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Mass Transfer Studies in Nickel/Cobalt Separation Using Pulsed Sieve-Plate Extraction Column

By

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A thesis submitted to the School of Graduate Studies in partial fulfillment of the requirements for the degree of M.A.Sc. in the Department of Chemical Engineering.

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ABSTRACT

Nickel/Cobalt separation was achieved in a pulsed sieve-plate extraction column using di(2-ethyl hexyl) phosphoric acid as the extractant. The liquid-liquid mass transfer involved in this process has been studied.

To evaluate the mass transfer characteristics of the operation, steady-state concentration profiles along the column were obtained by sampling both phases from each plate. Droplet size and interfacial area were estimated using a photographic method. From this information, the overall mass transfer coefficients in different sections of the column were calculated, and were found to vary with the concentration during the extraction, but remained rather constant during scrubbing and stripping.

The value of the coefficients were inthe 0.2×10^{-3} to 1.8×10^{-3} cm/sec. range for cobalt, and 0.5×10^{-3} to 2.4×10^{-3} cm/sec. for nickel.

By applying the pulsing technique to increase the degree of mixing between the two phases, the mass transfer rate was found to be significantly enhanced. The comparision of mass transfer coefficients with values obtained using different pulse amplitudes indicated that the coefficient value increased as the amplitude increased. The coefficient was also observed to be affected by the direction of mass transfer, such that the mass transfer coefficients for extraction were found to be higher than those obtained in stripping.

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Finally, the author would like to dedicate this thesis to his beloved parents whose understanding and encouragement made the study possible.

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NOMENCLATURE

N	:	Rate of Mass Transfer (g/sec)
k	:	Individual Mass Transfer Coefficient (cm/sec)
S	:	Surface area (cm^2)
C	:	Concentration (g/l)
m	:	Equilibrium Coefficient, $m=\frac{Co}{Ca}$
m'	:	See definition on eq (7)
$K_{o,org}$	:	Overall Mass Transfer coefficient based on organic phase (cm/sec)
u	:	Superficial Velocity (cm/sec)
V	:	Volumn (cm^3)
Z	:	Height (cm)
a	:	Interfacial Area per unit volumn (cm^2/cm^3)
d	:	Drop diameter (cm)
n	:	No. of drops
ϕ	:	Hold-up ratio
$\bar{d}_{32}$	:	Sauter mean diameter (cm^3/cm^2)
A	:	Amplitude of pulse (cycle/Min)
F	:	Frequency of Pulse (cm)
D	:	Diffusivity (cm^2/sec)
e_o	:	Axial diffusion coefficient (cm^2/sec)

Subscripts

0	:	Organic
a	:	Aqueous
i	:	Interfacial
1	:	Location 1

2 : Location 2

t : Total

DIMENSIONLESS GROUPS

$$Sh = \frac{kd}{D}$$

$$Re = \frac{\rho d u_c}{\mu}$$

$$We = \frac{u^2 d \rho_c}{\sigma}$$

$$Sc = \frac{\mu}{D \rho}$$

$$Gr = \frac{\rho d^3 \Delta\rho g}{\mu^2}$$

μ : Viscosity

ρ : Density

σ : Surface Tension

Chapter I

INTRODUCTION

Liquid-liquid extraction is usually used when distillation and rectification are difficult or ineffective. Extraction utilizes the differences in solubility or chemical selectivity rather than relative volatility. Therefore some close-boiling mixture or physically similar components can be separated economically by extraction techniques (1) (2). One of these applications is metallurgical processing.

For example, in the nuclear fuel industry, extraction is one of the most important operations in refining uranium fuel as well as in reprocessing the nuclear wastes (3). In recent years, this technique has been considered as an effective means of recovering copper (4) and other "3d" type transition metals, such as nickel and cobalt which we have investigated in this work.

Nickel and cobalt ores or concentrates can be leached by sulphuric acid solution, and then the metals separated from each other by liquid-liquid extraction using di-2-ethyl hexyl phosphoric acid (D2EHPA) as the extractant. The extraction process to separate cobalt from nickel is shown in figure 1. The metal bearing aqueous solution is fed into a contactor in which the two phases are mixed. In this step both nickel and cobalt are transfered from the aqueous phase to the organic phase. After settling, the aqueous raffinate is separated,and the loaded organic solvent goesto another contactor where it is scrubbed with a suitable aqueous solution to re-

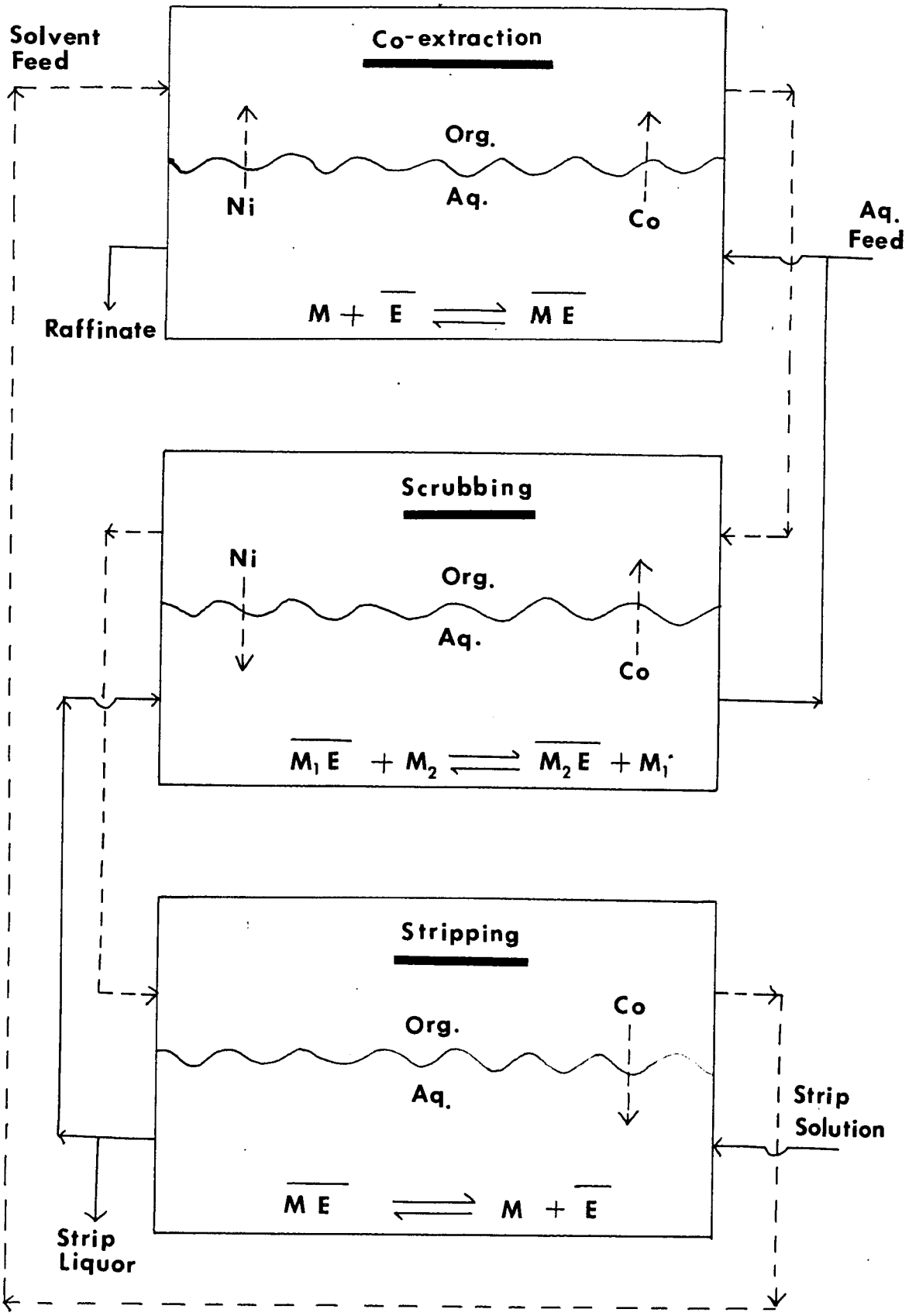


Fig.1 Extraction Process for Co/Ni Separation

move undesired metal, nickel in this study, or impurities co-extracted in the extraction step. After scrubbing, the loaded organic phase, containing essentially the desired metal— cobalt, passes to a third step in which the metal is stripped from the solvent by the acid solution. The strip liquor then goes to further processing for cobalt production, and the stripped solvent is recycled back to the extraction step. Each of the three steps described -- extraction, scrubbing and stripping -- may involve several contactors or extraction columns.

Through a laboratory test, Ritcey, Ashbrook and Lucas (5) proposed that a pulsed sieve-plate extraction column would be a suitable contactor for this separation process. A pilot scale column was constructed in the Department of Chemical Engineering, to further study this proposal.

Ni/Co separation in a pulsed column involves multicomponent mass transfer with chemical reaction between two phases. The uncertainty of the mass transfer mechanism of the co-extraction, stripping and scrubbing steps increases the complexity of the problem. In addition, the mixing effects and special configuration of the pulsed sieve-plate extraction column makes the process more complicated. A better understanding of the mass transfer performance in the contactor is necessary to help the design and optimization of the process. Therefore the purpose of this work was

to research the overall mass transfer coefficients and to evaluate extraction efficiencies.

Chapter 2

Literature Survey

This chapter is a review of the general background and some previous studies pertinent to this work, and is divided into four parts. In the first part, a review of the development of the process for separation of cobalt from nickel is presented. In the second part, the available information for designing and operating a pulsed column are presented. In the third part, hydrodynamic studies in basic drop phenomena and its experimental techniques are reported. Finally, basic theories and correlations in mass transfer studies for liquid-liquid extraction are briefly reviewed in the fourth section.

Development of Separation Process

Liquid-liquid extraction has long been a powerful separation technique for laboratory use. Its application for large scale industrial separation dates from the early 1930s, when it answered the need for a method of removing aromatic hydrocarbons from kerosene fraction during oil refining. Since then it has found ever-increasing application in a wide range of industries from copper production to the manufacture of antibiotics.

Its application in hydrometallurgy first came to general attention when, in 1955, the Atomic Energy Commision in U.S.A. declassified information concerning the solvent extraction process for uranium recovery and purification (8). The po-

tential of this new extractive technique quickly become apparent to those interested in the recovery of other metals such as vanadium, molybdenum, chromium, nickel, cobalt, zinc, and copper, with the result that research and development on solvent extraction processes in both laboratory and pilot plant gained phenomenal momentum. Many applications concerning the solvent extraction of metals are available. Basic theories and considerations can be found in the standard text by Treybal (2) and Rosenquist (9), and a review of recent developments by Hanson (10). Much valuable information has been published over the past decade in the proceedings of a series of International Solvent Extraction Conferences (I.S.E.C. meetings)(11-15), and in the regular reviews published by the Society of Chemical Industry (16). In addition, the notes for the professional development course in " Purification Techniques in Hydrometallurgy " (19), sponsored by the Chemical Engineering Department, University of Ottawa, are also a very valuable source of information.

In Canada, one of the methods for treating cobalt-nickel residues, ores, and concentrates is the acid sulphate leaching process. The leaching liquor containing iron, zinc, copper, and arsenic etc. is generally neutralized and followed by precipitation and filtration to remove these undesired metals(17).

The filtrate containing essentially cobalt and nickel as sulphate, is then suitable for solvent extraction purposes to

separate cobalt from nickel. In recent years, this separation method has become of increasing importance and much research effort has been devoted to the problem. A process has been developed using di-(2 ethyl hexyl) phosphoric acid (D2EHPA) as the reagent (18). This process decribed here (5) resulted from a continuing program by Eldorado Nuclear Limited and the Mines Branch, Department of Energy, Mines and Resources, Canada, on the application of solvent extraction as a process for the separation of metals from leach solutions, and it is to be incorporated in the new International Nickel Company (INCO) plant in Sudbury, Ontario.

Studies in the selection of extractant, diluent, and modifier by Ashbrook and Ritcey(19) proved the best extractant to be D2EHPA with Tributyl phosphate (T.B.P.) as modifier and Shell-140 kerosene as diluent. Bench-scale tests were performed and indicated that the optimum $_{p}H$ for cobalt extraction ($_{p}H$ to be from 5 to 6). To maintain this $_{p}H$ value, they suggested that preequilibrating ammonium hydroxide with D2EHPA will produce in the desired buffer effect. The distribution isotherms for Ni/Co separation were reported (5), but were studied intensively by Golding and coworkers(20), as fig. 3.

Previous work also showed that the extraction of cobalt and nickel by D2EHPA can be considered to be a liquid ion-exchange type of reaction in which the metal cations are exchanged for hydrogen ions of the solvent. The mechanism was

proposed as follows:

(1) Pre-equilibration of D2EHPA with $NH_4(OH)$:

$$(RO)_2\text{-}P\overset{=O}{\underset{OH}{<}} + NH_4OH \rightarrow (RO)_2\text{-}P\overset{=O}{\underset{ONH_4}{<}} + H_2O$$

(2) Co-extraction: (Step 1 of figure 1.)

$$7>PH>5$$

$$2(RO)_2\text{-}P\overset{=O}{\underset{ONH_4}{<}} + CoSO_4 \longleftrightarrow \left\{(RO)_2P\overset{=O}{\underset{O}{<}}\right\}_2\text{—}Co + (NH_4)_2SO_4$$

$$2(RO_2)\text{-}P\overset{=O}{\underset{ONH_4}{<}} + NiSO_4 \longleftrightarrow \left\{(RO)_2P\overset{=O}{\underset{O}{<}}\right\}_2\text{—}Ni + (NH_4)_2SO_4$$

(3) Scrubbing: (Step 2 of figure 1.)

$$\left\{(RO)_2\text{-}P\overset{=O}{\underset{O}{<}}\right\}_2\text{—}Ni + CoSO_4 \longleftrightarrow \left\{(RO)_2P\overset{=O}{\underset{O}{<}}\right\}_2\text{—}Co + NiSO_4$$

(4) Stripping of cobalt: (Step 3 of figure 1.)

$$\left\{(RO)_2P\overset{=O}{\underset{O}{<}}\right\}_2\text{—}Co + H_2SO_4 \xrightarrow{PH<2} 2(RO)_2P\overset{=O}{\underset{OH}{<}} + CoSO_4$$

Similar equations can be written for the extraction and stripping of nickel.

However, Ritcey and coworkers found the representation of the D2EHPA-Co complex in the organic phase in these equations as a 2:1 organic-metal complex could not be taken as implying that this is the actual species presente . Considerable evidence(21) showed that the actual complex in the organic phase could be a dimerised, or even a polymerized complex, although the stochiometric rating in the experiments was 2 : 1 for D2EHPA: Co. This uncertainty increases the complexity of the prediction of mass transfer coefficients.

Several preliminary pilot plant tests carried out by Ritcey

and coworkers(5) indicated the feasibility and necessity of applying a multi-stage contactor in the extraction process because of the chemical similarity between cobalt and nickel. A pulsed sieve-plate column was chosen.

Results obtained from their tests illustrated the capability of the process to separate cobalt from nickel. This information initiated our further studies in evaluating mass transfer performance of the pulsed column for Ni/Co separation.

