

LAPPEENRANTA-LAHTI UNIVERSITY OF TECHNOLOGY

LUT School of Engineering Science

Degree Program of Chemical Engineering



Master's Thesis

2019

Bershak Andrey

**PURIFICATION OF NICKEL SULFATE SOLUTIONS VIA SOLVENT
EXTRACTION METHOD**

Examiners:

Professor Tuomo Sainio

PhD Sami Virolainen

ABSTRACT

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This Thesis focuses on extractive separation of metal impurities from solution typical for hydrometallurgical nickel plants, containing nickel and cobalt. The research combines various experiments of residue metal extraction and provides an initial proposal of a solvent extraction process. Several classes of organic extractants, which are mainly applied in metals extraction were described in order to investigate the suitable extractant for Al, Mg, Mn, Fe, Zn, Ca ions: phosphorus-based acids, represented by Cyanex 272[®] (bis(2,4,4-trimethylpentyl) phosphinic acid), D2EHPA (di(2-ethylhexyl) phosphoric acid) and PC-88A (2-ethylhexyl phosphonic acid); hydroxyoximes (LIX 622N and LIX 84-I) and organic acids (Versatic 10). The main process steps, performed by loading, scrubbing and stripping stages were considered. The other methods of nickel and cobalt purification at synthetic leaching liquor was considered. Alternative methods as oxidative precipitation and ion exchange were described comprising description of developed appropriate conditions, where ion exchange resin application was tested experimentally.

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INTRODUCTION

Nickel is one of the most widespread and demanded component, especially in stainless austenitic steels, which contain from 8 to 33 % of Ni. Application of the last one is explained by corrosion-resistant and heat-resistant properties of Ni-based alloys. Another important application of Ni belongs to production of batteries, catalysts and magnetic semiconductors.

A large number of nickel-contain minerals have been identified, however several are abundant enough to be count as industrially important. These ores were shared as sulphides, laterites and arsenides. The most common ores in industrial processing are sulfides and laterites. The main source of Ni belonged to sulfides until 2003, where the level of laterite increased to 42 % and was expected to grow to 51 % in 2014. Therefore, the dominance of sulfide rocks became challenged, even due to 70 % of Ni contain in laterites (Figure 1). The growth of Ni extraction from the ores undergoes the rise about 4 % of rate and has followed economic cycles (Dalvi, et al., 2004).

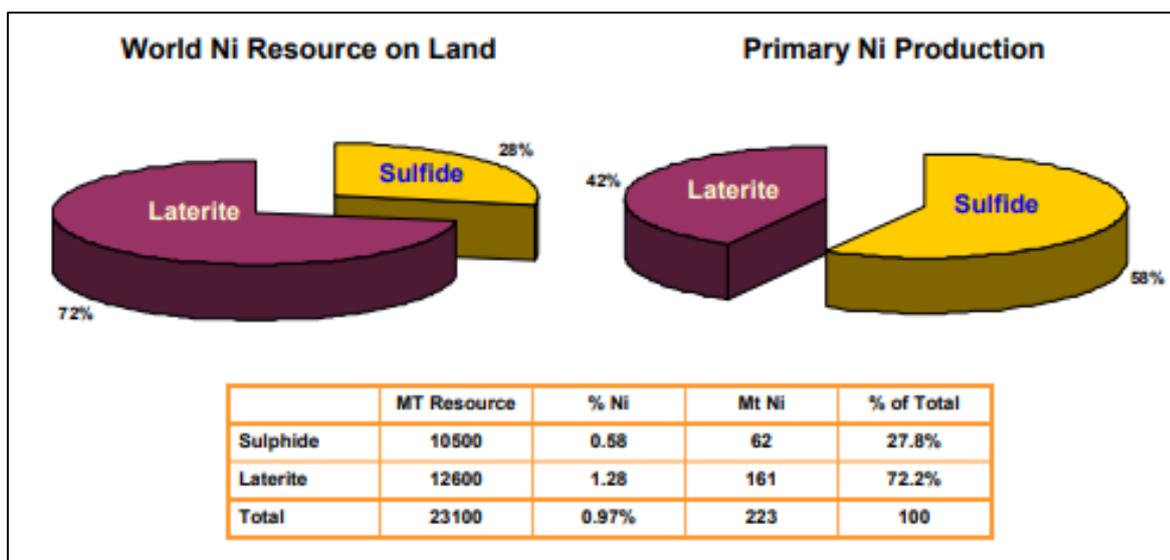


Figure 1. Distribution of Ni-contain rocks in the world and in production. Adapted from (Dalvi, et al., 2004)

Cobalt may substitute for transition metals in many minerals and chemical compounds and is commonly found in the place of iron and nickel as they share many similar chemical properties. The main cobalt mineral is heterogenite. It also occurs in pair with Ni in same ores and their presence was found in chrysocolla $[\text{CuOSiO}_2 \cdot 2\text{H}_2\text{O}]$, malachite $[\text{CuCO}_2 \cdot \text{Cu}(\text{OH})_2]$ and in gangue minerals such as siliceous dolomite $[\text{MgCO}_3 \cdot \text{CaCO}_3]$ and quartz (SiO_2). Extraction of cobalt is possible in the copper-cobalt oxide ores with 0.3 % of Co content (Cobalt Insitute, 2017).

As a result of leaching process of laterite and sulfide ores, production of clean Ni and Co becomes complicated, due to presence of significant volumes of certain impurities, such as iron, manganese, copper, zinc and magnesium. Appropriate solution is applied for separation of listed contaminants over Ni-Co and belongs mainly to preloading of organic extractants.

The widespread usage of energy batteries, used as the most convenient and ecological energy source, led to the increased of scrap production at the end of exploitation period. The question of utilization of hazardous waste from batteries involves serious ecological problems along with the fact that batteries was classified as dangerous waste (Zhang, et al., 1998). Consequently, the recycling of metal residues of cathode material (nickel, cobalt, lithium etc.) from spent battery corresponds to environmental demands and becomes significant economic measure of sustainability (Xu, et al., 2008).

Recovery of valuable metals from waste batteries typically consists of physical and chemical processing. Physical part provides separation of valuable powder fraction as zinc and manganese oxides, performing initial grinding of battery wastes, subsequent thermal processing of feedstock and the final rolling to produce dried material for separation of targeted powder (Appendix 1). Chemical processing of material occupies further treatment stage of produced powder, which is underwent leaching treatment by acids (Tanong, et al., 2014). Further recovery is accompanied by extraction procedure, consisting of loading, scrubbing and stripping procedures to cut off remained metal residues.

It is commonly applied to purify nickel sulphate solutions received from processing industry after nickel laterites leaching or battery leaching circuit. The presence of remained residue metals in nickel solution can cause harmful impact on electrodes as objectionable precipitate on the diaphragms during electrowinning step. According to the performed research by Guimaraes and Mansur (2014), selective removal of attending manganese and zinc from such liquors is quite effective under following conditions: Cyanex 272 = 20 % v/v, pH = 4, O/A = 1 and T = 50 °C, although extraction of magnesium and calcium may not be relevant for mentioned conditions. Aluminum and three-valent iron ions attending in solution does not complicate purification and can be easily removed in case of adaption of phosphorus based extractants. Improvement of extraction of magnesium and calcium may be obtained by D2EHPA application, which can be considered as the most effective liquid extractant to be implemented in purification process circuit. In addition, the application of phosphinic acids (Cyanex 272) is mostly aimed on cobalt and nickel separation, which does not correspond to project targets to remain cobalt in aqueous phase.

Experimental methodology consists of two sets of experiments as batch and pseudo counter-current processes. In turn, batch experiments included construction of pH isotherms and loading isotherms, based on D2EHPA liquid-liquid extraction of metals over solutions with two different compositions. Scrubbing and stripping isotherms were performed as part of the batch tests. Based on plotted isotherms, McCabe-Thiele method was implemented in order to determine the number of stages for counter-current experiments. As the outcome from provided experiments the influence of various operational parameters (as pH and O/A ratio) has to be investigated in order to improve impurities extraction efficiency and minimize nickel and cobalt losses.

1 Raw materials for Ni and Co

1.1 Content of sulfide ores

Sulfide ores includes Ni-contain mineral chiefly as mineral pentlandite $[(Ni,Fe)_9S_8]$ in combination with large amounts of pyrrhotite (Fe_7S_8) and chalcopyrite ($CuFeS_2$). Moreover, Ni-contain minerals may also include high varying level of Co, Fe, Cu and precious metals, such as Au and Ag. The chemical composition of nickel and its impurities placed in following range: Ni – 0.4-3.0 %; Cu – 0.2-3.0 %; Fe – 10-35 %; S – 5-25% and the rest, represented by oxides, as SiO_2 , Al_2O_3 , MgO and CaO.

The most known and volumetric deposits of sulfide ores are located in Sudbury, Ontario, Canada; in the Voisey's Bay deposit in northeastern Labrador, Canada; in the Thompson-Moak Lake area of Northern Manitoba, Canada; at Norilsk, Siberia, Russia; Kola Peninsula bordering Finland; in western Australia; and in South Africa.

1.2 Content of laterite ores

The placement of the following ore type corresponds the large deposits of several regions, such as Cuba, New Caledonia, Indonesia, the Philippines, and Central and South America. Formation of this ores type connected with specific climate processes that made the nickel to be leached from surface rock layers and precipitated at deeper layers. Figure 2 represents the PI-chart of distribution of laterite-nickel among world territories.

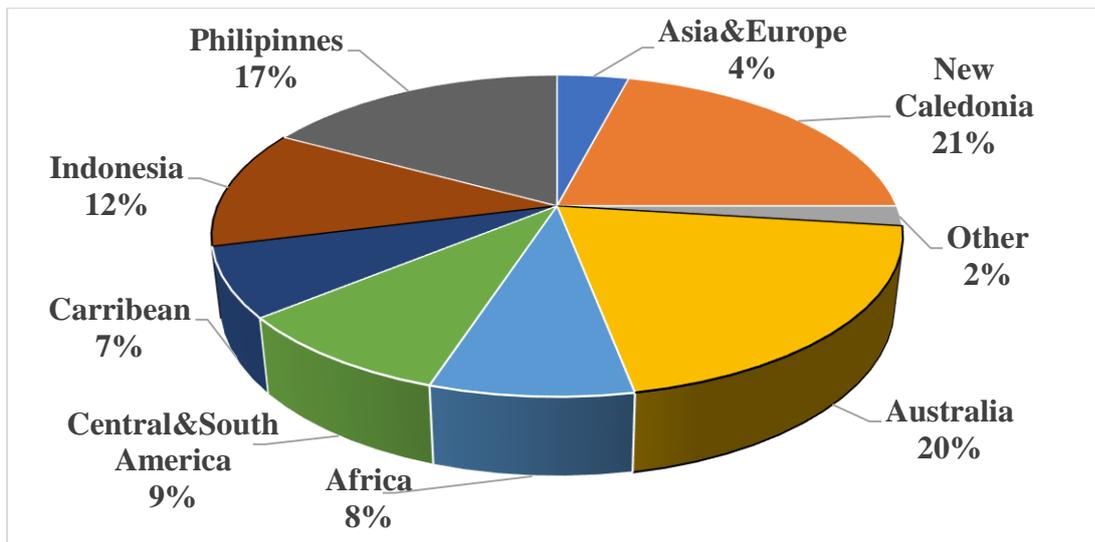


Figure 2. World nickel laterite resources. Adapted from (Dalvi, et al., 2004)

Described rock can be distinguished by two main Ni-content oxide ores: limonitic ore, which is mainly represented by mineral goethite $[(\text{Ni},\text{Fe})_2\text{O}_3 \cdot \text{H}_2\text{O}]$ with dispersed nickel and silicate ore, including the most common hydrated magnesium-iron-silicate goethite $[(\text{Ni},\text{Mg})_6\text{Si}_4\text{O}_{10}(\text{OH})_8]$. The typical content of oxide laterite ores varies and depends on the territory. Hence, the New Caledonian ores contains 2-3 % of Ni, 0.1 % of Co, 2 % Cr_2O_3 , and 10-25 % MgO, however Cuban ore contains chiefly limonitic type and has the structure as follows: 1.2-1.4 % Ni; 0.1-0.2 % Co; 3 % Cr_2O_3 ; and 35-50 % Fe.

Besides, laterite ores may be founded by other minerals, so called “ultramafic” rocks, which are comprised dunite (mainly monomineralic olivine), pyroxenite (orthopyroxene or clinopyroxene), serpentinite (serpentine $2\text{H}_4\text{Mg}_3\text{Si}_2\text{O}_9$), peridotite (olivine, pyroxene, and hornblende) and hornblendite (monomineralic hornblende). Figure 3 show the typical mineral placement according the deep of the layers in example of Western Australia and Indonesia with description of elements content.

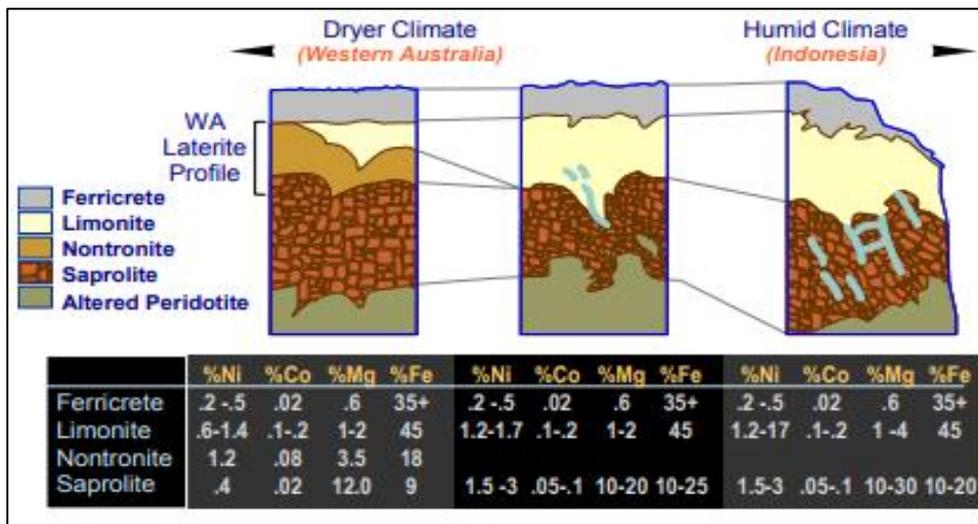


Figure 3. Laterite profiles. Adapted from (Dalvi, et al., 2004)

It is clear from the profile, that limonite and saprolite include the highest amount of desirable nickel and cobalt (0.6-1.4 % Ni and 0.1-0.2 % Co for dry climate and maximum content 17 % of Ni in wet conditions), which reports about the commercial benefits of Co-Ni extraction from special minerals (Dalvi, et al., 2004).

2 Purification of nickel and cobalt solution by solvent extraction

Conventionally, various methods of residue metals removal are still existing in aim to convert them as secondary resources and, mainly, to purify stock solution. These techniques include ion exchange purification, zeolite cation exchange and chromatography, however, solvent extraction method found the widespread application due to its flexibility properties, containing extraction, separation and concentration properties (Swain, et al., 2015).

Separation method, which is based on the diverse distribution component to be separated from two immiscible liquids concerns to solvent extraction and sometimes called liquid-liquid extraction. In simple terms, the procedure involves the extraction of specie (or any other impurities) from one solution to another liquid (Elvers, 2016).

2.1 Basic extraction principles

Detailed extraction mechanism explains, that the stock solution containing the desired compound becomes mixed with extractive substance, where the element of interest gets in contact with extractant to form the compound which is more soluble than in aqueous phase. As a result, the metal ion is transferred to organic solution (Rydberg, 2004). The raffinate is then rejected and underwent processing in order to recover remained metals in solution or going to the waste.

After extraction procedure, the loaded organic may be treated at next step by scrubbing process with suitable aqueous solution to scrub the metals and impurities co-extracted with target metals. The raffinate scrub is then recycled back to use in upstream circuits such as leaching stage.

After scrubbing stage, pregnant extractant passes to stripping stage where the metal is stripped by specially prepared aqueous solution represented as stripping agent and works as reverse to extraction reaction. The production outcome is represented by concentrated aqueous solution of the metal salt, which then transferred to end steps of metal production. Finally, processed solvent is recycled for repeated usage starting from extraction procedure (Ritcey, 2006). The diagram of described extraction steps is performed in Figure 4.

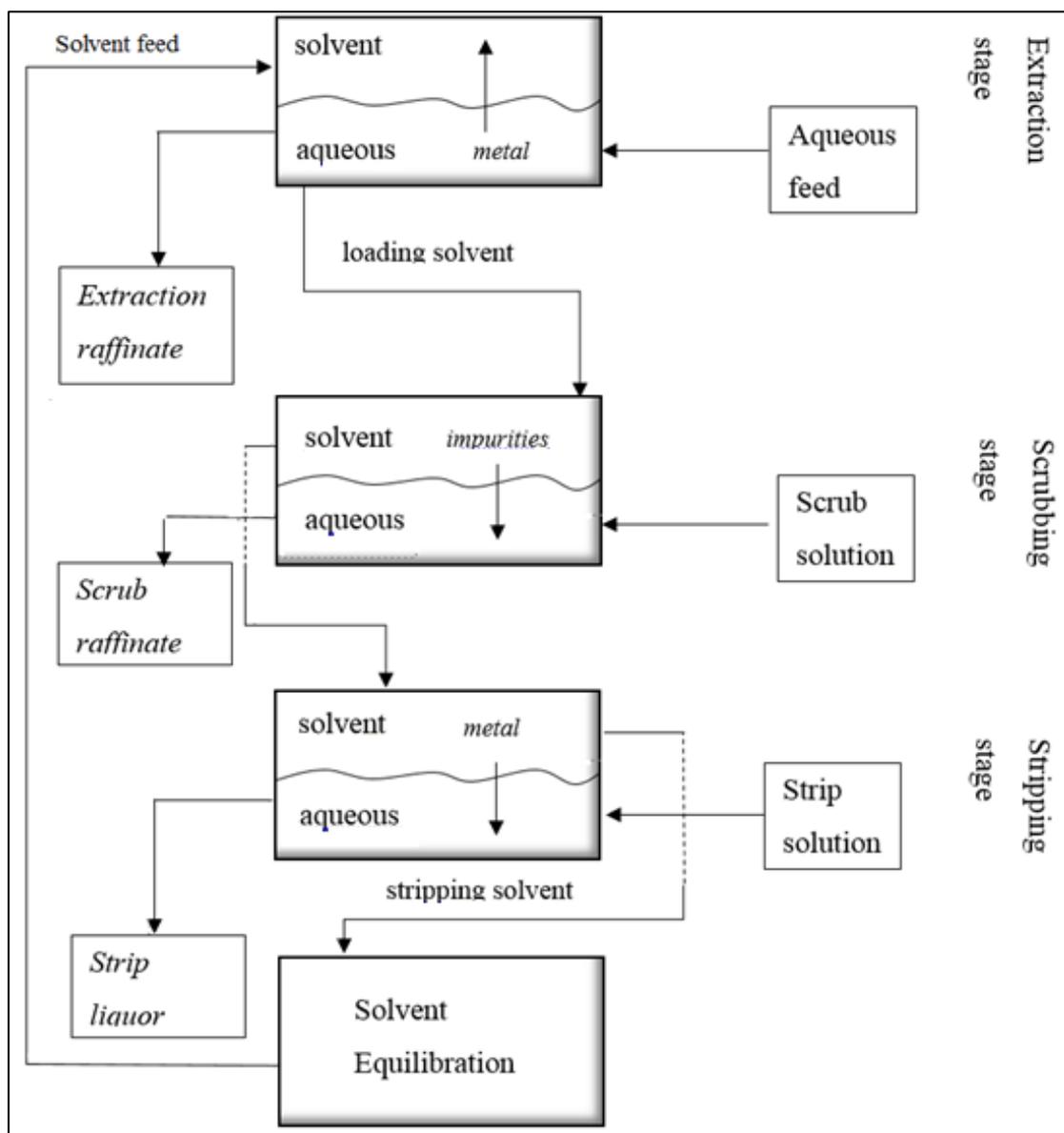


Figure 4. The practical process of solvent extraction. Adapted from (Ritcey, 2006)

Solvent extraction procedure is determined by several main objective parameters, which represent the extraction efficiency, such as distribution ratio D , percentage of extraction $\%E$ and separation factor β . Distribution coefficient is calculated as amount of metal ions in organic phase and the other listed parameters are defined as follows:

$$\%E = \frac{D}{D + \left(\frac{V_{\text{aq}}}{V_{\text{org}}}\right)} \cdot 100. \quad (1)$$

$$\beta = \frac{D_{\text{Co}}}{D_{\text{Ni}}} = \frac{\frac{[\text{Co}]_{\text{org}}}{[\text{Co}]_{\text{aq}}}}{\frac{[\text{Ni}]_{\text{org}}}{[\text{Ni}]_{\text{aq}}}}. \quad (2)$$

2.2 Industrial technologies

Nickel solutions purification by solvent extraction is stated as one of the vital targets of companies, owning hydrometallurgical plants in Australia to produce high purity nickel and cobalt. Therefore, several technologies are commonly used to remove Al, Fe, Zn, Mn and Mg over feed aqueous solution. List of existing technologies was compiled according to the principle, where main listed impurities are removed remaining Ni/Co in solution. Hence, Ni/Co separation processes were out of priority of consideration.

Inco company, placed in New Caledonia, proposes direct solvent SX process to separate cobalt and nickel from Mn, Mg and Ca impurities, where implemented technological scheme in Inco's Goro mine in New Caledonia were being exploited for two years (Mihaylov, et al., 2000). Industrial principle involves ion exchange (IX) extraction of Cu inclusions of leach liquor thereafter leaching of nickel laterites transitory to main SX stage to remove Mn, Ca and Mg impurities by Cyanex 301 treatment. Fe and Al along with other metals are removed during precipitation as a result of applied neutralization. Separation of zinc occurs by means of IX thereafter stripping stage of remained Ni, Co and Zn by 6 M HCl (Cheng, et al., 2004). Process branch on scheme of Ni-Co separation was not considered as it does not require to research purposes. General process scheme of Inco's Goro mine is represented in Figure 5.

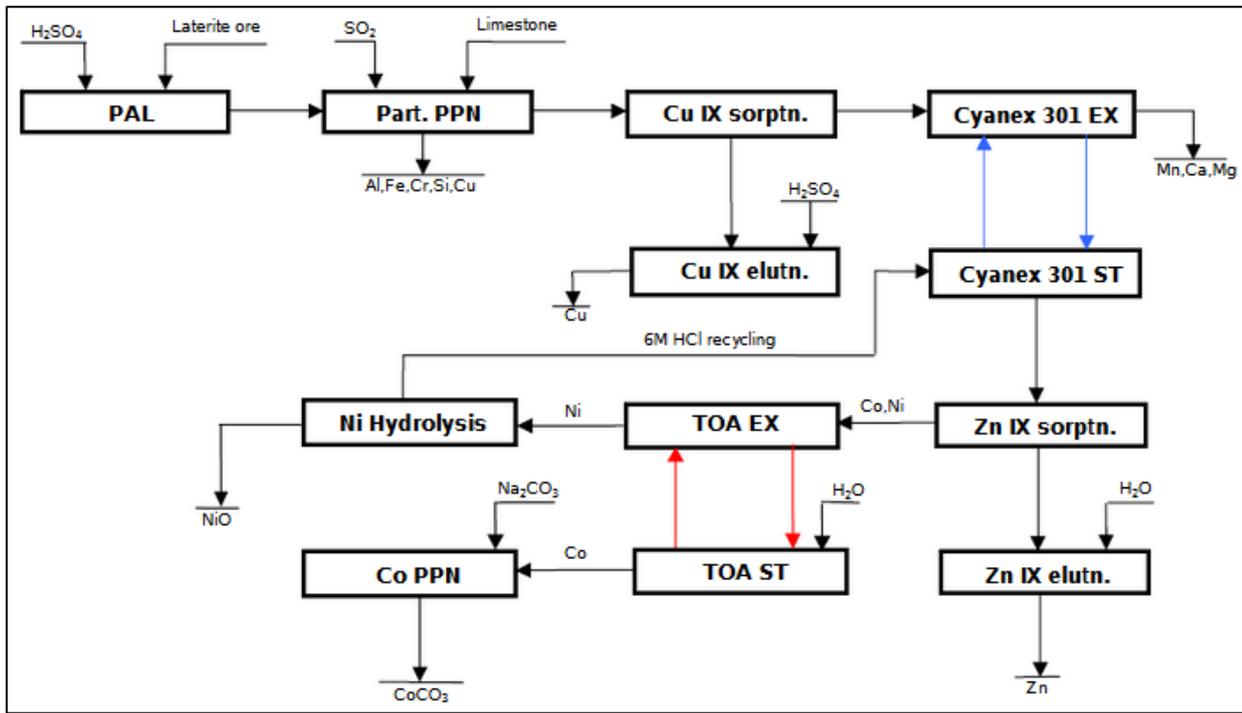


Figure 5. Conceptual flowsheet of Goro mine. Adapted from Mihaylov et al., 2000

Another solution for nickel and cobalt recovery by purification of solution from leaching residues was performed by AJ Parker Cooperative Research Centre for Hydrometallurgy / CSIRO Minerals (Cheng & Houchin, 2001). As in Goro process technology, Cr, Fe and Al are precipitated by neutralization. Treated solution is subjected to synergetic SX treatment in compound of Versatic 10 and decyl-4-pyridinecarboxylate ester to extract Ni, Co and Zn and to remain Mn, Ca and Mg in raffinate phase. Flowsheet of proposed technological process is provided in Figure 6.

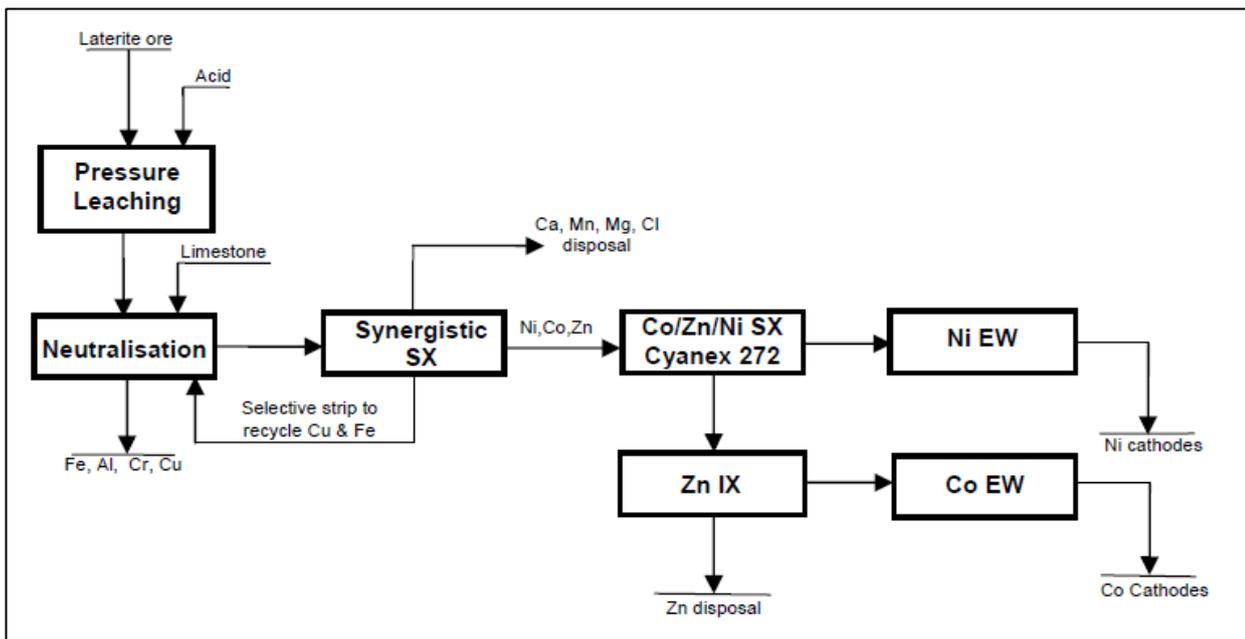


Figure 6. Flowsheet of the CSIRO DSX process. Adapted from Cheng & Houchin, 2001

CESL process is also established for Ni/Co solution refining, introducing treatment of received solution after acid pressure leaching of laterites and distributing one for two stages of purification with different acidity (Jones & Moore, 2001). First purification step is pointed to remove Cr, Al and Fe as limestone under pH 3.5, while Zn and remained traces of Fe are rejected at second purification point under pH 4.5-6.5 with lime. Removal of significant Mg amount is occurred at precipitation steps 1 and 2 by precipitating Ni, Co, Mn and Mg and subsequent Mg separation from precipitate. Proceeding of process belongs to re-leaching of Ni, Co, Mn and traces of Mg with following Mn extraction smoothly leading to Co SX separation by Cyanex 272 (Cheng & Houchin, 2001). Then, Ca and Mg are extracted again, transferring purified nickel to SX by LIX84I and to the final EW circuit (Figure 7).

