DEVELOPING A SOLVENT EXTRACTION PROCESS FOR THE SEPARATION OF COBALT AND IRON FROM NICKEL SULFATE SOLUTIONS

By

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DECLARATION

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ABSTRACT

Crude $NiSO_4$ solutions are often produced as a product of Sherrit based matte leach processes leading to iron and cobalt contaminated solutions of $NiSO_4$. To upgrade the quality of these solutions for either, the production of $NiSO_4$ crystals or cathode/precipitated nickel, the iron and cobalt must be removed.

Conventional processes use either pure or saponified Cyanex 272 in solvent extraction to extract iron and cobalt from pregnant nickel leach solutions. These processes require the addition of an alkali like NaOH to neutralise the protons being exchanged for the different metal species since extraction is a strong function of pH. Hence, while removing iron and cobalt from the solution, sodium is added instead. This limitation can be dealt with by pre-loading of Cyanex 272 with a portion of the purified nickel product prior to impurity extraction. During the extraction stage nickel is then exchanged for the impurities instead of hydrogen and no NaOH addition is necessary, resulting in a pure nickel product. The extracted metals are recovered from the organic phase by stripping it with H_2SO_4 and the organic phase is recycled.

A solvent extraction process that purifies an 80 g/l nickel sulfate solution from 1 g/l cobalt and 3 g/l iron was developed. The key variables include pH, organic/aqueous (O/A) mixing ratio, nickel loading, H_2SO_4 concentration, Cyanex 272 concentration, various organic diluents and temperature. These variables were investigated via preliminary and three 2^4 factorial design batch experiments which reduced the variables to pH/NaOH addition and O/A ratio for the pre-loading section, nickel loading and O/A ratio for the extraction section and H_2SO_4 concentration and A/O ratio for the stripping section. The reduced variables were considered in further batch experiments from which the data was used to develop models and design a simulation sheet in *Microsoft Excel* of the extraction circuit. These final batch tests revealed the conditions that resulted in the purest aqueous nickel product after extraction, where nickel and cobalt can selectively be stripped from iron and what H_2SO_4 concentration and A/O ratio is necessary to finally strip iron and regenerate the organic phase. Ultimately four tests were conducted on a mixer-settler setup to test the validity of the simulation sheet.

The proposed process conditions for the solvent extraction circuit are to use a 20V% Cyanex 272 solution in Shellsol D70 as diluent that are pre-loaded with an 80 g/l purified nickel product solution at an O/A ratio of 25 and a pH of 7 generating a nickel loading of 3.2 g/l for the extraction section. This loading at an O/A ratio of 1.5 produces a high pure nickel aqueous product (0.05 g/l Co, 0.01 g/l Fe). From the generated organic phase co-extracted nickel and cobalt can selectively be stripped with 0.1 M H_2SO_4 at an A/O ratio of 2.25 followed by an 1 M H_2SO_4 solution at an A/O ratio of 0.75 to strip the remaining iron. The temperature at all the stages should be controlled between 40-50°C to ensure phase separation.

Opsomming

Ongesuiwerde NiSO$_4$ oplossings word gedurig vervaardig as 'n produk van die *Sherrit* gebaseerde mat logingsproses wat lei tot yster en kobalt gekontamineerder oplossings van NiSO$_4$. Om die graad van hierdie oplossings op te gradeer vir die produksie van of NiSO$_4$ kristalle of katode/gepresipiteerde nikkel, moet die yster en kobalt eers verwyder word.

Meeste prosesse gebruik of suiwer Cyanex 272 of die natrium sout van Cyanex 272 in 'n vloeistof-vloeistof ekstraksie siklus om yster en kobalt vanuit versadigde nikkel oplossing te ekstraheer. Hierdie prosesse verg die gebruik van 'n alkali soos NaOH om die protone te neutraliseer wat geruil word vir die verskillende metaal spesies, aangesien ekstraksie 'n baie sterk funksie van pH is. Dit het tot gevolg dat natrium tot die oplossing bygevoeg word soos wat yster en kobalt verwyder word. Hierdie tekortkoming kan oorkom word deur Cyanex 272 eers te laai met nikkel deur 'n porsie van die gesuiwerde nikkel produk te gebruik voor die onsuiwerhede geëkstraheer word. Gedurende die ekstraksie stadium word nikkel dan geruil vir die onsuiwerhede, in plaas van waterstof, en geen NaOH toevoeging is nodig nie. Die gevolg is 'n suiwer nikkel oplossing. Die geëkstraheerde metaal word herwin vanaf die organies fase deur dit te stroop met 'n H$_2$SO$_4$ oplossing en die organiese fase kan weer gehersirkuleer word.

'n Vloeistof-vloeistof ekstraksie proses wat 'n 80 g/l nikkelsulfaat oplossing van 1 g/l kobalt en 3 g/l yster suiwer, is ontwikkel. Die belangrikste veranderlikes sluit in pH, organies/waterige (O/A) mengingsverhouding, nikkel lading, H$_2$SO$_4$ konsentrasie, Cyanex 272 konsentrasie, verskillende organiese oplosmiddels en temperatuur. Hierdie veranderlikes was ondersoek deur verskeie voorlopige en drie 2^4 faktoriaal ontwerp enkel-lading eksperimente wat gevolglik die veranderlikes verminder het na pH/NaOH toevoeging en O/A verhouding vir die voorbelading seksie, nikkel lading en O/A verhouding vir die ekstraksie seksie en H$_2$SO$_4$ konsentrasie en A/O verhouding vir die stroping seksie. Die verminderde veranderlikes was verder ondersoek in nog enkel-lading eksperimente, waarvan die data gebruik was om modelle op te stel en 'n simulasie sigblad in *Microsoft Excel* te ontwerp van die ekstraksie siklus. Die finale enkel-lading toetse het die kondisies weergegee wat die mees suiwer waterige nikkel produk sal oplewer na ekstraksie, waar kobalt en nikkel selektief van yster gestroop kan word en watter H$_2$SO$_4$ konsentrasie en A/O verhouding nodig is om yster finaal te stroop en die organiese fase te regenereer. Laastens is vier toetse gedoen op 'n menger-afskeidingstenk opstelling om die betroubaarheid van die simulasie sigblad te toets.

Die bedryfstoestande wat voorgestel word vir die vloeistof-vloeistof ekstraksie siklus is om 'n 20V% Cyanex 272 oplossing in Shellsol D70 as oplosmiddel vooraf te laai met 'n 80 g/l gesuiwerde nikkel produk oplossing by 'n O/A verhouding van 25 en 'n pH van 7 om 'n nikkel lading van 3.2 g/l vir die ekstraksie seksie te genereer. Hierdie lading by 'n O/A verhouding van 1.5 produseer 'n suiwer nikkel waterige oplossing produk (0.05 g/l Co, 0.01 g/l Fe). Vanaf die gegenereerde organiese fase kan die geëkstraheerde nikkel en kobalt selektief gestroop word met 0.1 M H$_2$SO$_4$ by 'n A/O verhouding van 2.25 gevolg deur 'n 1 M H$_2$SO$_4$ oplossing by 'n A/O verhouding van 0.75 om die oorblywende yster te stroop. Die temperatuur waarby al die stadiums beheer moet word is tussen 40-50°C om fase skeiding te verseker.

ACKNOWLEDGEMENTS

Galatians 2:20 (ESV): "I have been crucified with Christ. It is no longer I who live, but Christ who lives in me. And the life I now live in the flesh I live by faith in the Son of God, who loved me and gave himself for me"

First of all I would like to give all the Glory to Jesus Christ my Lord and Saviour. Without Him I can do nothing. He, through the Holy Spirit, is my primary source of favour, strength, endurance, knowledge and wisdom.

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Appendix A (Experimental and Modelling results)

NOMENCLATURE

Symbol	Description	Unit
A/O	Aqueous/organic mixing ratio (notation for stripping)	ml/ml
b_{1-6}	Modelling constants	-
β	Separation factor	-
C	Modelling constant	-
Co_{aq}	Cobalt concentration in the aqueous phase at equilibrium	g/l
Co_o	Cobalt concentration in the aqueous phase before mixing	g/l
Co_{org}	Cobalt concentration in the organic phase at equilibrium	g/l
D	Distribution coefficient	[g/l]/[g/l]
E	Percentage extracted	%
$f(y,x)$	Loading pH, extraction pH, cobalt and iron extraction and nickel, cobalt and iron stripping	-, %
F_{aq}	Aqueous flow rate	ml/min
fi	Modelled value used to determine R^2	g/l
F_{NaOH}	NaOH flow rate	ml/min
F_{org}	Organic flow rate	ml/min
Fe_{aq}	Iron concentration in the aqueous phase at equilibrium	g/l
Fe_o	Iron concentration in the aqueous phase before mixing	g/l
Fe_{org}	Iron concentration in the organic phase at equilibrium	g/l
K	Equilibrium constant (K)	-
[M]	Metal concentration in the aqueous phase at equilibrium	g/l
$[M]_o$	Metal concentration in the aqueous phase before mixing	g/l
$[M]_{org}$	Metal concentration in the organic phase at equilibrium	g/l
$MS_{between}$	Mean squares between groups	$(g/l)^2$
MS_{within}	Mean squares within groups	$(g/l)^2$
n	Number of repeated measurements	-
N_A	Moles of metal A in aqueous phase after extraction	mol
N_{AO}	Initial moles of metal A in the aqueous phase	mol
NaOH/Nio	Relative moles of NaOH added with respect to the initial moles of nickel in the aqueous phase	mol/mol
Ni_{aq}	Nickel concentration in the aqueous phase at equilibrium	g/l
Ni_o	Nickel concentration in the aqueous phase before mixing	g/l
Ni_{org}	Nickel concentration in the organic phase at equilibrium	g/l
O/A	Organic/aqueous mixing ratio (notation for pre-loading and extraction)	ml/ml
pH_{50}	pH at which 50% of the metal species is extracted	-
r	Repeatability	-
R^2	Model performance parameter	-
S	Percentage stripped	%

SS_{err}	Sum of squares of residuals	$(g/l)^2$
SS_{tot}	Total sum of squares	$(g/l)^2$
V_{aq}	Volume of the aqueous phase	ml
V_{org}	Volume of the organic phase	ml
x	Represent NaOH/Nio (pre-loading), O/A ratio (extraction) and H_2SO_4 concentration (stripping) in the respective models	mol/mol, ml/ml, M
Y	Represent O/A ratio (pre-loading), nickel loading (extraction) and A/O ratio (stripping) in the respective models	ml/ml, g/l, ml/ml
$\bar{y}$	Average of the experimental values used to determine R^2	-, g/l
y_i	Experimental value used to determine R^2	-, g/l

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

The mined ore being processed for PGM (platinum group metal) production typically consists of base metals such as nickel, copper, cobalt, and iron. Nickel, copper and cobalt are present in economically recoverable quantities while iron should be removed as an impurity. In order to recover the PGMs and base metals, the ore goes through various processing stages which usually include comminution, flotation, smelting and base metal refining.

Figure 1-1 gives a broad overview of a typical base metal refinery.
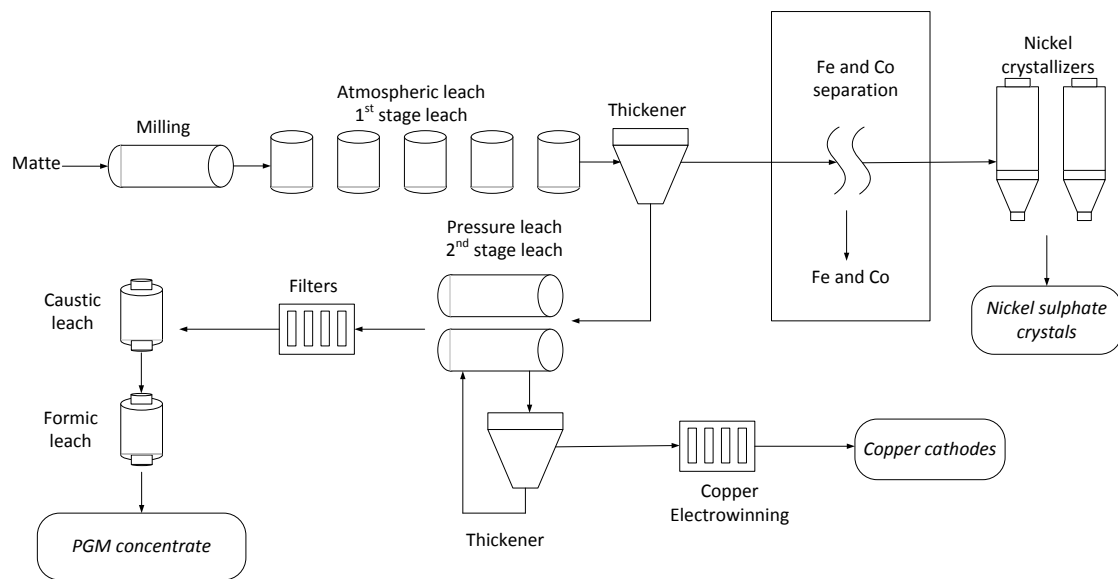
Figure 1-1: Process flow sheet of a typical base metal refinery

The matte from the smelter is ground in a closed circuit ball mill before being sent to the atmospheric leaching stage. During the first stage of atmospheric leaching nickel is dissolved from the nickel alloy and nickel sulphide phases in the matte using a sulphuric acid solution. The product stream from the first stage of leaching is sent to a thickener that separates the pregnant leach solution (rich in nickel) and the solid residue (rich in copper and PGMs). The overflow (pregnant solution) from the thickener is fed to a nickel crystallizer to produce nickel sulfate crystals as a hexa-hydrate in a rotary kiln (iron and cobalt removal prior to being fed to the crystallizer is discussed in sections 1.2 and 1.3). The residue from the

first stage thickener goes to the second stage of pressure leaching with the primary objective of leaching copper into solution, leaving the PGMs in the residue. Copper is recovered with electrowinning to produce copper cathodes. Filtering, caustic- and formic acid leaching are used to upgrade the PGM residue before it is sent to the precious metal refinery.

1.2 PROBLEM STATEMENT

As expected, some dissolution of copper, cobalt, iron and PGMs also occur during the atmospheric leaching stage. Consequently these metals are also present in the feed stream to the nickel crystallizer.

Precipitation processes are typically implemented to remove copper and PGMs from the leach solution prior to it being sent to the nickel crystallizer. The cobalt and iron present in the crystallizer feed stream do however reduce the quality of the crystals being produced. If cobalt and iron can be removed from the solution prior being sent to the nickel crystallizer, higher purity crystals can be produced allowing these to be sold at premium price. The recovered cobalt also has significant economic value.

1.3 OBJECTIVE

This project addresses the abovementioned deficiency by determining a feasible separation process and operating conditions to remove cobalt and iron from the pregnant nickel leach solution (with a composition of 1 g/l Co^{2+}, 3 g/l Fe^{2+} and 80 g/l Ni^{2+}) prior to being sent to the nickel crystallizer.

This was done by developing a solvent extraction circuit via the following approach:

- Preliminary and factorial design batch experiments were used to identify the key variables. These variables were considered during successive batch tests to determine the optimum operating conditions for the extraction circuit.
- The generated equilibrium data was then modelled and a simulation sheet for the extraction circuit was developed.
- Ultimately continuous tests were conducted to test the batch and simulated results.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

The current literature survey considers typical leach solution treatments. Typical extractants used in solvent extraction for cobalt and iron separation from nickel sulfate solutions are discussed and a selection is made of the best competitor. These extractants are rarely used in pure form and diluents and other organics that are also involved in solvent extraction are discussed accompanied with several extraction techniques. The best technique is selected and discussed in more depth. Important operating variables are also discussed as they will be investigated to design the solvent extraction circuit.

2.2 GENERAL LEACH SOLUTION TREATMENTS

Typical processes that are used to treat leach solutions include adsorption on activated charcoal, ion exchange, precipitation and solvent extraction.

2.2.1 ADSORPTION ON ACTIVATED CHARCOAL

Adsorption on activated charcoal is generally used for the extraction of gold and silver from cyanide solutions which are filtered through columns filled with granular activated charcoal. The metal species that needs to be removed adsorbs onto the activated charcoal. For this method maximum efficiency is obtained for dilute solutions, the kinetics is slow, and it has a relatively low capacity and cost (Habashi, 1999).

The leach solution that has to be treated in the present project is highly concentrated with nickel making this an unattractive approach that could cause blockages and regular overloading of nickel onto the charcoal.

2.2.2 ION EXCHANGE

Generally ion exchange is used for concentration of uranium from leach solutions as well as separation of individual members of lanthanides. An ion exchange resin comprises a matrix that has been functionalised either with positive or negative ions. The metal species to be extracted from the leach solution is exchanged for the ion on the resin. For this method maximum efficiency is obtained for dilute solutions, it has slow kinetics, is relatively expensive and has a high operating capacity (Habashi, 1999).

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Ion exchange is also not a popular choice for the same reasons as activated charcoal since the leach solution is highly concentrated with nickel, leading to overloading of nickel onto the resin.

2.2.3 PRECIPITATION

Typical precipitation processes include removal of iron from zinc sulfate solutions and precipitation of aluminium (Habashi, 1999). In precipitation solid particles are formed by changing operating conditions such as pH, addition of other reactants and the temperature of the solution. Addition of other reactants or increasing the pH, which will require the addition of an alkali like NaOH, defeats the purpose of purifying the pregnant nickel leach solution from cobalt and iron since new impurities are then added instead. Consequently this is not a good option.

2.2.4 SOLVENT EXTRACTION

Solvent extraction can be used for the extraction of U, Cu, Zn, Be, B, V, Cr, *Fe, Co, Ni*, Zr, Hf, Nb, Ta, Mo, W, As, PGMs, Au, Th, Pu and lanthanides from aqueous solutions (Habashi, 1999).

During solvent extraction the leach solution (aqueous phase) is contacted with an immiscible organic phase in either column or mixer-settler reactors. During agitation the metal ion from the aqueous phase reacts with the organic reagent (extractant) to form an organometallic complex. Once equilibrium is reached the two phases are allowed to separate and the metal species is extracted from the aqueous phase.

In practice extractants are rarely used in pure form. They are usually mixed with organic solvents known as diluents which should also be immiscible in water. Diluents are used to improve physical properties such as the viscosity of the organic phase. In contrast they may influence the extracting power of the extractant (Habashi, 1999).

In order to recover the extracted metal species from the organic phase as well as for recycling purposes of the reagent, the metal species in the organic phase is stripped with relatively strong acids such as H_2SO_4 or HCl. During the extraction process a hydrogen ion on the organic reagent is replaced with the metal species in the aqueous phase, but during the stripping process the hydrogen ion from the stripping agent (H_2SO_4 or HCl) replaces the metal species on the organic reagent. Hence during the stripping process the organic reagent is regenerated to its acidic form and recycled to serve as extracting reagent while the metal species is recovered for further processing. A schematic illustration of a typical solvent extraction circuit is shown in Figure 2-1:
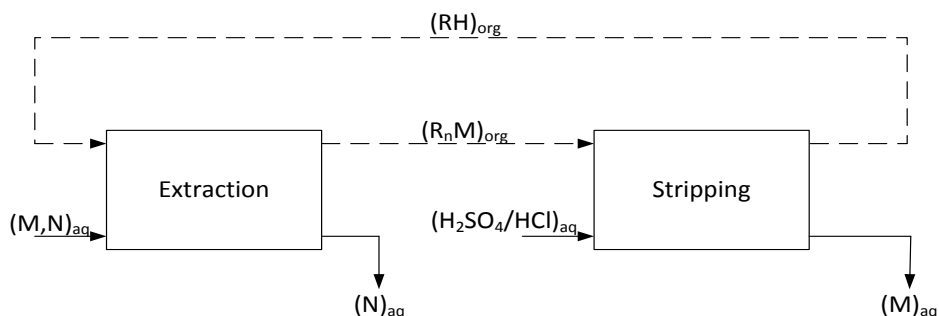
Figure 2-1: Schematic illustration of a solvent extraction circuit utilizing cation exchangers

Referring to Figure 2-1 the dashed and solid lines represent the organic and aqueous phases, respectively. In this scenario metal M is separated from metal N using the organic reagent RH. R represents a hydrocarbon anion and H is the proton replacing M during the extraction process.

Solvent extraction has a moderate cost relative to adsorption on activated charcoal and ion exchange and maximum efficiency can be obtained for concentrated solutions, the kinetics is rapid and it has a high operating capacity (Habashi, 1999).

Most frequently solvent extraction is the preferred separation process for cobalt, iron and nickel. This statement is justified with the significant amount of literature that is available in this field (Parhi *et al.*, 2008; Biswas *et al.*, 2007; Darvishi *et al.*, 2005; Lindell *et al.*, 2000; Devi *et al.*, 1998; Ajgaonkar and Dhadke, 1997; Gandhi *et al.*, 1993; Tait, 1993; Miralles *et al.*, 1992). Solvent extraction is also capable of tolerating higher metal concentrations than most of its competitors and its application range over a much wider range of different metal species (Habashi, 1999). It is therefore selected as the separation process for the extraction of iron and cobalt from the pregnant nickel leach solution.

2.3 EXTRACTING REAGENTS

2.3.1 BACKGROUND

In previous years the separation of cobalt and nickel presented problems due to their similar chemical and physical properties. Neither nickel nor cobalt forms anionic sulfato complexes which mean that they cannot be extracted with anion exchangers. Thus for nickel/cobalt separation in sulfate mediums a cation exchanger is required (Flett, 2005). The physical and chemical properties of iron and nickel differ much more than for cobalt and nickel and as a result the removal of iron from nickel will not be as challenging as for cobalt. The primary focus is therefore to find a suitable extractant for cobalt and nickel. The selected extractant will then be verified for the final selection with respect to its extractability towards iron from nickel sulfate solutions.

Solvent extraction technology dates back to the 1950s where the first major commercial plant was commissioned for the recovery of uranium as by-product from gold mining in South Africa. Following was the first copper solvent extraction plants in the late 1960s in Arizona and Zambia while the first Ni-

Co solvent extraction plant was commissioned in 1974 (Sole *et al.*, 2005). Currently there are a wide range of extractants being used for the extraction and purification of metal containing aqueous solutions. Organophosphorus extractants have proven to be of particular importance for the selective separation of cobalt and nickel (Flett, 2005). Table 2-1 summarizes the acid alkyl phosphorous extractants (cationic exchangers) that have been most widely investigated for the extraction of cobalt, iron and nickel:

Table 2-1: Most popular organophosphorus extractants for the separation of cobalt, iron and nickel (adapted from (Flett, 2005))

Type	Name	Commercial uses
Alkyl phosphoric acids	DEHPA/$C_{16}H_{35}O_4P$	Uranium extraction, rare earth extraction, cobalt/nickel separation, zinc extraction, etc.
Alkyl phosphonic acids	PC-88A or Ionquest 801/ $C_{16}H_{35}O_4P$	Cobalt/nickel separation, rare earth separation
Alkyl phosphinic acids	Cyanex 272, Ionquest 290, LIX 272/$(C_8H_{17})_2P(O)OH$ Cyanex 302/$(C_8H_{17})_2P(S)OH$ Cyanex 301/$(C_8H_{17})_2P(S)SH$	Cobalt/nickel separation, zinc and iron extraction, rare earth separation

A great deal of research were conducted up to the 1970s for the separation of cobalt and nickel with DEHPA, but at that stage the industry still remained eager for a selective extractant for cobalt and nickel (Ritcey *et al.*, 1975; Flett, 1972). It was during the early 1980s that Cyanex 272 and its thio analogues Cyanex 302 and Cyanex 301, was investigated in conjunction with DEHPA as extractant for nickel-cobalt separation (Flett, 2005). In section 2.3.2 phosphoric, phosphonic and phosphinic acids will be investigated by looking at DEHPA, PC-88A and Cyanex 272 respectively. The difference between Cyanex 272, 302 and 301 will be discussed in section 2.3.3.

In order to understand and quantify the performance of various extractants it is important to introduce the distribution coefficient, separation factor and percentage extraction (Habashi, 1999).

$$D_A = \frac{\text{Concentration of metal A (organic)}}{\text{Concentration of metal A (aqueous)}} \qquad [1]$$

$$\beta = \frac{D_A}{D_B} \qquad [2]$$

$$E_A = \frac{N_{AO} - N_A}{N_{AO}} \times 100 \qquad [3]$$

where: D_A, D_B = Distribution coefficients of metals A and B, respectively, at equilibrium

β = Separation factor

E_A = Percentage extracted of metal A

N_{AO} = Initial moles of metal A in the aqueous phase

N_A = Moles of metal A in aqueous phase after extraction

A high distribution coefficient (D) designates a high extractability of metal ions from the aqueous phase. The separation factor reflects how selectively metals are being extracted from the aqueous phase (a larger separation factor signifies better selectivity).

The pH of the aqueous solution is one of the most influential variables with respect to selective extraction. Finding the optimum pH that gives the highest separation factor is essential for obtaining selective extraction since different metal species are extracted at different pH values (Sarangi *et al.*, 1999b; Devi *et al.*, 1998). A good extracting reagent is classified as one that can extract two metal species at two completely different pH values, i.e. one that gives a high and low distribution coefficient for metals A and B, respectively, at a specific pH.

Another performance measurement tool is the pH_{50} value. This is the pH at which 50% of the metal species is extracted from solution. A large difference between the pH_{50} values of two metal species (pH_{50}^{Ni-Co} for example) implies that they can be separated selectively.

2.3.2 DEHPA, PC-88A AND CYANEX 272

Devi *et al.* (1994) investigated DEHPA, PC-88A and Cyanex 272 as extracting reagents for cobalt without the presence of nickel from sulfate mediums. Benzene was used as diluent and the experiments were conducted at an organic/aqueous (O/A) mixing ratio of 1. Cobalt (0.59 g/l) was extracted with various extractant concentrations (0.005-0.08 M). Practically 100% extraction was achieved for a reagent concentration of 0.04 M and the extraction behaviour of all 3 reagents was very similar giving the same extraction for cobalt as a function of extractant concentration. The pH at which these three reagents extracted cobalt was however different, with complete removal obtained at pH values of approximately 6, 6.5 and 7 for DEHPA, PC-88A and Cyanex 272, respectively. It was concluded that all 3 extracting reagents are equally capable of completely removing cobalt from aqueous solutions, i.e. give a high distribution coefficient. These experiments however do not report any valuable information regarding the ability of these three reagents to selectively separate cobalt from nickel.

Rodrigues and Mansur (2009) used DEHPA and Cyanex 272 in kerosene as diluent to extract cobalt (2 g/l) and nickel (14 g/l) in the presence of 1 g/l cadmium from a sulfate medium with an O/A mixing ratio of 1. The pH_{50}^{Ni-Co} values for DEHPA and Cyanex 272 was approximately 1 and 1.5 respectively. Darvishi *et al.* (2005) extracted cobalt and nickel (both 5 g/l) with 0.6 M DEHPA and Cyanex 272 also in kerosene with an O/A ratio of 1. pH_{50}^{Ni-Co} values of 0.5 and 3 were reported for DEHPA and Cyanex 272 respectively. Devi *et al.* (1998) used a 0.6 M solution of Cyanex 272, PC-88A and DEHPA in kerosene to extract cobalt and nickel (both 0.6 g/l) from a sulfate medium and obtained pH_{50}^{Ni-Co} values of approximately 3, 1.5 and 0.5 respectively. Separation factors ranging between 4000-7000, 70-1700 and

6-10 for Cyanex 272, PC-88A and DEHPA, respectively, have also been reported for aqueous solution consisting of 0.5-2 g/l cobalt and nickel (Sarangi *et al.*, 1999b; Devi *et al.*, 1998). Hence it is clear that Cyanex 272 is a better separation agent than either PC-88A or DEHPA for *dilute* cobalt and nickel solutions.

All three of these phosphorus based extractants have proven to be of particular importance in the past for the separation of cobalt and nickel but only Cyanex 272 is capable of treating solutions consisting of Ni:Co ratios higher than 100:1. The separation of minor quantities of cobalt from concentrated nickel solutions only became plausible since the development of Cyanex 272 and its thio analogues Cyanex 302 and Cyanex 301 (Flett, 2005).

It is well reported in the literature that the effectiveness of cobalt and nickel separation increases from phosphoric acids (DEHPA) to, phosphonic acids (PC-88A) to phosphinic acids (Cyanex 272) (Van de Voorde *et al.*, 2006). Hence the final reagent selection will be made between the three phosphinic acids Cyanex 272, Cyanex 302 or Cyanex 301.

2.3.3 CYANEX 272, 302 AND 301

Cyanex 272 is the best known reagent produced by Cytec. Figure 2-2 shows the chemical structure of Cyanex 272 and its thio analogues Cyanex 302 and Cyanex 301.
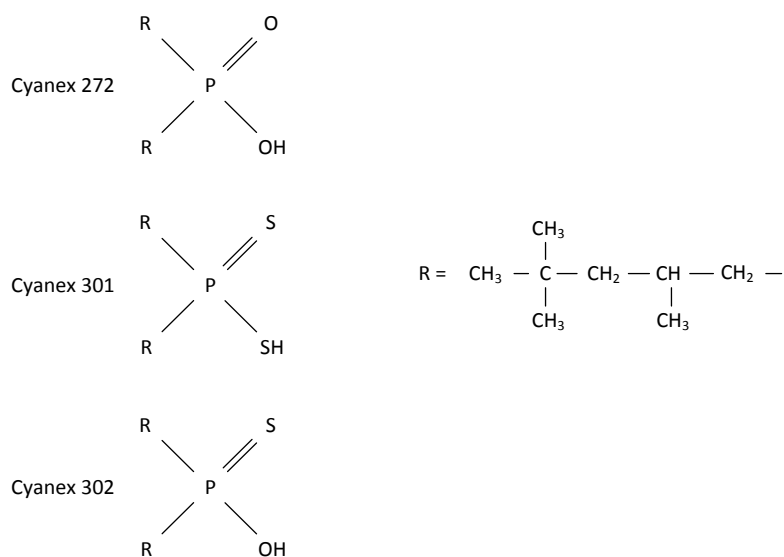
Figure 2-2: Chemical structure of Cyanex 272, 301 and 302 (adapted from (Tait, 1993))

Tait (1993) investigated the extraction behaviour of Cyanex 272, 302 and 301 on cobalt/nickel separation. Initial experiments were conducted where all three reagents were used to treat an aqueous solution consisting of 1.18 g/l cobalt and 1.18 g/l nickel. A reagent concentration of 0.25 M in toluene was used with an O/A mixing ratio of 1. The author found that the pH at which extraction occurred for cobalt and nickel differs much more for Cyanex 272 and Cyanex 302 than for Cyanex 301 with pH_{50}^{Ni-Co}

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values of approximately 2.5 compared to 1.5 respectively. The pH at which cobalt and nickel are extracted with Cyanex 301 is also much lower than for Cyanex 272 or 302 (1-3 compared to 4-7) which means that a stronger acid will be required to strip cobalt and nickel from the organic phase. It was therefore concluded by the author that Cyanex 272 and Cyanex 302 are more suitable extracting reagents than Cyanex 301 and another experiment was conducted by extracting cobalt (0.42 g/l) from a more concentrated nickel (22.3 g/l) solution with a reagent concentration of 0.14 M in toluene at an O/A ratio of 1. Under these experimental conditions the separation factors reported by Tait (1993) were 53 and 126 at a pH of 6 for Cyanex 272 and Cyanex 302 respectively. From these experimental results the author concluded that Cyanex 302 is a more effective separation reagent than Cyanex 272 for cobalt and nickel.

The ability of an extracting reagent to selectively separate different metal species is not the only factor that should be taken into consideration when selecting a reagent. Possible degradation of the extractant during operation should also be considered. It is important that the selected extractant remains stable during the solvent extraction cycle. Cyanex 301 can be used to extract cobalt and nickel at a lower pH than either Cyanex 272 or 302. Hence it is a stronger extracting reagent than either Cyanex 272 or 302. Cyanex 301, however, is not very stable and decomposes into elemental sulphur and Cyanex 272. Even though Cyanex 302 shows better separation characteristics than Cyanex 272 it also decomposes into elemental sulphur and Cyanex 272 during the solvent extraction cycle. Cyanex 272 on the other hand has been found to be very stable (Flett, 2005; Mihaylov, 2003).

Cyanex 272 is a weaker acid than any of its competitors (DEHPA, PC-88A, Cyanex 302 and Cyanex 301) and a weaker acid can therefore be used for stripping purposes.

Cyanex 272 is currently being used to produce more than 50% of the cobalt in the Western world. Most companies regard the use of Cyanex 272 as confidential which means that not a lot of plant and operating data are available. It is therefore concluded that Cyanex 272 is the obvious choice for extraction of cobalt from nickel solutions based on the following reasons:

- It is more stable than its thio analogues Cyanex 302 and Cyanex 301.
- It offers much higher separation factors than either DEHPA or PC-88A.
- It is the only reagent that can effectively separate Co from Ni at Co:Ni ratios as low as 1:100.
- It is also the weakest acid of all the organophosphorus acids which means that it is the easiest to strip.

The extraction characteristics of Cyanex 272 towards iron will be discussed next.

Miralles *et al.* (1992) investigated the extraction of iron (5.6 g/l) with Cyanex 272 from sulfate, chloride and nitrate mediums with 0.1 M Cyanex 272 in Isopar-H as diluent at an O/A ratio of 1. During these tests iron was completely removed from all three mediums at a pH lower than 2.2. This was however without the presence of cobalt and nickel in the solution. (Gandhi *et al.*, 1993) studied the sequential separation of iron, cobalt and nickel with Cyanex 272 dissolved in chloroform as diluent. It was found

that iron was selectively extracted at a pH of 3, cobalt at a pH of 8 and nickel was left in solution with 0.005 M Cyanex 272. The proposed method was reported to be simple, rapid and selective.

Based on the selective extractability of Cyanex 272 for iron from cobalt and nickel solutions as well as its superior separation characteristics for cobalt and nickel, it is concluded as the best choice of extractant for the current situation.

2.4 DILUENTS

As discussed previously, extractants are rarely used in pure form and are mixed with an organic solvent referred to as the diluent. Various diluents exist, both aromatic and aliphatic, and they range from straightforward molecules to complex mixtures. Gandhi *et al.* (1993) investigated some of the straightforward molecules most often used on laboratory scale as diluents for Cyanex 272 by extracting cobalt. The results are displayed in Table 2-2:

Table 2-2: Effect of various diluents on extraction of cobalt (0.0025 g/l) with Cyanex 272 (0.005 M) at a pH of 8 (adapted from (Gandhi *et al.*, 1993))

Diluents	% Extraction
n-hexane	60.8
Carbon tetrachloride	99.9
Cyclohexane	20.0
Benzene	99.9
Toluene	99.9
Xylene	99.9
Chloroform	99.9
Dichloromethane	98.3
1,2 dichloroethane	77.5
Nitrobenzene	56.5

Diluents may have a significant influence on the extracting behaviour of the extractant as shown in Table 2-2. This is caused by various interactions that may exist between diluents and extractants. Some of these interactions include dipole-dipole interaction, pi-electron interaction, hydrogen bonding and cavity formation. Some diluents also assist in the polymerization of the extractant. This will affect the cation exchange process, making the hydrogen atom on the extractant less free to react (Mohapatra *et al.*, 2007).

The commercial use of the diluents in Table 2-2 is often restricted due to environmental issues or economic considerations. Kerosene is one of the cheapest diluents that is often used on industrial scale. Major oil companies have also developed a range of diluents for commercial application in hydrometallurgy. These diluents typically consist of a mixture of naphthenic, paraffinic and aromatic hydrocarbons. Some of these companies include Exxon which produces the Escaid range of diluents (Escaid 100, Escaid 110, and Escaid 350) and Shell and Chevron with their range of diluents (Shellsol D series) (Foust *et al.*, 2008).

The interaction between diluents and extractants is poorly understood; hence a diluent is usually selected based on experimental data (Foust *et al.*, 2008).

2.5 PHASE SEPARATION & THIRD PHASE FORMATION

A serious problem encountered in solvent extraction is the formation of a third phase. This occurs due to solubility issues in the organic phase. What typically occurs is that during the phase separation stage, a third phase forms between the aqueous and organic interface (the third phase has an intermediate density between the aqueous and organic phase). This phase is primarily an organometallic complex-rich phase. Above this phase forms an organic phase that is rich in the diluent. From literature the following conclusions have been drawn regarding phase separation problems and third phase formation (Foust *et al.*, 2008):

- Suspended solids often result in phase separation problems.
- Overloading of the ligand/extractant can result in third phase formation.
- Third phase formation is temperature dependent. Increasing the temperature usually causes the third phase to disappear since the organic-aqueous solubility decreases as temperature increases.
- Third phase formation is more common with aliphatic diluents.
- Addition of a third phase modifier can help to overcome the formation of a third phase.

Typical third phase modifiers include isodecanol, 2-ethylhexanol, p-nonyl phenol and TBP (tri-n-butylphosphate). Most researchers use TBP as third phase modifier adding it between 2-5 volume percent to the organic phase (Rodrigues and Mansur, 2009; Reddy *et al.*, 2006; Swain *et al.*, 2006; Tsakiridis and Agatzini-Leonardou, 2004; Sarangi *et al*., 1999b; Devi *et al.*, 1998).

Experimental evidence has shown that, like diluents, a third phase modifier is not chosen arbitrarily but a selection is made based on experimental observation (Foust *et al.*, 2008). Most often an increase in temperature or extractant concentration causes the third phase to disappear and a third phase modifier is not necessary.

2.6 EXTRACTION AND STRIPPING CHEMISTRY

This section covers different extraction techniques associated with Cyanex 272 by specifically looking at the various chemical reactions. Restrictions linked with each technique will also be discussed. Finally a conclusion is drawn regarding which procedure will be the best choice for the purification of the pregnant nickel solution.

2.6.1 GENERAL REACTION

During solvent extraction a metal species is removed from the aqueous phase with a cation exchange reaction. If the interactions between diluents and extractants are ignored, this cation exchange reaction is presented with reaction 4 (Tsakiridis and Agatzini-Leonardou, 2004):

$$(M^{n+})_{aq} + (nRH)_{org} \leftrightarrow (MR_n)_{org} + (nH^+)_{aq} \tag{4}$$
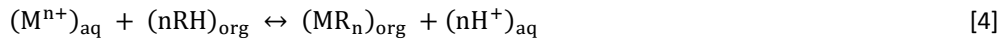
where M^{n+} is an n-valent metal cation, RH is a hydrocarbon (extractant) with proton H and subscripts "org" and "aq" represents the organic and aqueous phases respectively. Reaction 4 can be rewritten for the extraction of cobalt with Cyanex 272 as follows:

$$(Co^{2+})_{aq} + (2RH)_{org} \leftrightarrow (CoR_2)_{org} + (2H^+)_{aq} \tag{5}$$
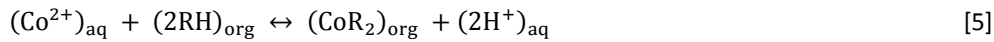
The release of hydrogen atoms into the aqueous phase during extraction will cause a drop in the pH of the aqueous solution. As discussed previously, the extraction of various components is a strong function of pH. Consequently the pH has to be controlled by adding OH^- to the system during operation (typically NaOH or NH_4OH). This will prevent excess H^+ formation that shifts the equilibrium of reaction 4 to the left. An improved representation for reaction 4 is shown in reaction 6 (a similar reaction can be written for NH_4OH) (Nogueira *et al.*, 2009):

$$(M^{n+})_{aq} + (nRH)_{org} + (nNaOH)_{aq} \leftrightarrow (MR_n)_{org} + (nH_2O)_{aq} + (nNa^+)_{aq} \tag{6}$$
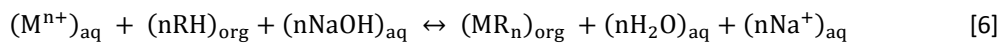
With a better understanding of the extraction procedure associated with Cyanex 272, the actual chemistry in the system will be discussed in more depth by taking the interactions between the extractant and diluent into consideration. The following reaction is a more general representation of how Cyanex 272 extracts different metal species from aqueous solutions (Flett, 2005):

$$(M^{n+})_{aq} + ((n+m)RH)_{org} \leftrightarrow (MR_n.mRH)_{org} + (nH^+)_{aq} \tag{7}$$
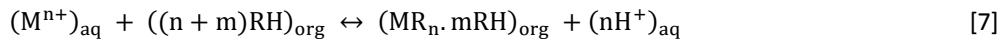
Reaction 7 can be rewritten where either NaOH or NH_4OH are used as base titrants:

$$(M^{n+})_{aq} + ((n+m)RH)_{org} + (nNaOH)_{aq} \leftrightarrow (MR_n.mRH)_{org} + (nH_2O)_{aq} + (nNa^+)_{aq} \tag{8}$$
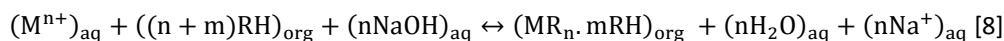
A significant amount of work has been done to determine the nature of the organometallic complex $MR_n.mRH$. Reaction 7 can be simplified to the following reaction for the extraction of cobalt and nickel with Cyanex 272 (Sahu *et al.*, 2004; Tsakiridis and Agatzini-Leonardou, 2004):

$$(M^{2+})_{aq} + ((1+m)(RH)_2)_{org} \leftrightarrow (MR_2.m(RH)_2)_{org} + (2H^+)_{aq} \tag{9}$$
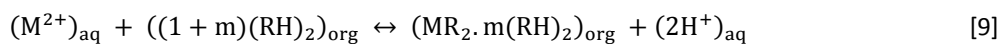
Slope analysis is a technique usually used to determine the nature of the organometallic complex $MR_2.m(RH)_2$. This is done via the definition of the equilibrium constant given by equation 10:

$$K = \frac{[H^+]^2[MR_2.m(RH)_2]}{[M^{2+}][(1+m)(RH)_2]} \tag{10}$$

By taking the logarithm and after some rearrangement of equation 10 the following expression is obtained (Tsakiridis and Agatzini-Leonardou, 2004):

$$logD_M - 2pH = logK + mlog[(RH)_2] \qquad [11]$$

where D_M is the distribution coefficient of metal M and $[(RH)_2]$ is the concentration of the extractant. A plot of $(logD_M–2pH)$ versus $log[(RH)_2]$ will yield a straight line of slope m and intercept logK. When m is known, the nature of the organometallic complex $MR_2.m(RH)_2$ is exposed. This has been reported as $CoA_2.(HR)_2$ and $NiR_2.2(HR)_2$ for the cobalt and nickel respectively (Yu *et al.*, 2001; Nogueira *et al.*, 2009). With m known reaction 9 simplifies to the following two expressions for the extraction of cobalt and nickel:

$$(Co^{2+})_{aq} + (2(RH)_2)_{org} \leftrightarrow (CoR_2.(RH)_2)_{org} + (2H^+)_{aq} \qquad [12]$$

$$(Ni^{2+})_{aq} + (3(RH)_2)_{org} \leftrightarrow (NiR_2.2(RH)_2)_{org} + (2H^+)_{aq} \qquad [13]$$
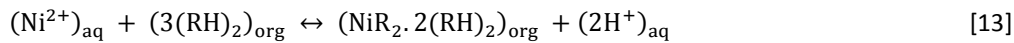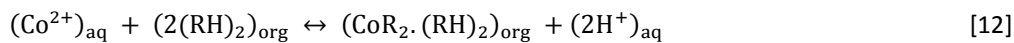
The following simplification of reaction 7 is suggested by Van de Voorde *et al.*, (2007) for ferric extraction with Cyanex 272 (reaction 14):

$$(Fe^{3+})_{aq} + ((3+m)(RH))_{org} \leftrightarrow (FeA_3.(RH)_m)_{org} + (3H^+)_{aq} \qquad [14]$$
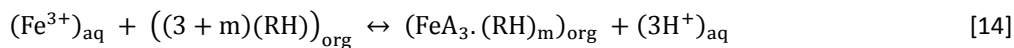
No research work has been discovered for the extraction of ferrous ions with Cyanex 272. It is however speculated that the reaction will be similar to reaction 9 due to the fact that ferrous ions also have a valence of 2 like cobalt and nickel.

It is therefore concluded that the chemistry involved with solvent extraction is not as simple as shown in reaction 4. This is caused by the interactions that exist between diluents and extractants as well as dimerization of extractants.

2.6.2 SAPONIFIED CYANEX 272

An alternative approach to using the acidic form of Cyanex 272 is to first prepare the sodium or ammonia salt of Cyanex 272 (saponified form of Cyanex 272) before extracting cobalt or iron. This will reduce the amount of sodium or ammonia hydroxide that has to be added to the extractor (extraction reactor) as shown in reactions 6 and 8 to control the pH. The two reactions involved with the extraction of divalent metal species (Co^{2+}, Ni^{2+}, Fe^{2+}) with saponified Cyanex 272 are as follows (Kang *et al.*, 2009; Reddy *et al.*, 2006; Swain *et al.*, 2006):

$$((Na, NH_4)OH)_{aq} + 1/2((RH)_2)_{org} \leftrightarrow ((Na, NH_4)R)_{org} + (H_2O)_{aq} \qquad [15]$$

$$(M^{2+})_{aq} + (2(Na, NH_4)R)_{org} + (m(RH)_2)_{org} \leftrightarrow (MR_2.m(RH)_2)_{org} + (2(Na^+, NH_4^+))_{aq} \qquad [16]$$
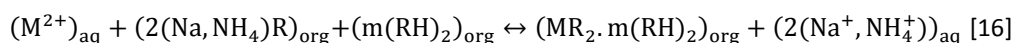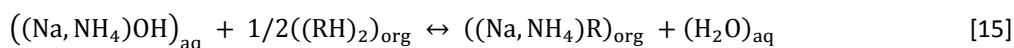
From reaction 16 it is seen that extraction still occurs via a cation exchange reaction, the only difference is that the metal being extracted is exchanged for Na^+ or NH_4^+ rather than H^+. By using this technique the large drop in pH as a function of extraction is significantly reduced and hence the amount of alkali that has to be added during the extraction process is reduced. From reactions 15 and 16 it is also seen that the acidic form of Cyanex 272 exists as a dimer (RH_2) and the saponified form as a monomer ((Na, NH_4)R)) (Kang *et al.*, 2009; Reddy *et al.*, 2006; Swain *et al.*, 2006).

2.6.3 SCRUBBING

As expected, complete separation of two different metal species is not always achieved and the undesired metal is often co-extracted with the desired one to a certain extent. One way to remove the undesired metal from the organic phase is to mix it with an aqueous solution consisting of the desired metal.

Say for instance cobalt and nickel are extracted with Cyanex 272. In order to remove any co-extracted nickel from the organic phase, it is mixed with an aqueous solution of cobalt which scrubs nickel from the organic phase according to reaction 17 (Nogueira *et al.*, 2009; Nogueira *et al.*, 2003):

$$(NiR_2.2(RH)_2)_{org} + (Co^{2+})_{aq} \leftrightarrow (CoR_2.(RH)_2)_{org} + ((RH)_2)_{org} + (Ni^{2+})_{aq} \qquad [17]$$
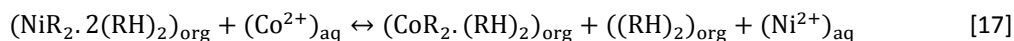
During scrubbing, only metal species with a higher chemical affinity for the extractant than the co-extracted metal can be used to scrub the undesired metal species from the organic phase. This is reflected in the pH at which Cyanex 272 extracts different metal species. The lower the pH at which Cyanex 272 extracts the metal species is, the higher the affinity for extraction will be with Cyanex 272. This means that metal species being extracted at lower pH values can be used to scrub/replace metal species that are extracted at higher pH values.

2.6.4 PRE-LOADING

Pre-loading is similar to scrubbing with respect to the chemistry as shown in reaction 17. The major difference between scrubbing and pre-loading is as follows:

- During scrubbing undesired and co-extracted nickel is replaced with cobalt in the organic phase by mixing the impure Ni-Co organic phase with a cobalt aqueous solution and in the ideal case will yield a pure Co-organic and a Ni-aqueous phase.
- During pre-loading an organic phase is first loaded with nickel. The nickel loaded organic phase is then used to remove cobalt from a cobalt-nickel aqueous phase also according to reaction 17.

Figure 2-3 shows a schematic illustration of the difference between scrubbing and pre-loading.
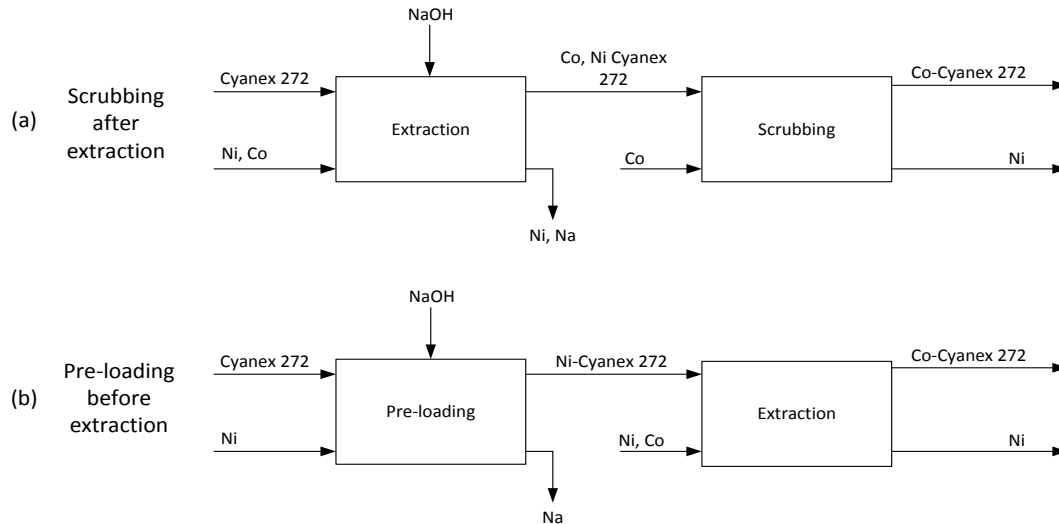
Figure 2-3: Schematic illustration of the difference between scrubbing and pre-loading

The technique shown in Figure 2-3 (a) will typically be used when a high purity cobalt product is of primary importance and the pre-loading technique in Figure 2-3 (b) will be used if a high purity nickel product is required. These two processes can be combined as well, but this is not of particular importance and will therefore not be discussed.

Pre-loading is based on the same principle as scrubbing regarding the fact that metal species being extracted at a higher pH value can be replaced in the organic phase with metal species being extracted at a lower pH value. Nickel, cobalt and iron are typically extracted in the pH range 7-8, 5-6 and 2-3, respectively, with Cyanex 272. Therefore, if a nickel salt of Cyanex 272 is agitated with an aqueous solution consisting of cobalt, iron and nickel, then iron and cobalt will replace nickel in the organic phase and increase the nickel concentration in the aqueous phase.

