

THE SEPARATION OF NICKELOUS AND COBALTOUS
CHLORIDES BY LIQUID-LIQUID EXTRACTION IN A SPRAY COLUMN

THE SEPARATION OF NICKELOUS AND COBALTOUS
CHLORIDES BY LIQUID-LIQUID EXTRACTION IN A SPRAY COLUMN

By

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ABSTRACT

Limiting liquid throughputs for a spray column $1\frac{1}{8}$ inches inside diameter and $68\text{-}\frac{3}{8}$ inches in length, with a distributor consisting of thirteen 0.01 inch nozzles, were determined using refined grade capryl alcohol and distilled water.

Extraction of CoCl_2 from $\text{CoCl}_2 - \text{HCl} - \text{water}$ and from $\text{CoCl}_2 - \text{NiCl}_2 - \text{HCl} - \text{water}$ solutions was carried out in this spray column, with the distributor consisting of ten 0.1 inch nozzles, using capryl alcohol as the solvent. $(\text{HTU})_{\text{OA}}$ values were found to be fairly constant at about 5 feet over the range of flow rates of the liquid phases investigated. $(\text{HTU})_{\text{OW}}$ values decrease rapidly with increasing alcohol rate and decrease slowly with decreasing water rate.

There is evidence that the degree of separation of the two salts is greater when carrying out the extraction continuously than is indicated by the ratio of the equilibrium distribution coefficients.

INTRODUCTION

Because of the similar properties of nickel and cobalt, their separation has presented considerable difficulty to the metallurgy industry. At present, the most widely used processes involve precipitation of the cobalt in the form of the hydrated cobaltic oxide ($\text{Co}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) 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, 12, 13}.

In 1947, Garwin⁴ carried out a systematic investigation of the possibility of the separation of the chlorides of nickel and cobalt by selective extraction with an organic solvent. On the basis of preliminary studies, capryl alcohol (2-octanol) was selected because of the wide difference in solubilities of the anhydrous salts in this solvent, the comparatively high solubility of the more soluble salt (CoCl_2) in the alcohol, the low solubility of the alcohol in water, the stability of the alcohol in contact with air and the aqueous solutions encountered, and the availability and moderate cost of the solvent.

Practically no CoCl_2 was extracted from the water solutions except at salt concentrations in the water phase near saturation. However, when certain electrolytes such as CaCl_2 and HCl were added, there was a marked improvement in the distribution coefficient of the cobalt. In all cases the extraction of the nickel was low. Separation factors of 40 to 90 were obtained when HCl was the added electrolyte, and 10 to 17 in the presence of CaCl_2 .

Distribution coefficients (K) for CoCl_2 and NiCl_2 in HCl solutions at 25°C , as a function of the total chloride concentration are shown in Figures 1, 2, and 3.

Geankoplis⁵ carried out the extraction of FeCl_3 from a 7.8 normal HCl solution in a spray column 1.45 inches in diameter and 2.57 feet long, using isopropyl ether as the solvent. The $(\text{HTU})_{\text{OW}}$ was found to vary from 0.45 to 2.5 feet, depending on the ether rate and inlet FeCl_3 concentration of the water phase. In all runs the water phase rate was constant. For the same ether rate, the $(\text{HTU})_{\text{OW}}$ decreased as the FeCl_3 concentration of the inlet water phase rate decreased. For a given inlet FeCl_3 concentration, the $(\text{HTU})_{\text{OW}}$ decreased with increasing ether rate. The curves of $(\text{HTU})_{\text{OW}}$ versus ether rate for different inlet FeCl_3 concentrations converged at the higher ether rates with the $(\text{HTU})_{\text{OW}}$ becoming constant at 0.45 feet.

STATEMENT OF THE PROBLEM

The quantitative distribution studies made by Garwin were under equilibrium conditions and no attempt was made to observe or predict extraction capacity coefficients which might be expected when carrying out the extraction countercurrently under steady state conditions in commercial-type equipment. The present work was undertaken in order that extraction capacity coefficients K_{Aa} and K_{Wa} and heights of a transfer unit $(HTU)_{OA}$ and $(HTU)_{OW}$ might be determined for the two systems: $CoCl_2 - HCl - water - capryl\ alcohol$ (Series II) and $NiCl_2 - CoCl_2 - HCl - water - capryl\ alcohol$ (Series III) when the extraction is carried out in continuous countercurrent fashion, and when the alcohol phase is dispersed.

Since, even under the most favorable conditions, the distribution coefficient for the $CoCl_2$ between the alcohol and water phases is less than 0.5, high ratios of alcohol to water rates must be employed to effect complete transfer of the $CoCl_2$ from the water phase to the alcohol. A spray column was chosen for this investigation because of the high liquid throughputs permissible¹ and because of the simplicity of construction. It was thought advisable to make a series of preliminary runs (Series I) in order to become familiar with the column operation and to determine the flooding characteristics of the column.

APPARATUS

A $1\frac{1}{4}$ inch inside diameter column 68- $\frac{3}{8}$ inches long, with end designs and disperser of the type suggested by Blanding and Elgin¹ and Johnson and Bliss⁹, respectively, was constructed of Plexiglas. For details, see Figures 4 and 5.

AUXILIARIES

Storage vessels for the aqueous feed, solvent, extract and raffinate were five-gallon Pyrex bottles.

Pressure for moving the aqueous feed and solvent was placed above the solutions by means of compressed nitrogen from a standard cylinder. Reduction of the pressure from cylinder pressure to 3 to 5 pounds per square inch was accomplished by means of a regulator commonly used in oxygen service. The pressure regulator was protected from hydrochloric acid vapor by the use of a section of standard 1 inch iron pipe filled with Ascarite and placed between the pressure regulator and the lines to the feed and solvent bottles.

Flow rates of the aqueous feed and solvent were indicated by the pressure drop across a capillary tube in the line. Inclined tube manometers were the pressure indicating devices. Control of the rates was accomplished by adjusting a screw clamp operating on a short length of rubber tubing, which gave a type of diaphragm valve.

A neoprene gasket between the bottom cover flange and the flange on the lower settling chamber of the column was found satisfactory.

The interface level inside the upper settling chamber was adjusted by the proper vertical positioning of a vented tee in the raffinate line.

The extract line, as well as the raffinate line, was vented to the atmosphere to prevent siphoning tendencies when the line was full of liquid.

All transfer lines were either 3/8-in. or 7/16-in. outside diameter Saran tubing, with fittings of Saran, glass and rubber.

A diagram of the extraction equipment and auxiliaries is given in Figure 6. Figure 7 is a photograph of the equipment in operation, as it appeared during the runs of Series II and Series III.

STRATHMORE PARCHMENT

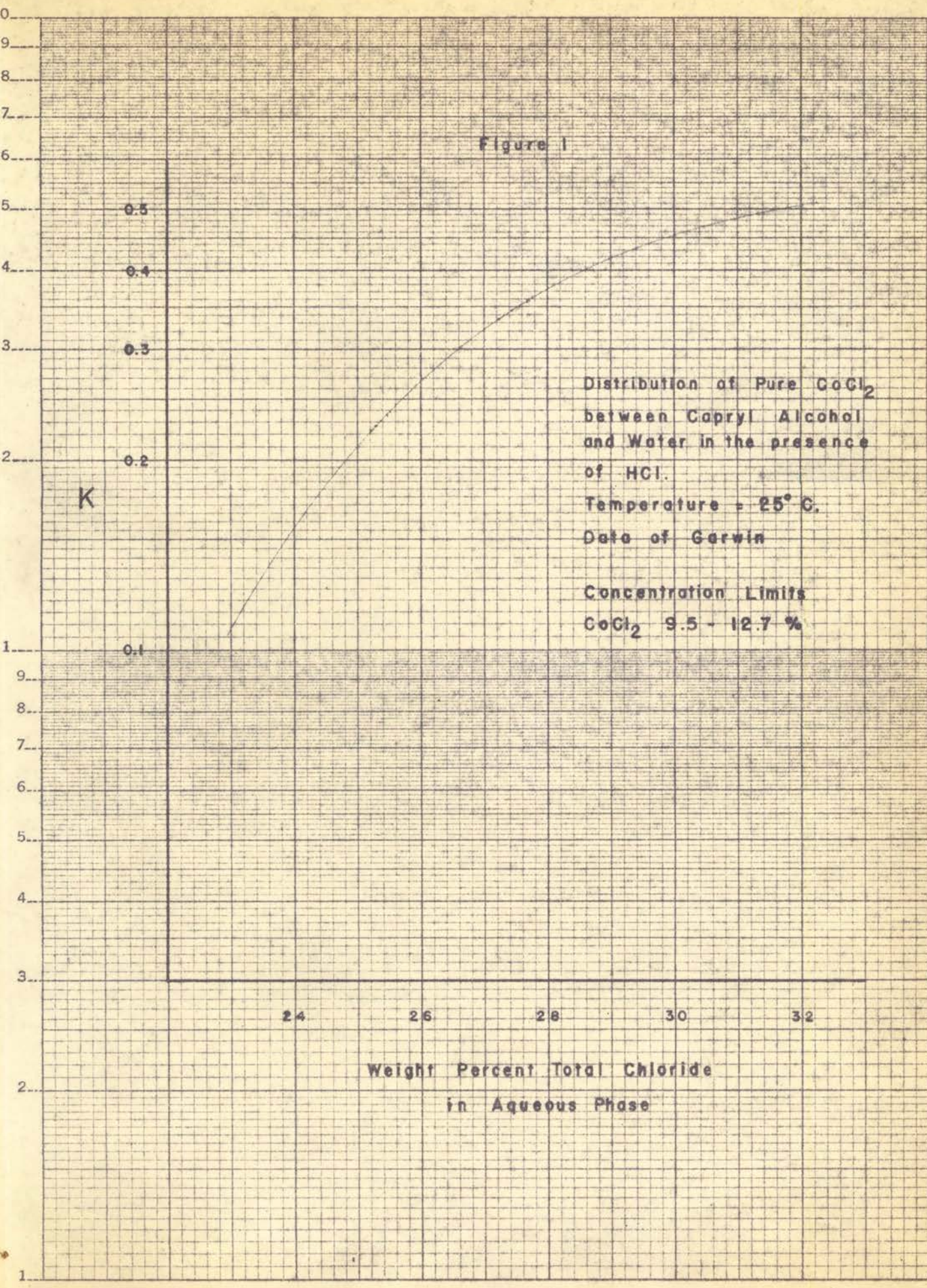
100% NAT. U.S.A.

Figure 1

Distribution of Pure CoCl_2
between Capryl Alcohol
and Water in the presence
of HCl.
Temperature = 25°C .
Date of Gerwin

Concentration Limits
 CoCl_2 9.5 - 12.7 %

K



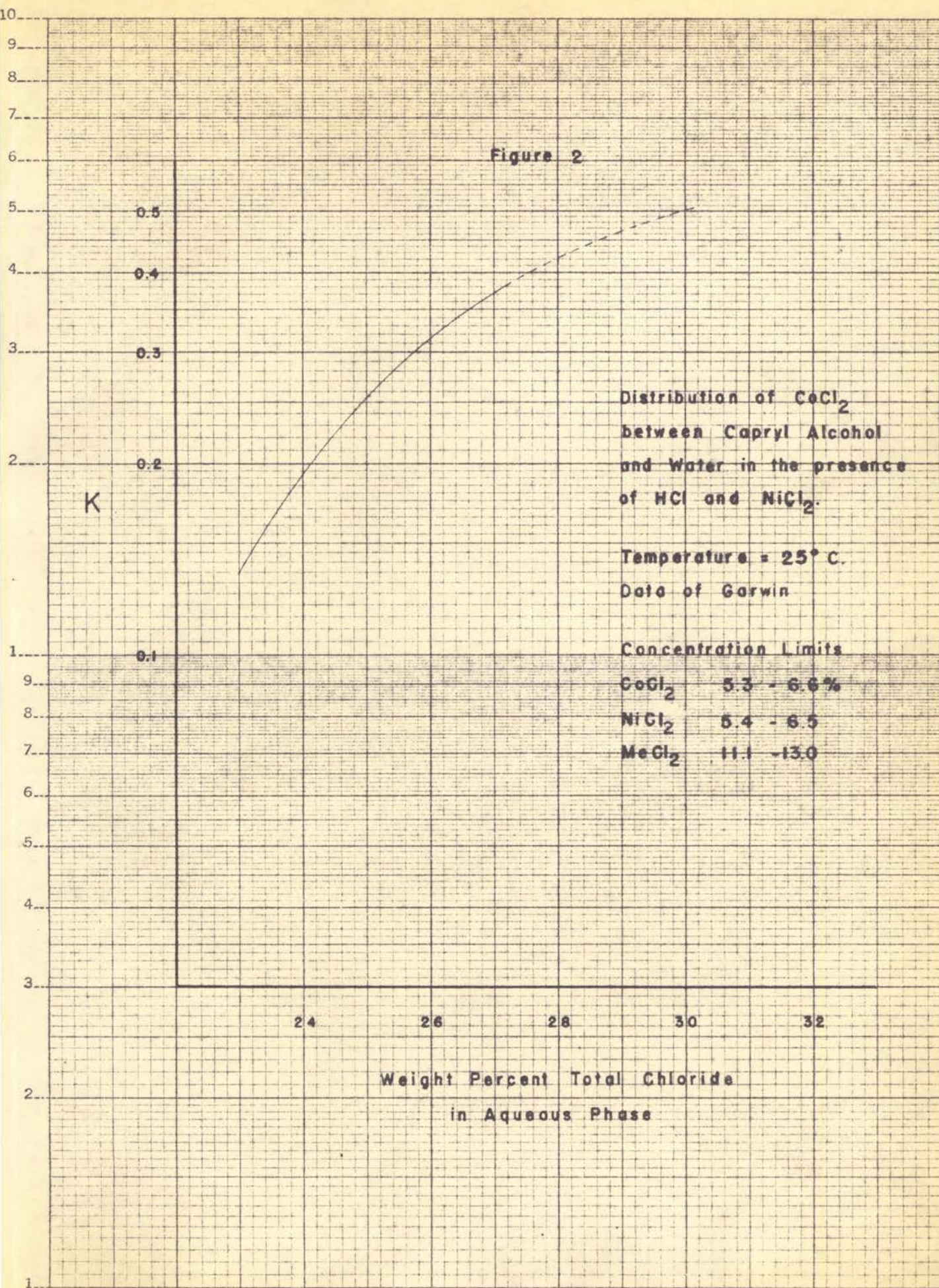


Figure 3

Distribution of NiCl_2 between
 Capryl Alcohol and Water in
 the presence of HCl and CoCl_2
 Temperature = 25°C .
 Date of Gerwin

