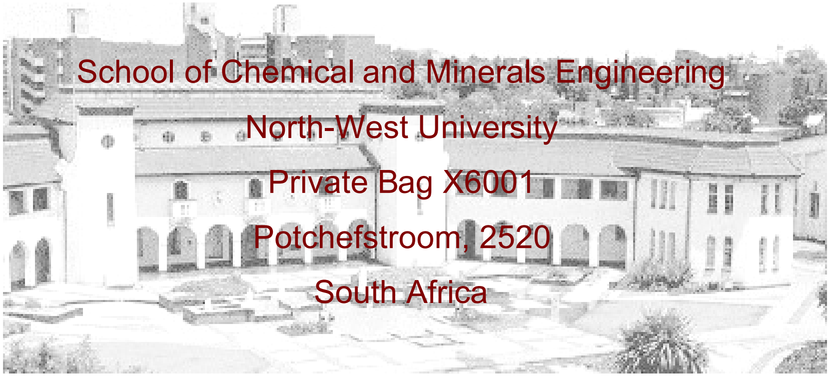
The evaluation of the mechanisms involved in the extraction of nickel from low concentration effluents by means of supported liquid membranes



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The evaluation of the mechanisms involved in the extraction of nickel from low concentration effluents by means of supported liquid membranes

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Declaration

The material in this thesis is my own work, except where indicated to the contrary. The material has not been submitted to another university for any other degree.

Signed

Leon Koekemoer

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Abstract

From an economic point of view, the use of membranes at the present time is intermediate between the development of first generation membrane processes and second generation processes such as supported liquid membranes. The objective of this research was to investigate the mechanisms involved in the extraction of nickel from low concentration effluents by means of supported liquid membranes (SLM).

A custom-made reactor/extractor was used for experimentation, based upon a process flow diagram that closely emulated the flow diagram of an industrial application and was used to determine the scientific and technical feasibility of the SLM process. The extraction equilibrium of the nickel/di-(2-ethylhexyl) phosphoric acid (Ni/D2EHPA) system is an integral part of the extraction process and was determined with extraction experiments.

The results of the extraction experiments showed that there is no significant influence of temperature on the equilibrium for the temperature range of 30 ˚C to 70 ˚C. It was assumed that the nickel-organic complex exists in two forms, one in which the nickel coordinates with two D2EHPA molecules and another one in which the nickel coordinates with six D2EHPA molecules. It was found that the experimental data supported this assumption. Another augmentation of the equilibrium model was the incorporation of the activity of the aqueous species, as well as the effect of aqueous speciation of the nickel species.

The SLM-process was modelled by solving a system of equations that describe all six steps involved in the extraction process and a special computer program was written to solve the system of equations. The process model showed that the nickel flux through the SLM is determined by the diffusion of the nickel through the feed boundary layer as well as the diffusion of the organo-metallic species through the membrane and although temperature does not have an effect on the extraction equilibrium, it does have a beneficial effect on both of these transfer steps. It was found that, as long as a sufficiently low pH ($\text{pH} < 2.0$) was kept in the strip solution, the strip side will not be rate limiting. The process model showed that there exists an extractant concentration at which the nickel flux is an optimum and that this optimum is dependent on temperature. The effect of all the variables involved in the extraction process are interdependent and the model is capable of predicting the effect of this interdependence.

The research reported in this thesis leads to a better understanding of the SLM process and suitable recommendations are made towards a possible industrial application of this technology.

Opsomming

Tans is membrane, vanuit ’n ekonomiese oogpunt, tussen die ontwikkeling van eerste generasie prosesse en tweede generasie prosesse soos ondersteunde vloeistof membrane. Die doelwit met die navorsing was om die meganismes wat betrokke is by die ekstraksie van nikkel met behulp van ondersteunde vloeistof membrane (OVM) te ondersoek.

’n Spesiaal-vervaardigde reaktor/ekstraheerder is gebruik vir eksperimentering en is gebaseer op ’n prosesvloeidiagram wat ’n industriële toepassing emuleer en is gebruik om die wetenskaplike en tegniese uitvoerbaarheid van die OVM-proses te bepaal. Die ekstraksie-ewewig van die nikkel/di-(e-etielheksiel)fosforsuur (Ni/D2EHPA) stelsel is ’n integrale deel van die ekstraksieproses en is bepaal met behulp van ekstraksie-eksperimente.

Die resultate van die ekstraksie-eksperimente het getoon dat die invloed van temperatuur op die ekstraksie-ewewig nie beduidend is in die temperatuurgebied van 30 ˚C tot 70 ˚C nie. Daar is aangeneem dat die nikkel-organiese kompleks twee vorme kan aanneem, een waarin die nikkel met twee D2EHPA molekules gekoördineer is en een waarin die nikkel met ses D2EHPA molekules gekoördineer is. Die eksperimentele data het hierdie aanname ondersteun. Nog ’n toevoeging tot die ewewigsdata was die inkorporering van die aktiwiteit van die waterige spesies, asook die waterige spesiëring van nikkel.

Die SLM-proses is gemodelleer met die gelyktydige oplos van ’n stelsel vergelykings, wat al ses stappe in die OVM beskryf. ’n Spesiale rekenaarprogram is geskryf om die stelsel van vergelykings op te los. Die prosesmodel het getoon dat die nikkelvloed deur die membraan bepaal word deur die voergrenslaag sowel as die diffusie van die spesies deur die membraan, en hoewel temperatuur nie ’n invloed op die ekstraksie-ewewig het nie, het ’n hoër temperatuur ’n voordelige effek op beide van hierdie oordragsmeganismes. Daar is gevind dat, solank die stroop-pH laag genoeg gehou word ($pH < 2.0$), sal die stroopkant nie die tempo-beheerende stap wees nie. Die prosesmodel het getoon dat daar ’n ekstraktantkonsentrasie bestaan waar die ekstraksie ’n maksimum is en dat hierdie konsentrasie afhanklik is van temperatuur. Die effek van al die veranderlikes in die ekstraksieproses is interafhanklik en die model is in staat om hierdie interafhanklikheid te bepaal.

Die navorsing wat gedoen is vir hierdie tesis lei tot ’n dieper begrip van die OVM proses en geskikte aanbevelings word gemaak ten opsigte van ’n moontlike industriële toepassing.

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Nomenclature

Symbol	Meaning	Units
a	Activity	(mol/m^3)
A	Area	(m^2)
A_{DH}	Debeye-Hückel constant	(kg$^{0.5}$/mol$^{0.5}$)
A_N	Nernst equation constant	(m^2/s·K)
B_{DH}	Debeye-Hückel constant	(kg$^{0.5}$/mol$^{0.5}$)
B_N	Nernst equation constant	(J/mol)
C_N	Nernst equation constant	(kg/mol)
d	Diameter	(m)
D	Distribution coefficient	(-)
D_{AB}	Diffusion coefficient of A in solvent B	(m^2/s)
D_{eff}	Effective diffusion coefficient	(m^2/s)
E	Fraction extracted	(-)
f	Fanning friction factor	(-)
F	Flow rate	(m^3/s)
G	Gibbs free energy	(J/mol)
I	Ionic strength	(mol/kg H_2O)
J	Flux	(mg/m^2·s)
k	Mass transfer constant	(m/s)
K	Equilibrium constant	(various)
K_1	Generic constant for NiR_2 species	(-)
K_{Zn1}	Generic constant for ZnR_2 species	(-)
K_{Zn2}	Generic constant for ZnR_3 species	(m^6/mol^2)
L	Tube length	(m)
M	Molecular weight	(g/mole)
m	Coordination number of molecule	(-)
n	Valence of metal ion	(-)
p	Amount of cations in solution	(mol)
P^0	Partition constant	(-)
q	Amount of anions in solution	(mol)
r	Radius	(m)

Symbol	meaning	Units
R	Universal gas constant	(J/mol·K)
$R_A, \ldots, R_E$	Riedel equation constants	(-)
Re	Reynolds number = $\rho \cdot v \cdot d / \mu$	(-)
Sc	Schmidt number = $\mu/(\rho \cdot D_{AB})$	(-)
Sh	Sherwood number = $k \cdot d/D_{AB}$	(-)
t	Time	(s)
t_b	Breakthrough time	(s)
T	Temperature	(K)
v	Velocity	(m/s)
V	Volume	(m^3)
Vr	Volume ratio = V_{aq}/V_o	(-)
x	Mass fraction	(-)
x_{mol}	Mole fraction	(-)
x_{vol}	Volume fraction	(-)
z	Charge number of ion	(-)

Acronyms / Abbreviations

AA	Atomic absorption spectrophotometer
CME	Capsule membrane extraction
D2EHPA	Di-(2-ethyllhexyl) phosphoric acid
ELM	Emulsion liquid membranes
ENPB	Electroless nickel plating bath
FFC	Flat-film contactor
GM	Generic model controller
HCC	Hydrodynamically characterised contactor
H^+	Hydronium ion
LLE	Liquid-liquid equilibrium
M	Metal ion
MCC	Multi-cell contactor
MR	Organo-metallic complex species
$MR_n(RH)_{m-n}$	Organo-metallic complex species
MTO	Metal turnovers

MXR	Organo-metallic complex species
NiR_2	Nickel-D2EHPA species; $Ni(C_8H_{17}O)_2P(O)O)_2$
$NiR_2(RH)_4$	Nickel-D2EHPA species; $Ni(C_8H_{17}O)_2P(O)O)_2(C_8H_{17}O)_2P(O)OH)_4$
NiR_6	Nickel-D2EHPA species; $NiR_2(RH)_4$ or $Ni(C_8H_{17}O)_2P(O)O)_2(C_8H_{17}O)_2P(O)OH)_4$
PID	Proportional-integral-derivative controller
R	Organic extractant
RH	D2EHPA monomer species
$(RH)_2$	D2EHPA dimer species
R^-	Organic phosphate ion
SFC	Slurry-flow contactor
SLE	Solid-liquid equilibrium
SLM	Supported liquid membranes
VLE	Vapour-liquid equilibrium
X	Anion species

Subscripts

aq	In aqueous solution
D	Dimerisation
f	Feed solution
FT	From feed tank
i	Interface
mem	Membrane
mix	Mixture
o	In organic solution
r	Raffinate solution
ref	Reference
s	Strip solution
sp	Control setpoint
ss	Steady state
ST	From strip tank
Tot	Total
+	Cation

-	Anion
±	Average between cation and anion

Superscripts

0	At infinite dilution
r	At position r

Greek letters

Symbol	meaning	Units
α_1	Regression constant	$(\mathrm{Pa \cdot m^2/K})$
α_2	Regression constant	(-)
γ	Activity coefficient	(-)
δ	Membrane thickness	(m)
ΔH^0	Standard reaction enthalpy	(J/mol)
ΔP	Pressure drop	(kPa)
λ	Ionic conductivity	$(\mathrm{S \cdot m^2/mol})$
μ	Viscosity	(mPa·s)
ρ	Density	$(\mathrm{kg/m^3})$
σ	Standard deviation	(Various)
τ	Shear stress	$(\mathrm{N/m^2})$
τ_w	Shear stress at wall	$(\mathrm{N/m^2})$

Chapter 1

Introduction

"In all things of nature there is something of the marvellous." - Aristotle

1.1 General Introduction

In the early days of environmentalism the general feeling was that "Technology equals pollution". Faced with the relentless march of industry and commerce, the green movement became mostly reactive: ecowarriors sailed into the paths of fishing boats or blockaded logging roads. Activists often got their way only by persuading governments to enact tough conservation and anti-pollution laws. While protesters and regulators haven't gone away, environmentalism is becoming much more proactive, and a new formula is gaining favour: "Technology equals solutions." (Geary, 1998:81).

In the field of separation science a central challenge is the development of processes that are economically profitable and at the same time environmentally friendly. One of the central questions in environmental engineering is: "How can the bad stuff be separated from the good stuff." As a method of separation, membrane processes are relatively new. For instance, membrane filtration was not considered a technically important separation process until 1975 (Mulder, 1988:7). Today membrane processes are used in a wide range of applications and the number of such applications is still growing. From an economic point of view, the present time is between the development of first generation membrane processes such as microfiltration, ultrafiltration, nanofiltration, reverse osmosis, electrodialysis, membrane electrolysis, diffusion dialysis and dialysis and the second generation membrane processes such as gas separation, vapour permeation, pervaporation, membrane distillation, membrane contactors and carrier-mediated processes. Supported liquid membranes are viewed as a carrier mediated process and have the potential to be one of these processes that is both environmentally friendly and economically viable.

1.2 Motivation

All the large chemical industries spend a substantial amount of money on the cleanup of the waste they generate and on publicity campaigns to let the general public know that they care for the environment. Some chemical companies were developed to cleanup the waste of other companies. In short: the recovery and upgrading of metal-containing waste have become not only a very demanding assignment, but also a lucrative business.

The cleaning of nickel from waste streams is no exception. 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 (14.40 US$/kg, London Metal Exchange, 2004) and thus a candidate for recovery from effluents.

Separation processes can be classified on grounds of the driving force that is used to effect the separation. Table 1.1 gives a summary of some separation processes in terms of the physical or chemical properties used for the process (Mulder, 1998:7). The processes usually used to treat metal containing effluents are:

- Precipitation
- Liquid-liquid extraction
- Nanofiltration
- Electroplating

Of these processes the most common one is precipitation, in which the nickel is removed by adjusting the solution pH to a point above the precipitation pH of nickel (Jackson, 1986:158). The disadvantage of this process is that the nickel-containing sludge has to be contained and it is usually not economically viable to recover the nickel from the sludge for re-use. Supported liquid membranes (SLM) can probably be used to recover the nickel and upconcentrate it to concentrations where it can be used again in an industrial process.

Table 1.1: Separation processes based on physical/chemical properties

Physical /chemical property	Separation process
Size	Filtration, microfiltration, ultrafiltration, dialysis, gas separation, gel permeation, chromatography
Vapour pressure	Distillation, membrane distillation
Freezing point	Crystallisation
Affinity	Adsorption, absorption, reverse osmosis, gas separation, pervaporation, affinity chromatography
Charge	Ion exchange, electrodialysis, electrophoresis, diffusion dialysis
Density	Centrifugation
Chemical nature	Liquid-liquid extraction, carrier mediated transport

1.3 Objectives

Various authors proved that nickel could be extracted with the use of supported liquid membranes (Verhaege *et al.*, 1987:331; Erlank, 1994:96; Juang & Jiang, 1995:163; Smit & Koekemoer, 1997:6). Although a number of process models have been developed in the past (Juang 1993:157; Zha *et al.*, 1995; Daiminger *et al.*, 1996; Hermandez-Cruz *et al.*, 1998), they tend to incorporate simplifications that are not valid for industrial applications. There are particular shortcomings in the prediction of the influence of temperature and aqueous speciation on the SLM process.

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

1. To develop and build a bench-scale apparatus to test the technical feasibility of a SLM process to extract nickel from low-concentration effluents.
2. To use the bench-scale apparatus to test the influence of the most important variables in the process on the extraction of nickel.
3. The determination of the effect of aqueous speciation on the nickel-D2EHPA equilibrium.
4. To develop a process model that can be used to understand the extraction mechanism of the supported liquid membrane system. Although many process models have been developed for supported liquid membranes, they all seem to focus on the scientific aspects of the transfer mechanism. The proposed research will be based on scientific aspects, but will focus more on the variables that are of relevance to engineering.

5. The method used to develop the Ni/D2EHPA equilibrium will be tested on Zn/D2EHPA system to determine if the same philosophy can be applied to other extraction systems.
6. To perform a limited number of experiments on the supported liquid membrane extraction of zinc in order to make comparative conclusions with regard to the extraction conditions.
7. The development of a computer simulation that can be used to accurately simulate the SLM process.

1.4 Scope of investigation

The research path adopted in this thesis is shown in Figure 1.1. The core of this research is the supported liquid membrane extraction of nickel and a bench-scale reactor/extractor was custom built for this investigation. The bench-scale reactor/extractor was designed in such a way that the process flow diagram closely resembles an industrial one. A statistical experimental design ensured that the experiments done on the reactor/extractor were distributed across a large range of values for the different variables and the results obtained with these experiments were used in conjunction with equilibrium data to develop a process model of the system. The extraction equilibrium constants were determined from experimental data and incorporated the effect of temperature and aqueous speciation. Finally, this model was used to develop a computer simulation of the supported liquid membrane process. The following constraints are applicable to this investigation:

1 The investigation focused on low concentration nickel effluents (less than 150 mg/l). Although a limited number of experiments were done on zinc to determine the technical feasability of the process, the main focus of the investigation was the extraction of nickel and the modelling of the nickel extraction.

2 Di-(2-ethylhexyl) phosphoric acid was the only extractant investigated.

3 Although it is noted that membrane stability is an important factor in the applicability of SLMs in industrial applications, it was not directly investigated in this study and only quantitative predictions were made with regard to the membrane stability.

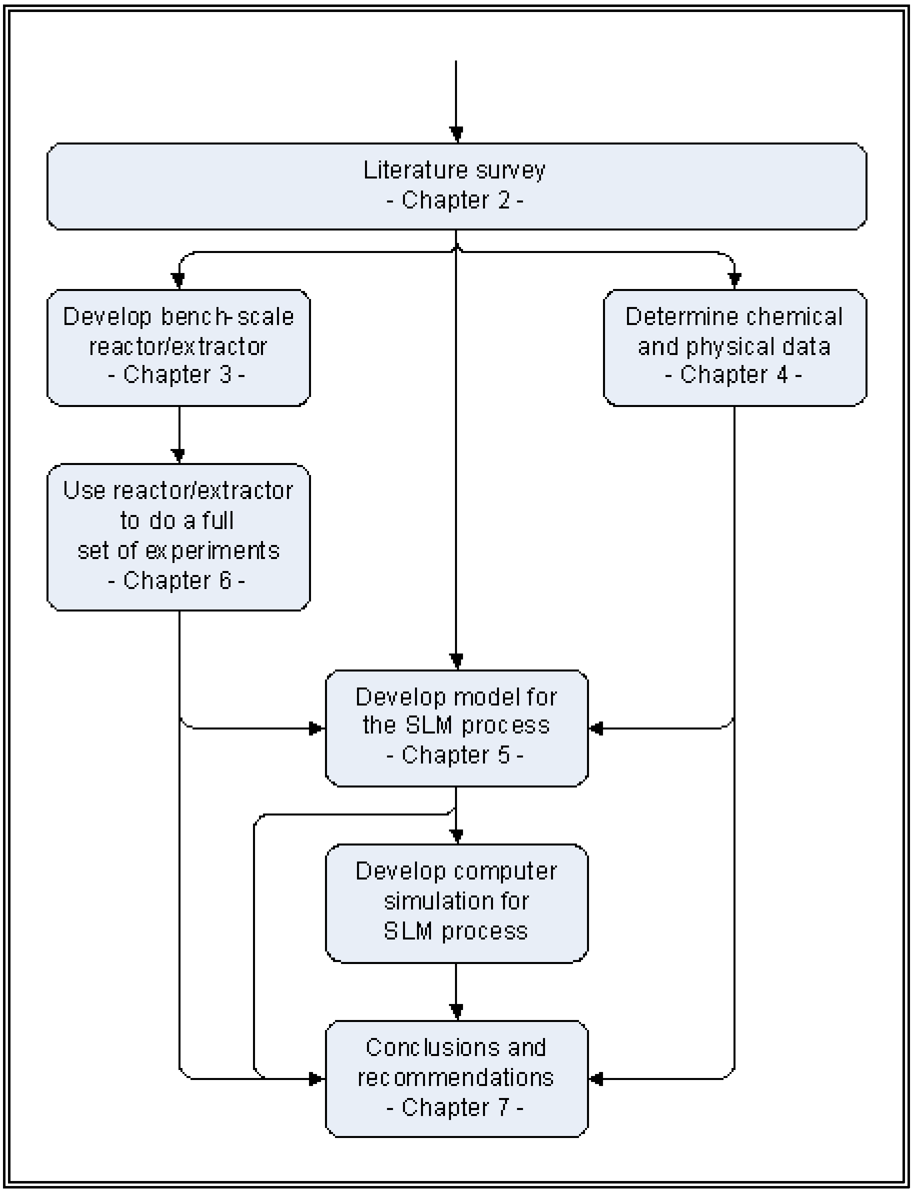

Fig. 1.1: Research path followed in investigation

Chapter 2

Literature survey and theory

"Many receive advice, only the wise profit by it." - *Syrus.*

2.1 Introduction

The literature, principles and data that are necessary to understand this thesis are discussed in this chapter. The concept of supported liquid membranes is discussed and an investigation is done into previous research which investigated supported liquid membranes to extract nickel. The investigation focuses on the approach of other researchers and the modelling of the SLM process. Reference is also made to work done to determine the extraction equilibrium constants. Additionally, some supplementary literature that is indirectly relevant to this thesis is given in Appendix A.

Supported liquid membranes were a further development of liquid-liquid extraction and emulsion membrane extraction and circumvented some of the problems of liquid-liquid extraction, such as poor phase separation and solvent entrainment (Babcock *et al.*, 1980:71). The first patent on supported liquid membranes appeared in 1967 (Li, 1967), but the use of supported liquid membranes are much older, since the transport of oxygen (using the haemoglobin-oxyhaemoglobin reaction) or carbon dioxide (using the carbonate-bicarbonate reaction) are in essence supported liquid membrane processes (Hemmingsen, 1962:733).

Although the use of supported liquid membranes in nature is very common, to date no real industrial application for SLMs has been reported in the literature. The Achilles heel of SLMs seems to be the following:

1. The low stability of the supported liquid membranes.
2. Low metal fluxes.
3. Osmosis through the membranes.
4. The relative high cost of the membrane support.

2.2 Supported liquid membranes (SLM)

2.2.1 Definition

Supported liquid membranes (SLM) represent an attractive alternative to liquid-liquid extraction for the selective removal and concentration of metal ions from solution. The permeation of metal species through SLMs can be described as the simultaneous extraction and stripping operation combined in a single stage. A thin layer of organic extraction reagent (extractant) is immobilized in a microporous inert support. This support is interposed between the feed solution (aqueous phase), in which the valuable metal is dissolved and the second (stripping) phase, in which enrichment of the metal occurs by transmembrane diffusion (Mulder, 1998:340).

Figure 2.1 gives the relationship between the concentration of the feed solution and the optimal metal flux that were obtained by other authors for various periodic group 4 transition metals, against the metal concentration in the feed solution, on a log-log scale. The data and references used for this graph can be seen in Appendix A.4. A few useful conclusions can be made from this graph:

1. It is clear that a large range of metal fluxes were obtained by these authors and it can be concluded that there are many other variables that influence the extraction process.
2. It should be noted that SLM extraction is essentially an extraction method dependent on the membrane area.
3. The fluxes are relatively low and in the light of point 2 it can be concluded that SLM's are more suitable for the extraction of small amounts of metal species from waste streams than it is for the extraction of high concentration leaching solutions.

2.2.2 Mechanism

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

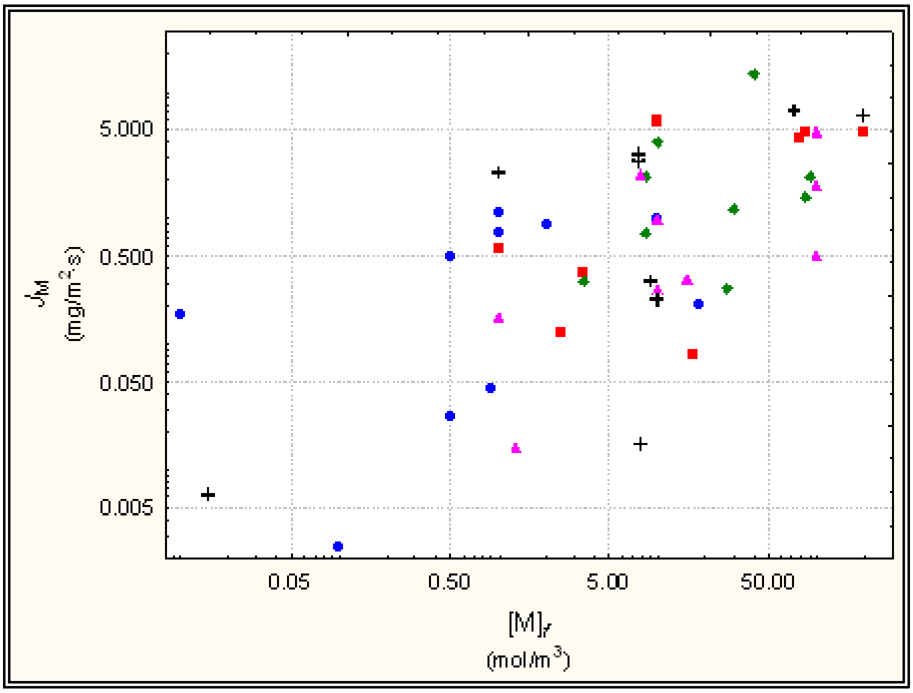

Fig. 2.1: Transmembrane flux for selected metal species. ●: Fe^{3+}; ■: Co^{2+}; ◆: Ni^{2+}; ▲: Cu^{2+}; ✚: Zn^{2+}

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

Two transport schemes mainly dominate the SLM process, 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 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 organic extractant, R, reacts with the metal ion to form a neutral complex, MR_n. This neutral complex can diffuse freely within the organic phase and move across the membrane to the second aqueous (strip) solution. At the interface the metal is released, the carrier reacts with a hydronium ion to obtain a neutral charge and diffuses back to the feed/membrane interface.

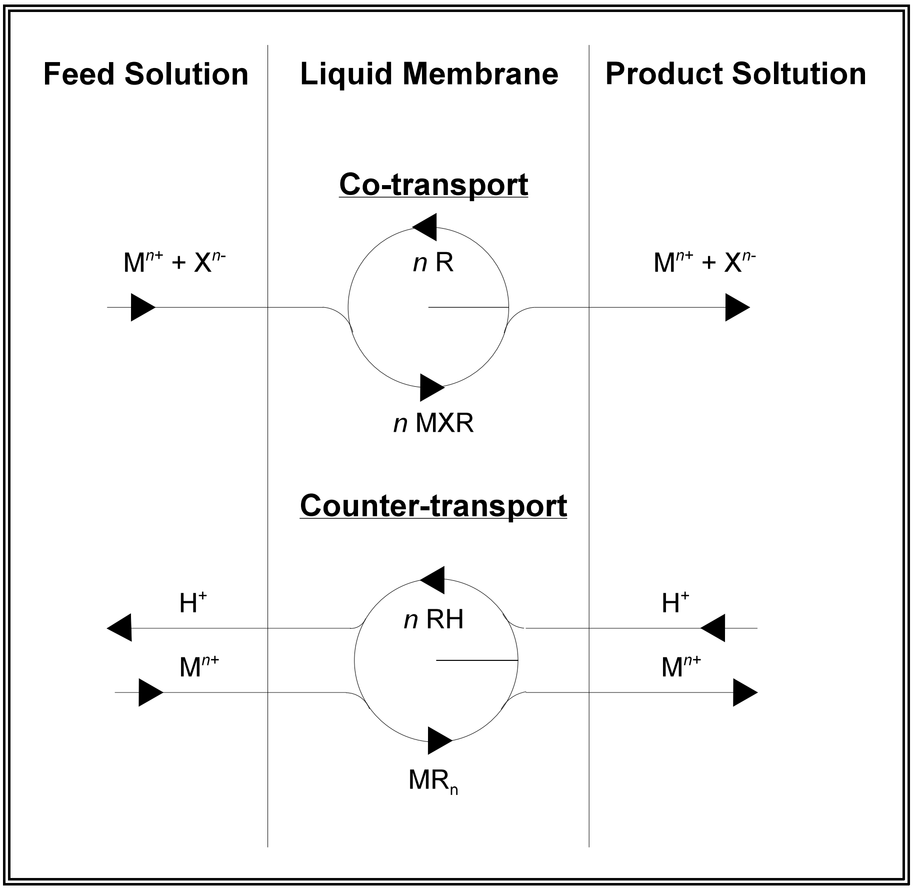

Fig. 2.2: Transport mechanisms across a supported liquid membrane

Previous work by Danesi (1984:876) demonstrated (and experimentally verified) that the steady state permeability across a SLM can be described by the following equilibrium equation:

$$K = \frac{[MR_n]_o \cdot [H^+]^n_{aq,s}}{[M^{n+}]_{aq,f} \cdot [RH]^n_o} \tag{2.1}$$

Equation 2.1 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.

Equation 2.1 describes the final steady state permeability and should not be confused with the extraction equilibrium as discussed in Section 2.3.

2.2.3 Process variables

The most important variables that influence the SLM extraction process are discussed briefly in the following paragraphs.

2.2.3.1 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 an increase in the extractant concentration, since viscosity of the extractant increases with concentration and this has a negative effect on the diffusion coefficient. This was proven in previous research by the author (Smit & Koekemoer, 1997:6) and it was found that the optimum extractant concentration is 60% (by volume) D2EHPA dissolved in Escaid 100. Other authors who also found optimum extractant concentrations and some of the optimum concentrations are mentioned in Table 2.1.

Table 2.1: Optimum extractant concentrations found for different SLM systems

Authors	Metal ion	Extractant	Diluent	Optimum concentration
Gherrou & Kerdjoudj, (2002)	Ag^+	DB18C6	Ethanol / chloroform	0.001 mol/l
Alguacil (2002)	Co^{2+}	DP-8R	Exxsol D100	>40% (vol)
Alguacil *et al.* (2002)	Cu^{2+}	Acorga M5640	Iberfluid	20% (vol)
Sarangi & Das (2003)	Cu^{2+}	D2EHPA	Kerosene	0.2 mol/l
Alguacil & Alonso (2000)	Fe^{3+}	Cyanex 921	Xylene	0.4 mol/l
Alguacil (2002)	Mn^{2+}	DP-8R	Exxsol D100	30% (vol)
Basualto *et al.*, (2003)	Mo^{6+}	Alamine 336	Kerosene	0.02 mol/l
Sarangi & Das (2003)	Zn^{2+}	D2EHPA	Kerosene	0.2 mol/l

2.2.3.2 The effect of pH

All chelating or acidic type extractants used in counter-current extraction processes, liberate a hydrogen ion on the extraction of a metal ion, as seen in Figure 2.2. 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, which in turn leads to a shift in the equilibrium and a decrease in the amount of metal extracted (Erlank, 1984:40, Alguacil *et al.*, 2002:269, Gherrou *et al.*, 2002:238, Yang *et al.,* 2002:40, Gherrou & Kerdjoudj, 2002:92, Basualto *et al.,* 2003:1005).

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

2.2.3.3 Aqueous phase composition

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

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

Conversely, if the metal species in the aqueous phase is uncharged, the 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. The ionic strength also has an effect on the activity of the metal species and therefore, the extraction equilibrium (Atkins, 1990:252, Sarangi & Das, 2003:4).

2.2.3.4 Metal ion concentration

If the metal ion concentration in the system is increased, with 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 (Alguacil *et al.*, 2002:269, Alguacil & Alonso, 2000:85, Gherrou *et al.*, 2002:238, Gherrou & Kerdjoudj, 2002:235, Sarangi & Das, 2003:4). Thus, a relative decrease in the extraction coefficient for that system could result in the limiting case of carrying capacity.

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 are usually replaced by concentration for the sake of simplicity, but activities can change substantially with increasing concentration of reactants.

2.2.3.5 Stirring of the aqueous phase

Hofman (1991) did research on the influence of agitation on a HCC flat sheet SLM (see Section 2.6.3) and found that the rate of extraction increased up to a Reynolds number of 7 000. A further increase in the agitation had little or no effect on the rate of extraction. This may 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. The optimum Reynolds number is dependent on the overall SLM system, but the trend has been confirmed by other authors (Alguacil *et al.*, 2002:268, Alguacil & Alonso, 2000:84, Yang *et al.,* 2002:41, Sarangi & Das, 2003:4)

2.2.3.6 Temperature

Although it is recognised that temperature is an important variable in all the steps in the SLM process and that an increase in temperature should result in an increase in flux (Monlinari *et al.*, 1989, Chaudry, *et al.,*1997:214 and Saito, 1991:1504), little research has been done on the effect of temperature. Gherrou *et al.* (2002:241) found a decrease in the extraction of silver and copper with an increase in temperature and attributed it to either the evaporation of the solvent or the degradation of the SLM due to increased viscosity. Rasul *et al.* (1995:3846) found that the flux of thorium through a SLM, with TBP as carrier and benzene as diluent, forms an optimum at 20 ˚C and attributed it to possible phase separation. Chaudrey *et al.* (1992:143) developed a simplified model that incorporated the Wilke-Chang equation to predict the influence of temperature on extraction. Rockman *et al.* (1995:2455) investigated the phenomenon of thermally enhanced transport, where the temperature gradient across the membrane, rather than a pH gradient is used to effect extraction. The application of this technique is limited by the fact that only a few of the common combinations of aqueous solutions/organic extraction solvents exhibit temperature sensitive equilibrium compositions. Rockman *et al.* (1995) modelled the extraction of citric acid with a tertiary amine with relative accuracy, although the experimental results that were used to verify the model were limited. With the exception of the work of Rockman *et al.* (1995) and Chaudrey *et al.* (1992) the author could not find any modelling of the effect of temperature on the SLM process.

2.2.4.7 The support characteristics

The support has an influence on both the stability and the metal flux through the membrane. The support should be highly hydrophobic for the extraction of metal species from aqueous solutions. The other fundamental properties for the support is the thickness and porosity of the membrane (Gherrou *et al.*, 2002:241, Gherrou & Kerdjoudj, 2002:92, Juang & Huang, 2003:129).

A thicker membrane results in lower flux if the diffusion through the membrane is the rate controlling step, but it also increases the capacity of the membrane to store the extractant solution and therefore, the stability of the membrane. A higher porosity results in a lower tortuosity for the diffusing organo-metallic complex and results in higher fluxes. The higher porosity also increases the capacity of the membrane, but this is countered by a lower support structure and there is a theoretical optimum porosity for optimum stability.

2.3 Di-(2-ethylhexyl)-phosphoric acid

2.3.1 Background

Different solvent extractants are available for the extraction of nickel. In the case of sulphuric acid systems, the extractants available for extraction of nickel perform best in the pH range 4 to 6 (Ritcey & Ashbrook, 1979: 111). Possible extractants are D2EHPA, LIX 64N, Kelex 100, Cyanex 272, PC-88A, Versatic 9 and Naphthenic Acid, among others. It was found that LIX 64N and Kelex 100 are non-selective and co-extracts iron and copper. The extraction characteristics of these two chelating extractants are similar, and pH-dependent, and will therefore give similar results in dilute nitric or hydrochloric acid systems as in the sulphuric acid system. 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.

2.3.2 Physical and chemical properties of D2EHPA

Di-(2-ethylhexyl) phosphoric acid (D2EHPA) is an organophosphorous extractant which is commercially used to extract a number of ions. Its preferred application is for acidic, aqueous metal salt solutions with pH values between 0.5 and 4.5 (Bayer, 1993:3). The structure of D2EHPA is shown in Figure 2.3 (Danesi *et al.*, 1985:438). During the modelling of the SLM process the density and viscosity of the D2EHPA in mixtures of kerosene at different temperatures are important, but this data was however not available in the literature.

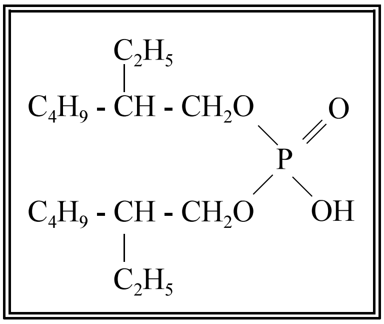

Fig. 2.3: Structure of D2EHPA

2.3.3 Solvent extraction with D2EHPA

The general extraction reaction of D2EHPA with a metal ion, M^{n+}, can be seen in Equation 2.2 and takes into account that, in nonpolar solvents, D2EHPA occurs in the form of dimeric molecules and that the electrically neutral metal complex MR_n is, in addition, coordinatively bound by electrically neutral D2EHPA molecules (Bayer, 1993:5).

General extraction reaction of D2EHPA:

$$M_{aq}^{n+} + \frac{1}{2} m (RH)_{2,o} \rightleftharpoons nH_{aq}^{+} + (MR_n (RH)_{m-n})_o \qquad (2.2)$$

with: M^{n+} : Metal ion in aqueous phase.
$(RH)_2$: D2EHPA dimer in organic phase.
H^+ : Proton in aqueous phase.
$MR_n(RH)_{m-n}$: Organo-metallic complex in organic phase.
n : Number of protons released = valence of metal ion.
m : Total number of bound D2EHPA molecules.

The composition of the metal complex depends on the reaction conditions. At high metal loadings the metal ion will coordinate solely with D2EHPA ions (m=n) to give an electrically neutral complex. At low metal loadings the complex will additionally be solvated by electrically neutral D2EHPA molecules, so that the total number of bound D2EHPA molecules (m) exceeds the charge number (n) of the metal ion (Bayer, 1993:5). In addition to the extra D2EHPA molecules it is also known that D2EHPA solubilises 5 to 6 water molecules (Kasaini, 2001:72).

A single-stage extraction processes can be described by means of distribution curves which illustrate the dependence of the distribution equilibrium on the pH value or by an extraction equilibrium constant K_{nm}:

$$K_{nm} = \frac{\left[MR_n(RH)_n\right]_o \cdot \left[H^+\right]_{aq}^n}{\left[M^{n+}\right]_{aq} \cdot \left[(RH)_2\right]_o^{m/2}} \tag{2.3}$$

The above-mentioned equation does not involve the rate at which equilibrium is attained. It does indicate that, when a reactant or product concentration is changed, the equilibrium will adjust itself so as to keep K_{nm} constant. Other ways to represent distribution equilibrium are:

- The distribution coefficient at equilibrium $D = [MR_n(RH)_{m-n}]_o / [M^{n+}]_{aq}$.
- The percentage extraction $\%E$.

Different K_{nm} values for the Ni/D2EHPA system are found in the literature depending on the aqueous phase and the diluent used. A summary of these values is given in Table 2.2. A possible reason for this large variation in values is that the above-mentioned theory is dependent on a number of assumptions. One of them is that the activity of the species is equal to the concentration of the species. Some of the available percentage extraction versus pH graphs are shown in Figures 2.4 & 2.5. As can be seen, the type of solution as well as the diluent, have an influence on the extraction characteristics.

Table 2.2: Extraction equilibrium constants for D2EHPA with nickel

Aqueous phase	Diluent	K_{25} (m^3/kmol)$^{0.5}$	K_{26} (m^3/kmol)	Reference
Dilute Watts rinse solution	n-heptane		1.40×10^{-4}	Juang & Jiang, 1995
Dilute Watts rinse solution	kerosene	1.16×10^{-5}	5.81×10^{-5}	Jiang, 1993
500 mol/m^3 (Na, H) SO_4	kerosene	1.38×10^{-6}	3.89×10^{-6}	Huang & Tsai, 1989
300 mol/m^3 NH_4NO_3	toluene		2.00×10^{-6}	Danesi *et al.*, 1985
500 mol/m^3 (Na, H) NO_3	n-heptane		4.50×10^{-5}	Komasawa *et al.*, 1981
500 mol/m^3 (Na, H) NO_3	toluene		1.20×10^{-6}	Komasawa *et al.*, 1981
1000 mol/m^3 (Na, H) NO_3	n-dodecaane		2.96×10^{-5}	Grim & Kolarik, 1974

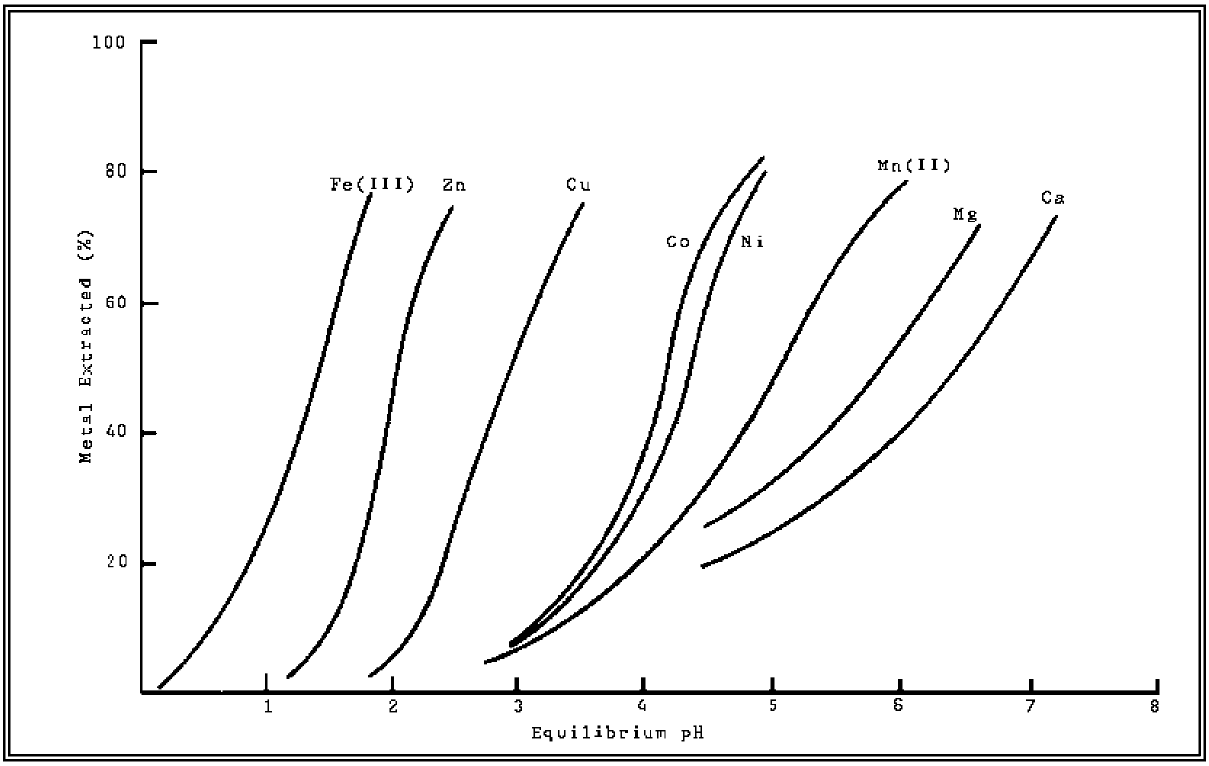

Fig. 2.4: Extraction by D2EHPA in sulphate solution (Ritchey & Ashbrook, 1979:105)

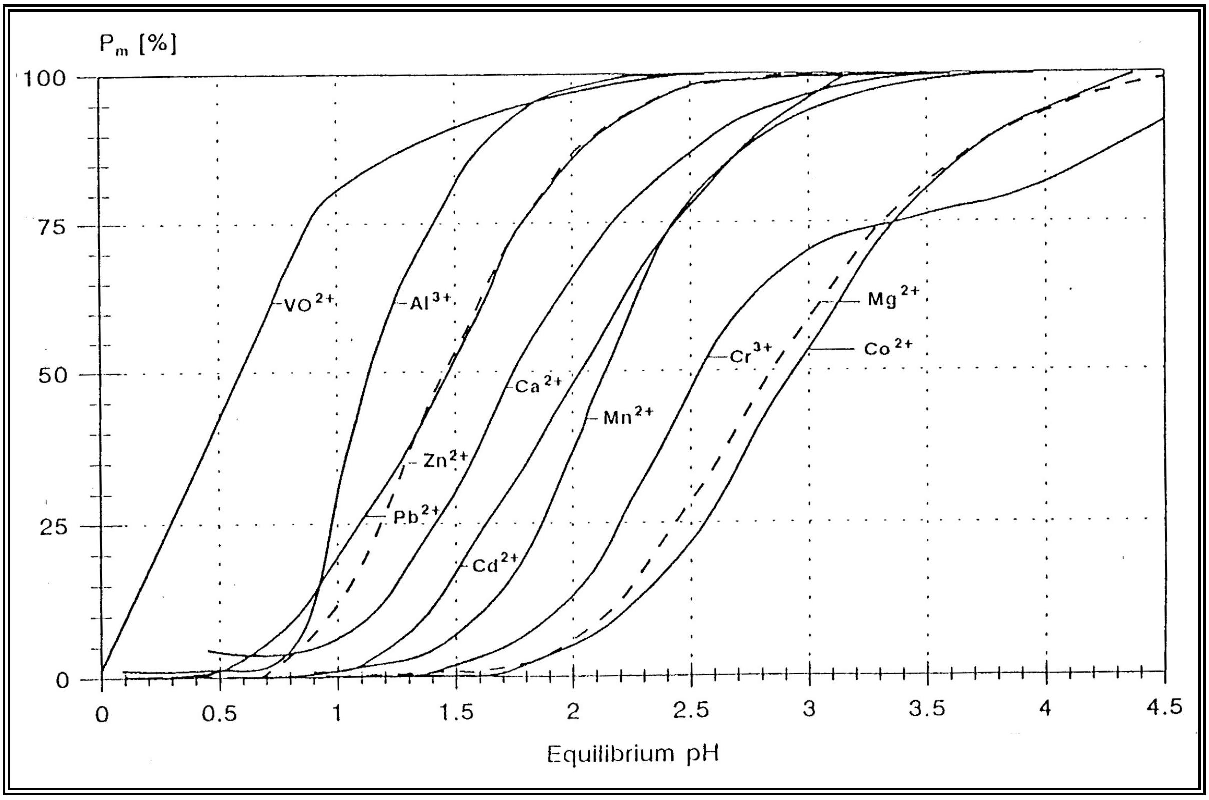

Fig. 2.5: Extraction of 20% D2EHPA with 10% isodecanol (Beyer, 2002:34)

2.4 Modelling of supported liquid membranes

Unlike solvent extraction, facilitated transport can be controlled by diffusion and/or 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 (Mulder, 1988:347).

A large number of process models have been proposed and applied to SLMs (see Table 2.3, page 20 and 21), both in flat sheet and hollow fibre configurations. Depending on the degree of complexity of the process model, the mathematics used can obscure the direct physical meaning of the role that chemical, hydrodynamic and geometric parameters play, making it difficult to clearly analyse the influence of changing these relevant parameters and this led to a preference for simplified models over the more complex process models. However, with the availability of high-speed computers and the development of faster algorithms, numerical simulations can be more readily performed, improving the usability of more complex process models (De Gyves &

De San Miguel, 1999:2183, Juang, 1993:912, Valenzuela *et al.*, 2002:385, Zhang *et al.*, 2002:107, Juang & Huang, 2003:129).

In general, the modelling of supported liquid membranes is based on the permeation of metal species across the SLM in six steps (Hofman, 1991:12; Elhassadi & Do, 1999:306; Juang, 1993:912; De Gyves & De San Miguel, 1999:2184):

1. Diffusion of the metal species (solute) from the bulk feed through the feedside boundary layer to the feed side surface of the SLM.
2. The reaction (or reactions) between the metal species and the extractant at the feed side surface of the SLM.
3. Diffusion across the SLM by the extractant-metal complex (or complexes).
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.
6. The extractant returns to the feed side of the membrane.

In addition to these steps the following two steps can also be included:

7. Diffusion of the extractant species across the aqueous boundary layers.
8. Chemical reaction of the metal-extractant complex with the extractant.

De Gyves and De San Miguel (1999) gave a good overview of existing process models which are summarised in Table 2.3. It is noticeable that almost all the process models deal with the application of Fick's first law and therefore assumes steady-state transfer across the membrane. Another problem with modelling is that different types of metal extraction mechanisms exist, depending on the pH of the aqueous phase, the distribution coefficients, acid dissociation constant, extractant concentration, etc. (Freiser, 1988).

Chemical reactions taking place simultaneously between the monomeric and dimeric species of the extractant and the metal ion (Kanungo and Mohapatra, 1995) and/or the diffusion of both extractant species in the membrane phase (Juang and Lee, 1996) have also been reported. In these process models the dimerisation constant is incorporated in the model as a new equation to be solved.

Table 2.3: Process models for SLM transport

Authors	Steps incorporated in model	Method of evaluation	Advantages	Restrictions
Cussler (1971)	2-4, 6, 8	Calculation of the steady-state flux of two solutes diffusing simultaneously across a carrier-containing membrane separating two well-stirred solutions applying the continuity equations for steady-state diffusion of the solute, the metal-extractant complex, and the extractant.	Analytical expressions for the fluxes and the maximum concentration difference were proposed. Equations show the roles that diffusion, facilitated diffusion, and pumping play.	Boundary layer resistance is not considered. Diffusion coefficients are assumed constant and equal for all the species, partition coefficients are assumed equal at both interfaces, and uncoupled fluxes are considered.
Baker *et al.* (1977)	2-4	Application of Fick's first law for the metal extractant complex in the membrane with the assumption of local equilibrium at the two interfaces. Steady-state flux.	Simple model. In its interval of validation the model correctly accounts for the influence of pH, maximum attainable concentration factor and coupling effects.	Boundary layer resistance is not considered; local equilibrium near the membrane is assumed.
Danesi *et al.* (1981), Komasawa *et al.* (1983)	1-3	Incorporation of the kinetic mechanism of metal extraction with Fick's first law for the diffusion of the metal-extractant complex in the membrane.	Simple model; an analytical solution is obtained.	The simplifications in the model do not allow explicit analysis of the influence of the driving force and calculation of the maximum solute concentration difference achievable. The model doesn't apply with additional resistances.
Ibáńez *et al.* (1989)	2-4, 6	Assumption of steady-state concentration of the extractant complex at both the source and receiving interfaces, combined with the mass balances of the metal ions and the equilibrium constant. Uses Fick's first law.	Allows for the determination of the equilibrium constant and the maximum initial flux. Analytical solu-tions for the metal concentration in receiving phase as a function time for different conditions.	Boundary layer resistance is not considered. Assumptions of equal diffusivity of the chemical species, steady-state concentrations and local equilibrium near the membrane are made.

Table 2.3: Process models for SLM transport (Continue)

Authors	Steps incorporated in model	Method of evaluation	Advantages	Restrictions
Kiani *et al.* (1984), Prasad *et al.* (1986) Prasad & Sirkar (1987) Zha *et al.* (1995)	1-8	The aqueous films and the membrane pore diffusion resistances are combined as a one-dimensional series of diffusion resistances in which the metal transport is described by simple film-type mass transfer coefficients.	The approach is similar to the treatment of liquid-liquid extraction in conventional solvent extractors.	Mass transfer in the films is stationary and of molecular nature. The concentrations have a linear profile; it is considered that equili-brium is instantaneously established at the interfaces.
Pluninshi & Nitsch (1988), Youn *et al.* (1995), Daiminger *et al.* (1996)	1-8	Application of Fick's first law in combination with the governing rate law for the chemical reaction taking place between the metal and the extractant. The resulting equations are numerically solved simultaneously in combination with the mass balance equations.	The metal ion flux can be estimated over a broad range of experimental conditions. If all the characteristic parameters are known, it leads to correct predictions.	Assumptions of steady-state and linear concentration gradients throughout the membrane and the aqueous boundary layers.
Hernández-Cruz *et al.* (1998)	2-4, 6, 8	Fick's second law is applied for the diffusion of the extractant species in the membrane, combined with the extraction equilibrium constant at the two interfaces and the aqueous complex equilibrium constants. Equations are numerically solved.	The model accounts for non-steady-state situations and predicts the concentration profiles of the chemical species within the membrane as a function of time, as well as the concentration of the metal species in the source of the receiving phase.	Diffusion through the membrane is considered to be rate-controlling; i.e., diffusion of the ion through the boundary layers is neglected.

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

A fair amount of work has been done in the past on the extraction of nickel with SLMs and even with emulsion liquid membranes (ELMs). The original work concentrated on the technical feasability of the extraction process with different organic extractants. Although some work is still done on the identification and evaluation of new extractants for the recovery of nickel, the focus of most of the research in recent years has shifted to either the selective recovery of the nickel from solutions containing other ions, or to the modelling of the extraction process. A more detailed discussion of each of these fields will be given in this section.

One of the first articles that reported on the technical feasability of nickel extraction with SLMs was by Cussler and Evans (1980:113) , who proved that nickel can be extracted using a SLM or ELM, with LIX-64N as extractant. The research on supported liquid membranes during the next couple of years was dominated by the research group of Pier Danesi, who also investigated the extraction of nickel (Danesi, 1984-5:857). The recovery of nickel, together with cobalt and iron, from ores, concentrates and residues were extensively researched by Chiarizia and Castagnola (1984:479) under a variety of extraction conditions. Verhaege *et al.* (1987:331), focusing on the Watts nickel bath rinse solution, investigated the possibility of nickel recovery by static membrane extraction. These first studies were typical exploratory studies with the focus on possible industrial applications. The transfer of the technology from bench-scale to pilot plant is however very limited. A four-year project involved in the recycling of nickel from electroplating baths and effluents was started in 1998 on a pilot plant with a total membrane area of 19 m^2 (Anon., 1998:4), but the results of this study were not found in the literature. Another pilot plant, in a bicycle factory in Austria, uses Emulsion Liquid Membranes (ELM) for the recovery of nickel with a throughput of 150 liter per hour (Rupert *et al.*, 1988:1666).

In the ELM-process an emulsion (water-in-oil) of the membrane phase and the stripping phase is prepared. In the permeation step, this emulsion is dispersed in the waste water phase. The only difference between ELM 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 wastewater and enriched by a factor of up to 1000 times the feed concentration. The most important problem with ELM is the osmosis effect. This effect causes water transport from the wastewater 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%. More recent work on the extraction of nickel with ELMs was done by Zhongmao *et al.* (1990:170), Juang and Jiang (1995:163) and Kasaini *et al.* (1998:159).

Several researchers focused on the use of different extractants mixtures to obtain a synergistic effect in the extraction process. Van de Voorde *et al.* (2004:16) tested different mictures containing D2EHPA, LIX 84-I, LIX 860-I, Cyanex 272 and Cyanex 302 and found the highest flux with a mixture of 400 mol/m^3 D2EHPA together with 400 mol/m^3 LIX 84-I. Erlank (1994:97) found that the addition of 18-crown-6-ether to D2EHPA increased the effective extraction of nickel. Gega *et al.* (2001:551) tested for the extraction of nickel and cobalt with D2EHPA, Cyanex® 272, 301 and 302 and found the best extraction with Cyanex® 301, but the best separation between the nickel and cobalt was obtained with Cyanex® 302.

The researchers who investigate the selective extraction of nickel with SLMs usually focus on the separation of cobalt from nickel (Matsuyama *et al.*, 1990:237; Juang, 1993:157; Youn *et al.*, 1997:231; Gega *et al.*, 2001:551; Joeng *et al.*, 2003:499), but studies have also been done on the separation of nickel from iron (Chiarizia *et al.*, 1984:479; Gill *et al.*, 2000:113) and copper (Gill *et al.*, 2000:113).

Gu *et al.* (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 2.6. Gu *et al.* (1986:131) suggested 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 the aqueous-organic interface more densely than the hydrated metal ions. This is favourable for the SLM process. Gu *et al.* (1986:132) tested several ligands and found that acetate gave the best results and the optimum acetate concentration was 0.10 mol/dm^3.

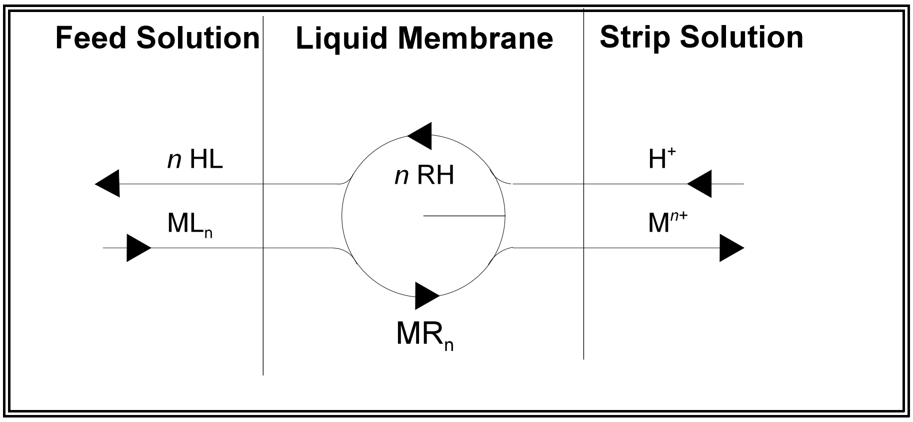

Fig. 2.6: Mechanism of ligand accelerated SLM extraction

The process models that were proposed for the extraction of nickel vary from simple analitical process models (Danesi, 1984-5:857; Van de Voorde *et al.*, 2004:16) to more complex process models that require computer software to solve the model (Juang, 1993:157; Youn *et al.*, 1997:231; Joeng *et al.*, 2003:499) and even process models that consider the non-steady state behaviour of the liquid membrane (Hernández-Cruz *et al.*, 1998:265) and process models that predict the selective extraction by the SLM process (Juang, 1993:157; Youn *et al.*, 1997:231; Joeng *et al.*, 2003:499).

Juang (1993:158) was one of the first researchers to employ the use of computers to solve the complex system of equations that describe the extraction of a multi-component system and he found a good agreement between the process model and the experimental data for the conditions studied. The equilibrium data that he used, however were derived for solutions with a constant amount of sulphate ions in the aqueous phase, which gave rise to the suspicion that the ionic species in the aqueous phase might have a significant influence on the extraction process.

Hernández-Cruz *et al.* (1998:265) developed a process model for the permeation of nickel ions from sulphate solutions through supported liquid membranes. The experimental setup uses two membrane supports with the liquid membrane in-between. This result in a very high capacitance of the membrane, which forced Hernández-Cruz *et al.* (1998:265) to use Fick's second law to describe the non-steady state transport through the membrane. Jeong *et al.* (2003:499) developed a process model for the transport of cobalt and cobalt-nickel mixtures through a Hollow-fiber SLM. The process model mainly focused on the extraction of cobalt and on calculating the concentration profiles along the tube-length.

Once again the main shortcomings of these models were that the effect of temperature, activity of the aqueous species and aqueous speciation, were not incorporated into the process model.

A substantial amount of research on the extraction of nickel with membrane capsules was done by the author (Smit & Koekemoer, 1996; Smit & Koekemoer, 1997). It was found that the membrane capsules did not extract enough nickel to make it economically viable without reuse of the capsules. Most of the variables in the extraction process were investigated and an optimum extractant concentration of 60% (by volume) were found. No modelling was done on the system.

2.6 Configurations for SLM extraction

One of the main goals of this project was to built a bench-scale SLM reactor/extractor. Different contacting devices or SLM reactors/extractors have been used in the past and a short description of these reactors/extractors follows in this section.

2.6.1 The Flat-film contactor

With this reactor/extractor (Figure 2.7) the sealed feed and strip compartments are separated by a suitably prepared SLM (Danesi, 1984:865, Shimidzu *et al.*, 1981:171, Teramoto *et al.*, 1993:3, Buonomenna *et al.,* 2002:259, Zhang *et al.,* 2003:68). Extraction proceeds until "equilibrium" (no further transport) is attained. The disadvantages of this reactor/extractor are:

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

The only advantage the FFC has is the ease of assembly, its cost effectiveness and the possibility of obtaining very rudimentary indicative "Yes/No" results.

2.6.2 The Multi-cell contactor (MCC)

This design endeavours to obviate the main disadvantages of the FFC *viz.* the single extraction result. The MCC is a flow-through variation of multiple FFC's (Baker *et al.*, 1977:220). From the schematic presentation (Figure 2.8) it is evident that each of four windows could effect a different strip solution and/or a different SLM exposed to either a different feed solution or the same feed solution. Any number of permutations and combinations is possible, which renders this reactor/extractor very flexible and able to give quick results to scan the extraction potential for a specific species (Sarangi & Das, 2003:3). Due to the MCC's small size no direct heating can be done, but heating, dosing and measurements can be done in the containers feeding the MCC.

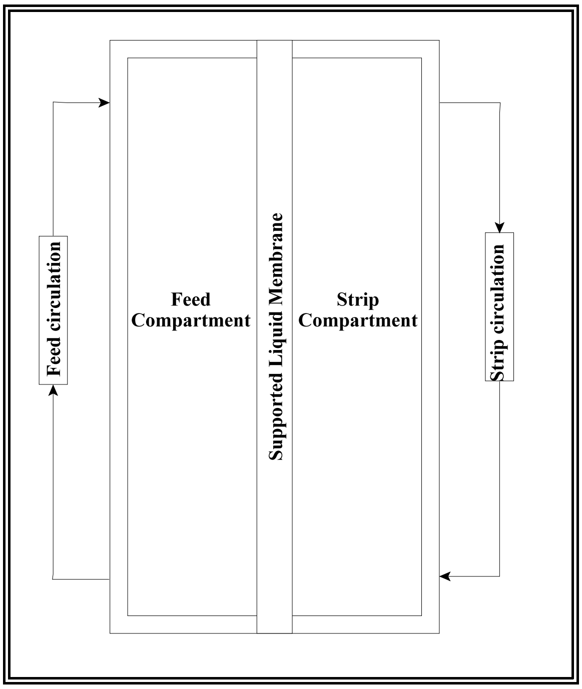

Fig. 2.7: Flat-film contactor (FFC)

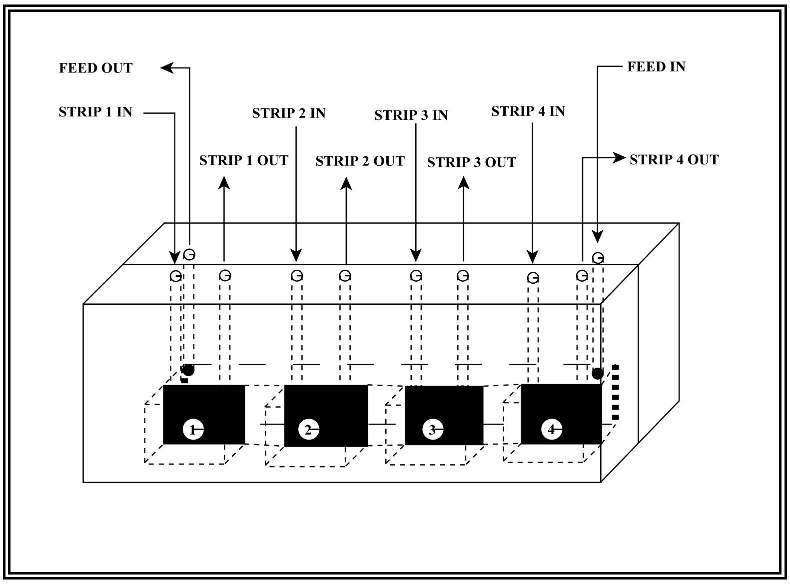

Fig. 2.8: Multi-cell contactor (MCC)

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 (Danesi *et al.*, 1987:122, Lamb *et al.*, 1988:18, Loiacono *et al.,* 1986:125, Ishizu *et al.*, 2003:213). With the variable agitation facility the boundary effects at the aqueous/membrane interfaces can be minimised and kept constant. These attributes render the HCC a powerful and accurate piece of equipment for studying transfer phenomena during SLM extraction. A diagram of a HCC can be seen in Figure 2.9.

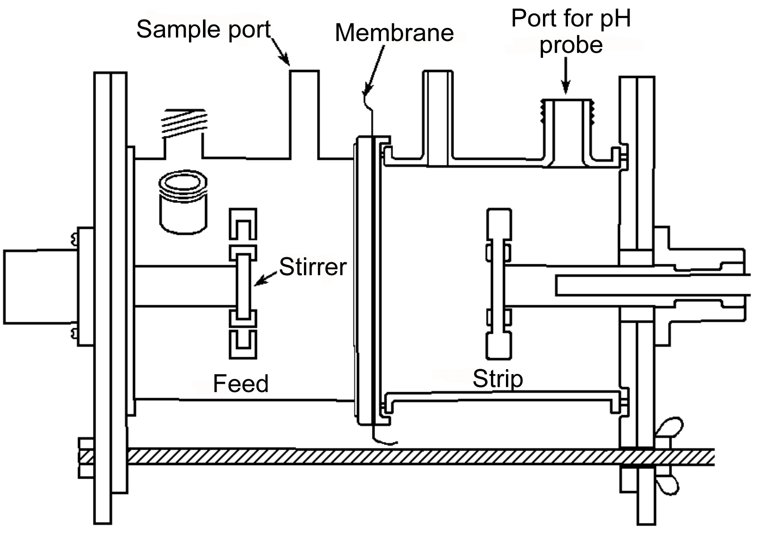

Fig. 2.9: Hydrodynamically characterised contactor (HCC)

2.6.4 The Slurry-flow contactor (SFC)

This configuration is a special reactor/extractor which was developed to demonstrate the possibility of extraction from a slurry into a slurry (Smit, 1994:29). 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 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 was fount that, by flowing these slurries past the membrane, the two aqueous boundary layers are minimised and become almost completely non-existent. A diagram of an SFC can be seen in Figure 2.10.

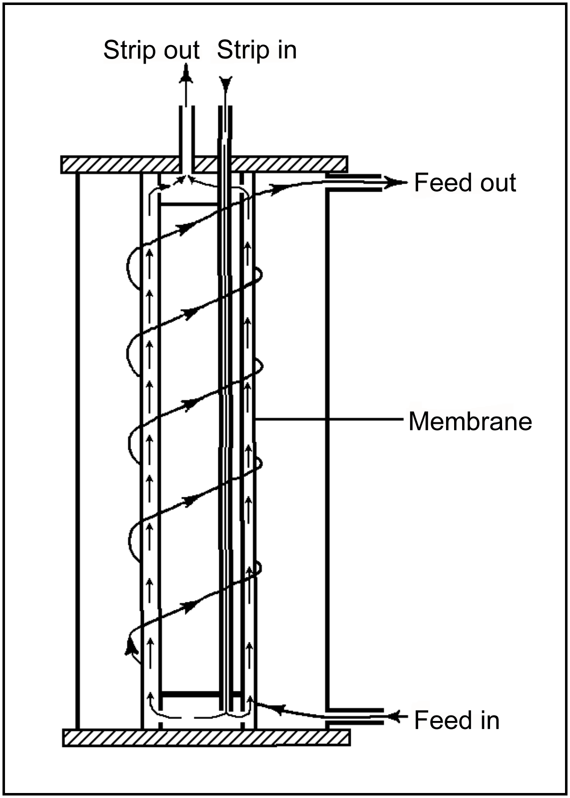

Fig. 2.10: Slurry-flow contactor (SFC)

2.6.5 Spiral-type flowing liquid membrane

This type of reactor/extractor was used by Matsuyama *et al.* (1990:237) and Ketzinel *et al.* (1976:525). In this type of reactor/extractor 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 reactor/extractor is shown in Figure 2.11.

Heavy metal ions were successfully recovered and concentrated from dilute solutions with this type of reactor/extractor. 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 reactor/extractor.

2.6.6 Double membrane contactor

In this reactor/extractor two sets of microporous hydrophobic membranes are used. The extractant solution is placed between the two membranes and is usually recycled (Guha, *et al.*,

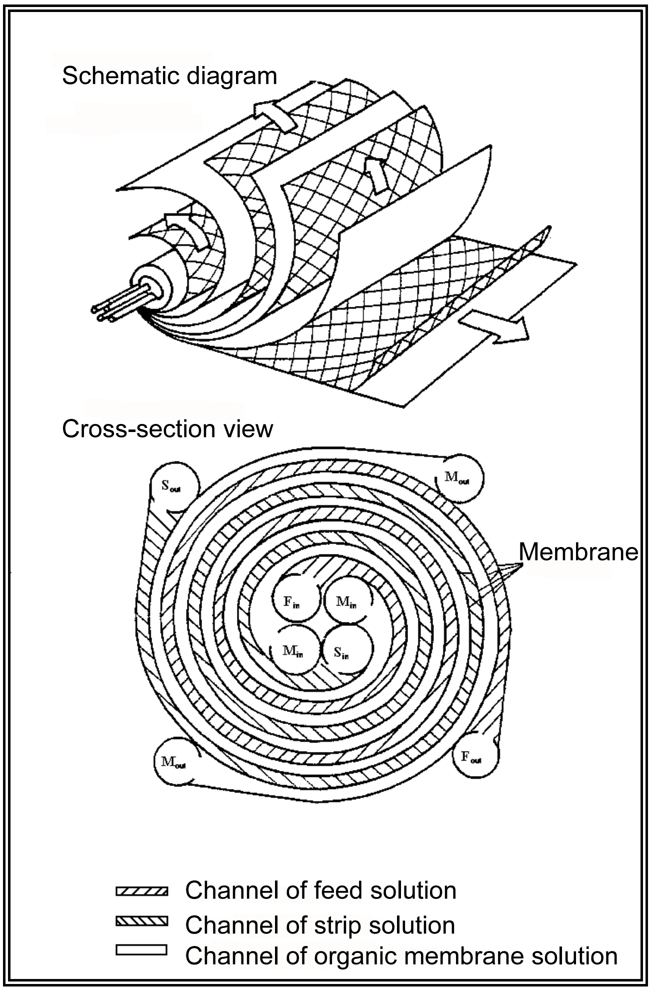

Fig. 2.11: Spiral-type flowing liquid membrane

1995:1999, Schlosser & Rothova, 1994:766, Sengupta, *et al.*, 1988:1699, Agrawal, 2002:876). The advantage of this reactor/extractor is that the problem of membrane stability is greatly reduced (possibly even eliminated). The disadvantage is that diffusion has to take place across two membranes and since this step is usually rate limiting, this can half the flux. The extra extractant also leads to a much larger membrane capacity and steady state conditions take much longer to reach.

2.6.7 Capsule membrane extraction (CME)

All of the above-mentioned reactor/extractor configurations (reactors/extractors) have the singular 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 (Koekemoer, 1996:95, Verhaege *et al.*, 1987:332) The extractant is supported in the membrane skin and the capsule is submerged in the feed solution. The CME configuration has the additional advantage that a very high acid concentration can be used in the strip solution without the risk of high corrosion. If the capsules are saturated in the reticulation system, tank or dam they can be retrieved by straining, followed by regeneration. The disadvantage of this configuration is that the capsules have to be broken to remove the strip solution. The process will therefore only be cost effective if the value of the metal extracted is substantially higher than the cost of the capsule. This is not the case for the extraction of nickel (Koekemoer, 1996:95)

2.6.8 Tubular membrane reactors

Another popular membrane configuration is the use of several membrane tubes or hollow fine fibres in a single configuration (Danesi, 1984:231, Dworzak & Naser, 1987:681, Kubaczka, *et al.*, 1998:906, Loiacono *et al.* 1986:126, Peretti *et al.*, 2001:193, Juang & Huang, 2003:129). These modules are usually “off the shelf” microfiltration modules and are not designed for supported liquid membranes. The significance of this is that the flow of the aqueous medium in microfiltration is through the membrane, while in supported liquid membranes, the flow is parallel to the membrane.

2.7 Applications in the industry

2.7.1 Introduction

The initial motivation for this project was to investigate an alternative to recover nickel from effluents that originate from the nickel plating industry. It is therefore appropriate to take a closer look at the requirements for effluent treatment in the South African context and the nickel plating process itself. 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.

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 nuisance value or otherwise with widely variable economic value. The basic needs for water recovery in industry and the environment are therefore contained in the following:

1. To demineralise effluents containing valuable metals with its associated cost incentive as the driving force.
2. To demineralise effluents containing nuisance metals to foster sustainable ecological development.
3. To decontaminate effluent of other chemical 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 both be economically and environmentally justifiable.

2.7.2 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) was used in electroplating.

The most common type of electroplating solution for nickel can be seen in Table 2.4 (Anon., 1970:684) and is known as the Watts solution. The rate of deposition is between 0.0008 and 0.0053 in/h (0.0203 - 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 in order to have the maximum amount of nickel ions available and to achieve a high current density.

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 (Figure 2.12 A). The degreasing action is sometimes assisted by an electric current. After degreasing, the articles are rinsed in a steel rinse tank (Figure 2.12 C), with flowing cold water. The articles are placed in a lead lined tank containing cold dilute acid, to etch the articles lightly (Figure 2.12 B).

Table 2.4: Composition and properties of a 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

The articles are placed in the nickel plating tank (Figure 2.12 D). The nickel plating solution is held in an open topped, lead or rubber lined tank. The solution is heated by submerged steam or electric heaters. A temperature of at least 35 ˚C is usual, but because faster electroplating can be achieved at higher temperatures, the baths are often operated at temperatures up to 65˚ or 70˚C. The plating solution is usually agitated by compressed air, which is blown in through a perforated pipe on the floor of the tank.

The tank is provided with a central metal rod at the top, from which the articles 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 intermittently.

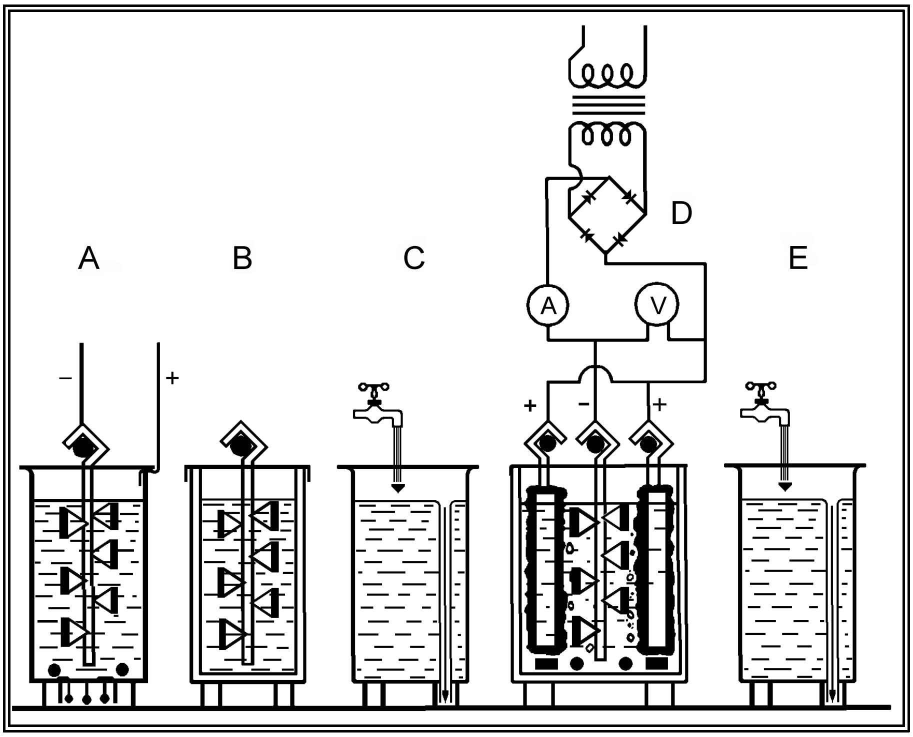

Fig. 2.12: Schematic representation of a simple plating plant

After the predetermined 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 (Figure 2.12 E) and then dried, usually in a current of warm air.

Many other types of nickel plating baths have been advocated, mostly based on nickel sulphate, although nickel chloride and nickel sulphate 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 depleted 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 less effluent (spent bath) must be discharged.

2.7.3 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 2.5 (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 in which no more MTO's could be attained.

Table 2.5: 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	

2.8 Conclusions

The following conclusions can be made from this literature review:

- Supported liquid membranes are a further development of liquid-liquid extraction and has the following advantages:
  - It circumvents the problems of poor phase separation and solvent entrainment.
  - Good separation and selectivity can be obtained.
  - The process can handle slurries.
- No commercial applications for SLMs were found in the literature. Possible reasons for the resistance for this technology to be applied in an industrial application is:
  - Low stability of SLMs
  - Low metal fluxes
  - Osmosis through membranes
  - Relative high cost of membranes
- The extraction mechanism is a combination of extraction equilibrium and diffusion.
- Although a large number of process models have been applied to SLM, they tend to make assumptions to simplify the system and to get analytical solutions for the process model. The process model usually concentrates on certain aspects of the extraction

process and there is a need for a process model which takes cognisance of all the variables involved in the SLM process.

- The most important variables in the SLM process are the extractant concentration, the pH of the feed and strip solutions, the aqueous phase composition, the metal ion concentrations of the feed and strip solutions and temperature.
- Di-(2-ethylhexyl) phosphoric acid (D2EHPA) is an organophosphorous extractant and can bind coordinatively in different forms with metal ions. The equilibrium constant for the nickel-D2EHPA system is very sensitive and a large range of values is given for the equilibrium constant(s) in the literature.
- No literature reference was found that describes the temperature dependence or the effect of ion speciation on the nickel-D2EHPA system.
- Different reactor/extractor configurations are available for SLMs. The disadvantage of most flat sheet membrane reactors is a low membrane area to reactor volume ratio. The problem with most of the tubular membrane reactors/extractors is that they are not designed for SLM, but for microfiltration and this results in unequal flow distributions between the feed and strip solutions.

Chapter 3

Development of bench scale reactor/extractor

"Unless you try to do something beyond what you have already mastered, you will never grow." - Ronald E. Osborn

3.1 Introduction

The development of a new technology from the original idea to a full-scale industrial factory usually takes the following path:

1. The conceptual idea is formed.
2. Laboratory tests are done to test the technical feasibility of the idea.
3. A bench-scale reactor is built to test the techno-economic feasibility of the idea.
4. A pilot plant is built and the final troubleshooting and upscaling is done.
5. The final plant is designed and built.

In recent years, with the dramatic advances in computer simulation software, step 4 is often replaced (if possible) by computer simulation before the final plant is built. The motivation for building a bench-scale reactor/extractor is the following:

1. The reactor/extractor is built according to a process flow diagram that will closely resemble an industrial application and the technical feasibility of the process, rather than just the technical feasibility of the scientific phenomenon is determined.
2. With the building of the bench-scale reactor/extractor, possible construction and operating pitfalls can be identified.
3. The bench-scale reactor/extractor is used to generate production data and this data can be used to develop a computer simulation of the process. The simulation will then take cognisance of variables that are important from both a scientific as well as an engineering point of view.
4. The bench-scale reactor will give a good idea of the scientific feasibility of the process, as well as a first indication of the economic feasibility of a possible industrial application.

A schematic diagram of the steps involved in developing the bench-scale apparatus in this study can be seen in Figure 3.1 (Coulson & Richardson, 1983:8). The design and development procedure is an iterative procedure and in this section, only the final iteration is discussed for each step.

3.2 Equipment

To give a realistic size to the reactor the design specification was defined as follows: The SLM reactor/extractor should extract 60% of the nickel in a 100 mg/litre solution with a flow rate of 10 litres/hr at optimum conditions. The requirement for the extraction of nickel from low concentration effluent streams would usually be much higher than the above-mentioned specification, but the experimental apparatus should also give enough leeway to investigate all the variables that were important in the extraction process. A secondary design specification was that a single experiment should take less than two hours to complete.

3.2.1 Membrane selection

The support for the supported liquid membrane is usually a commercial microfiltration membrane. This membrane should have the following properties (Gill *et al.*, 2000:114):

1. Thin membrane wall.
2. High porosity.
3. The membrane should be fairly flexible, yet have good mechanical strength.
4. Good chemical resistance.
5. Small pore size.
6. High hydrophobicity.
7. Low cost.

