A STATISTICAL APPROACH TO THE SEPARATION OF COBALT AND NICKEL WITH SODIUM DI(2-ETHYLHEXYL) PHOSPHATE

By David Ian Brandt, M.Sc., B.Sc.

A thesis submitted for the
Degree of Doctor of Philosophy
of the University of London

February 1986

Department of Metallurgy
and Materials Science,

Royal School of Mines,

Imperial College of Science
and Technology.

For:

My Mother and Father

I will arise and go now, and go to
Innisfree,
And a small cabin build there,
of clay and wattles made;
Nine bean rows will I have there...

From:

The Lake Isle of Innisfree

By

W.B. Yeats.

ABSTRACT

The separation of cobalt and nickel in aqueous sulphate solution, at elevated temperature, by solvent extraction with the sodium salt of di(2-ethylhexyl) phosphoric acid (D_2EHPA), has been studied using statistical methods of experimental design.

A full (2^5) factorial design has been used unreplicated to investigate the effects of five variables on the equilibrium distribution, at levels which could be expected in an industrial separation.

The variables studied were initial pH, initial aqueous Co and Ni concentrations, equilibrium temperature (at 50°C and 80°C) and initial aqueous Na_2SO_4 concentration. The results obtained are explained in terms of the known chemistry of the system.

Using multiple regression analysis, linear empirical polynomial expressions were obtained which describe the distribution of cobalt and nickel within the ranges studied.

In experiments prior to the factorial design, simple equilibrium expressions did not prove satisfactory for describing the distribution obtained.

CONTENTS

		Page
ABSTRACT		3
CONTENTS		4
LIST OF TABLES		9
LIST OF FIGURES		14
LIST OF SYMBOLS		16
CHAPTER 1. INTRODUCTION		20
1.1	Aim of the Study	21
1.2	General Aspects of the Separation of Cobalt and Nickel	22
1.3	Separation by Solvent Extraction with D_2EHPA	25
	1.3.1 Process Description	25
	1.3.2 The Nature of Extraction	29
	1.3.3 Solution Pretreatment and Separation pH	30
	1.3.4 Conversion of the Organic Phase to the Alkali-Salt Form	31
	1.3.5 Extraction and Scrubbing	31
	1.3.6 Stripping	33
CHAPTER 2. A LITERATURE SURVEY ON THE CHEMISTRY OF EXTRACTION		34
Introduction		35
2.1	Extraction Equations	35
2.2	The Extracted Species	39
2.3	A Chemical Basis for the Selectivity of the Extractant Towards Cobalt	48
2.4	The Polymerization of the Extracted Complex	50
	The Influence of the Diluent on Extraction	54

		Page
CHAPTER 3.	THE MODELLING OF EQUILIBRIUM DISTRIBUTION AND THE USE OF STATISTICAL METHODS OF EXPERIMENTAL DESIGN	57
3.1	General Introduction	58
3.2	Distribution Models	61
	Chemically-Based Models	61
	Semi-Empirical Models	64
	Empirical Models and Statistical Methods	66
3.3	Problems in Modelling	67
CHAPTER 4.	EXPERIMENTAL METHODS	73
4.1	Solvent Make-up and Conversion to Sodium-Salt Form	74
4.2	Equilibration of the Phases	76
4.3	Cross-Current Cascade Experiments	77
	Loading Experiments	77
	Scrubbing Experiments	78
4.4	Factorial Design Experiments	79
	Randomization of the Factorial Experiments	81
4.5	Analysis	82
	pH Measurements	82
	Analysis for Cobalt and Nickel by Atomic-Absorption Spectrophotometry	83
	A.A.S. for Cobalt	84
	A.A.S. for Nickel	84
4.6	Reagents	85

		Page
CHAPTER 5.	NON-FACTORIAL EXPERIMENTS: RESULTS AND DISCUSSION	87
5.1	Cross-Current Extraction Cascades	88
	Loading Experiments	88
	Scrubbing Experiments	93
5.2	The Treatment of Distribution Data by Chemical Equilibria	96
CHAPTER 6.	THE FACTORIAL DESIGN	102
6.1	Objectives of the Design	103
6.2	Selection of the Variables and their Levels	104
	Initial pH	104
	Initial Aqueous Cobalt Concentration and Initial Aqueous Nickel Concentration	106
	Equilibrium Temperature	108
	Initial Aqueous Sodium Sulphate Concentration	109
6.3	Other Conditions	110
6.4	The Experimental Matrix	112
6.5	Selection of the Responses	113
CHAPTER 7.	A STATISTICAL STUDY OF THE COBALT RESPONSE	115
7.1	Factorial Analysis	116
	Calculation of the Effects	116
	Significance Testing of the Effects	124
	Estimate of S.E.(Effect) from Higher-Order Interactions	127
	The Half-Normal Probability Plot	132
7.2	Regression Analysis	134

		Page
	The Method of Least-Squares	135
	Orthogonality and Least-Squares Regression	135
	The Regression Equation	136
	Equivalence of the Factorial Effect and Regression Parameter	140
	Goodness of Fit	142
	Distribution of the Residuals	143
	Regression of the Cobalt Response	144
	Discussion and Conclusions	169
7.3	Statistical Conclusions for the Cobalt Study	175
CHAPTER 8.	A STATISTICAL STUDY OF THE NICKEL RESPONSE	176
8.1	Factorial Analysis	177
	Calculation and Inspection of the Effects	177
	Significance Testing of the Effects	180
	The Half-Normal Probability Plot	184
8.2	Regression Analysis of the Nickel Response	186
	Regression Conclusions	196
8.3	Statistical Conclusions for the Nickel Study	198
CHAPTER 9.	A STATISTICAL STUDY OF THE EQUILIBRIUM pH RESPONSE	199
9.1	Factorial Analysis	200
	Calculation and Inspection of the Effects	200
	Significance Testing of the Effects	200
	The Half-Normal Probability Plot	207
9.2	Regression Analysis of the Equilibrium pH Response	207

Page

Regression Conclusions 223

9.3 Statistical Conclusions for the pH Study 226

CHAPTER 10. FACTORIAL EXPERIMENTS: DISCUSSION AND CONCLUSIONS 227

10.1 Influences on the Cobalt and Nickel Responses 228

The Meaning of the Effects 228

The Cobalt and Nickel Distribution Behaviour 235

Influence of Temperature 238

Similarity of the Cobalt and Nickel Effects 241

Non-Influencing Variables 245

10.2 Influences on the Equilibrium pH 247

The Meaning of the Effects 247

pH Behaviour 250

10.3 Quantitative Relationships 257

10.4 Conclusions 260

REFERENCES 264

APPENDICES 271

Appendix 1. Distribution Curves 272

Appendix 2. Statistical Appendices 276

ACKNOWLEDGEMENTS 285

LIST OF TABLES

No.	Title	Page
1.1	Processes for the separation of cobalt and nickel	23
1.2	Comparison of process variants	28
2.1	Sato and Nakamura's polymerization determinations	50
2.2	Approximate D_{Co} values at 75°C for different diluent/modifier combinations	56
5.1	Cross-current loading experiments at 80°C	90
5.2	Cross-current scrubbing experiments at 80°C and pH = 5.5	94
5.3	Equilibrium distribution data, and values for K_1/K_2 calculated according to Equation 5.12	99
6.1	The factorial variables and their levels	104
6.2	Combinations of cobalt and nickel factorial variables	107
6.3	Comparison of the compositions of the precipitated solid and some theoretical compounds	111
6.4	Experimental results from the factorial design. (The first six columns constitute the DESIGN MATRIX)	114
7.1	Calculated effects for the response: equilibrium organic cobalt concentration	118
7.2	Ranked absolute values of cobalt effects	121
7.3	Comparison between treatment combinations with variable D at the low level and at the high level	123

No.	Title	Page
7.4	Significance testing of the cobalt effects using two-tailed t-tests	126
7.5	Two-tailed t-tests for the cobalt effects using S.E.(3,4,5-f.i.)	131
7.6	Variables included in the cobalt regression runs	145
7.7	Statistical output from Computer Run 1. Regression model including variables B, C and D	146
7.8	Residuals and predicted response values for model fitted in Computer Run 1	148
7.9	Statistical output from Computer Run 2. Regression model including variables A, B, C and D	150
7.10	Residuals and predicted response values for model fitted in Computer Run 2	152
7.11	Statistical output from Computer Run 3. Model including variables B, C, D and E	153
7.12	Residuals and predicted response values for model fitted in Computer Run 3	155
7.13	Statistical output from Computer Run 4. Model including variables B, C and D and interaction BD	156
7.14	Residuals and predicted response values for model fitted in Computer Run 4	158
7.15	Statistical output from Computer Run 5. Regression model including variables B, C and D and interactions BD and CD	159
7.16	Residuals for model fitted in Computer Run 5	161
7.17	Statistical output from Computer Run 6. Regression model including variables B, C and D and interactions BC, BD and CD	162
7.18	Residuals and predicted response values for model fitted in Computer Run 6	164
7.19	Statistical output from Computer Run 7. Regression model including variables B, C and D and interactions BD, CD and BCD	165

No.	Title	Page
7.20	Residuals and predicted response values for model fitted in Computer Run 7	167
7.21	(At low level of cobalt variable). Mass-balance for equilibrium cobalt phase concentrations, and comparison with residuals from Computer Run 5	171
7.22	(At high level of cobalt variable). Mass-balance for equilibrium cobalt phase concentrations, and comparison with residuals from Computer Run 5	172
7.23	Real factors for the cobalt response	173
8.1	Calculated effects for the response: equilibrium organic nickel concentration	178
8.2	Ranked absolute values of nickel effects	179
8.3	Significance testing of the nickel response effects, using two-tailed t-tests and S.E.(4,5-f.i.)	181
8.4	Two-tailed t-tests for the nickel effects using S.E.(3,4,5-f.i.)	183
8.5	Variables included in the nickel regression runs	186
8.6	Statistical output from Computer Run 8. Regression model including variables B, C and D	187
8.7	Residuals and predicted response values for model fitted in Computer Run 8	189
8.8	Statistical output from Computer Run 12. Regression model including variables B, C and D and interactions BD and CD	192
8.9	Residuals and predicted response values for model fitted in Computer Run 12	195
8.10	Real factors for the nickel response	198
9.1	Calculated effects for the response: equilibrium pH	201
9.2	Ranked absolute values of pH effects	202

No.	Title	Page
9.3	Two-tailed t-tests for the pH effects using S.E.(4,5-f.i.)	204
9.4	Two-tailed t-tests for the pH effects using S.E.(3,4,5-f.i.)	205
9.5	Variables included in the equilibrium pH regression runs	208
9.6	Statistical output from Computer Run 16. Regression model including variables C and D	209
9.7	Residuals and predicted response values for model fitted in Computer Run 16	212
9.8	Statistical output from Computer Run 18. Regression model including variables A, C and D and interaction CD	214
9.9	Residuals and predicted response values for model fitted in Computer Run 18	216
9.10	Statistical output from Computer Run 23. Regression model with transformed response, and including variables A, C and D and interaction CD	219
9.11	Residuals and predicted response values for transformed response model (Computer Run 23)	222
9.12	Real factors for the equilibrium pH response	226
10.1	The factorial variables and their levels	230
10.2	Two-way table for $C_{Co}(i,aq)$ x T interaction, cobalt response	231
10.3	$C_{Ni}(i,aq)$ x T interaction, cobalt response	232
10.4	$C_{Co}(i,aq)$ x T interaction, nickel response	234
10.5	$C_{Ni}(i,aq)$ x T interaction, nickel response	235
10.6	Cobalt and nickel distribution behaviour	236
10.7	Extraction in the factorial experiments of cobalt and nickel combined	242

No.	Title	Page
10.8	Two-factor interaction $C_{Ni}(i,aq)$ x T, pH response	249

Appendix

1	Yates's algorithm for the cobalt response, 2^5 factorial design	281

LIST OF FIGURES

No.	Title	Page
1.1	A schematic representation of the separation with D_2EHPA	26
2.1	Sato and Nakamura's differential thermal and thermogravimetric analyses of the cobalt and nickel D_2EHPA complexes. Figure (a) T.G.A. and Figure (b) D.T.A.	42
5.1.a and 5.1.b	Representations of cross-current extractions cascades. a. loading cascade and b. scrubbing cascade	89
7.1	The half-normal probability plot for the cobalt effects	133
7.2.a and 7.2.b	Diagnostic plots for model fitted in Computer Run 1	147
7.3.a and 7.3.b	Diagnostic plots for model fitted in Computer Run 2	151
7.4.a and 7.4.b	Diagnostic plots for model fitted in Computer Run 3	154
7.5.a and 7.5.b	Diagnostic plots for model fitted in Computer Run 4	157
7.6.a and 7.6.b	Diagnostic plots for model fitted in Computer Run 5	160
7.7.a and 7.7.b	Diagnostic plots for model fitted in Computer Run 6	163
7.8.a and 7.8.b	Diagnostic plots for model fitted in Computer Run 7	166
7.9	Plot of predicted versus measured cobalt response for model including B, C, D, BD and CD (Computer Run 5)	173

No.	Title	Page
8.1	The half-normal probability plot for the nickel effects	185
8.2.a and 8.2.b	Diagnostic plots for model fitted in Computer Run 8	188
8.3.a and 8.3.b	Diagnostic plots for model fitted in Computer Run 12	193
8.4	Plot of predicted versus measured nickel response for model including B, C, D, BD and CD (Computer Run 12)	194
9.1	The half-normal probability plot for the equilibrium pH effects	206
9.2.a and 9.2.b	Diagnostic plots for model fitted in Computer Run 16	210
9.2.c	Plot of predicted versus measured pH response for model fitted in Computer Run 16	211
9.3.a and 9.3.b	Diagnostic plots for model fitted in Computer Run 18	215
9.4.a and 9.4.b	Diagnostic plots for model fitted in Computer Run 23	220
9.4.c	Plot of predicted versus measured response for transformed response model (Computer Run 23)	221
9.5	Plot of predicted versus measured equilibrium pH response for model including A, C, D and CD (Computer Run 18)	225
Appendix		
1a	D_2EHPA equilibrium distribution isotherms at $80^{\circ}C$ for cobalt, in the presence of fixed quantities of total distributed nickel	272
1b	Nickel extraction in the same equilibrations	272
2a	D_2EHPA equilibrium isotherms at $80^{\circ}C$ for nickel in the presence of fixed quantities of total distributed cobalt	275
2b	Cobalt extraction in the same equilibrations	275

LIST OF SYMBOLS

Non-Statistical

a - activity of the species indicated

aq - aqueous phase

C - concentration of species indicated

D - distribution ratio of species indicated

Δ - change in the quantity indicated

f - some function of

ΔG - free energy change of reaction

ΔH - enthalpy of reaction

i (non-subscripted) - initial

K - equilibrium constant

L - concentration ratio of initial metal ion to initial extractant

M - molar units

M, M^{n+} - metallic species

n - stoichiometric coefficient of a reaction

n - polymerization number (equation 3.10)

R - di(2-ethylhexyl) phosphate anion, or (2-ethylhexyl) group

ΔS - entropy of reaction

T - temperature or equilibrium temperature as indicated

v/o - percent by volume

v/v - volume to volume ratio

w/o - percent by weight

w/w - weight to weight ratio

X - some alkyl phosphoric group

{ } - activity of the species enclosed in the brackets

[ ] - equilibrium concentration of species enclosed in the brackets

$[\ ]^+$, etc. - complex ion

β_N^M - separation factor for species M and N

Statistical

A - code letter for variable 'initial pH'; also signifies the main-effect of the variable

a, ab, abc, cd, etc. - code for treatment or treatment combination

B - code letter for variable 'initial aqueous cobalt concentration'; also signifies the main-effect of the variable

C - code letter for variable 'initial aqueous nickel concentration'; also signifies the main-effect of the variable

D - code letter for variable 'equilibrium temperature'; also signifies the main-effect of the variable

d - residual

d_i - residual from ith observation

S.D.d. - standard deviation of the residuals

E - code letter for variable 'initial aqueous Na_2SO_4 concentration; also signifies the main-effect of the variable

2-f.i., 3-f.i., etc. - two-factor interaction, three-factor interaction, and so on

'L' - treatment code for treatment combination in which all factorial variables are at their low levels

N - total number of experiments in the factorial design

NS - statistically non-significant

n - number of factors in the factorial design

R^2 - multiple correlation coefficient

S - statistically significant

S.E.(effect) - standard error of an effect

S.E.(observation) - standard error of an observation

S.D.$\hat{y}$. - standard deviation of the predicted response value

t_c - calculated t-value

$t_{\alpha/2,\nu}$ - tabulated value of t from student's t-distribution, with level of probability $\alpha/2$ and ν degrees of freedom

V - variance

X_i - variable i in coded form

$X_{i,high}$ - high factorial level of variable i in coded form

$X_{i,low}$ - low factorial level of variable i in coded form

x_i - variable i in 'natural' (uncoded) form

$\bar{x}_i$ - mean level of variable i

$x_{i,high}$ - high factorial level of variable i in 'natural' form

$x_{i,low}$ - low factorial level of variable i in 'natural' form

Y - transformed response

y - response

y_i - response value for ith experiment

$\bar{y}$ - average value of the response

α - level of significance

β - regression parameter for 'natural' variable regression equation

β_o - regression parameter for 'dummy' variable x_o

β' - regression parameter for coded-variable regression equation

β'_o - regression parameter for 'dummy' variable X_o

ε - experimental error associated with measured response value

η - true value of response

ν - degrees of freedom

CHAPTER 1

INTRODUCTION

1.1 Aim of the Study

This study has been concerned with the distribution and hence the separation of cobalt and nickel at equilibrium in the di(2-ethylhexyl) phosphoric acid (D_2EHPA) extraction system.

In the preliminary stages of the investigation it was shown that the equilibrium distribution at 80°C could produce a good separation of the metals, giving both a high recovery of cobalt, and a cobalt-loaded organic phase of high purity (using a scrubbing step).

After the preliminary work, it was decided to determine which variables are of importance in influencing equilibrium distribution.

In applying postulated, simple chemical equilibria it was confirmed that the system is too complex for the approach to be of much use. Other hydrometallurgical systems, of a comparable complexity, which though in commercial operation, could not be explained or operated on the basis of their thermodynamics, had been made the subject of studies by the Hydrometallurgy Group. These studies aimed to investigate the application of statistical methods of experimental design and data analysis to the design of such processes. The application of statistical methods to the separation of cobalt and nickel therefore falls into place as one of a series on such applications of statistical methods.

1.2 General Aspects of the Separation of Cobalt and Nickel

Due to the great similarity in the chemical properties of cobalt and nickel, cobalt almost always occurs in association with nickel ores, as a minor constituent of the ore. Historically, cobalt has been recovered, if at all, as a by-product in the winning of the nickel, but recently, interest in the recovery of cobalt has grown, because of an increase in the metal price. The price increase was due to the discovery of new applications for cobalt, and particularly to concern for the security of its supply, hence cobalt has recently been termed a strategic metal.

There are several processes available for the industrial separation of cobalt and nickel, and these are summarized in Table 1.1. Of these processes, only the separation with D_2EHPA, and its more recently introduced derivatives, the organophosphonic and organophosphinic acid reagents, can make the separation from an acid-sulphate solution.

It was mainly this capacity that prompted the interest in the D_2EHPA separation in this work. The Hydrometallurgy Group had undertaken a project to develop a flowsheet and process for the recovery of cobalt and nickel from a metal scrap, and a possible separation route involved dissolution of the metal values using

TABLE 1.1 Processes for the Separation of Cobalt and Nickel

Process	References	Notes	Company/Location
Solvent Extraction			
a. Organophosphorous Extractants			
I di(2-ethylhexyl) phosphoric acid	1	-probably not operated commercially	Eldorado Nuclear Ltd.
	2,3	-used in the nickel refinery of a platinum group metal mine	Matthey Rustenberg Refiners
	4	-used until 1978 when replaced by the phosphonic extractant	Nippon Mining Co.
II di(2-ethylhexyl) phosphonic acid.	4	-now used at Hitachi plant	Nippon Mining Co..
III (unspecified alkyl) phosphinic acid group	4	not yet used commercially	-
b. Tertiary Amine Extractant	5	-treats chloride matte-leach liquor	Falconbridge
	6	-separates from chloride solution after solvent extraction with a carboxylic acid to transfer Co/Ni into chloride media.	Sumitomo Metal and Mining Co.
Sherritt Gordon (Pentammine) Type	7,8,9	-Well known process at Fort Saskatchewan, also under licence to Outokumpu for use in their cobalt refinery, and others (ref.8) under design.	Sherritt Gordon Mines Ltd.

... continued ...

TABLE 1.1 (continued)

	Process	References	Notes	Company/Location
Hydrometallurgical	Oxidation-Precipitation of Co(III) Hydrated Oxide			
	a. with sodium hypochlorite as oxidant	10	-process outmoded, since difficult to control and requires many stages	
	b. with Caro's acid as oxidant	10,11,12	proposed use	
	c. with nickelic hydroxide	13	2-stage precipitation in nickel refinery	Outokumpu Oy
Pyro/vapometallurgical	Carbonyl Process	14	The process is really a bulk clean of the nickel. A process (15) using D_2EHPA has been developed to treat carbonyl residue.	Inco

an acid-sulphate leach, followed by separation of the cobalt and nickel using D_2EHPA.

It was envisaged that the leach solution would be made under conditions of elevated temperature and pressure, and since the leach solution would emerge hot, advantage could be taken of the improved separation obtained with D_2EHPA at elevated separation temperature.

1.3 Separation by Solvent Extraction with D_2EHPA

1.3.1 Process Description.

The aim of the solvent extraction step is to extract the cobalt from a cobalt and nickel bearing solution, the feed, to obtain a pure cobalt-loaded organic phase which may be stripped to recover the cobalt. The nickel is left in the aqueous phase product from the extraction step, the raffinate, in which there should be left as little cobalt as possible. The nickel bearing raffinate is passed on to nickel recovery.

A schematic representation of the cobalt/nickel separation step is given in Figure 1.1. After suitable pre-treatment to remove impurities, the aqueous feed pH is adjusted to bring it into the range for extraction.

The production of a pure cobalt-loaded organic phase requires the steps of extraction and then scrubbing.

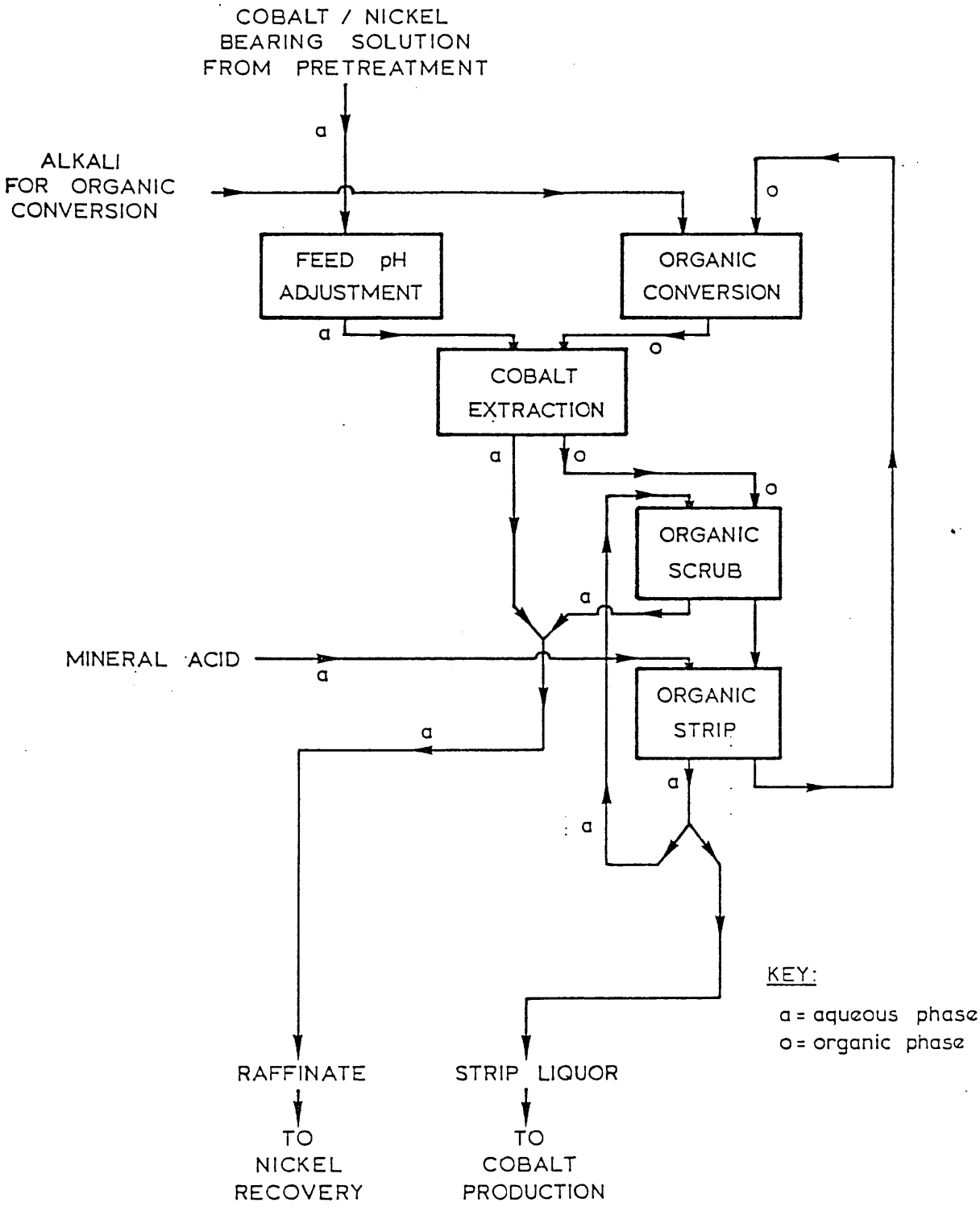


FIGURE 1.1. A schematic representation of the separation with D_2EHPA.

After these, the cobalt-loaded organic phase can be stripped with mineral-acid and the strip-liquor then reports for cobalt recovery.

The nickel-bearing raffinate now contains virtually no cobalt and reports for nickel recovery.

The stripped organic phase, with the extractant in its acid form after stripping, is regenerated by re-conversion to the alkali-salt form, and recycled back to extraction. It may be necessary to make up the organic phase to strength by adding fresh extractant during regeneration.

There are two known industrial variants of the separation, that reported by Ritcey, Ashbrook and Lucas[1] which has been operated at plant scale (though it is not clear whether it has been used in a commercial process), and the Matthey Rustenburg Refiners (MRR) Rustenburg process,[3] which produces an average of 90,000 lbs. of $CoSO_4$ crystal per year.

There are some differences between the variants, which are shown in Table 1.2. However, they are essentially similar in their chemistry and both conform to the scheme of Figure 1.1.

The process described by Ritecy et al. was reported in 1975. The chemistry of the improved MRR process was reported[2] in 1978, and the process itself was described in 1980.

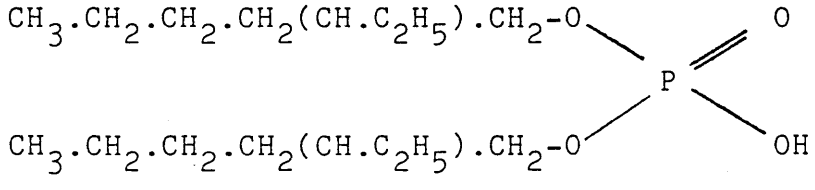
TABLE 1.2. Comparison of Process Variants

Feature	Ritcey's Eldorado Process	MRR Rustenberg Process
salt form of extractant	$(NH_4)D_2EHPA$	NaD_2EHPA
method of organic conversion	reaction with required amount of either gaseous ammonia or concentrated NH_4OH solution.	reaction with stoichiometric amount of 50 w/o NaOH solution.
extractant composition	20 v/o $(NH_4)D_2EHPA$ with 5 v/o tributyl phosphate (TBP) modifier.	0.5 M NaD_2EHPA with TBP modifier.
choice of diluent	probably Shell 140 kerosine type.	aromatic, probably Solvesso 150 (99% aromatic).
stripping agent	mineral acid depending on required product.	H_2SO_4
type of contactor		
1) for extraction and scrubbing	sieve-plate pulse column.	mixer-settler.
2) for stripping	mixer-settler	mixer-settler.
equilibrium temperature		
1) extraction	55-65°C	50°C
2) scrubbing	50-60°C	50°C
3) stripping	not specified	not specified
pH		
1) extraction	5.5-6.0	not specified
2) scrubbing	5.0	not specified

Some aspects of the process are now described further, mainly where they relate to the chemistry of extraction.

1.3.2 The Nature of Extraction.

The extractant used in the separation is the alkali-salt of di-(2-ethylhexyl) phosphoric acid (D_2EHPA). D_2EHPA is an organic alkylphosphoric acid of composition $(C_2H_5.C_6H_{12}O)_2POOH$ whose structural formula is:



As with other acidic extractants, in extraction with D_2EHPA the pH decreases during extraction, due to the exchange of hydrogen ions into the aqueous phase, according to a reaction such as:

$$M^{m+} + m\overline{(HR)_2} \rightleftharpoons \overline{M(R.HR)_m} + mH^+ \qquad (1.1)$$

where R is the di-(2-ethylhexyl) phosphate anion, a bar indicates an organic phase species, and M^{m+} is some metal ion.

The effect of the decrease in pH is to tend to stop further metal extraction. To prevent this,

in the separation of cobalt and nickel, the extraction is made with the extractant in its alkali-salt form, and not with the acidic extractant itself.

Metal extraction with the alkali-salt form of D_2EHPA may be represented by an equation such as:

$$M^{m+} + m\overline{RNa} \rightleftharpoons \overline{MR_m} + mNa^+ \qquad (1.2)$$

In extraction with the alkali-salt form, depending on the alkali-salt used, it is cations such as Na^+, Ca^{++} and NH_4^+ which are exchanged into the aqueous phase, and the pH is relatively unaffected.

1.3.3 Solution Pretreatment and Separation pH.

The solvent extraction separation step is made from weak-acid to neutral solution. Therefore, notwithstanding any pH adjustment which is part of the solution pretreatment, if the separation is made from a solution from an acid-sulphate leach, a neutralization step is required prior to solvent extraction in order to reduce the acidity.

Naturally, it is desirable to extract from as acidic a solution as possible in order to reduce neutralisation costs. Therefore, the extractant should have a relatively high acidity. That is, the extractant

should be willing to give hydrogen ions for metal ions (here Co and Ni) at a relatively low pH. With the alkali-salt form, this property is reflected in a preference for metal ions rather than aqueous hydrogen ions under the same conditions.

1.3.4 Conversion of the Organic Phase to the Alkali-Salt Form.

In the conversion, the organic phase, which contains the extractant as the acid (D_2EHPA), is contacted with the appropriate conversion reagent. In the Ritcey process this is either gaseous ammonia or concentrated ammonium hydroxide solution, and in the MRR process it is concentrated sodium hydroxide solution.

Whichever reagent is used, a single, homogenous phase is obtained on neutralization.

1.3.5 Extraction and Scrubbing.

The selectivity of D_2EHPA for cobalt over nickel is not very high, and both metals are extracted from a mixed solution. Several stages each of extraction and scrubbing are therefore required to obtain the required cobalt/nickel separation, even when advantage is taken of the increase of selectivity for cobalt with increase in extraction temperature.

Both the extraction and the scrubbing step use the counter-current stage configuration. This is usually the most economical in the number of stages required to achieve a certain level of extraction.

During extraction, an advantageous crowding out of nickel occurs in the organic phase, in which some of the nickel co-extracted in the early stages along with cobalt is displaced progressively in later stages by cobalt from the aqueous phase. For this to happen the organic phase must be nearly fully loaded with metal.

After extraction the organic phase is passed to the scrub stage, which is required to improve further the Co/Ni ratio in the organic phase. In this step the organic phase from extraction is contacted with an aqueous scrub feed, which is a solution concentrated in cobalt (e.g. 20 g/l Co as $CoSO_4$) and containing no nickel. A proportion of the cobalt strip solution can be recycled as the aqueous scrub feed, after its pH has been suitably adjusted.

The effect of the scrubbing step is to replace with cobalt the nickel remaining in the organic phase after extraction.

1.3.6 Stripping.

The cobalt-loaded organic phase is stripped with the mineral acid most appropriate to the requirements of the process. The reaction may be represented by

$$\overline{R_2Co} + 2H^+ \underset{\text{heat}}{\overset{\text{cool}}{\rightleftharpoons}} \overline{(RH)_2} + Co^{2+} \qquad (1.3)$$

For the acid-sulphate leaching route sulphuric acid is likely to be preferred.

It is easy to strip the cobalt in a few stages and mixer-settlers are therefore suitable contactors. As equation 1.3 indicates, stripping, the reverse of acid-form cobalt extraction, is favoured by low equilibrium temperatures.

CHAPTER 2

A LITERATURE SURVEY ON THE CHEMISTRY OF EXTRACTION

Introduction

This literature survey is presented as a description of the chemistry of extraction of cobalt and nickel with D_2EHPA. It will be seen that the system is complex and also that uncertainties still remain about the details of extraction even after much research effort. Both these factors contribute to great difficulty in the application of equations of chemical equilibrium to the modelling of distribution, and these difficulties may not be untypical of those encountered in other extraction systems.

2.1 Extraction Equations

The extraction of metal cations with alkylphosphoric acids, and particularly with D_2EHPA, has been represented by an equation of the generalised form:

$$M^{m+} + m\overline{(HX)_2} \rightleftharpoons \overline{M(X.HX)_m} + mH^+ \qquad (2.1)$$

where X is an alkylphosphoric acid anion, and M is a metal cation. In equation 2.1 the metal:organic extracted complex has the metal:extractant ratio of 1:2m.

For divalent metal extraction with D_2EHPA, equation 2.1 becomes

$$M^{2+} + 2\overline{(HR)_2} \rightleftharpoons \overline{M(R.HR)_2} + 2H^+ \qquad (2.2)$$

The main features of this description of extraction are that the metal:extractant ratio in the complex is 1:4, that the extractant dimer exchanges only one of its two available hydrogen ions with the metal cation, and that overall two moles of hydrogen ion are expelled into the aqueous phase per mole of metal extracted. For cobalt extraction the equation is

$$Co^{2+} + 2\overline{(HR)_2} \rightleftharpoons \overline{Co(R.HR)_2} + 2H^+ \qquad (2.3)$$

and similarly for nickel, the equation is

$$Ni^{2+} + 2\overline{(HR)_2} \rightleftharpoons \overline{Ni(R.HR)_2} + 2H^+ \qquad (2.4)$$

Brisk and McManamey[16,17] have described divalent metal extraction conditionally in this way for copper, cobalt and nickel, with the (initial metal ion:initial organic acid concentration) ratio L less than around 0.1:1 in each case.

One of the limitations of the above equations is that both hydrogen ions in the extractant dimer may be exchanged during metal extraction, usually at higher loadings. Brown and Sherrington,[18] for instance, have reported this in the extraction of trivalent lanthanides with D_2EHPA, as have Sato and Nakamura,[19] in a study

of the extraction of divalent copper, cobalt and nickel with D_2EHPA, in which a metal:extractant ratio of 1:2 was found, and not 1:4.

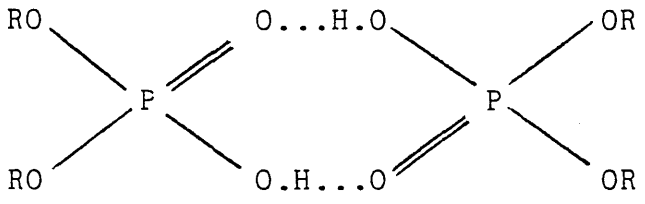
As applied to the extraction of cobalt and nickel with D_2EHPA, another limitation of the above equations is that they take no account of water which is known to be present in the organic phase. The possible nature of this water is discussed in Section 2.2.

These equations also do not take account of the known occurrance of the polymerization of the extracted complex. In the study by Brisk et al. already mentioned, the authors reported the polymerization of divalent copper, cobalt and nickel when L is greater than around 0.1, and they proposed the following equation for a typical polymerization step:

$$\overline{((MR_2)_{r-1}.H_2R_2)} + \overline{H_2R_2} + M^{2+} \rightleftharpoons \overline{((MR_2)_r.H_2R_2)} + 2H^+ \qquad (2.5)$$

In this case as the degree of polymerization increases the metal:extractant ratio increasingly approaches 1:2.

It is generally accepted that the acid-form of D_2EHPA exists as a dimer in the organic phases encountered in the solvent extraction of metals. The two monomeric D_2EHPA units are held together by hydrogen bonding, in a ring structure which is shown below.



When the organic phase is converted to its alkali-salt form, the dimeric units are broken up, since the bonding hydrogen ions are no longer present. The basic equation for extraction with the alkali-salt form is

$$M^{2+} + 2\overline{RNa} \rightleftharpoons \overline{R_2M} + 2Na^+ \qquad (2.6)$$

According to this representation, the metal:extractant ratio in the extracted complex is 1:2 even at low metal loadings, compared with that of 1:4 in similar conditions in extraction with the acid form.

The extraction equation for cobalt is

$$Co^{2+} + 2\overline{RNa} \rightleftharpoons \overline{R_2Co} + 2Na^+ \qquad (2.7)$$

and for nickel is

$$Ni^{2+} + 2\overline{RNa} \rightleftharpoons \overline{R_2Ni} + 2Na^+ \qquad (2.8)$$

The representations in equations 2.6-2.9 suffer from the inadequacies of their acid-form equivalents, in respect of water content and polymerization of the extracted complex.

2.2 The Extracted Species

For cobalt, two forms of extracted complex are recognized in extraction with D_2EHPA. A pink complex is obtained at low metal loadings and low temperature, and this changes to a blue complex when either the loading or the temperature are increased. For nickel, only one form of extracted complex has been reported with D_2EHPA. This is green in colour.

There has been a substantial amount of work carried out to determine the composition and nature of the complexes.

Ritcey et al., who found that a cobalt:extractant ratio of 1:2 in highly loaded organic phases is plausible, while a ratio of 1:4 is not, remarked that the representation of extraction they used (an equation of the form of 2.7) did not imply that $\overline{CoR_2}$ was the species actually present.

Sato and Nakamura[19] examined the extraction of copper, cobalt and nickel from sulphate solution. Later, Sato and Ueda[20] examined extraction from chloride solution. Comparable behaviour was obtained for each system. For cobalt, only the blue cobalt complex was discussed.

The authors concluded that under the conditions used for extraction the complexes present are:

$CoR_2.2H_2O$, tetrahedral

$(NiR_2.2H_2O)_3$, octahedral

and

$(CuR_2)_3$, square planar

These compositions, however, are not consistent with the authors' proposed extraction equation,

$$nM^{2+} + \overline{(n+1)HR_2} \rightleftharpoons \overline{M_nR_{2(n+1)}H_2} + 2nH^+ \qquad (2.9)$$

Further, Kolarik and Grimm[21], who also attempted to measure the polymeric size of the complexes by the same method, were unable to support the conclusions concerning polymeric size. (The polymerization of the extracted complexes is discussed in Section 2.4).

From their study of the visible and ultra-violet spectra of the complexes in cyclohexane, Sato and Nakamura found that the blue cobalt(II) complex has a tetrahedral co-ordination structure.

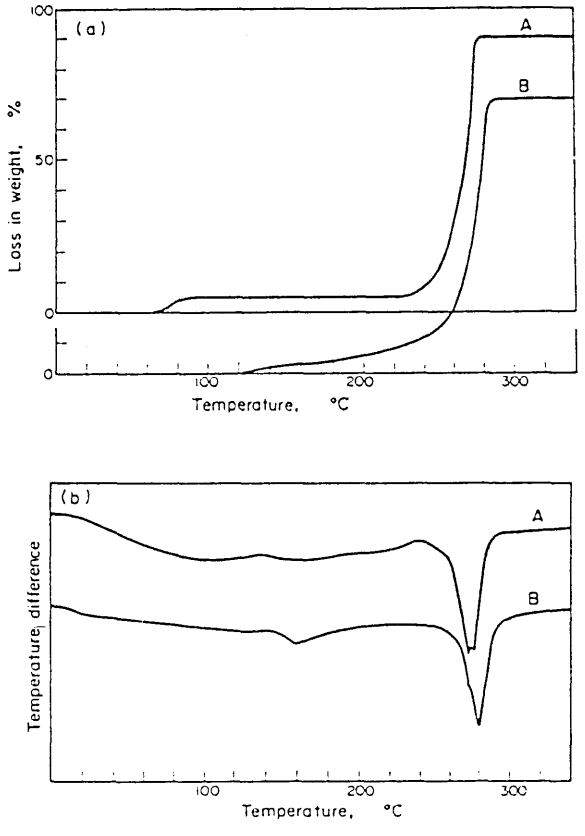
Sato and Nakamura examined the extracted complexes by infra-red spectroscopy, probably using the isolated complex. Due to hydrogen bonding, OH stretching and bending bands are seen in the spectrum of the D_2EHPA dimer, and the disappear in the spectrum of blue cobalt complex. (In the dimer, OH stretching bands are seen at frequencies of 2680 and 2350 cm^{-1} and OH bending bands at 1690 cm^{-1}).

The P=O band, which is visible in the dimer spectrum at 1230 cm^{-1}, is shifted to the lower frequency of 1196 cm^{-1} in the cobalt complex. This is interpreted as showing that the cobalt ion is bonded with the phosphoryl oxygen atom.

The water-content of a cobalt loaded organic phase was determined by Sato and Nakamura, by use of Karl-Fischer titration, and a H_2O:Co molar ratio of 2.1:1 was obtained. If the water present in the organic phase is directly associated with the complex, and if only the blue complex was present under the experimental conditions, then two molecules of water are associated with each cobalt ion.

Sato and Nakamura studied the isolated solid complex of cobalt by differential thermal analysis (D.T.A.) and thermogravimetric analysis (T.G.A.). The complex had been obtained by column chromatography of the organic phase. The T.G.A. and D.T.A. graphs of both the cobalt and nickel complex are shown in Figure 2.1.

With increase in temperature, the T.G.A. curve shows a plateau region between 85 and 225°C where no weight is lost. Above 225°C weight is lost continually, as water is liberated, until a second plateau is reached at 270°C, where water loss stops. Near this temperature the D.T.A. curve shows a sharp endothermic peak due to a lattice adjustment.

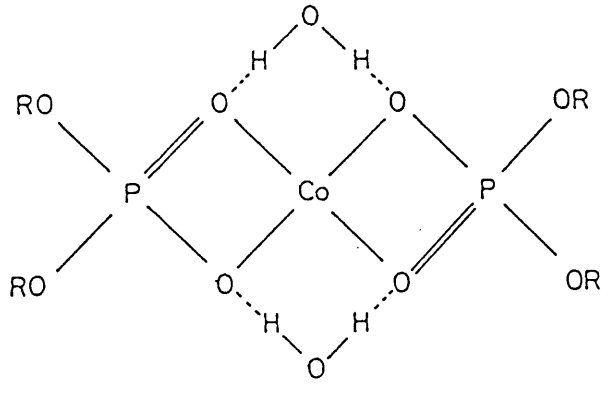


A = Cobalt

B = Nickel

FIGURE 2.1. Sato and Nakamura's differential thermal and thermogravimetric analyses of the cobalt and nickel D_2EHPA complexes. Figure (a) T.G.A. and Figure (b) D.T.A.

If it is possible to relate the situation in the isolated solid to that in the cobalt-loaded organic phase, then two molecules of water are associated with the blue tetrahedral complex (or its monomeric unit), but are not co-ordinated directly to the cobalt ion, since this would produce an octahedral complex. However, the exact stoichiometry of the water in the complex, and the endothermic adjustment of the lattice, suggest that the water is not merely loosely solvated. A structure such as that given below, where R is the 2-ethylhexyl group, may possibly account for these phenomena:



Barnes, Setchfield and Williams[22] observed both pink and blue complexes of cobalt in the organic phase. The pink complex is octahedrally co-ordinated, having a visible spectrum very similar to that of the octahedrally co-ordinated complex ion $[Co(H_2O)_6]^{2+}$, found in aqueous solution.

The authors describe an experiment in which a cobalt-loaded organic phase was dried in vacuo at 100°C

and finally by dessication over P_4O_{10} in vacuo. The organic phase remained deep blue even at low temperature but changed to the pink colour with dropwise addition of water. This was interpreted as evidence that the pink cobalt complex contains water. The authors proposed the relationship between the blue and pink complex given by the equation:

$$\underset{\text{pink}}{\overline{\overline{CoR_2.2H_2O}}} \quad \overset{\text{temperature, Co concentration}}{\rightleftharpoons} \quad \underset{\text{blue}}{\overline{R_2Co}} + 2H_2O \qquad (2.10)$$

Flett and West[2] determined the water content of the cobalt-loaded organic phase with TBP modifier present, using the method of Dean and Stark.[23] The analysed equilibrium phases contained differing cobalt concentrations, and hence different proportions of pink and blue complex. The phases also contained differing concentrations of NaD_2EHPA, with which water is also associated.

By assuming that the blue complex is anhydrous, and that both the pink cobalt complex and the sodium salt are hydrated, values of n and m for $\overline{CoR_2.nH_2O}$ and $\overline{NaR.mH_2O}$ (where n and m are assumed to be constant) could be calculated by using a water mass-balance for each of the phases analysed. Values of 2.2 for n and 8.9 for m were obtained, the value of n for the pink cobalt complex being consistent with the proposed formula $\overline{CoR_2.2H_2O}$. (The assumption that m is a constant is

certainly true if all the initial organic phases were prepared identically).

There is however, water present in an organic phase in which all the D_2EHPA is present as the blue cobalt complex, as may be seen from the authors' own data. Sato et al. also observed water in the cobalt-loaded organic phase which contained the blue complex, but it is not apparent what other water-containing species were present. Barnes et al., in discussing the pink/blue transformation, did not explicitly allocate a phase to the two water molecules expelled from the pink complex.

What is clear however, is that the blue tetrahedral complex is unable to have water directionally co-ordinated to the central cobalt ion.

Only one D_2EHPA complex is known for divalent nickel. The complex is yellow-green to green in colour.

As in the extraction of cobalt, in the extraction of nickel the metal:extractant ratio approaches 1:2 as loading increases.

The visible and ultra-violet spectra of the nickel complex in cyclohexane were studied by Sato and Nakamura. It was found that the main peak in absorbance occurs at a wavelength of approximately 400 nm. Overall, the spectra are characteristic of octahedral co-ordination.

The same authors also examined the extracted complex by infra-red spectroscopy, probably using the isolated solid complex. As with cobalt, it was found that nickel is bound to the phosphoryl oxygen atom. It was also found that the nickel spectrum has OH stretching and bending bands at frequencies of 3440 cm^{-1} (broad) and 1635 cm^{-1}. These are not present in the cobalt spectrum and are due, according to the authors, to directional water co-ordination in the extracted nickel complex.

Measurements by Sato and Nakamura on an organic phase containing nickel, gave a nickel:water molar ratio of 1:2, while Grimm and Kolařík[24] obtained a value of 1:3.6 for the same ratio, in an organic phase containing dodecane. Both sets of authors used Karl-Fischer titration.

Sato and Nakamura used D.T.A. and T.G.A. for the solid nickel complex, in the same manner as for cobalt. The graphs have already been shown in Figure 2.1.

The T.G.A. curve shows two successive regions of loss in weight: between 120°C and 150°C water is lost gradually and continuously, while between 250°C and 260°C the loss in weight is greater. No further loss in weight is observed above 280°C. The D.T.A. graph shows an endothermic lattice adjustment near 270°C, which corresponds to that seen with cobalt, but there is also a smaller endothermic adjustment at 260°C which is not seen with cobalt.

With the qualification expressed for cobalt, the D.T.A. and T.G.A. data tend to confirm that the extracted nickel complex contains co-ordinated water.

In producing an isolated solid nickel complex, in the same manner as for cobalt, Sato and Nakamura were fortunate to obtain a monomeric composition of $NiR_2.2H_2O$. Grimm et al.[24] reported a nickel:extractant ratio of 1:1.36 in their isolated octahedral complex, the remaining charge balance in the complex being supplied by either hydroxyl or nitrate ion. When Sato et al. heated their solid nickel complex for three hours, it exhibited thermochromism, showing a reversible colour change from yellow-green to violet. This was attributed to the equilibrium given by

$$NiR_2.2H_2O \rightleftharpoons \underset{\text{violet, tetrahedral}}{NiR_2} + 2H_2O \qquad (2.11)$$

Grimm et al., on heating the solid they had produced, were unable to obtain a similar conversion.

No change in complex comparable with that of equation 2.11 has been reported for the nickel complex in the organic phase. It seems safe to assume that in extraction, the nickel complex is always octahedrally co-ordinated.

2.3 A Chemical Basis for the Selectivity of the Extractant Towards Cobalt

Between cobalt and nickel D_2EHPA shows some selectivity in favour of cobalt (see Section 1.3.5). Barnes, Setchfield and Williams attributed the superior extraction of cobalt to the ability of the extracted cobalt complex to undergo the thermodynamically favourable change in co-ordination represented by the expression already given as equation 2.10, the thermochromic reaction. The nickel complex is unable to change co-ordination in the same way.

The transformation from pink to blue cobalt complex is favoured by increasing cobalt concentration and by temperature. It has been observed by Barnes et al. and Flett et al. that nickel extraction changes very little with temperature while cobalt extraction increases substantially with increase in temperature.

Barnes et al. studied the effect of temperature on the thermochromic reaction. They defined the equilibrium constant K for equation 2.10 as

$$K = \frac{[\text{Co tetrahedral}]}{[\text{Co octahedral}]} \qquad (2.12)$$

An organic phase containing cobalt was saturated with water, and the concentration of the blue form was estimated over the temperature range 25-200^{o}C by

spectrophotometry. The concentration of the pink form was obtained by difference and K for equation 2.12 could then be calculated over a range of temperature, T.

The calculated value of K varied from 0.15 at 25°C to 5.7 at 100°C.

Using the temperature dependence data, values of ΔH and ΔS for the proposed thermochromic reaction could be estimated from a plot of 1/T versus $-\log_{10}K$, by making the approximation that ΔH is constant over the temperature range and fitting a straight line to the data. Linear regression analysis gave a value of $+48.3$ KJ.mol^{-1} for ΔH and $+148$ J.mol^{-1}.°C^{-1} for ΔS.

If the above calculation (which does not take account of any polymerization of the extracted complex) is accepted, then the reaction, which is slightly endothermic, has a free energy change which is favourable overall because the entropy of transformation is positive. The authors postulate that the pcsitive entropy change is due to the loss of two water molecules from the cobalt co-ordination sphere. Thus the free energy change of the reaction, ΔG, given by

$$\Delta G = \Delta H - T.\Delta S \qquad (2.13)$$

becomes increasingly negative (i.e. increasingly favourable) as the quantity $T.\Delta S$ increases with increase in temperature.

2.4 The Polymerization of the Extracted Complex

It is generally accepted[21] that polymerization of the extracted complex does occur in the extraction of some metals with D_2EHPA. Expressions such as the already given equations 2.5 and 2.9 have been postulated to describe the polymerization.

Sato and Nakamura used vapour pressure osmometry (v.p.o.) to determine the apparent molecular weight of the extracted D_2EHPA complexes of cobalt, nickel and copper. Their results are shown in Table 2.1.

TABLE 2.1. Sato and Nakamura's Polymerization Determinations

Complex	Molecular Weight			Conclusion
	Observed	Theoretical	Observed/Theoretical	
$CoR_2.2H_2O$	770	737	1.06	monomer
$NiR_2.2H_2O$	2390	737	3.24	trimer
CuR_2	2080	706	2.95	trimer

The authors concluded that the extracted cobalt complex was present as a monomer under the conditions used for extraction.

Kolařík and Grimm[21] also used v.p.o. to determine the apparent molecular weight of several metal/D_2EHPA

complexes, but found both that the reproducibility of individual measurements was low, and also that each series of measurements gave a somewhat different curve. The v.p.o. method is very sensitive to variation in mean molecular weight, and it seems possible that the problems encountered were due to the complex polymerization behaviour of the extracted species.

Sato et al.'s determination of apparent molecular weight was made on an organic phase which probably contained cobalt at low and unspecified levels and possibly contained free D_2EHPA. Under these conditions a monomer is formed, but there is evidence that the cobalt complex does polymerize at high loadings.

Brisk and McManamey,[16] for instance, measured the specific viscosity of organic phases loaded to different extents with cobalt, and found a sharp rise in viscosity at a certain level of loading. Near saturation the colour of the extracted complex deepened from blue to violet.

Kolařík and Grimm[21] studied the polymerization behaviour of D_2EHPA complexes of copper (II), cadmium (II), zinc (II) and cobalt (II). The authors discarded v.p.o. methods and chose instead a method in which a variable amount of solid complex was distributed between two immiscible organic phases by equilibration, and the concentration in each phase measured. The lower phase was ethylene glycol and the upper phase was either wet benzene or

wet dodecane. The way the complex distributes with increasing complex concentration is dependent on its polymerization behaviour in each phase. It can be shown that a graph of the distribution coefficient, D, versus the total metal concentration in the lower phase, C_M, is a straight line with gradient (s-r)/r, if only one polymer predominates in each phase, an s-mer $(MA_2)_s$ in the upper and an r-mer $(MA_2)_r$ in the lower. If more species are present in one or both phases, a graph of log D versus C_M is a curve whose form, according to the authors, corresponds to the species present. From the empirical data and using a computer an interpretation can be made of the likely species present.

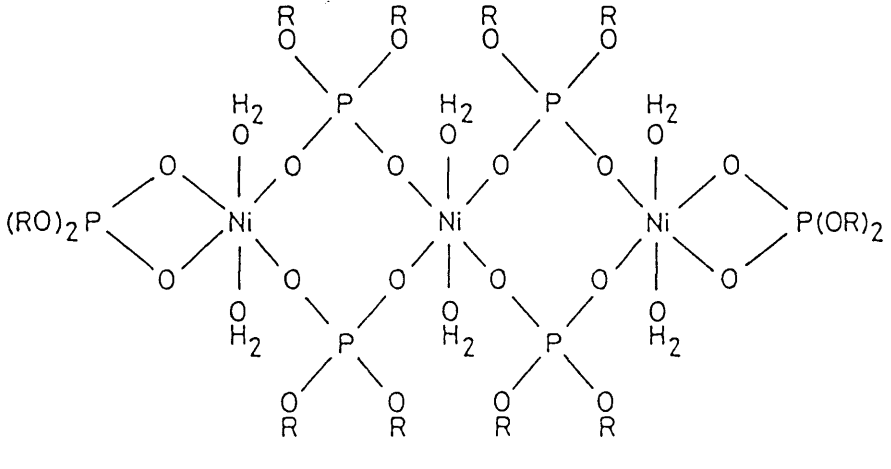
It was found that copper and cadmium do form polymeric groups in dodecane and benzene, but the results suggest that these are not as large as those formed by zinc and cobalt. The size of the copper and cadmium polymers are similar in both the upper (benzene or dodecane) phase and the lower ethylene glycol phase, so ethylene glycol does not depolymerize the complex.