Concentration	Limits
CoCl_2	5.3 - 6.6%
NiCl_2	5.4 - 6.5
MeCl_2	11.1 - 13.0

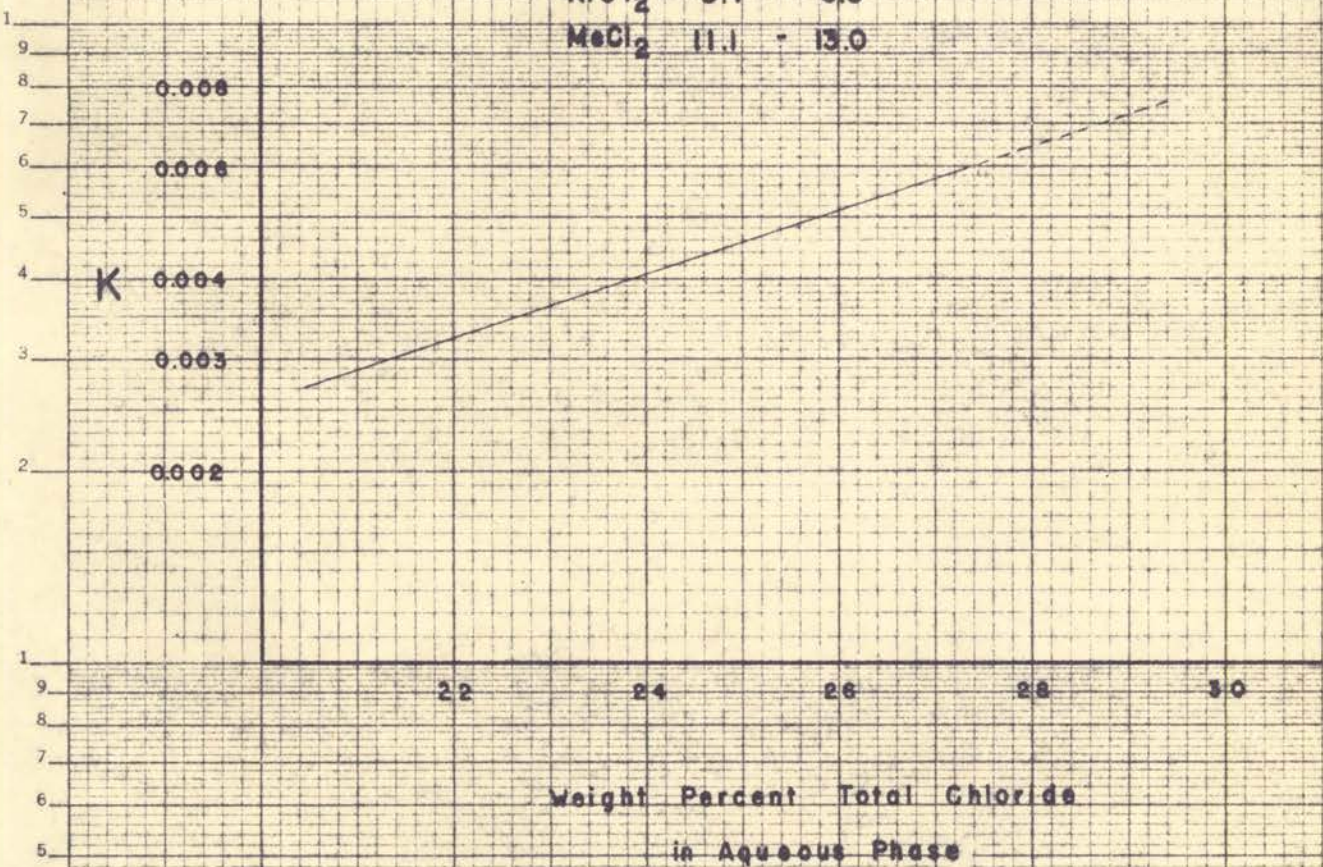


Figure 4
 Details of the Extraction
 Column Construction

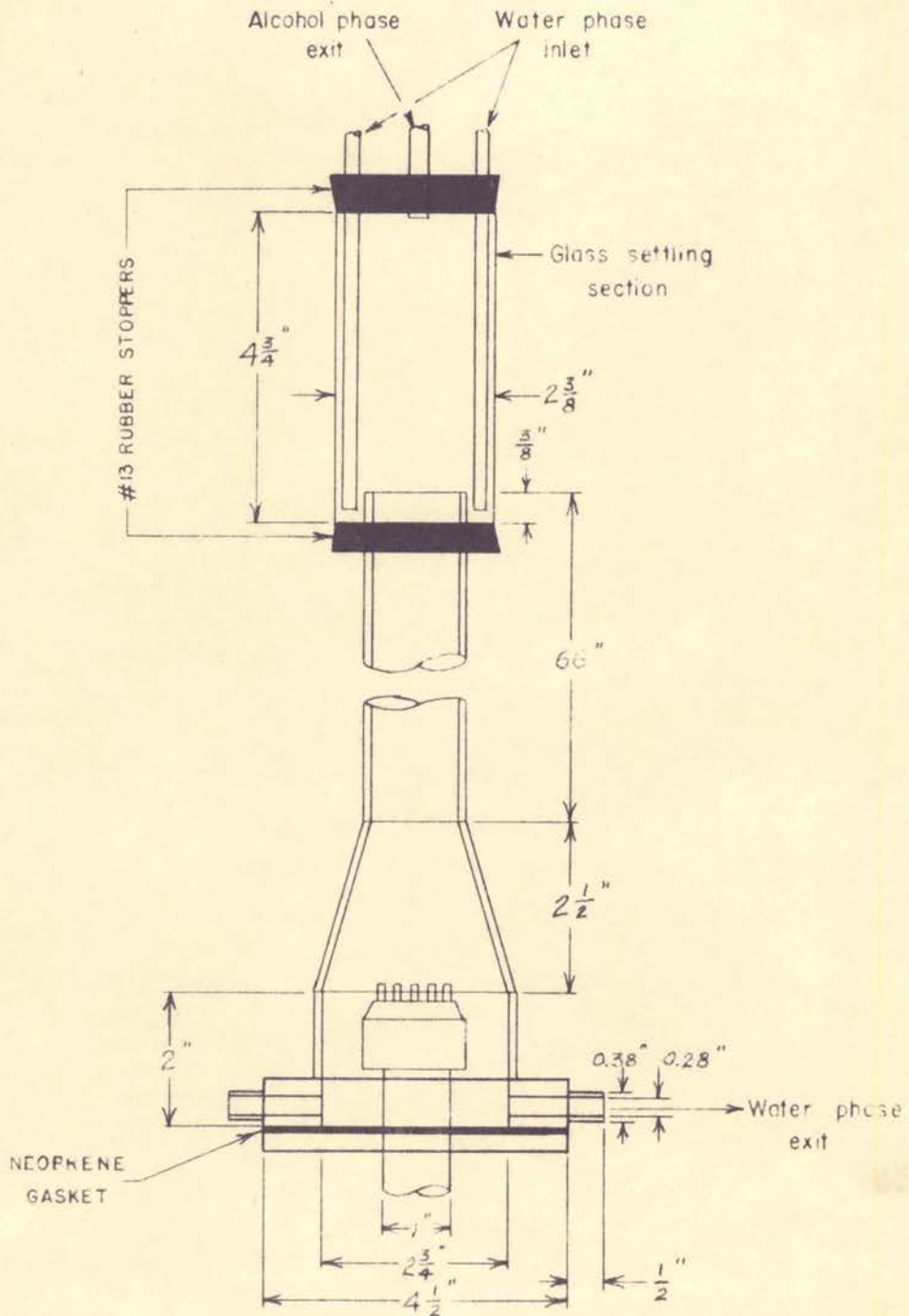


Figure 5
Details of the Disperser

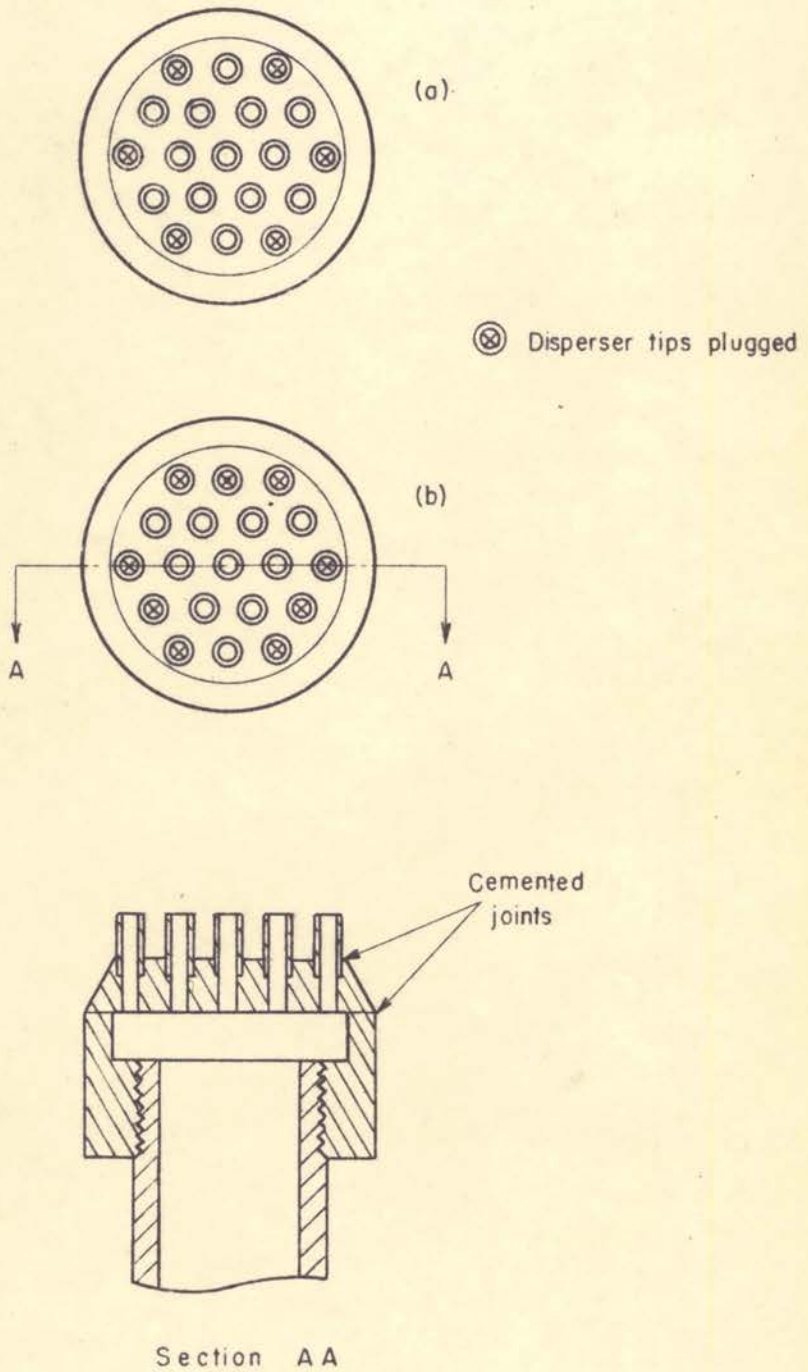


Figure 6
Diagram of Extraction Column
and Auxiliaries

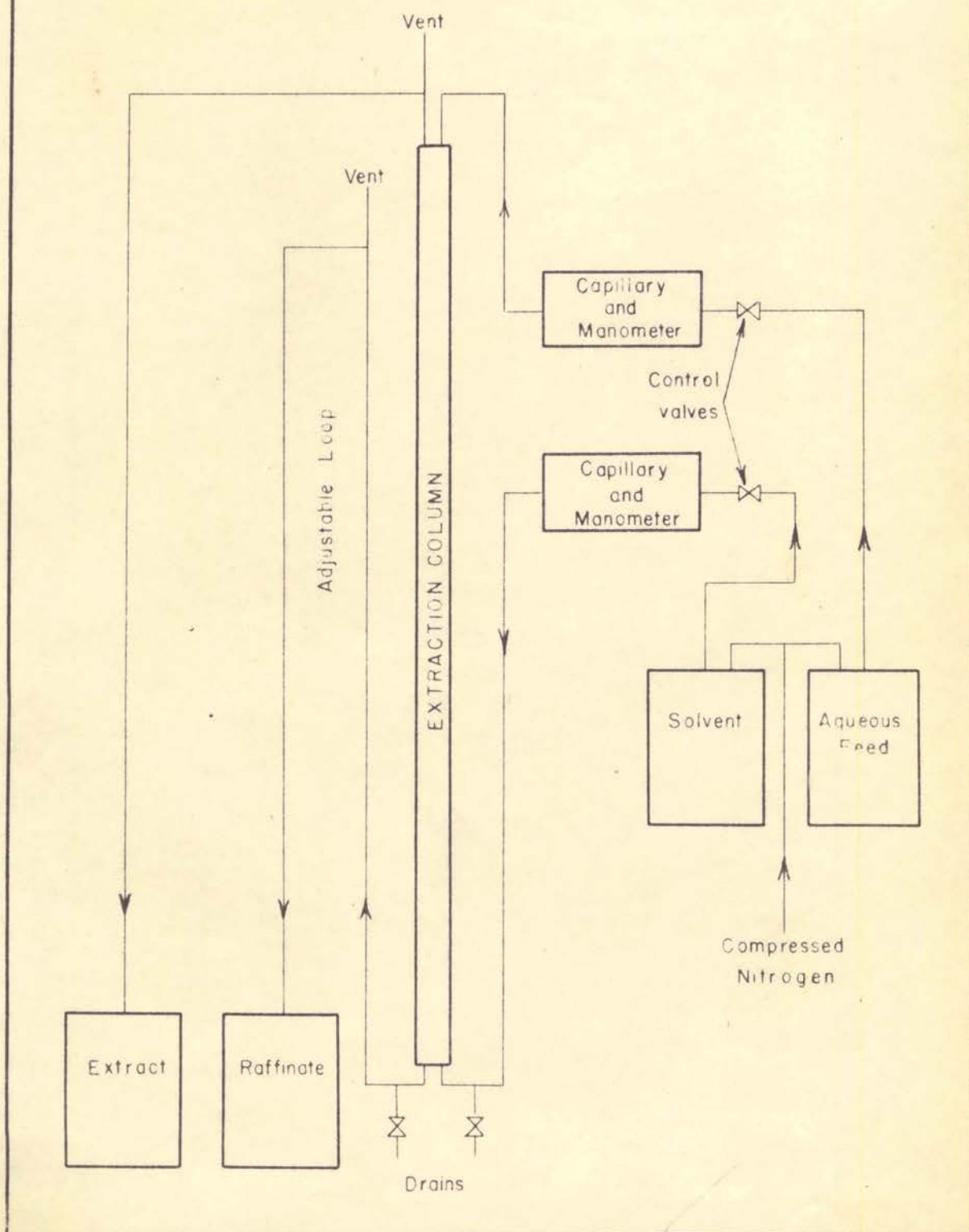


Figure 7

Photograph of Equipment in Operation



MATERIALS USED

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

Chemical grade capryl alcohol (2-octanol) for Series II and Series III extraction runs was also obtained from the Hardesty Company. It contained no more than 2.0% methyl hexyl ketone as the major impurity.

Eimer and Amend concentrated hydrochloric acid of tested purity (A.C.S. specifications) was used to bring the HCl concentration of the alcohol and aqueous phases to the proper value. Baker's Analyzed $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ were used in making up the aqueous feed solutions.

All reagents used in the analytical work met A.C.S. specifications for purity. Distilled water was used.

STRATHMORE PARCHMENT

100% RAG U.S.A.

PROCEDURE FOR SERIES I

Flooding Velocities

Calibration curves were made for the alcohol and water metering devices by observing the time required for 100 ml. of the fluid to be collected in a graduated cylinder for a given pressure drop across the capillary in the line. Volumetric flow rates expressed as cubic feet per hour were calculated and plotted versus manometer reading (see Figure 8).

The alcohol dispersing nozzle was as shown in Figure 5a.

Starting with the column and transfer lines empty, the water and alcohol storage vessels were first filled and pressure then applied above the liquids. The transfer lines were filled with liquid by opening the control valves momentarily. The alcohol rate was maintained at a very low value, just great enough to prevent the more dense water from displacing the alcohol in the disperser assembly while the column was being filled with water. When the column was full, the water rate was decreased to the proper rate for the run.

