Recovery of valuable metals from spent Li-ion batteries

A study of extraction and scrubbing parameters in a solvent extraction process

Bachelor's thesis in Chemical Engineering

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Abstract

Lithium-ion battery production is expected to rise and with it battery waste. Recycling of lithium-ion batteries through hydrometallurgy presents an important role in handling hazardous battery waste and recovery of metals. Two approaches were investigated to remove the impurity copper from a leached acid battery solution from spent lithium-ion batteries through solvent extraction or scrubbing. Solvent extraction with Acorga M5640, mixture of Acorga M5640 and Cyanex 272 as well as LIX 84-I were tested at different concentrations and pH values. The best results were achieved using Acorga M5640 20 v% (37% extraction of copper and co-extraction of 11% cobalt, at a pH of 0.8). In alternative, solvent extraction of manganese followed by scrubbing the impurities were tested. D2EHPA (0.5 M) was used as the extractant and the optimal pH for the solvent extraction of manganese was determined between 2.3-2.5 and the optimal O:A ratio 1:1 (Extraction Cu 22%, Co 14% Mn 75%). Scrubbing results using 4 g/L ($MnSO_4 \cdot H_2O$ and $MnCl_2 \cdot 4H_2O$) and 6 g/L manganese ($MnSO_4 \cdot H_2O$) showed the least co-extraction with 6 g/L manganese using $MnSO_4 \cdot H_2O$, in two stages. Stripping product of 21 g/L manganese and 0.4 g/L cobalt was obtained under the conditions (O:A 10:1, 0.5 M H_2SO_4 and 25 min contact time) in one stage.

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1 Introduction

With the increasing use of lithium-ion batteries (LiBs) in different applications such as portable computers, mobile phones, electric tools, and other devices, the amount of lithium-ion batteries waste is expected to increase by a significant amount over the next years [1]. Therefore, there is a need for efficient and effective methods to recycle spent LiBs, which represent a source of metals such as lithium, cobalt, manganese, nickel, aluminium, and copper [2]. Separation and recycling of these metals is important as spent LiBs are considered hazardous waste and need to be taken care of properly in order to not cause any health risks to humans, animals, and damage to the environment [1]. Additionally, recycling provides an excellent secondary source of metals [1, 3].

Lithium-ion batteries are sought after as they have many more advantages than disadvantages compared to other batteries such as lead-acid, nickel-cadmium, nickel-metal hydride, and rechargeable alkaline batteries [4]. Some of the advantages are relatively low self-discharge, low maintenance, and no memory effects as well as high energy density with potential for higher with future research [4]. These advantages make LiBs the technology of choice for powering portable devices as those previously mentioned and are important for a transition to renewable energy, electric vehicles and energy storage systems [2].

Spent LiBs are first treated by a mechanical treatment that can be followed by thermal treatment, leaching, precipitation, and solvent extraction [5]. Mechanical treatment includes for example the use of crushing, milling as well as separation by density and magnetic properties, [5]. Thermal pre-treatment is mostly used to remove organic compounds such as polyvinylidene fluoride (PVDF), a plastic that serves as a binder in LiBs. Graphite is used in the anode as an active material [5]. Leaching is used to dissolve metals in inorganic acids such as HCl. In solvent extraction, an organic extractor such as Acorga M5640, which is made to bind specifically to copper, can be used to separate the solved copper from the rest of the leach solution.

The leach solution obtained by the acid leaching of spent LiBs that was used in this study contains major metals and metal impurities. The metal impurities have been mostly removed in previous steps. The concentration of the impurities in the leach solution are: copper (6 mg/L), zinc (20 mg/L), magnesium (32 mg/L) and aluminium (270 mg/L). The major metals are cobalt (9440 mg/L), nickel (3960 mg/L), manganese (3320 mg/L) and lithium (2350 mg/L).

The purpose of this thesis is to find an optimal way to remove the impurity copper from an acid leach solution from spent lithium-ion batteries. Additionally, this work aimed to study the solvent extraction of manganese and the removal of copper and other impurities by scrubbing the loaded organic to purify the manganese product.

2 Theory

2.1 Battery components

A lithium-ion battery is made of several parts, some of them are the anode, cathode, electrolyte, and the separator. In current generation batteries, the anode is typically made of graphite and the cathode usually from nickel manganese cobalt oxide (NMC) [2]. Some other cathode materials are lithium cobalt oxide, lithium nickel cobalt aluminium oxide, and lithium iron phosphate [3]. In lithium-ion batteries, liquid electrolytes are used where lithium salts such as $LiPF_6$, $LiBF_4$ or $LiClO_4$ are in an organic solvent such as ethylene carbonate [6]. The separator is often made of a very thin polymeric membrane like polyvinylidene fluoride (PVDF) [7].

2.2 Recycling via Hydrometallurgy and Pyrometallurgy

LiBs can be recycled through the processes of hydrometallurgy and pyrometallurgy or a combination of both [2]. Hydrometallurgy consists of processes such as leaching, solvent extraction and precipitation, just to mention a few, while pyrometallurgy consists of smelting for refining and recovering the metals in a form of alloys [2].

Some of the advantages of hydrometallurgy over pyrometallurgy is low energy consumption, most metals can be recovered with high yields, and polymer compounds can be recovered [2, 5]. Some of the drawbacks of pyrometallurgy is that not all the metals can be recovered from the waste as well as organic and polymer components that were not separated in pre-treatment are burned off [5]. Metals such as cobalt, copper, and nickel form alloys, while other metals such as lithium end up in the slag and need to be recovered through hydrometallurgy processes [2].

2.3 Solvent Extraction

Solvent extraction is ideally used to separate specific metal ions within one liquid phase to another liquid phase leaving other metal ions behind. Usually, a polar aqueous phase and a non-polar organic phase are used. These liquids are immiscible and therefore separate into layers, which allows the separation of the two phases.

In hydrometallurgy, solvent extraction is used in order to separate metal ions in liquids [8]. There are different organic acid extractants, for example Acorga M5640, D2EHPA, Cyanex

272 and LIX 84-I. Each extractant has different selectivity for different metal ions. For example Acorga M5640 is used for extracting copper, while D2EHPA and Cyanex 272 are best suited for the extraction of manganese [9]. A mix of Acorga M5640 and Cyanex 272 has shown to have a synergistic effect extracting copper with a low co-extraction of cobalt at pH under 4 [10].

Extraction of the metals from aqueous phase to organic phase is affected by several factors, including the pH of the aqueous phase (if acidic extractants are used) and the organic to aqueous ratio (O:A) used. During extraction, the pH is expected to decrease (due to released hydrogen protons) and at lower pH there is less extraction occurring. Equation (1) shows the extraction mechanism using D2EHPA and causing a decrease in pH [11]. *M* represents the metal, while *HA* and MA_4H_2 represent D2EHPA in the organic phase and metal-organic complex, respectively [11].

$$M^{2+} + 2(HA)_2 \rightleftharpoons MA_4H_2 + 2H^+ \tag{1}$$
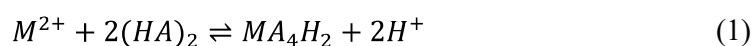
As seen in Figure 1, where a principle of solvent extraction is shown, the extraction moves the desired metal ions from aqueous feed solution to the organic phase (loaded organic) through the process of extraction. If the selectivity of the extractant is low, other unwanted metals are co-extracted as well. Scrubbing is used to remove the unwanted co-extracted metal ions from the loaded organic phase coming from the extraction stage using a solution based on the target metals (e.g. in a case of manganese – a solution containing manganese ions), so the co-extracted impurity will be replaced by metal cations. For example, when extracting manganese with the extractant D2EHPA and scrubbing away impurities, dissolved $MnSO_2 \cdot H_2O$ in milli-Q water can be used as a scrubbing solution [12]. Once the co-extracted metals are removed from the loaded organic, stripping is used to remove the metal ions from the loaded organic into the aqueous phase using a change of pH back to the acidic region. It can be performed using for example a stripping solution such as H_2SO_4, which will reverse the reaction of extraction according to Equation (1) [11, 12].
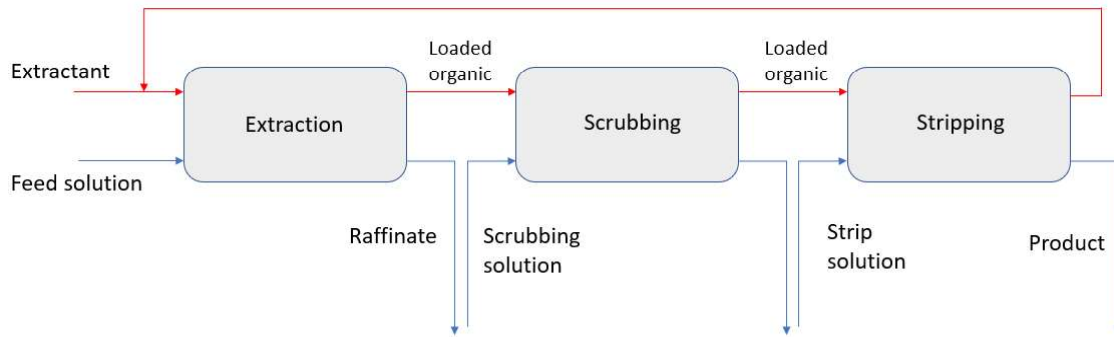
Figure 1: Solvent extraction, scrubbing and stripping steps used to separate specific metal ions from other metal ions. Blue lines represent aqueous phase, and organic (extractant) red. The extractant is regenerated and reused in the industry.

In the study of Nayl *et al.* [12], a leached solution containing impurities copper, aluminium and iron together with metals manganese, cobalt, nickel and lithium Acorga M5640 (20 v%, in kerosene) was used in order to remove the impurities [13]. The metals were leached using H_2SO_4 and the extractants were diluted with kerosene. A contact time of 5 min was used and the extraction was performed at a temperature of 30 °C with a 1:1 O:A ratio. The results showed negligible extraction of manganese, cobalt, nickel, and lithium between pH of 0-1.6. The extraction of impurities such as copper and aluminium increased with pH, with copper fully extracted at a pH of 1.0 and aluminium at 20%. At pH of 1.6, aluminium was extracted at about 90%.

Li *et al.* [12] studied the recovery of manganese from an acid leaching liquor of spent lithium-ion batteries using solvent extraction and the authors determined that the extraction could be performed in single stage extraction using D2EHPA 15% in kerosine and an O:A ratio of 1:1.

In an another study, using D2EHPA (0.5 M), an O:A ratio of 1.25:1 and an equilibrium pH of 3.5 was proposed by Vieceli *et al.* [11], for the solvent extraction of manganese from a synthetic solution based on LiBs.