2.6.5 STRIPPING

Once the metal species is extracted into the organic phase, it has to be recovered via a process called stripping. Stripping is basically the inverse of extraction and involves mixing the metal loaded organic with an acid. It is the same as reaction 7, but only in reverse as shown in reaction 18:

$$(MR_n \cdot mRH)_{org} + (nH^+)_{aq} \leftrightarrow (M^{n+})_{aq} + ((n+m)RH)_{org} \qquad [18]$$
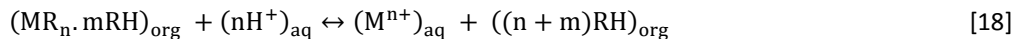
During stripping Cyanex 272 is regenerated to its acidic form and a new aqueous phase is produced consisting of the extracted metal species. Since iron, cobalt and nickel are extracted at different pH values, a possibility exist that they can also selectively be stripped by using different acid concentrations (selective stripping). If iron and cobalt are extracted from a concentrated nickel solution for instance, then a weaker acid may be used to strip cobalt followed by a stronger acid to strip iron since iron is extracted at a lower pH than cobalt. Limited research regarding selective stripping is however available.

Flett (2005) was the only author that reported that cobalt can selectively be stripped from any co-extracted iron or zinc with 150 g/l H_2SO_4 (0.6 M) in Cyanex 272.

2.6.6 CONCLUSIONS AND TECHNIQUE SELECTION

To date most research has focused on either using pure Cyanex 272 (pure Cyanex 272 refers to Cyanex 272 that has not been pre-loaded with nickel for the remainder of the text) or the saponified form of Cyanex 272 to extract cobalt, iron and nickel from aqueous solutions. Saponified Cyanex 272 will typically be preferred when large quantities of metal have to be extracted since this will minimize NH_4OH/NaOH additions to the extractor unit making pH control easier (it will however require a separate unit for the preparation of saponified Cyanex 272). Figure 2-4 shows how such a process flow sheet will typically look like for the selective separation of nickel, cobalt and iron (potential scrubbing that may be required is not included):
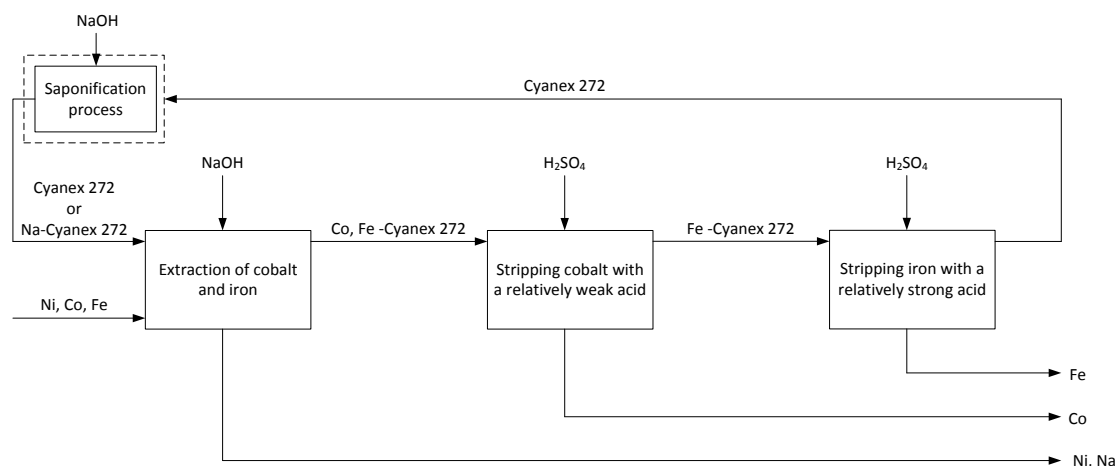
Figure 2-4: Process flow sheet for the extraction of cobalt and iron from nickel solutions when using either pure or saponified Cyanex 272

It is observed that according to reactions 6 and 16 the extraction of 1 mole of metal M with valence n+ will release n moles of Na^+ or NH_4^+ into the aqueous solution. If the objective for example is to remove 1 mole of Co^{2+} and 1 mole of Fe^{2+} from a concentrated nickel solution, then 4 moles of Na^+ or NH_4^+ will be added to the nickel solution. Thus while removing Co^{2+} and Fe^{+2} as impurities, double the amount of Na^+ or NH_4^+ is added as a new impurity during the extraction process. The objective of the project is to develop a solvent extraction circuit that will produce a high purity nickel product, but this is not achieved via the flow sheet shown in Figure 2-4.

An alternative solution is to pre-load the organic phase with nickel according to reaction 13 and then use the nickel loaded organic to extract cobalt and iron from the concentrated nickel solution according to reaction 17 (this reaction will be similar for iron). According to reaction 17 no Na^+ or NH_4^+ is added to the purified nickel stream. The proposed flow sheet is shown in Figure 2-5:

16
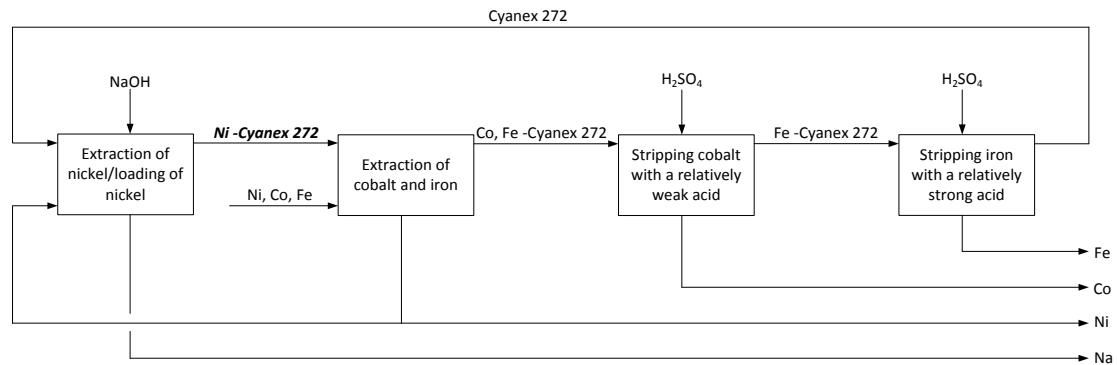
Figure 2-5: Process flow sheet for the extraction of cobalt and iron from nickel solutions with Ni-Cyanex 272

From Figure 2-5 a fraction of the purified nickel stream is recycled to be extracted by Cyanex 272. Consequently a nickel-loaded organic and a Na^+/NH_4^+ salt is produced. The loaded organic is then used to remove cobalt and iron and stripping occurs in the same way as in Figure 2-4. An advantage of this approach is the fact that the purified nickel stream does not come into direct contact with the added sodium or ammonia. Any sodium or ammonia used is recovered as a sulfate salt and, in the ideal scenario these are pure enough so that no further treatment is required.

Finally it is concluded that pre-loading Cyanex 272 with nickel and then using the generated nickel salt of Cyanex 272 to extract cobalt and iron, is the preferred process route to purify the pregnant nickel leach solution.

2.7 OPERATING VARIABLES

With an understanding of the extraction and stripping chemistry involved in solvent extraction, several operating variables will be considered next.

2.7.1 PH CONTROL

As mentioned previously, pH is one of the most important operating variables. Figure 2-6 shows how Cyanex 272 can extract various metal species (not only nickel, cobalt and iron) at different pH values. The cures in Figure 2-6 are only illustrative and will vary depending on the operating conditions and relative metal ion concentrations.
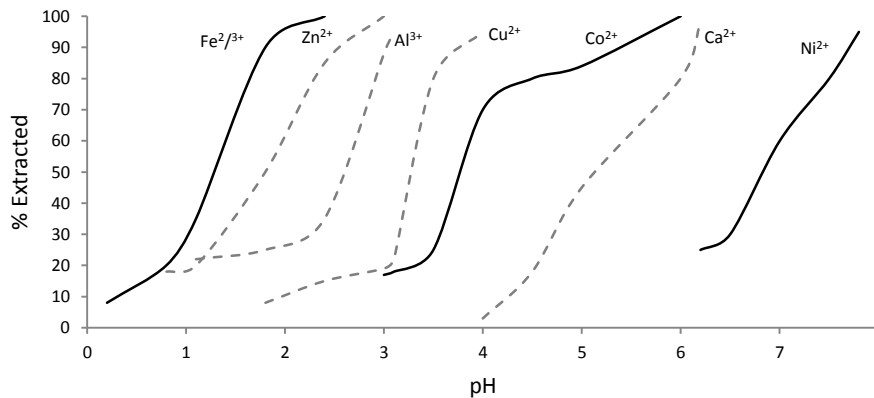
Figure 2-6: Comparison of typical pH values at which Cyanex 272 extracts different metal species (adapted from (Habashi, 1999))

Referring to Figure 2-6, Cyanex 272 has a pH_{50}^{Ni-Co} value of 3 for nickel and cobalt and a pH_{50}^{Co-Fe} value of 2 for cobalt and iron. This demonstrates the high selectivity that Cyanex 272 has for these three metals compared to copper and cobalt for example with a pH_{50}^{Co-Cu} value of only 0.5. Nonetheless only iron, cobalt and nickel are of interest and will be considered.

Typical base and acid titrants that are used to control pH in solvent extraction will be considered next. Base and acid titrants are used for extraction and stripping respectively (base titrants increases the pH so that there is extraction and acid titrants/stripping agents decreases the pH so that there is stripping).

2.7.1.1 BASE TITRANTS

In solvent extraction it is important that the solution pH does not increase above the precipitation point of the metal species in solution to prevent the formation of any double salts (Konishi and Takano, 2002). When using the nickel pre-loading technique there is no direct alkali addition to the cobalt and iron contaminated pregnant nickel leach solution. A base is only added to the recycled nickel stream that is used to pre-load Cyanex 272 (refer to Figure 2-5). Hence double salt formation is only a potential problem during the nickel pre-loading stage and not during the extraction stage. Operating below a pH of 7.5 at this unit will prevent any nickel double salt ($Ni(OH)_2$) formation (Nogueira *et al.*, 2009; Park and Mohapatra, 2006).

$NaOH$ and NH_4OH are common base titrants used in solvent extraction. Nogueira *et al.* (2009) studied the effect of $NaOH$ and NH_4OH as base titrants for the extraction of cobalt and cadmium from nickel solutions with nickel pre-loaded Cyanex 272 and DEHPA (nickel salt of Cyanex 272 and DEHPA), respectively. It was reported that the use of ammonia led to the formation of nickel amine precipitates. The used of $NaOH$ was subsequently preferred as the neutralizing agent since none of the precipitation issues were observed as with ammonia.

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An alternative base to use instead of NaOH or NH_4OH is $NiCO_3$ which can be used to remove H^+ according to reaction 19:

$$(NiCO_3)_s + (2H^+)_{aq} \leftrightarrow (Ni^{2+})_{aq} + (H_2O)_l + (CO_2)_g \qquad [19]$$
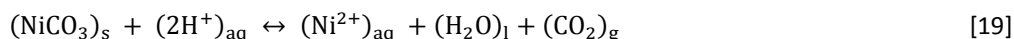
If reaction 19 is used to control pH, it prevents the addition of any new cations such as Na^+ or NH_4^+ into the system. Nickel carbonate can then directly be used to control the pH and no nickel pre-loading will be required while only water addition/formation occurs to the purified nickel product stream and the CO_2 gas can be purged off.

After modelling the solubility behaviour of $NiCO_3$ with the *OLI analyzer* software package, it was observer that $NiCO_3$ is only soluble in water at pH levels below 4 (i.e., there has to be significant H^+ present in a system for $NiCO_3$ to even dissolve). pH levels above 4 are required for complete cobalt removal with Cyanex 272. It is therefore concluded that NaOH as base titrant in a nickel pre-loading system is the best alternative.

2.7.1.2 STRIPPING AGENTS/ ACID TITRANTS

Different stripping agents for cobalt and iron will be discussed next. Gandhi *et al.* (1993) considered various stripping agents for the removal of cobalt from Cyanex 272 solutions as shown in Table 2-3.

Table 2-3: Effect of various stripping agents for the stripping of cobalt from 0.005 M Cyanex 272 (adapted from (Gandhi *et al.*, 1993))

Stripping agent (M)	% recovery				
	0.01	0.05	0.1	0.5	1-5
HCl	57	71	91.3	99.9	99.9
HNO_3	47.1	67.3	99.2	99.9	99.9
H_2SO_4	71.4	87.6	96.9	99.9	99.9
$HClO_4$	73.1	86	98	99.9	99.9
CH_3COOH	18.4	55.1	66.1	96	99.9

No stripping information for iron(II) from Cyanex 272 was discovered. Ajgaonkar and Dhadke (1997) however studied iron(III) stripping from a Cyanex 302 solutions. The results are displayed in Table 2-4:

Table 2-4: Effect of various stripping agents for the stripping of iron(III) from 0.005M Cyanex 302 (adapted from (Ajgaonkar and Dhadke, 1997))

Stripping agent (M)	% recovery				
	0.5	1	1.5	2	3
HCl	91.8	99.7	99.7	99.7	99.7
H_2SO_4	77.7	85	99.8	99.9	99.7
HNO_3	87	99.7	-	99.8	99.5
$HClO_4$	99.8	99.8	-	99.8	-

From Tables 2-3 and 2-4 higher acid concentrations are required for stripping of iron than for stripping of cobalt. When considering H_2SO_4, it is observed that more than 96% recovery is achieved for concentrations of 0.1 M and 1.5 M for cobalt and iron respectively. A slightly lower concentration than 1.5 M will be expected for iron since Cyanex 272 is a weaker acid than Cyanex 302. No data with respect to iron stripping with acid concentrations less than 0.5 M were reported. Consequently it is unclear what percentage stripping might be expected at lower acid concentrations. As mentioned in section 2.6.5, Flett (2005) was the only author who stated, without any published data, that cobalt can selectively be stripped from any co-extracted iron or zinc with 150 g/l H_2SO_4 (0.6 M) from Cyanex 272. It was not reported whether this was for ferric or ferrous ions. No published data with respect to selectively stripping an organic phase consisting of cobalt and iron were discovered. This is therefore an area that still requires attention.

2.7.2 AQUEOUS/ORGANIC PHASE MIXING RATIO

2.7.2.1 BACKGROUND

The relative volumetric quantities at which the aqueous and organic phases are being mixed with is referred to as the aqueous/organic phase mixing ratio (A/O ratio).

Varying the A/O or O/A ratio at a fixed pH and initial aqueous concentration in batch experiments is typically used to construct *extraction isotherms* which are plots of the concentration of the metal species in the aqueous phase versus the concentration of the metal species in the organic phase at equilibrium. Figure 2-7 is a classic example of an extraction isotherm:
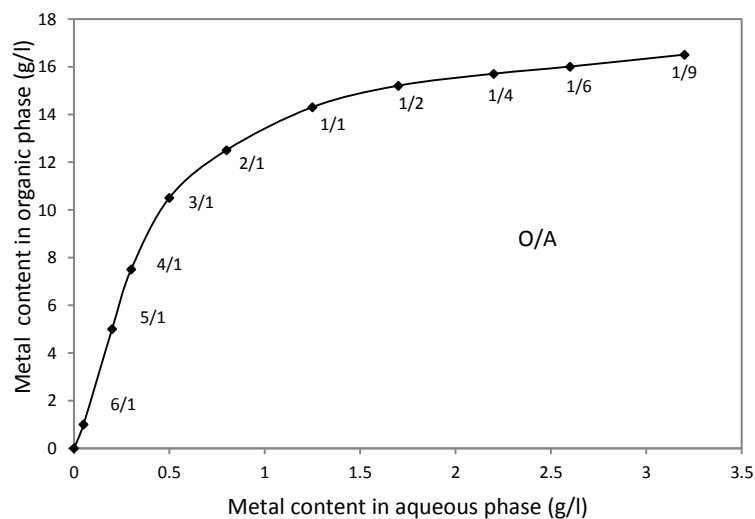
Figure 2-7: Example of a typical extraction isotherm constructed by varying the O/A ratio (adapted from (Tsakiridis and Agatzini-Leonardou, 2004))

Say for instance the aqueous phase initially contains 5 g/l of a particular metal species. From Figure 2-7 at a relatively low O/A ratio (1/8) most of the metal is still in the aqueous phase at equilibrium (3.2 g/l). The corresponding high concentration on the organic axis (16.2 g/l) is due to the fact that 1.8g of metal was transferred from 1l of an aqueous phase to $^1/_9$l of an organic phase. At a high O/A ratio (6/1) most of the metal is transferred to the organic phase as shown on the aqueous axis. The corresponding concentration on the organic axis is not particularly high due to the fact that 4.75g of metal from a 1l aqueous phase has been transferred to 6l of an organic phase.

Therefore higher O/A ratios result in higher metal extraction and lower O/A ratios result in lower metal extraction. Frequently lower O/A ratios as well as operating pH values, where complete extraction in a single stage is not attained, are used. To reach complete extraction at these conditions a stepped wise process is implemented as shown in Figure 2-8:
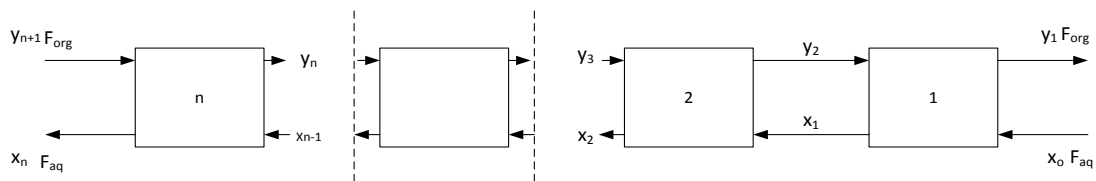
Figure 2-8: Staged counter-current extraction system

The organic and aqueous phases can also be fed in a co-current fashion, but the counter current manner shown in Figure 2-8 has proven to be more effective (Habashi, 1999).

If F_{aq}, F_{org}, y and x in Figure 2-8 represent the flow rate of the aqueous phase, the flow rate of the organic phase, the concentration of the metal species in the organic phase and the concentration of the metal species in the aqueous phase, respectively, the following straight line is derived via a material balance and some mathematical manipulation:

$$y_1 = \frac{F_{aq}}{F_{org}}(x_o - x_n) + y_{n+1}$$ [20]

where
y_1	=	Metal content in the organic phase leaving the system (*extract*)	
x_o	=	Metal content in aqueous phase that is to be extracted	
x_n	=	Metal content in the aqueous phase leaving the system (*raffinate*)	
y_{n+1}	=	Metal content in the organic phase entering the system	
n	=	Number of theoretical stages	
F_{aq}/F_{org}	=	Slope of the operating line (ratio at which the aqueous and organic phases are fed to the system in Figure 2-8)	

The straight line in equation 20, also referred to as the operating line, is used in conjunction with the extraction isotherm in Figure 2-7 to determine the number of theoretical stages required to decrease

the metal content in aqueous phase from x_o to x_n and to increase the metal content in the organic phase from y_{n+1} to y_1 as shown in Figure 2-9.
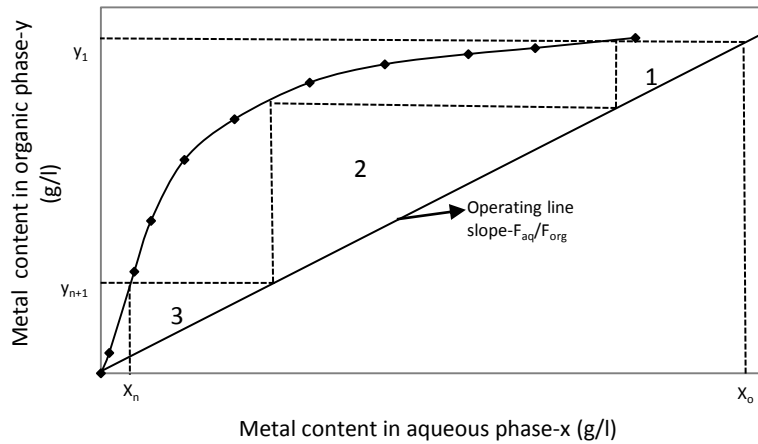
Figure 2-9: Example of a typical McCabe-Thiele diagram

From Figure 2-9 it is clear that three theoretical stages are required to reach the desired extraction as have been stepped off by the dotted lines for a specific F_{aq}/F_{org} or A/O feed ratio. The number of stages can be decreased by decreasing F_{aq}/F_{org} ratio (increasing the volume at which the organic phase is fed relative to the aqueous phase). This will cause a drop in the slope of the operating line and decrease the number of steps shown by the dotted lines.

Figure 2-9 is referred to as the McCabe-Thiele diagram and is used when designing the number of stages in a solvent extraction system at a specific pH. The methodology for determining the number of stages in stripping systems is similar to that for the extraction systems by using the McCabe-Thiele diagram.

2.7.2.2 NUMBER OF STAGES FOR NI, CO AND FE EXTRACTION

With a better understanding of the O/A feed ratio in a solvent extraction system and its implications on the number of theoretical stages, typical examples will be discussed with respect to nickel and cobalt extraction. No data regarding the number of stages required to remove iron with Cyanex 272 were discovered. Table 2-5 summarizes the number of stages calculated in literature when using Cyanex 272 with different O/A ratios and initial aqueous concentrations for cobalt and nickel:

Table 2-5: Summary of the typical number of theoretical stages obtained when extracting cobalt and nickel with Cyanex 272 and stripping the organic with H$_2$SO$_4$ with various A/O ratios

Author	Specifications	A/O ratio	Number of stages for more than 98% extraction
Devi *et al.* (1998)	Extracting cobalt (0.59 g/l) in the presence of 0.59 g/l nickel from a sulfate medium with 0.05 M of extractant	1	2
	Extracting nickel (0.59 g/l) from a sulfate medium with 0.05 M of extractant	1	2
	Stripping of the loaded organic (Co and Ni) with 0.02 M H$_2$SO$_4$	0.5	2
Kang *et al.* (2009)	Extraction of cobalt (13.8 g/l) from a 2 g/l lithium and 15 mg/l nickel solution from a sulfate medium with 0.4 M extractant	0.5	2
Park and Mohapatra (2006)	Extraction of cobalt (1.78 g/l) from a 16.78 g/l of nickel sulfate solution with 0.2 M of the extractant	1.5	2
Tsakiridis and Agatzini-Leonardou (2004)	Extraction of cobalt (0.63 g/l) in the presence of 3.8 g/l nickel and 5.75 g/l magnesium with 0.54 M of the extractant from a sulfate medium	2.5	2
	Extraction of nickel (3.8 g/l) with 0.54 M of the extractant from a sulfate medium	2.4	2
Reddy *et al.* (2006)	Extraction of cobalt (0.05 g/l) in the presence of 5.94 g/l of nickel with 0.03 M of the extractant from a sulfate medium	2	2
	Stripping of cobalt (0.149 g/l) with 6 M H$_2$SO$_4$	0.85	2
Li *et al.* (2009)	Extraction of cobalt (5.1 g/l) with 0.54 M of the extractant from a sulfate medium	1	2
Agatzini-Leonardou *et al.* (2009)	Extraction of nickel (3.6 g/l) with 0.27 M of the extractant from a sulfate medium	2.4	2
	Stripping of nickel (8.6 g/l) with 2 M H$_2$SO$_4$	2.4	3
	Cobalt extraction (0.66 g/l) with 0.27 M of the extractant from a sulfate medium	0.5	2
Swain *et al.* (2008)	Extraction of cobalt (22.08 g/l) in the presence of 5.43 g/l lithium with 1.3 M Cyanex 272 from a sulfate medium	1.5	2
	Stripping of cobalt (44.719 g/l) with 3 M H$_2$SO$_4$	0.4	3

Table 2-5 reflects the extensive amount of work that has already been done on the separation of cobalt and nickel with Cyanex 272. The small number of theoretical stages required for both extraction and

stripping (seldom larger than 2) proofs the superiority of Cyanex 272 with respect to cobalt and nickel refining. Most work reported on iron extraction is based on an O/A ratio of 1 while other variables such as extractant concentration and pH are varied. More than 90% of iron extraction was reported at an O/A ratio of 1(Biswas *et al.*, 2007). It was therefore speculated that quantitative extraction of iron will also be possible in less than 3 stages.

2.7.3 TEMPERATURE

As discussed in section 2.5, temperature influences phase separation given that the solubility of the organic phase in the aqueous phase typically decreases as temperature increases. In this section extraction as a function of temperature will be examined.

Bhaskara Sarma and Reddy (2002) studied the extraction of nickel at macro-level concentrations (29.345 g/l) with Cyanex 272 within the temperature range 30 to 45°C. It was reported that temperature had no influence on nickel extraction within the given temperature range.

Darvishi *et al.* (2005) found that the extraction of cobalt (5 g/l) and nickel (5 g/l) from aqueous solutions is endothermic when using mixtures of DEHPA and Cyanex 272 (1:1) as extractant within the temperature range 25-60°C. It was reported that the separation factor of cobalt and nickel increases from 9.93 to 51.8 when the temperature increases from 25°C to 60°C. Increasing the temperature by 35°C decreased the pH at which cobalt is extracted to a larger extent than that of nickel (roughly 0.4 and 0.8 for nickel and cobalt respectively). This explains the increased separation factor as temperature increases.

Sarangi *et al.* (1999b) extracted cobalt (0.5 g/l) and nickel (0.5 g/l) within the temperature range as shown in Figure 2-10:
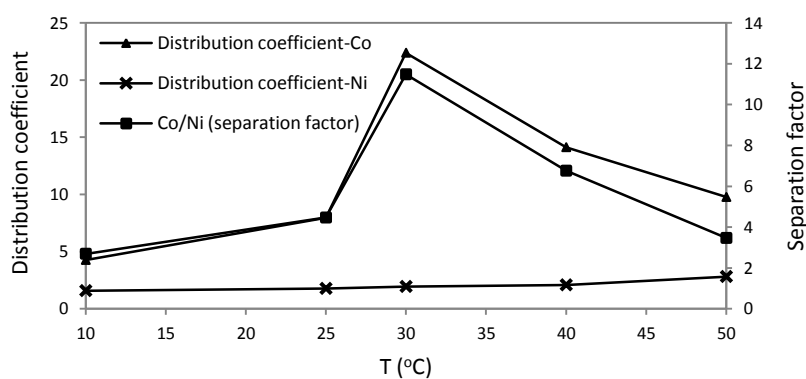
Figure 2-30: Effect of temperature on the extraction of cobalt (0.5 g/l) and nickel (0.5 g/l) with 0.025 M of Cyanex 272(adapted from (Sarangi *et al.*, 1999b))

From Figure 2-10 nickel extraction slightly increases as temperature increases. Cobalt extraction increases as temperature increases from 10 to 30°C and then decreases again within the temperature

range 30-50°C. It was reported that the decrease in cobalt extraction is caused by the fact that the organometallic complex becomes unstable at the elevated temperatures. The highest separation factor for the selective separation of cobalt and nickel (both 0.5 g/l) was obtained at 30°C. No temperature data with respect to iron extraction were discovered.

Based on this discussion, temperature only has a significant influence when extracting minor quantities of nickel and not when extracting major quantities of nickel. Increasing the temperature also increases the separation factor for cobalt and nickel (Darvishi *et al.*, 2005). The stability issue of the cobalt extracted complex at higher temperatures mentioned by Sarangi *et al.* (1999b) was not reported by Darvishi *et al.* (2005) who extracted cobalt at temperatures up to 60°C. The stability of the cobalt extracted complex at temperatures above 30°C therefore remains unclear even though Sarangi *et al.*, (1999b) and Darvishi *et al.* (2005) extracted metal species with different concentrations of 0.5 and 5 g/l respectively.

2.7.4 KINETICS/AGITATION TIME

The kinetics involved with cobalt, iron and nickel extraction will be focussed on in this section.

Hubicki and Hubicka (1996) and Lindell *et al.* (2000) investigated the extraction characteristics of cobalt (0.4 g/l and 3.5 g/l respectively) and nickel (58.7 g/l and 30 g/l respectively) with Cyanex 272 (0.27 M and 0.54 M respectively) as a function of contact time in a mechanical shaker and residence time in a co-current glass column reactor, respectively.

Hubicki and Hubicka (1996) found that equilibrium was reached after 90 seconds of agitation in a mechanical shaker. Lindell *et al.* (2000) stated that a residence time of 20 seconds in a glass column reactor was sufficient to reach equilibrium. A possible reason for the faster kinetics achieved in the latter case is that better mass transfer was obtained in the glass column reactor than in the mechanical shaker. In addition there are several authors that have reported that 5 minutes of agitation is sufficient to reach equilibrium for cobalt and nickel extraction and stripping (Parhi *et al.*, 2008; Devi *et al.*, 1998; Gandhi *et al.*, 1993).

Slower kinetics for iron(III) than either cobalt(II) or nickel(II) extraction with Cyanex 272 was reported with contact times as high as 30 minutes being used (Biswas and Singha, 2006). The pregnant leach solution however consists of ferrous ions (Fe^{2+}) and not ferric ions (Fe^{3+}). No kinetic data are available concerning ferrous extraction with Cyanex 272 and is consequently poorly understood.

2.8 PRE-LOADING EXTRACTION

The selected nickel pre-loading technique to extract cobalt and iron from the pregnant nickel leach solution will be considered next. Three papers that used the nickel salts of the extractant to remove impurities from a concentrated nickel stream will be discussed.

The first paper is a patent from O'Callaghan and Chamberlain (2002). The method involved contacting Cyanex 272 with a portion of a purified nickel solution and then using the pre-equilibrated cationic extractant to purify the impure nickel solution wherein the impure metal species are exchanged for nickel from Cyanex 272 (refer to Figure 2-5). An experiment was conducted by O'Callaghan and Chamberlain (2002) where 0.45 M of Cyanex 272 diluted in kerosene was contacted with 67.9 g/l of a nickel solution containing less than 50 mg/l of cobalt at 50°C and an O/A ratio of 1 for 5 minutes. The pH was adjusted to 5.97 and 6.26 for test 1 and 2, respectively, generating two different nickel loaded organic phases as shown in Table 2-6.

Table 2-6: Pre-loading Cyanex 272 (0.45 M) with 67.9 g/l of nickel at a pH of 5.97 and 6.27 (adapted from (O'Callaghan and Chamberlain, 2002))

	pH	Aqueous	Organic
Ni content before extraction (g/l)	4.97	67.9	0
Ni content after extraction (test 1) (g/l)	5.97	60.4	7.5
Ni content after extraction (test 2) (g/l)	6.26	54.2	13.7

From Table 2-6 the two organic phases that were generated that consisted of 7.5 and 13.7 g/l of nickel for test 1 and 2 respectively. The pre-equilibrated organic phase was then contacted with an impure nickel solution consisting of 71.98 g/l Ni, 6.5 g/l Co, 11 mg/l Cu, 5 mg/l Zn, and 11 mg/l Mn at 50°C and an O/A ratio of 1 for 5 minutes. The results from tests 1 and 2 are shown in Table 2-7.

Table 2-7: Extracting cobalt and other impurities from a nickel solution with the nickel salt of Cyanex 272 (adapted from (O'Callaghan and Chamberlain, 2002))

		Ni	Co	Cu	Zn	Mn
	Before extraction (g/l)	71.98	6.5	0.011	0.005	0.011
Test 1	After extraction (g/l)	78.1	0.085	0	0	0
	% extracted	-8.62	98.69	100	100	100
Test 2	After extraction (g/l)	79.72	0.04	0	0	0
	% extracted	-10.88	99.38	100	100	100

Referring to Table 2-7 most of the impurities are removed from the nickel solution with only trace quantities of cobalt remaining after extraction for both nickel loadings. The negative extraction of nickel designates nickel addition to the nickel solution. It was reported that the current invention is not limited to the experimental setup discussed above, but can be used to remove any impurity metal species that are extracted at a lower pH than nickel with Cyanex 272.

The second paper focussed on separating cobalt and cadmium from nickel sulfate solutions with the nickel salts of Cyanex 272 and DEHPA respectively (Nogueira *et al.*, 2009). Only cobalt separation with Cyanex 272 will be discussed since this is of primary concern. Typical leach liquors obtained from Ni-Cd batteries consists of 80 g/l Ni, 30 g/l Cd and 3 g/l Co. After cadmium removal with DEHPA the liquor consisted of 80 g/l Ni, 0.1 g/l Cd and 3 g/l Co which was the composition of the liquor that was treated with the nickel salt of Cyanex 272 by Nogueira *et al.* (2009).

An experiment was conducted where Cyanex 272 (0.5 M) was equilibrated with 80 g/l of a nickel solution at various O/A ratios and two different pH values (the extraction isotherms generated are displayed in Figure 2-11 (a)). The generated nickel organic phase was then used to remove cobalt from the leach liquor at a constant O/A ratio of 5 (Figure 2-11 (b))

(a)

(b)
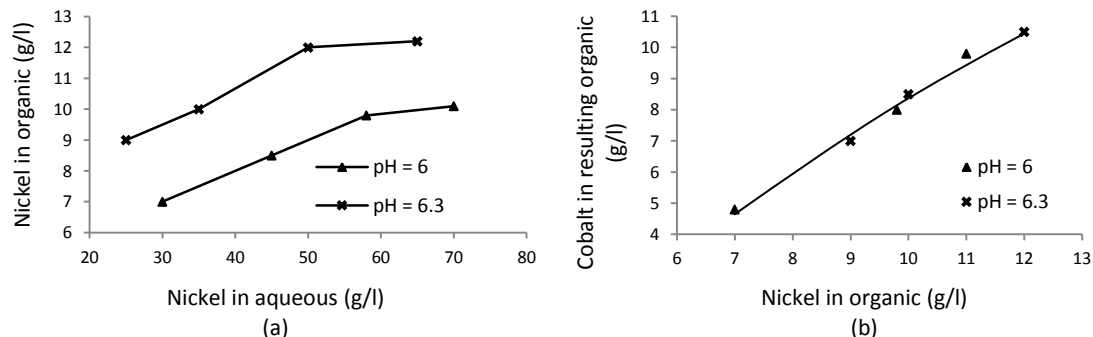
Figure 2-41: a: Extraction isotherms generated with 0.5 M Cyanex 272 and an initial nickel concentration of 80 g/l, b: extraction of cobalt (3 g/l) from an 83 g/l nickel solution at an A/O ratio of 1/5 with the generated nickel organic phase in Figure 2-11 (a) (adapted from (Nogueira *et al.*, 2009))

Referring to Figure 2-11 (b), increasing the nickel content in the organic phase causes an increase in cobalt extraction. This is also observed from Tables 2-6 and 2-7 where a higher nickel loading removed more cobalt from the aqueous phase. It is therefore concluded that nickel pre-loading can be used for the removal of cobalt from nickel solutions.

The third paper focussed on purifying a 100 g/l nickel solution from Ca and Mg with the nickel salt of a 20 V% DEHPA solution (Clark *et al.*, 1993). The purified raffinate contained less than 100 mg/l Mg and less than 5 mg/l Ca. The nickel salt of DEHPA can therefore also be used to purify the nickel solution. Cyanex 272 is however still selected as extractant since it is more selective than DEHPA with respect to cobalt- nickel separation.

No nickel pre-loading work with respect to removing iron from nickel solutions was discovered. It is however speculated that the pre-loading technique will also work for iron since iron is extracted at a lower pH that either cobalt or nickel.

The primary reason for rather using pre-loaded (Figure 2-5) than pure Cyanex 272 (Figure 2-4) is to minimize sodium additions to the nickel product stream. None of the authors reported any data with respect to sodium additions to the nickel product stream and only characterized the extraction behaviour of cobalt and other impurities with the nickel salt of the extractant. All the remaining papers that were reviewed only stated whether NaOH or NH_4OH were used to control the aqueous pH and what the concentration of these base titrants was. None of them reported any data with respect to the sodium or ammonia addition to the nickel product solution after extraction. A comparison of the relative sodium addition to the aqueous product solution after extraction when using Ni-Cyanex 272 or pure Cyanex 272 could therefore not be made.

CHAPTER 3

BATCH TESTS

3.1 INTRODUCTION

The objective of the batch experiments was to determine the operating variables for a solvent extraction circuit that will separate 1 g/l and 3 g/l of cobalt and iron, respectively, from an 80 g/l nickel sulfate solution by using the nickel-preloading technique. These variables included the following:

- pH/NaOH addition, O/A ratio and temperature for the pre-loading section
- nickel loading, O/A ratio and temperature for the extraction section
- H_2SO_4 concentration, A/O ratio and temperature for the stripping section

As expected, the same Cyanex 272 concentration and type of diluent will be used at each section as selected from the experimental data. Various batch experiments were conducted in a specific order since each set of experiments revealed essential information to continue with successive tests.

Initially the extraction kinetics was considered. After the minimum time required to reach equilibrium had been verified from the kinetic tests, the sodium addition to the purified nickel solution was investigated when using pure Cyanex 272 and when using the nickel salt of Cyanex 272. Once it was certain that using the nickel salt of Cyanex 272 is the preferred process route, various diluents were evaluated to identify any interactions that may exist between the extractant and diluents. After selecting a diluent, two 2^4 factorial designs for the pre-loading and extraction sections were conducted to discern the key and trivial variables as well as to identify any interactions there may exist between the design variables. Finally the O/A ratio was varied for the pre-loading and extraction sections with various NaOH additions and nickel loadings, respectively. From these tests the operating conditions for both sections were determined.

Next, stripping tests were carried out to see if selective stripping of cobalt, iron and nickel from the organic phase is possible as well as to see what operating conditions will be required to completely regenerate the extractant to its acidic form. Initially the stripping kinetics were considered to determine the minimum agitation periods for the rest of the experiments where after another 2^4 factorial design was performed to distinguish the vital and insignificant variables as well as to identify any important parameter interactions. Lastly the A/O ratio and acid concentration were varied simultaneously which revealed which operating conditions are needed for selective stripping of nickel, cobalt and iron.

3.2 METHOD

Following is a discussion of how the apparatus and solutions were used and prepared as well as the objectives of each set of experiments.

3.2.1 APPARATUS

Most published work with respect to cobalt, iron and nickel extraction with Cyanex 272 is conducted in a batch fashion. The organic/aqueous dispersion is either mixed via a wrist shaking action (Gandhi *et al.*, 1993) or with a mechanical agitator (Darvishi *et al.*, 2005) where after separation funnels are used to allow for phase separation (Parhi *et al.*, 2008). The metal content in the aqueous phase before and after each experimental run is most frequently determined via atomic absorption spectrophotometry (AAS). Inductively coupled plasma mass spectrometry (ICP-MS) was also used in some cases (Lothongkum *et al.*, 2009), but the majority of papers (Nogueira *et al.*, 2009; Reddy *et al.*, 2006; Rodrigues and Mansur, 2009; Sahu *et al.*, 2004; Tsakiridis and Agatzini-Leonardou, 2004) have reported that AAS is the preferred analytical technique used for analysis of the aqueous phase. ICPMS will often be preferred for very dilute solutions (parts per billion) since AAS is only capable of detecting metal concentrations as low as parts per million. The metal content in the organic phase was either determined via a mass balance or by stripping the organic phase with a very strong acid and then using AAS or ICP-MS to determine the metal content in the stripping agent afterwards by these authors.

In the current work three magnetic stirrer hot plates were used with either 100 ml or 500 ml beakers (depending on the dispersion volume) to serve as mixing reactors. The aqueous and organic solutions were preheated to the desired operating temperature by using a water heating bath. Pipettes were then used to transfer the organic and aqueous phases into the beakers. The hotplates were further used to control the temperature during agitation. An adjustable pipette was used to add NaOH in order to adjust the pH of the solution during agitation where necessary. After agitation was complete the pH was measured and the dispersion was transferred into 500 ml separation funnels allowing sufficient time for the two phases to separate. After phase separation was complete the aqueous phases were collected from the separation funnels and diluted to the concentration range required for analysis by AAS, and the samples were analyzed (0 – 100 mg/l). The metal content in the organic phase was determined via a mass balance from the AAS measurements.

3.2.2 SOLUTION PREPARATION

$CoSO_4.7H_2O$, $NiSO_4.6H_2O$ and $FeSO_4.7H_2O$ (CP grade) were supplied by KIMIX South Africa and were dissolved in distilled water to prepare synthetic representations of the pregnant leach solution and the aqueous solution used for nickel pre-loading. The metal contents in the synthetic solutions were verified via AAS.

Cyanex 272 was supplied by Cytec Inc. and was used without further purification. The concentration of Cyanex 272 required in the organic phase is dependent on the concentration of the metal species in the

aqueous phase. As expected, larger quantities of metal species in the aqueous phase will demand a higher Cyanex 272 concentration in the organic phase. The active component/ligand of Cyanex 272 is bis(2,4,4-trimethylpentyl)phosphinic acid and constitutes 85% of Cyanex 272 (Hubicki and Hubicka, 1996). Hence a 10V% solution of Cyanex 272 in a particular diluent represents a 0.27 M solution of bis(2,4,4-trimethylpentyl)phosphinic acid and a 20V% Cyanex 272 solution represents a 0.54 M solution of bis(2,4,4-trimethylpentyl)phosphinic acid. It has been reported that Cyanex 272 should not be operated at conditions were the ligand is loaded to higher than 60% of its total capacity according to the chemical reactions discussed previously (reactions 12-14). It has been observed that exceeding 60% of the loading capacity of Cyanex 272 causes an increase in the viscosity of the organic phase (O'Callaghan and Chamberlain, 2002; Devi *et al.*, 1994). An increase in viscosity will also cause phase separation issues which will complicate operating conditions.

The objective was to remove 1 g/l of Co and 3 g/l of Fe from an 80 g/l Ni solution. Estimating the concentration of the organic phase for an O/A ratio of 1 in a single stage will typically be as follows:

- According to reaction 17, 1 mole of a divalent ion is swapped for 1 mole of another divalent ion during the extraction stage. So if there is 1 g/l (0.017 M) and 3 g/l (0.054 M) of cobalt(II) and iron(II) in the impure nickel stream, respectively, then approximately 4.17 g/l (0.054 M + 0.017 M = 0.071 M) of nickel needs to be totally extracted during the pre-loading stage.
- If reaction 4 is used as a first approximation then a 2x0.071 M = 0.142 M Cyanex 272 solution is required if the ligand is to be 100% loaded. This increases to 0.24 M if viscosity issues due to exceeding the 60% loading capacity of the ligand are taken into consideration.

An approximation of the minimum Cyanex 272 concentration that will prevent ligand overloading at an O/A ratio of 1 is therefore 10V% (0.27 M). A higher concentration will typically be required since the pre-loading reaction is also more likely to occur via reaction 13 rather than reaction 4.

H_2SO_4 was also supplied by KIMIX South Africa and was used as stripping agent.

3.2.3 EXPERIMENTAL

Figure 3-1 summarizes the order in which the batch tests were conducted and is followed by a more in depth discussion of each set of pre-loading, extraction and stripping tests.
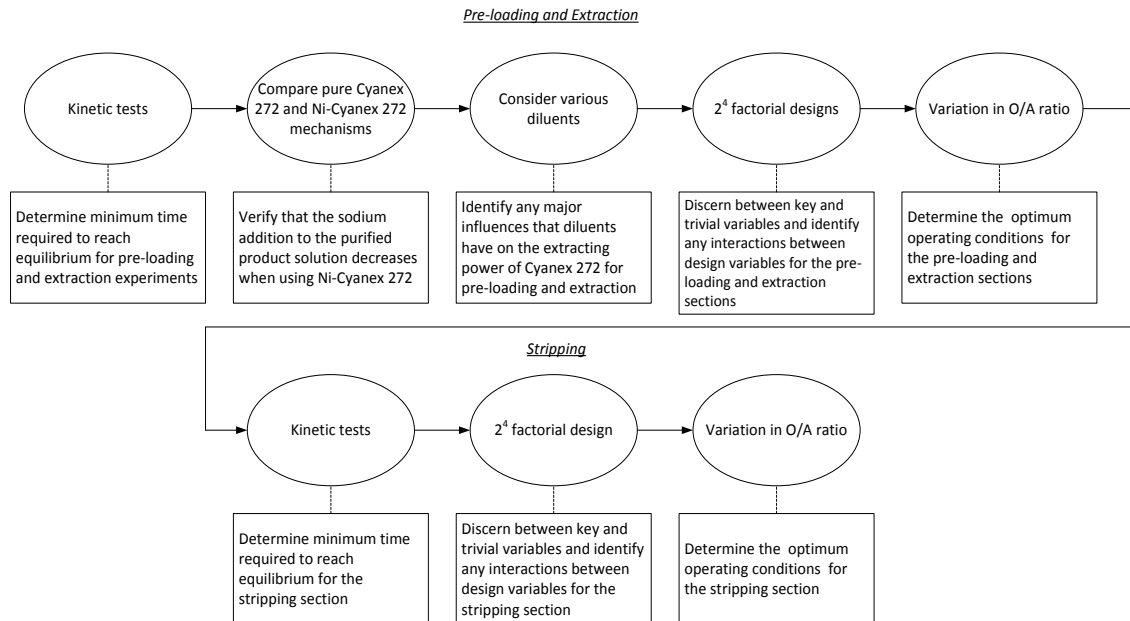
Figure 3-1: Schematic illustration of the order in which each set of batch experiments were conducted

3.2.3.1 PRE-LOADING AND EXTRACTION

3.2.3.1.1 Kinetics

Initially the extraction kinetics was investigated to determine the minimum agitation time for all succeeding extraction experiments. A 20V% (or 0.54 M) Cyanex 272 solution was used ensuring that the ligand is not overloaded resulting in viscosity and phase separation issues. An O/A ratio of 1 (20 ml/20 ml) was used throughout all the experimental runs at a temperature of 50°C.

Firstly the extraction kinetics of cobalt (1.05 g/l) and iron (3.3 g/l) from an 88 g/l nickel solution with pure Cyanex 272 (no pre-loading with nickel before extraction) in kerosene was investigated by allowing agitation to continue for 20, 40, 60, 100, 150 and 300 seconds. For each run 1 ml of a 3 M NaOH solution was added (approximately 1.95 mole of OH$^-$ for each mole of cobalt and iron that is initially in the aqueous phase).

Next the nickel loading kinetics of Cyanex 272 in kerosene was investigated. A 10.75 g/l nickel solution was used with a 3 M NaOH addition of 1 and 2 millilitres (there is approximately 0.8 and 1.6 moles of OH$^-$, respectively, for each mole of nickel that is initially in the aqueous phase) at agitation time intervals of 20, 40, 60, 80, 100, 150, 200, 250 and 300 seconds.

Finally the extraction kinetics with Ni-Cyanex 272 in kerosene and Shellsol D70 was investigated. After verifying the minimum agitation time to load Cyanex 272 with nickel, four organic batches were prepared consisting of 2.47 g/l, 4.09 g/l, 4.66 g/l and 8.48 g/l of nickel. These four batches were then used, respectively, to extract cobalt (1.07 g/l) and iron (3.3 g/l) from an 83.3 g/l nickel sulfate solution at agitation time intervals of 20, 40, 60, 100, 150 and 300 seconds.

3.2.3.1.2 Comparing Cyanex 272 and Ni-Cyanex 272

After verifying the extraction kinetics, two sets of experiments were conducted where cobalt (1 g/l) and iron (3 g/l) were extracted from a concentrated nickel (80 g/l) sulfate solution with pure Cyanex 272 as well as with the nickel salt of Cyanex 272 at various pH values/NaOH additions to the extraction circuit. The objective of these experiments was to determine to what extent using the nickel salt of Cyanex 272 decreases sodium additions to the purified nickel stream compared to using pure Cyanex 272. All the experiments were carried out at an A/O ratio of 1(20 ml/20 ml) and a temperature of 50°C.

For the case where pure Cyanex 272 was used (NaOH is directly added to the pregnant leach solution during extraction), a 20V% batch of Cyanex 272 in kerosene was prepared. The 3 M NaOH additions were 0.15, 0.35, 0.5, 0.65, 0.75, 0.85, 1, 1.3, 1.75, 2, 2.25 and 2.75 millilitres which are equivalent to 0.32, 0.74, 1.06, 1.37, 1.59, 1.80, 2.11, 2.75, 3.70, 4.23, 4.76 and 5.81 moles of OH^-, respectively, for each mole of cobalt and iron that are initially in the aqueous phase. This was sufficient to obtain a range of experimental data points for extraction as a function of pH for cobalt and iron since a good first approximation would be to add 2 moles of OH^- for each mole of a divalent ion that needs to be extracted as was seen previously.

For the scenario where the nickel salt of Cyanex 272 was first prepared prior to extraction (NaOH is only added in the unit where Cyanex 272 is converted into Ni-Cyanex 272 and not during the extraction stage), a 20V% batch of Cyanex 272 in kerosene was also prepared and were pre-loaded by using initial nickel aqueous concentrations of 6.15 g/l, 10.5 g/l and 21.2 g/l with 3 M NaOH additions of 0.25, 0.5, 0.75, 1, 1.3, 1.6, 2 and 2.25 millilitres each. The reason for using various initial nickel concentrations during the pre-loading stage was to see if higher initial nickel concentrations would result in higher loadings than lower initial nickel concentrations as a function of pH/NaOH addition. It will also be revealed whether using different initial nickel concentrations has an effect on cobalt and iron extraction or if only the final nickel loading on the organic phase is the determining factor of the extent of extraction.

3.2.3.1.3 Effect of various diluents

Next the effect of using various diluents was considered to identify any considerable influences they may have on the extracting power of the extractant. These results revealed whether a cautious decision should be made when selecting a diluent, or if economical considerations are the leading factor to consider.

The diluents that were used during the batch experiments included kerosene, heptane, toluene, xylene and Shellsol D70. Shellsol D70 is a 0% aromatic commercial diluent that is normally used with Cyanex 272 for the extraction of cobalt and nickel and was supplied by Shell Chemicals South Africa. The rest of the diluents were supplied by KIMIX South Africa and are CP grade.

10V% and 20V% Cyanex 272 solutions were prepared with all the diluents and was pre-loaded with a 10.3 g/l nickel solution with 3 M NaOH additions of 0.25, 0.5, 1 and 2 millilitres at an A/O ratio of 1 (20

ml/20 ml) and 50°C. The nickel salts of Cyanex 272 were then afterwards used to extract cobalt (1.05 g/l) and iron (2.99 g/l) from an 81.97 g/l nickel sulfate solution.

3.2.3.1.4 Factorial designs

After selecting a diluent a 2^4 factorial design was conducted for both the pre-loading and extraction sections. During the pre-loading design the influences of A/O ratio, extractant concentration, NaOH addition and temperature on nickel loading (initial nickel aqueous concentration was 9.76 g/l), sodium addition to the aqueous phase after extraction and pH were investigated. During the extraction design the influences of A/O ratio, extractant concentration, nickel loading and temperature on extraction and pH were investigated. The aim of these two designs was to eliminate variables that do not have a significant effect for subsequent experimental work as well as to identify any interactions between these variables. Three replicates were carried out of each run to check the repeatability of the experimental setup. The high and low values for the two designs are shown in Table 3-1.

Table 3-1: High and low values of the pre-loading and extraction 2^4 factorial designs (full design are in Table A-9 in Appendix A)

	Pre-loading				
	O/A ratio		Extractant concentration	NaOH addition	Temperature
	ml organic	ml aqueous	(V%)	3 M (ml)	(°C)
high	40	20	20	2	60
low	10	20	10	1	30
	Extraction				
	O/A ratio		Extractant concentration	Ni loading	Temperature
	ml organic	ml aqueous	(V%)	(g/l)	(°C)
high	40	20	20	4.76	60
low	10	20	10	2.83	30

Preliminary nickel pre-loading and extraction experiments were also conducted at 25°C with similar NaOH additions as the experiments conducted at 50°C (a 10V% and 20V% Cyanex 272 were used at both temperatures). These runs however presented various phase separation problems caused by solubility issues at these low temperatures as discussed during the literature survey. Nonetheless some data points could still be generated and were used in conjunction with the data obtained at 50°C to validate some of the claims made from the 2^4 factorial design with respect to the influence of temperature. A lower temperature of 30°C in the design was chosen to try and prevent solubility problems and a maximum of 60°C was chosen since the dispersion becomes too volatile at higher temperatures. The rest of the high and low values were chosen based the results obtained from the previous experiments.

