THE SEPARATION OF NICKELOUS AND COBALTOUS

CHLORIDES BY LIQUID-LIQUID EXTRACTION IN A PACKED COLUMN

By

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ABSTRACT

Limiting liquid throughputs were determined for the system capryl alcohol - water at two water rates in a column 2-inches i.d. and 82-1/2 inches in length, packed with 1/4" porcelain Raschig rings to a height of 72 inches.

Extraction of $CoCl_2$ from $CoCl_2$ - $NiCl_2$ - HCl - water solutions was carried out in this column using capryl alcohol as the solvent. $(HTU)_{OA}$ values were found to vary from 4 to 6 feet over the range of flow rates investigated. The $(HTU)_{OW}$ values increased as the alcohol rate was increased.

The recovery of $CoCl_2$ from the alcohol extract of the extraction runs was also carried out in this column, using a HCl - water solution as the solvent. The $(HTU)_{OA}$ and $(HTU)_{OW}$ increased when the alcohol rate was increased. The $(HTU)_{OA}$ values obtained indicated that the transfer of $CoCl_2$ from the discontinuous phase to the continuous phase was better than the transfer from the continuous to the discontinuous.

INTRODUCTION

The separation of nickel and cobalt has presented considerable difficulty to the metallurgy industry. The most widely used processes involve the precipitation of the cobalt in the form of the hydrated cobaltic oxide ($Co_2O_3 \cdot 3H_2O$) by the addition of an oxidizing agent to an alkaline solution of the divalent salts. Oxidizing agents commonly used are bleaching powder, sodium and potassium hypochlorite and hypobromite, and solid carbonates in conjunction with chlorine gas (4),(14),(19),(21),(26).

The preferential solubility of certain inorganic salts in organic solvents was noted by Garwin and Hixson(11) who 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. Capryl alcohol (2-octanol) was selected as the organic solvent on the basis of preliminary studies. The reasons for this selection were the wide difference in the solubilities of the anhydrous salts in the alcohol, 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 investigated, and the availability and moderate cost of the solvent.

Practically no $CoCl_2$ was extracted from the simple aqueous solution except at salt concentrations near saturation. The addition of an electrolyte such as $CaCl_2$ or HCl increased the distribution coefficient of $CoCl_2$. In all cases the extraction of $NiCl_2$ was very low. The distribution coefficients (K) for $CoCl_2$ and $NiCl_2$

in HCl solutions at 25°C are given as a function of the total chloride concentration in Figures 1 and 2, respectively (11).

Kylander and Garwin(16) investigated the extraction of $CoCl_2$ from aqueous HCl solutions of $CoCl_2$, and $CoCl_2$ and $NiCl_2$ with capryl alcohol in a spray column. The study was carried out in a column 1-1/4 inches i.d. and 68-3/8 inches in length. A distributor consisting of ten 0.1-inch dia. nozzles was used. Limiting liquid throughputs were also determined for refined grade capryl alcohol and distilled water. Values for $(HTU)_{OA}$ were found to be nearly constant at about 5 feet over the range of flow rates of the liquid phases. Values for $(HTU)_{OW}$ decreased rapidly with increasing alcohol rate and decreased slowly with decreasing water rate.

THE PERFORMANCE OF EXTRACTION EQUIPMENT

Investigations conducted prior to 1936 and shortly thereafter, made use of the theoretical stage theory and the transfer coefficient Ka for the expression of mass transfer. The recent trend has been toward the utilization of the HTU concept. The principal purpose of these mass transfer coefficients is to permit the adaption of small scale experimental results to the design of commercial size units.

Varteressian and Fenske(27) conducted investigations on the system benzene-water-ethyl alcohol, utilizing the theoretical plate concept to evaluate the performance in their packed column. The effect of a number of common variables on the column performance was indicated. The variables found to affect the column performance were shape and size of packing, and state of saturation of the feed streams. Variables found to have no effect upon column performance were the material of the packing, inversion of the continuous and discontinuous phases, and the rate of throughput of material.

The performance of spray and packed columns was studied by Appel and Elgin(1) with the system toluene-benzoic acid-water. It was found that the capacity of the packed column depended upon the feed rate of the discontinuous phase and only slightly upon the rate of the continuous phase. The capacity also varied with the drop size produced by the nozzle. In general, the dependence of holdup on these variables was similar to that of capacity. The effectiveness of a packed column relative to that of a spray column was believed to depend upon the drop size produced by the nozzle and the nature of the packing. The capacity of a packed column was believed to be determined largely by the rate of

flow and the geometry of the packing, rather than by the subdivision of the discontinuous phase at the nozzle.

Blanding and Elgin(3) studied the flooding velocities of a three-inch diameter by five-foot packed extraction column. The variables studied were drop size, type of packing, column design, packing support, and variation of the discontinuous and continuous phase rates. Data obtained covered the full range of discontinuous and continuous phase flow rate ratios and a description of the operation at flooding. The end design of the column was found to be important for maximum throughputs. The location of the disperser for best results was found to be just above the packing support and in the packing. Johnson and Bliss(15) made a comprehensive study of spray columns and compared the results with performances of packed and perforated plate columns.

Row, et. al.(22) studied the characteristics and performance of a nine-inch column packed with Raschig rings and Berl saddles. High flow rates for the continuous phase were found to have a profound influence on the over-all HTU. The tower packed with Raschig rings was found to have a greater capacity than when packed with Berl saddles.

Comings and Briggs(8) conducted experiments on four wetted-wall columns and four packed columns. Wetted-wall columns one-inch in diameter were found to give over-all coefficients twice those in packed columns and also were found to have capacities per unit of column cross-section as much as ten times those of the packed columns. Thus, a one-inch wetted-wall column can handle the same capacity as a three-inch packed tower, but it must be five times

6.

as high. The velocity of the dispersed phase was found to have the greater effect on the over-all coefficient and caused the same percentage variation in the film resistance of both phases. The velocity of the continuous phase was found to have a smaller effect, which was again the same in both phases. End effects may cause a four-fold change in the extraction capacity for a given volume of packing. This effect was found to be larger than that caused by changes in the dispersed phase velocity. A general tendency for larger and longer towers to give smaller coefficients was noticed.

Colburn and Welsh(7) made an attempt to determine individual film transfer units. The investigation was conducted with a column packed with 1/2-inch clay Raschig rings. The film HTU of the dis-continuous phase was found to be practically independent of either flow rate, while the film HTU of the continuous phase was found to increase with an increase in the discontinuous phase rate. The results indicated that the stream which is larger in amount should be made the discontinuous phase. A new method of interpreting over-all transfer data, obtained in similar packings, was obtained.

Gloyer(13) investigated the extraction of vegetable oils with furfural in a nine-foot high by two-inch diameter laboratory column packed with 1/2-inch Raschig rings and 1/2-inch Berl saddles. A series of runs was also conducted on a 22-inch diameter column at 64- and 87-feet heights. The results were that the longer column gave more efficient fractionation. The effect of column diameter was also determined using the data from 2-inch, 22-inch, and 66-inch diameter columns. The height per stage of separation was considerably

less for the 2-inch column than for the larger columns. The height
per stage was approximately the same for the 22- and 66-inch columns.
Therefore, the 2-inch column was more efficient per unit height and
it is necessary to have longer columns when the diameter is 22 inches
or greater in order to obtain the same degree of fractionation as
with the 2-inch column.

Visvanathan and Nandi(28) investigated the performance of an
air-agitated column for comparison with spray and packed columns.
It was ascertained that the order of efficiencies (decreasing values
of Ka) for various types of packing were as follows: With nitrobenzene
dispersed, (1) Lessing rings, (2) glass wool, (3) Raschig rings; with
aqueous acid dispersed, the order was (1) glass wool, (2) Lessing
rings, and (3) Raschig rings.

Laddha and Smith(18) investigated the individual film transfer
resistances in the systems, isobutyraldehyde-water and pentanol-water.
The HTU for the dispersed phase was found to be substantially constant
with changing rates of flow of either continuous or dispersed liquids.

Geankoplis and Hixson(12) determined the end-effects in a spray
tower for the extraction of ferric chloride from aqueous hydrochloric
acid with isopropyl ether using an internal sampling device. Contrary
to previous experience, the entire end-effect was produced by the
continuous inlet.

Morello and Beckmann(20) investigated the system diethylamine-
water-toluene using a 1.375-inch column packed with 4mm glass beads at
three different temperatures. The HTU for the water film was found to
be essentially zero, while that for the toluene film decreased with an
increase in temperature.

Claffey, et. al(6), investigating the extraction of water-
nicotine solutions by kerosene, found that the coefficient decreased
with an increase in temperature at all concentrations. At constant
temperature the coefficient increased with an increase in concen-
tration to a maximum and then decreased with further increase in
concentration. The extraction was 8 percent higher when the saddle
packing used was loosely packed. The saddle packing gave 5 percent
higher extraction than did the same size ring packing.

Scheibel(23, 25) reported efficiencies of from 10 to 100 percent
for a 1-inch diameter agitated packed column for the separation of
ethanol from water by the double solvent systems glycol-o-xylene
and glycol-methyl-n-amyl ketone, as the packed height varied from
1 to 8 inches. Scheibel and Karr(24), using a similar column but of
12-inch diameter, reported that stage efficiencies may reach 100
percent. Acetone and acetic acid were extracted with the solvent
pairs, water-methyl isobutyl ketone and water-o-xylene. The through-
put per unit cross-section of the 12-inch column at flooding was found
to be several times that in a 1-inch column.