3 Materials and Method

The feed solution also called the leached battery solution used in this study was provided by the Institute IME Process Metallurgy and Metal Recycling (RWTH Aachen University). The solution was obtained by acid leaching of the black mass of spent LiBs. The conditions of the leaching process were as follows: a solution of 4 M hydrochloric acid, 50 g/L hydrogen peroxide (concentration of 35%), leaching time of 120 min, S/L ratio of 100 g/L, temperature of 80°C and stirring speed of 300 rpm. The composition of the acid leach solution can be seen in Table 1. Cementation with iron was used which removed copper, then aluminium and iron was precipitated. Only small amount of copper and aluminium were left with no iron remining. This purified solution was used as feed solution for the experiments in this thesis and it had a pH of 4.1. The composition of the purified feed solution can be seen in Table 2 and a picture of it can be seen in Figure 14 in the Appendix. Notice that Table 1 is in g/L and Table 2 is in mg/L.

Table 1: Concentration of the leached solution before copper cementation and Al/Fe precipitation.

Source / element	Mg	Cu	Zn	Al	Mn	Ni	Li	Co
Liquid Sample (g/L)	0.1	3.1	0.1	2.1	7.5	7.9	4.0	18.0
Standard deviation (±)	<0.01	<0.1	<0.01	<0.1	<0.1	<0.1	<0.1	0.2

Table 2: Concentration of the leached solution after cementation and Al/Fe precipitation. Concentration is an average of two samples. pH 4.1.

Source / element	Mg	Cu	Zn	Al	Mn	Ni	Li	Co
Liquid Sample (mg/L)	31.8	6.3	20.4	269.3	3320.6	3966.3	2348.9	9438.5
Standard deviation (±)	<0.01	0.1	0.1	2.0	77.8	49.0	67.9	119.5

First, the approach adopted in this work was to remove the impurity copper from the feed solution using only solvent extraction, comparing different extractants and their effectiveness (section 3.1). Afterwards, the use of solvent extraction to extract manganese was tested and it was followed by the purification of the loaded organic by scrubbing to remove co-extracted impurities, such as copper (section 3.2). The organic acidic extractants used in this study can be seen in Table 3.

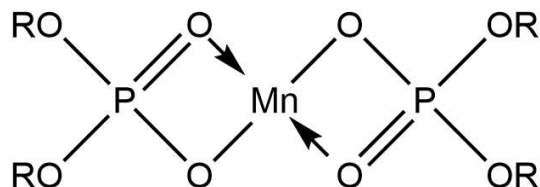| Organic acidic extractants	
Acorga M5640	5-nonylsalicylaldoxime modified with TXIB /2,2,4-trimethyl-1,3 pentanediol di-isobutyrate
D2EHPA	di-(2-ethylhexyl) phosphoric acid
Cyanex 272	bis(2,4,4-trimethylpentyl) phosphinic acid
LIX 84-I	2-hydroxy-5-nonylacetophenone oxime

Figure 2: Extractant D2EHPA extracting Mn.

3.1 Removal of impurities by solvent extraction

The extractants used in the solvent extraction tests were: Acorga M5640 (10 v%, 20 v% and 30 v%), LIX 84-I (20 v%), as well as two mixtures of Cyanex 272 and Acorga M5640. The mixtures were made from 0.15 M Cyanex 272 and 0.06 M Acorga M5640, and 0.30 M Cyanex 272 and 0.12 M Acorga M5640. These mixtures were tested in order to evaluate the synergetic effect proposed by Cheng *et al*. [10]. Isopar L (Exxon Mobil, USA) was used as diluent. An O:A ratio of 1:1 was used for all tests except those used for an O:A ratio analysis. Extractions experiments were performed in 3.5 ml vials and shaken using a shaking machine (IKA-Vibrax at 1000 rpm) for 15 min (contact time) and then were centrifuged for 5 minutes at 5000 rpm to promote the separation of phases. The equipment used can be seen in the Appendix (Figures 16 and 17).

The organic and aqueous phase were separated using autopipettes that can be seen in Figure 15 in Appendix. Organic residues on the pipette tip were cleaned off during separation using precision wipes as to not contaminate the aqueous phase. The aqueous phase pH was measured (Metrohm 827 pH lab) and the pH meter was calibrated before each test. Samples were made for ICP-OES analysis (Inductively Coupled Plasma—Optical Emission Spectroscopy, iCAP™ 6000 Series) for specific metal content, the ICP-OES and analysing samples can be seen in Figures 19 and 21 in the Appendix. Samples from the aqueous phase were taken from the feed solution and from the raffinate after extraction, scrubbing and stripping experiments. The samples were diluted using nitric acid (0.5 M) and analysed using ICP-OES as can be seen in

the flowsheet in Figure 3 and Figure 4. Samples were diluted to lower the concentration as it was too high for analysis otherwise.

The efficiency of extraction of a metal was calculated by Equation (2) where D represents the distribution ratio of a metal. V_{aq} and V_{org} represent the volume of aqueous and organic phases used during extraction, respectively [14].

$$\%E = \left(\frac{100 \times D_x}{D_x + \left(\frac{V_{aq}}{V_{org}} \right)} \right)$$ (2)

The distribution ratio (D) is defined as the ratio between the concentration of a metal in the organic phase compared to the concentration of the metal in the aqueous phase at equilibrium [14], and it can be determined by Equation (3). $[M]_{org}$ and $[M]_{aq}$ stand for the concentration of a metal in the organic and the aqueous phase, respectively.

$$D = \frac{[M]_{org}}{[M]_{aq}}$$ (3)

Mass balance was used to calculate the concentration of a metal extracted in the organic phase using Equation (4). $[M]_{aq,in}$ and $[M]_{org,in}$ are the concentrations of a metal entering the system through the aqueous phase (feed solution) and the organic phase, respectively. $V_{aq,in}$ and $V_{org,in}$ stand for the volume of the aqueous phase and the organic phase entering the system, respectively. $[M]_{org,out}$ and $[M]_{aq,out}$ are the concentrations of a metal leaving the system through the organic phase and the aqueous phase, respectively. Finally, $V_{org,out}$ and $V_{aq,out}$ are the volumes of the organic phase and aqueous phase, respectively, leaving the system.

$$[M]_{aq,in} \times V_{aq,in} + [M]_{org,in} \times V_{org,in} = [M]_{aq,out} \times V_{aq,out} + [M]_{org,out} \times V_{org,out}$$ (4)

The separation factor between two elements can be calculated using Equation (5). $[M]_x$ and $[M]_y$ are the concentration of metal x and y. D_x and D_y represent the distribution ratios of metal x and y [14].

$$\beta = \frac{[M_x]_{org}/[M_x]_{aq}}{[M_y]_{org}/[M_y]_{aq}} = \frac{D_x}{D_y} \tag{5}$$

The concentrations of metals in the scrubbing and stripping products were determined by continuous monitoring of the concentrations of metals in the feed solution and raffinates, and by mass balance.

The effect of pH on efficiency of extraction: Tests were performed using the original feed solution and varying the pH of the feed solution. An example of the process can be seen in Figure 3. Before the extraction, the pH was adjusted using 5 M, 1 M, 0.5 M NaOH or 6 M HCl. When using NaOH for increasing the pH, NaOH and the organic phase were first mixed thoroughly before adding the feed solution followed by immediate mixing as to not cause precipitation which ruins the sample. Adding NaOH directly to the feed solution caused instant precipitation which ruined the sample, the precipitation can be seen in Figure 20 in the Appendix. The different pH-levels that were tested were the original 4.1 as well as pH of 0.8, 1.1 and 1.4.

Pictures of samples after extraction using D2EHPA and Acorga M5640 can be seen in Figures 22 and 23 in the Appendix.
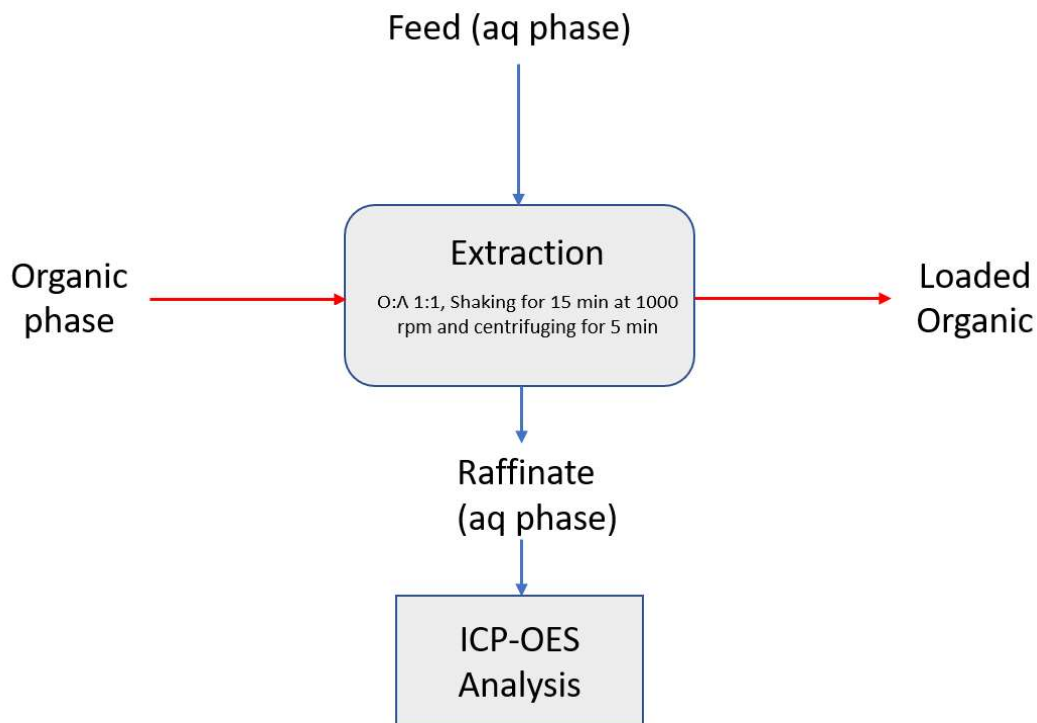
Figure 3: Example of the procedure of extraction performed during tests.

The effect of secondary extraction: Secondary stages of extraction were performed with the extractants Acorga M5640 (10 v%, 20 v% and 30 v%), LIX 84-I (20 v%), as well as the two mixtures of Cyanex 272 and Acorga M5640 made from 0.15 M and 0.06 M, 0.30 and 0.12 M, respectively. The secondary extraction was made using the raffinate from the previous test varying the pH (0.8, 1.1 and 1.4), combining the triplicates of each pH from the previous tests to have enough aqueous phase for a secondary extraction.