Pulsed Column Design and Operation

The pulsed sieve-plate column (as shown on figure 2) is an extractor wherein a rapid reciprocating motion of relatively small amplitude is applied to the liquid contents. With this motion, successive dispersion and coalescence of the liquid is accomplished by perforated plates. The agitation so produced has been found to give improved rates of extraction.

The principle originated with Van Dijck(21) and perhaps was first applied to uranium separation by C. Groot. Pulsed sieve-plate columns have found considerable favor, particularly in nuclear industry(23), because the device reduced tower heights by a factor of three to five (22) and consequently reduced the expense of massive shielding, and because pulsing provided a means of agitation not requiring moving parts, bearings and the like in contact with highly corrosive dangerous radioactive liquid. They have also been shown capable of handling solids in suspension and have been suggested for

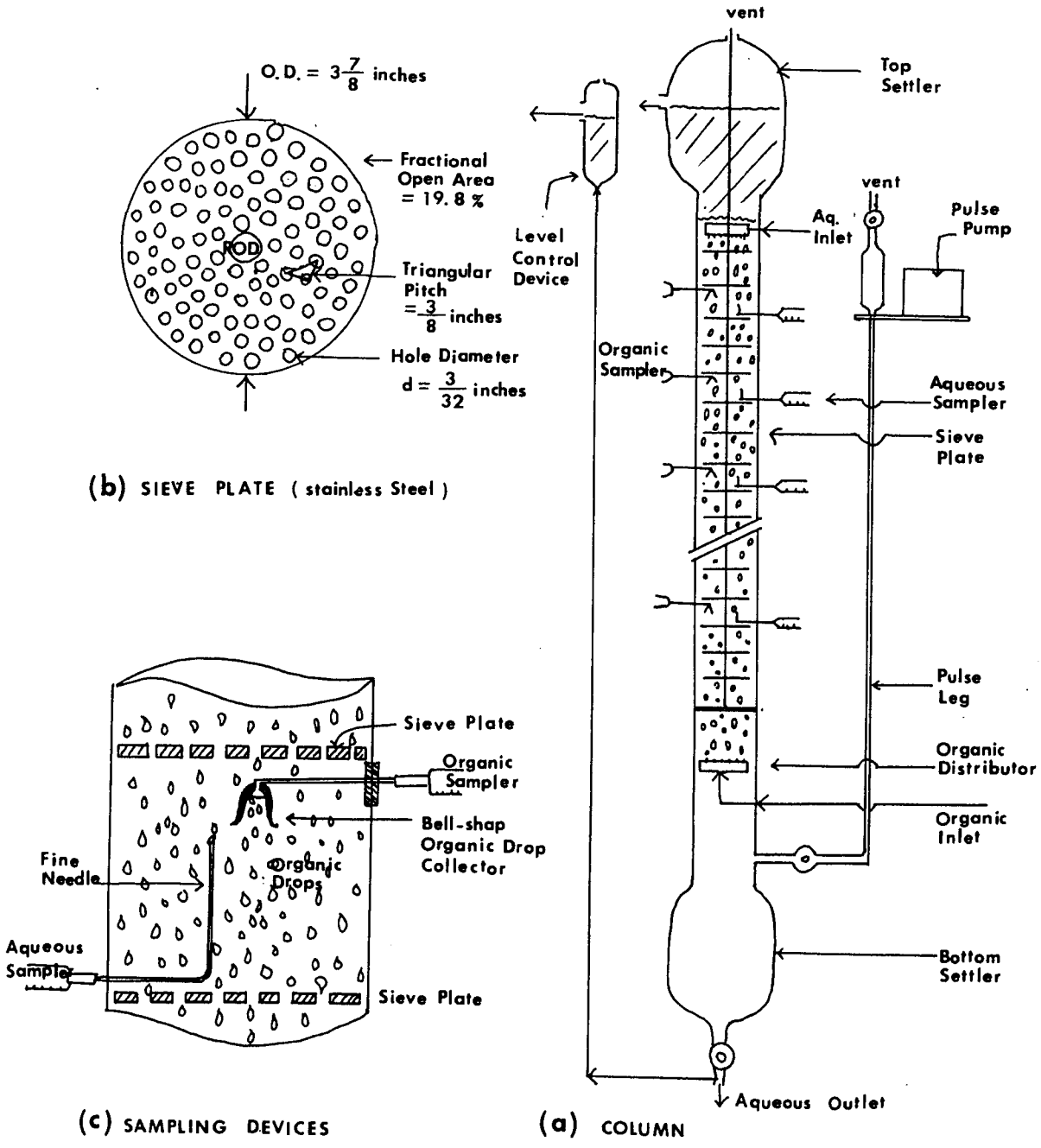


Fig. 2 Pulse–sieve–plate Column and Sampling Devices

solvent-in-pulp processing in the minerals industry (24). The information concerning the performance of the column is reasonably well documented (25).

Sege and Woodfield (26) provided a general description of the operational characteristics. Wiegundt and Von Berg (27) also reviewed the functions and performance of the apparatus. Refering to figure (4) there are several regions of operation which can be distinguished, depending on the flowrates and degree of pulsation. In the so-called mixer-settler region, the two phases separate into discrete layers between the plates during each reversal of the pulse cycle as shown on figure. At higher pulse-volume velocities, little or no coalescence takes place between the plates, and column then is in the emulsion region, and behaves as a truly differential contactor. The effects of operating regions on the extraction efficiency have been studied by several investigators (22) (26).

The capacity or throughput of the column depends on its flooding characteristics. McAllister et al (28) have correlated much of the published data on flooding rate for operation through the mixer-settler and emulsion regions. Smoot, Mar and Babb (29) have also published a correlation valid only for the emulsion region, and a comprehensive nomograph for calculating flooding velocities in pulsed sieve-plate column has been provided. Thornton (30) correlated the characteristic velocity, which can also be used to estimate flooding rates in the emulsion region.

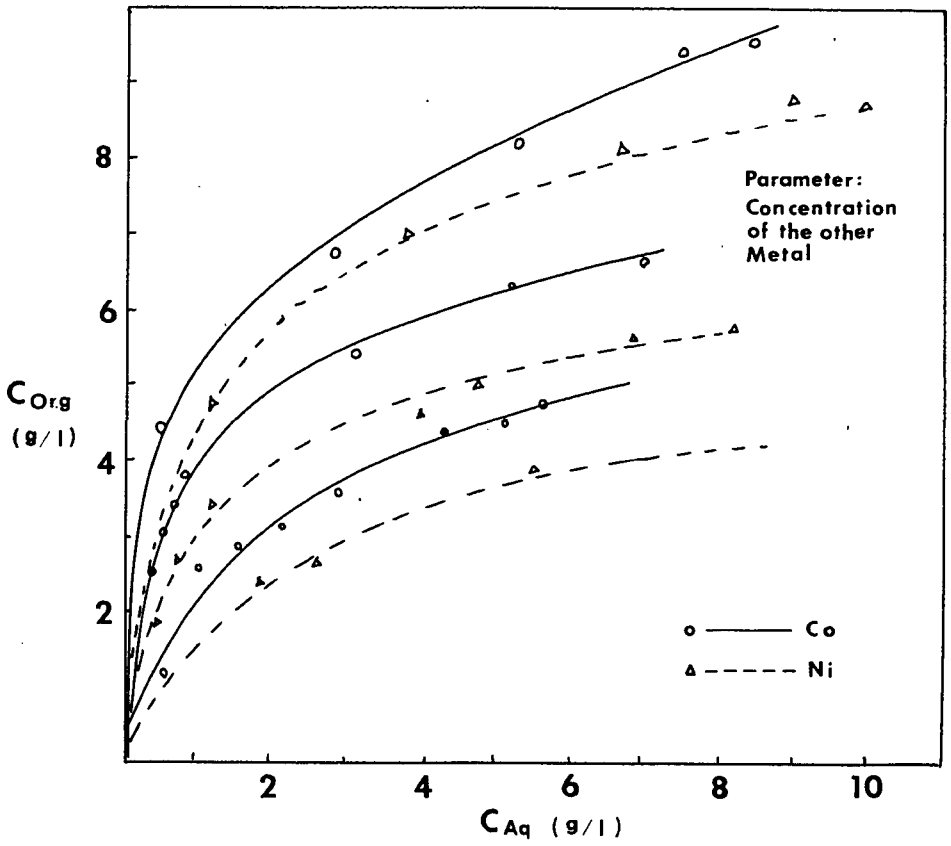


Fig. 3 Typical Equilibrium Curves for Ni/Co Extraction

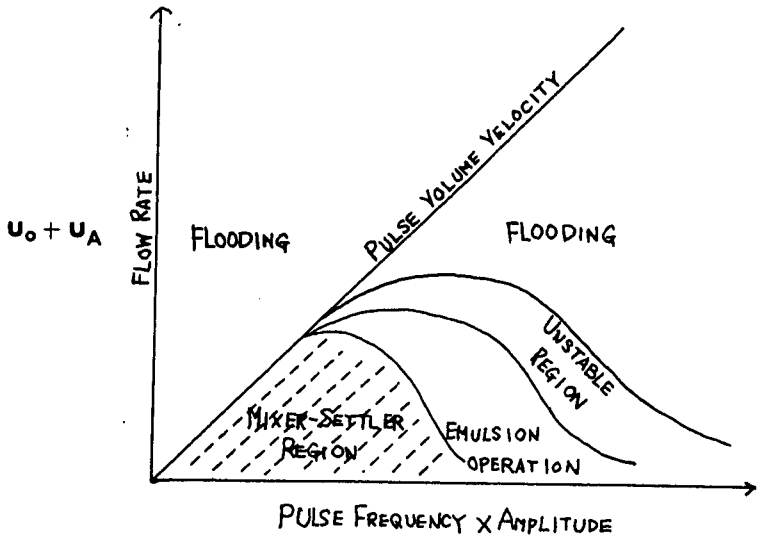


Fig. 4 Operation Regions of Pulsed Extraction Column

////// Operation Range in this Study

Another important factor in designing a pulsed sieve-plate column is the dispersed phase hold-up, which affects the total interfacial area and the residence time distribution during the extraction. Sehmel and Babb (31) intensively studied the effects of pulse amplitude, pulse frequency and phase flow rate on the dispersed phase hold-up, and it was found to be a minimum at the transition frequency between mixer-settler and emulsion type of operation. A simple empirical correlation was provided to predict this frequency for those systems they studied.

Due to the vigrous agitation and countercurrent contacting between the two phases, the extraction efficiency in the pulsed column has been found to be strongly affected by axial mixing. This mixing effect tends to reduce the effectiveness of mass transfer by flattening the axial concentration gradients in each phase and thus reducing the overall driving force. In some large scale columns, as much as 70 to 90 percent of the height has been found necessary to compensate for axial mixing effects. The phenomenon was studied by Babb and coworkers (32) (33), Miyauchi and Oya (34), and Baird (35) by applying either the steady-state technique (36) or the delta injection technique (37).

Smoot and Babb (7) also correlated mass transfer data in the form of a "true overall height of transfer unit" (the height corrected for axial mixing) by measuring the concen-

tration profile along the column. An experimental study, presented by Kagan et al (38), on the hydrodynamic and mass transfer problems in a pulsed column for the kerosene-water system is particularly applicable to hydrometallurgical applications.

The pulsed column used in this work was designed, constructed and set up according to the general information mentioned above and a note provided by Energy, Mines and Resources, Canada. Unfortunatly, most of the correlations were not quantitatively applicable because of insufficient information for the system we studied.

Drop Phenomena and Two Phases Dispersion

Since the residence time and interfacial area have significant effects on mass transfer efficiency, the study of drop formation, coalescence and redispersion became one of the most prosperous research topics in extraction studies. A series of reviews in the area of bubble and drop phenomena were presented by Tavlarides and coworkers (39) (40). Recent developments in coalescence and dispersion of liquid droplets were reported by Hanson et al (10).

To estimate the interfacial area in a pulsed column, special attention must be paid to the drop size distributions and drop mixing rates. General features of drop size distributions are summaried and several different equations were

developed to describe size distribution by Mugele et al (41). For agitated systems, interaction models such as population balance equations have been applied to predict interfacial area for batch contactors. Recently, data and correlations were also presented on both size distributions and droplet mixing frequency in an agitated flow vessel (42). Unfortunatly no such information could be found for predicting interfacial area of a pulsed column. Therefore, in this work, the unpredictable drop interactions became a major difficulty in evaluating the area-free mass transfer coefficients.

Experimental techniques for measuring interfacial area have been reviewed (43). The comparison of the methods indicate the advantages and disadvantages of the photographic method used in this work. The basic techniques for photographing liquid drops are reported by several investigators (44) (45), and can be found in a standard textbook (46).

Theories and Correlations for Liquid-liquid Mass Transfer

Although the mass transfer coefficient reported in this work is an overall coefficient including drop formation, rising and coalescence, a basic understanding of mass transfer theories is necessary for interpreting experimental results. A review of mass transfer between two phases has been published by Harriot (47), and a comprehensive survey for the fundamentals of mass transfer in liquid-liquid extraction presented by Johns, Beckmann and Ellis (48). Basic theories and

correlations can also be found in textbooks (2) (49).

Recent years, most efforts to investigate the mass transfer mechanism in dispersed liquid drops have used the "Model" approach. Basic models (48) have been devised which will, it is hoped, permit a mathematical approach to the interrelating factors of mass transfer, hydrodynamics, and interfacial phenomena. These models lead to several theoretical or semi-empirical solutions for single drop mass transfer, as tabulated briefly in Tables(1), (2) and (3), (50) (51). Attention has also been paid to the development of correlations for ensembles of drops (52) (53), and for mass transfer with chemical reaction (54) (55).

Because each model usually incorporates certain fundamental assumptions and limitations which are then inherent in the final solution, the utility of the proposed equations in rationalization of equipment performance is relatively low. Few applications were found in designing sieve-plate columns (56) and pulsed packed columns (57) using these theoretical and semi-empirical equations. For the pulsed sieve-plate column, empirical equations have been used for estimating the overall efficiency in relatively simple extraction systems (29) (7). No direct application in designing such an apparatus for metal separation process using theoretical equations was found.

The main difficulties come from the inability of predicting hydrodynamic behavior with which mass transfer occurs. The

other drawback is the unknown mechanism of the chemical reaction involved in metal separation. Low reproducibility for most experimental work is another obstacle. Due to the difficulties mentioned above and the time limitation, no attempt has been made to develop an "a priori" equation for predicting column performance in this work. Instead, an experimental measurements. of overall coefficients for the extractor were carried out to evaluate the performance of the different processing steps.

