The Extraction of Ionic and Chemical Species from Water by Membrane Extraction

JJ Smit • LR Koekemoer • AM van Wyk

Report to the Water Research Commission
by the
Department of Chemical Engineering
University of Potchefstroom for CHE

WRC Report No 761/1/98

THE EXTRACTION OF IONIC AND CHEMICAL SPECIES FROM WATER BY MEMBRANE EXTRACTION

Final Report to the

Water Research Commission

by

JJ Smit, LR Koekemoer and AM van Wyk

Department of Chemical Engineering
University of Potchefstroom for CHE
Private Bag X6001, Potchefstroom 2520 South Africa

WRC Report No 761/1/98
ISBN 1 86845 393 6

EXECUTIVE SUMMARY

THE EXTRACTION OF IONIC AND CHEMICAL SPECIES FROM WATER BY MEMBRANE EXTRACTION

by

JJ Smit, LR Koekemoer and AM van Wyk
Department of Chemical Engineering,University of Potchefstroom for CHE
Private Bag X6001, Potchefstroom 2520   South Africa

A.1 Introductory statement

This project is an extended investigation into the extraction potential of supported liquid membranes (SLM) for dissolved chemical species from aqueous solution. This emerging new technology involves the concept of an unconfined reactor which entails the membrane to be configured in the form of a capsule. This implies that no expensive reactor containment is necessary.

An important principle which motivated this research is the ever increasing environmental awareness fostered by a strong global drive towards sustainability. The depollution of waste waters (effluents) certainly ranks high in the priority list for at least two reasons:

a. The recovery of "clean", water and

b. the recovery of valuable dissolved chemical species.

The need to support this new, emerging technology was recognised by the WRC and the PU for CHE. A centre of expertise was consequently established through the financial subvention of various projects in this field of research. This participation led to networking with other instances like ESKOM with whom a joint project was configured.

The WRC part of the project entailed the extraction of nickel from aqueous solution. The results from this project served as starting point and indication to the ESKOM project which was focused on the extraction of lowly soluble cations (like barium, calcium and strontium)as well as the removal of TOC from boiler feedwater. This latter assignment posed extremely difficult problems with expensive analyses procedures because the concentrations involved were in the range of micrograms per liter.

Previous projects executed for the WRC on this research topic indicated the technical feasibility of nickel extraction with SLM (WRC Project K5/516). This report will therefore relate the results of two investigations which will cover (respectively) the WRC requirements and the requirements as set out by ESKOM (Refer to appendix C). These requirements and objectives are set out as follows for WRC and ESKOM respectively:

WRC objectives:

The development, design, evaluation and testing of a suitably qualified membrane support, in the form of a capsule, for the optimised extraction of nickel.

1. The application and qualification of this support and its peripheral components such as extractant in a typical extraction environment such as would be expected to yield maximum extraction of nickel.
2. The generation of an extraction equation from a six factorial experimental design to yield typical extraction rates for nickel.
3. The optimisation of the possible independent variables involved in the extraction protocol for nickel with capsule membranes.
4. The qualification of the system for plant use as well as for the widest possible application to other extraction system requirements such as the needs of ESKOM.

ESKOM objectives:

The design of an extraction system using the analogy from the protocol for nickel extraction.

1. The testing of various membrane supports (substrates) to effect extraction of cations and TOC from aqueous solutions.
2. The qualification of the basic extraction potential by shake-out solvent extraction techniques for the different species to be extracted.
3. The assessment of the extraction potential of SLM in general for the species involved at ESKOM.
4. The prognosis for the translation of the SLM results to the CME configuration using firstly higher concentrations of synthetic solutions followed by real solutions.

A.2 A summarised statement of the contract objectives

The joint objective for both projects can be summarised as an effort to translate the successes achieved with the capsule extraction of nickel to the extraction of cations and TOC from boiler feed water.

A.3 A brief summary of the results.

The integrity and the technical feasibility of the SLM and the CME systems were pointed out in previous research (Refer to WRC Report No. K5/617). The interest and eventual participation of ESKOM in this research caused the emphasis to be shifted to two virtually separate but similar projects. It can be stated that the two projects would develop along the same lines but out of phase. It is therefore logical to report the results separately

Nickel extraction refinement.

The extraction of nickel with suitably formed capsules gave extraction rates and total extraction values which were dependent on the five variables identified in previous research as mentioned in A.2. These variables are:

1. Temperature
2. Speed of agitation on the feed side (Reynolds number)
3. Acid concentration in the strip (inside) solution.
4. Special ligand concentration in the feed side solution.
5. Extractant concentration in the membrane.

Each of these variables increased the extraction rate and the combined nett effect was an increase of at least 100 times greater extraction than reported in literature. Furthermore an empirical rate equation was developed which yielded. a polynomial expression in terms of all the independent variables mentioned. This rate equation is a powerful tool to predict and determine the size of a plant using this technology. In final summary the experience gained from the nickel refinement experiments gave a very convincing platform from where the ESKOM assignment could be approached.

The application on lowly soluble cations and TOC (ESKOM)

The potential and response of the ESKOM chemical species were firstly investigated using shake-out tests followed by SLM experiments. This was necessary because the ESKOM project differed dramatically from the nickel and the following aspects complicated the direct use of results obtained with nickel:

1. The concentrations to be addressed in the ESKOM application were in the lower ranges of microgram per liter (ca.10-100 µg/liter).
2. The metals involved are not amongst those which are traditionally extracted and there is consequently a dearth of information regarding extractants and the like.

For these reasons the research protocol was slightly altered to qualify this extraction system regarding the extractants. The initial experiments were also performed on synthetic solutions to establish tendencies for the variables before the low concentration ,real solutions were attempted.

Suitable but low extraction was obtained with both shake-out tests as well as with SLM. It was however obvious that the four orders of magnitude lower concentration than the nickel had a dramatic effect and decreased the extraction rates to very low levels.

These low extraction values implied very large membrane surfaces and/or very long retention times both of which resulting in unfavourably large capital investment. The same experiments were repeated with the same configuration of capsules and the following observations were made:

1. The extractants were clearly not optimised for extraction of any of the cations or the TOC and substantial basic research is necessary.
2. Analysis had to be done at various different laboratories which raised serious doubts on the relative comparability of these.

In summary the CME system does not concentrate the cations well. The extractants used ranged from the mundane, off-the shelf types to very sophisticated macrocyclic polyethers with differing efficiencies. It was however obvious that the extraction is slow due to the low feed concentration the possibility of using an enhancing external driving force (like for example an electrical EMF) could improve the nett transfer tremendously.

The TOC values could not be extracted due to the non-availability of a suitable extractant mentioned in literature but unavailable in RSA.

A strongly positive indication was found that this technique could be used to concentrate analytical samples from the microgram/liter to the milligram per liter range. This will obviously have large cost and investment implications for analyses in these lower concentration ranges. The potential of electrochemical treatment also holds promise especially with the degradation of TOC coupled to the possibility of an external electrical driving force.

A.4 Assessment of the achievements of the research.

The project was completed satisfactorily with the nickel attaining all of its aims and objectives. The ESKOM project, being of a more exploratory nature, also attained its major objective viz.-- can CME be used for the extraction of lowly solubles? The answer is obviously negative - but with some very good indications of the possibilities of alternatives. The main objective namely to transfer the technology obtained with nickel to the ESKOM system was not attained.

A.5 Recommendations.

It is strongly recommended that this extraction technology be strongly supported by on-going research. It has potential to extract even low level concentrations from aqueous solution (effluents). It would therefore be able to desalinate (take out the not-so-harmful chemicals and ions) as well as the very obnoxious and/or toxic pollutants. The strongest and most attractive advantage of this concept is the fact that it demineralises. In the worst case an adjustment of pH might be necessary.

The capsule configuration is highly satisfactory and only the design of a cheaper capsule is necessary. The membrane material used in these experiments was extremely expensive. This cost factor reflected negatively on the cost of economically extracting nickel.

The research project led to various initiatives and exposure to the industrial and scientific public. The following are aspects which were directly derived from these research activities:

- Publications. The first article was entitled *The extraction of nickel with the use of supported liquid membrane capsules* and was publicized in *Water SA*, volume 22, number 3, July 1996. The second article was entitled *Optimization of nickel extraction with supported liquid membrane capsules* and is in the process of being refereed by the same journal..
- RSA patent.
- M (Eng)Chem. Dissertation by Mr. L.R. Koekemoer.
- A presentation of this emerging technology at the biennial forum of world leaders in potable water financing and research organisations. This event was organised by the American Water Works Association in Antwerp, Belgium, 5-8 May 1996.The WRC presented seven selected research topics from RSA at this distinguished event.

Acknowledgements

The authors hereby wishes to express their sincere gratitude towards the following people for their continuous support throughout the project.

Consultation:

Dr H Saayman (Water Research Commission)
Prof HS Steyn (Statistics Consultation Service: PU for CHE)
Dr FA Hawkins (Private consultant)
Mr G Lok (Corporative consultant: ESKOM)
Mr S Peters (Corporative consultant: ESKOM)
Dr RD Sanderson (IPS Stellenbosch University)
Dr TA du Plessis (MD of Grammatron Pty.Ltd.)
Mr D Saunders (Aquafund Pty. Ltd.)

Publications:

Me IG Buchan (Editor: *Water SA*)

All financial support is credited to the Water Research Commission and ESKOM.

Table of contents

Chapter 1

Chapter 2

Chapter 3

Chapter 4

Chapter 5

Chapter 6

Appendix A

Appendix B

Appendix C

List of tables

List of figures

List of photographs

Nomenclature

Unless otherwise stated, the symbols in this dissertation have the following meaning. The dimensions of the symbols are given in brackets

A	Area (cm^3).
AA	Atomic absorption spectrophotometer.
C	Concentration (mol/dm^3).
Cir	Circumference (m).
D	Impeller diameter (m)
E	Activated energy (J/mol).
Ex	Extractant.
Extr	Extraction (g/m^2).
H	Hydrogen
J	Flux ($\mu g/cm^2 s$).
k	Reaction constant.
k_0	Frequency factor.
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.
r	Rate of reaction ($mol/m^2 \cdot h$).
Rate	Rate of extraction ($g/m^2 \cdot h$).
Re	Reynolds number.
T	Temperature (K).
t	Time (s or h).
V	Volume (cm^3).
μ	Liquid viscosity ($N \cdot s/m^2$).
ρ	Density (kg/m^3).
ω	Rate of rotation.

Acronyms

Ac	Acetate.
CME	Capsule membrane extraction.
D2EHPA	Di-2-(ethylhexyl) phosphoric acid.
DSP	Double salt precipitation
EMF	Electro motoric force
fcc	Face-centred cubic.
FFC	Flat film contactor.
HCC	Hydrodynamically characterised contactor.
LMP	Emulsion liquid membrane permeation.
MCC	Multi cell contactor.
NMR	Nuclear magnetic resonance.
PVC	Polyvinyl chloride.
SFC	Slurry flow contactor.
SLM	Supported liquid membranes.
TBP	Tri-n-butyl phosphate
TOC	Total organic carbons

Superscript

b	Bulk solution.

Subscript

A	Component A.
f	Feed solution.
I	Initial.
o	Organic solution.
s	Strip 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 recovery and upgrading of metal-containing waste have become not only a very demanding assignment, but also a lucrative business (refer to photograph 1.1). The cleaning of nickel from waste streams is no exception. As one of the carcinogenic substances, nickel discharge to sewers or public water must be strictly limited (Zhongmao *et al.*, 1990:170). The trend in environmental legislation, world wide, is to limit the concentration of the common heavy metals to 1-2 mg/dm^3 for sewer discharge and 0.1 to 0.5 mg/dm^3 for open water discharge (Fane *et al.*, 1992:5). Nickel has the additional advantage that it is a very valuable metal (R 31.76/kg (Anon., 1996:S6)) and thus a candidate for recovery from effluents.

B.Sc. CHEMICAL ENGINEER
ENVIRONMENTAL
R 160 000 - R 180 000 PA
A dynamic projects company has an excellent opportunity for an engineer with either air or water pollution and environmental control experience. Contact Sheila Moran on (011) 488-9822.

Photograph 1.1: Advertisement in Sunday Times (PAG, 1996:15.)

An alloy of nickel was known in China more than 2000 years ago. Saxon miners were familiar with the reddish-coloured ore, NiAs, which resembles Cu_2O. The miners attributed their inability to extract copper from this ore to the work of the devil and named it "Kupfernickel" (Old Nick's copper). In 1751 A.F. Cronstedt isolated an impure metal from some Swedish ores and, identifying it with the metallic component of Kupfernickel, named the new metal "nickel" (Greenwood & Earnshaw, 1984:1328).

Nickel is a high melting element with a ductile crystal structure and with chemical properties which allow it to be combined with other elements. Nickel-base alloys provide excellent mechanical properties from cryogenic temperatures to temperatures in excess of 1000 °C (Tien & Howson, 1981:787). Nickel also has the face-centered cubic crystal structure which makes it highly formable but is relatively expensive (R 31.76/kg) and has a high density (8.9 g/cm^3) which limits its use (Smith, 1990:548).

Erlank (1994:96) proved that nickel can be extracted with the use of supported liquid membranes (SLM). A variation of the SLM configuration was found in the capsule membrane extraction (CME) configuration. Erlank found that extraction is strongly driven by a pH gradient between the feed and strip solution (1994:96). The results only showed the technical tendencies of CME and a full characterization and optimization still had to be done.

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.

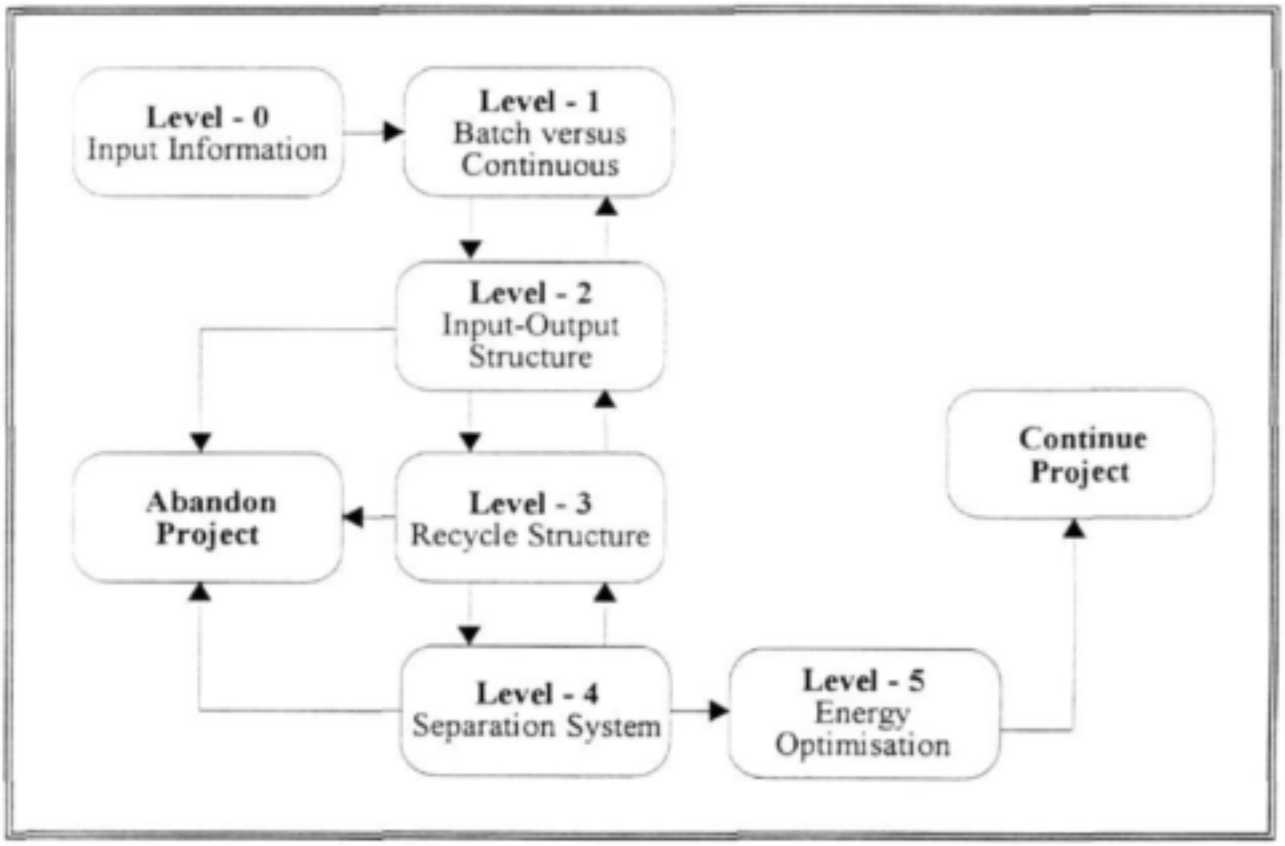


Fig. 1.1: Flowchart of hierarchial process design.

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 beneficiation of nickel is complicated. The oxide ores are not generally amenable to concentration by normal physical separations and so the whole ore body has to be treated. The sulfide ores (which are 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.

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 price quoted (R31.76/kg) 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 are expected to contribute to the general field of demineralization.

2.2 Statistical experimental design

2.2.1 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 factors are significant. The next step is to undertake 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 three-dimensional 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 were needed for a process with five factors (each having five different values). This process is unfortunately not very dependable. An example of an experiment which gives a false optimum can be seen in figure 2.1. In the experiment the X factor is kept constant at a value of x1 and the Y factor is varied. The optimum value for the X factor 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 factor. 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.

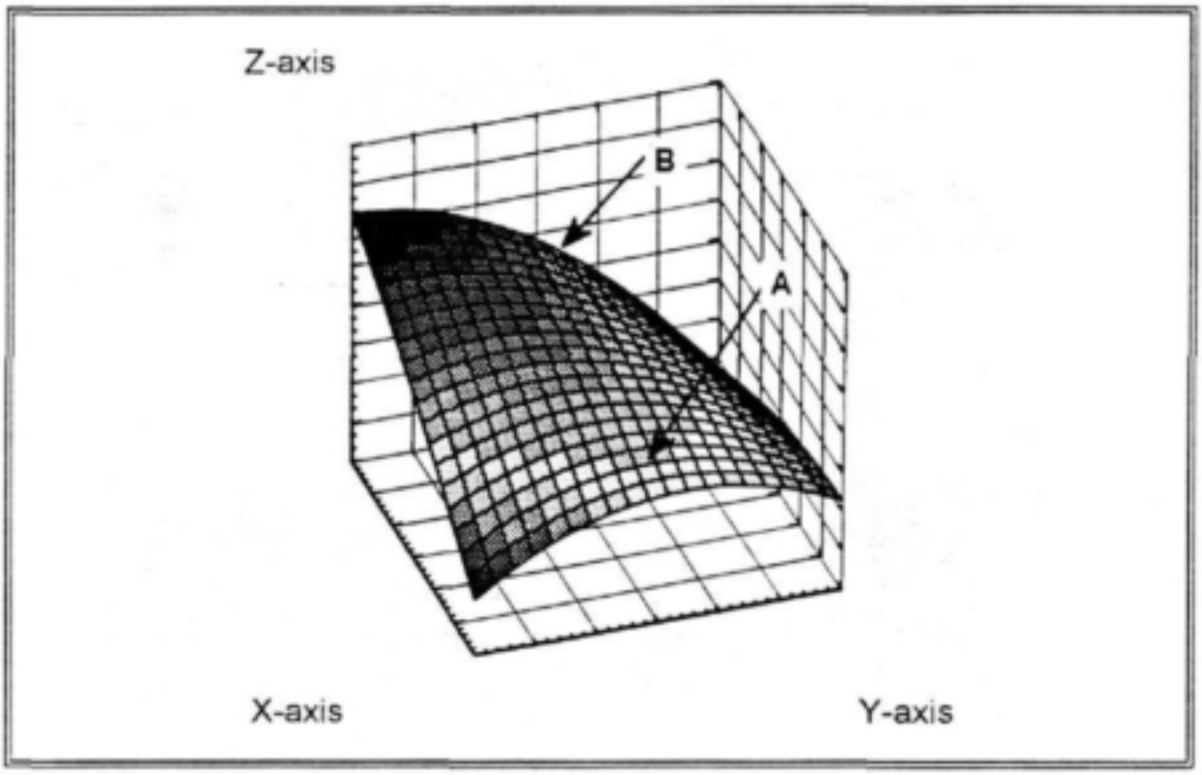


Fig. 2.1: False experimental optimum.

2.2.2 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.

2.3 Supported liquid membranes (SLM)

2.3.1 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).

2.3.2 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

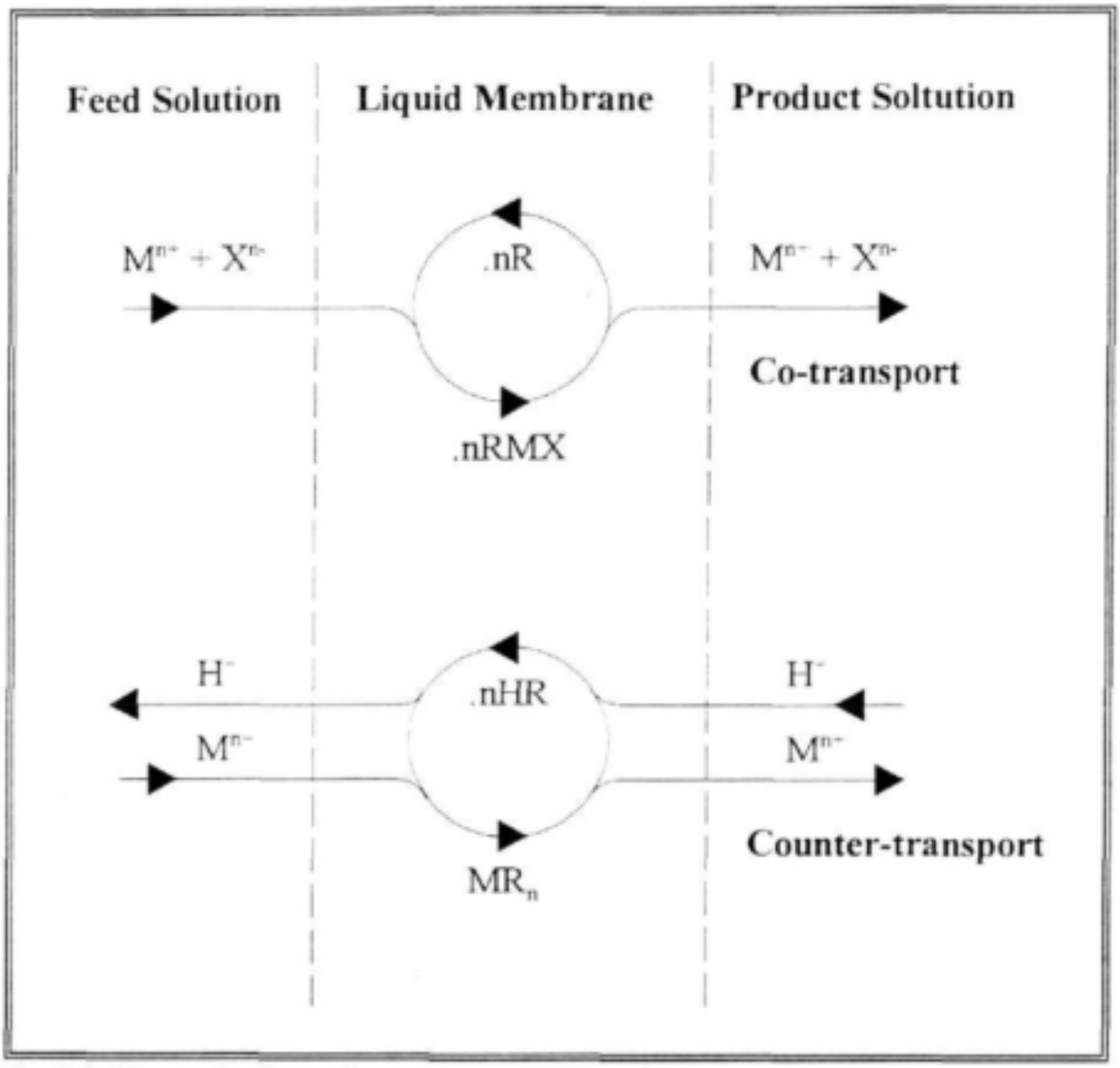


Fig. 2.2: The mechanisms of transport across a membrane.

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:

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

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.

2.3.3 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.

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

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 considered 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.

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

2.3.4 Process Variables

2.3.4.1 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).

2.3.4.2 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.

2.3.4.3 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 are 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 or by increased osmotic pressure displacing the organic from the membrane pores.

2.3.4.4 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

2.4.1 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 are therefor 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.

2.4.2 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 to 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 placed in a lead lined tank containing cold dilute acid, to etch the articles lightly (fig. 2.3 B).

The articles are 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.

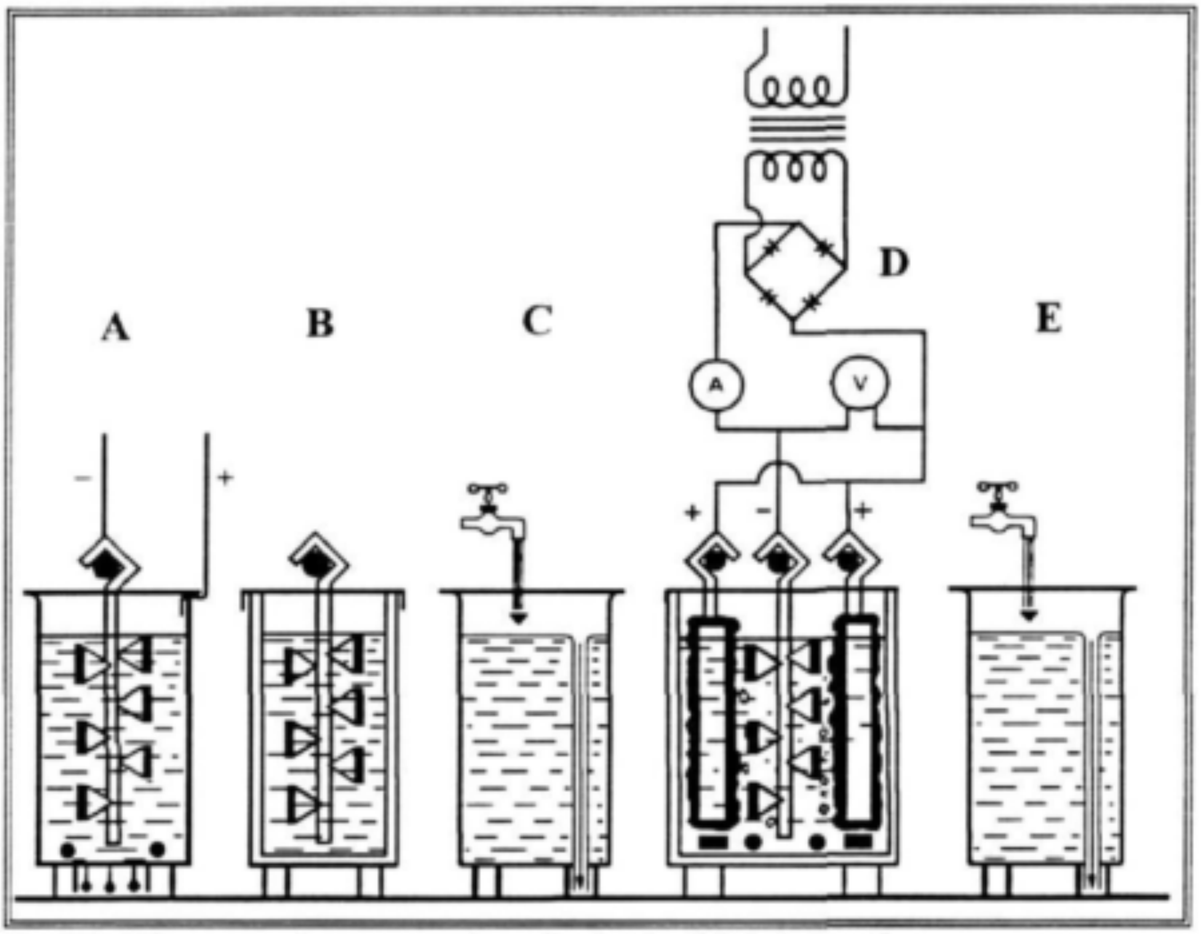


Fig. 2.3: Diagrammatic representation of a simple nickel plating plant.

The tank is provided with a central metal rod at the top, from which the articles hang. 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. The nickel anodes hang on these rods 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.

2.4.3 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).

It is evident that nickel effluent sources are of two kinds, namely the "drag out", which result from rinsing, as well as nickel to be recovered from "spent" baths where no more MTO's could be attained.

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	

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).

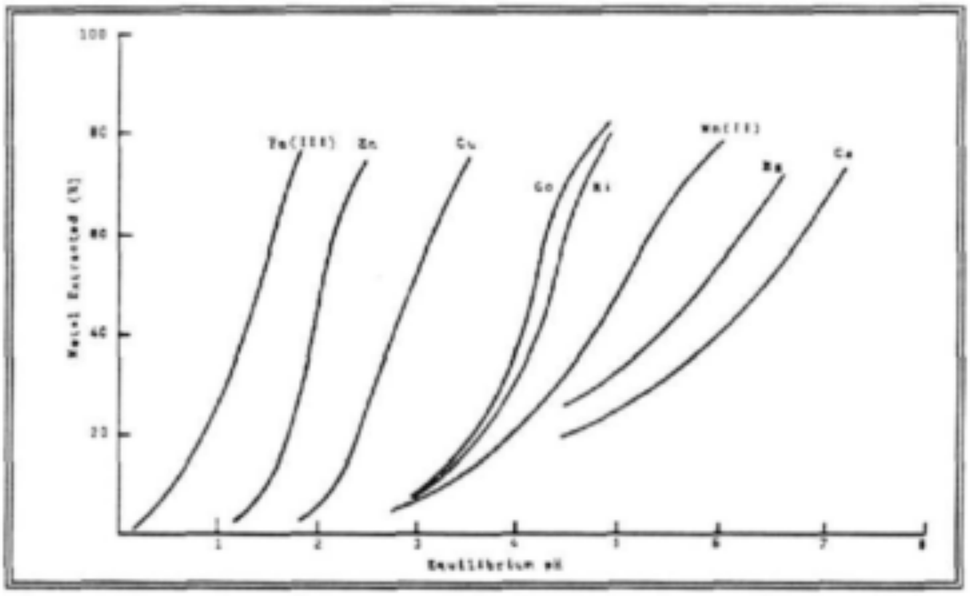


Fig. 2.4: Extraction of some metals by D2EHPA from sulphate solution.

Verhaege *et al.* (1987:331) investigated the possibility of nickel recovery by static 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.

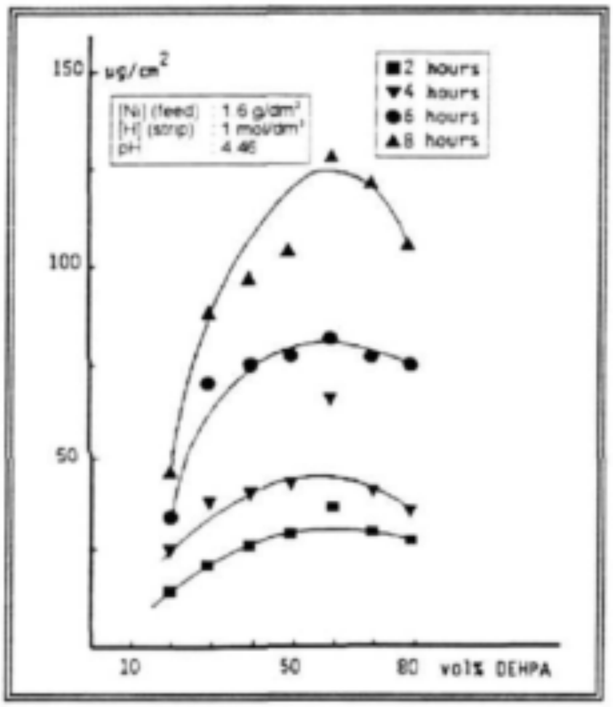


Fig. 2.5: Influence of membrane composition on mass transfer Verhaege *et al.* (1987:333).

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 as 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 obtained by Erlank 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.

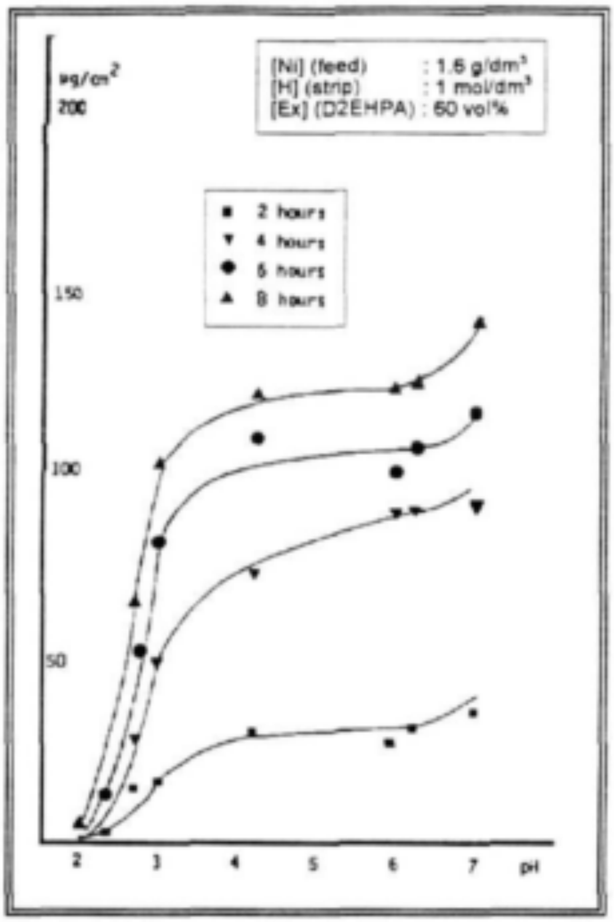


Fig. 2.6: Influence of feed pH on mass transfer
Verhaege *et al.* (1987:334).

Fane *et al.* (1992:5) outlined the requirements for metal recovery from wastewater, with particular reference to electroplating. The technical features of nanofiltration, ultrafiltration and supported liquid membranes were described. They found that a limitation of SLM is the need to avoid phase leakage. An advantage of SLM is the high selectivity of the process. Fane *et al.* (1992:16) came to the conclusion that the three membrane processes score favourably in terms of plating industry criteria, except for the aspect of simplicity, which needed further development.

Rupert *et al.* (1988:1659) used emulsion liquid membrane permeation (LMP) to recover Zn, Cd, Pb, Ni, NH_3 and phenol from aqueous solutions. In the LMP-process an emulsion of the membrane phase and the stripping phase is prepared. The emulsion type is water-in-oil. In the permeation step, this emulsion is dispersed in the waste water phase. The only difference between LMP and SLM is that the liquid membrane (extractant) is an emulsion and is not immobilised in a membrane. Rupert *et al.* (1988:1659) found that in this process harmful substances can be separated from the waste water and enriched by a factor of up to 1000 times the feed concentration. The most important problem with LMP is the osmosis effect. This effect causes water transport from the waste water through the organic membrane phase into the strip solution. This dilutes the product and the volume of the strip may increase by more than 100%. A LMP pilot plant for the recovery of nickel exists in a bicycle factory in Austria with a throughput of 150 liter per hour.

Gu and Wasan (1986:129) found that SLM extraction can be enhanced by the addition of anion ligands to the feed solution. The ligand effects on SLM are rationalised in terms of the labile nature of the ligand-metal complexes, the distribution coefficients of the metal ions, the interfacial and surface tensions and by the nuclear magnetic resonance (NMR) spectra of the metal-organic complexes.

The mechanism of ligand accelerated SLM extraction can be seen in figure 2.7. Gu and Wasan (1986:131) suggest that the water molecules in the hexa-aqueous nickel(II) complex, which were inert kinetically, were replaced by the ligand and the ligand-nickel(II) complex, which was labile kinetically, reacted quickly with the extractant, thus enhancing the reaction rate. Furthermore, the organic ligand has a hydrophobic-hydrophilic molecular structure. This is responsible for a surface active property, where the ligand-metal complex tends to populate at the aqueous-organic interface more than the hydrated metal ions do. This is favourable for the SLM process.

Gu and Wasan (1986:132) tested several ligands. Acetate gave the best results. The optimum acetate concentration was 0.10 mol/dm^3.

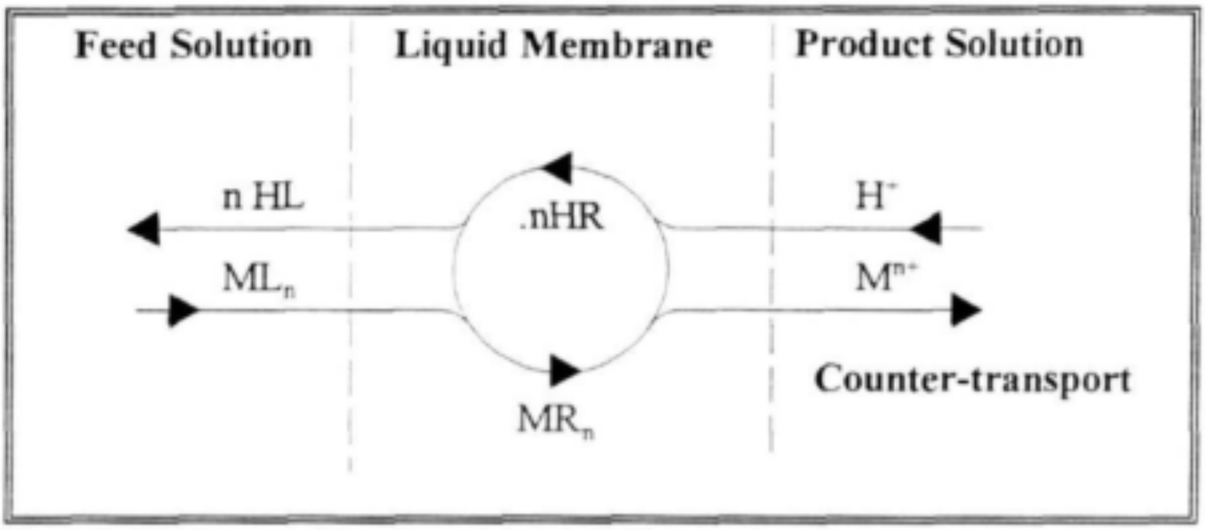


Fig. 2.7: Mechanism of ligand accelerated SLM extraction.

Abou-Nemeh and Van Peteghem (1992:149) investigated the metal extraction of a multi-component system with the use of SLM. Di-2-ethylhexyl phosphoric acid (D2EHPA) was used as a carrier with tri-n-butyl phosphate (TBP). The influence of TBP on the kinetics of metal extraction occupied a major part of the investigations. It was found that an optimum composition of extracting mixture exists (5.5 vol.% D2EHPA + 0.5 vol.%TBP) at which a maximum extraction efficiency can be achieved. It has also been proved that, although selectivity is relatively poor, it can be improved by varying the concentration of TBP in the membrane phase.

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.

2.6.1 The Flat film contactor

With this contactor (fig. 2.8) 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 fibre is essentially also a FFC, but Smit (1994:29) did not use this contactor in his evaluation due to its non-availability.

2.6.2 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 (fig. 2.9) 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 the MCC's small size no direct heating could be effected, but heating, dosing and measurements could be effected in the containers feeding the MCC.

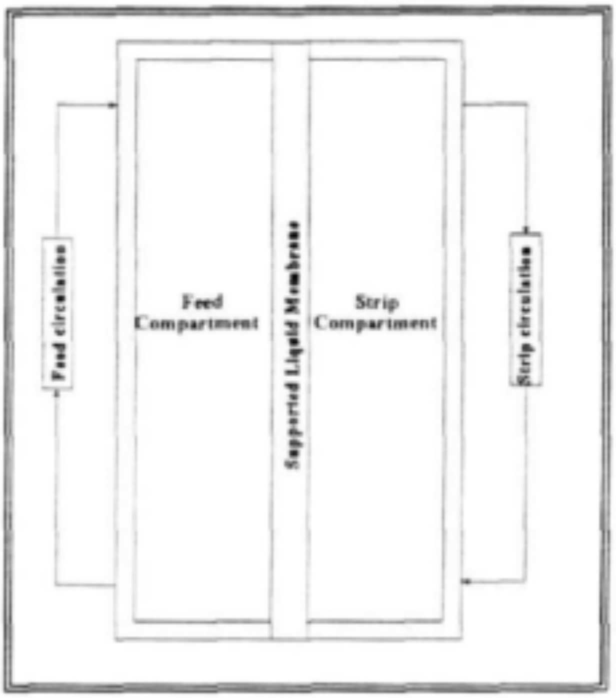


Fig. 2.8: Flat film contactor (FFC).

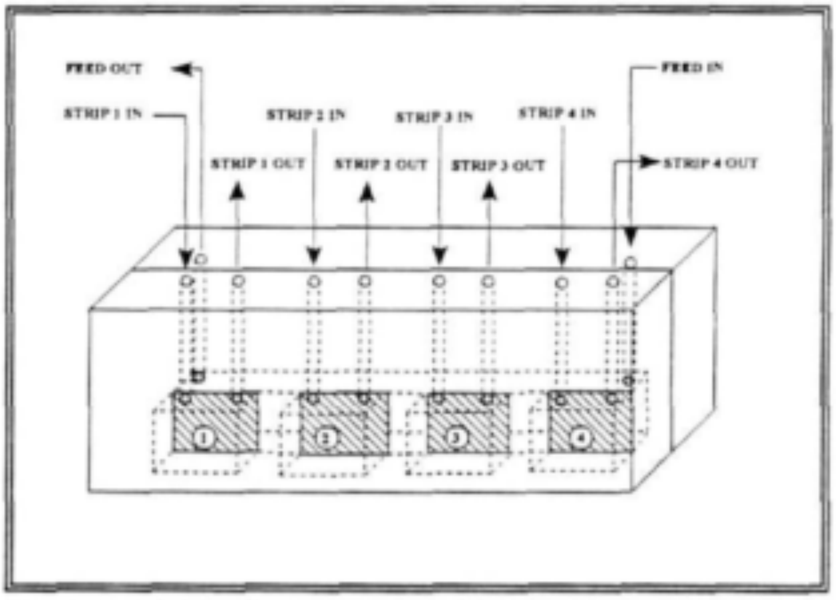


Fig. 2.9: Multi cell contactor (MCC).

2.6.3 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 2.10.

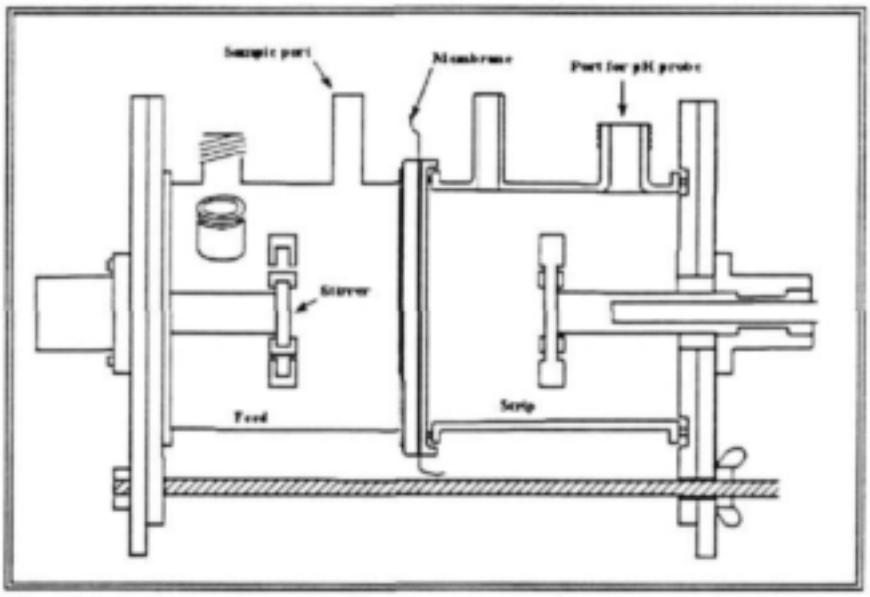


Fig. 2.10: Hydrodynamically characterised contactor (HCC).

2.6.4 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 precipitate and thus constitute 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 diagram of an SFC can be seen in figure 2.11.

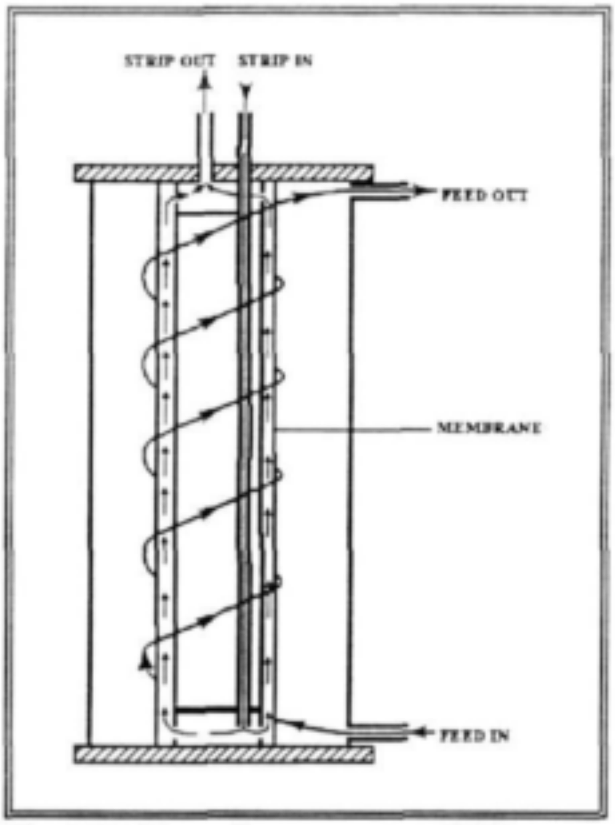


Fig. 2.11: Slurry flow contactor (SFC).

2.6.5 Spiral-type flowing liquid membrane

This type of contactor was developed by Matsuyama *et al.* (1990:237). In this type of contactor a liquid membrane solution containing an extractant flows in a thin channel between two hydrophobic microporous membranes which separate the membrane solution from the feed and strip solutions. A schematic diagram of the spiral type flowing membrane contactor is shown in figure 2.12.

Heavy metal ions were successfully recovered and concentrated from dilute solutions with this type of contactor. Furthermore, it was found that the selectivity of and the permeability could be controlled by adjusting the flow of the membrane solution. Such control of selectivity can only be accomplished by this type of contactor.

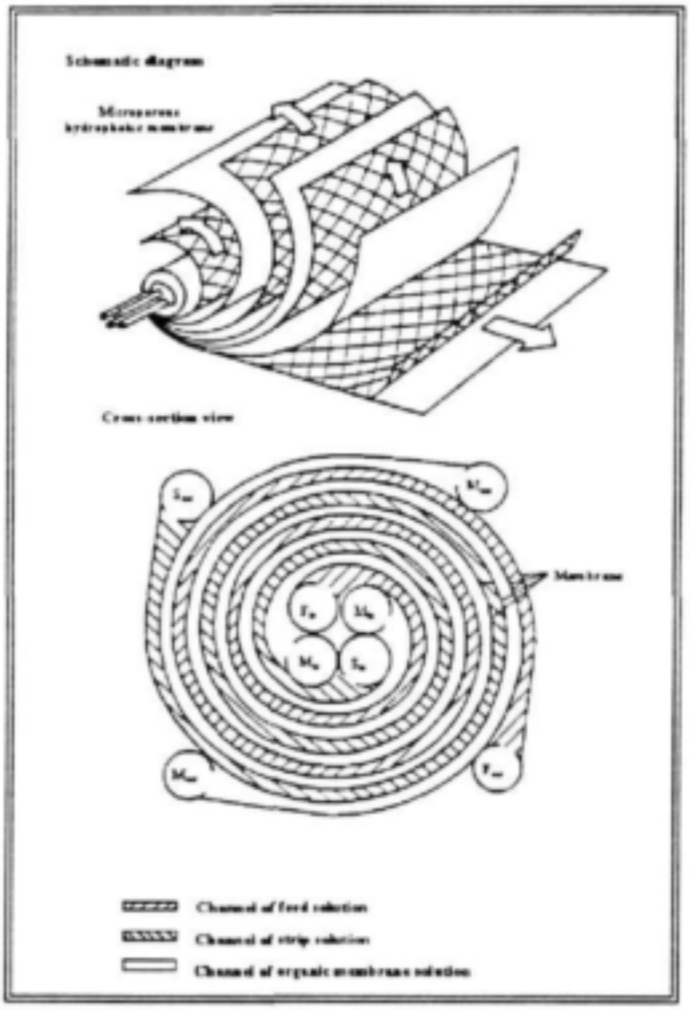


Fig. 2.12: Spiral-type flowing liquid membrane

2.6.6 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. If the capsules is saturated in the reticulation system, tank or dam it can be retrieved by straining followed by regeneration. The CME configuration is discussed in greater detail in chapter 3.2.

2.7 Conclusions

Nickel is a widely used metal and therefore subject to report in various effluents as a pollutant. The extraction of nickel at the current price (R 31.76/kg) 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 are expected to contribute to the general field of demineralization.

It is clear from the literature that nickel can be extracted from effluents with the use of SLM. Di-2(ethylhexyl) phosphoric acid (D2EHPA) is an efficient extractant for nickel and it is clear that extraction is strongly driven by a pH gradient between the feed and strip solution (Erlank, 1994:96).

Supported liquid membranes (SLM), even though they have passed the stage of scientific curiosity, has found little application in industry as yet. This can be contributed to the following problems:

1. The rate of extraction obtained with SLM is relatively low (0.147 $g/m^2 \cdot h$ by Verhaege *et al.*, 1987:337). This rate can be increased with the addition of anion ligands (Fu and Wasan, 1986:129).
2. A big disadvantage of SLM is the loss of the extractant from the membrane structure (Bromberg *et al.* 1992:41).
3. The sophistication of the various SLM reactors (with the exception of CME) implies high cost to manufacture, maintain and operate.

It was suspected that the above mentioned problems could be overcome with the use of CME, resulting in an economically viable process to recover nickel from industrial waste effluents.

Chapter 3
Characterisation of CME

3.1 Introduction

The first step in the systematic approach to design (Level 0) is to gather all the input information (fig. 3.1). The information which must normally be gathered at the initial stages of a design problem are (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 under different conditions. The dissertation by Erlank (1994:83) confirmed the feasibility of the CME process, but a characterisation and optimisation of process conditions still has to be done.

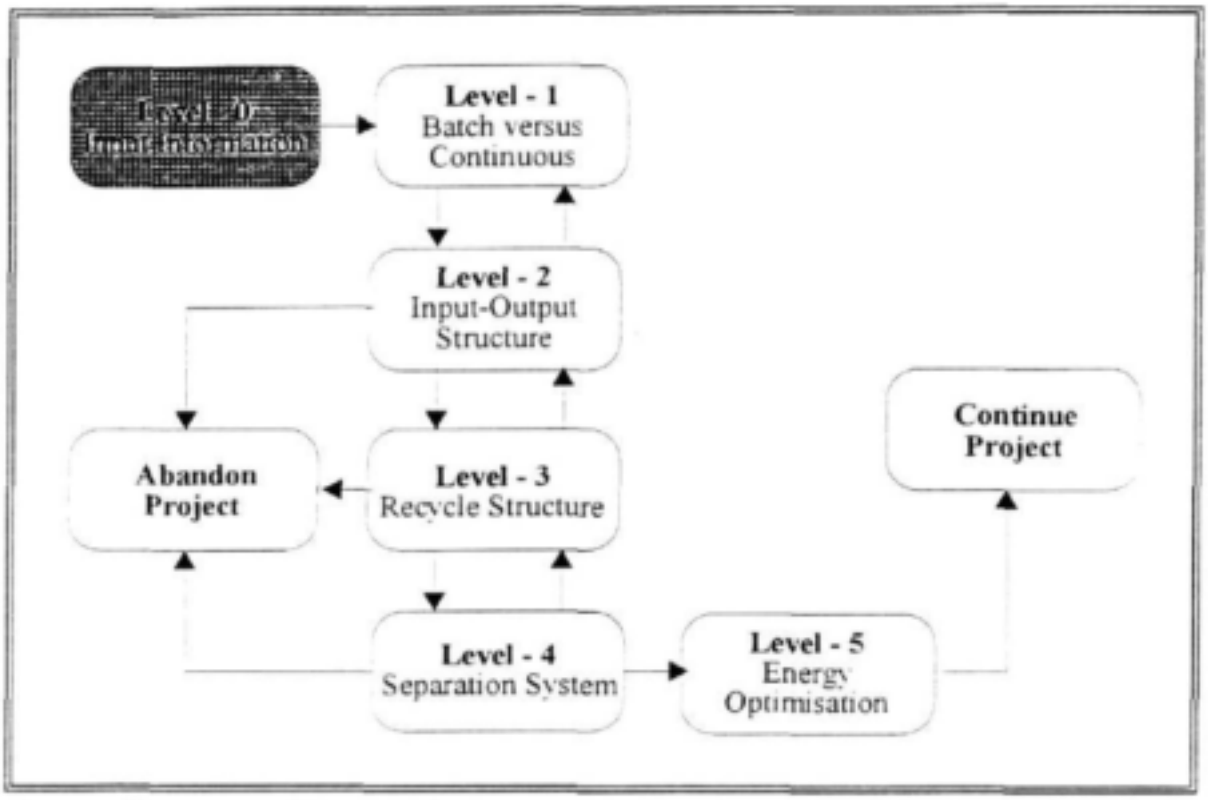


Fig. 3.1: Flowchart of hierarchial process design.

The purpose of this research in this chapter was to determine the influence of conditions like the pH and nickel concentration of the feed solution and the hydronium and nickel concentration of the strip solution on capsulated membrane extraction. Another objective was to determine the optimum extractant concentration and the influence of the above mentioned conditions on this optimum. These results could be used to determine the similarity (if any) between CME and SLM.

The research was focused on high hydronium strip concentrations, which is a prominent advantage of CME over SLM.

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 pores. The excess extractant (on the outside) 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 (refer to fig. 3.2). 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 sealed edges did not leak since that would defeat the integrity of the extraction system.

Photograph 3.1: Experimental configuration.

Photograph 3.2: Membrane Capsule.

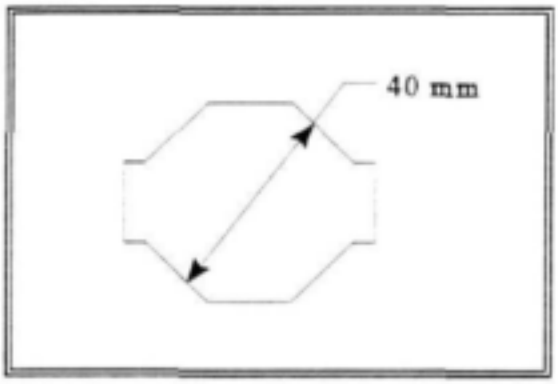


Fig. 3.2: Diagram of membrane capsule.

3.2.1 The Membrane

The hydrophobic organic phase forming the liquid membrane was immobilized within the pores of a Celgard® 4510 film (Celanese Separations Products, 1985:1). 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. The properties of the membrane are listed in table 3.1. Photograph 3.3 shows an enlargement (20 000×) of the membrane. 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.

Table 3.1: Properties of Celgard® 4510 film.

Property	**Value**
Nominal thickness	0.13 mm
Basis weight	30 g/m^2
Break strength	3.0×10^3 N/m
Tear initiation	13 N
Tear propagation	2.4 N
Porosity	45 %
Pore diameter	0.04 μm

Photograph 3.3: Celgard® 4510 film (20000× enlarged).

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 was 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 hydrophilic functional group is the phosphorous double bond to an oxygen and the monovalent bond to an hydroxyl 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.

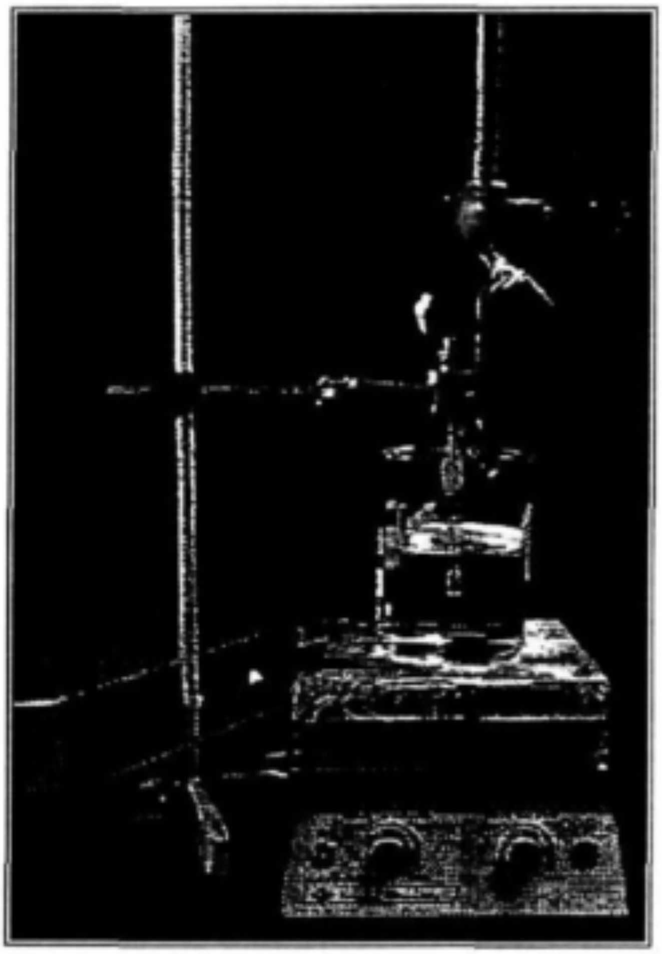
In general, heavier rare earth metals extract better than lighter metals. D2EHPA is mostly used in the extraction of Zn, Be, Cu, In, Ga, V, ect. and in the separation of copper from nickel in aqueous solutions.

The loss of the extractant from the membrane structure (a big disadvantage of SLM) is a minor problem with the extraction of nickel, because both the extractant (D2EHPA) and the membrane (Celgard® 4510) are highly hydrophobic.

3.3 Experimental procedure

An experimental design was performed to establish the conditions under which each experiment was to be performed (See paragraph 3.4). A beaker was filled with a feed solution of known pH and concentration. The prepared capsule, as explained in 3.2, was dropped into the filled beaker. The capsule was suspended in the feed solution with a piece of string (see photograph 3.1).

Samples were taken from the feed solution at five hour intervals for the first 25 hours with a micropipette. The pH of the feed solution was readjusted to the initial pH every two hours (see photograph 3.4) during the first 25 hours of the experiment with a diluted sodium hydroxide solution. The nickel concentration was readjusted every five hours (if extraction occured) to the initial nickel feed concentration with a 10 000 mg/dm^3 nickel solution. An example of the measuring results can be seen in table 3.2.



Photograph 3.4: Adjustment of pH.

Table 3.2: An example of measuring results.

Time (h)	**[Ni]$_{feed}$** (mg/dm^3)	**Volume (feed solution)** (dm^3)	**Adjustment with 10 g/dm^3 [Ni]** (dm^3×10^3)
0	1145	.405	0.0
5	1010	.400	0.0
10	912	.395	3.0
15	962	.390	1.0
20	1000	.390	0.0
25	938	.380	1.0
50	885	.400	-

The area of the membrane capsule was approximated as the area of a circle with the same circumference as the membrane capsule:

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

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

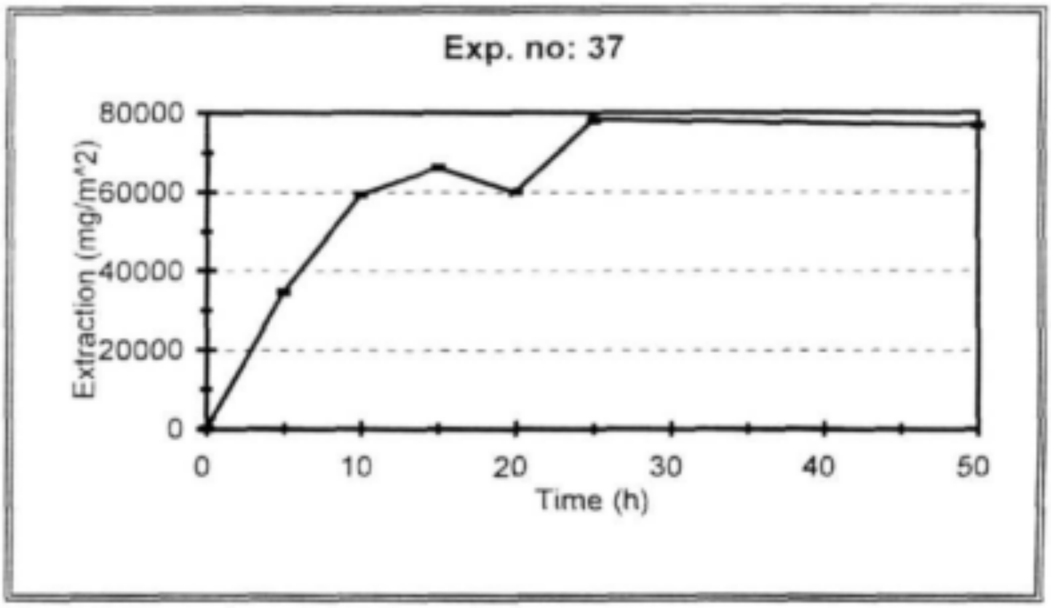


Fig. 3.3: Extraction of nickel over 50 hours.

3.4 The central composite experimental design

3.4.1 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:

7. The pH of the feed solution.
8. The hydronium concentration of the stripping solution.
9. The nickel concentration in the feed.
10. The nickel concentration in the strip.
11. The volume percentage of extractant in the membrane.
12. 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.

3.4.2 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 3.3. Table 3.4 shows the real values assigned to each factor.

Table 3.3: Design summary ($2^{(5-0)}$ second order central composite design).

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 3.3.a: Design summary.

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 3.3.b: 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

3.4.2 Determining the values for the factors

The first step to determine the values (variables) 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 3.4, represented in their transferred real values.

Table 3.4: The values of the experimental factors.

Factors	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%

3.4.4 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 second method.

3.5 Results

3.5.1 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. 3.2). This information was used to fit the following equation through the data:

$$Extr_{Ni} = a - b e^{-ct} \tag{3.2}$$

In this equation a, b and c are constants for every experiment. Extr$_{Ni}$ is the cumulative extraction of nickel (mg/m^2) with CME and t is the time (hours). 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 A.1.

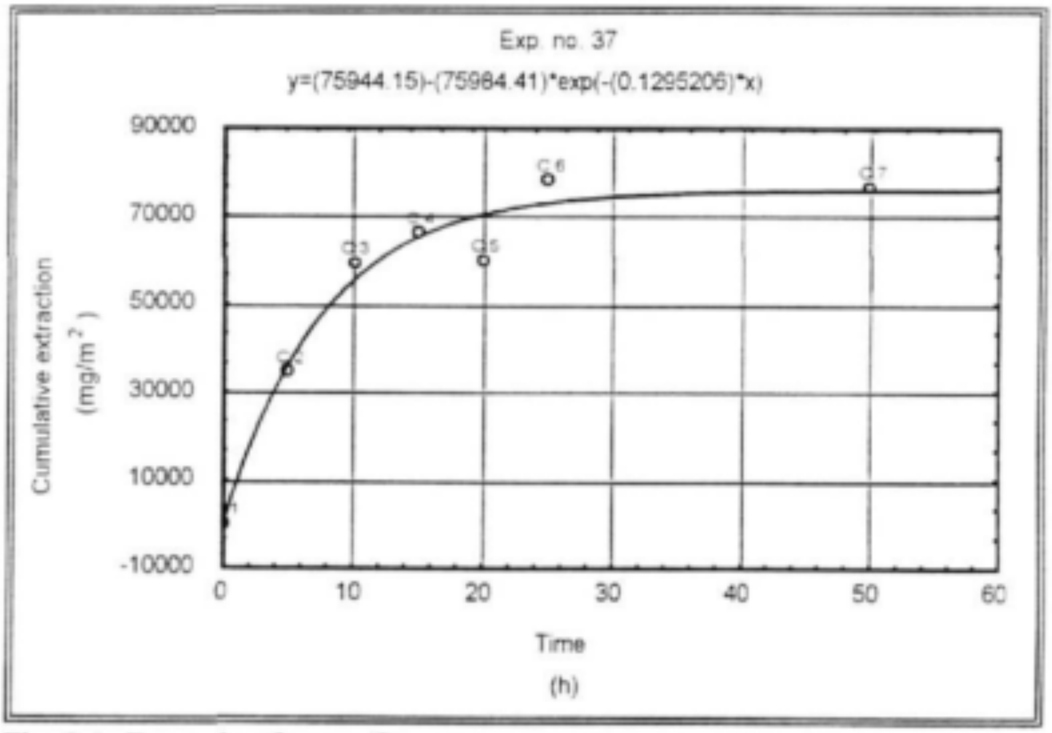


Fig. 3.4: Example of curve fit.

The maximum extraction of each experiment can be obtained from equation 3.2 by calculating Extr_{Ni} at $t=\infty$ and by subtracting Extr_{Ni} at $t=0$:

$$\begin{aligned} Extr_{\max} &= Extr_{Ni,\infty} - Extr_{Ni,0} \\ &= \left(a - b\,e^{-c\,\infty}\right) - \left(a - b\,e^{-c\,0}\right) \\ &= \left(a - b(0)\right) - \left(a - b(1)\right) \\ &= (a) - (a - b) \\ &= b \end{aligned} \tag{3.3}$$

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

$$\begin{aligned} Rate &= \tfrac{d}{dt}\left(a - b\,e^{-c\,t}\right) \\ &= b\,c\,e^{-c\,t} \\ If\ t &= 0: \\ Rate &= b\,c\,(1) \\ &= b\,c \end{aligned} \tag{3.4}$$

3.5.2 Results and discussion

The main effects and interaction of the different factors on the maximum (final) extraction (g/m^2 nickel) were evaluated. Two obvious outlier data points were overlooked and the following second order function was fitted through the remaining data:

$$\begin{aligned} Extr_{Max} = {} & -31.721\,pH - 6.959\,[H]_s + 0.4892\,[Ni]_f - 3.604\times10^{-3}\,[Ni]_s \\ & + 13.502[Ex] - 1.997\times10^{-2}\,pH^2 + 0.1868\,[H]_s^2 - 7.537\times10^{-5}[Ni]_f^2 \\ & + 2.329\times10^{-5}[Ni]_s^2 - 2.121\times10^{-2}\,[Ex]^2 - 0.2545\,pH\,[H]_s \\ & + 2.003\times10^{-2}\,pH\,[Ni]_f + 1.405\times10^{-3}\,pH\,[Ni]_s + 0.2433\,pH\,[Ex] \\ & + 2.080\times10^{-3}\,[H]_s[Ni]_f + 1.641\times10^{-3}\,[H]_s[Ni]_s - 4.974\times10^{-2}\,[H]_s[Ex] \\ & + 9.793\times10^{-5}\,[Ni]_f[Ni]_s - 8.458\times10^{-3}\,[Ni]_f[Ex] \\ & - 2.896\times10^{-3}[Ni]_s[Ex] - 503.445 \end{aligned} \tag{3.5}$$

The accuracy of this equation will be discussed in paragraph 3.5.3.

In similar fashion, three outlier data points were overlooked and the following second order function was fitted through the remaining data:

$$\begin{aligned} Rate = & - 0.5464\,pH - 3.065\,[H]_s - 2.653\times10^{-2}\,[Ni]_f + 1.155\times10^{-2}\,[Ni]_s \\ & - 4.875\times10^{-2}[Ex] + 0.1259\,pH^2 + 2.198\times10^{-2}\,[H]_s^2 + 1.237\times10^{-5}[Ni]_f^2 \\ & + 1.136\times10^{-6}[Ni]_s^2 + 2.499\times10^{-4}\,[Ex]^2 + 1.052\times10^{-2}\,pH\,[H]_s \\ & + 1.857\times10^{-3}\,pH\,[Ni]_f + 1.907\times10^{-4}\,pH\,[Ni]_s - 3.747\times10^{-2}\,pH\,[Ex] \\ & + 3.710\times10^{-4}\,[H]_s\,[Ni]_f - 8.814\times10^{-5}\,[H]_s\,[Ni]_s + 2.996\times10^{-2}\,[H]_s\,[Ex] \\ & - 3.684\times10^{-6}\,[Ni]_f\,[Ni]_s - 2.466\times10^{-4}\,[Ni]_f[Ex] \\ & - 2.711\times10^{-4}[Ni]_s\,[Ex] + 42.817 \end{aligned} \tag{3.6}$$

The experimental data together with calculated data for equation 3.5 and equation 3.6 are given in table 3.5. The data points which were overlooked are printed in bold italics.

Table 3.5: Observed and predicted data.

Exp. No	pH_{feed}	$[H]_{strip}$ (mol/dm^3)	$[Ni]_{feed}$ (mg/dm^3)	$[Ni]_{strip}$ (mg/dm^3)	[Ex] (Vol %)	Max. Extraction (g/m^2)	Eq. 3.5 (g/m^2)	Rate of Extraction (g/m^2.h)	Eq. 3.6 (g/m^2.h)
1	2.50	11	800	689	55	27.028	34.994	3.548	5.257
2	4.50	11	800	689	55	20.481	26.421	3.716	5.272
3	2.50	25	800	689	55	41.307	23.633	1.354	0.168
4	4.50	25	800	689	55	12.998	7.934	2.090	0.477
5	2.50	11	1200	689	55	43.951	40.474	***11.570***	***3.621***
6	4.50	11	1200	689	55	55.449	47.924	5.432	5.121
7	2.50	25	1200	689	55	11.833	40.761	0.522	0.609
8	4.50	25	1200	689	55	34.593	41.085	3.431	2.403
9	2.50	11	800	1689	55	21.351	27.401	9.425	7.053
10	4.50	11	800	1689	55	25.002	21.638	8.592	7.448
11	2.50	25	800	1689	55	44.854	39.014	***36.472***	***0.729***
12	4.50	25	800	1689	55	15.546	26.125	0.720	1.419
13	2.50	11	1200	1689	55	73.543	72.053	6.525	6.890
14	4.50	11	1200	1689	55	95.259	82.313	11.034	8.771
15	2.50	25	1200	1689	55	100.669	95.314	***12.795***	***2.644***
16	4.50	25	1200	1689	55	***35.367***	***98.448***	4.132	4.820
17	2.50	11	800	689	65	61.545	57.556	3.913	3.588
18	4.50	11	800	689	65	53.159	53.848	4.310	2.853
19	2.50	25	800	689	65	13.349	39.231	0.790	2.693
20	4.50	25	800	689	65	24.306	28.398	1.355	2.252
21	2.50	11	1200	689	65	35.946	29.203	1.544	0.965
22	4.50	11	1200	689	65	23.987	41.520	0.947	1.716
23	2.50	25	1200	689	65	25.058	22.527	1.300	2.147
24	4.50	25	1200	689	65	36.574	27.717	1.600	3.192

Table 3.5.a: Observed and predicted data.

Exp. No	pH_{feed}	$[H]_{strip}$ (mol/dm^3)	$[Ni]_{feed}$ (mg/dm^3)	$[Ni]_{strip}$ (mg/dm^3)	[Ex] (Vol %)	Max. Extraction (g/m^2)	Eq. 3.5 (g/m^2)	Rate of Extraction (g/m^2.h)	Eq. 3.6 (g/m^2.h)
25	2.50	11	800	1689	65	27.577	21.003	1.466	2.672
26	4.50	11	800	1689	65	33.407	20.105	1.680	2.319
27	2.50	25	800	1689	65	20.108	25.652	0.586	0.543
28	4.50	25	800	1689	65	20.882	17.629	1.218	0.484
29	2.50	11	1200	1689	65	19.630	31.822	0.744	1.523
30	4.50	11	1200	1689	65	45.106	46.949	1.710	2.655
31	2.50	25	1200	1689	65	52.292	48.120	2.190	1.471
32	4.50	25	1200	1689	65	50.323	56.120	4.542	2.898
33	3.50	18	1000	1189	60	29.293	28.993	1.021	1.033
34	3.50	18	1000	1189	60	27.099	28.993	0.696	1.033
35	1.12	18	1000	1189	60	38.108	29.221	1.643	0.889
36	5.88	18	1000	1189	60	24.893	28.539	1.624	2.603
37	3.50	1.351	1000	1189	60	75.984	82.074	9.842	10.007
38	3.50	34.649	1000	1189	60	90.780	79.470	4.185	4.244
39	3.50	18	524	1189	60	***48.129***	***-14.246***	3.317	3.373
40	3.50	18	1475	1189	60	43.321	38.096	4.114	4.286
41	3.50	18	1000	0	60	63.957	49.547	3.013	1.747
42	3.50	18	1000	2378.2	60	65.140	74.304	2.041	3.532
43	3.50	18	1000	1189	48.1	35.956	37.751	1.234	3.205
44	3.50	18	1000	1189	71.9	21.263	14.229	0.678	-1.068
45	3.50	18	1000	1189	60	28.085	28.993	1.030	1.033
46	3.50	18	1000	1189	60	35.090	28.993	1.201	1.033

The main effects and interaction of different factors on the maximum (final) extraction (g/m^2) and the rate of extraction (g/m^{2}h) will subsequently be discussed in greater detail.

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

The effect of the pH of the feed solution and the hydronium ion concentration of the strip solution on the final extraction of nickel 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 the hydronium ion concentration in the strip solution up to a point where the hydronium ion concentration is approximately 16 mol/dm^3. If the hydronium concentration is further increased, the final amount of extraction also increases. This result can be explained by the fact that the hydronium is transported through the membrane with the complexation reaction and the diffusion of hydronium through the membrane. If the hydronium ion concentration is increased, the rate of diffusion increases and less hydronium ions are available for the complexation reactions. At the point of approximately 16 mol/dm^3 (44.4 vol%) maximum diffusion of hydronium ions occurs. If the concentration of the sulfuric acid is further increased, the acid does not dissociate completely and the undissociated acid forms a hydronium ion reserve.

This theory is supported by the following:

1. At low hydronium ion 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 hydronium ion concentrations, the diffusion of hydronium is the controlling factor. The diffusion of hydronium ions is promoted by a high pH and less hydronium is available for the complexation reaction. The result is that at high hydronium concentrations, the maximum extraction occurs at low pH.
2. The capsules bulged during the experiment. This is an indication that osmosis has occurred.
3. At certain periods during the experiment retro-extraction occurred (fig. 3.4). This phenomenon was noted in all 46 experiments as well as in the experiments done by Erlank (1994) and Steyn & Janse van Rensburg (1994).

No conformation of this result could be found in the literature and further research on this phenomenon will be discussed in the following chapter.

The effect of the pH of the feed solution and the hydronium ion concentration of the strip solution on the initial rate of extraction can be seen in figure 3.6. The general shape of the plot is the same as for the final extraction, but the turning point for the minimum initial rate of extraction is at a hydronium ion concentration of approximately 21 mol/dm^3.

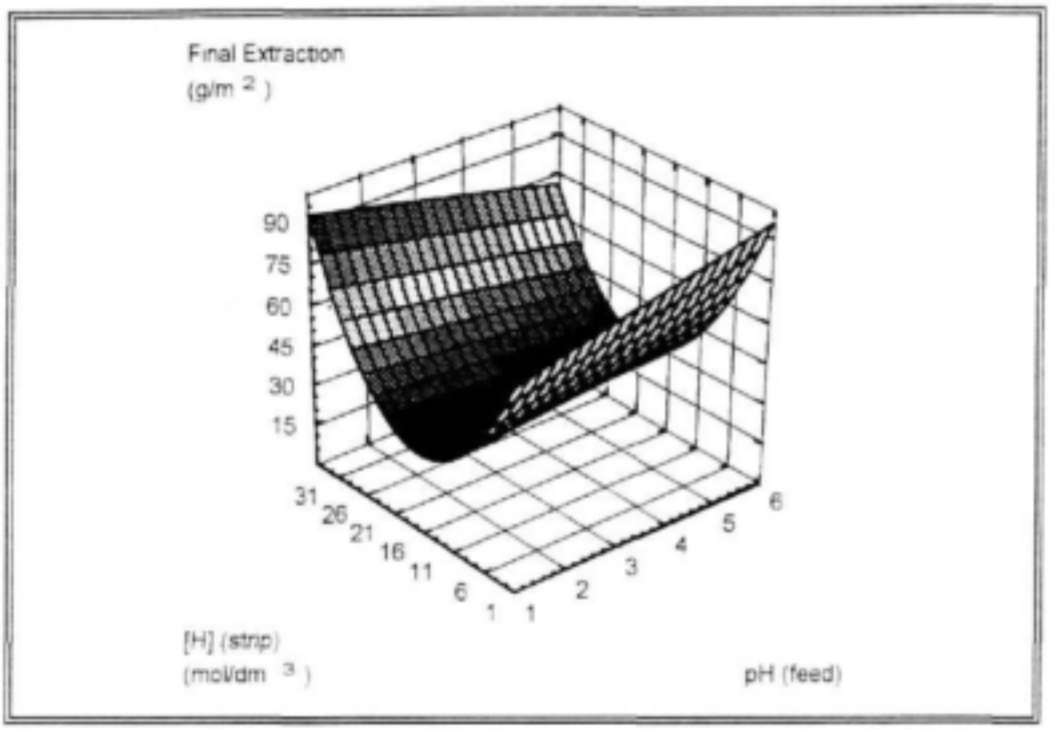


Fig. 3.5: The effect of pH_{feed} and $[H^+]_{strip}$ on the final extraction of nickel.

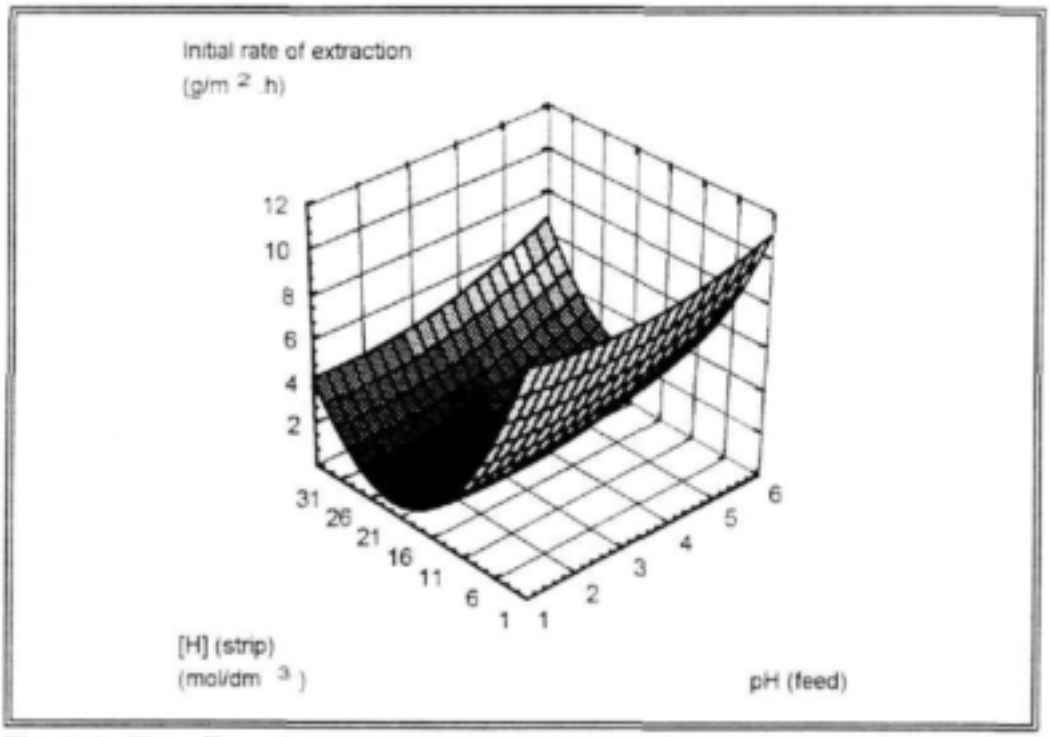


Fig. 3.6: The effect of pH_{feed} and $[H^+]_{strip}$ on the initial rate of nickel extraction.