3.2 Solvent extraction of manganese

The solvent extraction of manganese was tested using D2EHPA (0.5 M) as extractant. Isopar L (Exxon Mobil, USA) was also used as diluent and the tests were performed using the same procedures as described in section 3.1. The effect of the O:A ratio was evaluated and the purification of the loaded organic by scrubbing was also investigated. An example of the process flowsheet can be seen in Figure 4.

The effect of O:A ratio: Different O:A ratios were tested using D2EHPA 0.5 M and the feed solution. The tested O:A ratios were 5, 3, 2, 1.25, 1, 0.5, 0.33. The extraction was made with the same conditions as before with 3.5 ml vials, 15 min contact time at 1000 rpm and 5 min centrifuging at 5000 rpm. The equilibrium pH was set at 2.5 to allow comparing the extraction efficiency using different O:A ratios.

The effect of scrubbing and stripping: Scrubbing solutions of 4 g/L and 6 g/L of manganese in Milli-Q water were made using $MnSO_2 \cdot H_2O$ and a 4 g/L using $MnCl_2 \cdot 4\,H_2O$. A larger volume of loaded organic was required to perform the scrubbing tests. Therefore, the extraction step was made in multiple 8 ml vials or larger 100 ml plastic containers and the loaded organic obtained was used in the scrubbing tests. Right at the start of each extraction NaOH 5 M was added to achieve an equilibrium pH of 2.3 (aqueous pH after extraction), to obtain the loaded organic for the scrubbing tests with 4 g/L and 6 g/L manganese using $MnSO_2 \cdot H_2O$ and a pH of 2.5 for the scrubbing tests with 4 g/L manganese using $MnCl_2$. The extraction was performed using the same shaker (IKA-Vibrax at 1000 rpm) for 15 min, or if using the larger 100 ml plastic beaker, with a mixer (MSU 0.5, Figure 18 in the Appendix) at a rotation equivalent to 1000 rpm.

The loaded organic was scrubbed twice using an O:A of 10:1 in 8 ml glass vials for 15 min at 1000 rpm (IKA-Vibrax), each time taking a sample of the aqueous phase for ICP analysis. The samples scrubbed using $MnSO_2 \cdot H_2O$ were also stripped using H_2SO_4 0.5 M at O:A ratio of 10:1 for 25 min at 1000 rpm (IKA-Vibrax). No pH adjustment was done in the scrubbing and stripping tests.
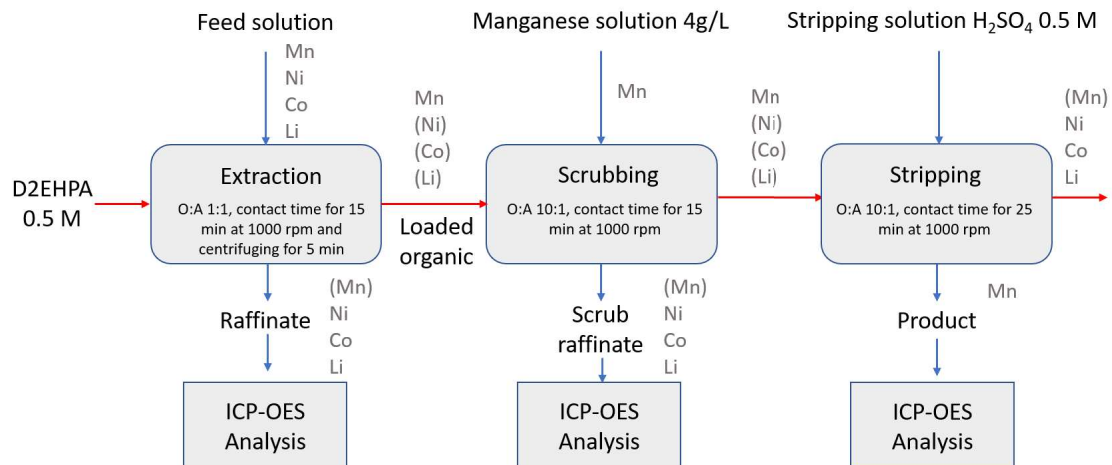
Figure 4: Example of the process flowsheet of extraction, scrubbing and stripping performed during tests. Blue lines represent aqueous phase and red the organic phase (extractant).

4 Results and Discussion

4.1 Removal of impurity by solvent extraction

Tests were performed to find suitable conditions to achieve a high extraction of the impurity copper and other impurities without co-extraction of unwanted major metals such as lithium, cobalt, nickel, and manganese.

4.1.1 Effect of extractants concentration and pH

As seen in Figure 5, the extraction efficiency of copper is increasing along with the concentration of Acorga M5640. However, the increase in efficiency is very slight when compared to the increase in the concentration of Acorga M5640 used (10 v%, 20 v% and 30 v%). When 10 v% of Acorga M5640 was used, 35% extraction of copper was achieved, while 37% of extraction of copper was reached when the concentration of Acorga was increased to 30 v%, which is not a noticeable increase in extraction compared to the increase of Acorga M5640 used. Also, the co-extraction is at about 14% for all the major metals.

As copper is present in low concentrations in the feed solution (about 6 mg/L) and only about 35% was extracted, when comparing to the co-extraction of about 14% of the major metals like cobalt (initial concentration of about 9500 mg/L), the impurity copper is not being removed efficiently and instead other metals are co-extracted. Because of the significant co-extraction and slight extraction of copper, it is not a suitable way to remove the impurity copper from the feed solution by solvent extraction, under the tested conditions. Same can be said for the two mixtures of Acorga M5640 and Cyanex 272 as well as LIX 84-I 20 v%.

The reason why the Acorga M5640 and Cyanex 272 mixture was used was to test their synergetic effect, which was proposed by Cheng *et al.* [10]. The authors claimed the extraction of copper and zinc at a pH range between 2 and 3.5, with no co-extraction of cobalt and nickel before a pH of 4, which was caused by a shift in the extraction curve of copper and zinc to lower pH by using the mixture of Acorga M5640 and Cyanex 272. As seen in Figure 5, the results show that there was co-extraction of cobalt from the tested feed solution. Therefore, even lower pH tests were made in order to see if a lower co-extraction of major metals, such as cobalt, could be obtained at lower pH.

For the tests using a feed solution at pH of 0.8, 1.1 and 1.4, the decrease of the pH was minimal for all extractants. However, when using the feed solution with unaltered pH of 4.1, the pH at

equilibrium varied with the different extractants. Using Acorga M5640 (10 v%, 20 v%, 30 v%), the equilibrium was pH 3.0. Using the Acorga M5640 and Cyanex 272 mixtures, the equilibrium pH was 2.4. Lastly, when using LIX 84-I (20 v%) the equilibrium pH was 3.4.
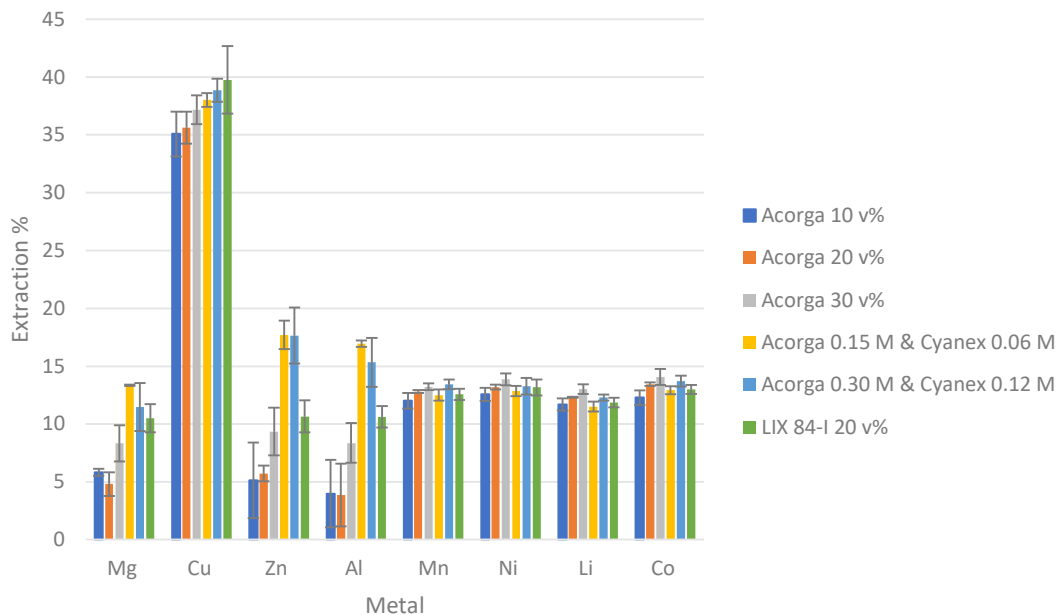
Figure 5: Extraction using different extractants at feed pH of 4.1. Conditions: Ratio 1:1, 15 min shaker at 1000 rpm, 5min centrifuge. Error bars made by triplicates. Data from Table 8.

Figure 6 shows the extraction at equilibrium pH of 0.8 and when comparing to Figure 5 at equilibrium pH of 3.0, the co-extraction of major metals is slightly lower for all extractants, except for LIX 84-I, which lead to a higher extraction of lithium at 27% compared to about 12% at pH 3.0. While the co-extraction at pH 0.8 is lower than for pH 3.0, the co-extraction is still too high and the extraction of copper too low.
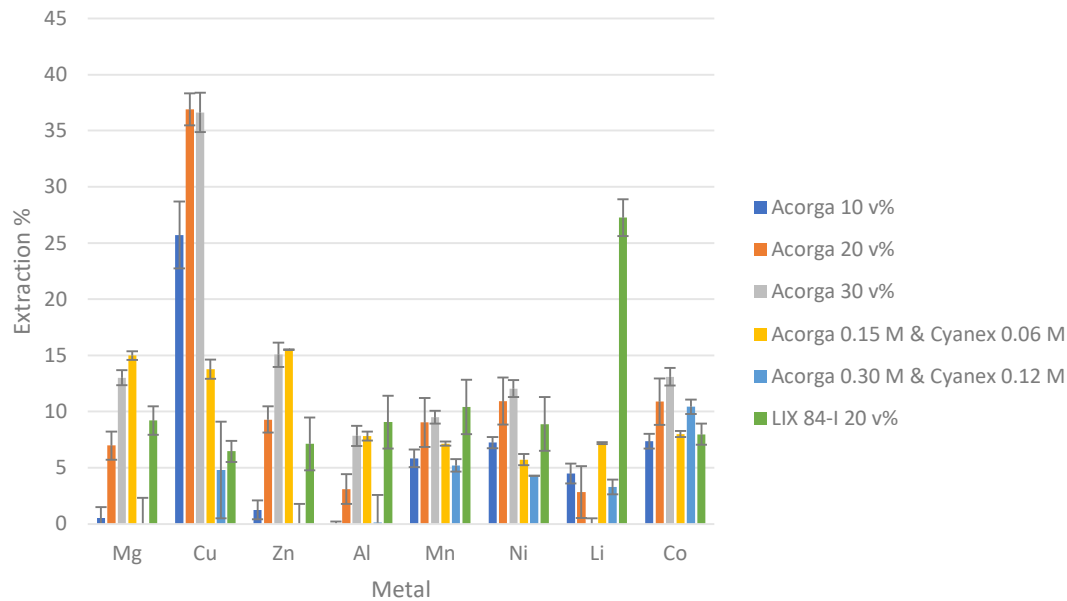
Figure 6: Extraction using different extractants at equilibrium pH of 0.8. Conditions: Extraction: O:A 1:1, 15 min contact time 1000 rpm, 5 min centrifuge 5000 rpm. Error bars made by triplicates.