Table 1

Equations for Predicting Aqueous Phase Mass Transfer Coefficients

Drop Conditions	Author	Equation	Limits
Rigid Spheres	Frössling	$Sh=0.552\ Re^{\frac{1}{2}}Sc^{1/3}$	$Re > 1$
	Linton	$Sh=0.582\ Re^{\frac{1}{2}}Sc^{1/3}$	$Re > 1$
	Rowe et al	$Sh=2.0 + 0.76\ Re^{\frac{1}{2}}Sc^{1/3}$	$Re > 1$
	Garner and Suckling	$Sh=2.0 + 0.95\ Re^{\frac{1}{2}}Sc^{1/3}$	$Re > 1$
Circulating	Hadamard	$Sh=0.65\left[\frac{\mu_c}{\mu_c + \mu_d}\right]^{\frac{1}{2}} Re^{\frac{1}{2}}Sc^{\frac{1}{2}}$	$Re < 1$
	Thorsen	$Sh=1.13\ f^{\frac{1}{2}}\ Re^{\frac{1}{2}}\ Sc^{\frac{1}{2}}$	$Re > 100$
		$f=1.0 - \frac{2+3\mu_d/\mu_c}{1+(\rho_d \mu_d/\rho_c \mu_c)^{\frac{1}{2}}} \frac{1.45}{Re^{\frac{1}{2}}}$	
Vigorous Circulation	Boussinesq, Higbie	$Sh=1.13\ Re^{\frac{1}{2}}\ Sc^{\frac{1}{2}}$	$Re > 300$ $We > 3.3$
Swarms Rigid Spheres	Frössling	$Sh=0.552\ Re^{\frac{1}{2}}\ Sc^{1/3}$	Drops Just Suspended
Swarms circulating Spheres	Heertjes	$Sh=0.8\ Re^{\frac{1}{2}}\ Sc^{\frac{1}{2}}$	"
	Calderbank	$Sh=0.42\ Sc^{\frac{1}{2}}Gr^{1/3}$	
Agitated Tank	Calderbank, Moo-Young	$Sh=0.13\ Sc^{-2/3}\left[\frac{(p/v)\mu_c}{\rho_c^2}\right]^{\frac{1}{4}}$	Strong Agitation

Table 2

Equations for Precting Dispersed Phase Mass Transfer Coefficients

Drop Conditions	With No Cont. Phase Resistance	; With continuous Phase Resistance
Diffusion (Stagnant Drops)	$k_D = -\frac{d}{6t} \ln \left[\frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(\frac{-n^2\pi^2 4Dt}{d^2}\right)\right]$ (Newman)	$k=-\frac{d}{6t} \ln \left[\frac{6}{\pi^2}\sum_{n=1}^{\infty}A_n \exp-\left(\frac{n^2\pi^2 4Dt}{d^2}\right)\right]$ (Calderbank)
Laminar circulation drops (Hadamard-Rybezinski) Re < 10 to 50	$k_D = -\frac{d}{6t} \ln \left[\frac{3}{8}\sum_{n=1}^{\infty}B_n^2 \exp\left(\frac{\lambda n\ 64\ Dt}{d^2}\right)\right]$ (Kronig, Brink)	as Kronig solution (Elzinga, Banchero) B_n and λ_n are functions of k_c
Vigorous circulation or oscillation drops Re > 300 We > 3.3	$k_D \simeq \frac{\lambda_1 V_d}{768(1+\frac{\mu_d}{\mu_c})}$ and $\lambda_1 = 2.88$ (Handlos, Baron)	As Handlos solution but $\lambda_1 = \lambda_1 (k_c)$ (Wellek, Skelland)
All flow regimes	Numerical solution (Johns, Beckmann)	Numerical solution (Patel, Wellek)

Table 3

Approximate Equations For Predicating Dispersed Phase Mass Transfer Coefficients

Drop Conditions	No Cont. Phase Resistance	With Continuous Phase Resistance
Diffusion (Stagnant drops)	$k_d \simeq -\frac{d}{6t} \ln\left[1 - \frac{2\pi\sqrt{Dt}}{d}\right]$ (Vermeulen)	$k_d \simeq -\frac{d}{6t} \ln\left[1 - 0.905\left(\frac{4RD\pi^2 t}{d^2}\right)^{1/2} - 0.0189\right]$
Laminar circulation drops	$k_d \simeq -\frac{d}{6t} \ln\left[1 - \frac{2\pi\sqrt{2.5Dt}}{d}\right]$ $\simeq 1.5\, k_D$ (Newman)	
Non-oscillating drops	$k_d \simeq 31.4 \frac{D}{d}\left(\frac{4Dt}{d}\right)^{-0.34}\left(\frac{\mu}{\bar{\rho} D}\right)^{-0.125}\left(\frac{dV_s^2 \rho_c}{\sigma}\right)^{0.37}$ (Skelland, Wollek)	
Oscillating drops	$k_d \simeq 0.32 \frac{D}{d}\left(\frac{4Dt}{d}\right)^{-0.14}\left(\frac{\rho_c d V_s}{\mu_c}\right)^{0.68}\left(\frac{\sigma^3 \rho_c^2}{g\mu_c \Delta\rho}\right)^{0.10}$	

Chapter 3

Theoretical Considerations

Two Film Theory

To investigate the mass transfer mechanism of Ni/Co separation, it is necessary to have an equation expressing the relationship between each individual phase resistance. Referring to figures(5) and(6), two fictitious films were postulated by Whitman (58) (59) to account for the total resistance to liquid-liquid mass transfer. Thus, at steady-state, the rate of transfer of solute through the interface can be expressed as follows:

$$dN = k_a ds\,(C_a - C_{i,a})$$

$$= k_o ds(C_{i,o} - C_o) \quad \text{---------- (1)}$$

$$\text{where } C_{i,o} = mC_{i,a} \quad \text{---------- (2)}$$

Due to the difficulty in measuring interfacial concentrations, "$C_{i,a}$" and "$C_{i,o}$", an overall coefficient was defined based on the assumption that the resistance to transfer can be accounted for entirely by only one phase (2), and the interfacial concentration on one side is taken to be in equilibrium with the bulk concentration of the other phase so that the rate of transfer become:

$$dN = K_{o,aq} dS(C_a - C_a^*)$$

$$= K_{o,org} dS(C_o^* - C_o) \quad \text{---------- (3)}$$

$$\text{where } C_o = mC_a^* \quad \text{---------- (4)}$$

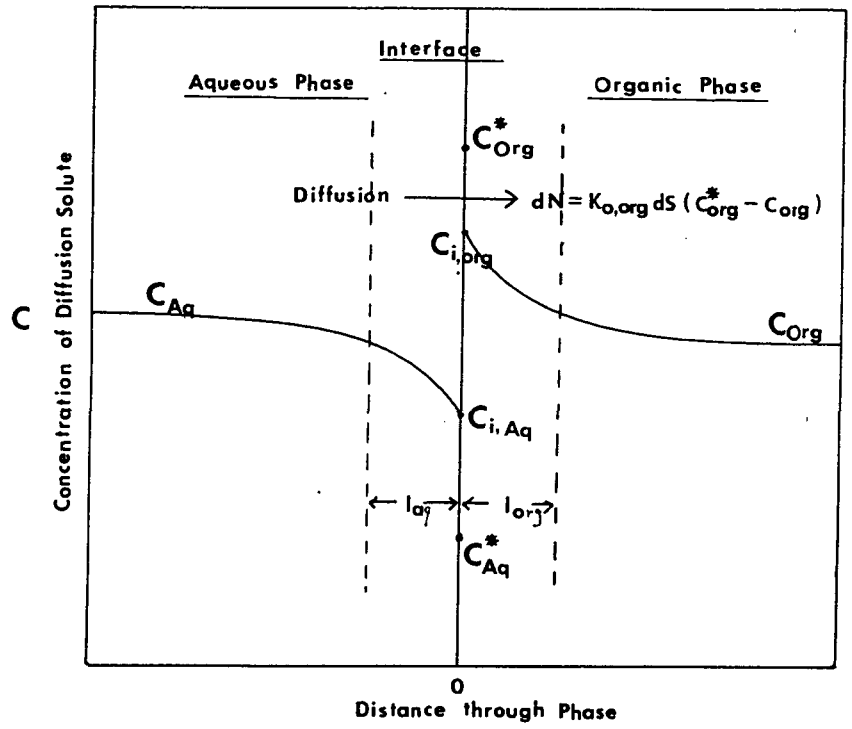


Fig.5 Two-film Model — Concentration Gradients at Phase Boundary

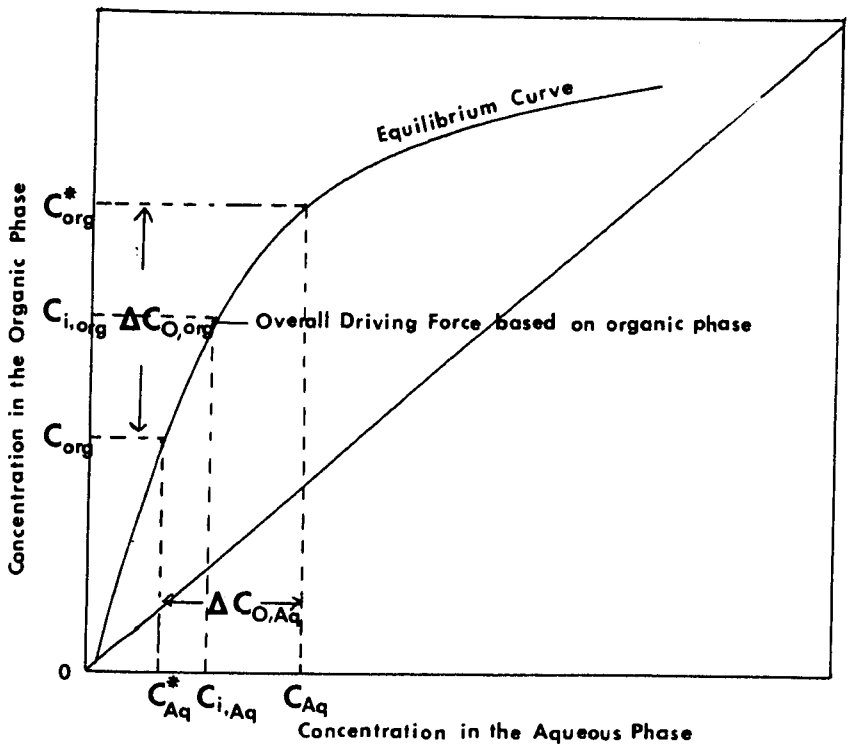


Fig.6 Overall Driving Force for Mass Transfer

If the equilibrium-distribution curve is a straight line, m is a constant for both equations (4) and (2). Therefore the individual coefficient "k" and the overall coefficient "K" can be related by eliminating "$C_{i,o}$", "$C_{i,a}$" and "C_a", and result in

$$dN = \frac{1}{(1/k_o) + (m/k_a)} dS(C_o^* - C_o) \quad \text{---------- (5)}$$

Comparison with equation (3) shows that

$$\frac{1}{K_{o\ org}} = \frac{1}{k_o} + \frac{m}{k_a} \quad \text{---------- (6)}$$

When, however, m varies with concentration, a graphical integration method must be used to obtain the mean value of "K" relating to successive values of "C_o". Also, if we define a new variable m' (60):

$$m' = \frac{C_o^* - C_{i,o}}{C_a - C_{i,a}} \quad \text{---------- (7)}$$

A relationship between k and K can be derived by equating (1), (2) and (7):

$$\frac{1}{K_{o,org}} = \frac{1}{k_o} + \frac{m'}{k_a} \quad \text{---------- (8)}$$

This equation is valid whenever m varies or not. It is a general expression which shows "$K_{o,org}$" can be a function of m' even if "k_o" and "k_a" remain constant. The experimental results obtained from the pulsed column then can be interpretated with this equation.

Equation for calculating $K_{o,org}$

Axial mixing in the countercurrent extractor makes it difficult to do a material balance for solutes distributed between two phases. No experimental measurement has been carried out to determine the axial mixing coefficients. Therefore, rigorous calculation of overall mass transfer coefficients in the pulsed column is impossible. For an approximate evaluation, an idealized diffusion model (10) (7) (61) was applied to the effective section of the pulsed sieve-plate extraction column. Both inlet and outlet end effects are not included in this model. With reference to figure 7, a solute mass balance over the element "dZ" for the organic phase yields the following differential equation.

Mass balance:

$$u_o S C_o \Big|_z - u_o S C_o \Big|_{z+\Delta z} + \left(-e_o \frac{dC_o}{dz}\right) S \Big|_z - \left(-e_o \frac{dC_o}{dz}\right) S \Big|_{z+\Delta z} + K_{o,org}\, aS\, \Delta z \left(C_o^* - C_o\right) = 0$$

Limit: $\Delta z \to o$

$$e_o \frac{d^2 C_o}{dz^2} - u_o \frac{dC_o}{dz} + K_{o,org}\, a\left(C_o^* - C_o\right) = 0 \qquad \text{--------(9)}$$

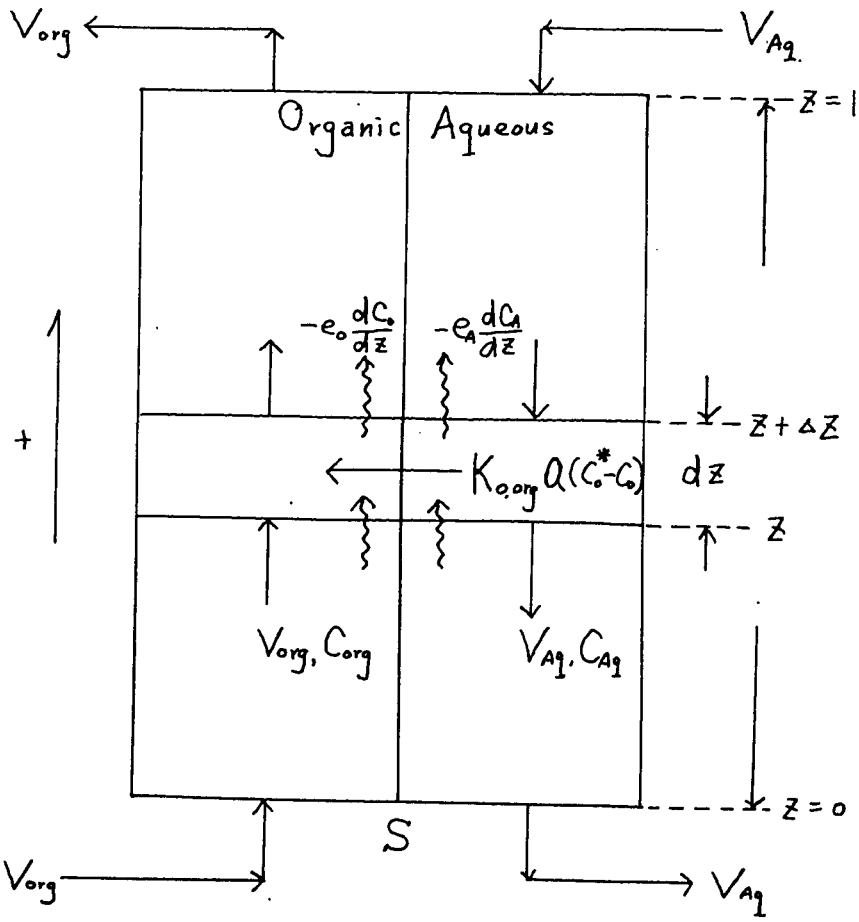


Fig.7 Diffusion Model for Two-phase Dispersion

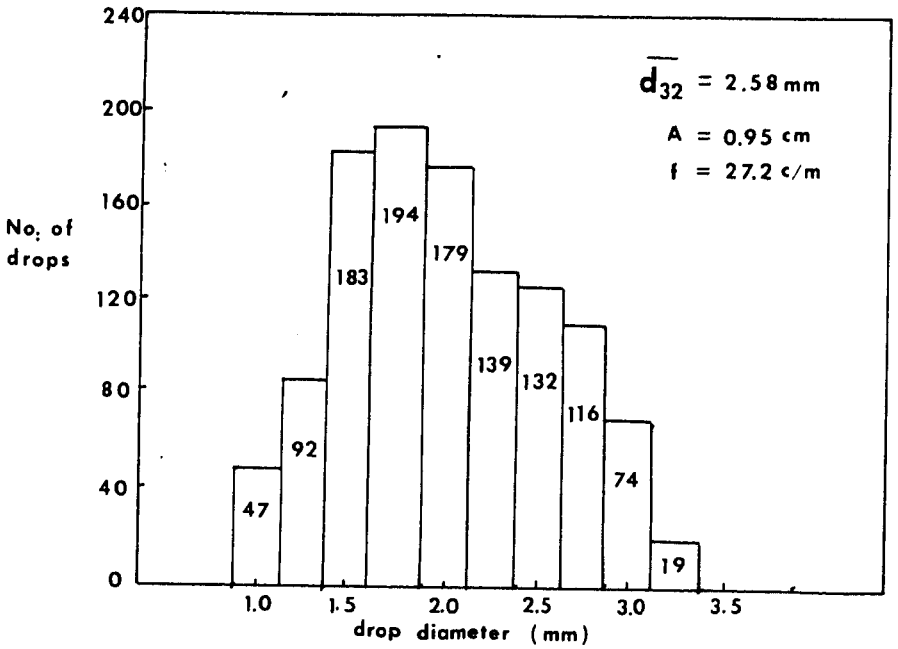


Fig.8 Typical drop size Distribution

From experimental observations and previous study (7), the axial mixing in the organic phase is insignificant and can be neglected under the low pulse frequency and amplitude used in this work. Therefore, "e_o" equals zero. Dropping out the axial mixing term, equation (9) become a first order differential equation as follows:

$$e_o \frac{d^2C_o}{dz} - u_o \frac{dC_o}{dz} + K_{o,org}\, a\left(C_o^* - C_o\right) = 0$$

$$K_{o,org}\, a\left(C_o^* - C_o\right) = u_o \frac{dC_o}{dz}$$

$$K_{o,org}\, dz = \frac{u_o dC_o}{a\left(C_o^* - C_o\right)} \qquad \text{----------(10)}$$

An integration over every two sample points was then applied to obtain the average overall mass transfer coefficient presuming "u_o" and "a" are constant and the concentration profiles can be suitably represented by a continuous smooth curve.

$$\bar{K}_{o,org} \int_{z1}^{z2} dz = \frac{u_o}{a} \int_{C_{o1}}^{C_{o2}} \frac{dC_o}{\left(C_o^* - C_o\right)}$$

$$\bar{K}_{o,org} = \frac{u_o}{a(z_2 - z_1)} \int_{C_{o1}}^{C_{o2}} \frac{dC_o}{\left(C_o^* - C_o\right)} \qquad \text{----------(11)}$$

The right hand side of equation (11) can be evaluated by direct graphical integration over the organic concentration profiles, and "a" can be calculated from photographic data.

Estimation of Interfacial Area

From the pictures taken during the experiments, a drop size distribution diagram can be obtained as shown in figure 8. With this diagram and the measured total hold-up ratio, one can calculate the interfacial area using the working equation derived as follows:

$$\bar{a} = \frac{\sum_i n_i d_i^2 \pi}{V_t}$$

$$= \frac{6 \sum_i n_i d_i^2 \left(\frac{\pi}{6}\right)}{V_t}$$

$$= 6 \left(\frac{V_{org}}{V_t}\right) \frac{\sum_i n_i d_i^2 (\pi/6)}{V_{org}}$$

$$= 6 \phi \, x \left(\frac{\sum_i n_i d_i^2 (\pi/6)}{\sum_i n_i d_i^3 (\pi/6)} \right)$$

$$= 6 \phi \, x \left(\frac{\sum_i n_i d_i^2}{\sum_i n_i d_i^3} \right)$$

Define the Sauter mean diameter $\bar{d}_{32} = \dfrac{\sum_i n_i d_i^2}{\sum_i n_i d_i^3}$

$$\bar{a} = \frac{6\,\phi}{\bar{d}_{32}} \qquad \text{----------(12)}$$

When applying equation (12) to the experimental data, an assumption was made that the hold-up ratio in each section of column is the same as the total hold-up ratio in the column. A simple computer program (Appendix 1) was set up to calculate the Sauter mean droplet diameter and the interfacial area.

Substituting equation (12) into (11):

$$\bar{K}_{o,org} = \frac{\bar{d}_{32}\, u_o}{6\phi(z_2 - z_1)} \int_{C_{o1}}^{C_{o2}} \frac{dC_o}{(C_o^* - C_o)} \qquad \text{---------(13)}$$

Where $\bar{d}_{32}$, U_o, ϕ, Z_1, and Z_2 were measured during experiment, and C_{o1}, C_{o2}, C_o^* were determined from the steady-state concentration profile. Hence, the average overall mass transfer coefficient "$\bar{K}_{o,org}$" can be evaluated.

Chapter 4

Experimental

The experimental program involved the measurement of concentration profiles and the evaluation of overall mass transfer coefficients in different sections of the pulsed column under various operating conditions.

For such an investigation, the organic phase was always dispersed as droplets in the column and contacted countercurrently with the continuous phase which was synthetic aqueous solution. The direction of mass transfer was from the aqueous phase to the organic phase during co-extraction, but the reverse during stripping.

Variables

Temperature, while not controlled exactly, was nearly constant at 28 degree Celsius, hence, the effects of temperature were neglected.

The configuration of column was maintained the same in all experiments. The plate spacing, plate thickness, sieve diameter, and fractional free plate area were also kept constant. In addition, the flow rates of both aqueous and organic inlets were not changed through the course of all experiments. The variables investigated in this work were the solute concentration and the pulse amplitude effects in the three different separation steps.

System

The system studied was D2EHPA-Nickel-Cobalt-Water, while D2EHPA was dissolved in the kerosene solvent.

In all experimental runs, the organic phase always contained 10% Vol. of D2EHPA, 5% Vol. of T.B.P. modifier, and 85% Vol. of kerosene diluent. Synthetic aqueous solutions were prepared by dissolving nickel and cobalt sulphate crystal in distilled water. The pH value of the aqueous feed was adjusted to 4 before each experiment by adding dilute sulphuric acid solution.

The important physical properties of these systems are presented in Table 4. Chemicals used and their purities are shown in Table 5.

Table 4

Summary Of Chemicals Used

Chemical	Supplier	Grade
T. B. P.	Anachemia Chemicals Ltd.	Technical
D2EHPA	Denison Co., Ltd.	Technical
Kerosene	Shell Oil Co., Ltd.	#140 Solvent
Sulphuric Acid	Fisher Scientific Co., Ltd.	Reagent 98% H_2SO_4
Amonium Hydroxide	McArthur Chemical Co., Ltd.	Reagent 28-30% NH_3
Nickel Sulfate	Fisher Scientific Co., Ltd.	C. P.
Cobaltous Sulfate	Fisher Scientific Co., Ltd.	C. P.

Table 5

Physical Properties Of The System At 25°C

	* ρ (g/c.c)	** μ (c.p.)	σ (dyne/cm)
Kerosene	0.793	1.244	38.4
T. B. P.	0.972	3.389	
D2EHPA	0.974	42.026	
10% D2EHPA + 5% T.B.P.+Solvent	0.818	1.611	
20% D2EHPA + 5% T.B.P.+Solvent	0.834	2.049	
30% D2EHPA + 5% T.B.P.+Solvent	0.855	2.699	
2 g/ℓ Co^{++} + 5 g/ℓ Ni^{++} Aqueous Solution	1.017	0.954	

* ρ: Measured by "Precision Density Meter DMA02C", with the following reference values:

$$\begin{cases} \rho_{H_2O} = 0.99709 \\ \rho_{n\text{-octane}} = 0.69882 \end{cases}$$

** μ: Measured by "Cannon Viscometer"

Apparatus

A pilot-scale pulsed sieve-plate extraction column was designed, constructed, and set up in the Chemical Engineering Department, University Ottawa. It provided a continuous contact between two immiscible phases. Figure 9 is a schematic diagram of the experimental set up.

Column

The column was 4 inches I. D. and 6 ft. high. It consisted of a series of short, cylindrical borosilicate glass sections, polyethylene gaskets, and twelve stainless steel sieve plates held by a central steel rod. Each end of the rod was fastened to flange plates at either end of the column. The sieve plates were spaced 3 inches apart from each other by stainless steel spacers. The dimensions of the column are summarized in Table 6.

Each plate, 1/16 inch thick, was drilled with 253 holes of 3/32 inch diameter on an 1/8 inch equilateral triangular pitch to give 19.8% free area. The clearance between plate and column wall was 1/32 inch.

Two 6-inch diameter phase disengaging sections were mounted at the top and bottom of the column to insure good disengagement between organic and aqueous phases.

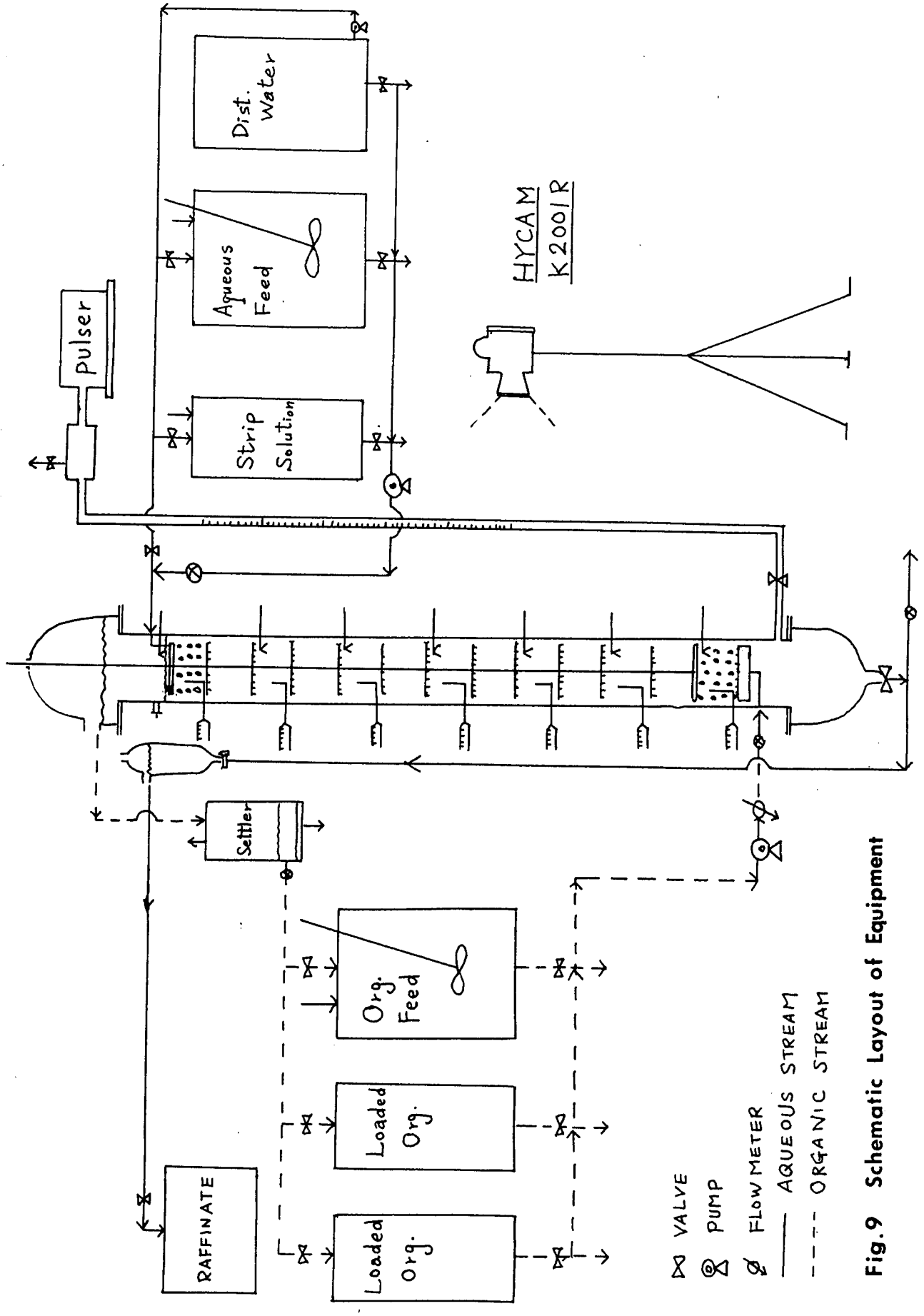


Fig.9 Schematic Layout of Equipment

Table 6

Dimensions Of Pulsed Column

Column O. D.	11.48 cm
Column I. D.	10.30 cm
Plate O. D.	9.85 cm
Plate Thickness	0.166 cm
Sieve Hole O. D.	0.24 cm
Average Plate Spacing	7.92 cm
Central Rod O. D.	0.970 cm
Top Distributor O. D.	6.58 cm
Bottom Distributor O. D.	8.66 cm
Fractional Free Area On Plate	19.80 %
No. Of Sieves On Each Plate	253
Height Of Column	186.8 cm
Effective Height	106.2 cm

Note: O. D. (outside diameter)

I. D. (inside diameter)

Both streams entering the column were pumped through stainless steel distributors of a conventional design to provide good distribution of the phases at either end of the effective section.

Since it was desired to measure the concentration profile of both phases, hypodermic needles were inserted into the column through the polyethylene gaskets at various points along each side of the column, as shown schematically in figure 2-c.

Sampling Devices

The sampling devices presented here were modifications of the original design of Gier & Hougen (6) and Smoot & Babb (7).

To sample the aqueous phase, a small stainless steel needle was inserted into the column through the gasket. The aqueous phase, which preferentially wet the stainless steel surface, could usually be sampled with 99% Vol. purity using an optimum sampling rate and a suitable size of needle.

In order to sample the organic phase, a small flared polyethylene sleeve was slipped over the end of a needle which was inserted through the gasket and positioned just below the sieve plate. The needle sleeve was pointed downward to trap the rising droplets. The organic liquid wet the polyethylene preferentially at the surface of the flare. Using this method, the purity of organic samples ranged from 85 to 95% Vol. if the sampling rates were controlled by a suitable size of needle.

Samples with less than 85% Vol. purity were discarded. The measured solute concentration of the organic samples with less than 98% Vol. purity were corrected according to the corresponding equilibrium and volume ratio of the other phase. The details of the correction method are given in reference 6. The use of proper sampling technique was very important in order to obtain a true concentration profile. The optimum sampling rate insured a "fresh" sample with high purity, and did not disturb the steady-state operation of the column. In this work, samples were taken at rates varying from 2.0 to 3.0 ml. per minute, which amounted to about 0.5 to 1.0% of the total column through-put.