Breckenfeld and Wilke(5) investigated flooding in a 2.6-inch
tower packed with 1/2-inch saddles and 1/4-inch carbon rings, using
a variety of liquid pairs in order to vary the physical properties
of the liquid pairs. Interfacial tension was introduced into a
flooding correlation for the first time. The correlation appeared
to fit the data of the authors and other previous workers.

Ballard and Piret(2) used columns of 2.03- and 3.75-inch
diameter with 1/4- and 1/2-inch ring packing. A variety of liquids

was used with water. For water as the dispersed phase, the flooding phenomena observed coincided with those found by previous investigators. However, with the water as the continuous phase, a new phenomenon -- a transition from normal operation to a type of flow involving considerable coalescence -- was observed. A correlation similar to that for gas-liquid flooding rates was derived.

Elgin and Foust(10) proposed that the same basic relationship exists for liquid-liquid extraction as that for solid particles falling through a countercurrently flowing liquid. The velocity of individual drops at flooding was related to the dispersed phase holdup, and the application of holdup data from fluidized beds of solids to the estimation of the spray tower flooding rates was shown.

Crawford and Wilke(9) reported data for limiting flows of various liquids in a 12-inch diameter tower packed with 1/2-, 1-, and 1-1/2-inch carbon Raschig rings. Comparison of the correlation obtained by Breckenfeld and Wilke(5) with data on fluids of high viscosity and large density difference in 1- and 1-1/2-inch packings gave favorable agreement. A new correlation was developed by analogy to the theory of settling spheres which gave good agreement with the data for columns packed with rings of 1/4- to 1/2-inch nominal diameter and 1/2-inch Berl saddles and clay spheres.

STATEMENT OF THE PROBLEM

The distribution studies made by Garwin and Hixson(11) were under equilibrium conditions and no attempt was made to observe or predict extraction capacity coefficients which might be expected when the extraction is carried out countercurrently in commercial type equipment. The extraction studies made by Kylander and Garwin(16) established capacity coefficients and heights of a transfer unit for $CoCl_2$ by countercurrent extraction with the systems: $CoCl_2$ - HCl - water - capryl alcohol and $NiCl_2$ - $CoCl_2$ - HCl - water - capryl alcohol in a spray column and with the alcohol phase dispersed. The present work was undertaken to determine the capacity coefficients $K_A a$ and $K_W a$ and heights of a transfer unit $(HTU)_{OA}$ and $(HTU)_{OW}$ for $CoCl_2$ with the system $NiCl_2$ - $CoCl_2$ - HCl - water - capryl alcohol by countercurrent extraction in a packed column with the alcohol phase dispersed.

It was thought advisable to conduct a series of preliminary runs (Series I) in order to become familiar with the column operation and to obtain a few flooding velocities. Series II was conducted to obtain data for the extraction of $CoCl_2$ from an aqueous solution containing $NiCl_2$, $CoCl_2$, and HCl with capryl alcohol. Series III was concerned with the recovery of $CoCl_2$ from the alcohol extract of Series II by extraction with an HCl - water mixture of approximately 23 wt. % HCl.

APPARATUS

A column with an over-all length of $82\frac{1}{2}$ inches was constructed of standard Pyrex glass pipe fittings. The packed section consisted of 8 reducing tees (2 inch to 1 inch) giving a total packed height of 72 inches. The side outlets of the tees were rotated 120° progressively from bottom to top. The diameter of the packed section was 2 inches. The one-inch side outlet of each tee was fitted with a rubber stopper containing a 3mm o.d. glass sampling tube. The stopper and the tube were inserted from the inside and forced out until the sampling tube was flush with the inside wall of the tee.

The end sections and disperser were constructed according to the suggestions of Blanding and Elgin(3) and Johnson and Bliss(15). They were constructed from Plexiglas and Pyrex glass pipe reducers. For more complete details, see figures 3, 4, 5, and 6.

13.

COLUMN DETAILS

FIGURE 3.

$\frac{7}{64}$" Drill

TOP PLATE CEMENTED
IN PLACE IN POSITION
& DISSOLVED IN ETHYLENE
DICHLORIDE.

$2\frac{3}{8}$"

$\frac{1}{8}$"

$2\frac{1}{8}$"

$1\frac{1}{6}$"

SECTION A-A

DIAGRAM OF EXTRACTION COLUMN
AND AUXILIARIES
FIGURE 5.
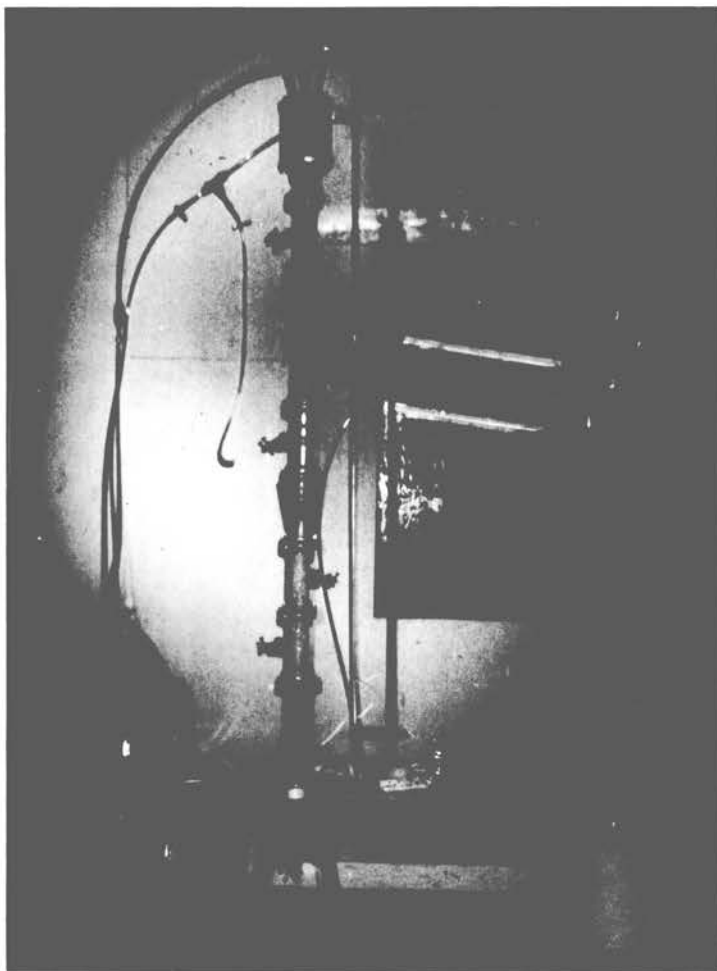
Figure 6.
Photograph of the Equipment in Operation

AUXILIARIES

Storage vessels for the aqueous feed, solvent, extract, and raffinate were 12-gallon Pyrex carboys.

Pressure for moving the aqueous feed and solvent was supplied by a cylinder of compressed nitrogen. The reduction of the pressure from the cylinder pressure to 6 or 9 pounds psig was accomplished by means of two regulators commonly used in oxygen service. The pressure regulators were protected from the hydrochloric acid vapor by the use of a wire basket filled with Ascarite and placed in the manifold between the feed vessels and the regulators. A U-tube manometer, with approximately 16 inches of mercury, was used as a safety valve.

Flow rates of the feed streams were indicated by the pressure drop across capillary tubes located in the lines. Inclined-tube manometers were used to indicate the amount of this pressure differential. Control of the flow was accomplished by adjusting a screw clamp upon a short section of Tygon tubing. This gave, in effect, a diaphram valve.

The interface level in the settling chamber was controlled by the vertical positioning of a vented tee in the raffinate line.

The extract and raffinate lines were vented to prevent siphoning tendencies when the lines were full of liquid.

All transfer lines were of 7/16-inch o.d. Saran tubing with fittings of Saran, glass, rubber, and 3/8-inch i.d. Tygon tubing. Tygon was used principally for the section of the raffinate line from the bottom of the column to the vented tee.

The packing material was 1/4-inch white porcelain Raschig rings manufactured by Maurice A. Knight. Packing characteristics are listed in Table I.

A sight glass constructed from 3mm o.d. glass tubing and connected to the column with Tygon was placed between the alcohol outlet and the first sampling point at the top of the column to facilitate the location of the interface during 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.

Chemical grade capryl alcohol (2-octanol) obtained from the Hardesty Chemical Company was used for Series II and Series III. The major impurity was no more than 2.0% methyl-hexyl-ketone.

Tap water was used for Series I, and distilled water was used for Series II and Series III.

Concentrated hydrochloric acid of tested purity, manufactured by Mallinckrodt, was used to adjust the HCl concentration of the alcohol and aqueous phases to the proper values.

Eimer & Amend's tested purity $CoCl_2 \cdot 6H_2O$ and $NiCl_2 \cdot 6H_2O$ were used in making up the aqueous phases to the proper values.

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

PROCEDURE FOR SERIES I

The column was packed from the bottom to the midpoint of the disperser with 1/2-inch Berl saddles. Then the column was filled with water and the 1/4-inch Raschig rings dumped in a few at a time on top of the Berl saddles. The settling chamber was placed in position and the transfer lines connected. Then the column was flushed several times with water and drained.