Comparing the extraction at pH of 1.1 (Figure 7) and the extraction at pH 0.8 (Figure 6) using Acorga M5640 as the extractant, it is possible to observe that the extraction of copper is similar for Acorga M5640 (20 v% and 30 v%), but the co-extraction of major metals is lower using a pH of 0.8. For the Acorga M5640 and Cyanex 272 mixtures in both Figure 6 and 7, the co-extraction of major metals is lower than for Acorga M5640 (20 v%, 30 v%) for all major metals, except for lithium. However, the extraction of copper is also much lower than using just Acorga M5640 (20 v%, 30 v%).

For LIX 84-I, the extraction differs greatly as lithium is being extracted the most at pH 0.8 (Li 26%, Co 8%) and cobalt at a pH of 1.1 (Li 5%, Co 27%). It could be noted in Figure 7 that LIX 84-I shows an extraction of cobalt at 27% and below 5% on all other metals. Therefore, LIX 84-I is not suitable at these conditions for the extraction of copper but maybe under more optimised conditions, it could be used to extract cobalt and the impurities could be scrubbed.

In the feed solution, the concentration of copper is at about a few milligrams (~ 6 mg/L) and with an extraction of 39% (using Acorga M5640 20 v%, pH 1.1) only a small portion of it was removed. In comparison, the concentration of major metals such as cobalt, nickel and manganese in the feed solution is much higher (g/L) and with an extraction at around 10-13% for these metals, the co-extraction is very high. It is not reasonable to remove copper under

15

these conditions as the selectivity for copper is too low. Lithium is the only major metal that had a very low co-extraction at 0-1% using Acorga 30 v% at pH of 0.8 and 1.1.
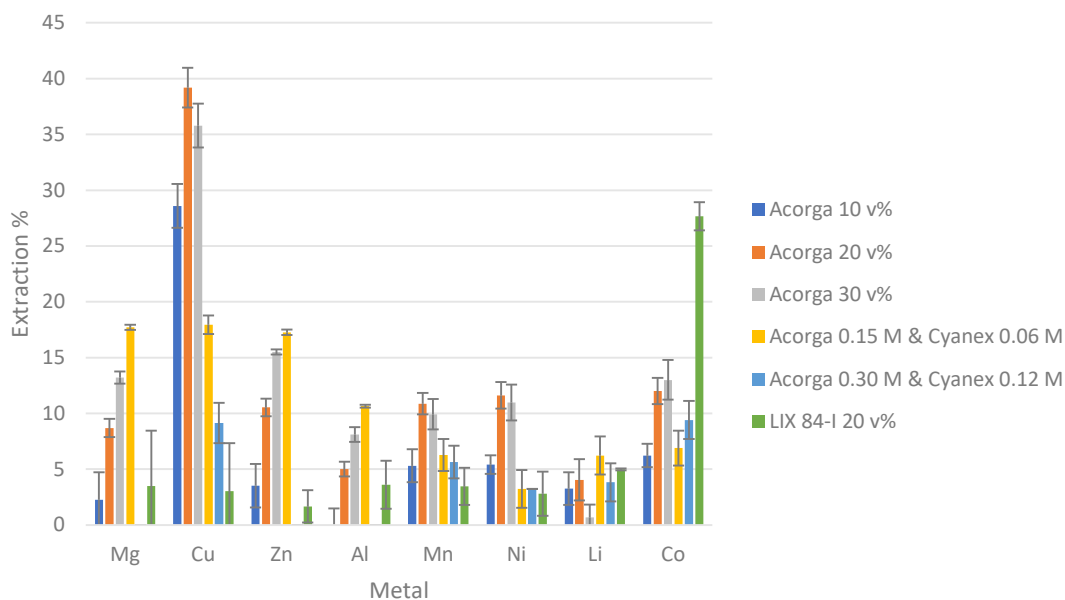
Figure 7: Extraction using different extractants at equilibrium pH of 1.1. Conditions: Extraction: O:A 1:1, 15 min contact time 1000 rpm, 5 min centrifuge 5000 rpm. Error bars made by triplicates.

Extraction using a pH of 1.4 can be seen in Figure 8 and when comparing the extraction results with Figure 6 showing extraction at pH of 0.8, there is an increase in the co-extraction of major metals at pH 1.4. At pH 1.4 (Figure 8) for example using Acorga M5640 20 v%, the extraction of manganese is at 13%, nickel at 18%, lithium at 9% and cobalt at 20% which at pH 0.8 (Figure 6) is 10% for manganese, 13% for nickel, 0-1% for lithium and 13% for cobalt. This indicates that extraction at 0.8 has a lower co-extraction of major metals, when compared to the other conditions tested (pH 1.1 and 1.4). However, even though the co-extraction is lower using a pH of 0.8, it is still significant when comparing with the low concentration of copper that is removed.
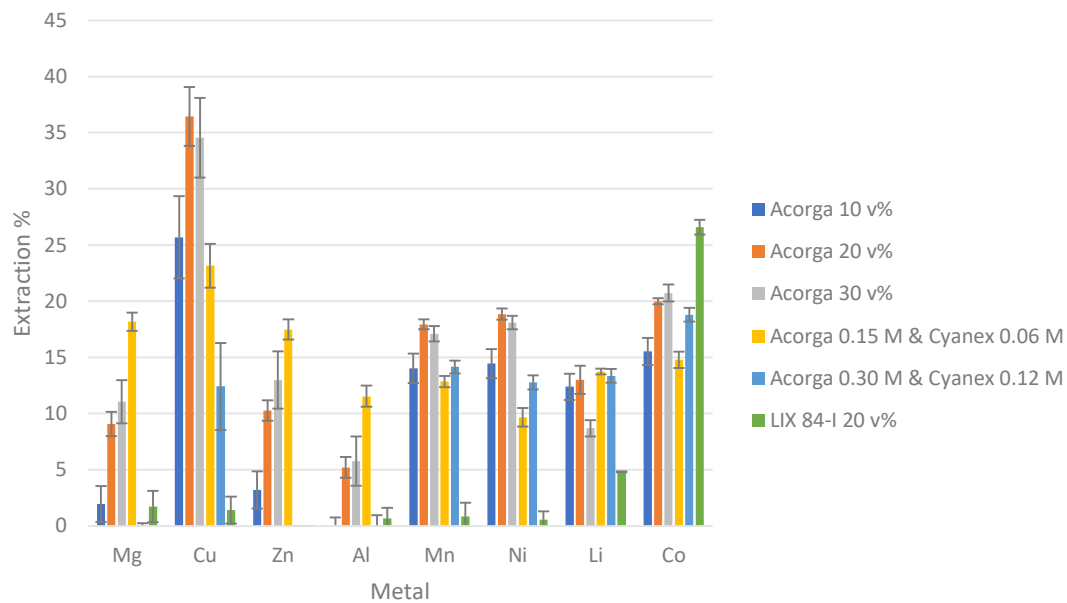
Figure 8: Extraction using different extractants at equilibrium pH of 1.4. Conditions: Extraction: O:A 1:1, 15 min shaking 1000 rpm, 5 min centrifuge 5000 rpm. Error bars made by triplicates.

The increase of co-extraction of major metals at higher pH using Acorga M5640 30 v% can be seen in Figure 9. At pH 1.4 the extraction is higher than at pH 3.0, which could be due to unexpected variation. Because of increase of co-extraction with pH, which can be seen in Figure 9, higher pH is not suitable for the removal of copper at these conditions.
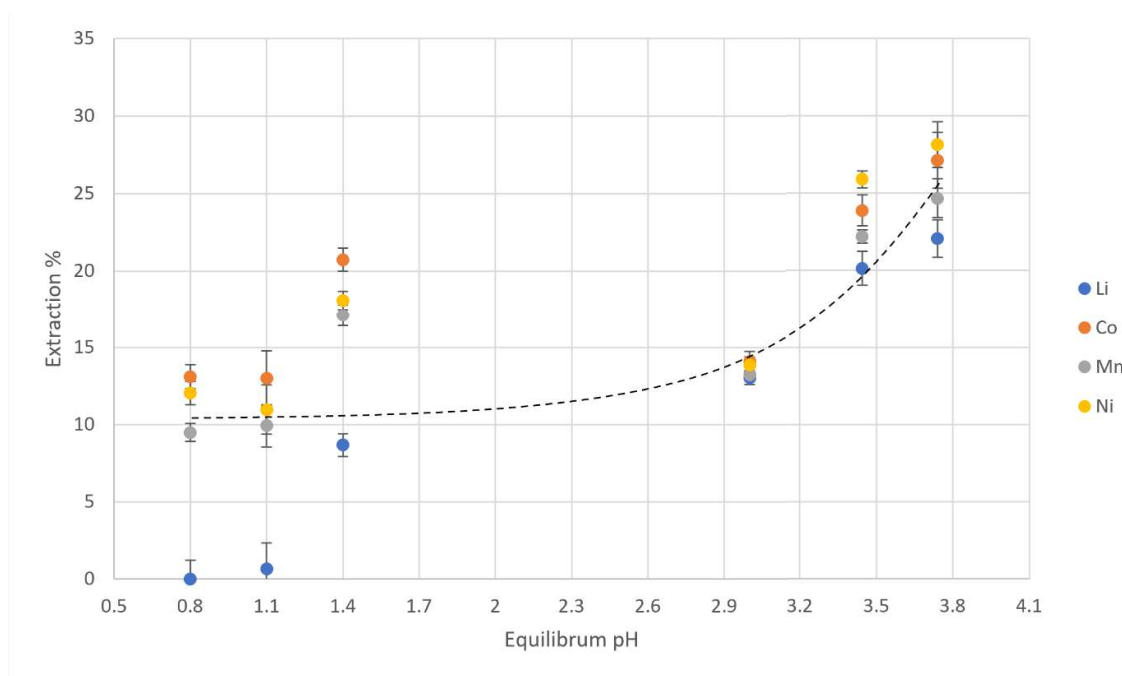
Figure 9: Extraction of major metals using Acorga M5640 30 v% at different pH. Extraction: O:A 1:1, 15 min shaking 1000 rpm, 5 min centrifuge 5000 rpm. Error bars for equilibrium pH 0.8, 1.1, 1.4, 3.0 made by triplicates, 3.4 and 3.7 by duplicates.

