Solvent extraction of nickel with phosphorus-containing extractants

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In this Master's thesis, the extraction of nickel using phosphorus-containing extractants and the effect of nickel concentration on extraction efficiency are investigated. The phosphorus-containing extractants studied in the literature review included di-(2-ethylhexyl) phosphoric acid (D2EHPA), 2-ethylhexyl hydrogen-2-ethylhexylphosphonate (HEHEHP), and bis(2,4,4-trimethylpentyl) phosphinic acid (BTMPPA). By comparing the pH_{50} values, D2EHPA extracts nickel at the lowest pH from these and BTMPPA extracts nickel at the highest pH, whereas HEHEHP falls between these two.

In the experimental part, pH isotherms for 0.5 and 1.0 M of D2EHPA and Cyanex 272 (BTMPPA) were constructed using nickel concentrations of 21–23, 51–59, and 110–118 g/L. The results confirmed that D2EHPA extracts nickel at a lower pH than Cyanex 272. In addition, increasing the nickel concentration shifted the extraction to a lower pH. Also, increasing the extractant concentration shifted the extraction to a lower pH. The effect of nickel and extractant concentration was evident for both extractants.

To study the effect of nickel concentration on the extraction efficiency, McCabe–Thiele analysis was done for 0.5 M D2EHPA at 55 °C and pH 4.00 (± 0.05) using 19, 49, and 113 g/L nickel feed solutions. In the analysis, ~4.58 g/L nickel loading of the organic phase was targeted, resulting in varying O/A ratios for the different nickel feeds. The results show that the higher the nickel concentration of the feed was, the more nickel remained in the raffinate. However, the percentage of extraction was increased with increasing feed concentration. The most significant differences were observed after the first ideal extraction stage, and as the number of extraction stages increased, the differences narrowed.

The results of this thesis show that increasing the nickel concentration shifts the equilibrium to a lower pH with phosphorus-containing extractants. In addition, it was demonstrated that higher nickel feed concentration increases extraction efficiency, although more nickel remains in the raffinate than with lower concentrations. The most significant differences between the different nickel feeds were seen after the first ideal extraction stage in terms of the extraction efficiency and the nickel concentration of the raffinate.

Keywords: Solvent extraction, Nickel, D2EHPA, HEHEHP, BTMPPA

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Tämän diplomityön tarkoituksena on tutkia nikkelin uuttamista fosforia sisältävillä uuttoreagensseilla sekä nikkelipitoisuuden vaikutusta uttotehokkuuteen. Kirjallisuuskatsauksessa käsitellyt fosforia sisältävät uuttoreagenssit olivat di-(2-etyyliheksyyli)fosforihappo (D2EHPA), 2-etyyliheksyyli vety-2-etyyliheksyylifosfonaatti (HEHEHP), ja bis(2,4,4-trimetyylipentyyli)fosfiinihappo (BTMPPA). Vertailemalla pH_{50} arvoja voidaan todeta, että D2EHPA:lla voidaan uuttaa nikkeliä alhaisimmissa pH arvoissa ja BTMPPA:lla korkeimmissa pH arvoissa, kun taas HEHEHP sijoittuu näiden kahden väliin.

Kokeellisessa osiossa tehtiin pH isotermit 0.5 ja 1.0 M D2EHPA:lle ja Cyanex 272:lle käyttäen 21–23, 51–59, ja 110–118 g/L nikkelipitoisuuksia. Tulokset vahvistivat, että D2EHPA uuttaa nikkeliä matalammassa pH:ssa kuin Cyanex 272. Lisäksi havaittiin, että nikkelipitoisuuden nostaminen siirsi nikkelin uuttumisen matalampaan pH arvoon. Myös uuttoreagenssin pitoisuuden nostaminen laski pH:ta, jossa nikkeli uuttui. Sekä nikkelin että uuttoreagenssin pitoisuuden vaikutus oli ilmeinen molemmilla uuttoreagensseilla.

Nikkelipitoisuuden vaikutusta uuttotehokkuuteen tutkittiin toteuttamalla McCabe–Thiele analyysi 0.5 M D2EHPA:lla 55 °C:ssa ja pH:ssa 4.00 (± 0.05) käyttäen 19, 49, ja 113 g/L nikkeliliuoksia. Analyysissä orgaanisen faasin nikkelipitoisuudeksi asetettiin ~4.58 g/L, jonka myötä eri nikkelipitoisuuksilla käytettiin eri O/A suhteita. McCabe–Thiele analyysin tulokset osoittavat, että mitä korkeampi syötön nikkelipitoisuus oli sitä enemmän nikkeliä jäi raffinaattiin. Toisaalta nikkelipitoisuuden kasvaessa myös uuttoaste kasvoi. Merkittävimmät erot havaittiin ensimmäisen ideaaliaskeleen jälkeen, ja askeleiden määrän kasvaessa erot pienenivät.

Diplomityön tulokset osoittavat, että nikkelipitoisuuden kasvattaminen siirtää tasapainoa matalampaan pH arvoon, kun fosforia sisältäviä uuttoreagensseja käytetään. Lisäksi tulokset osoittivat, että korkeampi syötön nikkelipitoisuus lisää uuttotehokkuutta, vaikka raffinaattiin jää enemmän nikkeliä kuin matalammilla syötön nikkelipitoisuuksilla. Merkittävimmät erot eri syöttöjen nikkelipitoisuuksilla näkyvät selkeimmin ensimmäisen ideaaliaskeleen jälkeen sekä uuttotehokkuuden että raffinaatin nikkelipitoisuuden suhteen.

Avainsanat: Neste-nesteuutto, nikkeli, D2EHPA, HEHEHP, BTMPPA

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Abbreviations

A/O	Aqueous to organic ratio
BMTPPA	Bis(2,4,4-trimethylpentyl) phosphinic acid
Cyanex 272	Bis(2,4,4-trimethylpentyl) phosphinic acid
Cyanex 302	Bis(2,4,4-trimethylpentyl) monothiophosphinic acid
Cyanex 801	2-ethylhexyl hydrogen-2-ethylhexylphosphonate
D2EHPA	Di-(2-ethylhexyl) phosphoric acid
HEHEHP	2-ethylhexyl hydrogen-2-ethylhexylphosphonate
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
Ionquest 801	2-ethylhexyl hydrogen-2-ethylhexylphosphonate
NNH	Norilsk Nickel Harjavalta Oy
O/A	Organic to aqueous ratio
PC88A	2-ethylhexyl hydrogen-2-ethylhexylphosphonate
PLS	Pregnant leachate solution
TBP	Tri-butyl phosphate
Versatic 10	Neodecanoic acid

Symbols

A	Extractant
b	Model specific parameter in the Langmuir adsorption isotherm model
C_0	Initial nickel concentration in aqueous phase (mg/L)
C_e	Equilibrium concentration of nickel in aqueous phase after extraction (mg/L)
C_{Ni}	Nickel concentration in the organic/aqueous phase (g/L or mol/L)
$C_{Reag.}$	Reagent concentration in the organic phase (mol/L)
$\%E$	Percentage of extraction (%)
H^+	Hydrogen ion
$L\%$	Percentage of metal loading in the organic phase (%)
M^{n+}	Metal ion
n	Metal valence
pH_{50}	pH value where 50% of the metal is extracted
q_e	Equilibrium concentration of the adsorbate in the adsorbent phase (mg/L)
Q_e	Monolayer adsorption capacity (mg/g)
V_{aq}	Volume of aqueous phase (mL)
V_{org}	Volume of organic phase (mL)
$V_{tot.}$	Total volume (mL)
ΔV	Difference between measured and calculated final volumes (%)

1 Introduction

Nickel is a widely used metal, with its primary use being in stainless steel production (66%), where it is used to enhance properties such as ductility and formability [1]. It is also used, for example, in batteries (16%) and other metal alloys (9%). To produce these, nickel must be separated from different metals that occur in primary and secondary raw materials. One of the hydrometallurgical methods for nickel purification is solvent extraction. In the solvent extraction process, organic extractants are used to remove impurities such as zinc, manganese, and copper from the nickel solution [2]. After purification, the pure nickel solution can be used, for example, in electrowinning to produce nickel cathodes, or it can be processed into different nickel chemicals. There are several types of extractants for solvent extraction, including the phosphorus-containing extractants.

Phosphorus-containing extractants include phosphoric, phosphonic, and phosphinic acids, i.e. D2EHPA, HEHEHP, and BTMPPA. In these extractants, there is a central phosphorus atom and an increasing number of alkyl groups bonded to it. The extraction mechanism of these extractants is cation exchange. The basicity of the extractants increases from phosphoric acid to phosphinic acid. Because of this, D2EHPA extracts nickel at the lowest pH and BTMPPA at the highest pH, while HEHEHP falls between these two, as seen in Figure 1. [3]

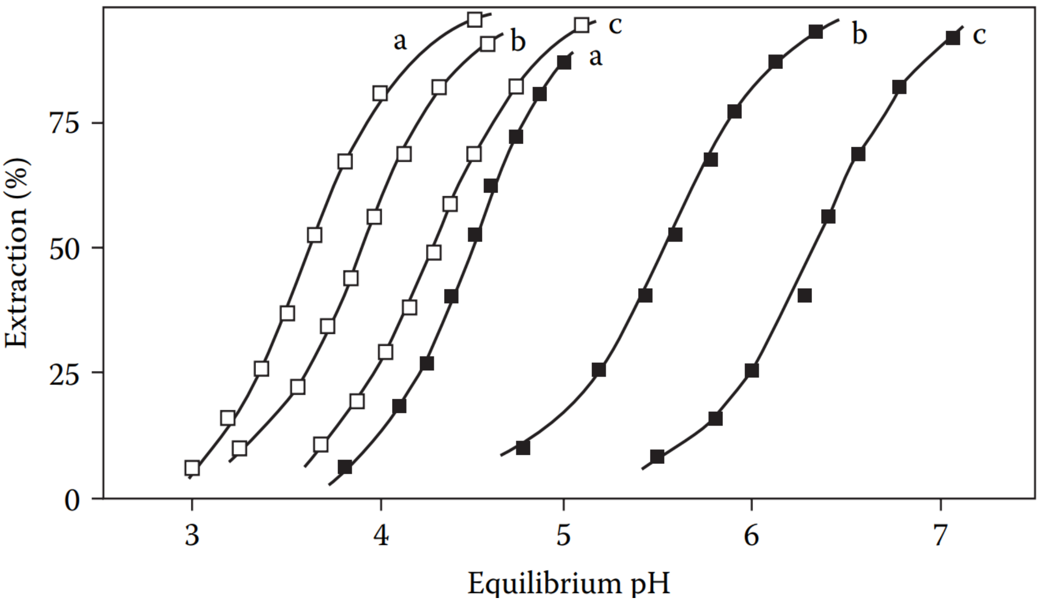


Figure 1. pH dependence of nickel (solid symbols) and cobalt (open symbols) extraction by (a) phosphoric acid, (b) phosphonic acid and (c) phosphinic acid in sulphate solutions. Reproduced from Sole [3]. Copyright 2008 Sole.

The purpose of this thesis is to investigate the effect of nickel concentration on extraction and extraction efficiency using phosphorus-containing extractants, as this type of comparison has not been conducted with high nickel concentrations. Extraction of nickel from high nickel concentrations can be used, for example, in nickel preloading, which is done to prevent neutralising agent cations from entering the purified aqueous solution and further processes [4]. The aim of the experimental part is to compare D2EHPA and BTMPPA in nickel extraction when three different levels of high nickel concentrations are used. Additionally, the effect of the extractant concentration is studied with three different levels of high nickel concentrations.

In this thesis, the AI-based language tool Grammarly has been used to assist with grammar and clarity of the writing. All interpretations, analyses and conclusions presented in the thesis are those of the authors.

2 Norilsk Nickel Harjavalta Oy

Norilsk Nickel Harjavalta Oy (NNH) is a significant nickel metals and chemicals refiner located in Harjavalta Suurteollisuuspuisto industrial park. NNH nickel production began in 1960, and it is a part of the global Nornickel Group. Nornickel Group is the world's largest producer of nickel and palladium. NNH products include nickel cathodes and briquettes, inorganic nickel salts, cobalt sulphate, and ammonium sulphate. The NNH production process includes leaching, extractions, electrolysis, reduction, and chemical plant. The process and products of NNH are presented in Figure 2. [5]

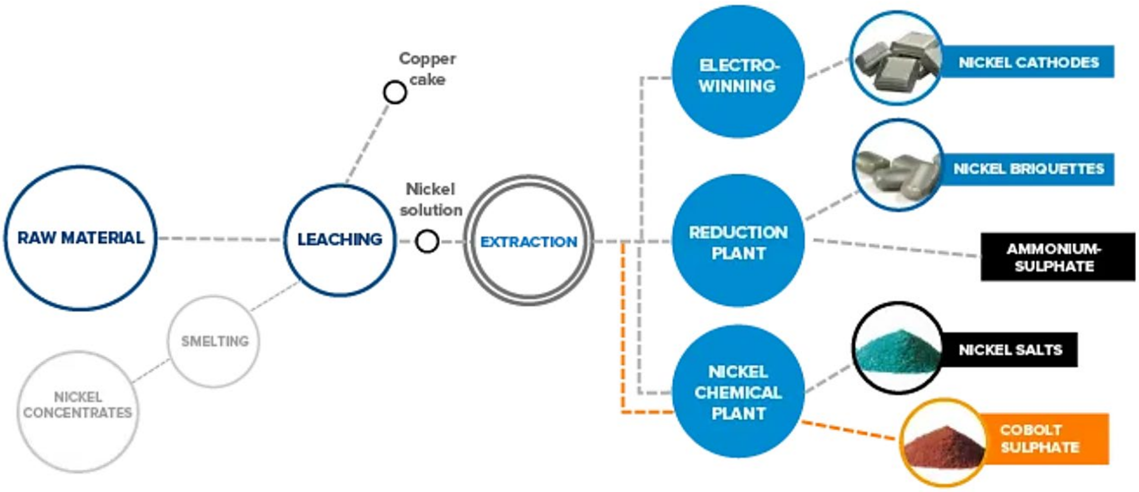


Figure 2. The process and products of NNH. Image reproduced with permission from [5]. Copyright 2021 Norilsk Nickel Harjavalta Oy.

In leaching, nickel raw material is leached to produce nickel raw solution. The nickel raw solution, used for cobalt extraction, is first cooled and washed with kerosene, after which cobalt extraction is done in sequential extraction cells. Some of the nickel sulphate solution from the leaching process is directed through calcium extraction, where calcium, iron, zinc, copper, and manganese are extracted, after which it is pumped to the cobalt extraction process. In cobalt extraction, cobalt and other impurities, such as iron, copper, lead, and zinc, are removed. The cobalt raw solution produced in the cobalt extraction is purified and pumped to the chemical plant, where cobalt sulphate is produced. The purified nickel solution is pumped to the electrolysis, reduction, and chemical plant. In electrolysis, nickel cathodes are produced via electrowinning. At the reduction plant, the nickel solution goes through hydrogen reduction to produce nickel powder, which is then briquetted. At the chemical plant, nickel solution is processed into hydroxycarbonates, hydroxides and sulphates in different production lines.

3 Solvent extraction

Solvent extraction is a hydrometallurgical process for concentrating and purifying solutions containing various metal ions. The solvent extraction process can be divided into three stages: extraction, scrubbing and stripping, as illustrated in Figure 3. In the extraction stage, an aqueous solution containing metal ions is mixed with an organic phase consisting of an organic extractant diluted in an organic solvent. When these immiscible phases are brought into contact in a mixing chamber, the target metal ions are selectively transferred from the aqueous phase to the organic phase. However, small concentrations of other impurity metal ions may be co-extracted with the target metals. These co-extracted impurities can be removed in the scrubbing stage, where the loaded organic containing the extracted metals is contacted with a suitable aqueous scrubbing solution. In this stage, impurities are selectively stripped from the organic phase back into the aqueous phase, leaving the target metal ions in the organic solution. The scrubbed organic phase then proceeds to the stripping stage, where it is mixed with an aqueous strip solution. In this step, the target metal ions are transferred from the organic phase back into the aqueous phase, producing a concentrated solution, known as strip liquor. This solution is further processed, for example, by electrowinning, to recover the final metal product. The stripped organic phase is regenerated and recycled back to the extraction stage.

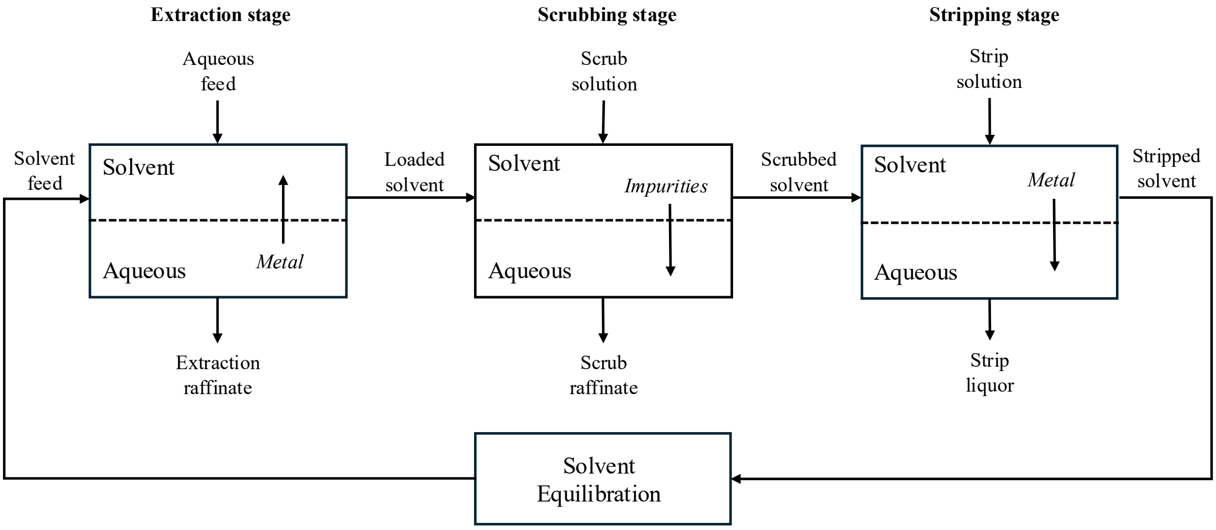


Figure 3. A schematic of the solvent extraction process. Adapted from Ritcey [6].

Each of the extraction stages may involve multiple extraction units to enhance efficiency. A commonly used extraction unit is the mixer-settler, which consists of mixing chambers and a settling chamber, is illustrated in Figure 4 [7]. In operation, the organic and aqueous phases are introduced into the first mixing chamber, where the phases are vigorously mixed to form a dispersion. This dispersion then flows into the second mixer, where the mixing is continued to allow for extended contact time. After mixing, the dispersion enters the settling chamber, where the two phases separate based on their density differences. The lighter organic phase rises to the top, while the denser aqueous phase settles at the bottom. The separated organic phase exits the settler via an overflow outlet, and the aqueous phase is removed through a launder.

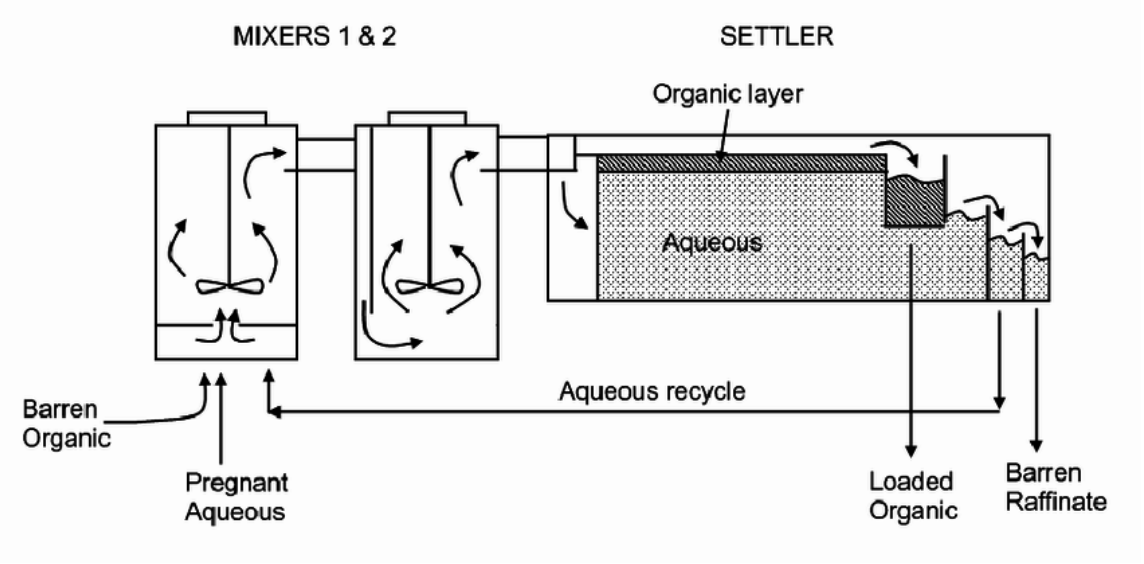


Figure 4. Schematic picture of a conventional mixer-settler. Reproduced from Littlejohn [7]. Copyright 2007 Littlejohn.

Solvent extraction often takes place in acidic environment and most extractants involve ion exchange, which is why acidic cation exchange extractants are often used in solvent extraction. This type of extraction reaction is presented Equation 1:

$$M^{n+} + \overline{nHA} \rightleftharpoons \overline{MA_n} + nH^{+}, \tag{1}$$

where the overline describes the organic solution, M^{n+} refers to the target metal ion, H^{+} is a proton, and A is the extractant [8]. As seen from Equation 1, the equilibrium concentration of reaction components is determined by the pH of the aqueous solution. The reaction equilibrium may be shifted to the right, where metals are extracted from the aqueous phase by neutralising the protons released from the extractant. The neutralisation can be done, for example, by addition of NaOH or NH_4OH [4].

4 Extractants for solvent extraction of nickel

4.1 Phosphorus-containing extractants

4.1.1 Di-(2-ethylhexyl) phosphoric acid (D2EHPA)

Di-(2-ethylhexyl) phosphoric acid, also known as D2EHPA, is extensively used for solvent extraction and separation of metals such as cobalt [9], scandium [10], manganese [11], vanadium [12], and iron [13]. The benefits of D2EHPA include limited solubility in aqueous acidic solutions, chemical stability, and high selectivity for metal ions [14].

Purification of synthetic laterite leach solution with D2EHPA has been studied by Cheng [15]. In the study, the organic solution consisted of 10% v/v D2EHPA, 5% v/v tri-butyl phosphate (TBP) as a phase modifier, and 85% kerosene. Before studying the synthetic laterite leach solution, pH isotherms for copper, cobalt, magnesium, manganese, nickel, zinc, and calcium were determined by using 3 g/L single metal solutions of each. The pH isotherms were determined at different pH values with O/A=1 at 23 °C, and H_2SO_4 and NH_4OH were used for pH adjusting. The pH isotherms using D2EHPA are presented in Figure 5.

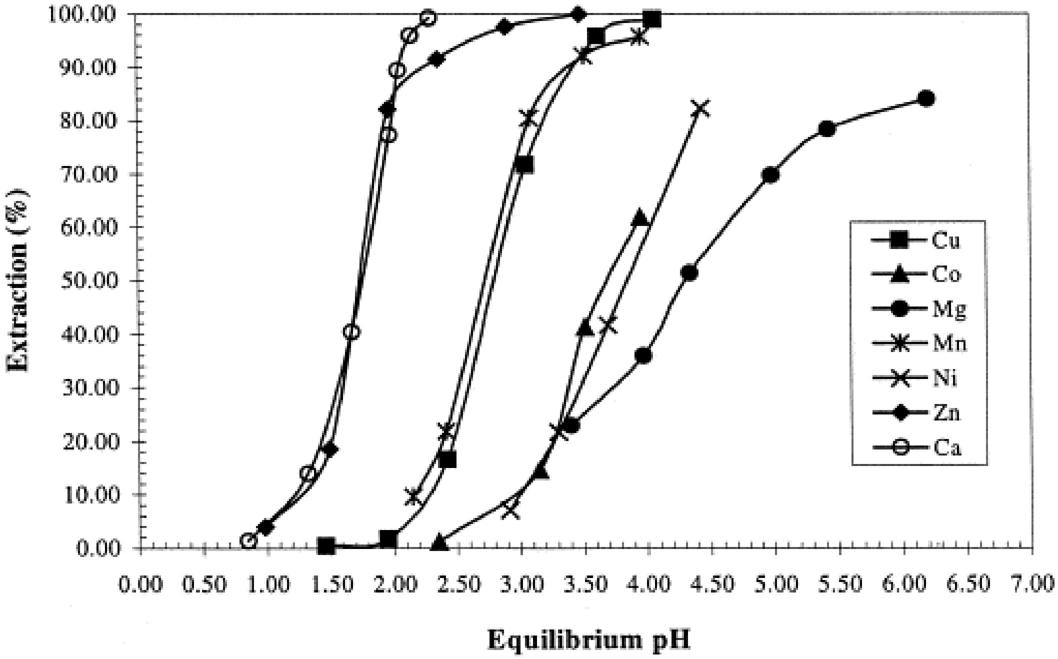


Figure 5. pH isotherm for 10 % v/v D2EHPA using solution containing copper, cobalt, magnesium, manganese, nickel, zinc, and calcium at 23 °C and O/A=1. Image reproduced with permission from [15]. Copyright 2000 Elsevier.

From Figure 5, it can be seen that the extraction order of metals was Zn > Ca > Mn > Cu > Co > Ni > Mg. The pH range for nickel extraction using D2EHPA was 2.9–3.9, and a maximum extraction (~82%) was reached at pH 3.9 [15]. The extraction order and pH range for nickel extraction differ from those reported by Sole, who described the extraction order as Zn > Ca > Mn > Cu > Mg > Co > Ni and the pH range as ~3.8–5.8 [3].

Gharabaghi et al. studied the separation of zinc and nickel in synthetic sulphate solutions using 1 M D2EHPA and Cyanex 272 [16]. In the extraction experiments using D2EHPA, aqueous solutions containing 0.1 g/L, 1 g/L, 3.2 g/L, and 10 g/L of zinc and nickel were studied at various pH levels. The pH was adjusted with H_2SO_4 and NaOH. The organic solution contained 1 M D2EHPA in hexane, and the temperature was 25 °C. In the experiments, equal amounts of aqueous solutions of different metal concentrations and organic solution were shaken for 30 minutes. The extraction of nickel took place in the pH range 1.5–5, as can be observed from Figure 6 [16].