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

The effect of the pH of the feed solution and the nickel concentration of the feed solution on the final extraction can be seen in figure 3.7 and the effect of these two factors on the initial rate of extraction can be seen in figure 3.8. It is clear that the amount of nickel which can be extracted, as well as the initial rate of extraction increase with an increase in the pH of the feed solution and the nickel concentration of the feed solution. This result is confirmed by Verhaege *et al.* (1987:333), who derived the following equation from conventional liquid-liquid equilibrium expressions:

$$\frac{[Ni^{2+}]_{feed}}{[Ni^{2+}]_{strip}} = \left(\frac{[H^{+}]_{feed}}{[H^{+}]_{strip}}\right)^2 \qquad (3.7)$$

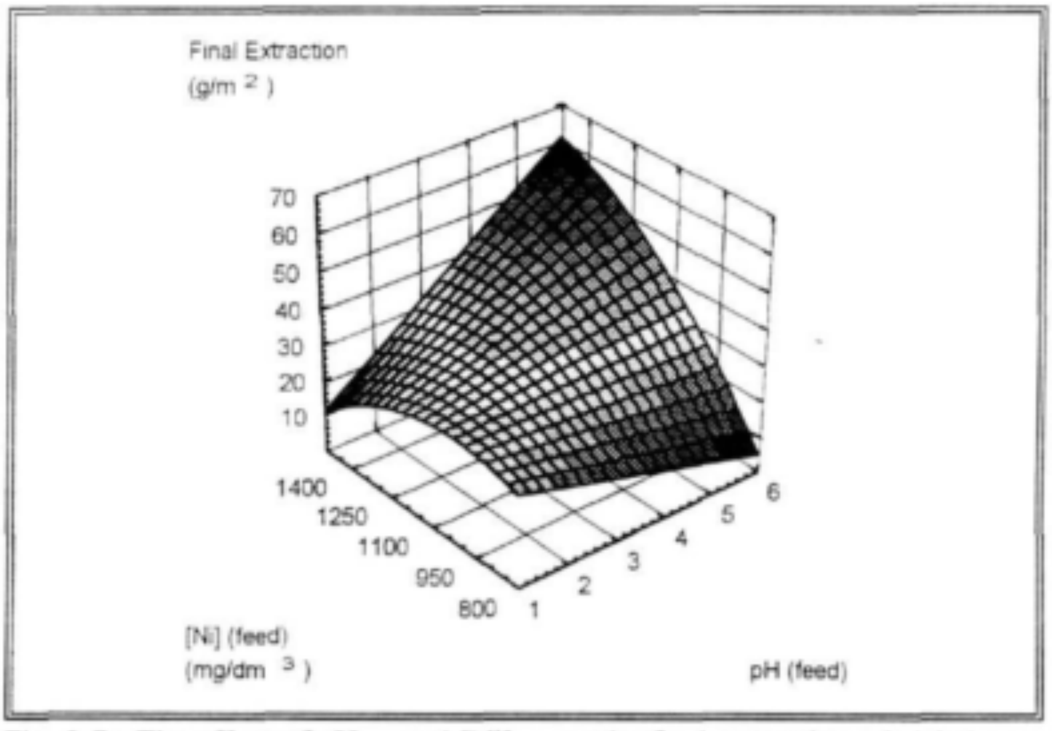


Fig. 3.7: The effect of pH_{feed} and $[Ni]_{feed}$ on the final extraction of nickel.

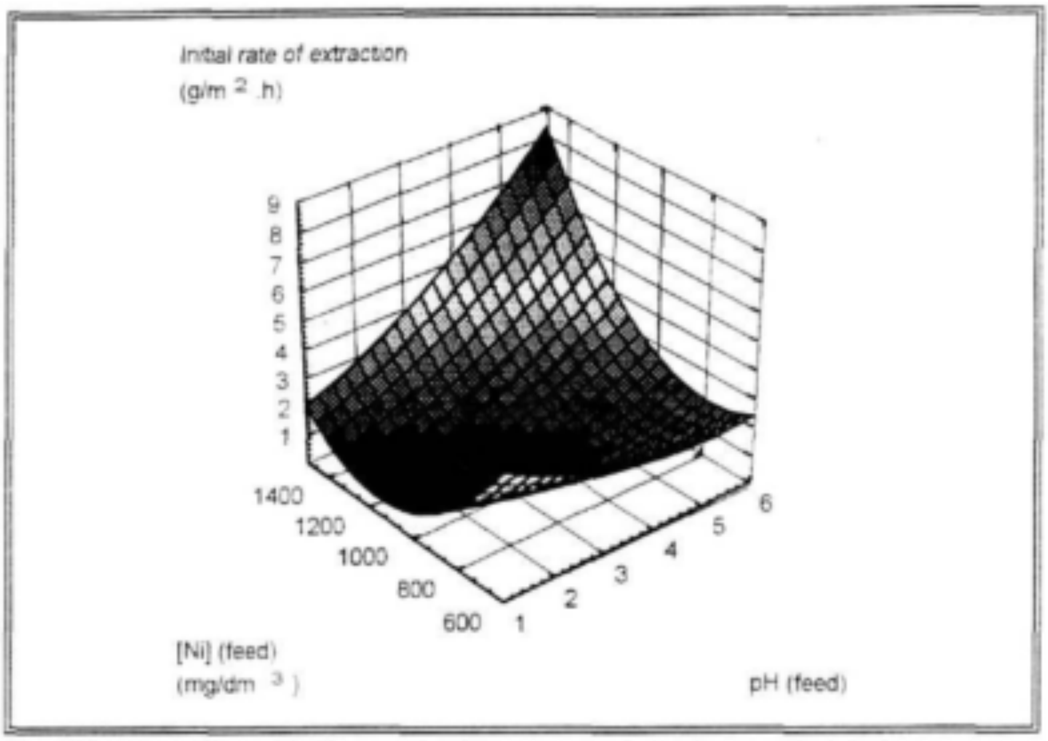


Fig. 3.8: The effect of pH_{feed} and $[Ni]_{feed}$ on the initial rate of nickel extraction.

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

The effect of these two factors on the final and initial rate of extraction can be seen in figures 3.9 and 3.10 respectively. It seems as if there is a point (± 1000 mg/dm^3) where the nickel concentration of the strip solution results in a minimum final extraction. If the nickel concentration of the strip solution is further increased, the final amount of nickel extracted also increases. This result contradicts previous results in literature, but can be explained by the following theory:

The extraction conditions in figures 3.9 and 3.10 was a hydronium ion concentration in the strip solution of 18 mol/dm^3, the nickel concentration in the feed solution was 1000 mg/dm^3 and the extractant concentration was 60 vol.% D2EHPA in Escaid. At these conditions osmosis has a large effect on the final and initial rate of extraction (refer to paragraph 3.5.2.1). The osmotic pressure is influenced by the dissolved ionic species (hydronium and nickel) in the feed and strip solution. If the nickel concentration of the strip solution is increased above the nickel concentration of the feed solution (1000 mg/dm^3 in figures 3.9 and 3.10) the osmotic pressure

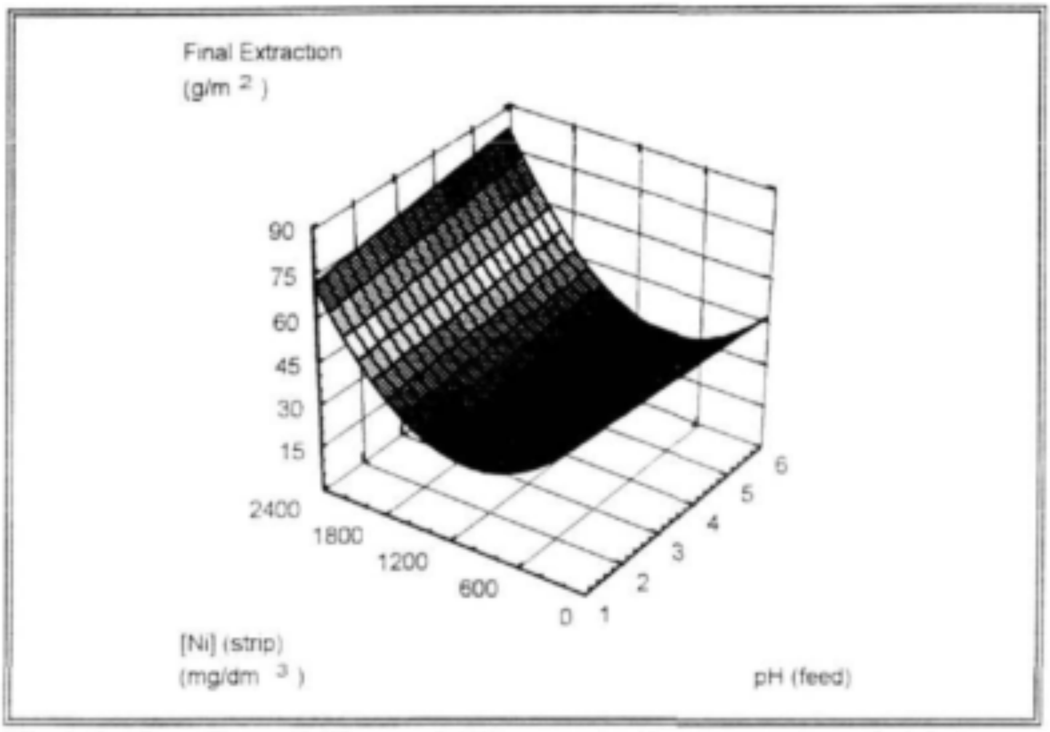


Fig. 3.9: The effect of pH_{feed} and $[Ni]_{strip}$ on the final extraction of nickel.

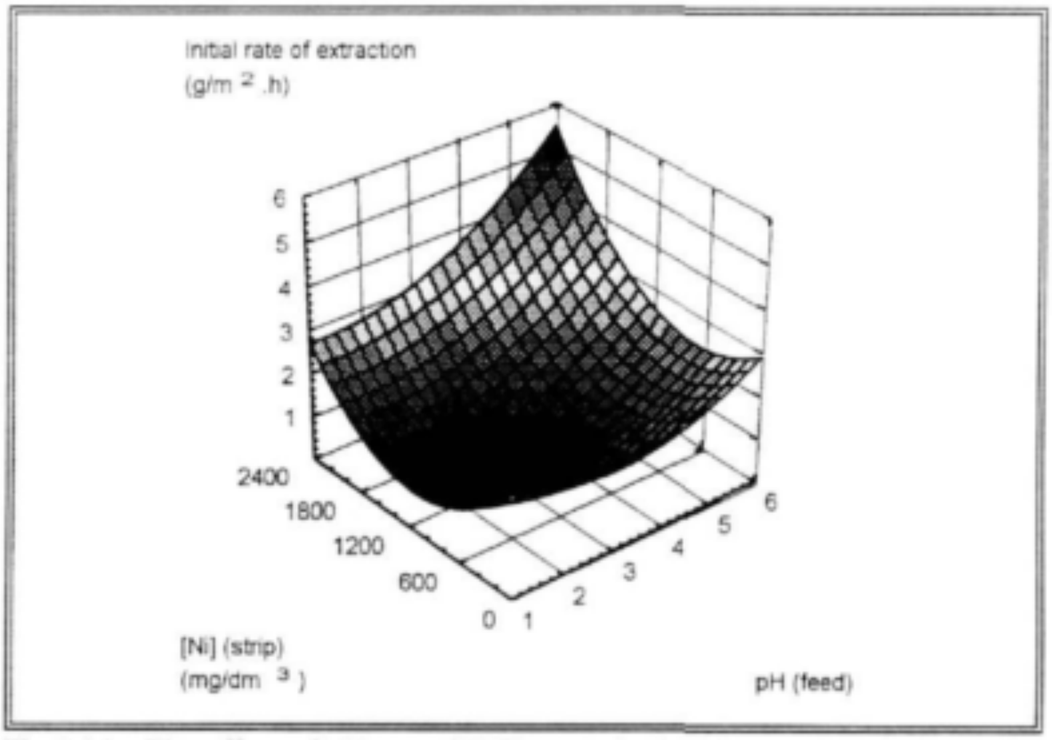


Fig 3.10: The effect of pH_{feed} and $[Ni]_{strip}$ on the initial rate of extraction.

difference across the membrane will also increase. This will result in a higher inflow of water into the membrane capsule and a subsequent dilution of the strip solution. It is clear from figure 3.5 (refer to paragraph 3.5.2.1) that a hydronium ion concentration below 18 mol/dm^3 is advantageous for the extraction of nickel. To summarise: an increase of the nickel concentration of the strip solution above 1000 mg/dm^3 at the above mentioned conditions, resulted in a higher osmotic flow of water into the membrane capsule. This resulted in a dilution of the hydronium ion concentration of the strip solution, which led to an increase in the final amount and initial rate of nickel extracted.

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

The effect of these two factors on the final extraction and initial rate of extraction can be seen in figures 3.11 and 3.12 respectively. At a lower feed pH, the optimum extractant concentration is also lower, at a higher feed pH the opposite happens. It is also clear that the initial rate of nickel extraction is higher at a high pH of the feed solution.

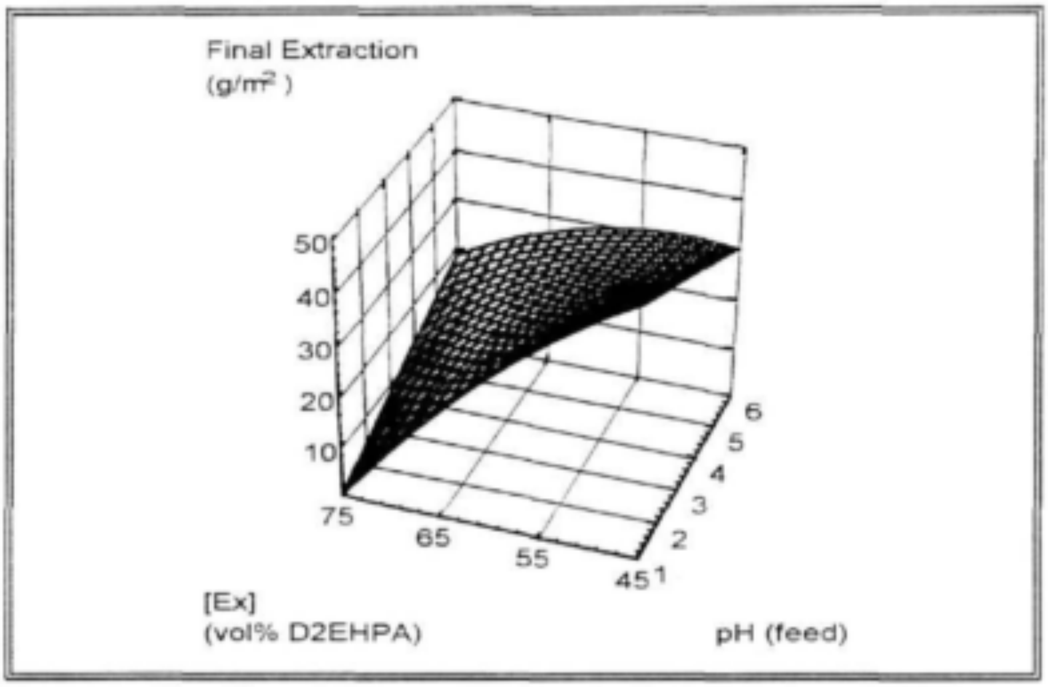


Fig. 3.11: The effect of pH_{feed} and [Ex] on the final extraction of nickel.

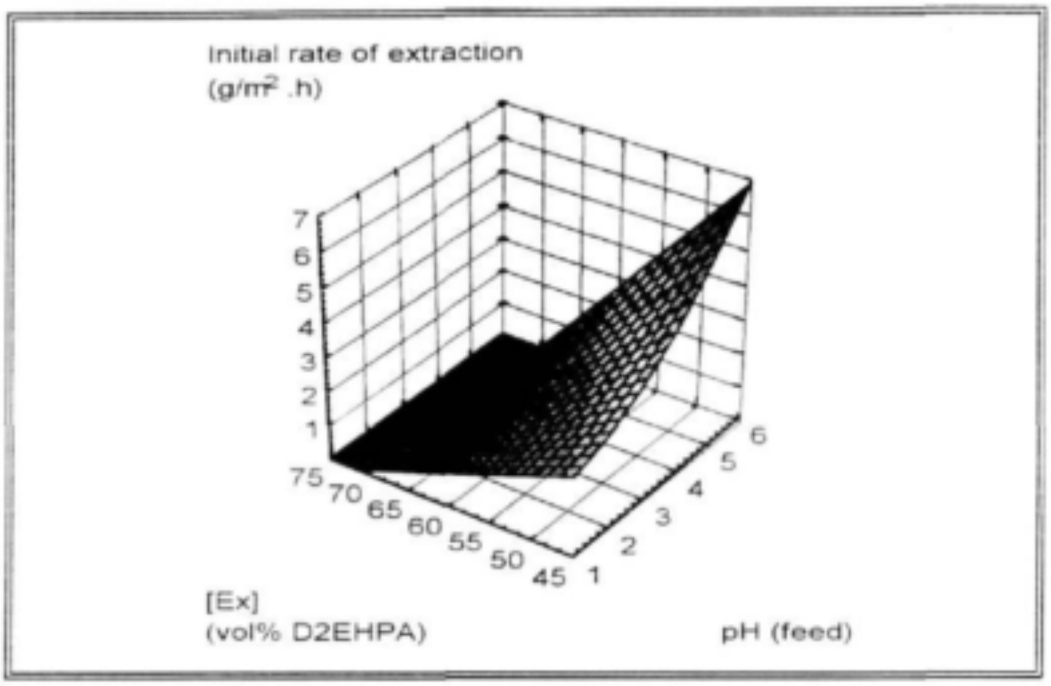


Fig. 3.12: The effect of pH_{feed} and [Ex] on the initial rate of extraction.

Verhaege *et al.* examined the influence of membrane composition on mass transfer at the following conditions (Table 3.6):

Table 3.6: Condition of experiments by Verhaege *et al.*

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

They found that the optimum extractant composition is 60% (vol.) D2EHPA in Solvesso 150 (refer to fig. 2.5). If a feed solution pH of 4.46, a hydronium strip concentration of 1.5 mol/dm^3, a nickel feed concentration of 1.4 g/dm^3 and a nickel strip concentration of 0 g/dm^3 are substituted into equation 3.5, the following equation results:

$$Extr = 9.551 + 2.671\,[Ex] - 2.121\times10^{-2}\,[Ex]^2 \tag{3.8}$$

The optimum extractant concentration can be obtained by differentiating equation 3.8:

$$\frac{d\,Extr}{d\,[Ex]} = 0 = 2.671 - 4.242\times10^{-3}\,[Ex] \qquad (3.9)$$

The optimum extractant concentration, at the above mentioned conditions, is 62.973 Vol% D2EHPA dissolved in Escaid 100 (see also fig.3.13).

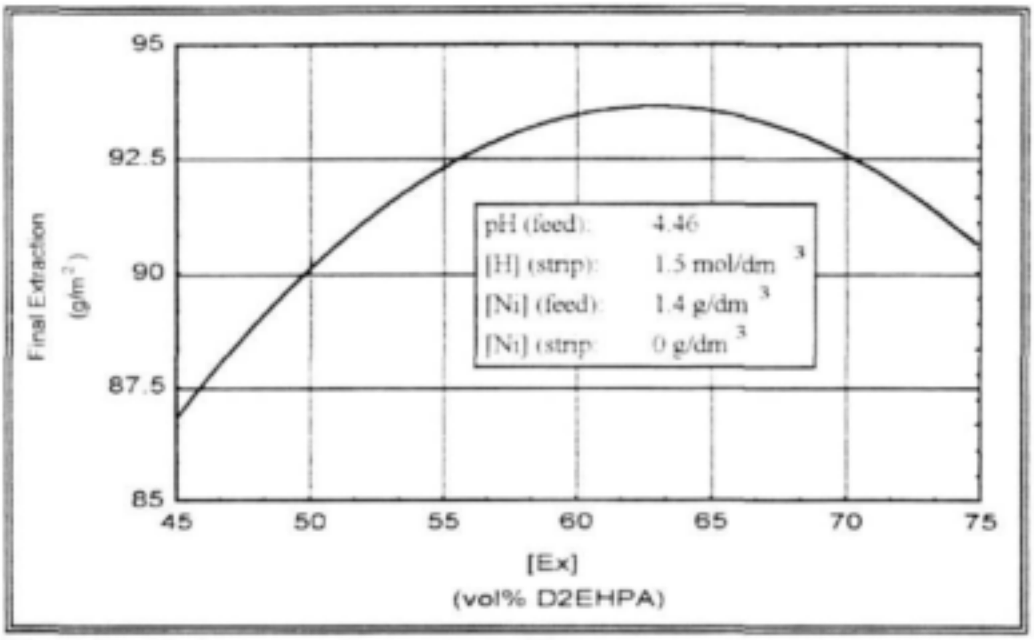


Fig. 3.13: Optimum membrane composition.

It can therefore be concluded that the results are compatible with the results of Verhaege *et al.*(1987:331). It is important to note that the optimum extractant concentration is very dependant on the nickel concentrations of the feed and strip solutions (refer to figures 3.22 and 3.24 in paragraph 3.5.2.9 and 3.5.2.10).

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

The effect of these two factors on the final extraction and initial rate of extraction can be seen in figures 3.14 and 3.15 respectively. The final amount of extraction and the initial rate of extraction is a maximum at high and low hydronium ion 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 (±16 mol/dm^3 for the final extraction and ± 21 mol/dm^3 for the initial rate of extraction).

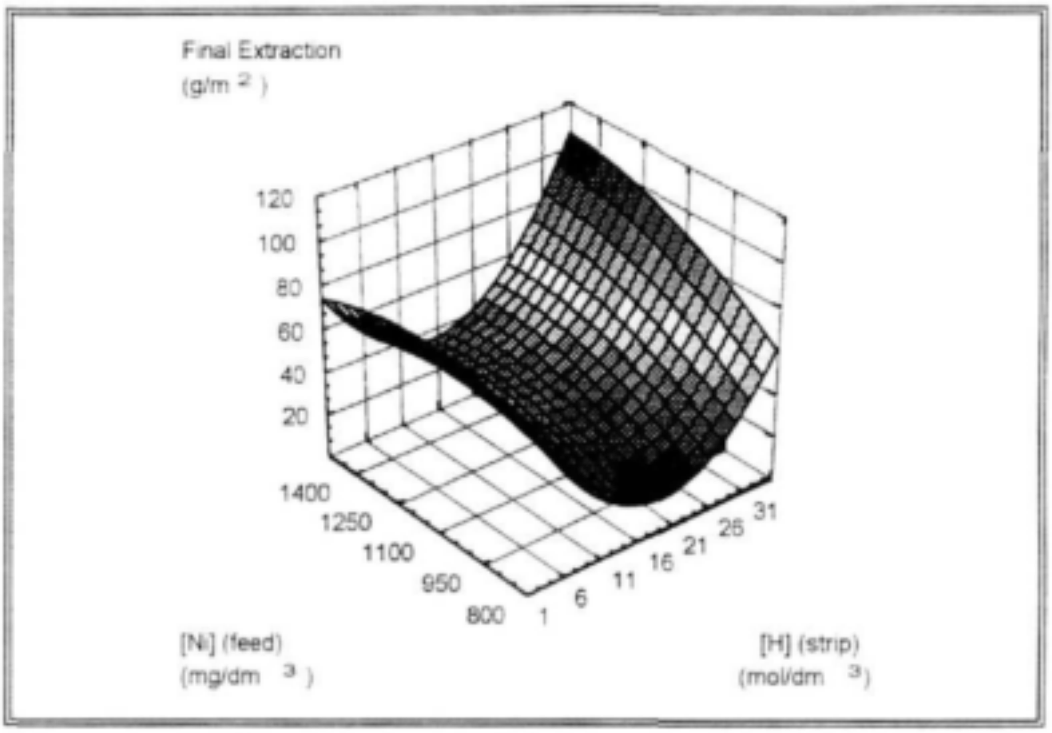


Fig. 3.14: The effect of $[H^+]_{strip}$ and $[Ni]_{feed}$ on the final extraction of nickel.

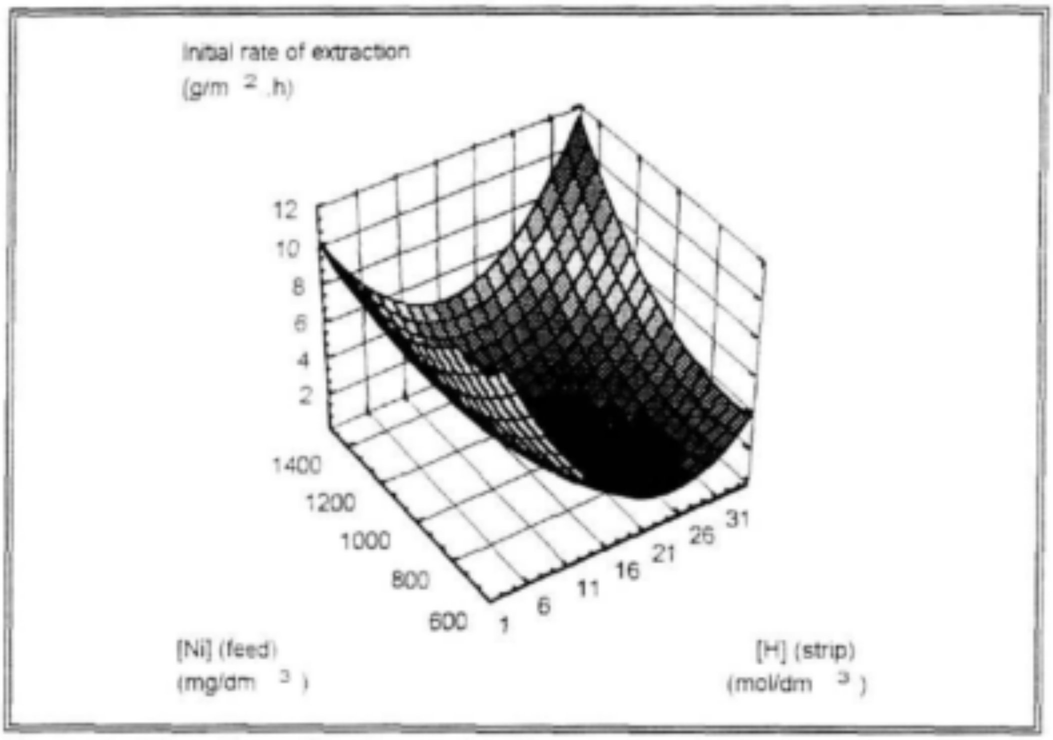


Fig 3.15: The effect of $[H^+]_{strip}$ and $[Ni]_{feed}$ on the initial rate of extraction.

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

Once again the final amount of extraction and initial rate of extraction is a maximum (fig. 3.16 and 3.17) at high and low hydronium ion concentrations of the strip solution (refer to paragraph 3.5.2.1). The final amount of extraction is a minimum at a nickel strip concentration of aproximately 1000 mg/dm³ (refer to paragraph 3.5.2.3).

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

The effect of these two factors on the final extraction can be seen in figure 3.18. The hydronium ion concentration of the strip solution does not have a large effect on the optimum extractant concentration with respect to the final amount of nickel extracted. The hydronium ion concentration of the strip solution has a much larger effect on the optimum extractant concentration with respect to the initial rate of extraction (fig. 3.19). The optimum extractant concentration is much lower for low hydronium ion strip solutions. The final extraction and initial rate of extraction is the highest at high and low hydronium ion concentrations in the strip solution.

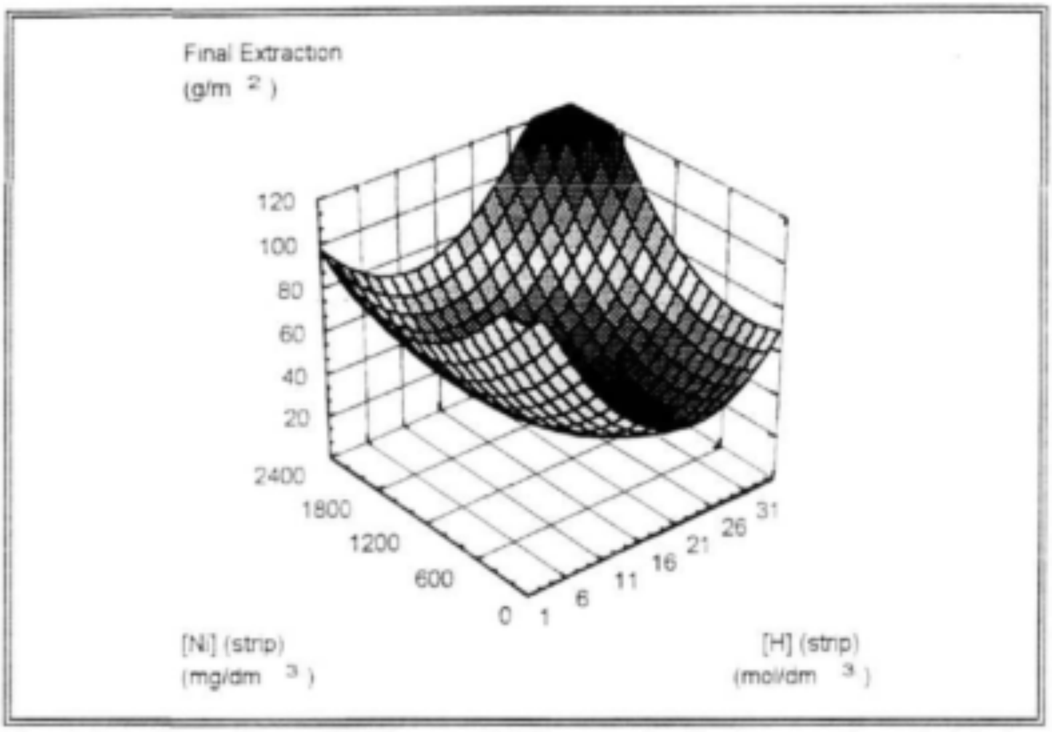


Fig. 3.16: The effect of $[H^+]_{strip}$ and $[Ni]_{strip}$ on the final extraction of nickel.

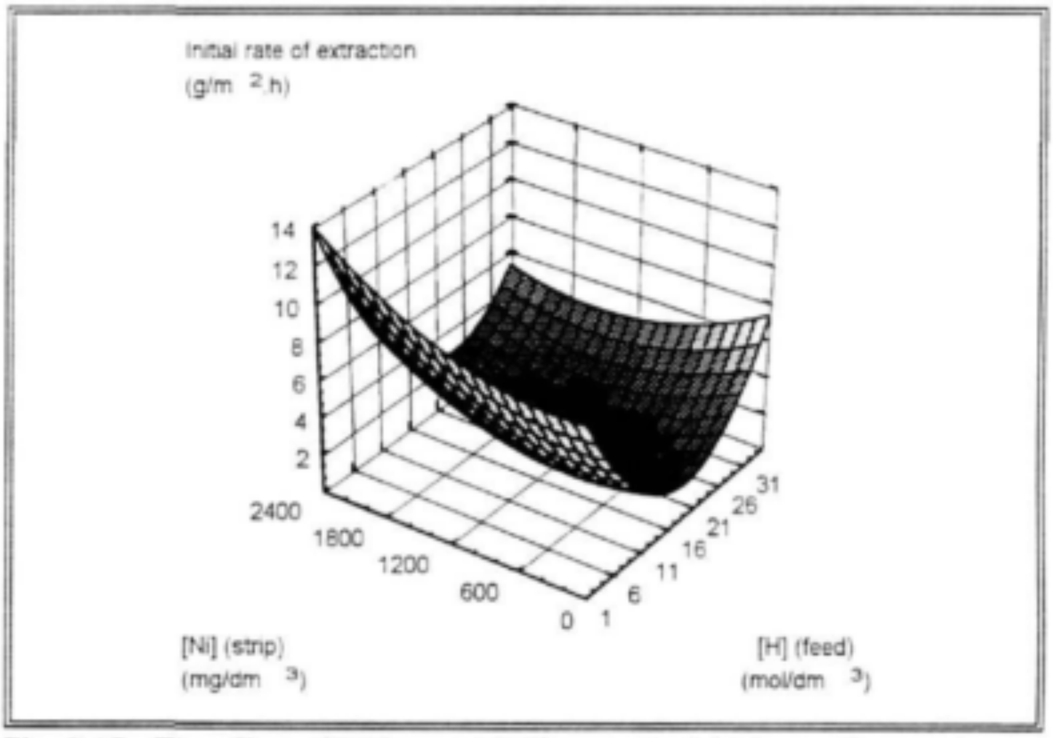


Fig. 3.17: The effect of $[H^+]_{strip}$ and $[Ni]_{strip}$ on the initial rate of extraction.

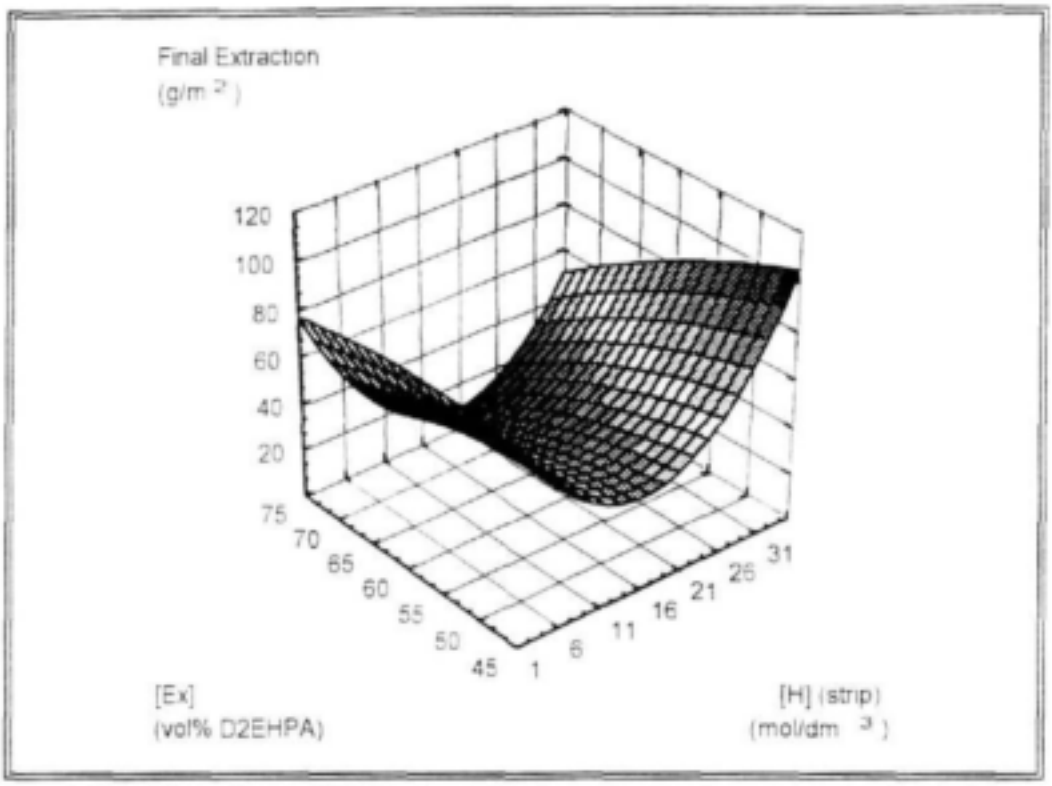


Fig. 3.18: The effect of $[H^+]_{strip}$ and [Ex] on the final extraction of nickel.

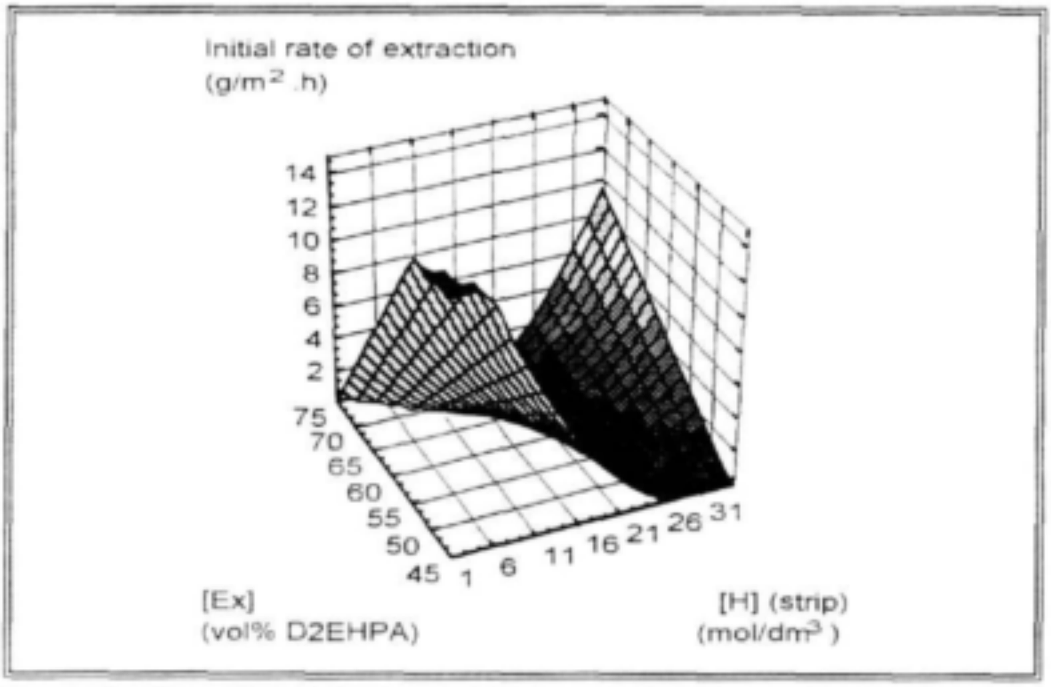


Fig. 3.19. The effect of $[H^+]_{strip}$ and [Ex] on the initial rate of extraction.

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

The effect of the nickel concentration of the feed solution and strip solution on the final extraction and initial rate of extraction can be seen in figure 3.20 and 3.21. The final extraction and initial rate of extraction increases if the nickel concentration of either the feed solution, or the strip solution is increased. The final extraction is a minimum at a nickel strip concentration of approximately 1000 mg/dm^3 (refer to paragraph 3.5.2.3).

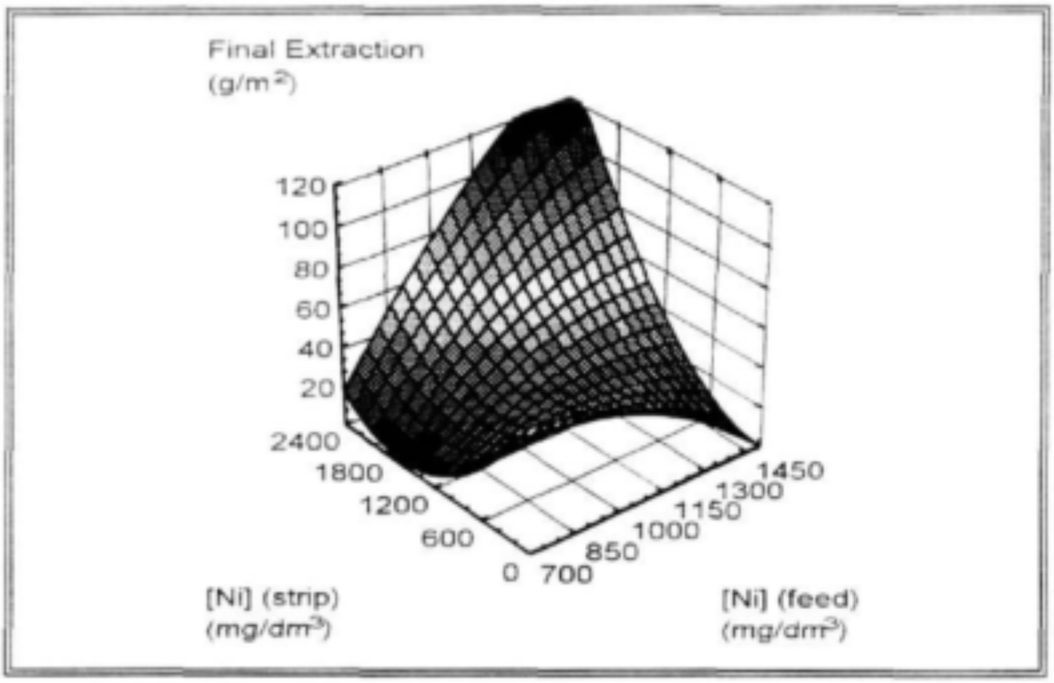


Fig. 3.20: The effect of the $[Ni]_{feed}$ and $[Ni]_{strip}$ on the final extraction of nickel.

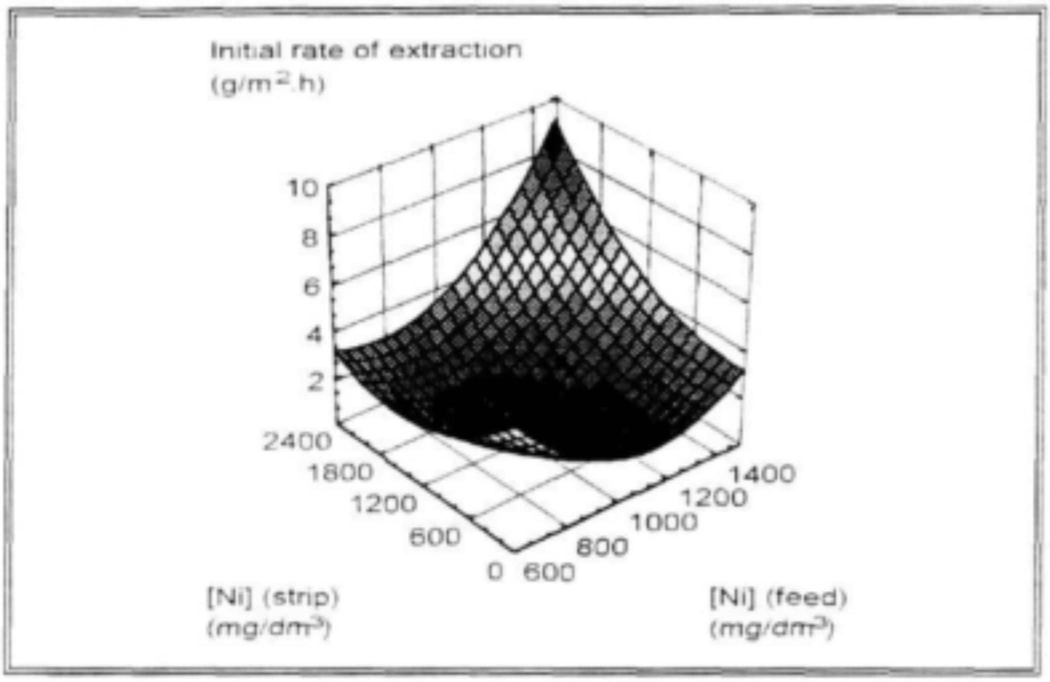


Fig. 3.21: The effect of $[Ni]_{feed}$ and $[Ni]_{strip}$ on the final extraction of nickel

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

The effect of these two factors on the final extraction and initial rate of extraction can be seen in figures 3.22 and 3.23. As previously mentioned the final extraction and initial rate of extraction increases if the nickel concentration of the feed solution increases (refer to paragraph 3.5.2.2, 3.5.2.5 and 3.5.2.8). The concentration of the nickel in the feed solution does have a great 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.

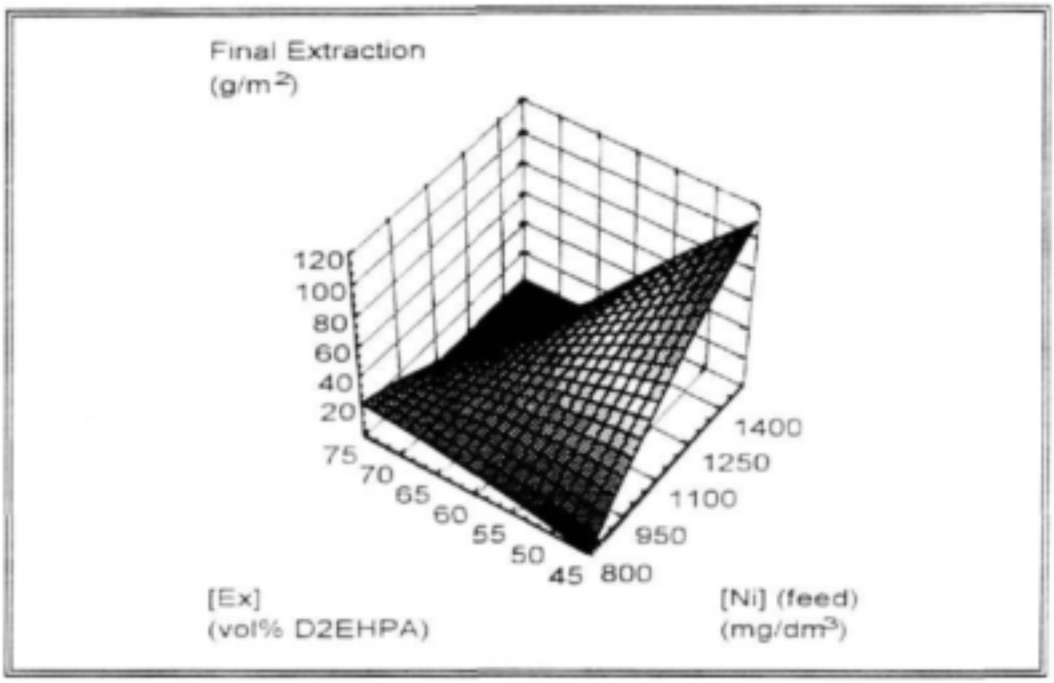


Fig 3.22: The effect of $[Ni]_{feed}$ and [Ex] on the final extraction of nickel.

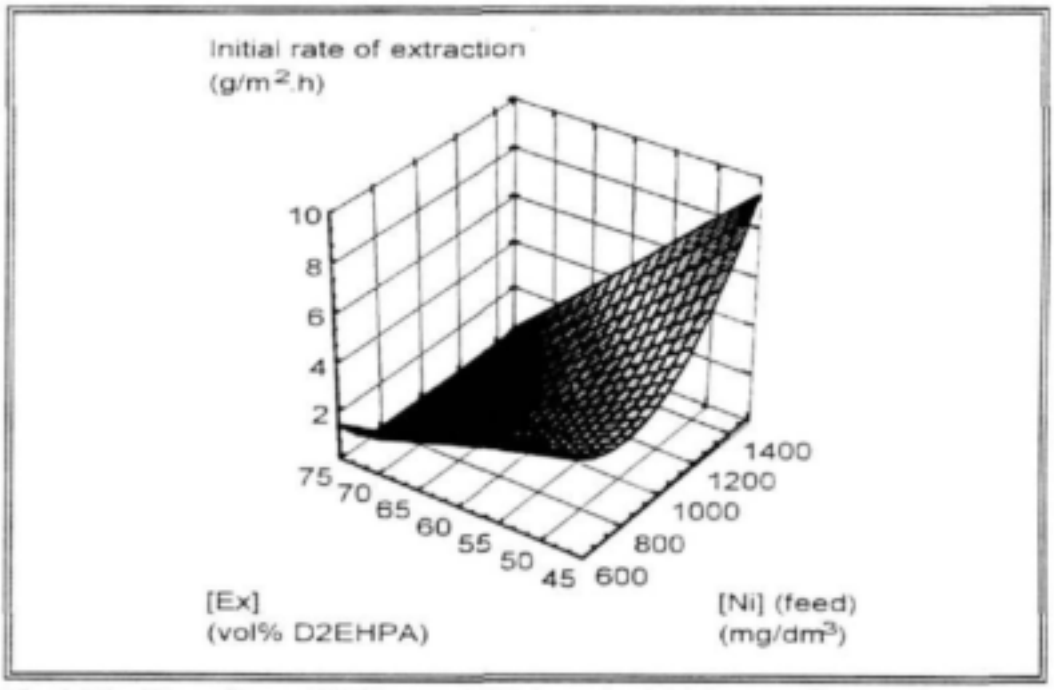


Fig 3.23: The effect of $[Ni]_{feed}$ and [Ex] on the initial rate of extraction.

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

The effect of the nickel strip concentration and the extractant concentration on the final extraction and initial rate of extraction can be seen in figures 3.24 and 3.25. Like the concentration of the nickel in the feed (paragraph 3.5.2.9), the concentration of the nickel in the strip has a great 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. The final extraction and initial rate of extraction is a minimum at a nickel strip concentration of approximately 1000 mg/dm^3 (refer to paragraph 3.5.2.3, 3.5.2.6 and 3.5.2.8).

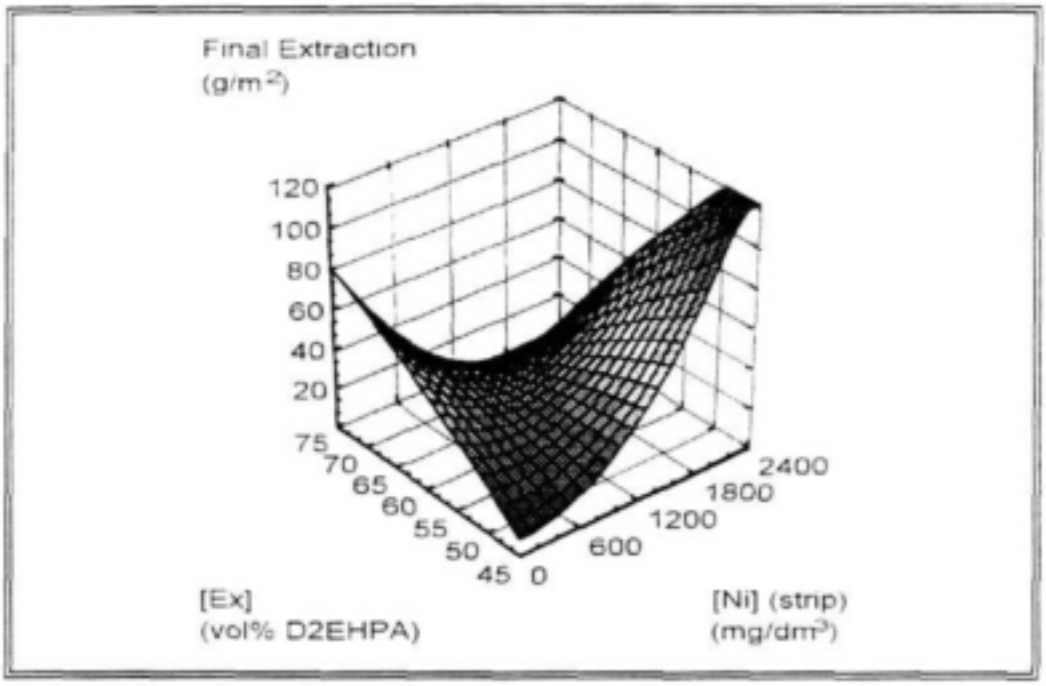


Fig 3.24: The effect of $[Ni]_{strip}$ and [Ex] on the final extraction of nickel.

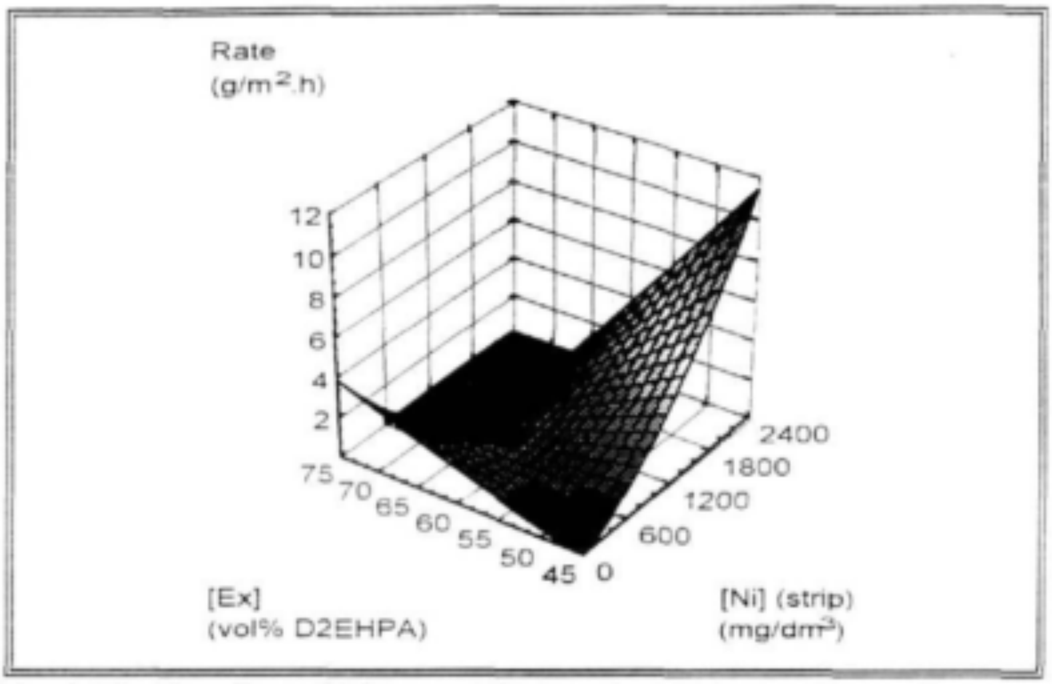


Fig. 3.25: The effect of $[Ni]_{strip}$ and [Ex] on the initial rate of extraction

3.5.3 Accuracy of characterisation experiments

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 which 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, could be identified and were omitted. This is a current statistically verified and accepted procedure. The final curve fit of the data could explain at least 85% of the variance for every experiment.

The temperature of the experiments could have been another cause of inaccuracy. The experiments had been performed over a three month period which stretched through the winter period and there was a difference in the temperature between the first and last experiments. The influence of temperature will be investigated and reported in more detail in the following chapter.

A second order function was fitted through the data for the maximum (final) extraction. Two outliers were omitted and another second order function (Eq. 3.5) was fitted through the remaining data. This equation could explain 81.0% of the variance. In similar fashion three outlier data points were omitted and a second order function (Eq. 3.6) was fitted through the remaining data. This equation could explain 81.7% of the variance. The variance explained for different data points omitted are displayed in Table 3.7. It is clear that the equation for the initial rate of extraction is more inaccurate than the equation for the maximum extraction. This can be explained by the fact that the rate of extraction is more dependent on temperature than the maximum extraction is.

A graphical representation of the observed and predicted values for equation 3.5 and 3.6 are given in figures 3.26 and 3.27 respectively.

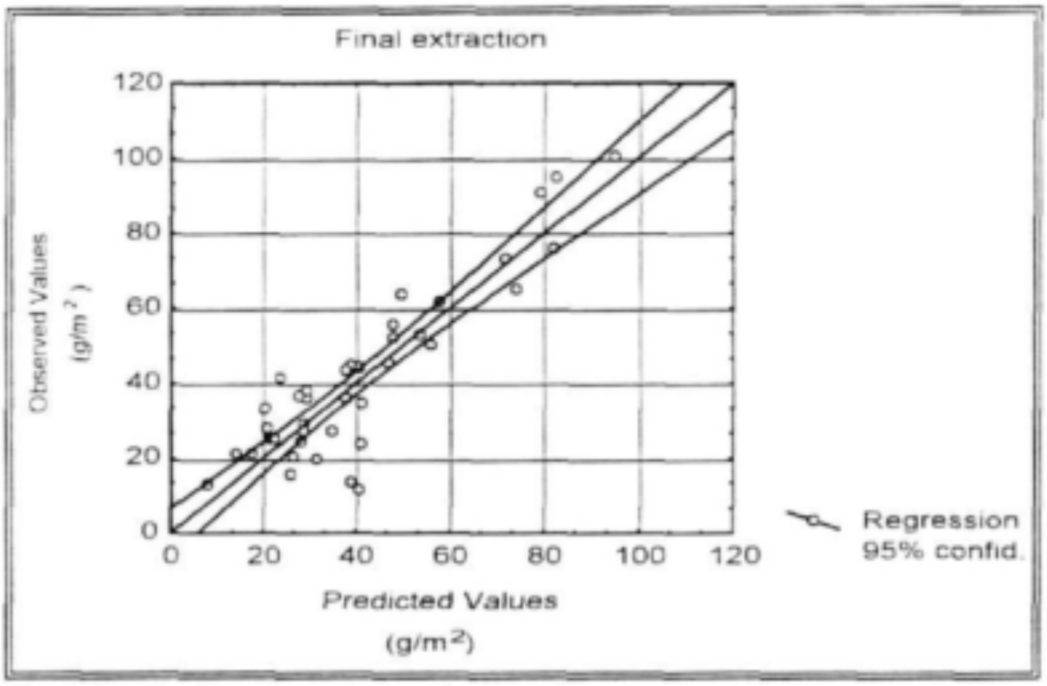


Fig. 3.26: Predicted vs. observed values for equation 3.5

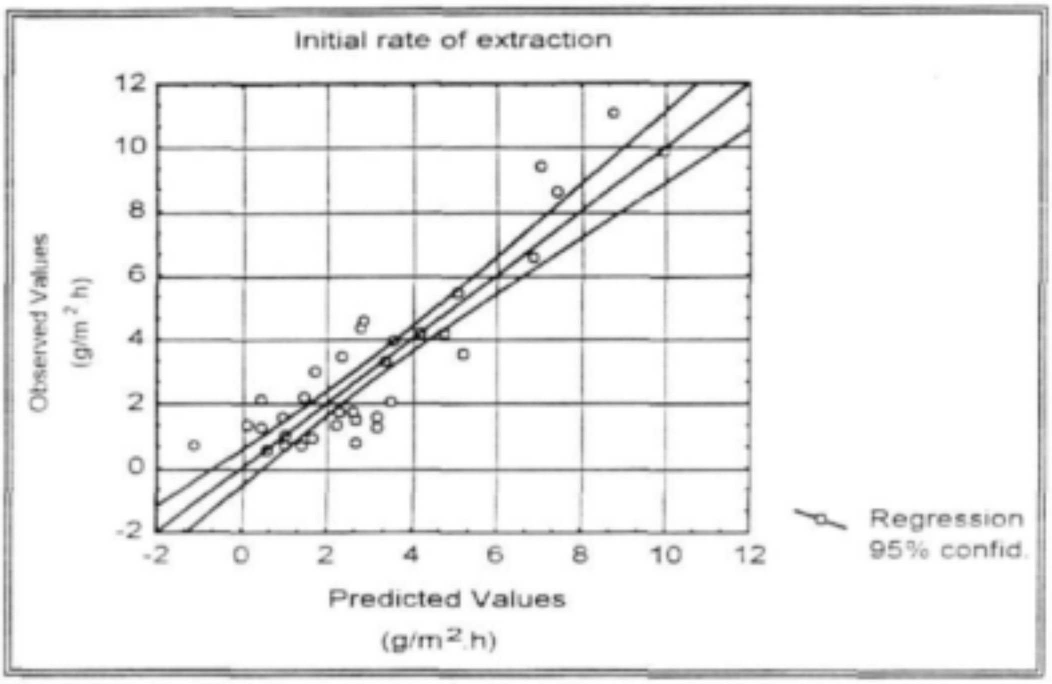


Fig. 3.27: Predicted vs. observed values for equation 3.6.

Table 3.7: Accuracy with outliers omitted.

Number of data (outliers) ignored	Variance explained (Eq. 3.5)	Variance explained (Eq. 3.6)
0	0.6398	0.4949
1	0.7311	0.6817
2	0.8098	0.7603
3	0.8772	0.8170
4	0.9305	0.8480

The following statistical criteria were used to determine whether a point is an outlier or not (Statistica, 1993):

Standard residual value: This is the standardized residual value (observed value minus predicted value divided by the square root of the residual mean square.

Deleted residual: The deleted residual is the standardized residual value for the respective data point (case), had it *not* been included in the regression analysis, that is, if one would exclude this case from all computations. If the deleted residual differs greatly from the respective standardized residual value, then this case is possibly an outlier because its exclusion changed the regression equation.

Cook's distance is another measure of the impact of the respective case on the regression equation. It indicates the difference between the computed coefficients and the coefficients one would have obtained, had the respective case been excluded. All distances should be of about equal magnitude; if not, then there is reason to believe that the respective case(s) biased the estimation of the regression coefficients.

Graphical representations of these criteria for the final equations can be seen in figures 3.28, 3.29 and 3.30 for equation 3.5 and in figures 3.31, 3.32 and 3.33 for equation 3.6.

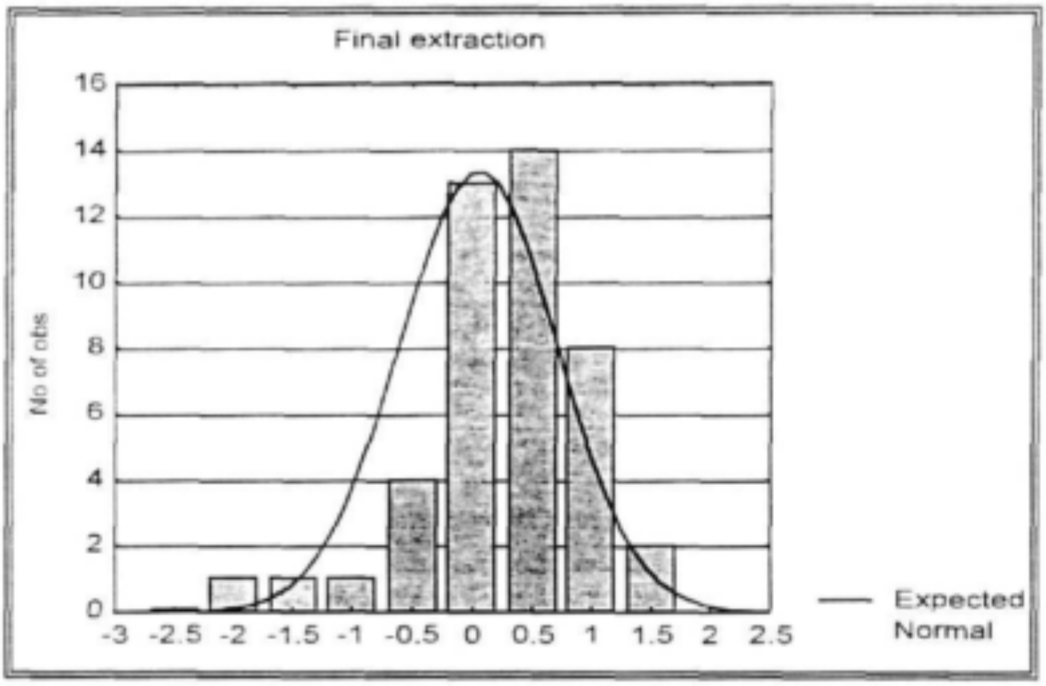


Fig. 3.28: Distribution of standard residuals for final extraction of nickel.

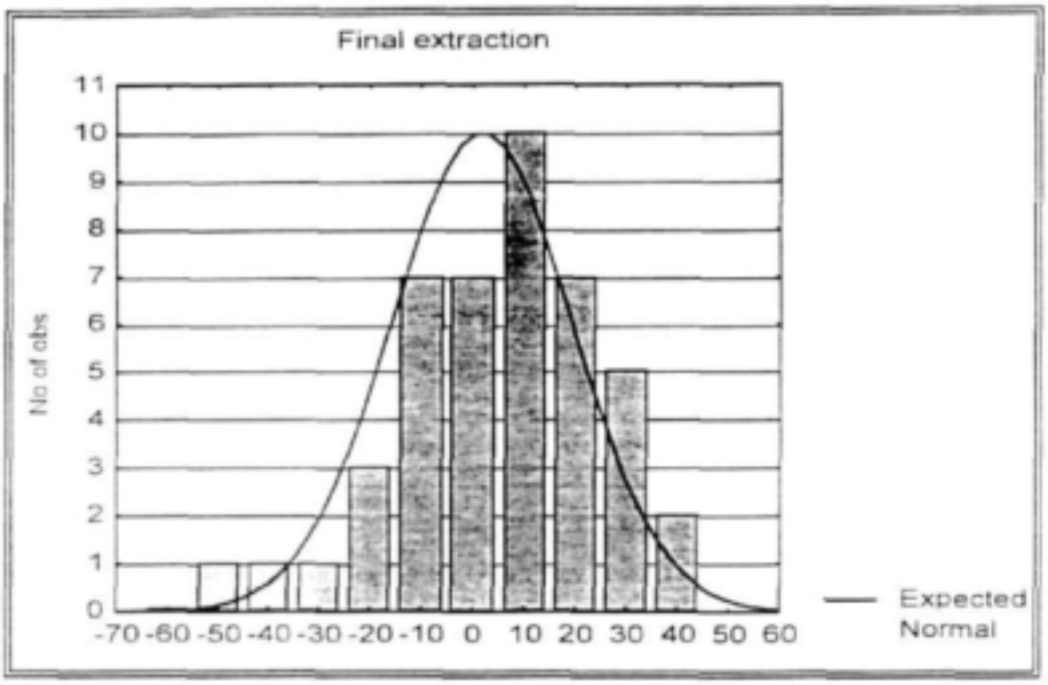


Fig. 3.29: Distribution of deleted residuals for final extraction of nickel

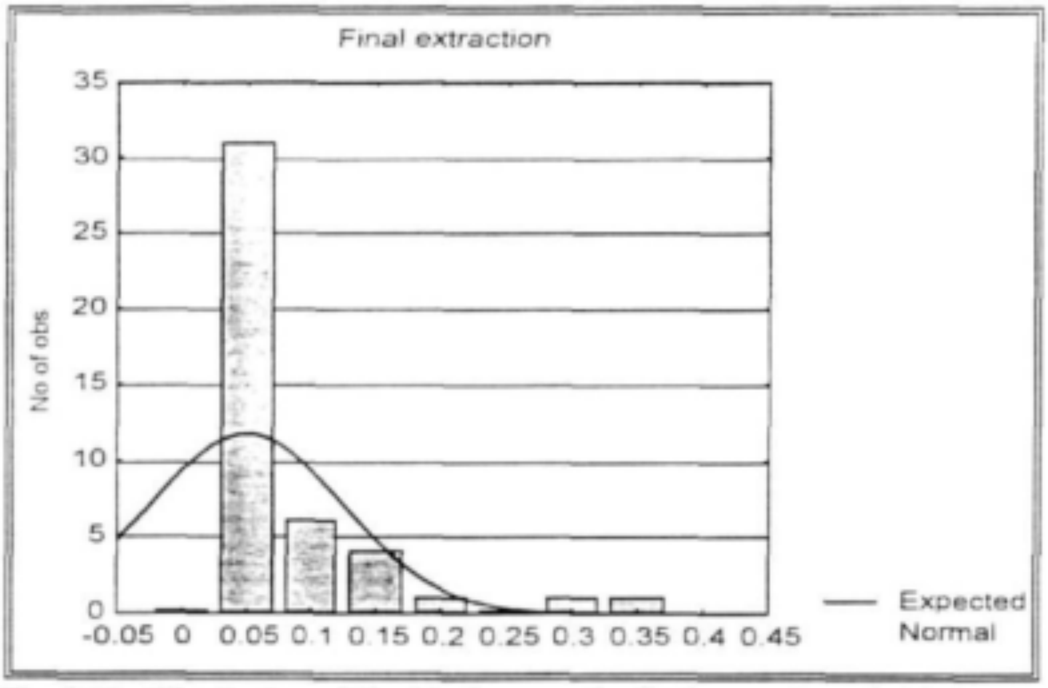


Fig. 3.30: Distribution of Cook's distances for final extraction of nickel

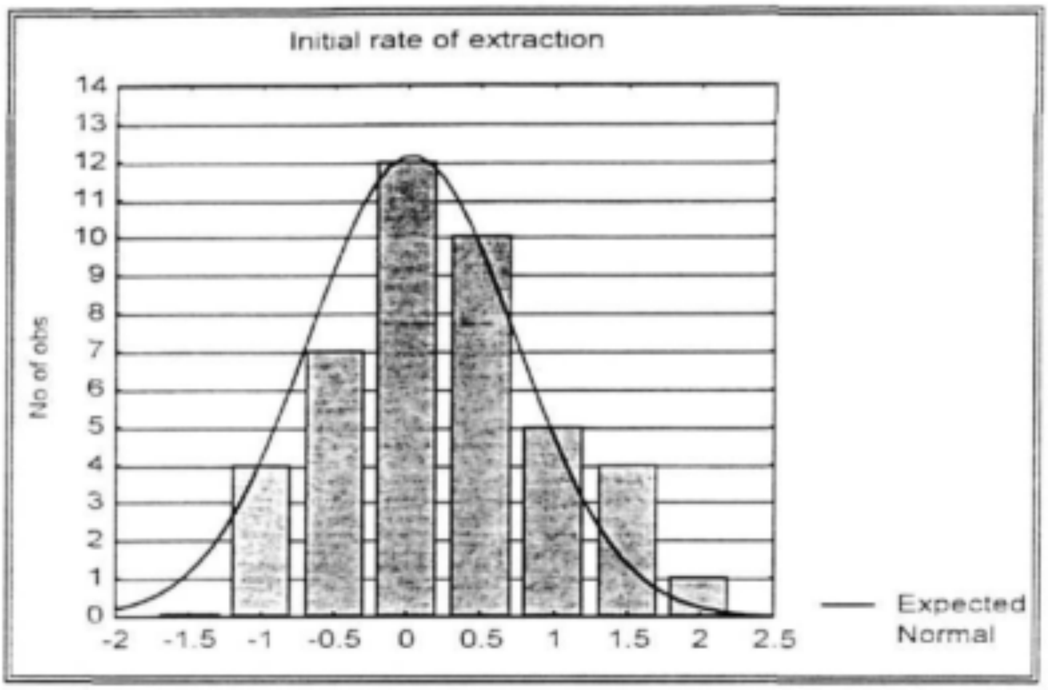


Fig. 3.31: Distribution of standard residuals for initial rate of extraction.

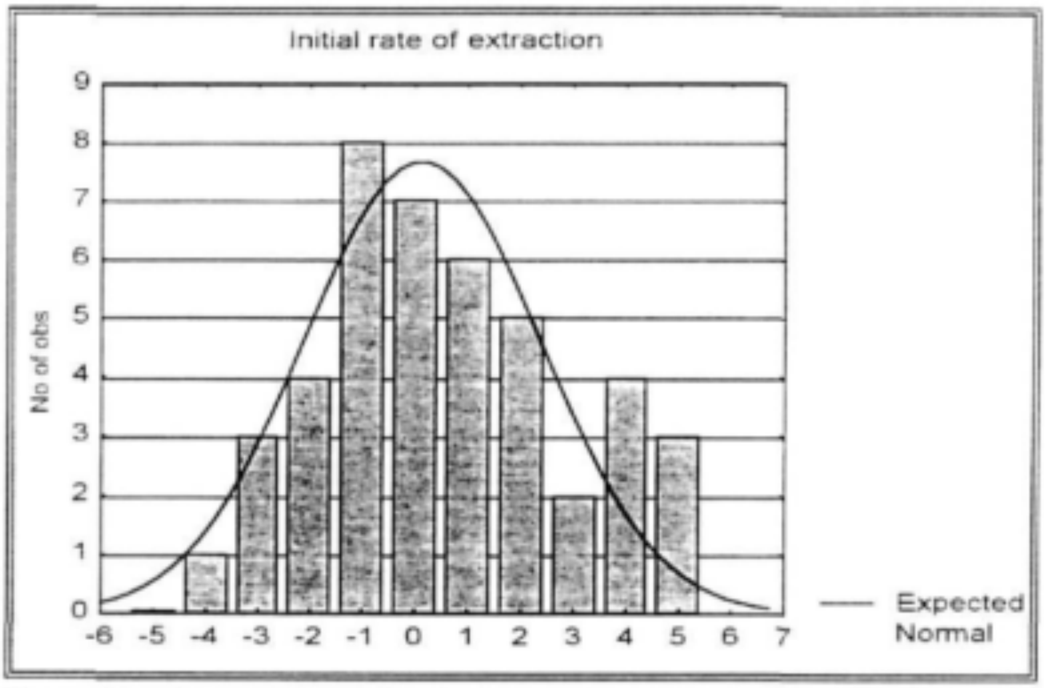


Fig. 3.32: Distribution of deleted residuals for initial rate of extraction.

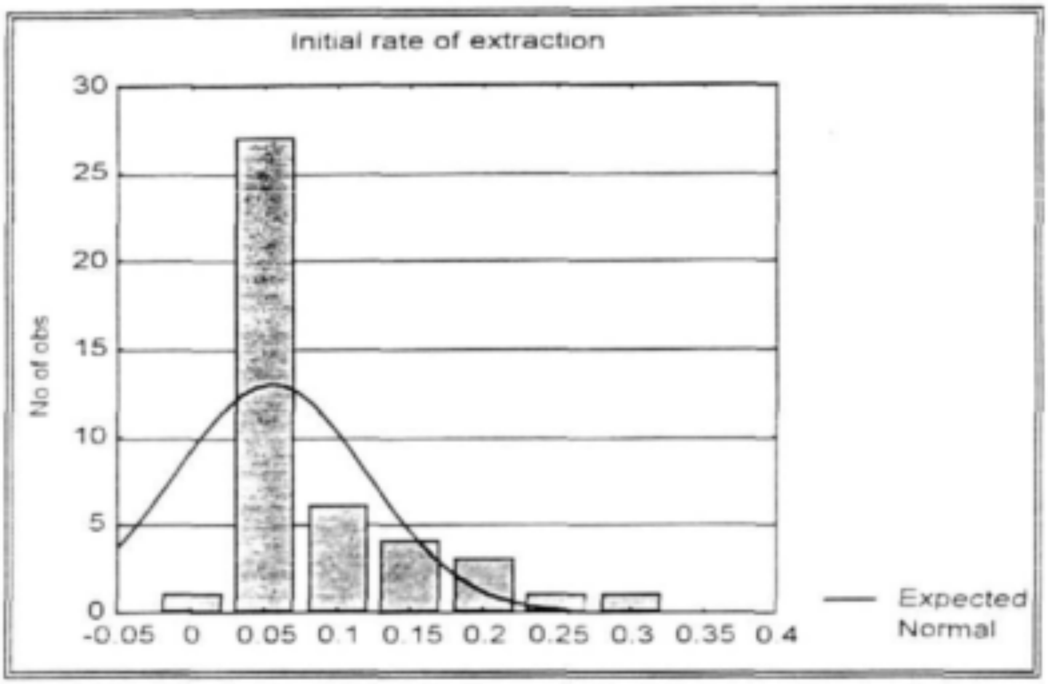


Fig. 3.33: Distribution of Cook's distances for initial rate of extraction.

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 3.8. The standard deviation for Eq. 3.5 was found to be 3.5789 (11.98 %). The standard deviation for Eq. 3.6 was found to be 0.1827 (18.51 %).

Table 3.8: Reproducibility test for experiments.

Experiment no.	**Eq. 5** (g/m^2)	**Eq. 6** ($g/m^2 \cdot h$)
33	29.293	1.021
34	27.099	0.696
45	28.085	1.030
46	35.090	1.201
Average:	29.8918	0.987
STD	3.5798	0.1827
STD (%)	11.98	18.51

3.6 Conclusions

The influence of different conditions on CME was determined. A central composite experimental design was executed to evaluate the influence of the different factors on the extraction of nickel with CME. The research was focused on high hydronium strip concentrations, which is a prominent advantage of CME over SLM. The two equations (Eq. 3.5 & 3.6) were shown to fit the experimental data to a highly acceptable accuracy and explained 81.0% and 81.7% of the variance respectively. The accuracy and reproducibility were both discussed and the experimental protocol showed an inherent accuracy of approximately 85%. In the light of these results it is possible to make the following conclusions on nickel extraction with CME:

1. It is obvious that the extremely high acidity difference (ΔH^+) which is tolerated between the strip solution and the feed solution is advantageous for the extraction of ionic species.
2. This driving force (ΔH^+) creates a system in which extraction proceeds against a concentration gradient of at least 1000:1 when considering the ratio between [Ni^{2+}] in the strip- and feed solutions at final extraction.
3. It is obvious from the fact that very little extraction occurs at a hydronium ion concentration of 0 mol/dm^3 and from Fig. 3.5, that an optimum hydronium ion concentration in the strip solution exists. This optimum will be explored in greater detail in the following chapter.
4. The CME yields at least two orders of magnitude higher extraction rates compared to traditional SLM configurations reported in literature (Verhaege *et al.*, 1987:332).
5. A detailed study of the influence of both temperature and the extractant concentration in the membrane will shed more light on the possible techno-economic feasibility of this extraction technique.
6. It is shown (Table 3.5) that an extraction of 95 g/m^2 (nickel) can be obtained at an initial rate of approximately 10 g/m^2·h.

Chapter 4
Optimisation of CME

4.1 Introduction

In the previous chapter research was focused on the extraction of nickel at high hydronium strip concentrations, which is a prominent advantage of CME over SLM. This led to a better understanding of this extraction method, but there are still unanswered questions. These questions are:

7. What is the optimum hydronium ion concentration for the strip solution?
8. What is the influence of temperature on the extraction of nickel with CME?
9. What is the influence of feed solution agitation on the extraction of nickel with CME?
10. Will anion ligands enhance the extraction of nickel with CME?

Research in this chapter is focused on answering these questions and on finding the optimum conditions for the extraction of nickel with the use of CME. This optimum will show the techno-economic feasibility of this extraction technique.

4.2 The Hydronium ion concentration of the strip solution

4.2.1 Introduction

It was shown in chapter 3.5.2.1 that osmosis has a negative effect on the extraction of nickel with CME. Osmosis has the additional disadvantage that it dilutes the hydronium ion concentration of the strip solution (the main driving force of CME).

It can be deduced from the fact that minimal extraction occurs at a hydronium ion concentration of 0 mol/dm^3 and from figure 3.5, that an optimum hydronium ion concentration in the strip solution exists. It is vital to quantitatively establish this optimum point before any applications of CME will be possible in the industry.

4.2.2 *Experimental configuration*

The capsule configuration was used for the experiments (refer to chapter 3.2). A thermally controlled water bath was used to maintain temperature at 25 °C.

4.2.3 Experimental procedure

A beaker was filled with a feed solution with a pH of 4.5 and nickel concentration of 1000 mg/dm^3. The prepared capsule, as explained in chapter 3.2, was suspended in the filled beaker (feed solution) with a piece of string (see photograph 3.1). The extractant concentration used for the experiments was 70% (vol.) D2EHPA dissolved in Escaid 100 (refer to chapter 3.2.2).

Samples were taken from the feed solution at different time intervals. The pH of the feed solution was readjusted to the initial pH at these sampling points with a diluted sodium hydroxide solution. The nickel concentration of the feed solution was not readjusted. An example of the results can be seen in table 4.1 showing the variation of the pH and the nickel concentration of the feed solution with time.

Table 4.1: An example of results.

Time (h)	**$[Ni]_{feed}$** (mg/dm^3)	**pH_{feed}**
0.00	1022	4.5
2.95	970	3.42
5.10	977	3.5
6.92	957	3.82
10.78	913	3.37
16.17	880	3.13
24.18	860	3
27.87	799	3.28
35.30	725	3.08
50.87	708	2.81

4.2.4 Results and discussion

These results were evaluated in the same manner as in chapter 3.5.1 to give the cumulative extraction of nickel (with CME) with respect to time. The result of a selected set of data can be seen in figure 4.1. The result of the other experiments are shown in Appendix A.2

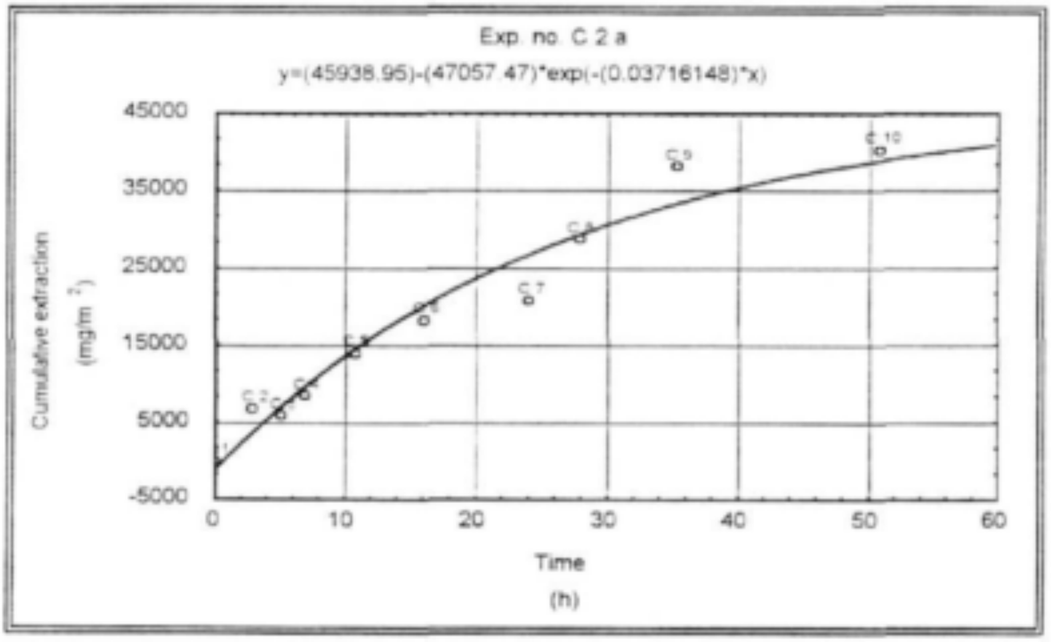


Fig. 4.1: Example of experimental results.