Pulsation Devices

The pulser provided by Energy, Mines, and Resources, Canada, is a modified 4 inch diaphram pump driven by a variable accentric cam attached to a wheel driven by a 1/4 hp, three-phase, 220 volts A. C. motor. The pulsation frequencies could be adjusted by changing the relative rotating speed. To minimize energy consumption, the pulser was placed at the same height as the top of the column, and the pulsation outlet was connected with the bottom of the column by a pulse leg made of a "1 inch Tygon tube".

Photographic Instruments

A K2001R model HYCAM high speed motion picture camera was used to obtain hydrodynamic information inside the column. Droplet movement, velocity, and size distribution could be evaluated from the pictures taken in each experiment. An X-L meter was used to help determine the optimum operating conditions

of the camera. Two 1000 watt tungsten lights provided the illumination. A light timing device was connected to the camera to synchronize the speed ofthe lighting and shutter. Kodak TRI-X 16 mm reversal film was used to take the picture of the two phases dispersion. Sample pictures for a pulse cycle have been shown in figure(4).

Experimental Procedure

(1) Preparation of organic solvent and aqueous feed solution.

Aqueous feed solution was prepared simply by dissolving nickel and cobalt sulphate crystals in distilled water, and then adjusting the pH value of aqueous solution to 4 by adding sulphuric acid.

Organic solvent was prepared by adding 10% vol. of D2EHPA and 5% vol. of T. B. P. to kerosene diluent. A five percent excess stochiometric amount of ammonium hydroxide was added to the organic phase as a buffer in order to maintain the equilibrium pH between 5 to 6.

The organic solvent had to be recovered after each cycle of experiments. The stripped organic phase was washed several times until 99.9% of the solutes and acid were removed. This recovered solvent could then be equilibrated with ammonium hydroxide and reused in the next experimental cycle. An "extraction shake out test" using a separatory funnel was made to test the quality of the solvent before each experimental run to insure consistent quality of the organic phase.

(2) Hydrodynamic Test

A hydrodynamic test was carried out before all the mass transfer experiments in order to understand the characteristics of the column. Kerosene and water were used as the two contact phases in this test. The column was operated at various pulse amplitudes and different drop size distributions. From such information, three favorable operating conditions were chosen in the mixer-settler region. The photographic method was also tested during these hydrodynamic experiments.

(3) Steady-State Operation

Steady-state mass transfer experiments were carried out according to the following procedures.

(i) Fill up the column with the continuous phase.

(ii) Adjust the pulse frequency and amplitude to the desired value.

(iii) Pump both aqueous and organic phases continuously into the column, and adjust and control the flow rate.

(iv) Adjust the location of the interface at the same height of the aqueous inlet.

(v) Wait until steady-state was reached. In this work, effluents were sampled every 15 minutes to test the constancy of the concentration. A minimum of two hours operation was found necessary to reach steady-state.

(vi) Take motion pictures with the HYCAM camera.

(vii) Take both organic and aqueous phase samples at the different sections of the column to obtain the steady-state concentration profile.

(viii) Close the inlet and outlet of both phases to measure the total column hold-up.

(4) Analysis Of Samples

A UNICAN SP90A Atomic Absorption spectrophotometer was used to analyse the concentration of nickel and cobalt ions. Organic samples were stripped with sulphuric acid, which was diluted with distilled water before the measurement. Aqueous samples, which were of higher concentration, were also diluted before analysis. The dilution ratio was in the 10 to 30 times range.

(5) Analysis Of Photographic Data

Pictures taken during the experiment were projected onto a scaled screen for measurement of the drop size and counting the number of drops. The drop size distribution was recorded from the details in the picture. A typical distribution is shown in figure 10. These data were then treated using a computer program (Appendix 1) to calculate Sauter-mean diameter and the interfacial area.

(6) From the concentration profiles and the measured interfacial area, the overall mass transfer coefficient was evaluated using equation (13) and a graphical integration.

FIGURE 10

A Sample Photograph

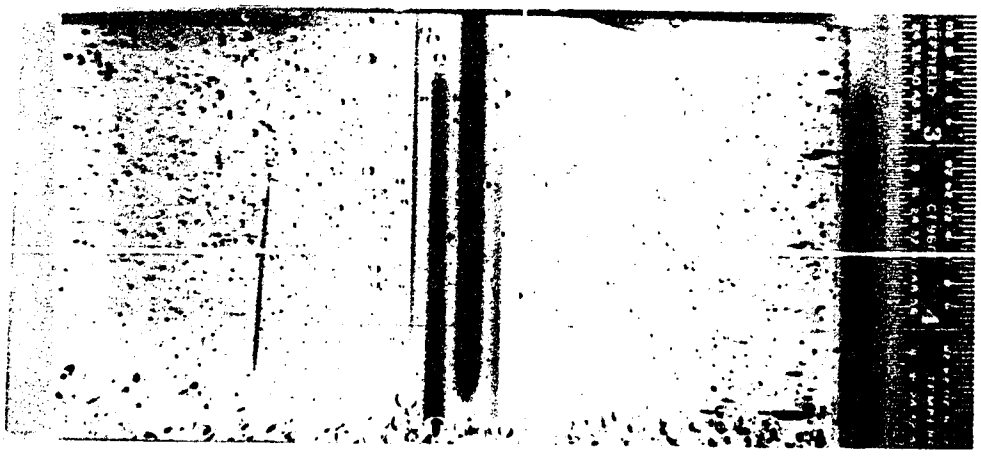
Showing the Drop Dispersion in a Pulse Cycle

(A) The quiescent period.

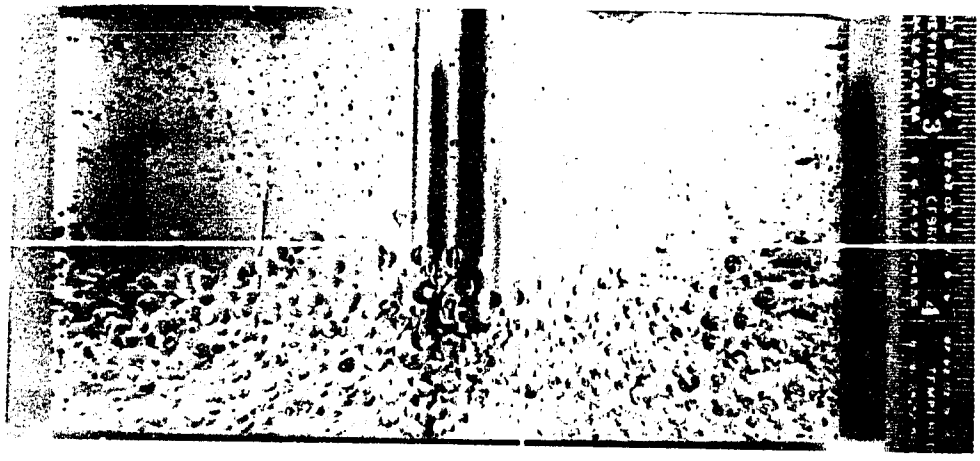
(B) Drops rising.

(C) Completely dispersed.

(D) Approach another quiescent period.



A



B

C

D

Chapter 5

Results And Discussion

Experiments were carried out for co-extraction, scrubbing and stripping which consisted of a cycle. Each cycle started from loading metal ions and ended by recovering solvents. The pulse amplitude was varied from one cycle to the next in order to compare the mass transfer coefficients for different operating conditions. The concentration profiles and calculated overall mass transfer coefficients at different sections of column are shown in Table(7) to Table(15).

In those experiments involved in metal transfer, distortion of organic drops and significant interaction between them was observed. These phenomena certainly differed from those in the hydrodynamic studies in which no metal was being transferred. Besides, the drop size distribution was found to vary slightly from plate to plate. These uncertainties made the estimation of interfacial area less accurate. In spite of such negative effects, the average values of the area-free mass transfer coefficients were calculated based on the average hold-up ratio and mean drop diameter. In addition, the values of the products of K and a were reported to provide more information of the overall column performance without separating the interfacial area from the mass transfer coefficients.

For the purpose of comparison, the experimental results are arranged in three groups according to the direction of mass transfer.

The coefficients in each group are then plotted against the organic phase concentration taking different pulse amplitude as a parameter. These average mass transfer coefficients are also correlated as a function of the organic concentration using a polynominal curve fitting method. The computer program for the curve fitting is shown in Appendix(2)and the obtained equations and plottings are shown in figures(11) to (16).

In the co-extraction group, the mass transfer coefficients are in 0.2×10^{-3} to 1.4×10^{-3} cm/sec range for cobalt and in 0.5×10^{-3} to 1.7×10^{-3} cm/sec range for nickel. The values of the coefficients increase as the organic phase concentration increases. This can be explained using equation (8) of the last chapter (58) (59) that indicates that the overall mass transfer coefficients will vary as " m' " varies if the two film resistances are of comparable magnitude. The curvature of the equilibrium line for two component system as shown in figure[3], (20), makes the variation of " m' " and " K " possible. Referring to figure 11 and 14, the slope of the fitted straight line is about 0.75 for cobalt and 0.55 for nickel. Comparison of the values between different operating conditions shows that the higher pulse amplitude gave a larger value of mass transfer coefficient.

In the scrubbing group, the coefficients remained rather constant in the different organic concentration. The values are in 1.1×10^{-3} to 1.8×10^{-3} cm/sec range for cobalt, and in 0.5×10^{-3} to 0.9×10^{-3} cm/sec range for nickel. The constancy of the mass transfer coefficients is due to the main resistance

lying in the organic phase is such that the variation of " m' " has an insignificant effect on the overall mass transfer coefficient. As observed in the co-extraction group, the larger the pulse amplitude the higher the value of the coefficient. This is consistant with the prediction correlations of the mass transfer coefficient for the circulating drops (Table 2) in which the smaller drops usually give a higher value of coefficient. The variations of drop diameter at different operating condition are recorded in Table(7) to(13).

The experimental results of the stripping process showed a slightly declining value of the mass transfer coefficients of nickel with the organic concentration, but a rather constant value for cobalt. The value of the coefficients are in 0.7×10^{-3} to 0.8×10^{-3} cm/sec range for cobalt, and in the 0.7×10^{-3} to 1.1×10^{-3} cm/sec range for nickel. Again a higher degree of agitation gave a larger value of area-free mass transfer coefficients.

The experimental error in the results mainly came from the measurement of concentration and the estimation of interfacial area. The sensitivity of Atomic Absorption Spectrophotometer which was used to measure metal ion concentration is 1 p.p.m. for cobalt and 2 p.p.m. for nickel in the operating scale. This deviation was amplified by the dilution of samples, and therefore usually gave 2 to 3 percent error in the measured concentration. Also a small amount of entrainment in the sample introduced another error although a concentration correction method was used.

According to the other investigators' reports (43), the photographic method usually has a 5 percent error in measuring the interfacial area. The neglecting of the differences in hold up ratio and drop size distribution between lower and upper sections of the column also contributed to a deviation in the calculation of mass transfer coefficients.

The material balance over the column for each component was checked, and an average 7 percent error was found.

The continuity of the aqueous concentration profiles were confirmed by sampling the aqueous phase at various heights between two plates, and it is believed to be true for the gentle agitating condition in this work.

The reproducibility of the experimental results was tested and were found to produce a 20 to 25 percent deviation, which is not very satisfactory. The difficulty in eliminating trace amounts of surface contaminants has made the reproducibility relatively low for most of the published works in liquid-liquid extraction, and it is believed that this is also the case in this work.

Table 7. Experimental Data

****

RUN NO. : 1 CO-EXTRACTION

TEMPERATURE = 28 ØC
AMPLITUDE = .95 CM FREQUENCY = 27.2 C/MIN
FLOWRATE (ML/MIN) AQ. = 320 ORG. = 480
ORGANIC SUPERFICIAL VELOCITY = .0962 CM/SEC
OVERALL ORGANIC HOLD-UP = 4.1 %
DROP SAUTER-MEAN DIAMETER = .258 CM
AVERAGE INTERFACIAL AREA = .9534 1/CM

CONCENTRATION PROFILE (G/LITER)

	SAMPLE POINT (CM):	Ø.ØØ	16.2Ø	32.3Ø	48.3Ø	64.1Ø	79.9Ø	97.1Ø	1Ø6.2Ø
COBALT:	AQ. CONC. =	.ØØ3	.ØØ8	.Ø19	.Ø42	.Ø85	.2Ø8	.312	.4Ø9
	ORG. CONC. =	Ø	.Ø14	.Ø56	.14	.221	.36	.571	.7Ø1
	EQUI. CONC.=	.31	.524	.965	1.32	1.73	1.946	2.Ø31	1.934
NICKEL:	AQ. CONC. =	.ØØ6	.Ø16	.Ø34	.Ø85	.187	.325	.618	.963
	ORG. CONC. =	Ø	.Ø42	.1Ø5	.275	.512	.9	1.475	1.745
	EQUI. CONC.=	.3Ø3	.7Ø2	1.Ø45	1.412	1.936	2.513	3.433	3.7Ø8

OVERALL MASS TRANSFER COEFFICIENTS (1ØØØØ*CM/SEC)

	SECTION :	Ø1	Ø2	Ø3	Ø4	Ø5	Ø6	Ø7
COBALT:	K (O,ORG) * A =	2.1Ø2	4.439	4.816	3.7Ø1	5.455	7.612	8.471
	K (O,ORG) =	2.2Ø5	4.656	5.Ø51	3.882	5.722	7.984	8.885
NICKEL:	K (O,ORG) * A =	6.71	5.527	1Ø.7Ø2	11.Ø38	14.192	15.749	14.556
	K (O,ORG) =	7.Ø38	5.797	11.225	11.577	14.886	16.518	15.267

Table 8. Experimental Data

****

RUN NO. : 2 CO-EXTRACTION

TEMPERATURE = 27.8 ºC
AMPLITUDE = .95 CM FREQUENCY = 27.2 C/MIN
FLOWRATE (ML/MIN) AQ. = 320 ORG. = 480
ORGANIC SUPERFICIAL VELOCITY = .0962 CM/SEC
OVERALL ORGANIC HOLD-UP = 4.18 %
DROP SAUTER-MEAN DIAMETER = .2578 CM
AVERAGE INTERFACIAL AREA = .9728 1/CM

CONCENTRATION PROFILE (G/LITER)

	SAMPLE POINT (CM):	0.00	16.20	32.30	48.30	64.10	79.90	97.10	106.20
COBALT:	AQ. CONC. =	.029	.033	.042	.072	.106	.318	.56	1.001
	ORG. CONC. =	.725	.764	.813	.841	.915	1.164	1.485	1.811
	EQUI. CONC.=	1.21	1.332	1.45	1.661	1.89	2.421	2.88	3.82
NICKEL:	AQ. CONC. =	.041	.044	.069	.104	.132	.341	.422	.763
	ORG. CONC. =	1.764	1.788	1.831	1.886	1.952	2.043	2.154	2.226
	EQUI. CONC.=	1.886	1.92	2.005	2.107	2.194	2.318	2.443	2.519

OVERALL MASS TRANSFER COEFFICIENTS (10000*CM/SEC)

	SECTION :	01	02	03	04	05	06	07
COBALT:	K (O,ORG) * A =	4.364	4.66	2.35	5.132	12.134	12.623	16.237
	K (O,ORG) =	4.486	4.79	2.416	5.275	12.473	12.976	16.69
NICKEL:	K (O,ORG) * A =	10.76	16.443	16.865	17.035	18.68	21.292	23.676
	K (O,ORG) =	11.061	16.903	17.336	17.511	19.202	21.887	24.338