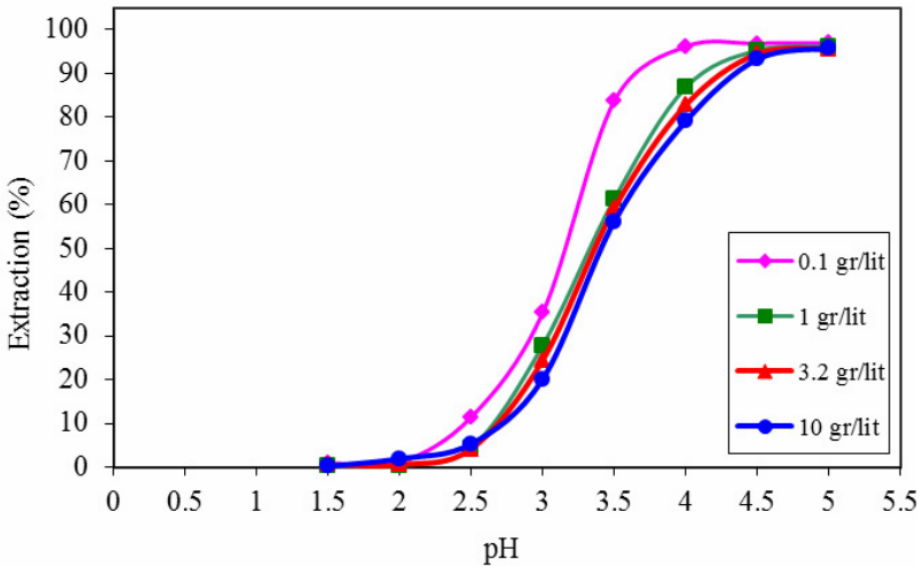


Figure 6. The effect of pH on nickel extraction was studied on various nickel concentrations. Extraction was done by mixing equal parts of 1 M D2EHPA and nickel solution for 30 minutes at 25 °C. Image reproduced from Gharabaghi et al. [16]. Copyright 2012 Gharabaghi, published by Physicochemical Problems of Mineral Processing.

From Figure 6, it can be seen that at pH 5.0, the percentage of extraction was similar for all nickel concentrations. There can be seen a slight increase in pH_{50} values as the nickel concentration increases, and the most notable change can be observed between 0.1 g/L and 1 g/L. In the experiment with 1 g/L nickel and zinc solution, the pH_{50} value of 3.35 was observed for nickel. A similar pH_{50} was observed in a study conducted by Babakhani et al., in which

D2EHPA and Cyanex 302 were studied for the selective separation of nickel and cadmium from sulphate solutions of spent Ni-Cd batteries [17]. In the study, a synthetic sulphate solution containing 2 g/L of both nickel and cadmium was contacted for 10 minutes with an equal volume of 0.6 M D2EHPA diluted with kerosene at 25 °C and the pH_{50} was observed to be 3.4 for nickel. When an aqueous solution containing 5 g/L of nickel and cobalt and 0.6 M D2EHPA at 25 °C was used by Darvishi et al., a pH_{50} value of 3.30 for nickel was obtained [18].

4.1.2 2-ethylhexyl hydrogen-2-ethylhexylphosphonate (HEHEHP)

2-ethylhexyl hydrogen-2-ethylhexyl phosphonate, also known by its trade names PC88A, Ionquest 801 and Cyanex 801, is commonly used for the separation of the rare earth elements [19] as well as for the separation and extraction of other metals such as cobalt, nickel and zinc [20]. The order of extraction for some common metals is Zn > Cu > Co > Ca > Mg > Ni, as shown in Figure 7 [3].

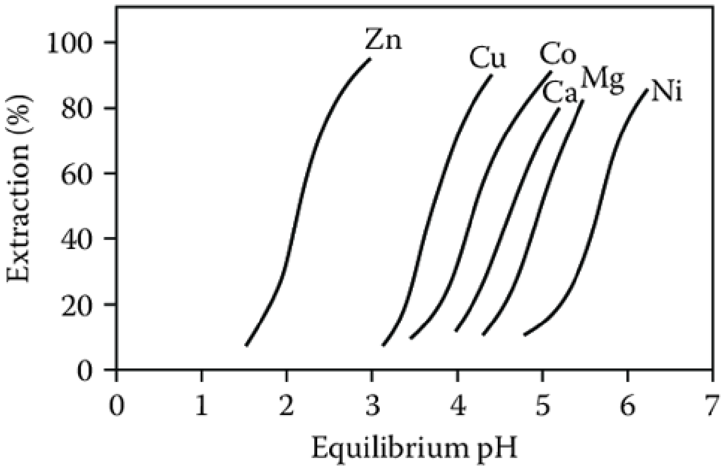


Figure 7. pH isotherm for Ionquest 801. Image reproduced from Sole [3]. Copyright 2008 Sole.

Devi et al. studied the separation and recovery of cobalt and nickel from sulphate solutions using the sodium salts of Cyanex 272, PC88A, and D2EHPA [9]. An aqueous solution containing 0.01 M cobalt and nickel was used in experiments studying the effect of pH on their extraction. The organic solution used in these experiments contained 60% neutralised extractant diluted in kerosene and 5 v% of phase modifier tri-butyl phosphate (TBP). The effect of pH was studied by mixing equal volumes of aqueous solution with 0.03, 0.05, and 0.06 M sodium salts of extractants for five minutes at 30 °C in a pH range of 2.5–7.0. These experiments showed that increasing the extractant concentration increases the extraction of nickel. The extraction of nickel with 0.03 M NaPC88A was negligible, however with 0.05 and 0.06 M, the extraction was ~20% at pH 6.4 and ~43% at pH 6.6, respectively. The effect of pH on nickel extraction is presented in Figure 8.

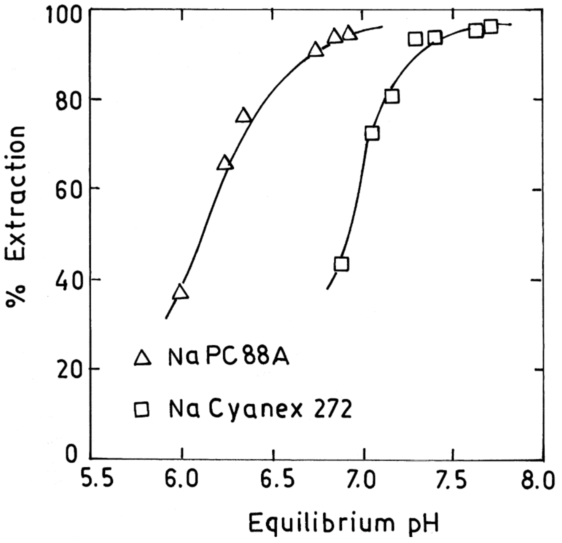


Figure 8. Effect of pH on nickel extraction using 0.05 M NaPC88A and NaCyanex 272. Image reproduced with permission from [9]. Copyright 1998 Elsevier.

Devi et al. constructed McCabe-Thiele plots for nickel extraction using 0.05 M for both NaPC88A and NaCyanex 272 by varying the organic to aqueous ratio from 1/5 to 5/1 [9]. The results suggested that over 99.8% of nickel could be extracted into the organic phase in two ideal stages at O/A=1/1, when 0.01 M nickel solution was used. The McCabe-Thiele plot for nickel extraction is presented in Figure 9.

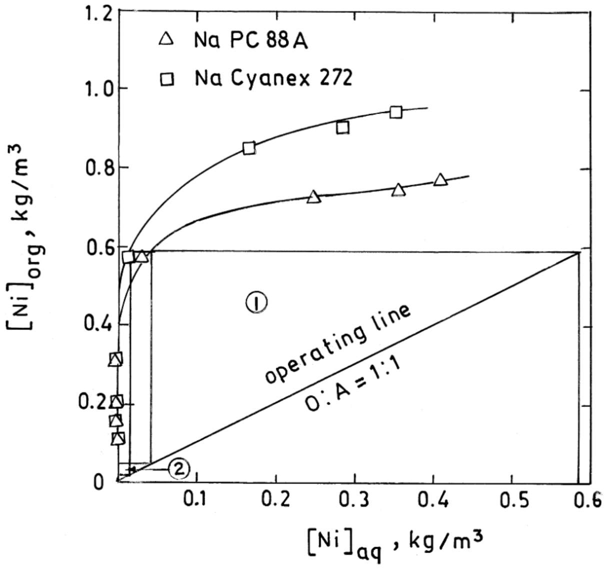


Figure 9. McCabe-Thiele plot for nickel extraction using 0.05 M NaPC88A and NaCyanex 272. Image reproduced with permission from [9]. Copyright 1998 Elsevier.

In a study conducted by Reddy et al., various extractant neutralisation levels and phase ratios were evaluated for the extraction of nickel from a solution containing nickel and $(NH_4)_2SO_4$ [21]. The aqueous solution contained 25.5 g/L of nickel and 18.1 g/L of $(NH_4)_2SO_4$, and the initial pH was ~5.0. The organic solution contained 1 M of PC88A diluted in kerosene. The temperature used in the experiments was 30 °C, and the mixing time was five minutes, although according to initial experiments, equilibrium was reached within one minute. First, the neutralisation of the organic phase was experimented with in the range of 20–65% with O/A=1. The neutralisation was done by the addition of NH_4OH. As the neutralisation level increased, the equilibrium pH increased. With 20% neutralisation, the equilibrium pH was 4.5 and the extraction of nickel was 16.00%. With 65% neutralisation, the equilibrium pH was 5.4 and the extraction was increased to 54.31%. It was estimated that with this level of extraction, more than six or seven extraction stages would be necessary to extract over 99% of the nickel. Because of these results, O/A ratios of two and three were then studied, varying the level of neutralisation within the same range as earlier. The highest nickel extraction was achieved with a neutralisation level of 65%, being 95.8% at O/A=3 and 85.2% at O/A=2. The effect of phase ratio and extractant neutralisation level on nickel extraction is presented in Table 1.

Table 1. Effect of phase ratio and extractant neutralisation level on nickel extraction. Adapted from Reddy et al. [21].

Neutralisation level,%	O/A	Equilibrium pH	Ni extraction,%
20	1	4.50	16.0
20	2	4.40	36.7
20	3	4.45	51.1
30	1	4.80	29.8
30	2	4.90	45.4
30	3	5.10	70.1
50	1	5.20	41.9
50	2	5.30	74.1
50	3	5.55	89.6
60	1	5.35	51.4
60	2	5.60	81.9
60	3	5.80	94.5
65	1	5.40	54.3
65	2	5.65	85.2
65	3	5.80	95.8

Two stage counter-current extraction of nickel was experimented with 50%, 55% and 60% neutralisation levels at O/A=2.5/1, resulting in 99.3%, 99.1% and 99.6% nickel extraction, respectively. A 50% neutralisation level was further experimented at O/A=2.2/1 in two, three and four stages, resulting in 95.3%, 99.7% and 99.9% nickel extraction, respectively. [21]

In a more recent study, Liu et al. studied the extraction and separation of zinc, cobalt and nickel with Ionquest 801, Cyanex 272 and their mixtures [20]. The aqueous solution used in the experiments contained 1 g/L of zinc, cobalt, and nickel. The effect of pH on metal extraction was studied using 0.1, 0.2, 0.3 and 0.4 M of extractant diluted in kerosene. The experiments were conducted at 40 °C and O/A=1, and 200 g/L NaOH was used to adjust the pH in the range of 1.5–6.5. In the experiments using Ionquest 801, it was seen that zinc and cobalt were extracted over nickel. It was also observed that increasing the extractant concentration shifted the extraction of each metal to a lower pH. For example, the pH_{50} values for nickel were 5.85 and 5.40, using 0.2 M and 0.3 M Ionquest 801, respectively. The maximum nickel extraction of ~98% was achieved at the end of the pH range at pH 6.5 using 0.3 M Ionquest 801. For 0.2 M Ionquest 801, the nickel extraction was ~84% at the end of the pH range. The metal extraction pH isotherm for Ionquest 801 is presented in Figure 10.

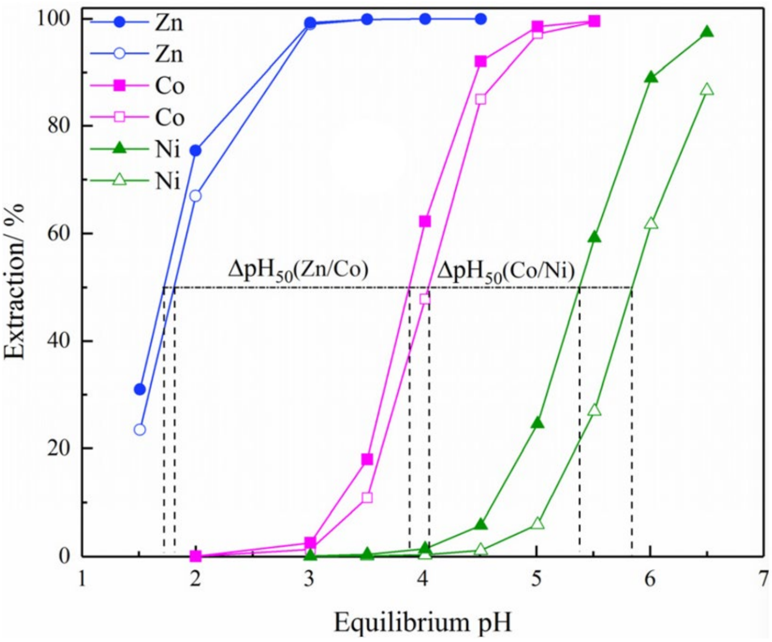


Figure 10. Extraction pH isotherm for Ionquest 801 for nickel, zinc and cobalt. Solid labels describe 0.3 M extractant concentration, and open labels 0.2 M extractant concentration. Image reproduced from Liu et al. [20]. Copyright 2021 Liu, published by MDPI.

4.1.3 Bis(2,4,4-trimethylpentyl) phosphinic acid (BTMPPA)

Bis(2,4,4-trimethylpentyl) phosphinic acid, also known as Cyanex 272, is commonly used for the separation of cobalt and nickel due to its high selectivity for cobalt over nickel [22]. It can also be used for the separation and extraction of zinc and copper [23] as well as magnesium [24]. The order of extraction for some common metals is Fe > Zn > Cu > Mn > Co > Mg > Ca > Ni, and the pH isotherm can be seen in Figure 11.

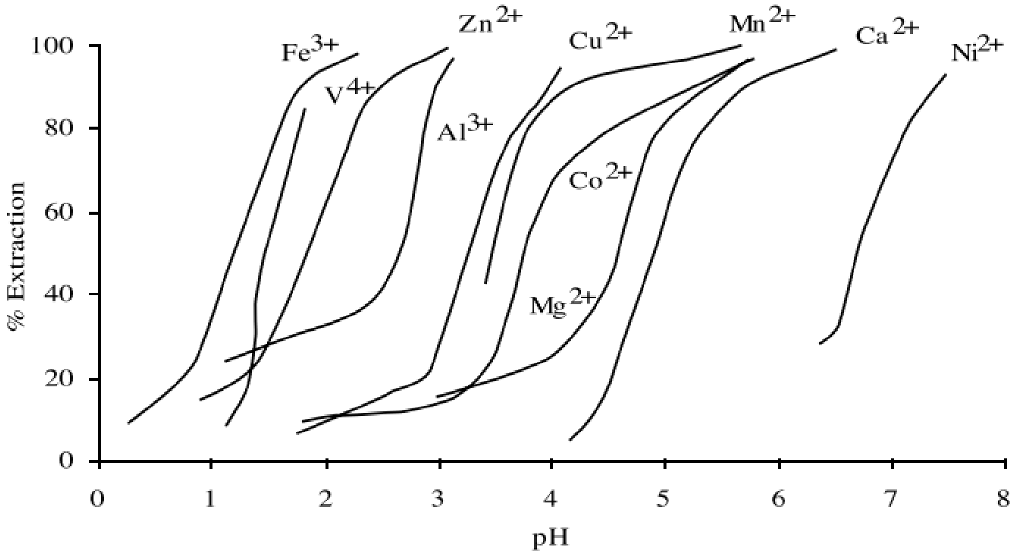


Figure 11. pH isotherm for Cyanex 272 in sulphate media. Image reproduced with permission from [22]. Copyright 2008 Syensqo.

Liu et al. studied the extraction and separation of zinc, cobalt and nickel with Ionquest 801, Cyanex 272 and their mixtures [20]. The aqueous solution contained 1 g/L of zinc, cobalt, and nickel. The effect of pH on metal extraction was studied using Cyanex 272 concentrations of 0.1, 0.2, 0.3 and 0.4 M diluted in kerosene. The experiments were conducted at 40 °C and O/A=1, and 200 g/L NaOH was used to adjust the pH in the range of 1.5–6.5. The pH_{50} values for nickel were 6.06, 6.28 and over 6.5, using 0.4, 0.3 and 0.2 M Cyanex 272, respectively. With 0.3 M Cyanex 272, ~71% of nickel was extracted at pH 6.5.

Begum et al. studied solvent extraction of copper, nickel, and zinc using Cyanex 272 [23]. In the experiments, pH, extractant concentration, and the concentrations of $[SO_4]^{2-}$ and $[Ac]^-$ ions were varied. The effect of each parameter was studied individually. The aqueous solution contained 20 mg/L Ni, 500 mg/L Cu, 20 mg/L Zn, 0.1 M $[SO_4]^{2-}$ and 0.25 M $[Ac]^-$. The organic solution contained 0.1 M of Cyanex 272 diluted in hexane. Experiments were conducted at room temperature, O/A=1 and mixing time of 20 minutes to ensure equilibrium was reached.

pH was adjusted by adding dilute NaOH. In the experiments investigating the effect of equilibrium pH, the initial pH was varied in the range of 4.48–12.0 for nickel, and the maximum extraction was achieved at an equilibrium pH of 7.45. In the experiments on the effect of extractant concentration, Cyanex 272 concentration was varied in the range of 0.01–0.4 M. The initial pH for nickel was 8.5, and it was seen that increasing the extractant concentration increased metal extraction, as could be expected. In the experiments on the effect of the $[SO_4]^{2-}$ concentration, 0.1 and 0.05 M Cyanex 272 concentrations were used, $[SO_4]^{2-}$ concentration was varied from 0.02 to 0.5 M, the $[Ac]^-$ concentration was kept constant, and an initial pH of 8.5 was used for nickel. In the 0.1 M Cyanex 272 system, nickel extraction decreased from 77.3% to 44.8%, and in the 0.05 M Cyanex 272 system, it decreased from 50.7% to 20.5%. The effect of $[Ac]^-$ concentration was studied in the range of 0.01–0.5 M of $[Ac]^-$. Cyanex 272 concentrations of 0.1 and 0.05 M, as well as an initial pH of 8.5 for nickel, were used. Increasing the $[Ac]^-$ concentration had an increasing effect on nickel extraction. In the 0.1 M Cyanex 272 system, extraction increased from 13.9% to 72.0%, and in the 0.05 M system, it increased from 6.6% to 47.5%.

4.2 Neodecanoic acid

Versatic 10, also known as neodecanoic acid, is a highly branched tertiary carboxylic acid that contains ten carbon atoms in total [25]. Versatic 10 is a cation exchanger and is used to extract nickel, cobalt, iron, and copper, as well as rare earth elements. It is a suitable extractant for nickel extraction as it extracts nickel over cobalt [26]. The order of extraction for Versatic 10 is Cu > Zn > Ni > Co > Mn > Ca > Mg [27]. The separation of metals is highly pH dependent, which is why precise control over pH is essential, as for example, the pH_{50} values for Ni^{2+}, Co^{2+}, and Fe^{2+} are 6.34, 6.55 and 6.72, respectively [28]. pH isotherm for Versatic 10 is presented in Figure 12.

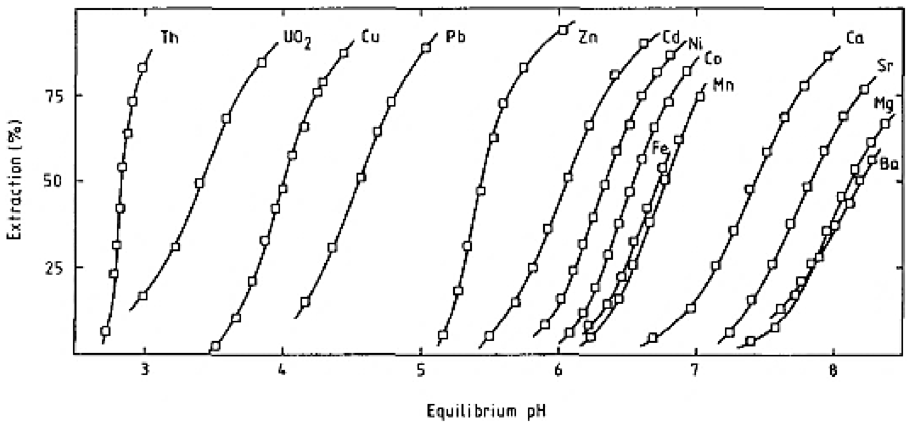


Figure 12. pH isotherms for Versatic 10 in xylene at 20 °C. Image reproduced with permission from [28]. Copyright 1985 Elsevier.

Versatic 10 was commercially used in direct solvent extraction of nickel from sulphate solutions at the now decommissioned Bulong Operations [29]. In the Bulong process, pregnant leachate solution (PLS) was purified in two separate solvent extraction circuits. The PLS contained 2.8 g/L Ni, 0.21 g/L Co, 0.002 g/L Fe, 0.03 g/L Zn, 0.003 g/L Cu, 0.75 g/L Mn, 16 g/L Mg, and 0.56 g/L Ca. In the first circuit, the solvent extraction of cobalt, cobalt, copper, zinc, and manganese were extracted using Cyanex 272 in five extraction stages. The raffinate from solvent extraction of cobalt, containing 2.8 g/L Ni, 0.003 g/L Mg, 0.0001 g/L Ca, 0.0006 g/L Co and 0.001 g/L Mn, was then used in the solvent extraction of nickel circuit. In the circuit, Versatic 10 was used to selectively extract nickel in four extraction stages at pH 6.5–6.8, leaving magnesium and calcium in the raffinate. After extracting nickel, the organic phase was scrubbed in two stages, and the nickel was stripped in three stages. In this process, 98.2% of nickel can be recovered from the PLS, and more than 99.8% nickel cathode could be produced.

Tsakiridis & Agatzini studied recovery of cobalt and nickel from sulphate solutions containing also magnesium and calcium by Versatic 10 and Cyanex 272 [30]. In the study, cobalt and nickel were recovered from a synthetic sulphate solution containing 0.65 g/L Co, 3.8 g/L Ni, 5.75 g/L Mg, and 0.25 g/L Ca in two extraction circuits. In the first circuit, Versatic 10 was used to co-extract nickel and cobalt from magnesium and calcium in two stages. The pH was 6.5, the organic phase consisted of 20% Versatic and 5% TBP in kerosene and the A/O was 2.3. Cobalt and nickel extraction at these conditions was 99.7% and 99.5%, respectively. Less than 0.5% co-extraction of calcium and magnesium was reached at these conditions. In the second circuit, Cyanex 272 was used to separate cobalt from nickel sulphate solution in two extraction stages. In this stage, the co-extraction of nickel was only 0.3%.

4.3 Comparison of the pH_{50} values between extractants

In the case of phosphorus-containing extractants, i.e., D2EHPA, HEHEHP, and BTMPPA, the selectivity order of metals is similar to each other when it comes to nickel. With all these extractants, nickel is last to be extracted. Another extractant that could be used for nickel extraction is neodecanoic acid, which extracts nickel before cobalt, manganese, calcium, and magnesium. When comparing pH_{50} values between phosphorus-containing extractants, it is seen that D2EHPA extracts nickel at the lowest pH (3.30–3.40 [16, 17, 18]), whereas BTMPPA extracts nickel at a higher pH (6.06–6.5 [16, 20]). The pH_{50} values using HEHEHP fall between these two, with values of approximately 5.05–5.35 ([18, 19]). With neodecanoic acid, the pH_{50} value is close to BTMPPA, it being ~6.3 [28, 31].

4.4 Nickel preloading

Solvent extraction is a process where precise pH control is crucial to extract metals selectively. The pH is often controlled by the addition of neutralisation agent, such as NaOH or NH_4OH. The cations of the used neutralisation agent end up in the extraction raffinate, which can cause problems such as contamination or precipitation further in the process. The problems caused by these cations can be avoided by preloading the organic phase. In the preloading, preneutralised organic phase, containing neutralising agent cations, is contacted with a pure solution containing product metal ions at a higher pH than the actual extraction of the impurity metals. In this process, cation exchange takes place, and the neutralising agent ions are exchanged with product metal ions. The aqueous solution containing the neutralising agent cations can be discarded from the process. [4]

Nickel preloading of the organic phase, which is preneutralised using NaOH, can be described by Equation 2 and extracting metal M^{2+} using the nickel preloaded organic phase can be described by Equation 3 [32].

$$Ni^{2+}_{(aq)} + 3\ (HA)_{2\,(org)} + 2\ NaOH_{(aq)} \rightleftharpoons NiA_2 \cdot 2(HA)_{2\,(org)} + 2\ H_2O_{(aq)} + 2\ Na^{+}_{(aq)} \quad (2)$$

$$M^{2+}_{(aq)} + NiA_2 \cdot 2(HA)_{2\,(org)} \rightleftharpoons MA_2 \cdot n(HA)_{2\,(org)} + (2-n)(HA)_{2\,(org)} + Ni^{2+}_{(aq)} \quad (3)$$

Nickel preloading of Cyanex 272 and D2EHPA in cobalt and cadmium extraction has been studied by Nogueira et al. [32]. In the study, an aqueous phase containing 80 g/L of nickel was contacted with both 1 M D2EHPA at pH 4.0 and 4.5, and 0.5 M Cyanex 272 at pH 6.0 and 6.3. With 1 M D2EHPA, it was possible to reach 16 g/L nickel loading of the organic phase at pH 4.5 in the O/A range of 4–5. When 0.5 M Cyanex 272, 7–8 g/L nickel loading was obtained at pH 6.3 and an O/A of 8, or at pH 6.0 and an O/A of 5. In the case of Cyanex 272, it was observed that during NaOH addition, partial precipitation of nickel occurred. The precipitation could be explained by the pH of the preloading process being close to the $Ni(OH)_2$ precipitation point in the aqueous phase. Nonetheless, the precipitates were redissolved after some mixing, and the phases were reported to be clean after 15 minutes of equilibration. It was suggested that the precipitation could be controlled by not increasing the pH above 6.3 and targeting organic nickel loading of under 9 g/L.

A process for nickel preloading of Cyanex 272 was also described by O'Callaghan and Chamberlain [33]. In the invention, a fraction of the purified nickel solution from the extraction stage is pre-equilibrated with Cyanex 272. In the pre-equilibration, 30–60 g/L nickel solution is diluted 1/1 ratio with water to avoid the formation of nickel double salts, which can form while neutralising concentrated nickel solutions with ammonia. The nickel preloaded extractant is then contacted with an impure nickel solution containing cobalt, and the nickel ions in the extractant are exchanged with cobalt ions in the aqueous phase. As an example, equal parts of 0.45 M Cyanex 272 diluted in Shellsol 2046 kerosene and nickel solution were contacted at 50 °C using a mixing speed of 1200 rpm and a mixing time of 5 min. The nickel solution was a raffinate from cobalt extraction, containing 67.9 g/L of nickel and less than 50 ppm of cobalt, and it was diluted in equal parts with water. The target pH of 6.0 was maintained by adding 12.5% ammonia solution. Under these conditions, 8.33 g/L nickel loading of the organic was achieved. At pH of 6.3, nickel loading of 13.48 g/L was achieved, and the organic phase was fully saturated. Cobalt extraction was then performed with 8.33 g/L nickel preloaded Cyanex 272, and 98.7% of the initial 6.50 g/L cobalt was extracted at pH 5.25, whereas with 13.48 g/L nickel preloaded Cyanex 272, 99.4% of cobalt was extracted at pH 5.75.