Several experiments were executed at different hydronium ion concentrations of the strip solution. The graphical representations of the influence of the hydronium ion concentration of the strip solution on the final extraction and initial rate of extraction can be seen in figures 4.2 and 4.3 respectively. It is clear that the suspicion of an optimum hydronium ion concentration in the strip solution was correct. The final amount of extraction and initial rate of extraction increases if the hydronium ion concentration of the strip solution is increased. At the point of approximately 4 mol/dm^3 a maximum extraction of nickel occurs. If the hydronium ion concentration of the strip solution is increased further, the osmotic pressure becomes greater than the hydrophobicity of the liquid membrane and osmosis occurs. This has a negative effect on the extraction process. The extraction of nickel decreases and there is a large loss of hydronium ions. The hydronium ions are extremely mobile and they migrate to the feed solution as soon as osmosis occurs. The osmotic effect can also result in the transport of contaminants to the strip solution in an industrial application due to so-called hydraulic short-circuiting.

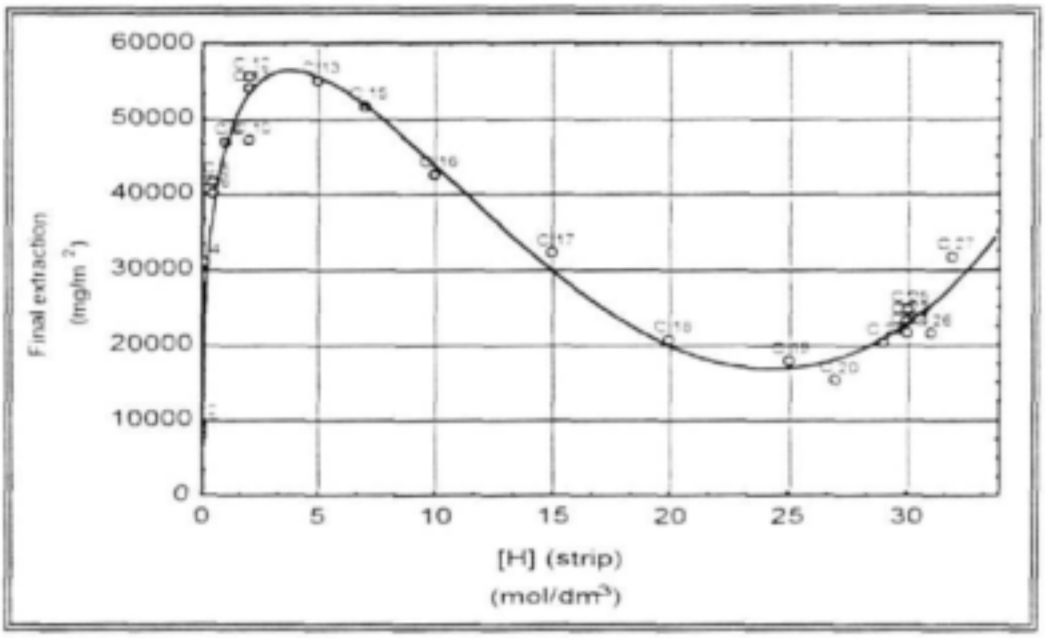


Fig. 4.2: The effect of $[H^+]_{strip}$ on the final extraction of nickel.

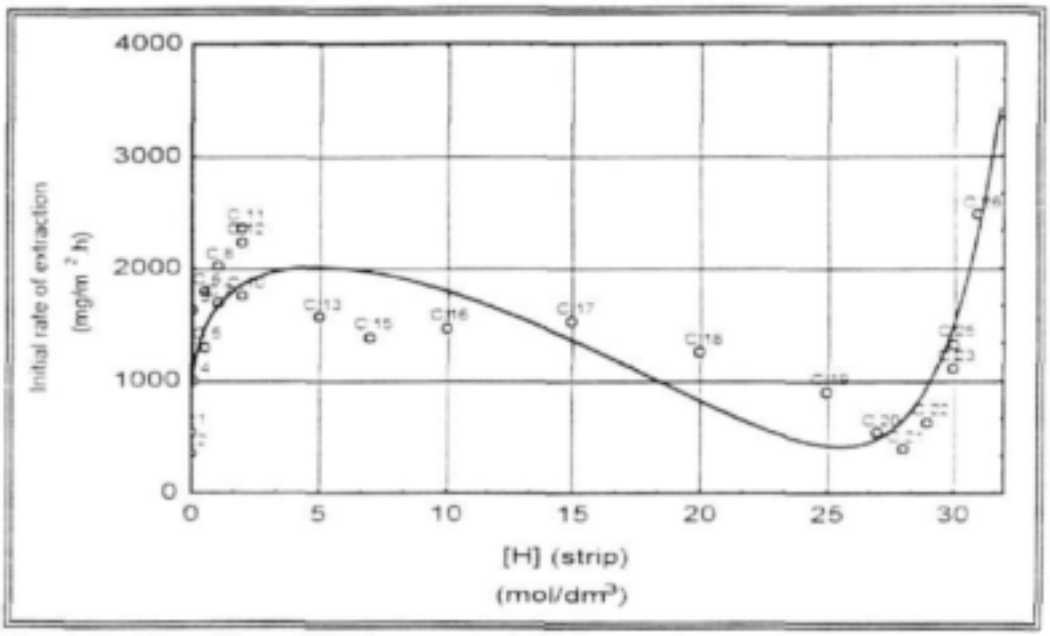


Fig. 4.3: The effect of $[H^+]_{strip}$ on the initial rate of extraction.

The effect of osmosis is a maximum at a hydronium ion concentration of approximately 25 mol/dm³. If the concentration of the sulfuric acid is increased further, the acid does not dissociate completely and the undissociated acid forms a hydronium ion reserve. The hydronium ion concentration in these experiments are given as hydronium available if H_2SO_4 dissociates completely. The actual hydronium ion concentration can be calculated with the use of dissociation constants. It is generally accepted that the diprotonic sulphuric acid dissociates in two steps (Cruywagen *et al.*, 1981:264):

$$H_2SO_4 + H_2O \rightarrow H_3O^+ + HSO_4^-$$
$$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$$

The first step is a complete dissociation, but the second step is only a partial dissociation with the following dissociation constant:

$$Ka_{HSO_4^-} = 2.162\times10^{-4} = \frac{[H_3O^+]\,[SO_4^{2-}]}{[H_2O][HSO_4^-]} \tag{4.1}$$

The sulphuric acid/water system is an equimolar solution at a concentration of 14 mol/dm³ H_2SO_4

In other words, if the sulphuric acid concentration is lower than 14 mol/dm^3, the solution consists of sulphuric acid diluted in water. If the sulphuric acid concentration is higher than 14 mol/dm^3, the solution consist of water diluted in sulphuric acid. The concentration of the hydronium ions can be calculated from the stoichiometric reactions and the dissociation constant. Figure 4.4 shows the hydronium ion concentration at different sulphuric acid concentrations (expressed as [H]). The calculations for this figure can be seen in appendix B.1.

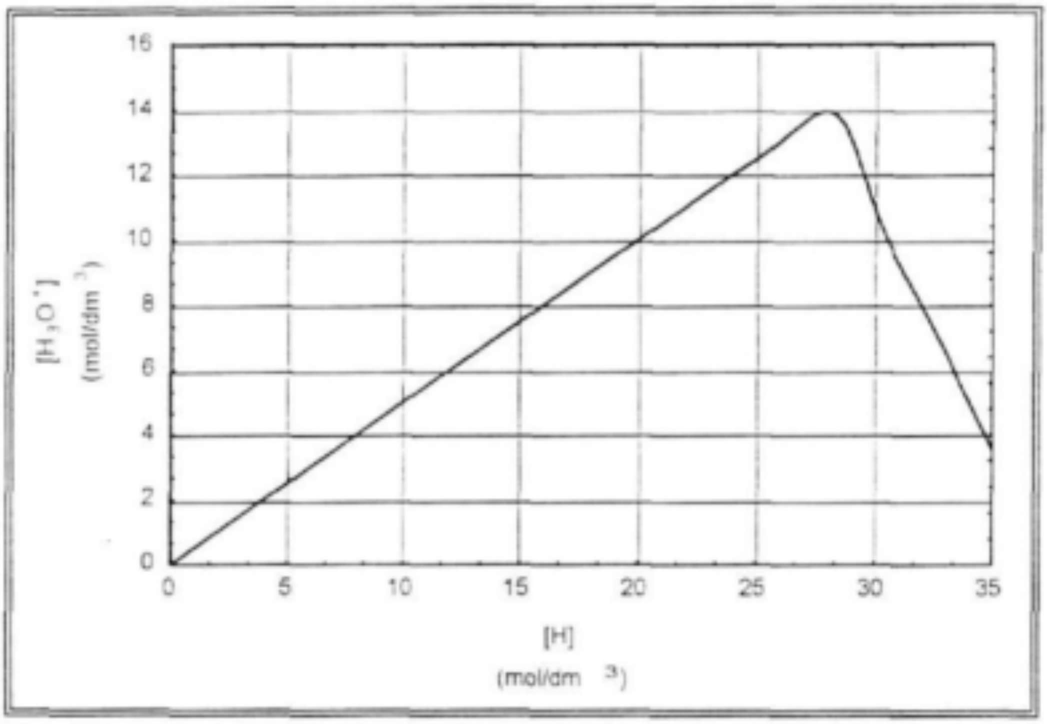


Fig. 4.4: Calculated [H_3O^+] at different H_2SO_4 concentrations (expressed as [H^+]).

The observed turning point for the osmotic effect in the experiments occurs at a hydronium ion concentration of approximately 25 mol/dm^3 (less than 28 mol/dm^3). This can be explained by the fact that the hydronium ion concentration of the strip solution is diluted as soon as osmosis occurs. A comparison between this set of experiments and the experiments of chapter 3 for the final extraction (Eq. 3.5) can be seen in figure 4.5. The value of the final extraction for the experiments in the previous chapter is higher than this set of experiments, because the nickel concentration of the feed solution was not readjusted to the initial concentration for this set of experiments. It is clear however that the form of the graph and the minimum extremity point of the final extraction is identical for the two sets of experiments.

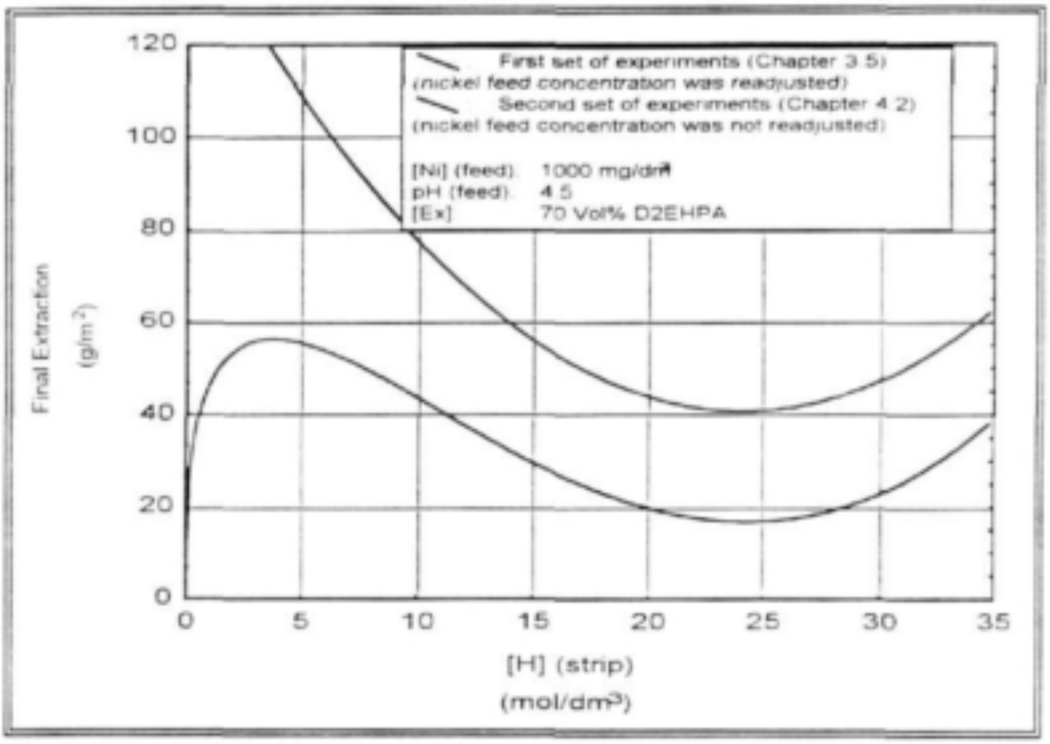


Fig. 4.5: Comparison between two sets of experiments.

The optimum hydronium ion concentration is very important for any industrial applications of CME. It can be concluded from figure 4.5 that the optimum hydronium ion concentration is approximately 3.8 mol/dm^3.

4.2.5 Accuracy of experiments

Some of the experiments were repeated to determine the reproducibility of the experiments. The results of these experiments can be seen in table 4.2. The standard deviation for the final extraction was found to be 6.86%.

Table 4.2: Reproducibility test for experiments

Experiment no.	**Final extraction (g/m²)**	
C 0.5	41.599	Average = 40.768
C 0.5 a	39.937	STD = 0.831
		STD (%) = 2.04
C 1	50.084	Average = 48.4895
C 1 a	46.895	STD = 1.595
		STD (%) = 3.29
C 2	39.238	Average = 48.966
C 2 a	47.057	STD = 6.468
C 2 b	53.959	STD (%) = 13.21
C 2 c	55.609	
C 5	54.974	Average = 49.655
C 5 a	44.336	STD = 5.319
		STD (%) = 10.71
C 30	23.026	Average = 23.101
C 30 a	21.711	STD = 1.167
C 30 b	24.567	STD (%) = 5.05
	STD (%)	**6.86**

4.3. The influence of temperature on CME

4.3.1 Introduction

Temperature was ignored as a factor in chapter 3, since very low rates of extraction were expected. With low rates of extraction, the possible increase in efficiency would not be economical if the cost of heating large volumes of liquid solutions is taken into account.

The extraction of nickel with CME yielded at least two orders of magnitude higher extraction rates compared to traditional SLM configurations reported in literature (Verhaege *et al.*, 1987:332). This positive result made the heating of the strip and feed solutions an economical possibility.

4.3.2 Experimental configuration

The capsule configuration was used for the experiments (refer to chapter 3.2). A thermally controlled water bath was used to maintain isothermal conditions.

4.3.3 Experimental procedure

A beaker was filled with a feed solution with a pH of 4.5 and nickel concentration of 1000 mg/dm^3. The prepared capsule, as explained in chapter 3.2, was suspended in the filled beaker (feed solution) with a piece of string (see photograph 3.1). The extractant concentration used for the experiments was 70% (vol.) D2EHPA dissolved in Escaid 100 (refer to chapter 3.2.2). The temperatures of the experiments were varied.

Samples were taken from the feed solution at different time intervals. The pH of the feed solution was readjusted to the initial pH at these sampling points with a diluted sodium hydroxide solution. The nickel concentration of the feed solution was not readjusted.

4.3.4 Results and discussion

The results were evaluated in the same manner as in chapter 3.5.1 to give the cumulative extraction of nickel with respect to time. A complete set of results can be seen in appendix A.3.

The graphical representation of the influence of the temperature of the feed solution on the final extraction and the initial rate of extraction can be seen in figures 4.7 and 4.8 respectively.

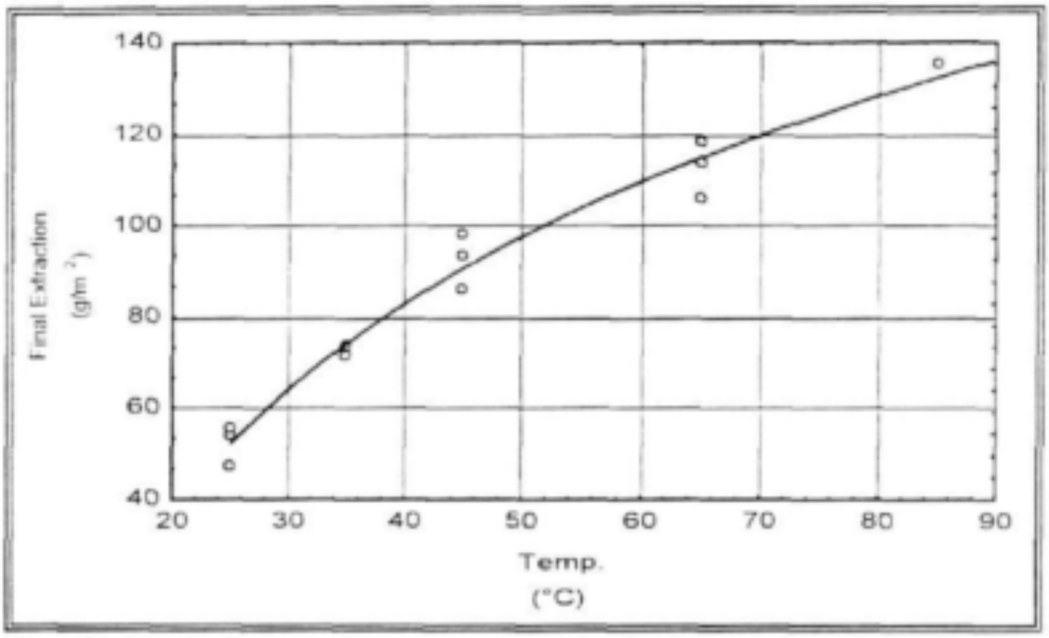


Fig. 4.7: The influence of temperature on the final extraction of nickel.

The final amount of nickel extracted with SLM increased with 154% when the temperature was increased from 25 °C to 85 °C. The initial rate of extraction increased with 253% when the temperature was increased from 25 °C to 85 °C. This confirms the suspicion that the initial rate of extraction is more dependent on temperature, than the final extraction of nickel.

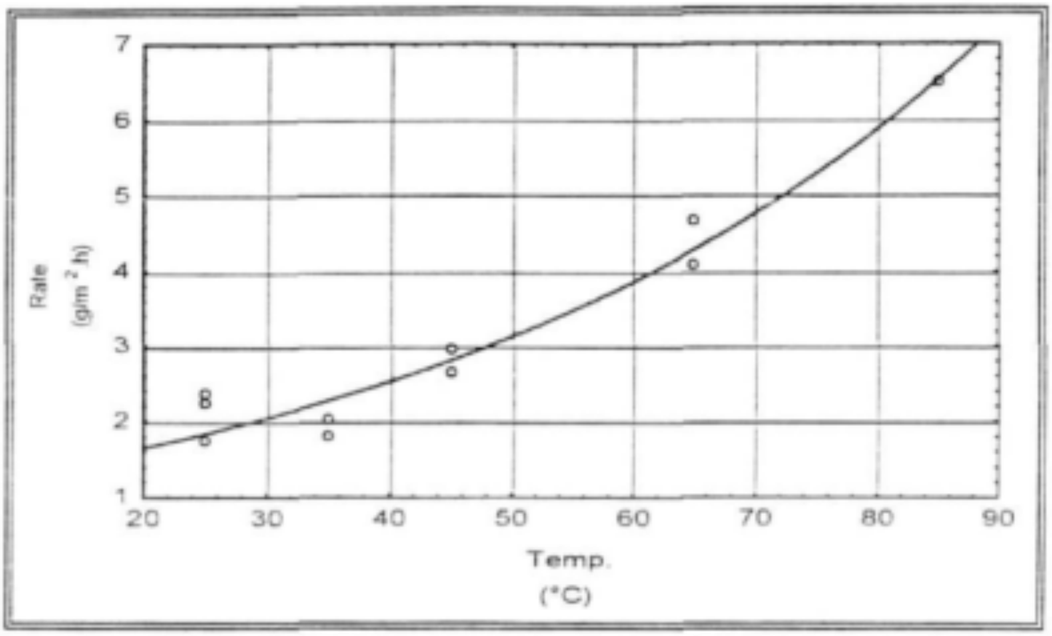


Fig. 4.8: The influence of temperature on the initial rate of extraction.

4.3.5 Accuracy of experiments

Some of the experiments were repeated to determine the reproducibility of the experiments. These results can be seen in table 4.3. The standard deviation for the final extraction was found to be 4.67%. The standard deviation for the initial rate of extraction was found to be 7.64%.

Table 4.3: Reproducibility tests for experiments.

Temperature	**Final Extraction** (g/m^2)		**Initial Rate of Extraction** ($g/m^2.h$)	
	Average	**STD (%)**	**Average**	**STD (%)**
25	52.2	7.09	2.12	12.5
35	73.1	1.59	1.88	6.01
45	92.5	5.35	2.87	5.59
65	112.5	4.63	4.47	6.45
		4.66		**7.67**

4.4 The influence of agitation on CME

4.4.1 Introduction

A factor which was not investigated in chapter 3 is the influence of agitation on the extraction of nickel. Hofman (1991:163) researched the influence of agitation on SLM. He found that the rate of extraction increased up to a Reynolds number of 7 000. A further increase in the agitation has little or no effect on the rate of extraction. This can be explained by the fact that at low agitation the liquid boundary layer of the feed solution is relatively large. If the agitation is increased, this boundary layer becomes thinner and results in a lower resistance to ion transport through the membrane which implies that this resistance to mass transfer is then not the controlling resistance.

4.4.2 Experimental configuration

The capsule configuration was used for the experiments (refer to chapter 3.2).

4.4.3 Experimental procedure

A beaker was filled with a feed solution with a pH of 4.5 and nickel concentration of 1000 mg/dm^3. The prepared capsule, as explained in chapter 3.2, was suspended in the filled beaker (feed solution) with a piece of string (see photograph 3.1). The extractant concentration used for the experiments was 70% (vol.) D2EHPA dissolved in Escaid 100 (refer to chapter 3.2.2). The feed solution was stirred with a magnetic stirrer. The stirrer's speed was varied for every experiment.

Samples were taken from the feed solution at different time intervals. The pH of the feed solution was readjusted to the initial pH at these sampling points with a diluted sodium hydroxide solution. The nickel concentration of the feed solution was not readjusted.

4.4.4 Results and discussion

The extraction of nickel was evaluated in the same manner as in chapter 3.5.1 to give the cumulative extraction of nickel with respect to time. The results of the experiments can be seen in appendix A.4. The rotational speed of the impeller was measured with a digital tachometer. The Reynolds number of the feed solutions was calculated with the following equation (Bird *et al.*, 1960:582):

$$Re = \frac{D^2 \omega \rho}{\mu} \tag{4.1}$$

In this equation D is the diameter of the impeller, ω is the rate of rotation, ρ is the liquid density of the feed solution and μ is the liquid viscosity of the feed solution.

The graphical representation of the influence of the agitation of the feed solution on the final extraction and the initial rate of extraction can be seen in figures 4.9 and 4.10 respectively.

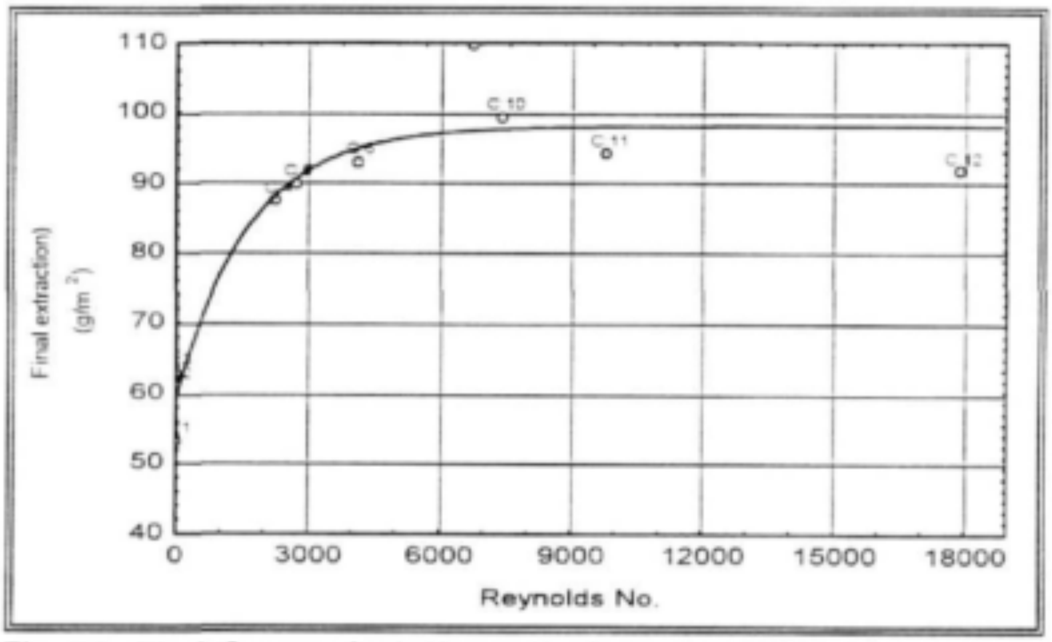


Fig. 4.9: The influence of agitation on the final extraction of nickel.

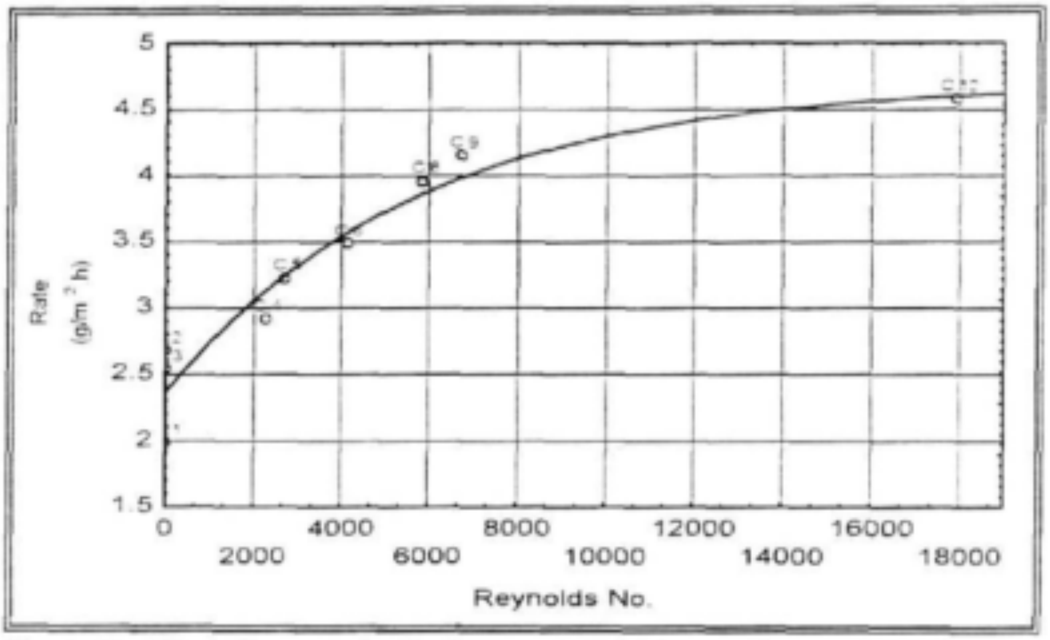


Fig. 4.10: The influence of agitation on the initial rate of extraction.

The final amount of nickel extracted with CME increased with 39.88 % and the initial rate of extraction increased with 49.86 % when the feed solution is agitated vigorously.

The most dramatic increase occurred when the Reynolds number of the feed solution increased from 0 to ±9000. This result correlates with the result obtained by Hofman (1991:163) for SLM systems.

4.5 The influence of anion ligands on CME

4.5.1 Introduction

Gu and Wasan (1986:129) found that SLM extraction could be enhanced by the addition of anion ligands to the feed solution (refer to chapter 2.5). Gu and Wasan (1986:132) tested several ligands. Acetate gave the best results. The optimum acetate concentration was 0.10 mol/dm^3. It was suspected that the same enhancement would apply to CME.

4.5.2 Experimental configuration

The capsule configuration was used for the experiments (refer to chapter 3.2). A thermally controlled water bath was used to experiment isothermally at 25 °C.

4.5.3 Experimental procedure

A beaker was filled with a feed solution with a nickel concentration of 1000 mg/dm^3. The feed solution had different sodium- and calcium acetate concentrations. The prepared capsule, as explained in chapter 3.2, was suspended in the filled beaker (feed solution) with a piece of string (see photograph 3.1). The extractant concentration used for the experiments was 70% (vol.) D2EHPA dissolved in Escaid 100 (refer to chapter 3.2.2).

Samples were taken from the feed solution at different time intervals. The pH of the feed solution was readjusted to 4.5 (if necessary) at these sampling points with a diluted sodium hydroxide solution. This readjustment was rarely necessary, since acetate is a pH buffer. The nickel concentration of the feed solution was not readjusted.

4.5.4 Results and discussion

The extraction of nickel was evaluated in the same manner as in chapter 3.5.1 to give the cumulative extraction of nickel with respect to time. The results of the experiments can be seen in appendix A.5.

The graphical representation of the influence of anion ligands in the feed solution on the final extraction and the initial rate of extraction can be seen in figures 4.11 and 4.12 respectively.

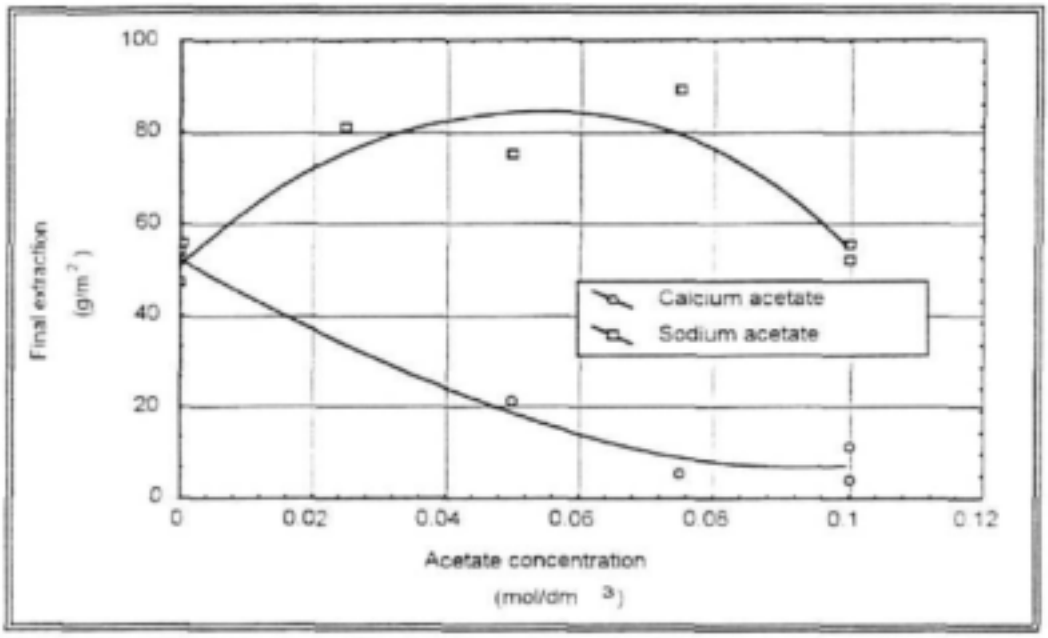


Fig. 4.11: The influence of anion ligands on the final extraction of nickel.

It is clear from figures 4.11 and 4.12 that calcium acetate inhibits the extraction of nickel with CME, while sodium acetate enhances the extraction. This can be explained by the fact that the divalent calcium acetate is a much larger ion than the monovalent sodium acetate. This larger ion causes a steric hindrance in the ligand accelerated mechanism proposed by Gu and Wasan (1986:131). The reduction of nickel extraction due to this hindrance can be as high as 92.3% for the final extraction of nickel and 78.4% for the initial rate of nickel extraction.

The addition of sodium acetate enhanced the extraction of nickel with CME. The optimum acetate concentration was found to be ±0.05 mol/dm^3 for the final extraction and ±0.10 mol/dm^3 for the initial rate of extraction. This result correlates with the result obtained by Gu and Wasan (1986:132).

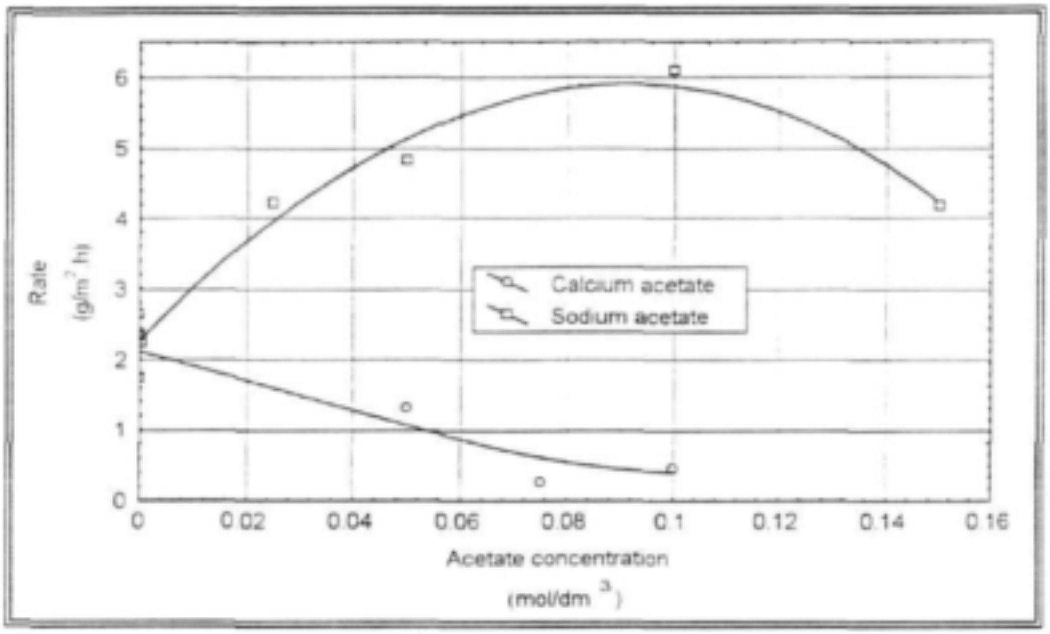


Fig. 4.12: The influence of anion ligands on the initial rate of extraction.

The addition of sodium acetate to the feed solution resulted in a maximum enhancement of 63.5% in the final extraction of nickel and an extremely high enhancement of 218.9% in the initial rate of nickel extraction.

4.5.5 Accuracy of experiments

Some of the experiments were repeated to determine the reproducibility of the experiments. These results can be seen in table 4.4. The standard deviation for the final extraction was found to be 5.54%. The standard deviation for the initial rate of extraction was found to be 7.87%.

Table 4.4: Reproducibility tests for experiments.

Acetate concentration (mol/dm^3)	**Final Extraction** (g/m^2)		**Initial Rate of Extraction** (g/m^2.h)	
	Average	**STD (%)**	**Average**	**STD (%)**
0	50.7	8.01	2.25	14.42
0.10	53.4	3.07	0.45	1.31
		5.54		**7.87**

4.6 The optimum extractant concentration

4.6.1 Introduction

The optimum conditions for the extraction of nickel with CME were determined in the previous paragraphs. It was shown in chapter 3.5.2 that the optimum extractant concentration is very dependant on other factors. It is thus necessary to determine the optimum extractant concentration at this optimum extraction conditions.

This set of experiments will also contain the result with the maximum extraction conditions. This result can be used to determine the techno-economic feasibility of this extraction technique.

4.6.2 Experimental configuration

The capsule configuration was used for the experiments (refer to chapter 3.2).

4.6.3 Experimental procedure

A beaker was filled with a feed solution with a nickel concentration of 7000 mg/dm^3 and a sodium acetate concentration of 0.10 mol/dm^3. Three prepared capsules, as explained in chapter 3.2, were suspended in the filled beaker (feed solution) with a piece of string. The capsules contained a 3 mol/dm^3 hydronium ion concentration. The extractant concentration used for the experiments varied. The experiments were done isothermally at 70 °C. The feed solution was stirred with a magnetic stirrer. The magnetic stirrer was used to control the Reynolds number of the feed solution at 9000.

Samples were taken from the feed solution at different time intervals. The pH of the feed solution was readjusted to 4.5 (if necessary) at these sampling points with a diluted sodium hydroxide solution. The nickel concentration of the feed solution was not readjusted.

4.6.4 Results and discussion

The extraction of nickel was evaluated in the same manner as in chapter 3.5.1 to give the cumulative extraction of nickel with respect to time. The results of the experiments can be seen in appendix A.6.

A graphical representation of the influence of the extractant concentration on the final extraction and the initial rate of extraction can be seen in figures 4.13 and 4.14 respectively.

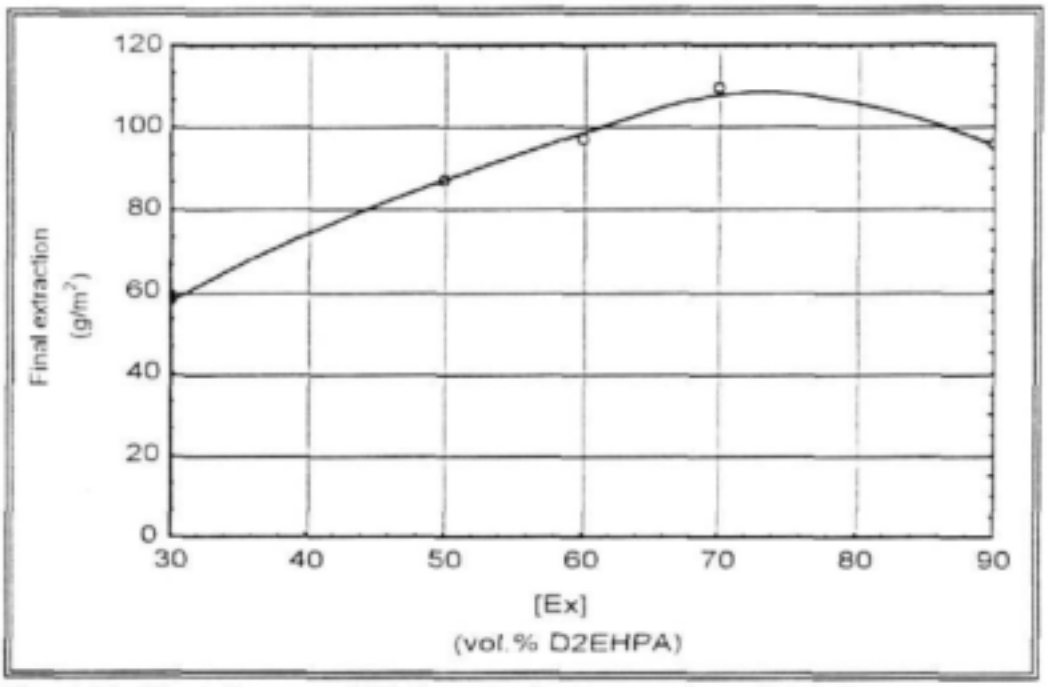


Fig. 4.13: The influence of [Ex] on the final extraction of nickel.

The optimum extractant concentration for the final extraction of nickel is ±70 vol.% D2EHPA dissolved in Escaid 100. The optimum extractant concentration for the initial rate of extraction is ±60 vol.% D2EHPA dissolved in Escaid 100. It is clear that the maximum nickel that can be extracted with CME is 109 g/m^2. This is equivalent to R 3.46 /m^2. The membranes used, cost approximately \$10 / m^2 (R 45.65 /m ^{2}). This implies that the membrane capsules should be recycled at least 14 times to obtain a profit under these adverse cost assumptions.

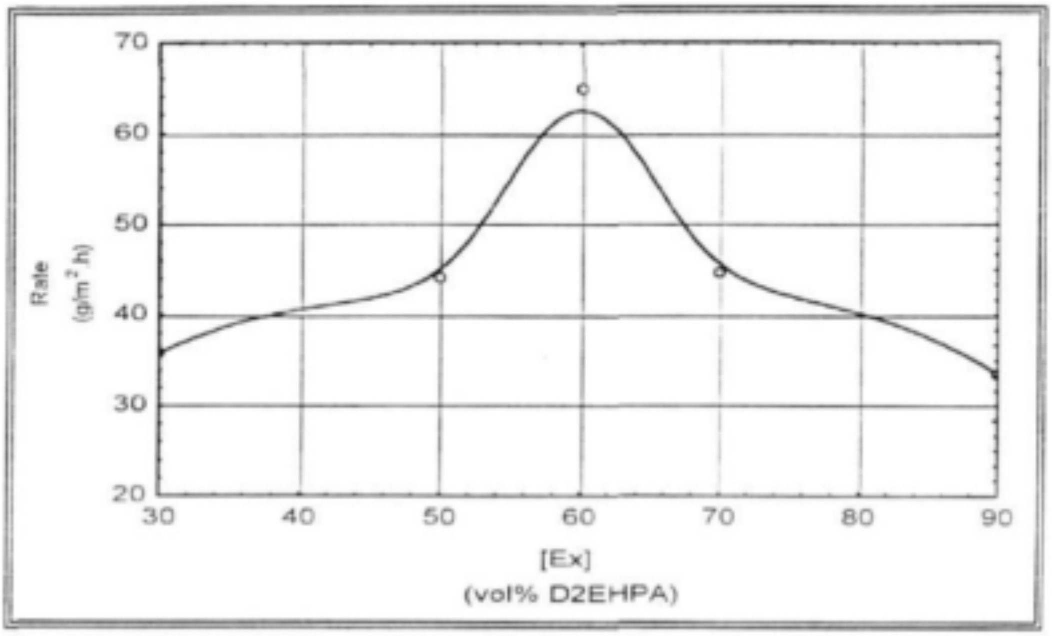


Fig. 4.14: The influence of [Ex] on the initial rate of nickel extraction.

The time needed to extract 90% of the final extraction can be calculated from equation 3.2:

$$\begin{aligned} Extr_{Ni} &= b\,(1-e^{-ct}) \\ \therefore 0.9\,b &= b\,(1-e^{-ct}) \\ \therefore 1-e^{-ct} &= 0.9 \\ \therefore -c\,t &= \ln\,0.1 \\ \therefore t &= -\frac{\ln\,0.1}{c} \end{aligned} \tag{4.2}$$

The time needed to extract 90% of the final extraction, if the extractant concentration is 60 vol% D2EHPA is 3.45 hours.

4.7 Conclusions

The research in this chapter was focused on clarifying the remaining uncertainties of CME and to find the optimum extraction conditions for CME. The following conclusions can be made from the results obtained in this chapter:

1. The final amount of extraction and initial rate of extraction increases if the hydronium ion concentration of the strip solution is increased. At the point of approximately 4 mol/dm^3 a maximum extraction of nickel occurs.
2. If the hydronium ion concentration of the strip solution is increased further, the osmotic pressure becomes greater than the hydrophobicity of the liquid membrane and osmosis occurs. This has a negative effect on the extraction process. The extraction of nickel decreases and there is a large loss of hydronium ions.
3. The osmotic effect can also result in the transport of contaminants to the strip solution in an industrial application due to so-called hydraulic short-circuiting.
4. The final amount of nickel extracted with SLM increased with 154% and the initial rate of extraction with 253% when the temperature was increased from 25 °C to 85 °C.
5. The final amount of nickel extracted with CME increased with 39.88 % and the initial rate of extraction increased with 49.86 % when the feed solution was agitated vigorously.
6. The most dramatic increase occurred when the Reynolds number of the feed solution was increased from 0 to ±9000.
7. Calcium acetate inhibits the extraction of nickel with CME, while sodium acetate enhances this extraction.
8. The optimum acetate concentration is ±0.10 mol/dm^3 and results in a 63.5% improvement on the final extraction of nickel and a 218.9% improvement on the initial rate of extraction.
9. The optimum extractant concentration was found to be ±60 vol% D2EHPA dissolved in Escaid 100.

10. If the abovementioned optimum conditions are used, it is possible to obtain a final extraction of ±109 g/m^2 at a rate where 90% of the extraction occurs within the first 3.45 hours.

11. The membrane capsules have to be recycled at least 14 times to obtain a profit at the current economic conditions. Alternatively a membrane costing less than R 3.46 /m^2 is necessary to make a profit.

Chapter 5

Development of a rate equation for CME

5.1 Introduction

In the past a great number of researchers have spent a large amount of time and energy to derive a theoretical rate equation for SLM systems (refer to chapter 2.3.3). All of these rate equations are subject to one ore more of the following weaknesses:

12. These equations are bulky and it is difficult to solve the constants in these multi-variable, nonlinear equations.
13. These equations are derived under assumptions which are not applicable to CME. For example: The assumption that the strip metal loading is neglible is not applicable to CME.
14. These equations do not make allowance for the influence of temperature, agitation and the influence of anion ligands.
15. These equations have a limited practical significance for calculation purposes.

To derive a theoretical equation which will overcome the abovementioned weaknesses will be a very difficult and time-consuming process. The equation will probably be very bulky and cumbersome to use. This leads to the concept that the CME system configured as thus can be viewed as a pseudo catalytic reaction. The rate equation for the CME system can thus be developed in an empirical way, such as traditionally applied to catalytic reactions. This is a bold assumption, but it subsequently has proven to be promising and fruitful and has resulted in a practical and elegant equation which has taken cognisance of all relevant effects.

5.2 Mathematical development of rate equation

5.2.1 Definition of the rate equation

The mathematical definition of a chemical reaction rate has been a source of confusion in chemical and chemical engineering literature for many years (Fogler, 1992:4). The earliest definition of reaction rates was developed from experiments in batch-type reactors in which the reaction vessel was closed and rigid. The reactants were mixed together at time t = 0 and the concentration of one of the reactants, C_A, was measured at various times t. The rate of reaction was determined from the slope of a plot of C_A as a function of time. Letting r_A be the rate of formation of A per unit volume (e.g., mol/s·dm^3), the investigators then defined and reported the chemical reaction rate as:

$$r_A = \frac{dC_A}{dt} \tag{5.1}$$

The reaction rate equation (i.e., the rate law) is essentially an algebraic equation involving the concentration of the different components involved in the reaction, not a differential equation (Fogler, 1992:4).

The rate equation for the CME system can be viewed as a pseudo catalytic reaction and the rate equation can be developed in an empirical way, such as traditionally applied to catalytic reactions. The rate equation must then be defined as the extraction rate of one of the ions (nickel in this case) per unit area of the membrane (e.g., mol/m^2·h). The rate equation is then an algebraic equation involving the concentrations of the different components involved in the extraction. The components involved in the extraction of nickel with CME is the nickel concentration of the feed solution, the nickel concentration of the strip solution, the hydronium ion concentration of the feed solution and the hydronium ion concentration of the strip solution (refer to chapter 3.4.1).

The following algebraic equation is analogous to the rate equations used to describe catalytic reactions:

$$Rate_{Ni} = k\,[Ni]_f^a\ [Ni]_s^b\ [H]_f^c\ [H]_s^d \tag{5.2}$$

In this equation k is the reaction constant and a, b, c and d are algebraic constants.

5.2.2 The influence of temperature

It was the Swedish chemist Arrhenius who first suggested that the temperature dependence of the specific reaction rate, k, could be correlated by an equation of the type (Fogler, 1992:62):

$$k(T) = k_0\,e^{-\frac{E}{RT}} \tag{5.3}$$

Where k_0 is the frequency factor, E is the activation energy (J/mol), R is the ideal gas constant (8.314 J/mol·K) and T is the absolute temperature.

This equation is also applicable on the CME rate equation.

5.2.3 The influence of feed solution agitation

The influence of agitation of the feed solution was investigated in chapter 4.4. This investigation showed that the rate of extraction increased up to a Reynolds number of 9 000 and that a further increase in the Reynolds number has little or no effect on the rate of extraction. The influence of this type of response on the rate equation can be described with the following exponential term:

$$a\,(1 - e^{b\,Re}) \tag{5.4}$$

Where Re is the Reynolds number and a and b are constants.

5.2.4 The influence of anion ligands

The influence of anion ligands on the extraction of nickel with CME was investigated in chapter 4.5. This investigation showed that the presence of sodium acetate enhances the extraction, but that an optimum ligand concentration exists. The influence of this kind of response on the rate equation can be described with the following polynomial factor:

$$[Ac]^{a} + b\,[Ac] + c \tag{5.5}$$

Where a, b and c is constants and [Ac] is the acetate concentration in mol/dm^3.

5.2.5 The optimum extractant concentration

It was shown in chapter 4.6 that an optimum extractant concentration exists. Once again the influence of the extractant concentration on the rate equation can be described with a polynomial factor:

$$[Ex]^{a} + b * [Ex] + c \tag{5.6}$$

Where a, b and c is constants and [Ex] is the volume fraction of D2EHPA dissolved in Escaid 100.

5.2.6 The development of the rate equation

A rate equation for the extraction of nickel with CME can be developed if all the above mentioned factors (Eq. 5.2 - Eq. 5.6) are combined in a single equation:

$$\begin{aligned} Rate_{Ni} = {} & k\,(-[Ac]^{a} + b\,[Ac] + 1)(-[Ex]^{c} + d\,[Ex])(1 - e^{-f\,Re})\left(e^{-\frac{E}{RT}}\right) \\ & \times [Ni]_{f}^{g}\,[Ni]_{s}^{h}\,[H]_{f}^{i}\,[H]_{s}^{j} + l \end{aligned} \tag{5.7}$$

5.3 Results

The results of the experiments in the previous chapter were used as data for solving the values of the constants in equation 5.7. The experiments yielded 484 data points. Seven outlier data points (1.44% of the total data points) were overlooked and the following function was fitted through the remaining data:

$$Rate_{Ni} = 441.31\,(-[Ac]^6 + 0.95142\,[Ac] + 1)(-[Ex]^4 - 9.8940\,[Ex])$$
$$\times(1 - e^{-0.90963\,Re})\left(e^{-\frac{461.72}{RT}}\right)[Ni]_f^{3.1532}\,[Ni]_s^{-0.10284}\,[H]_f^{-0.19790}\,[H]_s^{2} + 0.0169 \qquad (5.8)$$

The accuracy of this equation will be discussed in paragraph 5.4. There are a few significant conclusions that can be made from this equation:

1. The extractant concentration and the acetate concentration have an optimum concentration (refer to chapter 4.5 and 4.6).
2. The agitation of the feed solution is indeed a saturated exponential form (refer to chapter 4.4).
3. The Arrhenius equation describes the influence of temperature on the rate of extraction. The reaction is endothermic with an activation energy of 461.72 J/mol.
4. The positive exponents for the nickel feed- and hydronium ion strip concentrations show that high concentrations of nickel in the feed and high concentrations of hydronium ions in the strip solution are advantageous for the rate of extraction. This is consistent with all the literature.
5. The negative exponents for the nickel strip- and hydronium ion feed concentrations show on the other hand that high concentrations of nickel in the strip and high concentrations of hydronium ions in the feed solution are disadvantageous for the rate of extraction.
6. The equation is undefined for a nickel strip- and hydronium ion feed concentration of zero. The equation can however describe very low concentrations.

5.4 Accuracy of the rate equation

The two most important influences on the accuracy of equation 5.8 were the accuracy of the analytical methods and the distribution of the data points. 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 300 mg/dm^3 (30%). Thus, the accuracy which could be obtained with the AA was 28.5%. 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, could be identified and were omitted. This is a current statistically verified and accepted procedure. The final curve fit of the data could explain at least 85% of the variance for every experiment.

Statistica for Windows was used to solve equation 5.7. The standard residual values, the deleted residual values and the Cook's distances of the data points were used as criteria to identify seven outlier data points (refer to chapter 3.5.3) which where omitted. An equation (Eq. 5.8) was fitted through the remaining data points. This equation could explain 94.4% of the variance.

The fact that the variables (values) of the factors were not distributed across a large range for the different data points could be another reason for inaccuracy of equation 5.8. A graphical representation of the observed and predicted values for equation 5.8 are given in figure 5.1. This representation shows that, although the equation describes the data very well, the data points are not evenly distributed. This limits the application of equation 5.8. The value of equation 5.8 lies in the fact that this equation proves that CME system can be viewed as a pseudo catalytic reaction and that the extraction rate equation can be derived accordingly.

The graphical representation of the standard residual values, the deleted residual values and the Cook's distances for equation 5.8 can be seen in figures 5.2, 5.3 and 5.4 respectively. These graphical representations show that there are not any significant outlier data points if the seven previously identified outliers are ignored.

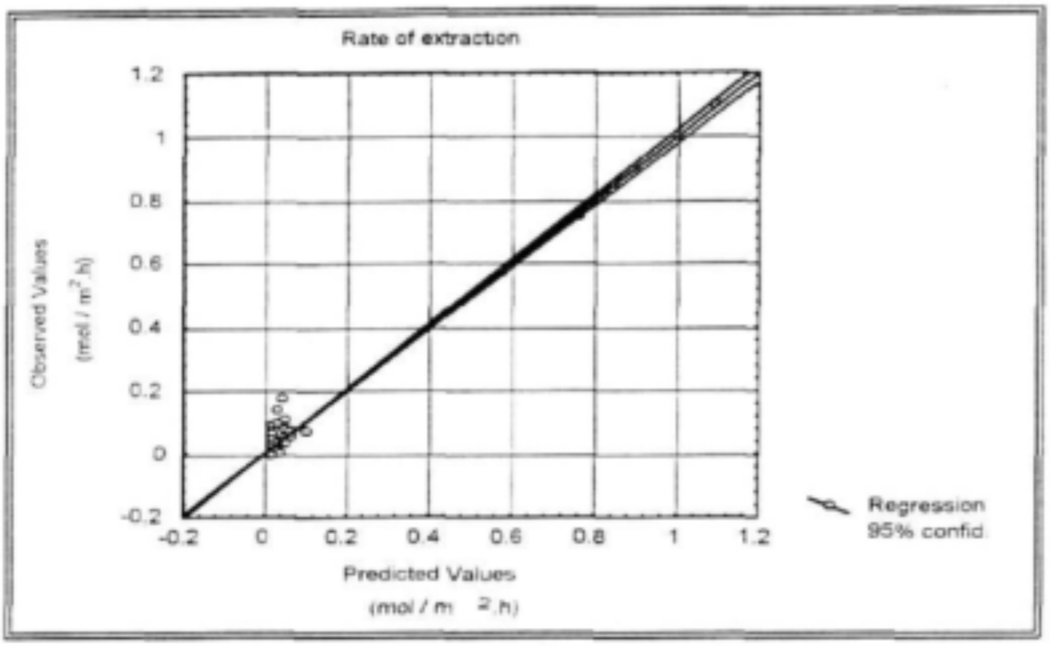


Fig. 5.1: Predicted vs. observed values for equation 5.8.

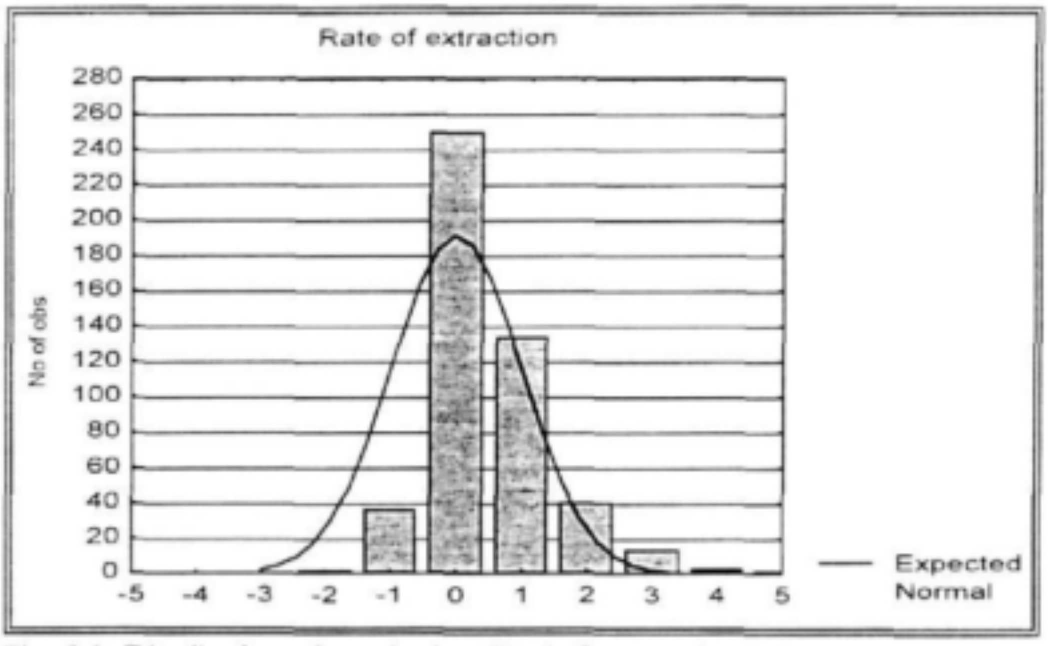


Fig. 5.2: Distribution of standard residuals for equation 5.8.

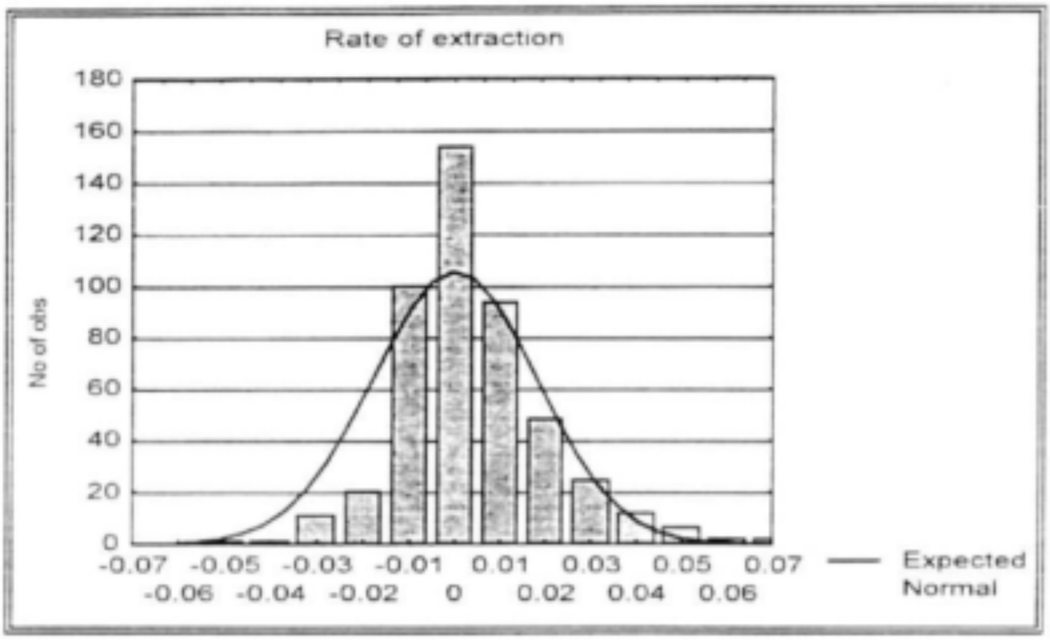


Fig 5.3: Distribution of deleted residuals for equation 5.8.

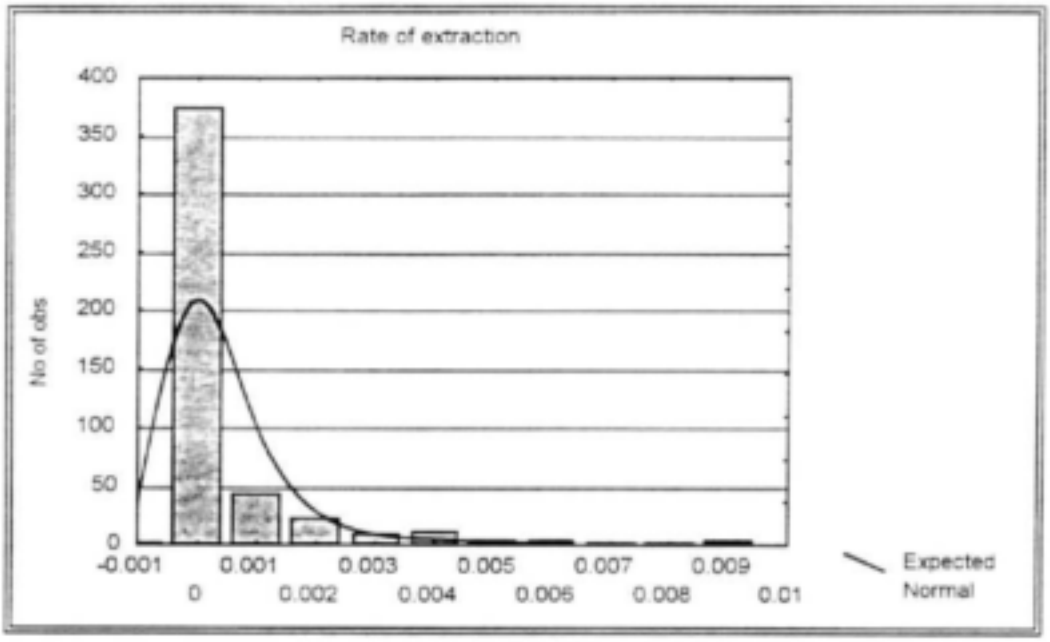


Fig. 5.4: Distribution of Cook's distances for equation 5.8.

5.5 Conclusions

The assumption was made that the CME system can be viewed as a pseudo catalytic reaction and that the rate equation of the extraction process can be developed in an empirical way. The rate equation (Eq. 5.8) was shown to fit the experimental data to a highly acceptable accuracy and explained 94.4% of the variance. This proved the assumption that the CME system can be viewed as a pseudo catalytic reaction.

The fact that the variables of the factors were not distributed across a large range for the different data points limits the application of equation 5.8. The equation can however be used to design a bench scale reactor for CME. A statistical experimental design can be used to determine the experiments done on this reactor. This will ensure that the data points are evenly distributed. The results of these experiments can be used to refine equation 5.8 and the new equation can then be used in industrial applications.

The following conclusions can be made from equation 5.8:

1. The extractant concentration and the acetate concentration have an optimum concentration (refer to chapter 4.5 and 4.6).
2. The agitation of the feed solution is indeed a saturated exponential form (refer to chapter 4.4).
3. The Arrhenius equation describes the influence of temperature on the rate of extraction. The reaction is endothermic with an activation energy of 461.72 J/mol.
4. The positive exponents for the nickel feed- and hydronium ion strip concentrations show that high concentrations of nickel in the feed and high concentrations of hydronium ions in the strip solution are advantageous for the rate of extraction. This is consistent with all the literature.
5. The negative exponents for the nickel strip- and hydronium ion feed concentrations show on the other hand that high concentrations of nickel in the strip and high concentrations of hydronium ions in the feed solution are disadvantageous for the rate of extraction.

6. The equation is undefined for a nickel strip- and hydronium ion feed concentration of zero. The equation can however describe very low concentrations.

Chapter 6
Final conclusions and recommendations

6.1 Final conclusions

Nickel is a widely used metal and therefore subject to report in various effluents as a pollutant. The extraction of nickel at the current price (R 31.76/kg) could consequently be a strong incentive to recover nickel from effluents from various industries but mainly from the plating and catalyst industries.

The influence of different conditions on CME was determined. A central composite experimental design was executed to evaluate the influence of the different factors on the extraction of nickel with CME. The first part of the research (chapter 3) was focused on high hydronium strip concentrations, which is a prominent advantage of CME over SLM. The two equations (Eq. 3.5 & 3.6) were shown to fit the experimental data to a highly acceptable accuracy and explained 81.0% and 81.7% of the variance respectively. The accuracy and reproducibility were both discussed and the experimental protocol showed an inherent accuracy of approximately 85%. In the light of these results it is possible to make the following conclusions on nickel extraction with CME:

7. It is obvious that the extremely high acidity difference (ΔH^+) which is tolerated between the strip solution and the feed solution is advantageous for the extraction of ionic species.
8. This driving force (ΔH^+) creates a system in which extraction proceeds against a concentration gradient of at least 1000:1 when considering the ratio between $[Ni^{2+}]$ in the strip- and feed solutions at final extraction.

The subsequent research (in chapter 4) was focused on clarifying the remaining uncertainties of CME and to find the optimum extraction conditions for CME. The following conclusions can be made from the results obtained:

1. The final amount of extraction and initial rate of extraction increases if the hydronium ion concentration of the strip solution is increased. At the point of approximately 4 mol/dm^3 a maximum extraction of nickel occurs.
2. If the hydronium ion concentration of the strip solution is increased further, the osmotic pressure becomes greater than the hydrophobicity of the liquid membrane and osmosis occurs. This has a negative effect on the extraction process. The extraction of nickel decreases and there is a large loss of hydronium ions.
3. The osmotic effect can also result in the transport of contaminants to the strip solution in an industrial application due to so-called hydraulic short-circuiting.
4. The final amount of nickel extracted with SLM increased with 154% and the initial rate of extraction with 253% when the temperature was increased from 25 °C to 85 °C.
5. The final amount of nickel extracted with CME increased with 39.88 % and the initial rate of extraction increased with 49.86 % when the feed solution was agitated vigorously.
6. The most dramatic increase occurred when the Reynolds number of the feed solution was increased from 0 to ±9000.
7. Calcium acetate inhibits the extraction of nickel with CME, while sodium acetate enhances this extraction.
8. The optimum acetate concentration is ±0.10 mol/dm^3 and results in a 63.5% improvement on the final extraction of nickel and a 218.9% improvement on the initial rate of extraction.
9. The optimum extractant concentration was found to be ±60 vol% D2EHPA dissolved in Escaid 100.
10. If the abovementioned optimum conditions are used, it is possible to obtain a final extraction of ±109 g/m^2 at a rate where 90% of the extraction occurs within the first 3.45 hours.

11. The membrane capsules have to be recycled at least 14 times to break even under the current economic conditions and adverse cost assumptions.

The extraction rate equation (Eq. 5.8) was shown to fit the experimental data to a highly acceptable accuracy and explained 94.4% of the variance. This proved the assumption that the CME system can be viewed as a pseudo catalytic reaction.

The following conclusions can be made from equation 5.8:

1. The extractant concentration and the acetate concentration have an optimum concentration.
2. The agitation of the feed solution is indeed a saturated exponential form.
3. The Arrhenius equation describes the influence of temperature on the rate of extraction.
4. The reaction is endothermic with an activation energy of 461.72 J/mol.
5. The positive exponents for the nickel feed- and hydronium ion strip concentrations show that high concentrations of nickel in the feed and high concentrations of hydronium ions in the strip solution are advantageous for the rate of extraction. This is consistent with all the literature.
6. The negative exponents for the nickel strip- and hydronium ion feed concentrations show on the other hand that high concentrations of nickel in the strip and high concentrations of hydronium ions in the feed solution are disadvantageous for the rate of extraction.
7. The equation is undefined for a nickel strip- and hydronium ion feed concentration of zero. The equation can however describe very low concentrations.

6.2 Recommendations

6.2.1 Introduction

The research in this report led to the publication of two articles. The first article was entitled *The extraction of nickel with the use of supported liquid membrane capsules* and was publicized in *Water SA*, volume 22, number 3, July 1996. The second article was entitled *Optimization of nickel extraction with supported liquid membrane capsules* and is in the process of being refereed by the same journal..

6.2.2 Recommendations from research

The extraction of nickel or any other metal ions from industrial effluents with CME is a very elegant method. The main advantage of this extraction method is that the extracted ions can be reclaimed. This extraction method only recovers the valuable ions (nickel) and none of the other, often undesired, ions in the feed solution. The capsule configuration also introduces the concept of an unconfined reactor, which implies that no fixed geometry (reactor containment) is required.

It is possible to make the following recommendations from this research towards an industrial application:

1. It was shown from the research that high hydronium ion concentration in the strip solution is very advantageous for the extraction process. If the hydronium ion concentration is too high, however, osmosis occurs. It is therefore recommended that the hydronium ion strip concentration used should be between 3 and 4 mol/dm^3.
2. The nickel concentration of the feed solution should be as high as possible. This recommendation is more for academic purposes, since the nickel concentration of the feed solution is usually an uncontrollable variable for an industrial application.
3. The pH of the feed solution should be as high as possible. The maximum pH which can be used is dependent of the precipitation point of nickel hydroxide. For example nickel hydroxide precipitates at a pH of 6.4 at 25 °C if the nickel concentration is 1

mol/dm^3 (Jackson, 1986:158).

4. The capsule membrane extraction process is an endothermic reaction, which implies that the temperature of the feed solution should be as high as possible. The maximum temperature is dependent on the boiling point of the feed solution (100 °C at 101.3 kPa).
5. It is recommended that the feed solution should be agitated. A Reynolds number of ±9000 is recommended. More vigourous agitation will result in little or no enhancement of the rate of extraction.
6. It is recommended that a sodium acetate solution of 0.1 mol/dm^3 acetate should be used for the feed solution to act as an ligand accelerator.
7. An extractant concentration of 60 vol% D2EHPA dissolved in Escaid 100 should be used.

6.2.3 Foreseeable problems

The research showed that at the current economical situation it will be necessary to recycle the capsules at least 17 times to break even. This recycling technology will probably be the biggest obstacle for the industrial application of CME. A large amount of energy will have to be invested in the development of such a recycle method for CME. An alternative is to use the knowledge gained with CME to develop a hollow tube reactor. The problem with a hollow tube reactor is to develop a cost effective reactor which will be able to endure the high hydronium ion strip concentrations needed for the supported liquid membrane process.

6.2.4 Future research

The recommended research path to develop an industrial application for the extraction of nickel with supported liquid membranes (or membrane capsules) can be seen in figure 6.1.

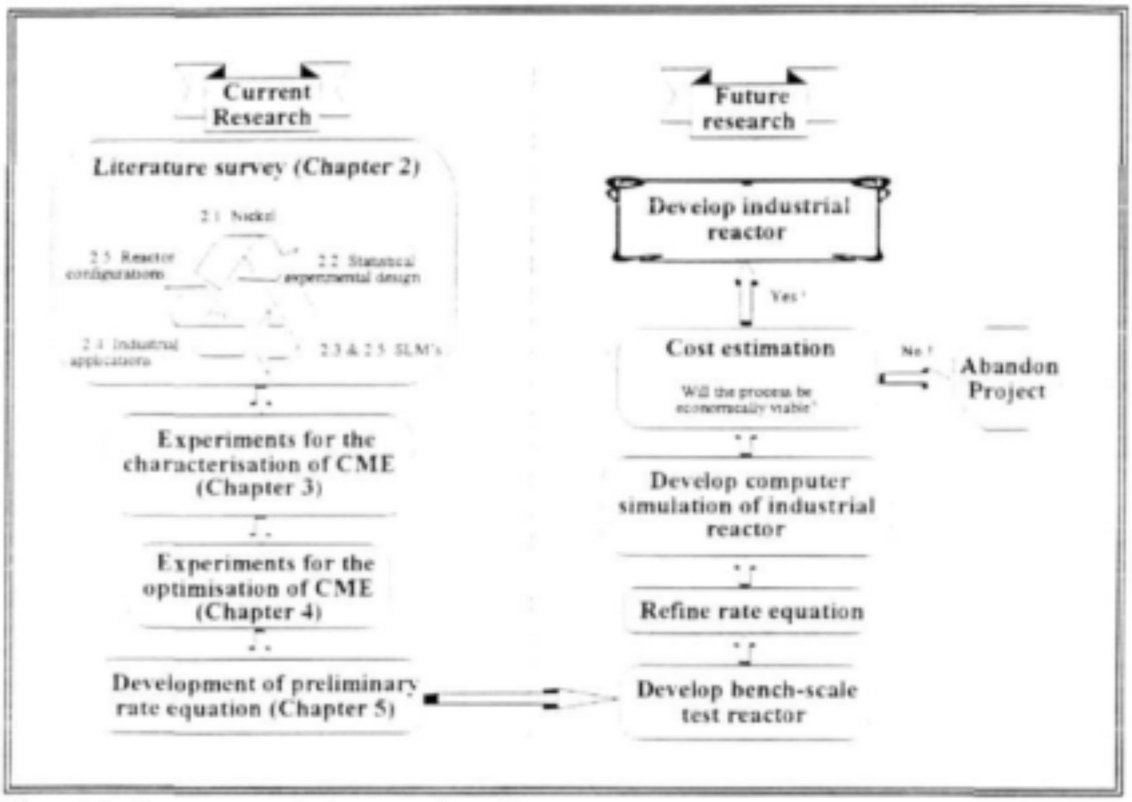


Fig. 6.1: Recommended research path.

It is essential to study current literature. This will ensure that the newest developments can be incorporated in an industrial process. Experiments to characterise and optimise the CME process have been done in this report (chapter 3 & 4). A preliminary rate equation has also been developed (chapter 5) and this equation can be used to design a bench-scale test reactor. A statistical experimental design will ensure that the experiments done on the test reactor is distributed across a large range of variables (values) for the different factors. The results obtained in these experiments can be used to refine the rate equation. This refined rate equation can be used to develop a computer simulation of an industrial reactor. This simulation can be used to optimise the industrial conditions and to do a cost estimation and financial evaluation. If the simulation shows that a commercial reactor would be economically viable, the project will be completed with the developing of an industrial reactor.

6.2.5 Closing remarks

The extraction of nickel with capsule membrane extraction is a relatively new and exiting research field. The increasing environmental pressure on industries to clean their effluents makes this a very actual technology. If the few remaining techno-economic problems of CME can be solved, this technology will be the newest membrane process used to clean industrial effluents and to reclaim valuable metals.

References

ABOU-NEMEH, I. & VAN PETEGHEM, A.P. 1992. Extraction of metals from simulated and industrial effluents by liquid surfactant membranes (LSM). *Hydrometallurgy*. 31 : 149-162.

ANON. 1996. Koerse, metale en beleggings. *Beeld*: S6, Augustus 16.

ANON. 1970. Nickel plating. (*In* Materials and Technology, 3:684-690.)

BABCOCK, W.C., BAKER, E.D., LACHPELLE, E.D. & SMITH, K.L. 1980. Coupled transport membranes II : The mechanism of uranium transport with tertiary ammine. *Journal of membrane science*, 7 : 71-81.

BIRD, R.B., STEWART, W.E. & LIGHTFOOT, E.N. 1960. Transport phenomena. New York : John Wiley & sons. 780 p.

BOGACKI, M.B., COTE, G. & SZYMANOWSKI, J. 1993. Modelling of nickel extraction between di-N-butyl phosphorodithioate and acid. *Industrial and Engineering Chemistry Research*, 32(11) : 2775-2780.

BROMBERG, L., LEVIN, G. & KEDEM, O. 1992. Transport of metals through gelled supported liquid membranes containing carrier. *Journal of Membrane Science*, 71 : 41-50.

CELANESE SEPARATIONS PRODUCTS. 1985. Microporous film and hollow fibres, Technical information. Brussels. 5 p.

CHIARIZIA, R. & CASTAGNOLA, A. 1984. Transfer rate and separation of Fe(III), Co(II) and Ni(II) chloride species by supported liquid membrane. *Solvent extraction and ion exchange*, 2(3) : 479-506.

CRUYWAGEN, J.J., HEYNS, J.B.B., RAUBENHEIMER, H.G. & VAN BERGE, P.C. 1981.

Inleiding tot die Anorganiese en Fisiese Chemie. 2de uitg. Durban : Butterworth. 423 p.

DANESI, P.R. 1985. Separation of metal species by supported liquid membranes. *Separation science and technology*, 19(11&12) : 857-894.

DANESI, P.R. & REICHLEY-YINGER, L. 1986. Origin and Significance of the Deviation from Pseudo First Order Rate Law in the Coupled Transport of Metal Species through Supported Liquid Membranes. *Journal of membrane science*, 29 : 195-206.

DOUGLAS, J.M., 1988. Conceptual Design of Chemical Processes. Singapore : McGraw-Hill International Editions. 601 p.

DRAPER, N.R. 1988. Response Surface Designs. (*In* Encyclopaedia of Statistical Sciences (John Wiley & Sons), 8:107-119.)

ERLANK, S.N. 1994. The application of supported liquid membranes (SLM) and double salt precipitation (DSP) for demineralization of calcium and nickel in agues solution. Potchefstroom : PU vir CHO. (Dissertation - M.Ing (Chem)) 141 p.

FANE, A.G., AWANG, A.R., BOLKO, M., MACOUN, R., SCHOFIELD, R., SHEN, Y.R. & ZHA, F. 1992. Metal recovery from wastewater using membranes. *Water Science and Technology*, 25(10) : 5-18.

FLETT, D.S. 1981. Some recent developments in the application of liquid extraction in hydrometallurgy. *Chemical engineering*, 321-324. July.

FOGLER, H.S. 1992. Elements of Chemical Reaction Engineering. London : Prentice-Hall. 838 p.

GREENWOOD, N.N. & EARNSHAW, A. 1984. Chemistry of the Elements. Oxford : Pergamon Press. 1542 p.

GU, Z.M. & WASAN, D.T. 1986. Ligand-accelerated liquid membrane extraction of metal ions. *Journal of membrane science.* 26(2) : 129-142.

HOFMAN, D.L. 1991. Development and modification of a supported liquid membrane extraction system for the recovery of cesium, strontium and uranium. Potchefstroom : PU vir CHO. (Thesis - Ph.D) 337 p.

MATSUYAMA, H., BOKU, J. & TERAMOTO, M. 1990. Separation and concentration of heavy metal ions by a spiral-type flowing liquid membrane module. *Water Treatment.* 5(2) : 237-252, Apr.

MELZNER, D., TILKOWSKI, J., MOHRMANN, A., POPPE, W., HALWACHS, W. & SCHUGERL, K. 1984. Selective extraction of metals by liquid membrane technique. *Hydrometallurgy*, 13 : 105-123.

JACKSON, E. 1986. Hydrometallurgical extraction and reclamation. New York : Ellis Horwood Limited. 266 p.

PAG. 1996. Executive & Engineering. *Sunday Times, Business Times* :15, March 3.

RITCEY, G.M. & ASHBROOK, A.W. 1984. Solvent extraction : Principles and applications to process metallurgy Part I. New York : Elsevier. 361 p.

RUPERT, M., DRAXLER, J & MARR, R. 1988. Liquid-membrane-permeation and its experiences in pilot-plant and industrial scale. *Separation science and technology*, 23(12):1659-1666, 1988.

SMIT, J.J. 1994. Extractive Purification of Industrial Effluents. Potchefstroom : PU for CHE. (Report - Water Research Commission) 75 p.

SMITH, W.S. 1990. Principles of Material Science and Engineering. Singapore : McGraw-Hill international editions. 864 p.

STATISTICA. 1993. Help screen on outliers in Statistica for windows, Release 4.5. StatSoft Inc. (Copy of program is registered to Statistical consultation service, PU for CHE).

TIEN, J.K. & HOWSON, T.E. 1981. Nickel and nickel alloys. (*In* Kirk-Othmer Encyclopaedia of Chemical Technology (John Wiley & Sons), 15:787-801.)

VERHAEGE, M., WETTINCK, E., VAN ROBAEYS, D. & LAUREYNS, F. 1987. Permeation of nickel through solid supported liquid membranes. *Separation Processes in hydrometallurgy*, Society of chemical industry, 32 : 331-338.

ZHONGMAO, G., QINGJIANG, Z. & LANRUI, J. 1990. Recovery of Ni (II) from nickel plating with liquid membranes. *Water Treatment*, 5(2) : 170-178.

Related literature

APRAHAMIAN, E.A.Jr. & FREISER, H. 1986. Role of the kinetics and mechanism of extraction of nickel by 8-Quinolinols. (*In* University of Arizona. ISEC '86 International solvent extraction conference held in Munich, West Germany on 11 to 16 September 1986. Munich : DECHEMA. p 385-392.)

BOX, G.E.P. & DRAPER, N.R. 1987. Empirical model-building and response surfaces. New York : Wiley. 405 p.

CORNELL, J.A. 1990. How to apply response surface methodology. Milwaukee : ASQC Quality Press. 669 p.

KHURI, A.I. & CORNELL, J.A. 1987. Response surfaces: designs and analyses. New York : Dekker. 82 p.

MEYERS, R.H. 1971. Response surface metrology. Boston : Allyn and Bacon. 246 p.

OSSEO-ASARE, K. & ZHENG, Y. 1986. Synergism, antagonism and selectivity in the Lix63-HDNNS metal extraction system. (*In* Pennsylvania State University. ISEC '86 International solvent extraction conference held in Munich, West Germany on 11 to 16 September 1986. Munich : DECHEMA. p 175-178.)

STEYN, H.S. & HIBBERT, E.S. 1984. Responsvlakke se toepassing by farmaseutiese doseervormontwerpe. *Suid-afrikaanse tydskrif vir Apteekwese:* 565-567, Des.