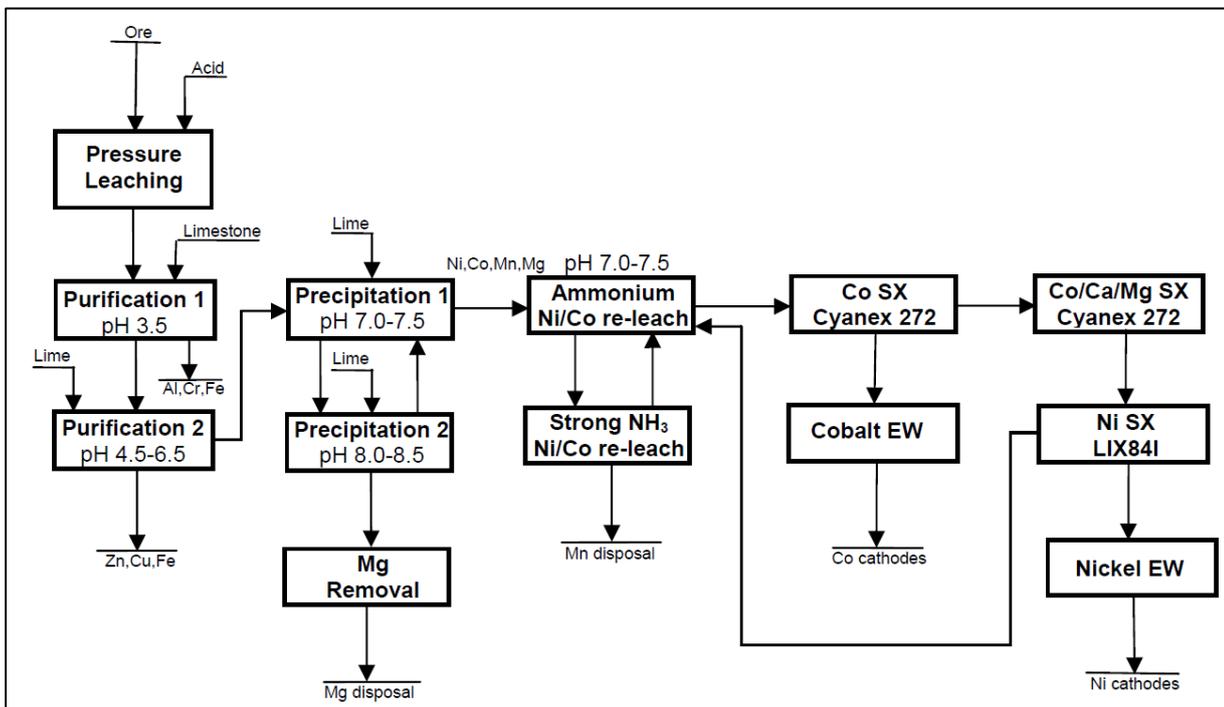


Figure 7. General technological scheme of CESL process. Adapted from Jones & Moore, 2001

The target of considered Murrin Murrin process (Figure 8) condensed in extraction of Mn, Mg and Ca over Ni/Co solution. Precipitate, containing Co, Ni and Zn is underwent pressure re-leaching in the presence of oxygen. Cyanex 272 application took place at SX circuit to separate zinc over remained solution (Motteram, et al., 1996).

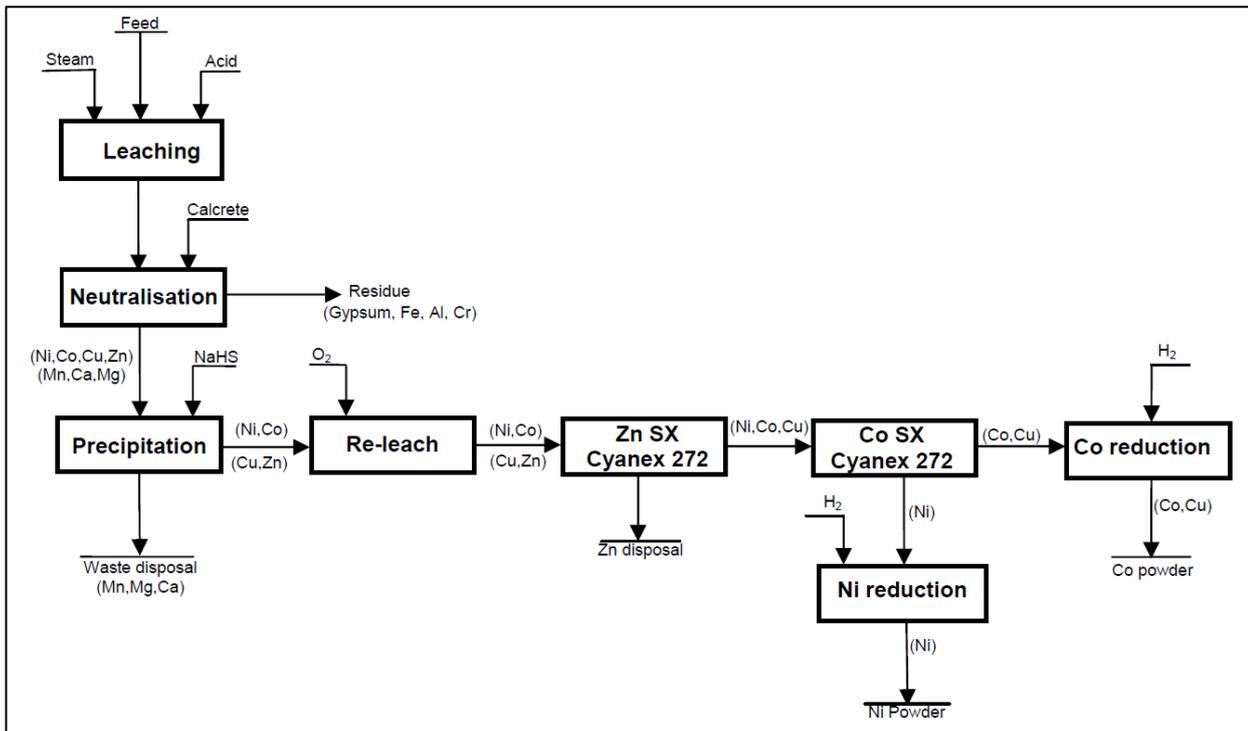


Figure 8. Flowsheet of Murrin Murrin process. Adapted from Motteram et al., 1996

Bulong process belongs to existing technologies of Australian hydrometallurgical plants and involves direct SX approach (Taylor & Cairns, 1997). The following process does not correspond to the current aims of project as it supposes initial nickel and cobalt separation during direct SX by Cyanex 272, however the process includes extraction of main impurities such as Ca, Mg, Zn and Mn. Thereafter separation of Ni/Co nickel raffinate underwent SX by Versatic 10 for target removal of Ca and Mg with further electrowinning process to recover Ni. The rest solution containing Co, Mn, Cu and Zn is transferred to sulphide precipitation – re-leach – SX circuit to achieve clean cobalt cathodes. Zinc and copper removal were carried out by D2EHPA and IX respectively (Cheng & Houchin, 2001). An accurate scheme of Bulong process is represented in Figure 9.

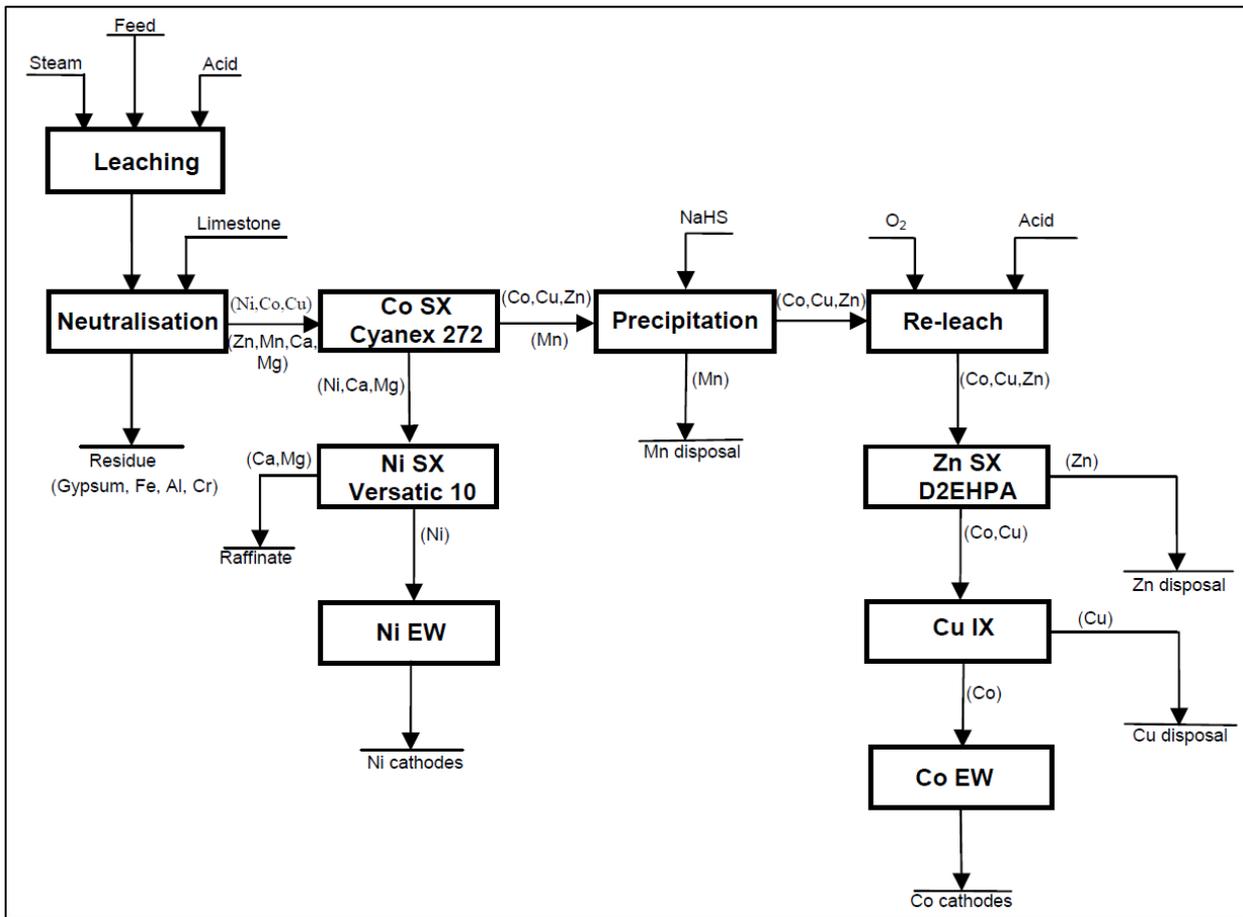


Figure 9. General flowsheet of Bulong process. Adapted from Taylor & Cairns, 1997

Sulphide/hydroxide precipitation – re-leach – SX are two technologies, which are applied respectively for Murrin Murrin and CESL processes and possesses several disadvantages, as high process complexity, metal losses as an outcome of incomplete precipitation and re-leach, environmental impact of used H_2S and NH_3 gases, elevated capital and operation costs. Moreover, Murrin Murrin process suffers from precipitation of Mn in compound with Ni and Co resulting to contamination of clean nickel and cobalt products. Advantages of applied processes are initial separation of main amounts of Mg, Ca and Mn; re-leach leads to elevated Ni and Co concentrations; availability of further processing and sale of intermediate products (Cheng & Houchin, 2001).

CSIRO DSX technology apply precipitation – re-leach – SX principle and has strengths as disposal of all general impurities such as Mg, Mn and Ca in first SX level, hence – smaller second SX circuit; exclusion of hazardous emissions as H_2S and NH_3 ; high metal recovery and low operation and capital costs. The weaknesses of the process are the need of intensive piloting as application of synergistic SX process and recovery of Versatic 10 by acidification (Cheng & Houchin, 2001).

Bulong process belongs to direct SX principle, which is appeared in relatively high costs and complexity of cobalt separation circuit due to the use of sulphide precipitation, solids/liquid separation and re-leach to separate manganese and zinc SX. Versatic 10 application leads to formation of gypsum, subsequently causes operational problems and nickel losses (Cheng & Houchin, 2001).

Goro process also belongs to direct SX technologies with several advantages as significant initial extraction of main impurities in first SX circuit; reduced costs due to absence of intermediate precipitation and re-leach; unnecessary of pH adjustment in extraction steps due to low pH operation value. However, the weaknesses of the following processes are the necessity of high concentrated HCl (6 M), high temperature (60 °C) and relatively long operation time (5 minutes) for stripping stage; facility requires high anti-corrosive material as operation with of high concentrated acid (Cheng & Houchin, 2001).

3 Extraction of metals using esters

Formation of esters is based on alcohols and inorganic acids interaction ability. Those acids, which are used in production of organics for extractive metallurgy, are represented by phosphoric acids in forms of phosphorus pentoxide (P₂O₅) and phosphoryl chloride (POCl₃). Reaction of dehydration of alcohols by P₂O₅ occurs producing unsaturated hydrocarbons or olefins. All esters, formatted by phosphoric acid are classified into acidic and neutral esters (Habashi, 1999). Classification is provided in Appendix 2.

Type of produced organic extractant is determined by molar ratio of reactants. As example, for alcohol/P₂O₅ ratio equals 2, an alkyl pyrophosphoric acid is produced:



D2EHPA and Cyanex 272[®] belongs to the most applicable extractants of acidic group. There are several rules corresponding to the acid esters properties, reporting that solubility of acidic esters in the aqueous phase declines with growing molecular chain length. Then, power of extraction increases simultaneously with chain length, however chain length in range C₈–C₁₂ are used due to economical issues. At last, low emulsifying behavior is reached by branching in the chain (Habashi, 1999).

Neutral esters are obtained by appropriate increase of ratio, where 6:1 leads to trialkyl phosphate is the outcome (common extractants are TBP and TOPO):



3.1 Extraction of metals using Cyanex 272®

3.1.1 General properties of bis(2,4,4-trimethylpentyl) phosphinic acid

The main mechanism of Cyanex 272® is introduced by phosphinic acid, which is selective for nickel and cobalt at certain pH range, based on cation exchange mechanism. It is extremely miscible in aliphatic and aromatic diluents and possesses of stability properties in heat and hydrolysis reactions. The reagent contains 85 % of bis(2,4,4-trimethylpentyl) phosphinic acid as extractant. The main target of bis(2,4,4-trimethylpentyl) phosphinic acid application aimed on the Ni/Co separation, which performs high selectivity of cobalt over nickel (Cytec Industries Inc., 2007). That fact is proved partially by pH-curves in Figure 10. As it seen, Cyanex 272 seems to be not applicable for implementation in current project as it poor selectivity of Mn and Mg over Co, moreover, Co and Ni selectivity is quite high, which does not correspond to project targets of remaining Co and Ni in aqueous solution.

The experiments provided by Cytec company in case of analysis of extractant stability report about absence of extractant degradation. Furthermore, there was not noticed any negative behavior in Ni-Co selectivity. Experimental procedure included settling of aqueous and organic fractions in stirred vessel, equilibrated at pH = 5 and 50 °C, with repeated returning of solvent into vessel during four-week contact. In addition, there were not detected any degradation of plants equipment after the 25-year period (Cytec Industries Inc., 2007).

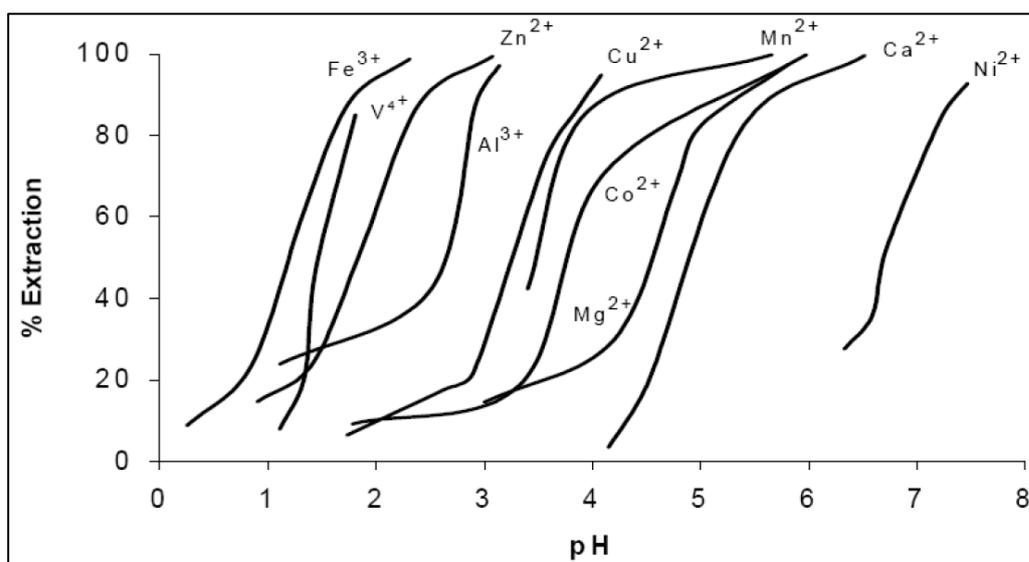


Figure 10. Basic extraction curves for Cyanex 272 at various pH. Adapted from (Roux, et al., 2007)

Along with the Cyanex 272[®] model, which was created mainly for the nickel and cobalt extraction, there is Cyanex 301[®] (dithiophosphinic acid) upgraded version of extractant. This modification ensures solvent extraction of Ni and Co under high acidic conditions neglecting the pH regulation, however Cyanex 272[®] stills more resistant to gypsum crystallization in stripping-electrowinning circuit, caused by calcium precipitation (Cytex Industries Inc., 2007). Table 1 illustrates the main advantages of Cyanex 272[®] application in comparison over other extractive substances.

However, Cyanex 272[®] possesses the main disadvantage, which caused by increasing of extractant viscosity up to 150 cSt in range of 12 to 20 g/dm³ of Co saturation. Obviously, this transformation leads to difficulties in mixing and pumping of solution or can make them even impossible. To avoid this, the amount of extracted cobalt should be adjusted in middle sizes. In addition, the elevated temperature is applied as solution for high viscosity problem (Ayanda, et al., 2013).

Table 1. Comparison of extractant properties. Adapted from Gotfryd, (2005)

Extractant	$\beta_{\text{CoNi}}^{\text{Co}}$	pH of optimal Co extraction	$\Delta\text{pH}_{50\%}^{\text{Ni-Co}}$	
			20 °C	50 °C
D2EHPA	14	3.6-3.8	0.35	0.70
PC-88A	280	5.0	1.21	1.48
Cyanex 272 [®]	7000	5.3-5.5	1.58	1.94

3.1.2 Iron extraction by Cyanex 272[®]

In targets of current research to purify nickel sulphate solution, iron has to be rejected firstly by SX to avoid difficulties at further steps of purification due to high content of dissolved iron in sulphate solution. For determination of the most effective extraction of Fe there were organized several experiments of solvent extraction, including participance of Cyanex 272 as extractant and kerosene as dilution agent (Debasis, et al., 1994). Research of iron removal along with other attending metals as Co, Mn, Zn, Ni and Cu were carried out with synthetic leaching solution, which composition is performed in Table 2.

According to experiments, the initial concentration of iron in pregnant solution equals 7.04 g/dm³. The sodium hydroxide was added beforehand, which is explained by necessity of pH regulation.

The temperature was regulated at range 30 ± 2 °C. It was assumed to equilibrate the A/O ratio as 1:1. The amount of added extractor was accurately measured in little concentration (around 0.2 m) in order to prevent the extraction of little volumes of other metals from pregnant solution by the same extractant (Debasis, et al., 1994). The general reaction of Fe removal is illustrated below in equation (3):



It was discovered that maximum efficiency of iron extraction is reached at pH equals 3.0. However, during the above equation pH becomes lower due to continuous production of hydrogen ions.

Table 2. Composition of investigated aqueous solution. Adapted from Debasis et al., 1994

Metal	Concentration, g/dm ³
Fe ³⁺	7.04
Ni ²⁺	2.82
Co ²⁺	0.184
Mn ²⁺	1.26
Zn ²⁺	0.05
Cu ²⁺	0.03

Moreover, aqueous pH value cannot be obtained higher than 3.0, due to iron hydrolysis. Therefore, it led to making the analysis at pH range of aqueous solution close to 3.0 (Ritcey & Ashbrook, 1979). The iron extraction occurred at 0.2 M and corresponds to 75 % of solvent neutralization. The results of analysis of aqueous phase after extraction are provided in Table 3.

Table 3. Iron extraction at different pH values. Adapted from Debasis et al., 1994

Initial pH	Equilibrium pH	Iron extraction (%)
1.90	2.30	30.8
2.15	2.35	33.3
2.50	2.60	50

During the analysis the end pH became less, although any attempts to increase this value led the aqueous phase to turbid form with occurrence of turbid particles. Thus, according to the received results, it can be stated that for described conditions (A/O = 1:1) the maximum Fe extraction level reached 50 %. The combination of possible conditions of extraction with different A/O ratios and degree of solvent neutralization resulted to a possibility to reach 95 % of iron extraction at

following parameters: 30 % of neutralized solvent and 1:5 A/O ratio. The same extraction can be achieved for 20 % of solvent neutralization (Ritcey & Ashbrook, 1979).

For completing of iron removal for industrial purposes the loaded organic solution is treated by stripping process by sulfuric acid with 78 % of efficiency of removal. Furthermore, the raffinate phase containing iron residue is processed through precipitation to extract the rest of iron (Ritcey & Ashbrook, 1979).

During the solvent extraction experiments in order to remove iron from sulphate solution, iron was almost totally extracted from aqueous phase, achieved 95 % of extraction from initial amount. Application of Cyanex 272 took place for other impurities in solution such as Cu, Mn, Zn were also extracted in a single stage exceeding 95 % of each. However, Cyanex 272 also touched cobalt with subsequent separation of Ni and Co in solution, which does not meet the objectives of current project. Experimental results for loading of organic were illustrated in Table 4 and prove the abovementioned conclusions.

Table 4. Extraction of impurities by Cyanex 272 from nickel sulphate solution

A:O ratio	Metal extraction (%)				
	Cu	Co	Mn	Zn	Ni
1:1	99.9	99.7	100	100	24.1
1:2	100	100	100	100	72.4
1:3	100	100	100	100	78.1
1:5	100	100	100	100	79.1
2:1	99	98.2	97.5	100	0.5
3:1	82.8	62.7	79.7	85.1	0.4
5:1	60.7	40.2	49.2	74.2	0.3

3.1.3 Zinc extraction using Cyanex 272[®]

The research of zinc extraction from sulfate media, using 0.1 M concentration of Cyanex 272 was provided. Feed aqueous solution contained 20 g/l of target zinc amount. Equilibrium pH variation occurred into range 1.4–3.6 for zinc (Jamaludin, 2012). The results reported about exponential growth of extracted zinc, reaching almost total extraction by the end of equilibrium pH variation (Figure 11). Described plot contains the extractive performance of copper and nickel ions.

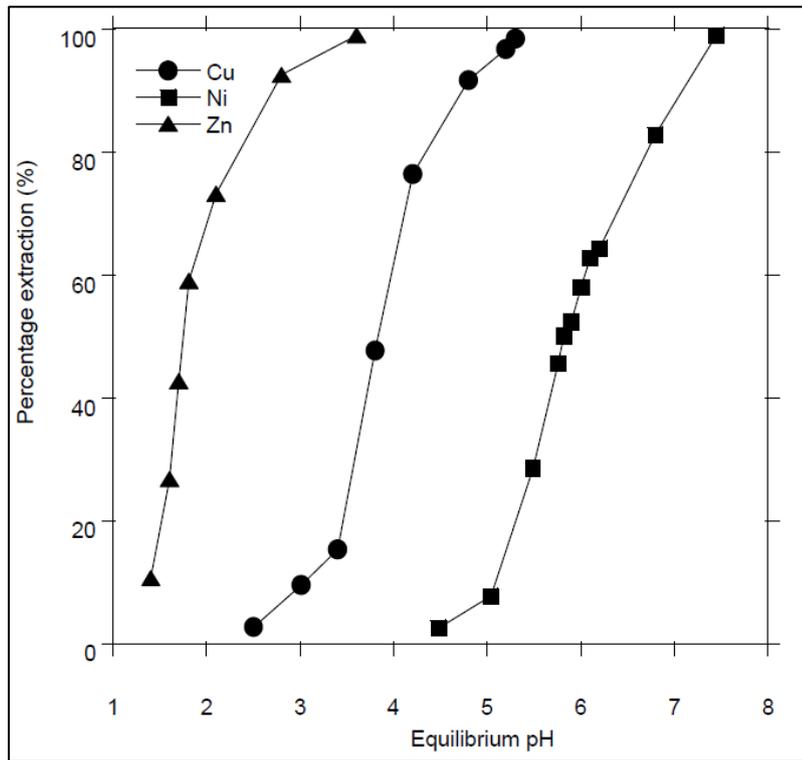


Figure 11. Effect of pH value on extraction percentage using Cyanex 272. Adapted from (Jamaludin, 2012)

Described research touched the topic of influence Cyanex 272 concentration of the extraction ability of zinc. Following concentration range were used in analysis from 0.01 to 0.4 M with initial pH 1.8 for aqueous solution with zinc (Jamaludin, 2012). The effect of concentration increase represented the obvious rise of zinc extraction (Figure 12).

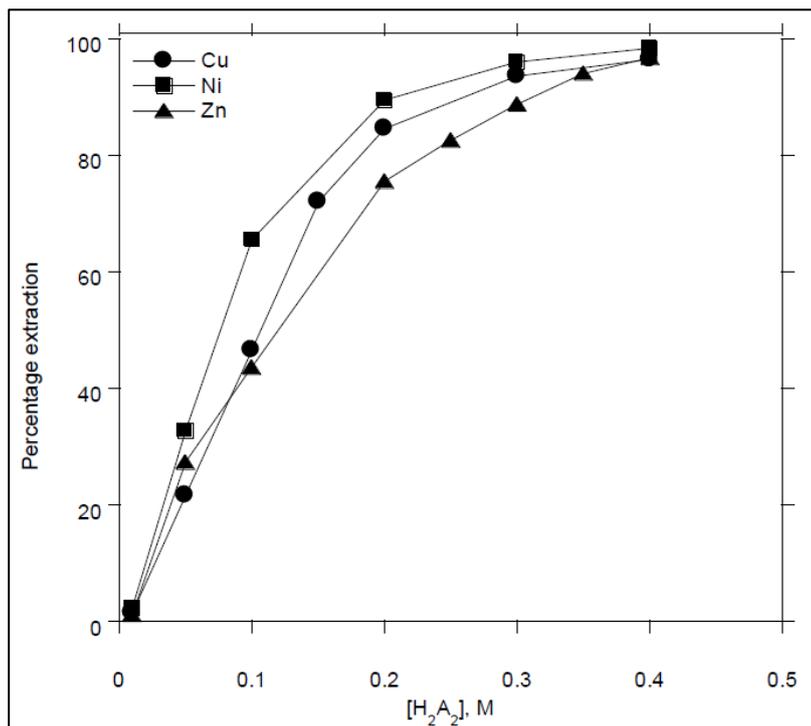


Figure 12. Effect of Cyanex 272 concentration on extraction percentage. Adapted from (Jamaludin, 2012)

Extraction of zinc by Cyanex 272 deserves evaluation as satisfactory as it possesses high selectivity over nickel ions, extracting Zn starting from high acidity value. That corresponds to effective removal of Zn without any Ni or Co ions losses, extracting at relatively low acidity by Cyanex 272 from sulphate solutions.

3.1.4 Aluminum and magnesium extraction using Cyanex 272[®]

Current research of Tsakiridis & Agatzini-Leonardou (2005) was provided as example for determination of aluminum and magnesium extraction parameters in presence of cobalt and nickel salts. This work aimed on wider field of extraction parameters, such as pH, temperature, O/A ratio and organics concentration.

Experimental parameters consisted of 25 % of extractant share, and the rest part of Exxsol D-80 for dilution. Composition of feed aqueous phase had the contained 5.85 g/L Al³⁺, 0.63 g/L Co²⁺, 3.8 g/L Ni²⁺ and 5.75 g/L Mg²⁺. Acidity adjustment was organized by 5 M NaOH solution while mixing took place in stirring conditions. Organic phase conditions were prepared according to the following parameters: 20% Cyanex 272 in Exxsol D-80 with 5% TBP, T – 40 °C.

As a result, extraction percentage achieved total removal of aluminum in 2.5–3.0 pH range with high selectivity over nickel and cobalt, while magnesium salts underwent significant difficulties in extraction due to co-extraction of cobalt ions (Tsakiridis & Agatzini-Leonardou, 2005). Extraction curves for all metals was placed together and represented in Figure 13.

Obtained results illustrate quite effective application of Cyanex 272 for Al from sulphate solution in presence of Ni, Co and Mg ions. It is achievable to extract 99.5 % of Al in one stage under 20 % v/v Cyanex 272 diluted in Exxsol D-80 with addition of 5 % of TBP at pH = 3.0, T = 40 °C and A/O = 2:1. Mg recovery was neglected as its close separation with Co ions, which has to be left in sulphate solution along with Ni ions. In terms of aluminum recovery at high selectivity over other contained Ni/Co ions, Cyanex 272 is the appropriate extractant, which removes Al at low pH values.

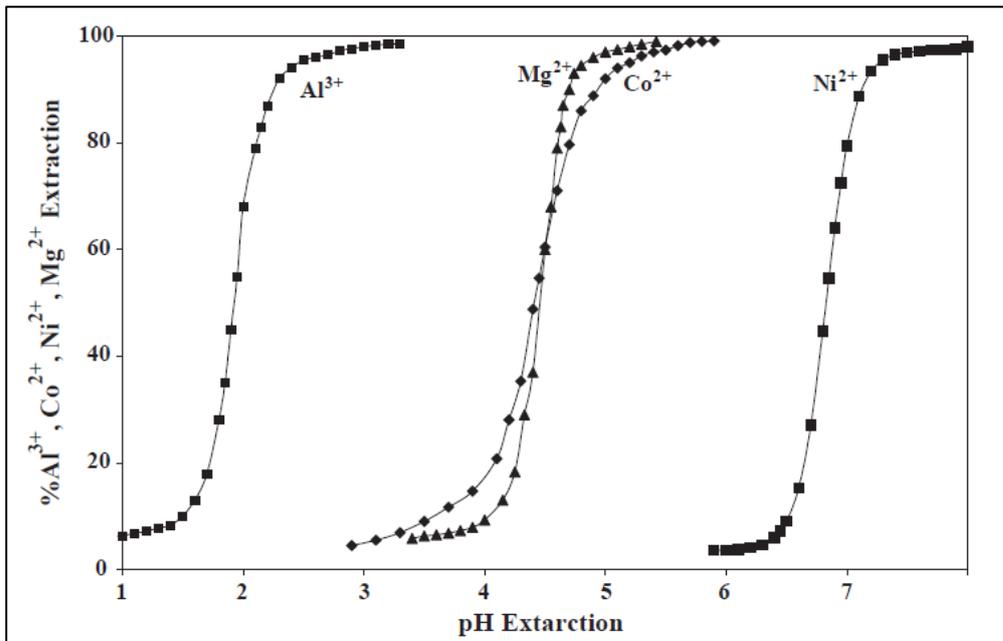


Figure 13. Al, Mg, Ni and Co extraction from sulphate solution by Cyanex 272. Adapted from (Tsakiridis & Agatzini-Leonardou, 2005)

3.1.5 Manganese extraction using Cyanex 272[®]

Additional analysis of Pérez-Garibay et al., (2012) of pH and residence time effect on manganese removal ability from sulphate solutions containing desirable manganese. In such authentic solution estimated manganese content reached 0.085 M, while several Cyanex 272 concentrations were also tested, equaled 5 %, 10 %, 15 %, 20 % and 25 % of volume. Experimental conditions consisted of 10 % of extractant concentration, O/A = 2, 1 minute of mixing time and 25 °C of reaction temperature. pH adjustment was provided by means of NH₄OH gas addition to the reactor.