After a screening process, in which different hydrophobic tubular microfiltration membranes were evaluated, it was decided to use the Accurel® PP Q3/2 membranes (see Fig. 3.2) The properties of this membrane can be seen in Table 3.1.

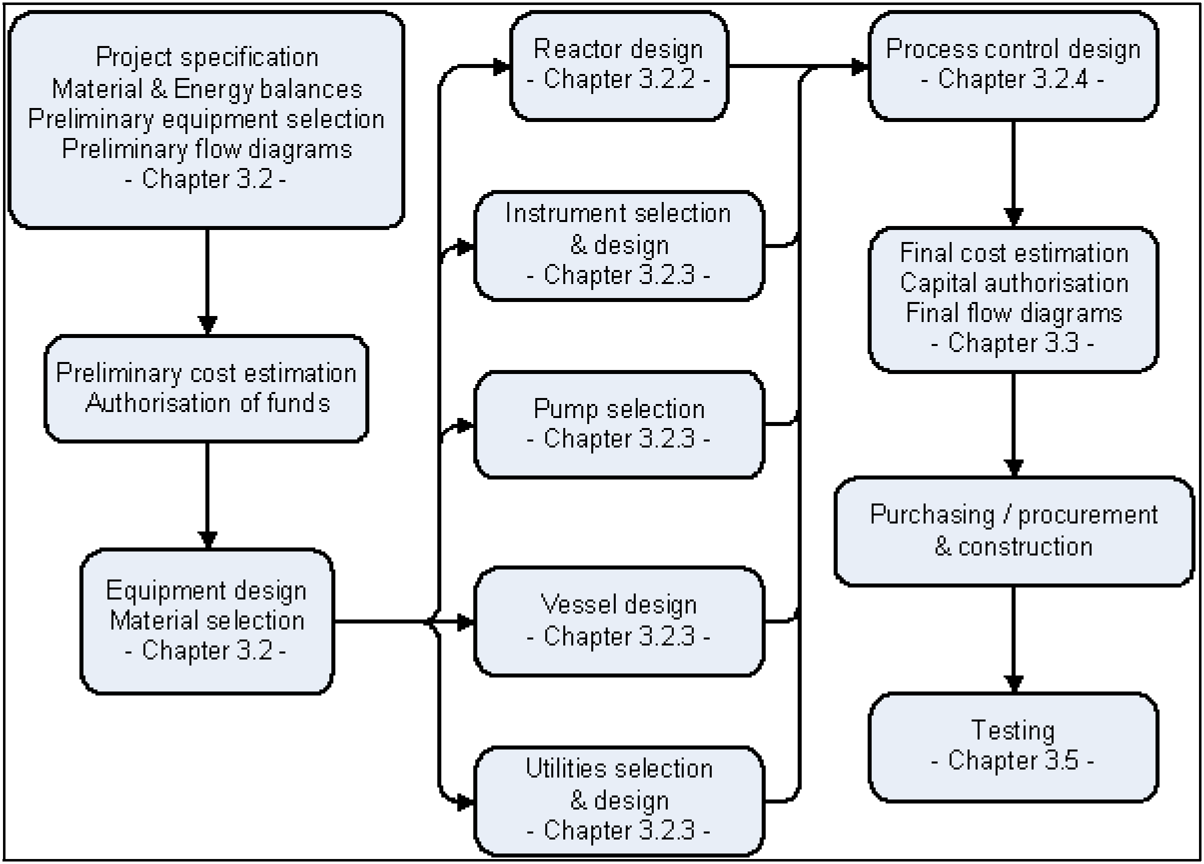

Fig. 3.1: Development procedure for bench-scale apparatus

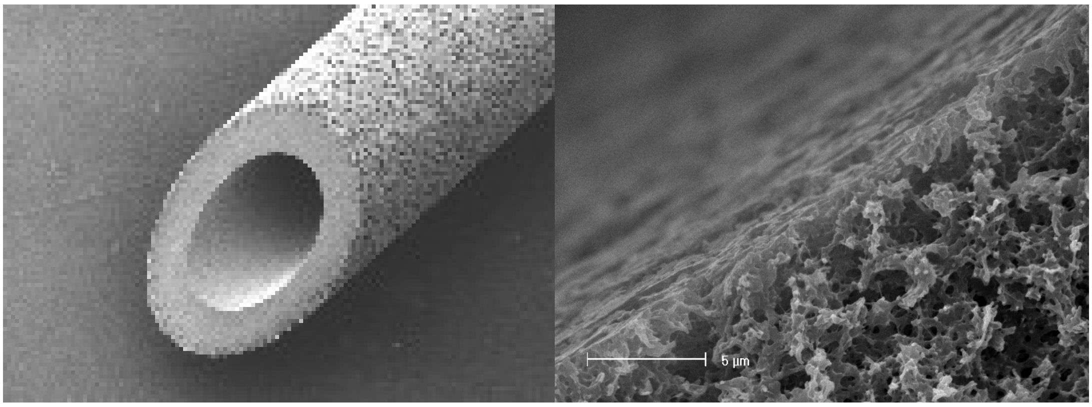

Fig. 3.2: Accurel® PP Q3/2 membrane. Membrane tube on left and magnification of membrane on right

Table 3.1: Properties of Accurel® PP Q3/2 membrane

Pore size	
nominal	0.2 μm
maximum	0.65 μm
Inside diameter	600 μm
Wall thickness	200 μm
Burst pressure	10 bar
Porosity	55 %

3.2.2 Reactor/extractor design

Different reactor/extractor configurations are available for supported liquid membranes, as discussed in Section 2.6. It was decided to use a tubular membrane module. This module use the same design method that is currently being used for the design of heat exchangers. The main reasons for using this type of reactor/extractor configuration are the following:

1. Ease of construction.
2. The membranes can be replaced if necessary.
3. All the relevant variables which influence the process can be easily measured or derived from measurements.
4. Relative low cost of construction.

From previous experiments it was shown that, at optimum extraction conditions, an extraction of 1.25 mg/m^2·s could be expected (Smit & Koekemoer, 1997:344). The design specification for the reactor was that the reactor/extractor must extract 60% of the nickel in a 100 mg/litre solution with a flow rate of 10 litres/hr at optimum conditions. This means that at a nickel flux of 1.25 mg/m^2·s, the minimum membrane area should be 0.133 m^2. A membrane length of 300mm requires that there should be at least 142 membranes in the reactor/extractor. The final design is summarised in Table 3.2 and a schematic diagram of the reactor/extractor and an endplate can be seen in Figures 3.3 and 3.4 (page 42). In the final design 159 membranes were used, so the reactor/extractor was overdesigned by 12%.

Table 3.2: Reactor/extractor design specifications

Number of tubes	159
Configuration	1 tube-pass and 3 shell-passes
Bundle diameter	35.7 mm
Shell diameter	40 mm
Tube pitch	2 mm square
Material of construction	Polypropylene

There are three baffles in the shell. The tubes are sealed into the end-pieces on the tube-bundle with a resin and the tube-bundle is in turn sealed inside the shell, by means of o-rings. There are two parameters that are important for the design of the reactor/extractor. The first is the amount of nickel that can be adsorbed into the membranes (i.e. the capacity of the membranes). The membrane support can hold 13.2 ml of liquid membrane and if a 1200 mol/m^3 D2EHPA solution is used, it can hold a maximum of 198 mg nickel (according to the equilibrium determined in section 4.3), if the aqueous solution has a nickel concentration of 60 mg/l with a pH of 4.0. If this is compared to the total nickel in the aqueous solution, it means that 15.7% of the nickel can be stored in the membrane. It was however found that the actual nickel concentration absorbed in the membrane during the experiment is much less (see Section 5.6). The other important parameter is the time it will take for the metal-organic complex to diffuse through the membrane (breakthrough time). The average breakthrough time (t_b) can be calculated with the following equation (Bird *et al.* 1960:126):

$$t_b = \frac{\delta^2}{16 \cdot D_{eff}} \tag{3.1}$$

Where D_{eff} is the effective diffusion coefficient as estimated by the Wilke-Chang estimation and δ is the membrane thickness. The breakthrough time was estimated to be 3.7 minutes, which is relatively fast, if it is considered that the time needed to reach steady state conditions in an experiment was 2 hours.

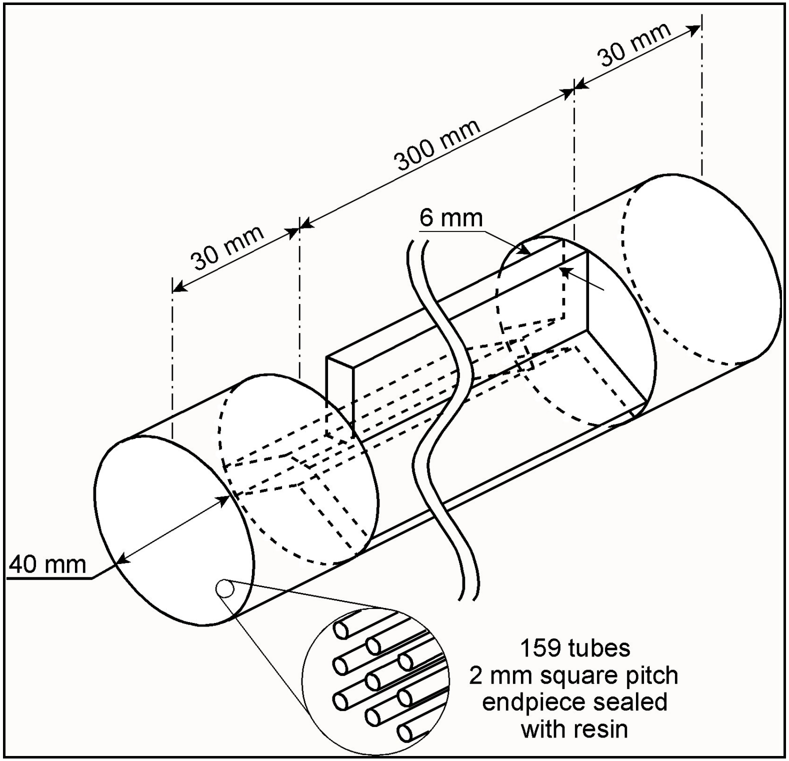

Fig. 3.3: Shell-side layout of reactor/extractor

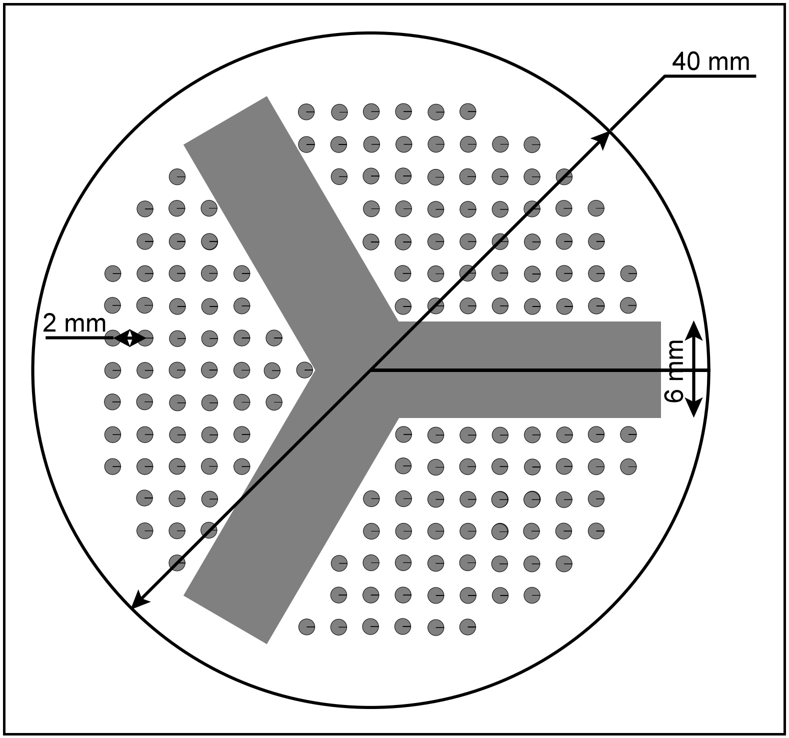

Fig. 3.4: Tube layout of reactor/extractor

3.2.3 Other equipment

A list of the other equipment used and the specification of the equipment can be seen in Table 3.3 (page 45).

3.2.4 Process control

The temperature of the feed and strip solutions as well as the pH of the feed solution was controlled, using Adam^{TM} control blocks in combination with the VisiDAQ software package. The flow through the reactor was controlled manually. The temperatures of the feed and strip solutions were controlled with a cascade control system, with the master control loop controlling the temperature of the bulk solution as it entered the reactor by changing the setpoint of the controller for the temperature near the heating elements. A normal PI-controller was used to control the pH.

3.3 Flow diagram

The flow diagram for the reactor/extractor system can be seen in Figure 3.5. The feed and strip solutions are kept in 0.021 m^3 tanks and are then fed to tank T01 (feed) and tank T02 (strip). The temperature of the feed- and strip solutions is controlled in the tanks using a cascaded control system. The pH of the feed solution is also adjusted in the feed tank using an automatic titrator. The feed and strip solutions are pumped to the reactor/extractor (R01), where the extraction occurs. The feed and strip solutions (also known as the raffinate and extract) are then recycled to T01 and T02 respectively. The flow of the feed and strip solutions through the reactor is controlled with valves and a direct recycle stream on each tank. Photographs of the bench-scale apparatus can be seen in Figures 3.6 - 3.9.

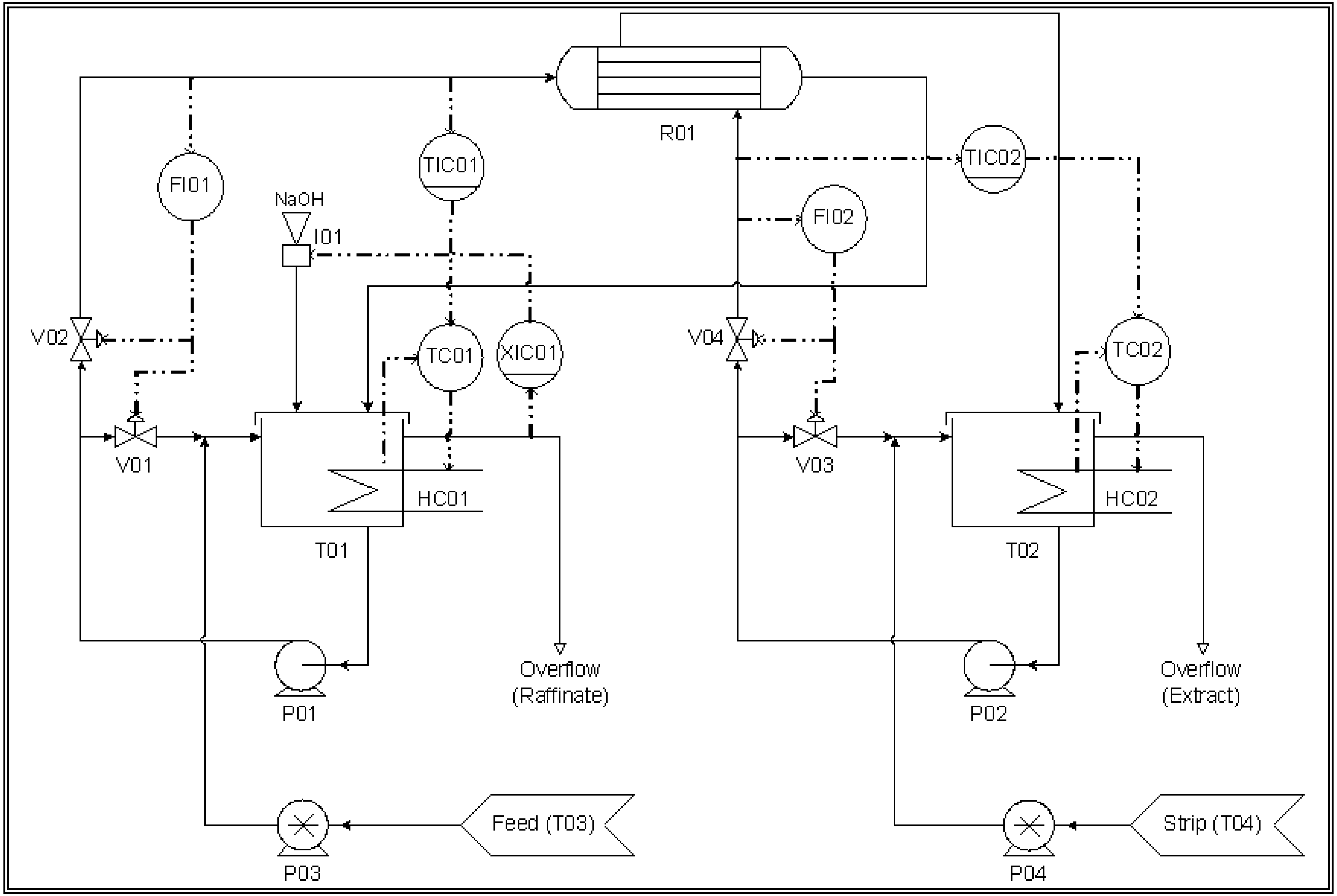

Fig. 3.5: Flow diagram of bench-scale apparatus

Table 3.3: Equipment list for process flow diagram

Equipment number	Type of equipment	Name and model of equipment	Specifications of equipment
FI01, FI02	Flowmeters	Two Krohne H250 C M9 rotameters	Measurement range = 63 - 630 l/hr
HC01, HC02	Utility	-	Two 1.5 kW electrical elements
P01, P02	Recycle pumps	Cole-Parmer E-75225-15 magnetic drive pumps	Maximum flow rate = 1590 l/hr ΔP (maximum) = 21.1 m Operating temperature = 0 - 90 ˚C
P03, P04	Feed pumps	Masterflex L/S 07520-40 peristaltic pumps	Maximum flow rate = 28.8 l/hr Operating temperature = 0-90 ˚C
R01	Reactor/extractor	-	See Table 3.2
T01, T02	Feed and strip recycle tanks	-	Volume (feed)[1] = 5 l Volume (strip) = 4.1 l
T03, T04	Feed and strip tanks	-	Volume = 21 l
TC01, TC02	Temperature measurement and control	Type "J" thermocouples	Control element temperature with GM controller
TIC01, TIC02	Temperature measurement and control	Type "J" thermocouples	Control reactor/extractor inlet temperature. Cascaded onto TC01 & TC02. Output is displayed on control computer
V01, V03	Control valves for recycle flow through reactor/extractor.	-	Globe valves
V02, V04	Valves in direct recycle to T01 and T02	-	Ball valves
XIC01	pH measurement and control	Metrohm 691 pH-meter	
I01	Sodium hydroxide titration	Metrohm dosimat 715 titrater	Syringe size = 20 ml Accuracy = 0.001 ml

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[1] The total volume (including the reactor volume and liquid holdup in the pipes)

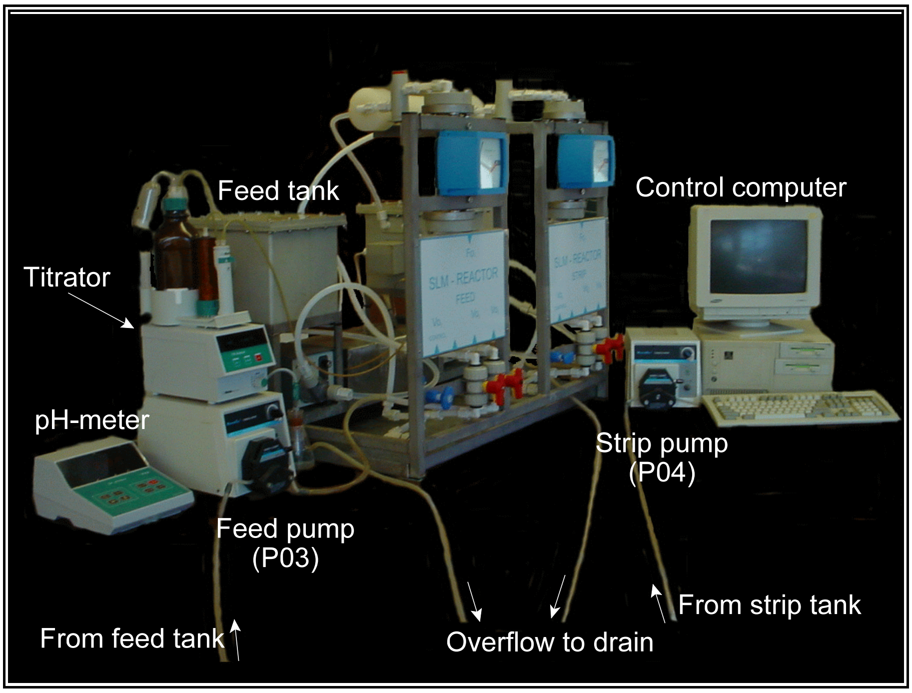


Fig. 3.6: Photograph of experimental setup, including control equipment

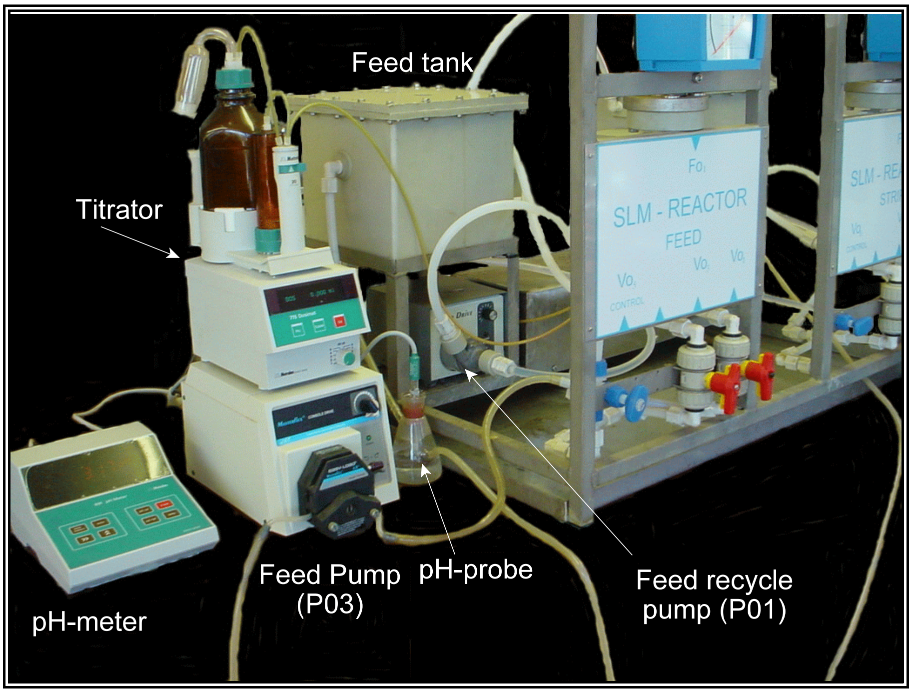


Fig. 3.7: Photograph of pH-meter, titrator and feed recycle tank

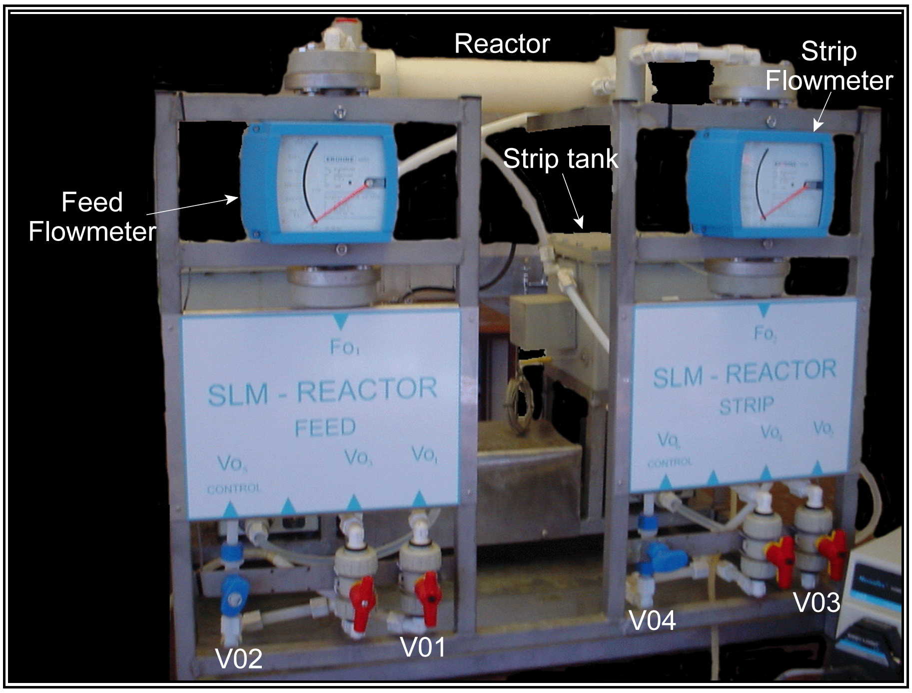


Fig. 3.8: Front view of experimental apparatus, showing feed and strip flowmeters

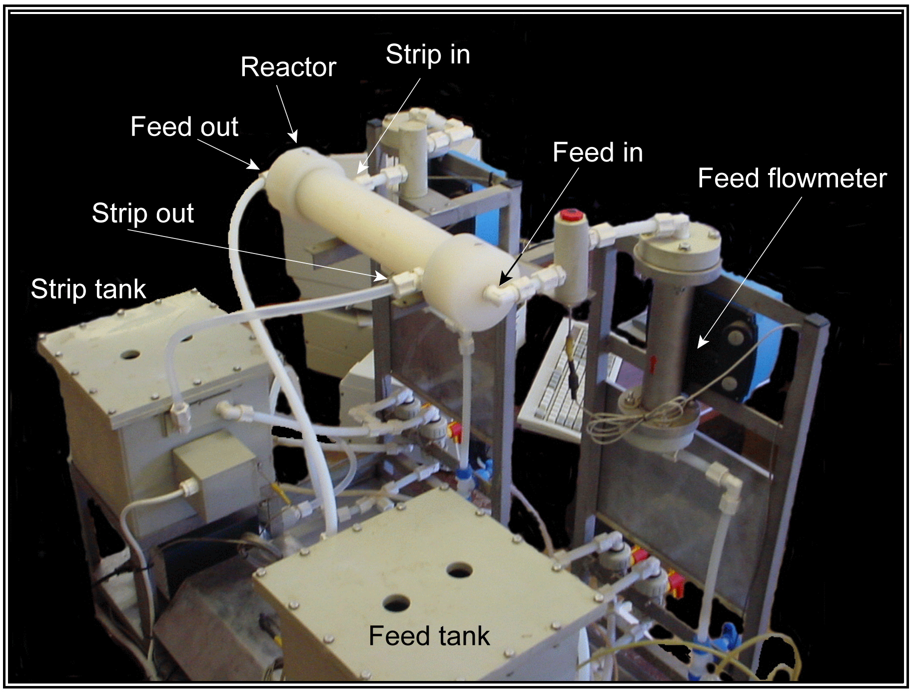


Fig. 3.9: Top view of experimental apparatus

3.4 Operating procedure

In an industrial plant the aim of the startup procedure is usually to achieve steady state conditions. In this thesis however, startup refers to the procedure that was followed in preparation for the point where measuring commenced. The operating procedure continued from the startup to the point where steady state conditions were obtained and was then directly followed by the shutdown procedure. The total procedure was designed in a way that the measurements would give accurate results with no contamination from previous experiments and in a way that the experiments were safe and efficient. A more comprehensive description of the operating procedure for the bench-scale apparatus can be seen in Appendix B.2.

The supported liquid membrane was prepared by disconnecting the reactor from the bench-scale experimental apparatus and filling it with the membrane solution (D2EHPA dissolved in kerosene) and leaving it for a minimum period of 30 minutes. The feed and shell side was then flushed with distilled water for 10 minutes each, to remove any excess membrane solution. This procedure was done once a day or after every two experiments (if more than two experiments were done on a day) to regenerate the liquid membrane.

3.5 Testing of bench-scale experimental apparatus

The main purpose during the testing phase of the bench-scale apparatus was to make sure that it could be used for the experiments. These experiments mainly focused on the following questions:

- Does all the equipment work as specified?
- Do the controllers work?
- Do the experiments result in reliable data (can the mass balance be reconciled)?
- Is steady state reached within a reasonable time?

To accomplish this, a number of experiments were done and the results showed that the equipment did indeed perform as specified. The controllers worked well (as discussed in Section 3.2.4). The flux through the membrane can be calculated from a dynamic mass balance over either the feed side or the strip side of the experimental apparatus (see Equation 5.1 and 5.2 in Section 5.3). If the nickel concentration of the feed and strip solutions are measured and used to calculate the flux through the membrane it should, therefore, give the same results. To test this an experiment was done under the following conditions:

- Nickel feed concentration = 60.4 mg/l
- Nickel strip concentration = 59.5 mg/l
- Setpoint for pH controller = 4.0
- pH of strip solution = 0.99
- Setpoint for temperature controller = 50 ˚C
- Recycle flow rate for feed solution 300 l/hr.
- Recycle flow rate for strip solution 300 l/hr.
- Extractant concentration = 1200 mol/m^3.

The results of the experiment can be seen in Figure 3.10. The difference between the calculation of the feed and strip solutions can be attributed to inaccuracy in the measurement of the nickel concentration of the feed and strip tanks. The results are satisfactory and there is a 98.2% correlation between the flux calculated with the feed solution and the flux calculated with the strip solution. This experiment also shows that the results reach steady state values at about 120 minutes.

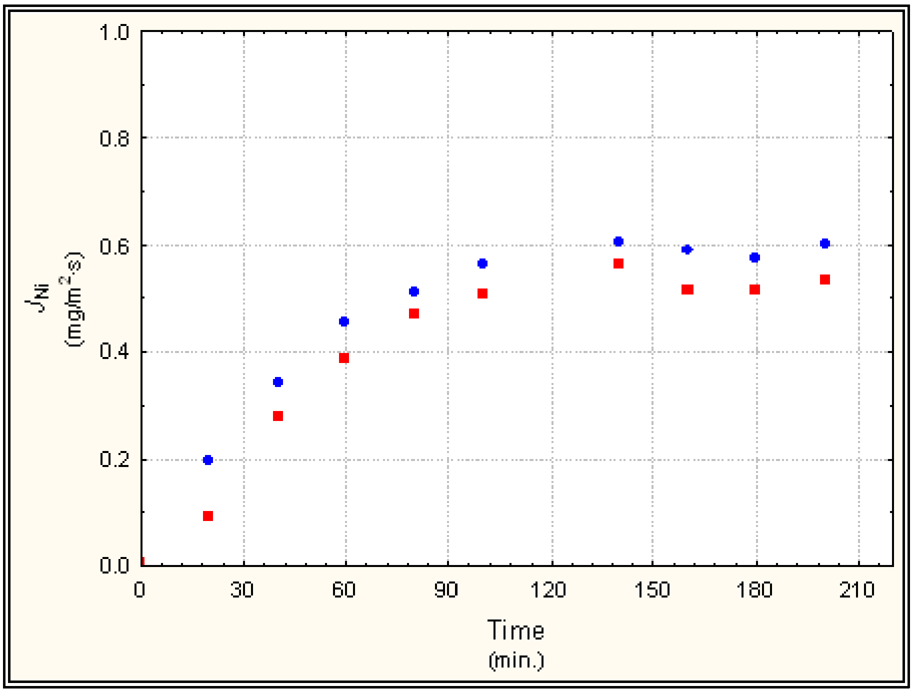


Fig. 3.10: Results of test experiment with $[Ni]_{FT}$ ≈ 60.4 mg/l, $[Ni]_{ST}$ ≈ 59.5 mg/l, $pH_{f,sp}$ = 4.00, pH_s ≈ 0.99, $F_f = F_s$ = 300 l/hr, T = 50 ˚C & $[RH]_{Total}$ = 1200 mol/m^3. ●: Flux calculated from feed. 🟥 : Flux calculated from strip.

Chapter 4

Determination of physical and chemical data

> *"Perfect as the wing of a bird may be, it will never enable the bird to fly if unsupported by the air. Facts are the air of science. Without them a man of science can never rise."* -
> *Ivan Pavlov*

4.1 Introduction

The determination of the physical data that was needed for the modelling of the process is discussed in this chapter. The development of software to determine the aqueous speciation that occurs under different conditions greatly improved the understanding of aqueous systems and one such program was used to investigate the nickel/sulphuric acid/water system. One of the important steps in the supported liquid extraction process is the reaction of the metal ion (nickel) with the organic extractant to form metal-extractant complexes. In Section 4.3 this equilibrium reaction is investigated and it is one of the critical parts of the process model as discussed in Chapter 5. Currently there is equilibrium data available for the Ni-D2EHPA system, but it is for ambient temperature conditions and the values obtained by different researchers differ to a large extent (1.20×10^9 - 1.40×10^7 m^3/mol, see Section 2.3.3). It was hoped that the use of aqueous speciation would increase the experimental range over which the derived equilibrium constant would be valid. A unique focus of this investigation was to investigate the influence of temperature. It is generally accepted that the temperature dependence of highly selective organic extractants is insignificant (Kasaini, 2003; Rockman *et al.*, 1995:2455), but it was important to confirm this, as most of the SLM experiments were done at elevated temperatures. The extraction of zinc was also investigated to see if the same philosophy could be used to develop an equilibrium model for the extraction of zinc, than was used for the Ni/D2EHPA system.

4.2 Aqueous speciation

OLIAnalyzer (produced by OLI systems Inc.) is a state-of-the-art and very comprehensive thermodynamic package for the simulation of aqueous solutions. The predictive modelling of the extraction equilibrium constants requires that the system be fully speciated. This will also allow for smoother extrapolation of experimental data. The program uses an aqueous model together with a known database of known thermodynamic properties to predict the distribution of species and is unique because it can predictively model the chemical speciation of a wide range of chemicals in water at almost any temperature and pressure of interest. The thermodynamic model also considers (and accurately predicts) phase behaviour (VLE, SLE and LLE), reactions between chemicals, solid formation, pH, the ionic composition and speciation of a given chemical mixture. All these properties make OLIAnalyzer a valuable tool for studying any water chemistry and all the values reported in this section were calculated with the OLIAnalyzer program, except where indicated to the contrary.

4.2.1 True species in aqueous phase

During experimentation the solutions were made up using nickel sulphate hexahydrate, sulphuric acid and pH control was achieved by adding sodium hydroxide to the raffinate recycle solution. The nickel concentrations measured during the AA analysis are the total nickel concentration of the solution, but actually the solution consists of many different ionic species. Table 4.1 gives a list of properties, including all the species (and the concentration of these species) of a solution that was made up of 0.5 mol/m^3 nickel(II) sulphate hexahydrate and 0.3 mol/m^3 sulphuric acid at a temperature of 50 °C and a pressure of 101.3 kPa. It is clear that the nickel in the solution is mainly present in two forms, namely as Ni^{2+} ions and a neutral dissolved $NiSO_4$ complex. Under the above-mentioned conditions about 13% of the nickel is in the form of the neutral $NiSO_4$ complex. Another interesting fact is that the activity coefficient of the Ni^{2+} is about 0.8 and it can, therefore, clearly not be assumed that the concentration of the aqueous species in the equilibrium studies is equal to the activity of the species. In the subsequent sections the influence of different process conditions on the solution properties will be investigated.

4.2.2 Dominant nickel species

The two dominant nickel species in the aqueous solution is Ni^{2+} and $NiSO_4$ (aqueous). The effect of pH, temperature, total nickel concentration and sodium sulphate concentration on the distribution between the two species can be seen in Figures 4.1 to 4.4 (page 55-56). The distribution between the two species was determined by the following equilibrium reaction:

$$Ni^{2+}_{aq} + SO_4^{2-}{}_{aq} \rightleftharpoons (NiSO_4)_{aq} \tag{4.1}$$

Table 4.1: Properties of a stream at 50°C and 101.3 kPa

Property	Value	Units
pH	3.29	-
Ionic strength	$2.527 \cdot 10^{-3}$	mol/kg H_2O
Osmotic pressure	3.982	kPa
Viscosity	$5.477 \cdot 10^{-4}$	$N \cdot s/m^2$
True species concentration		mol/m^3
H_2SO_4	$9.386 \cdot 10^{-16}$	
$Ni(OH)_2$	$1.660 \cdot 10^{-12}$	
$NiSO_4$	$6.341 \cdot 10^{-02}$	
SO_3	$1.781 \cdot 10^{-19}$	
HSO_4^{-1}	$5.742 \cdot 10^{-02}$	
H^{+1}	$5.353 \cdot 10^{-01}$	
OH^{-1}	$1.099 \cdot 10^{-07}$	
Ni^{+2}	$4.306 \cdot 10^{-01}$	
$NiOH^{+1}$	$4.922 \cdot 10^{-07}$	
$Ni(OH)_3^{-1}$	$7.168 \cdot 10^{-20}$	
SO_4^{-2}	$6.695 \cdot 10^{-01}$	
Species activity coefficients		-
HSO_4^{-1}	0.9441	
H^{+1}	0.9430	
OH^{-1}	0.9427	
Ni^{+2}	0.7915	
$Ni(OH)_2$ - Aq	1.0002	
$NiOH^{+1}$	0.9428	
$NiSO_4$ - Aq	1.0002	
$Ni(OH)_3^{-1}$	0.9439	
SO_4^{-2}	0.7910	
SO_3 - Aq	1.0002	
H_2SO_4 - Aq	1.0002	
Species self diffusivities		m^2/s
$HSO4^{-1}$	$2.299 \cdot 10^{-09}$	
H^{+1}	$1.322 \cdot 10^{-08}$	
OH^{-1}	$7.937 \cdot 10^{-09}$	
Ni^{+2}	$1.240 \cdot 10^{-09}$	
$Ni(OH)_2$ - Aq	$1.240 \cdot 10^{-09}$	
$NiOH^{+1}$	$1.238 \cdot 10^{-09}$	
$NiSO_4$ - Aq	$1.137 \cdot 10^{-09}$	
$Ni(OH)_3^{-1}$	$1.235 \cdot 10^{-09}$	
SO_4^{-2}	$1.833 \cdot 10^{-09}$	
SO_3 - Aq	$1.908 \cdot 10^{-10}$	
H_2SO_4 - Aq	$1.838 \cdot 10^{-09}$	

If the sulphate concentration in the solution is increased the equilibrium will shift to the right in accordance with Le Châtelier's principle. The pH of the solution is decreased by adding sulphuric acid and the added effect is an increase of sulphate ions and this explains the decrease in Ni^{2+} ions as the pH is decreased. A deviation from this trend occurs below a pH of 1.5 and can be attributed to the dramatic decrease in the activity of the Ni^{2+} species (see Section 4.2.3). It is important to remember that the equilibrium is determined by the activity of the species and not the concentration:

$$K_{NiSO_4} = \frac{a(NiSO_4)_{aq}}{a(Ni^{2+})_{aq} \cdot a(SO_4^{2-})_{aq}} = 0.208\ m^3/mol \tag{4.2}$$

Another effect that contributes to this phenomenon is the fact that the sulphate ions also take part in the following dissociation reaction:

$$HSO_{4,aq}^{-} \rightleftharpoons H_{aq}^{+} + SO_{4,aq}^{2-} \tag{4.3}$$

Below a pH of 1.5 most of the sulphates that are added to the solution are in the HSO_4^- form (see Figure 4.5) and this means that the decrease in the Ni^{2+} activity exceeds the increase in sulphate concentration and the equilibrium in Equation 4.1 moves to the right.

The equilibrium constants are dependent on temperature as given by Van't Hoff's equation (Atkins, 1990:219):

$$\ln\left(\frac{K}{K_{ref}}\right) = \frac{-\Delta H^0}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_{ref}}\right) \tag{4.4}$$

It is clear from Figure 4.2 that the reaction (Equation 4.1) is an endothermic reaction.

A sodium hydroxide solution was used for pH control in the experiments and this led to the formation of sodium sulphate which forced the reaction to the right as seen in Figure 4.4.

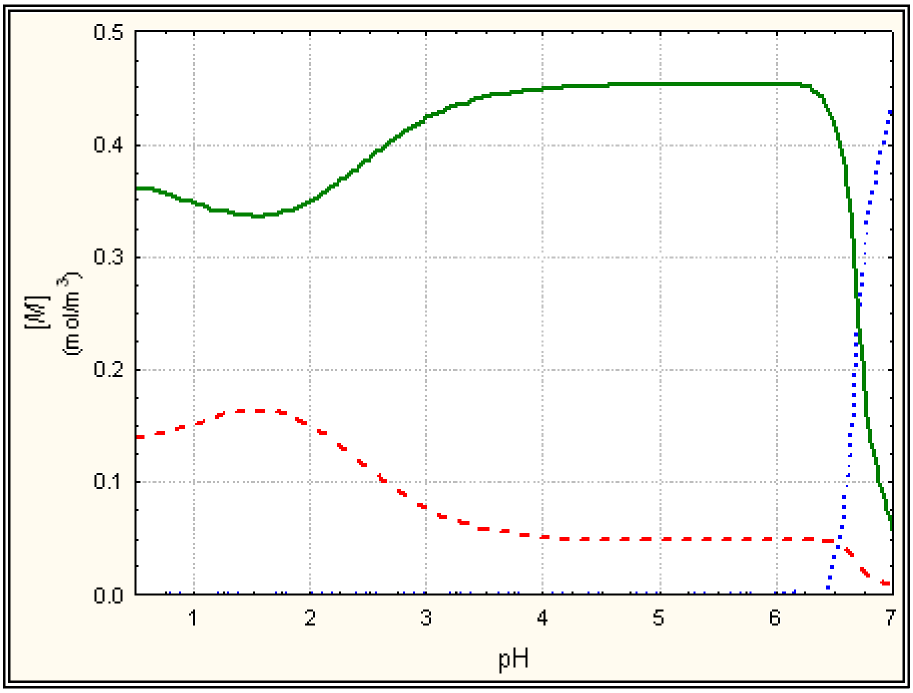


Fig. 4.1: Influence of pH on the nickel ion distribution in an aqueous solution. ——: Ni^{2+}, – –: $NiSO_4$, - - - -: $NiOH_2$, T = 50˚C

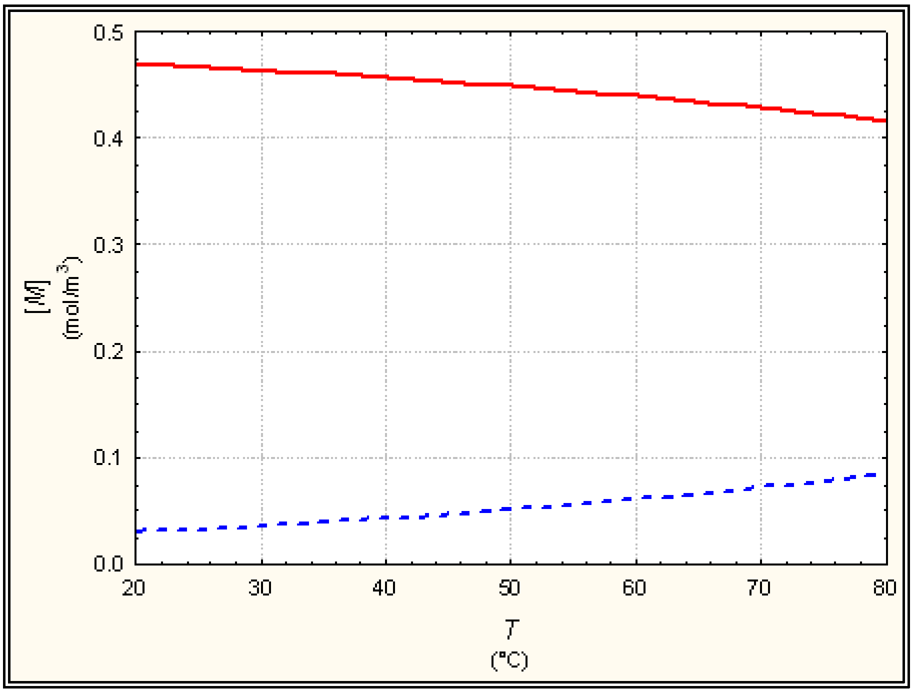


Fig. 4.2: Influence of temperature on the nickel ion distribution in an aqueous solution. ——: Ni^{2+}, – –: $NiSO_4$, pH = 4.0

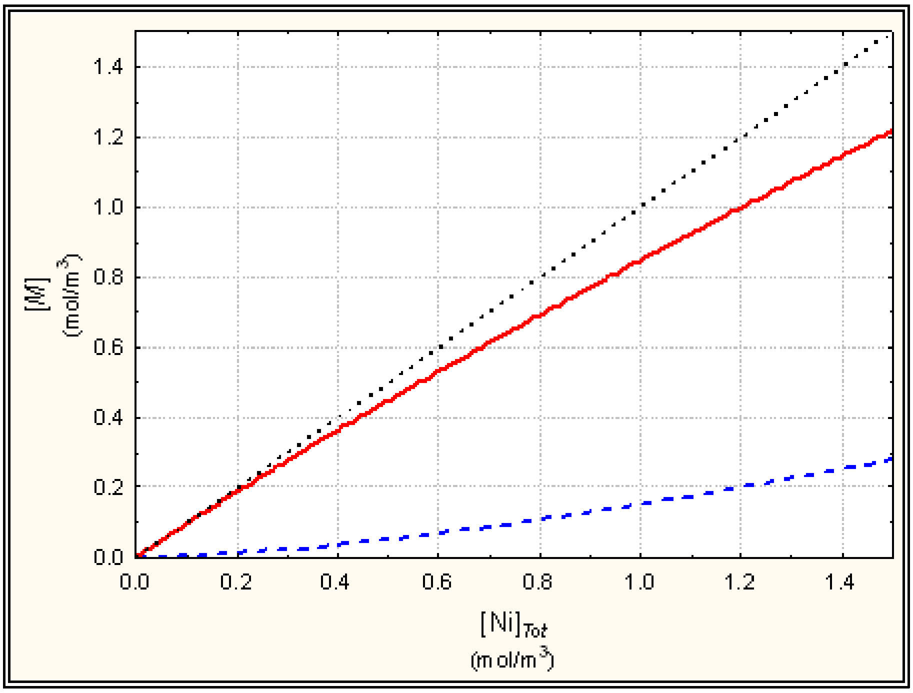


Fig. 4.3: Influence of total nickel concentration on the nickel ion distribution in an aqueous solution. ——: Ni^{2+}, — —: $NiSO_4$, ------ : Ni_{Tot}, T = 50˚C, pH = 4.0

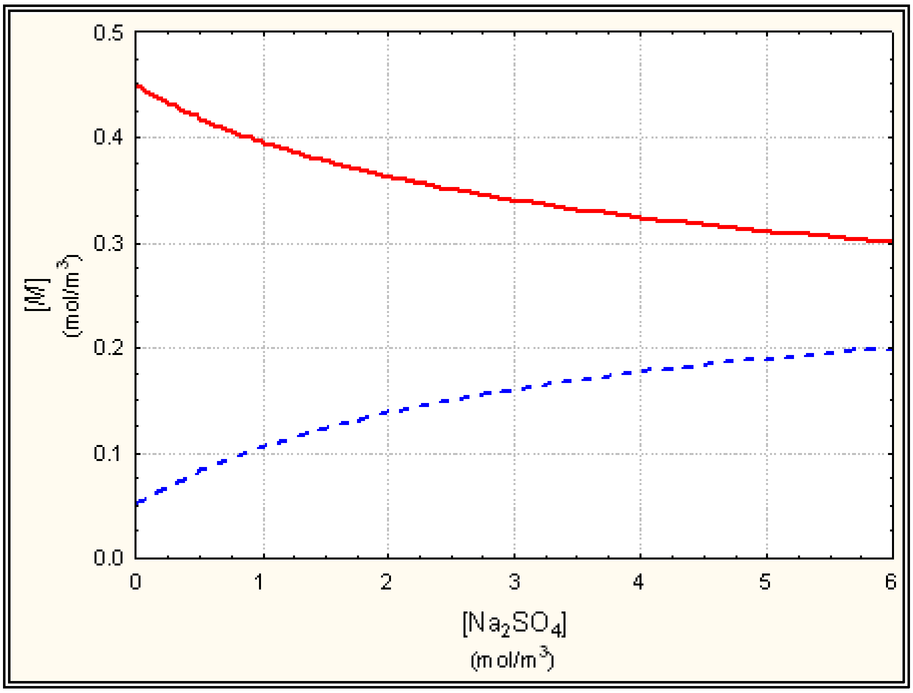


Fig. 4.4: Influence of sodium sulphate concentration on the nickel ion distribution in an aqueous solution. ——: Ni^{2+}, — —: $NiSO_4$, T = 50˚C, pH = 4.0

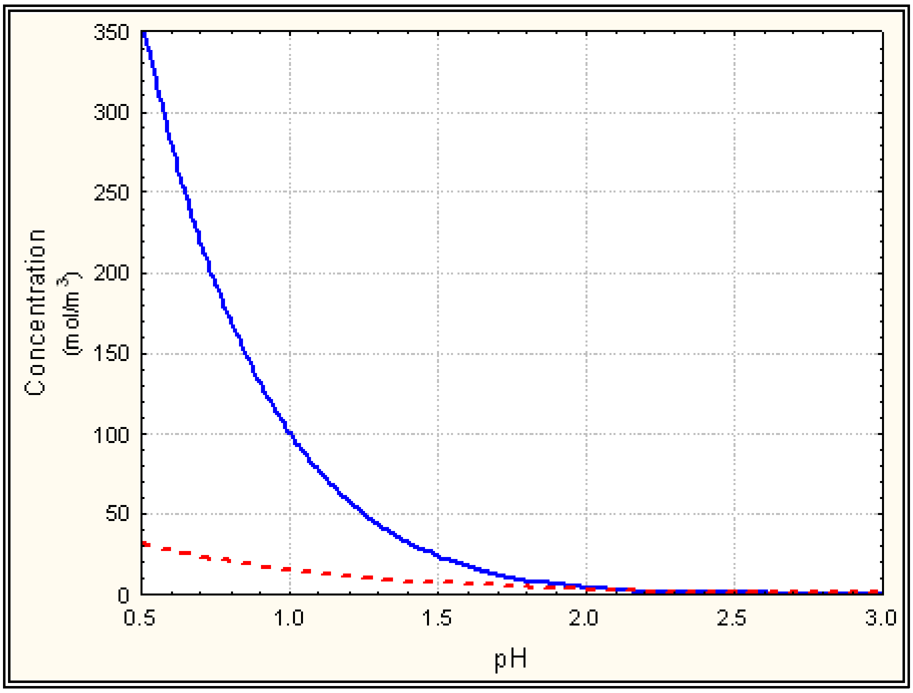


Fig. 4.5: Influence of pH on the sulphate/bisulphate equilibrium. ——: HSO_4^-, – –: SO_4^{2-}, T = 50°C

4.2.3 Activities of aqueous species

The activity of non-electrolytes can be approximated by the solution molalities (Atkins 1990:249). However, in ionic solutions, the interactions between ions are so strong that we can make this approximation only in very dilute solutions. Usually it can be assumed that the molality is equal to the activity if the concentration of the electrolyte is less than 1 mol/m^3, but for Ni^{2+} the activity deviates from the molality at an even lower concentration (see Figure 4.6). The activity coefficient (γ) of an ion depends on the composition, concentration and temperature of the aqueous solution (Atkins, 1990:249). The composition of the solution has an influence on the activity coefficient since cations have the tendency to be attracted by anions. The fact that the cations and anions are so co-dependent in a solution led to the introduction of a mean activity coefficient, as there is no way of disentangling the activity coefficients of the cations and anions experimentally. (It can however be done theoretically with the use of computer programs such as OLIAnalyzer):

$$\gamma_{\pm} = \left(\gamma_{+}^{p} \cdot \gamma_{-}^{q}\right)^{\frac{1}{p+q}} \tag{4.5}$$

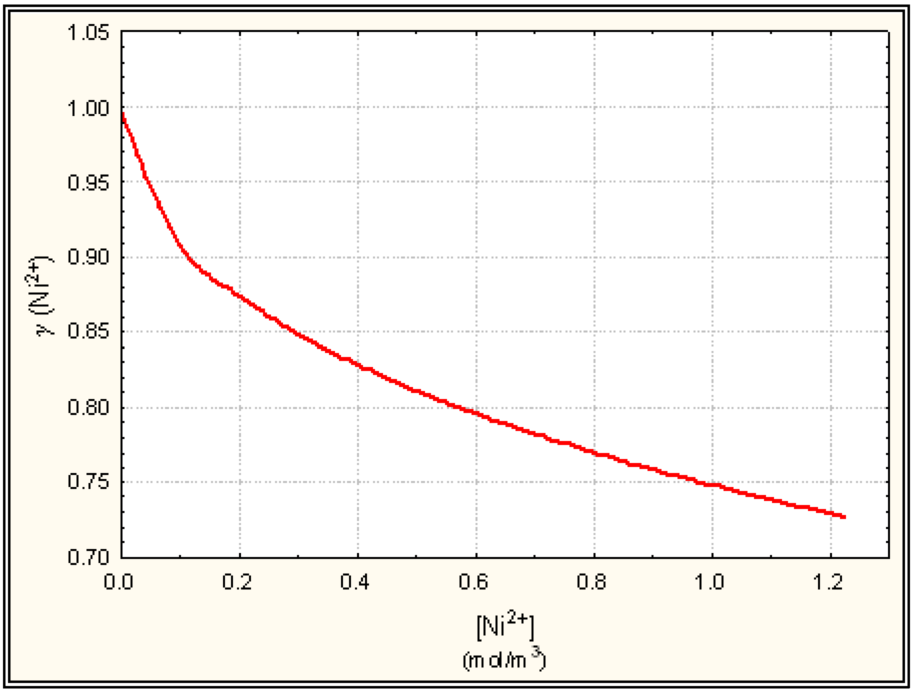


Fig 4.6: Influence of $[Ni^{2+}]$ on $\gamma\ (Ni^{2+})$, $T = 50^{\circ}C$

Where $\gamma_{\pm}$ is the mean activity coefficient, γ_{+} is the activity coefficient of the cation, γ_{-} is the activity coefficient of the anion in a solution of p cations and q anions. The extended Debeye-Hückel law (Atkens, 1990:251) gives the relationship between the mean activity coefficient and the ionic concentrations:

$$\ln(\gamma_{\pm}) = \frac{-A_{DH} \cdot |z_{+} \cdot z_{-}| \cdot \sqrt{I}}{1 + B_{DH} \cdot \sqrt{I}} \qquad I = \tfrac{1}{2}\sum z_i^2 \cdot [i] \tag{4.6}$$

Where I is the ionic strength of the solution, z is the charge number of an ion and A_{DH} and B_{DH} are constants. A_{DH} is equal to 0.509 $kg^{0.5}/mol^{0.5}$ for aqueous solutions at 25°C. In general A_{DH} depends on the relative permittivity and the temperature. B_{DH} can be interpreted as a measure of the closest approach of the ions. It is clear from the discussion above that the concentration of the nickel in solution, the pH of the solution, temperature and sodium sulfate concentration will have an effect on the activity coefficient of the Ni^{2+} species as can be seen in Figures 4.6-4.9.

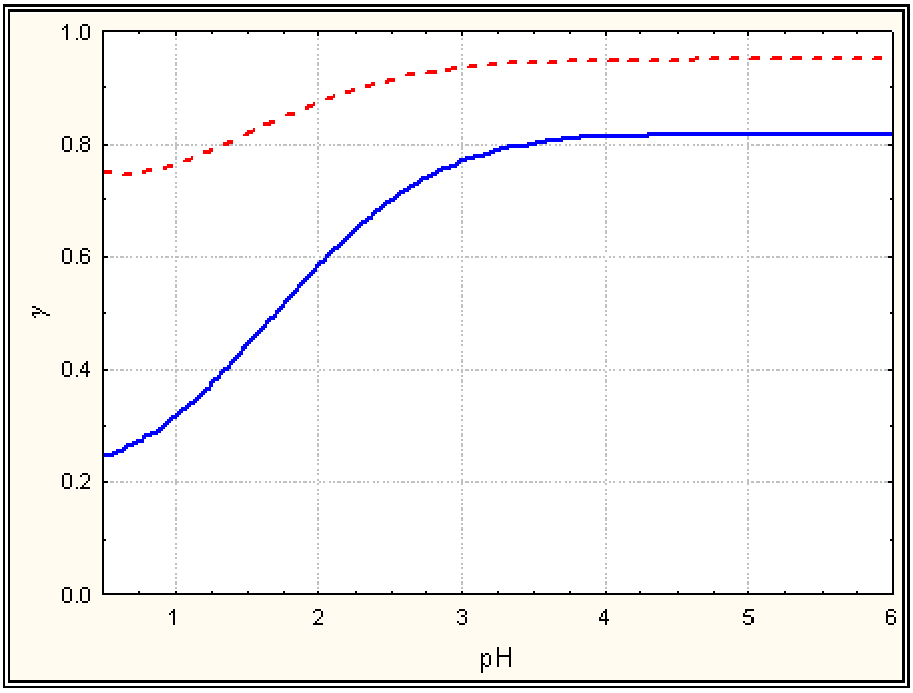


Fig 4.7: Influence of pH on activity coefficients of species, ——:$\gamma(\mathrm{Ni}^{2+})$, – –: $\gamma(\mathrm{H}^{+})$, T = 50°C

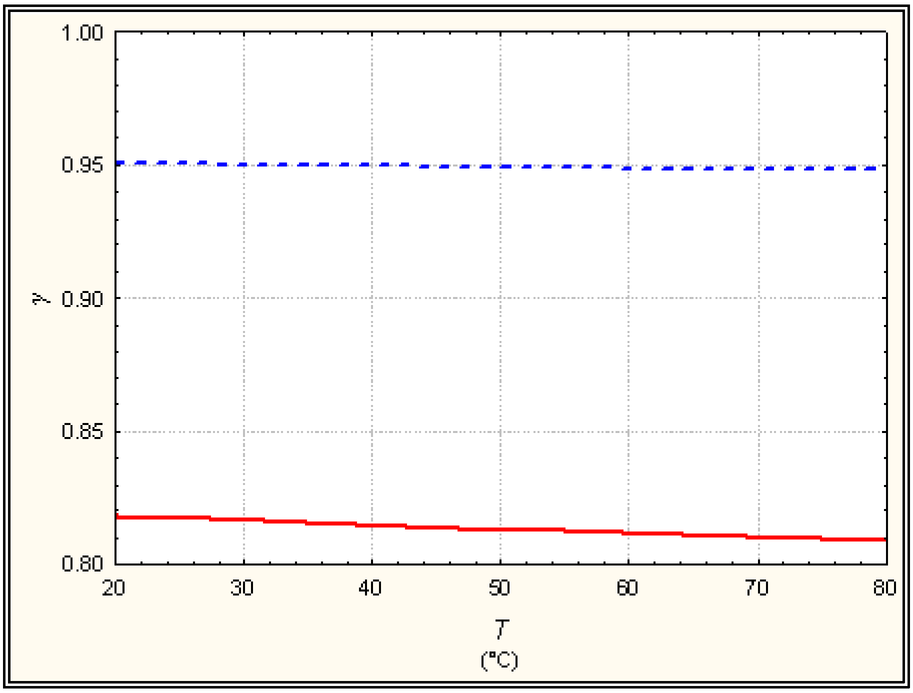


Fig 4.8: Influence of temperature on activity coefficients of species, ——:γ (Ni^{2+}), – –:γ (H^{+}), pH = 4.0

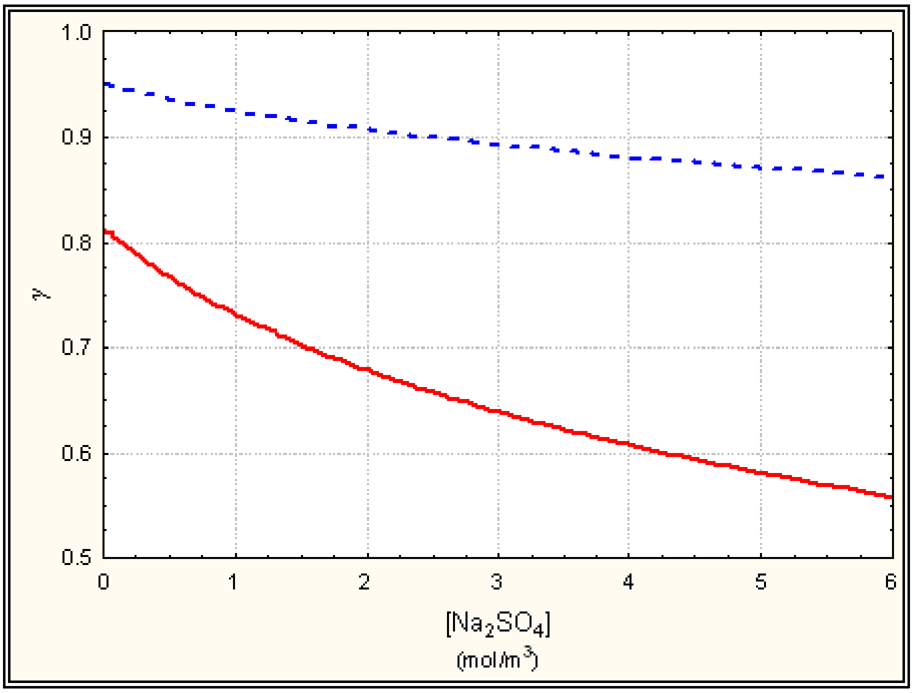


Fig 4.9: Influence of [Na_2SO_4] on activity coefficients of species, ——:γ (Ni^{2+}), — —:γ (H^+), $T = 50^\circ C$, pH = 4.0

4.2.4 Self diffusivities of aqueous species

As with the activity of ionic species, there is no way of experimentally disentangling the diffusivities of the cations and anions in a solution. Nerst developed the first equation for predicting diffusion coefficients of the cation and anion together in electrolyte solutions by relating the diffusivity to electrical conductivities (Hines & Maddox, 1985:34). His equation, which is valid at infinite dilution, is:

$$D_{AB}^{0} = \frac{R \cdot T}{F} \cdot \frac{\lambda_{+}^{0} \cdot \lambda_{-}^{0}}{\lambda_{+}^{0} + \lambda_{-}^{0}} \cdot \frac{|z_{-}| + |z_{+}|}{|z_{-} \cdot z_{+}|} \tag{4.7}$$

where F is the Faraday constant, D^{0}_{AB} the diffusion coefficient at infinite dilution and λ^0 the cationic or anionic conductance at infinite dilution. As the concentrations of other ions increase, the diffusion coefficient will decrease and this can be incorporated by using the ionic strength of the solution in a relationship similar to Equation 4.6. Although Equation 4.7 suggests a linear relationship between the diffusion coefficient and temperature, solutions away from infinite dilution tend to obey an Arrhenius expression (Hines & Maddox, 1985:38). Incorporating the above-mentioned variables into the Nernst equation results in an equation of the following form:

$$D_{AB} = A_N \cdot T \cdot \exp\left(\frac{-B_N}{R \cdot T} - C_N \cdot I \right) \tag{4.8}$$

with A_N, B_N and C_N constants. B_N has the units of J/mol and may be visualised simply as the energy necessary to raise an atom over a barrier. For liquids this may be interpreted as the energy required to break one-half of the bonds between a diffusing molecule and its nearest neighbours (Hines & Maddox, 1985:38).

In the experimental setup, the diffusion of the Ni^{2+} and H^+ species was of importance and the effect of pH and temperature on the self diffusivities of these species can be seen in Figures 4.10 and 4.11. The total nickel concentration and sodium sulfate concentration did not have a significant effect on the diffusion coefficients of Ni^{2+} and H^+ in the range from 0 to 3 mol/l.

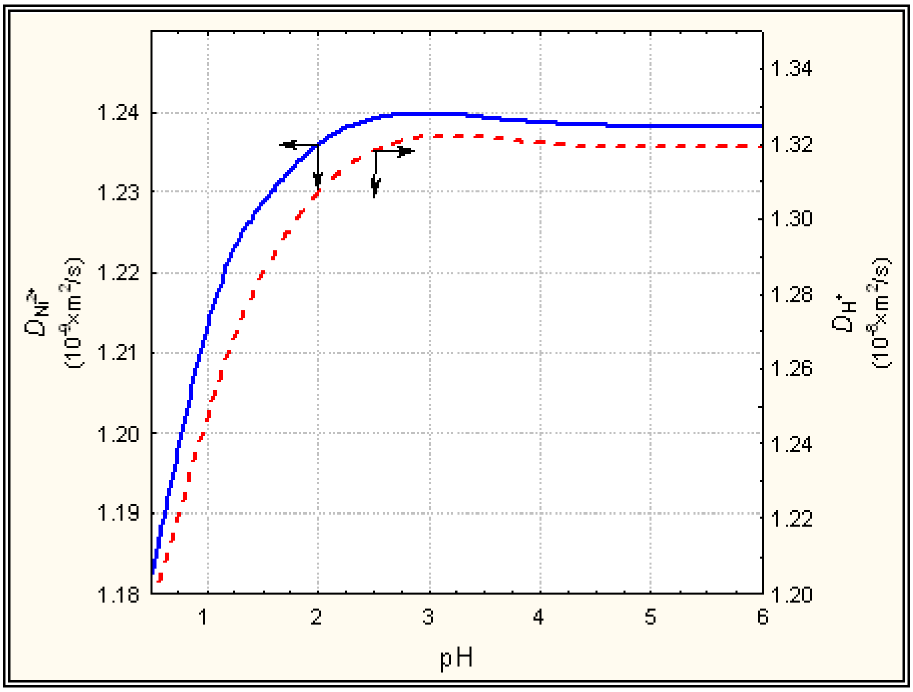


Fig 4.10: Influence of pH on the self diffusivities of Ni^{2+} (——; left axis) and H^+ (— —; right axis), T = 50˚C, pH = 4.0

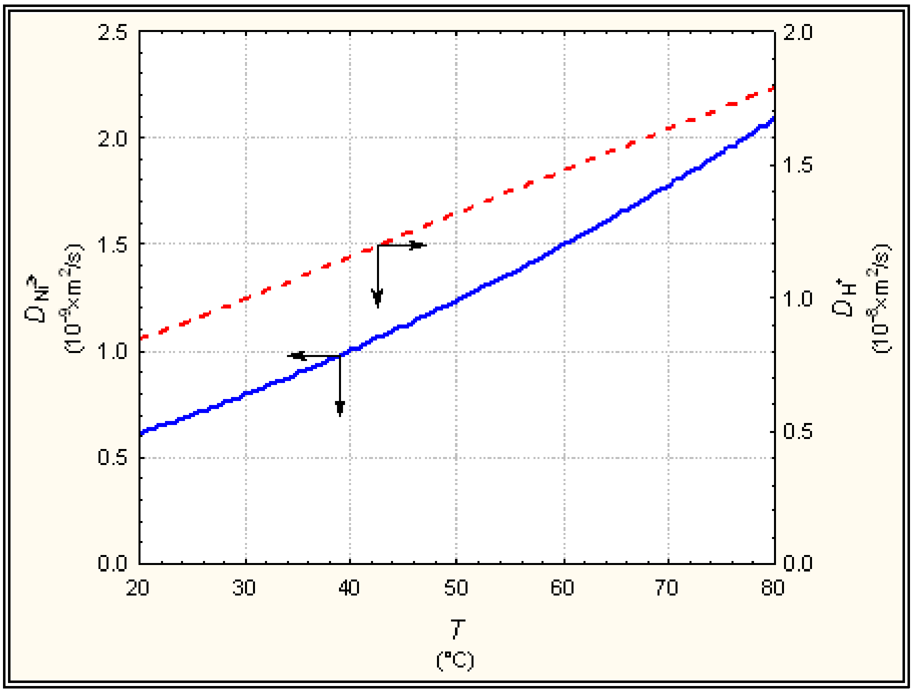


Fig 4.11: Influence of temperature on the self diffusivities of Ni^{2+} (——; left axis) and H$^+$ (— —; right axis), T = 50°C, pH = 4.0

4.2.5 Effect of pressure on aqueous speciation

The experiments were done at an altitude of 1 372 m, with an average atmospheric pressure of 85.9 kPa. It was found that the influence of pressure between 85.9 kPa and 101.3 kPa on the aqueous speciation properties mentioned in Section 4.2.1 to 4.2.4 was negligible.

4.3 Determination of the equilibrium data for the Ni/D2EHPA system

4.3.1 Theory

It was decided to use D2EHPA as an exctractant due to its commercial availability in South Africa and the substantial research that has been done on SLM extraction with this extractant (see Section 2.3.3). The equilibrium distribution of a solute between two immiscible liquids is described in terms of the partition law. The derivation of this law is described in Jackson (1986:109) and is summarised in this section. The derivation was adjusted for the Ni/D2EHPA system, using activities instead of concentrations where applicable.

If a solute is dissolved in two immiscible solvents, A and B, the free energy of the solute in the liquids may be expressed by:

$$G_A = G_A^0 + R \cdot T \cdot \ln(a(A)) \quad \text{and}$$
$$G_B = G_B^0 + R \cdot T \cdot \ln(a(B)) \tag{4.9}$$

when equilibrium is established, $G_A = G_B$ and:

$$\ln\left(\frac{a(A)}{a(B)}\right) = \frac{G_A^0 - G_B^0}{R \cdot T} \tag{4.10}$$

at a given temperature the righthand side of Equation 4.10 is constant and:

$$\ln\left(\frac{a(A)}{a(B)}\right) = \text{constant, or}$$
$$\frac{a(A)}{a(B)} = P^0 \tag{4.11}$$

P^0 is the partition constant and is dependent on the nature of the solute and the solvents involved as well as the temperature. In hydrometallurgy it is more useful to express the concentration of the metal in each phase as the distribution ratio (D):

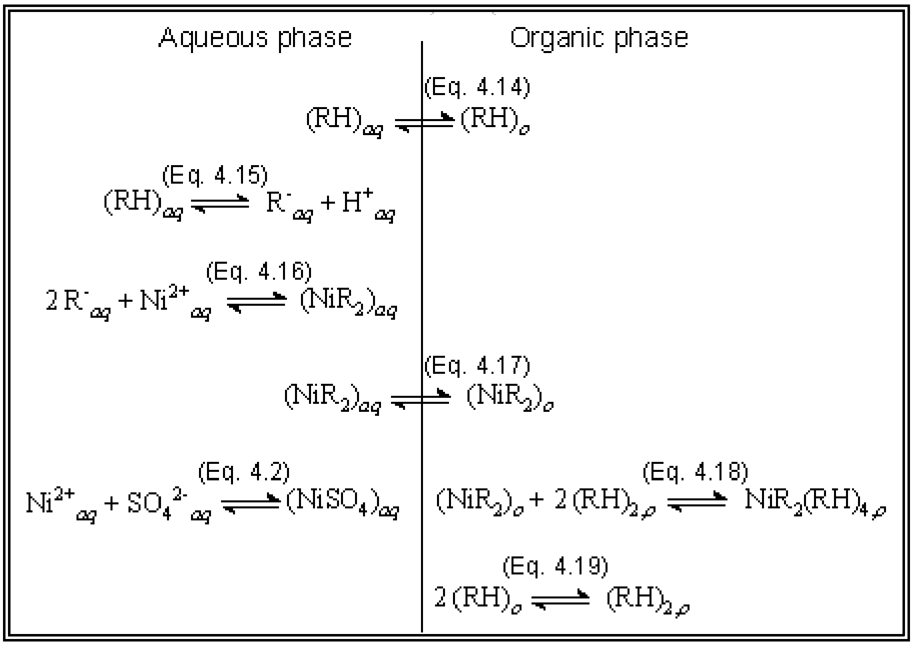
$$D = \frac{\sum [\text{Ni}]_o}{\sum [\text{Ni}]_{aq}} \tag{4.12}$$

or the percentage extraction (%E):

$$\%E = \frac{100 \cdot D}{D + \frac{V_{aq}}{V_o}} \tag{4.13}$$

where V_{aq} is the volume of the aqueous solution and V_o is the volume of the organic solution. The assumption was made that the system can be described by the reaction and partition equilibriums depicted in Figure 4.12. This assumption with a discussion concerning the equilibrium equations follow:

There is a partition equilibrium (P^0_{RH}) between the D2EHPA monomer in the organic phase and the aqueous phase and is expressed in terms of the activities, a, of the dissolved species:



(4.14)

Fig. 4.12: Steps involved in forming D2EHPA/Ni equilibrium.

The D2EHPA monomer dissociates (K_{RH}) in the aqueous phase to form an organic phosphate ion and a hydronium ion:

$$K_{\mathrm{RH}} = \frac{a\left(\mathrm{R}^-\right)_{aq} \cdot a\left(\mathrm{H}^+\right)_{aq}}{a\left(\mathrm{RH}\right)_{aq}} \tag{4.15}$$

The nickel in the aqueous phase takes part in an equilibrium reaction (K_{NiR2}) with the organic phosphate to form a chelate:

$$K_{\mathrm{NiR}_2} = \frac{a\left(\mathrm{NiR}_2\right)_{aq}}{a\left(\mathrm{R}^-\right)^2_{aq} \cdot a\left(\mathrm{Ni}^{2+}\right)_{aq}} \tag{4.16}$$

There is a partition equilibrium ($P^0{}_{\mathrm{NiR2}}$) between the chelate in the organic phase and the aqueous phase:

$$P^0_{\mathrm{NiR}_2} = \frac{a\left(\mathrm{NiR}_2\right)_o}{a\left(\mathrm{NiR}_2\right)_{aq}} \tag{4.17}$$

The chelate can react with additional D2EHPA molecules to form a second chelate in the organic phase. The equilibrium constant for this reaction is K_{NiR6}:

$$K_{\mathrm{NiR}_6} = \frac{a\left(\mathrm{NiR}_2(\mathrm{RH})_4\right)_o}{a\left(\mathrm{NiR}_2\right)_o \cdot a\left((\mathrm{RH})_2\right)_o^2} \tag{4.18}$$

The nickel ions form a complex with the sulphate ions in solution (Tur`yan & Ruvinskii, 1970), as discussed in Section 4.2.2. The equilibrium constant for this reaction is given by Equation 4.2. There is also an equilibrium (K_D) between the D2EHPA monomer and D2EHPA dimer (Juang & Su, 1992:2396; Huang & Juang, 1986:755; Komasawa et al., 1981:3351 ; Liem, 1971:191; Smelov & Chubukov, 1973:445):

$$K_D = \frac{a\left((\mathrm{RH})_2\right)_o}{a\left(\mathrm{RH}\right)_o^2} = 12\,\mathrm{m}^3/\mathrm{mol} \tag{4.19}$$

These equilibrium equations can be used to derive a final model to describe the Ni/D2EHPA equilibrium. The derivation of this model will be discussed in the subsequent paragraphs.

Using Equation 4.12, the distribution ratio for the system can be written as:

$$D = \frac{[\mathrm{NiR}_2]_o + [\mathrm{NiR}_2(\mathrm{RH})_4]_o}{[\mathrm{Ni}^{2+}]_{aq} + [\mathrm{NiSO}_4]_{aq} + [\mathrm{NiR}_2]_{aq}} \tag{4.20}$$

If it is assumed that $[\mathrm{NiR}_2]_{aq} << ([\mathrm{Ni}^{2+}]_{aq} + [\mathrm{NiSO}_4]_{aq})$ then Equation 4.20 becomes:

$$D = \frac{[\mathrm{NiR}_2]_o + [\mathrm{NiR}_2(\mathrm{RH})_4]_o}{[\mathrm{Ni}^{2+}]_{aq} + [\mathrm{NiSO}_4]_{aq}} \tag{4.21}$$

In terms of activity, Equation 4.21 becomes:

$$D = \frac{\dfrac{a(\mathrm{NiR}_2)_o}{\gamma(\mathrm{NiR}_2)_o} + \dfrac{a(\mathrm{NiR}_2(\mathrm{RH})_4)_o}{\gamma(\mathrm{NiR}_2(\mathrm{RH})_4)_o}}{\dfrac{a(\mathrm{Ni}^{2+})_{aq}}{\gamma(\mathrm{Ni}^{2+})_{aq}} + \dfrac{a(\mathrm{NiSO}_4)_{aq}}{\gamma(\mathrm{NiSO}_4)_{aq}}} \tag{4.22}$$

where γ is the activity coefficient of the species. Substituting Equations 4.2, 4.17 and 4.18 into Equation 4.22 gives:

$$D = \frac{P^0_{\mathrm{NiR_2}} \dfrac{a(\mathrm{NiR_2})_{aq}}{\gamma(\mathrm{NiR_2})_o} + \dfrac{K_{\mathrm{NiR_6}} \cdot P^0_{\mathrm{NiR_2}} \cdot a(\mathrm{NiR_2})_{aq} \cdot a((\mathrm{RH})_2)_o^2}{\gamma(\mathrm{NiR_2(RH)_4})_o}}{\dfrac{a(\mathrm{Ni^{2+}})_{aq}}{\gamma(\mathrm{Ni^{2+}})_{aq}} + \dfrac{K_{\mathrm{NiSO_4}} \cdot a(\mathrm{Ni^{2+}})_{aq} \cdot a(\mathrm{SO_4^{2-}})_{aq}}{\gamma(\mathrm{NiSO_4})_{aq}}} \tag{4.23}$$

Substituting the reaction equilibrium for the aqueous reaction (Equation 4.16) into equation 4.23 gives:

$$D = \frac{P^0_{\mathrm{NiR_2}} \cdot K_{\mathrm{NiR_2}} \cdot \left(\dfrac{a(\mathrm{R^-})_{aq}^2 \cdot a(\mathrm{Ni^{2+}})_{aq}}{\gamma(\mathrm{NiR_2})_o} + K_{\mathrm{NiR_6}} \cdot \dfrac{a(\mathrm{R^-})_{aq}^2 \cdot a(\mathrm{Ni^{2+}})_{aq} \cdot a((\mathrm{RH})_2)_o^2}{\gamma(\mathrm{NiR_2(RH)_4})_o} \right)}{\dfrac{a(\mathrm{Ni^{2+}})_{aq}}{\gamma(\mathrm{Ni^{2+}})_{aq}} + \dfrac{K_{\mathrm{NiSO_4}} \cdot a(\mathrm{Ni^{2+}})_{aq} \cdot a(\mathrm{SO_4^{2-}})_{aq}}{\gamma(\mathrm{NiSO_4})_{aq}}} \tag{4.24}$$

Substitution of the dimer dissociation (Equation 4.19) into Equation 4.24 gives:

$$D = \frac{P^0_{\mathrm{NiR_2}} \cdot K_{\mathrm{NiR_2}} \cdot K^2_{\mathrm{RH}} \cdot \left(\dfrac{a(\mathrm{RH})_{aq}^2 \cdot a(\mathrm{Ni^{2+}})_{aq}}{\gamma(\mathrm{NiR_2})_o} + K_{\mathrm{NiR_6}} \cdot \dfrac{a(\mathrm{RH})_{aq}^2 \cdot a(\mathrm{Ni^{2+}})_{aq} \cdot a((\mathrm{RH})_2)_o^2}{\gamma(\mathrm{NiR_2(RH)_4})_o} \right)}{\dfrac{a(\mathrm{Ni^{2+}})_{aq}}{\gamma(\mathrm{Ni^{2+}})_{aq}} + \dfrac{K_{\mathrm{NiSO_4}} \cdot a(\mathrm{Ni^{2+}})_{aq} \cdot a(\mathrm{SO_4^{2-}})_{aq}}{\gamma(\mathrm{NiSO_4})_{aq}}} \tag{4.25}$$

Finally the D2EHPA partition (Equation 4.14) can be substituted into Equation 4.25 and simplification gives:

$$D = \frac{K_1 \cdot \gamma(\mathrm{Ni^{2+}})_{aq} \cdot \gamma(\mathrm{NiSO_4})_{aq} \cdot a(\mathrm{RH})_o^2 \cdot \left(\gamma(\mathrm{NiR_2(RH)_4})_o + K_{\mathrm{NiR_6}} \cdot a((\mathrm{RH})_2)_o^2 \cdot \gamma(\mathrm{NiR_2})_o\right)}{\left(\gamma(\mathrm{NiR_2(RH)_4})_o \cdot \gamma(\mathrm{NiR_2})_o \cdot a(\mathrm{H^+})_{aq}^2\right) \cdot \left(\gamma(\mathrm{NiSO_4})_{aq} + K_{\mathrm{NiSO_4}} \cdot a(\mathrm{SO_4^{2-}})_{aq} \cdot \gamma(\mathrm{Ni^{2+}})_{aq}\right)} \tag{4.26}$$

with

$$K_1 = \frac{P^0_{NiR_2} \cdot K_{NiR_2} \cdot K^2_{RH}}{\left(P^0_{RH}\right)^2} \tag{4.27}$$

The chelate complexes and the aqueous nickel sulphate complex are neutral complexes with concentrations lower than 10 mol/m^3 and it can therefore be assumed that the activity coefficients are equal to 1 (Atkins,1990:249). Equation 4.26 then simplifies to:

$$D = \frac{K_1 \cdot \gamma\left(\mathrm{Ni}^{2+}\right)_{aq} \cdot a\left(\mathrm{RH}\right)_o^2 \cdot \left(1 + K_{\mathrm{NiR}_6} \cdot a\left(\left(\mathrm{RH}\right)_2\right)_o^2\right)}{a\left(\mathrm{H}^+\right)_{aq}^2 \cdot \left(1 + K_{\mathrm{NiSO}_4} \cdot a\left(\mathrm{SO}_4^{2-}\right)_{aq} \cdot \gamma\left(\mathrm{Ni}^{2+}\right)_{aq}\right)} \tag{4.28}$$

At any time the total D2EHPA concentration in the organic phase can be calculated from a simple mole balance:

$$[\mathrm{R}]_{Tot,o} = [\mathrm{RH}]_o + 2 \cdot [(\mathrm{RH})_2]_o + 2 \cdot [\mathrm{NiR}_2]_o + 6 \cdot [\mathrm{NiR}_2(\mathrm{RH})_4]_o \tag{4.29}$$

4.3.2 Experimental

The D2EHPA used in this research was supplied by Chem Quest (Pty) Ltd. The properties as analysed by the supplier are given in Table 4.2. The extraction Ni/D2EHPA equilibrium was determined with batch solvent extraction experiments. During extraction a predetermined volume of an aqueous nickel solution (feed) was mixed with a predetermined volume of D2EHPA/kerosene solution (extractant) in 250 ml conical flasks, using a magnetic stirrer to thoroughly mix the two phases. The volume ratio (*Vr*) between the aqueous solution and organic solution was 0.5, 0.7, 1, 2 and 5. In all the experiments the total solution volume (aqueous and organic) was 60 ml. The samples were then centrifuged at 30 000 rpm for 20 to 30 minutes to separate the phases and the pH and nickel concentrations of the aqueous solutions (both the feed and the raffinate) were measured.