When comparing the high co-extraction at low pH in this study with the negligible co-extraction results in the study of Nayl *et al.* [13], there is something that does decrease the selectivity of the extractants. In the study of Nayl *et al.* [13] kerosene was used as diluent and H_2SO_4 was used in the leaching process. It could be that the diluent Isopar L used for the extractants or that the acid HCl that is used during the leaching process decrease the selectivity for copper.

The results indicated that at these tested conditions, the co-extraction of major metals is very high and the removal of copper through solvent extraction is too low. Thus, it is not a reasonable way to remove copper from the feed solution.

4.1.2 Secondary extraction

The results of extraction on the pH of 0.8, 1.1 and 1.4 can be seen in Figure 6, 7, and 8. A second extraction was performed on these samples and the extraction was most likely constrained by the pH as there was a very low extraction of every metal. The highest copper extraction was achieved in the second extraction stage using a mixture of Cyanex 272 and Acorga M5640 (0.15 M and 0.06 M, respectively) at a feed pH of 1.4. The copper extraction was at 13% and most other metals were not extracted at all, except for magnesium (3 %).

Under the tested conditions, it was not possible to achieve a high selective extraction of copper by solvent extraction without significant co-extraction of other metals. Therefore, further tests focused on the solvent extraction of copper were not performed. Then, the focus shifted towards the extraction of manganese followed by the removal of the impurities by scrubbing.

4.2 Solvent extraction of manganese

These tests were performed in order to find suitable conditions to achieve high extraction of manganese and low co-extraction of other metals using solvent extraction. Then, the removal of co-extracted metals using scrubbing solutions to clean the loaded organic phase was tested. Finally, a stripping solution was used to force the metals in the loaded organic to the aqueous phase.

First the optimal pH for manganese extraction was investigated and determined. Then the most optimal O:A ratio was evaluated. Extraction using the determined pH and O:A ratio was performed, followed by the test of different scrubbing solutions, and final stripping stage.

4.2.1 The effect of pH on the solvent extraction of Mn

The extraction of major metals and impurities using D2EHPA (0.5 M) at different pH can be seen in Figure 10 and Figure 11. The figures were constructed using data from Table 9 (Appendix), which show the extraction and pH tested as well as standard deviation from triplicates. For all metals, the extraction is increasing with pH. The aim was to extract as much manganese from the feed solution and as little of other metals (co-extraction) as possible. As seen in Figure 10 and Figure 11, there is quite high extraction of manganese and low co-extraction of other major metals in the range between pH 2.3-2.5. At this range, the extraction of manganese is about 75%, cobalt at 14% and other major metals at about 8%. Therefore, the equilibrium pH of 2.3 and 2.5 were chosen to be used to produce the loaded organic for the scrubbing tests.
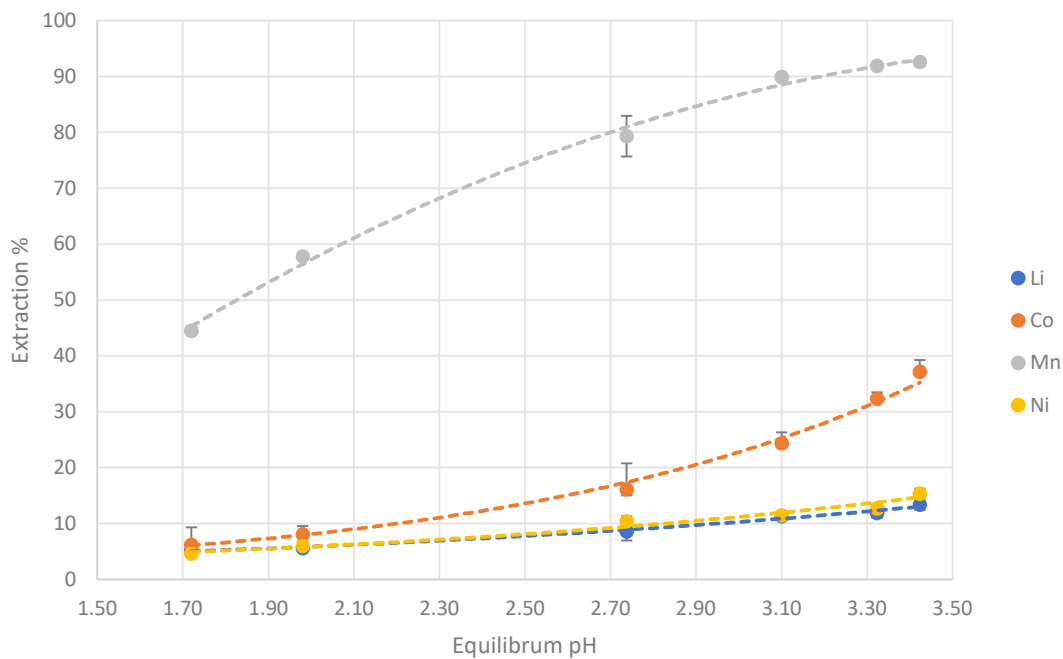
Figure 10: Extraction of major metals at different pH using D2EHPA 0.5 M. Conditions: O:A ratio 1:1, 15 min extraction at 1000 rpm. Data from Table 9 in (Appendix).
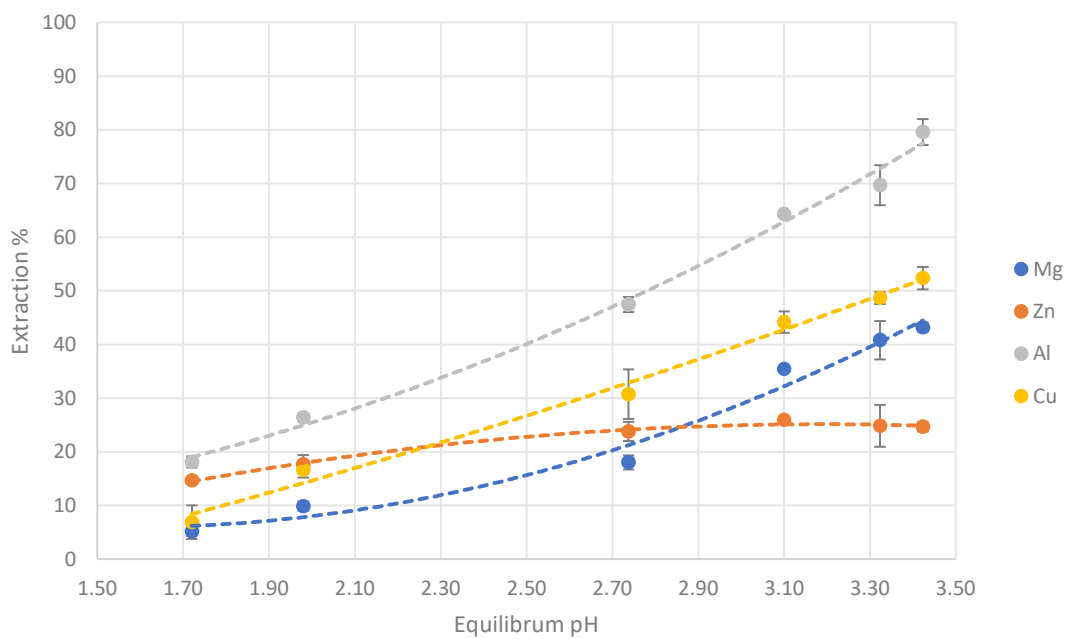
Figure 11: Extraction of impurities at different pH using D2EHPA 0.5M. Conditions: O:A ratio 1:1, 15 min extraction at 1000 rpm. Data from Table 9 in (Appendix).

4.2.2 The effect of O:A ratio

Tests were performed to study the effect of O:A ratio on the number of extraction stages needed to have full extraction of manganese from the aqueous phase. As seen in the McCabe-Thiele diagram in Figure 12, the extraction using O:A of 1:1 requires at least two extraction stages. The difference in concentrations of major metals and impurities caused by the change in O:A ratios can be seen in Tables 10 and Table 11 in the Appendix.
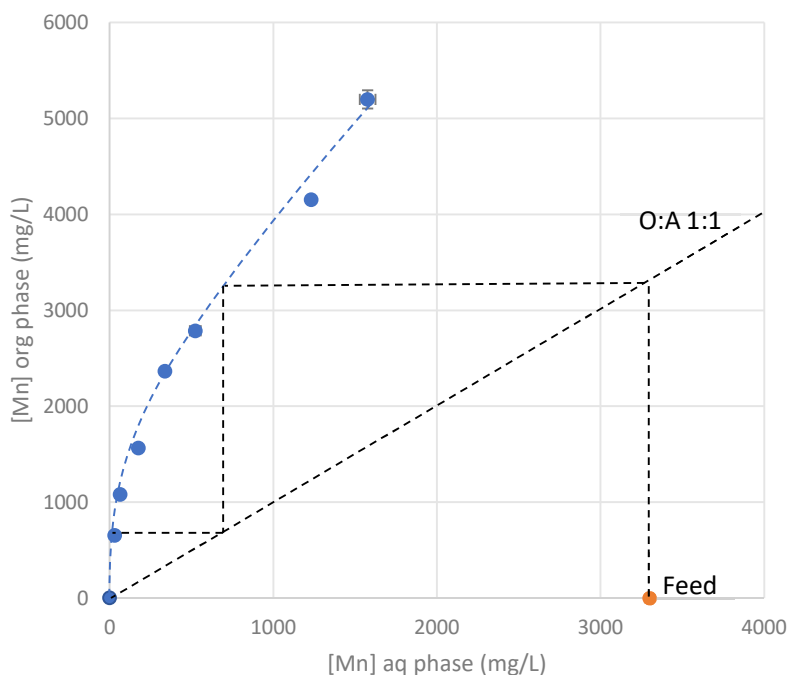
Figure 12: McCabe-Thiele diagram for the extraction stage of manganese using different O:A ratios with D2EHPA 0.5 M. Conditions: Concentration of Manganese in the feed solution:3300 mg/L; contact time 15 min, pH 2.5, O:A ratios tested, 5, 3, 2, 1.25, 1, 0.5, 0.33. Error bars made by triplicates. Data from Table 10.