The comparative plots were done depending of the incrementally changed initial pH before Mn extraction. Figure 14 shows the sharp leap of extraction percentage after pH = 8 for both Cyanex 272 and D2EHPA, which demands additional pH adjustment due to quite unstable rise. In addition, the D2EHPA extraction efficiency in pH range 5–8, obviously, seven times higher than Cyanex 272 (Perez-Garibay et al., 2012).

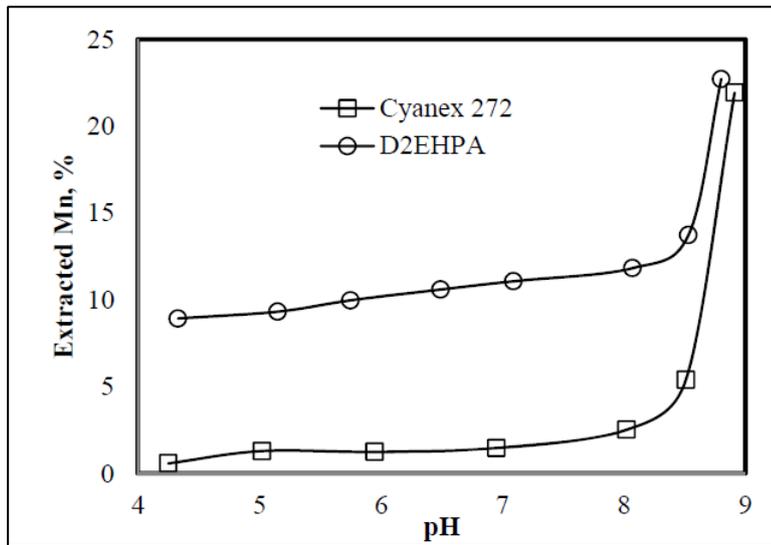


Figure 14. Effect of the pH on Mn extraction using Cyanex 272. Adapted from (Perez-Garibay et al., 2012)

The results of experiments with various extractant concentrations conclude the growth of manganese extraction as the extractant concentration increases as illustrated in Figure 15. Definitely, it is essential to apply higher concentrated organic to extract more manganese, although increase of extractant concentration may cause viscosity increase, subsequently reducing the mass transfer rate. Hence, the optimization of extractant concentration is required to avoid the extent of one (Perez-Garibay et al., 2012).

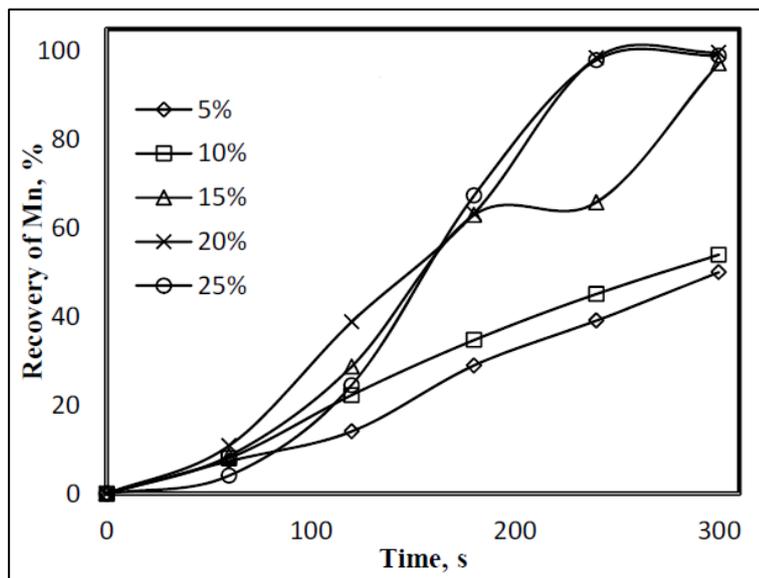


Figure 15. Effect of the extractant concentration on the manganese recovery. Adapted from (Pérez-Garibay, et al., 2012)

As a conclusion related to the current research problem, Cyanex 272 demonstrates less extraction efficiency than D2EHPA in case of Mn extraction from leach liquor as it requires achievement of

lower acidity (approximately pH = 9) to start transfer of significant amount of Mn ions. Hence, in case of current research, Cyanex 272 is not applicable as extractant for manganese removal from sulphate solution as D2EHPA seems to be more effective in solvent extraction tests.

3.1.6 Calcium extraction using Cyanex 272[®]

Suggested research (Guimaraes & Mansur, 2016) was provided for calcium to show the ability of Cyanex 272 to extract Ca from sulphate solution. According to the research, Cyanex 272 does not possess enough ability to remove high amounts of calcium from Ni-Co solutions, nevertheless investigation of extraction parameters should be provided, including Cyanex 272 and D2EHPA comparative analysis.

Experimental parameters correspond to calcium content equaled 0.57 g/l with initial pH of feed aqueous phase 2.0. Target organic composition corresponded to 20 % of Cyanex 272 and the rest of the Exxsol diluent. Figure 16 shows the curve of extraction, including curves for D2EHPA organic solution, where B-curve respects to 15 % Cyanex 272, 5 % of D2EHPA and C-curve suitable for 5 % of Cyanex 272 with 15 % D2EHPA. Experiment took place at O:A = 1 and corresponded to 200 ml of both phases volume. Temperature value was controlled at 50 °C (Guimaraes & Mansur, 2016).

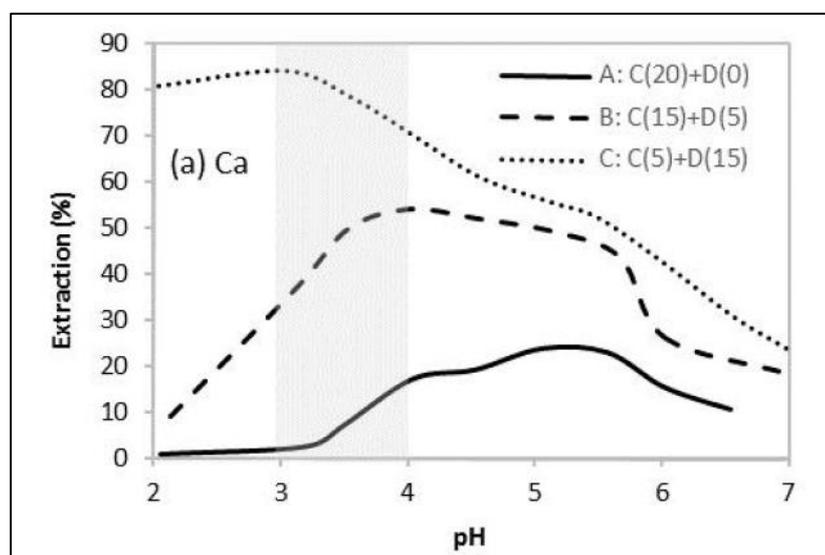


Figure 16. Extraction of calcium with Cyanex 272 and D2EHPA organic systems. Adapted from Guimaraes & Mansur, (2016)

Relatively to the calcium extraction, the weak extraction ability of Cyanex 272 is evidenced, in comparison with D2EHPA reagent mixture, which increase in the organics positively contributes to the calcium extraction. The explanation of the highlighted fact includes the nature background

of two extractants, as D2EHPA possesses higher acidity, explained by the molecular structure and higher content of oxygen atoms in the molecule, making D2EHPA more effective acidic extractant than Cyanex 272 (Guimaraes & Mansur, 2016).

The selectivity of calcium over nickel in solution was investigated at the same research, expressed in logarithm definition under following conditions: Ca – 0.57 g/L, Mg – 3.2 g/L, Ni – 99 g/L, A/O = 1:1 and T = 50 °C (Figure 17).

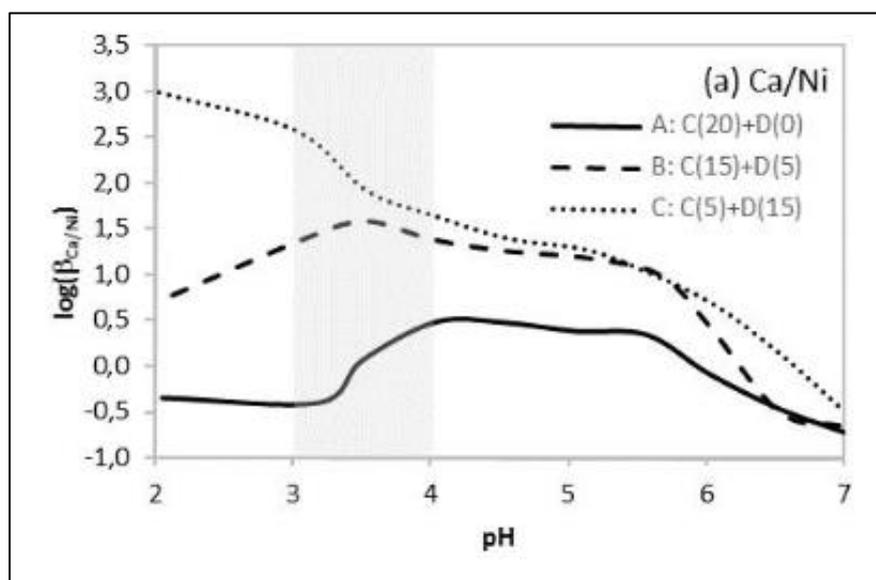


Figure 17. Selectivity of Ca/Ni with Cyanex 272 and D2EHPA organic systems. Adapted from Guimaraes & Mansur, (2016)

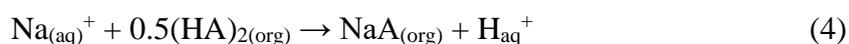
According to the studied selectivity performance of calcium and nickel, selectivity of mentioned metals is favored by predominance of D2EHPA, while higher acidity contributes to high selectivity as well. Subsequently it can be concluded, that high acidity has positive effect on Ca/Ni selectivity, explained by extraction of calcium under much lower pH value than for Ni extraction. Finally, in conditions of D2EHPA application and high acidity Ca extraction is elevated, resulting it minimized of Ni extraction. Application of organic mixtures with increased Cyanex 272 share still less effective and does not arrange equally high selectivity of Ca/Ni, where increasing of D2EHPA presence in organic leads to rise of Ca extraction share and selectivity.

3.1.7 Zinc and manganese extraction by Cyanex 272[®] using sodium salts

Devi et al. (1996) studied the influence of extractant sodium salts of NaCl, NaNO₃, NaSCN and Na₂SO₄ in compound with Cyanex 272[®] and 5 % TBP to extract Zn and Mn distilled at 0.5 M of each from sulphate solution. In aims of research of Zn and Mn extraction ability by Cyanex 272[®] there were performed several experiments to overcome the uncertainties during the removal of impurities in real process. However, it is suggested to extract the metals by production of sodium

salts, based on organic extractant. The extraction showed the unsatisfactory results of Zn and Mn removal from the aqueous phase at pure Cyanex 272[®], due to weak cation exchange. This fact explains the idea of addition of sodium salt into reagent.

Experiments included preparation of stock solutions containing 5 M of each sodium salt and 2.5 M of sodium sulphate for mixing with organic mixture. Organic extractant became mixed with NaOH component to achieve the neutralization (60 %) in presence of kerosene as diluent (reaction 6). The sample of 10 ml aliquot contained 0.01 M of dissolved metals and 0.1 M of Na₂SO₄ were contacted with beforehand prepared sodium-extractant solution during 5 min until completed equilibration. The pH value was under control of H₂SO₄/NaOH addition:



The zinc and manganese extractions were carried out until pH phase balance at 3.05-4.90 and 5.35-6.10, respectively (Devi, et al., 1996). The Figure 18 illustrates the behavior of the extraction percentage under the effect of pH growing.

Evidentially, the extraction increases while the equilibrium pH grows simultaneously. Moreover, the zinc began to extract at lower pH (almost 3 pH), while the manganese extraction started after pH = 5. It symbolized that Mn has the highest pH of separation which helps to divide the extractions of Zn and Mn by pH adjusting.

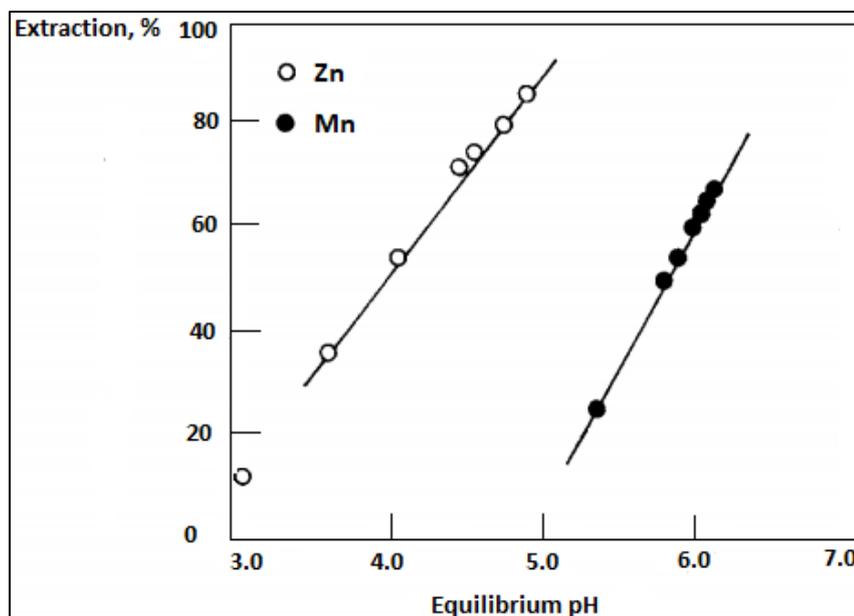


Figure 18. Extraction efficiency as function. Adapted from Devi et al., (1996)

The amount of extracted metal ions was investigated depending on the extractant concentration in the range 0.005-0.08 M. As it shown in Figure 19, the zinc and manganese extraction amount

climbed at ranges 10.0-99.99 % and 9.1-99.9 %, respectively. Increase of extractant concentration led to the pH leap, explaining the growing of extraction. At the level of extractant concentration equivalent 0.05 M reached the maximum for Zn and Mn extraction.

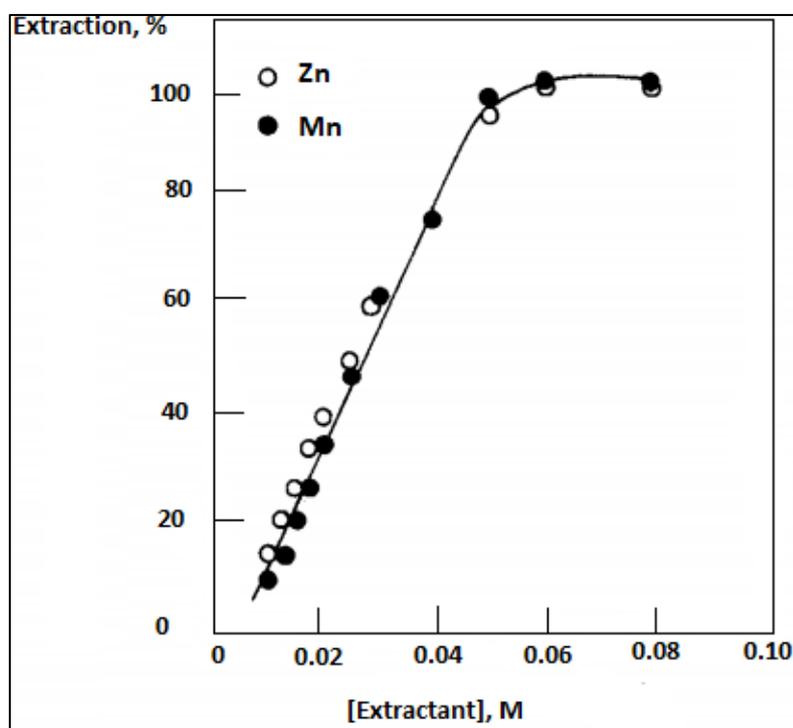
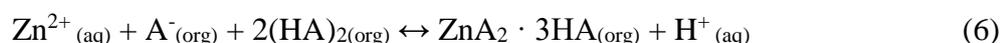


Figure 19. Extraction percentage as function of Na-Cyanex 272 concentration. Adapted from Devi et al., (1996)

The reaction mechanism is based on the neutral form of the organic defined as monomers in the beginning of the process. After the extraction the acidic form occurs by dimers in the organic (reactions 5-6).



The Figure 20 combined all traces, which were built according to the analysis of samples with several abovementioned salt species. Thus, NaNO_3 and NaCl salts did not affect significantly on the manganese extraction in any concentrations, however cyanide salt caused the 3.8 % of Mn extraction increase. Mentioned salts performed the same dynamic for zinc extraction and provide the leap of extraction ratio, except the NaSCN salt, which made the percentage untouched. However, the sodium sulphate salts caused the opposite effect on extraction procedure, and decreased the value for Zn and Mn from 54.0 % to 15.3 % and 30.0 %, respectively.

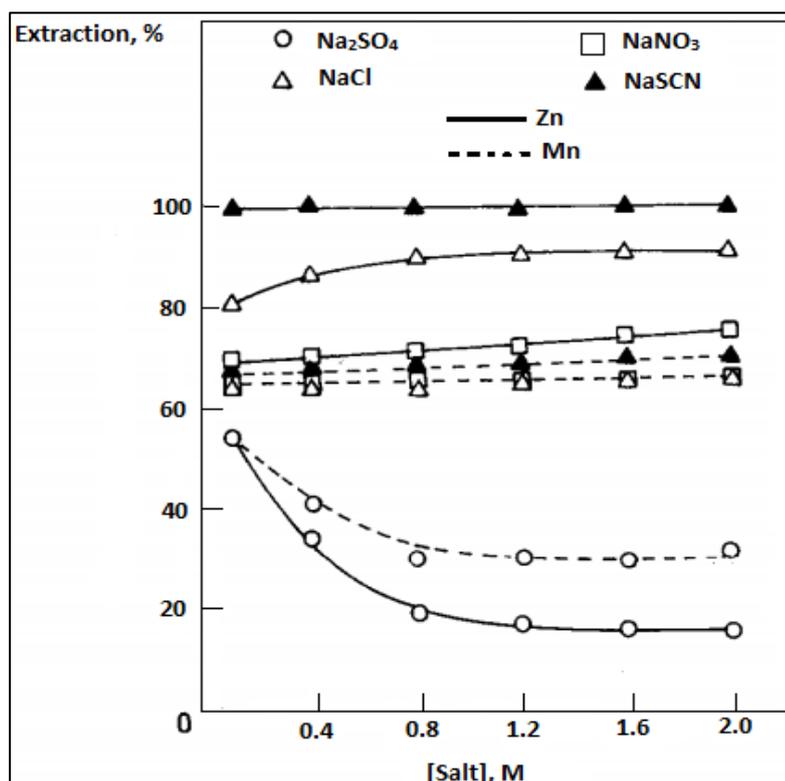


Figure 20. Extraction amount as function of salts concentration. Adapted from Devi et al., (1997)

3.2 Extraction of metals using D2EHPA

3.2.1 General properties of D2EHPA

According to the Cheng, (2000), the series of solvent extraction experiments were made for determination of D2EHPA properties, using organic mixture of 10 % di-2-ethylhexyl phosphoric acid, 5 % tri-butyl phosphate and 85 % of Shellsol 2046 as diluent to extract impurities from nickel-cobalt sulphate leach solution with following content: 3.0 g/l Ni, 0.3 g/l Co, 2.0 g/l Mn, 3.0 g/l Mg, 0.3 g/l Zn, 0.1 g/l Cu and 0.5 g/l Ca. Composition of aqueous phase was achieved by dissolution in distilled water of several hydrate salts as $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ with subsequent regulation of initial pH of aqueous phase at 4.5 and $T = 23^\circ\text{C}$.

SX tests (Cheng, 2000), started from pH range 2.0 – 2.5, corresponding to following percentage of metals removal as Zn – 83-93 % and Ca – 82-100 %, while Mn separation occupied 5-30 % range. Received data reports about high ability of D2EHPA to remove Ca and Zn at low steps of pH value. During the decremental acidity of tested aqueous solution, at pH 3.0-3.5 Mn extraction rose from 74 % to 92 % and Mg share equaled between 15 and 25 %, however cobalt extraction started as well from 12 % to 41 % along with nickel ranging in

10-32 % under the same pH range. Co-extracted cobalt and nickel leads to obligatory scrubbing of ones. The pH isotherm of extraction of present impurities overall investigated pH range is represented in Figure 21.

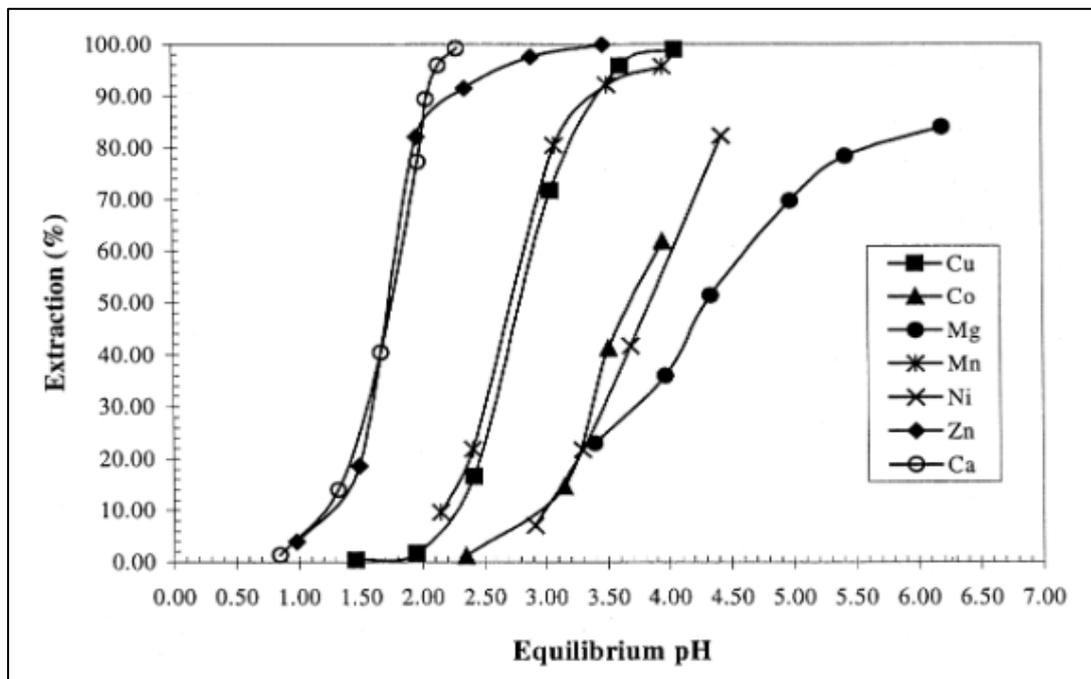


Figure 21. Extraction of several metals by D2EHPA from sulphate solution under $T = 23\text{ }^{\circ}\text{C}$.

Adapted from Cheng, (2000)

Temperature elevation outcome is represented graphically in Figure 22 to determine the effect of temperature on Mn and Cu separation over Ni and Co (Cheng, 2000). Considering the acidity point $\text{pH} = 3.0$ under $40\text{ }^{\circ}\text{C}$ the result of Cu and Mn equaled 64 % and 75 %, respectively, while Ni and Co share corresponded to 29 % and 47 %, respectively. The comparison was done for the same pH point under $23\text{ }^{\circ}\text{C}$, where Cu and Mn extractions reached 68 % and 73 % respectively, along with Ni and Co – 10 % and 12 %, respectively (Figure 22).

Thus, temperature increase forces the extraction of Co and Ni efficiency and remains extracted Mn and Cu at almost the same level. In case of achieving the highest impurity removal and minimization of Co/Ni extraction from sulphate solution, temperature leap is not required, moreover, it has negative influence contributing to Co/Ni co-extraction.

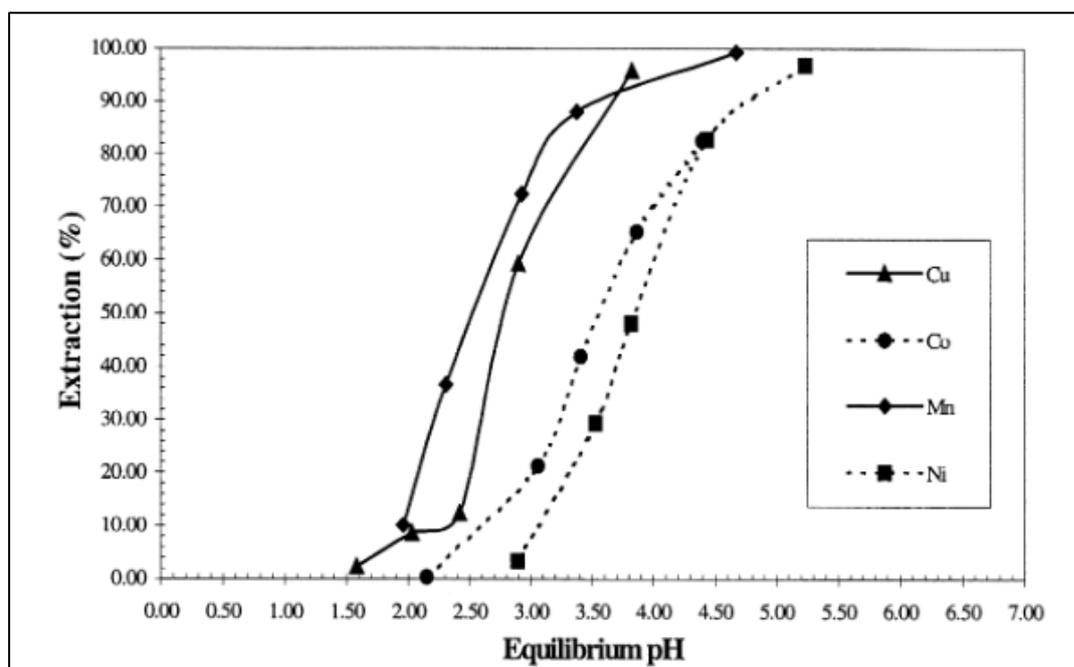


Figure 22. Extraction of several metals by D2EHPA from sulphate solution under T = 40 °C.

Adapted from Cheng, (2000)

Investigation of separation factor of manganese over nickel and cobalt was performed for various O/A ratio under 23 °C (Table 5). Decrease of separation factor is noticeable during the increase of aqueous phase volume. Separation factor growth is contributed by acidity decrease indicating higher separation of manganese over Co and Ni ions (Cheng, 2000).

Table 5. Separation factor of Mn over Ni and Co during SX under 23 °C. Adapted from Cheng, (2000)

Element	O/A ratio	$\beta_{Mn/M}$		
		pH = 2.0	pH = 3.0	pH = 3.5
Ni	2:1	49.7	309.1	690.4
	1:1	20.5	307.6	446.0
	1:2	56.8	262.7	571.8
	1:5	30.4	289.7	167.0
	1:10	50.3	198.1	114.3
Co	2:1	14.9	90.2	198.7
	1:1	20.5	98.3	142.7
	1:2	22.9	99.2	81.0
	1:5	19.7	111.0	67.1
	1:10	11.6	86.5	26.2

Table 6 represents the data of separation factor for 23, 40 and 60 °C reporting about the highest separation factor for room temperature 23 °C mostly, especially for Mn/Co separation.

Table 6. Separation factor of Mn over Ni and Co during SX under various temperature points.

Adapted from Cheng, (2000)

Element	O/A	$\beta_{Mn/M}$		
		23 °C	40 °C	60 °C
Ni	2:1	361.4	368.7	296.1
	1:1	434.2	430.5	205.9
	1:2	329.4	471.3	346.6
	1:5	225.0	738.7	277.1
	1:10	307.2	672.0	264.0
Co	2:1	119.3	36.9	78.1
	1:1	133.4	44.6	44.1
	1:2	132.9	33.0	37.6
	1:5	193.9	39.7	58.1
	1:10	340.6	37.2	56.6

According to the figure above, the extraction order for the several target elements as a function of pH was $Zn^{2+} > Ca^{2+} > Mn^{2+} > Cu^{2+} > Co^{2+} > Ni^{2+} > Mg^{2+}$. This confirmed that manganese would be extracted from sulfate solution ahead of cobalt and nickel. Extraction isotherms from solutions containing Zn, Ca, Mn, Cu, Co, Ni and Mg showed that the separation of zinc and calcium from the other elements was not difficult and the separation of copper and manganese from cobalt and nickel was achievable (Cheng, 2000).

3.2.2 Zinc and manganese extraction using D2EHPA

Provided research of Darvishi et al., (2011) demonstrates description of zinc and manganese separation from cobalt sulphate solution. All experiments included preparation of aqueous feed solution using sulphate salts, diluted in distilled water in 5 g/l concentration. Organic phase was prepared in concentration of 0.6 M of D2EHPA, diluted partially with kerosene according to the rule of extractant dilution to enhance fluid quality of one. Mixing conditions included 1:1 ratio of organic and aqueous phases with 20 ml of each under room temperature.

