The Extraction of Nickel with the use of Supported Liquid Membranes (SLM)

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EXECUTIVE SUMMARY

EXTRACTION OF NICKEL WITH THE USE OF SUPPORTED LIQUID MEMBRANES

1. MOTIVATION FOR THE PROJECT

The concept of using a supported liquid membrane (SLM) system to extract certain ionic species from solutions containing a mixture of various ions is not new.

The basic motivation for the current project, however, was to develop SLM extraction as a unit process to extract chemical species (selectively or non-selectivity) from mineralized industrial effluents. A secondary motivation for the project was to establish the potential for extracting chemical species with capsulated membrane configurations. Using the concept of an unconfined reactor would obviate the need for the use of costly containment of membranes in expensive flow-through contactors.

An initial feasibility study was conducted by the Department of Chemical Engineering of Potchefstroom University for the Water Research Commission. This showed some promise and the main thrust of the current follow-up project was the demonstration of the potential of the SLM extraction of various cations and anions from industrial effluents, such as the extraction of nickel from electroplating baths. A number of peripheral aspects were also to be investigated concurrently.

2. STATEMENT OF OBJECTIVES

2.1 Supported Liquid Membrane (SLM) qualification

The main objective was the determination of the interrelationship and the optimum rate of extraction between the various independent process variables associated with SLM extraction. The principal variables were:

- feed and strip concentration of the species to be extracted;
- acidity of feed and strip solutions;
- the concentration of extractant/diluent mix; and
- the effect of temperature.

This qualification implied the use of various cell configurations, of which a standard two-compartment cell, called the Hydrodynamically Characterised Cell (HCC), appeared to be the most appropriate. This cell configuration was required to provide the kinetic response and tendencies for the various variables.

2.2 Capsulated Membrane Extraction (CME)

It was hoped that the response from the HCC configuration would provide the extent and tendencies of the variables to be investigated by CME. A special factorial design experiment, using the STATISTICA computer package, could effect a dramatic reduction in the number of experiments to be conducted in order to optimize the five variables mentioned under 2.1

3. SUMMARY OF THE EXPERIMENTAL RESULTS

At the outset of the project it was felt that experiments should be conducted to illustrate the capability of SLM on more than one cationic species. For this purpose the cationic species of Nickel, Zinc, Chrome (III) and Calcium were selected. The rationale for this selection was to include a nuisance metal cation, such as Calcium, to demonstrate the possible extraction of Calcium from wastewater to render it more suitable for purification by reverse osmosis.

3.1 Results obtained by SLM extraction

The technical feasibility of SLM extraction by means of the HCC was demonstrated on a number of chemical species which could be summarised as follows:

- The extraction of anions such as HPO_3^{2-}, $H_2PO^-_2$, lactate and acetate was successfully achieved.

- The extraction of Calcium, Nickel, and Chrome was effected from a synthetic sulphate medium, as well as extraction of Zinc from an industrial penstock return solution obtained from Zincor.

These results exhibited extraction rates similar to those obtained by earlier researchers.

3.2 Results obtained by CME

Results obtained by CME on Nickel extraction clearly show that CME attains extraction rates of at least an order of magnitude higher than that achieved by SLM extraction. This was confirmed by a comparison between the SLM extraction of Nickel by earlier researchers and the extraction rate obtained currently with CME.

The design which was utilised for this experimental protocol is described in the report. The most important conclusion that could be drawn was that CME is a very viable technical possibility for the extraction and recovery of chemical species from aqueous media, such as industrial effluents.

4. CONCLUSIONS

The experimentation with regard to CME was successful and yielded very promising results on general design and technical features of the CME (unconfined reactor) concept. The following were the main results:

- Level 0 design parameters. (Input information needed for design).
- Provision of certain unique aspects of the concept, with regard to harsh chemical environment and superior transfer properties, as well as superior economic aspects such as size and configurational variables.
- The experimental design proved invaluable to attain the optima required, but it would have to be refined to higher levels of accuracy.

An extraction of 100 g/m^2 of nickel should be obtainable with the CME configuration. This is equivalent to approximately R3,00 /m^2 of membrane area.

5. RECOMMENDATION

The technique of CME is feasible from a technical point of view. To assess the commercial feasibility it would be necessary to obtain prices for the capsules made from a suitable membrane material. As there is no similar membrane type in capsule form available, costing was done on a prototype priced at about \$10 - 15/m^2 for quantities in excess of 100 m^2.

6. SUGGESTIONS FOR FURTHER RESEARCH AND TECHNOLOGY TRANSFER

The results obtained with CME were so encouraging that further research into its commercial applicability is warranted. It is for this reason that Eskom became interested to participate in a project concerning extraction of certain chemical pollutants still remaining in their boiler feed water, after ion exchange. Eskom is also willing to finance an extension of this project, but with a bias towards qualifying the CME to their need. For such a project, with technology transfer towards commercialization in mind, the following aspects would be of importance:

- Development and selection of a suitable extractant for the species to be extracted.
- Configuration and manufacture of a reusable capsule.
- Qualification of the extraction protocol, the capsule and the recovery of extracted species in the proposed industrial environment.
- A detailed study of the generalised critical extraction parameters governing CME.

A.5 Recommendation

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A.6 Suggestions for further research and technology transfer

The results obtain with CME are so encouraging that further research into the commercial potential is warranted. It is for this reason that Escom is interested to participate in a joint project concerning extraction of certain chemical pollutants still remaining in their boiler feed water after ion exchange. Escom is also willing to contribute towards an extension of this project, but with a bias towards qualifying the CME to their need. For such a joint project, with technology transfer towards commercialization in mind, the following aspects would be of importance:

- Development and selection of a suitable extractant for the species to be extracted.
- Configuration and manufacture of a reusable capsule.
- Qualification of the extraction protocol, the capsule and the recovery of extracted species in the proposed industrial environment.
- A detailed study of the generalised critical extraction parameters governing CME.

List of Photographs

Nomenclature

Unless otherwise stated, the symbols in this report have the following meaning: (The dimensions of the symbols are given in brackets).

A	Area (cm^2).
Ex	Extractant.
J	Flux ($\mu g/cm^2 s$).
k_{-1}	Mass transfer coefficient of reverse reaction.
k_1	Mass transfer coefficient of forward reaction.
K_E	Equilibrium constant.
M	Metal species.
R	Organic extractant.
t	Time (s or h).
V	Volume (cm^3).

Acronyms

CME	Capsulated membrane extraction.
D2EHPA	Di-2-(ethylhexyl) phosphoric acid.
DSP	Double salt precipitation
ENPB	Electroless Nickel plating bath
fcc	Face-centred cubic.
FFC	Flat film contactor.
HCC	Hydrodynamically characterised contactor.
MCC	Multi cell contactor.
MTO	Metal turnovers
SFC	Slurry flow contactor.
SLM	Supported liquid membranes.

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Table of Contents

Chapter 2

Chapter 3

Chapter 4

Appendix B

Appendix C

Appendix D

Appendix E

Appendix F

Appendix G

List of Tables

List of Figures

Superscript

b	Bulk solution.

Subscript

f	Feed solution.
o	Organic solution.

Chapter 1

Introduction

In the past few years there has been an increase in environmental awareness. This forced industries to be more careful with the waste they generate. The cleaning and upgrading of metal-containing waste have become not only a very demanding assignment, but also a lucrative business. The cleaning of nickel from waste streams is no exception. Nickel has the additional advantage that it is a very valuable metal (R 32.38/kg (Anon., 1995:S5)). The recovery of nickel from waste streams can be profitable.

This report is a continuation and extension of two previous reports viz. K5/617 (preliminary) and K5/431. In both the previous reports various configurations were shown to feasibly extract a wide variety of both cations and anions. A detailed description of the mechanisms involved were contained in both reports which ultimately confirmed the technical feasibility of the SLM concept. It was also evident that the sophistication of the various SLM reactor configurations implied high cost both to manufacture and operate. Consequently this project emphasizes the concept of an unconfined reactor which uses capsulated membrane extraction (CME). The technical feasibility of these capsules therefore was the main thrust of activities in this research report.

For this purpose a systematic approach to process design was followed. The design problem was reduced to a hierarchy of decisions (Douglas, 1988:16). The flowchart of the hierarchial process can be seen in figure 1.1. In this report only level zero (the input information) is researched.

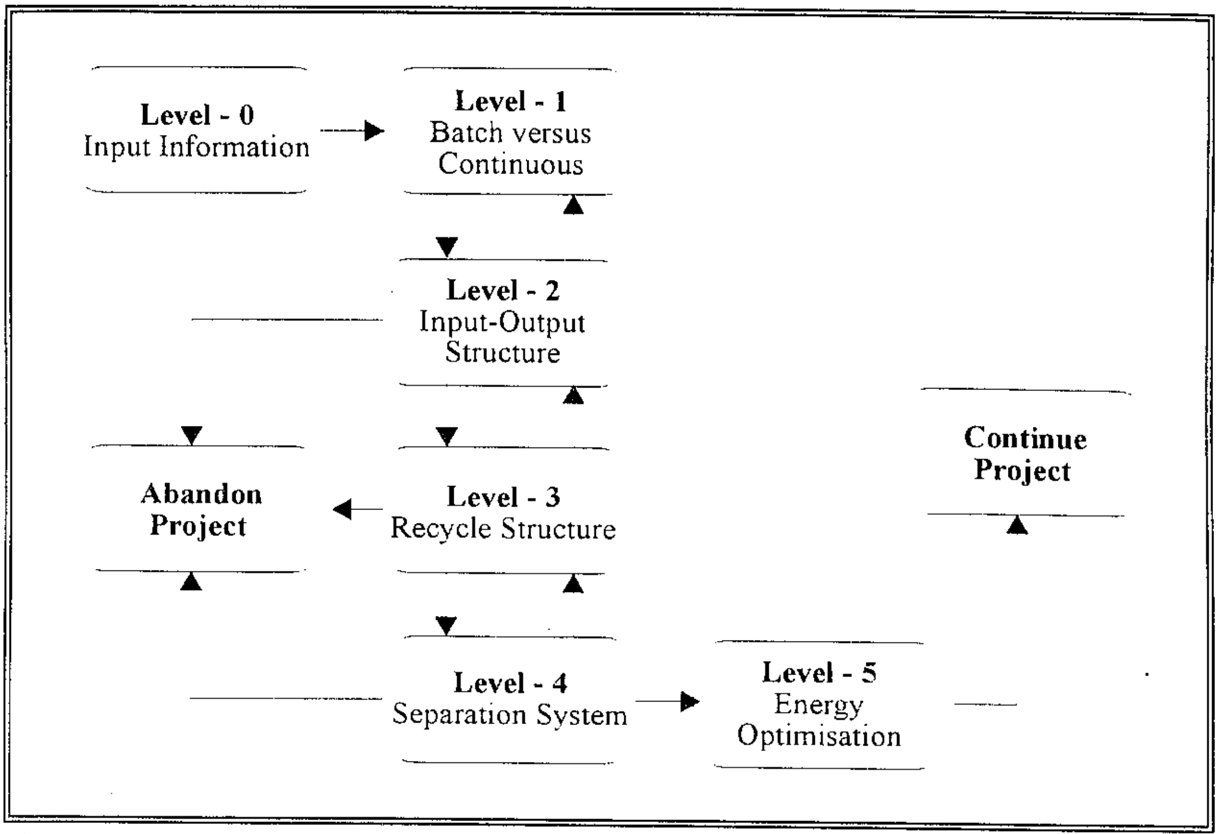


Fig. 1.1: Flowchart of hierarchial process design.

Chapter 2
Literature survey and theory

2.1 Nickel

Nickel is the seventh most abundant transition metal and the twenty-second most abundant element in the earth's crust (99 ppm). Its commercially important ores are of two types:

1. Laterites: Laterites are oxide/silicate ores such as garnierite. They are concentrated in tropical rainbelt areas such as New Caledonia, Cuba and Queensland.
2. Sulfides such as pentlandite: They are associated with metals such as copper, cobalt and other precious metals. These ores typically contain about 1% Ni and are found in more temperate regions such as Canada, the USSR and South Africa (Greenwood & Earnshaw, 1984:1329).

The production method of nickel is complicated. The oxide ores are not generally amenable to concentration by normal physical separations and so the whole ore has to be treated. The sulfide ores (as found in South Africa) can be concentrated by flotation and magnetic separations. This is the main reason why the sulfides provide the major part of the world's nickel (Tien & Hawson, 1981:797).

Some physical properties of nickel are given in table 2.1 (Tien & Hawson, 1981:788). Nickel has excellent corrosion-resistant properties. In general, nickel is very resistant to corrosion in marine and industrial atmospheres, outdoors, in distilled waters and flowing sea water. These properties are important to assess the amenability of nickel to be extracted by the proposed methods.

Table 2.1: Physical properties of nickel

Property	**Value**
atomic weight	58.71
crystal structure	fcc
lattice constant at 25°C, nm	0.35238
melting point, °C	1453
boiling point (by extrapolation), °C	2732
density at 20°C, g/cm^3	8.908
specific heat at 20°C, kJ/(kg·K)	0.44
av coefficient of thermal expansion × 10^{-6} per °C	
at 20-100°C	13.3
at 20-300°C	14.4
at 20-500°C	15.2
thermal conductivity, W/(m·K)	
at 100°C	82.8
at 300°C	63.6
at 500°C	61.9
electric resistivity at 20°C, μΩ·cm	6.97
temperature coefficient of resistivity at 0-100°C, (μΩ·cm)/°C	0.0071
Curie temperature, °C	353
saturation magnetization, T	0.617
residual magnetization, T	0.300
coercive force, A/m	239
initial permeability, mH/m	0.251
max permeability, mH/m	2.51-3.77
modulus of elasticity, × 10^3 MPa	
tension	206.0
shear	73.6
reflectivity, %	
at 0.30 μm	41
at 0.55 μm	64
at 3.0 μm	87
total emissivity μW/m^2	
at 20°C	45
at 100°C	60
at 500°C	120
at 1000°C	190

Wrought and cast nickel are used widely for nickel electrodeposition onto many base metals. Nickel also can be plated by an electroless process. Nickel plating provides resistance to corrosion for many commonly used articles such as pins, paper clips, scissors, keys, fasteners as well as for materials used in food processing.

Nickel plating is also used in the paper and pulp industries and the chemical industries which often are characterized by severely corrosive environments. Nickel plating is used in conjunction with chromium plating to provide decorative finishes and corrosion resistance to numerous articles. Nickel electroforming, in which nickel is electrodeposited onto a mold which subsequently is separated from the deposit, is used to form complex shapes such as printing plates, tubing, nozzles, screens and grids.

Nickel also is an important industrial catalyst. The most extensive use of nickel as a catalyst is in the food industry concerning the hydrogenation or dehydrogenation of organic compounds to produce edible fats and oils (Tien & Hawson, 1981:791).

Nickel is alloyed with about 32% copper to produce Monel 400 alloy which has relatively high strength weldability, and excellent corrosion resistance to many environments. A whole spectrum of nickel-base superalloys has been developed primarily for gas turbine parts which must be able to withstand high temperatures, high oxidizing conditions and be creep-resistant. Most wrought nickel-base superalloys consist of about 50 to 60% nickel, 15 to 20% chromium and 15 to 20% cobalt (Smith, 1990:548).

With these properties and end-uses in mind it is evident that nickel is a widely used metal and therefore subject to report in various effluents as a pollutant. The extraction of nickel at the prices quoted could consequently be a strong incentive to recover nickel from effluents from various industries but mainly from the plating and catalyst industries. It is for this purpose that the SLM and the newly proposed CME is expected to contribute to the general field of demineralization.

The same argument and procedures could be followed for other metal cations and consequently two separate but parallel projects were also conducted on the response of zinc and chrome III extraction with CME. These experiments and results are attached as addenda to this report to confirm the principle and procedure.

2.2 Supported Liquid Membranes (SLM)

2.2.1 Definition

Supported liquid membranes (SLM) represent an attractive alternative to liquid-liquid extraction for the selective removal and concentration of metal ions from solution. The permeation of metal species through SLMs can be described as the simultaneous extraction and stripping operation combined in a single stage. A thin layer of organic extraction reagent (extractant) is immobilized in a microporous inert support. This support is interposed between the feed solution (aqueous phase), in which the valuable metal is dissolved and the second (stripping) phase, in which enrichment of the metal occurs by transmembrane diffusion (Erlank, 1994:28).

2.2.2 Mechanism

The technique of SLM involves the transport of ions across the membrane under a concentration gradient by using a suitable carrier dissolved in a water immiscible organic diluent which is absorbed on a thin microporous polymeric film. The transport process takes place whenever the conditions of the aqueous feed and strip solutions are such that the distribution ratio of the permeating species at the aqueous feed solution membrane interface is much higher than at the aqueous strip solution-membrane interface (Chiarizia & Castagnola, 1984:481).

During extraction a metal-extractant complex is formed at the interface of the outer aqueous (feed) phase and the membrane phase. The complex permeates across the membrane and decomplexes at the interface yielding the metal species to the inner aqueous (strip) phase (Melzner *et al.*, 1984:107).

Two transport schemes mainly dominate the membrane processes, namely co-current transport and counter-current transport. These two modes of transport are depicted in figure 2.2, and although a number of variations do exist these two are illustrative of the principle involved. The mechanism of coupled transport, as illustrated in figure 2.2, shows that coupled transport is a reversible reaction of the permeating ion species with the metal carrier confined to the membrane

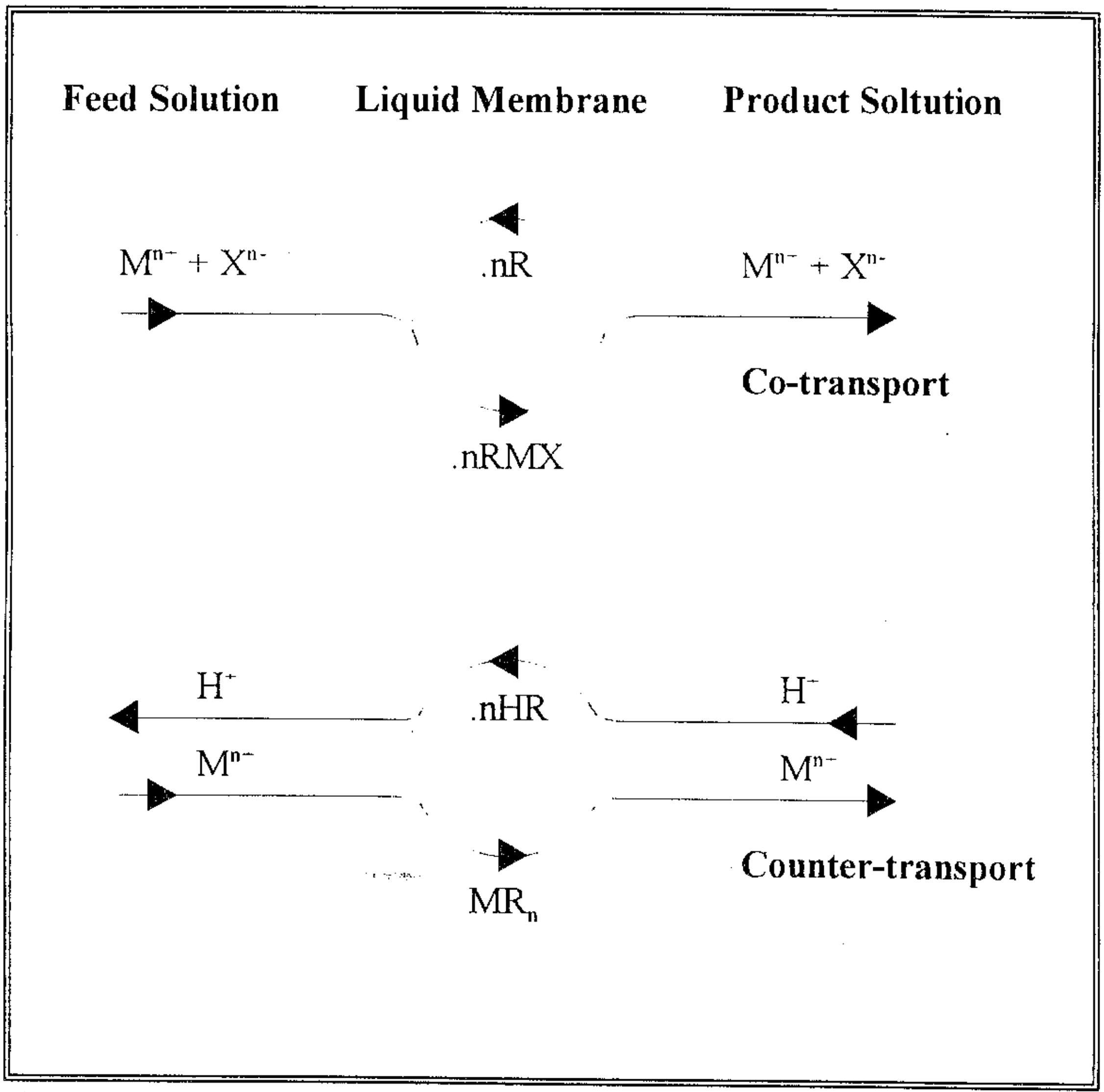


Fig. 2.2: The mechanisms of transport across a membrane.

phase (Babcock *et al.*, 1980:75). The permeant is an ionic species or chemical which cannot enter the membrane because of its low solubility in the hydrophobic organic solvent on the membrane. On the interface between the aqueous (feed) solution and organic solution, the metal carrier, R, reacts with the metal ion to form a neutral complex, MR_n. This neutral complex can diffuse freely within the organic phase and transports across the membrane to the second aqueous (strip) solution. At the interface the metal is released, the carrier reacts with a hydrogen cation to obtain a neutral charge, and diffuses back to the feed/membrane interface.

Previous work by Danesi *et al.* (1984:876) demonstrated (and experimentally verified) that the steady state permeability process can be described by the following equation:

$$M^{n+} + \overline{nHR} \rightleftharpoons \overline{MR_n} + nH^{+} \qquad 2.1$$

Where M = Metal species
n = valency
H = Hydrogen and
R = Organic extractant

The equation above is valid when the following conditions exist:

1. The metal ion concentration is low.
2. Fast interfacial reactions occur between the carrier and metal ion.
3. The distribution ratio of the permeating species at the strip membrane interface is very low.

The equilibrium constant (K_E) for the system is given by (Erlank, 1994:30):

$$K_E = \frac{(\overline{MR_n})(H^{+})^n}{(M^{n+})(\overline{HR})^n} \qquad 2.2$$

which is a mathematical expression of the Law of Mass Action which is very similar to the equilibrium constant for a simple reversible reaction. The overlined species represents the compounds in the organic phase. The above equation does not say anything about the rate at which equilibrium is attained. It does say that when a reactant or product concentration is changed, the equilibrium will adjust itself so as to maintain K_E constant. A constant K_E will be attained if the system variables are such as to allow for the changes to occur. These variables can now be selected to attain a specific selection or transport of species.

2.2.3 Kinetics

Unlike solvent extraction, facilitated transport is controlled by diffusion and chemical reaction rates. The mass transport process is established by a combination of the diffusion rate and the complexation reaction rate. The overall transfer rate in a facilitated transport system must therefore account for the interfacial reversible reaction kinetics as well as the diffusion process inherent in carrier-facilitated transport (Erlank, 1994:31).

A generalized model by Hofman (1991:12) is based on the permeation of metal species across the SLM in five steps:

1. Diffusion of the metal species from the bulk feed through the feedside boundary layer to the feed side of the SLM.
2. The reaction between the metal species and the extractant at the feedside surface of the SLM.
3. Diffusion across the SLM by the extractant-metal complex.
4. The chemical reaction between the extractant-metal complex and the strip solution on the strip side surface of the SLM.
5. Diffusion of the metal species from the strip side surface of the SLM, through the strip boundary layer, into the bulk strip solution.

Danesi (1985:862) developed a model for four cases where the assumptions are different for different experimental conditions. Danesi further assumed Fick's law of diffusion for steps 1, 3 and 5, and assumes that the chemical reactions in steps 2 and 4 are pseudo first order. Two parameters not considered in this model are the diffusion of the counter ion across the SLM, and the back diffusion of the extractant across the SLM after the metal has been stripped out of the SLM phase. The effect of the counter ion can be omitted if it is assumed that its mobility and chemical reaction are fast compared to that of the metal species. However, this assumption can not be applied to all systems and must be justified for each system which is modelled.

In the first case (Equation 2.3), Danesi assumed linear concentration gradients and that the strip metal loading is negligible. The first assumption is acceptable because of the small distances and concentration gradients in question. The second is made because Danesi had a system where he continuously added fresh strip, and hence he did not concentrate the metal species in the strip solution. This assumption is also acceptable for the studies done in this investigation. In most of the experimental procedures used during the investigation the initial strip solution was zero.

Also, the durations of the experiments were relatively short, thus preventing the strip phase to become too concentrated with the metal ion concentration.

$$\frac{J}{[M]_b^f} = P = \frac{k_1^f}{k_1^f \Delta a + k_{-1}^f \Delta o + 1} \qquad 2.3$$

In the second case, Danesi considered the chemical reaction at the feed-SLM interface to be fast. Hence k_1^f and k_{-1}^f are large and a local chemical equilibrium is found at the interface. Hofman (1991:27) extended the model to tubular and hollow fibre geometries.

In the third case Danesi considers the feed to have high metal ion concentration. A full recourse of the pertinent equations involved is given in the cited literature (Hofman, 1991:28). Danesi *et al.* extended this model to a fourth case (Equation 2.4) for situations where the strip metal concentration is not zero. This experimental condition was investigated to evaluate the extraction of metal ions against a gradient.

$$\ln\left[\frac{[M]_b^f}{[M]^o} - \frac{K_d^s}{K_d^f}\left(1 - \frac{[M]_b^f}{[M]^o}\right)\right] = -(P^f + P^s)\frac{At}{V} \qquad 2.4$$

2.2.4 Process Variables

2.2.4.1 Extractant concentrations

For a given metal concentration in the aqueous phase it is believed that the extraction coefficient will increase with an increase in extractant concentration. Extraction by a particular solvent, however, does not necessarily increase linearly with increase in the extractant concentration, since viscosity of the extractant increases with concentration. This might have an inhibiting effect on the carrier function that it must perform during transportation of metal species across the membrane. It is therefore necessary to evaluate each system individually in order to optimize the conditions for maximum results (Erlank, 1994:40).

2.2.4.2 The effect of pH

All chelating or acidic type extractants used in counter-current mode extraction processes, liberate a hydrogen ion on the extraction of a metal ion:

$$M^{n+} + \overline{nHR} \rightleftharpoons \overline{MR_n} + nH^{+} \qquad 2.1$$

Thus the greater the amount of metal extracted, the more hydrogen ions are produced and transferred to the feed side. This results in a decrease in pH of the feed side. The equilibrium will shift to the left and consequently results in a decrease in the amount of metal extracted (Erlank, 1984:40).

The pH of the system also affects both the metal ion and the extractant. If the pH on the feed side is increased, the metal will eventually hydrolyse and will not extract. Decrease in pH may result in the formation of non-extractable metal species as a result of complexation. At low pH values all extractants suffer protonation. If the extractant is unable to ionise it will not be able to form a complex with a metal ion, and extraction will not occur. It can thus be safely said that SLM extraction in this mode is pH-driven which implies the maintenance of a maximum pH difference across the membrane for optimum results.

2.2.4.3 Aqueous phase composition

Extraction of metals are affected by the type and concentration of the ionic species present in the aqueous phase. Where the metal complex in the aqueous phase has a stability constant greater than that of the metal-extractant complex, it can be predicted not to extract (Erlank, 1994:41).

If complexation of a metal in the aqueous phase produces a neutral species, it will not be extracted by an anionic or cationic extractant. The formation of a non-extractable metal-ion or ion-associated complex in the aqueous phase is dependent on the ion and on its concentration as well as chemical conditions such as pH.

Conversely, if the metal species in the aqueous phase is uncharged, then extraction with neutral or solvating extractants is more likely. However, increasing the ionic strength may seriously affect the extraction, either by the formation of stable metal complexes, or by the formation of unextractable charged species.

2.2.4.4 Metal ion concentration

If the metal ion concentration in the system is increased, all other conditions remaining constant, the concentration of extractant associated with the extractant species will increase with the result that the concentration of free extractant will decrease. Thus, a relative decrease in the extraction coefficient for that system could result in the limiting case of carrying capacity (Erlank, 1994:42).

Under certain controlled conditions, the extraction coefficient is independent of the metal ion concentration. This is not the case, however, at high metal concentrations. It must be kept in mind that activities were replaced by concentration for the sake of simplicity, but activities can change substantially with increasing concentration of reactants.

2.4 Applications in the Industry

2.3.1 Introduction

The requirements for environmentally sustainable development and the adverse economics of water recovery demand a new approach to the contaminants contained in effluents (Smit, 1994:14). These contaminants are chemical species with either a nuisance value or otherwise with widely variable economic value. The basic needs for water recovery in industry and the environment is therefore contained in the following:

1. To demineralise effluents of valuable metals with its associated cost incentive as the driving force.
2. To demineralise effluents of nuisance metals to foster sustainable ecological development.
3. To decontaminate effluent of other chemicals species having obnoxious, deleterious and/or hazardous effects in the ecology.

The extraction of nickel from electroplating wastewater is a classic example where the process can be both economically and environmentally justifiable.

2.3.2 Nickel plating

Nickel plating is by far the most important electroplating process (Anon., 1970:684), since a sufficiently thick coating of nickel protects iron and steel from rusting. Nickel is plated either by an electroplating process or by electroless nickel plating. Soon after the metal became commercially available, in about 1870, nickel plating became popular for the protection and embellishment of harness parts and bicycle parts. Subsequently it was used for all kinds of metal articles. Its use was further stimulated by the advent of the motor car, particularly after 1930. Out of the total consumption in the UK in 1965 of 36 300 tons of nickel it is estimated that about 5 000 tons (one seventh) were used in electroplating.

The most common type of electroplating solution for nickel can be seen in table 2.2 (Anon., 1970:684). This solution is known as the Watts solution. The rate of deposition is between

0.0008 and 0.0053 in/h (0.02032 - 0.3462 mm/h). The voltage necessary varies with the current density, the temperature and the size of the vat, but is in the range of 3 to 7 V. The solution is almost saturated with nickel salts, to have the maximum amount of nickel ions available and to achieve a high current density.

Table 2.2: Composition and properties of Watts nickel bath.

Nickel sulphate ($NiSO_4.7H_2O$)	250 g/l
Nickel chloride ($NiCl_2.6H_2O$)	37.5 g/l
Boric acid (H_3BO_3)	25 g/l
Acidity (pH)	3.0 - 5.8
Temperature	35 - 65 °C
Current density	1.39 - 9.29 A/m^2

In nickel plating maintenance of a steady, but very slight acidity is most important. Satisfactory nickel plating can only be obtained in the pH range 3.0 to 6.1, but in practice a much closer range is maintained (pH 5.2 to 5.8).

The first step in the plating process (Anon., 1970:685) is to attach the articles which that must be plated to wires or jigs. The wires or jigs are hung on a central metal rod at the top of the tanks. The articles are then placed in a tank with hot alkaline degreasing solution (fig. 2.3 A). The degreasing action is sometimes assisted by an electric current. After degreasing the articles are rinsed in a steel rinse tank (fig. 2.3 C), with flowing cold water. The articles are then placed in a lead lined tank containing cold dilute acid, to etch the articles lightly (fig 2.3 B).

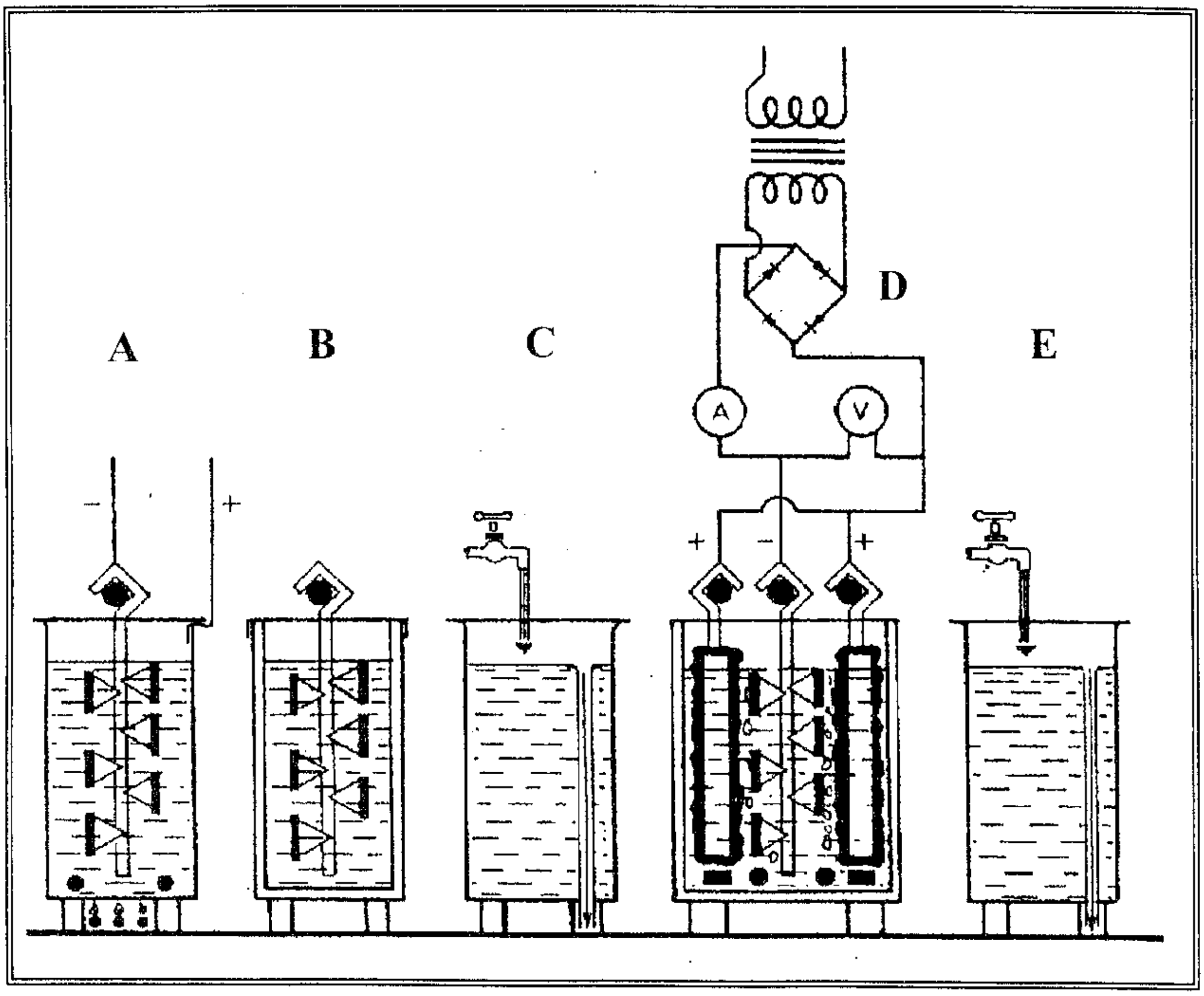


Fig. 2.3: Diagrammatic representation of a simple nickel plating plant.

The articles are then placed in the nickel plating tank (fig. 2.3 D). The nickel plating solution is held in an open topped, lead or rubber lined tank. The solution is heated by submerged steam or electric heaters. A temperature of at least 35 °C is usual, but because faster electroplating can be achieved at higher temperatures, the baths are often operated at temperatures up to 65° or 70°C. The plating solution is usually agitated by compressed air, which is blown in through a perforated pipe on the floor of the tank.

The tank is provided with a central metal rod at the top, from which the articles are hung. This rod is connected to the negative side of the low voltage direct current supply. Similar rods are arranged at the two opposite sides of the tank, and are connected to the positive side of the current supply. On these rods the nickel anodes are hung by metal hooks. Nickel anodes are usually cast from metal containing oxide and other trace elements to facilitate their dissolution. Nickel tends to release tiny metallic fragments into the solution as it dissolves. If these particles should settle on the articles being plated, a rough deposit would result. The anodes are therefore enclosed in heavy cotton twill bags. The nickel plating solution is also filtered, either continuously or from time to time.

After the selected period of electroplating the racks of wires carrying the articles are lifted out of the plating tank, thoroughly rinsed in running water to avoid stains (fig 2.3 E) and then dried, usually in a current of warm air.

Many other types of nickel plating have been advocated, mostly based on nickel sulphate, although nickel chloride and nickel sulphamate baths can be worked more quickly (Anon., 1970:689). With the nickel sulphate process the ENPB (electroless nickel plating bath) initially contains 7 g/dm^3 nickel (Smit, 1994:58). When the bath is operated for such a period that the nickel is "worked-out" to ± 1 - 3 g/dm^3 the nickel sulphate is replenished by addition. The number of times such a bath can "work out" the nickel is called the number of metal turnovers (MTO). Currently a bath can be operated for about 5 - 10 metal turnovers before a new ENPB has to be used. The number of metal turnovers is an indication of the bath's useful life. The higher the MTO's are the lesser effluent (spent bath) must be discharged.

2.3.3 Waste treatment

During the final rinsing step, valuable nickel plating solution inevitably adheres to the parts or is trapped in recesses. This is called "drag-out"(Anon., 1970:689).

In the nickel sulphate electroplating process "drag-out" also occurs, but there is the additional discharge of the spent bath after the ENPB has "worked-out" the number of metal turnovers. A typical analysis of a spent ENPB can be seen in table 2.3 (Smit, 1994:60).

Table 2.3: Analysis of a spent ENPB.

Species	**Concentration** (g/dm^3)
HPO_3^{2-}	97.98
$H_2PO_2^-$	24.10
HAC	98.20
LAC	95.77
Ni^{2-}	7.00
Operating conditions	
Temperature: 90 °C	
pH: 4.2 - 4.5	

It is thus evident that Nickel effluent sources are of two kinds viz. The "drag out" which result from rinsing as well as Nickel to be recovered from "spent" bath where no more MTO's could be attained.

2.5 Results of previous work done on extraction of Nickel with SLM

The recovery of nickel, together with cobalt and iron, from ores, concentrates and residues were extensively researched by Chiarizia *et al.* (1984:479) with a variety of extraction conditions. By studying the permeability coefficients of Fe^{3+} and Co^{2+} as functions of the feed chloride concentration, suitable conditions have been identified where a separation of Fe^{3+} from Co^{2+} and Ni^{2+}, and from Co^{2+} from Ni^{2+} can be performed.

Ritcey & Ashbrook (1979:105) reported that nickel can be extracted with the use of D2EHPA. Normally, extraction using D2EHPA is pH dependant. From sulphate solutions the order of extraction as function of pH is Fe^{3+} < Zn^{2+} < Cu^{2+} < Co^{2+} < Ni^{2+} < Mg^{2+} < Ca^{2+} (see fig. 2.4).

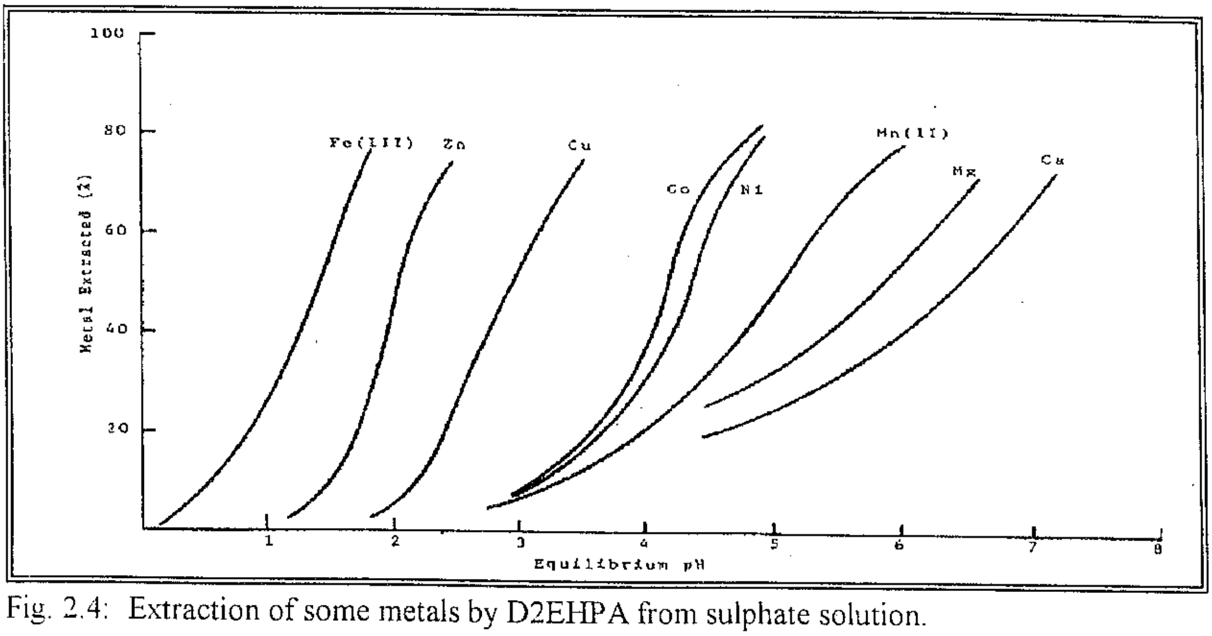


Fig. 2.4: Extraction of some metals by D2EHPA from sulphate solution.

Verhaege *et al.* (1987:331) investigated the possibility of nickel recovery by membrane extraction focussing on the Watts nickel bath rinse solution. Several solvent mixtures were prepared with D2EHPA dissolved in Solvesso 150. The feed solution contained 1.6 g/l Ni^{2+} and had a pH of 4.46. Their results are summarised in figure 2.5 and figure 2.6.