3.2.3.1.5 O/A ratio, nickel loading and NaOH addition

Ultimately the O/A ratio and nickel loading were varied simultaneously to determine the number of theoretical stages required for the extraction section. As will be seen during the results and discussion section a 20V% Cyanex 272 solution were chosen at a temperature of 50°C for the rest of the extraction

experiments. The O/A ratio was varied between 0.25, 0.5, 0.75, 1, 1.5, 2, 2.5 and 3 with nickel loadings of 0.56, 1.97, 2.94, 3.95, 4.69 and 5.73 g/l at each O/A ratio.

After selecting the O/A ratio and nickel loading for the extraction section, the O/A ratio and pH/NaOH addition for the pre-loading section were investigated. It was important to first determine the O/A ratio and nickel loading requirements for the extraction section before optimizing operating conditions for the pre-loading section. To prevent additional water addition to dilute the nickel pre-loading aqueous phase (or a portion of the recycled purified nickel aqueous phase), a very high O/A ratio will be required since an 80 g/l Ni stream will then be used instead of a 6-21.2 g/l Ni solution as was the case in the previous experiments. Based on mass balance calculations the O/A ratio for the pre-loading section ranged between 13.33 and 26.67 for nickel loadings of 6 g/l and 3 g/l respectively. Finally O/A ratios of 26.67, 20, 16 and 13.33 (80 ml/3 ml, 80 ml/4 ml, 80 ml/5 ml and 80 ml/6 ml respectively) and 3 M NaOH additions of 2.5, 3, 4, 5, 5.5 and 6 millilitres were selected as design variables to determine the number of theoretical stages and operating conditions for the pre-loading section. A 20V% Cyanex 272 solution was also used for these tests at 50°C as was concluded from previous experiments.

3.2.3.2 STRIPPING

3.2.3.2.1 Kinetics

The stripping kinetics was investigated next to determine minimum agitation periods to reach equilibrium. These results served as an indication for the rest of the stripping experiments regarding their agitation periods.

A 0.1 M and 0.5 M H_2SO_4 solution at agitation periods of 0.5, 1, 5, 7, 10 and 15 minutes were considered. An organic (20V% Cyanex 272 solution) composition of 4.5 g/l Ni, 1 g/l Co and 3 g/l Fe was used. The A/O ratio and temperature chosen were 1 and 50°C respectively.

3.2.3.2.2 Factorial design

Next a 2^4 factorial design was conducted for the stripping section as well. The influence of A/O ratio, acid concentration, temperature and the metal content of the organic phase on percentage stripped were investigated. The objective of the factorial design was to indentify the most important variables that would be taken into consideration in the next set of experiments. Each run were repeated three times to check for repeatability. The high and low values of the design are displayed in Table 3-2.

Table 3-2: High and low values of the stripping 2^4 factorial design (full design are in Table A-19 in Appendix A)

	A/O ratio		Acid concentration	Metal loading	Temperature
	ml organic	ml aqueous	(M)	(g/l Ni, Co, Fe)	(°C)
high	20	10	0.5	4.67, 1.03, 3.14	60
low	20	40	0.1	2.26, 0.52, 1.58	30

3.2.3.2.3 A/O ratio and acid concentration

Finally the A/O ratio and acid concentration was varied simultaneously to see if it would be possible to selectively strip nickel, cobalt and iron from the organic phase as well what the minimum acid concentration should be used to regenerate Cyanex 272 for recycling purposes. An A/O ratio of 0.5, 0.75, 1, 1.5, 2.25 and 3 with H_2SO_4 concentrations of 0.025, 0.05, 0.075, 0.1, 0.25, 0.5, 0.75, 1, 2 and 4 M were used during these tests.

3.3 RESULTS

3.3.1 PRE-LOADING AND EXTRACTION

The results for the pre-loading and extraction tests will be considered in the specific order as discussed in section 3.2.

3.3.1.1 KINETICS

The kinetic results for cobalt and iron extraction with pure Cyanex 272 are displayed in the Figure 3-2.
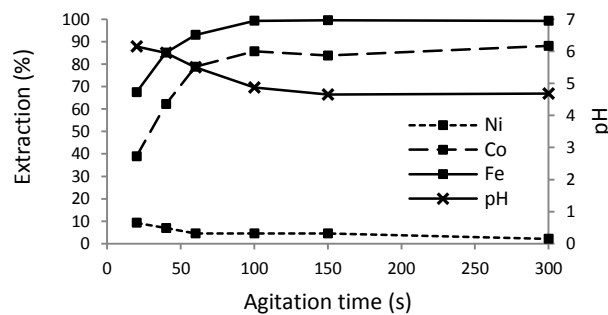
Figure 3-2: Extraction kinetics of cobalt (1.05 g/l), iron (3.3 g/l) and nickel (88 g/l) with pure Cyanex 272 (see Table A-1 in Appendix A for the experimental data and conditions)

From Figure 3-2 equilibrium is reached within 100 seconds which compares well with the time required to reach equilibrium determined by Hubicki and Hubicka, (1996) (see section 2.7.4). Hubicki and Hubicka, (1996) had an aqueous solution consisting of 0.4 g/l cobalt and 58.7 g/l nickel; hence purification of a nickel sulfate solution was also of primary concern and confirms the kinetics in Figure 3-2. It is observed that nickel extraction decreases over time. Referring to the pH, it is observed that as cobalt and iron is extracted, hydrogen is released into the aqueous phase causing the pH to drop. Assuming that some nickel was extracted within the first 20 seconds, the drop in pH can explain the drop in nickel extraction with time.

The nickel pre-loading kinetics of Cyanex 272 is displayed in Figure 3-3.
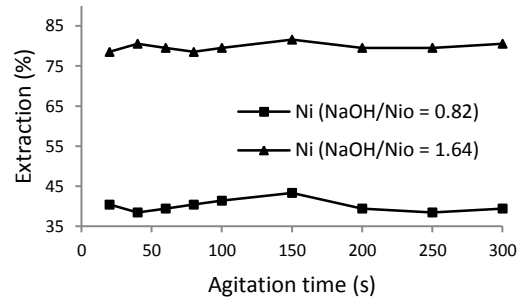
Figure 3-3: Pre-loading/Extraction kinetics of nickel (10.75 g/l) with pure Cyanex 272 (see Table A-2 in Appendix A for the experimental data and conditions)

As shown in Figure 3-3 the kinetics for pre-loading Cyanex 272 with nickel is faster than extraction of cobalt and iron with Cyanex 272 with equilibrium being reached in less than 20 seconds.

Figure 3-4 shows the kinetic results for nickel, cobalt and iron extraction with Ni-Cyanex 272.
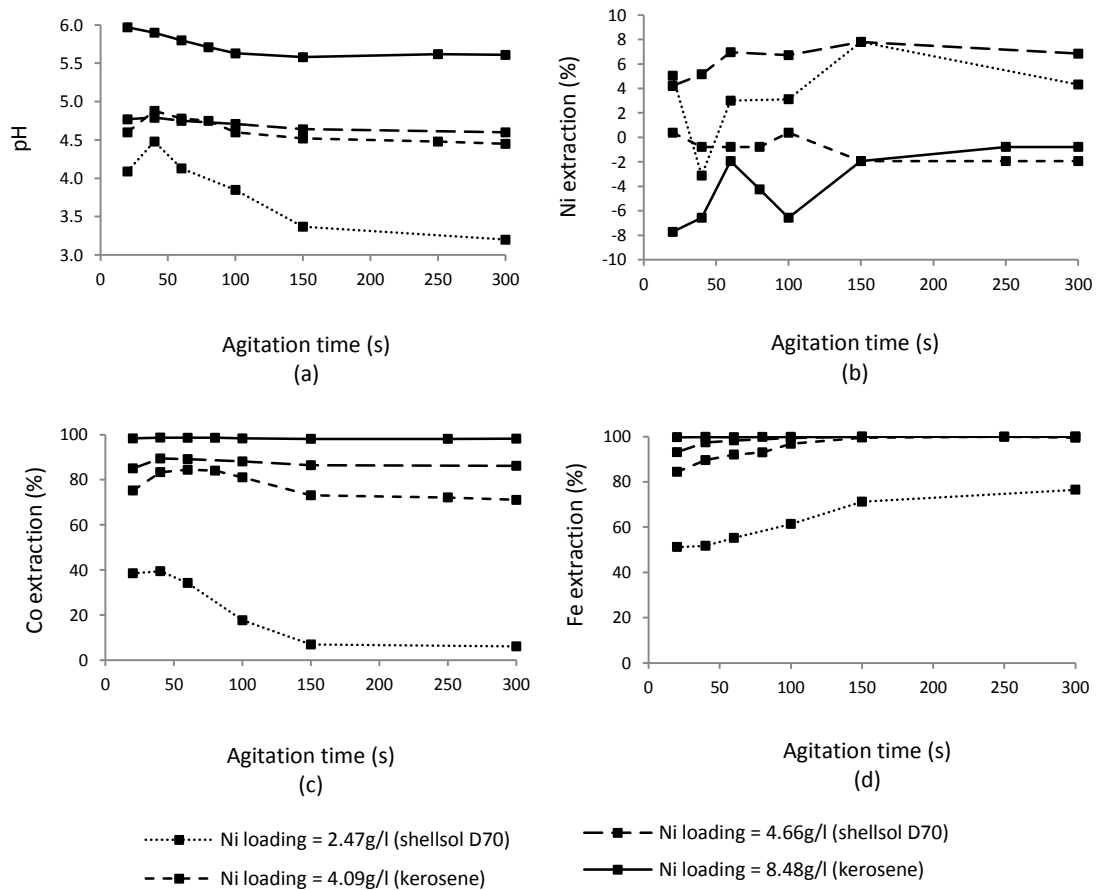
Figure 3-4: Extraction kinetics of cobalt (1.07 g/l), iron (3.3 g/l) and nickel (83.3 g/l) with Ni-Cyanex 272 (see Table A-3 in Appendix A for the experimental data and conditions)

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The kinetics with respect to cobalt and iron extraction with Ni-Cyanex are slower than when using pure Cyanex 272 with equilibrium being reached after 150 seconds compared to 100 seconds. The kinetic data regarding nickel extraction in Figure 3-4 (b) are scattered up to 150 seconds where after it becomes more stable. A possible explanation is that in the beginning the nickel cations in the organic phase are exchanged for cobalt and iron while the initial high pH also causes some nickel to be removed from the aqueous solution by the organic. The extracted nickel can then also be exchanged for cobalt and iron in the aqueous phase. The extent to which these reactions occur will depend on the nickel loading and pH as cobalt and iron removal proceeds.

The time to reach equilibrium decreases as the nickel loading on the organic phase increases for cobalt and iron extraction. This can be explained by considering typical rate laws that are functions of the reagent concentration/nickel loading. Hence lower and higher nickel loadings will decrease and increase the rate of cobalt and iron removal respectively. For lower nickel loadings, cobalt extraction initially increases and then starts decreasing again (Figure 3-4 (c)). A potential explanation can be given by considering the extraction chemistry and by looking at the behaviour of pH in Figure 3-4 (a). Initially the nickel in the organic phase is exchanged for cobalt and iron according to reaction 17. Once the nickel is exhausted from the organic phase the pH is still high enough for iron extraction to occur and the protons on the ligand are exchanged for iron according to reaction 7. This causes the pH to drop and cobalt is also exchanged from the organic phase into the aqueous phase for iron until iron becomes exhausted. For the case where a high nickel loading (8.48 g/l) was used there is sufficient nickel in the organic phase to be exchanged for both cobalt and iron. A drop in pH is however still observed but not to such an extent that cobalt is released back into the aqueous phase. This may also explain the faster kinetics observed for higher nickel loadings since extraction then mainly occurs via exchanging of nickel for cobalt and iron with the additional mechanism of cobalt being released back into the aqueous phase due to the drop in pH occurring to a lesser extent.

It was concluded that a total agitation period of 5 minutes will be allowed for successive extraction and pre-loading experiments. This corresponds well to the times used by several authors (Rodrigues and Mansur, 2009; Park and Mohapatra, 2006; Bhaskara Sarma and Reddy, 2002; Sarangi *et al.*, 1999a; Park, 2007; Sarangi *et al.*, 1999a).

3.3.1.2 COMPARING CYANEX 272 AND NI-CYANEX 272

Before comparing the sodium additions to the purified nickel stream after extraction, the effect of using different initial nickel concentrations during the pre-loading stage will be considered. The nickel loading of the organic phase after pre-loading with different nickel concentration aqueous solutions with varied NaOH additions and generated pH values are shown in Figure 3-5.
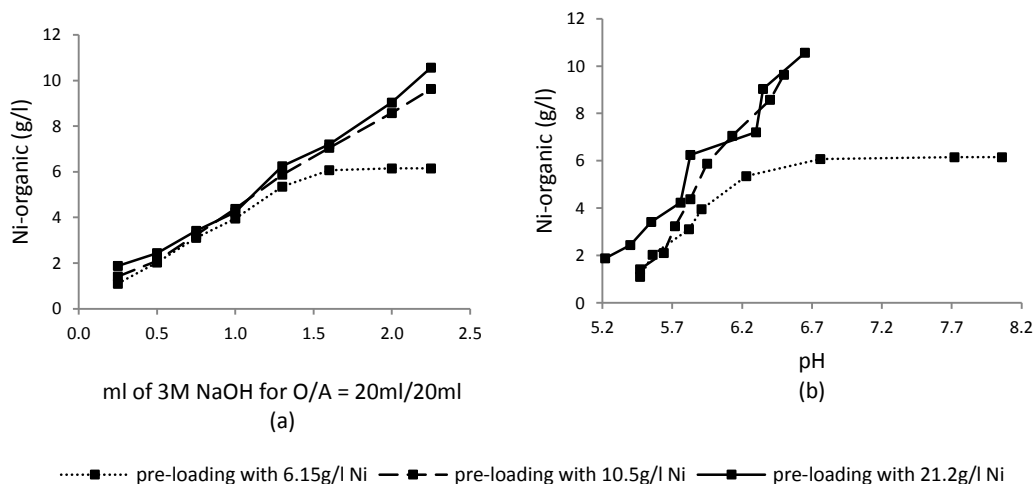
Figure 3-5: Nickel loading with different initial nickel aqueous concentrations as a function of NaOH addition and pH (see Table A-4 in Appendix A for the experimental data and conditions)

From Figure 3-5 (a) it is clear that the loading of nickel onto the organic phase remains similar for all three initial nickel concentrations at the same NaOH additions. Loading with the 6.15 g/l nickel solution is lower than the 10.5 g/l and 21.2 g/l solutions at 3 M NaOH additions higher than approximate 1.25 ml. This is due to the fact that basically all of the nickel from this solution is extracted at his point. Hence loading of nickel onto the organic phase is primarily a factor of the NaOH addition and not the initial nickel concentration used during pre-loading. From Figure 3-5 (b), higher initial nickel aqueous concentrations generates the same loading at lower pH values than lower aqueous concentrations do at higher pH values. A possible explanation is the fact that at the lower nickel concentrations the additional NaOH increases the solution pH once nickel in the aqueous phase becomes exhausted.

Figure 3-6 reveals what nickel loadings are required to extract cobalt and iron from the pregnant nickel solution at an O/A ratio of 1.
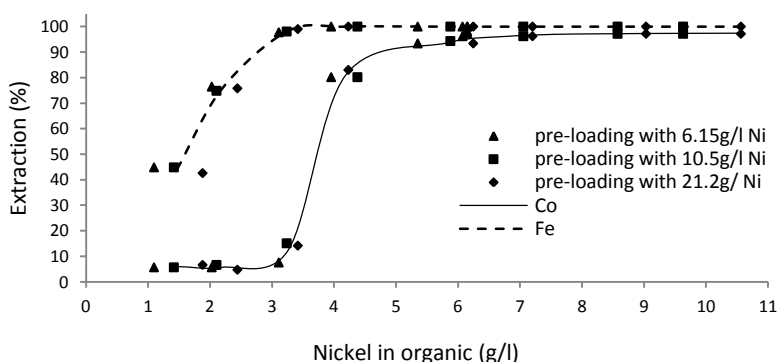
Figure 3-6: Extraction of cobalt (1 g/l) and iron (3 g/l) from the 80 g/l nickel solution as a function of nickel loading (see Table A-5 in Appendix A for the experimental data and conditions)

Referring to Figure 3-6, more than 90% extraction is achieved at nickel loadings of 3 g/l and 6 g/l for iron and cobalt respectively. The higher nickel loading (6 g/l) is more than the required loading according to the stoichiometry in reaction 17 where 1 mole of Ni has to be loaded for each mode of impurity being extracted (nickel loading of 6 g/l (0.1 mol/l) Ni to remove a total of 4 g/l (0.07 mol/l) of Co and Fe). O'Callaghan and Chamberlain (2002) and Nogueira *et al.* (2009) found that a nickel loading of 7.5 g/l is adequate to remove more than 98% of 6.5 g/l Co, 11 mg/l Cu, 5 mg/l Zn, and 11 mg/l Mn from a 78.1 g/l nickel solution at an A/O ratio of 1. Nogueira *et al.* (2009) reported that using nickel loadings ranging between 7 and 13 g/l are sufficient to purify an 83 g/l nickel stream from 3 g/l of cobalt at an A/O ratio of 0.2. These two publications compares well with the data displayed in Figure 3-6.

From Figure 3-6 it is also clear that using different initial nickel concentrations of 6.15, 10.5 and 21.2 g/l during pre-loading does not have a severe effect on extraction and that the final nickel loading (irrespective of the initial nickel aqueous concentration used during pre-loading) of Cyanex 272 will determine cobalt and iron extraction.

Next the sodium additions to the purified nickel stream will be considered. Figure 3-7 shows the extraction curves generated when using pure Cyanex 272 without any nickel pre-loading as well as the sodium additions to the product solution after extraction as a function of pH.
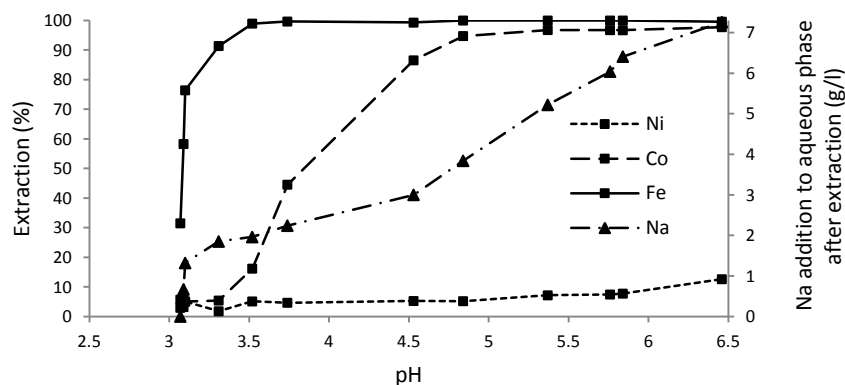
Figure 3-7: Extraction of cobalt (1 g/l), iron (3 g/l) and nickel (80 g/l) and sodium addition to the purified nickel product solution with pure Cyanex 272 (see Table A-6 in Appendix A for the experimental data and conditions)

Figure 3-7 shows that more than 95% of cobalt and iron are extracted from the nickel solution at pH values of 3.5 and 5, respectively, which corresponds well to typical pH values from literature (Miralles *et al.*, 1992; Hubicki and Hubicka, 1996, Park, 2007). The maximum nickel extraction is approximately 10% or 8 g/l at a pH of 6.5. At a pH of 5, approximately 4 g/l of sodium reports to the nickel product solution. Consequently, while 1 g/l cobalt and 3 g/l iron are being removed from the product solution, 4 g/l of sodium is added instead. Figure 3-8 shows the extraction curves generated when using the nickel salts of Cyanex 272 for cobalt and iron separation as well as the sodium addition to the nickel product solution as a function of pH.
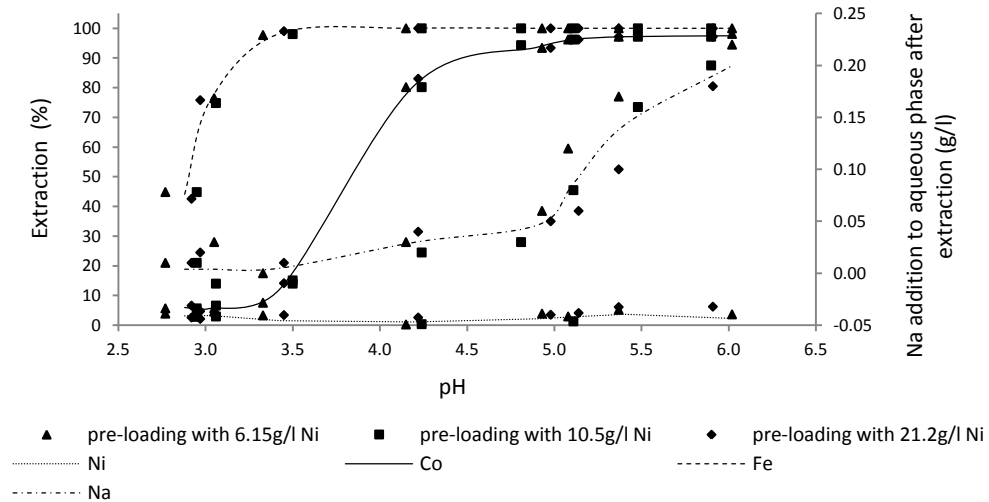
Figure 3-8: Extraction of cobalt (1 g/l), iron (3 g/l) and nickel (80 g/l) and sodium addition to the purified nickel product solution with the nickel salts of Cyanex 272 (see Table A-6 in Appendix A for the experimental data and conditions)

It is noted from Figures 3-6 and 3-8 that higher nickel loadings onto the organic phase results in higher equilibrium pH values. This is caused by the fact that when nickel is exhausted from the organic phase that hydrogen is exchanged for iron and then causes a drop in pH of the solution as discussed previously.

Cobalt and iron are extracted almost completely at pH values of 5 and 3.5, respectively, which correspond with the values obtained when using pure Cyanex 272. Maximum nickel extraction with Ni-Cyanex 272 is 5.18% compared to 12.61% with pure Cyanex 272. This is due to the fact that nickel is also released from the organic phase into the aqueous phase with Ni-Cyanex 272 and not only extracted. Very little sodium addition to the nickel product solution was observed. At a pH of 5 the removal of 1 g/l cobalt and 3 g/l iron from the product solution resulted in the addition of only 0.05 g/l sodium to the nickel product solution with Ni-Cyanex 272 compared to 4 g/l with pure Cyanex 272. It is therefore concluded that the pre-loading procedure is the best alternative based on the low sodium additions to the purified product solution.

3.3.1.3 EFFECT OF VARIOUS DILUENTS

Figure 3-9 and 3-10 shows the results for pre-loading Cyanex 272 and extraction with the pre-loaded Cyanex 272, respectively, by using various diluents. All the diluents gave good phase separation at 50°C which meant that no third phase modifier was necessary.
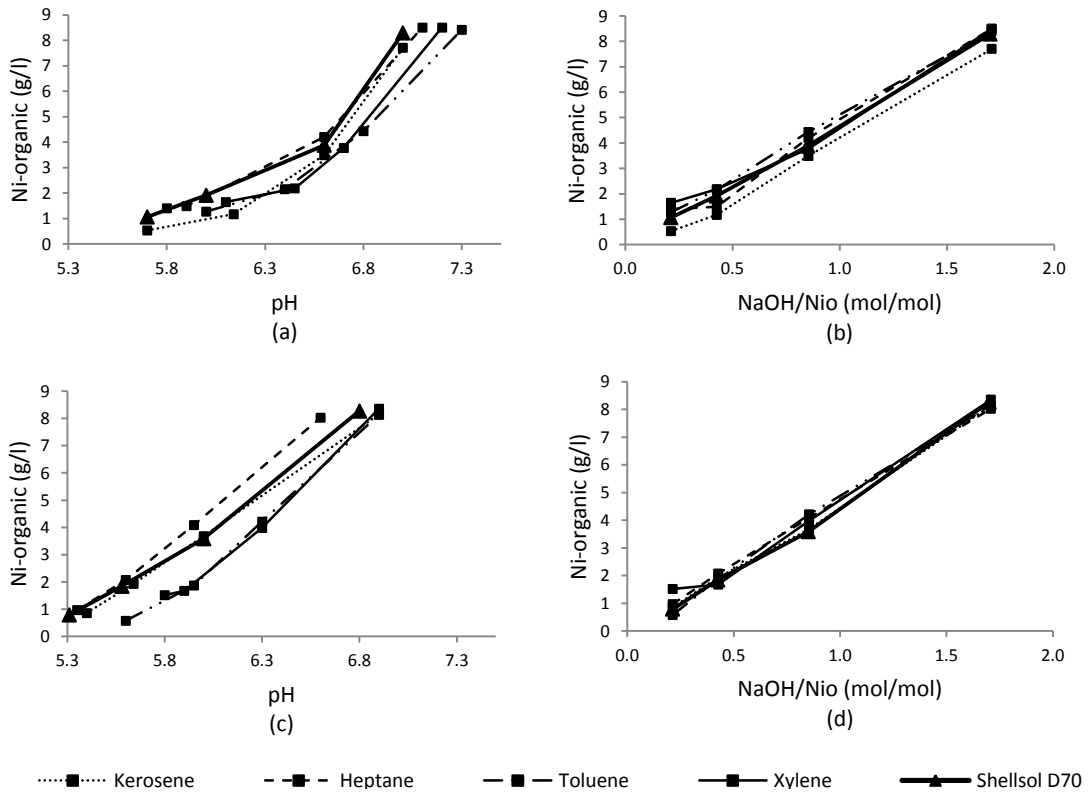
Figure 3-9: Effect of using various diluents on pre-loading as a function of (a) pH with 10V% Cyanex 272 (b) NaOH addition with 10V% Cyanex 272 (c) pH with 20V% Cyanex 272 (d) NaOH addition with 20V% Cyanex 272 (see Table A-7 in Appendix A for the experimental data and conditions)

Referring to Figure 3-9, all the diluents behaved very similar as a function of NaOH addition. In contrast they do however have an effect on the pH at which nickel extraction occurs as shown in Figures 3-9 (a) and (c). When considering Xylene and Heptane for example in Figures 3-9 (a) and (c), nickel loading differs approximately with 1 g/l and 2 g/l, respectively, at a pH of 6.3.

The loading curves in Figure 3-9 (d) (variance at NaOH/Nio values of 0.21, 0.43, 0.85 and 1.71 are *0.12, 0.02, 0.07 and 0.02,* respectively) are closer to each other than in Figure 3-9 (b) (variance at NaOH/Nio values of 0.21, 0.43, 0.85 and 1.71 are *0.18, 0.19, 0.14 and 0.11* respectively). A possible explanation is the fact that a higher concentration of Cyanex 272 is used in Figure 3-9 (d) (20V%) than in (b) (10V%) which means that the interactions between the diluent and ligand are less significant in the former than the latter case caused by the excess extractant.

Extraction of nickel, cobalt and iron with Ni-Cyanex 272 in Figure 3-10 is considered next.

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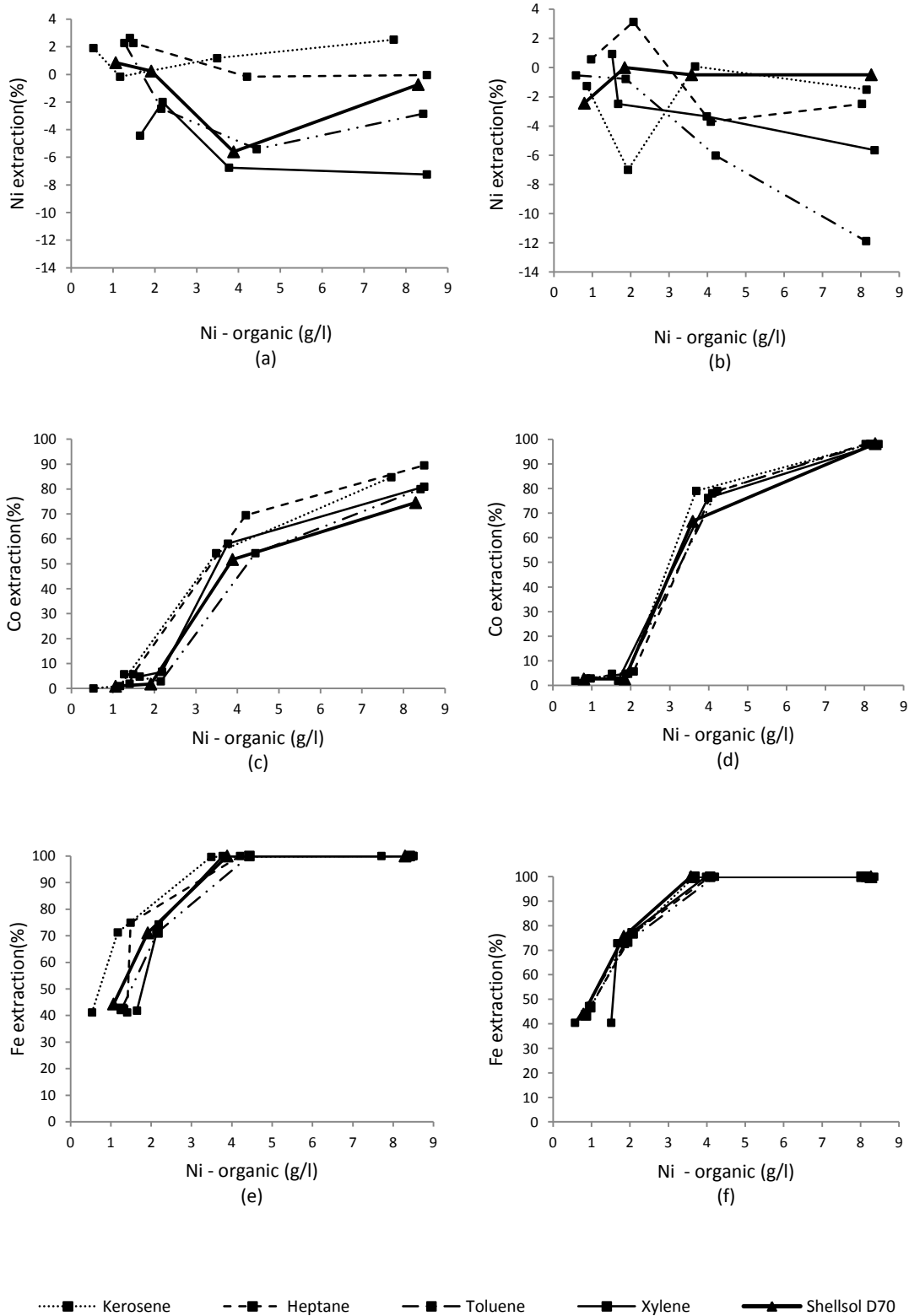
Figure 3-10: Effect of using various diluents for cobalt (1.05 g/l), iron (2.99 g/l) and nickel (81.97 g/l) extraction with Ni-Cyanex 272 as a function of nickel loading with (a, c and e) 10V% Cyanex 272 and (b, d and f) 20V% Cyanex 272 (see Table A-8 in Appendix A for the experimental data and conditions)

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For nickel extraction with Ni-Cyanex 272 the data is once again scattered (Figures 3-10 (a) and (b)) as was the case with the kinetic data (the negative extraction is due to the fact that more nickel is released from the organic than extracted from the aqueous phase). For all the diluents nickel extraction however remained below 4% which means that less than 3.28 g/l of nickel was lost from the 81.97 g/l solution, irrespective of the loading or diluent used. From Figures 3-10 (c)-(f) the diluents influence on the extracting power of Cyanex 272 for cobalt and iron once again becomes less severe when using a 20V% rather than a 10V% solution for the same reasons as discussed previously for pre-loading.

Since the various diluents do not have a significant effect on the extracting behaviour of Cyanex 272, Shellsol D70 was chosen as diluent for all subsequent experimental work given the fact that it is currently being used on industrial scale for the extraction of cobalt and nickel with Cyanex 272 (Flett, 2005).

3.3.1.4 FACTORIAL DESIGNS

The pre-loading and extraction factorial designs will be discussed in this section.

3.3.1.4.1 Pre-loading

The repeatability of the pre-loading setup will be considered prior to interpretation of the factorial design results. Equation 21 was used to define repeatability (Measey *et al.*, 2003):

$$r = \frac{MS_{between} - MS_{within}}{(MS_{between} + (n-1)MS_{within})} \qquad [21]$$

where: $MS_{between}$ =   Mean squares between groups (between run 1-16)

MS_{within} =   Mean squares within groups (within each run/3 repeats)

n   =   Number of repeated measurements

r   =   Repeatability

Repeatability varies from 0 to 1 and expresses the fraction of variation that is due to differences between groups not due to differences within groups. If the average group is consistent, then the average within group variation will be low which means that the ratio of among group variation to within group variation (the repeatability) will be high.

Table 3-3 gives qualitative terms to describe repeatability as calculated with equation 21.

Table 3-3: Terms to express the repeatability values calculated with equation 21 (adapted from (Measey *et al.*, 2003))

r less than 0.2	Slight repeatability
r between 0.2 and 0.4	Low repeatability
r between 0.4 and 0.7	Moderate repeatability
r between 0.7 and 0.9	High repeatability
r greater than 0.9	Very high repeatability

A single factor ANOVA on the pre-loading factorial design yielded the mean square (MS) values between and within groups for nickel loading, the sodium concentration in the aqueous solution after extraction and pH values. Equation 21 was subsequently used to calculate the repeatability, which is displayed in Table 3-4.

Table 3-4: Repeatability (r) values for the pre-loading factorial design

	Ni loading			Generated Na stream			pH		
	MS	n	**r**	MS	n	**r**	MS	n	**r**
Between Groups	114.15	3	**0.996**	5.20	3	**0.982**	1.09	3	**0.997**
Within Groups	0.17			0.03			0.0009		

According to the r-values in Table 3-4, pH gives the best repeatability followed by the nickel loading and then the sodium addition to the aqueous phase after extraction with r values of 0.997, 0.996 and 0.982 respectively. In all three instances, repeatability is considered as *very high* according to Table 3-3.

Two regression models were fitted to generated data from the pre-loading factorial design as shown in Table 3-5. The p-values for a 95% confidence interval for the two models are also shown.

Table 3-5: P-values for the pre-loading 2^4 factorial design with the high and low values shown in Table 3-1

	$y = z_o + z_1a + z_2b + z_3c + z_4d$				$y = z_o + z_1a + z_2b + z_3c + z_4d + z_5ab + z_6ac + z_7ad + z_8bc + z_9bd + z_{10}cd$		
Variable	Ni loading (g/l)	Na addition after extraction (g/l)	pH		Ni loading (g/l)	Na addition after extraction (g/l)	pH
A/O ratio (a)	6.E-22	0.23	5.E-24	a	2.E-50	0.22	4.E-31
Extractant concentration (b)	0.68	0.23	6.E-15	b	0.01	0.22	2.E-22
NaOH addition (c)	3.E-13	2.E-34	6.E-24	c	3.E-41	2.E-31	4.E-31
Temperature (d)	0.90	0.14	0.08	d	0.39	0.13	3.E-03
				ab	1.E-03	0.15	1.E-06
				ac	8.E-34	0.90	0.13
				ad	0.69	0.16	6.E-06
				bc	0.90	0.55	0.14
				bd	0.28	0.92	9.E-05
				cd	0.62	0.05	5.E-05

It is clear that A/O ratio and NaOH addition are the two dominating factors with respect to nickel loading with p-values of 6×10^{-22} and 3×10^{-13} respectively. Extractant concentration and temperature on the other hand do not affect nickel loading to such a large extent with p-values of 0.68 and 0.9 respectively. The following preliminary experiments confirm this statement.
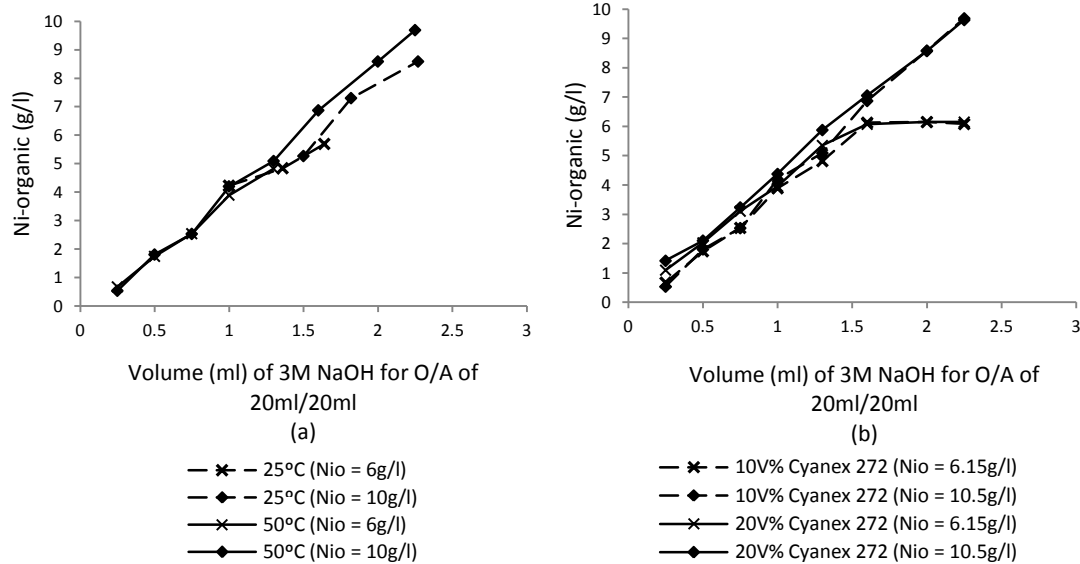
Figure 3-11: (a) Influence of temperature on nickel loading as a function of NaOH addition (b) Influence of extractant concentration on nickel loading as a function of NaOH addition (see Tables A-12 and A-13 in Appendix A for the experimental data and conditions)

From Figure 3-11 (a), nickel loading increases by approximately 1 g/l as temperature increases from 25°C to 50°C for 3 M NaOH additions higher than 1.25 ml. This has been confirmed by other authors as discussed during the literature review in section 2.7.3 (Bhaskara Sarma and Reddy, 2002; Sarangi *et al.*, 1999b). It was concluded that the effect of temperature on nickel loading is not as severe as O/A ratio and NaOH addition and all subsequent pre-loading tests were conducted at 50°C. Figure 3-11(b) confirms the relatively high p-value (0.68) for extractant concentration with respect to nickel loading in Table 3-5. Therefore only the influence of NaOH addition and A/O ratio on nickel loading was further investigated with respect to nickel loading.

Referring to Table 3-5 the Na addition to the aqueous solution after extraction is only influenced by the NaOH addition to the mixture. This means that most of the added sodium will exit with the aqueous raffinate stream used for pre-loading. All the variables except temperature have a significant influence on the pH. Most authors publish their results as a function of pH and not the quantity of NaOH added. Gandhi *et al*, (1993) for instance reported that extraction increases as the extractant concentration increases since extraction then occurs at a lower pH. This is not entirely true since the extractant concentration has an effect on the equilibrium pH and not extraction. Figure 3-12 illustrates this statement by plotting the same results from Figure 3-11(b) but only this time as a function of pH and pH as a function of NaOH addition.
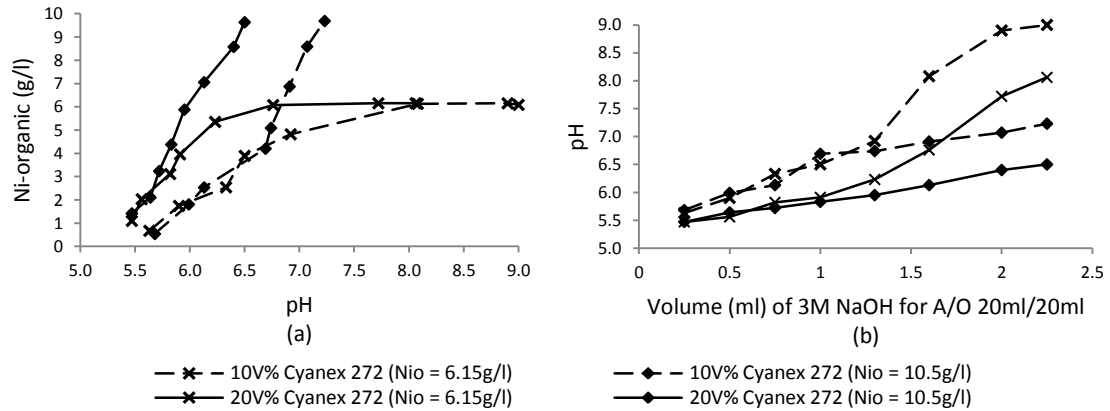
Figure 3-12: Influence of extractant concentration on nickel loading as a function of pH (see Tables A-12 and A-13 in Appendix A for the experimental data and conditions)

Referring to Figure 3-12 (a), higher extractant concentrations extract nickel to the same extent at lower pH values than lower extractant concentrations do at a higher pH values. Hence using more extractant decreases the pH at which extraction occurs caused by the extra protons being added to the system coming from the phosphinic acid (Cyanex 272) as shown in Figure 3-12 (b). This is not the case in Figure 3-11(b) where both extractant concentrations extract nickel to the same extent as a function of NaOH addition.

3.3.1.4.2 Extraction

Next the repeatability of the extraction runs will be considered followed by a discussion of the results obtained from the factorial design. The repeatability as calculated with equation 21 for nickel, cobalt and iron extraction as well as the generated equilibrium pH are shown in Table 3-6.

Table 3-6: Repeatability (r) values for the extraction factorial design

	Nickel extraction			Cobalt extraction			Iron extraction			pH		
	MS	n	r	MS	n	r	MS	n	r	MS	n	r
Between Groups	38.13	3	**0.371**	5675.46	3	**0.996**	1855.02	3	**0.988**	2.25	3	**0.990**
Within Groups	13.76			7.60			7.27			0.008		

According to Table 3-3, cobalt extraction, iron extraction and pH are considered as very highly repeatable with r-values very close to 1. Nickel extraction, however, is not repeatable according to the r-value of 0.371. Referring to equation 21 this can be explained by the fact that the mean square between groups (38.13) does not differ as much from the mean square within groups (13.76) as with cobalt, iron and pH. This was expected since nickel extraction rarely exceeded 10% resulting in the low MS (between groups) value of 38.13 compared to 5675.46 and 1855.02 for cobalt and iron. The MS value within groups of 13.76 for nickel compares better with the values of 7.6 and 7.27 for cobalt and iron. This, however, is an indication that the nickel extraction data remained relatively consistent and that the poor repeatability is a result of the low variance there was between the data groups.

Two regression models were fitted to the extraction tests. These models and the p-values for a 95% confidence interval for the extraction factorial design are shown in Table 3-7.

Table 3-7: P-values for the extraction 2^4 factorial design with the high and low values shown in Table 3-1

Variable	$y = z_o + z_1a + z_2b + z_3c + z_4d$					$y = z_o + z_1a + z_2b + z_3c + z_4d + z_5ab + z_6ac + z_7ad + z_8bc + z_9bd + z_{10}cd$			
	Extraction (%)					Extraction (%)			
	Ni	Co	Fe	pH		Ni	Co	Fe	pH
O/A ratio (a)	0.026	5.E-40	3.E-20	4.E-24	a	0.039	1.E-44	2.E-36	1.E-28
Extractant concentration (b)	0.130	0.572	0.604	2.E-06	b	0.283	0.330	0.103	4.E-10
Ni loading (c)	3.E-05	3.E-06	5.E-07	2.E-12	c	0.003	2.E-11	1.E-20	3.E-17
Temperature (d)	0.004	0.006	0.030	2.E-06	d	0.661	1.E-05	2.E-08	4.E-10
					ab	0.042	0.271	0.104	0.034
					ac	0.647	3.E-09	2.E-20	7.E-04
					ad	0.001	2.E-06	3.E-08	4.E-07
					bc	0.049	0.764	0.932	0.022
					bd	0.773	0.379	0.128	0.225
					cd	0.02	0.910	0.613	0.304

Due to the poor repeatability of the nickel extraction data it is difficult to come to any reasonable conclusions regarding its behaviour as a function of the design variables. The main objective is however to remove cobalt and iron from the pregnant nickel solution without losing too much nickel in the process. Hence predictions will only be made of the maximum and minimum nickel losses that can be expected in succeeding experiments.

O/A ratio with p-values of 5×10^{-40} and 3×10^{-20} and nickel loading with p-values of 3×10^{-6} and 5×10^{-7} are the dominating factors with respect to cobalt and iron extraction, respectively. Consequently these two variables were considered during the final experiments to determine the operating conditions for the extraction section. Extractant concentration once again does not appear to have a significant influence on cobalt and iron extraction according to their relatively high p-values (0.572 and 0.604). Figure 3-13 displays preliminary runs that were conducted to investigate the influence of extractant concentration.

■ 10V% Cyanex 272   □ 20V% Cyanex 272
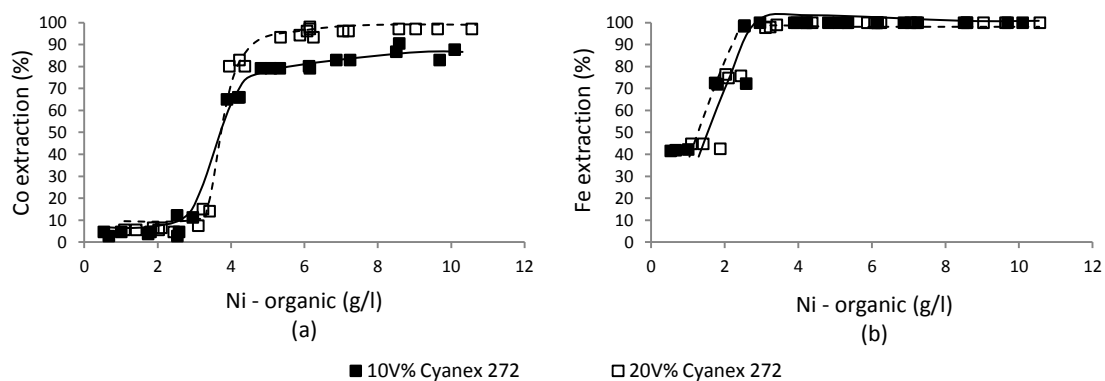
Figure 3-13: Effect of extractant concentration on cobalt and iron extraction with Ni-Cyanex 272 (see Table A-14 in Appendix A for the experimental data and conditions)

Based on Figure 3-13 (a) the use of a higher extractant concentration does in fact increase cobalt extraction for nickel loadings higher than 4.3 g/l which contradicts the results in Table 3-7. The maximum nickel loading that was used during the factorial design is 4.76 g/l (see Table 3-1). This is close to 4.3 g/l and with the O/A ratio being varied as well during the factorial design the effect of extractant concentration on cobalt extraction for higher nickel loadings was not revealed by the statistics. Extractant concentration does however, not have a significant effect on iron extraction as shown in Figure 3-13(b). It is well published in literature that cobalt extraction increases as the extractant concentration increases (Sarangi *et al.*, 1999b; Swain *et al.*, 2006, Park, 2007). Consequently it was concluded that a 20V% solution of Cyanex 272 will be used due to the higher extraction obtained for cobalt as well as for the fact that it reduces the probability of phase separation issues caused by overloading of the ligand. As the Cyanex 272 concentration increases, the organic phase viscosity increases. Typically Cyanex 272 concentrations of not higher than 20V% are used since the organic phase then becomes too viscous.

According to Table 3-7 temperature influences cobalt and iron extraction with p-values of 0.006 and 0.03 respectively. Figure 3-14 shows preliminary results that will clarify some of the influences that temperature may have on cobalt and iron extraction.
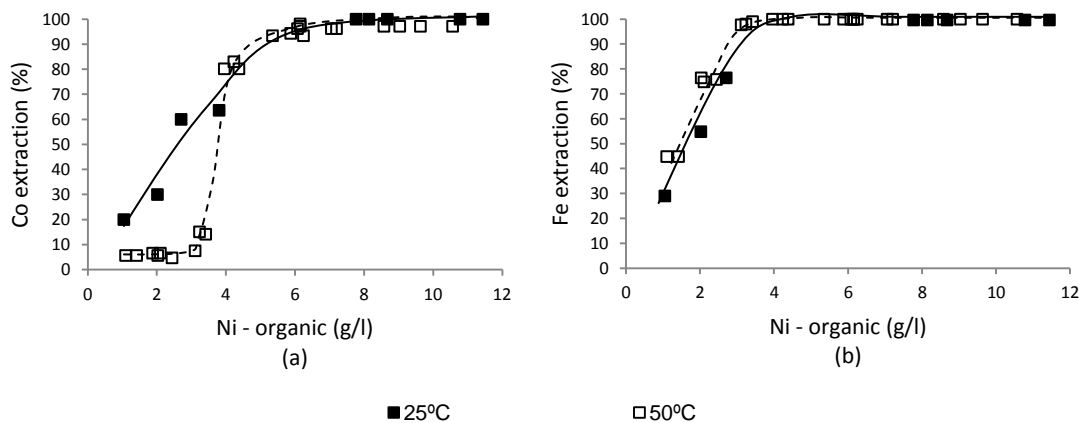
Figure 3-14: Effect of temperature on cobalt and iron extraction with Ni-Cyanex 272 (see Table A-15 in Appendix A for the experimental data and conditions)

Referring to Figure 3-14 (a), cobalt extraction increases as temperature decrease for nickel loadings less than approximately 4 g/l. Hence when there is not enough nickel present in the organic phase temperature does in fact influence cobalt extraction. Sarangi *et al.* (1999b) also observed that cobalt extraction decreases as temperature increases within the range 30-50°C as shown in Figure 2-10. According to Figure 3-14(b) temperature has no significant influence on iron extraction. Consequently the influence of temperature was not further considered since phase separation issues were observed at temperatures below 30°C (see section 2.5) and there will be sufficient nickel in the organic phase to ensure complete removal of cobalt and iron from the pregnant nickel solution. A temperature of 50°C was chosen for all the subsequent extraction experiments.

The interaction between O/A ratio and nickel loading for cobalt and iron extraction in Table 3-7 can be explained by the fact that cobalt and iron extraction are largely dependent on the quantity of nickel in the organic phase rather the concentration/loading. Hence a higher loading will be sufficient at a low O/A ratio and a lower loading at a higher O/A ratio. The A/O ratio and nickel loading should just be monitored to prevent overloading to greater than 60% of the ligand resulting in phase separation problems.

The equilibrium pH is influenced by all the variables (refer to Table 3-7). The O/A ratio and nickel loading influence can once again be explained by the fact that hydrogen will be exchanged for iron once nickel is exhausted from the organic phase when the pH is high enough. The influence of extractant concentration is due to the extra hydrogen atoms being added as discussed previously and temperature typically has an influence on pH as explained by the Nernst equation.