Table 4.2: Physical properties of D2EHPA (as supplied by Chem Quest (Pty) Ltd.)

Property	Value	Units
D2EHPA content	97 (min. 95)	weight %
Acidity	165-174	mg KOH/g
Water content	0.1 (max. 0.2)	Weight %
Density (at 20 ˚C)	960	kg/m^3
Viscosity (at 20 ˚C)	40	mPa·s
Setting point	-50	˚C
Flash point	150 (approx.)	˚C

Most of the experiments were done at ambient temperature except where the contrary is indicated. During the temperature experiments a water bath was used to maintain the desired temperature (temperatures of 30, 40, 50, 60 and 70 ˚C were used). The samples from the experiments done at different temperatures were centrifuged in five, 5 minute intervals (total 25 minutes) and the samples were replaced in the water bath between intervals to minimise the temperature loss of the samples. The feed solutions had nickel concentrations of approximately 20, 42, 66, 88 and 109 g/m^3 and the extractant solutions contained 300, 600, 800, 1000, 1200, 1400 and 1600 mol/m^3 D2EHPA as monomeric D2EHPA.

The pH of the raffinate solution was varied by adding either sulphuric acid or sodium hydroxide to the feed solution. The sulphuric acid was added to the feed solution before extraction. The sodium hydroxide was added during the extraction process to prevent the formation of nickel(II) hydroxide. This was done with a Metrohm 718 STAT Titrino automatic titrator. The sulphuric acid concentrations of the feed solutions were 0.570, 2.18, 3.90, 6.00 and 8.00 mol/m^3 (as sulphuric acid) after the addition of the sulphuric acid. The sodium hydroxide concentrations of the feed solutions were 0.67, 1.00 and 3.33 mol/m^3 after the addition of the sodium hydroxide.

Each experiment was done four times to determine the reproducibility of the experiment and evident outliers were ignored in calculations. A set of 2^k experiments was also done and although these experiments cannot be displayed graphically, it increased the confidence in the regression results. A summary of the experimental conditions and results obtained from the 2^k experiments can be seen in Table 4.3. The detailed results of all the experiments can be seen in Appendix C.2.

Table 4.3: Summary of 2^k solvent extraction experiments

Exp. Name	V_{aq}/V_o	Avg. $[Ni]_f$ (mol/m^3)	Acid added (mol/m^3 H_2SO_4)	D2EHPA (mol/m^3)	Avg. D	σ_D	Avg. %E	$\sigma_{\%E}$
K01	1	0.621	0	1000	4.688	0.57	82.4	1.8
K02	1	0.860	0	1400	7.553	0.68	88.3	0.9
K03	1	0.638	4	1000	0.465	-	31.7	-
K04	1	0.690	4	1400	1.428	0.10	58.8	1.1
K05	1	1.797	0	1000	2.611	0.00	72.3	1.6
K06	1	1.719	0	1400	6.121	0.65	86.0	1.3
K07	1	1.729	4	1000	0.415	0.20	29.3	10.0
K08	1	1.700	4	1400	0.934	0.15	48.3	3.9
K09	1	1.438	2	1200	1.64	0.19	62.1	2.7
K10	1	0.903	2	1200	1.948	0.33	66.1	3.8

4.3.3 Results and discussion

The distribution coefficient of each experiment was calculated by a simple mole balance:

$$D = \frac{[\mathrm{Ni}]_{aq,f} - [\mathrm{Ni}]_{aq,r}}{[\mathrm{Ni}]_{aq,r}} \cdot \frac{V_{aq}}{V_o} \tag{4.30}$$

The variance of a quantity y, that depends on two quantities a and b, with variance σ_a^2 and σ_b^2 respectively is given by the following equation (Kirup, 1994:97):

$$\sigma_y^2 = \left(\frac{\partial y}{\partial a}\right)^2 \cdot \sigma_a^2 + \left(\frac{\partial y}{\partial b}\right)^2 \cdot \sigma_b^2 \tag{4.31}$$

Using Equation 4.31 with regard to Equation 4.30 and 4.13 we can calculate the standard deviation of the distribution coefficient and % extraction:

$$\sigma(D) = \sqrt{\left(\frac{Vr}{[\mathrm{Ni}]_{aq,r}}\right)^2 \cdot \sigma([\mathrm{Ni}]_{aq,f})^2 + \left(\frac{Vr \cdot [\mathrm{Ni}]_{aq,f}}{[\mathrm{Ni}]_{aq,r}}\right)^2 \cdot \sigma([\mathrm{Ni}]_{aq,r})^2} \tag{4.32}$$

$$\sigma(\%E) = \sqrt{\left(\frac{100 \cdot Vr}{(D + Vr)^2}\right)^2 \cdot \sigma(D)^2} \tag{4.33}$$

The activity of the sulphate ions and the activity coefficient of the aqueous nickel were calculated using the OLIAnalizer software package (OLI Systems Inc.) The values of K_1 and K_{NiR6} were determined by regression using the simplex method (Jacoby *et al.*, 1972:79) in combination with Newton's method (Kreyszig, 1988:952) to solve Equations 4.19, 4.28 and 4.29 simultaneously. The standard error of the regression coefficients was determined with the Bootstrap method (Chernick, 1999:8). The detailed program code can be seen in Appendix D.5. The regression was done on all the experimental data points and a correlation coefficient (r^2) of 0.9979 was obtained. The regression results can be seen in Table 4.4 and the relationship between the predicted and observed percentage extraction values can be seen in Figure 4.13. The effect of different variables on the extraction equilibrium will be discussed below.

Table 4.4: Regression results for equilibrium constants for nickel

Variable	Value	Std. Err.	-95% confidence	+95% confidence
K_1 (-)	1.77×10^{-1}	0.32×10^{-1}	1.14×10^{-1}	2.45×10^{-1}
K_{NiR6} (m^6/mol^2)	8.3×10^{-6}	2.3×10^{-6}	4.9×10^{-6}	14.0×10^{-6}

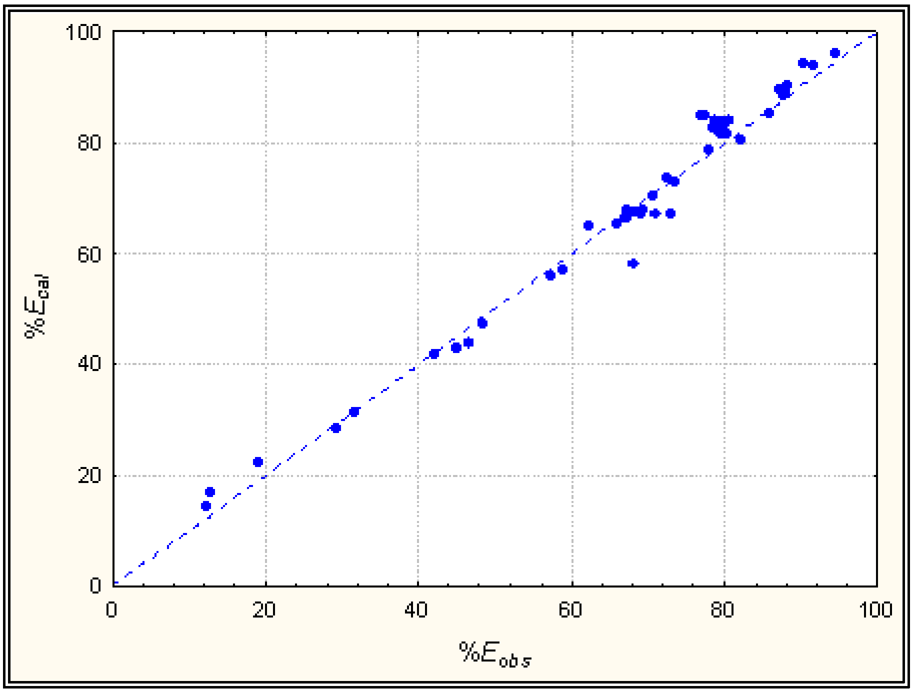


Fig. 4.13: Predicted *vs.* observed values for equilibrium regression (r^2=0.998)

4.3.3.1 Testing for equilibrium

A set of experiments was done to establish if equilibrium was reached within the extraction time. As can be seen in Figure 4.14 the reaction reached equilibrium in less than 10 minutes. This result is in agreement with results obtained by other researchers who also found that extraction with D2EHPA reached equilibrium in less than 10 minutes (Buch *et al.*, 2002:56; Hung & Juang, 1986:753; Biswas & Hayat, 2002:151, Huang & Tsai, 1989:1558). All other experiments were done for 30 minutes to ensure that equilibrium was reached.

4.3.3.2 The effect of temperature

It is generally accepted that the extraction equilibrium of highly selective extractants such as D2EHPA is not very sensitive to temperature (Agrawal, 2002:880; Reddy & Bhaskara Sarma, 2001:127; Bhaskara Sarma & Reddy, 2002:463). This was confirmed in a set of experiments where the temperatures were varied from 30 ˚C to 70 ˚C. It is clear from Figure 4.15 that the effect of temperature is negligible over the experimental range investigated. All other experiments were done at ambient temperature (≈25°C).

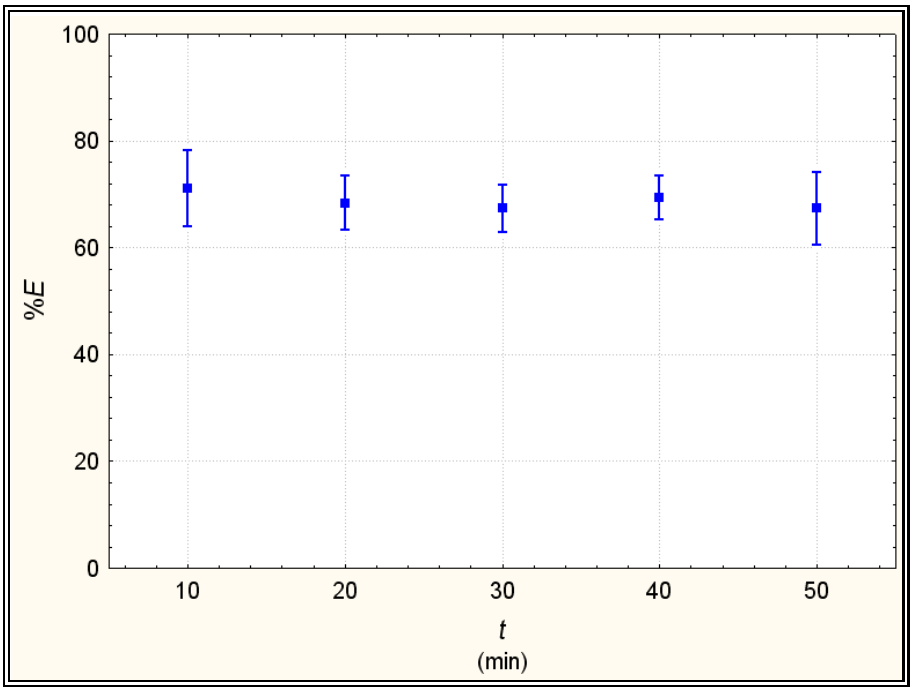


Fig. 4.14: Effect of time on % extraction. $Vr = 1$, $[\text{Ni}]_f \approx 1.8$ mol/m^3, $[\text{RH}]_{Tot} = 1200$ mol/m^3. ■: Experimental data with 95% confidence limits

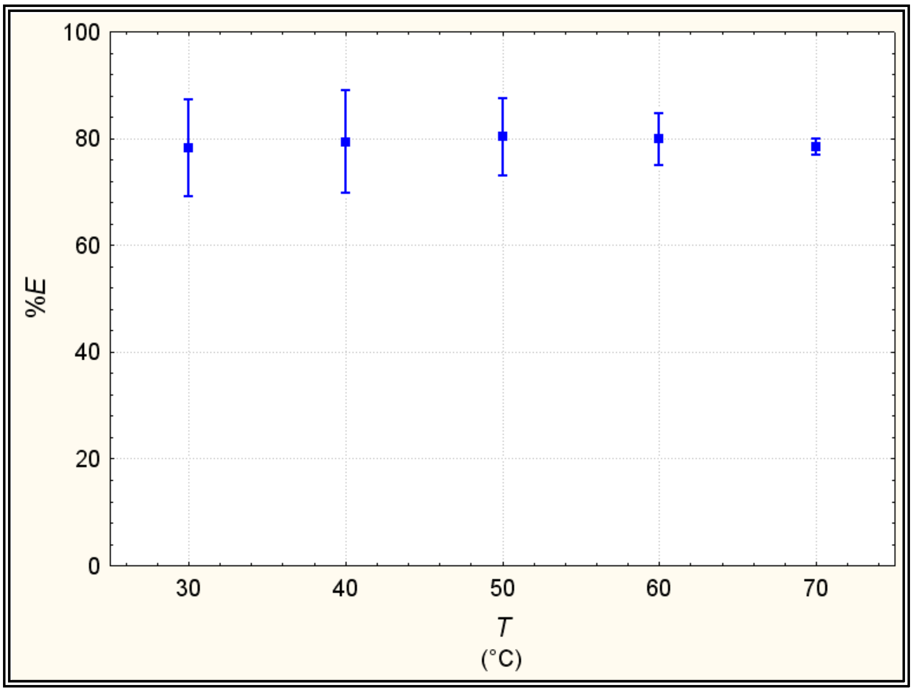


Fig. 4.15: The effect of temperature on the % extraction. $Vr = 1$, $[\text{Ni}]_f \approx 1.85$ mol/m^3, $[\text{RH}]_{Tot} = 1200$ mol/m^3. ■: Experimental data with 95% confidence limits

4.3.3.3 The effect of the total D2EHPA concentration

A set of experiments was done in which the total concentration of the D2EHPA was varied from 300 mol/m^3 to 1600 mol/m^3 (as total D2EHPA monomer). The results of the experiments can be seen in Figure 4.16 and it is clear that the equilibrium model (line) fits the data (squares) well. The predicted product distribution as % NiR_2 and % $NiR_2(RH)_4$ of the total nickel-organic species can be seen in Figure 4.17. The reaction equilibrium for the formation of $NiR_2(RH)_4$ (Equation 4.18) favours the formation of $NiR_2(RH)_4$ as the extractant concentration is increased. This is confirmed in the literature, from which it can be concluded that at high metal loadings the metal ion will coordinate solely with D2EHPA anions and at low metal loadings the complex is additionally solvated by electrically neutral D2EHPA molecules (Beyer, 1993:5). In other words m=2 in Equation 2.2.

4.3.3.4 The effect of the nickel concentration of the feed solution

A set of experiments was done in which the nickel concentration of the feed was varied. The results of these experiments can be seen in Figure 4.18. It is clear that an increase in the nickel concentration of the feed solution results in decreased extraction. At first sight this seems contrary to the reaction equilibrium (Equation 4.16), but a closer look at the data shows that, although the increased nickel in the feed solution results in an increase in the nickel concentration of the raffinate solution (positive effect), it also results in a drop in the pH, decrease in the activity coefficient of the nickel and an increase in the activity of the sulphate ions, all of which have a negative effect on the extraction process.

4.3.3.5 The effect of the raffinate pH

It is clear from the equilibrium model (Equation 4.28) that the pH of the raffinate solution will have a dramatic effect on the extraction equilibrium. A set of experiments was done to confirm this and Figure 4.19 shows the results of these experiments and the characteristic sigmoid-form predicted by the equilibrium model.

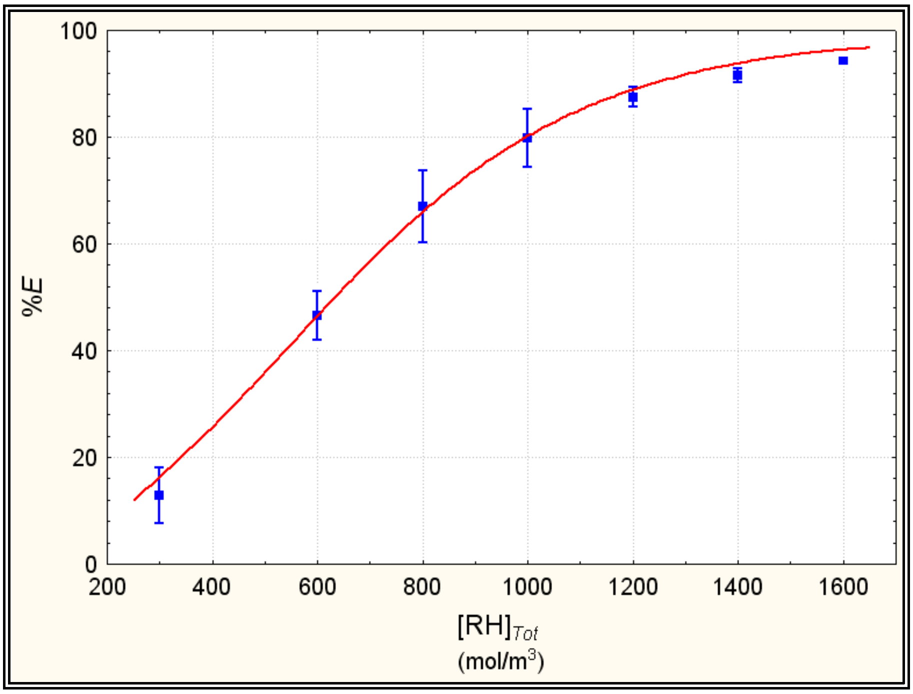


Fig. 4.16: Effect of $[RH]_{Tot}$ on % extraction. $Vr = 0.5$, $[Ni]_f \approx 1.85$ mol/m^3, ■: Experimental data with 95% confidence limits. ——: Equilibrium model ($r^2=0.999$)

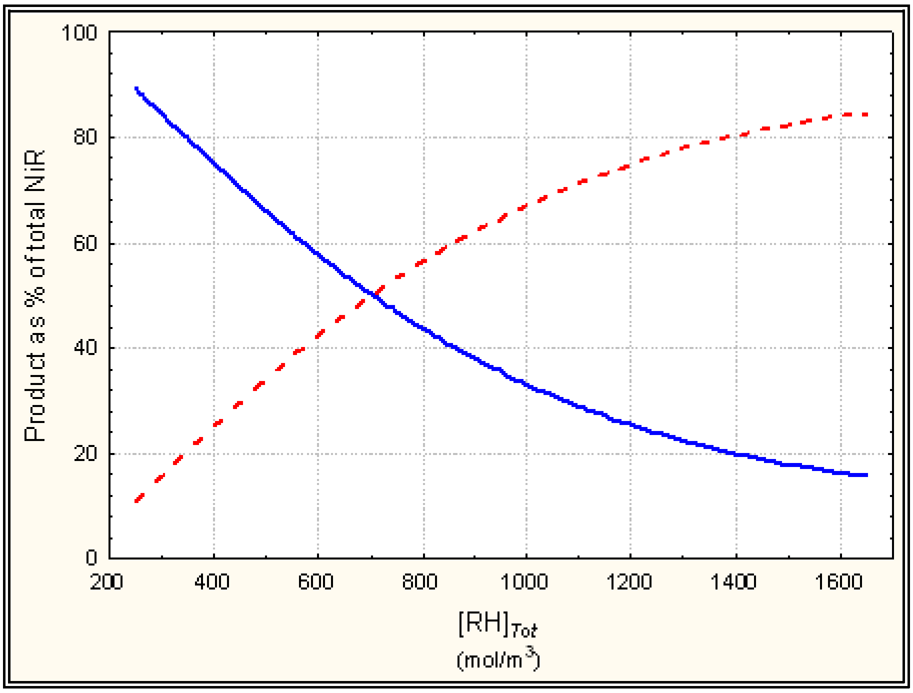


Fig. 4.17: Predicted product distribution of nickel-organic complexes. $Vr = 0.5$, $[Ni]_f = 1.85$ mol/m^3, ——: NiR_2, – –: NiR_6

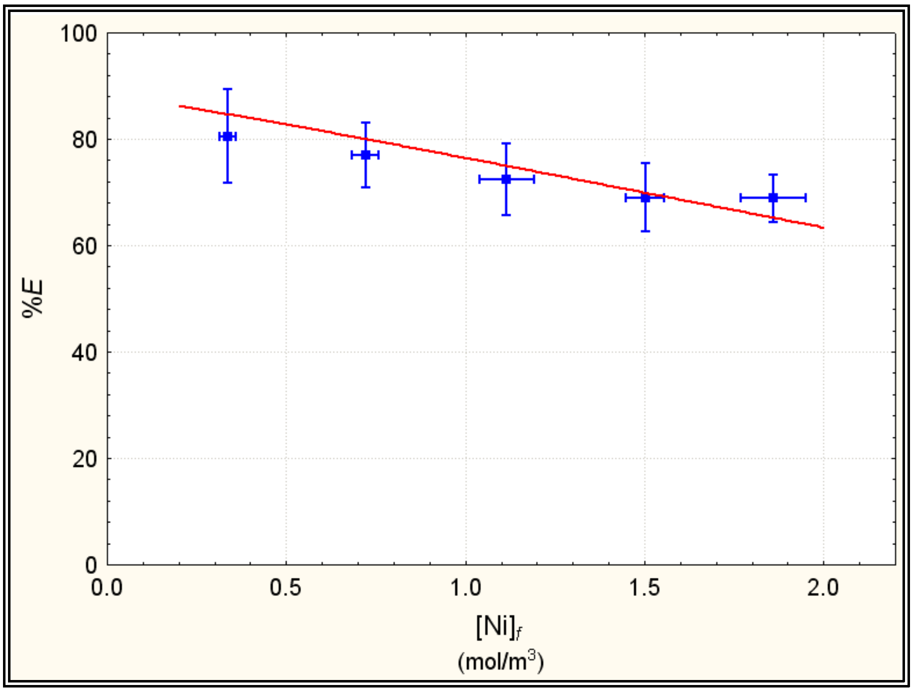


Fig. 4.18: Effect of $[Ni]_f$ on % extraction. $Vr = 1$, $[RH]_{Tot} = 1200$ mol/m^3. ■: Experimental data with 95% confidence limits. —: Equilibrium model (r^2=0.998)

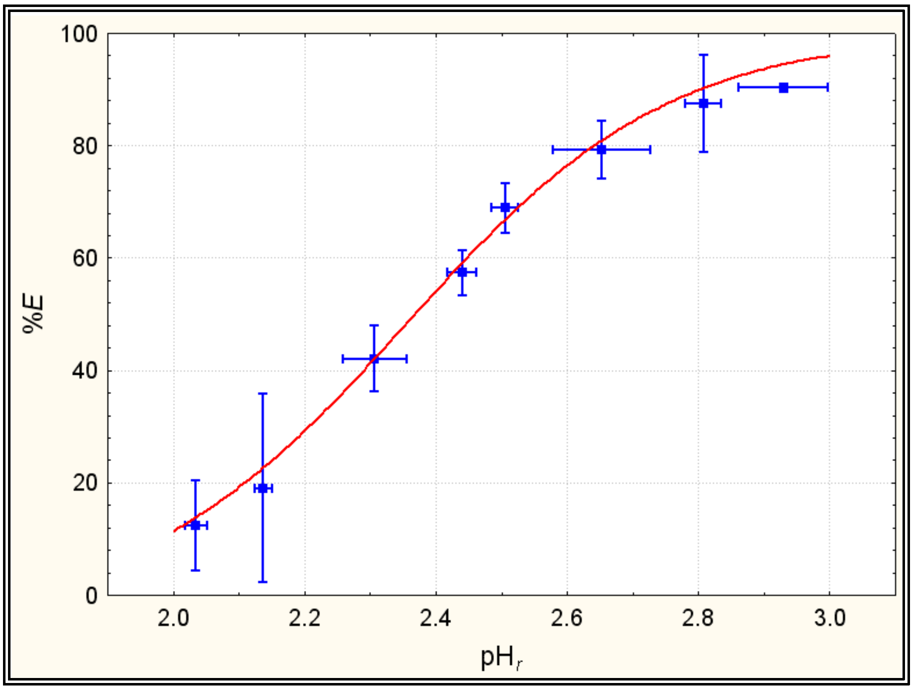


Fig. 4.19: Effect of pH_r on the % extraction. $Vr = 1$, $[Ni]_f \approx 1.8$ mol/m^3, $[RH]_{Tot} = 1200$ mol/m^3. ■: Experimental data with 95% confidence limits. —: Equilibrium model (r^2=0.999)

4.3.3.6 Effect of the volume ratio between the feed and organic solution

The volume ratio between the feed and organic solution influences all the parameters in the extraction process and a set of experiments was done to establish the overall effect of the extraction. This factor is not of direct importance to the establishment of the equilibrium but as with the 2^k experiments it increased the confidence in the equilibrium model. The results of these experiments can be seen in Figure 4.20. An increase in the volume ratio leads to a decrease in the %extraction, mainly due to the fact that there is more nickel that needs to be extracted in the feed and there is less organic solution to do it with.

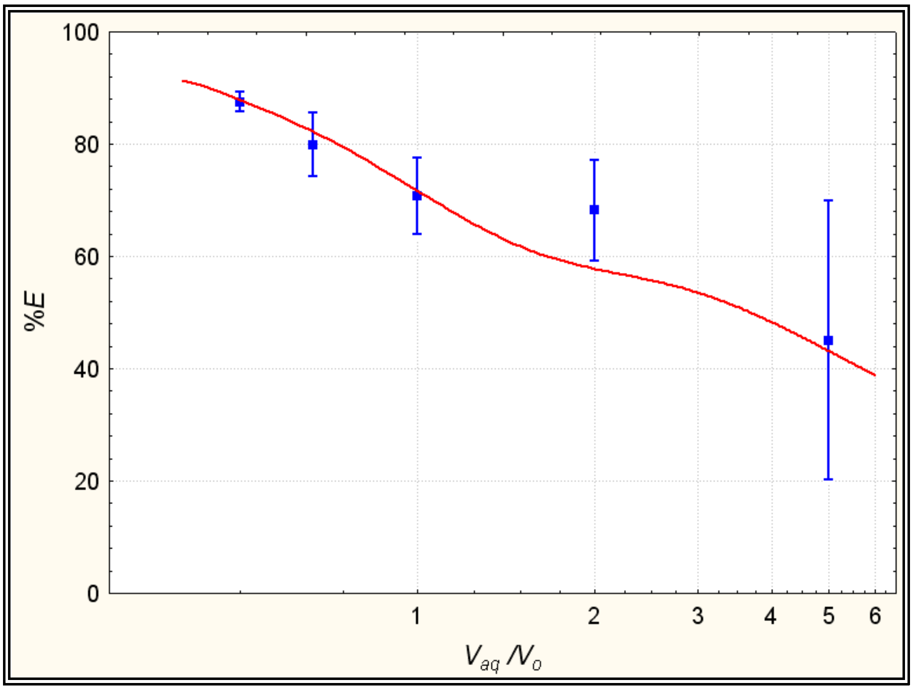


Fig. 4.20: Effect of Vr on % extraction. $[Ni]_f \approx 1.85$ mol/m^3, $[RH]_{Tot} = 1200$ mol/m^3. ■: Experimental data with 95% confidence limits. —: Equilibrium model (r^2=0.995)

4.4 Determination of the equilibrium data for the Zn/D2EHPA system

The equilibrium constants for the extraction were determined in the same manner as for the extraction of nickel. The extraction of zinc was not the main focus of this study and the detailed results are not discussed in the main text, but a summary of an article that resulted from this work can be seen in Appendix E. The most important difference between the extraction of nickel and the extraction of zinc is that zinc does not form a complex with the sulphate ions (Equation 4.1). This simplifies the distribution equation to the following:

$$D = \frac{K_{Zn1} \cdot a\left(\mathrm{RH}\right)_o^2 \cdot \gamma\left(\mathrm{Zn}^{2+}\right)_{aq}}{a\left(\mathrm{H}^+\right)_{aq}^2} + \frac{K_{Zn2} \cdot a\left(\left(\mathrm{RH}\right)_2\right)_o^{1.5} \cdot \gamma\left(\mathrm{Zn}^{2+}\right)_{aq}}{a\left(\mathrm{H}^+\right)_{aq}^2} \tag{4.34}$$

with

$$K_{Zn1} = \frac{P^0_{\mathrm{ZnR_2}} \cdot K_{\mathrm{ZnR_2}} \cdot K^2_{\mathrm{RH}}}{\left(P^0_{\mathrm{RH}}\right)^2} \tag{4.35}$$

$$K_{Zn2} = \frac{K_{\mathrm{ZnR_3}} \cdot P^0_{\mathrm{ZnR_2}} \cdot K_{\mathrm{ZnR_2}} \cdot K^2_{\mathrm{RH}}}{\left(P^0_{\mathrm{RH}}\right)^2} \tag{4.36}$$

The values of K_{Zn1} and K_{Zn2} were once again determined using a regression. The regression had a correlation coefficient (r^2) of 0.996 and the results can be seen in Table 4.5.

Table 4.5: Regression results for equilibrium constants for zinc

Variable	Value	Std. Err.
K_{Zn1} (-)	1.063×10^{-7}	0.0328×10^{-7}
K_{Zn2} (m^6/mol^2)	3.26	0.084

4.5 Determination of the viscosity and density of D2EHPA/ Kerosene mixtures

4.5.1 Background

The viscosity and density of D2EHPA/kerosene mixtures at different temperatures are important physical properties that were needed for the modelling of the SLM process (see Section 5.4.3). These values were, however, not available in the literature (Swain *et al.,* 2001: 234). Numerous attempts have appeared in the literature dealing with the development of reliable methods for estimating liquid viscosity of binary and multi-component mixtures. Despite all these efforts, a theoretical description of the viscosity of liquid mixtures nowadays remains insufficient due to the poor understanding of the liquid itself. Consequently, most of the estimation methods for liquid viscosity appearing in the literature are essentially empirical or semi-empirical in nature (Macías-Salinas *et al.,* 2003:319). In addition to this problem (theoretical grounds), kerosene is a petrol fraction and its composition and properties vary from one batch to another.

4.5.2 Experimental procedure

The mixtures were prepared at ambient temperature by adding kerosene to a known amount (mol) of D2EHPA. The mixture concentrations tested, can be seen in Table 4.6. The densities and viscosities of the mixtures were measured at temperatures ranging from 30 - 70 °C in 10 °C increments. The measurements were done in a water bath in combination with a Shinco DCS 300 temperature controller and the accuracy was estimated at ± 1 °C. The densities were measured by a hydrometer (accuracy ± 0.5 kg/m^3), while viscosities were measured by a thoroughly cleaned, dried and calibrated Ostwald U-tube viscometer, as described by Aulton (2002). The calibration constant for the meter was approximately 5.1×10^{-8} m^2/s^2. The precision of viscosity measurement was within ± 0.15%.

4.5.3 Results and discussion

The densities and viscosities of the pure components as well as the mixtures were determined, and are presented in Table 4.6 and 4.7. The viscosity of D2EHPA, as well as its density at 20 °C, was determined, to see if the results corresponded with those proposed by the manufacturer. The values found were 35.1 mPa·s and 970 kg/m^3, which differed slightly from the 40 mPa·s and 960 kg/m^3 specified by the manufacturer. These differences were ascribed to different batches of the D2EHPA being tested.

It is generally accepted that the density of an ideal mixture (ρ_{mix}) is given by the sum of the densities of the components (ρ_i) multiplied with the volume fraction of the component ($x_{vol,i}$):

$$\rho_{mix} = \sum_i x_{vol,i} \cdot \rho_i \tag{4.37}$$

This theory was tested for the D2EHPA/kerosene mixtures and a near perfect fit was obtained ($r^2 = 1.000$) as can be seen in Figure 4.21. This meant that the mixtures' density could be predicted accurately if an accurate correlation could be found for the density of the pure D2EHPA and kerosene as a function of temperature. It was found that a linear relationship existed for both components:

$$\rho_{kerosene} = 962.7 - 0.715 \cdot T \tag{4.38}$$

and

$$\rho_{\mathrm{D2EHPA}} = 1188.4 - 0.740 \cdot T \tag{4.39}$$

with the density in kg/m^3 and the temperature in K. This relationship can also be seen in Figure 4.22.

Table 4.6: Densities of D2EHPA/kerosene mixtures at different temperatures

Concentration (mole D2EHPA/m^3)	Density (kg/m^3)				
	T = 30 °C	T = 40 °C	T = 50 °C	T = 60 °C	T = 70 °C
0 (kerosene)	746	739	732	724.5	717.5
400	774	767	760	752.5	745.5
800	804	796.5	789.5	780	773.5
1000	818.5	811	804	797	789
1200	832.5	825	818.5	811	803
1400	847.5	840	833	825.5	818
1600	861.5	854.5	848	840	832
2100	897.5	890.5	883	875.5	869
2600	934	927	920.5	912.5	905
3008 (D2EHPA)	964	957	949.5	942	934.5

Table 4.7: Viscosities of D2EHPA/kerosene mixtures at different temperatures

Concentration (mole D2EHPA/m^3)	Viscosity (mPa·s)				
	T = 30 °C	T = 40 °C	T = 50 °C	T = 60 °C	T = 70 °C
0 (kerosene)	1.07	0.851	0.679	0.56	0.468
400	1.324	1.031	0.807	0.657	0.542
800	1.742	1.302	0.995	0.794	0.646
1000	2.035	1.501	1.136	0.896	0.72
1200	2.375	1.749	1.304	1.015	0.806
1400	2.822	2.061	1.519	1.165	0.916
1600	3.439	2.482	1.803	1.358	1.047
2100	5.724	3.982	2.806	2.069	1.569
2600	11.01	7.268	4.897	3.456	2.509
3008 (D2EHPA)	21.22	13.315	8.559	5.83	4.089

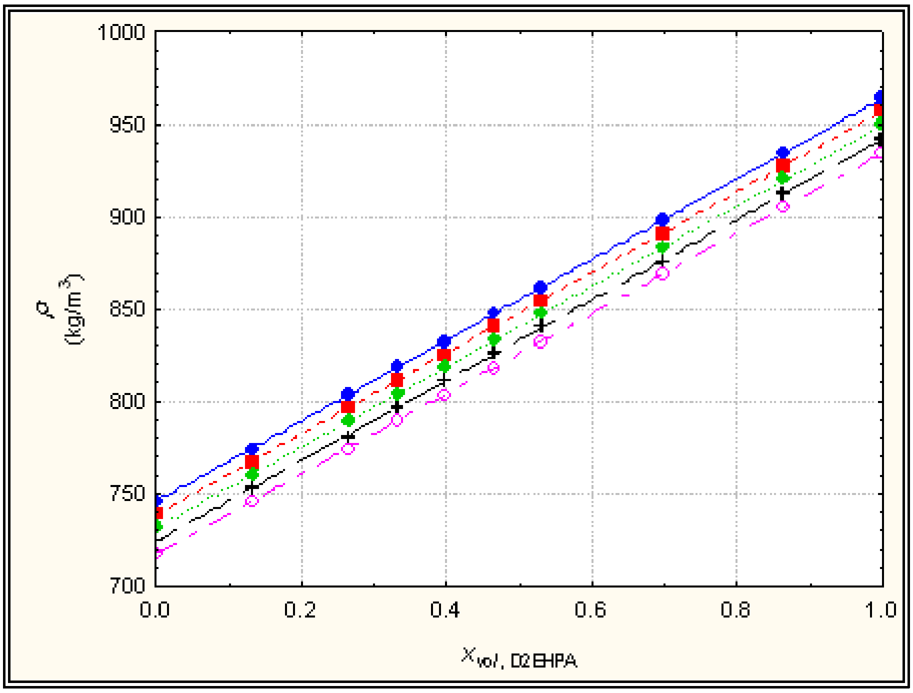


Fig. 4.21: Density of solution as a function of volume fraction. Data: (●) T = 30˚C; (■) T = 40˚C; (◆) = 50˚C; (✚) = 60 ˚C; (○) = 70 ˚C. Model: (——) T = 30˚C (r^2=1.000); (– –) T = 40˚C (r^2=1.000); (······) = 50˚C (r^2=1.000); (——) = 60 ˚C (r^2=1.000); (—— -) = 70 ˚C (r^2=1.000)

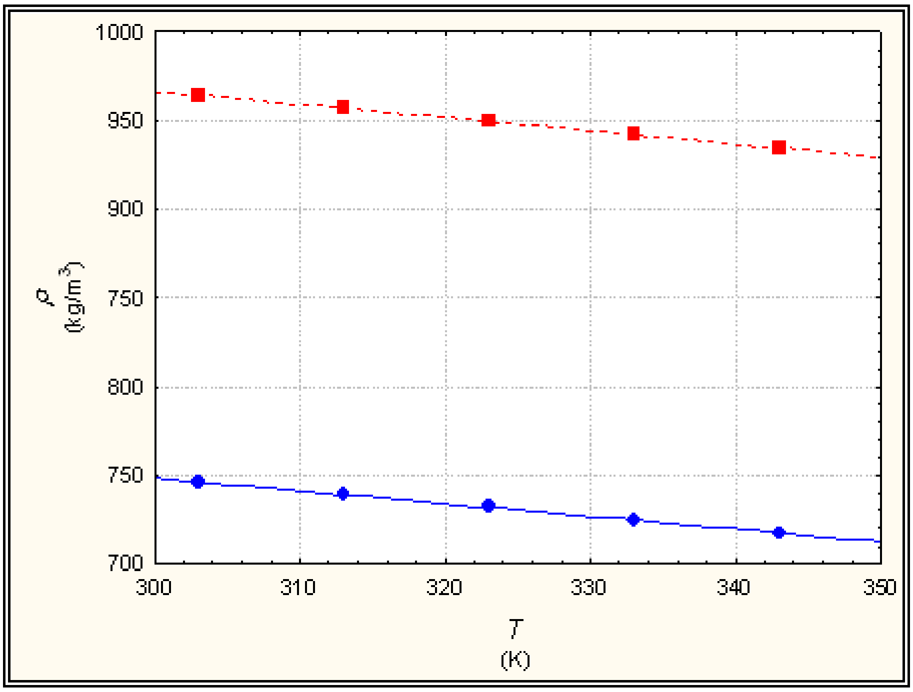


Fig. 4.22: Temperature dependence of pure component densities. Data: (●) Kerosene; (■) D2EHPA. Regression: (——) Kerosene (r^2=1.000); (– –) D2EHPA (r^2=1.000)

The viscosities of mixtures are usually determined by the Kendal and Monroe equation (Perry & Green, 1998 : 2-362):

$$\mu_{mix} = \left(\sum_i x_{mol,i} \cdot \mu_i^{1/3} \right)^3 \tag{4.40}$$

The problem with Equation 4.40 and the D2EHPA/kerosene system is that to calculate the mole fraction of the mixture, the molecular weight of kerosene is needed and this is not known since kerosene is a petrol fraction. If we however assume that the kerosene has an average molecular weight, M_{kerosene}, then the mole fraction can be calculated from the volume fraction:

$$x_{mol,j} = \frac{\left(x_{vol,j} \cdot \rho_j / M_j \right)}{\sum_i \left(x_{vol,i} \cdot \rho_i / M_i \right)} \tag{4.41}$$

For the D2EHPA/kerosene system we can then substitute Equation 4.41 into Equation 4.40 , which, with simplification gives:

$$\mu_{mix} = \left(\frac{M_{\text{kerosene}} \cdot x_{vol,\text{D2EHPA}} \cdot \rho_{\text{D2EHPA}} \cdot \left(\mu_{\text{D2EHPA}}\right)^{1/3} + M_{\text{D2EHPA}} \cdot x_{vol,\text{kerosene}} \cdot \rho_{\text{kerosene}} \cdot \left(\mu_{\text{kerosene}}\right)^{1/3}}{M_{\text{kerosene}} \cdot x_{vol,\text{D2EHPA}} \cdot \rho_{\text{D2EHPA}} + M_{\text{D2EHPA}} \cdot x_{vol,\text{kerosene}} \cdot \rho_{\text{kerosene}}} \right)^3 \tag{4.42}$$

In Equation 4.42 only the average molecular weight of the kerosene is unknown and was determined with the Levenberg-Marquardt non-linear regression method. It is important to note that, at the experimental temperatures, 98% of the D2EHPA was in the dimer form and the molecular weight of the D2EHPA dimer was used in Equation 4.42. The average molecular mass of the kerosene was calculated as 174.75 ± 0.98 g/mol, with a 0.999 correlation coefficient for all temperatures. The graphical representation of Equation 4.42, with the calculation done using the average molecular weight, as well as the data at temperatures between 30 ˚C and 70 ˚C can be seen in Figure 4.23.

It was found that the Riedel equation (Perry & Green, 1988:2-362) provided excellent representations of the temperature dependence of the pure component viscosities for both the D2EHPA and the kerosene:

$$\mu = \exp\left(R_A + \frac{R_B}{T} + R_C \cdot \ln(T) + R_D \cdot T^{R_E} \right) \tag{4.43}$$

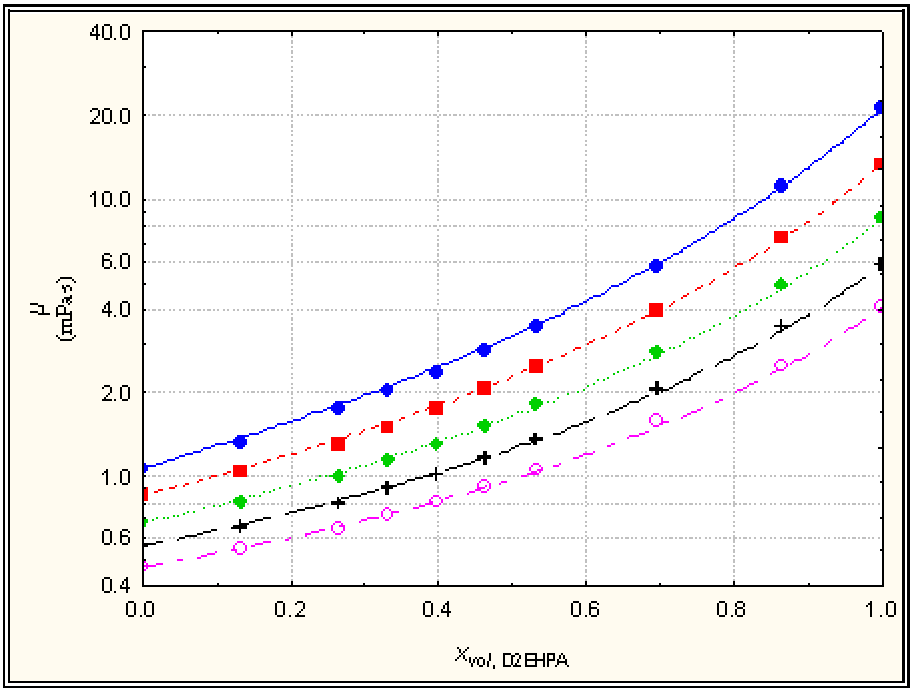


Fig. 4.23: Viscosity of solution as a function of volume fraction. Data: (●) T = 30°C; (■) T = 40°C; (◆) = 50°C; (✚) = 60 °C; (○) = 70 °C. Model: (——) T = 30°C (r^2=1.000); (— —) T = 40°C (r^2=1.000); (······) = 50°C (r^2=1.000); (——) = 60 °C (r^2=1.000); (—— ·) = 70 °C (r^2=1.000)

In Equation 4.43, μ is the viscosity of the liquid in mPa·s, T is the temperature in Kelvin, and R_A, R_B, R_C, R_D and R_E are constants. The last term is only used when the viscosity must be determined above the normal boiling point, while only the first two terms are applicable when viscosity is determined for small temperature intervals, as in this case. The values of R_A and R_B for D2EHPA and kerosene were determined with the Levenberg-Marquardt non-linear regression method and the results can be seen in Table 4.8. The data is presented graphically in Figure 4.24.

Table 4.8: Regression results for temperature dependence for the viscosity of D2EHPA and Kerosene

Component	R_A	Std. Err. (R_A)	R_B	Std. Err. (R_B)	r^2
Kerosene	-7.09	0.071	2169	98	1.000
D2EHPA	-11.4	0.14	4363	44	1.000

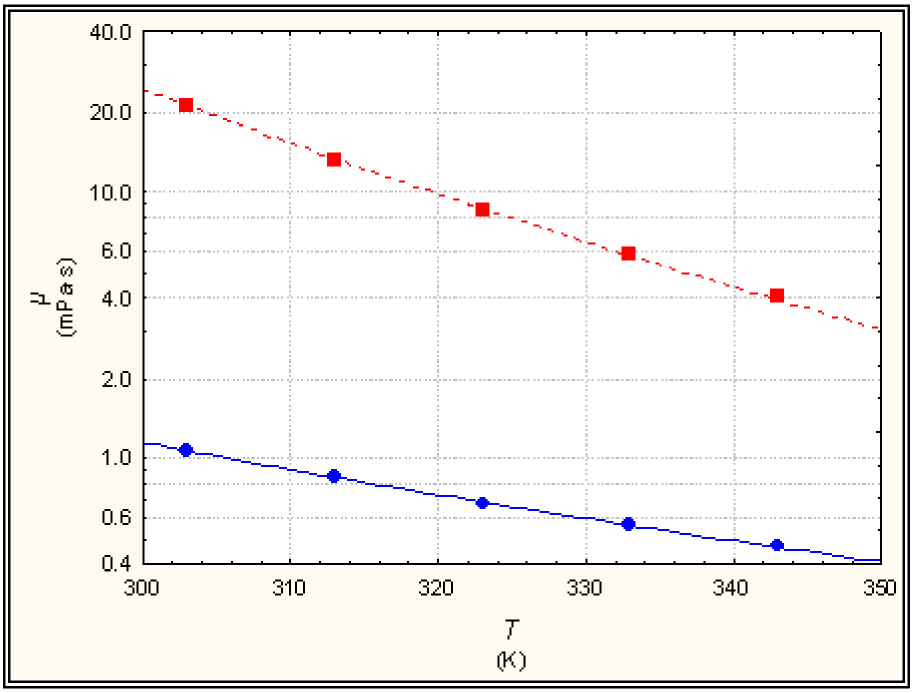


Fig. 4.24: Temperature dependence of pure component viscosities. Data: (●) Kerosene; (■) D2EHPA. Regression: (——) Kerosene (r^2=1.000); (– –) D2EHPA (r^2=1.000)

4.6 Determination of the friction factor within a SLM tube

4.6.1 Background

The friction factor of the aqueous solution flowing past the supported liquid membrane is an important variable in the determination of the mass transfer that occurs at the interface between the aqueous solution and the membrane. The fundamental theory of friction factors is derived from the definition of shear stress and viscosity and will be briefly discussed. If a liquid flows past a surface as a result of a force applied to the liquid, the shear stress (τ) of the liquid (for a Newtonian fluid) will be proportional to the velocity gradient ($\mathrm{d}v/\mathrm{d}y$) in the liquid (Wilkinson, 1960:1):

$$\tau = \mu \cdot \frac{\mathrm{d}v}{\mathrm{d}y} \tag{4.44}$$

μ is known as the Newtonian viscosity of the liquid. For flow of Newtonian fluids in a pipe or tube the shear stress at the wall is given by (Wilkinson, 1960:51):

$$\tau_w = \frac{r \cdot \Delta P}{2 \cdot L} \tag{4.45}$$

The Fanning friction factor is defined as:

$$f = \frac{2 \cdot \tau_w}{\rho \cdot v^2} \tag{4.46}$$

for laminar flow f = 16/Re (Wilkinson, 1960:59).

4.6.2 Experimental

A set of experiments was done with distilled water in which the pressure drop along the membrane tubes was measured at different flow rates. The experiments were done at 30, 35, 40, 50, 60 and 70 °C. The detailed results can be seen in Appendix C.4. The pressure drop as a function of flow rate at 50°C can be seen in Figure 4.25. It is clear that the pressure drop is much higher than calculated using the friction factor. If all the data points are plotted on a Moody diagram (Coulson & Richardson, 1990:54) we see that there is a large deviation from the theoretical 16/Re value for the friction factor (see Figure 4.26). To understand the nature of this deviation, we have to go back to the shear stress against the wall. Figure 4.27 shows the shear stress calculated with Equation 4.45 as a function of flow rate at 50 °C. Once again, we can see the deviation from the shear stress expected for laminar flow, but at all temperatures the shear stress was higher than predicted. This is attributed to the fact that the SLM wall is in fact a liquid and many of the assumptions that were made in the derivation of the original theory, such as no slip at the wall, is probably incorrect. This, combined with the fact that the SLM is highly hydrophobic, can lead to unusual interactions at the aqueous-organic interface. The definition of the friction factor is still valid if new correlations for the shear stress is used. It was proposed that an equation with the following form should be used for the prediction of the shear stress:

$$\tau_w = a_0 \cdot Re + a_1 \cdot Re^3 \tag{4.47}$$

In this correlation the first term is determined by the theoretical shear stress, while the second term can be subscribed to the non-ideality of the SLM-wall. The values of a_0 and a_1 are dependent on temperature and can be described by the Riedel equation (Equation 4.43). This temperature dependence was determined with a non-linear regression and the results are summarised in Table 4.9. The combination of Equation 4.47 and the temperature dependence of a_0 and a_1 had a correlation coefficient (r^2) of 0.994 for all the experiments. The predicted and observed shear stress values for all the experiments can be seen in Figure 4.28.

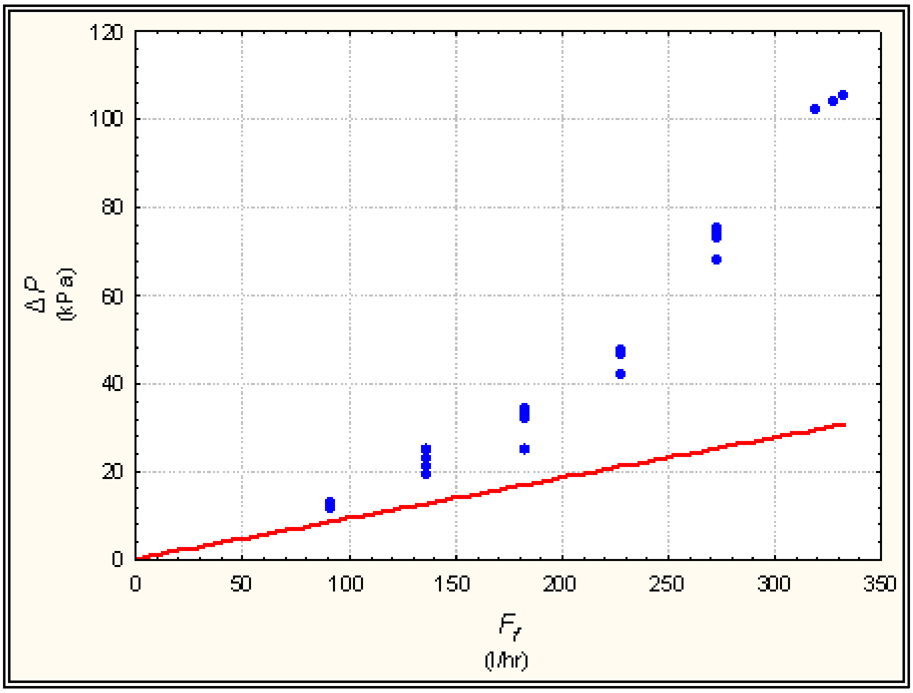


Fig. 4.25: Pressure drop *vs.* flow rate at 50°C. ●: Data. (—) Theory (r^2=0.573)

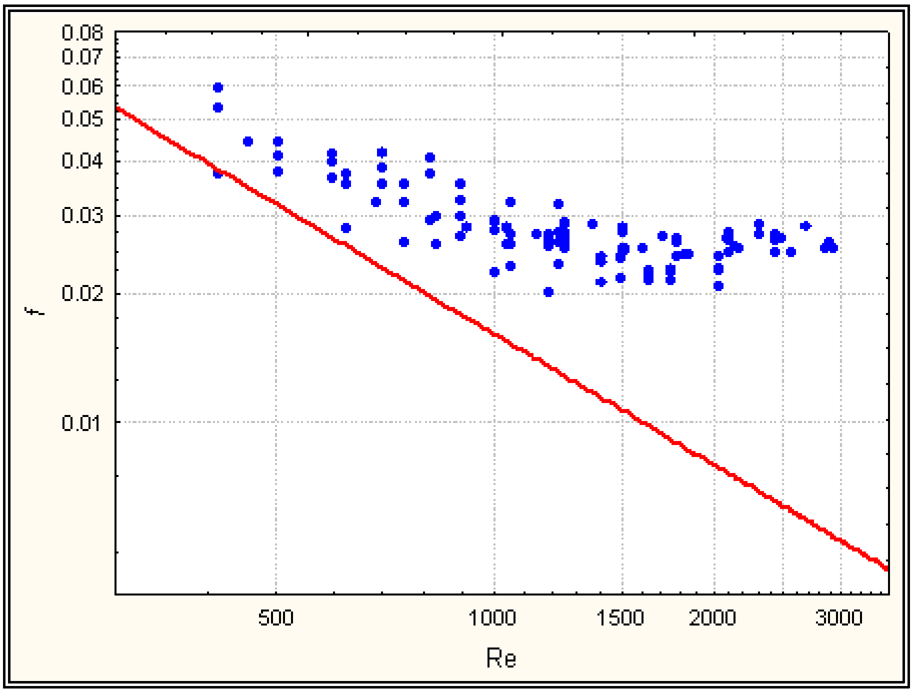


Fig. 4.26: Moody diagram for flow through SLM tube. ●: Data. (—) 16/Re (r^2=0.754)

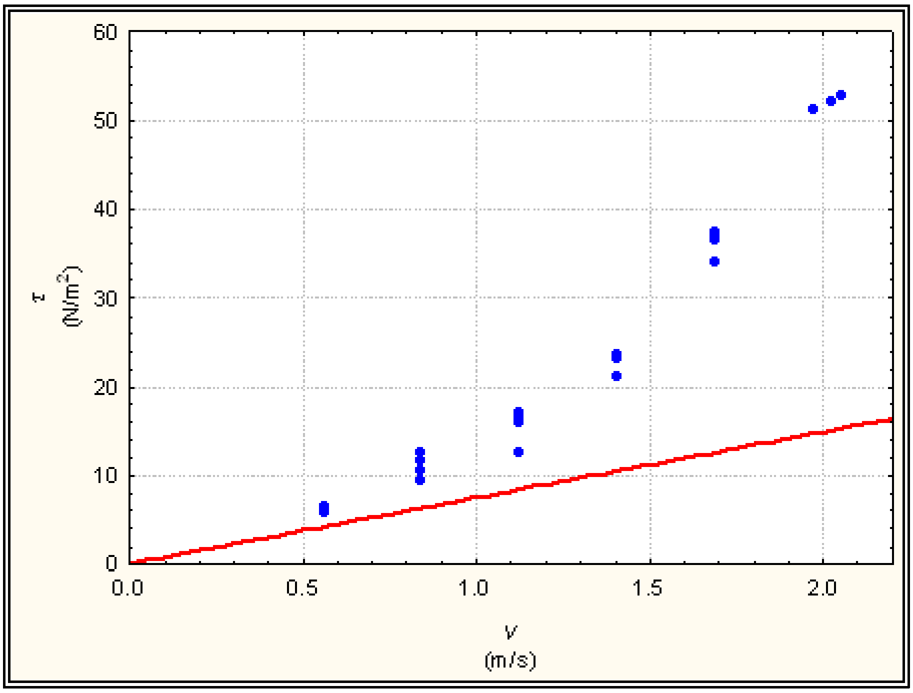


Fig. 4.27: Shear stress as a function of liquid velocity at 50°C. ●: Data. (——): Theory (r^2=0.573)

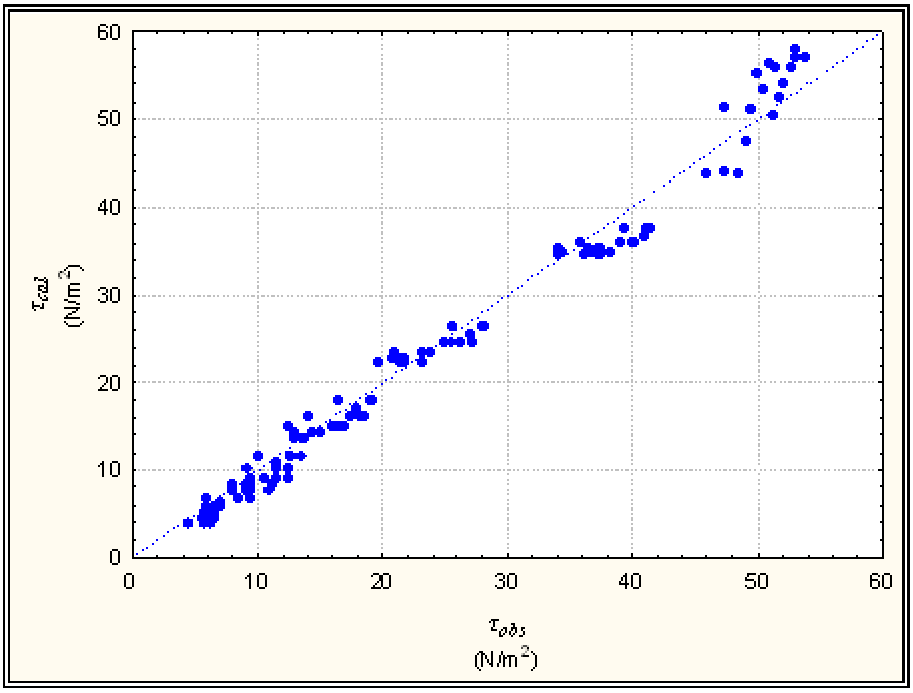


Fig. 4.28: Predicted *vs.* observed shear stress values (r^2=0.994)

Table 4.9: Riedel constants for shear stress coefficients

Coefficient	R_A	σ_{RA}	R_B	σ_{RB}	r^2
a_0	-16.1	0	3608	2	1.000
a_1	-33.3	0.4	4499	111	1.000

4.7 Conclusions

The complex thermodynamic calculations associated with aqueous systems are considerably simplified with the use of specialised software such as OLIAnalyzer. This software incorporates a database which increases the accuracy of calculations and variables such as the activity of species, the aqueous speciation and self diffusivities.

The extraction of nickel with D2EHPA can be adequately described by a system of seven equilibrium reactions, part of which is the formation of two nickel-organic species. The aqueous speciation and activity of the aqueous species are an integral part of these equilibrium reactions and can be easily calculated with modern software such as OLIAnalizer. It was found that the resulting equilibrium model could accurately predict the results from various experiments in which the total D2EHPA concentration, the concentration and pH of the raffinate solution and the volume ratio between the feed and solvent were varied. It was found that the effect of temperature was negligible. The Zn/D2EHPA liquid – liquid extraction system was described in the same way as the Ni/D2EHPA system, but the Zn forms different organo-metallic species and does not form an aqueous $ZnSO_4$ complex.

The densities and viscosities of pure D2EHPA and kerosene, as well as their mixtures, were determined. It was found that the Riedel equation provided excellent representations of the experimental data. The densities were found to be linear and it was found that the Kendal and Monroe equation could accurately predict the viscosity of the D2EHPA/kerosene mixtures if an average molecular weight of the kerosene is used.

It was found that the shear stress of water in a SLM tube is higher than predicted theoretically. This can possibly be explained by the fact that the SLM tube wall is in fact a liquid and some of the assumptions made in the development of the original theory is probably incorrect. There can also be some interactions between the kerosene and the aqueous solution that result in a higher shear stress. An empirical equation was derived to calculate the shear stress in the tube wall and it was found that this equation adequately describes the shear stress for the temperature range used in this thesis.

Chapter 5

Modelling the SLM process

> *"Reality is merely an illusion, albeit a very persistent one."*
> *-Albert Einstein*

5.1 Introduction

The development of a theoretical process model which accounts for the experimental data is essential in understanding the SLM process. It is also vital for accurate up-scaling of the process and although a number of process models have been developed in the past (refer to Section 2.4), they tend to incorporate simplifications that are not valid for industrial applications. There are especially shortcomings in the prediction of the influence of temperature on the SLM process. The importance of incorporating temperature in a usable process model is especially meaningful if one considers that it favourably influences most of the steps in the SLM process. Another shortcoming is the effect of aqueous speciation and the simplification made in most process models to assume that the molality is equal to the activity of the aqueous species. This was shown in Section 4.2.3 to be incorrect.

5.2 Assumptions

The following assumptions were made in developing the process model:

- The equilibrium constant of the extractant is independent of temperature.
- The flux through the membrane is in a pseudo-steady state.
- The reaction at the liquid-liquid interface is fast and proceeds to equilibrium.
- The concentration of the aqueous species in the reactor/extractor at a certain time is constant.

In the following paragraphs the reason behind each of the assumptions and its relevance will be discussed.

The equilibrium constant is independent of temperature

This was proved and discussed in Section 4.3.3.2.

The flux through the membrane is in a pseudo-steady state

To understand this assumption it is necessary to look at the process from both a macroscopic (the change of the nickel concentration in the feed and strip recycle tanks) and a microscopic point of view (the transport of nickel through the membrane). From the macroscopic point of view the extraction process is a dynamic process that can be explained with the use of a dynamic (non-steady state) mass balance. Since the macroscopic process time is larger than the time needed for the microscopic process, the microscopic process can be viewed as a pseudo-steady state process. The conditions for the microscopic process were therefore assumed to be constant at a certain time, although it is recognised that it changes over a longer time period. This assumption is confirmed by the fact that no delay was noticed from the time the nickel was removed from the feed phase to the time it appeared in the strip solution (see Figure 3.10).

The reaction at the liquid-liquid interface is fast

This assumption basically means that the interface reaction is not the rate-limiting step in the extraction process. This was confirmed by the fact that the overall activation energy of the process is 17.2 kJ/mol (see Section 6.5.6), showing that the process is diffusion-limited. This assumption was also made by other researchers (Alguacil & Alonso, 2000:83; Arous *et al.*, 2004:297; Basualto *et al.*, 2003:1004). Some researchers, however, chose to include the reaction kinetics (Akiba *et al.*, 1997:12; Kasaini *et al.*, 1998:161; Lin & Juang, 2002:146). It was decided, that, if the model gave good approximations for all of the variables, not to include the reaction kinetics. One would especially expect a deviation in the model from the experimental data in the prediction of the effect in temperature (see Figure. 6.10) if the assumption were not true, which was not the case.

The concentration of the aqueous species in the reactor/extractor at a certain time is constant

Other ways to express this assumption is to say that the reactor/extractor is perfectly mixed or that the reactor/extractor can be viewed as a differential element. The average residence time of the aqueous phase in the reactor is of the order of 0.2 s, With a typical nickel flux of 0.6 mg/m^2·s and aqueous nickel concentration of 50 mg/l, it means that the difference between the inlet and outlet concentration of the reactor is generally less than 1 mg/l.

5.3 Modelling of the metal concentration in the system

The concentration of the metal ions in the feed solution can be described by using a dynamic (non-steady state) mass-balance over the feed side:

$$V_f \cdot \frac{\mathrm{d}[\mathrm{Ni}]_f}{\mathrm{d}t} = F_{FT}\left([\mathrm{Ni}]_{FT} - [\mathrm{Ni}]_f\right) - J_{\mathrm{Ni}} \tag{5.1}$$

with: $[\mathrm{Ni}]_f$: The concentration of the nickel in the bulk of the feed solution (mol/m^3).

F_{FT} : The flow rate of the feed into the system from the feed tanks (m^3/s).

$[\mathrm{Ni}]_{FT}$: The concentration of the nickel in the feed solution (mol/m^3).

J_{Ni} : The flux of nickel across the membrane (mol/s).

Similarly, the concentration of the nickel in the strip side is given by:

$$V_s \cdot \frac{\mathrm{d}[\mathrm{Ni}]_s}{\mathrm{d}t} = F_{ST} \cdot \left([\mathrm{Ni}]_{ST} - [\mathrm{Ni}]_s\right) + J_{\mathrm{Ni}} \tag{5.2}$$

The calculation of the nickel flux across the membrane is the most difficult and complex step in solving Equation 5.1 and 5.2 and will be discussed in more detail in the following section.

5.4 Modelling of the metal flux through the membrane

As mentioned in Section 2.4, the modelling of supported liquid membranes is based on the permeation of metal species across the SLM in six steps. These steps can be represented by the concentration profile of each species through the SLM (see Figure 5.1). It should be noted, that the nickel can diffuse through the membrane as different species, either as Ni^{2+}_{aq} or as one of the nickel-organic species. The overall goal of the modelling is, however, to determine the transmembrane flux of the total nickel, irrespective of the form of the nickel species involved.

5.4.1 Diffusion through aqueous boundary layer

Diffusion of the nickel and hydronium ions in the feed and strip phase towards the membrane interface occur according to Fick's first law applied to film theory. Fick's first law, applied to nickel in the feed phase gives:

$$J'_{\mathrm{Ni}^{2+},f} = k_{\mathrm{Ni}^{2+},f} \cdot \left([\mathrm{Ni}^{2+}]_f - [\mathrm{Ni}^{2+}]_{fi}\right) \tag{5.3}$$

with $k_{\mathrm{Ni}^{2+},f}$: Mass transfer coefficient of nickel in the feed (m/s).

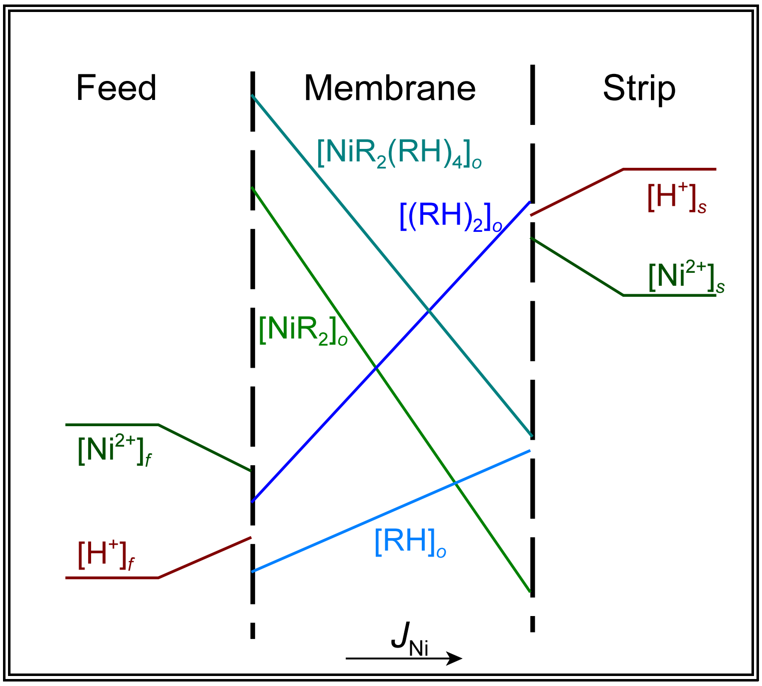


Fig. 5.1: Concentration profile of species through SLM

$[Ni^{2+}]_{fi}$: Concentration of nickel at the membrane interface on the feed side (mol/m^3).

$[Ni]_f$: The concentration of the nickel in the bulk of the feed solution (mol/m^3).

$J'_{Ni^{2+},f}$: Flux of nickel from the bulk to the interface (mol/m^2·s)

The mass transfer coefficient can be estimated by a dimensionless correlation. In this research the Chilton-Colburn analogy was used (Hines & Maddox, 1985:175) :

$$\mathrm{Sh} = \frac{f}{2} \cdot \mathrm{Re} \cdot \mathrm{Sc}^{1/3} \tag{5.4}$$

with Sh : Sherwood number = $k \cdot d_e / D_{AB}$

Re : Reynolds number = $\rho \cdot v \cdot d_e / \mu$

Sc : Schmidt number = $\mu / (\rho \cdot D_{AB})$

f : Fanning friction factor and is calculated with Eq. 4.46 & 4.47 (see Section 4.6)

The diffusion coefficient (D_{AB}) is usually calculated from the self-diffusivities of the ion pair that diffuses through the boundary layer, eg. for Ni^{2+} the ion pair that diffuses through the boundary layer is (Ni^{2+}/SO_4^{2-}), however for the SLM application the sulphate ions are spectator ions and the requirement of charge neutrality implies that the diffusion coefficient should be calculated for the

(Ni^{2+}/H^+) ion pair:

$$D_{Ni^{2+}/H^+} = \frac{D_{Ni^{2+}} \cdot D_{H^+}}{D_{Ni^{2+}} + D_{H^+}} \cdot \frac{\left|Z_{Ni^{2+}}\right| + \left|Z_{H^+}\right|}{\left|Z_{Ni^{2+}}\right| \cdot \left|Z_{H^+}\right|} = \frac{D_{Ni^{2+}} \cdot D_{H^+}}{D_{Ni^{2+}} + D_{H^+}} \cdot 1.5 \tag{5.5}$$

With $D_{Ni^{2+}}$ and D_{H^+} the values of the self-diffusivities of nickel and hydronium and can be calculated with modern thermodynamic software packages such as OLIAnalyzer.

The flux of the nickel from the bulk solution to the membrane interface can thus be calculated if the concentrations of nickel in the bulk of the feed and the strip solutions are known. In the same way the flux of the other ions in the feed and strip can be calculated:

$$J'_{H^+,f} = k_{H^+,f} \cdot \left(\left[H^+\right]_f - \left[H^+\right]_{fi}\right) \tag{5.6}$$

$$J'_{Ni^{2+},s} = k_{Ni^{2+},s} \cdot \left(\left[Ni^{2+}\right]_s - \left[Ni^{2+}\right]_{si}\right) \tag{5.7}$$

$$J'_{H^+,s} = k_{H^+,s} \cdot \left(\left[H^+\right]_s - \left[H^+\right]_{si}\right) \tag{5.8}$$

5.4.2 Reaction at the membrane interface

It is assumed that the reaction at the interface is relatively fast and is at equilibrium. The equilibrium of the Ni/D2EHPA system was discussed extensively in Section 4.3. The equilibrium at the membrane interface can be calculated by solving Equations 4.19, 4.28 and 4.29 simultaneously.

5.4.3 Diffusion through the liquid membrane

Diffusion of the NiR_2 and NiR_6 complexes (J_{NiR2} & J_{NiR6}) through a part of the liquid membrane with thickness dr is described by Fick's first law:

$$J_{NiR_2} = -A_{mem}(r) \cdot D_{NiR_2} \cdot \frac{d\left[NiR_2\right]}{dr} \tag{5.9}$$

$$J_{NiR_6} = -A_{mem}(r) \cdot D_{NiR_6} \cdot \frac{d\left[NiR_6\right]}{dr} \tag{5.10}$$

with A_{mem} : Membrane area (m^2)

D_{NiR2} & D_{NiR6} : Effective diffusion coefficient of the nickel-organic complexes through the membrane ($\mathrm{m^2/s}$).

d [$\mathrm{NiR_2}$] &
d [$\mathrm{NiR_6}$] : Concentration gradient across a differential element of the membrane ($\mathrm{mol/m^3}$).

Equation 5.9 and 5.10 can be solved numerically by discretisation. For a number of tubes (n_t), with a tube length of L at a point r in the membrane, Equations 5.9 and 5.10 become:

$$J_{\mathrm{NiR_2}} = 2 \cdot n_t \cdot \pi \cdot r \cdot L \cdot D_{\mathrm{NiR_2}} \cdot \frac{[\mathrm{NiR_2}]^{r} - [\mathrm{NiR_2}]^{r+\Delta r}}{\Delta r} \tag{5.11}$$

$$J_{\mathrm{NiR_6}} = 2 \cdot n_t \cdot \pi \cdot r \cdot L \cdot D_{\mathrm{NiR_6}} \cdot \frac{[\mathrm{NiR_6}]^{r} - [\mathrm{NiR_6}]^{r+\Delta r}}{\Delta r} \tag{5.12}$$

The total nickel flux through the membrane is then the sum of J_{NiR2} and J_{NiR6}:

$$J_{\mathrm{Ni}} = J_{\mathrm{NiR_2}} + J_{\mathrm{NiR_6}} \tag{5.13}$$

Equation 5.13 then forms a system of equations together with Equation 4.18, 4.19, 4.29, 5.11 and 5.12 that can be solved simultaneously for every point in the membrane. The membrane was divided into 20 such points across the thickness of the membrane and each point was solved with Newton's method.

It should be noted that there exists an equilibrium between the $\mathrm{NiR_2}$, $\mathrm{NiR_6}$, RH and $\mathrm{(RH)_2}$ species as discussed in Section 4.3, given by Equation 4.18 and 4.19:

$$K_{\mathrm{NiR_6}} = \frac{a\left(\mathrm{NiR_2(RH)_4}\right)_o}{a\left(\mathrm{NiR_2}\right)_o \cdot a\left(\mathrm{(RH)_2}\right)_o^2} \tag{4.18}$$

$$K_D = \frac{a\left(\mathrm{(RH)_2}\right)_o}{a\left(\mathrm{RH}\right)_o^2} = 12\ \mathrm{m^3/mol} \tag{4.19}$$

If the dimeric D2EHPA diffuses faster through the membrane, the equilibrium reaction will produce more $\mathrm{NiR_6}$ and less $\mathrm{NiR_2}$ species (Equation 4.18) and this will have an effect on the diffusion of these two species. This equilibrium exists at every point in the membrane and means that the diffusion effect of the monomeric and dimeric D2EHPA is indirectly incorporated in the diffusion of the NiR_2 and NiR_6 species.

The effective diffusion coefficients in Equation 5.10 and 5.11 are dependent on temperature and the viscosity of the organic solution. Different correlations are available to estimate diffusion coefficient of liquids; the simplest is probably the Stokes-Einstein equation (Hines & Maddox, 1985:27):

$$D = \frac{k_B \cdot T}{6 \cdot \pi \cdot r_{mol} \cdot \mu} \tag{5.14}$$

with D : Self-diffusion coefficient (m^2/s)

k_B : Boltzmann's constant (1.380×10^{-23} J/K)

T : Temperature (K)

r_{mol} : Radius of diffusing particle

μ : Solution viscosity (kg/m·s)

The Stokes-Einstein equation is, however, derived for spherical solute particles that are large compared to the solvent in which they move, a assumptions which are questionable for the Ni/D2EHPA/kerosene system. It can, however, be used as a starting point for estimating the diffusion coefficient of the process model. In this equation only the temperature and viscosity are not constant for the system and can therefore be simplified to the following:

$$D = \alpha \cdot \frac{T}{\mu} \tag{5.15}$$

with α a constant for the system. The viscosity of a component in turn is a function of temperature and was determined experimentally for the D2EHPA/kerosene system in Section 4.4. The relationship between the effective diffusion coefficient and the diffusion coefficient is given by (Hines & Maddox, 1985:46):

$$D_{eff} = D \cdot \frac{\varepsilon}{\tau} \tag{5.16}$$

with ε the porosity of the membrane support and τ the tortuosity of the diffusing molecule. It is commonly accepted that the tortuosity in porous membranes is the reciprocal of the tortuosity and Equation 5.15 can then be rewritten as:

$$D_{eff} = \alpha_1 \cdot \frac{T}{\mu} \tag{5.17}$$

5.5 Simulating the SLM extraction process

The first step in simulating the SLM process, is to solve the dynamic (unsteady state) mass balances of Equations 5.1 and 5.2 simultaneously. This can be done numerically by discretisation of the equations:

$$[\mathrm{Ni}]_{f,t+1} = [\mathrm{Ni}]_{f,t} + \frac{\Delta t}{V_f} \cdot \left(F_{FT} \cdot \left([\mathrm{Ni}]_{FT,t} - [\mathrm{Ni}]_{f,t}\right) - J_{\mathrm{Ni}}\right) \tag{5.18}$$

$$[\mathrm{Ni}]_{s,t+1} = [\mathrm{Ni}]_{s,t} + \frac{\Delta t}{V_s} \cdot \left(F_{ST} \cdot \left([\mathrm{Ni}]_{ST,t} - [\mathrm{Ni}]_{s,t}\right) + J_{\mathrm{Ni}}\right) \tag{5.19}$$

The calculation of J_{Ni} in Equations 5.18 and 5.19 is done by solving the equations discussed in section 5.4 according to the flow diagram in Figure 5.2. Newton's method is used to solve the concentrations at the membrane interface on the strip side and the concentration of the species in the membrane at 20 discreet points through the membrane. These algorithms are nested within another solving algorithm, that also uses Newton's method, to balance the flux through the feed boundary layer (Equation 5.3) and subsequently the nickel flux through the membrane. The only constants not known in the simulation are the values of α_1 for the effective diffusion coefficients of the nickel-organic species (in Equation 5.17). It was found that a slight adjustment of the Reynolds exponent in the Chilton-Coulbourn analogy gave a significant improvement in the regression results. The adjustment means that Equation 5.4 can be rewritten as Equation 5.20, adding another unknown (α_2) to the regression problem.

$$\mathrm{Sh} = \frac{f}{2} \cdot \mathrm{Re}^{\alpha_2} \cdot \mathrm{Sc}^{1/3} \tag{5.20}$$

The values of these constants were determined with the use of a Quasi-Newton regression (Jacoby *et al.*, 1972:117. See Appendix D.6 for program) and had a correlation coefficient (r^2) of 0.984 for all the experiments. The confidence intervals of the regression were determined with the likelihood ratio method (Ratkowsky, 1983:30). The results of the regression are summarised in Table 5.1 and the relationship between the observed nickel flux in the experiments and the nickel flux as predicted by the simulation for all 148 experiments and 844 time data points can be seen in Figure 5.3.