Also, cobalt or nickel preloading of D2EHPA was described by Lindell et al. [4]. This invention describes a process for removing zinc, iron, calcium, copper, and manganese from cobalt or nickel aqueous solutions. The aqueous solution contains 0–5 g/L Co, 50–120 g/L Ni, 0–1 g/L Fe, 0–10 g/L Zn, 0–0.6 g/L Cu and 0–10 g/L Mn. The process is described to include extraction, preloading, scrubbing, and stripping stages. In the extraction stage, the cobalt or nickel preloaded organic phase is contacted with the aqueous solution containing impurities, and cobalt or nickel ions in the organic phase are exchanged with the impurity metal ions. The pure extraction raffinate is fed to further processing, and a portion is used for preloading the organic phase. The organic phase from the extraction stage is fed to the scrubbing stage, where cobalt or nickel ions remaining in the organic phase are scrubbed back to the aqueous phase using a scrub solution containing impurity metal chlorides. After scrubbing, the impurity metals are stripped into the aqueous phase using diluted HCl in the stripping phase, after which the organic phase is preneutralised and used in the preloading stage. The aqueous solution containing impurity metals is fed to further processing and to the scrubbing stage. In the preloading stage, a portion of the extraction raffinate containing cobalt or nickel is contacted with preneutralised organic phase, and the neutralising agent cations are exchanged with cobalt or nickel. After preloading, the aqueous phase contains neutralising agent cations and is discarded as reject, while the cobalt or nickel loaded organic phase is fed to the extraction stage.

Based on the studies mentioned above, both D2EHPA and Cyanex 272 can be used effectively for nickel preloading. D2EHPA can be used at lower pH (4.0–4.5) to extract nickel, and there were no precipitation issues reported [32]. In contrast, extraction using Cyanex 272 requires pH values over 6.0, and precipitation of nickel was reported. It was therefore suggested to be used in conditions where a specific pH value or nickel loading of the organic phase is not exceeded, whereas such restrictions were not reported for D2EHPA.

5 Experimental procedure

5.1 Chemicals

Nikel sulphate solutions were prepared by dissolving $NiSO_4 \cdot 6\ H_2O$ (Norilsk Nickel Harjavalta Oy) in deionised water. Organic solutions were prepared by diluting BAYSOLVEX® D2EHPA (D2EHPA) provided by Lanxess Deutschland GmbH, and CYANEX® 272 (Cyanex 272) provided by Syensqo, in D100 kerosene. All organic solutions were washed by shaking equal parts of organic solution and 50 g/L H_2SO_4 for three minutes in a 5 L canister, after which the organic solution and H_2SO_4 were separated. NaOH (200 g/L) was used for pH control.

5.2 Equipment

Experiments were conducted in a 1 L jacketed glass reactor (ø 10 cm) equipped with baffles and a lid. Organic and aqueous phases were mixed using two GLS impellers (ø 5 cm) connected to IKA EUROSTAR digital overhead stirrer. The mixing speed in the experiments was set to 700 rpm. The temperature was controlled by Grant Instruments™ TC120 digital heated circulator and was set to 55 °C for the experiments.

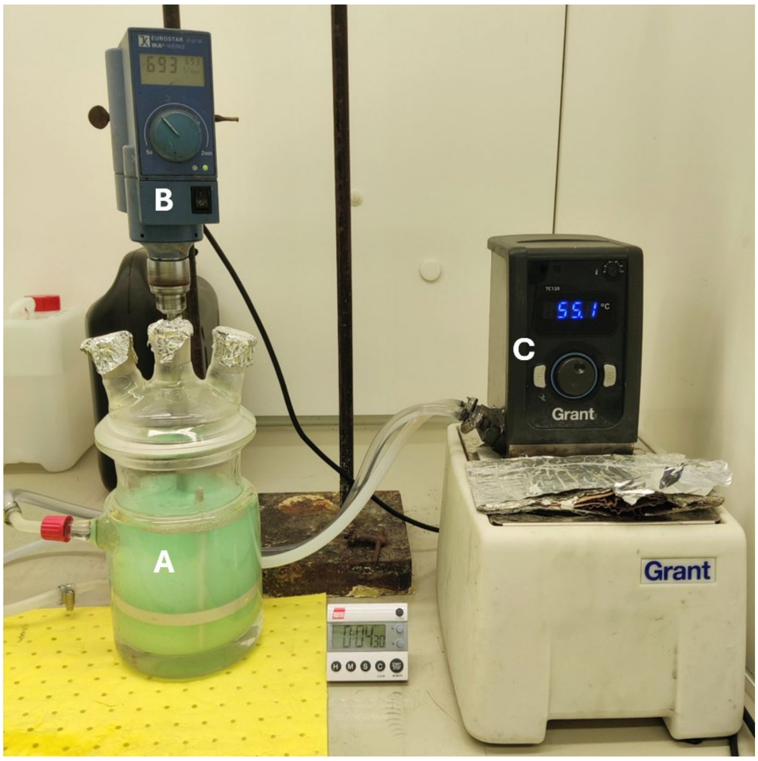


Figure 13. Experimental setup used for the experiments. A) Jacketed glass reactor equipped with a baffle and a lid. B) Overhead stirrer and impeller. C) Heated circulator.

5.3 Analytics

The pH in each experiment was measured using Mettler Toledo Seven2Go™ pH meter with a Mettler Toledo InLab® Max Pro-ISM probe. The pH meter was calibrated with pH 4.01 and 7.00 pH buffer solutions prior to each experiment.

Metal concentrations in the organic phase and aqueous phase were analysed with SPECTRO ARCOS ICP-OES analyser. Organic samples were diluted in D100 kerosene before analysis, and aqueous samples were syringe filtered and diluted with HNO_3 before analysis.

The active component concentration in the organic phase was determined by titration with a Mettler Toledo T9 titrator. The organic phase sample was diluted in 75 v% 2-propanol in deionised water and titrated using 0.1 M NaOH.

5.4 pH isotherms experiments

The effect of nickel concentration on the pH isotherms was studied using 0.5 and 1.0 M Cyanex 272 and D2EHPA, as well as synthetic nickel sulphate solutions with concentrations of 21–23, 51–59, and 110–118 g/L. In the experiments, the organic to aqueous ratio was varied for each nickel and reagent concentration. The O/A of each experiment was determined by setting the ratio of reagent to nickel amounts at five. The temperature was set at 55 °C for the experiments, and the solutions were preheated in a water bath prior to mixing.

In the experiments, the pH was controlled by constant volume NaOH (200 g/L) additions every 15 minutes. The volume of NaOH addition was determined by the sodium to nickel ratio. The first two additions were 0.1 times the nickel amount, and the rest were 0.2 times the nickel amount. NaOH additions were continued until the total ratio of added sodium and nickel was 2.2 or until two visually colourless aqueous samples were obtained. Samples were taken from the dispersion after 15 minutes of mixing, before NaOH addition. The first samples were taken after 15 minutes of mixing and before any NaOH addition. The volume of the dispersion sample was measured, as well as the volumes of the separated aqueous and organic samples. The aqueous sample was syringe filtered, and the pH was measured. After the experiment, the organic and aqueous phases were separated, and the volumes were measured. The percentage of extraction was calculated using Equation 4:

$$\%E = \frac{C_0 - C_e}{C_0} * 100\ \% \tag{4}$$

where C_0 is initial nickel concentration in aqueous phase and C_e is nickel equilibrium concentration in aqueous phase after extraction. Nickel loading of the organic phase was calculated using Equation 5:

$$L\% = \frac{3 * C_{Ni}}{C_{Reag.}} * 100\% \tag{5}$$

where C_{Ni} is the nickel concentration in the organic phase (mol/L) and $C_{Reag.}$ is the reagent concentration (mol/L). The parameters for each experiment can be seen in Table 2 and Table 3.

Table 2. Experiment parameters for Cyanex 272.

C_{Ni} [g/L]	**C_{Ni}** [mol/L]	**$C_{reag.}$** [mol/L]	**O/A** -	**V_{aq}** [mL]	**V_{org}** [mL]
23	0.37	0.5	3.7	214	786
52	0.90	0.5	9.0	100	900
118	2.00	0.5	20.0	48	953
22	0.37	1.0	1.9	347	653
51	0.90	1.0	4.5	182	818
114	2.00	1.0	10.0	91	909

Table 3. Experiment parameters for D2EHPA.

C_{Ni} [g/L]	**C_{Ni}** [mol/L]	**$C_{reag.}$** [mol/L]	**O/A** -	**V_{aq}** [mL]	**V_{org}** [mL]
21	0.37	0.5	3.8	214	786
59	0.90	0.5	9.2	100	900
116	2.00	0.5	20.0	48	953
21	0.37	1.0	1.8	347	653
57	0.90	1.0	4.4	182	818
110	2.00	1.0	9.8	91	909

5.5 Effect of equilibration time on the extraction

The effect of equilibration time on the extraction of nickel was studied using 0.5 M D2EHPA and 60 g/L nickel solution at O/A=8.3, $V_{tot.}$= 1000 mL and T=55 °C. The organic solution was allowed to preheat in the reactor, while the aqueous solution was preheated in a warm water bath. Preheated solutions were first mixed for 15 minutes before the addition of NaOH. After 15 minutes, a dispersion sample was taken, the organic and aqueous samples were separated from it. The aqueous sample was syringe filtered, and the pH was measured from it. After the first sample, mixing was continued, and 43 mL of NaOH, corresponding to sodium to nickel ratio of ~1.9, was added gradually, and the time taking was started. Samples were taken and pH was measured every 15 minutes for a total of 80 minutes. After the experiment, the organic and aqueous phases were separated, and the volumes were measured.

5.6 Effect of the ratio of reagent and nickel amount

The effect of the ratio of reagent and nickel amount on the extraction of nickel was studied using 0.5 M D2EHPA. The reagent to nickel ratio of 5.5 was studied using 57 g/L nickel solution at O/A=11, and the ratio of 7.2 was studied using 55 g/L nickel solution at O/A=13.8. The temperature in both experiments was set at 55 °C. Preheated organic and aqueous phases were mixed for 15 minutes prior to the addition of NaOH. After 15 min, a dispersion sample was taken, and the organic and aqueous samples were separated from it. The aqueous sample was syringe filtered, and the pH was measured from it. After the first sample, NaOH additions were made according to Table 4 every 15 minutes after sampling. After the experiment, the organic and aqueous phases were separated, and the volumes were measured.

Table 4. Sodium to nickel ratios used for reagent to nickel ratio experiments. Nickel solution used in the experiment for the reagent to nickel ratio of 5.5 was 57 g/L, and 55 g/L nickel solution was used in the experiment for the reagent to nickel ratio of 7.2.

NaOH addition point	**Reagent/Ni 5.5**	**Reagent/Ni 7.2**
1	0.0	0.0
2	1.1	1.4
3	1.3	1.7
4	1.5	2.1
5	1.7	2.5
6	1.8	2.7
7	2.0	-
8	2.4	-

5.7 Equilibrium isotherm and McCabe–Thiele analysis

The effect of nickel concentration on the nickel loading equilibrium was studied using 0.5 M DEHPA and 19 g/L, 49 g/L and 113 g/L nickel solutions. In the experiments, various organic to aqueous ratios were used for each nickel concentration. The temperature was set at 55 °C for the experiments, and the solutions were preheated in a water bath prior to mixing. The first

NaOH addition was made prior to the addition of the nickel solution. After the addition of the nickel solution, mixing was continued for 15 minutes, after which the organic and aqueous phases were allowed to separate, and the pH of the aqueous phase was measured. NaOH additions were made after every 15 minutes of mixing until the equilibrium pH 4.00 (± 0.05) was reached. At the equilibrium pH, samples from aqueous and organic phases were taken, and volumes of aqueous and organic phases were measured. The O/A and the volumes of the aqueous and organic phases for each experiment are presented in Table 5, Table 6 and Table 7.

Table 5. Aqueous and organic phase volumes, O/A ratios and organic nickel loading percentage for equilibrium experiments using 19 g/L nickel solution, 15 minutes mixing time, temperature of 55 ℃ and 700 rpm mixing speed.

V_{aq} [mL]	V_{org} [mL]	**O/A** -	**Loading** [%]
185	315	1.7	118
167	333	2.0	100
152	348	2.3	87
132	368	2.8	72
111	389	3.5	57
86	414	4.8	42
61	439	7.2	28
31	469	15.0	13

Table 6. Aqueous and organic phase volumes, O/A ratios and organic nickel loading percentage for equilibrium experiments using 49 g/L nickel solution, 15 minutes mixing time, temperature of 55 ℃ and 700 rpm mixing speed.

V_{aq} [mL]	V_{org} [mL]	**O/A** -	**Loading** [%]
86	414	4.8	116
77	423	5.5	101
68	432	6.4	87
57	443	7.8	71
46	454	9.8	57
35	465	13.3	42
38	762	20.2	28
24	976	41.0	14

Table 7. Aqueous and organic phase volumes, O/A ratios and organic nickel loading percentage for equilibrium experiments using 113 g/L nickel solution, 15 minutes mixing time, temperature of 55 ℃ and 700 rpm mixing speed.

V_{aq} [mL]	V_{org} [mL]	**O/A** -	**Loading** [%]
48	452	9.5	115
43	457	10.7	102
38	462	12.3	88
39	561	14.5	75
32	568	17.8	61
34	766	22.5	48
31	969	31.0	35
20	980	50.0	22

Aqueous and organic phase equilibrium concentrations were plotted against each other, and nonlinear Langmuir adsorption isotherm model was fitted to the data [34]. The model was used for a McCabe–Thiele analysis to determine the number of ideal extraction stages required to achieve the target metal concentration in the raffinate [35]. The nonlinear form of the Langmuir adsorption isotherm model is:

$$q_e = \frac{Q_0 b C_e}{1 + C_e} \tag{6}$$

where q_e is the equilibrium concentration (mg/L) of the adsorbate in the adsorbent phase, C_e is the equilibrium concentration (mg/L) of the adsorbate in the aqueous phase, Q_e is the monolayer adsorption capacity (mg/g), and b is the model specific parameter. The model was extrapolated by using the initial nickel concentration of each experiment as the last C_e in the model.

6 Results

6.1 pH isotherm experiments

6.1.1 Cyanex 272

The initial nickel concentrations in 0.5 M Cyanex 272 experiments were 23, 52 and 118 g/L. The pH isotherm using 0.5 M Cyanex 272 is shown in Figure 14. In all nickel concentrations, ~100% extraction was achieved. When using 118 g/L nickel solution, extraction took place at a lower pH, whereas with 23 g/L solution, extraction took place at a higher pH. A slightly greater difference in pH is observed between the 118 and 54 g/L solutions compared to the difference between the 54 and 22 g/L solutions. The pH_{50} values for 23, 52, and 118 g/L nickel solutions are 5.39, 5.26, and 5.00, respectively. The pH ranges in which extraction took place were 3.01–7.19, 2.79–7.10, and 2.60–7.28 for 23, 52, and 118 g/L nickel concentrations, respectively. All analyses from all Cyanex 272 experiments can be found in Appendix A.

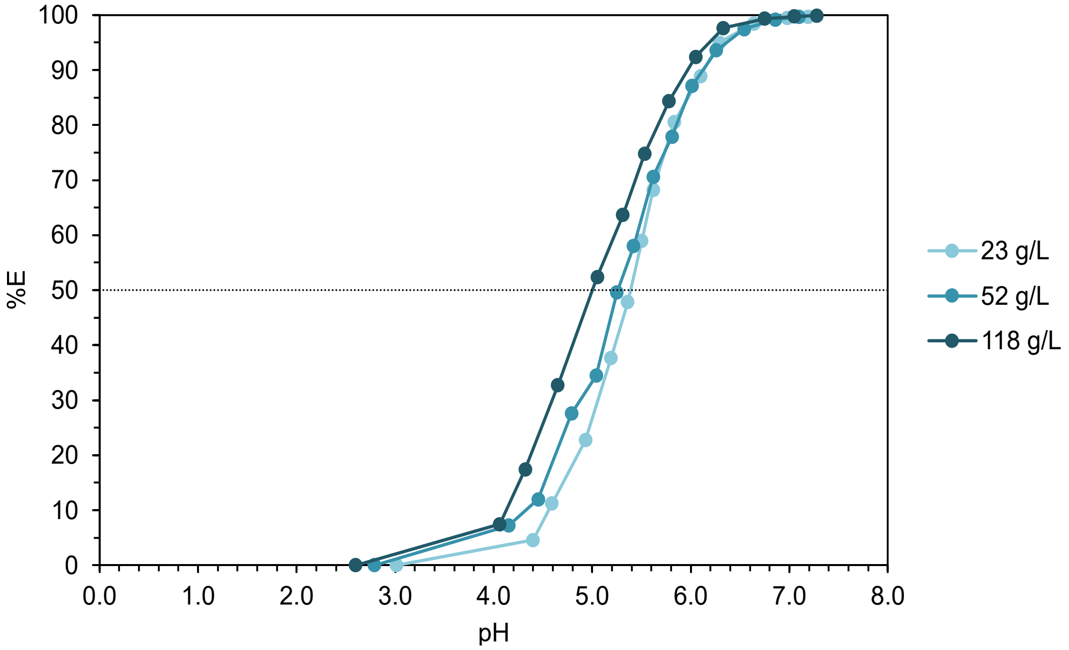


Figure 14. pH isotherm for 23, 52 and 118 g/L nickel solutions using 0.5 M Cyanex 272 and 15 minutes mixing time at 55 ℃. The O/A ratios were 3.7, 9.0 and 20.0 for 23, 52 and 118 g/L nickel solution experiments, respectively.

The initial nickel concentrations for 1.0 M Cyanex 272 experiments were 22, 51 and 114 g/L. The pH isotherm using 1.0 M Cyanex 272 is presented in Figure 15. Similarly to 0.5 M Cyanex 272, with 1.0 M Cyanex 272, there can be seen differences in the pH between the different nickel concentrations. The pH_{50} values for 22, 51 and 114 g/L nickel solutions are 5.14, 5.04

and 4.85, respectively. Extraction took place in the pH ranges of 2.91–6.81, 2.62–6.50, 2.41–6.78 for 22, 51 and 114 g/L nickel solutions, respectively. Within these pH ranges, ~100% extraction was achieved from 22 and 118 g/L nickel solutions, while ~98% was reached from 51 g/L nickel solution.

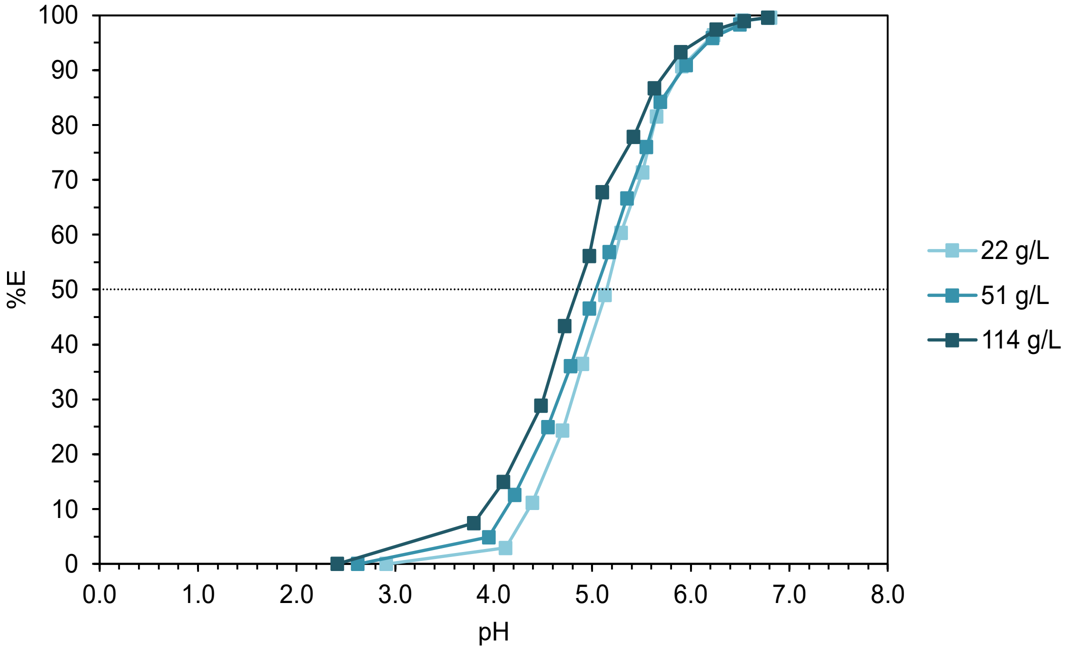


Figure 15. pH isotherm for 22, 52 and 114 g/L nickel solutions using 1.0 M Cyanex 272 and 15 minutes mixing time at 55 ℃. The O/A ratios were 1.9, 4.5 and 10.0 for 22, 52 and 114 g/L nickel solution experiments, respectively.

The final volumes of both phases were calculated, taking into account the NaOH additions and sample volumes. When comparing the initial volumes of the aqueous phase and organic phase with the final volumes, there can be seen differences in all experiments. In the aqueous solution volumes, the measured final volume was, in all cases, lower than the calculated volume, while the final measured volumes of the organic solution were slightly higher than the calculated volumes. The calculated and measured volumes of both organic and aqueous phases, as well as the difference between calculated and measured volumes as a percentage, are presented in Table 8. In the experiment where 118 g/L nickel solution and 0.5 M Cyanex 272 were used, there is a larger percentage difference between the calculated and measured volumes than in other experiments. The final separation of the organic and aqueous phases was difficult in this experiment, as the organic phase began to solidify during the separation. Since the separation of the phases was not successful, the measured volumes are not accurate. After the experiments, some precipitation could be seen inside the reactor in the liquid line and between the reactor and the lid.

Table 8. The volumes of the aqueous and organic phases were calculated by taking into account the sample volume and NaOH addition, the measured volumes of both phases and the difference between the calculated and measured volumes as a percentage.

C_{Ni} [g/L]	$C_{reag.}$ [mol/L]	O/A Initial -	$V_{aq\ calc.}$ [mL]	$V_{aq\ meas.}$ [mL]	ΔV [%]	$V_{org\ calc.}$ [mL]	$V_{org\ meas.}$ [mL]	ΔV [%]
23	0.5	3.7	224	188	-16.1	693	682	-1.5
52	0.5	9.0	115	90	-21.8	649	650	0.2
118	0.5	20.0	57	21*	-64.0	372	350*	-5.9
22	1.0	1.9	359	325	-9.4	564	590	4.7
51	1.0	4.5	217	186	-14.2	660	680	3.0
114	1.0	10.0	136	98	-27.9	570	583	2.3

*Solidification began during the separation of the phases, which is why a reliable measurement was not possible.

In Cyanex 272 experiments, sodium to nickel ratio of 2.2 was sufficient for over 99% extraction in all nickel and Cyanex 272 concentrations except when 51 g/L nickel and 1.0 M Cyanex 272 were used, in which case ~98% extraction was achieved. Sodium to nickel ratio of 2.4 was used in the experiments using 0.5 M Cyanex 272 with 23 and 52 g/L nickel solutions.

In experiments using 0.5 M Cyanex 272, it was observed that at higher pH levels, the organic phase began to solidify as it cooled down during sampling and final phase separation. Solidification occurred when the loading of the organic phase was over ~58%. The solidification was more rapid at higher organic loadings, whereas at lower loadings, solidification of some samples was not noticed until the next day. For this reason, it was decided to predilute the organic samples with fresh organic phase in ~1/1 ratio right after sampling in the experiments using 1.0 M Cyanex 272. The prediluted samples did not show any signs of solidifying. In addition, as the loading of the organic increased, the viscosity of the organic phase also increased, which in turn increased the separation times.

The organic samples, in which the loading of the organic phase was over ~58% and were not prediluted, could not be analysed. However, the samples from the 1.0 M Cyanex 272 experiments were analysed, and it was observed that with 22 and 114 g/L nickel solutions, the nickel concentration in the organic phase increased with increasing percentage of extraction until it decreased rapidly when 100% extraction was neared. In the experiment, where 51 g/L nickel solution was used, the nickel concentration in the organic phase and the percentage of extraction increased. In the experiments, the rate of the pH increase was slightly increased when the nickel concentration in the organic phase began to decrease. In Figure 16, the nickel concentration in the organic phase against the percentage of extraction in the 1.0 M Cyanex 272 experiments is presented.

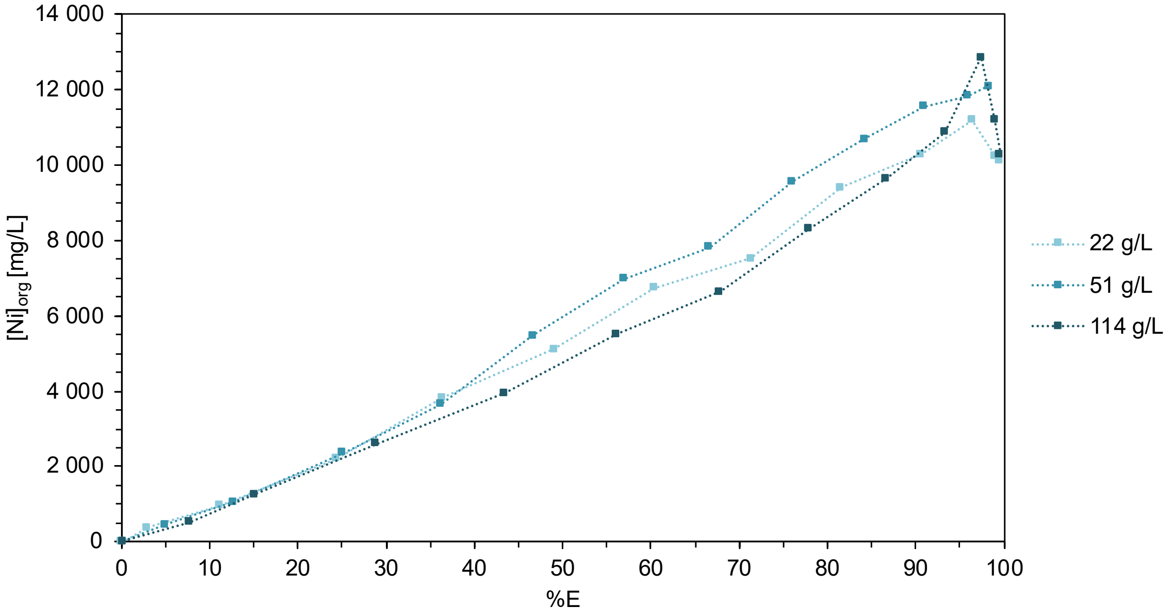


Figure 16. The nickel concentration in the organic phase plotted against the percentage of extraction using 1.0 M Cyanex 272.

6.1.2 D2EHPA

The initial nickel concentrations in 0.5 M D2EHPA experiments were 22, 59 and 116 g/L, and the pH isotherm for these concentrations is presented in Figure 17. Extraction took place in the pH range of 2.15–4.54 with 22 g/L nickel solution, 1.91–5.11 with 59 g/L solution and 1.58–5.62 with 116 g/L nickel solution. The maximum extraction percentages were ~97%, ~98%, and ~99%, and the pH_{50} values were 3.17, 3.06, and 2.85 for 22, 59, and 116 g/L nickel solutions, respectively. All analyses from all D2EHPA experiments can be found in Appendices B and C.