Table 9. Experimental Data

****

RUN NO. : 3 SCRUBBING

TEMPERATURE = 27.6 °C
AMPLITUDE = .95 CM FREQUENCY = 27.2 C/MIN
FLOWRATE (ML/MIN) AQ. = 320 ORG. = 480
ORGANIC SUPERFICIAL VELOCITY = .0962 CM/SEC
OVERALL ORGANIC HOLD-UP = 4.13 %
DROP SAUTER-MEAN DIAMETER = .2587 CM
AVERAGE INTERFACIAL AREA = .9582 1/CM

CONCENTRATION PROFILE (G/LITER)

	SAMPLE POINT (CM):	0.00	16.20	32.30	48.30	64.10	79.90	97.10	106.20
COBALT:	AQ. CONC. =	.131	.193	.279	.427	.666	.816	1.13	1.401
	ORG. CONC. =	1.468	1.635	1.933	2.135	2.301	2.763	3.183	3.375
	EQUI. CONC.=	2.185	2.524	2.96	3.382	3.764	4.282	4.764	5.122
NICKEL:	AQ. CONC. =	.464	.296	.182	.108	.068	.042	.04	.036
	ORG. CONC. =	2.201	2.091	1.96	1.853	1.705	1.54	1.415	1.346
	EQUI. CONC.=	1.516	1.039	.764	.542	.308	.274	.181	.098

OVERALL MASS TRANSFER COEFFICIENTS (10000*CM/SEC)

	SECTION :	01	02	03	04	05	06	07
COBALT:	K (O,ORG) * A =	12.826	15.855	11.81	11.375	14.051	13.344	13.045
	K (O,ORG) =	13.385	16.547	12.325	11.871	14.664	13.926	13.614
NICKEL:	K (O,ORG) * A =	6.41	6.883	5.128	6.539	7.269	5.486	5.993
	K (O,ORG) =	6.689	7.183	5.352	6.824	7.586	5.725	6.254

Table 10. Experimental Data

RUN NO. : 5 CO-EXTRACTION

TEMPERATURE = 28.2 °C
AMPLITUDE = .51 CM FREQUENCY = 27.2 C/MIN
FLOWRATE (ML/MIN) AQ. = 320 ORG. = 480
ORGANIC SUPERFICIAL VELOCITY = .0962 CM/SEC
OVERALL ORGANIC HOLD-UP = 5.41 %
DROP SAUTER-MEAN DIAMETER = .2764 CM
AVERAGE INTERFACIAL AREA = 1.1744 1/CM

CONCENTRATION PROFILE (G/LITER)

SAMPLE POINT (CM):	0.00	16.20	32.30	48.30	64.10	79.90	97.10	106.20
COBALT: AQ. CONC. =	.0025	.0075	.016	.039	.082	.197	.298	.386
ORG. CONC. =	0	.012	.053	.137	.229	.368	.559	.682
EQUI. CONC.=	.295	.415	.801	1.289	1.706	1.864	1.997	2.064
NICKEL: AQ. CONC. =	.005	.015	.034	.078	.164	.316	.588	.796
ORG. CONC. =	0	.043	.105	.246	.469	.827	1.368	1.571
EQUI. CONC.=	.306	.696	1.052	1.421	1.914	2.503	3.121	3.264

OVERALL MASS TRANSFER COEFFICIENTS (10000*CM/SEC)

SECTION :	01	02	03	04	05	06	07
COBALT: K (O,ORG) * A =	2.254	4.594	4.901	4.03	5.301	6.202	8.689
K (O,ORG) =	1.919	3.912	4.173	3.431	4.513	5.281	7.398
NICKEL: K (O,ORG) * A =	6.179	5.885	7.924	10.094	12.639	15.352	13.066
K (O,ORG) =	5.261	5.011	6.747	8.595	10.762	13.072	11.125

Table 11. Experimental Data

****

RUN NO. : 6 SCRUBBING

TEMPERATURE = 28.3 °C
AMPLITUDE = .51 CM FREQUENCY = 27.2 C/MIN
FLOWRATE (ML/MIN) AQ. = 320 ORG. = 480
ORGANIC SUPERFICIAL VELOCITY = .0962 CM/SEC
OVERALL ORGANIC HOLD-UP = 5.45 %
DROP SAUTER-MEAN DIAMETER = .2774 CM
AVERAGE INTERFACIAL AREA = 1.1788 1/CM

CONCENTRATION PROFILE (G/LITER)

SAMPLE POINT (CM):		0.00	16.20	32.30	48.30	64.10	79.90	97.10	106.20
COBALT:	AQ. CONC. =	.13	.186	.27	.417	.631	.788	1.016	1.275
	ORG. CONC. =	1.435	1.62	1.813	2.018	2.299	2.641	3.001	3.234
	EQUI. CONC.=	2.176	2.501	2.894	3.361	3.729	4.218	4.673	5.028
NICKEL:	AQ. CONC. =	.468	.291	.188	.11	.074	.043	.038	.032
	ORG. CONC. =	2.205	2.109	1.992	1.855	1.725	1.575	1.421	1.335
	EQUI. CONC.=	1.42	1.031	.768	.546	.315	.276	.201	.126

OVERALL MASS TRANSFER COEFFICIENTS (10000*CM/SEC)

SECTION :		01	02	03	04	05	06	07
COBALT:	K (O,ORG) * A =	13.289	12.105	10.413	12.554	13.906	13.254	14.525
	K (O,ORG) =	11.273	10.268	8.833	10.649	11.796	11.243	12.322
NICKEL:	K (O,ORG) * A =	6.098	6.22	6.421	5.666	6.565	6.197	7.103
	K (O,ORG) =	5.173	5.276	5.447	4.806	5.569	5.257	6.026

Table 12. Experimental Data

****

RUN NO. : 8 CO-EXTRACTION

TEMPERATURE = 27.9 °C
AMPLITUDE = 1.9 CM FREQUENCY = 27.1 C/MIN
FLOWRATE (ML/MIN) AQ. = 320 ORG. = 480
ORGANIC SUPERFICIAL VELOCITY = .0962 CM/SEC
OVERALL ORGANIC HOLD-UP = 3.93 %
DROP SAUTER-MEAN DIAMETER = .2312 CM
AVERAGE INTERFACIAL AREA = 1.0199 1/CM

CONCENTRATION PROFILE (G/LITER)

	SAMPLE POINT (CM):	0.00	16.20	32.30	48.30	64.10	79.90	97.10	106.20
COBALT:	AQ. CONC. =	.005	.013	.026	.067	.107	.243	.391	.639
	ORG. CONC. =	0	.026	.085	.233	.486	.781	1.156	1.334
	EQUI. CONC.=	.365	.613	1.101	1.64	2.037	2.245	2.384	2.565
NICKEL:	AQ. CONC. =	.009	.019	.033	.087	.161	.348	.668	.872
	ORG. CONC. =	0	.043	.143	.313	.605	1.059	1.56	1.813
	EQUI. CONC.=	.272	.538	1.062	1.384	1.95	2.562	2.961	3.164

OVERALL MASS TRANSFER COEFFICIENTS (10000*CM/SEC)

	SECTION :	01	02	03	04	05	06	07
COBALT:	K (O,ORG) * A =	3.372	6.288	8.407	9.778	11.069	12.74	14.842
	K (O,ORG) =	3.3062	6.165	8.243	9.587	10.853	12.491	14.552
NICKEL:	K (O,ORG) * A =	8.147	9.376	11.008	13.066	17.194	17.204	17.104
	K (O,ORG) =	7.988	9.193	10.793	12.811	16.858	16.868	16.77

Table 13. Experimental Data

****

RUN NO. : 9 SCRUBBING

TEMPERATURE = 28.3 ØC
AMPLITUDE = 1.9 CM FREQUENCY = 27.1 C/MIN
FLOWRATE (ML/MIN) AQ. = 320 ORG. = 480
ORGANIC SUPERFICIAL VELOCITY = .0962 CM/SEC
OVERALL ORGANIC HOLD-UP = 3.85 %
DROP SAUTER-MEAN DIAMETER = .2302 CM
AVERAGE INTERFACIAL AREA = 1.0035 1/CM

CONCENTRATION PROFILE (G/LITER)

	SAMPLE POINT (CM):	0.00	16.20	32.30	48.30	64.10	79.90	97.10	106.20
COBALT:	AQ. CONC. =	.12	.138	.167	.288	.495	.779	1.069	1.387
	ORG. CONC. =	1.355	1.558	1.787	2.05	2.355	2.601	2.868	3.071
	EQUI. CONC.=	1.985	2.253	2.596	2.873	3.441	3.832	4.103	4.264
NICKEL:	AQ. CONC. =	.405	.277	.146	.099	.068	.061	.05	.044
	ORG. CONC. =	2.488	2.383	2.27	2.129	1.981	1.821	1.656	1.551
	EQUI. CONC.=	1.921	1.694	1.28	.896	.665	.468	.221	.138

OVERALL MASS TRANSFER COEFFICIENTS (10000*CM/SEC)

	SECTION :	Ø1	Ø2	Ø3	Ø4	Ø5	Ø6	Ø7
COBALT:	K (O,ORG) * A =	17.595	16.478	18.272	18.016	15.087	15.728	16.754
	K (O,ORG) =	17.533	16.42	18.208	17.953	15.034	15.673	16.695
NICKEL:	K (O,ORG) * A =	9.602	8.189	8.402	7.458	7.014	7.744	8.097
	K (O,ORG) =	9.568	8.16	8.373	7.432	6.989	7.717	8.068

Table 14. Experimental Data

****

RUN NO. : 10 STRIPPING

TEMPERATURE = 28.4 °C
AMPLITUDE = .95 CM FREQUENCY = 27.2 C/MIN
FLOWRATE (ML/MIN) AQ. = 320 ORG. = 480
ORGANIC SUPERFICIAL VELOCITY = .0962 CM/SEC
OVERALL ORGANIC HOLD-UP = 4.09 %
DROP SAUTER-MEAN DIAMETER = .2567 CM
AVERAGE INTERFACIAL AREA = .9561 1/CM

CONCENTRATION PROFILE (G/LITER)

	SAMPLE POINT (CM):	0.00	16.20	32.30	48.30	64.10	79.90	97.10	106.20
COBALT:	AQ. CONC. =	2.383	2.067	1.694	1.405	1.145	.0921	.662	.531
	ORG. CONC. =	2.946	2.649	2.371	2.142	1.959	1.747	1.581	1.44
	EQUI. CONC.=	.169	.145	.125	.106	.092	.074	.058	.044
NICKEL:	AQ. CONC. =	2.743	2.319	1.866	1.375	.961	.725	.516	.406
	ORG. CONC. =	2.644	2.28	2.049	1.82	1.593	1.321	1.113	.982
	EQUI. CONC.=	.308	.284	.236	.191	.138	.102	.087	.061

OVERALL MASS TRANSFER COEFFICIENTS (10000*CM/SEC)

	SECTION :	01	02	03	04	05	06	07
COBALT:	K (O,ORG) * A =	6.793	7.026	6.571	6.301	7.101	5.766	7.412
	K (O,ORG) =	7.105	7.348	6.873	6.59	7.427	6.031	7.751
NICKEL:	K (O,ORG) * A =	10.029	7.19	8.061	8.98	10.565	10.352	10.719
	K (O,ORG) =	10.489	7.52	8.431	9.392	11.05	10.827	11.211

Table 15. Experimental Data

****

RUN NO. : 11 STRIPPING

TEMPERATURE =	27.7	°C	
AMPLITUDE =	1.9	CM	FREQUENCY = 27.1 C/MIN
FLOWRATE (ML/MIN) AQ. =	320	ORG. =	480
ORGANIC SUPERFICIAL VELOCITY =	.0962	CM/SEC	
OVERALL ORGANIC HOLD-UP =	3.9	%	
DROP SAUTER-MEAN DIAMETER =	.2307	CM	
AVERAGE INTERFACIAL AREA =	1.0143	1/CM	

CONCENTRATION PROFILE (G/LITER)

SAMPLE POINT (CM):	0.00	16.20	32.30	48.30	64.10	79.90	97.10	106.20
COBALT: AQ. CONC. =	2.011	1.865	1.646	1.416	1.14	.891	.68	.535
ORG. CONC. =	1.64	1.462	1.313	1.186	1.074	.962	.876	.837
EQUI. CONC.=	.146	.133	.121	.107	.092	.074	.056	.047
NICKEL: AQ. CONC. =	1.789	1.705	1.342	1.174	.932	.785	.601	.518
ORG. CONC. =	1.58	1.416	1.275	1.139	1.016	.898	.765	.716
EQUI. CONC.=	.233	.228	.204	.186	.164	.153	.118	.106

OVERALL MASS TRANSFER COEFFICIENTS (10000*CM/SEC)

SECTION :	01	02	03	04	05	06	07
COBALT: K (O,ORG) * A =	7.482	7.07	6.691	6.673	7.257	5.681	5.074
K (O,ORG) =	7.376	6.97	6.596	6.579	7.155	5.601	5.002
NICKEL: K (O,ORG) * A =	8.021	7.433	8.304	8.152	9.229	9.401	8.182
K (O,ORG) =	7.908	7.328	8.187	8.037	9.098	9.268	8.066