Li *et al.* [12] and Vieceli *et al.* [11], also investigated the solvent extraction of manganese from similar solution. In both studies, the co-extraction of cobalt increase with the O:A ratio and the same can be seen in Figure 13. Because of the increase in co-extraction of cobalt with O:A ratio, a ratio of 1:1 was chosen as the optimal ratio.
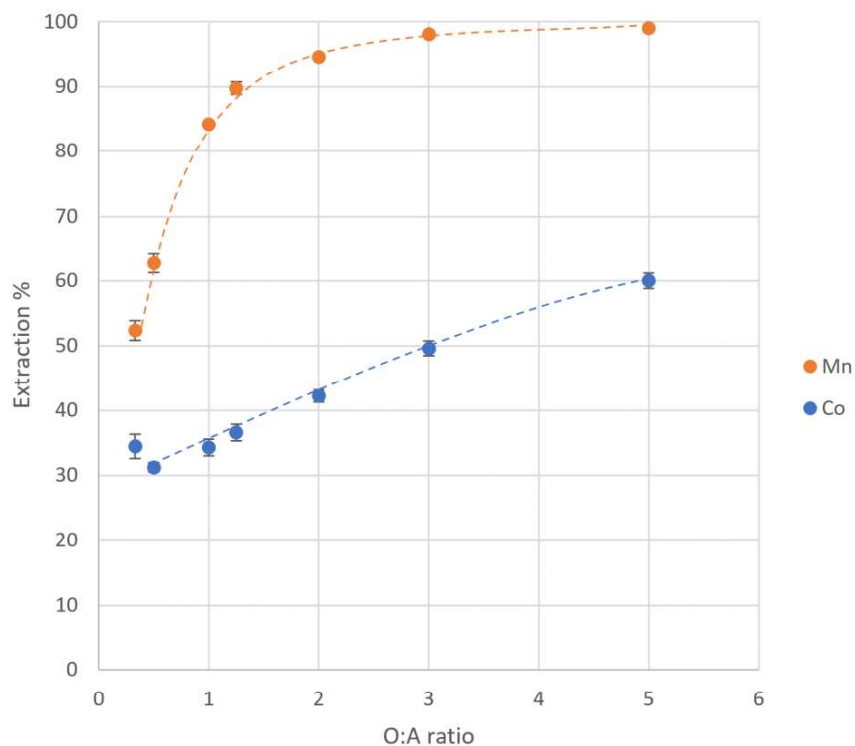
Figure 13: Extraction of manganese and cobalt at different O:A ratios with D2EHPA 0.5 M. Conditions: contact time 15 min, pH 2.5, O:A ratios tested, 5, 3, 2, 1.25, 1, 0.5, 0.33. Error bars made by triplicates.

4.2.3 Scrubbing and removal of impurities

The following Tables 4, 6 and 7 include the percentage of the feed solution and the distribution of the metals to the aqueous and organic phases through the extraction, scrubbing and stripping steps. The subsequent tests had some identical conditions such as contact time, shaking speed (rpm), O:A ratio and stripping solution. The two differences that were tested are the concentration of manganese in the scrubbing solution, as well as the source of manganese in the scrubbing solution.

The results for scrubbing in Tables 4 (4 g/L Mn) and 6 (6 g/L Mn), were obtained using $MnSO_4 \cdot H_2O$ as a source of manganese. Table 7 shows the results using 4 g/L manganese made using $MnCl_2 \cdot 4H_2O$. The raffinate in Tables 4 and 6 had an equilibrium pH of 2.3 and the raffinate in Table 7 had an equilibrium pH of 2.5 due to the added NaOH during extraction. Percentages were calculated for each step and stage based on the initial concentration of the feed solution and on the concentration of the raffinates, which were monitored throughout the process.

It should be noted that the feed solution, and in consequence the loaded organic used for the scrubbing using $MnCl_2$, has a higher concentration of metals than the tests performed using $MnSO_4$, which is a factor why there is a higher concentration of metals in the scrubbed organic in the $MnCl_2$ test. The concentrations of the tests can be seen in Tables 12, 13, and 14 in the Appendix. This variation in the concentration could be related to random errors in experimental measures, which cannot be predicted. For this reason, the concentration of the feed solution was followed throughout the different tests.

The stripping concentration results can be seen in Table 12 (Appendix) when 4 g/L manganese was used and in Table 13 when 6 g/L manganese was used. The standard deviations of these results can be seen in Tables 15 and 16 in the Appendix. Using scrubbed organic from the 4 g/L scrubbing solution, the concentration of manganese in the stripping product is 21000 mg/L and the standard deviation is 560. On the other hand, when using the scrubbed organic obtained using 6 g/L manganese, the concentration of manganese in the stripping product is 17500 mg/L and the standard deviation is ± 2600. With a higher concentration of manganese in the scrubbing solution using 6 g/L manganese compared to 4 g/L manganese, a higher concentration of manganese in the stripping product would be expected, however this is not the case. The high standard deviation could explain why the stripping product using 6 g/L manganese (17500 mg/L, Table 13) is lower than using 4 g/L manganese (21000 mg/L, Table 12) in the stripping product.

Table 4: Distribution of metals through the processes of extraction, scrubbing (using 4g/L manganese solution made from $MnSO_4 \cdot H_2O$) and stripping. Conditions: Extraction, O:A 1:1 using D2EHPA 0.5 M, 15 min contact time, 1000 rpm. Scrubbing, O:A 10:1, 15 min contact time. Stripping O:A 10:1, 25 min contact time with 0.5 M H_2SO_4.

Stage	% of the initial solution (feed)							
	Mg	Cu	Zn	Al	Mn	Ni	Li	Co
Feed	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Raffinate	86.0	84.1	84.3	8.7	23.0	94.0	89.3	89.2
Loaded organic	14.0	15.9	15.7	91.3	77.0	6.0	10.7	10.8
Scrub raffinate (1)	4.4	3.3	0.6	0.2	2.0	0.3	1.0	1.6
Scrub raffinate (2)	4.1	4.2	0.4	0.3	6.4	0.1	0.4	0.9
Scrubbed organic	5.5	8.4	14.7	90.7	92.7	5.5	9.3	8.4
Stripping product	2.6	8.2	4.1	2.2	62.3	0.1	0.2	0.4
Stripped organic	2.9	0.2	10.6	88.6	30.4	5.4	9.1	8.0

The test using a 4 g/L manganese scrubbing solution yielded a product with composition of 97.5% manganese, 1.9% cobalt, 0.3% aluminium, 0.2% lithium and 0.1% nickel as can be seen

in Table 5. Copper and magnesium were below 0.1%, and zinc about 0.1%. These compositions were calculated using the concentrations of the stripping product which are present in Tables 13 and 14 in the Appendix.

Table 5: Composition of the metals in the final stripping product in percentage based on grams. Calculated from the stripping product concentrations in Tables 12 and 13 in the appendix.

Scrubbing test	Composition of stripping product %							
	Mg	Cu	Zn	Al	Mn	Ni	Li	Co
4 g/L Mn	<0.1	<0.1	<0.1	0.3	97.5	0.1	0.2	1.9
6 g/L Mn	<0.1	<0.1	0.1	0.2	98.0	0.1	0.1	1.4

The results in Tables 4 and 6 show that after scrubbing using $MnSO_4$ there is between 2-12% (compared to the feed solution) manganese staying in the scrub raffinate. When using 4 g/L Mn from $MnCl_2$ as the scrubbing solution (Table 7) only less than 0.2% (compared to the feed solution) manganese stayed in the scrub raffinate. This shows that the vast majority of the manganese in the scrub solution is removed to the organic phase when using $MnCl_2$. Ideally the manganese would transfer from the scrubbed solution to the organic phase and the co-extracted metals be scrubbed away to the raffinate phase. However, as seen in Tables 4, 6 and 7, using $MnSO_4$ has the advantage of less co-extracted metals in the product and disadvantages of much more manganese in the scrub raffinate. For the test using $MnCl_2$ the opposite is true where the disadvantage is more co-extracted metals in the product and advantage of almost no manganese present in the scrub raffinate. As co-extraction is much higher using $MnCl_2$ 4 g/L manganese, higher concentration of manganese could be tested to see if co-extraction decreases.

It is important highlight that about 91% of the aluminium was extracted and less than one precent was scrubbed away in both of the scrubbing stages (Table 4 and Table 6). In the stripping step only 1.4% out of the 90% that were in the scrubbed organic ended up in the stripping product. Similarly, only a very small fraction of the other major metals such as nickel, lithium and cobalt were removed from the scrubbed organic to the stripping product.

Table 6: Distribution of metals through the processes of extraction, scrubbing (using 6g/L manganese solution made from $MnSO_4 \cdot H_2O$) and stripping. Conditions: Extraction O:A 1:1 using D2EHPA 0.5 M, 15 min contact time, 1000 rpm. Scrubbing, O:A 10:1, 15 min contact time. Stripping O:A 10:1, 25 min contact time with 0.5 M H_2SO_4.

Stage	% of the initial solution (feed)							
	Mg	Cu	Zn	Al	Mn	Ni	Li	Co
Feed	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Raffinate	86.0	84.1	84.3	8.7	23.0	94.0	89.3	89.2
Loaded organic	14.0	15.9	15.7	91.3	77.0	6.0	10.7	10.8
Scrub raffinate (1)	5.3	4.8	0.6	0.3	6.9	0.3	1.0	1.6
Scrub raffinate (2)	4.3	4.8	0.5	0.4	11.7	0.2	0.4	0.9
Scrubbed organic	4.5	6.3	14.7	90.6	94.6	5.5	9.3	8.2
Stripping product	1.6	6.3	5.3	1.4	57.7	<0.1	0.1	0.3
Stripped organic	2.8	<0.1	9.4	89.2	36.9	5.5	9.2	8.0

The test using a 6 g/L manganese scrubbing solution yielded a product with composition of 98.0% manganese, 1.4% cobalt, 0.2% aluminium, 0.1% lithium and 0.1% nickel, as can be seen in Table 5. The rest of the metals copper, magnesium and zinc were below 0.1%.

Using a scrubbing solution of 6 g/L of manganese yielded a slightly purer product of manganese (98.0% Mn), when compared to using a scrubbing solution of 4 g/L of manganese (97.5% Mn). Additionally, a slight decrease of cobalt (1.4% compared to 1.9%) was observed in the products, as can be seen in Table 5.