Table 5.1: Regression results for SLM process model

Variable	Value	-95% confidence	+95% confidence
$\alpha_{1,\mathrm{NiR2}}$ (Pa·m^2/K)	1.46×10^{-16}	1.39×10^{-16}	1.54×10^{-16}
$\alpha_{1,\mathrm{NiR6}}$ (Pa·m^2/K)	8.56×10^{-17}	8.03×10^{-17}	9.10×10^{-17}
α_2 (-)	0.8683	0.8637	0.8729

Equation 5.17 can be used to calculate the effective diffusion coefficients of the NiR_2 and the $NiR_2(RH)_4$ species at different temperatures and D2EHPA concentrations. The effective diffusion coefficient, for a D2EHPA concentration of 1200 mol/m^3, of the NiR_2 species varies from 1.86×10^{-11} m/s to 6.21×10^{-11} m/s between 30°C and 70°C, while the effictive diffusion coefficient of the $NiR_2(RH)_4$ species varies from 1.09×10^{-11} m/s to 3.64×10^{-11} m/s in the same temperature range. These values can be used, together with Equation 3.1, to calculate the average breakthrough time of the individual species. It was found that, for a D2EHPA concentration of 1200 mol/m^3, that the breakthrough time of the NiR_2 species varies from 0.7 to 2.2 minutes, while the breakthrough time for the $NiR_2(RH)_4$ species varies from 1.1 to 3.8 minutes. This is relativly fast in comparison with the 120 minutes needed for an experiment to reach steady state conditions and it supports the assumption of pseudo steady state conditions for the transmembrane flux.

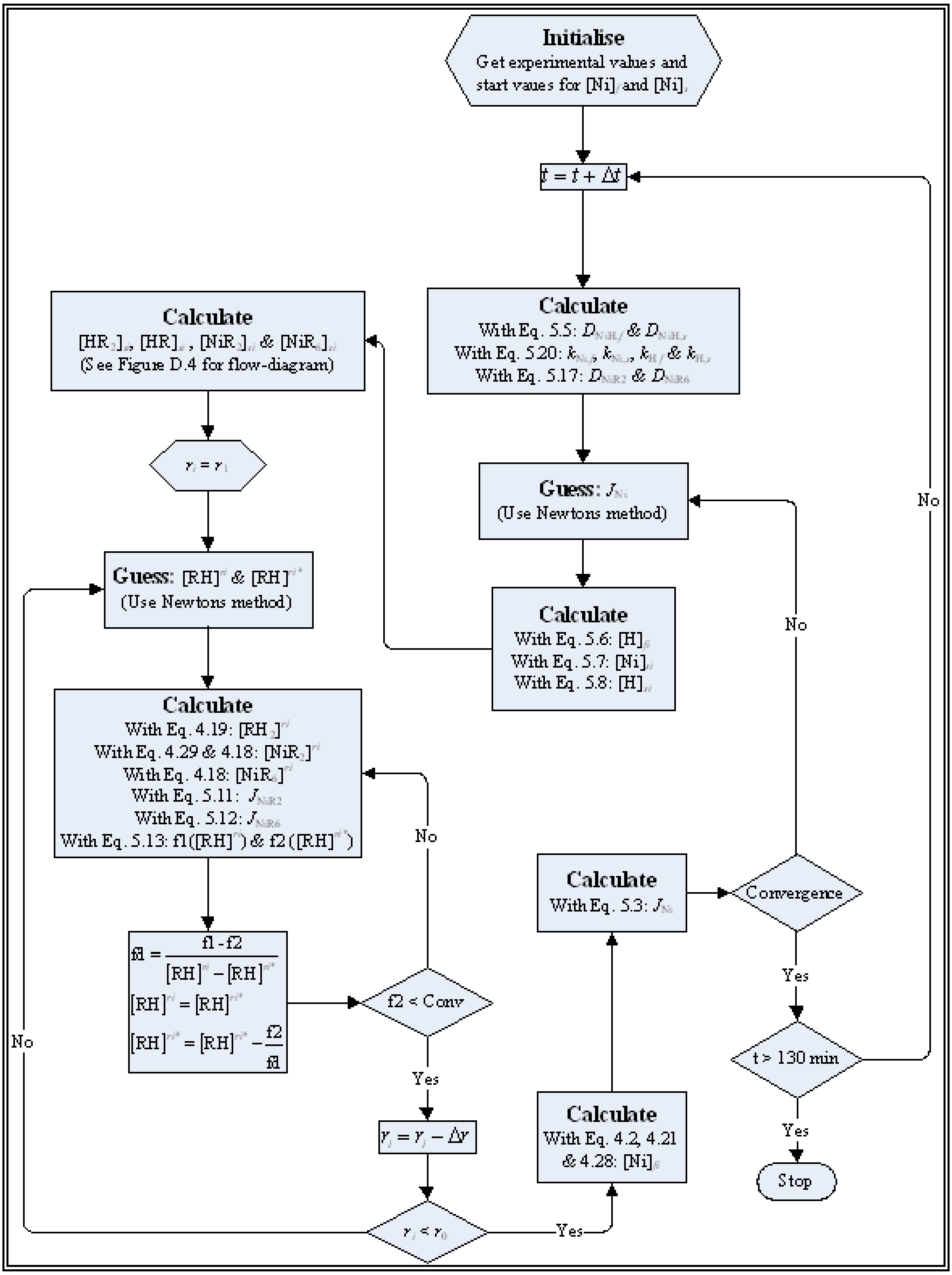


Fig. 5.2: Flow diagram for the calculation of nickel flux

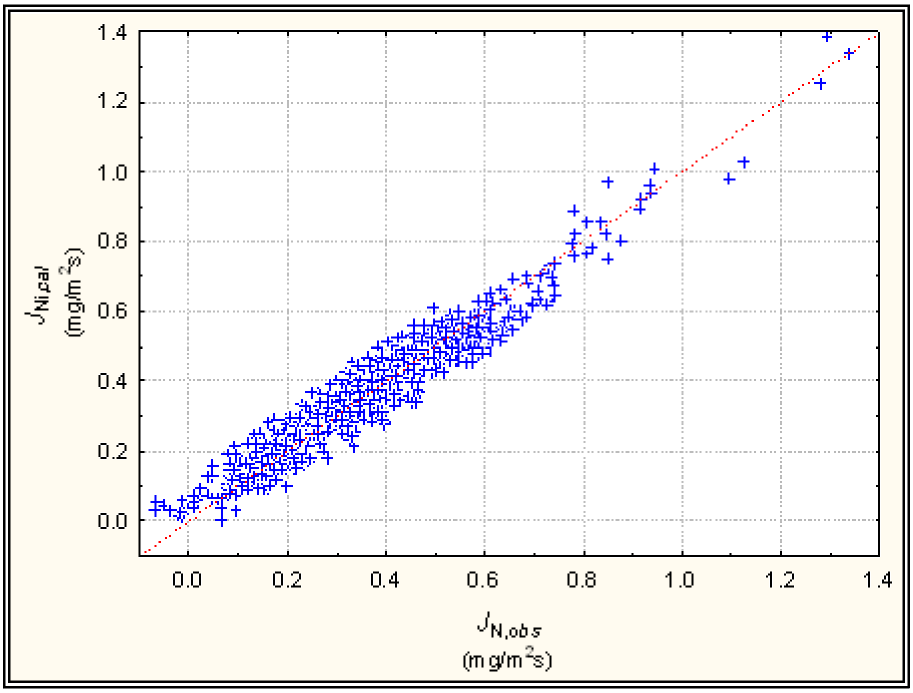
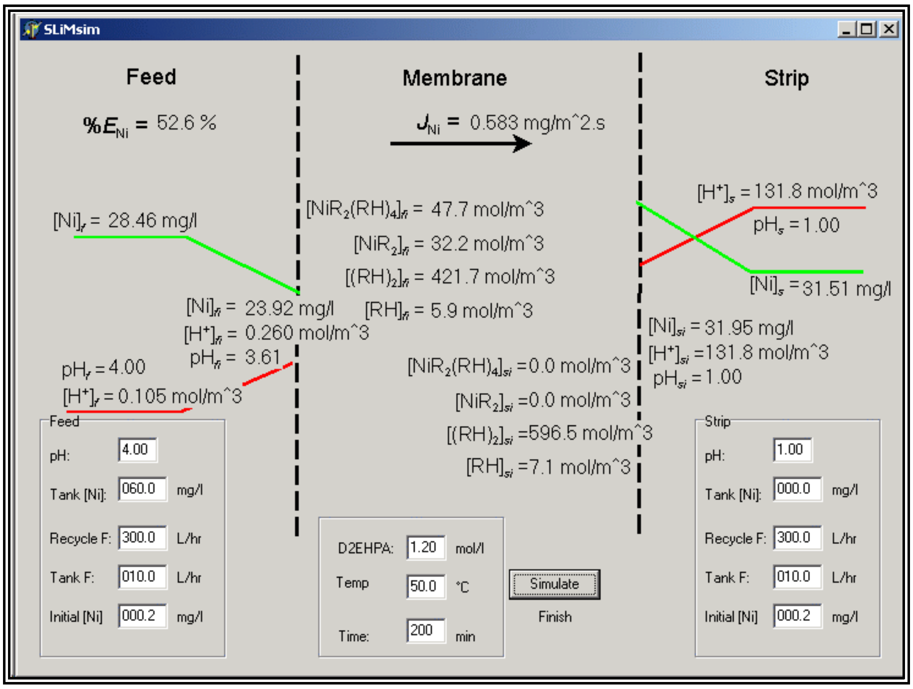


Fig. 5.3: Predicted *vs*. observed flux values for SLM regression (including dynamic or unsteady state experimental samples; r^2=0.984)

5.6 The SLiMsim program

Part of the objectives of this project was to write a computer simulation that is capable to accurately predict the SLM extraction of nickel. Although it would have been impossible to do the regression in Section 5.5 without such a program, it was decided to develop a more user-friendly interface for the simulation and to package it in a program that is easy to operate. The SLiMsim program was the product of this idea. The user input screen of the program can be seen in Figure 5.4. The user has to supply the following information:

- pH of the feed and strip solution.
- Nickel concentration of the feed and strip tanks (in mg/l).
- The recycle (reactor) flow rate of the feed and strip solutions (in l/hr).
- The flow rate from the feed and strip tanks (in l/hr).
- The initial nickel concentration of feed and strip solution (in mg/l).
- The total D2EHPA concentration as D2EHPA monomer (in mol/l).
- Temperature (in ˚C) and
- The final time of the experiment (in minutes).



$\%E_{Ni}$ = 52.6 %

J_{Ni} = 0.583 mg/m^2.s

$[Ni]_f$ = 28.46 mg/l

$[Ni]_{fi}$ = 23.92 mg/l

$[H^+]_{fi}$ = 0.260 mol/m^3

pH_{fi} = 3.61

pH_f = 4.00

$[H^+]_f$ = 0.105 mol/m^3

$[NiR_2(RH)_4]_{fi}$ = 47.7 mol/m^3

$[NiR_2]_{fi}$ = 32.2 mol/m^3

$[(RH)_2]_{fi}$ = 421.7 mol/m^3

$[RH]_{fi}$ = 5.9 mol/m^3

$[NiR_2(RH)_4]_{si}$ =0.0 mol/m^3

$[NiR_2]_{si}$ =0.0 mol/m^3

$[(RH)_2]_{si}$ =596.5 mol/m^3

$[RH]_{si}$ =7.1 mol/m^3

$[H^+]_s$ =131.8 mol/m^3

pH_s =1.00

$[Ni]_s$ =31.51 mg/l

$[Ni]_{si}$ = 31.95 mg/l

$[H^+]_{si}$ =131.8 mol/m^3

pH_{si} =1.00

Feed
pH: 4.00
Tank [Ni]: 060.0 mg/l
Recycle F: 300.0 L/hr
Tank F: 010.0 L/hr
Initial [Ni] 000.2 mg/l

D2EHPA: 1.20 mol/l
Temp 50.0 °C
Time: 200 min

Strip
pH: 1.00
Tank [Ni]: 000.0 mg/l
Recycle F: 300.0 L/hr
Tank F: 010.0 L/hr
Initial [Ni] 000.2 mg/l

Fig. 5.4: User interface of the SLiMsim program.

It took the experiments 130 minutes to reach steady state conditions, consequently the program will calculate the steady state conditions if a number larger than 130 minutes is supplied by the user for the time. The program will then calculate the flux through the membrane as well as the percentage extraction and the concentrations of all 12 species at the membrane interface (for both the feed and strip sides), as well as the concentration profile of the organic species through the membrane. Figure 5.5 gives a typical profile for an experiment and it is clear that the concentration profiles of the nickel-organic species is not linear due to both the changing diffusion area and the equilibrium that exist between the NiR_2 and then $NiR_2(RH)_4$ species. Another application of the program is that it can be used to calculate the actual capacity (amount of nickel absorbed in the membrane) of the liquid membrane. It was found, for the example shown in Figure 5.5, that the membrane held 34 mg of nickel. This is less than the 198 mg expected in the original design of the reactor/extractor (see Section 3.2.2). The program gave a better understanding of the SLM process and it is believed that it will be a valuable tool in future research to evaluate the profitability of a possible SLM pilot plant. All the process model predictions in Chapter 6 were done with this program. The install-CD of the program is attached to this thesis.

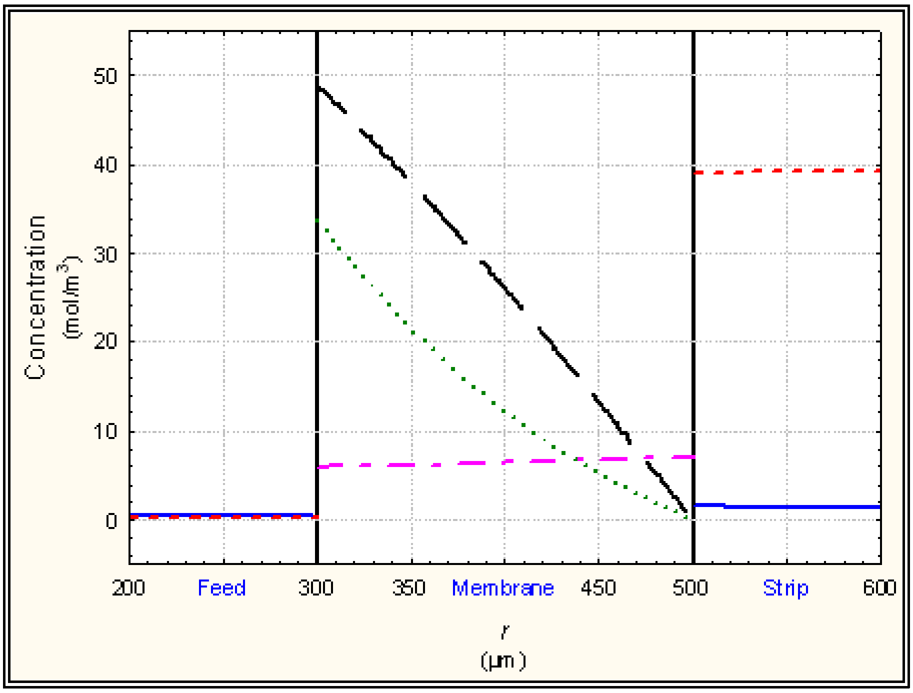


Fig. 5.5: Concentration profiles across the SLM. (———):$[Ni^{2+}]_{aq}$; (– –):$[H^+]_{aq}$; (······):$[NiR_2]_o$; (———):$[NiR_2(RH)_4]_o$; (—— -):$[RH]_o$; $[(RH)_2]_o \approx 506$ mol/m^3 (not shown)

There are two units used for the flux of the nickel species mol/s (in Equation 5.9, & 5.10) and mol/m^2·s (in Equation 5.3, 5.6,5.7 & 5.8). The difference is due to the membrane area. In this thesis the apparent membrane aria is used and not the effective or pore mouth area. In Chapter 6 the flux of the nickel is expressed in mol/m^2·s. In these instances the flux were taken relative to the outside membrane area.

The mechanisms of the mass transfer operations in supported liquid membranes are sometimes further elucidated by the relative transport resistance of each step (Lin & Juang, 2002:151; Ishizu *et al.*, 2003:217). Due to the complexity of the model and the influence of the activity of the aqueous nickel, the activity of the sulphate ions and especially the concentration of hydronium ions in the solution on the extraction equilibrium (Eq. 4.28), it would be very difficult (if not impossible) to use resistance analogy to make sensible conclusions with regard to the mass transfer operations involved in the transport process.

5.7 Conclusions from modelling

A more detailed discussion of the simulation results and the conclusions that can be drawn from it is presented in Chapter 6, together with the experimental results. The conclusions that can be drawn from the modelling can be summarised as follow;

1. The dynamic (unsteady state) modelling can be achieved by solving two differential equations (Eq. 5.1 and 5.2).
2. It can be assumed that the flux term in these equations is at pseudo-steady state and can be calculated by solving the reaction equilibrium at the membrane feed and strip interface together with the diffusion of the metal-organic species through the membrane.
3. In this process model there are three unknown constants which were calculated by regression by minimising the least squares of the error with the Quasi-Newton method.
4. The regression gave a correlation coefficient (r^2) of 0.984 and the regression constants had small standard deviations.
5. There exists a nonlinear concentration profile through the membrane, due to the variable area of the membrane and the equilibrium that exists between the nickel-organic species.

Chapter 6

Results and discussion

"The most exciting phrase to hear in science, the one that heralds new discoveries, is not 'Eureka!' but 'That's funny ...' " - Isaac Asimov

6.1 Introduction

As mentioned in Section 1.3, one of the main objectives of this project was to use the bench-scale reactor/extractor to investigate the influence of the main variables on the extraction of nickel with supported liquid membranes. The results of these experiments are briefly discussed and interpreted in this chapter. The modelling of the system gave a better understanding of the SLM system and the results predicted with the model are also discussed.

6.2 Experimental design

The modern trend in research is to use statistical methods to get the optimum (accurate and significant) results for the least amount of resources (time and money). The variables that are of importance to the process were briefly discussed in Section 2.2.3 and are listed below, together with the ranges of values investigated in this study:

1. Nickel concentration of the feed solution (20 - 140 mg/l)
2. Nickel concentration of the strip solution (0 - 5000 mg/l)
3. Hydronium ion concentration of the feed solution (pH: 3.0 - 5.0)
4. Hydronium ion concentration of the strip solution (pH: 0.4 - 1.9)
5. Recycle (reactor) flow rate of the feed solution (100 - 400 l/hr)
6. Recycle (reactor) flow rate of the strip solution (100 - 400 l/hr)
7. Temperature (30 - 70 °C)
8. Extractant concentration (800 - 1600 mol/m^3)

A monovariant experimental design was done to investigate these variables and a 2^8 design was superimposed on this design to investigate the interaction between these variables. A list of all the experiments done (including experimental conditions) can be seen in Appendix B.

6.3 Experimental procedure and representation

Each experiment was prepared according to the experimental design, following the procedure outlined in Section 3.4 and the following measurements were taken during the experiment:

1. The recycle flow rate of the feed and strip solutions.
2. The time when a sample was taken.
3. The feed and strip solution pH.
4. The nickel concentration of the feed and strip solution.

These results could be used to calculate the amount of nickel that was being extracted through the SLM system and can be expressed in one of two ways:

1. Flux: The amount of nickel (either as mg or mol) that passes through a square metre of membrane in one second.
2. % extraction: The amount of nickel that is extracted to the strip side as a fraction of the total nickel that would have been in the solution if no extraction occurred.

In membrane technologies the convention is usually to express the results in terms of the transmembrane flux, while in solvent extraction, the results are usually expressed in terms of recovery. Supported liquid membranes are a combination of the two technologies and it was decided to express the results in terms of flux, unless the observed phenomena could be better expressed by the concept of percentage extraction. The dynamic results of each experiment were measured and used for the regression as discussed in Section 5.5. The steady state flux is used in this chapter (with the exception of Section 6.4) to evaluate the effect of the different variables on the extraction process. The experimental results are also compared with the process model derived in Chapter 5.

6.4 Reproducibility of experiments

To assess the reproducibility of the experiments, eight experiments were done under the same conditions. These experiments were done throughout the whole experimental period and were also used to test if the experimental apparatus was still giving accurate results. The nickel flux as a function of time can be seen in Figure 6.1. The average standard deviation between the experiments was 5.9% and it can therefore be concluded that the experimental configuration gave

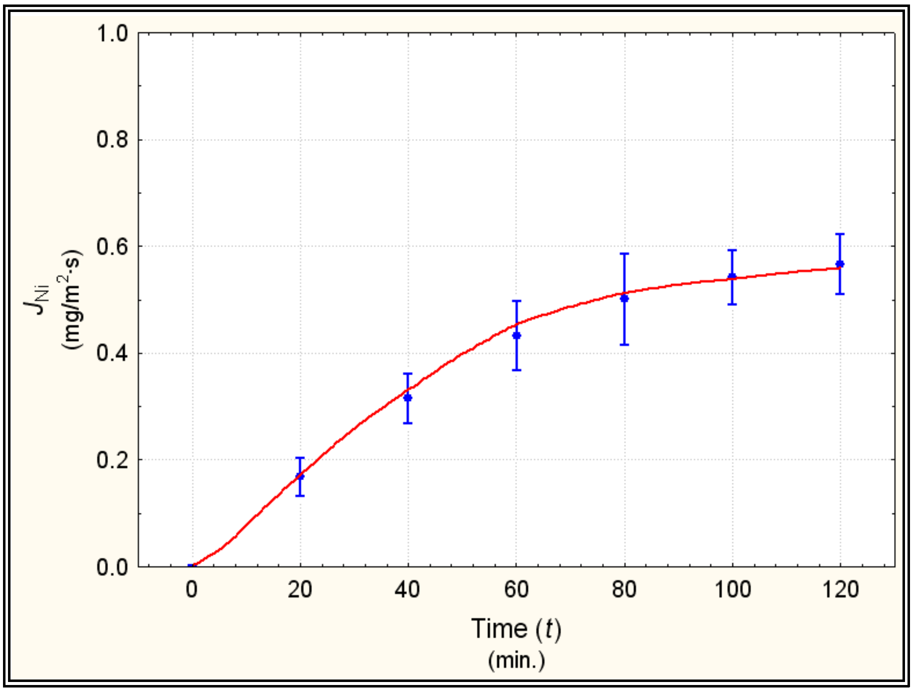


Fig. 6.1: Reproducibility test for SLM experiments with $[Ni]_{FT} \approx 57$ mg/l, $[Ni]_{ST} \approx 56$ mg/l, $pH_{f,sp} = 4.00$, $pH_s \approx 1.04$, $F_f = F_s = 300$ l/hr, $T = 50$ °C & $[RH]_{Tot} =$ mol/m^3.
●: Experimental data with 95% confidence limits. — : Process model (r^2=0.999)

accurate and reproducible results.

6.5 The influence of the different process conditions on the extraction of nickel

The influence of all the variables, mentioned in Section 6.2, on the extraction process were investigated through a comprehensive experimental study. The predictions from the model, derived in Chapter 5, were also compared with these experimental results.

6.5.1 The influence of the nickel concentration in the feed tank

A series of experiments were done to investigate the influence of the nickel concentration in the feed tank on the nickel flux through the membrane and the recovery. In these experiments the nickel concentration of the feed tank was varied from 20 mg/l to 157 mg/l. The results of the experiments can be seen in Figure 6.2. An increase in the nickel concentration in the feed tank results in higher organo-metallic concentrations at the feed interface and this results in an increase in the driving force across the membrane. The decrease in the % extraction with an increase in feed concentration cannot be understood intuitively. This can be explained by the fact that the extraction process is a membrane process and the % extraction is therefore proportional to

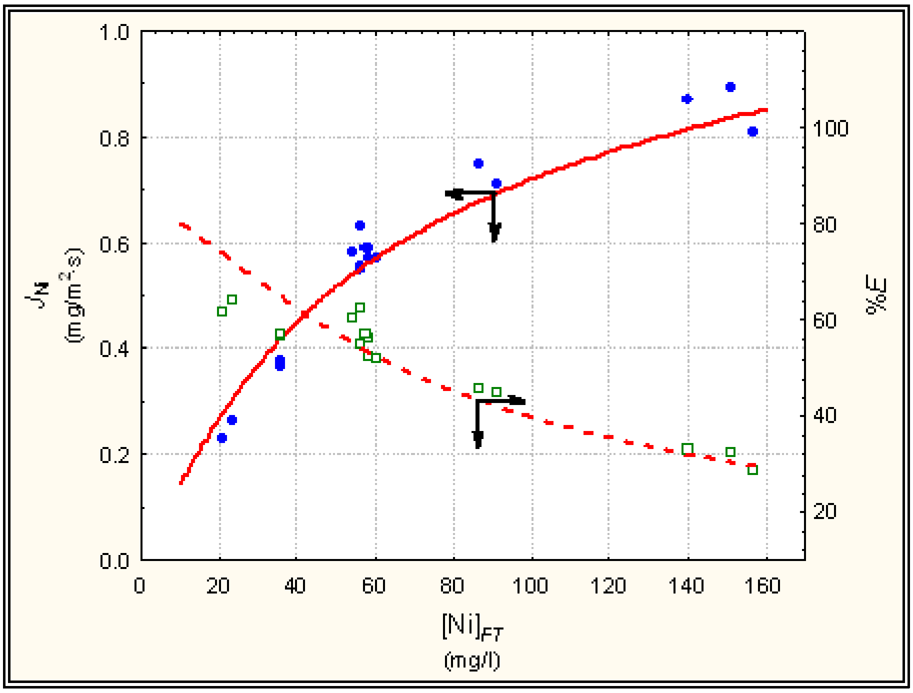


Fig. 6.2: Influence of $[\text{Ni}]_{FT}$ on nickel flux and % extraction with $[\text{Ni}]_{ST} \approx 56$ mg/l, $\text{pH}_{f,sp} = 4.00$, $\text{pH}_s \approx 1.05$, $F_f = F_s = 300$ l/hr, $T = 50$ ˚C & $[\text{RH}]_{Tot} = 1200$ mol/m^3. ●: Observed flux (left axis), ——: Predicted flux (r^2=0.995), ☐: Observed % extraction (right axis), – –: Predicted % extraction (r^2=0.990)

membrane area. In these experiments the membrane area was kept constant and this means that the same amount of membrane was used to extract nickel from a smaller number of nickel molecules, resulting in a higher recovery. The lower flux at these concentration was not enough to counter this phenomenon, resulting in the trend found. This is one of the main advantages of supported liquid membranes over other extraction processes such as liquid-liquid extraction and makes the process more usable for the scavenging of small amounts of valuable metal species from aqueous solutions. The percentage extraction and nickel flux predicted by the model is also shown in Figure 6.2. The increase in flux with an increase in the metal concentration is well documented in the literature (Juang, 1993:162; Youn *et al.*, 1997:233; Joeng *et al.*, 2003:506). It is however more difficult to make direct comparisons of the results, due to all the other variables that influence the SLM process, for instance Juang (1993:162) found that, if the concentrations of both nickel and cobalt are increased, the nickel flux will display an optimum. This can however be contributed to the competing flux of cobalt ions and the total metal flux increased with in increase in total metal concentration.

6.5.2 Influence of the nickel concentration in the strip tank

One of the main advantages of a supported liquid membrane system is that a high degree of upconcentration ($[Ni]_s/[Ni]_f$) can be achieved. The influence of the nickel concentration in the strip was investigated in a series of experiments in which the nickel concentration in the strip tank was varied from 0 mg/l to 5700 mg/l. The results are shown in Figure 6.3, with the nickel concentration in the strip tank on a logarithmic x-axes. An increase in the nickel concentration in the strip tank results in higher organo-metallic concentrations at the strip interface, but the resulting decrease in driving force is insignificant if it is compared to the concentration of the organo-metallic concentrations at the feed interface. The process model predict that the loss in driving force will be insignificant, even if the nickel strip concentration is increased to 292.5 g/l, the point where the nickel will precipitate (Perry & Green, 1984:3-17). One of the first accounts of the ability of supported liquid membranes to perform “uphill transport” is that of Matsuoka *et al.* (1980:11), who proved that uranium can be upconcentrated. Since then the phenomenon has been extensively researched in different systems (Juang & Chang, 1996:365; Shamsipur, 2000:217; Gholivand & Khorsandipoor, 2000:115; Alguacil *et al.*, 2001:13)

6.5.3 Influence of the feed pH on extraction

One of the most important variables in the extraction process is the pH of the feed stream and is the variable that is being investigated the most. The hydronium ion concentration in the feed stream has a dramatic effect on the equilibrium that is established between the nickel in the feed and the nickel-organic species in the membrane (see Figure 4.19). A series of experiments was done to quantify this effect and in these experiments the setpoint of the pH controller was varied from 3.00 to 5.00. If one considers Equation 4.28 it could be expected that the flux would increase exponentially as the pH of the feed solution is increased, but it is clear from Figure 6.4 that the flux stabilises at around 0.65 $mg/m^2 \cdot s$. This can be explained by (and is seen in the prediction made by the process model) the fact that as the flux increases, the concentration gradient across the feed boundary layer also increases and this impedes the extraction process, as the nickel cannot reach the membrane surface fast enough and the hydronium ions cannot be removed fast enough from the membrane interface. It should also be remembered that the maximum flux for the experimental conditions is around 1 $mg/m^2 \cdot s$ and this leads to the characteristic s-form of the graph. Verhaege *et al.* (1987:334) and Young *et al.* (1997:232) also found that the flux levels off at a pH higher than 4.

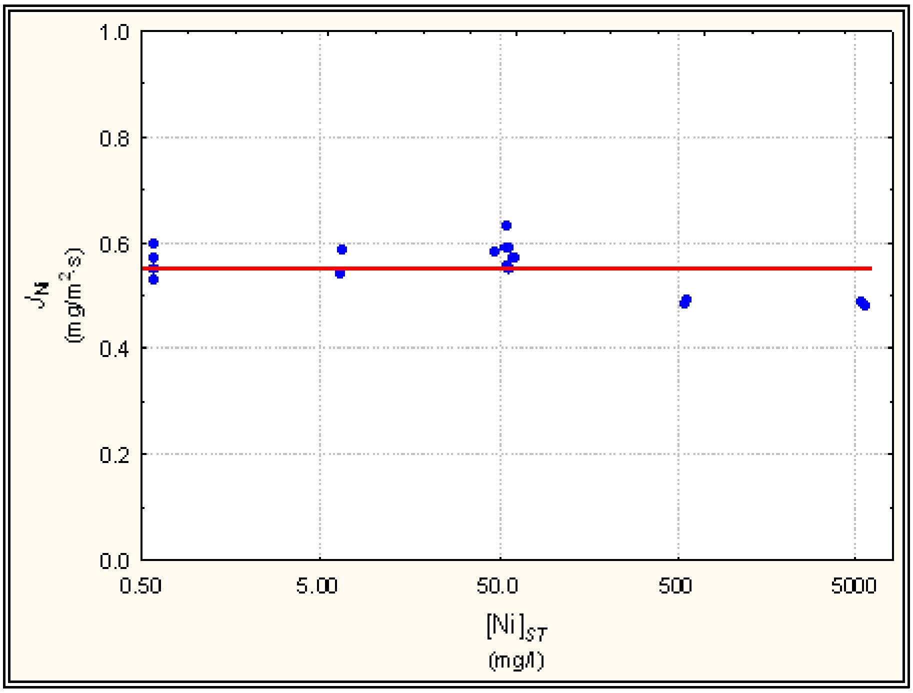


Fig. 6.3: Influence of $[Ni]_{ST}$ on nickel flux with $[Ni]_{FT} \approx 57$ mg/l, $pH_{f,sp} = 4.00$, $pH_s \approx 1.02$, $F_f = F_s = 300$ l/hr, $T = 50$ ˚C & $[RH]_{Tot} = 1200$ mol/m^3. ●: Experimental data. —— : Process model (r^2=0.994)

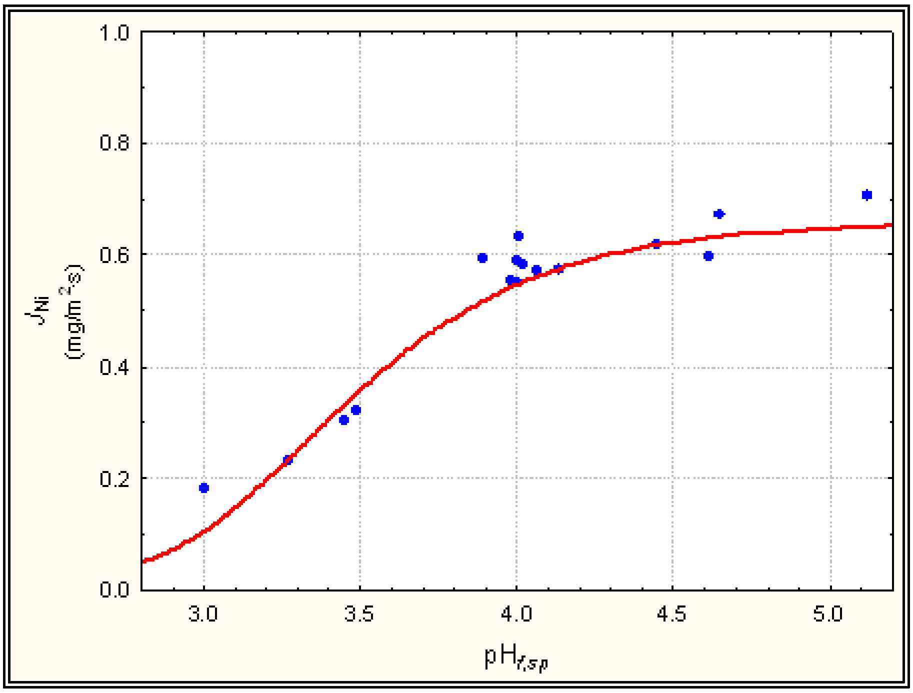


Fig. 6.4: Influence of $pH_{f,sp}$ on nickel flux with $[Ni]_{FT} \approx 57$ mg/l, $[Ni]_{ST} \approx 55$ mg/l, $pH_s \approx 1.04$, $F_f = F_s = 300$ l/hr, $T = 50$ ˚C & $[RH]_{Tot} = 1200$ mol/m^3. ●: Experimental data. —— : Process model (r^2=0.994)

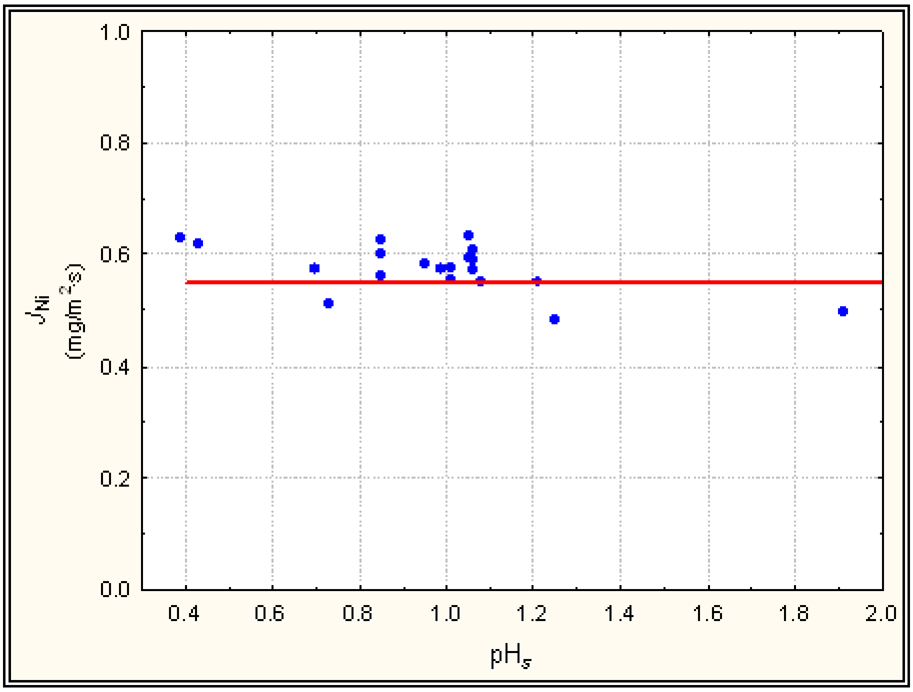


Fig. 6.5: Influence of pH_s on the nickel flux with $[Ni]_{FT} \approx 57$ mg/l, $[Ni]_{ST} \approx 56$ mg/l, $pH_{f,sp} \approx 4.00$, $F_f = F_s = 300$ l/hr, $T = 50$ ˚C & $[RH]_{Tot} = 1200$ mol/m^3. ●:Experimental data. —— : Process model (r^2=0.993)

6.5.4 Influence of the strip pH on extraction

As with the feed pH, the strip pH also affects the extraction at the membrane interface, but the influence is much less significant than that of the feed pH and can be explained by the fact that the extraction of nickel with D2EHPA usually varies from below 10% at a pH of 2.0 to above 90% at a pH of 3.0 (see Figure 4.19). In the experiments done to investigate the strip pH, the pH was varied from 0.4 to 1.91 (see Figure 6.5). It was seen in the predictions made by the process model that, at these low concentrations the stripping reaction is virtually complete and that the concentration of the nickel-organic complex at the strip interface is negligible, but the pH cannot be increased unconditionally and it is predicted by the process model that, if the pH rises above 2.5, there is a dramatic drop in the flux. The drop in flux, with a strip pH higher than 2.5, was reported in an set of experiments done by Joung (1993:164). An experiment was done with no acid in the strip solution and it confirmed that a very low flux will result (0.018 mg/m^2·s) if there is no acid present. Fortunately only a small amount of acid is necessary (0.1% mass) to lower the pH to below 2.0.

6.5.5 Influence of the reactor (recycle) flow rate on extraction

A series of experiments were done to investigate the influence of the flow rate through the reactor on the extraction. Two sets of experiments were done: In the first set the feed recycle flow rate was varied from 100 to 400 l/hr. There was an increase in flux as the flow rate increased, due to the decrease in the feed boundary layer (see Figure 6.6). At lower flow rates the observed flux was slightly lower than the flux predicted by the process model, but this phenomenon can be attributed to normal experimental errors. If the influence of the feed recycle flow rate on the error between the observed and predicted fluxes is considered for all the experiments (see Figure 6.7), including the 2^k-experimental set, it can be seen that the deviation between the predicted and observed flux is insignificant. The decrease of the boundary layer has the added effect that the hydronium ions that form at the membrane interface as a result of the extraction reaction, was removed faster and this leads to an increase in the pH at the membrane interface (see Figure 6.8). One would expect that the nickel concentration at the feed interface would increase with the increase of the flow rate, but the process model predicts the opposite (see Figure 6.8). This can be explained by the fact that the increase in pH at the membrane interface results in a higher nickel flux and this leads to an increased concentration drop across the boundary layer. The increased pH and reduced nickel concentration at the membrane interface result in two opposing influences on the organo-metallic concentrations at the feed interface (see Equation 4.28), with the increased pH having a positive effect on the organo-metallic concentration and the decreased nickel concentration a negative effect. The contribution of the hydronium concentration on the extraction equilibrium is, however, larger than the contribution of the nickel concentration, leading to an overall increase in the nickel flux.

The strip recycle flow rate was varied in the second set of experiments from 100 l/hr to 400 l/hr. Contrary to expectations, the strip flow rate through the reactor did not have a significant influence on the extraction of nickel (see Fig. 6.9). A higher strip recycle flow rate should reduce the strip side boundary layer and result in higher nickel fluxes, but as was shown with the nickel concentration of the strip solution and the pH of the strip solution, the strip side is not the rate limiting step in the extraction process and the increase in flux due to the reduced boundary layer is insignificant. The process model predictions of the influence of the recycle flow rate can also be seen in Figures 6.6 and 6.8.

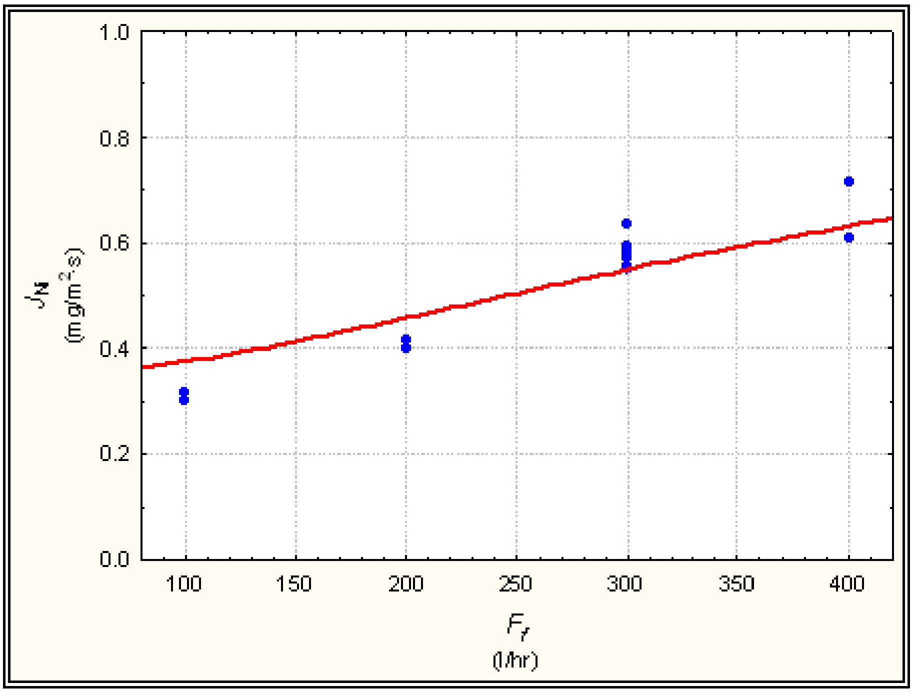


Fig. 6.6: Influence of F_f on the nickel flux with $[\text{Ni}]_{FT} \approx 56$ mg/l, $[\text{Ni}]_{ST} \approx 56$ mg/l, $\text{pH}_{f,sp} \approx 4.00$, $\text{pH}_s \approx 1.04$, $F_s = 300$ l/hr, $T = 50$ ˚C & $[\text{RH}]_{Tot} = 1200$ mol/m^3. ●: Experimental data. —— : Process model (r^2=0.991)

Joeng *et al.* (2003:507) also found an increase in the flux with a higher flow rate through a hollow fibre-supported liquid membrane. They found that film theory could not adequately describe the process and used a process model that uses the continuity mass-conservation equation for both the flow and the diffusion inside the fibre wall.

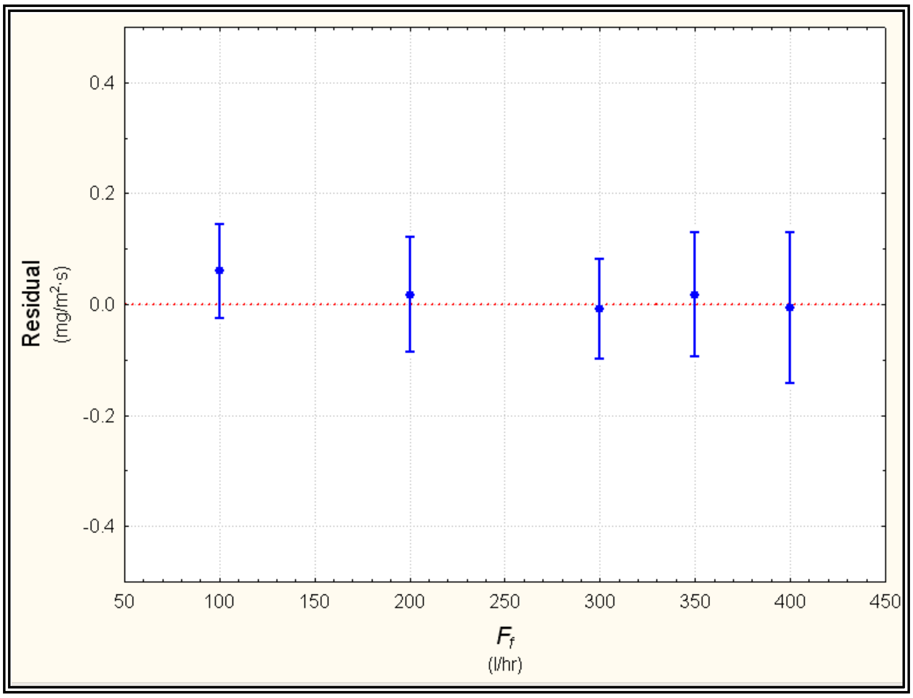


Fig. 6.7: Influence of F_f on the process model residuals. ●: Residuals with 95% confidence limits

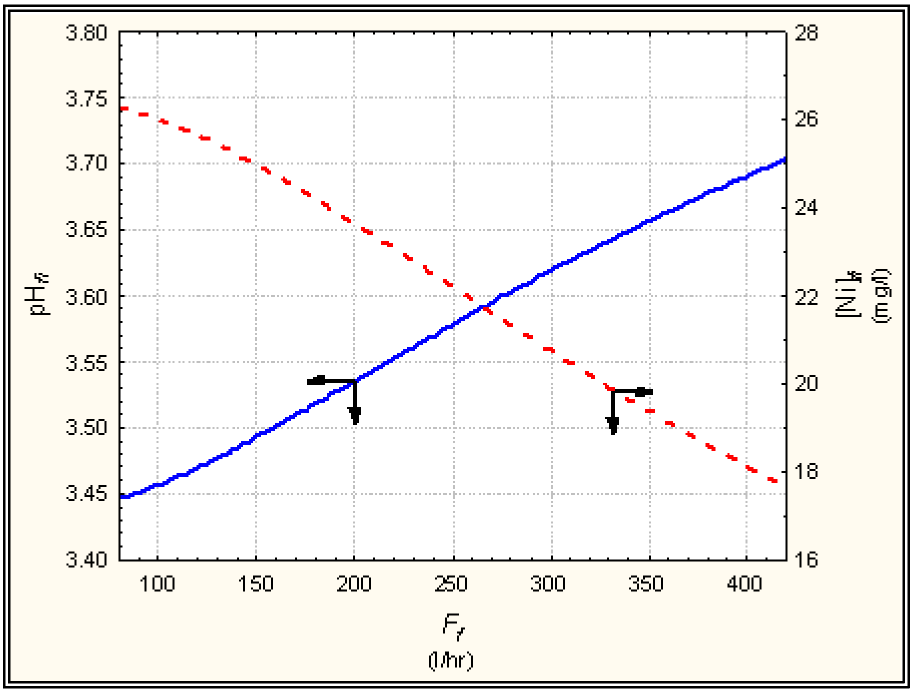


Fig. 6.8: Influence of F_f on the predicted pH_{fi} (—— ; left axis) and $[Ni]_{fi}$ (– – ; right axis)

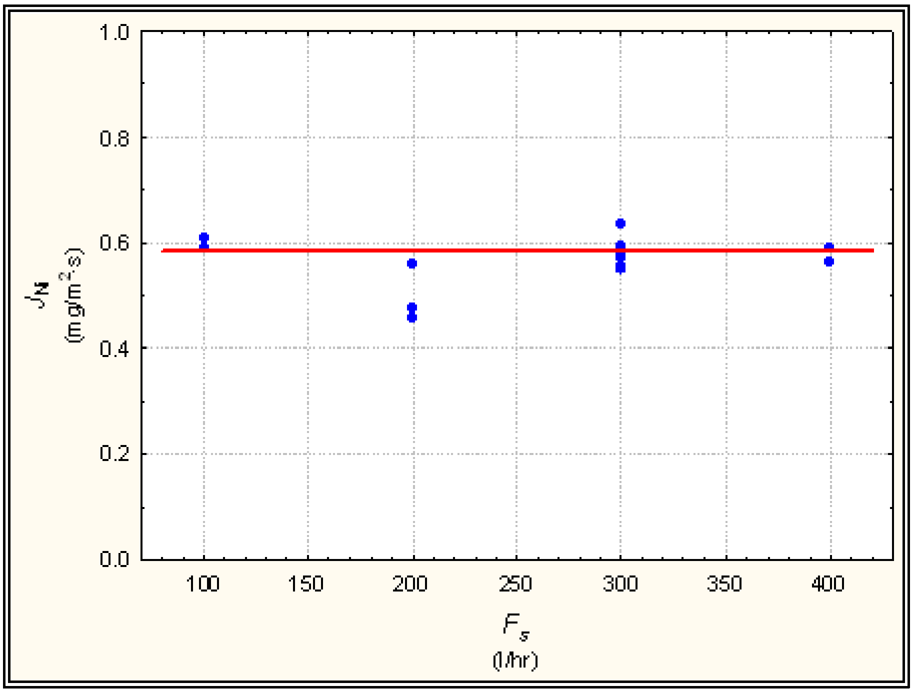


Fig. 6.9: Influence of F_s on the nickel flux with $[Ni]_{FT}$ ≈ 57 mg/l, $[Ni]_{ST}$ ≈ 56 mg/l, $pH_{f,sp}$ ≈ 4.00, pH_s ≈ 1.01, F_f = 300 l/hr, T = 50 °C & $[RH]_{Tot}$ = 1200 mol/m^3. ●: Experimental data. —— : Process model (r^2=0.993)

6.5.6 Influence of temperature on extraction

An important focus in this study was the incorporation of the effect of temperature into the process model. A series of experiments was done to investigate the influence of the temperature on extraction. In these experiments the temperature was varied from 30 to 70 °C. Although temperature does not have an effect on the nickel-organic equilibrium (see Figure 4.15), it does have an effect on the diffusion through the boundary layers as well as the diffusion through the membrane, leading to increased nickel flux through the membrane (see Figure 6.10). No reference was found in the literature on the effect of temperature in the SLM extraction of nickel. Some researchers did, however, investigate temperature as a variable in the extraction of other metals (see Section 2.2.3.6).

The typical way to represent the effect of temperature is with the use of an Arrhenius-type relationship. The value of the activation energy gives an indication if the process is reaction or diffusion limited and the rule of thumb is that if the activation energy is less than 50 kJ/mol the process is diffusion limited. The Arrhenius plot for the system can be seen in Figure 6.11. The activation energy was calculated as 17.2 ± 1.4 kJ/mol and it can therefore be concluded that the process is limited by film and/or transmembrane diffusion and not by the extraction reaction.

This supports the assumption that the reaction at the liquid-liquid interface is fast, as stated in Paragraph 5.2.

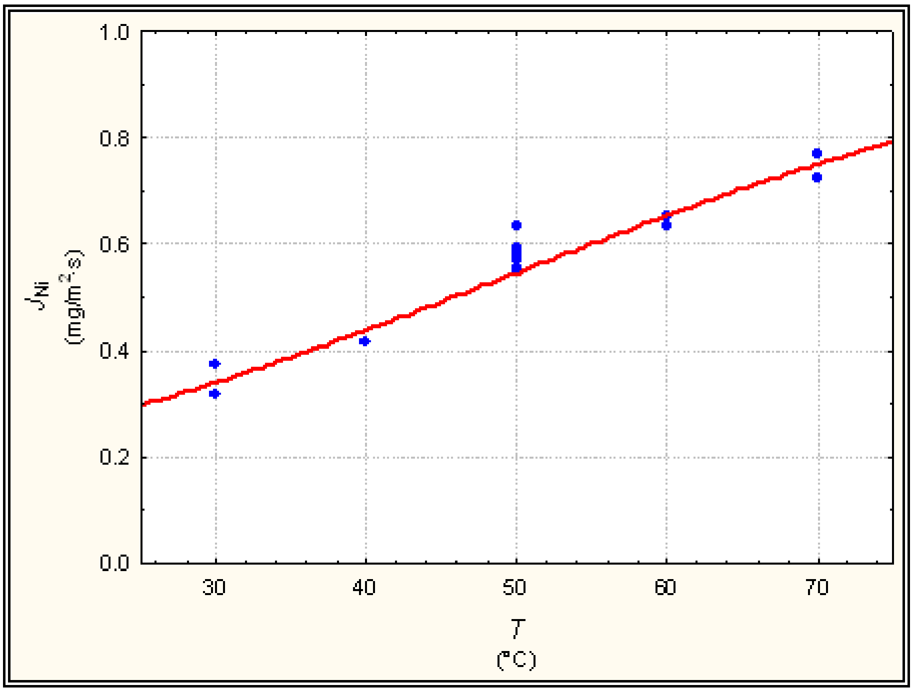


Fig. 6.10: Influence of T on the nickel flux with $[Ni]_{FT} \approx 57$ mg/l, $[Ni]_{ST} \approx 55$ mg/l, $pH_{f,sp} \approx 4.00$, $pH_s \approx 1.05$, $F_f = F_s = 300$ l/hr & $[RH]_{Tot} = 1200$ mol/m^3. ●: Experimental data. —— : Process model (r^2=0.997)

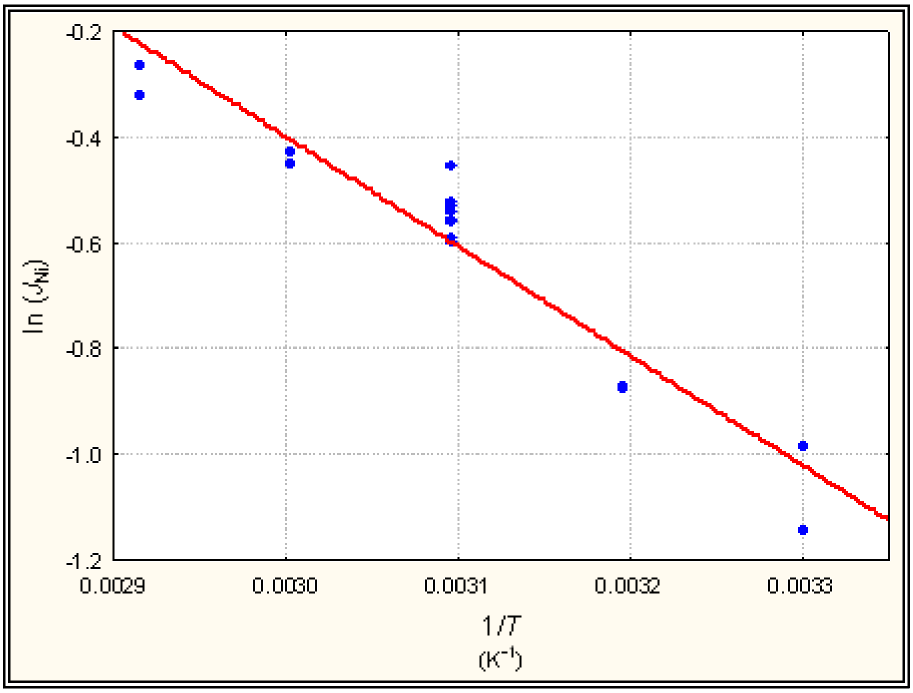


Fig. 6.11: Arrhenius plot for SLM system (r^2=0.989)

6.5.7 Influence of the extractant concentration

A series of experiments was done to investigate the influence of the extractant concentration (D2EHPA dissolved in Kerosene) on the nickel extraction. The extractant concentration was varied from 800 mol/m^3 to 1600 mol/m^3, with an additional two experiments done at zero extractant concentration to prove that no extraction takes place if the extractant is not present. An increase in extractant concentration resulted in higher organo-metallic concentrations, but it also resulted in an increase in the viscosity of the organic solution (see Figure 4.23), which in turn gave rise to a lower diffusion coefficient (see Equation 5.17). These two effects oppose each other and this usually results in an optimum extractant concentration. For the nickel-D2EHPA system it was found that this optimum is approximately 1200 mol/m^3 at ambient temperature (Verhaege *et al.*, 1987:333; Smit & Koekemoer, 1997:344). In this investigation a similar experimental result was obtained as seen in Figure 6.12, but with a less pronounced optimum. The process model does however predict a more dramatic drop in the extraction at concentrations outside the experimental range and it is expected that the elevated temperature of the experiments dampen this effect of viscosity on the diffusion coefficient. The viscosity of pure D2EHPA is 20 times higher than the viscosity of kerosene at 30 °C, this ratio, however, drops to about 9 at 70 °C (see Table 4.7). This phenomenon will be discussed in greater detail in Section 6.6.3.

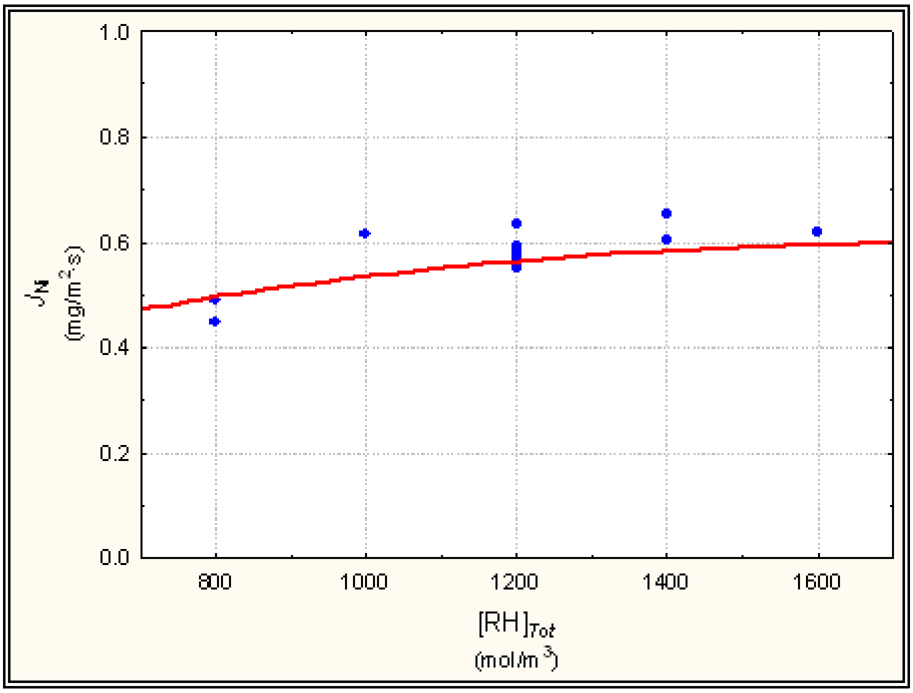


Fig. 6.12: Influence of $[RH]_{Tot}$ on the nickel flux with $[Ni]_{FT} \approx 57$ mg/l, $[Ni]_{ST} \approx 55$ mg/l, $pH_{f,sp} \approx 4.00$, $pH_s \approx 1.05$, $F_f = F_s = 300$ l/hr & $T = 50$ ˚C. ●: Experimental data. ——— : Process model (r^2=0.995)

6.6 Interaction between variables

A set of 2^k experiments was superimposed on the other experiments as discussed in Section 6.2. Although these experiments cannot be displayed graphically, they can be evaluated statistically and it greatly increased the accuracy of the process model and the predictions that can be made from it. Although all the abovementioned variables are interdependent, there are only a few that are significant and these variables are discussed in the following paragraphs. The term "interaction" as used in the following paragraphs implies that the effect obtained by varying two variables simultaneously is more or less than the sum of the effects obtained if the variables were varied independently.

6.6.1 Interaction between the feed solution pH and the nickel concentration in the feed tank

This interaction is depicted in Figure 6.13. As shown in Figure 6.4 and discussed in Section 6.5.2, the nickel flux through the membrane reaches an optimum, due to the limited amount of nickel that is available for extraction. This optimum is obviously dependent on the amount of nickel that is added to the system, resulting in the interaction between these two variables.

6.6.2 The influence of the feed recycle (reactor) flow rate on the extraction interactions

An increase in either the nickel concentration of the feed solution or the pH of the feed solution lead to an increase in the flux, but this increase is not linear because the increased flux leads to a higher concentration difference across the feed boundary layer. If the feed recycle flow rate is increased, this boundary layer is decreased and this leads to a higher slope in the transmembrane flux with regard to these variables (see Figures 6.14 & 6.15)

6.6.3 The influence of temperature on the extraction interactions

It was shown in Section 4.3.3.2 that temperature does not have an affect on the extraction reaction. Temperature does, however, have an effect on the diffusion through the boundary layer, leading to lower diffusion resistance across the boundary layer. The same rationalisation can be used to explain the interaction between the temperature and the nickel concentration of the feed solution, as well as the pH of the feed solution, than was used to explain the influence of the feed recycle flow rate on the interaction (see Section 6.6.2, Figure 6.16 & 6.17).

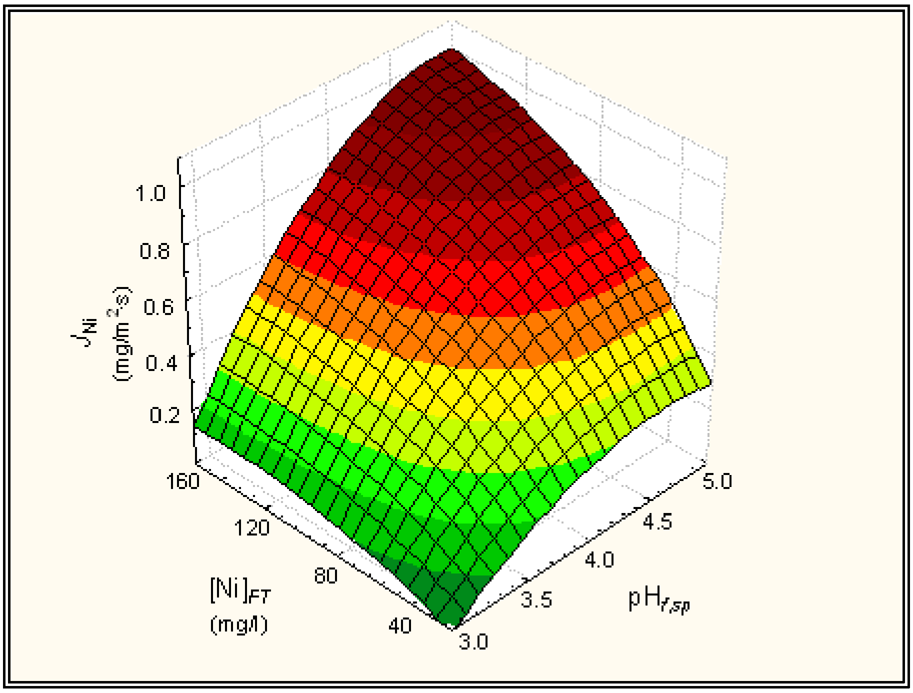


Fig. 6.13: Influence of $[Ni]_{FT}$ and $pH_{f,sp}$ on the nickel flux with $[Ni]_{ST} \approx 0$ mg/l, $pH_s \approx 1.0$, $F_f = F_s = 300$ l/hr, $T = 50$ °C & $[RH]_{Tot} = 1200$ mol/m^3

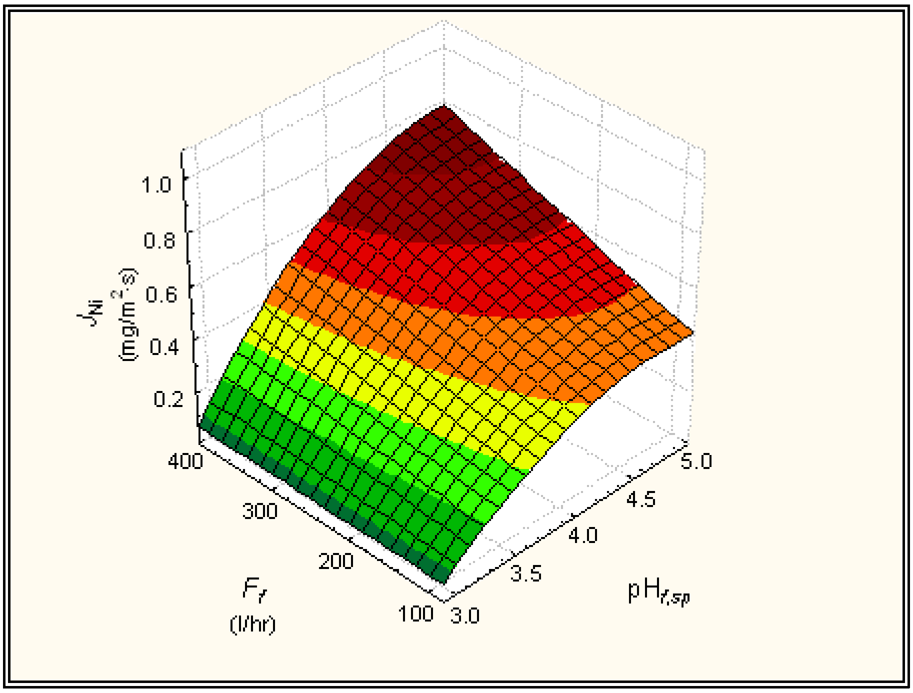


Fig. 6.14: Influence of F_f and pH$_{f,sp}$ on the nickel flux with $[Ni]_{FT}$ ≈ 60 mg/l, $[Ni]_{ST}$ ≈ 0 mg/l, pH$_s$ ≈ 1.0, F_s = 300 l/hr, T = 50 °C & $[RH]_{Total}$ = 1200 mol/m^3

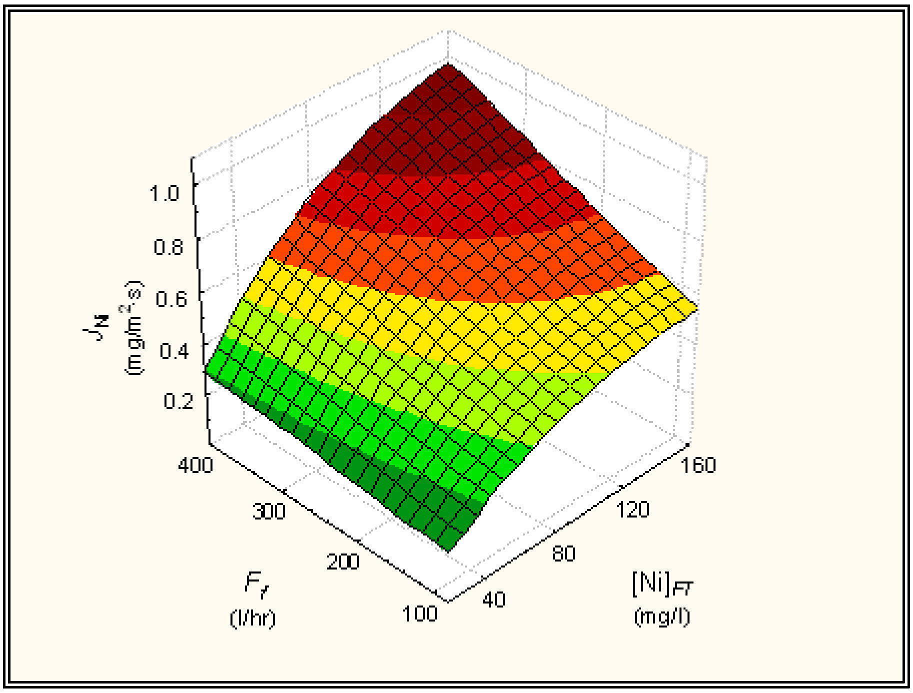


Fig. 6.15: Influence of F_f and $[Ni]_{FT}$ on the nickel flux with $[Ni]_{ST}$ ≈ 0 mg/l, pH$_{f,sp}$ ≈ 4.00, pH$_s$ ≈ 1.0, F_s = 300 l/hr, T = 50 °C & $[RH]_{Total}$ = 1200 mol/m^3

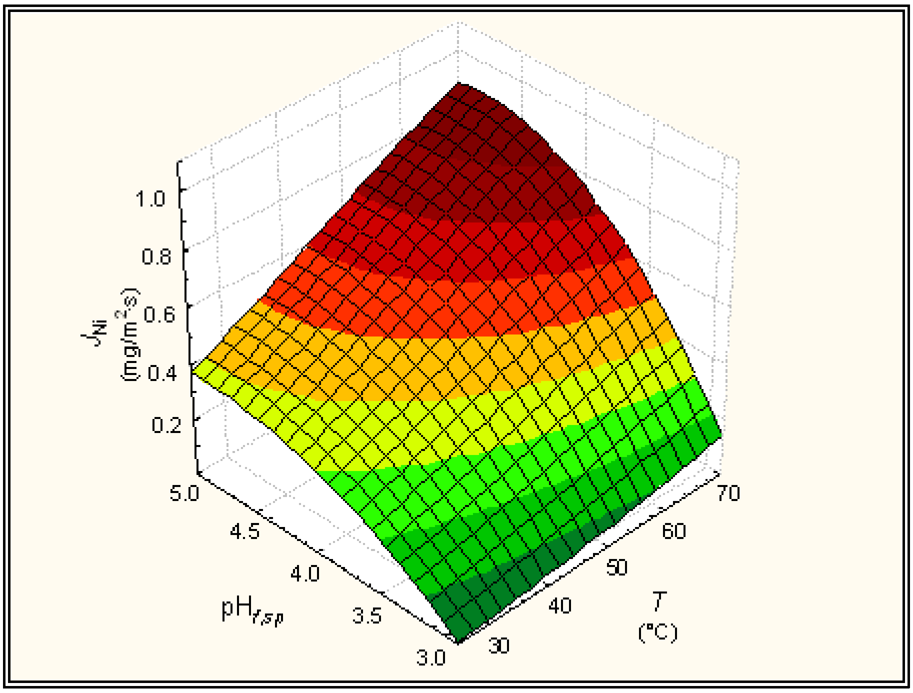


Fig. 6.16: Influence of pH$_{f,sp}$ and T on the nickel flux with $[Ni]_{FT}$ ≈ 60 mg/l, $[Ni]_{ST}$ ≈ 0 mg/l, pH$_s$ ≈ 1.0, $F_f = F_s$ = 300 l/hr & $[RH]_{Total}$ = 1200 mol/m^3

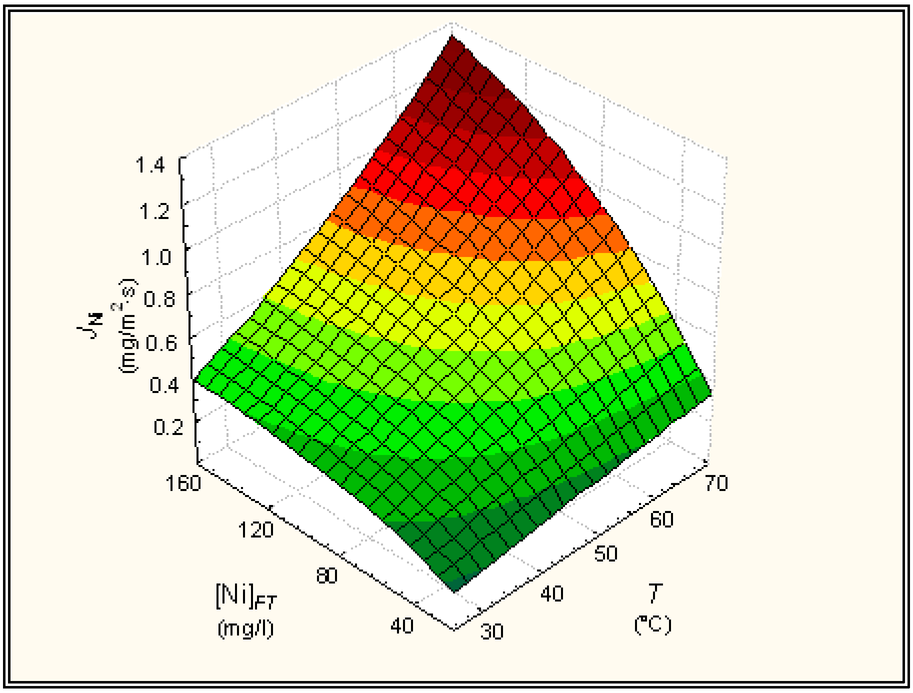


Fig. 6.17: Influence of $[Ni]_{FT}$ and T on the nickel flux with $[Ni]_{ST}$ ≈ 0 mg/l, pH$_{f,sp}$ ≈ 4.00, pH$_s$ ≈ 1.0, $F_f = F_s$ = 300 l/hr & $[RH]_{Total}$ = 1200 mol/m^3

There exist a tradeoff between the organo-metallic concentration and the diffusion resistance at different extractant concentrations, resulting in an optimum extractant concentration as discussed in Section 6.5.7 and in Section 2.2.3.1, but the diffusion through the membrane is dependent on temperature and this results in a shift in this optimum extractant concentration from 1500 mol/m^3 at 30˚C to 2000 mol/m^3 at 70 ˚C as seen in Figure 6.18.

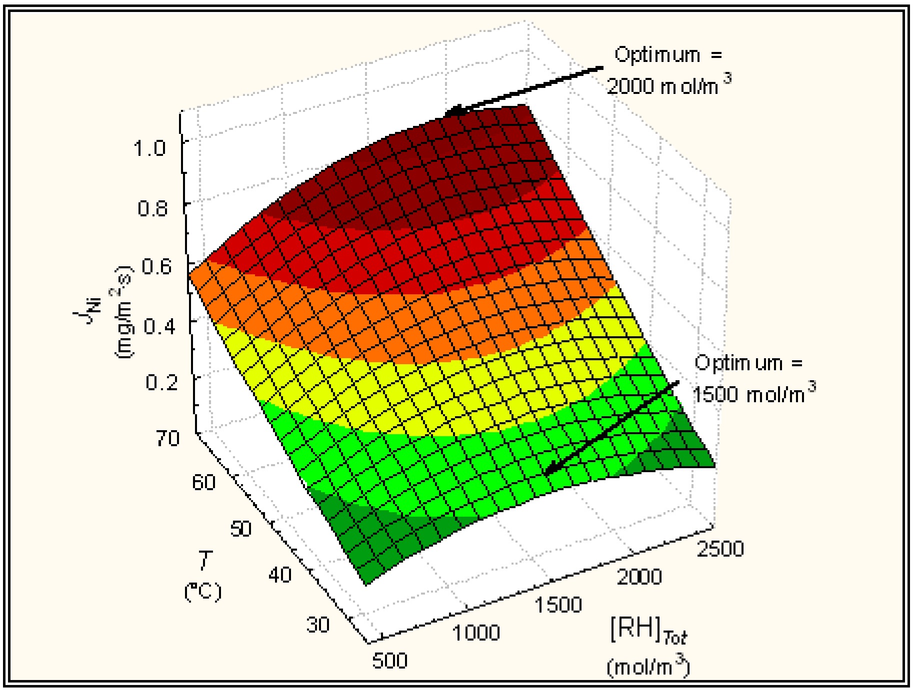


Fig. 6.18: Influence of T and $[RH]_{Tot}$ on the nickel flux with $[Ni]_{FT} \approx 60$ mg/l, $[Ni]_{ST} = 0$ mg/l, $pH_{f,sp} \approx 4.00$, $pH_s \approx 1.0$, $F_f = F_s = 300$ l/hr

6.7 The extraction of zinc with supported liquid membranes

It was decided to do two experimental sets to investigate the extraction of zinc with SLMs and to compare the results with those obtained for the extraction of nickel. In the first set of experiments, the pH of the feed solution was varied, since it is generally accepted that this is the most important factor in the extraction process (see Figure 6.19). In the second set the temperature (see Figure 6.20) was varied, since it was one of the unique variables in this study.

As can be seen in Figure 6.19, the extraction of zinc occurred at a lower pH, than that of nickel. Sarangi & Das (2004:192) also found that the extraction of zinc with SLMs varied in the pH range of 1.5 to 3.0 and Ata *et al.* (2004:898) investigated a pH range of 0.5 to 3.0. It is this difference in extraction pH that enables SLMs to selectively extract different ions from solution and, as mentioned in Section 2.5, a large amount of research has been done on this phenomenon in recent years.

It seems as if the extraction of zinc is slightly less dependent on temperature than the extraction of nickel. Further research will have to be done to confirm this and to determine the reason for it. More comprehensive research will also be needed before the process model derived in Chapter 5 can be adapted for the extraction of zinc with SLMs.

