
V	volume of the column, cu. ft.

Superscripts:

$*$	equilibrium value

Subscripts:

A	alcohol phase
B	bottom of the column
lm	log mean
OA	overall, based on the alcohol phase

OW	overall, based on the aqueous phase
T	top of the column
W	aqueous phase

BIBLIOGRAPHY

1. Blanding, F. H. and Elgin, J. C., Trans. Am. Inst. Chem. Engrs., 38, 305 (1942).

2. Bray, J. L., "Non-Ferrous Production Metallurgy", p. 79, New York, John Wiley and Sons, Inc., (1941).

3. Garwin, L. and Hixson, A. N., Ind. Eng. Chem., 41, 2298 (1949).

4. Garwin, L. and Hixson, A. N., Ind. Eng. Chem., 41, 2303 (1949).

5. Geankoplis, C. J. and Hixson, A. N., Ind. Eng. Chem., 42, 1141 (1950).

6. Hardy, J. V. E., Thesis for Degree of Chemical Engineer, Princeton University, (June 1939).

7. Hill, C. T. (to Pyrites Co., Ltd.), U. S. Patent 2,232,527 (Feb. 18, 1941).

8. Johnson, H. F., Jr., and Bliss, H., Trans. Am. Inst. Chem. Engrs., 42, 331 (1946).

9. Kylander, R. L., M. S. Thesis, Oklahoma A. & M. College, (1949).

10. Licht, W., Jr. and Conway, J. B., Ind. Eng. Chem., 42, 1151 (1950).

11. Mellor, J. W., "Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. XIV, p. 443, London, Longmans, Green, and Co., (1935).

12. Nandi, S. K. and Viswanathan, T. R., Current Science, 15, (India), 162 (June, 1946).

13. Rhodes, R. H. and Hosking, H. J., Ind. Eng. Chem., Anal. Ed., 2, 164 (1930).

14. Schaal, R. B. (to Ferro Enamel Co.), U. S. Patent 2,488,561 (Nov. 23, 1949).

15. Udy, N. J. and Ralston, O. E., U. S. Patent 1,365,358 (Jan. 11, 1921).

THESIS TITLE: Extraction of Cobaltous
Chloride in a Two Inch
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