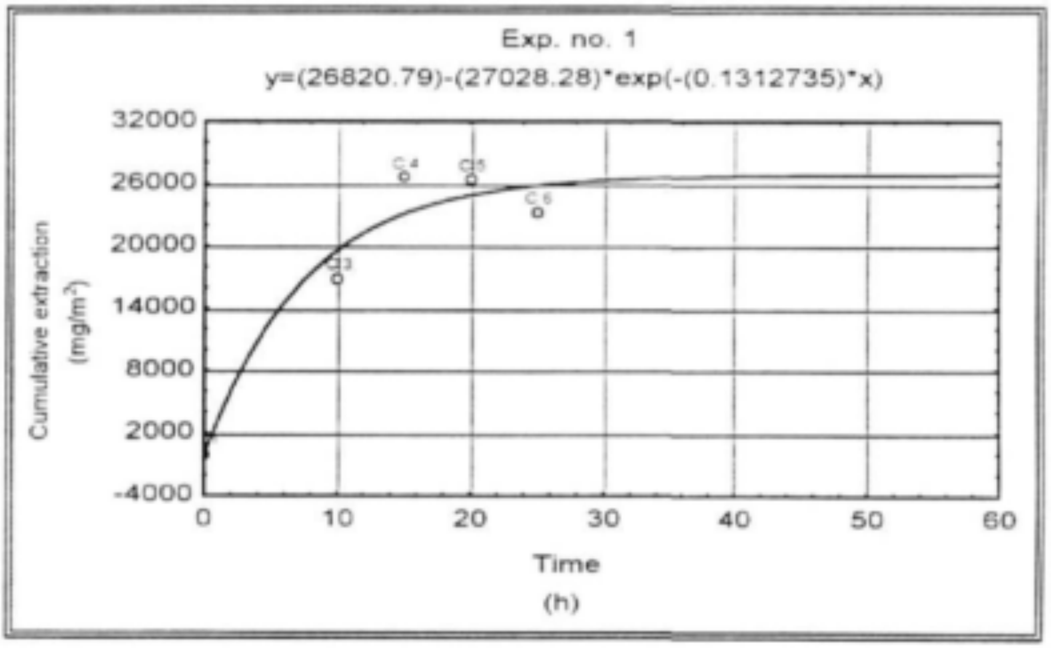
TERAMOTO, MASAAKI, SAKURAMOTO, TADASHI, TAKAYA, HITOSHI, KATAYAMA, YUJI, KOJIMA, ATSUSHI, MIYAKE, YOSHIKAZU, MATSUYAMA, HIDETO. 1986. Selectivity in the extraction of metals by liquid membranes. (*In* Kyoto institute of technology. ISEC '86 International solvent extraction conference held in Munich, West Germany on 11 to 16 September 1986. Munich : DECHEMA. p 545-552.)

Appendix A
Experimental Results

A.1 Results obtained from characterisation experiments

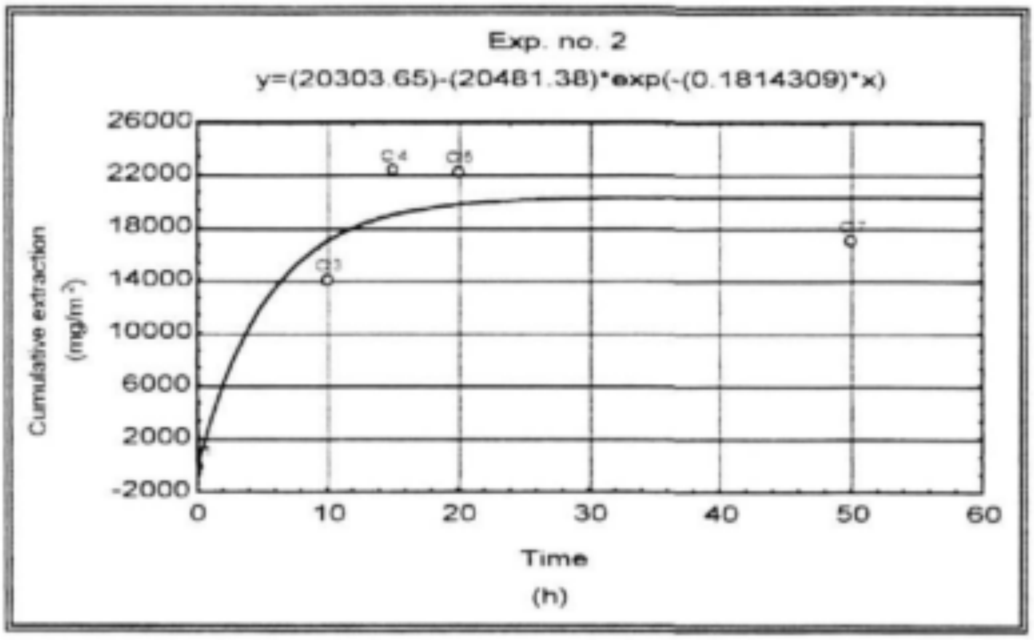
Exp. no: 1
Circum. 0.131 Area 0.0027312

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
Circum. 0.13 Area 0.002689
7

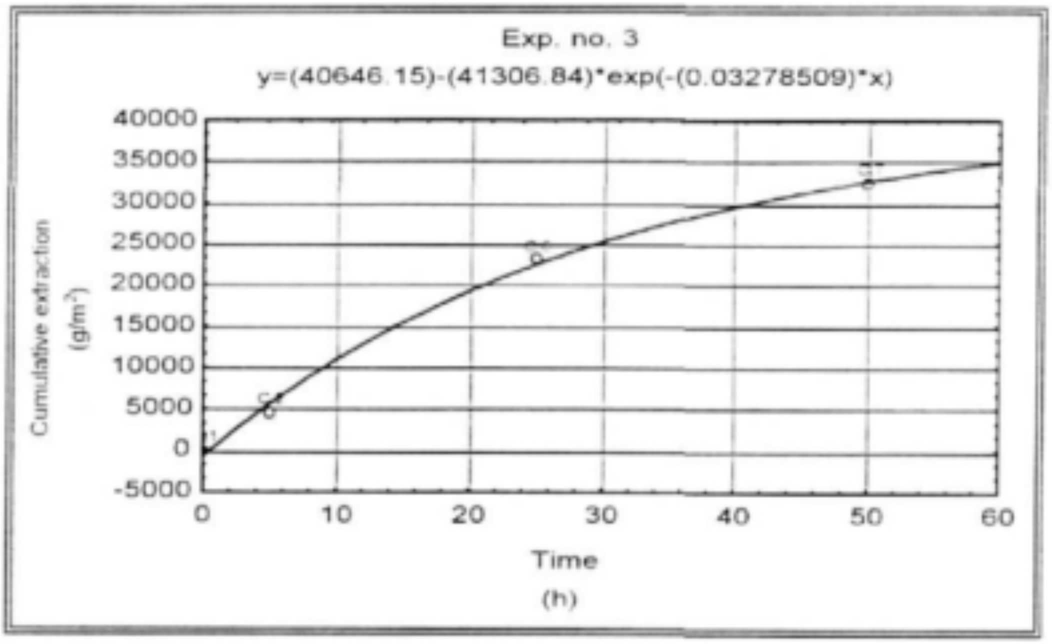
Time	[Ni] feed	Vol.	Adjust.	Extr.	Rate
0	800	0.400	0.000000	0	
5	639	0.400	0.007000	23943	4789
10	851	0.410	0.000000	14089	1409
15	796	0.405	0.000176	22370	1491
20	801	0.400	0.000000	22281	1114
25	818	0.410	0.000000	15223	609
50	816	0.400	0.000000	17066	341



Exp. no: 3

Circum. 0.144 Area 0.0033002

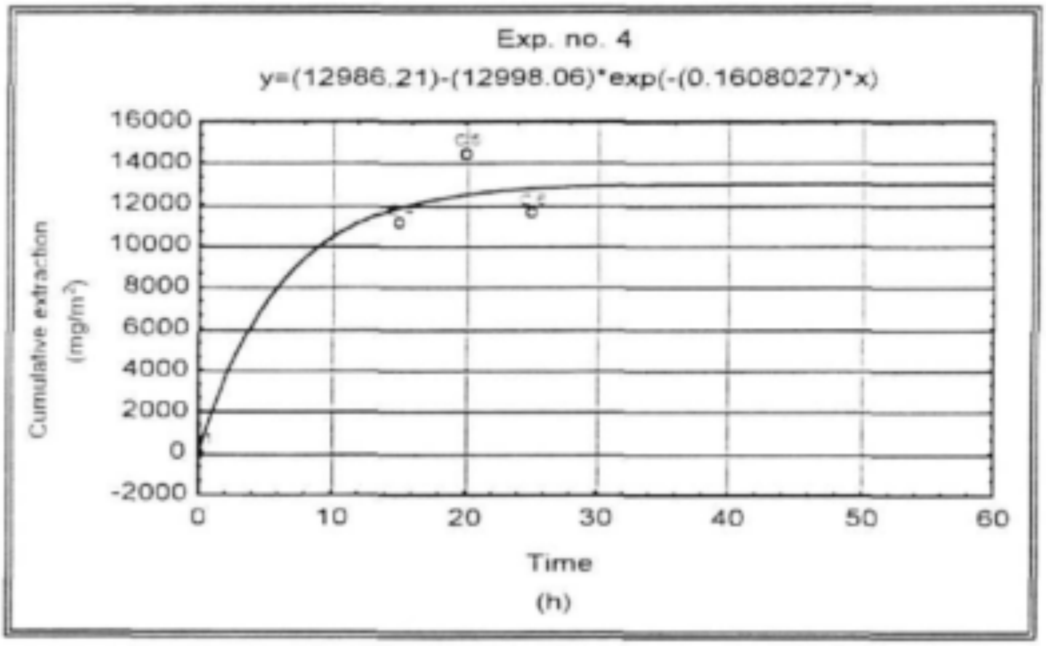
Time	[Ni] feed	Vol.	Adjust.	Extr.	Rate
0	800	0.400	0.000000	0	
5	663	0.460	0.006850	4551	910
10	803	0.475	0.000000	1139	114
15	784	0.470	0.000000	3845	256
20	770	0.400	0.001304	7763	388
25	667	0.400	0.005783	23032	921
50	735	0.395	0.000000	32415	648



Exp. no: **4**

Circum. 0.165 Area 0.0043329

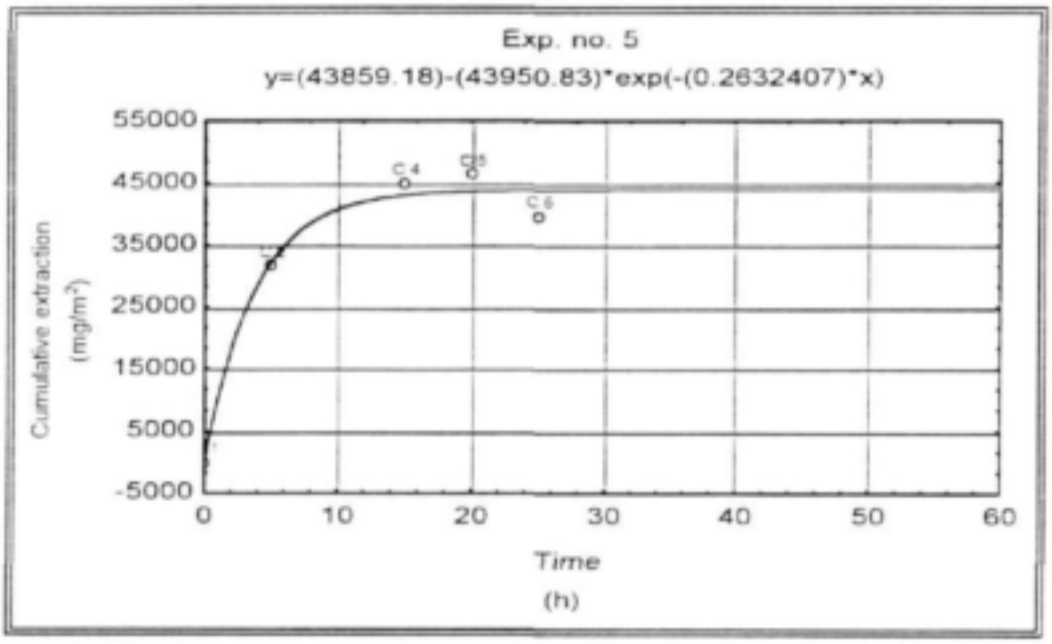
Time	[Ni] feed	Vol.	Adjust.	Extr.	Rate
0	800	0.400	0.000000	0	
5	629	0.488	0.009000	3011	602
10	794	0.500	0.000000	2274	227
15	704	0.405	0.004226	11050	737
20	773	0.400	0.001174	14434	722
25	824	0.400	0.000000	11543	462
50	743	0.398	0.000000	19409	388



Exp. no: 5

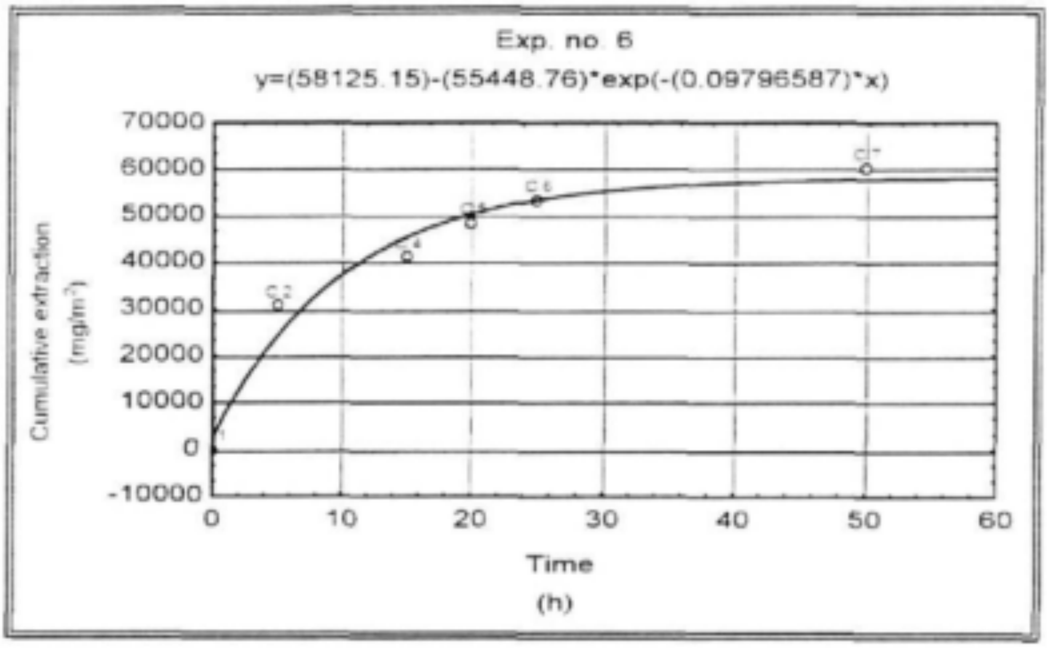
Circum. 0.129 Area 0.0026484

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
Circum. 0.14 Area 0.0031194

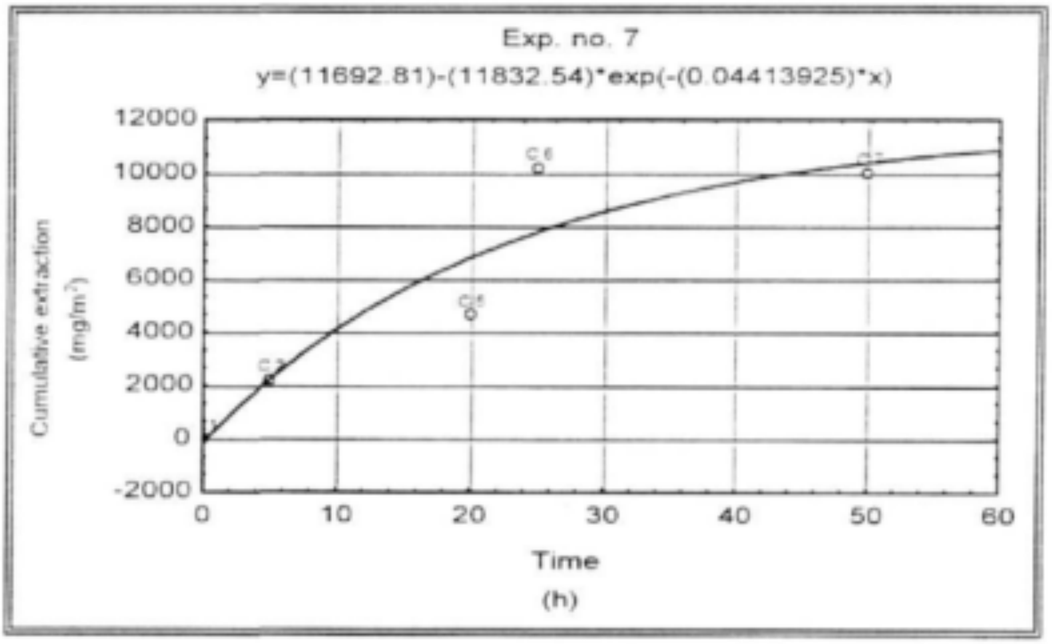
Time	[Ni] feed	Vol	Adjust.	Extr.	Rate
0	1200	0.400	0.000000	0	
5	938	0.410	0.012207	30589	6118
10	1248	0.412	0.000000	26672	2667
15	1144	0.405	0.002577	40975	2732
20	1137	0.405	0.002899	48312	2416
25	1170	0.400	0.001364	53385	2135
50	1156	0.398	0.000000	60292	1206



Exp. no: 7

Circum. 0.143 Area 0.0032545

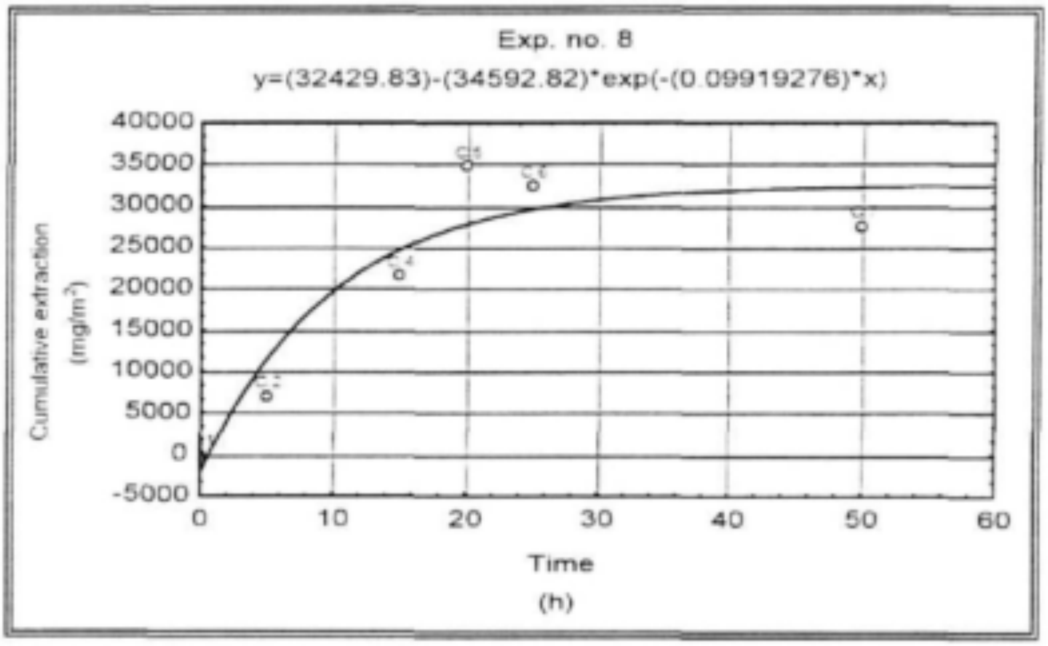
Time	[Ni] feed	Vol.	Adjust.	Extr.	Rate
0	1200	0.400	0.000000	0	
5	1087	0.435	0.005586	2198	440
10	1245	0.435	0.000000	-3427	-343
15	1176	0.440	0.001200	2076	138
20	1171	0.440	0.001450	4633	232
25	1124	0.450	0.003886	10190	408
50	1156	0.445	0.000000	19482	390



Exp. no: 8

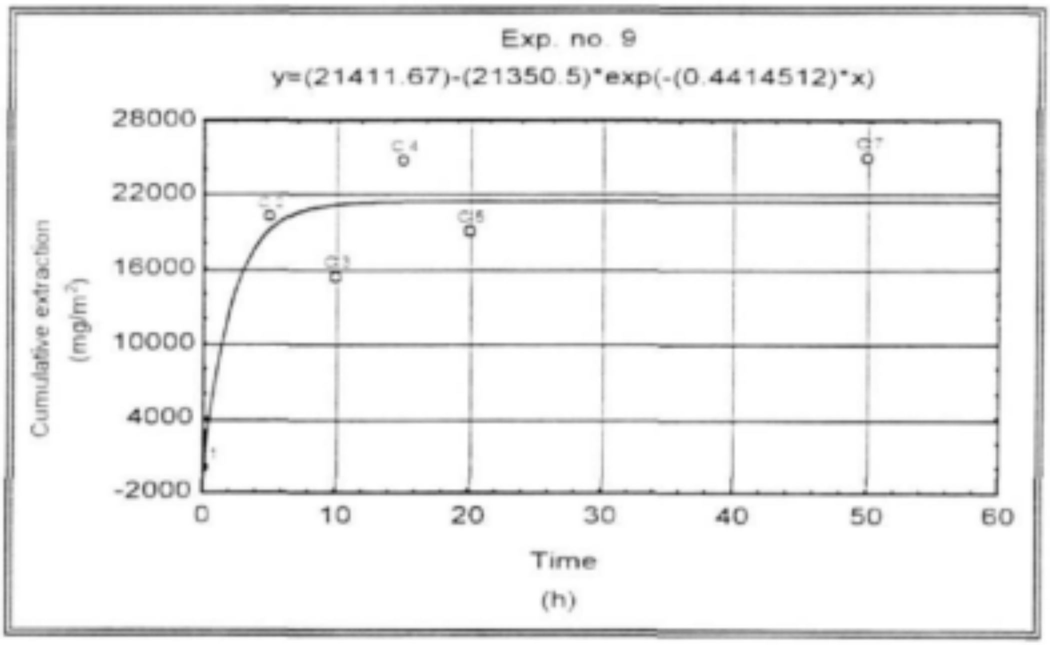
Circum. 0.137 Area 0.0029871

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
Circum. 0.131 Area 0.0027312

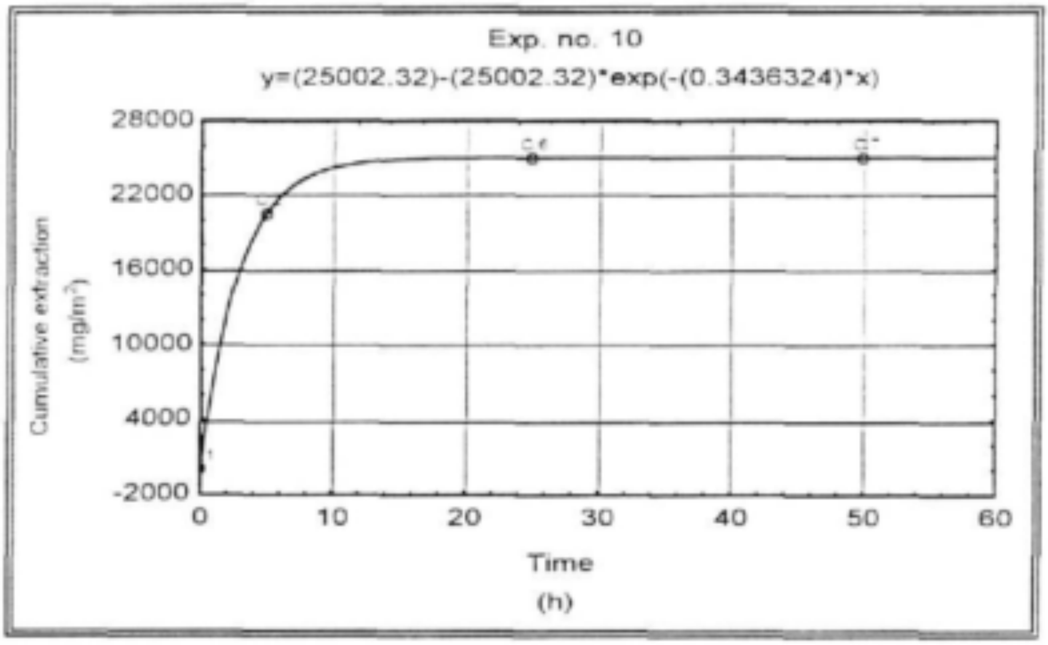
Time	[Ni] feed	Vol.	Adjust.	Extr.	Rate
0	800	0.400	0.000000	0	
5	662	0.400	0.006000	20210	4042
10	826	0.405	0.000000	15436	1544
15	766	0.398	0.001471	24784	1652
20	839	0.395	0.000000	19051	953
25	888	0.400	0.000000	8803	352
50	898	0.395	0.000000	9003	180



Exp. no: 10

Circum. 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



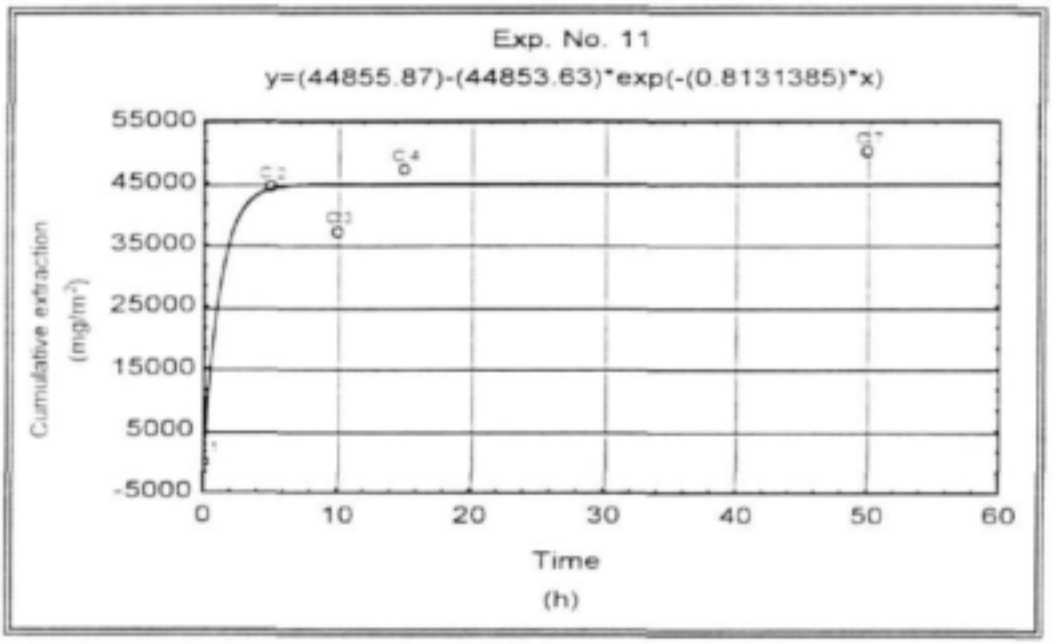
Exp. no. 10

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

Exp. no: 11

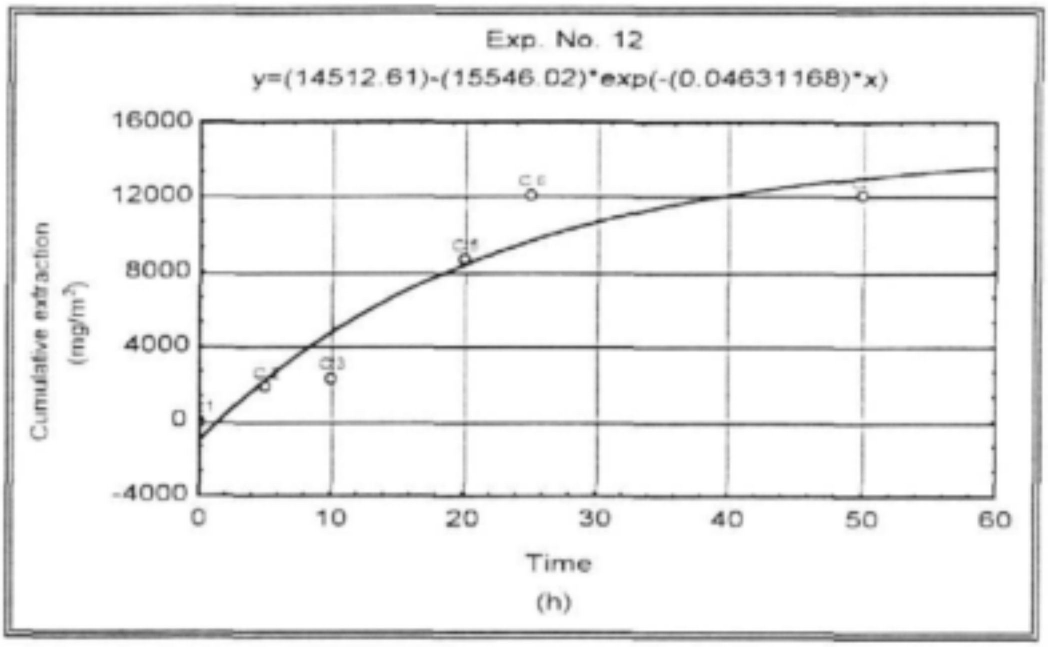
Circum. 0.129 Area 0.0026484

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: 12
Circum. 0.122 Area 0.0023688

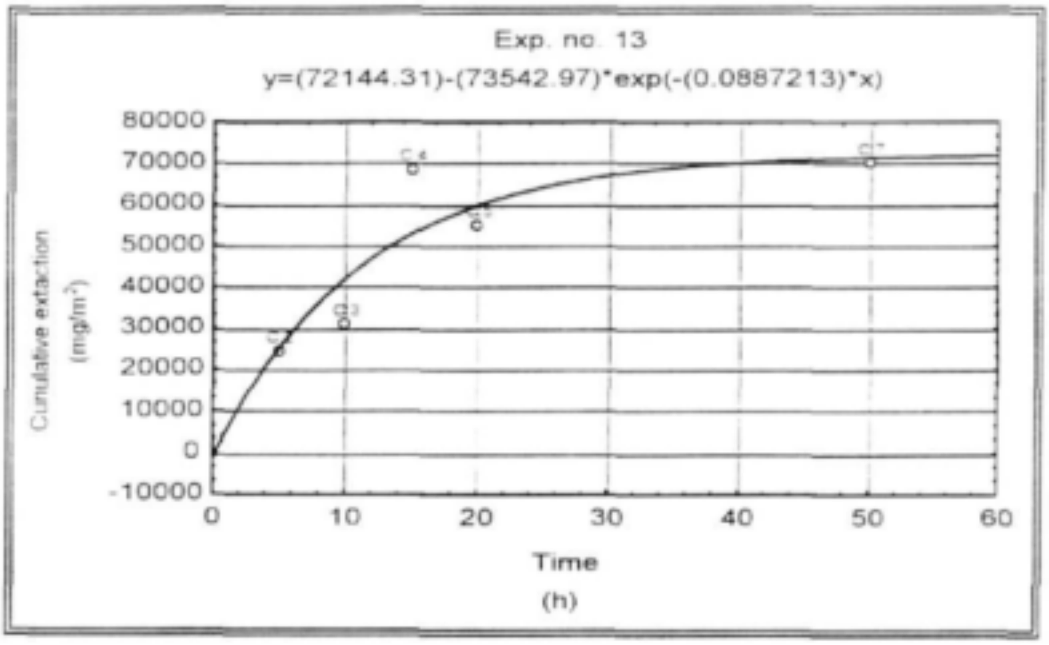
Time	[Ni] feed	Vol.	Adjust	Extr.	Rate
0	803	0.400	0.000000	0	
5	745	0.420	0.002000	1809	362
10	781	0.420	0.000000	2296	230
15	627	0.418	0.007000	28482	1899
20	895	0.420	0.000000	8662	433
25	845	0.430	0.000000	12071	483
50	855	0.430	0.000000	8451	169



Exp. no: 13

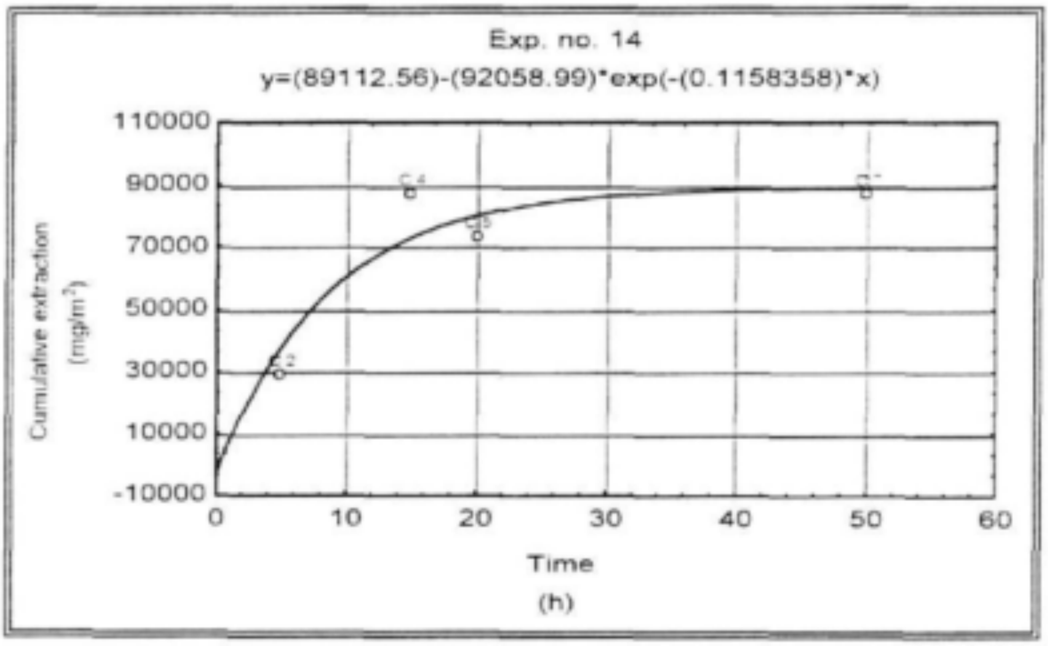
Circum. 0.138 Area 0.0030309

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



Exp. no: 14
Circum. 0.108 Area 0.0018563

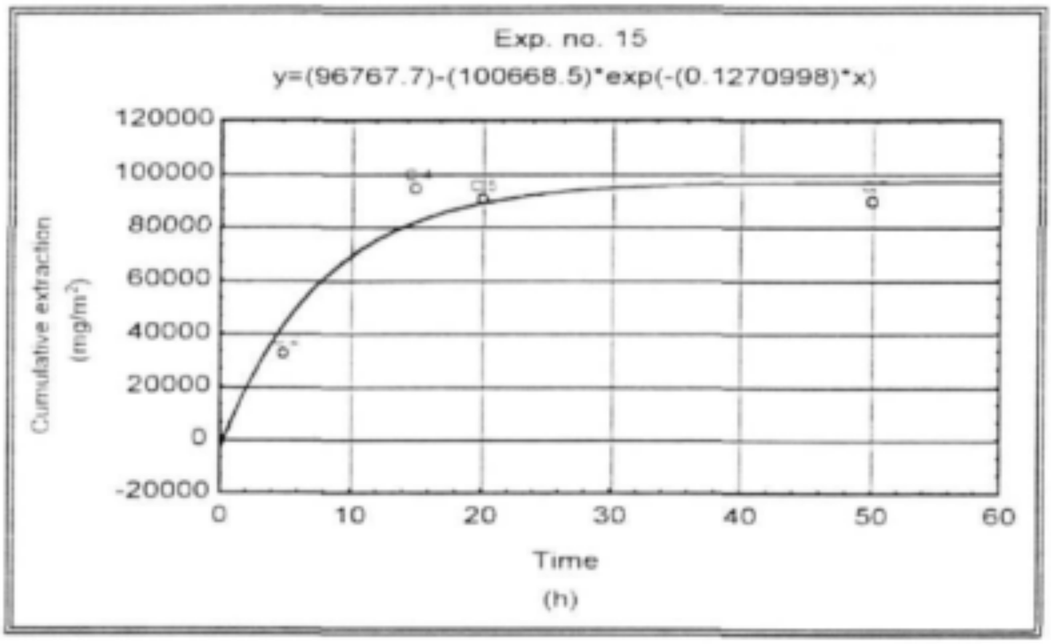
Time	[Ni] feed	Vol.	Adjust.	Extr.	Rate
0	1154	0.400	0.000000	0	
5	1005	0.400	0.008000	28997	5799
10	1197	0.410	0.000000	21566	2157
15	896	0.405	0.014000	87234	5816
20	1249	0.420	0.000000	73131	3657



Exp. no: 15

Circum. 0.102 Area 0.0016558

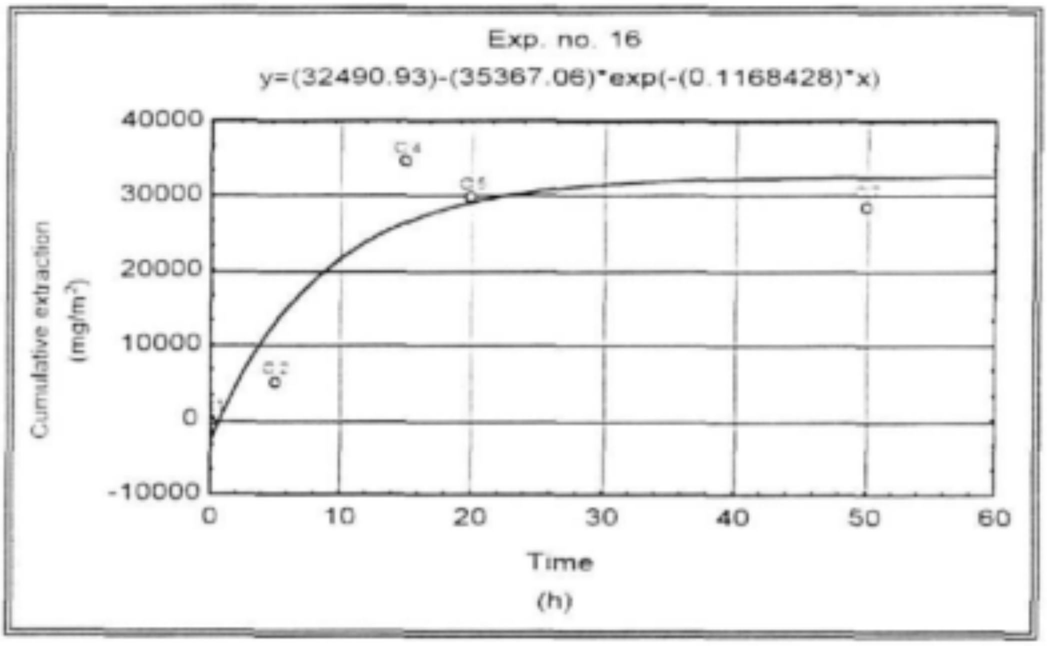
Time	[Ni] feed	Vol.	Adjust.	Extr.	Rate
0	1265	0.400	0.000000	0	
5	1115	0.400	0.003000	32415	6483
10	1188	0.400	0.000000	29532	2953
15	905	0.400	0.013000	94308	6287
20	1212	0.408	0.000000	90068	4503
25	1370	0.410	0.000000	45822	1833
50	1357	0.405	0.000000	49002	980



Exp. no: 16

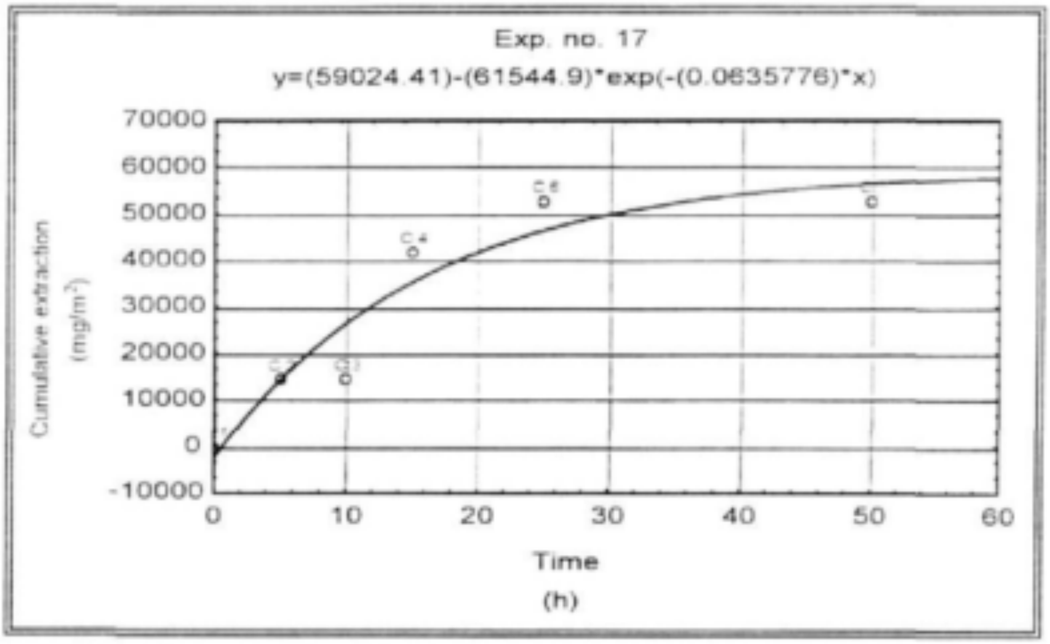
Circum. 0.129 Area 0.0026484

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



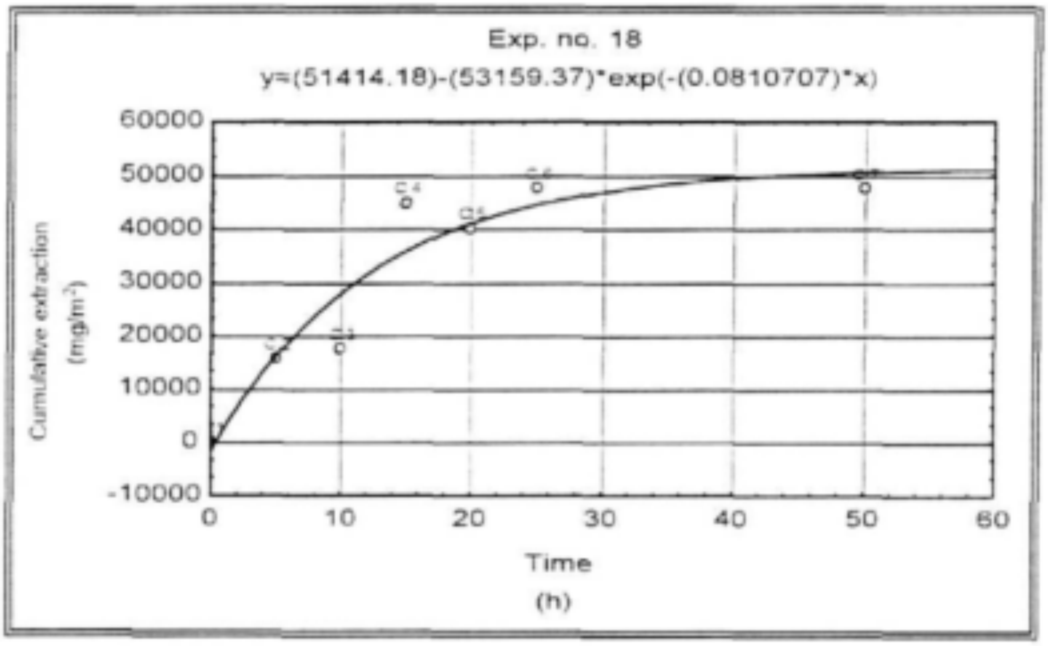
Exp. no: 17
Circum. 0.148 Area 0.0034861

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



Exp. no: 18
Circum. 0.152 Area 0.0036771

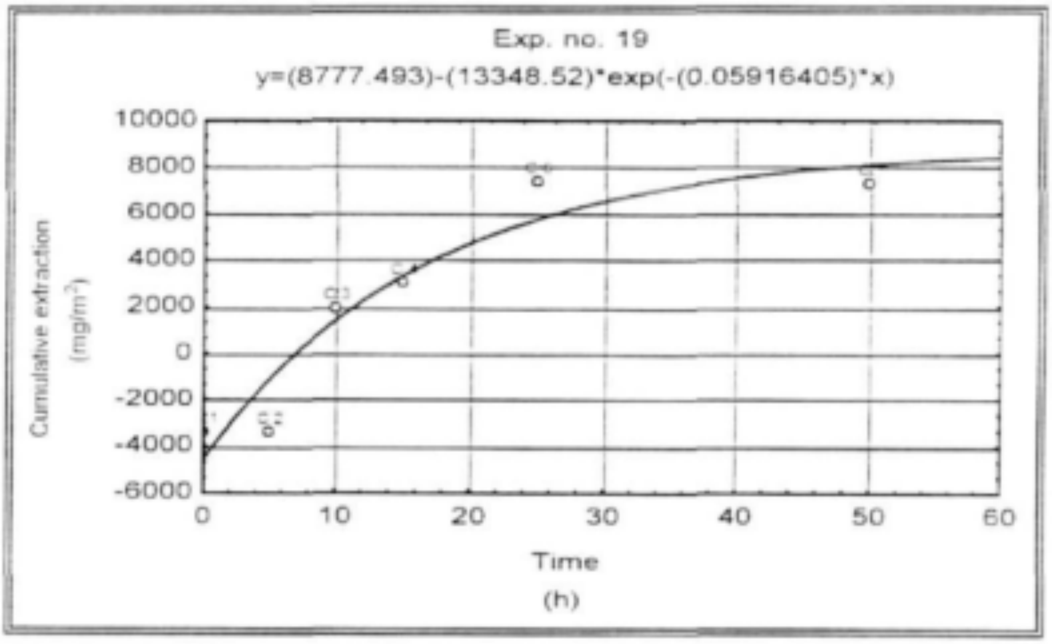
Time	[Ni] feed	Vol.	Adjust.	Extr.	Rate
0	808	0.400	0.000000	0	
5	657	0.398	0.006000	15685	3137
10	759	0.410	0.001000	17591	1759
15	542	0.400	0.011000	44948	2997
20	833	0.410	0.000000	40205	2010
25	757	0.410	0.000000	47547	1902
50	915	0.400	0.000000	31389	628



Exp. no: 19

Circum. 0.158 Area 0.0039731

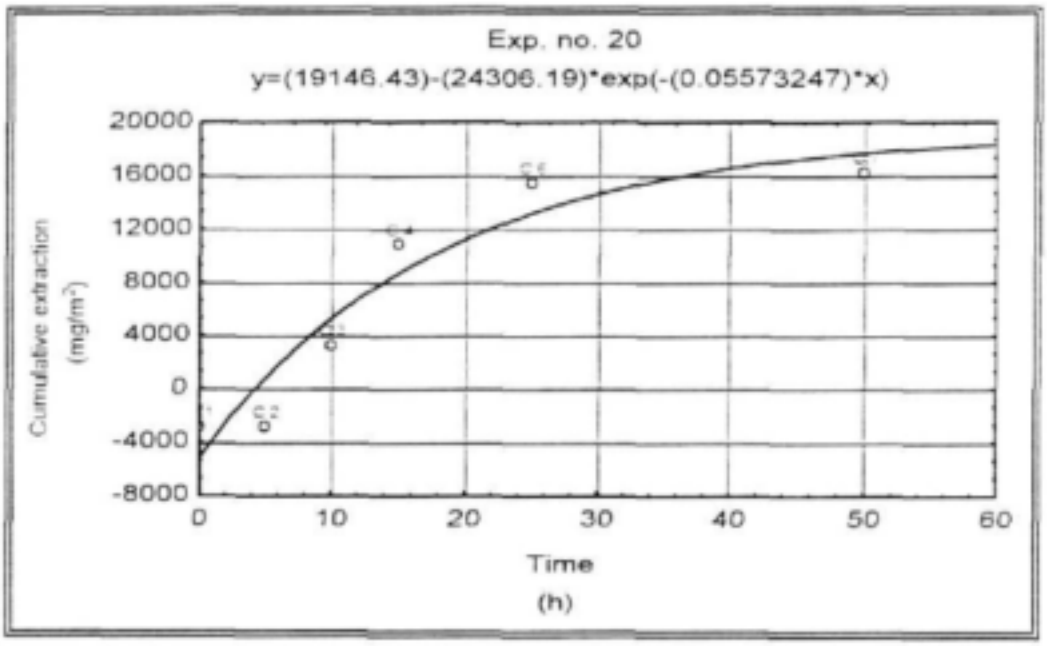
Time	[Ni] feed	Vol.	Adjust.	Extr.	Rate
0	803	0.400	0.000000	0	
5	735	0.450	0.003000	-3414	-683
10	730	0.460	0.003000	1941	194
15	716	0.500	0.004000	2985	199
20	810	0.495	0.000000	1342	67
25	746	0.500	0.000000	7357	294
50	783	0.488	0.000000	4127	83