The alcohol rate was increased to a value well below flooding and time was allowed for the proper positioning of the interface to a level inside the upper settling chamber.

When operation became satisfactory, the alcohol rate was increased a small amount and the interface adjusting loop lowered slightly to compensate for the decreased average density of the fluid within the column. Eventually, as the alcohol rate was increased, a limit was reached where operation was no longer satisfactory. This limiting pair of flow rates, considered as the flood point for the column, was characterized by the extreme non-uniformity in size of the alcohol drops, and is described in more detail under the discussion of the results of Series I.

Runs at different water rates were made in a similar manner. The resulting limiting alcohol and water rate combinations are indicated graphically in Figure 9.

Figure 8
Calibration of Capillary - Manometer
Combinations

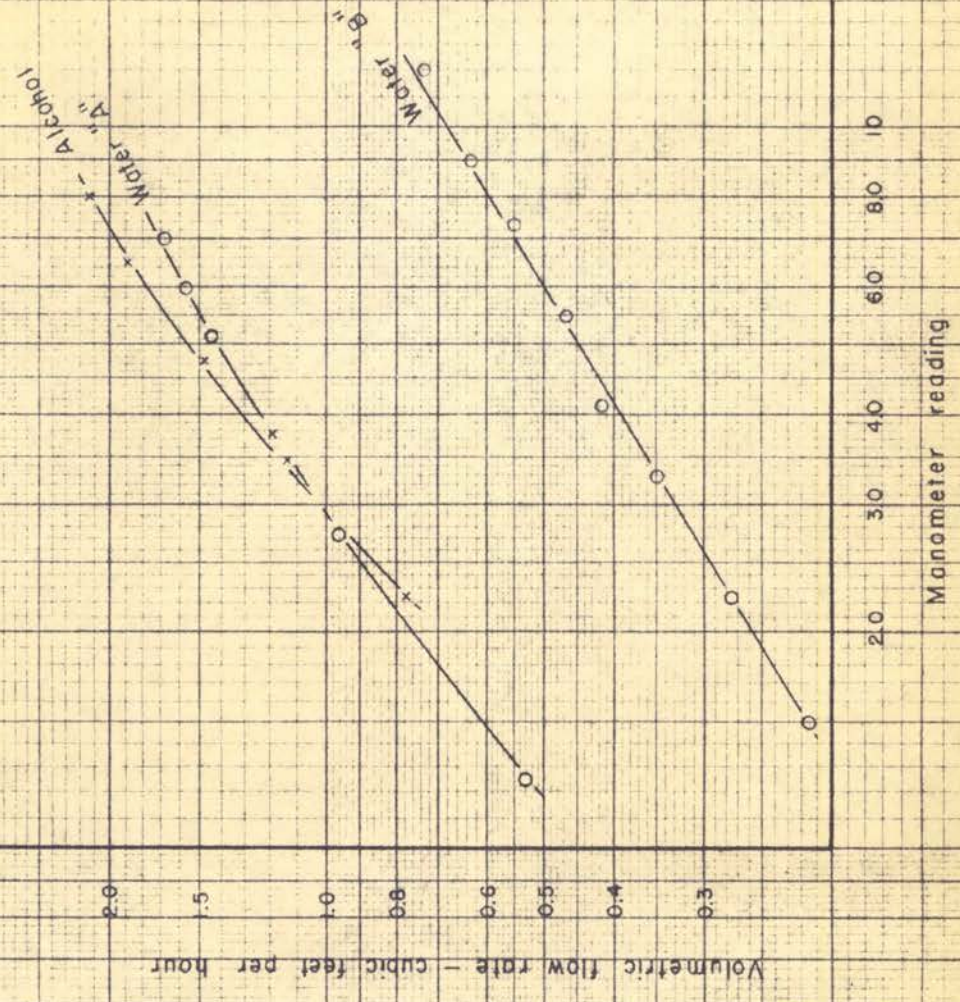
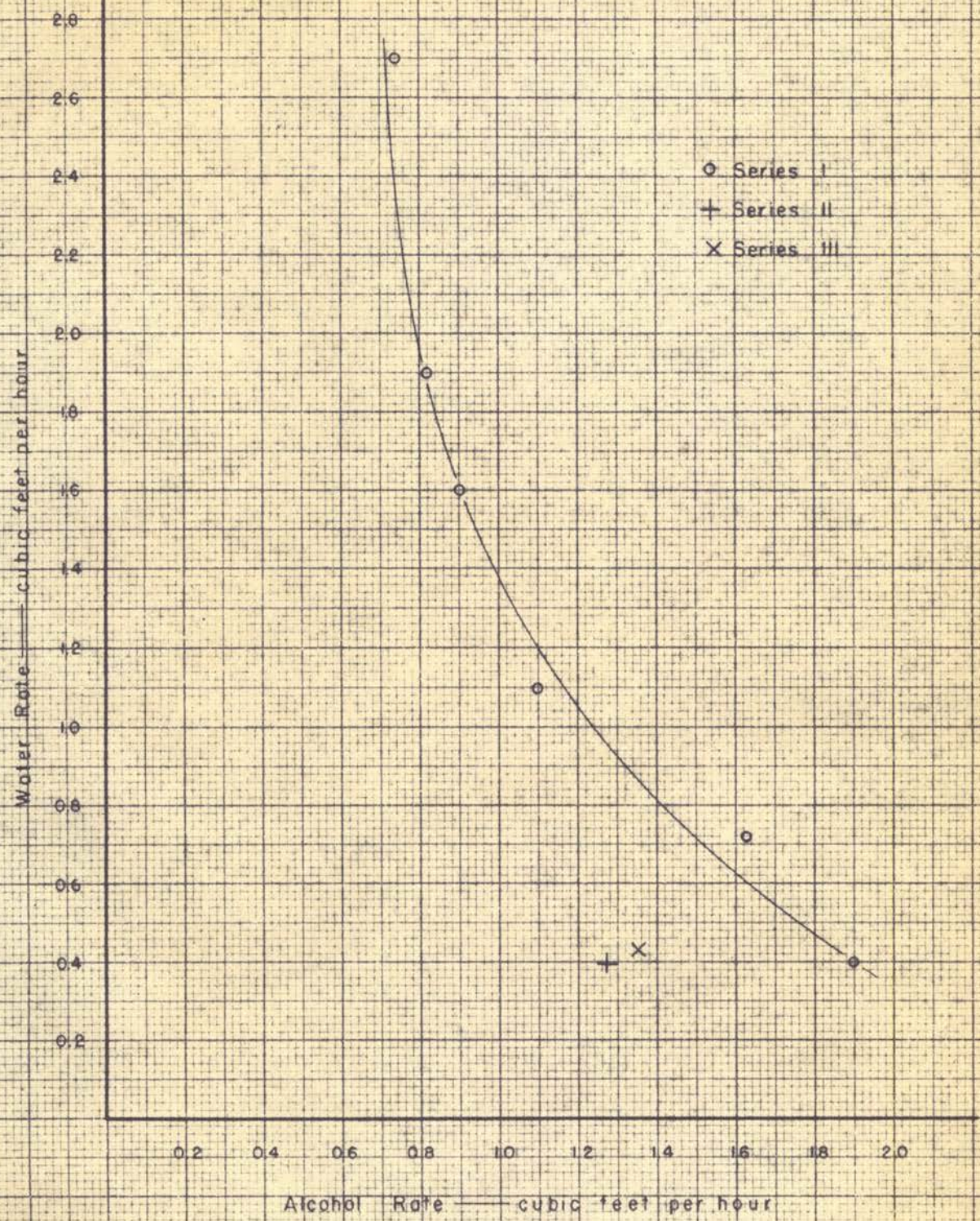


Figure 9
Flooding Velocities
of the Spray Column



MADE IN U.S.A.

PROCEDURE FOR SERIES II

CoCl₂ Extraction

Since it was desired that essentially no HCl be transferred as the solvent and feed flowed countercurrent through the column, the original solutions were prepared so that the aqueous and alcohol solutions contained HCl concentrations very nearly in equilibrium. The alcohol was brought to the proper HCl concentration by shaking with concentrated aqueous HCl and allowing the phases to separate. The acid phase was transferred to another container and was used to make up the aqueous feed. To this acid was added 10 pounds of CoCl₂·6H₂O and sufficient HCl to bring the total volume to about 5 gallons. The total chloride concentration was about 30% and the total anhydrous salt concentration about 8%.