Calibration curves for the alcohol and water metering devices were made by observing the time required for 100 ml. of fluid to be discharged through the transfer lines at a given pressure differential across the capillary tubing. Volumetric flow rates expressed as cubic feet per hour were calculated and plotted versus the manometer reading (see Figure 7). The flowmeters were used only as an indication of constancy of flow and the calibration values, therefore, were not used directly.

Starting with the column and the transfer lines empty, the water and alcohol carboys were filled and a pressure of 9 psig was applied above the liquids. The transfer lines were filled by opening the control valves momentarily. The alcohol rate was maintained at a low value while filling the column with water in order to prevent the more dense phase from displacing the alcohol in the disperser. When the column was full, the water rate was set at the desired value and the alcohol rate increased by small amounts at regular intervals until flooding occurred. Sufficient time was allowed for attainment of steady state between changes in the alcohol rate and the interface was maintained at a constant level by positioning of the vented tee in the raffinate line.

Flooding was taken as the condition where a layer of dispersed phase first appeared below the level of the 1/4-inch packing. This definition is the same as that of Breckenfeld and Wilke(5). Upon attainment of flooding, the alcohol rate was reduced and then increased by very slight amounts until the flooding point was again reached. After establishing the reproducibility of the flooding point, the alcohol rate was reduced to very slightly below flooding and the actual volumetric flow rate obtained by noting the time required for a definite volume to be discharged from the column. Several checks were taken and the average recorded.

Upon completion of the run, the alcohol rate was reduced and another water rate set. The foregoing procedure was then repeated for other flooding points.

PROCEDURE FOR SERIES II AND SERIES III

The procedures for Series II and Series III were the same as for Series I with the only exception being the nature of the solutions used. Series II was concerned with the extraction of $CoCl_2$ from an aqueous solution containing $NiCl_2$, $CoCl_2$, and HCl by contacting with capryl alcohol. Series III consisted of recovering the $CoCl_2$ from the alcohol extract of Series II by contacting the alcohol phase with an HCl - water mixture of approximately 23 wt. % HCl.

Starting with the column and transfer lines empty, a pressure of 9 psig was applied to the bottles containing the inlet liquids. The control valves were then opened slightly and the transfer lines filled. The water valve was left open until a slight layer of aqueous phase formed in the bottom of the column, then the alcohol valve was set at a maximum rate until three of the tee sections were filled with the alcohol phase. The alcohol rate was then reduced to a minimum and the water increased to a maximum until the column was completely filled, at which time the water and alcohol rates were set at the desired values. The initial layer of alcohol was found to facilitate the establishment of a constant interface level early in the operation of the column. The flow rates were checked by recording the time required for 100 ml. to 200 ml. of solution to be discharged from the column, and the control valves of the inlet streams were adjusted until the desired rates were obtained.

During the initial runs, samples of the outlet streams were taken after the first, second, third, and fourth changes of the continuous

phase to determine the time required for steady-state to be established. After four changes, samples were taken of the continuous phase at the eight intermediate points of the column. It was found that two complete changes of the continuous phase (based on the empty column) allowed sufficient time for the establishment of equilibrium.

Upon completion of a run, a new alcohol rate was set and sufficient time allowed for two complete changes of the continuous phase to occur. Samples of the outlet phases and of the continuous phase at the intermediate points were then taken. Since the available quantity of the inlet solutions was sufficient for several runs, samples of the inlet streams were taken before the initial run with each batch and used for successive runs with these mixtures.

ANALYTICAL METHODS

A. Aqueous Phase

1. **Total Chloride.** It was important to know the total chloride content as well as the salt concentrations of the aqueous phase since the distribution coefficients for the salts are given by Garwin and Hixson(11) as a function of the total chloride concentration. The Volhard method as recommended by Kylander(17) was chosen for the total chloride determination.

Samples of all runs for Series II and Series III were analyzed as follows: A 5 ml. portion of the sample was diluted to 100 ml., a 5 ml. aliquot was pipetted into a 125 ml. Erlenmeyer flask and 2 ml. to 3 ml. of boiled concentrated nitric acid was added. Sufficient standard $AgNO_3$ was added from a burette to completely precipitate the chloride, and provide a small excess. Two milliliters of nitrobenzene were added and the resulting mixture shaken vigorously to completely coagulate the AgCl precipitate. The precipitate was washed down from the sides of the flask and one ml. of saturated ferric ammonium sulfate was added. The excess $AgNO_3$ was then determined by titration with standard KCNS until a brownish tinge, indicating the formation of the iron-thiocyanate complex, marked the end-point.

2. **Total Salts.** A 25 ml. aliquot of the solution prepared from the sample for the total chloride analysis was pipetted into a 50 ml. Erlenmeyer flask and evaporated to dryness at temperatures below 105°C. The residue was dissolved in distilled water, transferred to a volumetric flask, and diluted to 100 ml.

A 25 ml. aliquot was pipetted into a 125 ml. Erlenmeyer flask and analyzed for chloride content in the same manner as in the total chloride analysis.

3. Nickel. The method described by Kylander(17) was found very satisfactory for the determination of nickel. The procedure used was as follows: A 25 ml. aliquot of the solution prepared from the sample for the total chloride analysis was pipetted into a 400 ml. beaker and diluted to approximately 200 ml. (approximately six times the volume of dimethylglyoxime reagent used). The solution was heated to near boiling, the dimethylglyoxime (0.5 ml. of a 1% solution of dimethylglyoxime in 95% ethyl alcohol for each mg. of total metals present) was added. Concentrated NH_4OH was added dropwise, while stirring, until the red dimethylglyoxime precipitate formed, or the vapors given off turned red litmus blue. The precipitate was allowed to stand over night before being filtered on a weighed sintered-glass-bottom crucible, then washed with hot distilled water and dried in an oven at about 110°C for one hour. The dried precipitate was weighed and the percentage of nickel in the original sample calculated. No nickel was found to be present in the alcohol extracts of Series II.

4. Cobalt. The $CoCl_2$ concentration of the samples taken from the runs of Series II and III was determined as the difference between the total salt concentration and the nickel chloride concentration. The system of Series III did not contain any nickel since the alcohol extracts of Series II gave no trace of nickel.

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

B. Alcohol Phase. The HCl and dissolved salts were washed from the alcohol phase with water. Essentially all of the solutes were transferred to the water phase since they favor this phase at low chloride concentrations.

The washing technique used was as follows: A 25 ml. aliquot of the alcohol phase sample was pipetted into a 200 ml. volumetric flask containing approximately 150 ml. of water. The contents of the flask were shaken vigorously and the phases allowed to separate. Further additions of water were made, with thorough mixing and settling, until the alcohol-water interface reached the 200 ml. mark. Most of the alcohol was decanted and the resulting aqueous solution used for the analyses. The general procedure for the analyses was the same as that for the aqueous phase previously described. Modifications of the procedure appear below:

1. Total Chloride. The total chloride content was determined in order that the HCl concentration of the alcohol phase would be readily available if desired. An aliquot of 5 ml. or 10 ml. of the above aqueous extract was given the same treatment as the aqueous phase samples.

2. Total Salts. A 25 ml. aliquot of the above aqueous extract was dried and processed in the same manner as the aqueous phase samples.

3. Nickel. A 25-150 ml. aliquot of the aqueous extract from above was treated similarly to the aqueous phase samples.

However, the nickel dimethylglyoxime precipitate did not form immediately when the solution was treated with concentrated NH_4OH. The presence of sufficient NH_4OH was indicated by the characteristic red color of the cobalt complex, and also by the change of moist red litmus paper to blue in the vapors above the solution. The samples were allowed to stand for 24 hours, then 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.

INTERFACIAL TENSION MEASUREMENTS

A du Nouy ring tensiometer was used to measure the inter-facial tension of a few selected mixtures. Where samples taken during runs were used, equal volumes of the alcohol and aqueous phases were shaken together in order to attain equilibrium dis-tribution of the solutes. The mixture was poured into the tensiometer dish and allowed to separate into two phases. The measurement was then made and the temperature recorded. The results are tabulated in Table IV.

the first stagnant layer appeared at the disperser section. The
Ballard and Piret correlation gave much closer agreement to the
actual flooding points as shown by Table II. The quantity
$(U_c^{\frac{1}{2}} \neq U_d^{\frac{1}{2}})$ is equal to a constant for the two flooding points.
It was possible to operate the column at a slightly higher rate than
the flood point, but the interface became uncontrollable. During
all flooding runs, the interface was maintained approximately two
to three inches above the top of the weir.

Series II and III. The extraction capacity coefficient curves
of Figures 9 and 10 indicate an increase of Ka as the dispersed
phase rate is increased. Figures 11 and 12 show an increase in the
$(HTU)_{OW}$ for Series II, and $(HTU)_{OW}$ and $(HTU)_{OA}$ for Series III with an
increase in the dispersed phase rate. The $(HTU)_{OA}$ of Series II
remains essentially constant at a range of from 4 to 6 feet. This
agrees very well with the $(HTU)_{OA}$ of approximately 5 feet found by
Kylander and Garwin(16). An $(HTU)_{OA}$ of approximately 5 feet, there-
fore, is suitable for a preliminary design of either a spray or packed
column. Figure 13 is a replot of the $(HTU)_{OA}$ curves of Figures 11 and
12. This figure shows that the transfer of $CoCl_2$ in the recovery runs
of Series III is better than that for the runs of Series II. This
indicates that the transfer is better from the discontinuous to the
continuous phase than from the continuous to the discontinuous phase.
The higher salt concentration levels in Series II over those prevailing
in Series III may be an important factor in this effect.