Investigation also included the experiments with D2EHPA and Cyanex 272 mixture, producing the data curve represented within Figure 23 as data curve for D2EHPA application.

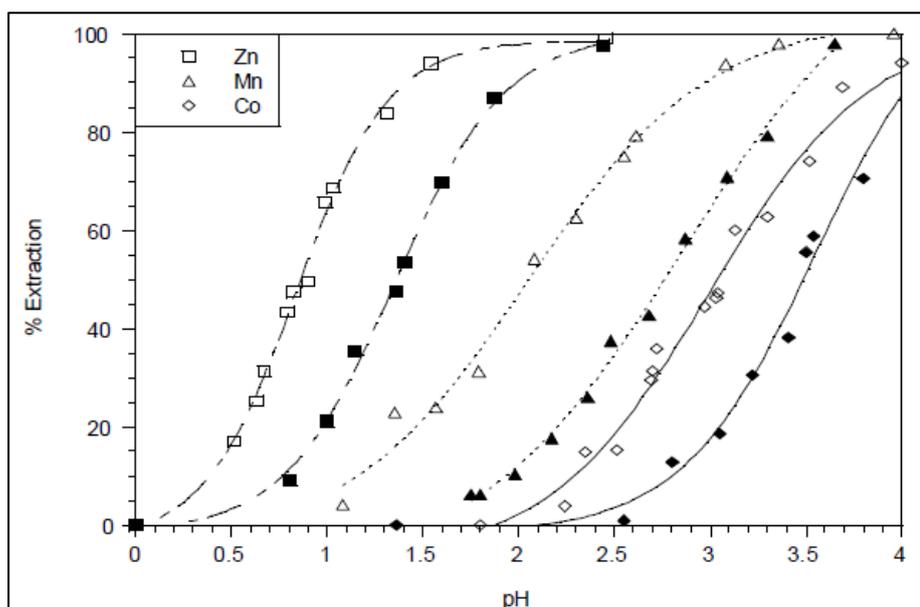


Figure 23. Effect of pH on extraction of zinc, manganese and cobalt (hollow symbols are related to 0.6 M D2EHPA; solid symbols correspond to 0.3 to 0.3 mixture of D2EHPA and Cyanex 272®). Adapted from Darvishi et al., (2011)

According to the received results, zinc extraction with clean D2EHPA occurred totally at pH 1.5–2. It can be assumed that zinc extraction does not cause any significant obstacles due to its high selectivity over cobalt. Manganese extraction causes co-extraction of cobalt at all extraction range, therefore other methods of separation should be applied as increase of number of extraction stages, scrubbing of co-extracted cobalt or establishment of temperature where the highest separation factor is avoided. According to the described experiments, separation factor of clean 0.6 M D2EHPA reached highest value, almost 44.5 for Mn and Co, in comparison with D2EHPA mixtures with Cyanex products. Table 7 contains all calculated values, resulted from described range of completed experiments with D2EHPA and its mixtures with Cyanex 272 and Cyanex 302 (Darvishi, et al., 2011)

Table 7. Values of for different mixtures of D2EHPA with Cyanex 302, D2EHPA with Cyanex 272 and individual D2EHPA. Adapted from (Darvishi, et al., 2011)

pH	D2EHPA/Cyanex 302	D2EHPA/Cyanex 272	Individual D2EHPA
	$\beta_{Mn/Co}$	$\beta_{Mn/Co}$	$\beta_{Mn/Co}$
1.8	-	-	-
2.0	6.33	-	44.50
2.2	4.71	26.00	20.29
2.4	3.33	14.00	14.67
2.6	2.79	13.60	12.50
2.8	2.41	10.09	11.96
3.0	2.09	9.00	11.10

3.2.3 Calcium and magnesium extraction using D2EHPA

Research material of Pakarinen & Paatero, (2008) with SX experiments related to purification of sulphate solution with dissolved Mn, Mg, Ca and Na sulphate salts by 25 % organic mixture of D2EHPA including the investigation of temperature influence.

Experiments were done in 5 °C and 25 °C in sulphate solution, where the composition was as follows: 5.3 g/L Mn, 2.2 g/L Mg, 0.26 g/L Ca and 2.2 g/L Na (initial pH of feed solution – 2.2). Organic/aqueous ratio equaled 1:1.5 with 25 % of D2EHPA concentration in organic. pH variation was the main parameter in the experiments, organized by NH₃ addition to the mixing vessel (Pakarinen & Paatero, 2008). Experimental data was converted to the pH isotherm, illustrated in Figure 24.

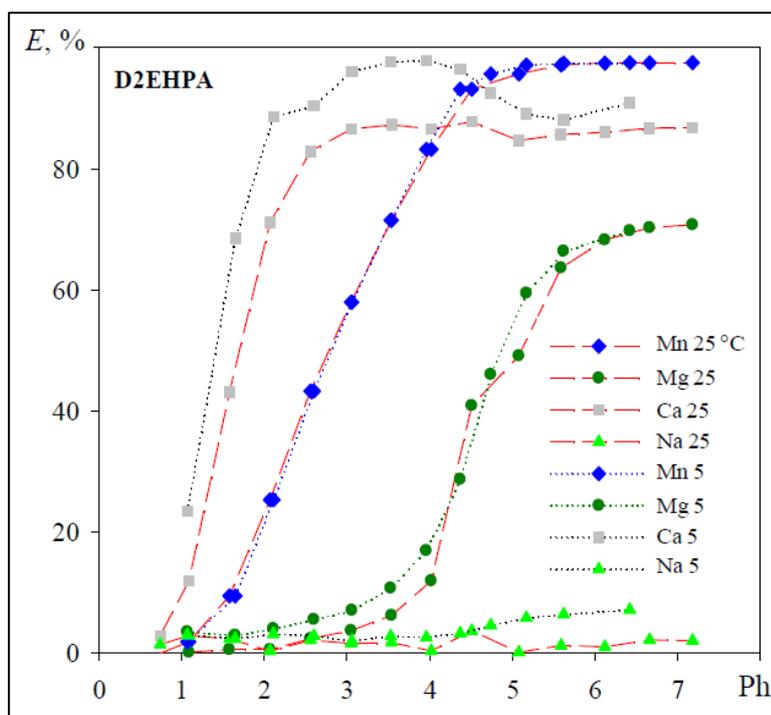


Figure 24. Extraction isotherms for Mn, Mg, Ca and Na at 5 and 25 °C. Adapted from (Pakarinen & Paatero, 2008)

Particularly, calcium extraction reached the top at almost 100 % of extraction at acidity value – 3.0, while magnesium extraction occurred at higher pH without visible difference in extraction under both temperatures (Pakarinen & Paatero, 2008).

The research of magnesium removal was done with 4.40 g/L Ni(II), 0.08 g/L Co(II), and 32.20 g/L Mg(II) content of aqueous sulfate solution. In the solvent extraction by D2EHPA, extraction

percentage of Mg(II) was much higher than that of Co(II), which establish the extraction order of these three metals by D2EHPA (Aguilar & Cortina, 2008).

Besides, manesium extration by D2EHPA reached the highest point, co-extraction only 4.0 % of nickel and 30 % of cobalt, making suitable its application in purification of nickel-cobalt solutions (Table 8).

Table 8. Extraction results obtained by various mixtures of extractants at equal volume ratio of organic to aqueous from the synthetic solution pH of 6. Adapted from (Lee, et al., 2011)

Extractant	Ni(%)	Co(%)	Mg(%)
D2EHPA	4.0	30.0	80.0
PC88A	5.0	40.0	80.0
Cyanex 272	10.0	70.0	20.0
TBP	1.0	1.0	2.0
Alamine 336	10.0	20.0	20.0
D2EHPA+TBP	10.0	40.0	80.0
D2EHPA+TOPO	7.0	40.0	70.0
D2EHPA+Alamine 336	10.0	40.0	80.0
PC88A+TBP	2.0	30.0	20.0
PC88A+TOPO	4.0	10.0	10.0
PC88A+ Alamine 336	1.0	8.0	4.0
Cyanex 272+TBP	1.0	>99.0	6.0
Cyanex 272+TOPO	1.0	6.0	4.0
Cyanex 272+Alamine 336	1.0	90.0	6.0

Volume ratio slightly affected on the extraction percentage of Co(II), while extraction percentage of Mg(II) increased with increasing volume ratio of organic to aqueous. The data in Figure 25 imply that Mg(II) can be separated from the synthetic solution by using D2EHPA, however co-extraction of Ni and Co takes place.

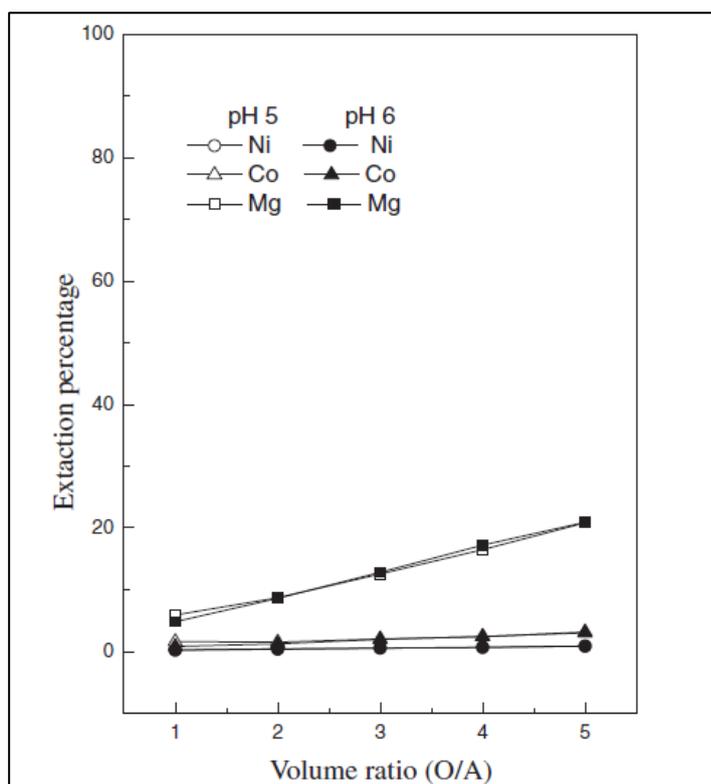


Figure 25. Effect of volume ratio of organic to aqueous on the extraction of metals by 0.3 kmol/m³ D2EHPA from the synthetic solution of pH 5 and 6. Adapted from (Lee, et al., 2011)

3.3 Extraction of metals using PC-88A

PC-88A is an organic extractant, applied at the stage of solvent extraction process and used mainly for Co/Ni separation (Flett, 2004). The extractant belongs to group of phosphonic acids (Nguyen et al., 2015) and represented by 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (Chemserve Co., 2008).

Zhang et al., (1998) stated the application of PC-88A as extractant for cobalt and lithium, containing in wasted battery solution, which allow satisfactory quality of Li and Co separation to produce metals with high purity. It was discovered that described extractant has satisfactory chemical stability, low toxicity and enough separating efficiency of Li and Co which makes the PC-88A appropriate reagent of cobalt separation from various sulfate and chloride solutions at various concentrations of cobalt and nickel ions.

3.3.1 Aluminum extraction using PC-88A

In addition to high selectivity of cobalt over nickel, extraction of zinc occurs at lower pH which corresponds to D2EHPA performance and suitable for Zn separation (Ritcey, 2006). Due to the problem existence related to the aluminum contamination of nickel solutions, there were done

several researches to test Al extraction over Ni ions in aqueous solution applying PC-88A extractant.

Experiments included test of three leading extractants as D2EHPA, Cyanex 272 (produced nowadays with other tradenames) and PC-88A in 0.45 M concentration. Analyzed feed solution contained 3.25 g/l Al³⁺ and 85 g/l Ni²⁺. Variation of equilibrium pH occupied 1.0 – 7.0 range. Figure 26 illustrates the comparative results as isotherms for Al extraction from nickel solution.

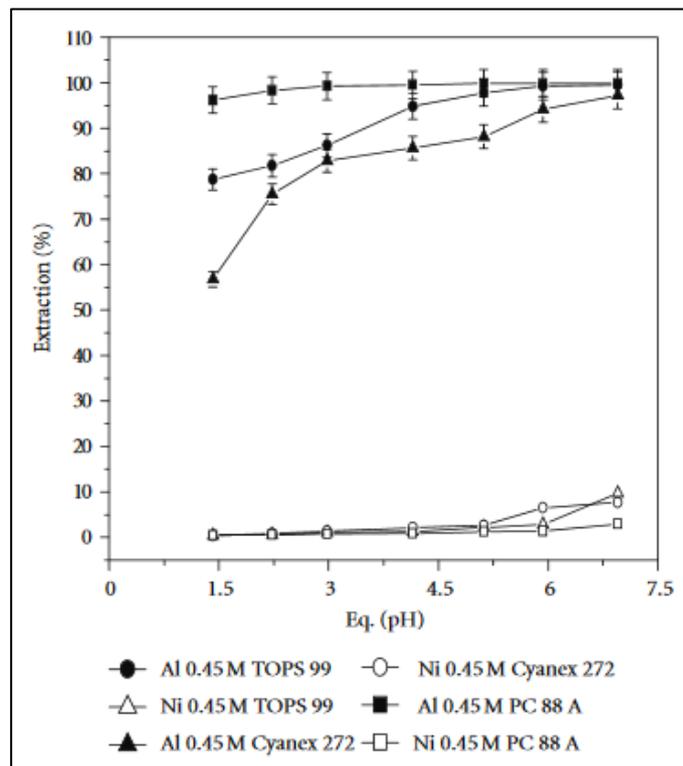


Figure 26. Equilibrium pH on percentage extraction of Al and Ni. Adapted from (Dong, et al., 2012)

The results reports about the most effective aluminum removal over nickel of PC-88A application for sulphate solutions. Extractant demonstrated the > 99 % of extraction efficiency, achieved at two stages, O:A = 1:2 and pH = 2.23 (Dong, et al., 2012).

3.3.2 Manganese separation using PC-88A

At current chapter, the single research was provided with 0.02 M Co, Cu and Mn stock sulphate solution. Experiment performed test of three 0.1 M organics, as PC-88A, PC-88A+Cyanex 272 (1:1) and Cyanex 272. In spite of synergetic effect was obtained with coefficient of synergy for Cyanex 272 equaled 0.5, the extractability of the mixed and single systems follows as PC-88A > Cyanex 272 + PC-88A > Cyanex272 (Wang, et al., 2012), which is indicated according to the distribution ratio curves in Figure 27.

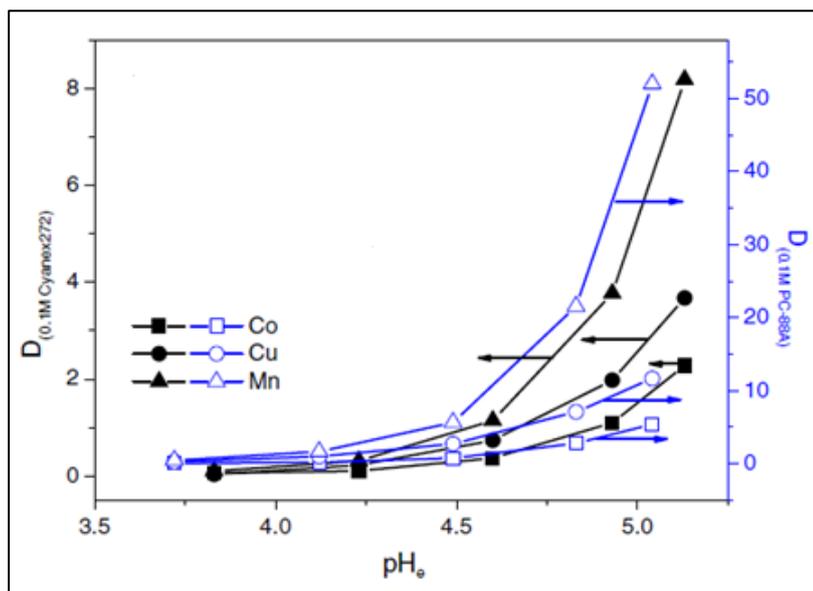


Figure 27. Comparison of distribution ratios in different systems under the same extraction conditions. Adapted from (Wang, et al., 2012)

According to the obtained results, the highest extraction of manganese belongs to single Cyanex 272 application, however making it increase of cobalt co-extraction (Wang, et al., 2012).

4 Metals extraction using hydroxyoximes

Oximes are the group of extractants, belonging to the group including =N-OH group. The mechanism of extraction exploits chelation procedure, where neutral metal chelate is insoluble in the aqueous phase but is able to solute in the diluent. Chelate definition includes the situation, where organic molecule consists of acidic and basic function making compound with metallic ion. In case of operative ability of both functions, chelate salt is formed.

As main representatives of oximes, there are the compounds named hydroxyoximes, aimed to the copper extraction. One of the common representatives is 5,8-diethyl-7-6-dodecanone oxime with commercial name LIX-63, supplied by Henkel Corporation (Habashi, 1999).

Industrial implementation of hydroxyoximes, as example LIX 63, occurred as catalytic additive under 40 °C to extractants containing 2-hydroxy-benzophenone oxime derivatives, as LIX 65N and LIX 70. LIX 64 found commercial interests mostly for copper and germanium extraction, while LIX 65 N is applied for copper removal from sulphate solutions at pH higher 1.5. The accurate list of commercial hydroxyoximes extractants is shown in Appendix 3.

4.1 Application of LIX 622N and LIX 84-I

According to the research of Panigrahi et al., (2009), hydroxyoximes possesses the highest extraction efficiency relatively to Cu over sulphate solutions. Several SX experiments were carried out to determine the parameters of Cu and Zn removal over Ni/Co by LIX 84-I and LIX 622N from sulphate solution with content 13.0 g/l copper, 15.6 g/l nickel, 2.6 g/l cobalt and 2.6 g/l zinc.

The copper extraction procedure is accompanied by using extractant 2-hydroxy-5-nonylacetophenone oxime, registered as LIX[®]84-I organic extractant (BASF, 2015). Another option of copper extraction includes the usage of mixture of 5-nonylsalicylaldoxime with tridecanol with commercial name of LIX[®]622N (Panigrahi, et al., 2009).

Extraction process involves transfer of Cu²⁺ ions to organic phase making the leach solution free of copper ions and recycling it back for leaching, while the pregnant organic part underwent stripping leading to conversion back to concentrated electrolyte solution for further copper cathodes formation by electrowinning (Ruiz, et al., 2017).

Preparation of organic phase was completed under concentration of 15 % for both LIX[®]84-I and LIX[®]622N, including dilution by kerosene without purification of extractants. The experiments of determination of pH influence on metals extraction were carried out at similar amount of aqueous and organic ratios (0.01 L of both phases). The sampling was performed at pH range 0.5-4.6, however the maximum copper loading of organic phase was reached at 1.27 and 1.19 for LIX 84-I and LIX 622N, respectively (Figure 28).

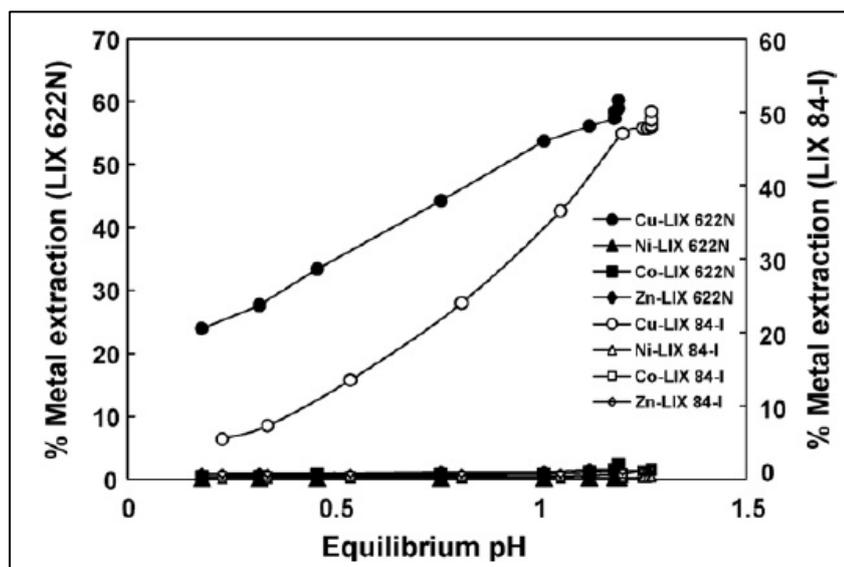


Figure 28. Effect of pH on metal extraction percentage. Adapted from Panigrahi et al., (2009)

During the mixing with LIX 84-I the amount of extracted copper underwent significant increase from 5.46 to 50.08 % and from 24.0 to 60.2 % for LIX 622N, although the extraction percentage of other dissolved metals remained low and did not climb higher than 3 % (Panigrahi et al., 2009).

Figure 29 illustrates the performance of extraction within 2.5 – 25.0 % range of extractant concentration from leach liquor with initial pH = 4.0 at O/A = 1:1. Equilibrium pH values were installed at 2.12-1.16 and 1.98-1.07 for LIX 84-I and LIX 622N, respectively. The result was received, that Cu extraction was at more than five times elevated from almost 13.0 % up to 73.0 %, while Ni and Co co-extraction remains at minor percentage (reached approximately 2.0 %) in all range of extractant concentration variation (2.5-25.0 %) (Panigrahi et al., 2009).

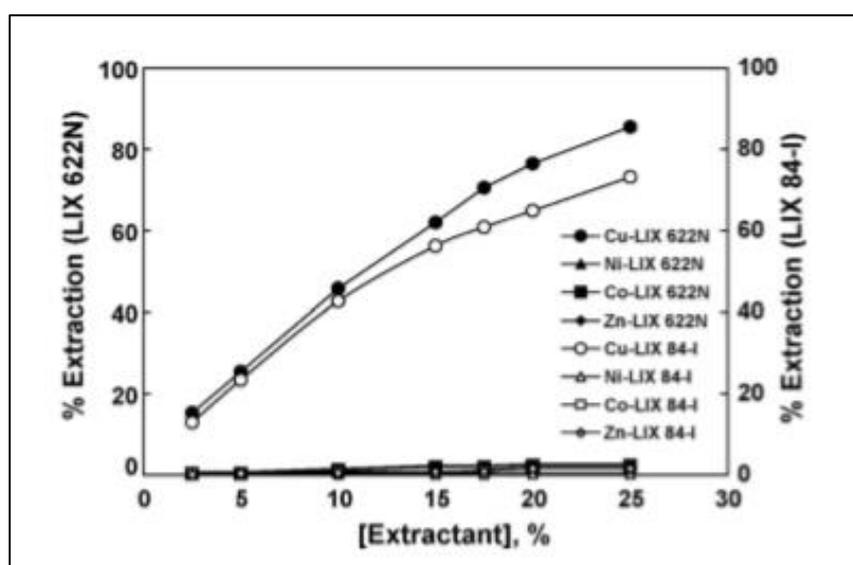


Figure 29. Effect of extractant concentration on extraction efficiency. Adapted from Panigrahi et al., (2009)

Experiments with SX of Mg and Ca was provided by Ndlovu & Mahlangu, (2008) with application of 0.5 M LIX 84-IC at 40 °C and O/A = 1:1 under different values of equilibrium pH. The graphic interpretation of pH isotherm of Ni, Mg and Ca loading is shown in Figure 30.

As obvious from represented chart (Figure 30), Ni removal curve starts earlier, climbing up to almost 90 % while at pH = 6.0 Ca and Mg curves represent 0 and 10 %, respectively, of extraction share and, hence, less efficiency to remove impurities over Ni-sulphate solution. In general, Ca and Mg SX performed poor percentage even at higher pH, where pH = 8.0 point corresponds to 30 % of both Mg and Ca ion transfer to organic.

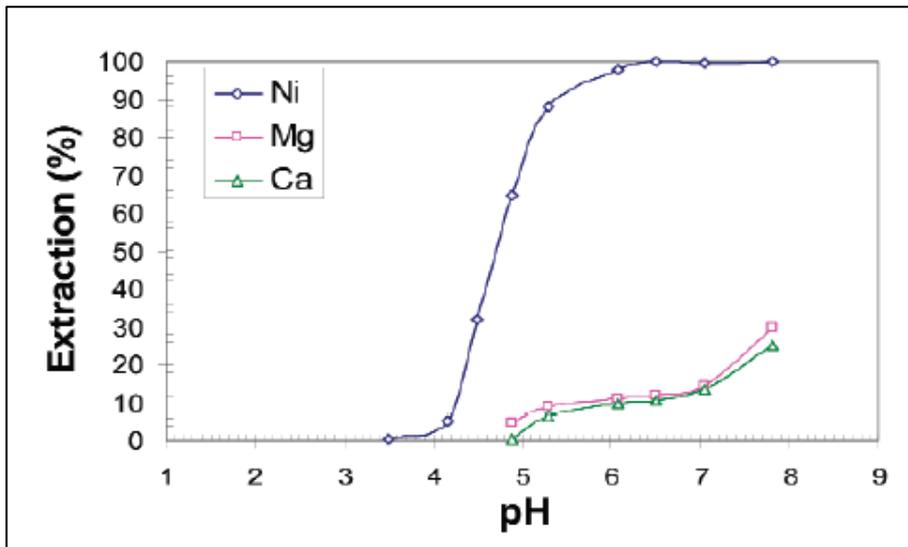


Figure 30. pH isotherm of Ni, Ca and Mg extraction by LIX 84-I. Adapted from Ndlovu & Mahlangu, (2008)

Ndlovu & Mahlangu, (2008) performed experiments with determination of LIX 84-IC concentration effect on extraction process at fixed equilibrium pH = 4.0 in variation of the extractant concentration from 0.1 to 0.6 M. Results also demonstrated high removal of Ni, while Mg and Ca remained in solution. The effect of the extractant concentration increase did not make sense as extraction of Mg and Ca even dropped from initial 20 % and 10 % to almost 5 % and 3 %, respectively (Figure 31).

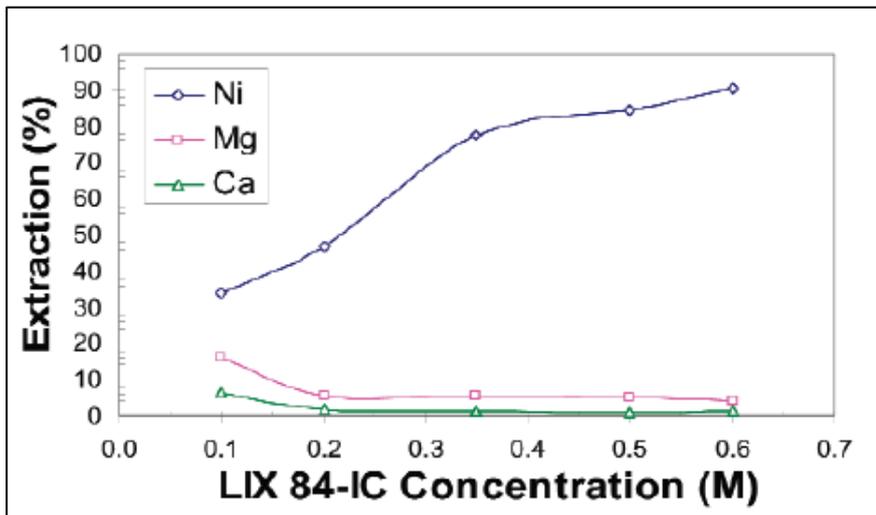


Figure 31. pH isotherm of Ni, Ca and Mg extraction by LIX 84-I. Adapted from Ndlovu & Mahlangu, (2008)

Finally, the other metals remained in solution and did not show noticeable transfer to organic phase. It can be concluded, that results of completed series experiments prove the hydroxyoximes effective usage mostly for Cu (II) extraction and should be aimed for copper recovery industry.

Moreover, Zn removal remained at relatively low percentage, which reports about poor efficiency of Zn removal from sulphate solutions. As a result of LIX 84-I application, pH isotherm of Ni extraction was shifted to lower pH range, while Mg and Ca placed at lower acidity. Therefore, application of hydroxyoximes for purification of Ni-Co from such impurities as Zn, Ca and Mg does not make sense due to low extraction ability of hydroxyoximes relatively to listed metals.

5 Solvent extraction by organic acids

The theory of extraction by organic compounds applying acidic properties and containing carboxyl group establish the organic acids extraction principle. The main representatives of organic acids class are fatty acids or carboxylic acids, which corresponds to decreasing of solubility as increasing of molecular weight. Palmitic and stearic acids are introduced as extractants, however the common application deserved Versatic 10, known as 2-methyl-2-ethylheptanoic acid (neodecanoic acid) with common structural formula $R_1R_2CH_2COOH$ (Habashi, 1999).

5.1 Metals extraction using Versatic 10

Cheng et al., (2010) provided experiments of impurities extraction from sulphate solution over Co ions with following composition as $[Co] = 0.195 \text{ g/L}$, $[Cu] = 0.145 \text{ g/L}$, $[Zn] = 1.164 \text{ g/L}$, $[Mn] = 44.61 \text{ g/L}$, $[Mg] = 25.71 \text{ g/L}$, $[Ca] = 0.462 \text{ g/L}$, $[Fe] = 0.010 \text{ g/L}$ under O/A = 1:2 and $T = 40 \text{ }^\circ\text{C}$ by applying Versatic 10 acid and its synergetic mixture with hydroxyoximes, where the last one represented by LIX 63. Experiments were organised as shakeout test in stainless-steel vessel under temperature and pH control. Aqueous solution was prepared by dissolving of the required amount of analytical grade of hydrate-sulphate salts, containing listed metal ions. The performance of SX by Versatic 10 in pH isotherm is represented in Figure 32.