The zinc and cobalt complexes do form large polymeric groups in the benzene or dodecane phase, but not in ethylene glycol, i.e. they are depolymerized by ethylene glycol. The size of the cobalt and zinc polymers is difficult to determine precisely, due to the difficulty in interpreting the very steep gradients of the log D versus C_M graph at higher complex concentrations, but for zinc in dodecane $s > 400$.

The authors measured the viscosity of the cobalt complex in both benzene and dodecane. It was found that the solutions containing no free D_2EHPA were very viscous, but the viscosity decreased substantially on the addition of D_2EHPA, further indicating that large polymers are present, and that these are depolymerized by excess or free D_2EHPA.

It seems safe to assume that the cobalt complex is also polymerized in the organic phases used in solvent extraction. The difficulties that Kolařík and Grimm encountered in trying to obtain a reproducible value of the mean molecular weight of the polymer using v.p.o. show that the polymerization behaviour is too complex to be described with stability constants even if several are used for each system.

The only reported evidence concerning the polymerization of the extracted nickel complex is Sato and Nakamura's v.p.o. determination. It was concluded that a trimer was present under the conditions of extraction. Overall from their studies the authors concluded that the complex had the composition $\overline{(NiR_2.2H_2O)_3}$, and the following structure:



It is not necessarily the case that the extracted nickel complex is trimeric under all circumstances, and it may polymerize beyond the trimer. Whatever the case, if the polymerization behaviour of the extracted D_2EHPA complexes of cobalt and nickel are markedly different, the difference would provide another reason for the selectivity of the extractant towards cobalt.

The Influence of the Diluent on Extraction

Grimm and Kolařík[24] studied the absorption spectra of the copper, nickel and cobalt complexes in various organic solutions.

It was found that the blue cobalt complex is tetrahedrally co-ordinated in dodecane, cyclohexane, benzene, carbon tetrachloride and chloroform and its closed structure is stable even towards electron donors such as methyl iso-butyl ketone and free D_2EHPA. Of the solvents studied only 2-ethyl hexanol is able to co-ordinate with the central Co^{2+} ion with consequent rearrangement of the bonding geometry.

The spectrum of the nickel (II) complex does not change with solvent for the above range, including 2-ethyl hexanol. An exception is for the addition of free D_2EHPA to the complex in cyclohexane, although the complex remains octahedral. It is plausible that in this case free D_2EHPA displaces water molecules in the central co-ordination sites.

The above results show that the basic nature of the extracted complexes of cobalt and nickel will be unaffected by choice of diluent within the limits of those normally employed in commercial solvent extraction.

Nevertheless, there is some influence of the diluent on the distribution of the metals, as Flett and West[2] have shown.

For each metal three commercial diluents of different aromacity were compared, each tried with both isodecanol (IDA), and then TBP modifier.

The distribution coefficient of the metal, D_M, where

$$D_M = \frac{\bar{C}_M}{C_M} \qquad (2.14)$$

was measured for each diluent/modifier combination over a range of extraction temperatures, keeping all other conditions constant. Some values of D_M taken from the authors' graphs are shown in Table 2.2. The combination of high aromatic diluent and TBP modifier gave comparatively high D_{Co} values and also low D_{Ni} values, making it suitable for the cobalt/nickel separation.

TABLE 2.2. Approximate D_{Co} values at 75°C for Different Diluent/Modifier Combinations.

Diluent	Aromatic Content %	Modifier	
		IDA	TBP
Escaid 111/25	0.3	500	700
Escaid 100/25	20	740	1450
Escaid 350	97	870	1220

Finally, it is worth mentioning that in Kolařík and Grimm's polymerization studies, differences in the polymerization behaviour of the cobalt-D_2EHPA complex could be detected between benzine and dodecane.

CHAPTER 3

THE MODELLING OF EQUILIBRIUM DISTRIBUTION AND THE USE OF STATISTICAL METHODS OF EXPERIMENTAL DESIGN

3.1 General Introduction

In the solvent extraction of metals, the distribution of a metal at equilibrium is usually represented by the distribution isotherm, in which the equilibrium organic phase metal concentration, $C_M(org)$, is plotted against the equilibrium aqueous phase metal concentration, $C_M(aq)$.

The distribution isotherm may be used in conjunction with the McCabe-Thiele or Varteressian-Fenske construction[25] to predict the phase concentrations in a separation where extraction takes place in several equilibrium stages, often in counter-current configuration.

The combination of distribution isotherm and McCabe-Thiele construction is of some practical use, but its application is confined to separations where only one metal is extracted into the organic phase.

Using acidic extractants as an example, if the following general equation is used to represent extraction,

$$M^{n+} + n\overline{RH} \rightleftharpoons \overline{R_2M} + nH^+ \qquad (3.1)$$

where R is an acidic extractant anion, then it can be seen that extraction is not only dependent on $C_M(aq)$. The functional relationship between the variables is given by:

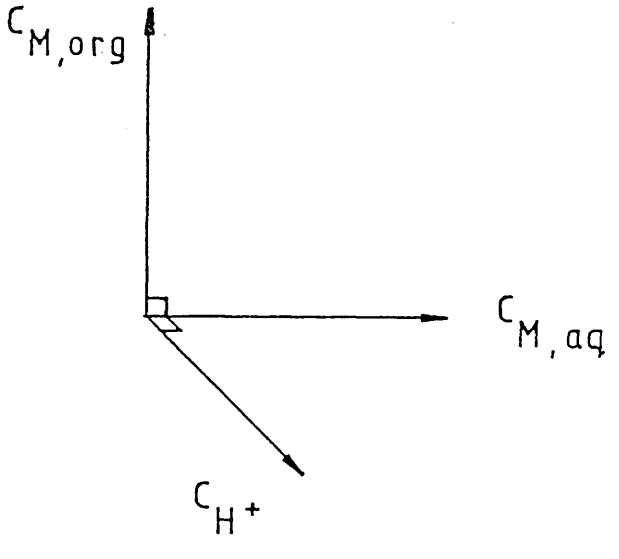
$$C_M(org) = f(C_M,(aq),C_{H^+}(aq),\ C_R total(org)) \qquad (3.2)$$

where $C_{H^+}(aq)$ is the equilibrium aqueous hydrogen ion concentration and $C_R total(org)$ is the total extractant concentration.

In the case where a fixed level of total extractant concentration is being considered, the relationship is given by:

$$C_M(org) = f(C_M(aq),\ C_{H^+}(aq)) \qquad (3.3)$$

This second functional relationship may be represented by a surface in three dimensions, with axes arranged in the following way:



The distribution isotherm applies to extraction with a fixed aqueous feed composition (in the acidic extraction example this means fixed feed C_M and feed C_{H^+}). The isotherm is obtained by the method of contacts

(usually shake-out tests) in which only the phase-ratio is varied. The organic feed and aqueous feed compositions are set at the levels of the staged process it is wished to model. The resulting isotherm (see Hughes et al.[26]) is a particular section of the distribution surface. Because each isotherm is for a given feed, when it is wished to determine the effect of a change in aqueous feed, a fresh isotherm has to be made by shake-out tests using the new feed.

However, when the distribution surface can be described mathematically, the McCabe-Thiele construction can be performed numerically on the surface by computer,[26] and the effect of each change in the aqueous feed can be predicted without further experiment.

Using the above three-dimensional correlation, distribution with each extractant concentration is described by a fresh surface. Unless the effect of changing the extractant concentration can be extrapolated from data acquired at other concentrations (and usually this is only possible with a chemically-based model), fresh distribution data will be required, and the new surface fitted before the McCabe-Thiele construction can be applied for that concentration. Similarly fresh experimental effort will be required if just the distribution isotherm is used.

In separations where two or more metals are co-extracted, the relationship between the distributed species

can no longer be represented in three dimensions. Also the McCabe-Thiele construction cannot be used for staged process predictions. Unless a mathematical model of distribution can be obtained and incorporated into a staged process calculation, a prediction of distribution in the staged process can only be obtained by making the separation at bench or pilot scale, or by using a simulation described by Treybal.[27] The drawback with these procedures is that they require a lot of experimental effort, and the information derived from them is very specific. The distribution model, on the other hand, can be manipulated numerically to determine the effect on the separation of changing the conditions.

3.2 Distribution Models

There are several kinds of distribution model, which may be classified, after a survey by Forrest and Hughes,[28] into chemically-based models, semi-empirical models and empirical models.

Chemically-Based Models

The chemically-based model or fundamental model is based on an equilibrium constant, K. The constant is defined from a postulated extraction equation, by use of the law of mass-action.

Harrington,[29] for example, used the following extraction equation to describe the extraction of uranium in nitrate media by solvation with tri-butyl phosphate, (TBP):

$$UO_2^{2+} + 2NO_3^- + 2\overline{TBP} \rightleftharpoons \overline{UO_2(NO_3)_2.2TBP} \qquad (3.4)$$

The extraction equilibrium constant for the reaction is:

$$K = \frac{\{\overline{UO_2(NO_3)_2.2TBP}\}}{\{UO_2^{2+}\}\{NO_3^-\}^2\{\overline{TBP}\}^2} \qquad (3.5)$$

where the { } brackets denote the activity of the species.

Whewell and Hughes[30] have used a chemically-based model to describe the extraction of copper from acid-sulphate solution with LIX-64N, a β hydroxyoxime extractant.

Even though only one metal is extracted, the system is probably as complex chemically as any to which a chemically-based model has been applied.

The overall extraction equation is

$$Cu^{2+} + 2\overline{HR} \rightleftharpoons \overline{CuR_2} + 2H^+ \qquad (3.6)$$

with an equilibrium constant (here a step stability constant, β_2) defined by

$$\beta_2 = \frac{\overline{[Cu]}.h^2}{\overline{[RH]}^2.b} \qquad (3.7)$$

where R represents the active oxime radical, and h and b are the equilibrium aqueous concentrations of free hydrogen ion and free cupric ion respectively.

The oxime extractant is said to associate in the organic phase, and this is represented in the model by an equilibrium between the unassociated oxime species which is available for extraction and the aggregated species which is not.

The model also includes additional aqueous phase equilibria, as will be discussed in Section 3.3.

The process of modelling involves the simultaneous solution of both mass-balance and equilibrium equations, utilizing experimental distribution data to obtain best-fit estimates of β_2 and the parameter expressing oxime aggregation.

The model predicts the distribution of copper and the pH of the raffinate, and has been applied to extraction in a counter-current cascade. In its extended form, the influence of the diluent on extraction of a number of diluents is incorporated,[31] again on a chemical basis.

Another chemically-based model has been described by Bauer and Chapman,[32] for the extraction of copper

from acid-sulphate solution using Kelex 100, a (branched hydroxyquinolene) chelating extractant.

The extraction equation used,

$$Cu^{2+} + 2\overline{HR} \rightleftharpoons \overline{CuR_2} + 2H^{+} \qquad (3.8)$$

where R is the 'Kelex' anion, is similar to that used by Whewell and Hughes for the LIX 64N separation. The treatment of the organic phase can be simpler than in the LIX 64N system, since according to Bauer et al., Kelex 100 does not aggregate in the organic phase.

The incorporation of the Bauer model in stage calculations for counter-current extraction, has been described by Chapman,[33] together with similar models for the extraction of two metals. One of these, not as yet seen by the present author, is for the extraction of copper and nickel from acidic solution with D_2EHPA.

Semi-Empirical Models

Semi-empirical models in the solvent extraction of metals are based on analogies with other physico-chemical phenomena. Two types have been reported, these being models by analogy with adsorption, and models by analogy with liquid-vapour equilibrium.

The adsorption type model is developed by using an analogy with gas adsorption by a solid. Ellis[34]

had noticed that the distribution curve in solvent extraction is similar (when there is extraction by chemical reaction) to the Langmuir adsorption isotherm.

A modification of the idea, in which the analogy is with the Freundlich adsorption isotherm (the Freundlich isotherm can be derived from equilibria), has been applied by Lloyd and Oetel[35] to metal extraction with amines. The predictions of the model for the co-extraction of two metals were too high over most of the range.

The liquid-vapour equilibria type model is developed by analogy with Raoult's law behaviour of liquid-vapour equilibria.

In the model, the organic phase is analogous to the vapour phase and the aqueous to the liquid phase. By analogy, the equilibrium organic phase concentration of a component is proportional to the aqueous phase mole fraction, having as its constant of proportionality (in an 'ideal' system), the organic phase concentration of the single component determined under standard conditions. The model includes extra terms for departures from 'ideality'.

Ioannu et al.[36] have modelled in this way the extraction of lanthanides in acid-chloride solutions with D_2EHPA.

Empirical Models and Statistical Methods

Empirical modelling involves fitting some kind of algebraic expression to distribution data, using regression analysis. The measured response is correlated against the regression variables, whose values are known.

In any regression analysis one of the problems in obtaining a satisfactory correlation is to select the correct variables. Where the important variables are not known through previous experience or understanding of the system, many combinations of controlled variables will have to be considered. One of the advantages of statistical methods of experimental design, and particularly factorial design methods, it will be seen, is that the design shows which variables are of significant importance, and hence which should be included in the correlation.

Experimental designs also generate a correlation expression, which describes the behaviour under study. If this expression is not itself satisfactory as a model, it can be extended and improved using model-building statistical methods.[37]

Robinson and Paynter[38,39] used an empirical model to describe the extraction of copper from acid-sulphate solution by LIX 64N.

The authors found that copper extraction was dependent on the following variables:

(1) the total concentration of the active oxime,

(2) the copper concentration in the aqueous feed,

(3) the sulphuric acid concentration in the aqueous feed.

Both a three-dimensional correlation for fixed extractant concentration, and a full four-dimensional correlation were made.

Recently, Valdes, Cooper and Bacon[40] have reported the use of factorial experimentation to study the extraction of copper from ammoniacal sulphate and acid-sulphate solution by mixtures of LIX 64N and SME 529, another hydroxyoxime reagent. The factorial variables studied were:

(1) the aqueous copper concentration in the feed,

(2) the sulphuric acid or ammonia concentration in the feed,

(3) the total organic phase concentration of SME 529,

(4) the total organic phase concentration of LIX 64N.

An incomplete (i.e. fractional) factorial design at three levels was used for each system.

3.3 Problems in Modelling

Several problems may arise when the chemically-based model is applied to a given system.

One of the main problems with the approach is that the equilibrium constant is defined in terms of activities. In general with aqueous solutions, and particularly with the many relatively concentrated solutions which are encountered in hydrometallurgy, the activity of a component is substantially less than its concentration, and it is very difficult to estimate the activity of a species in mixed, concentrated solution. (The Debye-Huckel theory cannot be used to estimate the activity coefficients because the ionic strength of such solutions is very much higher than the applicability of the theory).

Whewell and Hughes,[30] for example, did not use activities in the copper/LIX 64N model. The activity/concentration behaviour was approximated by defining additional aqueous phase equilibria, for copper ion-pair formation.

$$Cu^{2+}(aq) + SO_4^{2-}(aq) \rightleftharpoons CuSO_4(aq) \qquad (3.9)$$

which reduced the free cupric-ion concentration available for extraction, and for the sulphate/bisulphate equilibrium, which accounts for a reduction in the effective acid concentration.

A sufficient amount is known about the copper/acid-sulphate system to justify the approach in this case, and Chapman[41] has reported the use of the same approach with other systems, but using different equilibria.

In general, however, the approach will not always be acceptable. It is well known that if concentration terms are used in the equilibrium constant expression in place of activities, K can vary considerably.

For the organic phase species, the activity coefficients usually tend to unity, and concentrations may therefore be used in place of activities in the equilibrium constant expression. This is because organic phases are non-electrolytes, so there are no ions present, and the inter-ionic interactions, which according to the Debye-Huckel theory cause a decrease in the activity of aqueous species, do not occur.

With the organic phase species, the distribution of the metal is affected not only by the species which appear in the extraction equation. Other reactions involving the extractant which are known to occur in the organic phase, must be included in the chemically-based model.

Depending on the extraction system concerned, these reactions include such phenomena as self-association (aggregation) of the extractant, solvation of the extracted species by the diluent, interactions between diluent and extractant, and polymerisation of the extracted species.

The need for inclusion of these reactions can easily be seen by considering extractant self-association. If an extractant associates to a significant extent and only the unassociated or free form is directly available

for extraction, then the effective concentration of extractant available for metal extraction is reduced.

The incorporation of these reactions into the model on a chemical basis involves defining an extra equilibrium expression for each pertinent behaviour. This means the addition of a simultaneous equation for the equilibrium to the model together with additional equations to account for mass-balance constraints.

There is another problem apart from that of the additional computational burden that these reactions cause. The behaviour may not adequately be described by one equation, or even several. In the case of polymerization, for example, writing an equation involves defining a single polymerization number, n. For the blue cobalt complex of D_2EHPA the polymerization reaction can be represented by

$$\overline{nCoR_2} \rightleftharpoons \overline{(CoR_2)_n} \qquad (3.10)$$

However, when the polymerization is extensive, n need not take on a single number.

Even when a satisfactory equation does exist, if the system under study is a newly introduced one, it will not be known which potential behaviours occur.

So far the difficulties described in applying a chemically-based model relate to systems where the organic phase is easily characterised and where its composition (to

all intents and purposes) is fully known. In systems used for industrial separations this is not usually the case. The organic phase is more complex than a single solute (the extractant) dissolved in a single organic solvent (the diluent), because of the use of additives (modifiers) such as third phase inhibitors; and of synergistic combinations of two or more extractants (the modifier may serve as one of these). In some cases, the composition of an organic phase may not even be known precisely, due to the use of proprietory reagents.

In modelling a particular system, one of the semi-empirical models may provide a form of expression which is suitable to be fitted to distribution data that has already been acquired. A more general application of semi-empirical models appears to be improbable, since, unlike with chemically-based models, the parameters which are used in semi-empirical modelling do not necessarily have any physical significance. If the analogy used in the modelling breaks down, the model parameters may fail to remain constant over the full extraction range, leading to a systematic failure of the model.

In empirical modelling the model parameters do not have any physical significance at all. However, the construction of an empirical model using first experimental design methods and then model building methods, should result in the development of an empirical model which has an adequate fit over the full extraction range.

In Part II of the present study, a component part of this modelling process is examined for the present separation, in a study of the application of experimental design methods.

CHAPTER 4

EXPERIMENTAL METHODS

4.1 Solvent Make-up and Conversion to Sodium-Salt Form

Throughout the present work, the extractant was used unpurified, in the form it was received. This was considered appropriate, as the study concerns the factors which influence distribution in the industrial process, in which the extractant would almost certainly be used unpurified. The extractant is anyway quite pure ($\geq$ 96% D_2EHPA).

It was required that in the conversion of the solvent to its salt-form, the neutralization of the extractant should be exact. In this way superfluous changes in pH during extraction would be avoided. In order to achieve this the acid-value of the extractant was determined, from which the neutralization requirement of alkali could be calculated.

The acid-value was determined by potentiometric titration of D_2EHPA in wet ethanol, using a combination glass electrode and pH meter. The titrant, a standard 1 M solution of sodium hydroxide, was delivered in the required aliquot by a Mettrome Dosimat. Bromo-cresol green indicator was used as a visual check for the end point, at which it gave a colour change of yellow to blue-green. Only one equivalence point was detected, and it was found in general that within experimental error, the acid-value of the D_2EHPA was equivalent to its molecular weight.

Incidentally, it was found that the acid-value of the made-up solvent could be determined, if required, by potentiometric titration with 1 M NaOH. This could only be done if the solvent was dissolved in wet ethanol, and the addition of titrant had to be made with caution, since at some points in the titration, turbidity was observed, and it was necessary to wait for this to disperse, before making the next addition of titrant. The practice of titrating the solvent was not adopted for the experimental programmes.

To convert the solvent to its alkali-salt form, the required weight of D_2EHPA for a given strength of solvent was dissolved in a certain amount of diluent and the required volume of TBP modifier. To this solvent was added the exact required weight of a freshly made up 50 w/o sodium hydroxide solution, which had been standardized by titration of a known weight with standard 0.1 M hydrochloric acid solution.

This mixture was shaken vigorously in a large separating funnel, becoming turbid and hot, and the funnel was immediately cooled under a running tap, to take conversion to completion. The product of the conversion is a single, translucent phase of solvent. This solvent was made up to volume with diluent. The solvent was now ready for use.

It is clear that the solvent takes up water during conversion, both from the sodium hydroxide solution and

the water produced chemically by neutralization. It is a possibility that during extraction the water is exchanged into the aqueous phase and this may produce a slight distortion of the phase-ratio. The amount of water potentially involved is small, and it was assumed that the error produced by the assumption that the phase ratio is constant is negligible compared with other experimental errors.

4.2 Equilibration of the Phases

In all the experiments, the method of equilibration was the same. Equilibration was carried out using a Baird and Tatlock type 304/1700 heated, deep form water bath with thermostatic temperature control (~±1°C), fitted with a Baird and Tatlock shaking tray attachment.

Sealed, boro-silicate glass flasks were used to hold the equilibrating phases. The required volume of each phase was run into the flask, the screw-top was fitted, and the flask was then placed in the water bath shaking tray, which retained the flask so that it was partially immersed in the water bath. If required, several flasks could be accommodated at once. The flask was then allowed to stand for 30 minutes, so that the contents could warm up to room temperature. When this time had elapsed, the shaking tray, which agitates by a horizontal reciprocal motion, the speed and throw of which are variable, was then switched on, and the flasks

were equilibrated, also for a period of 30 minutes. It had been determined at the outset of the experimental programme that this equilibration time was adequate for the phases to come to equilibrium.

After equilibration, the shaking was stopped, the flasks were removed and their contents transferred quickly into warmed separating funnels. The phases were allowed to disengage and were then immediately separated.

4.3 Cross-Current Cascade Experiments

Loading Experiments

In the loading cascade experiment, a single volume of organic phase was contacted at an extraction temperature of 80°C with successive volumes of an aqueous feed solution. The composition of the solvent phase to be loaded was 0.5 M NaD_2EHPA with 5% TBP by volume in Solvesso 150.

The following procedure was used. The aqueous feed solution was made-up by dissolving the required amounts of hydrated cobalt and nickel sulphate in distilled water to give a solution containing around 20 g/L cobalt and 50 g/L nickel. The pH of the aqueous feed was then adjusted to the required value by the dropwise addition of either sodium hydroxide solution or sulphuric acid solution. Next, an exact volume of 100 ml of solvent in its alkali-salt form was pipetted into one of the

boro-silicate glass flasks, together with the same amount of aqueous feed solution.

The phases were equilibrated and separated by the method given, and then allowed to cool to room temperature. An exact 10 ml sample of the organic phase was taken by pipette, for subsequent analysis, and the remainder of the organic retained for the next equilibration. The pH of the raffinate was measured, a sample taken for analysis, and the remainder discarded.

This procedure was then repeated, using the retained organic phase and an equal volume of fresh aqueous feed solution, until the required number of equilibrations had been made.

The sample solutions collected were analysed for cobalt, nickel and pH using the methods described presently.

Scrubbing Experiments

In the scrubbing experiments, an organic phase, loaded with both cobalt and nickel, is scrubbed of nickel by contact with successive volumes of an aqueous scrub solution, the scrub feed.

The organic phase for scrubbing was obtained by cross-current loading in which a fresh organic phase was contacted with three successive volumes of aqueous feed solution.

The aqueous scrub feed was made up by dissolving hydrated cobalt sulphate in distilled water to the required concentration. The pH of this solution was then adjusted to the required value by the dropwise addition of either dilute sodium hydroxide or dilute sulphuric acid solution.

The procedure used was identical to that for the cross-current loading experiments, except that the aqueous scrub feed replaces the aqueous feed solution of the loading experiment.

4.4 Factorial Design Experiments

The equilibration procedure for the factorial experiments was quite straightforward. Each factorial experiment consisted of a single contact of an aqueous and an organic phase. The equilibration of the phases could therefore be carried out using the method already described.

It was essential that the set levels of the factorial variables were achieved consistently and accurately in the experiments. The procedure for making up the aqueous phase took account of this.

At the beginning of the experimental programme, solid hydrated cobalt sulphate, in a quantity sufficient for all the experiments, was finely ground in a pestle and mortar, and then dried. A representative sample was obtained by coning and quartering on black-glazed

paper, and this was assayed for cobalt, using atomic absorption spectrophotometry to determine the cobalt concentration of a solution containing a known weight of solid. The same was done with a sufficient quantity of the solid hydrated nickel sulphate. Both these prepared solids were then stored under dessication in order to stabilise the moisture content.

The aqueous phase for a factorial experiment was then made up in the following way: The required accurate weights of the finely ground cobalt sulphate and nickel sulphate were successively weighed out using an electronic balance. A 100 ml beaker was placed on a sheet of black glazed paper, and the portions of cobalt and nickel sulphate were transferred into the beaker. By using the paper, any spillage of the metal sulphate during transfer could be seen and remedied, as the grains stand out against the black background. Using this procedure, the large number of weighings could be done relatively quickly yet with the required accuracy. Next, if the treatment combination in that factorial experiment included initial sodium sulphate concentration at the high level, a volume of 50 ml of 1 M Na_2SO_4 solution was added by pipette to the beaker, and the contents stirred with a glass stirring rod. The solution in the beaker was then made up to nearly 100 ml with distilled water, and the contents dissolved completely, if necessary applying gentle heating by placing the beaker on a hot-plate. After the solids had dissolved and the contents of the beaker had cooled

to room temperature, the pH of the solution was measured and adjusted to the required factorial value by dropwise addition of dilute solutions of either sodium hydroxide or sulphuric acid as required. Finally, the solution was transferred into a 100 ml volumetric flask, with sparing washing, made up to volume with the few drops of distilled water required, and shaken. The aqueous phase was then ready for equilibration.

The temperature control of the water bath had been adjusted until the temperature of the bath was stable over a period of time at the level required by the factorial treatment. Then, 100 ml of organic phase in its sodium-salt form was pipetted into a glass equilibration flask, and the prepared aqueous phase added. The phase equilibration and phase separation were carried out using the method described. The separated phases were put into glass storage bottles and allowed to cool to room temperature. The pH of the raffinates was measured and the solutions were analysed for cobalt and nickel.

Randomization of the Factorial Experiments

Due to statistical considerations, the order in which the factorial experiments were carried out was to be random.

To do this, the random order of experiments given in Appendix 2.a was drawn up. For ideal randomization, each experiment in the random order would have been carried

out to completion, including solution preparation, equilibration and solution analysis, before the next experiment was begun. However, this was not practicable, and it was decided that the factorial design would be sufficiently randomized if every phase of the experimental method were carried out in the random order. Thus the aqueous phases were prepared in the randomized order, then the equilibrations were carried out in random order, then the procedures used in the analysis were carried out in random order, etc., etc..

4.5 Analysis

pH Measurements

The pH measurements were carried out using a Russell combination glass electrode and a Pye Unicam PW 9409 glass electrode.

The pH meter was calibrated using 0.05 M potassium hydrogen phthalate buffer (pH = 4.008 at T = 25°C) and phosphate buffer, containing 0.025 M Na_2HPO_4 and 0.025 M KH_2PO_4 (pH = 6.865 at T = 25°C).

Since the pH was measured with the solutions at room temperature, and not the temperature of extraction, the reported pH values do not have thermodynamic significance, and do not represent the actual hydrogen ion activity in the phase at equilibrium.

Analysis for Cobalt and Nickel by Atomic-Absorption Spectrophotometry

The aqueous phase of cobalt and nickel concentrations were determined directly, by atomic absorption spectrophotometry (A.A.S.). A variable diluter was used to dilute the samples.

The analysis of the organic phase for cobalt and nickel was made by stripping a sample of the organic phase with hydrochloric acid solution, and analysing the aqueous strip product by A.A.S.

This was done by the following method. A 5 ml sample of the organic phase to be analysed was taken by bulb pipette, and run into a glass vial, to which was added a pipetted 10 ml volume of 1:1 v/v HCl solution. A cap was fitted to the vial, it was then shaken vigorously to strip the organic phase, and the phases were allowed to separate. A volume of the lower phase, the aqueous strip phase was withdrawn by pipette, care being taken not to withdraw any organic phase as well. Samples of this aqueous strip product were then analysed for cobalt and nickel by A.A.S. in the same way as the aqueous phase samples. The organic phase concentration of the metal could then be calculated from its aqueous strip concentration.

In diluting solutions with the variable diluter, care was taken to use the higher dilution ranges, which have less error. As few as possible different dilutions

were used, so as to obtain maximum precision. Usually, x10 and x100 dilution steps were made.

A Perkin Elmer 306 double-beam atomic absorption spectrophotometer was used. The instrument has a digital output display. The conditions used were as recommended in the manufacturer's handbook.[42] For both elements, a lean, blue,air-acetylene flame was used.

A.A.S. for Cobalt

The most sensitive wavelength for cobalt, 240.7 nm was used, together with a slit width of 0.2 nm. Under these conditions a linear calibration was obtained up to 4 ppm cobalt. A set of standards of 1, 2, 3 and 4 ppm cobalt were used for calibration, and a straight line was fitted for the calibration by least-squares.

The standards were made up from A.A. standard solutions using high grade bulb pipettes and volumetric flasks, and it was ensured that the background matrix in the standards was similar to that of the sample.

A.A.S. for Nickel

The most sensitive wavelength for nickel, 232.0 nm was used, together with a slit width of 0.2 nm. Under these conditions, a linear calibration was obtained up to 5 ppm nickel.

The analysis was made in the same manner as for cobalt, using 1, 2, 3, 4 and 5 ppm nickel standards.

4.6 Reagents

The reagent used, the grade or purity and the supplier are given.

1. For the solvent:

   D_2EHPA; $\geq$ 96% pure; Koch-lite Chemicals, now Genzyme Ltd.

   TBP; approx. 98%; Koch-lite.

   Solvesso 150 (Esso Chemicals); 99% aromatic; Rutpen Ltd.

2. For the aqueous feeds:

   cobalt sulphate, $CoSO_4\ 7H_2O$; GPR, min. assay 97%, max. limit Ni impurity, 0.5%; BDH.

   nickel sulphate, $NiSO_4\ xH_2O$; GPR, 20.8-22.4% nickel, max. limit Co impurity, 0.5%; BDH.

3. For titrations:

   0.1 M HCl solution; 'convol'; BDH.

   0.1 M NaOH solution; " "

   1 M NaOH solution; " "

   Bromo-Cresol Green pH indicator, water soluble; pH 3.6-5.2; BDH.

4. For pH measurements:

KH phthalate, anhydrous; Analar; BDH.

KH_2PO_4, anhydrous; Analar; BDH.

Na_2HPO_4, anhydrous; Analar; BDH.

5. A.A.S. Standard Solutions:

Co: cobaltous nitrate, 1000 ppm Co; 'SpectrosoL'; BDH.

Ni: nickel nitrate, 1000 ppm Ni; 'SpectrosoL'; BDH.

6. Others:

ethanol; Analar 96 v/o; various.

hydrochloric acid; Analar Sp. Gr. 1.84; various.

sulphuric acid; Analar Sp. Gr. 1.18; various.

sodium sulphate, Na_2SO_4 anhydrous; GPR; BDH.

sodium hydroxide pellets; Analar; BDH.

CHAPTER 5

NON-FACTORIAL EXPERIMENTS: RESULTS AND DISCUSSION

5.1 Cross-Current Extraction Cascades

Each set of these experiments simulates a continuous extraction process in which mixer-settlers (or any other discreet-stage contactors) are used as equilibrium stages in a cross-current cascade.

The attraction of using this configuration, where two-metal extraction is concerned, is that unlike the counter-current cascade (see Section 3.1), the cross-current cascade may readily be simulated with batch experiments.

Although the cross-current cascade is unlikely to be employed in industrial practice, because it exploits distribution inefficiently, the simulation is of use in studying the cobalt/nickel separation. Equilibrium distribution data is obtained, and some idea is given of the degree of separation that can be obtained in the organic phase. It can be expected that the same degree of separation will be obtained in a counter-current configuration with greater efficiency.

Loading Experiments

A schematic representation of the loading cascade is given in Figure 5.1.a. In the figure, each stage represents an equilibrium stage in a continuous cascade, or a single equilibration in the experiments.

In Table 5.1 the results are given for a set of loading experiments in which the aqueous feed solution

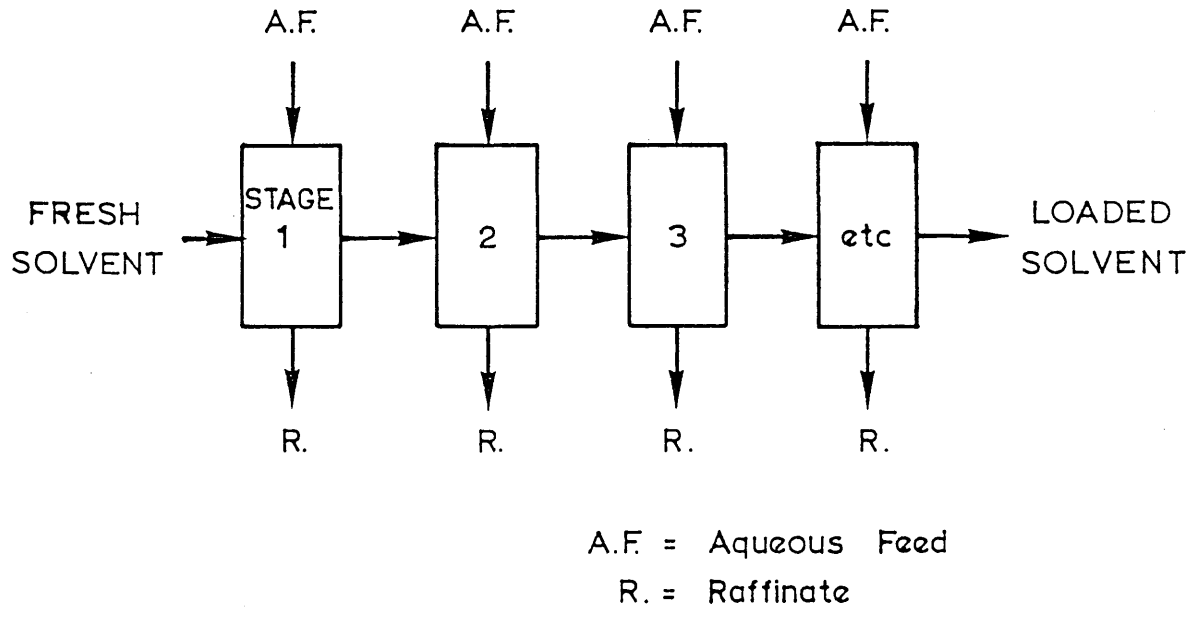


Figure a.

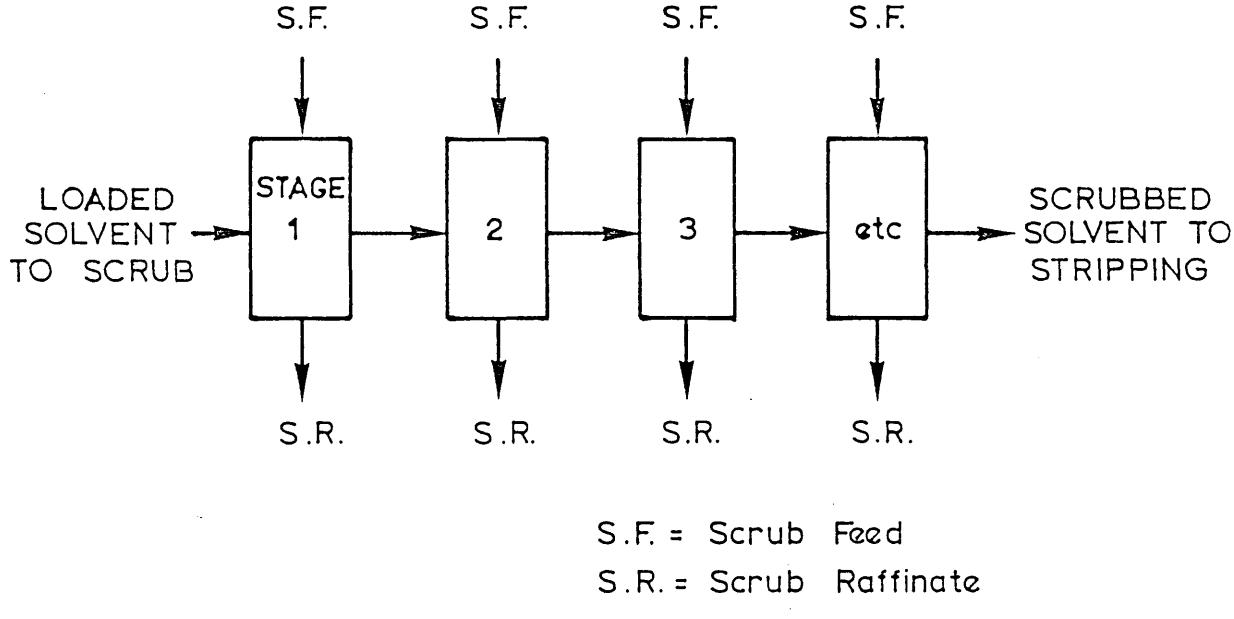


Figure b.

FIGURES 5.1.a and 5.1.b. Representations of cross-current extractions cascades. a. loading cascade and b. scrubbing cascade.

TABLE 5.1 Cross-Current Loading Experiments at 80°C

	pH	Aqueous Concentration		Organic Concentration		Distribution Ratio		Separation Factor	Sum of Concentrations	Molar Concentration Ratio
		Cobalt (g/L)	Nickel (g/L)	Cobalt (g/L)	Nickel (g/L)	D_{Co}	D_{Ni}	β_{Ni}^{Co}	$\overline{[Co]} + \overline{[Ni]}$ (M)	Co:Ni
aqueous feed	4.12	18.8	42.7	-	-	-	-	-	-	0.44:1
organic feed	-	-	-	none	none	-	-	-	-	-
equilibrium stage 1	4.65	7.6	38.4	11.3	3.16	1.49	0.082	18.1	0.246	3.6:1
2	4.59	17.1	44.6	13.4	1.54	0.78	0.035	22.7	0.253	8.7:1
3	4.98	19.6	42.5	13.4	1.52	0.68	0.036	19.1	0.253	8.8:1
4	5.08	15.6	43.6	14.2	1.28	0.91	0.029	30.9	0.262	11.1:1
5	5.09	20.4	49.3	14.4	1.34	0.71	0.027	26.0	0.267	10.8:1

that was used contained approximately 20 g/L cobalt and 40 g/L nickel at a pH of approximately 4.0.

The composition of the organic phase for loading was 0.5 M NaD_2EHPA with 5 v/o TBP in Solvesso 150, and the phase volume ratio was 1:1 throughout.

The results show that after the first stage, an improvement in the cobalt:nickel concentration ratio was seen, from a value of 0.44:1 in the aqueous feed to 3.6:1 in the equilibrated organic phase. Downstream through the stages, the ratio for the organic phase increased until stage 5, where, allowing for experimental error, a terminal value of around 11:1 was reached. In fact, in stage 5 there was little change at all in the feed and equilibrium compositions of each phase (except a rather high and unlikely value for the equilibrium aqueous nickel concentration).

The selectivity of the extractant for cobalt can be seen from the way in which nickel was crowded out of the organic phase in successive stages. The stage concentrations show that nickel in the organic phase coming from the previous stage was displaced in the next stage by cobalt from the aqueous feed to that stage.

According to theory, an organic phase of composition 0.5 M NaD_2EHPA has a stoichiometric capacity for divalent metals of 0.25 M, assuming extraction as the metal cation.

The sum of the organic phase cobalt and nickel concentrations, $\overline{[Co]} + \overline{[Ni]}$, where square brackets denote the equilibrium concentration of the species in the bracket, was calculated for each stage of the cascade, and in each case, within experimental error, values very close to the stoichiometric capacity were obtained. In fact, within experimental error, the theoretical stoichiometric capacity was never exceeded in the present study.

The effect on the stability of the pH of using the sodium form of D_2EHPA can be seen in Table 5.1, by comparing the feed and raffinate values of pH. Instead of the substantial decrease in pH that would occur during extraction with the acid form of D_2EHPA, which would tend to stop further extraction, there is only a slight overall increase in pH during extraction.

The distribution ratio of a metal is defined by

$$D_M = \frac{C_M(org)}{C_M(aq)} \qquad (5.1)$$

at equilibrium, it is defined by

$$D_M = \frac{\overline{[M]}}{[M]} \qquad (5.2)$$

The distribution ratio is often used as a parameter for extraction, though it does not have fundamental significance. D_M is not usually a constant, and in acidic extraction it varies with total metal concentration and pH.

In systems where two metals M and N (or more) are extracted, the separation factor, β_N^M, defined by

$$\beta_N^M = \frac{D_M}{D_N} \qquad (5.3)$$

is used to give an idea of the relative extractability of the two metals. However, since the distribution ratios are not constants, and each further varies with the concentration of the other metal, β_N^M is also not a constant.

In Table 5.1, the parameters D_{Co}, D_{Ni} and β_{Ni}^{Co} have been calculated for each equilibrium stage. As expected, D_{Co} and D_{Ni} vary from stage to stage, as does β_{Ni}^{Co}. In all the stages D_{Co} is larger than D_{Ni}, hence β_{Ni}^{Co}, reflecting the preference of D_2EHPA for cobalt, is always larger than one, and reaches a maximum value of around 30.

Scrubbing Experiments

A schematic representation of the scrub cascade is given in Figure 5.1.b. In the figure, as before, each stage represents an equilibrium stage in a continuous cascade, or a single equilibration in the experiments.

In Table 5.2 results are given for a set of scrubbing experiments in which a $CoSO_4$ aqueous scrub feed was used which contained approximately 20 g/L of cobalt at a pH of 5.5.

The organic phase for scrubbing contained 12.0 g/L cobalt and 2.68 g/L nickel. Prior to loading its composition

TABLE 5.2 Cross-Current Scrubbing Experiments at 80°C and pH = 5.5

	Aqueous Concentration		Organic Concentration		Distribution Ratio		Separation Factor	Sum of Concentrations	Molar Concentration Ratio
	Cobalt (g/L)	Nickel (g/L)	Cobalt (g/L)	Nickel (g/L)	D_{Co}	D_{Ni}	β_{Ni}^{Co}	$\overline{[Co]} + \overline{[Ni]}$ (M)	Co:Ni
aqueous scrub feed	19.8	0.082	-	-	-	-	-	-	
organic for scrubbing	-	-	12.0	2.68	-	-	-	0.249	4.5
equilibrium stage 1	16.8	2.05	13.1	0.778	0.78	0.38	2.1	0.235	16.8
2	18.2	0.67	14.3	0.266	0.79	0.40	1.7	0.248	53.8
3	18.1	0.29	13.9	0.023	0.77	0.08	9.63	0.236	604
4	19.8	0.08	14.4	0.007	0.73	0.09	6.99	0.243	2050

was 0.5 M NaD_2EHPA with 5 v/o TBP in Solvesso 150. The phase volume ratio used was 1:1 throughout.

The organic phase for scrubbing in these experiments contained less cobalt and more nickel than had been obtained in the final organic phase in loading experiments, so these scrubbing experiments represent a less favourable set of circumstances for scrubbing than might be required in a process.

The results show that the combined loading of cobalt and nickel remained constant in each stage, but nickel in the organic phase was progressively replaced with cobalt with each stage. The cobalt:nickel concentration ratio in the organic phase increased from 4.5:1 in the organic scrub feed to approximately 2000:1 in the final stage.

The distribution ratio D_{Co} changed very little from stage to stage in these experiments, due to the similarity of the cobalt compositions in each stage. D_{Ni}, however showed a marked reduction in size as nickel was scrubbed out. In the latter stages at the cascade D_{Ni} is the ratio of two very low nickel concentrations.

The cobalt losses in the scrubbing cascade are represented by the raffinate cobalt concentrations. The cross-current configuration and phase ratio used result in losses which would be unacceptable in an actual process. Even using a cross-current cascade though, the losses at each stage could be reduced by using a higher organic:

aqueous phase volume ratio, say 5:1, than that of 1:1 used here.

However, the scrub cascade experiments do demonstrate that a satisfactory level of cobalt separation can be achieved in the organic phase.

5.2 The Treatment of Distribution Data by Chemical Equilibria

Consider the following representations for extraction by the sodium-salt of D_2EHPA. For cobalt extraction (as the blue complex),

$$\overline{2RNa} + Co^{2+} \rightleftharpoons \overline{R_2Co} + 2Na^+ \qquad (5.4)$$

and for nickel extraction,

$$\overline{2RNa} + Ni^{2+} \rightleftharpoons \overline{R_2Ni} + 2Na^+ \qquad (5.5)$$

According to equations 5.4 and 5.5, the equilibrium constants for cobalt and nickel respectively are defined by,

$$K_{Co} = \frac{a_{\overline{R_2Co}} \cdot a_{Na^+}^2}{a_{\overline{RNa}}^2 \cdot a_{Co^{2+}}} \qquad (5.6)$$

where a is the activity of the species indicated, and by

$$K_{Ni} = \frac{a_{\overline{R_2Ni}} \cdot a^2_{Na^+}}{a^2_{\overline{RNa}} \cdot a_{Ni^{2+}}} \qquad (5.7)$$

Equation 5.6 may be rearranged to give

$$\frac{a^2_{Na^+}}{a^2_{\overline{RNa}}} = \frac{K_{Co} \cdot a_{Co^{2+}}}{a_{\overline{R_2Co}}} \qquad (5.8)$$

and equation 5.7 rearranged to give

$$\frac{a^2_{Na^+}}{a^2_{\overline{RNa}}} = \frac{K_{Ni} \cdot a_{Ni^{2+}}}{a_{\overline{R_2Ni}}} \qquad (5.9)$$

With both cobalt and nickel present in an extraction system, equations 5.8 and 5.9 may be equated with each other, and the resulting expression rearranged, so that

$$\frac{K_{Co}}{K_{Ni}} = \frac{a_{\overline{R_2Co}} \cdot a_{Ni^{2+}}}{a_{\overline{R_2Ni}} \cdot a_{Co^{2+}}} \qquad (5.10)$$

For a given extraction temperature, K_{Co}/K_{Ni} is a constant, since K_{Co} and K_{Ni} are constants by definition.

If it is assumed, as is common in solvent extraction studies, that the activity coefficients of the extracted species tend to unity, then the organic phase activities in the equation may be replaced by concentrations.

The activity/concentration behaviour of several transition metal sulphate solutions is known to be virtually the same[43]. This should therefore be the case with cobalt and nickel.

In mixed solution it is reasonable to assume that their activity coefficients will be very similar, so that concentrations may again replace activities. With these changes, equation 5.10 becomes:

$$\frac{K_{Co}}{K_{Ni}} = \frac{[\overline{R_2Co}]\ [Ni^{2+}]}{[\overline{R_2Ni}]\ [Co^{2+}]} \qquad (5.11)$$

If $\overline{R_2Co}$ and $\overline{R_2Ni}$ are the only extracted forms of the metals, then the specific species concentrations can be replaced by analytical concentrations, as in equation 5.12. In this equation, K_{Co}/K_{Ni} is equivalent to the separation factor, β^{Co}_{Ni}, as

$$\frac{K_{Co}}{K_{Ni}} = \frac{[\overline{Co}]\ [Ni^{2+}]}{[\overline{Ni}]\ [Co^{2+}]} = \beta^{Co}_{Ni} \qquad (5.12)$$

If the above argument holds true, then for any equilibration at a given temperature, values of K_{Co}/K_{Ni} calculated according to equation 5.12 should converge on a single value.

In Table 5.3, K_{Co}/K_{Ni} has been calculated in this way, from equilibrium distribution data which was obtained with an extraction temperature of 80°C, an organic phase of original composition 0.5 M NaD_2EHPA with 5% v/v TBP in Solvesso 150, and a phase volume ratio of 1:1. The data are derived from various non-factorial experiments

TABLE 5.3. Equilibrium distribution data, and values for K_1/K_2 calculated according to Equation 5.12.

	Equilibrium pH	Equilibrium Aqueous Concentration		Equilibrium Organic Concentration		$K_{Co}/K_{Ni} = \beta^{Co}_{Ni}$
		Cobalt	Nickel	Cobalt	Nickel	
		(M)	(M)	(M)	(M)	
1	5.80	0.178	0.835	0.153	0.061	11.80
2	3.90	0.304	0.927	0.163	0.029	17.40
3	5.78	0.314	0.917	0.171	0.024	20.80
4	5.75	0.314	0.876	0.178	0.025	19.70
5	6.01	0.329	0.879	0.175	0.027	17.10
6	5.94	0.163	0.825	0.144	0.054	13.50
7	+	0.322	0.866	0.171	0.029	15.86
8	5.82	0.343	0.864	0.178	0.024	18.60
9	5.86	0.348	0.835	0.178	0.028	15.00
10	5.89	0.392	0.814	0.171	0.030	11.90
11	5.31	0.176	0.899	0.239	0.048	25.20
12	5.35	0.353	0.974	0.246	0.026	25.90
13	5.76	0.397	0.920	0.271	0.022	28.30
14	5.40	0.396	0.947	0.254	0.042	14.50
15	5.77	0.400	0.940	0.263	0.022	28.70
16	4.56	0.348	0.027	0.292	4×10^{-4}	56.63
17	4.61	0.358	0.002	0.277	8×10^{-5}	19.34
18	4.82	0.351	0.001	0.284	5×10^{-5}	16.18
19	4.66	0.355	0.001	0.306	4×10^{-5}	21.55
20	(a)5.60	0.284	0.035	0.222	0.013	2.10
21	"	0.309	0.011	0.243	0.005	1.73
22	"	0.307	0.005	0.236	4×10^{-4}	9.61
23	"	0.335	1.4×10^{-4}	0.234	1×10^{-4}	6.99
24	4.65	0.129	0.654	0.192	0.054	18.07
25	4.59	0.290	0.760	0.227	0.026	22.70
26	4.98	0.333	0.724	0.227	0.026	19.12
27	5.08	0.265	0.743	0.240	0.022	30.90
28	5.09	0.346	0.840	0.244	0.023	25.97
29	4.59	0.132	0.656	0.193	0.065	14.73
30	4.77	0.294	0.763	0.232	0.033	18.29
31	4.76	0.319	0.734	0.229	0.718	20.36
32	+	0.316	0.794	0.229	0.026	21.68
33	5.49	0.178	0.741	0.186	0.065	11.95
34	5.32	0.159	0.722	0.189	0.059	14.45
35	5.36	0.168	0.722	0.186	0.059	13.50

+ = missing value

made by the present author, including the cascade experiments reported here.

The values of K_{Co}/K_{Ni} obtained ranged from about 1.7 to 30, though in one case a value of 56.6 was obtained. This variation in value is too large to be explained by experimental errors, which come mainly from the analysis for cobalt and nickel, and it was concluded that the approach does not give a satisfactory description of distribution in the system.

Some of the problems in the above approach will be apparent from discussions in other chapters. It has been seen that equations 5.3 and 5.4 are likely to be of limited use because of uncertainties relating to the water content of the extracted complex and also because the cobalt and nickel complexes are unalike in their co-ordination. At the same time it is not clear what equations would be better used in this kind of analysis.

The assumption that only one extracted complex of each metal occurs in the organic phase does not hold good, because of the polymerization of the cobalt and possibly the nickel complex; because of the occurrence of both pink and blue cobalt complexes; and because any excess D_2EHPA present may co-ordinate in the extracted complexes.

Roughly speaking, for the activity coefficients of the extracted species to be unity (i.e. ideal behaviour)

as was assumed in obtaining equation 5.11, there should be no enthalpy of mixing of the complex and diluent. If there is a significant enthalpy of mixing, the alternative assumption, that the activity coefficients of the cobalt and nickel complexes are similar, may not hold since the complexes are differently co-ordinated and differ in water content.

CHAPTER 6

THE FACTORIAL DESIGN

6.1 Objectives of the Design

It was decided to apply an experimental design to the task of examining several variables in the chemistry of the system. The experimental design chosen as suitable was a full factorial design at two levels, i.e. a 2^n FACTORIAL DESIGN. In a 2^n design which is UNREPLICATED, that is one in which each treatment combination is executed only once, n FACTORS can be examined in N experiments, where $N = 2^n$. In limiting the size of experimental programme for practical reasons, it was considered satisfactory to examine five factors (the terms FACTOR and VARIABLE are interchangeable) identified as being of potential importance. Thus $N = 2^5 = 32$ experiments would be required.

Each experiment in the design pattern consists of a single contact of a cobalt and nickel bearing aqueous feed with an organic phase containing D_2EHPA as its sodium salt. Within the experiment the variables under study are set at the required levels while the other conditions are held constant. Once at equilibrium, the phases are separated, allowed to cool, and analysed.

Each experiment represents an extraction equilibrium stage, and the purpose of the factorial design as a whole is to determine the effects of the variables on the separation achieved in an extraction stage.

6.2 Selection of the Variables and their Levels

The variables and levels chosen are shown in Table 6.1. In the statistical analysis of the results, the variables will be represented by code letters for convenience, and these are given in the table.

TABLE 6.1 The Factorial Variables and Their Levels

Variable	Variable Code Letter	Levels of Variables		
		Low	High	(Units)
initial pH	A	4.0	5.5	pH units
initial aqueous cobalt concentration	B	10.0	25.0	g/L
initial aqueous nickel concentration	C	20.0	50.0	g/L
equilibrium temperature	D	323 (50^{o})	353 (80^{o})	K(^{o}C)
initial aqueous sodium sulphate concentration	E	0	0.5	(M)

The reasons for each choice are now discussed.

Initial pH

As was described earlier, the extraction of metals with D_2EHPA is dependent on pH according to a reaction such as

$$M^{2+} + \overline{(RH)_2} \rightleftharpoons \overline{M(R.HR)_2} + 2H^+ \qquad (6.1)$$

Although it was clear that the extraction of both cobalt and nickel will be affected by pH, what was not apparent was whether there is an appreciable difference between the metals in this dependance which could be exploited in their separation. This was one of the questions it was thought that the factorial design could answer. In any case, the pH is of course, an important factor to be taken into account with any hydrometallurgical process.

Since the pH is difficult to maintain at a set value during extraction, and since when using the sodium salt of D_2EHPA, the pH does not change very much during extraction, it was decided to use initial pH as the factorial variable.

In a factorial design it is customary to refer to the two levels of a factorial variable as the LOW LEVEL and the HIGH LEVEL. The low level of initial pH of 4.0 was selected from previous experience as being within the lower pH limit for cobalt extraction. The high level of initial pH of 5.5 was again selected from previous experience, as being within the limit of pH above which hydrolysis of cobalt and nickel occurs in the aqueous phase.

Hydrolysis of cobalt and nickel and precipitation of the product occurs according to the reaction:

$$M^{2+} + 2H_2O \rightleftharpoons M(OH)_{2(s)} + 2H^+ \qquad (6.2)$$

If for any reason hydrolysis occurs during solvent extraction, it gives rise to the problem of third-phase formation.

Initial Aqueous Cobalt Concentration and Initial Aqueous Nickel Concentration

The obvious choice of cobalt and nickel variables for a distribution study were initial aqueous cobalt concentration and initial aqueous nickel concentration and these were selected.