The results are not as precise as desired. The quantity of $CoCl_2$
transferred was small because of the fact that the alcohol to water

EQUATIONS FOR EXTRACTION CAPACITY COEFFICIENTS

AND HEIGHT OF A TRANSFER UNIT

For solute transfer across a liquid film in extraction, under steady-state conditions, at any point in a continuously functioning apparatus,

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

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

In packed columns the interfacial area is not measurable, and dA is replaced by adV. Assuming that the driving force for mass transfer is linear in mass transfer, equation (1) may be integrated to give the following:

$$N = K_A a \, (\triangle C_A)_{lm} V \qquad (3)$$

or

$$K_A a = \frac{N}{V(\triangle C_A)_{lm}} \qquad (4)$$

N is defined as

$$N = S(L_{A_T} C_{A_T} - L_{A_B} C_{A_B}) \qquad (5)$$

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

$$N = SL_A(C_{A_T} - C_{A_B}) \qquad (6)$$

The over-all height of a transfer unit based on the alcohol phase is:

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

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

RESULTS

Series I flooding determinations are given in Table II.

The calculated values of Ka and HTU for Series II and Series III are given in Table III in the Appendix. This table contains the observed experimental data and all intermediate calculated values from which the capacity coefficients were obtained. The results are plotted as Ka and HTU versus the alcohol phase rate, at a constant water rate. See Figures 9, 10, 11, 12, and 13. It was not possible to calculate the capacity coefficients for Run W1 of Series III since the driving force based upon either of the phases was negative. This is theoretically impossible since the operating line cannot cross the equilibrium curve.

The salt concentrations at intermediate sampling points are shown in Table V. These were not used since the change in concentration from point to point along the column was very small and the capacity coefficients calculated with these values would have been considerably in error.

Table VI gives the maximum percent error in the capacity coefficients resulting from an assumed analytical error of 0.05 ml. in the chloride titration.

DISCUSSION OF RESULTS -- CONCLUSIONS

Series I. A study of the flooding characteristics of the column was made to become familiar with the operation of the column and to obtain additional data to check against the correlations of Breckenfeld and Wilke(5) and Ballard and Piret(2).

Blanding and Elgin found that a certain pair of flow rates, a layer of the dispersed phase appeared below the packing and the column ceased to operate satisfactorily. Breckenfeld and Wilke also found this condition in their investigations. However, Ballard and Piret found three types of flooding to occur, depending upon which phase was dispersed and the physical properties of the liquids. They found that the flooding described by previous investigators (type 1) occurred only with solvents of medium or high density and with systems of high interfacial tension. The second type of operation was found to occur in most of their runs under all conditions of operation. In these runs a gradual transition or phase reversal occurred from dropwise movement of the dispersed organic solvent through the continuous water phase, to a film-wise movement of the water phase over the packing through a predominant solvent phase. The third type of behavior occurred in many of the runs in which the interfacial tension was low. This phenomenon was characterized by surging of the interface and a sudden formation of a layer of the organic solvent near the disperser which then passed on through the packing and out the column. This operation repeated itself periodically.

The transition points defined by Ballard and Piret were below the flooding points found by previous investigations. Crawford and
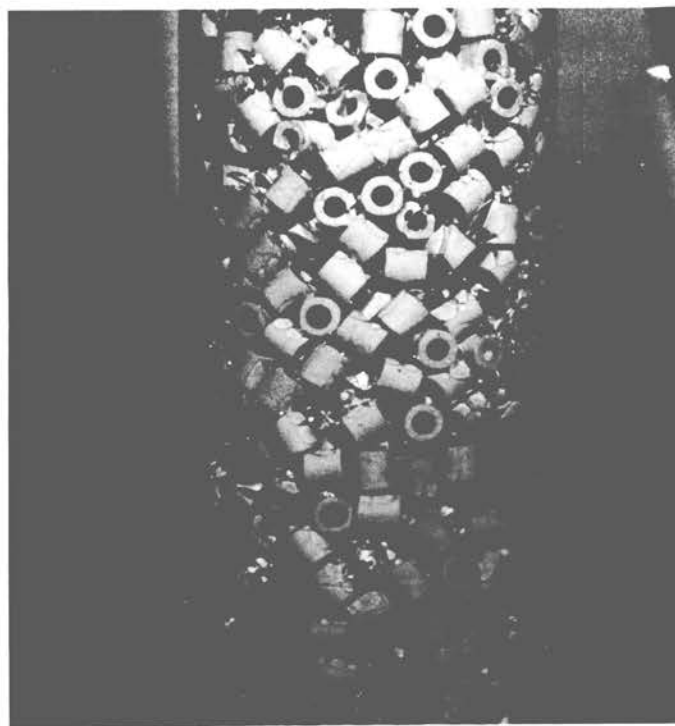
Figure 8.
Appearance of the Column Near Flooding

Wilke(9), in investigating limiting flow through larger packings, calculated transition points with the Ballard and Piret correlation and compared them with the flooding points they themselves obtained, using the criterion of flooding as proposed by Blanding and Elgin. The transition points were for the most part about 40 percent lower than the flooding points.

The type of flooding found in this investigation was similar to the third type found by Ballard and Piret. In approaching the flooding point, the bubble size was noted to increase slightly. An accumulation of bubbles in the more open sections of the packing was noticed as shown by Figure 8. At flooding, a layer of the dispersed alcohol phase formed just above the disperser. This layer increased in thickness to a certain point and then began to pass up the column as a unit. However, it did not pass out of the column as a unit, but decreased in depth and finally disappeared, at which time another layer of solvent had formed at the disperser. This operation was repeated at regular intervals. Since the packed section was 72 inches in length, the packing was able to disperse the solvent layer. The surging of the interface allowed the solvent to disengage itself from the disperser and thus move up into the column. The interfacial tension and density difference was low, as shown in Table II. All flooding determinations were made with alcohol and water previously saturated with respect to each other.