As it seen from pH curves of single Versatic 10 application, Cu and Zn climbed to 90 % almost at 4.5 and 5.5 of acidity value, respectively. Extraction of Co started from pH = 6 and at the end point pf 7.5 reached 60 %. Mn and Mg removal did not exceed 20 %, while Ca removal curve did not rise in general. According to the close position of pH-curves of Mg, Mn and Ca relatively to Co, it can be outlined that single application of Versatic 10 does not provide enough selectivity to separate following metals over Co ions. poor extraction percentage of Mg, Mn and especially Ca reports about evidential useless of Versatic 10 to purify Co sulphate solution from Mg, Mn and Ca, providing undesirable Co co-extraction at significant amounts (30 % at pH = 7).

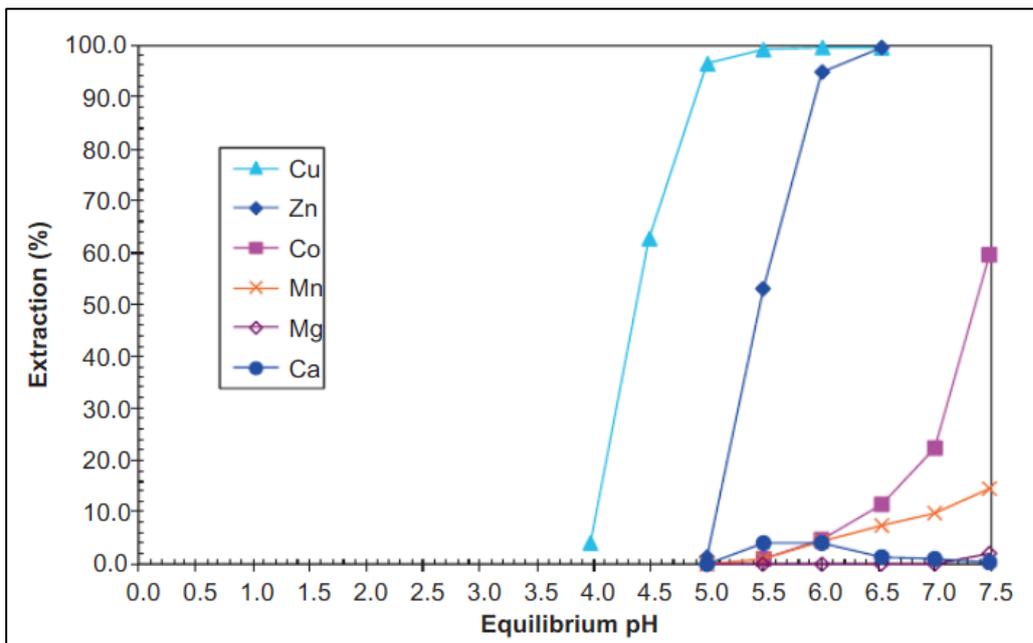


Figure 32. Metal extraction pH isotherms Versatic 10 acid alone. Adapted from Cheng et al., (2010)

Another developed solution by Cheng et al., (2010), suggested to use synergy of 0.5 M Versatic 10 and 0.4 M LIX 63 (5,8 diethyl-7-hydroxy-6-dodecanone oxime) to purify sulphate solution of the same content provided above, due to relatively high separation extent of cobalt over manganese. Experiments were carried out with 0.5 M of Versatic 10 and 0.4 M of LIX 63 diluted in Shellsol D70 and the received data were illustrated on pH isotherm (Figure 33).

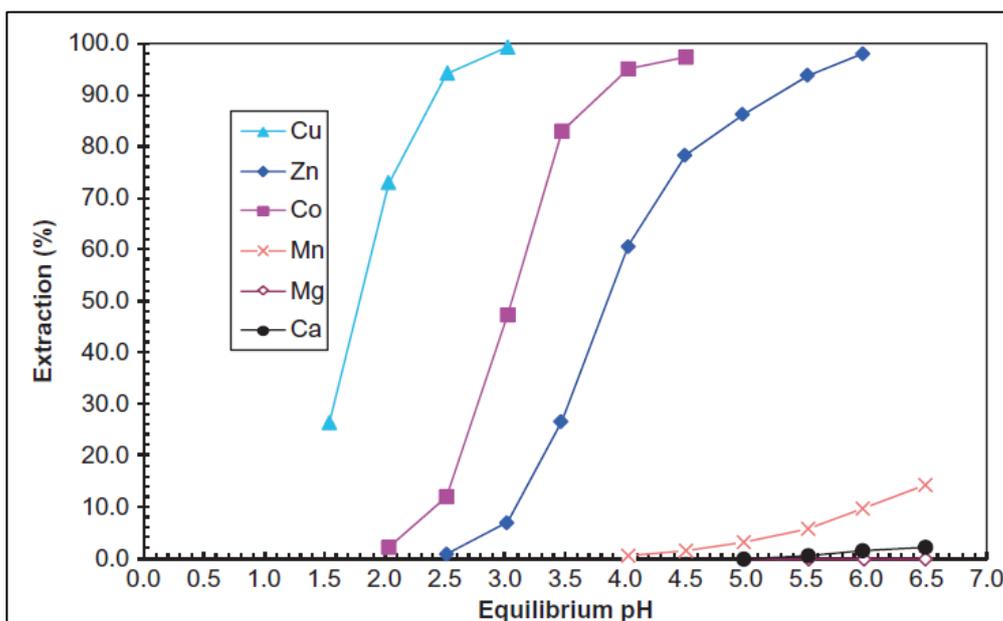


Figure 33. pH isotherm of manganese extraction with 0.5 M Versatic 10 and 0.4 M of LIX 63. Adapted from (Cheng, et al., 2010)

After leaching circuit, the Ni-Co solution is often produced with major impurities, represented by alkaline earth metals Ca and Mg, which contaminate produced metal cathode (Santos, et al., 2015). At this case, the separation of calcium and magnesium from Co can be gained by SX with Versatic 10, however, it does not meet the targets of impurities removal and remaining of Co in aqueous phase, making the extraction of Co more effective and at higher acidity (Co extraction – 90 % under pH = 3.5).

Guimaraes & Mansur, (2014) proposed method of sulphate solution purification with following content as [Ca] = 0.50 g/L; [Co] = 2.10 g/L; [Cu] = 0.25 g/L; [Mg] = 3.50 g/L; [Mn] = 0.55 g/L; [Ni] = 75.0 g/L; [Zn] = 0.06 g/L by organic mixture of Cyanex 272 with 20 % v/v share and neodecanoic acid (Versatic 10) with several concentrations as 0, 5, 10 and 20 % v/v to identify extraction ability of Versatic 10. All experiments were carried out by mixing procedure in glass reactor (volume 1 L) at O/A = 1:1 (300 mL of each) under heating of both phases up to 50 °C. Adjustment of pH was provided by incremental addition of NaOH. Mixing were carried out at 10 minutes in water bath to control temperature with electrode for pH control.

SX experiments under abovementioned conditions represented Ca and Mg removal ability, which should be definitely separated from Ni ions in sulphate aqueous phase. Figure 34 illustrates dependence of Ca extraction from pH under several listed concentrations of Versatic 10. Thus, extraction of calcium underwent positive effect during the increase of Versatic 10 share, reaching the peak at 40 %. A plateau of 30-40 % was observed at pH range between 4.5 – 5.5 in spite of the increase of Versatic 10 share in organics.

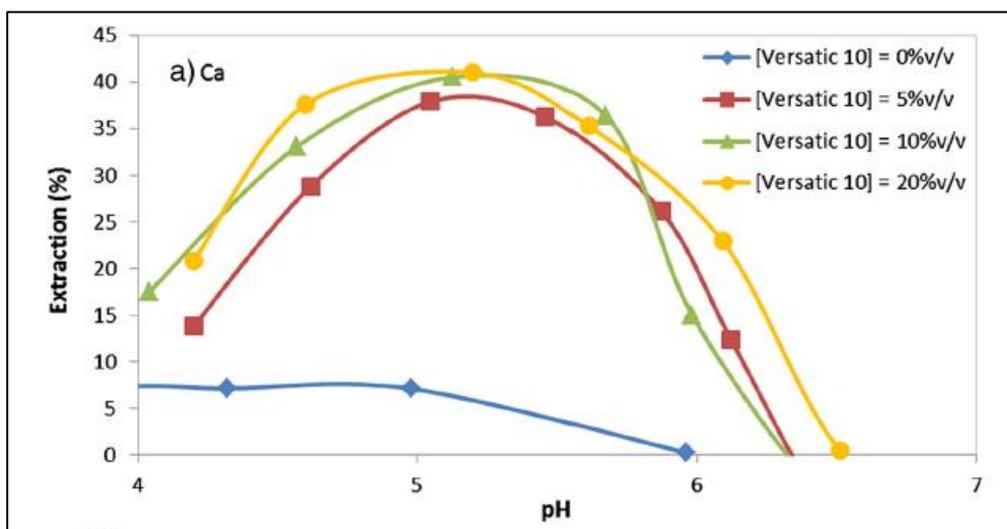


Figure 34. Effect of pH variation of Ca extraction under various neodecanoic acid concentration with 20 % v/v of Cyanex 272. Adapted from Guimaraes & Mansur, (2014)

According to Guimaraes & Mansur, (2014), analysis of Mg amount extraction pointed decremental influence of increase of neodecanoic acid concentration on Mg removal ability. Thus, at point of pH = 5.5 it decreased from 80 % to 46 % while using 5 % and 20 % Versatic 10, respectively, although absence of Versatic 10 in organics (0 % curve) did not rise the Mg extraction and the corresponded curve placed almost at same level as 10 %-curve (Figure 35).

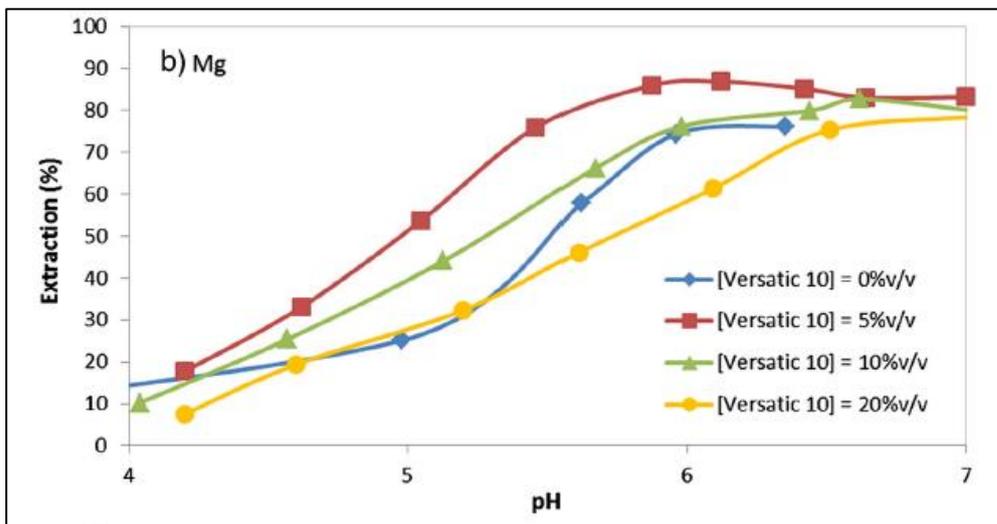


Figure 35. Effect of pH variation of Mg extraction under various neodecanoic acid concentration with 20 % v/v of Cyanex 272. Adapted from Guimaraes & Mansur, (2014)

Extraction of Ni (Figure 36) sharply rose after pH = 5 which coincides with Ca extraction drop starting from the same acidity value point. Hence, organic phase underwent scrubbing of Ca due to high content of Ni in aqueous phase compared to Ca ions content (initial concentration ratio of Ni/Ca – 150) (Guimaraes & Mansur, 2014).

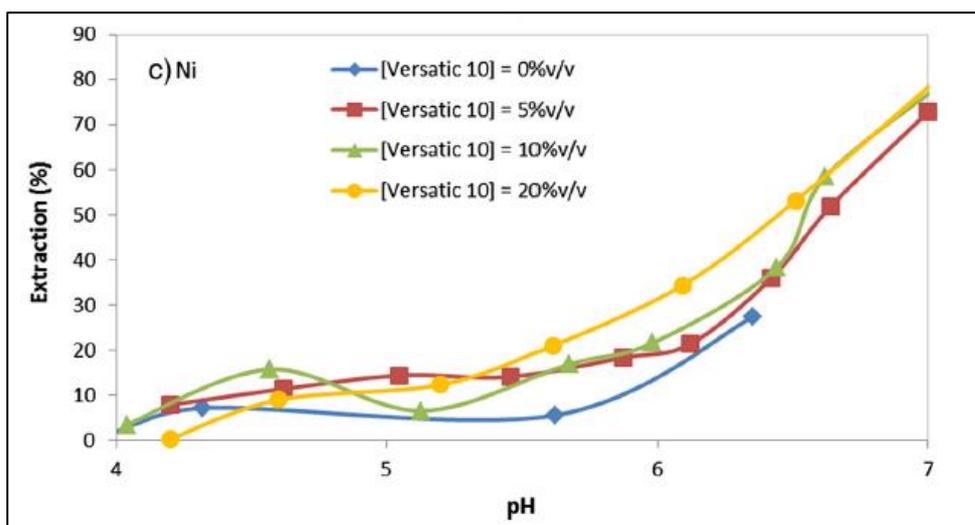


Figure 36. Effect of pH variation of Ni extraction under various neodecanoic acid concentration with 20 % v/v of Cyanex 272. Adapted from Guimaraes & Mansur, (2014)

Calculated separation factors (Table 9) of Ni/Ca and Ni/Mg helps to conclude that the target to separate impurities from sulphate solution is achievable under following conditions as [Cyanex 272] = 20 % v/v + [Versatic 10] = 10 % v/v at pH = 5.1 and [Cyanex 272] = 20 % v/v + [Versatic 10] = 20 % v/v at pH = 4.2. However, all selected parameters left the Ni extraction at relatively high level. 10 % of Versatic 10 and 20 % Cyanex 272 under pH 5.1 provides the optimal extraction of Ca and Mg at 40 %, even though 10 % of Ni removal is attained.

Table 9. Selectivity of Ca and Mg over Ni ions in sulphate solutions with Versatic 10. Adapted from Guimaraes & Mansur, (2014)

Concentration, % v/v	pH	$\beta_{Ca/Ni}$	$\beta_{Mg/Ni}$
5	4.2	1.9	2.5
	4.7	3.1	3.8
	5.1	3.6	6.9
	5.5	3.5	19
	5.9	1.6	27
	6.1	0.5	24
	6.4	-	10
	6.6	-	4.5
	7.0	-	1.8
	10	4.0	5.7
4.6		2.6	1.8
5.1		10	11
5.7		2.8	10
6.4		-	6.4
6.6		-	3.4
7.1		-	1.0
20	4.2	79	24
	4.6	6.1	2.4
	5.2	4.9	3.4
	5.6	2.1	3.2
	6.1	0.6	3.0
	6.5	< 0.1	2.7
	7.1	-	0.8

6 Alternative methods of nickel and cobalt purification

6.1 Oxidative precipitation

The process is considered as alternative way of impurities separation over Ni/Co and involve usage of various strong oxidants such as chlorine, ammonium persulphate, Caro's acid, ozone and pressured air (Burkin, 1987).

Chlorine oxidation for cobalt extraction demands high pH regulation for process optimization. It found the application by INCO and Falconbridge in Canada and by Jinchuan Group Ltd in China.

Electrolytically generated nickelic hydroxide is applied for cobalt removal from unpurified nickel solution, created by Outokumpu Oy in Finland (Flett, 1987). Production of Ni(OH)₃ is based on black Ni(OH)₂ electrolytic oxidation with subsequent mixing of nickel solution to precipitate the Co(OH)₃. In fact, the sedimentation contains the biggest part of nickel, which is removed by sulfuric acid processing to manufacture clean cobalt. The process is also occurred in Rustenberg Base Metal Refinery in South Africa.

Caro's acid oxidation technology involves the preparation of concentrated sulphuric acid from hydrogen peroxide and applied directly for metals removal in solutions of recycled NiCd batteries (Wyborn & McDonagh, 1996).

The ozone oxidation did not provide any commercial application, which can be explained by slow rate of reaction. The cobalt production may be accelerated by including sedimentation seeds. The process reaches the optimal separation at pH range 2.5 – 4.0 (Nishimura & Umetsu, 1992).

Precipitation of metals including the use of SO₂/O₂ or SO₂/air mixtures as an oxidant due to reduced costs in comparison with ozone or hydrogen peroxide. The process is mainly applied for manganese removal from nickel cobalt solutions attracting by simplicity and low-cost properties for Mn extraction from Ni-Co leach liquors (Menard & Demopoulos, 2007). The oxidation reactions were carried out at equations below (7-10):



The reaction occurred below pH = 7 at high redox potential to precipitate Mn to MnO₂ form. Reaction corresponds to pH range from 5 to 7 for Mn₂O₃ formation:



During the reactions, sulfur dioxide reacted with oxygen to form the sulfuric acid:



For acid neutralization hydrated lime was added to produce the gypsum:



According to the plotted diagram of Mn and Co precipitation in Figure 37, percentage as SO₂ changing, the optimal ration of extraction is reached at SO₂ part equals 3 % in air, corresponding

to the 13 % in O₂. It should be stated, that high SO₂/O₂ ratios lead to slow kinetics and the longer residence time is required for oxidation.

As it was discovered, the extent of Mn precipitation is directly depends on O₂ amount in the gas mixture. O₂ increase causes the growth of amount of Mn saturation due to slow kinetics under higher SO₂/O₂ ratios than optimal value (Mulaudzi & Mahlangu, 2009).

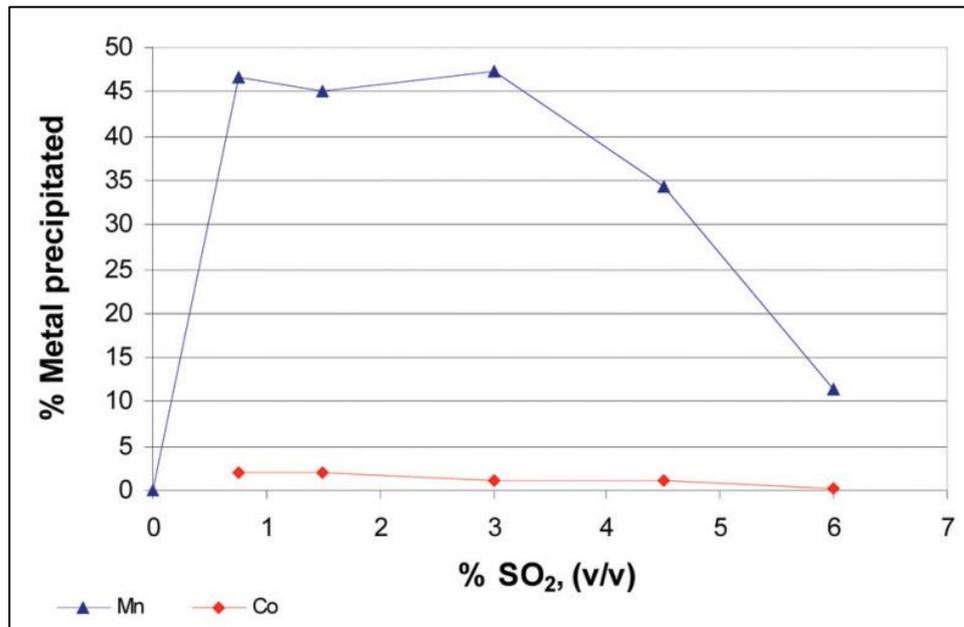


Figure 37. The influence of SO₂ concentration in air on Mn and Co precipitation. Adapted from Mulaudzi & Mahlangu, (2009)

The effect of pH in range 2-4 on Mn and Co sedimentation formation was investigated and illustrated in graph at Figure 38. It is noticeable that Mn and Co precipitation dynamic remained constant until value 3, however the sharp increase of precipitation was observed at range of pH from 3 to 4. This reports about independency of metals extraction from pH under 3. The loss of cobalt sedimentation is explained by increase of Mn production, hence the Mn sedimentation procedure should be adjusted to avoid the cobalt losses (Zhang, et al., 2002).

Listyawan et al., (2014) provided the study of iron removal (Initial Fe content – 20 g/L) from nickel sulphate leach solution by precipitation method using sodium hydroxide additive under atmospheric pressure, elevated temperature (95 °C). Changing pH value was tested for determination of optimal acidity for highest Fe separation over Ni-sulphate liquor. Incremental of pH occurred as follows: 1.3, 1.9, 2.7 and 3.5. Current research provided the oxidative precipitation experiments for Mn removal (Initial Mn content – 3.6 g/L) via application of hydrogen peroxide reagent and permanganate solution to oxidize Mn ions to Mn dioxides under 50 °C.

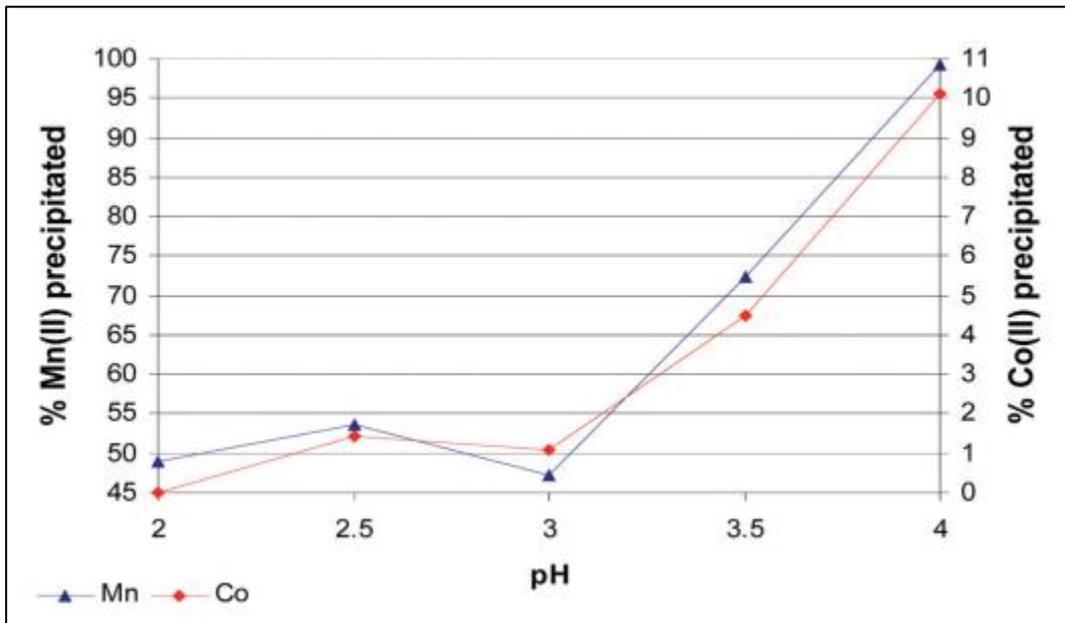


Figure 38. Percentage of Mn and Co precipitation dependency from pH varying. Adapted from Mulaudzi & Mahlangu, (2009)

Experimental results of iron precipitation contain the outcome that the decrease of acidity leads to increase of the iron precipitated. Based on Figure 39, which represents the amount of precipitated iron during the increment of pH value, it was observed that by 2.8 pH point the amount of iron in sulphate phase dropped from 20 g/L to 0.25 g/L and reached 98.7 % of total extraction, approximately. Proceed of acidity decrease resulted in 0.075 g/L of Fe concentration at pH = 3 in aqueous phase, thereafter equilibration of pH = 3.21 Fe was removed completely.

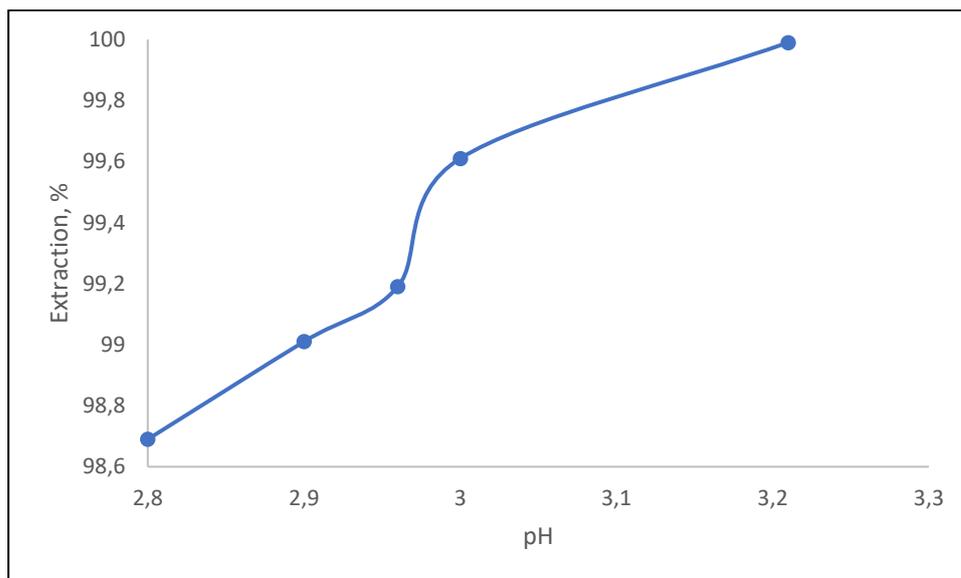


Figure 39. Dependence of precipitated Fe percentage from acidity. Adapted from Listyawan et al., (2014)

During Fe removal via precipitation, partial Ni removal from aqueous solution occurred, increased with acidity reduction, which is explained by co-extraction during the Fe hydrolysis process. Thus, by pH increase up to 3.2 Ni losses are estimated already at 4 %. As acidity decrease occurred beyond the pH = 3.2, Ni ions started to leave the solution, reaching the 32 % of total losses (68 % of retention in solution) at pH = 4.8 (Listyawan, et al., 2014).

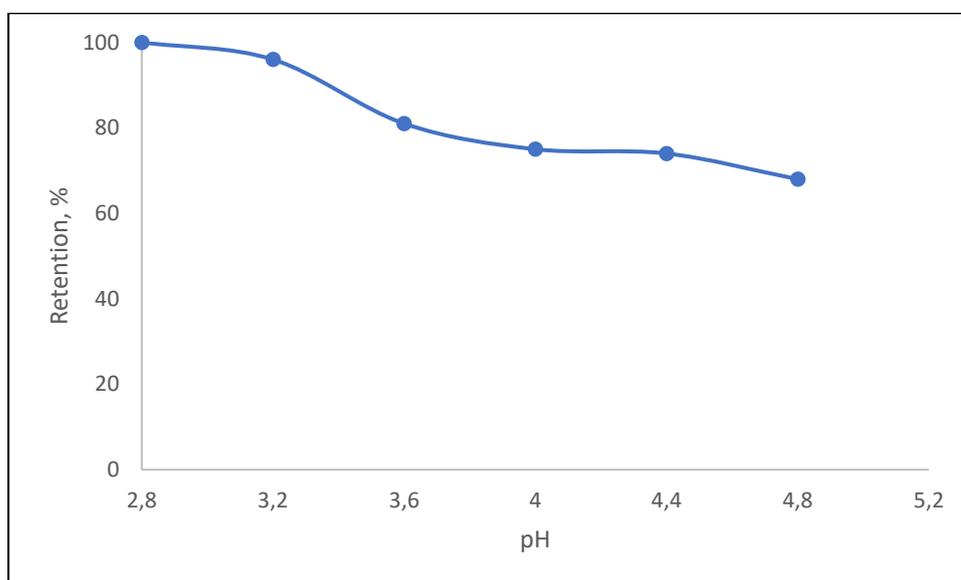


Figure 40. Nickel retention in aqueous phase vs. pH value during iron precipitation experiments.

Adapted from Listyawan et al., (2014)

As conclusion, proposed process implementation directly depends on tolerance of target Fe removal and Ni loss. The optimal acidity value for iron removal by precipitation from sulphate solutions equals 3.0, while Ni losses are almost neglected (less than 1 %) and Fe precipitation achieved 99.5 %, approximately.

At the same research, along with iron separation, manganese precipitation process was observed

6.2 Selective sorption using chelating ion exchange resins

The other alternative to the widespread solvent extraction of metals after high pressure leaching is the ion exchange technique, which suggested the productive and economical manufacturing of recovered Ni and Co from pregnant leach solutions (Kotze et al., 2001). Furthermore, considered technology possesses reduced environmentally loading including decreased water consumption and the presence of water retreatment facilities. The economic advantages contain low capital and

operating cost, moreover the technology provides relatively high selectivity and separation ability resulted at high quality of metal recovery (Zontov, 2001).

Chelating resins mechanism was created to achieve selectively adsorption of desirable metal ions by means of formation strong bonds between resins and metals (or chelates). There are several commercially produced ion exchange resins for nickel and cobalt recovery, which are listed in Table 10.

Table 10. Several commercially available ion exchange polymeric resins used for Ni and Co purification. Adapted from Mendes & Martins, (2004)

Resin	Manufacturer	Functional group	Matrix
Dowex M4195 [®]	Dow Chemical	Bis-picolylamine	Macroporous styrene divinylbenzene
Amberlite IRC748 [®]	Rohm and Haas	Iminodiacetic acid	Macroporous styrene divinylbenzene
Ionac SR-5 [®]	Sybron	Iminodiacetic acid	Macroporous styrene divinylbenzene
S 930 [®]	Purolite	Iminodiacetic acid	Macroporous styrene divinylbenzene

The first position in the table, Dowex M4195[®] exploited the mechanism of complexes formation between metals and free electron pair-bearing nitrogen atom, while the other representatives of commercial resins present convenient chelating functional group (iminodiacetic acid).