In applying the statistical methods for the first time, the present author felt that it would be of guidance in planning the design to have a prior indication of the influence of some of the variables. This was available for the cobalt and nickel variables, through the extraction curves obtained in the hydrometallurgy group at Imperial College by M.J. Rogers. These are shown in Appendix 1.

These distribution curves represent a classical 'one-at-a-time' investigation of the variables, as one variable is studied at once while the others are held constant. One advantage of the factorial design approach is that, unlike that of the 'one-at-a-time', interactions between variables can be detected, as will be seen.

Incidentally, the present author calculated the K_{Co}/K_{Ni} ratio according to equation 5.12 for these equilibrations. As before, it was found that the variation observed was too large to be explained by experimental error (see Section 5.2).

In cobalt/nickel processing, the feed to the separation will usually have already been treated in one of a number of ways to remove the bulk of the nickel initially present. This tends to produce a uniformity of cobalt:nickel concentration ratio in separation feeds, since, whichever pretreatment is used, the nickel removal can be carried out without contamination of the product with cobalt, until the nickel concentration in the residue is reduced to about that of cobalt. Thus feeds to a cobalt/nickel separation often contain roughly equal concentrations of cobalt and nickel.

This was taken account of in setting the factorial levels of the cobalt and nickel. The combinations straddle a ratio of unity, as can be seen from Table 6.2.

TABLE 6.2 Combinations of Cobalt and Nickel Factorial Variables.

Variable Level Combination		Variable Level g/L		Molar Concentration Ratio in Feed	Combined Concentration in Feed
Co	Ni	Co	Ni	Co:Ni	M
high	low	25	20	1:0.8	0.765
high	high	25	50	1:2	1.276
low	low	10	20	1:2	0.510
low	high	10	50	1:5	1.021

Not only were the concentration ratios appropriate, the concentrations themselves were in line with those of typical cobalt/nickel separation feeds, since the solutions were fairly concentrated but were not subject to the danger of metal sulphate precipitation.

Equilibrium Temperature

The separation is profoundly influenced by the temperature of extraction, due to the thermochromic change in the extracted cobalt complex. Though the effect of temperature on separation is understood qualitatively, and some quantitative data is available in the literature (for the effect of temperature on D_{Co} and D_{Ni}), it was decided to include equilibrium temperature as a factorial variable, especially as only one extraction temperature had been used by the present author up to this point.

For the high level of equilibrium temperature, 353K ($80^{o}C$) was selected. This is the practical upper limit of temperature for the experimental method, and would allow comparison of the factorial data with the earlier experiments. For the low level, 323K ($50^{o}C$) was selected. It was known from Flett et al.[2] that the relationship between temperature and β_{Ni}^{Co} is fairly linear between 50^{o} and $80^{o}C$.

This is perhaps an appropriate point to mention that with a factorial design that has quantitative variables, it is an implicit assumption that the relationship between each variable will be (in mathematical language) continuous,

i.e. that as the variable level is changed, the response is either static or changes smoothly without jumps or interruptions. This should be remembered when selecting the variables and their levels, and the responses, since only under these conditions can the variable be incorporated into the eventual polynomial model.

Initial Aqueous Sodium Sulphate Concentration

In extraction with the sodium form of D_2EHPA, as cobalt and nickel are extracted, ionic sodium species are exchanged into the aqueous phase to produce sodium sulphate, according to an equation such as:

$$M^{2+} + 2\overline{RNa} \rightleftharpoons \overline{R_2M} + 2Na^{+} \qquad (6.3)$$

This equation shows the possible importance of the influence of sodium ion concentration on metal distribution. Sodium ion concentration is also of interest as a process variable, since in considering an equilibrium stage there will be sodium present in the aqueous feed due to previous extraction stages.

As the only anionic species present in the extraction system is sulphate, and it was undesirable to introduce new species which might affect the extraction chemistry, the factorial variable selected was initial aqueous sodium sulphate concentration.

In all the previous experiments there had been no aqueous sodium sulphate present, and this was adopted as the low factorial level. To give an adequate range of concentration, the high level was 0.5 M, Na_2SO_4. With the phase ratio and NaD_2EHPA concentration used, this is in excess of that available from the extractant for exchange.

6.3 Other Conditions

The remaining conditions were not varied in the experiments.

As before, an organic phase containing 0.5 M NaD_2EHPA with 5 v/o TBP in Solvesso 150, and a phase volume ratio of 1:1 were used.

In all the experiments up to this point, tributyl phosphate (TBP) was included in the solvent. TBP is used in many separations because it inhibits third-phase formation during extraction by increasing the solubility of the extracted species in the organic phase. Before including TBP in the solvent for the factorial design experiments, extraction of cobalt was tried without TBP modifier present.

An aqueous feed containing 20 g/L cobalt as cobalt sulphate at pH = 5.5 was equilibrated at 353K ($80^{o}C$) with an organic phase containing 0.5 M NaD_2EHPA in Solvesso 150.

During extraction, a third phase was observed. On filtering both the phases together, a blue solid residue,

similar in colour to the cobalt-loaded organic phase, was obtained. The solid was allowed to dry thoroughly, remaining blue, but when ground the powder became pink, on standing over a long period. An analysis of the substance is given in Table 6.3. The value given for percent oxygen was calculated by difference.

TABLE 6.3. Comparison of the Compositions of the Precipitated Solid and Some Theoretical Compounds.

Element	Analysis (% weight)	Composition of Theoretical Compound (% weight)			
		CoR_2	$Co(III)R_3$	Co(OH)R	CoR.2HR
Co	16.2 ± 0.3	8.4	5.76	14.83	4.38
Ni	0.06 ± 0.01	-	-	-	-
C	36.12	54.77	56.34	48.36	57.09
H	6.53	9.77	10.05	8.88	10.33
O	32.12	18.24	18.76	20.13	19.01
P	9.03	8.83	9.08	7.79	9.20

The analysis was made on the material unpurified, as insufficient was collected for a recrystallization. The composition of the solid appears to be closer to a mono(2-ethylhexyl) phosphate than a di(2-ethylhexyl) phosphate compound.

The matter was not investigated further, since the TBP modifier was clearly needed. The modifier was included

in the solvent for the factorial experiments at its previous concentration, i.e. 5 v/o TBP.

6.4 The Experimental Matrix

The DESIGN MATRIX of experimental conditions for the factorial design is shown in Table 6.4, in which each row relates to one experiment.

Each experiment has a TREATMENT CODE which gives, in shorthand, the level of each factorial variable in that experiment. The combination of levels in that experiment is known as the TREATMENT COMBINATION. The notation used for the treatment code in this study is that if a variable code letter appears in the treatment code in lower case (i.e. a for variable A), then the variable is at its high level in the treatment combination. If the lower case is absent from the combination, then that variable is at its low level. The letter 'L' for a treatment code refers to the treatment combination in which all the variables are at their low levels.

The order of the treatments in Table 6.4 is the so-called YATES'S or STANDARD ORDER, and not the order in which the experiments were carried out, which is given in Appendix 2.a. By writing out the treatment combinations in this way, it is possible to calculate the main effects and interactions for a response by hand, using Yates' hand algorithm, as will be seen.

6.5 Selection of the Responses

The results of the experiments are given in columns 7-11 of Table 6.4. It can be seen that the same measurements were made in the factorial experiments as in the earlier experiments.

A RESPONSE is a quantity or variable which is evaluated to see whether it has any relationship with the factorial variables.

It was decided that of the equilibrium metal concentrations, the organic concentrations of cobalt and nickel would be treated formally as responses. It was not considered necessary to so treat the aqueous cobalt and nickel concentrations, since they are related to the organic concentrations by mass conservation, and this saved a large amount of superfluous calculation.

The equilibrium pH was also selected as a response, because of its importance in the chemistry of the system. Another reason for the selection was to do with process modelling. Unless there is some form of pH control in extraction, the equilibrium pH in one stage is the feed pH to the next stage. It is therefore desirable, if possible, to produce a correlation relating initial and equilibrium pH.

TABLE 6.4. Experimental Results from the Factorial Design. (The first six columns constitute the DESIGN MATRIX).

Treatment Code	Level of Variable					Responses					
	Variable A (pH)	Variable B (Co)	Variable C (Ni)	Variable D (T)	Variable E (Na_2SO_4)	Equilibrium Aqueous Concentration		Equilibrium Organic Concentration		Equilibrium pH	Separation Factor β^{Co}_{Ni}
						Co	Ni	Co	Ni		
		g/L	g/L	^oC	M	g/L	g/L	g/L	g/L		
L	4.0	10.0	20.0	50	0	2.23	13.5	8.26	6.10	5.46	8.20
a	5.5	10.0	20.0	50	0	2.23	13.4	8.28	6.22	5.52	7.99
b	4.0	25.0	20.0	50	0	11.75	18.4	13.20	1.32	5.28	15.6
ab	5.5	25.0	20.0	50	0	11.75	18.4	13.56	1.37	5.35	15.50
c	4.0	10.0	50.0	50	0	4.34	40.4	6.36	7.72	5.20	7.67
ac	5.5	10.0	50.0	50	0	4.56	40.2	6.16	7.74	5.17	7.02
bc	4.0	25.0	50.0	50	0	13.55	45.0	12.08	2.76	4.82	14.54
abc	5.5	25.0	50.0	50	0	13.90	45.5	11.04	3.42	5.20	10.57
d	4.0	10.0	20.0	80	0	1.28	14.3	9.25	5.26	5.03	19.65
ad	5.5	10.0	20.0	80	0	1.28	14.5	9.37	5.34	4.96	19.88
bd	4.0	25.0	20.0	80	0	11.50	18.8	14.02	1.08	4.73	21.22
abd	5.5	25.0	20.0	80	0	11.75	18.5	13.20	1.56	5.18	13.32
cd	4.0	10.0	50.0	80	0	2.62	41.9	8.24	6.34	4.89	20.78
acd	5.5	10.0	50.0	80	0	2.58	41.0	7.92	6.18	4.81	20.37
bcd	4.0	25.0	50.0	80	0	12.80	46.1	12.36	2.35	5.06	18.94
abcd	5.5	25.0	50.0	80	0	13.15	45.7	12.40	2.37	5.06	18.18
e	4.0	10.0	20.0	50	0.5	2.40	14.5	8.44	5.62	5.46	9.07
ae	5.5	10.0	20.0	50	0.5	2.39	14.1	7.96	5.72	5.48	8.21
be	4.0	25.0	20.0	50	0.5	11.70	18.8	13.52	1.29	5.43	16.84
abe	5.5	25.0	20.0	50	0.5	11.70	18.6	13.48	1.33	5.51	16.11
ce	4.0	10.0	50.0	50	0.5	4.68	41.0	5.96	7.43	4.67	7.03
ace	5.5	10.0	50.0	50	0.5	4.52	41.2	6.76	7.80	5.02	7.90
bce	4.0	25.0	50.0	50	0.5	13.15	44.8	11.80	2.62	5.02	15.34
abce	5.5	25.0	50.0	50	0.5	13.25	48.8	12.04	2.60	4.92	17.05
de	4.0	10.0	20.0	80	0.5	1.32	14.7	9.24	5.32	5.18	19.34
ade	5.5	10.0	20.0	80	0.5	1.27	14.7	9.32	5.28	5.15	20.43
bde	4.0	25.0	20.0	80	0.5	11.90	18.1	12.92	1.79	5.10	10.98
abde	5.5	25.0	20.0	80	0.5	12.30	18.1	13.48	1.32	5.19	15.02
cde	4.0	10.0	50.0	80	0.5	2.60	41.9	8.36	6.28	4.85	21.45
acde	5.5	10.0	50.0	80	0.5	2.58	41.8	8.16	6.22	4.92	21.25
bcde	4.0	25.0	50.0	80	0.5	13.65	46.0	12.36	2.28	4.98	18.27
abcde	5.5	25.0	50.0	80	0.5	13.10	45.4	11.60	2.23	5.12	18.03

CHAPTER 7

A STATISTICAL STUDY OF THE COBALT RESPONSE

7.1 Factorial Analysis

Calculation of the Effects

Collectively, the main-effects and the interaction effects for a response are called the response EFFECTS.

For the cobalt response, the effects were calculated by hand using YATES'S ALGORITHM. The method of calculation and the calculation itself are given in Appendix 2.b. The calculated effects are given in Table 7.1, where the treatment codes are presented in Yates' order to agree with the full calculation.

In Table 7.1, the quantity in the first row of column (III) is the GRAND MEAN, which is the mean value of the response over all the experiments. If the response in a given experiment is y_i, then the grand mean,

$$\bar{y} = \frac{\sum_{1}^{i=N} y_i}{N} \qquad (7.1)$$

Thus the grand mean value of the equilibrium organic cobalt concentration in the factorial design was 10.35 g/L.

The (2^n-1) remaining values in column (III) are the effects, and they are identified in column (IV). The MAIN-EFFECT of each variable is denoted by its single upper case variable letter (i.e. B for variable B), and the various interaction effects by a combination of upper-case letters (e.g. BC is the TWO-FACTOR INTERACTION between variables B and C).

It has been seen that in interpreting the results of a 2^n design, the effects are not calculated laboriously from the definition of each effect. Instead, a hand algorithm such as Yates' analysis or a computer algorithm are generally used.

However, if each effect were so calculated, it would be found that each effect is the equivalent of the difference between two averages, $\bar{y}_+$ and $\bar{y}_-$, so that

$$\text{effect} = \bar{y}_+ - \bar{y}_- \tag{7.2}$$

where $\bar{y}_+$ is the average response of one half of the 2^n observations, and $\bar{y}_-$ is the average response for the other half.

For each effect, the group of observations which make up $\bar{y}_+$ and the group which make up $\bar{y}_-$ are termed the CONTRASTS of the effect. Which contrast a given observation is assigned to depends on the effect being calculated.

For example, if the effect is a main-effect, say B, then the observations in the $\bar{y}_+$ contrast would consist of all the responses whose treatment combination contained variable B at its high level. The $\bar{y}_-$ contrast would contain the other half of the observations, in which variable B is at its low level.

On inspecting the effects in Table 7.1, it is found that the largest effect is B, the main-effect of variable B, the initial aqueous cobalt concentration.

TABLE 7.1. Calculated effects for the response:equilibrium organic cobalt concentration.

Treatment Code	Response (g/L)	Estimated Effect	Identity
Column (I)	(II)	(III)	(IV)
L	8.26 ± 0.348	10.3468	Average
a	8.28 ± 0.348	-0.1025 ± 0.123	A
b	13.20 ± 0.348	4.6888 ± 0.123	B
ab	13.56 ± 0.348	-0.0800 ± 0.123	AB
c	6.36 ± 0.348	-1.4938 ± 0.123	C
ac	6.16 ± 0.348	-0.0775 ± 0.123	AC
bc	12.08 ± 0.348	0.0313 ± 0.123	BC
abc	11.04 ± 0.348	-0.1200 ± 0.123	ABC
d	9.25 ± 0.348	0.8313 ± 0.123	D
ad	9.37 ± 0.348	-0.0600 ± 0.123	AD
bd	14.02 ± 0.348	-0.6288 ± 0.123	BD
abd	13.20 ± 0.348	-0.0025 ± 0.123	ABD
cd	8.24 ± 0.348	0.3188 ± 0.123	CD
acd	7.92 ± 0.348	-0.0700 ± 0.123	ACD
bcd	12.36 ± 0.348	-0.0813 ± 0.123	BCD
abcd	12.40 ± 0.348	0.1525 ± 0.123	ABCD
e	8.44 ± 0.348	-0.0188 ± 0.123	E
ae	7.96 ± 0.348	0.1280 ± 0.123	AE
be	13.52 ± 0.348	-0.0638 ± 0.123	BE
abe	13.48 ± 0.348	0.0550 ± 0.123	ABE
ce	5.96 ± 0.348	0.0788 ± 0.123	CE
ace	6.76 ± 0.348	0.0725 ± 0.123	ACE
bce	11.80 ± 0.348	-0.0163 ± 0.123	BCE
abce	12.04 ± 0.348	-0.1350 ± 0.123	ABCE
de	9.24 ± 0.348	-0.1463 ± 0.123	DE
ade	9.32 ± 0.348	-0.0450 ± 0.123	ADE
bde	12.92 ± 0.348	-0.1763 ± 0.123	BDE
abde	13.48 ± 0.348	0.0075 ± 0.123	ABDE
cde	8.36 ± 0.348	-0.0238 ± 0.123	CDE
acde	8.16 ± 0.348	-0.3250 ± 0.123	ACDE
bcde	12.36 ± 0.348	-0.0338 ± 0.123	BCDE
abcde	11.60 ± 0.348	-0.1575 ± 0.123	ABCDE

A MAIN-EFFECT is defined as the average difference in the response between the high and low levels of that factorial variable. A positive sign for a main-effect means that in going from the low to the high level of the factorial variable there is an increase in the response. A negative sign means that in going from the low to the high level of the factorial variable, there is a decrease in the response.

The main-effect B is +4.69 g/L so the cobalt response increases by an average of 4.69 g/L in going from the low to the high level of initial aqueous cobalt concentration.

Apart from any previous knowledge of the D_2EHPA separation, it is clear by inspection of the factorial data that the main-effect B is a real effect, and is not merely a quantity that arises from experimental error.

Looking first not at the effects, but at the response values for different treatment combinations, if any two treatment combinations are compared which differ only in the factorial level of variable B (for example bd and d, abcd and acd, b and L), there is consistently an increase in the response in going from the low level to the high level of the variable. This is the case regardless of the levels of the other variables in the treatment combination. For the above pairs of treatments, the increases in the response are +4.77, +4.48 and +4.94 g/L respectively. From such an examination, it is obvious that the influence of variable B on the response is a real one.

The same conclusion would also be drawn by considering the effect itself. A main-effect represents an average change in the response as defined above. For B, the change is much larger than would be expected if the value arose only due to experimental error. Also, the sign of B is consistent with the expected trend indicated by the non-factorial work.

To make the interpretation of the effects easier, in Table 7.2 the effects are given in order of size. Because both positive and negative effects occur, the ordering is according to absolute magnitude. The effects have the units of the original response. From the table, it is seen that the most conspicuous of the remaining effects are the MAIN-EFFECTS C and D and the TWO-FACTOR INTERACTION, BD. These effects are respectively the next three largest in magnitude after B, and the two-factor interaction (2-f.i) is composed of two of the large main-effects.

As C is a main-effect, the likelihood that it is a real effect can easily be determined by inspection in the same manner as for B. In comparing the pairs of treatments which differ only in the level of variable C (e.g. ac and a, abce and abe etc.), it would be found that with every pair there is a perceptible decrease in the response in going from the low level to the high level of C. The decrease and the negative sign of the calculated effect are consistent with each other.

C is the main-effect of the variable initial aqueous nickel concentration. The calculated value of the

TABLE 7.2. Ranked absolute values of cobalt effects.

Order	Effect	Absolute Value	Effect Sign
1	B	4.689	+
2	C	1.494	-
3	D	0.831	+
4	BD	0.629	-
5	ACDE	0.325	-
6	CD	0.319	+
7	BDE	0.176	-
8	ABCDE	0.158	-
9	ABCD	0.153	+
10	DE	0.146	-
11	ABCE	0.135	-
12	AE	0.127	+
13	ABC	0.120	-
14	A	0.103	-
15	BCD	0.0813	-
16	AB	0.0800	-
17	CE	0.0788	+
18	AC	0.0775	-
19	ACE	0.0725	+
20	ACD	0.0700	-
21	BE	0.0638	-
22	AD	0.0600	-
23	ABE	0.0550	+
24	ADE	0.0450	-
25	BCDE	0.0338	-
26	BC	0.0313	+
27	CDE	0.0238	-
28	E	0.0188	-
29	BCE	0.0163	-
30	ABDE	0.00750	+
31	ABD	0.00250	-

effect is -1.49 g/L. The effect means that the cobalt response decreases with increase in the variable initial aqueous nickel concentration.

For the main-effect D, the comparison of pairs of treatment combinations is shown in Table 7.3. It is seen that in most, but not all pairs, there is an increase in the response in going from the low to the high level of variable D. There is no apparent relationship between the pairs which show a decrease, and the decrease may possibly be explained by experimental error.

Incidentally, a main-effect may easily be calculated in the way shown in Table 7.3. It is often recommended that the calculation of the effects by algorithm is checked by the hand calculation of several of the main-effects.

D is the main-effect of the variable equilibrium temperature. The calculated value of the effect is +0.83 g/L. The effect means that the cobalt response increases with increase in equilibrium temperature.

A TWO-FACTOR INTERACTION between two variables, say B and D, is defined as half the difference between the average effect of one variable, say B, on the response when the runs were carried out at high level of variable D, and the average effect of variable B on the response when the runs were carried out at the low level of variable D.

In a 2^n design the above definition would be equally valid if B and D are interchanged, and the same numerical

TABLE 7.3. Comparison between Treatment Combinations with Variable D at the Low Level and at the High Level

Row	Treatment Combinations		Cobalt Response (g/L)		Difference in response: =y(high)-y(low) (g/L)
	High Level	Low Level	High Level	Low Level	
1	d	L	9.25	8.26	0.99
2	ad	a	9.37	8.28	1.09
3	bd	b	14.02	13.20	0.82
4	abd	ab	13.20	13.56	-0.36
5	cd	c	8.24	6.36	1.88
6	acd	ac	7.92	6.16	1.76
7	bcd	bc	12.36	12.08	0.24
8	abcd	abc	12.40	11.04	1.36
9	de	e	9.24	8.44	0.80
10	ade	ae	9.32	7.96	1.36
11	bde	be	12.92	13.52	-0.60
12	abde	abe	13.48	13.48	0.00
13	cde	ce	8.36	5.96	2.40
14	acde	ace	8.16	6.76	1.40
15	bcde	bce	12.36	11.80	0.56
16	abcde	abce	11.60	12.04	-0.44

Mean difference = main-effect D = 0.83 g/L

result and sign would be obtained on calculating the effect, whichever definition was used.

The 2-f.i. can be thought of as indicating the consistency of the effect of a variable on the response, over the range of the other variable. It is laborious and unnecessary to scrutinize each of the two-factor and other interactions individually in order to ascertain whether they are real effects, since the significance testing which follows will perform this function more effectively.

Significance Testing of the Effects

The concept in statistics of an observation being an imperfect 'sample' from a population of observations is a familiar one. In the factorial experiments, each of the effects is an imperfect sample from the population of observations that would be obtained if the effect was sampled a sufficient number of times. The sample effect obtained from the factorial experiment is therefore termed an estimate of an effect.

Any non-real effect, whether a main-effect or an interaction effect, will have a true value of zero, (in statistical terms, will have a population mean of zero), but the estimated value obtained from the factorial design can be different from zero due to experimental error. The purpose of the test of statistical significance is to determine whether the estimated effect of a given value is likely or not to have come from a non-existent or non-

real effect. An appropriate test[44] is the TWO-TAILED t-TEST.

The NULL HYPOTHESIS (H_o) of the test is that the (estimated) effect is not statistically different from zero. The ALTERNATIVE HYPOTHESIS (H_1) is that the effect is significantly different from zero. Each of the effects is tested. Tests for the cobalt effects are given in Table 7.4.

The calculated t-value, t_c, given in column (III) of the table, is defined by:

$$t_c = \frac{\text{effect}}{\text{S.E.(effect)}} \qquad (7.3)$$

where S.E.(effect) is the STANDARD ERROR OF AN EFFECT.

If a result is judged significant at a given significance level, say at the $100(1-\alpha) = 99\%$ level, this means that in ninety-nine of a hundred cases a result of that size would not occur due to chance fluctuation or experimental error.

The reference t-values given in columns (IV) and (VI) are the tabulated values having ν degrees of freedom. In a two-tailed t-test, at a LEVEL OF SIGNIFICANCE $(1-\alpha)$, reference values of $t_{\alpha/2,\nu}$ are used.

For a given effect, if

$$|t_c| > t_{\alpha/2,\nu} \qquad (7.4)$$

TABLE 7.4. Significance testing of the cobalt effects using two-tailed t-tests.

Column I	II	III	IV	V	VI	VII
Effect Identity	Effect Value	$t_c = \frac{\text{Effect}}{\text{S.E.(Effect)}}$	$t_{0.005}$ $\nu = 6$	Significance at 99% Probability Level	$t_{0.025}$ $\nu = 6$	Significance at 95% Probability Level
Average	10.347	-	-	-	-	-
A	-0.1025	-0.603	3.707	NS	2.447	NS
B	4.6888	27.581	3.707	S	2.447	S
AB	-0.0800	-0.471	3.707	NS	2.447	NS
C	-1.4938	-8.787	3.707	S	2.447	S
AC	-0.0775	-0.456	3.707	NS	2.447	NS
BC	0.0313	0.184	3.707	NS	2.447	NS
ABC	-0.1200	-0.706	3.707	NS	2.447	NS
D	0.8313	4.890	3.707	S	2.447	S
AD	-0.0600	-0.353	3.707	NS	2.447	NS
BD	-0.6288	-3.699	3.707	NS	2.447	S
ABD	-0.0025	-0.015	3.707	NS	2.447	NS
CD	0.3188	1.875	3.707	NS	2.447	NS
ACD	-0.0700	-0.412	3.707	NS	2.447	NS
BCD	-0.0813	-0.478	3.707	NS	2.447	NS
ABCD	0.1525	0.897	3.707	NS	2.447	NS
E	-0.0188	-0.110	3.707	NS	2.447	NS
AE	0.1275	0.750	3.707	NS	2.447	NS
BE	-0.0638	0.375	3.707	NS	2.447	NS
ABE	0.0550	0.324	3.707	NS	2.447	NS
CE	0.0788	0.463	3.707	NS	2.447	NS
ACE	0.0725	0.426	3.707	NS	2.447	NS
BCE	-0.0163	-0.096	3.707	NS	2.447	NS
ABCE	-0.1350	-0.794	3.707	NS	2.447	NS
DE	-0.1463	-0.860	3.707	NS	2.447	NS
ADE	-0.0450	-0.265	3.707	NS	2.447	NS
BDE	-0.1763	-1.037	3.707	NS	2.447	NS
ABDE	0.0075	0.044	3.707	NS	2.447	NS
CDE	-0.0238	-0.140	3.707	NS	2.447	NS
ACDE	-0.3250	-1.912	3.707	NS	2.447	NS
BCDE	-0.0338	-0.199	3.707	NS	2.447	NS
ABCDE	-0.1575	-0.926	3.707	NS	2.447	NS

S = Significant

NS = Non-significant

then at that level of significance the null hypothesis is discredited and the effect is said to be statistically significant.

According to this set of t-tests the following judgements may be made about the cobalt effects.

The main effects B, C and D are highly significant at the $100(1-\alpha) = 99\%$ level of probability. At this probability level none of the two-factor interactions are significant, although BD is very nearly so ($|t_c| = 3.699$ compared with $t_{\alpha/2,\nu=6} = 3.707$). At the lower (but still stringent) 95% probability level BD is comfortably significant.

The next largest plausible effect, the 2-f.i.CD (which is smaller in value than the implausible 4-f.i.ACDE) cannot be judged significant at either level of probability.

Very importantly, two main-effects, A and E, of the 31 effects ranked 14th and 28th largest respectively, are firmly judged non-significant. Inspection of the effects confirms A and E non-significant.

Estimate of S.E.(Effect) from Higher-Order Interactions

No direct estimate of S.E.(effect) is available in an unreplicated design, where no treatment combination is run more than once.

In this situation, in order to obtain an estimate of S.E.(effect) for use in the t-test, it is usual, in

the absence of contrary indications, to assume[45,46] that the higher-order interactions are negligible or do not exist, and their effects are therefore measures of experimental error.

S.E.(effect) in the t-tests given in Table 7.4 was obtained using all five four-factor interactions (4-f.i)'s and the single five-factor interaction (5-f.i.), i.e. the interactions ABCD, ABCE, ABDE, ACDE, BCDE and ABCDE. A value of S.E.(4,5-f.i.) = 0.170 g/L with ν = 6 degrees of freedom (d.o.f.) was obtained. The calculation of S.E.(effect) is shown in Appendix 2.c.

If the higher-order interactions assumption is true in a given case then the selected interaction effects measure only error. In that case each selected effect should be a sample error of a single population of errors. The hypothesis that the selected $(\text{effect})^2$ are measures of a single POPULATION VARIANCE may be tested using Bartlett's criterion.[47]

This test was applied to the 4- and 5-f.i.'s assumed negligible. The calculation may be found in Appendix 2.d.

It was found that there was no evidence of heterogeneity of variance, and hence no evidence to discredit the higher order interactions assumption.

There is nothing in the analysis of the cobalt effects so far to suggest that any of the three-factor interactions are real effects. The largest three-factor

interaction, BDE, has a component main-effect E which is almost certainly non-significant, so that BDE is very likely to be non-significant. Moreover, BCD is smaller than the improbable 4-f.i. ACDE.

Therefore, providing the higher-order assumption holds, the three-factor interactions may be added to the 4-f.i.'s and the 5-f.i. to give an improved estimate of S.E.(effect), S.E.(3,4,5-f.i.). By doing this S.E.(effect) now has $\nu = 16$ degrees of freedom.

S.E.(3,4,5-f.i.) was calculated in the same manner as for S.E.(4,5-f.i.), and a value of 0.123 g/L with $\nu = 16$ d.o.f. was obtained. The contributing interaction effects were tested for homogeneity of variance using the approximation of Bartlett's criterion described by Davis,[48] as no tabulated values for the criterion were available for $\nu = 16$. It was found that there was no evidence of heterogeneity of variance.

An estimate of the standard error of an observation may be obtained from the estimate of the standard error of an effect. This is due to the fact that each effect is obtained from the difference of two averages of the observations. The relationship is given by[49]

$$(\text{S.E.(effect)})^2 = \frac{4}{2^n.r} (\text{S.E.(observation)})^2 \qquad (7.5)$$

where r (in a replicated 2^n) is the number of treatments. For an unreplicated design, r=1. On substituting

S.E.(3,4,5-f.i.) = 0.123 in equation 7.5, an estimated value of S.E.(observation) = 0.348 g/L is obtained for the cobalt response. These are the values of S.E.(effect) and S.E.(observation) used in Table 7.1.

The t-tests for the cobalt effects using S.E.(3,4,5-f.i.) are shown in Table 7.5. The effects B,C,D and BD are judged significant at the 99% level of significance. In the previous tests, BD was significant at the 95% but not at the 99% level of significance.

At the 95% level of significance ACDE and also CD were also judged significant.

ACDE, the larger in magnitude of the two effects, was assumed to be a measure of error and was one of the effects used in estimating S.E.(effect) for that test. It is implausible as a real effect, as two of its component effects are firmly non-real and its significance at 95% could well be disregarded, which would be convenient, since the estimate of SE used in the test would remain undisturbed.

However if ACDE is discounted as a real effect, and attributed to error, it would be logical to exclude CD in the same way, because of its smaller size. On the other hand, if CD is regarded as real, it would be difficult to exclude ACDE from being judged real.

One reason for so excluding ACDE would be if (say) one or two of the treatments had produced quite spurious response values, which, while not large enough to distort

TABLE 7.5. Two-tailed t-tests for the cobalt effects using S.E.(3,4,5-f.i.)

Effect Identity	Effect Value	$t_c = \frac{\text{Effect}}{\text{S.E.(Effect)}}$	$t_{0.005}$ $\nu = 16$	Significance at 99% Probability Level	$t_{0.025}$ $\nu = 16$	Significance at 95% Probability Level
Average	10.347	-	-	-	-	-
A	-0.1025	-0.833	2.921	NS	2.120	NS
B	4.6888	38.120	2.921	S	2.120	S
AB	-0.0800	-0.650	2.921	NS	2.120	NS
C	-1.4938	-12.144	2.921	S	2.120	S
AC	-0.0775	-0.630	2.921	NS	2.120	NS
BC	0.0313	0.254	2.921	NS	2.120	NS
ABC	-0.1200	-0.976	2.921	NS	2.120	NS
D	0.8313	6.758	2.921	S	2.120	S
AD	-0.0600	-0.487	2.921	NS	2.120	NS
BD	-0.6288	-5.112	2.921	S	2.120	S
ABD	-0.0025	-0.020	2.921	NS	2.120	NS
CD	0.3188	2.592	2.921	NS	2.120	S
ACD	-0.0700	-0.569	2.921	NS	2.120	NS
BCD	-0.0813	-0.661	2.921	NS	2.120	NS
ABCD	0.1525	1.240	2.921	NS	2.120	NS
E	-0.0188	-0.153	2.921	NS	2.120	NS
AE	0.1275	1.037	2.921	NS	2.120	NS
BE	-0.0638	-0.519	2.921	NS	2.120	NS
ABE	0.0550	0.447	2.921	NS	2.120	NS
CE	0.0788	0.641	2.921	NS	2.120	NS
ACE	0.0725	0.589	2.921	NS	2.120	NS
BCE	-0.0163	-0.132	2.921	NS	2.120	NS
ABCE	-0.1350	-1.098	2.921	NS	2.120	NS
DE	-0.1463	-1.189	2.921	NS	2.120	NS
ADE	-0.0450	-0.365	2.921	NS	2.120	NS
BDE	-0.1763	-1.433	2.921	NS	2.120	NS
ABDE	0.0075	0.061	2.921	NS	2.120	NS
CDE	-0.0238	-1.193	2.921	NS	2.120	NS
ACDE	-0.3250	-2.642	2.921	NS	2.120	S
BCDE	-0.0338	-0.274	2.921	NS	2.120	NS
ABCDE	-0.1575	-1.280	2.921	NS	2.120	NS

S = Significant
NS = Non-significant.

the large effects very much, had some influence on the smaller effects.

A problem of interpretation like this would probably arise less frequently with a design in which there was replication, both because the independent estimate of error that is obtained, would allow a more secure statistical judgement than with the interactions assumption S.E.(effect) estimate, and because the occurrences giving rise to the distortions would affect the estimate less strongly.

Although the use of replication diminishes such interpretative problems, it is extremely costly in experimental effort.

In any case, the problem in interpreting ACDE and CD is neither critical, nor perhaps insuperable, as will be seen in the regression analysis of the factorial data.

The Half-Normal Probability Plot

Another means by which the effects may be examined statistically is the use of the half-normal probability (H.N.P.) plot, developed by Daniel.

The advantage of the H.N.P. plot is that no assumption that higher-order interactions are insignificant is required for its use. Thus the method is independent of the t-test. It is usually used in conjunction with other statistical tools, however, since its interpretation requires a subjective assessment of straightness.

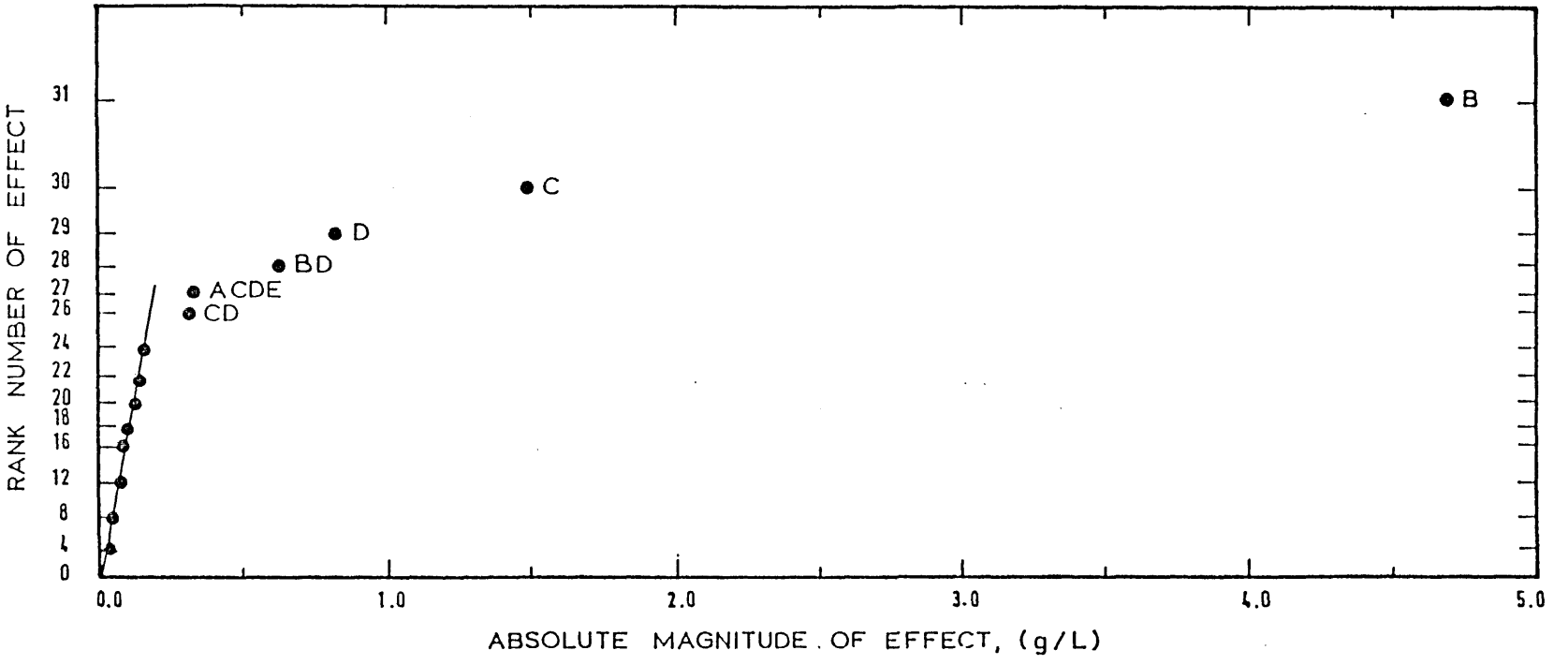


FIGURE 7.1. The half-normal probability plot for the cobalt effects.

The plot is based on the idea that if none of the (2^n-1) effects are real, they are samples of an effects error population, which will be approximately normally distributed.

The vertical scale of the plot is special, and depends on the number of factors in the design. An appropriate scale may be copied from Daniel[50] onto a graph paper with ordinary horizontal axis. On the vertical scale is plotted the rank number of the effect when ordered by increasing absolute magnitude. The absolute magnitude of the effect is plotted on the horizontal axis. With 2^5 plots, only each second one of the smaller effects is plotted. Non-real effects plot as a straight line through the origin, while real effects fall off the line.

The plot of the cobalt effects is given in Figure 7.1. The effects B, C, D and BD are again found significant. The H.N.P. plot suggest that ACDE and CD are significant, in support of one of the t-tests. If ACDE is rejected as a real effect on the grounds previously given, the H.N.P. plot gives B, C, D, BD and CD as the real effects.

7.2 Regression Analysis

A close link exists between the factorial analysis of the factorial design, and the analysis of the data by multiple linear least-squares regression analysis. By the further examination of the factorial data through regression,

it should be possible to reinforce and possibly improve the assessments of the effects made so far.

The Method of Least-Squares

Briefly, the method of least-squares is based upon the principle of least-squares, which states that the errors given by $(y_i-\hat{y}_i)$, where $\hat{y}_i$ is the predicted value of the response, are to be minimized in the direction perpendicular or normal to the factorial variables. This gives rise to the well-known normal equations, which are solved to yield the least-squares estimates.

In regression analysis the term CONTROLLED VARIABLE is often used to describe the variables in the correlation whose values could be set or controlled. The factorial variables may be termed controlled variables.

In applying the method of least-squares it is assumed:

1) that the levels of the controlled variables are known accurately.
2) that the experimental error is distributed homogeneously and independently throughout the data set.

Orthogonality and Least-Squares Regression

Two-level full factorial designs belong to a class of experimental design called ORTHOGONAL DESIGNS, in which

the data set generated has the properties[51] of ORTHOGONALITY. Thus with 2^n designs it can be shown that:

1) the factorial effects are least-squares estimates

and 2) that each effect is independently estimated.

By independent estimation it is meant that the value which is placed on one effect does not depend on the value placed on another effect.

Incidentally, if at some later stage it is wished to extend the range of conditions covered by the factorial design, it is desirable to plan the experiments so as to preserve the orthogonality of the data set. One way of doing this with a factorial design is to COMPOSITE[52] the design.

The Regression Equation

In the regression analysis of the response, an empirical, POLYNOMIAL expression is fitted to the data using the method of least-squares. The general form of equation is:

$$\hat{y} = \beta_o x_o + \beta_1 x_1 + \beta_2 x_2 + \ldots . \beta_i x_i \qquad (7.6)$$

where x_o, x_1, ... x_i are the controlled variables in their 'natural' or uncoded form, and β_o, β_1, ..., β_i are the REGRESSION PARAMETERS, which for a given regression are constants.

Equation 7.6 is an example of a FIRST-ORDER polynomial, since the x_i's are not raised to any powers. In the regression of 2^n factorial data, only first order expressions should be fitted, since the design includes only two-levels of each variable.

It is often useful to make x_o a 'dummy' variable, by setting $x_o = 1$ throughout. This gives:

$$\hat{y} = \beta_o + \beta_1 x_1 + \beta_2 x_2 \ldots., + \beta_i x_i \qquad (7.7)$$

and the equation has a constant term, the regression parameter β_o, where

$$\beta_o = \hat{y}_{x_1, x_2 \ldots x_i} \qquad (7.8)$$

at $$x_1 = x_2 = x_3 \ldots = x_i = 0 \qquad (7.9)$$

In working with factorial design data, it is often convenient to translate the controlled variables, i.e. the x_i's, into a coded form, X_i. For a two-level factorial, the coding takes the form

$$X_i = (x_i - \bar{x}_i)/(\bar{x}_i - x_{i,low}) \qquad (7.10)$$

where $\bar{x}_i$ is the mean level of the variable x_i, and $x_{i,low}$ is the low factorial level of that variable.

By using the coded variable forms, the factorial levels of the variable take on the convenient values

$$X_i(\text{high}) = +1 \tag{7.11}$$

$$X_i(\text{low}) = -1 \tag{7.12}$$

and the regression equation now becomes:

$$\hat{y} = \beta'_o + \beta'_1 X_1 + \beta'_2 X_2 \ldots \beta'_i X_i \tag{7.13}$$

In this form, the constant term

$$\beta'_o = \hat{y}_{X_1, X_2 \ldots X_i} \tag{7.14}$$

at $$X_1 = X_2 \ldots X_i = 0 \tag{7.15}$$

$\hat{y}_{X_1=X_2 \ldots X_i=0}$ is the predicted value of the response for the factorial levels at their mid points. It is a property of the orthogonal factorial data set that

$$\hat{y}_{X_1=X_2 \ldots =X_i=0} = \bar{y} \tag{7.16}$$

where $\bar{y}$ is the GRAND MEAN, or overall mean value of the response over all the treatments, as defined in equation 7.1.

In its factorial form, equation 7.13 includes terms for the variables, for the interactions between two variables, between three variables and so on. With coded variables and a dummy variable X_o, the general factorial form is:

$$\hat{y} = \beta'_o + \beta'_1 X_1 + \beta'_2 X_2 + \beta'_3 X_3 \ldots.$$
$$+ \beta'_{12} X_1 X_2 + \beta'_{13} X_1 X_3 \ldots.$$
$$+ \beta'_{123} X_1 X_2 X_3 \ldots \text{ etc} \qquad (7.17)$$

where the two-number suffix on β'_{12}, the three-number suffix on β'_{123} etc. indicate respectively the regression parameters for the two variable interaction between the variables X_1 and X_2, and the three variable interaction between X_1, X_2 and X_3, and so on. For a 2^n design, if all the variables and their interactions were considered significant, then with all the terms explicitly written, equation 7.17 would have (2^n-1) terms in addition to β'_o.

A purpose-designed computer routine is usually used to fit regression equations, though this may be done by hand for factorial data using YATES' REVERSE ALGORITHM[53] if so desired. However, the computer routine can allow rapid and scrutiny of many regression models. Daniel,[54] gives the advice about such routines:

> Do not consider any programme that does not compute and print residuals automatically, preferably rounded to two digits.

Such a computer routine is the regression facility of MINITAB, a general purpose statistical computing package developed by Ryan, Joiner and Ryan,[55,56], and available on the Imperial College computer network. This was the package used.

The data from the factorial design was submitted to MINITAB with the variable levels in the coded form shown in equation 7.10. The regression equations fitted were all coded-variable forms and all used a dummy X_o variable to give a constant term β'_o.

In addition to the regression parameters the MINITAB regression output also gives the following statistics and information associated with the regression: the estimated regression coefficients and their standard errors (or standard deviations) as well as the t-values of each coefficient, the standard error of the observed value, the multiple correlation coefficient, the residual and total sum of squares as well as the sum of squares explained by each variable considered and the number of degrees of freedom associated with them. Finally, the diagnostic plots could be given.

Equivalence of the Factorial Effect and Regression Parameter

In fact, in the regression of 2^n factorial data, when a regression expression in the form of equation 7.17 is acceptable there is no need to perform the regression calculation. This is because the factorial effects, which

are least-squares estimates, are directly related to the β' regression parameters of that form of expression. The relationship between each effect and its corresponding β' parameter is given by

$$\text{effect} = 2\beta' \tag{7.18}$$

the factor of two occurring because the effect measures changes in the response between the low and high factorial levels, i.e. two coded units, whereas β' measures changes in response per unit variable.

Further, because each parameter is independently estimated, if a regression equation of the same form as equation 7.17 but with fewer terms is to be fitted, the parameters of the terms included retain the same values as they have in the full equation.

This means that MINITAB is not actually required for the computing of the regression parameters in a given regression. It is used however to examine the apparent adequacy of fit of each equation, particularly in respect of the goodness-of-fit, and the equation's residuals.

Through the examination of fit, the main objectives of the regression analysis may be achieved.

The first objective is to obtain support, if possible, for the factorial analysis of the response. If a term, whether for a variable or for a variable interaction,

has a real influence on the response, an improvement in fit should be evident when it is included in the regression equation.

The second objective, is to obtain a regression model which gives a satisfactory description of the data.

Goodness of Fit

A measure of the goodness-of-fit of a regression equation is given by the MULTIPLE CORRELATION COEFFICIENT, R^2, which is defined by:

$$R^2 = \frac{\Sigma(\hat{y}_i-\bar{y})^2}{\Sigma(y_i-\bar{y})^2} \qquad (7.19)$$

The numerator of the quotient is the variation due to the model, and the denominator is the total variation in the response. Thus R^2 expresses the proportion in the total variation that is explained by the model. R^2 is often expressed as a percentage. A value of $R^2 = 1$ or $R^2 = 100\%$ indicates that a regression equation gives a perfect fit.

Although the multiple correlation coefficient gives a quantitative measure of fit, it does not say anything about how consistent the fit is in different regions of the response range. This may be found from a graph of the predicted response $\hat{y}_i$ versus the measured response, y_i. Here, a perfect fit would be indicated if the plotted points fall on a straight line of gradient = 1.

Distribution of the Residuals

The regression equation seeks to describe, if not fundamentally then at least quantitatively, the functional relationship between the variables and the response. In the 'ideal' model, i.e. a model which has no systematic lack-of-fit, the true value of the response η_i, at a given combination of variable levels, will be closely approximated by the predicted response $\hat{y}_i$ from the model, differing only by a small, but unknown, random amount ε_i such that

$$\eta_i = \hat{y}_i + \varepsilon_i \tag{7.20}$$

In general

$$\varepsilon = \eta - \hat{y} \tag{7.21}$$

The least-squares assumption of homogeneity of variance is that the magnitude and sign of ε are independent of the size of $\hat{y}$. It may further be assumed that ε is distributed in an approximately normal distribution.

If an entertained regression equation is an adequate fit of the data, then the equation's residuals, given by

$$d_i = y_i - \hat{y}_i \tag{7.22}$$

should be due principally to experimental error, and not to any systematic lack-of-fit in the model. Then, the residuals should be samples of the error population of ε and should be approximately normally distributed.

The residuals may therefore be used diagnostically to suggest systematic lack-of-fit in a model. If normally distributed, the 'normal' plot of (standardized) residuals should yield an approximately straight line.

The apparent homogeneity of variance may be examined by the plot of standardized residuals versus predicted $\hat{y}$ values. Here, the residuals should be randomly distributed with size of $\hat{y}$.

Regression of the Cobalt Response

The combinations of variables included in the regression equations are shown in Table 7.6.

Initially, the response was regressed on the three factorial variables whose main-effects had already been judged significant in the factorial analysis, the variables B, C and D. This is the model fitted in Computer Run 1.

A part of the MINITAB regression output for this regression is shown in Table 7.7. The residuals and predicted response values are shown in Table 7.8. The normal plot of residuals, and the plot of standardized residuals (standardized residual = residual ÷ standard error of the residuals) versus $\hat{y}$, are shown in Figures 7.2.a and 7.2.b respectively.

The model fitted in Computer Run 1 appears to give a fairly satisfactory fit. The value of R^2 = 96.8%

TABLE 7.6. Variables Included in the Cobalt Regression Runs.

Computer Runs	Terms Included For		
	Variables	Two-factor Interactions	Three-factor Interactions
No. 1	B, C, D		
2	A, B, C, D		
3	B, C, D, E		
4	B, C, D	BD	
5	B, C, D	BD, CD	
6	B, C, D	BC, BD, CD	
7	B, C, D	BD, CD	BCD

for the multiple correlation coefficient is relatively high, there is no marked non-normality in the residuals, and they are reasonably evenly distributed in size over the response range.

Next, the other two factorial variables, variables A and E were considered, since, even though they had been judged non-significant in the factorial analysis, it was wished to determine how each of them would influence the fit of the regression model.

Variable A was introduced into the model in Computer Run 2. The information from this regression is shown in

THE REGRESSION EQUATION IS
Y = 10.3 + 2.34 X1 - .747 X2
+ .416 X3

	COLUMN	COEFFICIENT	ST. DEV. OF COEF.	T-RATIO = COEF/S.D.
	--	10.3469	0.0852	121.38
X1	INIT.CO	2.34437	0.08525	27.50
X2	INIT.NI	-0.74687	0.08525	-8.76
X3	EQU.TEMP	0.41563	0.08525	4.88

THE ST. DEV. OF Y ABOUT REGRESSION LINE IS
S = 0.4822
WITH (32- 4) = 28 DEGREES OF FREEDOM

R-SQUARED = 96.8 PERCENT
R-SQUARED = 96.5 PERCENT, ADJUSTED FOR D.F.

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF
REGRESSION	3	199.2531	66.4177
RESIDUAL	28	6.5111	0.2325
TOTAL	31	205.7643	

FURTHER ANALYSIS OF VARIANCE
SS EXPLAINED BY EACH VARIABLE WHEN ENTERED IN THE ORDER GIVEN

DUE TO	DF	SS
REGRESSION	3	199.2531
INIT.CO	1	175.8750
INIT.NI	1	17.8503
EQU.TEMP	1	5.5278

TABLE 7.7. Statistical output from Computer Run 1. Regression model including variables B, C and D.

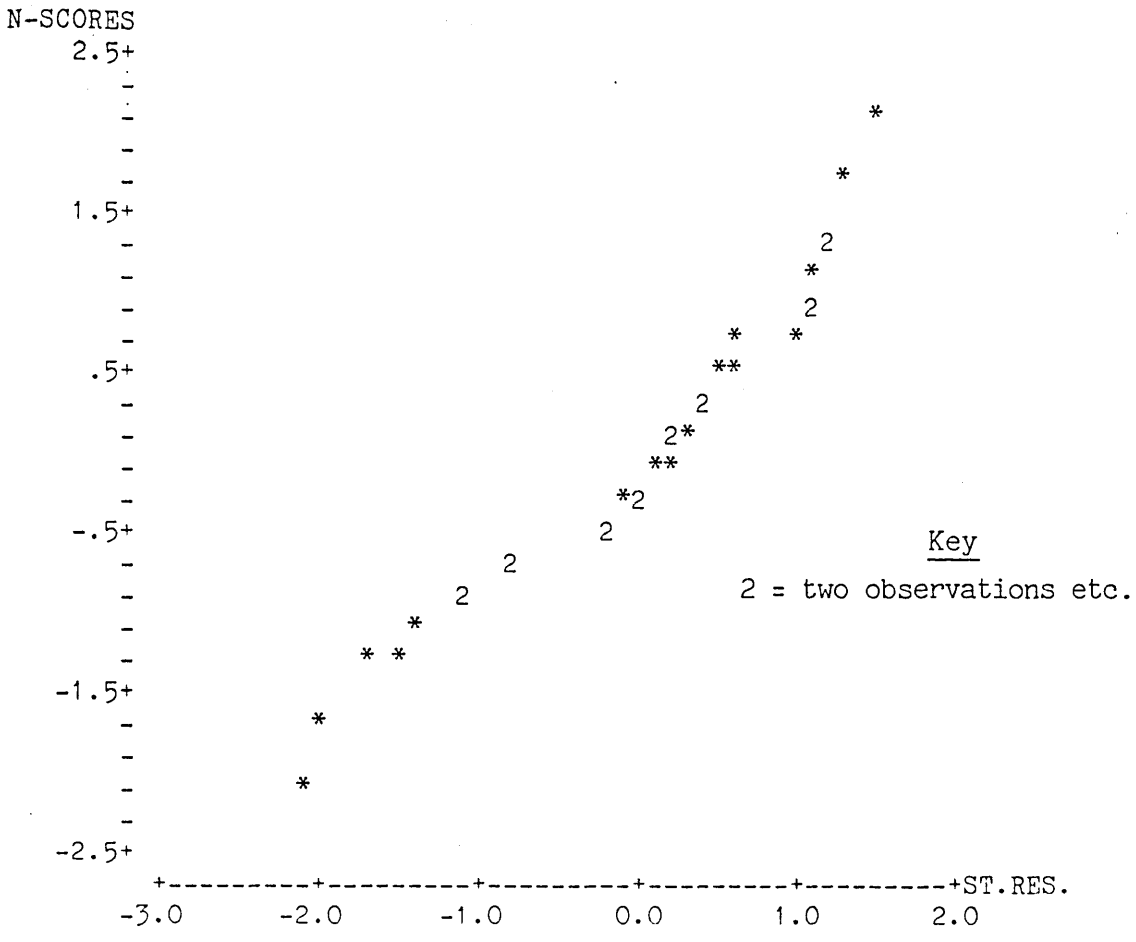


Figure (A)

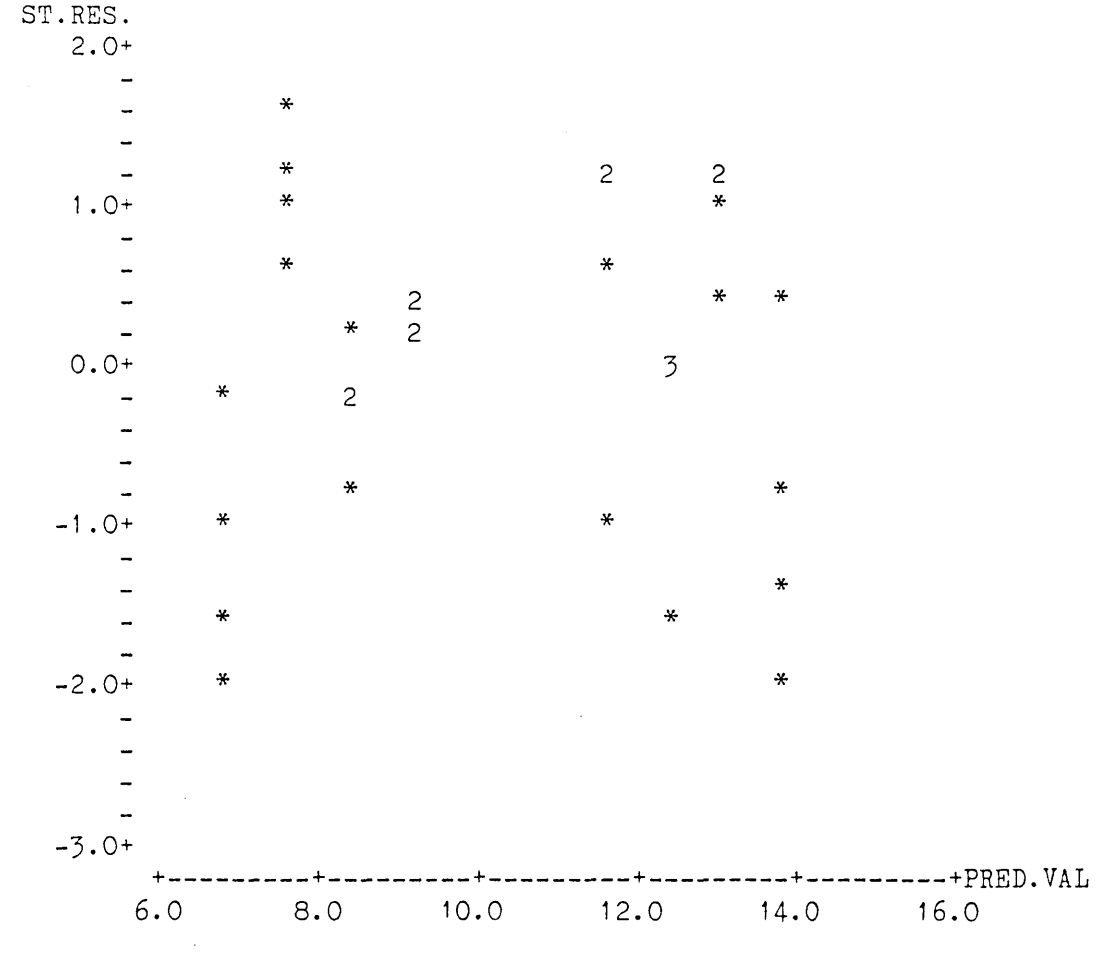


Figure (B)

FIGURES 7.2.a and 7.2.b. Diagnostic plots for model fitted in Computer Run 1.