3.3.1.5 O/A RATIO, NICKEL LOADING AND NaOH ADDITION

The nickel loading and O/A ratio requirements for the extraction section were studied prior to the pre-loading section since it is important to first determine the loading requirements for the extraction section. Figure 3-15 reveals what typical nickel losses and sodium additions to the purified nickel stream might be expected after extraction.
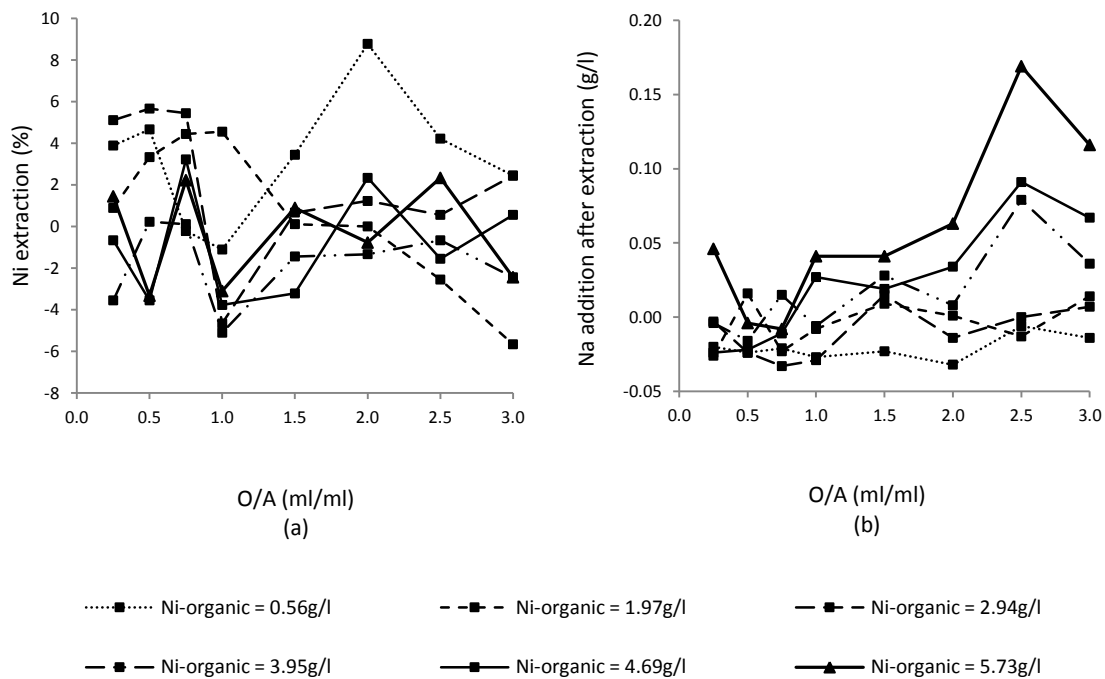
Figure 3-15: Nickel (80 g/l) extraction from and sodium addition to the product solution after extraction as a function of nickel loading and O/A (see Table A-16 in Appendix A for the experimental data and conditions)

The negative extraction of nickel in Figure 3-15(a) is caused by the fact that more nickel is transferred from the organic to the aqueous phase than from the aqueous to the organic phase. The nickel extraction data are once again relatively scattered and ranges between -6 and 6 percent with the exception of 8.77% when using a nickel loading of 0.56 g/l at an O/A ratio of 2. Apart from this exception maximum nickel losses of approximately 4.8 g/l can be expected. Referring to Figure 3-15(b) the sodium additions to the purified nickel stream predominantly increases as the nickel loading increases for O/A ratios higher than 1 (The negative sodium additions are due to impure sodium that was in the salts used to prepare the synthetic representation of the pregnant nickel leach solution which was then also extracted and typically ranges between 0.05-0.1 g/l). This can be explained by the fact that higher nickel loadings during the pre-loading stage demands higher NaOH additions and consequently increases the probability of sodium uptake by the extractant causing the higher sodium additions to the purified pregnant nickel solution. Nonetheless typical maximum sodium additions of 0.1 g/l might be expected during the extraction section with the exception of 0.17 g/l for a high nickel loading of 5.73 g/l and an O/A ratio of 2.5.

Next cobalt and iron separation will be considered as a function of O/A ratio and nickel loading.
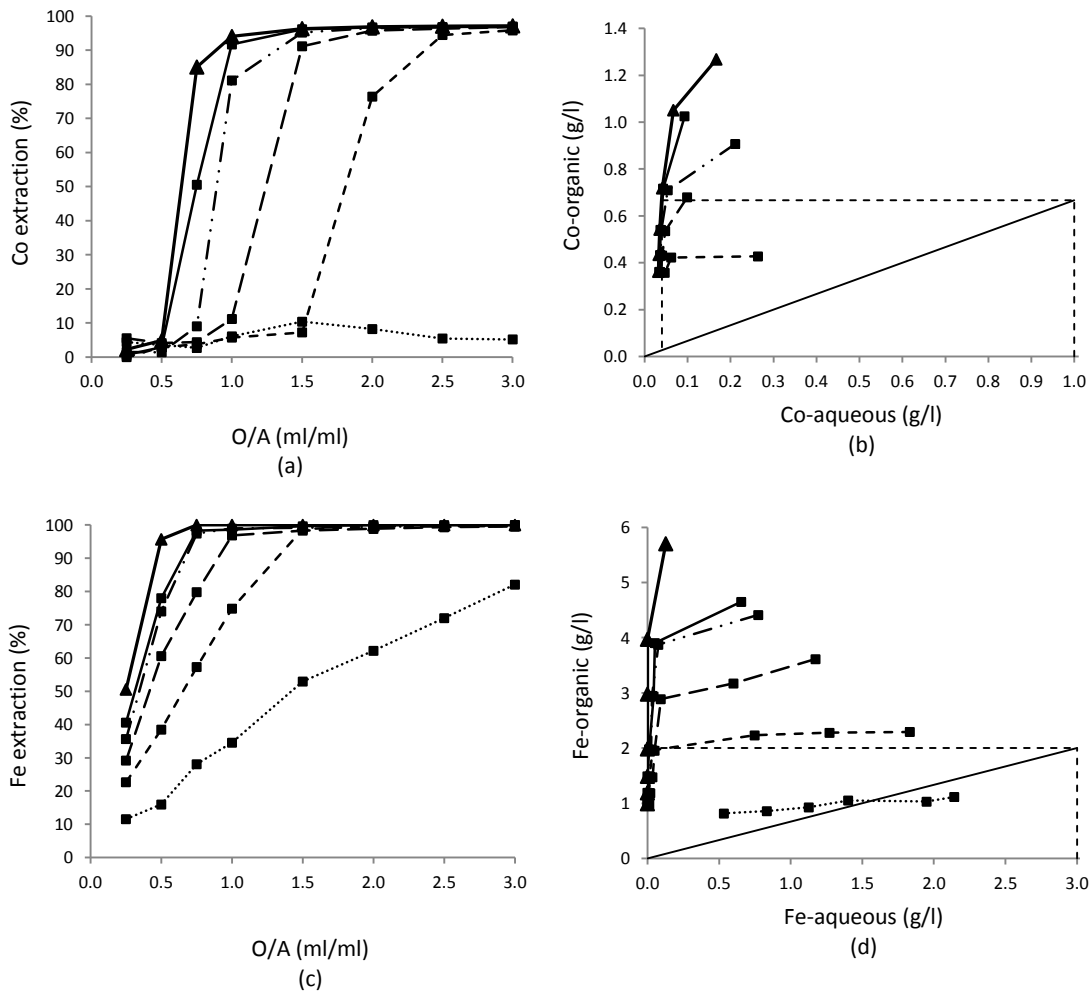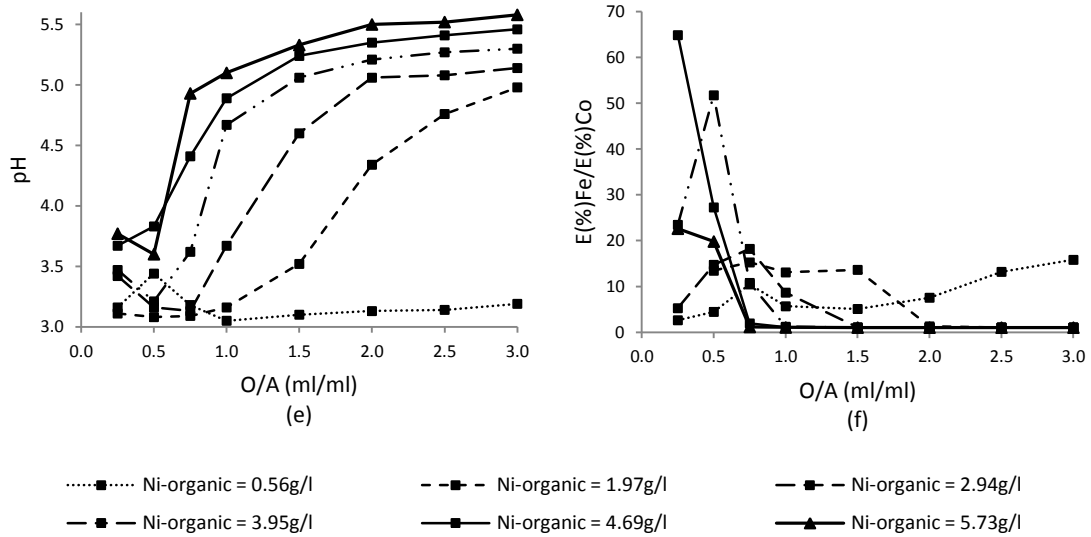
Figure 3-16: Variation in O/A ratio and nickel loading for pH and cobalt (1 g/l) and iron (3 g/l) extraction (see Table A-16 in Appendix A for the experimental data and conditions)

Referring to Figure 3-16 (a) and (c), higher nickel loadings reduce the O/A ratio at which cobalt and iron extraction occurs which confirms the earlier statement in section 3.3.1.4.2 that extraction is largely a function of the nickel content in the organic phase rather than the nickel concentration. This is also reflected in Figure 3-16(e) where higher nickel loadings, or rather the nickel content in the organic phase, increase the equilibrium pH.

Most frequently extraction McCabe-Thiele diagrams are reported as a function of pH. This means that NaOH is added within each stage to control the solution pH. This approach, however, is limited when using the pre-loading procedure since the McCabe-Thiele diagrams are generated at various nickel loadings. It will be more challenging to control the nickel loading between extraction stages than having to control the pH (to do this a separate pre-loading section will be required within each extraction stage). The McCabe-Thiele diagrams (Figures 3-16 (b) and (d)) will therefore only be used to confirm that the selected nickel loading and O/A ratio are sufficient to extract cobalt and iron in a single stage.

Referring to Figure 3-16, two different scenarios will be considered. In the first one the selective extraction of iron and cobalt will be discussed followed by a discussion of the simultaneous extraction of cobalt and iron.

Referring to Figure 3-16 (f), a plot is given of iron extraction divided by cobalt extraction $(E(\%)_{Fe}/E(\%)_{Co})$ as a function of nickel loading and O/A ratio. The aim of this plot is to identify a nickel loading and O/A ratio that can selectively separate iron and cobalt from the pregnant solution. The higher the value for $(E(\%)_{Fe}/E(\%)_{Co})$ the better the selectivity. The highest value for $E(\%)_{Fe}/E(\%)_{Co}$ is 64.4 at an O/A ratio of 0.25 and a nickel loading of 4.69 g/l. At these conditions cobalt extraction is very low (0.63%) but only 40.6% iron extraction is reached, referring to Figures 3-16 (a) and (c), respectively. The second highest value obtained for $(E(\%)_{Fe}/E(\%)_{Co})$ is 52 at an O/A ratio of 0.5 and a nickel loading of 3.95 g/l. 75% iron extraction is attained at these conditions as shown in Figure 3-16(c). The third best value for

$(E(\%)_{Fe}/E(\%)_{Co})$ is 23 at an O/A ratio of 0.25 and a nickel loading of 5.73 g/l with iron being extracted up to 50%. Referring to Figure 3-16 (f), the highest values for $E(\%)_{Fe}/E(\%)_{Co}$ are reached at O/A ratios less than 0.5. Even though very little cobalt extraction occurs at these conditions, phase separation issues were encountered caused by ligand overloading (see section 2.5). Ultimately the best operating conditions with respect to selectivity would be at an O/A ratio of 1.5 and a nickel loading of 1.97 g/l giving 7.25% cobalt and 98.79% iron extraction resulting in no phase separation problems.

For the second scenario, only cobalt extraction has to be considered since sufficient iron extraction is expected at these conditions. Referring to Figures 3-16 (a) and (c), an O/A ratio of 1.5 with a nickel loading of 3.2 g/l is selected since it gives maximum cobalt (95-96%) and iron (99-100%) extraction (this loading was selected via interpolation). This is a high enough O/A ratio which reduces possible ligand overloading and the nickel loading is relatively low compared to the other higher loadings which minimizes the quantity of nickel that has to be recycled from the purified product solution for pre-loading. From the McCabe-Thiele diagrams in Figures 3-16 (b) and (d), a single stage is sufficient to extract cobalt and iron at this O/A ratio and nickel loading.

The primary objective of the project is to purify the concentrated nickel solution while selective separation of cobalt and iron are secondary. Due to the unpredictability of the nickel extraction data, a pure cobalt and iron product cannot be guaranteed with the selective extraction approach and the second scenario was selected as the best alternative. This also eliminates the additional pre-loading unit that will be required (one before iron extraction and one before cobalt extraction). Selective stripping of cobalt, iron and any nickel that may still be left in the organic phase was subsequently considered.

From Figure 3-16 (b), cobalt is still present in quantities ranging between 0.03-0.05 g/l after extraction for the highest nickel loadings and O/A ratios. For complete cobalt extraction minor additions of NaOH to the extractor unit will ensure complete cobalt removal as well since this will slightly increase the pH. An approximation of the additional sodium that will end up in the nickel product solution to remove a remaining 0.05 g/l of cobalt is 0.04 g/l [(0.05/59)(2)(23) = (concentration of cobalt left after extraction/atomic weight of cobalt)(moles of sodium required to neutralize the total moles of H^+ being released for cobalt)(atomic weight of sodium)].

Next the O/A ratio and pH for the pre-loading section will be considered. If a portion of the purified nickel stream is used (80 g/l) to pre-load Cyanex 272 (refer to Figure 2-5), then the corresponding O/A ratio to reach these loadings (assuming complete nickel extraction at the pre-loading unit) is determined via the following equation which is derived via a mass-balance:

$$\frac{O}{A} = \frac{V_{org}}{V_{aq}} = \frac{Ni_{aq}}{Ni_{org}} \qquad\qquad\qquad [22]$$

where   O/A   =   Organic/aqueous mixing ratio [ml/ml]

V_{org}; V_{aq} =   Volumes of the organic and aqueous phase [g/l]

Ni_{org}; Ni_{aq} =   Nickel concentration of the organic and aqueous phases [g/l]

The aim was to generate nickel loadings ranging between 3-6 g/l with an 80 g/l nickel aqueous solution. The reason for using such a high nickel concentration was to eliminate unnecessary water additions to the system to dilute the purified nickel stream used for pre-loading. If 3 g/l and 6 g/l are substituted in equation 22 the O/A ratio interval generated is 13.33-26.667. The pre-loading results as functions of the O/A ratio and pH are shown in Figure 3-17:
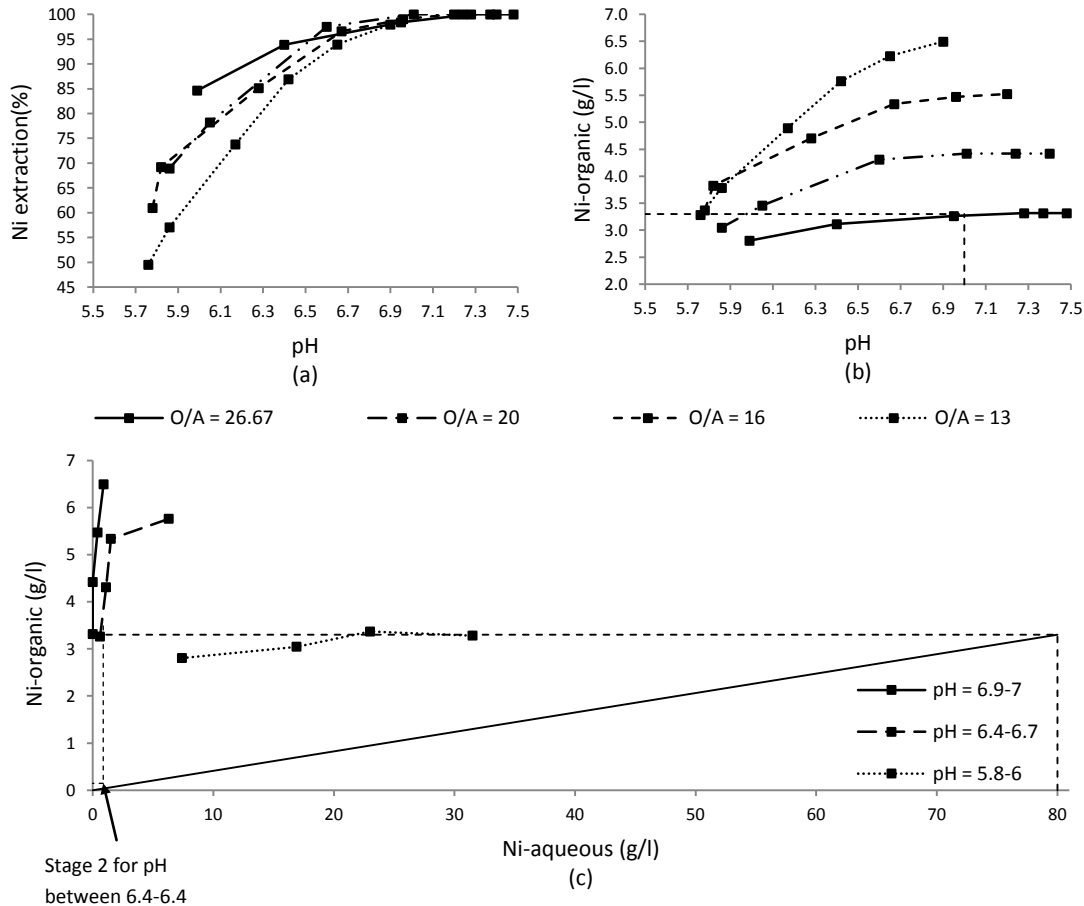
Figure 3-17: Variation in O/A ratio and pH with respect to nickel loading of Cyanex 272 (see Table A-17 in Appendix A for the experimental data and conditions)

Referring to Figure 3-17 (a), at pH values higher than 6.7 the O/A ratio does not have a significant influence on extraction and at a pH higher than 7.1 all of the nickel is extracted irrespective of the O/A ratio. As expected the nickel loading decreases when using higher O/A ratios as shown in Figure 3-17 (b). To remove cobalt and iron from the pregnant solution a nickel loading of 3.2 g/l is required as discussed previously: substituting this in equation 22 results in an O/A ratio of 25. From Figure 3-17(a) a pH of approximately 7 will be sufficient to completely extract nickel at this O/A ratio and generate the required loading in a single stage as shown in Figure 3-17(c). Decreasing the pH to values ranging between 6.4 and 6.7 will require an additional stage to extract the remaining nickel as indicated in Figure 3-17 (c). The higher pH of 7 is, however, proposed since a single pre-loading unit will then be required instead of two units.

3.3.2 STRIPPING

Nickel was also loaded onto the organic phase along with cobalt and iron during the stripping tests. The aim was to see whether selective stripping of nickel, cobalt and iron is possible. The stripped nickel can then be rejoined with the purified pregnant solution while pure cobalt and iron are recovered from the organic phase.

3.3.2.1 KINETICS

The results for the kinetic tests with respect to stripping are shown in Figure 3-18.
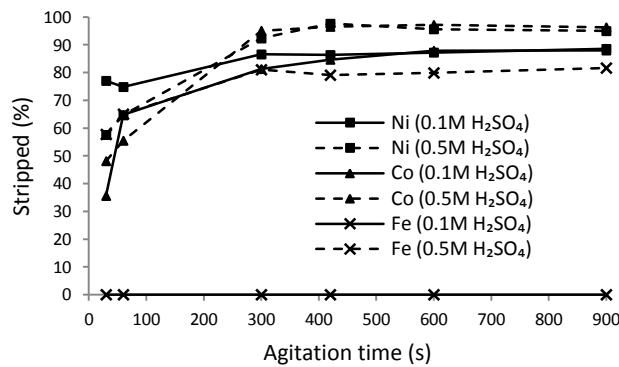
Figure 3-18: Stripping kinetics of an organic loaded with nickel (4.5 g/l), cobalt (1.04 g/l) and iron (2.96 g/l) (see Table A-18 in Appendix A for the experimental data and conditions)

Form Figure 3-18 it is clear that the stripping kinetics are slower than the extraction kinetics with Ni-Cyanex 272 with equilibrium being reached after approximately 410 seconds compared to 150 seconds (refer to Figure 3-4). An agitation period of 600 seconds was therefore allowed for succeeding stripping tests.

3.3.2.2 FACTORIAL DESIGN

The repeatability that was calculated with equation 21 for the factorial design with respect to percentage nickel, cobalt and iron stripped as well as the equilibrium pH is shown in Table 3-8.

Table 3-8: Repeatability (r) values for the stripping factorial design

	Nickel stripping			Cobalt stripping			Iron stripping			pH		
	MS	n	**r**	MS	n	**r**	MS	n	**r**	MS	n	**r**
Between Groups	595.56	3	**0.962**	2996.12	3	**0.993**	3683.11	3	**0.996**	5.32	3	**0.997**
Within Groups	7.71			7.52			4.34			0.006		

All the r-values in Table 3-8 are very close to 1 which means that the stripping tests are also highly repeatable according to Table 3-3.

The p-values for the two regression models fitted to the stripping factorial design data, as shown in Table 3-9 will be considered next.

Table 3-9: P-values for the stripping 2^4 factorial design with the high and low values shown in Table 3-2

	$y = z_o + z_1a + z_2b + z_3c + z_4d$				$y = z_o + z_1a + z_2b + z_3c + z_4d + z_5ab + z_6ac + z_7ad + z_8bc + z_9bd + z_{10}cd$		
	Stripped (%)				Stripped (%)		
Variable	Ni	Co	Fe		Ni	Co	Fe
A/O ratio (a)	3.E-04	2.E-03	2.E-06	a	1.E-08	7.E-07	1.E-13
Acid concentration (b)	2.E-04	4.E-04	9.E-22	b	6.E-09	3.E-08	3.E-31
Metal loading (c)	7.E-06	6.E-05	0.08	c	2.E-11	1.E-09	6.E-04
Temperature (d)	7.E-03	0.399	0.911	d	6.E-06	0.13	0.82
				ab	1.E-06	3.E-06	1.E-11
				ac	0.01	1.E-05	5.E-04
				ad	0.117	0.458	2.E-05
				bc	9.E-10	4.E-08	3.E-03
				bd	0.8	0.825	0.07
				cd	0.274	0.511	0.05

Referring to Table 3-9, temperature only influences nickel stripping. Nickel stripping, however, only increased with values ranging between 5-10% as the temperature increased. This effect was considered as being not large enough and a temperature of 50°C was chosen for all subsequent stripping experiments for the same reasons as the pre-loading and extraction runs.

A high and low metal loading were chosen to see if the metal content in the organic phase influences the percentage of metal stripped or if the acid concentration and A/O ratio are the two dominating factors. This is important since the O/A ratio used during the extraction section will determine the metal concentration in the organic phase and possibly influence the extent of stripping. From Table 3-9 it is clear that the metal concentration does, in fact, influence the percentage of metal stripped, with p-values well below 0.05 except for iron with a p-value of 0.08. This means that the metal loadings that will be used for the remaining stripping tests will be based on the O/A ratio of the extraction section.

Interactions also exist between the metal loading with A/O ratio and the acid concentration. The only exception is for nickel where there is not a significant interaction between the metal loading and A/O ratio. A possible explanation is the fact that nickel is stripped more easily than cobalt or iron and the acid concentrations used were high enough to ensure that cobalt and iron striping also occurred. Hence there was sufficient H^+ for nickel to be stripped irrespective of the A/O ratio used. Stripping is therefore primarily dependent on the quantity of H^+ cations available in the strip solution, i.e., the quantity of metal being removed from the organic phase is determined by the H^+ content in the aqueous phase rather than the concentration of H^+ in the aqueous phase.

As expected the A/O ratio and acid concentration are the two dominating factors with respect to stripping; hence these two variables were further investigated to determine operating conditions to regenerate the organic phase as well as possibilities for selective stripping.

3.3.2.3 A/O RATIO AND ACID CONCENTRATION

Next the A/O ratio and H_2SO_4 concentration were considered. Table 3-10 indicates where phase separation issues (a single emulsion formed) were encountered as well as the relative concentrations at which nickel, cobalt and iron were stripped.

Table 3-10: Phase separation and selectivity defined by the relative quantities stripped of each metal

H_2SO_4 (M)	A/O 0.50			0.75			1.00			1.50			2.25			3.00		
0.025	Poor			Poor			Poor			Poor			Poor			Poor		
	43	Inf	Inf	85	Inf	Inf	86	Inf	Inf	inf	Inf	Inf	262	Inf	Inf	1.7	Inf	Inf
0.05	Poor			Poor			Poor			Good			Good			Good		
	277	Inf	Inf	160	Inf	Inf	1.7	Inf	Inf	1	Inf	Inf	1	Inf	Inf	1	Inf	Inf
0.075	Poor			Poor			Poor			Good			Good			Good		
	332	Inf	Inf	1.5	Inf	Inf	1	Inf	Inf	1	Inf	Inf	1.2	Inf	Inf	1	Inf	Inf
0.1	Poor			Poor			Poor			Good			Good			Good		
	78	Inf	Inf	1	Inf	Inf	1	Inf	Inf	1	Inf	Inf	1.2	Inf	Inf	1	Inf	Inf
0.25	Poor			Poor			Good			Good			Good			Good		
	1	602	645	1	3.3	3.5	1	2.3	2.4	1	1.9	2	1.1	1.9	2.1	1	2	2.3
0.5	Good			Good			Good			Good			Good			Good		
	1	1.4	1.5	1	1.2	1.2	1	1.1	1.2	1	1.2	1.2	1	1.2	1.2	1	1.2	1.3
0.75	Good			Good			Good			Good			Good			Good		
	1	1.2	1.3	1	1.1	1.1	1	1.1	1.1	1	1	1.2	1	1.2	1.2	1	1.3	1.2
1	Good			Good			Good			Good			Good			Good		
	1	1.3	1.4	1	0.9	0.9	1	1	1	1	1	1	1	1	1	1	1	1
2	Good			Good			Good			Good			Good			Good		
	1	1	1.1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
4	Good			Good			Good			Good			Good			Good		
	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1

*Legend for interpretation of Table 3-10

Phase separation		
$S(\%)_{Ni}/S(\%)_{Co}$	$S(\%)_{Co}/S(\%)_{Fe}$	$S(\%)_{Ni}/S(\%)_{Fe}$

The nickel, cobalt and iron stripped as well as pH as a function of acid concentration and A/O ratio are revealed in Figure 3-19.
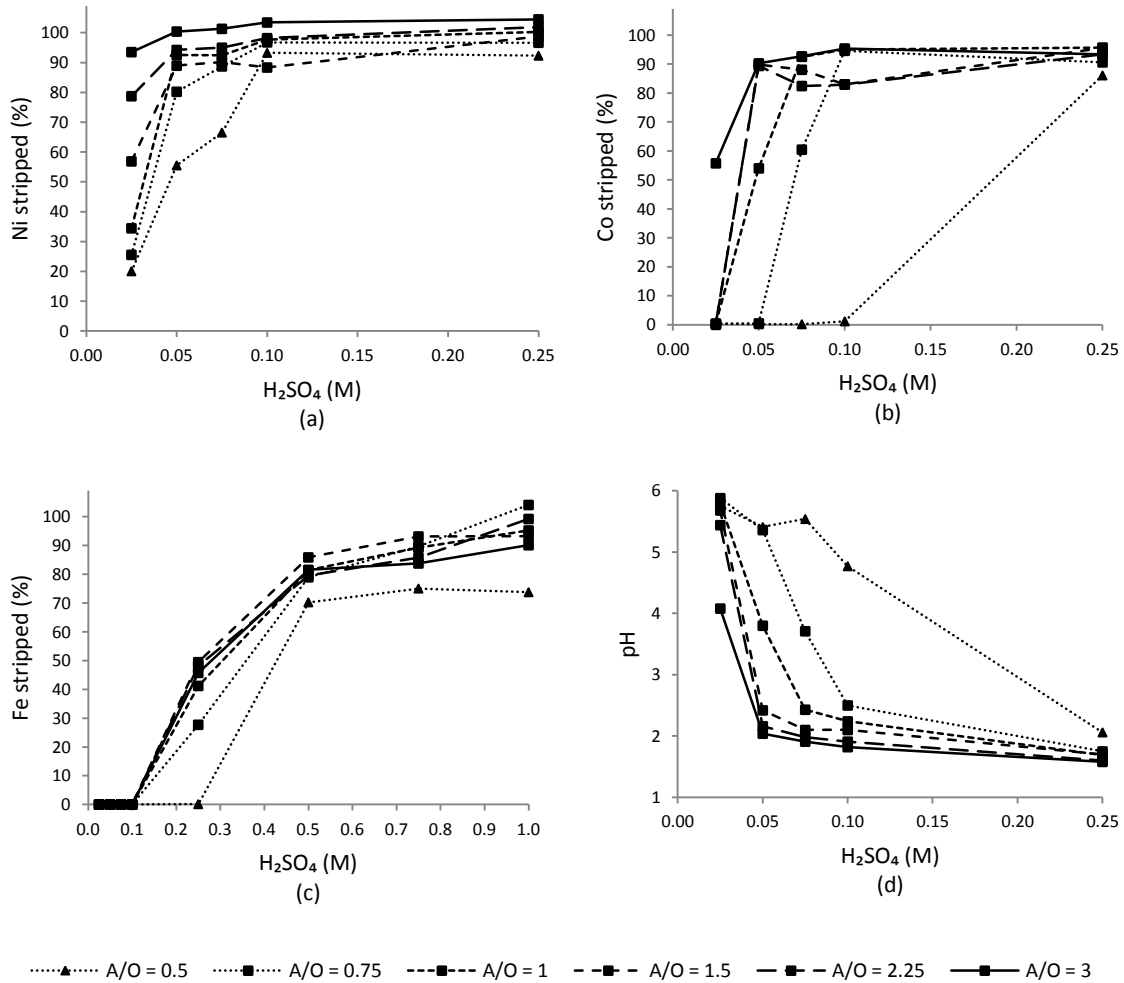
Figure 3-19: Nickel (2.69 g/l), cobalt (0.75 g/l) and iron (2.08 g/l) stripping as a function of H₂SO₄ concentration and A/O ratio (see Table A-21 in Appendix A for the experimental data and conditions)

Lower cobalt and iron loadings were used than those initially present in the pregnant solution since an O/A ratio of 1.5 was decided on for the extraction section. Ideally this would yield an organic phase with a loading of 0.7 g/l (1/1.5) Co and 2 g/l (3/1.5) Fe. Slightly higher concentrations were generated to rather overdesign the operating variables. 2.69 g/l of nickel was also loaded onto the organic phase to investigate selective removal of any co-extracted nickel as well.

From Figure 3-19 it is clear that stripping increases as the acid concentration and A/O ratio increases, with nickel being stripped initially followed by cobalt and then iron. First selective stripping of nickel and cobalt will be considered. *Inf* in Table 3-10 refers to infinity and was used when no stripping occurred for the component in the denominator as shown in the legend (i.e., when there was perfect separation). This occurred for nickel and cobalt at an A/O ratio of 1.5 and a H₂SO₄ concentration of 0.025 M. Even though no cobalt stripping occurred at these conditions only 56.9% of the nickel was stripped which is not considerably high. The second highest value of nickel relative to cobalt stripped (S(%)$_{Ni}$/S(%)$_{Co}$) is 332 at an A/O ratio of 0.5 and a H₂SO₄ concentration of 0.075 M. At these conditions nickel and cobalt are 66.52% and 0.2% stripped, respectively. The best operating conditions for selective stripping of

nickel and cobalt are at an A/O ratio of 0.75 and a H_2SO_4 concentration of 0.1 M generating a $S(\%)_{Ni}/S(\%)_{Co}$ value of 78 with 93.25% and 1.2% of nickel and cobalt being stripped respectively. A major drawback from the stripping tests was the fact that various phase separation issues were encountered as indicated with the shaded area in Table 3-10. A general trend is observed that at low acid concentrations and A/O ratios phase separation problems occur (i.e., when there is not sufficient H^+ present in the aqueous phase). This was also the case for the factorial design at both the high and low temperatures. In Table 3-10 all the high values for $S(\%)_{Ni}/S(\%)_{Co}$ are within the shaded areas. Therefore even though nickel and cobalt may selectively be removed from the organic phase this operation will be limited due to phase separation problems. No literature for the selective stripping of cobalt and nickel from Cyanex 272 was discovered. The phase separation dilemma where a single emulsion forms is a possible explanation.

Referring to Figure 3-19(c) no iron stripping is observed for H_2SO_4 concentrations equal or less than 0.1 M irrespective of the A/O ratio. This is reflected with all the *inf* values for $S(\%)_{Ni}/S(\%)_{Fe}$ and $S(\%)_{Co}/S(\%)_{Fe}$ indicated in Table 3-10 for these low acid concentrations since iron stripping is zero. The highest stripping for cobalt and nickel at these *inf* values are at A/O ratios between 2.25-3 and a H_2SO_4 concentration of 0.1 M where basically all of the nickel and cobalt are removed leaving an organic phase primarily consisting of iron (an A/O ratio of 2.25 is selected since less acid will then be used and a more concentrated nickel and cobalt solution will be generated than at an A/O ratio of 3). This compares well with literature, as shown in Table 2-3. No phase separation problems are encountered at these conditions making this a much more practical operation. Referring to Figure 3-19(d) the pH at which this stripping unit will have to be controlled at is 1.82.

According to Figure 3-8 iron is only completely extracted with Ni-Cyanex 272 at a pH of 3.5 which is higher than 1.82. Therefore the metal content in each respective phase differs as a function of pH during stripping and extraction at equilibrium which means that the metal ions are relatively stable once they are in the organic phase as reflected by the low pH values needed for stripping (the same is true for nickel and cobalt).

From Figure 3-19(c) a H_2SO_4 concentration of 1 M at an A/O ratio of 0.75 are sufficient to regenerate the organic phase from iron. This is lower than the 1.5 M H_2SO_4 required for the stripping of iron from Cyanex 302 found in literature (refer to Table 2-4) which is expected since Cyanex 302 is a stronger acid than Cyanex 272. A relatively low A/O ratio is chosen to generate a more concentrated iron solution rather than a dilute solution. The corresponding pH measurement was 1.41.

CHAPTER 4

MODELLING AND SIMULATION

4.1 INTRODUCTION

The data generated from the batch tests with respect to variation in O/A ratio and NaOH addition for the pre-loading section, O/A ratio and nickel loading for the extraction section and A/O ratio and H_2SO_4 concentration for the stripping section were used to model and develop a process simulation sheet in Microsoft Office Excel® that can be used to approximate operating design variables at equilibrium.

4.2 METHOD

For the pre-loading section the nickel loading model was derived from the equilibrium constant obtained from reaction 13.

$$K = \frac{[H^+]^2[NiA_2.2(RH)_2]}{[(RH)_2]^3[Ni^{2+}]} \qquad \text{[23]}$$

By taking the logarithm on each side and after some mathematical manipulation with respect to the fact that pH is defined as –log [H⁺] and the distribution coefficient which is defined via equation 1, equation 23 can be rewritten as shown in equation 24:

$$\log D_{Ni} = \log K + 3\log[(RH)_2] + 2pH \qquad \text{[24]}$$

where: D_{Ni} =   Distribution coefficients
       K   =   Equilibrium constant
       $[(RH)_2]$ =   Concentration of the extractant/Cyanex 272 (dimer form)

Equation 25 displays the distribution coefficient as a function of percentage extraction (E) and O/A ratio (Swain *et al.*, 2008):

$$D_{Ni} = \left(\frac{E}{O/A \ (100-E)}\right) \qquad \text{[25]}$$

Substituting equation 25 in equation 24 results in equation 26 after some rearrangement:

$$E = 100 \times \left(\frac{O/A\left(K \times 10^{[(RH)_2]^3 + 2pH} \right)}{1 + O/A\left(K \times 10^{[(RH)_2]^3 + 2pH} \right)} \right) \qquad [26]$$

Since the values typically calculated for $[(RH)_2]^3$ are two to three orders of magnitude smaller than the values calculated for the pH term, it was assumed that this term $[(RH)_2]^3$ would have a negligible effect in order to simplify the derivation of the model. Extraction can also be defined as the nickel concentration in the organic phase at equilibrium divided by the initial nickel aqueous concentration multiplied by the O/A ratio and a 100. Equation 26 then simplifies to equation 27 which is rearranged to give equation 28:

$$E = 100 \times \left(\frac{O/A\left(K \times 10^{2pH} \right)}{1 + O/A\left(K \times 10^{2pH} \right)} \right) = \left(\frac{Ni_{org}}{Nio_{aq}} \right) O/A \times 100 \qquad [27]$$

$$Ni_{org} = Nio_{aq} \times \left(\frac{\left(K \times 10^{2pH} \right)}{1 + O/A\left(K \times 10^{2pH} \right)} \right) \qquad [28]$$

where: Ni_{org} = Nickel concentration in the organic phase at equilibrium/nickel loading (g/l)

  Nio_{aq} = Initial nickel aqueous concentration (g/l)

Assuming that pH is proportional to the relative moles of NaOH added with respect to the initial moles of nickel in the aqueous phase (NaOH/Nio), equation 29 was derived to predict nickel loading.

$$Ni_{org} = Nio_{aq} \times \left(\frac{\left(K \times 10^{NaOH/Nio} \right)}{1 + O/A\left(K \times 10^{NaOH/Nio} \right)} \right) \qquad [29]$$

A similar equation to equation 29 could not be derived as a function of the operating variables for the loading pH, extraction and stripping data. The sigmoid function, which was also used by Swain *et al.* (2008) to model cobalt and lithium extraction with Cyanex 272, (see equation 30 and Figure 4-1) was used as origin to model the remaining data. Equation 29 gave a better fit for the nickel loading data than the sigmoid function (R^2 value, as calculated with equation 34 in section 4.3, of 0.97 and 0.95 respectively). The sigmoid function also poorly extrapolated the nickel loading data compared to equation 29.

$$f(x) = \frac{K}{C + \exp(Px)} \qquad [30]$$
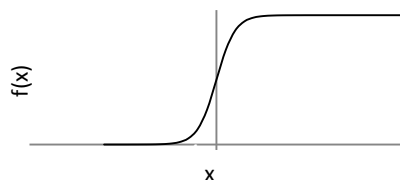
Figure 4-1: Characteristic S shape of the sigmoid function

Referring to Figure 4-1, the sigmoid function has a characteristic S shape which is typical for the pre-loading, extraction and stripping curves that were generated in the previous chapter. Consequently it gave a good fit for the loading pH, extraction pH, cobalt and iron extraction and nickel, cobalt and iron stripping data (Refer to Figures 3-16 [a, c and e] and 3-19 [a, b and c]. The loading pH data are displayed shortly).

Referring to equation 30, it is noticed that the sigmoid function is only two dimensional (in other words pre-loading, extraction and stripping are only modelled as a function of NaOH/Nio, O/A ratio and H_2SO_4 concentration respectively). After inspection it was observed that the constant, P, varies in a polynomial manner as a function of O/A ratio, nickel loading and A/O ratio for pre-loading, extraction and stripping respectively. Consequently a third dimension was added to equation 30 by expanding the constant P as shown in equation 31 (third and lower order polynomials were found adequate).

$$f(y, x) = \frac{K}{C + \exp\left((b_1 + b_2 y + b_3 y^2) \times (x + b_4 + b_5 y + b_6 y^2)\right)} \qquad [31]$$

where: $f(y,x)$ = Loading pH, extraction pH, cobalt and iron extraction (%) and nickel, cobalt and iron stripping (%)

K, C, b_{1-6} = Modelling constants

y = O/A ratio (pre-loading), nickel loading (extraction) and A/O ratio (stripping)

x = NaOH/Nio (pre-loading), O/A ratio (extraction) and H_2SO_4 concentration (stripping)

The supplementary expansion (addition of $b_4 + b_5 y + b_6 y^2$ to x) was to allow the graph in Figure 4-1 to shift to the left and right to give a better fit where necessary. Most frequently not all the polynomial terms were necessary and equation 31 was simplified by lowering the polynomial order (see Table A-22 in Appendix A which contains all the solved values for K, C and b_1-b_6 for the different models). Allocating y to be nickel loading and x to be O/A and not vice versa for the extraction section was chosen through a process of trial and error to see which combination results in the best fit and was accordingly chosen as allocated in the above glossary. The same is applicable for the loading pH and stripping models.

For the purpose of developing a process simulation sheet it is important that the models also predict the aqueous concentrations in the exit streams for the extraction and stripping sections. The aqueous product concentration of the pre-loading section can be determined via a mass-balance. Equations 32 and 33 below were used to convert $f(y,x)$/percentage extracted and stripped into aqueous concentration at equilibrium for the extraction and stripping sections respectively.

$$f(y, x) = \left(\frac{[M]_o - [M]}{[M]_o}\right) 100 \qquad \text{(Extraction)}$$

$$\rightarrow [M] = [M]_o \left(1 - \frac{f(y,x)}{100}\right) = [M]_o \left(1 - \frac{\frac{K}{C + \exp\left((b_1 + b_2 y + b_3 y^2) \times (x + b_4 + b_5 y + b_6 y^2)\right)}}{100}\right) \qquad [32]$$

$$f(y, x) = \left(\frac{[M]}{[M]_{org}}\right)\frac{A}{O}100 \qquad \text{(Stripping)}$$

$$\rightarrow [M] = \left.\frac{[M]_{org}\frac{O}{A}f(y,x)}{}\right/100 = [M]_{org}\left(\left.\frac{\frac{O}{A}K}{C+\exp((b_1+b_2y+b_3y^2)\times(x+b_4+b_5y+b_6y^2))}\right/100\right) \qquad [33]$$

where: [M]   =   Metal concentration in the aqueous phase at equilibrium (g/l)

[M]$_o$ =   Initial metal concentration in the aqueous phase (g/l)

[M]$_{org}$ =   Metal loading on the organic phase (g/l)

4.3 RESULTS

The modelling results with respect to nickel loading (equation 29), metal concentration in the aqueous phase for the extraction and stripping sections (equation 32 and 33) and the loading and extraction pH (equation 31) will be considered. Three-dimensional (3D) graphs of each model can be found in Appendix A as well as two-dimensional (2D) graphs which are the same as those that will be consider next but only on separate axes since the curves are frequently close to each other and plotting them on separate axes results in a better visual indication of each fit.

The quality of each model fit was quantified by calculating the R^2 value (see equation 34) for the overall 3D surface as well as for various 2D curves at specific O/A ratios, nickel loadings and A/O ratios for the pre-loading, extraction and stripping sections respectively. A R^2 value of 1 signifies a perfect model fit, in other words the closer the R^2 value is to 1, the better the fit (generally a R^2 value higher than 0.95 is regarded as a good fit). The formula used to calculate R^2 is shown in equation 34.

$$R^2 = 1 - \frac{SS_{err}}{SS_{tot}} = \frac{\sum(y_i - f_i)^2}{\sum(y_i - \bar{y})^2} \qquad [34]$$

where: SS$_{err}$ =   Sum of squares of residuals

SS$_{tot}$ =   Total sum of squares

y_i =   Experimental value

$\bar{y}$ =   Average of the experimental values

f_i =   Modelled value

The predicted/modelled values were also plotted against the experimental values which give a visual indication of how good each fit is. For a perfect fit all of the points should be on a straight line with a y-intercept of 0 and a slope of 1.

4.3.1 PRE-LOADING

Figure 4-2 shows the pH and nickel loading modelling results for the pre-loading section. The R^2 values for each model are found in Table 4-1.
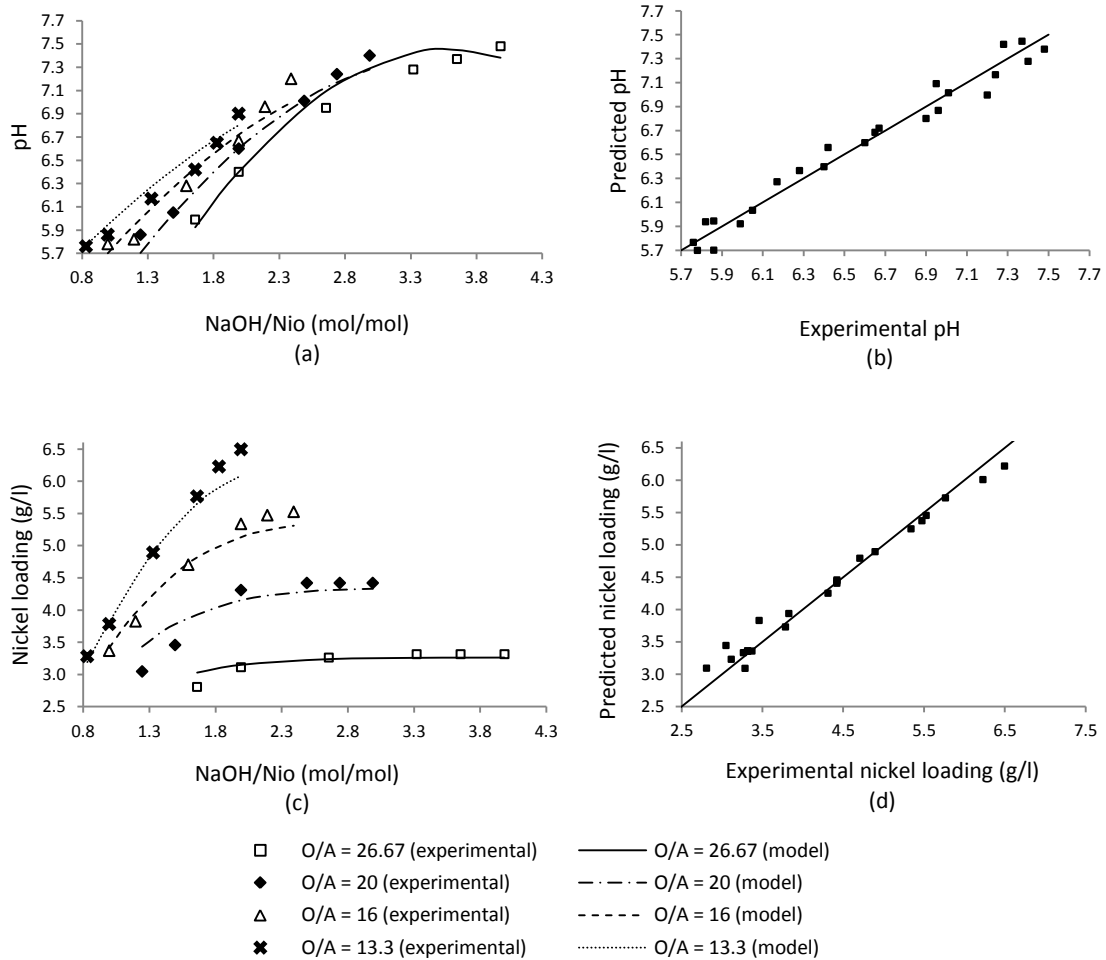
Figure 4-2: Model results for nickel loading and equilibrium pH for the pre-loading section

Table 4-1: R^2 values of the models developed for equilibrium pH and nickel loading for the pre-loading section

O/A (ml/ml)	26.67	20.00	16.00	13.33	Overall for 3D model
pH	0.97	0.98	0.95	0.95	**0.97**
Nickel loading	0.70	0.83	0.96	0.97	**0.97**

Referring to Figure 4-2 (a) it is noticed that the loading pH is predominantly influenced by NaOH/Nio and not by the O/A ratio, resulting in the lines being so close to each other. The model accurately predicts the loading pH behaviour with R^2 values higher than 0.95 at all the O/A ratios as well as for the overall 3D model. This is also reflected in Figure 4-2 (b) with all the points being closely positioned on the straight line. Nickel loading is accurately predicted by the model for O/A ratios of 16 and 13.33 with R^2

values of 0.96 and 0.97, respectively. The low R^2 value of 0.7 at an O/A ratio of 26.67 is caused by the fact that the nickel loading do not vary significantly at this high O/A ratio and the slightest under or over prediction will have a significant influence on the R^2 value which is the case at NaOH/Nio values less than 1.8 mol/mol. The model also over predicts the nickel loading at an O/A ratio of 20 for NaOH/Nio additions less than 1.8 mol/mol by approximately 0.4 g/l and as a result has a R^2 value of 0.83. From Figure 4-2 (d) it is clear that a more accurate model prediction is attained for nickel loadings higher than 3.5 g/l with all the points being closer to the straight line than the points at loadings lower than 3.5 g/l. Even so, the overall R^2 value of 0.97 signifies a generally good fit, implying that the nickel loading model can be used to accurately predict loadings.

4.3.2 EXTRACTION

The model results for extraction pH and cobalt and iron concentrations in the aqueous phase at equilibrium are considered next. Refer to Figure A-5 in Appendix A where graphs might be unclear.

The R^2 values for each fit are displayed in Table 4-2.