Exp. no: 20

Circum. 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



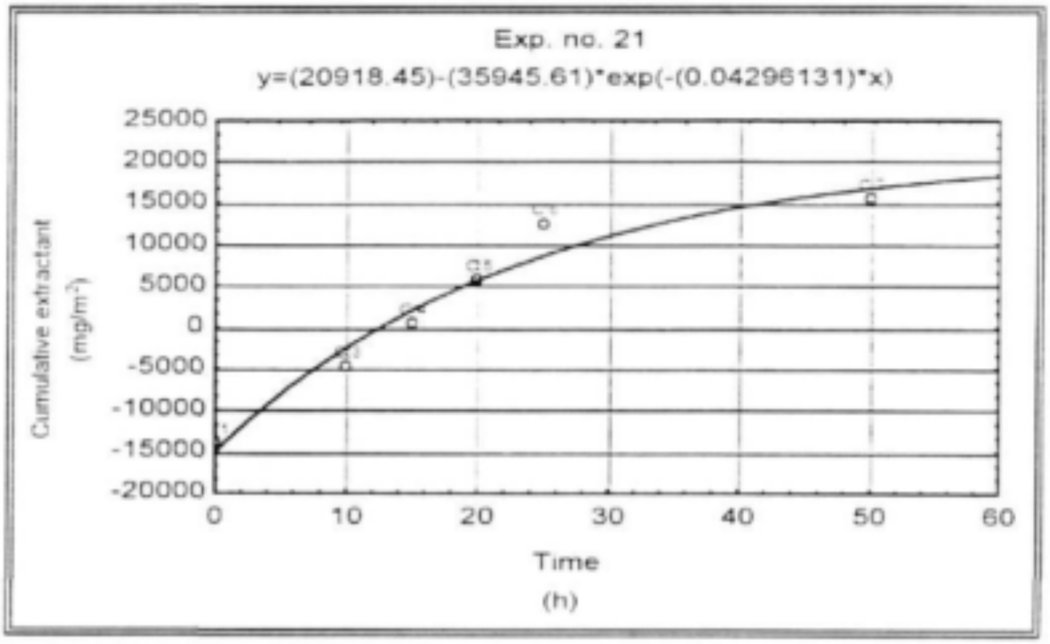
Exp. no: 21

Circum. 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



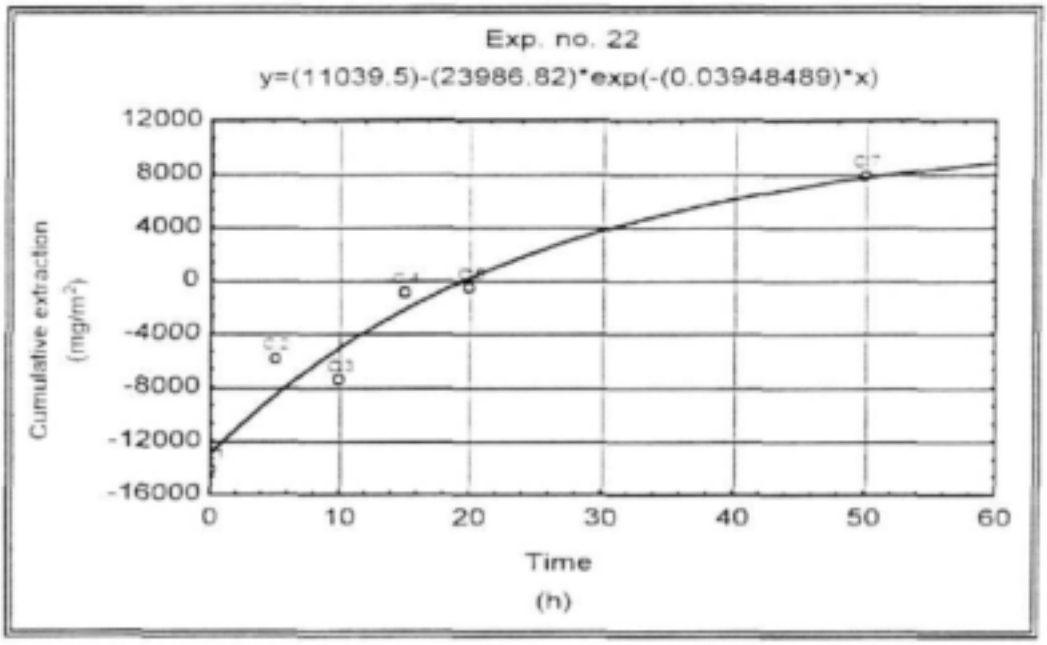
Exp. no: 22

Circum 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



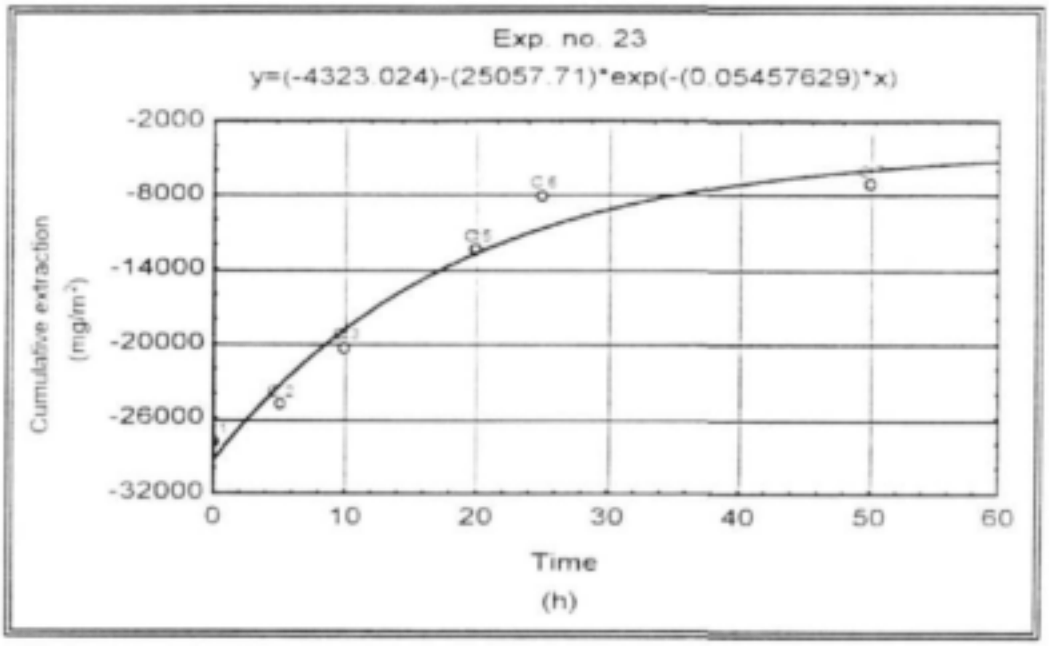
Exp. no: 23

Circum. 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



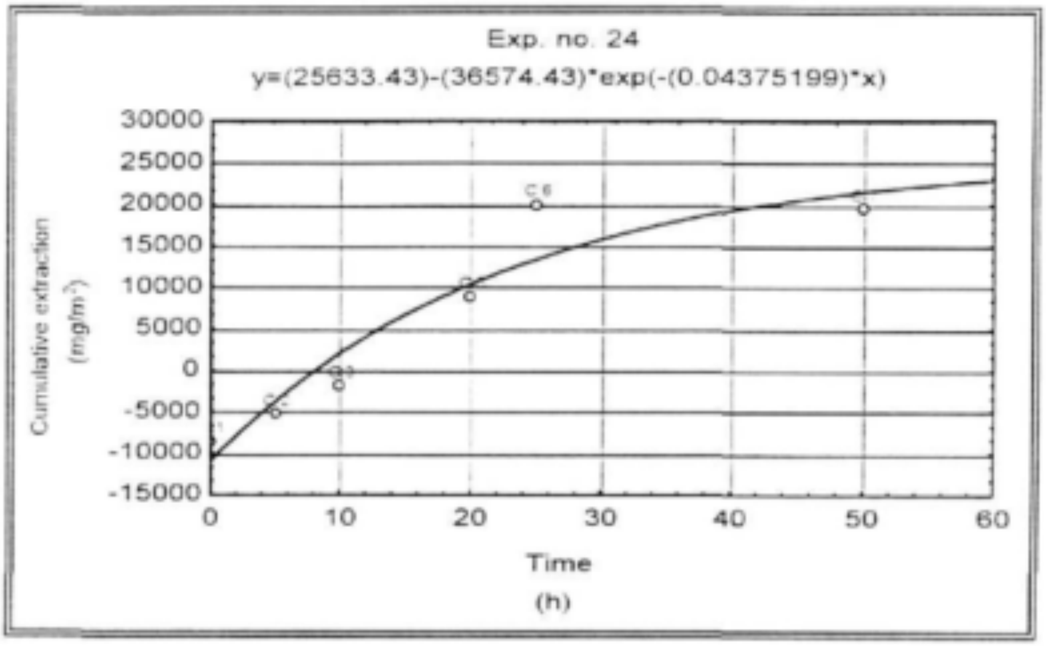
Exp. no: 24

Circum. 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



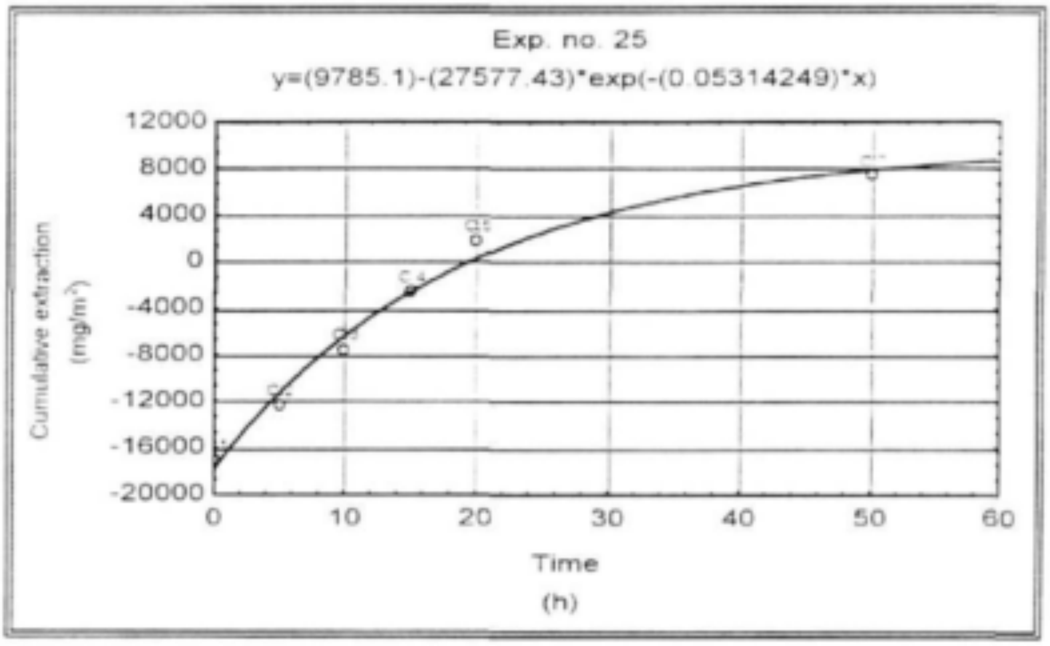
Exp. no: 25

Circum. 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



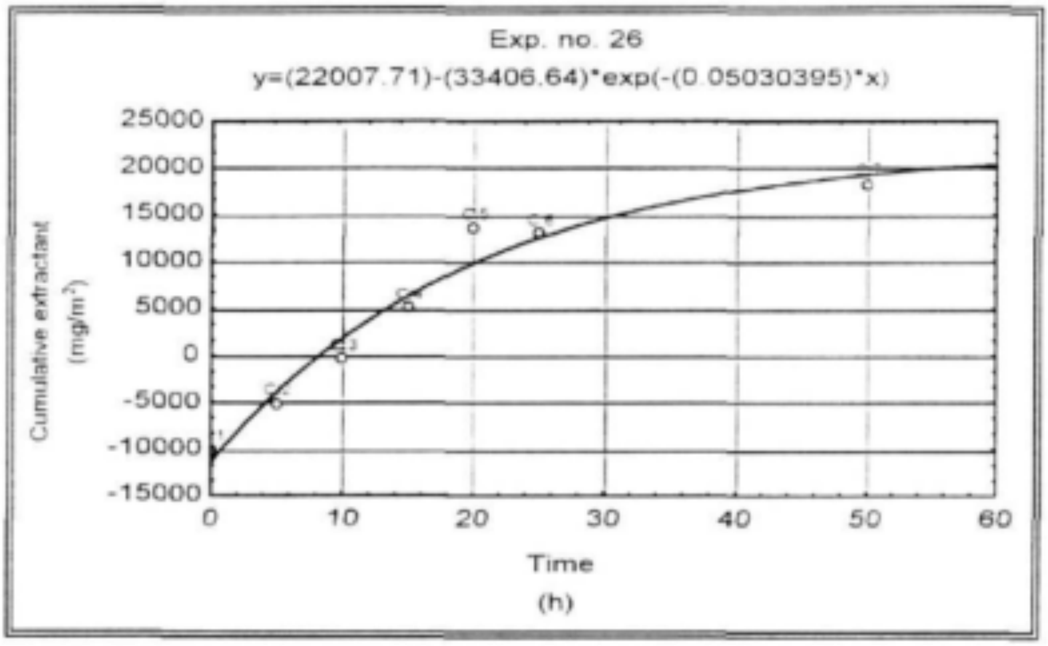
Exp. no: 26

Circum. 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



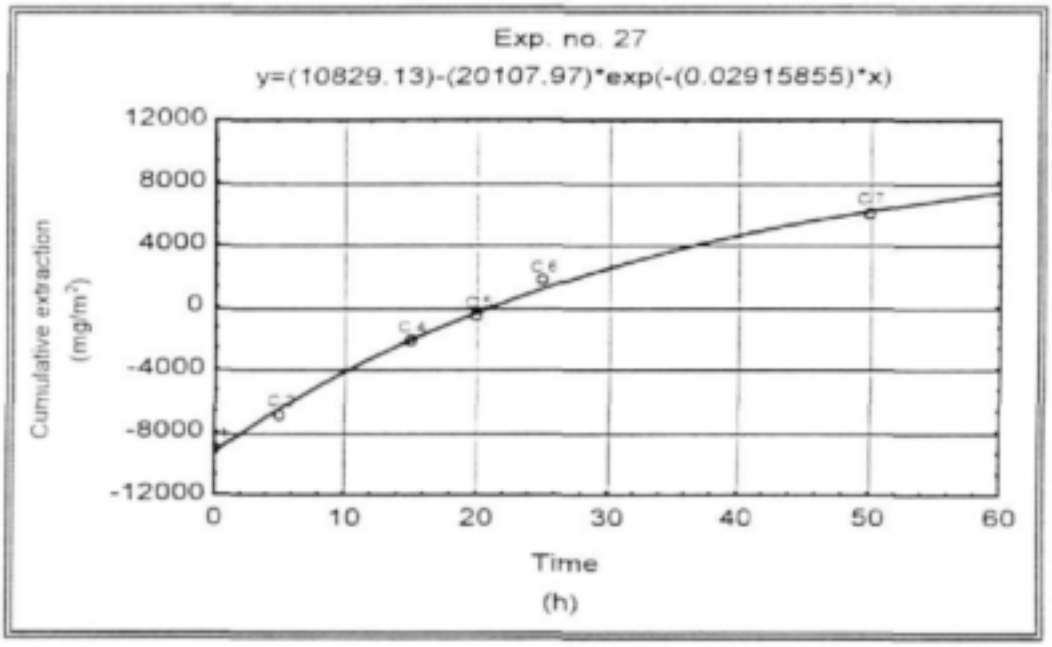
Exp. no: 27

Circum. 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



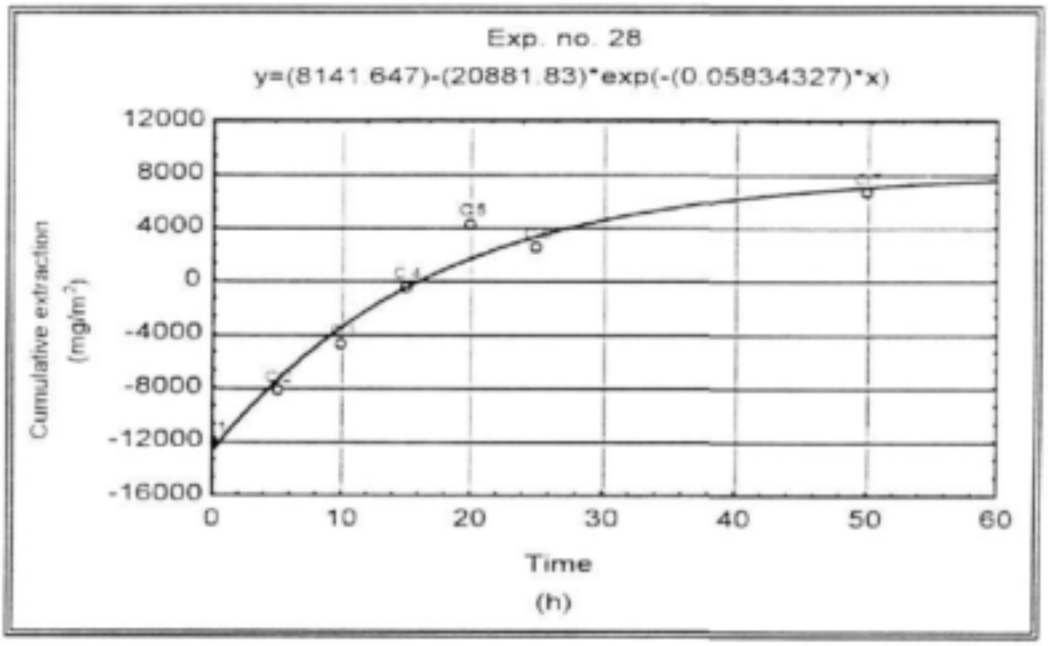
Exp. no: 28

Circum. 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



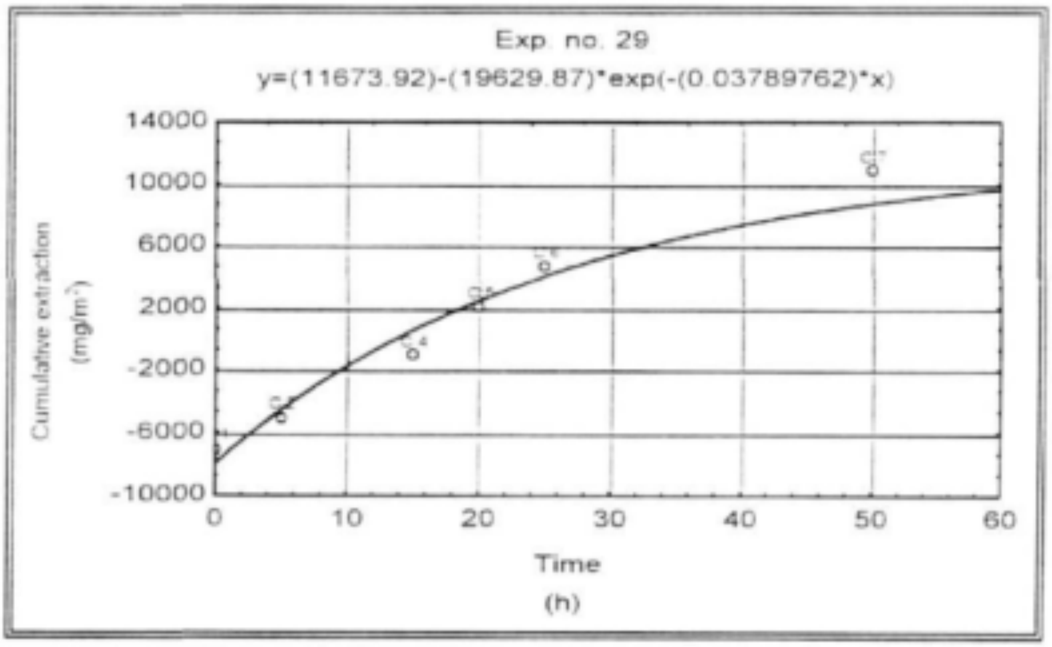
Exp. no: 29

Circum 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



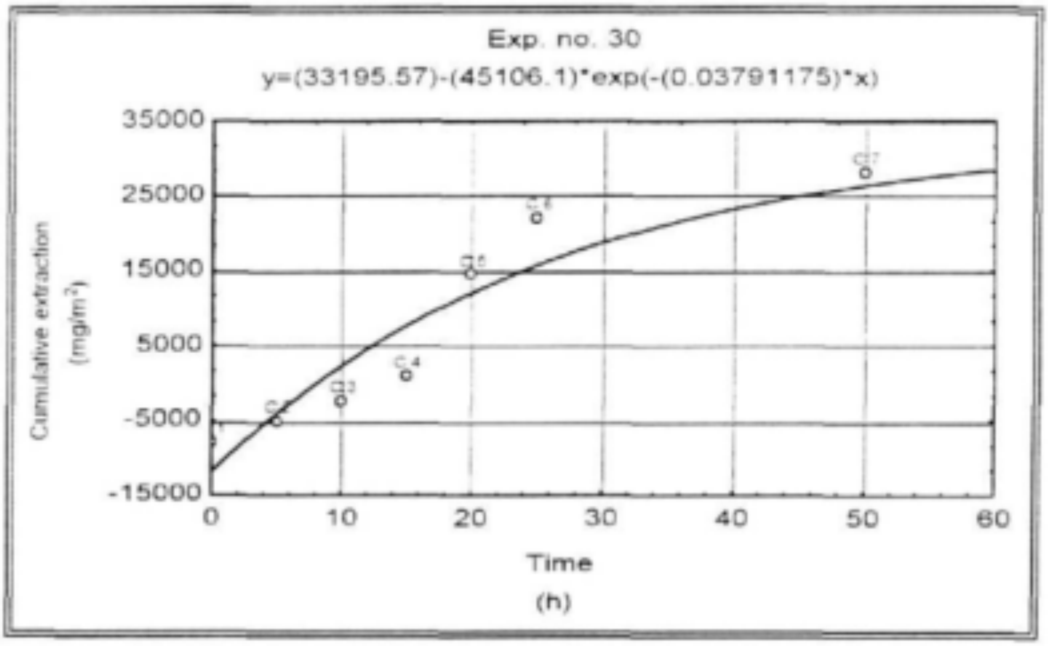
Eksp. no: 30

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

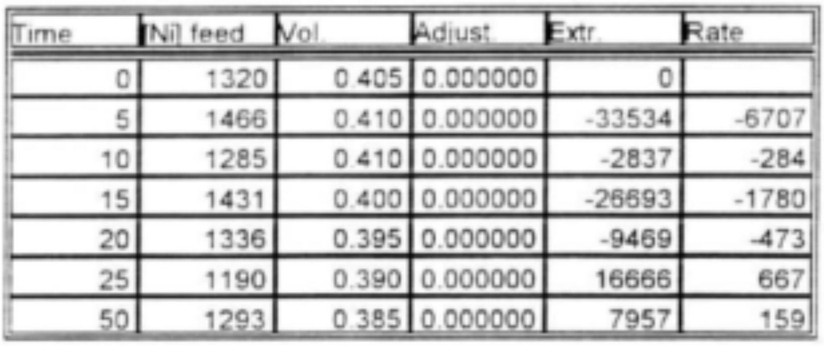


Exp. no: 31

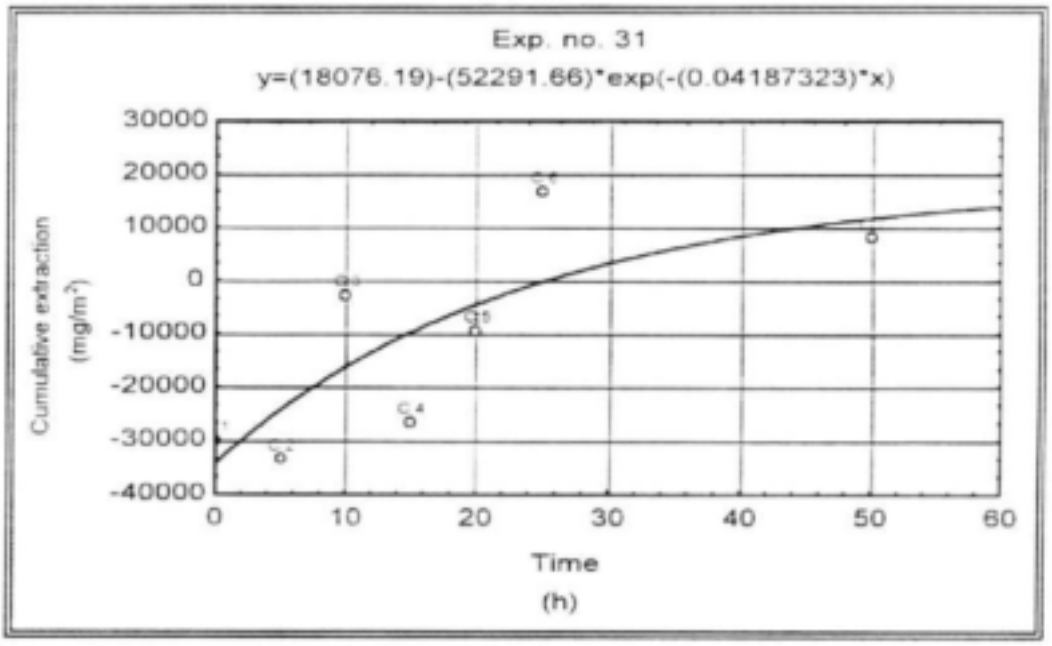
Circum. 0.117

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



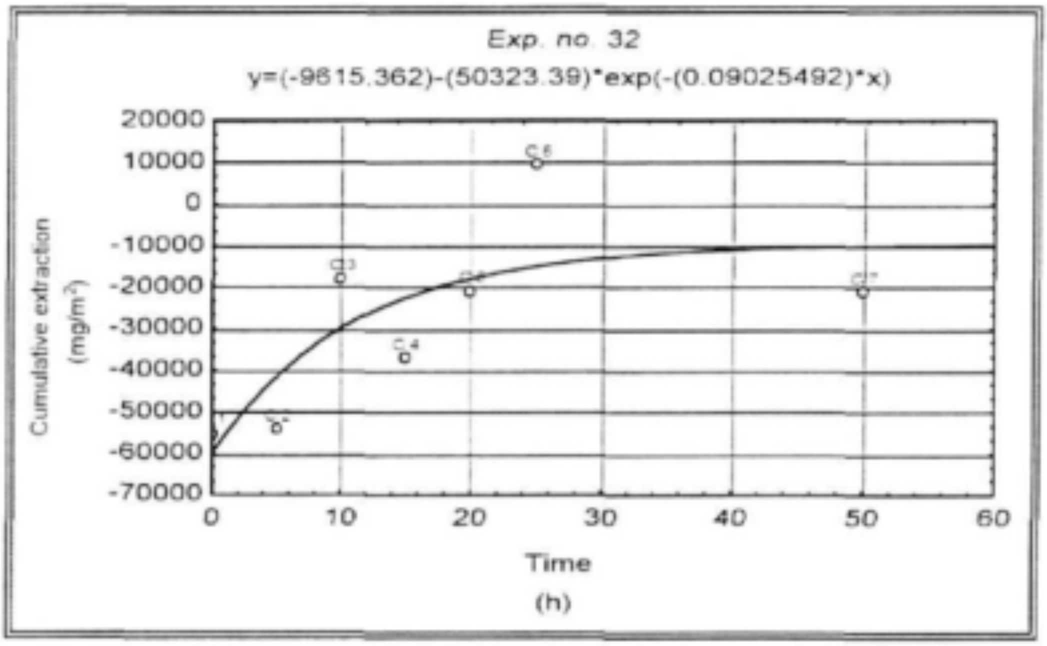
Exp. no: 32

Circum. 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



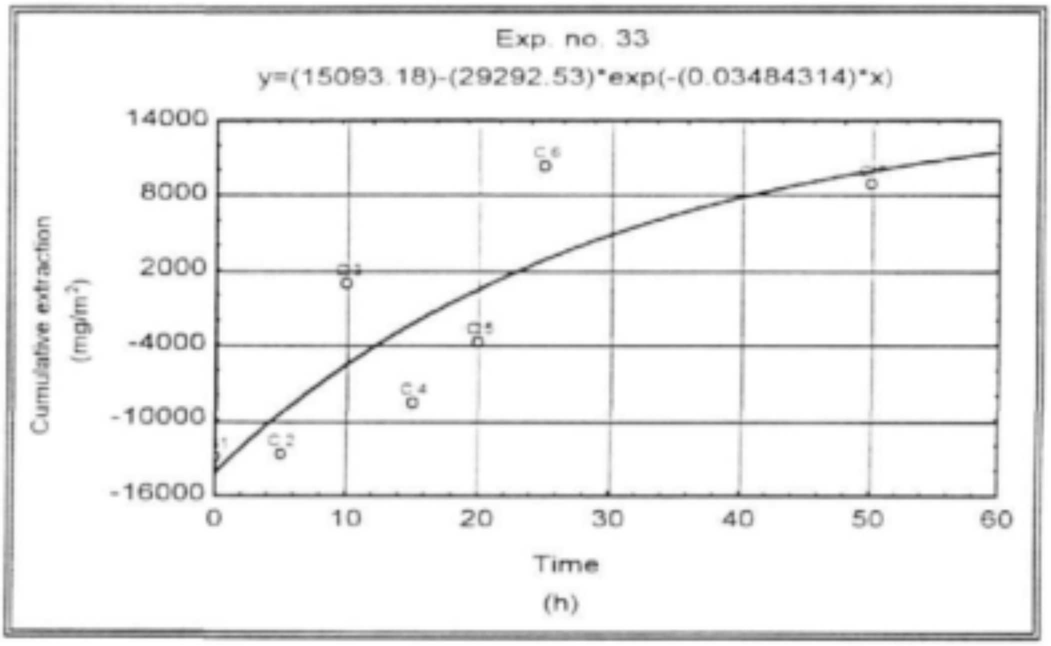
Exp. no: 33

Circum. 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



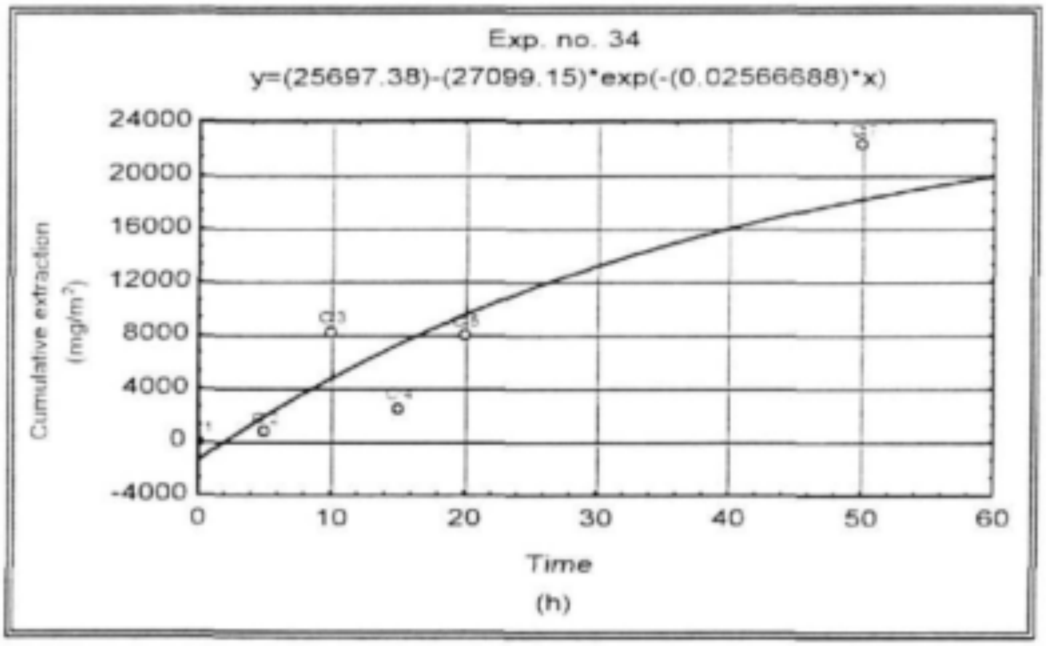
Exp. no: 34

Circum. 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



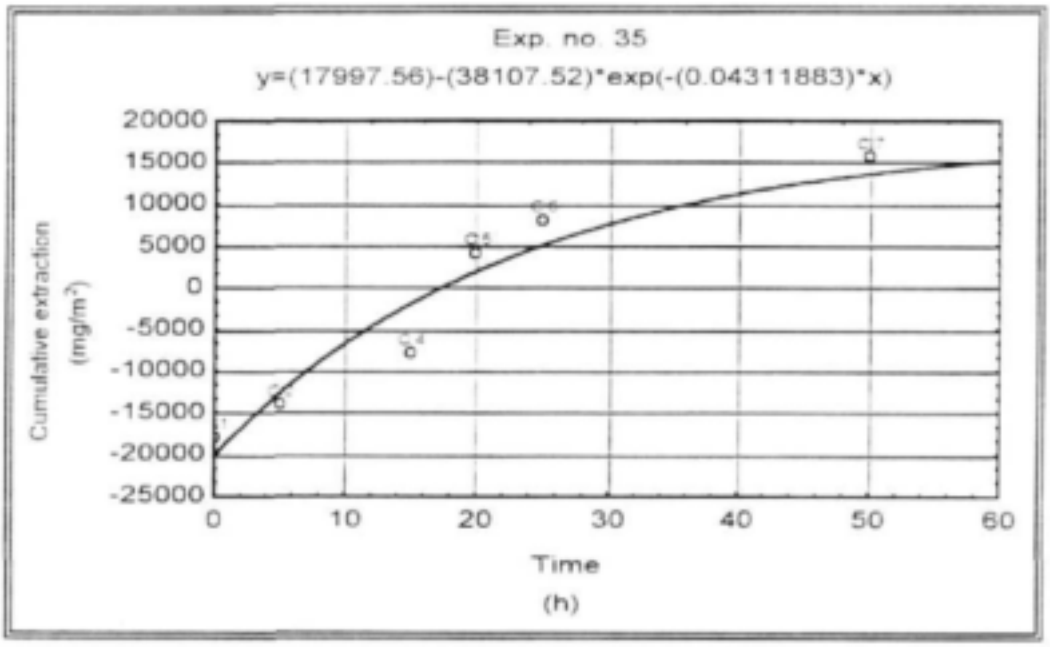
Exp. no: 35

Circum. 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



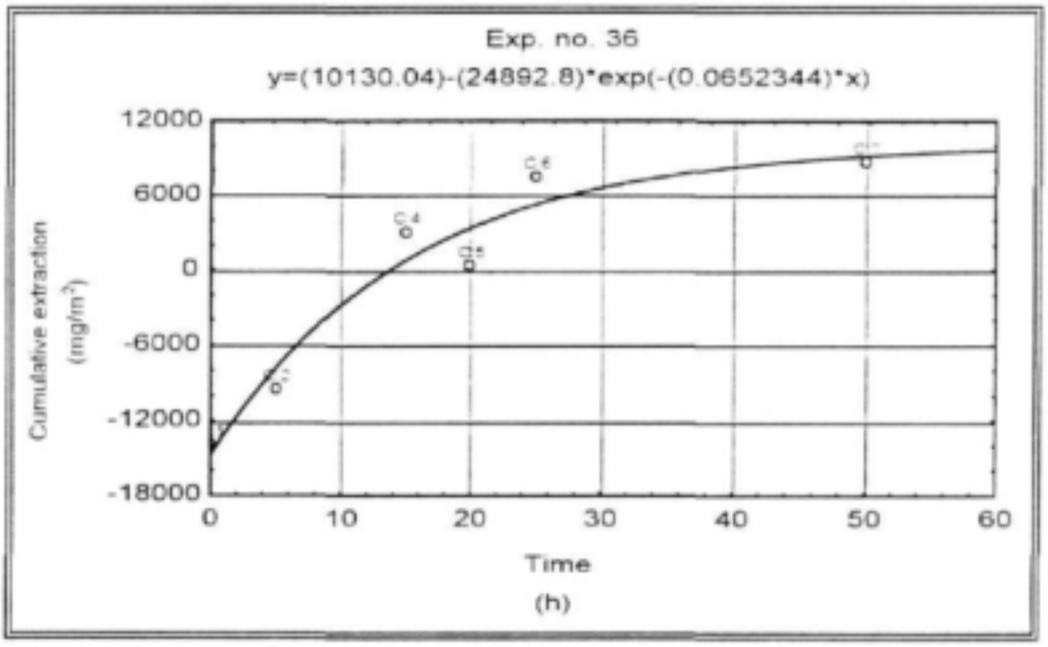
Exp. no: 36

Circum. 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



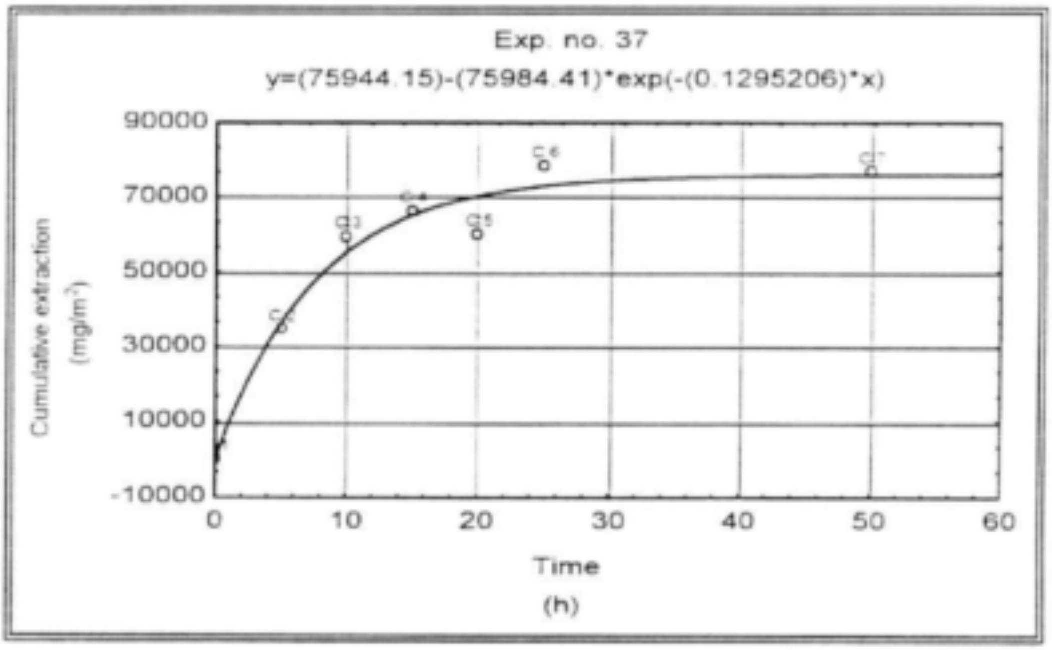
Exp. no: 37

Circum 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



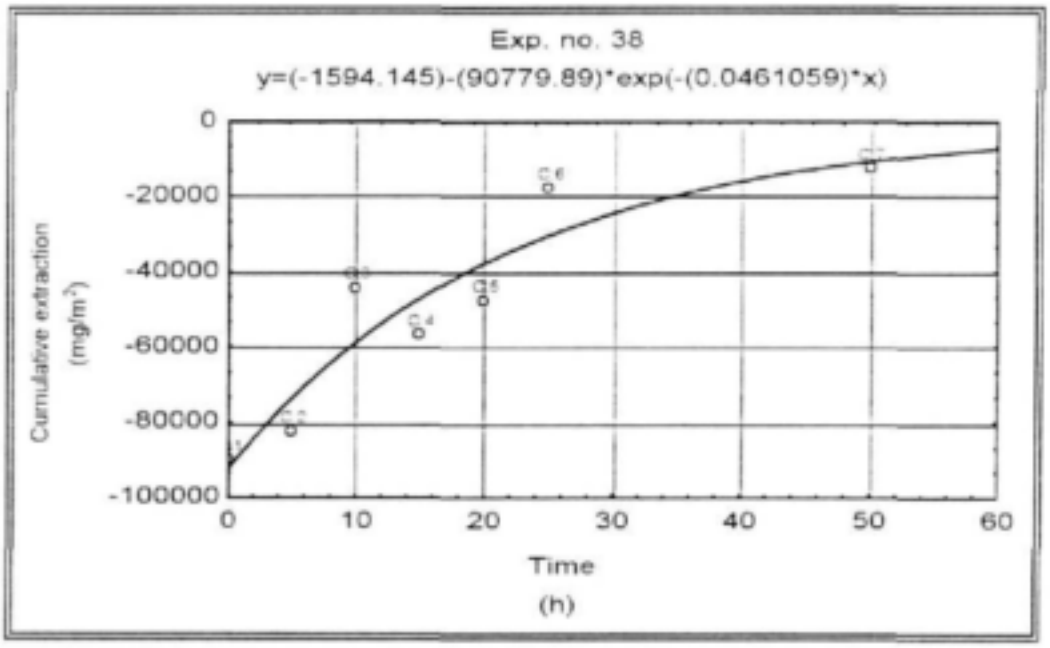
Exp. no: 38

Circum 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



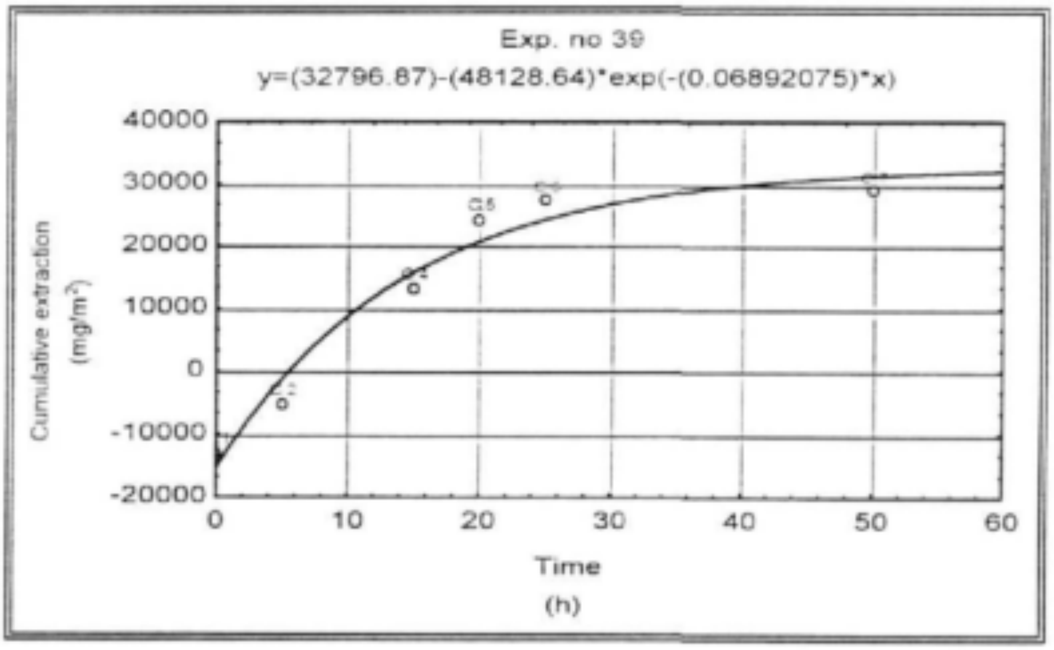
Exp. no: 39

Circum. 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



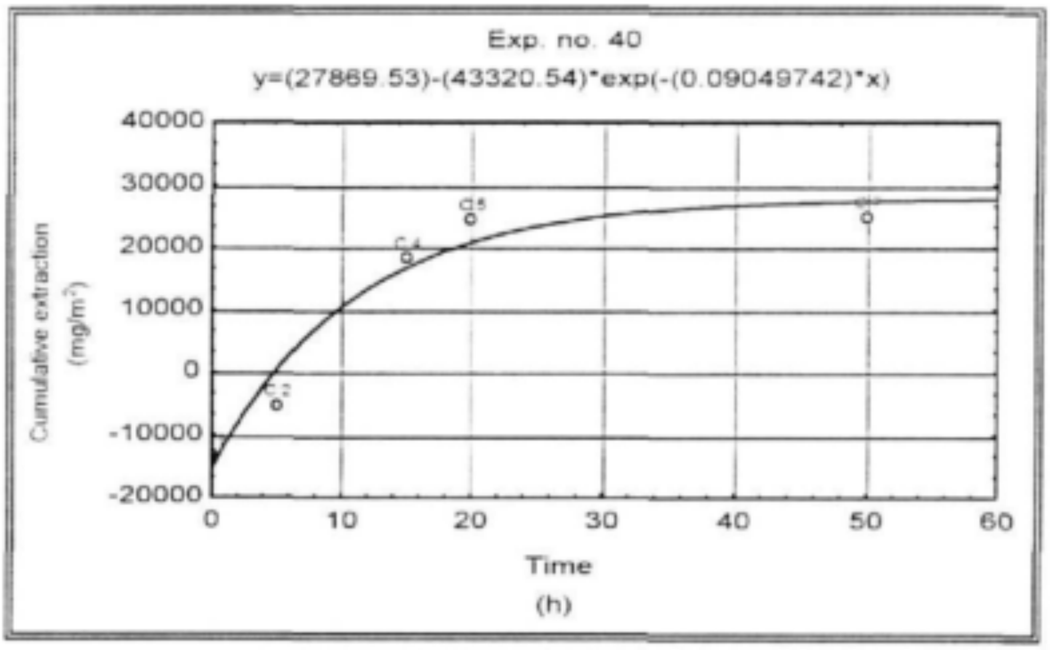
Exp. no: 40

Circum. 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



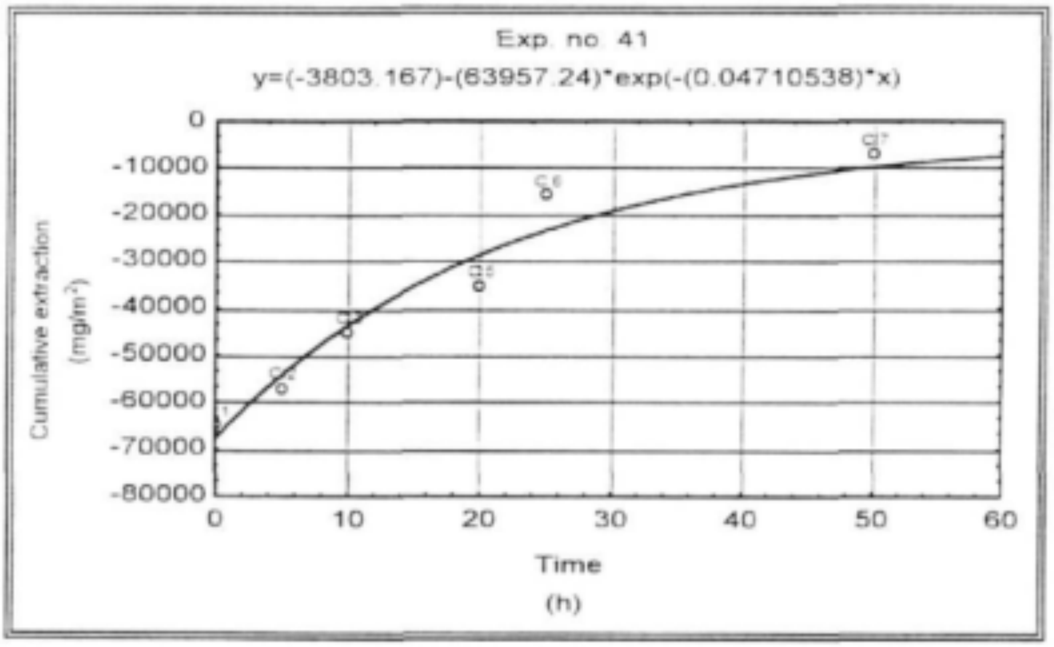
Exp. no: 41

Circum 0.118

Area

0.0022161

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



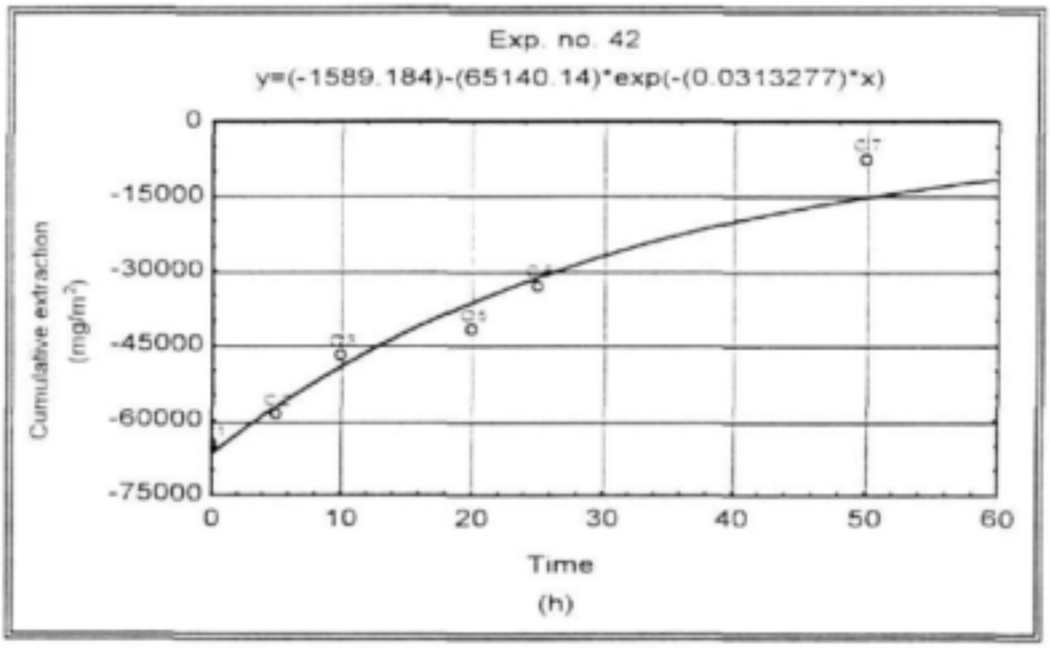
Exp. no: 42

Circum. 0.124

Area

0.0024472

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



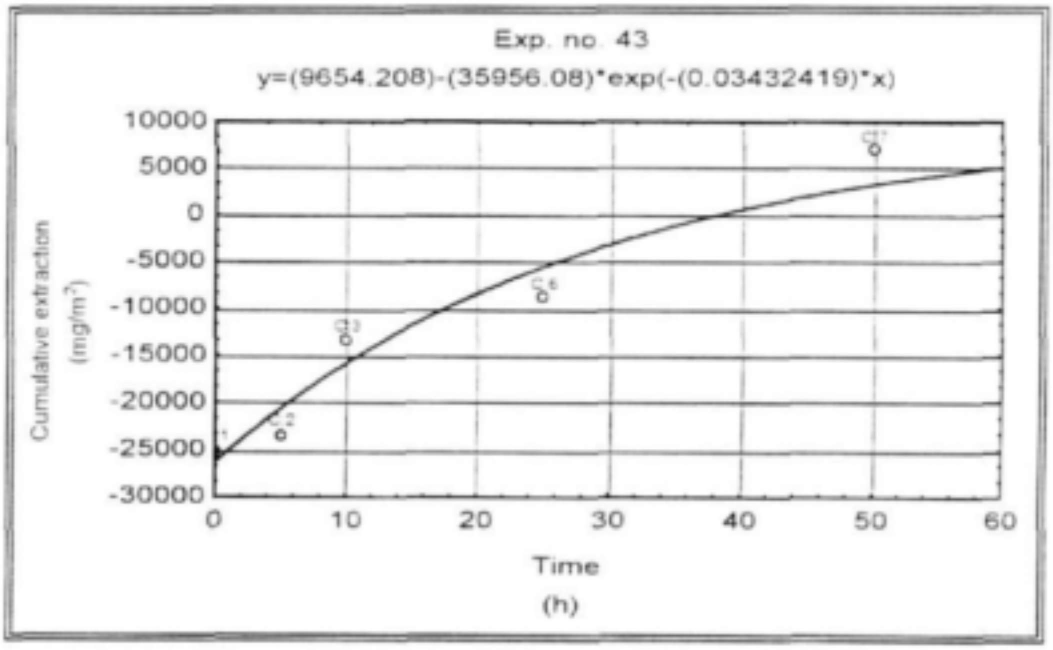
Exp. no: 43

Circum: 0.119

Area

0.0022538

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



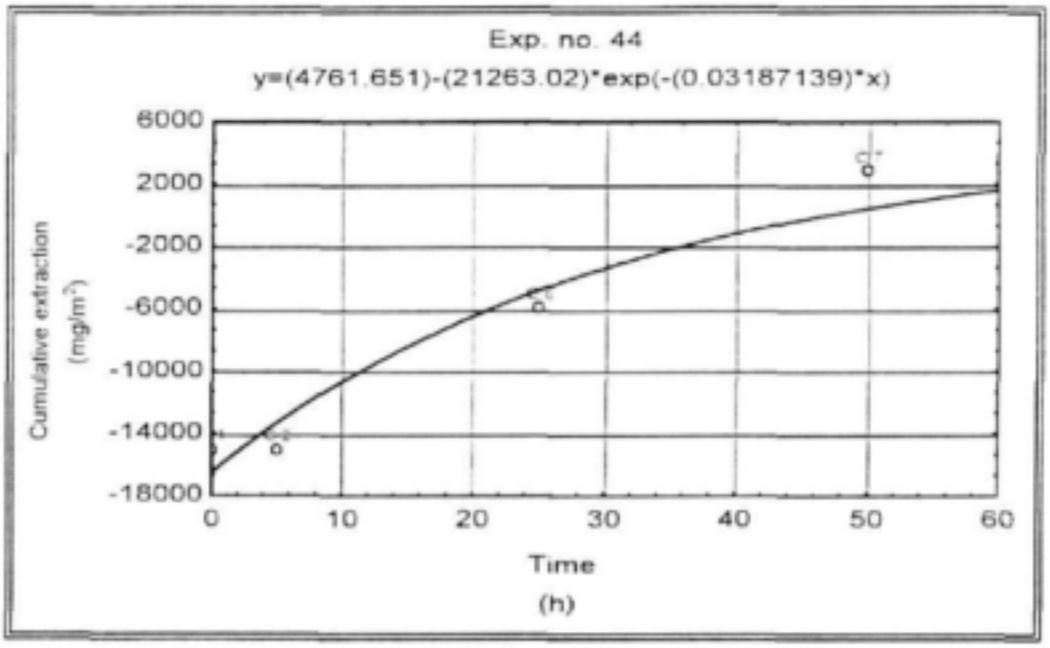
Exp. no 44

Circum 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



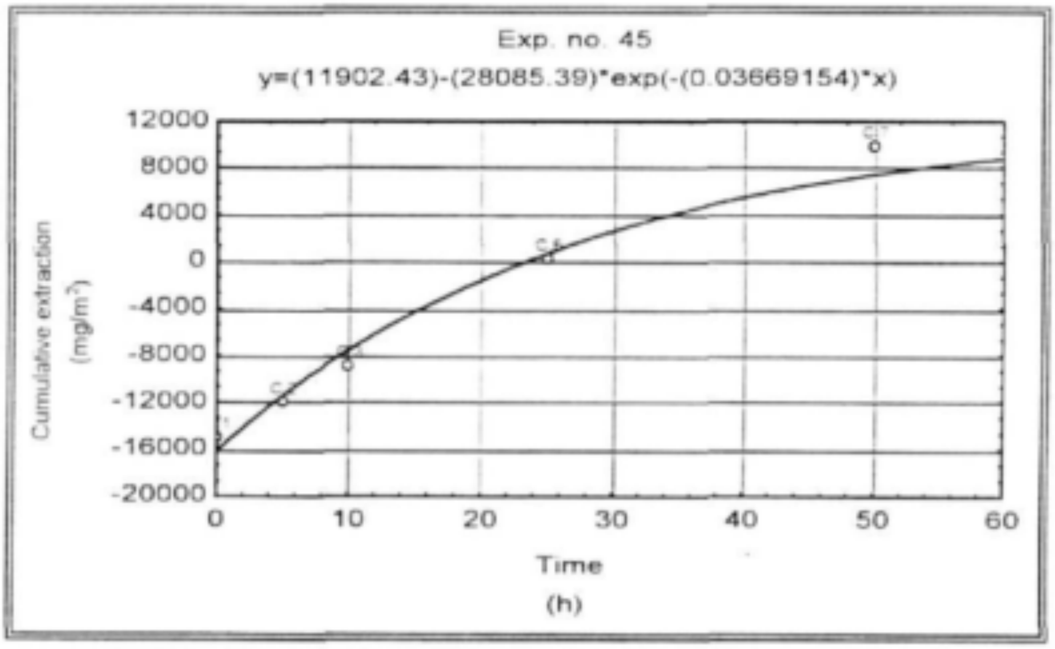
Exp. no 45

Circum. 0.117

Area

0.0021787

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



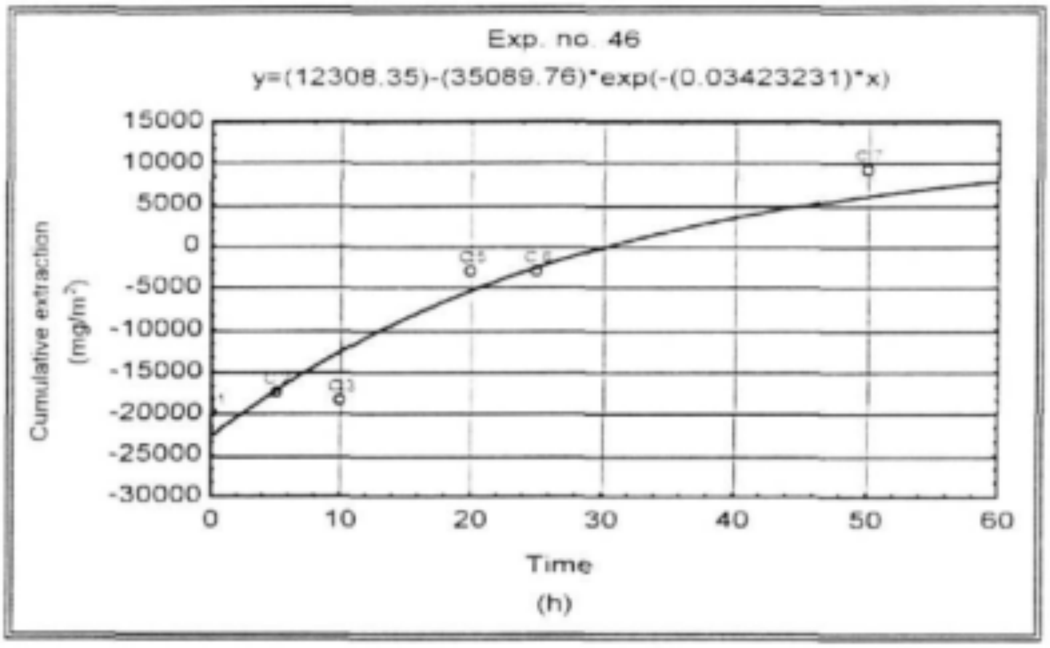
Exp. no: 46

Circum. 0.128

Area

0.0026076

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



A.2 Experimental results for establishing the optimum hydronium ion concentration of the strip solution

Exp. no.: C 0 [H] 1E-05

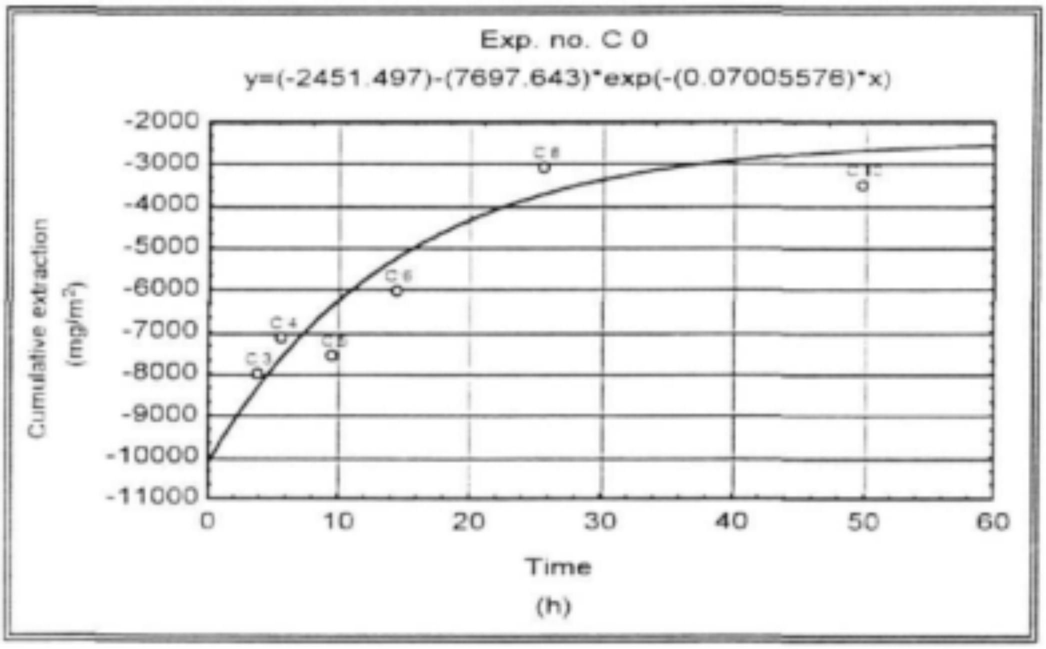
Temp. 25 pH 4.5

Vol. 0.4 0.005

Circum.: 0.134

Area 0.0028578

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	940	0	4.5	0.000	0.0000	0.0000
1.85	977	-5179	4.09	0.000	0.0000	-0.0882
3.83	997	-7978	3.94	0.000	0.0000	-0.1359
5.73	991	-7138	3.88	0.000	0.0000	-0.1216
9.63	994	-7558	3.83	0.000	0.0000	-0.1288
14.43	983	-6019	3.85	0.000	0.0000	-0.1025
22.60	952	-1680	3.79	0.000	0.0000	-0.0286
25.68	962	-3079	4.48	0.000	0.0000	-0.0525
32.03	1000	-8398	4.33	0.000	0.0000	-0.1431
49.77	965	-3499	4.33	0.000	0.0000	-0.0596



Exp. no.: C 0.01 [H] 0.01

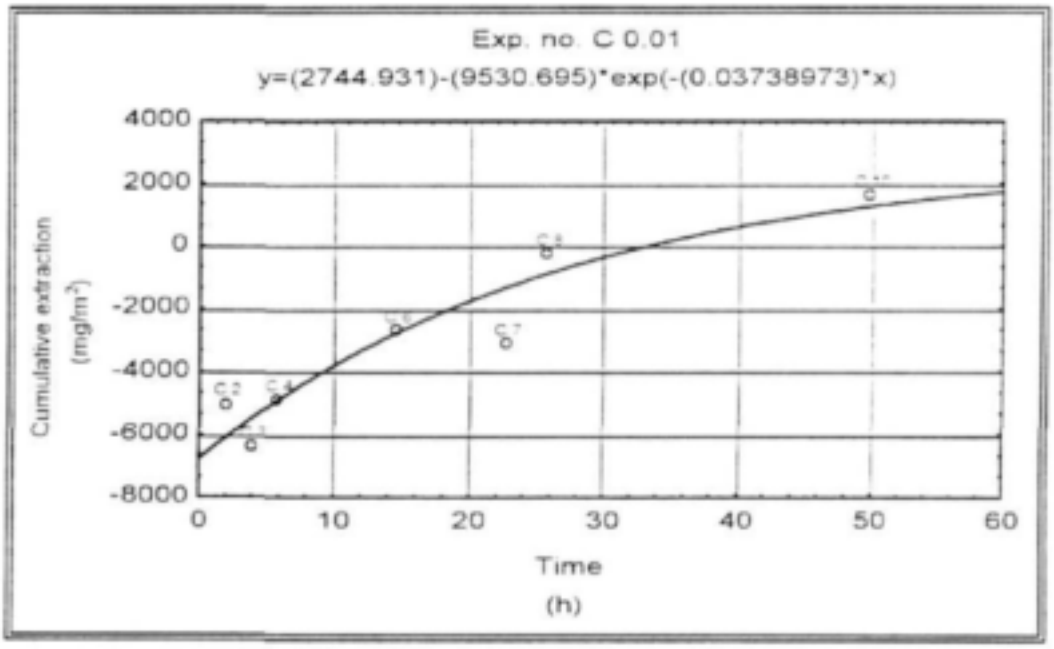
Temp. 25 pH 4.5

Vol. 0.4 0.005

Circum.: 0.136

Area 0.0029437

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	950	0	4.5	0.010	0.0000	0.0000
1.97	987	-5028	3.88	0.002	0.0136	-0.0856
3.95	997	-6386	3.75	0.000	0.0170	-0.1088
5.85	986	-4892	4.47	0.000	0.0170	-0.0833
9.75	1006	-7609	4.21	0.000	0.0170	-0.1296
14.58	970	-2718	4.12	0.000	0.0170	-0.0463
22.73	973	-3125	4.06	0.000	0.0170	-0.0532
25.80	952	-272	4.06	0.000	0.0170	-0.0046
32.15	989	-5299	4.02	0.000	0.0170	-0.0903
49.88	938	1631	4.02	0.000	0.0170	0.0278



Exp. no.: C 0.05 [H] 0.05

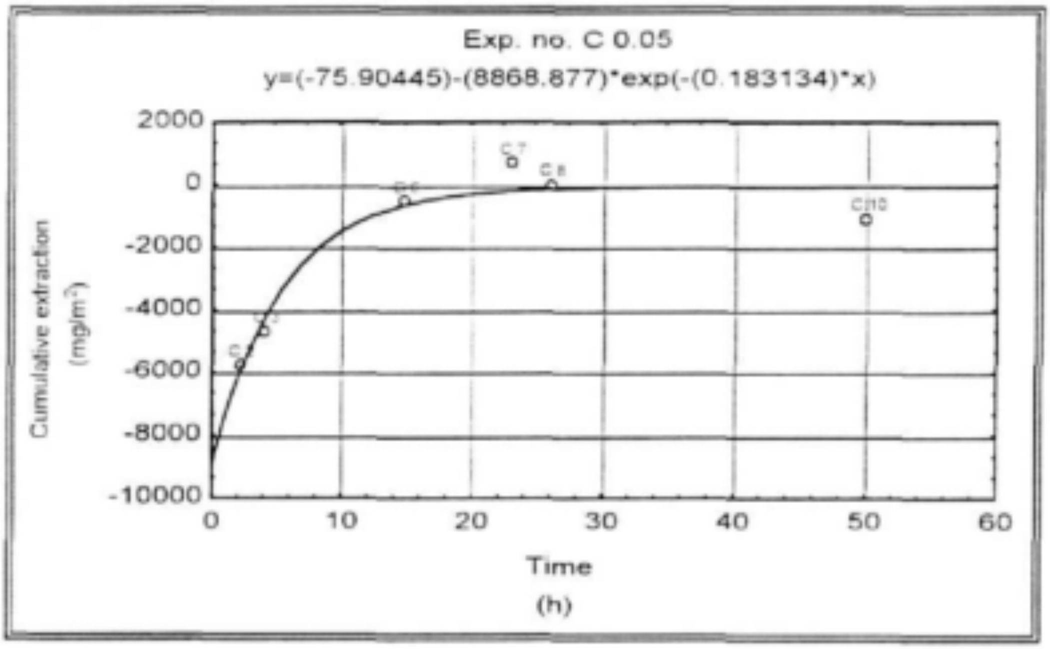
Temp. 25 pH 4.5

Vol. 0.4 0.005

Circum.: 0.137

Area 0.0029872

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	957	0	4.5	0.050	0.0000	0.0000
2.17	1000	-5758	3.73	0.038	0.0207	-0.0981
4.13	992	-4687	3.62	0.021	0.0486	-0.0798
6.03	1006	-6561	3.7	0.008	0.0711	-0.1118
9.93	1000	-5758	3.7	0.000	0.0837	-0.0981
14.77	961	-536	4.1	0.000	0.0837	-0.0091
22.92	952	670	3.96	0.000	0.0837	0.0114
26.00	957	0	3.96	0.000	0.0837	0.0000
32.33	1021	-8570	3.92	0.000	0.0837	-0.1460
50.07	965	-1071	3.92	0.000	0.0837	-0.0182



Exp. no.: C 0.1 [H] 0.1

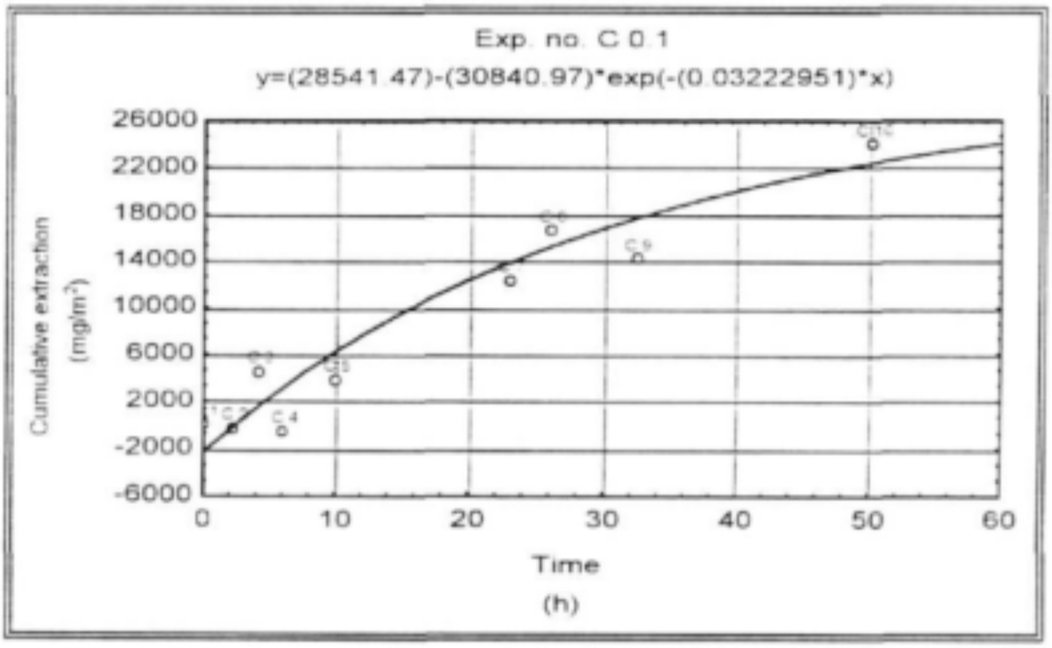
Temp. 25 pH 4.5

Vol. 0.4 0.005

Circum.: 0.133

Area 0.0028153

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	985	0	4.5	0.100	0.0000	0.0000
2.25	987	-284	3.7	0.087	0.0239	-0.0048
4.22	953	4547	3.58	0.068	0.0567	0.0775
6.12	989	-568	3.92	0.061	0.0693	-0.0097
10.03	958	3836	3.19	0.019	0.1440	0.0654
14.85	967	2557	3.28	0.000	0.1776	0.0436
23.02	898	12361	3.11	0.000	0.1776	0.2106
26.08	868	16623	3.38	0.000	0.1776	0.2832
32.42	885	14208	3.33	0.000	0.1776	0.2420
50.15	816	24012	3.33	0.000	0.1776	0.4091



Exp. no.: C 0.5 [H] 0.5

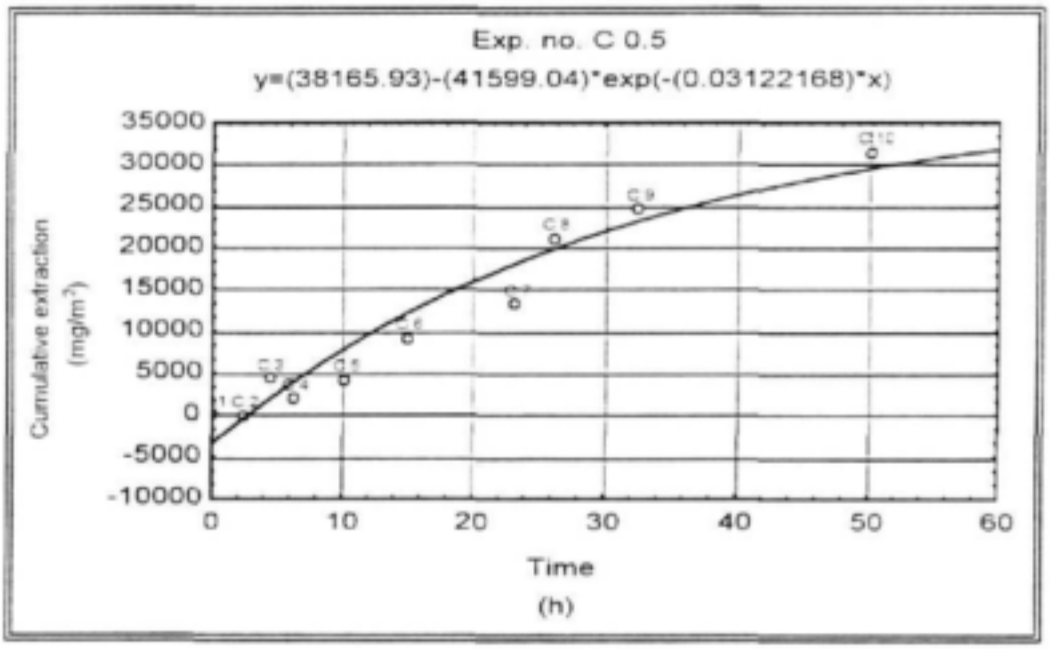
Temp. 25 pH 4.5

Vol. 0.4 0.005

Circum.: 0.139

Area 0.003075

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	1012	0	4.5	0.500	0.0000	0.0000
2.42	1013	-130	3.61	0.483	0.0278	-0.0022
4.38	979	4293	3.52	0.461	0.0630	0.0731
6.30	997	1951	3.61	0.444	0.0908	0.0332
10.20	980	4163	3.33	0.409	0.1475	0.0709
15.02	942	9106	3.23	0.365	0.2200	0.1551
23.28	911	13138	3.05	0.296	0.3318	0.2238
26.25	850	21073	3.39	0.266	0.3807	0.3590
32.60	823	24585	3.06	0.199	0.4899	0.4188
50.32	770	31479	3.06	0.132	0.5991	0.5363



Exp. no.: C 0.5 b [H] 0.5

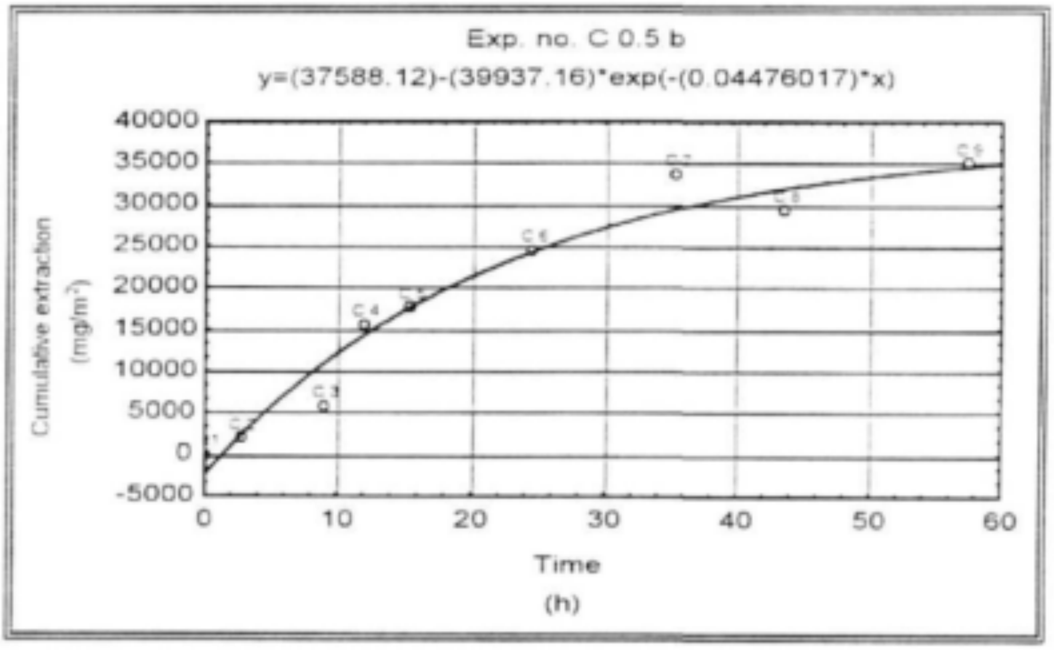
Temp. 25 pH 4.5

Vol. 0.4 0.006

Circum.: 0.131

Area 0.0027313

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	1083	0	4.5	0.500	0.0000	0.0000
2.73	1070	1900	3.53	0.482	0.0386	0.0324
9.05	1044	5761	3.17	0.439	0.1330	0.0981
12.00	977	15531	3.26	0.405	0.2088	0.2646
15.48	963	17520	3.43	0.382	0.2586	0.2985
24.57	916	24501	3.06	0.326	0.3815	0.4174
35.38	854	33600	2.95	0.254	0.5412	0.5724
43.57	883	29281	3.19	0.213	0.6311	0.4988
57.35	844	34992	3.19	0.172	0.7211	0.5961



Exp. no.: C 1 [H] 1

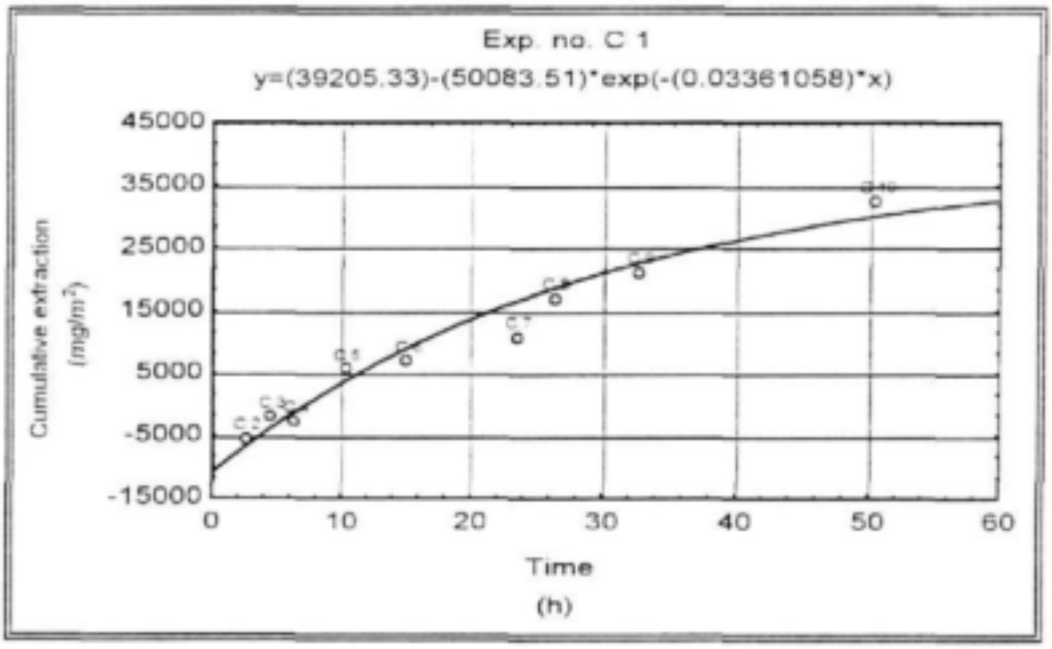
Temp. 25 pH 4.5

Vol. 0.4 0.005

Circum.: 0.138

Area 0.0030309

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	990	0	4.5	1.000	0.0000	0.0000
2.55	1031	-5411	3.48	0.976	0.0395	-0.0922
4.53	1005	-1980	3.7	0.963	0.0617	-0.0337
6.38	1011	-2771	4	0.957	0.0707	-0.0472
10.32	947	5675	3.24	0.919	0.1335	0.0967
15.15	937	6995	3.2	0.871	0.2125	0.1192
23.57	908	10822	3.04	0.801	0.3287	0.1844
26.37	861	17024	3.38	0.770	0.3796	0.2900
32.72	830	21116	3.14	0.714	0.4710	0.3597
50.43	744	32465	3.14	0.659	0.5624	0.5531



Exp. no.: C 1 b [H] 1

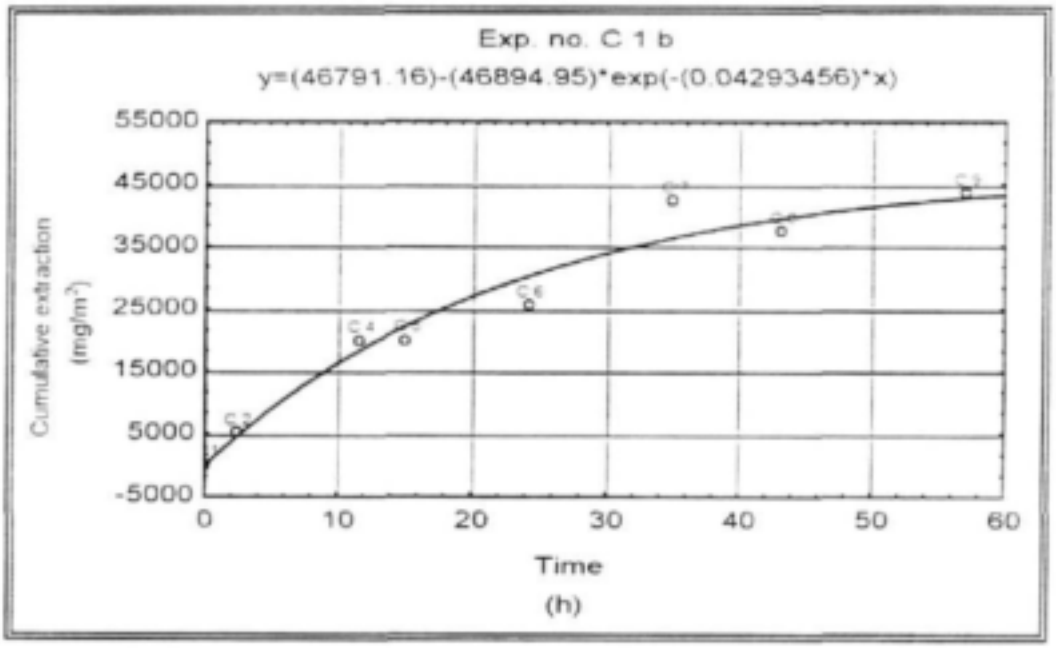
Temp. 25 pH 4.5

Vol. 0.4 0.004

Circum.: 0.134

Area 0.0028578

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	1104	0	4.5	1.000	0.0000	0.0000
2.37	1070	5011	3.61	0.979	0.0299	0.0854
9.68	1062	6178	3.21	0.920	0.1118	0.1052
11.63	968	19949	3.29	0.872	0.1792	0.3398
15.12	968	19983	3.32	0.827	0.2417	0.3404
24.20	930	25528	3.04	0.739	0.3650	0.4349
35.00	816	42186	2.95	0.630	0.5176	0.7187
43.20	849	37375	3.04	0.542	0.6408	0.6367
56.98	807	43454	3.04	0.454	0.7640	0.7403



Exp. no. C 2 [H]2

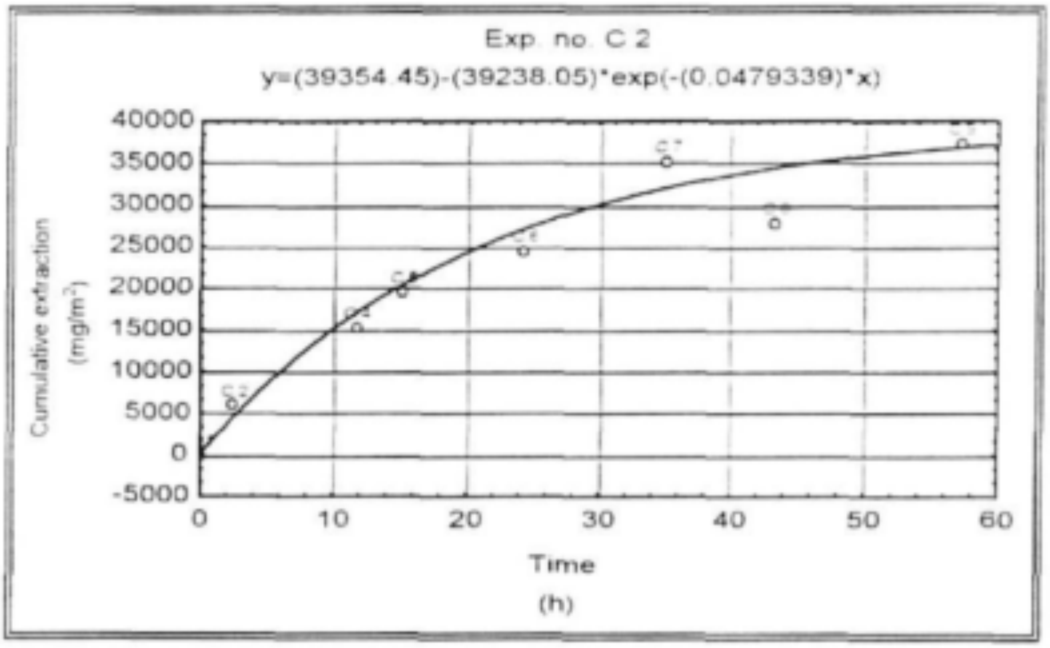
Temp 25 pH 4.5

Vol 0.4 0.006

Circum.: 0.136

Area 0.0029437

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	1090	0	4.5	2.000	0.0000	0.0000
2.48	1046	5929	3.51	1.982	0.0377	0.1010
8.82	1075	2058	3.09	1.929	0.1438	0.0351
11.75	978	15279	3.16	1.885	0.2336	0.2603
15.25	946	19527	3.19	1.844	0.3170	0.3327
24.32	909	24546	3.11	1.795	0.4182	0.4182
35.13	831	35240	2.91	1.715	0.5810	0.6003
43.32	885	27873	3.05	1.658	0.6979	0.4748
57.10	815	37350	3.05	1.600	0.8147	0.6363



Exp. no.: C 2 a [H] 2

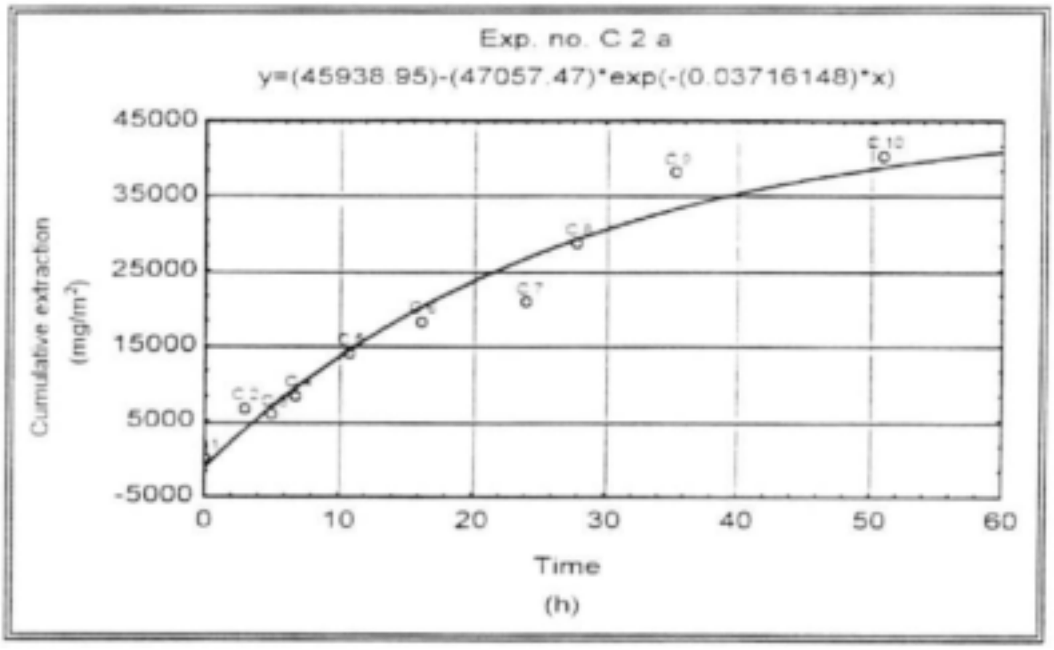
Temp 25 pH 4.5

Vol. 0.4 0.005

Circum.: 0.14

Area 0.0031194

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	1022	0	4.5	2.000	0.0000	0.0000
2.95	970	6668	3.42	1.972	0.0447	0.1136
5.10	977	5770	3.5	1.949	0.0812	0.0983
6.92	957	8335	3.82	1.940	0.0965	0.1420
10.78	913	13977	3.37	1.908	0.1472	0.2381
16.17	880	18208	3.13	1.851	0.2382	0.3102
24.18	860	20773	3	1.774	0.3624	0.3539
27.87	799	28595	3.28	1.734	0.4256	0.4871
35.30	725	38084	3.08	1.670	0.5282	0.6488
50.87	708	40264	2.81	1.549	0.7228	0.6859



Exp. no.: C 2 b [H] 2

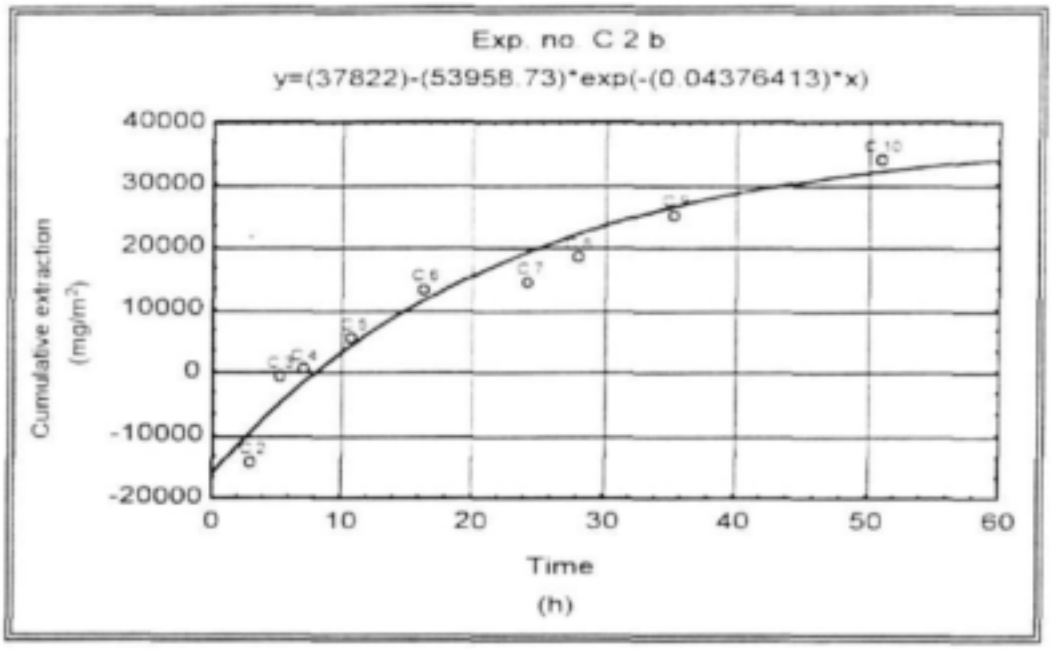
Temp 25 pH 4.5

Vol. *0.4 0.005*

Circum.: 0.136

Area 0.0029437

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	997	0	4.5	2.000	0.0000	0.0000
3.05	1103	-14403	3.47	1.975	0.0417	-0.2454
5.20	1003	-815	3.45	1.950	0.0857	-0.0139
7.02	995	272	3.77	1.939	0.1044	0.0046
10.88	958	5299	3.25	1.896	0.1766	0.0903
16.27	900	13181	3.38	1.865	0.2289	0.2245
24.30	892	14268	3	1.788	0.3605	0.2431
27.97	863	18208	3.32	1.752	0.4212	0.3102
35.42	813	25002	3.23	1.707	0.4969	0.4259
50.97	748	33835	2.85	1.597	0.6846	0.5764



Exp. no.: C 2 c [H] 2

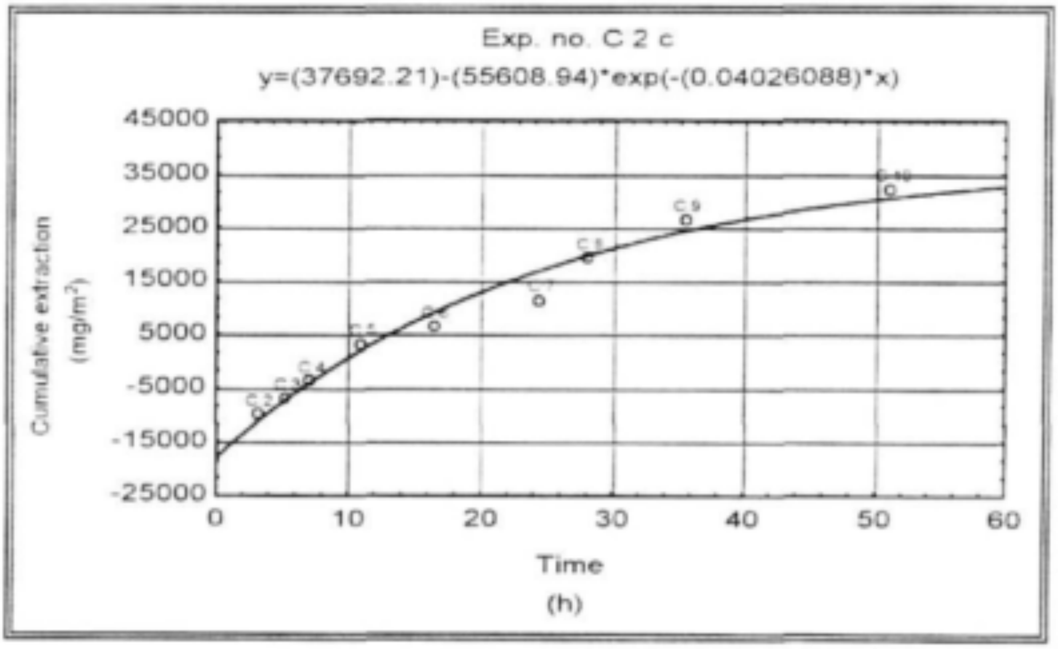
Temp. 25 pH 4.5

Vol. 0.4 0.005

Circum.: 0.141

Area 0.0031642

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	948	0	4.5	2.000	0.0000	0.0000
3.20	1027	-9987	3.48	1.976	0.0379	-0.1701
5.35	1003	-6953	3.39	1.946	0.0854	-0.1184
7.15	978	-3792	3.61	1.929	0.1124	-0.0646
11.02	923	3160	3.37	1.897	0.1623	0.0538
16.40	898	6321	3.11	1.838	0.2565	0.1077
24.43	858	11377	3.01	1.762	0.3760	0.1938
28.10	796	19215	3.28	1.723	0.4383	0.3273
35.55	738	26547	3.15	1.668	0.5238	0.4523
51.10	693	32236	2.8	1.544	0.7202	0.5492



Exp. no.: C 5 [H] 5

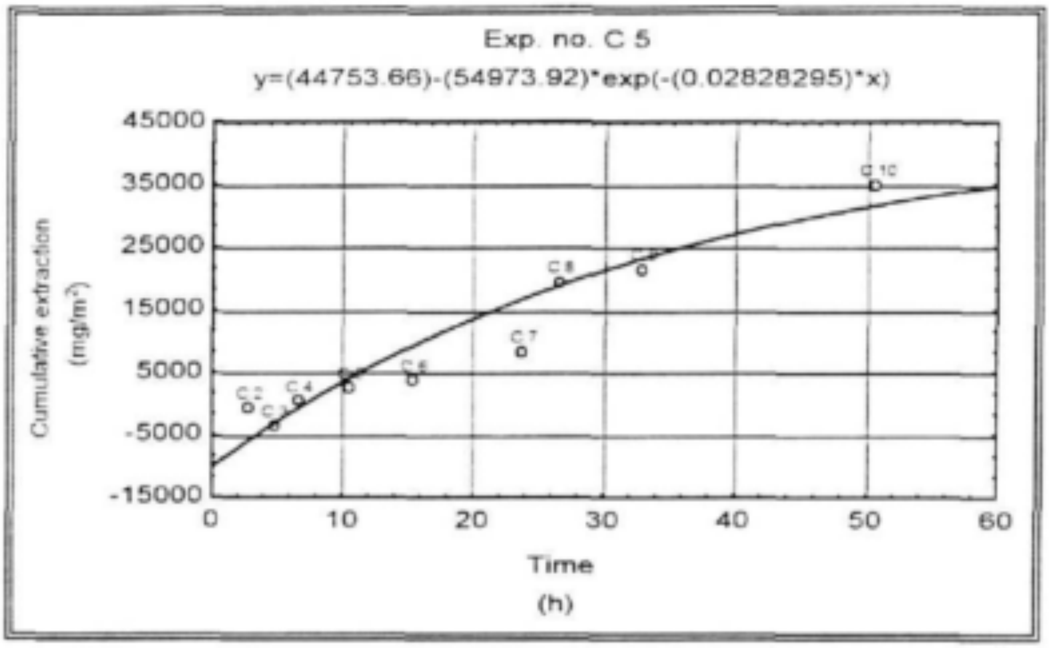
Temp. 25 pH 4.5

Vol. 0.4 0.005

Circum.: 0.128

Area 0.0026076

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	966	0	4.5	5.000	0.0000	0.0000
2.82	970	-614	3.42	4.972	0.0535	-0.0105
4.80	989	-3528	3.61	4.955	0.0863	-0.0601
6.68	963	460	3.88	4.947	0.1016	0.0078
10.58	950	2454	3.25	4.913	0.1677	0.0418
15.42	942	3682	3.24	4.869	0.2511	0.0627
23.85	911	8437	3.03	4.797	0.3894	0.1437
26.63	839	19482	3.42	4.769	0.4429	0.3319
32.98	826	21476	3.11	4.709	0.5571	0.3659
50.70	738	34975	3.11	4.650	0.6713	0.5958



Exp. no.: C 5 b [H] 5

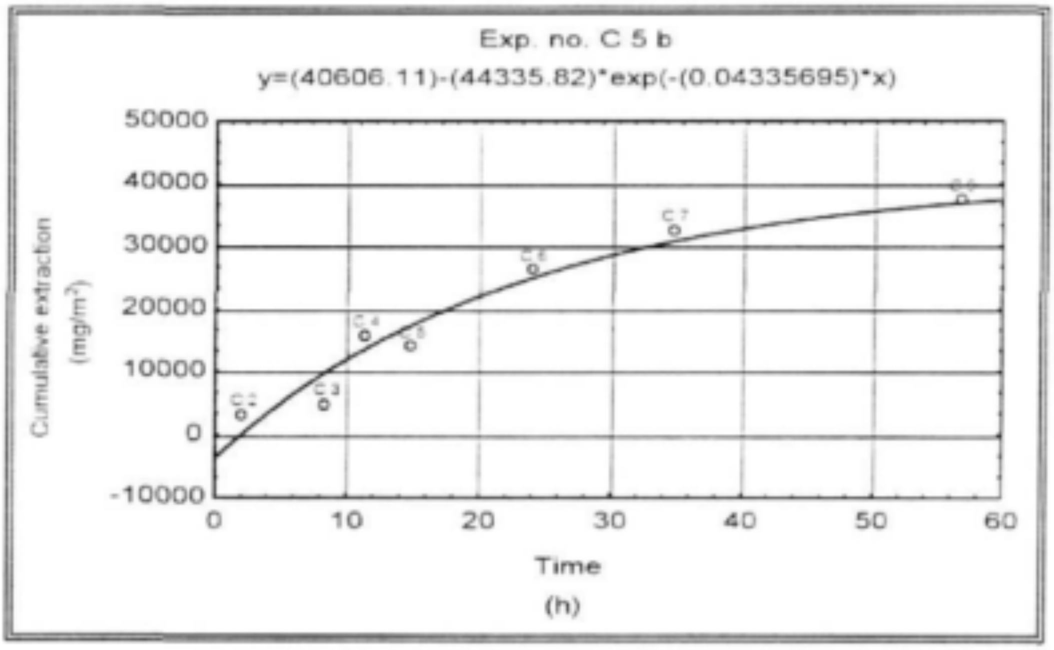
Temp. 25 pH 4.5

Vol. 0.4 0.005

Circum.: 0.131

Area 0.0027313

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	1097	0	4.5	5.000	0.0000	0.0000
2.10	1075	3245	3.55	4.980	0.0366	0.0553
8.43	1064	4843	3.25	4.938	0.1144	0.0825
11.37	990	15696	3.22	4.892	0.1980	0.2674
14.85	1002	13961	3.17	4.840	0.2924	0.2378
23.93	918	26240	3.09	4.778	0.4068	0.4470
34.73	875	32560	2.95	4.691	0.5665	0.5547
42.93	933	24007	3.02	4.617	0.7017	0.4090
56.72	842	37340	3.02	4.543	0.8369	0.6361



Exp. no.: C 7 [H] 7

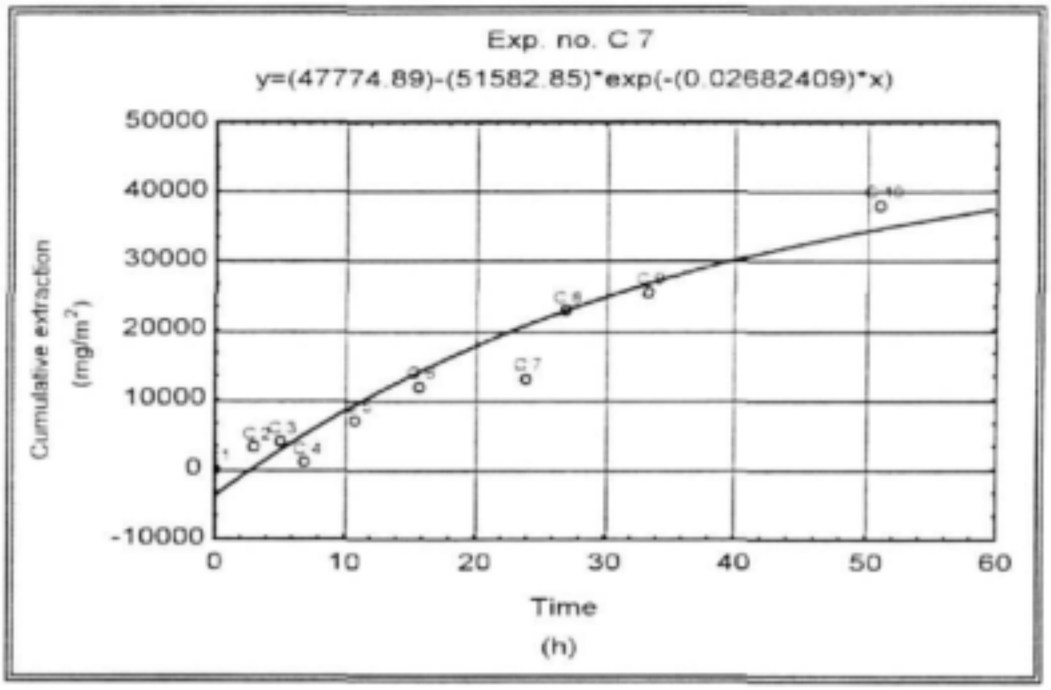
Temp. 25 pH 4.5

Vol. 0.4 0.005

Circum.: 0.139

Area 0.003075

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	996	0	4.5	7.000	0.0000	0.0000
3.10	972	3122	3.33	6.965	0.0567	0.0532
5.10	966	3902	3.43	6.938	0.1009	0.0665
7.00	989	911	3.58	6.919	0.1310	0.0155
10.90	942	7024	3.25	6.877	0.2001	0.1197
15.70	905	11837	3.24	6.833	0.2708	0.2017
23.93	896	13008	3.01	6.758	0.3938	0.2216
26.93	822	22634	3.3	6.720	0.4549	0.3856
33.28	801	25366	3.04	6.650	0.5694	0.4321
50.98	705	37853	3.04	6.579	0.6839	0.6449



Exp. no.: C 10 [H] 10

Temp. 25

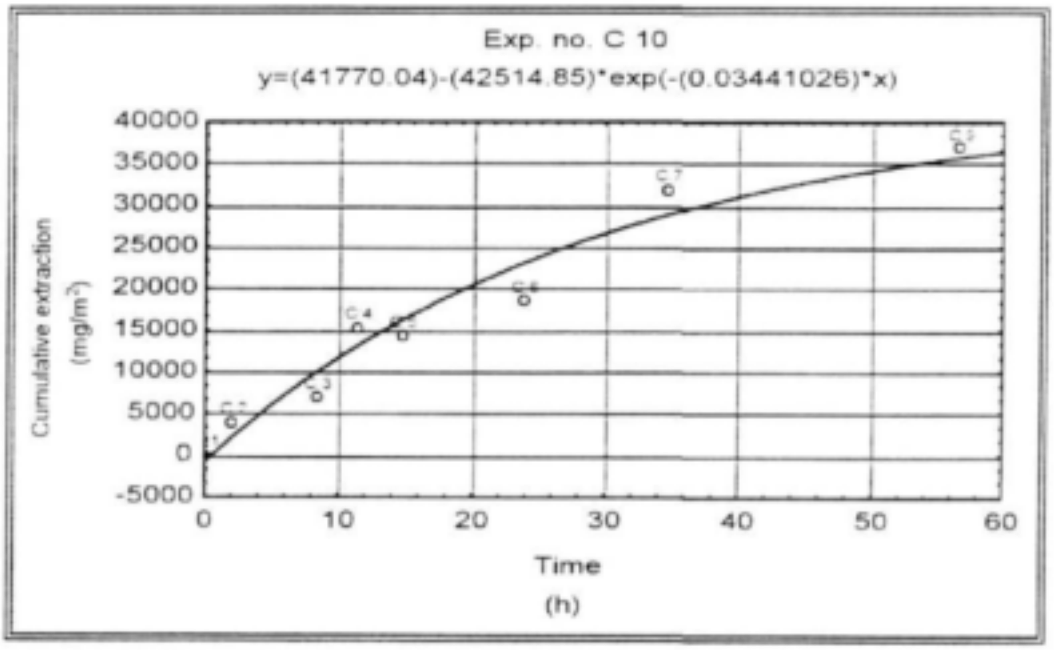
pH 4.5

Vol. 0.4 0.004

Circum.: 0.137

Area 0.0029872

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	1112	0	4.5	10.000	0.0000	0.0000
2.05	1083	3888	3.75	9.985	0.0196	0.0662
8.37	1061	6865	3.14	9.916	0.1123	0.1170
11.38	998	15276	3.07	9.834	0.2221	0.2602
14.78	1005	14294	3.41	9.798	0.2699	0.2435
23.85	974	18446	2.96	9.692	0.4125	0.3142
34.68	874	31886	2.83	9.547	0.6064	0.5432
42.87	911	26933	2.93	9.433	0.7595	0.4588
56.65	837	36802	2.93	9.319	0.9125	0.6269



Exp. no.: C 15 [H] 15

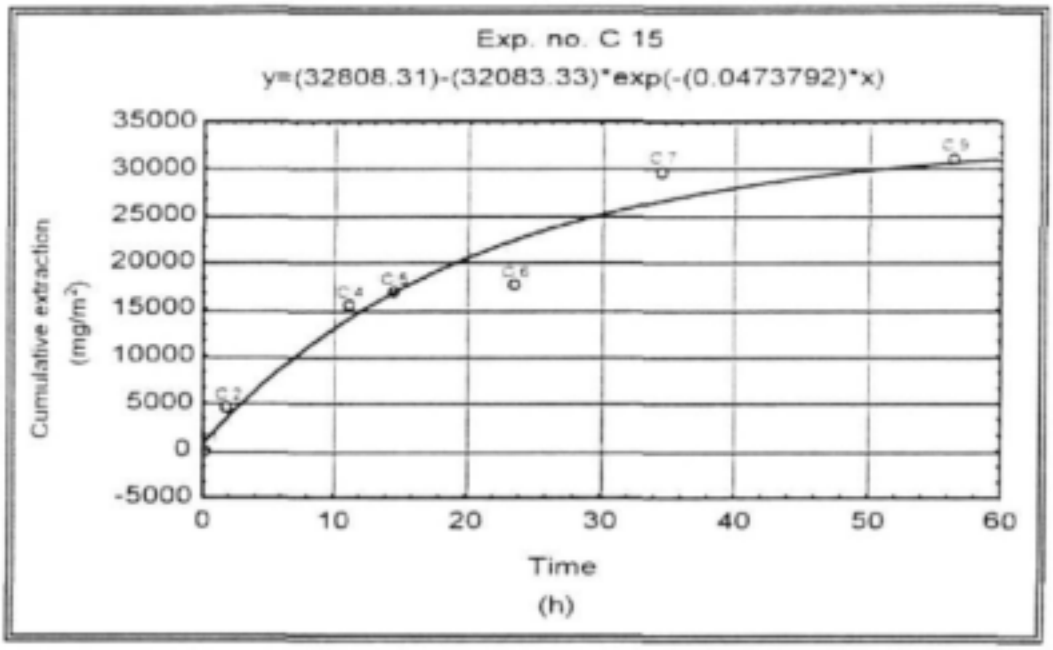
Temp. 25 pH 4.5

Vol. 0.4 0.006

Circum.: 0.137

Area 0.0029872

Time(h)	[Ni]	Extr.
0.13	1097	0
1.85	1064	4468
8.17	1051	6191
11.18	983	15314
14.58	972	16723
23.65	967	17474
34.47	875	29679
42.53	935	21693
56.32	866	30943



Exp. no.: C 20 [H] 20

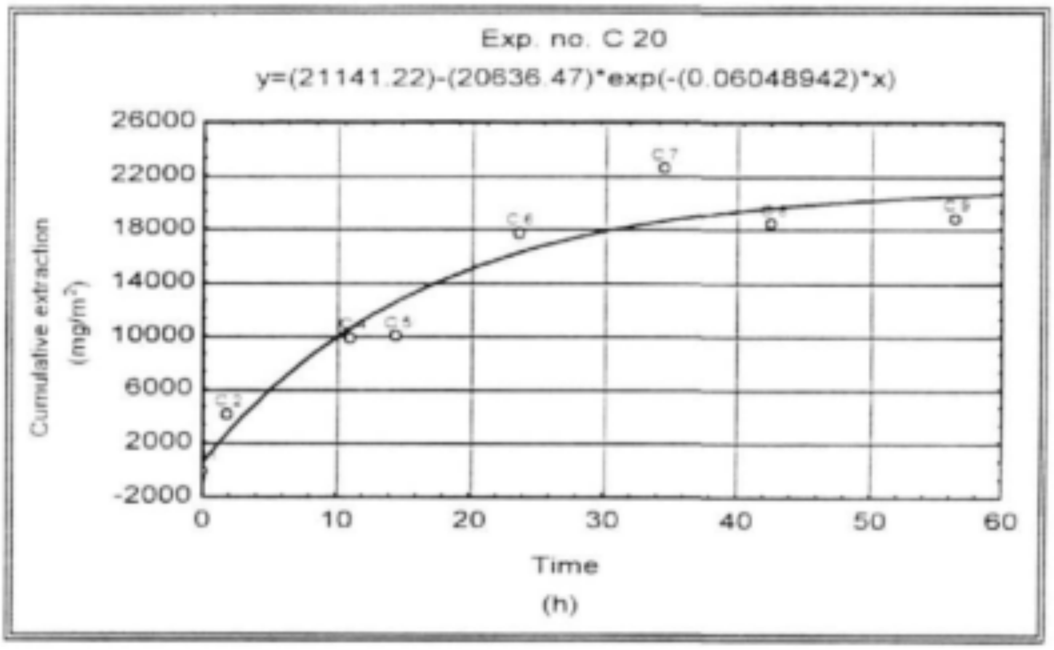
Temp. 25 pH 4.5

Vol. 0.4 0.005

Circum.: 0.135

Area 0.0029006

Time(h)	[Ni]	Extr.
0.00	1080	0
1.80	1050	4095
8.10	1073	982
11.13	1009	9830
14.52	1008	9931
23.60	952	17641
34.42	917	22488
42.62	947	18394
56.40	944	18736