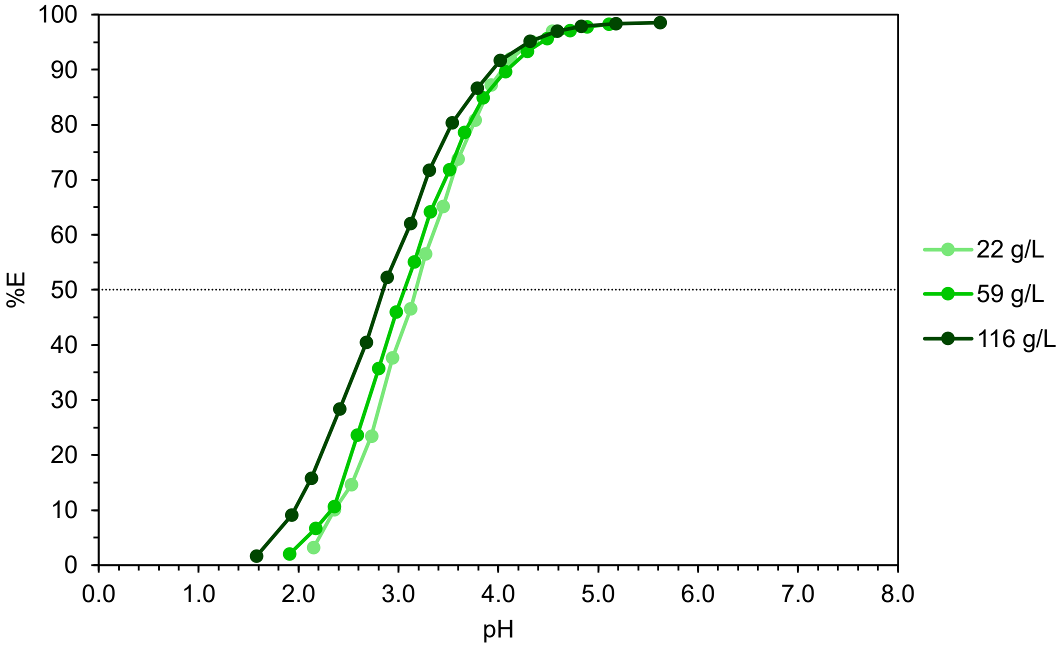


Figure 17. pH isotherm for 22, 59 g/L and 116 g/L nickel solutions using 0.5 M D2EHPA and 15 minutes mixing time at 55 ℃. The O/A ratios were 3.8, 9.2 and 20.0 for 22, 59 and 116 g/L nickel solution experiments, respectively.

The initial nickel concentrations for 1.0 M D2EHPA experiments were 20, 57, and 110 g/L. The pH isotherm for 1.0 M D2EHPA is presented in Figure 18. The pH_{50} values for 20, 57, and 110 g/L nickel solutions are 2.95, 2.82, and 2.74, respectively. Extraction took place in the pH ranges of 1.99–4.80, 1.74–5.17, and 1.50–5.40 for 20, 57, and 110 g/L nickel solutions, respectively. The maximum extraction percentage was ~99% for 20 g/L nickel solution, and ~98% for 57 and 110 g/L nickel solutions.

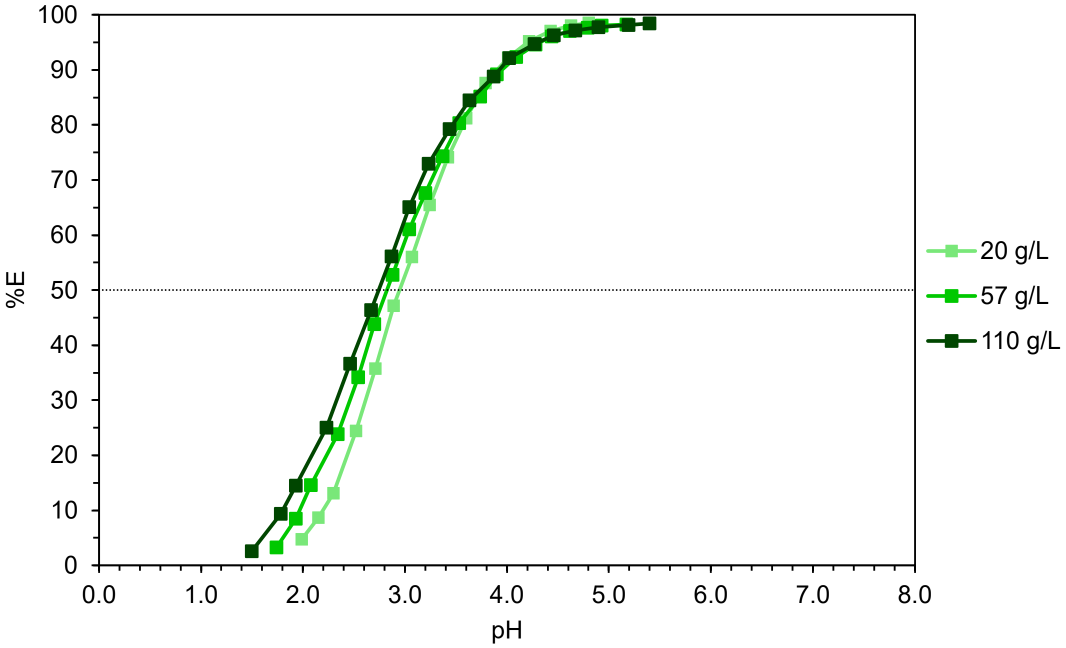


Figure 18. pH isotherm for 20, 57 and 110 g/L nickel solutions using 1.0 M D2EHPA and 15 minutes mixing time at 55 ℃. The O/A ratios were 1.8, 4.4 and 9.8 for 20, 57 and 110 g/L nickel solution experiments, respectively.

NaOH additions corresponding to sodium to nickel ratio of 2.2 were not sufficient for the extraction of nickel using D2EHPA. In Table 9, the initial nickel concentrations with both extractant concentrations, as well as the highest percentages of extraction and sodium to nickel ratios corresponding to them, are presented. With 1.0 M D2EHPA, a higher sodium to nickel ratio was needed as the nickel concentration increased, while with 0.5 M D2EHPA, this was not as evident, as the percentage of extraction also slightly increased as the ratio slightly increased.

Table 9. Sodium to nickel ratios and percentage of extraction for each nickel and reagent concentration in pH isotherm experiments.

***C**$_{Ni}$* [g/L]	***C**$_{reag.}$* [mol/L]	***%E*** [%]	**Na/Ni**
22	0.5	97.0	2.5
59	0.5	98.2	2.7
116	0.5	98.5	2.8
21	1.0	98.5	3.0
57	1.0	98.2	3.3
110	1.0	98.4	3.7

Similarly to Cyanex 272 experiments, as the loading of the organic phase increased, the viscosity of the organic phase increased, which in turn increased the separation time. Also, the calculated and measured final volumes were compared. In the aqueous solution volumes, the measured final volume was lower than the calculated volume in all cases, except with 116 g/L nickel solution, while the final measured volumes of the organic solution were slightly higher than the calculated volumes. In the experiment, where 116 g/L nickel solution and 0.5 M D2EHPA were used, there is a significant percentage difference between the calculated and measured volumes. Towards the end of this experiment, the volumes of the phases were so low that air was mixed into the dispersion. The separation time was also longer toward the end, and the final phase separation was slow, which made measuring the final volumes difficult. The calculated and measured volumes of both organic and aqueous phases, as well as the difference as a percentage of calculated and measured volumes, are presented in Table 10.

Table 10. The volumes of aqueous and organic phases calculated by taking into account the sample volume and NaOH addition, the measured volumes of both phases and the difference between the calculated and measured volumes as a percentage.

c_{Ni} [g/L]	$c_{reag.}$ [mol/L]	$V_{aq\ calc.}$ [mL]	$V_{aq\ meas.}$ [mL]	ΔV [%]	$V_{org\ calc.}$ [mL]	$V_{org\ meas.}$ [mL]	ΔV [%]
22	0.5	213	191	-10.2	678	693	2.2
59	0.5	104	70	-32.7	530	550	3.8
116	0.5	64	75	17.8*	365	752	105.8*
21	1.0	367	320	-12.8	548	576	5.1
57	1.0	256	183	-28.6	624	679	8.8
110	1.0	162	92	-43.3	510	567	11.2

*Phase separation was slow, making measuring the volumes accurately difficult.

In the experiments, it was also observed that, towards the end of the experiment, the nickel concentration in the organic phase decreased, while the percentage of extraction from the aqueous solution and the pH increased. In the Figure 19 and Figure 20, nickel concentration in the organic phase is plotted against the percentage of extraction. From Figure 19, it can be seen that the nickel concentration in the organic phase decreased with all nickel concentrations using 0.5 M D2EHPA. The most significant decrease is observed with 116 g/L nickel solution, where nickel concentration decreased from ~5.5 g/L to ~4.6 g/L. The second most significant decrease is observed with 22 g/L nickel, where nickel concentration decreases from ~5.6 g/L to ~5.2 g/L. As the nickel concentration decreased, the pH increased at a clearly faster rate than in the previous points, where the nickel concentration in the organic phase was increasing.

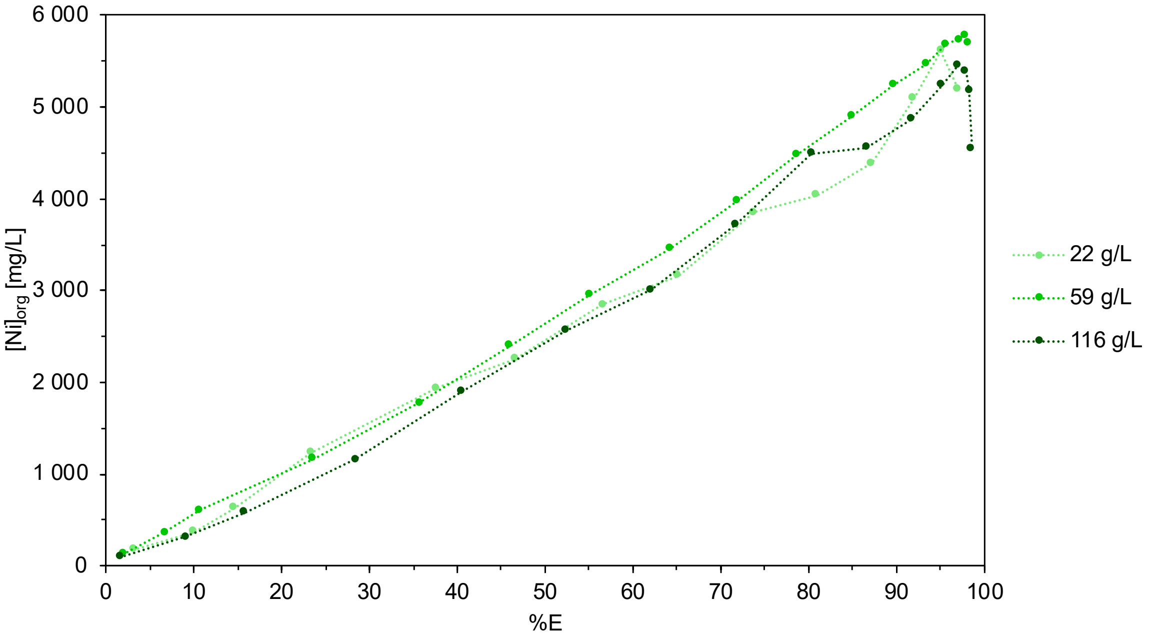


Figure 19. The nickel concentration in the organic phase plotted against the percentage of extraction using 0.5 M D2EHPA.

From Figure 20, it can be seen that the increase of nickel concentration in the organic phase also stopped and began to rapidly decrease in 1.0 M D2EHPA experiments. In experiments with 21 and 57 g/L nickel concentrations, there can be seen nickel concentration spiking to over 11 g/L in the organic solution. With 21 g/L nickel solution, the decrease in the nickel concentration in the organic is ~0.7 g/L. In the experiment with 57 g/L nickel, the nickel concentration decreased from ~11.8 g/L to ~10.3 g/L, and in the experiment with 110 g/L nickel, the decrease was from ~10.9 g/L to ~9.3 g/L. Similarly to 0.5 M experiments, the pH was observed to begin to increase exponentially and was nearly vertical when maximum extraction was achieved.

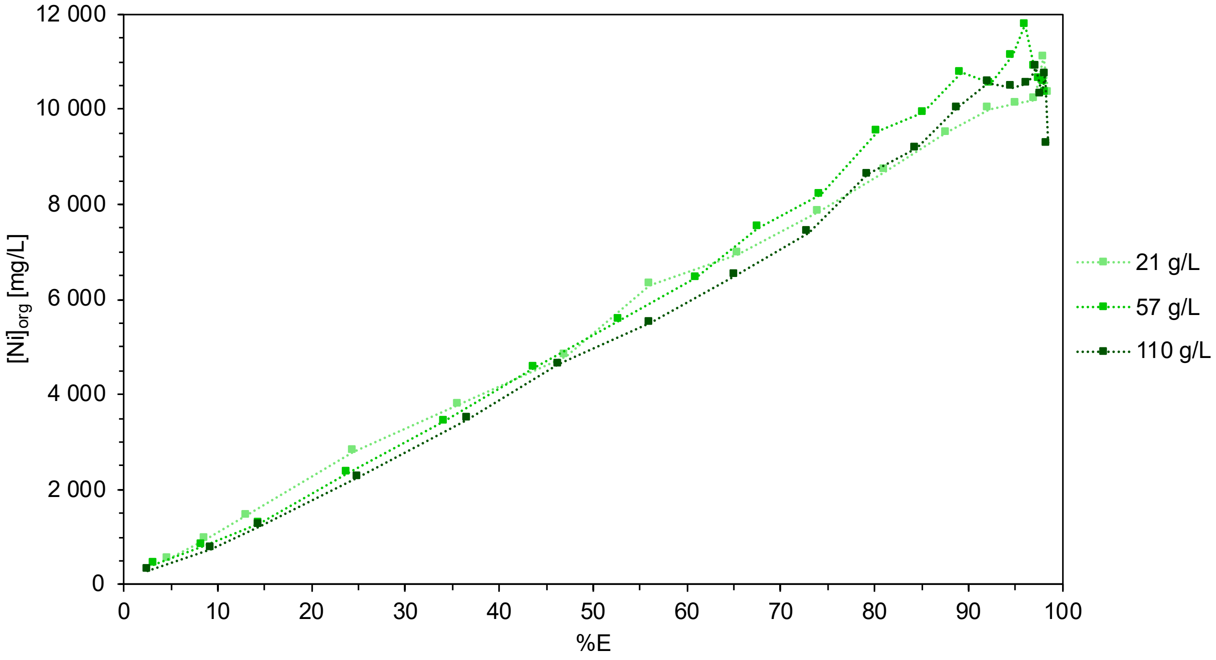


Figure 20. The nickel concentration in the organic phase plotted against the percentage of extraction using 1.0 M D2EHPA.

6.2 Effect of equilibration time on the extraction

The effect of equilibration time on the extraction was studied as described in section 5.5. After the initial mixing, before the addition of NaOH, the pH was 1.84, and the percentage of extraction was ~2.8%. Mixing was continued after NaOH addition, and after every 15 minutes of mixing, the pH was measured to be in the range of 4.01–4.04. The percentage of extraction was ~87% in all experiment points.

6.3 Effect of the ratio of reagent and nickel amount on the extraction

The effect of the ratio of reagent and nickel amount on the extraction was studied as described in section 5.6. With the reagent to nickel ratio of 5.5, the maximum percentage of extraction was ~94.5% from 57 g/L of nickel at sodium to nickel ratio of 2.4. With the reagent to nickel ratio of 7.2 with 55 g/L nickel solution, the percentage of extraction was ~96.8% at sodium to nickel ratio of 2.7, and ~93.4% at sodium to nickel ratio of 2.5. When the reagent to nickel ratio of 5.0 was used with 59 g/L nickel solution, the percentage of extraction was ~98.2% at sodium to nickel ratio of 2.7, and ~97.8% at sodium to nickel ratio of 2.5.

6.4 Equilibrium isotherm and McCabe–Thiele analysis

In the construction of the equilibrium isotherm, 19, 49 and 113 g/L nickel solutions and 0.5 M D2EHPA were used. D2EHPA was selected as the extractant, as it proved to extract nickel at low pH values. The curve fitting to the equilibrium data was done with the nonlinear Langmuir adsorption model. From Figure 19, it can be seen that as the nickel concentration decreased, the curve became steeper. Analyses from equilibrium isotherm experiments can be found in Appendix D.

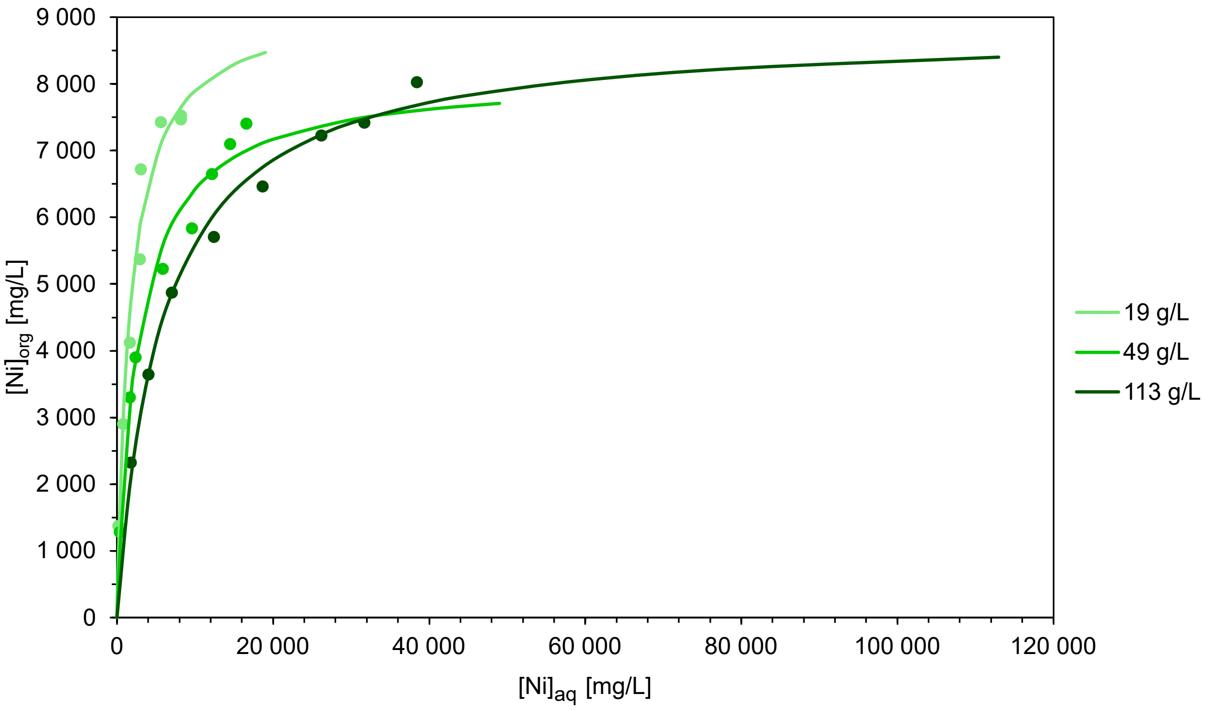


Figure 21. Loading isotherm of 0.5 M D2EHPA using 19, 49 and 113 g/L nickel solutions with 15 minutes mixing time, various O/A and at 55 °C.

In the McCabe–Thiele analysis, 45% loading of the organic was targeted for each nickel concentration. With 0.5 M D2EHPA, this corresponds to ~4.58 g/L of nickel in the organic. As the nickel loading of the organic was set to 4.58 g/L and the initial aqueous concentrations of 19, 49, and 113 g/L were used, the operating lines were at O/A 4.1, 10.7 and 24.7, respectively. In Figure 22, Figure 23 and Figure 22, the equilibrium isotherms and McCabe–Thiele analyses are presented. Based on the figures, two ideal extraction stages would be needed to extract all nickel from each aqueous solution.

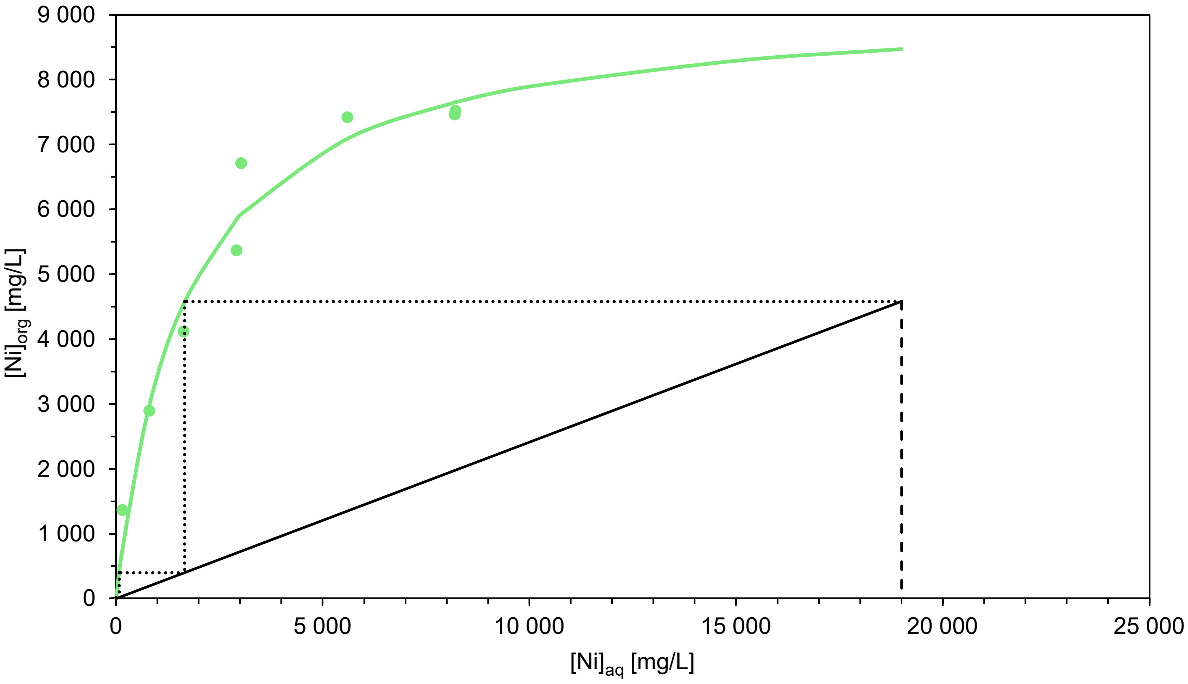


Figure 22. Equilibrium isotherm and McCabe–Thiele analysis of 0.5 M D2EHPA and 19 g/L nickel solution at 55 °C and pH 4.00 (± 0.05). The green dots are the equilibrium points from the experiments, the green line is the equilibrium model, black solid line is the operating line at O/A=4.1, black dashed line is the aqueous concentration, and the black dotted line is the ideal stage lines.

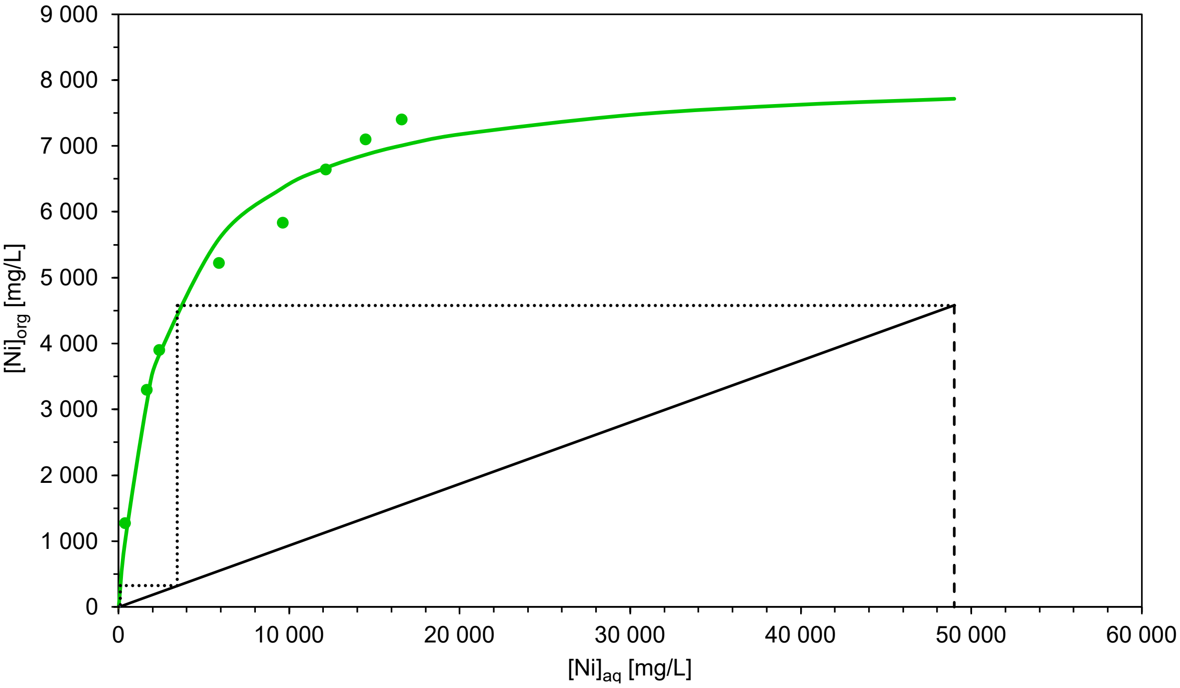


Figure 23. Equilibrium isotherm and McCabe–Thiele analysis of 0.5 M D2EHPA and 49 g/L nickel solution at 55 °C and pH 4.00 (± 0.05). The green dots are the equilibrium points from the experiments, the green line is the equilibrium model, black solid line is the operating line at O/A=10.7, black dashed line is the aqueous concentration, and the black dotted line is the ideal stage lines.