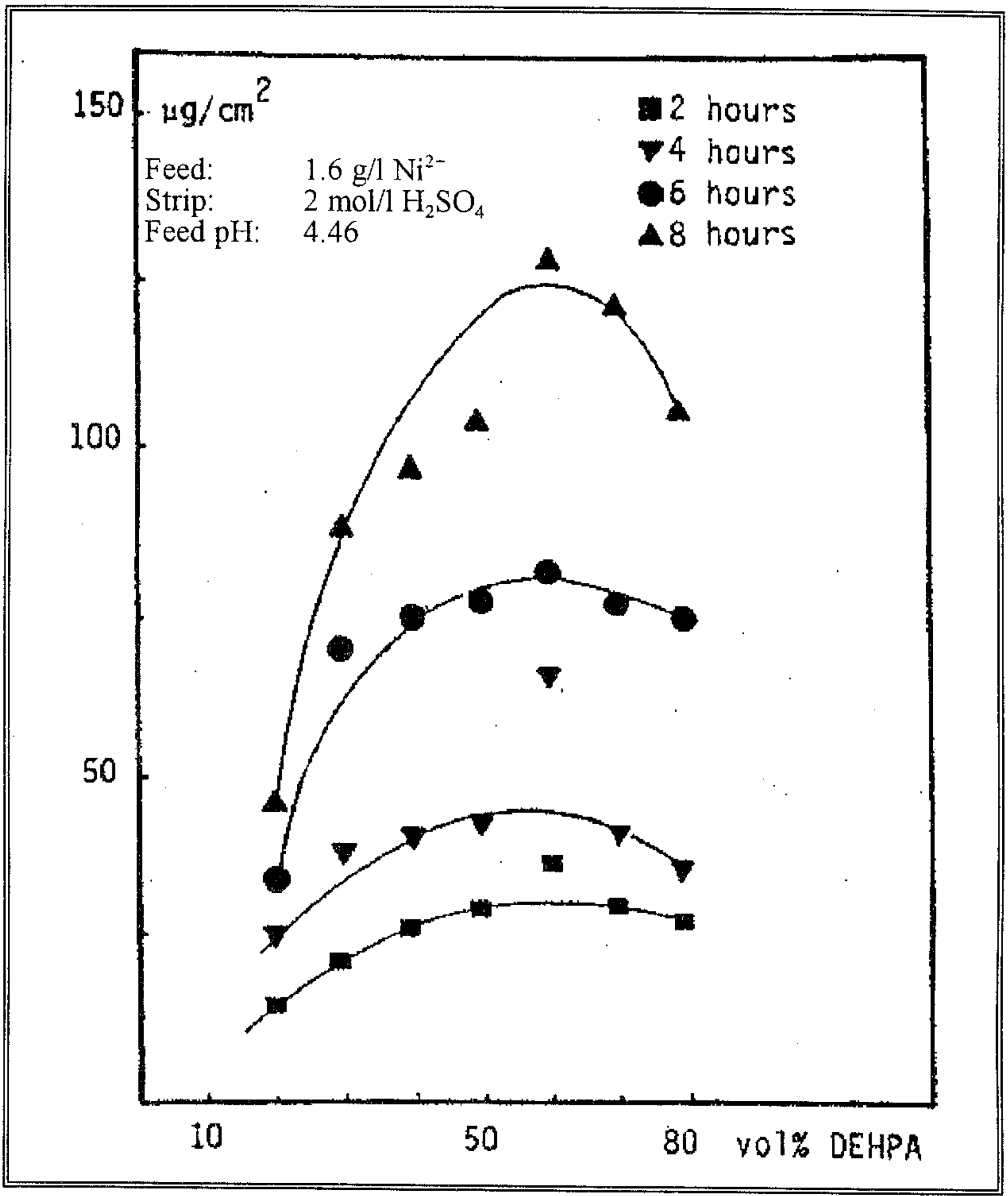


Fig. 2.5: Influence of membrane composition on mass transfer.

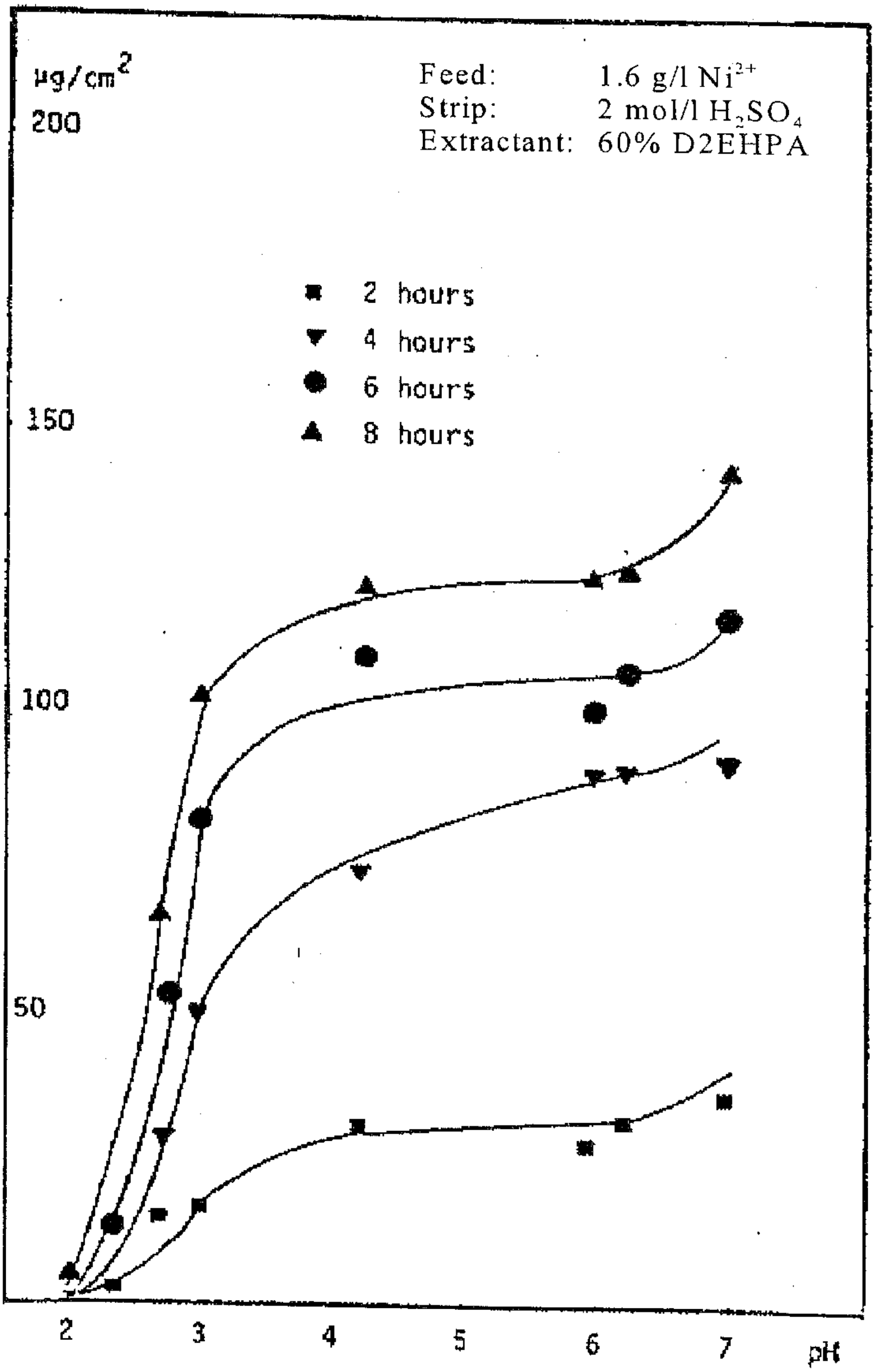


Fig. 2.6: Influence of feed pH on mass transfer.

In the case of a sulphuric acid system, the extractants available for extraction of nickel perform best in the pH range 4 to 6 (Ritcey & Ashbrook, 1979: 111). It was found that LIX 64N and Kelex 100 are non-selective and co-extracts iron and copper in this pH region. The extraction characteristics of these two chelating extractants are similar, and pH dependant, and will therefore give similar results in dilute nitric or hydrochloric acid systems than the sulphuric acid system.

Bogacki *et al.* (1993:2775) came to the conclusion that the use of hydrochloric acid for stripping instead of sulphuric acid, increases the transfer of nickel from the feed to the strip.

Flett (1981:321) reported the slow rate of extraction of nickel by a mixture of alpha-hydroxyoximes and lauric acid to be due to specific interfacial effects caused by the interaction between nickel and lauric acid.

Erlank (1994:97) also found that nickel can be extracted with SLM. The preliminary results showed a general increase of nickel extraction with CME compared with SLM. The addition of 18-crown-6-ether to D2EHPA had a positive synergistic effect and increased the effective extraction of nickel.

2.6 Configurations for SLM extraction

Smit (1994:29) developed four different contacting devices for SLM-extraction namely the Flat film contactor (FFC), the Multi cell contactor (MCC), the Hydrodynamically characterised contactor (HCC) and the Slurry flow contactor (SFC). Each of these contactor (reactor) configurations will be discussed in greater detail.

2.5.1 The Flat film contactor

With this contactor (fig. 2.7) the sealed feed and strip compartments are separated by a suitably prepared SLM. Extraction proceeds until "equilibrium" (no further transport) is attained. The disadvantages of this contactor are:

1. No possibility to influence the boundary layers by flow or agitation.
2. No possibility of effecting addition/withdrawal of chemical species.
3. No possibility of researching the influence of temperature as variable.

The only advantage the FFC has is in the ease of assembly, its cost effectiveness and the possibility of obtaining very rudimentary indicative "Yes/No" results. A tubule or hollow fine fibres is essentially also a FFC, but was not used in the evaluation due to its non-availability.

2.5.2 The Multi cell contactor (MCC)

This design endeavours to obviate the main disadvantages of the FFC viz. the singular extraction result. The MCC is a flow-through variation of multiple FFC's. From the schematic presentation (Figure 2.8) it is evident that each of four windows could effect a different strip solution and/or a different SLM exposed to either a different feed solution or the same feed solution. Any number of permutations and combinations is possible which renders this contactor very flexible and able to give quick results to scan the extraction potential for a specific species. Due to its small size, however, no direct heating can be effected but heating, dosing and measurements could be effected in the containers feeding the MCC.

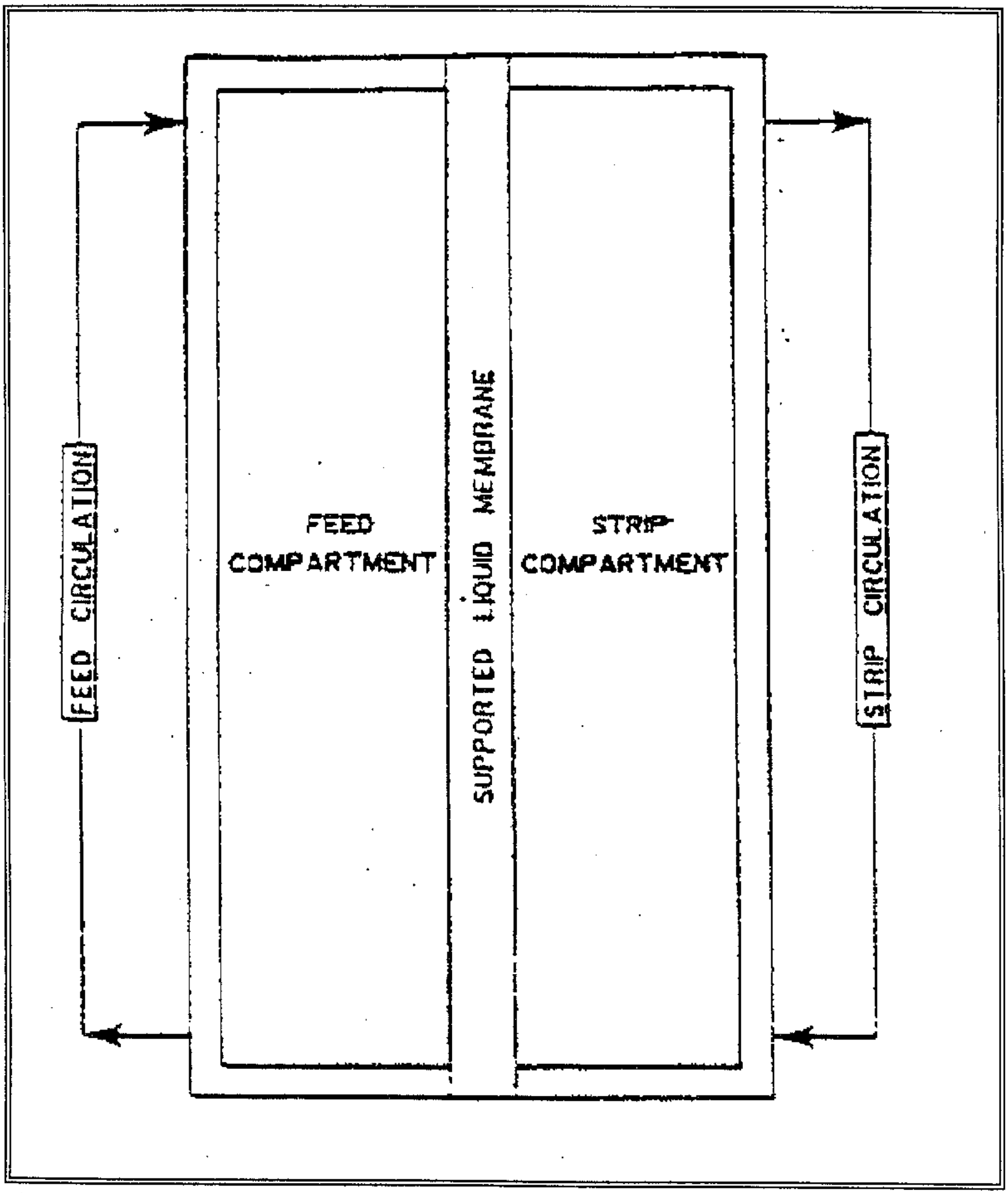


Fig. 2.7: Flat film contractor (FFC).

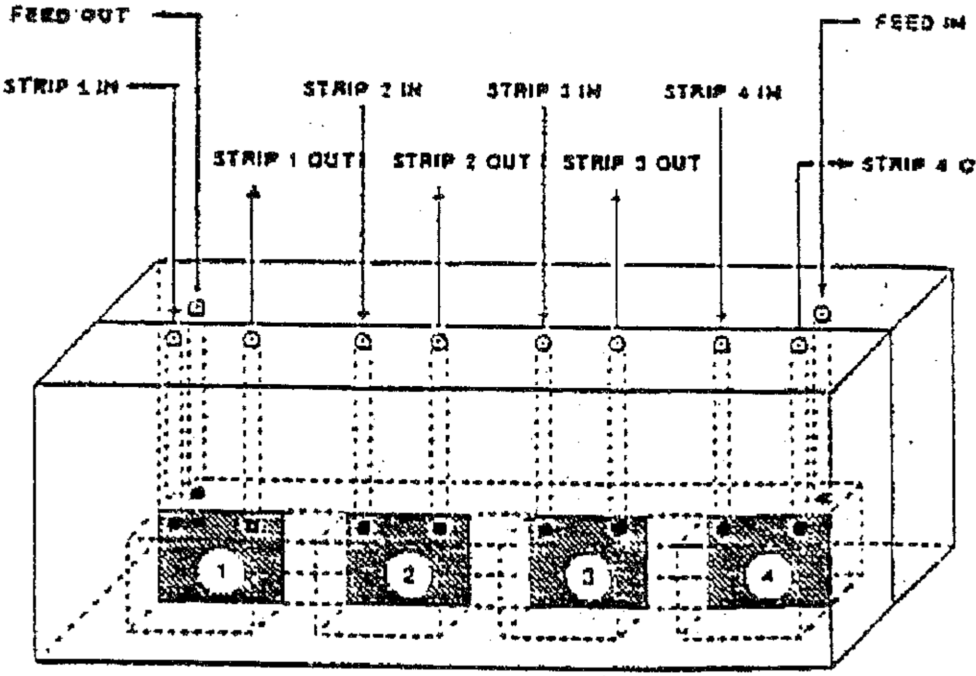


Fig. 2.8: Multi cell contactor (MCC).

2.5.3 Hydrodynamically characterised contactor (HCC)

Experimentation with the HCC enables the meticulous evaluation of optimised transport through the membrane at various temperatures and with the possibility to add and withdraw chemicals during the experiment. By the variable agitation facility the boundary effects at the aqueous/membrane interphases can be minimised and kept constant. These attributes render the HCC a powerful but accurate piece of equipment for studying transfer phenomena during SLM extraction. Several prototypes were tried and the latest seems to be satisfactory also with regard to the harsh chemical conditions (low and high pH) often required for the facilitated (sympathetic) driving force. A diagram of a HCC can be seen in figure 2.9.

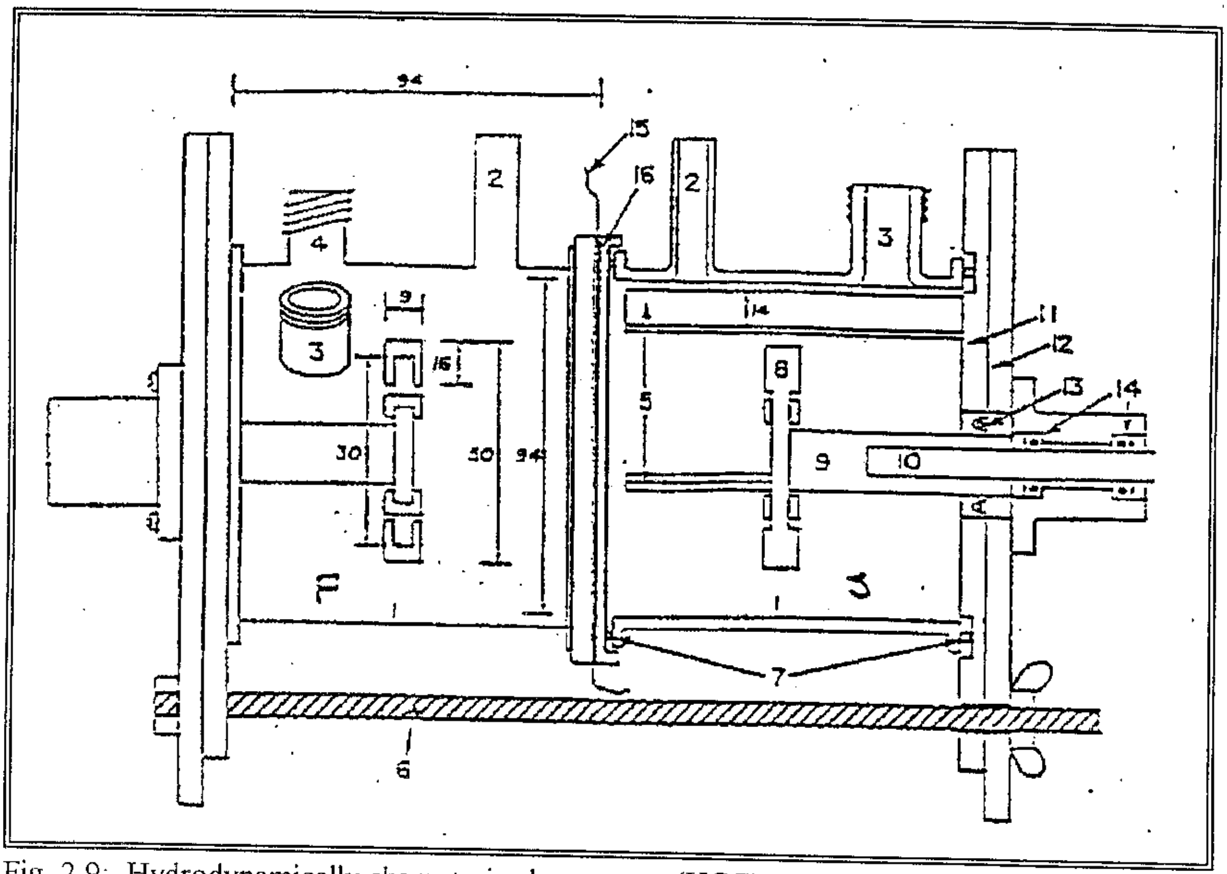


Fig. 2.9: Hydrodynamically characterised contactor (HCC).

2.5.4 The Slurry flow contactor (SFC)

This configuration is a special contactor which was developed to demonstrate the possibility of extraction from a slurry (feed side) into a slurry (strip side). This configuration illustrates the direct extraction of a chemical species from an unclarified leach slurry (± 5 - 10% solids) into a strip solution in which the extracted species precipitates and thus constitutes a strip slurry. It is firstly interesting to note that for hydrometallurgical applications the need for a very well clarified feed solution to a liquid-liquid extraction (solvent extraction) process can now be obviated. It is secondly also important to realise that by precipitating the extracted chemical species in the strip solution, it is removed from any chemical equilibrium reaction thereby effecting the maximum possible yield of reagent to product. Thirdly it is evident that by flowing these slurries past the membrane the two aqueous boundary layers are destroyed and completely non-existent. A diagramme of an SFC can be seen in figure 2.10.

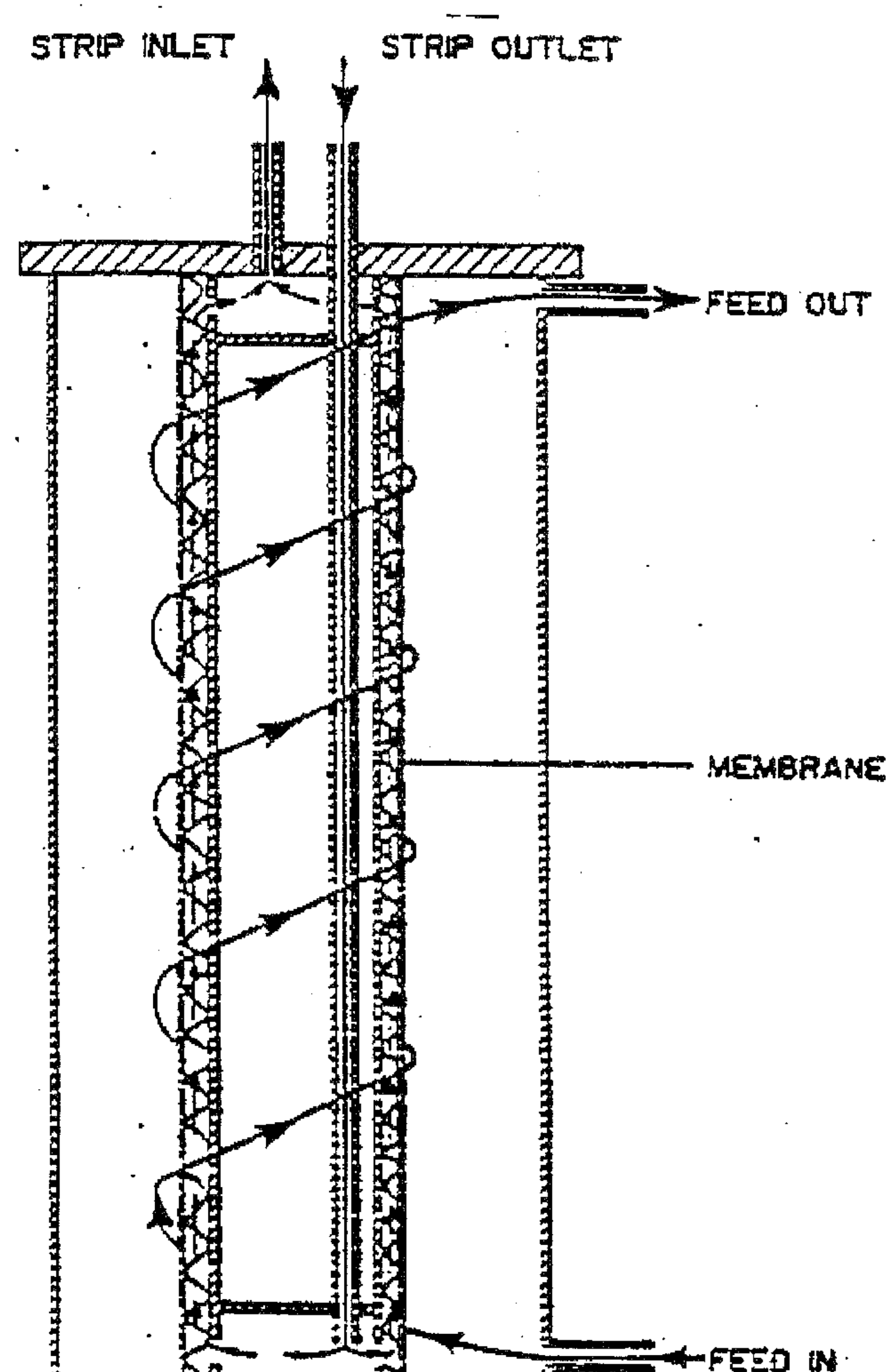


Fig. 2.10: Slurry flow contactor (SFC).

2.5.5 Capsule membrane extraction (CME)

All of the above mentioned contactor configurations (reactors) have the simple disadvantage of excessively high cost to obtain the required packing density (m^2/m^3) in the available spatial configuration used to configure the particular reactor. The concept of an unconfined reactor was used to overcome this problem. In this configuration a membrane capsule is made with the strip solution on the inside. The extractant is supported in the membrane skin. This capsule is submerged in the feed solution. The CME configuration has the additional advantage that very high acid concentration can be used in the strip solution without the risk of high corrosion. The CME configuration is discussed in greater detail in chapter 3.2.

Chapter 3
Optimization of CME

3.1 Introduction

The fist step in the systematic approach to design (Level 0) is to gather all the input information (fig. 3.1). The information that must normally be gathered at the initial stages of a design problem is (Douglas, 1988:99):

1. The reactions and reaction conditions.
2. The desired production rate.
3. The desired product purity, or some information about price versus purity.
4. The raw materials and/or some information about price versus purity.
5. Information about the rate of the reaction.
6. Any processing constraints.
7. Other plant and site data.
8. Physical properties of all components.
9. Information about the safety, toxicity and environmental impact of the materials involved in the process.
10. Cost data for by-products, equipment and utilities.

Some of the information above was gathered during the literature survey, others are not applicable to this specific process design, but the most important information still lacking is the information about the rate of the reactions, more specifically, about the rate of extraction during different conditions. The dissertation by Erlank (1994:83) confirmed the feasibility of the CME process, but an optimisation of process conditions still has to be done.

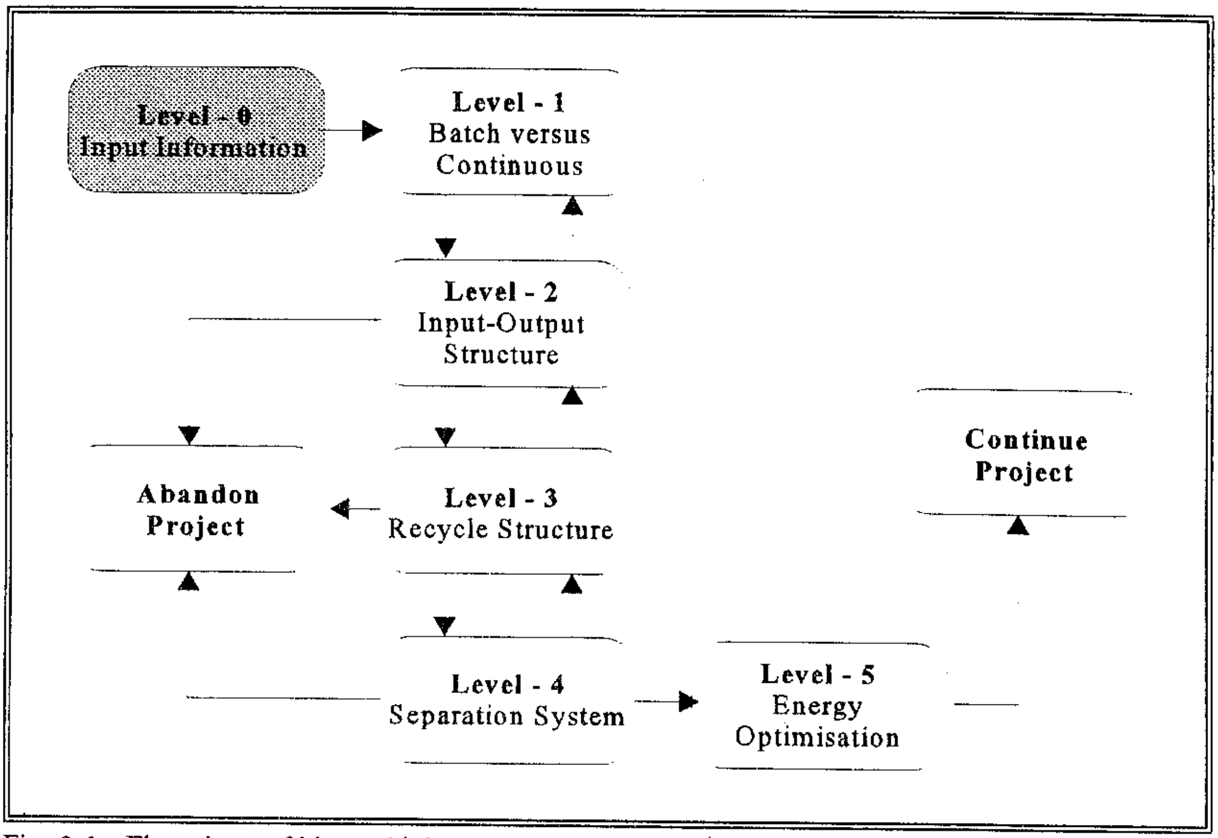
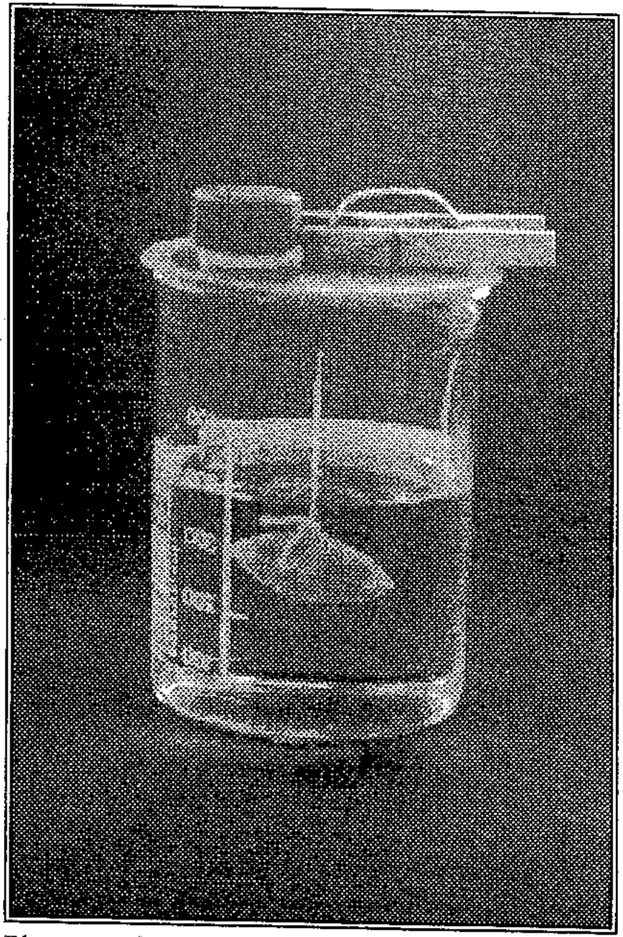


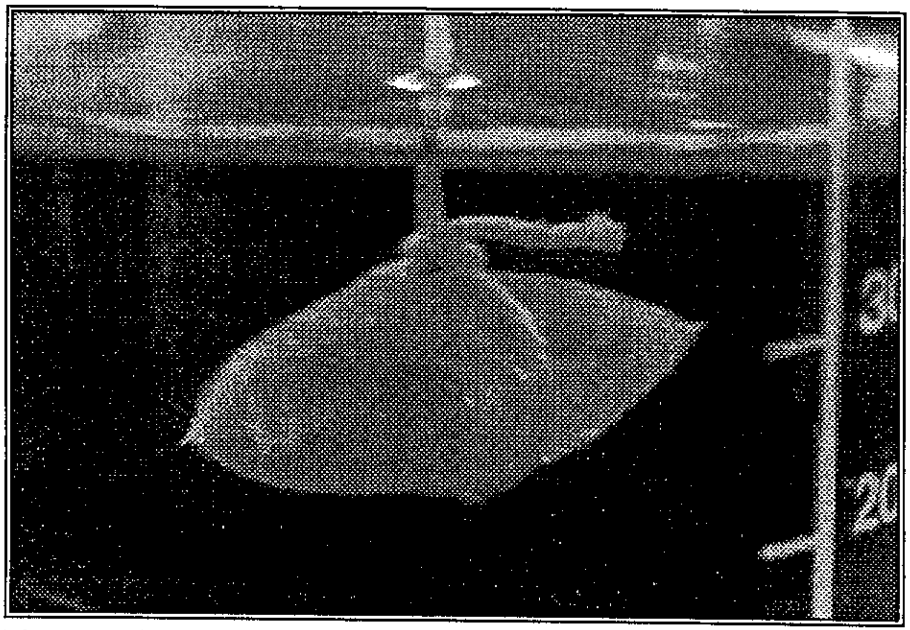
Fig. 3.1: Flowchart of hierarchial process design.

3.2 Experimental Configuration

The capsule configuration was used for the experiments (Erlank, 1984:50). The membrane was folded double and a hot wire sealer was used to seal all the edges, except for one. The capsule was then impregnated by leaving the capsule in the extractant and allowing the extractant to load into the membrane. The excess extractant was removed by blotting. The capsule was filled with strip solution at the open edge and then completely sealed. The capsules varied in size, but had an average diameter of approximately 40 mm. The average contact area of a membrane capsule is approximately 26 cm^2. A string was used to keep the capsule suspended in the bulk aqueous feed solution (Photograph 3.1 and 3.2). It was vital that the capsule did not leak since that would defeat the integrity of the extraction system.



Photograph 3.1: Experimental configuration.



Photograph 3.2: Membrane Capsule.

3.2.1 The Membrane

The hydrophobic organic phase forming the liquid membrane was immobilized within the pores of a Celgard 4510 film (Erlank, 1994:49). This hydrophobic laminate has been designed by Celanese Plastics Co. It is a heat-embossed laminate of Celgard 2500 bonded to a nonwoven polypropylene web. This membrane is approximately 0.13 mm thick with a porosity of 45% and a pore diameter in the order of 0.04 µm. Filling the pores of the membranes with an extractant was accomplished by immersing the membrane in the organic phase. The pores were immediately filled by capillary forces and suitable adherence was attained due to the hydrophobicity of the substrate.

3.2.2 The Extractant

The extractant used in this study was a commercial solvent extraction agent. To be suitable for the extraction of metals from aqueous solutions, the extractant should comply with certain requirements (Erlank, 1994:52):

1. It should have a low solubility in the aqueous phase.

2. It should have good chemical stability regarding the aqueous solutions it would be in contact with.
3. It should have a high metal loading capacity.
4. The loaded metal should be stripped easily from the extractant.
5. It should be non-volatile and nontoxic for safety reasons.
6. A high solubility in aliphatic and aromatic solvents is necessary.
7. It should have good extraction kinetics.

The extraction agents were diluted with Escaid 100, an aromatic solvent. Diluents are inert and do not participate in the mechanism of extraction apart from acting as the solvation medium.

Due to above mentioned reasons it was decided to use D2EHPA as an extractant. This versatile alkylphosphoric acid has been used since 1949 for the extraction of a variety of metals (Erlank, 1994:54). The chemical name is di-2-ethylhexyl phosphoric acid and the structure is represented by $(OR)_2POOH$ with R representing an alkyl group. The functional group is the phosphorous double bond to an oxygen and the monovalent bond to an alcohol group. D2EHPA is a commonly used extractant because its many good qualities renders it superior to other extractants. These qualities include:

1. Reliable chemical stability.
2. General favourable extraction kinetics.
3. Good metal loading and strip characteristics.
4. Very low solubility in water.
5. Availability in commercial quantities.
6. Versatility in extraction of a variety of ions.

In general, heavier rare earth metals extract better than lighter metals. D2EHPA is mostly used in the extraction of Zn, Be, Cu, In, Ga, V, ect. and in the separation of copper from nickel in aqueous solutions.

3.3 Experimental Procedure

3.3.1 Introduction

The dissertation by S.N. Erlank (1994) showed that the extraction of nickel with the use of SLM is potentially feasible. The dissertation also showed which variables are significant. The next step is to do an experimental design and to execute the experiments. The purpose of experimental design is to plan the experimentation so that the number of experiments to be executed is minimized, but the results are still accurate. The method of response surfaces was used for the experimental design. Empirical equations are set up to draw tree-dimensional and contour plots of responses studied. Thereby the influences of a number of factors on the response are simultaneously obtained, and the optimum conditions for the extraction of nickel are obtained.

The classical way to find the optimum for a process with a number of factors which influence the process is to keep all the factors (except one) constant. One factor at a time was varied and the response was measured. This meant that 25 experiments are needed for a process with five factors (each having five different values). This process is unfortunately not very dependable. An example of an experiment that gives a false optimum can be seen in figure 3.2. In the experiment the X variable is kept constant at a value of x1 and the Y variable is varied. The optimum value for the X variable is found at point A. If the classical way of experimentation is used, the following step would be to keep the value of Y constant at a value of A and to vary the X variable. The optimum according to the experiment is then at point B, but the true optimum is at a lower value of Y. Another disadvantage of the method is that there is no mathematical response for the different factors.

Another way to obtain the optimum is to do all the possible combinations of experiments.

Response surfaces are more reliable than the classical way of experimentation. The number of experiments for a process with five factors (each having five different values) needs 46 experiments. Another advantage of response surfaces is that a mathematical response can be attained for the different factors.

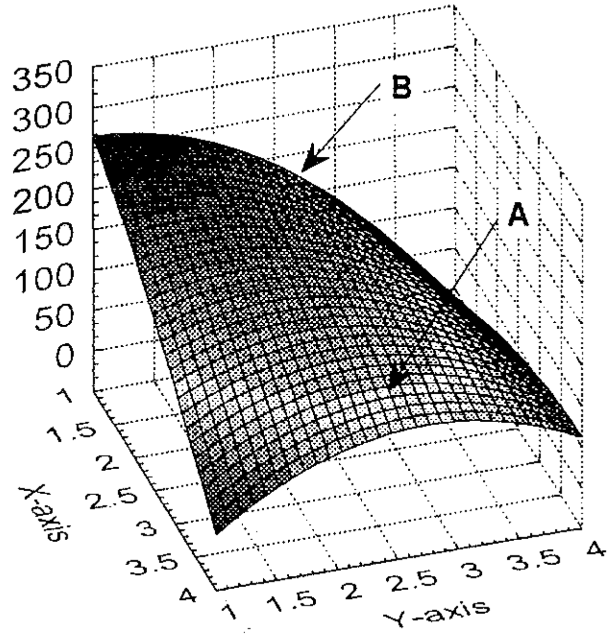


Fig. 3.2: False experimental optimum.

3.3.2 Response surfaces

Draper (1988:107) describes a response surface as follows: "Suppose we have a set of observations y_u, ξ_{1u}, ξ_{2u}, .. ,ξ_{ku}, u = 1,2, . ,n, taken on a response variable y and on k predictor variables ξ_1, ξ_2, .. ,ξ_k. A response surface model is a mathematical model fitted to y as a function of the ξ's in order to provide a summary representation of the behaviour of y."

The purpose of response surface design is to fit a n-dimensional surface to the surface with the method of least squares. The surface can then be analysed mathematically and the relationship between the different factors and the optimum response can be determined.

The goal of this experimental design is to design a set of experiments to determine the mathematical relationship between the different factors which influence the extraction of nickel.

3.3.3 Design factors

The first step of the experimental design is to list all the factors (dependant variables) which influence the rate of nickel extraction in order of decreasing importance:

1. The pH of the feed solution.
2. The pH of the stripping solution.
3. The nickel concentration in the feed.
4. The nickel concentration in the strip.
5. The volume percentage of extractant in the membrane.
6. The temperature of the feed.

The effect of the first four factors is very important and a response surface design is needed to determine the relationship between these factors. The temperature of the feed greatly affects the rate of extraction, but the possible increase in efficiency should be weighed against the cost of heating large volumes of liquid solutions.

The cost of experiments makes it important that the design should be streamline and only the most significant experiments should be done.

3.3.4 Experimental design

Statistica for Windows was used to do a central composite design with the use of response surface methods to effect a second order composite design (Draper, 1988:107).

A total number of 27 experiments are needed to fit a mathematical model for the first four factors. An additional ten experiments have to be done to prove that the volume percentage of the extractant is independent of the first four factors.

The minimum number of experiments needed to fit a mathematical model through the first five factors is 30. A more reliable fit can be obtained if 46 experiments are done (Central composite designs require a certain number of central points, cube points and star points and the number of experiments cannot be chosen arbitrarily).

The minimum number of experiments needed to fit a mathematical model through all six factors is 47. A more reliable fit requires 79 experiments.

The temperature of the feed is less important and it was decided to do a response surface design on the first five factors. Another set of five experiments would be done with the optimum results of the first five factors to establish the effect of temperature. The experimental design was done with Statistica for Windows. The experimental profile of the 46 experiments in normalised 5-point form can be seen in table 3.1. Table 3.2 shows the real values assigned to each variable.

Run	Block	pH (feed)	[H] (strip)	[Ni] (feed)	[Ni] (strip)	Percentage Extractant
1	1	-1.00000	-1.00000	-1.00000	-1.00000	-1.00000
2	1	1.00000	-1.00000	-1.00000	-1.00000	-1.00000
3	1	-1.00000	1.00000	-1.00000	-1.00000	-1.00000
4	1	1.00000	1.00000	-1.00000	-1.00000	-1.00000
5	1	-1.00000	-1.00000	1.00000	-1.00000	-1.00000
6	1	1.00000	-1.00000	1.00000	-1.00000	-1.00000
7	1	-1.00000	1.00000	1.00000	-1.00000	-1.00000
8	1	1.00000	1.00000	1.00000	-1.00000	-1.00000
9	1	-1.00000	-1.00000	-1.00000	1.00000	-1.00000
10	1	1.00000	-1.00000	-1.00000	1.00000	-1.00000
11	1	-1.00000	1.00000	-1.00000	1.00000	-1.00000
12	1	1.00000	1.00000	-1.00000	1.00000	-1.00000

Table 3.1: Design summary ($2^{(5-0)}$ second order central composite design).

Run	Block	pH (feed)	[H] (strip)	[Ni] (feed)	[Ni] (strip)	Percentage Extractant
13	1	-1.00000	-1.00000	1.00000	1.00000	-1.00000
14	1	1.00000	-1.00000	1.00000	1.00000	-1.00000
15	1	-1.00000	1.00000	1.00000	1.00000	-1.00000
16	1	1.00000	1.00000	1.00000	1.00000	-1.00000
17	1	-1.00000	-1.00000	-1.00000	-1.00000	1.00000
18	1	1.00000	-1.00000	-1.00000	-1.00000	1.00000
19	1	-1.00000	1.00000	-1.00000	-1.00000	1.00000
20	1	1.00000	1.00000	-1.00000	-1.00000	1.00000
21	1	-1.00000	-1.00000	1.00000	-1.00000	1.00000
22	1	1.00000	-1.00000	1.00000	-1.00000	1.00000
23	1	-1.00000	1.00000	1.00000	-1.00000	1.00000
24	1	1.00000	1.00000	1.00000	-1.00000	1.00000
25	1	-1.00000	-1.00000	-1.00000	1.00000	1.00000
26	1	1.00000	-1.00000	-1.00000	1.00000	1.00000
27	1	-1.00000	1.00000	-1.00000	1.00000	1.00000
28	1	1.00000	1.00000	-1.00000	1.00000	1.00000
29	1	-1.00000	-1.00000	1.00000	1.00000	1.00000
30	1	1.00000	-1.00000	1.00000	1.00000	1.00000
31	1	-1.00000	1.00000	1.00000	1.00000	1.00000
32	1	1.00000	1.00000	1.00000	1.00000	1.00000
33	1	0.00000	0.00000	0.00000	0.00000	0.00000
34	1	0.00000	0.00000	0.00000	0.00000	0.00000
35	2	-2.37841	0.00000	0.00000	0.00000	0.00000
36	2	2.37841	0.00000	0.00000	0.00000	0.00000

Table 3.1.a: Design summary.

Run	Block	pH (feed)	[H] (strip)	[Ni] (feed)	[Ni] (strip)	Percentage Extractant
37	2	0.00000	-2.37841	0.00000	0.00000	0.00000
38	2	0.00000	2.37841	0.00000	0.00000	0.00000
39	2	0.00000	0.00000	-2.37841	0.00000	0.00000
40	2	0.00000	0.00000	2.37841	0.00000	0.00000
41	2	0.00000	0.00000	0.00000	-2.37841	0.00000
42	2	0.00000	0.00000	0.00000	2.37841	0.00000
43	2	0.00000	0.00000	0.00000	0.00000	-2.37841
44	2	0.00000	0.00000	0.00000	0.00000	2.37841
45	2	0.00000	0.00000	0.00000	0.00000	0.00000
46	2	0.00000	0.00000	0.00000	0.00000	0.00000

Table 3.1.b: Design summary.