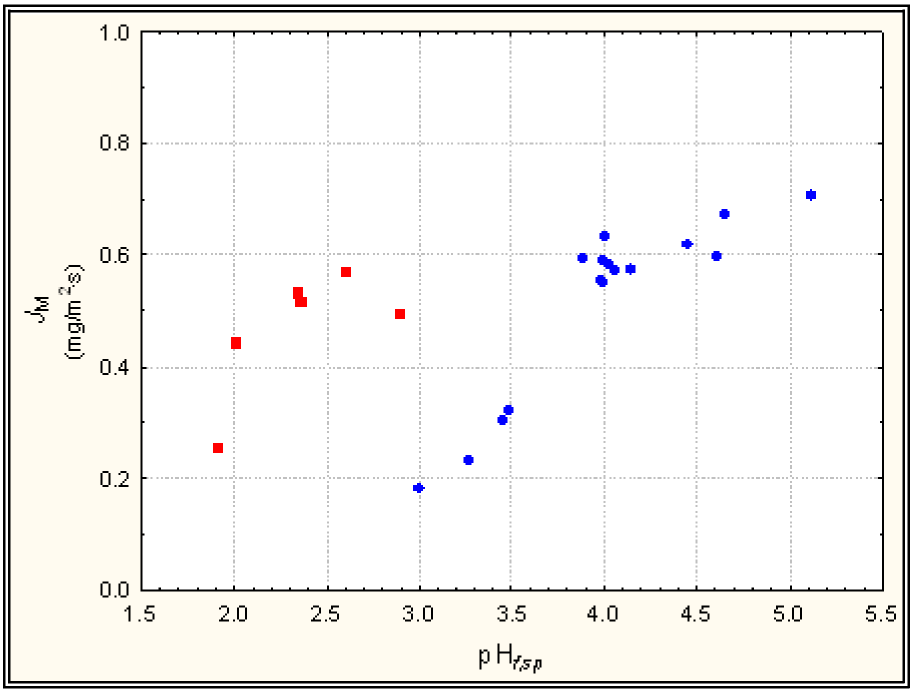


Fig. 6.19: Influence of pH$_{f,sp}$ on the transmembrane flux. ●: Nickel; 🟥: Zinc

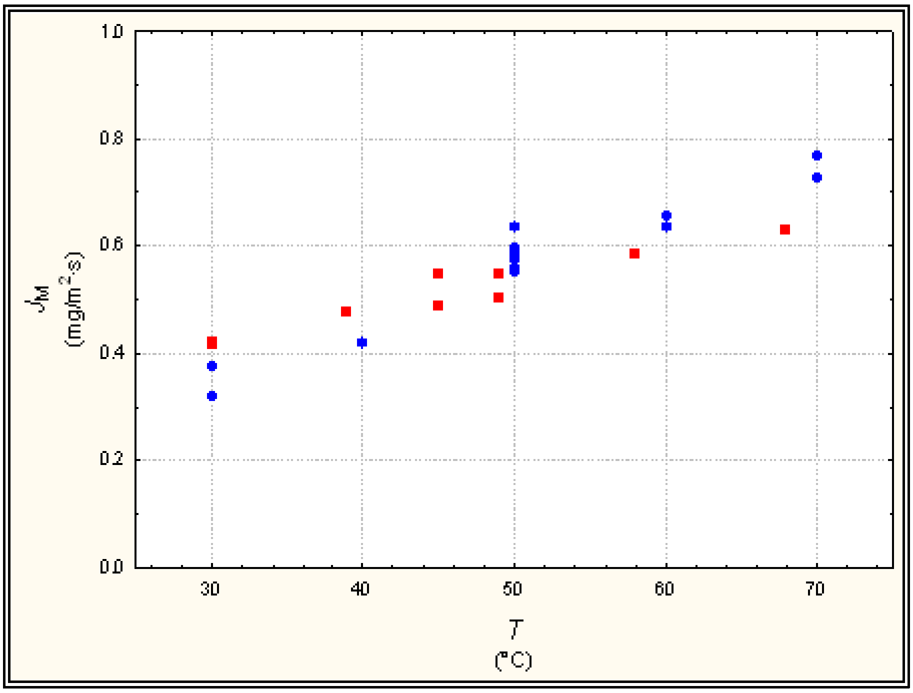


Fig. 6.20: Influence of temperature on the transmembrane flux. ●: Nickel; 🟥: Zinc

6.8 Conclusions from results

The conclusions that can be made from the results can be summarised as follow:

1. The process model is capable of accurately describing the effect of all the major variables in the SLM process.
2. There is a synergistic effect between four sets of variables and the process model is capable of describing these effects.
3. There exists an optimum extractant concentration that is dependent on temperature.
4. The effective extraction of zinc occurs at a lower pH than the extraction of nickel and this phenomenon will make it possible to selectively extract zinc from nickel/zinc solutions.

Chapter 7

Final conclusions and recommendations

> "*Engineering is the art or science of making practical.*" - *Samuel C. Florman*

7.1 Final conclusions

From an economic point of view, the use of membranes at the present time is intermediate between the development of first generation processes and second generation processes such as supported liquid membranes. The supported liquid membrane process has the potential to be both environmentally friendly and economically viable. It also has the advantage that it circumvents the problems associated with liquid-liquid extractions, such as poor phase separation and solvent entrainment.

The extraction mechanism in the SLM-process is a combination of extraction equilibrium and diffusion and can be divided into six separate steps and the process can be modelled by solving a system of equations that describes the equilibrium at both the feed and strip interface as well as the diffusion through the aqueous boundary layers and the membrane. A computer simulation was developed to solve these equations and to simulate the SLM process. Much of the physical and chemical data needed for this process model was not known and were determined through different experiments. The following conclusions can be made from these experiments:

1. The interaction between ionic solutions are so strong that the difference between the solution activity and molality cannot be ignored, an error which is very common among researches who model the SLM process. An advanced thermodynamic program was used and the effect of aqueous speciation was incorporated into the extraction equilibrium.
2. There are seven equilibrium equations involved in the extraction of nickel with D2EHPA, taking into consideration the formation of two organo-metallic species. These equations can, however, be condensed to three equations that can be solved numerically.

3. At low extractant concentrations, below 700 mol/m^3, the first reaction (forming NiR_2) dominates the extraction reaction, while the second reaction (forming $NiR_2(RH)_4$) dominates at higher extractant concentrations.
4. The temperature-dependent viscosity and density data for D2EHPA/kerosene mixtures were not available in the literature and were determined experimentally. It was found that the mixture exhibited ideal behaviour and the viscosity of the mixture could be described with the use of the Kendal and Monroe Equation (Eq. 4.40).
5. It was found that the pressure drop along a SLM tube cannot be described by standard fluid dynamic theory and an empirical equation was derived to describe shear stress along the SLM wall as a function of the Reynolds number. The shear stress could then be used to calculate the Fanning friction factor, which in turn could be used in the calculation of the boundary layer diffusion.

Different reactor/extractor configurations are available for SLMs. The disadvantage of most flat sheet membrane reactors is the low membrane area to volume ratio, while “off the shelf” tubular membrane reactors are designed for microflitration and this results in unequal flow distributions between the feed and strip solutions. To overcome this problem a custom-made reactor/extractor was designed and built for the experiments reported in this thesis. The following conclusions can be made from the results generated with the reactor/extractor:

6. Supported liquid membranes provide an area-driven extraction method, which means that the recovery of metal species will be higher at lower concentrations. This makes SLMs ideal for scavenging metal ions form effluent streams rather than a means to extract metal ions from high concentration leaching solutions.
7. Higher nickel concentrations in the feed solution increase the flux through the membrane. This increase is not linear and is hindered by the fact that higher fluxes result in a higher concentration drop across the feed boundary layer.
8. A higher feed pH also results in a higher nickel flux and, as with the nickel concentration in the feed solution, this increase is hindered by the increase in the concentration drop across the feed boundary layer. The pH of the feed solution is probably the most important factor in the extraction process and should be controlled accurately in a possible industrial applications.
9. An increase in the feed recycle (reactor) flow rate reduces the size of the feed boundary

layer and this results in an increase of the nickel flux through the membrane. It also has an synergistic effect with the pH and nickel concentration of the feed solution and should be kept high. The downside of a high recycle flow rate is that it results in an increased pressure drop across the membrane and can result in loss of extractant and subsequently in decreased membrane stability. The pressure drop along the tube wall is also higher for SLM tubes than for solid surface tubes and this amplifies the above-mentioned effect. The author recommends that, as a rule of thumb, the flow velocity through a membrane tube should be less than 2.5 m/s.

10. The diffusion across the strip side boundary layer is generally not the rate limiting step and the system is not susceptible to changes in the strip conditions, as long as a sufficiently low pH ($pH < 2.0$) is maintained.
11. An increase in temperature results in higher nickel fluxes. This is due to the following:
    1. The increased temperature leads to a reduction in the boundary layer resistance and
    2. The increased temperature leads to a reduction in the transmembrane diffusion resistance.
12. There is an optimum extractant concentration at which point the flux through the membrane is a maximum. This is due to the fact that a higher extractant concentration leads to a higher concentration gradient of organo-metallic species across the membrane, but it also leads to a decrease in the transmembrane diffusion coefficient, due to an increase in the viscosity of the organic solution. This maximum is temperature-dependent, due to the temperature dependence of the organic mixture's viscosity and rises from 1500 mol/m^3 at 30 °C to 2000 mol/m^3 at 70 °C.
13. All the above-mentioned variables are interdependent and the process model is capable of predicting the influence of this interdependence on the nickel flux through the membrane.

7.2 Recommendations for future research

The next step would be to do a full investigation into the stability of the membrane. This study can then be used to do a full economic study of the SLM process and to determine what is the economic resistance to the use of SLMs in industry.

7.3 Contribution from investigation

The use of supported liquid membranes has its historical roots in both membrane technology and liquid- liquid extraction and the following contributions emanated from this investigation:

1 The thermodynamic equilibrium of the Ni/D2EHPA system was expanded to incorporate the following:
   1.1 The nickel forms two nickel-organic species in the organic phase.
   1.2 The nickel in the aqueous phase exists as Ni^{2+} ions and a neutral $NiSO_4$ complex.
   1.3 The difference between the activity and molality of the aqueous species.
2 The philosophy that was used to describe the Ni/D2EHPA system was used to develop an equilibrium model for the Zn/D2EHPA system.
3 Some of the physical data needed for this project, such as the temperature dependence of the D2EHPA/kerosene mixture properties, was determined.
4 A model for the SLM extraction of nickel was derived and some of the unique features of this model are the following:
   4.1 The process model incorporates the equilibrium mentioned in item 1 above.
   4.2 Diffusion of both nickel-organic species is described.
   4.3 The nonlinear concentration profile of the nickel-organic species, due to the varying area and the equilibrium that exist between the two nickel organic species is incorporated in the transmembrane diffusion.
   4.4 The effect of temperature is incorporated into the process model.
   4.5 The process model uses an empirical correlation that compensates for the fact that both the pressure drop and the film theory that apply along a SLM tube deviate from standard transport phenomena.

7.4 Closing remarks

The use of supported liquid membranes is a novel idea that has the possibility of being both economically profitable and environmentally friendly. This idea is now beyond the point of a scientific curiosity and it is important to bridge the gap between science and industry. To do this, researchers will need to know how large this gap is and it is the hope of the author that this thesis will bring a better understanding of this gap and give rise to new ideas of how to cross it, in the spirit of the words of George Bernard Shaw: *"Imagination is the beginning of creation. You imagine what you desire, you will what you imagine and at last you create what you will."*

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Publications

The publications in this section are divided into three parts. The first part consist of publications by the author in the research field, prior to this investigation. The second part is a list of publications that resulted from this investigation and have been submitted for publication and the third part are papers that were presented at peer reviewed conferences.

Journal publications

Published

SMIT. JJ & KOEKEMOER LR. 1996. The Extraction of nickel with the use of supported liquid membrane capsules. *Water SA*, 22(3):249-255.

SMIT. JJ & KOEKEMOER LR. 1997. The Optimisation of nickel extraction with the use of supported liquid membrane capsules. *Water SA* 23(4):339-343.

KOEKEMOER, L.R., BUYS, J. & ROLLINGS, J.E. 2000. Use of supported liquid membranes for sulphate extraction from acidic wastewaters. *Separation Science and Technology*. 35(8):1233-1245.

Submitted

KOEKEMOER, L.R., VAN JAARSVELD, J., EVERSON, R.C. & LACHMANN, G. Liquid-liquid extraction equilibrium for the Nickel / Di-(2-ethylhexyl) phosphoric acid system with multiple reactions. *Hydrometallurgy*.

KOEKEMOER, L.R., BADENHORST, M.J.G. & EVERSON, R.C. Determination of Viscosity and Density of Di-(2-ethylhexyl) phosphoric acid in solutions of aliphatic kerosene. *Chemical Engineering Data*.

KOEKEMOER, L.R., VAN JAARSVELD, J., EVERSON, R.C., LACHMANN, G. Liquid-liquid extraction equilibrium for the Zinc / Di-(2-ethylhexyl) phosphoric acid system with multiple reactions. *Hydrometallurgy*.

Peer reviewed conference presentations

SMIT. JJ & KOEKEMOER LR. 1997. The extraction of nickel with the use of supported liquid membrane capsules at high hydronium strip concentrations. (Proceedings of the 8th national meeting of the South African Institution of Chemical Engineers, 1997, Cape Town, South Africa)

KOEKEMOER, L.R. & EVERSON, R.C. 2003. The extraction of nickel with the use of supported liquid membranes (SLM) at elevated temperatures. (Proceedings of the 10th national meeting of the South African Institution of Chemical Engineers, 2003, Sun City, South Africa)

Appendix A

Additional literature

Contents

A.1 Introduction

This appendix is used for additional literature. The literature is not of direct importance for the understanding of the project, but entails background information and methods or tools which was used in the project and is not general knowledge. References used in this appendix are cited in the reference list in the main text.

A.2 Nickel

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 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 in excess of 1000 °C (Tien & Howson, 1981:787). Nickel also has the face-centred cubic crystal structure which makes it highly formable but relatively expensive (14.40 US$/kg, London Metal Exchange, 2004) and has a high density (8.9 g/cm^3) which limits its use (Smith, 1990:548).

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 A.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. 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 is also 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).

Table A.1: Physical properties of nickel (adapted from Tien & Hawson, 1981:788)

Property	Value
Atomic weight, g/mol	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
Avg. 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 magnetisation, T	0.617
Residual magnetisation, 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

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 (14.40 US$/kg) could consequently be a strong incentive to recover nickel from effluents from various industries but mainly from the plating and catalyst industries.

A.3 Statistical experimental design

A.3.1 Introduction

The purpose of experimental design is to plan the experimentation so that the number of experiments to be executed is minimised, but the results are still accurate. The classical way to find the optimum for a process with a number of variables which influence the process is to keep all the variables (except one) constant. One variable at a time is then varied and the response is measured. This means that 25 experiments are needed for a process with five variables (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 A.1. In the experiment the X variable is kept constant at a value of x1 and the Y variable is varied. The optimum value for the X variable is found at point A. If the classical way (mono-variant) of experimentation is used, the following step would be to keep the value of Y constant at a value of A and to vary the X variable. The optimum according to the experiment is then at point B, but the true optimum is at a higher value of Y.

Another way to obtain the optimum is to do all the possible combinations of experiments, but this is usually not a practical solution. Central composite experimental designs are more reliable than the classical way of experimentation. The number of experiments for a process with five variables

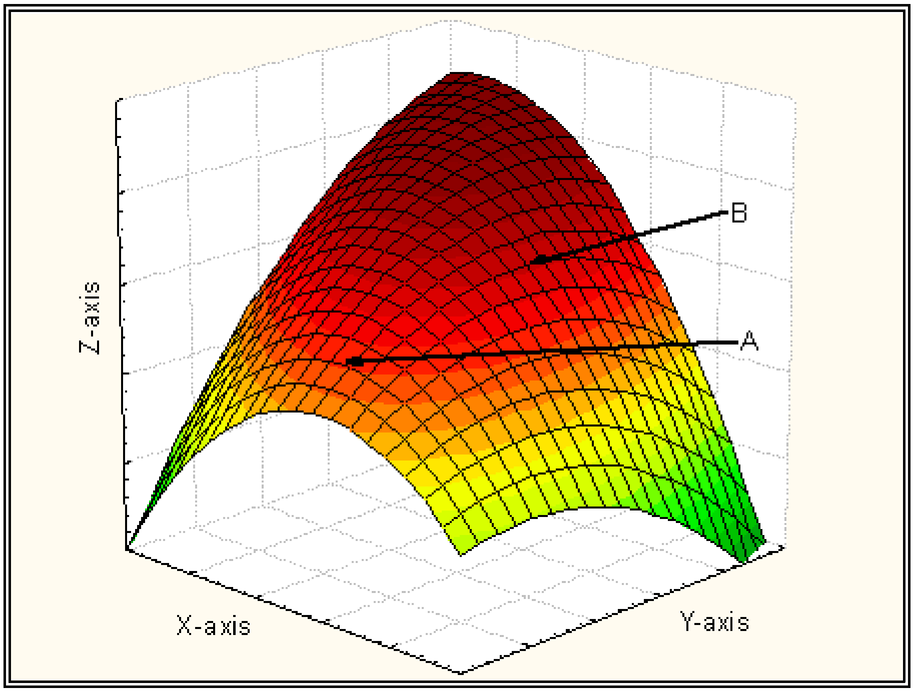

Fig. A.1: An example of a false experimental optimum

(each having five different values) needs 46 experiments.

A.3.2 Response surfaces

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

The purpose of response surface design is to fit a n-dimensional surface to the surface with the method of least squares. The surface can then be analysed mathematically and the relationship between the different variables and the optimum response can be determined. The goal of the experimental design in this thesis was to design a set of experiments to determine the mathematical relationship between the different variables which influence the extraction of nickel with supported liquid membranes. The data obtained from these experiments should be sufficient to do the required modelling.

A.4 Other work on supported liquid membranes

Typical fluxes obtained by other authors for supported liquid membranes can be seen in Table A.2.

Table A.2: Typical results obtained for supported liquid membranes

Species	Conc. (mol/m^3)	Flux (mg/m^2·s)	Extractant	Reference
Ag^{1+}	10	0.575	D2EHPA	Gherrou *et al.* (2002)
Ag^{1+}	1.0	0.101	DB18C6	Gherrou & Kerdjoudj (2002)
Au^{1+}	3.16	0.196	DB18C6	Gherrou *et al.* (2002)
Au^{1+}	0.05	8.79×10^{-3}	LIX 79	Kumar & Sastre (2000)
Co^{2+}	200	4.71	D2EHPA	Juang (1993)
Co^{2+}	85	4.72	D2EHPA	Youn *et al.* (1997)
Co^{2+}	78.6	4.25	PC-88A	Teramoto *et al.* (1987)
Co^{2+}	17.0	8.19×10^{-2}	DP-8R	Alguacil (2002)
Co^{2+}	10.0	5.89	D2EHPA	Gega *et al.* (2001)
Co^{2+}	3.39	0.361	PC-88	Matsuyama *et al.* (1990)
Co^{2+}	2.50	0.124	TEA	Bukhari *et al.* (2004)
Co^{2+}	1.00	0.588	TLAHCl	Chiarizia & Castagnola (1984)
Cu^{2+}	236	63.6	LIX 64 N	Loiacono *et al.* (1986)
Cu^{2+}	100	4.77	Acorga P5100	Largman & Sifniades (1978)
Cu^{2+}	100	3.24	Acorga P5300	Largman & Sifniades (1978)
Cu^{2+}	100	2.54	Kelex 100	Largman & Sifniades (1978)
Cu^{2+}	100	2.16	LIX 64 N	Largman & Sifniades (1978)
Cu^{2+}	100	1.78	LIX 64 N	Largman & Sifniades (1978)
Cu^{2+}	100	0.502	LIX 64 N	Baker *et al.* (1977)
Cu^{2+}	15.7	0.324	LIX 84	Gill *et al.* (2000)
Cu^{2+}	10.0	10.5	β-hydroxy oximes	Danesi *et al.* (1983)
Cu^{2+}	10.0	0.953	SME 529	Teramoto & Tanimoto (1983)
Cu^{2+}	10.0	0.262	D2EHPA	Gherrou *et al.* (2002)
Cu^{2+}	7.86	2.192	D2EHPA	Sarangi & Das (2003)

Table A.2: Typical results obtained for supported liquid membranes (continue)

Species	Conc. (mol/m^3)	Flux (mg/m^2·s)	Extractant	Reference
Cu^{2+}	1.30	1.46×10^{-2}	Acorga M5640	Alguacil *et al.* (2002)
Cu^{2+}	1.00	2.31	β-hydroxy oximes	Danesi *et al.* (1983)
Cu^{2+}	1.00	0.160	D2EHPA	Danesi (1984)
Cr^{3+}	1.90	0.520	Dinonyl-naphtalene sulfonic acid	Loiacono *et al.* (1986)
Cr^{6+}	92.3	20.8	Tri-n-octylamine	Chaudry *et al.* (1997)
Cr^{6+}	38.4	9.36	Alamine 336	Smith *et al.* (1981)
Fe^{3+}	17.9	0.201	LIX 84	Gill *et al.* (2000)
Fe^{3+}	10.0	0.977	β-hydroxy oximes	Danesi *et al.* (1983)
Fe^{3+}	2.00	0.894	Cyanex 921	Alguacil & Alonso (2000)
Fe^{3+}	1.00	1.114	TLAHCl	Chiarizia & Castagnola (1984)
Fe^{3+}	1.00	0.760	β-hydroxy oximes	Danesi *et al.* (1983)
Fe^{3+}	0.90	0.044	D2EHPA	Zhang *et al.* (2002)
Fe^{3+}	0.50	0.503	Cyanex 921	Alguacil & Alonso (2000)
Fe^{3+}	0.50	2.67×10^{-2}	3-phenyl-5-isoxazolone	Buonomenna *et al.* (2002)
Fe^{3+}	0.10	2.38×10^{-3}	EHPA	Akiba *et al.* (1997)
Fe^{3+}	0.01	0.168	Cyanex 921	Alguacil & Alonso (2000)
Hf^{4+}	0.28	0.571	TNOA	Yang *et al.* (2002)
K^{+}	100	2.07×10^{-3}	Dicyclohexano-18-crown-6	Lamb *et al.* (1988)
La^{3+}	1.00	0.945	HEH(EHP)	Guobin *et al.* (1995)
Mn^{2+}	1.46	0.901	DP-8R	Alguacil (2002)
Mo^{6+}	1.00	1.44	Alamine 336	Basualto *et al.* (2003)
Na^{+}	100	480	Monensin	Choy *et al.* (1974)
Ni^{2+}	89.7	2.15	PC-88A	Teramoto *et al.* (1987)

Table A.2: Typical results obtained for supported liquid membranes (continue)

Species	Conc. (mol/m^3)	Flux (mg/m^2·s)	Extractant	Reference
Ni^{2+}	85.0	1.47	D2EHPA	Youn *et al.* (1997)
Ni^{2+}	40.0	13.9	D2EHPA	Smit & Koekemoer (1996)
Ni^{2+}	30.0	1.17	D2EHPA	Juang (1993)
Ni^{2+}	27.3	0.278	D2EHPA	Verhaege *et al.* (1987)
Ni^{2+}	10.0	4.11	D2EHPA	Gega *et al.* (2001)
Ni^{2+}	8.50	2.14	LIX 84-I + D2EHPA	Van de Voorde *et al.* (2004)
Ni^{2+}	8.50	0.777	D2EHPA	Hernandez-cruz *et al.* (1998)
Ni^{2+}	3.41	0.31	PC-88	Matsuyama *et al.* (1990)
NO_3^-	4.00	1.22	Tetra-octyl-ammonium	Neplenbroek *et al.* (1992)
O_2	12.1	57.0	Haemoglobin	Hemmingsen (1962)
Pb^{2+}	50.0	0.11	Dicyclohexano-18-crown-6	Lamb *et al.* (1988)
Penicillin	200	-	Amberlite LA-2	Wang & Lee (1995)
U	10.0	0.357	D2EHPA	Elhassadi & Do (1986)
U	16.8	11.7	Alamine 336	Babcock *et al.* (1980)
Y	7.50	8.89×10^{-4}	PC88-A	Chitra *et al.* (1997)
Zn^{2+}	200	6.34	D2EHPA	Juang (1993)
Zn^{2+}	72.7	7.16	D2EHPA	Teramoto *et al.* (1987)
Zn^{2+}	10.0	0.222	Cryptands	Arous *et al.* (2004)
Zn^{2+}	9.17	0.317	Aliquat 336	Juang *et al.* (2004)
Zn^{2+}	7.83	1.6×10^{-2}	D2EHPA	Juang & Huang (2003)
Zn^{2+}	7.64	3.17	TOPS-99	Swain *et al.* (2004)
Zn^{2+}	7.64	2.82	D2EHPA	Sarangi & Das (2003)
Zn^{2+}	1.00	2.28	DP-8R	Alguacil & Alonso (2004)
Zn^{2+}	0.015	6.3×10^{-3}	Dithizone-CCl_4	Plucinski & Nitsch (1988)
Zr^{4+}	0.55	10.3	TNOA	Yang *et al.* (2002)

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Appendix B

Supported liquid membrane results

Contents

B.1 Introduction

This Appendix focuses on the experimental procedure and the raw experimental data for the SLM experiments. A comprehensive description of the operating procedure is given in Section B.2, while a list of the experiments done for the SLM extraction, with the corresponding page numbers in the appendix is given in Table B.1 for nickel and Table B.2 for zinc. A list of the experimental conditions are given in Table B.3 for nickel and in Table B.4 for zinc.

B.2 Operating procedure

B.2.1 Startup procedure

1. Fill the feed and strip tanks with distilled water
2. Close valves V02 and V04
3. Open valves V01 and V03
4. Start pumps P03 and P04 and wait until the recycle tanks are full
5. Open valves V02 and V04
6. Start secondary temperature controller and wait until temperature is within 10% of setpoint
7. Close Valve V01 and V03
8. Control the feed and strip flow rates using V02 and V04
9. Start primary temperature controller

B.2.2 Operating procedure during experiments

1. Replace distilled water in feed and strip tank with process water
2. Start pH controller
3. Take samples of feed and strip solution every 20 minutes.

B.2.3 Shutdown procedure

1. Stop all control loops
2. Flush system with distilled water for two hours
3. Stop all pumps
4. Open all valves and drain system

Table B.1: List of detailed experimental results given in appendix for nickel together with the corresponding page numbers

Name	Page	Name	Page	Name	Page	Name	Page	Name	Page	Name	Page
Ctr 01	B11	pHf 09	B15	Nis 01	B19	Ext 03	B23	Int 18	B27	Int 43	B31
Ctr 02	B11	Flf 01	B15	Nis 02	B19	Ext 04	B23	Int 19	B27	Int 44	B32
Ctr 03	B11	Flf 02	B15	Nis 03	B19	Ext 05	B23	Int 20	B28	Int 45	B32
Ctr 04	B11	Flf 03	B15	Nis 04	B19	Ext 06	B24	Int 21	B28	Int 46	B32
Ctr 05	B11	Flf 04	B15	Nis 05	B20	Ext 07	B24	Int 22	B28	Int 47	B32
Ctr 06	B11	Flf 05	B16	Nis 06	B20	Ext 08	B24	Int 23	B28	Int 48	B32
Ctr 07	B12	Flf 06	B16	Nis 07	B20	Ext 09	B24	Int 24	B28	Int 49	B32
Ctr 08	B12	Flf 07	B16	Nis 08	B20	Ext 10	B24	Int 25	B28	Int 50	B33
Nif 01	B12	Flf 08	B16	Nis 09	B20	Int 01	B24	Int 26	B29	Int 51	B33
Nif 02	B12	Tmp 01	B16	Nis 10	B20	Int 02	B25	Int 27	B29	Int 52	B33
Nif 03	B12	Tmp 02	B16	pHs 01	B21	Int 03	B25	Int 28	B29	Int 53	B33
Nif 04	B12	Tmp 03	B17	pHs 02	B21	Int 04	B25	Int 29	B29	Int 54	B33
Nif 05	B13	Tmp 04	B17	pHs 03	B21	Int 05	B25	Int 30	B29	Int 55	B33
Nif 06	B13	Tmp 05	B17	pHs 04	B21	Int 06	B25	Int 31	B29	Int 56	B34
Nif 07	B13	Tmp 06	B17	pHs 05	B21	Int 07	B25	Int 32	B30	Int 57	B34
Nif 08	B13	Tmp 07	B17	pHs 06	B21	Int 08	B26	Int 33	B30	Int 58	B34
Nif 09	B13	Tmp 08	B17	pHs 07	B22	Int 09	B26	Int 34	B30	Int 59	B34
pHf 01	B13	Fls 01	B18	pHs 08	B22	Int 10	B26	Int 35	B30	Int 60	B34
pHf 02	B14	Fls 02	B18	pHs 09	B22	Int 11	B26	Int 36	B30	Int 61	B34
pHf 03	B14	Fls 03	B18	pHs 10	B22	Int 12	B26	Int 37	B30	Int 62	B35
pHf 04	B14	Fls 04	B18	pHs 11	B22	Int 13	B26	Int 38	B31	Int 63	B35
pHf 05	B14	Fls 05	B18	pHs 12	B22	Int 14	B27	Int 39	B31	Int 64	B35
pHf 06	B14	Fls 06	B18	pHs 13	B23	Int 15	B27	Int 40	B31	Max 01	B35
pHf 07	B14	Fls 07	B19	Ext 01	B23	Int 16	B27	Int 41	B31		
pHf 08	B15	Fls 08	B19	Ext 02	B23	Int 17	B27	Int 42	B31		

Table B.2: List of detailed experimental results given in appendix for zinc together with the corresponding page numbers

Name	Page	Name	Page	Name	Page
ZCt 01	B38	ZpH 01	B38	ZTp 01	B39
ZCt 02	B38	ZpH 02	B38	ZTp 02	B39
ZCt 03	B38	ZpH 03	B39	ZTp 03	B39
ZCt 04	B38	ZpH 04	B39	ZTp 03	B39

B.3 Experimental conditions for nickel experiments

The meaning of the titles as used in Table B.3 are the following:

Name	: A short descriptive name is given to each experiment to keep track of the data.
$[\mathrm{Ni}]_f$	: The nickel concentration in the feed tank as measured. The solutions was prepared to approximate concentrations and then the exact value was measured (mg/l).
$\mathrm{pH}_{\mathrm{f,sp}}$	: The setpoint of the feed pH controller.
$[\mathrm{Ni}]_s$	: The nickel concentration in the strip tank as measured (mg/l).
$V_{\mathrm{H},s}$	: The amount of pure sulphuric acid used to make up strip solution (ml in a 21l tank).
pH_s	: The pH of the strip tank as measured.
T_{sp}	: The temperature setpoint for the controller (˚C).
F_f	: The feed recycle flow rate (l/hr)
F_s	: The strip recycle flow rate (l/hr)
$[\mathrm{RH}]_{Tot}$	: The concentration of the extractant as D2EHPA monomer (mol/l).

Table B.3: Summary of experimental conditions for the SLM extraction of nickel

Name	$[\mathrm{Ni}]_f$ (mg/l)	$\mathrm{pH}_{f,sp}$	$[\mathrm{Ni}]_s$ (mg/l)	$V_{\mathrm{H},s}$ (ml/21l)	pH_s	T_{sp} (˚C)	F_f (l/hr)	F_s (l/hr)	$[\mathrm{RH}]_{Tot}$ (mol/l)
Ctr 01	60.10	4.00	60.80	90	1.08	50	300	300	1.2
Ctr 02	58.29	4.00	59.50	90	0.98	50	300	300	1.2
Ctr 03	58.50	4.00	55.20	87	1.05	50	300	300	1.2
Ctr 04	56.10	4.00	57.80	95	1.10	50	300	300	1.2
Ctr 05	57.70	4.00	57.10	130	1.05	50	300	300	1.2

Table B.3: Summary of experimental conditions for the SLM extraction of nickel (continue)

Name	$[Ni]_f$ (mg/l)	$pH_{f,sp}$	$[Ni]_s$ (mg/l)	$V_{\mathrm{H},s}$ (ml/21l)	pH_s	T_{sp} (˚C)	F_f (l/hr)	F_s (l/hr)	$[RH]_{Tot}$ (mol/l)
Ctr 06	56.20	4.00	56.53	130	0.99	50	300	300	1.2
Ctr 07	56.10	4.00	56.17	130	1.10	50	300	300	1.2
Ctr 08	54.23	4.00	47.23	130	0.97	50	300	300	1.2
Nif 01	20.90	4.00	58.10	103	1.06	50	300	300	1.2
Nif 02	23.30	4.50	54.90	110	1.05	50	300	300	1.2
Nif 03	35.80	4.00	57.60	115	1.02	50	300	300	1.2
Nif 04	35.30	4.00	55.10	110	1.07	50	300	300	1.2
Nif 05	91.20	4.00	59.90	115	1.05	50	300	300	1.2
Nif 06	86.60	4.00	52.00	120	1.05	50	300	300	1.2
Nif 07	150.80	4.00	54.30	120	1.06	50	300	300	1.2
Nif 08	157.20	4.00	56.90	120	1.04	50	300	300	1.2
Nif 09	140.00	4.00	57.00	120	1.05	50	300	300	1.2
pHf 01	57.50	3.00	58.20	130	1.03	50	300	300	1.2
pHf 02	58.40	3.00	57.13	130	1.00	50	300	300	1.2
pHf 03	59.43	3.50	58.65	130	1.02	50	300	300	1.2
pHf 04	58.50	3.50	55.85	130	1.01	50	300	300	1.2
pHf 05	55.00	4.50	55.00	110	1.06	50	300	300	1.2
pHf 06	53.10	4.50	44.20	110	1.10	50	300	300	1.2
pHf 07	53.10	4.50	50.00	110	1.09	50	300	300	1.2
pHf 08	55.00	5.00	55.00	120	1.10	50	300	300	1.2
pHf 09	57.07	5.00	53.76	130	1.01	50	300	300	1.2
Flf 01	54.50	4.00	55.60	130	1.01	50	100	300	1.2
Flf 02	52.70	4.00	53.60	130	1.09	50	100	300	1.2
Flf 03	53.00	4.00	53.65	130	1.14	50	200	300	1.2
Flf 04	49.70	4.00	43.97	130	1.07	50	200	300	1.2
Flf 05	48.70	4.00	46.63	130	1.12	50	400	300	1.2
Flf 06	56.60	4.00	56.60	130	0.90	50	400	300	1.2

Table B.3: Summary of experimental conditions for the SLM extraction of nickel (continue)

Name	$[Ni]_f$ (mg/l)	$pH_{f,sp}$	$[Ni]_s$ (mg/l)	$V_{H,s}$ (ml/21l)	pH_s	T_{sp} (˚C)	F_f (l/hr)	F_s (l/hr)	$[RH]_{Tot}$ (mol/l)
Flf 07	57.30	4.00	56.77	130	0.94	50	400	300	1.2
Flf 08	48.20	4.00	53.33	130	1.11	50	200	300	1.2
Tmp 01	55.50	4.00	54.40	125	1.05	30	300	300	1.2
Tmp 02	57.30	3.50	54.80	130	1.02	30	300	300	1.2
Tmp 03	54.40	4.00	51.00	130	1.04	40	300	300	1.2
Tmp 04	57.00	4.00	48.90	130	1.04	40	300	300	1.2
Tmp 05	56.80	4.00	54.60	130	1.07	60	300	300	1.2
Tmp 06	55.40	4.00	52.80	130	1.08	60	300	300	1.2
Tmp 07	56.00	4.00	56.00	130	1.08	70	300	300	1.2
Tmp 08	56.00	4.00	50.00	130	1.06	70	300	300	1.2
Fls 01	57.53	4.00	55.73	130	1.01	50	300	100	1.2
Fls 02	59.16	4.00	57.03	130	0.98	50	300	100	1.2
Fls 03	54.23	4.00	52.97	130	0.95	50	300	200	1.2
Fls 04	53.86	4.00	49.66	130	0.97	50	300	200	1.2
Fls 05	55.20	4.00	54.80	130	0.98	50	300	200	1.2
Fls 06	53.55	4.00	51.85	120	1.05	50	300	400	1.2
Fls 07	57.33	4.00	58.60	125	1.00	50	300	400	1.2
Fls 08	56.17	4.00	53.20	130	0.97	50	300	400	1.2
Nis 01	60.20	4.00	0.00	120	1.02	50	300	300	1.2
Nis 02	56.70	4.00	0.00	130	1.02	50	300	300	1.2
Nis 03	56.60	4.00	0.00	130	1.02	50	300	300	1.2
Nis 04	57.30	4.00	0.00	130	1.02	50	300	300	1.2
Nis 05	55.70	4.00	6.47	130	0.94	50	300	300	1.2
Nis 06	56.70	4.00	6.70	130	0.96	50	300	300	1.2
Nis 07	55.70	4.00	554	130	1.00	50	300	300	1.2
Nis 08	56.70	4.00	563	130	1.01	50	300	300	1.2
Nis 09	55.00	4.00	5426	130	1.02	50	300	300	1.2
Nis 10	57.10	4.00	5690	130	1.06	50	300	300	1.2

Table B.3: Summary of experimental conditions for the SLM extraction of nickel (continue)

Name	$[Ni]_f$ (mg/l)	$pH_{f,sp}$	$[Ni]_s$ (mg/l)	$V_{H,s}$ (ml/21l)	pH_s	T_{sp} (°C)	F_f (l/hr)	F_s (l/hr)	$[RH]_{Tot}$ (mol/l)
pHs 01	57.70	4.00	55.77	0	3.99	50	300	300	1.2
pHs 02	55.40	4.00	55.40	10	1.90	50	300	300	1.2
pHs 03	57.00	4.00	56.77	50	1.20	50	300	300	1.2
pHs 04	55.50	4.00	53.65	50	1.24	50	300	300	1.2
pHs 05	57.90	4.00	56.47	90	1.00	50	300	300	1.2
pHs 06	55.80	4.00	55.17	90	1.00	50	300	300	1.2
pHs 07	55.40	4.00	55.27	170	0.84	50	300	300	1.2
pHs 08	56.00	4.00	55.17	170	0.85	50	300	300	1.2
pHs 09	57.60	4.00	57.40	210	0.89	50	300	300	1.2
pHs 10	55.00	4.00	52.23	210	0.72	50	300	300	1.2
pHs 11	57.60	4.00	57.83	210	0.70	50	300	300	1.2
pHs 12	59.30	4.00	57.73	500	0.43	50	300	300	1.2
pHs 13	54.00	4.00	50.00	500	0.39	50	300	300	1.2
Ext 01	50.40	5.50	44.37	130	0.96	50	300	300	0.0
Ext 02	54.93	4.00	51.90	110	1.03	50	300	300	0.0
Ext 03	56.30	4.00	57.27	110	1.09	50	300	300	0.8
Ext 04	59.20	4.00	60.40	120	1.10	50	300	300	0.8
Ext 05	59.80	4.00	60.37	130	0.83	50	300	300	1.0
Ext 06	56.70	4.00	56.17	130	0.82	50	300	300	1.0
Ext 07	56.10	4.00	56.87	120	0.97	50	300	300	1.4
Ext 08	56.30	4.00	56.47	120	1.19	50	300	300	1.4
Ext 09	56.00	4.00	55.97	120	0.93	50	300	300	1.6
Ext 10	52.40	4.00	50.70	120	0.97	50	300	300	1.6
Int 01	83.00	3.50	0.10	90	1.08	40	200	200	1.0
Int 02	34.63	4.50	0.40	90	1.05	40	200	200	1.0
Int 03	34.30	3.50	0.40	90	1.05	40	350	350	1.0
Int 04	34.10	3.50	487	170	0.83	60	200	350	1.0
Int 05	74.90	3.50	519	90	1.10	40	200	350	1.0

Table B.3: Summary of experimental conditions for the SLM extraction of nickel (continue)

Name	[Ni]$_f$ (mg/l)	pH$_{f,sp}$	[Ni]$_s$ (mg/l)	$V_{\mathrm{H},s}$ (ml/21l)	pH$_s$	T_{sp} (˚C)	F_f (l/hr)	F_s (l/hr)	[RH]$_{Tot}$ (mol/l)
Int 06	32.65	4.50	464	90	1.09	40	200	350	1.0
Int 07	39.50	4.50	490	90	1.06	60	200	350	1.0
Int 08	76.60	3.50	1.03	170	0.88	60	350	350	1.0
Int 09	33.30	4.50	489	90	1.09	60	350	350	1.0
Int 10	77.80	3.50	0.67	170	0.81	40	200	350	1.0
Int 11	33.60	4.00	0.23	170	0.81	40	200	350	1.0
Int 12	86.50	3.50	509	90	1.08	60	350	350	1.0
Int 13	36.40	4.50	0.13	170	0.79	60	350	350	1.0
Int 14	92.40	3.50	598	170	0.75	40	200	200	1.0
Int 15	34.80	4.50	534	170	0.76	40	200	200	1.0
Int 16	78.50	3.50	500	170	0.77	60	350	200	1.0
Int 17	34.60	3.50	0.47	170	0.95	60	200	350	1.0
Int 18	35.20	4.50	522	170	0.84	60	350	200	1.0
Int 19	65.10	4.50	0.57	170	0.76	60	200	200	1.0
Int 20	84.00	4.50	1.37	90	1.06	60	200	350	1.0
Int 21	35.10	3.50	481	90	1.11	60	200	200	1.0
Int 22	34.90	3.50	0.27	170	0.89	40	350	200	1.0
Int 23	85.80	4.50	500	90	1.11	60	200	200	1.0
Int 24	32.70	3.50	0.23	170	0.82	60	200	200	1.0
Int 25	85.20	4.50	0.87	170	0.79	40	350	200	1.0
Int 26	32.43	3.50	467	170	0.80	40	350	350	1.0
Int 27	34.80	3.50	540	90	1.05	40	350	200	1.0
Int 28	85.10	4.50	0.30	90	1.06	40	350	350	1.0
Int 29	35.80	5.00	0.20	90	1.08	60	350	200	1.0
Int 30	84.50	3.50	0.93	90	1.05	60	350	200	1.0
Int 31	82.10	4.50	429	170	0.81	40	350	350	1.0
Int 32	35.60	4.50	509	90	1.19	60	200	350	1.4
Int 33	35.10	4.50	0.53	90	1.22	60	200	200	1.4

Table B.3: Summary of experimental conditions for the SLM extraction of nickel (continue)

Name	$[Ni]_f$ (mg/l)	$pH_{f,sp}$	$[Ni]_s$ (mg/l)	$V_{H,s}$ (ml/21l)	pH_s	T_{sp} (°C)	F_f (l/hr)	F_s (l/hr)	$[RH]_{Tot}$ (mol/l)
Int 34	35.03	4.50	0.80	170	1.03	60	200	350	1.4
Int 35	78.30	3.50	448	90	1.28	40	350	350	1.4
Int 36	34.20	4.50	464	90	1.22	40	350	350	1.4
Int 37	38.20	3.50	514	90	1.23	40	200	200	1.4
Int 38	36.40	3.50	0.37	170	1.04	40	200	200	1.4
Int 39	78.40	3.50	0.67	170	0.88	40	350	350	1.4
Int 40	86.20	4.50	0.90	170	0.89	40	350	350	1.4
Int 41	35.50	4.50	0.47	170	0.86	40	200	200	1.4
Int 42	36.43	3.50	436	170	0.83	40	200	350	1.4
Int 43	34.90	4.50	522	170	0.84	40	350	200	1.4
Int 44	76.43	4.50	354	170	0.85	40	200	350	1.4
Int 45	34.90	3.50	0.65	90	1.14	60	350	350	1.4
Int 46	32.90	4.50	0.40	90	1.54	40	350	200	1.4
Int 47	87.60	4.50	1.03	90	1.16	60	350	350	1.4
Int 48	36.50	3.50	487	90	1.16	60	350	200	1.4
Int 49	81.30	4.50	542	90	1.14	40	200	200	1.4
Int 50	77.00	4.50	471	90	1.44	60	350	200	1.4
Int 51	32.10	3.50	0.73	170	1.22	60	350	200	1.4
Int 52	32.50	4.50	519	170	1.30	60	200	200	1.4
Int 53	33.15	3.50	0.43	90	1.32	40	200	350	1.4
Int 54	87.00	4.50	0.82	170	1.13	60	350	200	1.4
Int 55	31.60	3.50	481	170	1.09	60	350	350	1.4
Int 56	82.10	4.50	0.10	90	1.29	40	200	350	1.4
Int 57	83.30	3.50	0.70	90	1.31	40	350	200	1.4
Int 58	80.20	4.50	500	170	1.24	60	350	350	1.4
Int 59	95.70	3.50	0.97	90	1.22	60	200	200	1.4

Table B.3: Summary of experimental conditions for the SLM extraction of nickel (continue)

Name	$[Ni]_f$ (mg/l)	$pH_{f,sp}$	$[Ni]_s$ (mg/l)	$V_{H,s}$ (ml/21l)	pH_s	T_{sp} (˚C)	F_f (l/hr)	F_s (l/hr)	$[RH]_{Tot}$ (mol/l)
Int 60	85.98	3.50	550	170	1.01	40	350	200	1.4
Int 61	94.10	3.50	0.97	170	1.02	60	200	350	1.4
Int 62	80.90	4.50	625	90	1.23	60	200	200	1.0
Int 63	75.40	3.50	479	90	1.26	60	350	350	1.0
Int 64	76.30	4.50	2.23	170	1.02	60	200	200	1.0
Max 01	129.40	5.00	0.13	170	1.20	70	300	350	1.6

B.4 Detailed results of SLM experiments for nickel

The meaning of the titles as used in the tables in this section is as follow:

Exp. Name:	A short descriptive name (same as in Table B.3) of the experiment.
J_{fin}	: The final flux of nickel across the membrane (mg/m^2·s).
F_{FT}	: The flow rate from the feed tank to the feed recycle tank (l/hr).
F_{ST}	: The flow rate from the strip tank to the strip recycle tank (l/hr).
F_f	: The feed recycle flow rate (l/hr).
F_s	: The strip recycle flow rate (l/hr).
T_{sp}	: The temperature setpoint for the controller (˚C).
$[RH]_{Tot}$	: The concentration of the extractant as D2EHPA monomer (mol/l).
Time	: The time when samples were taken (min).
$[Ni]_f$	: The nickel concentration of the feed as measured in the recycle tank (mg/l).
pH_f	: The pH of the feed as measured in the recycle tank.
$[Ni]_s$	: The nickel concentration of the strip as measured in the recycle tank (mg/l).
pH_s	: The pH of the strip as measured in the recycle tank.
V_{NaOH}	: The volume of a 1 mol/l NaOH solution titrated by the pH controller (ml).
Tank	: The concentration and pH in the feed and strip tanks.

Exp. Name: Ctr 01

J_{fin}=0.571 mg/m^2·s

F_{FT}=10.08 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=10.08 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	[Ni]$_f$ (mg/l)	pH$_f$	[Ni]$_s$ (mg/l)	pH$_s$	V_{NaOH} (ml)
0	0.50	4.06	0.60	3.67	0.00
20	22.60	3.97	38.60	1.27	2.24
40	29.90	3.94	62.30	1.11	5.36
60	31.80	4.12	75.50	1.09	8.78
80	33.00	4.09	83.20	1.05	12.16
100	28.90	3.99	85.60	1.05	15.58
117	28.90	4.09	86.10	1.08	18.32
Tank	60.10	8.33	60.80	3.67	-

Exp. Name: Ctr 02

J_{fin}=0.573 mg/m^2·s

F_{FT}=9.54 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=10.06 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	[Ni]$_f$ (mg/l)	pH$_f$	[Ni]$_s$ (mg/l)	pH$_s$	V_{NaOH} (ml)
0	0.10	3.83	0.30	3.61	0.00
20	17.40	4.37	38.10	1.24	3.09
40	24.00	4.13	62.90	1.07	7.02
60	25.80	4.37	75.20	1.02	11.32
80	26.90	4.16	82.30	0.99	15.69
100	26.00	4.15	85.70	0.99	20.18
140	25.60	4.10	89.50	0.98	29.20
Tank	58.29	5.64	59.50	0.99	-

Exp. Name: Ctr 03

J_{fin}=0.594 mg/m^2·s

F_{FT}=10.63 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=1044 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	[Ni]$_f$ (mg/l)	pH$_f$	[Ni]$_s$ (mg/l)	pH$_s$	V_{NaOH} (ml)
0	0.30	4.02	0.20	3.93	0.00
20	20.90	3.85	38.00	1.25	2.24
40	27.30	3.80	60.70	1.12	6.28
60	27.90	4.01	73.20	1.06	10.94
80	27.60	3.98	79.10	1.04	15.88
100	28.80	3.93	83.20	1.06	20.63
120	28.30	3.77	85.00	1.05	25.55
Tank	58.50	4.00	60.80	1.03	-

Exp. Name: Ctr 04

J_{fin}=0.550 mg/m^2·s

F_{FT}=9.84 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=10.23 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	[Ni]$_f$ (mg/l)	pH$_f$	[Ni]$_s$ (mg/l)	pH$_s$	V_{NaOH} (ml)
0	0.20	4.11	1.40	2.89	0.00
20	17.40	3.82	38.60	1.27	1.58
40	23.90	3.90	63.50	1.13	5.68
60	25.20	3.87	76.20	1.08	9.70
80	25.30	4.00	82.10	1.08	13.96
100	25.40	4.02	85.70	1.06	18.34
120	25.50	3.99	88.50	1.10	22.74
Tank	56.10	5.16	57.80	1.03	-

Exp. Name: Ctr 05

J_{fin}=0.588 mg/m^2·s

F_{FT}=9.83 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=9.83 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	[Ni]$_f$ (mg/l)	pH$_f$	[Ni]$_s$ (mg/l)	pH$_s$	V_{NaOH} (ml)
0	0.60	4.00	2.30	2.51	0.00
20	18.30	3.76	35.70	1.26	2.21
40	24.60	3.88	61.30	1.15	6.50
60	25.30	3.97	77.00	1.09	11.47
80	25.90	4.00	84.60	1.07	16.46
100	25.60	3.99	89.60	1.07	21.08
120	24.50	4.00	89.60	1.05	25.80
Tank	57.70	4.17	57.10	1.07	-

Exp. Name: Ctr 06

J_{fin}=0.556 mg/m^2·s

F_{FT}=9.94 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=10.00 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	[Ni]$_f$ (mg/l)	pH$_f$	[Ni]$_s$ (mg/l)	pH$_s$	V_{NaOH} (ml)
0	2.50	3.81	57.50	1.90	0.00
20	19.50	3.82	61.70	1.15	3.06
40	24.80	3.90	72.30	1.08	7.16
60	25.20	3.99	79.00	1.02	11.81
80	24.90	4.00	83.00	1.03	16.39
100	26.20	3.92	83.10	1.00	20.02
120	25.80	4.03	82.70	0.99	25.19
Tank	56.20	5.25	56.53	1.00	-

Exp. Name: Ctr 07

J_{fin}=0.635 mg/m^2·s

F_{FT}=9.78 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=10.26 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.20	3.88	1.40	2.66	0.00
20	17.60	3.78	40.30	0.97	2.47
40	22.40	3.89	65.50	0.86	7.15
60	22.40	3.95	77.30	0.91	12.03
80	22.50	3.99	83.20	0.99	17.22
100	21.60	3.98	85.20	1.05	22.52
120	21.90	4.06	88.50	1.1	27.82
Tank	57.03	5.38	56.17	0.97	-

Exp. Name: Ctr 08

J_{fin}=0.582 mg/m^2·s

F_{FT}=9.78 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=9.77 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.20	3.76	2.60	1.91	0.00
20	16.90	3.78	22.90	1.01	3.81
40	22.90	3.92	70.60	0.98	8.99
60	23.10	3.98	76.00	0.91	14.43
80	20.90	4.02	81.10	0.92	19.87
100	22.30	4.01	80.80	0.97	24.96
120	22.20	4.03	80.90	0.97	30.14
Tank	54.23	5.49	47.23	0.90	-

Exp. Name: Nif 01

J_{fin}=0.228 mg/m^2·s

F_{FT}=9.72 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=9.45 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	1.00	5.00	0.50	4.22	0.00
20	6.30	3.92	32.40	1.33	1.44
40	7.20	3.99	49.20	1.18	5.24
60	7.90	4.01	58.40	1.13	8.62
80	7.80	4.01	64.30	1.08	12.45
100	8.00	4.02	67.20	1.06	15.83
120	8.10	4.03	69.50	1.06	19.19
Tank	20.90	3.45	58.10	1.04	-

Exp. Name: Nif 02

J_{fin}=0.266 mg/m^2·s

F_{FT}=9.79 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=9.75 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.30	4.11	0.60	3.30	0.00
20	6.20	4.09	33.80	1.28	2.94
40	8.30	4.20	51.30	1.11	6.35
60	8.30	4.22	61.20	1.10	9.92
80	8.30	4.06	66.60	1.09	13.43
100	8.40	4.12	68.60	1.07	16.95
120	8.50	4.26	69.00	1.05	20.28
Tank	23.30	3.66	54.90	1.05	-

Exp. Name: Nif 03

J_{fin}=0.365 mg/m^2·s

F_{FT}=9.89 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=10.30 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.60	4.07	1.40	3.07	0.00
20	9.60	3.81	36.50	1.21	2.20
40	13.60	4.03	58.10	1.10	5.53
60	15.10	3.97	66.00	1.02	8.87
80	15.10	4.02	69.30	1.00	12.30
100	15.10	4.05	70.00	1.01	15.91
120	15.50	4.06	71.30	1.02	19.37
Tank	35.80	3.96	57.60	1.01	-

Exp. Name: Nif 04

J_{fin}=0.378 mg/m^2·s

F_{FT}=10.43 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=11.74 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	1.60	3.93	7.00	1.96	0.00
20	10.90	3.86	43.70	1.20	2.35
40	13.70	3.99	59.20	1.12	5.45
60	14.80	4.04	65.90	1.07	8.76
80	14.90	3.91	68.30	1.07	12.03
100	14.90	4.05	69.40	1.09	15.05
106	15.20	4.06	68.70	1.07	16.20
Tank	35.30	4.44	55.10	1.09	-

Exp. Name: Nif 05

$J_{fin}=0.714$ mg/m^2·s

$F_{FT}=9.60$ l/hr $F_f=300$ l/hr $T_{sp}=50$ °C

$F_{ST}=10.15$ l/hr $F_s=300$ l/hr $[RH]_{Tot}=1.2$ mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.40	3.98	2.10	2.61	0.00
20	32.90	3.83	39.00	1.28	3.04
40	43.70	3.88	65.40	1.10	8.69
60	48.80	3.92	84.60	1.05	14.80
80	50.80	3.83	92.20	1.06	20.06
100	50.30	3.99	96.20	1.07	26.68
120	49.30	3.94	94.10	1.05	32.89
Tank	91.20	3.76	59.90	1.00	-

Exp. Name: Nif 06

$J_{fin}=0.749$ mg/m^2·s

$F_{FT}=10.38$ l/hr $F_f=300$ l/hr $T_{sp}=50$ °C

$F_{ST}=9.97$ l/hr $F_s=300$ l/hr $[RH]_{Tot}=1.2$ mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	1.90	3.73	9.80	2.23	0.00
20	36.00	3.77	49.60	1.26	3.93
40	44.50	3.89	69.90	1.15	9.54
60	50.60	3.96	86.00	1.06	15.64
80	49.80	3.97	85.90	1.08	21.78
100	45.60	4.01	91.90	1.05	28.01
120	48.40	4.01	91.90	1.05	34.18
Tank	86.60	4.04	52.00	1.04	-

Exp. Name: Nif 07

$J_{fin}=0.896$ mg/m^2·s

$F_{FT}=10.05$ l/hr $F_f=300$ l/hr $T_{sp}=50$ °C

$F_{ST}=10.35$ l/hr $F_s=300$ l/hr $[RH]_{Tot}=1.2$ mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.10	4.06	0.90	3.11	0.00
20	63.10	3.67	39.80	1.27	3.57
40	93.60	3.84	67.30	1.07	11.30
60	98.80	3.94	84.70	1.03	19.54
80	102.20	4.02	89.30	1.04	27.61
100	102.80	4.04	93.30	1.06	35.94
120	101.00	4.03	93.10	1.06	44.56
Tank	150.80	3.46	54.30	1.04	-

Exp. Name: Nif 08

$J_{fin}=0.809$ mg/m^2·s

$F_{FT}=9.91$ l/hr $F_f=300$ l/hr $T_{sp}=50$ °C

$F_{ST}=10.30$ l/hr $F_s=300$ l/hr $[RH]_{Tot}=1.2$ mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.70	3.97	1.40	2.99	0.00
20	61.90	3.71	42.60	1.22	3.07
60	103.70	4.00	88.40	1.09	16.85
80	106.20	4.06	98.80	1.03	24.38
100	109.20	4.04	102.30	1.04	31.48
120	111.40	4.04	103.00	1.04	38.71
Tank	157.20	4.50	56.90	1.02	-

Exp. Name: Nif 09

$J_{fin}=0.870$ mg/m^2·s

$F_{FT}=10.26$ l/hr $F_f=300$ l/hr $T_{sp}=50$ °C

$F_{ST}=10.08$ l/hr $F_s=300$ l/hr $[RH]_{Tot}=1.2$ mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	1.20	3.86	4.50	2.28	0.00
20	61.80	3.69	44.20	1.21	4.51
40	84.50	3.87	78.20	1.18	11.30
60	90.60	3.96	93.70	1.09	18.76
80	96.50	3.98	98.30	1.06	26.32
100	90.80	4.00	102.70	1.06	34.08
120	94.60	4.00	100.80	1.05	40.92
Tank	140.00	3.75	57.00	1.03	-

Exp. Name: pHf 01

$J_{fin}=0.229$ mg/m^2·s

$F_{FT}=9.73$ l/hr $F_f=300$ l/hr $T_{sp}=50$ °C

$F_{ST}=9.79$ l/hr $F_s=300$ l/hr $[RH]_{Tot}=1.2$ mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.30	3.98	2.20	2.64	0.00
20	21.50	3.55	37.80	1.21	0.00
40	34.30	3.37	61.20	1.08	0.00
60	42.40	3.31	67.10	1.06	0.00
80	43.00	3.28	69.90	1.02	0.00
100	42.90	3.27	70.90	1.00	0.00
120	43.00	3.27	71.30	1.03	0.00
Tank	57.50	4.34	58.20	1.03	-

Exp. Name: pHf 02

J_{fin}=0.180 mg/m^2·s

F_{FT}=9.30 l/hr F_f=300 l/hr T_{sp}=50 ˚C

F_{ST}=9.88 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.70	3.72	3.70	2.30	0.00
20	26.80	3.03	35.70	1.23	0.00
40	41.80	3.00	52.60	1.09	3.11
60	47.20	3.00	58.30	1.06	5.89
80	44.20	3.00	62.20	1.02	8.69
100	44.30	3.00	63.20	1.00	11.62
120	48.80	3.00	62.80	1.00	14.46
Tank	58.40	2.89	57.13	1.00	-

Exp. Name: pHf 03

J_{fin}=0.320 mg/m^2·s

F_{FT}=10.50 l/hr F_f=300 l/hr T_{sp}=50 ˚C

F_{ST}=9.83 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.20	3.79	2.40	2.43	0.00
20	25.70	3.39	38.80	1.20	1.35
40	37.50	3.47	58.60	1.08	8.50
60	40.70	3.48	68.30	1.05	15.15
80	42.30	3.47	72.30	1.03	22.52
100	42.30	3.50	74.80	1.02	30.07
120	42.60	3.50	76.20	1.02	37.01
Tank	59.43	2.94	58.65	1.02	-

Exp. Name: pHf 04

J_{fin}=0.301 mg/m^2·s

F_{FT}=9.81 l/hr F_f=300 l/hr T_{sp}=50 ˚C

F_{ST}=9.82 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.30	3.73	3.30	2.35	0.00
20	24.00	3.37	36.50	1.22	2.18
40	34.10	3.47	55.50	1.10	7.08
60	38.10	3.49	61.60	1.04	12.06
80	41.20	3.49	70.00	1.02	17.10
100	42.00	3.28	72.10	1.02	20.00
120	40.10	3.59	74.90	1.01	27.63
Tank	58.50	3.10	55.85	1.01	-

Exp. Name: pHf 05

J_{fin}=0.597 mg/m^2·s

F_{FT}=9.75 l/hr F_f=300 l/hr T_{sp}=50 ˚C

F_{ST}=9.77 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	1.00	3.80	11.80	2.12	0.00
20	15.30	3.95	47.70	1.26	3.91
40	18.40	4.20	60.40	1.14	9.91
60	18.10	4.42	68.50	1.12	16.47
80	19.60	4.92	70.00	1.11	22.93
100	20.20	4.53	74.60	1.12	29.04
120	20.00	4.51	76.40	1.10	35.26
Tank	53.10	3.79	44.20	1.09	-

Exp. Name: pHf 06

J_{fin}=0.675 mg/m^2·s

F_{FT}=9.84 l/hr F_f=300 l/hr T_{sp}=50 ˚C

F_{ST}=10.00 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.50	3.79	3.00	2.33	0.00
20	14.80	3.94	40.30	1.30	5.03
40	17.10	4.20	67.00	1.21	12.07
60	17.20	4.60	81.50	1.16	19.25
80	17.80	4.56	87.80	1.13	25.84
100	16.70	4.54	87.90	1.10	32.52
120	17.70	4.72	80.40	1.06	39.02
Tank	55.00	4.22	55.00	1.05	-

Exp. Name: pHf 07

J_{fin}=0.0.618 mg/m^2·s

F_{FT}=10.07 l/hr F_f=300 l/hr T_{sp}=50 ˚C

F_{ST}=9.49 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.40	3.90	7.30	2.27	0.00
20	18.80	3.98	43.40	1.31	3.69
40	21.70	4.20	65.40	1.17	9.07
60	21.50	4.38	76.90	1.15	14.95
80	19.90	4.34	80.70	1.12	20.75
100	20.80	4.51	82.00	1.10	26.71
120	20.20	4.51	81.90	1.09	32.61
Tank	53.10	4.37	50.00	1.08	-

Exp. Name: pHf 08

J_{fin}=0.706 mg/m^2·s

F_{FT}=9.94 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=10.00 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.20	3.90	2.50	2.51	0.00
20	14.20	4.09	38.10	1.27	4.48
40	16.30	4.35	64.70	1.16	10.57
60	16.70	4.69	78.80	1.18	17.11
80	16.70	4.93	85.70	1.14	23.81
100	16.60	5.32	87.60	1.17	30.33
120	16.20	5.12	87.00	1.10	36.80
Tank	55.00	5.62	55.00	1.05	-

Exp. Name: pHf 09

J_{fin}=0.761 mg/m^2·s

F_{FT}=10.11 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=9.71 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.20	3.79	2.50	2.61	0.00
20	15.20	4.01	40.00	1.25	4.64
40	17.80	4.27	68.60	1.08	11.27
60	17.10	4.82	86.00	1.06	18.93
80	17.00	5.00	89.70	1.03	25.99
100	16.40	5.21	88.70	1.02	33.23
120	16.40	5.37	90.00	1.01	40.00
Tank	57.07	3.99	53.76	1.01	-

Exp. Name: Flf 01

J_{fin}=0.316 mg/m^2·s

F_{FT}=10.01 l/hr F_f=100 l/hr T_{sp}=50 °C

F_{ST}=9.88 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.10	3.89	1.00	2.87	0.00
20	21.20	3.91	37.10	1.25	1.92
40	31.70	3.94	55.90	1.15	4.32
60	35.40	3.99	62.00	1.07	7.10
80	36.50	4.00	64.50	1.02	9.86
100	35.90	4.01	70.90	1.05	12.66
120	37.10	4.00	70.00	1.01	15.32
Tank	54.50	4.17	55.60	1.08	-

Exp. Name: Flf 02

J_{fin}=0.301 mg/m^2·s

F_{FT}=10.07 l/hr F_f=100 l/hr T_{sp}=50 °C

F_{ST}=9.78 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.50	3.82	0.10	2.38	0.00
20	18.50	3.90	31.10	1.26	2.22
40	32.10	3.96	58.80	1.13	4.99
60	36.60	3.99	65.30	1.10	8.08
80	34.80	4.00	65.00	1.09	11.16
100	36.10	4.00	68.60	1.09	14.13
120	35.50	4.02	70.40	1.09	17.37
Tank	52.70	3.93	53.60	1.04	-

Exp. Name: Flf 03

J_{fin}=0.400 mg/m^2·s

F_{FT}=10.06 l/hr F_f=200 l/hr T_{sp}=50 °C

F_{ST}=9.87 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.00	3.84	1.60	2.71	0.00
20	18.80	3.85	35.30	1.31	1.64
40	26.40	3.94	51.80	1.19	4.37
60	30.80	3.96	60.40	1.12	7.40
80	30.70	3.98	63.00	1.09	10.52
100	33.90	4.00	68.20	1.13	13.71
120	33.00	3.99	68.00	1.14	16.77
Tank	55.50	4.28	53.65	1.07	-

Exp. Name: Flf 04

J_{fin}=0.369 mg/m^2·s

F_{FT}=9.91 l/hr F_f=200 l/hr T_{sp}=50 °C

F_{ST}=9.76 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.40	4.02	1.70	2.63	0.00
20	19.80	3.84	34.90	1.24	1.62
40	28.90	3.94	55.80	1.09	4.23
60	30.50	3.99	63.90	1.06	7.10
80	32.40	3.98	67.00	1.09	9.78
100	30.40	4.01	64.70	1.12	12.91
120	33.20	4.01	65.20	1.07	15.72
Tank	49.70	4.18	43.97	1.02	-

Exp. Name: Flf 05

J_{fin}=0.480 mg/m^2·s

F_{FT}=9.93 l/hr F_f=400 l/hr T_{sp}=50 ˚C

F_{ST}=9.87 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.20	4.02	1.90	2.58	0.00
20	17.00	3.85	37.10	1.24	2.10
40	18.00	3.91	54.00	1.13	5.57
60	25.40	3.97	60.10	1.12	9.40
80	24.40	3.99	61.00	1.13	13.30
100	22.30	4.01	61.40	1.11	17.06
120	21.10	3.98	60.80	1.12	21.35
Tank	48.70	4.22	46.63	1.04	-

Exp. Name: Flf 06

J_{fin}=0.725 mg/m^2·s

F_{FT}=9.96 l/hr F_f=400 l/hr T_{sp}=50 ˚C

F_{ST}=10.02 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.30	3.82	2.50	2.88	0.00
20	18.60	3.76	40.70	1.13	3.05
40	21.70	3.87	66.20	1.04	8.06
60	19.70	3.93	86.10	0.98	13.96
80	20.00	3.99	87.70	0.95	19.95
100	19.40	4.00	90.40	0.94	25.95
120	19.60	4.03	90.40	0.94	31.92
Tank	57.30	5.70	56.77	0.95	-

Exp. Name: Flf 07

J_{fin}=0.610 mg/m^2·s

F_{FT}=10.25 l/hr F_f=400 l/hr T_{sp}=50 ˚C

F_{ST}=9.63 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.70	3.74	6.70	1.89	0.00
20	18.70	3.79	43.20	0.98	2.73
40	24.20	3.90	67.30	0.93	7.14
60	24.60	3.96	79.30	0.92	12.20
80	23.60	3.99	85.20	0.92	17.54
100	24.30	3.96	84.90	0.91	22.23
120	23.00	4.04	89.60	0.90	27.53
Tank	56.60	5.63	56.60	0.91	-

Exp. Name: Flf 08

J_{fin}=0.415 mg/m^2·s

F_{FT}=9.78 l/hr F_f=200 l/hr T_{sp}=50 ˚C

F_{ST}=9.65 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	4.30	3.85	27.90	2.31	0.00
20	18.80	3.88	48.10	1.32	0.68
40	23.90	3.93	57.60	1.19	4.75
60	27.40	3.98	64.10	1.15	9.66
80	28.00	3.99	67.40	1.14	15.18
100	27.50	3.99	67.10	1.12	20.00
120	28.40	4.00	65.50	1.11	23.09
Tank	51.87	2.96	53.33	1.09	-

Exp. Name: Tmp 01

J_{fin}=0.319 mg/m^2·s

F_{FT}=9.85 l/hr F_f=300 l/hr T_{sp}=30 ˚C

F_{ST}=10.59 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.60	3.93	2.00	2.92	0.00
20	21.10	3.81	35.40	1.22	1.86
40	30.50	4.01	56.90	1.08	5.32
60	34.40	4.06	66.40	1.08	8.68
80	37.20	4.00	68.80	1.01	12.00
100	36.90	4.08	70.20	1.08	15.37
117	36.50	4.03	70.30	1.05	18.07
Tank	55.50	4.07	54.40	1.03	-

Exp. Name: Tmp 02

J_{fin}=0.374 mg/m^2·s

F_{FT}=10.24 l/hr F_f=300 l/hr T_{sp}=30 ˚C

F_{ST}=9.95 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.90	5.38	3.90	2.24	0.00
20	19.40	4.29	38.40	1.27	2.47
40	29.40	4.46	57.60	1.08	6.00
60	33.50	4.57	66.50	1.04	9.65
80	34.60	4.55	68.50	1.05	13.25
100	36.20	4.23	69.20	1.03	16.78
120	36.90	3.58	71.60	1.02	20.23
Tank	57.30	4.12	54.80	1.03	-

Exp. Name: Tmp 03

J_{fin}=0.417 mg/m^2·s

F_{FT}=9.86 l/hr F_f=300 l/hr T_{sp}=40 °C

F_{ST}=9.97 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.30	4.04	3.00	2.45	0.00
20	19.00	3.93	35.10	1.22	1.97
40	26.50	3.98	54.00	1.09	4.90
60	28.40	4.01	61.60	1.03	8.12
80	28.20	4.04	66.20	1.02	11.36
100	31.50	3.98	67.90	1.04	14.61
120	31.30	4.05	67.10	1.04	17.79
Tank	54.40	3.77	51.00	1.04	-

Exp. Name: Tmp 04

J_{fin}=0.419 mg/m^2·s

F_{FT}=10.15 l/hr F_f=300 l/hr T_{sp}=40 °C

F_{ST}=9.90 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.30	5.07	2.40	2.49	0.00
20	19.80	3.93	34.80	1.24	1.55
40	27.80	4.04	53.50	1.16	4.37
60	30.70	4.07	63.00	1.05	7.43
80	33.10	4.00	64.30	1.04	10.63
100	33.70	4.11	64.20	1.04	13.64
120	34.00	4.13	69.30	1.04	16.81
Tank	57.00	4.16	48.90	1.04	-

Exp. Name: Tmp 05

J_{fin}=0.636 mg/m^2·s

F_{FT}=9.69 l/hr F_f=300 l/hr T_{sp}=60 °C

F_{ST}=9.82 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.60	3.89	2.10	2.67	0.00
20	16.90	3.84	39.60	1.25	3.24
40	20.00	3.91	64.80	1.18	8.10
60	20.30	4.08	83.80	1.16	14.09
80	20.30	4.10	91.10	1.10	19.76
100	19.50	4.09	93.10	1.07	25.45
120	19.90	3.98	93.60	1.12	31.52
Tank	55.40	3.56	54.60	1.06	-

Exp. Name: Tmp 06

J_{fin}=0.654 mg/m^2·s

F_{FT}=9.95 l/hr F_f=300 l/hr T_{sp}=60 °C

F_{ST}=9.75 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.20	3.93	3.30	2.47	0.00
20	16.80	3.83	43.00	1.27	2.95
40	20.50	3.95	66.10	1.17	8.01
60	20.20	4.06	82.80	1.08	13.91
80	20.40	4.06	87.80	1.06	19.72
100	19.90	4.06	91.90	1.08	25.65
120	19.70	4.05	92.10	1.09	31.56
Tank	55.40	3.67	52.80	1.08	-

Exp. Name: Tmp 07

J_{fin}=0.726 mg/m^2·s

F_{FT}=9.86 l/hr F_f=300 l/hr T_{sp}=70 °C

F_{ST}=9.81 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.10	3.95	1.10	2.91	0.00
20	15.10	3.85	42.20	1.25	4.20
40	15.90	4.00	68.90	1.13	10.58
60	14.80	4.04	85.30	1.07	17.67
80	14.40	4.09	91.50	1.07	24.58
100	13.90	4.08	92.70	1.08	31.63
120	14.20	4.04	90.60	1.08	38.30
Tank	53.60	4.23	38.20	1.01	-

Exp. Name: Tmp 08

J_{fin}=0.768 mg/m^2·s

F_{FT}=9.92 l/hr F_f=300 l/hr T_{sp}=70 °C

F_{ST}=9.92 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.20	3.79	4.00	2.36	0.00
20	15.10	3.73	46.20	1.30	3.42
40	15.00	3.83	68.30	1.14	9.29
60	13.50	3.94	82.50	1.07	16.12
80	13.50	4.00	82.60	1.05	23.13
100	14.30	4.04	89.60	1.09	29.93
120	14.80	4.00	85.50	1.06	36.61
Tank	56.00	3.93	50.00	1.06	-

Exp. Name: Fls 01

J_{fin}=0.590 mg/m^{2}·s

F_{FT}=9.79 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=9.64 l/hr F_s=100 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	1.30	3.70	4.60	1.91	0.00
20	17.40	3.83	41.00	1.36	3.72
40	23.40	3.91	65.90	1.06	8.55
60	24.80	3.98	77.20	1.03	13.76
80	23.60	3.98	82.90	1.02	18.76
100	25.40	4.03	83.30	1.01	23.90
120	24.10	4.06	86.30	1.01	29.08
Tank	57.53	4.07	55.73	1.00	-

Exp. Name: Fls 02

J_{fin}=0.606 mg/m^{2}·s

F_{FT}=10.14 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=9.53 l/hr F_s=100 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	1.20	3.84	24.00	1.55	0.00
20	19.60	3.77	48.70	1.11	2.94
40	25.10	3.88	69.20	1.07	7.74
60	25.90	3.97	79.30	1.06	12.64
80	26.00	4.00	83.60	0.99	17.74
100	27.30	3.98	86.70	0.98	22.45
120	26.30	4.02	89.00	0.98	27.80
Tank	59.16	3.90	57.03	1.02	-

Exp. Name: Fls 03

J_{fin}=0.475 mg/m^{2}·s

F_{FT}=9.45 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=9.54 l/hr F_s=200 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.40	3.74	10.10	1.93	0.00
20	17.70	3.82	41.20	1.14	2.85
40	23.40	3.91	62.40	1.02	6.97
60	26.00	3.97	71.60	0.98	11.21
80	26.20	3.99	76.30	0.97	15.99
100	26.70	3.98	80.00	0.96	20.18
120	26.10	4.00	78.40	0.95	24.71
Tank	54.23	4.22	52.97	0.93	-

Exp. Name: Fls 04

J_{fin}=0.457 mg/m^{2}·s

F_{FT}=10.37 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=9.88 l/hr F_s=200 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.20	3.83	9.10	1.94	0.00
20	19.60	3.79	39.60	1.18	2.23
40	27.40	3.91	57.50	1.05	6.18
60	30.00	3.97	67.70	0.98	10.48
80	30.00	4.00	73.00	0.97	14.74
100	30.70	4.01	72.40	0.98	19.09
120	28.90	4.06	74.60	0.97	23.13
Tank	53.86	4.07	49.66	0.95	-

Exp. Name: Fls 05

J_{fin}=0.558 mg/m^{2}·s

F_{FT}=9.90 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=9.70 l/hr F_s=200 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.40	3.82	7.50	2.12	0.00
20	18.10	3.84	40.10	1.20	2.48
40	24.40	3.89	63.50	1.06	6.39
60	25.10	3.97	77.00	1.00	10.99
80	24.30	4.00	84.00	0.99	15.67
100	25.40	4.03	85.40	1.01	20.08
120	24.10	4.01	85.10	0.98	24.51
Tank	55.20	5.63	54.80	0.97	-

Exp. Name: Fls 06

J_{fin}=0.405 mg/m^{2}·s

F_{FT}=9.52 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=10.05 l/hr F_s=400 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	2.90	3.58	9.70	1.86	0.00
20	19.30	3.90	39.60	1.20	3.20
40	26.30	3.96	57.40	1.07	6.39
60	29.30	3.99	66.20	1.06	9.79
80	31.40	4.00	69.50	1.06	13.15
100	32.40	3.99	69.90	1.06	16.40
120	32.00	3.99	69.60	1.05	19.60
Tank	53.55	4.11	51.85	1.05	-

Exp. Name: Fls 07

J_{fin}=0.589 mg/m^2·s

F_{FT}=9.98 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=10.38 l/hr F_s=400 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.40	3.92	2.50	2.48	0.00
20	20.60	3.83	38.80	1.16	2.23
40	26.40	3.88	63.40	1.04	6.23
60	26.10	3.96	74.80	1.00	10.82
80	25.40	3.99	82.60	0.99	15.62
100	26.30	3.99	85.25	1.01	19.89
120	25.30	4.04	87.70	1.00	24.85
Tank	57.33	6.51	58.60	1.00	-

Exp. Name: Fls 08

J_{fin}=0.561 mg/m^2·s

F_{FT}=10.33 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=9.83 l/hr F_s=400 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.20	3.88	1.20	2.95	0.00
20	19.20	3.78	38.30	1.18	2.35
40	25.80	3.90	63.80	1.02	6.49
60	27.30	3.97	76.40	0.99	11.15
80	27.80	3.99	82.00	0.97	15.97
100	27.30	3.98	84.70	0.97	20.09
120	25.90	4.00	85.70	0.97	24.56
Tank	56.17	4.72	53.20	0.95	-

Exp. Name: Nis 01

J_{fin}=0.599 mg/m^2·s

F_{FT}=10.25 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=10.01 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.40	3.94	0.60	3.59	0.00
20	19.30	3.79	3.90	1.08	1.46
40	25.70	3.90	9.30	1.08	5.48
60	28.20	3.98	14.00	1.06	10.07
80	27.40	4.00	18.20	1.03	14.65
100	29.00	4.00	22.90	1.03	19.19
120	28.20	4.01	26.50	1.02	23.56
Tank	60.43	5.59	0.00	1.02	-

Exp. Name: Nis 02

J_{fin}=0.551 mg/m^2·s

F_{FT}=10.31 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=10.01 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.40	3.95	0.40	3.79	0.00
20	18.90	3.78	3.30	1.02	2.02
40	24.10	3.90	7.10	1.02	5.98
60	25.60	3.97	10.90	1.03	10.61
80	25.70	4.00	13.50	1.02	15.01
100	27.10	4.03	16.70	1.02	19.39
120	29.20	3.98	19.20	1.02	22.80
Tank	57.10	5.39	0.00	1.02	-

Exp. Name: Nis 03

J_{fin}=0.532 mg/m^2·s

F_{FT}=9.62 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=9.62 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	1.70	3.94	0.80	3.59	0.00
20	18.00	3.79	3.20	1.08	1.80
40	24.00	3.90	6.20	1.08	5.59
60	25.60	3.98	9.60	1.06	9.57
80	26.90	4.00	12.90	1.03	13.59
100	26.20	4.00	15.90	1.03	17.70
120	25.70	4.01	19.10	1.02	21.83
Tank	56.67	5.59	0.00	1.02	-

Exp. Name: Nis 04

J_{fin}=0.570 mg/m^2·s

F_{FT}=10.08 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=10.07 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.50	4.10	0.30	3.65	0.00
20	17.00	3.80	2.80	1.04	2.42
40	22.10	3.88	6.90	1.03	6.88
60	24.40	3.97	14.30	1.02	11.81
80	25.20	3.98	18.50	1.02	16.42
100	27.20	3.89	22.50	1.02	20.00
120	26.50	4.00	26.20	1.02	25.02
Tank	57.83	5.31	0.00	1.03	-

Exp. Name: Nis 05

J_{fin}=0.541 mg/m^2·s

F_{FT}=9.67 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=9.73 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.70	3.90	4.80	2.37	0.00
20	18.50	3.80	12.50	1.16	2.28
40	23.90	3.91	22.00	1.02	6.17
60	25.90	3.96	29.00	0.96	10.55
80	26.20	4.01	32.40	0.95	14.99
100	25.60	4.01	34.20	0.95	19.48
120	25.30	4.02	34.60	0.94	23.61
Tank	56.23	6.01	6.47	0.94	-

Exp. Name: Nis 06

J_{fin}=0.585 mg/m^2·s

F_{FT}=9.93 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=10.01 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.50	4.14	1.50	2.91	0.00
20	16.90	3.77	12.70	1.24	1.20
40	22.50	3.90	23.50	1.10	4.28
60	24.40	3.95	30.80	1.05	7.80
80	24.70	3.99	34.20	1.04	11.50
100	24.00	3.99	35.50	1.02	15.21
120	24.90	3.99	36.00	1.01	19.05
Tank	57.00	5.81	5.81	0.97	-