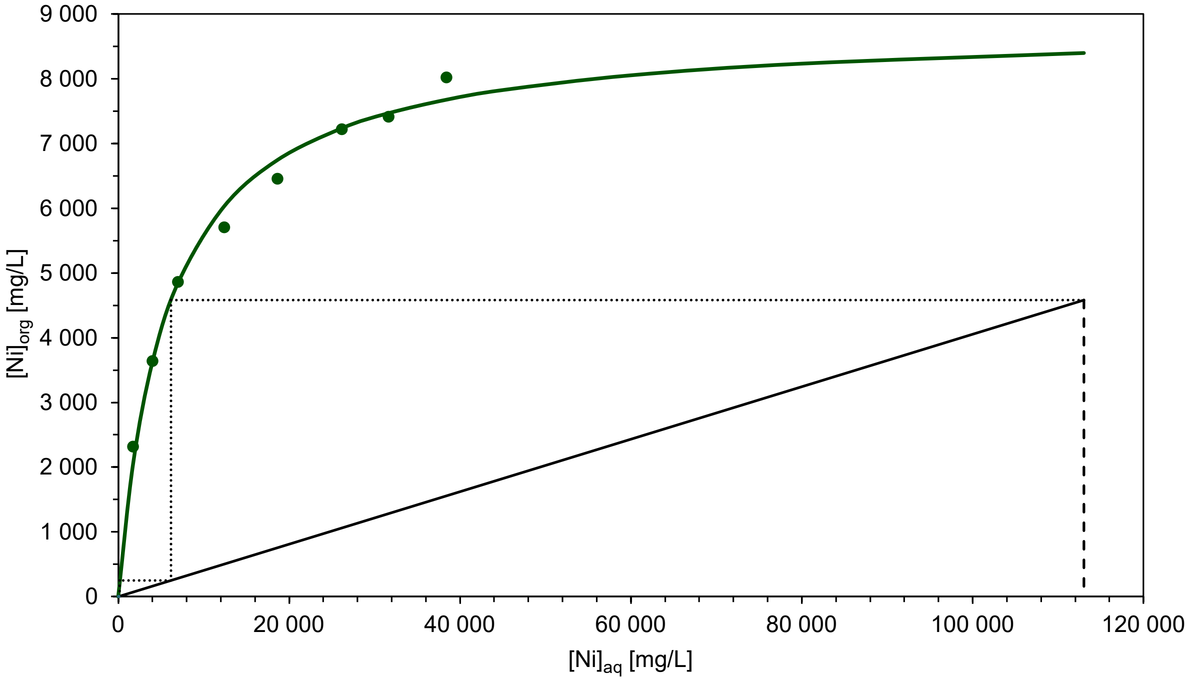


Figure 24. Equilibrium isotherm and McCabe–Thiele analysis of 0.5 M D2EHPA and 113 g/L nickel solution at 55 °C and pH 4.00 (± 0.05). The green dots are the equilibrium points from the experiments, the green line is the equilibrium model, black solid line is the operating line at O/A=24.7, black dashed line is the aqueous concentration, and the black dotted line is the ideal stage lines.

Although the figures indicate that two ideal stages would be sufficient to remove all nickel in each initial concentration, there will be nickel left in the raffinate. In the model with an initial nickel concentration of 19 g/L, there is ~76 mg/L of nickel left in the raffinate after two ideal stages. With an initial nickel concentration of 49 g/L, there is ~111 mg/L left in the raffinate after two ideal stages, and with 113 g/L initial nickel concentration, there is ~168 mg/L left in the raffinate after two ideal stages. Nickel concentrations in the raffinate after each stage are presented in Table 11. The most significant differences in the nickel concentrations in the raffinate can be seen after the first stage. However, these differences become smaller after each stage, and after the third stage, the difference between the raffinate nickel concentrations is negligible.

Table 11. The nickel concentrations in the raffinate after each stage. O/A of 4.1, 10.7 and 24.7 were used for the initial nickel concentrations of 19, 49 and 113 g/L at 55 °C and pH 4.00 (± 0.05).

Extraction stage	**19 g/L Ni** [mg/L]	**49 g/L Ni** [mg/L]	**113 g/L Ni** [mg/L]
1	1658	3452	6191
2	76	111	168
3	3.4	3.4	4.4

To study the effect of the initial nickel concentration on the stage efficiency, the percentage of extraction after each stage was calculated. These results are presented in Table 12. The most significant difference can be seen after the first ideal stage, where ~91.27% from 19 g/L nickel feed, ~92.96% from 49 g/L nickel feed and ~94.52% from 113 g/L nickel feed are extracted. After the second stage, the differences are only 0.08–0.17 percentage points between the initial nickel concentrations. After the third stage, all nickel is practically extracted.

Table 12. The percentage extracted from each nickel concentration after each stage. O/A of 4.1, 10.7 and 24.7 were used for the initial nickel concentrations of 19, 49 and 113 g/L at 55 °C and pH 4.00 (± 0.05).

Extraction stage	**19 g/L Ni** [%]	**49 g/L Ni** [%]	**113 g/L Ni** [%]
1	91.27	92.96	94.52
2	99.60	99.77	99.85
3	99.98	99.99	100.00

7 Discussion

7.1 pH isotherm experiments

In the pH isotherm experiments, the effect of the aqueous nickel concentration on extraction was studied using 21–23, 51–59, and 110–118 g/L nickel solutions with 0.5 and 1.0 M D2EHPA and Cyanex 272. The results show that increasing the nickel concentration shifts the extraction to lower pH. This was observed with both extractants and extractant concentrations. The effect of the nickel concentration was previously studied with lower nickel concentrations (0.1, 1, 3.2, and 10 g/L) using 1 M D2EHPA, and it was found that increasing the nickel concentration shifts the extraction to a slightly higher pH [16]. The results presented here are opposite and clearly show that increasing nickel concentration shifts the extraction to lower pH. On the other hand, a few other studies show a similar effect of the increasing nickel concentration as presented here. For example, increasing nickel concentration from 2 g/L to 5 g/L using 0.6 M D2EHPA shifted the pH_{50} value from 3.4 to 3.3 [17], [18]. The results here indicate that at higher nickel concentrations, the pH_{50} values change more slowly than at lower concentrations, as described in the studies above. The pH_{50} values for D2EHPA were lower in the present experiments than the values reported in the literature. This was also observed for Cyanex 272, where a previously reported pH_{50} value of 6.06 was obtained with 1 g/L nickel solution and 0.4 M Cyanex 272 [20].

For both extractants, increasing the extractant concentration decreased the extraction pH. This has also been previously reported. For example, Liu et al. reported that increasing the Cyanex 272 concentration from 0.2 M to 0.5 M decreased the pH_{50} value from over 6.5 to 6.06 [20]. In the present experiments, increasing the Cyanex 272 concentration from 0.5 M to 1.0 M decreased the pH_{50} value from 5.39 (23 g/L nickel solution) to 5.14 (22 g/L nickel solution). Although the experiments show the same effect as in the previous study, the change in pH_{50} value is not as significant as in the previous study.

When comparing the results of D2EHPA and Cyanex 272 experiments, it is seen that D2EHPA extracts nickel at a lower pH than Cyanex 272, as expected. Regardless of the extractant concentration, 100% extraction was not achieved with D2EHPA, while it was achieved with Cyanex 272. Both of these effects were also reported by Darvishi et al., where 5 g/L nickel solution was used [18]. In the study, ~93% extraction was achieved, which is lower than in the present experiments. The previously reported pH range for nickel extraction using 0.6 M D2EHPA was ~2.3–4.3, and for 0.6 M Cyanex 272 it was ~4–8, while in the experiments here, the range for 0.5 M D2EHPA was 2.15–5.54 (22 g/L nickel solution) and for 0.5 M Cyanex 272 it was 3.01–7.19 (23 g/L solution). Incomplete extraction of nickel was also reported by Gharabaghi et al., where ~96% extraction was achieved using 1 M D2EHPA [16]. Also, the results from the experiments, which studied the effects of mixing time and reagent to nickel ratio, show that the percentage of extraction was not increased despite higher reagent to nickel ratios or longer mixing times. The previous studies and the results presented here suggest that 100% extraction cannot be achieved in a single stage with D2EHPA, regardless of the nickel concentration.

The results show that sodium to nickel ratio of 2.2 was sufficient neutralisation to achieve over 99% extraction using Cyanex 272, while with D2EHPA, ratios of 2.8–3.7 were needed (~97–99% extraction). According to Equation 2, two moles of sodium would be necessary to extract one mole of nickel, therefore sodium to nickel ratio of 2.2 should have been sufficient for complete extraction. One important thing to keep in mind when comparing the previous studies with the results here is that the nickel concentrations in the earlier studies are lower than in these experiments, and in some of the earlier studies, aqueous solutions contained other metals in addition to nickel. Also, pH isotherm experiments are often conducted at O/A=1, which means that, for example, while the nickel concentration is changed, also the reagent to nickel ratio is changed, whereas this ratio was kept constant in these experiments.

It was observed for both Cyanex 272 and D2EHPA that as the percentage of extraction was nearing 100%, the nickel concentration in the organic phase decreased. This was not observed in the 0.5 M Cyanex 272 experiments, as the decrease would likely have been measured from the solidified samples. In experiments using 1.0 M Cyanex, a decrease was observed with 22 and 114 g/L nickel concentrations, whereas with 51 g/L nickel concentration, a decrease was not observed. In 0.5 M D2EHPA experiments, a noticeable decrease was seen with 22 and 116 g/L nickel solutions, whereas with 59 g/L nickel solution, the decrease was negligible. In 1.0 M D2EHPA experiments, the most significant decrease was seen with 110 and 57 g/L nickel solutions, whereas the decrease was clearly lower with 21 g/L nickel solution. With both extractants, a change in the pH increasing rate was also observed just before the nickel concentration decreased. In 0.5 M Cyanex 272 experiments, the rate at which the pH increased was slightly faster than before the nickel concentration decrease. In D2EHPA experiments with both extractant concentrations, the pH began to grow exponentially before the nickel concentration was decreased. This change in pH increasing rate could indicate that, in the case of Cyanex 272, the extractant is becoming fully used as there are fewer protons released that

NaOH can neutralise. In the case of D2EHPA, the pH rise was eventually close to vertical, indicating there are no protons to be neutralised. This, along with the fact that longer equilibration time or a higher reagent to nickel ratio did not improve nickel extraction, suggests that complete nickel extraction is not achievable at these nickel concentrations with D2EHPA.

Some of the variation in nickel concentrations in the organic phases may be due to analytical accuracy. In addition, in 1.0 M Cyanex 272 experiments, predilution of the organic samples can affect the accuracy. Moreover, the increase in the percentage of extraction, while nickel concentration in the organic phase decreased, can partly be due to the precipitation of nickel. During the experiments, the level of the dispersion decreased due to sampling and evaporation, and some precipitation was seen inside the reactor. In addition, the pH in the Cyanex 272 experiments was above 6.3, at which Nogueira et al. reported the partial precipitation of nickel began [32]. According to Park et al., nickel started to precipitate at a pH of 6.6 with D2EHPA [36]. These pH values were exceeded in experiments using Cyanex 272, but in D2EHPA experiments, the pH reached a maximum pH value of 5.6.

Solidification of the organic phase was observed in Cyanex 272 experiments when the loading of the organic exceeded 58%. This is due to the extractant being overloaded, and exceeding this percentage should be avoided. Alternatively, using D2EHPA could be considered, as it did not show similar behaviour at the same loading percentages. Nonetheless, excessive loading of the phase should be avoided, as it was observed for both D2EHPA and Cyanex 272 that the organic phase viscosity increased, resulting in longer separation times.

7.2 Equilibrium isotherm and McCabe–Thiele analysis

The equilibrium isotherm experiments for McCabe–Thiele analysis were conducted with 19, 49, and 113 g/L nickel solutions and 0.5 M D2EHPA, and the Langmuir adsorption isotherm model was used. It can be seen that the beginning of the model becomes steeper as the initial nickel concentration decreases, i.e. the distribution ratio is higher for lower nickel concentration. The model does not provide the best fit to the equilibrium data. In the cases of 49 and 113 g/L of nickel solutions, it can be seen that at the equilibrium points with higher aqueous concentrations, the organic nickel concentration has a rising trend. In contrast, the increase of the organic concentration is usually expected to slow down, as can be seen, for example, in the study conducted by Devi et al. [9]. With 19 g/L nickel, this settling can be seen, but some data clearly deviate from the model. This can happen if the measured equilibrium pH of the point was off the target (4.00 ± 0.05). Although the fit is not optimal at higher equilibrium concentrations, it is satisfactory at lower equilibrium concentrations, where the McCabe–Thiele analysis is used in this case. If the model were used at a higher organic phase nickel loading, the model fitting would begin to affect the results. In addition to the Langmuir adsorption isotherm model, the equilibrium isotherms can be drawn by connecting the data with straight lines, as was done by Agarwal et al. [37]. However, the Langmuir model fitting was satisfactory for this purpose, as mentioned.

By visual inspection of the McCabe–Thiele analysis, it can be seen that two ideal stages would be sufficient for complete extraction. When comparing the extraction stages numerically, the most significant difference between the initial nickel concentrations is observed after the first ideal stage, where the higher the initial concentration was, the more nickel is left in the raffinate. After the second ideal stage, there can still be seen differences in the raffinate concentration. However, the nickel concentration of the raffinate was less than 200 mg/L in all initial concentrations. After the third stage, the differences were negligible. Although more nickel remains in the raffinate after the first and second ideal extraction stages, the extraction efficiency increased as the initial nickel concentration increased, when the efficiency is measured as a percentage of extraction from the initial nickel concentration. The most significant differences were observed after the first ideal extraction stage, and after the second ideal extraction stage, the differences were minor in terms of percentages of extraction. Although the extraction efficiency was highest with the 113 g/L nickel feed, a higher organic to aqueous ratio was also required to reach 4.58 g/L of nickel in the organic phase. With the 113 g/L nickel feed, an O/A ratio of 24.7 was needed, whereas with the 49 g/L nickel feed, the O/A ratio was 10.7, and with the 19 g/L nickel feed, an O/A ratio of 4.1 was needed. As the organic to aqueous ratio increases, more organic solution is required in circulation.

In the McCabe–Thiele analysis, it is important to consider that the extraction stages are ideal, i.e., the extraction efficiency in each stage is assumed to be 100%, which is not achievable in practice. In addition, the experiments were conducted at a specific temperature and pH, and therefore, they are applicable only under similar conditions. When planning the number of stages for industrial applications, it is important to consider the acceptable nickel content in the raffinate. If the desired nickel concentration in the raffinate is, let's say, less than 500 mg/L, in this case, two ideal stages would be needed. As 100% extraction efficiency is not possible, one additional stage would be sound to add in a real-life application. If extremely low raffinate concentrations are required, it is worth noting that adding stages means adding extraction units, which increases costs.

8 Conclusions

The purpose of this thesis was to investigate the effect of nickel concentration on the extraction and extraction efficiency using phosphorus-containing extractant, and the aim was to study it by comparing two concentrations of D2EHPA and Cyanex 272 (BTMPPA) and three different levels of high nickel concentration.

The literature review revealed that with D2EHPA, nickel could be extracted at the lowest pH, with pH_{50} values ranging from ~3.30 to 3.40. In contrast, with BTMPPA, the pH_{50} values were above 6.06. HEHEHP was shown to fall between these two, with pH_{50} values ranging from 5.05 to 5.25. For all these extractants, it was found that higher extractant concentration results in slightly decreased equilibrium pH. There were also indications that increasing nickel concentration would lower the pH_{50} value. In the literature, relatively low nickel concentrations have been used to study the extraction using phosphorus-containing extractants. Higher concentrations were primarily used in experiments studying nickel preloading of the organic phase using either BTMPPA or D2EHPA.

In the experimental part, where the effect of nickel concentration on the extraction was studied, nickel concentrations of 21–23, 51–59, and 110–118 g/L were used with 0.5 and 1.0 M of D2EHPA and Cyanex 272. The results showed that increasing the nickel concentration shifts the extraction to a lower pH. Additionally, increasing the extractant concentration lowers the extraction pH. These effects were observed with both extractants. It was also found that with D2EHPA, complete extraction of nickel could not be reached in a single stage, regardless of the nickel concentration. With Cyanex 272, complete extraction of nickel was achieved. Although D2EHPA extracts nickel at a lower pH than Cyanex 272, more NaOH was required for extraction with D2EHPA. It was also found that loading Cyanex 272 above 58% results in solidification of the organic phase.

The effect of nickel concentration on extraction efficiency was investigated using McCabe–Thiele analysis with 0.5 M D2EHPA and nickel concentrations of 19, 49, and 113 g/L. It was found that a lower initial nickel concentration results in a higher distribution ratio. From the McCabe–Thiele analysis, it was found that two ideal extraction stages would result in a raffinate containing less than 200 mg/L of nickel. The most significant differences were observed after the first ideal extraction stage, where the more nickel was in the feed, the more nickel remained in the raffinate. This was still seen after the second ideal extraction stage, and after the third stage, the differences are negligible. The effect on efficiency was investigated as the percentage of extraction. The most significant differences were seen after the first stage, where ~91.27% of 19 g/L nickel, ~92.96% of 49 g/L nickel, and ~94.52% of 113 g/L nickel were extracted. This shows that increasing the nickel concentration increases the extraction efficiency of the first ideal stage. After the second ideal stage, the differences in the efficiencies were only 0.08–0.17 percentage points.

In the future, the effect of nickel concentration should be studied using HEHEHP, as it is expected to fall between D2EHPA and Cyanex 272 (BTMPPA) in terms of equilibrium pH. It would also be beneficial to investigate whether complete nickel extraction can be achieved with this extractant using reasonable NaOH additions, similar to those with Cyanex 272. Additionally, the maximum loading capacity of it should be studied to see if it exhibits a similar solidification effect to Cyanex 272. Also, to further investigate the impact of nickel concentration on extraction and extraction efficiency, similar experiments should be performed for all three extractants at both high and low nickel concentrations using both extractant concentrations. This way, it can be seen whether the effect of the nickel concentration is the same across a broader range of nickel and extractant concentrations.

References

[1] ‘Nickel Institute | Knowledge for a brighter future’. Accessed: Oct. 08, 2025. [Online]. Available: https://nickelinstitute.org/en

[2] S. Kursunoglu, Z. T. Ichlas, and M. Kaya, ‘Solvent extraction process for the recovery of nickel and cobalt from Caldag laterite leach solution: The first bench scale study’, *Hydrometallurgy*, vol. 169, pp. 135–141, May 2017, doi: 10.1016/j.hydromet.2017.01.001.

[3] K. Sole, ‘Solvent extraction in the hydrometallurgical processing and purification of metals: process design and selected applications’, in *Solvent Extraction and Liquid Membranes: Fundamentals and Application in New Materials*, Boca Raton: CRC Press, 2008, pp. 141–200.

[4] E. Lindell, R. Luoma, and A. Oja, ‘Menetelmä sinkin, raudan, kalsiumin, kuparin ja mangaanin erottamiseksi koboltin ja/tai nikkelin vesiliuoksista’, FI 120943 B Accessed: May 08, 2025. [Online]. Available: https://patentimages.storage.googleapis.com/f9/81/8f/a95d0b5ca06ce9/FI120943B.pdf

[5] ‘Nickel processing Harjavalta | World-class expert’. Accessed: Sept. 03, 2025. [Online]. Available: https://www.nornickel.fi/en-gb

[6] G. M. Ritcey, *Solvent Extraction Principles and Applications to Process Metallurgy. Vol. 1.*, Revised Edition. Ottawa, Canada, 2006.

[7] Littlejohn, ‘Technical Review - Copper Solvent Extraction in Hydrometallurgy’. Accessed: Mar. 25, 2025. [Online]. Available: https://citeseerx.ist.psu.edu/document?repid=rep1&type=pdf&doi=1a215f29629b63cac40cb0fd8acf4cd0d37c74e1

[8] M. L. Free, *Hydrometallurgy: Fundamentals and Applications*. in The Minerals, Metals & Materials Series. Cham: Springer International Publishing, 2022. doi: 10.1007/978-3-030-88087-3.

[9] N. B. Devi, K. C. Nathsarma, and V. Chakravortty, ‘Separation and recovery of cobalt(II) and nickel(II) from sulphate solutions using sodium salts of D2EHPA, PC 88A and Cyanex 272’, *Hydrometallurgy*, vol. 49, no. 1, pp. 47–61, June 1998, doi: 10.1016/S0304-386X(97)00073-X.

[10] W. Wang, Y. Pranolo, and C. Y. Cheng, ‘Recovery of scandium from synthetic red mud leach solutions by solvent extraction with D2EHPA’, *Sep. Purif. Technol.*, vol. 108, pp. 96–102, Apr. 2013, doi: 10.1016/j.seppur.2013.02.001.

[11] J.-H. Jeon, J.-X. Wen, and M.-S. Lee, ‘Separation of Co(II), Mn(II) and Ni(II) from the sulfuric acid leaching solution of lithium-ion battery by solvent extraction’, *J. Min. Metall. Sect. B Metall.*, vol. 60, no. 3, pp. 395–405, 2024, doi: 10.2298/JMMB240731032J.

[12] G. Hu *et al.*, ‘Extraction of vanadium from chloride solution with high concentration of iron by solvent extraction using D2EHPA’, *Sep. Purif. Technol.*, vol. 125, pp. 59–65, Apr. 2014, doi: 10.1016/j.seppur.2014.01.031.

[13] Y. Jin, Y. Ma, Y. Weng, X. Jia, and J. Li, ‘Solvent extraction of Fe3+ from the hydrochloric acid route phosphoric acid by D2EHPA in kerosene’, *J. Ind. Eng. Chem.*, vol. 20, no. 5, pp. 3446–3452, Sept. 2014, doi: 10.1016/j.jiec.2013.12.033.

[14] P. A. Yudaev, N. A. Kolpinskaya, and E. M. Chistyakov, ‘Organophosphorous extractants for metals’, *Hydrometallurgy*, vol. 201, p. 105558, May 2021, doi: 10.1016/j.hydromet.2021.105558.

[15] C. Y. Cheng, ‘Purification of synthetic laterite leach solution by solvent extraction using D2EHPA’, *Hydrometallurgy*, vol. 56, no. 3, pp. 369–386, July 2000, doi: 10.1016/S0304-386X(00)00095-5.

[16] M. Gharabaghi, M. Irannajad, and A. R. Azadmehr, 'Separation of nickel and zinc ions in a synthetic acidic solution by solvent extraction using D2EHPA and Cyanex 272', *Physicochem. Probl. Miner. Process. ISSN 2084-4735*, 2013, doi: 10.5277/PPMP130121.

[17] A. Babakhani, F. Rashchi, A. Zakeri, and E. Vahidi, 'Selective separation of nickel and cadmium from sulfate solutions of spent nickel–cadmium batteries using mixtures of D2EHPA and Cyanex 302', *J. Power Sources*, vol. 247, pp. 127–133, Feb. 2014, doi: 10.1016/j.jpowsour.2013.08.063.

[18] D. Darvishi, D. F. Haghshenas, E. K. Alamdari, S. K. Sadrnezhaad, and M. Halali, 'Synergistic effect of Cyanex 272 and Cyanex 302 on separation of cobalt and nickel by D2EHPA', *Hydrometallurgy*, vol. 77, no. 3–4, pp. 227–238, June 2005, doi: 10.1016/j.hydromet.2005.02.002.

[19] J. E. Quinn, K. Soldenhoff, and G. W. Stevens, 'Alternatives to 2-Ethylhexyl Phosphonic Acid, Mono-2-Ethylhexyl Ester for the Separation of Rare Earths', in *Extraction 2018*, Cham: Springer International Publishing, 2018, pp. 2765–2775. doi: 10.1007/978-3-319-95022-8_234.

[20] W. Liu, J. Zhang, Z. Xu, J. Liang, and Z. Zhu, 'Study on the Extraction and Separation of Zinc, Cobalt, and Nickel Using Ionquest 801, Cyanex 272, and Their Mixtures', *Metals*, vol. 11, no. 3, p. 401, Mar. 2021, doi: 10.3390/met11030401.

[21] B. R. Reddy, C. Parija, and P. V. R. B. Sarma, 'Processing of solutions containing nickel and ammonium sulphate through solvent extraction using PC-88A', *Hydrometallurgy*, vol. 53, no. 1, pp. 11–17, July 1999, doi: 10.1016/S0304-386X(99)00036-5.

[22] Syensqo, 'Cyanex 272 Extractant brochure'. 2008.

[23] N. Begum, Z. Bari, S. B. Jamaludin, and K. Hussin, 'Solvent extraction of copper, nickel and zinc by Cyanex 272', *Int. J. Phys. Sci.*, vol. 7, no. 22, June 2012, doi: 10.5897/JCIIR12.116.

[24] P. E. Tsakiridis and S. Agatzini-Leonardou, 'Process for the recovery of cobalt and nickel in the presence of magnesium from sulphate solutions by Cyanex 272 and Cyanex 302', pp. 913–923, July 2004.

[25] Hexion Inc., 'Versatic Acid 10'. June 26, 2019.

[26] E. Jääskeläinen and E. Paatero, 'Properties of the ammonium form of Versatic 10 in a liquid–liquid extraction system', *Hydrometallurgy*, vol. 51, no. 1, pp. 47–71, Jan. 1999, doi: 10.1016/S0304-386X(98)00071-1.

[27] A. S. Guimarães, G. P. De Souza Resende, I. D. Dos Santos, Y. M. Vera, and M. B. Mansur, 'Evaluating cationic extractant systems containing Versatic 10 on the solvent extraction of metals from an Ni lateritic sulfuric solution', *Sep. Purif. Technol.*, vol. 328, p. 125060, Jan. 2024, doi: 10.1016/j.seppur.2023.125060.

[28] J. S. Preston, 'Solvent extraction of metals by carboxylic acids', *Hydrometallurgy*, vol. 14, no. 2, pp. 171–188, July 1985, doi: 10.1016/0304-386X(85)90032-5.

[29] S. Donegan, 'Direct solvent extraction of nickel at Bulong operations', *Miner. Eng.*, vol. 19, no. 12, pp. 1234–1245, Sept. 2006, doi: 10.1016/j.mineng.2006.03.003.

[30] P. E. Tsakiridis and S. L. Agatzini, 'Process for the recovery of cobalt and nickel in the presence of magnesium and calcium from sulphate solutions by Versatic 10 and Cyanex 272', *Miner. Eng.*, vol. 17, no. 4, pp. 535–543, Apr. 2004, doi: 10.1016/j.mineng.2003.12.003.

[31] B. Ndlovu and T. Mahlangu, 'Calcium and magnesium rejection from sulphate solutions in Iateritic nickel solvent extraction using Versatic 10 acid-LIX®84-IC system', *J. South. Afr. Inst. Min. Metall.*, vol. 108, Apr. 2008.

[32] C. A. Nogueira, Oliveira ,Paula C., and F. M. and Pedrosa, 'Separation of Cadmium, Cobalt, and Nickel by Solvent Extraction using the Nickel Salts of the Extractants',

Solvent Extr. Ion Exch., vol. 27, no. 2, pp. 295–311, Mar. 2009, doi: 10.1080/07366290802672352.

[33] J. O'CALLAGHAN and T. Chamberlain, 'SOLVENT EXTRACTION OF IMPURITY METALS FROM A VALUABLE METAL SULPHATE SOLUTION', WO 01/48252 A1

[34] R. Ezzati, 'A new insight into the surface adsorption in the solution phase: A modification of the Langmuir isotherm', *Water Environ. Res.*, vol. 96, no. 4, p. e11019, 2024, doi: 10.1002/wer.11019.