Aqueous feed and solvent were charged to the feed vessels and the tower and lines were filled as in Series I. Flow rates of both phases were adjusted to the desired values, measurements being made by observing the time required for a given quantity (usually 100 ml.) of exit fluid to be collected. The inclined tube manometers were used only as indicating devices for maintaining the flow rates constant. The manometer and capillary tube combinations were not calibrated for measurement of flow rates because of possible inaccuracies arising from slight variations in solute concentrations and temperature for the different runs.

Steady-state operation was assumed to be reached after about three complete changes of the continuous phase. Samples of the extract and raffinate were collected and stoppered. The flows of aqueous feed and solvent were stopped and the column and lines emptied. Samples of the aqueous feed and solvent were taken from the storage bottles either just before the run was begun or immediately after the run was completed.

It was necessary to recover both the CoCl_2 and the capryl alcohol because of the limited supply of each available and their comparative high cost. This was done by repeated washing of the extract with about 25% aqueous hydrochloric acid solution. Although removal of the CoCl_2 was not complete with this operation, the salt concentration was lowered to 0.5% or less, depending on the thoroughness of washing. Separation of this aqueous extract was effected by simple distillation of the HCl and water to the point of CoCl_2 dryness. Since HCl and water form an azeotrope containing approximately 20% HCl, HCl vapor came off first in the distillation. This HCl was absorbed in previously distilled azeotrope to bring its HCl concentration up to 25%.

The solid CoCl_2 recovered from the distillation was dissolved in the raffinate from the run just completed so that the resulting solution was suitable for use as the next aqueous feed without further treatment.

PROCEDURE FOR SERIES III

Separation of NiCl_2 and CoCl_2

Except for the preparation of the original aqueous feed, the procedure for this series was exactly the same as for Series II.

The aqueous feed from Series II was diluted with hydrochloric acid and water so that the total salt concentration after addition of NiCl_2 would be about 10%. Approximately 10 pounds of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ was dehydrated at 130 to 140° C. and added to the above CoCl_2 - HCl - water solution to obtain a feed solution containing about 4% NiCl_2 , 6% CoCl_2 , and a total chloride concentration of about 28%.

ANALYTICAL METHODS

A. Aqueous Phase.

1. Total Chloride. Since the distribution coefficients for the salts are known as a function of the total chloride concentration, it was important to know the total chloride content as well as the metal chlorides concentration of the aqueous feed and raffinate. The Volhard method¹⁰ was chosen for the total chloride determination because it is much faster than gravimetric methods, because cobalt and nickel ions do not interfere with the detection of the end point, and because the titrations are carried out in acid solution, whereas other volumetric methods for chloride (Mohr, Fajans') must be carried out in essentially neutral solution. Samples from runs 1 through 19 were analyzed for total chloride as follows: a 1 ml. portion of the sample was diluted to 100 ml., a 25 ml. aliquot was pipetted into a 125 ml. Erlenmeyer flask and 3 to 5 ml. of concentrated nitric acid was added. Sufficient standard AgNO_3 was added from a burette to completely precipitate the chloride, and provide a small excess. One ml. of saturated ferric ammonium sulfate and 1 to 3 ml. of nitrobenzene were added and the resulting mixture shaken well to completely coagulate the AgCl precipitate. The excess AgNO_3 was determined by addition of standard KCNS until the brownish tinge, marking the formation of an iron complex with the thiocyanate radical, indicated the end point.

In analyzing samples from runs 20 through 23, a 5 ml. portion of the sample was diluted to 100 ml. and a 5 ml. aliquot taken for the chloride determination. The use of larger samples and smaller aliquot portions gave slightly more accurate results.

2. Total salts. Samples of Series II, containing only CoCl_2 as the dissolved salt, were analyzed for CoCl_2 by placing an accurately

weighed 2 to 3 gram sample in a weighing bottle, evaporating to dryness at about 100° C., dehydrating the solids at 130 to 140° C. overnight, or an equivalent length of time, and weighing the residue.

Considerable difficulty was encountered in the determination of total salts when NiCl_2 was present. When the dehydration procedure described above was used for total salts determination in Series III, inconsistent results were obtained. Results varied as much as 3% for determinations made under identical conditions. The residues, instead of being flaky, as in the case of CoCl_2 residues, were hard and sometimes covered with a shiny crust, indicating that dehydration of the salts might be incomplete. The use of smaller samples, weighing about 0.3 gram, seemed to yield results of no greater reliability.

As a last attempt to analyze for total salts directly, 0.1 to 0.2 gram of asbestos fibers, which had been previously washed and dried by the manufacturer, were placed in the weighing bottle and dehydrated at 130 to 140° C. An accurately weighed sample 1 to 1.5 grams was added, dried for 2 hours at 95 to 100°C., dehydrated 10 to 12 hours at 130 to 140° C. and weighed. The results seemed to be slightly more reproducible, but still subject to errors of 1 to 2 percent, presumably due to the formation of basic nickel salts during dehydration. This was the method finally used, even though it was not entirely satisfactory. Multiple determinations were made in each case and average values used in the calculations.

3. Nickel. The method described by Garwin⁴ was found satisfactory for the determination of nickel in the samples of Series III. It was used as follows: A 5 ml. portion of the sample was diluted to a volume of 100 ml. A 10 ml. aliquot was pipetted into a 250 ml. beaker and diluted to a volume approximately six times the volume of dimethylglyoxime

reagent to be used. The solution was heated to nearly boiling, the dimethylglyoxime (0.5 ml. of a 1% solution of dimethylglyoxime in 95% alcohol for each mg. of total metals present) was added and concentrated NH_4OH was added dropwise with stirring until the red dimethylglyoxime precipitate formed. After standing for four to eight hours, the nickel precipitate was filtered onto a weighed sintered glass bottom crucible, washed well with hot water and dried in an oven at about 110°C . for one hour. The dried precipitate was weighed and the percentage nickel in the original sample calculated.

4. Cobalt. The CoCl_2 concentration of the samples taken from runs of Series III was calculated as the difference between the total salt concentration and the nickel chloride concentration.

5. Specific gravity. All specific gravities are reported at room temperature with respect to water at 4°C . A Westphal balance was used.

B. Alcohol phase. Both HCl and dissolved salts were washed from the alcohol phase with water. Since these solutes greatly favor the water phase at low chloride concentrations in the water phase, essentially all of the solutes were transferred to the water when the washing was carried out as follows: A 10 or 25 ml. alcohol phase sample was pipetted into a 250 ml. volumetric flask which already contained about 150 ml. of water. The mixture was shaken well and the phases allowed to separate. Further additions of water were made, with thorough mixing and settling, until the alcohol-water interface was at the 250 ml. mark. Most of the alcohol was decanted and the water phase, containing the solutes, was used for the analyses. In general, analyses of this water phase were made in the same

manner as the analyses of the aqueous samples previously described.

Modifications of these procedures appear below:

1. Total chloride. Although knowledge of the total chloride concentration in the alcohol phase was not required, it was determined so that in case the HCl concentration was desired, the information would be readily available. An aliquot of 25 or 10 ml. of the above aqueous extract was given the same treatment as the aqueous phase samples.

2. Total salts. A 20 ml. aliquot of the aqueous extract was dried and dehydrated in the same manner as the aqueous phase samples.

3. Nickel. A 150 ml. aliquot of the aqueous extract from above was treated similarly to the aqueous phase samples. However, when the concentrated NH_4OH was added, the nickel dimethylglyoxime precipitate did not form immediately. The presence of sufficient NH_4OH was indicated by the characteristic red color of the cobalt complex. After allowing to stand for at least 20 hours, the nickel precipitate was filtered, dried and weighed as before.

4. Cobalt. Cobalt chloride was determined as the difference between the total salts and the nickel chloride.

5. Specific gravity of the alcohol samples was determined by the same method as the aqueous phase samples.

Surface and Interfacial Tension Measurements

A du Nouy ring tensiometer was used to measure the surface and interfacial tension of a few selected solutions. Where samples taken during the runs were used, equal volumes of the alcohol and water phases were shaken in order to reach equilibrium distribution of the solutes. The mixture was allowed to separate into two phase and the measurement then made. The results are tabulated in Table III.

EQUATIONS FOR EXTRACTION CAPACITY COEFFICIENTS

AND HEIGHT OF A TRANSFER UNIT

At any point in an extraction column operating under steady-state conditions, the rate at which material is being transferred is represented by the following equations:

$$dN/\theta = K_A(C_A^* - C_A) dA \quad (1)$$

$$dN/\theta = K_W(C_W - C_W^*) dA \quad (2)$$

Inserting adV for dA , assuming the equilibrium line to be linear, and integrating equation (1), the following is obtained:

$$N/\theta = K_A a (\Delta C_A)_{lm} V \quad (3)$$

or

$$K a = \frac{N/\theta}{V(\Delta C_A)_{lm}} \quad (4)$$

N/θ is defined as

$$N/\theta = S(L_{A1}C_{A1} - L_{A2}C_{A2}) \quad (5)$$

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

$$N/\theta = SL_A(C_{A1} - C_{A2}) \quad (6)$$

The overall height of a transfer unit⁵ based on the alcohol phase rate is:

$$(\text{HTU})_{OA} = \frac{L_A}{K_A a} \quad (7)$$

Similar equations may be derived for the water phase in which the subscript W is substituted for subscript A in equations (3) through (7).

CORRELATION OF RESULTS

Series I flooding determinations were correlated by plotting the water phase rate versus the corresponding alcohol phase rate where flooding occurs. See Figure 9. Also included are the two flood points for the Series II and III runs. These represent the conditions for runs 4 and 23, made just at the flood point.

The calculated values of K_a and HTU for Series II and III are given in Tables I and II in the Appendix. These tables also contain the data and intermediate calculations from which these capacity coefficients were obtained. The results are correlated by plotting K_a and HTU values versus the alcohol phase rate, at constant water rate. See Figures 12, 13, 14, 15, 16, 17, 18 and 19.

DISCUSSION OF RESULTS - CONCLUSIONS

Series I. The study of the flooding characteristics of the column was made in order to get an approximation of the velocities which might be reached without exceeding the limiting values, and also to confirm the findings of Blanding and Elgin¹.

Blanding and Elgin found that at a certain pair of flow rates, a condition of high drop holdup would develop at the top of the column and proceed uncontrolled down the column until the whole column was filled with closely packed drops. Even though the column would operate satisfactorily under these conditions, they considered this to represent column flooding.

The original studies to produce flooding in this investigation were made with the column as shown in Figures 4 and 5a, except that there was no upper settling chamber. The water phase was introduced through a piece of glass tubing which extended about six inches below the exit of the alcohol phase. A side outlet located $1\frac{1}{2}$ inches below the top of the column was used to withdraw the alcohol phase.

It was found that as long as the interface (in this work, defined as the lowest point where coalescence of the dispersed phase occurred) remained above the inlet of the water phase, the column operated under normal (low) holdup of the dispersed phase. However, it was not practical to maintain the interface above the water inlet at the higher alcohol rates, since it was felt important to provide sufficient settling space to prevent water from being carried over the top with the alcohol. As soon as the interface was dropped to the level of the water inlet, a region of high holdup would form immediately and continue down the column until it stopped at some equilibrium position. The depth of the high holdup region

was then dependent entirely on the flow rates and on the position of the interface. Figures 10 and 11 show the appearance of the regions of low and high holdup, respectively.

Since this behavior was so different from the observations of Blanding and Elgin, the difficulty was believed to lie in the arrangement of the top of the column.

Modifications were made to the column to incorporate the new upper end design. This was the one used in all of the extraction runs of Series II and III, as well as the Series I flooding runs.

With this end design it was found that much higher alcohol rates, for a given water rate, could be reached before the column ceased to operate satisfactorily. Even so, flooding of the type described by Blanding and Elgin was never observed, provided the interface was maintained above the water inlet. Flooding for this column was taken as the condition where drops of alcohol would collect in the conical section at the point of attachment to the main length of the extraction column to such an extent as to provide interference with drop formation from the jets issuing from the disperser. This resulted in non-uniformly sized alcohol drops. Often these drops were as large as $\frac{1}{2}$ inch and would rise along the wall of the column or in the bulk of the liquid phase for some distance before being broken into smaller drops.

In all measurements of the flooding velocities, the interface was maintained at such a level that the lowest point where coalescence of the drops occurred was well above the top end of the column proper. Later, it was observed that by lowering the interface so that the lowest point of coalescing drops was even with the top of the plastic column, a region of

high holdup appeared in the column, and that the depth of this high hold-up region apparently could be adjusted over the entire length of the column by very slight alterations of the interface level adjusting loop.

Factors responsible for flooding characteristics different from the type observed by Blanding and Elgin may include slight differences in column design, as well as differences in the physical properties of the systems employed.



Figure 10

Appearance of the Column with High Holdup



Figure 11

Appearance of the Column with Low Holdup

Series II and III. The extraction capacity coefficient curves (Figures 12, 13, 14, 15) indicate that the K_A increases with increased dispersed phase rate until the flood point is reached. At the flood point the interfacial area is decreased because of the formation of large drops of the dispersed phase, and as a direct result, the K_A decreases. It was not possible to reach flooding at the 0.2 cu.ft./hr. water rate because of an insufficient supply of alcohol.