Exp. no.: C 25 [H] 25

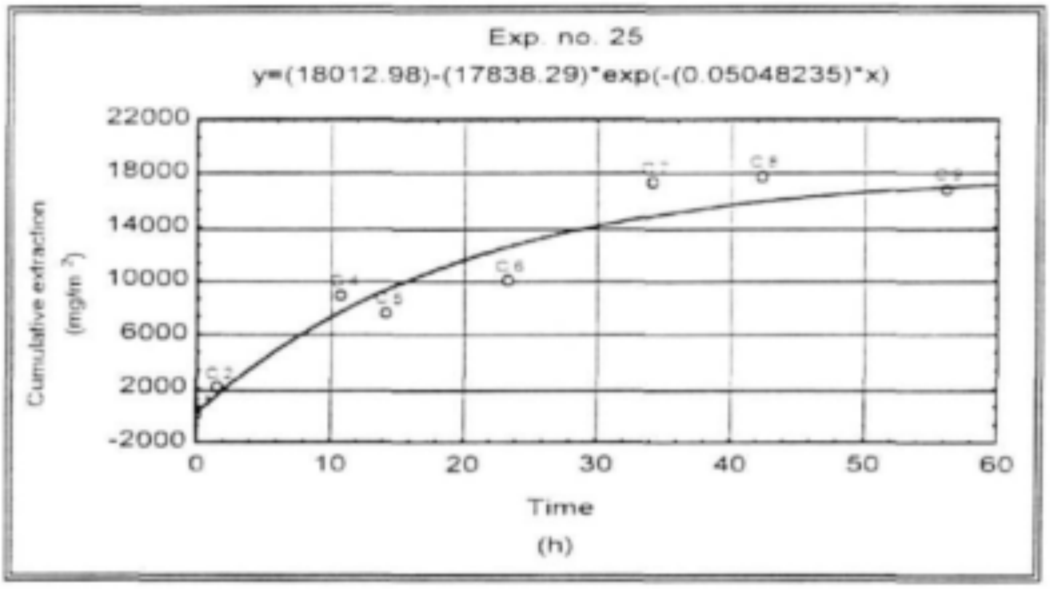
Temp. 25 pH 4.5

Vol. 0.4 0.006

Circum.: 0.136

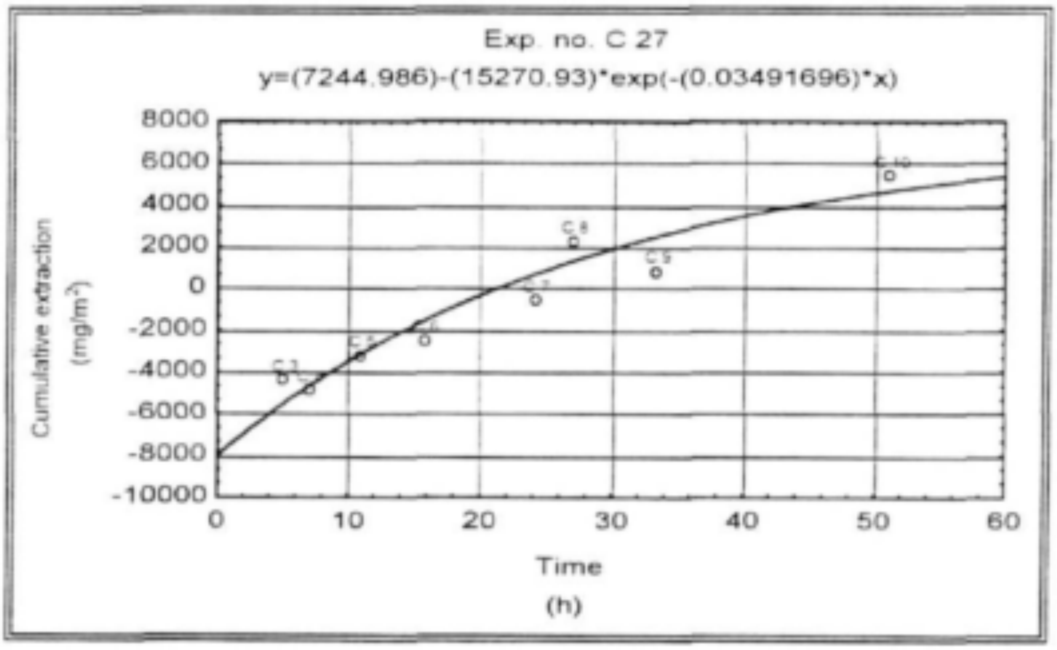
Area 0.0029437

Time(h)	[Ni]	Extr.
0.00	995	0
1.57	980	2049
7.87	980	1988
10.90	929	8915
14.28	939	7624
23.38	921	10015
34.18	868	17307
42.38	864	17784
56.17	871	16848



Exp. no.: C 27 [H] 27
Temp. 25 pH 4.5
Vol. 0.4 0.005
Circum.: 0.145
Area 0.0033462

Time(h)	[Ni]	Extr.
0.00	976	0
3.20	993	-2032
5.18	1013	-4423
7.07	1017	-4901
10.98	1003	-3228
15.78	997	-2510
24.15	981	-598
27.02	957	2271
33.37	969	837
51.07	931	5379



Exp. no.: C 28 [H] 28

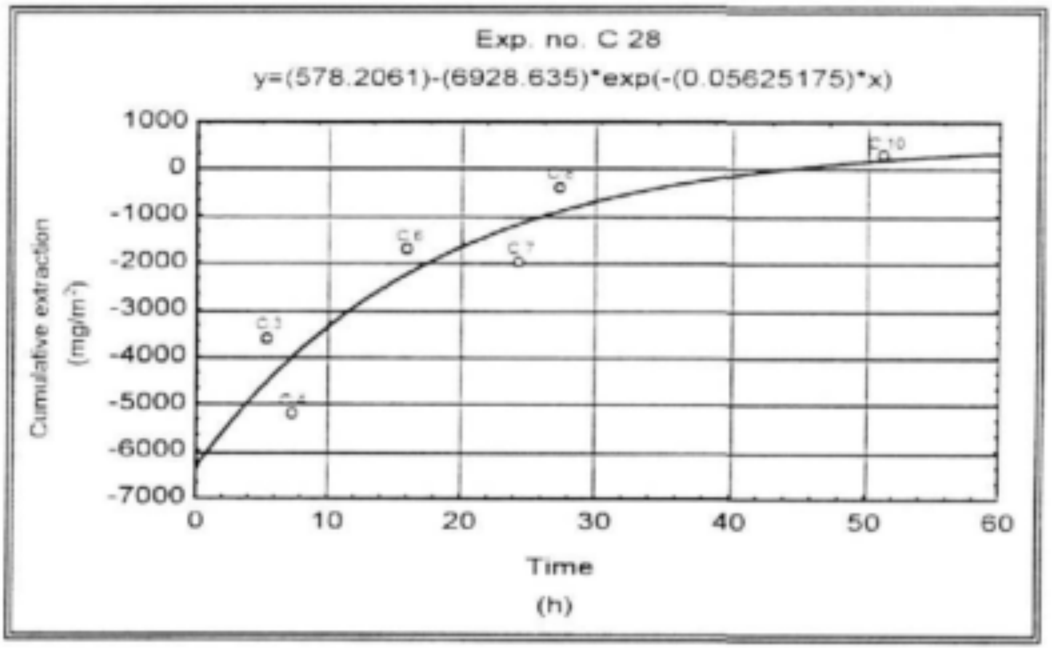
Temp. 25 pH 4.5

Vol. 0.4 0.005

Circom.: 0.137

Area 0.0029872

Time(h)	[Ni]	Extr.
0.00	1007	0
3.42	1023	-2142
5.42	1034	-3615
7.28	1046	-5222
11.25	980	3615
16.03	1020	-1741
24.32	1022	-2009
27.25	1010	-402
33.60	1032	-3348
51.28	1005	268



Exp. no.: C 29 [H] 29

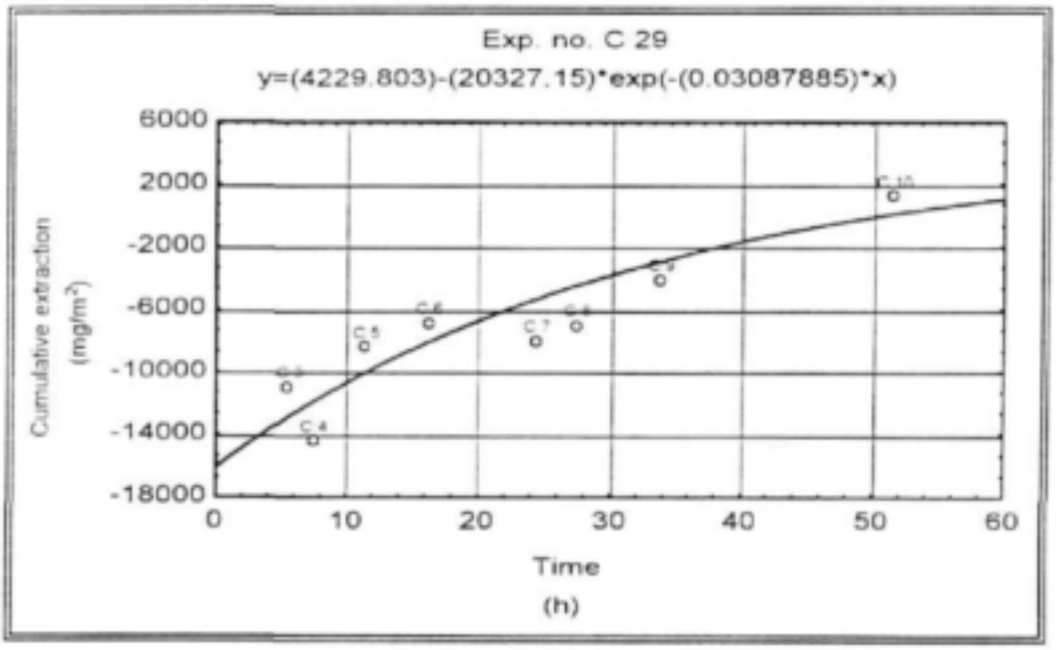
Temp. 25 pH 4.5

Vol. 0.4 0.005

Circum.: 0.134

Area 0.0028578

Time(h)	[Ni]	Extr.
0.00	940	0
3.57	995	-7698
5.58	1018	-10918
7.45	1043	-14417
11.42	1000	-8398
16.18	989	-6858
24.33	997	-7978
27.40	990	-6998
33.75	969	-4059
51.43	931	1260



Exp. no.: C 30,a [H] 30

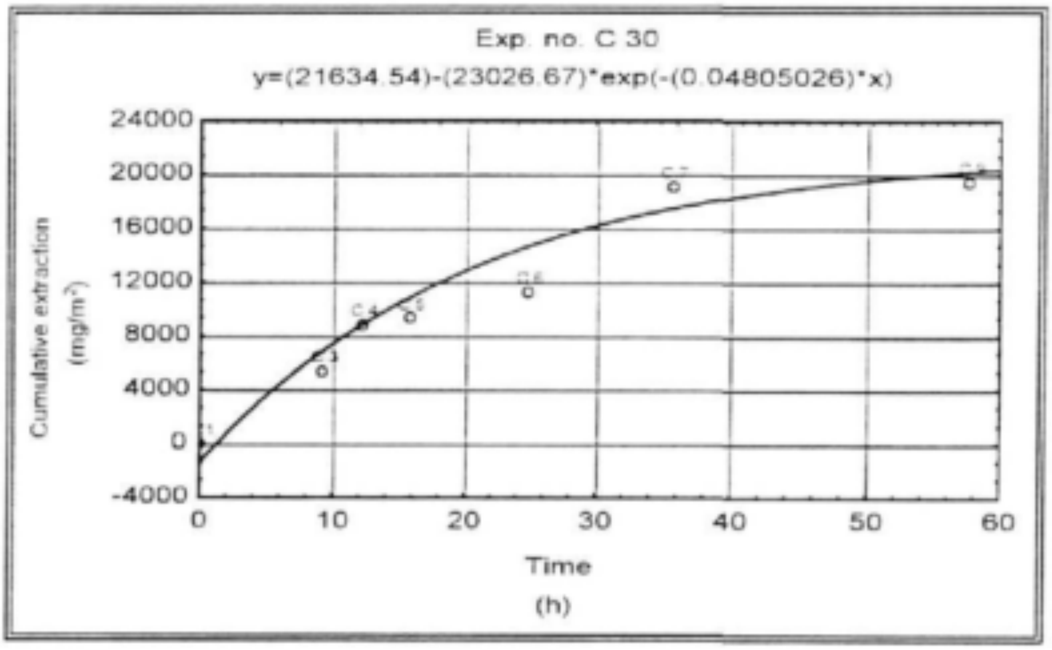
Temp. 25 pH 4.5

Vol. 0.4 0.006

Circum.: 0.138

Area 0.0030309

Time(h)	[Ni]	Extr.
0.00	1027	0
3.03	986	5414
9.33	986	5407
12.28	960	8833
15.78	957	9281
24.87	942	11261
35.67	882	19072
43.87	1023	464
57.65	880	19422



Exp. no.: C 30 a [H] 30

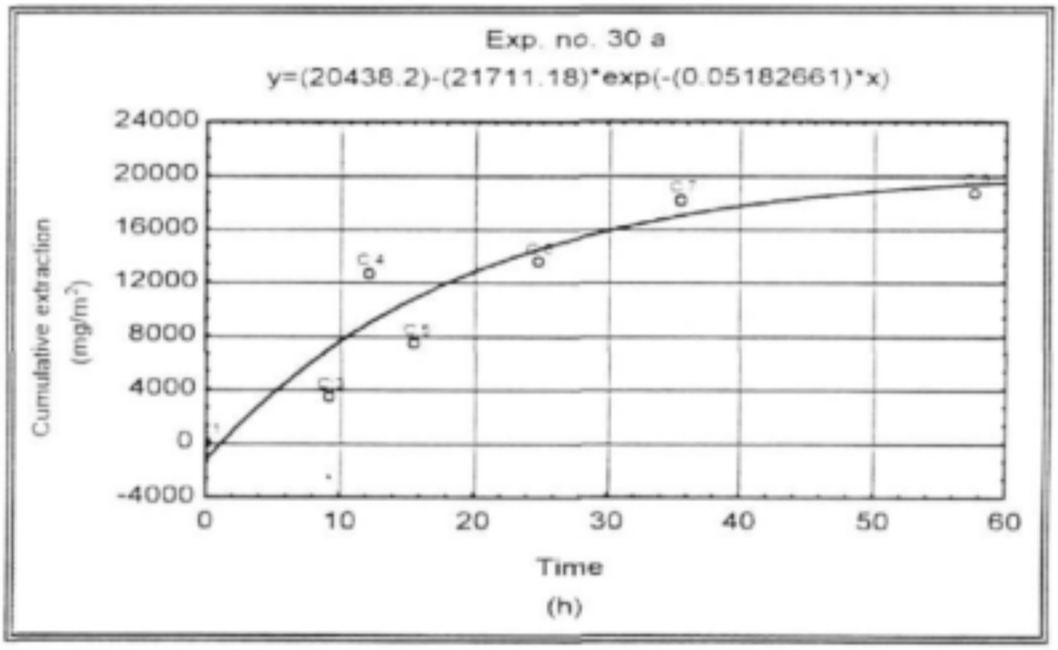
Temp. 25 pH 4.5

Vol. 0.4 0.006

Circum.: 0.138

Area 0.0030309

Time(h)	[Ni]	Extr.
0.00	1076	0
2.95	1034	5596
9.27	1050	3383
12.23	980	12612
15.72	1020	7366
24.80	974	13448
35.60	939	18094
43.80	1021	7260
57.60	935	18665



Exp no.: C 30 b [H] 30

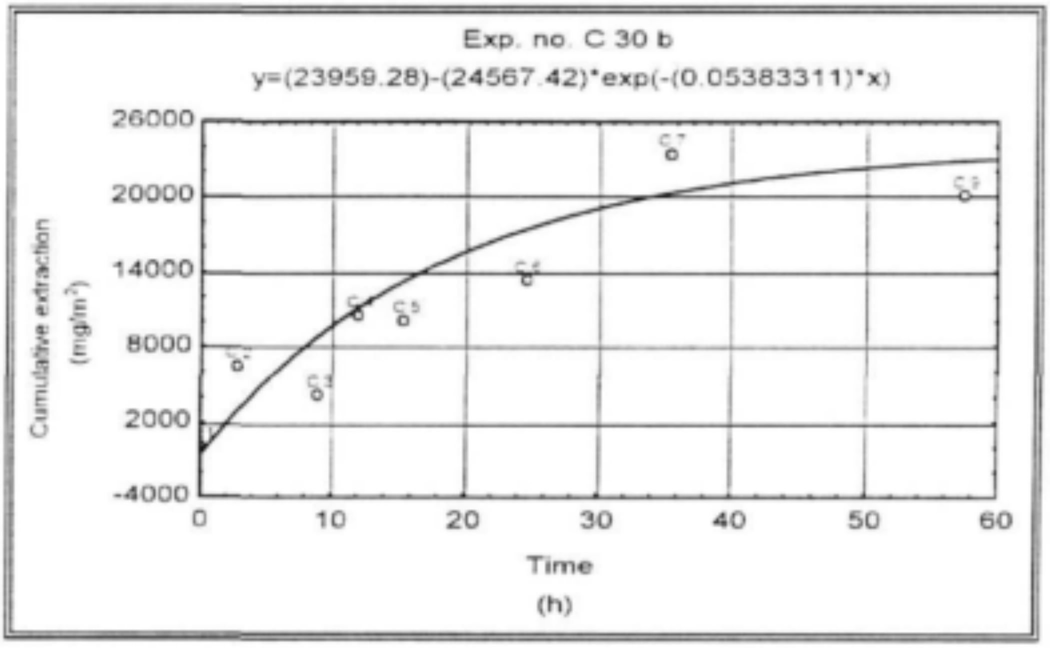
Temp. 25 pH 4.5

Vol. 0.4 0.005

Circum.: 0.129

Area 0.0026485

Time(h)	[Ni]	Extr.
0.00	1076	0
2.80	1034	6384
9.10	1049	4106
12.07	1007	10479
15.55	1009	10091
24.63	988	13263
35.45	921	23374
43.63	967	16486
57.42	943	20045



Exp. no.: C 31 [H] 31

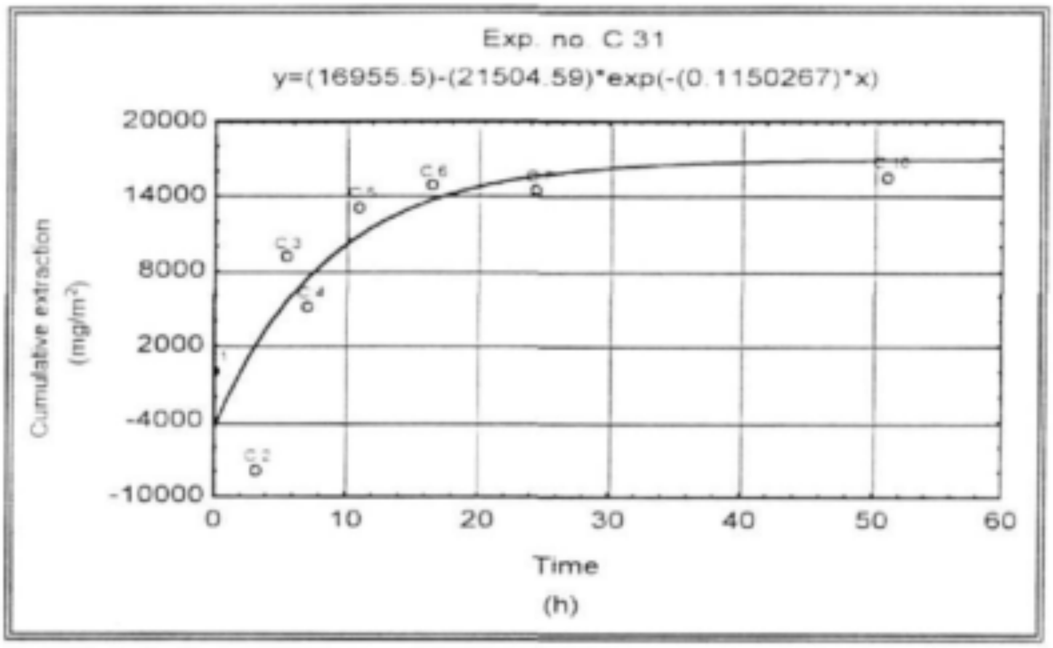
Temp. 25 pH 4.5

Vol. 0.4 0.005

Circum.: 0.143

Area 0.0032546

Time(h)	[Ni]	Extr.
0.00	1065	0
3.25	1129	-7866
5.40	991	9095
7.22	1023	5162
11.07	958	13151
16.45	944	14871
24.48	947	14503
28.15	1145	-9832
35.60	1023	5162
51.15	938	15609



Exp. no.: C 32 [H] 32

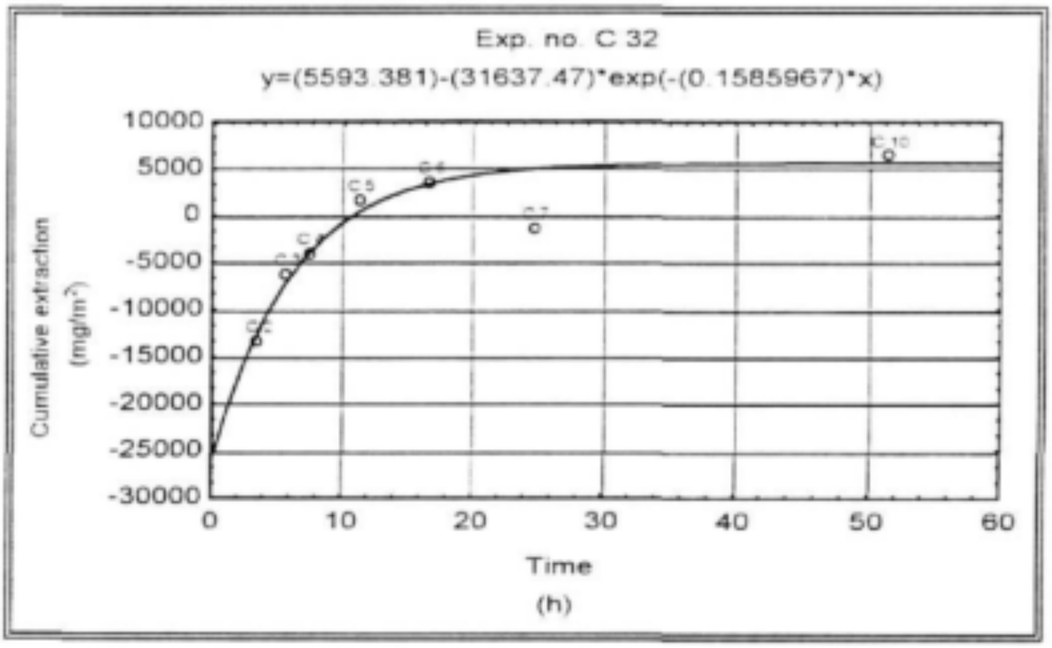
Temp. 25 pH 4.5

Vol. 0.4 0.005

Circum.: 0.136

Area 0.0029437

Time(h)	[Ni]	Extr.
0.00	975	0
3.53	1073	-13316
5.70	1021	-6251
7.50	1005	-4076
11.35	963	1631
16.73	949	3533
24.75	985	-1359
28.43	1220	-33291
35.88	1041	-8968
51.43	928	6386



Exp. no.: C 33 [H] 33

Temp. 25

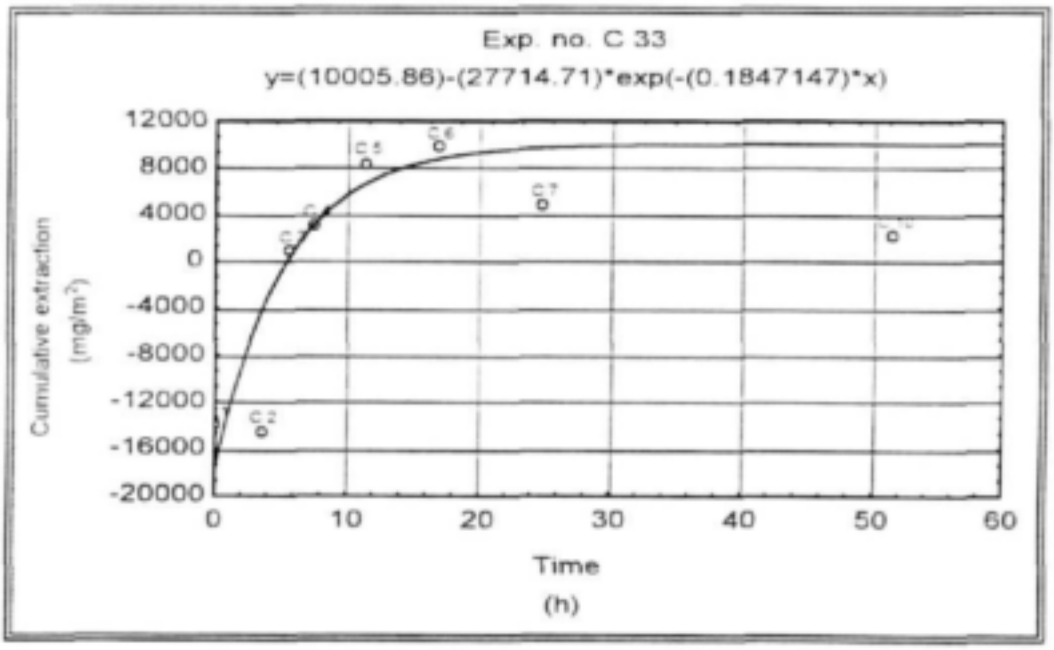
pH 4.5

Vol. 0.4 0.005

Circum.: 0.135

Area 0.0029006

Time(h)	[Ni]	Extr.
0.00	994	0
3.62	1099	-14480
5.78	988	827
7.58	972	3034
11.43	933	8412
16.82	923	9791
24.85	959	4827
28.52	1128	-18479
35.97	1058	-8826
51.53	978	2206



Exp. no.: C 35 [H] 35

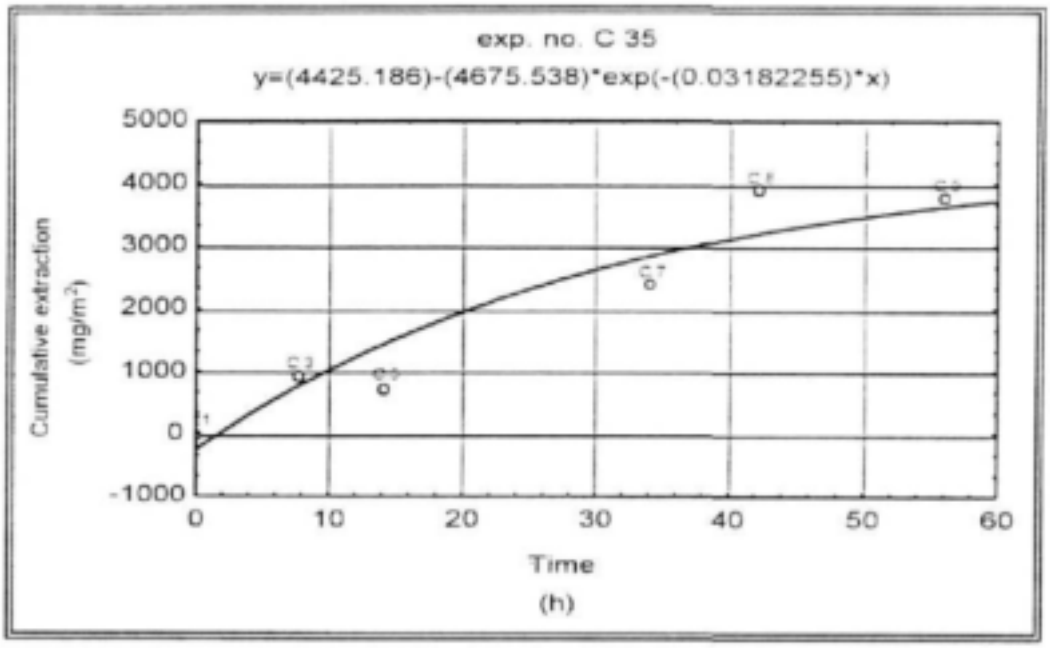
Temp 25 pH 4.5

Vol 0.4 0.007

Circum.: 0.146

Area 0.0033925

Time(h)	[Ni]	Extr.
0.00	1037	0
1.50	1016	2462
7.78	1029	915
10.82	1016	2460
14.20	1031	734
23.30	1041	-506
34.10	1017	2373
42.30	1004	3879
56.08	1005	3760



A.3 Experimental results obtained from temperature experiments

Exp. no.: T 1 a [H] 2

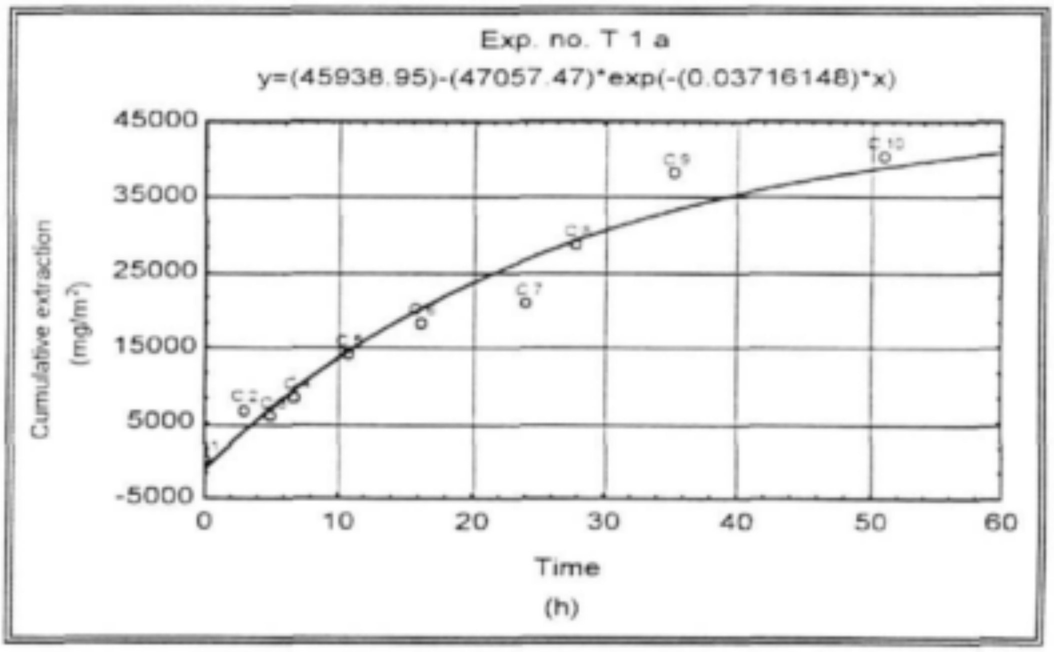
Temp. 25 pH 4.5

Vol. 0.4 0.005

Circum.: 0.14

Area 0.0031194

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	1022	0	4.5	2.000	0.0000	0.0000
2.95	970	6668	3.42	1.972	0.0447	0.1136
5.10	977	5770	3.5	1.949	0.0812	0.0983
6.92	957	8335	3.82	1.940	0.0965	0.1420
10.78	913	13977	3.37	1.908	0.1472	0.2381
16.17	880	18208	3.13	1.851	0.2382	0.3102
24.18	860	20773	3	1.774	0.3624	0.3539
27.87	799	28595	3.28	1.734	0.4256	0.4871
35.30	725	38084	3.08	1.670	0.5282	0.6488
50.87	708	40264	2.81	1.549	0.7228	0.6859



Exp. no.: T 1 b [H] 2

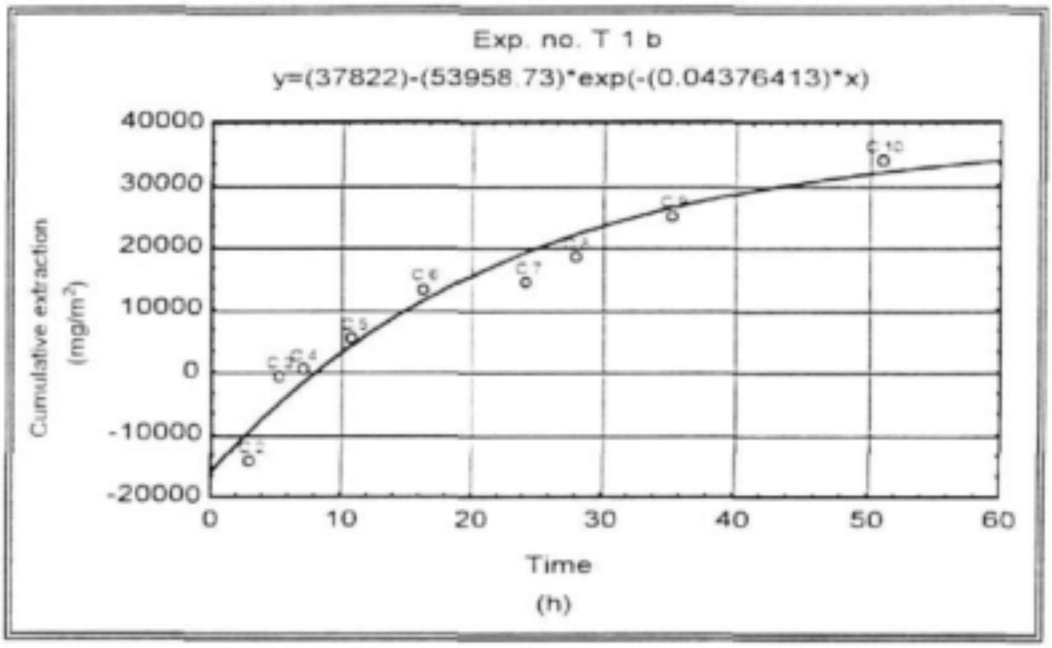
Temp. 25 pH 4.5

Vol. 0.4 0.005

Circum.: 0.136

Area 0.0029437

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	997	0	4.5	2.000	0.0000	0.0000
3.05	1103	-14403	3.47	1.975	0.0417	-0.2454
5.20	1003	-815	3.45	1.950	0.0857	-0.0139
7.02	995	272	3.77	1.939	0.1044	0.0046
10.88	958	5299	3.25	1.896	0.1766	0.0903
16.27	900	13181	3.38	1.865	0.2289	0.2245
24.30	892	14268	3	1.788	0.3605	0.2431
27.97	863	18208	3.32	1.752	0.4212	0.3102
35.42	813	25002	3.23	1.707	0.4969	0.4259
50.97	748	33835	2.85	1.597	0.6846	0.5764



Exp. no.: T 1 c [H] 2

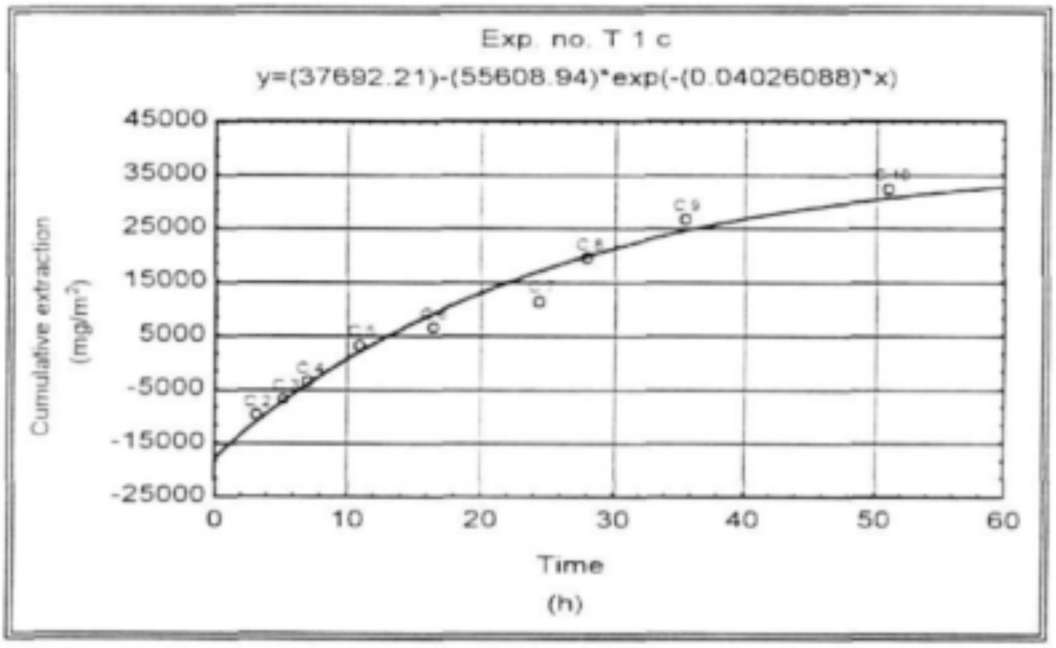
Temp. 25 pH 4.5

Vol. 0.4 0.005

Circum.: 0.141

Area 0.0031642

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	948	0	4.5	2.000	0.0000	0.0000
3.20	1027	-9987	3.48	1.976	0.0379	-0.1701
5.35	1003	-6953	3.39	1.946	0.0854	-0.1184
7.15	978	-3792	3.61	1.929	0.1124	-0.0646
11.02	923	3160	3.37	1.897	0.1623	0.0538
16.40	898	6321	3.11	1.838	0.2565	0.1077
24.43	858	11377	3.01	1.762	0.3760	0.1938
28.10	796	19215	3.28	1.723	0.4383	0.3273
35.55	738	26547	3.15	1.668	0.5238	0.4523
51.10	693	32236	2.8	1.544	0.7202	0.5492



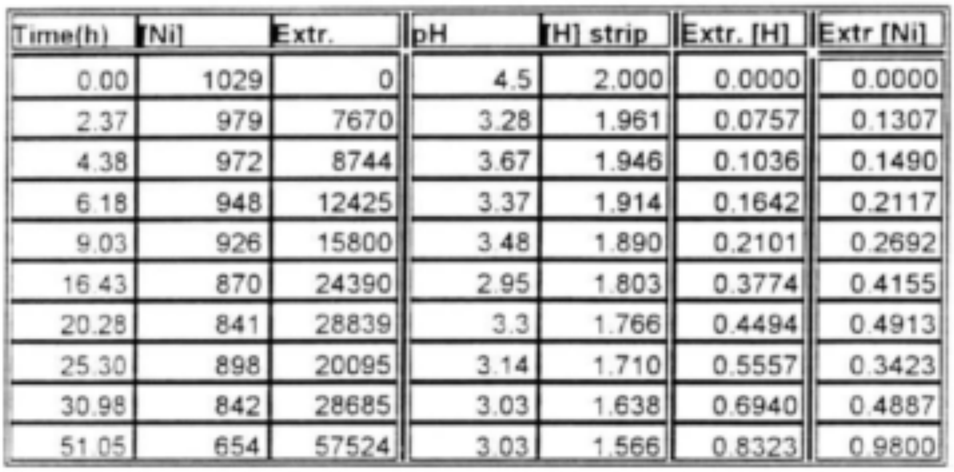
Exp. no.: T 2 a [H] 2

Temp. 35 pH 4.5

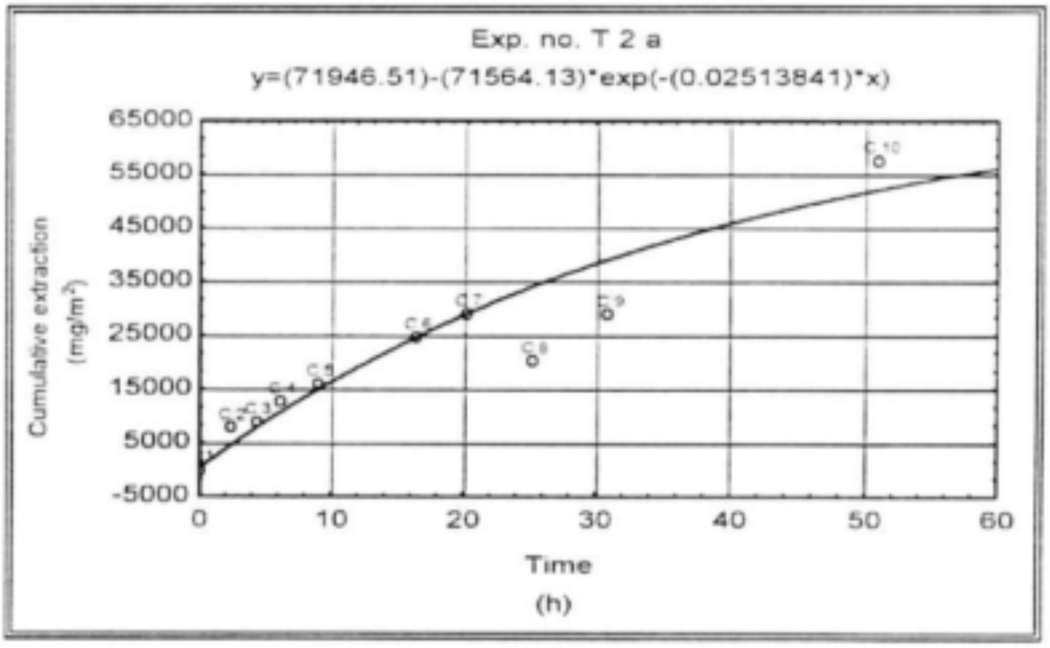
Vol. 0.4 0.005

Circum.: 0.128

Area 0.0026076



Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	1029	0	4.5	2.000	0.0000	0.0000
2.37	979	7670	3.28	1.961	0.0757	0.1307
4.38	972	8744	3.67	1.946	0.1036	0.1490
6.18	948	12425	3.37	1.914	0.1642	0.2117
9.03	926	15800	3.48	1.890	0.2101	0.2692
16.43	870	24390	2.95	1.803	0.3774	0.4155
20.28	841	28839	3.3	1.766	0.4494	0.4913
25.30	898	20095	3.14	1.710	0.5557	0.3423
30.98	842	28685	3.03	1.638	0.6940	0.4887
51.05	654	57524	3.03	1.566	0.8323	0.9800



Exp. no.: T 2 b [H] 2

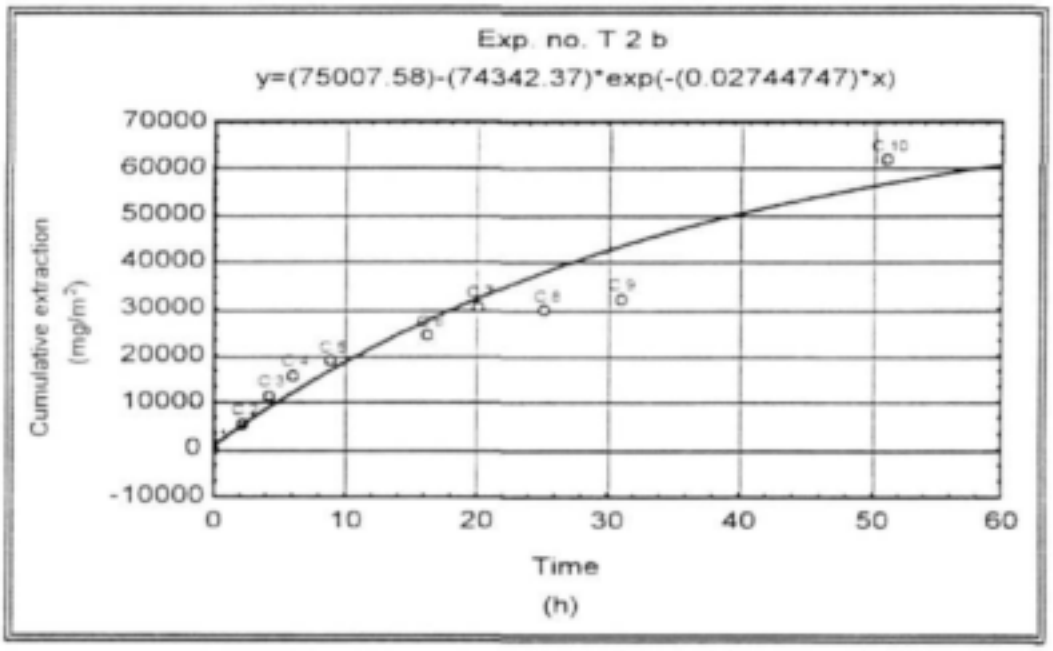
Temp. 35 pH 4.5

Vol. 0.4 0.005

Circum.: 0.129

Area 0.0026485

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	1022	0	4.5	2.000	0.0000	0.0000
2.32	986	5437	3.28	1.961	0.0745	0.0926
4.33	946	11478	3.61	1.943	0.1068	0.1955
6.13	917	15858	3.41	1.915	0.1608	0.2702
8.97	898	18728	3.52	1.893	0.2016	0.3190
16.37	861	24316	2.9	1.795	0.3870	0.4142
20.13	820	30508	3.25	1.753	0.4671	0.5197
25.32	826	29602	3.15	1.698	0.5693	0.5043
31.02	809	32169	3.08	1.634	0.6901	0.5480
51.07	613	61771	3.08	1.570	0.8109	1.0523



Exp. no.: T 2 c [H] 2

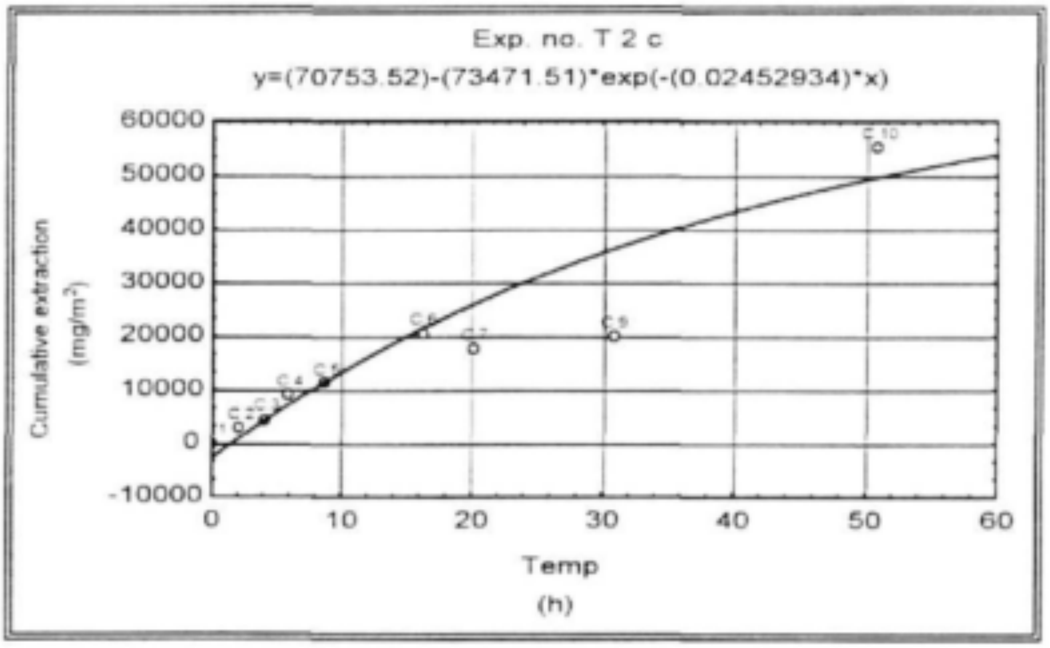
Temp. 35 pH 4.5

Vol. 0.4 0.005

Circum.: 0.127

Area 0.002567

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	989	0	4.5	2.000	0.0000	0.0000
2.12	971	2805	3.33	1.965	0.0680	0.0478
4.13	960	4519	3.61	1.948	0.1013	0.0770
5.93	931	9038	3.63	1.932	0.1329	0.1540
8.77	917	11219	3.22	1.886	0.2218	0.1911
16.18	857	20569	2.92	1.792	0.4043	0.3504
20.12	876	17608	3.35	1.759	0.4689	0.3000
25.13	896	14492	3.05	1.690	0.6029	0.2469
30.82	861	19945	3.13	1.634	0.7135	0.3398
50.87	634	55317	3.13	1.577	0.8241	0.9424



Exp. no.: T 3 a [H] 2

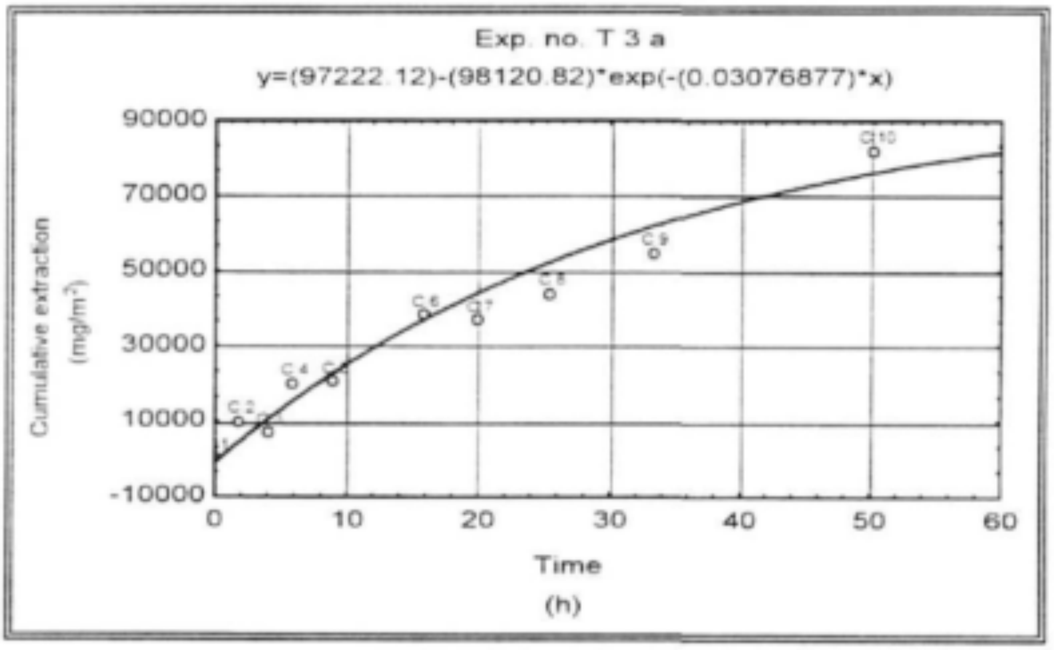
Temp. 45 pH 4.5

Vol. 0.4 0.005

Circum.: 0.139

Area 0.003075

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	1035	0	4.5	2.000	0.0000	0.0000
1.90	958	10016	3.14	1.945	0.0901	0.1706
4.07	983	6764	3.2	1.897	0.1681	0.1152
5.93	881	20032	3.28	1.857	0.2322	0.3413
9.05	879	20292	2.97	1.774	0.3675	0.3457
15.88	742	38113	2.69	1.613	0.6290	0.6493
19.98	753	36683	3.07	1.548	0.7356	0.6249
25.50	697	43967	2.89	1.447	0.8990	0.7490
33.27	615	54634	2.65	1.271	1.1861	0.9307
50.33	404	82080	2.45	0.989	1.6436	1.3983



Exp. no.: T 3 b [H] 2

Temp. 45.

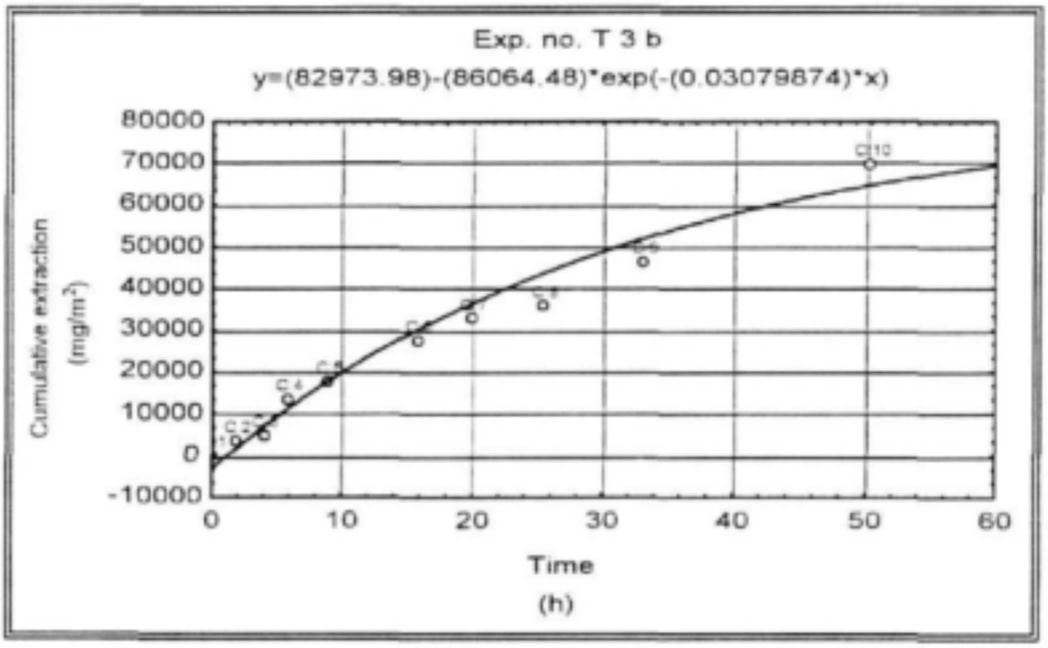
pH 4.5

Vol. 0.4 0.005

Circum.: 0.129

Area 0.0026485

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	1000	0	4.5	2.000	0.0000	0.0000
1.85	977	3474	3.26	1.959	0.0782	0.0592
4.03	969	4682	3.14	1.903	0.1829	0.0798
5.90	911	13442	3.56	1.884	0.2197	0.2290
9.00	884	17519	3.06	1.816	0.3464	0.2985
15.83	818	27487	2.75	1.677	0.6102	0.4683
19.93	784	32622	3.24	1.633	0.6924	0.5557
25.47	763	35794	3.13	1.576	0.7996	0.6098
33.22	693	46366	2.72	1.427	1.0826	0.7899
50.27	539	69624	2.49	1.170	1.5665	1.1861



Exp. no.: T 3 c [H] 2

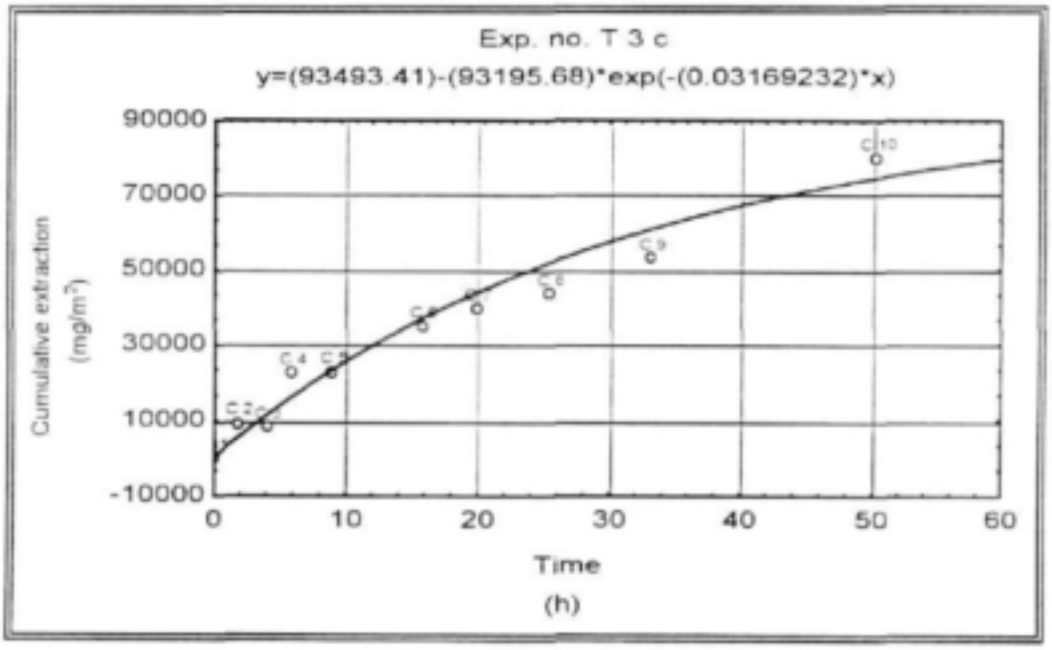
Temp. 45 pH 4.5

Vol. 0.4 0.005

Circum.: 0.133

Area 0.0028153

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	1023	0	4.5	2.000	0.0000	0.0000
1.82	958	9235	3.16	1.947	0.0938	0.1573
4.00	966	8099	3.23	1.903	0.1730	0.1380
5.87	865	22449	3.34	1.869	0.2334	0.3824
8.97	863	22733	3.07	1.803	0.3499	0.3873
15.82	778	34810	2.72	1.653	0.6161	0.5930
19.90	744	39641	3.21	1.606	0.6992	0.6753
25.43	717	43477	2.99	1.527	0.8401	0.7407
33.18	649	53138	2.7	1.370	1.1191	0.9053
50.25	461	79850	2.45	1.089	1.6187	1.3603



Exp. no.: T 4 a [H] 2

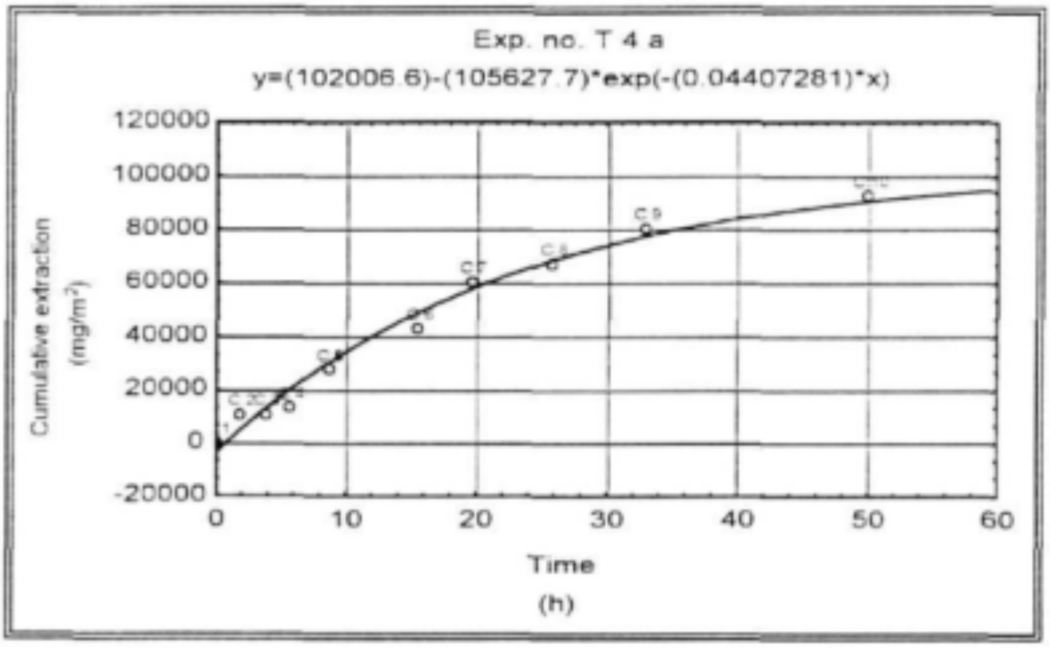
Temp. 65 pH 4.5

Vol. 0.4 0.004

Circum.: 0.126

Area 0.0025267

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	1039	0	4.5	2.000	0.0000	0.0000
1.88	971	10765	2.96	1.894	0.1686	0.1834
3.82	971	10765	3.35	1.852	0.2343	0.1834
5.70	957	12981	3.04	1.764	0.3737	0.2211
8.75	864	27704	2.89	1.638	0.5726	0.4720
15.58	769	42743	2.5	1.325	1.0682	0.7282
19.68	658	60315	3.03	1.235	1.2109	1.0275
25.88	615	67122	2.98	1.134	1.3717	1.1435
32.98	531	80420	2.86	0.999	1.5852	1.3700
50.02	454	92609	3.14	0.929	1.6949	1.5777



Exp. no.: T 4 b [H] 2

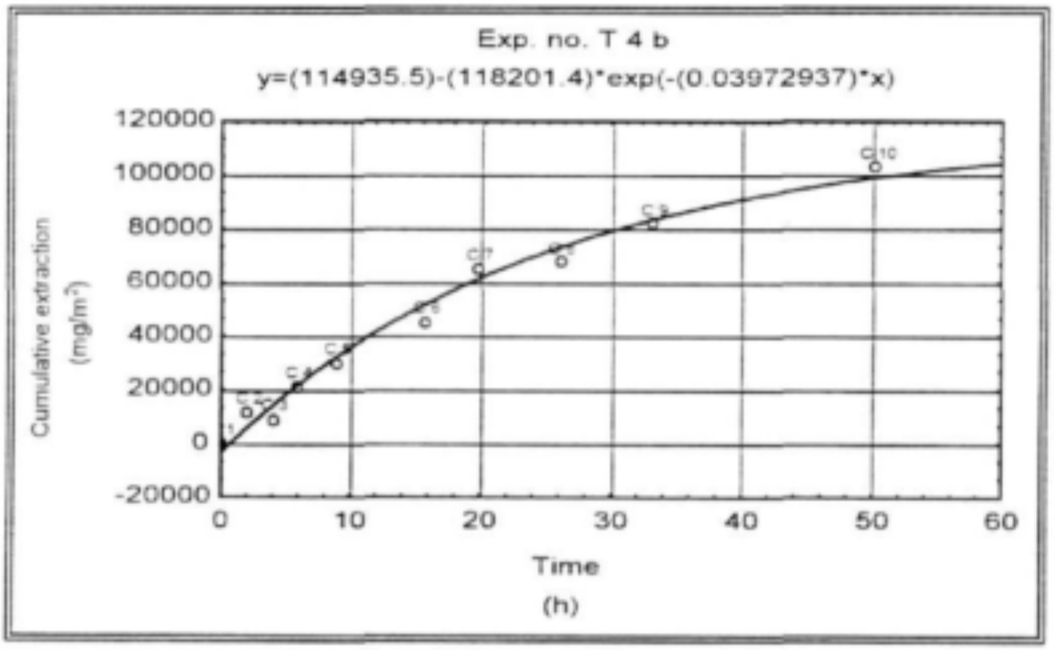
Temp. 65 pH 4.5

Vol. 0.4 0.0045

Circum.: 0.128

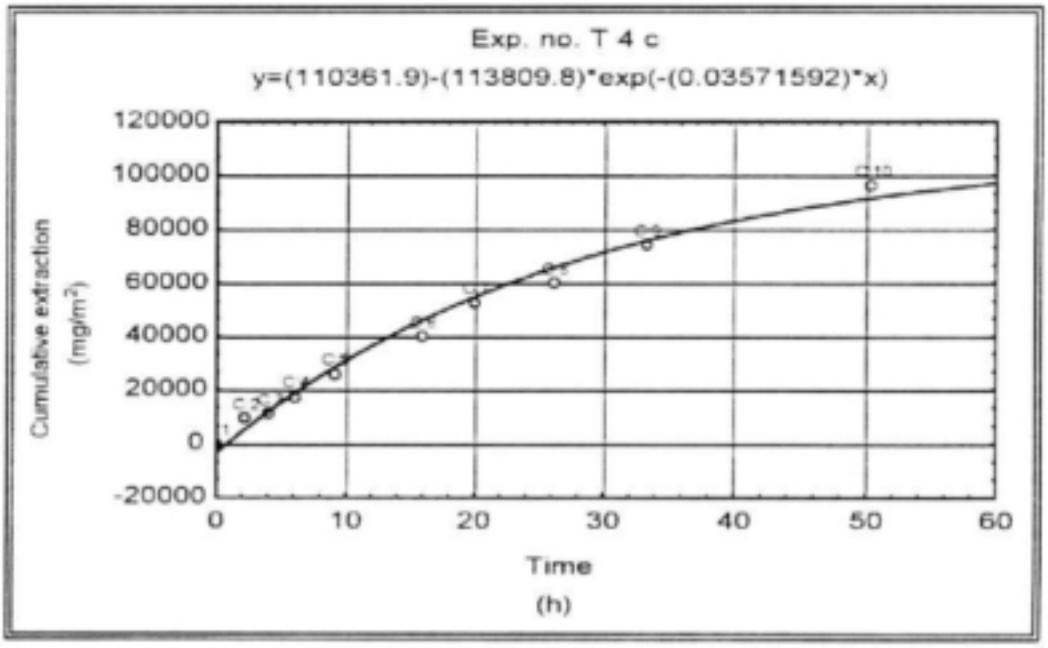
Area 0.0026076

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	1030	0	4.5	2.000	0.0000	0.0000
2.10	954	11658	2.88	1.886	0.1974	0.1986
4.03	971	9050	3.27	1.841	0.2749	0.1542
5.93	893	21016	3.2	1.787	0.3668	0.3580
8.97	835	29913	2.79	1.646	0.6108	0.5096
15.78	735	45252	2.39	1.287	1.2308	0.7709
19.90	607	64887	3.2	1.234	1.3228	1.1054
26.12	591	67342	2.8	1.095	1.5610	1.1472
33.20	498	81608	2.7	0.921	1.8623	1.3903
50.22	360	102777	2.69	0.742	2.1706	1.7509



Exp. no.: T 4 c [H] 2
Temp. 65
pH 4.5
Vol. 0.4 0.005
Circum.: 0.133
Area 0.0028153

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	1030	0	4.5	2.000	0.0000	0.0000
2.23	965	9235	2.93	1.909	0.1624	0.1573
4.17	952	11082	3.38	1.878	0.2172	0.1888
6.08	907	17476	3.09	1.815	0.3282	0.2977
9.12	846	26143	2.85	1.705	0.5244	0.4454
15.92	749	39925	2.6	1.506	0.8768	0.6802
20.03	660	52570	3.15	1.452	0.9729	0.8956
26.15	608	59958	2.68	1.288	1.2652	1.0214
33.33	507	74308	2.89	1.187	1.4438	1.2659
50.35	353	96189	2.25	0.740	2.2383	1.6387



Exp. no.: T 5 a [H] 2

Temp. 85

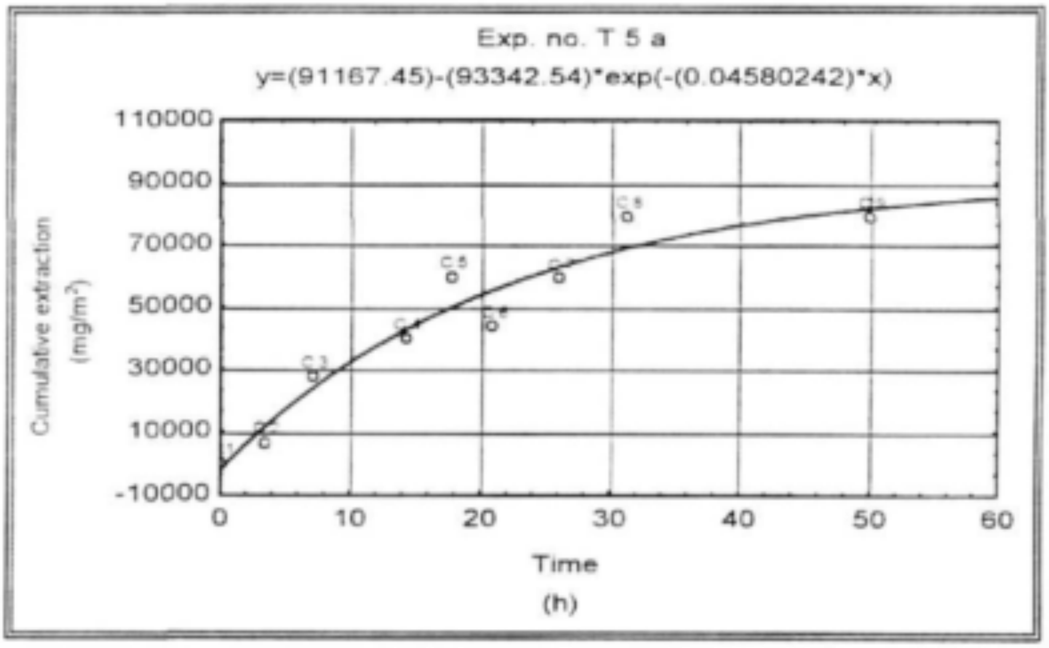
pH 4.5

Vol. 0.4 0.005

Circum.: 0.125

Area 0.0024868

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	1005	0	4.5	2.000	0.0000	0.0000
3.50	964	6595	2.24	1.542	0.9205	0.1123
7.18	833	27666	2.89	1.442	1.1226	0.4713
14.25	757	39891	2.47	1.173	1.6626	0.6796
17.77	634	59675	3.03	1.101	1.8076	1.0166
20.97	733	43751	2.89	1.000	2.0097	0.7453
26.08	638	59032	2.48	0.738	2.5373	1.0057
31.38	513	79138	2.87	0.633	2.7492	1.3482



Exp. no.: T 5 b [H] 2

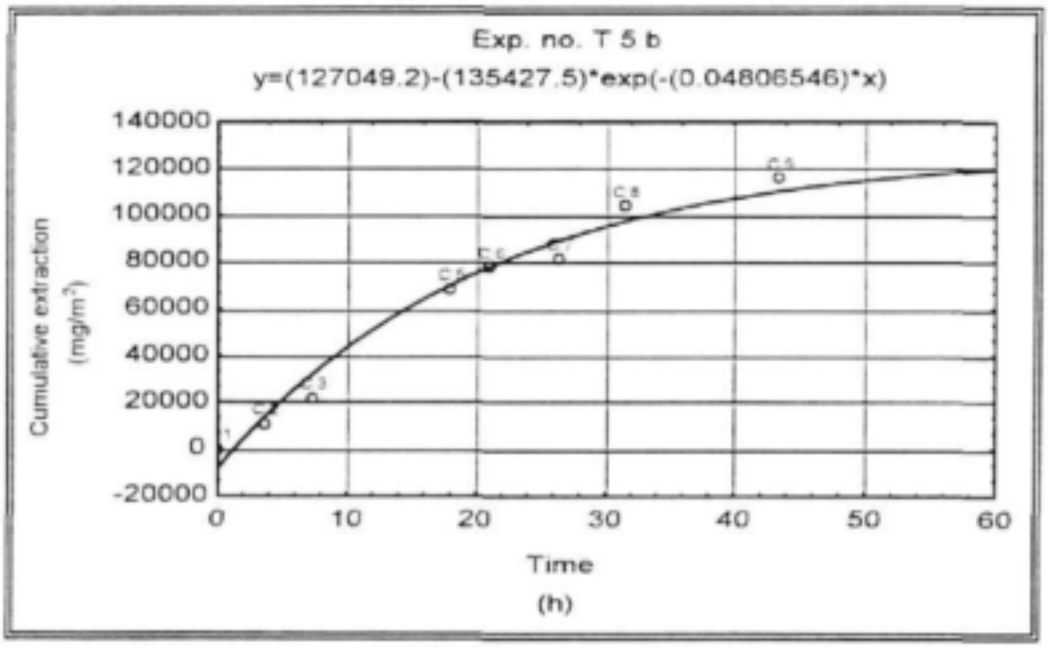
Temp. 85 pH 4.5

Vol. 0.4 0.005

Circum.: 0.125

Area 0.0024868

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	1005	0	4.5	2.000	0.0000	0.0000
3.63	937	10938	2.12	1.396	1.2151	0.1863
7.32	869	21876	2.88	1.293	1.4220	0.3727
14.35	1121	-18659	2.77	1.159	1.6901	-0.3179
17.98	580	68361	4.5	1.159	1.6901	1.1646
21.08	522	77690	3.04	1.089	1.8317	1.3235
26.38	499	81390	2.69	0.928	2.1550	1.3865
31.50	359	103909	2.96	0.843	2.3263	1.7702
43.40	285	115812	2.57	0.630	2.7542	1.9729
50.75	664	54850	4.5	0.630	2.7542	0.9344

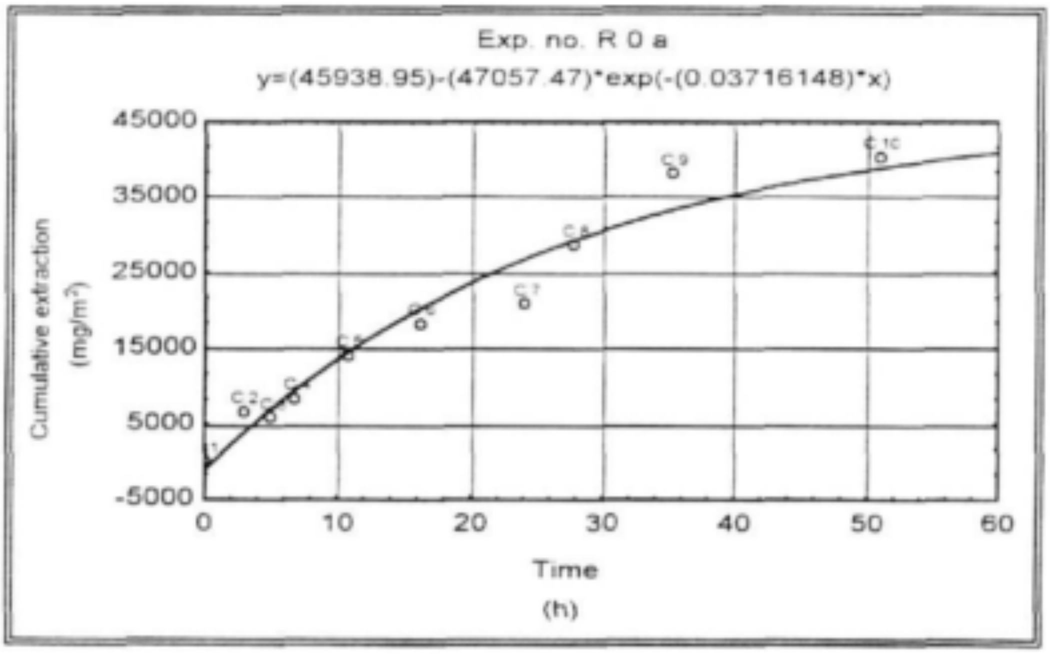


A.4 Experimental results obtained from agitation experiments

Exp. no.: R 0 a [H] 2
Temp. 25 Impeller 0.04
pH 4.5
Vol. 0.4 0.005
Circum.: 0.14
Area 0.0031194

Time(h)	RPM	Re	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	0	0	1022	0	4.5	2.000	0.0000	0.0000
2.95	0	0	970	6668	3.42	1.972	0.0447	0.1136
5.10	0	0	977	5770	3.5	1.949	0.0812	0.0983
6.92	0	0	957	8335	3.82	1.940	0.0965	0.1420
10.78	0	0	913	13977	3.37	1.908	0.1472	0.2381
16.17	0	0	880	18208	3.13	1.851	0.2382	0.3102
24.18	0	0	860	20773	3	1.774	0.3624	0.3539
27.87	0	0	799	28595	3.28	1.734	0.4256	0.4871
35.30	0	0	725	38084	3.08	1.670	0.5282	0.6488
50.87	0	0	708	40264	2.81	1.549	0.7228	0.6859

0



Exp. no.: R 0 b [H] 2

Temp. 25 Impeller 0.04

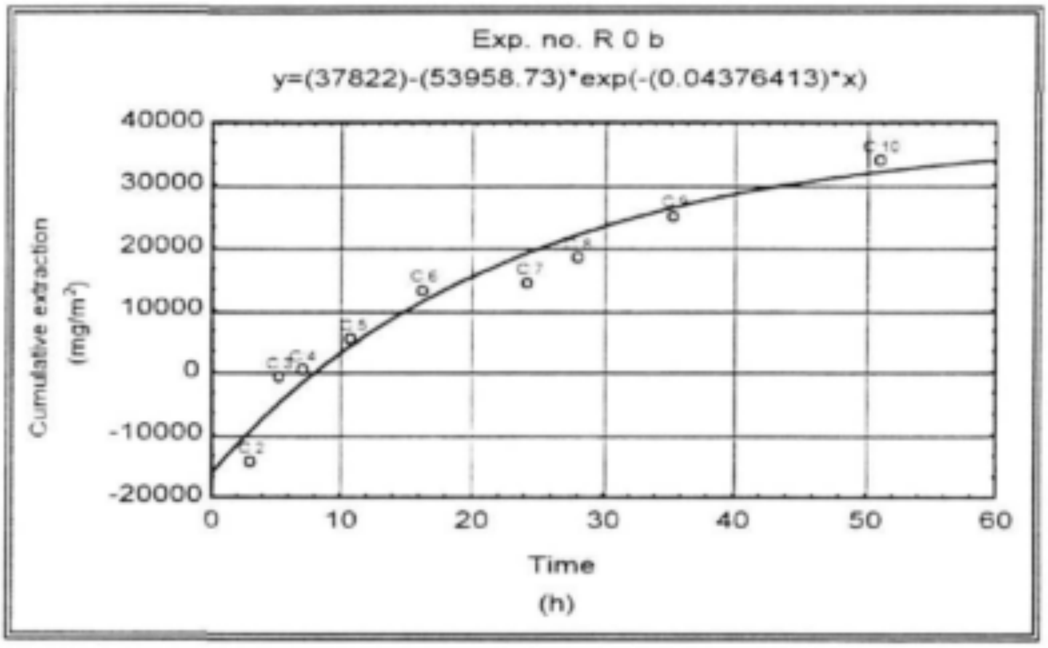
pH 4.5

Vol. 0.4 0.005

Circum.: 0.136

Area 0.0029437

Time(h)	RPM	Re	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	0	0	997	0	4.5	2.000	0.0000	0.0000
3.05	0	0	1103	-14403	3.47	1.975	0.0417	-0.2454
5.20	0	0	1003	-815	3.45	1.950	0.0857	-0.0139
7.02	0	0	995	272	3.77	1.939	0.1044	0.0046
10.88	0	0	958	5299	3.25	1.896	0.1766	0.0903
16.27	0	0	900	13181	3.38	1.865	0.2289	0.2245
24.30	0	0	892	14268	3	1.788	0.3605	0.2431
27.97	0	0	863	18208	3.32	1.752	0.4212	0.3102
35.42	0	0	813	25002	3.23	1.707	0.4969	0.4259
50.97	0	0	748	33835	2.85	1.597	0.6846	0.5764



Exp. no.: R 0 c [H] 2

Temp. 25 Impeller 0.04

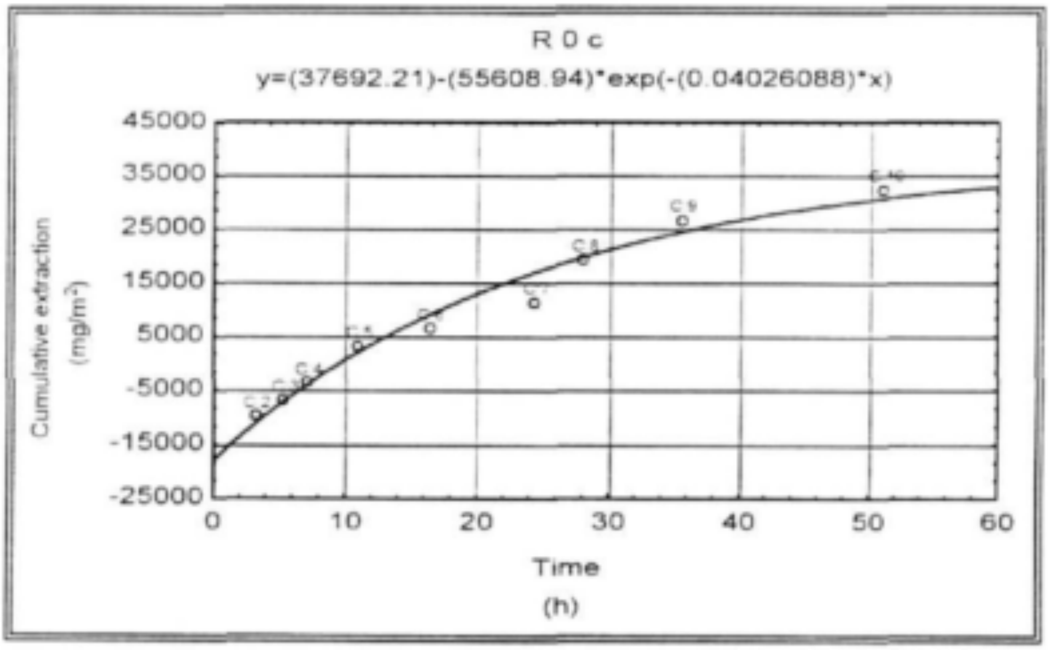
pH 4.5

Vol. 0.4 0.005

Circum.: 0.141

Area 0.0031642

Time(h)	RPM	Re	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	0	0	948	0	4.5	2.000	0.0000	0.0000
3.20	0	0	1027	-9987	3.48	1.976	0.0379	-0.1701
5.35	0	0	1003	-6953	3.39	1.946	0.0854	-0.1184
7.15	0	0	978	-3792	3.61	1.929	0.1124	-0.0646
11.02	0	0	923	3160	3.37	1.897	0.1623	0.0538
16.40	0	0	898	6321	3.11	1.838	0.2565	0.1077
24.43	0	0	858	11377	3.01	1.762	0.3760	0.1938
28.10	0	0	796	19215	3.28	1.723	0.4383	0.3273
35.55	0	0	738	26547	3.15	1.668	0.5238	0.4523
51.10	0	0	693	32236	2.8	1.544	0.7202	0.5492