3.3.5 Determining the values for the factors

The first step to determine the values for the factors is to select the range of values for the experiments. The second step is to calculate the values according to the levels, as calculated with Statistica for Windows. The values of the factors can be seen in table 3.2. represented in their transferred real values.

Variables	Levels					Units
	-2.3784	-1.0	0.0	1.0	2.3784	
pH (feed)	1.12	2.5	3.5	4.5	5.88	
[H] (strip)	1.351	11	18	25	34.649	Mol/dm^3
[Ni] (feed)	524	800	1000	1200	1475	mg/dm^3
[Ni] (strip)	0	689	1189	1689	2378.2	mg/dm^3
[Extractant]	48.1	55	60	65	71.9	Vol %

Table 3.2: The values of the experimental factors.

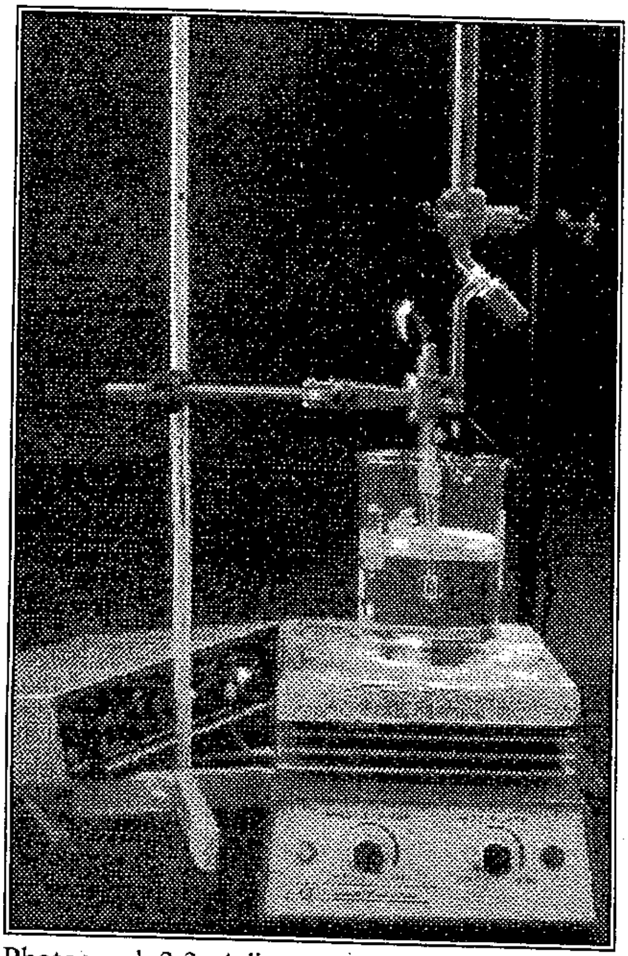
3.3.6 Block effects

Statistica for Windows makes provision for block effects. The experiments can be divided into two blocks which can give slightly different results. An example of block effects is when two different methods are used to analyse the response. The experiments can then be divided into two blocks. The first block can be analysed with the first method and the second block with the other method, which would yield a comparative response result.

3.3.7 Experimental Procedure

A beaker is filled with a feed solution of known pH and concentration. The prepared capsule, as explained in 3.2, is dropped into the filled beaker. The capsule is suspended in the feed solution with a piece of string (see photograph 3.1).

Samples are taken at five hour intervals for the first 25 hours with a micropipette. The pH of the feed solution is adjusted every two hours (see photograph 3.3) during the first 25 hours of the experiment with a diluted sodium hydroxide solution. The nickel concentration is adjusted every five hours if needed with a 10 000 ppm nickel solution. An example of the measuring results can be seen in table 3.3.



Photograph 3.3: Adjustment of pH.

The circumference of the membrane capsule (Cir_{mem}) was measured and the area of the membrane (A_{mem}) was calculated with the following equation:

$$A_{mem} = \frac{\frac{1}{2}(Cir_{mem})^2}{\pi} \qquad 3.1$$

Time (hours)	**$[Ni]_{feed}$** (mg/l)	**Volume** (Litres)	**Adjustment** (Litre)
0	1145	.405	0.000000
5	1010	.400	0.000000
10	912	.395	0.003000
15	962	.390	0.001000
20	1000	.390	0.000000
25	938	.380	0.000000
50	885	.400	0.000000

Table 3.3: An example of measuring results.

The above mentioned information was used to calculate the cumulative extraction of nickel (Ex_{Ni}) (in mg/m^2) at the different time intervals (see fig. 3.3).

The following equation was fitted through the data:

$$Ex_{Ni} = a - be^{-ct} \quad 3.2$$

Where a, b and c are constant for every experiment and t is the time in hours. The influence of the different conditions on b and c was determined for various experimental conditions.

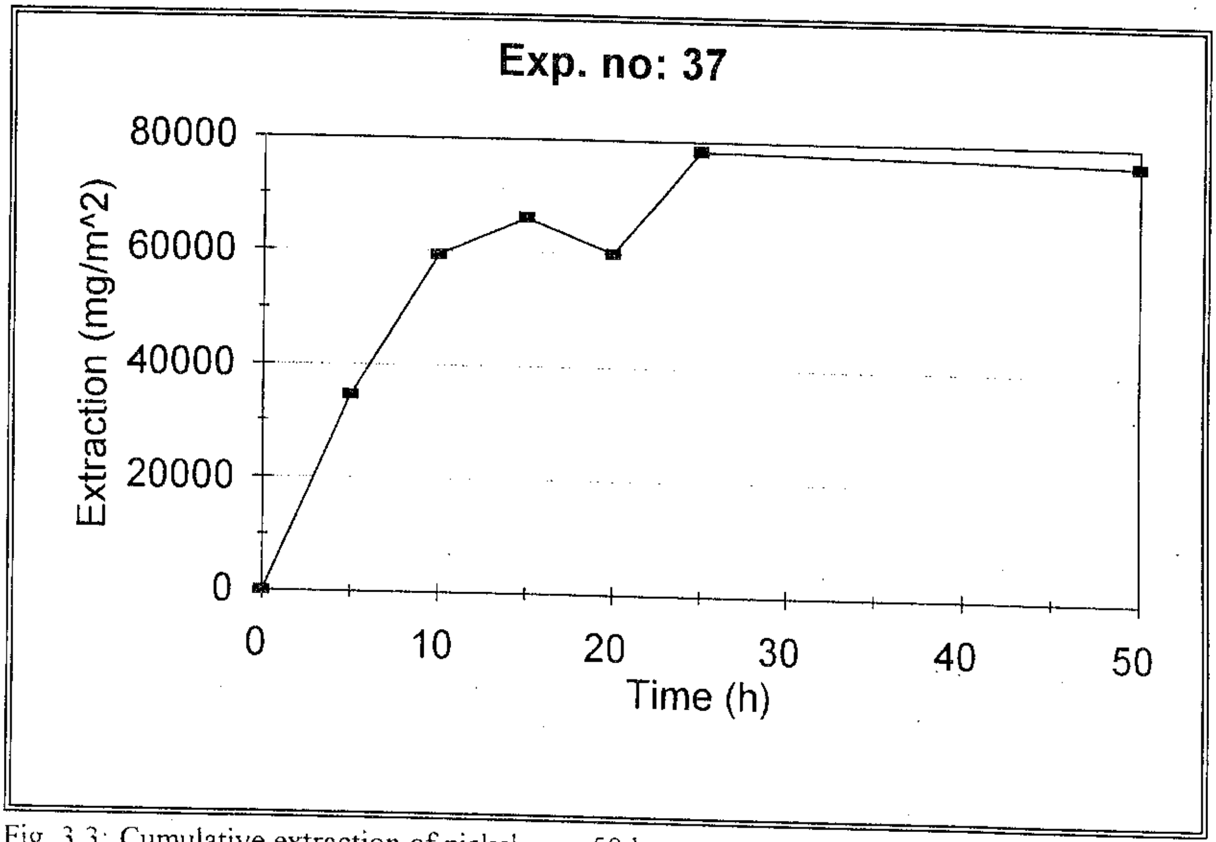


Fig. 3.3: Cumulative extraction of nickel over 50 hours.

3.4 Experimental Results

3.4.1 Mathematical background

The first step in evaluating the results was to calculate the extraction of nickel (in mg/m^2) at the different time intervals (refer to fig. 3.3 and equation 3.2). A selected example of such a curve fit can be seen in figure 3.4 for a set of experimental results. The results of the other experiments can be seen in appendix B.

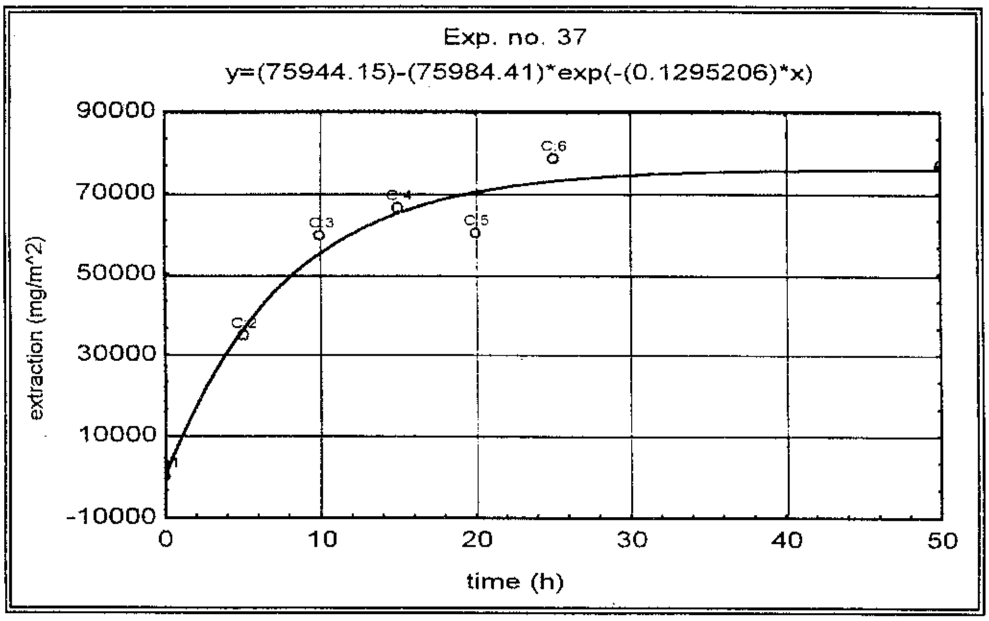


Fig. 3.4: Example of curve fit for the extraction of Nickel over time.

The maximum extraction of each experiment can be obtained from equation 3.2 by calculating Ex_{Ni} at $t = \infty$:

$$\begin{aligned} Ex_{Ni,\infty} &= a - b\,e^{-c\infty} \\ &= a - b(0) \\ &= a \end{aligned} \qquad 3.3$$

The amount of contamination that occurred during the experiment is equal to the intercept of equation 3.2. In other words by substituting t with the value zero:

$$\begin{aligned} Ex_{Ni,0} &= a - b\,e^{-c0} \\ &= a - b(1) \\ &= a - b \end{aligned} \qquad 3.4$$

This contamination can be the result of dirty equipment or evaporation of the feed solution as well as evaporation of the standards used to calibrate the AA. To obtain a more accurate value of the maximum extraction, the amount of contamination (Eq. 3.4)has to be subtracted from the final extraction (Eq.. 3.3):

$$\begin{aligned} Ex_{Ni,\infty} &= (a) - (a - b) \\ &= b \end{aligned} \qquad 3.5$$

The initial rate of extraction can be obtained by differentiating equation 3.2:

$$\begin{aligned} Rate &= \frac{d}{dt}\left(a - b\,e^{-ct}\right) \\ &= b\,c\,e^{-ct} \\ If\ t &= 0: \\ Rate &= b\,c\,(1) \\ &= b\,c \end{aligned} \qquad 3.6$$

3.4.2 Maximum extraction

The influence of the different variables on the maximum (final) extraction was evaluated. The following second order function was fitted through the experimental data with Statistica for Windows:

$$\begin{aligned} b = & -1.816A - 1.791B + 6.346C + 3.522D - 3.262E - 0.696A^2 \\ & + 8.476B^2 + 1.819C^2 + 5.146D^2 - 1.207E^2 - 4.056AB \\ & + 1.733AC - 0.970AD + 2.889AE + 1.239BC + 3.471BD \\ & 0.533BE + 7.520CD - 6.184CE - 5.568DE + 27.002 \end{aligned} \qquad 3.7$$

With:

$$A = pH_{feed} - 3.5 \qquad 3.8$$

$$B = \frac{H_{strip} - 18}{7} \qquad 3.9$$

$$C = \frac{[Ni]_{feed} - 1000}{200} \qquad 3.10$$

$$D = \frac{[Ni]_{strip} - 1189}{500} \qquad 3.11$$

$$E = \frac{[Ex] - 60}{5} \qquad 3.12$$

3.4.2.1 The effect of pH_{feed} and $[H^+]_{strip}$

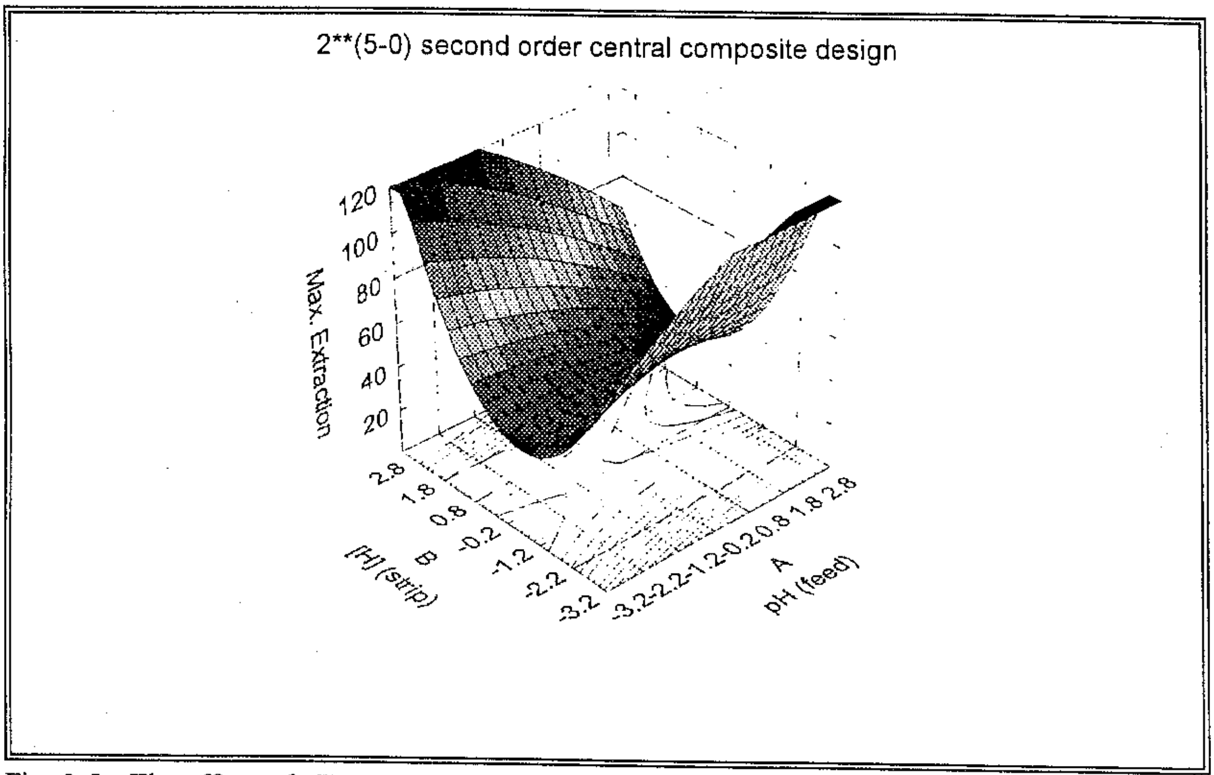


Fig. 3.5: The effect of pH_{feed} and H^-_{strip} on the final extraction of Nickel.

The effect of the pH of the feed and the hydrogen concentration of the strip on the final extraction can be seen in figure 3.5. It is clear that the final amount of nickel that can be extracted with the CME decreases with an increase of hydrogen concentration in the strip up to a point where the hydrogen concentration is approximately 16.6 mol/dm^3. If the hydrogen concentration is further increased, the final amount of extraction also increases. This result can be explained by the fact that the hydrogen is transported through the membrane with the complexation reaction and the diffusion of hydrogen through the membrane. If the hydrogen concentration is increased, the rate of diffusion increases and less hydrogen ions are available for the complexation reactions. At the point of approximately 16.6 mol/dm^3 (44.4 vol%) maximum diffusion of hydrogen occurs. If the concentration of the sulfuric acid is further increased, the acid does not dissociate completely and the undissociated acid forms a hydrogen reserve. This explains the fact that at low hydrogen concentrations the maximum extraction occurs at the highest pH, since the complexation reaction is then the controlling reaction and this reaction increases if the pH increases. At higher hydrogen concentration the diffusion of hydrogen is the controlling factor. The diffusion of hydrogen is promoted by a high pH and less hydrogen is available for the complexation reaction. The result is that at high hydrogen concentration, the maximum extraction occurs at low pH.

3.4.2.2 The effect of pH_{feed} and $[Ni]_{feed}$

The effect of the pH of the feed and the nickel concentration of the feed on the final extraction can be seen in figure 3.6. It is clear that the amount of nickel that can be extracted increases with an increase in the pH of the feed and the nickel concentration of the feed. This result is confirmed by Verhaege *et al.* (1987:333), who derived the following equation from conventional liquid-liquid equilibrium expressions:

$$\frac{[Ni^{2+}]_{feed}}{[Ni^{2+}]_{strip}} = \left(\frac{[H^{+}]_{feed}}{[H^{+}]_{strip}}\right)^{2} \tag{3.13}$$

3.4.2.3 The effect of pH_{feed} and $[Ni]_{strip}$

The effect of these two variables can be seen in if figure 3.7. It seems as if there is a point where the nickel concentration of the strip results in a minimum final extraction. This result is unexpected and thus far unexplainable. It also contradicts previous results in literature (Verhaege, 1987:333). This result could be inaccurate due to the difference of temperature of the experiments. The effect of the pH of the feed seems to be minimal. The difference in the final extraction at different nickel strip concentrations is also relatively small and it can be concluded that this variable is relatively unimportant.

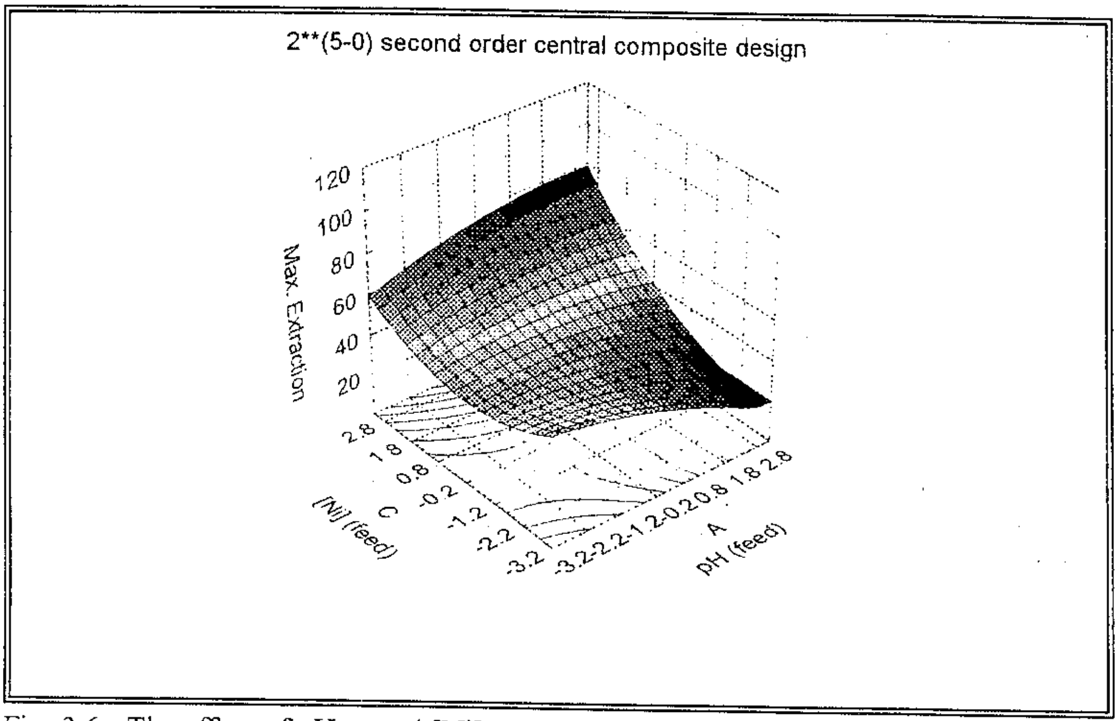


Fig. 3.6: The effect of pH_{feed} and $[Ni]_{feed}$ on the final extraction.

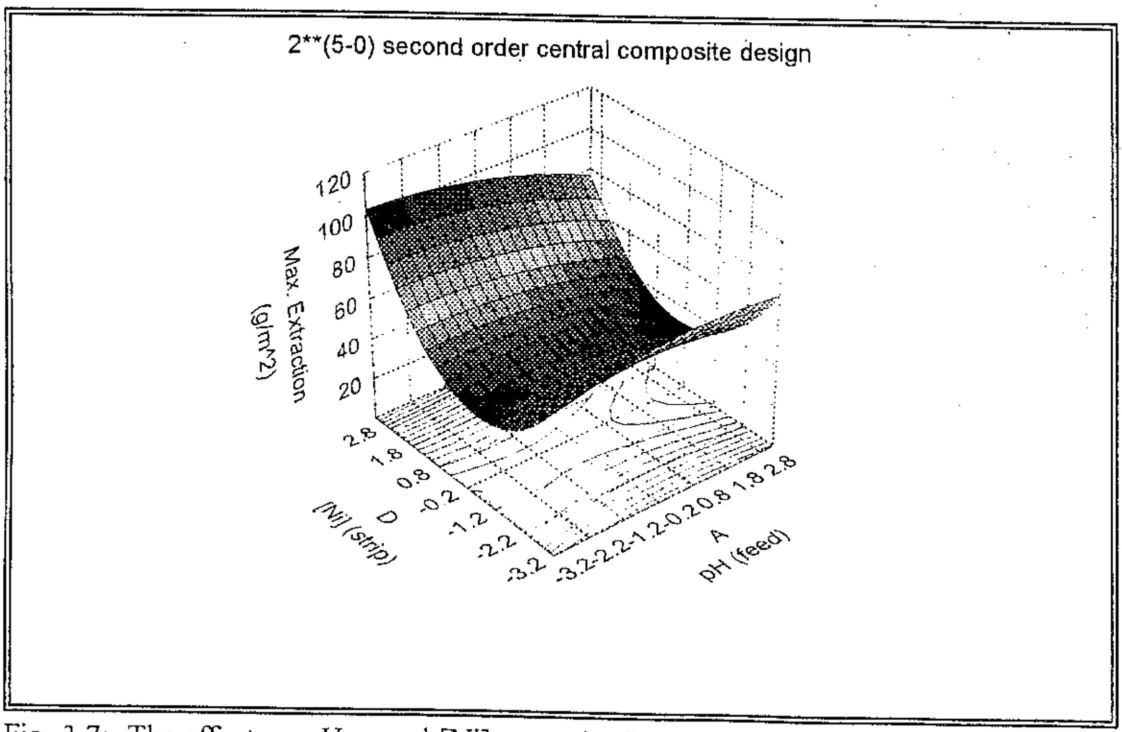


Fig. 3.7: The effect op pH_{feed} and $[Ni]_{strip}$ on the final extraction.

3.4.2.4 The effect of pH_{feed} and [Ex]

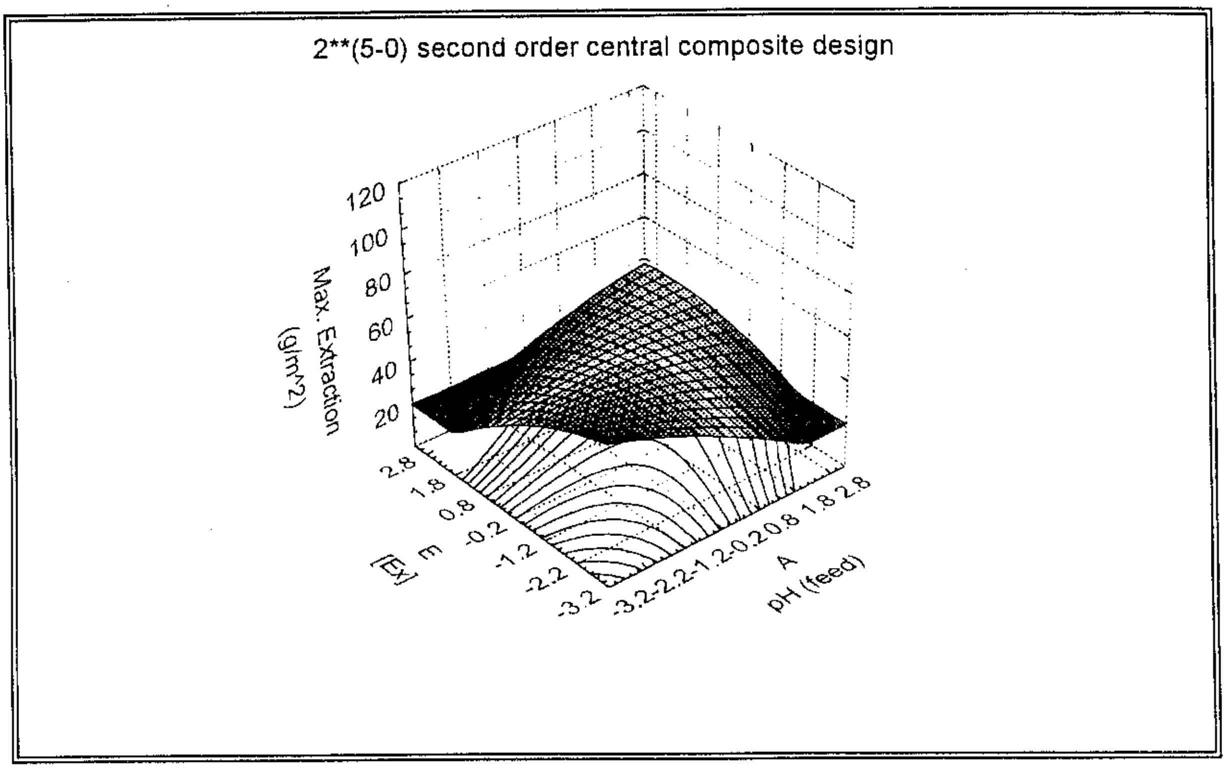


Fig. 3.8: The effect of pH_{feed} and [Ex] on the final extraction.

The effect of these two variables can be seen in figure 3.8. At a lower feed pH, the optimum extractant concentration is also lower, at a higher feed pH the opposite happens. Verhaege *et al.* examined the influence of membrane composition on mass transfer at the following conditions (Table 3.4):

pH (feed)	4.46
[H] (strip)	1 mol/dm^3
[Ni] (feed)	1 600 mg/dm^3
[Ni] (strip)	0 mg/dm^3

Table 3.4: Condition of experiments by Verhaege *et al.*

They found that the optimum extractant composition is 60% (vol) D2EHPA in Solvesso 150 (fig. 2.5). The conditions are substituted into equation 3.7 to give the following:

$$b = 104.020 - 3.932E - 1.207E^2 \qquad 3.14$$

with the value of E as calculated in equation 3.12. The optimum extractant concentration can be obtained by differentiating equation 3.14:

$$\frac{db}{dE} = 0 = -3.932 - 2.414E \tag{3.15}$$

The optimum extractant concentration is where E = -1.629 or an extractant concentration of 51.855% of D2EHPA dissolved in Escaid 100 (see also fig.3.9).

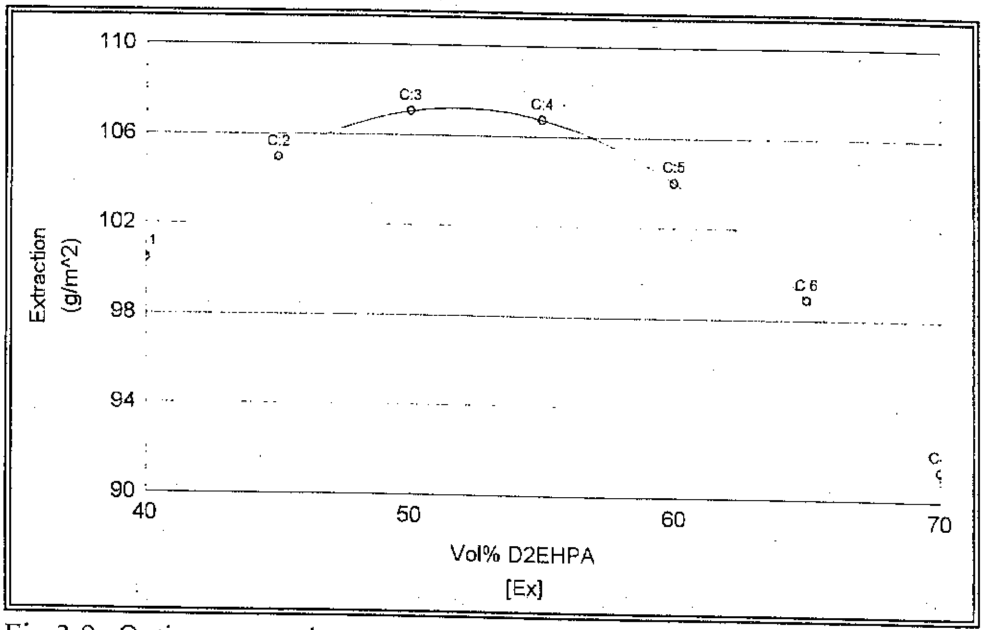


Fig.3.9: Optimum membrane composition using experimental conditions of Verhaege *et al.*

It can therefore be concluded that the results are compatible with the results of Verhaege *et al.*

3.4.2.5 The effect of $[H^+]_{strip}$ and $[Ni]_{feed}$

The effect of these two variables can be seen in figure 3.10. The final amount of extraction is a maximum at high and low hydronium concentrations in the strip solution (refer to paragraph 3.5.2.1). The final extraction increases as the nickel concentration of the feed increases (refer to paragraph 3.5.2.2) and again a minimum final extraction is obtained at a certain hydronium ion concentration.

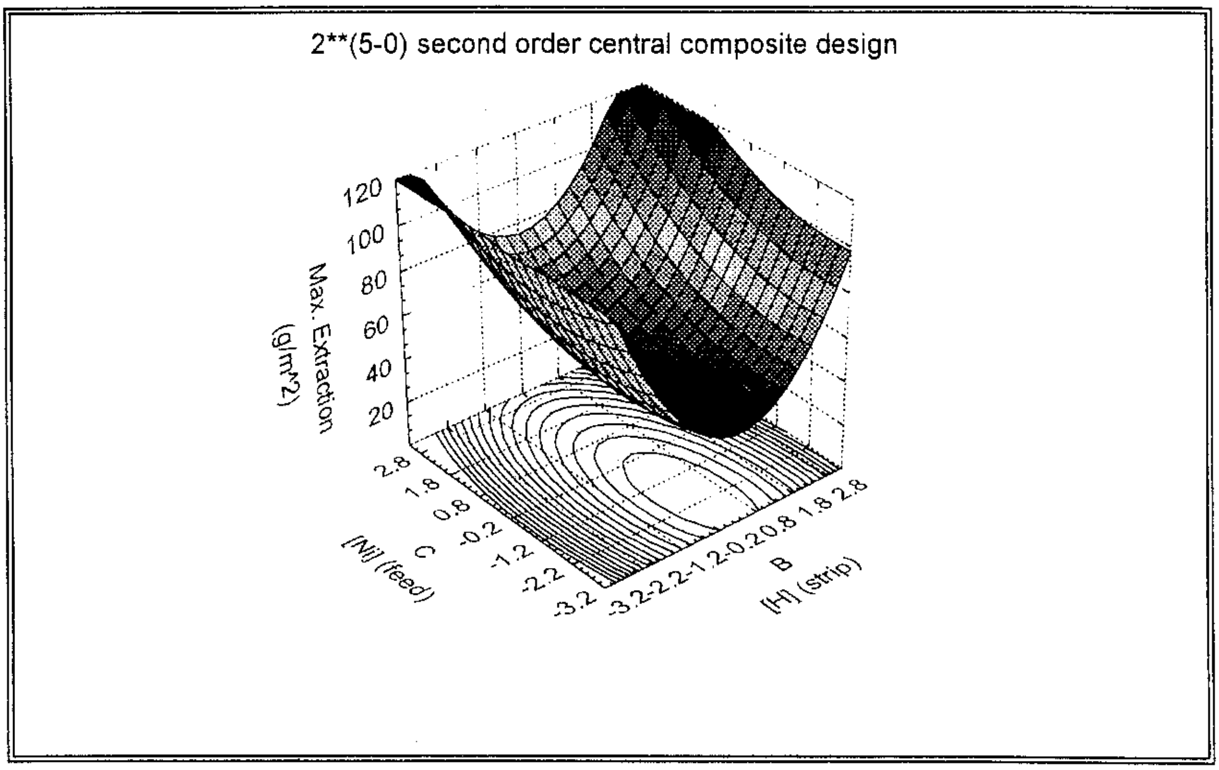


Fig. 3.10: The effect of $[H^-]_{strip}$ and $[Ni]_{feed}$ on the final extraction.

3.4.2.6 The effect of $[H^+]_{strip}$ and $[Ni]_{strip}$

Once again the final amount of extraction is a maximum (fig.3.11) at high and low hydronium ion and feed concentrations of the strip solution (refer to paragraph 3.5.2.3).

3.4.2.7 The effect of $[H^+]_{strip}$ and [Ex]

The effect of these two factors can be seen in figure 3.12. The hydronium ion concentration of the strip does not have an effect on the optimum extractant concentration. The final extraction is the highest at high and low hydronium ion concentrations in the strip.

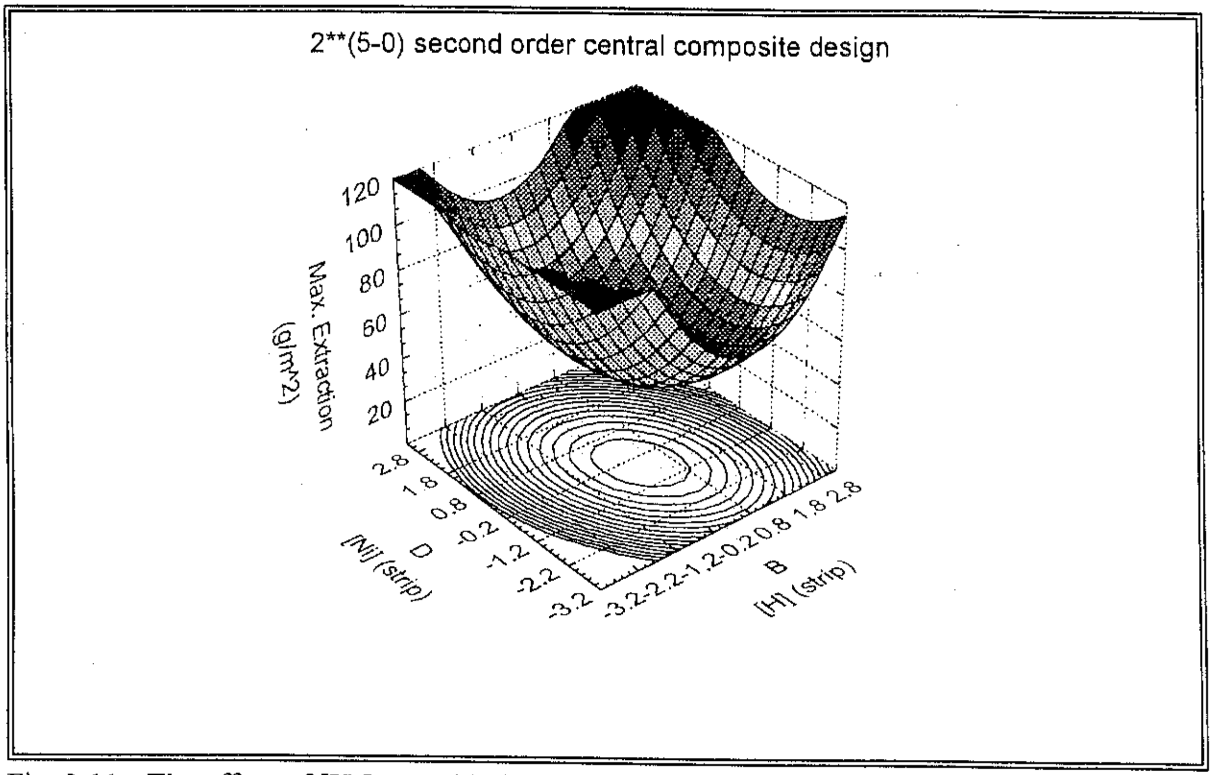


Fig. 3.11: The effect of $[H^+]_{strip}$ and $[Ni]_{strip}$.

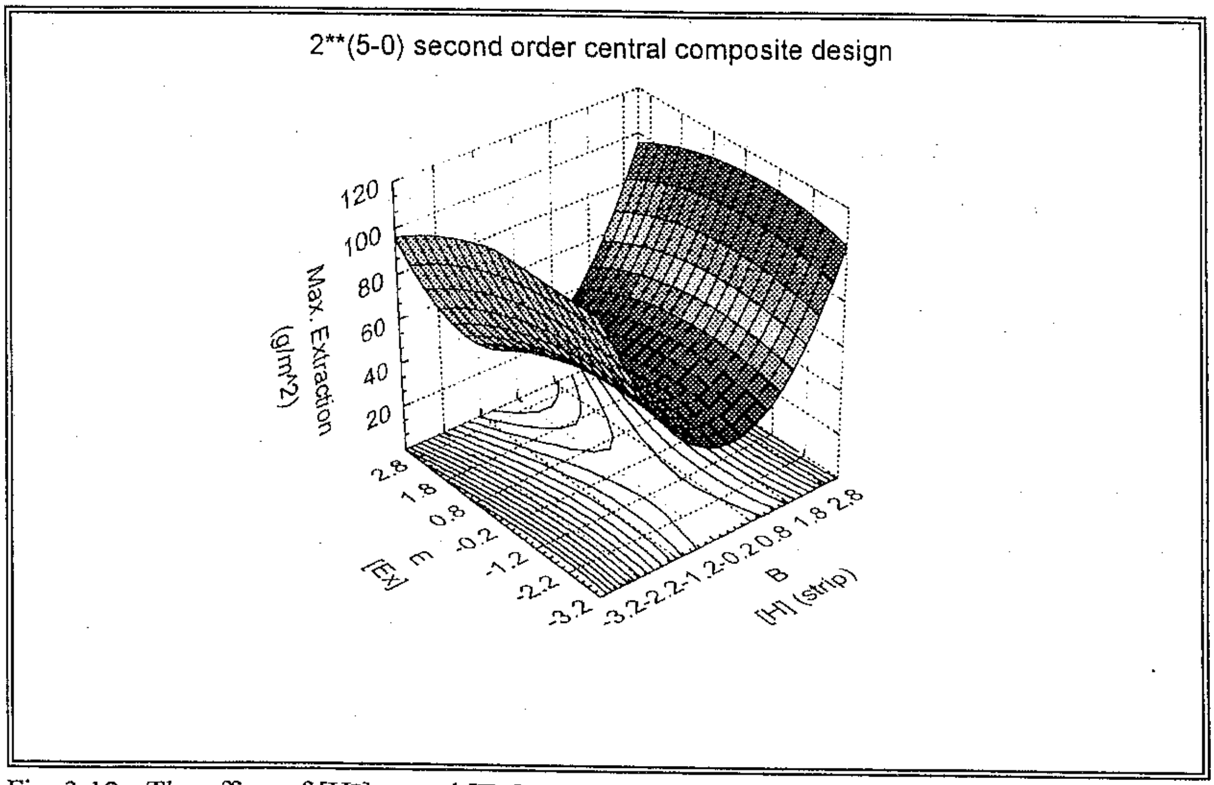


Fig. 3.12: The effect of $[H^+]_{strip}$ and [Ex].

3.4.2.8 The effect of $[Ni]_{feed}$ and $[Ni]_{strip}$

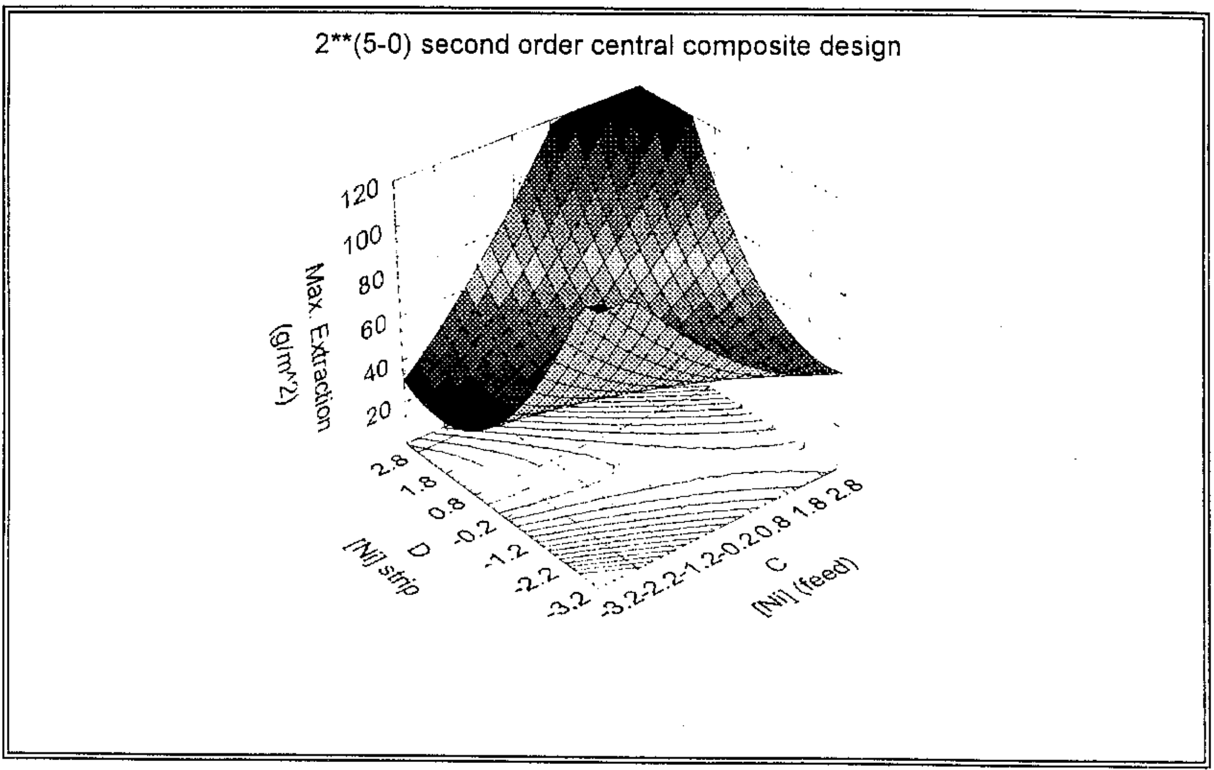


Fig. 3.13: The effect of $[Ni]_{feed}$ and $[Ni]_{strip}$ on the final extraction.