Exp. Name: Nis 07

J_{fin}=0.485 mg/m^2·s

F_{FT}=9.87 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=9.86 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.60	4.13	29	3.17	0.00
20	20.60	3.74	332	1.21	1.16
40	26.90	3.89	464	1.08	4.76
60	30.20	3.99	524	1.03	8.36
80	29.10	4.00	566	1.05	12.15
100	28.20	4.00	545	1.01	15.78
120	28.40	4.01	575	1.00	19.46
Tank	55.20	5.92	554	1.00	-

Exp. Name: Nis 08

J_{fin}=0.495 mg/m^2·s

F_{FT}=9.68 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=9.88 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.50	4.14	7.80	2.91	0.00
20	18.90	3.77	312	1.24	1.20
40	26.80	3.90	454	1.10	4.28
60	28.70	3.95	527	1.05	7.80
80	28.30	3.99	558	1.04	11.50
100	28.20	3.99	577	1.02	15.21
120	28.50	3.99	581	1.01	19.05
Tank	56.53	4.99	563	1.00	-

Exp. Name: Nis 09

J_{fin}=0.488 mg/m^2·s

F_{FT}=10.09 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=9.97 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.20	3.90	0.50	3.33	0.00
20	19.30	3.79	3020	1.27	2.25
40	24.70	3.91	4330	1.12	6.23
60	25.70	3.99	5010	1.08	10.64
80	27.10	3.99	5230	1.04	14.53
100	26.90	4.00	5330	1.03	18.70
120	28.20	4.01	5610	1.02	22.55
Tank	54.00	5.24	5426	1.02	-

Exp. Name: Nis 10

J_{fin}=0.481 mg/m^2·s

F_{FT}=10.00 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=9.98 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.50	3.92	1.00	3.98	0.00
20	20.40	3.82	3030	1.29	1.84
40	27.30	3.91	4430	1.14	5.31
60	26.80	3.98	5060	1.11	9.11
80	28.30	3.99	5560	1.10	12.94
100	29.10	4.01	5700	1.08	16.70
120	30.20	3.95	5690	1.06	20.39
Tank	55.70	5.76	5690	1.06	-

Exp. Name: pHs 01

J_{fin}=0.018 mg/m^2·s

F_{FT}=10.29 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=10.04 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.60	3.83	5.00	2.59	0.00
20	21.10	3.86	37.90	2.99	2.14
40	33.90	3.98	53.60	3.48	4.90
60	39.80	4.09	55.10	3.78	7.28
80	46.30	4.13	57.00	3.93	8.71
100	50.50	4.06	56.20	4.00	9.23
120	54.20	4.03	56.60	3.99	9.51
Tank	56.03	5.23	55.77	5.18	-

Exp. Name: pHs 02

J_{fin}=0.499 mg/m^2·s

F_{FT}=10.29 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=10.09 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	2.30	3.91	2.30	3.87	0.00
20	21.90	3.80	39.80	2.11	1.63
40	28.60	3.86	61.10	1.99	5.03
60	27.90	3.94	72.70	1.93	9.41
80	27.80	3.98	79.10	1.92	13.94
100	26.80	3.99	80.80	1.90	18.29
120	30.90	4.00	75.80	1.90	22.49
Tank	55.07	5.16	55.40	1.87	-

Exp. Name: pHs 03

J_{fin}=0.550 mg/m^2·s

F_{FT}=10.11 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=10.12 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.90	3.92	9.70	2.03	0.00
20	20.20	3.79	46.60	1.33	1.86
40	26.60	3.88	65.60	1.25	5.64
60	27.90	3.96	77.00	1.23	9.91
80	28.00	3.97	82.40	1.21	14.23
100	27.70	4.00	84.10	1.21	18.90
120	27.70	3.99	83.30	1.20	21.83
Tank	57.33	5.25	56.77	1.19	-

Exp. Name: pHs 04

J_{fin}=0.482 mg/m^2·s

F_{FT}=10.45 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=10.51 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.60	3.89	1.40	3.64	0.00
20	19.90	3.82	41.40	1.46	2.12
40	27.70	3.91	62.50	1.33	5.74
60	28.90	3.97	71.80	1.29	9.68
80	28.20	4.00	75.20	1.27	13.81
100	30.10	4.02	78.20	1.25	17.92
117	30.90	4.01	77.50	1.24	21.83
Tank	55.50	5.45	53.65	1.22	-

Exp. Name: pHs 05

J_{fin}=0.607 mg/m^2·s

F_{FT}=9.88 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=9.96 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.80	4.01	4.80	1.90	0.00
20	18.30	3.74	39.30	1.21	1.51
40	23.80	3.86	65.90	1.06	5.91
60	24.90	3.95	79.50	1.01	11.01
80	24.00	4.00	84.20	1.00	16.07
100	24.90	4.00	86.80	1.00	21.73
120	24.40	4.03	87.80	1.00	26.16
Tank	57.97	4.91	56.47	1.00	-

Exp. Name: pHs 06

J_{fin}=0.577 mg/m^2·s

F_{FT}=10.14 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=10.08 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.40	3.80	4.60	2.33	0.00
20	18.90	3.81	43.80	1.09	2.54
40	25.00	3.90	65.50	1.03	6.62
60	26.00	3.98	77.00	1.03	11.25
80	26.00	4.00	82.50	1.03	15.87
100	25.40	3.93	84.10	1.01	20.36
120	25.20	4.02	84.90	1.00	25.03
Tank	56.23	4.84	55.17	1.00	-

Exp. Name: pHs 07

J_{fin}=0.561 mg/m^2·s

F_{FT}=10.32 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=9.77 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.90	3.81	9.90	2.18	0.00
20	16.60	3.78	43.00	1.08	2.77
40	23.70	3.90	66.20	0.91	7.28
60	24.00	3.98	77.60	0.87	12.44
80	25.40	3.99	85.20	0.85	17.32
100	27.60	3.73	87.60	0.85	20.00
120	25.10	4.07	88.60	0.84	27.25
Tank	56.00	5.87	55.27	0.90	-

Exp. Name: pHs 08

J_{fin}=0.600 mg/m^2·s

F_{FT}=10.30 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=9.72 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.20	3.78	1.10	2.63	0.00
20	19.00	3.79	40.70	0.92	3.27
40	24.30	3.93	66.40	0.87	7.97
60	26.00	3.98	79.50	0.86	12.83
80	26.40	4.00	84.10	0.85	17.71
100	25.80	3.98	86.80	0.84	22.61
120	24.60	4.01	88.10	0.85	27.47
Tank	56.93	4.97	55.17	0.83	-

Exp. Name: pHs 09

J_{fin}=0.626 mg/m^2·s

F_{FT}=10.28 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=10.35 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.60	3.87	11.60	1.82	0.00
20	20.50	3.76	50.60	0.70	2.50
40	26.10	3.89	68.80	0.69	6.72
60	27.40	3.95	78.00	0.80	11.47
80	25.90	3.98	81.40	0.82	16.28
100	25.50	3.98	82.40	0.85	21.01
120	25.60	4.00	83.00	0.89	25.46
Tank	58.37	5.80	57.40	0.68	-

Exp. Name: pHs 10

J_{fin}=0.511 mg/m^2·s

F_{FT}=9.96 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=10.13 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.30	3.83	6.40	2.00	0.00
20	19.30	3.80	42.30	0.92	2.19
40	25.80	3.90	62.70	0.80	6.10
60	27.40	3.97	72.00	0.78	10.52
80	27.40	4.00	80.00	0.74	15.00
100	26.10	4.00	81.70	0.73	19.55
120	26.10	4.01	82.50	0.72	23.97
Tank	54.13	5.47	52.23	0.73	-

Exp. Name: pHs 11

J_{fin}=0.573 mg/m^2·s

F_{FT}=9.93 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=10.24 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.40	3.78	7.90	2.10	0.00
20	18.70	3.79	44.80	0.91	2.58
40	24.70	3.87	67.20	0.77	6.87
60	25.40	3.98	81.30	0.72	12.22
80	26.20	4.00	87.80	0.70	16.93
100	28.70	4.00	87.40	0.70	21.48
120	24.80	4.04	83.40	0.70	26.12
Tank	57.93	5.52	57.83	0.69	-

Exp. Name: pHs 12

J_{fin}=0.620 mg/m^2·s

F_{FT}=10.29 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=9.88 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.10	3.84	2.00	2.65	0.00
20	18.50	3.80	38.90	0.65	2.85
40	24.60	3.90	62.50	0.51	7.31
60	28.00	3.97	76.80	0.48	12.09
80	26.70	4.00	80.90	0.42	17.02
100	27.10	3.99	82.20	0.43	21.86
120	25.90	4.01	84.10	0.43	26.84
Tank	59.47	5.52	57.73	0.44	-

Exp. Name: pHs 13

J_{fin}=0.631 mg/m^2·s

F_{FT}=9.69 l/hr F_f=300 l/hr T_{sp}=50 ˚C

F_{ST}=10.17 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.60	3.79	7.30	2.04	0.00
20	14.90	3.83	33.80	0.54	3.50
40	18.90	3.93	63.50	0.41	8.07
60	21.10	3.98	77.60	0.39	13.31
80	20.50	4.00	81.70	0.39	18.42
100	21.00	4.01	79.60	0.39	22.95
120	20.20	4.01	83.90	0.39	27.72
Tank	56.40	5.45	50.00	0.39	-

Exp. Name: Ext 01

J_{fin}=0.000 mg/m^2·s

F_{FT}=9.73 l/hr F_f=300 l/hr T_{sp}=50 ˚C

F_{ST}=9.96 l/hr F_s=300 l/hr $[RH]_{Tot}$=0.0 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.60	4.45	2.80	1.80	0.00
20	25.50	4.60	33.30	1.06	0.00
40	40.70	4.80	46.40	0.96	0.00
60	46.10	5.12	50.60	0.96	0.00
80	50.40	5.29	50.90	0.96	0.00
100	47.50	5.36	43.70	0.96	0.00
120	46.10	5.45	46.30	0.96	0.00
Tank	48.10	5.56	44.37	0.96	-

Exp. Name: Ext 02

J_{fin}=0.016 mg/m^2·s

F_{FT}=9.84 l/hr F_f=300 l/hr T_{sp}=50 ˚C

F_{ST}=9.90 l/hr F_s=300 l/hr $[RH]_{Tot}$=0.0 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	3.00	4.01	3.80	1.86	0.00
20	24.40	4.02	32.90	1.24	0.00
40	41.80	4.05	48.70	1.10	0.00
60	48.30	4.05	52.60	1.05	0.00
80	52.20	4.06	55.30	1.04	0.00
100	55.00	4.07	60.00	1.04	0.00
120	48.70	4.07	57.10	1.03	0.00
Tank	54.93	4.00	51.90	0.98	-

Exp. Name: Ext 03

J_{fin}=0.448 mg/m^2·s

F_{FT}=9.90 l/hr F_f=300 l/hr T_{sp}=50 ˚C

F_{ST}=10.19 l/hr F_s=300 l/hr $[RH]_{Tot}$=0.8 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	1.60	3.85	2.90	2.89	0.00
20	19.40	3.85	37.70	2.08	2.46
40	27.00	3.94	61.90	1.13	5.93
60	28.90	3.96	70.20	1.11	9.62
80	30.20	4.00	75.20	1.09	13.39
100	31.10	4.00	77.70	1.09	17.40
120	31.60	3.99	78.00	1.09	20.34
Tank	56.45	4.96	57.27	1.09	-

Exp. Name: Ext 04

J_{fin}=0.490 mg/m^2·s

F_{FT}=10.35 l/hr F_f=300 l/hr T_{sp}=50 ˚C

F_{ST}=10.20 l/hr F_s=300 l/hr $[RH]_{Tot}$=0.8 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	1.00	3.82	7.90	2.00	0.00
20	22.50	3.85	45.90	1.10	1.68
40	31.90	3.91	61.10	1.07	4.60
60	33.90	3.96	68.10	1.08	8.00
80	35.10	4.03	71.40	1.07	11.40
100	37.00	4.05	72.40	1.10	14.63
120	31.50	5.24	77.20	1.10	20.74
Tank	59.80	5.50	60.40	1.06	-

Exp. Name: Ext 05

J_{fin}=0.656 mg/m^2·s

F_{FT}=9.85 l/hr F_f=300 l/hr T_{sp}=50 ˚C

F_{ST}=9.88 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.0 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.60	3.88	5.80	2.17	0.00
20	17.40	3.79	41.90	1.03	3.05
40	22.00	3.91	64.90	0.91	7.40
60	22.80	4.00	76.70	0.84	12.11
80	23.80	4.00	81.30	0.85	16.71
100	24.00	3.98	83.80	0.85	20.96
120	23.20	3.99	85.90	0.83	25.56
Tank	59.80	4.00	60.37	0.80	-

Exp. Name: Ext 06

J_{fin}=0.616 mg/m^2·s

F_{FT}=9.88 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=10.09 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.0 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.70	3.87	5.40	2.23	0.00
20	15.60	3.81	36.90	1.09	1.59
40	23.50	3.88	61.60	0.92	4.84
60	25.80	3.93	73.30	0.83	9.03
80	24.80	4.00	76.90	0.85	13.33
100	22.70	4.00	78.70	0.82	17.64
120	24.30	3.90	79.90	0.82	21.29
Tank	58.07	4.03	56.17	0.83	-

Exp. Name: Ext 07

J_{fin}=0.653 mg/m^2·s

F_{FT}=9.87 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=10.38 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.4 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.50	3.84	4.30	2.30	0.00
20	16.00	3.78	41.00	1.15	3.17
40	19.70	3.91	65.90	1.04	7.92
60	21.40	3.98	77.40	1.01	12.93
80	20.40	4.00	81.10	0.98	17.86
100	21.60	4.01	85.90	0.96	22.70
120	21.00	4.01	86.80	0.97	27.50
Tank	57.30	6.70	56.87	0.96	-

Exp. Name: Ext 08

J_{fin}=0.604 mg/m^2·s

F_{FT}=9.93 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=9.77 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.4 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.20	3.86	4.10	2.32	0.00
20	17.00	3.80	40.00	1.39	2.17
40	22.50	3.90	65.10	1.26	6.11
60	22.30	3.96	76.60	1.21	10.48
80	23.60	3.99	82.90	1.19	15.02
100	23.70	3.99	84.40	1.20	19.46
120	23.40	4.00	84.80	1.19	23.91
Tank	56.73	6.44	56.47	1.13	-

Exp. Name: Ext 09

J_{fin}=0.699 mg/m^2·s

F_{FT}=10.01 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=9.68 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.6 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	2.90	3.90	18.50	1.82	0.00
20	15.90	3.77	48.10	1.13	3.36
40	17.70	3.90	71.40	0.99	8.45
60	16.30	3.99	82.50	0.96	13.97
80	19.00	4.00	87.10	0.94	19.44
100	18.10	4.01	89.20	0.94	24.73
120	17.80	4.01	90.40	0.93	29.99
Tank	56.00	5.82	55.97	0.92	-

Exp. Name: Ext 10

J_{fin}=0.619 mg/m^2·s

F_{FT}=10.00 l/hr F_f=300 l/hr T_{sp}=50 °C

F_{ST}=9.91 l/hr F_s=300 l/hr $[RH]_{Tot}$=1.6 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.20	3.80	1.80	2.70	0.00
20	15.60	3.78	41.40	1.19	2.83
40	20.60	3.88	70.50	1.04	7.32
60	20.50	3.95	82.40	0.99	12.63
80	19.20	3.99	84.10	0.99	18.03
100	16.20	4.17	86.10	0.98	24.41
120	20.90	3.90	86.60	0.97	28.58
Tank	52.40	6.06	50.70	0.96	-

Exp. Name: Int 01

J_{fin}=0.214 mg/m^2·s

F_{FT}=9.58 l/hr F_f=200 l/hr T_{sp}=40 °C

F_{ST}=9.34 l/hr F_s=200 l/hr $[RH]_{Tot}$=1.0 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.10	3.86	1.20	3.22	0.00
20	30.50	3.58	7.50	1.30	0.00
40	47.80	3.44	11.60	1.15	0.53
60	61.60	3.50	14.30	1.09	1.76
80	63.40	3.49	16.40	1.07	2.99
100	66.80	3.51	17.20	1.08	4.13
120	69.30	3.50	17.40	1.08	5.38
Tank	83.00	5.56	0.10	1.08	-

Exp. Name: Int 02

J_{fin}=0.389 mg/m^2·s

F_{FT}=9.95 l/hr F_f=200 l/hr T_{sp}=40 °C

F_{ST}=9.95 l/hr F_s=200 l/hr $[RH]_{Tot}$=1.0 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	2.50	3.87	2.10	2.16	0.00
20	9.20	4.51	6.70	1.24	5.68
40	11.30	4.52	12.70	1.10	9.61
60	11.80	4.54	16.10	1.08	13.16
80	13.00	4.49	18.50	1.04	17.11
100	12.90	4.52	19.20	1.07	20.91
120	13.20	4.45	19.80	1.05	24.09
Tank	34.63	5.90	0.40	1.03	-

Exp. Name: Int 03

J_{fin}=0.216 mg/m^2·s

F_{FT}=9.80 l/hr F_f=350 l/hr T_{sp}=40 °C

F_{ST}=9.79 l/hr F_s=350 l/hr $[RH]_{Tot}$=1.0 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.10	3.86	2.40	2.57	0.00
20	12.20	3.63	5.80	1.28	0.00
40	19.60	3.50	8.80	1.13	0.00
60	21.70	3.47	10.00	1.08	0.43
80	21.70	3.50	11.00	1.05	0.99
100	21.60	3.50	11.60	1.06	1.48
120	22.00	3.50	11.90	1.05	1.93
Tank	34.30	5.80	0.40	1.05	-

Exp. Name: Int 04

J_{fin}=0.252 mg/m^2·s

F_{FT}=9.76 l/hr F_f=200 l/hr T_{sp}=60 °C

F_{ST}=9.60 l/hr F_s=350 l/hr $[RH]_{Tot}$=1.0 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	1.10	3.80	5	2.99	0.00
20	11.40	3.59	271	1.35	0.00
40	18.20	3.50	365	0.88	0.00
60	20.30	3.48	418	0.85	0.60
80	18.60	3.50	481	0.83	1.12
100	19.20	3.50	482	0.83	1.56
120	20.20	3.50	494	0.83	2.02
Tank	34.10	5.71	487	0.83	-

Exp. Name: Int 05

J_{fin}=0.298 mg/m^2·s

F_{FT}=9.73 l/hr F_f=200 l/hr T_{sp}=40 °C

F_{ST}=9.45 l/hr F_s=350 l/hr $[RH]_{Tot}$=1.0 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	1.80	3.52	61	1.67	0.00
20	36.20	3.36	360	1.25	1.20
40	45.10	3.47	484	1.15	4.94
60	52.00	3.49	499	1.11	9.00
80	50.90	3.49	506	1.09	12.80
100	54.10	3.49	497	1.07	17.57
120	61.60	3.43	545	1.10	21.69
Tank	74.90	5.70	519	1.07	-

Exp. Name: Int 06

J_{fin}=0.314 mg/m^2·s

F_{FT}=9.97 l/hr F_f=200 l/hr T_{sp}=40 °C

F_{ST}=10.17 l/hr F_s=350 l/hr $[RH]_{Tot}$=1.0 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.20	3.96	2	3.35	0.00
20	10.20	4.69	289	1.29	3.20
40	12.70	4.36	376	1.16	5.81
60	13.40	4.52	433	1.12	8.76
80	13.60	4.62	444	1.10	11.45
100	14.00	4.56	445	1.09	14.12
120	17.10	4.42	481	1.09	16.77
Tank	32.65	4.34	464	1.05	-

Exp. Name: Int 07

J_{fin}=0.413 mg/m^2·s

F_{FT}=10.01 l/hr F_f=200 l/hr T_{sp}=60 °C

F_{ST}=9.92 l/hr F_s=350 l/hr $[RH]_{Tot}$=1.0 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.20	3.79	1	3.37	0.00
20	9.90	4.49	320	1.28	3.20
40	13.50	4.46	461	1.15	5.81
60	14.90	4.44	533	1.07	8.76
80	15.30	5.22	553	1.07	11.45
100	15.90	4.59	556	1.06	14.12
120	17.60	4.52	516	1.06	16.77
Tank	39.50	5.00	490.00	1.06	-

Exp. Name: Int 08

J_{fin}=0.606 mg/m^2·s

F_{FT}=9.80 l/hr F_f=350 l/hr T_{sp}=60 °C

F_{ST}=10.02 l/hr F_s=350 l/hr $[RH]_{Tot}$=1.0 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.40	3.84	21.70	2.45	0.00
20	32.50	3.44	18.40	1.07	0.14
40	46.30	3.45	21.70	0.94	2.86
60	44.60	3.49	27.10	0.90	6.03
80	47.80	3.50	30.80	0.88	9.60
100	41.00	3.50	32.00	0.89	12.61
120	42.20	3.50	32.00	0.88	15.96
Tank	76.60	5.75	1.03	0.83	-

Exp. Name: Int 09

J_{fin}=0.486 mg/m^2·s

F_{FT}=9.70 l/hr F_f=350 l/hr T_{sp}=60 °C

F_{ST}=9.64 l/hr F_s=350 l/hr $[RH]_{Tot}$=1.0 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.90	3.68	7	1.91	0.00
20	3.90	4.39	273	1.35	6.42
40	4.70	4.50	430	1.19	11.79
60	5.10	4.54	519	1.19	17.32
80	5.80	4.53	509	1.10	22.54
100	5.40	4.59	504	1.10	28.03
120	5.70	4.51	504	1.09	33.33
Tank	33.30	5.45	489	1.07	-

Exp. Name: Int 10

J_{fin}=0.326 mg/m^2·s

F_{FT}=9.75 l/hr F_f=200 l/hr T_{sp}=40 °C

F_{ST}=10.05 l/hr F_s=350 l/hr $[RH]_{Tot}$=1.0 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.40	3.82	18.40	2.40	0.00
20	38.20	3.32	12.30	0.98	0.85
40	51.90	3.42	12.30	0.86	6.12
60	55.70	3.46	14.50	0.82	12.94
80	52.30	3.49	16.30	0.81	20.00
100	53.70	3.51	17.10	0.82	27.61
120	57.80	3.49	17.90	0.81	35.76
Tank	77.80	5.96	0.67	0.79	-

Exp. Name: Int 11

J_{fin}=0.292 mg/m^2·s

F_{FT}=9.68 l/hr F_f=200 l/hr T_{sp}=40 °C

F_{ST}=9.78 l/hr F_s=350 l/hr $[RH]_{Tot}$=1.0 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	2.90	3.80	6.30	1.62	0.00
20	9.70	4.37	9.30	0.99	7.10
40	13.30	4.35	14.40	0.87	15.13
60	13.90	4.82	16.10	0.84	25.42
80	14.60	4.53	18.50	0.82	35.23
100	15.80	4.45	17.80	0.81	47.38
120	18.40	3.85	18.20	0.81	59.40
Tank	33.60	5.35	0.23	0.81	-

Exp. Name: Int 12

J_{fin}=0.629 mg/m^2·s

F_{FT}=9.85 l/hr F_f=350 l/hr T_{sp}=60 °C

F_{ST}=9.91 l/hr F_s=350 l/hr $[RH]_{Tot}$=1.0 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.10	3.70	2	2.10	0.00
20	34.80	3.39	411	1.20	3.92
40	42.30	3.31	428	1.16	6.71
60	64.80	3.12	455	1.10	35.63
80	49.50	3.84	522	1.11	44.62
100	48.50	3.63	527	1.09	51.32
120	51.20	3.55	555	1.08	59.40
Tank	86.50	4.98	509	1.04	-

Exp. Name: Int 13

J_{fin}=0.524 mg/m^2·s

F_{FT}=9.46 l/hr F_f=350 l/hr T_{sp}=60 °C

F_{ST}=10.00 l/hr F_s=350 l/hr $[RH]_{Tot}$=1.0 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.80	3.68	16.50	2.50	0.00
20	4.40	4.44	18.80	1.02	8.32
40	5.10	4.49	23.90	0.89	14.02
60	5.50	4.54	26.00	0.85	19.73
80	5.40	4.56	26.60	0.79	25.60
100	5.90	4.49	26.60	0.77	31.00
120	5.90	4.50	26.70	0.79	36.20
Tank	36.40	5.01	0.13	0.76	-

Exp. Name: Int 14

$J_{fin}=0.402$ mg/m^2·s

$F_{FT}=9.73$ l/hr $F_f=200$ l/hr $T_{sp}=40$ °C

$F_{ST}=10.10$ l/hr $F_s=200$ l/hr $[RH]_{Tot}=1.0$ mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.10	3.97	5	1.61	0.00
20	37.50	3.56	357	0.97	0.00
40	59.50	3.47	506	0.82	0.75
60	65.70	3.49	583	0.80	1.95
80	68.20	3.52	581	0.75	3.22
100	66.70	3.51	568	0.75	4.69
120	69.80	3.50	582	0.75	5.94
Tank	92.40	4.70	598	0.76	-

Exp. Name: Int 15

$J_{fin}=0.334$ mg/m^2·s

$F_{FT}=9.57$ l/hr $F_f=200$ l/hr $T_{sp}=40$ °C

$F_{ST}=10.15$ l/hr $F_s=200$ l/hr $[RH]_{Tot}=1.0$ mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	2.70	3.72	1	1.81	0.00
20	11.10	4.34	356	0.96	3.12
40	14.40	4.41	480	0.86	5.69
60	15.10	4.45	550	0.81	8.70
80	15.20	4.51	522	0.77	11.49
100	15.30	4.50	561	0.77	14.48
120	15.70	4.49	564	0.76	17.14
Tank	34.80	5.83	533	0.76	-

Exp. Name: Int 16

$J_{fin}=0.559$ mg/m^2·s

$F_{FT}=9.98$ l/hr $F_f=350$ l/hr $T_{sp}=60$ °C

$F_{ST}=10.12$ l/hr $F_s=200$ l/hr $[RH]_{Tot}=1.0$ mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.20	3.82	13	2.27	0.00
20	32.00	3.42	350	1.03	0.20
40	40.50	3.47	490	0.85	2.89
60	53.60	3.49	521	0.84	5.73
80	46.10	3.49	527	0.78	8.62
100	49.50	3.50	521	0.80	11.57
120	58.60	3.50	533	0.77	14.50
Tank	78.50	6.06	500	0.75	-

Exp. Name: Int 17

$J_{fin}=0.222$ mg/m^2·s

$F_{FT}=9.78$ l/hr $F_f=200$ l/hr $T_{sp}=60$ °C

$F_{ST}=10.09$ l/hr $F_s=350$ l/hr $[RH]_{Tot}=1.0$ mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.30	3.68	10.00	2.38	0.00
20	13.10	3.39	8.00	1.18	0.32
40	20.60	3.44	8.40	1.05	3.95
60	21.20	3.47	9.90	1.00	8.74
80	21.30	3.48	10.70	1.00	13.76
100	21.90	3.49	11.10	0.96	18.94
120	22.30	3.49	11.20	0.95	24.61
Tank	34.60	5.91	0.47	0.94	-

Exp. Name: Int 18

$J_{fin}=0.529$ mg/m^2·s

$F_{FT}=10.23$ l/hr $F_f=350$ l/hr $T_{sp}=60$ °C

$F_{ST}=9.67$ l/hr $F_s=200$ l/hr $[RH]_{Tot}=1.0$ mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.20	3.81	0	3.05	0.00
20	4.90	4.48	339	1.05	6.87
40	6.40	4.41	502	0.92	11.95
60	6.70	4.49	549	0.82	17.93
80	6.60	4.47	561	0.84	22.80
100	6.80	4.53	555	0.83	28.37
120	7.00	4.50	556	0.84	33.79
Tank	35.20	6.01	522	0.78	-

Exp. Name: Int 19

$J_{fin}=0.552$ mg/m^2·s

$F_{FT}=9.63$ l/hr $F_f=200$ l/hr $T_{sp}=60$ °C

$F_{ST}=9.91$ l/hr $F_s=200$ l/hr $[RH]_{Tot}=1.0$ mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.40	3.90	7.60	2.51	0.00
20	25.50	4.43	17.20	0.99	5.48
40	37.10	4.43	29.90	0.81	11.60
60	26.60	4.55	31.80	0.80	17.53
80	31.00	4.55	32.30	0.77	23.88
100	32.80	4.55	33.60	0.75	29.90
120	36.00	4.43	31.80	0.76	35.63
Tank	65.10	5.21	0.57	0.75	-

Exp. Name: Int 20

J_{fin}=0.605 mg/m^2·s

F_{FT}=9.56 l/hr F_f=200 l/hr T_{sp}=60 ˚C

F_{ST}=10.31 l/hr F_s=350 l/hr $[RH]_{Tot}$=1.0 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.40	3.56	1.50	2.56	0.00
20	28.20	4.33	14.50	1.28	7.40
40	37.60	4.36	25.10	1.15	18.10
60	42.00	4.55	31.20	1.09	30.30
80	49.40	3.79	33.20	1.07	41.60
100	47.40	4.59	34.30	1.06	54.50
120	47.70	4.66	34.60	1.06	66.79
Tank	84.00	6.10	1.37	1.03	-

Exp. Name: Int 21

J_{fin}=0.245 mg/m^2·s

F_{FT}=9.63 l/hr F_f=200 l/hr T_{sp}=60 ˚C

F_{ST}=10.05 l/hr F_s=200 l/hr $[RH]_{Tot}$=1.0 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	1.20	4.01	3	2.31	0.00
20	11.30	3.67	333	1.29	0.00
40	17.50	3.50	491	1.17	0.34
60	19.70	3.46	527	1.13	1.14
80	19.60	3.52	543	1.09	1.55
100	19.60	3.49	504	1.10	2.04
120	21.50	3.50	502	1.11	2.04
Tank	35.10	3.50	480	1.03	-

Exp. Name: Int 22

J_{fin}=0.290 mg/m^2·s

F_{FT}=10.35 l/hr F_f=350 l/hr T_{sp}=40 ˚C

F_{ST}=9.88 l/hr F_s=200 l/hr $[RH]_{Tot}$=1.0 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	1.60	5.76	2.60	3.13	0.00
20	12.80	4.59	6.70	0.85	0.00
40	20.10	3.99	9.60	0.83	0.00
60	22.30	3.77	10.40	0.88	0.00
80	21.10	3.68	10.70	0.93	0.00
100	18.90	3.64	10.40	0.93	0.00
120	19.80	3.62	10.00	0.89	0.00
Tank	34.90	6.70	0.27	0.91	-

Exp. Name: Int 23

J_{fin}=0.748 mg/m^2·s

F_{FT}=10.12 l/hr F_f=200 l/hr T_{sp}=60 ˚C

F_{ST}=9.85 l/hr F_s=200 l/hr $[RH]_{Tot}$=1.0 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	1.00	3.97	3	1.93	0.00
20	28.40	4.28	310	1.33	5.75
40	38.20	4.38	433	1.15	13.37
60	42.20	4.38	500	1.13	22.39
80	45.70	4.53	535	1.12	32.26
100	43.50	4.48	516	1.10	42.59
120	45.10	4.42	521	1.11	51.57
Tank	85.80	6.54	500	1.04	-

Exp. Name: Int 24

J_{fin}=0.086 mg/m^2·s

F_{FT}=9.80 l/hr F_f=200 l/hr T_{sp}=60 ˚C

F_{ST}=9.87 l/hr F_s=200 l/hr $[RH]_{Tot}$=1.0 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	1.40	3.71	21.00	2.37	0.00
20	15.90	3.50	11.70	1.08	2.43
40	25.30	3.47	8.00	0.92	12.75
60	23.90	3.73	8.40	0.86	26.94
80	29.30	3.26	5.70	0.86	36.47
100	28.60	3.46	5.50	0.83	51.95
120	24.60	3.34	5.50	0.82	65.17
Tank	32.70	5.95	0.23	0.82	-

Exp. Name: Int 25

J_{fin}=0.608 mg/m^2·s

F_{FT}=10.27 l/hr F_f=350 l/hr T_{sp}=40 ˚C

F_{ST}=9.64 l/hr F_s=200 l/hr $[RH]_{Tot}$=1.0 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	1.10	4.02	0.60	2.59	0.00
20	31.70	4.01	7.50	1.02	3.39
40	45.10	4.23	18.10	0.90	8.86
60	48.40	4.40	25.90	0.86	14.27
80	49.10	4.53	30.70	0.83	19.90
100	53.70	4.76	32.60	0.81	25.59
120	52.10	4.64	32.20	0.79	30.59
Tank	85.20	6.28	0.87	0.82	-

Exp. Name: Int 26

J_{fin}=0.116 mg/m^2·s

F_{FT}=6.74 l/hr F_f=350 l/hr T_{sp}=40 ˚C

F_{ST}=10.26 l/hr F_s=350 l/hr $[RH]_{Tot}$=1.0 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	3.70	3.49	7	2.58	0.00
20	8.90	3.52	331	1.04	0.82
40	13.40	3.50	476	0.86	1.21
60	16.40	3.50	534	0.84	1.71
80	18.50	3.50	568	0.82	2.29
100	19.10	3.50	578	0.84	2.78
120	22.30	3.53	551	0.80	3.18
Tank	32.43	6.09	467	0.79	-

Exp. Name: Int 27

J_{fin}=0.175 mg/m^2·s

F_{FT}=10.33 l/hr F_f=350 l/hr T_{sp}=40 ˚C

F_{ST}=9.75 l/hr F_s=200 l/hr $[RH]_{Tot}$=1.0 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.20	3.97	11	2.39	0.00
20	13.30	3.74	350	1.28	0.00
40	18.90	3.63	496	1.14	0.00
60	22.60	3.58	571	1.07	0.00
80	24.70	3.56	601	1.05	0.00
100	24.30	3.55	577	1.08	0.00
120	25.00	3.54	580	1.05	0.00
Tank	34.80	5.98	540	1.03	-

Exp. Name: Int 28

J_{fin}=0.580 mg/m^2·s

F_{FT}=8.91 l/hr F_f=350 l/hr T_{sp}=40 ˚C

F_{ST}=10.02 l/hr F_s=350 l/hr $[RH]_{Tot}$=1.0 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.20	3.88	5.20	2.90	0.00
20	25.00	4.10	10.10	1.28	3.84
40	38.50	4.30	19.00	1.13	8.41
60	43.90	4.43	25.00	1.09	13.44
80	48.70	4.50	30.50	1.07	18.66
100	51.90	4.49	33.40	1.07	23.71
120	43.50	4.51	32.60	1.06	28.88
Tank	85.10	6.19	0.37	1.05	-

Exp. Name: Int 29

J_{fin}=0.487 mg/m^2·s

F_{FT}=9.91 l/hr F_f=350 l/hr T_{sp}=60 ˚C

F_{ST}=10.04 l/hr F_s=200 l/hr $[RH]_{Tot}$=1.0 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.30	3.89	1.70	2.86	0.00
20	8.10	4.08	9.00	1.26	3.09
40	9.00	4.24	17.10	1.16	7.36
60	8.70	4.41	21.90	1.09	12.27
80	8.60	4.53	23.80	1.05	17.03
100	10.30	4.06	22.60	1.07	20.62
120	8.40	4.93	24.30	1.08	26.83
Tank	35.80	6.00	0.20	1.03	-

Exp. Name: Int 30

J_{fin}=0.752 mg/m^2·s

F_{FT}=10.68 l/hr F_f=350 l/hr T_{sp}=60 ˚C

F_{ST}=9.58 l/hr F_s=200 l/hr $[RH]_{Tot}$=1.0 mol/l

Time (min)	$[Ni]_f$ (mg/l)	$pH_f[Ni]_s$ (mg/l)	pH_sV_{NaOH} (ml)	Time (min)	$[Ni]_f$ (mg/l)
0	0.20	3.99	1.20	2.56	0.00
20	37.10	3.56	8.20	1.29	0.00
40	48.90	3.45	12.20	1.14	0.39
60	58.40	3.51	15.20	1.11	1.78
80	51.00	3.50	17.30	1.06	2.86
100	50.90	3.50	18.10	1.05	3.92
120	63.80	3.50	18.40	1.05	4.87
Tank	84.50	6.19	0.93	1.02	-

Exp. Name: Int 31

J_{fin}=0.549 mg/m^2·s

F_{FT}=10.12 l/hr F_f=350 l/hr T_{sp}=40 ˚C

F_{ST}=9.84 l/hr F_s=350 l/hr $[RH]_{Tot}$=1.0 mol/l

p H_f $[Ni]_s$ (mg/l)	pH_sV_{NaOH} (ml)				
0	0.20	4.10	1	2.86	0.00
20	27.30	4.10	294	1.03	6.32
40	44.50	4.03	367	0.89	9.65
60	40.70	4.66	450	0.84	17.94
80	53.90	4.15	484	0.84	20.16
100	49.90	4.20	488	0.81	24.42
120	51.50	4.39	445	0.81	29.43
Tank	82.10	6.19	429	1.02	-

Exp. Name: Int 32

J_{fin}=0.377 mg/m^2·s

F_{FT}=10.26 l/hr F_f=200 l/hr T_{sp}=60 °C

F_{ST}=10.35 l/hr F_s=350 l/hr $[RH]_{Tot}$=1.4 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.30	4.01	2	2.60	0.00
20	11.10	4.20	358	1.35	2.09
40	14.60	4.38	430	1.75	5.33
60	14.70	4.46	493	1.19	8.01
80	15.50	4.50	522	1.20	11.12
100	15.10	4.51	526	1.20	14.08
120	15.90	4.48	538	1.19	16.95
Tank	35.60	6.03	509	1.14	-

Exp. Name: Int 33

J_{fin}=0.347 mg/m^2·s

F_{FT}=9.42 l/hr F_f=200 l/hr T_{sp}=60 °C

F_{ST}=10.69 l/hr F_s=200 l/hr $[RH]_{Tot}$=1.4 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.90	3.91	15.20	2.65	0.00
20	9.40	4.44	10.30	1.39	3.43
40	12.20	4.53	12.20	1.26	6.18
60	13.90	4.56	15.20	1.22	9.22
80	13.80	4.52	14.40	1.23	12.13
100	14.70	4.45	15.90	1.23	14.86
120	14.60	4.60	16.20	1.22	17.47
Tank	35.10	6.12	0.53	1.19	-

Exp. Name: Int 34

J_{fin}=0.340 mg/m^2·s

F_{FT}=9.37 l/hr F_f=200 l/hr T_{sp}=60 °C

F_{ST}=10.24 l/hr F_s=350 l/hr $[RH]_{Tot}$=1.4 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.10	4.10	0.80	3.27	0.00
20	9.30	4.47	5.80	1.22	2.59
40	13.50	4.42	11.80	1.08	5.26
60	14.30	4.59	15.10	1.04	8.78
80	15.00	4.44	16.90	1.04	11.16
100	14.70	4.50	17.70	1.02	14.05
120	14.80	4.44	18.40	1.03	16.99
Tank	35.03	5.73	0.80	0.98	-

Exp. Name: Int 35

J_{fin}=0.490 mg/m^2·s

F_{FT}=8.33 l/hr F_f=350 l/hr T_{sp}=40 °C

F_{ST}=10.59 l/hr F_s=350 l/hr $[RH]_{Tot}$=1.4 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.20	3.93	1	2.89	0.00
20	26.70	3.56	274	1.43	0.00
40	41.80	3.47	380	1.31	0.50
60	46.50	3.49	428	1.29	1.86
80	44.30	3.50	427	1.26	3.19
100	44.20	3.50	451	1.27	4.58
120	45.50	3.50	464	1.28	5.84
Tank	78.30	5.71	449	1.26	-

Exp. Name: Int 36

J_{fin}=0.360 mg/m^2·s

F_{FT}=9.18 l/hr F_f=350 l/hr T_{sp}=40 °C

F_{ST}=10.45 l/hr F_s=350 l/hr $[RH]_{Tot}$=1.4 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	1.20	3.88	25	2.39	0.00
20	8.60	4.11	356	1.38	2.38
40	11.00	4.30	498	1.27	5.91
60	11.00	4.46	540	1.23	9.76
80	12.20	4.52	531	1.23	13.29
100	12.00	4.55	503	1.21	16.83
118	12.70	4.59	510	1.22	19.92
Tank	34.20	6.13	464	1.20	-

Exp. Name: Int 37

J_{fin}=0.209 mg/m^2·s

F_{FT}=8.44 l/hr F_f=200 l/hr T_{sp}=40 °C

F_{ST}=10.48 l/hr F_s=200 l/hr $[RH]_{Tot}$=1.4 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.30	4.03	9	2.84	0.00
20	10.50	3.77	335	1.42	0.00
40	18.20	3.60	468	1.29	0.00
60	20.20	3.55	513	1.26	0.00
80	22.90	3.52	538	1.22	0.00
100	23.10	3.51	552	1.25	0.00
120	23.20	3.51	544	1.23	0.00
Tank	38.20	5.80	514	1.18	-

Exp. Name: Int 38

$J_{fin}=0.217$ mg/m$^2\cdot$s

$F_{FT}=10.68$ l/hr $F_f=200$ l/hr $T_{sp}=40$ °C

$F_{ST}=9.75$ l/hr $F_s=200$ l/hr $[RH]_{Tot}=1.4$ mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	4.10	3.99	3.40	1.58	0.00
20	14.60	3.80	5.80	1.18	0.00
40	20.60	3.67	8.90	1.10	0.00
60	23.10	3.61	10.50	1.04	0.00
80	23.90	3.58	10.90	1.04	0.00
100	24.40	3.59	11.20	1.05	0.00
120	25.10	3.56	11.80	1.04	0.00
Tank	36.40	6.00	0.37	1.01	-

Exp. Name: Int 38

$J_{fin}=0.349$ mg/m$^2\cdot$s

$F_{FT}=9.00$ l/hr $F_f=350$ l/hr $T_{sp}=40$ °C

$F_{ST}=8.56$ l/hr $F_s=350$ l/hr $[RH]_{Tot}=1.4$ mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.30	4.01	0.90	2.23	0.00
20	32.60	3.58	6.70	1.11	0.00
40	50.80	3.43	11.80	0.96	0.45
60	54.10	3.50	15.70	0.92	2.56
80	57.50	3.50	19.00	0.90	3.92
100	55.60	3.49	20.60	0.90	5.35
120	55.60	3.50	21.00	0.88	6.71
Tank	78.40	5.87	0.67	0.86	-

Exp. Name: Int 40

$J_{fin}=0.535$ mg/m$^2\cdot$s

$F_{FT}=7.35$ l/hr $F_f=350$ l/hr $T_{sp}=40$ °C

$F_{ST}=7.33$ l/hr $F_s=350$ l/hr $[RH]_{Tot}=1.4$ mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	4.20	4.87	4.30	1.75	0.00
20	13.60	3.90	11.80	1.07	3.00
40	41.00	4.12	25.20	0.97	8.89
60	42.30	4.40	34.40	0.93	15.54
80	43.00	4.49	39.30	0.93	22.20
100	43.00	4.48	42.00	0.90	28.62
120	44.20	4.49	43.00	0.89	35.60
Tank	86.20	6.20	0.90	0.81	-

Exp. Name: Int 41

$J_{fin}=0.254$ mg/m$^2\cdot$s

$F_{FT}=8.91$ l/hr $F_f=200$ l/hr $T_{sp}=40$ °C

$F_{ST}=9.92$ l/hr $F_s=200$ l/hr $[RH]_{Tot}=1.4$ mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.30	4.00	2.10	2.78	0.00
20	11.10	4.20	4.70	1.07	2.40
40	14.80	4.36	9.90	0.93	4.83
60	16.70	4.48	13.20	0.89	7.53
80	18.00	4.51	14.70	0.88	10.17
100	18.20	4.55	15.40	0.87	12.78
120	20.20	4.65	15.10	0.86	15.48
Tank	35.50	6.34	0.47	0.77	-

Exp. Name: Int 42

$J_{fin}=0.219$ mg/m$^2\cdot$s

$F_{FT}=10.42$ l/hr $F_f=200$ l/hr $T_{sp}=40$ °C

$F_{ST}=9.60$ l/hr $F_s=350$ l/hr $[RH]_{Tot}=1.4$ mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.30	4.22	1	2.05	0.00
20	12.90	3.80	342	1.04	0.00
40	19.90	3.63	481	0.92	0.00
60	22.00	3.57	530	0.86	0.00
80	24.30	3.53	524	0.82	0.00
100	24.30	3.53	500	0.82	0.00
120	24.10	3.52	514	0.83	0.00
Tank	36.43	6.03	437	0.82	-

Exp. Name: Int 43

$J_{fin}=0.425$ mg/m$^2\cdot$s

$F_{FT}=9.62$ l/hr $F_f=350$ l/hr $T_{sp}=40$ °C

$F_{ST}=9.74$ l/hr $F_s=200$ l/hr $[RH]_{Tot}=1.4$ mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.60	4.03	20	2.15	0.00
20	9.30	4.08	343	1.03	2.84
40	10.90	4.28	506	0.89	6.93
60	10.60	4.45	568	0.85	11.50
80	10.80	4.54	592	0.84	15.61
100	10.60	4.57	581	0.83	19.95
120	11.10	4.51	572	0.84	23.82
Tank	34.90	5.60	522	0.82	-

Exp. Name: Int 44

J_{fin}=0.641 mg/m^{2}·s

F_{FT}=9.98 l/hr F_{f}=200 l/hr T_{sp}=40 ˚C

F_{ST}=9.63 l/hr F_{s}=350 l/hr [RH]$_{Tot}$=1.4 mol/l

Time (min)	[Ni]$_f$ (mg/l)	pH$_f$	[Ni]$_s$ (mg/l)	pH$_s$	V_{NaOH} (ml)
0	0.30	4.07	8	2.56	0.00
20	32.90	4.09	331	1.06	2.73
40	50.40	4.21	478	0.91	6.81
60	54.70	4.38	343	0.87	11.48
80	43.20	4.39	375	0.83	17.06
100	44.10	4.45	377	0.85	22.00
120	43.90	4.47	384	0.85	27.42
Tank	76.43	5.62	354	0.82	-

Exp. Name: Int 45

J_{fin}=0.236 mg/m^{2}·s

F_{FT}=7.36 l/hr F_{f}=350 l/hr T_{sp}=60 ˚C

F_{ST}=8.73 l/hr F_{s}=350 l/hr [RH]$_{Tot}$=1.4 mol/l

Time (min)	[Ni]$_f$ (mg/l)	pH$_f$	[Ni]$_s$ (mg/l)	pH$_s$	V_{NaOH} (ml)
0	0.20	3.84	5.60	2.75	0.00
20	12.00	3.58	7.50	1.31	0.00
40	18.30	3.47	9.70	1.19	0.11
60	20.30	3.50	11.30	1.16	1.01
80	19.60	3.50	12.10	1.14	1.76
100	15.80	3.47	10.50	1.12	2.83
120	18.70	3.51	15.10	1.14	4.12
Tank	34.90	5.93	0.65	1.10	-

Exp. Name: Int 46

J_{fin}=0.430 mg/m^{2}·s

F_{FT}=10.44 l/hr F_{f}=350 l/hr T_{sp}=40 ˚C

F_{ST}=10.32 l/hr F_{s}=200 l/hr [RH]$_{Tot}$=1.4 mol/l

Time (min)	[Ni]$_f$ (mg/l)	pH$_f$	[Ni]$_s$ (mg/l)	pH$_s$	V_{NaOH} (ml)
0	0.40	4.87	1.00	3.06	0.00
20	12.50	4.60	5.30	0.96	1.21
40	13.50	4.13	10.20	0.97	4.45
60	13.40	4.31	11.50	1.14	8.79
80	12.10	4.46	17.20	1.34	13.74
100	11.70	4.57	18.50	1.49	18.50
120	10.70	4.54	22.00	1.54	22.59
Tank	32.90	5.71	0.40	1.55	-

Exp. Name: Int 47

J_{fin}=1.149 mg/m^{2}·s

F_{FT}=10.09 l/hr F_{f}=350 l/hr T_{sp}=60 ˚C

F_{ST}=10.08 l/hr F_{s}=350 l/hr [RH]$_{Tot}$=1.4 mol/l

Time (min)	[Ni]$_f$ (mg/l)	pH$_f$	[Ni]$_s$ (mg/l)	pH$_s$	V_{NaOH} (ml)
0	0.50	3.82	0.30	1.56	0.00
20	26.50	3.84	14.20	1.33	4.16
40	32.20	4.02	31.70	1.20	11.80
60	36.40	4.02	38.40	1.17	19.07
80	27.90	4.61	50.40	1.17	30.30
100	26.00	4.70	54.80	1.16	40.32
120	25.80	4.68	57.90	1.16	50.33
Tank	87.60	5.84	1.03	1.17	-

Exp. Name: Int 48

J_{fin}=0.314 mg/m^{2}·s

F_{FT}=10.28 l/hr F_{f}=350 l/hr T_{sp}=60 ˚C

F_{ST}=10.32 l/hr F_{s}=200 l/hr [RH]$_{Tot}$=1.4 mol/l

Time (min)	[Ni]$_f$ (mg/l)	pH$_f$	[Ni]$_s$ (mg/l)	pH$_s$	V_{NaOH} (ml)
0	0.70	4.32	3	3.08	0.00
20	13.50	3.71	363	1.36	0.00
40	21.30	3.50	514	1.22	0.00
60	22.20	3.48	564	1.17	0.83
80	20.00	3.50	562	1.17	1.55
100	20.60	3.50	533	1.16	2.23
120	19.20	3.50	561	1.16	2.84
Tank	36.50	5.83	487	1.13	-

Exp. Name: Int 49

J_{fin}=0.520 mg/m^{2}·s

F_{FT}=10.48 l/hr F_{f}=200 l/hr T_{sp}=40 ˚C

F_{ST}=10.39 l/hr F_{s}=200 l/hr [RH]$_{Tot}$=1.4 mol/l

Time (min)	[Ni]$_f$ (mg/l)	pH$_f$	[Ni]$_s$ (mg/l)	pH$_s$	V_{NaOH} (ml)
0	0.10	3.83	1	3.55	0.00
20	31.20	4.06	333	1.34	3.37
40	48.10	4.32	481	1.21	7.88
60	53.50	4.50	543	1.16	12.31
80	52.70	4.49	566	1.16	16.68
100	52.50	4.48	566	1.17	20.89
120	54.50	4.53	570	1.14	25.21
Tank	81.30	5.68	543	1.15	-

Exp. Name: Int 50

J_{fin}=0.971 mg/m^{2}·s

F_{FT}=10.48 l/hr F_f=350 l/hr T_{sp}=60 °C

F_{ST}=10.43 l/hr F_s=200 l/hr [RH]$_{Tot}$=1.4 mol/l

Time (min)	[Ni]$_f$ (mg/l)	pH$_f$	[Ni]$_s$ (mg/l)	pH$_s$	V_{NaOH} (ml)
0	5.20	3.86	8	4.21	0.00
20	33.40	3.84	369	1.55	5.16
40	35.80	4.01	514	1.44	13.90
60	30.00	4.18	550	1.41	24.18
80	29.50	4.45	564	1.41	34.88
100	27.50	4.45	549	1.41	45.62
120	27.60	4.66	528	1.44	54.65
Tank	77.00	6.21	471	1.41	-

Exp. Name: Int 51

J_{fin}=0.285 mg/m^{2}·s

F_{FT}=10.29 l/hr F_f=350 l/hr T_{sp}=60 °C

F_{ST}=10.39 l/hr F_s=200 l/hr [RH]$_{Tot}$=1.4 mol/l

Time (min)	[Ni]$_f$ (mg/l)	pH$_f$	[Ni]$_s$ (mg/l)	pH$_s$	V_{NaOH} (ml)
0	0.30	3.71	1.80	3.41	0.00
20	10.80	3.54	6.90	1.33	0.00
40	15.00	3.48	9.00	1.26	0.43
60	17.60	3.49	10.50	1.24	1.22
80	17.00	3.49	11.50	1.22	2.02
100	17.30	3.50	11.80	1.22	2.89
120	16.30	3.50	12.80	1.22	3.61
Tank	32.10	5.73	0.73	1.22	-

Exp. Name: Int 52

J_{fin}=0.378 mg/m^{2}·s

F_{FT}=10.29 l/hr F_f=200 l/hr T_{sp}=60 °C

F_{ST}=10.01 l/hr F_s=200 l/hr [RH]$_{Tot}$=1.4 mol/l

Time (min)	[Ni]$_f$ (mg/l)	pH$_f$	[Ni]$_s$ (mg/l)	pH$_s$	V_{NaOH} (ml)
0	1.10	3.91	2	1.89	0.00
20	11.80	3.92	322	1.23	0.25
40	13.20	4.11	468	1.18	3.95
60	12.90	4.38	501	1.20	8.19
80	12.70	4.58	526	1.15	12.26
100	12.90	4.63	514	1.13	16.05
120	12.90	4.52	532	1.13	19.53
Tank	32.50	5.81	520	1.16	-

Exp. Name: Int 53

J_{fin}=0.188 mg/m^{2}·s

F_{FT}=10.29 l/hr F_f=200 l/hr T_{sp}=40 °C

F_{ST}=10.01 l/hr F_s=350 l/hr [RH]$_{Tot}$=1.4 mol/l

Time (min)	[Ni]$_f$ (mg/l)	pH$_f$	[Ni]$_s$ (mg/l)	pH$_s$	V_{NaOH} (ml)
0	0.10	3.87	1.50	3.16	0.00
20	12.20	3.66	4.50	1.45	0.00
40	17.10	3.54	6.50	1.37	0.00
60	20.30	3.47	7.70	1.34	0.06
80	22.60	3.50	9.80	1.32	0.84
100	23.30	3.50	10.00	1.29	1.02
120	21.70	3.49	9.60	1.32	1.13
Tank	33.15	5.44	0.43	1.34	-

Exp. Name: Int 54

J_{fin}=0.918 mg/m^{2}·s

F_{FT}=9.97 l/hr F_f=350 l/hr T_{sp}=60 °C

F_{ST}=10.03 l/hr F_s=200 l/hr [RH]$_{Tot}$=1.4 mol/l

Time (min)	[Ni]$_f$ (mg/l)	pH$_f$	[Ni]$_s$ (mg/l)	pH$_s$	V_{NaOH} (ml)
0	1.00	3.94	1.90	2.41	0.03
20	13.00	3.77	27.60	1.25	4.00
40	34.30	3.98	27.00	1.14	11.29
60	33.10	4.15	39.00	1.17	20.20
80	38.80	5.38	38.80	1.16	29.45
100	37.90		28.00	1.18	37.49
120	34.20	4.28	42.00	1.13	44.57
Tank	87.00	5.42	0.82	1.16	-

Exp. Name: Int 55

J_{fin}=0.276 mg/m^{2}·s

F_{FT}=9.53 l/hr F_f=350 l/hr T_{sp}=60 °C

F_{ST}=10.33 l/hr F_s=350 l/hr [RH]$_{Tot}$=1.4 mol/l

Time (min)	[Ni]$_f$ (mg/l)	pH$_f$	[Ni]$_s$ (mg/l)	pH$_s$	V_{NaOH} (ml)
0	0.30	3.78	1	3.26	0.00
20	10.00	3.55	299	1.29	0.00
40	15.00	3.45	413	1.14	0.38
60	16.70	3.49	455	1.14	1.46
80	16.60	3.50	465	1.13	2.45
100	17.00	3.50	468	1.08	3.43
120	14.40	3.50	497	1.09	4.40
Tank	31.60	5.27	481	1.14	-

Exp. Name: Int 56

J_{fin}=0.523 mg/m^{2}·s

F_{FT}=10.25 l/hr F_f=200 l/hr T_{sp}=40 °C

F_{ST}=10.36 l/hr F_s=350 l/hr $[RH]_{Tot}$=1.4 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	1.40	3.98	64.10	1.82	0.00
20	34.80	4.09	28.20	1.39	2.73
40	50.80	4.27	21.60	1.29	6.55
60	56.60	4.42	21.30	1.28	10.74
80	57.50	4.38	21.40	1.27	14.96
100	56.30	4.47	22.20	1.26	19.29
120	52.60	4.46	23.90	1.29	23.73
Tank	82.10	5.09	0.07	1.27	-

Exp. Name: Int 57

J_{fin}=0.499 mg/m^{2}·s

F_{FT}=11.47 l/hr F_f=350 l/hr T_{sp}=40 °C

F_{ST}=11.67 l/hr F_s=200 l/hr $[RH]_{Tot}$=1.4 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.10	3.90	23.30	1.51	0.00
20	46.10	3.52	6.50	1.41	0.00
40	59.10	3.46	8.70	1.34	1.36
60	63.40	3.50	11.10	1.32	3.13
80	59.30	3.50	13.00	1.32	4.87
100	59.40	3.50	14.20	1.31	6.63
108	58.00	3.50	14.80	1.31	7.22
Tank	83.30	4.96	0.77	1.26	-

Exp. Name: Int 58

J_{fin}=0.947 mg/m^{2}·s

F_{FT}=9.44 l/hr F_f=350 l/hr T_{sp}=60 °C

F_{ST}=10.38 l/hr F_s=350 l/hr $[RH]_{Tot}$=1.4 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	3.60	5.40	17	2.10	0.00
20	18.50	3.95	285	1.07	6.73
40	26.70	3.90	290	1.01	12.80
60	29.50	4.30	475	1.04	21.80
80	25.60	4.35	537	1.09	30.71
100	24.60	4.49	581	1.23	39.70
120	24.90	4.58	592	1.24	48.69
Tank	80.20	3.75	500	1.24	-

Exp. Name: Int 59

J_{fin}=0.501 mg/m^{2}·s

F_{FT}=9.65 l/hr F_f=200 l/hr T_{sp}=60 °C

F_{ST}=9.75 l/hr F_s=200 l/hr $[RH]_{Tot}$=1.4 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.60	3.85	4.10	2.97	0.00
20	30.00	3.49	8.90	1.45	0.00
40	53.50	3.47	13.90	1.31	1.60
60	63.70	3.50	17.41	1.23	3.68
80	64.90	3.50	19.00	1.23	5.72
100	64.80	3.42	20.00	1.20	6.92
120	63.70	3.58	18.90	1.22	9.89
Tank	95.70	4.95	0.97	1.18	-

Exp. Name: Int 60

J_{fin}=0.453 mg/m^{2}·s

F_{FT}=10.50 l/hr F_f=350 l/hr T_{sp}=40 °C

F_{ST}=10.50 l/hr F_s=200 l/hr $[RH]_{Tot}$=1.4 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	3.20	3.78	53	1.89	0.00
20	42.90	3.43	474	1.12	0.92
40	58.60	3.48	590	1.05	3.31
60	64.00	3.49	642	1.02	5.79
80	67.30	3.51	573	1.00	8.21
100	62.10	3.49	551	1.00	10.59
120	60.90	3.50	538	1.01	13.08
Tank	85.98	4.30	550	0.98	-

Exp. Name: Int 61

J_{fin}=0.453 mg/m^{2}·s

F_{FT}=9.82 l/hr F_f=200 l/hr T_{sp}=60 °C

F_{ST}=9.69 l/hr F_s=350 l/hr $[RH]_{Tot}$=1.4 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	6.50	3.62	10.20	2.09	0.00
20	42.30	3.37	14.50	1.21	0.68
40	56.10	3.44	21.40	1.10	4.75
60	62.60	3.47	25.40	1.05	9.66
80	70.10	3.49	23.00	1.03	15.18
100	68.10	3.45	24.40	1.02	20.00
120	79.80	3.30	19.20	1.02	23.09
Tank	94.10	5.67	0.97	1.00	-

Exp. Name: Int 62

J_{fin}=0.628 mg/m^2·s

F_{FT}=9.83 l/hr F_f=200 l/hr T_{sp}=60 ˚C

F_{ST}=10.16 l/hr F_s=200 l/hr $[RH]_{Tot}$=1.0 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	5.00	4.17	10	2.33	0.00
20	30.50	4.02	79	1.94	0.68
40	47.30	4.01	452	1.33	4.75
60	48.00	4.20	622	1.28	9.66
80	51.00	4.00	573	1.24	15.18
100	58.30	4.32	599	1.24	20.00
120	44.60	5.76	683	1.23	23.09
Tank	80.90	3.11	625.00	1.19	-

Exp. Name: Int 63

J_{fin}=0.333 mg/m^2·s

F_{FT}=10.20 l/hr F_f=350 l/hr T_{sp}=60 ˚C

F_{ST}=10.00 l/hr F_s=350 l/hr $[RH]_{Tot}$=1.0 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	7.10	4.53	25	1.84	0.00
20	30.30	3.44	280	1.38	0.68
40	46.00	3.44	417	1.30	4.75
60	53.30	3.48	456	1.28	9.66
80	53.60	3.49	465	1.27	15.18
100	55.60	3.49	477	1.26	20.00
120	56.10	3.40	496	1.26	23.09
Tank	75.40	2.74	479	1.19	-

Exp. Name: Int 64

J_{fin}=0.653 mg/m^2·s

F_{FT}=10.15 l/hr F_f=200 l/hr T_{sp}=60 ˚C

F_{ST}=9.90 l/hr F_s=200 l/hr $[RH]_{Tot}$=1.0 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	6.70	4.18	42.20	2.19	0.00
20	31.50	3.92	29.00	1.20	0.68
40	38.50	4.10	26.30	1.11	4.75
60	41.00	4.36	28.90	1.04	9.66
80	43.30	3.97	29.00	1.03	15.18
100	48.20	4.74	24.10	1.03	20.00
120	31.50	6.25	31.70	1.02	23.09
Tank	76.30	3.24	2.23	1.00	-

Exp. Name: Max 01

J_{fin}=1.368 mg/m^2·s

F_{FT}=9.98 l/hr F_f=300 l/hr T_{sp}=70 ˚C

F_{ST}=9.88 l/hr F_s=350 l/hr $[RH]_{Tot}$=1.6 mol/l

Time (min)	$[Ni]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	6.00	3.72	14.60	2.02	0.00
20	35.60	4.15	40.30	1.31	11.67
40	53.00	3.64	63.00	1.21	40.00
60	44.60	5.94	81.90	1.21	77.55
80	51.40	5.08	83.40	1.21	109.47
100	52.60	4.41	81.60	1.20	146.80
120	57.00	6.44	82.90	1.20	180.00
Tank	129.40	4.57	0.13	1.09	-

B.5 Experimental conditions for zinc experiments

The meaning of the titles as used in Table B.4 is the following:

Name	: A short descriptive name is given to each experiment to keep track of the data.
$[Zn]_f$	: The zinc concentration in the feed tank as measured. The solutions was prepared to approximate concentrations and then the exact value was measured (mg/l).
$pH_{f,sp}$	: The setpoint for the feed pH controller.
$[Zn]_s$	: The zinc concentration in the strip tank as measured (mg/l).
$V_{H,s}$	: The amount of pure sulphuric acid used to make up strip solution (ml in a 21l tank).
pH_s	: The pH of the strip tank as measured.

T_{sp} : The temperature setpoint for the controller (˚C).

F_f : The feed recycle flow rate (l/hr)

F_s : The strip recycle flow rate (l/hr)

$[RH]_{Tot}$: The concentration of the extractant as D2EHPA monomer (mol/l).

Table B.4: Summary of experimental conditions for the SLM extraction of zinc

Name	$[Zn]_f$ (mg/l)	$pH_{f,sp}$	$[Zn]_s$ (mg/l)	$V_{H,s}$ (ml/21l)	pH_s	T_{sp} (˚C)	F_f (l/hr)	F_s (l/hr)	$[RH]_{Tot}$ (mol/l)
ZCt 01	48.16	2.30	2.49	100	0.92	50	200	200	1.2
ZCt 02	50.54	2.30	0.14	100	0.99	50	200	200	1.2
ZCt 03	51.70	2.30	0.26	100	1.10	50	200	200	1.2
ZCt 04	50.71	2.30	0.20	100	1.05	50	200	200	1.2
ZpH 01	50.74	2.00	0.19	100	1.05	50	200	200	1.2
ZpH 02	44.98	2.90	0.30	100	1.06	50	200	200	1.2
ZpH 03	50.22	2.60	0.14	100	1.01	50	200	200	1.2
ZpH 04	50.77	1.70	0.30	100	0.98	50	200	200	1.2
ZTp 01	51.87	2.30	0.30	100	1.05	70	200	200	1.2
ZTp 02	50.54	2.30	0.57	100	1.06	60	200	200	1.2
ZTp 03	51.52	2.30	0.37	100	1.09	40	200	200	1.2
ZTp 04	52.35	2.30	0.30	100	1.21	30	200	200	1.2

B.6 Detailed results of SLM experiments for zinc

The meaning of the titles as used in the tables in this section is as follow:

Exp. Name : A short descriptive name (same as in Table B.4) of the experiment.

J_{fin} : The final flux of zinc across the membrane (mg/m^2·s).

F_{FT} : The flow rate from the feed tank to the feed recycle tank (l/hr).

F_{ST} : The flow rate from the strip tank to the strip recycle tank (l/hr).

F_f : The feed recycle flow rate (l/hr).

F_s : The strip recycle flow rate (l/hr).

T_{sp} : The temperature setpoint for the controller (˚C).

$[RH]_{Tot}$: The concentration of the extractant as D2EHPA monomer (mol/l).

Time : The time when samples were taken (min).

$[\mathrm{Zn}]_f$: The nickel concentration of the feed as measured in the recycle tank (mg/l).

pH_f : The pH of the feed as measured in the recycle tank.

$[\mathrm{Zn}]_s$: The nickel concentration of the strip as measured in the recycle tank (mg/l).

pH_s : The pH of the strip as measured in the recycle tank.

V_{NaOH} : The volume of a 1 mol/l NaOH solution titrated by the pH controller (ml).

Tank : The concentration and pH in the feed and strip tanks.

Exp. Name: ZCt 01

J_{fin}=0.488 mg/m^2·s

F_{FT}=9.87 l/hr F_f=200 l/hr T_{sp}=45 °C

F_{ST}=9.89 l/hr F_s=200 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Zn]_f$ (mg/l)	pH_f	$[Zn]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	2.2	2.29	5.3	1.68	0.00
20	12.4	2.37	5.9	1.19	6.90
40	14.9	2.28	15.9	1.02	10.17
60	19.1	2.30	19.7	0.98	15.27
80	18.7	2.29	22.6	0.95	22.00
100	20.3	2.30	24.6	0.91	28.92
120	21.2	2.30	24.5	0.92	34.16
Tank	48.16	2.09	2.49	0.94	-

Exp. Name: ZCt 02

J_{fin}=0.458 mg/m^2·s

F_{FT}=10.17 l/hr F_f=200 l/hr T_{sp}=45 °C

F_{ST}=10.18 l/hr F_s=200 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Zn]_f$ (mg/l)	pH_f	$[Ni]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	2.6	2.34	5.8	1.64	0.00
20	13.8	2.30	8.7	1.21	0.87
40	19.5	2.29	17.1	1.07	3.60
60	18.8	2.35	20.4	1.05	8.40
80	19.5	2.29	22.4	1.00	11.81
100	20.5	2.30	24.9	1.01	15.11
120	21.8	2.29	27.5	0.99	17.81
Tank	50.54	2.24	0.14	0.99	-

Exp. Name: ZCt 03

J_{fin}=0.513 mg/m^2·s

F_{FT}=10.11 l/hr F_f=200 l/hr T_{sp}=49 °C

F_{ST}=9.95 l/hr F_s=200 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Zn]_f$ (mg/l)	pH_f	$[Zn]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	1.4	3.25	5.0	0.95	0.00
20	16.2	2.56	7.4	1.03	0.00
40	22.3	2.43	16.8	1.07	0.00
60	22.9	2.38	20.9	1.09	0.00
80	22.6	2.41	25.2	1.08	0.00
100	24.3	2.34	28.1	1.09	0.00
120	24.0	2.35	28.5	1.10	0.00
Tank	51.70	2.40	0.26	1.10	-

Exp. Name: ZCt 04

J_{fin}=0.531 mg/m^2·s

F_{FT}=10.24 l/hr F_f=200 l/hr T_{sp}=49 °C

F_{ST}=10.44 l/hr F_s=200 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Zn]_f$ (mg/l)	pH_f	$[Zn]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	8.2	2.18	13.7	1.58	0.00
20	16.6	2.35	15.0	1.23	11.72
40	22.6	2.35	21.3	1.14	11.72
60	22.4	2.37	24.3	1.11	11.72
80	23.9	2.35	26.7	1.06	11.72
100	22.4	2.36	27.6	1.05	11.72
120	21.2	2.32	26.4	1.05	11.72
Tank	50.71	2.41	0.20	1.04	-

Exp. Name: ZpH 01

J_{fin}=0.488 mg/m^2·s

F_{FT}=9.87 l/hr F_f=200 l/hr T_{sp}=49 °C

F_{ST}=10.23 l/hr F_s=200 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Zn]_f$ (mg/l)	pH_f	$[Zn]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	3.2	2.42	6.8	1.89	0.00
20	17.4	2.11	10.1	1.30	0.00
40	24.6	2.00	15.4	1.13	0.26
60	26.0	1.99	19.8	1.10	4.73
80	26.1	1.99	20.8	1.07	11.18
100	25.2	2.03	24.1	1.06	20.00
120	26.4	2.03	28.4	1.05	27.66
Tank	50.74	2.00	0.19	1.14	-

Exp. Name: ZpH 02

J_{fin}=0.492 mg/m^2·s

F_{FT}=10.28 l/hr F_f=200 l/hr T_{sp}=49 °C

F_{ST}=9.82 l/hr F_s=200 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Zn]_f$ (mg/l)	pH_f	$[Zn]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.4	3.27	10.5	1.14	0.00
20	11.6	2.94	10.8	1.09	0.00
40	15.9	2.81	13.7	1.06	0.00
60	16.2	3.32	17.8	1.06	12.29
80	18.7	2.90	22.1	1.05	12.36
100	17.9	2.90	24.5	1.07	14.20
120	19.0	2.90	31.4	1.06	16.35
Tank	44.98	2.99	0.30	1.06	-

Exp. Name: ZpH 03

J_{fin}=0.567 mg/m^2·s

F_{FT}=10.29 l/hr F_f=200 l/hr T_{sp}=49 °C

F_{ST}=10.06 l/hr F_s=200 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Zn]_f$ (mg/l)	pH_f	$[Zn]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	0.9	3.79	7.1	1.11	0.00
20	15.0	2.54	7.7	1.08	0.42
40	18.3	2.57	13.9	1.05	16.81
60	20.5	2.61	18.4	1.03	24.67
80	20.0	2.61	23.2	1.03	35.00
100	19.6	2.62	23.1	1.02	45.59
120	20.4	2.60	27.0	1.01	54.83
Tank	50.22	2.41	0.14	1.04	-

Exp. Name: ZpH 04

J_{fin}=0.156 mg/m^2·s

F_{FT}=10.03 l/hr F_f=200 l/hr T_{sp}=49 °C

F_{ST}=10.60 l/hr F_s=200 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Zn]_f$ (mg/l)	pH_f	$[Zn]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	1.3	3.56	14.7	1.09	0.00
20	36.7	1.89	18.8	1.05	0.00
40	45.0	1.70	25.3	1.05	1.49
60	45.0	1.71	26.9	1.01	2.34
80	42.6	1.69	26.4	1.02	8.79
100	36.7	1.72	24.3	1.03	25.35
120	37.2	1.70	24.6	0.98	35.63
Tank	50.77	1.64	0.30	1.04	-

Exp. Name: ZTp 01

J_{fin}=0.630 mg/m^2·s

F_{FT}=10.28 l/hr F_f=200 l/hr T_{sp}=68 °C

F_{ST}=10.05 l/hr F_s=200 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Zn]_f$ (mg/l)	pH_f	$[Zn]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	1.2	2.99	5.4	1.21	0.00
20	6.6	2.49	7.6	1.13	0.00
40	11.0	2.38	13.3	1.11	0.00
60	14.2	2.35	19.1	1.08	0.00
80	16.0	2.24	24.6	1.06	3.76
100	15.8	2.36	27.4	1.06	4.71
120	19.6	2.30	32.0	1.05	6.61
Tank	51.87	2.43	0.30	1.07	ZTp 01

Exp. Name: ZTp 02

J_{fin}=0.587 mg/m^2·s

F_{FT}=10.27 l/hr F_f=200 l/hr T_{sp}=58 °C

F_{ST}=10.09 l/hr F_s=200 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Zn]_f$ (mg/l)	pH_f	$[Zn]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	1.1	3.62	7.5	1.20	0.00
20	13.3	2.55	9.3	1.19	0.00
40	16.9	2.33	16.4	1.15	6.18
60	19.5	2.38	19.9	1.11	9.92
80	19.7	2.35	24.7	1.10	14.39
100	17.2	2.29	27.0	1.12	16.91
120	20.1	2.36	29.1	1.06	29.22
Tank	50.54	2.26	0.57	1.08	ZTp 02

Exp. Name: ZTp 03

J_{fin}=0.478 mg/m^2·s

F_{FT}=10.21 l/hr F_f=200 l/hr T_{sp}=39 °C

F_{ST}=10.02 l/hr F_s=200 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Zn]_f$ (mg/l)	pH_f	$[Zn]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	1.2	3.57	8.9	1.21	0.00
20	19.3	2.48	9.5	1.18	0.00
40	24.9	2.30	14.3	1.15	0.00
60	26.1	2.30	18.0	1.12	4.45
80	24.5	2.25	20.6	1.10	20.00
100	26.2	2.31	25.9	1.10	20.09
120	26.7	2.30	25.0	1.09	24.51
Tank	51.52	2.26	0.37	1.16	-

Exp. Name: ZTp 04

J_{fin}=0.420 mg/m^2·s

F_{FT}=9.91 l/hr F_f=200 l/hr T_{sp}=30 °C

F_{ST}=9.76 l/hr F_s=200 l/hr $[RH]_{Tot}$=1.2 mol/l

Time (min)	$[Zn]_f$ (mg/l)	pH_f	$[Zn]_s$ (mg/l)	pH_s	V_{NaOH} (ml)
0	1.3	3.51	11.7	1.26	0.00
20	20.0	2.60	11.3	1.23	0.00
40	25.7	2.42	14.8	1.23	0.00
60	28.5	2.38	18.8	1.22	0.00
80	28.9	2.35	21.7	1.22	0.00
100	29.5	2.36	22.2	1.21	0.00
120	28.7	2.48	24.9	1.21	18.20
Tank	52.35	0.97	0.30	1.20	-

List of Tables

Appendix C

Physical and chemical data - detailed results -

Contents

C.1 Introduction

A comprehensive list of the equilibrium experiments done and the raw results are given in Table C.1. The processed results of each experiment is given in Table C.2. The raw pressure drop results are given in Table C.3 and the processed results are given in Table C.4.

C.2 Raw equilibrium results

The meaning of the titles as used in Table C.1 are the following:

Name : A name is given to each experiment to keep track of the data.
Rep. : The number of reproducibility test.
V_{aq} : Volume aqueous solution (ml).
V_o : Volume organic solution (ml).
$[Ni]_f$: Nickel concentration of feed solution.
$[Ni]_r$: Nickel concentration of raffinate solution.
$[RH]_{Tot}$: D2EHPA concentration in organic solution as D2EHPA monomer (mol/l).
pH_r : pH of raffinate solution.
$[H_2SO_4]$: Concentration of sulphuric acid added to aqueous solution (mol/m^3).
$[NaOH]$: Concentration of sodium hydroxide added to aqueous solution (mol/m^3).