Init.pH	Init.Co	Init.Ni	Equ.T	Na2SO4	y	$\hat{y}$	S.D.$\hat{y}$.	Resid,d	S.D.d.	Std.Res
-1	-1	-1	-1	-1	8.260	8.334	0.171	-.074	.458	-.163
+1	-1	-1	-1	-1	8.280	8.334	0.171	-.054	.458	-.119
-1	+1	-1	-1	-1	13.200	13.022	0.171	.178	.458	.393
+1	+1	-1	-1	-1	13.560	13.022	0.171	.538	.458	1.192
-1	-1	+1	-1	-1	6.360	6.840	0.171	-.480	.458	-1.064
+1	-1	+1	-1	-1	6.160	6.840	0.171	-.680	.458	-1.507
-1	+1	+1	-1	-1	12.080	11.529	0.171	.551	.458	1.222
+1	+1	+1	-1	-1	11.040	11.529	0.171	-.489	.458	-1.084
-1	-1	-1	+1	-1	9.250	9.165	0.171	.085	.458	.188
+1	-1	-1	+1	-1	9.370	9.165	0.171	.205	.458	.454
-1	+1	-1	+1	-1	14.020	13.854	0.171	.166	.458	.369
+1	+1	-1	+1	-1	13.200	13.854	0.171	-.654	.458	-1.449
-1	-1	+1	+1	-1	8.240	7.671	0.171	.569	.458	1.261
+1	-1	+1	+1	-1	7.920	7.671	0.171	.249	.458	.551
-1	+1	+1	+1	-1	12.360	12.360	0.171	.000	.458	.000
+1	+1	+1	+1	-1	12.400	12.360	0.171	.040	.458	.089
-1	-1	-1	-1	+1	8.440	8.334	0.171	.106	.458	.236
+1	-1	-1	-1	+1	7.960	8.334	0.171	-.374	.458	-.829
-1	+1	-1	-1	+1	13.520	13.022	0.171	.498	.458	1.103
+1	+1	-1	-1	+1	13.480	13.022	0.171	.458	.458	1.014
-1	-1	+1	-1	+1	5.960	6.840	0.171	-.880	.458	-1.951
+1	-1	+1	-1	+1	6.760	6.840	0.171	-.080	.458	-.177
-1	+1	+1	-1	+1	11.800	11.529	0.171	.271	.458	.601
+1	+1	+1	-1	+1	12.040	11.529	0.171	.511	.458	1.133
-1	-1	-1	+1	+1	9.240	9.165	0.171	.075	.458	.166
+1	-1	-1	+1	+1	9.320	9.165	0.171	.155	.458	.344
-1	+1	-1	+1	+1	12.920	13.854	0.171	-.934	.458	-2.070
+1	+1	-1	+1	+1	13.480	13.854	0.171	-.374	.458	-.829
-1	-1	+1	+1	+1	8.360	7.671	0.171	.689	.458	1.527
+1	-1	+1	+1	+1	8.160	7.671	0.171	.489	.458	1.084
-1	+1	+1	+1	+1	12.360	12.360	0.171	.000	.458	.000
+1	+1	+1	+1	+1	11.600	12.360	0.171	-.760	.458	-1.685

TABLE 7.8. Residuals and predicted response values for model fitted in Computer Run 1.

Tables 7.9 and 7.10 and Figures 7.3.a and 7.3.b. The inclusion of variable A in the model apparently does not improve the model fit. The value of the correlation coefficient, R^2 = 96.9%, is virtually unchanged from the first regression.

The regression parameter for variable A is β' = -0.0152. This is not statistically different from zero, as can be determined by inspection, since the presence of β' would change the predicted value of the cobalt response, $\hat{y}$, by 2 x 0.0152 g/L between the low and high levels of variable A.

Alternatively, the regression parameter β' can be subjected to a t-test, with the null hypothesis, H_o that β' is not statistically significant from zero, tested against the alternative hypothesis, H_1, that $\beta \neq 0$.

There is no indication of an improvement in fit from the diagnostic plots, although at the same time they contain nothing to firmly discredit the model.

Overall then, the inclusion of variable A did nct improve the model fit, and it was dropped from the model.

Variable E was introduced into the model in Computer Run 3. It can be seen from Tables 7.11 and 7.12 that no improvement in fit is observed either in R^2, with a value of 96.8%, or in the diagnostic plots. Therefore variable E was dropped from the model.

In the earlier factorial analysis, significant two-factor interactions (2-f.i's) had been found. In the next

THE REGRESSION EQUATION IS
Y = 10.3 - .0512 X1 + 2.34 X2
- .747 X3 + .416 X4

	COLUMN	COEFFICIENT	ST. DEV. OF COEF.	T-RATIO = COEF/S.D.
	--	10.3469	0.0862	119.97
X1	INIT.PH	-0.05125	0.08625	-0.59
X2	INIT.CO	2.34437	0.08625	27.18
X3	INIT.NI	-0.74687	0.08625	-8.66
X4	EQU.TEMP	0.41563	0.08625	4.82

THE ST. DEV. OF Y ABOUT REGRESSION LINE IS
S = 0.4879
WITH (32- 5) = 27 DEGREES OF FREEDOM

R-SQUARED = 96.9 PERCENT
R-SQUARED = 96.4 PERCENT, ADJUSTED FOR D.F.

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF
REGRESSION	4	199.3372	49.8343
RESIDUAL	27	6.4271	0.2380
TOTAL	31	205.7643	

FURTHER ANALYSIS OF VARIANCE
SS EXPLAINED BY EACH VARIABLE WHEN ENTERED IN THE ORDER GIVEN

DUE TO	DF	SS
REGRESSION	4	199.3372
INIT.PH	1	0.0840
INIT.CO	1	175.8750
INIT.NI	1	17.8503
EQU.TEMP	1	5.5278

TABLE 7.9. Statistical output from Computer Run 2. Regression model including variables A, B, C and D.

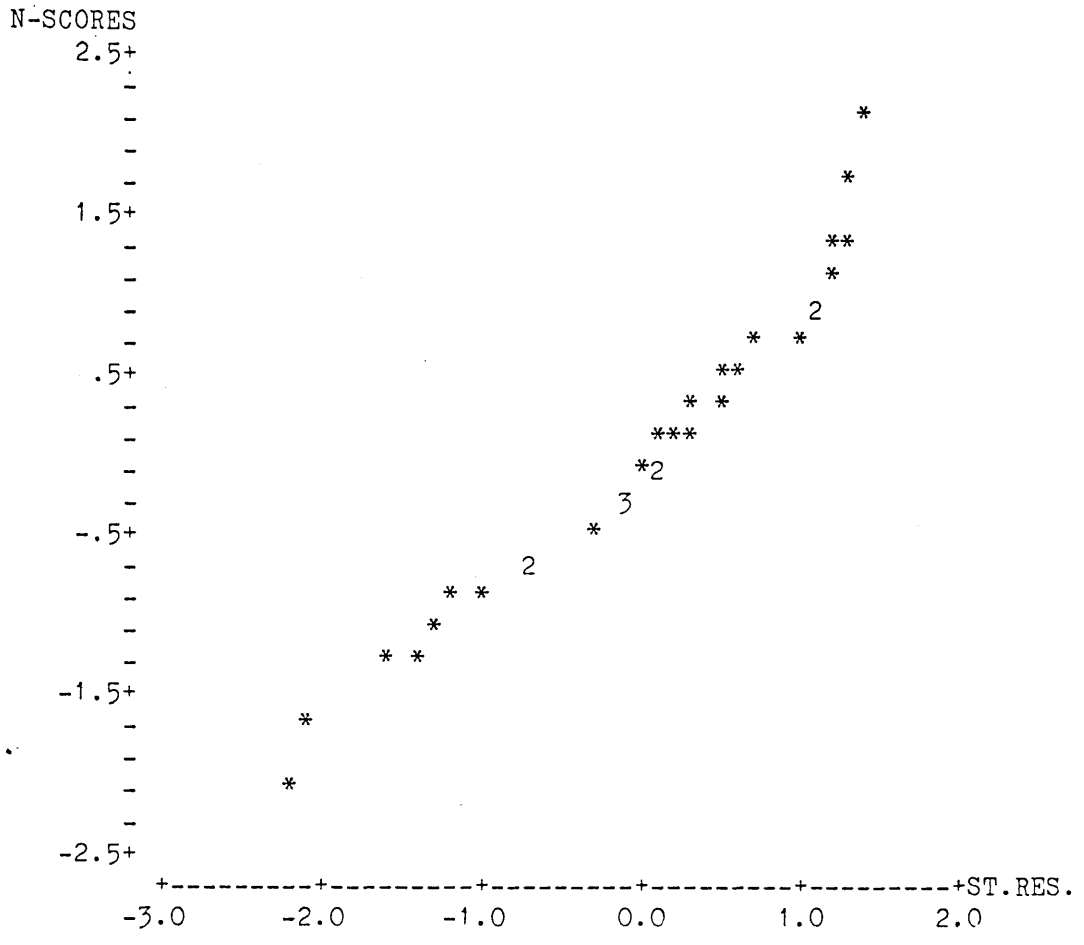


Figure (A)

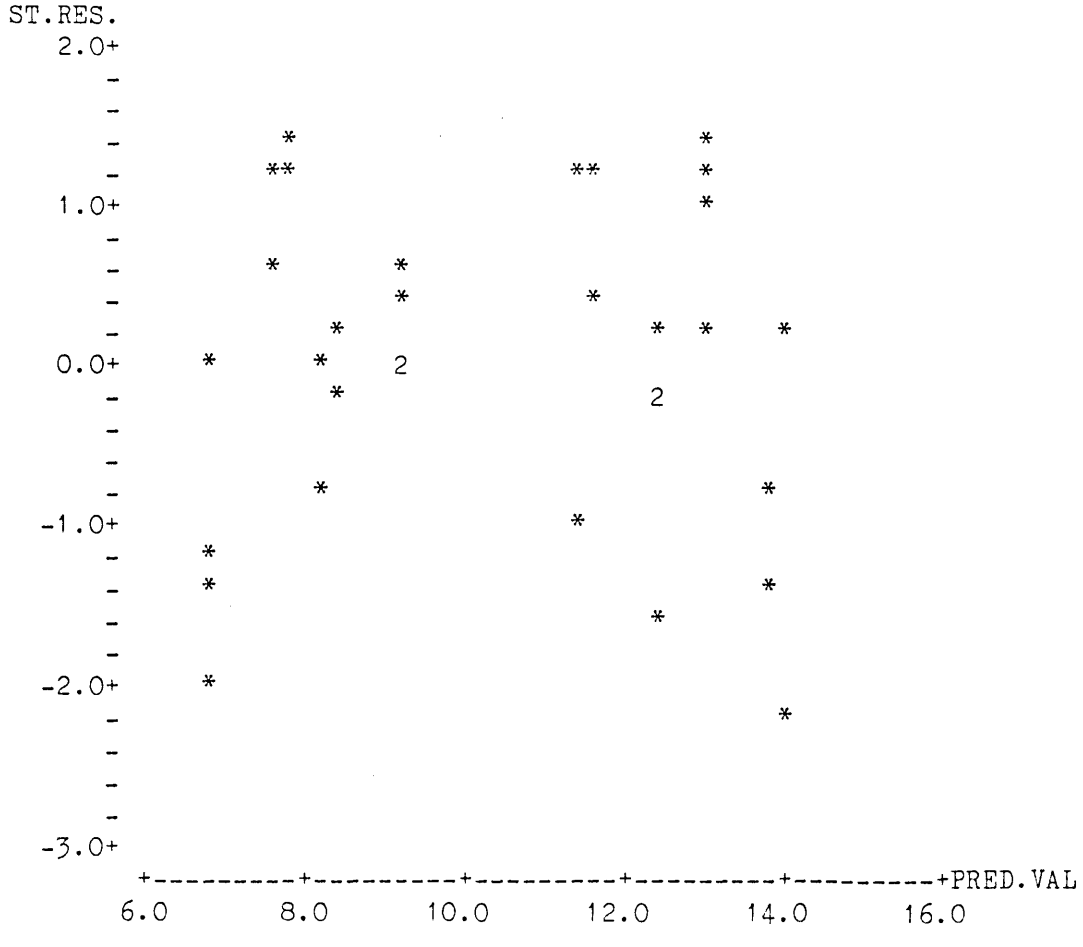


Figure (B)

FIGURES 7.3.a and 7.3.b. Diagnostic plots for model fitted in Computer Run 2.

Init.pH	Init.Co	Init.Ni	Equ.T	Na2SO4	y	$\hat{y}$	S.D.$\hat{y}$.	Resid,d	S.D.d.	Std.Res
-1	-1	-1	-1	-1	8.260	8.385	0.193	-.125	.455	-.279
+1	-1	-1	-1	-1	8.280	8.282	0.193	-.002	.455	-.006
-1	+1	-1	-1	-1	13.200	13.074	0.193	.126	.455	.282
+1	+1	-1	-1	-1	13.560	12.971	0.193	.589	.455	1.314
-1	-1	+1	-1	-1	6.360	6.891	0.193	-.531	.455	-1.185
+1	-1	+1	-1	-1	6.160	6.789	0.193	-.629	.455	-1.403
-1	+1	+1	-1	-1	12.080	11.580	0.193	.500	.455	1.116
+1	+1	+1	-1	-1	11.040	11.477	0.193	-.437	.455	-.976
-1	-1	-1	+1	-1	9.250	9.216	0.193	.034	.455	.075
+1	-1	-1	+1	-1	9.370	9.114	0.193	.256	.455	.572
-1	+1	-1	+1	-1	14.020	13.905	0.193	.115	.455	.257
+1	+1	-1	+1	-1	13.200	13.802	0.193	-.602	.455	-1.344
-1	-1	+1	+1	-1	8.240	7.722	0.193	.518	.455	1.155
+1	-1	+1	+1	-1	7.920	7.620	0.193	.300	.455	.669
-1	+1	+1	+1	-1	12.360	12.411	0.193	-.051	.455	-.114
+1	+1	+1	+1	-1	12.400	12.309	0.193	.091	.455	.204
-1	-1	-1	-1	+1	8.440	8.385	0.193	.055	.455	.123
+1	-1	-1	-1	+1	7.960	8.282	0.193	-.322	.455	-.720
-1	+1	-1	-1	+1	13.520	13.074	0.193	.446	.455	.996
+1	+1	-1	-1	+1	13.480	12.971	0.193	.509	.455	1.135
-1	-1	+1	-1	+1	5.960	6.891	0.193	-.931	.455	-2.078
+1	-1	+1	-1	+1	6.760	6.789	0.193	-.029	.455	-.064
-1	+1	+1	-1	+1	11.800	11.580	0.193	.220	.455	.491
+1	+1	+1	-1	+1	12.040	11.477	0.193	.563	.455	1.255
-1	-1	-1	+1	+1	9.240	9.216	0.193	.024	.455	.053
+1	-1	-1	+1	+1	9.320	9.114	0.193	.206	.455	.460
-1	+1	-1	+1	+1	12.920	13.905	0.193	-.985	.455	-2.198
+1	+1	-1	+1	+1	13.480	13.802	0.193	-.322	.455	-.720
-1	-1	+1	+1	+1	8.360	7.722	0.193	.638	.455	1.422
+1	-1	+1	+1	+1	8.160	7.620	0.193	.540	.455	1.205
-1	+1	+1	+1	+1	12.360	12.411	0.193	-.051	.455	-.114
+1	+1	+1	+1	+1	11.600	12.309	0.193	-.709	.455	-1.581

TABLE 7.10. Residuals and predicted response values for model fitted in Computer Run 2.

THE REGRESSION EQUATION IS
Y = 10.3 + 2.34 X1 - .747 X2
+ .416 X3 - .0094 X4

	COLUMN	COEFFICIENT	ST. DEV. OF COEF.	T-RATIO = COEF/S.D.
	--	10.3469	0.0868	119.22
X1	INIT.CO	2.34437	0.08679	27.01
X2	INIT.NI	-0.74687	0.08679	-8.61
X3	EQU.TEMP	0.41563	0.08679	4.79
X4	NA2SO4	-0.00937	0.08679	-0.11

THE ST. DEV. OF Y ABOUT REGRESSION LINE IS
S = 0.4910
WITH (32- 5) = 27 DEGREES OF FREEDOM

R-SQUARED = 96.8 PERCENT
R-SQUARED = 96.4 PERCENT, ADJUSTED FOR D.F.

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF
REGRESSION	4	199.2559	49.8140
RESIDUAL	27	6.5083	0.2410
TOTAL	31	205.7643	

FURTHER ANALYSIS OF VARIANCE
SS EXPLAINED BY EACH VARIABLE WHEN ENTERED IN THE ORDER GIVEN

DUE TO	DF	SS
REGRESSION	4	199.2559
INIT.CO	1	175.8750
INIT.NI	1	17.8503
EQU.TEMP	1	5.5278
NA2SO4	1	0.0028

TABLE 7.11. Statistical output from Computer Run 3. Model including variables B, C, D and E.

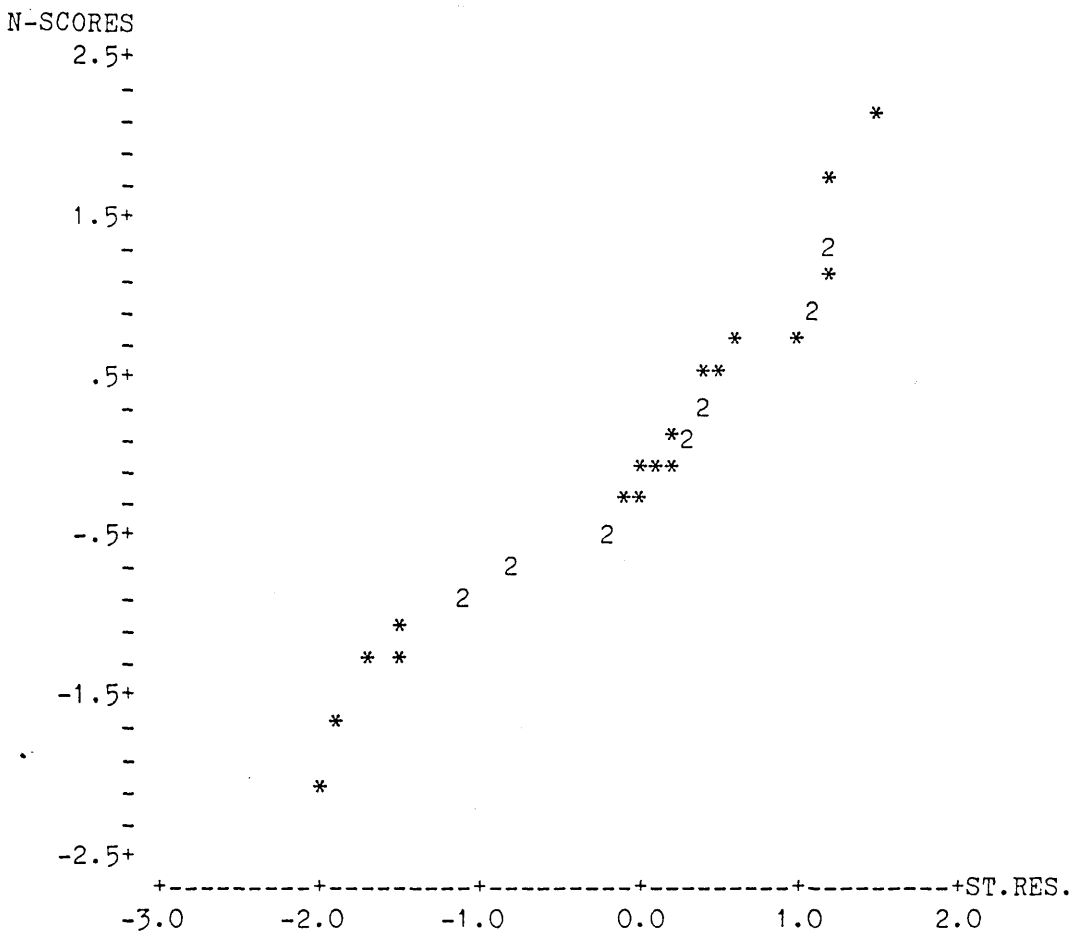


Figure (A)

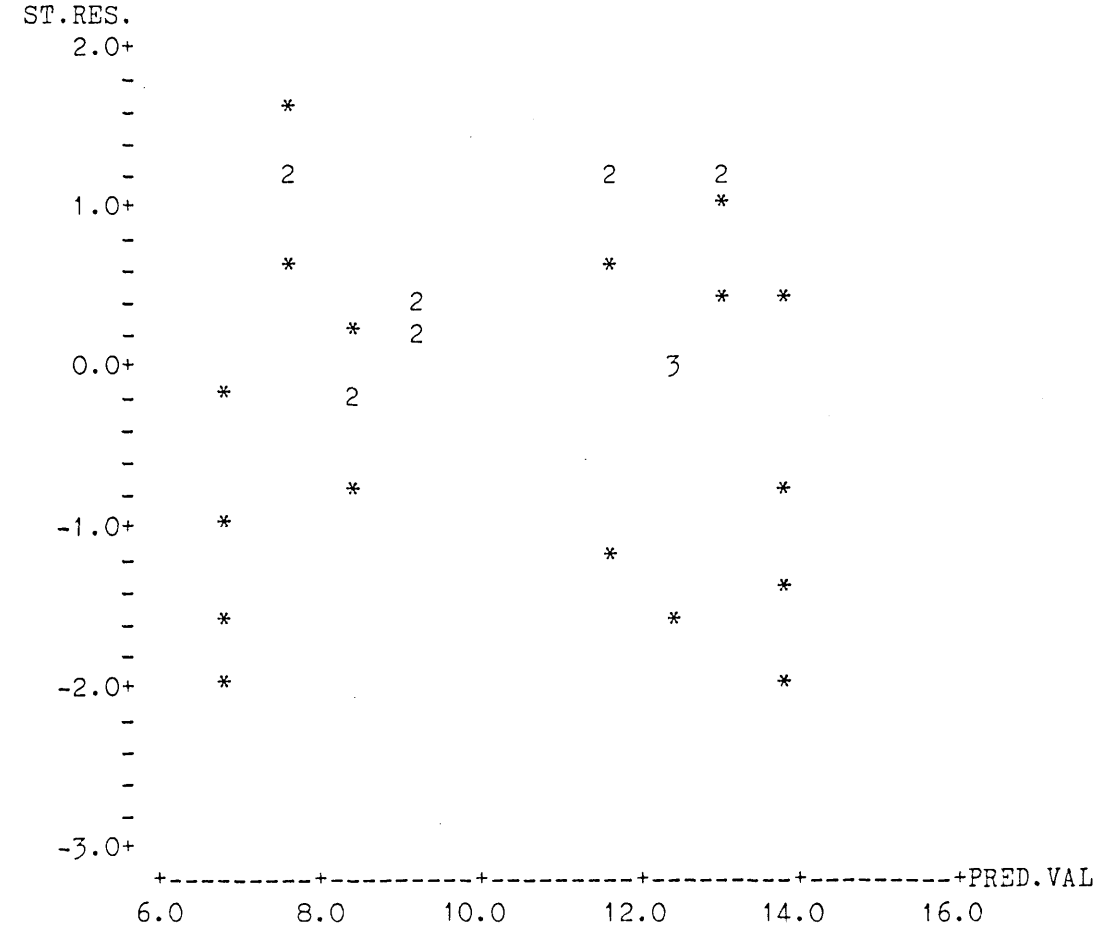


Figure (B)

FIGURES 7.4.a and 7.4.b. Diagnostic plots for model fitted in Computer Run 3.

Init.pH	Init.Co	Init.Ni	Equ.T	Na2SO4	y	$\hat{y}$	S.D.$\hat{y}$.	Resid,d	S.D.d.	Std.Res
-1	-1	-1	-1	-1	8.260	8.343	0.194	-.083	.458	-.184
+1	-1	-1	-1	-1	8.280	8.343	0.194	-.063	.458	-.140
-1	+1	-1	-1	-1	13.200	13.032	0.194	.168	.458	.373
+1	+1	-1	-1	-1	13.560	13.032	0.194	.528	.458	1.171
-1	-1	+1	-1	-1	6.360	6.849	0.194	-.489	.458	-1.085
+1	-1	+1	-1	-1	6.160	6.849	0.194	-.689	.458	-1.529
-1	+1	+1	-1	-1	12.080	11.538	0.194	.542	.458	1.202
+1	+1	+1	-1	-1	11.040	11.538	0.194	-.498	.458	-1.105
-1	-1	-1	+1	-1	9.250	9.174	0.194	.076	.458	.168
+1	-1	-1	+1	-1	9.370	9.174	0.194	.196	.458	.434
-1	+1	-1	+1	-1	14.020	13.863	0.194	.157	.458	.348
+1	+1	-1	+1	-1	13.200	13.863	0.194	-.663	.458	-1.470
-1	-1	+1	+1	-1	8.240	7.681	0.194	.559	.458	1.240
+1	-1	+1	+1	-1	7.920	7.681	0.194	.239	.458	.531
-1	+1	+1	+1	-1	12.360	12.369	0.194	-.009	.458	-.021
+1	+1	+1	+1	-1	12.400	12.369	0.194	.031	.458	.068
-1	-1	-1	-1	+1	8.440	8.324	0.194	.116	.458	.256
+1	-1	-1	-1	+1	7.960	8.324	0.194	-.364	.458	-.808
-1	+1	-1	-1	+1	13.520	13.013	0.194	.507	.458	1.124
+1	+1	-1	-1	+1	13.480	13.013	0.194	.467	.458	1.035
-1	-1	+1	-1	+1	5.960	6.831	0.194	-.871	.458	-1.931
+1	-1	+1	-1	+1	6.760	6.831	0.194	-.071	.458	-.157
-1	+1	+1	-1	+1	11.800	11.519	0.194	.281	.458	.622
+1	+1	+1	-1	+1	12.040	11.519	0.194	.521	.458	1.154
-1	-1	-1	+1	+1	9.240	9.156	0.194	.084	.458	.187
+1	-1	-1	+1	+1	9.320	9.156	0.194	.164	.458	.364
-1	+1	-1	+1	+1	12.920	13.844	0.194	-.924	.458	-2.050
+1	+1	-1	+1	+1	13.480	13.844	0.194	-.364	.458	-.808
-1	-1	+1	+1	+1	8.360	7.662	0.194	.698	.458	1.548
+1	-1	+1	+1	+1	8.160	7.662	0.194	.498	.458	1.105
-1	+1	+1	+1	+1	12.360	12.351	0.194	.009	.458	.021
+1	+1	+1	+1	+1	11.600	12.351	0.194	-.751	.458	-1.664

TABLE 7.12. Residuals and predicted response values for model fitted in Computer Run 3.

THE REGRESSION EQUATION IS
Y = 10.3 + 2.34 X1 - .747 X2
+ .416 X3 - .314 X4

	COLUMN	COEFFICIENT	ST. DEV. OF COEF.	T-RATIO = COEF/S.D.
	--	10.3469	0.0623	166.20
X1	INIT.CO	2.34437	0.06225	37.66
X2	INIT.NI	-0.74687	0.06225	-12.00
X3	EQU.TEMP	0.41563	0.06225	6.68
X4	CO*TEMP	-0.31437	0.06225	-5.05

THE ST. DEV. OF Y ABOUT REGRESSION LINE IS
S = 0.3522
WITH (32- 5) = 27 DEGREES OF FREEDOM

R-SQUARED = 98.4 PERCENT
R-SQUARED = 98.1 PERCENT, ADJUSTED FOR D.F.

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF
REGRESSION	4	202.4157	50.6039
RESIDUAL	27	3.3485	0.1240
TOTAL	31	205.7643	

FURTHER ANALYSIS OF VARIANCE
SS EXPLAINED BY EACH VARIABLE WHEN ENTERED IN THE ORDER GIVEN

DUE TO	DF	SS
REGRESSION	4	202.4157
INIT.CO	1	175.8750
INIT.NI	1	17.8503
EQU.TEMP	1	5.5278
CO*TEMP	1	3.1626

TABLE 7.13. Statistical output from Computer Run 4. Model including variables B, C and D and interaction BD.

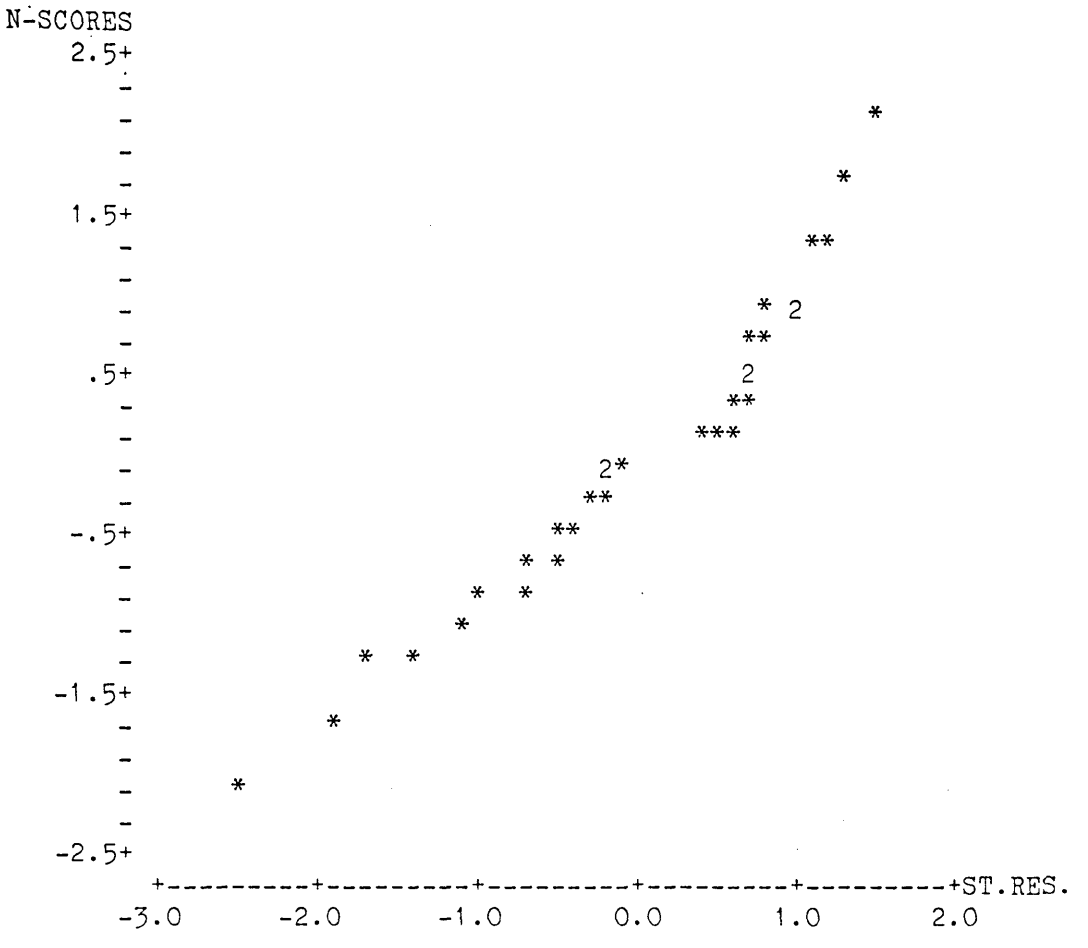


Figure (A)

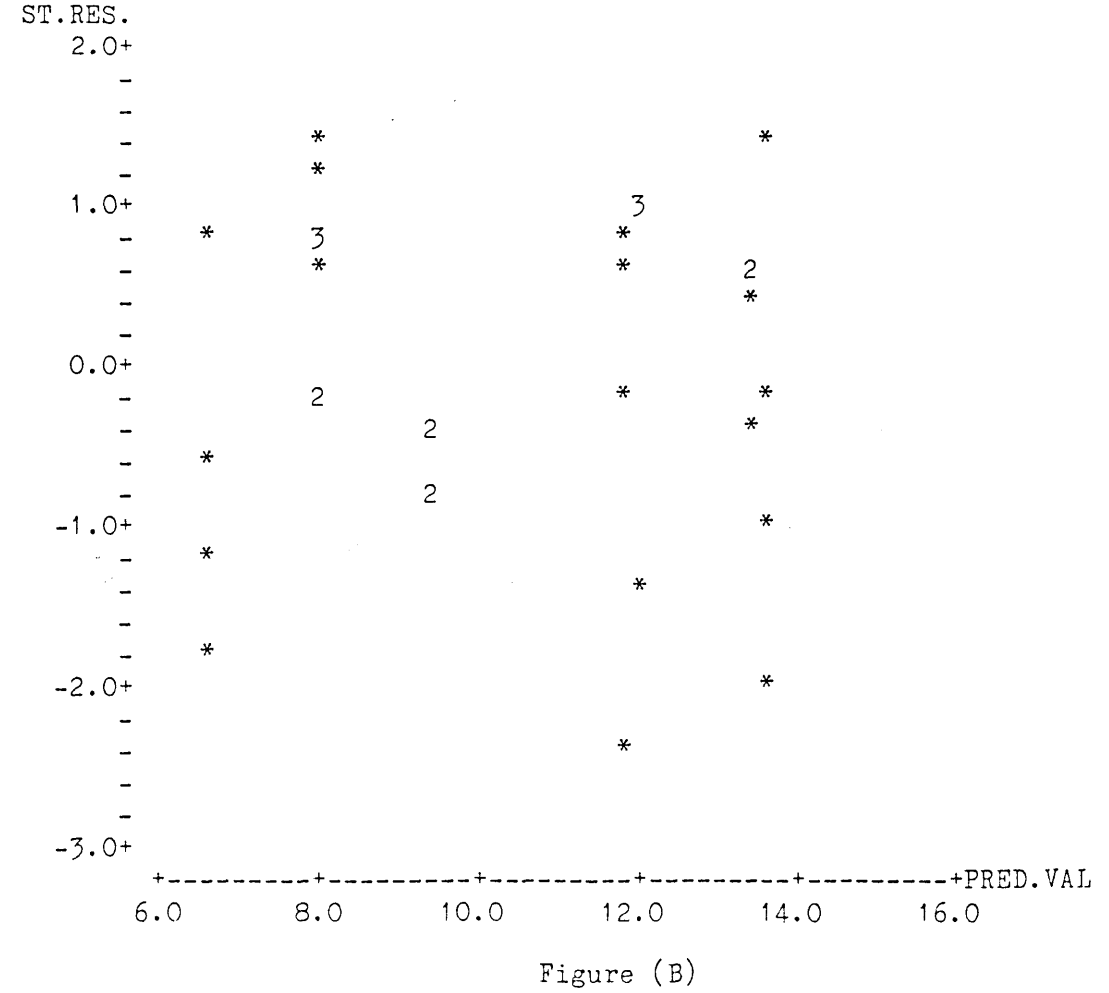


Figure (B)

FIGURES 7.5.a and 7.5.b. Diagnostic plots for model fitted in Computer Run 4.

Init.pH	Init.Co	Init.Ni	Equ.T	Na2SO4	y	$\hat{y}$	S.D.$\hat{y}$.	Resid,d	S.D.d.	Std.Res
-1	-1	-1	-1	-1	8.260	8.019	0.139	.241	.329	.744
+1	-1	-1	-1	-1	8.280	8.019	0.139	.261	.329	.806
-1	+1	-1	-1	-1	13.200	13.337	0.139	-.137	.329	-.423
+1	+1	-1	-1	-1	13.560	13.337	0.139	.223	.329	.690
-1	-1	+1	-1	-1	6.360	6.526	0.139	-.166	.329	-.512
+1	-1	+1	-1	-1	6.160	6.526	0.139	-.366	.329	-1.130
-1	+1	+1	-1	-1	12.080	11.843	0.139	.237	.329	.732
+1	+1	+1	-1	-1	11.040	11.843	0.139	-.803	.329	-2.483
-1	-1	-1	+1	-1	9.250	9.479	0.139	-.229	.329	-.709
+1	-1	-1	+1	-1	9.370	9.479	0.139	-.109	.329	-.338
-1	+1	-1	+1	-1	14.020	13.539	0.139	.481	.329	1.486
+1	+1	-1	+1	-1	13.200	13.539	0.139	-.339	.329	-1.049
-1	-1	+1	+1	-1	8.240	7.986	0.139	.254	.329	.786
+1	-1	+1	+1	-1	7.920	7.986	0.139	-.066	.329	-.203
-1	+1	+1	+1	-1	12.360	12.046	0.139	.314	.329	.972
+1	+1	+1	+1	-1	12.400	12.046	0.139	.354	.329	1.095
-1	-1	-1	-1	+1	8.440	8.019	0.139	.421	.329	1.300
+1	-1	-1	-1	+1	7.960	8.019	0.139	-.059	.329	-.184
-1	+1	-1	-1	+1	13.520	13.337	0.139	.183	.329	.566
+1	+1	-1	-1	+1	13.480	13.337	0.139	.143	.329	.442
-1	-1	+1	-1	+1	5.960	6.526	0.139	-.566	.329	-1.749
+1	-1	+1	-1	+1	6.760	6.526	0.139	.234	.329	.725
-1	+1	+1	-1	+1	11.800	11.843	0.139	-.043	.329	-.133
+1	+1	+1	-1	+1	12.040	11.843	0.139	.197	.329	.609
-1	-1	-1	+1	+1	9.240	9.479	0.139	-.239	.329	-.740
+1	-1	-1	+1	+1	9.320	9.479	0.139	-.159	.329	-.493
-1	+1	-1	+1	+1	12.920	13.539	0.139	-.619	.329	-1.915
+1	+1	-1	+1	+1	13.480	13.539	0.139	-.059	.329	-.184
-1	-1	+1	+1	+1	8.360	7.986	0.139	.374	.329	1.157
+1	-1	+1	+1	+1	8.160	7.986	0.139	.174	.329	.539
-1	+1	+1	+1	+1	12.360	12.046	0.139	.314	.329	.972
+1	+1	+1	+1	+1	11.600	12.046	0.139	-.446	.329	-1.378

TABLE 7.14. Residuals and predicted response values for model fitted in Computer Run 4.

THE REGRESSION EQUATION IS
Y = 10.3 + 2.34 X1 - .747 X2
+ .416 X3 - .314 X4 + .159 X5

	COLUMN	COEFFICIENT	ST. DEV. OF COEF.	T-RATIO = COEF/S.D.
	--	10.3469	0.0552	187.42
X1	INIT.CO	2.34437	0.05521	42.47
X2	INIT.NI	-0.74687	0.05521	-13.53
X3	EQU.TEMP	0.41563	0.05521	7.53
X4	CO*TEMP	-0.31437	0.05521	-5.69
X5	NI*TEMP	0.15937	0.05521	2.89

THE ST. DEV. OF Y ABOUT REGRESSION LINE IS
S = 0.3123
WITH (32- 6) = 26 DEGREES OF FREEDOM

R-SQUARED = 98.8 PERCENT
R-SQUARED = 98.5 PERCENT, ADJUSTED FOR D.F.

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF
REGRESSION	5	203.2286	40.6457
RESIDUAL	26	2.5357	0.0975
TOTAL	31	205.7643	

FURTHER ANALYSIS OF VARIANCE
SS EXPLAINED BY EACH VARIABLE WHEN ENTERED IN THE ORDER GIVEN

DUE TO	DF	SS
REGRESSION	5	203.2286
INIT.CO	1	175.8750
INIT.NI	1	17.8503
EQU.TEMP	1	5.5278
CO*TEMP	1	3.1626
NI*TEMP	1	0.8128

TABLE 7.15. Statistical output from Computer Run 5. Regression model including variables B, C and D and interactions BD and CD.

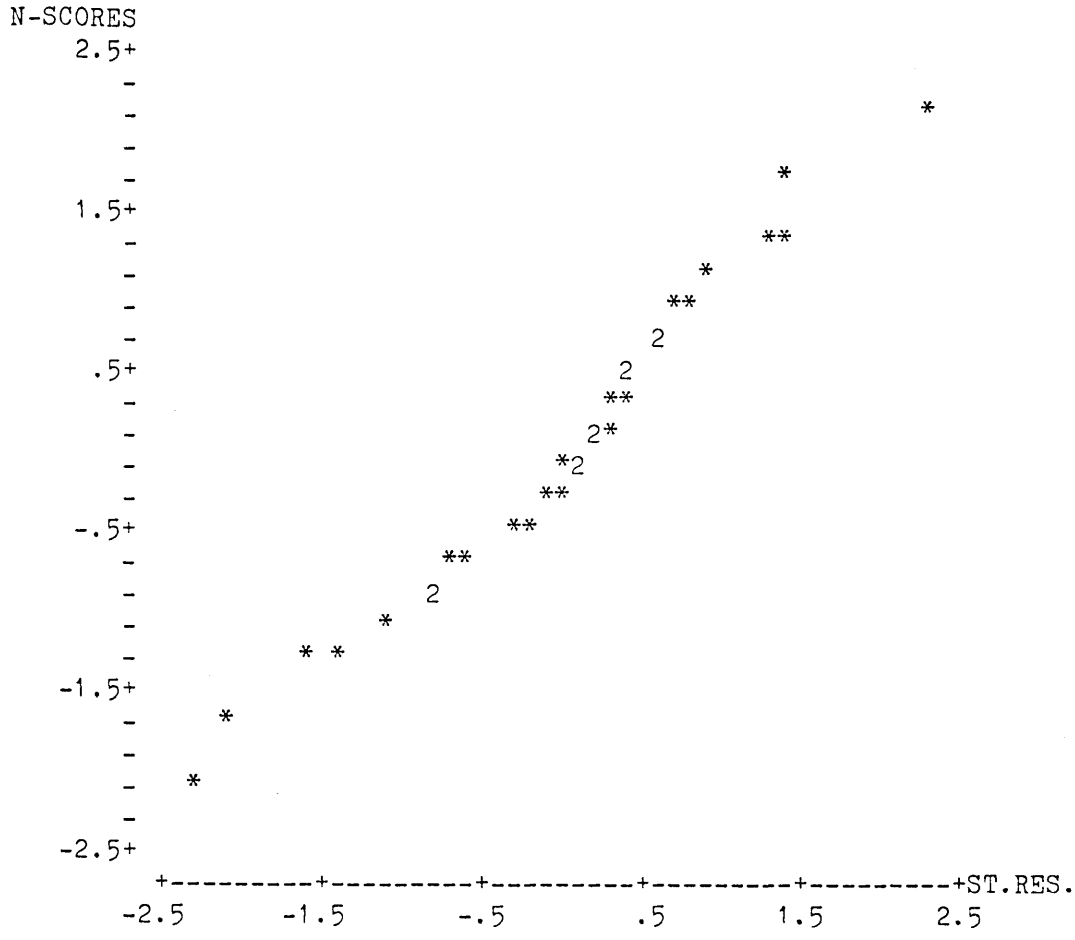


Figure (A)

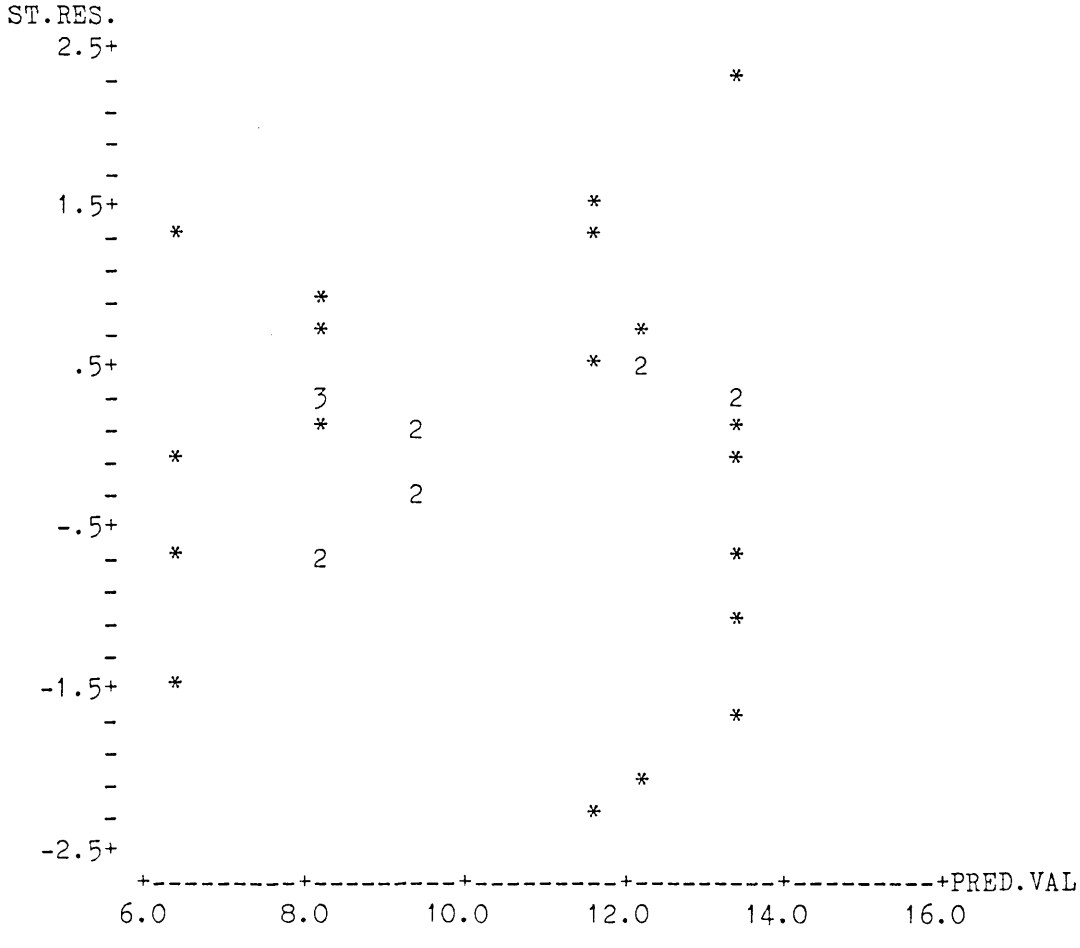


Figure (B)

FIGURES 7.6.a and 7.6.b. Diagnostic plots for model fitted in Computer Run 5.

Init.pH	Init.Co	Init.Ni	Equ.T	Na2SO4	y	$\hat{y}$	S.D.$\hat{y}$.	Resid,d	S.D.d.	Std.Res
-1	-1	-1	-1	-1	8.260	8.179	0.135	.081	.286	.289
+1	-1	-1	-1	-1	8.280	8.179	0.135	.101	.286	.360
-1	+1	-1	-1	-1	13.200	13.496	0.135	-.296	.286	-1.052
+1	+1	-1	-1	-1	13.560	13.496	0.135	.064	.286	.226
-1	-1	+1	-1	-1	6.360	6.366	0.135	-.006	.286	-.022
+1	-1	+1	-1	-1	6.160	6.366	0.135	-.206	.286	-.733
-1	+1	+1	-1	-1	12.080	11.684	0.135	.396	.286	1.408
+1	+1	+1	-1	-1	11.040	11.684	0.135	-.644	.286	-2.287
-1	-1	-1	+1	-1	9.250	9.320	0.135	-.070	.286	-.249
+1	-1	-1	+1	-1	9.370	9.320	0.135	.050	.286	.178
-1	+1	-1	+1	-1	14.020	13.380	0.135	.640	.286	2.274
+1	+1	-1	+1	-1	13.200	13.380	0.135	-.180	.286	-.639
-1	-1	+1	+1	-1	8.240	8.145	0.135	.095	.286	.337
+1	-1	+1	+1	-1	7.920	8.145	0.135	-.225	.286	-.799
-1	+1	+1	+1	-1	12.360	12.205	0.135	.155	.286	.551
+1	+1	+1	+1	-1	12.400	12.205	0.135	.195	.286	.693
-1	-1	-1	-1	+1	8.440	8.179	0.135	.261	.286	.928
+1	-1	-1	-1	+1	7.960	8.179	0.135	-.219	.286	-.777
-1	+1	-1	-1	+1	13.520	13.496	0.135	.024	.286	.084
+1	+1	-1	-1	+1	13.480	13.496	0.135	-.016	.286	-.058
-1	-1	+1	-1	+1	5.960	6.366	0.135	-.406	.286	-1.443
+1	-1	+1	-1	+1	6.760	6.366	0.135	.394	.286	1.399
-1	+1	+1	-1	+1	11.800	11.684	0.135	.116	.286	.413
+1	+1	+1	-1	+1	12.040	11.684	0.135	.356	.286	1.266
-1	-1	-1	+1	+1	9.240	9.320	0.135	-.080	.286	-.284
+1	-1	-1	+1	+1	9.320	9.320	0.135	.000	.286	.000
-1	+1	-1	+1	+1	12.920	13.380	0.135	-.460	.286	-1.634
+1	+1	-1	+1	+1	13.480	13.380	0.135	.100	.286	.355
-1	-1	+1	+1	+1	8.360	8.145	0.135	.215	.286	.764
+1	-1	+1	+1	+1	8.160	8.145	0.135	.015	.286	.053
-1	+1	+1	+1	+1	12.360	12.205	0.135	.155	.286	.551
+1	+1	+1	+1	+1	11.600	12.205	0.135	-.605	.286	-2.149

TABLE 7.16. Residuals for model fitted in Computer Run 5.

THE REGRESSION EQUATION IS
Y = 10.3 + 2.34 X1 - .747 X2
+ .416 X3 + .0156 X4 - .314 X5
+ .159 X6

	COLUMN	COEFFICIENT	ST. DEV. OF COEF.	T-RATIO = COEF/S.D.
	--	10.3469	0.0562	184.07
X1	INIT.CO	2.34437	0.05621	41.71
X2	INIT.NI	-0.74687	0.05621	-13.29
X3	EQU.TEMP	0.41563	0.05621	7.39
X4	CO*NI	0.01563	0.05621	0.28
X5	CO*TEMP	-0.31437	0.05621	-5.59
X6	NI*TEMP	0.15937	0.05621	2.84

THE ST. DEV. OF Y ABOUT REGRESSION LINE IS
S = 0.3180
WITH (32- 7) = 25 DEGREES OF FREEDOM

R-SQUARED = 98.8 PERCENT
R-SQUARED = 98.5 PERCENT, ADJUSTED FOR D.F.

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF
REGRESSION	6	203.2364	33.8727
RESIDUAL	25	2.5279	0.1011
TOTAL	31	205.7643	

FURTHER ANALYSIS OF VARIANCE
SS EXPLAINED BY EACH VARIABLE WHEN ENTERED IN THE ORDER GIVEN

DUE TO	DF	SS
REGRESSION	6	203.2364
INIT.CO	1	175.8750
INIT.NI	1	17.8503
EQU.TEMP	1	5.5278
CO*NI	1	0.0078
CO*TEMP	1	3.1626
NI*TEMP	1	0.8128

TABLE 7.17. Statistical output from Computer Run 6. Regression model including variables B, C and D and interactions BC, BD and CD.