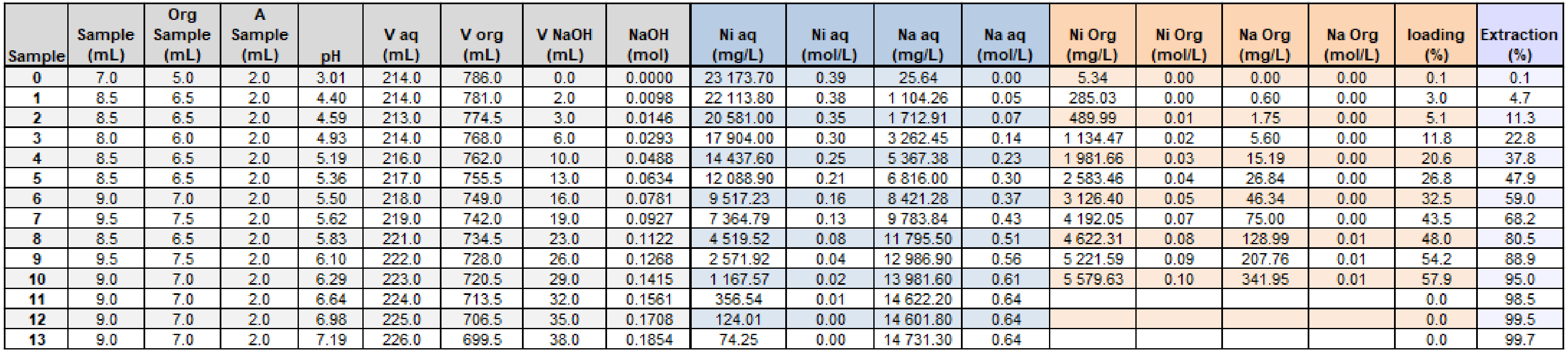
[35] V. S. Kislik, *Solvent Extraction: Classical and Novel Approaches*. Chantilly, NETHERLANDS, THE: Elsevier, 2011. Accessed: Oct. 27, 2025. [Online]. Available: http://ebookcentral.proquest.com/lib/kutu/detail.action?docID=862042

[36] K. H. Park, B. R. Reddy, S. H. Jung, and D. Mohapatra, 'Transfer of cobalt and nickel from sulphate solutions to spent electrolyte through solvent extraction and stripping', *Sep. Purif. Technol.*, vol. 51, no. 3, pp. 265–271, Oct. 2006, doi: 10.1016/j.seppur.2006.02.007.

[37] V. Agarwal, M. K. Khalid, A. Porvali, B. P. Wilson, and M. Lundström, 'Recycling of spent NiMH batteries: Integration of battery leach solution into primary Ni production using solvent extraction', *Sustain. Mater. Technol.*, vol. 22, p. e00121, Dec. 2019, doi: 10.1016/j.susmat.2019.e00121.

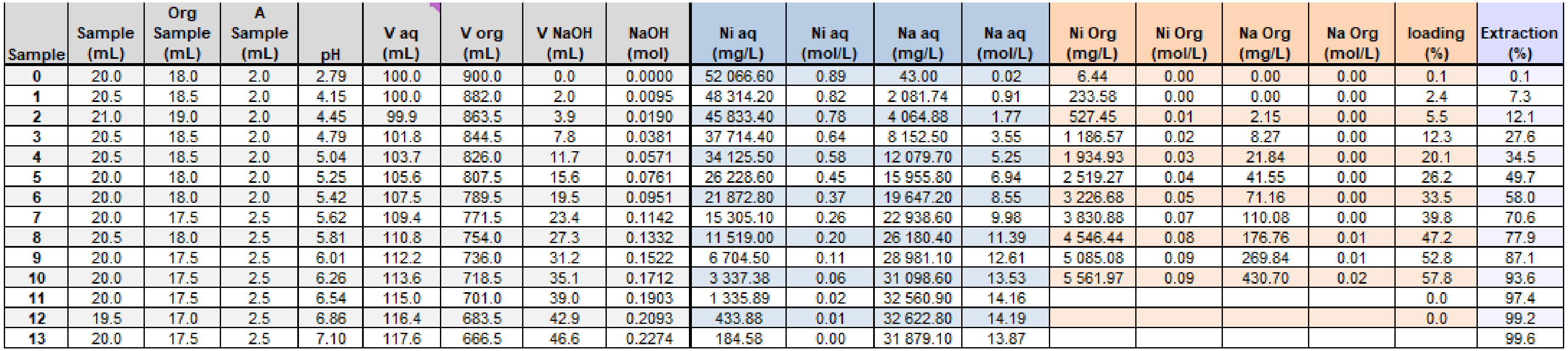
Appendices

Appendix A: Analyses and calculations for Cyanex 272 pH isotherm experiments



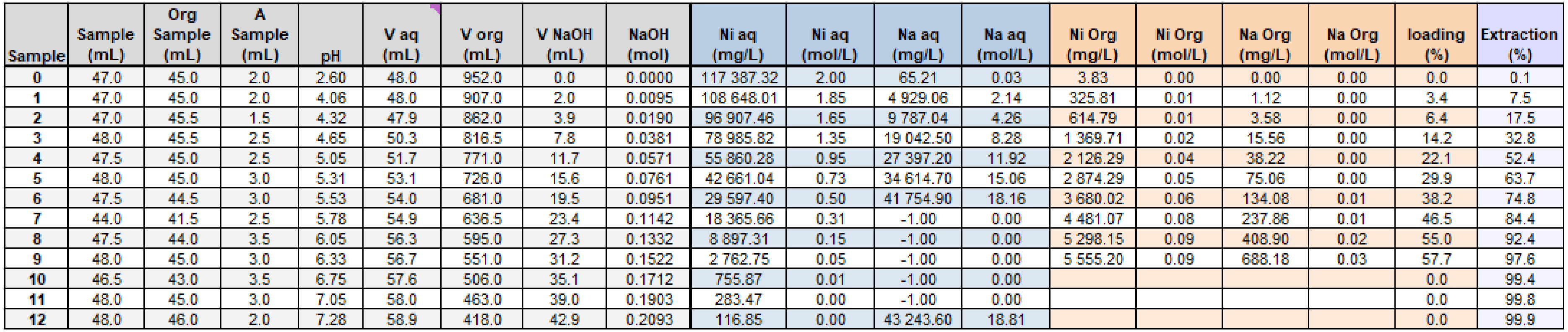
Sample	Sample (mL)	Org Sample (mL)	A Sample (mL)	pH	V aq (mL)	V org (mL)	V NaOH (mL)	NaOH (mol)	Ni aq (mg/L)	Ni aq (mol/L)	Na aq (mg/L)	Na aq (mol/L)	Ni Org (mg/L)	Ni Org (mol/L)	Na Org (mg/L)	Na Org (mol/L)	loading (%)	Extraction (%)
0	7.0	5.0	2.0	3.01	214.0	786.0	0.0	0.0000	23 173.70	0.39	25.64	0.00	5.34	0.00	0.00	0.00	0.1	0.1
1	8.5	6.5	2.0	4.40	214.0	781.0	2.0	0.0098	22 113.80	0.38	1 104.26	0.05	285.03	0.00	0.60	0.00	3.0	4.7
2	8.5	6.5	2.0	4.59	213.0	774.5	3.0	0.0146	20 581.00	0.35	1 712.91	0.07	489.99	0.01	1.75	0.00	5.1	11.3
3	8.0	6.0	2.0	4.93	214.0	768.0	6.0	0.0293	17 904.00	0.30	3 262.45	0.14	1 134.47	0.02	5.60	0.00	11.8	22.8
4	8.5	6.5	2.0	5.19	216.0	762.0	10.0	0.0488	14 437.60	0.25	5 367.38	0.23	1 981.66	0.03	15.19	0.00	20.6	37.8
5	8.5	6.5	2.0	5.36	217.0	755.5	13.0	0.0634	12 088.90	0.21	6 816.00	0.30	2 583.46	0.04	26.84	0.00	26.8	47.9
6	9.0	7.0	2.0	5.50	218.0	749.0	16.0	0.0781	9 517.23	0.16	8 421.28	0.37	3 126.40	0.05	46.34	0.00	32.5	59.0
7	9.5	7.5	2.0	5.62	219.0	742.0	19.0	0.0927	7 364.79	0.13	9 783.84	0.43	4 192.05	0.07	75.00	0.00	43.5	68.2
8	8.5	6.5	2.0	5.83	221.0	734.5	23.0	0.1122	4 519.52	0.08	11 795.50	0.51	4 622.31	0.08	128.99	0.01	48.0	80.5
9	9.5	7.5	2.0	6.10	222.0	728.0	26.0	0.1268	2 571.92	0.04	12 986.90	0.56	5 221.59	0.09	207.76	0.01	54.2	88.9
10	9.0	7.0	2.0	6.29	223.0	720.5	29.0	0.1415	1 167.57	0.02	13 981.60	0.61	5 579.63	0.10	341.95	0.01	57.9	95.0
11	9.0	7.0	2.0	6.64	224.0	713.5	32.0	0.1561	356.54	0.01	14 622.20	0.64					0.0	98.5
12	9.0	7.0	2.0	6.98	225.0	706.5	35.0	0.1708	124.01	0.00	14 601.80	0.64					0.0	99.5
13	9.0	7.0	2.0	7.19	226.0	699.5	38.0	0.1854	74.25	0.00	14 731.30	0.64					0.0	99.7

Figure A1. Analyses and calculations for 23 g/L nickel initial concentration using 0.5 M Cyanex 272.



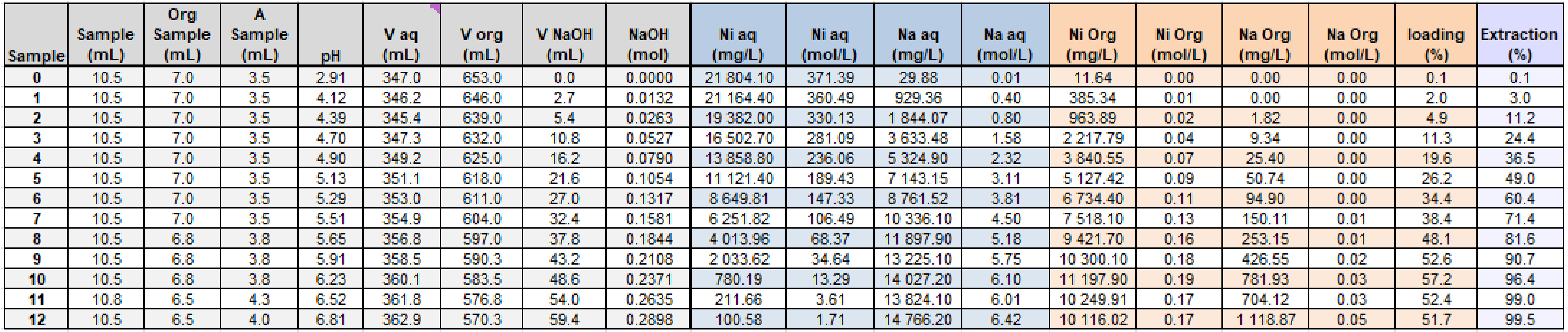
Sample	Sample (mL)	Org Sample (mL)	A Sample (mL)	pH	V aq (mL)	V org (mL)	V NaOH (mL)	NaOH (mol)	Ni aq (mg/L)	Ni aq (mol/L)	Na aq (mg/L)	Na aq (mol/L)	Ni Org (mg/L)	Ni Org (mol/L)	Na Org (mg/L)	Na Org (mol/L)	loading (%)	Extraction (%)
0	20.0	18.0	2.0	2.79	100.0	900.0	0.0	0.0000	52 066.60	0.89	43.00	0.02	6.44	0.00	0.00	0.00	0.1	0.1
1	20.5	18.5	2.0	4.15	100.0	882.0	2.0	0.0095	48 314.20	0.82	2 081.74	0.91	233.58	0.00	0.00	0.00	2.4	7.3
2	21.0	19.0	2.0	4.45	99.9	863.5	3.9	0.0190	45 833.40	0.78	4 064.88	1.77	527.45	0.01	2.15	0.00	5.5	12.1
3	20.5	18.5	2.0	4.79	101.8	844.5	7.8	0.0381	37 714.40	0.64	8 152.50	3.55	1 186.57	0.02	8.27	0.00	12.3	27.6
4	20.5	18.5	2.0	5.04	103.7	826.0	11.7	0.0571	34 125.50	0.58	12 079.70	5.25	1 934.93	0.03	21.84	0.00	20.1	34.5
5	20.0	18.0	2.0	5.25	105.6	807.5	15.6	0.0761	26 228.60	0.45	15 955.80	6.94	2 519.27	0.04	41.55	0.00	26.2	49.7
6	20.0	18.0	2.0	5.42	107.5	789.5	19.5	0.0951	21 872.80	0.37	19 647.20	8.55	3 226.68	0.05	71.16	0.00	33.5	58.0
7	20.0	17.5	2.5	5.62	109.4	771.5	23.4	0.1142	15 305.10	0.26	22 938.60	9.98	3 830.88	0.07	110.08	0.00	39.8	70.6
8	20.5	18.0	2.5	5.81	110.8	754.0	27.3	0.1332	11 519.00	0.20	26 180.40	11.39	4 546.44	0.08	176.76	0.01	47.2	77.9
9	20.0	17.5	2.5	6.01	112.2	736.0	31.2	0.1522	6 704.50	0.11	28 981.10	12.61	5 085.08	0.09	269.84	0.01	52.8	87.1
10	20.0	17.5	2.5	6.26	113.6	718.5	35.1	0.1712	3 337.38	0.06	31 098.60	13.53	5 561.97	0.09	430.70	0.02	57.8	93.6
11	20.0	17.5	2.5	6.54	115.0	701.0	39.0	0.1903	1 335.89	0.02	32 560.90	14.16					0.0	97.4
12	19.5	17.0	2.5	6.86	116.4	683.5	42.9	0.2093	433.88	0.01	32 622.80	14.19					0.0	99.2
13	20.0	17.5	2.5	7.10	117.6	666.5	46.6	0.2274	184.58	0.00	31 879.10	13.87						99.6

Figure A2. Analyses and calculations for 52 g/L nickel initial concentration using 0.5 M Cyanex 272.



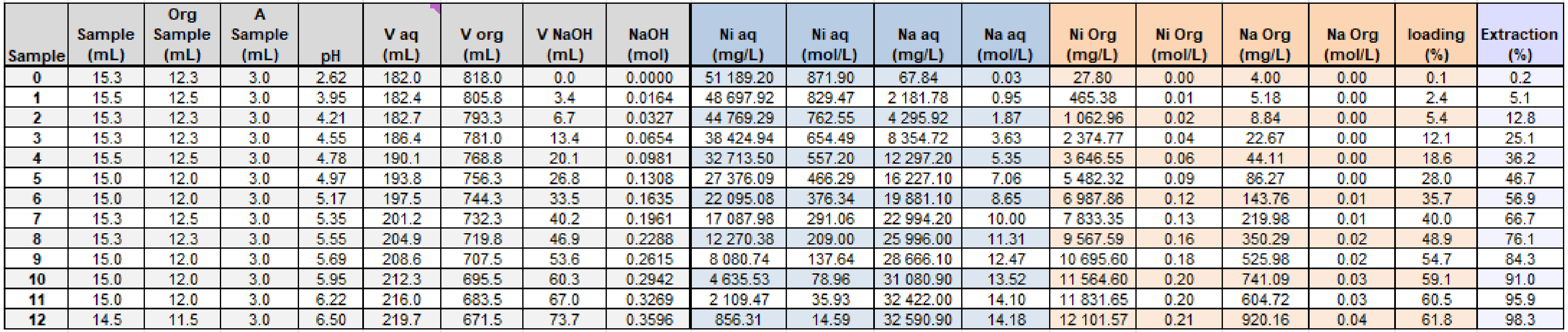
Sample	Sample (mL)	Org Sample (mL)	A Sample (mL)	pH	V aq (mL)	V org (mL)	V NaOH (mL)	NaOH (mol)	Ni aq (mg/L)	Ni aq (mol/L)	Na aq (mg/L)	Na aq (mol/L)	Ni Org (mg/L)	Ni Org (mol/L)	Na Org (mg/L)	Na Org (mol/L)	loading (%)	Extraction (%)
0	47.0	45.0	2.0	2.60	48.0	952.0	0.0	0.0000	117 387.32	2.00	65.21	0.03	3.83	0.00	0.00	0.00	0.0	0.1
1	47.0	45.0	2.0	4.06	48.0	907.0	2.0	0.0095	108 648.01	1.85	4 929.06	2.14	325.81	0.01	1.12	0.00	3.4	7.5
2	47.0	45.5	1.5	4.32	47.9	862.0	3.9	0.0190	96 907.46	1.65	9 787.04	4.26	614.79	0.01	3.58	0.00	6.4	17.5
3	48.0	45.5	2.5	4.65	50.3	816.5	7.8	0.0381	78 985.82	1.35	19 042.50	8.28	1 369.71	0.02	15.56	0.00	14.2	32.8
4	47.5	45.0	2.5	5.05	51.7	771.0	11.7	0.0571	55 860.28	0.95	27 397.20	11.92	2 126.29	0.04	38.22	0.00	22.1	52.4
5	48.0	45.0	3.0	5.31	53.1	726.0	15.6	0.0761	42 661.04	0.73	34 614.70	15.06	2 874.29	0.05	75.06	0.00	29.9	63.7
6	47.5	44.5	3.0	5.53	54.0	681.0	19.5	0.0951	29 597.40	0.50	41 754.90	18.16	3 680.02	0.06	134.08	0.01	38.2	74.8
7	44.0	41.5	2.5	5.78	54.9	636.5	23.4	0.1142	18 365.66	0.31	-1.00	0.00	4 481.07	0.08	237.86	0.01	46.5	84.4
8	47.5	44.0	3.5	6.05	56.3	595.0	27.3	0.1332	8 897.31	0.15	-1.00	0.00	5 298.15	0.09	408.90	0.02	55.0	92.4
9	48.0	45.0	3.0	6.33	56.7	551.0	31.2	0.1522	2 762.75	0.05	-1.00	0.00	5 555.20	0.09	688.18	0.03	57.7	97.6
10	46.5	43.0	3.5	6.75	57.6	506.0	35.1	0.1712	755.87	0.01	-1.00	0.00					0.0	99.4
11	48.0	45.0	3.0	7.05	58.0	463.0	39.0	0.1903	283.47	0.00	-1.00	0.00					0.0	99.8
12	48.0	46.0	2.0	7.28	58.9	418.0	42.9	0.2093	116.85	0.00	43 243.60	18.81					0.0	99.9

Figure A3. Analyses and calculations for 117 g/L nickel initial concentration using 0.5 M Cyanex 272.



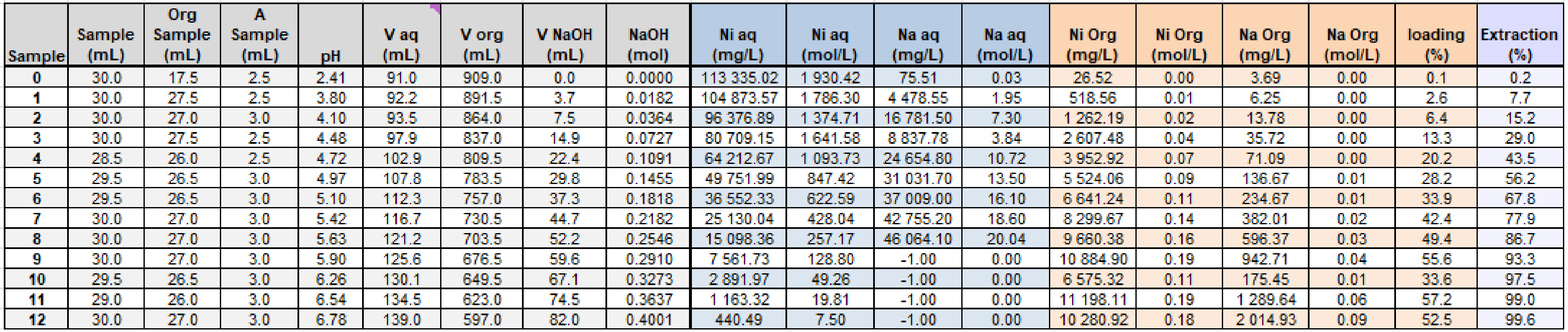
Sample	Sample (mL)	Org Sample (mL)	A Sample (mL)	pH	V aq (mL)	V org (mL)	V NaOH (mL)	NaOH (mol)	Ni aq (mg/L)	Ni aq (mol/L)	Na aq (mg/L)	Na aq (mol/L)	Ni Org (mg/L)	Ni Org (mol/L)	Na Org (mg/L)	Na Org (mol/L)	loading (%)	Extraction (%)
0	10.5	7.0	3.5	2.91	347.0	653.0	0.0	0.0000	21 804.10	371.39	29.88	0.01	11.64	0.00	0.00	0.00	0.1	0.1
1	10.5	7.0	3.5	4.12	346.2	646.0	2.7	0.0132	21 164.40	360.49	929.36	0.40	385.34	0.01	0.00	0.00	2.0	3.0
2	10.5	7.0	3.5	4.39	345.4	639.0	5.4	0.0263	19 382.00	330.13	1 844.07	0.80	963.89	0.02	1.82	0.00	4.9	11.2
3	10.5	7.0	3.5	4.70	347.3	632.0	10.8	0.0527	16 502.70	281.09	3 633.48	1.58	2 217.79	0.04	9.34	0.00	11.3	24.4
4	10.5	7.0	3.5	4.90	349.2	625.0	16.2	0.0790	13 858.80	236.06	5 324.90	2.32	3 840.55	0.07	25.40	0.00	19.6	36.5
5	10.5	7.0	3.5	5.13	351.1	618.0	21.6	0.1054	11 121.40	189.43	7 143.15	3.11	5 127.42	0.09	50.74	0.00	26.2	49.0
6	10.5	7.0	3.5	5.29	353.0	611.0	27.0	0.1317	8 649.81	147.33	8 761.52	3.81	6 734.40	0.11	94.90	0.00	34.4	60.4
7	10.5	7.0	3.5	5.51	354.9	604.0	32.4	0.1581	6 251.82	106.49	10 336.10	4.50	7 518.10	0.13	150.11	0.01	38.4	71.4
8	10.5	6.8	3.8	5.65	356.8	597.0	37.8	0.1844	4 013.96	68.37	11 897.90	5.18	9 421.70	0.16	253.15	0.01	48.1	81.6
9	10.5	6.8	3.8	5.91	358.5	590.3	43.2	0.2108	2 033.62	34.64	13 225.10	5.75	10 300.10	0.18	426.55	0.02	52.6	90.7
10	10.5	6.8	3.8	6.23	360.1	583.5	48.6	0.2371	780.19	13.29	14 027.20	6.10	11 197.90	0.19	781.93	0.03	57.2	96.4
11	10.8	6.5	4.3	6.52	361.8	576.8	54.0	0.2635	211.66	3.61	13 824.10	6.01	10 249.91	0.17	704.12	0.03	52.4	99.0
12	10.5	6.5	4.0	6.81	362.9	570.3	59.4	0.2898	100.58	1.71	14 766.20	6.42	10 116.02	0.17	1 118.87	0.05	51.7	99.5

Figure A4. Analyses and calculations for 22 g/L nickel initial concentration using 1.0 M Cyanex 272.



Sample	Sample (mL)	Org Sample (mL)	A Sample (mL)	pH	V aq (mL)	V org (mL)	V NaOH (mL)	NaOH (mol)	Ni aq (mg/L)	Ni aq (mol/L)	Na aq (mg/L)	Na aq (mol/L)	Ni Org (mg/L)	Ni Org (mol/L)	Na Org (mg/L)	Na Org (mol/L)	loading (%)	Extraction (%)
0	15.3	12.3	3.0	2.62	182.0	818.0	0.0	0.0000	51 189.20	871.90	67.84	0.03	27.80	0.00	4.00	0.00	0.1	0.2
1	15.5	12.5	3.0	3.95	182.4	805.8	3.4	0.0164	48 697.92	829.47	2 181.78	0.95	465.38	0.01	5.18	0.00	2.4	5.1
2	15.3	12.3	3.0	4.21	182.7	793.3	6.7	0.0327	44 769.29	762.55	4 295.92	1.87	1 062.96	0.02	8.84	0.00	5.4	12.8
3	15.3	12.3	3.0	4.55	186.4	781.0	13.4	0.0654	38 424.94	654.49	8 354.72	3.63	2 374.77	0.04	22.67	0.00	12.1	25.1
4	15.5	12.5	3.0	4.78	190.1	768.8	20.1	0.0981	32 713.50	557.20	12 297.20	5.35	3 646.55	0.06	44.11	0.00	18.6	36.2
5	15.0	12.0	3.0	4.97	193.8	756.3	26.8	0.1308	27 376.09	466.29	16 227.10	7.06	5 482.32	0.09	86.27	0.00	28.0	46.7
6	15.0	12.0	3.0	5.17	197.5	744.3	33.5	0.1635	22 095.08	376.34	19 881.10	8.65	6 987.86	0.12	143.76	0.01	35.7	56.9
7	15.3	12.5	3.0	5.35	201.2	732.3	40.2	0.1961	17 087.98	291.06	22 994.20	10.00	7 833.35	0.13	219.98	0.01	40.0	66.7
8	15.3	12.3	3.0	5.55	204.9	719.8	46.9	0.2288	12 270.38	209.00	25 996.00	11.31	9 567.59	0.16	350.29	0.02	48.9	76.1
9	15.0	12.0	3.0	5.69	208.6	707.5	53.6	0.2615	8 080.74	137.64	28 666.10	12.47	10 695.60	0.18	525.98	0.02	54.7	84.3
10	15.0	12.0	3.0	5.95	212.3	695.5	60.3	0.2942	4 635.53	78.96	31 080.90	13.52	11 564.60	0.20	741.09	0.03	59.1	91.0
11	15.0	12.0	3.0	6.22	216.0	683.5	67.0	0.3269	2 109.47	35.93	32 422.00	14.10	11 831.65	0.20	604.72	0.03	60.5	95.9
12	14.5	11.5	3.0	6.50	219.7	671.5	73.7	0.3596	856.31	14.59	32 590.90	14.18	12 101.57	0.21	920.16	0.04	61.8	98.3

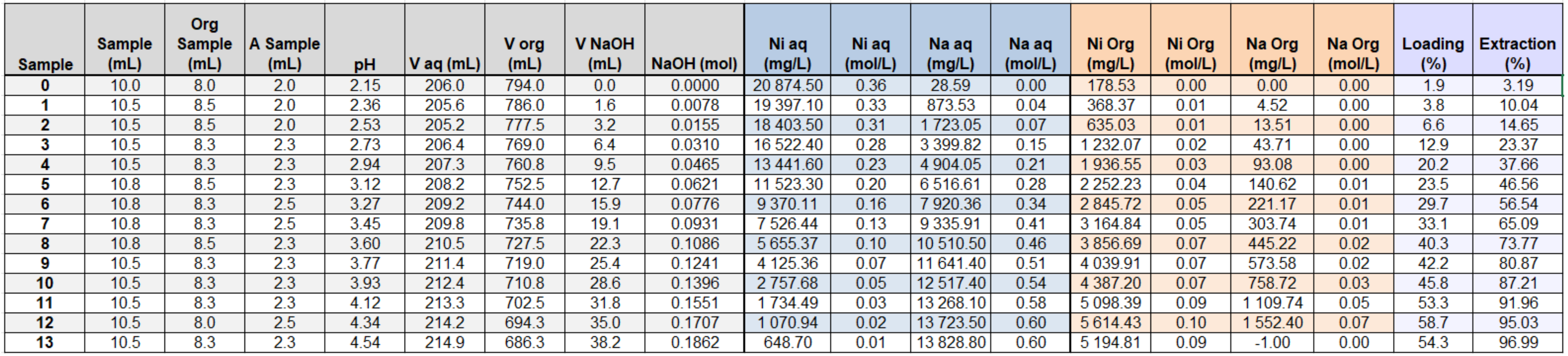
Figure A5. Analyses and calculations for 51 g/L nickel initial concentration using 1.0 M Cyanex 272.