It is important to mention that other alternative scrubbing solutions could be tested. Chen *et al.* [15] investigated the solvent extraction of manganese from a leachate from LiBs using D2EHPA and the use of diluted oxalic acid was tested to remove the cobalt loaded by scrubbing. Almost 100% of efficiency was achieved, which was attributed to the formation of more stable $CoC_2O_4 \cdot 2H_2O$ precipitate. Joo *et al.* [16] also investigate the solvent extraction of manganese from the leach solution of spent batteries but using a PC88A/Versatic 10 acid system. In this case, an EDTA solution was used as the scrubbing solution. The results demonstrated that impurities such as cobalt, nickel, and lithium were removed completely from the loaded organic, while the loss of manganese was less than 0.4%. However, although alternative scrubbing solutions could increase the removal of unwanted co-extracted metals from the loaded organic, they can limit the possibility of connecting different streams in the solvent extraction circuit.

In Table 7 $MnCl_2$ was used as the source of manganese for the scrubbing solution, and the reason for the change was because the leaching process used HCl. Thus, using a scrubbing

solution also based on chlorides would allow connecting the streams in the solvent extraction circuit. Therefore, the scrubbing solution was changed to see if it would provide better results in lowering the concentration of the unwanted co-extracted metals in the loaded organic. In this case, no stripping test was performed.

As seen in Table 7 (using $MnCl_2$) there is almost no manganese in the scrubbing raffinate, meaning that almost all of the manganese in the scrub solution was transferred to the organic phase. Thus, the scrub raffinate has almost only co-extracted metals. It could be investigated if a portion of the stripping product could be diluted (to e.g. 4 g/L) to be used as the scrub solution in the process.

Table 7: Distribution of metals through the processes of extraction, scrubbing (using 4g/L manganese solution made from $MnCl_2 \cdot 4H_2O$) and stripping. Conditions: Extraction, O:A 1:1 using D2EHPA 0.5 M, 15 min contact time, 1000 rpm. Scrubbing, O:A 10:1, 15 min contact time. Stripping O:A 10:1, 25 min contact time with 0.5 M H_2SO_4.

Stage	% of the initial solution (feed)							
	Mg	Cu	Zn	Al	Mn	Ni	Li	Co
Feed	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Raffinate	81.3	74.2	81.6	46.0	18.1	87.9	87.5	85.1
Loaded organic	18.7	25.8	18.4	54.0	81.9	12.1	12.5	14.9
Scrub raffinate (1)	3.4	1.6	0.4	0.1	0.2	0.4	0.9	1.6
Scrub raffinate (2)	4.2	3.3	0.2	0.1	<0.1	0.2	0.4	0.1
Scrubbed organic	11.0	20.9	17.8	53.7	103.1	11.5	11.2	13.2

The second scrubbing stage was less effective than the first on all three experiments, especially using $MnCl_2$ as the scrubbed away cobalt in the first scrubbing was 1.6% (of initial feed solution), which was much higher than in the second 0.1%. In the other two scrubbing tests (using $MnSO_4$), both also had a scrubbing of cobalt of 1.6 % in the first stage and 0.9 % in the second scrubbing. These results suggest that a second scrubbing is more effective using $MnSO_4$ than when using $MnCl_2$, under the tested conditions.

Thus, further tests should be performed to optimize the removal of impurities from the loaded organic. Different conditions can affect this operation and some of the factors that could be additionally investigated include: different O:A ratios, contact times and different concentrations of manganese in the scrubbing solution. Furthermore, directly testing the stripping of the loaded organic could be explored as another alternative.

5 Conclusion

Removal of impurities through solvent extraction using Acorga M5640 (10 v%, 20 v%, 30 v%), LIX 84-I (20 v%) as well as the two mixtures of Acorga M5640 and Cyanex 272 (0.15 M and 0.06 M, 0.30 and 0.12 M, respectively) did not show any results where only copper without co-extraction of majors was achieved at pH of 0.8, 1.1, 1.4 and 4.1. The best results were achieved with Acorga (20 v%) at feed solution pH at 0.8, which extracted copper at around 37%, with a co-extraction of manganese at 10%, nickel 11%, cobalt 13%, and lithium at around 0-1%. Under these conditions there is a high co-extraction of major metals, considering that the concentration of major metals in the feed solution is much higher than the concentration of copper. As the goal of using these extractants is to extract mostly copper and possibly other impurities without the co-extraction of major metals, this method was not a reasonable way to remove copper, under the tested conditions. The low selectivity of the extractants could be due to the diluent Isopar L used for the extractants or the HCl used for the leaching process.

Secondary extractions were performed on the pH of 0.8, 1.1 and 1.4 with the six different extractants mentioned above. The highest extraction was achieved using Acorga M5640 and Cyanex 272 (0.15 M and 0.06 M respectively), at a pH of 1.4. The most optimal result showed extraction of copper at 13% and magnesium at 3% and no other co-extraction, most likely due to extraction being constrained by the pH.

Solvent extraction of manganese was performed using D2EHPA (0.5 M) at pH range between of 1.7 and 3.4. The results showed an optimal extraction of manganese at pH range between 2.3 and 2.5, extracting between 70-75% manganese and co-extracting cobalt at around 12-13%. Therefore, pH of 2.3 and 2.5 were chosen for the target equilibrium pH for the subsequent scrubbing experiments.

The effect of O:A ratio on manganese extraction was studied using D2EHPA (0.5 M) and O:A ratios ranging from 0.33 to 5. The McCabe-Thiele diagram showed that two extraction stages are theoretically necessary for an O:A ratio of 1:1 at pH of 2.5.

The most optimal scrubbing of co-extracted metals was achieved with $MnSO_4$, 6 g/L of manganese and was slightly better than 4 g/L manganese scrub solution. Both scrubbing tests of $MnSO_4$ performed better with more scrubbed co-extracted metals than when using 4g/L of manganese scrubbing solution using $MnCl_2$. This was even more noticeable in the second

scrubbing stage, where the $MnCl_2$ scrubbing was not very effective as only a small amount of cobalt and other co-extracted metals were removed to the scrub raffinate.

The concentration of manganese in the stripping product was higher using a scrubbing solution of 4 g/L than using 6 g/L $MnSO_4$. However, the amount of manganese could be larger due to the high standard deviation of the two samples used for measuring the 6 g/L manganese stripping test.

Comparing both approaches tested to remove the impurity copper – by solvent extraction and removing the impurities by scrubbing – the results indicate that using scrubbing is a reasonable way to remove impurities, under the tested conditions. When using solvent extraction at the tested conditions, major metals have high co-extraction. In comparison, scrubbing does decrease the concentration of impurities and other co-extracted metals yielding a high purity product of manganese of 98% with 1.4% cobalt, when using a scrubbing solution containing manganese prepared with 6 g/L $MnSO_4$, in two scrubbing stages.

6 References

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7 Appendix

Appendix A: Equipment
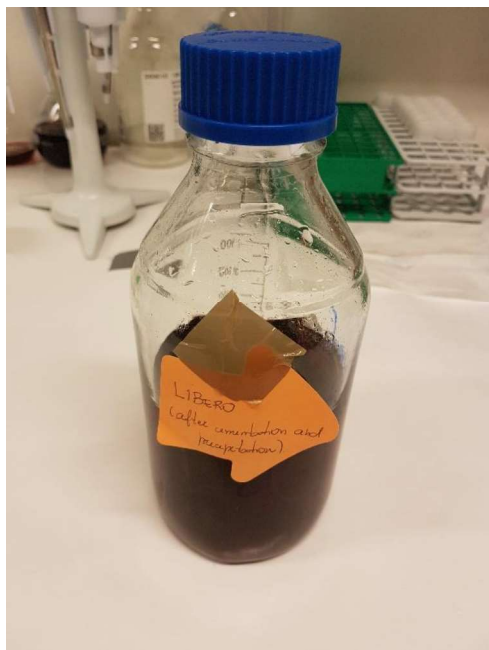
Figure 14: Leached battery solution (Feed solution)

Figure 15: Autopipettes

Figure 16: From left to right. First bottle used for ICP analysis of aqueous phase, 15ml. Second bottle used for pH analysis of aqueous phase, 15ml. Third glass bottle used for extraction where the organic and aqueous phase mixed in the shaker, 3.5 ml. Fourth bottle were used for keeping aqueous phase from small scale scrubbing.
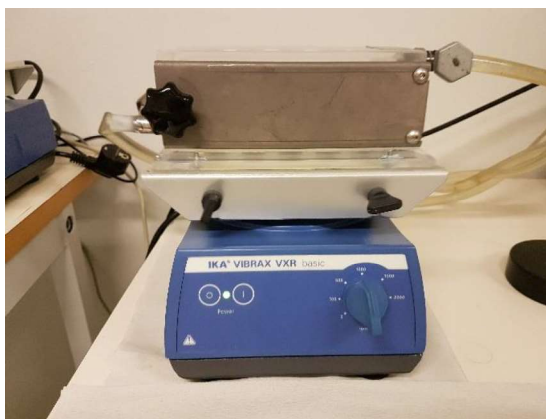
Figure 17: Shaker machine (IKA-Vibrax, 1000 vibrations/min)

Figure 18: Mixer used instead of the shaker when making bigger volumes of organic for scrubbing.

Figure 19: ICP-OES

Figure 20: Extraction with added NaOH where precipitation occurred ruining the sample.

Figure 21: Samples being analysed by ICP-OES.

Figure 22: Picture taken after centrifuging. Aqueous feed at the bottom and the extractant D2EHPA at the top. The transparent D2EHPA turns blue during contact time.
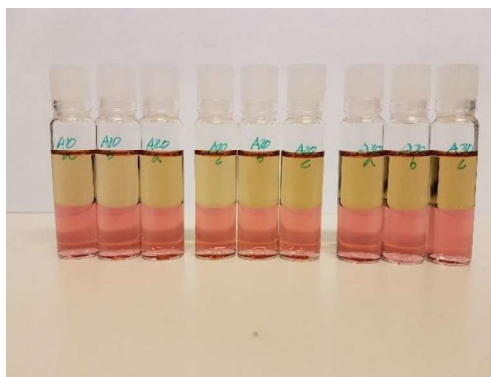
Figure 23: Picture taken after centrifuging. Aqueous feed at the bottom and the extractant Acorga M5640 at the top. From left triplicates of 10v%, 20v% and 30v% Acorga M5640.

Appendix B: Tables

Extraction at feed pH

Table 8: Average Extraction. CA 1: 0.15 M Cyanex and 0.06 M Acorga M5640, CA2: 0.30 M Cyanex 272 and 0.12 M Acorga M5640. Conditions: O:A ratio 1:1, 15 min extraction at 1000 rpm. Average data from triplets.