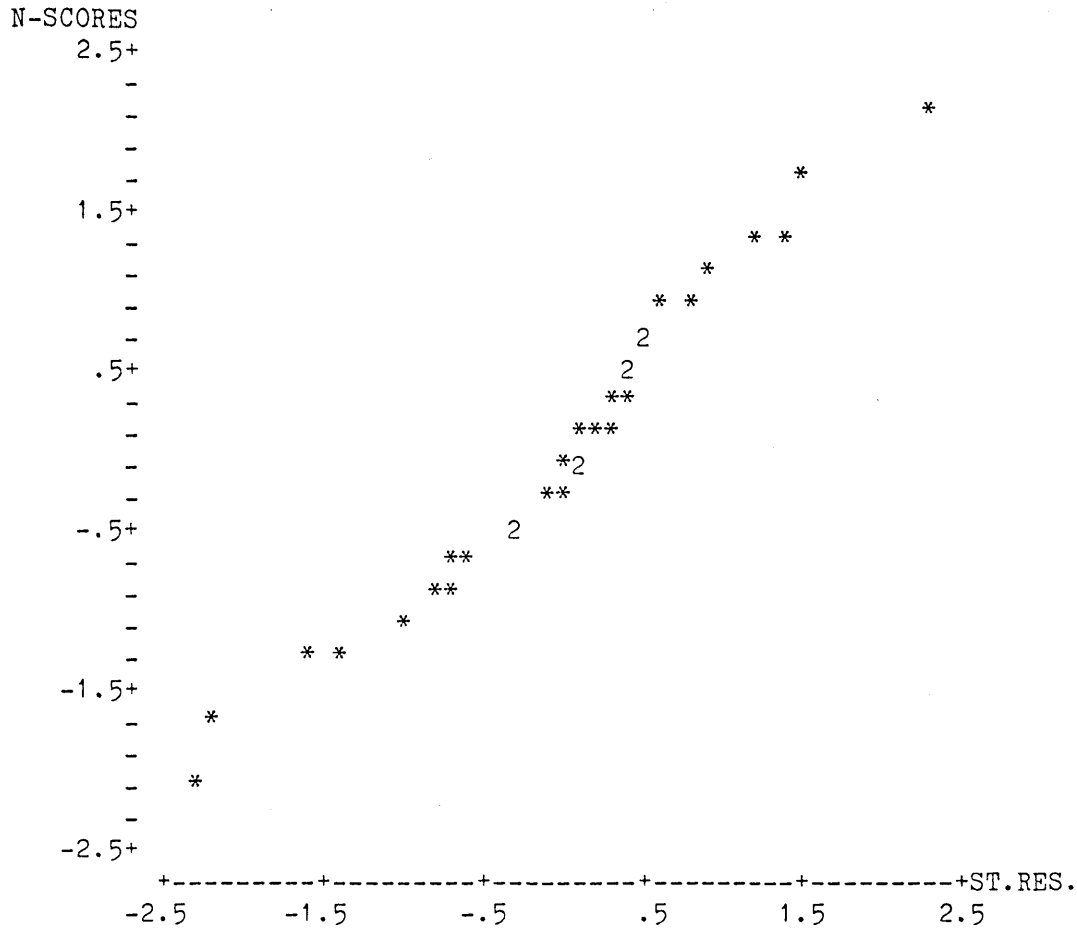


Figure (A)

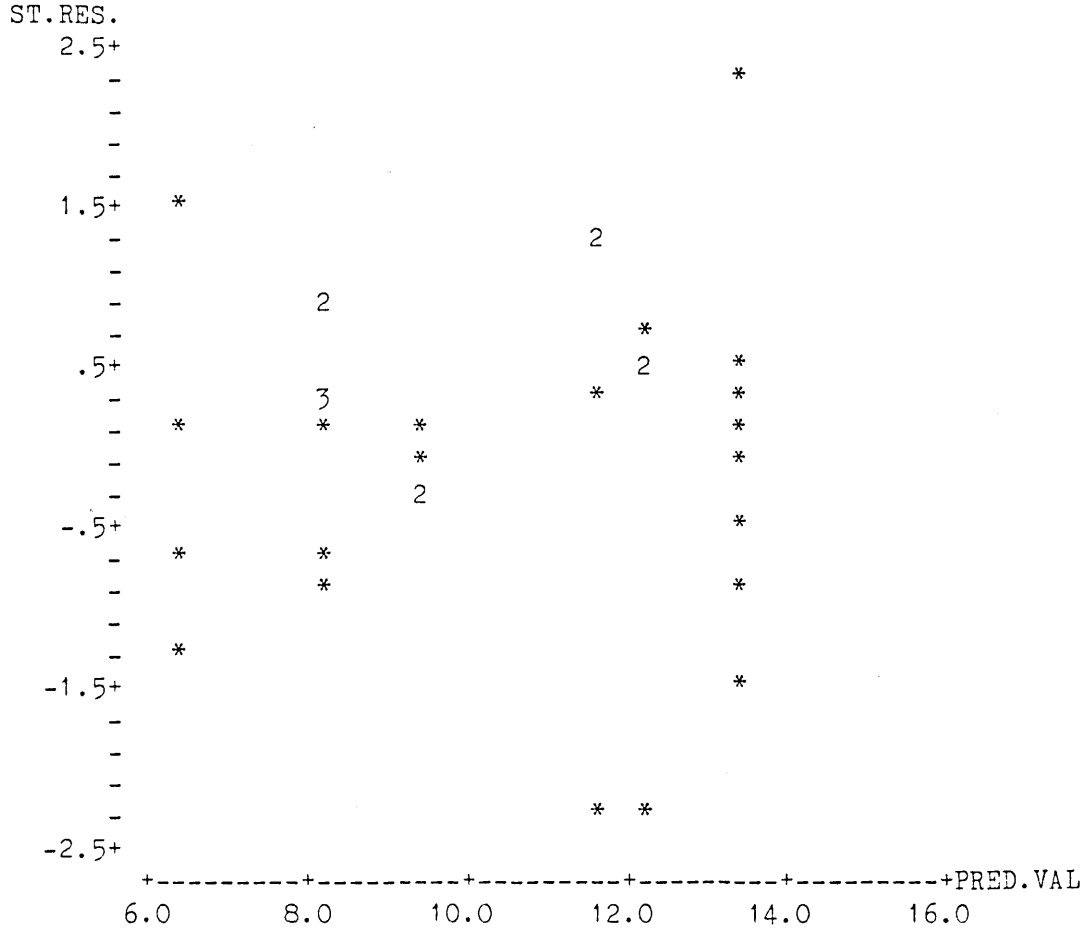


Figure (B)

FIGURES 7.7.a. and 7.7.b. Diagnostic plots for model fitted in Computer Run 6.

Init.pH	Init.Co	Init.Ni	Equ.T	Na2SO4	y	$\hat{y}$	S.D.$\hat{y}$.	Resid,d	S.D.d.	Std.Res
-1	-1	-1	-1	-1	8.260	8.194	0.149	.066	.286	.233
+1	-1	-1	-1	-1	8.280	8.194	0.149	.086	.286	.305
-1	+1	-1	-1	-1	13.200	13.481	0.149	-.281	.286	-.998
+1	+1	-1	-1	-1	13.560	13.481	0.149	.079	.286	.282
-1	-1	+1	-1	-1	6.360	6.351	0.149	.009	.286	.033
+1	-1	+1	-1	-1	6.160	6.351	0.149	-.191	.286	-.678
-1	+1	+1	-1	-1	12.080	11.699	0.149	.381	.286	1.354
+1	+1	+1	-1	-1	11.040	11.699	0.149	-.659	.286	-2.346
-1	-1	-1	+1	-1	9.250	9.336	0.149	-.086	.286	-.305
+1	-1	-1	+1	-1	9.370	9.336	0.149	.034	.286	.122
-1	+1	-1	+1	-1	14.020	13.364	0.149	.656	.286	2.333
+1	+1	-1	+1	-1	13.200	13.364	0.149	-.164	.286	-.585
-1	-1	+1	+1	-1	8.240	8.129	0.149	.111	.286	.394
+1	-1	+1	+1	-1	7.920	8.129	0.149	-.209	.286	-.745
-1	+1	+1	+1	-1	12.360	12.221	0.149	.139	.286	.496
+1	+1	+1	+1	-1	12.400	12.221	0.149	.179	.286	.638
-1	-1	-1	-1	+1	8.440	8.194	0.149	.246	.286	.874
+1	-1	-1	-1	+1	7.960	8.194	0.149	-.234	.286	-.834
-1	+1	-1	-1	+1	13.520	13.481	0.149	.039	.286	.140
+1	+1	-1	-1	+1	13.480	13.481	0.149	-.001	.286	-.002
-1	-1	+1	-1	+1	5.960	6.351	0.149	-.391	.286	-1.390
+1	-1	+1	-1	+1	6.760	6.351	0.149	.409	.286	1.457
-1	+1	+1	-1	+1	11.800	11.699	0.149	.101	.286	.358
+1	+1	+1	-1	+1	12.040	11.699	0.149	.341	.286	1.212
-1	-1	-1	+1	+1	9.240	9.336	0.149	-.096	.286	-.340
+1	-1	-1	+1	+1	9.320	9.336	0.149	-.016	.286	-.056
-1	+1	-1	+1	+1	12.920	13.364	0.149	-.444	.286	-1.581
+1	+1	-1	+1	+1	13.480	13.364	0.149	.116	.286	.411
-1	-1	+1	+1	+1	8.360	8.129	0.149	.231	.286	.821
+1	-1	+1	+1	+1	8.160	8.129	0.149	.031	.286	.109
-1	+1	+1	+1	+1	12.360	12.221	0.149	.139	.286	.496
+1	+1	+1	+1	+1	11.600	12.221	0.149	-.621	.286	-2.208

TABLE 7.18. Residuals and predicted response values for model fitted in Computer Run 6.

THE REGRESSION EQUATION IS
Y = 10.3 + 2.34 X1 - .747 X2
+ .416 X3 - .314 X4 + .159 X5
- .0406 X6

	COLUMN	COEFFICIENT	ST. DEV. OF COEF.	T-RATIO = COEF/S.D.
	--	10.3469	0.0557	185.73
X1	INIT.CO	2.34437	0.05571	42.08
X2	INIT.NI	-0.74687	0.05571	-13.41
X3	EQU.TEMP	0.41563	0.05571	7.46
X4	CO*TEMP	-0.31437	0.05571	-5.64
X5	NI*TEMP	0.15937	0.05571	2.86
X6	CO*NI*T	-0.04062	0.05571	-0.73

THE ST. DEV. OF Y ABOUT REGRESSION LINE IS
S = 0.3151
WITH (32- 7) = 25 DEGREES OF FREEDOM

R-SQUARED = 98.8 PERCENT
R-SQUARED = 98.5 PERCENT, ADJUSTED FOR D.F.

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF
REGRESSION	6	203.2814	33.8802
RESIDUAL	25	2.4829	0.0993
TOTAL	31	205.7643	

FURTHER ANALYSIS OF VARIANCE
SS EXPLAINED BY EACH VARIABLE WHEN ENTERED IN THE ORDER GIVEN

DUE TO	DF	SS
REGRESSION	6	203.2814
INIT.CO	1	175.8750
INIT.NI	1	17.8503
EQU.TEMP	1	5.5278
CO*TEMP	1	3.1626
NI*TEMP	1	0.8128
CO*NI*T	1	0.0528

TABLE 7.19. Statistical output from Computer Run 7. Regression model including variables B, C and D and interactions BD, CD and BCD.

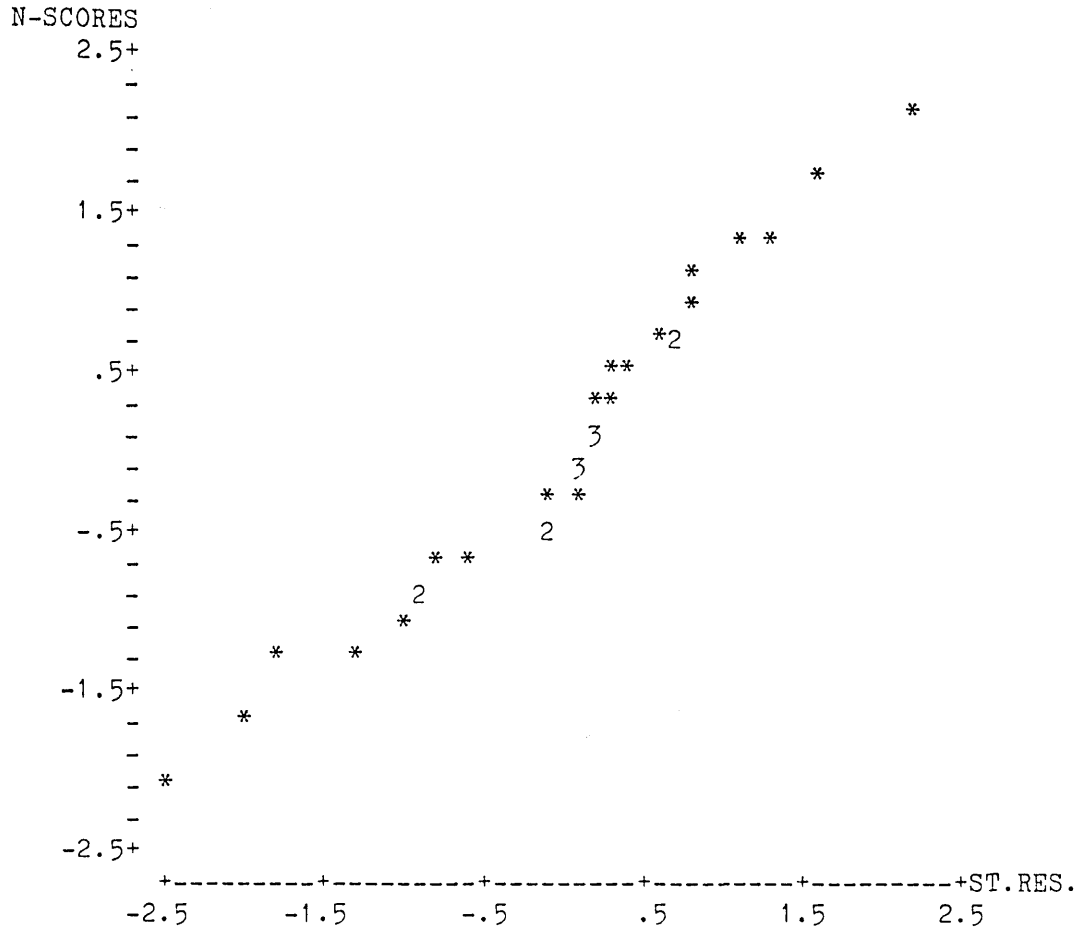


Figure (A)

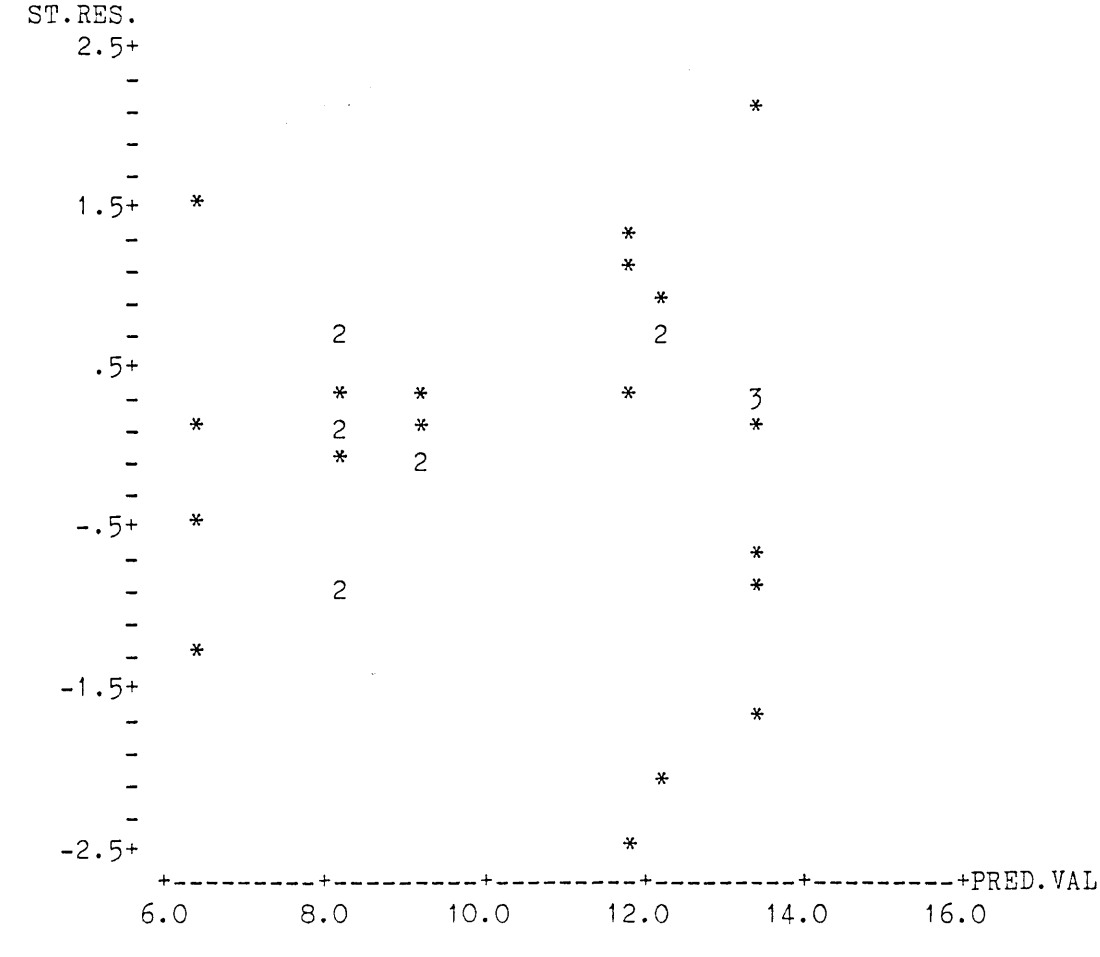


Figure (B)

FIGURES 7.8.a and 7.8.b. Diagnostic plots for model fitted in Computer Run 7.

Init.pH	Init.Co	Init.Ni	Equ.T	Na2SO4	y	$\hat{y}$	S.D.$\hat{y}$.	Resid,d	S.D.d.	Std.Res
-1	-1	-1	-1	-1	8.260	8.219	0.149	.041	.283	.146
+1	-1	-1	-1	-1	8.280	8.219	0.149	.061	.283	.218
-1	+1	-1	-1	-1	13.200	13.456	0.149	-.256	.283	-.918
+1	+1	-1	-1	-1	13.560	13.456	0.149	.104	.283	.375
-1	-1	+1	-1	-1	6.360	6.326	0.149	.034	.283	.123
+1	-1	+1	-1	-1	6.160	6.326	0.149	-.166	.283	-.595
-1	+1	+1	-1	-1	12.080	11.724	0.149	.356	.283	1.277
+1	+1	+1	-1	-1	11.040	11.724	0.149	-.684	.283	-2.457
-1	-1	-1	+1	-1	9.250	9.279	0.149	-.029	.283	-.105
+1	-1	-1	+1	-1	9.370	9.279	0.149	.091	.283	.325
-1	+1	-1	+1	-1	14.020	13.421	0.149	.599	.283	2.152
+1	+1	-1	+1	-1	13.200	13.421	0.149	-.221	.283	-.792
-1	-1	+1	+1	-1	8.240	8.186	0.149	.054	.283	.195
+1	-1	+1	+1	-1	7.920	8.186	0.149	-.266	.283	-.954
-1	+1	+1	+1	-1	12.360	12.164	0.149	.196	.283	.702
+1	+1	+1	+1	-1	12.400	12.164	0.149	.236	.283	.846
-1	-1	-1	-1	+1	8.440	8.219	0.149	.221	.283	.792
+1	-1	-1	-1	+1	7.960	8.219	0.149	-.259	.283	-.931
-1	+1	-1	-1	+1	13.520	13.456	0.149	.064	.283	.231
+1	+1	-1	-1	+1	13.480	13.456	0.149	.024	.283	.088
-1	-1	+1	-1	+1	5.960	6.326	0.149	-.366	.283	-1.313
+1	-1	+1	-1	+1	6.760	6.326	0.149	.434	.283	1.559
-1	+1	+1	-1	+1	11.800	11.724	0.149	.076	.283	.271
+1	+1	+1	-1	+1	12.040	11.724	0.149	.316	.283	1.133
-1	-1	-1	+1	+1	9.240	9.279	0.149	-.039	.283	-.141
+1	-1	-1	+1	+1	9.320	9.279	0.149	.041	.283	.146
-1	+1	-1	+1	+1	12.920	13.421	0.149	-.501	.283	-1.797
+1	+1	-1	+1	+1	13.480	13.421	0.149	.059	.283	.213
-1	-1	+1	+1	+1	8.360	8.186	0.149	.174	.283	.626
+1	-1	+1	+1	+1	8.160	8.186	0.149	-.026	.283	-.092
-1	+1	+1	+1	+1	12.360	12.164	0.149	.196	.283	.702
+1	+1	+1	+1	+1	11.600	12.164	0.149	-.564	.283	-2.026

TABLE 7.20. Residuals and predicted response values for model fitted in Computer Run 7.

stage of the regression analysis, the model was extended by the addition of plausible VARIABLE-INTERACTION terms to those for the variables B, C and D. The two-variable interactions considered were BD, CD and BC.

With the introduction of BD into the model (Computer Run 4) the fit is improved, as can be seen from Tables 7.13 and 7.14 and Figures 7.5.a and 7.5.b. There are no irregularities in the diagnostic plots, and the value of R^2 is increased to 98.4%. From the plot of standardized residuals (std. res.) versus $\hat{y}$, it appears that the residuals are fairly homogenous. The regression parameter for BD is $\beta' = -0.314$. BD was retained in the regression model.

The further introduction of CD into the model (Computer Run 5) resulted in another appreciable improvement in fit, as can be seen from Tables 7.15 and 7.16 and Figures 7.6.a and 7.6.b. The diagnostic plots are in good order and a value of $R^2 = 98.8\%$, was obtained. The CD regression parameter, $\beta' = +0.159$. CD was retained.

The introduction of BC in Computer Run 6 (Tables 7.17 and 7.18 and Figures 7.7.a and 7.7.b) appears to have any influence at all, either on the model fit, with $R^2 = 98.8\%$, or on the diagnostic plots. The regression parameter for BC, with a value of $\beta' = +0.016$, is statistically non-significant. BC was discarded from the model.

The only plausible three-factor interaction is BCD, which was judged insignificant in the factorial analysis. It was introduced into the model in Computer Run 7. Like BC, the introduction of BCD appears to have little effect on the model. There is no improvement in fit, with R^2 = 98.8%, and the diagnostic plots are very similar indeed to those for Computer Run 6. The parameter obtained, β' = -0.041, is statistically insignificant.

Discussion and Conclusions

In the earlier factorial analysis, significance testing of the effects themselves had found firmly significant the main-effects B, C and D and the two-factor interaction BD. The interactions CD and ACDE were on the borderline of significance. The main-effects A and E had been found firmly non-significant.

In the regression analysis, all the models appear to describe the data satisfactorily. The most acceptable model however, in that it obtains the highest correlation with greatest economy in number of regression parameters, and has good normality and homogeneity of residiuals, is the model which includes B, C, D, BD and CD, which was fitted in Computer Run 5.

The variables A and E, and the interactions BC and BDE, do not enhance the description of the data given by this model, thus the regression analysis confirms that, on the present data, these effects are non-significant,

or in other words cannot be distinguished from experimental error.

In accepting the above model, CD is taken as a real effect. In the factorial analysis, CD was of equivocal significance, and accepting it as a real effect implied likewise accepting the implausible four-factor interaction ACDE. It was suggested in that section, that ACDE might be inflated in size due to the presence of bad or faulty values in the response. Three of the model's residuals were 'flagged' by the regression package as being greater than two standard deviations from the mean residual, those of row 8, 11 and 32 (treatments abc, bd, and abcde respectively). The observations which gave rise to these residuals give similarly large residuals in Computer Runs 4, 6 and 7, which are the better fitting models. These observations (response values) give rise to markedly non-normal residuals, as they appear at the extreme ends of the normal plot of residuals, so it is quite possible that they are bad values. However there was no apparent correlation between those observations and those that produced the large residuals with the other responses.

Confirmation of the possibility that these residuals are due to bad response values was sought from the calculation of the cobalt mass-balances, as shown in Tables 7.21 and 7.22. No obvious correlation was observed between the observations giving the possibly suspect residuals, and distortions in the associated concentration-balance.

TABLE 7.21 (At Low Level of Cobalt Variable). Mass-Balance for Equilibrium Cobalt Phase Concentrations, and Comparison with Residuals from Computer Run 5

Treatment Code	Row in Table 8.12	Response Value g/L	Standardized Residual	Sum of [Co] and $\overline{[Co]}$	Deviation of Sum From Mean Sum
L	1	8.26	0.29	10.49	-0.19
a	2	8.28	0.36	10.51	-0.17
c	5	6.36	-0.02	10.70	0.02
ac	6	6.16	-0.73	10.72	0.04
d	9	9.25	-0.25	10.53	-0.15
ad	10	9.37	0.18	10.65	-0.03
cd	13	8.24	0.34	10.86	0.18
acd	14	7.92	-0.80	10.50	-0.18
e	17	8.44	0.93	10.84	0.16
ae	18	7.96	-0.78	10.35	-0.33
ce	21	5.96	-1.44	10.64	-0.04
ace	22	6.76	1.40	11.28	0.60
de	25	9.24	-0.28	10.56	-0.12
ade	26	9.32	0.00	10.59	-0.09
cde	29	8.36	0.76	10.96	0.28
acde	30	8.16	0.05	10.74	0.06

Level Mean = 10.68

Standard Deviation of Sum = 0.224

TABLE 7.22. (At High Level of Cobalt Variable). Mass-Balance for Equilibrium Cobalt Phase Concentrations, and Comparison with Residuals From Computer Run 5.

Treatment Code	Row in Table 8.12	Response Value g/L	Standardized Residual	Sum of [Co] and $\overline{[Co]}$	Deviation of Sum From Mean Sum
b	3	13.20	-1.05	24.95	-0.32
ab	4	13.56	0.23	25.31	0.04
bc	7	12.08	1.41	25.63	0.36
abc	8	11.04	-2.29	24.94	-0.33
bd	11	14.02	2.27	25.52	0.25
abd	12	13.20	-0.64	24.95	-0.32
bcd	15	12.36	0.55	25.16	-0.11
abcd	16	12.40	0.69	25.55	0.28
be	19	13.52	0.08	25.62	0.35
abe	20	13.48	-0.06	25.18	-0.09
bce	23	11.80	0.41	24.95	-0.32
abce	24	12.04	1.27	25.29	0.02
bde	27	12.92	-1.63	24.82	-0.45
abde	28	13.48	0.36	25.78	0.50
bcde	31	12.36	0.55	26.01	0.74
abcde	32	11.60	-2.15	24.70	-0.57

Level Mean = 25.27

Standard Deviation of Sum = 0.38

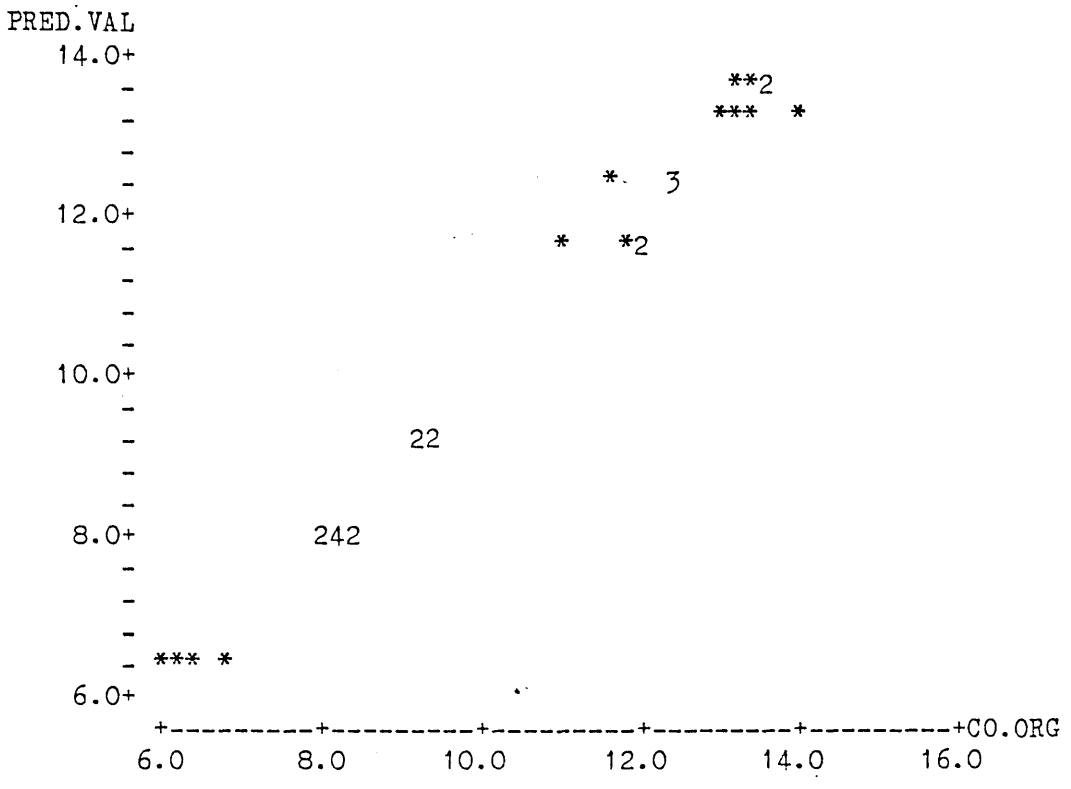


FIGURE 7.9. Plot of predicted versus measured cobalt response for model including B, C, D, BD and CD (Computer Run 5).

Whatever the reason for the spuriously large value of the ACDE effect, there seems little doubt that the model including B, C, D, BD and CD gives the most convincing fit. Thus, on the present data, the regression equation which best describes the response behaviour, strictly within the ranges of the variables studied, and under the present conditions of experimentation, is:

$$\hat{y} = 10.35 + 2.344X_1 - 0.747X_2 + 0.416X_3 - 0.314X_4 + 0.159X_5 \qquad (7.23)$$

where $\hat{y}$ is the predicted value of the equilibrium organic cobalt concentration, and the coded variables X_1, X_2,...,X_5 correspond to the natural variables B, C, D,..., CD as follows:

$X_1 \rightarrow$ B

$X_2 \rightarrow$ C

$X_3 \rightarrow$ D

$X_4 = X_1X_3 \rightarrow$ BD

$X_5 = X_2X_3 \rightarrow$ CD

The coded variables are related to the natural variables by the following equations:

$$X_1 = \frac{x_1 - 17.5}{7.5} \qquad (7.24)$$

$$X_2 = \frac{x_2 - 35}{15} \qquad (7.25)$$

$$X_3 = \frac{x_3 - 338}{15} \qquad (7.26)$$

where x_1, x_2 and x_3 are the initial aqueous cobalt concentration (g/L), the initial aqueous nickel concentration (g/L) and equilibrium temperature (degrees K) respectively.

The plot of the predicted versus the measured value of the response for this model is shown in Figure 7.9.

7.4 Statistical Conclusions for the Cobalt Study

It is concluded that of the factorial variables studied, those which have a real influence on the response EQUILIBRIUM ORGANIC COBALT CONCENTRATION are the variables B, C and D. There are real two-factor interactions between B and D, and between C and D. The factorial variables are identified in Table 7.23.

TABLE 7.23. Real Factors for the Cobalt Response.

Factor or Interaction	Identity	Effect Value g/L
B	Initial aqueous cobalt concentration	+4.69
C	Initial aqueous nickel concentration	-1.49
D	Equilibrium temperature	+0.83
BD	Two-factor interaction between B and D	-0.63
CD	Two-factor interaction between C and D	+0.32

CHAPTER 8

A STATISTICAL STUDY OF THE NICKEL RESPONSE

8.1 Factorial Analysis

Calculation and Inspection of the Effects

For the nickel response, rather than using the laborious Yates' hand algorithm, the effects were calculated using the computer program FACEXP[57] and then cross-checked by the hand calculation of three of the main-effects.

The effects are given in Standard or Yates's order in Table 8.1 and in order of absolute magnitude in Table 8.2. The response values from which they are obtained are to be found in Table 6.4.

Because cobalt and nickel compete to extract into the organic phase, it had been anticipated that there would be some relation between the results of the statistical analysis of the cobalt response and that of the nickel response, so that information gained in the study of the cobalt response would be of use in making the interpretation of the nickel response.

This has indeed been found to be the case. However, the statistical analysis of the nickel response is sufficiently robust to require only the minimum of external comparison.

From Table 8.2 it is seen that the five largest in magnitude of the nickel effects, the main-effects B, C and D, and the 2-f.i's BD and CD, are the effects which were concluded to be significant for the cobalt response, and are in the same order of magnitude.

TABLE 8.1. Calculated effects for the response:equilibrium organic nickel concentration

Treatment Code	Response (g/L)	Estimated Effect	Identity
L	6.10 ± 0.190	4.1331	Average
a	6.22 ± 0.190	0.0713 ± 0.067	A
b	1.32 ± 0.190	-4.3050 ± 0.067	B
ab	1.37 ± 0.190	0.0175 ± 0.067	AB
c	7.72 ± 0.190	1.2762 ± 0.067	C
ac	7.74 ± 0.190	0.0263 ± 0.067	AC
bc	2.76 ± 0.190	-0.0800 ± 0.067	BC
abc	3.42 ± 0.190	0.0375 ± 0.067	ABC
d	5.26 ± 0.190	-0.6163 ± 0.067	D
ad	5.34 ± 0.190	-0.0963 ± 0.067	AD
bd	1.08 ± 0.190	0.4000 ± 0.067	BD
abd	1.56 ± 0.190	0.0025 ± 0.067	ABD
cd	6.34 ± 0.190	-0.3638 ± 0.067	CD
acd	6.18 ± 0.190	-0.0638 ± 0.067	ACD
bcd	2.35 ± 0.190	0.0375 ± 0.067	BCD
abcd	2.37 ± 0.190	-0.0100 ± 0.067	ABCD
e	5.62 ± 0.190	-0.1250 ± 0.067	E
ae	5.72 ± 0.190	-0.0875 ± 0.067	AE
be	1.29 ± 0.190	0.0288 ± 0.067	BE
abe	1.33 ± 0.190	-0.1263 ± 0.067	ABE
ce	7.43 ± 0.190	-0.0525 ± 0.067	CE
ace	7.80 ± 0.190	0.0500 ± 0.067	ACE
bce	2.62 ± 0.190	-0.1438 ± 0.067	BCE
abce	2.60 ± 0.190	-0.0238 ± 0.067	ABCE
de	5.32 ± 0.190	0.1550 ± 0.067	DE
ade	5.28 ± 0.190	-0.0425 ± 0.067	ADE
bde	1.79 ± 0.190	0.0063 ± 0.067	BDE
abde	1.32 ± 0.190	0.0013 ± 0.067	ABDE
cde	6.28 ± 0.190	-0.0350 ± 0.067	CDE
acde	6.22 ± 0.190	0.0875 ± 0.067	ACDE
bcde	2.28 ± 0.190	0.0613 ± 0.067	BCDE
abcde	2.23 ± 0.190	0.1063 ± 0.067	ABCDE

TABLE 8.2. Ranked absolute values of nickel effects.

Order	Effect	Absolute Value	Effect Sign
1	B	4.305	-
2	C	1.276	+
3	D	0.616	-
4	BD	0.400	+
5	CD	0.364	-
6	DE	0.155	+
7	BCE	0.144	-
8	ABE	0.126	-
9	E	0.125	-
10	ABCDE	0.107	+
11	AD	0.0963	-
12/13	ACDE/AE	0.0875	+/-
14	BC	0.0800	-
15	A	0.0713	+
16	ACD	0.0638	-
17	BCDE	0.0613	+
18	CE	0.0525	-
19	ACE	0.0500	+
20	ADE	0.0425	-
21/22	BCD/ABC	0.0375	+/+
23	CDE	0.0350	-
24	BE	0.0288	+
25	AC	0.0263	+
26	ABCE	0.0238	-
27	AB	0.0175	+
28	ABCD	0.0100	-
29	BDE	0.00625	+
30	ABD	0.00250	-
31	ABDE	0.00125	+

The five effects form a plausible set of real effects, since they consist of main-effects of variables and some of the two-factor interactions between them. Also, and this does not necessarily have to be the case, the main-effects are each larger in magnitude than the interactions.

Significance Testing of the Effects

To subject the nickel effects to a formal test of significance, an estimate is required of the standard error of an effect for the nickel response. As with the cobalt response, this was obtained on the assumption that higher order interactions are negligible or do not exist.

For the set of two-tailed t-tests shown in Table 8.3, an estimate of the S.E.(effect) was obtained from the five four-factor interactions and the single five-factor interaction. A value of S.E. (4,5-f.i.) = 0.0624 g/L with ν = 6 d.o.f. was found. The selected effects were tested according to Bartlett's criterion and there was no evidence of heterogeneity of variance.

Five effects were judged to be significant at the $100(1-\alpha)$ = 99% level of significance. These are the set already identified as a likely set of real effects, and comprise B, C, D, BD and CD. From the tests in Table 8.3, they form by far the most convincing set of real effects. At this stringent significance level, not only are they

TABLE 8.3. Significance testing of the nickel response effects, using two-tailed t-tests and S.E.(4,5-f.i.)

Effect Identity	Effect Value	$t_c = \frac{\text{Effect}}{\text{S.E.(Effect)}}$	$t_{0.005}$ $\nu = 6$	Significance at 99% Probability Level	$t_{0.025}$ $\nu = 6$	Significance at 95% Probability Level
Average	4.1331	-	-	-	-	-
A	0.0713	1.142	3.707	NS	2.447	NS
B	-4.3050	-68.990	3.707	S	2.447	S
AB	0.0175	0.280	3.707	NS	2.447	NS
C	1.2762	20.452	3.707	S	2.447	S
AC	0.0263	0.421	3.707	NS	2.447	NS
BC	-0.0800	-1.282	3.707	NS	2.447	NS
ABC	0.0375	0.601	3.707	NS	2.447	NS
D	-0.6163	-9.877	3.707	S	2.447	S
AD	-0.0963	-1.543	3.707	NS	2.447	NS
BD	0.4000	6.410	3.707	S	2.447	S
ABD	0.0025	0.040	3.707	NS	2.447	NS
CD	-0.3638	-5.830	3.707	S	2.447	S
ACD	-0.0638	-1.022	3.707	NS	2.447	NS
BCD	0.0375	0.601	3.707	NS	2.447	NS
ABCD	-0.0100	-0.160	3.707	NS	2.447	NS
E	-0.1250	-2.003	3.707	NS	2.447	NS
AE	-0.0875	1.402	3.707	NS	2.447	NS
BE	0.0288	0.462	3.707	NS	2.447	NS
ABE	-0.1263	-2.024	3.707	NS	2.447	NS
CE	-0.0525	-0.841	3.707	NS	2.447	NS
ACE	0.0500	0.801	3.707	NS	2.447	NS
BCE	-0.1438	-2.304	3.707	NS	2.447	NS
ABCE	-0.0238	-0.381	3.707	NS	2.447	NS
DE	0.1550	2.483	3.707	NS	2.447	S
ADE	-0.0425	-0.681	3.707	NS	2.447	NS
BDE	0.0063	0.101	3.707	NS	2.447	NS
ABDE	0.0013	0.021	3.707	NS	2.447	NS
CDE	-0.0350	-0.561	3.707	NS	2.447	NS
ACDE	0.0875	1.402	3.707	NS	2.447	NS
BCDE	0.0613	0.982	3.707	NS	2.447	NS
ABCDE	0.1063	1.704	3.707	NS	2.447	NS

S = Significant

NS = Non-significant

judged significant according to the criterion already given, that

$$|t_c| > t_{\alpha/2,\nu} \qquad (8.1)$$

but in each case, $|t_c|$ (t_c is a quotient) is substantially larger than the tabulated t-value.

At the lower $100(1-\alpha) = 95\%$ level of significance, an additional effect, the 2-f.i. DE is judged significant.

In spite of the significance test, DE is not particularly plausible as a real effect. One of the reasons for this is that of the two component main-effects D and E of DE, only D is convincing as a real effect, E being rejected as such by t-test and by regression analysis. Another reason is that DE is only marginally significant at this lower level of significance, since the value of $|t_c| = 2.484$ is just larger than $t_{\alpha/2,\nu} = 2.447$.

As with the interpretation of the cobalt response, there was no evidence that any three-factor interaction was a probable real effect. On the assumption that the higher-order interactions are negligible or do not exist, the three-factor interactions were pooled in with the four and five-factor interactions to obtain an improved estimate of S.E.(effect).

All the 3-f.i., 4-f.i. and 5-f.i's were included, and a value of S.E.(3,4,5-f.i.) = 0.0673 with $\nu = 16$ d.o.f.

TABLE 8.4. Two-tailed t-tests for the nickel effects using S.E.(3,4,5-f.i.)

Effect Identity	Effect Value	$t_c = \frac{\text{Effect}}{\text{S.E.(Effect)}}$	$t_{0.005}$ $\nu = 16$	Significance at 99% Probability Level	$t_{0.025}$ $\nu = 16$	Significance at 95% Probability Level
Average	4.1331	-	-	-	-	-
A	0.0713	1.059	2.921	NS	2.120	NS
B	-4.3050	-63.997	2.921	S	2.120	S
AB	0.0175	0.260	2.921	NS	2.120	NS
C	1.2762	18.963	2.921	S	2.120	S
AC	0.0263	0.390	2.921	NS	2.120	NS
BC	-0.0800	-1.189	2.921	NS	2.120	NS
ABC	0.0375	0.557	2.921	NS	2.120	NS
D	-0.6163	-9.158	2.921	S	2.120	S
AD	-0.0963	-1.431	2.921	NS	2.120	NS
BD	0.4000	5.944	2.921	S	2.120	S
ABD	0.0025	0.037	2.921	NS	2.120	NS
CD	-0.3638	-5.408	2.921	S	2.120	S
ACD	-0.0638	-0.948	2.921	NS	2.120	NS
BCD	0.0375	0.557	2.921	NS	2.120	NS
ABCD	-0.0100	-0.149	2.921	NS	2.120	NS
E	-0.1250	-1.858	2.921	NS	2.120	NS
AE	-0.0875	-1.301	2.921	NS	2.120	NS
BE	0.0288	0.427	2.921	NS	2.120	NS
ABE	-0.1263	-1.877	2.921	NS	2.120	NS
CE	-0.0525	-0.780	2.921	NS	2.120	NS
ACE	0.0500	0.743	2.921	NS	2.120	NS
BCE	-0.1438	-2.137	2.921	NS	2.120	S
ABCE	-0.0238	-0.353	2.921	NS	2.120	NS
DE	0.1550	2.304	2.921	NS	2.120	S
ADE	-0.0425	-0.632	2.921	NS	2.120	NS
BDE	0.0063	0.093	2.921	NS	2.120	NS
ABDE	0.0013	0.019	2.921	NS	2.120	NS
CDE	-0.0350	-0.521	2.921	NS	2.120	NS
ACDE	0.0875	1.301	2.921	NS	2.120	NS
BCDE	0.0613	0.911	2.921	NS	2.120	NS
ABCDE	0.1063	1.579	2.921	NS	2.120	NS

S = Significant
NS = Non-significant

was obtained. From this estimate, an estimate of the standard error of an observation was calculated for the nickel response, giving a value of $\pm$0.190 g/L. These are the standard error values used in Table 8.1.

Tests of significance using S.E.(3,4,5-f.i.) are shown in Table 8.4. This set of t-tests produces an interpretation of the effects almost identical to those of Table 8.3.

At the 99% level of significance, the effects B, C, D, BD and CD are judged significant. At the lower 95% level of significance, in addition to these effects, the effects DE, and for the first time the three-factor interaction, BCE, are judged significant. DE is no more plausible than before as a real effect. BCE can almost certainly be regarded as not real, since it is very marginal in significance and also because a component 2-f.i. BC is not significant.

The Half-Normal Probability Plot

The H.N.P. plot for the nickel effects is given in Figure 8.1. On the basis of the plot, the effects B, C, D, BD and CD may certainly be judged real. It is difficult from the plot to be conclusive about the effects DE and BCE. DE appears to fall slightly off the selected line, while BCE, for which there is no marked position on the vertical scale since it is the 25th marked effect,

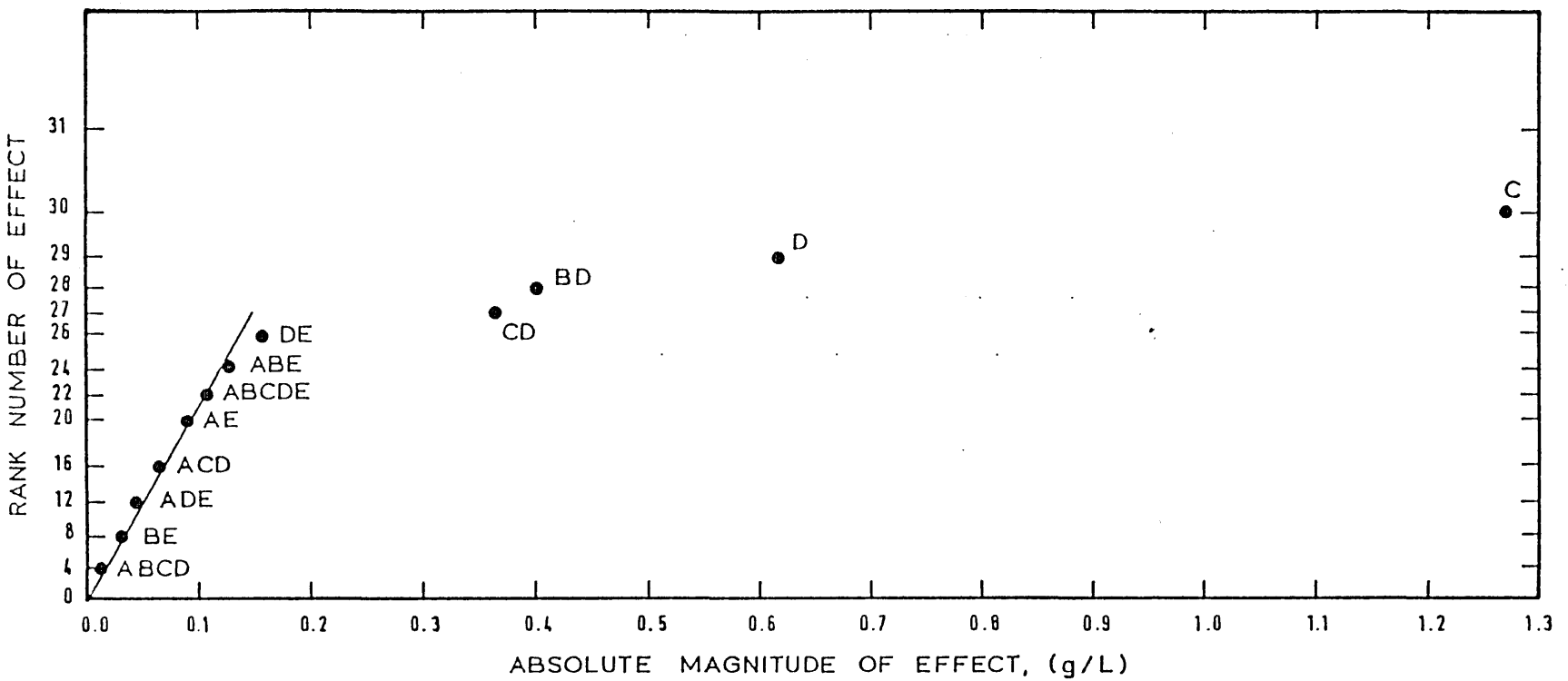


FIGURE 8.1. The half-normal probability plot for the nickel effects.

probably does also. This would judge them real effects. On the other hand, like the t-tests, the plot does not compel them to be so.

8.2 Regression Analysis of the Nickel Response

The combinations of variables included in the regression equations are shown in Table 8.5.

Initially, the response was regressed on the three factorial variables whose main-effects had already been judged significant in the earlier factorial analysis, the variables B, C and D. This is the model fitted in Computer Run 8, the information for which is given in Tables 8.6 and 8.7 and figures 8.2.a and 8.2.b.

TABLE 8.5. Variables Included in the Nickel Regression Runs

Computer Run	Terms included for		
	Variables	Two-factor Interactions	Three-factor Interactions
No. 8	B,C,D	-	-
9	A,B,C,D	-	-
10	B,C,D,E	-	-
11	B,C,D	BD	-
12	B,C,D	BD,CD	-
13	B,C,D	BC,BD,CD	-
14	B,C,D	BD,CD	BCD
15	B,C,D,E	BD,CD,DE	-

THE REGRESSION EQUATION IS
Y = 4.13 - 2.15 X1 + .638 X2
- .308 X3

	COLUMN	COEFFICIENT	ST. DEV. OF COEF.	T-RATIO = COEF/S.D.
	--	4.13312	0.06249	66.14
X1	INIT.CO	-2.15250	0.06249	-34.45
X2	INIT.NI	0.63812	0.06249	10.21
X3	EQU.TEMP	-0.30812	0.06249	-4.93

THE ST. DEV. OF Y ABOUT REGRESSION LINE IS
S = 0.3535
WITH (32- 4) = 28 DEGREES OF FREEDOM

R-SQUARED = 97.9 PERCENT
R-SQUARED = 97.7 PERCENT, ADJUSTED FOR D.F.

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF
REGRESSION	3	164.3328	54.7776
RESIDUAL	28	3.4989	0.1250
TOTAL	31	167.8317	

FURTHER ANALYSIS OF VARIANCE
SS EXPLAINED BY EACH VARIABLE WHEN ENTERED IN THE ORDER GIVEN

DUE TO	DF	SS
REGRESSION	3	164.3328
INIT.CO	1	148.2642
INIT.NI	1	13.0305
EQU.TEMP	1	3.0381

TABLE 8.6. Statistical output from Computer Run 8. Regression model including variables B, C and D.

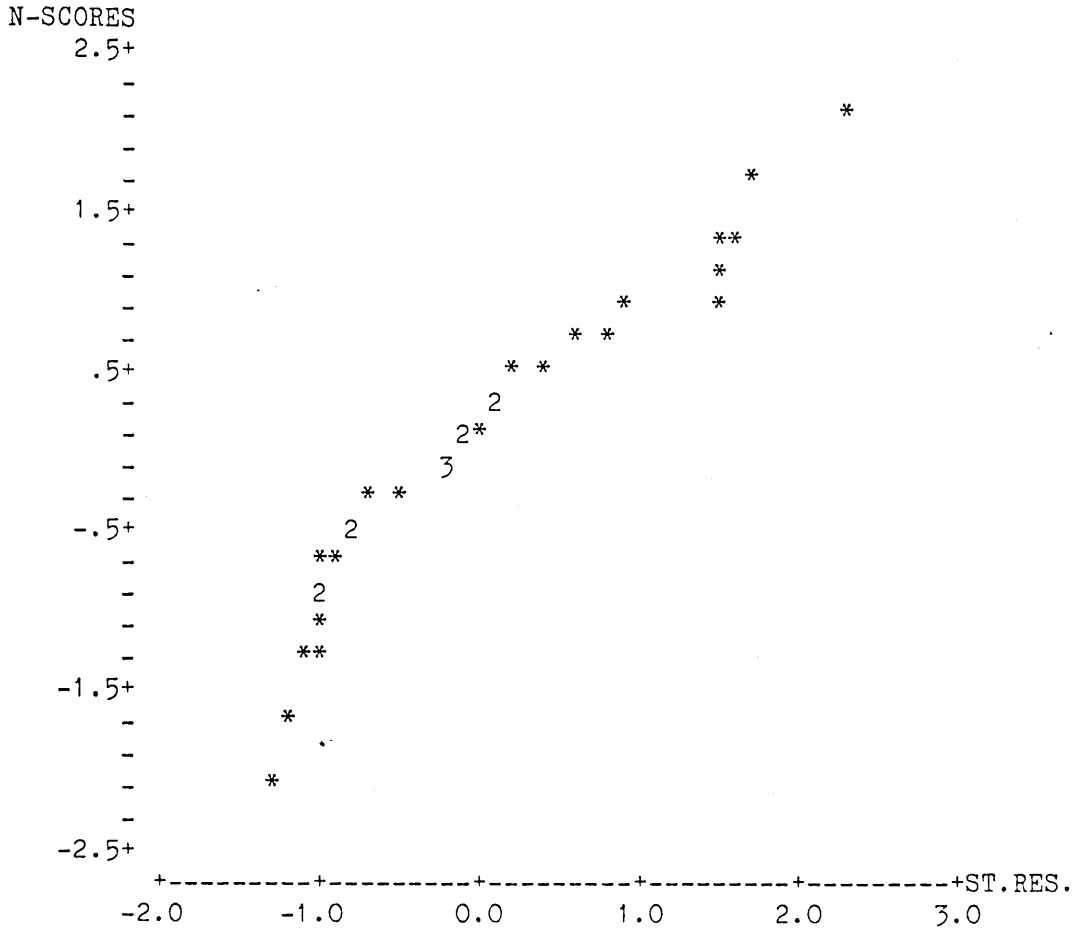


Figure (A)

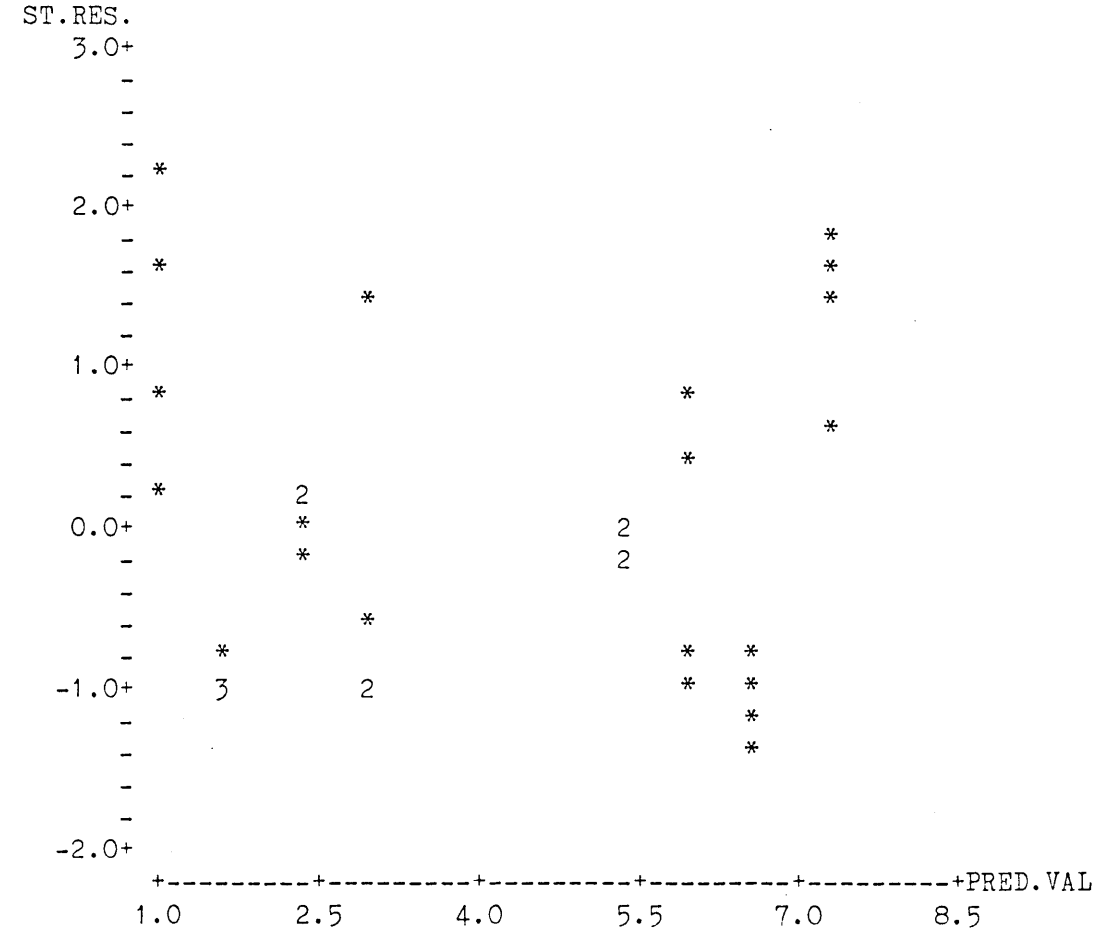


Figure (B)

FIGURES 8.2.a and 8.2.b. Diagnostic plots for model fitted in Computer Run 8.