The good material balances for runs of Series II indicate that steady-state operation had been reached and that the methods of analysis are good (if it can be assumed that there are no compensating errors). Therefore, the K_A and HTU values should be reliable within the limits of experimental error in the determination of the total chloride and CoCl_2 concentrations and the quantities derived from these analytical results.

Poor material balances for the runs of Series III are believed caused by the faulty method for total salts analysis, as previously discussed. An average N/θ was used here as in Series II. Since the extracts contained essentially no NiCl_2 , no difficulties were encountered in the total salts analysis of the extract phase and errors in $K_A a$ and $(\text{HTU})_{OA}$ are due primarily to the errors in N/θ . However, in the calculations of $K_W a$ and $(\text{HTU})_{OW}$, the log mean driving force, as well as the average N/θ , was obtained from the water phase analyses. It is not known whether the combination of errors in the driving force and the average N/θ is compensating or additive. The K_A and HTU values are, consequently, not as reliable as those for Series II.

The interfacial measurements (see Table III) indicate that the aqueous solutions containing only CoCl_2 as the dissolved salt in contact

with alcohol at equilibrium had a slightly higher interfacial tension than those containing both NiCl_2 and CoCl_2 . Assuming the viscosities the same, higher interfacial tension should lead to larger drop formation and higher permissible throughputs for the cobalt solutions. However, visual observation of the column indicated that with runs 4 and 23, both made under flooding conditions, the flooding rate for the nickel-cobalt run was higher than for the cobalt run, which is just opposite to what might be expected. On examination of the specific gravities of the alcohol and water phases (see Tables I and II), it is seen that their difference is noticeably greater for the nickel-cobalt runs. For the 0.4 cu.ft./hr. water rate runs, this average difference in specific gravity for Series III runs is about 6% greater than the corresponding difference for the runs of Series II. This is to be expected, since the nickel concentration of the water phase remains essentially constant, making a change in specific gravity due to the transfer of CoCl_2 only. The effect of the greater difference in specific gravity in Series III apparently more than compensates for the lower interfacial tension, so that higher throughputs are permissible.

Flooding for Series II and III runs at much lower throughputs than for Series I is due to the smaller alcohol phase drops (smaller interfacial tension) and the lower difference in specific gravities of the phases.

The relatively small distribution coefficient (K) indicates that the alcohol film presents the major resistance to diffusion of the CoCl_2 . The $(\text{HTU})_{\text{OA}}$ is found to be almost independent of the flow rates of either phase. For design purposes, an $(\text{HTU})_{\text{OA}}$ of about five feet is probably a good value to use at flow rates near flooding.

Lower $K_{\text{W}}a$ values and higher $(\text{HTU})_{\text{OW}}$ values than those observed by Geankoplis are probably due primarily to the higher viscosity of the solvent used in this investigation.

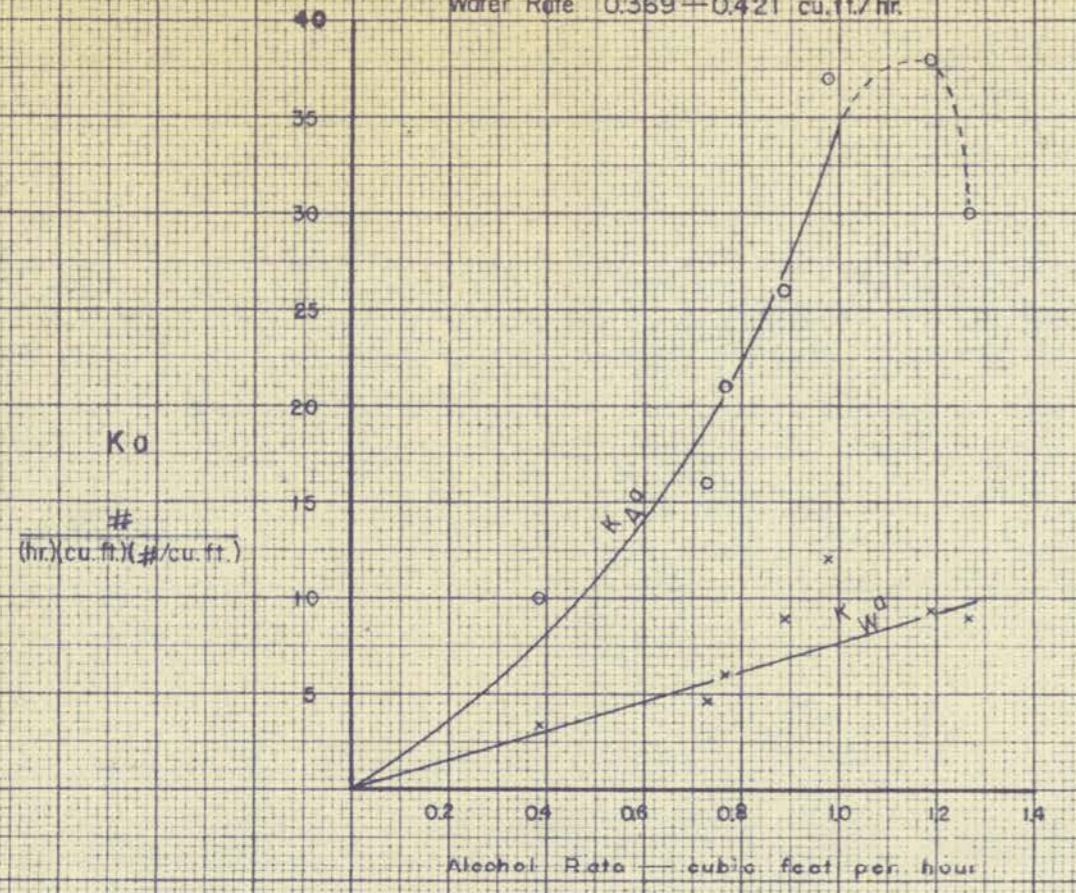
The ratio of CoCl_2 to NiCl_2 extracted under steady-state operating conditions, based on the alcohol phase analyses, averages about 200 to 1, which is appreciably greater than the equilibrium separation factor. This would indicate that the rate of diffusion of the CoCl_2 is greater than that of NiCl_2 .

There was no tendency for emulsion formation and no difficulties were experienced in this regard.

No study was made of the effect of column length and diameter on the performance of the column.

Figure 12

Water Rate 0.369—0.421 cu.ft./hr.



SERIES II

Figure 13

Water Rate 0.185—0.197 cu. ft./hr.

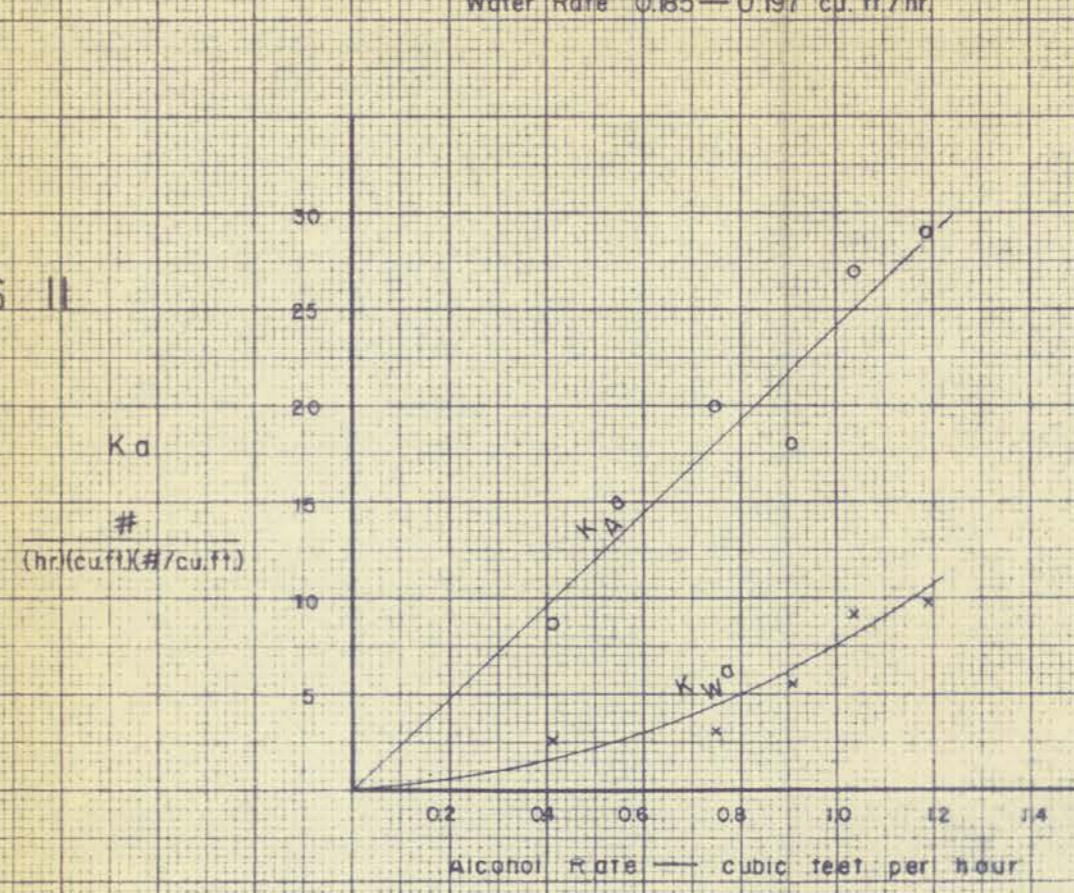
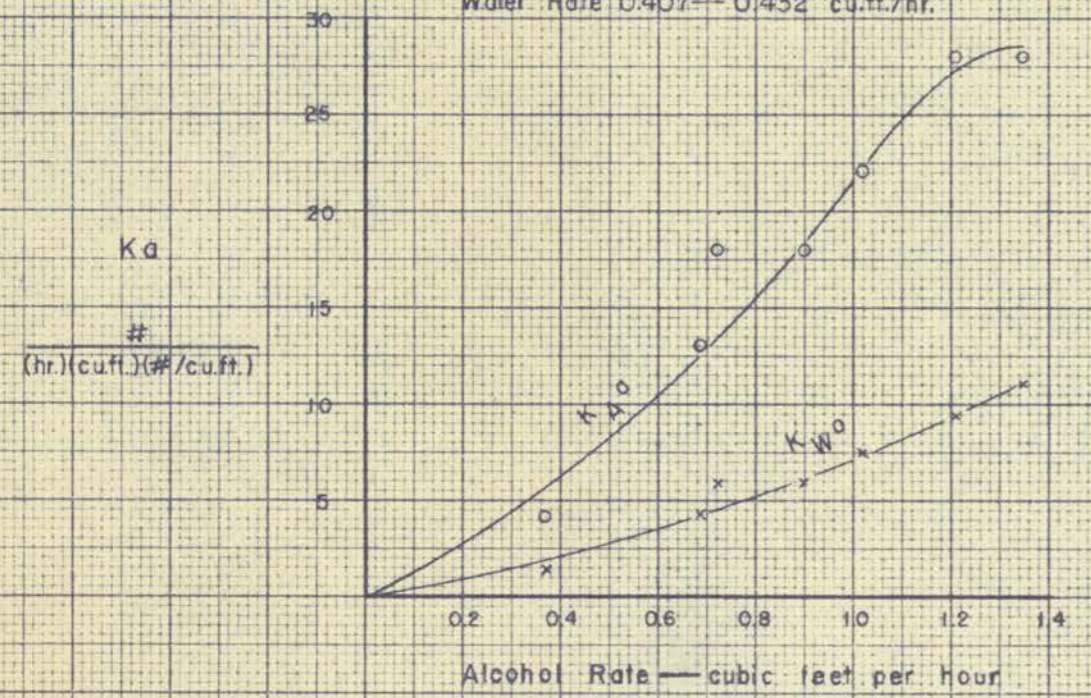


Figure 14

Water Rate 0.407—0.432 cu.ft./hr.



SERIES III

Figure 15

Water Rate 0.194—0.201 cu.ft./hr.