(a)

(b)

(c)

(d)

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(e)

■	Ni loading = 0.56g/l (experimental)	——————	Ni loading = 0.56g/l (modell)
◇	Ni loading = 1.97g/l (experimental)	··············	Ni loading = 1.97g/l (model)
▲	Ni loading = 2.94g/l (experimental)	- - - - -	Ni loading =2.94g/l (modell)
□	Ni loading = 3.95g/l (experimental)	— — — -	Ni loading = 3.95g/l (model)
+	Ni loading = 4.69g/l (experimental)	—·—·—	Ni loading = 4.69g/l (model)
○	Ni loading = 5.73g/l (experimental)	——————	Ni loading = 5.73g/l (model)
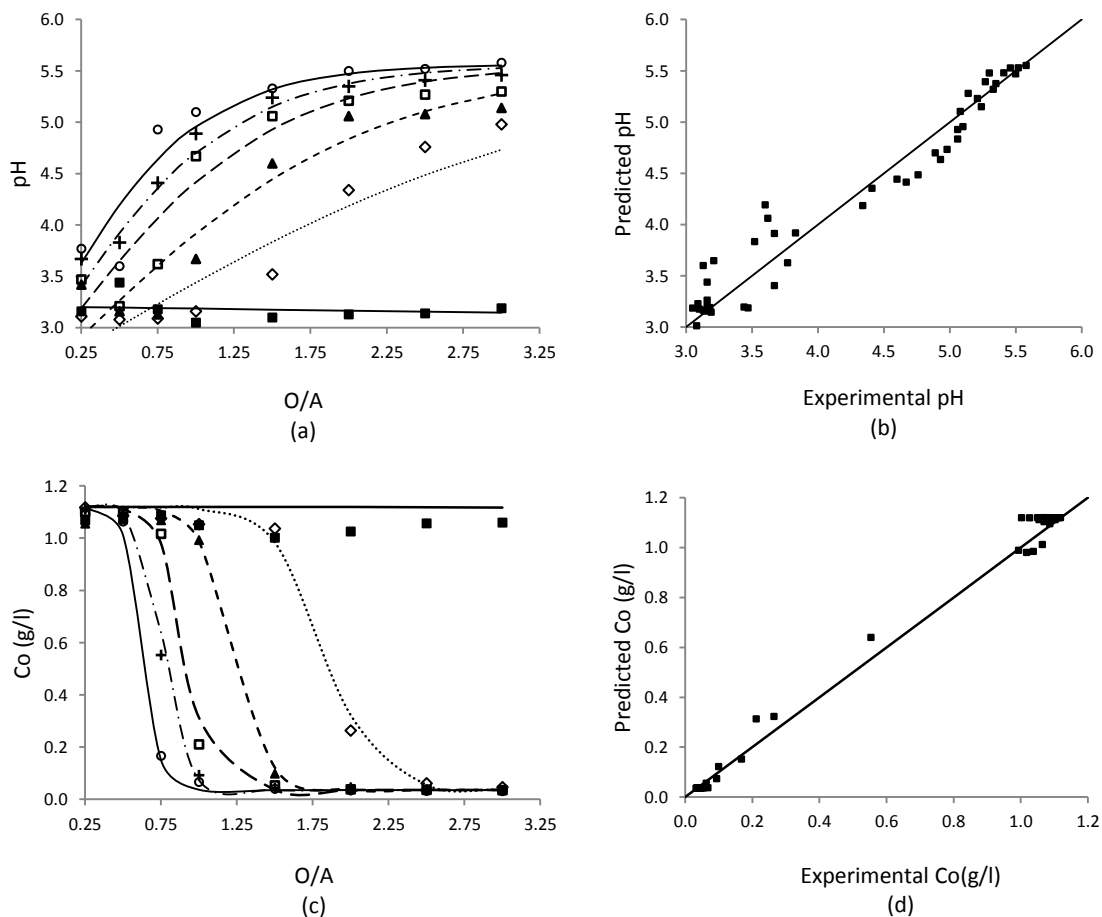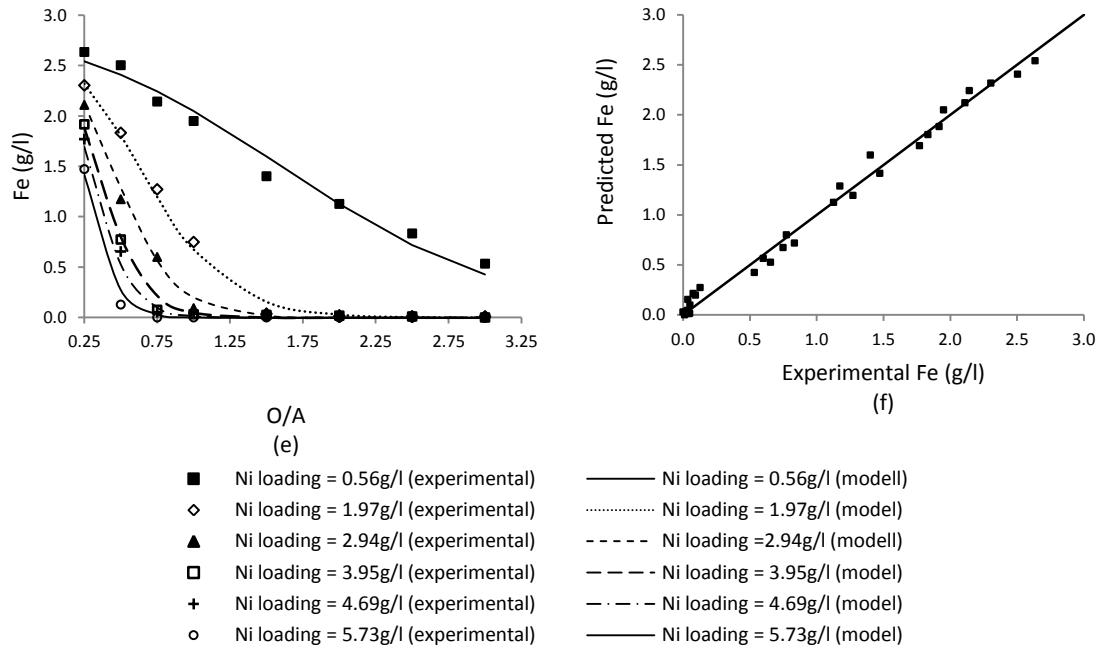
Figure 4-3: Model results for equilibrium pH and cobalt and iron concentration in the pregnant nickel solution at equilibrium for the extraction section

Table 4-2: R^2 values of the models developed for equilibrium pH and cobalt and iron concentration in the aqueous phase at equilibrium

Nickel loading (g/l)	0.56	1.97	2.94	3.95	4.69	5.73	**Overall for 3D model**
pH	0.06	0.90	0.89	0.89	0.96	0.89	**0.94**
Co	-6.23	0.99	1.00	0.99	0.99	1.00	**0.99**
Fe	0.98	1.00	0.99	0.99	0.99	0.99	**0.99**

From Figure 4-3 (b) it is clear that the model gives a better fit for pH values higher than 4 with the points being closer to the straight line than for pH predictions lower than 4. Referring to Figure A-5 it is visually observed that the pH-model gives a better fit as the nickel loading increases as a function of O/A ratio. The R^2 value of 0.06 at a loading of 0.56 g/l is once again caused by the fact that the pH data at this loading remains steady and a slight deviation in the model prediction will have severe influence on the R^2 value. The same applies to the R^2 value of -6.23 for cobalt at a nickel loading of 0.56 g/l.

The models perform exceptionally well when predicting the aqueous concentration of cobalt and iron at equilibrium with R^2 values higher and equal to 0.98 for all scenarios apart from the single exception regarding cobalt just mentioned. This exception is also responsible for all the points that deviate from the straight line for cobalt concentrations higher than 1 g/l in Figure 4-3 (d). Referring to Figure 4-3 (c and e) it is noted that the aqueous cobalt concentration at equilibrium is more sensitive for variations in O/A ratio and nickel loading than the aqueous iron concentration at equilibrium, in other words there is a sudden drop in cobalt concentration whereas the iron concentration has a more gradual decrease as the O/A ratio and nickel loading increases. This sudden drop is accurately predicted by the model as indicated in Figure A-5 and can therefore be used to accurately predict the cobalt and iron behaviour in the extraction section.

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4.3.3 STRIPPING

The modelling results for the nickel, cobalt and iron concentration in the aqueous phase at equilibrium are shown in Figure 4-4 (refer to Figure A-6 where graphs may appear unclear). The R^2 values of each model are found in Table 4-3.
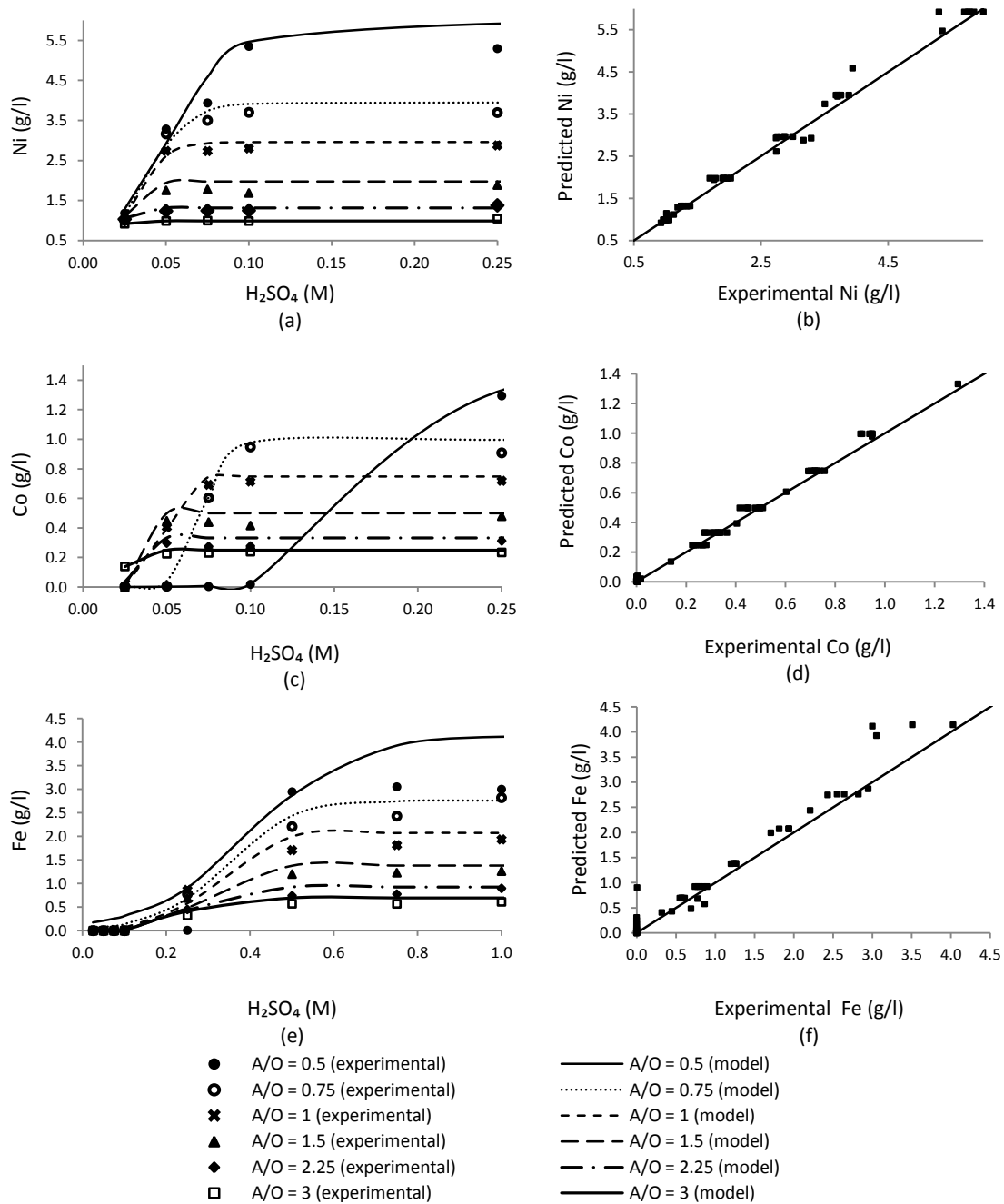
Figure 4-4: Model results for nickel, cobalt and iron concentration in the aqueous phase at equilibrium for the stripping section

Table 4-3: R^2 values of the models developed for nickel, cobalt and iron concentration in the aqueous phase at equilibrium for the stripping section

A/O (ml/ml)	0.50	0.75	1.00	1.50	2.25	3.00	**Overall for 3D model**
Ni	0.95	0.93	0.95	0.72	0.68	0.24	**0.99**
Co	0.98	0.98	0.98	0.93	0.89	0.78	**0.98**
Fe	0.88	0.98	0.96	0.96	0.95	0.90	**0.94**

The nickel model accurately fits the experimental data with an overall R^2 value of 0.99. The relatively low R^2 values of 0.72, 0.68 and 0.24 at A/O ratios of 1.5, 2.25 and 3, respectively, are once again caused by the relatively constant experimental data as discussed previously. Referring to Figure 4-4 (a) it is clear that the model accurately predicts these trends as well.

Referring to Figure 4-4 (d) the cobalt model is also performing superbly with the majority of points being close to the straight line. This is also reflected in the high R^2 value of 0.98 for the model.

The iron model is performing the worst of the three models when comparing Figure 4-4 (f) to Figures 4-4 (b and d). This is also reflected in the R^2 value of 0.94 compared to 0.98 and 0.99 for cobalt and nickel, respectively. It is noted that the iron model over predicts the iron concentration at acid concentrations less than 0.2 M and larger than 0.5 M for an A/O ratio of 0.5. This is reflected in Figure 4-4 (f) for experimental iron concentrations equal to 0 g/l and larger than 3 g/l. Besides this, the model also accurately predicts iron concentrations at the remaining A/O ratios, with R^2 values higher and equal to 0.9.

4.4 SIMULATION

4.4.1 SIMULATION SHEET

Figure 4-5 shows the simulation sheet that was developed in *Microsoft Excel* from the derived models. The dark and light grey boxes represent the organic and aqueous phases respectively. The *italic* values are the input values and the remaining values are the output values. The input values include the metal concentrations and flow rates of the pregnant solution, the O/A ratio for the pre-loading and extraction sections, A/O ratio for the stripping sections, the relative moles of NaOH being added with respect to nickel in the aqueous feed (NaOH/Nio), the NaOH concentration used for the pre-loading section and the H_2SO_4 concentration of the two streams being fed to the stripping sections. The output values include the flow rate of all the remaining feed and product streams, percentage extracted and stripped at the relevant stages, the pH at the pre-loading and extraction stages and the metal concentration in the remaining streams.

The stream concentrations in the flow sheet that are not determined by the models are resolved via mass balance calculations. These include the nickel concentration of the pre-loading aqueous product solution as well as the metal loading of the organic phase after extraction and stripping. No models were developed for the nickel behaviour in the pregnant solution at the extraction stage or for the sodium behaviour in pre-loading and extraction aqueous product solutions. For the sake of simplicity the

amount of nickel extracted from the pregnant solution can be selected as indicated by the italic value in the extraction box/unit. It is also assumed in the sheet that no sodium ends up in the pregnant solution and that all the sodium entering the pre-loading stage is exiting at the aqueous product of this stage. When not all the metal is stripped at the final stage it will be indicated in the organic feed to the pre-loading stage.
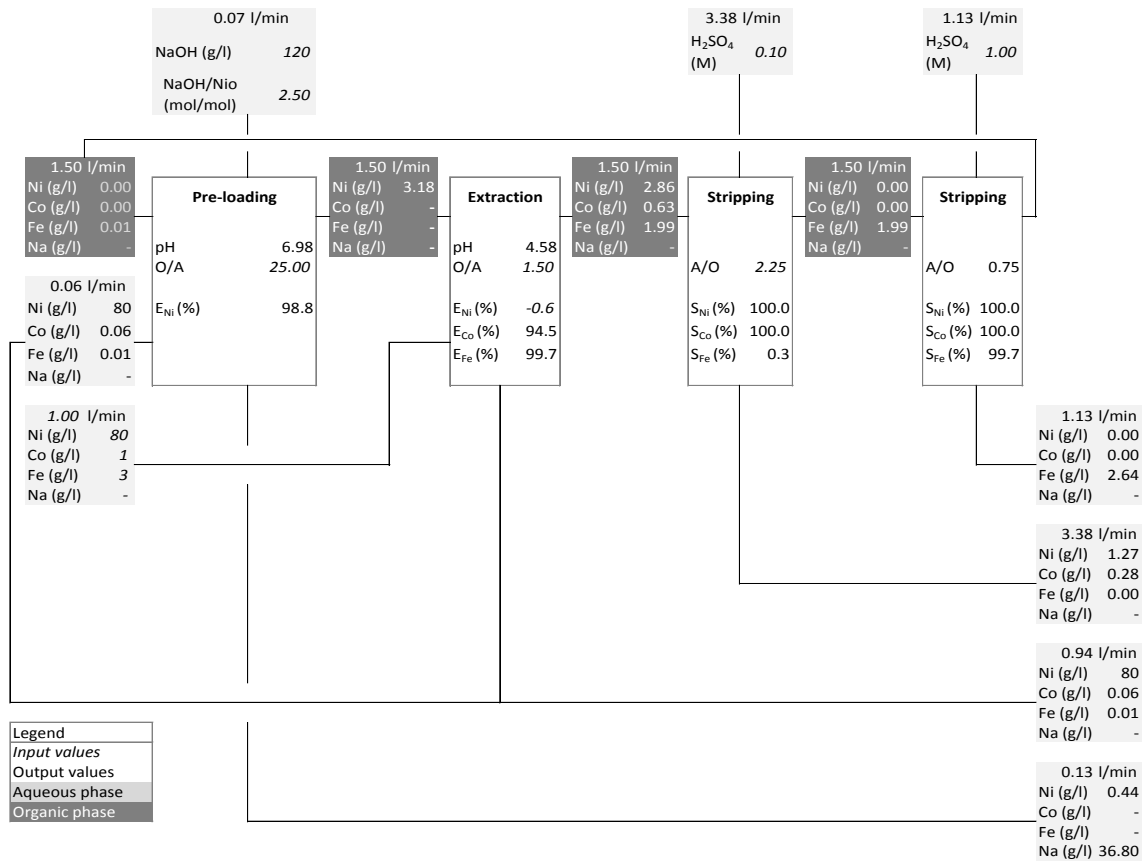
Figure 4-5: Process simulation sheet in *Microsoft Excel*

The process conditions in Figure 4-5 are set as they were selected from the batch tests (nickel extraction was chosen as -0.6%). This simulation accurately resembles what was observed from the batch tests with respect to cobalt (94.9%) and iron (99.7%) extraction, selective stripping of cobalt (100%) and nickel (100%) from iron (0.3%) at the first stripping stage and iron stripping at the final stage (99.7%).

4.4.2 MODEL LIMITATIONS

The limitations associated with the models developed for the simulation sheet in Figure 4-5 are considered next. In order to do this, model predictions were made outside the original range of the experimental conditions used to generate the equilibrium data.

Table 4-4, 4-5 and 4-6 reveal the extrapolated model results for the pre-loading, extraction and stripping sections, respectively. Predictions made at the maximum, minimum and selected intermediate conditions are also included in these Tables and are indicated within the shaded areas. The experimental results at the maximum and minimum conditions are also included within brackets.

Table 4-4: Extrapolated model results for the pre-loading section

		O/A ratio					
		7	13.33	16	20	26.67	35
		Nickel loading (g/l)/Nickel extraction (%)					
	0.5	2.41/19.1	2.05/31.0	1.93/35	1.78/40.2	1.57/47.3	1.37/54.1
	0.83	4.23/33.5	3.25/48.9 (3.28/49.52)	2.96/53.5	2.61/59	2.18/65.7	1.81/71.6
	1	5.39/42.7	3.89/58.6	3.48/63 (3.37/60.97)	3.01/68	2.45/73.9	1.99/78.8
	1.24	7.12/56.4	4.72/71.1	4.13/74.7	3.48/78.7 (3.05/68.93)	2.76/83.1	2.19/86.6
NaOH/Nio	1.66	9.61/77.3	5.65/86.6	4.82/88.6	3.94/90.7	3.03/92.8 (2.81/84.65)	2.35/94.4
(mol/mol)	1.99	10.93/87.9	6.09/93.3 (6.5/97.96)	5.13/94.3	4.15/95.4	3.15/96.5	2.42/97.3
	2.39	11.97/94.8	6.45/97.2	5.4/97.7 (5.53/100)	4.34/98.1	3.27/98.6	2.5/98.9
	2.99	12.46/98.6	6.58/99.3	5.49/99.4	4.4/99.5 (4.42/100)	3.3/99.6	2.52/99.7
	3.98	12.61/99.99	6.63/99.99	5.52/99.9	4.42/100	3.31/100 (3.32/100)	2.53/100
	5	12.63/100	6.63/100	5.52/100	4.42/100	3.31/100	2.53/100
		Loading pH					
	0.5	6.24	5.39	5.04	4.55	3.78	2.95
	0.83	6.44	5.77 (5.76)	5.49	5.08	4.44	3.7
	1	6.54	5.95	5.71 (5.78)	5.35	4.77	4.09
	1.24	6.67	6.19	5.99	5.7 (5.86)	5.21	4.64
NaOH/Nio	1.66	6.87	6.56	6.43	6.24	5.92 (5.99)	5.53
(mol/mol)	1.99	6.99	6.8 (6.9)	6.72	6.6	6.4	6.15
	2.39	7.12	7.03	7 (7.2)	6.95	6.86	6.75
	2.99	7.23	7.26	7.27	7.28 (7.4)	7.3	7.33
	3.98	7.25	7.29	7.31	7.34	7.38 (7.48)	7.44
	5	7.05	6.91	6.85	6.76	6.61	6.42

Referring to Table 4-4, the model realistically extrapolates the nickel loading in that it increases and decreases to sensible maximum and minimum loadings as NaOH/Nio increases and decreases and the O/A ratio decreases and increases, respectively (percentage extraction does not exceed 100% at the highest O/A ratios and NaOH/Nio values). The nickel loading predictions at the maximum and minimum experimental conditions seldom differ more than 0.4 g/l from the experimental results. Consequently the nickel loading model can be used to predict loadings beyond the borders of the original experimental conditions.

Referring to the loading pH in Table 4-4, the model unrealistically predicts the pH at NaOH/Nio values higher than 3.98 since the pH decreases as NaOH/Nio increases. Apart from this, the model provides sensible predictions beyond the original experimental borders in that pH decreases as the O/A ratio increases and NaOH/Nio decreases. The differences between the model predictions and experimental pH do not differ more than 0.2 at the highest and lowest values in the shaded areas. Therefore the pH

model can be used to forecast a loading pH outside the shaded area except at NaOH/Nio values higher than 3.98.

Table 4-5: Extrapolated model results for the extraction section

		O/A ratio			
		0.15	0.25	3	4
		Co$_{aq}$ (g/l)/Cobalt extraction (%)			
Ni-loading (g/l)	0.3	1/0.4	1/0.7	1/8.6	1/11.5
	0.56	1/0.4	1/0.7 (1.07/4.38)	1/8.8 (1.06/5.19)	0.98/12.8
	5.73	1/0.5	1/0.9 (1.09/2.24)	0.03/97.1 (0.03/97.1)	0.03/97.2
	6.3	1/0.5	1/0.9	0.03/97.1	0.03/97.2
		Fe$_{aq}$ (g/l)/Iron extraction (%)			
Ni-loading (g/l)	0.3	2.62/12.9	2.59/14.2	1.03/68.7	0.52/84.7
	0.56	2.61/13.5	2.56/15.3 (2.64/11.58)	0.43/86.8 (0.53/82.08)	0.13/96.1
	5.73	2.05/31.9	1.43/52.8 (1.47/50.57)	0/100 (0/100)	0/100
	6.3	1.97/34.6	1.27/57.9	0/100	0/100
		Extraction pH			
Ni-loading (g/l)	0.3	<u>3.4</u>	<u>3.38</u>	<u>2.84</u>	<u>2.64</u>
	0.56	<u>3.21</u>	<u>3.2</u> (3.16)	<u>3.14</u> (3.19)	<u>3.12</u>
	5.73	3.37	3.63 (3.77)	5.55 (5.58)	5.56
	6.3	3.41	3.68	5.56	5.57

From Table 4-5, the model realistically extrapolates cobalt and iron extractions so that both increase and decrease as the nickel loading and O/A ratio increase and decrease, respectively, (iron and cobalt extractions do not exceed 97.1% and 100%, respectively, at the maximum nickel loading and O/A ratio). The cobalt and iron concentrations in the shaded areas rarely differ more that 0.1 g/l. It is therefore concluded that the model can be used to realistically predict cobalt and iron extractions beyond the borders of the shaded areas.

At nickel loadings equal to and less than 0.56 g/l the model does not resemble the expected pH behaviour for the extraction section which normally increases and decreases as the O/A ratio and nickel loading increase and decrease, respectively. Instead an irregular trend is observed where the pH increases from 3.38 to 3.4 and decreases from 2.84 to 2.64 as the O/A ratio decreases from 0.25 to 0.15 and increases from 3 to 4, respectively, at a nickel loading of 0.3 g/l. On the other hand, the pH decreases from 3.21 to 3.12 as the O/A ratio increases from 0.15 to 4 at a nickel loading of 0.56 g/l. This fluctuation, however, remains within realistic boundaries of 2.64 and 3.4 which are typical pH values that can be expected at nickel loadings less than 0.56 g/l. Apart from this, the model rationally extrapolates the extraction pH so that it increases as nickel loading and O/A ratio increase. The experimental and predicted pH also do not differ more than 0.1 in the shaded area. The model can therefore be used to extrapolate realistic pH values for nickel loadings higher than 0.56 g/l.

Table 4-6: Extrapolated model results for the stripping section

		A/O ratio			
		0.25	0.5	3	4
		Ni_{aq} (g/l)/Nickel stripped (%)			
	0.01	1.36/11.4	0.68/11.5	0.12/12.3	0.09/12.6
	0.025	1.88/15.9	1.28/21.7 (1.19/20.02)	0.92/92.8 (0.92/93.5)	0.73/98.4
H_2SO_4 (M)	1	11.84/100	5.92/100 (5.76/99.65)	0.99/100 (0.96/99.96)	0.74/100
	4	11.84/100	5.92/100 (5.8/100)	0.99/100 (1/100)	0.74/100
	5	11.84/100	5.92/100	0.99/100	0.74/100
		Co_{aq} (g/l)/Cobalt stripped (%)			
	0.01	0/0.1	0/0	0/0	0/0
	0.025	0/0	0/0.1 (0.01/0.47)	0.14/55.1 (0.14/55.75)	0.18/96.4
H_2SO_4 (M)	1	0/0	1.5/100 (1.3/91.05)	0.25/100 (0.27/100))	0.19/100
	4	0/0	1.5/100 (1.45/100)	0.25/100 (0.24/99.98)	0.19/100
	5	0/0	0/0	0.25/100	0.19/100
		Fe_{aq} (g/l)/Iron stripped (%)			
	0.01	0.66/7.9	0.15/3.6	0/0	0/0
	0.025	0.7/8.4	0.17/4.1 (0/0)	0/0 (0/0)	0/0
H_2SO_4 (M)	1	7.01/84..2	4.12/99.1 (3.9/98.2)	0.69/99.8 (0.69/99.7)	0.52/99.8
	4	8.3/99.8	4.15/100 (4.1/100)	0.69/100 (0.6/100)	0.52/99.8
	5	8.3/99.8	4.15/99.8	0.69/99.8	0.52/99.8

Referring to Table 4-6, the model realistically extrapolates the nickel concentration in the aqueous phase during stripping since the nickel concentration increases and decreases as the H_2SO_4 concentration increases and decreases and as the A/O ratio decreases and increases respectively. The modelled and experimental nickel concentrations do not differ more than 0.2 g/l at the maximum, minimum and intermediate experimental H_2SO_4 concentrations and A/O ratios. Consequently the model can be used to predict realistic values for the quantity of nickel stripped beyond the borders of the shaded area.

At an A/O ratio of 0.5 and H_2SO_4 concentration of 5 M, the model unrealistically predicts that no cobalt is stripped. Apart from this, the expected trend that percentage cobalt stripped increases and decreases as the acid concentration and A/O ratio increases and decreases is observed outside the shaded area. Referring to an A/O ratio of 0.5 at the intermediate H_2SO_4 concentration of 1 M, the model predicts that most of the cobalt is stripped and realistically also predicts this at 4 M; hence the sharp decline only occurs for acid concentrations higher than 4 M. The maximum difference between the experimental and predicted aqueous cobalt concentrations is 0.2 g/l. It is therefore concluded that up to H_2SO_4 concentrations of 4 M, the model can be used to realistically extrapolate cobalt stripping.

Referring to iron stripping in Table 4-6, the model over- and under- predicts the iron concentration in the aqueous phase at H_2SO_4 concentrations of 0.025 M and 4 M, respectively, relative to the experimental data with a maximum of 0.17 g/l. The expected trend where the percentage iron stripped increases and decreases as the acid concentration and A/O increase and decrease, respectively, is however predicted by the model outside the shaded area. The model can therefore be use to

extrapolate iron stripping. It is however important to notice that this will be a slight over- and under-prediction of not more than 0.17 g/l at the higher and lower acid concentrations, respectively.

4.4.3 QUANTIFYING THE NUMBER OF STAGES

The simulation sheet in Figure 4-5 can also be used to determine the number of stages to reach desired nickel-loadings, percentage cobalt and iron extraction and percentage nickel, cobalt and iron stripped at the pre-loading, extraction and stripping sections, respectively. Since the models allow for variation in the inlet aqueous and organic concentrations (see equations 29, 32 and 33), the concentration of the aqueous or organic product streams become the new feed concentration of the next stage and is typed into the simulation sheet accordingly (this is done after determining it from a simulation for the previous stage).

Two different scenarios were considered. During the first simulation, generating a nickel loading of 3.2 g/l at an O/A ratio of 25 and different pH values from an 80 g/l nickel aqueous solution were considered with a counter-current configuration as explained in Figure 2-8. Table 4-7 shows the predicted nickel concentration in the aqueous product at each stage. As mentioned in section 3.3.1.5, even though controlling the nickel loading at various stages is possible from a theoretical point of view, this is not always a practical operation and was consequently not considered with respect to the number of stages at different operating conditions. Another approach of how the simulation sheet can be helpful is to consider A/O ratios and H_2SO_4 concentrations where complete cobalt and nickel stripping is not attained. This reduces iron stripping as well and the result is a purer cobalt and nickel aqueous product by using multiple stages. As mentioned in section 3.3.2.3, low acid concentrations and A/O ratios where complete cobalt and nickel stripping was not reached, resulted in phase separation problems which limits this approach. The final scenario therefore considered was to use different acid concentrations at the selected A/O ratio of 0.75 to strip a 2 g/l iron-loaded organic solution (see Table 4-8).

Table 4-7: Nickel concentration (g/l) in the aqueous product at different stages to generate a nickel loading of 3.2 g/l from an 80 g/l nickel feed solution at an O/A ratio of 25 as predicted by the simulation sheet

pH	1st stage	2nd stage	3rd stage	4th stage	5th stage
5.5	7.295	1.014	0.148	0.022	0.003
6	3.467	0.255	0.019	0.001	0.000
6.5	1.411	0.047	0.002	0.000	0.000
7	0.409	0.004	0.000	0.000	0.000

Table 4-8: Iron concentration (g/l) in the organic phase at different stages as predicted by the simulation sheet to strip a 2 g/l iron loaded organic phase at an A/O ratio of 0.75

H_2SO_4 (M)	1st stage	2nd stage	3rd stage	4th stage	5th stage
0.3	1.243	0.772	0.480	0.298	0.185
0.4	0.639	0.204	0.065	0.021	0.007
0.5	0.239	0.029	0.003	0.000	0.000
0.75	0.016	0.000	0.000	0.000	0.000
1	0.005	0.000	0.000	0.000	0.000

Referring to Table 4-7, it is clear that the nickel concentration in the aqueous product decreases at each stage as the pH increases. 0.022 g/l of nickel for example is left in the aqueous product solution at the

4th stage for a pH of 5.5 compared to 0.001 g/l at the same stage but when controlling the pH at 6. From Table 4-8, the same goes for the iron concentration in the organic product which decreases at each stage as the H_2SO_4 concentration increases.

During stripping a fresh H_2SO_4 solution is fed to each stage compared to the pH being controlled during pre-loading. Consequently there will be various aqueous products compared to the single aqueous raffinate stream for pre-loading. The single stage at a pH of 7 and 1 M H_2SO_4 solution for the nickel pre-loading and iron stripping sections are, however, still selected as operating conditions (the iron concentration in the 2nd stage will be lower since the model under-predicts iron concentration as discussed in section 4.4.2). This is justified by the fact that the quantity of NaOH required to extract nickel in several stages will be similar to the quantity of NaOH in a single stage. This reasoning is also applicable to the quantity of H_2SO_4 that will be required to strip iron and that adding additional stages will not add any value with respect to the purity of the product as it would have done for cobalt and nickel stripping as discussed previously.

4.4.4 SENSITIVITY ANALYSIS

The sensitivity with respect to the extent to which cobalt and iron are extracted and nickel, cobalt and iron are stripped for variations in the feed concentrations at the selected operating conditions is considered next. Prior to varying the inlet concentrations in the simulation sheet, different McCabe-Thiele diagrams will be discussed to obtain a better understanding of the simulated results to follow.

Figure 4-6 reveals the McCabe-Thiele diagrams for iron extraction (feed concentrations of 2 g/l, 4 g/l and 5.5 g/l) at O/A feed ratios of 1.5 (a) and 2 (b) with nickel loadings of 2.94 g/l and 3.95 g/l.
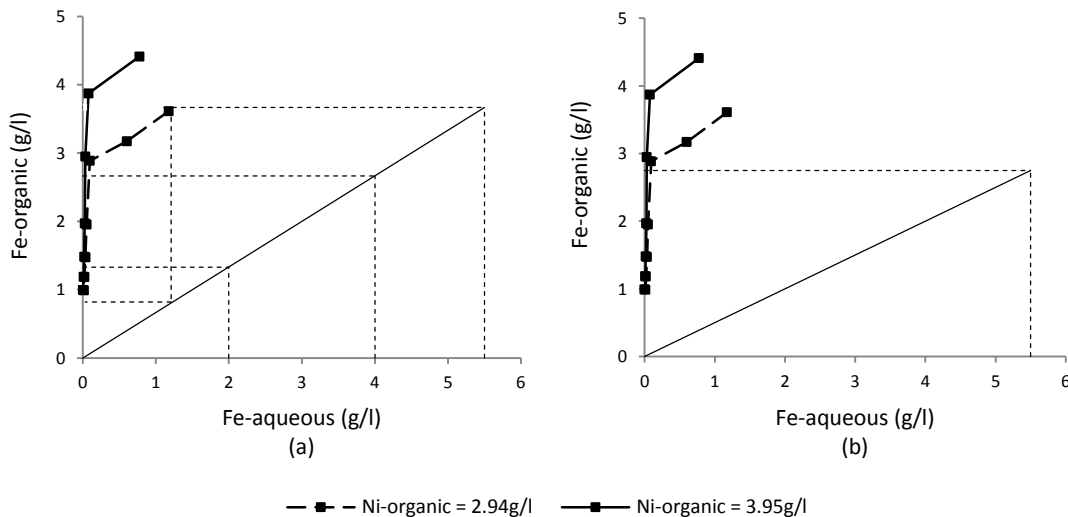
Figure 4-6: McCabe-Thiele diagrams for nickel loadings of 2.94 g/l and 3.95 g/l with an O/A feed ratio of 1.5 (a) and 2 (b) to extract 4 g/l and 5.5 g/l of iron

Referring to Figure 4-6 (a), decreasing and increasing the iron concentration in the feed stream from the original 3 g/l to 2 g/l and 4 g/l, respectively, does not significantly influence iron extraction (concentration in the product stream in both cases is close to 0 g/l) at a nickel loading of 2.94 g/l. Consequently it will also not significantly influence iron extraction at the selected nickel loading of 3.2 g/l. Increasing the feed concentration to 5.5 g/l, however, requires an additional extraction stage at a nickel loading of 2.94 g/l and O/A ratio of 1.5. This additional stage can be prevented by either increasing the nickel loading to 3.95 g/l as shown in Figure 4-6 (a), or by increasing the O/A ratio to 2 as shown in Figure 4-6 (b). The McCabe-Thiele diagram for cobalt extraction also has a very steep slope at these nickel loadings (refer to Figure 3-16 (b). Consequently cobalt and iron extraction will not be sensitive for increases in the aqueous feed concentrations. Upper limits, however, do exist like the 5.5 g/l for iron extraction at an O/A ratio of 1.5 and nickel loading of 2.94 g/l (this will be higher for the selected nickel loading of 3.2 g/l though). The upper limit determined for cobalt in the same manner as shown in Figure 4-6 for iron at a nickel loading and O/A ratio of 2.94 g/l and 1.5 is approximately 1.5 g/l. This will also be higher at the selected nickel loading of 3.2 g/l.

The McCabe-Thiele diagrams for the nickel, cobalt and iron stripping also have very steep slopes. Figure 4-7, for example, shows the McCabe-Thiele diagram for nickel at the selected A/O ratio and acid concentration of 2.25 and 0.1 M for the first stripping section.
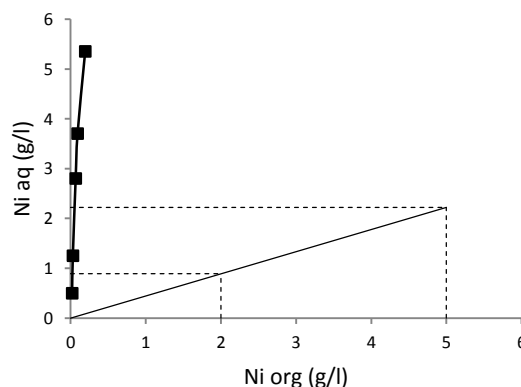
Figure 4-7: McCabe-Thiele diagram for stripping 2 g/l and 5 g/l of nickel with 0.1 M H$_2$SO$_4$ at an A/O feed ratio of 2.25

Referring to Figure 4-7, decreasing and increasing the nickel concentration to 2 g/l and 5 g/l, respectively, compared to the originally selected 2.69 g/l (see section 3.3.2.3), does not significantly influence the nickel concentration in the product stream (close to 0 g/l in both cases). Likewise it can be proven that increasing the cobalt and iron organic loading to 5 g/l at the selected acid concentrations and A/O ratios will not significantly influence the loading of the organic product. Increasing all three nickel, cobalt and iron organic loadings beyond 5 g/l will result in third phase formation caused by the ligand being overloaded. Realistic upper limits therefore do not exist as for cobalt and iron extraction.

The sensitivity analysis in Table 4-9, that was conducted with the simulation sheet, reveals the sensitivity with respect to extraction and stripping for variations in the feed concentration.

Table 4-9: Sensitivity analysis with respect to variations in the feed concentration to the extraction and stripping sections as predicted by the simulation sheet

Cobalt and iron extraction at an O/A ratio of 1.5 and nickel loading of 3.2 g/l				
Run	Cobalt in aqueous feed (g/l)	Cobalt in aqueous product (g/l)	Iron in aqueous feed (g/l)	Iron in aqueous product (g/l)
1	1	0.057	3	0.008
2	1.5	0.085	4	0.01
3	2	0.113	5	0.013

Nickel and cobalt stripping at an A/O ratio of 2.25 with 0.1 M H_2SO_4						
	Nickel in organic feed (g/l)	Nickel in organic product (g/l)	Cobalt in organic feed (g/l)	Cobalt in organic product (g/l)	Iron in organic feed (g/l)	Iron in organic product (g/l)
4	2.96	0.0006	0.67	0.0003	2	1.9939
5	4	0.0009	1	0.0005	4	3.9877
6	5	0.0011	3	0.0014	5	4.9847

Iron stripping at an A/O ratio of 0.75 with 1 M H_2SO_4		
	Iron in organic feed (g/l)	Iron in organic product (g/l)
7	2	0.005
8	4	0.011
9	5	0.013

Referring to Table 4-9, it is observed that increasing the feed concentration does, in fact, increase the metal content in the product streams. This is expected by looking at Figures 4-6 and 4-7 which reveal that even though the extraction isotherms generally have very steep slopes, they are in fact not vertical and that an increase in the feed concentration will increase the product concentration. If the absolute concentrations in the respective aqueous and organic product streams are of primary importance, then apart from cobalt yielding an aqueous product of 0.113 g/l at a feed concentration of 2 g/l compared to 0.057 g/l and 0.085 g/l at feed concentrations of 1 g/l and 1.5 g/l, respectively; the simulation sheet predicts that the selected operating variables for the extraction circuit are robust towards variations in the feed concentration for the extraction and stripping sections.

CHAPTER 5

CONTINUOUS TESTS

5.1 INTRODUCTION

A wide range of multistage extractor/contactor designs exist in solvent extraction. Essentially all of them can be categorized into *differential* or *stage-wise* contactors (Habashi, 1999). With differential contactors the organic and aqueous phases are continuously in contact with each other and complete phase separation is only reached at the end of the unit. Typical examples include spray, packed, perforated plate, pulse and rotating disk columns (Perry and Green, 2007; Richardson *et al.*, 2002; Habashi, 1999). The height of these columns depends on the number of stages required. Stage-wise contactors consist of a series of physical stages in which the phases are mixed and separated at each stage. The most common example is the mixer-settler system which consists of a series of mixing and settling chambers. The organic and aqueous phases are mixed with a rotating impeller in the mixing chamber and then flow to the settling chamber where phase separation occurs.

From the batch tests in chapter 3 it was observed that the extraction and stripping kinetics are fast with equilibrium being reached within 5 and 10 minutes, respectively. It was also noticed that a single stage is sufficient to attain the desired metal extraction and stripping at the chosen operating conditions. Consequently a mixer-settler system was selected instead of a column design for the continuous tests since column designs are frequently used when several stages are required to extract or strip a single metal and the mixer-settler system will not be too large based on the fast kinetics which can be problematic when floor space is limited.

Four continuous tests were conducted to examine the proposed process conditions from the simulation sheet. In the first two tests pre-loading and extraction were considered and in the final two tests stripping was considered. The sole purpose of the continuous tests was to evaluate the batch and simulated results. Pilot and plant scale tests will differ from the tests conducted in this section.

5.2 MIXER-SETTLER SETUP

A four-stage mixer-settler setup having 320 ml capacity in the mixers and 1350 ml capacity in the settlers, manufactured from borosilicate/Pyrex glass, was purchased from *SX Kinetics Canada*. Clear and yellow tubing connecting each stage were used for the aqueous and organic phases respectively. The yellow organic tubing is specifically designed for organic solutions (Tygon B-44-3) and the clear tubing is made from Tygon F-4040-A suitable for aqueous solutions. The connectors between the tubing and mixing and settling chambers were manufactured from polypropylene. Peristaltic pumps with a capacity of 20-200 ml/min were used to feed the organic and aqueous phases to the system. Four variable-speed

mixer agitators (40-2000 rpm) with curved-blade impellers manufactured from polypropylene were used for agitation in the mixers (a stirring speed of 1000 rpm was used for all the tests). Seven litre stainless steel containers were used as organic and aqueous inventories and were pre-heated by placing them in a heating bath to control the temperature. Temperature and pH monitors were mounted above each stage and were used to monitor the temperature and pH respectively. In order to control the pH for the pre-loading stage, a flow meter was connected to a tube attached to a valve at the bottom of a chamber filled with NaOH solution, the flow of which was adjusted depending on the flow meter reading. Gravity was used to ensure flow by mounting the NaOH chamber approximately 20cm above the mixing chamber.

The O/A ratio at each stage during operation was determined by sampling a 10 ml aliquot with a pipette from the mixing chamber into a measuring cylinder which revealed the O/A ratio once the two phases separated. Each pump's flow rate was calibrated by measuring the time it took to fill a 200 ml flask at various capacities (0-100%) as indicated on the pump knob. These flow rates were confirmed during operation by measuring the time it took to fill a 200 ml flask from each product stream.

Figure 5-1 illustrates the flow through the mixers and settlers.
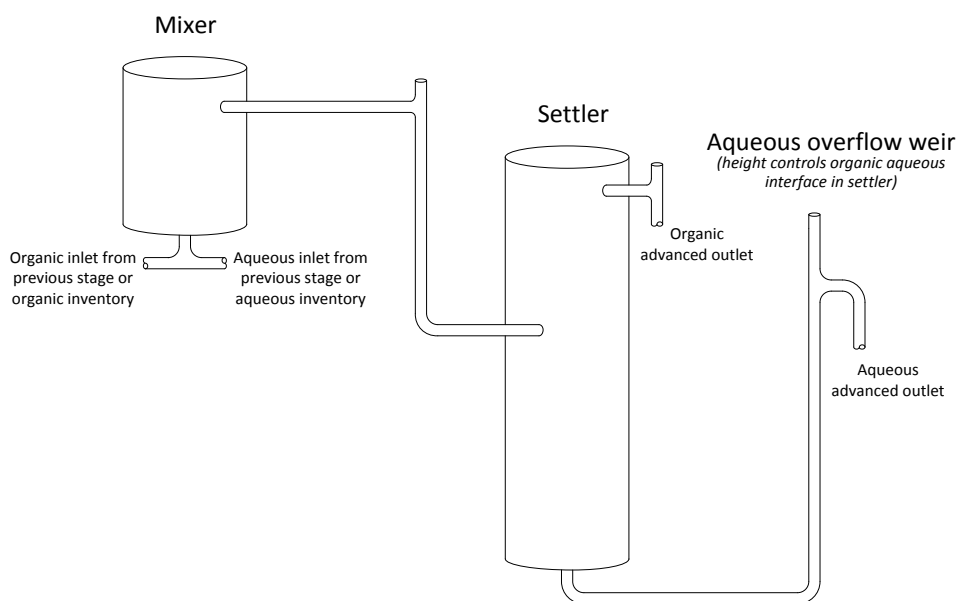
Figure 5-1: Schematic illustration of the organic and aqueous flow through the mixers and settlers

Referring to Figure 5-1 the organic and aqueous phases are fed to the bottom of each mixer where after the dispersion advances through the mixer overflow weir to the settling chamber where the aqueous and organic phases separate and exit at the bottom and top, respectively. The position of the organic-aqueous interface in the settlers is controlled by the position of the aqueous over-flow weir which can be raised or lowered.

See Figures A-7 and A-8 in Appendix A for photographs of the setup.

5.3 MIXER-SETTLER CONFIGURATIONS

Figures 5-2 to 5-5 show the four configurations and process conditions that were used to test the predictions made by the simulation sheet. The dotted lines signify the organic streams and the solid lines the aqueous streams.
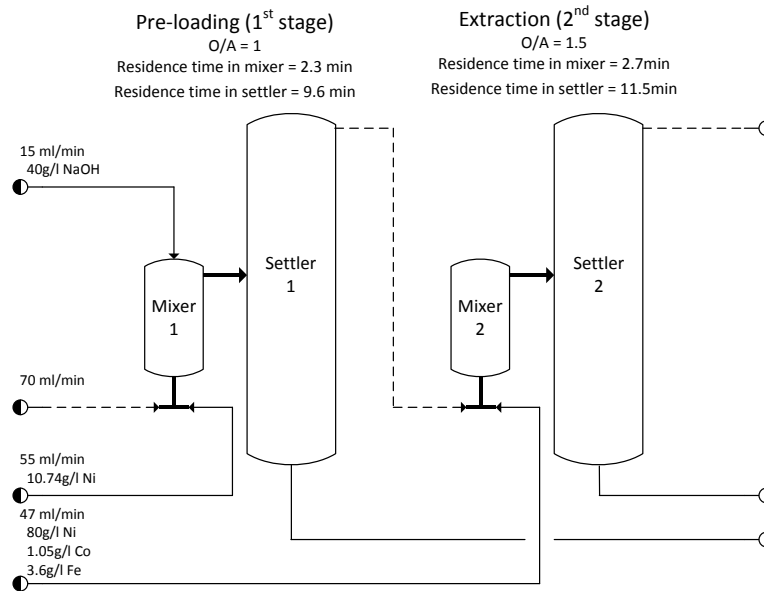
Figure 5-2: Mixer-settler configuration for pre-loading and extraction when generating a lower nickel loading on the organic phase (process conditions and results are shown in Table A-23 in Appendix A)
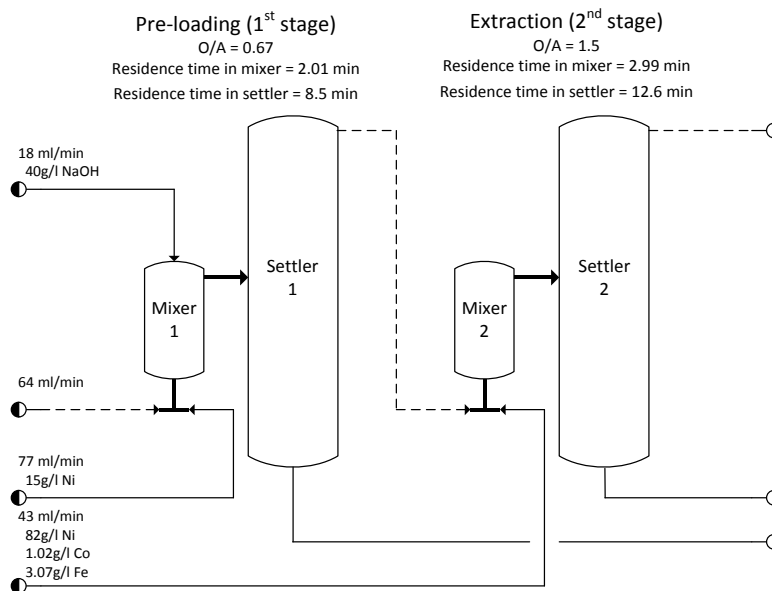
Figure 5-3: Mixer-settler configuration for pre-loading and extraction when generating a higher nickel loading on the organic phase (process conditions and results are shown in Table A-24 in Appendix A)

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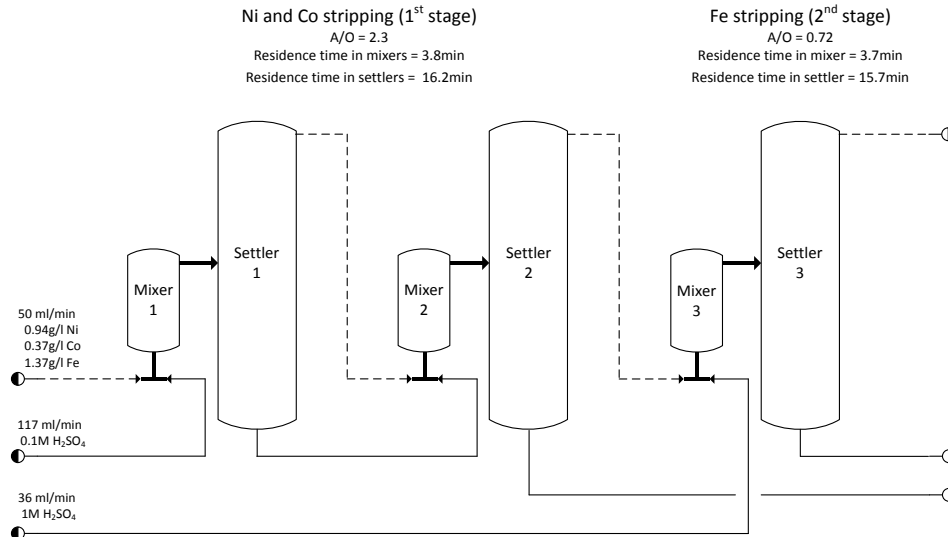
Figure 5-4: Mixer-settler configuration when stripping an organic phase with a lower metal loading (process conditions and results are shown in Table A-25 in Appendix A)
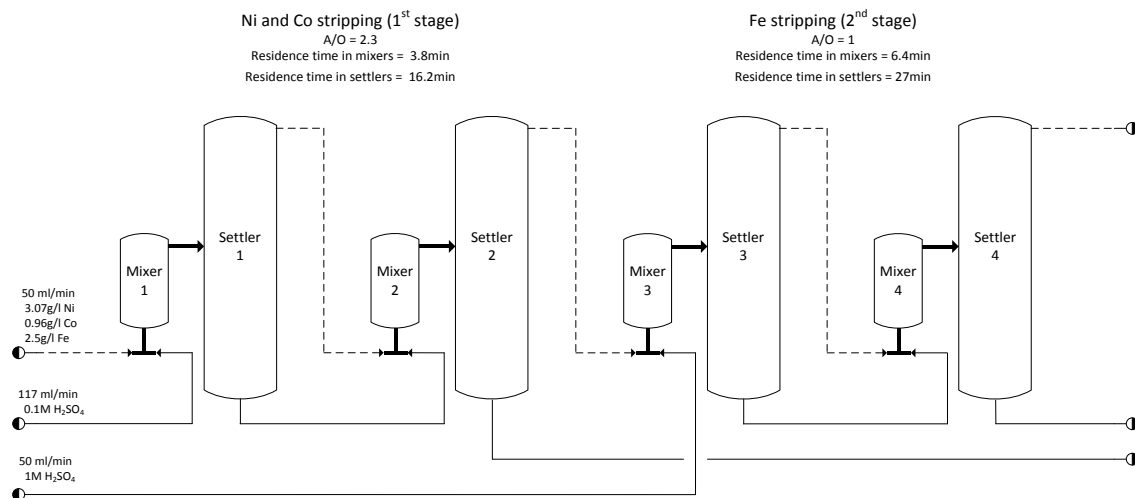
Figure 5-5: Mixer-settler configuration when stripping an organic phase with a higher metal loading (process conditions and results are shown in Table A-26 in Appendix A)

In all tests a 20V% Cyanex 272 solution in Shellsol D70 was used while the temperature in each stage was controlled between 40°C and 50°C by adjusting the heating bath temperature.