FIGURE 11-16

Variation of Mass Transfer Coefficients

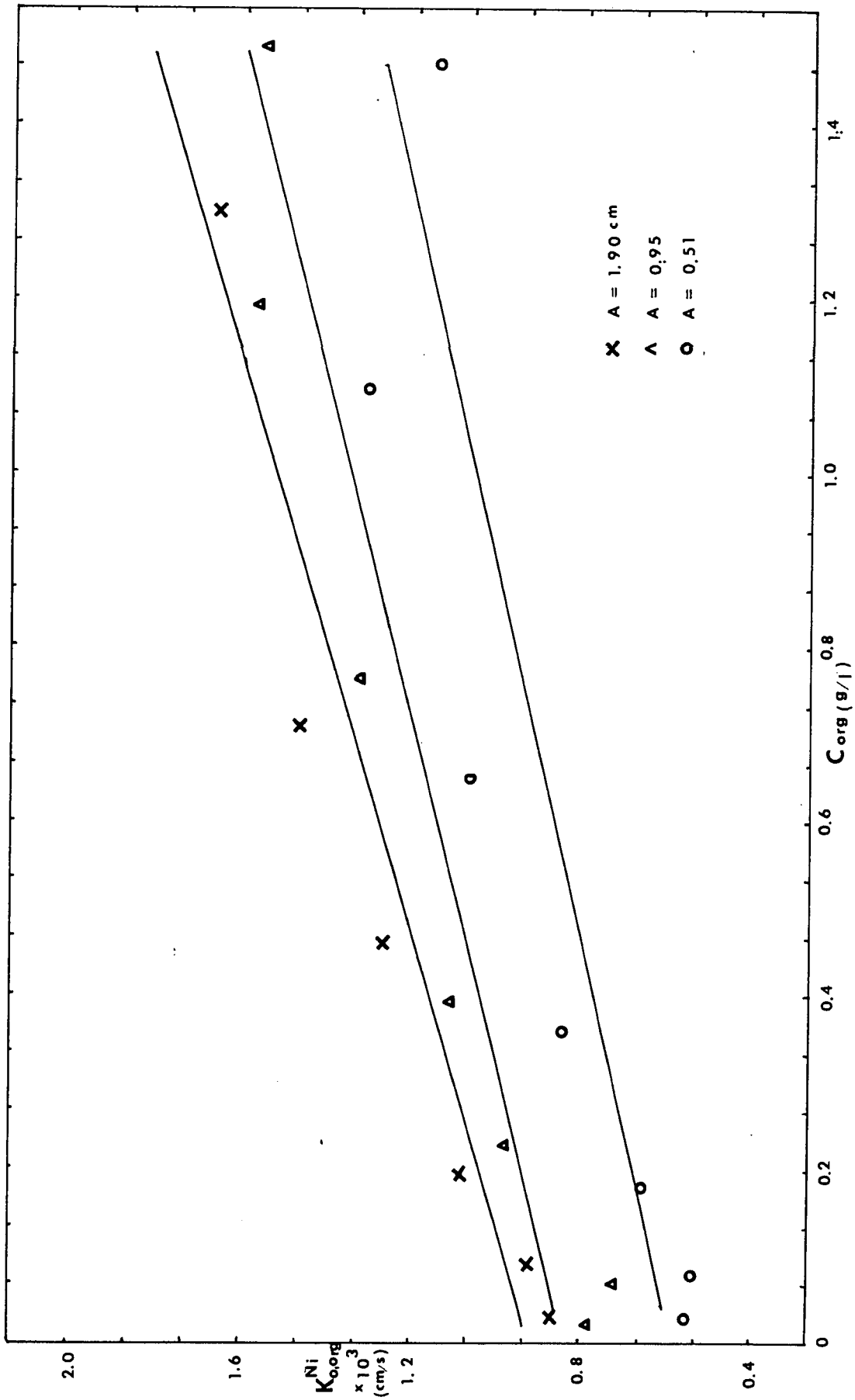


Fig. 11 K^{Ni} vs. C for Extraction

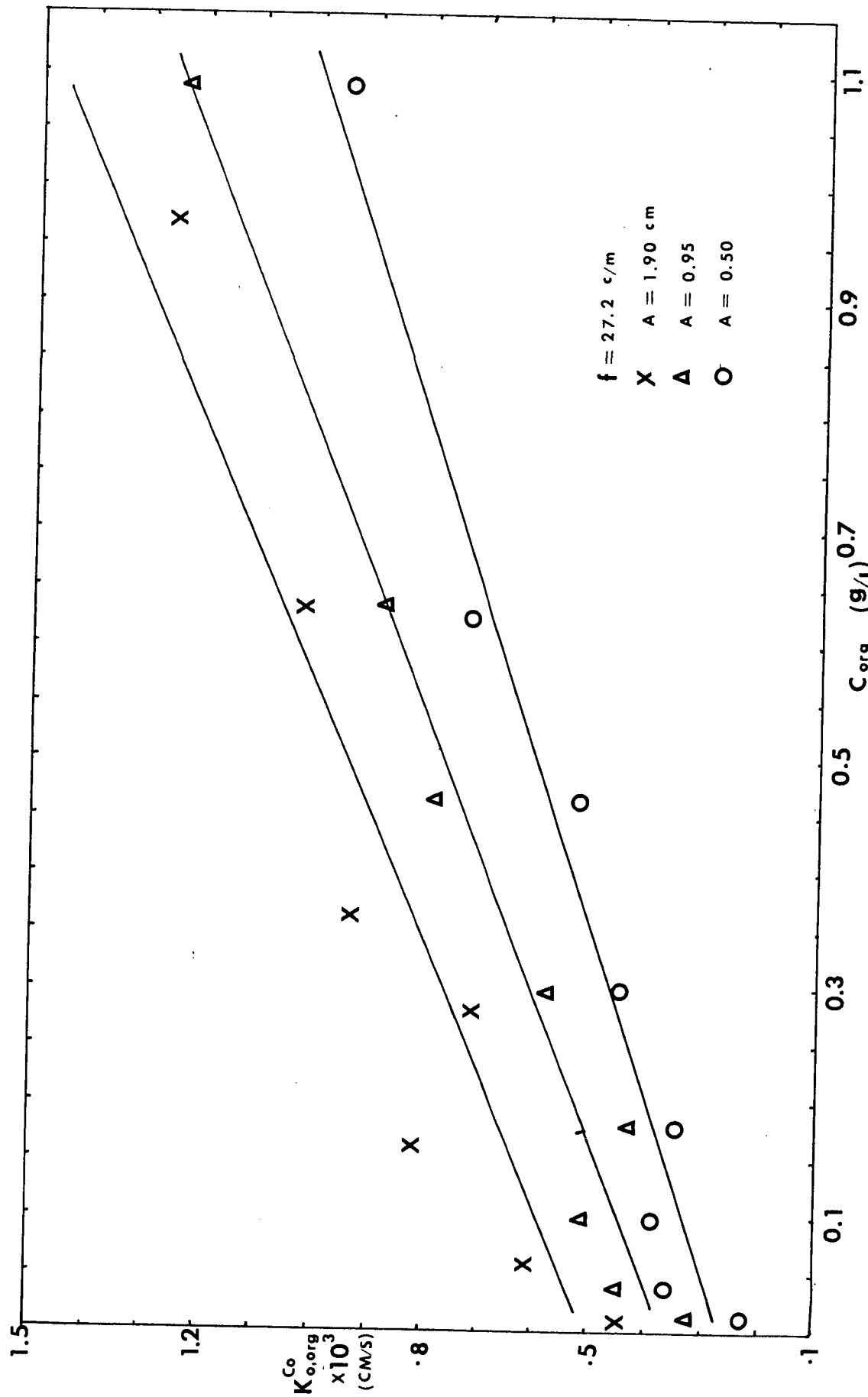


Fig.12 K^{Co} vs. C for EXTRACTION

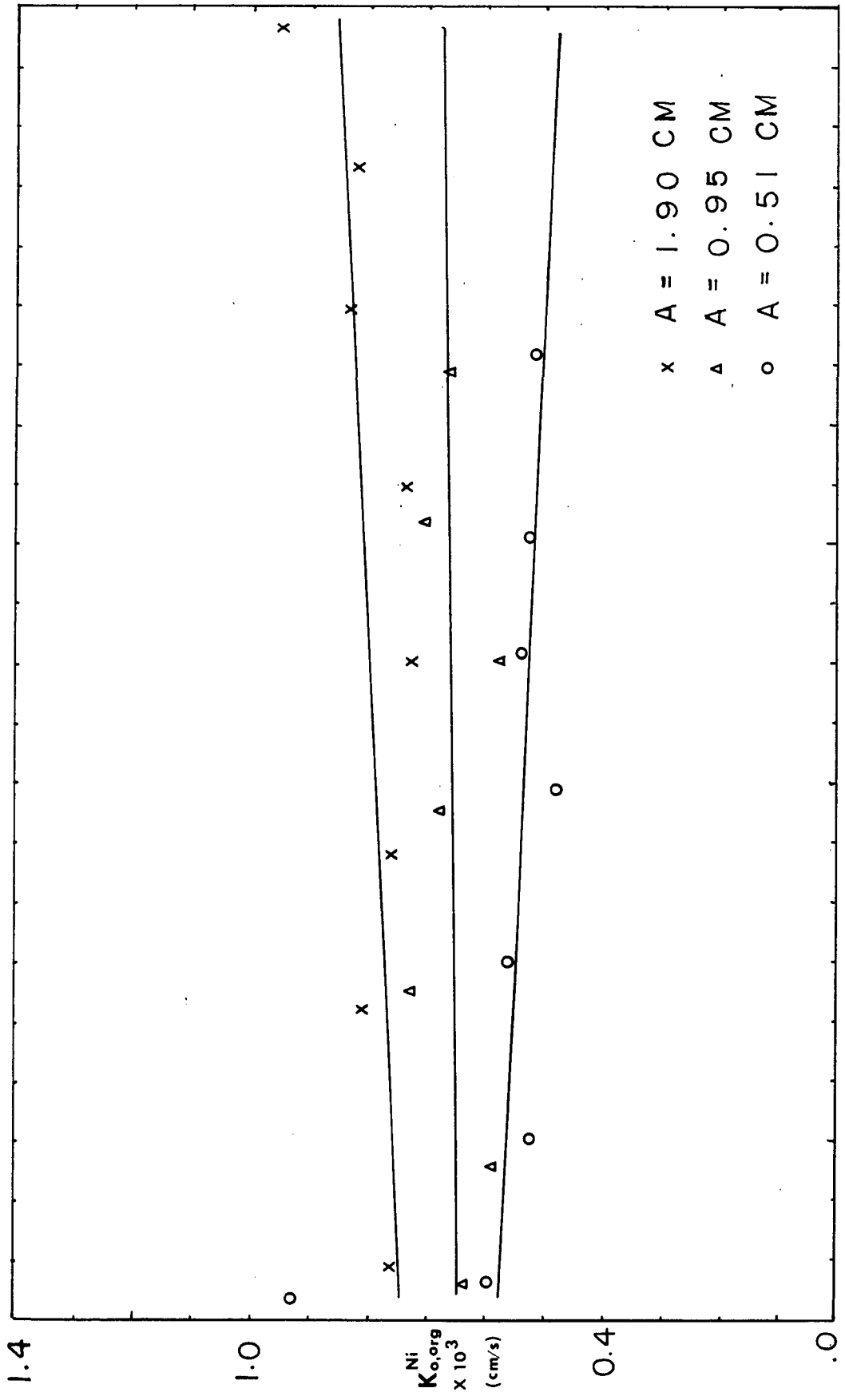


Fig.13 K^{Ni} vs C for Scrubbing

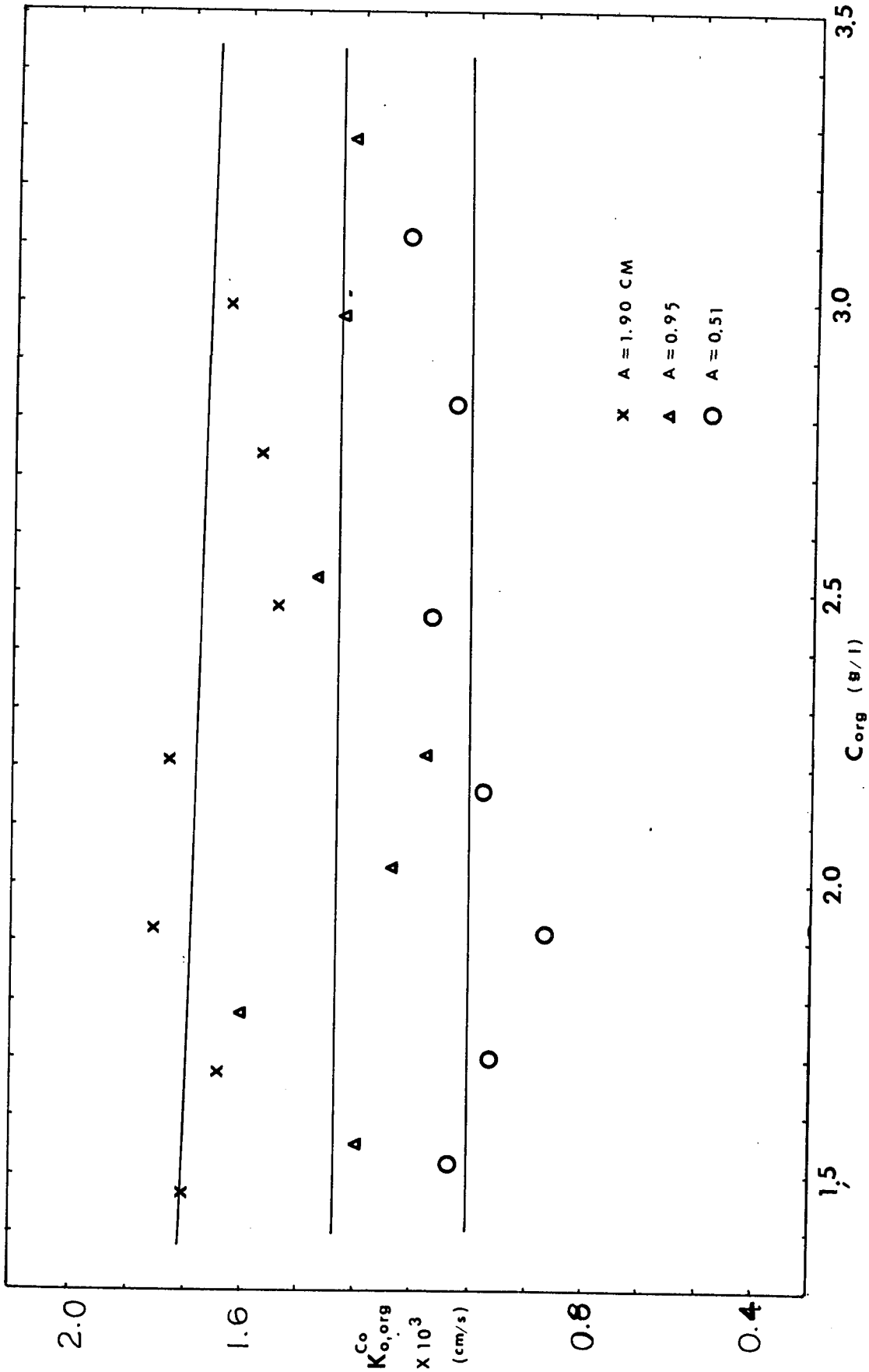


Fig.14 K^{Co} vs. C for Scrubbing

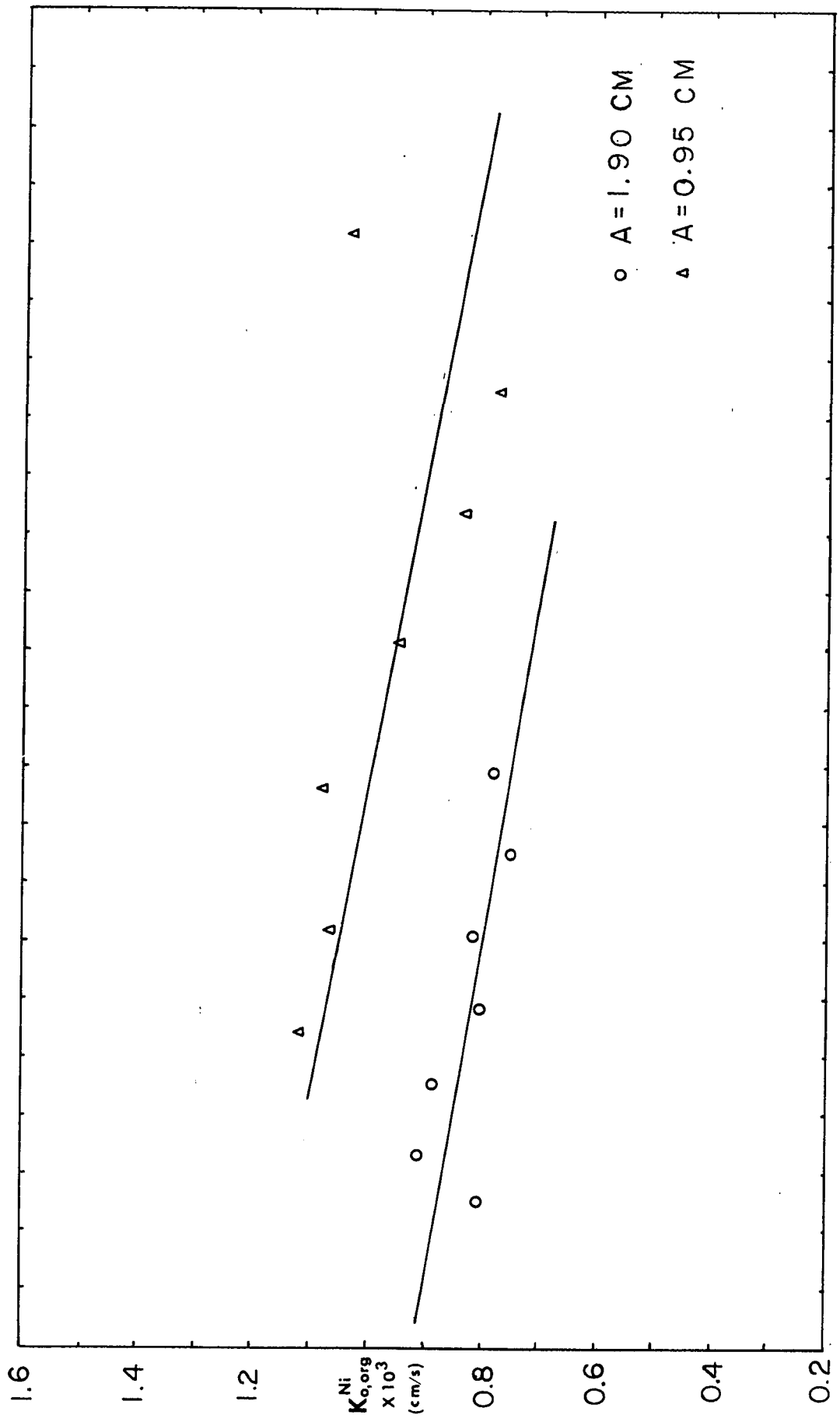


Fig.15 K^{Ni} vs. C for STRIPPING

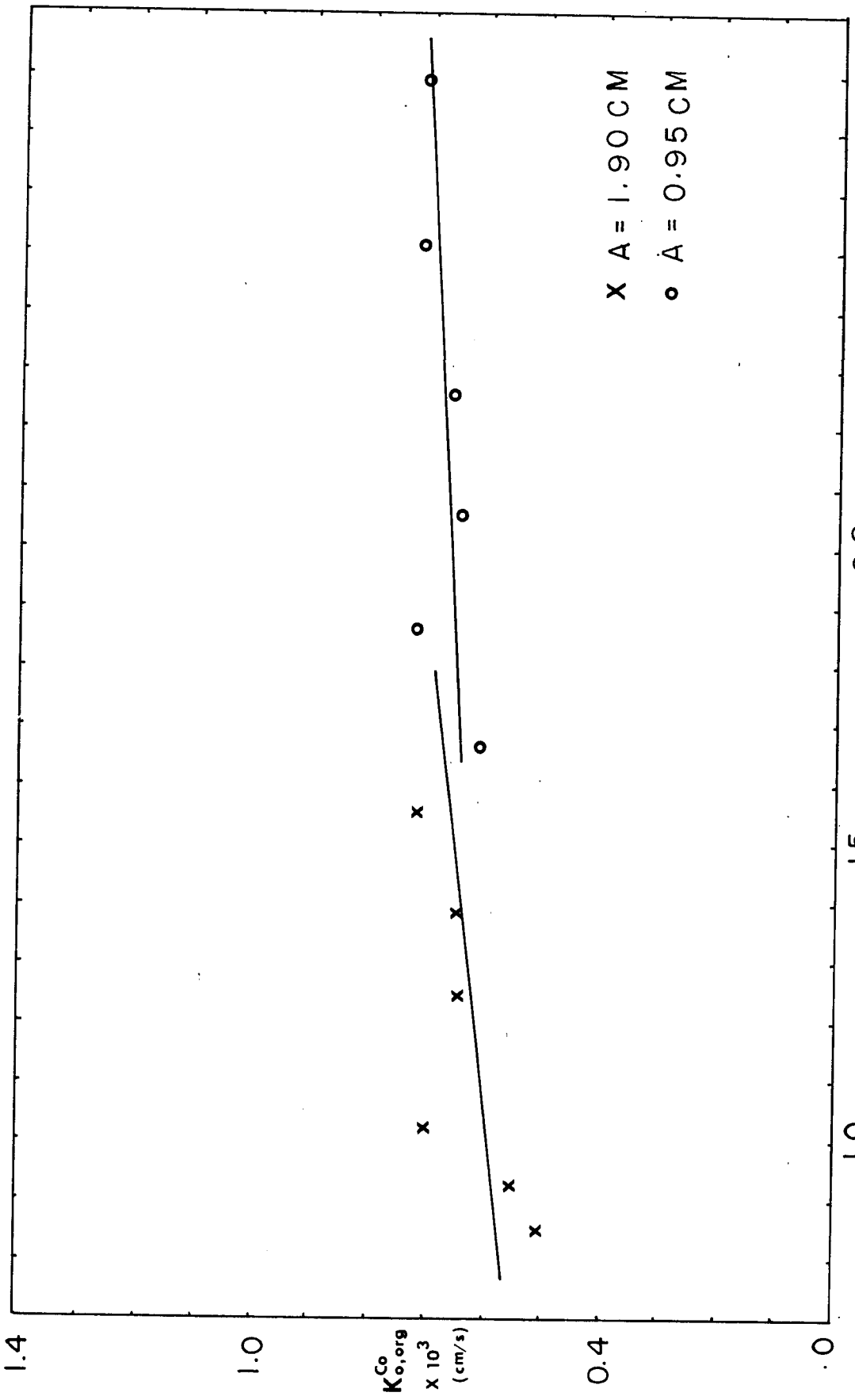


Fig.16 K^{Co} vs. C for STRIPPING

Chapter 6

Conclusion And Recommendation

Several conclusions can be made as follows:

(1) A 4" I.D. pulsed sieve-plate extraction column was successfully constructed, and either co-extraction, scrubbing or stripping process can be carried out in this column to separate nickel from cobalt.

(2) By using modified sampling devices, concentration profiles along the column were obtained. This provided suitable information to permit evaluation of the mass transfer performance in the pulsed column for the three different separation steps.

(3) Experimental results indicated the importance of the effect of the direction of transfer on the overall mass transfer coefficients. During co-extraction, the value of coefficients increased as the organic phase concentration increased, but these values remained constant during scrubbing and stripping.

(4) Comparison of the coefficients at different operating conditions showed that a higher pulse amplitude gave larger value of the coefficients within the range investigated. But a reduction in total hold-up ratio at such higher amplitudes (as recorded in Table 7 to 13) had a negative influence on the overall extraction rate.

(5) Some understanding of the separation process in the pulse sieve-plate extraction column was obtained through this preliminary study.

Based on the results of this work, the following recommendations for further studies are made:

(1) More precise data on the hydrodynamics of the column are required. The factors such as drop size and hold-up ratio, varied significantly from case to case, especially when charged metal ions were transfer from one phase to the other. The effects of interfacial tension on mass transfer increases the complexity of the problem. With further hydrodynamic information, more precise value of area-free mass transfer coefficient can be obtained.

(2) Intensive study on the effects of the degree of agitation on extraction efficiency is necessary for optimizing the pulse column performance.

(3) In order to obtain more accurate information, the axial mixing coefficients in the apparatus have to be measured to correct the mixing effects, especially during the operation with higher pulse amplitude and frequency.

(4) The surface contaminants in both phases have an uncertain effect on mass transfer. Therefore the elimination of such impurities can improve the reproducibility of the experimental results.

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APPENDIX I

Computer Program for Calculation of Sauter-mean Diameter

(BASIC)

```
LIST
1   REM    CALCULATION OF SAUTER-MEAN DIAMETER
2   REM    PLOTTING OF DROP SIZE DISTRIBUTION
3   REM    JOHNSEE LEE ; CHEM. ENG.
4   REM    N:NO. OF DROPS
5   REM    D: MEASURED PHOTO DIAMETER
6   REM    R: REAL SCALE; P: PHOTO SCALE
7   REM    DATA START FROM 600
10   LET T= 0
20   LET V= 0
30   LET X= 0
35   PRINT
36   PRINT "------------------------------------------------------------"
37   PRINT
40   READ N
50   READ D
60   IF N= 0 GOTO  500
70   LET S=N*(D↑3)
80   LET W=N*(D↑2)
90   LET X=X+N
100   LET T=T+S
110   LET V=V+W
130   GOTO  40
500   LET D1=T/V
505   PRINT
510   PRINT "------------------------------------------------------------"
520   PRINT
530   PRINT
535   INPUT R
536   INPUT P
537   LET R1=R/P
538   LET D2=D1*R1
539   PRINT
540   PRINT "                SAUTER-MEAN DIAMETER = ",D2,"M.M."
550   PRINT
560   PRINT "          TOTAL NO. OF DROPS SAMPLED = ",X