Partial resin sorption of Al, Mg, Mn, Cu and Zn (1 g/l of each) over Ni/Co in sulphate liquid was studied by Mendes & Martins, (2004), who involved performance of four resins, listed in Table 10 at quantity of 1 g for each batch test, according to the main parameters such as time, pH and initial concentration of desirable metals. The all listed models were tested at different acidity conditions in order to determine the most appropriate resin for impurities removal. The experiments were carried out by taking 50 mL of aqueous solution mixing with 1 g of resin in 250 mL flask under 200 rpm of rotation velocity at 25 °C for 24 h to reach the completed reaction. The opportunity to remove all metals from solution was investigated for all listed resins and visualized at plotted charts.

Figure 41 demonstrates the results of sorption of metals, where the highest Cu selectivity over other metals was clearly visualized. Acidity value played the main role of removal percentage regulator, while pH reducing to 1 guided to Cu recovery decrease. The copper recovery template

is also applicable for other metals, however all of them, except Ni, was extracted not higher than 20 % of total amount. Amberlite IRC 747 and SR-5 demonstrated the most effective recovery, however still inefficient of Mn and g separation over Co due to low selectivity. Ni selectivity over other metals achieved better results, although earlier Ni recovery than impurity metals does not correspond to the targets, which requires Ni remaining in sulphate phase.

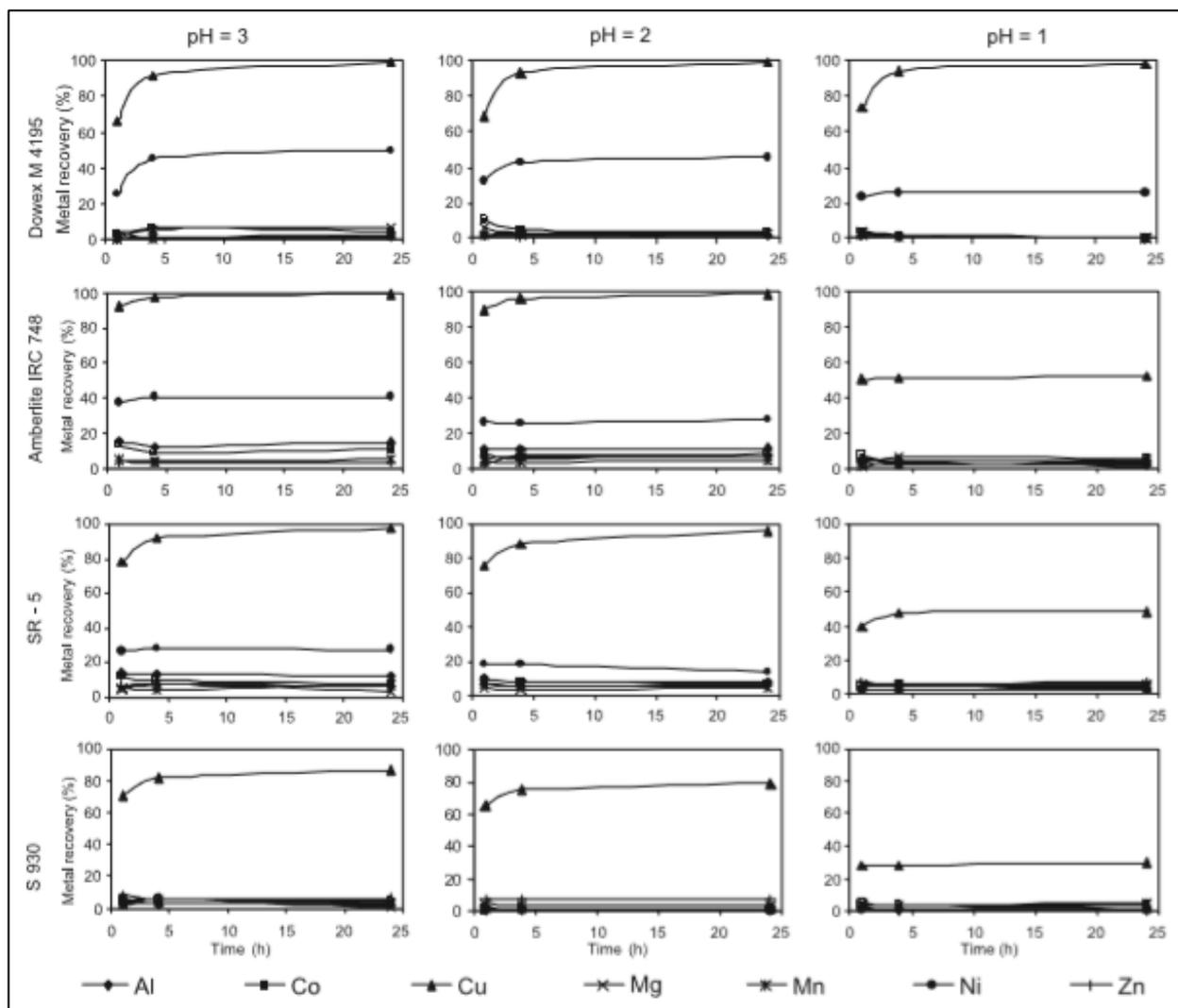


Figure 41. Sorption performance of resins for different metals. Adapted from Mendes & Martins, (2004)

All suggested resins were accurately tested separately to check individual properties and recovery ability. Thus, Dewax M4195 was tested under pH incremental variation from 1 to 4 at 24 hours. As performed in Figure 42, the highest selectivity is reached at the highest pH value, however the extraction order was remained as follows: Cu > Ni > Co (Mendes & Martins, 2004). As it was said, the obtained results do not meet the aims of research to remain Co/Ni in solution at the same time recovery all contaminating metals. Hence, Dewax M4195 is not applicable for purification of Ni/Co sulphate solution in frames of current research.

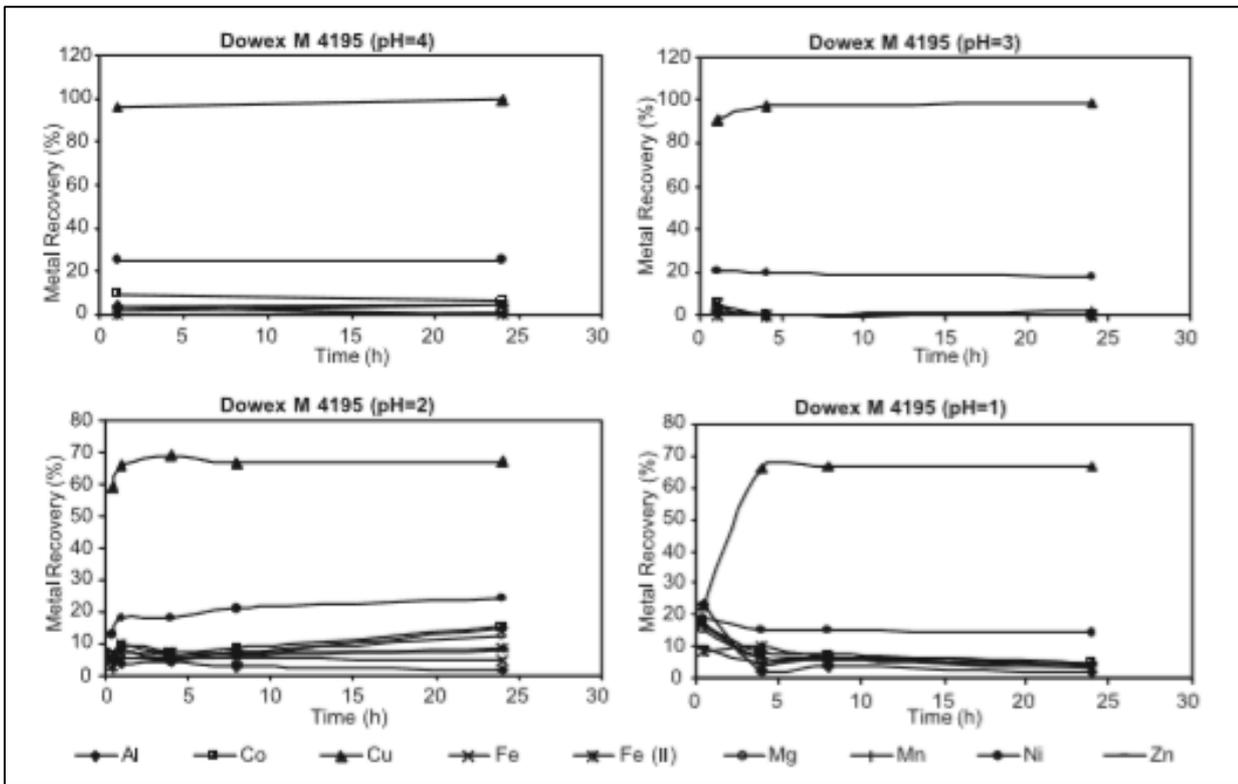


Figure 42. Recovery ability of Dowex M4195. Adapted from Mendes & Martins, (2004)

Amberlite® 748 was investigated as well for its extraction ability under acidity variation. As shown in Figure 43, the recovery of all target metals reaches less than 10 % of all amount. During the pH increase, copper extraction obtained 100 % mark, while Ni and Co rised up to 30 and 15 %, respectively (Mendes & Martins, 2004).

Amberlite® IRC747 is a styrene divinylbenzene copolymer (-CH₂-NH-CH₂-PO₃Na₂) as alternative for Ca and Mg removal over Ni/Co, having macroporous structure and aminophosphonic groups, forming complexes with metal ions and producing free sodium ions (Lenntech, 2019):



where M²⁺ - metal ions.

The relative affinity for cations of described resin is as follows: Zn²⁺ > Mg²⁺ > Ca²⁺ > Ni²⁺ > Co²⁺. In addition, the resin can operate at various media as neutral, alkaline and acidic conditions, where cations sorption corresponds to concrete pH values as Zn²⁺ - 2.5, Ca²⁺ - 3, Mg²⁺, Ni²⁺, Co²⁺ - 4.5 (Lenntech, 2019).

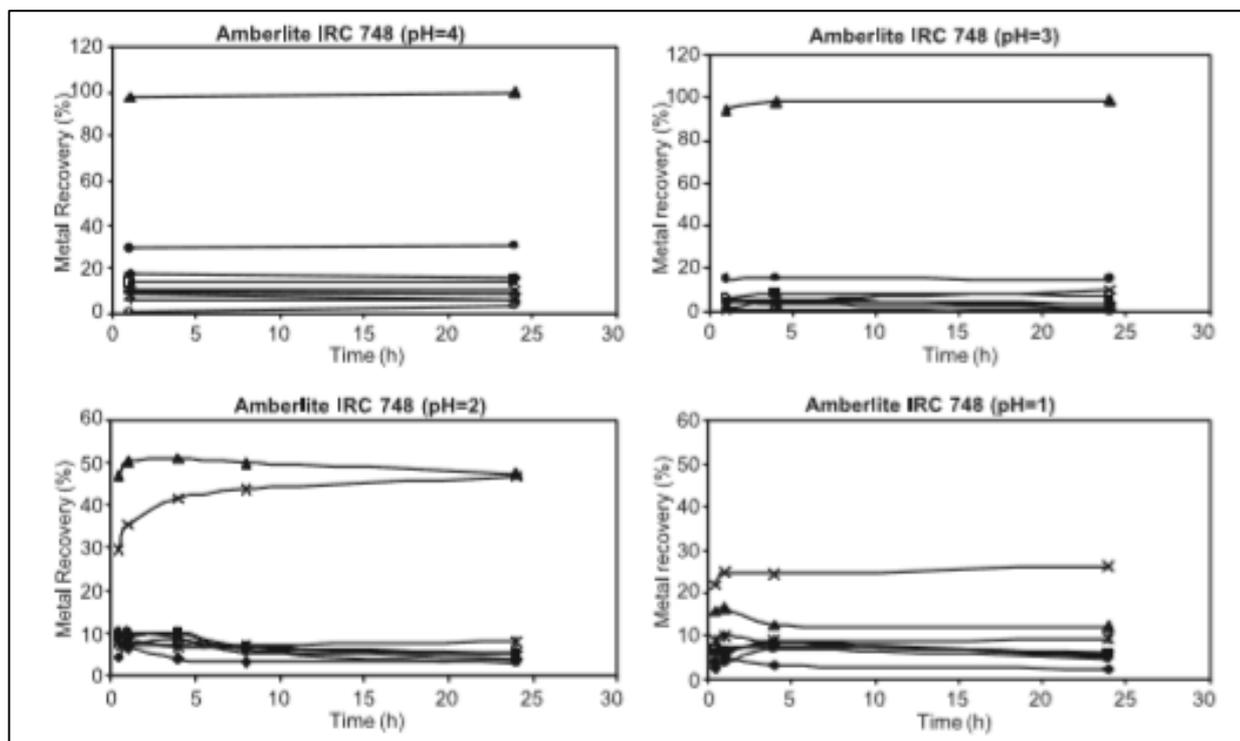


Figure 43. Recovery ability of Amberlite® IRC748. Adapted from Mendes & Martins, (2004)

Figure 44 illustrates the dynamic of metals sorption by commercial product Ionac SR-5® at pH values from 1 to 4 (Mendes & Martins, 2004). Acidity value 1 and 2 is characterized by relatively high Fe retention with high selectivity of one over other metals followed by Cu ions. Recovery other metals at the same pH remained under 10 %, while after pH increase to 3 Cu sorption percentage reached almost 100 %, however amount of extracted iron decreased even though remaining higher level than Ni sorption. At pH = 4 the resin becomes mostly selective for Ni and Co, 24 and 15 %, respectively, leaving the impurities in sulphate phase.

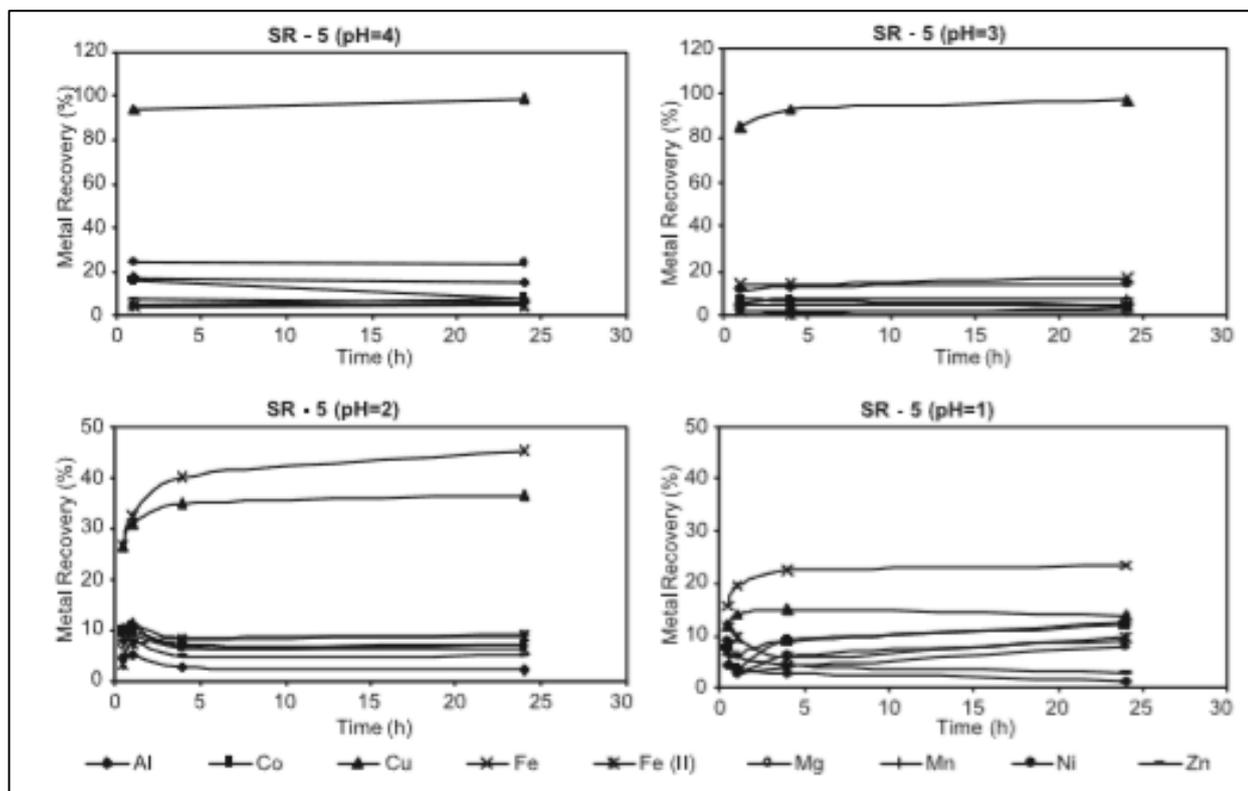


Figure 44. Recovery ability of Ionac SR-5[®]. Adapted from Mendes & Martins, (2004)

Figure 45 demonstrates sorption process of commercial resin S 930[®] which reports about high selectivity of Cu, while other metals remained under 10 %. Hence, the resin is not applicable for impurities removal due to extremely low uptake percentage of impurity metals.

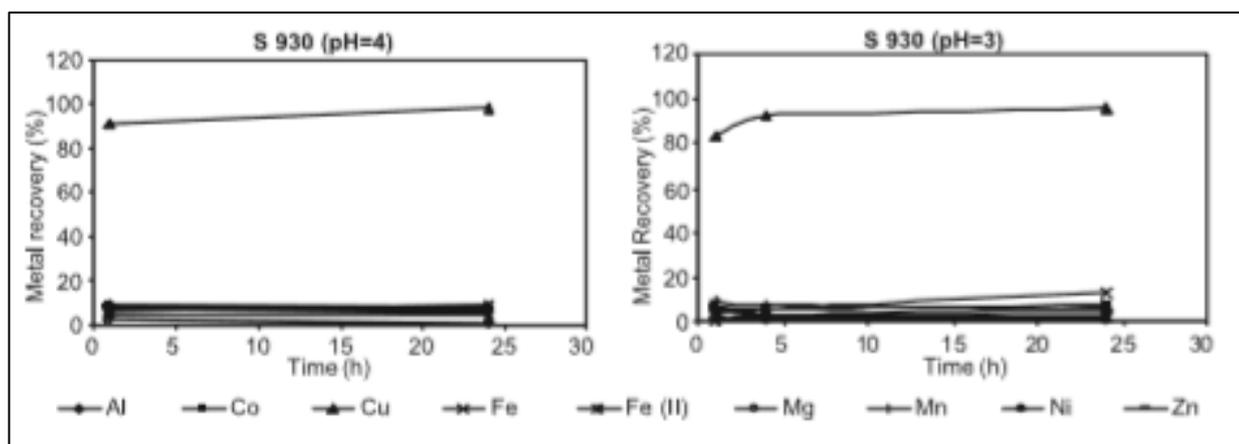


Figure 45. Recovery ability of S 930[®]. Adapted from Mendes & Martins, (2004)

After the metal sorption to chelating resin, the metals should be removed at elution procedure. The elution of commercial resins saturated by metals was carried out by sulfuric acid, ammonia hydroxide and hydrochloric acid and the outcomes of metals extraction were combined in Table 6. In comparison of elution agents for Dowex M4195[®], HCl removes more nickel but less iron and cobalt than H₂SO₄. Nevertheless, NH₄OH removes the biggest part of copper at Dowex M4195[®]

elution under pH = 4, however it was not efficient in removal of other metal from Dowex M4195[®] resin.

NH₄OH did not show the effective elution for Amberlite IRC 748[®] resin as well. The best results provided sulphuric acid processing of Amberlite IRC 748[®] removed the highest amount of nickel cobalt and other metals (except zinc) (Mendes & Martins, 2004).

Table 11. Elution results for the resins loaded at pH 4. Adapted from Mendes & Martins, (2004)

Share, %	Al	Co	Cu	Fe	Mg	Mn	Ni	Zn
Dowex M4195 [®] (1 M H ₂ SO ₄)	8.8	64.3	49.7	88.7	10.0	6.7	78.2	100
Dowex M4195 [®] (1 M NH ₄ OH)	9.2	5.3	82.1	54.7	44.7	0.5	46.2	100
Dowex M4195 [®] (1.6 M HCl)	na	29.81	na	10.1	na	na	96.4	na
Amberlite IRC 748 [®] (1 M H ₂ SO ₄)	80.7	100	100	100	66.5	39.4	100	98.9
Amberlite IRC 748 [®] (1.6 M HCl)	85.9	61.4	100	100	21.1	35.9	96	100
Amberlite IRC 748 [®] (1 M NH ₄ OH)	na	0.1	na	0.01	na	na	0.1	na
Ionac SR-5 [®] (1 M H ₂ SO ₄)	65.2	88.4	100	69	48.1	48.1	100	100

Generally, all resins proposed relatively high selectivity of copper over impurity metals, while Ni were extracted at even higher quantities than Zn, Mg, Al and Mn which reports about weak ability of suggested resins to purify Ni/Co sulphate solutions. However, proposed product Amberlite[®] IRC747 owns promised quality of Mg and Ca separation over Ni and Co, thus the resin can be counted as possible solution of Mg separation problem.

EXPERIMENTAL PART

Experimental part of the thesis includes description of laboratory scale experiments of extraction procedures and provides information about experimental methods, performance and results.

7 Aims and the content of the experimental part

The main objective of the experimental part was to investigate separation process for removal of metal impurities from nickel-cobalt sulfate solution. After production of nickel via hydrometallurgical process, solution usually contains attached cobalt due to similarity of nickel and cobalt chemical structures. However, before cobalt nickel-cobalt separation, solution had to be purified from other metal impurities occurred in Ni-Co solution, such as aluminum, manganese, iron, magnesium copper, calcium and zinc. Research part includes series of solvent extraction experiments using organic extractants to remove impurity ions as sulfate salts. Experimental part also described experimental performance of ion exchange resin sorption, using for magnesium ions separation over cobalt and nickel.

8 Materials

According to the made literature search, it was decided to apply di-2ethylhexyl phosphoric acid for extraction. Due to high viscosity of selected extractant, the diluent kerosene Exxsol™ D80 was added to upgrade properties of solvent.

For preparation of aqueous solution with definite metal ions concentrations, there were used range of sulphate salts listed in Table 12.

Table 12. Salts used in experiments

Salts	Metal ions	Ion concentration in WP1 solution, g/l	Ion concentration in WP2 solution, g/l
NiSO ₄ ·6H ₂ O	Ni ²⁺	40	40
CoSO ₄ ·7H ₂ O	Co ²⁺	10	10
MnSO ₄ ·4H ₂ O	Mn ²⁺	10	5
MgSO ₄ ·7H ₂ O	Mg ²⁺	-	10
Al ₂ (SO ₄) ₃ ·18H ₂ O	Al ²⁺	1	-
ZnSO ₄ ·7H ₂ O	Zn ²⁺	-	1

$\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$	Fe^{3+}	1	0.1
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Ca^{2+}	-	0.5

9 Equipment

Experiment was carried out in glass vessel with 1000 ml volume. Experiments were performed in batch mode using 4-blade impeller connected with electronic stirrer Heidolph RZR 2050. Acidity adjustment was done by addition of ammonia gas to the mixture measuring by Consort C833 pH-meter. Temperature control was organized by Lauda Eco E 4 at keep temperature at 23 °C for all experiments. Baffles was placed for providing better mixing in vessel (Figure 34).

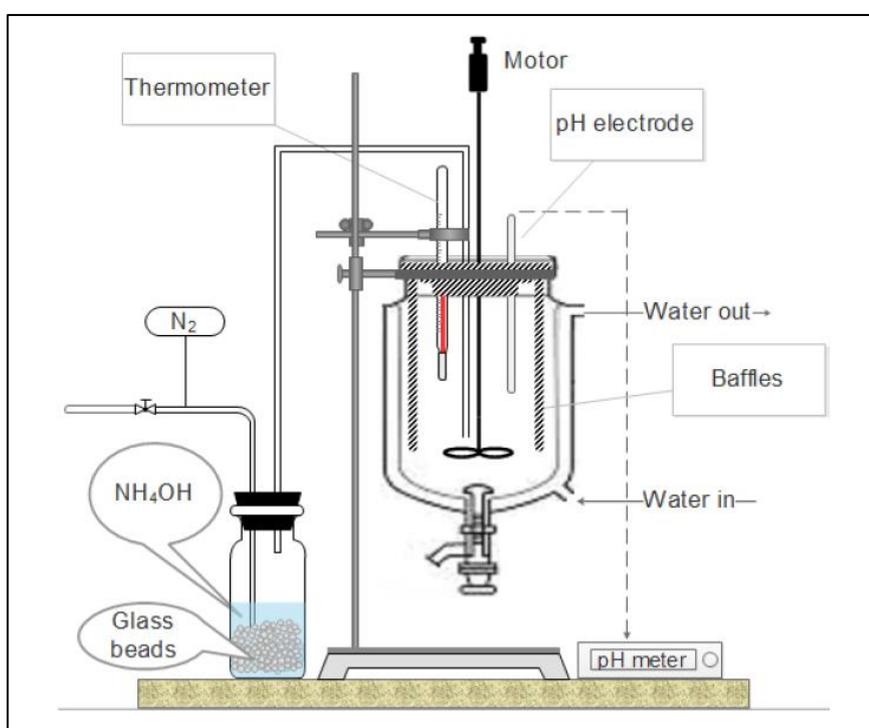


Figure 46. General scheme of laboratory facility

10 Methods

Experimental methods were divided at experiments providing batch tests for plotting pH isotherm, loading isotherm and pseudo counter-current experiments.

First experimental step occupied preparation of WP1 and WP2 solutions including ion composition according to the Table 12. Prepared solutions were filtered to prevent penetration of sediments and undissolved particles to the vessel. Chemical ICP-analysis of prepared feed solutions were performed with representing of real composition in Tables 13-20. Used extractant was mixed with

kerosene to get solvents with 0.6 M and 1 M concentrations. The first series of experiments included determination of appropriate D2EHPA concentration containing the results for pH isotherm. pH isotherm experiments included mixing of organic-aqueous solution in vessel until acid equilibration of mixture (fixed pH value) and then, further incremental increase of pH by ammonia gas at 0.2-0.3 value.

After sampling of both phases in each pH change, the organic samples underwent stripping by 5 M hydrochloric acid and was shaken at 20 min to transfer extracted metals to the aqueous phase for analysis. All collected samples were diluted with DF = 10000 and underwent analysis in Agilent 7900 ICP-MS (Inductively Coupled Plasma Mass Spectrometry) using argon plasma.

RESULTS AND DISCUSSION

11 pH isotherm experiments

11.1 D2EHPA concentration

As it is mentioned earlier, WP1 solution was prepared according to the Table 12 and contained following amount of dissolved metal ions with slightly different concentrations (Table 13).

Table 13. Chemical analysis of composition of WP1 feed solution

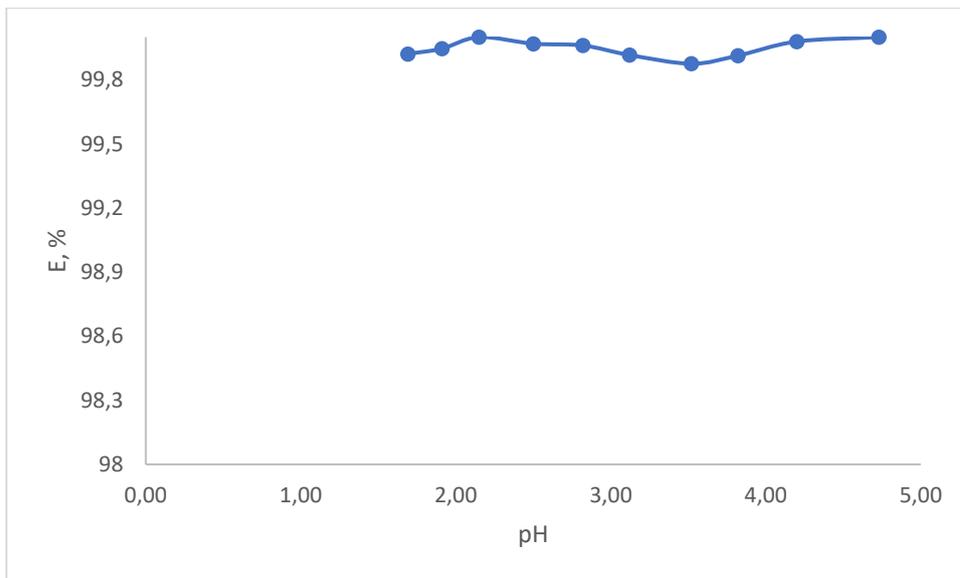
Ions	Ni ²⁺	Co ²⁺	Fe ³⁺	Mn ²⁺	Al ²⁺
Concentration, g/L	41.19	10.30	1.036	10.28	1.39

For the first step of the experiments belongs to comparison of performance of two D2EHPA concentrations 0.6 M and 1 M. Organic-aqueous ratio equaled 1:1 and the volumes of both phases were taken 400 ml of each. Rotation speed was taken uniform for all experiments and was maintained at 200 rpm. Grow of pH was adjusted step-by-step method from equilibration value up to 4.7 roughly and was the sampling were done at fixed pH points as follows in Table 14.