Figures 5-2 and 5-3 reveal the configuration that were used for the extraction tests. The pump capacities did not allow for the high O/A ratio of 25 in the pre-loading section (maximum is (200 ml/min)/(20 ml/min) = 10). Consequently only the designed process conditions for the extraction section were considered. Lower nickel aqueous concentrations and O/A ratios were used for the pre-loading section to generate the required nickel loading for the extraction section. For the first extraction test in Figure 5-2 the O/A ratio of 1, 40 g/l NaOH flow rate of 15 ml/min and nickel aqueous feed concentration of

10.74 g/l in the pre-loading stage were chosen based on the previous batch tests to produce a nickel loading ranging between 3-3.5 g/l. For the extraction section a higher iron concentration (3.6 instead of 3 g/l) was used in the pregnant solution to observe if the generated loading was still adequate at the selected O/A ratio of 1.5 to produce a pure nickel product solution as well as to see if the model could predict the variation regarding this metal inlet concentration. In the second extraction test (Figure 5-3) a lower O/A ratio of 0.67, a higher 40 g/l NaOH flow rate of 18 ml/min and a higher nickel aqueous feed concentration of 15 g/l were chosen to see if generating a higher nickel loading at the same O/A ratio of 1.5 in the extraction section would result in a purer nickel product solution. In the second extraction test the iron concentration was lowered to 3.07 g/l while the cobalt and nickel concentrations remained between 1.02-1.05 g/l and 80-82 g/l, respectively.

Referring to Figures 5-4 and 5-5, higher and lower organic loadings relative to those that were selected in the simulation sheet (2.89 g/l Ni, 0.63 g/l Co and 2 g/l Fe) were used. This was to see if the selected A/O ratio and H_2SO_4 concentration used in the simulation was still sufficient to selectively strip cobalt and nickel as well as to see whether the model allows for variations in metal loading. For the stripping test in Figure 5-4 organic loadings of 0.94 g/l Ni, 0.37 g/l Co and 1.37 g/l Fe were stripped with a H_2SO_4 concentration of 0.1 M and an A/O ratio of 2.3 at the first stage and a H_2SO_4 concentration of 1 M and an A/O ratio of 0.72 at the second stage. These A/O ratios that were measured compared well with those that were selected in the simulation sheet of 2.25 and 0.75, respectively. The high A/O ratio of 2.3 at the first stage demanded a high acid flow rate resulting in a residence time of 1.9 minutes which is much less than the 10 minutes allowed for the batch tests to reach equilibrium. In order to increase this to a total mixing time of 3.8 minutes, the organic and aqueous product from the first settler were connected to the second mixer as indicated in Figure 5-4. An extra mixer was not added to the second stripping stage since the residence time was already 3.7 minutes. For the second stripping test in Figure 5-5 the organic loading was increased to 3 g/l Ni, 0.96 g/l Co and 2.5 g/l Fe. A second mixer was also added to the second stage to increase the residence time at this stage as shown in Figure 5-5. A higher A/O ratio of 1 was also used to accommodate for the fact that equilibrium might not be reached and try to strip all the metal still left in the organic phase.

5.4 EXPERIMENTAL PROCEDURE

All stock solutions were prepared in the same manner as those in the batch tests. Metal aqueous concentrations were determined via atomic absorption spectrophotometry and the metal loadings were accordingly calculated via a mass balance. The following general start-up, operating and shut-down procedure was used for both the extraction and stripping tests in this specific order.

5.4.1 START UP PROCEDURE

- The heating baths were turned on by adjusting the knob of the heaters to the desired temperature.
- The system was then configured as per the test design.
- All the fittings were firmly fastened (finger tight).
- The position of the impellers was adjusted to the centre of the mixers and close to the bottom without touching the bottom or the sides.

- All the chucks of the impellers were securely tightened.
- A container filled with demineralised water was placed in the heating bath (approximately 5 l). This was used during start-up.
- Next the pre-loading, pregnant leach, stripping and NaOH stock solutions were prepared and also placed in the heating baths.
- The first stage settler and mixer were then filled half full with the nickel aqueous pre-loading solution and the remaining mixers and settlers was filled half full with the demineralised water (This was only done for the extraction tests, the first stage was also filled with water for the stripping configurations).
- 10 ml samples of each stock solution were then taken to confirm the metal content in each batch via AAS.
- The organic stock solutions were then prepared and all the remaining settlers and mixers were filled to their overflow weirs.
- The remaining organic solution was then also placed in the heating bath.
- Next the NaOH feed chamber was filled with the NaOH stock solution (only applicable to the extraction configurations).
- The temperature and pH sensors were then turned on and the corresponding probes were placed in the mixer and aqueous overflow weirs respectively.
- The 1st stage aqueous feed and product tubes were then placed in the nickel pre-loading inventory so that the aqueous product from the 1st stage is recycled back to the pre-loading inventory (only applicable to the extraction configurations).
- Next the aqueous feed and product tubes for the rest of the stages were placed in the container filled with demineralised water so that these aqueous product streams are also recycled back to this inventory.
- The organic feed tubing for the first stage as well as the organic product tube from the final stage was then placed in the organic stock solution so that the organic phase is also recycled back to the organic inventory. Initially pure and not loaded organic was used for the stripping tests.
- The impellers were then turned on and the speed was adjusted to 1000 rpm.
- The knobs on the feed pumps were then adjusted to the desired flow rates and they were all activated simultaneously.
- 10 ml samples after 5 minutes from each mixer were taken to determine the O/A ratio in each stage and the pumping rates were adjusted accordingly to obtain the desired O/A ratio.
- A sample from the 1st stage aqueous product was taken to confirm that no loading has occurred yet (only applicable to the extraction configurations).
- The liquid interface at each settler was examined and had to remain constant to ensure that the system was at steady state (the aqueous overflow flow weir was shifted up and down to shift the liquid interface up and down in the settler).
- All the product tubes were then placed in the product containers and the feed tubing from the water feed as well as the organic feed tube in the loaded organic inventory for the stripping tests were placed in their respective inventory feeds.
- The valve for the NaOH feed to the 1st stage was then adjusted to the desired flow rate as shown on the flow metre (only applicable to the extraction configurations).

5.4.2 OPERATING PROCEDURE

- During operation it was important to ensure that the NaOH inventory remained full by consistently adding NaOH since the container only had a volume of 500 ml (only applicable to the extraction configurations).
- A sample was taken every 10 minutes from each aqueous product stream.
- The pH, temperature and O/A were also regulated every 10 minutes.

5.4.3 SHUT DOWN PROCEDURE

- During shut down the feed pumps were switched off first.
- The impellers were then turned off.
- The organic and aqueous phases were then drained from the system.
- The mixers, settlers, over-flow weirs, and tubing were rinsed with water.
- The mixers and pumps were cleaned with a mild soap or detergent solution).

5.5 RESULTS

5.5.1 EXTRACTION

The nickel loading, sodium concentration in the aqueous product solution and pH for the pre-loading stage for the two configurations in Figures 5-2 and 5-3 are shown in Figures 5-6 (a) and 5-7 (a), respectively. Nickel, cobalt and iron extraction as well as sodium addition to the purified nickel product solution and pH for the extraction section for the two configurations in Figures 5-2 and 5-3 are shown in Figures 5-6 (b) and 5-7 (b), respectively. Zero minutes represents the time after the NaOH valve was opened.
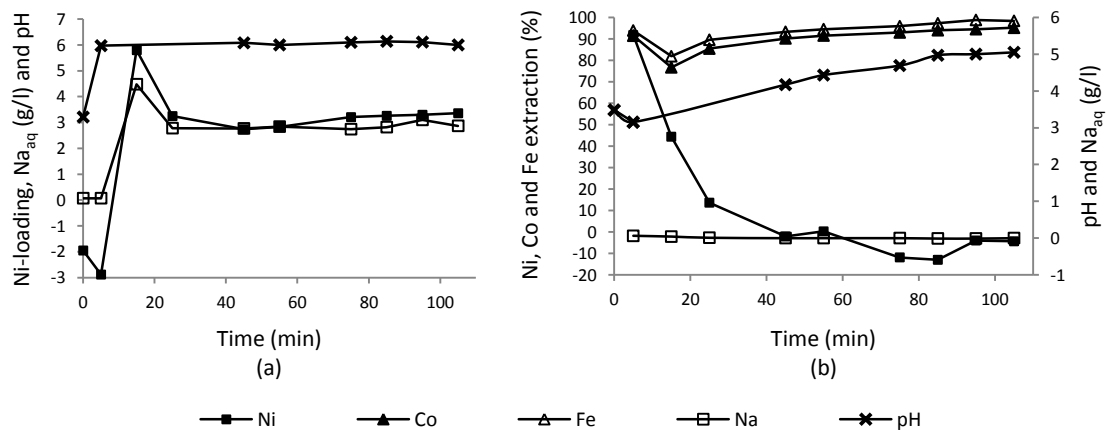
Figure 5-6: Results for pre-loading (1ˢᵗ stage (a)) and extraction (2ⁿᵈ stage (b)) when generating a lower nickel loading on the organic phase (process conditions and results are shown in Table A-23 in Appendix A)
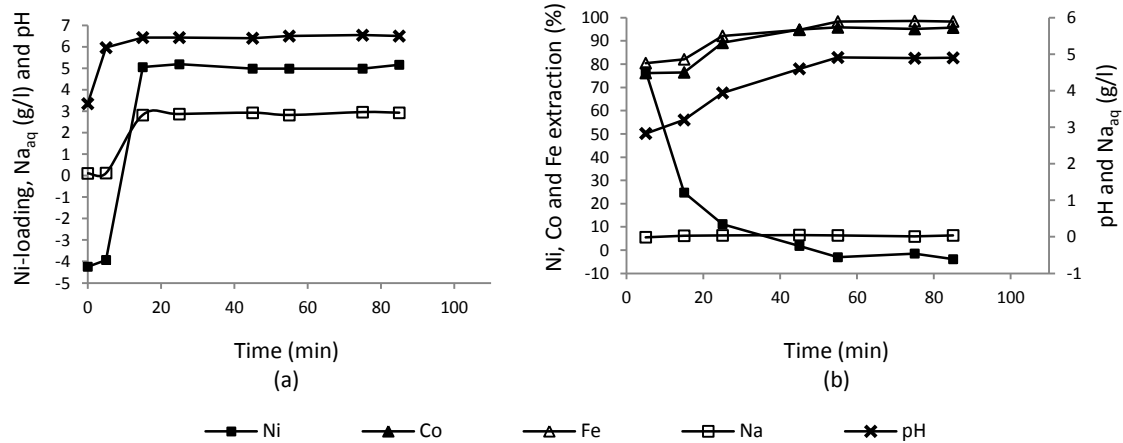
Figure 5-7: Results for pre-loading (1ˢᵗ stage (a)) and extraction (2ⁿᵈ stage (b)) when generating a higher nickel loading on the organic phase (process conditions and results are shown in Table A-24 in Appendix A)

During all the extraction tests no phase separation problems were encountered and a third phase barely even formed in the settlers. Referring to Figure 5-6 (a) there are peaks at 15 minutes in the nickel loading and sodium concentration in the aqueous product solution of 5.8 g/l and 4.48 g/l, respectively. This was caused by a momentarily increase in the NaOH flow rate between 0 and 10 minutes. For the time period between 15 and 25 minutes (Figure 5-6 (a, b)) the pH probes were removed from the aqueous product solutions so that this sudden increase in pH did not interfere with the probes calibration (this is why there are no pH data for this time period).

The negative nickel loading between 0-5 minutes in Figures 5-6 (a) and 5-7 (a) can be explained by referring to equation 35 that was used to calculate nickel loading.

$$Ni_{org} = \frac{Nio_{aq}F_{aq} - Ni_{aq}(F_{aq} + F_{NaOH})}{(O/A)(F_{aq} + F_{NaOH})}$$

[35]

where:

Ni_{org}	=	Nickel concentration in the organic phase at equilibrium/nickel loading (g/l)
Nio_{aq}	=	Nickel concentration in the aqueous feed (g/l)
Ni_{aq}	=	Nickel concentration in the aqueous product (g/l)
F_{aq}	=	Aqueous flow rate nickel pre-loading solution (ml/min)
F_{NaOH}	=	NaOH flow rate (ml/min)

During the start-up procedure nickel is initially circulated with the organic phase in the first stage without opening the NaOH valve. Consequently five minutes after the NaOH has been opened the effect of the extra volume added by the NaOH stream to the aqueous product stream has not yet been detected in the sample and the loading should in fact be zero by setting F_{NaOH} equal to zero in equation 35. The nickel loading at steady state is however of primary interest therefore equation 35 was still used in this regard irrespective of the time period after the NaOH valve has been opened.

The initial high extraction for nickel, cobalt and iron in Figures 5-6 (b) and 5-7 (b) is due to the fact that the aqueous product from this stage is still largely water that was used during the start-up procedure before the NaOH valve was opened. Hence it may appear as if nickel, cobalt and iron have been extracted, but this is only because they have not yet made their way through the mixer and settler. Nickel extraction can be used as indication to see when all the demineralised water has been removed from the system (this will typically be when it approaches zero).

From Figure 5-6, steady state was reached approximately 85 minutes after the NaOH valve was opened since al the curves are reaching or are already at a consistent value. The steady state nickel loading ranges between 3.26 and 3.36 g/l. This is close to the loading of 3.2 g/l selected as the optimum loading at an O/A ratio of 1.5 for the extraction section. The pH and cobalt and iron extraction at steady state, range between 4.97-5.05, 94-95% and 97-98% respectively. At nickel loadings ranging between 3.26-3.36 g/l and an O/A ratio of 1.5, the simulation sheet returns a pH and cobalt and iron extraction range of 4.62-4.67, 95-96% and 99-99%, respectively, which compares well with the experimental results. The nickel loading and O/A ratio were adequate to remove the extra iron added to the pregnant nickel solution (3.6 g/l instead of 3 g/l) as predicted and proven by the simulation sheet and experimental results, respectively.

As mentioned previously the second extraction test was conducted to see if generating a higher nickel loading results in a purer nickel product (in other words if higher cobalt and iron extraction is achieved). Referring to Figure 5-7, steady state was reached after approximately 55 minutes. At steady state the nickel loading ranges between 4.98 and 5.16 g/l and the pH and cobalt and iron extraction between 4.89-4.91, 95-96% and 98-99%, respectively. At the same nickel loading and O/A ratio the simulation sheet returns a pH and cobalt and iron extraction range of 5.21-5.24, 97-98% and 99-100% respectively. Even though there is a slight increase in cobalt and iron extraction as predicted and proven by the second test and simulation, this effect is not severe enough to increase the nickel loading for a purer nickel product. The model under predicts the extraction pH for the lower nickel loading and over predicts the extraction pH at the higher nickel loading whereas it slightly over predicts extraction for both the low and high loading.

The sodium addition to the purified nickel product solution ranges between -0.01-0 g/l and 0.1-0.4 for the low and high nickel loading tests, respectively. The negative addition for the low nickel loading case is due to impure sodium that was in the stock solutions and was subtracted from the concentration given by the AAS (in other words some of the sodium was also extracted). It is also observed that the sodium addition increases as the nickel loading increases. This also justifies why it would be better to rather use the lower loading since the negligible extra extraction obtained from the higher nickel loading comes at the cost of having more sodium in the purified nickel product stream.

5.5.2 STRIPPING

The percentage nickel, cobalt and iron stripped in both stages for the two configurations in Figures 5-4 and 5-5 are shown in Figures 5-8 and 5-9, respectively. Zero minutes represents the time after each feed

tube is switched from the water and pure organic inventory to the stripping and loaded organic inventory solutions.
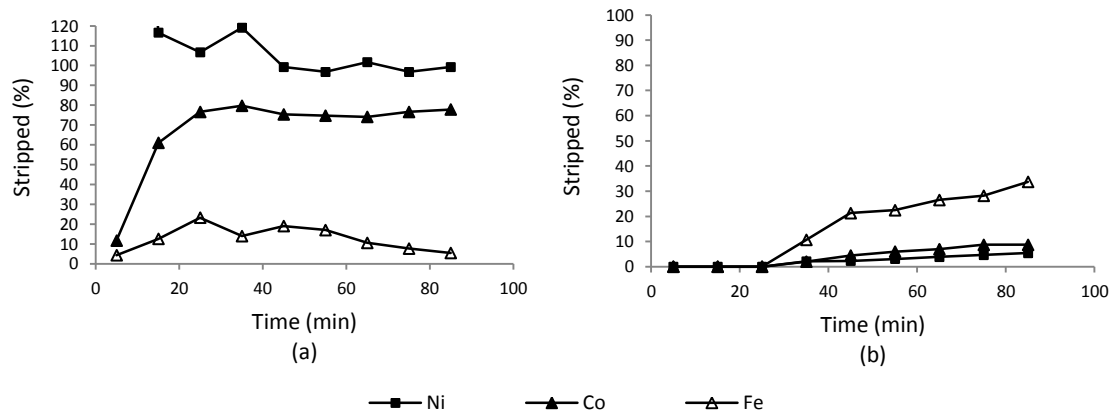
Figure 5-8: Results for stripping the organic phase with the lower metal loading; (a) and (b) represent the 1st and 2nd stages respectively (process conditions and results are shown in Table A-25 in Appendix A)
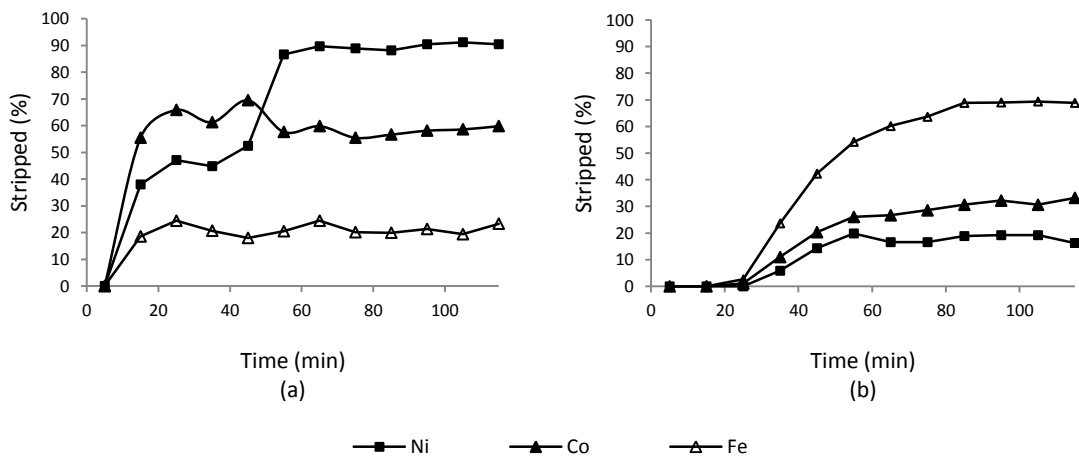
Figure 5-9: Results for stripping the organic phase with the higher metal loading; (a) and (b) represent the 1st and 2nd stages respectively (process conditions and results are shown in Table A-26 in Appendix A)

The percentage stripped in both stages was calculated with respect to the metal loading being fed to the first stage. This reveals what percentage of the metal fed to the stripping section ends up in which product stream.

For the stripping tests there were also no phase separation problems with the two phases almost completely disengaging as they flow from the mixer over flow weir to the settler where a third phase was hardly observed. The percentage nickel stripped at 5 minutes after start-up was calculated to be 366.41%. This is not indicated in Figure 5-8 (a) as the y-axis has been reduced to 120% to give a better visual indication of the rest of the data. A possible cause for this unrealistic value is the fact that some of the aqueous phase was still suspended in the loaded organic phase after the two phases were separated

and could not visually be observed. This then descended to the bottom of the container after a certain time period and was pumped by the organic pump to the 1st stage mixer. Most of the cobalt and iron were extracted while preparing this batch but not all of the nickel; hence this only affected the percentage nickel stripped in Figure 5-8 (a). This problem did not occur for the second stripping test as indicated in Figure 5-9 (a).

Figure 5-8 shows the results for the scenario where the organic phase with the lower metal loading of 0.94 g/l Ni, 0.37 g/l Co and 1.37 g/l Fe was stripped. In the first stage steady state with respect to nickel and cobalt stripping was reached approximately after 45 minutes. Steady state is however not reached with respect to iron stripping. This is also the case in the second stage where iron stripping increases and does not become consistent like nickel and cobalt. From 65 to 85 minutes the percentage of nickel, cobalt and iron stripped in the 1st stage ranges between 97-101%, 74-78% and 11-5% and in the 2nd stage between 4-5%, 7-9% and 27-34%, respectively. The simulated percentage nickel, cobalt and iron stripped for this metal loading and process conditions as shown in Figure 5-4 for the first stage are 99.98%, 99.95% and 0.28% and for the second stage are 0.02%, 0.05% and 99.45%, respectively. The almost ideal separation of nickel and cobalt from iron predicted by the models is not reflected in the experimental results. Referring to Figure 3-18 a mixing time of approximately 410 seconds or 6.83 minutes is required for equilibrium. This is almost double the residence time of 3.8 and 3.7 minutes used for the 1st and 2nd stage mixers, respectively. The simulated and experimental results with respect to nickel stripping corresponds the best. A likely explanation, when considering the stripping kinetics in figure 3-18, is the fact that nickel is stripped faster than either cobalt or iron with more than half the nickel being stripped after 60 seconds. The opposite can be applied with respect to iron stripping, since the stripping kinetics in this regard are slower than nickel or cobalt and therefore the residence time of 3.7 minutes is not enough to reach equilibrium in the second stage. This is reflected in the low percentage of iron stripped as opposed to the high stripping predicted by the model.

Next the stripping results of the higher metal loading configuration in Figure 5.5 (3.07 g/l Ni, 0.95 g/l Co and 0.95 g/l Fe) will be considered. Due to the poor iron stripping obtained (maximum of 33.72%) in the 2nd stage in Figure 5.8 an extra mixer and settler were added to the 2nd stage as discussed previously to increase the residence time. This adjustment increased the 2nd stage mixer residence time to 6.4 minutes while the 1st stage mixer residence time remained at 3.8 minutes. A higher A/O ratio of 1 was also used with the aim of increasing iron extraction at this stage. Referring to Figure 5.9, steady state was reached approximately after 85 minutes which was the duration for the previous stripping test. Consequently larger inventories were prepared for the second stripping test which successfully yielded steady state. At steady state the percentage nickel, cobalt and iron stripped in the 1st stage ranges between 88-90%, 57-60% and 20-23% and in the 2nd stage between 16-19%, 31-32% and 69-70%, respectively. The simulated percentage nickel, cobalt and iron stripped for the first stage is 99.98%, 99.95% and 0.28% and for the second stage is 0.02%, 0.05% and 99.48%, respectively. The simulated results once again predict excellent separation of nickel and cobalt from iron which is not the case for the experimental results. The additional nickel and cobalt loaded onto the organic phase decreased the nickel and cobalt stripping by approximately 10% in the 1st stage while the remainder ended up in the second stage aqueous product stream. As expected, the increased residence time and A/O increased iron stripping in the second stage even though a higher loading was used. Complete stripping of the organic phase was however again not attained.

It is clear that the simulation sheet made more accurate predictions for the extraction tests than for the stripping tests. This is probably due to the fact that the extraction tests came much closer to equilibrium than the stripping tests did. Even though the stripping tests did not generate the favourable results the extraction tests did, it is still speculated that selective stripping of cobalt and nickel from iron can be achieved by doing some fine tuning with respect to the A/O ratio and H_2SO_4 concentration at each stripping stage as well as increasing the residence time for iron stripping.

CHAPTER 6
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CONCLUSIONS

The following conclusions are made from the literature review, batch tests, modelling and simulations and continuous tests. Recommendations for future work are also given.

6.1 LITERATURE REVIEW

Solvent extraction with Cyanex 272 as extracting reagent is the most popular separation process to remove cobalt and iron from pregnant nickel leach solutions. This is based on the extensive amount of research accompanied with favourable results that are available as well as for the fact that it is currently being applied in industry specifically for selective extraction of cobalt from nickel (Flett, 2005).

Most research focuses on either using saponified Cyanex 272 or pure Cyanex 272 during the extraction process. This however contaminates the aqueous product solution with sodium. A limited amount of research is available regarding the use of nickel salts of Cyanex 272 to extract cobalt and iron from nickel sulfate solutions which eliminates any sodium additions to the purified nickel aqueous product solution.

Equilibrium pH/NaOH addition, A/O feed ratio, extractant concentration, temperature, agitation time, nickel loading onto the organic and acid concentration are the most important operating variables in solvent extraction for this system.

6.2 BATCH TESTS

The pre-loading, extraction and stripping experimental setup are considered as being highly repeatable with a minimum r-value of 0.96 for the three replicates for all the factorial designs. The only exception was with nickel extraction during the extraction factorial design which yielded a r-value of 0.371. This was due to the fact that nickel extraction remained between 0-10% and is consequently hard to reproduce like cobalt and iron extraction since the mean square within groups do not differ significantly from the mean square between groups.

The pre-loading kinetics are the fastest followed by extraction with pure Cyanex 272, then extraction with the nickel salts of Cyanex 272 and then stripping, with equilibrium roughly being reached within 20, 100, 150 and 410 seconds, respectively.

Provided there is enough nickel available in the aqueous phase, nickel loading of Cyanex 272 is primarily a function of the NaOH addition and not the initial nickel aqueous concentration. In other words nickel

loading of Cyanex 272 is a function of the quantity of OH^- ions that can be used to neutralise the H^+ ions being exchanged for nickel in the aqueous phase; hence using higher initial nickel aqueous concentrations will not generate higher loadings.

When comparing pure Cyanex 272 and the nickel salt of Cyanex 272 to remove 1 g/l Co and 3 g/l Fe from an 80 g/l Ni solution, 4 g/l and 0.05 g/l of sodium ends up in the purified nickel product streams, respectively. Hence using the nickel salt of Cyanex 272 is the more attractive approach if minimization of sodium contamination in the product solution is of concern.

Increasing the extractant concentration decreases the effect the diluents have on the extracting power of Cyanex 272. These effects were however not large enough, even at the low concentrations, and Shellsol D70 was chosen as diluent for subsequent experimental work since it is one of diluents currently being manufactured for the extraction of cobalt and nickel with Cyanex 272 by Shell Chemicals in South Africa.

From the pre-loading factorial design, O/A ratio and NaOH addition are the two dominating factors with respect to nickel pre-loading. Temperature and extractant concentration on the other hand do not influence nickel loading to a significant extent. The equilibrium pH at which loading occurs decreases as the extractant concentration increases caused by the excess H^+ being added to the dispersion.

According to the factorial design for the extraction section, O/A ratio and nickel loading are the most influential factors with respect to cobalt and iron extraction. Preliminary experiments revealed that increasing the extractant concentration from 10 V% to 20 V% increases cobalt extraction but has no significant effect on iron extraction. According to the factorial design extractant concentration does not influence either cobalt or iron extraction. Consequently a 20V% Cyanex 272 solution was chosen for subsequent tests since it increases cobalt extraction and decreases possible ligand overloading leading to phase separation problems. Temperature influences cobalt and iron extraction at nickel loadings lower than approximately 4 g/l and an O/A ratio of 1 with cobalt and iron extraction decreasing and increasing, respectively, as temperature increases. At nickel loadings higher than 4 g/l for an O/A ratio of 1 temperature does not have a significant influence on cobalt and iron extraction. A temperature of 50°C was chosen for the pre-loading and extraction sections since it minimizes phase separation problems and nickel loadings and O/A ratios close to 4 g/l and 1, respectively, are recommended.

The nickel extraction data with Ni-Cyanex 272 was scattered as a function of nickel loading and O/A ratio but consistently remained within -6% and 6% with a single exception of 8.77% at a nickel loading of 0.56 g/l and an O/A ratio of 2. The sodium addition to the purified nickel product solution increases as the O/A ratio and nickel loading increases. This is caused by the fact that higher nickel loadings demand higher sodium additions in the pre-loading section which increases the probability of sodium uptake by the organic phase and which consequently ends up in the purified nickel stream.

In essence all of the (99-100%) iron is removed from the pregnant solution for the selected nickel loading and O/A ratio (1.5 and 3.2 g/l respectively). A small quantity of cobalt however still remains after extraction (95-96%) even at the maximum nickel loadings and O/A ratios tested.

From the nickel loading extraction isotherms, one theoretical stage is calculated to generate the required loading (3.2 g/l) at a pH of 7 and an O/A ratio of 25 from the 80 g/l purified nickel solution.

A/O ratio and acid concentration are the most influential factors with respect to stripping. The metal loading on the organic phase also influences stripping and as a result different metal loadings will require different A/O ratios and stripping agent concentrations. Temperature only influences nickel stripping. This effect is however not large and a temperature of 50°C was used for the subsequent stripping tests as well.

Stripping occurs at a lower pH than extraction; hence the metal complexes are more stable in the organic phase than in the aqueous phase.

Selective stripping of nickel and cobalt are possible to a certain extent but are limited by phase separation problems and hence not practical. Selective stripping of nickel and cobalt from iron is however possible and do not present any phase separation problems.

A 0.1 M H_2SO_4 solution at an A/O ratio of 2.25 is recommended to strip cobalt and nickel and a 1 M H_2SO_4 solution at an A/O ratio of 0.75 to strip the remaining iron from the organic phase.

6.3 MODELLING AND SIMULATION

The model derived from the equilibrium constant for nickel loading as a function of NaOH/Nio and O/A ratio gave a good fit with a R^2 value of 0.97.

The sigmoid function was also successfully manipulated to model the loading pH as a function of NaOH/Nio and O/A ratio, the concentration of cobalt and iron in the extraction aqueous product solution and extraction pH as a function of nickel loading and O/A ratio and nickel, cobalt and iron concentration in the aqueous product strip solution as a function of H_2SO_4 concentration and A/O ratio. The lowest R^2 value out of all these fits with the modified sigmoid function was 0.94 for iron concentration in the stripped product solution and the extraction pH which was still regarded as a good model fit.

Using these models and mass-balance calculations, a simulation sheet was successfully developed to predict all the aqueous and organic product concentrations (except for nickel in the extraction product solutions which can be selected arbitrarily) as well as the extraction or stripping at each stage and pH for the pre-loading and extraction stages. The input values that can be varied include the metal concentrations and flow rate of the pregnant solution, the O/A ratio for the pre-loading and extraction sections, A/O ratio for the stripping sections, the relative moles of NaOH being added with respect to nickel in the aqueous feed (NaOH/Nio), the NaOH concentration used for the pre-loading section and the H_2SO_4 concentration of the two streams being fed to the stripping sections

After conducting a sensitivity analysis with the simulation sheet, it was concluded that the selected operating variables for the extraction circuit are robust towards variations in the feed concentration for the extraction and stripping sections.

6.4 CONTINUOUS TESTS

The mixer-settler setup was successfully used to extract cobalt and iron from the pregnant nickel solution by using the pre-loading procedure.

The predictions made regarding cobalt extraction, iron extraction and extraction pH by the simulation sheet were accurately re-produced during the two extraction tests.

The O/A ratio of 1.5 and nickel loading ranging between 3.26 g/l and 3.36 g/l at steady state, which is close to the 3.2 g/l selected as the optimum during the batch tests, were adequate to remove the additional iron (3.6 g/l instead of 3 g/l) and cobalt (1 g/l) from the concentrated nickel solution.

Increasing the nickel loading so that it ranges between 4.98 g/l and 5.16 g/l at steady state did not have a significant influence on cobalt and iron extraction (even though the iron concentration was decreased to 3 g/l in the pregnant solution). This increase in nickel loading also increased the sodium addition to the purified nickel solution from -0.01-0 g/l to 0.1-0.4 g/l and it was concluded that the lower loading is still the better option.

The stripping results did not accurately reflect the predictions made by the simulations. A possible cause is that equilibrium was not reached in each stage as the pump capacities did not allow for low enough flow rates. This statement was justified during the second stripping test where iron extraction increased as the residence time increased by adding an additional mixer and settler to the second stripping stage.

Even though the selected H_2SO_4 concentration and A/O ratio of 0.1 M and 2.25, respectively, to selectively strip nickel and cobalt from iron did not completely achieve this goal, it is believed that this is still possible through some fine tuning of these two variables. The same goes for the failed attempt to regenerate the organic phase and completely strip iron with 1 M H_2SO_4 at an A/O ratio of 0.75 and 1 (increasing the residence time will also increase iron extraction).

6.5 FUTURE WORK

The following comments are made regarding future work:

- Modify the mixer-settler setup to test the simulation sheet with respect to pre-loading the organic with 80 g/l Ni.

- Use the mixer-settler setup to find the optimum conditions (H_2SO_4 concentration and A/O ratio) to selectively strip nickel and cobalt from iron as well as to completely remove iron after nickel and cobalt have been stripped.
- Conduct a fundamental study regarding the phase separation problems (single emulsion that formed) that were encountered during the stripping tests by considering factors like viscosity and liquid interface tension.
- Conduct a kinetic study regarding the reaction mechanism by which Ni-Cyanex 272 removes cobalt and iron from the concentrated nickel sulfate solution. This will provide a more fundamental understanding of the behaviour of nickel, cobalt and iron in the pregnant solution during extraction.

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APPENDIX A (EXPERIMENTAL AND MODELLING RESULTS)

A1 BATCH TESTS

Table A-1: Extraction kinetics of nickel, cobalt and iron with pure Cyanex 272

Diluent:	Kerosene
Cyanex 272 (V%):	20
Temperature (°C):	50
3 M NaOH (ml):	1
O/A (ml/ml):	20/20

Agitation period (s)	pH	Ni_o aqueous (g/l)	Co_o aqueous (g/l)	Fe_o aqueous (g/l)	Ni aqueous (g/l)	Co aqueous (g/l)	Fe aqueous (g/l)	Ni extracted (%)	Co extracted (%)	Fe extracted (%)
20	6.15	88	1.05	3.3	76	0.611	1.022	9.32	38.90	67.48
40	5.95	88	1.05	3.3	78	0.378	0.468	6.93	62.20	85.11
60	5.5	88	1.05	3.3	80	0.212	0.219	4.55	78.80	93.03
100	4.87	88	1.05	3.3	80	0.143	0.021	4.55	85.70	99.33
150	4.65	88	1.05	3.3	80	0.162	0.014	4.55	83.80	99.55
300	4.68	88	1.05	3.3	82	0.119	0.022	2.16	88.10	99.30

Table A-2: Pre-loading kinetics of Cyanex 272 with nickel

Diluent:	Kerosene
Cyanex 272 (V%):	20
Temperature (°C):	50
O/A (ml/ml):	20/20

3 M NaOH (ml)	Agitation period (s)	Ni_o aqueous (g/l)	Ni aqueous (g/l)	Ni extracted (%)
1	20	10.75	6.1	40.42
1	40	10.75	6.3	38.47
1	60	10.75	6.2	39.44
1	80	10.75	6.1	40.42
1	100	10.75	6	41.40
1	150	10.75	5.8	43.35
1	200	10.75	6.2	39.44
1	250	10.75	6.3	38.47
1	300	10.75	6.2	39.44
2	20	10.75	2.1	78.51
2	40	10.75	1.9	80.56
2	60	10.75	2	79.53
2	80	10.75	2.1	78.51
2	100	10.75	2	79.53
2	150	10.75	1.8	81.58
2	200	10.75	2	79.53
2	250	10.75	2	79.53
2	300	10.75	1.9	80.56

Table A-3: Extraction kinetics of nickel, cobalt and iron with the nickel salt of Cyanex 272

Cyanex 272 (V%):	20
Temperature (°C):	50
O/A (ml/ml):	20/20

Nickel loading (g/l)	Diluent	Agitation period (s)	Ni_o aqueous (g/l)	Co_o aqueous (g/l)	Fe_o aqueous (g/l)	Ni aqueous (g/l)	Co aqueous (g/l)	Fe aqueous (g/l)	Ni extracted (%)	Co extracted (%)	Fe extracted (%)
2.47	shellsol D70	20	83.30	1.07	2.88	79.10	0.66	1.41	5.04	38.50	51.22
2.47	shellsol D70	40	83.30	1.07	2.88	85.90	0.65	1.39	-3.12	39.44	51.74
2.47	shellsol D70	60	83.30	1.07	2.88	80.80	0.70	1.29	3.00	34.21	55.21
2.47	shellsol D70	100	83.30	1.07	2.88	80.70	0.88	1.11	3.12	17.66	61.39
2.47	shellsol D70	150	83.30	1.07	2.88	76.80	1.00	0.83	7.80	6.92	71.22
2.47	shellsol D70	300	83.30	1.07	2.88	79.70	1.01	0.68	4.32	6.07	76.53
4.09	kerosene	20	86.33	1.08	3.30	86.00	0.27	0.52	0.38	75.23	84.39
4.09	kerosene	40	86.33	1.08	3.30	87.00	0.18	0.34	-0.78	83.40	89.58
4.09	kerosene	60	86.33	1.08	3.30	87.00	0.17	0.26	-0.78	84.42	92.03
4.09	kerosene	80	86.33	1.08	3.30	87.00	0.17	0.23	-0.78	84.04	93.00
4.09	kerosene	100	86.33	1.08	3.30	86.00	0.20	0.11	0.38	81.08	96.79
4.09	kerosene	150	86.33	1.08	3.30	88.00	0.29	0.01	-1.93	73.10	99.58
4.09	kerosene	250	86.33	1.08	3.30	88.00	0.30	0.00	-1.93	72.17	99.94
4.09	kerosene	300	86.33	1.08	3.30	88.00	0.31	0.02	-1.93	71.06	99.45
4.66	shellsol D70	20	83.30	1.07	2.88	79.80	0.16	0.20	4.20	85.05	93.09
4.66	shellsol D70	40	83.30	1.07	2.88	79.00	0.11	0.07	5.16	89.44	97.43
4.66	shellsol D70	60	83.30	1.07	2.88	77.50	0.12	0.05	6.96	89.16	98.30
4.66	shellsol D70	100	83.30	1.07	2.88	77.70	0.13	0.02	6.72	88.13	99.44
4.66	shellsol D70	150	83.30	1.07	2.88	76.80	0.15	0.00	7.80	86.45	100.00
4.66	shellsol D70	300	83.30	1.07	2.88	77.60	0.15	0.00	6.84	86.17	100.00
8.48	kerosene	20	86.33	1.08	3.30	93.00	0.02	0.01	-7.73	98.33	99.73
8.48	kerosene	40	86.33	1.08	3.30	92.00	0.01	0.01	-6.57	98.70	99.85
8.48	kerosene	60	86.33	1.08	3.30	88.00	0.02	0.01	-1.93	98.61	99.70
8.48	kerosene	80	86.33	1.08	3.30	90.00	0.02	0.01	-4.25	98.61	99.82
8.48	kerosene	100	86.33	1.08	3.30	92.00	0.02	0.01	-6.57	98.33	99.85
8.48	kerosene	150	86.33	1.08	3.30	88.00	0.02	0.00	-1.93	98.14	99.88
8.48	kerosene	250	86.33	1.08	3.30	87.00	0.02	0.00	-0.78	98.14	99.88
8.48	kerosene	300	86.33	1.08	3.30	87.00	0.02	0.00	-0.78	98.24	99.91

Table A-4: Pre-loading of Cyanex 272 with different initial nickel aqueous concentrations

Diluent:	Kerosene
Temperature (°C):	50
Agitation period (min):	5
O/A (ml/ml):	20/20

Cyanex 272 (V%)	3 M NaOH (ml)	Ni_o aqueous (g/l)	Ni aqueous (g/l)	Ni extracted (%)	Ni-loading (g/l)	pH
10	0.25	6.15	5.41	10.93	0.67	5.63
10	0.5	6.15	4.3	28.33	1.74	5.9
10	0.75	6.15	3.48	41.29	2.54	6.33
10	1	6.15	2.15	63.29	3.89	6.5
10	1.3	6.15	1.25	78.35	4.82	6.92
10	1.6	6.15	0.02	99.65	6.13	8.08
10	2	6.15	0	100.00	6.15	8.9
10	0.25	10.5	9.84	5.11	0.54	5.68
10	0.5	10.5	8.48	17.22	1.81	5.99
10	0.75	10.5	7.68	24.11	2.53	6.13
10	1	10.5	6	40.00	4.20	6.69
10	1.3	10.5	5.08	48.47	5.09	6.74
10	1.6	10.5	3.36	65.44	6.87	6.91
10	2	10.5	1.74	81.77	8.59	7.07
10	2.25	10.5	0.73	92.27	9.69	7.23
10	0.25	21.2	19.9	4.77	1.01	6
10	0.5	21.2	18.2	12.20	2.59	6.2
10	0.75	21.2	17.6	13.97	2.96	6.35
10	1	21.2	16.2	19.96	4.23	6.53
10	1.3	21.2	14.9	25.15	5.33	6.55
10	1.6	21.2	12.9	34.18	7.25	6.78
10	2	21.2	11.5	40.12	8.51	6.79
10	2.25	21.2	9.98	47.63	10.10	6.81
20	0.25	6.15	4.99	17.85	1.10	5.47
20	0.5	6.15	4.02	33.00	2.03	5.56
20	0.75	6.15	2.93	50.57	3.11	5.82
20	1	6.15	2.09	64.32	3.96	5.91
20	1.3	6.15	0.75	87.01	5.35	6.23
20	1.6	6.15	0.07	98.77	6.07	6.76
20	2	6.15	0	100.00	6.15	7.72
20	2.25	6.15	0	100.00	6.15	8.06
20	0.25	10.5	8.97	13.50	1.42	5.47
20	0.5	10.5	8.19	20.05	2.11	5.64
20	0.75	10.5	7	30.83	3.24	5.72
20	1	10.5	5.83	41.70	4.38	5.83
20	1.3	10.5	4.34	55.98	5.88	5.95
20	1.6	10.5	3.19	67.19	7.05	6.13
20	2	10.5	1.75	81.67	8.58	6.4
20	2.25	10.5	0.78	91.74	9.63	6.5
20	0.25	21.2	19.1	8.87	1.88	5.22
20	0.5	21.2	18.3	11.52	2.44	5.4
20	0.75	21.2	17.1	16.12	3.42	5.55
20	1	21.2	16.2	19.96	4.23	5.76
20	1.3	21.2	14	29.47	6.25	5.83
20	1.6	21.2	13	33.98	7.20	6.3
20	2	21.2	11.1	42.61	9.03	6.35
20	2.25	21.2	9.56	49.83	10.56	6.65

Table A-5: Sodium addition to nickel product solution as a function of cobalt and iron extraction with the nickel loadings of Cyanex 272 as generated in Table A-4

Diluent:	Kerosene
Temperature (°C):	50
Agitation period (min):	5
O/A (ml/ml):	20/20

Cyanex 272 (V%)	Ni-loading (g/l)	Ni_o aqueous (g/l)	Co_o aqueous (g/l)	Fe_o aqueous (g/l)	Na_o aqueous (g/l)	Ni aqueous (g/l)	Co aqueous (g/l)	Fe aqueous (g/l)	Na aqueous (g/l)	Ni extracted (%)	Co extracted (%)	Fe extracted (%)	Na addition to aqueous phase after extraction (g/l)	pH
10	0.67	85	1.06	3.1	0.26	81	1.03	1.8	0.26	4.71	2.83	41.94	0	2.9
10	1.74	85	1.06	3.1	0.26	79.9	1.02	0.85	0.31	6	3.77	72.58	0.05	3.18
10	2.54	85	1.06	3.1	0.26	83.8	1.03	0.04	0.28	1.41	2.83	98.71	0.02	3.65
10	3.89	85	1.06	3.1	0.26	78.4	0.37	0	0.3	7.76	65.09	100	0.04	4.81
10	4.82	85	1.06	3.1	0.26	80.2	0.22	0	0.3	5.65	79.25	100	0.04	5.24
10	6.13	85	1.06	3.1	0.26	77.5	0.21	0	0.57	8.82	80.19	100	0.31	5.86
10	6.15	85	1.06	3.1	0.26	74.5	0.22	0	1.14	12.35	79.25	100	0.88	6.4
10	0.54	85	1.06	3.1	0.26	78.2	1.01	1.81	0.23	8	4.72	41.61	-0.03	3.12
10	1.81	85	1.06	3.1	0.26	81	1.01	0.87	0.26	4.71	4.72	71.94	0	3.16
10	2.53	85	1.06	3.1	0.26	84.4	0.93	0.05	0.28	0.71	12.26	98.39	0.02	3.91
10	4.2	85	1.06	3.1	0.26	87.4	0.36	0	0.25	-2.82	66.04	100	-0.01	4.85
10	5.09	85	1.06	3.1	0.26	85.9	0.22	0	0.33	-1.06	79.25	100	0.07	5.3
10	6.87	85	1.06	3.1	0.26	87	0.18	0	0.28	-2.35	83.02	100	0.02	5.84
10	8.59	85	1.06	3.1	0.26	87.2	0.1	0	0.33	-2.59	90.57	100	0.07	6.43
10	9.69	85	1.06	3.1	0.26	87.2	0.18	0	0.3	-2.59	83.02	100	0.04	6.51
10	1.01	85	1.06	3.1	0.26	81.9	1.01	1.79	0.27	3.65	4.72	42.26	0.01	3.2
10	2.59	85	1.06	3.1	0.26	82.9	1.01	0.86	0.26	2.47	4.72	72.26	0	3.69
10	2.96	85	1.06	3.1	0.26	85.5	0.94	0	0.29	-0.59	11.32	100	0.03	4.05
10	4.23	85	1.06	3.1	0.26	86.1	0.36	0	0.28	-1.29	66.04	100	0.02	4.84
10	5.33	85	1.06	3.1	0.26	83.7	0.22	0	0.26	1.53	79.25	100	0	5.14
10	7.25	85	1.06	3.1	0.26	85.6	0.18	0	0.31	-0.71	83.02	100	0.05	5.57
10	8.51	85	1.06	3.1	0.26	84.1	0.14	0	0.28	1.06	86.79	100	0.02	6.27
10	10.1	85	1.06	3.1	0.26	83.4	0.13	0	0.49	1.88	87.74	100	0.23	6.56

Cyanex 272 (V%)	Ni-loading (g/l)	Ni_o aqueous (g/l)	Co_o aqueous (g/l)	Fe_o aqueous (g/l)	Na_o aqueous (g/l)	Ni aqueous (g/l)	Co aqueous (g/l)	Fe aqueous (g/l)	Na aqueous (g/l)	Ni extracted (%)	Co extracted (%)	Fe extracted (%)	Na addition to aqueous phase after extraction (g/l)	pH
20	1.1	85	1.06	3.1	0.26	81.7	1	1.71	0.27	3.88	5.66	44.84	0.01	2.77
20	2.03	85	1.06	3.1	0.26	81.1	1	0.73	0.29	4.59	5.66	76.45	0.03	3.05
20	3.11	85	1.06	3.1	0.26	82.2	0.98	0.07	0.26	3.29	7.55	97.74	0	3.33
20	3.96	85	1.06	3.1	0.26	84.8	0.21	0	0.29	0.24	80.19	100	0.03	4.15
20	5.35	85	1.06	3.1	0.26	81.7	0.07	0	0.38	3.88	93.4	100	0.12	4.93
20	6.07	85	1.06	3.1	0.26	82.5	0.04	0	0.64	2.94	96.23	100	0.38	5.08
20	6.15	85	1.06	3.1	0.26	80.6	0.03	0	1.84	5.18	97.17	100	1.58	5.37
20	6.15	85	1.06	3.1	0.26	81.9	0.02	0	1.61	3.65	98.11	100	1.35	6.02
20	1.42	85	1.06	3.1	0.26	82.6	1	1.71	0.27	2.82	5.66	44.84	0.01	2.95
20	2.11	85	1.06	3.1	0.26	82.5	0.99	0.78	0.25	2.94	6.6	74.84	-0.01	3.06
20	3.24	85	1.06	3.1	0.26	86.8	0.9	0.06	0.25	-2.12	15.09	98.06	-0.01	3.5
20	4.38	85	1.06	3.1	0.26	84.7	0.21	0	0.28	0.35	80.19	100	0.02	4.24
20	5.88	85	1.06	3.1	0.26	85.9	0.06	0	0.29	-1.06	94.34	100	0.03	4.81
20	7.05	85	1.06	3.1	0.26	83.9	0.04	0	0.34	1.29	96.23	100	0.08	5.11
20	8.58	85	1.06	3.1	0.26	85.3	0.03	0	0.42	-0.35	97.17	100	0.16	5.48
20	9.63	85	1.06	3.1	0.26	87.7	0.03	0	0.46	-3.18	97.17	100	0.2	5.9
20	1.88	85	1.06	3.1	0.26	82.8	0.99	1.78	0.27	2.59	6.6	42.58	0.01	2.92
20	2.44	85	1.06	3.1	0.26	83.2	1.01	0.75	0.28	2.12	4.72	75.81	0.02	2.97
20	3.42	85	1.06	3.1	0.26	82.1	0.91	0.03	0.27	3.41	14.15	99.03	0.01	3.45
20	4.23	85	1.06	3.1	0.26	82.8	0.18	0	0.3	2.59	83.02	100	0.04	4.22
20	6.25	85	1.06	3.1	0.26	82	0.07	0	0.31	3.53	93.4	100	0.05	4.98
20	7.2	85	1.06	3.1	0.26	81.5	0.04	0	0.32	4.12	96.23	100	0.06	5.14
20	9.03	85	1.06	3.1	0.26	79.8	0.03	0	0.33	6.12	97.17	100	0.07	5.37
20	10.56	85	1.06	3.1	0.26	79.7	0.03	0	0.31	6.24	97.17	100	0.05	5.91

Table A-6: Sodium addition to nickel product solution as a function of cobalt and iron extraction with pure Cyanex 272

Diluent:	Kerosene
Temperature (°C):	50
Agitation period (min):	5
O/A (ml/ml):	20/20