Exp. no.: R 1 [H] 2

Temp. 26.9 Impeller 0.04

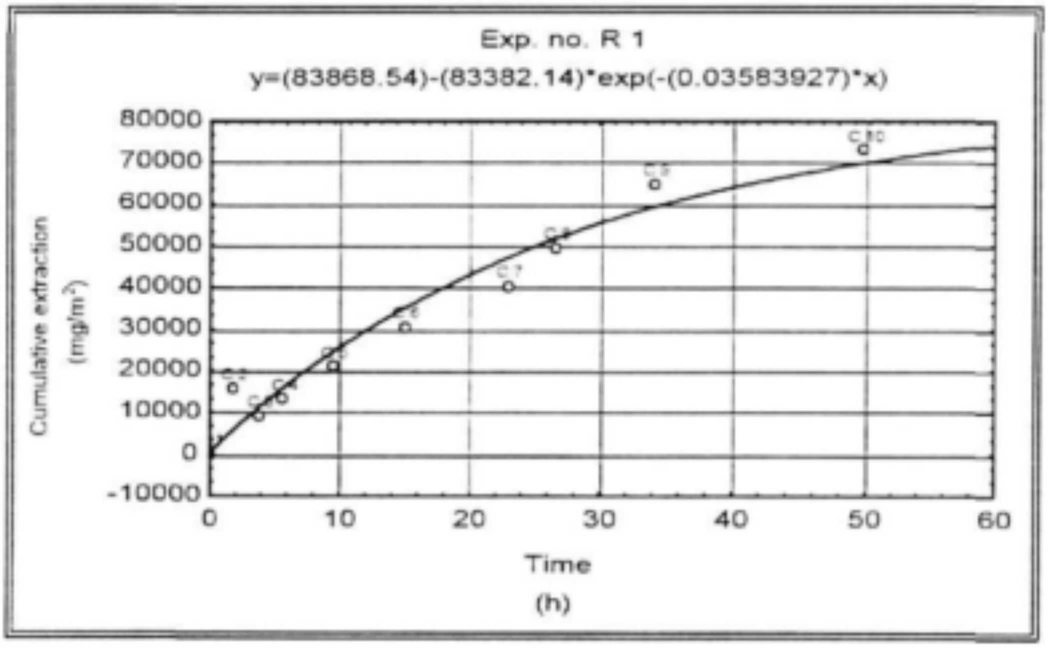
pH 4.5

Vol. 0.4 0.005

Circum.: 0.137

Area 0.0029872

Time(h)	RPM	Re	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	79	2107	1032	0	4.5	2.000	0.0000	0.0000
1.77	104	2774	913	15935	3.34	1.966	0.0570	0.2715
3.87	102	2721	963	9239	3.22	1.920	0.1334	0.1574
5.75	105	2801	933	13257	3.67	1.906	0.1578	0.2258
9.57	104	2774	875	21023	2.99	1.826	0.2906	0.3581
15.00	107	2854	803	30664	2.91	1.730	0.4511	0.5224
22.95	107	2854	730	40439	2.84	1.617	0.6404	0.6889
26.63	106	2827	663	49411	3.16	1.565	0.7288	0.8418
34.15	106	2827	548	64810	2.84	1.451	0.9182	1.1041
49.85	102	2721	487	72979	2.68	1.287	1.1937	1.2432
	Avg:	2726						



Exp. no.: R 2 [H] 2

Temp. 26 Impeller 0.04

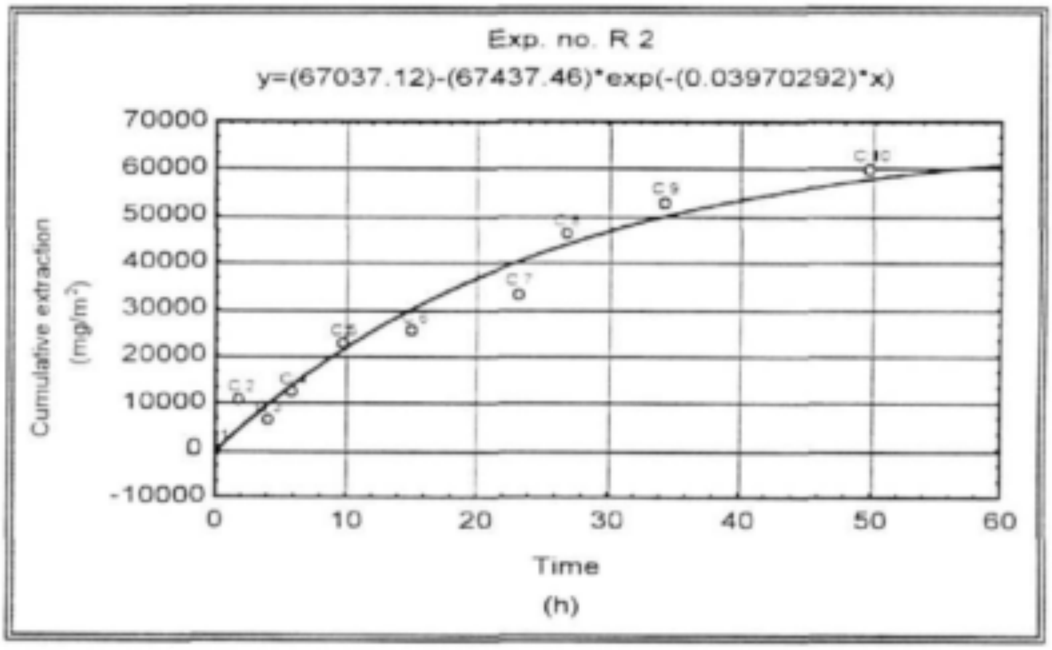
pH 4.5

Vol. 0.4 0.005

Circum.: 0.142

Area 0.0032092

Time(h)	RPM	Re	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	164	4374	1032	0	4.5	2.000	0.0000	0.0000
1.92	184	4908	948	10470	3.3	1.962	0.0585	0.1784
4.00	179	4774	983	6107	3.28	1.923	0.1200	0.1040
5.87	179	4774	935	12090	3.34	1.889	0.1730	0.2060
9.70	178	4748	852	22435	3.04	1.819	0.2828	0.3822
15.13	185	4934	830	25178	2.95	1.731	0.4187	0.4289
23.10	188	5014	766	33155	2.86	1.623	0.5868	0.5648
26.77	187	4988	664	45868	3.12	1.565	0.6774	0.7814
34.28	182	4854	608	52848	2.86	1.457	0.8455	0.9003
49.83	182	4854	553	59703	2.71	1.304	1.0846	1.0171
	Avg:	4822						



Exp. no.: R 3 [H] 2

Temp. 26.9 Impeller 0.04

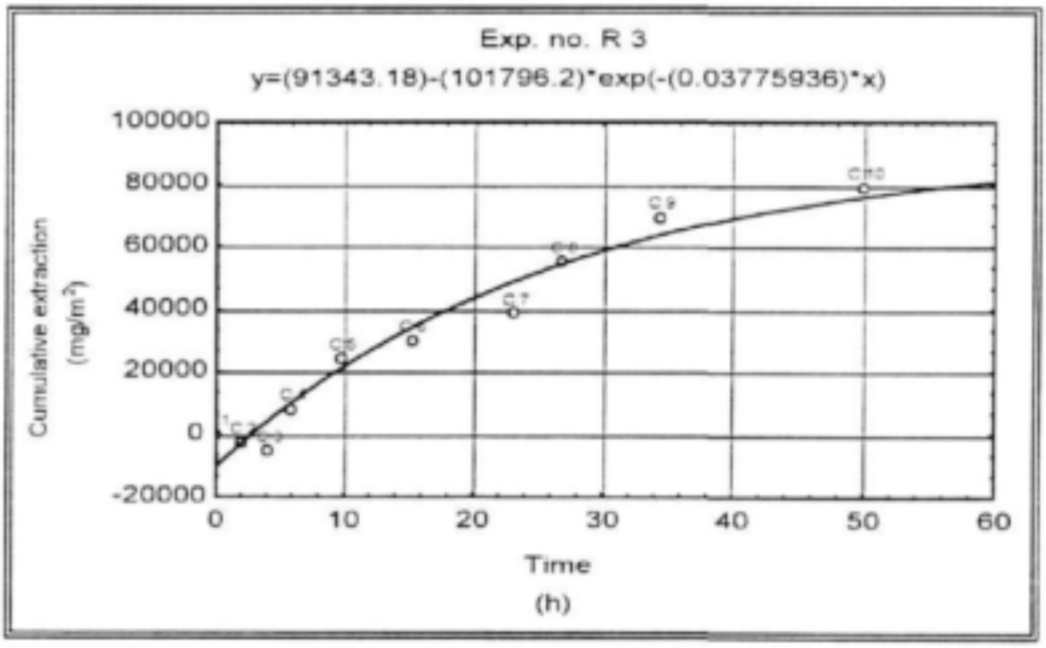
pH 4.5

Vol. 0.4 0.005

Circum.: 0.122

Area 0.0023689

Time(h)	RPM	Re	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	228	6081	1025	0	4.5	2.000	0.0000	0.0000
2.07	255	6801	1041	-2702	3.29	1.962	0.0813	-0.0460
4.15	255	6801	1057	-5403	3.25	1.919	0.1709	-0.0921
6.00	250	6668	977	8105	3.29	1.881	0.2521	0.1381
9.83	261	6961	882	24147	3.02	1.807	0.4081	0.4114
15.27	261	6961	847	30057	2.93	1.715	0.6011	0.5120
23.23	249	6641	797	38499	2.84	1.602	0.8398	0.6559
26.90	259	6908	700	54879	3.11	1.543	0.9656	0.9349
34.40	257	6855	614	69400	2.84	1.429	1.2043	1.1823
49.97	255	6801	556	79194	2.71	1.276	1.5282	1.3491
	Avg:	6748						



Exp. no.: R 4 [H] 2

Temp. 28.35 Impeller 0.02

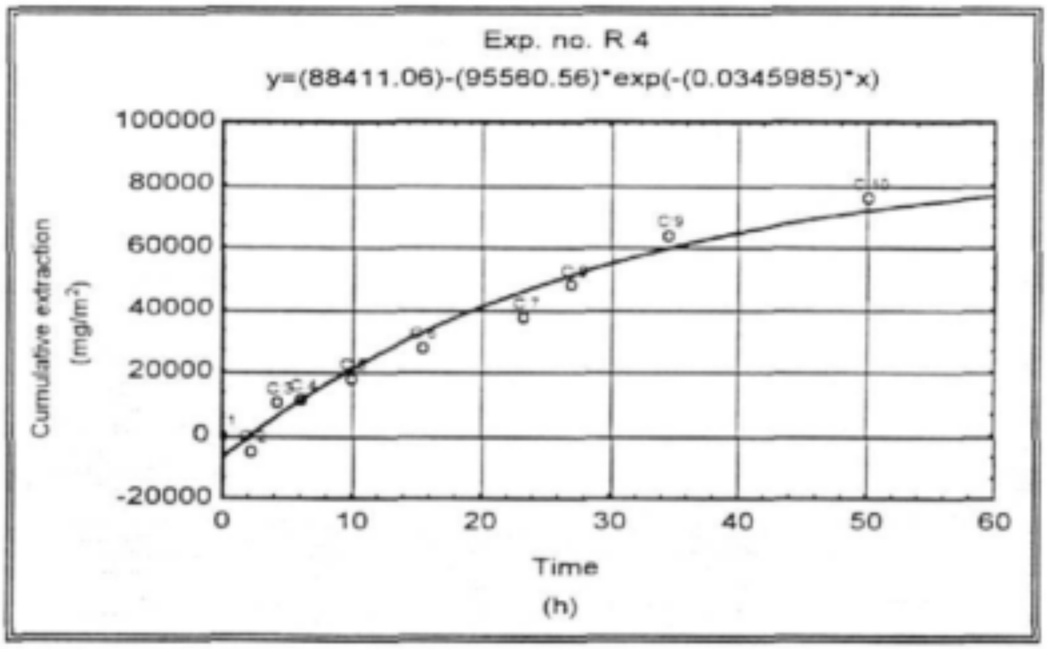
pH 4.5

Vol. 0.4 0.005

Circum.: 0.126

Area 0.0025267

Time(h)	RPM	Re	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	1110	7401	988	0	4.5	2.000	0.0000	0.0000
2.27	1128	7522	1020	-5066	3.2	1.952	0.0949	-0.0863
4.35	1010	6735	924	10132	3.19	1.903	0.1921	0.1726
6.20	1129	7528	918	11081	3.28	1.863	0.2702	0.1888
10.03	1120	7468	875	17889	2.96	1.778	0.4387	0.3047
15.47	1131	7542	813	27704	2.89	1.678	0.6377	0.4720
23.43	1129	7528	752	37360	2.79	1.551	0.8894	0.6365
27.10	1132	7548	687	47650	3.06	1.483	1.0223	0.8118
34.60	1130	7535	586	63639	2.8	1.359	1.2682	1.0841
50.17	1127	7515	511	75512	2.66	1.187	1.6095	1.2864
	Avg:	7432						



Exp. no.: R 5 [H] 2

Temp. 26.6 Impeller 0.04

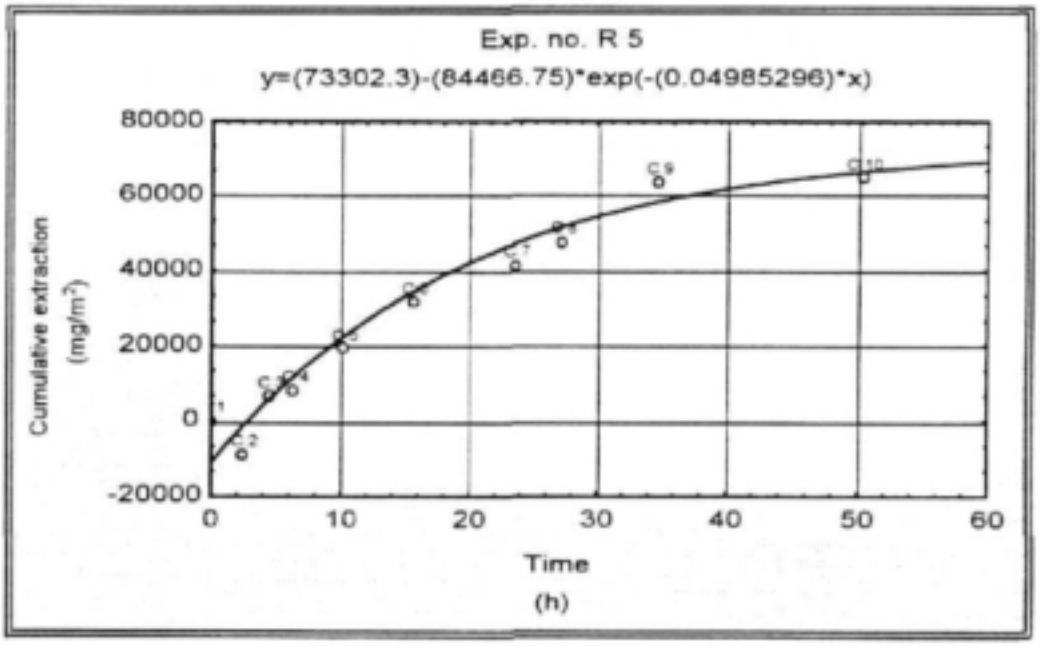
pH 4.5

Vol. 0.4 0.005

Circum.: 0.134

Area 0.0028578

Time(h)	RPM	Re	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	790	21071	1019	0	4.5	2.000	0.0000	0.0000
2.45	802	21391	1084	-9098	3.15	1.946	0.0947	-0.1550
4.53	750	20004	974	6299	3.17	1.894	0.1849	0.1073
6.38	750	20004	962	7978	3.23	1.850	0.2629	0.1359
10.22	751	20031	882	19176	2.96	1.765	0.4119	0.3267
15.63	690	18404	794	31493	2.88	1.662	0.5920	0.5365
23.62	684	18244	723	41431	2.81	1.540	0.8044	0.7058
27.28	689	18377	679	47589	3.05	1.471	0.9247	0.8107
34.77	402	10722	565	63546	2.81	1.350	1.1370	1.0826
50.35	403	10749	556	64805	2.56	1.132	1.5181	1.1040
	Avg:	17900						



Exp. no.: R 6 [H] 2

Temp. 32.2 Impeller 0.04

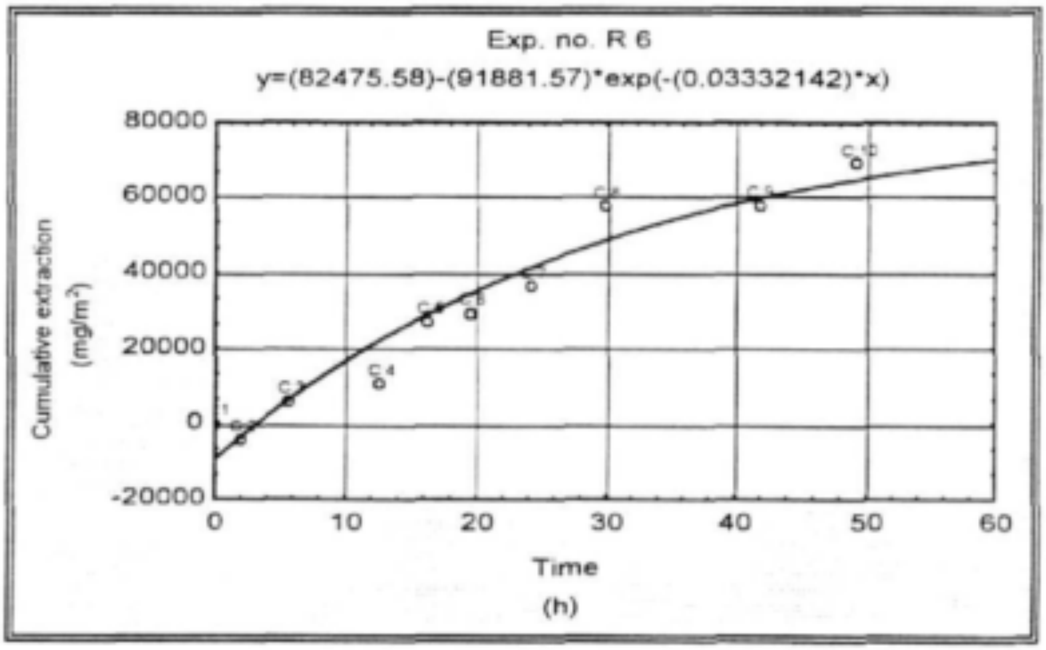
pH 4.5

Vol. 0.4 0.004

Circum.: 0.135

Area 0.0029006

Time(h)	RPM	Re	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	94	2507	1031	0	4.5	2.000	0.0000	0.0000
2.03	109	2907	1063	-4413	3.09	1.922	0.1077	-0.0752
5.75	87	2320	989	5792	2.98	1.820	0.2478	0.0987
12.67	79	2107	955	10481	2.81	1.669	0.4570	0.1785
16.35	68	1814	836	26891	2.95	1.560	0.6074	0.4581
19.53	73	1947	819	29235	3.04	1.472	0.7288	0.4980
24.23	84	2240	768	36268	2.84	1.330	0.9237	0.6179
29.93	82	2187	615	57367	2.83	1.185	1.1234	0.9773
41.82	87	2320	613	57643	2.63	0.954	1.4423	0.9820
49.27	88	2347	532	68813	2.75	0.779	1.6831	1.1723
	Avg:	2270						



Exp. no.: R 7 [H] 2

Temp. 31.1 Impeller 0.04

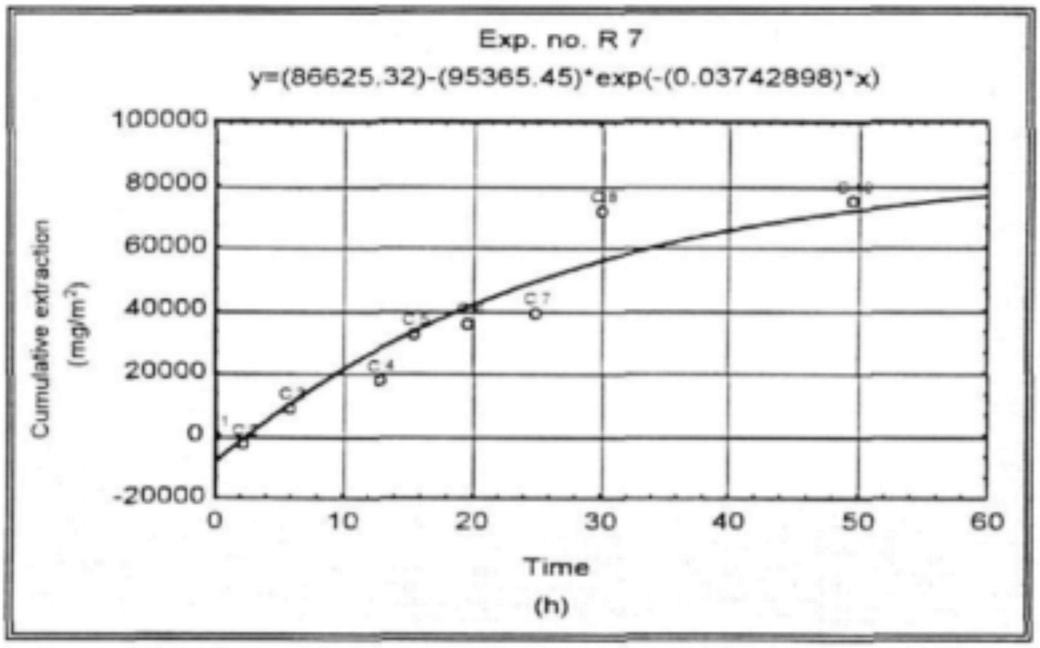
pH 4.5

Vol. 0.4 0.0045

Circum.: 0.126

Area 0.0025267

Time(h)	RPM	Re	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	154	4107	1015	0	4.5	2.000	0.0000	0.0000
2.27	158	4214	1033	-2850	3.02	1.918	0.1462	-0.0485
5.97	152	4054	959	8865	2.96	1.823	0.3147	0.1510
12.88	151	4027	902	17889	2.75	1.668	0.5913	0.3047
16.58	143	3814	810	32453	2.97	1.576	0.7559	0.5529
19.75	158	4214	788	35936	2.96	1.481	0.9245	0.6122
24.97	161	4294	768	39102	2.81	1.346	1.1646	0.6661
30.15	162	4321	562	71713	2.81	1.211	1.4048	1.2217
42.03	160	4268	499	81686	2.62	1.001	1.7796	1.3916
49.48	153	4081	544	74562	2.76	0.849	2.0497	1.2702
	Avg:	4139						



Exp. no.: R 8 [H] 2

Temp. 31.4 Impeller 0.04

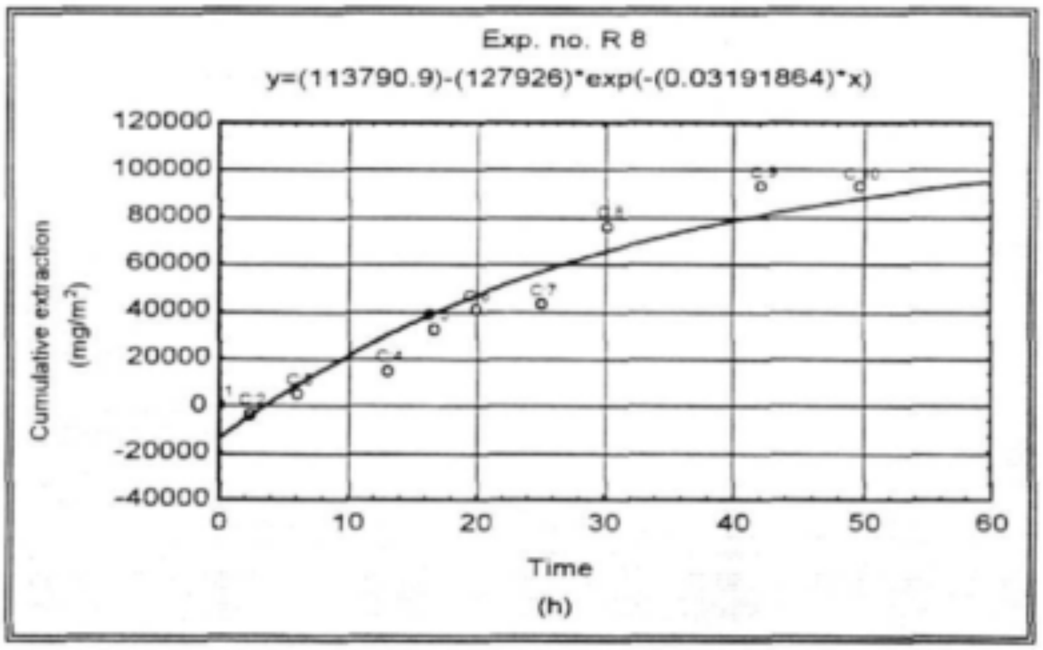
pH 4.5

Vol. 0.4 0.005

Circum.: 0.128

Area 0.0026076

Time(h)	RPM	Re	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	220	5868	1021	0	4.5	2.000	0.0000	0.0000
2.48	220	5868	1045	-3682	2.93	1.909	0.1754	-0.0627
6.18	221	5895	989	4909	2.89	1.808	0.3681	0.0836
13.12	219	5841	925	14726	2.7	1.651	0.6694	0.2509
16.80	210	5601	810	32367	2.9	1.553	0.8576	0.5514
19.97	224	5975	758	40344	2.91	1.457	1.0415	0.6873
25.20	227	6055	744	42491	2.76	1.320	1.3032	0.7239
30.37	226	6028	526	75932	2.77	1.187	1.5589	1.2936
42.25	219	5841	416	92806	2.6	0.989	1.9393	1.5810
49.70	217	5788	419	92346	2.73	0.842	2.2201	1.5732
	Avg:	5876						



Exp. no.: R 9 [H] 2

Temp. 32.05 Impeller 0.04

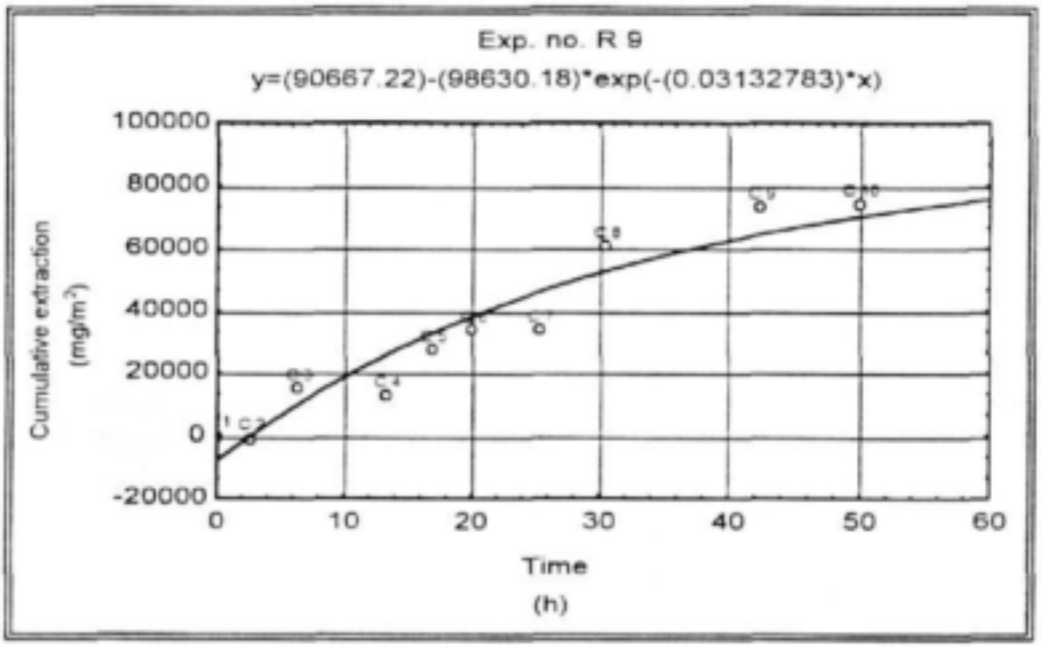
pH 4.5

Vol. 0.4 0.005

Circum.: 0.136

Area 0.0029437

Time(h)	RPM	Re	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	365	9735	1005	0	4.5	2.000	0.0000	0.0000
2.67	375	10002	1012	-951	2.91	1.904	0.1629	-0.0162
6.37	419	11176	896	14811	2.91	1.808	0.3257	0.2523
13.30	150	4001	912	12637	2.74	1.665	0.5687	0.2153
16.98	376	10029	805	27176	2.88	1.562	0.7435	0.4630
20.15	374	9975	758	33563	2.91	1.466	0.9064	0.5718
25.38	462	12322	758	33563	2.75	1.327	1.1438	0.5718
30.57	509	13576	560	60468	2.78	1.196	1.3650	1.0301
42.43	335	8935	470	72697	2.6	0.998	1.7020	1.2384
49.88	315	8402	460	74056	2.76	0.861	1.9338	1.2616
	Avg:	9815						



A.5 Experimental results obtained from ligand acceleration experiments

Exp. no.: CaAc 0.05 [H] 2

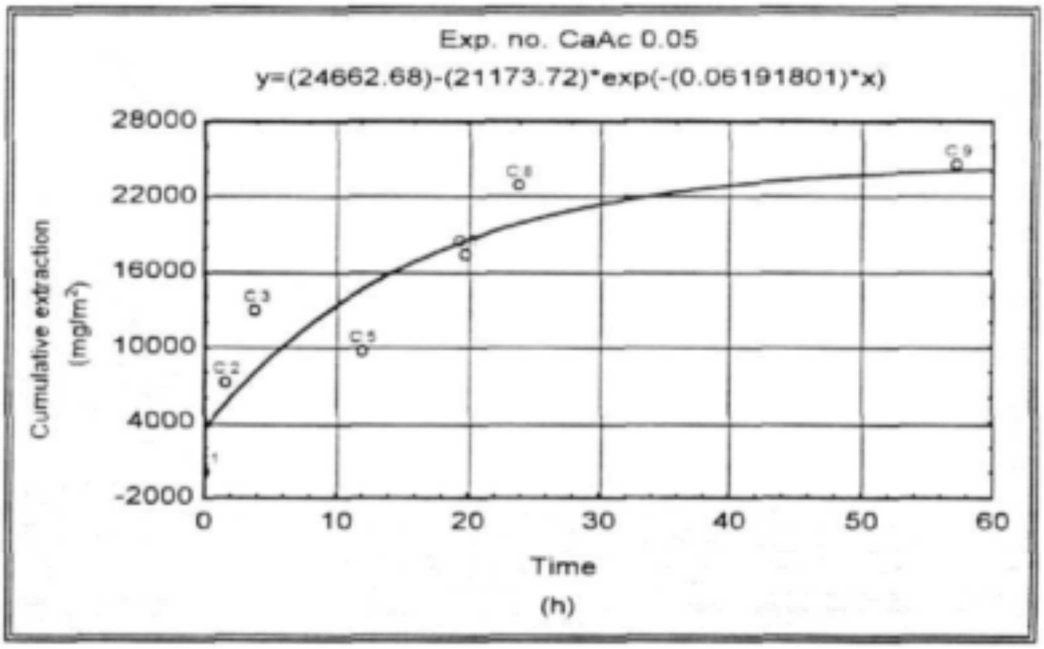
Temp. 25 pH 4.5

Vol. 0.4 0.005

Circum.: 0.135

Area 0.0029006

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	1000	0	5.13	2.000	0.0000	0.0000
1.57	948	7200	5.02	1.755	0.4229	0.1227
3.85	907	12876	4.89	1.561	0.7563	0.2194
8.98	981	2631	4.53	1.910	0.1545	0.0448
11.97	930	9692	4.75	1.670	0.5692	0.1651
14.83	941	8169	4.56	1.722	0.4798	0.1392
19.80	874	17307	4.45	1.410	1.0165	0.2948
23.82	834	22845	4.31	1.222	1.3417	0.3892
57.20	822	24507	4.4	1.165	1.4393	0.4175



Exp. no.: CaAc 0.075 [H] 2

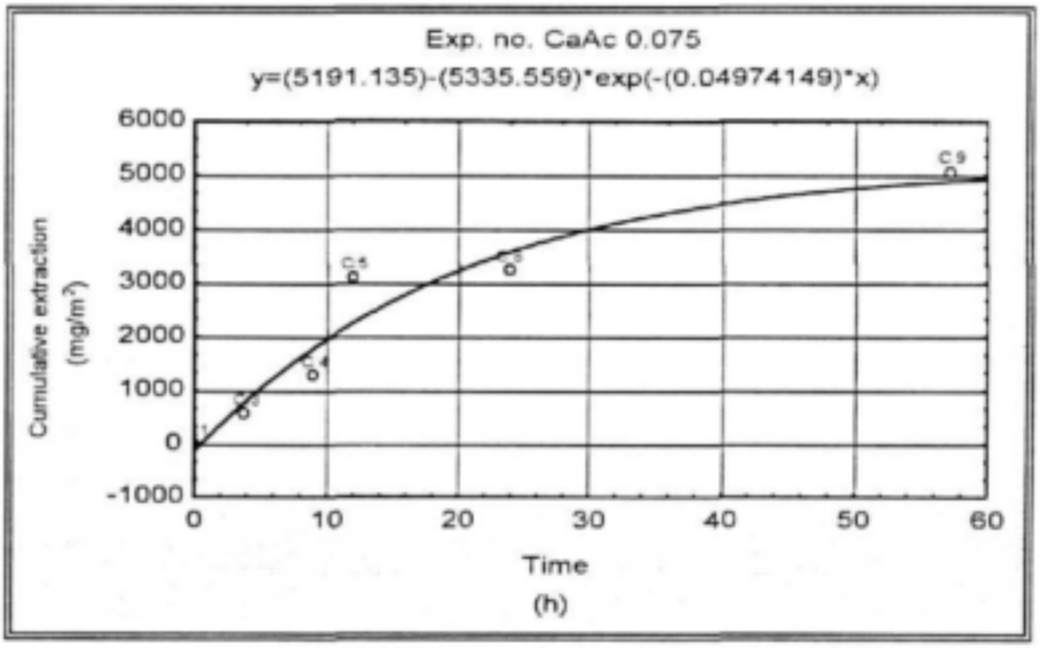
Temp. 25 pH 4.5

Vol. 0.4 0.005

Circum.: 0.132

Area 0.0027731

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	1000	0	6.71	2.000	0.0000	0.0000
1.60	1045	-6467	6.23	2.220	-0.3973	-0.1102
3.87	996	562	5.64	1.981	0.0345	0.0096
9.00	991	1265	5.34	1.957	0.0777	0.0216
11.98	979	3093	5.13	1.895	0.1900	0.0527
14.87	950	7170	5.16	1.756	0.4405	0.1221
19.82	1016	-2249	5.07	2.077	-0.1382	-0.0383
23.85	978	3233	5	1.890	0.1986	0.0551
57.22	965	5061	4.85	1.828	0.3109	0.0862



Exp. no.: CaAc 0.1 a [H] 2

Temp. 25

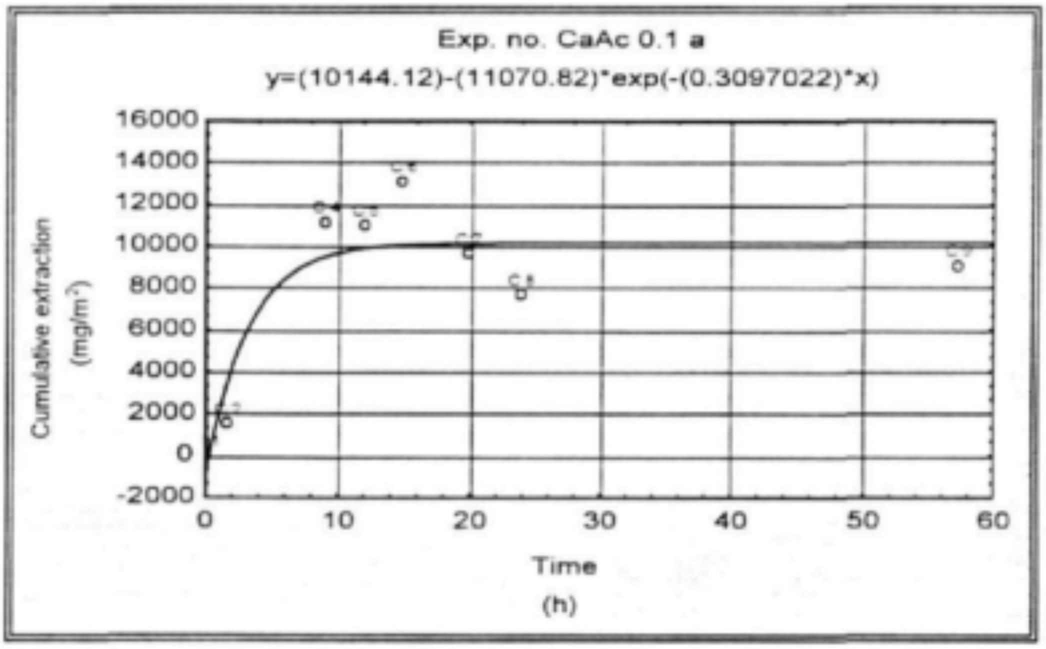
pH 4.5

Vol. 0.4 0.005

Circum.: 0.129

Area 0.0026485

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	1000	0	7.45	2.000	0.0000	0.0000
1.55	990	1534	6.32	1.948	0.0987	0.0261
3.83	895	15898	6.11	1.458	1.0226	0.2708
8.97	926	11156	5.97	1.620	0.7176	0.1901
11.97	927	11017	5.72	1.625	0.7086	0.1877
14.83	913	13109	5.33	1.553	0.8432	0.2233
19.78	936	9622	5.26	1.672	0.6189	0.1639
23.82	949	7670	5.18	1.739	0.4934	0.1307
57.18	940	9065	5.07	1.691	0.5831	0.1544



Exp. no.: CaAc 0.1 b [H] 2

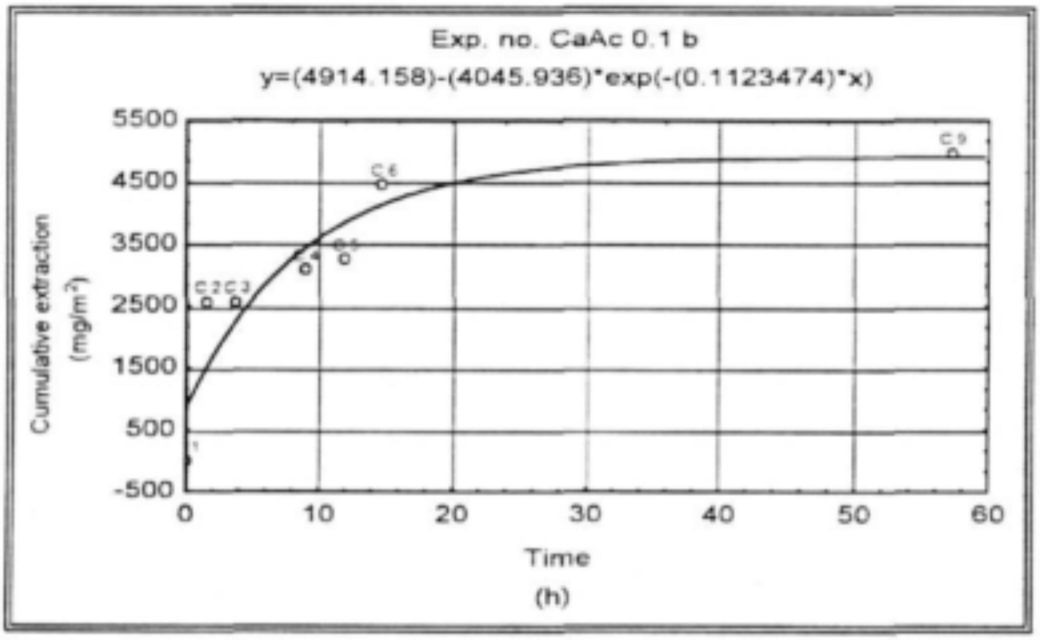
Temp. 25 pH 4.5

Vol. 0.4 0.005

Circum.: 0.121

Area 0.0023302

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	1000	0	7.51	2.000	0.0000	0.0000
1.53	985	2537	6.36	1.914	0.1855	0.0432
3.82	985	2537	5.99	1.914	0.1855	0.0432
8.97	982	3044	5.76	1.896	0.2226	0.0519
11.95	981	3213	5.35	1.891	0.2349	0.0547
14.82	974	4397	5.31	1.850	0.3215	0.0749
19.78	992	1353	5.24	1.954	0.0989	0.0230
23.80	988	2029	4.31	1.931	0.1484	0.0346
57.15	971	4905	5.08	1.833	0.3586	0.0836



Exp. no.: CaAc 0.2 [H] 2

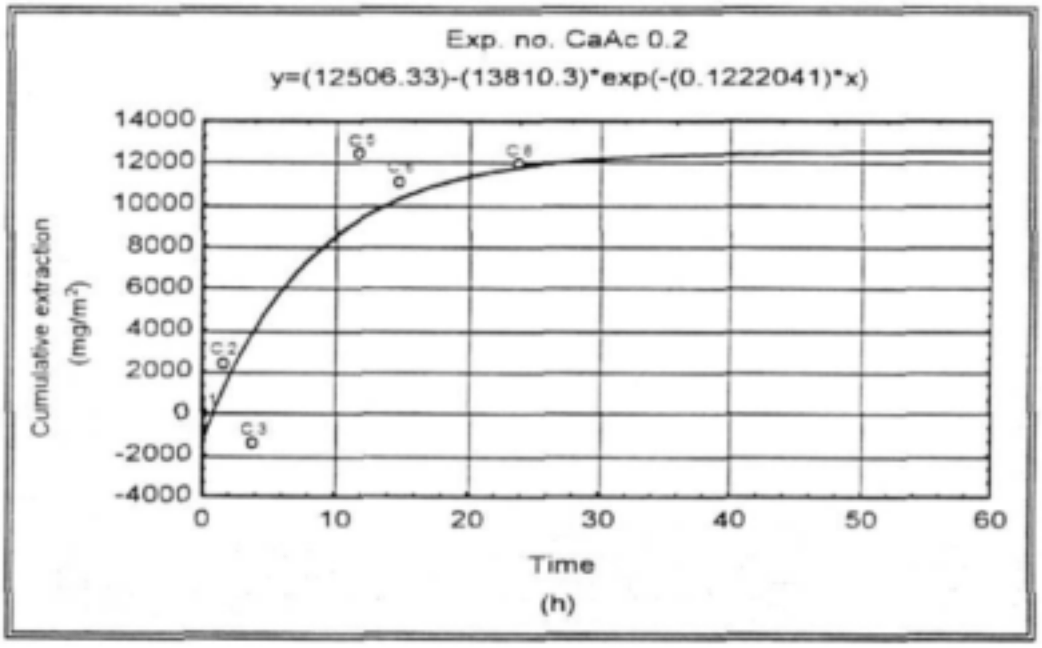
Temp. 25 pH 4.5

Vol. 0.4 0.005

Circum.: 0.125

Area 0.0024868

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	1000	0	7.62	2.000	0.0000	0.0000
1.52	986	2195	6.54	1.925	0.1504	0.0374
3.80	1008	-1317	6.14	2.045	-0.0902	-0.0224
8.95	916	13465	6.06	1.541	0.9224	0.2294
11.93	930	11270	5.65	1.616	0.7720	0.1920
14.80	937	10099	5.64	1.656	0.6918	0.1720
19.77	1019	-3074	5.55	2.105	-0.2106	-0.0524
23.78	933	10831	5.53	1.631	0.7420	0.1845
57.13	1018	-2927	3.19	2.100	-0.2005	-0.0499



Exp. no.: NaAc 0 [H] 2

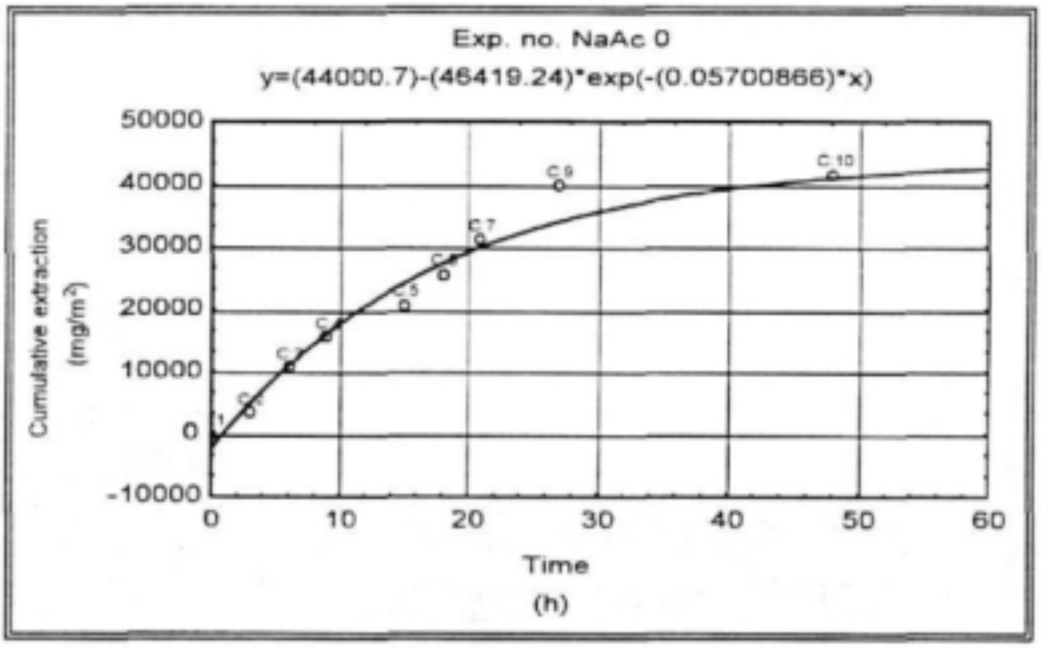
Temp. 25 pH 4.5

Vol. 0.4 0.005

Circum.: 0.126

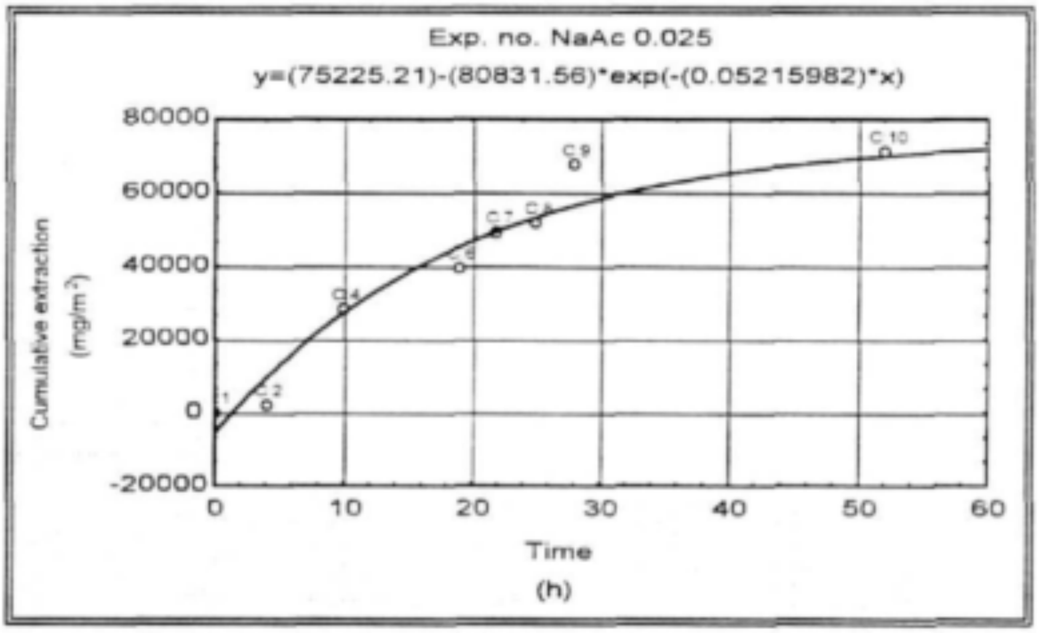
Area 0.0025267

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	1000	0	5.53	2.000	0.0000	0.0000
3.00	979	3306	3.01	1.887	0.2229	0.0563
6.00	933	10652	3.12	1.637	0.7182	0.1815
9.00	901	15610	3.18	1.468	1.0525	0.2659
15.00	869	20752	2.82	1.293	1.3992	0.3535
18.00	838	25711	3.1	1.124	1.7335	0.4380
21.00	803	31186	3.15	0.937	2.1026	0.5313
24.00	704	46859	3.12	0.403	3.1593	0.7983
27.00	749	39735	3.19	0.646	2.6790	0.6769
48.00	737	41635	2.48	0.581	2.8071	0.7093



Exp. no.:	NaAc 0.025 [H] 2
Temp.	25 pH 4.5
Vol.	0.4 0.005
Circum.:	0.122
Area	0.0023689

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	1029	0	6.98	2.000	0.0000	0.0000
4.00	1016	2195	6.1	1.925	0.1579	0.0374
6.00	1119	-15197	5.18	2.518	-1.0929	-0.2589
10.00	862	28199	4.92	1.039	2.0280	0.4804
16.00	1031	-338	4.73	2.012	-0.0243	-0.0058
19.00	796	39344	4.52	0.659	2.8294	0.6703
22.00	738	49138	4.36	0.326	3.5337	0.8371
25.00	723	51670	4.31	0.240	3.7159	0.8802
28.00	630	67374	4.26	-0.296	4.8452	1.1478
52.00	607	71258	4.09	-0.428	5.1245	1.2139



Exp. no.: NaAc 0.05 [H] 2

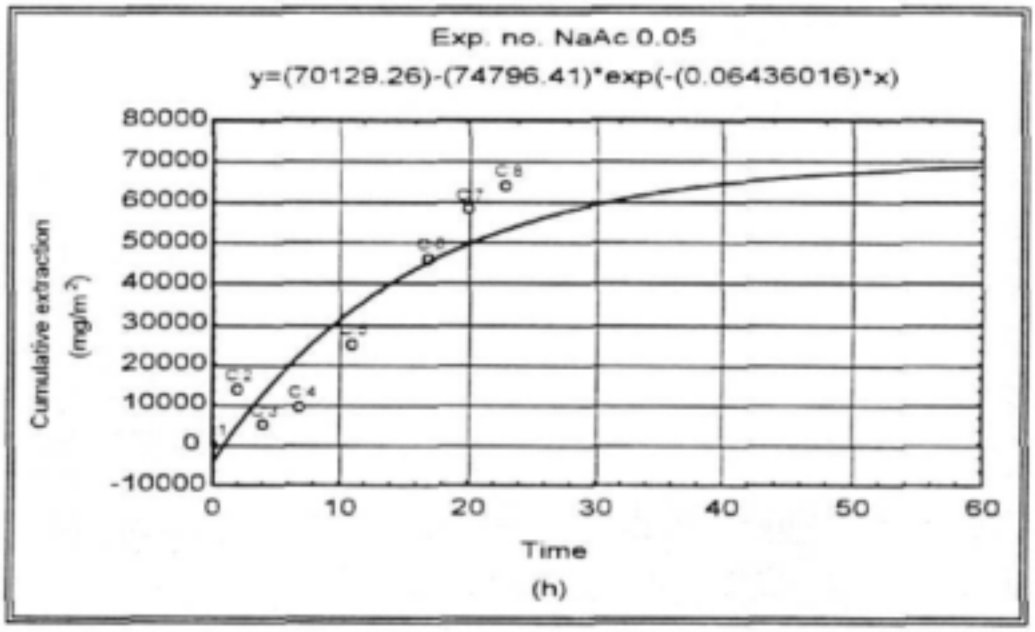
Temp. 25 pH 4.5

Vol. 0.4 0.005

Circum.: 0.131

Area 0.0027313

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	1026	0	6.61	2.000	0.0000	0.0000
2.00	932	13767	6.08	1.531	0.8587	0.2345
4.00	993	4833	5.66	1.835	0.3014	0.0823
7.00	961	9519	5.36	1.676	0.5938	0.1622
11.00	855	25043	4.91	1.147	1.5620	0.4266
17.00	712	45986	4.68	0.433	2.8683	0.7834
20.00	630	57995	4.6	0.024	3.6174	0.9880
23.00	588	64146	4.56	-0.186	4.0010	1.0928
32.00	753	39982	4.56	0.638	2.4938	0.6811
52.00	1013	1904	4.63	1.935	0.1188	0.0324



Exp. no.: NaAc 0.075 [H] 2

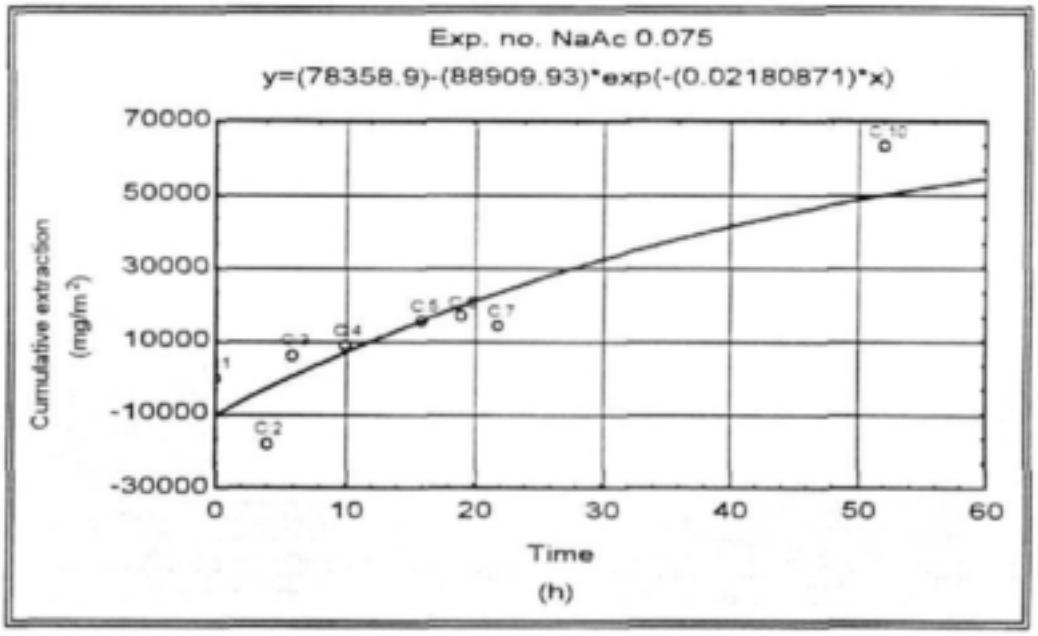
Temp. 25 pH 4.5

Vol. 0.4 0.005

Circum.: 0.119

Area 0.0022538

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	959	0	7.42	2.000	0.0000	0.0000
4.00	1060	-17925	6.58	2.611	-1.3549	-0.3054
6.00	924	6212	5.73	1.788	0.4695	0.1058
10.00	909	8874	5.45	1.698	0.6708	0.1512
16.00	870	15796	5.17	1.462	1.1939	0.2691
19.00	865	16683	5.03	1.432	1.2610	0.2842
22.00	879	14198	5.01	1.516	1.0732	0.2419
25.00	1027	-12069	4.99	2.411	-0.9122	-0.2056
28.00	962	-532	5.01	2.018	-0.0402	-0.0091
52.00	603	63182	5.02	-0.153	4.7758	1.0764



Exp. no.: NaAc 0.1 a [H] 2

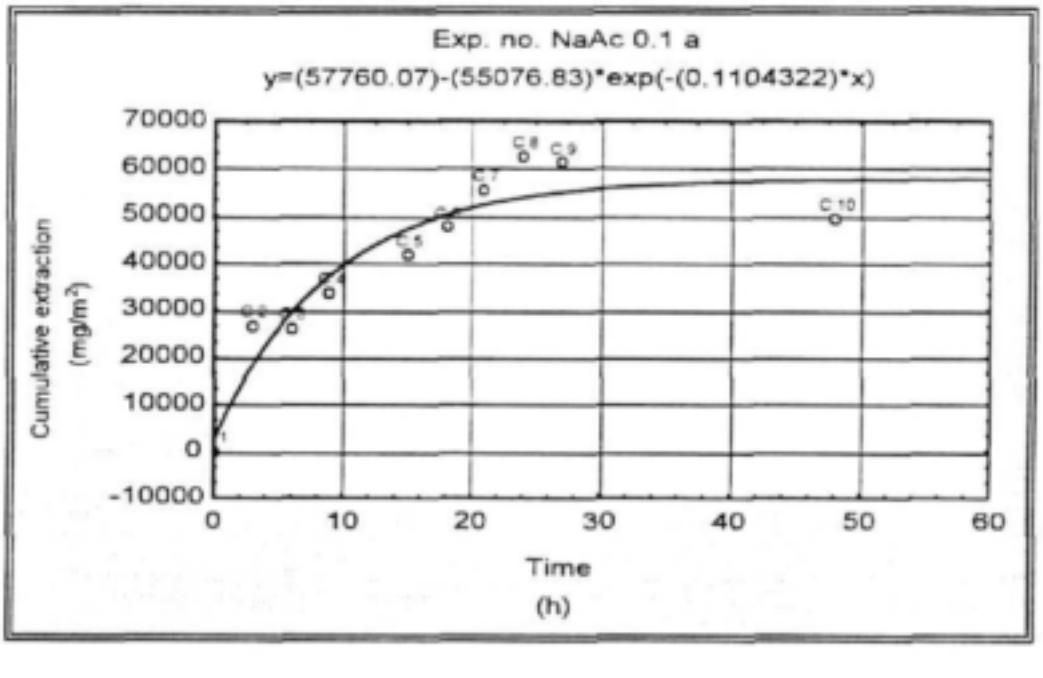
Temp. 25 pH 4.5

Vol. 0.4 0.005

Circum.: 0.132

Area 0.0027731

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	1000	0	7.28	2.000	0.0000	0.0000
3.00	815	26621	6.81	1.093	1.6354	0.4535
6.00	819	26064	6.18	1.112	1.6011	0.4440
9.00	767	33638	5.64	0.854	2.0664	0.5730
15.00	711	41658	5.41	0.581	2.5591	0.7097
18.00	671	47456	5.15	0.383	2.9153	0.8084
21.00	616	55389	5.06	0.113	3.4026	0.9436
24.00	567	62457	5.02	-0.128	3.8368	1.0640
27.00	576	61159	5.06	-0.084	3.7571	1.0419
48.00	658	49331	5.02	0.319	3.0305	0.8404



Exp. no.: NaAc 0.1 b [H] 2

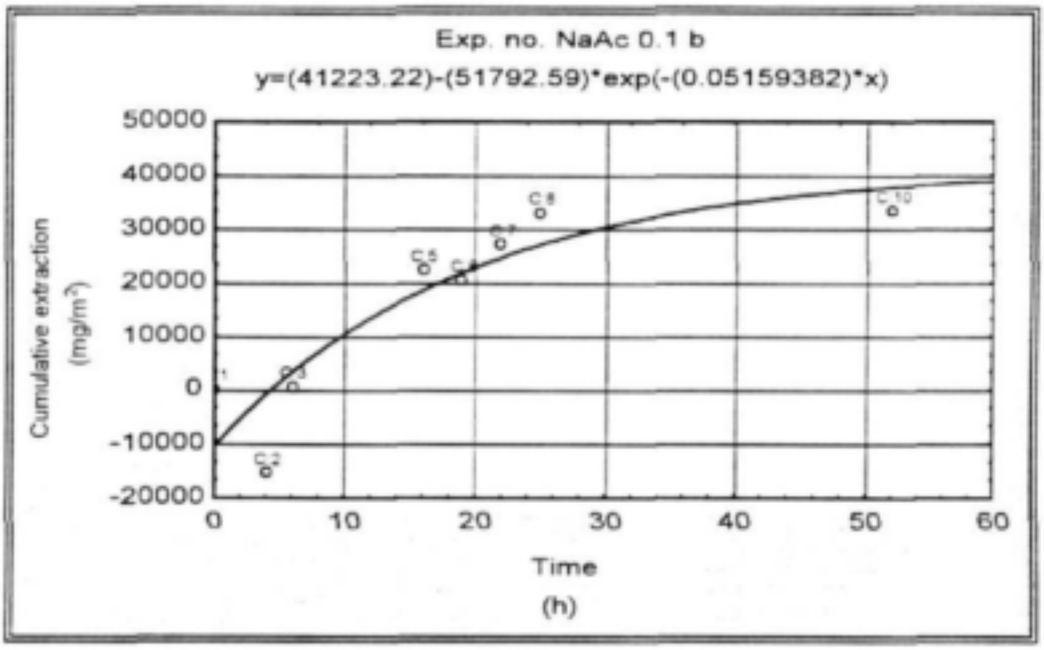
Temp. 25 pH 4.5

Vol. 0.4 0.005

Circum.: 0.119

Area 0.0022538

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	956	0	7.51	2.000	0.0000	0.0000
4.00	1043	-15441	6.59	2.526	-1.1671	-0.2630
6.00	953	532	5.77	1.982	0.0402	0.0091
10.00	835	21475	5.52	1.268	1.6232	0.3658
16.00	831	22185	5.13	1.244	1.6769	0.3779
19.00	841	20410	5.62	1.305	1.5427	0.3477
22.00	804	26977	5.13	1.081	2.0391	0.4596
25.00	770	33011	5.12	0.875	2.4952	0.5624
28.00	724	41175	5.15	0.597	3.1123	0.7014
52.00	768	33366	5.16	0.863	2.5220	0.5684



Exp. no.: NaAc 0.15 [H] 2

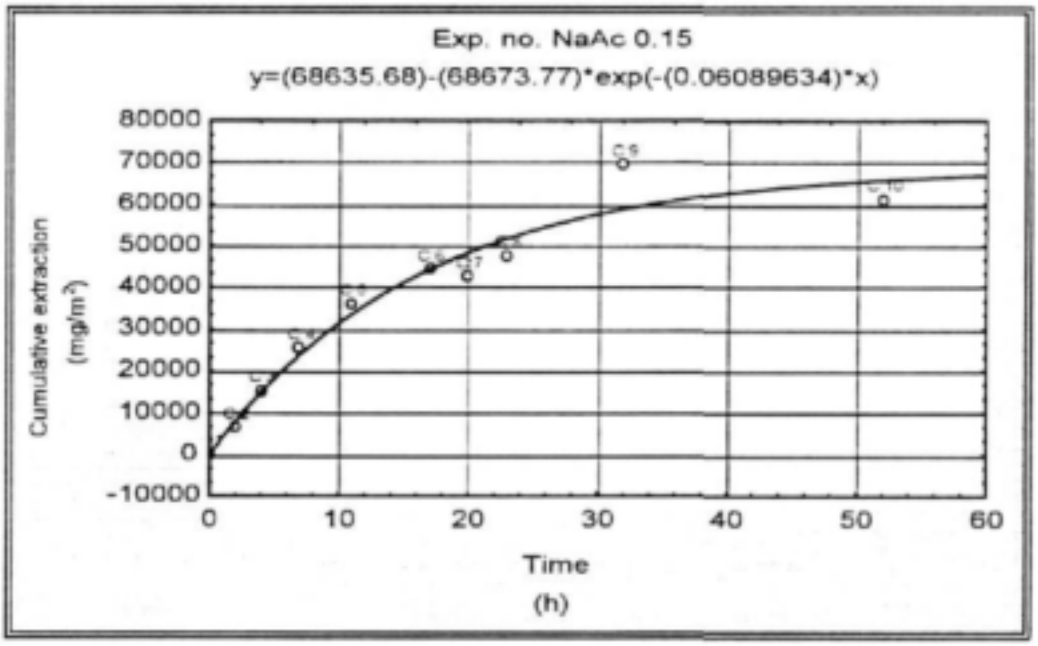
Temp. 25 pH 4.5

Vol. 0.4 0.005

Circum.: 0.125

Area 0.0024868

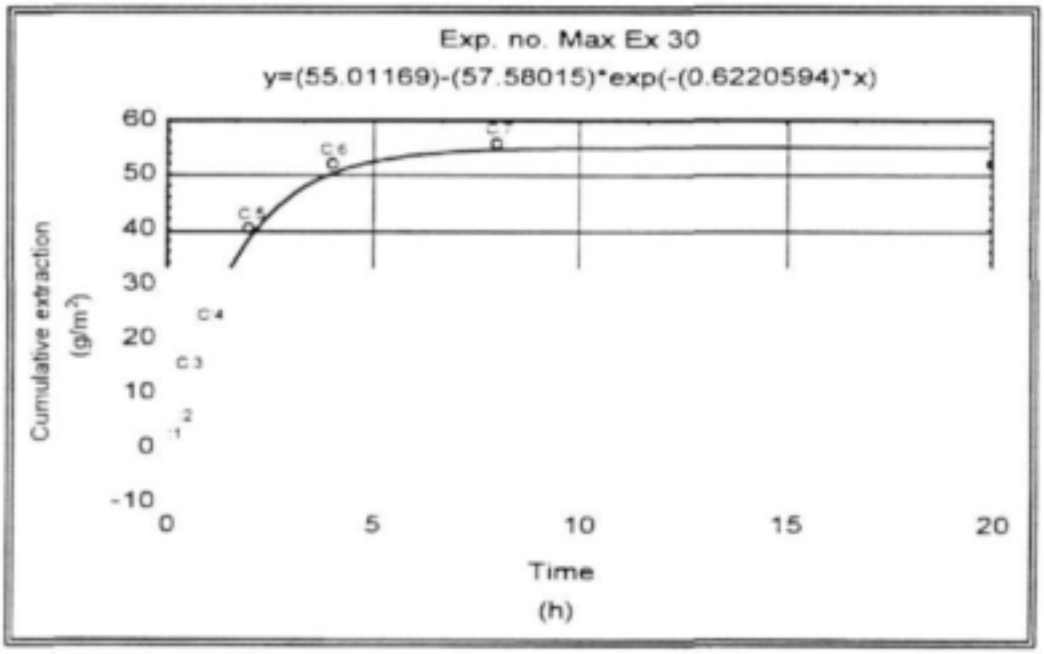
Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	1007	0	7.33	2.000	0.0000	0.0000
2.00	967	6434	6.22	1.781	0.4408	0.1096
4.00	912	15281	6.13	1.479	1.0468	0.2603
7.00	849	25414	5.71	1.134	1.7410	0.4330
11.00	784	35869	5.38	0.778	2.4572	0.6111
17.00	732	44234	5.24	0.493	3.0302	0.7536
20.00	743	42464	5.24	0.553	2.9090	0.7234
23.00	711	47611	5.28	0.378	3.2616	0.8111
32.00	576	69326	5.28	-0.362	4.7492	1.1810
52.00	626	61284	5.34	-0.088	4.1982	1.0440



A.6 Experimental results used to determine the optimum extractant concentration

Exp. no.: Max Ex 30 [H] 3
Temp. 70 pH 4.5
Vol. 0.4 0.015
Circum.: 0.122 0.127 0.128
Area 0.0075435

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	6.979	0.000	5.7	3.000	0.0000	0.0000
0.25	6.916	3.341	5.24	2.886	0.2263	0.0569
0.50	6.736	12.885	4.95	2.561	0.8730	0.2195
1.00	6.569	21.741	4.53	2.259	1.4729	0.3704
2.00	6.220	40.247	4.16	1.629	2.7267	0.6856
4.00	5.996	52.125	3.97	1.224	3.5315	0.8880
8.00	5.925	55.889	3.99	1.096	3.7865	0.9521
16.00	6.831	7.848	4.43	2.733	0.5317	0.1337



Exp. no.: Max Ex 50 [H] 3

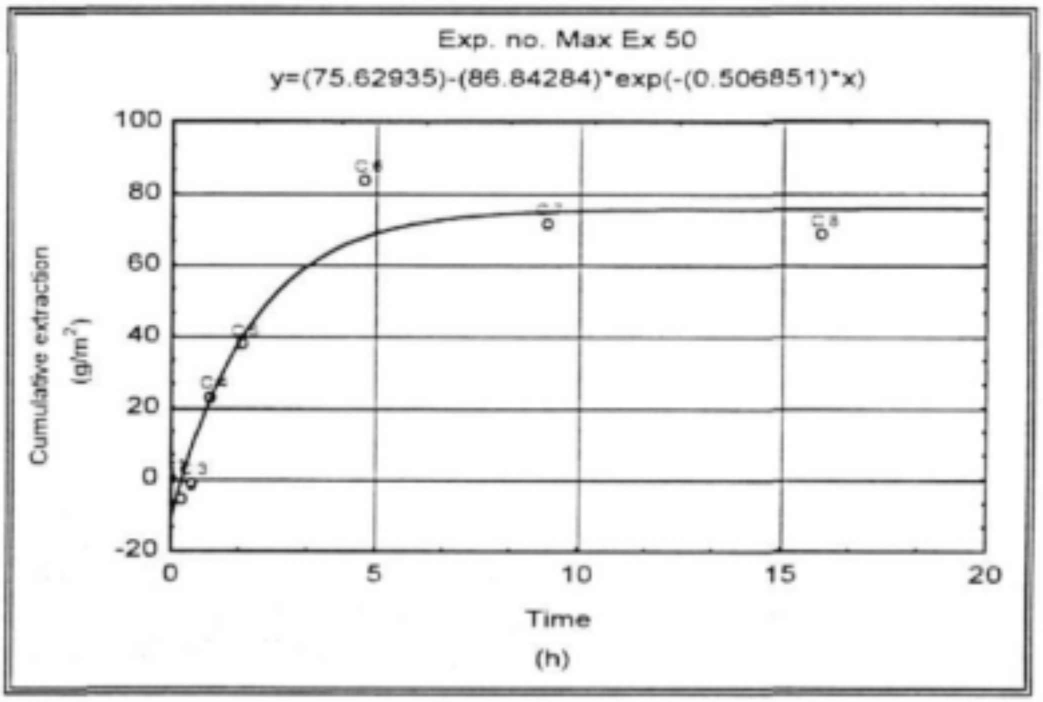
Temp. 70 pH 4.5

Vol. 0.4 0.015

Circum.: 0.124 0.127 0.122

Area 0.007383

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	6.852	0.000	5.52	3.000	0.0000	0.0000
0.25	6.956	-5.635	4.8	3.192	-0.3900	-0.0960
0.50	6.876	-1.300	4.59	3.044	-0.0900	-0.0222
1.00	6.425	23.134	4.29	2.212	1.6014	0.3941
1.75	6.157	37.654	4.11	1.717	2.6065	0.6415
4.75	5.309	83.597	3.52	0.152	5.7868	1.4241
9.25	5.530	71.624	4.47	0.560	4.9580	1.2202
16.00	5.588	68.481	4.55	0.667	4.7405	1.1666



Exp. no.: Max Ex 60 [H] 3

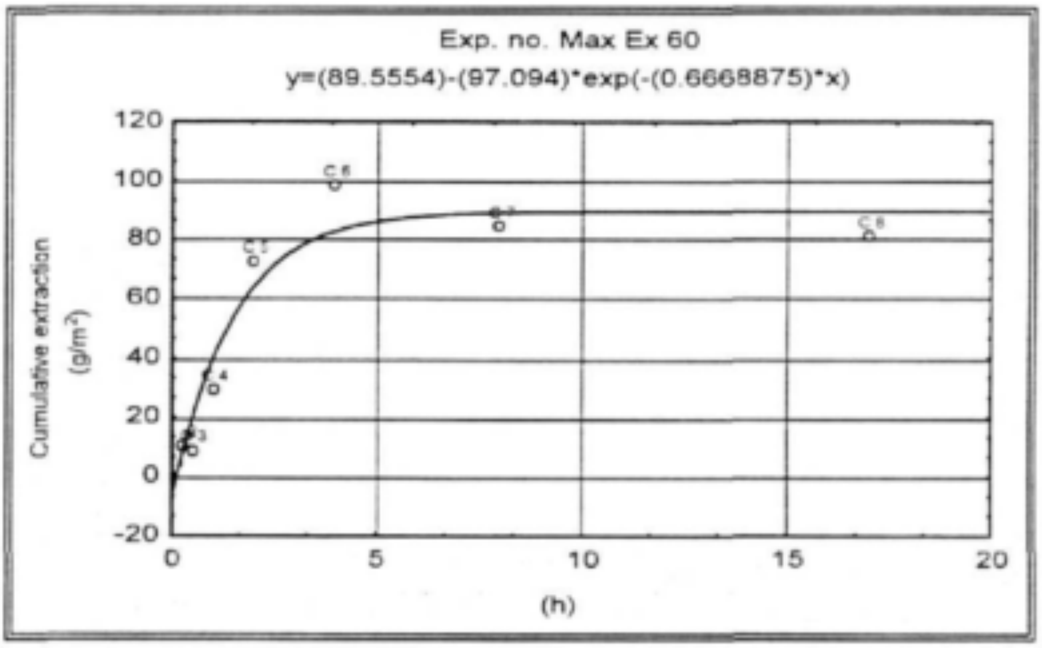
Temp. 70 pH 4.5

Vol. 0.4 0.015

Circum.: 0.127 0.126 0.128

Area 0.0077013

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	7.226	0.000	5.99	3.000	0.0000	0.0000
0.25	7.028	10.284	5.19	2.650	0.6825	0.1752
0.50	7.056	8.830	4.91	2.699	0.5859	0.1504
1.00	6.662	29.294	4.5	2.002	1.9440	0.4990
2.00	5.828	72.611	4.06	0.526	4.8186	1.2370
4.00	5.329	98.528	3.82	-0.357	6.5385	1.6785
8.00	5.601	84.401	4.43	0.124	5.6010	1.4378
17.00	5.666	81.025	4.52	0.239	5.3769	1.3803



Exp. no.: Max Ex 70 [H] 3

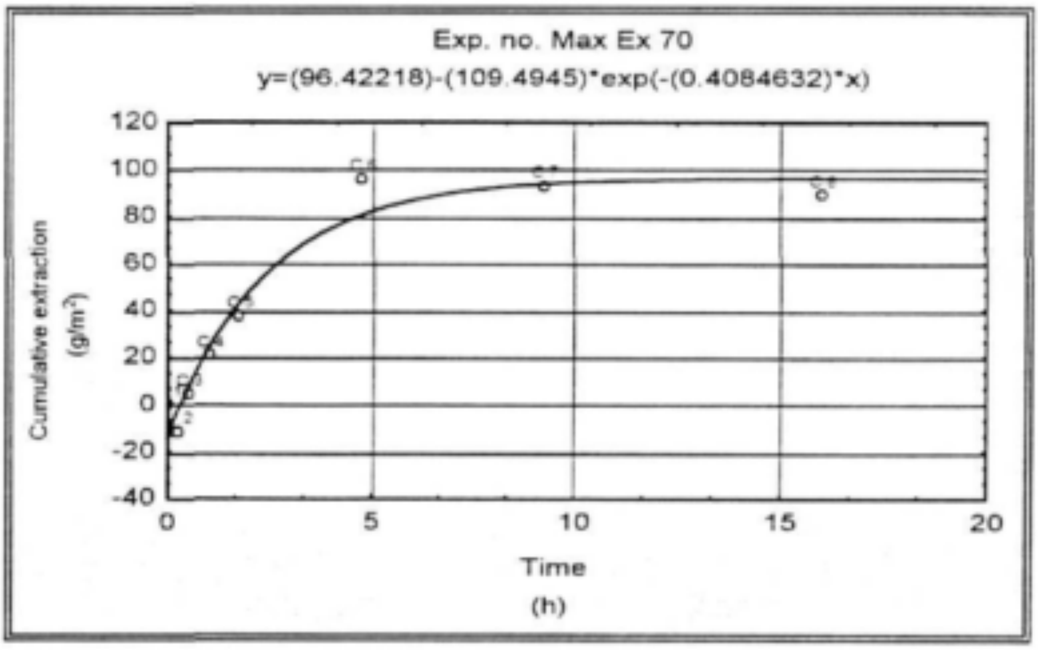
Temp. 70 pH 4.5

Vol. 0.4 0.015

Circum.: 0.119 0.122 0.124

Area 0.0070698

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	6.950	0.000	5.18	3.000	0.0000	0.0000
0.25	7.150	-11.316	4.95	3.386	-0.8180	-0.1928
0.50	6.876	4.187	4.78	2.857	0.3027	0.0713
1.00	6.588	20.481	4.55	2.302	1.4806	0.3489
1.75	6.290	37.342	4.3	1.728	2.6994	0.6361
4.75	5.255	95.901	3.53	-0.267	6.9326	1.6337
9.25	5.306	93.015	4.12	-0.169	6.7240	1.5846
16.00	5.370	89.394	4.52	-0.046	6.4622	1.5229



Exp. no.: Max Ex 90 [H] 3

Temp. 70

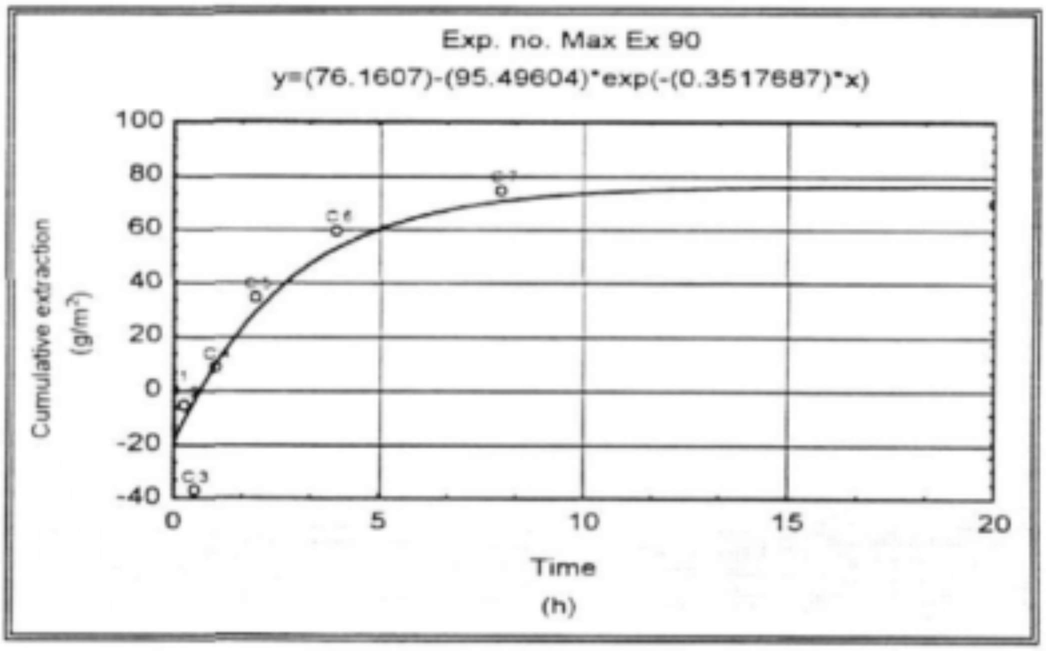
pH 4.5

Vol. 0.4 0.015

Circum.: 0.12 0.124 0.12

Area 0.0070308

Time(h)	[Ni]	Extr.	pH	[H] strip	Extr. [H]	Extr [Ni]
0.00	6.895	0.000	5.71	3.000	0.0000	0.0000
0.25	7.000	-5.974	5.71	3.204	-0.4342	-0.1018
0.50	7.553	-37.435	5.09	4.275	-2.7212	-0.6377
1.00	6.750	8.249	4.08	2.719	0.5997	0.1405
2.00	6.296	34.078	4.23	1.839	2.4772	0.5806
4.00	5.851	59.396	3.82	0.976	4.3175	1.0118
8.00	5.589	74.301	4.09	0.468	5.4010	1.2658
16.00	5.998	51.032	4.36	1.261	3.7096	0.8694



Appendix B

Calculations

B.1 Calculations to determine the hydronium ion concentration at different acid concentrations

It is generally accepted that the diprotonic sulphuric acid dissociates in two steps (Cruywagen *et al.*, 1981:264):

$$
\begin{aligned}
H_2SO_4 + H_2O &\rightarrow H_3O^+ + HSO_4^- \\
HSO_4^- + H_2O &\rightleftharpoons H_3O^+ + SO_4^{2-}
\end{aligned}
$$

The first step is a complete dissociation, but the second step is only a partial dissociation with the following dissociation constant:

$$Ka_{HSO_4^-} = 2.162\times10^{-4} = \frac{[H_3O^+]\,[SO_4^{2-}]}{[H_2O]\,[HSO_4^-]} \tag{B.1}$$

The sulphuric acid/water system is an equimolar solution at a concentration of 14 mol/dm^3 H_2SO_4. In other words, if the sulphuric acid concentration is lower than 14 mol/dm^3, the solution consists of sulphuric acid diluted in water. If the sulphuric acid concentration is higher than 14 mol/dm^3, the solution consist of water diluted in sulphuric acid. The concentration of the hydronium ions can be calculated from the stoichiometric reactions and the dissociation constant.

If the acid concentration is lower than 14 mol/dm^3 the following is true:

The first dissociation step is complete and this means (from simple stoichiometry) that the mol bisulphate ions formed in the first dissociation step is equal to the initial mol sulphuric acid. A part of the bisulphate ions dissociates in the second step to form sulphate ions. The initial sulphuric acid concentration is thus equal to the summation of the final bisulphate ion and sulfate ion concentrations :

$$\begin{aligned}[H_2SO_4]_i &= [HSO_4^-] + [SO_4^{2-}] \\ \therefore\ [SO_4^{2-}] &= [H_2SO_4]_i - [HSO_4^-] \qquad (B.2)\end{aligned}$$

Where $[H_2SO_4]_i$ is the initial sulphuric acid concentration before dissociation occurred. Since water is the excess reagent, it follows that the final water concentration is equal to the initial water concentration minus the final hydronium ion concentration:

$$[H_2O] = [H_2O]_i - [H_3O^+] \qquad (B.3)$$

where $[H_2O]_i$ is the initial concentration of the water before dissociation occurred. Equation B.2 and B.3 are substituted in equation B.1 to give the following:

$$Ka_{HSO_4^-} = \frac{[H_3O^+]\,([H_2SO_4] - [HSO_4^-])}{([H_2O]_i - [H_3O^+])\,[HSO_4^-]} \qquad (B.4)$$

From simple stoichiometry it follows that the final hydronium ion concentration is equal to the summation of the hydronium ions formed in the first and second dissociation steps. The first dissociation step is complete and the mol hydronium ions formed in this step is equal to the initial mol sulphuric acid. The hydronium ions formed in the second dissociation step is equal to the final mol sulphate ions. The final hydronium ion concentration is thus equal to the summation of the initial sulphuric acid concentration and the final sulphate ion concentration:

$$[H_3O^+] = [H_2SO_4]_i + [SO_4^{2-}] \qquad (B.5)$$

Substitute equation B.2 in equation B.5:

$$\begin{aligned}[H_3O^+] &= [H_2SO_4]_i + ([H_2SO_4]_i - [HSO_5^-]) \\ &= 2\,[H_2SO_4]_i - [HSO_4^-]\end{aligned} \tag{B.6}$$

If the initial sulphuric acid concentration is known, equations B.4 and B.6 can be solved simultaneously to give the final hydronium ion- and bisulphate ion concentrations.