Init.pH	Init.Co	Init.Ni	Equ.T	Na2SO4	y	$\hat{y}$	S.D.$\hat{y}$.	Resid,d	S.D.d.	Std.Res
-1	-1	-1	-1	-1	6.100	5.956	0.125	.144	.336	.437
+1	-1	-1	-1	-1	6.220	5.956	0.125	.264	.336	.800
-1	+1	-1	-1	-1	1.320	1.651	0.125	-.331	.336	-1.000
+1	+1	-1	-1	-1	1.370	1.651	0.125	-.281	.336	-.849
-1	-1	+1	-1	-1	7.720	7.232	0.125	.488	.336	1.476
+1	-1	+1	-1	-1	7.740	7.232	0.125	.508	.336	1.537
-1	+1	+1	-1	-1	2.760	2.927	0.125	-.167	.336	-.505
+1	+1	+1	-1	-1	3.420	2.927	0.125	.493	.336	1.491
-1	-1	-1	+1	-1	5.260	5.339	0.125	-.079	.336	-.240
+1	-1	-1	+1	-1	5.340	5.339	0.125	.001	.336	.002
-1	+1	-1	+1	-1	1.080	1.034	0.125	.046	.336	.138
+1	+1	-1	+1	-1	1.560	1.034	0.125	.526	.336	1.590
-1	-1	+1	+1	-1	6.340	6.616	0.125	-.276	.336	-.834
+1	-1	+1	+1	-1	6.180	6.616	0.125	-.436	.336	-1.317
-1	+1	+1	+1	-1	2.350	2.311	0.125	.039	.336	.119
+1	+1	+1	+1	-1	2.370	2.311	0.125	.059	.336	.180
-1	-1	-1	-1	+1	5.620	5.956	0.125	-.336	.336	-1.015
+1	-1	-1	-1	+1	5.720	5.956	0.125	-.236	.336	-.713
-1	+1	-1	-1	+1	1.290	1.651	0.125	-.361	.336	-1.091
+1	+1	-1	-1	+1	1.330	1.651	0.125	-.321	.336	-.970
-1	-1	+1	-1	+1	7.430	7.232	0.125	.198	.336	.599
+1	-1	+1	-1	+1	7.800	7.232	0.125	.568	.336	1.718
-1	+1	+1	-1	+1	2.620	2.927	0.125	-.307	.336	-.928
+1	+1	+1	-1	+1	2.600	2.927	0.125	-.327	.336	-.989
-1	-1	-1	+1	+1	5.320	5.339	0.125	-.019	.336	-.059
+1	-1	-1	+1	+1	5.280	5.339	0.125	-.059	.336	-.180
-1	+1	-1	+1	+1	1.790	1.034	0.125	.756	.336	2.285
+1	+1	-1	+1	+1	1.320	1.034	0.125	.286	.336	.864
-1	-1	+1	+1	+1	6.280	6.616	0.125	-.336	.336	-1.015
+1	-1	+1	+1	+1	6.220	6.616	0.125	-.396	.336	-1.196
-1	+1	+1	+1	+1	2.280	2.311	0.125	-.031	.336	-.093
+1	+1	+1	+1	+1	2.230	2.311	0.125	-.081	.336	-.244

TABLE 8.7. Residuals and predicted response values for model fitted in Computer Run 8.

The regression parameters for B, C and D are respectively $\beta' = -2.153$, $\beta' = 0.638$ and $\beta' = -0.308$, and each parameter obviously measures a real change in the response, whether judged by inspection or significance test.

The obtained value of $R^2 = 97.9\%$ indicates that the model gives a comparatively good fit. However, the diagnostic plots suggest that the model has some systematic lack of fit. The normal plot of residuals does not give a straight line, and the plot of residuals versus $\hat{y}$ values shows that the residuals are not randomly distributed over the response range. Nevertheless, all three variables are obviously significant and each was retained in the model.

As in the factorial analysis, variable A was judged to be non-significant. Its introduction into the model in Computer Run 9 did not result in an improvement in fit. A value of $R^2 = 97.9\%$ was obtained, and the diagnostic plots show some systematic lack of fit. The fitted regression parameter for A was $\beta' = 0.036$. A was not retained in the model.

Variable E was also judged to be non-significant, as in the factorial analysis. With its introduction into the model in Computer Run 10, there was no substantial improvement in fit, either in the R^2 value of 98.0%, or in the diagnostic plots. The fitted regression parameter for E was $\beta' = -0.063$. Variable E was not retained in the model.

The two-factor interaction BD was judged to be significant, as in the factorial analysis. Its introduction into the model in Computer Run 10 resulted in a definite improvement in fit, giving a value of R^2 = 98.7%. Some improvement was also evident in the diagnostic plots. The regression parameter for BD was $\beta' = 0.200$. BD was retained in the model.

The two-factor interaction CD, which had been judged significant in the factorial analysis, was also found significant in the regression analysis. On its introduction into the model in Computer Run 12, there was again an increase in fit, as can be seen from Tables 8.8 and 8.9 and Figures 8.3.a and 8.3.b. An increase in R^2 to 99.3% was observed, and the diagnostic plots look better than in the previous runs. In particular, the plot of residuals versus $\hat{y}$ values showed a more random distribution of residuals. The fitted regression parameter for CD was $\beta' = -0.182$. CD was retained in the regression model.

The 2-f.i. BC was judged to be non-significant, as in the factorial analysis. There was no improvement in fit on its introduction into the model in Computer Run 13. A value of R^2 = 99.3% was obtained, and the regression parameter for BC was $\beta' = -0.040$.

The three-factor interaction BCD might be expected to be a real effect, as it is an interaction between three significant variables. It was introduced into the model

THE REGRESSION EQUATION IS
Y = 4.13 - 2.15 X1 + .638 X2
- .308 X3 + .200 X4 - .182 X5

	COLUMN	COEFFICIENT	ST. DEV. OF COEF.	T-RATIO = COEF/S.D.
	--	4.13312	0.03735	110.67
X1	INIT.CO	-2.15250	0.03735	-57.64
X2	INIT.NI	0.63812	0.03735	17.09
X3	EQU.TEMP	-0.30812	0.03735	-8.25
X4	CO*TEMP	0.20000	0.03735	5.36
X5	NI*TEMP	-0.18187	0.03735	-4.87

THE ST. DEV. OF Y ABOUT REGRESSION LINE IS
S = 0.2113
WITH (32- 6) = 26 DEGREES OF FREEDOM

R-SQUARED = 99.3 PERCENT
R-SQUARED = 99.2 PERCENT, ADJUSTED FOR D.F.

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF
REGRESSION	5	166.6713	33.3343
RESIDUAL	26	1.1603	0.0446
TOTAL	31	167.8317	

FURTHER ANALYSIS OF VARIANCE
SS EXPLAINED BY EACH VARIABLE WHEN ENTERED IN THE ORDER GIVEN

DUE TO	DF	SS
REGRESSION	5	166.6713
INIT.CO	1	148.2642
INIT.NI	1	13.0305
EQU.TEMP	1	3.0381
CO*TEMP	1	1.2800
NI*TEMP	1	1.0585

TABLE 8.8. Statistical output from Computer Run 12. Regression model including variables B, C and D and interactions BD and CD.

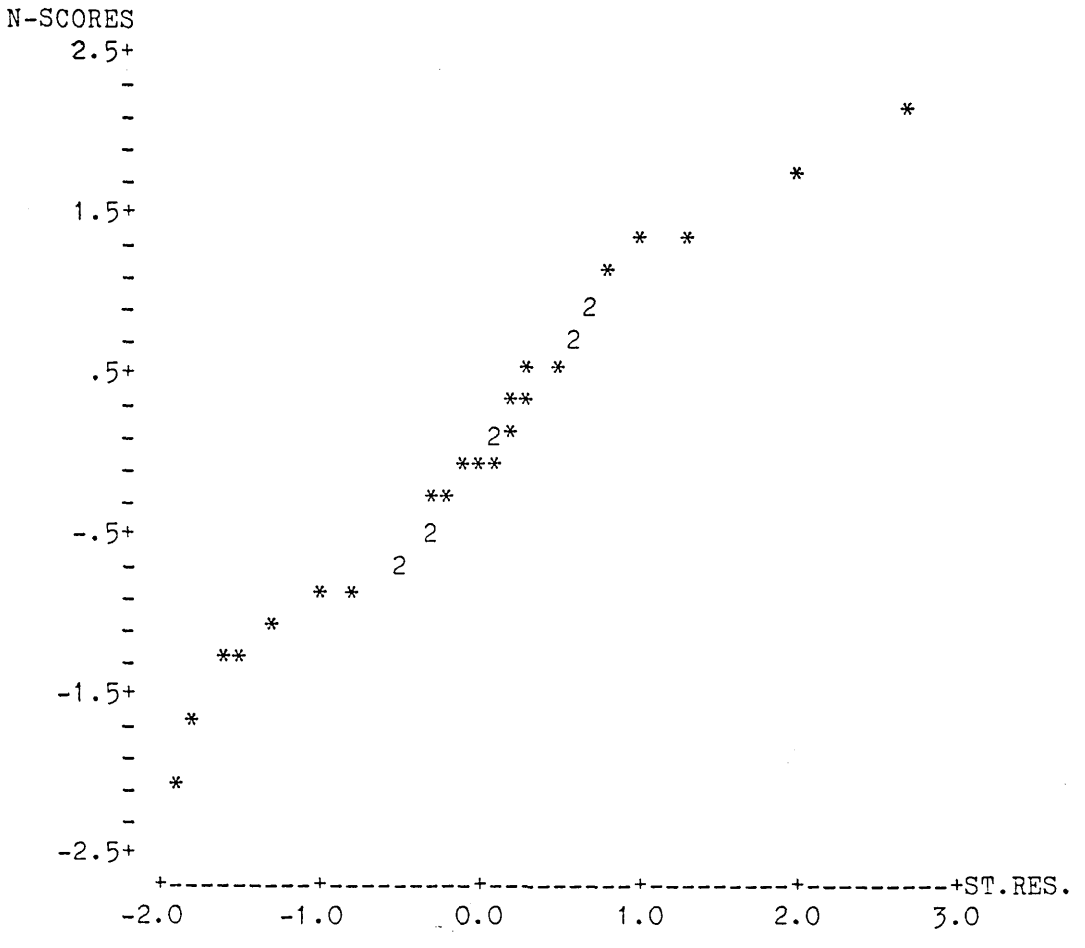


Figure (A)

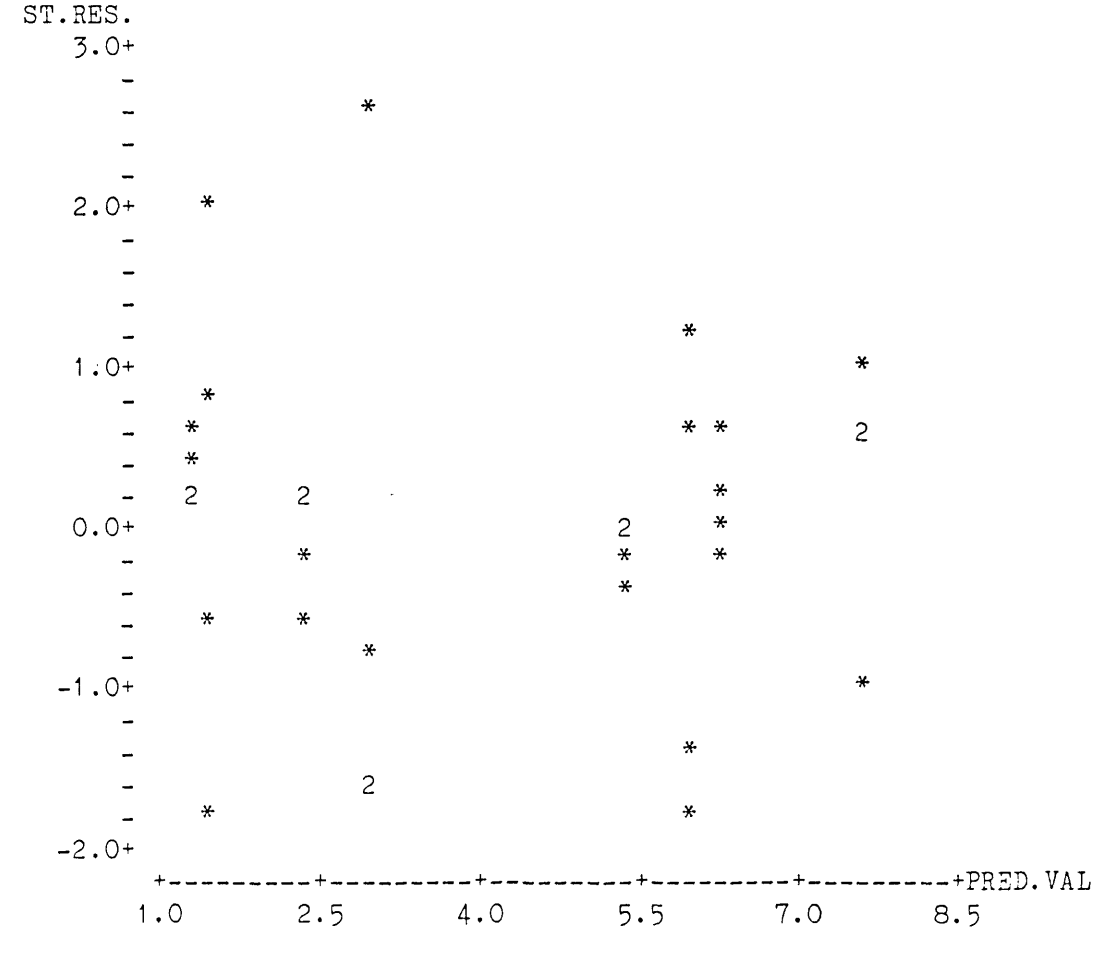


Figure (B)

FIGURES 8.3.a and 8.3.b. Diagnostic plots for model fitted in Computer Run 12.

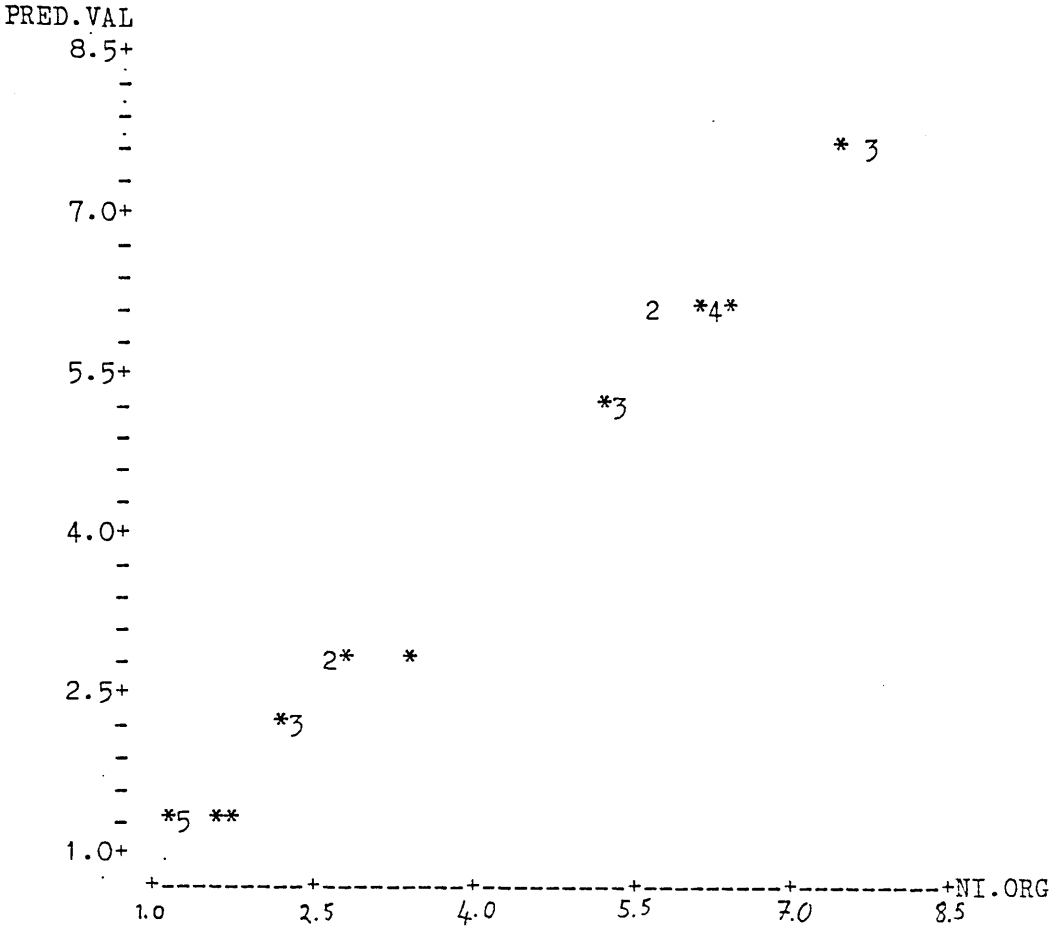


FIGURE 8.4. Plot of predicted versus measured nickel response for model including B, C, D, BD and CD (Computer Run 12).

Init.pH	Init.Co	Init.Ni	Equ.T	Na2SO4	y	$\hat{y}$	S.D.$\hat{y}$.	Resid,d	S.D.d.	Std.Res
-1	-1	-1	-1	-1	6.100	5.974	0.092	.126	.193	.663
+1	-1	-1	-1	-1	6.220	5.974	0.092	.246	.193	1.293
-1	+1	-1	-1	-1	1.320	1.269	0.092	.051	.193	.269
+1	+1	-1	-1	-1	1.370	1.269	0.092	.101	.193	.532
-1	-1	+1	-1	-1	7.720	7.614	0.092	.106	.193	.558
+1	-1	+1	-1	-1	7.740	7.614	0.092	.126	.193	.663
-1	+1	+1	-1	-1	2.760	2.909	0.092	-.149	.193	-.781
+1	+1	+1	-1	-1	3.420	2.909	0.092	.511	.193	2.685
-1	-1	-1	+1	-1	5.260	5.321	0.092	-.061	.193	-.322
+1	-1	-1	+1	-1	5.340	5.321	0.092	.019	.193	.098
-1	+1	-1	+1	-1	1.080	1.416	0.092	-.336	.193	-1.766
+1	+1	-1	+1	-1	1.560	1.416	0.092	.144	.193	.755
-1	-1	+1	+1	-1	6.340	6.234	0.092	.106	.193	.558
+1	-1	+1	+1	-1	6.180	6.234	0.092	-.054	.193	-.282
-1	+1	+1	+1	-1	2.350	2.329	0.092	.021	.193	.112
+1	+1	+1	+1	-1	2.370	2.329	0.092	.041	.193	.217
-1	-1	-1	-1	+1	5.620	5.974	0.092	-.354	.193	-1.858
+1	-1	-1	-1	+1	5.720	5.974	0.092	-.254	.193	-1.333
-1	+1	-1	-1	+1	1.290	1.269	0.092	.021	.193	.112
+1	+1	-1	-1	+1	1.330	1.269	0.092	.061	.193	.322
-1	-1	+1	-1	+1	7.430	7.614	0.092	-.184	.193	-.965
+1	-1	+1	-1	+1	7.800	7.614	0.092	.186	.193	.978
-1	+1	+1	-1	+1	2.620	2.909	0.092	-.289	.193	-1.516
+1	+1	+1	-1	+1	2.600	2.909	0.092	-.309	.193	-1.621
-1	-1	-1	+1	+1	5.320	5.321	0.092	-.001	.193	-.007
+1	-1	-1	+1	+1	5.280	5.321	0.092	-.041	.193	-.217
-1	+1	-1	+1	+1	1.790	1.416	0.092	.374	.193	1.963
+1	+1	-1	+1	+1	1.320	1.416	0.092	-.096	.193	-.505
-1	-1	+1	+1	+1	6.280	6.234	0.092	.046	.193	.243
+1	-1	+1	+1	+1	6.220	6.234	0.092	-.014	.193	-.072
-1	+1	+1	+1	+1	2.280	2.329	0.092	-.049	.193	-.256
+1	+1	+1	+1	+1	2.230	2.329	0.092	-.099	.193	-.519

TABLE 8.9. Residuals and predicted response values for model fitted in Computer Run 12.

in Computer Run 14. As in the factorial analysis, it was judged to be non-significant.

For completeness, the two-factor introduction DE was considered, since it was judged to be on the borderline of significance in the statistical analysis. Since E is a component of DE, a term for E was also included.

As with the earlier analysis, it was not possible to be confident that DE is a real effect. With its introduction in computer Run 15, there was probably no increase in fit, although R^2 was increased to 99.5%. The regression parameter for DE, $\beta' = 0.078$ was not significant at the 99% level of significance when submitted to a t-test ($t_{calc} = 2.34$, $t_{\alpha/2=0.005} = 2.807$), and the diagnostic plots do not suggest any improvement in fit over runs 12-14. The estimated value of the standard deviation of $\hat{y}$ of 0.094 is slightly larger than that of the best value, obtained in Computer Run 12.

While on the presented evidence DE is not considered a real effect, the possibility that it is should be borne in mind when any further experimental data is interpreted.

Regression Conclusions

All the entertained models describe the data moderately well. The model which is considered to provide the best fit for the data set is that fitted in Computer Run 12. As with the cobalt response, this is the model which includes terms for the variables B,C,D,BD and CD.

This model gives a high multiple correlation coefficient while being economical in the number of terms used. It has good homogeneity and normality of residuals. Also, it has the smallest predicted standard deviation of $\hat{y}$ of the models considered.

Thus, on the present data, the regression equation which best describes the response behaviour, strictly within the ranges of the variables studied and under the present conditions of experimentation, is:

$$\hat{y} = 4.13 - 2.15X_1 + 0.638X_2 - 0.308X_3 + 0.200X_4 - 0.182X_5 \qquad (8.2)$$

where $\hat{y}$ is the predicted value of the equilibrium organic nickel concentration, and the coded variables $X_1, X_2 \ldots, X_5$ correspond to the natural variables B, C,...,CD as follows:

$X_1 \rightarrow$ B
$X_2 \rightarrow$ C
$X_3 \rightarrow$ D
$X_4 = X_1X_3 \rightarrow$ BD
$X_5 = X_2X_3 \rightarrow$ CD

The coded variables are related to the natural variables by the following equations:

$$X_1 = \frac{x_1 - 17.5}{7.5} \qquad (8.3)$$

$$X_2 = \frac{x_2 - 35}{15} \tag{8.4}$$

$$X_3 = \frac{x_3 - 338}{15} \tag{8.5}$$

where x_1, x_2 and x_3 are the initial aqueous cobalt concentration (g/L), the initial aqueous nickel concentration (g/L) and the equilibrium temperature (degrees K) respectively.

The plot of the predicted versus the measured value of the response for this model is shown in Figure 8.4.

8.3 Statistical Conclusions for the Nickel Study

It is concluded that of the factors studied, those which have a real influence on the response Equilibrium Organic Nickel Concentration are the factors B, C and D. There are real two-factor interactions between B and D, and between C and D. The factors can be identified in Table 8.10.

TABLE 8.10. Real Factors for the Nickel Response.

Factor or Interaction	Identity	Effect Value (g/L)
B	Initial aqueous cobalt concentration	-4.31
C	Initial aqueous nickel concentration	+1.27
D	Equilibrium temperature	-0.62
BD	Two-factor interaction between B and D	+0.40
CD	Two-factor interaction between C and D	-0.36

CHAPTER 9

A STATISTICAL STUDY OF THE EQUILIBRIUM pH RESPONSE

9.1 Factorial Analysis

Calculation and Inspection of the Effects

The effects are given in standard or Yates's order in Table 9.1 and in order of absolute magnitude in Table 9.2. They were calculated using the computer program FACEXP.

The first value in the effects column of Table 9.1 is $\bar{y}_{pH}$, the average value of the response over all the treatments. A value of $\bar{y}_{pH} = 5.116$ was obtained.

At first sight the significant effects seem to be the main-effects C and D, and the two-factor interaction CD. This is so because they are the three largest effects in magnitude, and the interaction is composed of the two main-effects.

With the possible exception of A, none of the other effects look particularly plausible as real effects, since no coherent pattern emerges from amongst the larger of them. Also, as the effects are in the units of the response, their sizes suggest that they exert little influence on the response.

Significance Testing of the Effects

As before, an estimate of S.E.(effect) was obtained on the assumption that higher-order interactions are negligible or do not exist.

TABLE 9.1. Calculated effects for the response:equilibrium pH

Treatment Code	Response (pH units)	Estimated Effect	Identity
L	5.46 ± 0.122	5.1163	Average
a	5.52 ± 0.122	0.0875 ± 0.0431	A
b	5.28 ± 0.122	0.0113 ± 0.0431	B
ab	5.35 ± 0.122	0.0513 ± 0.0431	AB
c	5.20 ± 0.122	-0.2688 ± 0.0431	C
ac	5.17 ± 0.122	0.0038 ± 0.0431	AC
bc	4.82 ± 0.122	0.0700 ± 0.0431	BC
abc	5.20 ± 0.122	-0.0375 ± 0.0431	ABC
d	5.03 ± 0.122	-0.2063 ± 0.0431	D
ad	4.96 ± 0.122	-0.0163 ± 0.0431	AD
bd	4.73 ± 0.122	0.0675 ± 0.0431	BD
abd	5.18 ± 0.122	0.0475 ± 0.0431	ABD
cd	4.89 ± 0.122	0.1650 ± 0.0431	CD
acd	4.81 ± 0.122	-0.0425 ± 0.0431	ACD
bcd	5.06 ± 0.122	0.0388 ± 0.0431	BCD
abcd	5.06 ± 0.122	-0.0238 ± 0.0431	ABCD
e	5.46 ± 0.122	0.0175 ± 0.0431	E
ae	5.48 ± 0.122	-0.0100 ± 0.0431	AE
be	5.43 ± 0.122	0.0563 ± 0.0431	BE
abe	5.51 ± 0.122	-0.0763 ± 0.0431	ABE
ce	4.67 ± 0.122	-0.1063 ± 0.0431	CE
ace	5.02 ± 0.122	0.0338 ± 0.0431	ACE
bce	5.02 ± 0.122	0.0075 ± 0.0431	BCE
abce	4.92 ± 0.122	-0.0325 ± 0.0431	ABCE
de	5.18 ± 0.122	0.0788 ± 0.0431	DE
ade	5.15 ± 0.122	0.0063 ± 0.0431	ADE
bde	5.10 ± 0.122	-0.0625 ± 0.0431	BDE
abde	5.19 ± 0.122	0.0250 ± 0.0431	ABDE
cde	4.85 ± 0.122	0.0225 ± 0.0431	CDE
acde	4.92 ± 0.122	0.0425 ± 0.0431	ACDE
bcde	4.98 ± 0.122	-0.0238 ± 0.0431	BCDE
abcde	5.12 ± 0.122	0.0813 ± 0.0431	ABCDE

TABLE 9.2. Ranked absolute values of pH effects

Order	Effect	Absolute Value	Effect Sign
1	C	0.269	-
2	D	0.206	-
3	CD	0.165	+
4	CE	0.106	-
5	A	0.0875	+
6	ABCDE	0.0813	+
7	DE	0.0788	+
8	ABE	0.0763	-
9	BC	0.0700	+
10	BD	0.0675	-
11	BDE	0.0625	-
12	BE	0.0563	+
13	AB	0.0513	+
14	ABD	0.0475	+
15/16	ACD/ACDE	0.0425	-/+
17	BCD	0.0388	+
18	ABC	0.0375	-
19	ACE	0.0338	+
20	ABCE	0.0325	-
21	ABDE	0.0250	+
22/23	BCDE/ABCD	0.0238	-/-
24	CDE	0.0225	+
25	E	0.0175	+
26	AD	0.0163	-
27	B	0.0113	+
28	AE	0.0100	-
29	BCE	0.00750	+
30	ADE	0.00625	+
31	AC	0.00375	+

The t-tests of the effects are identical in nature to those for the other responses.

For the t-tests in Table 9.3, an estimate of S.E.(effect) was obtained from the 4-f.i.'s and 5-f.i.'s. A value of S.E.(4,5-f.i.) = 0.04324 pH units with $\nu = 6$ d.o.f. was found.

According to these t-tests, three effects are judged significant, the main-effects C and D, and the 2-f.i. CD. This is so whichever level of significance is accepted. None of the other effects are significant, except the 2-f.i. CE, which is just significant at the lower level of significance.

As with the other responses, since there was no evidence of any real three-factor interaction, the 3-f.i.'s were pooled with the 4 and 5-f.i.'s to obtain a new estimate of S.E.(effect), S.E.(3,4,5-f.i.). All of the 3, 4 and 5-f.i.'s were included, giving a value of S.E.(3,4,5-f.i.) = 0.0431 pH units with $\nu = 16$ d.o.f. From this estimate of S.E.(effect) an estimate was calculated of S.E.(observation) for the pH response, and this is the value used in Table 9.1. Tests of significance using S.E.(3,4,5-f.i.) are shown in Table 9.4.

At the 99% level of significance the effects C, D and CD are judged significant, as before.

At the lower 95% level of significance, in addition to these effects, the 2-f.i. CE is judged significant, and the main-effect A is near significance. Of the two

TABLE 9.3. Two-tailed t-tests for the pH effects using S.E.(4,5-f.i.)

Effect Identity	Effect Value	$t_c = \frac{\text{Effect}}{\text{S.E.(Effect)}}$	$t_{0.005}$ $\nu = 6$	Significance at 99% Probability Level	$t_{0.025}$ $\nu = 6$	Significance at 95% Probability Level
Average	5.1163	-	-	-	-	-
A	0.0875	2.024	3.707	NS	2.447	NS
B	0.0113	0.261	3.707	NS	2.447	NS
AB	0.0513	1.185	3.707	NS	2.447	NS
C	-0.2688	-6.213	3.707	S	2.447	S
AC	0.0038	0.087	3.707	NS	2.447	NS
BC	0.0700	1.619	3.707	NS	2.447	NS
ABC	-0.0375	-0.867	3.707	NS	2.447	NS
D	-0.2063	-4.764	3.707	S	2.447	S
AD	-0.0163	-0.376	3.707	NS	2.447	NS
BD	0.0675	1.561	3.707	NS	2.447	NS
ABD	0.0475	1.099	3.707	NS	2.447	NS
CD	0.1650	3.817	3.707	S	2.447	S
ACD	-0.0425	-0.983	3.707	NS	2.447	NS
BCD	0.0388	0.896	3.707	NS	2.447	NS
ABCD	-0.0238	-0.549	3.707	NS	2.447	NS
E	0.0175	0.405	3.707	NS	2.447	NS
AE	-0.0100	-0.231	3.707	NS	2.447	NS
BE	0.0563	1.301	3.707	NS	2.447	NS
ABE	-0.0763	-1.764	3.707	NS	2.447	NS
CE	-0.1063	-2.457	3.707	NS	2.447	S
ACE	0.0338	0.781	3.707	NS	2.447	NS
BCE	0.0075	0.173	3.707	NS	2.447	NS
ABCE	-0.0325	-0.752	3.707	NS	2.447	NS
DE	0.0788	1.821	3.707	NS	2.447	NS
ADE	0.0063	0.145	3.707	NS	2.447	NS
BDE	-0.0625	-1.445	3.707	NS	2.447	NS
ABDE	0.0250	0.578	3.707	NS	2.447	NS
CDE	0.0225	0.520	3.707	NS	2.447	NS
ACDE	0.0425	0.983	3.707	NS	2.447	NS
BCDE	-0.0238	-0.549	3.707	NS	2.447	NS
ABCDE	0.0813	1.879	3.707	NS	2.447	NS

S = Significant
NS = Non-significant

TABLE 9.4. Two-tailed t-tests for the pH effects using S.E.(3,4,5-f.i.)

Effect Identity	Effect Value	$t_c = \frac{\text{Effect}}{\text{S.E.(Effect)}}$	$t_{0.005}$ $\nu = 16$	Significance at 99% Probability Level	$t_{0.025}$ $\nu = 16$	Significance at 95% Probability Level
Average	5.1163	-	-	-	-	-
A	0.0875	2.033	2.921	NS	2.120	NS
B	0.0113	0.263	2.921	NS	2.120	NS
AB	0.0513	1.192	2.921	NS	2.120	NS
C	0.2688	6.244	2.921	S	2.120	S
AC	0.0038	0.088	2.921	NS	2.120	NS
BC	0.0700	1.626	2.921	NS	2.120	NS
ABC	-0.0375	-0.871	2.921	NS	2.120	NS
D	-0.2063	-4.792	2.921	S	2.120	S
AD	-0.0163	-0.379	2.921	NS	2.120	NS
BD	0.0675	1.568	2.921	NS	2.120	NS
ABD	0.0475	1.103	2.921	NS	2.120	NS
CD	0.1650	3.833	2.921	S	2.120	S
ACD	-0.0425	-0.987	2.921	NS	2.120	NS
BCD	0.0388	0.901	2.921	NS	2.120	NS
ABCD	-0.0238	-0.553	2.921	NS	2.120	NS
E	0.0175	0.407	2.921	NS	2.120	NS
AE	-0.0100	-0.232	2.921	NS	2.120	NS
BE	0.0563	1.308	2.921	NS	2.120	NS
ABE	-0.0763	-1.772	2.921	NS	2.120	NS
CE	-0.1063	-2.469	2.921	NS	2.120	S
ACE	0.0338	0.785	2.921	NS	2.120	NS
BCE	0.0075	0.174	2.921	NS	2.120	NS
ABCE	-0.0325	-0.754	2.921	NS	2.120	NS
DE	0.0788	1.831	2.921	NS	2.120	NS
ADE	0.0063	0.146	2.921	NS	2.120	NS
BDE	-0.0625	-1.452	2.921	NS	2.120	NS
ABDE	0.0250	0.581	2.921	NS	2.120	NS
CDE	0.0225	0.522	2.921	NS	2.120	NS
ACDE	0.0425	0.987	2.921	NS	2.120	NS
BCDE	-0.0238	-0.553	2.921	NS	2.120	NS
ABCDE	0.0813	1.889	2.921	NS	2.120	NS

S = Significant
NS = Non-significant.

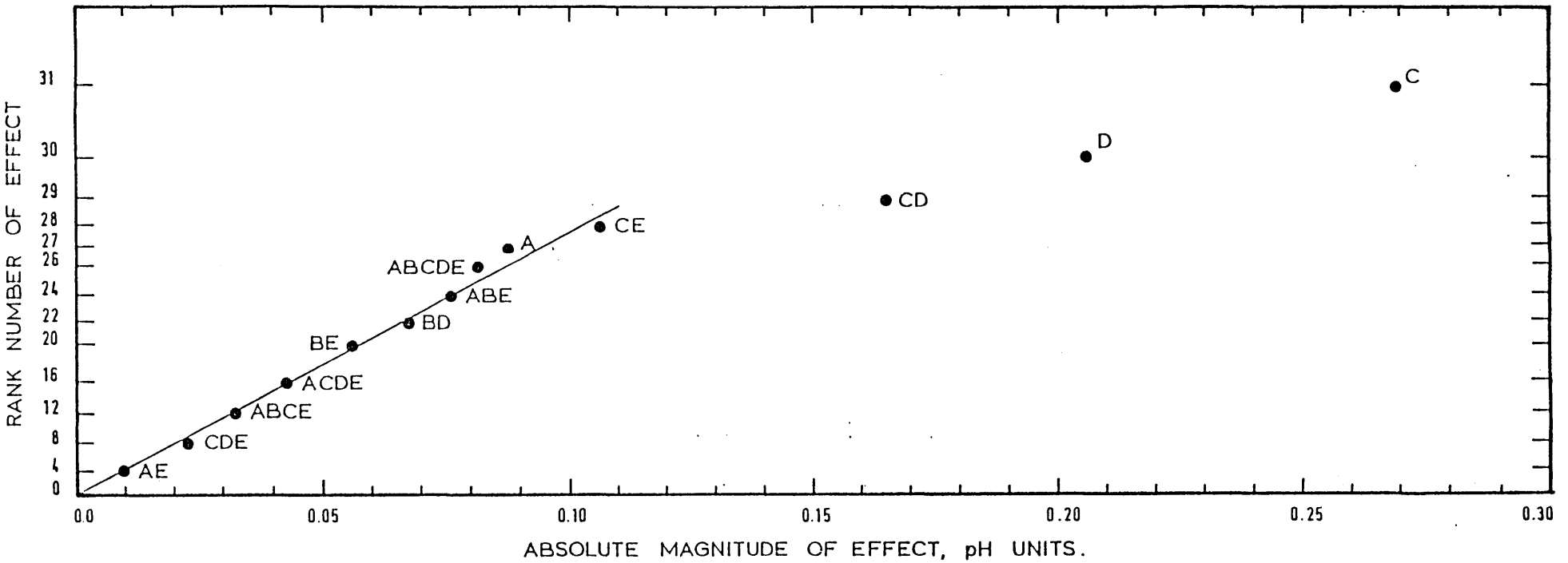


FIGURE 9.1. The half-normal probability plot for the equilibrium pH effects.

effect estimates, CE is the larger but A is more plausible as a real effect, being the main-effect of the variable initial pH.

The Half-Normal Probability Plot

The H.N.P. plot for the equilibrium pH effects is given in Figure 9.1. On the basis of the plot, the effects C, D and CD may certainly be judged real.

It is difficult from the plot to be conclusive about the effect CE, since the judgement depends rather finely on the placing of the line. With the line chosen as best, CE is probably not real.

On the basis of the plot there is no difficulty about A. With any acceptable line, A would be judged not real.

9.2 Regression Analysis of the Equilibrium pH Response

The combinations of variables included in the regression equations are shown in Table 9.5.

Initially, the response was regressed on the two factorial variables C and D, whose main-effects had already been judged firmly significant in the factorial analysis. This was the model fitted in Computer Run 16. Information about this regression can be found in Tables 9.6 and 9.7 and Figures 9.2.a, 9.2.b and 9.2.c.

TABLE 9.5 Variables Included in the Equilibrium pH Regression Runs.

Computer Run	Terms Included for			Response
	Variables	Two-Factor Interactions	Three-Factor Interactions	
16	C,D		-	equilibrium pH
17	C,D	CD	-	equilibrium pH
18	A,C,D	CD	-	equilibrium pH
19	A,B,C,D	CD	-	equilibrium pH
20	A,C,D,E	CD	-	equilibrium pH
21	A,C,D	AC,CD	-	equilibrium pH
22	A,C,D	AD,CD	-	equilibrium pH
23	A,C,D	CD	-	$\{H^+\}$

The fitted regression parameter for variable C was $\beta' = -0.134$. As always, the effects have the same units as the original response, so the presence of the β' parameter for C in the regression equation decreases the predicted value of the equilibrium pH, $\hat{y}$, by an average of 2 x 0.134 pH units in going from the low to the high level of variable C.

This suggests that variable C is a real effect. Variable C is also judged to be a real effect if its regression parameter is subjected to a t-test.

THE REGRESSION EQUATION IS
Y = 5.12 - .134 X1 - .103 X2

	COLUMN	COEFFICIENT	ST. DEV. OF COEF.	T-RATIO = COEF/S.D.
	--	5.11625	0.02908	175.95
X1	INIT.NI	-0.13437	0.02908	-4.62
X2	EQU.TEMP	-0.10312	0.02908	-3.55

THE ST. DEV. OF Y ABOUT REGRESSION LINE IS
S = 0.1645
WITH (32- 3) = 29 DEGREES OF FREEDOM

R-SQUARED = 53.9 PERCENT
R-SQUARED = 50.7 PERCENT, ADJUSTED FOR D.F.

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF
REGRESSION	2	0.91812	0.45906
RESIDUAL	29	0.78463	0.02706
TOTAL	31	1.70275	

FURTHER ANALYSIS OF VARIANCE
SS EXPLAINED BY EACH VARIABLE WHEN ENTERED IN THE ORDER GIVEN

DUE TO	DF	SS
REGRESSION	2	0.91812
INIT.NI	1	0.57781
EQU.TEMP	1	0.34031

TABLE 9.6. Statistical output from Computer Run 16. Regression model including variables C and D.

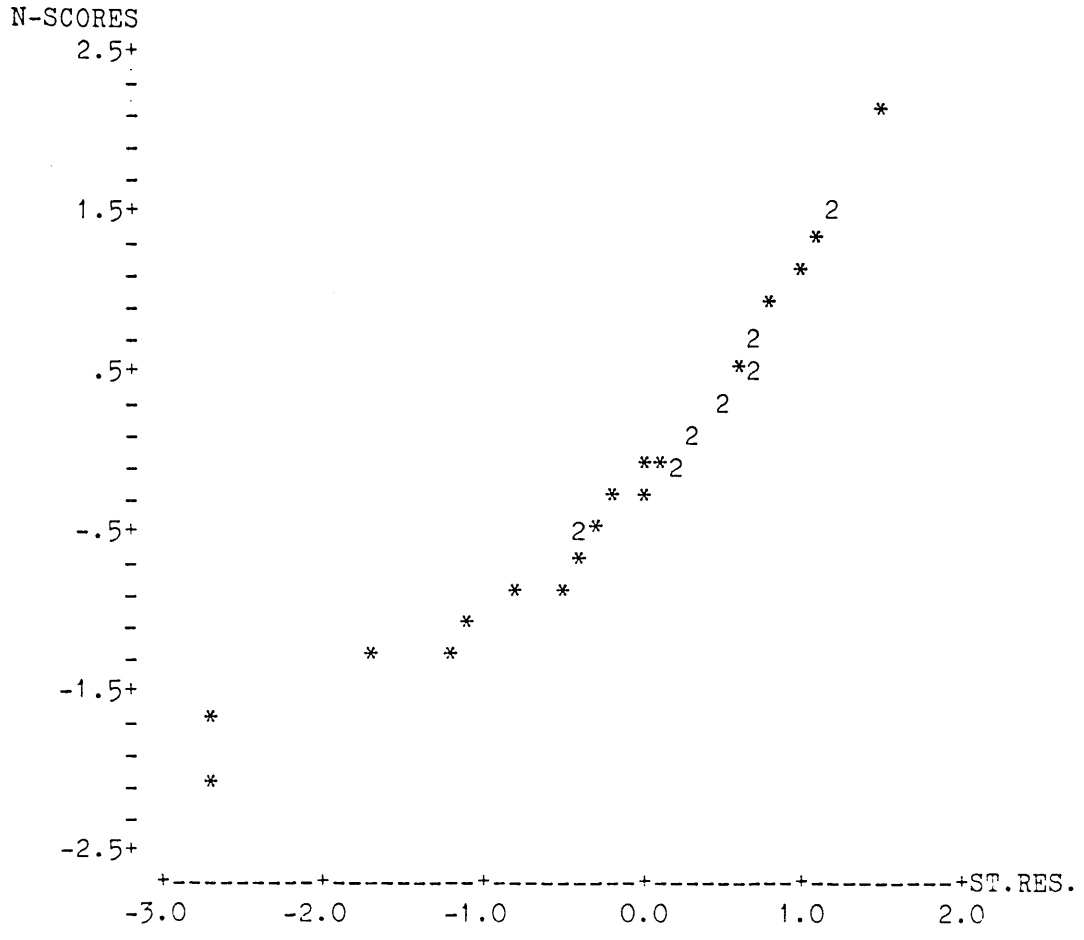


Figure (A)

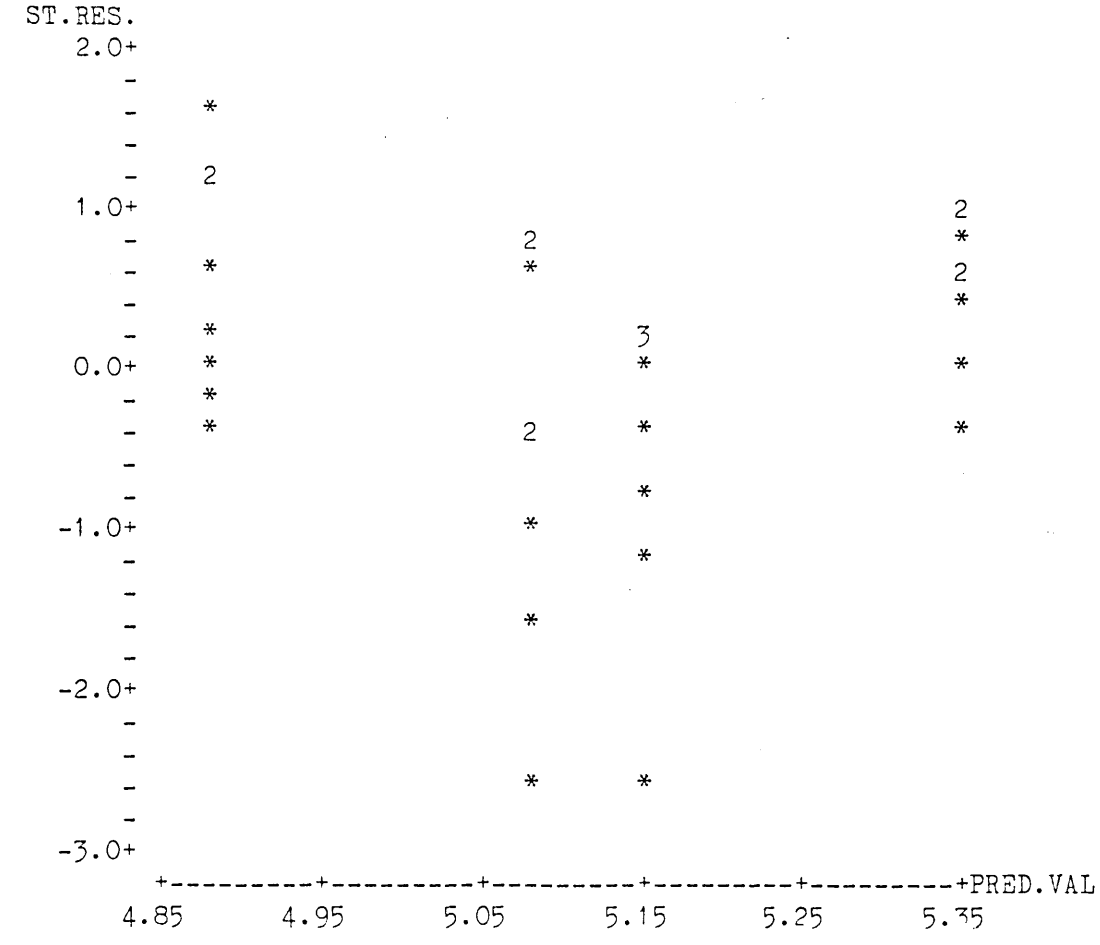


Figure (B)

FIGURES 9.2.a and 9.2.b. Diagnostic plots for model fitted in Computer Run 16.

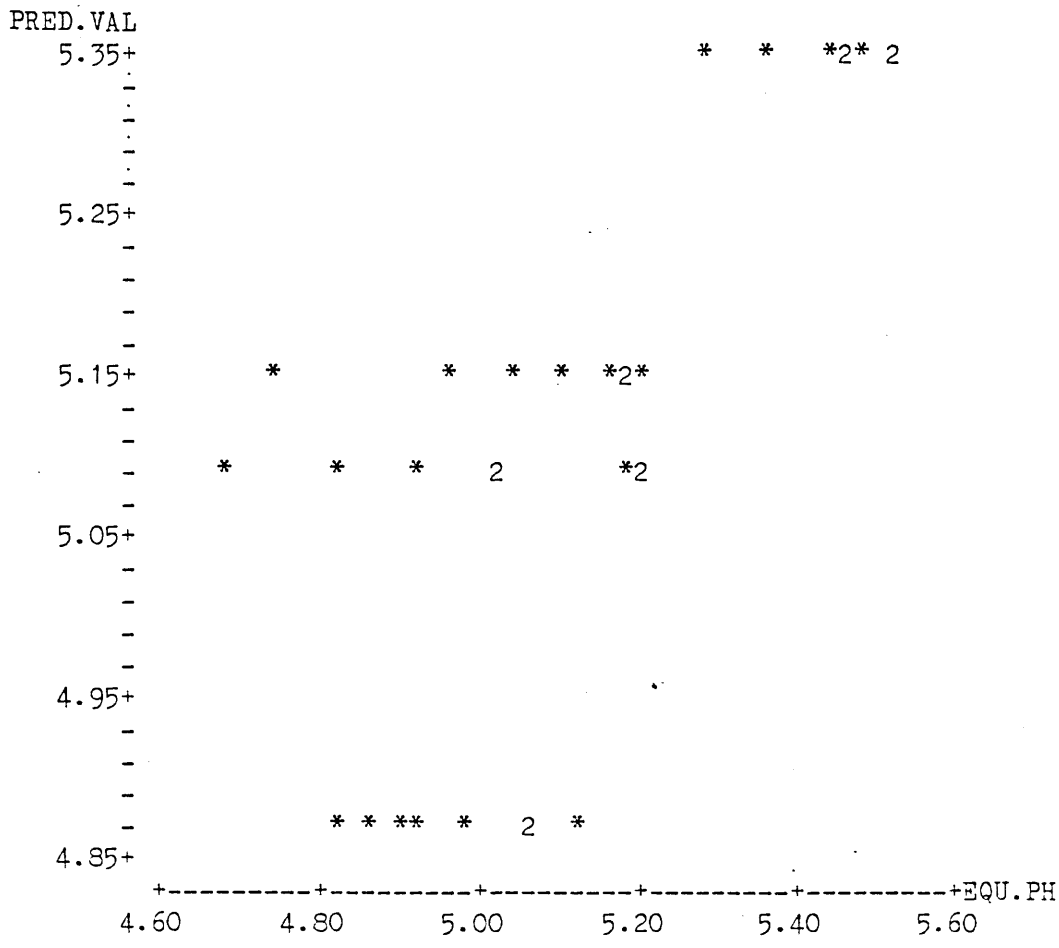


Figure (C)

FIGURE 9.2.c. Plot of predicted versus measured pH response for model fitted in Computer Run 16.

Init.pH	Init.Co	Init.Ni	Equ.T	Na2SO4	y	$\hat{y}$	S.D.$\hat{y}$.	Resid,d	S.D.d.	Std.Res
-1	-1	-1	-1	-1	5.460	5.354	0.050	.106	.159	.679
+1	-1	-1	-1	-1	5.520	5.354	0.050	.166	.159	1.062
-1	+1	-1	-1	-1	5.280	5.354	0.050	-.074	.159	-.471
+1	+1	-1	-1	-1	5.350	5.354	0.050	-.004	.159	-.024
-1	-1	+1	-1	-1	5.200	5.085	0.050	.115	.159	.734
+1	-1	+1	-1	-1	5.170	5.085	0.050	.085	.159	.543
-1	+1	+1	-1	-1	4.820	5.085	0.050	-.265	.159	-1.692
+1	+1	+1	-1	-1	5.200	5.085	0.050	.115	.159	.734
-1	-1	-1	+1	-1	5.030	5.147	0.050	-.117	.159	-.750
+1	-1	-1	+1	-1	4.960	5.147	0.050	-.187	.159	-1.197
-1	+1	-1	+1	-1	4.730	5.147	0.050	-.417	.159	-2.666
+1	+1	-1	+1	-1	5.180	5.147	0.050	.033	.159	.208
-1	-1	+1	+1	-1	4.890	4.879	0.050	.011	.159	.072
+1	-1	+1	+1	-1	4.810	4.879	0.050	-.069	.159	-.439
-1	+1	+1	+1	-1	5.060	4.879	0.050	.181	.159	1.158
+1	+1	+1	+1	-1	5.060	4.879	0.050	.181	.159	1.158
-1	-1	-1	-1	+1	5.460	5.354	0.050	.106	.159	.679
+1	-1	-1	-1	+1	5.480	5.354	0.050	.126	.159	.806
-1	+1	-1	-1	+1	5.430	5.354	0.050	.076	.159	.487
+1	+1	-1	-1	+1	5.510	5.354	0.050	.156	.159	.998
-1	-1	+1	-1	+1	4.670	5.085	0.050	-.415	.159	-2.650
+1	-1	+1	-1	+1	5.020	5.085	0.050	-.065	.159	-.415
-1	+1	+1	-1	+1	5.020	5.085	0.050	-.065	.159	-.415
+1	+1	+1	-1	+1	4.920	5.085	0.050	-.165	.159	-1.054
-1	-1	-1	+1	+1	5.180	5.147	0.050	.033	.159	.208
+1	-1	-1	+1	+1	5.150	5.147	0.050	.003	.159	.016
-1	+1	-1	+1	+1	5.100	5.147	0.050	-.047	.159	-.303
+1	+1	-1	+1	+1	5.190	5.147	0.050	.043	.159	.271
-1	-1	+1	+1	+1	4.850	4.879	0.050	-.029	.159	-.184
+1	-1	+1	+1	+1	4.920	4.879	0.050	.041	.159	.263
-1	+1	+1	+1	+1	4.980	4.879	0.050	.101	.159	.647
+1	+1	+1	+1	+1	5.120	4.879	0.050	.241	.159	1.541

TABLE 9.7. Residuals and predicted response values for model fitted in Computer Run 16.

Similarly, the fitted regression parameter for variable D is $\beta' = -0.103$, and variable D is judged a real effect.

In spite of the fact that the parameters for C and D are both significant, a low standard of fit is obtained from the model. This is particularly evident from the plot of $\hat{y}$ versus y. It is also apparent from the other diagnostic plots, and from R^2, which has the low value of 53.9%. It was decided to introduce into the model next, the two-variable interaction CD, in the hope of improving the fit. This was done in Computer Run 17.

CD is judged to be a real effect, in agreement with the factorial analysis, since a definite improvement in fit was obtained in the run. R^2 was increased to 66.7% and the model's residuals were homogeneously distributed. The value of the regression parameter for CD is $\beta' = 0.083$. CD was retained in the model.

Variable A had been judged non-significant in the factorial analysis of the response, although it was near to significance. From the regression analysis it is tentatively concluded that it is a significant variable, since with its introduction in Computer Run 18, there was an improvement in fit, as can be seen from Tables 9.8 and 9.9 and Figures 9.3.a and 9.3.b. A value of $R^2 = 70.3\%$ was obtained, and the diagnostic plots, while still not good, are as acceptable as any for this response.

THE REGRESSION EQUATION IS
Y = 5.12 + .0438 X1 - .134 X2
- .103 X3 + .0825 X4

	COLUMN	COEFFICIENT	ST. DEV. OF COEF.	T-RATIO = COEF/S.D.
	--	5.11625	0.02419	211.50
X1	INIT.PH	0.04375	0.02419	1.81
X2	INIT.NI	-0.13437	0.02419	-5.55
X3	EQU.TEMP	-0.10312	0.02419	-4.26
X4	NI*TEMP	0.08250	0.02419	3.41

THE ST. DEV. OF Y ABOUT REGRESSION LINE IS
S = 0.1368
WITH (32- 5) = 27 DEGREES OF FREEDOM

R-SQUARED = 70.3 PERCENT
R-SQUARED = 65.9 PERCENT, ADJUSTED FOR D.F.

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF
REGRESSION	4	1.19717	0.29929
RESIDUAL	27	0.50558	0.01873
TOTAL	31	1.70275	

FURTHER ANALYSIS OF VARIANCE
SS EXPLAINED BY EACH VARIABLE WHEN ENTERED IN THE ORDER GIVEN

DUE TO	DF	SS
REGRESSION	4	1.19717
INIT.PH	1	0.06125
INIT.NI	1	0.57781
EQU.TEMP	1	0.34031
NI*TEMP	1	0.21780

TABLE 9.8. Statistical output from Computer Run 18. Regression model including variables A, C and D and interaction CD.