The Breckenfeld and Wilke correlation predicted a limiting flow of the dispersed phase of from 50 to 100 percent higher than that actually obtained, the flood point being defined as the point where
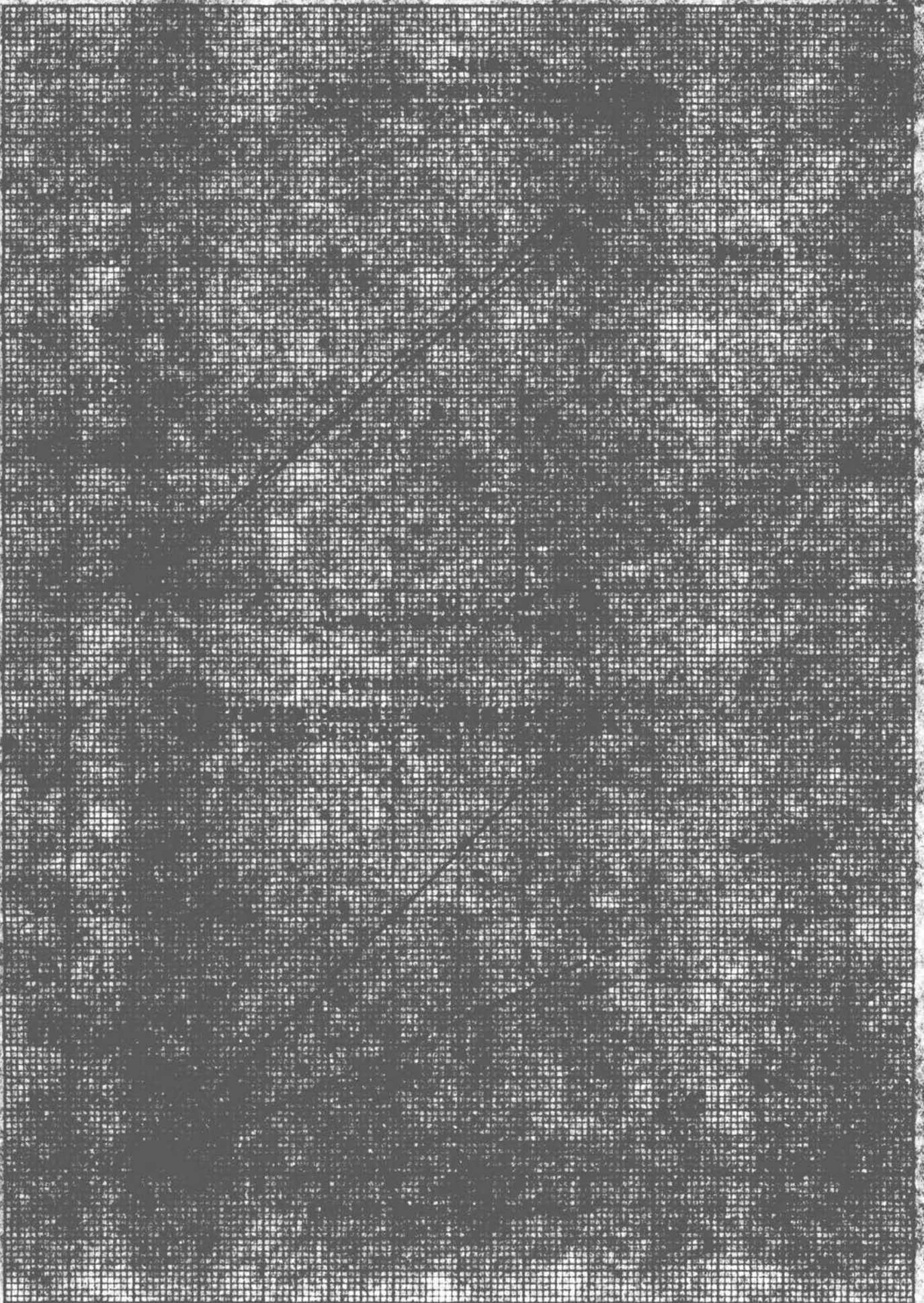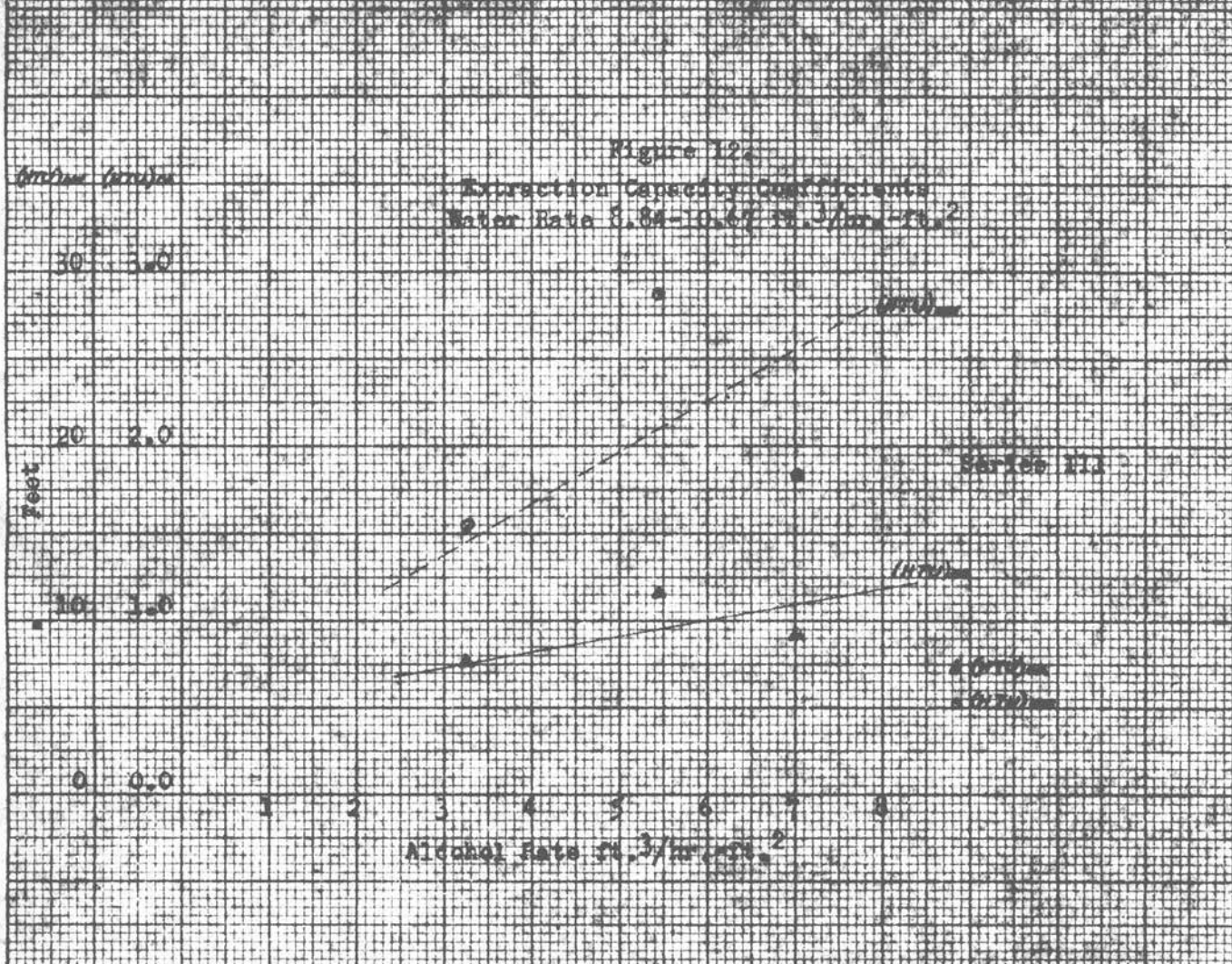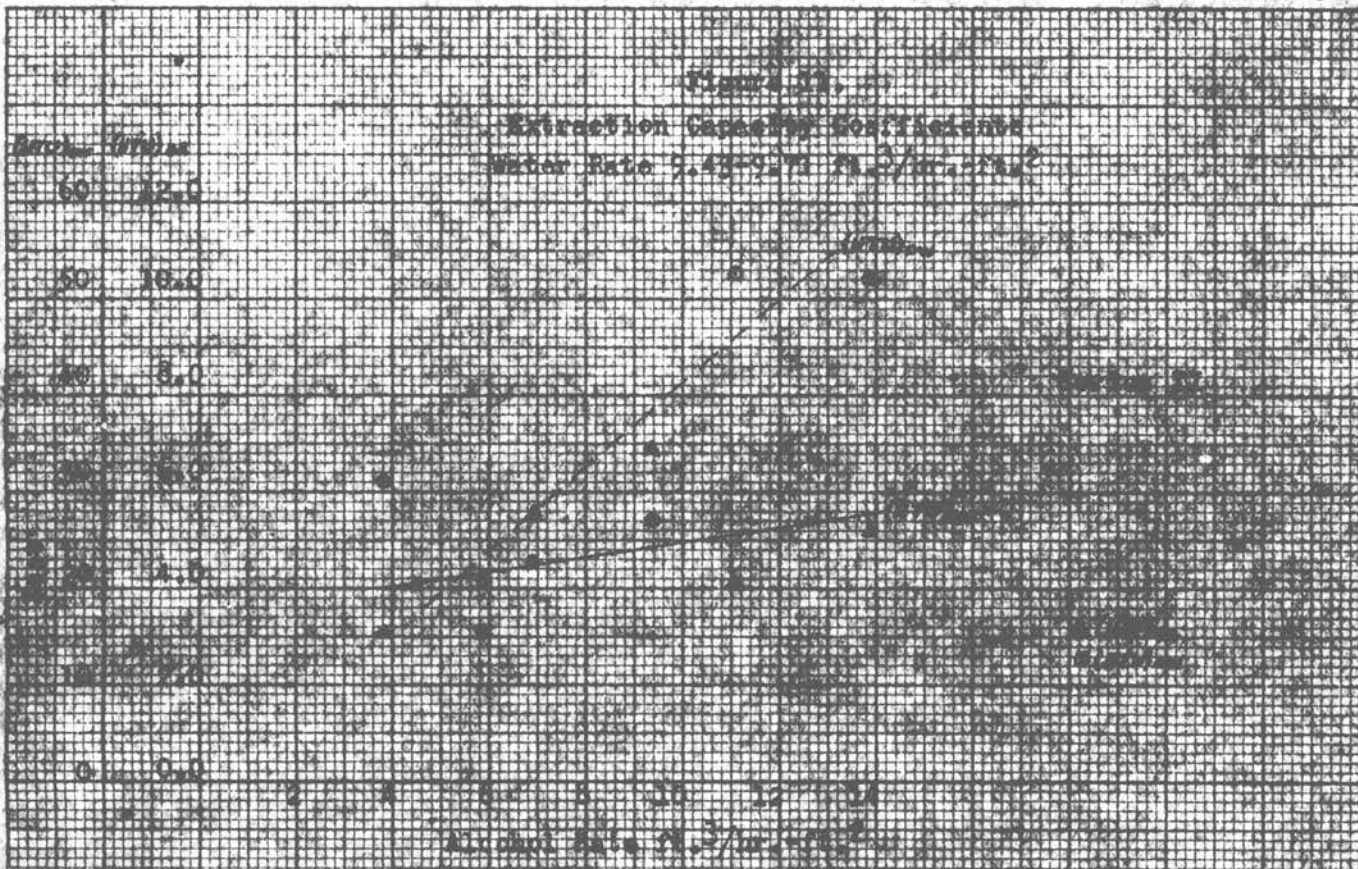
Figure 11.
Extraction Capacity Coefficient
Water Rate 9.45-9.74 M.3/hr.-ft.2