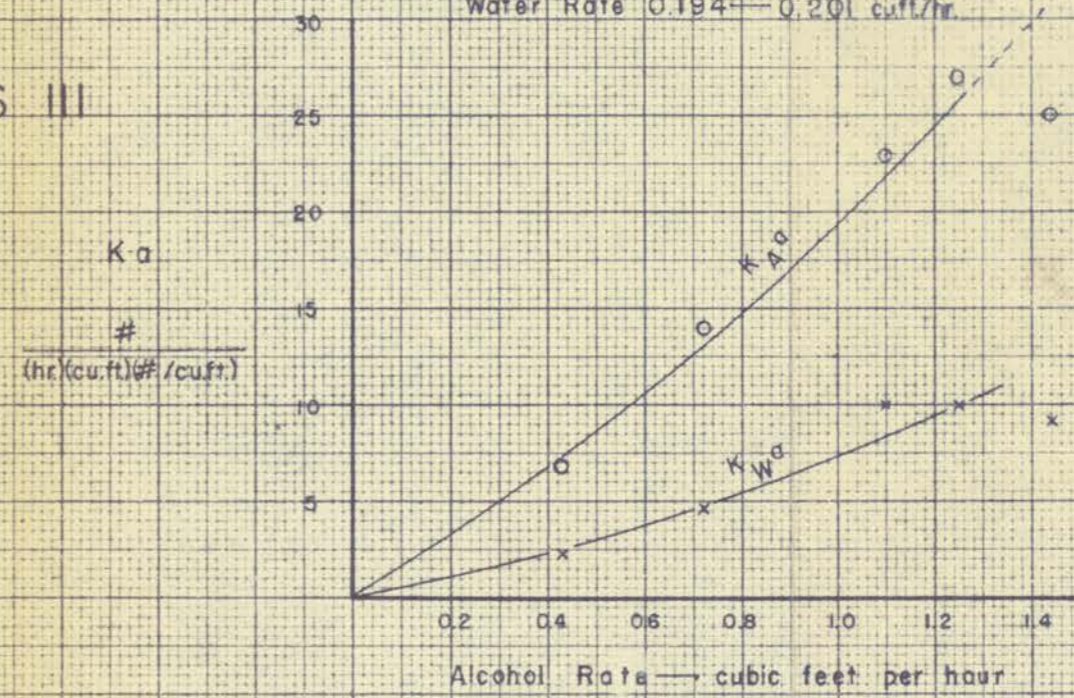
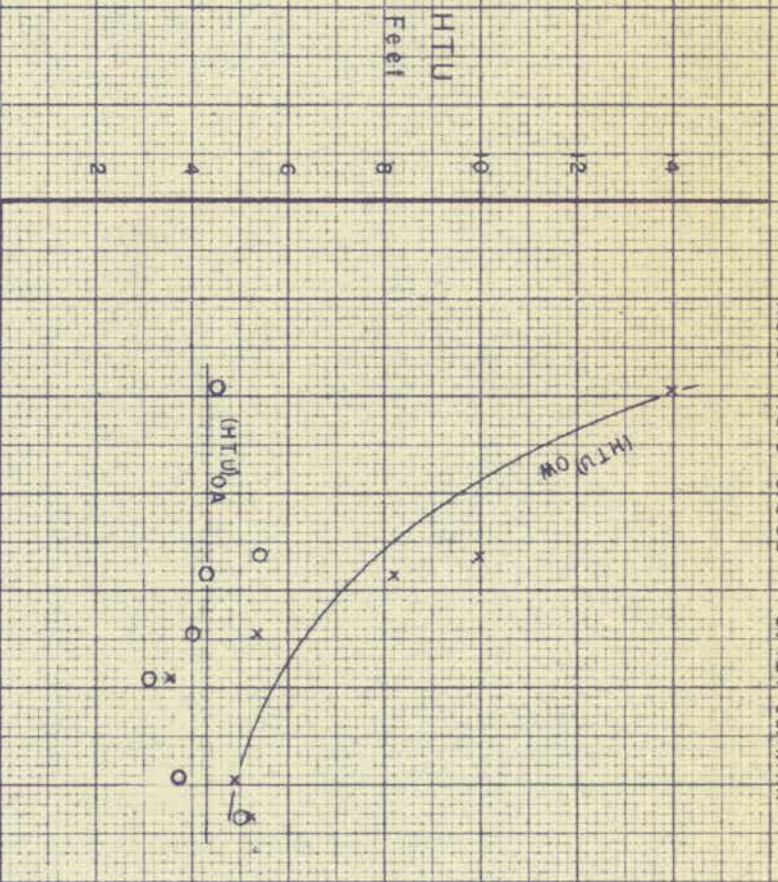


Figure 16
Water Rate 0.369—0.421 cu.ft./hr.



SERIES II

Figure 17
Water Rate 0.185—0.197 cu.ft./hr.

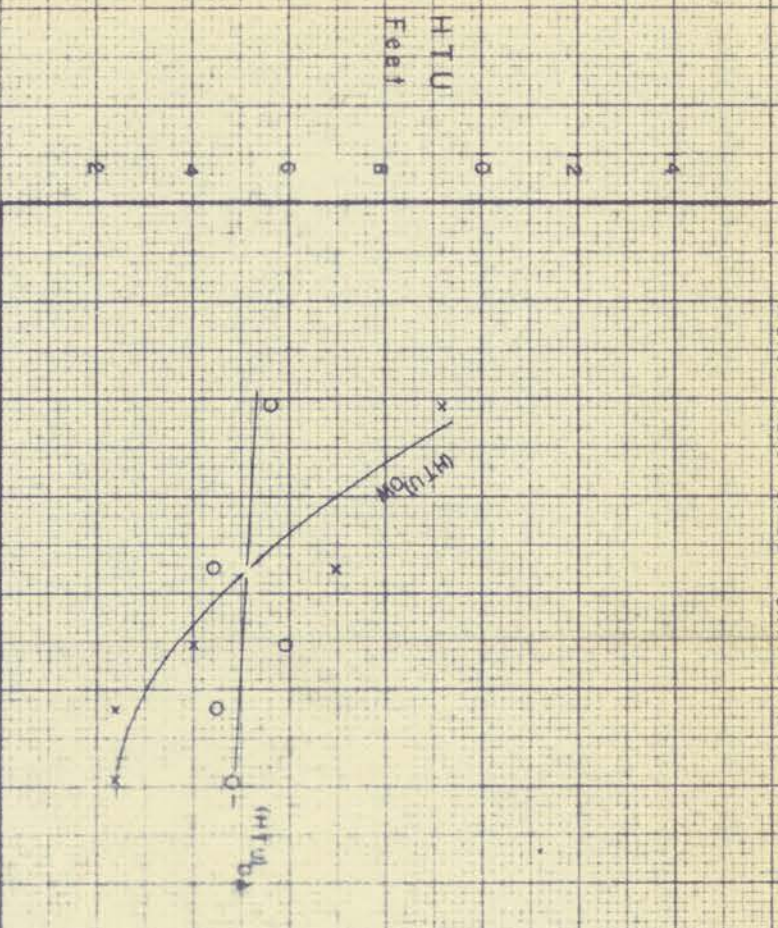
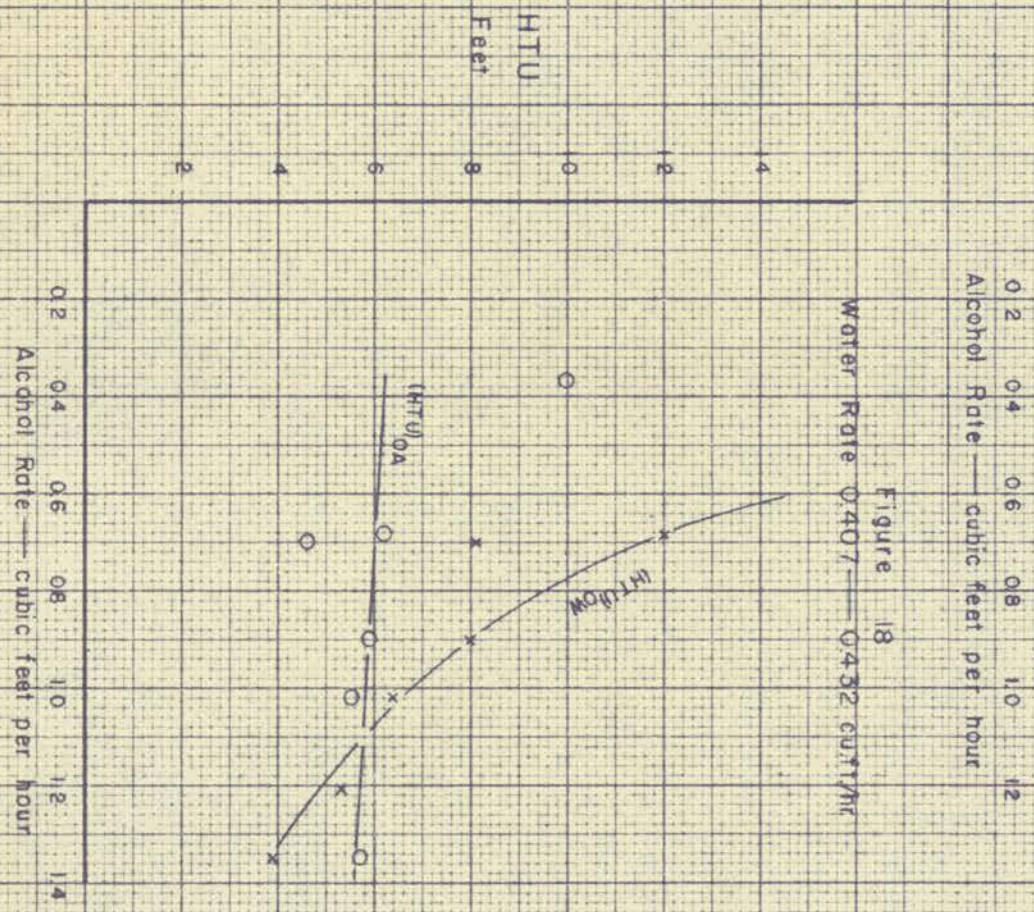
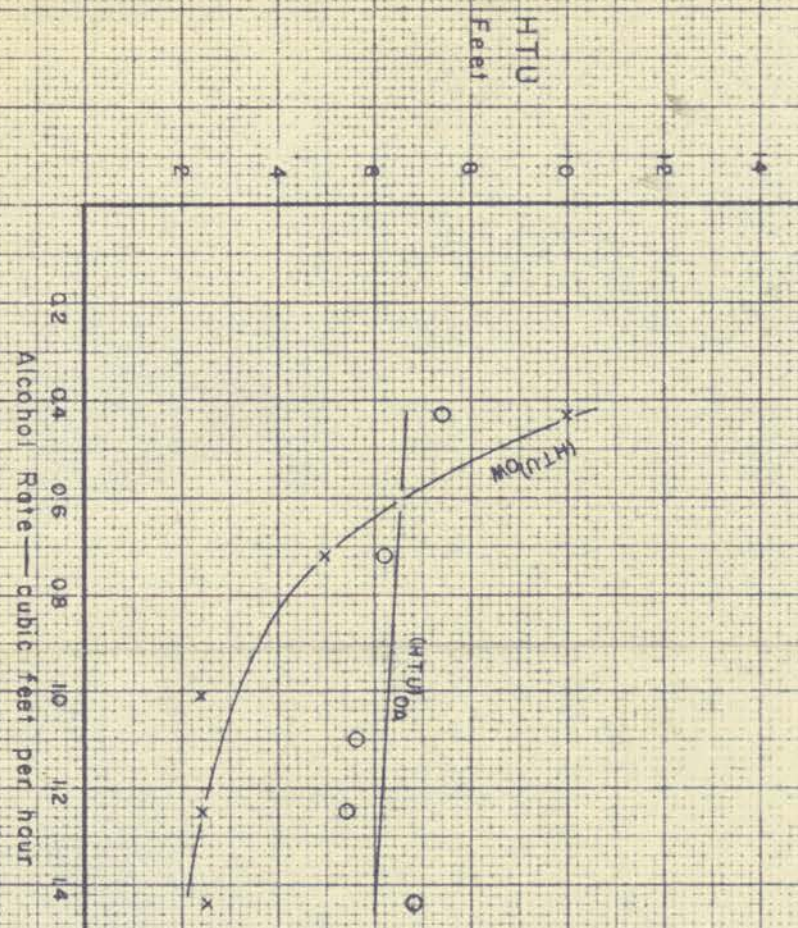


Figure 18
Water Rate 0.407—0.432 cu.ft./hr.



SERIES III

Figure 19
Water Rate 0.194—0.201 cu.ft./hr.



SUMMARY

A study of the continuous extraction of CoCl_2 from solutions containing $\text{CoCl}_2 - \text{HCl} - \text{water}$ and $\text{CoCl}_2 - \text{NiCl}_2 - \text{HCl} - \text{water}$ was made, using capryl alcohol as the solvent. The equilibrium distribution data of the salts between the two phases used in the present work are those found by Garwin.

A spray column $1\frac{1}{2}$ inches inside diameter and $68\text{-}3/8$ inches long was used for the flooding and extraction studies. The end design and the disperser design for the column were those found satisfactory by previous investigators. A new criterion for flooding was found convenient and limiting liquid throughputs for the column are reported using this definition of the flooded state.

For the extraction, the overall height of a transfer unit based on the alcohol phase, $(\text{HTU})_{\text{OA}}$, was approximately constant at 5 feet over the range of liquid rates used. The overall height of a transfer unit based on the water phase rate, $(\text{HTU})_{\text{OW}}$, was found to vary widely. As the alcohol rate increased, a marked decrease in $(\text{HTU})_{\text{OW}}$ was observed.

Flooding of the column when operating with the cobalt and nickel-cobalt solutions was found to take place at a lower throughput than when distilled water and capryl alcohol were used. This is likely due to the difference in the physical properties of the fluids containing the solutes. Interfacial tensions of the cobalt and nickel-cobalt solutions are much lower than that for capryl alcohol-water, causing smaller drops of the dispersed phase when the solutes are present. The difference in specific gravities of the two phases is also much lower when the solutes are present. These two effects lead to flooding at lower liquid throughputs.

Based on the alcohol phase analyses, the ratio of CoCl_2 to NiCl_2 extracted from solutions containing both CoCl_2 and NiCl_2 in approximately a 1:1 ratio averages about 200 to 1. This is more favorable than the ratio of equilibrium distribution coefficients would indicate.