Sample	Sample (mL)	Org Sample (mL)	A Sample (mL)	pH	V aq (mL)	V org (mL)	V NaOH (mL)	NaOH (mol)	Ni aq (mg/L)	Ni aq (mol/L)	Na aq (mg/L)	Na aq (mol/L)	Ni Org (mg/L)	Ni Org (mol/L)	Na Org (mg/L)	Na Org (mol/L)	loading (%)	Extraction (%)
0	30.0	17.5	2.5	2.41	91.0	909.0	0.0	0.0000	113 335.02	1 930.42	75.51	0.03	26.52	0.00	3.69	0.00	0.1	0.2
1	30.0	27.5	2.5	3.80	92.2	891.5	3.7	0.0182	104 873.57	1 786.30	4 478.55	1.95	518.56	0.01	6.25	0.00	2.6	7.7
2	30.0	27.0	3.0	4.10	93.5	864.0	7.5	0.0364	96 376.89	1 374.71	16 781.50	7.30	1 262.19	0.02	13.78	0.00	6.4	15.2
3	30.0	27.5	2.5	4.48	97.9	837.0	14.9	0.0727	80 709.15	1 641.58	8 837.78	3.84	2 607.48	0.04	35.72	0.00	13.3	29.0
4	28.5	26.0	2.5	4.72	102.9	809.5	22.4	0.1091	64 212.67	1 093.73	24 654.80	10.72	3 952.92	0.07	71.09	0.00	20.2	43.5
5	29.5	26.5	3.0	4.97	107.8	783.5	29.8	0.1455	49 751.99	847.42	31 031.70	13.50	5 524.06	0.09	136.67	0.01	28.2	56.2
6	29.5	26.5	3.0	5.10	112.3	757.0	37.3	0.1818	36 552.33	622.59	37 009.00	16.10	6 641.24	0.11	234.67	0.01	33.9	67.8
7	30.0	27.0	3.0	5.42	116.7	730.5	44.7	0.2182	25 130.04	428.04	42 755.20	18.60	8 299.67	0.14	382.01	0.02	42.4	77.9
8	30.0	27.0	3.0	5.63	121.2	703.5	52.2	0.2546	15 098.36	257.17	46 064.10	20.04	9 660.38	0.16	596.37	0.03	49.4	86.7
9	30.0	27.0	3.0	5.90	125.6	676.5	59.6	0.2910	7 561.73	128.80	-1.00	0.00	10 884.90	0.19	942.71	0.04	55.6	93.3
10	29.5	26.5	3.0	6.26	130.1	649.5	67.1	0.3273	2 891.97	49.26	-1.00	0.00	6 575.32	0.11	175.45	0.01	33.6	97.5
11	29.0	26.0	3.0	6.54	134.5	623.0	74.5	0.3637	1 163.32	19.81	-1.00	0.00	11 198.11	0.19	1 289.64	0.06	57.2	99.0
12	30.0	27.0	3.0	6.78	139.0	597.0	82.0	0.4001	440.49	7.50	-1.00	0.00	10 280.92	0.18	2 014.93	0.09	52.5	99.6

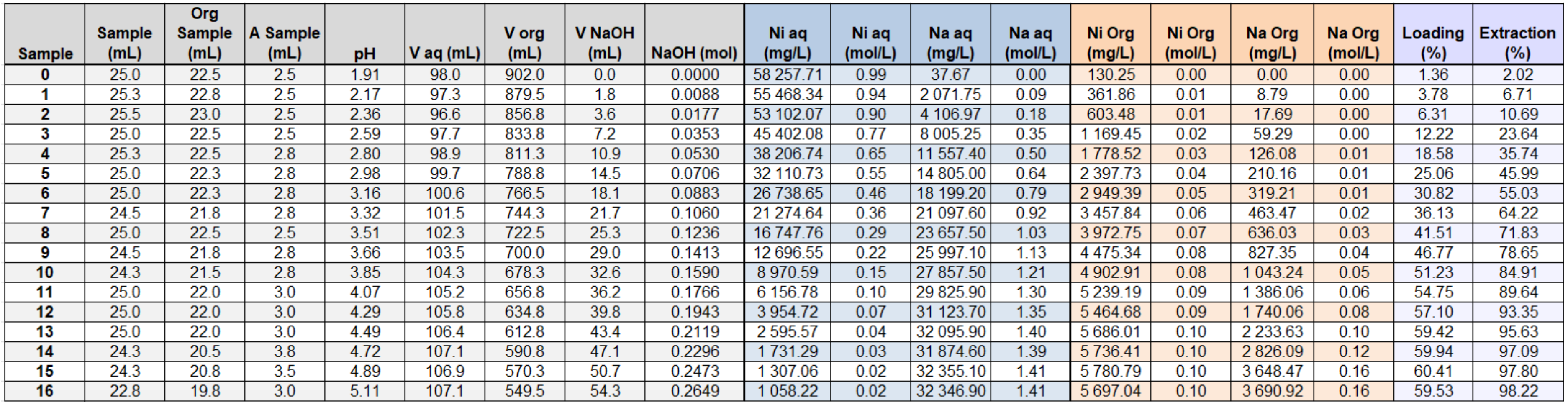
Figure A6. Analyses and calculations for 114 g/L nickel initial concentration using 1.0 M Cyanex 272.

Appendix B: Analyses and calculations for D2EHPA pH isotherm experiments



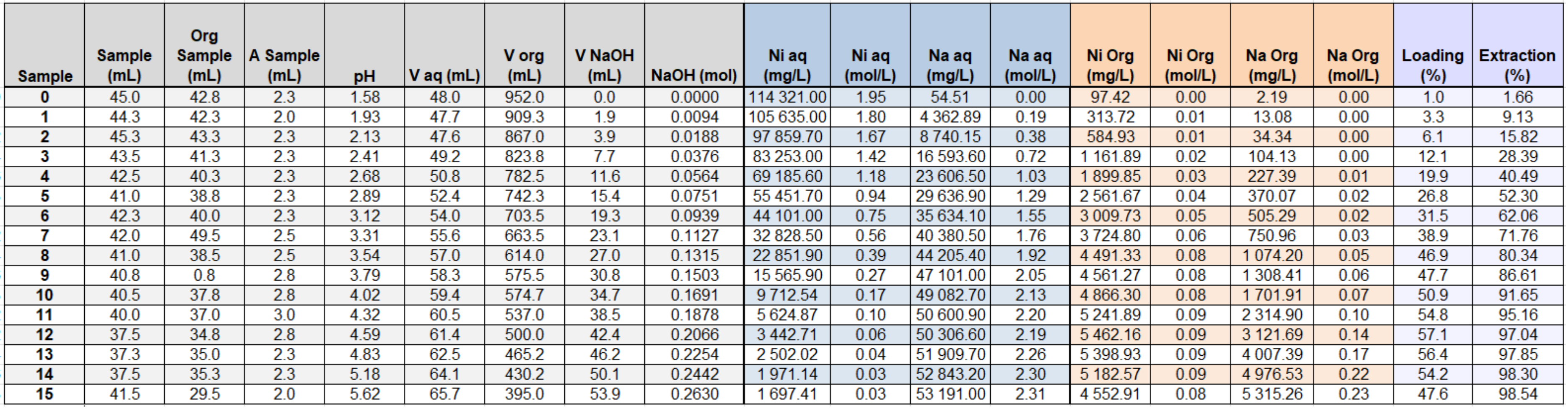
Sample	Sample (mL)	Org Sample (mL)	A Sample (mL)	pH	V aq (mL)	V org (mL)	V NaOH (mL)	NaOH (mol)	Ni aq (mg/L)	Ni aq (mol/L)	Na aq (mg/L)	Na aq (mol/L)	Ni Org (mg/L)	Ni Org (mol/L)	Na Org (mg/L)	Na Org (mol/L)	Loading (%)	Extraction (%)
0	10.0	8.0	2.0	2.15	206.0	794.0	0.0	0.0000	20 874.50	0.36	28.59	0.00	178.53	0.00	0.00	0.00	1.9	3.19
1	10.5	8.5	2.0	2.36	205.6	786.0	1.6	0.0078	19 397.10	0.33	873.53	0.04	368.37	0.01	4.52	0.00	3.8	10.04
2	10.5	8.5	2.0	2.53	205.2	777.5	3.2	0.0155	18 403.50	0.31	1 723.05	0.07	635.03	0.01	13.51	0.00	6.6	14.65
3	10.5	8.3	2.3	2.73	206.4	769.0	6.4	0.0310	16 522.40	0.28	3 399.82	0.15	1 232.07	0.02	43.71	0.00	12.9	23.37
4	10.5	8.3	2.3	2.94	207.3	760.8	9.5	0.0465	13 441.60	0.23	4 904.05	0.21	1 936.55	0.03	93.08	0.00	20.2	37.66
5	10.8	8.5	2.3	3.12	208.2	752.5	12.7	0.0621	11 523.30	0.20	6 516.61	0.28	2 252.23	0.04	140.62	0.01	23.5	46.56
6	10.8	8.3	2.5	3.27	209.2	744.0	15.9	0.0776	9 370.11	0.16	7 920.36	0.34	2 845.72	0.05	221.17	0.01	29.7	56.54
7	10.8	8.3	2.5	3.45	209.8	735.8	19.1	0.0931	7 526.44	0.13	9 335.91	0.41	3 164.84	0.05	303.74	0.01	33.1	65.09
8	10.8	8.5	2.3	3.60	210.5	727.5	22.3	0.1086	5 655.37	0.10	10 510.50	0.46	3 856.69	0.07	445.22	0.02	40.3	73.77
9	10.5	8.3	2.3	3.77	211.4	719.0	25.4	0.1241	4 125.36	0.07	11 641.40	0.51	4 039.91	0.07	573.58	0.02	42.2	80.87
10	10.5	8.3	2.3	3.93	212.4	710.8	28.6	0.1396	2 757.68	0.05	12 517.40	0.54	4 387.20	0.07	758.72	0.03	45.8	87.21
11	10.5	8.3	2.3	4.12	213.3	702.5	31.8	0.1551	1 734.49	0.03	13 268.10	0.58	5 098.39	0.09	1 109.74	0.05	53.3	91.96
12	10.5	8.0	2.5	4.34	214.2	694.3	35.0	0.1707	1 070.94	0.02	13 723.50	0.60	5 614.43	0.10	1 552.40	0.07	58.7	95.03
13	10.5	8.3	2.3	4.54	214.9	686.3	38.2	0.1862	648.70	0.01	13 828.80	0.60	5 194.81	0.09	-1.00	0.00	54.3	96.99

Figure B1. Analyses and calculations for 22 g/L nickel initial concentration using 0.5 M D2EHPA.



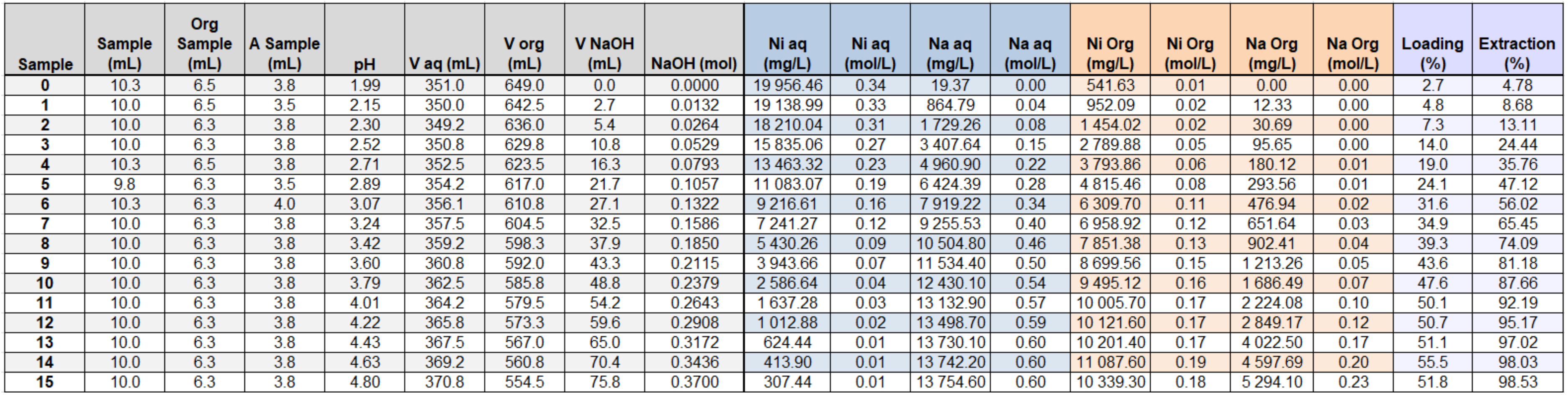
Sample	Sample (mL)	Org Sample (mL)	A Sample (mL)	pH	V aq (mL)	V org (mL)	V NaOH (mL)	NaOH (mol)	Ni aq (mg/L)	Ni aq (mol/L)	Na aq (mg/L)	Na aq (mol/L)	Ni Org (mg/L)	Ni Org (mol/L)	Na Org (mg/L)	Na Org (mol/L)	Loading (%)	Extraction (%)
0	25.0	22.5	2.5	1.91	98.0	902.0	0.0	0.0000	58 257.71	0.99	37.67	0.00	130.25	0.00	0.00	0.00	1.36	2.02
1	25.3	22.8	2.5	2.17	97.3	879.5	1.8	0.0088	55 468.34	0.94	2 071.75	0.09	361.86	0.01	8.79	0.00	3.78	6.71
2	25.5	23.0	2.5	2.36	96.6	856.8	3.6	0.0177	53 102.07	0.90	4 106.97	0.18	603.48	0.01	17.69	0.00	6.31	10.69
3	25.0	22.5	2.5	2.59	97.7	833.8	7.2	0.0353	45 402.08	0.77	8 005.25	0.35	1 169.45	0.02	59.29	0.00	12.22	23.64
4	25.3	22.5	2.8	2.80	98.9	811.3	10.9	0.0530	38 206.74	0.65	11 557.40	0.50	1 778.52	0.03	126.08	0.01	18.58	35.74
5	25.0	22.3	2.8	2.98	99.7	788.8	14.5	0.0706	32 110.73	0.55	14 805.00	0.64	2 397.73	0.04	210.16	0.01	25.06	45.99
6	25.0	22.3	2.8	3.16	100.6	766.5	18.1	0.0883	26 738.65	0.46	18 199.20	0.79	2 949.39	0.05	319.21	0.01	30.82	55.03
7	24.5	21.8	2.8	3.32	101.5	744.3	21.7	0.1060	21 274.64	0.36	21 097.60	0.92	3 457.84	0.06	463.47	0.02	36.13	64.22
8	25.0	22.5	2.5	3.51	102.3	722.5	25.3	0.1236	16 747.76	0.29	23 657.50	1.03	3 972.75	0.07	636.03	0.03	41.51	71.83
9	24.5	21.8	2.8	3.66	103.5	700.0	29.0	0.1413	12 696.55	0.22	25 997.10	1.13	4 475.34	0.08	827.35	0.04	46.77	78.65
10	24.3	21.5	2.8	3.85	104.3	678.3	32.6	0.1590	8 970.59	0.15	27 857.50	1.21	4 902.91	0.08	1 043.24	0.05	51.23	84.91
11	25.0	22.0	3.0	4.07	105.2	656.8	36.2	0.1766	6 156.78	0.10	29 825.90	1.30	5 239.19	0.09	1 386.06	0.06	54.75	89.64
12	25.0	22.0	3.0	4.29	105.8	634.8	39.8	0.1943	3 954.72	0.07	31 123.70	1.35	5 464.68	0.09	1 740.06	0.08	57.10	93.35
13	25.0	22.0	3.0	4.49	106.4	612.8	43.4	0.2119	2 595.57	0.04	32 095.90	1.40	5 686.01	0.10	2 233.63	0.10	59.42	95.63
14	24.3	20.5	3.8	4.72	107.1	590.8	47.1	0.2296	1 731.29	0.03	31 874.60	1.39	5 736.41	0.10	2 826.09	0.12	59.94	97.09
15	24.3	20.8	3.5	4.89	106.9	570.3	50.7	0.2473	1 307.06	0.02	32 355.10	1.41	5 780.79	0.10	3 648.47	0.16	60.41	97.80
16	22.8	19.8	3.0	5.11	107.1	549.5	54.3	0.2649	1 058.22	0.02	32 346.90	1.41	5 697.04	0.10	3 690.92	0.16	59.53	98.22

Figure B2. Analyses and calculations for 59 g/L nickel initial concentration using 0.5 M D2EHPA.



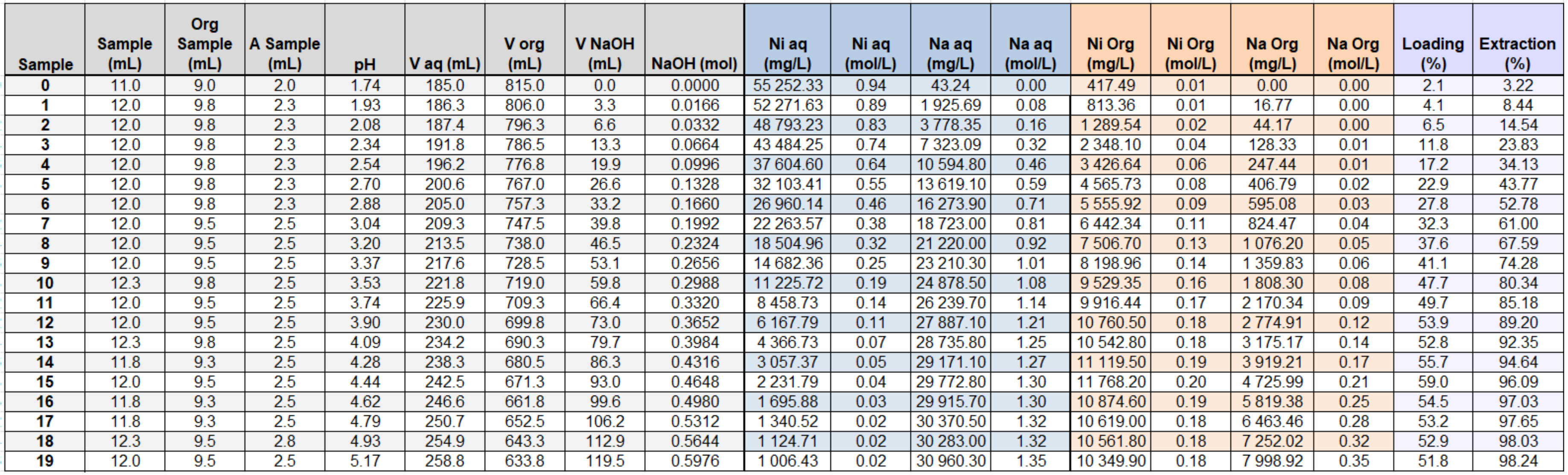
Sample	Sample (mL)	Org Sample (mL)	A Sample (mL)	pH	V aq (mL)	V org (mL)	V NaOH (mL)	NaOH (mol)	Ni aq (mg/L)	Ni aq (mol/L)	Na aq (mg/L)	Na aq (mol/L)	Ni Org (mg/L)	Ni Org (mol/L)	Na Org (mg/L)	Na Org (mol/L)	Loading (%)	Extraction (%)
0	45.0	42.8	2.3	1.58	48.0	952.0	0.0	0.0000	114 321.00	1.95	54.51	0.00	97.42	0.00	2.19	0.00	1.0	1.66
1	44.3	42.3	2.0	1.93	47.7	909.3	1.9	0.0094	105 635.00	1.80	4 362.89	0.19	313.72	0.01	13.08	0.00	3.3	9.13
2	45.3	43.3	2.3	2.13	47.6	867.0	3.9	0.0188	97 859.70	1.67	8 740.15	0.38	584.93	0.01	34.34	0.00	6.1	15.82
3	43.5	41.3	2.3	2.41	49.2	823.8	7.7	0.0376	83 253.00	1.42	16 593.60	0.72	1 161.89	0.02	104.13	0.00	12.1	28.39
4	42.5	40.3	2.3	2.68	50.8	782.5	11.6	0.0564	69 185.60	1.18	23 606.50	1.03	1 899.85	0.03	227.39	0.01	19.9	40.49
5	41.0	38.8	2.3	2.89	52.4	742.3	15.4	0.0751	55 451.70	0.94	29 636.90	1.29	2 561.67	0.04	370.07	0.02	26.8	52.30
6	42.3	40.0	2.3	3.12	54.0	703.5	19.3	0.0939	44 101.00	0.75	35 634.10	1.55	3 009.73	0.05	505.29	0.02	31.5	62.06
7	42.0	49.5	2.5	3.31	55.6	663.5	23.1	0.1127	32 828.50	0.56	40 380.50	1.76	3 724.80	0.06	750.96	0.03	38.9	71.76
8	41.0	38.5	2.5	3.54	57.0	614.0	27.0	0.1315	22 851.90	0.39	44 205.40	1.92	4 491.33	0.08	1 074.20	0.05	46.9	80.34
9	40.8	0.8	2.8	3.79	58.3	575.5	30.8	0.1503	15 565.90	0.27	47 101.00	2.05	4 561.27	0.08	1 308.41	0.06	47.7	86.61
10	40.5	37.8	2.8	4.02	59.4	574.7	34.7	0.1691	9 712.54	0.17	49 082.70	2.13	4 866.30	0.08	1 701.91	0.07	50.9	91.65
11	40.0	37.0	3.0	4.32	60.5	537.0	38.5	0.1878	5 624.87	0.10	50 600.90	2.20	5 241.89	0.09	2 314.90	0.10	54.8	95.16
12	37.5	34.8	2.8	4.59	61.4	500.0	42.4	0.2066	3 442.71	0.06	50 306.60	2.19	5 462.16	0.09	3 121.69	0.14	57.1	97.04
13	37.3	35.0	2.3	4.83	62.5	465.2	46.2	0.2254	2 502.02	0.04	51 909.70	2.26	5 398.93	0.09	4 007.39	0.17	56.4	97.85
14	37.5	35.3	2.3	5.18	64.1	430.2	50.1	0.2442	1 971.14	0.03	52 843.20	2.30	5 182.57	0.09	4 976.53	0.22	54.2	98.30
15	41.5	29.5	2.0	5.62	65.7	395.0	53.9	0.2630	1 697.41	0.03	53 191.00	2.31	4 552.91	0.08	5 315.26	0.23	47.6	98.54

Figure B3. Analyses and calculations for 116 g/L nickel initial concentration using 0.5 M D2EHPA.



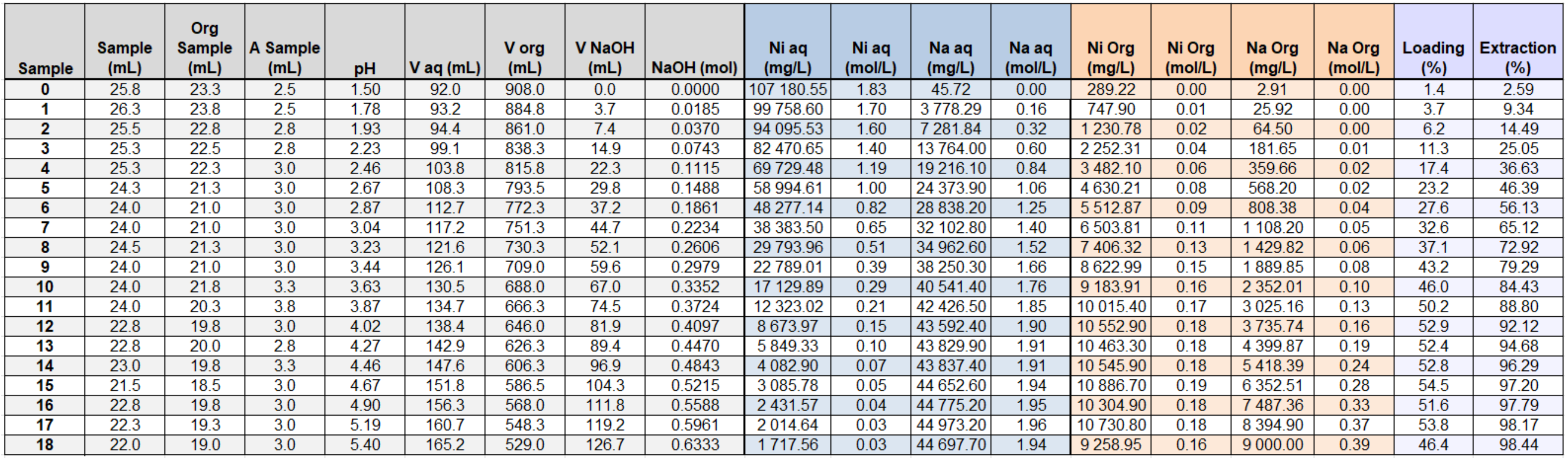
Sample	Sample (mL)	Org Sample (mL)	A Sample (mL)	pH	V aq (mL)	V org (mL)	V NaOH (mL)	NaOH (mol)	Ni aq (mg/L)	Ni aq (mol/L)	Na aq (mg/L)	Na aq (mol/L)	Ni Org (mg/L)	Ni Org (mol/L)	Na Org (mg/L)	Na Org (mol/L)	Loading (%)	Extraction (%)
0	10.3	6.5	3.8	1.99	351.0	649.0	0.0	0.0000	19 956.46	0.34	19.37	0.00	541.63	0.01	0.00	0.00	2.7	4.78
1	10.0	6.5	3.5	2.15	350.0	642.5	2.7	0.0132	19 138.99	0.33	864.79	0.04	952.09	0.02	12.33	0.00	4.8	8.68
2	10.0	6.3	3.8	2.30	349.2	636.0	5.4	0.0264	18 210.04	0.31	1 729.26	0.08	1 454.02	0.02	30.69	0.00	7.3	13.11
3	10.0	6.3	3.8	2.52	350.8	629.8	10.8	0.0529	15 835.06	0.27	3 407.64	0.15	2 789.88	0.05	95.65	0.00	14.0	24.44
4	10.3	6.5	3.8	2.71	352.5	623.5	16.3	0.0793	13 463.32	0.23	4 960.90	0.22	3 793.86	0.06	180.12	0.01	19.0	35.76
5	9.8	6.3	3.5	2.89	354.2	617.0	21.7	0.1057	11 083.07	0.19	6 424.39	0.28	4 815.46	0.08	293.56	0.01	24.1	47.12
6	10.3	6.3	4.0	3.07	356.1	610.8	27.1	0.1322	9 216.61	0.16	7 919.22	0.34	6 309.70	0.11	476.94	0.02	31.6	56.02
7	10.0	6.3	3.8	3.24	357.5	604.5	32.5	0.1586	7 241.27	0.12	9 255.53	0.40	6 958.92	0.12	651.64	0.03	34.9	65.45
8	10.0	6.3	3.8	3.42	359.2	598.3	37.9	0.1850	5 430.26	0.09	10 504.80	0.46	7 851.38	0.13	902.41	0.04	39.3	74.09
9	10.0	6.3	3.8	3.60	360.8	592.0	43.3	0.2115	3 943.66	0.07	11 534.40	0.50	8 699.56	0.15	1 213.26	0.05	43.6	81.18
10	10.0	6.3	3.8	3.79	362.5	585.8	48.8	0.2379	2 586.64	0.04	12 430.10	0.54	9 495.12	0.16	1 686.49	0.07	47.6	87.66
11	10.0	6.3	3.8	4.01	364.2	579.5	54.2	0.2643	1 637.28	0.03	13 132.90	0.57	10 005.70	0.17	2 224.08	0.10	50.1	92.19
12	10.0	6.3	3.8	4.22	365.8	573.3	59.6	0.2908	1 012.88	0.02	13 498.70	0.59	10 121.60	0.17	2 849.17	0.12	50.7	95.17
13	10.0	6.3	3.8	4.43	367.5	567.0	65.0	0.3172	624.44	0.01	13 730.10	0.60	10 201.40	0.17	4 022.50	0.17	51.1	97.02
14	10.0	6.3	3.8	4.63	369.2	560.8	70.4	0.3436	413.90	0.01	13 742.20	0.60	11 087.60	0.19	4 597.69	0.20	55.5	98.03
15	10.0	6.3	3.8	4.80	370.8	554.5	75.8	0.3700	307.44	0.01	13 754.60	0.60	10 339.30	0.18	5 294.10	0.23	51.8	98.53

Figure B4. Analyses and calculations for 21 g/L nickel initial concentration using 1.0 M D2EHPA.