Figure 12.
Extraction Capacity Coefficient
Water Rate 8.84-10.67 M.3/hr.-ft.2

Feet

Alcohol Rate M.3/hr-ft.2
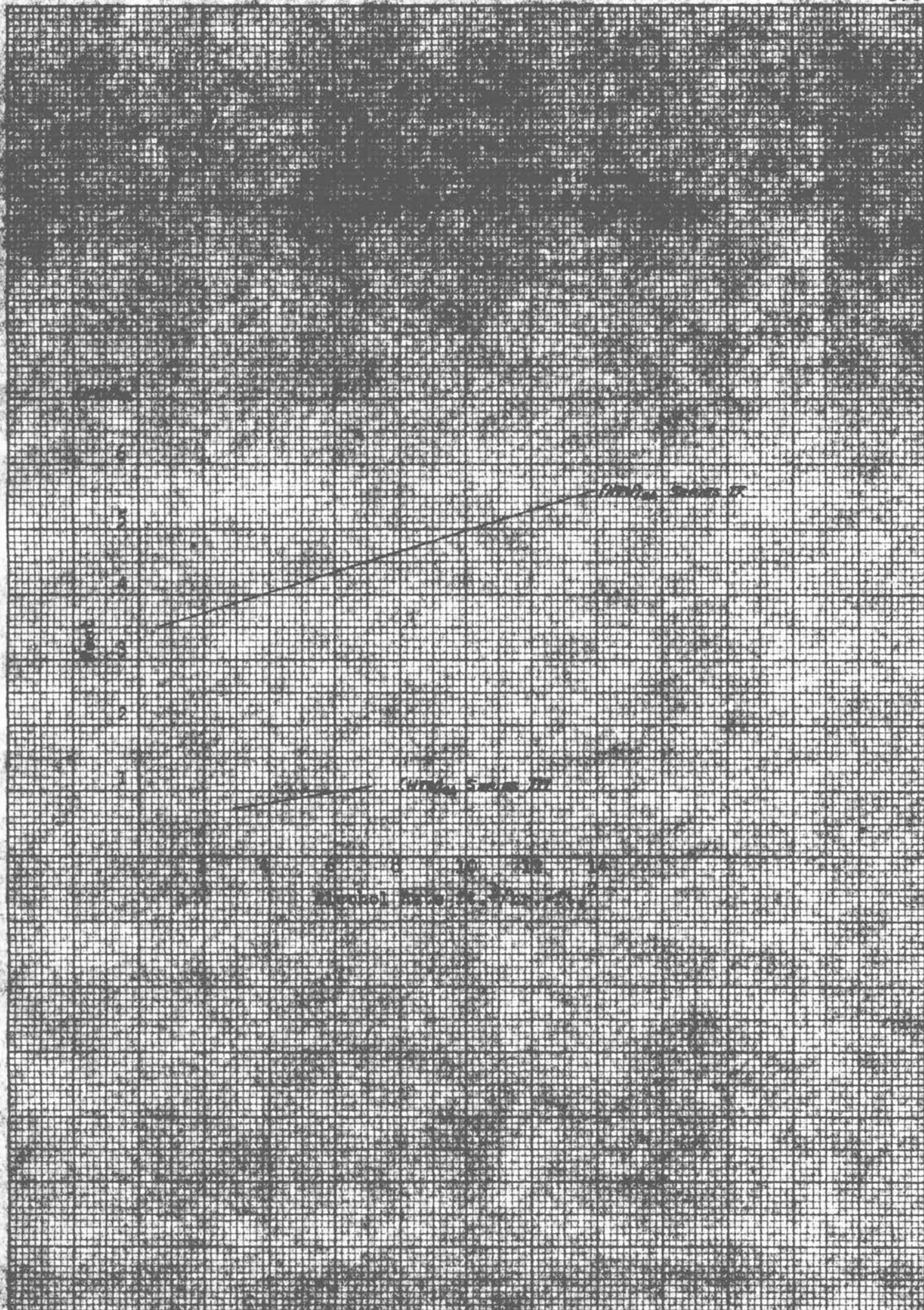
rates studied were not high and the equilibrium distribution tends to favor the aqueous phase. Calculations of the quantity of $CoCl_2$ transferred are obtained from differences in inlet and outlet stream concentrations. Therefore, they are subject to considerable percentage error when such differences are small. It is believed, however, that the data are sufficiently reliable for preliminary design calculations. With the experimental coefficients reported, it is possible to design columns for the separation of $NiCl_2$ and $CoCl_2$, and for the recovery of $CoCl_2$ from the alcohol extract.

SUMMARY

A study was made of the continuous extraction of $CoCl_2$ with capryl alcohol from a solution containing $CoCl_2$ - $NiCl_2$ - HCl - water and the recovery of $CoCl_2$ from the alcohol extract with an HCl - water mixture. The equilibrium distribution data of the salts between the two phases used in the present work are those found by Garwin and Hixson(11).

A column 2-inches i.d. and 82-1/2-inches long, packed with 1/4-inch porcelain Raschig rings to a height of 72 inches, was used for the flooding and extraction studies. The end design and disperser design for the column were similar to those found satisfactory by previous investigators. Flooding was defined as the pair of flow rates at which a layer of the dispersed phase first appeared near the disperser.

For the extraction, the over-all $(HTU)_{OA}$ varied from 4 to 6 feet over the range of liquid rates used. The over-all $(HTU)_{OW}$ varied widely and showed a general increase as the alcohol rate increased. A replotting of the $(HTU)_{OA}$ curves for Series II and III indicated that the transfer of $CoCl_2$ was better from the discontinuous to the continuous phase than from the continuous to the discontinuous phase.

Flooding rates determined for the system capryl alcohol - water were compared with those calculated with the Breckenfeld and Wilke(5) and Ballard and Piret(2) correlations. The actual flooding velocities were found to agree more closely with those predicted by the Ballard and Piret correlation. The operation of the column at flooding was the same as that reported by Ballard and Piret for systems with low interfacial tension and density difference.

RECOMMENDATIONS

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

1. Development of a volumetric method of analysis for cobalt or nickel in solutions containing both salts.

2. Investigation of higher alcohol to water ratios.

3. Determination of extraction capacities with other types of packing and packing material.

4. Inversion of the extraction column so that operation with the water phase dispersed may be studied.

APPENDIX

TABLE I

Packing Characteristics[1]

Size of packing, inch	0.25
Type of material	Unglazed Porcelain
Apparent density, #/cu.ft.	139.5
Sizes	
Outside diameter, inch	0.25
Inside diameter, inch	0.125
Length, inch	0.25
Surface area factor, A, sq.ft./cu.ft.	202.0
Fractional free volume, F	0.559

- - - -

TABLE II

Limiting Flows

Run	Water Rate (U_c) ft.^{3}/hr.-ft.^{2}	Alcohol Rate (U_d) ft.^{3}/hr.-ft.^{2}	U_d Calculated by Recent Correlations (5)	(2)	$(U_c^{\frac{1}{2}} + U_d^{\frac{1}{2}})$
F-1	10.3	24.5	38.9	16.7	8.1
F-2	19.5	7.98	22.3	9.74	7.7

Temperature = 29.5°C

σ = 11.1 dynes/cm.

ρc = 1.000 g./ml.

ρd = 0.921 g./ml.

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1 Obtained from Maurice A. Knight, Akron, Ohio

TABLE III

Run	Flow Rate Cu.Ft./Hr. Alcohol (1)	Water (2)	Cu.Ft./Hr.-Sq.Ft. Alcohol (3)	Water (4)	Specific Gravity Alcohol In (5)	Out (6)	Water In (7)	Out (8)	Salt Concentration - Water Phase In Weight Percent MeCl₂ ᵃ (9)	NiCl₂ (10)	CoCl₂ (11)	# Salt/Cu.Ft. MeCl₂ ᵃ (12)	NiCl₂ (13)	CoCl₂ (14)	Salt Concentration - Water Phase Out Weight Percent MeCl₂ ᵃ (15)	NiCl₂ (16)	CoCl₂ (17)	# Salt/Cu.Ft. MeCl₂ ᵃ (18)	NiCl₂ (19)	CoCl₂ (20)
Series II																				
Ex 1	0.0820	0.206	3.76	9.43	0.872	0.880	1.190	1.188	7.79	3.48	4.31	5.78	2.58	3.20	7.56	3.50	4.06	5.60	2.60	3.00
2	0.130	0.209	5.94	9.57	0.872	0.879	1.190	1.188	7.79	3.48	4.31	5.78	2.58	3.20	7.39	3.50	3.89	5.48	2.60	2.88
3	0.151	0.209	6.92	9.57	0.876	0.874	1.189	1.179	8.66	3.07	5.59	6.43	2.28	4.15	8.12	3.04	5.08	5.97	2.24	3.73
4	0.205	0.216	9.39	9.89	0.876	0.876	1.189	1.184	8.66	3.07	5.59	6.43	2.28	4.15	8.21	3.03	5.18	6.07	2.24	3.83
5	0.243	0.210	11.13	9.62	0.876	0.879	1.189	1.184	8.66	3.07	5.59	6.43	2.28	4.15	7.67	3.01	4.66	5.67	2.23	3.44
6	0.304	0.212	13.92	9.71	0.876	0.878	1.189	1.184	8.66	3.07	5.59	6.43	2.28	4.15	7.82	3.01	4.81	5.78	2.23	3.55
Series III																				
W 1	0.0385	0.205	1.76	9.38	0.869	0.866	1.121	1.123	0.139	0.000	0.139	0.096	0.000	0.096	1.08	0.000	1.08	0.758	0.000	0.758
2	0.0707	0.193	3.24	8.84	0.869	0.868	1.120	1.120	0.139	0.000	0.139	0.096	0.000	0.096	1.25	0.000	1.25	0.874	0.000	0.874
3	0.119	0.226	5.45	10.35	0.882	0.875	1.128	1.133	0.000	0.000	0.000	0.000	0.000	0.000	0.436	0.000	0.436	0.308	0.000	0.308
4	0.154	0.233	7.05	10.67	0.882	0.874	1.128	1.134	0.000	0.000	0.000	0.000	0.000	0.000	0.667	0.000	0.667	0.472	0.000	0.472