Cyanex 272 (V%)	3 M NaOH (ml)	Ni_o aqueous (g/l)	Co_o aqueous (g/l)	Fe_o aqueous (g/l)	Na_o aqueous (g/l)	Ni aqueous (g/l)	Co aqueous (g/l)	Fe aqueous (g/l)	Na aqueous (g/l)	Ni extracted (%)	Co extracted (%)	Fe extracted (%)	Na addition to aqueous phase after extraction (g/l)	pH
10	0.15	82	1.02	3	0.56	79	1.01	2.03	0.59	2.94	-0.25	31.83	0.03	3.05
10	0.35	82	1.02	3	0.56	79	1.00	1.40	1.20	1.97	-0.25	52.52	0.64	3.34
10	0.5	82	1.02	3	0.56	78	0.99	0.83	1.68	2.50	0.02	71.64	1.12	3.37
10	0.65	82	1.02	3	0.56	77	0.96	0.21	2.20	3.05	2.34	92.77	1.64	3.40
10	0.75	82	1.02	3	0.56	78	0.83	0.04	2.58	1.31	15.16	98.62	2.02	3.81
10	0.85	82	1.02	3	0.56	76	0.62	0.02	2.92	3.38	36.32	99.31	2.36	4.24
10	1	82	1.02	3	0.56	75	0.29	0.02	3.34	3.96	70.00	99.30	2.78	4.90
10	1.3	82	1.02	3	0.56	73	0.16	0.05	4.26	5.19	83.21	98.23	3.70	5.21
10	1.75	82	1.02	3	0.56	71	0.08	0.03	5.68	5.84	91.43	98.91	5.12	6.20
10	2	82	1.02	3	0.56	66	0.07	0.02	6.09	11.46	92.41	99.27	5.53	6.82
10	2.25	82	1.02	3	0.56	66	0.08	0.02	6.64	10.46	91.23	99.26	6.08	6.82
10	2.75	82	1.02	3	0.56	63	0.06	0.01	8.19	12.61	93.28	99.62	7.63	6.82
20	0.15	82	1.02	3	0.56	79	0.95	2.04	0.55	2.94	5.70	31.49	0.00	3.07
20	0.35	82	1.02	3	0.56	78	0.94	1.23	1.23	3.21	5.77	58.28	0.67	3.09
20	0.5	82	1.02	3	0.56	76	0.94	0.69	1.88	5.00	5.07	76.43	1.32	3.10
20	0.65	82	1.02	3	0.56	78	0.93	0.25	2.41	1.79	5.40	91.40	1.85	3.31
20	0.75	82	1.02	3	0.56	75	0.82	0.03	2.52	5.11	16.18	98.96	1.96	3.52
20	0.85	82	1.02	3	0.56	75	0.54	0.01	2.80	4.65	44.54	99.65	2.24	3.74
20	1	82	1.02	3	0.56	74	0.13	0.02	3.56	5.24	86.55	99.30	3.00	4.53
20	1.3	82	1.02	3	0.56	73	0.05	0.00	4.40	5.19	94.75	100.00	3.84	4.84
20	1.75	82	1.02	3	0.56	70	0.03	0.00	5.78	7.16	96.79	100.00	5.22	5.37
20	2	82	1.02	3	0.56	69	0.03	0.00	6.60	7.44	96.75	100.00	6.04	5.76
20	2.25	82	1.02	3	0.56	68	0.03	0.00	6.97	7.74	96.71	100.00	6.41	5.84
20	2.75	82	1.02	3	0.56	63	0.02	0.01	7.82	12.61	97.76	99.62	7.26	6.46

Table A-7: Effect of various diluents on nickel pre-loading

Temperature (°C):	50					
Agitation period (min):	5					
O/A (ml/ml):	20/20					

Diluent	Cyanex 272 (V%)	NaOH/Nio (mol/mol)	Ni_o aqueous (g/l)	Ni aqueous (g/l)	Ni extracted (%)	Ni-loading (g/l)	pH
Kerosene	10	0.21	10.30	9.65	5.17	0.53	5.7
Kerosene	10	0.43	10.30	8.91	11.36	1.17	6.14
Kerosene	10	0.85	10.30	6.49	33.86	3.49	6.6
Kerosene	10	1.71	10.30	2.36	74.80	7.71	7
Kerosene	20	0.21	10.30	9.33	8.31	0.86	5.4
Kerosene	20	0.43	10.30	8.17	18.72	1.93	5.64
Kerosene	20	0.85	10.30	6.31	35.70	3.68	6
Kerosene	20	1.71	10.30	1.96	79.07	8.15	6.9
Heptane	10	0.21	10.30	8.79	13.62	1.40	5.8
Heptane	10	0.43	10.30	8.6	14.45	1.49	5.9
Heptane	10	0.85	10.30	5.81	40.79	4.20	6.6
Heptane	10	1.71	10.30	1.64	82.49	8.50	7.1
Heptane	20	0.21	10.30	9.22	9.40	0.97	5.35
Heptane	20	0.43	10.30	8.03	20.12	2.07	5.6
Heptane	20	0.85	10.30	5.92	39.67	4.09	5.95
Heptane	20	1.71	10.30	2.07	77.90	8.03	6.6
Toluene	10	0.21	10.30	8.92	12.34	1.27	6
Toluene	10	0.43	10.30	7.95	20.91	2.15	6.4
Toluene	10	0.85	10.30	5.59	43.03	4.43	6.8
Toluene	10	1.71	10.30	1.72	81.64	8.41	7.3
Toluene	20	0.21	10.30	9.61	5.56	0.57	5.6
Toluene	20	0.43	10.30	7.23	28.07	1.87	5.95
Toluene	20	0.85	10.30	5.8	40.89	4.21	6.3
Toluene	20	1.71	10.30	1.97	78.97	8.14	6.9
Xylene	10	0.21	10.30	8.55	15.98	1.65	6.1
Xylene	10	0.43	10.30	7.92	21.21	2.19	6.45
Xylene	10	0.85	10.30	6.22	36.61	3.77	6.7
Xylene	10	1.71	10.30	1.64	82.49	8.50	7.2
Xylene	20	0.21	10.30	8.68	14.70	1.51	5.8
Xylene	20	0.43	10.30	8.42	16.24	1.67	5.9
Xylene	20	0.85	10.30	6.02	38.65	3.98	6.3
Xylene	20	1.71	10.30	1.77	81.10	8.36	6.9
Shellsol D70	10	0.21	10.35	9.17	10.29	1.07	5.7
Shellsol D70	10	0.43	10.35	8.23	18.50	1.91	6
Shellsol D70	10	0.85	10.35	6.16	37.51	3.88	6.6
Shellsol D70	10	1.70	10.35	1.87	80.13	8.29	7
Shellsol D70	20	0.21	10.35	9.44	7.65	0.79	5.31
Shellsol D70	20	0.43	10.35	8.3	17.80	1.84	5.58
Shellsol D70	20	0.85	10.35	6.44	34.67	3.59	6
Shellsol D70	20	1.70	10.35	1.89	79.91	8.27	6.8

Table A-8: Effect of various diluents on cobalt and iron extraction with Ni-Cyanex 272

Temperature (°C):	50
Agitation period (min):	5
O/A (ml/ml):	20/20

Diluent	Cyanex 272 (V%)	Ni-loading (g/l)	Ni_o aqueous (g/l)	Co_o aqueous (g/l)	Fe_o aqueous (g/l)	Ni aqueous (g/l)	Co aqueous (g/l)	Fe aqueous (g/l)	Ni extracted (%)	Co extracted (%)	Fe extracted (%)
Kerosene	10	0.53	81.96	1.05	2.99	80.4	1.05	1.76	1.91	0.00	41.14
Kerosene	10	1.17	81.96	1.05	2.99	82.1	1.04	0.86	-0.16	0.95	71.24
Kerosene	10	3.49	81.96	1.05	2.99	81	0.48	0.01	1.18	54.29	99.67
Kerosene	10	7.71	81.96	1.05	2.99	79.9	0.16	0	2.52	84.76	100.00
Kerosene	20	0.86	81.96	1.05	2.99	83	1.02	1.69	-1.26	2.86	43.48
Kerosene	20	1.93	81.96	1.05	2.99	87.7	1	0.79	-6.99	4.76	73.58
Kerosene	20	3.68	81.96	1.05	2.99	81.9	0.22	0	0.08	79.05	100.00
Kerosene	20	8.15	81.96	1.05	2.99	83.2	0.02	0	-1.50	98.10	100.00
Heptane	0.27	1.40	81.96	1.05	2.99	79.8	1.03	1.76	2.64	1.90	41.14
Heptane	0.27	1.49	81.96	1.05	2.99	80.1	0.99	0.75	2.28	5.71	74.92
Heptane	0.27	4.20	81.96	1.05	2.99	82.1	0.32	0	-0.16	69.52	100.00
Heptane	0.27	8.50	81.96	1.05	2.99	82	0.11	0	-0.04	89.52	100.00
Heptane	0.54	0.97	81.96	1.05	2.99	81.5	1.02	1.59	0.57	2.86	46.82
Heptane	0.54	2.07	81.96	1.05	2.99	79.4	0.99	0.69	3.13	5.71	76.92
Heptane	0.54	4.09	81.96	1.05	2.99	85	0.23	0	-3.70	78.10	100.00
Heptane	0.54	8.03	81.96	1.05	2.99	84	0.02	0	-2.48	98.10	100.00
Toluene	0.27	1.27	81.96	1.05	2.99	80.1	0.99	1.72	2.28	5.71	42.47
Toluene	0.27	2.15	81.96	1.05	2.99	84	1.02	0.86	-2.48	2.86	71.24
Toluene	0.27	4.43	81.96	1.05	2.99	86.4	0.48	0	-5.41	54.29	100.00
Toluene	0.27	8.41	81.96	1.05	2.99	84.3	0.21	0	-2.85	80.00	100.00
Toluene	0.54	0.57	81.96	1.05	2.99	82.4	1.03	1.78	-0.53	1.90	40.47
Toluene	0.54	1.87	81.96	1.05	2.99	82.6	1	0.82	-0.77	4.76	72.58
Toluene	0.54	4.21	81.96	1.05	2.99	86.9	0.22	0	-6.02	79.05	100.00
Toluene	0.54	8.14	81.96	1.05	2.99	91.7	0.02	0	-11.87	98.10	100.00
Xylene	0.27	1.65	81.96	1.05	2.99	85.6	1	1.74	-4.43	4.76	41.81
Xylene	0.27	2.19	81.96	1.05	2.99	83.6	0.98	0.77	-1.99	6.67	74.25
Xylene	0.27	3.77	81.96	1.05	2.99	87.5	0.44	0	-6.75	58.10	100.00
Xylene	0.27	8.50	81.96	1.05	2.99	87.9	0.2	0	-7.24	80.95	100.00
Xylene	0.54	1.51	81.96	1.05	2.99	81.2	1	1.78	0.94	4.76	40.47
Xylene	0.54	1.67	81.96	1.05	2.99	84	1.03	0.81	-2.48	1.90	72.91
Xylene	0.54	3.98	81.96	1.05	2.99	84.7	0.25	0	-3.33	76.19	100.00
Xylene	0.54	8.36	81.96	1.05	2.99	86.6	0.02	0	-5.65	98.10	100.00
Shellsol D70	0.27	1.07	82.1	1.14	3.25	81.4	1.13	1.81	0.85	0.88	44.31
Shellsol D70	0.27	1.91	82.1	1.14	3.25	81.9	1.12	0.94	0.24	1.75	71.08
Shellsol D70	0.27	3.88	82.1	1.14	3.25	86.7	0.55	0	-5.60	51.75	100.00
Shellsol D70	0.27	8.29	82.1	1.14	3.25	82.7	0.29	0	-0.73	74.56	100.00
Shellsol D70	0.54	0.79	82.1	1.14	3.25	84.1	1.11	1.82	-2.44	2.63	44.00
Shellsol D70	0.54	1.84	82.1	1.14	3.25	82.1	1.11	0.79	0.00	2.63	75.69
Shellsol D70	0.54	3.59	82.1	1.14	3.25	82.5	0.38	0	-0.49	66.67	100.00
Shellsol D70	0.54	8.27	82.1	1.14	3.25	82.5	0.02	0	-0.49	98.25	100.00

Table A-9: High and low values of the pre-loading and extraction 2^4 factorial designs

	Pre-loading											
Run	O/A ratio			Extractant concentration			NaOH addition			Temperature		
	a	ml organic	ml aqueous	b	(V%)		c	3 M ml		d	(°C)	
1	-1	40	20	-1	10		-1	1		-1	30	
2	1	10	20	-1	10		-1	1		-1	30	
3	-1	40	20	1	20		-1	1		-1	30	
4	1	10	20	1	20		-1	1		-1	30	
5	-1	40	20	-1	10		1	2		-1	30	
6	1	10	20	-1	10		1	2		-1	30	
7	-1	40	20	1	20		1	2		-1	30	
8	1	10	20	1	20		1	2		-1	30	
9	-1	40	20	-1	10		-1	1		1	60	
10	1	10	20	-1	10		-1	1		1	60	
11	-1	40	20	1	20		-1	1		1	60	
12	1	10	20	1	20		-1	1		1	60	
13	-1	40	20	-1	10		1	2		1	60	
14	1	10	20	-1	10		1	2		1	60	
15	-1	40	20	1	20		1	2		1	60	
16	1	10	20	1	20		1	2		1	60	
	Extraction											
Run	O/A ratio			Extractant concentration			Ni loading			Temperature		
	a	ml organic	ml aqueous	b	(V%)		c	g/l		d	(°C)	
1	-1	40	20	-1	10		-1	2.83		-1	30	
2	1	10	20	-1	10		-1	2.83		-1	30	
3	-1	40	20	1	20		-1	2.47		-1	30	
4	1	10	20	1	20		-1	2.47		-1	30	
5	-1	40	20	-1	10		1	4.76		-1	30	
6	1	10	20	-1	10		1	4.76		-1	30	
7	-1	40	20	1	20		1	4.66		-1	30	
8	1	10	20	1	20		1	4.66		-1	30	
9	-1	40	20	-1	10		-1	2.83		1	60	
10	1	10	20	-1	10		-1	2.83		1	60	
11	-1	40	20	1	20		-1	2.47		1	60	
12	1	10	20	1	20		-1	2.47		1	60	
13	-1	40	20	-1	10		1	4.76		1	60	
14	1	10	20	-1	10		1	4.76		1	60	
15	-1	40	20	1	20		1	4.66		1	60	
16	1	10	20	1	20		1	4.66		1	60	

Table A-10: Results for the pre-loading factorial design as shown in Table A-9

Diluent:		Shellsol D70				
Agitation period (min):		5				
Run/Repeat	Ni_o aqueous (g/l)	Na_o aqueous (g/l)	Ni aqueous (g/l)	Na aqueous (g/l)	Ni-loading (g/l)	Na addition to aqueous phase after extraction (g/l)	pH
1/1	9.76	0.02	5.66	3.17	1.91	3.15	6.11
1/2	9.76	0.02	5.69	3.17	1.89	3.15	6.1
1/3	9.76	0.02	5.33	3.24	2.08	3.22	6.14
2/1	9.76	0.02	4.92	2.71	9.19	2.69	6.82
2/2	9.76	0.02	5.34	2.91	8.31	2.89	6.83
2/3	9.76	0.02	5.14	3.17	8.73	3.15	6.81
3/1	9.76	0.02	5.38	3.23	2.05	3.21	5.63
3/2	9.76	0.02	5.33	3.14	2.08	3.12	5.63
3/3	9.76	0.02	5.35	3.07	2.07	3.05	5.62
4/1	9.76	0.02	5.63	3.05	7.70	3.03	6.46
4/2	9.76	0.02	5.31	3.18	8.38	3.16	6.46
4/3	9.76	0.02	5.35	2.74	8.28	2.72	6.46
5/1	9.76	0.02	1.46	5.26	4.08	5.24	6.94
5/2	9.76	0.02	1.42	5.60	4.10	5.58	6.94
5/3	9.76	0.02	1.41	5.53	4.10	5.51	6.95
6/1	9.76	0.02	1.07	5.66	17.16	5.64	7.84
6/2	9.76	0.02	0.65	5.86	18.09	5.84	7.83
6/3	9.76	0.02	0.63	5.97	18.13	5.95	7.87
7/1	9.76	0.02	1.34	5.66	4.14	5.64	6.33
7/2	9.76	0.02	1.39	5.80	4.11	5.78	6.3
7/3	9.76	0.02	1.45	5.76	4.08	5.74	6.29
8/1	9.76	0.02	1.12	5.73	17.05	5.71	7.28
8/2	9.76	0.02	1.11	5.95	17.09	5.93	7.3
8/3	9.76	0.02	1.13	5.85	17.03	5.83	7.29
9/1	9.76	0.02	5.31	2.96	2.09	2.94	6.25
9/2	9.76	0.02	5.43	3.29	2.03	3.27	6.26
9/3	9.76	0.02	5.42	3.14	2.03	3.12	6.23
10/1	9.76	0.02	5.27	3.01	8.44	2.99	6.68
10/2	9.76	0.02	5.44	3.12	8.10	3.10	6.71
10/3	9.76	0.02	4.80	2.81	9.43	2.79	6.65
11/1	9.76	0.02	5.38	2.76	2.05	2.74	5.65
11/2	9.76	0.02	5.40	3.15	2.04	3.13	5.66
11/3	9.76	0.02	5.40	3.17	2.05	3.15	5.63
12/1	9.76	0.02	5.40	3.21	8.19	3.19	6.56
12/2	9.76	0.02	5.32	3.24	8.35	3.22	6.53
12/3	9.76	0.02	5.39	3.27	8.21	3.25	6.58
13/1	9.76	0.02	1.46	5.63	4.08	5.61	6.82
13/2	9.76	0.02	1.39	5.77	4.12	5.75	6.85
13/3	9.76	0.02	1.38	5.91	4.12	5.89	6.86
14/1	9.76	0.02	0.93	5.01	17.48	4.99	7.35
14/2	9.76	0.02	0.66	5.32	18.07	5.30	7.45
14/3	9.76	0.02	0.90	4.98	17.55	4.96	7.25
15/1	9.76	0.02	1.22	5.52	4.21	5.50	6.42
15/2	9.76	0.02	1.41	5.31	4.11	5.29	6.41
15/3	9.76	0.02	1.19	5.92	4.22	5.90	6.43
16/1	9.76	0.02	0.91	5.36	17.51	5.34	7.16
16/2	9.76	0.02	0.86	5.80	17.62	5.78	7.18
16/3	9.76	0.02	0.99	5.30	17.34	5.28	7.12

Table A-11: Results for the extraction factorial design as shown in Table A-9

Diluent:		Shellsol D70							
Agitation period (min):		5							

Run/Repeat	Ni_o aqueous (g/l)	Co_o aqueous (g/l)	Fe_o aqueous (g/l)	Ni aqueous (g/l)	Co aqueous (g/l)	Fe aqueous (g/l)	Nickel extracted (%)	Cobalt extracted (%)	Iron extracted (%)	pH
1/1	85.30	1.09	2.96	83.10	0.14	0.03	2.58	87.10	98.89	5.04
1/2	85.30	1.09	2.96	79.00	0.16	0.00	7.39	85.07	100.00	4.97
1/3	85.30	1.09	2.96	82.80	0.17	0.00	2.93	84.79	100.00	4.87
2/1	85.30	1.09	2.96	82.00	1.03	1.82	3.87	5.16	38.48	3.55
2/2	85.30	1.09	2.96	76.80	0.97	1.95	9.96	10.23	34.26	3.70
2/3	85.30	1.09	2.96	79.90	0.97	1.70	6.33	10.97	42.57	3.40
3/1	85.30	1.09	2.96	78.30	0.24	0.03	8.21	77.88	98.92	4.45
3/2	85.30	1.09	2.96	77.90	0.23	0.00	8.68	78.99	100.00	4.55
3/3	85.30	1.09	2.96	81.40	0.22	0.00	4.57	80.00	100.00	4.60
4/1	85.30	1.09	2.96	78.50	0.86	1.70	7.97	20.83	42.57	3.76
4/2	85.30	1.09	2.96	77.60	0.94	1.99	9.03	13.55	32.70	3.87
4/3	85.30	1.09	2.96	77.70	1.00	1.96	8.91	7.47	33.82	3.60
5/1	85.30	1.09	2.96	84.30	0.02	0.00	1.17	97.79	100.00	5.64
5/2	85.30	1.09	2.96	78.60	0.02	0.00	7.85	97.79	100.00	5.70
5/3	85.30	1.09	2.96	83.40	0.02	0.00	2.23	97.97	100.00	5.70
6/1	85.30	1.09	2.96	78.00	0.92	1.09	8.56	15.30	63.31	4.64
6/2	85.30	1.09	2.96	77.50	0.89	1.09	9.14	18.34	63.07	4.72
6/3	85.30	1.09	2.96	81.10	0.91	0.91	4.92	15.76	69.19	4.50
7/1	85.30	1.09	2.96	80.30	0.02	0.00	5.86	98.34	100.00	5.27
7/2	85.30	1.09	2.96	78.60	0.02	0.00	7.85	98.25	100.00	5.27
7/3	85.30	1.09	2.96	78.40	0.02	0.00	8.09	98.43	100.00	5.27
8/1	85.30	1.09	2.96	83.80	0.98	1.00	1.76	9.31	66.39	4.05
8/2	85.30	1.09	2.96	76.50	0.90	1.11	10.32	17.42	62.60	4.20
8/3	85.30	1.09	2.96	83.00	1.04	0.77	2.70	4.61	73.89	3.80
9/1	85.30	1.09	2.96	78.80	0.17	0.00	7.62	84.24	100.00	4.93
9/2	85.30	1.09	2.96	79.00	0.18	0.00	7.39	83.87	100.00	4.80
9/3	85.30	1.09	2.96	75.10	0.19	0.00	11.96	82.67	100.00	4.81
10/1	85.30	1.09	2.96	75.10	1.05	1.59	11.96	2.95	46.25	3.32
10/2	85.30	1.09	2.96	76.20	1.07	1.62	10.67	1.20	45.24	3.33
10/3	85.30	1.09	2.96	88.50	1.05	1.75	-3.75	3.23	40.81	3.27
11/1	85.30	1.09	2.96	71.20	0.19	0.00	16.53	82.40	100.00	4.24
11/2	85.30	1.09	2.96	72.50	0.22	0.00	15.01	80.09	100.00	4.32
11/3	85.30	1.09	2.96	72.00	0.20	0.00	15.59	82.03	100.00	4.27
12/1	85.30	1.09	2.96	79.60	1.08	1.45	6.68	0.46	51.01	3.04
12/2	85.30	1.09	2.96	79.60	1.05	1.35	6.68	3.23	54.49	3.06
12/3	85.30	1.09	2.96	77.20	1.09	1.54	9.50	0.00	48.14	3.10
13/1	85.30	1.09	2.96	78.90	0.02	0.00	7.50	98.16	100.00	5.68
13/2	85.30	1.09	2.96	80.80	0.01	0.00	5.28	99.08	100.00	5.71
13/3	85.30	1.09	2.96	78.70	0.01	0.00	7.74	98.89	100.00	5.66
14/1	85.30	1.09	2.96	88.20	1.06	0.73	-3.40	2.67	75.34	3.77
14/2	85.30	1.09	2.96	80.00	1.06	0.64	6.21	2.12	78.28	3.73
14/3	85.30	1.09	2.96	79.50	1.08	0.66	6.80	0.18	77.60	3.65
15/1	85.30	1.09	2.96	79.00	0.01	0.00	7.39	99.08	100.00	5.25
15/2	85.30	1.09	2.96	79.40	0.01	0.00	6.92	99.26	100.00	5.22
15/3	85.30	1.09	2.96	79.90	0.01	0.00	6.33	98.89	100.00	5.26
16/1	85.30	1.09	2.96	80.80	1.07	0.65	5.28	1.29	78.14	3.25
16/2	85.30	1.09	2.96	89.20	1.05	0.55	-4.57	3.59	81.28	3.27
16/3	85.30	1.09	2.96	90.00	1.00	0.55	-5.51	7.83	81.32	3.35

Table A-12: Effect of temperature on nickel loading of Cyanex 272

Cyanex 272 (V%):	10			
Diluent:	Kerosene			
Agitation period (min):	5			
O/A (ml/ml):	20/20			
T (°C)	3 M NaOH (ml)	Ni_o aqueous (g/l)	Ni aqueous (g/l)	Ni-loading (g/l)
25	1	5.8	1.5	4.23
25	1.36	5.8	0.9	4.84
25	1.64	5.8	0.1	5.69
25	1.5	8.6	3.1	5.27
25	1.82	9.7	2.2	7.30
25	2.27	9.7	1	8.59
50	0.25	6.15	5.41	0.66
50	0.5	6.15	4.3	1.51
50	0.75	6.15	3.48	2.4
50	1	6.15	2.15	3.19
50	1.3	6.15	1.25	4.23
50	0.25	10.5	9.84	0.54
50	0.5	10.5	8.48	1.81
50	0.75	10.5	7.68	2.53
50	1	10.5	6	4.20
50	1.3	10.5	5.08	5.09
50	1.6	10.5	3.36	6.87
50	2	10.5	1.74	8.59
50	2.25	10.5	0.73	9.69

Table A-13: Effect of Cyanex 272 concentration on nickel loading of Cyanex 272

T (°C):	50
Diluent:	Kerosene
Agitation period (min):	5
O/A (ml/ml):	20/20

Cyanex 272 (V%)	3 M NaOH (ml)	Ni_o aqueous (g/l)	Ni aqueous (g/l)	Ni-loading (g/l)	pH
10	0.25	6.15	5.41	0.67	5.63
10	0.5	6.15	4.3	1.74	5.9
10	0.75	6.15	3.48	2.54	6.33
10	1	6.15	2.15	3.89	6.5
10	1.3	6.15	1.25	4.82	6.92
10	1.6	6.15	0.02	6.13	8.08
10	2	6.15	0	6.15	8.9
10	2.25	6.15	0.06	6.08	9
10	0.25	10.5	9.84	0.54	5.68
10	0.5	10.5	8.48	1.81	5.99
10	0.75	10.5	7.68	2.53	6.13
10	1	10.5	6	4.20	6.69
10	1.3	10.5	5.08	5.09	6.74
10	1.6	10.5	3.36	6.87	6.91
10	2	10.5	1.74	8.59	7.07
10	2.25	10.5	0.73	9.69	7.23
20	0.25	6.15	4.99	1.10	5.47
20	0.5	6.15	4.02	2.03	5.56
20	0.75	6.15	2.93	3.11	5.82
20	1	6.15	2.09	3.96	5.91
20	1.3	6.15	0.75	5.35	6.23
20	1.6	6.15	0.07	6.07	6.76
20	2	6.15	0	6.15	7.72
20	2.25	6.15	0	6.15	8.06
20	0.25	10.5	8.97	1.42	5.47
20	0.5	10.5	8.19	2.11	5.64
20	0.75	10.5	7	3.24	5.72
20	1	10.5	5.83	4.38	5.83
20	1.3	10.5	4.34	5.88	5.95
20	1.6	10.5	3.19	7.05	6.13
20	2	10.5	1.75	8.58	6.4
20	2.25	10.5	0.78	9.63	6.5

Table A-14: Effect of Cyanex 272 concentration on cobalt and iron extraction with Ni-Cyanex 272

T(°C):	50
Diluent:	Kerosene
Agitation period (min):	5
O/A (ml/ml):	20/20

Cyanex 272 (V%)	Ni-loading (g/l)	Ni_o aqueous (g/l)	Co_o aqueous (g/l)	Fe_o aqueous (g/l)	Ni aqueous (g/l)	Co aqueous (g/l)	Fe aqueous (g/l)	Nickel extracted (%)	Cobalt extracted (%)	Iron extracted (%)
10	0.67	85	1.06	3.1	81	1.03	1.8	4.71	2.83	41.94
10	1.74	85	1.06	3.1	79.9	1.02	0.85	6.00	3.77	72.58
10	2.54	85	1.06	3.1	83.8	1.03	0.04	1.41	2.83	98.71
10	3.89	85	1.06	3.1	78.4	0.37	0	7.76	65.09	100.00
10	4.82	85	1.06	3.1	80.2	0.22	0	5.65	79.25	100.00
10	6.13	85	1.06	3.1	77.5	0.21	0	8.82	80.19	100.00
10	6.15	85	1.06	3.1	74.5	0.22	0	12.35	79.25	100.00
10	0.54	85	1.06	3.1	78.2	1.01	1.81	8.00	4.72	41.61
10	1.81	85	1.06	3.1	81	1.01	0.87	4.71	4.72	71.94
10	2.53	85	1.06	3.1	84.4	0.93	0.05	0.71	12.26	98.39
10	4.20	85	1.06	3.1	87.4	0.36	0	-2.82	66.04	100.00
10	5.09	85	1.06	3.1	85.9	0.22	0	-1.06	79.25	100.00
10	6.87	85	1.06	3.1	87	0.18	0	-2.35	83.02	100.00
10	8.59	85	1.06	3.1	87.2	0.1	0	-2.59	90.57	100.00
10	9.69	85	1.06	3.1	87.2	0.18	0	-2.59	83.02	100.00
10	1.01	85	1.06	3.1	81.9	1.01	1.79	3.65	4.72	42.26
10	2.59	85	1.06	3.1	82.9	1.01	0.86	2.47	4.72	72.26
10	2.96	85	1.06	3.1	85.5	0.94	0	-0.59	11.32	100.00
10	4.23	85	1.06	3.1	86.1	0.36	0	-1.29	66.04	100.00
10	5.33	85	1.06	3.1	83.7	0.22	0	1.53	79.25	100.00
10	7.25	85	1.06	3.1	85.6	0.18	0	-0.71	83.02	100.00
10	8.51	85	1.06	3.1	84.1	0.14	0	1.06	86.79	100.00
10	10.10	85	1.06	3.1	83.4	0.13	0	1.88	87.74	100.00
20	1.10	85	1.06	3.1	81.7	1	1.71	3.88	5.66	44.84
20	2.03	85	1.06	3.1	81.1	1	0.73	4.59	5.66	76.45
20	3.11	85	1.06	3.1	82.2	0.98	0.07	3.29	7.55	97.74
20	3.96	85	1.06	3.1	84.8	0.21	0	0.24	80.19	100.00
20	5.35	85	1.06	3.1	81.7	0.07	0	3.88	93.40	100.00
20	6.07	85	1.06	3.1	82.5	0.04	0	2.94	96.23	100.00
20	6.15	85	1.06	3.1	80.6	0.03	0	5.18	97.17	100.00
20	6.15	85	1.06	3.1	81.9	0.02	0	3.65	98.11	100.00
20	1.42	85	1.06	3.1	82.6	1	1.71	2.82	5.66	44.84
20	2.11	85	1.06	3.1	82.5	0.99	0.78	2.94	6.60	74.84
20	3.24	85	1.06	3.1	86.8	0.9	0.06	-2.12	15.09	98.06
20	4.38	85	1.06	3.1	84.7	0.21	0	0.35	80.19	100.00
20	5.88	85	1.06	3.1	85.9	0.06	0	-1.06	94.34	100.00
20	7.05	85	1.06	3.1	83.9	0.04	0	1.29	96.23	100.00
20	8.58	85	1.06	3.1	85.3	0.03	0	-0.35	97.17	100.00
20	9.63	85	1.06	3.1	87.7	0.03	0	-3.18	97.17	100.00
20	1.88	85	1.06	3.1	82.8	0.99	1.78	2.59	6.60	42.58
20	2.44	85	1.06	3.1	83.2	1.01	0.75	2.12	4.72	75.81
20	3.42	85	1.06	3.1	82.1	0.91	0.03	3.41	14.15	99.03
20	4.23	85	1.06	3.1	82.8	0.18	0	2.59	83.02	100.00
20	6.25	85	1.06	3.1	82	0.07	0	3.53	93.40	100.00
20	7.20	85	1.06	3.1	81.5	0.04	0	4.12	96.23	100.00
20	9.03	85	1.06	3.1	79.8	0.03	0	6.12	97.17	100.00
20	10.56	85	1.06	3.1	79.7	0.03	0	6.24	97.17	100.00

Table A-15: Effect of temperature on the cobalt and iron extraction with Ni-Cyanex 272

Cyanex 272 (V%):	20
Diluent:	Kerosene
Agitation period (min):	5
O/A (ml/ml):	20/20

T(°C)	Ni-loading (g/l)	Ni_o aqueous (g/l)	Co_o aqueous (g/l)	Fe_o aqueous (g/l)	Ni aqueous (g/l)	Co aqueous (g/l)	Fe aqueous (g/l)	Nickel extracted (%)	Cobalt extracted (%)	Iron extracted (%)
25	1.05	72	1	3.1	67	0.8	2.2	6.94	20.00	29.03
25	2.02	72	1	3.1	69	0.7	1.4	4.17	30.00	54.84
25	2.71	72	1	3.1	71	0.4	0.73	1.39	60.00	76.45
25	3.81	72	1.1	3.1	72	0.4	1.02	0.00	63.64	67.10
25	8.14	72	1.1	3.1	72	0	0.01	0.00	100.00	99.68
25	7.77	72	1.1	3.1	72	0	0.01	0.00	100.00	99.68
25	10.78	72	1.1	3.1	72	0	0.01	0.00	100.00	99.68
25	12.77	72	1.1	3.1	69	0	0.01	4.17	100.00	99.68
25	8.68	72	1.1	3.1	70	0	0.01	2.78	100.00	99.68
25	11.44	72	1.1	3.1	70	0	0.01	2.78	100.00	99.68
25	13.60	72	1.1	3.1	71	0	0.02	1.39	100.00	99.35
50	1.10	85	1.06	3.1	81.7	1	1.71	3.88	5.66	44.84
50	2.03	85	1.06	3.1	81.1	1	0.73	4.59	5.66	76.45
50	3.11	85	1.06	3.1	82.2	0.98	0.07	3.29	7.55	97.74
50	3.96	85	1.06	3.1	84.8	0.21	0	0.24	80.19	100.00
50	5.35	85	1.06	3.1	81.7	0.07	0	3.88	93.40	100.00
50	6.07	85	1.06	3.1	82.5	0.04	0	2.94	96.23	100.00
50	6.15	85	1.06	3.1	80.6	0.03	0	5.18	97.17	100.00
50	6.15	85	1.06	3.1	81.9	0.02	0	3.65	98.11	100.00
50	1.42	85	1.06	3.1	82.6	1	1.71	2.82	5.66	44.84
50	2.11	85	1.06	3.1	82.5	0.99	0.78	2.94	6.60	74.84
50	3.24	85	1.06	3.1	86.8	0.9	0.06	-2.12	15.09	98.06
50	4.38	85	1.06	3.1	84.7	0.21	0	0.35	80.19	100.00
50	5.88	85	1.06	3.1	85.9	0.06	0	-1.06	94.34	100.00
50	7.05	85	1.06	3.1	83.9	0.04	0	1.29	96.23	100.00
50	8.58	85	1.06	3.1	85.3	0.03	0	-0.35	97.17	100.00
50	9.63	85	1.06	3.1	87.7	0.03	0	-3.18	97.17	100.00
50	1.88	85	1.06	3.1	82.8	0.99	1.78	2.59	6.60	42.58
50	2.44	85	1.06	3.1	83.2	1.01	0.75	2.12	4.72	75.81
50	3.42	85	1.06	3.1	82.1	0.91	0.03	3.41	14.15	99.03
50	4.23	85	1.06	3.1	82.8	0.18	0	2.59	83.02	100.00
50	6.25	85	1.06	3.1	82	0.07	0	3.53	93.40	100.00
50	7.20	85	1.06	3.1	81.5	0.04	0	4.12	96.23	100.00
50	9.03	85	1.06	3.1	79.8	0.03	0	6.12	97.17	100.00
50	10.56	85	1.06	3.1	79.7	0.03	0	6.24	97.17	100.00

Table A-16: Variation in O/A ratio and nickel loading for nickel, cobalt and iron extraction

Cyanex 272 (V%):	20
Diluent:	Shellsol D70
Agitation period (min):	5
T(°C):	50

O/A (ml/ml)	Ni-loading (g/l)	Ni_o aqueous (g/l)	Co_o aqueous (g/l)	Fe_o aqueous (g/l)	Na_o aqueous (g/l)	Ni aqueous (g/l)	Co aqueous (g/l)	Fe aqueous (g/l)	Na aqueous (g/l)	Nickel extracted (%)	Cobalt extracted (%)	Iron extracted (%)	Ni-organic (g/l)	Co-organic (g/l)	Fe-organic (g/l)	Na addition to aqueous phase after extraction (g/l)	pH
5/20	0.56	90.1	1.12	2.98	0.08	86.6	1.07	2.64	0.06	3.88	4.38	11.58	14.56	0.2	1.38	-0.02	3.16
10/20	0.56	90.1	1.12	2.98	0.08	85.9	1.08	2.5	0.06	4.66	3.58	15.97	8.96	0.08	0.95	-0.02	3.44
15/20	0.56	90.1	1.12	2.98	0.08	90.3	1.09	2.14	0.06	-0.22	2.68	28.09	0.3	0.04	1.12	-0.02	3.18
20/20	0.56	90.1	1.12	2.98	0.08	91.1	1.05	1.95	0.06	-1.11	6.08	34.56	-0.44	0.07	1.03	-0.03	3.05
30/20	0.56	90.1	1.12	2.98	0.08	87	1	1.4	0.06	3.44	10.38	52.95	2.63	0.08	1.05	-0.02	3.1
40/20	0.56	90.1	1.12	2.98	0.08	82.2	1.03	1.13	0.05	8.77	8.23	62.18	4.51	0.05	0.93	-0.03	3.13
50/20	0.56	90.1	1.12	2.98	0.08	86.3	1.06	0.83	0.08	4.22	5.46	72.01	2.08	0.02	0.86	-0.01	3.14
60/20	0.56	90.1	1.12	2.98	0.08	87.9	1.06	0.53	0.07	2.44	5.19	82.08	1.3	0.02	0.82	-0.01	3.19
5/20	1.97	90.1	1.12	2.98	0.08	89.3	1.12	2.3	0.06	0.89	0	22.68	5.17	0	2.7	-0.03	3.11
10/20	1.97	90.1	1.12	2.98	0.08	87.1	1.09	1.83	0.1	3.33	2.86	38.49	7.97	0.06	2.29	0.02	3.08
15/20	1.97	90.1	1.12	2.98	0.08	86.1	1.08	1.27	0.06	4.44	3.76	57.32	7.3	0.06	2.28	-0.02	3.09
20/20	1.97	90.1	1.12	2.98	0.08	86	1.05	0.75	0.07	4.55	5.72	74.87	6.07	0.06	2.23	-0.01	3.16
30/20	1.97	90.1	1.12	2.98	0.08	90	1.04	0.04	0.09	0.11	7.25	98.79	2.03	0.05	1.96	0.01	3.52
40/20	1.97	90.1	1.12	2.98	0.08	90.1	0.26	0.01	0.08	0	76.39	99.53	1.97	0.43	1.48	0	4.34
50/20	1.97	90.1	1.12	2.98	0.08	92.4	0.06	0.01	0.07	-2.55	94.45	99.6	1.05	0.42	1.19	-0.01	4.76
60/20	1.97	90.1	1.12	2.98	0.08	95.2	0.05	0.01	0.1	-5.66	95.8	99.63	0.27	0.36	0.99	0.01	4.98
5/20	2.94	90.1	1.12	2.98	0.08	85.5	1.06	2.11	0.08	5.11	5.55	29.19	21.34	0.25	3.48	0	3.42
10/20	2.94	90.1	1.12	2.98	0.08	85	1.07	1.17	0.06	5.66	4.11	60.6	13.14	0.09	3.61	-0.02	3.16
15/20	2.94	90.1	1.12	2.98	0.08	85.2	1.07	0.6	0.05	5.44	4.38	79.83	9.47	0.07	3.17	-0.03	3.13
20/20	2.94	90.1	1.12	2.98	0.08	94.3	0.99	0.09	0.05	-4.66	11.18	96.88	-1.26	0.13	2.89	-0.03	3.67
30/20	2.94	90.1	1.12	2.98	0.08	89.5	0.1	0.05	0.1	0.67	91.14	98.32	3.34	0.68	1.95	0.02	4.6
40/20	2.94	90.1	1.12	2.98	0.08	89	0.05	0.04	0.07	1.22	95.71	98.83	3.49	0.54	1.47	-0.01	5.06
50/20	2.94	90.1	1.12	2.98	0.08	89.6	0.04	0.02	0.08	0.55	96.33	99.33	3.14	0.43	1.18	0	5.08
60/20	2.94	90.1	1.12	2.98	0.08	87.9	0.04	0.01	0.09	2.44	96.78	99.56	3.67	0.36	0.99	0.01	5.14

O/A (ml/ml)	Ni-loading (g/l)	Ni_o aqueous (g/l)	Co_o aqueous (g/l)	Fe_o aqueous (g/l)	Na_o aqueous (g/l)	Ni aqueous (g/l)	Co aqueous (g/l)	Fe aqueous (g/l)	Na aqueous (g/l)	Nickel extracted (%)	Cobalt extracted (%)	Iron extracted (%)	Ni-organic (g/l)	Co-organic (g/l)	Fe-organic (g/l)	Na addition to aqueous phase after extraction (g/l)	pH
5/20	3.95	90.1	1.12	2.98	0.08	93.3	1.1	1.92	0.08	-3.55	1.52	35.67	-8.85	0.07	4.25	0	3.47
10/20	3.95	90.1	1.12	2.98	0.08	89.9	1.1	0.77	0.07	0.22	1.43	74.03	4.35	0.03	4.41	-0.02	3.21
15/20	3.95	90.1	1.12	2.98	0.08	90	1.02	0.08	0.1	0.11	9.03	97.45	4.08	0.13	3.87	0.02	3.62
20/20	3.95	90.1	1.12	2.98	0.08	94.7	0.21	0.03	0.08	-5.11	81.13	98.93	-0.65	0.91	2.95	-0.01	4.67
30/20	3.95	90.1	1.12	2.98	0.08	91.4	0.05	0.03	0.11	-1.44	95.17	99.16	3.08	0.71	1.97	0.03	5.06
40/20	3.95	90.1	1.12	2.98	0.08	91.3	0.04	0.02	0.09	-1.33	96.51	99.4	3.35	0.54	1.48	0.01	5.21
50/20	3.95	90.1	1.12	2.98	0.08	90.7	0.04	0.01	0.16	-0.67	96.69	99.66	3.71	0.43	1.19	0.08	5.27
60/20	3.95	90.1	1.12	2.98	0.08	92.3	0.04	0	0.12	-2.44	96.78	100	3.21	0.36	0.99	0.04	5.3
5/20	4.69	90.1	1.12	2.98	0.08	90.7	1.11	1.77	0.06	-0.67	0.63	40.6	2.29	0.03	4.84	-0.02	3.67
10/20	4.69	90.1	1.12	2.98	0.08	93.3	1.09	0.66	0.06	-3.55	2.86	78.02	-1.71	0.06	4.65	-0.02	3.83
15/20	4.69	90.1	1.12	2.98	0.08	87.2	0.55	0.05	0.07	3.22	50.54	98.26	8.56	0.75	3.9	-0.01	4.41
20/20	4.69	90.1	1.12	2.98	0.08	93.5	0.09	0.04	0.11	-3.77	91.68	98.56	1.29	1.03	2.94	0.03	4.89
30/20	4.69	90.1	1.12	2.98	0.08	93	0.04	0.01	0.1	-3.22	96.15	99.63	2.76	0.72	1.98	0.02	5.24
40/20	4.69	90.1	1.12	2.98	0.08	88	0.04	0	0.12	2.33	96.69	100	5.74	0.54	1.49	0.03	5.35
50/20	4.69	90.1	1.12	2.98	0.08	91.5	0.04	0	0.17	-1.55	96.78	100	4.13	0.43	1.19	0.09	5.41
60/20	4.69	90.1	1.12	2.98	0.08	89.6	0.03	0	0.15	0.55	96.96	100	4.86	0.36	0.99	0.07	5.46
5/20	5.73	90.1	1.12	2.98	0.08	88.8	1.09	1.47	0.13	1.44	2.24	50.57	10.93	0.1	6.03	0.05	3.77
10/20	5.73	90.1	1.12	2.98	0.08	93.1	1.06	0.13	0.08	-3.33	4.83	95.7	-0.27	0.11	5.7	0	3.6
15/20	5.73	90.1	1.12	2.98	0.08	88.1	0.17	0	0.07	2.22	85.06	100	8.39	1.27	3.97	-0.01	4.93
20/20	5.73	90.1	1.12	2.98	0.08	92.9	0.07	0	0.12	-3.11	94.01	100	2.93	1.05	2.98	0.04	5.1
30/20	5.73	90.1	1.12	2.98	0.08	89.3	0.04	0	0.12	0.89	96.33	100	6.26	0.72	1.99	0.04	5.33
40/20	5.73	90.1	1.12	2.98	0.08	90.8	0.04	0	0.15	-0.78	96.87	100	5.38	0.54	1.49	0.06	5.5
50/20	5.73	90.1	1.12	2.98	0.08	88	0.03	0	0.25	2.33	97.05	100	6.57	0.43	1.19	0.17	5.52
60/20	5.73	90.1	1.12	2.98	0.08	92.3	0.03	0	0.2	-2.44	97.14	100	4.99	0.36	0.99	0.12	5.58

Table A-17: Variation in O/A ratio and NaOH addition for nickel loading of Cyanex 272

Cyanex 272 (V%):	20
Diluent:	Shellsol D70
Agitation period (min):	5
T (°C):	50

O/A (ml/ml)	3 M NaOH (ml)	Ni_o aqueous (g/l)	Na_o aqueous (g/l)	Ni aqueous (g/l)	Na aqueous (g/l)	Ni - extracted (%)	Ni-loading (g/l)	pH
80/3	2.5	88.4	0.4	7.4	34	84.65	2.81	5.99
80/3	3	88.4	0.4	2.7	34.9	93.89	3.11	6.4
80/3	4	88.4	0.4	0.6	33	98.42	3.26	6.95
80/3	5	88.4	0.4	0	26	100.00	3.32	7.28
80/3	5.5	88.4	0.4	0	26.2	100.00	3.32	7.37
80/3	6	88.4	0.4	0	26.4	100.00	3.32	7.48
80/4	2.5	88.4	0.4	16.9	27.8	68.93	3.05	5.86
80/4	3	88.4	0.4	11	33.9	78.22	3.46	6.05
80/4	4	88.4	0.4	1.1	30.6	97.51	4.31	6.6
80/4	5	88.4	0.4	0	27.7	100.00	4.42	7.01
80/4	5.5	88.4	0.4	0	28	100.00	4.42	7.24
80/4	6	88.4	0.4	0	25.9	100.00	4.42	7.4
80/5	2.5	88.4	0.4	23	21.7	60.97	3.37	5.78
80/5	3	88.4	0.4	17	25.7	69.23	3.83	5.82
80/5	4	88.4	0.4	7.3	30.7	85.14	4.70	6.28
80/5	5	88.4	0.4	1.5	32.5	96.61	5.34	6.67
80/5	5.5	88.4	0.4	0.4	30.8	99.05	5.47	6.96
80/5	6	88.4	0.4	0	31.2	100.00	5.53	7.2
80/6	2.5	88.4	0.4	31.5	20.9	49.52	3.28	5.76
80/6	3	88.4	0.4	25.3	24.2	57.07	3.78	5.86
80/6	4	88.4	0.4	13.9	28.4	73.79	4.89	6.17
80/6	5	88.4	0.4	6.3	29.9	86.93	5.76	6.42
80/6	5.5	88.4	0.4	2.8	31.1	93.93	6.23	6.65
80/6	6	88.4	0.4	0.9	32.6	97.96	6.50	6.9

Table A-18: Data for the stripping kinetics of nickel, cobalt and iron

Diluent:	Shellsol D70
Cyanex 272 (V%)	20
Temperature (°C):	50
A/O (ml/ml):	20/20

Agitation period (s)	H_2SO_4 (M)	Ni_o organic (g/l)	Co_o organic (g/l)	Fe_o organic (g/l)	Ni aqueous (g/l)	Co aqueous (g/l)	Fe aqueous (g/l)	Ni stripped (%)	Co stripped (%)	Fe stripped (%)
30	0.1	4.52	1.05	2.96	3.48	0.37	0.00	77.03	35.57	0.00
60	0.1	4.52	1.05	2.96	3.38	0.68	0.00	74.81	64.74	0.00
300	0.1	4.52	1.05	2.96	3.91	0.85	0.00	86.54	81.29	0.00
420	0.1	4.52	1.05	2.96	3.90	0.89	0.00	86.32	84.63	0.00
600	0.1	4.52	1.05	2.96	3.94	0.92	0.00	87.21	87.88	0.00
900	0.1	4.52	1.05	2.96	4.00	0.92	0.00	88.53	87.98	0.00
30	0.5	4.52	1.05	2.96	2.60	0.50	1.71	57.55	48.10	57.73
60	0.5	4.52	1.05	2.96	2.92	0.58	1.93	64.63	55.47	65.02
300	0.5	4.52	1.05	2.96	4.17	0.99	2.40	92.30	95.06	81.03
420	0.5	4.52	1.05	2.96	4.41	1.01	2.34	97.61	96.49	79.07
600	0.5	4.52	1.05	2.96	4.32	1.02	2.37	95.62	97.16	79.88
900	0.5	4.52	1.05	2.96	4.29	1.01	2.42	94.95	96.30	81.63

Table A-19: High and low values of the stripping 2^4 factorial design

Run	O/A ratio			Acid concentration			Metal loading		Temperature	
	a	ml organic	ml aqueous	b	M	c	g/l Ni, Co, Fe	d	(°C)	
1	-1	20	40	-1	0.1	-1	2.26, 0.52, 1.58	-1	30	
2	1	20	10	-1	0.1	-1	2.26, 0.52, 1.58	-1	30	
3	-1	20	40	1	0.5	-1	2.26, 0.52, 1.58	-1	30	
4	1	20	10	1	0.5	-1	2.26, 0.52, 1.58	-1	30	
5	-1	20	40	-1	0.1	1	4.67, 1.03, 3.14	-1	30	
6	1	20	10	-1	0.1	1	4.67, 1.03, 3.14	-1	30	
7	-1	20	40	1	0.5	1	4.67, 1.03, 3.14	-1	30	
8	1	20	10	1	0.5	1	4.67, 1.03, 3.14	-1	30	
9	-1	20	40	-1	0.1	-1	2.26, 0.52, 1.58	1	60	
10	1	20	10	-1	0.1	-1	2.26, 0.52, 1.58	1	60	
11	-1	20	40	1	0.5	-1	2.26, 0.52, 1.58	1	60	
12	1	20	10	1	0.5	-1	2.26, 0.52, 1.58	1	60	
13	-1	20	40	-1	0.1	1	4.67, 1.03, 3.14	1	60	
14	1	20	10	-1	0.1	1	4.67, 1.03, 3.14	1	60	
15	-1	20	40	1	0.5	1	4.67, 1.03, 3.14	1	60	
16	1	20	10	1	0.5	1	4.67, 1.03, 3.14	1	60	