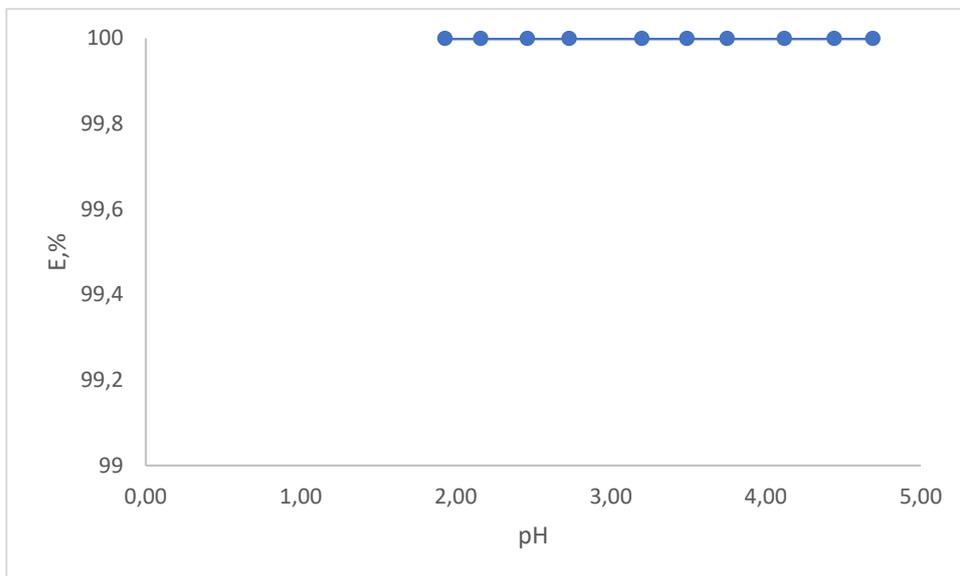
Table 14. Numbers of pH of aqueous phase for both experiments with 1 M and 0.6 M organics for WP 1 solution

1 M organic test	1.69	1.91	2.15	2.5	2.82	3.12	3.52	3.82	4.2	4.73
0.6 M organic test	1.93	2.16	2.46	2.73	3.20	3.49	3.75	4.12	4.44	4.69

Both organics solutions successfully remove iron over aqueous phase already at starting values of pH, which is clearly shown in Figure 47a,b.



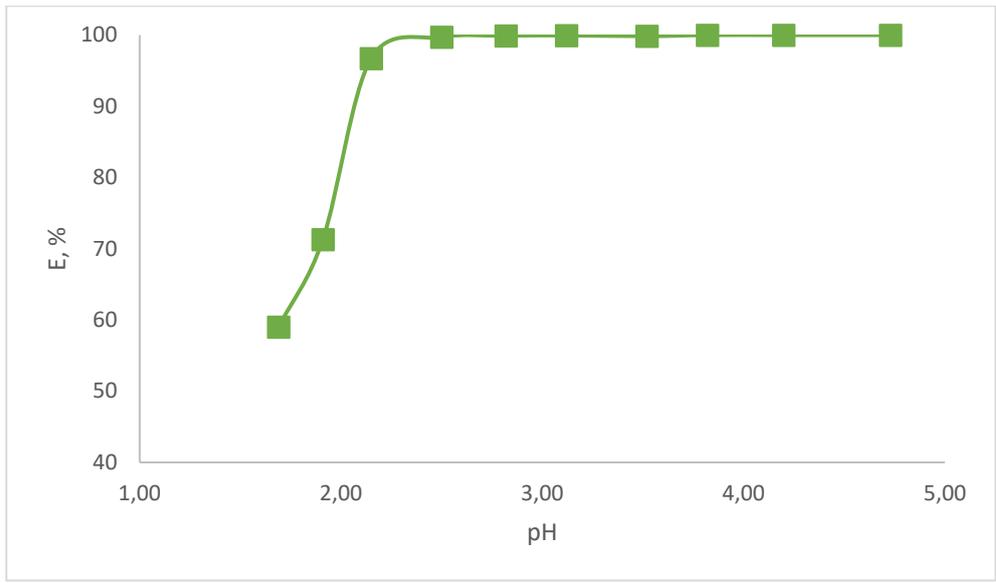
a)



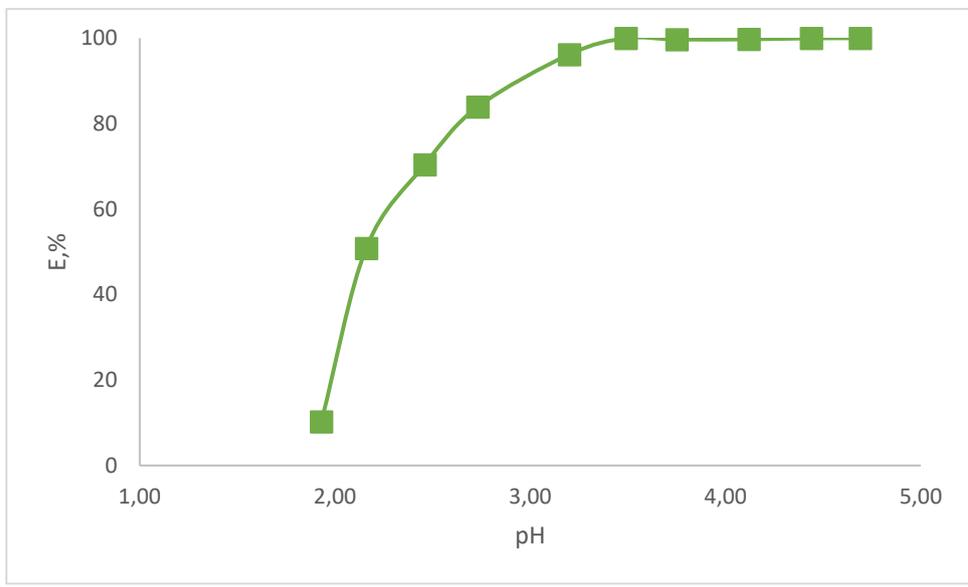
b)

Figure 47. Iron extraction during the pH change: a) 1 M D2EHPA b) 0.6 M D2EHPA

Aluminum extraction shown the total removal of one, however 1 M organic started removal from 60 % and reached the 100 % even at pH = 2.5, while for the 0.6 M organic pH = 2.5 corresponds to 60 % of removal and reaches 100 % extraction at pH = 3.5 (Figure 48a,b).



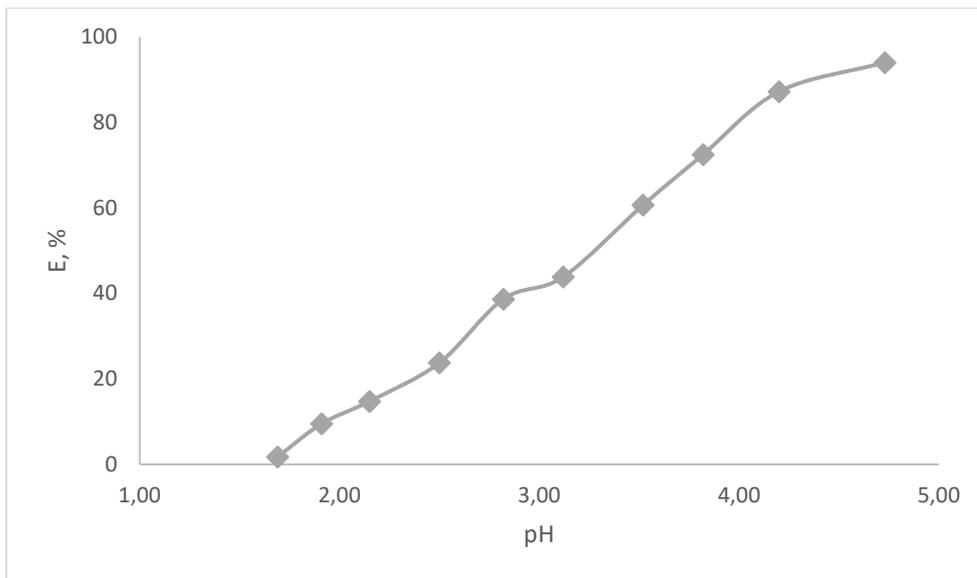
a)



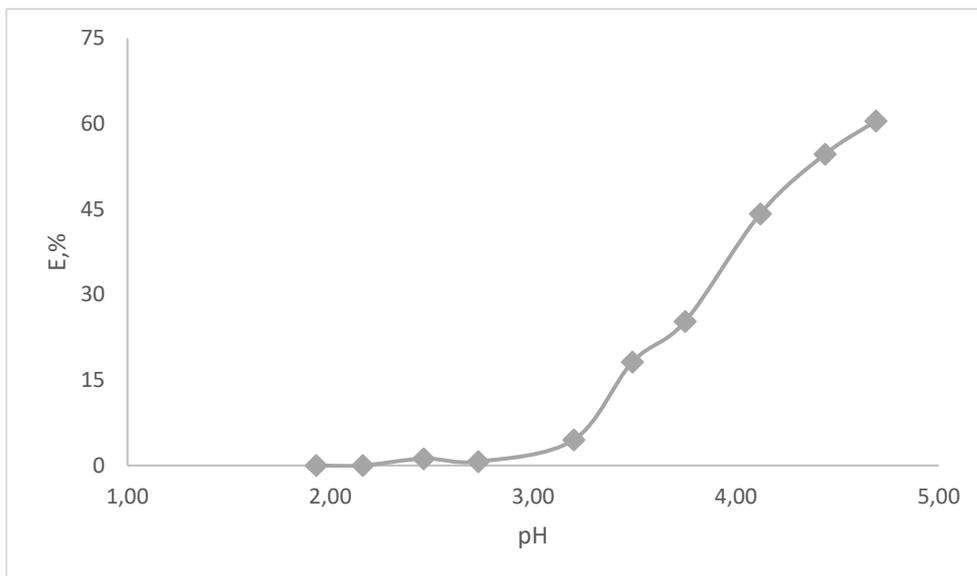
b)

Figure 48. pH loading isotherm for Al removal: a) 1 M D2EHPA b) 0.6 M D2EHPA

The highest manganese extraction efficiency belongs to 1 M D2EHPA reaching 60 % of total extraction amount at pH = 3.5 and climbing up to 90 %, while 0.6 M D2EHPA reaching 60 % only at the end of pH range (Figure 49a,b).



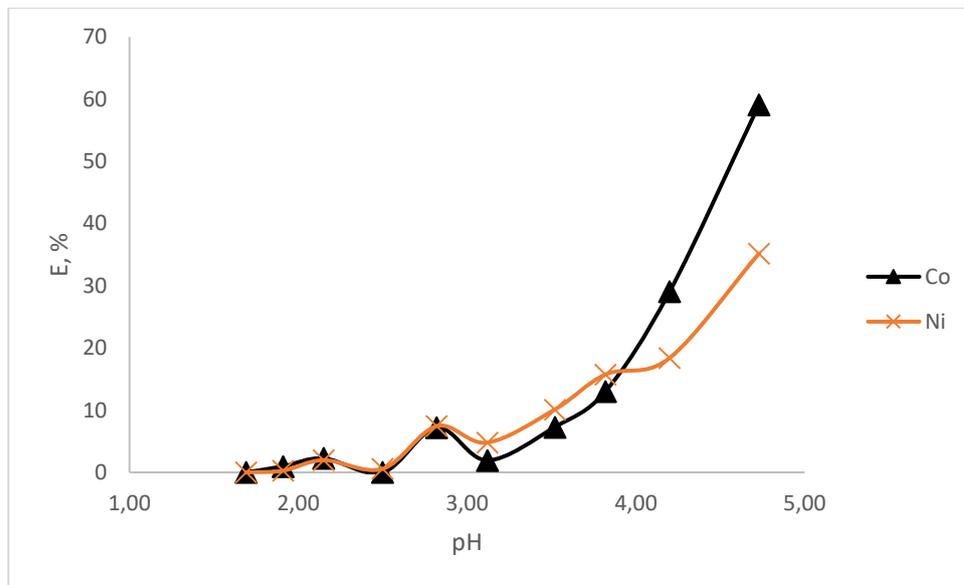
a)



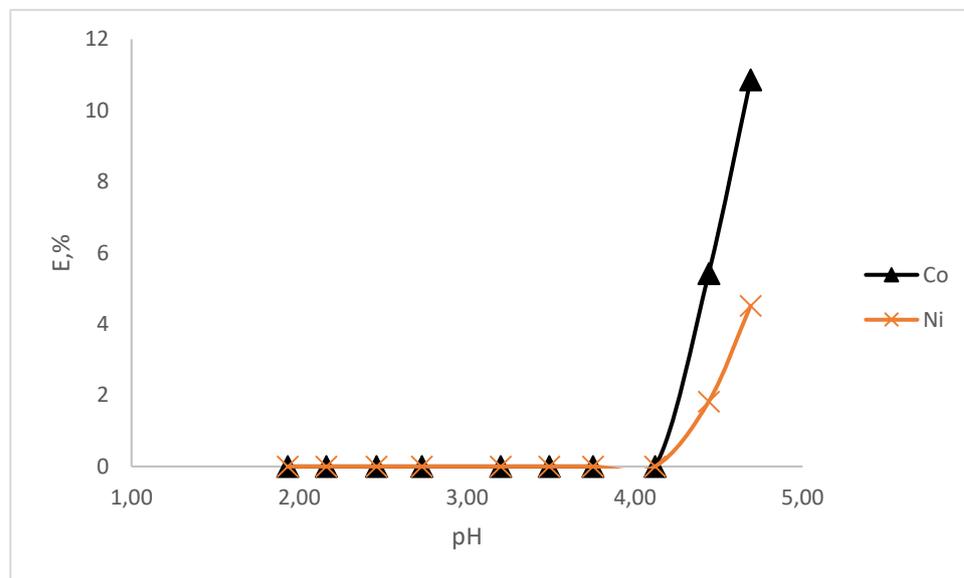
b)

Figure 49. pH isotherm of manganese extraction: a) 1 M D2EHPA b) 0.6 M D2EHPA

Although, extraction of cobalt and nickel becomes undesirable process, which has to be reduced as much as possible. Thus, 0.6 M shown less extraction percentage of these elements and became more effective in terms of nickel and cobalt remaining in aqueous phase (Figure 50a,b).



a)



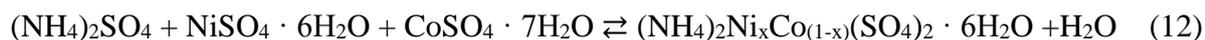
b)

Figure 50. pH isotherm of Ni-Co extraction: a) 1 M D2EHPA b) 0.6 M D2EHPA

According to the abovementioned data description organic solvent 1 M much more effective than 0.6 M due to higher affinity of iron, aluminum and especially manganese. Nickel and cobalt partial extraction reaches almost 35 % and 60 % respectively, consequently the pH range 3.5 – 4.5 was assumed as much appropriate for loading isotherm experiments and pseudo counter-current experiments, taking into account good extraction extent of manganese (90 % in the last point). However, the noticeable co-extraction of Co ions along with Mn ions required extra measures for decrease of Co amount by implementation of scrubbing procedure, for instance, hence additional tests of scrubbing are required.

In addition to the digit data, there were other visual changes during the experimental process. Firstly, during the incremental grow of pH the organic phase started to change its color drastically from dark green to the intensive blue one. Described effect can be explained by transfer of cobalt to the organic at relatively high pH where cobalt extraction starts. Moreover, organic phase underwent increase of viscosity during the pH growth. It can be assumed that mentioned phenomenon is the consequence of extractant saturation by cobalt likewise.

Turquoise sedimentation in aqueous phase at the end of pH increase is another consequence from extraction process, which reports, about presence if nickel-ammonia double sulphate salts in loaded organic going to precipitate due to pH rise afterwards. That phenomenon was earlier described by Ghosh et al., (2018), reporting about turquoise precipitate is known as Tutton's salt, isomeric hydrated complexes with empirical formula $M_2M'(SO_4)_2 \cdot 6H_2O$, where $M - S, K, NH_4, Rb, Tl$; $M' - Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, V, Zn$. Reaction of Ni-Co Tutton's salts formation is provided below (equation 12):



Collected samples for visualization of described phenomena are shown in Figure 51.



Figure 51. Samples of aqueous (left) and organic (right) phases after the extraction procedure

11.2 WP2 authentic solution

Solution WP2 contained more elements, including zinc and magnesium, where the composition is as follows in Table 15, while equilibrium pH values for sampling of organic and aqueous phases were as follows: 1.70; 2.08; 2.37; 2.54; 2.89; 3.28; 3.54; 4.01; 4.45 and 4.89.

Table 15. Chemical analysis of composition of WP1 feed solution

Ions	Ni ²⁺	Co ²⁺	Fe ³⁺	Mn ²⁺	Zn ²⁺	Mg ²⁺	Ca ²⁺
Concentration, g/L	31.22	7.61	0.077	3.87	0.79	7.92	0.34

Experimental method used for WP1 solution identically applied for experiments with WP2. Parameters of mixing remained identical, where O/A = 1:1, $T_{\text{reaction}} = 23\text{ }^{\circ}\text{C}$, $N = 200\text{ rpm}$. The range of acidity adjustment started from 1.7 and stepwise changed until upper boarder 4.9, considering pH of feed aqueous solution equaled 3.14. At the end of data treatment, the plot combining extraction isotherm for all metals was constructed and illustrated in Figure 52.

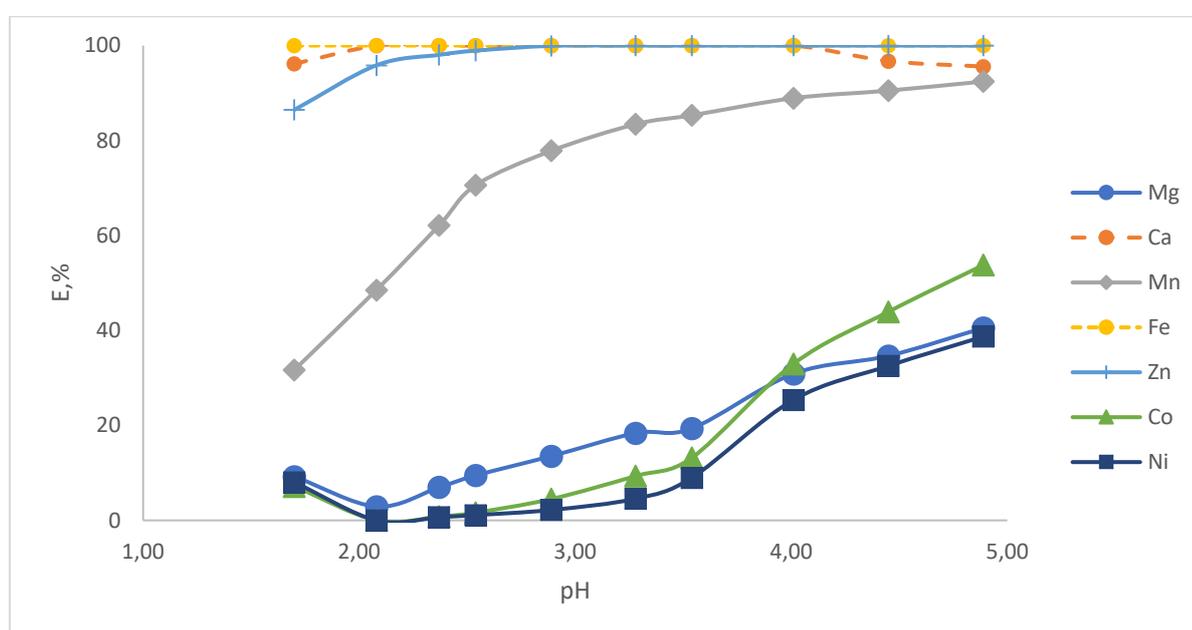


Figure 52. pH isotherm for ions extraction over WP2 solution

Illustrated chart represent high extent of zinc, iron and calcium extraction leaped from 80 % to 100 %. Manganese removal performed steady growth up to 90 % and seemed to be quite satisfactory. Selectivity of manganese over nickel and cobalt at pH 3.5 demonstrated sufficient selectivity, keeping the Co and Ni extraction under 20 % and rejecting manganese higher than 80 %.

However, magnesium removal exposed unacceptable results of selectivity, extracting simultaneously with nickel and cobalt, which is proved by close isotherms. Hence, the additional treatment of solution is required to ensure more effective Mg extraction, maintaining Ni and Co in the aqueous phase.

12 Loading isotherm experiments

The extraction isotherm represents the ratio of the increasing concentration in the organic phase to the limiting concentration in the aqueous phase.

For experiments were taken O/A starting in the range 1:10 and rising to 2:1 incrementally adding 1/10 or 20 ml of organic to the mixture. Experiment started from 200 ml of aqueous phase and 20 ml of organic phase. Each growth of organic amount was equilibrated in vessel by controlling pH and sampled. Loading isotherm experiments were performed for fixed pH value such as 4.5, 4.0 and 3.5. Therefore, each element would have three plots of O/A distribution. In Figures 53-55 are illustrated loading isotherms for all metal ions.

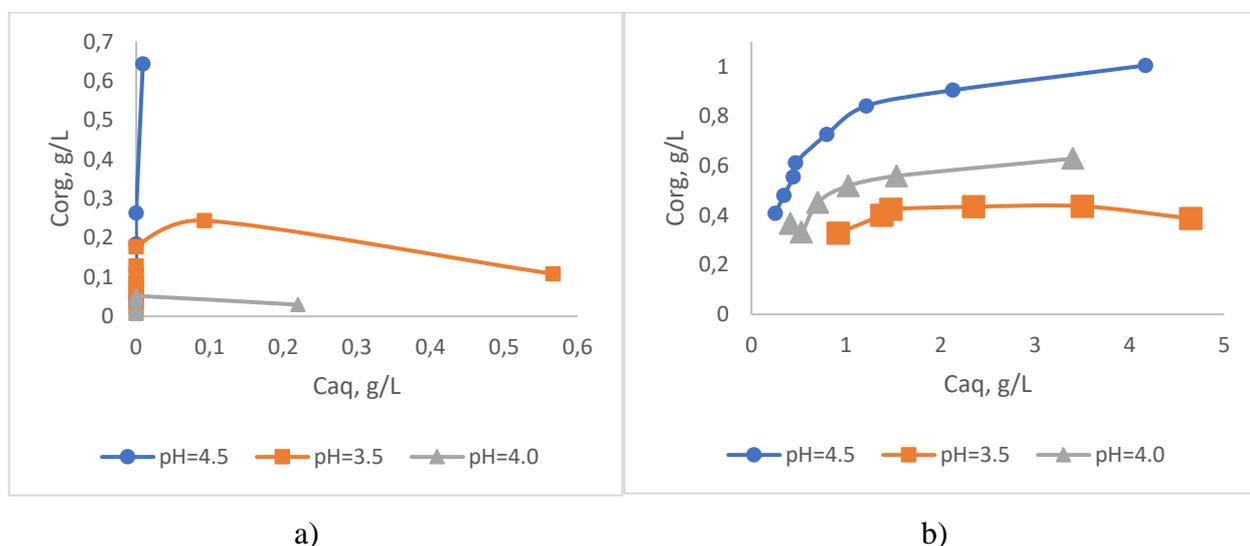


Figure 53. Loading isotherms for: a) Al and b) Mn

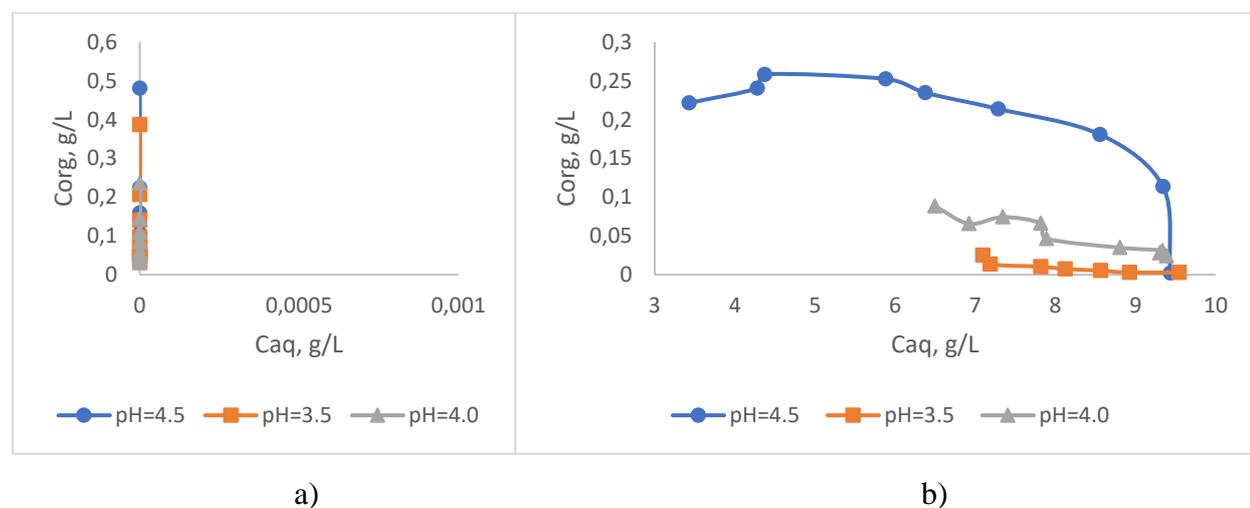


Figure 54. Loading isotherms for: a) Fe and b) Co

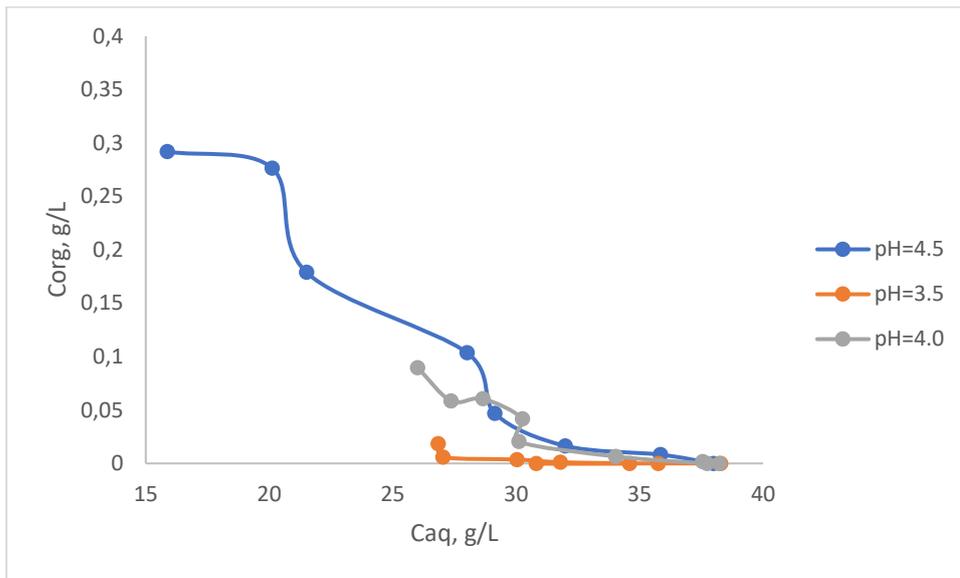


Figure 55. Loading isotherms for Ni

Obviously, lower acidity conditions support the growth of ion transfer to organics and represent higher loading of one than lower pH values. That fact suitable to the aims of research to remove impurities, but negatively affects as co-extraction of nickel and cobalt.

After processing of data McCabe-Thiele method was applied to determine the minimum number of theoretical stages to obtain the removal of residues from the solution (Figures 56a,b and Figure 57). It was decided to select two stages in further pseudo counter-current process. Evidentially, that Fe and Al extraction did not require 2-stage extraction, while they were separated almost right after extraction started.

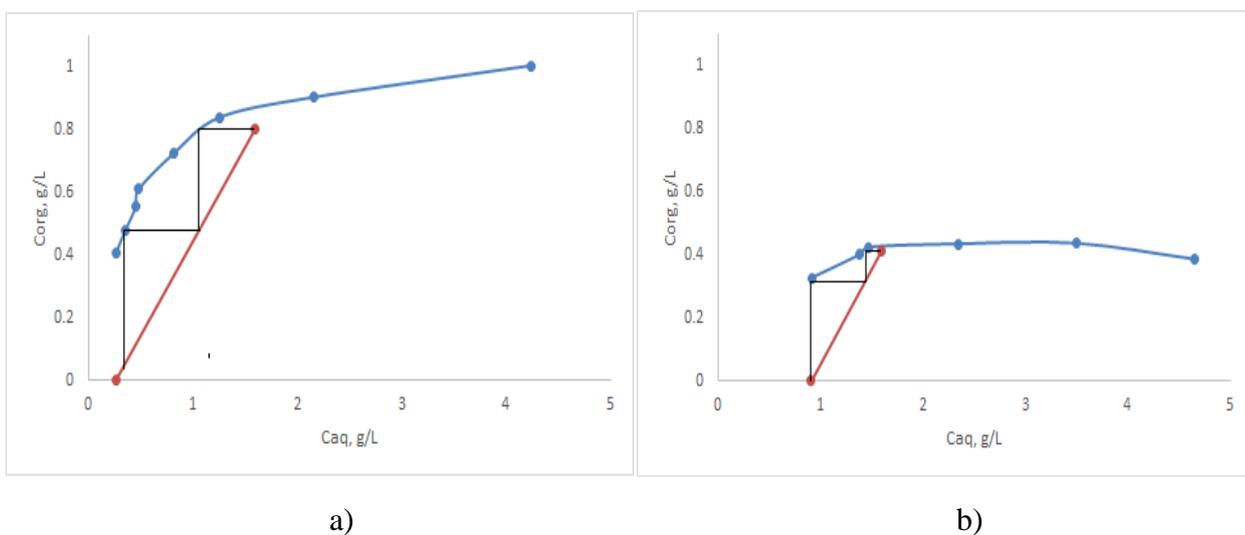


Figure 56. McCabe-Thiele method for Mn loading isotherm at O:A = 5:3: a) equilibrium pH = 4.5; b) equilibrium pH = 3.5

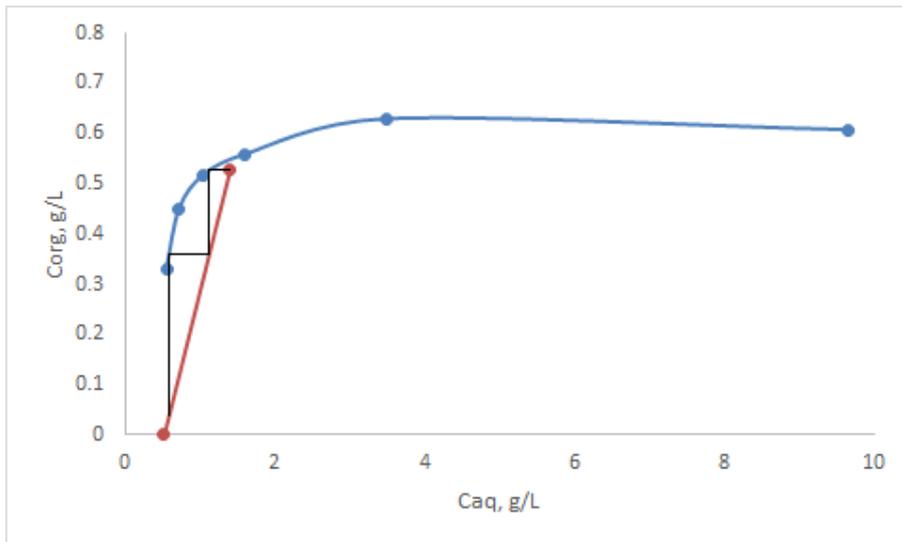


Figure 57. McCabe-Thiele method for Mn loading isotherm at O:A = 5:3: at equilibrium pH = 4.0

13 Scrubbing experiments. Manganese removal

Scrubbing experiments were aimed to scrub co-extracted cobalt from organic phase. Experiment were carried out by step-by-step addition of 20 g/L manganese sulphate salt to the loaded organic from O/A 10:1 to 1:1. Procedure started from 360 mL of loaded organic and 36 mL of aqueous manganese solution. For preparation of scrubbing solution tetrahydrate of manganese sulphate were used, which were balanced to initial pH of feed aqueous equaled 4.0 roughly. Scrubbing isotherms for three elements are represented in Figure 58a,b.