Run	Salt Concentration - Alcohol Phase In Weight Percent MeCl₂ ᵃ (21)	NiCl₂ (22)	CoCl₂ (23)	# Salt/Cu.Ft. MeCl₂ ᵃ (24)	NiCl₂ (25)	CoCl₂ (26)	Salt Concentration - Alcohol Phase Out Weight Percent MeCl₂ ᵃ (27)	NiCl₂ (28)	CoCl₂ (29)	# Salt/Cu.Ft. MeCl₂ ᵃ (30)	NiCl₂ (31)	CoCl₂ (32)	# MeCl₂ Transferred Per Hour Water Phase (33)	Alcohol Phase (34)	Average (35)	% Total Deviation (36)	# CoCl₂ Transferred Per Hour Water Phase (37)	Alcohol Phase (38)	Average (39)	% Total Deviation (40)
Series II																				
Ex 1	0.000	0.000	0.000	0.000	0.000	0.000	1.29	0.000	1.29	0.708	0.000	0.708	0.0371	0.0581	0.0476	− 44.2	0.0412	0.0581	0.0497	− 34.1
2	0.000	0.000	0.000	0.000	0.000	0.000	1.21	0.000	1.21	0.664	0.000	0.664	0.0627	0.0864	0.0746	− 31.8	0.0877	0.0864	0.0871	+ 1.49
3	0.0305	0.000	0.0305	0.0167	0.000	0.0167	0.848	0.000	0.848	0.463	0.000	0.463	0.0962	0.0673	0.0818	+ 35.3	0.0877	0.0673	0.0775	+ 26.3
4	0.0305	0.000	0.0305	0.0167	0.000	0.0167	0.890	0.000	0.890	0.492	0.000	0.492	0.0777	0.0973	0.0875	− 22.4	0.0692	0.0973	0.0833	− 33.7
5	0.0305	0.000	0.0305	0.0167	0.000	0.0167	0.991	0.000	0.991	0.544	0.000	0.544	0.160	0.128	0.144	+ 29.2	0.151	0.128	0.140	+ 16.4
6	0.0305	0.000	0.0305	0.0167	0.000	0.0167	0.974	0.000	0.974	0.534	0.000	0.534	0.138	0.157	0.148	− 12.8	0.127	0.157	0.142	− 21.1
Series III																				
W 1	1.58	0.000	1.58	0.858	0.000	0.858	0.0383	0.000	0.0383	0.0205	0.000	0.0205	0.136	0.0322	0.084	+124	0.136	0.0322	0.084	+ 124
2	1.58	0.000	1.58	0.858	0.000	0.858	0.0465	0.000	0.0465	0.025	0.000	0.025	0.150	0.0588	0.105	+86.7	0.150	0.0588	0.105	+ 86.7
3	1.03	0.000	1.03	0.567	0.000	0.567	0.0103	0.000	0.0103	0.0056	0.000	0.0056	0.0697	0.0668	0.0683	+ 4.24	0.0697	0.0668	0.0683	+ 4.24
4	1.03	0.000	1.03	0.567	0.000	0.567	0.0088	0.000	0.0088	0.0048	0.000	0.0048	0.110	0.0866	0.0985	+ 23.4	0.110	0.0866	0.0985	+ 23.4

TABLE III (Cont.)

% Cl Top (In) (41)	K (42)	% Cl Bottom (Out) (43)	K (44)	Wt% Top (Out) (45)	Wt% Bottom (In) (46)	#/Cu.Ft. Top (Out) (47)	#/Cu.Ft. Bottom (In) (48)	ΔC Bottom (49)	ΔC Top (50)	ΔC Log Mean (51)	K_A^a (52)	(HTU)$_{OA}$ Ft. (53)	Wt% Top (In) (54)	Wt% Bottom (Out) (55)	#/Cu.Ft. Top (In) (56)	#/Cu.Ft. Bottom (Out) (57)	ΔC Top (58)	ΔC Bottom (59)	ΔC Log Mean (60)	K_W^a (61)	(HTU)$_{OW}$ Ft. (62)
47	0.342	26.26	0.330	1.47	1.34	0.808	0.730	0.730	0.100	0.317	1.20	3.14	3.77	0.000	2.83	0.000	0.370	3.00	1.26	0.301	31.4
47	0.342	26.18	0.327	1.47	1.27	0.807	0.692	0.692	0.143	0.348	1.91	3.11	3.54	0.000	2.65	0.000	0.550	2.88	1.40	0.469	20.4
98	0.253	24.98	0.253	1.42	1.29	0.775	0.705	0.688	0.312	0.477	1.24	5.58	3.36	0.066	2.50	0.0478	1.65	3.24	2.46	0.241	23.0
98	0.253	25.08	0.258	1.42	1.34	0.776	0.733	0.716	0.284	0.467	1.36	6.91	3.52	0.0647	2.64	0.0468	1.51	3.36	2.32	0.274	27.1
98	0.253	24.83	0.243	1.42	1.13	0.779	0.618	0.601	0.235	0.391	2.73	4.07	3.92	0.0683	2.94	0.0494	1.21	2.95	1.95	0.547	52.6
98	0.253	24.92	0.248	1.42	1.19	0.778	0.651	0.634	0.244	0.408	2.65	5.25	3.85	0.0673	2.89	0.0488	1.26	3.06	2.01	0.538	52.3
58	0.299	25.20	0.221	0.0416	0.239	0.0361	0.207	0.651	-0.016	---	---	---	0.128	6.92	0.09	5.13	-0.006	4.37	---	---	---
66	0.192	24.11	0.162	0.0267	0.202	0.0232	0.176	0.682	0.002	0.192	4.18	0.775	0.244	9.44	0.171	7.14	0.075	6.27	1.42	0.57	15.5
18	0.220	24.98	0.209	0.000	0.091	0.000	0.0795	0.487	0.0056	0.111	4.67	1.17	0.0468	4.92	0.033	3.69	0.033	3.38	1.44	0.36	28.8
09	0.216	25.04	0.212	0.000	0.141	0.000	0.124	0.443	0.0048	0.099	7.63	0.92	0.0407	4.86	0.029	3.55	0.029	3.08	1.29	0.58	18.4

Column groups:
- % Cl in Water Phase & Corresponding K: Top (In) [% Cl (41), K (42)], Bottom (Out) [% Cl (43), K (44)]
- Equilibrium CoCl2 Concentration in Alcohol [b]: Weight % [Top (Out) (45), Bottom (In) (46)], #/Cu. Ft. [Top (Out) (47), Bottom (In) (48)]
- ΔC - # CoCl2/Cu. Ft. Based on Alcohol Phase Conc.: Bottom (49), Top (50), Log Mean (51)
- K_A^a #/Hr. Cu.Ft.-#/Cu.Ft. (52)
- (HTU)$_{OA}$ Ft. (53)
- Equilibrium CoCl2 Concentration in Water Phase [c]: Weight % [Top(In) (54), Bottom(Out) (55)], #/Cu. Ft. [Top(In) (56), Bottom(Out) (57)]
- ΔC - #CoCl2/Cu.Ft. Based on Water Phase Concentration: Top (58), Bottom (59), Log Mean (60)
- K_W^a #/Hr. Cu.Ft.-#/Cu.Ft. (61)
- (HTU)$_{OW}$ Ft. (62)

Notes:

a. $MeCl_2 = CoCl_2 + NiCl_2$

b. Specific gravity of the equilibrium alcohol phase is assumed to be equal to that actually measured under steady-state conditions of operation (see columns 5 & 6) - used for calculation of columns 47 & 48.

c. Specific gravity of the water phase at equilibrium is assumed as follows:

Series II		Series III	
Weight % $CoCl_2$	Specific Gravity	Weight % $CoCl_2$	Specific Gravity
4	1.20	9	1.21
3	1.19	7	1.19
2	1.18	6	1.18
1	1.17	5	1.17
0	1.16	4	1.16
		3	1.15
		2	1.14
		1	1.13

TABLE IV

| System | Interfacial Tension | |
	Observed	Literature Values(17)
Refined Grade Capryl Alcohol - Distilled Water	11.1 (29.5°C)	10.5 (30-35°C)
Solvent - Aqueous Feed Run Ex. 1, Equal Volumes Equilibrated	2.37 (29°C)	2.5 (30-35°C) (For a comparable mixture - not identical with actual system used.)