Table C.1: Raw equilibrium results

Name	Rep.	V_{aq} (ml)	V_o (ml)	$[Ni]_f$ (mg/l)	$[Ni]_r$ (mg/l)	$[RH]_{Tot}$ (mol/l)	pH_r	$[H_2SO_4]$ (mol/m^3)	[NaOH] (mol/m^3)
S01	1	30	30	114.0	30.97	1.20	2.48	0.00	0.00
S01	2	30	30	109.4	34.42	1.20	2.51	0.00	0.00
S01	3	30	30	109.9	34.10	1.20	2.51	0.00	0.00
S01	4	30	30	110.4	28.55	1.20	2.51	0.00	0.00
S02	1	30	30	110.4	37.07	1.20	2.51	0.00	0.00
S02	2	30	30	108.0	32.84	1.20	2.51	0.00	0.00
S02	3	30	30	109.9	35.65	1.20	2.50	0.00	0.00
S02	4	30	30	110.4	33.34	1.20	2.51	0.00	0.00
S03	1	30	30	106.1	37.23	1.20	2.51	0.00	0.00
S03	2	30	30	107.5	33.24	1.20	2.51	0.00	0.00
S03	3	30	30	108.0	35.02	1.20	2.51	0.00	0.00
S03	4	30	30	107.0	34.48	1.20	2.51	0.00	0.00
S04	1	30	30	109.0	34.95	1.20	2.52	0.00	0.00
S04	2	30	30	110.4	31.56	1.20	2.51	0.00	0.00
S04	3	30	30	107.5	34.59	1.20	2.50	0.00	0.00
S04	4	30	30	109.9	32.84	1.20	2.51	0.00	0.00
S05	1	30	30	112.5	35.97	1.20	2.51	0.00	0.00
S05	2	30	30	102.0	34.93	1.20	2.50	0.00	0.00
S05	3	30	30	111.7	29.28	1.20	2.48	0.00	0.00
S05	4	30	30	108.3	28.81	1.20	2.50	0.00	0.00
N01	1	20	40	116.2	14.31	1.20	2.66	0.00	0.00
N01	2	20	40	118.8	14.31	1.20	2.65	0.00	0.00
N01	3	20	40	115.7	15.64	1.20	2.62	0.00	0.00
N01	4	20	40	114.7	15.53	1.20	2.64	0.00	0.00
N02	1	20	40	114.3	14.36	1.20	2.62	0.00	0.00
N02	2	20	40	112.8	14.19	1.20	2.63	0.00	0.00
N02	3	20	40	114.3	13.43	1.20	2.62	0.00	0.00
N02	4	20	40	114.3	13.22	1.20	2.62	0.00	0.00

Table C.1: Raw equilibrium results (continue)

Name	Rep.	V_{aq} (ml)	V_o (ml)	$[Ni]_f$ (mg/l)	$[Ni]_r$ (mg/l)	$[RH]_{Tot}$ (mol/l)	pH_r	$[H_2SO_4]$ (mol/m^3)	[NaOH] (mol/m^3)
T01	1	30	30	111.5	22.06	1.20	2.63	0.00	0.00
T01	2	30	30	111.5	24.20	1.20	2.62	0.00	0.00
T01	3	30	30	111.5	29.38	1.20	2.62	0.00	0.00
T01	4	30	30	111.5	21.36	1.20	2.61	0.00	0.00
T02	1	30	30	111.5	29.19	1.20	2.66	0.00	0.00
T02	2	30	30	111.5	20.32	1.20	2.66	0.00	0.00
T02	3	30	30	111.5	26.75	1.20	2.66	0.00	0.00
T02	4	30	30	111.5	21.89	1.20	2.66	0.00	0.00
T03	1	30	30	111.5	19.57	1.20	2.71	0.00	0.00
T03	2	30	30	111.5	25.74	1.20	2.66	0.00	0.00
T03	3	30	30	111.5	22.86	1.20	2.60	0.00	0.00
T03	4	30	30	111.5	19.74	1.20	2.64	0.00	0.00
T04	1	30	30	105.4	20.87	1.20	2.68	0.00	0.00
T04	2	30	30	102.7	22.28	1.20	2.69	0.00	0.00
T04	3	30	30	105.8	22.81	1.20	2.61	0.00	0.00
T04	4	30	30	106.8	18.79	1.20	2.69	0.00	0.00
T05	1	30	30	105.4	22.96	1.20	2.74	0.00	0.00
T05	2	30	30	104.3	22.25	1.20	2.61	0.00	0.00
T05	3	30	30	103.8	21.71	1.20	2.70	0.00	0.00
T05	4	30	30	103.2	22.60	1.20	2.70	0.00	0.00
R01	1	20	40	113.7	99.41	0.30	2.42	0.00	0.00
R01	2	20	40	114.2	100.80	0.30	2.46	0.00	0.00
R01	3	20	40	111.1	98.50	0.30	2.43	0.00	0.00
R01	4	20	40	115.1	97.13	0.30	2.46	0.00	0.00
R02	1	20	40	117.1	63.43	0.60	2.50	0.00	0.00
R02	2	20	40	117.1	62.01	0.60	2.47	0.00	0.00
R02	3	20	40	114.2	60.54	0.60	2.45	0.00	0.00
R02	4	20	40	115.2	58.63	0.60	2.45	0.00	0.00

Table C.1: Raw equilibrium results (continue)

Name	Rep.	V_{aq} (ml)	V_o (ml)	$[Ni]_f$ (mg/l)	$[Ni]_r$ (mg/l)	$[RH]_{Tot}$ (mol/l)	pH_r	$[H_2SO_4]$ (mol/m^3)	[NaOH] (mol/m^3)
R03	1	20	40	111.6	40.15	0.80	2.54	0.00	0.00
R03	2	20	40	113.0	34.47	0.80	2.55	0.00	0.00
R03	3	20	40	109.7	37.63	0.80	2.54	0.00	0.00
R03	4	20	40	111.7	34.85	0.80	2.55	0.00	0.00
R04	1	20	40	114.0	20.49	1.00	2.60	0.00	0.00
R04	2	20	40	109.2	24.09	1.00	2.61	0.00	0.00
R04	3	20	40	109.7	24.31	1.00	2.60	0.00	0.00
R04	4	20	40	109.2	20.61	1.00	2.60	0.00	0.00
R05	1	20	40	116.8	9.94	1.40	2.68	0.00	0.00
R05	2	20	40	112.1	9.20	1.40	2.67	0.00	0.00
R05	3	20	40	108.5	9.34	1.40	2.68	0.00	0.00
R05	4	20	40	107.0	9.02	1.40	2.68	0.00	0.00
R06	1	20	40	114.8	6.30	1.60	2.71	0.00	0.00
R06	2	20	40	112.7	6.22	1.60	2.7	0.00	0.00
R06	3	20	40	111.6	6.28	1.60	2.69	0.00	0.00
R06	4	20	40	110.1	6.12	1.60	2.7	0.00	0.00
F01	1	30	30	89.7	28.94	1.20	2.51	0.00	0.00
F01	2	30	30	88.5	28.94	1.20	2.51	0.00	0.00
F01	3	30	30	87.5	24.74	1.20	2.50	0.00	0.00
F01	4	30	30	87.1	26.68	1.20	2.49	0.00	0.00
F02	1	30	30	64.8	16.87	1.20	2.56	0.00	0.00
F02	2	30	30	65.2	16.74	1.20	2.56	0.00	0.00
F02	3	30	30	67.8	19.13	1.20	2.55	0.00	0.00
F02	4	30	30	64.2	19.67	1.20	2.56	0.00	0.00
F03	1	30	30	42.3	10.55	1.20	2.65	0.00	0.00
F03	2	30	30	43.5	10.55	1.20	2.65	0.00	0.00
F03	3	30	30	42.0	8.97	1.20	2.69	0.00	0.00
F03	4	30	30	41.7	8.97	1.20	2.68	0.00	0.00

Table C.1: Raw equilibrium results (continue)

Name	Rep.	V_{aq} (ml)	V_o (ml)	$[Ni]_f$ (mg/l)	$[Ni]_r$ (mg/l)	$[RH]_{Tot}$ (mol/l)	pH_r	$[H_2SO_4]$ (mol/m^3)	[NaOH] (mol/m^3)
F04	1	30	30	20.4	4.42	1.20	2.67	0.00	0.00
F04	2	30	30	19.4	4.32	1.20	2.68	0.00	0.00
F04	3	30	30	19.4	3.36	1.20	2.68	0.00	0.00
F04	4	30	30	19.7	3.26	1.20	2.66	0.00	0.00
V01	1	24	36	120.4	21.40	1.20	2.59	0.00	0.00
V01	2	24	36	114.5	24.69	1.20	2.59	0.00	0.00
V01	3	24	36	120.9	25.01	1.20	2.23	0.00	0.00
V01	4	24	36	115.2	30.50	1.20	2.23	0.00	0.00
V02	1	30	30	117.9	33.69	1.20	2.53	0.00	0.00
V02	2	30	30	118.3	33.35	1.20	2.52	0.00	0.00
V02	3	30	30	104.1	32.63	1.20	2.54	0.00	0.00
V02	4	30	30	105.0	38.95	1.20	2.54	0.00	0.00
V03	1	40	20	104.7	34.59	1.20	2.57	0.00	0.00
V03	2	40	20	97.9	28.81	1.20	2.56	0.00	0.00
V03	3	40	20	106.9	33.63	1.20	2.56	0.00	0.00
V03	4	40	20	100.8	29.69	1.20	2.57	0.00	0.00
V04	1	50	10	104.8	37.12	1.20	2.65	0.00	0.00
V04	2	50	10	102.7	49.83	1.20	2.64	0.00	0.00
V04	3	50	10	103.1	60.89	1.20	2.64	0.00	0.00
V04	4	50	10	90.5	49.29	1.20	2.63	0.00	0.00
P01	1	30	30	112.6	25.52	1.20	2.71	0.00	0.67
P01	2	30	30	112.6	23.22	1.20	2.71	0.00	0.67
P01	3	30	30	108.9	25.52	1.20	2.75	0.00	0.67
P01	4	30	30	105.3	25.16	1.20	2.72	0.00	0.67
P02	1	30	30	99.6	10.05	1.20	2.96	0.00	0.67
P02	2	30	30	104.6	9.96	1.20	2.94	0.00	0.67
P02	3	30	30	100.8	9.70	1.20	2.91	0.00	0.67
P02	4	30	30	102.1	9.87	1.20	2.91	0.00	0.67

Table C.1: Raw equilibrium results (continue)

Name	Rep.	V_{aq} (ml)	V_o (ml)	$[Ni]_f$ (mg/l)	$[Ni]_r$ (mg/l)	$[RH]_{Tot}$ (mol/l)	pH_r	$[H_2SO_4]$ (mol/m^3)	[NaOH] (mol/m^3)
P03	1	30	30	107.7	27.10	1.20	2.57	0.57	0.00
P03	2	30	30	106.3	28.83	1.20	2.56	0.57	0.00
P03	3	30	30	103.2	17.03	1.20	2.55	0.57	0.00
P03	4	30	30	104.0	35.36	1.20	2.55	0.57	0.00
P04	1	30	30	107.6	45.89	1.20	2.43	2.18	0.00
P04	2	30	30	109.0	46.49	1.20	2.5	2.18	0.00
P04	3	30	30	103.6	45.01	1.20	2.44	2.18	0.00
P04	4	30	30	109.5	48.28	1.20	2.44	2.18	0.00
P05	1	30	30	108.2	64.88	1.20	2.32	3.90	0.00
P05	2	30	30	110.1	62.53	1.20	1.98	3.90	0.00
P05	3	30	30	112.9	61.54	1.20	2.29	3.90	0.00
P05	4	30	30	106.4	64.55	1.20	2.31	3.90	0.00
P06	1	30	30	101.7	84.27	1.20	2.14	6.00	0.00
P06	2	30	30	102.2	76.04	1.20	2.13	6.00	0.00
P06	3	30	30	106.8	88.63	1.20	2.14	6.00	0.00
P06	4	30	30	106.3	88.63	1.20	2.14	6.00	0.00
P07	1	30	30	99.5	83.54	1.20	2.03	8.00	0.00
P07	2	30	30	99.0	90.06	1.20	2.03	8.00	0.00
P07	3	30	30	101.1	88.00	1.20	2.04	8.00	0.00
P07	4	30	30	99.8	88.39	1.20	2.04	8.00	0.00
P08	1	30	30	109.3	23.02	1.20	2.69	0.00	0.67
P08	2	30	30	109.3	23.14	1.20	2.69	0.00	0.67
P08	3	30	30	108.0	21.40	1.20	2.7	0.00	0.67
P08	4	30	30	108.0	20.61	1.20	2.69	0.00	0.67
P09	1	30	30	111.6	24.50	1.20	2.76	0.00	1.00
P09	2	30	30	107.0	23.65	1.20	2.71	0.00	1.00
P09	3	30	30	106.1	21.07	1.20	2.7	0.00	1.00
P09	4	30	30	107.0	22.70	1.20	2.7	0.00	1.00

Table C.1: Raw equilibrium results (continue)

Name	Rep.	V_{aq} (ml)	V_o (ml)	$[Ni]_f$ (mg/l)	$[Ni]_r$ (mg/l)	$[RH]_{Tot}$ (mol/l)	pH_r	$[H_2SO_4]$ (mol/m^3)	[NaOH] (mol/m^3)
P10	1	30	30	119.2	9.10	1.20	2.82	0.00	3.33
P10	2	30	30	113.4	16.62	1.20	2.81	0.00	3.33
P10	3	30	30	118.9	15.72	1.20	2.8	0.00	3.33
P10	4	30	30	113.4	16.42	1.20	2.8	0.00	3.33
K01	1	30	30	36.5	5.93	1.00	2.73	0.00	0.00
K01	2	30	30	33.3	6.83	1.00	2.72	0.00	0.00
K01	3	30	30	35.8	6.60	1.00	2.71	0.00	0.00
K01	4	30	30	40.2	6.26	1.00	2.71	0.00	0.00
K02	1	30	30	47.7	6.40	1.40	2.73	0.00	0.00
K02	2	30	30	52.0	5.61	1.40	2.71	0.00	0.00
K02	3	30	30	50.7	6.08	1.40	2.71	0.00	0.00
K02	4	30	30	51.6	5.53	1.40	2.70	0.00	0.00
K03	1	30	30	33.9	29.83	1.00	2.30	4.00	0.00
K03	2	30	30	33.1	32.68	1.00	2.29	4.00	0.00
K03	3	30	30	37.5	25.57	1.00	2.29	4.00	0.00
K03	4	30	30	29.6	38.44	1.00	2.29	4.00	0.00
K04	1	30	30	40.9	19.66	1.40	2.35	4.00	0.00
K04	2	30	30	56.7	16.94	1.40	2.35	4.00	0.00
K04	3	30	30	40.2	16.25	1.40	2.35	4.00	0.00
K04	4	30	30	58.1	16.88	1.40	2.36	4.00	0.00
K05	1	30	30	106.5	27.34	1.00	2.61	0.00	0.00
K05	2	30	30	104.7	25.93	1.00	2.59	0.00	0.00
K05	3	30	30	106.5	29.77	1.00	2.58	0.00	0.00
K05	4	30	30	104.3	30.52	1.00	2.58	0.00	0.00
K06	1	30	30	102.2	13.81	1.40	2.62	0.00	0.00
K06	2	30	30	103.1	12.89	1.40	2.62	0.00	0.00
K06	3	30	30	103.9	14.37	1.40	2.62	0.00	0.00
K06	4	30	30	94.4	15.61	1.40	2.62	0.00	0.00

Table C.1: Raw equilibrium results (continue)

Name	Rep.	V_{aq} (ml)	V_o (ml)	$[Ni]_f$ (mg/l)	$[Ni]_r$ (mg/l)	$[RH]_{Tot}$ (mol/l)	pH_r	$[H_2SO_4]$ (mol/m^3)	[NaOH] (mol/m^3)
K07	1	30	30	108.2	81.04	1.00	2.29	4.00	0.00
K07	2	30	30	106.8	77.66	1.00	2.28	4.00	0.00
K07	3	30	30	95.5	64.34	1.00	2.29	4.00	0.00
K07	4	30	30	95.5	64.01	1.00	2.29	4.00	0.00
K08	5	30	30	104.4	55.23	1.40	2.29	4.00	0.00
K08	6	30	30	102.7	50.80	1.40	2.27	4.00	0.00
K08	7	30	30	101.0	50.07	1.40	2.27	4.00	0.00
K08	8	30	30	91.2	50.25	1.40	2.27	4.00	0.00
K09	1	30	30	84.7	28.97	1.20	2.47	2.00	0.00
K09	2	30	30	84.3	33.38	1.20	2.49	2.00	0.00
K09	3	30	30	84.5	31.41	1.20	2.49	2.00	0.00
K09	4	30	30	84.2	34.11	1.20	2.49	2.00	0.00
K10	1	30	30	50.1	18.73	1.20	2.48	2.00	0.00
K10	2	30	30	55.0	13.91	1.20	2.48	2.00	0.00
K10	3	30	30	59.9	17.85	1.20	2.48	2.00	0.00
K10	4	30	30	47.0	17.35	1.20	2.48	2.00	0.00

C.3 Processed equilibrium results

The meaning of the titles as used inTable C.2 is as follow:

Name : A short name of the experiment

Vr : Volume ratio = V_{aq}/V_o

$[Ni]_f$: Concentration of the nickel in the feed solution (mol/m^3).

$\sigma([Ni]_f)$: Standard deviation of $[Ni]_f$.

$[Ni]_r$: Concentration of the nickel in the raffinate solution (mol/m^3).

$\sigma([Ni]_r)$: Standard deviation of $[Ni]_r$.

pH_r : Average pH of raffinate solution.

$\sigma(pH_r)$: Standard deviation of pH_r.

$a(H_r)$: Activity of hydronium ions in raffinate solution (mol/m^3).

$\gamma(Ni_r)$: Activity coefficient of the nickel in the raffinate solution.

$a(SO4_r)$: Activity of the Sulphate ions in raffinate solution (mol/m^3).

$\%E$: % extraction of nickel ions as calculated with Equation 4.13.

$\sigma(\%E)$: Standard deviation of $\%E$.

Table C.2: Processed equilibrium results

Name	Vr	$[Ni]_f$ (mol/m^3)	$\sigma([Ni]_f)$ (mol/m^3)	$[Ni]_r$ (mol/m^3)	$\sigma([Ni]_r)$ (mol/m^3)	pH_r	$\sigma(pH_r)$	$a(H_r)$ (mol/m^3)	$\gamma(Ni_r)$	$a(SO_{4,r})$ (mol/m^3)	$\%E$	$\sigma(\%E)$
S01	1.00	1.889	0.036	0.545	0.047	2.50	0.02	3.144	0.702	1.370	71.1	2.6
S02	1.00	1.869	0.020	0.591	0.034	2.51	0.00	3.108	0.702	1.372	68.3	1.8
S03	1.00	1.825	0.014	0.596	0.028	2.51	0.00	3.090	0.701	1.374	67.3	1.6
S04	1.00	1.860	0.022	0.570	0.027	2.51	0.01	3.090	0.703	1.363	69.3	1.5
S05	1.00	1.850	0.081	0.604	0.013	2.50	0.01	3.181	0.699	1.396	67.4	1.6
Stot	1.00	1.859	0.043	0.579	0.037	2.51	0.01	3.123	0.702	1.375	68.9	2.1
N01	0.50	1.982	0.030	0.255	0.013	2.64	0.02	2.278	0.747	0.996	87.2	0.7
N02	0.50	1.940	0.013	0.235	0.010	2.62	0.00	2.385	0.745	1.018	87.9	0.5
Ntot	0.50	1.961	0.031	0.245	0.015	2.63	0.02	2.331	0.746	1.007	87.5	0.8
T01	1.00	1.899	0.000	0.413	0.062	2.62	0.01	2.399	0.731	1.088	78.2	3.3
T02	1.00	1.899	0.000	0.392	0.057	2.66	0.00	2.188	0.735	0.994	79.4	3.0
T03	1.00	1.899	0.000	0.374	0.050	2.65	0.05	2.226	0.734	0.940	80.3	2.6
T04	1.00	1.791	0.030	0.361	0.031	2.67	0.04	2.150	0.737	0.857	79.9	1.7
T05	1.00	1.774	0.016	0.381	0.009	2.67	0.05	2.138	0.743	1.015	78.5	0.5
Ttot	1.00	1.852	0.052	0.384	0.044	2.65	0.04	2.220	0.736	0.979	79.3	2.4
R01	0.50	1.934	0.029	1.686	0.026	2.44	0.02	3.610	0.644	1.922	12.8	1.9
R02	0.50	1.974	0.025	1.056	0.025	2.49	0.02	3.273	0.676	1.600	46.5	1.4
R03	0.50	1.899	0.023	0.626	0.045	2.55	0.01	2.851	0.707	1.317	67.0	2.4
R04	0.50	1.883	0.040	0.381	0.036	2.60	0.01	2.497	0.731	1.122	79.8	2.0
R05	0.50	1.892	0.074	0.160	0.007	2.68	0.01	2.101	0.762	0.886	91.6	0.5
R06	0.50	1.913	0.034	0.106	0.001	2.70	0.01	1.984	0.771	0.827	94.5	0.1
F01	1.00	1.502	0.019	0.465	0.035	2.50	0.01	3.144	0.707	1.335	69.0	2.3

Table C.2: Processed equilibrium results (continue)

Name	Vr	$[Ni]_f$ (mol/m^3)	$\sigma([Ni]_f)$ (mol/m^3)	$[Ni]_r$ (mol/m^3)	$\sigma([Ni]_r)$ (mol/m^3)	pH_r	$\sigma(pH_r)$	$a(H_r)$ (mol/m^3)	$\gamma(Ni_r)$	$a(SO_{4,r})$ (mol/m^3)	%E	σ(%E)
F02	1.00	1.116	0.027	0.308	0.026	2.56	0.00	2.770	0.728	1.154	72.4	2.4
F03	1.00	0.722	0.014	0.166	0.016	2.67	0.02	2.150	0.760	0.904	77.0	2.2
F04	1.00	0.336	0.008	0.065	0.010	2.67	0.01	2.126	0.769	0.849	80.5	3.2
V01	0.67	2.006	0.057	0.404	0.034	2.59	0.00	2.570	0.727	1.149	79.9	1.8
V02	1.00	1.932	0.138	0.566	0.009	2.53	0.01	2.934	0.707	1.325	70.7	2.1
V03	2.00	1.747	0.068	0.556	0.044	2.57	0.01	2.723	0.714	1.253	68.2	2.8
V04	5.00	1.708	0.113	0.938	0.140	2.64	0.01	2.291	0.703	1.319	45.1	8.9
P01	1.00	1.871	0.060	0.423	0.019	2.71	0.01	1.935	0.725	1.179	77.4	1.2
P02	1.00	1.733	0.037	0.169	0.003	2.93	0.02	1.175	0.773	0.818	90.3	0.3
P03	1.00	1.793	0.035	0.476	0.021	2.56	0.01	2.770	0.717	1.233	73.4	1.3
P04	1.00	1.830	0.046	0.780	0.013	2.44	0.01	3.631	0.626	2.202	57.4	1.3
P05	1.00	1.864	0.047	1.079	0.027	2.31	0.02	4.936	0.644	1.970	42.1	2.1
P06	1.00	1.776	0.046	1.437	0.101	2.14	0.00	7.286	0.582	2.801	19.1	6.1
P07	1.00	1.701	0.015	1.490	0.047	2.04	0.01	9.226	0.555	3.207	12.4	2.9
P08	1.00	1.851	0.014	0.375	0.021	2.69	0.01	2.030	0.726	1.182	79.7	1.2
P09	1.00	1.838	0.042	0.391	0.025	2.70	0.01	1.980	0.717	1.273	78.7	1.4
P10	1.00	1.979	0.056	0.246	0.061	2.81	0.01	1.558	0.681	1.739	87.6	3.1
K01	1.00	0.621	0.049	0.109	0.007	2.72	0.01	1.916	0.775	0.800	82.4	1.8
K02	1.00	0.860	0.034	0.101	0.007	2.71	0.01	1.939	0.774	0.810	88.3	0.9
K03	1.00	0.638	-	0.436	-	2.29	0.00	5.099	0.664	1.788	31.7	-
K04	1.00	0.690	0.008	0.284	0.007	2.35	0.01	4.441	0.646	2.074	58.8	1.1
K05	1.00	1.797	0.019	0.498	0.028	2.59	0.01	2.570	0.721	1.193	72.3	1.6
K06	1.00	1.719	0.075	0.241	0.019	2.62	0.00	2.399	0.744	1.020	86.0	1.3
K07	1.00	1.729	0.118	1.222	0.151	2.29	0.00	5.158	0.621	2.276	29.3	10.0
K08	1.00	1.700	0.101	0.879	0.042	2.28	0.01	5.309	0.631	2.171	48.3	3.9
K09	1.00	1.438	0.004	0.544	0.039	2.49	0.01	3.273	0.701	1.388	62.1	2.7
K10	1.00	0.903	0.096	0.306	0.012	2.48	0.00	3.311	0.712	1.303	66.1	3.8

C.4 Raw pressure drop results

The meaning of the titles used in Table C.3 are the following:

Temp. : Temperature (˚C)
Flow rate : Measured flow rate through reactor (l/hr)
P in : Inlet pressure (kPa)
P out : Outlet pressure (kPa)

Table C.3: Raw pressure drop results

Temp. (˚C)	Flow rate (l/hr)	P in (kPa)	P out (kPa)
30	100	12	0
30	150	20	0
30	200	33	0
30	250	52	1
30	300	82	3
40	100	12	0
40	150	19	0
40	200	28	0
40	250	50	0
40	300	73	1
50	100	13	0
50	150	19	0
50	200	25	0
50	250	42	0
50	300	68	0
60	100	11	0
60	150	16	0
60	200	26	0
60	250	44	1
60	300	71	2
60	330	96	4
35	250	54	0
35	300	84	2
35	350	103	4
40	100	13	0
40	150	25	0
40	200	35	0
40	250	51	0
40	300	80	2
40	340	103	5
50	100	13	0
50	150	25	0
50	200	34	0
50	250	47	1
50	300	77	3
50	350	107	5
60	100	12	0
60	150	18	0
60	200	29	0
60	250	44	1
60	300	78	2
60	330	102	5

Table C.3: Raw pressure drop results (continue)

Temp. (˚C)	Flow rate (l/hr)	P in (kPa)	P out (kPa)
70	100	9	0
70	150	16	0
70	200	27	1
70	250	42	3
70	300	72	4
70	330	101	6
35	100	14	0
35	150	23	0
35	200	36	0
30	250	58	1
30	300	85	2
30	365	111	5
40	100	14	0
40	150	23	0
40	200	37	0
40	250	53	1
40	300	83	2
40	365	108	5
50	100	12	0
50	150	21	0
50	200	32	0
50	250	47	1
50	300	75	2
50	360	108	4
70	100	12	0
70	150	18	0
70	200	28	1
70	250	48	2
70	300	75	3
70	350	100	5
30	100	19	0
30	150	26	0
30	200	39	0
30	200	38	0
30	250	57	1
30	300	85	2
30	365	110	3
40	100	14	0
40	150	25	0
40	200	37	0
40	250	55	0
40	300	82	2
40	370	109	3
50	100	13	0
50	150	23	0
50	200	33	0
50	250	48	1
50	300	77	2

Table C.3: Raw pressure drop results (continue)

Temp. (˚C)	Flow rate (l/hr)	P in (kPa)	P out (kPa)
60	100	13	0
60	150	19	0
60	200	29	0
60	250	42	0.5
60	300	76.5	2
60	355	108	4.5
70	100	11.5	0
70	150	19	0
70	200	27	0
70	250	44	0.5
70	300	77	2
70	355	105	4
30	100	17	0
30	150	27	0
50	365	108	2.5
60	100	13	0
60	150	22.5	0
60	200	30.5	0.5
60	250	45	1.5
60	300	76	2.5
60	365	106	4
70	100	12.5	0
70	150	22	0
70	200	29	1.5
70	250	45	2
70	300	77.5	3
70	360	102	2

C.5 Processed pressure drop results

The meaning of the titles used in Table C.4 are the following:

Temp : Temperature (K)

ρ : Density of water (kg/m^3)

μ : Viscosity of water

F : Flow rate (l/hr)

v: : Flow velocity (m/s)

Re : Reynolds number

ΔP : Pressure drop (kPa)

ΔP_{theo} : Theoretical pressure drop (kPa)

f : Fanning friction factor

f_{theo} : Theoretical Fanning friction factor

τ_w : Shear stress at wall (N/m^2)

$\tau_{w,theo}$: Theoretical shear stress at wall (N/m^2)

Table C.4: Processed pressure drop results

Temp (K)	ρ (kg/m^3)	μ (mPa·s)	F (l/hr)	v (m/s)	Re	ΔP (kPa)	ΔP_{theo} (kPa)	f	f_{theo}	τ_w (N/m^2)	$\tau_{w,theo}$ (N/m^2)
303	996	0.812	92	0.565	416	12.0	12.2	0.0377	0.0384	6.0	6.1
303	996	0.812	137	0.848	624	20.0	18.4	0.0279	0.0256	10.0	9.2
303	996	0.812	183	1.131	832	33.0	24.5	0.0259	0.0192	16.5	12.2
303	996	0.812	229	1.414	1041	51.5	30.6	0.0259	0.0154	25.8	15.3
303	996	0.812	275	1.696	1249	79.0	36.7	0.0276	0.0128	39.5	18.4
303	996	0.812	92	0.565	416	19.0	12.2	0.0597	0.0384	9.5	6.1
303	996	0.812	137	0.848	624	25.5	18.4	0.0356	0.0256	12.8	9.2
303	996	0.812	183	1.131	832	38.5	24.5	0.0302	0.0192	19.3	12.2
303	996	0.812	229	1.414	1041	56.5	30.6	0.0284	0.0154	28.3	15.3
303	996	0.812	275	1.696	1249	83.0	36.7	0.0290	0.0128	41.5	18.4
303	996	0.812	334	2.064	1519	106.0	44.7	0.0250	0.0105	53.0	22.3
303	996	0.812	92	0.565	416	17.0	12.2	0.0534	0.0384	8.5	6.1
303	996	0.812	137	0.848	624	27.0	18.4	0.0377	0.0256	13.5	9.2
303	996	0.812	183	1.131	832	38.0	24.5	0.0298	0.0192	19.0	12.2
303	996	0.812	229	1.414	1041	56.0	30.6	0.0281	0.0154	28.0	15.3
303	996	0.812	275	1.696	1249	82.5	36.7	0.0288	0.0128	41.3	18.4
303	996	0.812	334	2.064	1519	107.5	44.7	0.0253	0.0105	53.8	22.3
308	994	0.736	91	0.565	457	14.0	11.1	0.0442	0.0350	7.0	5.5
308	994	0.736	137	0.847	686	23.0	16.6	0.0322	0.0233	11.5	8.3
308	994	0.736	183	1.130	915	36.0	22.2	0.0284	0.0175	18.0	11.1
308	994	0.736	229	1.412	1144	54.0	27.7	0.0273	0.0140	27.0	13.9
308	994	0.736	274	1.694	1372	82.0	33.3	0.0287	0.0117	41.0	16.6
308	994	0.736	320	1.977	1601	99.0	38.8	0.0255	0.0100	49.5	19.4

Table C.4: Processed pressure drop results (continue)

Temp (K)	ρ (kg/m^3)	μ (mPa·s)	F (l/hr)	v (m/s)	Re	ΔP (kPa)	ΔP_{theo} (kPa)	f	f_{theo}	τ_w (N/m^2)	$\tau_{w,theo}$ (N/m^2)
313	991	0.669	91	0.564	501	12.0	10.1	0.0380	0.0319	6.0	5.0
313	991	0.669	137	0.846	752	18.5	15.1	0.0261	0.0213	9.3	7.6
313	991	0.669	183	1.128	1002	28.0	20.1	0.0222	0.0160	14.0	10.1
313	991	0.669	228	1.410	1253	50.0	25.2	0.0254	0.0128	25.0	12.6
313	991	0.669	274	1.692	1504	72.0	30.2	0.0254	0.0106	36.0	15.1
313	991	0.669	91	0.564	501	13.0	10.1	0.0412	0.0319	6.5	5.0
313	991	0.669	137	0.846	752	25.0	15.1	0.0352	0.0213	12.5	7.6
313	991	0.669	183	1.128	1002	35.0	20.1	0.0277	0.0160	17.5	10.1
313	991	0.669	228	1.410	1253	51.0	25.2	0.0259	0.0128	25.5	12.6
313	991	0.669	274	1.692	1504	78.0	30.2	0.0275	0.0106	39.0	15.1
313	991	0.669	310	1.918	1704	98.5	34.2	0.0270	0.0094	49.3	17.1
313	991	0.669	91	0.564	501	14.0	10.1	0.0444	0.0319	7.0	5.0
313	991	0.669	137	0.846	752	23.0	15.1	0.0324	0.0213	11.5	7.6
313	991	0.669	183	1.128	1002	36.5	20.1	0.0289	0.0160	18.3	10.1
313	991	0.669	228	1.410	1253	52.5	25.2	0.0266	0.0128	26.3	12.6
313	991	0.669	274	1.692	1504	80.5	30.2	0.0284	0.0106	40.3	15.1
313	991	0.669	333	2.059	1829	103.0	36.8	0.0245	0.0087	51.5	18.4
313	991	0.669	91	0.564	501	14.0	10.1	0.0444	0.0319	7.0	5.0
313	991	0.669	137	0.846	752	25.0	15.1	0.0352	0.0213	12.5	7.6
313	991	0.669	183	1.128	1002	37.0	20.1	0.0293	0.0160	18.5	10.1
313	991	0.669	228	1.410	1253	54.5	25.2	0.0276	0.0128	27.3	12.6
313	991	0.669	274	1.692	1504	80.0	30.2	0.0282	0.0106	40.0	15.1
313	991	0.669	338	2.087	1854	106.0	37.3	0.0245	0.0086	53.0	18.6
323	986	0.559	91	0.563	596	12.5	8.4	0.0400	0.0268	6.3	4.2
323	986	0.559	137	0.844	894	19.0	12.6	0.0270	0.0179	9.5	6.3
323	986	0.559	182	1.126	1192	25.0	16.8	0.0200	0.0134	12.5	8.4
323	986	0.559	228	1.407	1490	42.0	21.0	0.0215	0.0107	21.0	10.5

Table C.4: Processed pressure drop results (continue)

Temp (K)	ρ (kg/m^3)	μ (mPa·s)	F (l/hr)	v (m/s)	Re	ΔP (kPa)	ΔP_{theo} (kPa)	f	f_{theo}	τ_w (N/m^2)	$\tau_{w,theo}$ (N/m^2)
323	986	0.559	273	1.688	1789	68.0	25.2	0.0242	0.0089	34.0	12.6
323	986	0.559	91	0.563	596	13.0	8.4	0.0416	0.0268	6.5	4.2
323	986	0.559	137	0.844	894	25.0	12.6	0.0356	0.0179	12.5	6.3
323	986	0.559	182	1.126	1192	34.0	16.8	0.0272	0.0134	17.0	8.4
323	986	0.559	228	1.407	1490	46.5	21.0	0.0238	0.0107	23.3	10.5
323	986	0.559	273	1.688	1789	74.5	25.2	0.0265	0.0089	37.3	12.6
323	986	0.559	319	1.970	2087	102.5	29.3	0.0268	0.0077	51.3	14.7
323	986	0.559	91	0.563	596	11.5	8.4	0.0368	0.0268	5.8	4.2
323	986	0.559	137	0.844	894	21.0	12.6	0.0299	0.0179	10.5	6.3
323	986	0.559	182	1.126	1192	32.0	16.8	0.0256	0.0134	16.0	8.4
323	986	0.559	228	1.407	1490	46.5	21.0	0.0238	0.0107	23.3	10.5
323	986	0.559	273	1.688	1789	73.0	25.2	0.0260	0.0089	36.5	12.6
323	986	0.559	328	2.026	2146	104.0	30.2	0.0257	0.0075	52.0	15.1
323	986	0.559	91	0.563	596	13.0	8.4	0.0416	0.0268	6.5	4.2
323	986	0.559	137	0.844	894	23.0	12.6	0.0327	0.0179	11.5	6.3
323	986	0.559	182	1.126	1192	33.0	16.8	0.0264	0.0134	16.5	8.4
323	986	0.559	228	1.407	1490	47.5	21.0	0.0243	0.0107	23.8	10.5
323	986	0.559	273	1.688	1789	75.0	25.2	0.0267	0.0089	37.5	12.6
323	986	0.559	332	2.054	2176	105.5	30.6	0.0253	0.0074	52.8	15.3
333	982	0.471	91	0.561	701	11.0	7.1	0.0356	0.0228	5.5	3.5
333	982	0.471	136	0.842	1052	16.0	10.6	0.0230	0.0152	8.0	5.3
333	982	0.471	182	1.123	1403	26.0	14.1	0.0210	0.0114	13.0	7.1
333	982	0.471	227	1.403	1753	43.5	17.6	0.0225	0.0091	21.8	8.8
333	982	0.471	273	1.684	2104	69.0	21.2	0.0248	0.0076	34.5	10.6
333	982	0.471	300	1.852	2314	92.0	23.3	0.0273	0.0069	46.0	11.6
333	982	0.471	91	0.561	701	12.0	7.1	0.0388	0.0228	6.0	3.5
333	982	0.471	136	0.842	1052	18.0	10.6	0.0259	0.0152	9.0	5.3
333	982	0.471	182	1.123	1403	29.0	14.1	0.0234	0.0114	14.5	7.1

Table C.4: Processed pressure drop results (continue)

Temp (K)	ρ (kg/m^3)	μ (mPa·s)	F (l/hr)	v (m/s)	Re	ΔP (kPa)	ΔP_{theo} (kPa)	f	f_{theo}	τ_w (N/m^2)	$\tau_{w,theo}$ (N/m^2)
333	982	0.471	227	1.403	1753	43.0	17.6	0.0222	0.0091	21.5	8.8
333	982	0.471	273	1.684	2104	76.5	21.2	0.0275	0.0076	38.3	10.6
333	982	0.471	300	1.852	2314	97.0	23.3	0.0288	0.0069	48.5	11.6
333	982	0.471	91	0.561	701	13.0	7.1	0.0420	0.0228	6.5	3.5
333	982	0.471	136	0.842	1052	19.0	10.6	0.0273	0.0152	9.5	5.3
333	982	0.471	182	1.123	1403	29.0	14.1	0.0234	0.0114	14.5	7.1
333	982	0.471	227	1.403	1753	41.5	17.6	0.0215	0.0091	20.8	8.8
333	982	0.471	273	1.684	2104	74.5	21.2	0.0268	0.0076	37.3	10.6
333	982	0.471	323	1.993	2490	103.5	25.1	0.0266	0.0064	51.8	12.5
333	982	0.471	91	0.561	701	13.0	7.1	0.0420	0.0228	6.5	3.5
333	982	0.471	136	0.842	1052	22.5	10.6	0.0323	0.0152	11.3	5.3
333	982	0.471	182	1.123	1403	30.0	14.1	0.0242	0.0114	15.0	7.1
333	982	0.471	227	1.403	1753	43.5	17.6	0.0225	0.0091	21.8	8.8
333	982	0.471	273	1.684	2104	73.5	21.2	0.0264	0.0076	36.8	10.6
333	982	0.471	332	2.049	2560	102.0	25.8	0.0248	0.0063	51.0	12.9
343	976	0.402	91	0.560	817	9.0	6.0	0.0294	0.0196	4.5	3.0
343	976	0.402	136	0.840	1225	16.0	9.0	0.0232	0.0131	8.0	4.5
343	976	0.402	181	1.120	1633	26.0	12.0	0.0212	0.0098	13.0	6.0
343	976	0.402	227	1.400	2042	39.5	15.0	0.0206	0.0078	19.8	7.5
343	976	0.402	272	1.680	2450	68.0	18.0	0.0247	0.0065	34.0	9.0
343	976	0.402	299	1.848	2695	95.0	19.8	0.0285	0.0059	47.5	9.9
343	976	0.402	91	0.560	817	11.5	6.0	0.0376	0.0196	5.8	3.0
343	976	0.402	136	0.840	1225	18.0	9.0	0.0261	0.0131	9.0	4.5
343	976	0.402	181	1.120	1633	27.5	12.0	0.0225	0.0098	13.8	6.0
343	976	0.402	227	1.400	2042	46.5	15.0	0.0243	0.0078	23.3	7.5
343	976	0.402	272	1.680	2450	72.5	18.0	0.0263	0.0065	36.3	9.0

Table C.4: Processed pressure drop results (continue)

Temp (K)	ρ (kg/m^3)	μ (mPa·s)	F (l/hr)	v (m/s)	Re	ΔP (kPa)	ΔP_{theo} (kPa)	f	f_{theo}	τ_w (N/m^2)	$\tau_{w,theo}$ (N/m^2)
343	976	0.402	317	1.960	2858	95.0	21.0	0.0253	0.0056	47.5	10.5
343	976	0.402	91	0.560	817	11.5	6.0	0.0376	0.0196	5.8	3.0
343	976	0.402	136	0.840	1225	19.0	9.0	0.0276	0.0131	9.5	4.5
343	976	0.402	181	1.120	1633	27.0	12.0	0.0221	0.0098	13.5	6.0
343	976	0.402	227	1.400	2042	43.5	15.0	0.0227	0.0078	21.8	7.5
343	976	0.402	272	1.680	2450	75.0	18.0	0.0272	0.0065	37.5	9.0
343	976	0.402	322	1.988	2899	101.0	21.3	0.0262	0.0055	50.5	10.6
343	976	0.402	91	0.560	817	12.5	6.0	0.0408	0.0196	6.3	3.0
343	976	0.402	136	0.840	1225	22.0	9.0	0.0319	0.0131	11.0	4.5
343	976	0.402	181	1.120	1633	27.5	12.0	0.0225	0.0098	13.8	6.0
343	976	0.402	227	1.400	2042	43.0	15.0	0.0225	0.0078	21.5	7.5
343	976	0.402	272	1.680	2450	74.5	18.0	0.0270	0.0065	37.3	9.0
343	976	0.402	326	2.016	2940	100.0	21.6	0.0252	0.0054	50.0	10.8

C.6 Pressure drop regressions

The regression results of Equation 4.47 for each of the experimental temperatures are shown in this section. The value of a_0 is the theoretical value for laminar flow and was calculated. The value of a_1 were calculated with the Levenberg-Marquart nonlinear regression method. The meaning of the titles as used in Table C.5 are the following:

Temp : Temperature (K)
a_0 : Theoretical value of a_0 (N/m^2) in Equation 4.47.
a_1 : Regressed value of a_1 calculated from experimental data (N/m^2).
SE(a_1) : Standard error of a_1 (N/m^2).
r^2 : Correlation coefficient for regression.

Table C.5: Regression results for shear stress coefficients

Temp (K)	a_0 (N/m^2)	a_1 (N/m^2)	SE(a_1) (N/m^2)	r^2
303	0.01471	9.81×10^{-9}	0.37×10^{-9}	0.949
308	0.01212	8.04×10^{-9}	0.43×10^{-9}	0.965
313	0.01005	6.17×10^{-9}	0.19×10^{-9}	0.952
323	0.0070	3.90×10^{-9}	0.08×10^{-9}	0.977
333	0.0050	2.62×10^{-9}	0.06×10^{-9}	0.971
343	0.0037	1.71×10^{-9}	0.04×10^{-9}	0.973

List of Tables

Appendix D

Computer programs

Contents

D.1 Introduction

The code of all the computer programs that were specifically written for this investigation are given in this appendix. The general philosophy of each program together with a flow diagram are given, as well as the Delphy (Visual Pascal) code.

D.2 Simplex method

D.2.1 Background

There is many non-linear regression programs available on the market today, but they all have some shortcomings and is usually not suitable for specialised applications. Some of the shortcomings are:

- They cannot solve systems of equations
- The input function must be in a certain form
- They cannot solve equations with differentials or integrals

The simplex method was developed by Nelder and Mead (1965) and is based on the comparison of the objective function values at the (n + 1) vertices of a general simplex (in n dimensions) and moving the simplex towards the optimum point (Jacoby *et al.*, 1972:79). This movement is achieved by three basic operations:

1. Reflection: x^h is replaced by

$$x^r = 2 \cdot x^0 - x^h \tag{D.1}$$

2. Contraction: The simplex is contracted:

$$x^c = 0.5 \cdot x^h + 0.5 \cdot x^0 \tag{D.2}$$

3. Expansion: x^r is expanded in the direction along which a further improvement of the function value may be expected:

$$x^e = 2 \cdot x^r - x^0 \tag{D.3}$$

The following notation is used in the equations:

x^h : This is the vertex corresponding to the highest value of the objective function:

$$M\left(x^h\right) = \max_i\left(x^i\right), \quad i = 1, 2, \ldots, (n+1) \tag{D.4}$$

x^s : This is the vertex with the second highest value of M.

x^l : This is the vertex with the lowest value of M.

x^0 : This is the centroid of all x^i except $i = h$, given by

$$x^0 = \frac{1}{n}\sum_{\substack{i=1\\ i\neq h}}^{n+1} x^i \tag{D.5}$$

The first step is to estimate a minimum $x^l = (x_1, x_2, ..., x_n)$. The next step is to form an initial simplex, using two auxiliary values p_n and q_n:

$$\begin{aligned} p_n &= \frac{\sqrt{n+1} - 1 + n}{n \cdot \sqrt{2}} \cdot S \\ q_n &= \frac{\sqrt{n+1} - 1}{n \cdot \sqrt{2}} \cdot S \end{aligned} \tag{D.6}$$

where S is a scaling factor (the estimate for x^l is usually used) . The n+1 vertices of a regular simplex with edge of length S are given by:

$$\begin{aligned} x^1 &= (x_1,\ x_2,\ ...,\ x_n)^T \\ x^2 &= (p_n + x_1,\ q_n + x_2,\ q_n + x_3,\ ...\ ,q_n + x_n)^T \\ x^3 &= (q_n + x_1,\ p_n + x_2,\ q_n + x_3,\ ...\ ,q_n + x_n)^T \\ x^4 &= (q_n + x_1,\ q_n + x_2,\ p_n + x_3,\ ...\ ,q_n + x_n)^T \\ &\cdot \\ &\cdot \\ &\cdot \\ x^{n+1} &= (q_n + x_1,\ q_n + x_2,\ q_n + x_3,\ ...\ ,p_n + x_n)^T \end{aligned} \tag{D.7}$$

The construction of the initial simplex assures that its vertices span the full n-dimensional space.

To test for convergence, the standard deviation of the function at the (n +1) vertices of the current simplex is compared with some preselected tolerance ζ > 0:

$$\left\{\sum_{i=1}^{n+1}\frac{\left[M\left(x^{i}\right)-M\left(x^{0}\right)\right]^{2}}{n}\right\}^{\frac{1}{2}}\leq\zeta \tag{D.8}$$

The process is terminated if Equation D.8 is satisfied.

D.2.2 Flow diagram

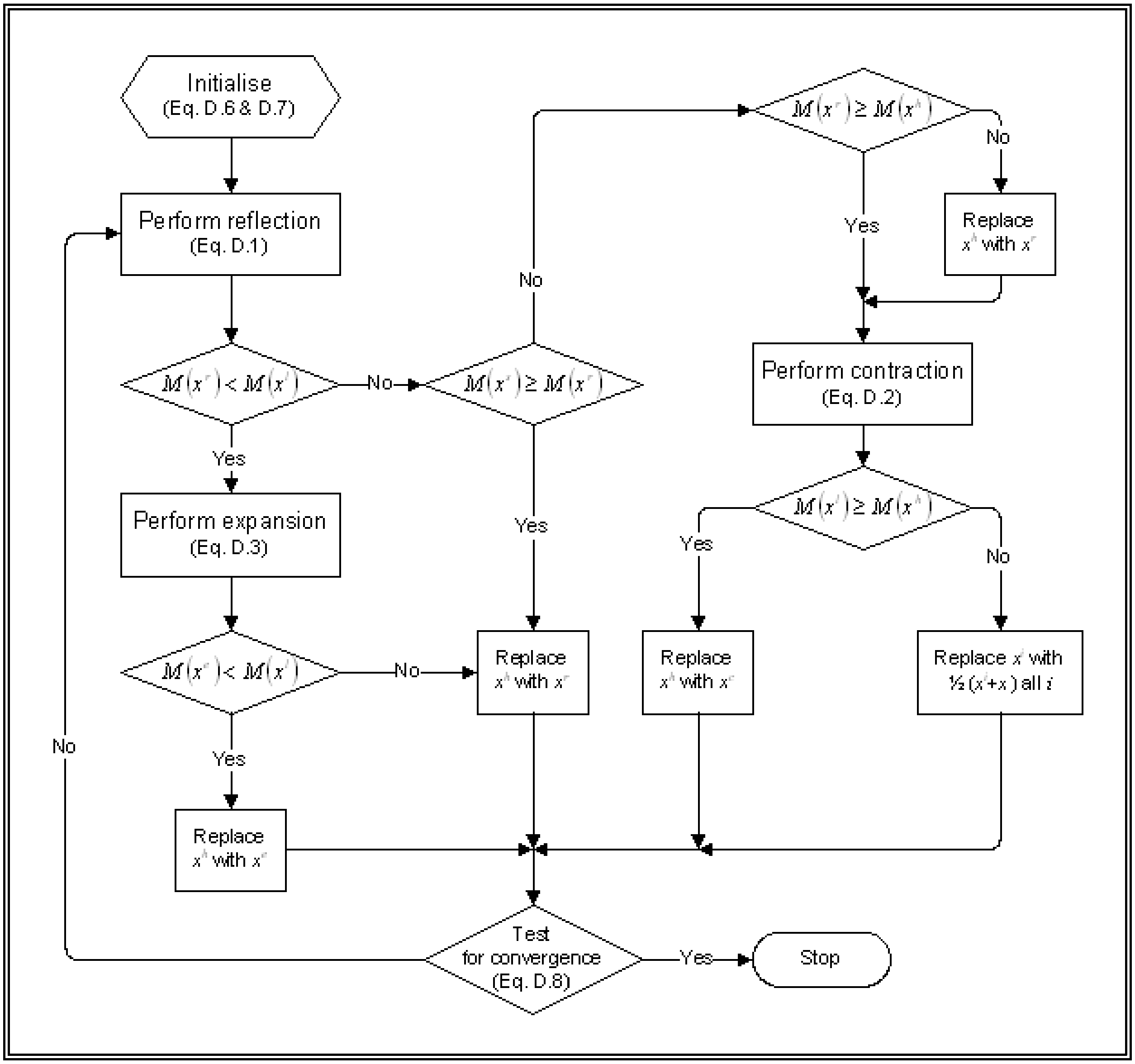

Fig. D.1: Flow diagram of the Simplex method

D.2.3 Code

In the code that follows the value of the M function is minimised.

```
procedure Simplex;
Var
            i,j : Integer;
            h, s, l  : Integer;
            High, Sec, low, sum, tsi : Double;
            Mx : Array[0..n+1] of Double;
            Mxr, Mxe, Mxc : Double;
begin


  Repeat
    For i := 0 to n+1 do
      Mx[i] := M(x[i]);

    High := 0;
    Sec := 0;
    low := Mx[0];
    l := 0;
    h := 0;
    s:=0;
    i := 0;
    Repeat
      If Mx[i] > high then
        Begin
          high := Mx[i];
          h := i;
          i := -1;
        End
      Else
        If (Mx[i] > sec) and (Mx[i] < high) then
          Begin
            sec := Mx[i];
            s := i;
            i := -1;
          end
        Else
          If Mx[i] < low then
              Begin
                  low := Mx[i];
                  l := i;
                  i := -1;
              end;
      i := i+1;
  Until i > n+1;

{Calculate centerpoint without h}
    for i := 0 to n do
      Begin
```

```
        sum := 0;
        for j := 0 to (n+1) do
          If j <> h then
            sum := sum + x[j,i];
        x0[i] := sum/(n+1);
      end;

{Perform reflection}
    for i := 0 to n do
      xr[i] := 2*x0[i] - x[h,i];
    Mxr := M(xr);
    If Mxr < Mx[l] then
      Begin {yes}
{Expansion}
        For i := 0 to n do
          xe[i] := 2*xr[i] - x0[i];
        Mxe := M(xe);
        If Mxe < Mx[l] then
          Begin
            for i := 0 to n do
              x[h,i] := xe[i];
          End
        Else
          Begin
            for i := 0 to n do
              x[h,i] := xr[i];
          end;
      End

    Else {no}
      Begin
        If Mx[s] >= Mxr then
          Begin
            for i := 0 to n do
              x[h,i] := xr[i];
          end
        Else
          Begin
            If Mxr < Mx[h] then
              Begin  {no no. 2}
                for i := 0 to n do
                  x[h,i] := xr[i];
              End;
{Contraction}
          for i := 0 to n do
            xc[i] := 0.5*x[h,i] + 0.5*x0[i];
          Mxc := M(xc);
          If Mxc < Mx[h] then
             Begin
                for i := 0 to n do
                  x[h,i] := xc[i];
              End
            Else
```

```
       Begin
        for j := 0 to (n+1) do
         for i := 0 to n do
          x[j,i] := 0.5*(x[j,i]+x[l,i]);
       End;
     End;
   End;
  tsi := 0;
  for i := 0 to (n+1) do
   tsi := tsi + sqr (Mx[i]-Mx[0]);
  tsi := sqrt (tsi/(n+1));

 Until tsi < con;

end;
```

D.3 The Quasi-Newton method

D.3.1 Background

The Quasi-Newton method is part of a larger group of optimisation methods known as steepest decent techniques (Jacoby *et al.*, 1972:117). The method usually reach the optimum value faster than the simplex method, but the method tends to be more unstable. The method is a second-order gradient technique and uses the Hessian matrix, Hess(x), in computing the local steepest decent direction. The Hessian matrix for the objective function (M (x)) is defined as follow:

$$\mathrm{Hess}(x) = \begin{bmatrix} h_{11} & \cdots & h_{1n} \\ \cdots & \cdots & \cdots \\ h_{n1} & \cdots & h_{nn} \end{bmatrix} \qquad \text{with} \quad h_{ij} = \frac{\partial^2 M(x)}{\partial x_i \, \partial x_j} \tag{D.9}$$

The direction of steepest decent (s) is then calculated with the following equation:

$$s = -\left[\mathrm{Hess}(x)\right]^{-1} \cdot \nabla M(x) \tag{D.10}$$

Once the direction of steepest decent has been determined, the next step is to calculate the decent steplength (λ). The decent steplength is defined as the distance in the direction of steepest decent ($x + \lambda \cdot s$), at which point $M(\lambda)$, assumes its minimum. This minimum is reached if the first order differential of M in the direction of s is equal to 0:

$$\frac{d\,M(\lambda)}{d\,\lambda} = \left[\nabla M(x + \lambda \cdot s)\right]^T \cdot s \tag{D.11}$$

D.3.2 Flow diagram

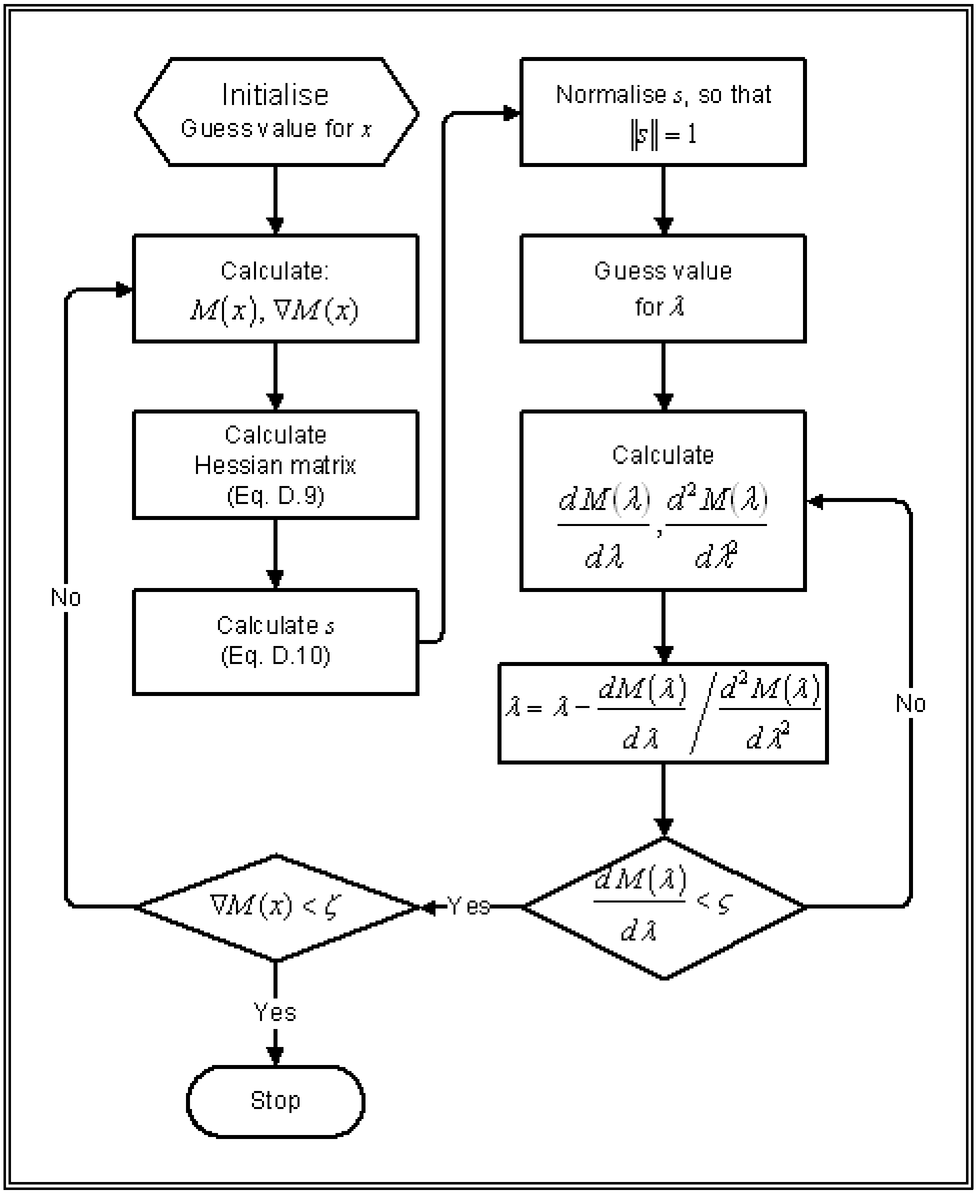

Fig. D.2: Flow diagram for the Quasi-Newton method

D.3.3 Code

In the code that follows the value of the M function is minimised.

```
procedure QuasiNewton;
Var
            dM, xc1, xc2, xc3, xs  : Array [0..n] of double;
            Hes, Hcalc, Hesinv : array[0..n,0..n] of double;
            dM2, fgj, abss, absM, absdx, xhold,  delk, tau, lamb, lamb0, dMl,
            d2Ml, Mc1, Mc2, Mc3, M0hold, Ml0, Ml0hold, dlamb : double;
            i, j, k : integer;
Begin
  tau := TSS*convqn;

{initilase}
  for i := 0 to n do
    for j := 0 to n do
      Begin
        Hes[i,j] := 0;
        If (i=j) then Hesinv[i,j] := 1
        Else Hesinv[i,j] := 0;
      end;

  M0 := M(x0);
  telregr := 0;
  Repeat
    telregr := telregr + 1;
{calculate dMdx and Hessian}
    for i := 0 to n do
      Begin
        For j := 0 to n do
          Begin
            xc2[j] := x0[j];
            if (i = j) then
              Begin
                xc1[j] := x0[j]*(1-1e-5);
                xc3[j] := x0[j]*(1+1e-5);
              end
            Else
              begin
                xc1[j] := x0[j];
                xc3[j] := x0[j];
              end;
          end;
        Mc1 := M(xc1);
        Mc2 := M(xc2);
        Mc3 := M(xc3);
        dM[i] := (Mc3-Mc2)/(x0[i]*1e-5);
        Hes[i,i] := (Mc1 -2*Mc2 + Mc3)/(sqr(x0[i]*1e-5));
      end;
```

```
  for i := 0 to (n-1) do
   Begin
    For j := (i+1) to n do
     Begin
      For k := 0 to n do
       Begin
        If (k = i) then
         xc1[k] := x0[k]*(1+1e-5)
        Else
         xc1[k] := x0[k];
        If (k = j) then
         xc2[k] := xc1[k]*(1+1e-5)
        Else
         xc2[k] := xc1[k];
       end;
      Mc1  := M(xc1);
      Mc2  := M(xc2);
      dM2  := (Mc2-Mc1)/(x0[j]*1e-5);
      Hes [i,j] := (dM2-dM[j])/(x0[i]*1e-5);
      Hes [j,i] := Hes[i,j];
     end;
   end;

{calculate inverse Hessian}
  for i := 0 to n do
   for j := 0 to n do
    Hcalc [i,j] := Hes[i,j];

{Guass Jordan elimination}
   for i := 0 to (n-1) do
    for j := (i+1) to (n) do
     Begin
      fgj := Hcalc[j,i]/Hcalc[i,i];
      for k := 0 to n do
       Begin
        Hcalc [j,k] := Hcalc[j,k] - fgj*Hcalc[i,k];
        Hesinv [j,k] := Hesinv[j,k] - fgj*Hesinv[i,k];
       end;
     end;
   for i := 0 to n do
    Begin
     fgj := 1/Hcalc[i,i];
     for k := 0 to n do
      Begin
       Hcalc [i,k] := fgj*Hcalc [i,k];
       Hesinv [i,k] := fgj*Hesinv[i,k];
      end;
    end;

   for i := 0 to (n-1) do
    for j := (i+1) to n do
     Begin
      fgj := Hcalc[(n-j),(n-i)]/Hcalc[(n-i),(n-i)];
```

```
          for k := 0 to n do
            Begin
              Hcalc [(n-j),k] := Hcalc[(n-j),k] - fgj*Hcalc[(n-i),k];
              Hesinv [(n-j),k] := Hesinv[(n-j),k] - fgj*Hesinv[(n-i),k];
            end;
        end;

{calculate xs}
     abss := 0;
     for i := 0 to n do
       Begin
         xs[i] := 0;
         for j := 0 to n do
            xs[i] := xs[i] + Hesinv[i,j]*dM[j];

         abss := abss + sqr(xs[i]);
       end;
     abss := sqrt(abss);
     for i := 0 to n do
       xs[i] := xs[i]/abss;

{calculate normalised derivative in decent direction}
     xhold := 0;
     For i := 0 to n do
       xhold := xhold + xs[i]*dM[i];

     absM := 0;
     for i := 0 to n do
       absM :=absM + sqr(dM[i]);
     absM := sqrt(absM);

     delk := abs (xhold)/absM;


     If xhold >= 0 then
       For i := 0 to n do
         xs[i] := -1*xs[i];

{Find minimum in direction of xs}
     lamb := abss;
     Ml0 := 0;
     Repeat
       dlamb := 1e-5*lamb;
       For i := 0 to n do
         Begin
           xc1[i] := x0[i]+(lamb-dlamb)*xs[i];
           xc2[i] := x0[i]+ lamb*xs[i];
           xc3[i] := x0[i]+ (lamb+dlamb)*xs[i];
         end;
       Mc1 := M(xc1);
       Mc2 := M(xc2);
       Mc3 := M(xc3);
       Ml0hold := Ml0;
```

```
      Ml0 := Mc2;
      dMl := (Mc3 - Mc2)/(dlamb);
      d2Ml := (Mc1 - 2*Mc2 + Mc3)/( sqr(dlamb));
      If d2Ml = 0 then
        lamb := lamb + dlamb
      else
       lamb := lamb - (dMl/d2Ml);

    Until (abs(Ml0-Ml0hold) < tau) ;

    For i := 0 to n do
      x0[i] := x0[i]+(lamb*xs[i]);

    M0hold := M0;
    M0 := M(x0);

  Until (abs(M0 - M0hold) < tau);

end;
```

D.4 Bootstrap method

D.4.1 Background

The bootstrap method is one of a larger class of statistical methods that resample from the original data set and thus are called resampling procedures (Chernick, 1999:1). In this investigation the bootstrap method is used to calculate the standard error and confidence intervals of the results obtained from the non-linear regression methods (see Section D.2 & D.3). There are a lot of variations on the bootstrap method. In this investigation Efron's version is used in combination with the Monte Carlo approximation (Chernick, 1999:8) and can be sumarised as follow:

1. Generate a bootsrap sample of size n (where n is the origenal sample size) with replacement from the empirical distribution. The detail of this step is duscussed below.
2. Compute the values of interest by using the bootstrap sample in place of the origenal sample.
3. Repeat steps 1 and 2, k times.

The procedure for bootstrapping the residuals of a regressing is as follow (Chernick, 1999:72):
Take a general regression model:

$$y_i = g(x, c_i) + \varepsilon_i \tag{D.12}$$

The functions $g(x, c_i)$ are of known form and may depend on a fixed vector of covariates c_i. The vector x is a $p \times 1$ vector of unknown parameters and ε_i are the errors of each data point. The value of x is usually calculated by minimising the distance measure with the least squares method (see Section D.2 & D.3):

$$M(y,x,c) = \sum_{i=1}^{n} \left(y_i - g(x,c_i)\right)^2 \tag{D.13}$$

Now by taking $x' = \{x$ such that M is minimised$\}$ we have our parameter estimate of x. The residuals are obtained as:

$$\varepsilon'_i = y_i - g(x',c_i) \tag{D.14}$$

We then bootstrap the residuals ε_i^* for i = 1,2...,n where ε_i^* are obtained by sampling independently (randomly) from ε_i'. We can then generate a bootstrap sample data set:

$$y_i^* = g(x',c_i) + \varepsilon_i^* \quad \text{for } i = 1, 2, \ldots, n \tag{D.15}$$

For each such bootstrap data set y^* we obtain $x^* = \{x$ such that M is minimised$\}$ (step 2 of the Monte Carlo approximation). The procedure is repeated k times (step 3 of the Monte Carlo approximation) and the variance and confidence intervals of x is approximately the same as the variance and confidence interval of x^*.

D.4.2 Flow diagram

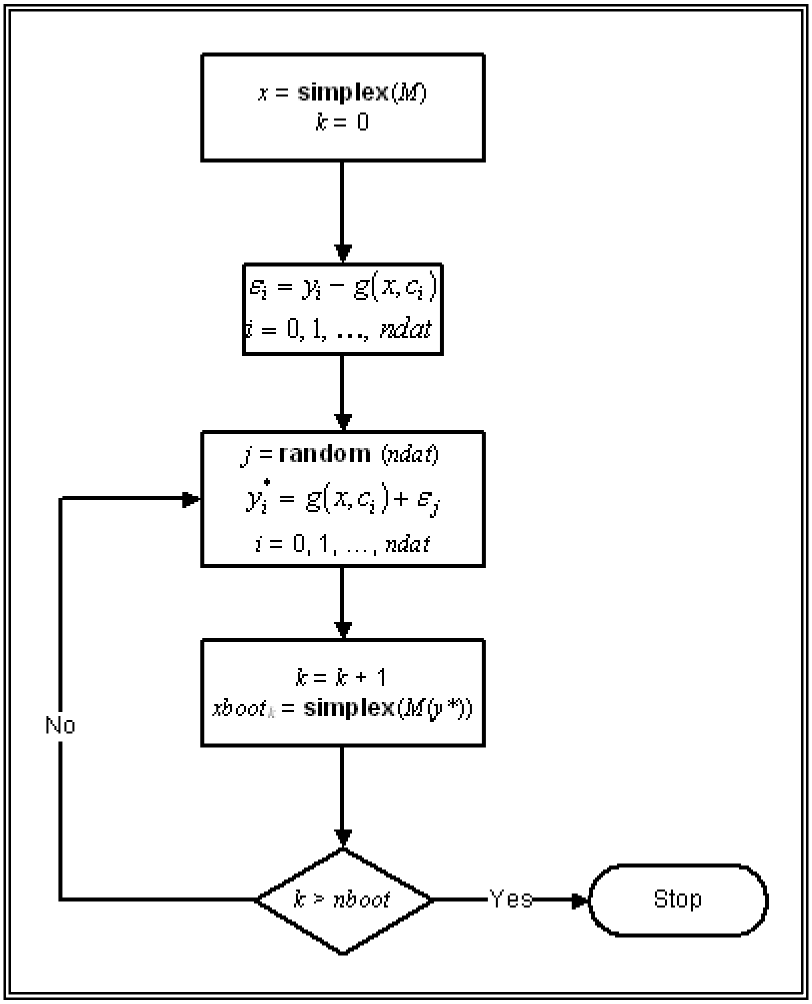

Fig. D.3: Flow diagram for the Bootstrap method

D.4.3 Code

In the code that follows a bootstrap is performed on the variable E.

```
Procedure TForm1.BootstrapClick(Sender: TObject);
Var
  i, j, k, l, km, kp,k0, tel1 : Integer;
  change : Boolean;
  khold, Dpred : double;
  datfile2 : Textfile;

begin
 Boot := true;
```

```
 km := round (0.025*(nboot));
 kp := round (0.975*(nboot));
 k0 := round (0.5*(nboot));

 For i := 0 to ndat do
  Begin
   Es[i] := Eobs[i];
   Ds[i] := D[i];
   E[i] := Eobs[i]-Epred[i];
   If W[i] <> 0 then W[i] := 1;
  end;

 x0r := x0;
 Randomize;

 For k := 0 to nboot do
  Begin

{Bootstrap residuals}
   For i := 0 to ndat do
    Begin
     j := Random (ndat);
     Dpred := F (x0r,i);
     Epred[i] := (Dpred*100/ (Dpred + Vr[i]));
     Eobs[i] := Epred[i] + E[j];
     If Eobs[i] > 99 then Eobs[i] := 99;
     If Eobs[i] < 1 then Eobs[i] := 1;
     D[i]:= (Vr[i]*Eobs[i])/(100-Eobs[i]);
    end; {i}

    x[0,0] := x0r[0];
    x[0,1] := x0r[1];
    p := (sqrt (n+2) - 1 + (n+1))/((n+1)*sqrt(2))*Sf;
    q := (sqrt (n+2) - 1)/((n+1)*sqrt(2))*Sf;
    For i := 1 to n+1 do
     For j := 0 to n do
      Begin
       If i = (j+1) then
        x[i,j] := p*x[0,j]+x[0,j]
       Else
        x[i,j] := q*x[0,j]+x[0,j];
      end; {j}
    Simplex;
    For i := 0 to n do
      xboot[i,k] := x0[i];
  end; {k}

{calculate standard deviation and sort xboot in order to calculate 95% confidence interval}
  For i := 0 to n do
   Begin
    SE[i] := StdDev (xboot[i]);

    If xboot[i,0] < xboot[i,1] then
```

```
        Begin
          xbs[i,0] := xboot[i,0];
          xbs[i,1] := xboot[i,1];
        end
      Else
        Begin
          xbs[i,0] := xboot[i,1];
          xbs[i,1] := xboot[i,0];
        end;
      For k := 2 to nboot do
        Begin
          j := -1;
          change := false;
          Repeat
            j := j+1;
            If xboot[i,k] <= xbs[i,j] then
              Begin
                For l := 0 to (k-j) do
                  xbs[i,k-l] := xbs[i,k-l-1];
                xbs[i,j] := xboot[i,k];
                change := true;
              End;
          Until ((change) or (j>(k-2)) );
          If (not (change)) then
            xbs[i,k] := xboot[i,k];
        end;{k}
    end; {i}

{replace origenal values}
  for i := 0 to ndat do
    Begin
      Eobs[i] := Es[i];
      D[i]  := Ds[i];
    end;

end;
```

D.5 Equilibrium regression

D.5.1 Background

The regression of the equilibrium constants is a typical example where off-the-shelf regression programs cannot be used, as the system consist of three equations that have to be solved simultaneously. The Newton method (Kreyszig, 1988:952) was used to solve the equations.

D.5.2 Flow diagram

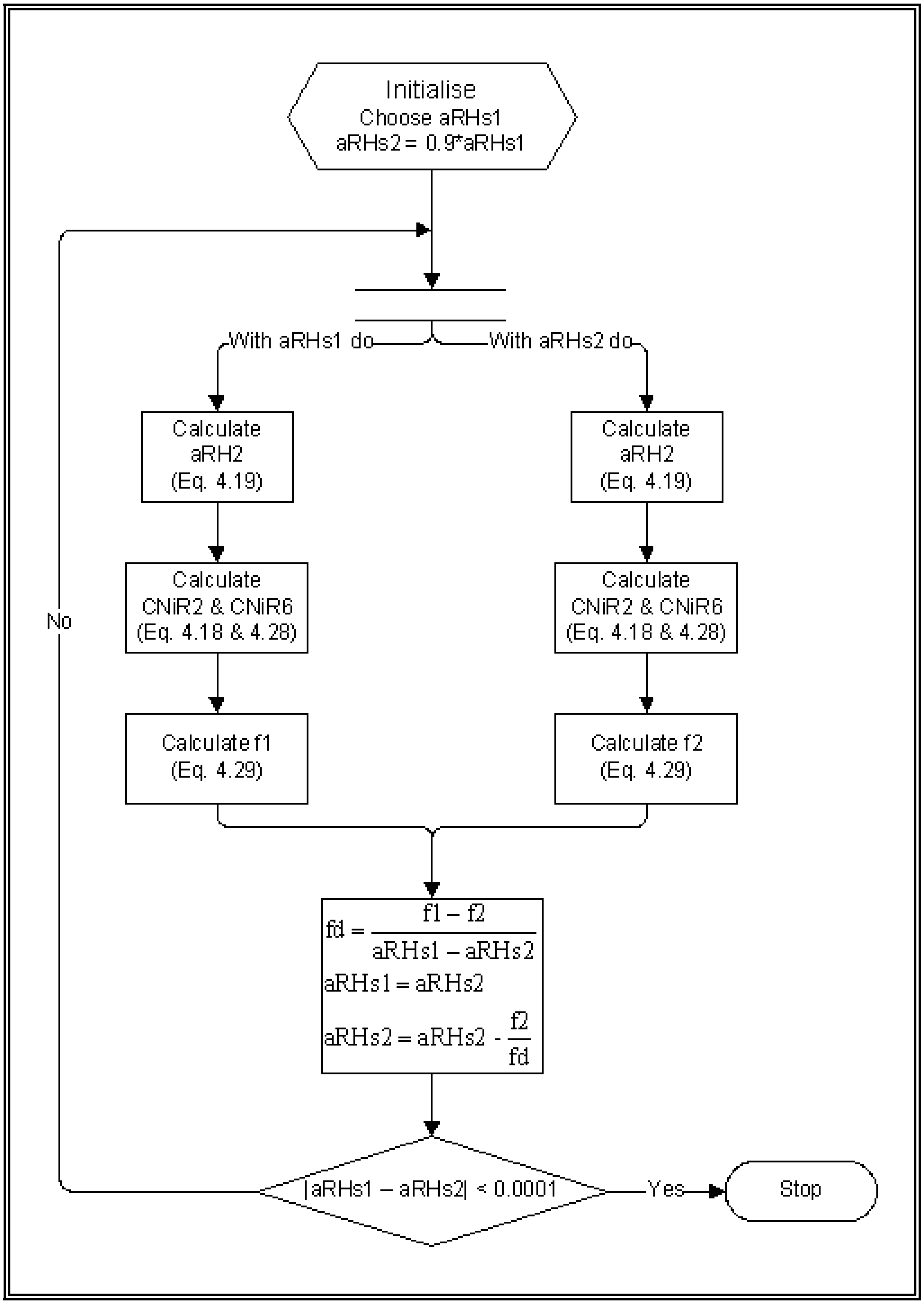

Fig. D.4: Flow diagram for equilibrium regression program

D.5.3 Code

```
Function F (xm : Array of Double; i : integer) : Double;
Var
  hold, aRHs1, aRHs2, f1, f2, fd, K1, K2 : double;

Begin
 {Initialise}
  aRHs1 := sqrt (CRT[i]/(2*Kd));
  aRHs2 := 0.9*aRHs1;
  K1 := xm[0];
  K2 := xm[1];

  Repeat
    aRH2[i] := Kd*sqr(aRHs1);
    CNiR2[i] := (K1* ( (aRH2[i]*GamNi[i]) / (Sqr(aH[i])*(1+KSO4*aSO4[i]*GamNi[i]))  ))*CNi[i];
    CNiR6[i] := (K2* ( (power(aRH2[i],3)*GamNi[i]) / (Sqr(aH[i])*(1+KSO4*aSO4[i]*GamNi[i])) ))*CNi[i];
    f1 := CRT[i]-2*aRH2[i]-2*CNiR2[i]-6*CNiR6[i] - aRHs1;

    aRH2[i] := Kd*sqr(aRHs2);
    CNiR2[i] := (K1* ( (aRH2[i]*GamNi[i]) / (Sqr(aH[i])*(1+KSO4*aSO4[i]*GamNi[i])) ))*CNi[i];
    CNiR6[i] := (K2* ( (power(aRH2[i],3)*GamNi[i]) / (Sqr(aH[i])*(1+KSO4*aSO4[i]*GamNi[i])) ))*CNi[i];
    f2 := CRT[i]-2*aRH2[i]-2*CNiR2[i]-6*CNiR6[i] - aRHs2;

    fd := (f1-f2)/(aRHs1-aRHs2);

    aRHs1 := aRHs2;
    aRHs2 := aRHs2 - f2/fd;

  Until (abs(aRHs1 - aRHs2) < 0.0001);
  aRH[i] := aRHs2;
  aRH2[i] := Kd*sqr(aRH[i]);
  CNiR2[i] := (K1* ( (aRH2[i]*GamNi[i]) / (Sqr(aH[i])*(1+KSO4*aSO4[i]*GamNi[i])) ))*CNi[i];
  CNiR6[i] := (K2* ( (power(aRH2[i],3)*GamNi[i]) / (Sqr(aH[i])*(1+KSO4*aSO4[i]*GamNi[i])) ))*CNi[i];

  hold := (CNiR2[i]+CNiR6[i])/CNi[i];
  F := hold;
end;
```

D.6 SLiMsim simulation program

D.6.1 background

The simulation of the SLM-process was one of the main objectives of this project. The general approached that was followed to do this was discussed in detail in Chapter 5.