The effect of the nickel concentration of the feed and strip on the final extraction can be seen in figure 3.13. The final extraction increases if the nickel concentration of the feed is increased. The effect of the nickel concentration of the strip remains unexplained.

3.4.2.9 The effect of $[Ni]_{feed}$ and [Ex]

The effect of these two variables on the final extraction can be seen in figure 3.14. As previously mentioned the final extraction increases if the nickel concentration of the feed increases (refer to paragraph 3.4.2.2, 3.4.2.5 and 3.4.2.8). The concentration of the nickel in the feed does seem to have an effect on the optimum extractant concentration. At lower nickel feed concentrations the optimum extractant concentration occurs at a higher volume percentage than at higher nickel feed concentrations.

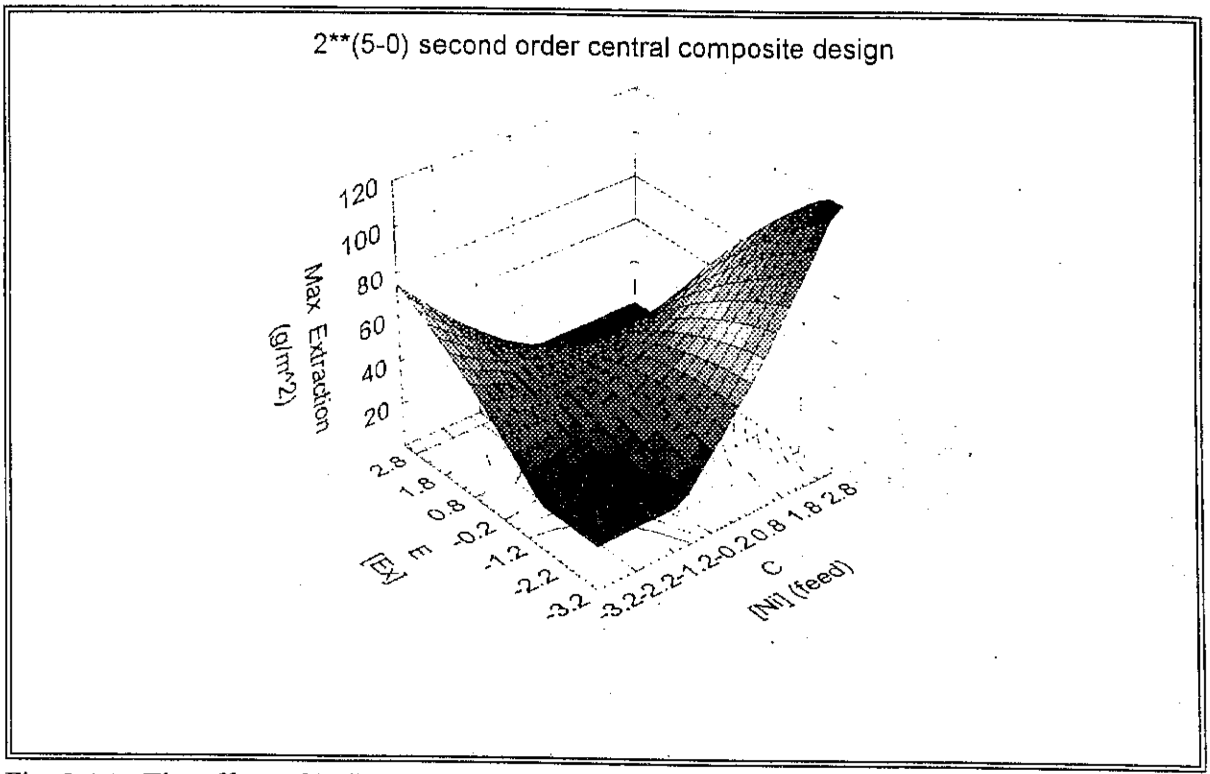


Fig. 3.14: The effect of $[Ni]_{feed}$ and [Ex] on the final extraction.

3.4.2.10 The effect of $[Ni]_{strip}$ and [Ex]

The effect of the nickel strip concentration and the extractant concentration on the final extraction can be seen in figure 3.15. Just like the concentration of the nickel in the feed (paragraph 3.4.2.9), the concentration of the nickel in the strip does seem to have an effect on the optimum extractant concentration. At lower nickel strip concentrations the optimum extractant concentration occurs at a higher volume percentage than at higher nickel strip concentrations.

3.4.3 The rate of extraction

The influence of the different variables on c in equation 3.2 was evaluated. The following second order function was fitted through the experimental data with Statistica for windows:

$$\begin{aligned} c = {} & -0.0150A - 0.0091B - 0.0277C + 0.0232D - 0.0525E + 0.0100A^2 \\ & + 0.0160B^2 + 0.0150C^2 + 0.0074D^2 + 0.0063E^2 - 0.0110AB \\ & + 0.0184AC - 0.0263AD + 0.0268AE - 0.0006BC + 0.0159BD \\ & + 0.0077BE - 0.0342CD + 0.0354CE - 0.0350DE + 0.0513 \end{aligned} \qquad 3.16$$

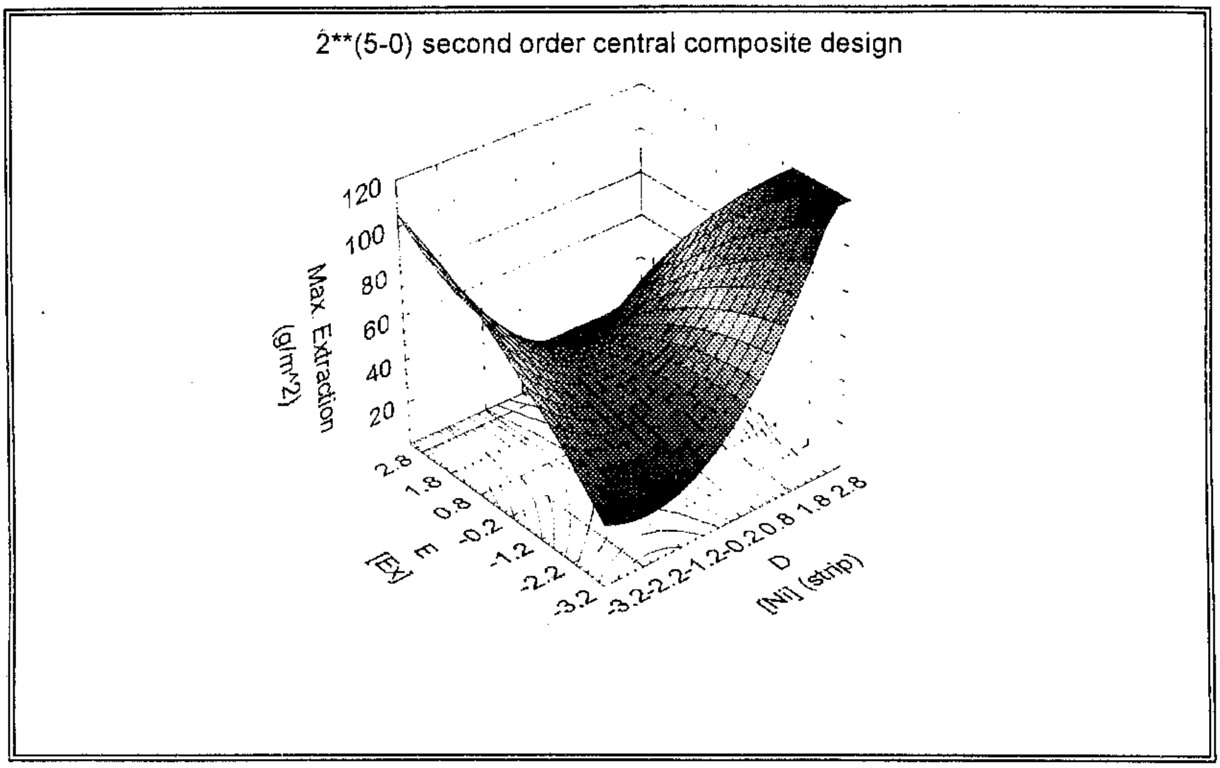


Fig. 3.15: The effect of $[Ni]_{strip}$ and [Ex] on the final extraction.

with the value A, B, C, D and E the same as in equations 3.8 - 3.12. The results were unfortunately inconsistent and will not be discussed in great detail. The reason for the inconsistency will be discussed in paragraph 3.5.4. The five results, with the highest rate of extraction and their conditions can be seen in table 3.5 (refer also to fig. 3.15).

Experiment No.	**Conditions**					**Rate of Extraction**
	pH_{feed}	$[H]_{strip}$ Mol/dm^3	$[Ni]_{feed}$ mg/dm^3	$[Ni]_{strip}$ mg/dm^3	[Ex] Vol. %	g/m^{2}h
Verhaege *et al.*	4.46	1	1600	0	60	0.147
9	2.5	11	800	1689	55	9.425
37	3.5	1.351	1000	1189	60	9.841
14	4.5	11	1200	1689	55	11.034
5	2.5	11	1200	689	55	11.570
15	2.5	25	1200	1689	55	12.795

Table 3.5: Best results obtained with experiments.

It is clear that the optimum extractant concentration is very important (about 55 Vol.%).

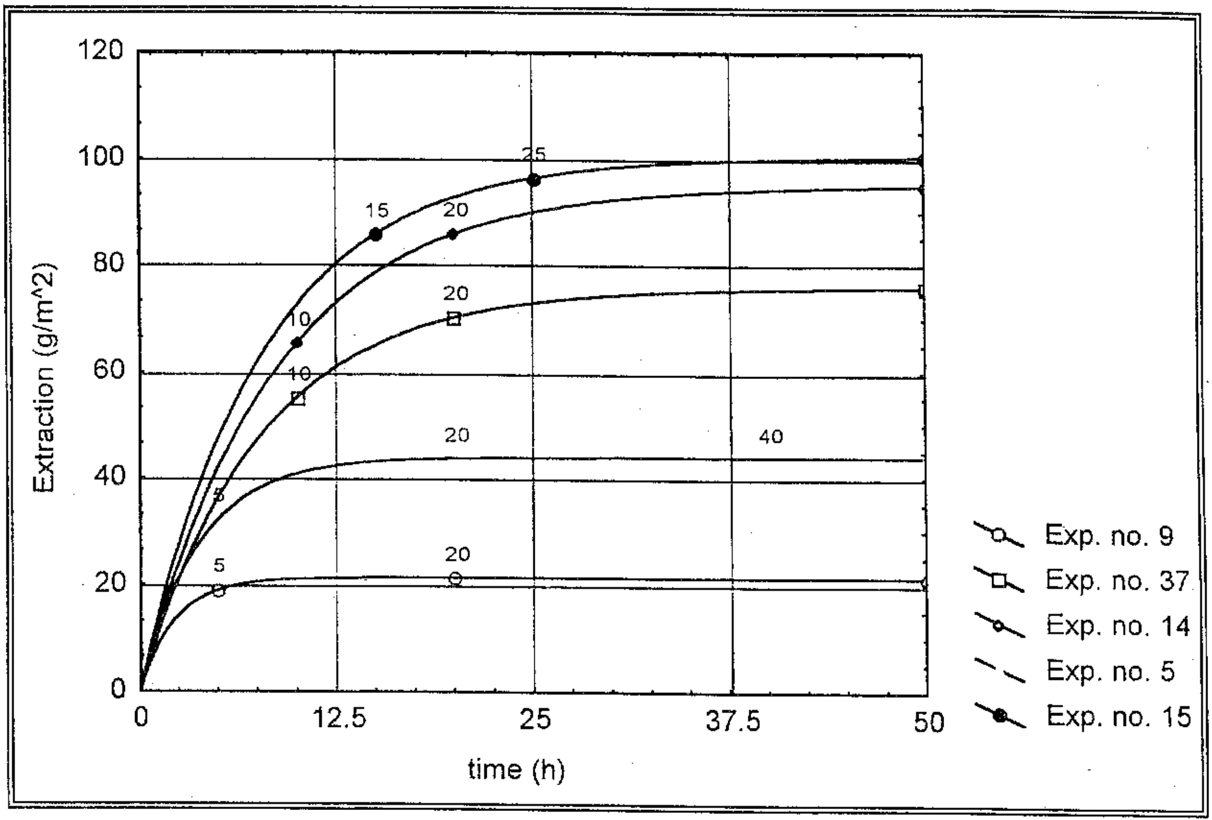


Fig. 3.15: Experiments with fastest rate of extraction.

3.4.4 Accuracy

The two most important influences on the accuracy of the experiments were the accuracy of the analytical methods and the influence of temperature on the experiments. An AA spectrometer was used to analyse the feed concentrations. The AA had an accuracy of 95% and higher, but the average drop in the nickel concentration was about 100 mg/dm^3 (10%). Thus, the accuracy that could be obtained with the AA was 9.5%. Statistical methods were used to perform a curve fit on the data. This increased the accuracy, since inaccurate data points, where obvious experimental deviations occurred, were ignored. The final curve fit of the data was at least 85% accurate for every experiment.

The temperature of the experiments was the other cause of inaccuracy. The experiments were performed over a three month period which stretched through the winter period and there is a large difference in the temperature between the first and last experiments, yielding a significant source of inaccuracy.

The curve fit for the maximum (final) extraction (Eq. 3.7) was 64.86% accurate. If the five worst points were ignored, the accuracy was 78.26% accurate. The curve fit of the rate of extraction had an average fault of 120.75% (see Appendix A.2 for calculations). This can be explained by the fact that the rate of extraction is more dependant on temperature than the maximum extraction.

Four of the experiments in the experimental design were repeated to determine the reproducibility of the experiments. The results of these four experiments can be seen in table 3.6. The standard deviation for the value of b was found to be 3.5789 (11.98 %). The standard deviation for the value of c was found to be 0.004884 (14.87 %).

Experiment no.	**b** (g/m^2)	**c** (h^{-1})
33	29.293	0.0348
34	27.099	0.0257
45	28.085	0.0367
46	35.090	0.0342
Average:	29.8918	0.03285
STD	3.5798	0.004884
STD (%)	11.98	14.87

Table 3.6: Reproducibility test for experiments.

Chapter 4

Conclusions and Recommendations

4.1 Conclusions

Most of the information needed for level zero of the process design have been gathered in this report. A central composite experimental design was executed to evaluate the influence of the different variables on the extraction of nickel. The CME configuration was used for the experiments. In this configuration a membrane capsule is made with the strip solution on the inside. The extractant is supported in the membrane skin. This capsule is submerged in the feed solution. The CME configuration has the following advantages:

1. A relatively low cost.
2. Very high acid concentrations can be used in the strip solution without the risk of high corrosion.

An equation (Eq. 3.7) was fitted through the data and extensively discussed in paragraph 3.4.2. The optimum conditions for the extraction of nickel have been established with the use of a computer program (See Appendix C.1 for program).

The following conclusions can be made with respect to the maximum extraction:

1. The hydronium concentration of the strip should be very high. The use of pure sulfuric acid is not recommended since there would be insufficient hydrolysis of acid. An acid concentration of 35 mol/dm^3 is recommended. This is a feature of this reactor and technique which renders its performance beyond that of the currently used reactors and configurations.

2. With this high hydronium strip concentration a low feed pH is recommended. This is not essential since the pH of the feed would drop drastically after the CME-process has started. This also means that no adjustment of the pH of the feed is necessary.
3. The nickel concentration of the feed should be as high as possible.
4. No conclusion can be made about the nickel concentration of the strip. This is not an obstacle since the nickel concentration of the strip would be zero in practice.
5. Further research needs to be done regarding the optimum extractant concentration, but at the above-mentioned conditions the optimum extractant concentration would probably be in the order of 45 vol. %.

With the above-mentioned conditions an extraction of more than 100 g/m^2 should be obtainable.

The average value for c in the experiments was 0.1014 h^{-1}. The time needed to extract 90% of the maximum extraction can be calculated with the following formula:

$$\begin{aligned} 0.9\,b &= b(1-e^{ct}) \\ \therefore 1-e^{ct} &= 0.9 \\ \therefore -c\,t &= \ln 0.1 \\ \therefore t &= -\frac{\ln 0.1}{c} \end{aligned} \tag{3.17}$$

The average time needed to extract 90% of the maximum extraction is thus 22.7 hours.

4.2 Recommendations

4.2.1 Introduction

Extensive research has been done on the extraction of nickel with CME. Very positive results have been obtained on the maximum amount of nickel that can be extracted with CME. These results can be used in developing a process where nickel can be extracted in industry with the use of CME. There is still some uncertainty about the rate of extraction, but on average 90% of the maximum nickel that can be extracted, can be extracted within 23 hours.

4.2.2 Further experiments

It is recommended that further experiments should be done to establish the effect of temperature and agitation. Additional experiments should also be done to establish the optimum extractant concentration. The following should be remembered in the experiments:

1. A hydronium strip concentration of approximately 30 mol/dm^3 should be used.
2. A constant feed pH (say 4.5) should be used. It is not necessary to adjust the pH during the experiment.
3. A nickel feed concentration of 1000 mg/dm^3 should be used. This concentration must not be adjusted in order to minimise the error made with analysing.
4. There must be no nickel in the strip solution.
5. The experiments must be done over a short period of time (say two weeks) to minimise the effect of the surrounding temperature.

4.2.3 Proposed process

A proposed process for the extraction of nickel with SLM can be seen in figure 4.1. The first step is to adjust the nickel waste water to a pH of approximately 7.5 with sodium hydroxide. At this pH nickel hydroxide ($Ni(OH)_2$) will form and precipitate. This is done to reduce the volume of the waste that has to be treated. The concentrated nickel hydroxide slurry is then placed in a tank together with the membrane capsules. The capsules will cause a drop in the pH of the solution and the nickel hydroxide will dissolve again. The capsules will continue to extract the nickel until the capsules are saturated with nickel and the waste solution depleted. This solution is recycled to the original waste water and the nickel is recovered from the capsules. It is recommended that experiments should be done to test this proposed process.

An extraction of 100 g/m^2 should be obtainable with the CME configuration. This is equivalent to R3.24 /m^2. The membranes used cost approximately \$10 - 15/m^2 (R36 - 55/m^2). It is clear that the membrane should be recycled at least 17 times to obtain a profit under these adverse cost assumptions.

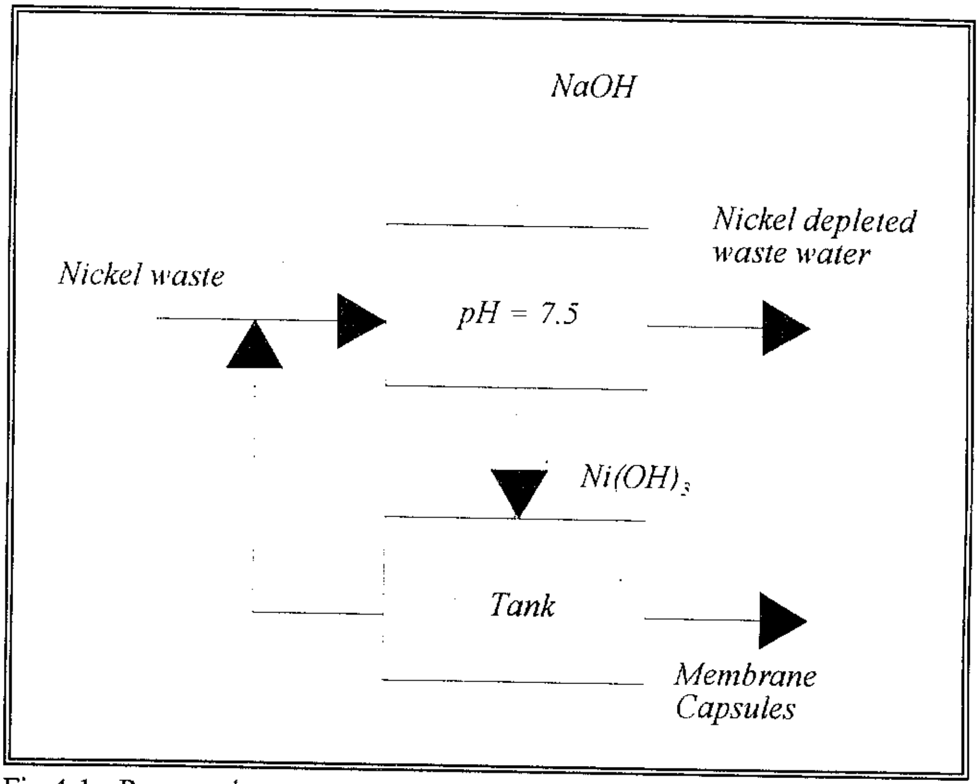


Fig 4.1: Proposed process

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Appendix B

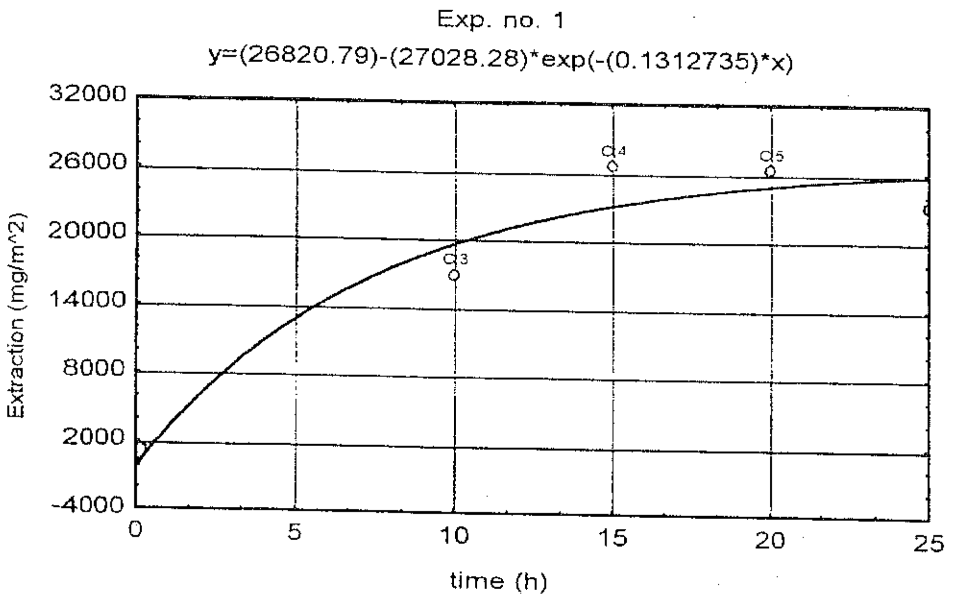
Results

B.1 Results of experiments done for optimization of CME

Eksp. no: 1

Circom. 0.131 Area 0.0027312

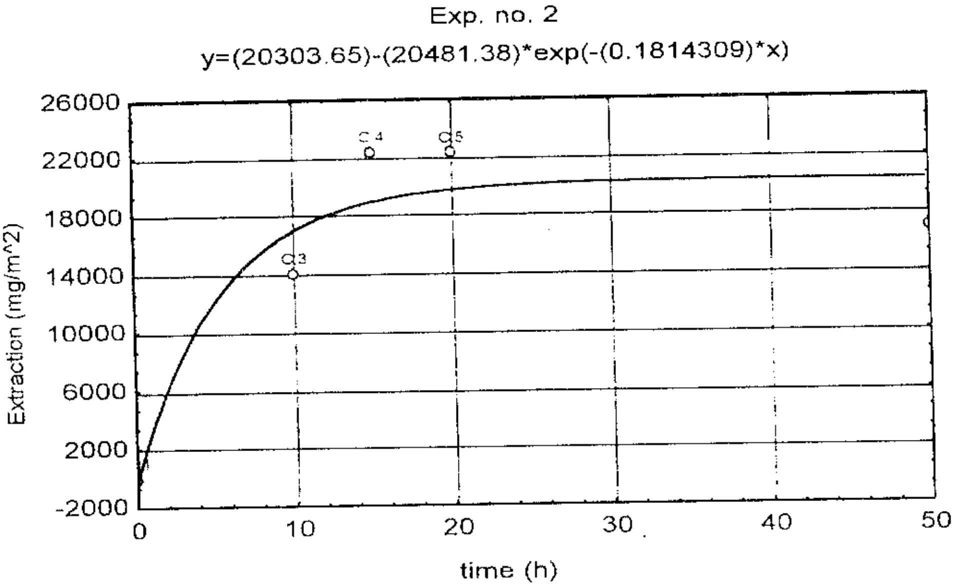
Time	[Ni] feed	Vol.	Adjust.	Extr.	Rate
0	800	0.400	0.000000	0	
5	638	0.400	0.007000	23725	4745
10	841	0.405	0.000000	16917	1692
15	785	0.395	0.000644	26556	1770
20	803	0.390	0.000000	26343	1317
25	825	0.385	0.000000	23242	930
50	846	0.380	0.000000	20344	407



Exp. no: 2

Circom. 0.13 Area 0.0026897

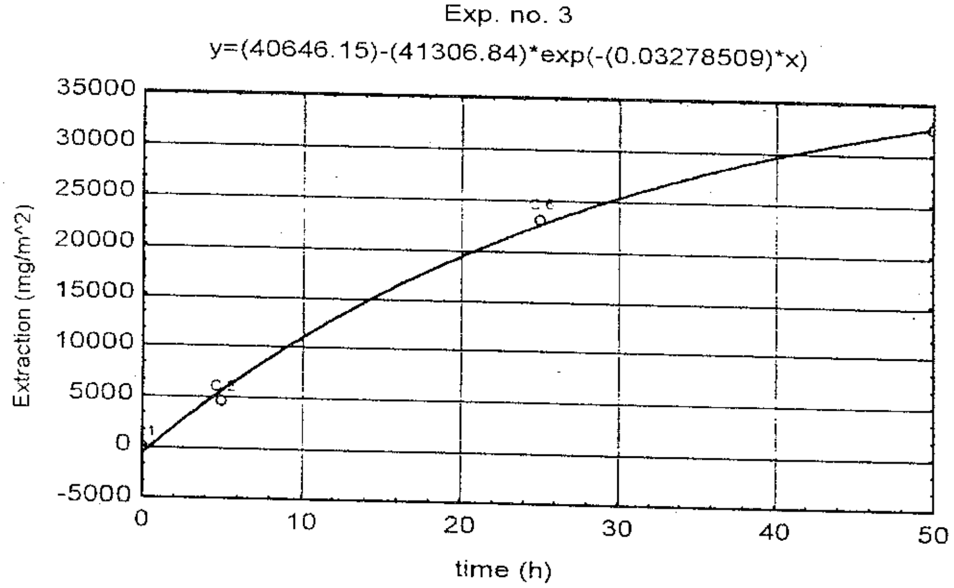
Time	[Ni] feed	Vol.	Adjust.	Extr.	Rate
0	800	0.400	0.000000	0	
5	639	0.400	0.007000	23943	4789
10	851	0.410	0.000000	14089	1409
15	796	0.405	0.000176	22370	1491
20	801	0.400	0.000000	22281	1114
25	818	0.410	0.000000	15223	609
50	816	0.400	0.000000	17066	341



Exp. no: 3

Circom. 0.144 Area 0.0033002

Time	[Ni] feed	Vol.	Adjust.	Extr.	Rate
0	800	0.400	0.000000	0	
5	663	0.460	0.006850	4551	910
10	803	0.475	0.000000	1139	114
15	784	0.470	0.000000	3845	256
20	770	0.400	0.001304	7763	388
25	667	0.400	0.005783	23032	921
50	735	0.395	0.000000	32415	648



Exp. no. 3

y=(40646.15)-(41306.84)*exp(-(0.03278509)*x)

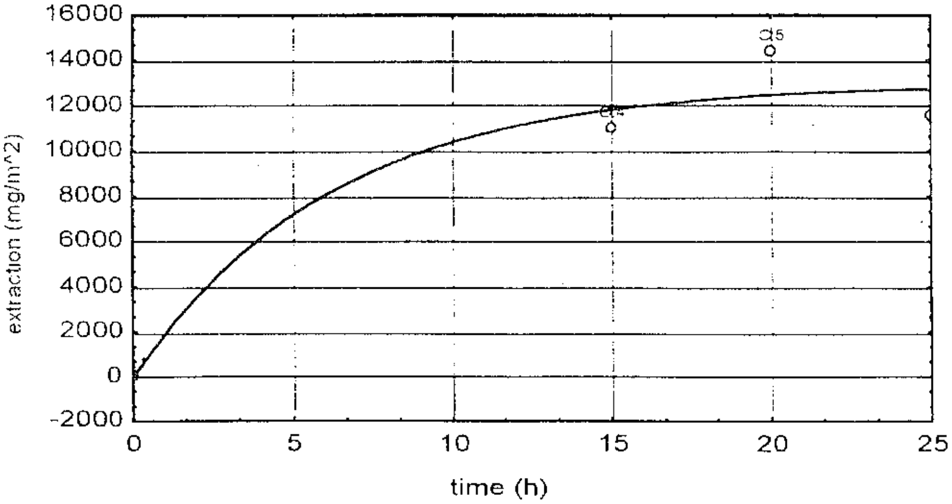
Exp. no: 4

Circom. 0.165 Area 0.0043329

Time	[Ni] feed	Vol.	Adjust.	Extr.	Rate
0	800	0.400	0.000000	0	
5	629	0.488	0.009000	3011	602
10	794	0.500	0.000000	2274	227
15	704	0.405	0.004226	11050	737
20	773	0.400	0.001174	14434	722
25	824	0.400	0.000000	11543	462
50	743	0.398	0.000000	19409	388

Exp. no. 4

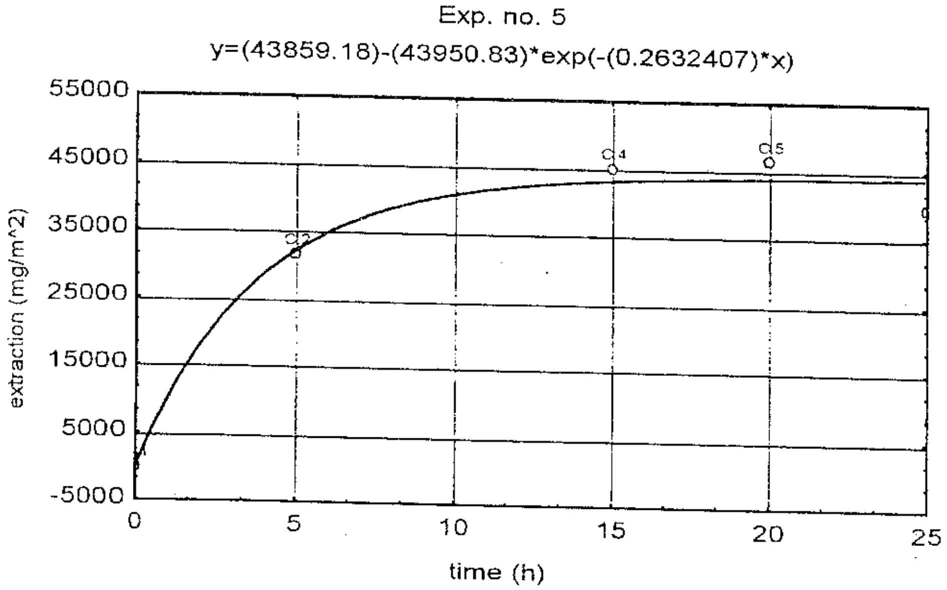
y=(12986.21)-(12998.06)*exp(-(0.1608027)*x)



Exp. no: 5

Circom. 0.129 Area 0.0026484

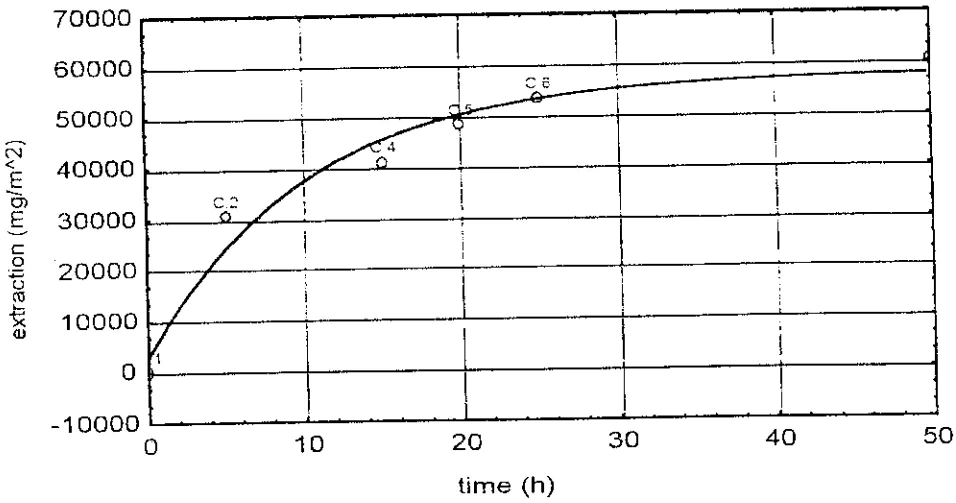
Time	[Ni] feed	Vol.	Adjust.	Extr.	Rate
0	1200	0.400	0.000000	0	
5	991	0.400	0.010000	31565	6313
10	1291	0.405	0.000000	19706	1971
15	1124	0.400	0.003455	44927	2995
20	1218	0.390	0.000000	46251	2313
25	1247	0.390	0.000000	39681	1587
50	1312	0.390	0.000000	30110	602



Exp. no: 6

Circom. 0.14 Area 0.0031194

Time	[Ni] feed	Vol.	Adjust.	Extr.	Rate
0	1200	0.400	0.000000	0	
5	938	0.410	0.012207	30589	6118
10	1248	0.412	0.000000	26672	2667
15	1144	0.405	0.002577	40975	2732
20	1137	0.405	0.002899	48312	2416
25	1170	0.400	0.001364	53385	2135
50	1156	0.398	0.000000	60292	1206

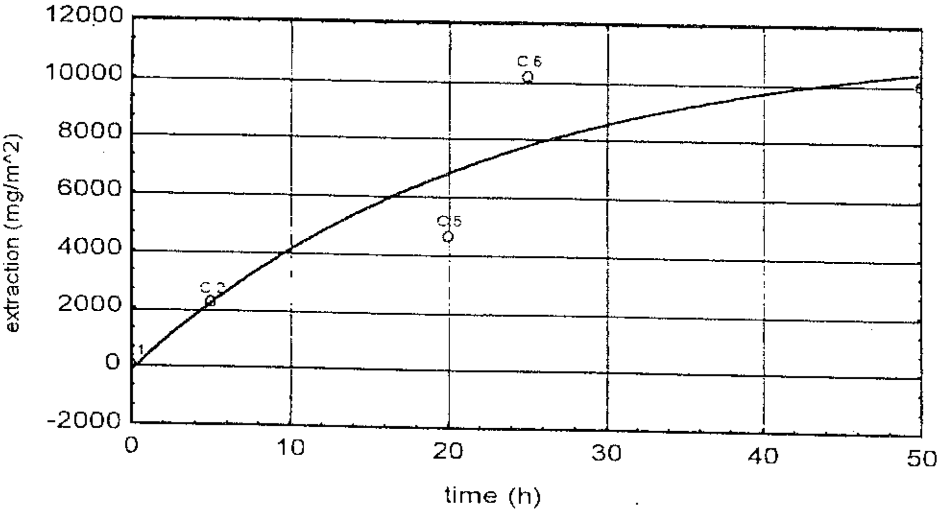


Exp. no. 6

y=(58125.15)-(55448.76)*exp(-(0.09796587)*x)

Exp. no: 7
Circom. 0.143 Area 0.0032545

Time	[Ni] feed	Vol.	Adjust.	Extr.	Rate
0	1200	0.400	0.000000	0	
5	1087	0.435	0.005586	2198	440
10	1245	0.435	0.000000	-3427	-343
15	1176	0.440	0.001200	2076	138
20	1171	0.440	0.001450	4633	232
25	1124	0.450	0.003886	10190	408
50	1156	0.445	0.000000	19482	390

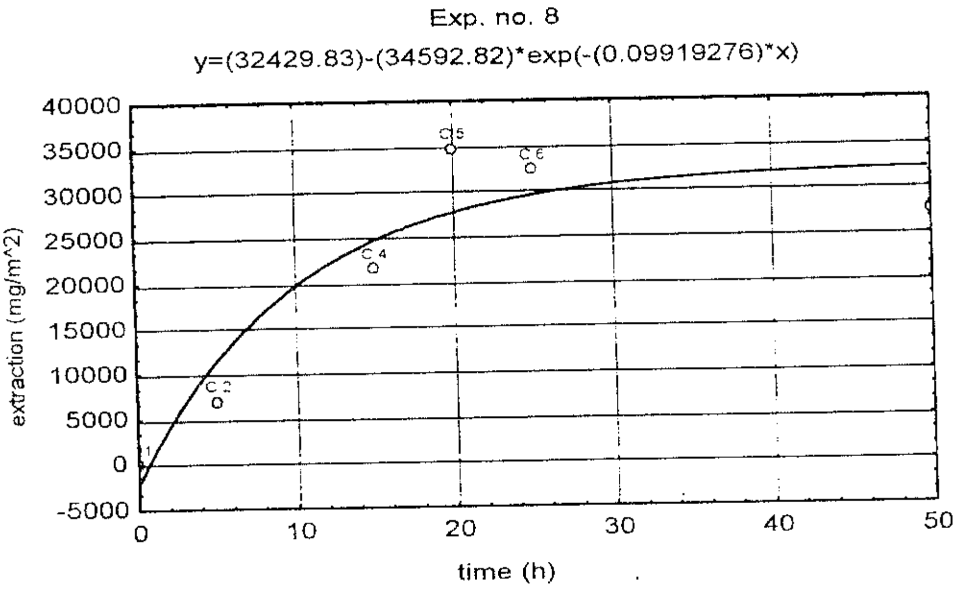


Exp. no. 7
y=(11692.81)-(11832.54)*exp(-(0.04413925)*x)

Exp. no: 8

Circom. 0.137 Area 0.0029871

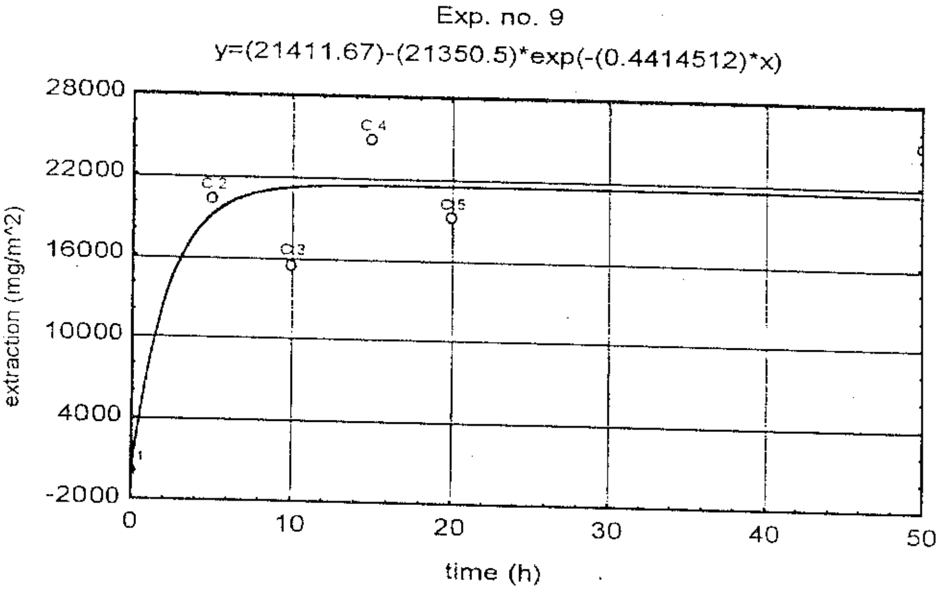
Time	[Ni] feed	Vol.	Adjust.	Extr.	Rate
0	1200	0.400	0.000000	0	
5	1080	0.425	0.005795	7030	1406
10	1238	0.430	0.000000	72	7
15	1100	0.420	0.004773	21547	1436
20	1107	0.420	0.004439	34699	1735
25	1188	0.430	0.000586	32339	1294
50	1264	0.420	0.000000	27594	552



Exp. no: 9

Circom. 0.131 Area 0.0027312

Time	[Ni] feed	Vol.	Adjust.	Extr.	Rate
0	800	0.400	0.000000	0	
5	662	0.400	0.006000	20210	4042
10	826	0.405	0.000000	15436	1544
15	766	0.398	0.001471	24784	1652
20	839	0.395	0.000000	19051	953
25	888	0.400	0.000000	8803	352
50	898	0.395	0.000000	9003	180



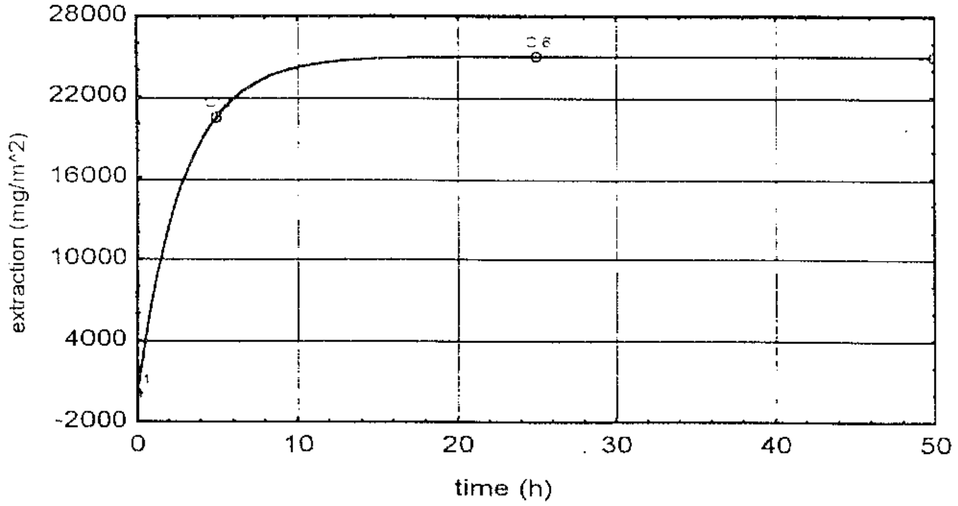
Exp. no: 10

Circom. 0.14 Area 0.0031194

Time	[Ni] feed	Vol.	Adjust.	Extr.	Rate
0	800	0.400	0.000000	0	
5	640	0.400	0.006957	20517	4103
10	839	0.405	0.000000	14929	1493
15	832	0.405	0.000000	14493	966
20	855	0.410	0.000000	8803	440
25	871	0.410	0.000000	5330	213
50	843	0.410	0.000000	8966	179