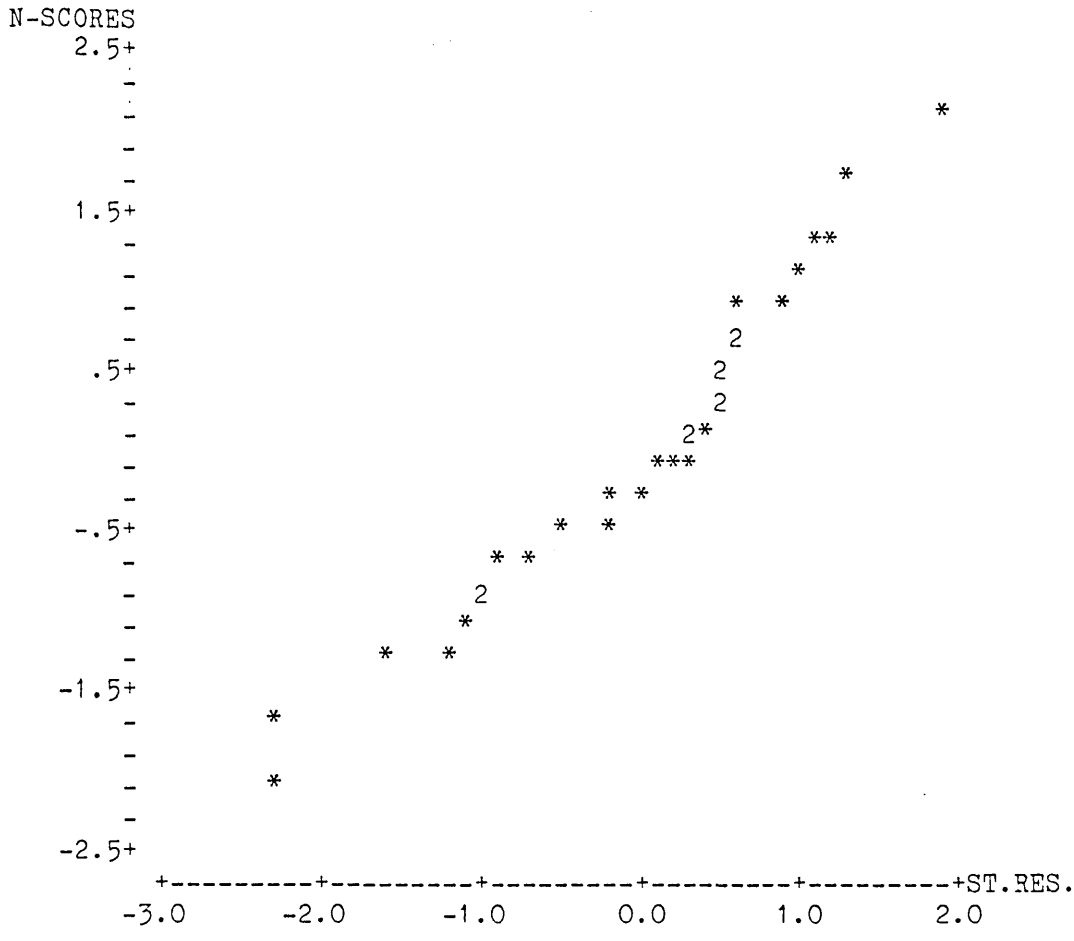


Figure (A)

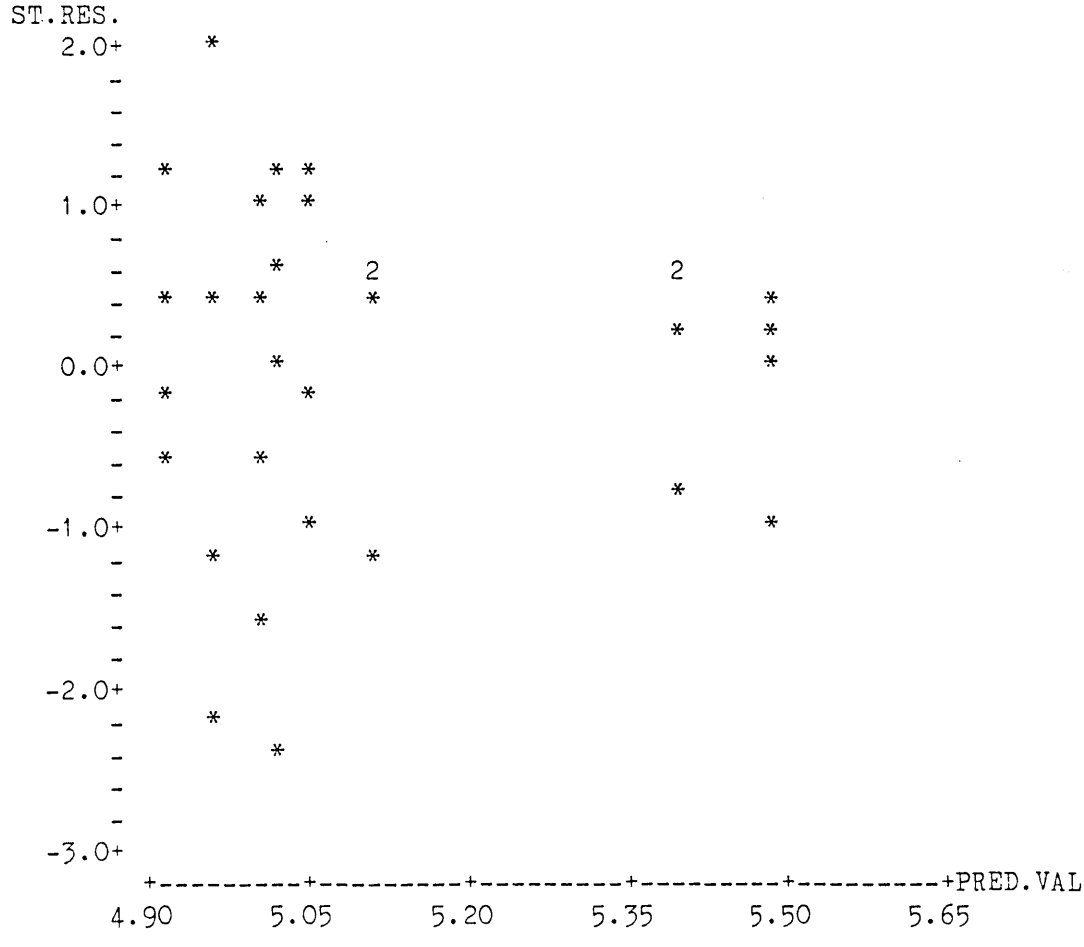


Figure (B)

FIGURES 9.3.a and 9.3.b. Diagnostic plots for model fitted in Computer Run 18.

Init.pH	Init.Co	Init.Ni	Equ.T	Na2SO4	y	$\hat{y}$	S.D.$\hat{y}$.	Resid,d	S.D.d.	Std.Res
-1	-1	-1	-1	-1	5.460	5.392	0.054	.068	.128	.537
+1	-1	-1	-1	-1	5.520	5.480	0.054	.040	.128	.318
-1	+1	-1	-1	-1	5.280	5.392	0.054	-.112	.128	-.895
+1	+1	-1	-1	-1	5.350	5.480	0.054	-.130	.128	-1.034
-1	-1	+1	-1	-1	5.200	4.959	0.054	.241	.128	1.919
+1	-1	+1	-1	-1	5.170	5.046	0.054	.124	.128	.985
-1	+1	+1	-1	-1	4.820	4.959	0.054	-.139	.128	-1.104
+1	+1	+1	-1	-1	5.200	5.046	0.054	.154	.128	1.223
-1	-1	-1	+1	-1	5.030	5.021	0.054	.009	.128	.070
+1	-1	-1	+1	-1	4.960	5.109	0.054	-.149	.128	-1.183
-1	+1	-1	+1	-1	4.730	5.021	0.054	-.291	.128	-2.317
+1	+1	-1	+1	-1	5.180	5.109	0.054	.071	.128	.567
-1	-1	+1	+1	-1	4.890	4.917	0.054	-.027	.128	-.219
+1	-1	+1	+1	-1	4.810	5.005	0.054	-.195	.128	-1.551
-1	+1	+1	+1	-1	5.060	4.917	0.054	.143	.128	1.134
+1	+1	+1	+1	-1	5.060	5.005	0.054	.055	.128	.438
-1	-1	-1	-1	+1	5.460	5.392	0.054	.068	.128	.537
+1	-1	-1	-1	+1	5.480	5.480	0.054	.000	.128	.000
-1	+1	-1	-1	+1	5.430	5.392	0.054	.038	.128	.298
+1	+1	-1	-1	+1	5.510	5.480	0.054	.030	.128	.239
-1	-1	+1	-1	+1	4.670	4.959	0.054	-.289	.128	-2.297
+1	-1	+1	-1	+1	5.020	5.046	0.054	-.026	.128	-.209
-1	+1	+1	-1	+1	5.020	4.959	0.054	.061	.128	.487
+1	+1	+1	-1	+1	4.920	5.046	0.054	-.126	.128	-1.004
-1	-1	-1	+1	+1	5.180	5.021	0.054	.159	.128	1.263
+1	-1	-1	+1	+1	5.150	5.109	0.054	.041	.128	.328
-1	+1	-1	+1	+1	5.100	5.021	0.054	.079	.128	.627
+1	+1	-1	+1	+1	5.190	5.109	0.054	.081	.128	.646
-1	-1	+1	+1	+1	4.850	4.917	0.054	-.067	.128	-.537
+1	-1	+1	+1	+1	4.920	5.005	0.054	-.085	.128	-.676
-1	+1	+1	+1	+1	4.980	4.917	0.054	.063	.128	.497
+1	+1	+1	+1	+1	5.120	5.005	0.054	.115	.128	.915

TABLE 9.9. Residuals and predicted response values for model fitted in Computer Run 18.

There is room for doubt however, since the fitted regression parameter for A, with a value of $\beta' = 0.044$, is not significant at the 95% level of significance, according to a t-test.

As in the statistical analysis, the variable B was judged non-significant. There was no real improvement in fit with its introduction in Computer Run 19. A value of $R^2 = 70.4\%$ was obtained.

Similarly, the variable E was judged non-significant, as before. For completeness, the two-factor interactions AC and AD were considered, though there had been little in the earlier analysis to suggest that they were real effects. They were again judged non-significant.

It is a common procedure in regression analysis to make a transformation of a variable or of the response in order to achieve an improvement in the way the model fits the data. A transformation in the response is made when the response is modified so that the transformed response,

$$Y_i = f(y_i) \tag{9.1}$$

A common transformation, is to set

$$Y_i = \log y_i \tag{9.2}$$

In the case of the equilibrium pH response, of course, the response as presented can be thought of as being in a

transformed form, since

$$pH = -\log_{10}\{H^+\} \qquad (9.3)$$

It was decided to see whether an improved fit of the data could be obtained with the response transformed (back) to equilibrium hydrogen-ion activity, $\{H^+\}$, by the transformation

$$\{H^+\} = 10^{-pH} \qquad (9.4)$$

In Computer Run 23, the response was transformed for the model which had produced the best fit so far, that of Computer Run 18. The transformation model is transformed response, Y = $\{H^+\}$ regressed with variables A, C, D and interaction CD. The results are shown in Tables 9.10 and 9.11 and Figures 9.4.a, 9.4.b and 9.4.c.

With the introduction of the transformation, the fit is less good than in the 'untransformed' equilibrium pH model. A value of R^2 = 49.2% was obtained for the $\{H^+\}$ model, as opposed to R^2 = 70.3% for the equivalent equilibrium pH model.

The diagnostic $\hat{y}$ versus y plot shows a strong trend in the residuals, with the size of the residuals increasing with decrease in pH. A plot of this type, which shows a trend with response value, is usually interpreted as showing that a transformation of the response is needed.

```
THE REGRESSION EQUATION IS
Y =   .0000 - .0000 X1 + .0000 X2
    + .0000 X3 - .0000 X4

                                          ST. DEV.    T-RATIO =
       COLUMN     COEFFICIENT           OF COEF.    COEF/S.D.
       --       0.0000087628       0.0000006239        14.05
X1     INIT.PH  -1.04750E-06       0.0000006239        -1.68
X2     INIT.NI   0.0000023005      0.0000006239         3.69
X3     EQU.TEMP  0.0000014626      0.0000006239         2.34
X4     NI*TEMP  -1.27648E-06       0.0000006239        -2.05

THE ST. DEV. OF Y ABOUT REGRESSION LINE IS
S = 0.000003529
WITH (  32- 5) =  27 DEGREES OF FREEDOM

R-SQUARED = 49.2 PERCENT
R-SQUARED = 41.6 PERCENT, ADJUSTED FOR D.F.

ANALYSIS OF VARIANCE

 DUE TO     DF           SS       MS=SS/DF
REGRESSION   4 3.250527E-10  8.126317E-11
RESIDUAL    27 3.362700E-10  1.245445E-11
TOTAL       31 6.613227E-10

FURTHER ANALYSIS OF VARIANCE
SS EXPLAINED BY EACH VARIABLE WHEN ENTERED IN THE ORDER GIVEN

 DUE TO     DF           SS
REGRESSION   4 3.250527E-10
INIT.PH      1 3.511223E-11
INIT.NI      1 1.693482E-10
EQU.TEMP     1 6.845114E-11
NI*TEMP      1 5.214115E-11
```

TABLE 9.10. Statistical output from Computer Run 23. Regression model with transformed response, and including variables A, C and D and interaction CD.

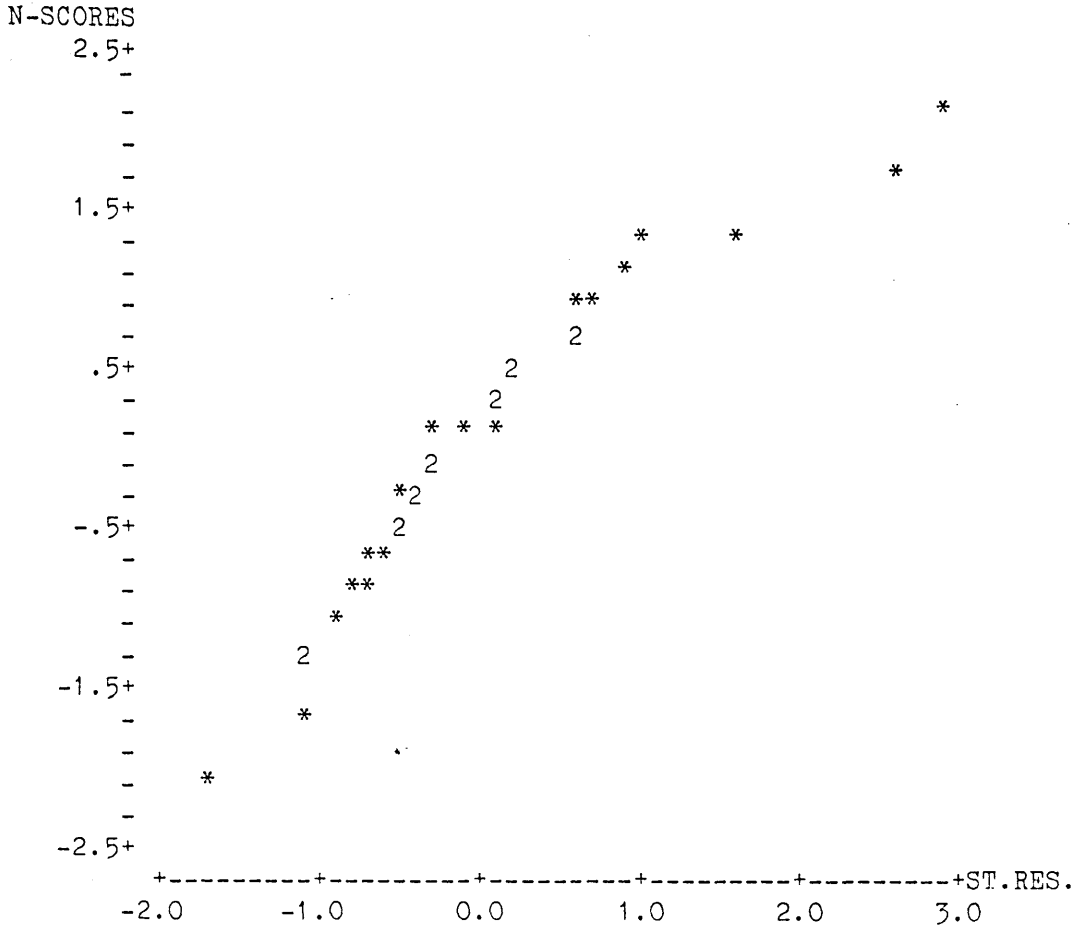


Figure (A)

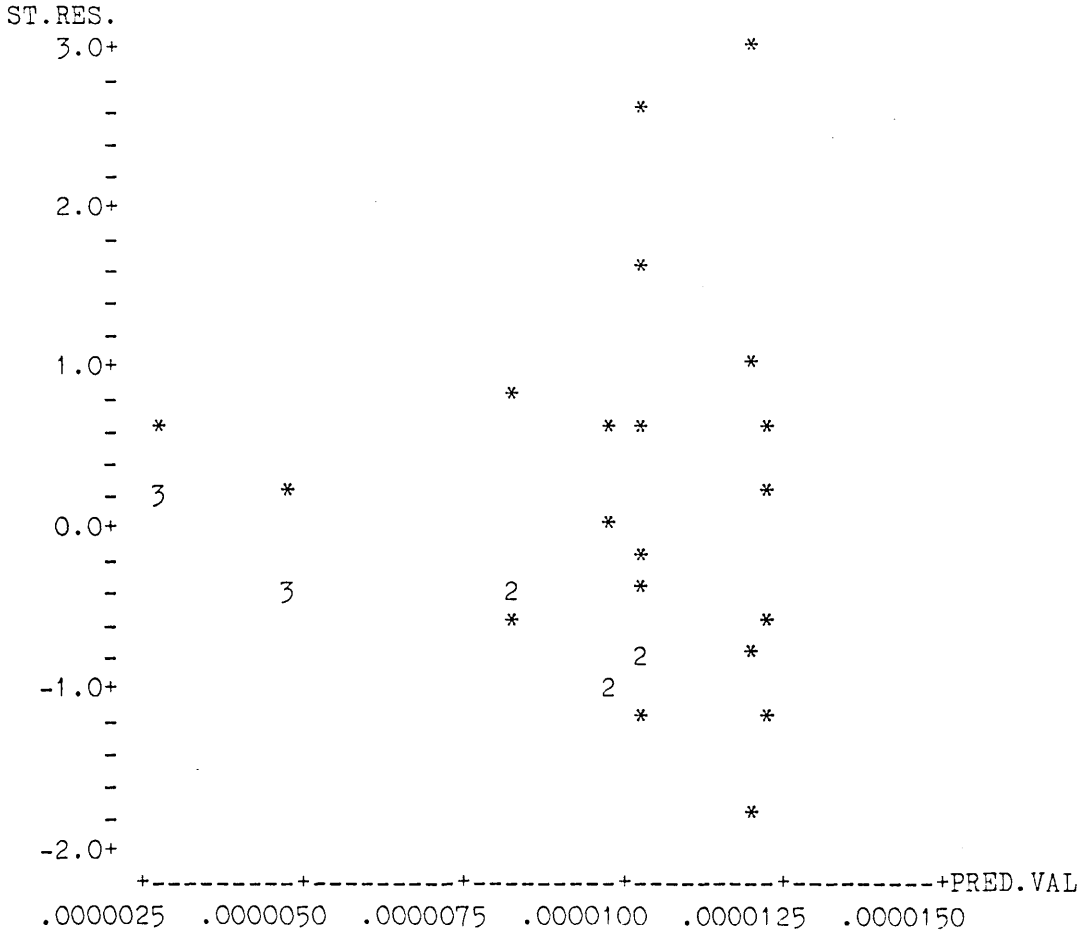


Figure (B)

FIGURES 9.4.a and 9.4.b. Diagnostic plots for model fitted in Computer Run 23.

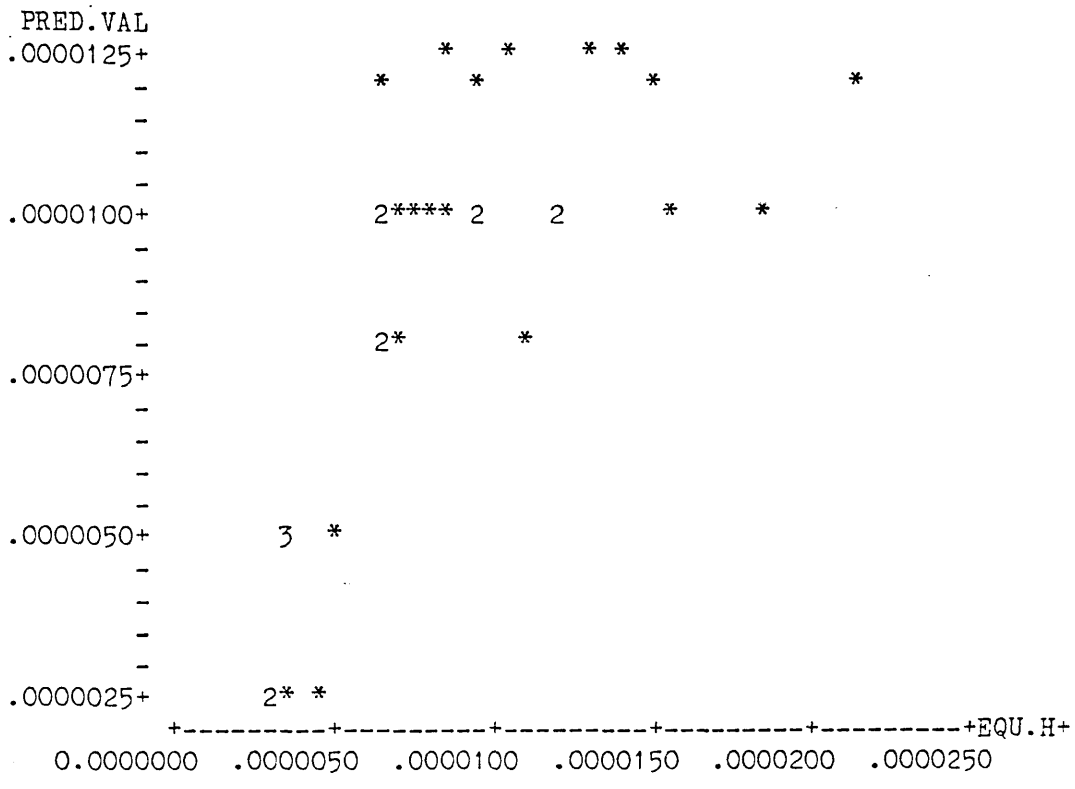


Figure (C)

FIGURE 9.4.c. Plot of predicted versus measured response for transformed response model (Computer Run 23).

Init.pH	Init.Co	Init.Ni	Equ.T	Na2SO4	y	$\hat{y}$	S.D.$\hat{y}$.	Resid,d	S.D.d.	Std.Res
-1	-1	-1	-1	-1	.347	.477	1.0	-.130	.329	-.402
+1	-1	-1	-1	-1	.302	.268	1.0	.034	.329	.106
-1	+1	-1	-1	-1	.525	.477	1.0	.048	.329	.147
+1	+1	-1	-1	-1	.447	.268	1.0	.179	.329	.552
-1	-1	+1	-1	-1	.631	1.192	1.0	-.562	.329	-1.732
+1	-1	+1	-1	-1	.676	.983	1.0	-.307	.329	-.947
-1	+1	+1	-1	-1	1.514	1.192	1.0	.321	.329	.991
+1	+1	+1	-1	-1	.631	.983	1.0	-.352	.329	-1.086
-1	-1	-1	+1	-1	.933	1.025	1.0	-.092	.329	-.283
+1	-1	-1	+1	-1	1.096	.815	1.0	.281	.329	.867
-1	+1	-1	+1	-1	1.862	1.025	1.0	.837	.329	2.583
+1	+1	-1	+1	-1	.661	.815	1.0	-.155	.329	-.477
-1	-1	+1	+1	-1	1.288	1.230	1.0	.059	.329	.181
+1	-1	+1	+1	-1	1.549	1.020	1.0	.529	.329	1.631
-1	+1	+1	+1	-1	.871	1.230	1.0	-.359	.329	-1.107
+1	+1	+1	+1	-1	.871	1.020	1.0	-.149	.329	-.460
-1	-1	-1	-1	+1	.347	.477	1.0	-.130	.329	-.402
+1	-1	-1	-1	+1	.331	.268	1.0	.064	.329	.196
-1	+1	-1	-1	+1	.372	.477	1.0	-.106	.329	-.326
+1	+1	-1	-1	+1	.309	.268	1.0	.041	.329	.128
-1	-1	+1	-1	+1	2.138	1.192	1.0	.945	.329	2.917
+1	-1	+1	-1	+1	.955	.983	1.0	-.028	.329	-.086
-1	+1	+1	-1	+1	.955	1.192	1.0	-.237	.329	-.733
+1	+1	+1	-1	+1	1.202	.983	1.0	.219	.329	.676
-1	-1	-1	+1	+1	.661	1.025	1.0	-.364	.329	-1.123
+1	-1	-1	+1	+1	.708	.815	1.0	-.107	.329	-.331
-1	+1	-1	+1	+1	.794	1.025	1.0	-.231	.329	-.711
+1	+1	-1	+1	+1	.646	.815	1.0	-.170	.329	-.524
-1	-1	+1	+1	+1	1.413	1.230	1.0	.183	.329	.564
+1	-1	+1	+1	+1	1.202	1.020	1.0	.182	.329	.562
-1	+1	+1	+1	+1	1.047	1.230	1.0	-.183	.329	-.563
+1	+1	+1	+1	+1	.759	1.020	1.0	-.262	.329	-.807

TABLE 9.11. Residuals and predicted response values for transformed response model (Computer Run 23).

Regression Conclusions

With this response, none of the entertained models give a particularly good description of the data. The highest multiple correlation coefficient obtained was R^2 = 70.4%. This means that only about 70% of the overall variation in the response is explained by a model.

The model which is considered to provide the best fit of the data set is that fitted in Computer Run 18. It is the model which includes terms for the variables A, C, D and CD and uses the equilibrium pH response untransformed.

This model gives the highest value of R^2, with economy in the number of terms required, and the residuals have satisfactory homogeneity and no marked non-normality.

Thus, on the present data, the regression equation which best describes the response behaviour, strictly within the ranges of the variables studied, and under the present conditions of experimentation, is:

$$\hat{y} = 5.12 + 0.044X_1 - 0.134X_2 - 0.103X_3 + 0.083X_4 \qquad (9.5)$$

where $\hat{y}$ is the predicted value of the equilibrium pH, and the coded variables X_1, X_2, ..., X_4 correspond to the natural variables A, C, ..., CD as follows:

$X_1 \rightarrow A$

$X_2 \rightarrow C$

$X_3 \rightarrow D$

$X_4 = X_2X_3 \rightarrow CD$

The coded variables are related to the natural variables by the following equations:

$$X_1 = \frac{10^{-x_1} - 5.16 \times 10^{-5}}{4.84 \times 10^{-5}} \qquad (9.6)$$

$$X_2 = \frac{x_2 - 17.5}{15} \qquad (9.7)$$

$$X_3 = \frac{x_3 - 65}{15} \qquad (9.8)$$

where x_1, x_2 and x_3 are the initial pH, initial aqueous nickel concentration (g/L), and equilibrium temperature (^{o}C) respectively.

In equation 9.6, the initial pH variable is coded in terms of hydrogen-ion concentration, using the mean value of $\{H^+\}$ (initial) = 5.16×10^{-5} M and the interval = 4.84×10^{-5} M, according to the coding defined in equation 7.10. It is believed that this will provide a better correlation than coding in terms of equilibrium pH, due to the logarithmic nature of pH.

The plot of the predicted response versus the measured response for this model is shown in Figure 9.5.

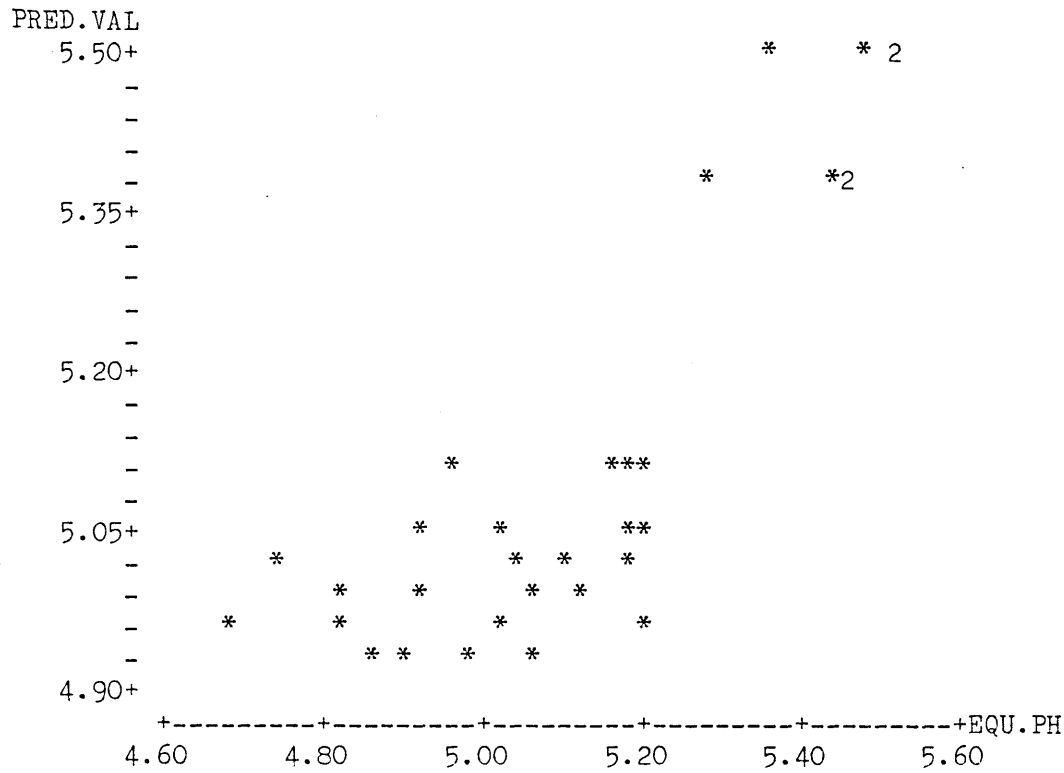


FIGURE 9.5. Plot of predicted versus measured equilibrium pH response for model including A, C, D and CD (Computer Run 18).

9.3 Statistical Conclusions for the pH Study

It is concluded that of the factorial variables studied, those that have a real influence on the response EQUILIBRIUM pH are the variables A, C and D. There is a real two-factor interaction between C and D. The factorial variables are identified in Table 9.12.

TABLE 9.12. Real factors for the equilibrium pH response.

Factor or Interaction	Identity	Effect Value (pH units)
A	Initial pH	+0.088
C	Initial aqueous nickel concentration	-0.269
D	Equilibrium temperature	-0.206
CD	Two-factor interaction between C and D	+0.165

CHAPTER 10

FACTORIAL EXPERIMENTS: DISCUSSION AND CONCLUSIONS

10.1 Influences on the Cobalt and Nickel Responses

The Meaning of the Effects

For the cobalt response, three variables, the initial aqueous cobalt concentration, the initial aqueous nickel concentration, and the equilibrium temperature, produced significant effects.

The effects showed that, within the ranges of the variables studied, and under the present experimental conditions, the equilibrium organic cobalt concentration increases with increase in initial aqueous cobalt concentration; decreases with initial aqueous nickel concentration and increases with equilibrium temperature.

For a given variable, the overall trend in the response with that variable is given by the main-effect of the variable. The main-effect, as defined earlier, gives the average change in the response, over all the levels of the other variables, in going from the low to the high factorial level of the variable.

For the cobalt response, the presence of a real main-effect of the variable initial aqueous cobalt concentration (B = +4.69 g/L Co) means that the equilibrium organic cobalt concentration increases by a mean value of +4.69 g/L in going from the low factorial level (10 g/L (0.170 M) Co) to the high factorial level (25 g/L (0.42 M) Co) of the variable.

Similarly, the presence of a real main-effect (C = -1.49 g/L Co) for the variable initial aqueous nickel

concentration, means that there is an average decrease in the equilibrium organic cobalt concentration in going from the low factorial level (20 g/L (0.34 M) Ni) to the high factorial level (50 g/L (0.85 M) Ni) of the variable.

These trends reflect the competition for loading of cobalt and nickel when both are present. Increasing the aqueous cobalt concentration increases the organic cobalt concentration, and increasing the aqueous nickel concentration increases the organic nickel concentration.

The absence for the cobalt response of a real two-factor interaction (BC) between the variables initial aqueous cobalt concentration, $C_{Co}(i,aq)$, and the initial aqueous nickel concentration, $C_{Ni}(i,aq)$ should be noted. It means that, within the ranges of the variables studied, the effect of increasing the $C_{Co}(i,aq)$ is consistent over the range of $C_{Ni}(i,aq)$, and vice-versa.

For the cobalt response, the presence of a real main-effect (D = +0.83 g/L Co) for the variable equilibrium temperature, means that there is a increase in the response in going from the low to the high level of the variable. For ease of reference, Table 6.1, which shows the factorial variables and their levels, is reproduced here as Table 10.1.

For the cobalt response, real two-factor interactions were found to be present. These are the interactions between the variables initial aqueous cobalt concentration and equilibrium temperature, (T); and the interaction between initial aqueous nickel concentration and equilibrium temperature.

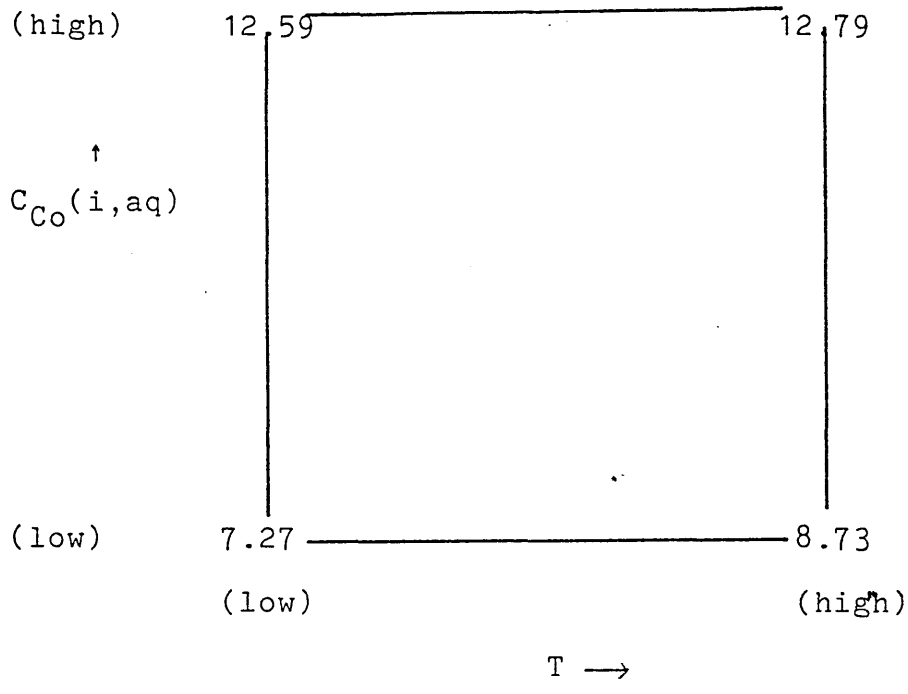
TABLE 10.1 The Factorial Variables and Their Levels

Variable	Variable Code Letter	Levels of Variables		
		Low	High	(Units)
initial pH	A	4.0	5.5	pH units
initial aqueous cobalt concentration	B	10.0	25.0	g/L
initial aqueous nickel concentration	C	20.0	50.0	g/l
equilibrium temperature	D	323 (50°)	353 (80°)	K(°C)
initial aqueous sodium sulphate concentration	E	0	0.5	(M)

When there is a real interaction between variables, the effects of the variables must be considered jointly.

The nature of the two-factor interaction between $C_{Co}(i,aq)$ and T (the $C_{Co}(i,aq)$ x T interaction) can be seen from Table 10.2, which shows the average value of the response for each level combination of the two variables. The table is called a two-way table. It is seen that the interaction arises because the effect on the response of increasing $C_{Co}(i,aq)$ is smaller (= 12.79-8.73 = 4.06 g/L Co) at the high level of equilibrium temperature than (= 12.59 - 7.27 = 5.32 g/L Co) at the low level.

TABLE 10.2 Two-way Table for $C_{Co}(i,aq)$ x T Interaction, Cobalt Response.

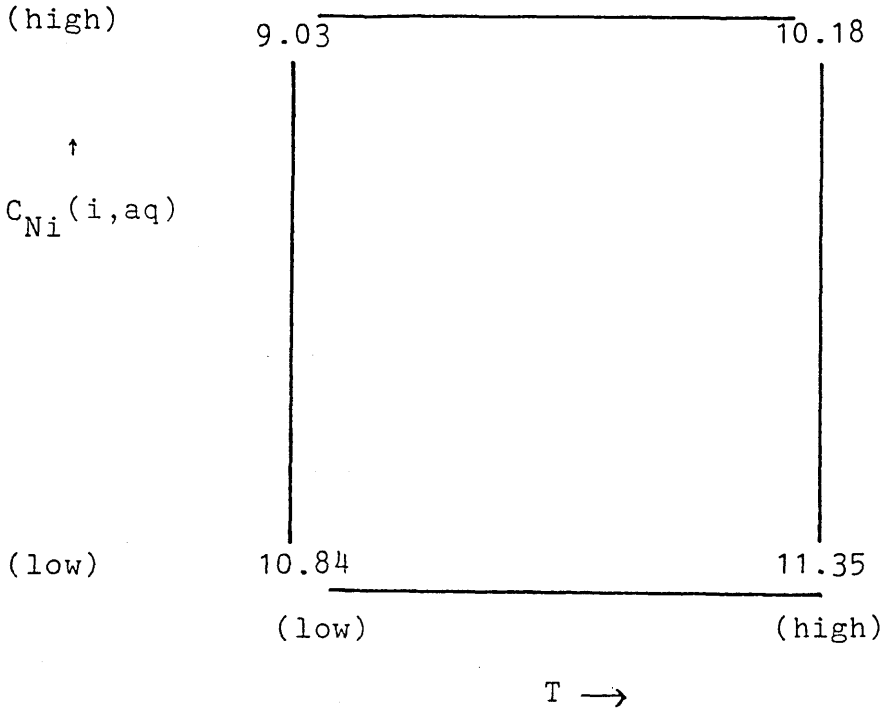


It would be equivalent to say that the interaction arises because the effect on the response of increasing equilibrium temperature is smaller at the high level of $C_{Co}(i,aq)$ than at the low level.

Similarly, from Table 10.3 it can be seen that the 2-f.i. $C_{Ni}(i,aq)$ x T arises because the effect on the response of increasing $C_{Ni}(i,aq)$ is smaller at the high level of equilibrium temperature than at the low level.

The sign of each two-factor interaction can be interpreted in the following way. Whichever way of seeing the interaction is chosen, if the effect of a variable on the response is an increase in going from the low to the high level of the other variable, or if the effect on the

TABLE 10.3 $C_{Ni}(i,aq)$ x T Interaction, Cobalt Response



response is a reduction in the decrease (as with $C_{Ni}(i,aq)$ x T), then the 2-f.i. has a positive sign. Conversely, if a decrease in the response, or a decrease in the increase of the response is obtained, then the 2-f.i. has a negative sign.

For the nickel response, three of the factorial variables, the initial aqueous cobalt concentration, the initial aqueous nickel concentration, and the equilibrium temperature, produced significant effects. These are of course the same variables that produced significant effects with the cobalt response.

The effects showed that, within the ranges of the variables studied, and under the present experimental

conditions, the equilibrium organic nickel concentration decreases with increase in the initial aqueous cobalt concentration; increases with increase in the initial aqueous nickel concentration; and (with cobalt present) decreases with increase in equilibrium temperature.

The overall trend in the response is given by the main-effect of the variable. For the nickel response, the presence of a real main-effect (B = -4.31 g/L Ni) for the variable $C_{Co}(i,aq)$, means that there is a decrease in the response in going from the low to the high factorial level of the variable.

Similarly, the presence of a real main-effect (C = +1.29 g/L Ni) for the variable initial aqueous nickel concentration, means that there is an increase in the equilibrium organic nickel concentration in going from the low to the high level of the variable.

As with the cobalt response, with the nickel response the absence of a 2-f.i. (BC) between the variables $C_{Co}(i,aq)$ and $C_{Ni}(i,aq)$, means that, within the ranges studied, the effect of increasing $C_{Co}(i,aq)$ is consistent over the range of $C_{Ni}(i,aq)$, and vice-versa.

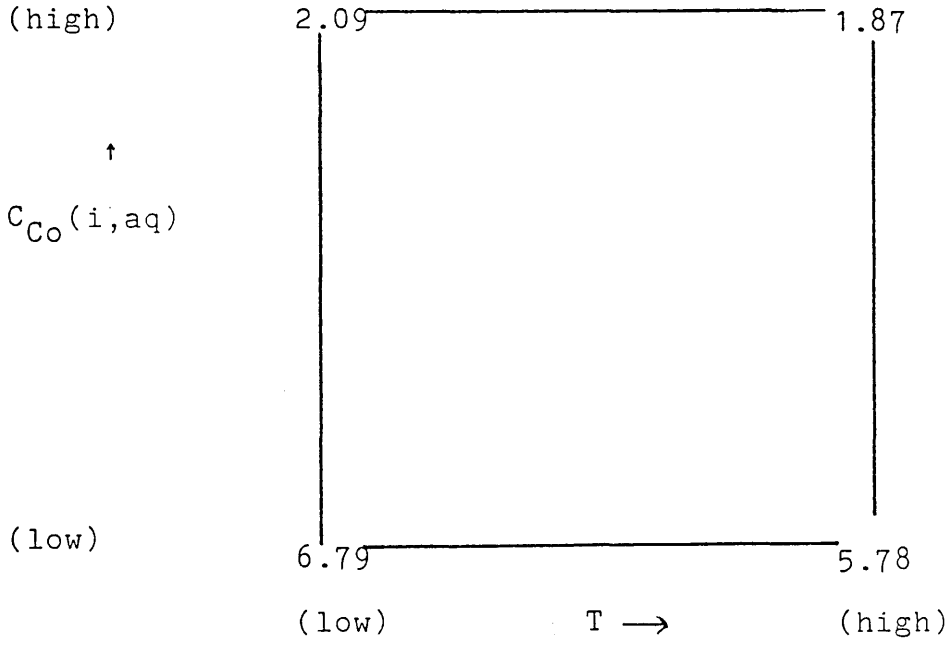
For the nickel response, the presence of a real main-effect (D = -0.62 g/L Ni) for the variable equilibrium temperature, means that, under the present experimental conditions (i.e. with cobalt present), there is a decrease in the equilibrium organic nickel concentration in going

from the low to the high level of the variable. The response is decreased by a mean value of 0.62 g/L Ni.

For the nickel response, the same real two-factor interactions were found to be present as with the cobalt response. These are the interactions between the variables $C_{Co}(i,aq)$ and T,(BD); and between the variables $C_{Ni}(i,aq)$ and T ,(CD).

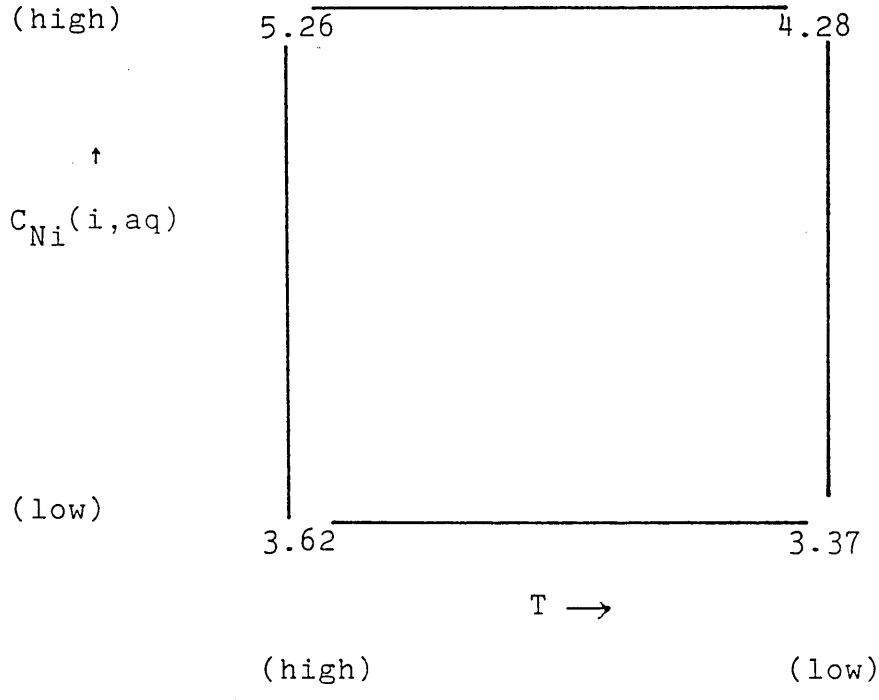
From table 10.4 it can be seen that the interaction $C_{Co}(i,aq)$ x T arises because the effect on the nickel response of increasing the initial aqueous cobalt concentration is smaller at the high level of equilibrium temperature than at the low level.

TABLE 10.4 $C_{Co}(i,aq)$ x T Interaction, Nickel Response.



Similarly, it can be seen from Table 10.5 that for the nickel response, the interaction between initial aqueous nickel concentration and equilibrium temperature arises because the effect on the response of increasing the $C_{Ni}(i,aq)$ is smaller at the high level of equilibrium temperature than at the low level.

TABLE 10.5 $C_{Ni}(i,aq)$ x T Interaction, Nickel Response



Cobalt and Nickel Distribution Behaviour

For ease of reference, the cobalt and nickel effects are brought together in Table 10.6.

TABLE 10.6.

Effect	Effect Value For	
	Co Response	Ni Response
	g/L	g/L
Mean Response Value	10.35	4.13
B	+4.69	-4.31
C	-1.49	+1.29
D	+0.83	-0.62
BD	-0.63	+0.40
CD	+0.32	-0.36
Standard error of an effect	±0.123	±0.067

Dropping now the formal terminology of experimental design methods, the following trends in the distribution behaviour of cobalt and nickel, within the ranges of the variables studied, and under the present experimental conditions, can be discerned in the effects.

Cobalt and nickel, initially present in the aqueous phase, are in competition to be extracted by the sodium-salt form of the solvent, which is initially free of the metals to be extracted.

Increasing the initial aqueous cobalt concentration increases the organic cobalt concentration. A measure of the effect is given by the main-effect B for the cobalt response. B has the value +4.69 g/L Co. Due to the competition between cobalt and nickel to be loaded, the increase in organic cobalt concentration results in less

nickel being extracted. A measure of this effect is the main-effect B for the nickel response. B has the value -4.65 g/L Ni.

Increasing the initial aqueous nickel concentration, increases the equilibrium organic nickel concentration. A measure of the effect is the main-effect C for the nickel response. C has the value +1.29 g/L Ni. Due again to the competition between cobalt and nickel to be extracted, the increase in the equilibrium organic nickel concentration results in less cobalt being extracted. A measure of this effect is the main-effect C for the cobalt response. C has the value -1.49 g/L Co.

The selectivity of the extractant for cobalt over nickel may be approximately gauged by comparing the effect of increasing the aqueous cobalt concentration on the cobalt response with the effect of increasing the aqueous nickel concentration on the nickel response. B = +4.69 g/L measures the average increase in the cobalt response in increasing the $C_{Co}(i,aq)$ from 10 to 25 g/L Co. C = +1.29 g/L Ni measures the average increase in the nickel response in increasing the $C_{Ni}(i,aq)$ from 20 to 50 g/L Ni. Since the atomic weights of cobalt and nickel are close to each other, these results can be compared directly. Clearly, the extractant is quite selective towards cobalt.

Influence of Temperature

The effect on the distribution of increasing the equilibrium temperature is to improve the separation of cobalt from nickel, by increasing the amount of cobalt extracted and decreasing the amount of nickel extracted.

The maximum cobalt extraction obtained in the factorial experiments occurs when both equilibrium temperature and $C_{Co}(i,aq)$ are at their high levels, and $C_{Ni}(i,aq)$ is at its low level. Under these conditions, average values of the equilibrium organic cobalt concentration, $\overline{[Co]}$, and the equilibrium organic nickel concentration, $\overline{[Ni]}$, of 13.50 and 1.50 g/L were obtained, giving a separation factor of $\beta_{Ni}^{Co} = 14.1$.

The maximum nickel extraction obtained in the factorial experiments occurs when both equilibrium temperature and $C_{Co}(i,aq)$ are at their low levels, and $C_{Ni}(i,aq)$ is at its high level. Under these conditions, average values for $\overline{[Ni]}$ and $\overline{[Co]}$ of 7.65 and 6.30 g/L respectively were obtained, giving $\beta_{Ni}^{Co} = 10.0$.

The increase in cobalt extraction with increase in temperature is reflected in the main-effect of equilibrium temperature (main-effect D) and the two-factor interactions $C_{Co}(i,aq) \times T$ and $C_{Ni}(i,aq) \times T$ for the cobalt response.

The equilibrium organic cobalt concentration increases with increasing initial aqueous cobalt concentration and with increasing equilibrium temperature. However, the rate

of increase of equilibrium organic cobalt concentrations with increasing initial aqueous cobalt concentration, $\Delta[\overline{Co}]/\Delta C_{Co}(i,aq)$ where Δ is a change in a quantity, gets smaller with increasing equilibrium temperature, as indicated by $C_{Co}(i,aq) \times T$ for the cobalt response.

The equilibrium organic cobalt concentration decreases with increase in $C_{Ni}(i,aq)$ but the rate of decrease, $\Delta[\overline{Co}]/\Delta C_{Ni}(i,aq)$ gets smaller with increasing temperature, as indicated by $C_{Ni}(i,aq) \times T$ for the ccbalt response.

The decrease in nickel extraction with increase in temperature, when cobalt is present, is reflected in the main-effect of equilibrium temperature (main-effect D) and the two-factor interactions $C_{Co}(i,aq) \times T$ (BD) and $C_{Ni}(i,aq) \times T$ (CD) for the nickel response.

The equilibrium organic nickel concentration increases with increase in $C_{Ni}(i,aq)$ but the rate of increase, $\Delta[\overline{Ni}]/\Delta C_{Ni}(i,aq)$ gets smaller with increasing temperature,as indicated by $C_{Ni}(i,aq) \times T$ for the nickel response.

The equilibrium organic nickel concentration decreases with both increasing $C_{Co}(i,aq)$ and with increasing temperature. However, the rate of decrease, given by $\Delta[\overline{Ni}]/\Delta C_{Co}(i,aq)$ gets smaller with increasing temperature, as indicated by $C_{Ni}(i,aq) \times T$ for the nickel response.

From the interpretation of the effects, it is seen that the effect of increasing temperature in the system in

which both cobalt and nickel are present, is to increase cobalt extraction and decrease nickel extraction. Because the cobalt and nickel responses mutually influence each other, it is not possible with the present factorial design to determine what the effect of temperature is on cobalt alone or nickel alone, though it is clear, of course, that the effect does not work independently on each metal.

In fact, from the literature, it can be seen that the increase in selectivity for cobalt over nickel observed here can be accounted for by the tendency of cobalt to give a substantial increase in extraction with temperature, and the tendency for nickel to give a slight increase in extraction. In mixed extraction, the net result of these trends is that with increasing temperature, between 50°C and 80°C, cobalt extraction increases at the expense of nickel extraction, as the factorial results show.

As has been seen in Chapter 2, the tendency for cobalt extraction to increase with temperature is due primarily to the ability of the extracted cobalt complex to undergo the thermochromic change in co-ordination given by the equation:

$$\underset{\text{pink}}{\overline{\qquad}CoR_2.2H_2O} \overset{\text{temperature, concentration}}{\rightleftharpoons} \underset{\text{blue}}{\overline{\quad}CoR_2} + 2H_2O \qquad (10.1)$$

The effects $C_{Co}(i,aq) \times T$ and $C_{Ni}(i,aq) \times T$ for the cobalt response measure a trend of the effect of

temperature to decrease with increasing temperature. It can be assumed that they reflect the exact temperature and concentration dependence of $\overline{CoR_2}$ in equation 10.1.

Similarity of the Cobalt and Nickel Effects

In examining the results of the statistical analysis, it becomes increasingly obvious that the link between the cobalt results and the nickel results is very strong. Not only do the responses have the same set of real effects, but, as is evident from Table 10.6, the value of a factorial effect for one response is very close to the value of the same effect for the other response, and for each response the signs of the effects are always opposite.

The calculation shown in Table 10.7 suggests that within the ranges of the variables studied, the solvent phase is virtually loaded to capacity with a combination of cobalt and nickel. If, at equilibrium, species other than cobalt and nickel are present to any appreciable extent, their concentrations will be small.

Under these circumstances, for the cobalt and nickel responses, any change in the factorial variables which produces a change in one of the responses should automatically produce a change in the other response. If, as expected, the metal:extractant ratio is 1:2 in both the extracted cobalt and nickel complexes, then changes in the two responses should be equimolar, and will be approximated by the change in response in g/L.

TABLE 10.7. Extraction in the Factorial Experiments of Cobalt and Nickel Combined.

Row	Treatment Code	Sum of Concentrations, $\overline{[Co]}+\overline{[Ni]}$
		(M)
1	L	0.244
2	a	0.246
3	b	0.246
4	ab	0.253
5	c	0.240
6	ac	0.236
7	bc	0.252
8	abc	0.246
9	d	0.247
10	ad	0.250
11	bd	0.256
12	abd	0.251
13	cd	0.248
14	acd	0.240
15	bcd	0.250
16	abcd	0.251
17	e	0.239
18	ae	0.232
19	be	0.251
20	abe	0.251
21	ce	0.228
22	ace	0.248
23	bce	0.245
24	abce	0.249
25	de	0.247
26	ade	0.248
27	bde	0.250
28	abde	0.251
29	cde	0.249
30	acde	0.244
31	bcde	0.249
32	abcde	0.235

If this is so, there should be an exact correspondence in the magnitude of the effects for the two responses, and they should differ only in their signs.

One explanation for the difference in the observed magnitudes of the effects is that it is due to a lower value of the average metal:extractant ratio in the extracted nickel complex than in the cobalt complex. However, it is difficult to explain how this would arise, especially in extraction at high metal loading.

It is much easier to explain the apparent difference in the magnitude of the cobalt and nickel effects as being due to a consistent bias within a set of observations, either the cobalt response set, or the nickel response set, or possibly both.

By having a consistent bias it is meant that the observations within the relevant set have good precision or reproducibility, but are subject to a bias in accuracy.