RECOMMENDATIONS

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

1. The development of a more satisfactory method for the total salts analysis of solutions containing both NiCl_2 and CoCl_2 .
2. Inversion of the extraction column so that operation with the water phase dispersed may be studied.
3. Determination of extraction capacities with packed and perforated-plate columns.
4. Investigation of the possibility of the use of a more expensive grade of capryl alcohol, such as the refined grade. This would necessitate a redetermination of distribution coefficients, as well as a study of the extraction rates.
5. The use of other solvents, particularly the higher alcohols, such as nonyl alcohol, which have recently become commercially available.

APPENDIX

RED	% DEVIATION FROM AVERAGE $\frac{(33)-(34)}{(35)} \times 100$	# CoCl ₂ TRANSFERRED PER HOUR			% DEVIATION FROM AVERAGE $\frac{(37)-(38)}{(39)} \times 100$	% Cl IN WATER PHASE AND CORRESPONDING K				EQUILIBRIUM CoCl ₂ CONCENTRATION IN ALCOHOL PHASE (SEE NOTE 2)				$\Delta C = f$ CoCl ₂ /cu.ft. BASED ON ALCOHOL PHASE CONCENTRATIONS			K _A $\frac{f}{hr.-cu.ft.-f.}$	(HTU) _{OA} Ft.	EQUILIBRIUM CoCl ₂ CONCENTRATION IN WATER PHASE (SEE NOTE 3)				$\Delta C = f$ CoCl ₂ /cu.ft. BASED ON WATER PHASE CONCENTRATIONS			K _W $\frac{f}{hr.-cu.ft.-f.}$	(HTU) _{OW} Ft.
		Water Phase	Alcohol Phase	Average		Top (In)	Bottom (Out)	% Cl	K	% Cl	K	Top (Out)	Bottom (In)	Top (Out)	Bottom (In)	Bottom			Top	Log Mean	Top (In)	Bottom (Out)	Top (In)	Bottom (Out)	Top		
Average	(35)	(37)	(38)	(39)	(40)	(41)	(42)	(43)	(44)	(45)	(46)	(47)	(48)	(49)	(50)	(51)	(52)	(53)	(54)	(55)	(56)	(57)	(58)	(59)	(60)	(61)	(62)
0.208	- 18	0.185	0.226	0.206	- 20	28.6	0.450	29.3	0.480	2.66	2.57	1.49	1.45	1.34	0.77	1.03	4.1	10	2.87	0.41	2.13	0.30	2.32	3.71	2.96	1.4	35
0.522	+ 20	0.583	0.468	0.526	+ 22	28.6	0.450	29.3	0.480	2.66	2.80	1.49	1.12	1.01	0.70	0.85	13	6.2	3.13	0.41	2.33	0.30	2.12	2.80	2.45	4.4	12
0.631	+ 13	0.660	0.586	0.623	+ 12	29.0	0.468	28.2	0.432	2.77	1.66	1.55	0.93	0.82	0.60	0.70	18	4.6	3.59	0.44	2.69	0.32	1.76	2.54	2.12	6.0	8.1
0.759	+ 24	0.830	0.664	0.747	+ 22	29.1	0.472	28.8	0.459	3.04	1.77	1.71	0.99	0.88	0.86	0.87	18	5.9	3.18	0.41	2.36	0.30	2.50	2.56	2.53	6.1	8.0
0.871	+ 12	0.890	0.815	0.852	+ 9	29.1	0.472	28.5	0.445	3.04	1.60	1.71	0.90	0.79	0.80	0.80	22	5.5	3.39	0.43	2.52	0.31	2.34	2.36	2.35	7.5	6.4
0.995	+ 11	0.930	0.887	0.909	+ 5	29.0	0.468	28.4	0.441	2.77	1.35	1.55	0.76	0.65	0.71	0.68	28	5.2	3.21	0.43	2.39	0.31	2.06	1.94	2.00	9.4	5.3
1.09	+ 24	1.17	0.95	1.06	+ 21	28.3	0.437	28.2	0.432	2.8	1.21	1.6	0.67	0.65	0.9	0.77	28	5.7	2.98	0.70	2.21	0.51	2.61	1.46	1.98	11	3.9
0.298	+ 25	0.330	0.261	0.296	+ 23	29.1	0.472	28.2	0.432	2.86	1.66	1.60	0.92	0.87	0.94	0.90	6.8	7.4	2.50	0.22	1.86	0.16	2.70	2.70	2.70	2.3	9.9
0.487	+ 29	0.547	0.416	0.487	+ 20	29.1	0.472	28.1	0.428	2.86	1.04	1.60	0.58	0.53	0.97	0.73	14	6.2	2.37	0.22	1.76	0.16	2.80	1.64	2.17	4.6	5.0
0.602	+ 16	0.616	0.554	0.585	+ 11	28.5	0.445	28.5	0.445	2.40	0.58	1.34	0.32	0.30	0.82	0.52	23	5.6	2.13	0.67	1.50	0.49	2.40	0.47	1.20	10	2.4
0.642	- 9	0.584	0.664	0.624	- 13	28.4	0.441	27.4	0.383	2.29	0.54	1.27	0.30	0.29	0.73	0.48	27	5.4	2.21	0.51	1.64	0.37	2.26	0.62	1.27	10	2.4
0.748	+ 10	0.748	0.701	0.725	+ 6	28.2	0.432	28.0	0.423	2.73	0.58	1.51	0.32	0.31	1.01	0.59	25	6.8	2.09	0.47	1.55	0.34	3.20	0.67	1.62	9.2	2.5

TABLE II

RUN	FLOW RATE				SPECIFIC GRAVITY				SALT CONCENTRATION--WATER PHASE IN						SALT CONCENTRATION--WATER PHASE OUT						SALT CONCENTRATION--ALCOHOL PHASE IN						SALT CONCENTRATION--ALCOHOL PHASE OUT						# MeCl_2 TRANSFER PER HOUR	
	Cu.ft./hr.		Cu.ft./hr.--sq.ft.		Alcohol		Water		Weight Percent			# Salt/cu.ft.			Weight Percent			# Salt/cu.ft.			Weight Percent			# Salt/cu.ft.			Weight Percent			# Salt/cu.ft.			Water	Alcohol
	Alcohol	Water	Alcohol	Water	In	Out	In	Out	MeCl_2	NiCl_2	CoCl_2	MeCl_2	NiCl_2	CoCl_2	MeCl_2	NiCl_2	CoCl_2	MeCl_2	NiCl_2	CoCl_2	MeCl_2	NiCl_2	CoCl_2	MeCl_2	NiCl_2	CoCl_2	MeCl_2	NiCl_2	CoCl_2	MeCl_2	NiCl_2	CoCl_2	Phase	Phase
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)	(19)	(20)	(21)	(22)	(23)	(24)	(25)	(26)	(27)	(28)	(29)	(30)	(31)	(32)	(33)	(34)
12	0.371	0.419	42.5	49.2	0.900	0.898	1.205	1.200	10.2	4.28	5.92	7.67	3.22	4.45	9.64	4.28	5.36	7.22	3.21	4.01	0.20	0.0	0.20	0.11	0.0	0.11	1.29	0.003	1.29	0.722	0.002	0.720	0.189	0.227
13	0.685	0.432	80.4	50.7	0.900	0.899	1.205	1.195	10.2	4.28	5.92	7.67	3.22	4.45	8.50	4.34	4.16	6.34	3.24	3.10	0.20	0.0	0.20	0.11	0.0	0.11	1.42	0.006	1.41	0.796	0.003	0.793	0.575	0.470
16	0.792	0.415	82.4	48.7	0.895	0.900	1.207	1.194	10.1	4.19	5.91	7.60	3.16	4.45	8.03	4.18	3.85	5.98	3.12	2.86	0.19	0.0	0.19	0.11	0.0	0.11	1.69	0.008	1.68	0.940	0.004	0.945	0.673	0.589
14	0.90	0.415	106	48.7	0.898	0.903	1.208	1.192	10.3	3.85	6.45	7.76	2.90	4.86	7.67	3.81	3.86	5.71	2.83	2.88	0.19	0.0	0.19	0.11	0.0	0.11	1.51	0.006	1.50	0.850	0.003	0.847	0.851	0.667
15	1.02	0.407	120	47.8	0.898	0.903	1.208	1.190	10.3	3.85	6.45	7.76	2.90	4.86	7.40	3.80	3.60	5.49	2.82	2.67	0.19	0.0	0.19	0.11	0.0	0.11	1.62	0.003	1.62	0.912	0.002	0.910	0.924	0.818
17	1.21	0.423	142	49.6	0.895	0.900	1.207	1.186	10.1	4.19	5.91	7.60	3.16	4.45	7.08	4.02	3.06	5.24	2.97	2.27	0.19	0.0	0.19	0.11	0.0	0.11	1.51	0.008	1.50	0.847	0.004	0.845	0.990	0.891
23	1.35	0.426	159	50.0	0.889	0.894	1.205	1.181	10.5	4.09	6.4	7.90	3.08	4.82	6.83	4.02	2.81	5.03	2.86	2.07	0.03	0.0	0.03	0.02	0.0	0.02	1.30	0.003	1.30	0.726	0.002	0.724	1.22	0.953
18	0.428	0.194	50.3	22.8	0.891	0.897	1.207	1.192	10.2	4.14	6.06	7.68	3.12	4.56	8.00	4.15	3.86	5.08	3.08	2.86	0.095	0.0	0.095	0.05	0.0	0.05	1.18	0.00	1.18	0.660	0.00	0.660	0.335	0.261
19	0.720	0.198	84.5	23.2	0.891	0.898	1.207	1.181	10.2	4.14	6.06	7.68	3.12	4.56	6.59	4.15	2.44	4.86	3.06	1.80	0.095	0.0	0.095	0.05	0.0	0.05	1.12	0.00	1.12	0.628	0.00	0.628	0.558	0.416
20	1.10	0.200	129	23.5	0.887	0.892	1.200	1.173	9.47	4.07	5.40	7.09	3.05	4.04	5.27	3.96	1.31	3.86	2.90	0.96	0.03	0.0	0.03	0.02	0.0	0.02	0.947	0.005	0.942	0.527	0.003	0.524	0.646	0.558
21	1.25	0.201	147	23.6	0.885	0.889	1.201	1.168	9.25	4.05	5.20	6.93	3.03	3.90	5.33	3.96	1.37	3.88	2.89	0.99	0.02	0.0	0.02	0.01	0.0	0.01	0.973	0.008	0.965	0.546	0.004	0.542	0.613	0.670
22	1.44	0.200	169	23.5	0.888	0.890	1.204	1.172	10.4	4.08	6.32	7.81	3.07	4.75	5.30	3.92	1.38	3.88	2.87	1.01	0.02	0.0	0.02	0.01	0.0	0.01	0.905	0.009	0.896	0.502	0.005	0.497	0.786	0.709

Note 1. $\text{MeCl}_2 = \text{NiCl}_2 + \text{CoCl}_2$

Note 2. Specific gravities of the alcohol phase at equilibrium are assumed to be equal to those measured for steady-state conditions of countercurrent operation (See columns (5) and (6)).

Note 3. Specific gravities of the water phase at equilibrium are assumed as follows:

Weight % CoCl_2	Sp. Gr.
3	1.19
2	1.18
1	1.17

TABLE III

Surface and Interfacial Tension Measurements

Temperature = 30 to 35° C.