Exp. no. 10

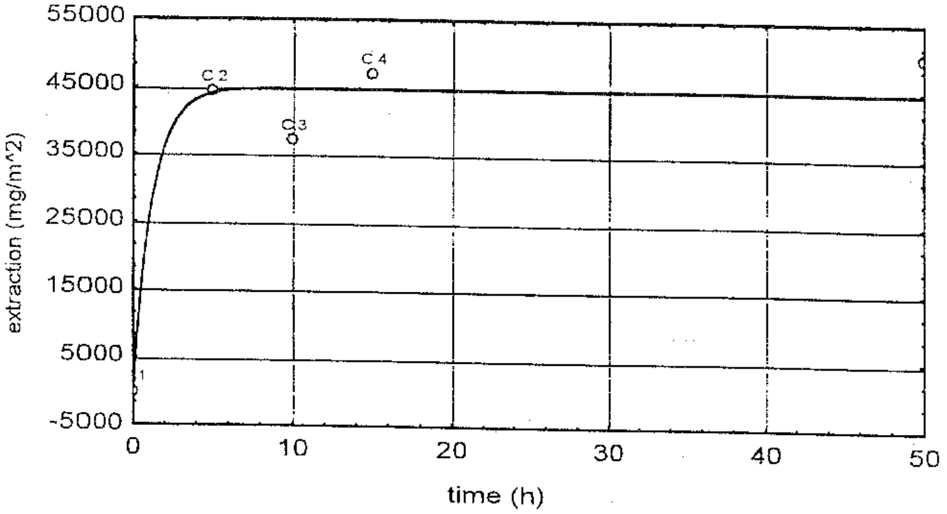
y=(25002.32)-(25002.32)*exp(-(0.3436324)*x)



Eksp. no: 11

Circom. 0.129 Area 0.0026484

Time	[Ni] feed	Vol.	Adjust.	Extr.	Rate
0	823	0.388	0.000000	0	
5	764	0.400	0.001000	44348	8870
10	797	0.400	0.000000	37163	3716
15	703	0.400	0.004000	47132	3142
20	809	0.400	0.000000	27749	1387
25	771	0.410	0.001292	12318	493
50	784	0.400	0.000696	11750	235

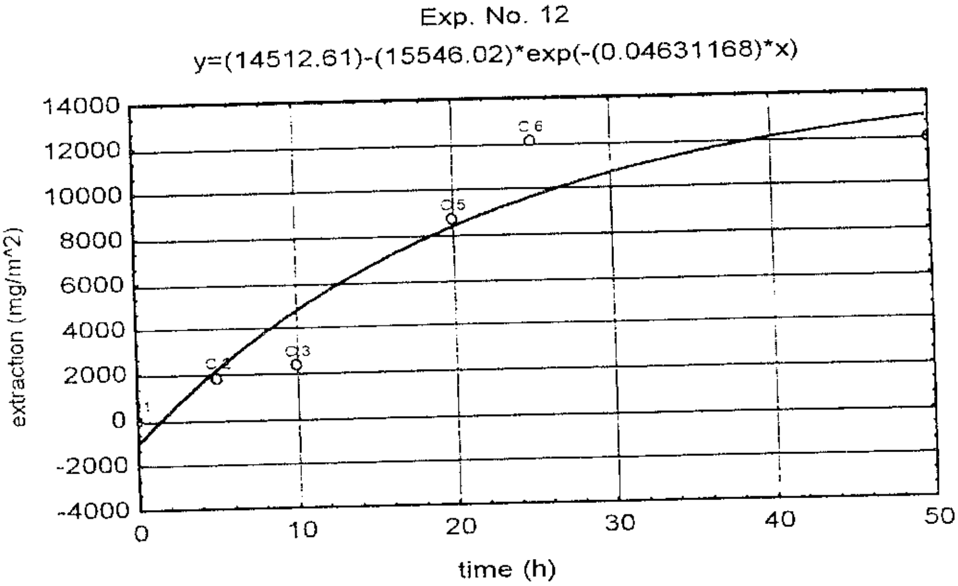

Exp. No. 11

y=(44855.87)-(44853.63)*exp(-(0.8131385)*x)

Eksp. no: 12

Circom. 0.122 Area 0.0023688

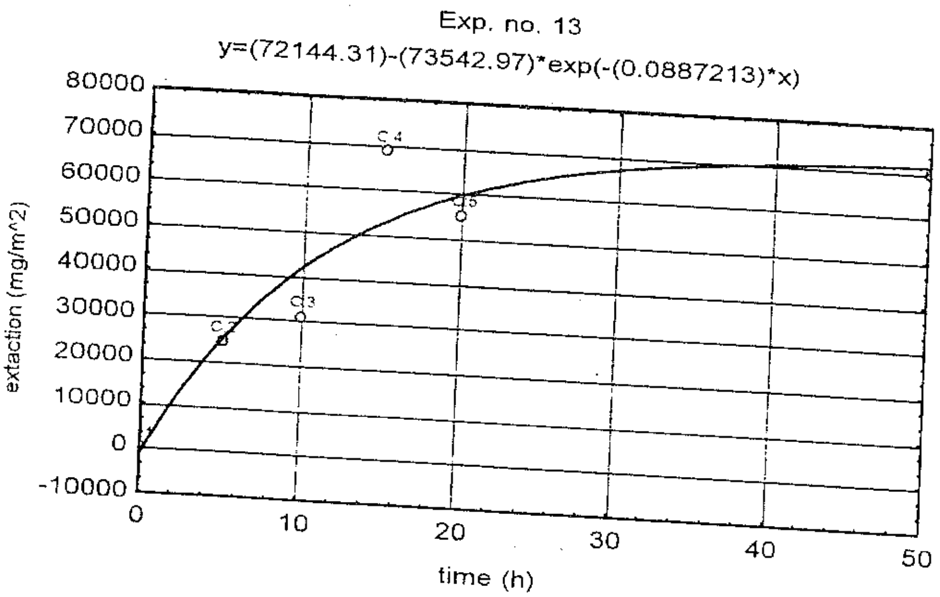
Time	[Ni] feed	Vol.	Adjust.	Extr.	Rate
0	803	0.400	0.000000	0	
5	745	0.420	0.002000	1809	362
10	781	0.420	0.000000	2296	230
15	627	0.418	0.007000	28482	1899
20	895	0.420	0.000000	8662	433
25	845	0.430	0.000000	12071	483
50	855	0.430	0.000000	8451	169



Eksp. no: 13

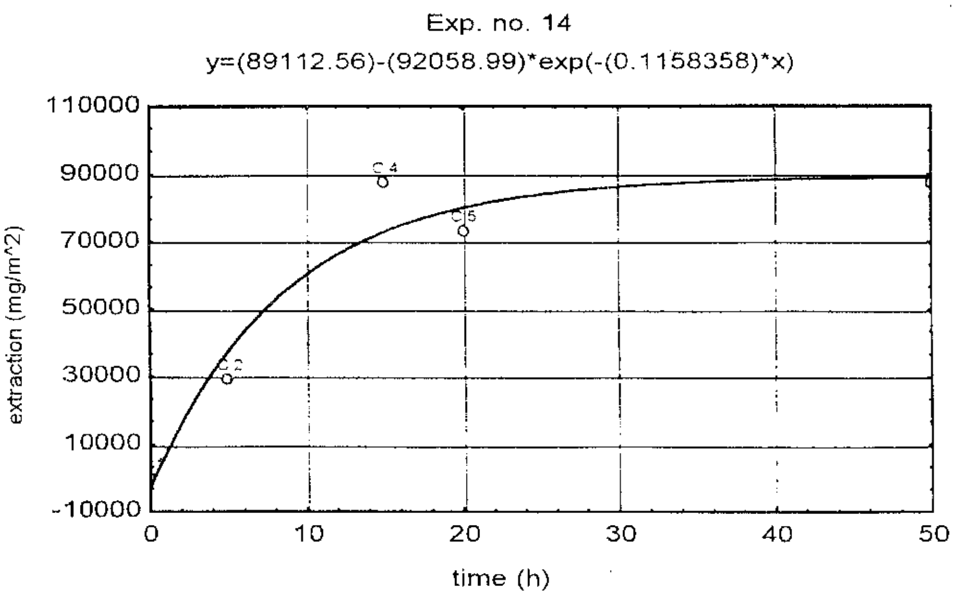
Circom. 0.138 Area 0.0030309

Time	[Ni] feed	Vol.	Adjust.	Extr.	Rate
0	1184	0.400	0.000000	0	
5	996	0.395	0.009000	24501	4900
10	1153	0.398	0.002000	30949	3095
15	903	0.398	0.013000	68474	4565
20	1297	0.405	0.000000	55143	2757



Eksp. no: 14
Circom. 0.108 Area 0.0018563

Time	[Ni] feed	Vol.	Adjust.	Extr.	Rate
0	1154	0.400	0.000000	0	
5	1005	0.400	0.008000	28997	5799
10	1197	0.410	0.000000	21566	2157
15	896	0.405	0.014000	87234	5816
20	1249	0.420	0.000000	73131	3657

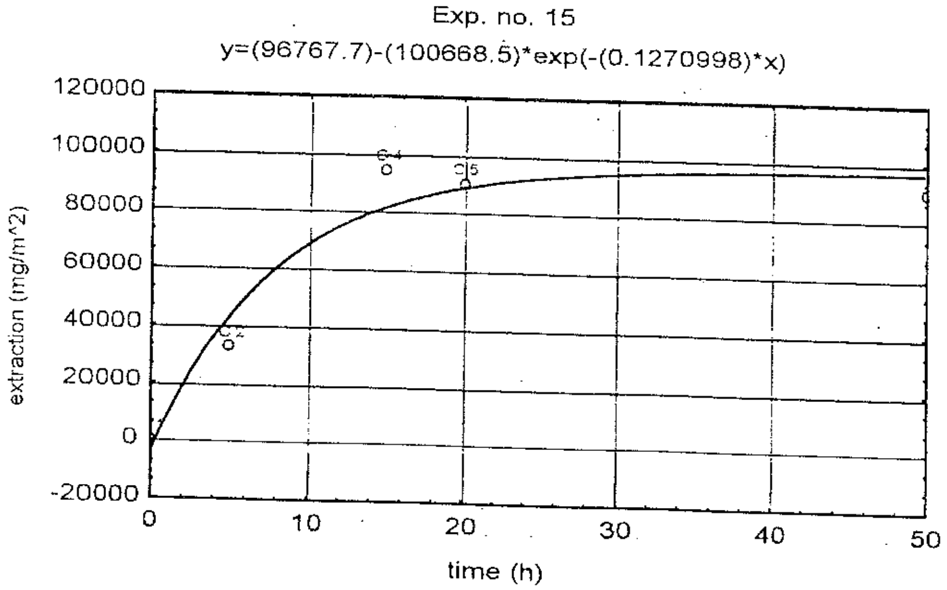


Exp. no. 14
y=(89112.56)-(92058.99)*exp(-(0.1158358)*x)

Eksp. no: 15

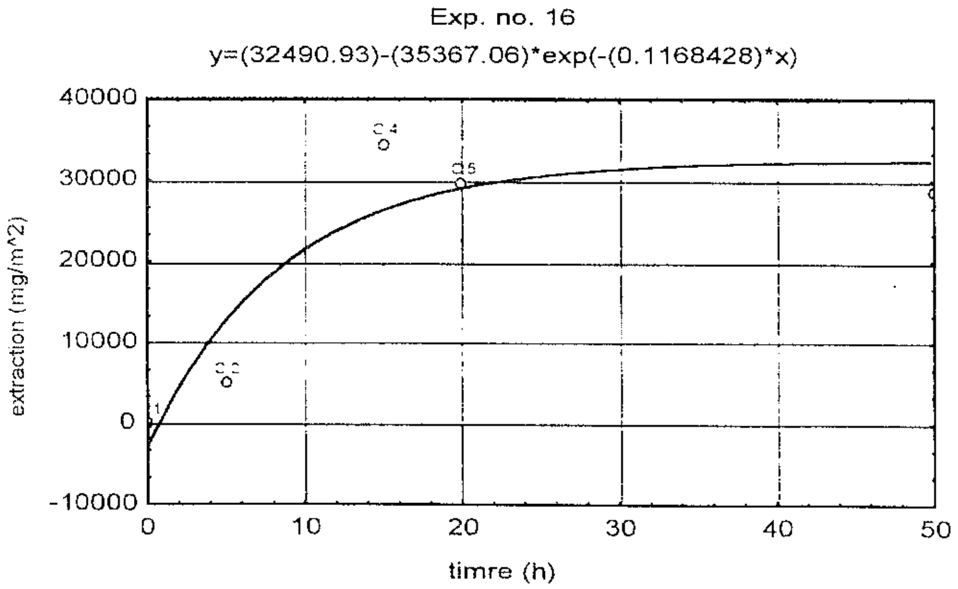
Circom. 0.102 Area 0.0016558

Time	[Ni] feed	Vol.	Adjust.	Extr.	Rate
0	1265	0.400	0.000000	0	
5	1115	0.400	0.003000	32415	6483
10	1188	0.400	0.000000	29532	2953
15	905	0.400	0.013000	94308	6287
20	1212	0.408	0.000000	90068	4503
25	1370	0.410	0.000000	45822	1833
50	1357	0.405	0.000000	49002	980



Eksp. no: 16
Circom. 0.129 Area 0.0026484

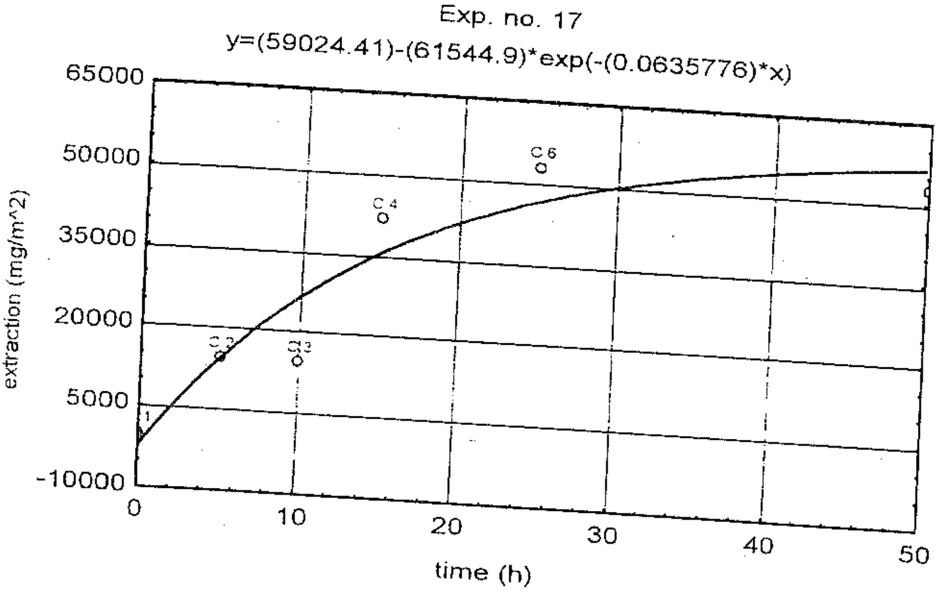
Time	[Ni] feed	Vol.	Adjust.	Extr.	Rate
0	1230	0.400	0.000000	0	
5	1099	0.430	0.004000	5014	1003
10	1174	0.435	0.001000	3649	365
15	989	0.438	0.013000	34474	2298
20	1269	0.450	0.000000	29636	1482
25	1352	0.458	0.000000	9054	362
50	1246	0.450	0.000000	28595	572



Eksp. no: 17

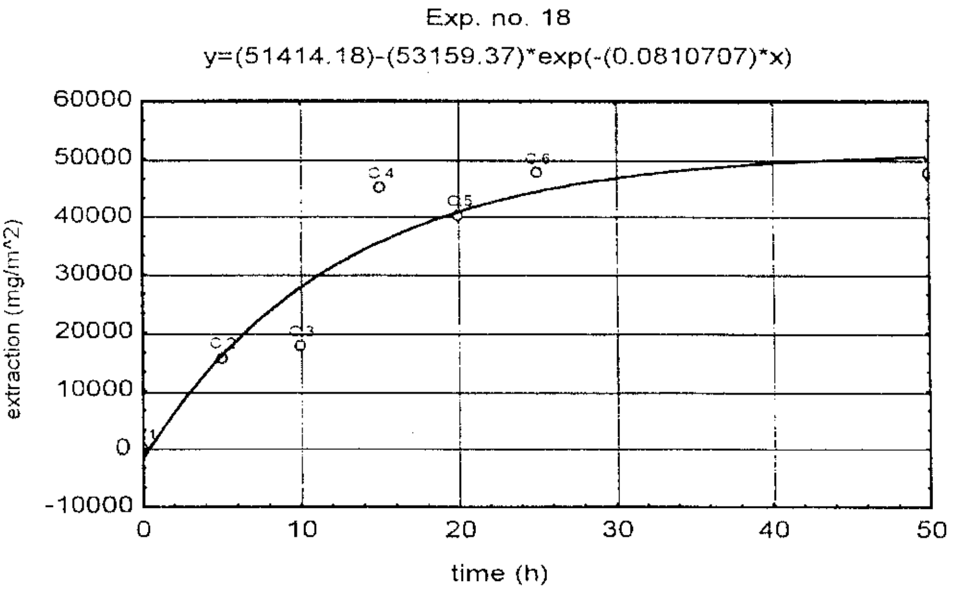
Circom. 0.148 Area 0.0034861

Time	[Ni] feed	Vol.	Adjust.	Extr.	Rate
0	813	0.400	0.000000	0	
5	677	0.400	0.005000	14439	2888
10	803	0.395	0.000000	14505	1450
15	545	0.400	0.011000	41804	2787
20	942	0.410	0.000000	24322	1216
25	688	0.410	0.000000	52844	2114
50	955	0.400	0.000000	23195	464



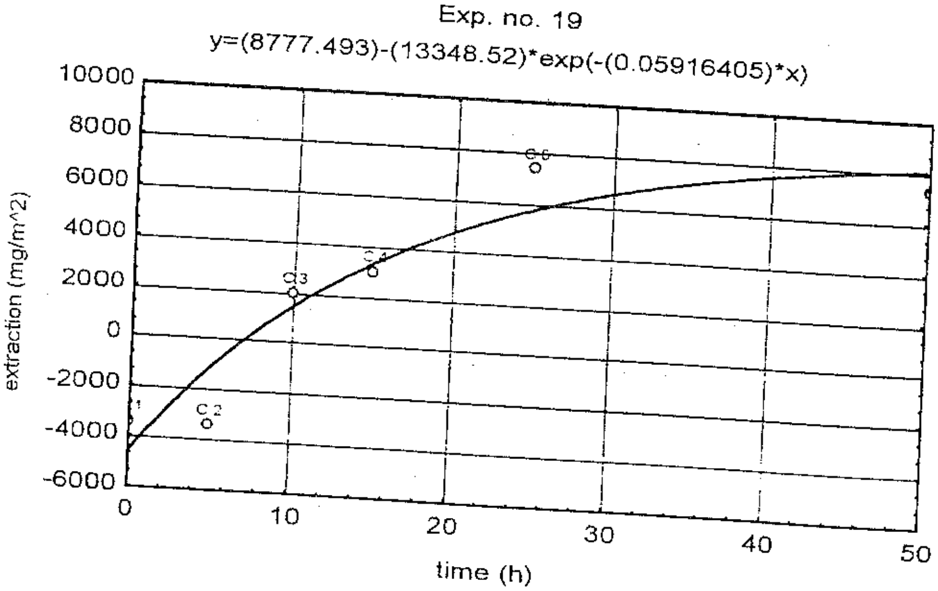
Eksp. no: 18
Circom. 0.152 Area 0.0036771

Time	[Ni] feed	Vol.	Adjust.	Extr.	Rate
0	808	0.400	0.000000	0	
5	657	0.398	0.006000	15685	3137
10	759	0.410	0.001000	17591	1759
15	542	0.400	0.011000	44948	2997
20	833	0.410	0.000000	40205	2010
25	757	0.410	0.000000	47547	1902
50	915	0.400	0.000000	31389	628



Eksp. no: 19
Circom. 0.158 Area 0.0039731

Time	[Ni] feed	Vol.	Adjust.	Extr.	Rate
0	803	0.400	0.000000	0	
5	735	0.450	0.003000	-3414	-683
10	730	0.460	0.003000	1941	194
15	716	0.500	0.004000	2985	199
20	810	0.495	0.000000	1342	67
25	746	0.500	0.000000	7357	294
50	783	0.488	0.000000	4127	83



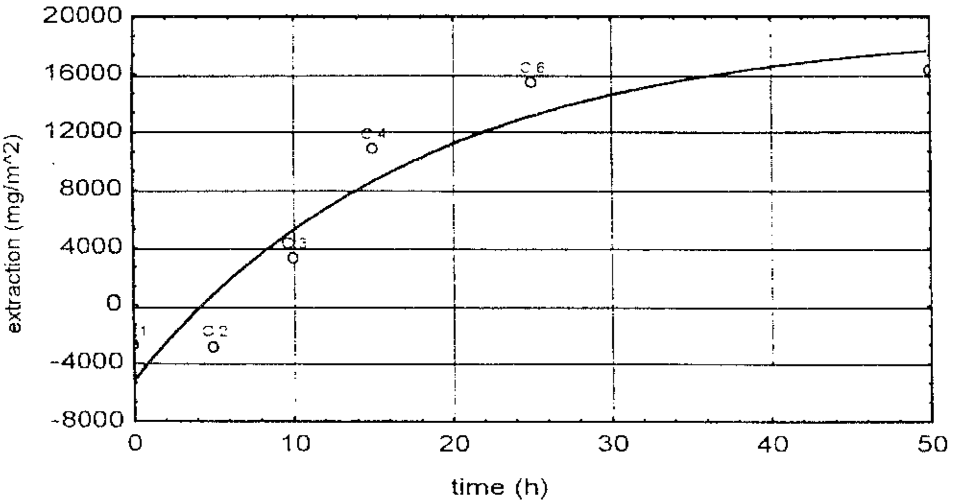
Eksp. no: 20

Circom. 0.148 Area 0.0034861

Time	[Ni] feed	Vol.	Adjust.	Extr.	Rate
0	801	0.400	0.000000	0	
5	717	0.455	0.004000	-2821	-564
10	739	0.462	0.003000	3269	327
15	711	0.480	0.004000	10854	724
20	825	0.480	0.000000	5612	281
25	745	0.480	0.000000	15444	618
50	747	0.470	0.000000	16243	325

Exp. no. 20

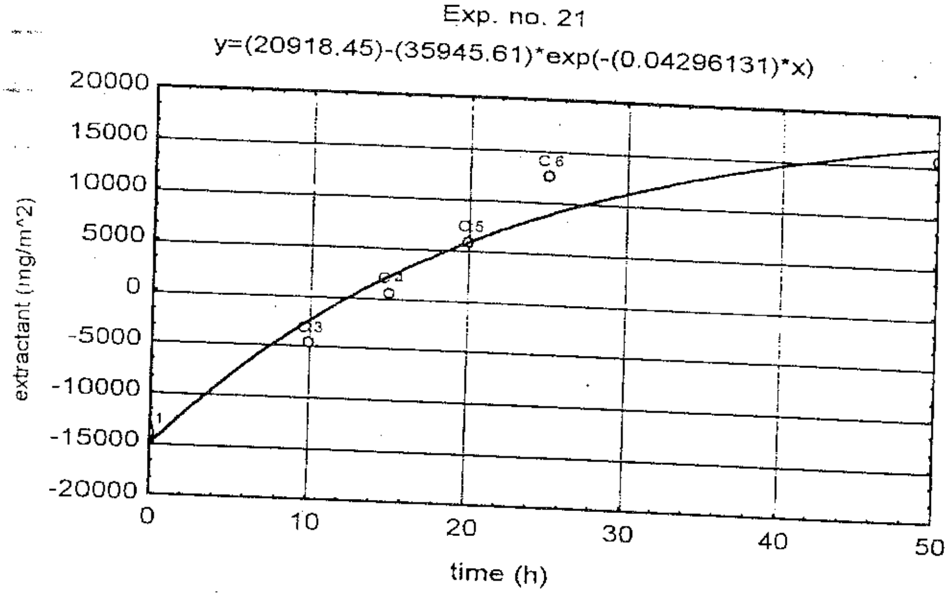
y=(19146.43)-(24306.19)*exp(-(0.05573247)*x)



Eksp. no: 21

Circom. 0.138 Area 0.0030309

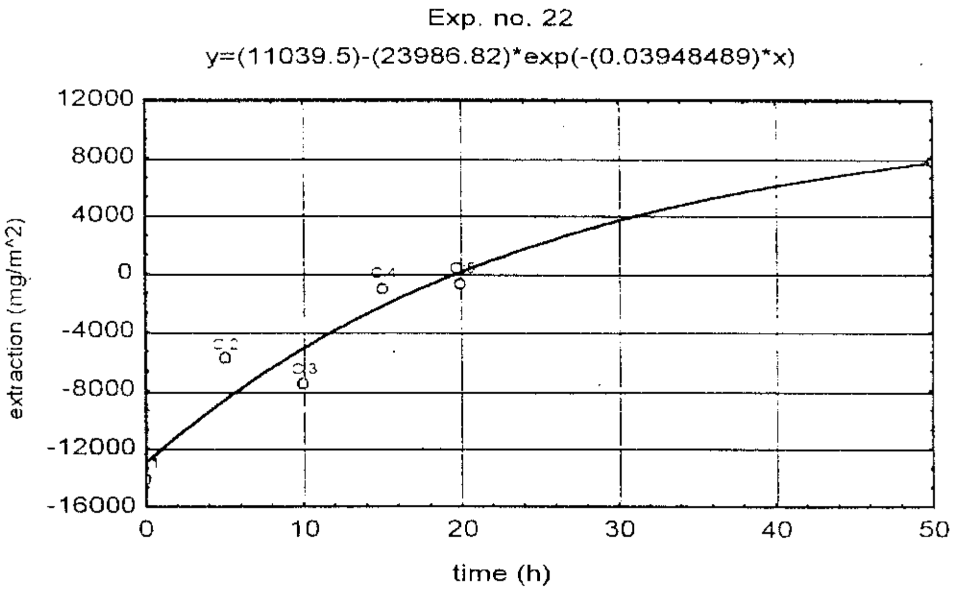
Time	[Ni] feed		Vol.	Adjust.	Extr.	Rate
0	1217	0.400	0.000000		0	
5	1217	0.400	0.000000		-2008	-402
10	1253	0.390	0.000000		-4632	-463
15	1213	0.385	0.000000		449	30
20	1186	0.375	0.000000		5790	290
25	1131	0.370	0.003000		12504	500
50	1071	0.405	0.000000		15494	310



Eksp. no: 22

Circom. 0.136 Area 0.0029437

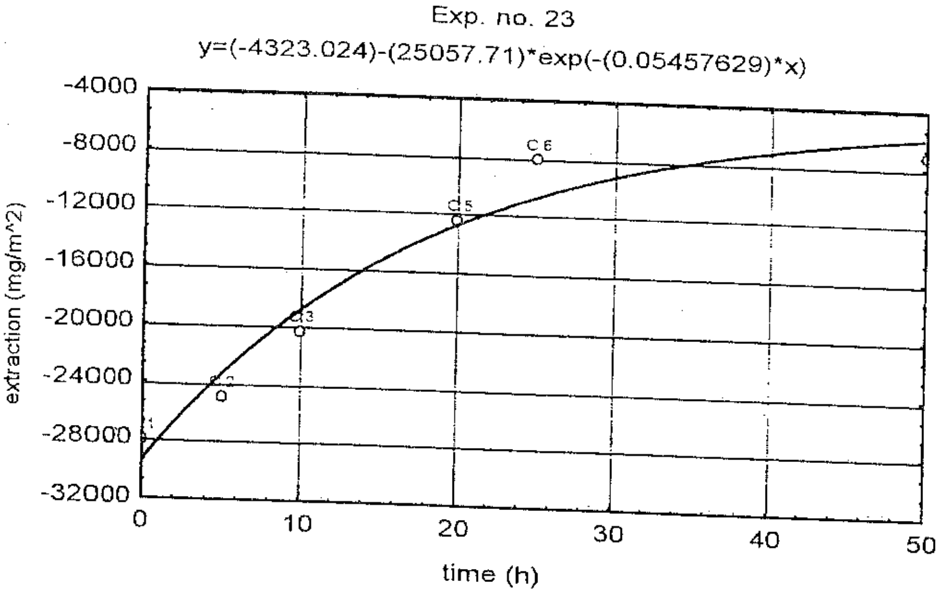
Time	[Ni] feed		Vol.	Adjust.	Extr.	Rate
0	1169	0.400	0.000000		0	
5	1146	0.418	0.002000		-5868	-1174
10	1215	0.410	0.000000		-7516	-752
15	1153	0.410	0.002000		-944	-63
20	1215	0.400	0.000000		-617	-31
25	1134	0.395	0.003000		10252	410
50	1229	0.390	0.000000		7857	157



Eksp. no: 23

Circom. 0.13 Area 0.0026897

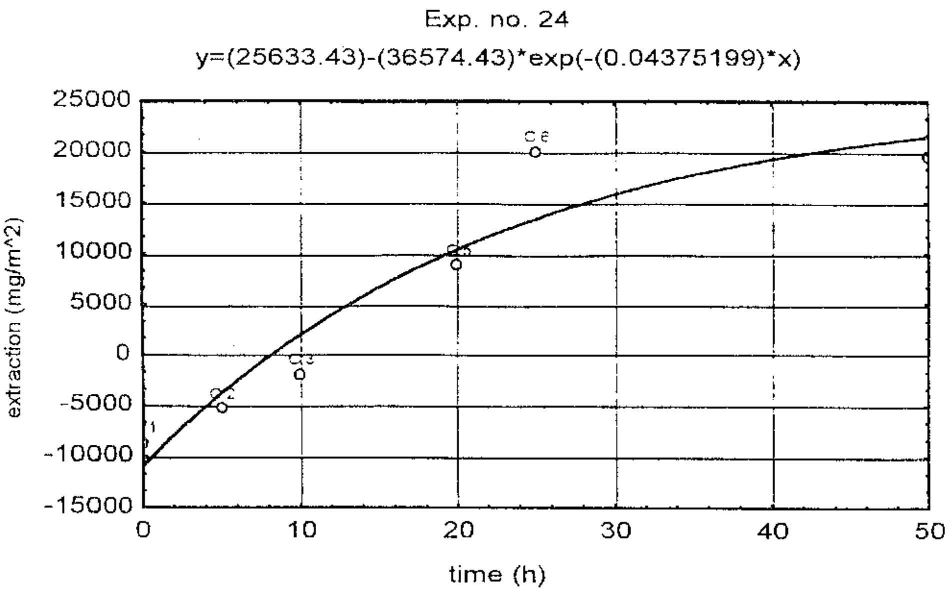
Time	[Ni] feed		Vol.	Adjust.	Extr.	Rate	
0	1082	0.400	0.000000		0		
5	1075	0.460	0.006000		-24951		-4990
10	1167	0.460	0.001000		-20376		-2038
15	1188	0.460	0.000000		-22419		-1495
20	1129	0.455	0.003000		-12438		-622
25	1132	0.465	0.003000		-8099	-324	
50	1179	0.465	0.000000		-7175	-144	



Eksp. no: 24

Circom. 0.136 Area 0.0029437

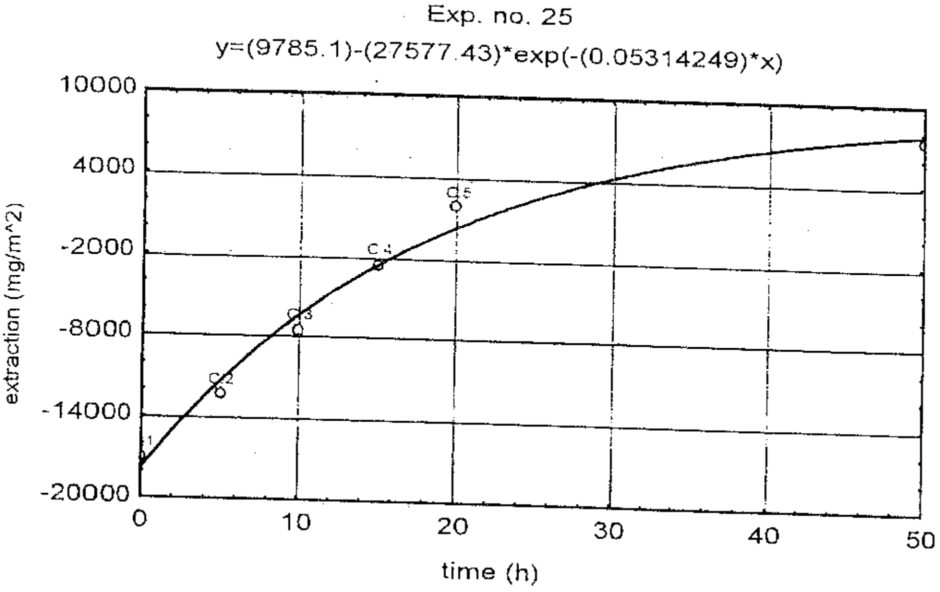
Time	[Ni] feed		Vol.	Adjust.	Extr.	Rate
0	1244	0.400	0.000000		0	
5	1165	0.435	0.001000		-5230	-1046
10	1165	0.430	0.001000		-1833	-183
15	1160	0.430	0.002000		316	21
20	1162	0.420	0.002000		8795	440
25	1117	0.420	0.004000		20036	801
50	1203	0.420	0.000000		19457	389



Eksp. no: 25

Circom. 0.123 Area 0.0024078

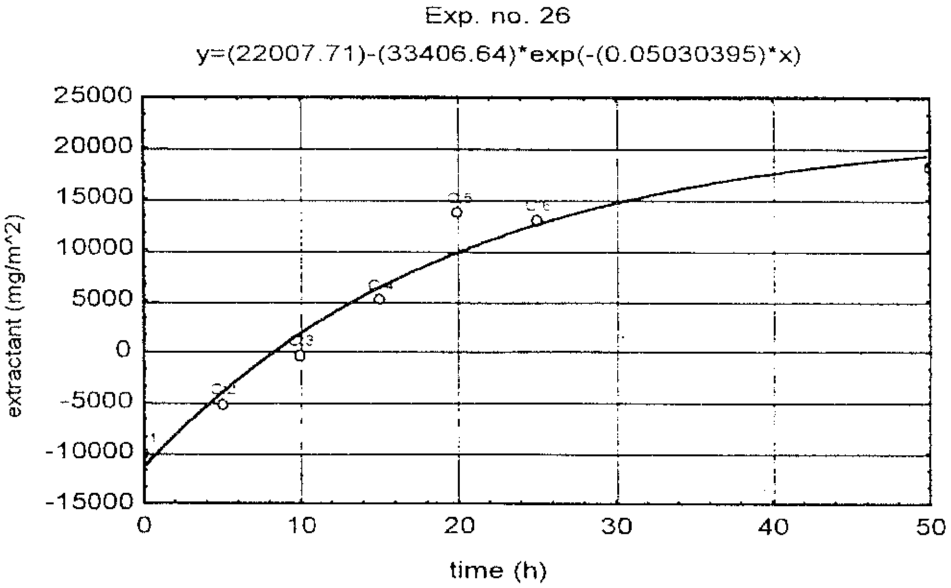
Time	[Ni] feed		Vol.	Adjust.	Extr.	Rate	
0	895	0.400	0.000000		0		
5	946	0.405	0.000000		-12295		-2459
10	917	0.400	0.000000		-7478	-748	
15	887	0.395	0.000000		-2556	-170	
20	860	0.390	0.000000		1817	91	
25	772	0.400	0.001000		11078	443	
50	809	0.400	0.000000		7405	148	



Eksp. no: 26

Circom. 0.131 Area 0.0027312

Time	[Ni] feed		Vol.	Adjust.	Extr.	Rate
0	742	0.400	0.000000		0	
5	749	0.410	0.002000		-5126	-1025
10	776	0.400	0.001000		-386	-39
15	764	0.395	0.001000		5011	334
20	739	0.385	0.002000		13594	680
25	786	0.385	0.000000		12939	518
50	710	0.400	0.000000		18314	366

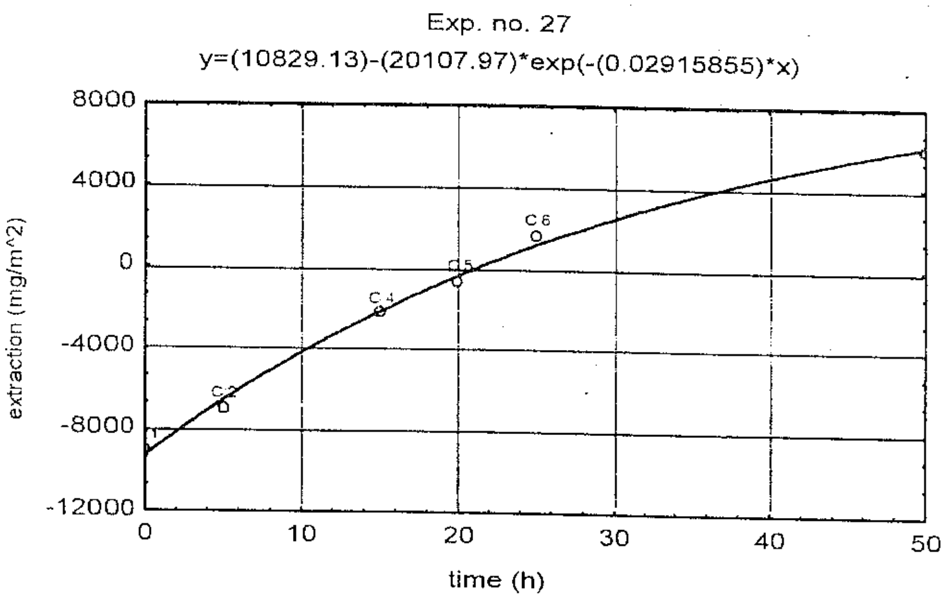


Eksp. no: 27

Circom. 0.139 Area 0.0030750

Time	[Ni] feed		Vol.	Adjust.	Extr.	Rate
0	732	0.400	0.000000		0	
5	722	0.430	0.003000		-6933	-1387
10	804	0.430	0.000000		-9818	-982
15	749	0.425	0.002000		-2216	-148
20	785	0.420	0.000000		-629	-31
25	759	0.420	0.001000		1646	66
50	769	0.405	0.000000		6032	121

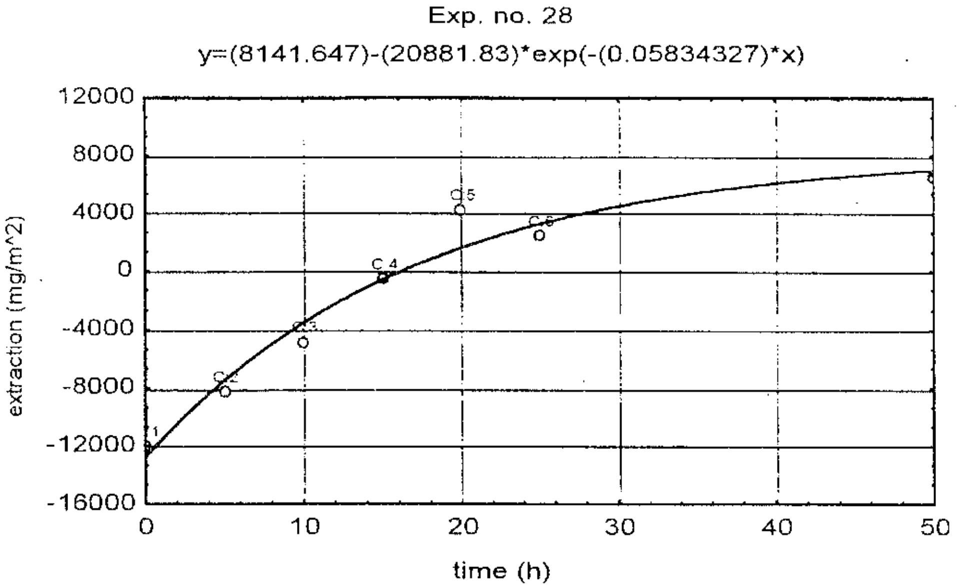
e



Eksp. no: 28

Circom. 0.141 Area 0.0031641

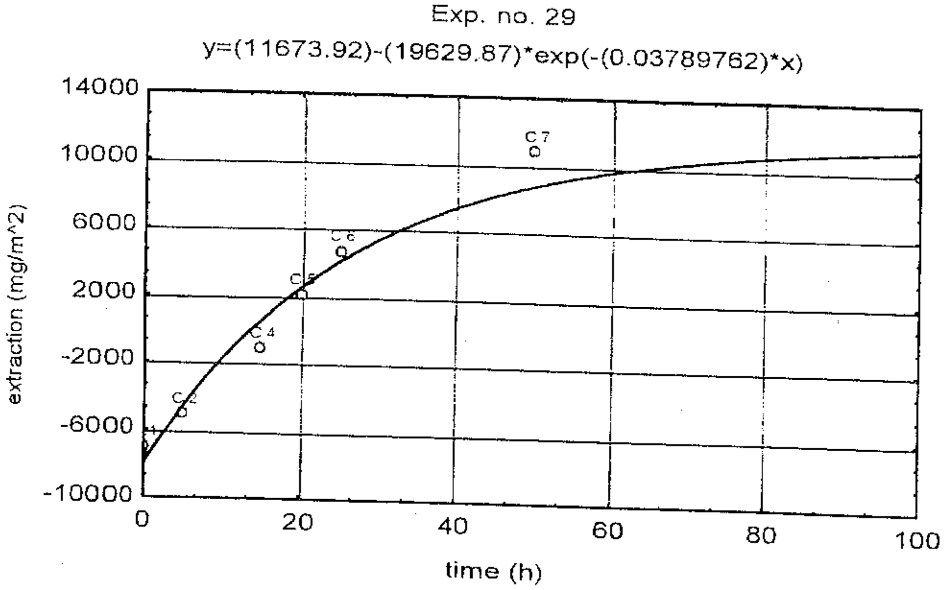
Time	[Ni] feed		Vol.	Adjust.	Extr.	Rate
0	745	0.400	0.000000		0	
5	712	0.450	0.004000		-8257	-1651
10	769	0.450	0.001000		-4846	-485
15	761	0.445	0.001000		-561	-37
20	749	0.440	0.002000		4268	213
25	799	0.440	0.000000		2452	98
50	760	0.440	0.000000		6613	132



Eksp. no: 29

Circom. 0.147 Area 0.0034391

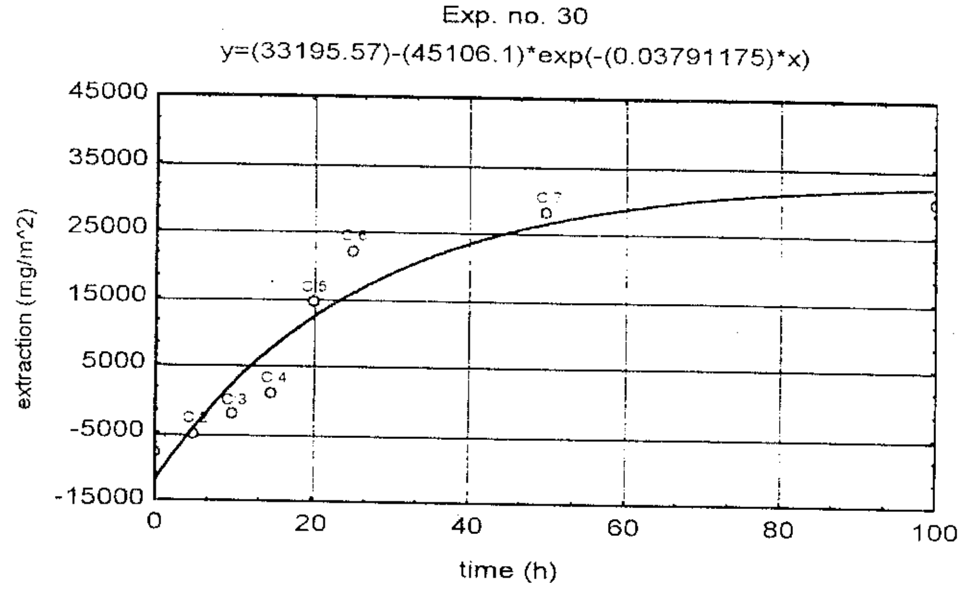
Time	[Ni] feed		Vol.	Adjust.	Extr.	Rate
0	1211	0.400	0.000000		0	
5	1209	0.410	0.000000		-5043	-1009
10	1204	0.405	0.000000		-4455	-445
15	1175	0.400	0.001000		-1082	-72
20	1158	0.400	0.002000		2095	105
25	1171	0.400	0.001000		4715	189
50	1143	0.395	0.000000		10838	217