TABLE V

Salt Concentrations at Intermediate Sampling Points

Run	#1 MeCl₂	NiCl₂	CoCl₂	#2 MeCl₂	NiCl₂	CoCl₂	#3 MeCl₂	NiCl₂	CoCl₂	#4 MeCl₂	NiCl₂	CoCl₂	#5 MeCl₂	NiCl₂	CoCl₂	#6 MeCl₂	NiCl₂	CoCl₂	#7 MeCl₂	NiCl₂	CoCl₂	#8 MeCl₂	NiCl₂	CoCl₂
Ex 1	7.64	3.50	4.14	7.64	3.48	4.16	7.71	3.50	4.21	7.92	3.52	4.40	7.85	3.51	4.34	7.76	3.48	4.28	7.85	3.50	4.35	7.92	3.48	4.44
2	8.75	3.61	5.14	7.79	3.52	4.27	No Sample			7.97	3.59	4.38	7.85	3.61	4.24	8.05	3.66	4.39	8.03	3.63	5.60	7.85	3.44	4.41
3	8.32	2.86	5.46	8.32	3.03	5.29	8.36	3.07	5.29	8.45	3.08	5.37	8.61	3.08	5.53	8.61	3.10	5.51	8.70	3.08	5.62	8.61	3.05	5.56
4	8.76	2.93	5.83	8.64	2.69	5.95	8.56	3.02	5.54	8.58	3.04	5.54	8.58	3.06	5.52	8.67	3.06	5.81	8.88	3.08	5.70	8.58	3.02	5.56
5	8.10	3.02	5.08	7.89	3.06	4.83	8.05	3.08	4.97	8.05	3.02	5.03	8.19	3.06	5.13	8.30	3.08	5.22	8.34	3.08	5.26	8.38	3.08	5.30
6	7.45	3.04	4.41	7.69	2.97	4.72	7.94	2.98	4.96	7.69	3.08	4.61	8.10	3.04	5.06	7.99	3.00	4.99	8.19	2.98	5.21	8.19	3.04	5.15
W 1	0.19	0.00	0.19	0.06	0.00	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.23	0.00	0.23	0.00	0.00	0.00
2	0.24	0.00	0.24	0.15	0.00	0.15	0.10	0.00	0.10	0.05	0.00	0.05	0.07	0.00	0.07	0.07	0.00	0.07	0.07	0.00	0.07	0.05	0.00	0.05
3	0.41	0.00	0.41	0.22	0.00	0.22	0.19	0.00	0.19	0.18	0.00	0.18	0.08	0.00	0.08	0.06	0.00	0.06	0.06	0.00	0.06	0.05	0.00	0.05
4	NO INTERMEDIATE SAMPLES TAKEN																							

TABLE VI

Maximum % Error in Capacity Coefficients Resulting from an Assumed Analytical Error of 0.05 ml. in the Chloride Titration.

Column Number (Table III)	Maximum % Error Resulting from that Inherent in Analytical Procedure									
	Ex 1	Ex 2	Ex 3	Ex 4	Ex 5	Ex 6	W 1	W 2	W 3	W 4
(52) K_Aa	30	10	24	19	75	51	--	32	28	18
(53) $(HTU)_{OA}$	23	8	20	16	300	100	--	25	20	22
(61) K_Wa	22	24	14	11	13	4	--	12	33	50
(62) $(HTU)_{OW}$	18	19	51	23	70	67	--	11	33	50

SAMPLE CALCULATIONS

Run number 3, Series II.

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

$$(12) = \frac{62.4 \times (7) \times (9)}{100} = \frac{62.4 \times 1.189 \times 8.66}{100} = 6.43 \ \#MeCl_2/cu.ft.$$

$$(13) = \frac{62.4 \times (7) \times (10)}{100} = \frac{62.4 \times 1.189 \times 3.07}{100} = 2.28 \ \#NiCl_2/cu.ft.$$

$$(14) = (12) - (13) = 6.43 - 2.28 = 4.15 \ \#CoCl_2/cu.ft.$$

$$(18) = \frac{62.4 \times (8) \times (16)}{100} = \frac{62.4 \times 1.179 \times 8.12}{100} = 5.97 \ \#MeCl_2/cu.ft.$$

$$(19) = \frac{62.4 \times (8) \times (16)}{100} = \frac{62.4 \times 1.179 \times 3.04}{100} = 2.24 \ \#NiCl_2/cu.ft.$$

$$(20) = (18) - (19) = 3.73 \ \#CoCl_2/cu.ft.$$

$$(24) = \frac{62.4 \times (5) \times (21)}{100} = \frac{62.4 \times 0.876 \times 0.0305}{100} = 0.0167 \ \#MeCl_2/cu.ft.$$

$$(25) = \frac{62.4 \times (5) \times (22)}{100} = \frac{62.4 \times 0.876 \times 0.0}{100} = 0.0 \ \#NiCl_2/cu.ft.$$

$$(26) = (24) - (25) = 0.0167 - 0.0 = 0.0167 \ \#CoCl_2/cu.ft.$$

$$(30) = \frac{62.4 \times (6) \times (27)}{100} = \frac{62.4 \times 0.874 \times 0.848}{100} = 0.463 \ \#MeCl_2/cu.ft.$$

$$(31) = \frac{62.4 \times (6) \times (28)}{100} = \frac{62.4 \times 0.874 \times 0.0}{100} = 0.0 \ \#NiCl_2/cu.ft.$$

$$(32) = (30) - (31) = 0.463 - 0.0 = 0.463 \ \#CoCl_2/cu.ft.$$

$$(33) = (2) \times [(12)-(18)] = 0.209 \ [6.43 - 5.97] = 0.0962 \ \#MeCl_2/hr.$$

$$(34) = (1) \times [(30)-(24)] = 0.151 \ [0.463 - 0.0167] = 0.0673 \ \#MeCl_2/hr.$$

$$(35) = \frac{(33) + (34)}{2} = \frac{0.0962 + 0.0673}{2} = 0.0818 \ \#MeCl_2/hr.$$

$$(36) = \frac{(33) - (34)}{(35)} \times 100 = \frac{0.0962 - 0.0673}{0.0818} \times 100 = +35.3\%$$

$$(37) = (2) \times [(14) - (20)] = 0.209 [4.15 - 3.73] = 0.877 \text{ } \#CoCl_2/hr.$$

$$(38) = (1) \times [(32) - (26)] = 0.151 [0.463 - 0.0167] = 0.0673 \text{ } \#CoCl_2/hr.$$

$$(39) = \frac{(37) + (38)}{2} = \frac{0.0877 + 0.0673}{2} = 0.0775 \text{ } \#CoCl_2/hr.$$

$$(40) = \frac{(37) - (38)}{(39)} \times 100 = \frac{0.0877 - 0.0673}{0.0775} \times 100 = +26.3\%$$

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

$$(45) = (11) \times (42) = 5.59 \times 0.253 = 1.42\% \text{ } CoCl_2$$

$$(46) = (17) \times (44) = 5.08 \times 0.253 = 1.29\% \text{ } CoCl_2$$

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.

$$(47) = \frac{62.4 \times (6) \times (45)}{100} = \frac{62.4 \times 0.874 \times 1.42}{100} = 0.775 \text{ } \#CoCl_2/cu.ft.$$

$$(48) = \frac{62.4 \times (5) \times (46)}{100} = \frac{62.4 \times 0.876 \times 1.29}{100} = 0.705 \text{ } \#CoCl_2/cu.ft.$$

$$(49) = (48) - (26) = 0.705 - 0.0167 = 0.688 \text{ } \#CoCl_2/cu.ft.$$

$$(50) = (47) - (32) = 0.775 - 0.463 = 0.312 \text{ } \#CoCl_2/cu.ft.$$

$$(51) = \frac{(49) - (50)}{\ln \frac{(49)}{(50)}} = \frac{0.688 - 0.312}{\ln \frac{0.688}{0.312}} = 0.477 \text{ } \#CoCl_2/cu.ft.$$

The effective tower volume is 0.131 cu.ft.

$$(52) = \frac{(39)}{0.131 \times (51)} = \frac{0.0775}{0.131 \times 0.477} = 1.24 \frac{\#CoCl_2/hr.}{(cu.ft.)(\#/cu.ft.)}$$

$(53) = \dfrac{(3)}{(52)} = \dfrac{6.92}{1.24} = 5.58$ feet

$(54) = \dfrac{(29)}{(42)} = \dfrac{0.848}{0.253} = 3.36\%\ CoCl_2$

$(55) = \dfrac{(23)}{(44)} = \dfrac{0.0167}{0.253} = 0.066\%\ CoCl_2$

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

$(56) = \dfrac{62.4 \times sp.gr. \times (54)}{100} = \dfrac{62.4 \times 1.19 \times 3.36}{100} = 2.50\ \#CoCl_2/cu.ft.$

$(57) = \dfrac{62.4 \times sp.gr. \times (55)}{100} = \dfrac{62.4 \times 1.16 \times 0.066}{100} = 0.0478\ \#CoCl_2/cu.ft.$

$(58) = (14) - (56) = 4.15 - 2.50 = 1.65\ \#CoCl_2/cu.ft.$

$(59) = (20) - (57) = 3.73 - 0.0478 = 3.24\ \#CoCl_2/cu.ft.$

$(60) = \dfrac{(59) - (58)}{\ln \dfrac{(59)}{(58)}} = \dfrac{3.24 - 1.65}{\ln \dfrac{3.24}{1.65}} = 2.46\ \#CoCl_2/cu.ft.$

$(61) = \dfrac{(39)}{0.131 \times (60)} = \dfrac{0.0775}{0.131 \times 2.46} = 0.241\ \dfrac{\#CoCl_2/hr.}{(Cu.ft.)(\#/cu.ft.)}$

$(62) = \dfrac{(4)}{(61)} = \dfrac{9.57}{0.241} = 23.0\ ft.$

NOMENCLATURE

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

dA = differential interfacial area, sq.ft.

C = $CoCl_2$ concentration, #/cu.ft.

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

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

HTU = height of a transfer unit, feet.

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)$(\triangle C_A)$.

Ka = extraction capacity coefficient, #/(hr.)(cu.ft. of column)$(\triangle C)$.

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

$MeCl_2$ = $NiCl_2 + CoCl_2$

N = 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.

B = bottom of the column.

c = continuous phase.

d = discontinuous phase.

lm = log mean.

OA = over-all, based on the alcohol phase.

OW = over-all, based on the water phase.

T = top of column.

U = superficial velocity at flooding point, cu.ft./(sq.ft.)(hr.).

W = water phase.

1,2,3 = first, second, or third sampling point from the bottom.

Superscript

* = equilibrium value.

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THESIS TITLE: The Separation of Nickelous and Cobaltous
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