D.6.2 Flow diagram

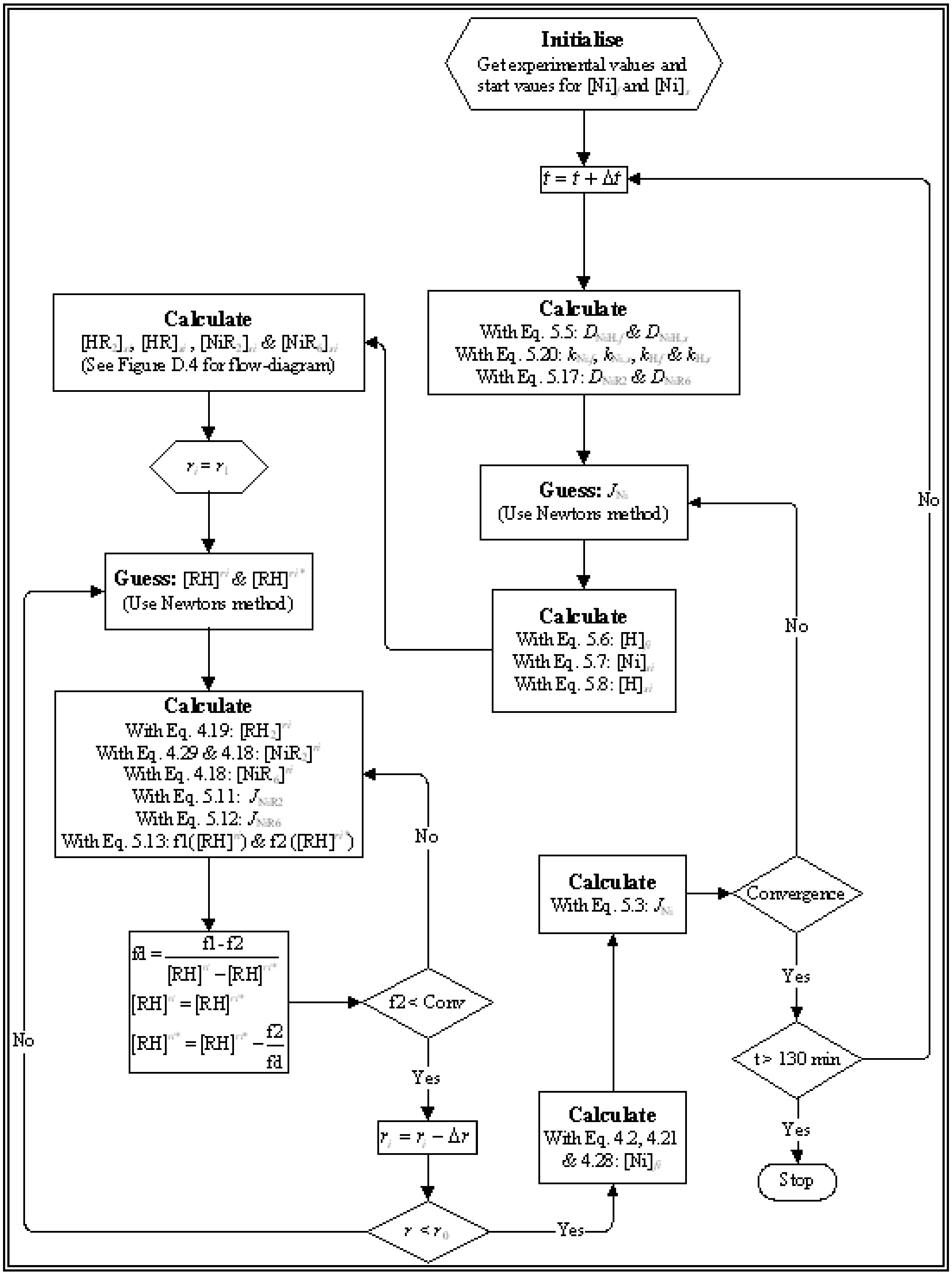

Fig. D.5: Flow diagram for SLiMsim program

D.6.3 Code

```
Function FluxNi (xm : Array of double; i, j : Integer; JNi : double) : Double;
Var
 hold, alfa2,alfa6, bet, DNiR2, DNiR6, JH, JNi1, JNi2, f1c, f2c, fdc, f1j, f2j, fdj, GamNifi,  GamNisi, aSO4fi,
 aSO4si, aRH1,  aRHs1, JNiR2, JNiR6, Dc, JNic, Isfi, Issi, GamHfi, GamHsi, Jmax, dr, ri : Double;
 telitc, telitj, telr, rk  : Integer;

Begin
 alfa2 := alf1*1e-15;
 alfa6 := alf3*1e-15;
 DNiR2 := (alfa2*T/(muor));
 DNiR6 := (alfa6*T/(muor));

 telitj := 0;

 JMax := 2*nt*PI*Lt*DNiR2*( (CRHt/2)/(ln(r2/r1)));
 If (2*nt*PI*Lt*DNiR6*( (CRHt/6)/(ln(r2/r1)))) > JMax then
   JMax := 2*nt*PI*Lt*DNiR6*( (CRHt/6)/(ln(r2/r1)));
 If (kf*Amem1*CNif) < Jmax then
   Jmax := kf*Amem1*CNif;
 If (ks*Amem*CHs*0.5) < Jmax then
   Jmax := ks*Amem*CHs*0.5;

 JNi1 := JNi;
 While JNi1 > JMax do
   JNi1 := JNi1/1.1;

 JH := 2*JNi1;
 CNifi := (kf*Amem1*CNif - JNi1)/(kf*Amem1);
 CNisi := (JNi1 + ks*Amem*CNis)/(ks*Amem);
 CHfi := (JH + kf*Amem1*CHf)/(kf*Amem1);
 CHsi := (ks*Amem*CHs - JH)/(ks*Amem);

 {*** calculate with OLI ***}
  Isfi := (0.0004783*CHfi+0.001243*CNifi+0.001224*CNaSO4)*EXP(286.13/T);
  If Isfi <0 then Isfi := 0;

  Issi := (0.5*CHsi+CNisi)*0.001*EXP(251/T);
  If Issi <0 then Issi := 0;

  GamNifi := EXP(-5.115*SQRT(Isfi)/(1+1.663*SQRT(Isfi)));
  GamNisi := EXP(-5.594*SQRT(Issi)/(1+1.741*(power(CHsi,0.05))*SQRT(Issi) ));

  GamHfi := EXP(-1.308*SQRT(Isfi)/(1+1.854*SQRT(Isfi)));
  GamHsi := EXP(-1.462*SQRT(Issi)/(1+1.686*(power(CHsi,0.1))*SQRT(Issi)));

  aHfi := GamHfi*CHfi;     aHsi := GamHsi*CHsi;
  aSO4fi := (0.5*Chfi+CNifi+CNaSO4)/(1+263.05*EXP(-2349/T)*aHfi+2.284*EXP(-474.4/T)*
          GamNifi*power(10,(0.15*CNifi)));
  aSO4si := (0.5*CHsi+CNisi)/(1+845.7*EXP(-2776/T)*aHsi + 2.286*EXP(-643.73/R2)*GamNisi*CNisi);
 {*** --- ***}
```

```
 {calculate organic concentrations on strip side}
 {initialise}
 aRHs1 := sqrt (CRHT/(2*Kd));
 aRH2s := Kd*sqr(aRHs1);
 Dc := (K1*GamNisi*sqr(aRHs1)*(1+KNiR6*sqr(aRH2s)))/ (Sqr(aHsi)*(1+KNiSO4*aSO4si*GamNisi));
 CNiR2s := (Dc*CNisi)/(1+KNiR6*sqr(aRH2s));
 CNiR6s :=  KNiR6* CNiR2s*sqr(aRH2s);
 f1c := CRHT-2*aRH2s-2*CNiR2s-6*CNiR6s - aRHs1;

 aRHs2 := 0.99*aRHs1;

 {Newton method}
 Repeat
   aRH2s := Kd*sqr(aRHs2);
   Dc := (K1*GamNisi*sqr(aRHs2)*(1+KNiR6*sqr(aRH2s)))/(Sqr(aHsi)*(1+KNiSO4*aSO4si*GamNisi));
   CNiR2s := (Dc*CNisi)/(1+KNiR6*sqr(aRH2s));
   CNiR6s :=  KNiR6* CNiR2s*sqr(aRH2s);
   f2c := CRHT-2*aRH2s-2*CNiR2s-6*CNiR6s - aRHs2;

   fdc := (f1c-f2c)/(aRHs1-aRHs2);

   aRHs1 := aRHs2;
   aRHs2 := aRHs2 - f2c/fdc;
   f1c := f2c;

 Until (abs(aRHs1 - aRHs2)+ abs(f2c) < convc);

{Calculate flux through membrane}
 dr := (r2-r1)/nr;
 CNiR2[0] := CNiR2s;
 CNiR6[0] := CNiR6s;
 aRH[0] := aRHs2;
 aRH2[0] := aRH2s;

 For telr := 0 to (nr-1) do
  Begin
   ri := r2 - telr*dr;
   rk := telr+1;
   aRH[rk] := aRH[rk-1];

   {solve equations}
   aRH2[rk] := Kd*sqr(aRH[rk]);
   CNiR2[rk] := (CRHT -2*aRH2[rk] - aRH[rk])/ (2 + 6*KNiR6*(sqr(aRH2[rk])));
   CNiR6[rk] := KNiR6*(CNiR2[rk])*(sqr(aRH2[rk]));

   JNiR2 := 2*nt*PI*ri*Lt*DNiR2*((CNiR2[rk]-CNiR2[rk-1])/dr);
   JNiR6 := 2*nt*PI*ri*Lt*DNiR6*((CNiR6[rk]-CNiR6[rk-1])/dr);
   f1c := JNi1 - JNiR2 - JNiR6;

   aRH1 := 0.999*aRH[rk];

   Repeat
     aRH2[rk] := Kd*sqr(aRH1);
     CNiR2[rk] := (CRHT -2*aRH2[rk] - aRH1)/ (2 + 6*KNiR6*(sqr(aRH2[rk])));
```

```
      CNiR6[rk] := KNiR6*(CNiR2[rk])*(sqr(aRH2[rk]));

      JNiR2 := 2*nt*PI*ri*Lt*DNiR2*((CNiR2[rk]-CNiR2[rk-1])/dr);
      JNiR6 := 2*nt*PI*ri*Lt*DNiR6*((CNiR6[rk]-CNiR6[rk-1])/dr);
      f2c := JNi1 - JNiR2 - JNiR6;

      fdc := (f1c-f2c)/(aRH[rk]-aRH1);

      aRH[rk] := aRH1;
      aRH1 := aRH1 - f2c/fdc;
      If aRH1 < 0 then
        aRH1 := 0.5*aRH[rk];
      If aRH1 > CRHT then
        aRH1 := 0.5*(aRH[rk]+CRHT);

      f1c := f2c;

    Until (abs(f2c) < convj);
    aRH[rk] := aRH1;

  end; {dr}

aRHf := aRH[nr]; aRH2f := aRH2[nr]; CNiR2f := CNiR2[nr]; CNiR6f := CNiR6[nr];

Dc := (K1*GamNifi*sqr(aRHf)*(1+KNiR6*sqr(aRH2f)))/(Sqr(aHfi)*(1+KNiSO4*aSO4fi*GamNifi));
CNifi := (CNiR6f + CNiR2f)/(Dc*(1+KNiSO4*aSO4fi*GamNifi));
JNic := Amem1*kf*(CNif-CNifi);

f1j := JNi1 - Jnic;

{Newton method for flux}
telitj := 0;
JNi2 := (JNi1*(1-1e-5));
JH := 2*JNi2;

CNisi := (JNi2 + ks*Amem*CNis)/(ks*Amem);
CHfi := (JH + kf*Amem1*CHf)/(kf*Amem1);
CHsi := (ks*Amem*CHs - JH)/(ks*Amem);

Repeat
   {*** Calculate with OLI ***}
   Isfi := (0.0004783*CHfi+0.001243*CNifi+0.001224*CNaSO4)*EXP(286.13/T);
   If Isfi < 0 then Isfi := 0;

   Issi := (0.5*CHsi+CNisi)*0.001*EXP(251/T);

   GamNifi := EXP(-5.115*SQRT(Isfi)/(1+1.663*SQRT(Isfi)));
   GamNisi := EXP(-5.594*SQRT(Issi)/(1+1.741*(power(CHsi,0.05))*SQRT(Issi) ));{0.3}

   GamHfi := EXP(-1.308*SQRT(Isfi)/(1+1.854*SQRT(Isfi)));
   GamHsi := EXP(-1.462*SQRT(Issi)/(1+1.686*(power(CHsi,0.1))*SQRT(Issi)));

   aHfi := GamHfi*CHfi;     aHsi := GamHsi*CHsi;
   aSO4fi := (0.5*CHfi+CNifi+CNaSO4)/(1+263.05*EXP(-2349/T) *aHfi+2.284*EXP(-474.4/T)*GamNifi*
```

```
    power(10,(0.15*CNifi)));
aSO4si := (0.5*CHsi+CNisi)/(1+845.7*EXP(-2776/T)*aHsi+ 2.286*EXP(-643.73/R2)*GamNisi*CNisi);
{*** --- ***}

{calculate organic concentrations on strip side}
{initialise}
aRH2s := Kd*sqr(aRHs1);
Dc := (K1*GamNisi*sqr(aRHs1)*(1+KNiR6*sqr(aRH2s)))/
   (Sqr(aHsi)*(1+KNiSO4*aSO4si*GamNisi));
CNiR2s := (Dc*CNisi)/(1+KNiR6*sqr(aRH2s));
CNiR6s :=  KNiR6* CNiR2s*sqr(aRH2s);
f1c := CRHT-2*aRH2s-2*CNiR2s-6*CNiR6s - aRHs1;

aRHs2 := 0.99*aRHs1;
telitc := 0;

{Newton method}
Repeat
  aRH2s := Kd*sqr(aRHs2);
  Dc := (K1*GamNisi*sqr(aRHs2)*(1+KNiR6*sqr(aRH2s)))/(Sqr(aHsi)*(1+KNiSO4*aSO4si*GamNisi));
  CNiR2s := (Dc*CNisi)/(1+KNiR6*sqr(aRH2s));
  CNiR6s :=  KNiR6* CNiR2s*sqr(aRH2s);
  f2c := CRHT-2*aRH2s-2*CNiR2s-6*CNiR6s - aRHs2;

  fdc := (f1c-f2c)/(aRHs1-aRHs2);

  aRHs1 := aRHs2;
  aRHs2 := aRHs2 - f2c/fdc;
  f1c := f2c;

Until (abs(aRHs1 - aRHs2)+ abs(f2c) < convc);

{Calculate flux through membrane}
CNiR2[0] := CNiR2s;
CNiR6[0] := CNiR6s;
aRH[0] := aRHs2;
aRH2[0] := aRH2s;

For telr := 0 to (nr-1) do
  Begin
    ri := r2 - telr*dr;
    rk := telr+1;
    aRH[rk] := aRH[rk-1];
    {solve equations}

    aRH2[rk] := Kd*sqr(aRH[rk]);
    CNiR2[rk] := (CRHT -2*aRH2[rk] - aRH[rk])/ (2 + 6*KNiR6*(sqr(aRH2[rk])));
    CNiR6[rk] := KNiR6*(CNiR2[rk])*(sqr(aRH2[rk]));

    JNiR2 := 2*nt*PI*ri*Lt*DNiR2*((CNiR2[rk]-CNiR2[rk-1])/dr);
    JNiR6 := 2*nt*PI*ri*Lt*DNiR6*((CNiR6[rk]-CNiR6[rk-1])/dr);
    f1c := JNi2 - JNiR2 - JNiR6;

   aRH1 := 0.999*aRH[rk];
```

```
      Repeat
        aRH2[rk] := Kd*sqr(aRH1);
        CNiR2[rk] := (CRHT -2*aRH2[rk] - aRH1)/ (2 + 6*KNiR6*(sqr(aRH2[rk])));
        CNiR6[rk] := KNiR6*(CNiR2[rk])*(sqr(aRH2[rk]));

        JNiR2 := 2*nt*PI*ri*Lt*DNiR2*((CNiR2[rk]-CNiR2[rk-1])/dr);
        JNiR6 := 2*nt*PI*ri*Lt*DNiR6*((CNiR6[rk]-CNiR6[rk-1])/dr);
        f2c := JNi2 - JNiR2 - JNiR6;

        fdc := (f1c-f2c)/(aRH[rk]-aRH1);

        aRH[rk] := aRH1;
        aRH1 := aRH1 - f2c/fdc;
        If aRH1 < 0 then
          aRH1 := 0.5*aRH[rk];
        If aRH1 > CRHT then
          aRH1 := 0.5*(aRH[rk]+CRHT);

        f1c := f2c;

      Until (abs(f2c) < convj);
      aRH[rk] := aRH1;
    end; {dr}

  aRHf := aRH[nr]; aRH2f := aRH2[nr]; CNiR2f := CNiR2[nr]; CNiR6f := CNiR6[nr];

  Dc := (K1*GamNifi*sqr(aRHf)*(1+KNiR6*sqr(aRH2f)))/(Sqr(aHfi)*(1+KNiSO4*aSO4fi*GamNifi));
  CNifi := (CNiR6f + CNiR2f)/(Dc*(1+KNiSO4*aSO4fi*GamNifi));
  JNic := Amem1*kf*(CNif-CNifi);

  f2j := JNi2 - JNic;

  fdj := (f1j-f2j)/(JNi1-Jni2);
  JNi1 := JNi2;
  JNi2 := JNi2-(f2j/fdj);
  f1j := f2j;

  If JNi2 > Jmax then
    JNi2 := 0.5*(Jmax+JNi1);
  If JNi2 <0 then
    JNi2 := 0.5*JNi1;

  JH := 2*JNi2;
  CNisi := (JNi2 + ks*Amem*CNis)/(ks*Amem);
  CHfi := (JH + kf*Amem1*CHf)/(kf*Amem1);
  CHsi := (ks*Amem*CHs - JH)/(ks*Amem);

 Until (abs (f2j) < convj);

 hold := JNi2;
 FluxNi := hold;
end;
```

```
Procedure Simexp (xm : Array of double;i : Integer);
var
          j, j2, jt, jtm : Integer;
          taus, JNi : double;
Begin
{initiate}
  CNifc[i,0] := CNif[i,0];      CNisc[i,0] := CNis[i,0];
  aHfc[i,0] := aHf[i,0];        aHsc[i,0] := aHs[i,0];
  CNaSO4[i,0] := 0;
  j2 := 1;
  JNi := 0;
  For j := 1 to ntp do
    Begin
      jt := round (time[i,j2]/dt);
      if (j > jt) and (j2<6) then
        Begin
          j2 := j2 +1;
          jt := round (time[i,j2]/dt);
        end;
      jtm := round(time[i,j2-1]/dt);

      aHfc[i,j] := aHfc[i,j-1] + (1/(jt-jtm))*( aHf[i,j2] - aHf[i,j2-1]);
      aHsc[i,j] := aHsc[i,j-1] + (1/(jt-jtm))*( aHs[i,j2] - aHs[i,j2-1]);

{*** Na2SO4 Total ***}
      CNaSO4[i,j] := CNaSO4[i,j-1] + (dt/Volf)*(FNa[i]*(0.5*CNaOH)-
              FFT[i]*CNaSO4[i,j-1]);

{*** Ni in bulk solution ***}
      CNifc[i,j] := CNifc[i,j-1] + (dt/Volf)*(FFT[i]*(CNiFT[i]-CNifc[i,j-1])
        - JNi);
      CNisc[i,j] := CNisc[i,j-1] + (dt/Vols)*(FST[i]*(CNiST[i]-CNisc[i,j-1])
        + JNi);

      {*** From OLI ***}
      Iss[i,j] :=(0.001095*aHsc[i,j]+ 0.003639*CNisc[i,j]
        - 0.000006674*CNis[i,j]*T[i])*EXP(111.5/T[i]);
      If Iss[i,j] <0 then Iss[i,j] := 0;

      Isf[i,j] :=(0.0005744*aHfc[i,j]+0.001202*CNifc[i,j]+0.001179*CNaSO4[i,j])
        *EXP(294.4/T[i]);

      If Isf[i,j] <0 then Isf[i,j] := 0;

      xmolH2SO4s[i,j] := aHsc[i,j]*exp(0.6573*(-log10(aHsc[i,j]/1000))+ 3.8383*   (power(Iss[i,j],0.1))+
             0.003382*T[i]-15.7192);

      DNif[i,j] := 691.861e-9*EXP(-2047/T[i]); {1.24e-9}
      DNis[i,j] := 670.61e-9*EXP(-2040/(T[i]-5.22*Iss[i,j]));
      DHf[i,j] := 61.08e-8*EXP(-1246.5/T[i]); {7.9e-9}
      DHs[i,j] := 58.73e-8*EXP(-1241/(T[i]-12.94*Iss[i,j]));
      GamHf[i,j] := EXP(-1.308*SQRT(Isf[i,j])/(1+1.854*SQRT(Isf[i,j])));
      GamHs[i,j] := EXP(-1.46*SQRT(Iss[i,j])/(1+1.739*(power(aHsc[i,j],0.1))*SQRT(Iss[i,j])));
{*** --- ***}
```

```
    CHfc[i,j] := (aHfc[i,j]/gamHf[i,j]);
    CHsc[i,j] := (aHsc[i,j]/gamHs[i,j]);

    xvolH2SO4s[i,j] := (rhow[i]*xmolH2SO4s[i,j]*MH2SO4)/( xmolH2SO4s[i,j]*MH2SO4*rhow[i] +
          Mw*rhoH2SO4[i] - Mw*rhoH2SO4[i]*xmolH2SO4s[i,j]);

    rhos[i,j] := xvolH2SO4s[i,j]*rhoH2SO4[i] + (1-xvolH2SO4s[i,j])*rhow[i];
    mus[i,j] := power ( xmolH2SO4s[i,j]*power(muH2SO4[i],(1/3)) + (1-xmolH2SO4s[i,j])*
          power(muw[i],(1/3)) ,3);

    Fs[i,j] := Fsm[i]*(sqrt(1189)/(sqrt(rhos[i,j])));
    vs[i,j] := Fs[i,j]/Acs;
    Res[i,j] := rhos[i,j]*vs[i,j]*de/(mus[i,j]);

    DNiHf[i,j] := (1.5*DNif[i,j]*DHf[i,j])/(DNif[i,j]+DHf[i,j]);
    DNiHs[i,j] := (1.5*DNis[i,j]*DHs[i,j])/(DNis[i,j]+DHs[i,j]);

    Scf[i,j] := muw[i]/(rhow[i]*DNiHf[i,j]);
    Scs[i,j] := mus[i,j]/(rhos[i,j]*DNiHs[i,j]);

    taus := a0[i]*Res[i,j] + a1[i]*power(Res[i,j],3);
    frics[i,j] := (2*taus)/(rhos[i,j]*sqr(vs[i,j]));

    Shf[i,j] := 0.5*fricf[i]*(power(Ref[i],xm[1]))*(power(Scf[i,j],xm[2]));
    Shs[i,j] := 0.5*frics[i,j]*(power(Res[i,j],xm[1]))*power(Scs[i,j],xm[2]);

    kf[i,j] := (Shf[i,j]*DNiHf[i,j])/d1;
    ks[i,j] := (Shs[i,j]*DNiHs[i,j])/de;

    If j = 1 then
       JNi := 0.5*kf[i,j]*CNifc[i,j];
    JNi := FluxNi(xm,i,j,JNi);
   end;
End;
```

List of Figures

Appendix E

Liquid-liquid extraction equilibrium for the zinc/di-(2-ethylhexyl) phosphoric acid system

Contents

E.1 Introduction

In this appendix a summary is given of the Zn/D2EHPA equilibrium system. The most important differences between the Ni/D2EHPA and the Zn/D2EHPA system are:

- Zinc does not form a neutral complex with the sulphate ions.
- The zinc forms different organo-metallic complexes (see Section E.2).

In this study, the effect of the aqueous activity coefficient was incorporated in a new equilibrium model and it was assumed that the zinc ions reacts with the monomeric D2EHPA in the aqueous phase. This equilibrium model was verified with a set of experiments in which the factors affecting the equilibrium was varied.

E.2 Literature survey

The extraction of zinc with Di-(2-ethylhexyl) phosphoric acid (D2EHPA) was recently adopted as a reactive liquid-extraction test system by the European Federation of Chemical Engineering for validating liquid-liquid extraction equipment design procedures when both mass transfer and chemical reaction rates are significant (Mansur *et al.*, 2004). The Zn/D2EHPA system has been under considerable investigation and the constraints of previous work are summarised in Table E.1. The main shortcomings of these publications are that the researchers did not take into account that the activity of the zinc differ from the molality (event at very low zinc concentrations). There has also been some recent developments, leading to a better understanding of the extraction mechanism as discussed below. It was found by Sainz-Diaz *et al.* (1996) that zinc is extracted according to the following mechanism:

$$Zn^{2+}_{aq} + 1.5\left(RH\right)_{2,o} \rightleftharpoons ZnR_2\left(RH\right)_o + 2H^+_{aq} \tag{E.1}$$

This mechanism was proved by slope analysis and the result was that the dimeric extractant/zinc stiochiometric ratio was 1.6. The results of a FT - IR spectroscopy study showed that the stochiometric ratio of Zn/D2EHPA in the organic phase is near 3, which supports the formation of the ZnR2(RH) organo-metallic species. In 1999 Bart and Rousselle used this reaction again, with

Table E.1: A summary of previous research on the Zn/D2EHPA system

	Bart and Rousselle (1999)	Forrest (1977)	Zimmermann and Robl (1997)	Mansur *et al.* (2002)	This study
Type of study	Extraction	Extraction	Stripping	Stripping	Extraction
Number of data points	43	92	44	8	50
$[Zn]_{aq}$ (mol/m^3)	5 and 50	30 - 615	0	0	0.5 - 3.5
$[Zn]_{o,\,t=0}$ (mol/m^3)	0	0	26.2, 38.0 & 46.4	39.7	0
$[RH]_{Tot}$ (mol/m^3)	5 - 200	300 & 600	80, 120 & 150	120	10 - 100
Diluent	Isodecane	Kerosene	n-heptane	n-heptane	Kerosene
$[H_2SO_4]_{aq,\,t=0}$ (mol/m^3)	0 - 10	0 - 200	1000, 2000 & 3000	500, 1000 & 2000	3 - 22
Vr (V_{aq}/V_o)	1	0.1 - 10	0.05 - 1.0	0.5, 1 & 2	0.5 - 5

the value of *n* equal to1.5, but showed that the two rate determining steps were an aqueous phase reaction and an organic phase reaction (Reactions E.2 & E.3).

Aqueous phase reaction:

$$Zn^{2+}_{aq} + 2\left(RH\right)_{2,aq} \rightleftharpoons ZnR_{2,aq} + 2H^{+}_{aq} \tag{E.2}$$

Organic phase reaction:

$$ZnR_{2,o} + n\left(RH\right)_{2,o} \rightleftharpoons ZnR_{2}\left(RH\right)_{o} + 2\left(RH\right)_{o} \tag{E.3}$$

In 2002 an equilibrium model was proposed, for the system with n-heptane as diluent, by Mansur *et al.* (2002), since the reactions above were not able to describe the whole process by assuming a constant value of *n*. They postulated that a heterogeneous interfacial reaction can be assumed to produce $ZnR_2(RH)$ and a homogeneous reaction follows in the organic phase to produce a free D2EHPA dimer and a ZnR_2 organo-metallic complex.

Interfacial reaction:

$$\mathrm{Zn}_i^{2+} + n\left(\mathrm{RH}\right)_{2,i} \rightleftharpoons \mathrm{ZnR}_2\left(\mathrm{RH}\right)_{2(n-1),i} + 2\mathrm{H}_i^{+} \tag{E.4}$$

Organic phase reaction:

$$\mathrm{ZnR}_2\left(\mathrm{RH}\right)_{2(n-1),o} \rightleftharpoons \mathrm{ZnR}_2\left(\mathrm{RH}\right)_{(m-2),o} + \left(n - \frac{m}{2}\right)\left(\mathrm{RH}\right)_{2,o} \tag{E.5}$$

According to Mansur *et al.* (2002) the first reaction alone can explain the equilibrium behaviour at low loading conditions; however, both reactions have to be considered at intermediate and high loading conditions. This equilibrium model is an improvement of the one postulated by Sainz-Diaz *et al.* (1996), because it did not give an inconsistent value for *n*. There were, however, two questionable assumptions made in this equilibrium model. Firstly, the assumption was made that the activity coefficients of the aqueous species are equal to 1. Due to the charge of the aqueous species the activity differs from the molality, even at very low aqueous concentrations (Atkins, 1998: 248). Secondly, it is questionable if the zinc will react with the D2EHPA dimer on the interface. The reaction probably takes place in a very thin boundary layer in the aqueous phase and it is known that the dimer is much less soluble in the aqueous phase than the monomer (Huang & Juang, 1986).

E.3 Theory

The assumption was made that the Zn/D2EHPA system can be described by the reactions and partition equilibriums depicted in Figure E.1. This assumption, with a discussion concerning the equilibrium equations, follow:

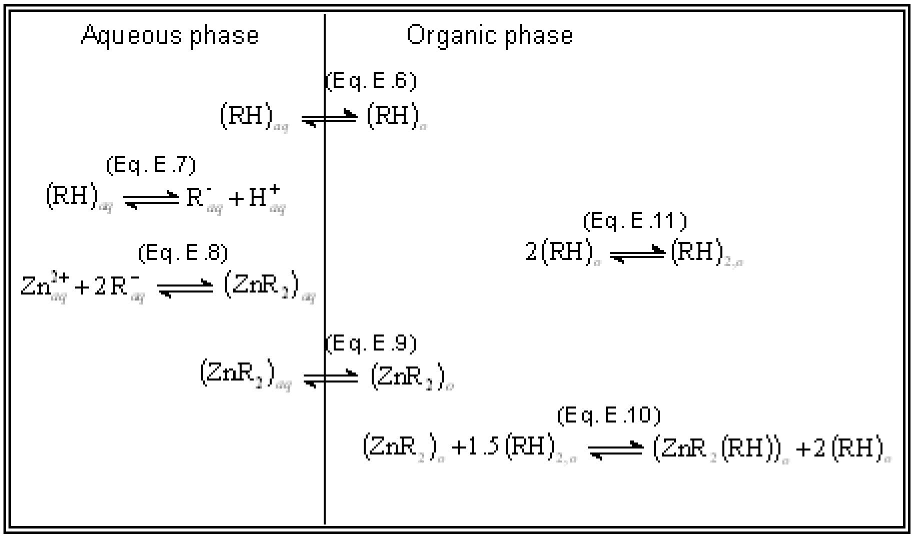

Fig. E.1: Steps involved in forming Zn/D2EHPA equilibrium

The partition equilibrium between the D2EHPA monomer in the organic and aqueous phase is expressed by the following in term of the activities (*a*):

$$P^0_{\mathrm{RH}} = \frac{a(\mathrm{RH})_o}{a(\mathrm{RH})_{aq}} \tag{E.6}$$

The D2EHPA monomer dissociates in the aqueous phase to form an organic phosphate ion and a hydronium ion:

$$K_{\mathrm{RH}} = \frac{a(\mathrm{R}^-)_{aq} \cdot a(\mathrm{H}^+)_{aq}}{a(\mathrm{RH})_{aq}} \tag{E.7}$$

The zinc in the aqueous phase takes part in an equilibrium reaction with the organic phosphate to form a ZnR_2 chelate:

$$K_{\mathrm{ZnR}_2} = \frac{a(\mathrm{ZnR}_2)_{aq}}{a(\mathrm{R}^-)^2_{aq} \cdot a(\mathrm{Zn}^{2+})_{aq}} \tag{E.8}$$

There is a partition equilibrium between the ZnR_2 chelate in the organic phase and the aqueous phase:

$$P^{0}_{ZnR_2} = \frac{a(\mathrm{ZnR}_2)_o}{a(\mathrm{ZnR}_2)_{aq}} \tag{E.9}$$

The ZnR_2 chelate can react with additional D2EHPA dimer molecule to form a second $ZnR_2(RH)$ chelate in the organic phase. The equilibrium constant is:

$$K_{ZnR_3} = \frac{a(\mathrm{ZnR}_2(\mathrm{RH}))_o \cdot a(\mathrm{RH})_o^2}{a(\mathrm{ZnR}_2)_o \cdot a((\mathrm{RH})_2)_o^{1.5}} \tag{E.10}$$

There is also an equilibrium between the D2EHPA monomer and dimer (Juang & Su, 1992; Huang & Juang, 1986; Komasawa et al., 1981):

$$K_D = \frac{a((\mathrm{RH})_2)_o}{a(\mathrm{RH})_o^2} = 12\,\mathrm{m}^3/\mathrm{mol} \tag{E.11}$$

These equilibrium equations can be used to derive the final model in terms of distribution ratio and this equilibrium model will be used to describe the Zn/D2EHPA equilibrium. The derivation of this equilibrium model will be discussed in the subsequent paragraphs.

Using Equation 4.12, the distribution ratio for the system can be written as:

$$D = \frac{[\mathrm{ZnR}_2]_o + [\mathrm{ZnR}_2(\mathrm{RH})]_o}{[\mathrm{Zn}^{2+}]_{aq} + [\mathrm{ZnR}_2]_{aq}} \tag{E.12}$$

If it is assumed that $[ZnR_2]_{aq} << [Zn^{2+}]_{aq}$, then Equation E.12 simplifies to:

$$D = \frac{[\mathrm{ZnR}_2]_o + [\mathrm{ZnR}_2(\mathrm{RH})]_o}{[\mathrm{Zn}^{2+}]_{aq}} \tag{E.13}$$

In terms of activity, Equation E.13 becomes:

$$D = \frac{\dfrac{a(\mathrm{ZnR}_2)_o}{\gamma(\mathrm{ZnR}_2)_o} + \dfrac{a(\mathrm{ZnR}_2(\mathrm{RH}))_o}{\gamma(\mathrm{ZnR}_2(\mathrm{RH}))_o}}{\dfrac{a(\mathrm{Zn}^{2+})_{aq}}{\gamma(\mathrm{Zn}^{2+})_{aq}}} \tag{E.14}$$

Substitution of the aqueous phase reaction equilibrium (Equations E.8), the partition equilibrium of the ZnR_2 species (Equation E.9), and the organic phase reaction equilibrium (Equation E.10) into Equation E.14 gives:

$$D = \frac{\dfrac{P^0_{\mathrm{ZnR}_2} \cdot K_{\mathrm{ZnR}_2} \cdot a(R^-)^2_{aq} \cdot a(Zn^{2+})_{aq}}{\gamma(ZnR_2)_o} + \dfrac{K_{\mathrm{ZnR}_3} \cdot P^0_{\mathrm{ZnR}_2} \cdot K_{\mathrm{ZnR}_2} \cdot a(R^-)^2_{aq} \cdot a(Zn^{2+})_{aq} \cdot a((RH)_2)^{1.5}_o}{a(RH)^2_o \cdot \gamma(ZnR_2(RH))_o}}{\dfrac{a(Zn^{2+})_{aq}}{\gamma(Zn^{2+})_{aq}}} \tag{E.15}$$

Substitution of the monomer dissociation (Equation E.7) into Equation E.15 gives:

$$D = \frac{\dfrac{P^0_{\mathrm{ZnR}_2} \cdot K_{\mathrm{ZnR}_2} \cdot K^2_{\mathrm{RH}} \cdot a(\mathrm{RH})^2_{aq} \cdot a(\mathrm{Zn}^{2+})_{aq}}{\gamma(\mathrm{ZnR}_2)_o \cdot a(\mathrm{H}^+)^2_{aq}} + \dfrac{K_{\mathrm{ZnR}_3} \cdot P^0_{\mathrm{ZnR}_2} \cdot K_{\mathrm{ZnR}_2} \cdot K^2_{\mathrm{RH}} \cdot a(\mathrm{RH})^2_{aq} \cdot a(\mathrm{Zn}^{2+})_{aq} \cdot a((\mathrm{RH})_2)^{1.5}_o}{a(\mathrm{RH})^2_o \cdot \gamma(\mathrm{ZnR}_2(\mathrm{RH}))_o \cdot a(\mathrm{H}^+)^2_{aq}}}{\dfrac{a(\mathrm{Zn}^{2+})_{aq}}{\gamma(\mathrm{Zn}^{2+})_{aq}}} \tag{E.16}$$

The final step is to substitute the D2EHPA partition equilibrium (Equation E.6) into Equation E.16 and simplification gives:

$$D = \frac{K_{\mathrm{Zn}1} \cdot a(\mathrm{RH})^2_o \cdot \gamma(\mathrm{Zn}^{2+})_{aq}}{\gamma(\mathrm{ZnR}_2)_o \cdot a(\mathrm{H}^+)^2_{aq}} + \frac{K_{\mathrm{Zn}2} \cdot a((\mathrm{RH})_2)^{1.5}_o \cdot \gamma(\mathrm{Zn}^{2+})_{aq}}{\gamma(\mathrm{ZnR}_2(\mathrm{RH}))_o \cdot a(\mathrm{H}^+)^2_{aq}} \tag{E.17}$$

with

$$K_{Zn1} = \frac{P^0_{ZnR_2} . K_{ZnR_2} . K^2_{RH}}{\left(P^0_{RH}\right)^2} \tag{E.18}$$

and

$$K_{Zn2} = \frac{K_{ZnR_3} \cdot P^0_{ZnR_2} . K_{ZnR_2} . K^2_{RH}}{\left(P^0_{RH}\right)^2} \tag{E.19}$$

At any time the total D2EHPA concentration in the organic phase can be calculated from a mol balance:

$$[R]_{Tot,o} = [RH]_o + 2 \cdot [(RH)_2]_o + 2 \cdot [ZnR_2]_o + 3 \cdot [ZnR_2(RH)]_o \tag{E.20}$$

E.4 Experimental procedure

The Zn/D2EHPA extraction equilibrium was determined with batch solvent extraction experiments. The experimental procedure that was followed is the same as the procedure discussed in Section 4.3.2. The factors that were investigated are the concentration of extractant (D2EHPA) in the organic phase, the concentration of zinc in the aqueous phase, the volume ratio of the phases, pH and reaction temperature. Each experiment was done four times to determine the reproducibility of the experiment. A set of 2^k experiments was also done and although these experiments cannot be displayed graphically, it increased the confidence in the regression results. The detailed results of all the experiments can be seen in Table E.2 (see Section E.7).

E.5 Results and discussion

The activity coefficients of the aqueous zinc were calculated using the OLIAnalyzer software package (OLI System Inc.), which uses a database of known thermodynamic properties and mathematical algorithms to predict the properties and component distributions of aqueous solutions. The values of K_{Zn1} and K_{Zn2} were determined by regression using the Simplex method (Jacoby *et al.*, 1972:79) in combination with Newton's method (Kreyszig, 1988:952) to solve Equations E.11, E.17 and E.20 simultaneously. The distribution ratio observed for each experiment was calculated with a simple mole balance:

$$D_{obs} = \frac{\sum[\mathrm{M}_o]}{\sum[\mathrm{M}_{aq}]} = \frac{\left([\mathrm{Zn}^{2+}]_{aq,f} - [\mathrm{Zn}^{2+}]_{aq,r}\right)\dfrac{\mathrm{V}_{aq}}{\mathrm{V}_o}}{[\mathrm{Zn}^{2+}]_{aq,r}} \qquad \text{(E.21)}$$

The regression was done on all the experimental data points and had a correlation coefficient (r^2) of 0.996. The standard error of the regression were determined with the Bootstrap method (Chernick, 1999:8). The regression results can be seen in Table 4.5 and in Figure E.2, where the percentage extraction ($\%E_{cal}$), calculated with the equilibrium model is plotted against the observed percentage extraction ($\%E_{obs}$), as calculated with Equations E.21 and 4.13.

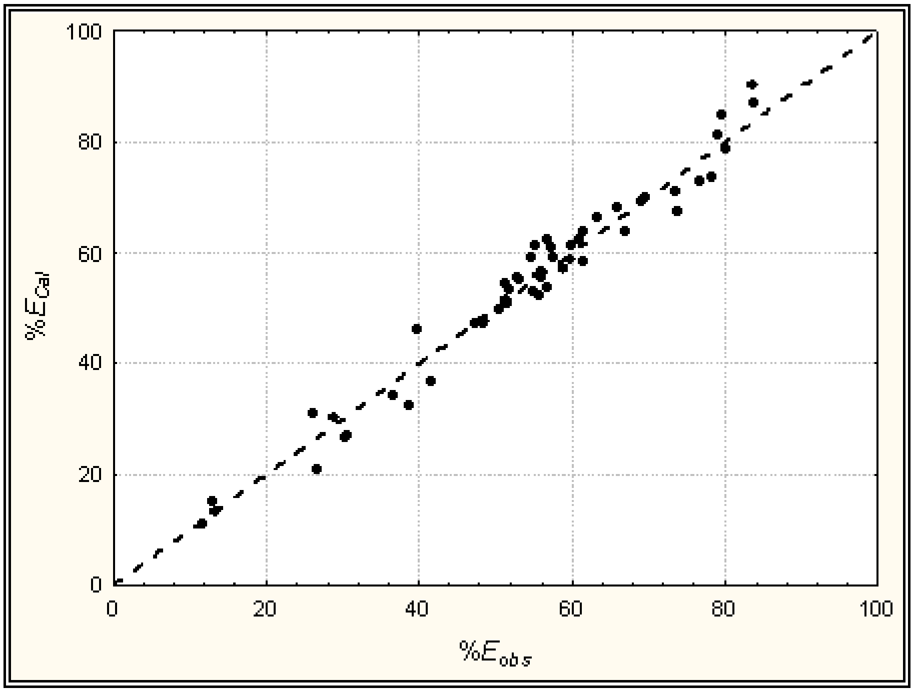

Fig. E.2: Predicted *vs.* observed values for the equilibrium model of the Zn/D2EHPA system

E.5.1 Testing for equilibrium

One of the first objectives in the experimental design was to ensure that equilibrium conditions were reached. This was done by varying the extraction time from 10 to 50 minutes and observing the percentage zinc extracted. Figure E.3 shows that the equilibrium was reached within 10 minutes.

E.5.2 The effect of temperature

The effect of temperature on the Zn/D2EHPA system was determined by changing the temperature from 30˚C to 70˚C in a temperature bath and as was the case with the extraction of nickel, the temperature showed no significant temperature dependence (see Figure E.4)

E.5.3 The effect of the total D2EHPA concentration

An experiment was done where the D2EHPA concentration was varied from 10 - 100 mol/m^3 (see Figure E.5). An increase of the D2EHPA concentration lead to an increase of the monomer in the feed solution (Equation E.6), resulting in an increase of the organic phosphate ions (Equation E.7). The amount of organic phosphate ions in the feed is directly proportional to the amount of zinc ions used to form the ZnR_2 complex as well as percentage zinc extracted.

E.5.4 The effect of the zinc concentration of the feed solution

The percentage extraction lowered with an increase in the zinc concentration of the feed solution. This seems contrary to Equation E.8, but it can be explained by the fact that, although an increase in the zinc concentration of the feed leads to an increase in the zinc concentration of the raffinate solution (a positive effect), it also results in a decrease of the zinc activity coefficient and a lower raffinate pH (both negative effects). It can be seen in Figure E.6 that the equilibrium model accurately predicts this behaviour.

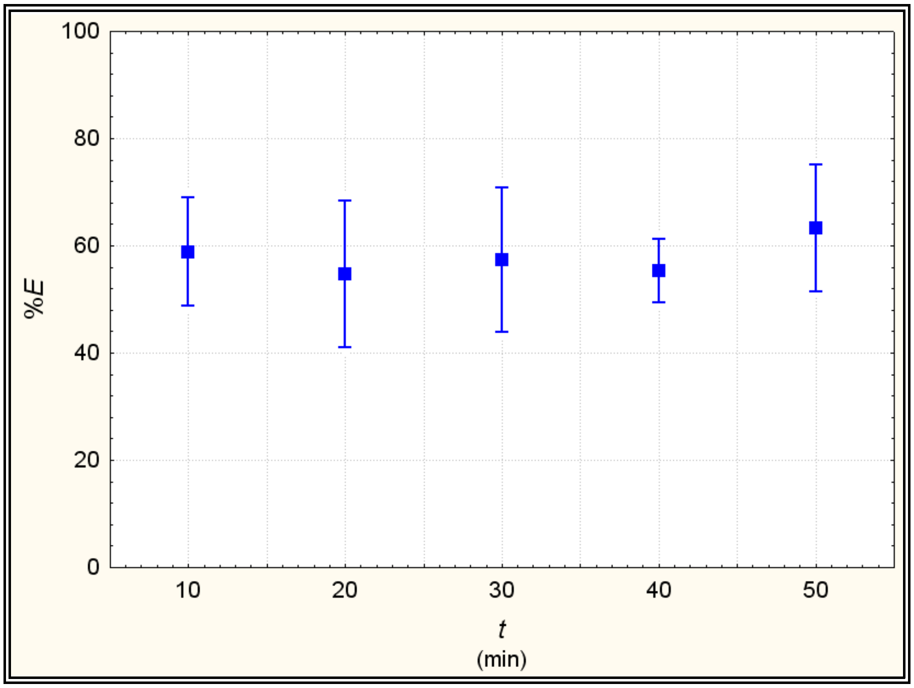

Fig. E.3: Effect of time on % extraction. Vr = 2, $[\mathrm{Zn}]_f \approx 1.5$ mol/m^3, $[\mathrm{RH}]_{Tot}$ = 50 mol/m^3. ■: Experimental data with 95% confidence limits

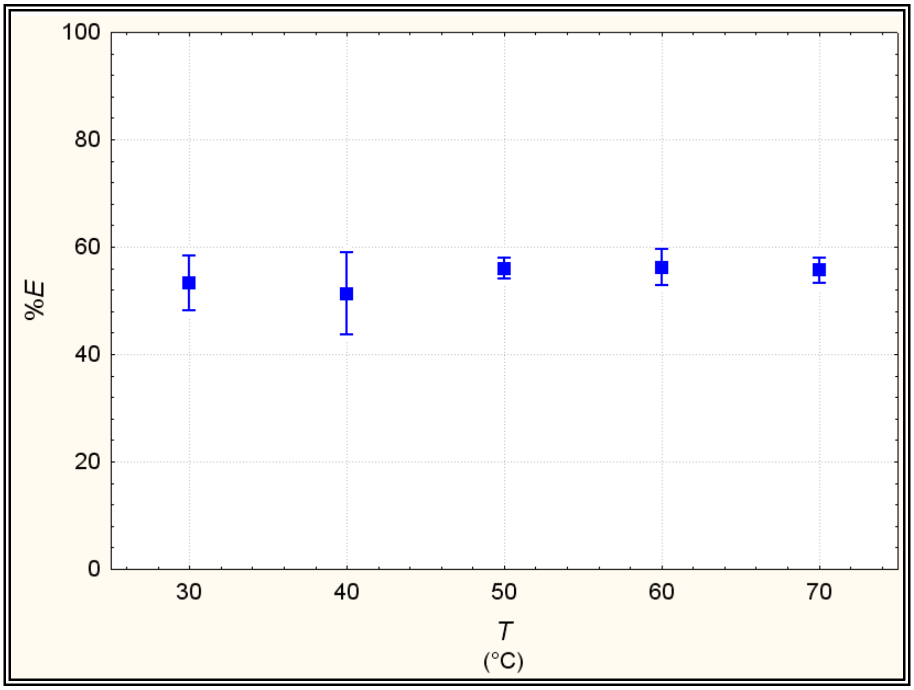

Fig. E.4: Effect of temperature on the % extraction. Vr = 2, $[\mathrm{Zn}]_f \approx 2.0$ mol/m^3, $[\mathrm{RH}]_{Tot}$ = 50 mol/m^3. ■: Experimental data with 95% confidence limits

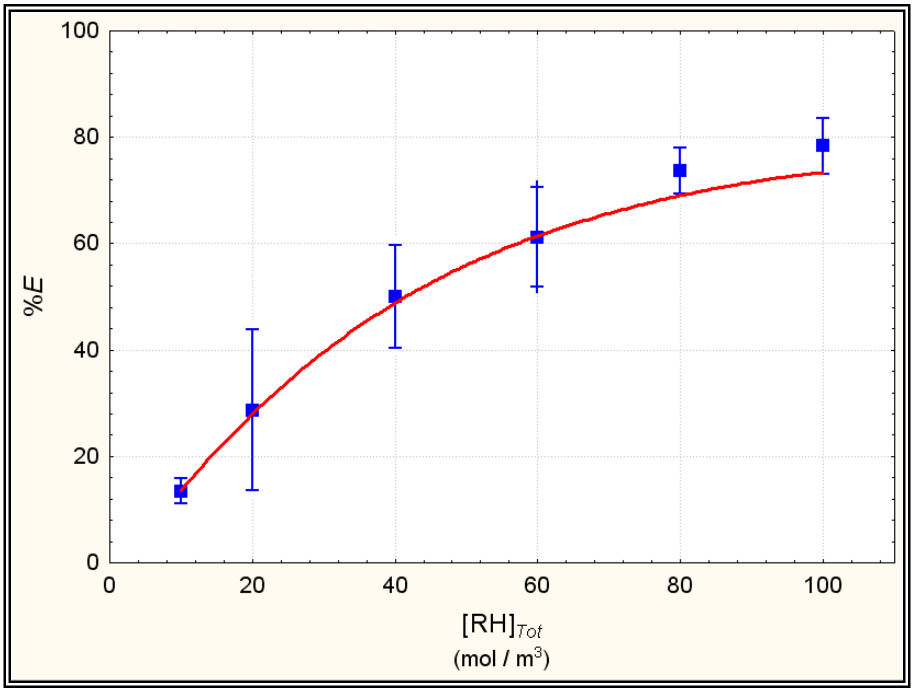

Fig. E.5: Effect of $[\mathrm{RH}]_{Tot}$ on % extraction. $Vr = 2$, $[\mathrm{Zn}]_f \approx 1.9$ mol/m^3, ■: Experimental data with 95% confidence limits. ━━: Equilibrium model

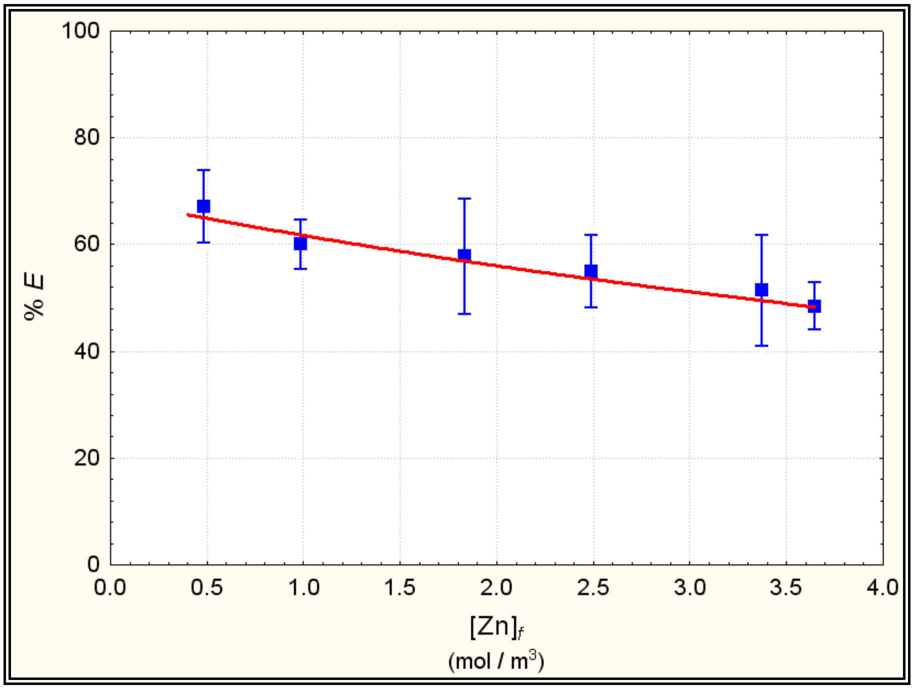

Fig. E.6: Effect of $[\mathrm{Zn}]_f$ on % extraction. $Vr = 2$, $[\mathrm{RH}]_{Tot} = 50$ mol/m^3. ■: Experimental data with 95% confidence limits. ━━ : Equilibrium model

E.5.5 The effect of the raffinate pH

Figure E.7 illustrates the significant effect of pH on the percentage extraction. If the pH of the aqueous feed solvent is increased, the equilibrium of Equation E.7 shifts to the right and this leads to an increase of the organic phosphate ions in the aqueous phase and subsequently in increased extraction.

E.5.6 The effect of the volume ratio between the feed and organic solutions

The effect of the ratio between the volume of the aqueous solvent and the volume of the organic extractant was also tested. The result from Figure E.8 shows that the extraction is better when the volume of the extractant is bigger with respect to the volume of the aqueous phase. This is simply due to the fact that if larger volumes of extractant are used, more moles of D2EHPA are available to extract the zinc.

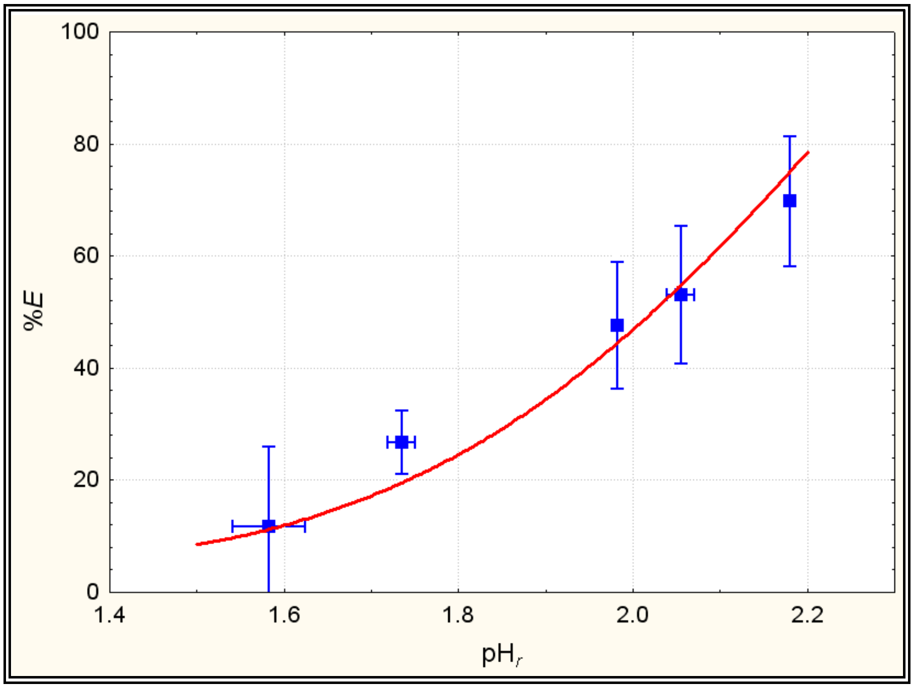

Fig. E.7: Effect of pH_r on % extraction. $Vr = 2$, $[Zn]_f \approx 1.7$ mol/m^3, $[RH]_{Tot} = 50$ mol/m^3. ■: Experimental data with 95% confidence limits. ——: Equilibrium model

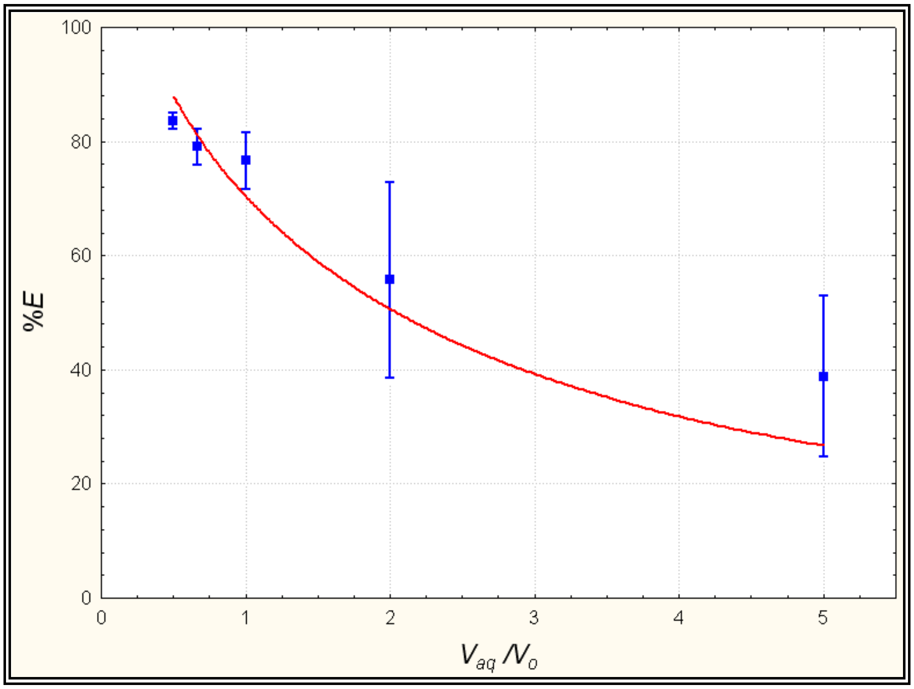

Fig. E.8: Effect of *Vr* on % extraction. $[Zn]_f \approx 1.9$ mol/m^3, $[RH]_{Tot} = 50$ mol/m^3. ■: Experimental data with 95% confidence limits. ——: Equilibrium model

E.6 Conclusions

The Zn/D2EHPA liquid- liquid extraction system was investigated with kerosene as diluent to derive a new equilibrium model and in this model the aqueous activities were used instead of concentrations where it was applicable. The effects of volume ratio, D2EHPA concentration, zinc concentration, pH and temperature on the equilibrium distribution were investigated in this study and the activity of the aqueous species was calculated with appropriate software. It was found that the effect of temperature was negligible and it was proposed that the equilibrium reactions form two chelates, ZnR_2 and $ZnR_2(RH)$. Two constants, K_{Zn1} and K_{Zn2}, in the distribution ratio model were determined through regression in terms of the observed percentage extraction. With a correlation coefficient of 0.996, the proposed model, successfully described the equilibrium of the Zn/D2EHPA system.

E.7 Raw equilibrium results

The meaning of the titles as used in Table E.2 are the following:

Name	: A name is given to each experiment to keep track of the data.
Rep.	: The number of reproducibility test.
V_{aq}	: Volume aqueous solution (ml).
V_o	: Volume organic solution (ml).
$[Zn]_f$	: Nickel concentration of feed solution (mol/m^3).
$[Zn]_r$	: Nickel concentration of raffinate solution (mol/m^3).
$[RH]_{Tot}$	: D2EHPA concentration in organic solution as D2EHPA monomer (mol/m^3).
pH_r	: pH of raffinate solution.
$[H_2SO_4]$	: Concentration of sulphuric acid added to aqueous solution (mol/m^3).

Table E.2: Raw equilibrium results for the extraction of zinc

Name	Rep.	V_{aq} (ml)	V_o (ml)	$[Zn]_f$ (mol/m^3)	$[Zn]_r$ (mol/m^3)	$[RH]_{Tot}$ (mol/m^3)	pH_r	$[H_2SO_4]$ (mol/m^3)
Ext 01	1	40	20	2.064	1.586	10	2.17	4.75
Ext 01	2	40	20	2.231	1.574	10	2.16	4.75
Ext 01	3	40	20	2.007	1.562	10	2.15	4.75
Ext 01	4	40	20	2.014	1.550	10	2.14	4.75
Ext 02	1	40	20	1.673	1.296	20	2.17	4.75
Ext 02	2	40	20	1.729	1.338	20	2.16	4.75
Ext 02	3	40	20	1.454	1.378	20	2.16	4.75
Ext 02	4	40	20	1.843	1.337	20	2.17	4.75
Ext 03	1	40	20	1.686	0.931	40	2.12	4.75
Ext 03	2	40	20	1.871	0.904	40	2.11	4.75
Ext 03	3	40	20	1.592	0.840	40	2.08	4.75
Ext 03	4	40	20	1.656	0.824	40	2.08	4.75

Table E.2 Raw equilibrium results for the extraction of zinc (continue)

Name	Rep.	V_{aq} (ml)	V_o (ml)	$[Zn]_f$ (mol/m^3)	$[Zn]_r$ (mol/m^3)	$[RH]_{Tot}$ (mol/m^3)	pH_r	$[H_2SO_4]$ (mol/m^3)
Ext 04	1	40	20	1.834	0.736	60	2.02	4.75
Ext 04	2	40	20	1.947	0.679	60	2.02	4.75
Ext 04	3	40	20	1.728	0.715	60	2.02	4.75
Ext 04	4	40	20	1.804	0.658	60	2.02	4.75
Ext 05	1	40	20	1.953	0.480	80	2.00	4.75
Ext 05	2	40	20	1.835	0.470	80	2.00	4.75
Ext 05	3	40	20	1.811	0.459	80	2.00	4.75
Ext 05	4	40	20	1.916	0.490	80	2.00	4.75
Ext 06	1	40	20	1.677	0.367	100	1.99	4.75
Ext 06	2	40	20	1.671	0.412	100	1.99	4.75
Ext 06	3	40	20	1.919	0.432	100	1.99	4.75
Ext 06	4	40	20	1.570	0.362	100	1.99	4.75
Znf 01	1	40	20	0.477	0.156	50	2.10	4.75
Znf 01	2	40	20	0.457	0.153	50	2.10	4.75
Znf 01	3	40	20	0.579	0.176	50	2.10	4.75
Znf 01	4	40	20	0.431	0.156	50	2.08	4.75
Znf 02	1	40	20	0.980	0.373	50	2.11	4.75
Znf 02	2	40	20	1.023	0.373	50	2.08	4.75
Znf 02	3	40	20	0.980	0.395	50	2.10	4.75
Znf 02	4	40	20	0.972	0.440	50	2.07	4.75
Znf 03	1	40	20	1.635	0.692	50	2.08	4.75
Znf 03	2	40	20	1.576	0.730	50	2.07	4.75
Znf 03	3	40	20	1.606	0.677	50	2.09	4.75
Znf 03	4	40	20	1.723	0.529	50	2.09	4.75
Znf 04	1	40	20	2.104	0.813	50	2.13	4.75
Znf 04	2	40	20	1.657	0.668	50	2.11	4.75
Znf 04	3	40	20	1.775	0.695	50	2.09	4.75
Znf 04	4	40	20	1.794	0.922	50	2.06	4.75

Table E.2 Raw equilibrium results for the extraction of zinc (continue)

Name	Rep.	V_{aq} (ml)	V_o (ml)	$[Zn]_f$ (mol/m^3)	$[Zn]_r$ (mol/m^3)	$[RH]_{Tot}$ (mol/m^3)	pH_r	$[H_2SO_4]$ (mol/m^3)
Znf 05	1	40	20	2.339	1.285	50	2.08	4.75
Znf 05	2	40	20	2.574	1.116	50	2.03	4.75
Znf 05	3	40	20	2.522	1.060	50	2.05	4.75
Znf 05	4	40	20	2.522	1.032	50	2.06	4.75
Znf 06	1	40	20	2.818	1.662	50	2.04	4.75
Znf 06	2	40	20	2.765	1.334	50	2.03	4.75
Znf 06	3	40	20	2.871	1.161	50	2.06	4.75
Znf 06	4	40	20	2.871	1.452	50	2.03	4.75
Znf 07	1	40	20	3.371	1.378	50	2.06	4.75
Znf 07	2	40	20	3.371	1.901	50	2.07	4.75
Znf 07	3	40	20	3.371	1.693	50	2.09	4.75
Znf 07	4	40	20	3.371	1.587	50	2.07	4.75
Znf 08	1	40	20	3.335	1.968	50	2.05	4.75
Znf 08	2	40	20	3.570	1.767	50	2.05	4.75
Znf 08	3	40	20	4.175	1.811	50	2.02	4.75
Znf 08	4	40	20	3.503	1.974	50	2.02	4.75
pHr 01	1	40	20	1.710	1.683	50	1.60	22.0
pHr 01	2	40	20	1.951	1.760	50	1.59	22.0
pHr 01	3	40	20	1.989	1.544	50	1.57	22.0
pHr 01	4	40	20	1.805	1.594	50	1.57	22.0
pHr 02	1	40	20	2.024	1.385	50	1.74	13.5
pHr 02	2	40	20	2.151	1.341	50	1.74	13.5
pHr 02	3	40	20	1.891	1.307	50	1.73	13.5
pHr 02	4	40	20	1.720	1.331	50	1.73	13.5
pHr 03	1	40	20	1.886	0.921	50	1.97	5.50
pHr 03	2	40	20	1.643	0.818	50	1.98	5.50
pHr 03	3	40	20	1.848	0.940	50	2.21	5.50
pHr 03	4	40	20	1.617	0.989	50	2.00	5.50

Table E.2 Raw equilibrium results for the extraction of zinc (continue)

Name	Rep.	V_{aq} (ml)	V_o (ml)	$[Zn]_f$ (mol/m^3)	$[Zn]_r$ (mol/m^3)	$[RH]_{Tot}$ (mol/m^3)	pH_r	$[H_2SO_4]$ (mol/m^3)
pHr 04	1	40	20	1.564	0.691	50	2.05	4.75
pHr 04	2	40	20	0.983	0.722	50	2.05	4.75
pHr 04	3	40	20	0.921	0.600	50	2.06	4.75
pHr 04	4	40	20	1.443	0.751	50	2.06	4.75
pHr 05	1	40	20	1.244	0.360	50	2.18	3.03
pHr 05	2	40	20	1.545	0.388	50	2.18	3.03
pHr 05	3	40	20	1.382	0.474	50	2.18	3.03
pHr 05	4	40	20	1.426	0.474	50	2.18	3.03
Vr 01	1	20	40	1.992	0.321	50	2.15	4.75
Vr 01	2	20	40	1.826	0.314	50	2.19	4.75
Vr 01	3	20	40	1.851	0.300	50	2.17	4.75
Vr 01	4	20	40	1.975	0.321	50	2.17	4.75
Vr 02	1	24	36	1.791	0.413	50	2.06	4.75
Vr 02	2	24	36	1.989	0.385	50	2.06	4.75
Vr 02	3	24	36	1.848	0.371	50	2.09	4.75
Vr 02	4	24	36	1.922	0.413	50	2.06	4.75
Vr 03	1	30	30	2.050	0.445	50	2.07	4.75
Vr 03	2	30	30	2.107	0.425	50	2.07	4.75
Vr 03	3	30	30	1.968	0.499	50	2.04	4.75
Vr 03	4	30	30	1.862	0.492	50	2.05	4.75
Vr 04	1	40	20	1.863	0.844	50	2.03	4.75
Vr 04	2	40	20	1.764	0.770	50	2.03	4.75
Vr 04	3	40	20	1.729	0.738	50	2.03	4.75
Vr 04	4	40	20	1.608	0.728	50	2.02	4.75
Vr 05	1	50	10	1.815	1.069	50	2.07	4.75
Vr 05	2	50	10	2.029	1.058	50	2.07	4.75
Vr 05	3	50	10	1.707	1.193	50	2.08	4.75
Vr 05	4	50	10	1.924	1.251	50	2.07	4.75

Table E.2 Raw equilibrium results for the extraction of zinc (continue)

Name	Rep.	V_{aq} (ml)	V_o (ml)	$[Zn]_f$ (mol/m^3)	$[Zn]_r$ (mol/m^3)	$[RH]_{Tot}$ (mol/m^3)	pH_r	$[H_2SO_4]$ (mol/m^3)
Tmp 01	2	40	20	1.975	0.956	50	2.02	4.75
Tmp 01	3	40	20	2.214	1.026	50	2.01	4.75
Tmp 01	4	40	20	2.207	0.942	50	2.02	4.75
Tmp 02	1	40	20	2.132	0.942	50	2.04	4.75
Tmp 02	2	40	20	2.071	0.942	50	2.06	4.75
Tmp 02	3	40	20	1.972	0.938	50	2.04	4.75
Tmp 02	4	40	20	1.782	1.049	50	2.02	4.75
Tmp 03	1	40	20	2.344	0.925	50	2.02	4.75
Tmp 03	2	40	20	2.165	0.899	50	2.02	4.75
Tmp 03	3	40	20	2.010	0.915	50	2.02	4.75
Tmp 03	4	40	20	1.739	0.892	50	2.02	4.75
Tmp 04	1	40	20	2.153	0.863	50	2.00	4.75
Tmp 04	2	40	20	2.590	0.818	50	2.01	4.75
Tmp 04	3	40	20	1.684	0.840	50	2.00	4.75
Tmp 04	4	40	20	1.306	0.869	50	2.01	4.75
Tmp 05	1	40	20	1.700	0.834	50	2.05	4.75
Tmp 05	2	40	20	1.956	0.862	50	2.02	4.75
Tmp 05	3	40	20	2.090	0.826	50	2.02	4.75
Tmp 05	4	40	20	1.837	0.844	50	2.02	4.75
Ctr 01	1	40	20	1.592	0.538	50	2.07	4.75
Ctr 01	2	40	20	1.343	0.589	50	2.07	4.75
Ctr 01	3	40	20	1.349	0.568	50	2.06	4.75
Ctr 01	4	40	20	1.441	0.659	50	2.06	4.75
Ctr 02	1	40	20	1.383	0.588	50	2.08	4.75
Ctr 02	2	40	20	1.529	0.665	50	2.08	4.75
Ctr 02	3	40	20	1.663	0.665	50	2.08	4.75
Ctr 02	4	40	20	1.354	0.765	50	2.11	4.75

Table E.2 Raw equilibrium results for the extraction of zinc (continue)

Name	Rep.	V_{aq} (ml)	V_o (ml)	$[Zn]_f$ (mol/m^3)	$[Zn]_r$ (mol/m^3)	$[RH]_{Tot}$ (mol/m^3)	pH_r	$[H_2SO_4]$ (mol/m^3)
Ctr 03	1	40	20	1.565	0.557	50	2.10	4.75
Ctr 03	2	40	20	1.571	0.641	50	2.13	4.75
Ctr 03	3	40	20	1.386	0.732	50	2.10	4.75
Ctr 03	4	40	20	1.593	0.679	50	2.10	4.75
Ctr 04	1	40	20	1.313	0.615	50	2.12	4.75
Ctr 04	2	40	20	1.502	0.639	50	2.09	4.75
Ctr 04	3	40	20	1.264	0.608	50	2.10	4.75
Ctr 04	4	40	20	1.362	0.569	50	2.12	4.75
Ctr 05	1	40	20	1.430	0.538	50	2.18	4.75
Ctr 05	2	40	20	1.529	0.607	50	2.18	4.75
Ctr 05	3	40	20	1.600	0.538	50	2.14	4.75
Ctr 05	4	40	20	1.491	0.538	50	2.12	4.75
N01	1	40	20	2.105	1.700	40	1.72	13.6
N01	2	40	20	2.119	1.799	40	1.73	13.6
N01	3	40	20	2.058	1.864	40	1.76	13.6
N01	4	40	20	2.058	1.832	40	1.71	13.6
N02	1	40	20	1.682	0.677	40	2.21	2.70
N02	2	40	20	1.664	0.617	40	2.21	2.70
N02	3	40	20	1.548	0.718	40	2.23	2.70
N02	4	40	20	1.493	0.695	40	2.22	2.70
N03	1	24	36	2.139	1.234	40	1.73	13.6
N03	2	24	36	2.078	1.310	40	1.71	13.6
N03	3	24	36	2.159	1.412	40	1.71	13.6
N03	4	24	36	1.925	1.283	40	1.71	13.6
N04	1	24	36	1.980	0.419	40	2.10	2.70
N04	2	24	36	1.849	0.284	40	2.10	2.70
N04	3	24	36	1.870	0.352	40	2.12	2.70
N04	4	24	36	1.767	0.352	40	2.09	2.70

Table E.2 Raw equilibrium results for the extraction of zinc (continue)

Name	Rep.	V_{aq} (ml)	V_o (ml)	$[Zn]_f$ (mol/m^3)	$[Zn]_r$ (mol/m^3)	$[RH]_{Tot}$ (mol/m^3)	pH_r	$[H_2SO_4]$ (mol/m^3)
N05	1	40	20	2.138	1.484	60	1.80	13.6
N05	2	40	20	2.416	1.522	60	1.79	13.6
N05	3	40	20	1.901	1.478	60	1.78	13.6
N05	4	40	20	2.042	1.403	60	1.77	13.6
N06	1	40	20	1.746	0.640	60	2.12	2.70
N06	2	40	20	1.809	0.513	60	2.13	2.70
N06	3	40	20	1.774	0.543	60	2.12	2.70
N06	4	40	20	1.532	0.483	60	2.12	2.70
N07	1	24	36	2.113	0.997	60	1.81	13.6
N07	2	24	36	1.928	0.890	60	1.76	13.6
N07	3	24	36	1.882	0.991	60	1.73	13.6
N07	4	24	36	2.033	1.111	60	1.71	13.6
N08	1	24	36	1.891	0.256	60	2.09	2.70
N08	2	24	36	2.019	0.284	60	2.09	2.70
N08	3	24	36	1.651	0.280	60	2.10	2.70
N08	4	24	36	1.938	0.315	60	2.10	2.70
N09	1	40	20	2.443	1.632	40	2.20	2.70
N09	2	40	20	6.357	2.015	40	2.21	2.70
N09	3	40	20	7.800	1.600	40	2.18	2.70
N09	4	40	20	4.454	1.749	40	2.21	2.70
N10	1	24	36	4.836	2.595	40	1.71	13.6
N10	2	24	36	3.605	2.684	40	1.74	13.6
N10	3	24	36	5.843	2.355	40	1.81	13.6
N10	4	24	36	3.721	2.595	40	1.79	13.6
N11	1	24	36	4.996	1.551	40	2.11	2.70
N11	2	24	36	3.242	1.496	40	2.10	2.70
N11	3	24	36	3.307	1.551	40	2.11	2.70
N11	4	24	36	3.436	1.463	40	2.10	2.70

Table E.2 Raw equilibrium results for the extraction of zinc (continue)

Name	Rep.	V_{aq} (ml)	V_o (ml)	$[Zn]_f$ (mol/m^3)	$[Zn]_r$ (mol/m^3)	$[RH]_{Tot}$ (mol/m^3)	pH_r	$[H_2SO_4]$ (mol/m^3)
N12	1	40	20	3.613	3.026	60	1.81	13.6
N12	2	40	20	5.286	3.026	60	1.68	13.6
N12	3	40	20	4.146	3.183	60	1.74	13.6
N12	4	40	20	3.946	3.026	60	1.77	13.6
N13	1	40	20	2.942	1.315	60	2.18	2.70
N13	2	40	20	3.196	1.406	60	2.16	2.70
N13	3	40	20	3.461	1.380	60	2.18	2.70
N13	4	40	20	3.917	1.406	60	2.25	2.70
N14	1	24	36	3.898	2.650	60	1.74	13.6
N14	2	24	36	4.368	2.911	60	1.67	13.6
N14	3	24	36	4.839	2.435	60	1.74	13.6
N14	4	24	36	4.907	2.605	60	1.72	13.6
N15	1	24	36	4.286	0.841	60	2.09	2.70
N15	2	24	36	3.200	0.841	60	2.09	2.70
N15	3	24	36	3.901	0.827	60	2.11	2.70
N15	4	24	36	3.710	0.763	60	2.12	2.70
N16	1	30	30	3.028	1.212	50	1.99	5.14
N16	2	30	30	2.963	1.299	50	2.00	5.14
N16	3	30	30	3.880	1.439	50	1.99	5.14
N16	4	30	30	2.898	1.245	50	1.97	5.14

E.8 Processed equilibrium results

The meaning of the titles as used in Table E.3 are as follow:

Name : A short code of the experiment.

Vr : Volume ratio = V_{aq}/V_o.

$[Zn]_f$: Concentration of the nickel in the feed solution (mol/m^3).

$\sigma([Zn]_f)$: Standard deviation of $[Zn]_f$.

$[Zn]_r$: Concentration of the nickel in the raffinate solution (mol/m^3).

$\sigma([Zn]_r)$: Standard deviation of $[Zn]_r$.

pH_r : Average pH of raffinate solution.

$\sigma(pH_r)$: Standard deviation of pH_r.

$a(H_r)$: Activity of hydronium ions in raffinate solution (mol/m^3).

$\gamma(Zn_r)$: Activity coefficient of the nickel in the raffinate solution.

$\%E$: % extraction of nickel ions. Calculated with Equation 4.13.

$\sigma(\%E)$: Standard deviation of $\%E$.

Table E.3: Processed results for extraction equilibrium of zinc

Name	Vr	$[Zn]_f$ (mol/m^3)	$\sigma([Zn]_f)$ (mol/m^3)	$[Zn]_r$ (mol/m^3)	$\sigma([Zn]_r)$ (mol/m^3)	pH_r	$\sigma(pH_r)$	$a(H_r)$ (mol/m^3)	$\gamma(Zn_r)$	$\%E$	$\sigma(\%E)$
Ext 01	2.0	1.81	0.10	1.57	0.02	2.155	0.013	7.0	0.584	13.5	0.9
Ext 02	2.0	1.99	0.16	1.42	0.13	2.165	0.006	7.2	0.586	28.7	6.6
Ext 03	2.0	1.99	0.12	0.99	0.08	2.098	0.021	8.1	0.589	50.0	4.2
Ext 04	2.0	1.99	0.09	0.77	0.08	2.020	0.000	9.0	0.584	61.2	4.0
Ext 05	2.0	1.99	0.07	0.52	0.04	2.000	0.000	9.5	0.586	73.6	1.9
Ext 06	2.0	1.81	0.15	0.39	0.03	1.990	0.000	10.2	0.582	78.3	1.9
Znf 01	2.0	0.49	0.06	0.16	0.01	2.095	0.010	8.0	0.620	67.0	4.9
Znf 02	2.0	0.99	0.02	0.40	0.03	2.090	0.018	8.1	0.608	60.0	3.3
Znf 03	2.0	1.63	0.20	0.66	0.09	2.083	0.010	8.3	0.596	59.8	7.3
Znf 04	2.0	1.83	0.19	0.77	0.12	2.098	0.030	8.0	0.598	57.7	7.7
Znf 05	2.0	2.49	0.10	1.12	0.11	2.055	0.021	8.8	0.576	54.9	4.9
Znf 06	2.0	2.83	0.05	1.40	0.21	2.040	0.014	9.1	0.565	50.5	7.5
Znf 07	2.0	3.37	0.27	1.64	0.22	2.073	0.013	8.5	0.565	51.4	7.5
Znf 08	2.0	3.65	0.37	1.88	0.11	2.035	0.017	9.2	0.551	48.4	3.2
pHr 01	2.0	1.86	0.13	1.65	0.10	1.583	0.015	26.2	0.443	11.7	5.1
pHr 02	2.0	1.83	0.18	1.34	0.03	1.735	0.006	18.4	0.488	26.7	1.8

Table E.3: Processed results for extraction equilibrium of zinc (continue)

Name	*Vr*	$[Zn]_f$ (mol/m^3)	$\sigma([Zn]_f)$ (mol/m^3)	$[Zn]_r$ (mol/m^3)	$\sigma([Zn]_r)$ (mol/m^3)	pH_r	$\sigma(pH_r)$	$a(H_r)$ (mol/m^3)	$\gamma(Zn_r)$	%*E*	σ(%*E*)
pHr 03	2.0	1.75	0.14	0.92	0.07	2.040	0.114	10.4	0.578	47.6	4.1
pHr 04	2.0	1.47	0.32	0.69	0.07	2.055	0.006	8.8	0.589	53.0	4.4
pHr 05	2.0	1.40	0.12	0.42	0.06	2.180	0.000	6.6	0.632	69.7	4.2
Vr 01	0.5	1.91	0.08	0.31	0.01	2.170	0.016	6.8	0.634	83.5	0.5
Vr 02	0.7	1.89	0.09	0.40	0.02	2.068	0.015	8.6	0.603	79.0	1.1
Vr 03	1.0	2.00	0.11	0.47	0.04	2.058	0.015	8.8	0.598	76.7	1.8
Vr 04	2.0	1.74	0.11	0.77	0.11	2.028	0.005	9.4	0.582	55.8	6.2
Vr 05	5.0	1.87	0.14	1.14	0.09	2.073	0.005	8.5	0.580	38.8	5.1
Tmp 01	2.0	2.07	0.16	0.97	0.04	2.018	0.005	8.5	0.575	53.2	1.8
Tmp 02	2.0	1.99	0.15	0.97	0.05	2.040	0.016	8.7	0.580	51.3	2.7
Tmp 03	2.0	2.06	0.26	0.91	0.02	2.020	0.000	8.5	0.583	56.0	0.7
Tmp 04	2.0	1.93	0.56	0.85	0.02	2.005	0.006	8.4	0.582	56.2	1.2
Tmp 05	2.0	1.90	0.17	0.84	0.02	2.028	0.015	8.6	0.588	55.6	0.8
Ctr 01	2.0	1.43	0.12	0.59	0.05	2.065	0.006	8.6	0.591	58.9	3.6
Ctr 02	2.0	1.48	0.14	0.67	0.07	2.088	0.015	8.2	0.593	54.7	4.9
Ctr 03	2.0	1.53	0.10	0.65	0.07	2.108	0.015	7.8	0.597	57.4	4.8
Ctr 04	2.0	1.36	0.10	0.61	0.03	2.108	0.015	7.8	0.598	55.3	2.1
Ctr 05	2.0	1.51	0.07	0.56	0.06	2.155	0.030	7.0	0.610	63.3	4.3
N01	2.0	2.07	0.03	1.80	0.01	1.730	0.022	18.6	0.481	13.0	0.6
N02	2.0	1.76	0.09	0.68	0.04	2.218	0.010	6.1	0.626	61.6	2.5
N03	0.7	2.07	0.11	1.31	0.07	1.715	0.010	19.3	0.485	36.7	3.6
N04	0.7	1.76	0.09	0.35	0.06	2.103	0.013	7.9	0.617	80.1	3.1
N05	2.0	2.07	0.22	1.47	0.05	1.785	0.013	16.4	0.500	28.8	2.4
N06	2.0	1.76	0.13	0.54	0.07	2.123	0.005	7.5	0.610	69.1	3.9
N07	0.7	2.07	0.10	1.00	0.09	1.753	0.043	17.7	0.498	51.8	4.4
N08	0.7	1.76	0.16	0.28	0.02	2.095	0.006	8.0	0.613	83.9	1.4
N09	2.0	4.04	2.33	1.75	0.32	2.200	0.014	6.3	0.583	56.7	8.0

Table E.3: Processed results for extraction equilibrium of zinc (continue)

Name	Vr	$[\text{Zn}]_f$ (mol/m^3)	$\sigma([\text{Zn}]_f)$ (mol/m^3)	$[\text{Zn}]_r$ (mol/m^3)	$\sigma([\text{Zn}]_r)$ (mol/m^3)	pH_r	$\sigma(\text{pH}_r)$	$a(\text{H}_r)$ (mol/m^3)	$\gamma(\text{Zn}_r)$	$\%E$	$\sigma(\%E)$
N10	0.7	4.40	1.05	2.56	0.21	1.763	0.046	17.4	0.472	41.8	4.8
N11	0.7	4.04	0.84	1.52	0.06	2.105	0.006	7.9	0.569	62.5	1.5
N12	2.0	4.40	0.73	3.06	0.19	1.750	0.055	16.9	0.474	30.3	4.4
N13	2.0	4.04	0.42	1.38	0.25	2.193	0.039	6.4	0.586	65.9	6.1
N14	0.7	4.40	0.47	2.65	0.09	1.718	0.033	19.2	0.463	39.7	2.1
N15	0.7	4.04	0.45	0.82	0.07	2.103	0.015	7.9	0.580	79.8	1.7
N16	1.0	3.00	0.46	1.30	0.10	1.988	0.013	10.3	0.552	56.8	3.3

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