Eksp. no: 30

Circom. 0.129 Area 0.0026484

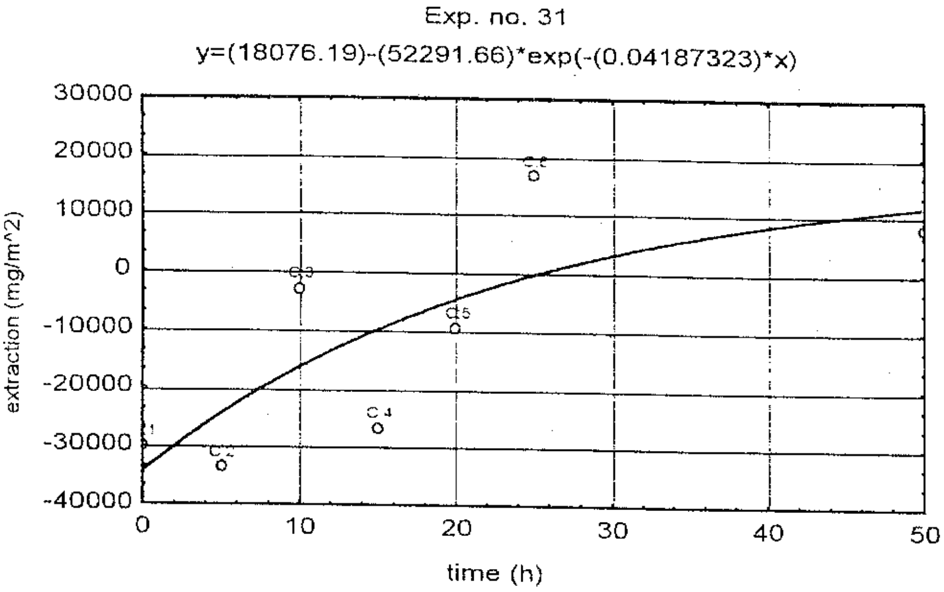
Time	[Ni] feed		Vol.	Adjust.	Extr.	Rate
0	1203	0.400	0.000000		0	
5	1177	0.415	0.001000		-5010	-1002
10	1156	0.420	0.002000		-2349	-235
15	1169	0.420	0.001000		959	64
20	1107	0.415	0.004000		14450	722
25	1155	0.410	0.002000		22122	885
50	1165	0.405	0.000000		28144	563



Eksp. no: 31

Circom. 0.117 Area 0.0021786

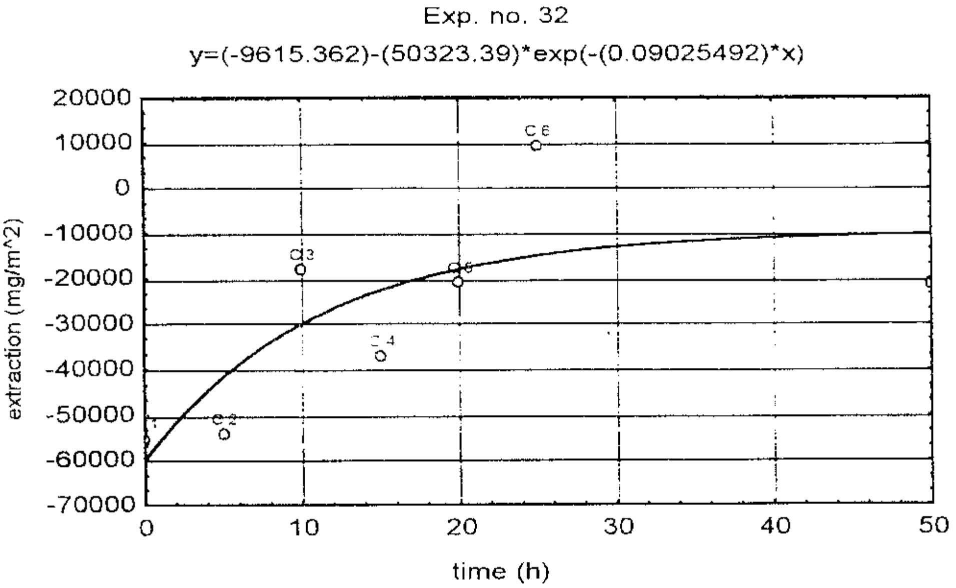
Time	[Ni] feed		Vol.	Adjust.	Extr.	Rate	
0	1320	0.405	0.000000		0		
5	1466	0.410	0.000000		-33534		-6707
10	1285	0.410	0.000000		-2837	-284	
15	1431	0.400	0.000000		-26693		-1780
20	1336	0.395	0.000000		-9469	-473	
25	1190	0.390	0.000000		16666	667	
50	1293	0.385	0.000000		7957	159	



Eksp. no: 32

Circom. 0.108 Area 0.0018563

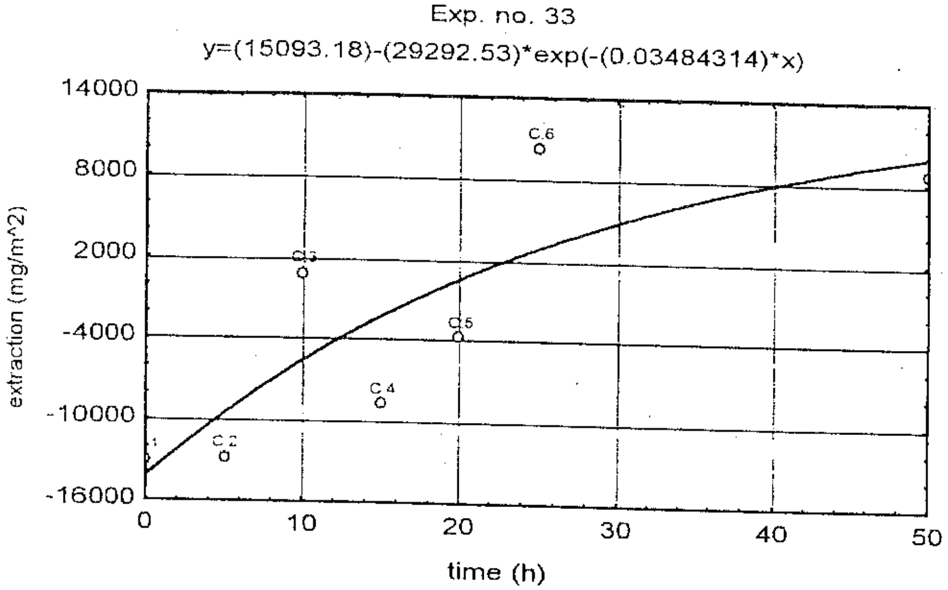
Time	[Ni] feed		Vol.	Adjust.	Extr.	Rate
0	1237	0.400	0.000000		0	
5	1403	0.420	0.000000		-54216	-10843
10	1226	0.420	0.000000		-17949	-1795
15	1328	0.410	0.000000		-37174	-2478
20	1269	0.400	0.000000		-20885	-1044
25	1113	0.400	0.000000		9311	372
50	1241	0.400	0.000000		-21267	-425



Eksp. no: 33

Circom. 0.112 Area 0.0019964

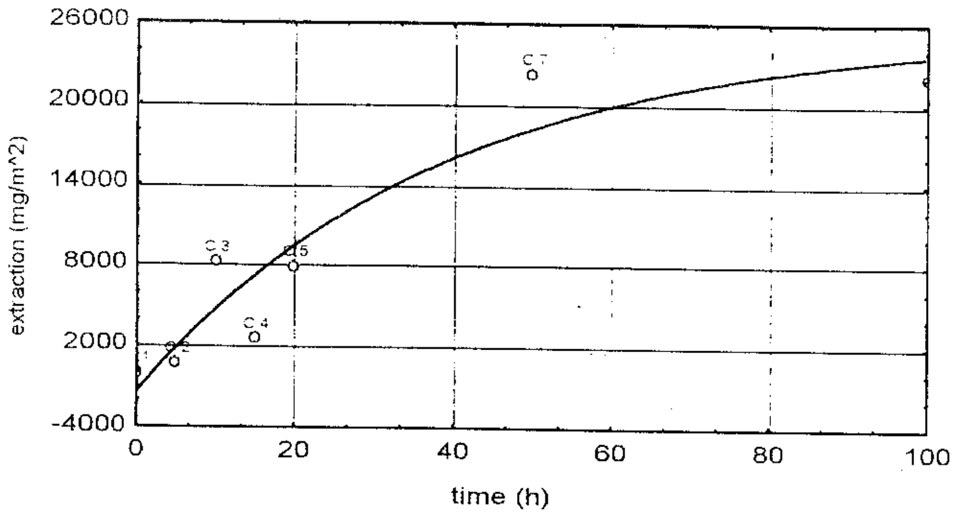
Time	[Ni] feed		Vol.	Adjust.	Extr.	Rate	
0	1049	0.400	0.000000		0		
5	1086	0.405	0.000000		-12760		-2552
10	1018	0.400	0.000000		864	86	
15	1080	0.390	0.000000		-8698	-580	
20	1041	0.390	0.000000		-3784	-189	
25	968	0.385	0.000000		10293	412	
50	927	0.400	0.000000		8811	176	



Eksp. no: 34

Circom. 0.114 Area 0.0020683

Time	[Ni] feed		Vol.	Adjust.	Extr.	Rate
0	1064	0.400	0.000000		0	
5	1047	0.400	0.000000		716	143
10	995	0.400	0.000000		8241	824
15	1038	0.390	0.000000		2538	169
20	959	0.405	0.001000		7970	399
25	805	0.400	0.000000		42587	1703
50	900	0.400	0.000000		22269	445



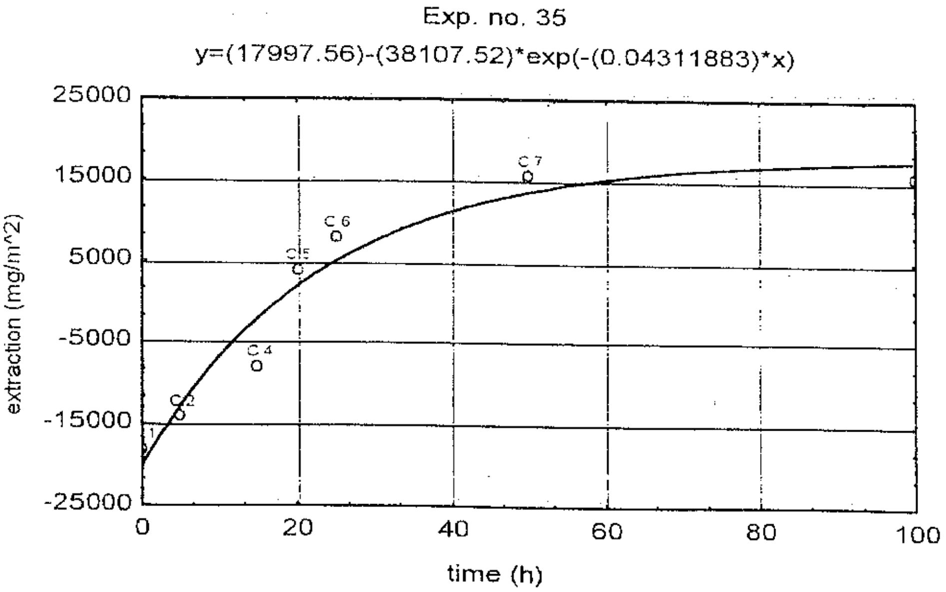
Exp. no. 34

y=(25697.38)-(27099.15)*exp(-(0.02566688)*x)

Eksp. no: 35

Circom. 0.109 Area 0.0018909

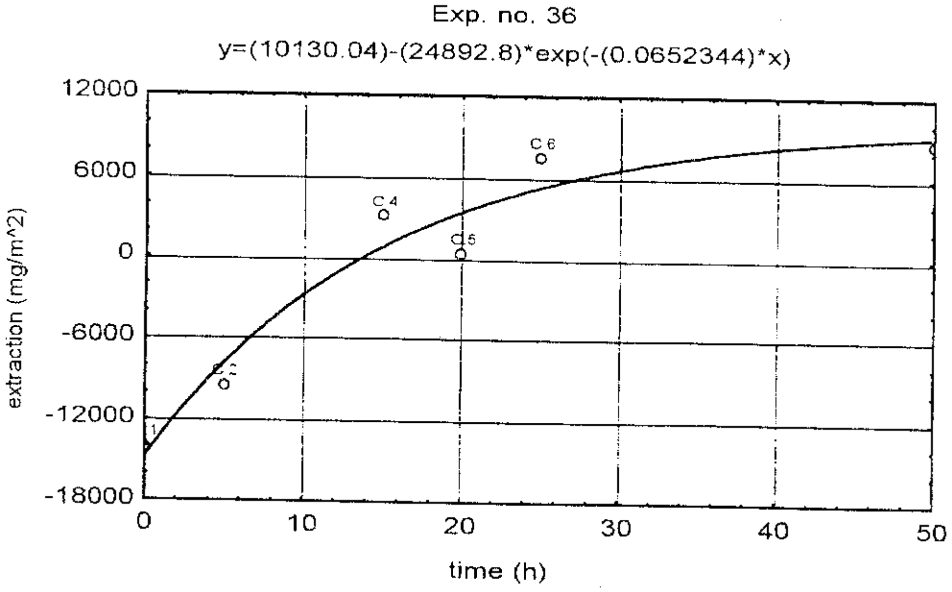
Time	[Ni] feed		Vol.	Adjust.	Extr.	Rate	
0	1044	0.400	0.000000		0		
5	1084	0.405	0.000000		-14088		-2818
10	951	0.400	0.002000		14046	1405	
15	1093	0.400	0.000000		-7930	-529	
20	1049	0.390	0.000000		4035	202	
25	1043	0.380	0.000000		8015	321	
50	942	0.400	0.000000		15590	312	



Eksp. no: 36

Circom. 0.109 Area 0.0018909

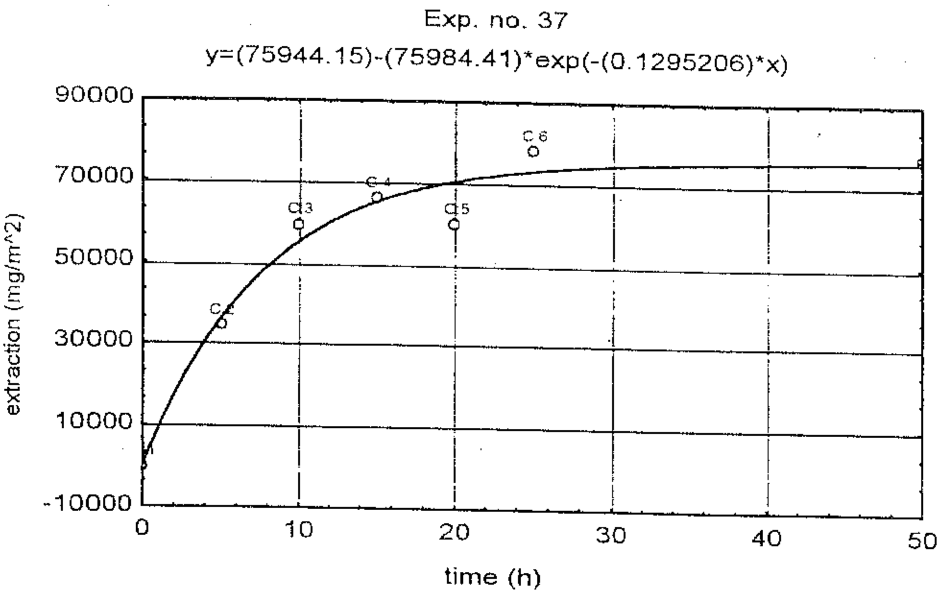
Time	[Ni] feed		Vol.	Adjust.	Extr.	Rate
0	1057	0.405	0.000000		0	
5	1075	0.410	0.000000		-9493	-1899
10	972	0.410	0.001000		9998	1000
15	1042	0.400	0.000000		3049	203
20	1042	0.400	0.000000		294	15
25	995	0.400	0.000000		7480	299
50	977	0.400	0.000000		8657	173



Eksp. no: 37

Circom. 0.099 Area 0.0015598

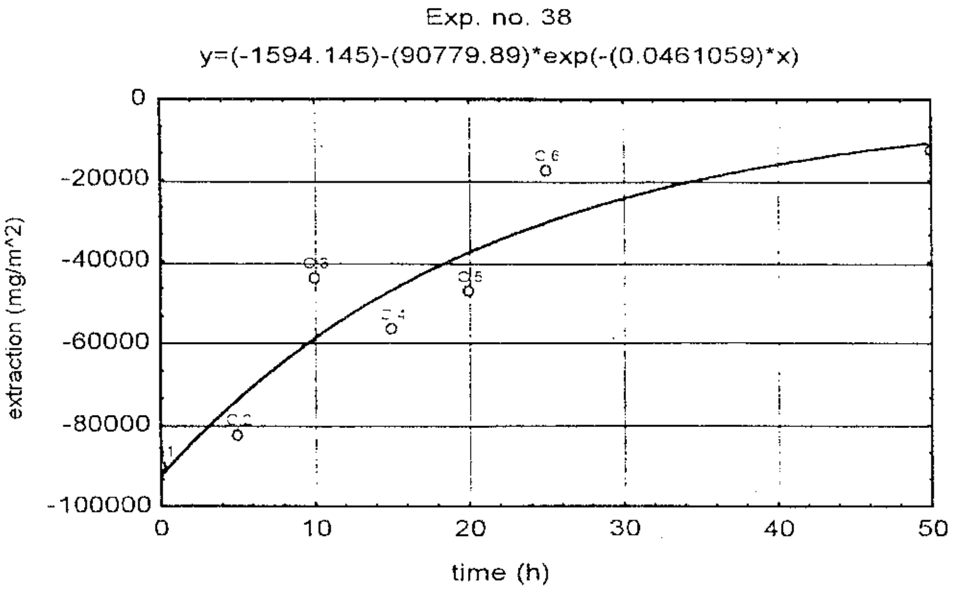
Time	[Ni] feed		Vol.	Adjust.	Extr.	Rate
0	1145	0.405	0.000000		0	
5	1010	0.400	0.000000		34618	6924
10	912	0.395	0.003000		59434	5943
15	962	0.390	0.001000		66165	4411
20	1000	0.390	0.000000		59992	3000
25	938	0.380	0.000000		78301	3132
50	885	0.400	0.000000		76859	1537



Eksp. no: 38

Circom. 0.096 Area 0.0014667

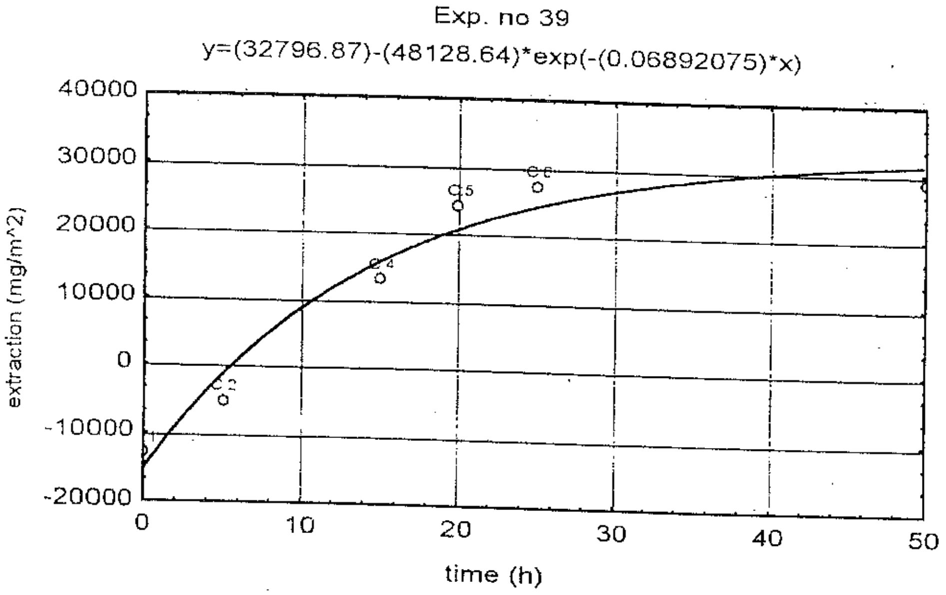
Time	[Ni] feed		Vol.	Adjust.	Extr.	Rate	
0	1033	0.405	0.000000		0		
5	1271	0.420	0.000000		-82235		-16447
10	1084	0.435	0.000000		-44107		-4411
15	1127	0.430	0.000000		-56713		-3781
20	1082	0.430	0.000000		-47363		-2368
25	991	0.420	0.000000		-17617		-705
50	973	0.415	0.000000		-12524		-250



Eksp. no: 39

Circom. 0.106 Area 0.0017882

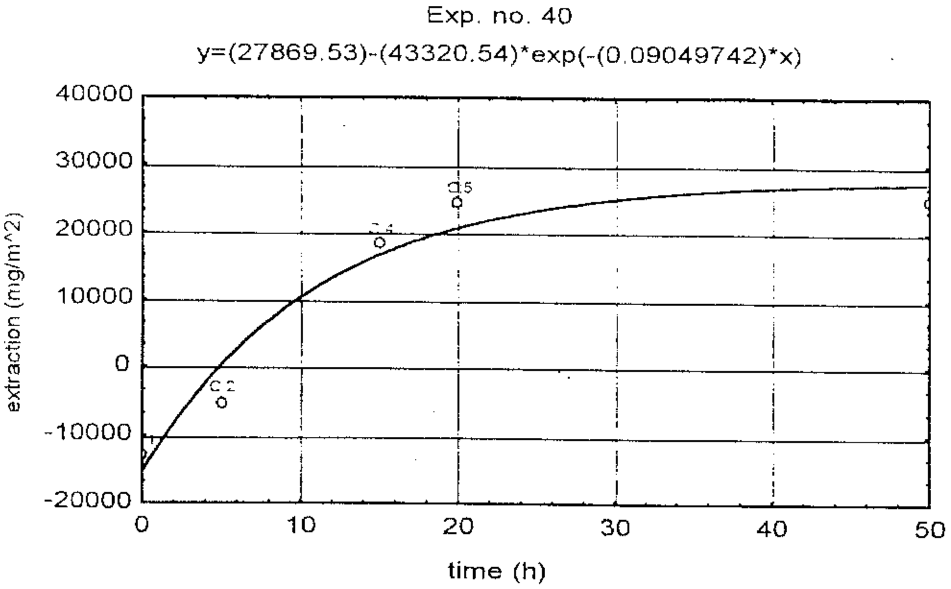
Time	[Ni] feed		Vol.	Adjust.	Extr.	Rate
0	528	0.400	0.000000		0	
5	538	0.405	0.000000		-5217	-1043
10	422	0.400	0.004000		20730	2073
15	551	0.400	0.000000		13063	871
20	494	0.400	0.001000		24272	1214
25	519	0.385	0.000000		27244	1090
50	486	0.400	0.000000		28821	576



Eksp. no: 40

Circom. 0.097 Area 0.0014974

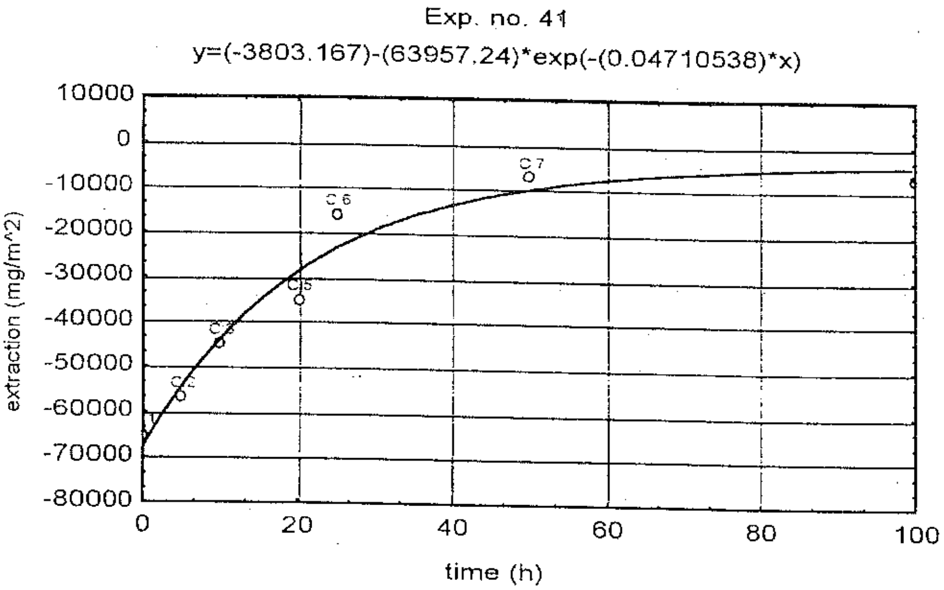
Time	[Ni] feed		Vol.	Adjust.	Extr.	Rate
0	1535	0.400	0.000000		0	
5	1535	0.400	0.000000		-5125	-1025
10	1351	0.400	0.005000		38898	3890
15	1536	0.400	0.000000		18361	1224
20	1532	0.390	0.000000		24531	1227
25	1620	0.390	0.000000		-3503	-140
50	1494	0.400	0.000000		14347	287



Eksp. no: 41

Circom. 0.118 Area 0.0022160

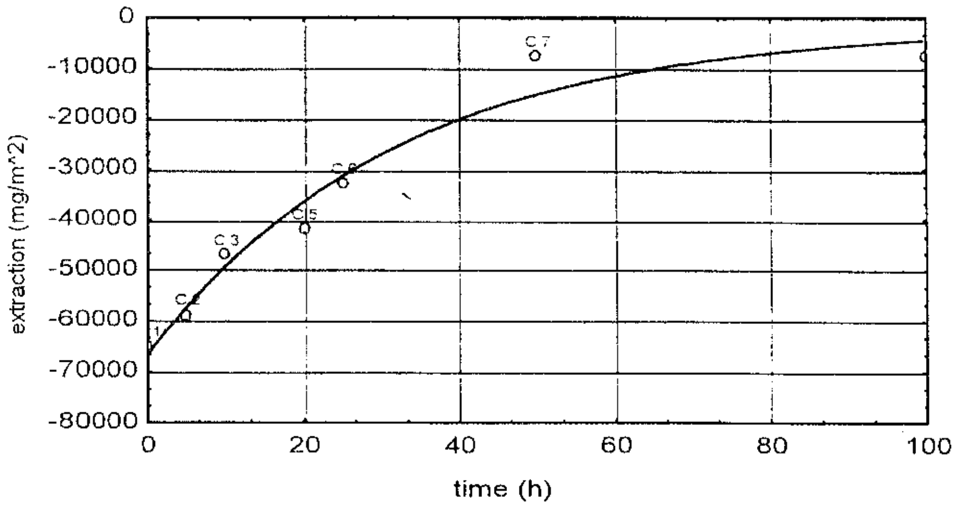
Time	[Ni] feed	Vol.	Adjust.	Extr.	Rate
0	1214	0.400	0.000000	0	
5	1477	0.410	0.000000	-56875	-11375
10	1412	0.405	0.000000	-44996	-4500
15	1169	0.400	0.000000	-1135	-76
20	1360	0.395	0.000000	-35179	-1759
25	1251	0.390	0.000000	-15997	-640
50	1216	0.380	0.000000	-7173	-143



Eksp. no: 42

Circom. 0.124 Area 0.0024471

Time	[Ni] feed	Vol.	Adjust.	Extr.	Rate
0	1070	0.398	0.000000	0	
5	1376	0.410	0.000000	-58701	-11740
10	1305	0.405	0.000000	-46950	-4695
15	1173	0.400	0.000000	-25374	-1692
20	1275	0.395	0.000000	-41838	-2092
25	1219	0.390	0.000000	-32914	-1317
50	1072	0.380	0.000000	-7597	-152



Exp. no. 42

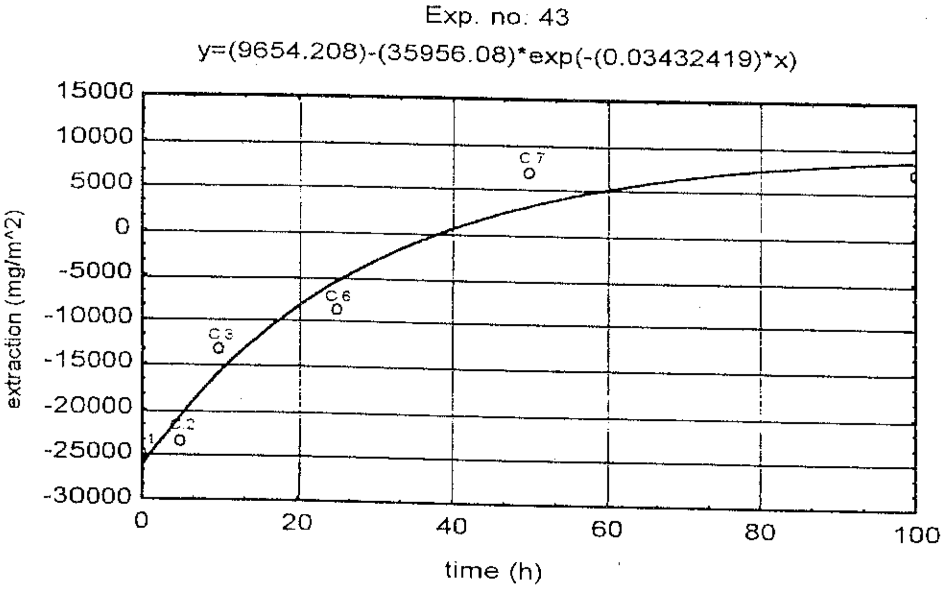
y=(-1589.184)-(65140.14)*exp(-(0.0313277)*x)

Eksp. no: 43

Circom. 0.119 Area 0.0022537

Max Extr: 6880

Time	[Ni] feed	Vol.	Adjust.	Extr.	Rate
0	1043	0.405	0.000000	0	
5	1146	0.410	0.000000	-23365	-4673
10	1104	0.400	0.000000	-13369	-1337
15	1023	0.395	0.000000	827	55
20	1160	0.390	0.000000	-22879	-1144
25	1092	0.380	0.000000	-8841	-354
50	1011	0.370	0.000000	6880	138



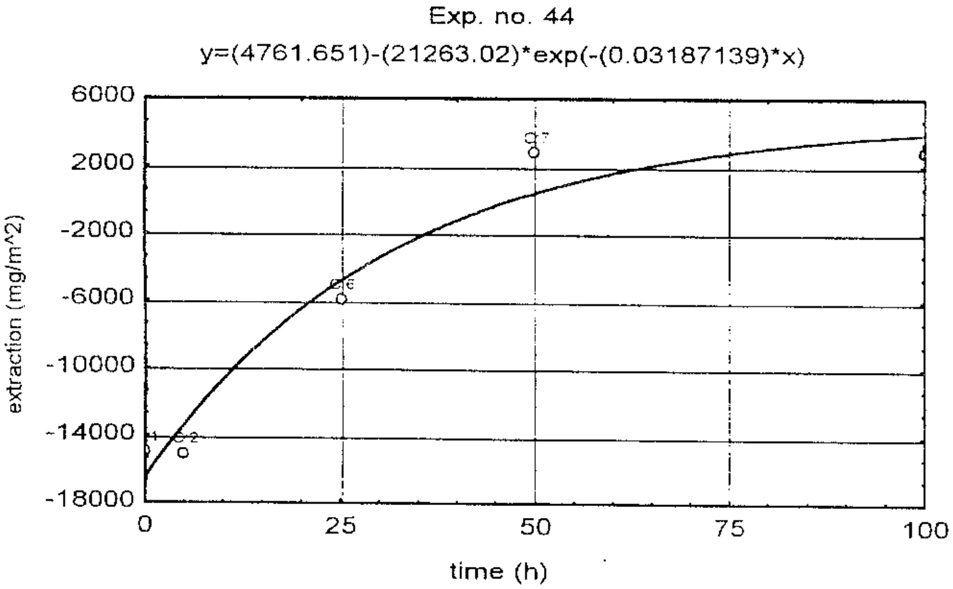
Exp. no: 43

y=(9654.208)-(35956.08)*exp(-(0.03432419)*x)

Eksp. no: 44

Circom. 0.13 Area 0.0026897

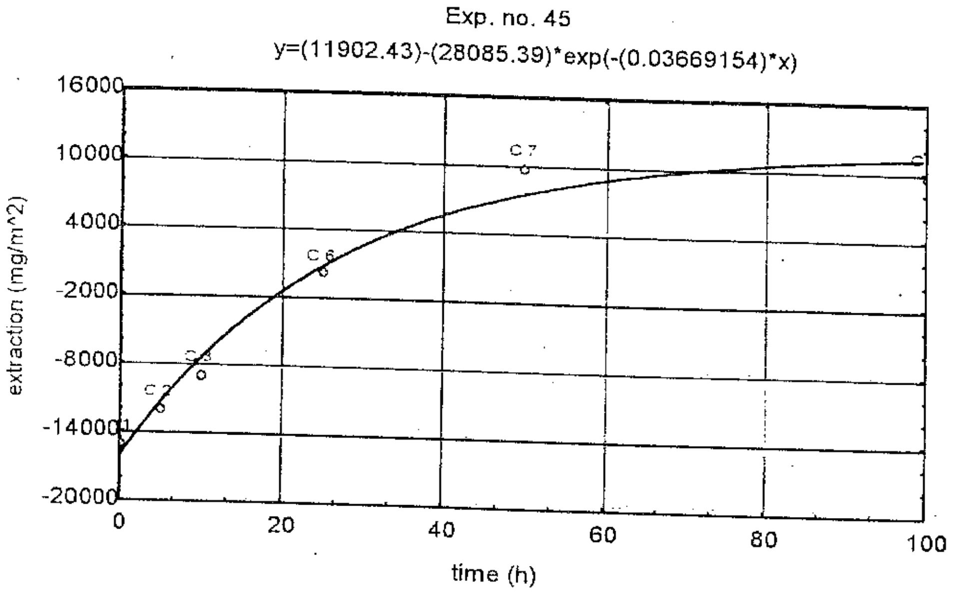
Time	[Ni] feed	Vol.	Adjust.	Extr.	Rate
0	1026	0.410	0.000000	0	
5	1126	0.405	0.000000	-15057	-3011
10	1159	0.400	0.000000	-19965	-1996
15	1015	0.400	0.000000	-705	-47
20	1148	0.395	0.000000	-20236	-1012
25	1063	0.385	0.000000	-5936	-237
50	1001	0.380	0.000000	2824	56



Eksp. no: 45

Circom. 0.117 Area 0.0021786

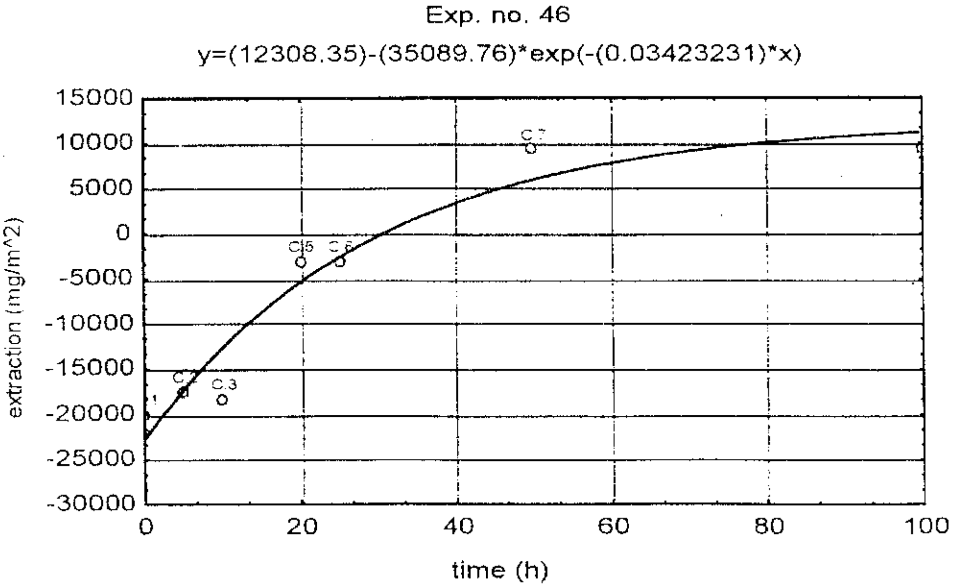
Time	[Ni] feed	Vol.	Adjust.	Extr.	Rate
0	1059	0.400	0.000000	0	
5	1111	0.400	0.000000	-11977	-2395
10	1094	0.395	0.000000	-8895	-890
15	1030	0.390	0.000000	2561	171
20	1154	0.385	0.000000	-19351	-968
25	1042	0.380	0.000000	184	7
50	999	0.370	0.000000	9878	198



Eksp. no: 46

Circom. 0.128 Area 0.0026075

Time	[Ni] feed	Vol.	Adjust.	Extr.	Rate
0	983	0.405	0.000000	0	
5	1089	0.403	0.000000	-17513	-3503
10	1089	0.400	0.000000	-18348	-1835
15	966	0.395	0.001000	284	19
20	1014	0.390	0.000000	-3060	-153
25	1014	0.385	0.000000	-3060	-122
50	942	0.375	0.000000	9238	185



Eksp. no: 22 A

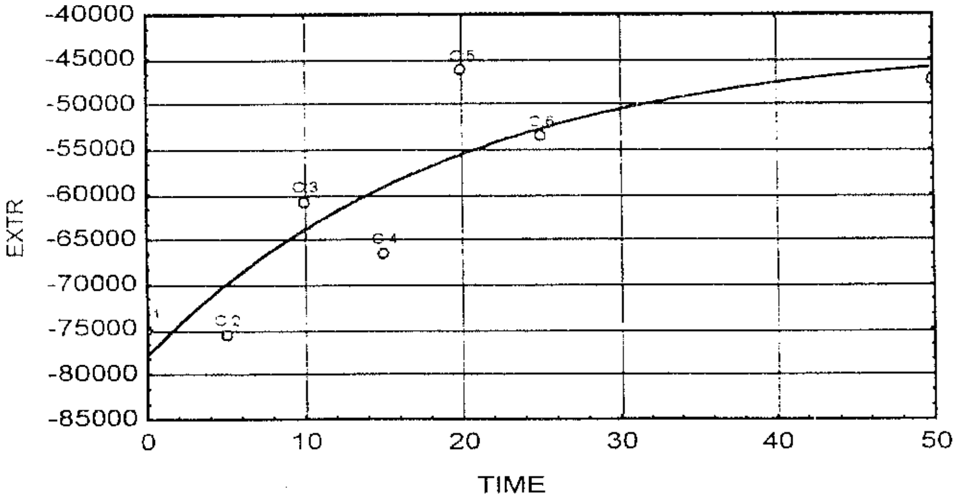
Circom. 0.111 Area 0.0019609

Time	[Ni] feed	Vol.	Adjust.	Extr.	Rate
0	1183	0.400	0.000000	0	
5	1136	0.393	0.002000	10626	2125
10	1191	0.385	0.000000	11765	1176
15	1185	0.380	0.000000	12927	862
20	1201	0.380	0.000000	6805	340
25	1212	0.370	0.000000	7792	312
50	992	0.365	0.000000	48742	975

Eksp. no: 23 A

Circom. 0.129 Area 0.0026484

Time	[Ni] feed	Vol.	Adjust.	Extr.	Rate
0	1070	0.403	0.006000	0	
5	1674	0.410	0.000000	-75696	-15139
10	1577	0.405	0.000000	-60863	-6086
15	1595	0.405	0.000000	-66592	-4439
20	1461	0.400	0.000000	-46355	-2318
25	1491	0.400	0.000000	-53644	-2146
50	1467	0.390	0.000000	-47295	-946



Exp. 23 A

y=(-43301.19)-(34677.49)*exp(-(0.051895)*x)

Eksp. no: 27 A

Circom. 0.123 Area 0.0024078

55134037

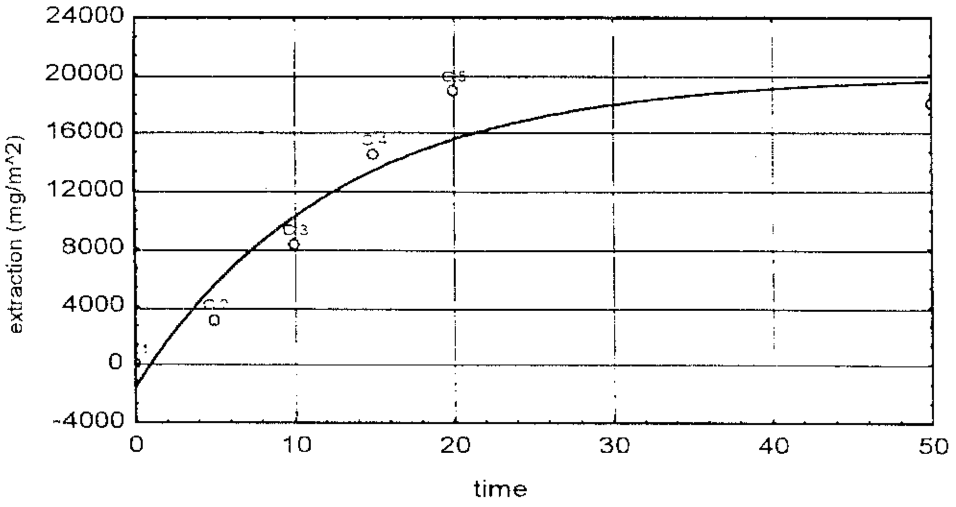
28

Time	[Ni] feed	Vol.	Adjust.	Extr.	Rate
0	705	0.400	0.004000	0	
5	995	0.410	0.000000	-37160	-7432
10	993	0.405	0.000000	-36823	-3682
15	956	0.400	0.000000	-25693	-1713
20	1027	0.400	0.000000	-44457	-2223
25	986	0.390	0.000000	-35683	-1427
50	938	0.383	0.000000	-27229	-545

Eksp. no: 38

Circom. 0.14 Area 0.0031194

Time	[Ni] feed	Vol.	Adjust.	Extr.	Rate
0	893	0.400	0.004000	0	
5	958	0.400	0.001000	3057	611
10	942	0.395	0.002000	8288	829
15	944	0.390	0.002000	14450	963
20	960	0.385	0.000000	18886	944
25	1091	0.380	0.001000	2928	117
50	1084	0.370	0.000000	8713	174



Exp. no. 38 A

y=(19957.74)-(21500.87)*exp(-(0.07925094)*x)

B.2 Accuracy

Exp. no.	b g/m^2	b Theo g/m^2	% falt	Rate g/h.m^2	Rate Theo	% falt
1	27.0283	38.1488	41.1440	3.5481	8.0019	125.5256
2	20.4813	35.3238	72.4686	3.7159	3.9832	7.1916
3	41.3068	32.1922	22.0658	1.3542	5.3699	296.5192
4	12.9981	13.1450	1.1307	2.0901	0.3411	83.6825
5	43.9508	42.2250	3.9267	11.5696	4.9596	57.1330
6	55.4488	46.3319	16.4419	5.4321	4.2986	20.8668
7	11.8325	41.2258	248.4104	0.5223	2.9938	473.2141
8	34.5928	29.1106	15.8479	3.4314	0.1096	96.8048
9	21.3505	36.2870	69.9586	9.4252	13.2101	40.1569
10	25.0023	29.5817	18.3157	8.5916	7.8372	8.7813
11	44.8536	44.2146	1.4246	36.4722	17.0497	53.2530
12	15.5460	21.2871	36.9299	0.7200	5.1452	614.6416
13	73.5430	70.4415	4.2172	6.5248	9.3925	43.9509
14	95.2590	70.6681	25.8148	11.0344	7.6501	30.6702
15	100.6685	83.3266	17.2268	12.7949	12.6630	1.0315
16	35.3671	67.3310	90.3777	4.1324	5.6726	37.2720
17	61.5449	48.2833	21.5479	3.9129	1.7709	54.7428
18	53.1594	57.0158	7.2545	4.3097	2.4866	42.3022
19	13.3485	44.4583	233.0576	0.7898	1.1418	44.5811
20	24.3062	36.9686	52.0956	1.3546	-0.4085	130.1572
21	35.9456	27.6228	23.1538	1.5443	2.3192	50.1789
22	23.9868	43.2873	80.4627	0.9471	7.2045	660.6801
23	25.0577	28.7553	14.7562	1.3004	2.0195	55.3029
24	36.5744	28.1976	22.9036	1.6002	3.0604	91.2502
25	27.5774	24.1503	12.4271	1.4655	1.1808	19.4309
26	33.4066	29.0025	13.1834	1.6805	1.6730	0.4452
27	20.1080	34.2096	70.1297	0.5863	3.4531	488.9419
28	20.8818	22.8396	9.3757	1.2183	1.4973	22.8999
29	19.6299	33.5682	71.0058	0.7439	-1.3384	279.9156
30	45.1061	45.3523	0.5458	1.7101	1.9322	12.9920
31	52.2917	48.5849	7.0885	2.1896	0.4790	78.1242
32	50.3234	44.1469	12.2737	4.5419	2.1262	53.1874
33	29.2925	27.0022	7.8188	1.0206	1.3854	35.7380
34	27.0992	27.0022	0.3578	0.6956	1.3854	99.1806
35	38.1075	27.3844	28.1391	1.6432	3.9385	139.6937
36	24.8928	18.7471	24.6886	1.6239	1.3579	16.3771
37	75.9844	79.2062	4.2400	9.8415	12.9589	31.6754

38	90.7799	70.6890	22.1314	4.1855	8.4771	102.5355
39	48.1286	22.1971	53.8796	3.3171	4.4796	35.0463
40	43.3205	52.3832	20.9200	4.1143	3.6663	10.8890
41	63.9572	47.7377	25.3600	3.0127	1.8108	39.8951
42	65.1401	64.4906	0.9971	2.0407	9.5708	368.9961
43	35.9561	27.9345	22.3093	1.2342	5.9186	379.5614
44	21.2630	12.4158	41.6085	0.6777	-0.4690	169.2033
45	28.0854	27.0022	3.8568	1.0305	1.3854	34.4403
46	35.0898	27.0022	23.0482	1.2012	1.3854	15.3345
		AVG	35.1374		AVG	120.7477

Appendix C

Computer program

C.1 Introduction

A small Pascal program was used to solve the optimum point of the equation. The program uses five loops that vary the variables of the equation until the optimum point is found.