Such a bias might be expected to manifest itself in the set of effects in the following way. Each effect is composed of the difference between two contrasts. In non-real effects the contrasts differ only due to random errors within the contrasts, each contrast being obtained from an identical set of treatments. A consistent bias in the observations would therefore cancel out, and an average effect of zero would still be obtained on repeated sampling.

With real effects, the contrasts are subject to random error, and the treatments in each contrast differ from the other contrast due to the effect concerned. With a bias present, the contrasts for a real effect would also differ due to the bias. The result of bias would be a distortion in the estimated value of the effect.

The presence of a bias of this nature in a set of factorial observations should not vitiate the statistical significance tests, however, since the non-real effects used to provide the error estimate would not be influenced by the bias.

In the present experimental design, there is very little scope for the introduction of a differential bias such as that postulated here between the cobalt and the nickel response, since they are determined through the same experiments. One possible source of bias in these experiments is the dilution of the samples for analysis. Because the cobalt response is fairly consistently higher than the nickel response in these experiments, the required dilution factor for cobalt is generally higher than that required for nickel, and different dilution combinations would be used. The use of a different setting on the variable diluter might introduce a bias which would account for the differences in effect values observed here.

Non-Influencing Variables

It was concluded in the statistical studies of the cobalt and nickel responses that for the variable initial pH there were no real effects.

This means that, within the ranges of the variables studied, and under the present experimental conditions, both the equilibrium organic cobalt concentration, and the equilibrium organic nickel concentration, are independent of the initial pH.

It is well known that the extraction of both cobalt and nickel with the sodium salt of D_2EHPA is pH-dependent. If, as a simplification, the extraction of cobalt and nickel is represented by the equation

$$M^{2+} + 2\overline{RNa} \rightleftharpoons \overline{R_2M} + 2Na^+ \qquad (10.2)$$

as in equations 5.4 and 5.5, then the dependence on pH of metal extraction can be represented by:

$$M^{2+} + \overline{(RH)_2} \rightleftharpoons \overline{R_2M} + 2H^+ \qquad (10.3)$$

According to the above representations, the equilibrium organic cobalt concentrations are given by $[\overline{R_2Co}]$ and $[\overline{R_2Ni}]$ respectively.

The conclusion that the equilibrium organic cobalt concentration is independent of the initial pH, within the

ranges of the variables studied, must show that, under these conditions, the equilibrium represented by equation 10.3 is shifted very little in changing the initial pH between pH = 4.0 and pH = 5.5.

The same argument must also apply within the ranges studied to nickel extraction. The equilibrium represented by equation 10.3 is shifted very little in changing the initial pH within the range of initial pH 4.0-5.5.

It will be apparent from equation 10.3 that at lower initial pH values, and at lower $C_{Co}(i,aq)$ and $C_{Ni}(i,aq)$ values than included in the factorial design, the level of pH will influence the cobalt and nickel responses. Thus the proviso attached to the factorial design conclusions, that they apply strictly within the ranges studied, must be particularly binding with the initial pH variable.

As with the initial pH, it was concluded in the statistical studies of the cobalt and nickel responses that there were no real effects for the variable initial aqueous sodium sulphate concentration, $C_{Na_2SO_4}(i,aq)$.

The analysis of the effects shows that, within the ranges studied, there is no difference in either the observed loading of cobalt, or of nickel, between the low level of $C_{Na_2SO_4}(i,aq)$, none present, and the high level, 0.5 M Na_2SO_4.

Again using simplified extraction equations, cobalt extraction using the sodium-salt is given by

$$Co^{2+} + 2\overline{RNa} \rightleftharpoons \overline{R_2Co} + 2Na^+ \qquad (10.4)$$

and nickel extraction is given by

$$Ni^{2+} + 2\overline{RNa} \rightleftharpoons \overline{R_2Ni} + 2Na^+ \qquad (10.5)$$

The argument is the same as for the effect of initial pH. Because of the extent of cobalt and nickel loading, within the ranges studied the equilibrium concentration of $\overline{RNa}$ must be very low, so the equilibria represented by equations 10.4 and 10.5 will be well over to the right. Since both responses are independent of $C_{Na_2SO_4}(i,aq)$, the equilibria represented by these equations are shifted very little in changing the initial aqueous sodium sulphate concentration, within the range 0-0.5 M Na_2SO_4. Since at equilibrium almost all of the sodium ion initially present in the organic phase must be displaced, the aqueous phase at equilibrium will have contained 0.5 M Na^+ in addition to the initial level, giving up to a maximum equilibrium aqueous sodium sulphate concentration of 0.75 M, hence $[Na^+] \simeq 1.5$ M. Even with this concentration present, the equilibria represented apparently remain over to the right.

10.2 Influences on the Equilibrium pH

The Meaning of the Effects

For the equilibrium pH response, three of the factorial variables, the initial pH, the initial aqueous nickel

concentration and the equilibrium temperature, produced real effects.

The effects showed that, within the ranges of the variables studied, and under the present conditions of experimentation, that the equilibrium pH increases with increasing initial pH; decreases with increasing initial aqueous nickel concentration; and decreases with increasing equilibrium temperature.

The overall trend in response with a variable is given by the main-effect of the variable. For the equilibrium pH response, the presence of a real main-effect (A = +0.0875 pH units) means that, averaged over the levels of the other variables, there is an increase in the equilibrium pH in going from the low to the high level of the variable.

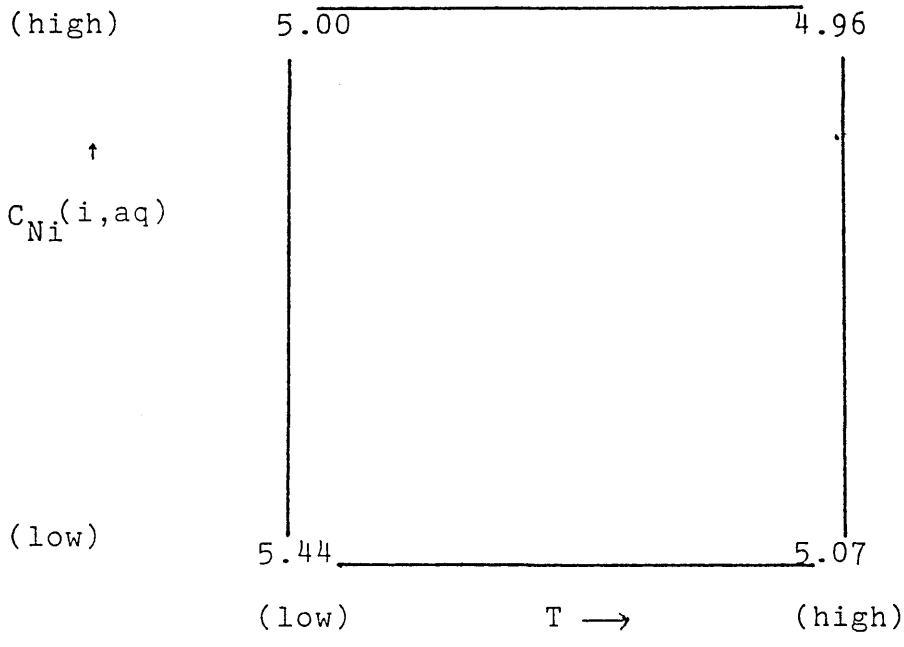
Similarly, the presence of a real main-effect for the variable initial aqueous nickel concentration (C = -0.269 pH units) means that, over the levels of the other variables, there is a decrease in the equilibrium pH in going from the low to the high level of the variable.

For the equilibrium pH response, the presence of a real main-effect for the variable equilibrium temperature (D = -0.206 pH units) means that there is a decrease in the response in going from the low to the high level of the variable.

For the pH response, a real two-factor interaction (CD = +0.165 pH units) was found to be present between the

variables initial aqueous nickel concentration and equilibrium temperature. The nature of the interaction can be seen from Table 10.8.

TABLE 10.8. Two-factor Interaction $C_{Ni}(i,aq)$ x T, pH Response.



The interaction arises because, at a combination of low $C_{Ni}(i,aq)$ and low equilibrium temperature, a high equilibrium pH is obtained, and at a combination of high $C_{Ni}(i,aq)$ and high T, a low equilibrium pH is obtained.

It can be seen from Table 10.8 that neither the effect on the response of increasing $C_{Ni}(i,aq)$ nor the effect of increasing T is consistent over the range of the other variable (e.g. the effect of increasing $C_{Ni}(i,aq)$ is 5.00-5.44 = -0.44 pH units at the low level of T, and

4.96-5.07 = -0.11 pH units at the high level of T, c.f. main-effect of $C_{Ni}(i,aq)$ = -0.269 pH units). The inconsistency is what the interaction measures. The strength of the interaction $C_{Ni}(i,aq)$ x T for the pH response is indicated by the fact that it has the same order of magnitude as its component main-effects (CD = +0.165, C = -0.269, and D = -0.206 pH units).

pH Behaviour

The changes in pH that occur during extraction due to processes involving the factorial variables are measured by the factorial effects. In the factorial experiments, an underlying change in pH could have occurred during extraction if there had been an inexactness in the neutralization of the extractant in the conversion of the solvent to its sodium-salt form.

If there was a shortfall in the amount of alkali used, the solvent would remain slightly acid after conversion, and if a slight excess of alkali was used, the excess would be held in the single phase that is obtained on conversion. Depending on which was the case, the result would be the exchange of hydrogen ions or hydroxide ions into the aqueous phase during extraction. Since all the solvent for the factorial experiments was converted in one batch, the quantity exchanged during extraction would be constant throughout the experiments.

With the exception of the main-effect of initial pH (main-effect A), the values of the factorial effects would not be affected by this occurrence, since the change would cancel out in the contrasts which make up each effect (see Section 7.1).

With the main-effect of initial pH, such a change would distort the effect value, since the liberation of a fixed quantity of acid or alkali into the aqueous phase would not produce the same change in pH at the low and high level of initial pH.

If such a distortion has occurred, it seems probable that the value of the effect is smaller than its true value, since the change in response measured by the effect (A = +0.0875 pH units) is much smaller than the change in initial pH (from pH = 4 to pH = 5.5).

The two-factor and other interaction effects involving the initial pH variable would not be distorted in this way. The absence for the pH response of real interactions involving initial pH means that, over the ranges of the variables studied, the effect of initial pH on the response is independent of the other factorial variables.

Although the statistical analysis shows that the equilibrium pH is dependent on the initial aqueous nickel concentration, this does not mean that the equilibrium pH is in turn dependent on the equilibrium organic nickel concentration. In fact, the equilibrium pH is not so

dependent. This is apparent because, in extraction where both cobalt and nickel are present, the largest influence on the equilibrium organic nickel concentration is the variable $C_{Co}(i,aq)$, and this variable was found to have no influence on the equilibrium pH.

In the range of pH in which cobalt and nickel are extracted, the possibility that extraction of neutral species occurs can be discounted, so only cationic exchange needs to be considered. There are several possible causes of variable-related changes in pH during extraction, for extraction using the sodium salt of D_2EHPA.

One cause of a decrease in pH during extraction could be the postulated cationic extraction of hydrolysed cobalt and nickel species such as $[Co(OH)]^+$ and $[Ni(OH)]^+$, or their hydrated equivalents. These species form according to an equation such as:

$$M^{2+} + H_2O \rightleftharpoons MOH^+ + H^+ \qquad (10.6)$$

and would be extracted according to an equation such as:

$$MOH^+ + RNa \rightleftharpoons R.MOH + H^+ \qquad (10.7)$$

The extraction of MOH^+ would cause the hydrolysis of fresh M^{2+}, to maintain equilibrium 10.6, thus decreasing the pH.

Another cause of a decrease in pH during extraction could be the aqueous phase hydrolysis of cobalt or nickel or both, when the aqueous phase is heated up to extraction temperature. Hydrolysis can be represented by the reaction

$$M^{2+} + 2H_2O \rightleftharpoons M(OH)_2 + 2H^+ \qquad (10.8)$$

In general, and with cobalt and nickel, the hydrolysis behaviour shown in equations 10.6 and 10.8 will increase with increasing metal concentration and temperature.

The most likely cause of an increase in pH during extraction, relating to the factorial variables, is the extraction of hydrogen ions according to a reaction such as:

$$2H^+ + 2\overline{RNa} \rightleftharpoons \overline{(RH)_2} + 2Na^+ \qquad (10.9)$$

It is not possible on the available evidence to give a firm explanation for the observed dependence of the equilibrium pH. Three possible explanations are now put forward.

One explanation for the observed dependence is, that under the extraction conditions least favourable to metal extraction, the sodium-salt co-extracts hydrogen ion, in addition to the metal ions, according to equation 10.9, and under more favourable conditions only cobalt and nickel are extracted.

It is reasonable to expect that the least likely conditions for full loading of cobalt and nickel are the combined conditions of low equilibrium temperature, where cobalt extraction is relatively low because of the temperature dependence of cobalt extraction, and low initial aqueous nickel concentration, where any shortfall in the cobalt loading is less likely to be made up by nickel extraction.

Thus (see Figure 10.8) the combination of low $C_{Ni}(i,aq)$ and low temperature would produce the highest equilibrium pH, the combination of high $C_{Ni}(i,aq)$ and high temperature would produce the lowest pH, and the other combinations of the two variables would produce an intermediate equilibrium pH.

If the co-extraction of hydrogen ion does occur under these circumstances, a correlation would be expected between the equilibrium pH and the sum of the concentrations, $\overline{[Co]} + \overline{[Ni]}$, although the quantity of hydrogen-ion extraction required to produce the observed change in pH is small.

The factorial data was analysed in a number of ways to detect such a correlation, but none was found. This could be due to random error in the cobalt and nickel responses (e.g., the estimated standard error of an observation for $\overline{[Co]}$ is ± 0.348 g/L (0.006 M)), or it could be due to the suspected bias in one of the two responses.

A second explanation of the observed dependence of the equilibrium pH is that it could be due to the

co-extraction with cobalt and nickel cations of a hydrolysed nickel species such as $[Ni(OH)]^+$, as a function of the aqueous phase concentration present, according to a reaction similar to:

$$NiOH^+ + \overline{RNa} \rightleftharpoons \overline{R.NiOH} + Na^+ \qquad (10.10)$$

Thus under the combination of low $C_{Ni}(i,aq)$ and low temperature, a relatively low aqueous concentration of $NiOH^+$, and hence according to equations 10.6 and 10.10, a higher equilibrium pH, would be expected, as is observed. Under the combination of conditions of high $C_{Ni}(i,aq)$ and high temperature, a relatively low $[NiOH^+]$, and hence according to equations 10.6 and 10.10, a lower equilibrium pH, would be expected, again as observed. Under an intermediate combination of conditions, by the same argument, an intermediate pH would be expected, as observed.

The hydrolysis behaviour of cobalt and nickel is very similar, so there is no reason to suppose that there should be a great difference between the concentrations of the cobalt and nickel hydrolysed species. Therefore to be consistent with the observed effects, it would have to be assumed that the hydrolysed nickel species is extracted more than its cobalt counterpart.

The only evidence in the literature in support of the extraction of a hydrolysed nickel complex is that Grimm et al. reported the presence of hydroxide ion in the isolated

extracted nickel complex, as discussed in Section 2.2. In the complex, the metal:extractant ratio found was 1:1.37, and not the 1:2 expected for $\overline{NiR_2.2H_2O}$. The authors reported that the ratio for the isolated extracted cobalt complex was 1:2, so the cobalt complex was not hydrolysed.

It is not clear how solvent loading would be affected by the extraction of a hydrolysed nickel species, relative to extraction of the (hydrated) cation. It seems plausible that loading would increase with the hydrolysed species, since hydrolysis would lower the effective valency of nickel.

Whatever the effect on loading, the extraction of a hydrolysed species would not easily be detected in the factorial effects for the cobalt and nickel responses, since nickel extraction overall is dependent on the factor $C_{Co}(i,aq)$, which does not influence the extent of formation of the hydrolysed nickel species.

A third explanation for the observed dependence of equilibrium pH is that it is due to an irreversible aqueous phase hydrolysis of nickel that could occur when the aqueous feed solution is heated to extraction temperature, according to the reaction

$$Ni^{2+} + 2H_2O \rightleftharpoons Ni(OH)_2\ aq + 2H^+ \qquad (10.11)$$

(although it is more likely that the hydrolysed species would be polynuclear and hydrated). The hydrolysis reaction would be expected to increase with increasing $C_{Ni}(i,aq)$ and with

increasing equilibrium temperature, so that the trend in equilibrium pH with the combination of the nickel and temperature variables would be the same as before.

Of the three explanations of the pH behaviour, irreversible aqueous phase hydrolysis is the least credible. To account for the observed effects it would have to be postulated either that cobalt hydrolyses less than nickel, or that cobalt hydrolysis is reversible at elevated temperature and nickel hydrolysis is not. Both of these alternatives run contrary to what is known of cobalt and nickel hydrolysis. Stability constant data for hydrolysis of cobalt and nickel indicate that the species are hydrolysed to very similar extents, and neither cobalt nor nickel are known to hydrolyse irreversibly.

Both of the other explanations of the pH response behaviour are credible. It is not possible to say which is the more likely explanation however, on the present data.

10.3 Quantitative Relationships

In an equilibrium stage in which a cobalt and nickel bearing aqueous sulphate solution is contacted with a solvent phase containing 0.5 M NaD_2EHPA with 5 v/o TBP in Solvesso 150, at a phase volume ratio of 1:1, quantitative empirical polynomial expressions have been obtained to relate the equilibrium distributions and initial levels of the variables studied.

Within the ranges of the variables studied, the predicted values $\hat{y}_{\overline{Co}}$, $\hat{y}_{\overline{Ni}}$ and $\hat{y}_{pH}$ of the equilibrium organic cobalt concentration, equilibrium organic nickel concentration, and equilibrium pH respectively, are related to the coded levels X_1, X_2..., X_n of the factorial variables by the following equations:

$$\hat{y}_{\overline{Co}} = 10.35 + 2.344X_2 - 0.747X_3 + 0.416X_4 - 0.314X_5 + 0.159X_6 \quad (10.12)$$

$$\hat{y}_{\overline{Ni}} = 4.13 - 2.15X_2 + 0.638X_3 - 0.308X_4 + 0.200X_5 - 0.182X_6 \quad (10.13)$$

$$\hat{y}_{pH} = 5.12 + 0.044X_1 - 0.134X_3 - 0.103X_4 + 0.083X_6 \quad (10.14)$$

These equations are the regression equations which were considered to give the best fit of the data for each of the three responses, and have been given as equations 7.23, 8.2 and 9.5 respectively. However, the subscripts used with the coded variables have been altered so that each subscript number is common to a particular variable, in all three equations. The coded variables now correspond to the natural variables as follows:

X_1 → initial pH

X_2 → initial aqueous cobalt concentration

X_3 → initial aqueous nickel concentration

X_4 → equilibrium temperature

and $X_5 = X_2X_4$

$X_6 . X_3X_4$

The coding of the variables is made according to equation 7.10. Thus the coded variables are related to the natural variables x_1, x_2, ..., x_4 by the following equations:

$$X_1 = \frac{10^{-x_1} - 5.16 \times 10^{-5}}{4.84 \times 10^{-5}} \qquad (10.15)$$

$$X_2 = \frac{x_2 - 17.5}{7.5} \qquad (10.16)$$

$$X_3 = \frac{x_3 - 35}{15} \qquad (10.17)$$

$$X_4 = \frac{x_4 - 338}{15} \qquad (10.18)$$

where x_1 is the initial pH, x_2 is the initial aqueous cobalt concentration in g/L, x_3 is the initial aqueous nickel concentration in g/L, and x_4 is the equilibrium temperature in degrees Kelvin.

The predicted values $\hat{y}_{Co}$ and $\hat{y}_{Ni}$ of the equilibrium aqueous cobalt concentration and the equilibrium aqueous nickel concentration respectively, can be obtained from the predicted organic concentrations by difference with the initial aqueous concentrations, due to the constraint of conservation of mass. Since the phase volume ratio is 1:1,

$$\hat{y}_{Co} = x_2 - \hat{y}_{\overline{Co}} \qquad (10.19)$$

and $$\hat{y}_{Ni} = x_3 - \hat{y}_{\overline{Ni}} \qquad (10.20)$$

Equations 10.14-10.16 are the first-order polynomial equations which best fit the factorial design data. The presence of real two-factor interactions ($X_5 = X_2X_4$, $X_6 = X_3X_4$) in these equations indicate that, if required, an improved model of each response behaviour could be obtained using second-order polynomial expressions. In order to fit second-order polynomials, it would be necessary to carry out further experiments, at new levels of the factorial variables. An experimental design method of doing this is to composite (augment) the factorial design (see Section 7.2, orthogonality).

10.4 Conclusions

The effects of five variables and their interactions on the equilibrium distributions have been studied for the separation of cobalt and nickel in acid-sulphate solution by the sodium salt of D_2EHPA.

Throughout, the solvent composition was 0.5 M NaD_2EHPA with 5 v/o TBP in Solvesso 150, and the phase volume ratio was 1:1.

The variables and their levels studied were: the initial pH, at pH = 4.0 and 5.5; initial aqueous cobalt concentration, at 10 g/L (0.170 M) and 25 g/L (0.42 M); the initial aqueous nickel concentration, at 20 g/L (0.34 M) and 50 g/L (0.85 M); the equilibrium temperature, at 50°C

(323 K) and 80°C (353 K); and the initial aqueous sodium sulphate concentration, at none present and 0.5 M Na_2SO_4.

The three responses studied were the equilibrium organic cobalt concentration, the equilibrium organic nickel concentration and the equilibrium pH.

Strictly within the ranges of the variables studied, and under the present conditions of extraction, the conclusions are:

For the Cobalt and Nickel Responses:

1) Both the equilibrium organic cobalt concentration and the equilibrium organic nickel concentration are independent of the initial pH.

2) The equilibrium organic cobalt concentration increases, and the equilibrium organic nickel concentration decreases with increase in initial aqueous cobalt concentration.

3) The effect of increasing equilibrium temperature is to increase the equilibrium organic cobalt concentration. The two-factor interactions which are present indicate that the rate of increase (given by $\Delta\overline{[Co]}/\Delta T$) is not linear, and decreases with increasing temperature.

4) When both cobalt and nickel are present, the effect of increasing equilibrium temperature is to decrease the equilibrium organic nickel concentration.

The two-factor interactions which are present indicate that the rate of decrease, $\Delta[\overline{Ni}]/\Delta T$, is not linear, and decreases with increasing temperature.

5) Both the equilibrium organic cobalt concentration and the equilibrium organic nickel concentration, are independent of the initial aqueous sodium sulphate concentration.

6) The observed dependences of the cobalt and nickel responses can be explained in terms of the known extraction chemistry of the separation.

For the Equilibrium pH Response:

7) The equilibrium pH increases with increasing initial pH.

8) The equilibrium pH decreases with increasing initial aqueous nickel concentration.

9) The equilibrium pH decreases with increasing temperature.

10) There is a strong interaction between the initial aqueous nickel concentration and the equilibrium temperature.

11) The equilibrium pH is independent of the initial aqueous cobalt concentration.

12) The equilibrium pH is independent of the initial aqueous sodium sulphate concentration.

13) It is not possible to give a definite explanation of the behaviour of the equilibrium pH response, on the present evidence. However, credible explanations are put forward.

For All Three Responses:

14) Empirical polynomial expressions are given which quantitatively describe the dependences of the responses on the variables studied, within the ranges studied, and under the present experimental conditions.

REFERENCES

1. RITCEY G.M., ASHBROOK A.W. and LUCAS B.H. (1975). "Development of a Solvent Extraction Process for the Separation of Cobalt from Nickel". C.I.M. Bulletin, January, pp.111-123.
2. FLETT D.S. and WEST D.W. (1979). "Improved Solvent Extraction Process for Cobalt-Nickel Separation in Sulphate Solution by use of Di(2-ethylhexyl) Phosphoric Acid". Proceedings of Symposium of Complex Metallurgy, I.M.M., London, pp.49-57.
3. CLEMENTE D. De J., DEWAR B.I. and HILL J. (1980). Paper presented at 10th Annual Hydrometallurgical Meeting, Canadian Institute of Mining and Metallurgy, Edmonton. October 26-28th.
4. PRESTON J.S. (1982). "Solvent Extraction of Cobalt and Nickel by Organophosphorus Acids. 1. Comparison of Phosphoric, Phosphonic and Phosphinic Acid Systems". Hydrometallurgy, 9, pp. 115-133.
5. WIGSTØL E. and FROYLAND K. (1972). "Solvent Extraction in Nickel Metallurgy. The Falconbridge Matte Leach Process". Het Ingenieursblad, 41(17), pp.476-480.
6. FUJIMORI M., ONO N., ITASAKO S. and FUKUI I. (1980). "Solvent Extraction in S.M.M.'s Cobalt Refining Process". Paper, presented at 10th Annual Hydrometallurgical Meeting, C.I.M., Edmonton, October 26-28th.

7. MACKIW V.N. and VELTMAN H. (1980). "Recovery of Metals by Pressure Hydrometallurgy: The Sherritt Technology". Paper, presented at 10th Annual Hydrometallurgical Meeting, C.I.M., Edmonton, October 26-28th.

8. BURKIN A.R. (1966). The Chemistry of Hydrometallurgical Processes, E and F.N. Spon Ltd., London, pp.1-4.

9. BOLDT JR J.R. (1967). The Winning of Nickel, ed. Queneau P., Methuen, London, pp. 299-313.

10. HOWLING H.L. and SHANLEY E.S. (1961). "Cobalt-Nickel Separation". United States Patent 2,977,221.

11. LEVER F.M., MacGREGOR J.J. and WESTWOOD W. (1974). "Preparation of Group VIII Metal Compounds". United States Patent 3,806,591.

12. MOBBS D.B. and MOUNSEY D.M. (1981). "The Use of Caro's Acid in the Separation of Cobalt and Nickel". Trans. I.M.M., 90, pp. C103-C110.

13. OJANEN A. (1980). "Integrated Treatment of Cobalt Bearing Materials at Outokumpu Oy". Paper presented at 10th Annual Hydrometallurgical Meeting, C.I.M., Edmonton, October 26-28th.

14. As reference 9, pp.374-383.

15. FLETT D.S. (1979). "Solvent Extraction in Scrap and Waste Processing". J. Chem. Tech. Biotechnol., 29(4), pp.258-272.

16. BRISK M.L. and McMANAMEY W.J. (1969). "Liquid Extraction of Metals from Sulphate Solutions by Alkylphosphoric Acids. 1. Equilibrium Distributions of Cu, Co and Ni with D_2EHPA". J. app. Chem., 19, April, pp.103-108.

17. BRISK M.L. and McMANAMEY W.J. (1969). "Liquid Extraction of Metals from Sulphate Solutions by Alkylphosphoric Acids. 2. Kinetics of the Extraction of Cu and Co with D_2EHPA". J. app. Chem., 19, April, pp.109-114.

18. BROWN C.G. and SHERRINGTON L.G. (1979). J. Chem. Tech. Biotechnol., 29(4), pp.193-209.

19. SATO T. and NAKAMURA T. (1972). J. Inorg. Nucl. Chem., 34, pp.3721-3730.

20. SATO T. and UEDA M. (1974). Proceedings of the International Solvent Extraction Conference, Lyon, 1, pp.871-91.

21. KOLAŘÍK Z. and GRIMM R. (1976). J. Inorg. Nucl. Chem., 38, pp.1721-7.

22. BARNES J.E., SETCHFIELD J.H. and WILLIAMS G.O.R. (1976). "Solvent Extraction with D_2EHPA: A Correlation Between Selectivity and the Structure of the Complex". J. Inorg. Nucl. Chem., 38, 2, pp.1065-7.

23. WELCHER F.J. ed. (1963). Standard Methods of Chemical Analysis, 6th edition, Vol(II) part B, D. Van Nostrand, Princeton, U.S.A., pp.2282-5. (Determination by azeotropic distillation).

24. GRIMM R. and KOLARIK Z. (1976). "Acidic Organo-phosphorus Extractants - XXV. Properties of Complexes formed by Cu (II), Co (II), Ni (II), Zn (II) and Cd (II) with D_2EHPA in Organic Solvents". J. Inorg. Nucl. Chem., 38, pp.1493-1500.

25. MARTIN F.S. and HOLT R.J.W. (1959). Liquid-Liquid Extraction in Inorganic Chemistry". Quarterly Reviews of Chemical Society, Vol.13, pp.327-352.

26. HUGHES M.A., ANDERSSON S. and FORREST C. (1975). "Distribution Surfaces in Solvent Extraction Systems". International Journal of Mineral Processing, 2, pp.267-276.

27. TREYBAL R.E. (1963). Liquid Extraction, 2nd ed., McGraw-Hill, New York etc., pp.361-9.

28. FORREST C. and HUGHES M.A. (1975). "The Modelling of Equilibrium Data for the Liquid-Liquid Extraction of Metals. Part 1. A Survey of Existing Models". Hydrometallurgy, 1, pp.25-37.

29. HARRINGTON C.D. (1959). Uranium Production Technology, Van Nostrand, New York.

30. WHEWELL R.J. and HUGHES M.A. (1979). "The Modelling of Equilibrium Data for the Liquid-Liquid Extraction of Metals. Part (III). An Improved Chemical Model for the Copper/LIX 64N System". Hydrometallurgy, 4, pp.109-124.

31. WHEWELL R.J., HUGHES M.A. and MIDDLEBROOK P.D. (1979). "The Modelling of Equilibrium Data for the Liquid-Liquid Extraction of Metals. Part (IV). The Effect of the Diluent on the Copper/LIX 64N System". Hydrometallurgy, 4, pp.125-133.

32. BAUER G.L. and CHAPMAN T.W. (1976). Metallurgical Transactions B, 7B, pp.519-27.

33. CHAPMAN T.W. (1978). "Equilibrium Stage Calculations for the Solvent Extraction of Metals". A.I.Ch.E. Symposium Series, 74, No. 173, pp.120-126.

34. ELLIS D.A. (1960). Ind. and Eng. Chem., 52, pp.251-252.

35. LLOYD P.J. and OERTEL M.K. (1963). International Symposium on Hydrometallurgy, Dallas, Gordon and Breach, New York, pp.453-477.

36. IOANNU T.K., BAUTISTA G. and SMUTZ M. (1971). Proc. Int. Solvent Extr. Conf., London, 2, pp.957-65.

37. BOX G.E.P., HUNTER W.G. and HUNTER J.S. (1978). Statistics for Experimenters, Wiley, New York etc., U.S.A., Part (IV).

38. FORREST C. and HUGHES M.A. (1975). "The Modelling of Equilibrium Data for the Liquid-Liquid Extraction of Metals, Part (II). Models for the Copper/LIX 64N and Chromate/Aliquat 336 Systems". Hydrometallurgy, 1, pp.139-154.

39. ROBINSON C.G. and PAYNTER J.C. (1971). Proc. Int. Solvent. Extr. Conf., London, 2, pp.1409-15.

40. VALDES C.J., COOPER W.C. and BACON D.W. (1983). Metallurgical Transactions B, 14B, pp. 159-70.

41. CHAPMAN T.W. (1984). "Solvent Extraction of Metals - Metal Transfer Rates and Contactor Design". Hydrometallurgical Process Fundamentals, ed. Bautista R.G., Plenum, Nato Conference Series, Series (IV), Materials Science.

42. PERKIN-ELMER (1971). Analytical Methods for Atomic Absorption Spectrophotometry. Perkin Elmer Corp., Norwalk, Connecticut, U.S.A.

43. HARNED H.S. and OWEN B.B. (1958). The Physical Chemistry of Electrolytic Solutions, 3rd ed., Reinhold, New York, U.S.A., p.565.

44. AGATZINI S. (1981). 'A Statistical Approach to the Precipitation of Iron as "Goethite", Ph.D. Thesis, University of London, pp.133-4.

45. As reference 37, p.327.

46. DAVIES O.L., Editor (1967). The Design and Analysis of Industrial Experiments, 2nd ed., Oliver and Boyd, London, pp.286-7.

47. Ibid., p.287.

48. Ibid., p.287.

49. As reference 37, p.320.

50. DANIEL C. (1959). "Use of Half-Normal Plots in Interpreting Factorial Two-Level Experiments", Technometrics, 1(4), pp.311-341.

51. As reference 46, pp.271-273.

52. As reference 44, pp.82-89.

53. As reference 37, p.344.

54. DANIEL C. (1976). Applications of Statistics to Industrial Experimentation, John Wiley and Sons, New York etc., p.6.

55. RYAN JR T.A., JOINER B.L. and RYAN B.F. (1978). Minitab (II) Reference Manual, (on-line).

56. RYAN JR T.A., JOINER B.L. and RYAN B.F. (1976). Minitab Student Handbook, Duxbury Press, North Scituate, Massachusetts, U.S.A.

57. JAMES N. (1977). "User's Manual, Interactive Statistics Instructional System, Draft 2". Imperial College Computer Centre.

58. FISHER R.A. (1953). The Design of Experiments, 6th ed., Oliver and Boyd, Edinburgh.

59. As reference 37, Chapter 4.

60. As reference 54, p.22.

61. DUCKWORTH W.E. (1968). Statistical Techniques in Technological Research, Methuen, London, pp.135-138.

APPENDICES

Appendix 1. Distribution Curves.

Appendix 2. Statistical Appendices.

2.a. Randomization of the Experiments.

2.b. Yates's Algorithm for the Calculation of the Effects.

2.c. An Estimate of the Standard Error of an Effect from Higher-Order Interactions.

2.d. Bartlett's Criterion for the Homogeneity of Variances.

FIGURE 1.a. D_2EHPA* equilibrium distribution isotherms at 80°C for cobalt, in the presence of fixed quantities of total distributed nickel (by M.J. Rogers).

FIGURE 1b. Nickel extraction in the same equilibrations.

*0.5 M D_2EHPA with 5 v/o TBP in Solvesso 150.

Legend

Symbol	total nickel, gms (per litre of aqueous phase)
▲	50
△	30
❶	10
○	0
----	part of curve interpolated, due to phase entanglement problems.
T.S.C.=	total stoichiometric capacity of solvent for metal

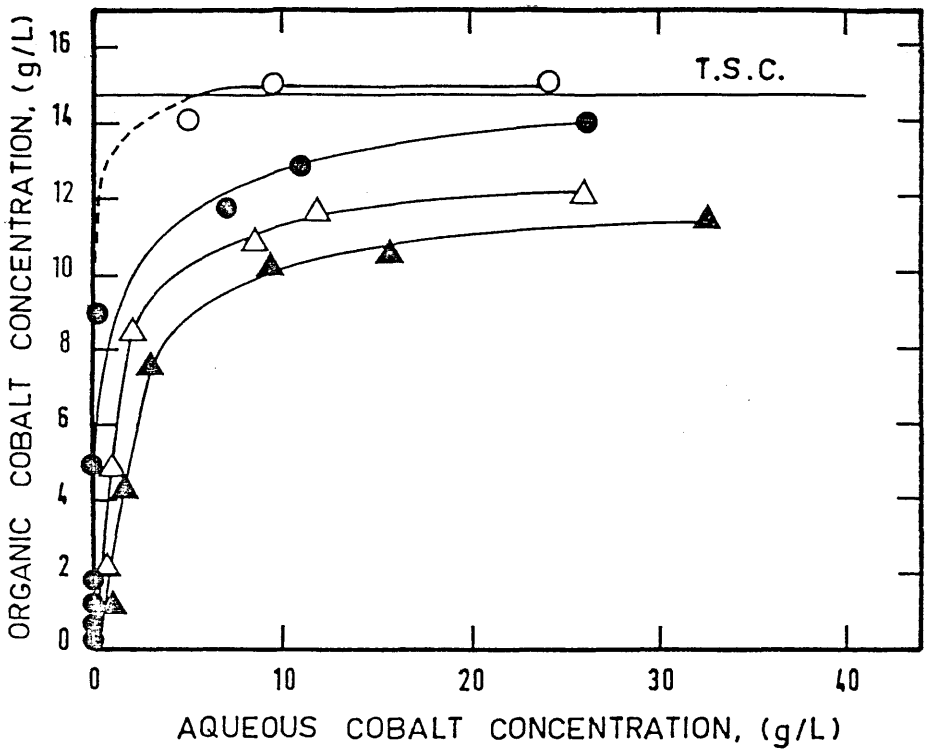


Figure 1a.

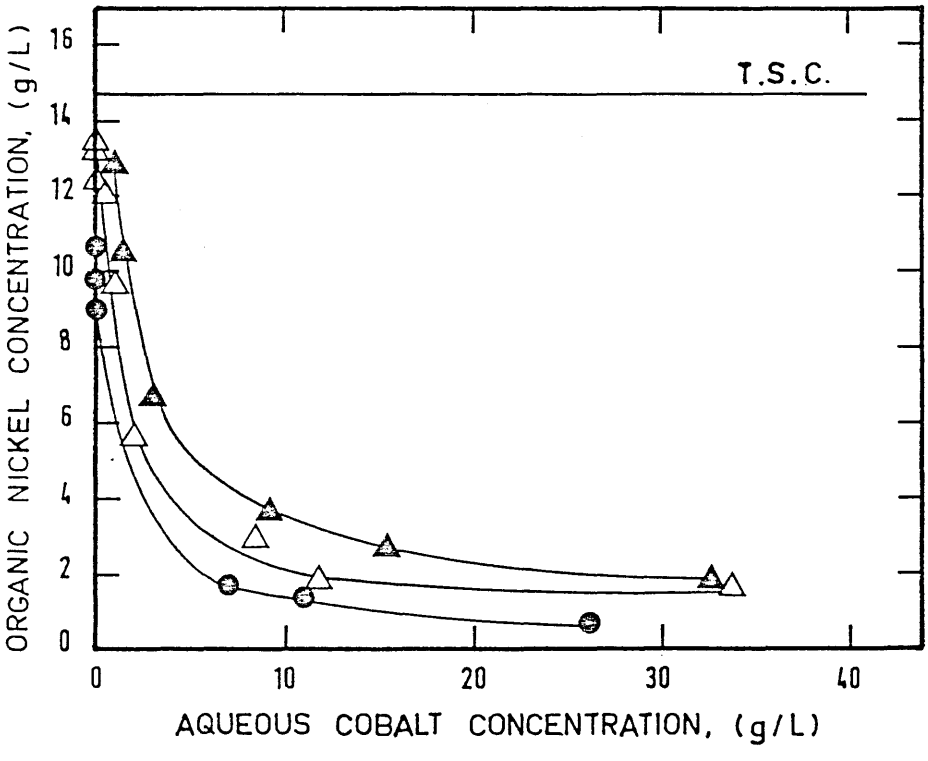


Figure 1b.

FIGURE 2a. D_2EHPA* equilibrium isotherms at 80°C for nickel, in the presence of fixed quantities of total distributed cobalt (by M.J. Rogers).

FIGURE 2b. Cobalt extraction in the same equilibrations.

*0.5 M D_2EHPA with 5 v/o TBP in Solvesso 150.

Legend

symbol	total cobalt, gms (per litre of aqueous phase)
▲	50
△	30
●	10
○	0

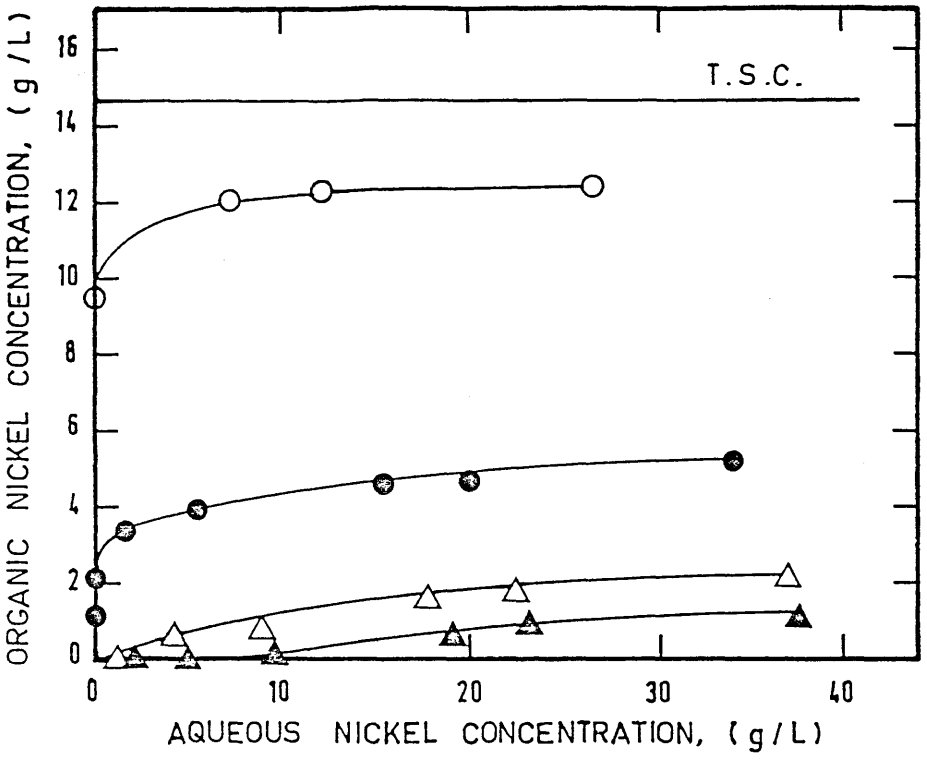


Figure 2a.

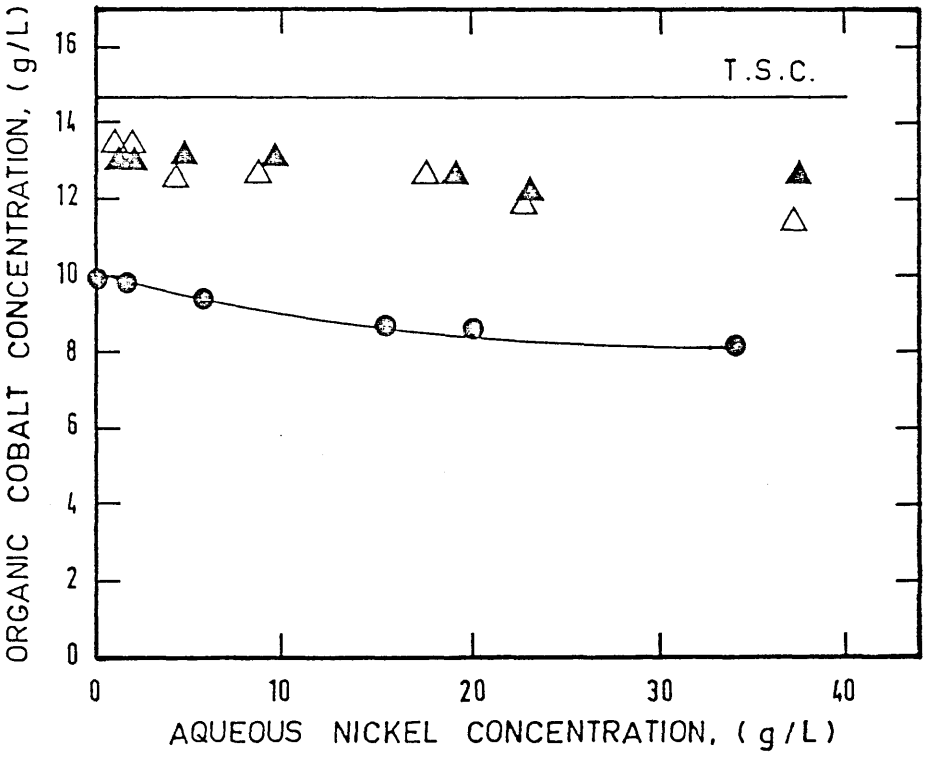


Figure 2b.

APPENDIX 2.a. Randomization of the Experiments

The application of randomization to statistical experiments was developed by Fisher[58], and both Box, Hunter and Hunter[59], and Daniel[60], for example, give useful discussions on the subject.

By randomizing the experiments it is meant that treatment combinations are randomly applied to experiments.

By randomizing the experiments, the validity of the application of the statistical tests of significance is ensured. It is highly desirable to randomize the experiments for this reason. There are a few circumstances, however, where it is not necessary (or even possible) to go to the effort of randomizing, as Daniel has discussed. An example is the case where randomizing is highly detrimental to the experimental procedure.

In the present work, randomization was introduced by randomization of the experimental order. Methods of randomizing the experimental order are given in most statistical textbooks. The procedure used here was that described by Duckworth[61], and is as follows.

(1) The treatment combinations are written down in standard order and numbered from 1 to N.

(2) Using a Table of Random Numbers which lists M items (M > N) one should decide on some arbitrary

scheme of selecting entries from the table (i.e. choose to use any of the columns or rows, or some other way) and of selecting the digits in the entry (i.e. choose to use the first two digits, the last two digits etc., in the entry). The number of digits chosen has to be equal to the number of digits in N.

(3) For each number selected the number is divided by N. If the remainder from the division has been obtained previously, it is discarded. If not, it is allocated to the first vacant treatment combination in the standard order list, as the experimental run number. The procedure is repeated until all (N-1) possible remainders have been allocated. The remaining treatment combination is run last.

(4) To avoid any bias in favour of some remainders, the pool of random numbers which may be selected should include only a complete multiple of N, e.g., for the design used here, since N = 32, only random numbers between 1 and 96 were selected.

For the present design, using the above method the following randomised experimental order was obtained:

Run Number	Treatment Combination	Run Number	Treatment Combination
1	abc	17	abde
2	bde	18	bce
3	abe	19	bcde
4	c	20	ae
5	bcd	21	L
6	abd	22	bc
7	ade	23	bd
8	ace	24	ce
9	b	25	be
10	abce	26	de
11	a	27	ad
12	abcd	28	d
13	cd	29	ac
14	cde	30	acde
15	e	31	acd
16	ab	32	abcde

APPENDIX 2.b. Yates's Algorithm for the Calculation of the Effects

The calculation of the effects using Yates's algorithm is exemplified in Table 1, which shows the calculation for the cobalt response.

The treatment combinations are written out in STANDARD ORDER, and the corresponding value of the response is entered in the response column.

In column (i) of Yates's algorithm, the first $2^n/2$ (here $2^5/2 = 16$) entries are obtained by adding pairs of responses together: In Table 1 the first pair 8.28 + 8.26 = 16.54, the second pair 13.20 + 13.56 = 26.76, and so on. The second $2^n/2$ entries are obtained by subtracting the top result from the bottom result for each pair of responses. Thus 8.28 - 8.26 = 0.02, the 17th entry in column (i); 13.56 - 13.20 = 0.36, the 18th entry, and so on.

In exactly the same way as column (i) is obtained from the responses, column (ii) is obtained from column (i), column (iii) is obtained from column (ii), column (iv) is obtained from column (iii), and finally column (v) is obtained from column (iv). The entries in column (v) are divided by the appropriate divisor to give the effects values. The divisor is 16 for the effects, except for the first entry, which is divided by 32 to give the average.

The cobalt effects are identified in the last column of Table 1.

In order to prevent mistakes in the addition and subtraction, it is convenient to check the calculation as each column is obtained. This can be done by calculating the sum of entries for each column, and the sum of every second entry. The check is that the sum of every second entry in column (i) is equal to half of the sum of entries in column (i + 1). The check is shown in the last two rows of Table 1.

Generalising the Yates's algorithm for the case of a 2^n design, n columns (i), (ii), ... (n) will be generated by adding and subtracting appropriate pairs of numbers. The first divisor will be 2^n, and the remaining divisors will be 2^{n-1}. If a factorial design is replicated, the Yates's algorithm is started by working with the response totals for each treatment combination rather than the response averages. Then the effects are obtained by dividing the entries in column (n) by N for the average and N/2 for the remaining effects, where N is the total number of experiments. ($N = 2^n.r$ where r is the number of replications).

TABLE 1. Yates's Algorithm for the Cobalt Response, 2^5 Factorial Design

Treatment Code	Response	Yates's Analysis (i)	(ii)	(iii)	(iv)	(v)	divisor	estimate	Identification
L	8.26	16.54	43.30	78.94	165.70	331.10	32	10.347	Average
a	8.28	26.76	35.64	86.70	165.40	-1.64	16	-0.1025	A
b	13.20	12.52	45.84	79.96	-1.84	75.02	16	4.6888	B
ab	13.56	23.12	40.92	85.44	0.20	-1.28	16	-0.0800	AB
c	6.36	18.62	43.40	-0.86	38.20	-23.90	16	-1.4938	C
ac	6.16	27.22	36.56	-0.98	37.00	-1.24	16	-0.0775	AC
bc	12.08	16.16	44.96	0.52	-1.08	0.50	16	0.0313	BC
abc	11.04	24.76	40.48	-0.32	-0.20	-1.92	16	-0.1200	ABC
d	9.25	16.40	0.38	20.82	-12.58	13.20	16	0.8313	D
ad	9.37	27.00	-1.24	17.20	-11.32	-0.96	16	-0.0600	AD
bd	14.02	12.72	-0.70	21.72	-1.20	-10.06	16	-0.6288	BD
abd	13.20	23.84	-0.28	15.28	-0.04	-0.04	16	-0.0025	ABD
cd	8.24	18.56	-0.52	-0.50	0.38	5.10	16	0.3188	CD
acd	7.92	26.40	1.04	-0.58	0.12	-1.12	16	-0.0700	ACD
bcd	12.36	16.52	0.64	-0.12	0.12	-1.30	16	-0.0813	BCD
abcd	12.40	23.96	-0.96	-0.08	-2.04	2.44	16	0.1525	ABCD
e	8.44	0.02	10.22	-7.66	7.82	-0.30	16	-0.0188	E
ae	7.96	0.36	10.60	-4.92	5.48	2.04	16	0.1280	AE
be	13.52	-0.20	8.60	-6.84	-0.12	-1.02	16	-0.0638	BE
abe	13.48	-1.04	8.60	-4.48	-0.84	0.88	16	0.0550	ABE
ce	5.96	0.12	10.60	-1.62	-3.62	1.26	16	0.0788	CE
ace	6.76	-0.82	11.12	0.42	-6.44	1.16	16	0.0725	ACE
bce	11.80	-0.32	7.84	1.56	-0.08	-0.26	16	-0.0163	BCE
abce	12.04	0.04	7.44	-1.60	0.04	-2.16	16	-0.1350	ABCE
de	9.24	-0.48	0.34	0.38	2.74	-2.34	16	-0.1463	DE
ade	9.32	-0.04	-0.34	0.00	2.36	-0.72	16	-0.0450	ADE
bde	12.92	0.80	-0.94	0.52	2.04	-2.82	16	-0.1763	BDE
abde	13.48	0.24	0.36	-0.40	-3.16	0.12	16	0.0075	ABDE
cde	8.36	0.08	0.44	-1.18	-0.38	-0.38	16	-0.0238	CDE
acde	8.16	0.56	-0.56	1.30	-0.92	-5.20	16	-0.3250	ACDE
bcde	12.36	-0.20	0.48	-1.00	2.48	-0.54	16	-0.0338	BCDE
abcde	11.60	-0.76	-0.56	-1.04	-0.04	-2.52	16	-0.1575	ABCDE
Column total:		329.46	403.20	376.64	384.00	371.20			
Total of alternates:		201.66	188.32	192.00	185.60				

APPENDIX 2.c. An Estimate of the Standard Error of an Effect from Higher-Order Interactions

In an unreplicated factorial design, on the assumption that higher-order interactions are negligible or do not exist, an estimate of the standard error of an effect, S.E. (effect), can be obtained from the higher-order interactions.

For example, an estimate of S.E. (effect) for the cobalt response, S.E. (4,5-f.i.), can be obtained from the four and five factor interactions. For the cobalt response, the interactions are:

Interaction	Effect (g/L)	$(\text{Effect})^2$	Degrees of Freedom
ABCD	0.1525	0.0233	1
ABCE	-0.1350	0.0182	1
ABDE	0.0075	5.6×10^{-5}	1
ACDE	-0.3250	0.1056	1
BCDE	-0.0338	0.0011	1
ABCDE	-0.1575	.0248	1
	Sum	0.1731	6

Accordingly, an estimate of S.E. (effect) for the cobalt response, having $\nu = 6$ degrees of freedom, is

$$\text{S.E.}(4,5\text{-f.i.}) = \sqrt{\frac{0.1731}{6}} = 0.170 \text{ g/L.}$$

APPENDIX 2.d. Bartlett's Criterion for the Homogeneity of Variances

To test the hypothesis that k mean squares, V_1, V_2, ... V_i ... V_k, are estimates of the same variance and may therefore be used as an estimate of error, the Bartlett's criterion can be used.

If the mean squares are based on ν_1, ν_2, ..., ν_k degrees of freedom respectively, and ν is the total number of degrees of freedom, then the average variance is $V = \Sigma(\nu_i V_i)/\nu_i$. The criterion measuring the divergence in the V's is $M = \nu \ln V - \Sigma \nu_i \ln V_i$. The significance points for M when each mean square has a single degree of freedom are given in the following table (from reference (47)).

Significance Points for M.

(Each estimate has one degree of freedom)

Value of k	2	3	4	5	6	7	8	9	10
5% point	5.1	7.7	10.0	12.0	14.1	15.9	17.9	19.6	21.3
1% point	8.3	11.5	14.0	16.5	18.9	21.0	23.1	25.2	27.2

For S.E. (4,5-f.i.) for the cobalt response, the calculations are as follows:

Interaction	$(\text{Effect})^2$	$V_i = \text{Mean Square} = 2^{(n-2)}(\text{Effect})^2$	$\ln V_i$	ν_i
ABCD	0.0233	0.1864	-1.6799	1
ABCE	0.0182	0.1456	-1.9269	1
ABDE	5.6×10^{-5}	4.96×10^{-4}	-7.7072	1
ACDE	0.1056	0.8448	-0.1687	1
BCDE	0.0011	0.0088	-4.7330	1
ABCDE	0.0248	0.1984	-1.6175	1
		$\Sigma V_i = 1.3844$	$\Sigma \ln V_i = -17.8332$	$\nu = 6$

$$V = 0.2307$$

$$\ln V = 1.4665$$

$$6 \ln V = -8.7990$$

$$M = 6 \ln V - \Sigma \ln V_i = 9.0342$$

Consulting the table, it is seen that a value of 14.1 is required for significance at the 5% level of significance. Therefore there is no evidence of heterogeneity.

ACKNOWLEDGEMENTS

I would like to offer many thanks to Professor A.R. Burkin, for all aspects of his supervision of this project, but particularly for showing patience above and beyond the call of duty.

To all members of the Hydrometallurgy Group, both past and present, who have offered me friendship, help and encouragement, I would like to extend my thanks, especially to Fiona Doyle and Luiz-Alberto Teixeira, and including June Rogers.

I would like to acknowledge Stella Agatzini and Mizé Dias, whose theses have helped me a great deal.

Deserving of mention and thanks are my friends W.G. Fahy, J.P. Latham and T. Vargas, with whom, amongst other things, I shared many lunch-time and late evening conversations about my work.

There are not a few whom I would like to thank for showing their friendship through not always the easiest of times. I hope their forebearance can be repaid.

For their financial support for this work I would like to thank the Science Research Council.

I would like to thank Sylvia Greenwood, both for the high quality of her typing of this thesis, and for her indulgence of my flexible approach to deadlines.

For the diagrams I thank Judy Healey.

The last word is for my family, in tribute to them for so many things.