Sample	Sample (mL)	Org Sample (mL)	A Sample (mL)	pH	V aq (mL)	V org (mL)	V NaOH (mL)	NaOH (mol)	Ni aq (mg/L)	Ni aq (mol/L)	Na aq (mg/L)	Na aq (mol/L)	Ni Org (mg/L)	Ni Org (mol/L)	Na Org (mg/L)	Na Org (mol/L)	Loading (%)	Extraction (%)
0	11.0	9.0	2.0	1.74	185.0	815.0	0.0	0.0000	55 252.33	0.94	43.24	0.00	417.49	0.01	0.00	0.00	2.1	3.22
1	12.0	9.8	2.3	1.93	186.3	806.0	3.3	0.0166	52 271.63	0.89	1 925.69	0.08	813.36	0.01	16.77	0.00	4.1	8.44
2	12.0	9.8	2.3	2.08	187.4	796.3	6.6	0.0332	48 793.23	0.83	3 778.35	0.16	1 289.54	0.02	44.17	0.00	6.5	14.54
3	12.0	9.8	2.3	2.34	191.8	786.5	13.3	0.0664	43 484.25	0.74	7 323.09	0.32	2 348.10	0.04	128.33	0.01	11.8	23.83
4	12.0	9.8	2.3	2.54	196.2	776.8	19.9	0.0996	37 604.60	0.64	10 594.80	0.46	3 426.64	0.06	247.44	0.01	17.2	34.13
5	12.0	9.8	2.3	2.70	200.6	767.0	26.6	0.1328	32 103.41	0.55	13 619.10	0.59	4 565.73	0.08	406.79	0.02	22.9	43.77
6	12.0	9.8	2.3	2.88	205.0	757.3	33.2	0.1660	26 960.14	0.46	16 273.90	0.71	5 555.92	0.09	595.08	0.03	27.8	52.78
7	12.0	9.5	2.5	3.04	209.3	747.5	39.8	0.1992	22 263.57	0.38	18 723.00	0.81	6 442.34	0.11	824.47	0.04	32.3	61.00
8	12.0	9.5	2.5	3.20	213.5	738.0	46.5	0.2324	18 504.96	0.32	21 220.00	0.92	7 506.70	0.13	1 076.20	0.05	37.6	67.59
9	12.0	9.5	2.5	3.37	217.6	728.5	53.1	0.2656	14 682.36	0.25	23 210.30	1.01	8 198.96	0.14	1 359.83	0.06	41.1	74.28
10	12.3	9.8	2.5	3.53	221.8	719.0	59.8	0.2988	11 225.72	0.19	24 878.50	1.08	9 529.35	0.16	1 808.30	0.08	47.7	80.34
11	12.0	9.5	2.5	3.74	225.9	709.3	66.4	0.3320	8 458.73	0.14	26 239.70	1.14	9 916.44	0.17	2 170.34	0.09	49.7	85.18
12	12.0	9.5	2.5	3.90	230.0	699.8	73.0	0.3652	6 167.79	0.11	27 887.10	1.21	10 760.50	0.18	2 774.91	0.12	53.9	89.20
13	12.3	9.8	2.5	4.09	234.2	690.3	79.7	0.3984	4 366.73	0.07	28 735.80	1.25	10 542.80	0.18	3 175.17	0.14	52.8	92.35
14	11.8	9.3	2.5	4.28	238.3	680.5	86.3	0.4316	3 057.37	0.05	29 171.10	1.27	11 119.50	0.19	3 919.21	0.17	55.7	94.64
15	12.0	9.5	2.5	4.44	242.5	671.3	93.0	0.4648	2 231.79	0.04	29 772.80	1.30	11 768.20	0.20	4 725.99	0.21	59.0	96.09
16	11.8	9.3	2.5	4.62	246.6	661.8	99.6	0.4980	1 695.88	0.03	29 915.70	1.30	10 874.60	0.19	5 819.38	0.25	54.5	97.03
17	11.8	9.3	2.5	4.79	250.7	652.5	106.2	0.5312	1 340.52	0.02	30 370.50	1.32	10 619.00	0.18	6 463.46	0.28	53.2	97.65
18	12.3	9.5	2.8	4.93	254.9	643.3	112.9	0.5644	1 124.71	0.02	30 283.00	1.32	10 561.80	0.18	7 252.02	0.32	52.9	98.03
19	12.0	9.5	2.5	5.17	258.8	633.8	119.5	0.5976	1 006.43	0.02	30 960.30	1.35	10 349.90	0.18	7 998.92	0.35	51.8	98.24

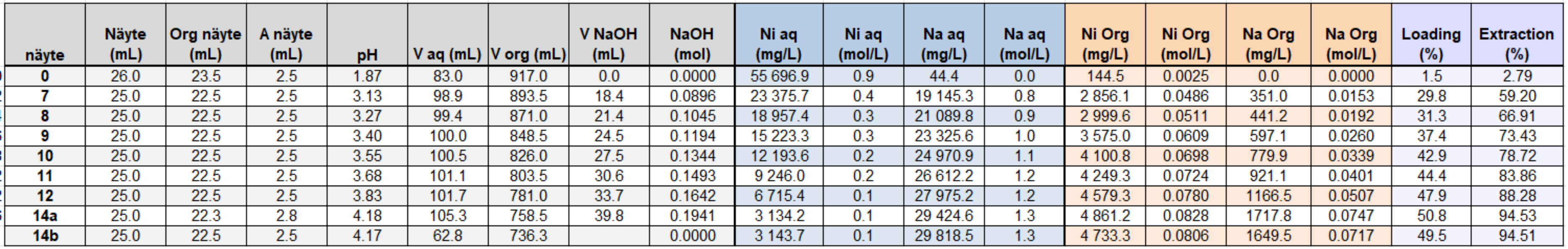
Figure B5. Analyses and calculations for 57 g/L nickel initial concentration using 1.0 M D2EHPA.



Sample	Sample (mL)	Org Sample (mL)	A Sample (mL)	pH	V aq (mL)	V org (mL)	V NaOH (mL)	NaOH (mol)	Ni aq (mg/L)	Ni aq (mol/L)	Na aq (mg/L)	Na aq (mol/L)	Ni Org (mg/L)	Ni Org (mol/L)	Na Org (mg/L)	Na Org (mol/L)	Loading (%)	Extraction (%)
0	25.8	23.3	2.5	1.50	92.0	908.0	0.0	0.0000	107 180.55	1.83	45.72	0.00	289.22	0.00	2.91	0.00	1.4	2.59
1	26.3	23.8	2.5	1.78	93.2	884.8	3.7	0.0185	99 758.60	1.70	3 778.29	0.16	747.90	0.01	25.92	0.00	3.7	9.34
2	25.5	22.8	2.8	1.93	94.4	861.0	7.4	0.0370	94 095.53	1.60	7 281.84	0.32	1 230.78	0.02	64.50	0.00	6.2	14.49
3	25.3	22.5	2.8	2.23	99.1	838.3	14.9	0.0743	82 470.65	1.40	13 764.00	0.60	2 252.31	0.04	181.65	0.01	11.3	25.05
4	25.3	22.3	3.0	2.46	103.8	815.8	22.3	0.1115	69 729.48	1.19	19 216.10	0.84	3 482.10	0.06	359.66	0.02	17.4	36.63
5	24.3	21.3	3.0	2.67	108.3	793.5	29.8	0.1488	58 994.61	1.00	24 373.90	1.06	4 630.21	0.08	568.20	0.02	23.2	46.39
6	24.0	21.0	3.0	2.87	112.7	772.3	37.2	0.1861	48 277.14	0.82	28 838.20	1.25	5 512.87	0.09	808.38	0.04	27.6	56.13
7	24.0	21.0	3.0	3.04	117.2	751.3	44.7	0.2234	38 383.50	0.65	32 102.80	1.40	6 503.81	0.11	1 108.20	0.05	32.6	65.12
8	24.5	21.3	3.0	3.23	121.6	730.3	52.1	0.2606	29 793.96	0.51	34 962.60	1.52	7 406.32	0.13	1 429.82	0.06	37.1	72.92
9	24.0	21.0	3.0	3.44	126.1	709.0	59.6	0.2979	22 789.01	0.39	38 250.30	1.66	8 622.99	0.15	1 889.85	0.08	43.2	79.29
10	24.0	21.8	3.3	3.63	130.5	688.0	67.0	0.3352	17 129.89	0.29	40 541.40	1.76	9 183.91	0.16	2 352.01	0.10	46.0	84.43
11	24.0	20.3	3.8	3.87	134.7	666.3	74.5	0.3724	12 323.02	0.21	42 426.50	1.85	10 015.40	0.17	3 025.16	0.13	50.2	88.80
12	22.8	19.8	3.0	4.02	138.4	646.0	81.9	0.4097	8 673.97	0.15	43 592.40	1.90	10 552.90	0.18	3 735.74	0.16	52.9	92.12
13	22.8	20.0	2.8	4.27	142.9	626.3	89.4	0.4470	5 849.33	0.10	43 829.90	1.91	10 463.30	0.18	4 399.87	0.19	52.4	94.68
14	23.0	19.8	3.3	4.46	147.6	606.3	96.9	0.4843	4 082.90	0.07	43 837.40	1.91	10 545.90	0.18	5 418.39	0.24	52.8	96.29
15	21.5	18.5	3.0	4.67	151.8	586.5	104.3	0.5215	3 085.78	0.05	44 652.60	1.94	10 886.70	0.19	6 352.51	0.28	54.5	97.20
16	22.8	19.8	3.0	4.90	156.3	568.0	111.8	0.5588	2 431.57	0.04	44 775.20	1.95	10 304.90	0.18	7 487.36	0.33	51.6	97.79
17	22.3	19.3	3.0	5.19	160.7	548.3	119.2	0.5961	2 014.64	0.03	44 973.20	1.96	10 730.80	0.18	8 394.90	0.37	53.8	98.17
18	22.0	19.0	3.0	5.40	165.2	529.0	126.7	0.6333	1 717.56	0.03	44 697.70	1.94	9 258.95	0.16	9 000.00	0.39	46.4	98.44

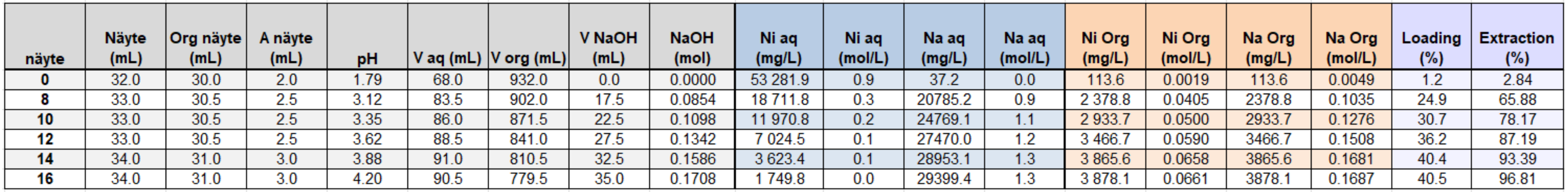
Figure B6. Analyses and calculations for 110 g/L nickel initial concentration using 1.0 M D2EHPA.

Appendix C: Analyses and calculations for additional 0.5 M D2EHPA experiments



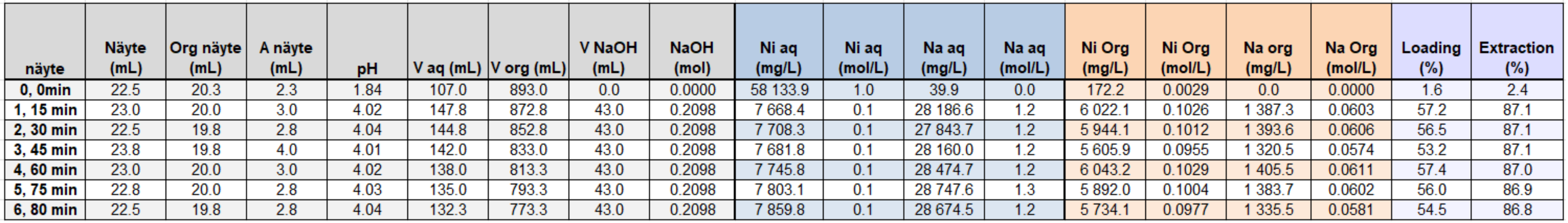
näyte	Näyte (mL)	Org näyte (mL)	A näyte (mL)	pH	V aq (mL)	V org (mL)	V NaOH (mL)	NaOH (mol)	Ni aq (mg/L)	Ni aq (mol/L)	Na aq (mg/L)	Na aq (mol/L)	Ni Org (mg/L)	Ni Org (mol/L)	Na Org (mg/L)	Na Org (mol/L)	Loading (%)	Extraction (%)
0	26.0	23.5	2.5	1.87	83.0	917.0	0.0	0.0000	55 696.9	0.9	44.4	0.0	144.5	0.0025	0.0	0.0000	1.5	2.79
7	25.0	22.5	2.5	3.13	98.9	893.5	18.4	0.0896	23 375.7	0.4	19 145.3	0.8	2 856.1	0.0486	351.0	0.0153	29.8	59.20
8	25.0	22.5	2.5	3.27	99.4	871.0	21.4	0.1045	18 957.4	0.3	21 089.8	0.9	2 999.6	0.0511	441.2	0.0192	31.3	66.91
9	25.0	22.5	2.5	3.40	100.0	848.5	24.5	0.1194	15 223.3	0.3	23 325.6	1.0	3 575.0	0.0609	597.1	0.0260	37.4	73.43
10	25.0	22.5	2.5	3.55	100.5	826.0	27.5	0.1344	12 193.6	0.2	24 970.9	1.1	4 100.8	0.0698	779.9	0.0339	42.9	78.72
11	25.0	22.5	2.5	3.68	101.1	803.5	30.6	0.1493	9 246.0	0.2	26 612.2	1.2	4 249.3	0.0724	921.1	0.0401	44.4	83.86
12	25.0	22.5	2.5	3.83	101.7	781.0	33.7	0.1642	6 715.4	0.1	27 975.2	1.2	4 579.3	0.0780	1166.5	0.0507	47.9	88.28
14a	25.0	22.3	2.8	4.18	105.3	758.5	39.8	0.1941	3 134.2	0.1	29 424.6	1.3	4 861.2	0.0828	1717.8	0.0747	50.8	94.53
14b	25.0	22.5	2.5	4.17	62.8	736.3		0.0000	3 143.7	0.1	29 818.5	1.3	4 733.3	0.0806	1649.5	0.0717	49.5	94.51

Figure C1. Analyses and calculations of the study of the effect of ratio of reagent and nickel amount on the extraction using 57 g/L nickel initial concentration and ratio of 5.5.



näyte	Näyte (mL)	Org näyte (mL)	A näyte (mL)	pH	V aq (mL)	V org (mL)	V NaOH (mL)	NaOH (mol)	Ni aq (mg/L)	Ni aq (mol/L)	Na aq (mg/L)	Na aq (mol/L)	Ni Org (mg/L)	Ni Org (mol/L)	Na Org (mg/L)	Na Org (mol/L)	Loading (%)	Extraction (%)
0	32.0	30.0	2.0	1.79	68.0	932.0	0.0	0.0000	53 281.9	0.9	37.2	0.0	113.6	0.0019	113.6	0.0049	1.2	2.84
8	33.0	30.5	2.5	3.12	83.5	902.0	17.5	0.0854	18 711.8	0.3	20785.2	0.9	2 378.8	0.0405	2378.8	0.1035	24.9	65.88
10	33.0	30.5	2.5	3.35	86.0	871.5	22.5	0.1098	11 970.8	0.2	24769.1	1.1	2 933.7	0.0500	2933.7	0.1276	30.7	78.17
12	33.0	30.5	2.5	3.62	88.5	841.0	27.5	0.1342	7 024.5	0.1	27470.0	1.2	3 466.7	0.0590	3466.7	0.1508	36.2	87.19
14	34.0	31.0	3.0	3.88	91.0	810.5	32.5	0.1586	3 623.4	0.1	28953.1	1.3	3 865.6	0.0658	3865.6	0.1681	40.4	93.39
16	34.0	31.0	3.0	4.20	90.5	779.5	35.0	0.1708	1 749.8	0.0	29399.4	1.3	3 878.1	0.0661	3878.1	0.1687	40.5	96.81

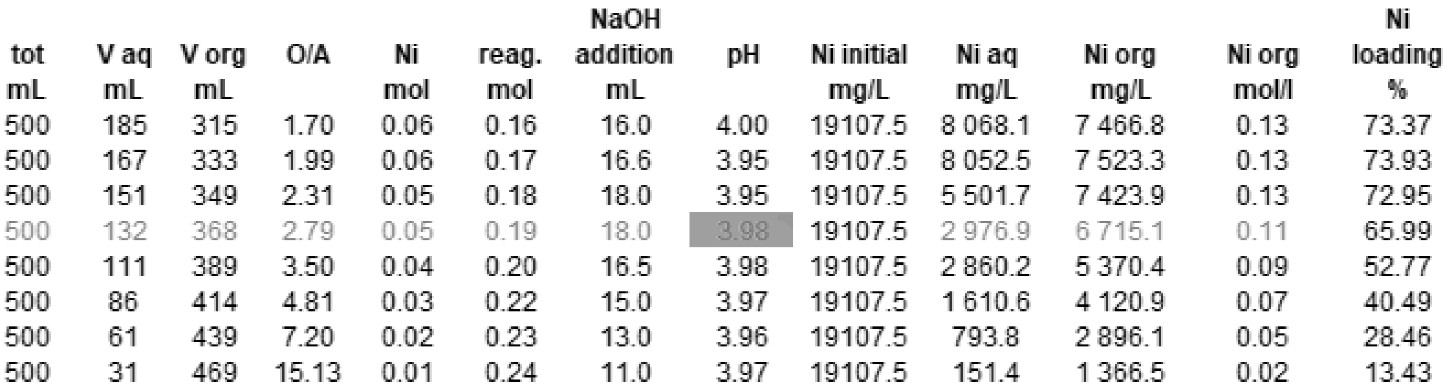
Figure C2. Analyses and calculations of the study of the effect of ratio of reagent and nickel amount on the extraction using 55 g/L nickel initial concentration and ratio of 7.2.



näyte	Näyte (mL)	Org näyte (mL)	A näyte (mL)	pH	V aq (mL)	V org (mL)	V NaOH (mL)	NaOH (mol)	Ni aq (mg/L)	Ni aq (mol/L)	Na aq (mg/L)	Na aq (mol/L)	Ni Org (mg/L)	Ni Org (mol/L)	Na org (mg/L)	Na Org (mol/L)	Loading (%)	Extraction (%)
0, 0min	22.5	20.3	2.3	1.84	107.0	893.0	0.0	0.0000	58 133.9	1.0	39.9	0.0	172.2	0.0029	0.0	0.0000	1.6	2.4
1, 15 min	23.0	20.0	3.0	4.02	147.8	872.8	43.0	0.2098	7 668.4	0.1	28 186.6	1.2	6 022.1	0.1026	1 387.3	0.0603	57.2	87.1
2, 30 min	22.5	19.8	2.8	4.04	144.8	852.8	43.0	0.2098	7 708.3	0.1	27 843.7	1.2	5 944.1	0.1012	1 393.6	0.0606	56.5	87.1
3, 45 min	23.8	19.8	4.0	4.01	142.0	833.0	43.0	0.2098	7 681.8	0.1	28 160.0	1.2	5 605.9	0.0955	1 320.5	0.0574	53.2	87.1
4, 60 min	23.0	20.0	3.0	4.02	138.0	813.3	43.0	0.2098	7 745.8	0.1	28 474.7	1.2	6 043.2	0.1029	1 405.5	0.0611	57.4	87.0
5, 75 min	22.8	20.0	2.8	4.03	135.0	793.3	43.0	0.2098	7 803.1	0.1	28 747.6	1.3	5 892.0	0.1004	1 383.7	0.0602	56.0	86.9
6, 80 min	22.5	19.8	2.8	4.04	132.3	773.3	43.0	0.2098	7 859.8	0.1	28 674.5	1.2	5 734.1	0.0977	1 335.5	0.0581	54.5	86.8

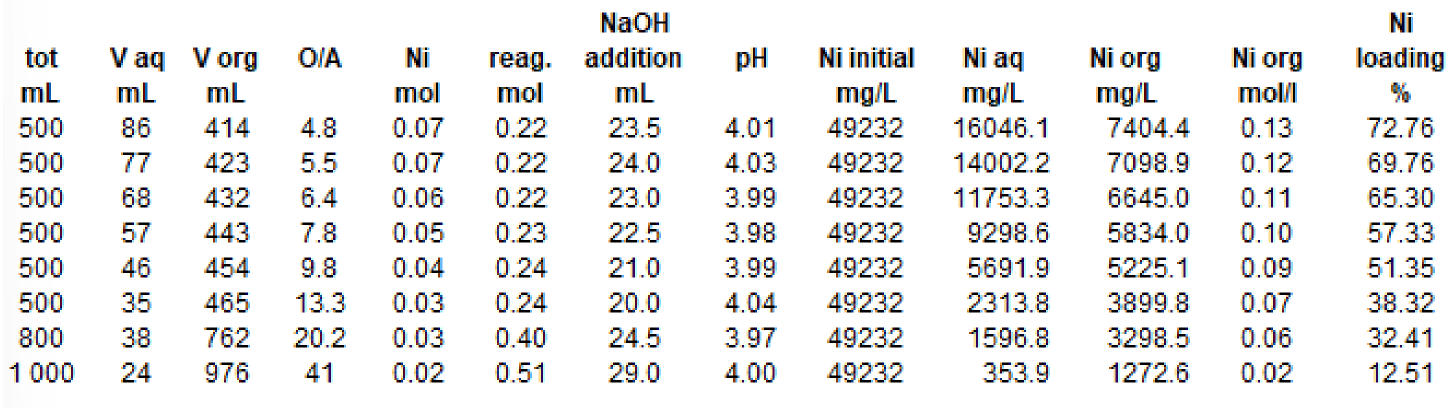
Figure C3. Analyses and calculations of the study of the effect of equilibration time on the extraction using 60 g/L nickel initial concentration.

Appendix D: Analyses for equilibrium isotherms using 0.5 M D2EHPA



tot mL	V aq mL	V org mL	O/A	Ni mol	reag. mol	NaOH addition mL	pH	Ni initial mg/L	Ni aq mg/L	Ni org mg/L	Ni org mol/l	Ni loading %
500	185	315	1.70	0.06	0.16	16.0	4.00	19107.5	8 068.1	7 466.8	0.13	73.37
500	167	333	1.99	0.06	0.17	16.6	3.95	19107.5	8 052.5	7 523.3	0.13	73.93
500	151	349	2.31	0.05	0.18	18.0	3.95	19107.5	5 501.7	7 423.9	0.13	72.95
500	132	368	2.79	0.05	0.19	18.0	3.98	19107.5	2 976.9	6 715.1	0.11	65.99
500	111	389	3.50	0.04	0.20	16.5	3.98	19107.5	2 860.2	5 370.4	0.09	52.77
500	86	414	4.81	0.03	0.22	15.0	3.97	19107.5	1 610.6	4 120.9	0.07	40.49
500	61	439	7.20	0.02	0.23	13.0	3.96	19107.5	793.8	2 896.1	0.05	28.46
500	31	469	15.13	0.01	0.24	11.0	3.97	19107.5	151.4	1 366.5	0.02	13.43

Figure D1. Analyses for the equilibrium isotherm of 19 g/L nickel and 0.5 M D2EHPA.



tot mL	V aq mL	V org mL	O/A	Ni mol	reag. mol	NaOH addition mL	pH	Ni initial mg/L	Ni aq mg/L	Ni org mg/L	Ni org mol/l	Ni loading %
500	86	414	4.8	0.07	0.22	23.5	4.01	49232	16046.1	7404.4	0.13	72.76
500	77	423	5.5	0.07	0.22	24.0	4.03	49232	14002.2	7098.9	0.12	69.76
500	68	432	6.4	0.06	0.22	23.0	3.99	49232	11753.3	6645.0	0.11	65.30
500	57	443	7.8	0.05	0.23	22.5	3.98	49232	9298.6	5834.0	0.10	57.33
500	46	454	9.8	0.04	0.24	21.0	3.99	49232	5691.9	5225.1	0.09	51.35
500	35	465	13.3	0.03	0.24	20.0	4.04	49232	2313.8	3899.8	0.07	38.32
800	38	762	20.2	0.03	0.40	24.5	3.97	49232	1596.8	3298.5	0.06	32.41
1 000	24	976	41	0.02	0.51	29.0	4.00	49232	353.9	1272.6	0.02	12.51

Figure D2. Analyses for the equilibrium isotherm of 49 g/L nickel and 0.5 M D2EHPA.

tot mL	V aq mL	V org mL	O/A	Ni mol	reag. mol	NaOH addition mL	pH	Ni initial mg/L	Ni aq mg/L	Ni org mg/L	Ni org mol/l	Ni loading %
500	48	452	9.5	0.09	0.24	27.5	4.01	113394.9	38433.2	8021.6	0.14	78.83
500	43	457	10.7	0.08	0.24	27.0	4.01	113394.9	31669.9	7415.9	0.13	72.87
500	38	462	12.3	0.07	0.24	27.0	4.03	113394.9	26192.0	7223.9	0.12	70.99
600	39	561	14.5	0.07	0.29	31.0	4.02	113394.9	18674.1	6458.2	0.11	63.46
600	32	568	17.8	0.06	0.30	30.0	3.98	113394.9	12410.3	5706.0	0.10	56.07
800	34	766	22.5	0.07	0.40	37.0	4.02	113394.9	7014.9	4865.3	0.08	47.81
1 000	31	969	31	0.06	0.50	40.0	3.97	113394.9	4029.5	3642.7	0.06	35.80
1 000	20	980	50	0.04	0.51	35.5	3.97	113394.9	1753.1	2321.6	0.04	22.81

Figure D3. Analyses for the equilibrium isotherm of 113 g/L nickel and 0.5 M D2EHPA.