C.1 Program for the solving of the optimum point.

```
Program solve;
uses crt,printer;
var
  a, b, c, d, e, Ha, Hb, Hc, Hd, He, Max, hf : real;
  Ta, Tb, Tc, Td, Te : integer;

Function F(a,b,c,d,e : real): real;
Begin
   F := -1.816*a-1.791*b+6.346*c+3.522*d-3.262*e-0.696*a*a
       +8.476*b*b+1.819*c*c+5.146*d*d-1.207*e*e-4.056*a*b+1.733*a*c
       -0.97*a*d+2.889*a*e+1.239*b*c+3.471*b*d+0.533*b*e
       +7.520*c*d-6.184*c*e-5.568*d*e+27.002;

end;

BEgin
clrscr;
```

```
Max := 0;
ha := -10; hb := -10; hc := -10; hd := -10; he := -10;
for ta := 2 to 10 do
  BEgin
    For tb := 2 to 10 do
     Begin
      For Tc := 2 to 10 do
       BEgin
        For td := 2 to 10 do
         Begin
         For te := 2 to 10 do
         BEgin
            A := (ta-6)/2; B := (tb - 6)/2;
            C := (tc-6)/2; D := (td-6)/2;
            E := (te-6)/2;
            hf := f(a,b,c,d,e);

            if (hf) > Max then
              BEgin
                ha := A;  hb := B;
                hc := C;  hd := D;
                he := E;
                Max := hf;
              end;
         end;
         end;
       end;
     End;
 end;
clrscr;
writeln (ha :5:4,';  ',hb :5:4,';  ', hc :5:4,';  ',hd :5:4,'; ',he:5:4,' '
      ,max:5:2);
readln;
end.
```

Appendix D

The application of SLM and DSP for demineralization of Calcium and Nickel

D.1 Introduction

Experimental results obtained and reported previously by Erlank (1994) are summarised and illustrated to demonstrate the demineralization effect of both SLM and CME on Calcium as well as the effects of DSP on Nickel and Calcium.

D.2 DSP from nickel sulphate solution

A series of experiments were launched to investigate to what extent this success would be repeated in precipitating nickel from solution by the method of DSP.

From figure D.1 it is evident that the difference in the amount of nickel precipitated is very small for the different pH conditions. The curves indicate that the decrease in nickel concentrations was similar in both cases. A precipitation of up to 90% was reached with the addition of 650 g/l ammonium sulphate to the bulk nickel solution. Also, the curves reach a mutual point indicating that a change in pH has a negligible effect.

X-ray diffraction was used to analyse the precipitated salt. It was found that the compound formed was not crystalline but colloidal. It is, however, mentioned in literature that nickel reacts with ammonium sulphate to form a hydrated nickel salt, $NiSO_4(NH_4)_2.3H2O$. This salt can be heated to 110 °C to remove the water and can finally be converted to $NiSO_4$ by heating to 500°C.

This phenomenon could therefore be used to recover nickel from concentrated nickel effluents.

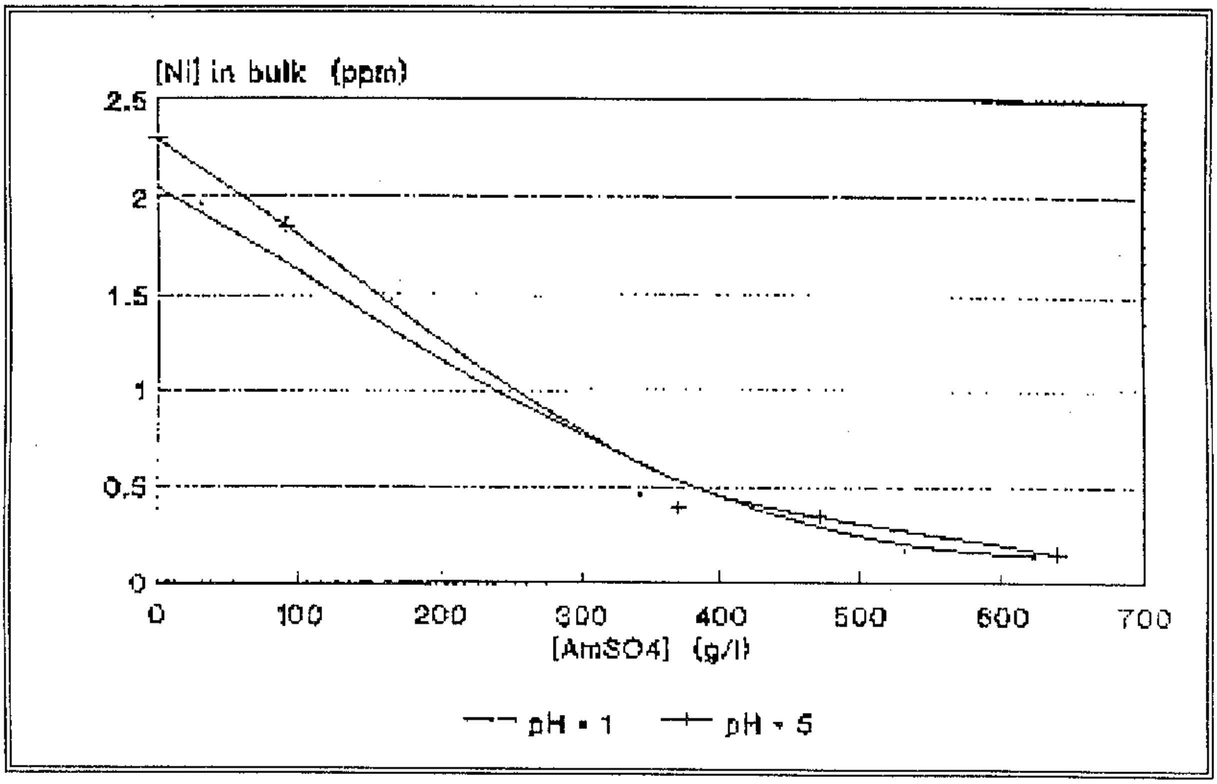


Fig. D.1: DSP of nickel from a sulphate solution with the addition of $(NH_4)_2SO_4$ at 23°C

D.3 SLM extraction of Calcium

Experiments were done with D2EHPA, 18-crown-6-ether, LIX, nTOPO and an acid base combination of D2EHPA:TOA. Due to the exploratory nature of this investigation, no attempts were made to maintain the pH values or the concentrations on respectively the feed and strip side (pH), as well as on the feed side for calcium. This decision was made to establish the initial extraction rates for subsequent kinetic studies, as well as to demonstrate the technical feasibility of this concept of demineralisation. In almost all the cases it was not necessary to reset the pH value of the calcium feed solution, since the value dropped less than one unit.

A large number of experiments were performed of which only selected graphical results are reported to illustrate the response (Fig. D.2).

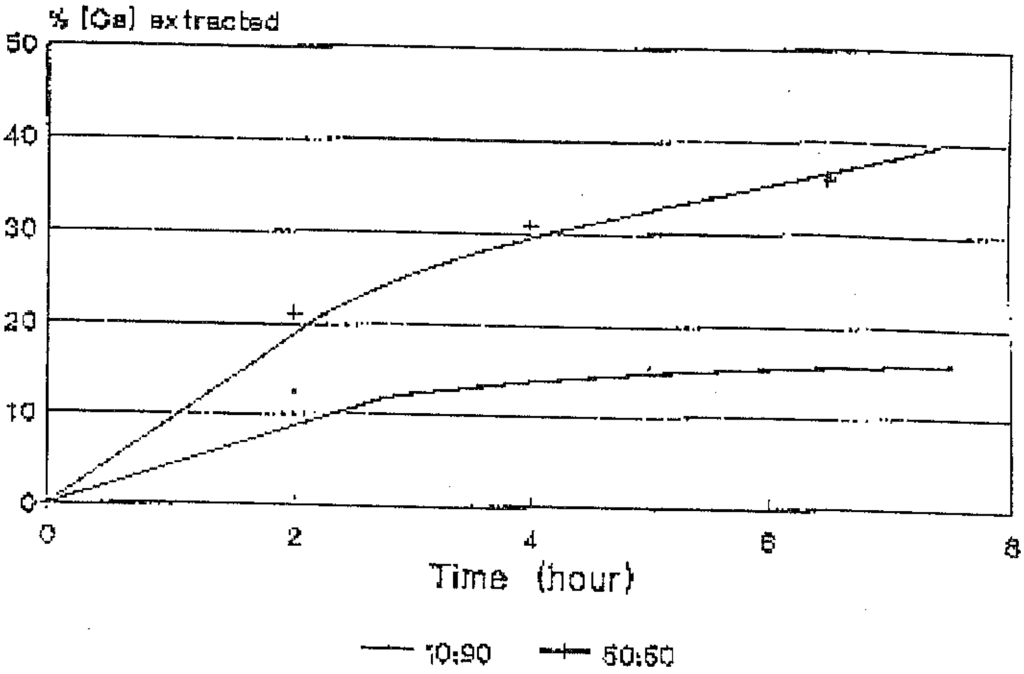


Fig. D.2: Extraction of $CaCO_3$ with 0.0125M 18-crown-ether in 10% and 50% ratio with 0.125M D2EHPA at feed pH = 4.

D.4 Double salt precipitation of calcium

In the following series of experiments it was the aim to precipitate calcium from a solution by the addition of ammonium sulphate. Firstly it was investigated what the influence of the molar ratio [Ca2+]:[NH4+] was on the percentage calcium precipitated. The method used was to add a certain volume of ammonium sulphate solution to a calcium solution in order to create the required experimental conditions.

Using the results of these preliminary experiments, further work was done using a slightly different method. A calcium solution was agitated while continuously adding ammonium sulphate. A calcium salt precipitated and the decrease in calcium concentration of the bulk solution was analysed.

D.4.1 Precipitation from calcium carbonate solutions.

Initially, an experiment was done to see what influence the ratio between the calcium in the feed, and the ammonium added, has on the amount of calcium precipitated from solution. Figure D.3 indicates that the relation is not linear, contrary to prediction. As the ratio [Ca]:[NH4+] became larger (calcium in excess), the amount of calcium precipitated decreased. This is because, as the ratio becomes larger, the relatively decreasing amount of ammonium is not sufficient to react with the relatively increasing amount of calcium. Maximum precipitation seems to occur for the ratios [Ca]:[NH4+] being less than one. Subsequent experiments were done concentrating on this region and investigating the influence of differences in:

1. initial calcium carbonate concentration, and
2. pH-variation.

Results are given in Figure D.3

For a given set of calcium-ammonium molar ratios, 10 g/l and 20 g/l CaCO3 solutions were tested. The separate curves in figure D.3 show a similar trend but it does seem that, at smaller molar ratios (ammonium being in excess), the lower feed concentration will result in a higher precipitation percentage compared to the higher concentration.

The results for the different pH conditions are within close range of each other. Again the trend of decreasing precipitation with increasing molar ratio can be noticed. Thus, a variation in solution pH has minimal effects on the precipitation of calcium from carbonate solutions. The addition of extra chemicals, with the intention to change the pH is therefore unnecessary. This is advantageous in terms of economics, time and effort.

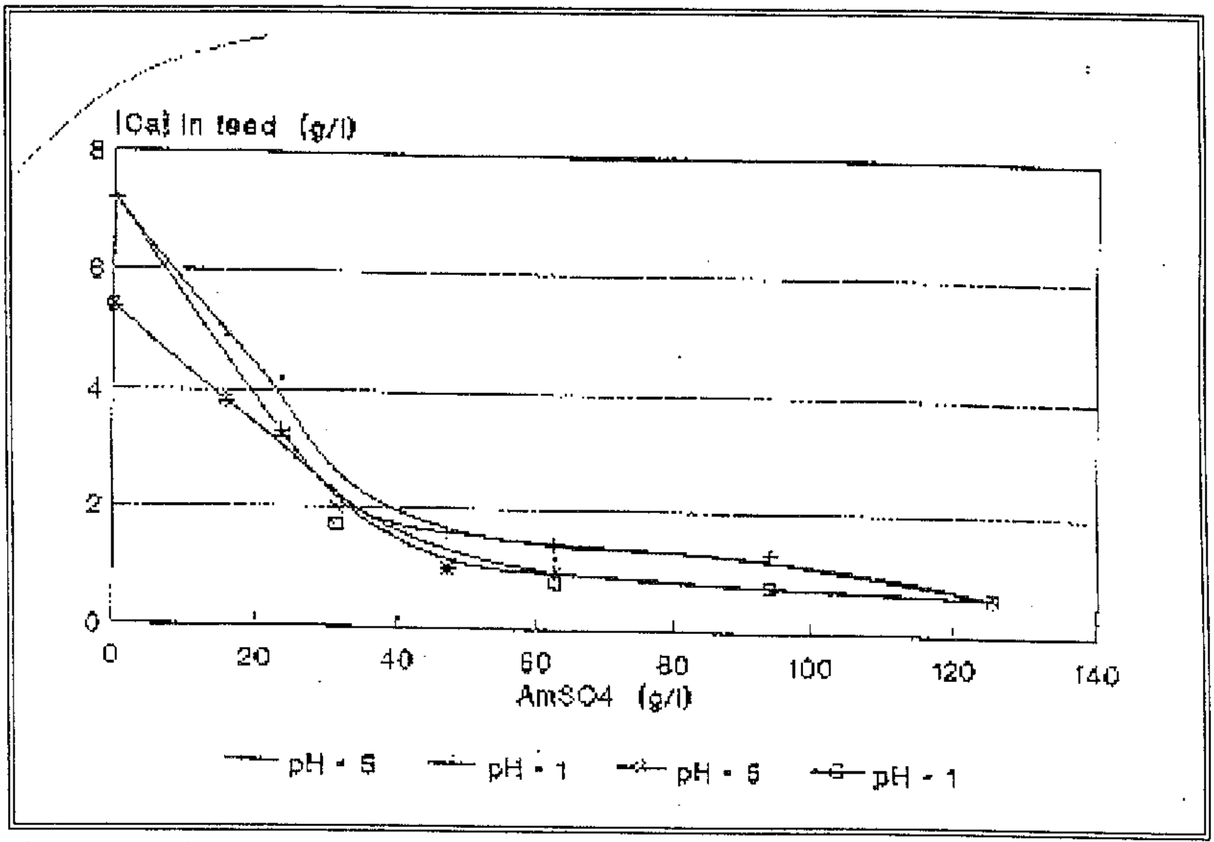


Fig. D.3: Precipitation of $CaCO_3$-solutions at different pH values with the addition of ammonium sulphate.

Appendix E

Herwinning van sink uit 'n uitskotstroom

E.1 Inleiding

Die resultate verkry deur Steyn & Janse van Rensburg (1994) word opgesom en illustreer die herwinning van sink uit 'n uitskotstroom.

E.2 Berekening van die Vloed

Die sink wat deur die sakkies opgeneem is word in die volgende drie tabelle getoon, waar die temperature verander word by 'n konstante pH.

Stropings medium: $H2SO4$ met pH = 0.8, 5 ml
Membraan: 20% D2EHPA, 80% Escaid
Voer: 250 ml, 30 maal verdun.

Tabel E.1: Sink onttrek by pH = 3.2 en verskillende T.

Tyd (min)	Sink (mg) by T = 10 °C	Sink (mg) by T = 30 °C	Sink (mg) by T = 50 °C
0	0.00	0.00	0.00
5	1.75	2.75	3.00
10	3.75	4.75	5.75
15	4.50	6.00	7.25
20	5.00	7.25	9.00
25	5.75	8.50	10.75
30	6.50	9.50	11.25
35	7.50	9.25	11.00
60	9.75	9.25	11.00
90	9.00	9.00	10.75

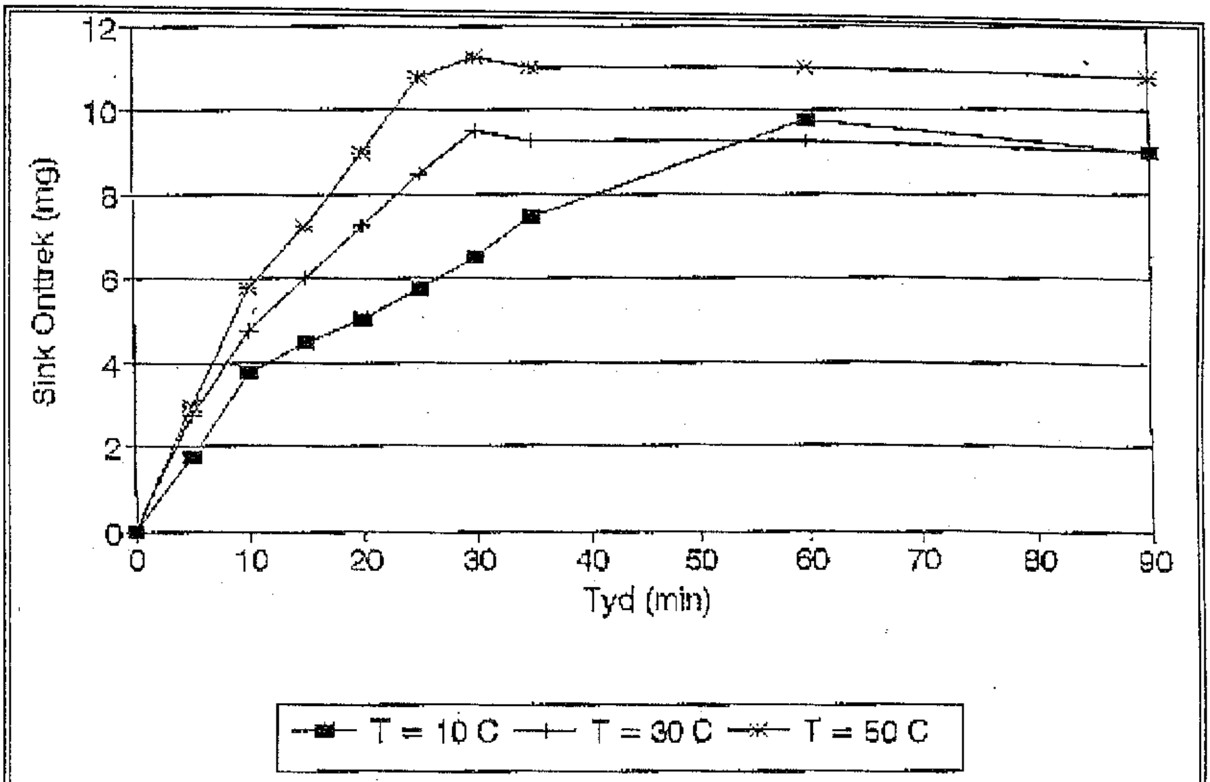
Table E.2: Sink onttrek by pH = 2.0 en verskillende T.

Tyd (min)	Sink (mg) by T = 10 °C	Sink (mg) by T = 30 °C	Sink (mg) by T = 50 °C
0	0.00	0.00	0.00
5	0.75	1.25	1.75
10	1.75	2.50	3.50
15	2.25	3.25	5.00
20	2.75	4.00	6.00
25	3.25	4.50	5.25
30	4.00	4.75	5.50
35	4.50	4.50	5.25
60	6.00	4.25	5.25
90	7.50	4.50	5.75
120	8.25	4.25	5.25
180	9.50	4.50	5.50
240	9.25	4.25	5.75

Tabel E.3: Sink onttrek by pH = 1.5 en verskillende T.

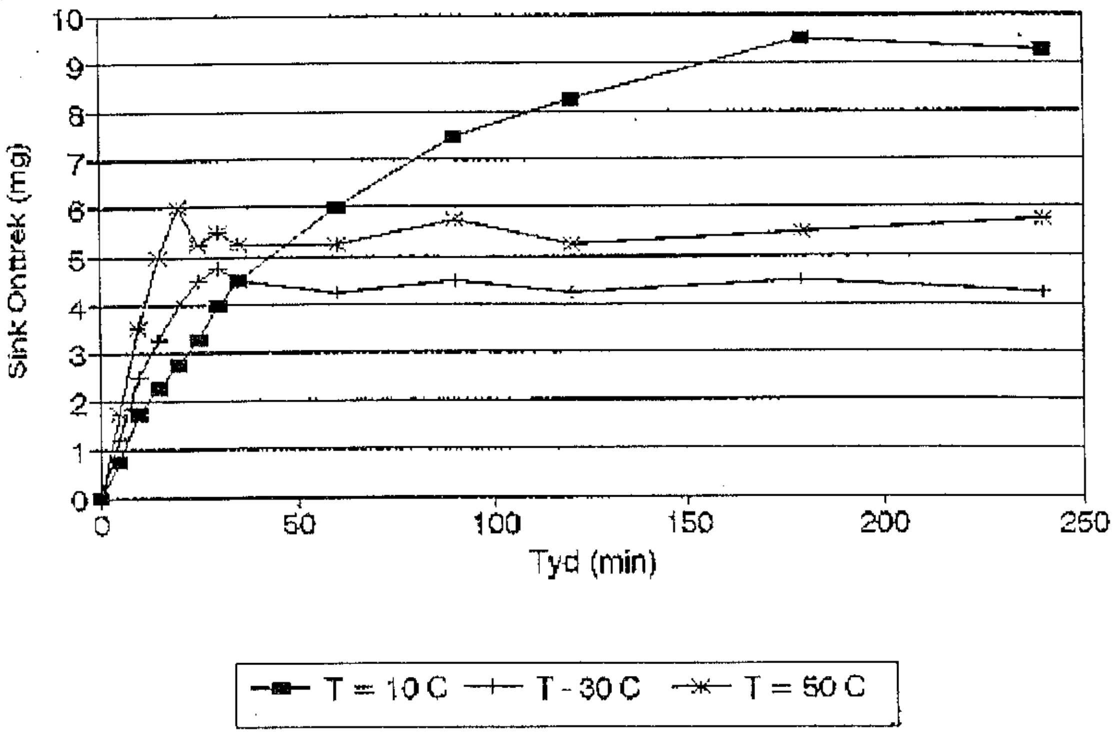
Tyd (min)	Sink (mg) by T = 10 °C	Sink (mg) by T = 30 °C	Sink (mg) by T = 50 °C
0	0.00	0.00	0.00
5	0.25	0.75	1.00
10	0.50	1.50	1.50
15	1.00	2.25	1.75
20	1.25	3.00	2.25
25	1.50	3.25	3.25
30	2.00	3.50	3.75
35	2.25	3.75	3.25
60	3.00	4.50	3.50
90	3.50	4.25	3.25
120	3.75	4.00	3.00
180	4.00	4.25	3.50
240	3.75	4.25	3.25

Uit Figure E.1 tot E.3 kan gesien word dat, by al die temperature, sinkopname gewoonlik bevoordeel word deur 'n hoë pH. In al die gevalle word sink die vinnigste onttrek as die pH hoër is. Dit kan toegeskryf word aan die feit dat die waterstof konsentrasiegradiënt groter is hoe hoër die pH is. Dus sal die sink vinniger die sakkie in beweeg, as gevolg van die waterstof wat vinniger uitbeweeg. Die hoeveelheid sink wat onttrek is, was ook in alle gevalle die meeste by die hoogste pH. By 10°C was die maksimum 9.75 mg, by 30°C was die maksimum 9.50 mg en by 50°C was die maksimum 11.25 mg. Al drie hierdie maksimums was by die hoogste pH van 3.2.



STROPINGS OPLOSSING	MEMBRAAN	EKSTRAKTANT	VOER
H_2SO_4 pH = 0.8	Polipropileen 40% porieus 0.03 μm opening	20% D2EHPA 80% ESCAID	Afvalstroom 30 x Verdun T, pH = var

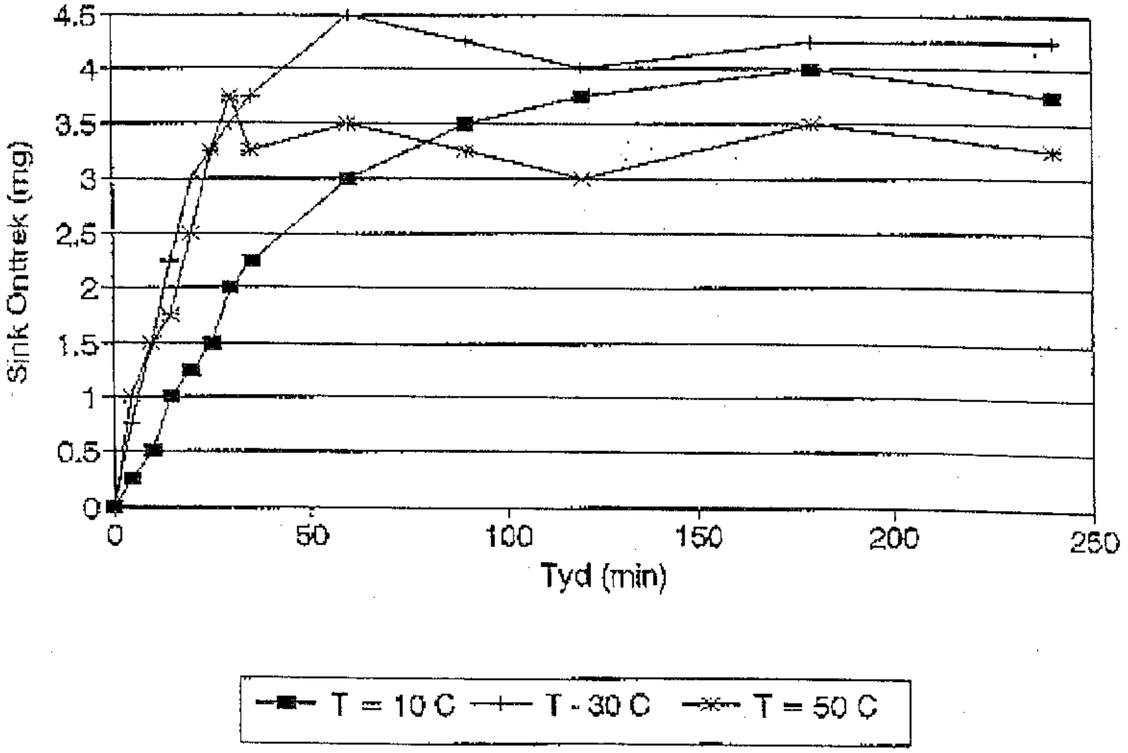
Fig. E.1: Sink onttrek by pH = 3.2.



STROPINGS OPLOSSING	MEMBRAAN	EKSTRAKTANT	VOER
H_2SO_4 pH = 0.8	Polipropileen 40% porieus 0.03 µm Opening	20% D2EHPA 80% ESCAID	Afvalstroom 30 x Verdun T, pH = var

Fig. E.2: Sink onttrek by pH = 2.0.

Die grafieke waar die temperature vergelyk word by konstante pH (Figure E.1 tot E.3), was moeilik om te interpreteer. Een faktor wat konstant bly, is dat die aanvanklike tempo waarteen sink onttrek word, vinniger is by hoër temperature. By al drie grafieke was die aanvanklike tempo van sink onttrekking as volg: 50°C die vinnigste, 30°C die tweede vinnigste en 10°C die stadigste. Die rede hiervoor kan wees dat 'n verhoging in die energie die kinetika van die reaksie versnel. Die feit dat daar by 'n pH van 2.0 en 1.5 meer sink opgeneem is by 10°C as by 50°C is egter moeilik verklaarbaar.



STROPINGS OPLOSSING	MEMBRAAN	EKSTRAKTANT	VOER
H_2SO_4 pH = 0.8	Polipropileen 40% porieus 0.03 µm Opening	20% D2EHPA 80% ESCAID	Afvalstroom 30 x Verdun T, pH = var

Fig. E.3: Sink onttrek by pH = 1.5

'n Verskynsel wat by al die kondisies na vore gekom het, is dat die sink in die sakkie toegeneem het tot 'n maksimum, en toe 'n bietjie sink teruggestort het in die voer voordat dit konstant gebly het. Dit kan moontlik verklaar word as dat die sink so sterk deur die membraan gedryf word, dat die versadigingspunt oorskrei word. Die oortollige sink ruil dan met die waterstof in die voer om die ewewig te herstel.

E.3. Reaksieorde en reaksiekonstante

Die inligting wat verkry is, word in die volgende drie tabelle aangetoon (E4 - E6). Let op dat die term $\ln(M_{Zn}/M_{ZnO})$ in die tabelle met die simbool D voorgestel word.

Tabel E.4: Toets vir eerste orde reaksie by 10°C.

Tyd (s)	D by pH = 3.2	D by pH = 2.0	D by pH = 1.5
0	0.00	0.00	0.00
600	-0.16	-0.07	-0.02
1200	-0.22	-0.12	-0.05
1800	-0.30	-0.17	-0.08
3600	-0.49	-0.27	-0.12

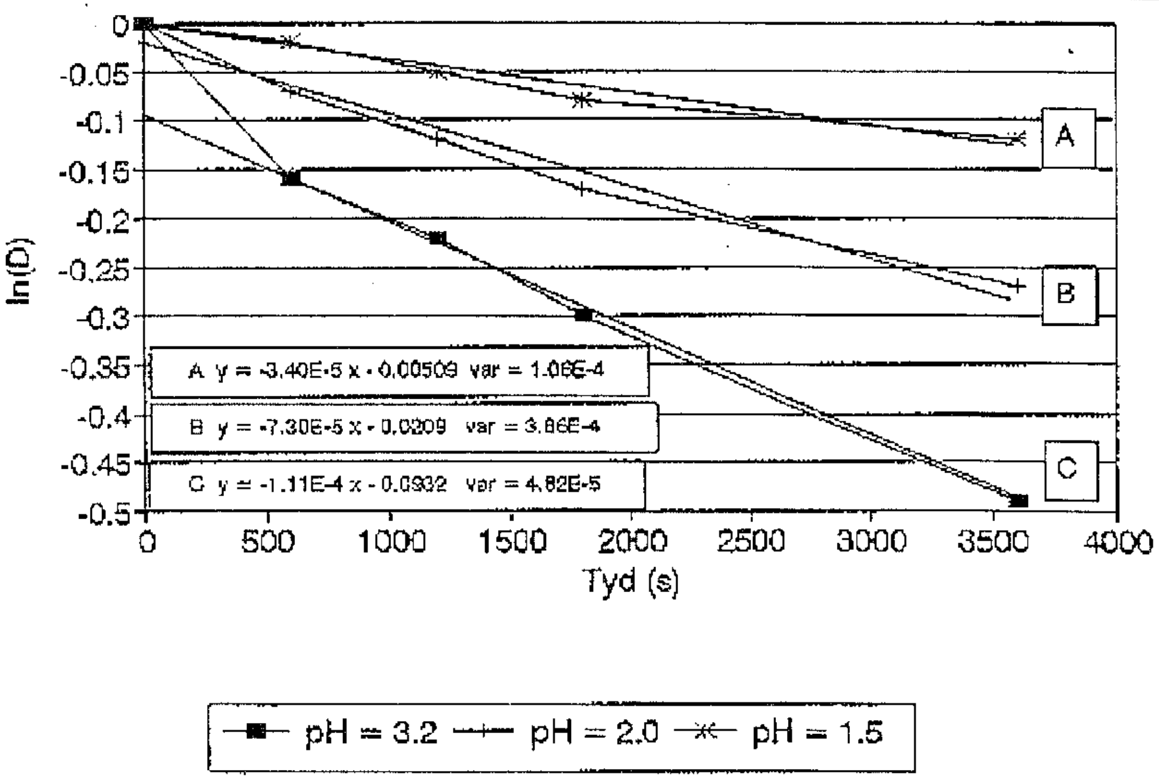
Tabel E.5: Toets vir eerste orde reaksie by 30°C.

Tyd (s)	D by pH = 3.2	D by pH = 2.0	D by pH = 1.5
0	0.00	0.00	0.00
300	-0.12	-0.05	-0.03
600	-0.21	-0.11	-0.06
900	-0.27	-0.14	-0.09
1200	-0.34	-0.17	-0.12

Tabel E.6: Toets vir eerste orde reaksie by 50°C.

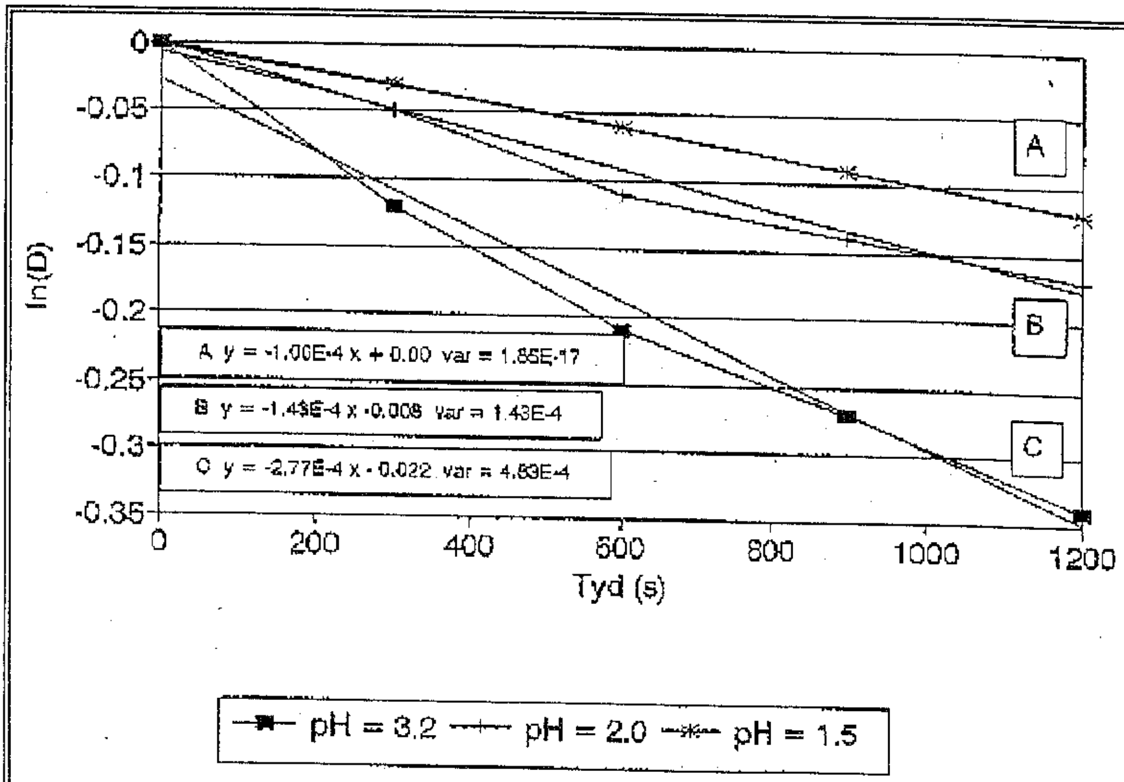
Tyd (s)	D by pH = 3.2	D by pH = 2.0	D by pH = 1.5
0	0.00	0.00	0.00
300	-0.13	-0.07	-0.04
600	-0.26	-0.15	-0.06
900	-0.34	-0.22	-0.07
1200	-0.45	-0.27	-0.11

Die inhoud van die vorige drie tabelle (E4 - E6) is grafies voorgestel in Figure E.4 tot E.6. Telkens is 'n reguit lyn deur die datapunte gepas. Hierdie reguit lyne is met A, B, en C genommer. Die vergelyking van die reguit lyne, met die variansie en maksimum afwyking van elke lyn word onder aan die grafiek geplaas en ook genommer met die toepaslike A, B of C.



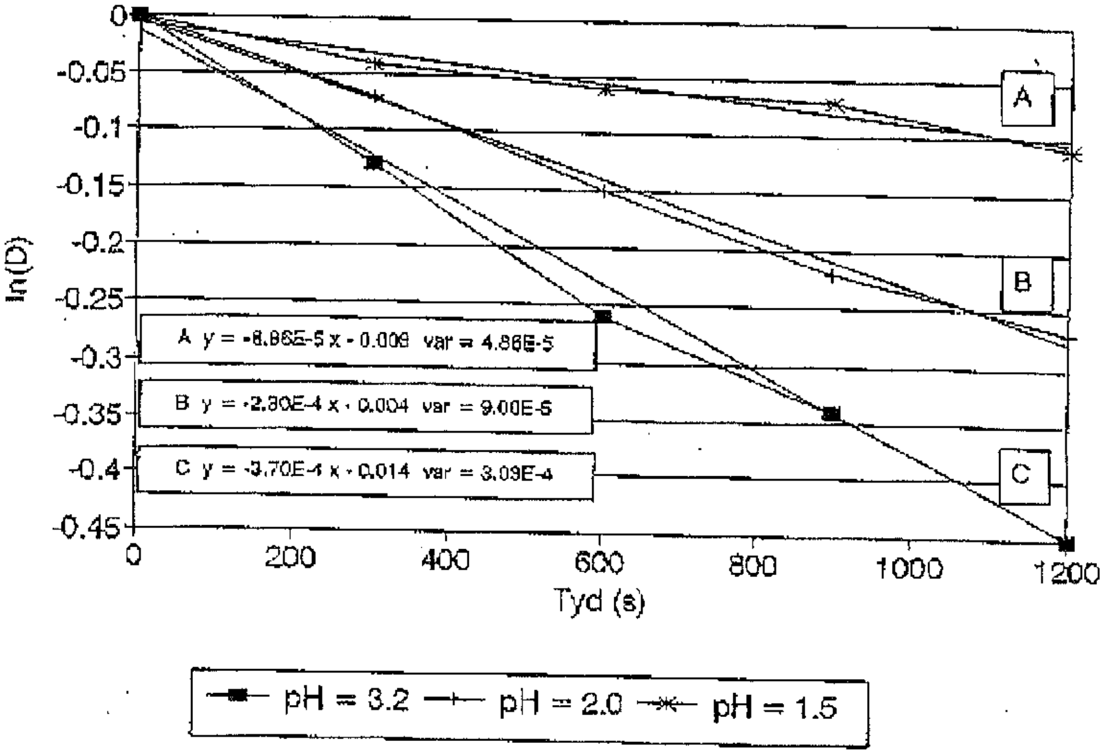
STROPINGS OPLOSSING	MEMBRAAN	EKSTRAKTANT	VOER
H_2SO_4 pH = 0.8	Polipropileen 40% porieus 0.03 μm Opening	20% D2EHPA 80% ESCAID	Afvalstroom 30 x Verdun T, pH = var

Fig. E.4: Orde bepaling by T=10°C.



STROPINGS OPLOSSING	MEMBRAAN	EKSTRAKTANT	VOER
H_2SO_4 pH = 0.8	Polipropileen 40% porieus 0.03 µm Opening	20% D2EHPA 80% ESCAID	Afvalstroom 30 x Verdun T, pH = var

Fig. E.5: Orde bepaling by T = 30°C.



STROPINGS OPLOSSING	MEMBRAAN	EKSTRAKTANT	VOER
H_2SO_4 pH = 0.8	Polipropileen 40% porieus 0.03 µm Opening	20% D2EHPA 80% ESCAID	Afvalstroom 30 x Verdun T, pH = var

Fig. E.6: Orde bepaling by T = 50°C.

Dit was moontlik om reguit lyne deur al die datapunte te pas. As daar na die lae waardes van die variansies en maksimum afwyking gekyk word, lyk dit asof dit 'n baie goeie passing was. Slegs op Figuur E.4 by die pH = 3.2 was daar in probleem. Die laaste deel van die datapunte lê op 'n goeie reguit lyn, maar die eerste kort deel is heeltemal van die lyn af. 'n Lyn is toe deur die laaste vier punte gepas. Dit is onduidelik waarom slegs hierdie kurwe 'n afwyking toon.

Tabel E.7: Reaksiekonstantes (S^{-1}) by verskillende T en pH.

	pH = 3.2	pH = 2.0	pH = 1.5
T = 10 °C	1.11E-4	7.30E-5	3.40E-5
T = 30 °C	2.77E-4	1.43E-4	1.00E-4
T = 50 °C	3.70E-4	2.30E-4	8.88E-5

Die hellings van die reguit lyne is die negatief van die reaksiekonstante. Vanuit die vergelykings onder aan elke grafiek kon die helling en dus die reaksiekonstante gekry word. Dit lyk dus asof die reaksie eerste orde is. Tabel E.7 gee die waardes van die reaksiekonstante (k) in s^{-1}.