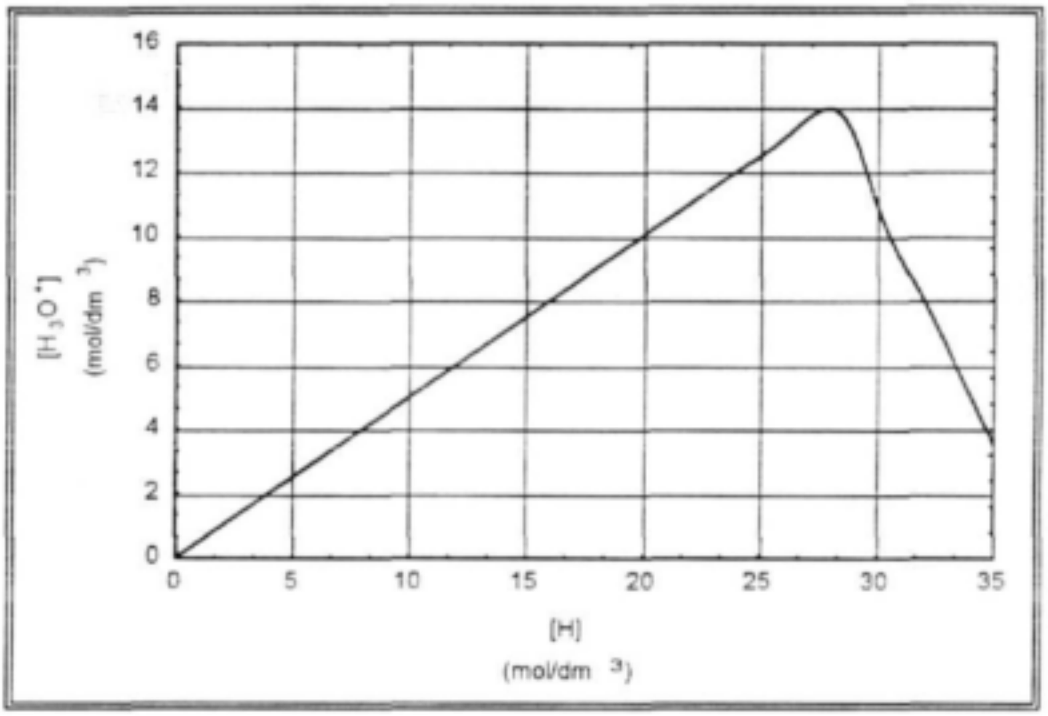
If the sulphuric acid concentration is higher that 14 mol/dm^3 water becomes the limiting reagent in the dissociation process. This means that all the water dissociates to form hydronium ions:

$$[H_2O]_i = [H_3O^+] \tag{B.7}$$

The results of the above mentioned calculations can be seen in the following table. The concentration of the sulphuric acid is expressed as [H]:

[H]	**$[H_3O^+]$**	**[H]**	**$[H_3O^+]$**	**[H]**	**$[H_3O^+]$**
0.0	0.000	13.0	6.506	25.0	12.501
1.0	0.511	14.0	7.006	26.0	13.001
2.0	1.011	15.0	7.506	27.0	13.500
3.0	1.511	16.0	8.005	28.0	13.949
4.0	2.010	17.0	8.505	29.0	12.464
5.0	2.510	18.0	9.004	30.0	10.980
6.0	3.009	19.0	9.504	31.0	9.496
7.0	3.509	20.0	10.003	32.0	8.012
8.0	4.009	21.0	10.503	33.0	6.528
9.0	4.508	22.0	11.003	34.0	5.043
10.0	5.008	23.0	11.502	35.0	3.559
11.0	5.507	24.0	12.002	36.0	0.000
12.0	6.007				

A graphical representation of the table can be seen in the following figure:



Appendix C
ESKOM Research Report

TECHNOLOGY GROUP

RESEARCH REPORT

INITIATED BY	:	PROF JJ SMIT
ISSUED BY	:	AM VAN WYK

TITLE	:	EXTRACTION OF LOWLY SOLUBLE DISSOLVED CHEMICAL SPECIES WITH CAPSULED MEMBRANE EXTRACTION (CME)
PROJECT No	:	2TB23294
BY	:	AM VAN WYK
SECTION or CONTRACTOR	:	PU VIR CHO, DEPT OF CHEMICAL ENGINEERING, CENTRE FOR SEPARATION TECHNOLOGY

C.1 RESEARCH REPORT SUMMARY

EXTRACTION OF LOWLY SOLUBLE DISSOLVED CHEMICAL SPECIES WITH CAPSULED MEMBRANE EXTRACTION (CME)

OVERVIEW

BACKGROUND

Eskom envisaged some problems with the organic content and the ionic species present in the boiler reuse water at the Matimba power station near Ellisras. The chemical engineering department of the Potchefstroom University has been awarded a grant from Eskom to do research on this problem. This report contains the results of this research.

OBJECTIVES

The main objectives of the research can be summarised as follows:

- The organic content of the Matimba reuse water is too high. An extensive literature survey was undertaken and experiments were performed to remove these organic compounds.
- The ionic species present in the reuse water were also too high. Experiments were conducted to remove most of it.

Membranes in a capsuled configuration were to be used in both the above mentioned experiments.

APPROACH

After the project had been awarded to the chemical engineering department of the Potchefstroom university, an extensive literature survey was undertaken to determine the extend of research done in the past on membrane extraction. A visit to the Matimba power station gave the researchers some first hand knowledge of the problems experienced by Eskom. Experiments were conducted using membrane technology as well as electrochemical processes to find solutions for these problems.

RESULTS

The results showed that membrane extraction is a solution for the extraction of ions from the Matimba reuse water, but the rate of extraction is too slow for practical use. However, membranes can be used very successful in the analytical chemistry applications because of its concentrating ability. The electrochemical treatment of the Matimba reuse sample showed a high reduction in organic contents (>50%) and it is recommended that future research be done in this regard.

INDUSTRY PERSPECTIVE

From an industry point of view, membrane extraction is not the answer for the treatment of large volumes. Electrochemical processes offer an elegant method for the removal of both organic and inorganic substances from water.

KEYWORDS
Membrane extraction, electrochemical extraction, water purification, organic extraction, inorganic extraction, supported liquid membranes, capsuled membrane extraction.

C.1 INTRODUCTION

The main objective of the project was the removal of organics from the Matimba boiler feedwater. The problem however, is the low organic content of this feedwater. It is essential to find not only an effective, but also an economical process to extract this lowly soluble organics.

It is also important to extract as many as possible cations from the boiler feedwater. The cations and anions present in the boiler feedwater, combine and precipitate on the tubes of the boiler, causing an increase in the heat resistance of the tubes.

C.2. LITERATURE SURVEY

C.2.1 SUPPORTED LIQUID MEMBRANES (SLM)

C.2.1.1 Definition

A supported liquid membrane is described as a thin layer of organic solution consisting of solvent extraction reagents, immobilised on microporous inert supports interposed between two aqueous solutions for the selective removal of metal ions from a mixture (Danesi, 1985:857). The organic extractant extracts the metal species present in the first aqueous solution (referred to as the feed solution), while the second aqueous solution is necessary to strip the metal species from the organic phase present in the membrane (referred to as the strip solution).

The organic extractant, also referred to as the metal carrier, is usually diluted in a water immiscible organic diluent before being absorbed into a microporous polymeric film that acts as the solid support for the liquid membrane. The thickness of this polymeric membrane, made from polypropylene, is typically between 25 and 30 µm and has pore sizes ranging from 0.02 and 0.2 µm.

The traditional extraction methods used for the selective removal and concentration of metal ions from solutions are ion exchange techniques and liquid-liquid extraction. SLMs represent an attractive alternative to these conventional techniques. Some of the advantages displayed by SLMs are:

- Small volumes of organic extractants are needed. The extractants are constantly regenerated which makes it economically feasible to utilise some of the more exotic and expensive extractants available.
- The permeation of metal species through SLMs can be described as the simultaneous extraction and stripping operation combined in a single stage, and hence eliminates some process steps that would be required by conventional solvent extraction.
- SLMs can operate in unclarified feed solutions eliminating the need of a filter.
- The only waste generated by a SLM is the exhausted membrane after a period when regeneration is no longer effective. This represents a far smaller volume to be disposed of compared to the volume of the spent resin used in a liquid-liquid extraction unit.
- The equipment required, is simple and has a very low energy consumption.
- The limitations present in liquid-liquid extraction, such as flooding, independent phase flow rates, the requirement of density differences and the inability to handle particulates, are avoided.

Although these advantages should result in higher efficiencies and low operating costs, very few process applications of SLMs have been reported so far. One of the main reasons which has limited the widespread use of SLMs probably is the lack of information presently available on the membrane lifetime. Most processes require relatively long-lived SLMs in order for their use to be cost effective. Moreover, even for those processes where periodical and frequent reimpregnation of the support is acceptable, predictable lifetimes are required. Danesi and his colleagues investigated the factors influencing the stability of the membranes and they drew the following conclusions (Danesi et al., 1987:141):

- The SLMs appear to be stable when the two aqueous solutions separated by the membrane have approximately the same ionic concentration, providing the metal carrier is sufficiently water-insoluble.
- The membrane tends to become unstable when an osmotic pressure gradient is present across the SLM, as a result of the different ionic concentrations of the feed and strip solutions. The degree of stability depends on the composition of the SLM and increases with an increasing osmotic pressure gradient.
- The instability of SLMs increases with their ability to transport water.
- A critical osmotic pressure gradient is present at SLMs subjected to progressively increasing osmotic pressure gradients. This critical osmotic pressure gradient represents the maximum osmotic pressure gradient the SLM can withstand before the water flow starts to displace the organic phase from the pores of the support.
- Water transport through the SLM occurs mainly through support pores which have become devoid of the organic phase. This displacement of organics is caused by the osmotic flow of massive quantities of water through the organic phase.
- The displacement of the organic liquid from the pores of the support does not appear to take place simultaneously; it seems to be a statistical phenomenon.

The following guidelines maximise the lifetime of an SLM:

- Use organic liquid phases exhibiting low tendency to solubilise water and high organic/water interfacial tension.
- Minimise, whenever possible, the concentration difference of the bulk solutes between feed and strip solutions.
- Use porous supports having small pore radii and high hydrophobicity.

C.2.1.2 Mechanism

The permeation of the metal species from the feed solution to the strip solution will be facilitated by the highest possible distribution coefficient, K_d, of the feed to favour extraction, and the lowest possible K_d on the strip side of the membrane to ensure maximum stripping (Chiarizia & Castagnola, 1984:481). This distribution coefficient is defined as the ratio of the concentration of metal species in the organic phase to the concentration of metal species in the aqueous phase:

$$K_d = \frac{[M]_o}{[M]_a} \quad (C.2.1)$$

A metal-extractant complex is formed at the interface of the outer aqueous (feed) phase and the organic phase present in the membrane during extraction. This complex permeates across the membrane and decomplexes at the interface of the organic phase and the strip solution (Melzner et al., 1984:107).

The transport of metal species through the membrane is described as a coupled transport mechanism because the transport of the metal species is accompanied by a counter ion (Danesi, 1985:859). Depending of the nature of the counter ion, the coupled transport can be divided in a counter- or a co-transport phenomenon.

C.2.1.2.1. Counter-transport

If the metal carrier is an acidic extractant, HX, the transport mechanism is referred to as a counter-transport mechanism. This meganism is illustrated in figure 1.1. The H^+ counter ion permeates in the opposite direction as the metal ion M^{n+} and the difference in K_d between the feed and strip sides of the SLM is generally achieved by a pH gradient. The following chemical reaction takes place during the counter-transport mechanism:

$$M^{n+} + nHX_{membrane} \underset{\text{strip side}}{\overset{\text{feed side}}{\rightleftarrows}} nMX_{membrane} + nH^{+} \qquad (C.2.2)$$

2.1.2.2. Co-transport

If the metal carrier is a neutral or basic extractant, E, the transport is referred to as co-transport and is illustrated in figure 1.2. The X^- counter ion permeates in the same direction as the metal ion M^{n+} through the membrane and the difference in K_d is generally obtained by a concentration gradient of X^-. The chemical reaction is:

$$M^{n+} + X^{-} + E_{membrane} \underset{\text{strip side}}{\overset{\text{feed side}}{\rightleftarrows}} EMX_{membrane} \qquad (C.2.3)$$

C.2.1.3. Generalised Model

Although pH and counter ion concentration gradients are most often used as driving forces to ensure transportation, any other expedient which assures a large chemical potential gradient between the two

opposite sides of the membrane can be used, provided that coupled transport of metal ions and some other chemical species occur through the SLM.

It is possible to transport metal ions across the membrane against their concentration gradient, because the metal ion concentration is not necessarily a driving force. This type of "uphill" transport will continue until all the metal species which can permeate the SLM have been transferred from the feed to the strip side, providing that the driving force for the process is kept constant. In practice, this situation occurs when very dilute solutions of metal species are involved or when, in the case of more concentrated metal solutions, the concentration of the chemicals responsible for the driving force is continuously adjusted to keep it constant. Therefore very high concentration factors can be obtained in a SLM process by using a volume of the strip solution which is much lower than that of the feed solutions. Moreover, very clean separation processes can be performed by using carrier molecules, HX or E, which is very selective to given metal species. Since the carrier acts as a shuttle during the permeation process, very small amounts of carrier are used and therefore expensive, tailor-made extractants can be used economically.

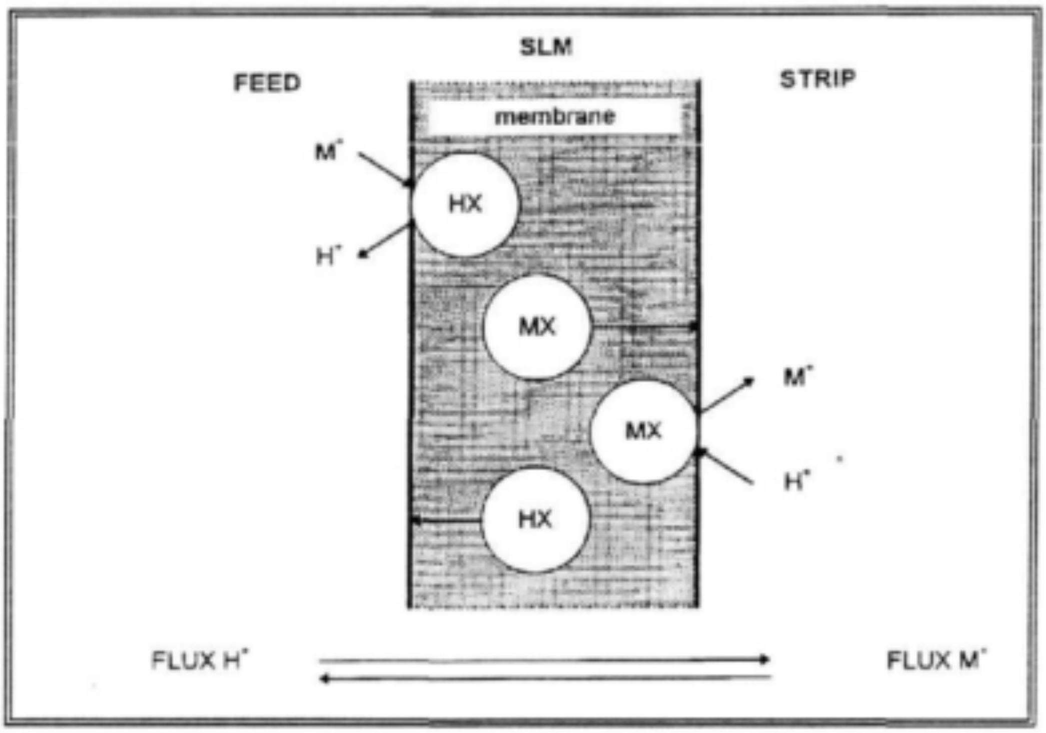


Fig. C.1.1: Counter transport for metal species across a SLM.

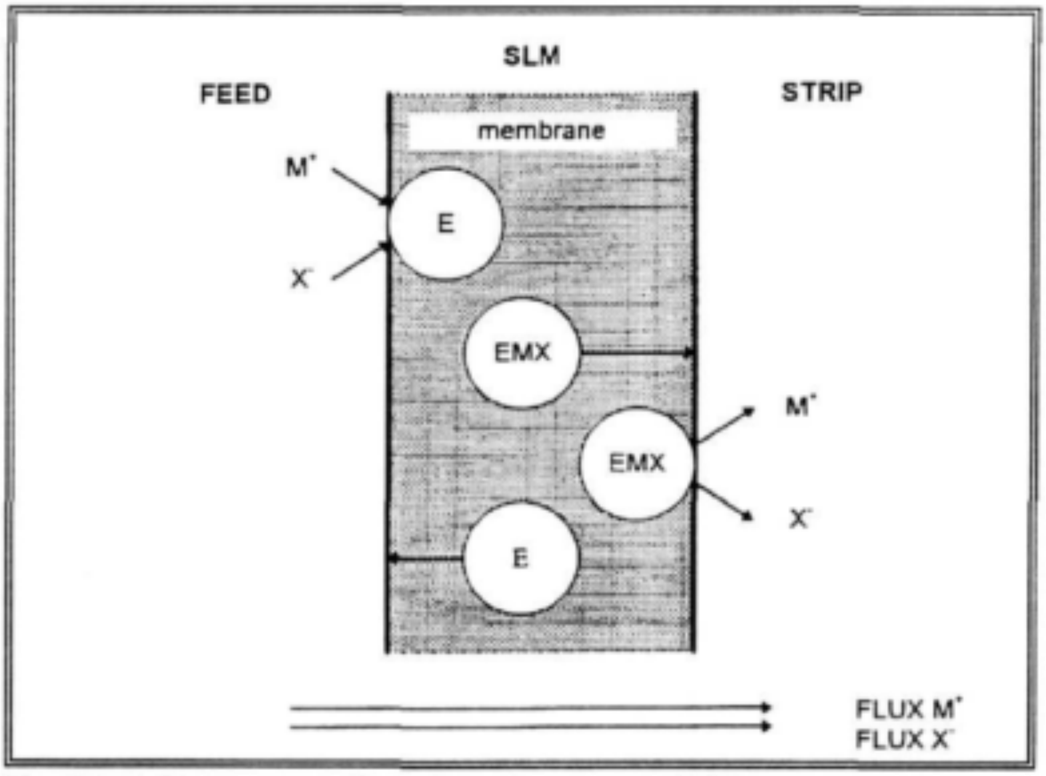


Fig. C.1.2: Co-transport of metal species across a SLM.

A generalised model for the processes controlling membrane permeability has been devised, assuming:

- steady state conditions
- a linear metal concentration throughout the SLM (Danesi et al., 1981:203).

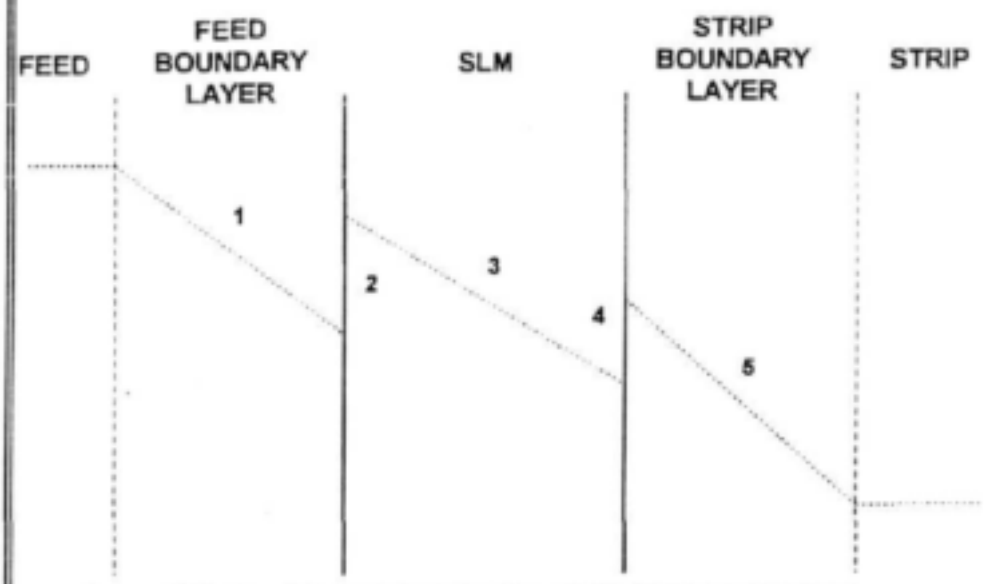
In spite of their simplicity, above assumptions do hold well enough in those cases where coupled transport through liquid membranes has been measured with well-stirred aqueous solutions and with chemical systems characterised by fast chemical reactions (Caracciolo et al., 1975:1960).

This model is schematically illustrated in figure 2, describing the processes controlling membrane permeability in five steps:

1. Diffusion of metal species from the bulk feed solution through the aqueous boundary layer to the feed side of the membrane.
2. The slow chemical reaction between the metal species and the extractant on the surface of the SLM on the feed side.
3. The membrane diffusion of the metal-extractant complex.
4. The slow decomplexing reaction between the metal-extractant complex and the strip solution.
5. Diffusion of the metal species from the surface of the SLM through the aqueous strip boundary layer into the bulk strip solution.

After considering above steps, it seems obvious that two important aspects have been left out. These two factors are the diffusion of the counter ion across the SLM and the diffusion of the regenerated extractant back to the feed side of the membrane after the metal species have been stripped. The former is important because the counter ion concentration gradient is the driving force, and the reason for its omission would appear that it is generally assumed that the chemical reactions or diffusion through the SLM are significantly slower and hence rate controlling. Another possibility is the assumption that the mobility of the counter ion is substantially higher than that of the metal species being complexed with the metal carrier in the membrane phase. The latter omission can be justified if the diffusion of the regenerated extractant is accounted for in an overall diffusion coefficient for diffusion in the SLM (Hofman, 1991:23).

Danesi further assumed Fick's law of diffusion for steps 1, 3 and 5 and assumed that the chemical reactions in 2 and 4 are pseudo first order (Danesi, 1985:862).



1 Diffusion of the metal species through the feed boundary layer.
2 Chemical reaction of metal species with extractant at surface of SLM on feed side to form a complex.
3 Diffusion of metal-extractant complex through SLM.
4 Chemical reaction of metal-extractant complex with strip solution.
5 Diffusion of metal species through strip boundary layer into bulk strip solution.

Fig. C.2: Model for SLM permeation showing a typical concentration gradient.

C.2.2. SUPPORTED POLYMERIC LIQUID MEMBRANES (SPLMs)

C.2.2.1. Introduction

An intensive literature investigation was done into the removal of organic residues from dilute aqueous solutions. The Matimba water has a relatively high organic content and it is advisable that these organics must be removed to prevent pollution to the environment.

The removal or elimination of organic residues from aqueous waste streams represents a major need in the chemical industry. Ho recognised this problem and developed a new class of membrane called supported polymeric liquid membranes (SPLM's) capable of removing and concentrating low molecular weight organic compounds from dilute aqueous solutions, especially those containing a high concentration of inorganic salts. These membranes are prepared by impregnated microfiltration or ultrafiltration membranes with functional, polymeric liquids having affinity for the organic compounds of interest. He found that supported polyglycol liquid membranes were remarkably resilient against tremendous osmotic pressure differentials between dilute solutions and those containing 10 to 20 wt% inorganic salts. Mr Ho has been contacted and he is sending his publications to us for further study. If the organic content of the Matimba sample is fully known, experiments shall be conducted using this concept (Ho, 1996:160).

C.2.2.2. Mechanism

The transport through the composite membranes is by chemical interaction, not by size difference. A key property of these membranes is that they effectively reject charged species in solution. These include both small ions (ions generated by salts, H^+ and OH^-) and larger charged molecules. Only neutral compounds can pass through. Thus, the membranes can be used to recover organics from an aqueous saline waste as illustrated in Figure 3. For effective separation across such a membrane, a driving force should be provided and the strip solution should provide an environment (a "sink") which limits the back diffusion of the compound across the membrane into the waste solution. This could be accomplished in several ways including pH range, reaction, chemical complexation, biodegradation, pervaporation, etc.

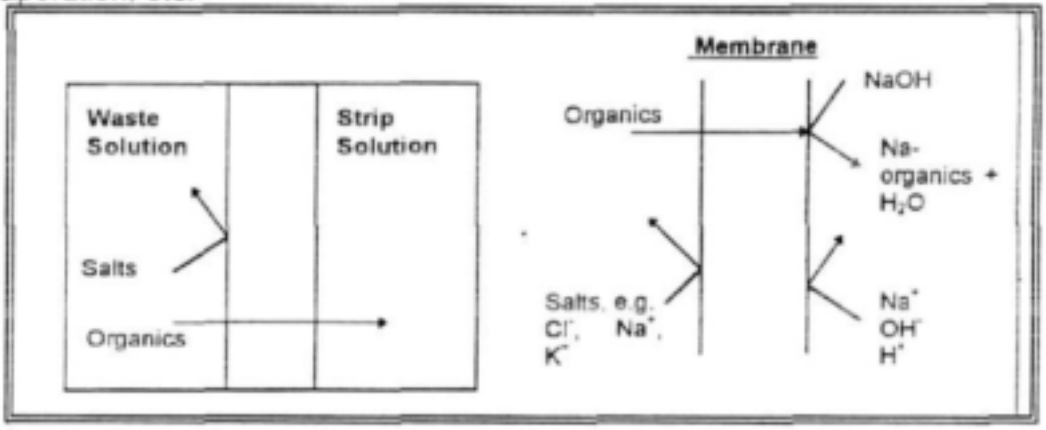


Fig. 3: Composite membrane for organic/salt separation.

C.2.3. THE LIQUID MEMBRANE

The liquid membrane consists of the extractant, diluted in a suitable diluent. This extractant-diluent mixture is absorbed into the pores of the solid support, and is held in place by capillary action. The composition of this liquid membrane is a very important factor in the design of a supported liquid membrane unit from the point of view of stability and life expectancy. These factors must be kept in mind when extractants or diluents are selected; the best suited for liquid-liquid extraction may not necessarily be best for SLM. The choice of liquid membrane determines the economically feasibility of the process.

C.2.3.1. The Solid Support

The solid support that will be eventually chosen for an SLM, will be the one ensuring the highest stability for the SLM. This solid support must be preferably manufactured of a hydrophobic material for reducing the wettability of the SLM. The size of the pores must be kept as small as possible as to hold the extractant-diluent solution in the pores by capillary action, but care must be taken that they are not too small for diffusion resistance to be increased. Finally, the thickness of the solid support must be kept at a minimum so as to minimise the diffusional resistance across the SLM (Hofman, 1991:42).

The literature survey showed that polypropylene membranes are the most widely used (Charizim et al., 1987:641, Danesi et al., 1986:149 and Dworzak et al., 1987:677). Komasano et al. (1983:127) and Nakano et al. (1987:326) used polytetrafluoro-ethylene (PTFE) membranes. Babcock et al. (1978:2) used polysulphone membranes, Akiba et al. (1983:831) used polyolefin membranes while Fernandez et al. (1987:1578) used polyvinylidene membranes. An important consideration when choosing a solid support is its ability to withstand the possible corrosive nature of the aqueous solutions with which it is in constant contact. A polysulphone solid support will probably be unsuitable for an environment with an aqueous solution containing a strong acid.

The solid support used for this experimentation was Celgard 4510 film, a heat embossed laminate of Celgard 2500 bonded to a nonwoven polypropylene web supplied by Celanese Plastics Co. The scanning electron microscope of the Potchefstroom University was used to examine this membrane more closely. This membrane is approximately 0.13 mm thick with a porosity of 45% and a pore diameter in the order of 0.04 µm.

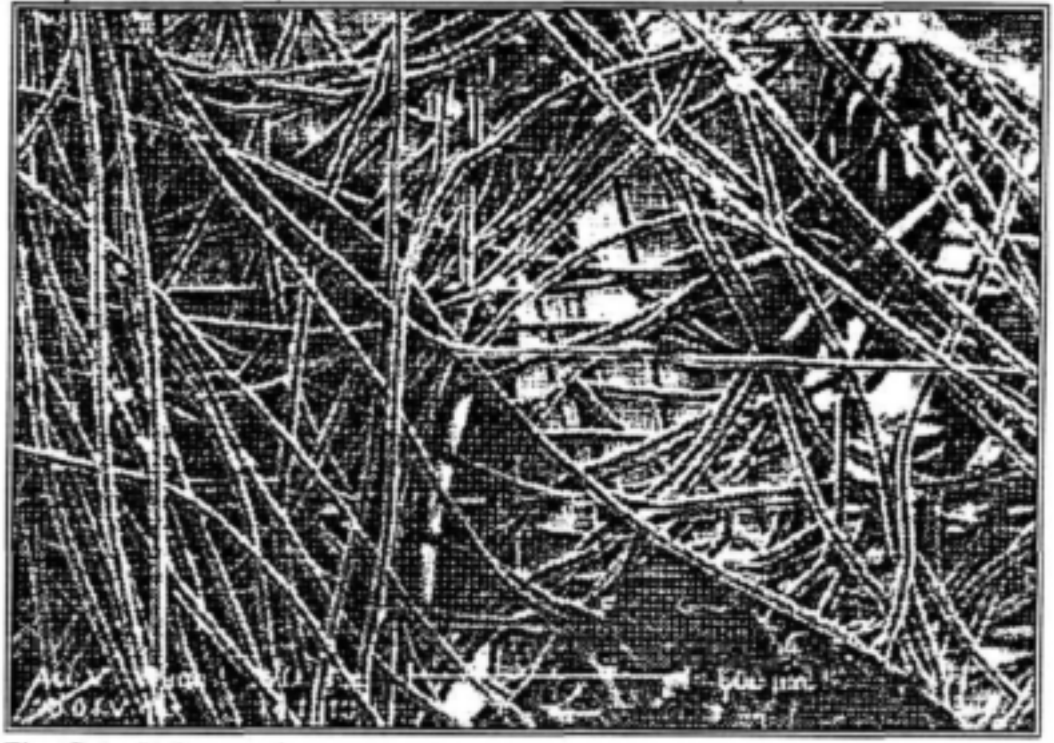


Fig. C.4: Polypropylene support.

Figure 1 shows the nonwoven web of polypropylene that supports the thin layer of Celgard 2500 membrane.

The main function of this polypropylene web is supporting the membrane. Without this support the membrane will be flexible, and can be easily torn in the presence of a strong pressure gradient over it.

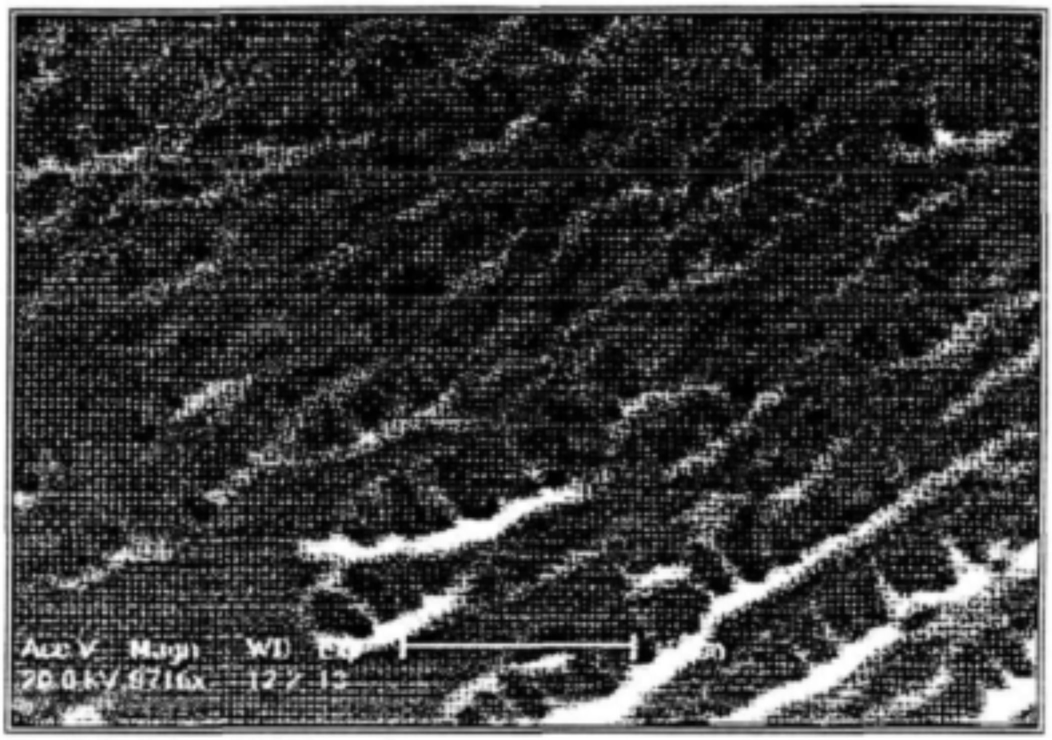


Fig. C.5: Celgard 2500 membrane.

The thin layer of Celgard 2500 membrane is shown in figure 2. The membrane is approximately 0.13 mm thick with a porosity of 45% and a pore diameter in the order of 0.04 µm

The organic phase is impregnated in the pores of this membrane, and it is important that the osmotic pressure difference over this membrane must not be too high. A high pressure will blow the organic phase from the pores, and either the feed solution or the stripping solution will be carried through the membrane. This will of course render the membrane useless.

The cross section of the membrane is shown in Figure 6. The relative thickness of the membrane and polypropylene support can easily be seen.

C.2.3.2. The Extractant

A major advantage of the process involving SLMs is the property of selectively extracting metal species. The extractant used in the SLM must therefore be selective for the metal species involved. There exist two major requirements for the extractant which promote the stability of the membrane: it must not be highly soluble in the aqueous solutions adjacent to the membrane, and it must be immiscible with water. Only a small amount of extractant is needed for impregnation into the membrane, therefore tailor-made, expensive extractants can be utilised. The molecules of the extractant must be small enough for impregnation into the pores of the membrane to ensure mobility in the membrane.

The extractant considered for use in the SLM can be evaluated using the distribution coefficient, K_d. The value of K_d on the feed side must be as high as possible, implying that the extractant must have an affinity for metal species by extracting it. The value of K_d on the strip side however, must be as small as possible, implying that the extractant must readily release the metal species to the strip solution.

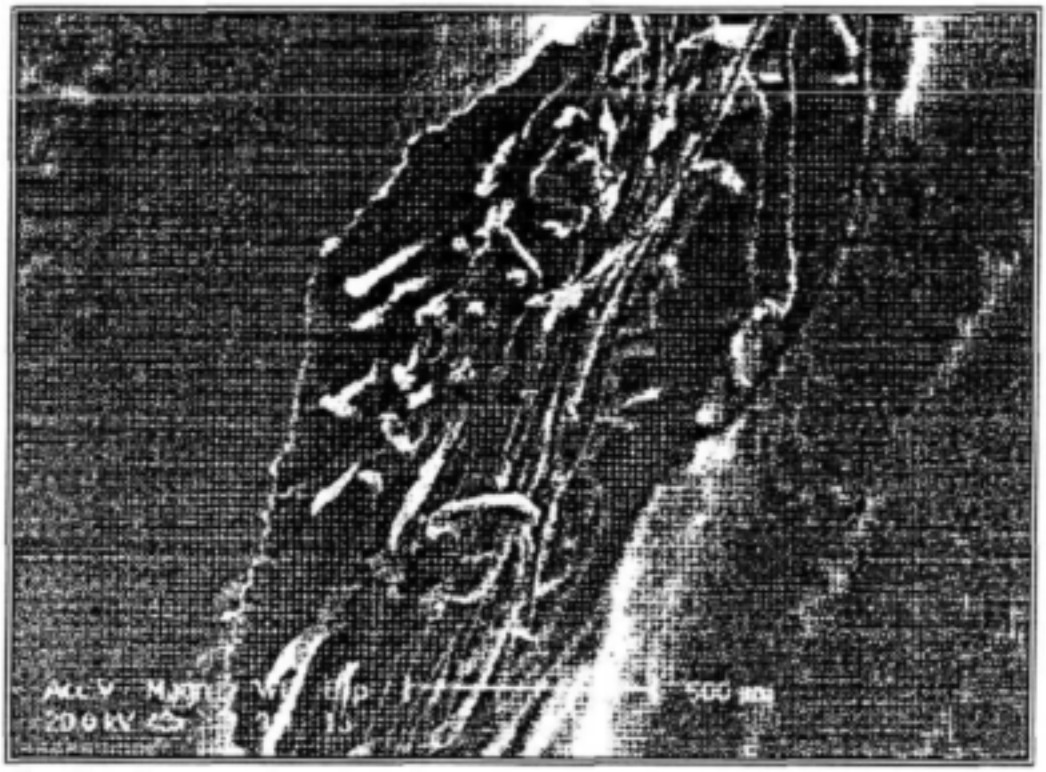


Fig. C.6: Cross section of membrane.

The diffusion of the metal species through the membrane is dependent on the viscosity of the extractant according to the Stokes-Einstein equation:

$$D_R = \frac{kT}{6\pi r\mu} \tag{C.2.4}$$

The viscosity of the extractant must be as low as possible to promote the diffusion of metal species through the membrane (Smith et al., 1981:316).

C.2.3.3. The Diluent

The diluent is the other important organic liquid that forms part of the liquid membrane. The concentration of the diluent is nearly always higher than the concentration of the extractant and therefore it has a higher contribution to the stability of the membrane. The diluent must be insoluble in water, it must not be a surfactant and the viscosity must be as low as possible.

C.2.4. SURFACTANT MEMBRANES

In the study of a water-organic-water surfactant membrane, the membrane phase usually consists of three components: the carrier (extractant), the solvent, and the surfactant. Each of these three components is indispensable in the three component system.

Feng-Jee and his associates discovered a two-component liquid membrane system which differs in composition and nature from the above mentioned three-component membrane systems (Feng-Jee et al., 1985:138). In this two-component membrane system, one of the components acts as both carrier and surfactant.

Usually, the carriers and surfactants which are commonly used in three-component liquid membrane systems are not suitable for the carrier-solvent two-component system because the carriers used possess rather weak surface activity, and the surfactants used show very low complexing capacity with the solute.

In their study, polyethylene glycol and 1,2-dichloroethane were chosen to form the carrier-solvent two-component liquid membrane system; the former compound acts both as carrier and surfactant, and the latter as solvent.

The polyethylene glycol incorporated in the membrane phase will not only stabilise the membrane, but will also form stable complexes with cations, and transport them quickly into internal droplets through the membrane phase. Furthermore polyethylene glycol is a kind of extractant which is similar to crown ethers in structure and nature, and has been widely applied to comparison studies with crown ethers.

The extraction ability of polyethylene glycol increases with increasing molecular weight. The order of extraction selectivity for alkali metals are:

$$Mg^{2+} < Ca^{2+} << Ba^{2+}$$

This property of polyethylene glycol makes it an important extractant for the extraction of alkali metals, especially for Ba-ions.

C.2.5. SELECTIVE EXTRACTANTS

The main purpose for this investigation was to identify extractants for the selective removal of barium and strontium from boiler feed water. This was obtained from Matimba power station situated near Ellisras in the Northern Province.

C.2.5.1. Synergistic Effect of Crown Ethers

The potential of crown ethers (size selective macrocyclic polyethers) as the next generation of specific extracting agents for metal ions, especially alkali and alkaline earth metal cations, has been widely reported (Charewicz et al., 1982:2094, 1982:2300; Izatt et al., 1986:69; Cussler et al., 1974:399). These molecules selectively complex cations by wrapping around them. The major advantage of the macrocyclic polyethers one can choose a polyether selective for almost any ion. Since the polyether is uncharged, the selective complex with a cation often involves the formation of an ion pair with a nearby anion. The formation of this ion pair is probably less selective for anions than the polyether cation interaction (Cussler et al., 1974:409).

The strength of association of the crown ether with the metal ion appears to be greater when there is a correspondence between the ionic diameter and the size of the cavity in the polyether ring. It is therefore possible to effect a selective interaction of the various metals with crown ethers by varying the size of the polyether ring.

Kinard et al. (1981:2947-2953) and McDowell et al. (1983:1483-1507) found that a mixture of an organic phase soluble metal extractants produces a synergistic effect in the extraction of metal ions. This synergistic effect is size selective; it tends to be greater for those ions that best fit the cavity of the crown ether. The metal ion is held in the centre of the cavity of the polyether by Van der Waal's forces. Extraction may occur whether the crown ether is present in the SLM system or not, but complexation with the crown ether enhances extraction of the metal species by making the formed complex even more hydrophobic.

The solubility of crown ethers in both the aqueous and the organic phases is very important. If the crown ether shows a high solubility in the aqueous phase, it will form a complex with the aqueous phase resulting in low extraction. The organic solubility of the crown ether in the organic phase is important to promote extraction. Therefore, maximising the organic solubility and minimising the aqueous solubility of the crown ether will result in an increase of the metal carrying capability of the organic phase.

C.2.5.2. Extraction of Alkaline Earth Cations

Strzelbickl et al. (1981:2247) investigated the extraction of Ba, Sr, Ca and Mg from aqueous solutions by crown ether carboxylic acids. They used *sym*-dibenzo-16-crown-5-oxyacetic acid (1), *sym*-dibenzo-13-crown-4-oxyacetic acid (2) and *sym*-dibenzo-19-crown-6-oxyacetic acid (3) to extract these metal ions in chloroform as the organic phase. A 0.1 M HCl solution was used as the stripping solution. In terms of extraction efficiency and selectivity, it was found that the order for the crown ether carboxylic acids is 1>3>2. Tables 1 and 2 show the diameters of the cavities of the crown ether carboxylic acids, and the alkaline earth cations respectively.

Marked differences in the efficiency and selectivity order are noted for single ion and competitive extractions using *sym*-dibenzo-16-crown-5-oxyacetic acid (1). Although chloroform phase extraction complexes of MA_2 are indicated for each crown ether carboxylic acid, 1 surpasses 2 and 3 in extraction efficiency and selectivity. This can be explained in terms of the cavity size of the crown ether carboxylic acid. The small cavity size of 2 confines interactions with the alkaline earth metals to the carboxylate group. The dimunitions of metal extractability produced by the ring enlargement of 1 to 3 may also be understood on the basis of competitive polyether and carboxylate group interactions.

Table C.1: Crown ether carboxylic acids

No	Name	Ring size (Å)
1	*sym*-dibenzo-16-crown-5-oxyacetic acid	2.0-2.4
2	*sym*-dibenzo-13-crown-4-oxyacetic acid	< 1.2
3	*sym*-dibenzo-19-crown-6-oxyacetic acid	3.0-3.5

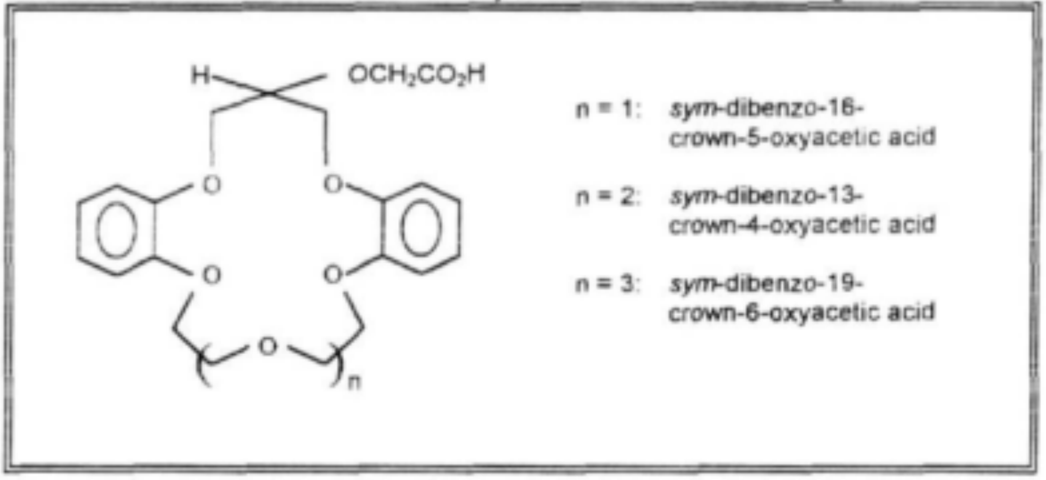
Table C.2: Alkaline earth metals

Metal cation	Ionic diameter (Å)
Mg^{2+}	1.56
Ca^{2+}	2.12
Sr^{2+}	2.54
Ba^{2+}	2.83

On the basis of single ion extraction results, the selectivity order was found to be Ca>Ba>Sr>Mg in basic pH regions. It was also found that 85% of the complexing agent remained in the organic phase for Ba, Sr and Ca which makes it suitable for use in liquid membranes.

Results from competitive extractions of aqueous solutions of alkaline earth cations reported a change in selectivity order to Ba>Ca>Sr>Mg. Thus, the selectivity order for Ba and Ca is the opposite of that reported in single ion extraction studies.

The structures of the crown ether carboxylic acids are shown in Figure 7.



n = 1: *sym*-dibenzo-16-crown-5-oxyacetic acid

n = 2: *sym*-dibenzo-13-crown-4-oxyacetic acid

n = 3: *sym*-dibenzo-19-crown-6-oxyacetic acid

Fig. C.7: Crown ether carboxylic acids.

C.2.5.1. Extractants for Barium

The literature survey showed that not much research has been done regarding the extraction of barium using liquid membranes. Izatt et al. (1986:69-76) reported that dichloromethane (CH_2Cl_2) extracts barium from aqueous solutions with the help of 0.001M dicyclohexano-18-crown-6 ether. It seems that di-2-ethylhexyl phosphoric acid (D2EHPA) is a good extractant for barium (Van Wyk, 1996:2).

C.2.5.2. Extractants for Strontium

Smelov et al., (1974:4) and Bray (1964) reported that D2EHPA extracts strontium from aqueous solutions in the pH range 4.5 to 6. The strontium was stripped from this organic phase with the use of a dilute acid. It is reported that 4-sec-butyl-2-(α-methyl-benzyl)-phenol (BAMBP) can be used as extractant for strontium in the pH range 5 to 11. Bray (1964) also reported that D2EHPA shows a synergistic effect when used in conjunction with other extractants.

C.2.6. SELECTION OF DILUENTS

Although the diluent does not play such a direct role in the SLM mechanism as the extractant or solid support, it is the key to the stability of the SLM and the use of the correct diluent is therefore vital. The diluent acts as the solvent for the metal extractant and its viscosity directly influences the diffusion tempo. It is important that the metal-extractant complex is also soluble in the diluent.

The surface tension of the diluent is another important property that plays a role in extraction. Since the diluent is held in the pores of the solid support by capillary action, the surface tension between the solid support and the diluent must be sufficient to prevent the diluent from being washed out , and large enough to prevent small pressure differentials "blowing" it out of the pores (Hofman, 1991:78).

Kerosene is the traditional diluent used in conjunction with the metal extractants. Its viscosity is relatively low, it exhibits a higher surface tension with most solid supports than other diluents such as xylene, benzene and carbon tetrachloride. Escaid 110, a commercial kerosene product, was therefore used as a diluent throughout the work.

C.3. EXPERIMENTAL

C.3.1. EXPERIMENT 1: BARIUM EXTRACTION

C.3.1.1. Introduction

The literature survey produced no suitable extractant for barium. It was decided to conduct an experiment using D2EHPA as extractant for the recovery of barium in the stripping solution.

C.3.1.2. Experimental solution

A synthetic solution containing 100 ppm Ba was made up by dissolving 0.178g $BaCl_2 \cdot 2H_2O$ in water and filling it to 1L. The pH of this solution was measured as 4.61. This solution was treated in a capsule arrangement as a first approach.

C.3.1.3. Capsule

Celgard microporous polypropylene film was used in the experiment. The capsule was formed by fusing two of these films together using an electrical heat sealer. The circumference of the membrane capsule was measured and the area of the membrane was calculated with the following equation:

$$A_{membrane} = \frac{0.5(Cir_{membrane})^2}{\pi}$$

C.3.1.4. Mobile phase

The mobile phase consists of a mixture of the extractant and the carrier (both organic liquids). The extractant used was D2EHPA (di-2-ethylhexyl-phosphoric acid) and the carrier Escaid. The empty capsule was drenched with the mobile phase for 5 minutes before the stripping solution was sealed in the capsule.

C.3.1.5. Stripping solution

H_2SO_4 was used as stripping solution for stripping the Ba from the synthetic solution. 1M H_2SO_4 was sealed into the capsule.

C.3.1.6 Standards

The standards used for the Atomic Absorption Spectrophotometer (AA) was made up by dissolving $BaCl_2 \cdot 2H_2O$ in water, and the following standards were used:

- 50 mg/mL
- 70 mg/mL
- 90 mg/mL
- 100 mg/mL

C.3.1.7. Experimental procedure

The capsule was placed in the synthetic solution and samples were taken after 0, 0.5, 1, 2, 4, 8 and 10 hours. The pH of the solution was adjusted after every 2 hours because every Ba ion extracted, was substituted by 2 H^+ ions. This adjustment was done by using H_2SO_4 and NaOH.

C.3.1.8. Conclusion

The high extraction rate of the Ba confirms the effectiveness of D2EHPA as suitable extractant for barium. The literature survey showed that Sr is also extracted by D2EHPA.

If the pH of the ESKOM analysis of the Matimba water is between 4 and 6, only D2EHPA is needed to extract most of the barium and strontium.

C.3.2. EXPERIMENT 2: BARIUM AND STRONTIUM EXTRACTION

C.3.2.1. Experimental Configuration

The capsuled configuration proposed by Erlank was used for the experiments (Erlank, 1984:50). The edges of two layers of the membrane were welded together in the form of a capsule, leaving one edge unsealed. The capsule was dosed in the extractant/diluent organic mixture for long enough to allow the solution to enter the pores of the membrane. The access of organics was removed and the capsule was filled with the strip solution. The last edge of the capsule was also sealed and the capsule was then checked for any leaks.

The experimental program designed for the barium and strontium extraction comprised of the following:

- Shake out tests were performed to measure the extraction and stripping coefficients of various metal carriers.
- Capsuled membranes were constructed and used to determine the extraction of metal ions from the Matimba boiler feed water sample.

C.3.2.2. Shake Out Tests

The shake out tests were carried out to investigate the stability of the extractant/diluent solution. These tests gave an indication of the chemical suitability of the extractant/diluent solution for the extraction of the metal species.

The shake out tests were performed by using 100 ml of the extractant/diluent solution. Synthetic solutions containing the desired metal species were used to determine the extraction. The shake out tests were performed in separatory funnels using 100 ml of synthetic feed solution and 100 ml of extractant/diluent solution. This was shaken for five minutes and then the two layers were given time to separate. A 50 ml sample of both these solutions were taken for analyses. The remaining 50 ml of organic extractant/diluent mixture was shaken in the separatory funnel with 50 ml of aqueous strip solution for a further five minutes, and allowed to separate before being taken as samples. Five samples were taken for every shake out test: the original feed solution, the feed after the first shake, the extractant/diluent mixture after the first shake, the extractant/diluent mixture after the second shake and finally the strip solution after the second shake.

It was now possible to calculate the distribution coefficient, K_d, for extraction and stripping. The following equations could be used:

$$K_d(feed) = \frac{Concentration\ of\ organic\ after\ extraction}{Concentration\ of\ feed\ after\ extraction} \qquad (C.3.1)$$

$$K_d(strip) = \frac{Concentration\ of\ organic\ after\ stripping}{Concentration\ of\ strip\ after\ stripping} \qquad (C.3.2)$$

As it was not possible to analyse the organic phase for metal species, it was necessary to calculate it using a mass balance as follows:

$$\left[\frac{Organic\ concentration}{after\ extraction}\right] = \left[\frac{Feed\ concentration}{before\ extraction}\right] - \left[\frac{Feed\ concentration}{after\ extraction}\right] \qquad (C.3.4)$$

$$\left[\frac{Organic\ concentration}{after\ stripping}\right] = \left[\frac{Organic\ concentration}{before\ extraction}\right] - \left[\frac{Strip\ concentration}{after\ extraction}\right] \qquad (C.3.4)$$

These two equations hold true because equal aqueous and organic solutions are used and because the strip solution is initially free of metal species.

An overall extraction efficiency was calculated using the following equation:

$$\eta = 2 \times \frac{[M]_s}{[M]_f}\frac{V_s}{V_f} \times 100 \qquad (3.5)$$

The factor of 2 accounts for the fact that half the mass of the metal species in the organic phase is removed from the system as only half of the organic solution is shaken with the strip solution whose volume is half that of the feed (Hofman, 1991:84).

C.3.2.2.1. Barium shake out tests

The experimental program followed for the shake out tests to find a suitable extractant for barium, is shown in Table 3.

Table C.3: Barium shake out tests

Test no	Extractant/diluent used	Feed concentration (ppm)	Feed pH	Strip solution
1	0.25 M BAMBP in Escaid + 0.0022g dicyclohexyl-18-crown-6 ether	100	10.3	1 M HNO_3
2	0.25 M D2EHPA in Escaid	100	10.3	1 M H_2SO_4

C.3.2.2.2. Strontium shake out tests

Table 4 shows the experimental program followed to identify a suitable extractant for the recovery of strontium.

Table 4: Strontium shake out tests

Test no	Extractant/diluent used	Feed concentration (ppm)	Feed pH	Strip solution
1	0.25 M D2EHPA in Escaid	100	10.3	1 M HNO_3
2	0.25 M D2EHPA in Escaid + 0.0022g dicyclohexyl-18-crown-6 ether	100	10.3	1 M H_2SO_4
3	0.25 M EHPA/D2EHPA mixture in Escaid	100	10.3	1 M H_2SO_4

C.3.2.3. Experimental Discussion

C.3.2.3.1. Shake out tests

The analysis for the aqueous solutions containing the barium and strontium was done with atomic absorption techniques. The metal ion concentrations in the organic solutions could not be determined, therefore mass balances were used to determine these values. The obtained values for metal concentrations could then be used to determine the distribution coefficients, K_d.

$$K_d(feed) = \frac{Concentration\ of\ organic\ after\ extraction}{Concentration\ of\ feed\ after\ extraction} = \frac{C_1 - C_2}{C_2} \qquad (C.3.6)$$

$$K_d(strip) = \frac{Concentration\ of\ organic\ after\ stripping}{Concentration\ of\ strip\ after\ stripping}$$
$$= \frac{C_1 - C_2 - C_3}{C_3}$$

with C_1 = concentration of the metal ions in the aqueous feed phase before extraction

C_2 = concentration of the metal ions in the aqueous feed phase after first shake

C_3 = concentration of the metal ions in the aqueous strip phase after stripping

The value of K_d (feed) should be as high as possible, while the value of K_d (strip) must be as low as possible to ensure a high extraction.

C.3.2.3.2. Barium shake out tests

The K_d values for the barium shake out tests are shown in Figure 8, while its efficiencies are shown in Figure 9.

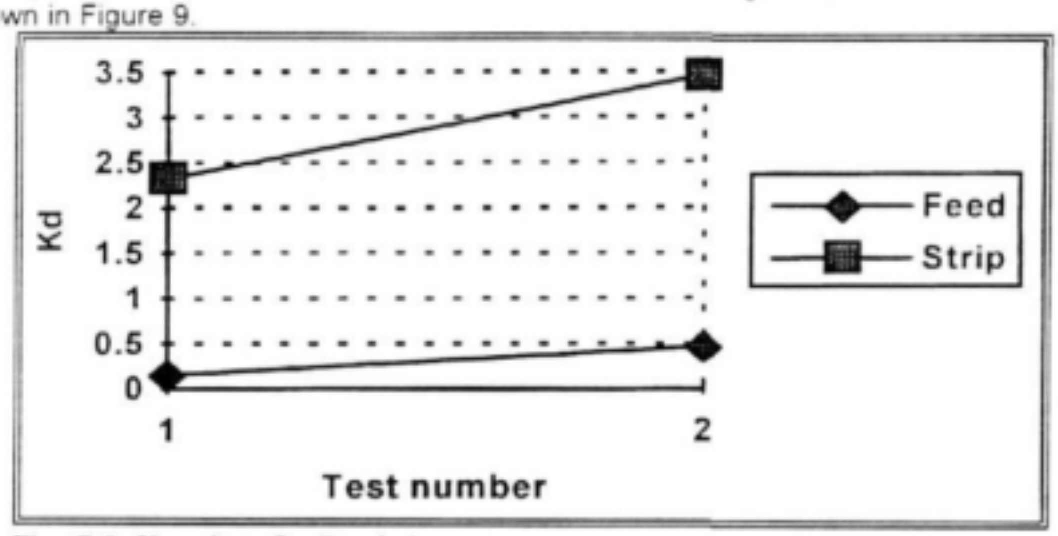


Fig. C.8: K_d values for Ba shake out tests

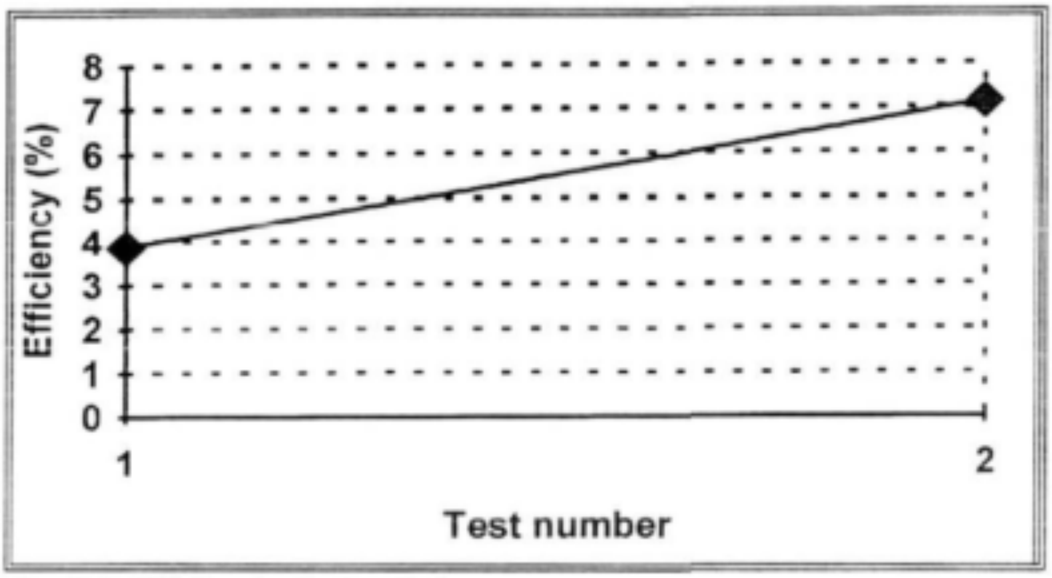


Fig. C.9: Efficiencies for Ba shake out tests.

Figure 8 shows a low value for K_d on the feed side of the membrane, and a relatively high value on the strip side. This is not ideal because the K_d value for the feed must be as high as possible while the value must be as low as possible for the strip side. The low efficiencies for the barium shake out tests as depicted in Figure 9 are indicative of low barium extraction.

C.3.2.3.3. Strontium shake out tests

The K_d values for the strontium shake out tests are shown in Figure 10, and the efficiencies of these tests in Figure 11.

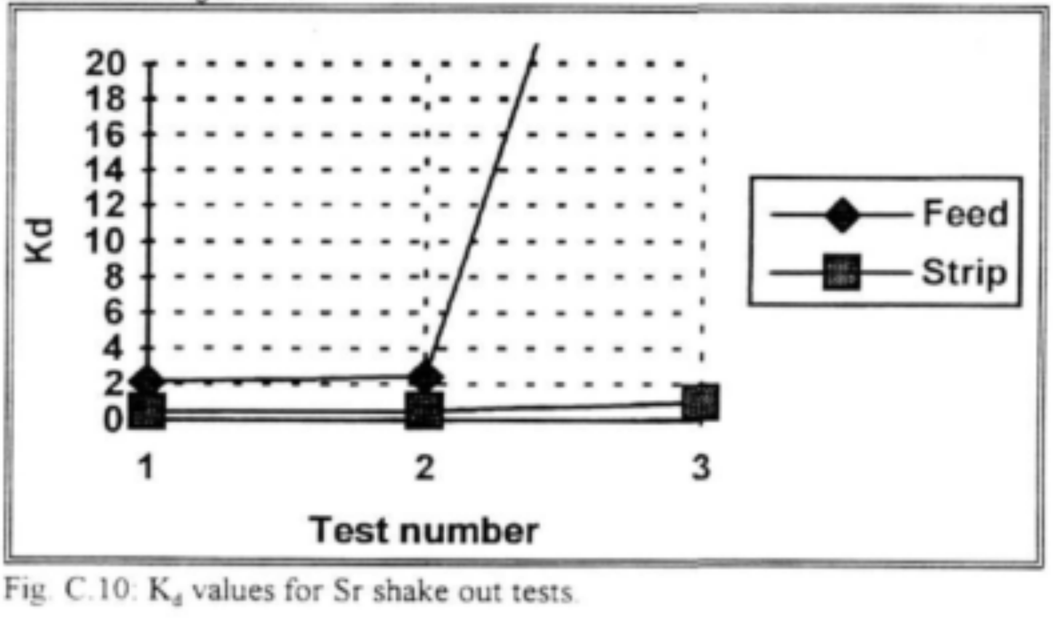


Fig. C.10: K_d values for Sr shake out tests.

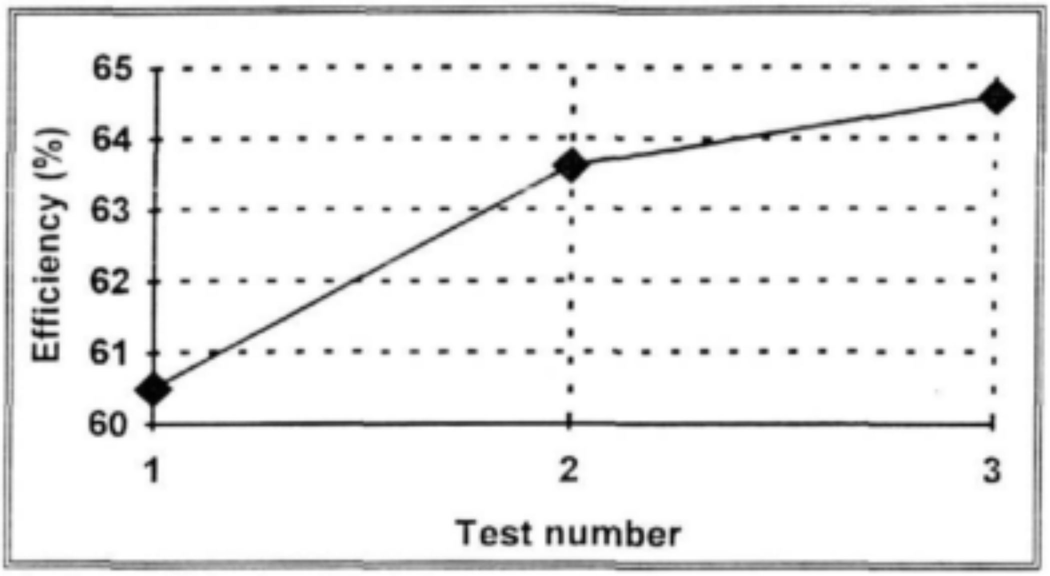


Fig. C.11: Efficiencies of Sr shake out tests.

The results obtained from the strontium shake out tests seems far better than those for barium. Figure 10 shows high values for K_d on the feed side and low K_d values on the strip side. The efficiencies calculated for these tests show relatively high efficiencies, especially considering the possible synergism with experiments 2 and 3 where a mixture of two extractants were used.

C.3.2.4. Conclusions

C.3.2.4.1. Barium extraction

The low efficiencies from the two experiments conducted to test the suitability of D2EHPA and BAMBP as extractants for barium, showed that neither one of these is suitable. More extractants must be investigated to find a suitable extractant. D2EHPA proved to be more suitable for the extraction because of its slightly higher efficiency.

C.3.2.4.2. Strontium extraction

All three of the extractants used in the shake out tests for the extraction of strontium seem to be efficient to extract strontium from aqueous solutions. The mixture of EHPA and D2EHPA showed the highest efficiency for strontium extraction (64.57%) and this gives support to the theory that D2EHPA has a synergistic effect on the extraction of strontium when used in conjunction with other extractants.

When D2EHPA was used as extractant without any additives, the efficiency was reported as 60.51%. This is the lowest efficiency calculated for strontium extraction, but is still high enough to investigate D2EHPA further as a possible extractant.

The efficiency of D2EHPA as extractant was raised by dissolving 0.0022g of dicyclohexyl-18-crown-6-ether in the organic phase. The cavity size of this crown ether is reported to be 2.6 to 3.2 D. The ionic diameter of the divalent strontium cation is 2.54 D. These two dimensions is of the same order and that may be the reason for the higher efficiency.

C.3.3. EXPERIMENT 3: INVESTIGATION OF EXTRACTANTS FOR THE EXTRACTION OF BARIUM AND STRONTIUM

C.3.3.1. Experimental Procedure

A range of extractants for the removal of cations from solutions have been tested for their ability to remove Ba and Sr from solutions. Synthetic solutions containing 100 ppm Ba and 100 ppm Sr respectively have been used to determine the extraction capabilities for these cations. The experiments were done by doing shake-out tests; that is by shaking 100 ml of synthetic solution with 100 ml of organic diluent containing the extractant for five minutes. During this time the Ba and Sr was extracted from the synthetic solution and transferred into the organic solution.

The second part of the experiments was done by shaking 50 ml of this Ba and Sr containing organics with 50 ml of stripping solution, which consisted of 1M HNO_3. Table 5 shows the conditions for these experiments:

Table C.5: Experimental conditions

Test no.	Feed concentration		Extractant used	Strip concentration
	Ba (ppm)	Sr (ppm)		
1	109.2	90.0	30 % T$_2$EHPA	1M HNO_3
2	110.0	89.8	30 % LIX984	1M HNO_3
3	110.3	90.2	30 % KELEX100	1M HNO_3
4	110.3	88.4	30 % CYANEX471X	1M HNO_3
5	110.2	85.5	30 % CYANEX272	1M HNO_3
6	110.3	87.1	30 % VERSATIC10	1M HNO_3
7	109.6	85.4	30 % CYANEX923	1M HNO_3
8	109.5	87.6	30 % EHPA EN D$_2$EHPA	1M HNO_3

C.3.4. EXPERIMENT 4: CAPSULED MEMBRANE EXTRACTION (CME) LABORATORY TESTS

C.3.4.1. Introduction

The shake out tests conducted in the preliminary experiments showed that EHPA/D2EHPA can extract both barium and strontium. These tests were all done on synthetic solutions and not on the actual Matimba samples. The CME tests were carried out to determine the effect of a mixture of EHPA/D2EHPA on the extraction of metal cations from the Matimba reuse sample.

C.3.4.2. Experimental Procedure

A 0.25 M EHPA/D2EHPA mixture was used as organic extractant in Escaid. The capsuled membrane was dosed with this solution, after which the capsule was filled with 1 M H_2SO_4. The experiment was done by using five 4 L Matimba feed solutions, each containing 5 capsuled membranes. The feed solutions were agitated at 50 rpm to reduce the aqueous boundary layer at the feed side of the membrane.

One of the experiments was terminated after 1, 2, 5 and 20 hours respectively. A 2.5 L sample of every experiment were taken and the analysis was done by Eskom TRI.

C.4. CONCLUSION

C.4.1. EXTRACTION OF BARIUM

C.4.1.1 Experiment 1

The results of the initial tests showed clearly that D2EHPA is a suitable extractant of barium. The barium concentration of the feed solution was reduced from 97 to 5 ppm in 10 hours, which represents an extraction of nearly 95%. 1M D2EHPA was used as extractant and the strip solution used was 0.25M H_2SO_4.

C.4.1.2. Experiment 2

The results of the shake out tests of experiment 2 showed that the extraction rate for barium is strongly dependant on the time of extraction. 0.25M D2EHPA was used as extractant and the extraction was allowed to go on for 5 minutes. The barium concentration of the feed solution was reduced from 107 to 72.96 ppm resulting in an efficiency of 7.13%.

When BAMBP was used as the extractant, the barium concentration was reduced from 107 to 93.18 ppm, representing an efficiency of 3.89%.

Both the experiments showed that D2EHPA is a suitable extractant for the removal of barium from a solution. It can also be concluded that D2EHPA is a more effective extractant than BAMBP.

C.4.2. EXTRACTION OF STRONTIUM

The extraction of strontium from an aqueous solution was investigated in experiment 2. The 0.25M EHPA/D2EHPA mixture as extractant reduced the strontium concentration in the synthetic feed solution from 88.95 to 1.74 ppm representing an efficiency of 64.57%. This is the highest efficiency for the three extractants used and it can be concluded that EHPA/D2EHPA is an efficient extractant for the removal of strontium from an aqueous solution.

C.4.3. EXTRACTANTS FOR THE SIMULTANEOUS EXTRACTION OF BARIUM AND STRONTIUM FROM THE MATIMBA SAMPLE

The extraction of cations for different extractants used in the membranes was investigated in experiment 3. The concentrations of the cations in every sample are summarised in Figure 12.

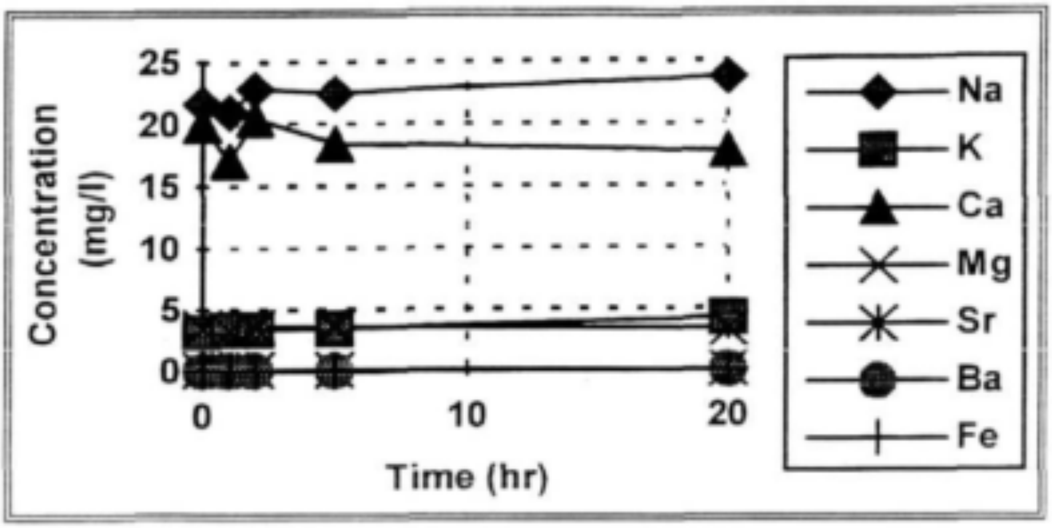


Fig. C.12: Concentration of cations after extraction.

From Figure 12, it is clear that the concentrations of the cations show no definite trend: they are not increasing or decreasing but rather fluctuating. This can be explained by the fact that some of the capsules leaked during the experiments, resulting in the release of the cation concentration in the stripping solution into the Matimba feedwater sample. This was probably also due to the high agitation speed during the experiments but might also be a result of the difficulty of analysing in the ppb range.

C.5. PROPOSED FUTURE RESEARCH

C.5.1. ELECTROCHEMICAL TREATMENT OF MATIMBA REUSE WATER

C.5.1.1. Definition

An electrochemical cell consists of at least two conducting electrodes that are suspended in the electrolyte containing the ionic species. These two electrodes are externally connected through a power source, so that one electrode has a positive polarity (anode) and the other a negative polarity (cathode). When an external potential difference exist between the two electrodes, the anode will start to corrode to form cations and electrons. At the cathode the H^+ ions will be reduced to hydrogen gas.

C.5.1.2. Background

The department of chemical engineering at the Potchefstroom University has done extensive research on the electrochemical treatment of water under professor JJ Smit.

The use of electrolysis as a method for water treatment is known for a long time. Some patents were already taken out at the end of the previous century. An inconsistent electricity supply and passivation of electrodes posed problems for this method which resulted in the development of alternative processes. The following reasons prompted the industry and research facilities during the previous decade to investigate electrolysis again closely:

- Unlike conventional chemical treatment processes, electrolysis does not remove certain minerals by the addition of other chemical substances. Present environmental conditions make this highly desirable.

- The systems governing electrical supply and control has developed vastly which resulted in optimum control conditions for the processes. This results in an increase of efficiency and it is also more convenient than most chemical dosing systems.
- The relative cost of electricity to chemicals has decreased significantly.

The electrochemical process can best be described as the electrolytical solution of a metal ion (e.g. iron) with the associated formation of hydrogen by electrolysis according to the following reactions:

$$Fe \rightarrow Fe^{2+} + 2e^{-}$$
$$2H^{+} + 2e^{-} \rightarrow H_2(gas)$$

The H^+ thus removed as hydrogen gas causes an increase of pH. At this increased pH various salts of the associated dissolved metal cation (in this case Fe^{2+}) becomes insoluble which causes it to precipitate out of the solution. In this way the dissolved iron cations as well as the unwanted anions and excessive acids are removed.

C.5.1.3. Removal of Organics

No references for the removal of organics by electrochemical processes could be found in the literature. It was decided to investigate the removal of organics from the Matimba sample by using iron, aluminium and zinc electrodes alternatively. The sample was treated for 10 minutes at a current of 2 A. The treated samples as well as the untreated sample were analysed by Rand Water Scientific Services and are shown in Table 6.

Table C.6: Organic removal from Matimba reuse

Quality Variable	Untreated sample	Fe electrodes	Al electrodes	Zn electrodes
Total Organic Carbon (TOC) in mg/l	11	4.7	4.2	4.4

It is clear from Table 6 that the electrolytical process removes a high amount (>50%) of TOC.

C.5.2. ANALYTICAL CONCENTRATION OF DILUTE SAMPLES

Although the use of capsuled membranes could not extract all the cations from the Matimba sample, it concentrated it to a large extend. This is an important observation which identifies an application in analytical chemistry.

Analytical scientists experience much difficulty in analysing the concentrations of dilute samples. There exist various high technology equipment on the market which are able to make these measurements, but none of them are very accurate. Accuracy is lost in the way the dilute chemicals are concentrated before the final analysis can be made.

Capsuled membrane extraction (CME) offers a unique way to measure the concentration of dilute samples accurately. As the diffusion rate of a chemical species is known for the different membranes on the market, it will be possible to calculate the concentration of this chemical species in the sample after the concentration in the capsuled membrane is measured. Accurate measurements of the concentration of the concentrated chemical species in the capsule can be made with conventional equipment because of the higher concentration.

C.5.3. PROPOSAL REGARDING 5.1. AND 5.2.

In lieu of the results obtained it might be advisable to reconfigure this project and redirect it as follows:

- Proceed with SLM in the capsule configuration but put more emphasis on its potential as a strong contender for preconcentration of chemicals to be analysed in the ppb range. Once concentrated the analyses could proceed by more reliable and accurate conventional methods already well qualified in the mg/l range.
- The response of TOC to electrochemical treatment is an exhilarating means of reducing TOC by the strongly oxidising atmosphere created in the proximity of the electrodes. This reduction could be enhanced by addition of for example ozone or some similar oxidising agent right at the electrodes.

C.6. REFERENCES

AKIBA, K.L. & KANNO, T., "Transport of uranium(VI) through a supported liquid membrane containing LIX 63", *Separation Science and Technology*, 18(9):831-841.

BABCOCK, W.C., BAKER, R.W. KELLY, D.J. & LONSDALE, H.K., "Coupled Transport Membranes for metal separations. Final; Report, phase III", United States Department of the Interior, 1978:1-79.

BRAY, L.A., "Synergism in the Solvent Extraction of Alkali Metals", Letter to Editor, 1964. *Nuclear Science Engineering.*

CHAREWICZ, W.A. & BARTSCH, H., "Competitive Transport of Alkali Metal Ions from Aqueous Solutions into Toluene by Highly Lipophilic Crown Ether Carboxylic Acids", *Analytical Chemistry*, 1982. 54:2300-2303.

CHAREWICZ, W.A., HEO, G.S. & BARTSCH, R.A., "Comparison of Highly Lipophilic Crown Ether Carboxylic Acids for Transport of Alkali Metal Cations from Aqueous Solutions into Chloroform", *Analytical Chemistry*, 1982, 54:2094-2097.

CHARIZIM, R.L. & DANESI, P.R., "A double liquid membrane system for the removal of actinides and lanthanides from acidic nuclear wastes", *Separation Science and Technology*, 1987, 22:641-655.

CUSSLER, E.L. & Evans D.F., "How to Design Liquid Membrane Separations", *Separation and Purification Methods*, 1974, 3(2):399-421.

DANESI, P.R., HORWITZ, E.P., VANDEGRIFT, G.F. & CHIARIZIA, R., "Mass Transfer Rate through Liquid Membranes: Interfacial Chemical Reactions and Diffusion as Simultaneous Permeability Controlling Factors", *Separation Science and Technology*, 1981, 16(2):201-211.

DANESI, P.R. & RICKERT, P.G., "Some observation on the performancy of hollow-fiber supported liquid membranes for Co-Ni separations", *Solvent Extraction and Ion Exchange*, 1986, 4:149-164.

DANESI, P.R., REICHLEY-YINGER, L. & RICKERT, P.G., Lifetime of Supported Liquid Membranes: The influence of interfacial properties, chemical composition and water transport on the long-term stability of the membranes, *Journal of Membrane Science*, 1987, 31:117-145.

DWORZAK, W.R. & NASER, A.J., "Pilot scale evaluation of supported liquid membrane extraction", *Separation Science and Technology*, 1987, 22:677-689.

ERLANK, S.N., "The Application of Supported Liquid Membranes (SLM) and double salt precipitation (DSP) for demineralization of calcium and nickel in Aqueous Solution". Potchefstroom University, Dissertation M. Eng, 1994:1-141.

FENG-JEE, C., BAO-LONG, T., MING-XIA, X., QING-JIN, Q. and LAN-YING, Z., "A Study on a Two-Component Liquid Membrane System", *Journal of Membrane Science*, 1985, 23:137-154.

FERNANDEZ, L., APARICIO, J. & MOHAMMED, M., "The role of feed metal concentration in the coupled transport of zinc through a Bis-(2-ethylhexyl)-phosphoric acid Solid Supported Liquid Membrane from Aqueous Perchlorate Media", *Separation Science and Technology*, 1987, 22(6):1577-1595.

HO, S.V., "A new Membrane Process for Recovering Organics from Aqeuous Wastes", *Industrial Environmental Chemistry*, 1992, 229-245.

HOFMAN, D.L., "The development and Modelling of a Supported Liquid Membrane Extraction System for the Recovery of Cesium, Strontium and Uranium", Potchefstroom University, Ph. D Thesis, 1991:1-376.

HORNER, D.E., CROUSE, K.B., BROWN, K.B., and WEAVER, B., "Fission Product Recovery from Waste Solutions by Solvent Extraction", Nucl. Sci. Eng., 1963.

KINARD, W.F. & McDOWELL, W.J., "Crown Ethers as Size Selective Synergists in Solvent Extraction Systems: A New Selectivity Parameter", *Journal of Inorganic Chemistry*, 1981, 43(11):2947-2953.

KOMASANO, I., OTAKE, T. & YEMASHITA, T., "Mechanism and Kinetics of Copper Permeation through a Supported Liquid Membrane containing a Hydroxyoxime as a Mobile Carrier", *Industrial and Engineering Chemistry Fundamentals*, 1983, 22(1):127-131.

McDOWELL, W.J., CASE, G.N. & ALDRAP, D.W., "Investigations of Ion-Size-Selective Synergism in Solvent Extraction", *Separation Science and Technology*, 1983, 18(14&15):1483-1507.

NAKANO, M., TAKAHASHI, K. & TAKENCHI, H., "A Method for continuous operation of supported liquid membranes", *Journal of Chemical Engineering in Japan*, 1987, 20(3): 326-328.

SMELOV, V.S. & LUNIN, V.P., "Effect of Temperature on Extraction of Alkali and Alkaline Earth Elements by D2EHPA", Radiokhimiya, 1974:4.

SMITH, K.L., BABCOCK, W.C., BAKER, R.W. & CONROD, M.G., "Coupled Transport Membranes for Removal of Chromium from Electroplating Rinse Solutions", *Chemical Water Reuse*, 1981, 1:311-324.