Extraction % Standard deviation (±)								
Extractant	Mg	Cu	Zn	Al	Mn	Ni	Li	Co
Acorga v10%	5.8	35.1	5.1	4.0	12.0	12.6	11.7	12.3
STD	0.3	1.9	3.3	2.9	0.7	0.6	0.5	0.6
Acorga v20%	4.8	35.6	5.7	3.9	12.8	13.2	12.3	13.4
STD	1.0	1.4	0.7	2.7	0.1	0.2	0.0	0.2
Acorga v30%	8.3	37.2	9.4	8.4	13.2	13.9	13.0	14.1
STD	1.6	1.2	2.1	1.7	0.3	0.5	0.4	0.7
Cyanex & Acorga 1	13.3	38.0	17.7	16.9	12.5	12.8	11.5	12.9
STD	0.1	0.6	1.2	0.3	0.5	0.4	0.4	0.3
Cyanex & Acorga 2	11.5	38.9	17.7	15.3	13.4	13.3	12.3	13.7
STD	2.1	1.0	2.4	2.1	0.4	0.7	0.3	0.5
LIX 84-I v20%	10.5	39.8	10.7	10.6	12.6	13.2	11.8	13.0
STD	1.2	2.9	1.4	0.9	0.5	0.7	0.4	0.4

Extraction at different pH

Table 9: Extraction using D2EHPA 0.5 M at different pH. Conditions: O:A ratio 1:1, 15 min extraction at 1000 rpm. Average data from triplets.

| pH	Extraction (%) and Standard deviation (±)							
	Mg	Cu	Zn	Al	Mn	Ni	Li	Co
1.72	5.1	6.9	14.7	18.1	44.5	4.6	5.2	6.2
STD	0.8	3.1	0.4	1.0	0.7	0.4	0.4	0.3
1.98	9.9	16.7	17.7	26.4	57.8	6.0	5.6	8.1
STD	0.8	1.5	1.7	0.8	0.5	0.8	0.2	0.5
2.74	18.0	30.7	23.8	47.4	79.3	10.4	8.5	16.1
STD	1.3	4.6	1.8	1.4	3.6	0.9	1.6	1.1
3.10	35.4	44.2	25.9	64.3	89.9	11.5	11.3	24.4
STD	0.6	2.0	0.1	0.6	0.2	0.1	0.0	0.7
3.32	40.8	48.7	24.8	69.7	91.8	12.7	11.9	32.3
STD	3.6	1.1	3.9	3.7	0.1	0.3	0.9	0.2
3.42	43.2	52.4	24.6	79.6	92.6	15.4	13.4	37.2
STD	0.9	2.1	0.9	2.4	0.1	0.9	0.9	0.5

O:A ratios tables

Table 10: Concentration of major metals after extraction using D2EHPA 0.5 M at different O:A ratios. Conditions: 15 min extraction, 5 min centrifuge. Average data from triplets.

	Concentration mg/L and Standard deviation (±)							
	Mn		Ni		Li		Co	
O:A	**aq**	**org**	**aq**	**org**	**aq**	**org**	**aq**	**org**
5	31	656	2594	448	1647	149	4378	1314
STD	4	1	69	14	50	10	128	26
3	64	1082	3022	604	1732	220	5518	1811
STD	4	1	57	19	47	16	123	41
2	177	1566	3121	856	1831	281	6330	2310
STD	10	5	33	16	30	15	102	51
1.25	339	2366	3298	1222	1884	406	6938	3195
STD	33	26	61	49	40	32	139	110
1	523	2786	3434	1399	2039	354	7189	3761
STD	8	8	77	77	38	38	139	139
0.5	1233	4153	3527	2611	2098	591	7535	6829
STD	47	95	29	58	18	36	78	156
0.33	1577	5197	3344	4465	2012	1143	7168	11346
STD	50	149	92	275	58	173	205	614

Table 11: Concentration of metals impurities after extraction using D2EHPA 0.5 M at different O:A ratios. Conditions: 15 min extraction, 5 min centrifuge. Average data from triplets.

	Concentration mg/L and Standard deviation (±)							
	Mg		Cu		Zn		Al	
O:A	**aq**	**org**	**aq**	**org**	**aq**	**org**	**aq**	**org**
5	10.9	4.9	2.1	0.7	14.2	2.3	25.1	50.4
STD	1.4	0.3	0.1	0.0	0.5	0.1	6.1	1.2
3	15.2	6.7	2.8	1.0	16.1	3.1	45.7	77.1
STD	1.0	0.3	0.1	0.0	0.5	0.2	6.1	2.0
2	22.0	6.6	3.3	1.2	16.3	4.6	97.3	89.9
STD	0.3	0.2	0.1	0.0	0.3	0.1	13.5	6.7
1.25	24.7	8.4	3.7	1.6	16.7	7.0	112.6	131.0
STD	0.4	0.3	0.1	0.1	0.5	0.4	5.9	4.7
1	25.4	9.8	3.9	1.8	16.1	9.4	117.2	159.9
STD	2.5	2.5	0.4	0.4	1.5	1.5	5.2	5.2
0.5	30.9	8.7	4.8	1.7	17.8	15.4	175.8	202.4
STD	0.1	0.3	0.1	0.2	0.2	0.3	13.3	26.7
0.33	29.4	17.6	4.7	2.7	16.7	26.1	155.5	364.6
STD	0.4	1.2	0.1	0.2	0.2	0.5	25.1	75.4

Scrubbing

Table 12: Metal concentrations after extraction, scrubbing (using 4g/L manganese solution made from $MnSO_4 \cdot H_2O$) and stripping. Conditions: Extraction, O:A 1:1 using D2EHPA 0.5 M, 15 min contact time, 1000 rpm. Scrubbing, O:A 10:1, 15 min contact time. Stripping O:A 10:1, 25 min contact time with 0.5 M H_2SO_4. Average data from duplicates

Concentration mg/L								
Sample	Mg	Cu	Zn	Al	Mn	Ni	Li	Co
Feed	31.8	6.3	20.4	269.3	3320.6	3966.3	2348.9	9438.5
Raffinate	27.3	5.3	17.2	23.5	762.8	3729.9	2097.0	8419.9
Loaded organic	4.5	1.1	3.2	245.7	2557.8	236.4	252.0	1018.5
Scrub raffinate (1)	14.1	2.1	1.2	6.6	657.5	124.2	237.0	1466.4
Scrub raffinate (2)	13.2	2.7	0.9	7.8	2136.6	54.0	93.0	820.2
Scrubbed organic	1.7	0.6	3.0	244.3	3078.4	218.6	219.0	789.9
Stripping product	8.4	5.6	8.6	59.8	21221.5	26.3	42.7	403.1

Table 13: Metal concentrations after extraction, scrubbing (using 6g/L manganese solution made from $MnSO_4 \cdot H_2O$) and stripping. Conditions: Extraction O:A 1:1 using D2EHPA 0.5 M, 15 min contact time, 1000 rpm. Scrubbing, O:A 10:1, 15 min contact time. Stripping O:A 10:1, 25 min contact time with 0.5 M H_2SO_4. Average data from duplicates.

Concentration mg/L								
Sample	Mg	Cu	Zn	Al	Mn	Ni	Li	Co
Feed	31.8	6.3	20.4	269.3	3320.6	3966.3	2348.9	9438.5
Raffinate	27.3	5.3	17.2	23.5	762.8	3729.9	2097.0	8419.9
Loaded organic	4.5	1.0	3.2	245.7	2557.8	236.4	252.0	1018.5
Scrub raffinate (1)	16.9	3.0	1.1	7.7	2283.2	118.0	225.8	1531.8
Scrub raffinate (2)	13.5	3.0	0.9	10.6	3885.1	61.2	105.3	867.5
Scrubbed organic	1.4	<0.1	3.0	243.9	3140.9	218.4	218.9	778.6
Stripping product	5.3	4.1	11.1	37.4	17552.3	16.0	26.0	251.9

Table 14: Metal concentrations after extraction, scrubbing (using 4g/L manganese solution made from $MnCl_2 \cdot 4H_2O$) and stripping. Conditions: Extraction O:A 1:1 using D2EHPA 0.5 M, 15 min contact time, 1000 rpm. Scrubbing, O:A 10:1, 15 min contact time. Stripping O:A 10:1, 25 min contact time with 0.5 M H_2SO_4. Average data from triplets.

Concentration mg/L								
Sample	Mg	Cu	Zn	Al	Mn	Ni	Li	Co
Feed	38.5	5.1	29.1	351.1	3741.9	4494.9	2586.8	10456.4
Raffinate	28.4	3.6	20.0	130.7	675.8	3951.8	2264.1	8898.8
Loaded organic	6.5	1.3	4.5	153.2	3066.1	543.1	322.7	1557.6
Scrub raffinate (1)	12.0	0.8	0.9	3.0	58.5	171.6	222.7	1711.4
Scrub raffinate (2)	14.8	1.6	0.5	4.2	6.5	90.7	97.9	97.9
Scrubbed organic	3.8	1.0	4.4	152.5	3859.6	516.9	290.6	1376.7

Table 15: Complementary table showing the standard deviation of scrubbing and stripping for Scrubbing (using 4g/L manganese solution made from $MnSO_4 \cdot H_2O$) and stripping. Conditions: Extraction O:A 1:1 using D2EHPA 0.5 M, 15 min contact time 1000 rpm. Scrubbing, O:A 10:1, 15 min contact time. Stripping O:A 10:1, 25 min contact time with 0.5 H_2SO_4.

Standard deviation (±)								
Stage	Mg	Cu	Zn	Al	Mn	Ni	Li	Co
Scrub raffinate (1)	0.2	0.2	<0.1	0.4	62.4	8.5	10.9	60.6
Scrub raffinate (2)	0.7	<0.1	<0.1	0.2	12.2	0.4	1.2	16.9
Stripping product	0.9	0.3	2.3	1.1	560.3	2.1	0.7	33.2

Table 16: Complementary table showing the standard deviation of scrubbing and stripping for Table 13. Scrubbing (using 6g/L manganese solution made from $MnSO_4 \cdot H_2O$) and stripping. Conditions: Extraction O:A 1:1 using D2EHPA 0.5 M, 15 min contact time 1000 rpm. Scrubbing, O:A 10:1, 15 min contact time. Stripping O:A 10:1, 25 min contact time with 0.5 H_2SO_4.

Standard deviation (±)								
Stage	Mg	Cu	Zn	Al	Mn	Ni	Li	Co
Scrub raffinate (1)	0.8	0.1	<0.1	0.5	91.1	7.6	12.1	76.5
Scrub raffinate (2)	0.1	0.1	<0.1	1.2	39.4	2.0	4.7	20.5
Stripping product	0.2	<0.1	2.3	2.8	2616.0	0.3	1.4	2.8