600   DATA  1, 1, 4, 1.5, 8, 2, 28, 2.5, 45, 3, 53, 3.5
610   DATA  71, 4, 139, 4.5, 144, 5, 153, 5.5, 147, 6
620   DATA  132, 6.5, 102, 7, 66, 7.5, 29, 8, 16, 8.5
630   DATA  13, 9, 9, 9.5, 4, 10, 3, 10.5, 1, 11
640   DATA  0, 0
120 PRINT D; TAB(N/2.5);"*";N
```

APPENDIX II

Computer program for

Polynominal Curve Fitting.

(BASIC)

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LIST
10   REM      INPUT DATA: S,T,E(1,S),Y(S)
20   REM      STATEMENT NO. FOR INPUT DATA: 1600---1699
21   REM      S: NO. OF SETS OF GIVEN DATA
22   REM      T: DEGREE OF POLYNOMIAL (ONE VARIABLE ONLY)
30   PRINT
35   PRINT
40   PRINT "      ================================================="
45   PRINT
50   GOSUB  1010
60   LET N=T+1
70   LET M=T+2
195   PRINT
196   PRINT
197   GOSUB  400
200   PRINT "******* THE SOLUTIONS :  *******"
205   FOR I=1 TO N
210     PRINT "           X(";I;")=",A[I,M]
215   NEXT I
230   LET X=8.5
232   LET S0= 0
234   PRINT
235   PRINT
240   FOR I=1 TO 69
250     PRINT "-";
260   NEXT I
262   PRINT
269   LET R=A[1,M]
270   FOR I=2 TO N
280     LET V[I]=A[I,M]*X↑(I-1)
290     LET R=R+V[I]
300   NEXT I
305   IF S0= 0 GOTO  310
306   PRINT "      Y=   ",R
307   IF X= 0 GOTO  390
308   GOTO  384
310   IF R>220 GOTO  380
315   IF R< 0 GOTO  380
317   IF X>100 GOTO  380
320   PRINT X; TAB (R/3.1);"*";R
330   LET X=X+2.5
340   GOTO  269
360   FOR I=1 TO 69
381     PRINT "-";
382   NEXT I
384   INPUT X
385   LET S0=5
386   GOTO  262
390   STOP
400   PRINT
440   LET L=N
452   FOR L=1 TO N
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455     LET K=A[L,L]
457     IF K= 0 GOTO  475
460     FOR J=1 TO M
465       LET A[L,J]=A[L,J]/K
470     NEXT J
472     GOTO  500
475     FOR J=1 TO M
477       LET D[L,J]=A[L+1,J]
479       LET A[L+1,J]=A[L,J]
481       LET A[L,J]=D[L,J]
483     NEXT J
485     IF A[L,L]= 0 GOTO  489
487     GOTO  455
489     FOR J=1 TO M
491       LET D[L,J]=A[L+2,J]
492       LET A[L+2,J]=A[L,J]
493       LET A[L,J]=D[L,J]
494     NEXT J
495     GOTO  455
500     FOR I=1 TO N
550       FOR J=1 TO M
590         IF I=L GOTO  640
600         LET C[I,J]=A[L,L]*A[I,J]-A[I,L]*A[L,J]
630         GOTO  660
640         LET C[I,J]=A[I,J]
660       NEXT J
680     NEXT I
685     PRINT
686     PRINT
687     FOR I=1 TO N
688       FOR J=1 TO M
689         LET A[I,J]=C[I,J]
690       NEXT J
691     NEXT I
695   NEXT L
700   RETURN
1010   READ S,T
1020   DIM Y[S]
1023   LET T2=T*2
1025   DIM E[T2,S]
1027   DIM F[T+1,S]
1028   LET T2=2*T
1029   DIM H[T*3],G[T2]
1030   FOR I=1 TO S
1040     READ E[1,I]
1050     READ Y[I]
1051   NEXT I
1052   PRINT
1053   PRINT "  **** INPUT DATA: ****"
1054   PRINT
1055   FOR I=1 TO S
1056     PRINT E[1,I],Y[I]
1057   NEXT I
1063   FOR I=1 TO T2
1065     LET H[I]= 0
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1067  NEXT I
1068  FOR I=1 TO T+1
1069    LET G[I]= 0
1070  NEXT I
1075  FOR I=1 TO T2-1
1080    FOR J=1 TO S
1090      LET E[I+1,J]=E[I,J]*E[1,J]
1100    NEXT J
1110  NEXT I
1120  FOR I=1 TO T+1
1130    FOR J=1 TO S
1140      LET F[I,J]=E[I,J]*Y[J]
1150    NEXT J
1160  NEXT I
1200  FOR I=1 TO T2
1210    FOR J=1 TO S
1220      LET H[I]=H[I]+E[I,J]
1230    NEXT J
1240  NEXT I
1242  FOR I=1 TO S
1244    LET G[1]=G[1]+Y[I]
1246  NEXT I
1250  FOR I=2 TO T+1
1260    FOR J=1 TO S
1270      LET G[I]=G[I]+F[I-1,J]
1280    NEXT J
1290  NEXT I
1360  LET A[1,1]=S
1400  FOR I=1 TO T
1415    LET A[1,I+1]=H[I]
1420  NEXT I
1450  LET P=1
1455  LET Q=P+1
1460  FOR I=P TO T+P
1472    LET A[Q,I-P+1]=H[I]
1480  NEXT I
1500  LET P=P+1
1505  IF P>T GOTO  1550
1510  GOTO  1455
1550  PRINT
1570  FOR I=1 TO T+1
1585    LET A[I,T+2]=G[I]
1587  NEXT I
1599  RETURN
1600  DATA  17, 2
1610  DATA  100, 0, 84, 10, 73, 20, 62, 30, 56, 40, 49.5, 50
1620  DATA  43.5, 60, 44, 70, 39.5, 80, 35, 90, 31.8, 100
1630  DATA  30, 110, 27, 120, 22.5, 140, 17.5, 160, 12.5, 180, 0, 200
1700  END
RUN
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