Table A-20: Results for the stripping factorial design as shown in table 5-19

	Diluent:	Shellsol D70								
	Agitation period (min):	10								
Run/Repeat	Ni$_o$ organic (g/l)	Co$_o$ organic (g/l)	Fe$_o$ organic (g/l)	Ni aqueous (g/l)	Co aqueous (g/l)	Fe aqueous (g/l)	Nickel stripped (%)	Cobalt stripped (%)	Iron stripped (%)	pH
11	2.26	0.52	1.58	1.08	0.25	0.05	95.72	96.82	6.20	1.98
12	2.26	0.52	1.58	1.03	0.24	0.06	91.29	91.86	6.96	1.80
13	2.26	0.52	1.58	1.14	0.23	0.06	101.04	87.67	7.97	1.77
21	2.26	0.52	1.58	4.21	1.00	0.00	93.29	95.58	0.00	2.67
22	2.26	0.52	1.58	4.12	0.95	0.00	91.29	90.82	0.00	2.68
23	2.26	0.52	1.58	4.16	0.99	0.00	92.18	94.53	0.00	2.64
31	2.26	0.52	1.58	1.10	0.26	0.70	97.50	98.73	88.80	1.47
32	2.26	0.52	1.58	1.07	0.25	0.70	94.84	94.91	89.06	1.42
33	2.26	0.52	1.58	1.08	0.24	0.66	95.72	91.86	83.62	1.40
41	2.26	0.52	1.58	4.20	0.97	1.73	93.07	92.34	54.84	1.51
42	2.26	0.52	1.58	4.01	0.91	1.62	88.86	87.10	51.27	1.47
43	2.26	0.52	1.58	3.96	0.93	1.53	87.75	88.81	48.23	1.48
51	4.67	1.03	3.14	1.83	0.37	0.07	78.36	71.11	4.59	1.88
52	4.67	1.03	3.14	1.95	0.39	0.06	83.50	75.37	3.76	1.87
53	4.67	1.03	3.14	1.84	0.38	0.03	78.79	73.04	2.17	1.89
61	4.67	1.03	3.14	4.96	0.01	0.00	53.10	0.44	0.00	5.59
62	4.67	1.03	3.14	4.93	0.01	0.00	52.78	0.44	0.00	5.97
63	4.67	1.03	3.14	5.42	0.01	0.00	58.02	0.39	0.00	5.67
71	4.67	1.03	3.14	2.08	0.44	1.27	89.07	85.44	81.02	1.50
72	4.67	1.03	3.14	2.08	0.45	1.33	89.07	87.96	84.84	1.42
73	4.67	1.03	3.14	2.00	0.42	1.24	85.64	81.76	79.17	1.40
81	4.67	1.03	3.14	8.47	1.86	1.50	90.68	89.90	23.90	1.54
82	4.67	1.03	3.14	8.37	1.76	1.47	89.61	85.25	23.46	1.51
83	4.67	1.03	3.14	8.65	1.78	1.40	92.60	86.12	22.29	1.47
91	2.26	0.52	1.58	1.13	0.27	0.00	100.16	101.77	0.00	1.81
92	2.26	0.52	1.58	1.30	0.26	0.00	107.25	98.34	0.00	1.74
93	2.26	0.52	1.58	1.23	0.24	0.00	109.02	93.01	0.00	1.77
101	2.26	0.52	1.58	4.29	0.95	0.00	95.06	90.63	0.00	2.87
102	2.26	0.52	1.58	4.10	0.96	0.00	90.85	91.67	0.00	2.85
103	2.26	0.52	1.58	4.36	0.99	0.00	96.61	94.63	0.00	2.88
111	2.26	0.52	1.58	1.19	0.26	0.59	105.47	97.20	75.14	1.41
112	2.26	0.52	1.58	1.11	0.26	0.55	98.38	100.63	68.94	1.34
113	2.26	0.52	1.58	1.14	0.25	0.52	101.04	96.82	65.78	1.30
121	2.26	0.52	1.58	4.45	1.02	2.09	98.60	97.58	66.07	1.50
122	2.26	0.52	1.58	4.36	0.95	1.90	96.61	90.24	60.12	1.40
123	2.26	0.52	1.58	4.30	1.01	2.09	95.28	96.34	66.07	1.33
131	4.67	1.03	3.14	2.23	0.47	0.00	95.49	90.87	0.00	2.18
132	4.67	1.03	3.14	2.13	0.44	0.00	91.21	85.83	0.00	2.09
133	4.67	1.03	3.14	2.16	0.45	0.00	92.50	87.57	0.00	2.00
141	4.67	1.03	3.14	5.69	0.01	0.00	60.91	0.24	0.00	5.04
142	4.67	1.03	3.14	5.31	0.00	0.00	56.85	0.10	0.00	5.18
143	4.67	1.03	3.14	5.60	0.00	0.00	59.95	0.19	0.00	5.20
151	4.67	1.03	3.14	2.31	0.48	1.26	98.92	93.77	80.32	1.57
152	4.67	1.03	3.14	2.39	0.49	1.27	102.34	94.35	80.57	1.48
153	4.67	1.03	3.14	2.27	0.49	1.23	97.21	94.94	78.09	1.49
161	4.67	1.03	3.14	9.41	2.00	2.73	100.74	96.78	43.39	1.62
162	4.67	1.03	3.14	9.20	1.94	2.65	98.49	94.16	42.20	1.57
163	4.67	1.03	3.14	9.02	1.93	2.80	96.56	93.29	44.54	1.58

Table A-21: Variation in O/A ratio and aid concentration for nickel, cobalt and iron stripping

Cyanex 272 (V%)	20
Diluent:	Shellsol D70
Agitation period (min):	10
T(°C)	50

A/O (ml/ml)	H_2SO_4 (M)	Ni_o organic (g/l)	Co_o organic (g/l)	Fe_o organic (g/l)	Ni aqueous (g/l)	Co aqueous (g/l)	Fe aqueous (g/l)	Nickel stripped (%)	Cobalt stripped (%)	Iron stripped (%)	pH
10/20	0.025	2.96	0.75	2.08	1.19	0.01	0.00	20.02	0.47	0.00	5.75
15/20	0.025	2.96	0.75	2.08	1.01	0.00	0.00	25.55	0.30	0.00	5.88
20/20	0.025	2.96	0.75	2.08	1.02	0.00	0.00	34.44	0.40	0.00	5.79
30/20	0.025	2.96	0.75	2.08	1.12	0.00	0.00	56.88	0.00	0.00	5.68
45/20	0.025	2.96	0.75	2.08	1.04	0.00	0.00	78.71	0.30	0.00	5.44
60/20	0.025	2.96	0.75	2.08	0.92	0.14	0.00	93.50	55.75	0.00	4.08
10/20	0.05	2.96	0.75	2.08	3.29	0.00	0.00	55.51	0.20	0.00	5.41
15/20	0.05	2.96	0.75	2.08	3.17	0.01	0.00	80.21	0.50	0.00	5.36
20/20	0.05	2.96	0.75	2.08	2.74	0.40	0.00	92.49	54.02	0.00	3.8
30/20	0.05	2.96	0.75	2.08	1.76	0.45	0.00	88.94	89.85	0.00	2.42
45/20	0.05	2.96	0.75	2.08	1.24	0.30	0.00	94.21	89.35	0.00	2.16
60/20	0.05	2.96	0.75	2.08	0.99	0.23	0.00	100.39	90.25	0.00	2.04
10/20	0.075	2.96	0.75	2.08	3.94	0.00	0.00	66.52	0.20	0.00	5.54
15/20	0.075	2.96	0.75	2.08	3.50	0.60	0.00	88.72	60.47	0.00	3.71
20/20	0.075	2.96	0.75	2.08	2.74	0.69	0.00	92.39	92.52	0.00	2.43
30/20	0.075	2.96	0.75	2.08	1.78	0.44	0.00	90.16	88.04	0.00	2.1
45/20	0.075	2.96	0.75	2.08	1.25	0.27	0.00	94.97	82.43	0.00	1.98
60/20	0.075	2.96	0.75	2.08	1.00	0.23	0.00	101.30	92.66	0.00	1.91
10/20	0.1	2.87	0.75	2.10	5.36	0.02	0.00	93.25	1.20	0.00	4.77
15/20	0.1	2.87	0.75	2.10	3.71	0.95	0.00	96.78	94.58	0.00	2.5
20/20	0.1	2.87	0.75	2.10	2.80	0.71	0.00	97.65	94.98	0.00	2.24
30/20	0.1	2.87	0.75	2.10	1.69	0.42	0.00	88.34	83.01	0.00	2.1
45/20	0.1	2.87	0.75	2.10	1.25	0.28	0.00	98.19	82.91	0.00	1.91
60/20	0.1	2.87	0.75	2.10	0.99	0.24	0.00	103.44	95.38	0.00	1.82
10/20	0.25	2.87	0.75	2.10	5.30	1.29	0.01	92.29	86.07	0.14	2.06
15/20	0.25	2.87	0.75	2.10	3.70	0.91	0.78	96.64	90.59	27.74	1.75
20/20	0.25	2.87	0.75	2.10	2.88	0.72	0.87	100.27	95.65	41.23	1.69
30/20	0.25	2.87	0.75	2.10	1.89	0.48	0.69	98.73	95.58	49.48	1.7
45/20	0.25	2.87	0.75	2.10	1.38	0.31	0.45	101.87	93.39	48.15	1.6
60/20	0.25	2.87	0.75	2.10	1.05	0.23	0.32	104.48	93.39	45.76	1.58
10/20	0.5	2.87	0.75	2.10	6.00	1.48	2.95	104.48	98.64	70.26	1.6
15/20	0.5	2.87	0.75	2.10	3.76	0.95	2.21	98.11	94.28	78.97	1.46
20/20	0.5	2.87	0.75	2.10	2.75	0.70	1.71	95.88	93.25	81.46	1.45
30/20	0.5	2.87	0.75	2.10	1.98	0.49	1.20	103.17	98.57	85.87	1.4
45/20	0.5	2.87	0.75	2.10	1.24	0.32	0.74	97.17	95.48	79.58	1.39
60/20	0.5	2.87	0.75	2.10	1.02	0.25	0.57	106.57	98.97	81.51	1.38
10/20	0.75	2.89	0.72	2.03	5.70	1.33	3.05	98.64	93.01	75.05	1.5
15/20	0.75	2.89	0.72	2.03	3.88	0.95	2.43	100.71	99.37	89.68	1.43
20/20	0.75	2.89	0.72	2.03	2.87	0.72	1.82	99.13	100.35	89.23	1.42
30/20	0.75	2.89	0.72	2.03	2.02	0.45	1.23	104.89	94.76	90.71	1.39
45/20	0.75	2.89	0.72	2.03	1.28	0.33	0.78	99.80	103.14	85.73	1.36
60/20	0.75	2.89	0.72	2.03	0.96	0.26	0.57	99.65	108.59	83.78	1.34
10/20	1	2.89	0.72	2.03	5.79	1.39	3.00	100.11	97.41	73.77	1.4
15/20	1	2.89	0.72	2.03	3.70	0.90	2.82	95.94	94.55	104.09	1.39
20/20	1	2.89	0.72	2.03	2.99	0.74	1.94	103.56	103.14	95.23	1.37
30/20	1	2.89	0.72	2.03	1.97	0.50	1.26	102.03	104.61	93.14	1.3
45/20	1	2.89	0.72	2.03	1.34	0.34	0.90	103.93	105.34	99.23	1.29
60/20	1	2.89	0.72	2.03	0.96	0.27	0.61	99.96	104.82	90.12	1.27
10/20	2	2.89	0.72	2.03	5.76	1.30	3.51	99.65	91.05	86.28	<1.27
15/20	2	2.89	0.72	2.03	3.68	0.94	2.55	95.47	98.32	94.10	<1.28
20/20	2	2.89	0.72	2.03	2.86	0.73	1.94	99.02	101.75	95.18	<1.29
30/20	2	2.89	0.72	2.03	1.91	0.50	1.27	99.18	104.40	93.29	<1.30
45/20	2	2.89	0.72	2.03	1.33	0.34	0.85	103.31	106.60	93.47	<1.31
60/20	2	2.89	0.72	2.03	1.00	0.27	0.55	103.80	109.01	81.12	<1.32
10/20	4	2.89	0.72	2.03	5.85	1.44	4.03	101.24	100.35	99.04	<1.33
15/20	4	2.89	0.72	2.03	3.76	0.95	2.64	97.49	99.58	97.42	<1.34
20/20	4	2.89	0.72	2.03	3.00	0.76	1.94	103.80	105.80	95.28	<1.35
30/20	4	2.89	0.72	2.03	1.91	0.51	1.24	99.13	106.71	91.37	<1.36
45/20	4	2.89	0.72	2.03	1.34	0.36	0.80	104.40	106.92	88.94	<1.37
60/20	4	2.89	0.72	2.03	1.05	0.28	0.59	103.80	109.01	86.43	<1.38

A2 MODELLING AND SIMULATION

Table A-22: Constants solved my minimizing the square of the error in *Microsoft Excel* for the models developed in the process simulations sheet

	K	C	b1	b2	b3	b4	b5	b6
Loading pH	14.42	1.000	-208.8	122.2	-17.07	-0.0003	-	-
Nickel loading (g/l)	0.0106	-	-	-	-	-	-	-
Extraction pH	7.432	1.335	0.2959	-0.5106	0.0205	-1.411	0.4319	-0.0348
Cobalt concentration in aqueous phase at equilibrium for the extraction section (g/l)/Cobalt extraction (%)	0.0019	0.00002	-	-3.018	-	-	-	-
Iron concentration in aqueous phase at equilibrium for the extraction section (g/l)/Iron extraction (%)	12.47	0.1246	-0.4788	-1.438	-	-	-	-
Nickel concentration in aqueous phase at equilibrium for the stripping section (g/l)/Nickel stripped (%)	12.84	0.1284	0.9778	-100.7	-	-	-	-
Cobalt concentration in aqueous phase at equilibrium for the stripping section (g/l)/Cobalt stripped (%)	0.0385	0.0004	6.827	-396.5	-0.3856	-0.0258	-	-
Iron concentration in aqueous phase at equilibrium for the stripping section (g/l)/Iron stripped (%)	20.00	0.2005	3.527	-16.72	-	-	-	-
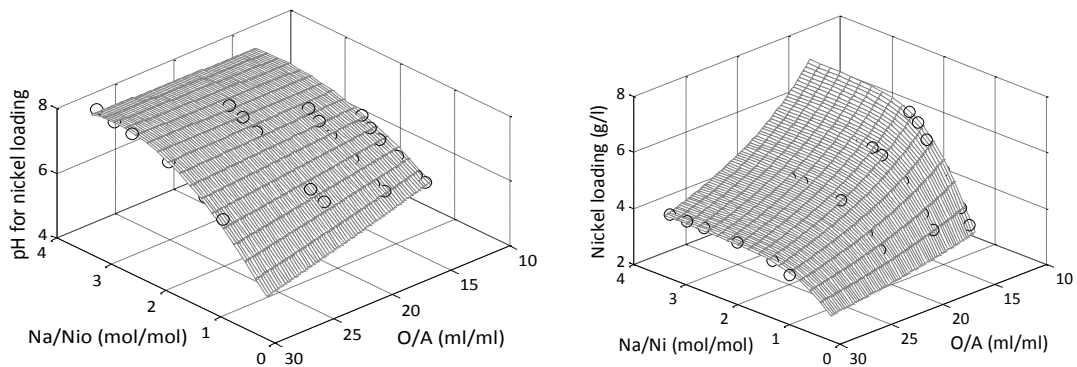
Figure A-1: Three dimensional graphs of the models developed for pH and nickel loading for the pre-loading section

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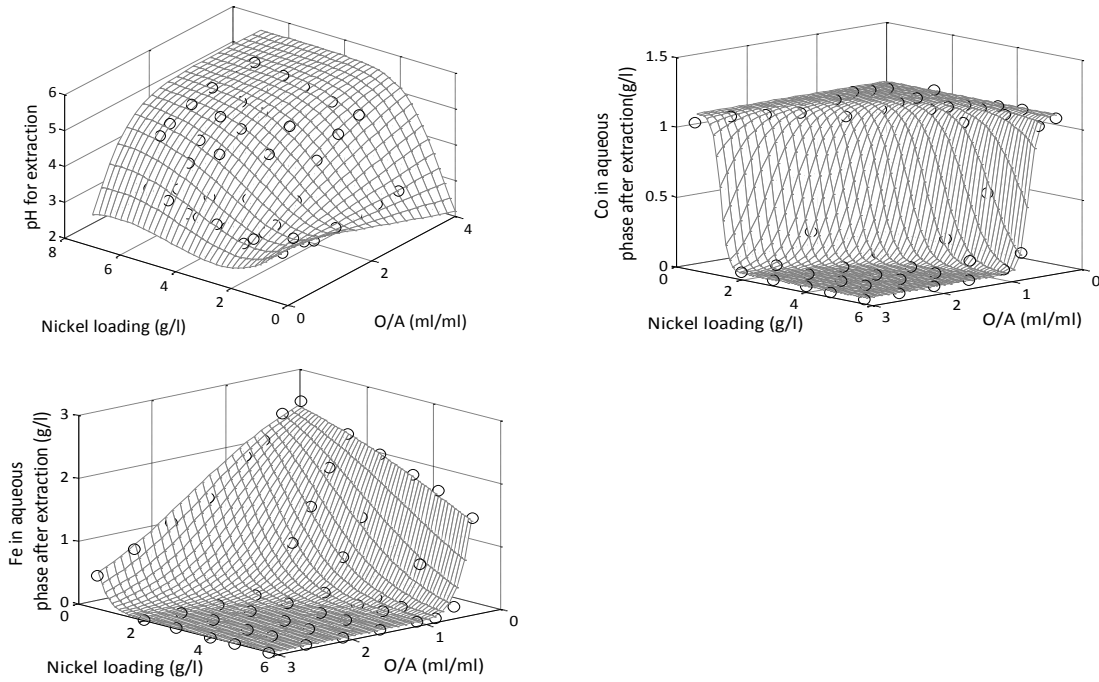
Figure A-2: Three dimensional graphs of the models developed for pH and cobalt and iron concentration in the aqueous phase at equilibrium for the extraction section
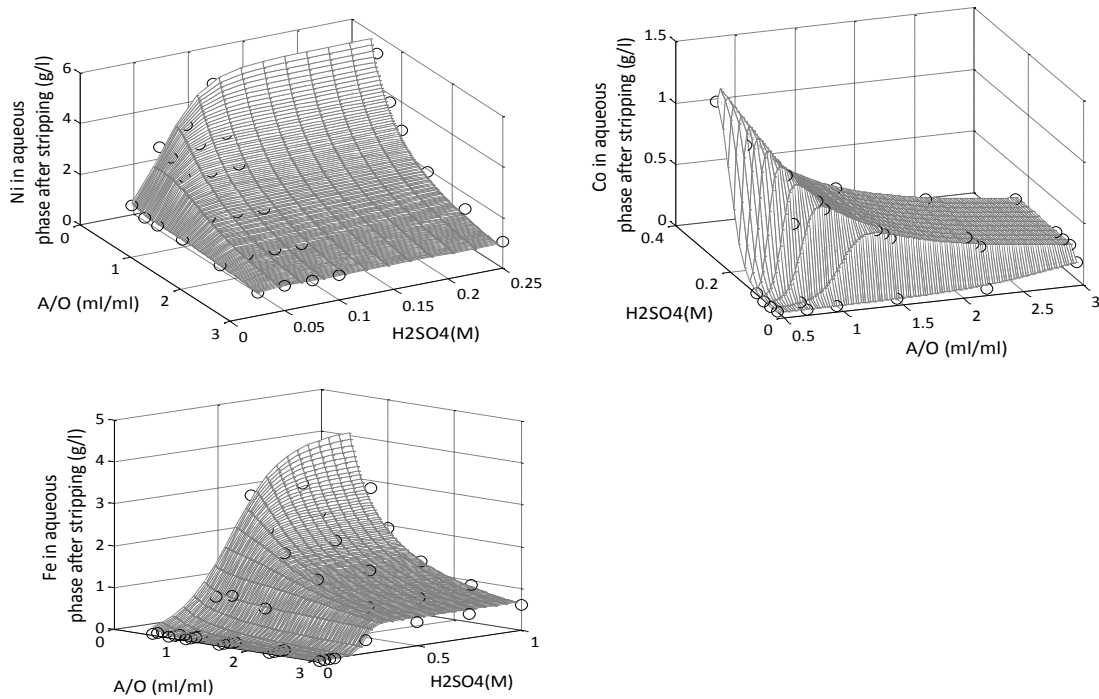
Figure A-3: Three dimensional graphs of the models developed for nickel, cobalt and iron concentration at equilibrium in the aqueous phase for the stripping section
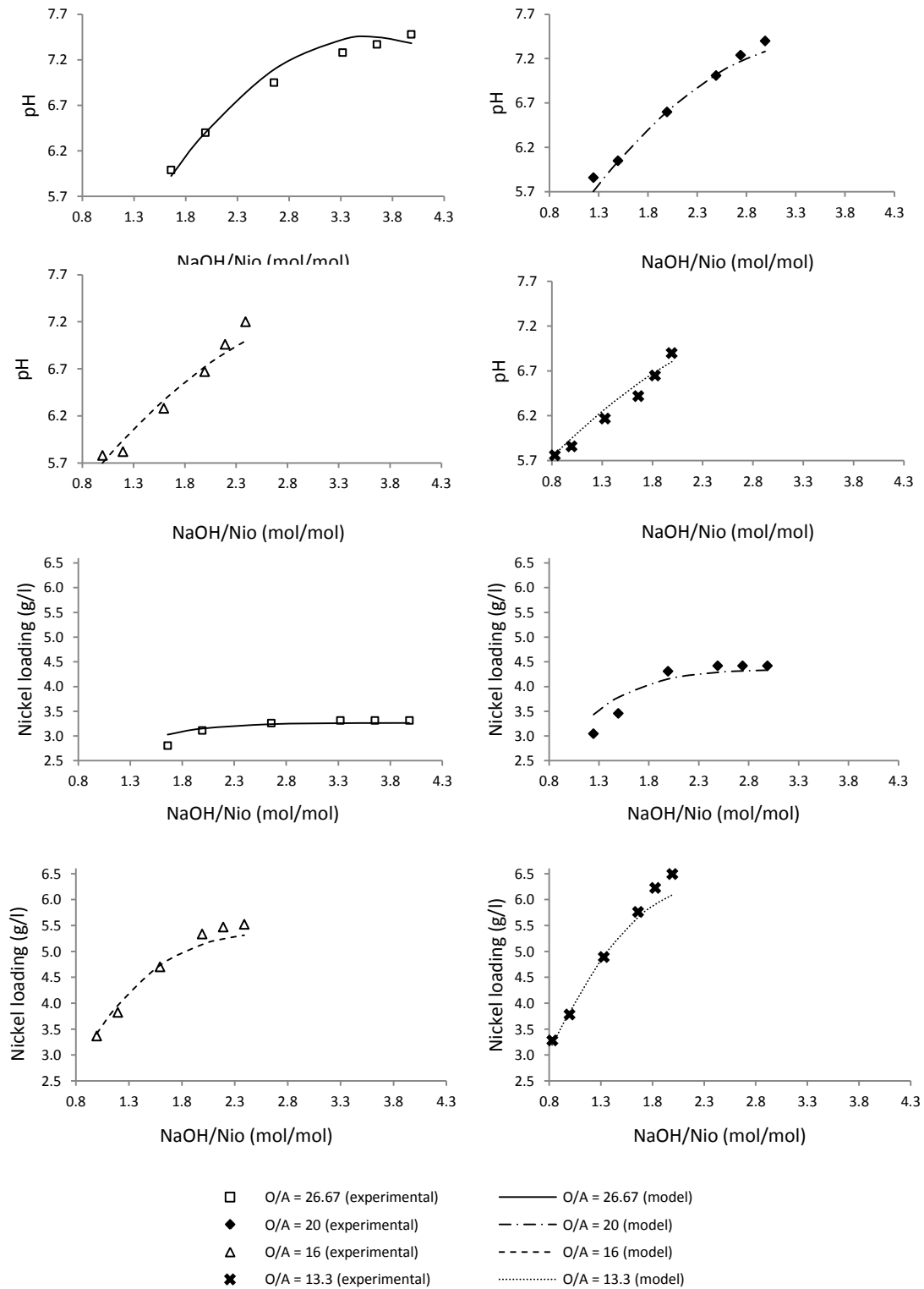
Figure A-4: Model results at various O/A ratios as a function of NaOH addition for pH and nickel loading at equilibrium for the pre-loading section

■ Ni loading = 0.56g/l (experimental)	—— Ni loading = 0.56g/l (modell)
♦ Ni loading = 1.97g/l (experimental)	·········· Ni loading = 1.97g/l (model)
▲ Ni loading = 2.94g/l (experimental)	– – – Ni loading =2.94g/l (modell)
✕ Ni loading = 3.95g/l (experimental)	— — Ni loading = 3.95g/l (model)
+ Ni loading = 4.69g/l (experimental)	– · – · Ni loading = 4.69g/l (model)
● Ni loading = 5.73g/l (experimental)	—— Ni loading = 5.73g/l (model)
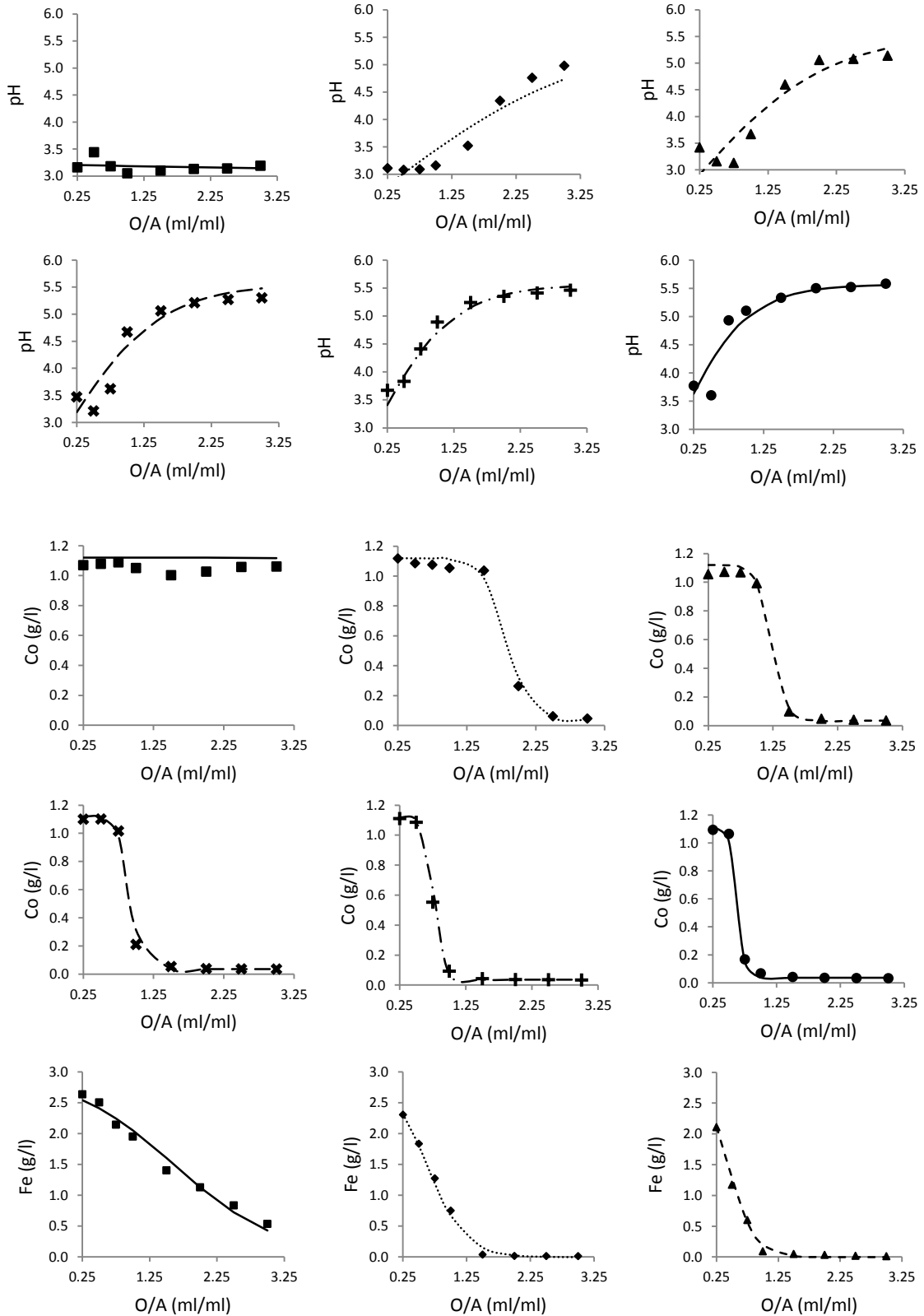
Figure A-5: Model results at various nickel loadings as a function of O/A ratio for pH and cobalt and iron concentration in the aqueous phase at equilibrium for the extraction section

Figure A-6: Model results at various A/O ratios as a function of H$_2$SO$_4$ concentration for nickel, cobalt and iron concentration in the aqueous phase at equilibrium for the stripping section

A3 CONTINUOUS TESTS

Table A-23: Process conditions and results for the pre-loading (1st stage) and extraction (2nd stage) test when generating a lower nickel loading

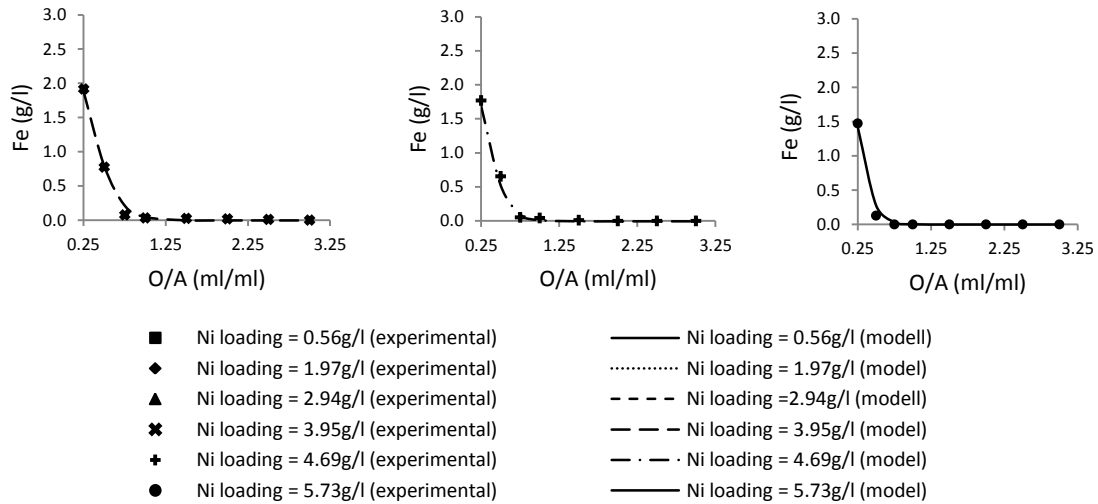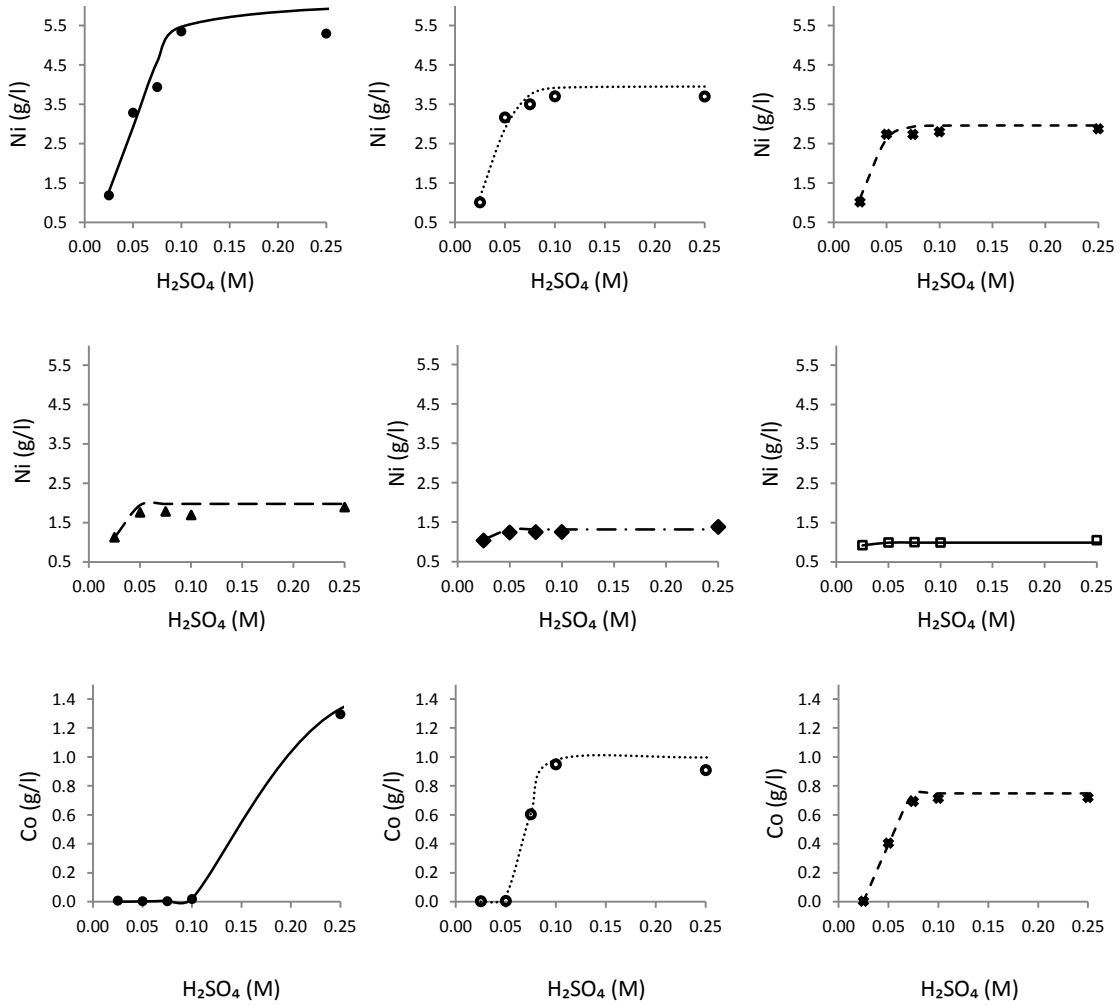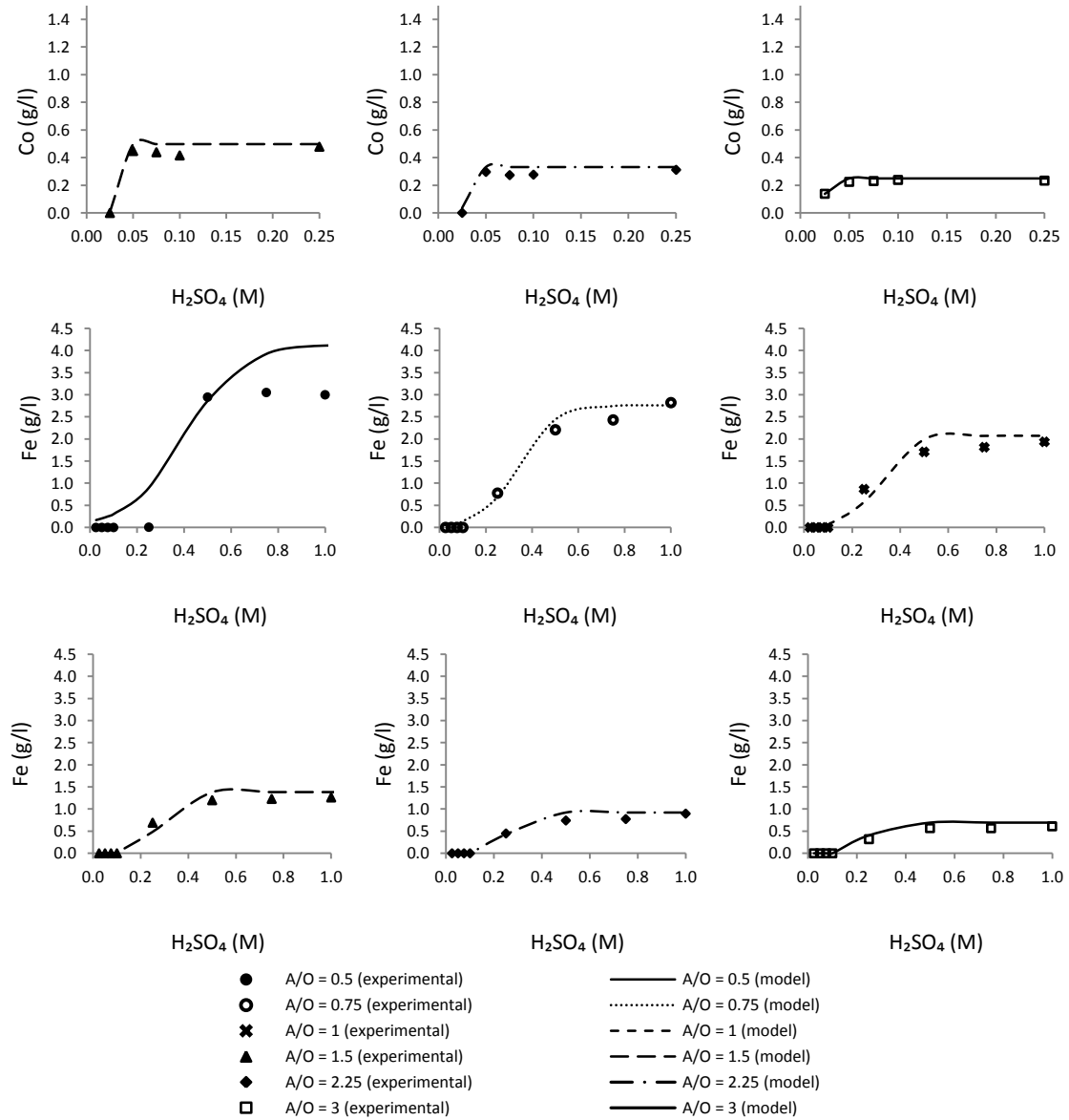|			
1st stage (pre-loading)			
Ni_o - aqueous		g/l	10.74
Cyanex 272		V%	20
Diluent		-	Shellsol D70
T		°C	40-50
O/A		ml/ml	1
F_{aq}		ml/min	55
F_{org}		ml/min	70
F_{NaOH}		ml/min	15
NaOH		g/l	40
Residence time in mixer		min	2.3
Residence time in settler		min	9.6

Time after start-up	Ni - aqueous (g/l)	Na - aqueous (g/l)	pH	Ni-loading (g/l)
0	9.72	0.07	3.21	-1.95
5	9.69	0.07	5.97	-2.89
15	1.97	4.48	-	5.80
25	4.52	2.78	-	3.25
45	5.03	2.77	6.08	2.74
55	4.94	2.84	6	2.83
75	4.56	2.74	6.1	3.21
85	4.51	2.82	6.14	3.26
95	4.47	3.1	6.11	3.30
105	4.41	2.87	6	3.36

2nd stage (extraction)			
Ni_o - aqueous		g/l	80
Co_o - aqueous		g/l	1.05
Fe_o - aqueous		g/l	3.6
Na_o - aqueous		g/l	0.08
Cyanex 272		V%	20
Diluent		-	Shellsol D70
T		°C	40-50
O/A		ml/ml	1.5
F_{aq}		ml/min	47
F_{org}		ml/min	70
Residence time in mixer		min	2.7
Residence time in settler		min	11.5

Time after start-up	Ni - aqueous (g/l)	Co - aqueous (g/l)	Fe - aqueous (g/l)	Na – aqueous (g/l)	pH	Ni extracted (%)	Co extracted (%)	Fe extracted (%)	Na addition to aqueous phase after extraction (g/l)
0	-	-	-	-	3.48	-	-	-	-
5	6.6	0.09	0.22	0.14	3.15	91.75	91.44	93.89	0.06
15	44.5	0.245	0.652	0.12	-	44.38	76.69	81.88	0.04
25	69.1	0.153	0.375	0.09	-	13.63	85.44	89.58	0.01
45	81.7	0.103	0.242	0.08	4.17	-2.13	90.20	93.28	0
55	79.8	0.089	0.197	0.08	4.43	0.25	91.53	94.53	0
75	89.5	0.074	0.148	0.08	4.69	-11.88	92.96	95.89	0
85	90.4	0.063	0.099	0.07	4.97	-13.00	94.01	97.25	-0.01
95	83.2	0.058	0.043	0.07	5	-4.00	94.48	98.81	-0.01
105	83.5	0.051	0.058	0.08	5.05	-4.38	95.15	98.39	0

Table A-24: Process conditions and results for the pre-loading (1st stage) and extraction (2nd stage) test when generating a higher nickel loading

1st stage (pre-loading)				
Ni_o - aqueous		g/l	15	
Cyanex 272		V%	20	
Diluent		-	Shellsol D70	
T		°C	40-50	
O/A		ml/ml	0.67	
F_{aq}		ml/min	77	
F_{org}		ml/min	64	
F_{NaOH}		ml/min	18	
NaOH		g/l	40	
Residence time in mixer		min	2.01	
Residence time in settler		min	8.5	

Time after start-up	Ni - aqueous (g/l)	Na - aqueous (g/l)	pH	Ni-loading (g/l)
0	15	0.105	3.35	-4.24
5	14.79	0.12	5.96	-3.93
15	8.805	2.82	6.43	5.05
25	8.715	2.865	6.43	5.19
45	8.85	2.925	6.4	4.98
55	8.85	2.82	6.5	4.98
75	8.85	2.955	6.54	4.98
85	8.73	2.925	6.5	5.16

2nd stage (extraction)				
Ni_o - aqueous		g/l	82	
Co_o - aqueous		g/l	1.02	
Fe_o - aqueous		g/l	3.07	
Na_o - aqueous		g/l	0.08	
Cyanex 272		V%	20	
Diluent		-	Shellsol D70	
T		°C	40-50	
O/A		ml/ml	1.5	
F_{aq}		ml/min	43	
F_{org}		ml/min	64	
Residence time in mixer		min	2.99	
Residence time in settler		min	12.6	

Time after start-up	Ni - aqueous (g/l)	Co - aqueous (g/l)	Fe - aqueous (g/l)	Na – aqueous (g/l)	pH	Ni extracted (%)	Co extracted (%)	Fe extracted (%)	Na addition to aqueous phase after extraction (g/l)
0	-	-	-	-	3.28	-	-	-	-
5	18.9	0.244	0.6	0.07	2.83	76.95	76.17	80.46	-0.01
15	61.7	0.241	0.55	0.11	3.2	24.76	76.46	82.08	0.03
25	72.8	0.111	0.24	0.12	3.94	11.22	89.16	92.18	0.04
45	80.5	0.053	0.16	0.13	4.6	1.83	94.82	94.79	0.05
55	84.5	0.043	0.05	0.12	4.91	-3.05	95.80	98.37	0.04
75	83.2	0.05	0.045	0.09	4.89	-1.46	95.12	98.53	0.01
85	85.2	0.044	0.05	0.12	4.9	-3.90	95.70	98.37	0.04

Table A-25: Process conditions and results when stripping the organic phase with the lower metal loading

		1st stage (Ni and Co stripping)				
Ni - organic	g/l	0.94				
Co - organic	g/l	0.37				
Fe - organic	g/l	1.37				
Cyanex 272	V%	20				
Diluent	-	Shellsol D70				
T	°C	40-50				
A/O	ml/ml	2.3				
F_{aq}	ml/min	117				
F_{org}	ml/min	50				
H_2SO_4	M	0.1				
Residence time in mixer	min	3.8				
Residence time in settler	min	16.2				
Time after start-up	Ni - aqueous (g/l)	Co - aqueous (g/l)	Fe – aqueous (g/l)	Ni stripped (%)	Co stripped (%)	Fe stripped (%)
5	1.34	0.017	0.023	366.41	11.67	4.30
15	0.47	0.098	0.074	116.62	61.02	12.56
25	0.43	0.123	0.137	106.69	76.59	23.26
35	0.48	0.128	0.082	119.10	79.70	13.92
45	0.4	0.121	0.112	99.25	75.35	19.02
55	0.39	0.12	0.1	96.77	74.72	16.98
65	0.41	0.119	0.062	101.73	74.10	10.53
75	0.39	0.123	0.045	96.77	76.59	7.64
85	0.4	0.125	0.032	99.25	77.84	5.43
		2nd stage (Fe stripping)				
Ni - organic	g/l	dependent on previous stage				
Co - organic	g/l	dependent on previous stage				
Fe - organic	g/l	dependent on previous stage				
Cyanex 272	V%	20				
Diluent	-	Shellsol D70				
T	°C	40-50				
A/O	ml/ml	0.72				
F_{aq}	ml/min	36				
F_{org}	ml/min	50				
H_2SO_4	M	1				
Residence time in mixer	min	3.7				
Residence time in settler	min	15.7				
Time after start-up	Ni - aqueous (g/l)	Co - aqueous (g/l)	Fe - aqueous (g/l)	Ni stripped (%)	Co stripped (%)	Fe stripped (%)
5	0	0	0	0.00	0.00	0.00
15	0	0	0	0.00	0.00	0.00
25	0	0	0	0.00	0.00	0.00
35	0.03	0.0113	0.22	2.13	2.01	10.67
45	0.03	0.023	0.404	2.31	4.44	21.29
55	0.04	0.031	0.426	3.08	5.99	22.45
65	0.05	0.036	0.503	3.85	6.96	26.50
75	0.06	0.045	0.535	4.62	8.70	28.19
85	0.07	0.045	0.64	5.39	8.70	33.72

Table A-26: Process conditions and results when stripping the organic phase with the higher metal loading

1st stage (Ni and Co stripping)						
Ni - organic	g/l	3.07				
Co - organic	g/l	0.96				
Fe - organic	g/l	2.5				
Cyanex 272	V%	20				
Diluent	-	Shellsol D70				
T	°C	40-50				
A/O	ml/ml	2.3				
F_{aq}	ml/min	117				
F_{org}	ml/min	50				
H_2SO_4	M	0.1				
Residence time in mixer	min	3.8				
Residence time in settler	min	16.2				

Time after start-up	Ni - aqueous (g/l)	Co - aqueous (g/l)	Fe – aqueous (g/l)	Ni stripped (%)	Co stripped (%)	Fe stripped (%)
5	0	0	0	0.00	0.00	0.00
15	0.5	0.229	0.199	38.00	55.49	18.55
25	0.62	0.272	0.262	47.12	65.91	24.42
35	0.59	0.253	0.222	44.84	61.30	20.70
45	0.69	0.287	0.193	52.44	69.54	17.99
55	1.14	0.238	0.22	86.64	57.67	20.51
65	1.18	0.247	0.262	89.69	59.85	24.42
75	1.17	0.229	0.216	88.93	55.49	20.14
85	1.16	0.234	0.214	88.17	56.70	19.95
95	1.19	0.24	0.229	90.45	58.15	21.35
105	1.2	0.242	0.208	91.21	58.64	19.39
115	1.19	0.247	0.25	90.45	59.85	23.31

2nd stage (Fe stripping)						
Ni - organic	g/l	dependent on previous stage				
Co - organic	g/l	dependent on previous stage				
Fe - organic	g/l	dependent on previous stage				
Cyanex 272	V%	20				
Diluent	-	Shellsol D70				
T	°C	40-50				
A/O	ml/ml	1				
F_{aq}	ml/min	50				
F_{org}	ml/min	50				
H_2SO_4	M	1				
Residence time in mixer	min	6.4				
Residence time in settler	min	27				

| Time after start-up	Ni - aqueous (g/l)	Co - aqueous (g/l)	Fe – aqueous (g/l)	Ni stripped (%)	Co stripped (%)	Fe stripped (%)
5	0	0	0	0.00	0.00	0.00
15	0	0	0	0.00	0.00	0.00
25	0	0.01	0.066	0.00	1.04	2.64
35	0.18	0.106	0.592	5.86	11.01	23.65
45	0.44	0.196	1.059	14.33	20.35	42.31
55	0.61	0.251	1.358	19.87	26.06	54.25
65	0.51	0.257	1.506	16.61	26.69	60.17
75	0.51	0.275	1.593	16.61	28.56	63.64
85	0.58	0.295	1.724	18.89	30.63	68.88
95	0.59	0.31	1.728	19.22	32.19	69.04
105	0.59	0.295	1.737	19.22	30.63	69.40
115	0.5	0.32	1.724	16.29	33.23	68.88
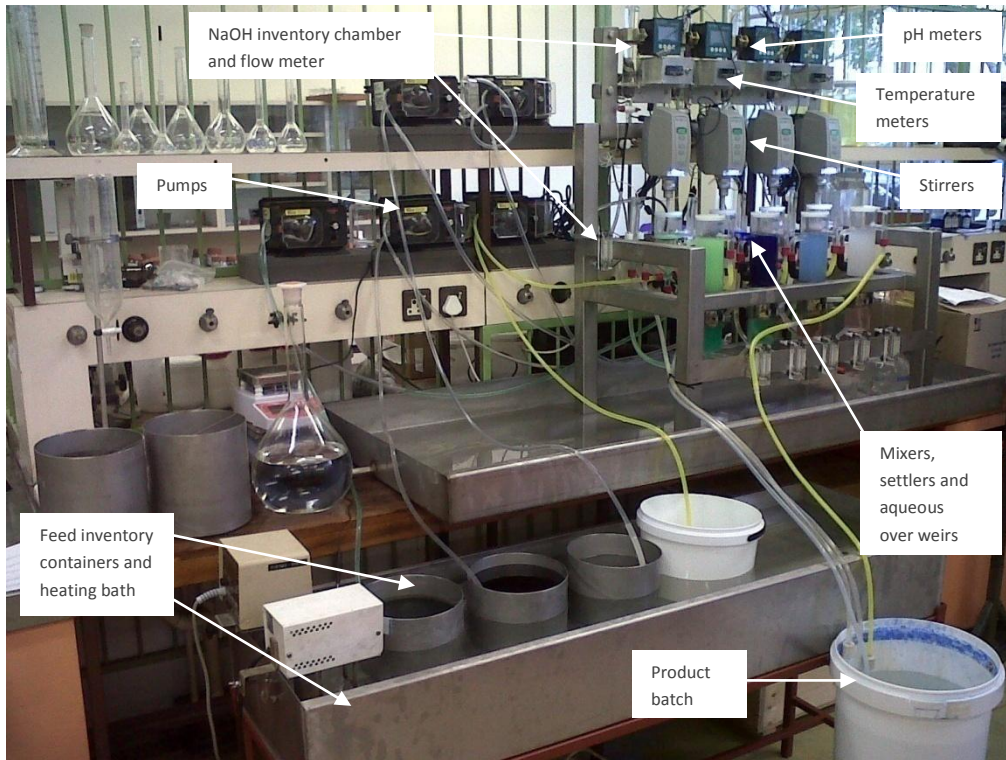
Figure A-7: Photograph of the mixer-settler setup

Figure A-8: Photograph of the agitators, mixers, settlers and aqueous overflow weirs

APPENDIX B (PUBLICATIONS)

Paper prepared for submission to refereed journal

Olivier, MC, Dorfling, C, and Eksteen, JJ, (2011), "Evaluating a solvent extraction process route incorporating nickel preloading of Cyanex 272 for the removal of cobalt and iron from nickel sulfate solutions", *Minerals Engineering*

Refereed full length paper in the proceedings of international symposia

Olivier, MC, Dorfling, C, and Eksteen, JJ, (2011), "Extraction of cobalt(II) and iron(II) from nickel(II) solutions with nickel salts of Cyanex 272", International Solvent Extraction Conference 2011, Santiago, Chile, 3-7 October 2011

Presentations at national conferences

Olivier, MC, Dorfling, C, and Eksteen, JJ, (2011), "Developing a solvent extraction process for the extraction of cobalt (II) and iron (II) from nickel (II) solutions with nickel salts of Cyanex 272", Mineral Processing 2011, Western Cape Branch of SAIMM, Cape Town, South Africa, 4-5 August 2011

Olivier, MC, Dorfling, C, and Eksteen, JJ, (2010), "Developing a solvent extraction process for the separation of cobalt and iron from nickel sulfate solutions", Mineral Processing 2010, Western Cape Branch of SAIMM, Cape Town, South Africa, 5-6 August 2010