<u>Materials Used</u>	<u>Observed dynes/cm.</u>	<u>Surface Tension</u>
		<u>Literature Values dynes/cm.</u>
Distilled water	71.7	71.2 (30°C.), 70.4 (35°C.) ⁸
Eastman Kodak Co. ketone-free capryl alcohol	27.6	25.5 (30°C.), 24.7 (40°C.) ⁶
E. K. Co. capryl alcohol saturated with water	27.6	
Extract, run 22	28.7	
Raffinate, run 22	37	
Solvent, run 23	28.5	
Extract, run 23	28.7	
<u>Interfacial Tension</u>		
E. K. Co. capryl alcohol - distilled water	10.3	9.6 (30°C.), 10.0 (40°C.) ⁶
Hardesty refined grade capryl alcohol - distilled water	10.5	
Solvent, run 14 - aqueous feed, run 14	2.5	
Solvent, run 14 - raffinate, run 14	2.8	
Extract, run 22 - 8% CoCl ₂ , 25% HCl	3.4	

SAMPLE CALCULATIONS

I. Run number 2 of Series II.

The numbers in parentheses refer to the numbers heading the columns in Table I. Columns (1) through (12), (21), and (23) contain observed experimental data.

$$(13) = \frac{62.4 \times (9) \times (5)}{100} = \frac{62.4 \times 0.899 \times 0.21}{100} = 0.12 \text{ \#CoCl}_2/\text{cu.ft.}$$

$$(14) = \frac{62.4 \times (10) \times (6)}{100} = \frac{62.4 \times 0.912 \times 2.33}{100} = 1.33 \text{ \#CoCl}_2/\text{cu.ft.}$$

$$(15) = \frac{62.4 \times (11) \times (7)}{100} = \frac{62.4 \times 1.199 \times 7.7}{100} = 5.77 \text{ \#CoCl}_2/\text{cu.ft.}$$

$$(16) = \frac{62.4 \times (12) \times (8)}{100} = \frac{62.4 \times 1.163 \times 3.42}{100} = 2.48 \text{ \#CoCl}_2/\text{cu.ft.}$$

$$(17) = [(16) - (15)] (2) = (5.77 - 2.48) (0.369) = 1.21 \text{ \#CoCl}_2/\text{hr.}$$

$$(18) = [(14) - (13)] (1) = (1.33 - 0.12) (0.979) = 1.18 \text{ \#CoCl}_2/\text{hr.}$$

$$(19) = \frac{(17) + (18)}{2} = \frac{1.21 + 1.18}{2} = 1.20 \text{ \#CoCl}_2/\text{hr.}$$

$$(20) = \frac{(17) - (18)}{(19)} \times 100 = \frac{1.21 - 1.18}{1.20} \times 100 = + 2.5\%$$

(22) and (24) are the distribution coefficients (K) corresponding to the total chloride concentration in the water phase (see Figure 1.)

$$(25) = (22) \times (7) = 0.465 \times 7.7 = 3.58 \text{ \%CoCl}_2$$

$$(26) = (24) \times (8) = 0.379 \times 3.42 = 1.30 \text{ \%CoCl}_2$$

For the calculation of (27) and (28), the specific gravity of the alcohol phase which would be in equilibrium with the bulk of the water was assumed to be the observed alcohol phase gravity.

$$(27) = \frac{62.4 \times (10) \times (25)}{100} = \frac{62.4 \times 0.912 \times 3.58}{100} = 2.04 \text{ \#CoCl}_2/\text{cu.ft.}$$

$$(28) = \frac{62.4 \times (9) \times (26)}{100} = \frac{62.4 \times 0.899 \times 1.30}{100} = 0.73 \text{ \#CoCl}_2/\text{cu.ft.}$$

$$(29) = (28) - (13) = 0.73 - 0.12 = 0.61 \text{ \#CoCl}_2/\text{cu.ft.}$$

$$(30) = (27) - (14) = 2.04 - 1.33 = 0.71 \text{ \#CoCl}_2/\text{cu.ft.}$$

$$(31) = \frac{(30) - (29)}{\ln \frac{(30)}{(29)}} = \frac{0.71 - 0.61}{\ln \frac{0.71}{0.61}} = 0.66 \text{ \#CoCl}_2/\text{cu.ft.}$$

The effective volume of the column is 0.0486 cu. ft.

$$(32) = \frac{(19)}{(31) \times 0.0486} = \frac{1.20}{0.66 \times 0.0486} = \frac{37 \text{ \#/hr.}}{(\text{cu.ft.}) (\text{\#/cu.ft.})}$$

$$(33) = \frac{(3)}{(32)} = \frac{115}{37} = 3.1 \text{ feet}$$

$$(34) = \frac{(6)}{(22)} = \frac{2.33}{0.465} = 5.01 \text{ \%CoCl}_2$$

$$(35) = \frac{(5)}{(24)} = \frac{0.21}{0.379} = 0.55 \text{ \%CoCl}_2$$

See Note 3, Table I, for the specific gravities used in the calculation of (36) and (37).

$$(36) = \frac{62.4 \times \text{sp.gr.} \times (34)}{100} = \frac{62.4 \times 1.17 \times 5.01}{100} = 3.66 \text{ \#CoCl}_2/\text{cu.ft.}$$

$$(37) = \frac{62.4 \times \text{sp.gr.} \times (35)}{100} = \frac{62.4 \times 1.13 \times 0.55}{100} = 0.39 \text{ \#CoCl}_2/\text{cu.ft.}$$

$$(38) = (15) - (36) = 5.77 - 3.66 = 2.11 \text{ \#CoCl}_2/\text{cu.ft.}$$

$$(39) = (16) - (37) = 2.48 - 0.39 = 2.09 \text{ \#CoCl}_2/\text{cu.ft.}$$

$$(40) = \frac{(38) - (39)}{\ln \frac{(38)}{(39)}} = \frac{2.11 - 2.09}{\ln \frac{2.11}{2.09}} = 2.10 \text{ \#CoCl}_2/\text{cu.ft.}$$

$$(41) = \frac{(19)}{(40) \times 0.0486} = \frac{1.20}{2.10 \times 0.0486} = 12 \frac{\text{\#CoCl}_2/\text{hr.}}{(\text{cu.ft.}) (\text{\#CoCl}_2/\text{cu.ft.})}$$

$$(42) = \frac{(4)}{(41)} = \frac{43.3}{12} = 3.6 \text{ feet}$$

II. Run number 13 of Series III.

Columns (1) through (11), (15), (16), (17), (21), (22), (23), (27), (28), (29), (41) and (43) contain observed experimental data.

$$(12) = \frac{62.4 \times (7) \times (9)}{100} = \frac{62.4 \times 1.205 \times 10.2}{100} = 7.67 \text{ \#MeCl}_2/\text{cu.ft.}$$

$$(13) = \frac{62.4 \times (7) \times (10)}{100} = \frac{62.4 \times 1.205 \times 10.2}{100} = 3.22 \text{ \#NiCl}_2/\text{cu.ft.}$$

$$(14) = (12) - (13) = 7.67 - 3.22 = 4.45 \text{ \#CoCl}_2/\text{cu.ft.}$$

$$(18) = \frac{62.4 \times (8) \times (15)}{100} = \frac{62.4 \times 1.195 \times 8.50}{100} = 6.34 \text{ \#MeCl}_2/\text{cu.ft.}$$

$$(19) = \frac{62.4 \times (8) \times (16)}{100} = \frac{62.4 \times 1.195 \times 4.34}{100} = 3.24 \text{ \#NiCl}_2/\text{cu.ft.}$$

$$(20) = (18) - (19) = 6.34 - 3.24 = 3.10 \text{ \#CoCl}_2/\text{cu.ft.}$$

$$(24) = \frac{62.4 \times (5) \times (21)}{100} = \frac{62.4 \times 0.900 \times 0.20}{100} = 0.11 \text{ \#MeCl}_2/\text{cu.ft.}$$

$$(25) = \frac{62.4 \times (5) \times (22)}{100} = \frac{62.4 \times 0.900 \times 0.0}{100} = 0.0 \text{ \#NiCl}_2/\text{cu.ft.}$$

$$(26) = (24) - (25) = 0.11 - 0.0 = 0.11 \text{ \#CoCl}_2/\text{cu.ft.}$$

$$(30) = \frac{62.4 \times (6) \times (27)}{100} = \frac{62.4 \times 0.899 \times 1.42}{100} = 0.796 \text{ \#MeCl}_2/\text{cu.ft.}$$

$$(31) = \frac{62.4 \times (6) \times (28)}{100} = \frac{62.4 \times 0.899 \times 0.006}{100} = 0.003 \text{ \#NiCl}_2/\text{cu.ft.}$$

$$(32) = (30) - (31) = 0.796 - 0.003 = 0.793 \text{ \#CoCl}_2/\text{cu.ft.}$$

$$(33) = (2) \times (12) - (18) = 0.432 \times (7.67 - 6.34) = 0.575 \text{ \#MeCl}_2/\text{hr.}$$

$$(34) = (1) \times (30) - (24) = 0.685 \times (0.796 - 0.11) = 0.470 \text{ \#MeCl}_2/\text{hr.}$$

$$(35) = \frac{(33) + (34)}{2} = \frac{0.575 + 0.470}{2} = 0.522 \text{ \#CoCl}_2/\text{hr.}$$

$$(36) = \frac{(33) - (34)}{(35)} = \frac{0.575 - 0.470}{0.522} = + 20\%$$

$$(37) = (2) \times [(14) - (20)] = 0.432 \times (4.45 - 3.10) = 0.583 \text{ \#CoCl}_2/\text{hr.}$$

$$(38) = (1) \times [(32) - (26)] = 0.685 \times (0.793 - 0.11) = 0.468 \text{ \#CoCl}_2/\text{hr.}$$

$$(39) = \frac{(37) + (38)}{2} = \frac{0.583 + 0.468}{2} = 0.526 \text{ \#CoCl}_2/\text{hr.}$$

$$(40) = \frac{(37) - (38)}{(39)} \times 100 = \frac{0.583 - 0.468}{0.526} \times 100 = + 22\%$$

(42) and (44) are the distribution coefficients (K) corresponding to the total chloride concentration in the water phase (see Figure 2).

$$(45) = (11) \times (42) = 5.92 \times 0.450 = 2.66 \text{ \%CoCl}_2$$

$$(46) = (17) \times (44) = 4.16 \times 0.480 = 2.00 \text{ \%CoCl}_2$$

For the calculation of (47) and (48), the specific gravity of the alcohol phase which would be in equilibrium with the bulk of the water phase was assumed to be equal to the observed alcohol phase gravity.

$$(47) = \frac{62.4 \times (6) \times (45)}{100} = \frac{62.4 \times 0.899 \times 2.66}{100} = 1.49 \text{ \#CoCl}_2/\text{cu.ft.}$$

$$(48) = \frac{62.4 \times (5) \times (46)}{100} = \frac{62.4 \times 0.900 \times 2.00}{100} = 1.12 \text{ \#CoCl}_2/\text{cu.ft.}$$

$$(49) = (48) - (26) = 1.12 - 0.11 = 1.01 \text{ \#CoCl}_2/\text{cu.ft.}$$

$$(50) = (47) - (32) = 1.49 - 0.793 = 0.70 \text{ \#CoCl}_2/\text{cu.ft.}$$

$$(51) = \frac{(49) - (50)}{\ln \frac{(49)}{(50)}} = \frac{1.01 - 0.70}{\ln \frac{1.01}{0.70}} = 0.85 \text{ \#CoCl}_2/\text{cu.ft.}$$

$$(52) = \frac{(39)}{0.0486 \times (51)} = \frac{0.526}{0.0486 \times 0.85} = 13 \frac{\text{\#CoCl}_2/\text{hr.}}{(\text{cu.ft.})(\text{\#}/\text{cu.ft.})}$$

$$(53) = \frac{(3)}{\frac{(15)}{(52)}} = \frac{80.4}{13} = 6.2 \text{ feet}$$

$$(54) = \frac{(29)}{(42)} = \frac{1.41}{0.450} = 3.13 \% \text{CoCl}_2$$

$$(55) = \frac{(23)}{(44)} = \frac{0.20}{0.480} = 0.41 \% \text{CoCl}_2$$

For the specific gravity of the water phase used in the calculation of (56) and (57), see Note 3, Table II.

$$(56) = \frac{62.4 \times \text{sp.gr.} \times (54)}{100} = \frac{62.4 \times 1.19 \times 3.13}{100} = 2.33 \# \text{CoCl}_2 / \text{cu.ft.}$$

$$(57) = \frac{62.4 \times \text{sp.gr.} \times (55)}{100} = \frac{62.4 \times 1.17 \times 0.41}{100} = 0.30 \# \text{CoCl}_2 / \text{cu.ft.}$$

$$(58) = (14) - (56) = 4.45 - 2.33 = 2.12 \# \text{CoCl}_2 / \text{cu.ft.}$$

$$(59) = (20) - (57) = 3.10 - 0.30 = 2.80 \# \text{CoCl}_2 / \text{cu.ft.}$$

$$(60) = \frac{(59) - (58)}{\ln \frac{(59)}{(58)}} = \frac{2.80 - 2.12}{\ln \frac{2.80}{2.12}} = 2.45 \# \text{CoCl}_2 / \text{cu.ft.}$$

$$(61) = \frac{(39)}{0.0486 \times (60)} = \frac{0.526}{0.0486 \times 2.45} = 4.4 \frac{\# \text{CoCl}_2 / \text{hr.}}{(\text{cu.ft.})(\# \text{CoCl}_2 / \text{cu.ft.})}$$

$$(62) = \frac{(4)}{(61)} = \frac{50.7}{4.4} = 12 \text{ feet}$$

NOMENCLATURE

a = interfacial area per unit volume, sq.ft./cu.ft.

dA = differential interfacial area, sq.ft.

C = CoCl_2 concentration, #/cu.ft.

$\Delta C_A = (C_A^* - C_A)$ at any point in the column, #/cu.ft.

$\Delta C_W = (C_W - C_W^*)$ at any point in the column, #/cu.ft.

HTU = height of a transfer unit

K = distribution coefficient, (weight percent salt in the alcohol phase at equilibrium)/(weight percent salt in the water phase at equilibrium)

K_A = extraction coefficient based on the alcohol phase,
#/(hr.)(sq.ft. of interfacial area)(ΔC)

K_a = extraction capacity coefficient, #/(hr.)(cu.ft. of column)(ΔC)

L = liquid rate, (cu.ft.)/(hr.)(sq.ft.)

N/θ = rate of CoCl_2 transfer, #/hr.

S = cross-sectional area of the column, sq. ft.

V = volume of the column, cu.ft.

Subscripts

A = alcohol phase

lm = log mean

OA = overall, based on the alcohol phase

OW = overall, based on the water phase

W = water phase

1 = top of column

2 = bottom of column

Superscript

* = equilibrium value

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