Dit lyk dus asof die reaksiekonstante toeneem soos die temperatuur verhoog word. Ook 'n pH verhoging het 'n reaksiekonstante verhoging tot gevolg. Dit klop met wat voorheen voorgestel is, dat 'n hoër pH en temperatuur vinniger onttrekking tot gevolg het. Die reaksie is dus vinniger en die reaksiekonstante moet dus hoër wees.

E.4. Berekening van termodinamiese veranderlikes

D monsterberekeninge is gedoen vir In(k) en l/T, wat gebruik is om E_a te bereken. Die volgende drie tabelle (E8 - E10) stel hierdie data voor vir die drie verskillende PH's:

Tabel E.8: ln(k) en 1/T vir pH = 3.2.

T (K)	ln(k)	1/T (K^{-1})
283	-9.106	3.53E-3
303	-8.191	3.30E-3
323	-7.902	3.10E-3

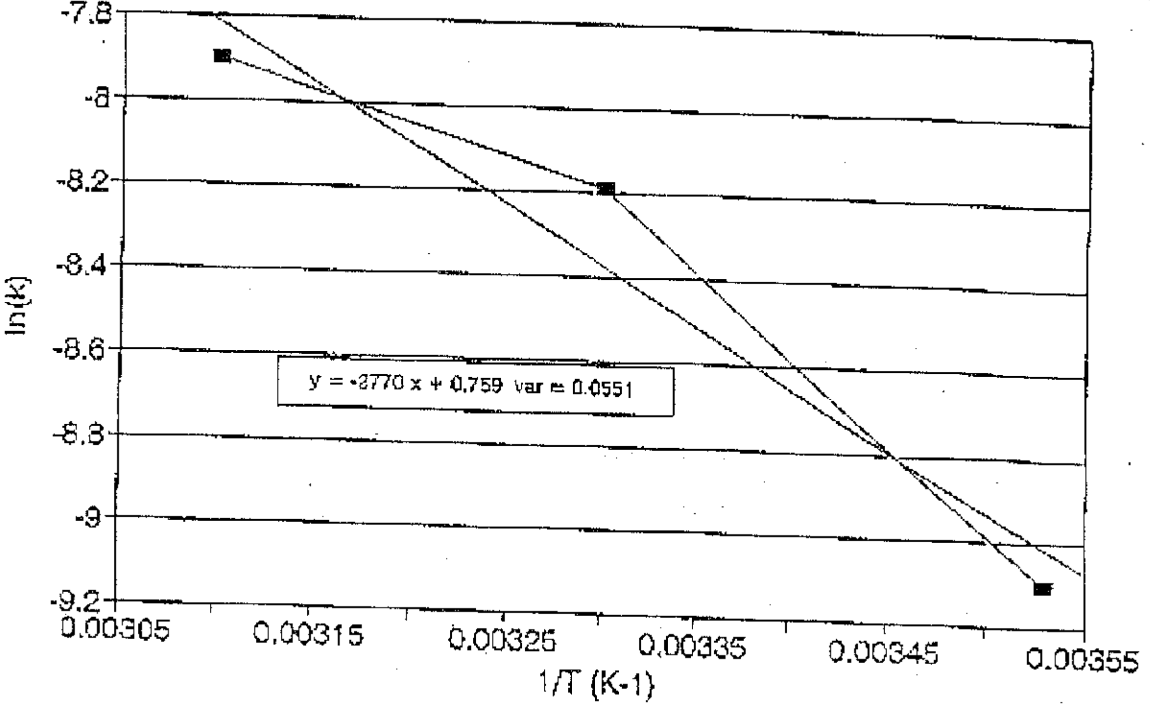
Tabel E.9: ln(k) en 1/T vir pH = 2.0.

T (K)	ln(k)	1/T (K^{-1})
283	-9.525	3.53E-3
303	-8.853	3.30E-3
323	-8.377	3.10E-3

Tabel E.10: ln(k) en 1/T vir pH = 1.5.

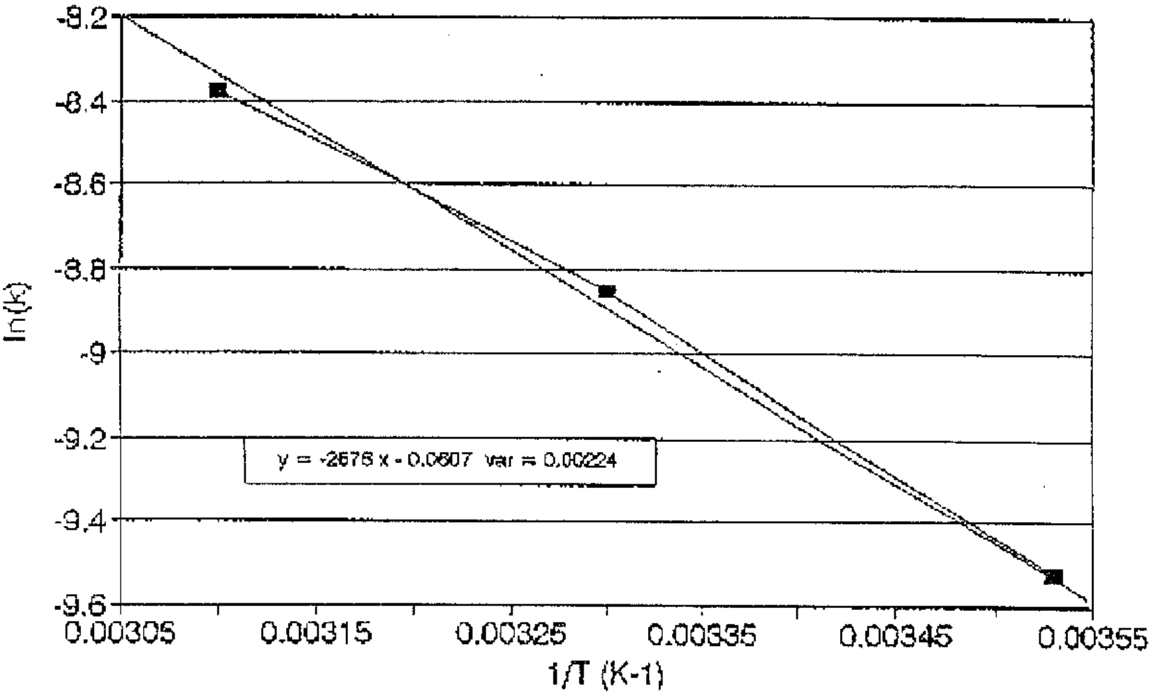
T (K)	ln(k)	1/T (K^{-1})
283	-10.289	3.53E-3
303	-9.210	3.30E-3
323	-9.329	3.10E-3

Uit hierdie tabelle is ln(k) teen 1/T geplot vir al drie pH's. Die vergelykings van die lyne verskyn onder aan die grafieke (Figure E.7 tot E.9). Reguit lyne is deur al die stel data gepas. By 'n pH van 3.2 en 2.0 was die variansie en maksimum afwyking van die passing relatief laag, wat daarop dui dat dit 'n goeie reguit lyn is. Dit lyk dus asof daar by 'n hoër pH slegs een meganisme betrokke is by die onttrekking van sink. Aangesien die H^+-konsentrasiegradiënt groter is by 'n hoër pH, lyk dit asof diffusie teen 'n konsentrasiegradiënt in hierdie gevalle beherend is. By 'n pH van 1.5 was die passing egter baie swakker, wat daarop kan dui dat die helling van die lyn verander. Dit kan wees omdat daar meer as een meganisme betrokke is by die onttrekkingsproses by 'n lae pH. Dit wil se hoe laer die H^+konsentrasie is, hoe kleiner rol speel diffusie. Die volgende tabel (E.11) toon die aktiveringsenergie by verskillende pH's.



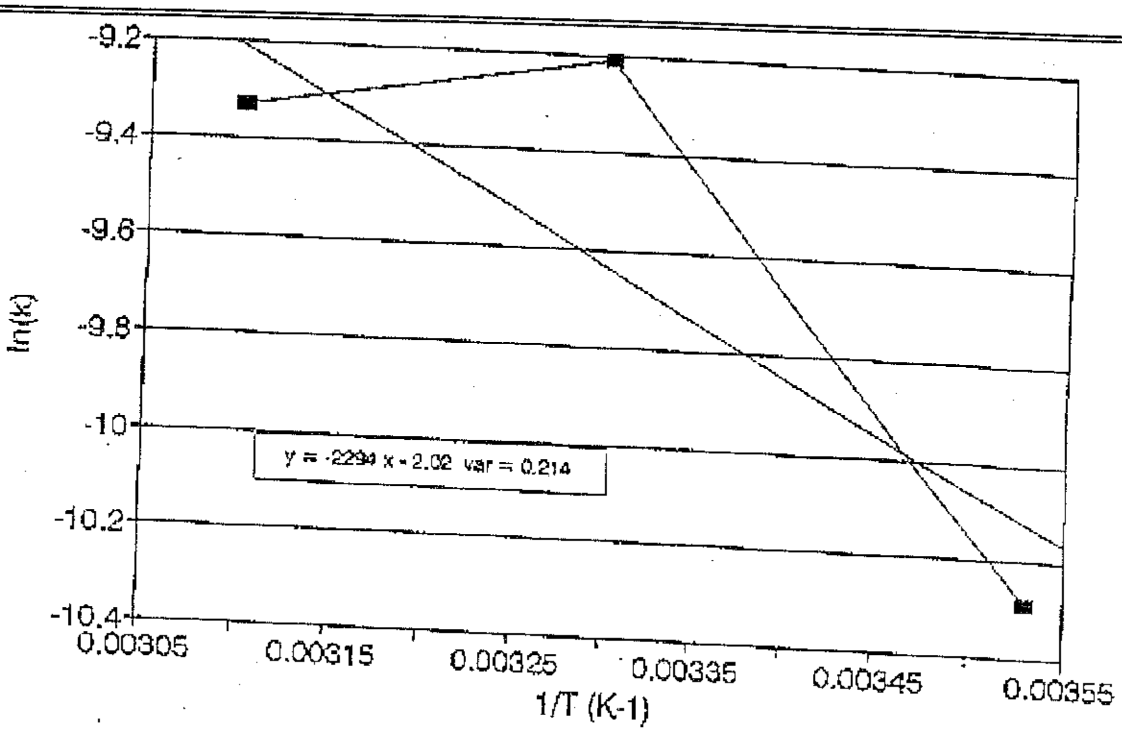
STROPINGS OPLOSSING	MEMBRAAN	EKSTRAKTANT	VOER
H_2SO_4 pH = 0.8	Polipropileen 40% porieus 0.03 µm opening	20% D2EHPA 80% ESCAID	Afvalstroom 30 x Verdun T, pH = var

Fig. E.7: ln(k) teen 1/T by pH = 3.2.



STROPINGS OPLOSSING	MEMBRAAN	EKSTRAKTANT	VOER
H_2SO_4 pH = 0.8	Polipropileen 40% porieus 0.03 μm Opening	20% D2EHPA 80% ESCAID	Afvalstroom 30 x Verdun T, pH = var

Fig. E.8: ln (k) teen 1/T by pH = 2.0.



STROPINGS OPLOSSING	MEMBRAAN	EKSTRAKTANT	VOER
H_2SO_4 pH = 0.8	Polipropileen 40% porieus 0.03 µm Opening	20% D2EHPA 80% ESCAID	Afvalstroom 30 x Verdun T, pH = Var

Fig. E.9: ln(k) teen 1/T by pH = 1.5.

Tabel E.11: Aktiveringsenergie by verskillende pH.

pH	E_a (kJ/mol)
1.5	19.072
2.0	22.248
3.2	23.030

Die lae waardes van die aktiveringsenergie dui eenduidig daarop dat die onttrekking van die sink diffusiebeherend is. Indien reaksie 'n noemenswaardige rol gespeel het, sou die aktiveringsenergie baie hoër gewees het (aktiveringsenergie vir reaksies is gewoonlik meer as 100 kJ/mol). Selfs by 'n pH van 1.5 speel diffusie 'n baie groot rol. Die afwyking van 'n reguit lyn kan slegs daarop dui dat reaksie 'n groter rol hier speel as in die ander gevalle. Die feit dat E_a meer word met toenemende pH, dui daarop dat dit moeiliker sal wees om die reaksie om te keer by 'n hoër pH. Dus sal die sink moeiliker uit die sakkie uitbeweeg by 'n pH van 3.2 as by 'n pH van 2.0. Dit is omdat die sink teen 'n groter pH-gradiënt sal inbeweeg by 3.2 as by 2.0.

Die volgende drie tabelle (E.12- E14) gee die resultate van al die berekeninge gedoen vir 1/T en ln [$k*h/(k_B*T)$] by verskillende pH's. (ln [$k*h/(k_B*T)$]) word met die simbool F aangedui in beide die tabelle en grafieke).

Tabel E.12: 1/T en F vir pH = 3.2.

1/T (K^{-1})	F
3.53E-3	-38.51
3.30E-3	-37.66
3.1E-3	-37.44

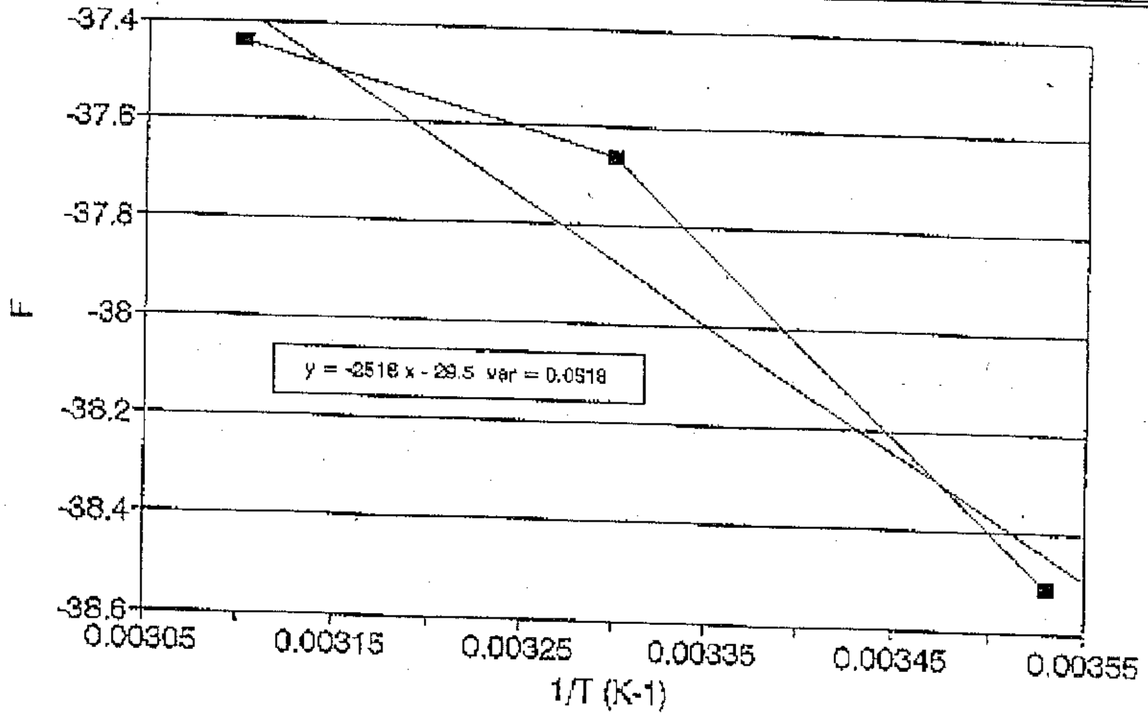
Tabel E.13: 1/T en F vir pH = 2.0.

1/T (K^{-1})	F
3.53E-3	-38.93
3.30E-3	-37.33
3.1E-3	-37.91

Tabel E.14: 1/T en F vir pH = 1.5.

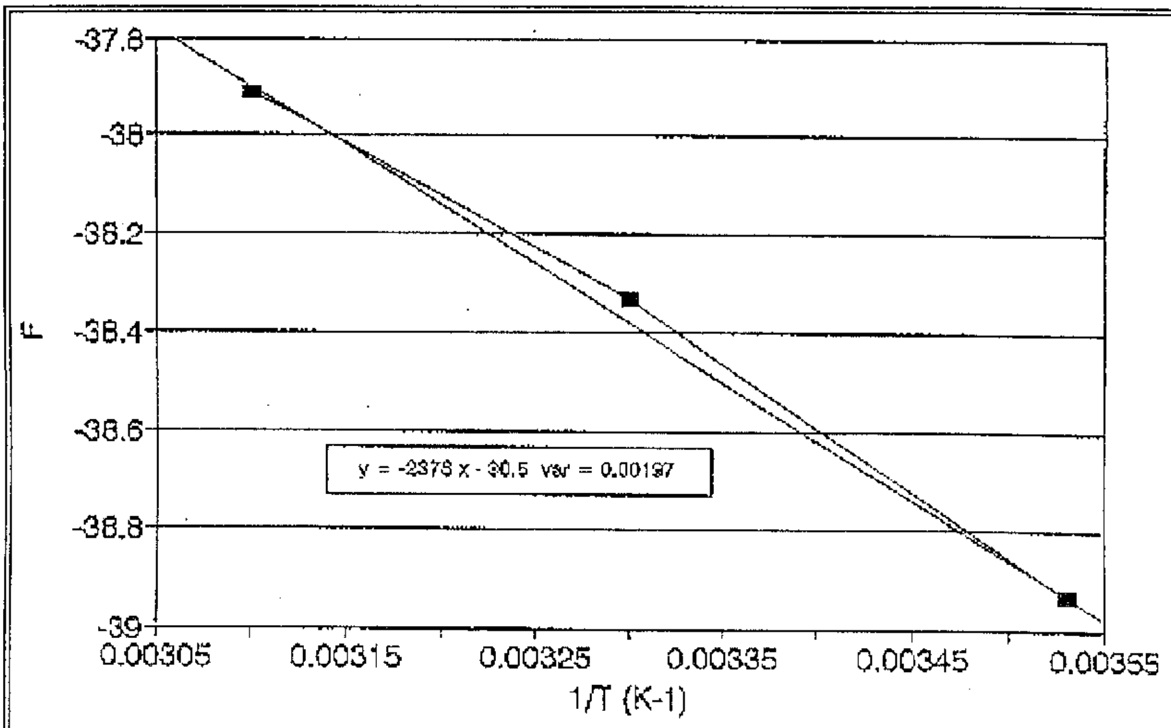
1/T (K^{-1})	F
3.53E-3	-39.69
3.30E-3	-38.68
3.1E-3	-38.87

Die tabelle word grafies getoon in figure E.10 - E.12. Die vergelykings van die lyne verskyn onder aan die grafiek.



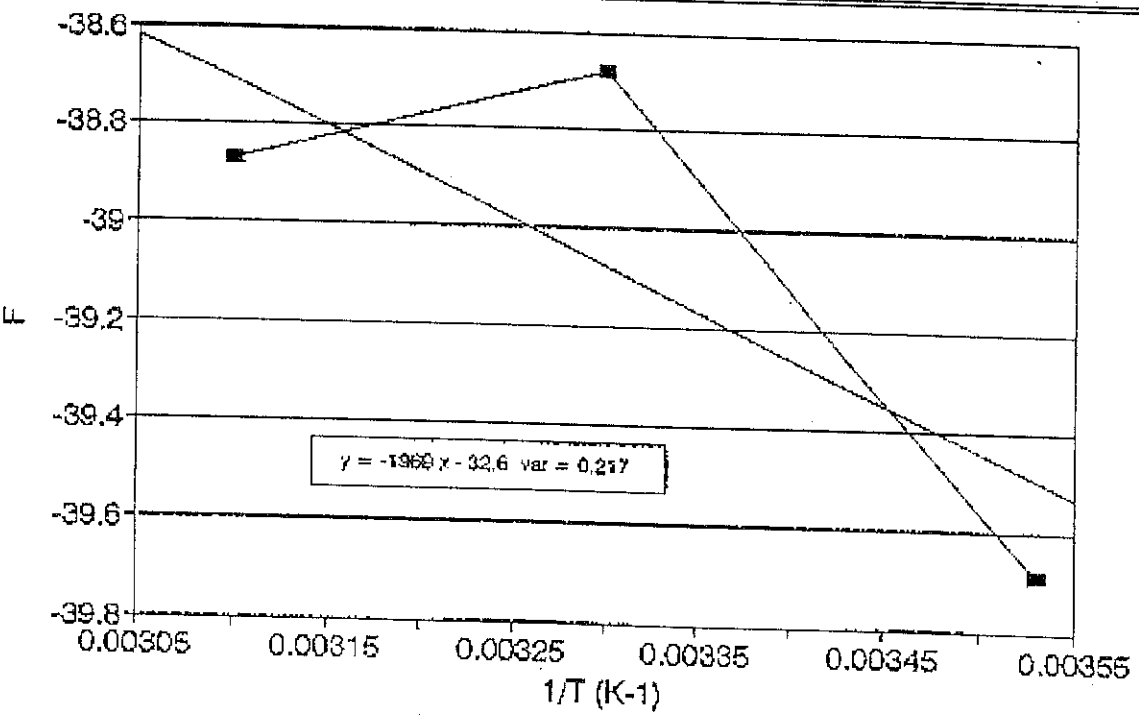
STROPINGS OPLOSSING	MEMBRAAN	EKSTRAKTANT	VOER
H_2SO_4 pH = 0.8	Polipropileen 40% porieus 0.03 µm Opening	20% D2EHPA 80% ESCAID	Afvalstroom 30 x Verdun T, pH = var

Fig. E.10: F teen 1/T vir pH = 3.2.



STROPINGS OPLOSSING	MEMBRAAN	EKSTRAKTANT	VOER
H_2SO_4 pH = 0.8	Polipropileen 40% porieus 0.03 µm Opening	20% D2EHPA 80% ESCAID	Afvalstroom 30 x Verdun T, pH = var

Fig. E.11: F teen 1/T vir pH = 2.0.



STROPINGS OPLOSSING	MEMBRAAN	EKSTRAKTANT	VOER
H_2SO_4 pH = 0.8	Polipropileen 40% porieus 0.03 µm Opening	20% D2EHPA 80% ESCAID	Afvalstroom 30 x Verdun T, pH = var

Fig. E.12: F teen 1/T vir pH = 1.5.

Vanaf die hellings en Y-afsnitte van die grafieke is die aktiveringsentalpie en aktiveringsentropie bereken. Die volgende tabel (E.15) toon die waardes wat bereken is by verskillende pH's:

Tabel E.15: $\delta H^{=}$ en $\delta S^{=}$ by verskillende pH.

pH	δH^{-} (kJ/mol)	δS^{-}
1.5	16.37	-0.271
2.0	19.77	-0.254
3.2	20.93	-0.245

Uit die positiewe teken van δH^{-} kan gesien word dat die reaksie endotermies is. Ook hier is dit duidelik dat die energie om die reaksie om te keer hoër is hoe hoër die pH is. Dit strook met die afleiding wat gemaak is oor aktiveringsenergie. Die negatiewe teken van δS^{-} dui daarop die chaos in die sisteem verminder het. Dit is as gevolg van die feit dat die sakkie sinkione wat wanordelik rondbeweeg, uit die sisteem onttrek. Die wanordelikheid van die sisteem neem dus af.

E.5. Gevolgtrekking

Uit die resultate soos gekry in die projek kan die volgende gevolgtrekkings gemaak word:

Uit graffieke E.1 -E.3 kan gesien word dat 'n hoë pH sinkopname bevoordeel. Hierdie verksynsel kan toegskryf word aan die feit dat die waterstof konsentrasiegradient groter is by 'n hoë pH.

Uit grafiek E.1 toon dat by hoër temperature sinkopname ook bevoordeel word. Die pH en die temperatuur kan egter nie onbepaald verhoog word nie as gevolg van die feit dat by 'n hoë pH sal sink uitsak en by hoë temperature sal die proses kostes verhoog en moederoplossing sal verdamp. Die flukskurwes toon die tempo waar teen die sink in die sakkie in gediffundeer het. Dit kan ook gebruik word as bewys om bogenoemde te staaf.

Uit die resultate is gevind dat die reaksie eerste orde is en die reaksie konstante is ook bereken. Soos verwag word, word hoër reaksiekonstantes verkry by 'n hoër pH en temperatuur. Die tempo van die reaksie neem dus toe.

Uit die aktiveringsenergie is gesien dat die reaksie diffusiebeherend is. By 'n lae pH is egter gevind dat reaksiebeheer en diffusiebeheer beide 'n rol speel. Hierdie gevolgtrekking is gemaak uit die feit dat daar 'n afwyking van 'n reguit lyn is, soos gesien kan word in figuur E.9.

Die aktiveringsentropie dui daarop dat die wanordelikheid van die sisteem afneem soos die sink uit die oplossing onttrek word.

Appendix F

Herwinning van Chroom uit 'n uitskotstroom

F.1 Inleiding

Die resultate verkry deur Coetzee & Van Wyk (1995) word opgesom en illustreer die herwinning van chroom uit 'n uitskotstroom.

F.2 Eksperimentele ontwerp

Die eerste stap in die eksperimentele ontwerp is om 'n lys te maak van al die moontlike parameters wat die tempo van chroom ekstraksie kan beïnvloed (in dalende volgorde van belangrikheid). Dit kan as volg gelys word:

- Die pH van die moederoplossing
- Die waterstof konsentrasie van die stropingsmiddel
- Die chroom konsentrasie van die moederoplossing
- Die ekstraktant konsentrasie in die draer fase

Die Windows uitgawe van Statistica is bebruik om 'n sentrale saamgestelde ontwerp, met die gebruik van respons oppervlakte metodes, te doen. 'n Tweede orde saamgestelde ontwerp is hierna opgestel. Die eksperimentele ontwerp vir die eksperiment word getoon in tabel F.1.

Tabel F.1: Eksperimentele vlakke van eksperiment:

Eksp. No.	pH	[H] molaar H^+	[Cr] ppm	[Ekstrak] % TOA
1	-1	-1	-1	-1
2	1	-1	-1	-1
3	-1	1	-1	-1
4	1	1	-1	-1
5	-1	-1	1	-1
6	1	-1	1	-1
7	-1	1	1	-1
8	1	1	1	-1
9	-1	-1	-1	1
10	1	-1	-1	1
11	-1	1	-1	1
12	1	1	-1	1
13	-1	-1	1	1
14	1	-1	1	1
15	-1	1	1	1
16	1	1	1	1
17	0	0	0	0
18	0	0	0	0
19	-2	0	0	0
20	2	0	0	0
21	0	-2	0	0
22	0	2	0	0
23	0	0	-2	0
24	0	0	2	0
25	0	0	0	-2
26	0	0	0	2
27	0	0	0	0

F.2.1 Bepaling van waardes van eksperimentele parameters

Die eerste stap in die bepaling van die waardes van die eksperimentele parameters is om die bereik van waardes vir die eksperiment te bepaal. Die tweede stap is om die waardes van die vlakke te normaliseer en te bereken met Statistica. Die resultate word getoon in tabel F.2.

Tabel F.2: Interpretering van vlakke

Parameters	Vlakke				
	-2	-1	0	1	2
pH van voer	1	1.5	2	2.5	3
[H] molaar H^-	2	10	18	26	34
[Cr] ppm	200	400	600	800	1000
[Ekstrak] % TOA	5	7.5	10	12.5	15

F.3 Resultate en bespreking

F.3.1 Eksperiment 1

Hierdie eksperiment is uitgevoer om 'n growwe bepaling van die pH waar optimum ekstraksie plaasvind te bepaal. Die resultate het getoon dat die beste ekstraksie uit die moederoplossing by 'n pH van 2 voorgekom het. Omrede hierdie eksperiment slegs 'n rowwe bepaling van die pH opgelewer het is die pH gebied vasgestel op 'n pH tussen 1 en 3. Aanvanklik is die gevolgtrekking gemaak dat hoë ekstraksie bo 'n pH van 7 plaasvind, maar na verdere literatuur ondersoeke is gevind dat chroom (III) begin neerslaan in die vorm van $Cr(OH)_3$ bo 'n pH van 5 (Holland, 1975).

F.3.2 Eksperiment 2

'n Growwe bepaling van die optimum persentasie TOA in die draer fase is in hierdie eksperiment bepaal. Die beste ekstraksie vind plaas by 'n ekstraktant konsentrasie laer as 15 % in Escaid. Dit moet egter beklemtoon word dat eksperimente 1 en 2 slegs die gebied rofweg afbaken waarin optimale ekstraksie plaasvind.

F.3.3 Eksperiment 3

Die gebiede afgebaken vir die pH- en ekstraktant konsentrasie parameters is gebruik om die bereik van die eksperimente op te stel. Aangesien die uitskotstroom van die leerlooiery nagenoeg 1 g/l chroom bevat is die chroom konsentrasie gevarieër tussen 200 tot 1000 ppm.

Die resultate van eksperiment 3 word in figuur F.1 tot figuur F.6 weergegee. Die grafiek se x en y asse is ingedeel volgens die vlakke soos bereken in die eksperimentele ontwerp (sien tabel F.1).

Uit figuur F.1 kan gesien word dat die chroom ekstraksie bevoordeel word deur 'n toename in pH en 'n toename in waterstof konsentrasie ($[H^+]$).

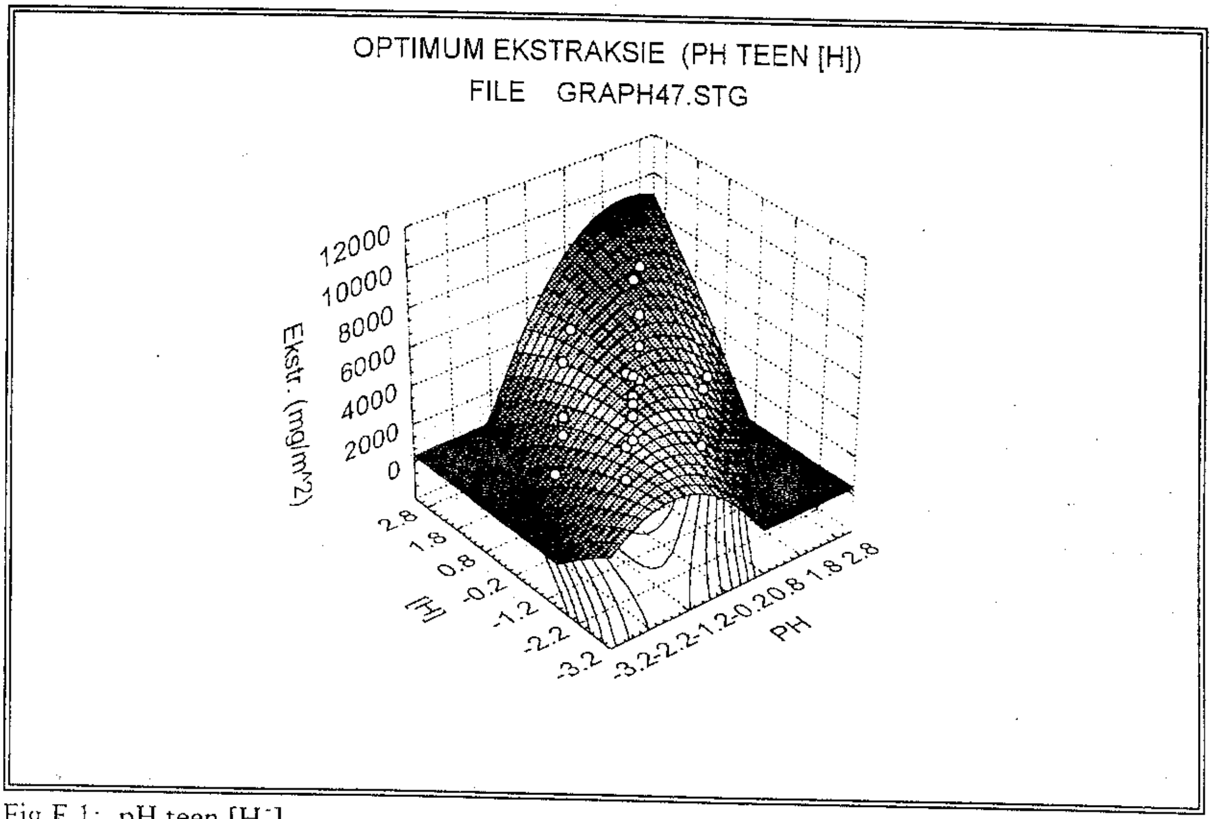


Fig F.1: pH teen $[H^-]$.

Figuur F.2 toon 'n toename in ekstraksie indien die pH toeneem en die chroom konsentrasie toeneem. Die pH en chroom konsentrasie moet dus so hoog as moontlik wees vir optimum ekstraksie.

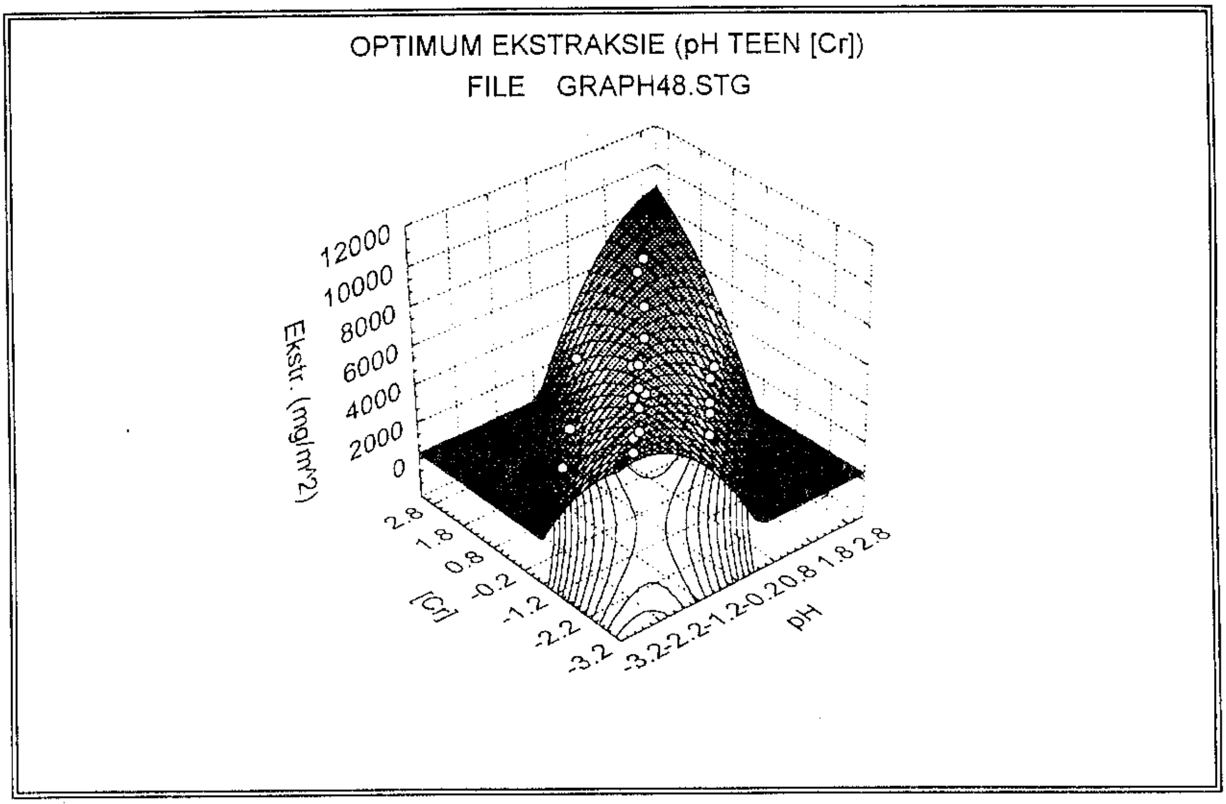


Fig. F.2: [Cr] teen pH

Figuur F.3 toon dat die maksimum ekstraksie verkry word by 'n gemiddelde ekstraktant konsentrase by 'n gemiddelde pH. Dit is verder duidelik dat ekstraksie van chroom benadeel word deur 'n baie lae pH (meer suur) en lae ekstraktant konsentrasie.

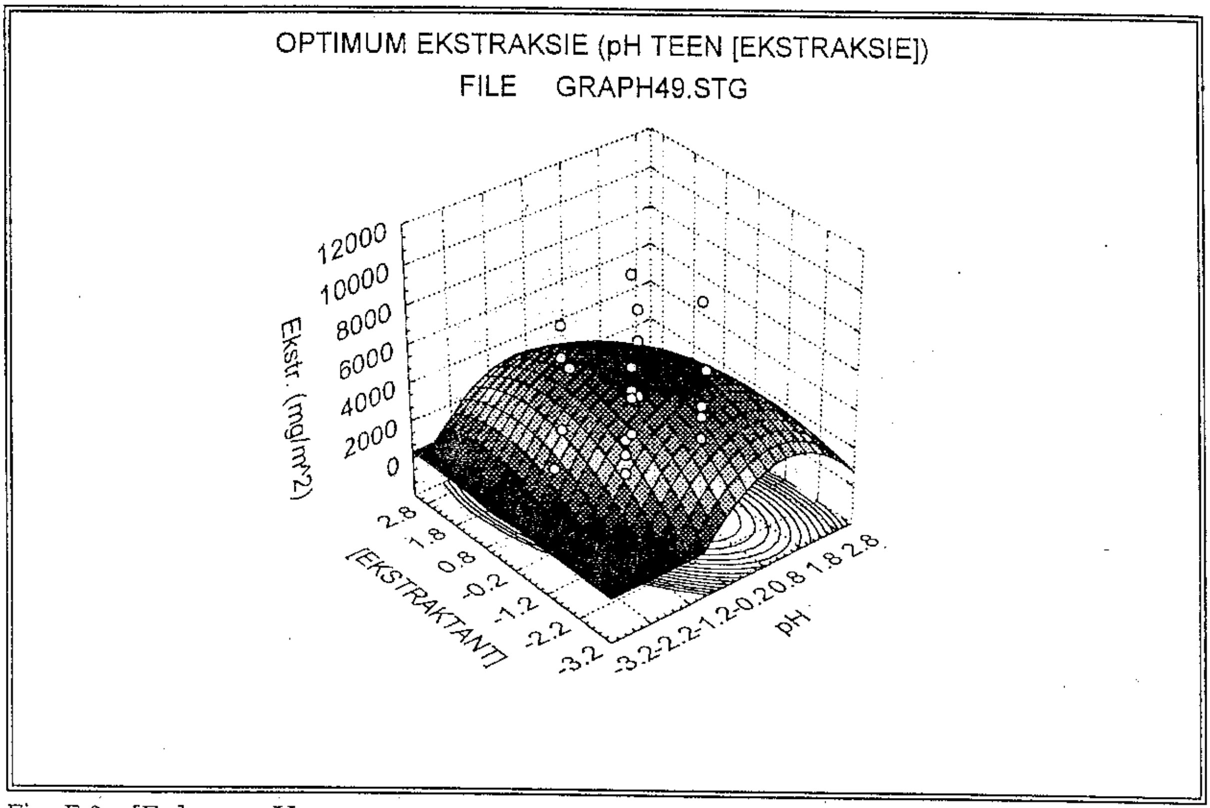


Fig. F.3: [Ex] teen pH

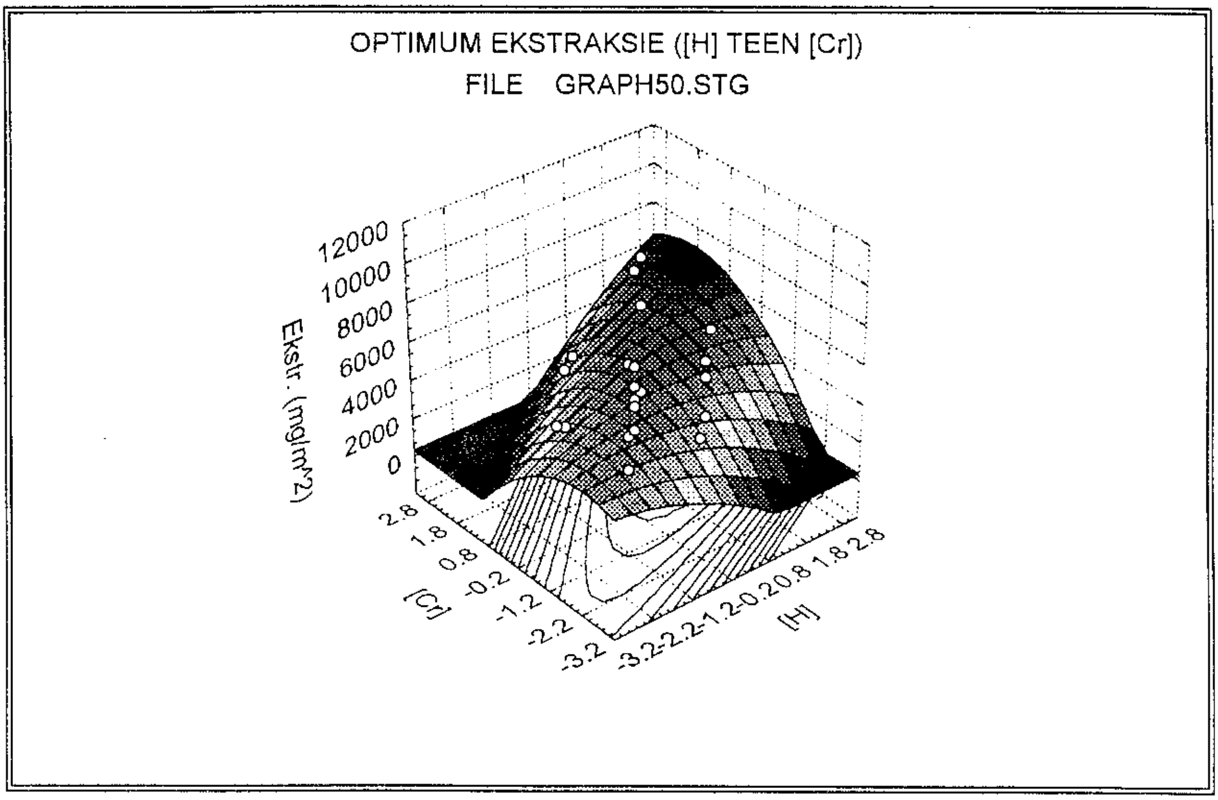


Fig.F.4: [Cr] teen [H].

Figuur F.4 voorspel dat 'n hoë chroom ekstraksie verkry sal word by 'n hoë chroom konsentrasie in die moederoplossing, mits 'n hoë waterstof konsentrasie gehandhaaf word. 'n Verlaging van die waterstof konsentrasie sal 'n skerp afname in ekstraksie tot gevolg hê.

In figuur F.5 word aangetoon dat ekstraksie bevoordeel word by 'n hoë waterstof konsentrasie en 'n gemiddelde ekstraktant konsentrasie. Die volgende kondisies lei tot 'n afname in chroom ekstraksie:

- 'n hoë waterstof konsentrasie in die kapsule en 'n hoë ekstraktant konsentrasie.
- 'n lae waterstof konsentrasie in die kapsule en 'n lae ekstraktant konsentrasie.

Figuur F.6 toon geen ekstraksie by 'n lae chroom konsentrasie in die moederoplossing en 'n lae ekstraktant konsentrasie nie. Matige ekstrakie vind plaas by 'n gemiddelde chroom konsentrasie en 'n gemiddelde ekstraktant konsentrasie.