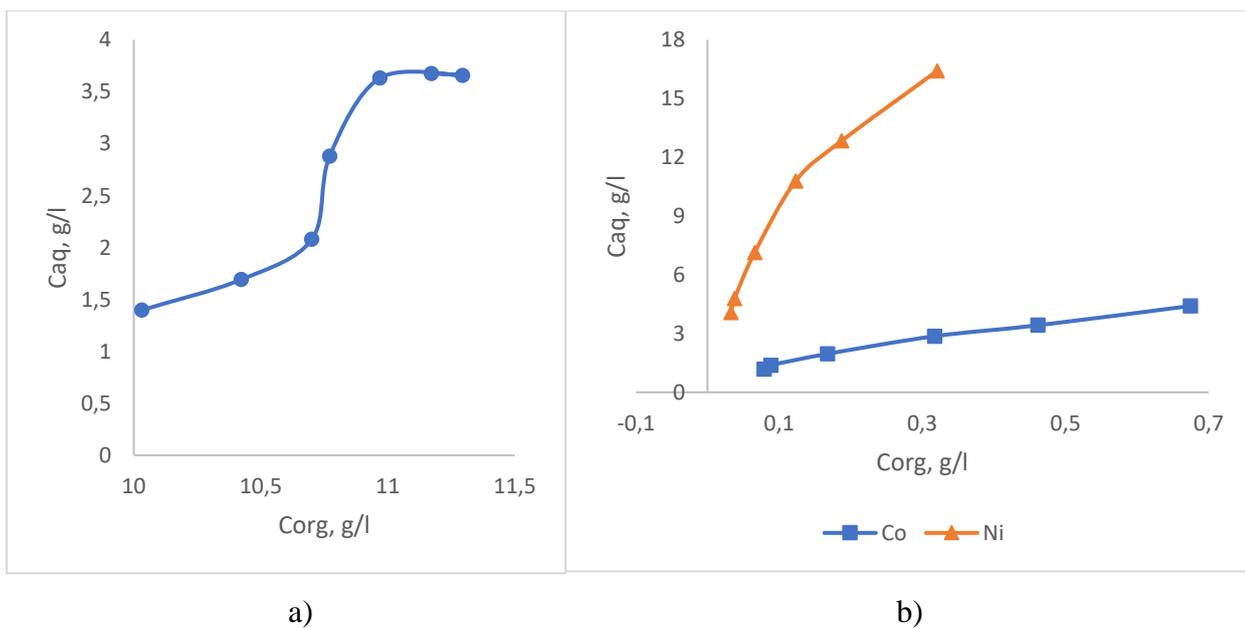


Figure 58. Scrubbing isotherms: a) Mn scrubbing, b) Co/Ni scrubbing

Data from charts report about stronger scrubbing of nickel than cobalt, which demanded further experiments with scrubbing tests. Modifications of experiments were done relatively to the manganese sulphate salts content in solution. The pH adjustment was organized without ammonia gas addition until equilibration of acidity value.

Initial pH of scrubbing solution equaled 3.8 with 20 g/l of MnSO₄ dissolved salt and 4.93 g/l of Mn²⁺ (calculation of exact Mn ions concentration is provided below). During experiment, pH dropped to 3.66 when O/A ratio reached 1/1 value. Figure 59a,b represents the processed data as scrubbing curves.

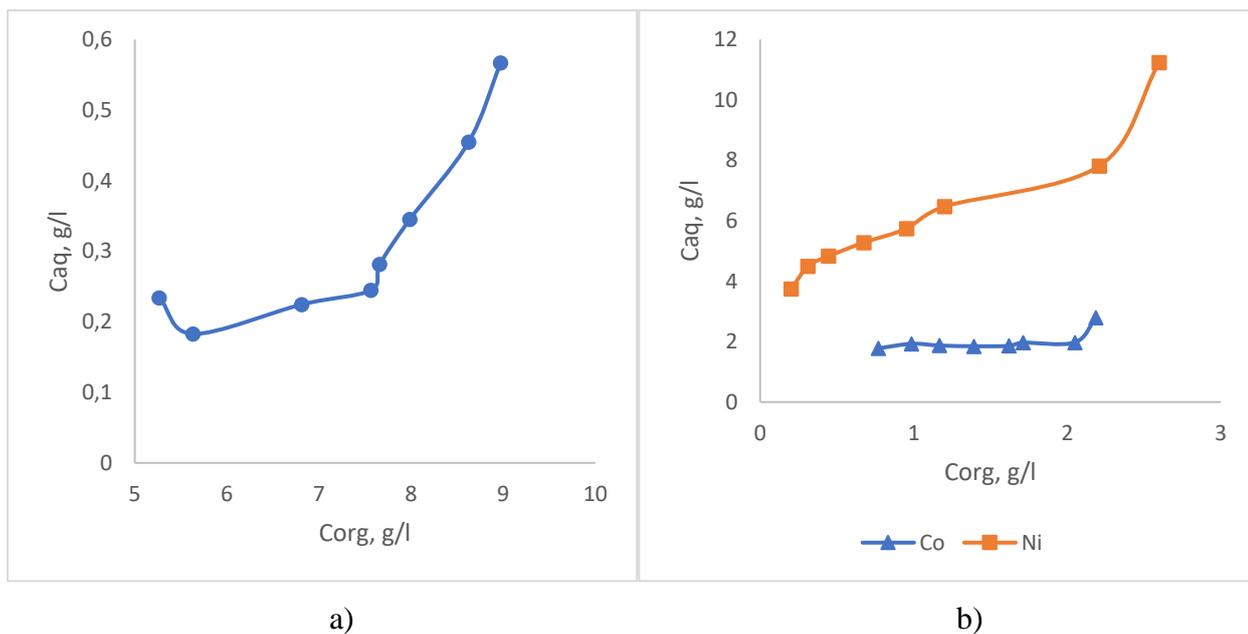
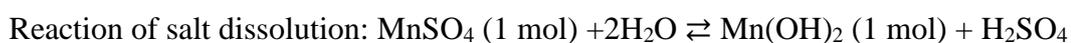


Figure 59. Scrubbing isotherm, 20 g/L MnSO₄ second experiment: a) Mn scrubbing; b) Ni, Co scrubbing

Obtained results repeated the reached data received earlier from first scrubbing tests despite the changing in pH regulation. The same experiments were done with 60 g/L of manganese sulphate salt concentration, where free Mn ions concentration reached 14.78 g/L (according to the calculations below).

$$M_{\text{MnSO}_4 \cdot 4\text{H}_2\text{O}} = 223 \text{ g/mol}$$

$$M_{\text{Mn}^{2+}} = 54.94 \text{ g/mol}$$



$$C_{20\text{Mn}^{2+}} = \frac{M_{\text{Mn}^{2+}}}{M_{\text{MnSO}_4 \cdot 4\text{H}_2\text{O}}} \cdot m_{\text{MnSO}_4 \cdot 4\text{H}_2\text{O}} = \frac{54.94}{223} \cdot 20 = 4.93 \text{ g/L}$$

$$C_{60_{Mn^{2+}}} = \frac{54.94}{223} \cdot 60 = 14.78 \text{ g/L}$$

Composition of loaded organic and aqueous scrub solution, involved in scrubbing experiments with 20 g/L and 60 g/L Mn scrub solution is represented in Table 16.

Table 16. Analytical data of composition of organic/aqueous phases of scrubbing tests

Experiment	Phase	Al	Mn	Fe	Ni	Co
20 g/L of MnSO ₄	loaded organic	0.48	4.95	0.47	4.12	2.60
	aqueous feed	6.85E-04	4.86	6.14E-04	6.09E-03	1.99E-04
60 g/L of MnSO ₄	loaded organic	0.43	5.05	0.48	4.27	2.55
	aqueous feed	1.71E-04	14.08	8.77E-05	4.66E-04	3.60E-03

Feed of aqueous equilibrated at 5.48 and fell down to 3.6 after incremental addition of scrubbing feed to O/A mixture while reaction took place. Figure 60 illustrates the data of scrubbing by 60 g/L scrubbing solution.

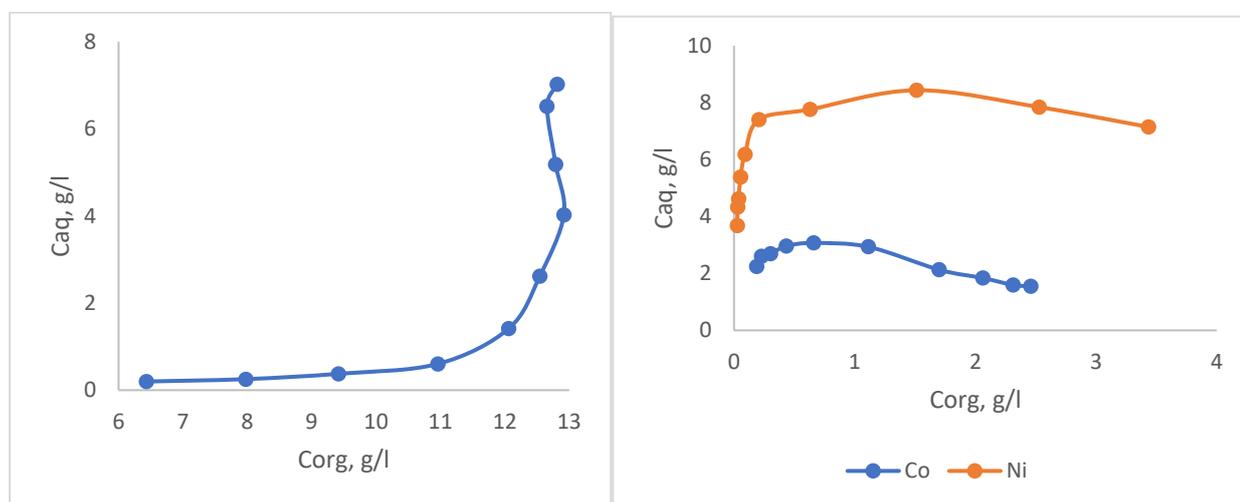


Figure 60. Scrubbing isotherm, 60 g/L MnSO₄, third experiment: a) Mn scrubbing; b) Ni, Co scrubbing

During the scrubbing tests there were noticed several visual changes of mixture properties. Intensive blue color of loaded organic smoothly changed to the violet due to possible saturation of organic by exchanged manganese from the scrubbing solution and removal of Co. Aqueous phase

changed the color from the light violet and became darker due to saturation by scrubbed metals (Figure 61).

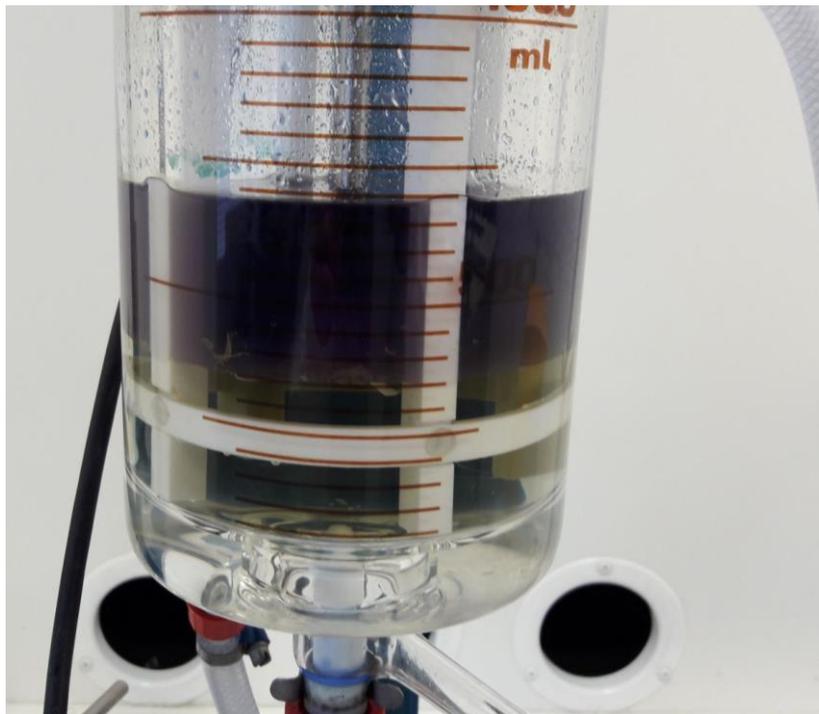


Figure 61. Visual changing of scrubbing solution and scrubbed organic

As a result, scrubbing tests of 20 g/L shown the highest exchange ability of Mn/Co than 60 g/L Mn scrubbing solution. Thus, for 60 g/L chart, the Mn quantity in aqueous phase point of 7 g/L in aqueous corresponds to 13 g/L of Mn content in organic demonstrating relatively poor exchange capacity of Mn between aqueous-organic. Another option was reached by 20 g/L scrub solution, performing the 9 g/l of transferred Mn ions in organic and 0.7 g/L of Mn in aqueous phase in the last point. In addition, all scrubbing isotherm points satisfy to the conclusion, that ratio of Mn concentration of organic to aqueous is higher for 20 g/L tests than 60 g/L, reporting about better exchange ability of Mn.

However, Co transfer during 60 g/L Mn tests possesses slightly higher transfer, reaching 3 g/L of transferred cobalt ions almost at 1 g/L of remained Co in organic. In general, Co exchange curve fluctuates within limits of 2 g/L of Co in organic, while 20 g/L Mn tests also remained the Co exchange curve at 2 g/L limits in organic. It can be concluded that Co exchange is almost the same for 20 g/L Mn and 60 g/L scrub solution.

Higher Mn transfer form aqueous to organic for 20 g/L tests, remaining the same exchange quantities of Co, is explained by higher Ni transfer reaching 12 g/L and 10 g/L in aqueous phases for 20 g/L ad 60 g/L tests, respectively.

Comparing Ni and Co exchange abilities of both scrub solutions and Mn transfer to organic, it can be stated that 20 g/L Mn solution is rather more effective in scrubbing, hence preparation of high concentrated Mn scrub solution does not make sense as it spends much manganese sulphate salts. Moreover, less concentrated scrub solution removes Ni better than more concentrated, while Co removal from organic is remained at the same levels.

14 Stripping experiments

Stripping experiments provided results of transfer of extracted metal ions from organic to the aqueous phase as last stage of solvent extraction process to deliver it at precipitation facility. For stripping solution 2 M sulphuric acid was introduced exploiting stepwise method of acid addition. Ratio of O/A solution varied from 10:1 to 1:1 and volumes of both phases at each step equaled to the scrubbing experiments. Initial composition, which were treated by acid underwent scrubbing and had the composition as it follows in Table 17.

Table 17. Composition of organic phase, which were tested at stripping procedure

	Al	Mn	Fe	Ni	Co
Concentration, g/l	1.165386	11.17172	1.092761	0.070081	0.029176

After incremental adding of acid to the organic, the last one started to change the color and finally became light. Viscosity of organics significantly decreased while aqueous phase was painted to the light pink due to transfer of Mn and Co ions (Figure 62).



Figure 62. Stripping procedure: a) stripping process (mixing), b) pregnant aqueous phase

Results of stripping procedure were provided at isotherm in Figure 63 with Mn stripping example. Other elements can be found in Appendix 4. Also, McCabe-Thiele method was applied to determine required number of stripping stages to strip all remained Mn after scrubbing procedure. O/A = 1/1 was selected as ratio for pregnant organic to acid phase.

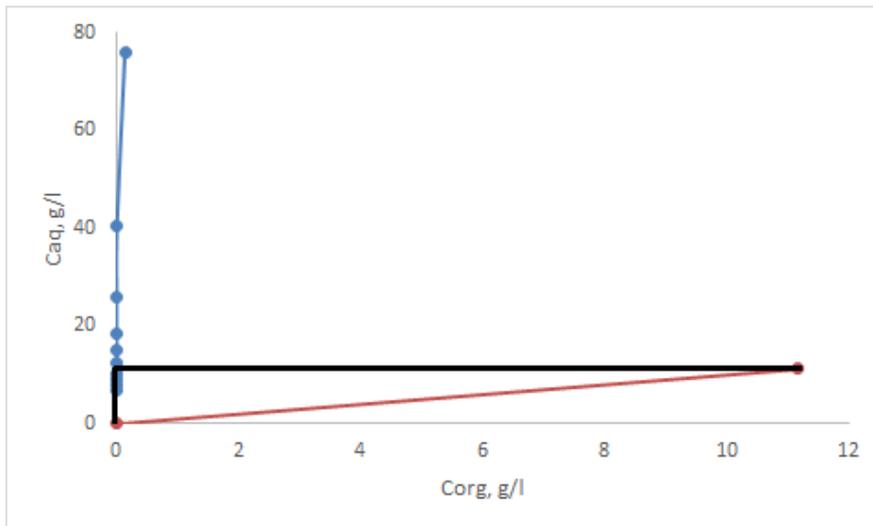


Figure 63. Manganese stripping isotherm at O:A = 1:1

Its clearly illustrated from above chart that even at low organic share in mixture required one-stage process to strip Mn from organic. In order to reduce the usage of expensive material, as highly concentrated acids for stripping, O/A ratio was modified, and illustrated in Figures 64-65.

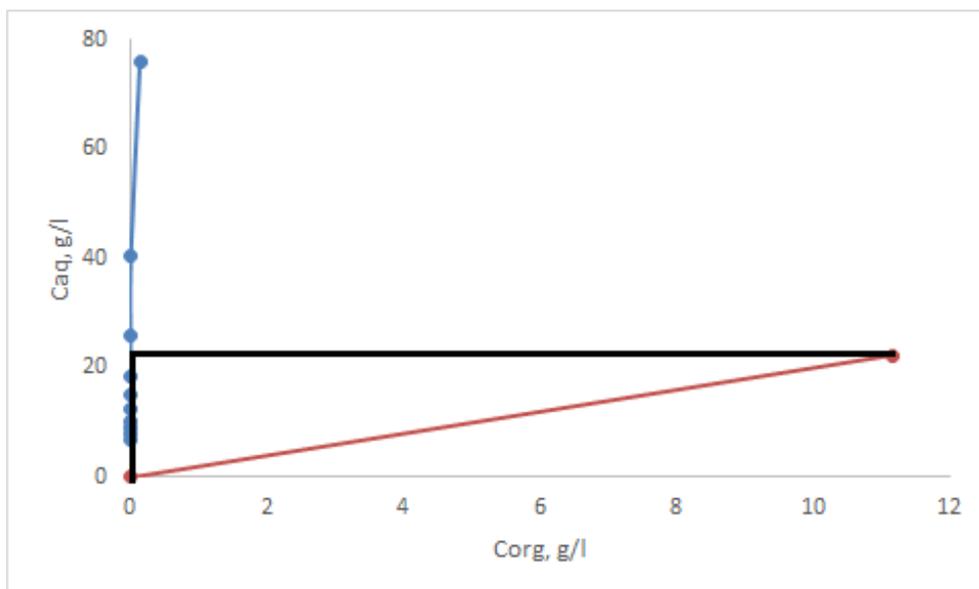


Figure 64. Manganese stripping isotherm at O:A = 2:1

Experimental outcome shows the significant noise in data for Fe, Al, Ni and Co, which leads to conclusion that stripping of listed metals does not occurred properly and demands modifications of stripping parameters e.g. acid concentration.

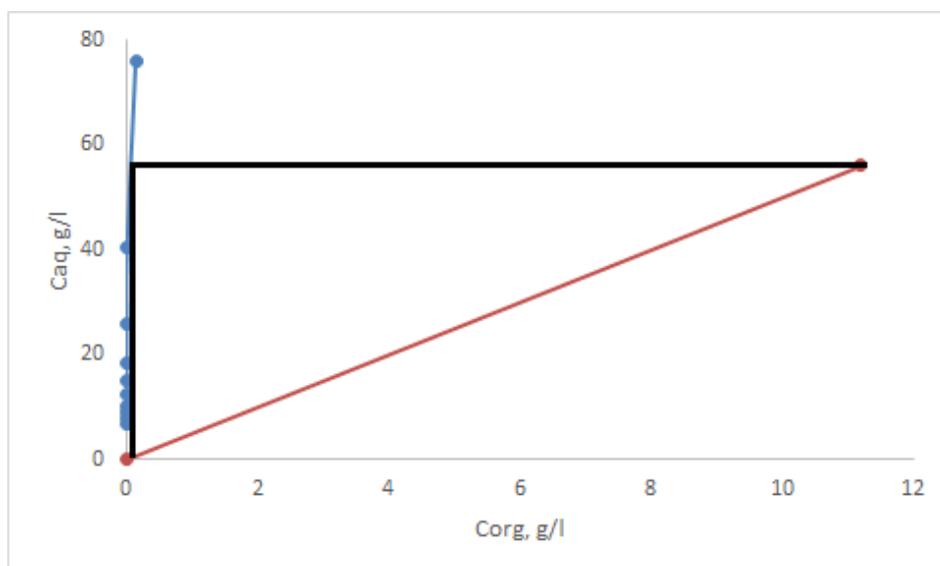


Figure 65. Manganese stripping isotherm at O:A = 5:1

According to constructed curves and applied McCabe-Thiele method, it was stated that reduced O:A ratio leads to economy of acid for stripping remaining one-stage total stripping of Mn. Hence, it does not necessary to increase acid volume to reach O:A 2:1 and 1:1 making the stripping process at significantly lower aqueous phase share.

15 Pseudo counter-current experiments

Pseudo counter-current extraction provided the results of multistage extraction aimed on complete recovery of desired metals using limited volume of the solvent. The process involves principle of crossed aqueous and organic phases forming layers and stages. Number of stages is formed by addition to the mixing volume fresh aqueous and/or organic starting the new stage. Thus, “A” mixing (Figure 66) starts from addition of feed aqueous and clean organic phase. Then, raffinate from “A” is transferred to the next B2 mixing, where the raffinate is processed again by clean organic and starting the new stage (second stage) of pseudo c-c experiment. According to the same principle, the third stage is formed going further until required number of stages is achieved. During the A and B2 mixings as start of new stages, the used organic becomes saturated by extracted metals, still saving its ability of extraction though. Hence, pregnant organic is transferred to the next mixing sets forming new layers of pseudo c-c extraction at first stage of experiment by addition of feed aqueous solution (as B1, C1, D1 etc.). At upper stages, pregnant organic is mixed with raffinate also producing the elements of stages and layers (at three-stage process and higher).

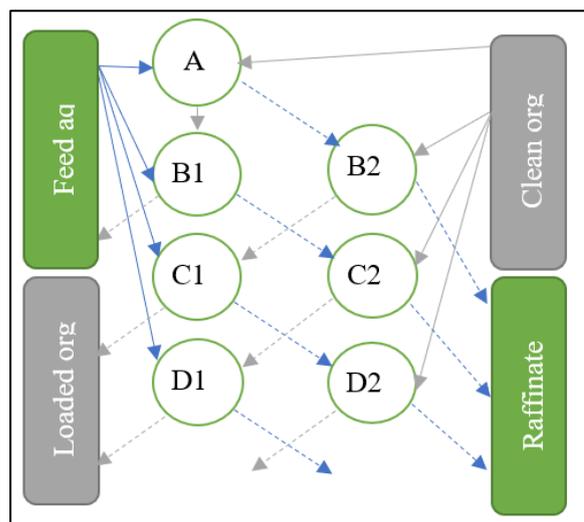


Figure 66. Scheme of organization of pseudo two-stage counter-current experiment

15.1 Loading and scrubbing

Experimental parameters consist of Initial pH of feed aqueous - 2.6 and O/A = 5:3 (500 and 300 ml respectively). Following procedure contained 10 layers and 2 stages. pH adjustment at each stage was remained at 3.5 with insignificant deviations from that value. After each batch mixing the phases were sampled and stored. Feed solution contained following ions concentrations: $\text{Ni}^{2+} = 41.68 \text{ g/L}$, $\text{Co}^{2+} = 10.41 \text{ g/L}$, $\text{Mn}^{2+} = 10.41 \text{ g/L}$, $\text{Fe}^{3+} = 0.95 \text{ g/L}$ and $\text{Al}^{2+} = 1.55 \text{ g/L}$. The results were plotted in Figure 67 for manganese and in Figures 68-71 for other metals.

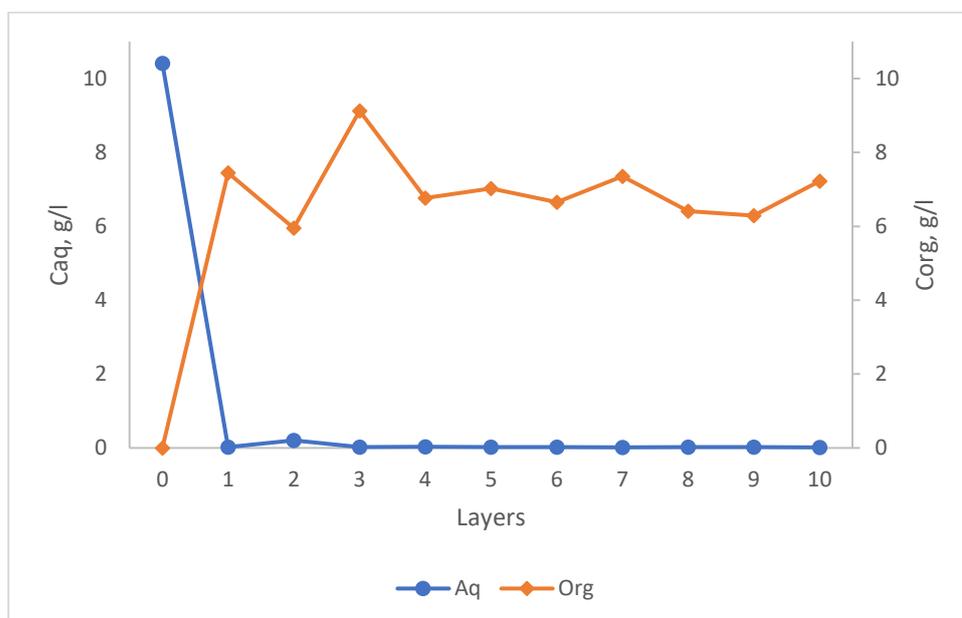


Figure 67. Pseudo c-c loading isotherm for manganese (O:A = 5:3)

The level of manganese transfer to the organic from aqueous feed solution was firstly reached at 9.12 g/L at third layer and then the steady state was caught around 7 g/l, taking 75 % of total

manganese removal. Cobalt extraction reached 4 g/l of transferred ions, which corresponding to 40 % of extraction and 4 g/l for nickel equaled 10 % of total amount. In that case, scrubbing counter-current tests were required to separate co-extracted Ni and Co from organics.

Each mixture in batches of first stage with feed aqueous and loaded organic phase was accompanied by sedimentation described earlier. Organics changed to the intensive blue and increased viscosity.

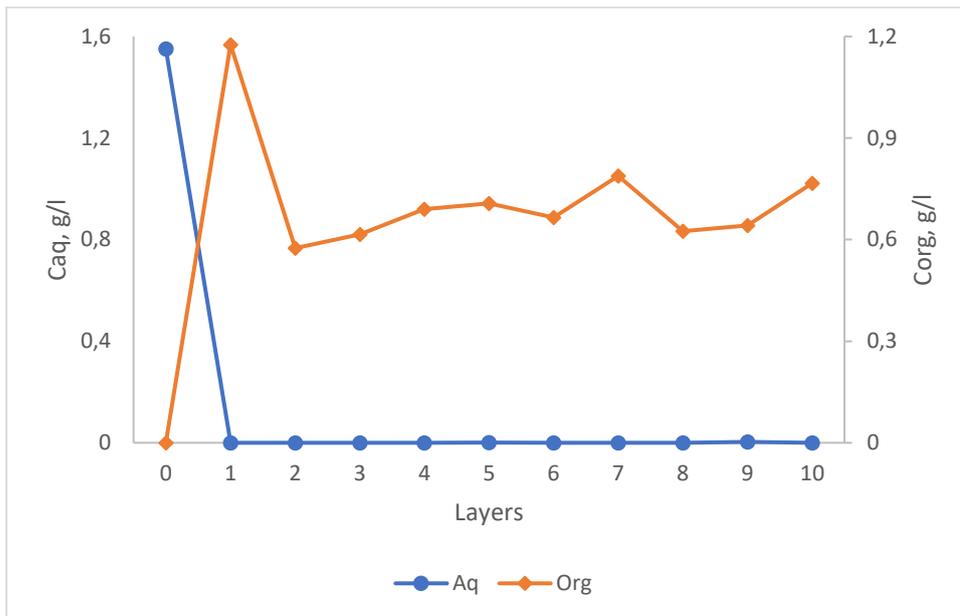


Figure 68. Pseudo c-c loading isotherm for aluminum (O:A = 5:3)

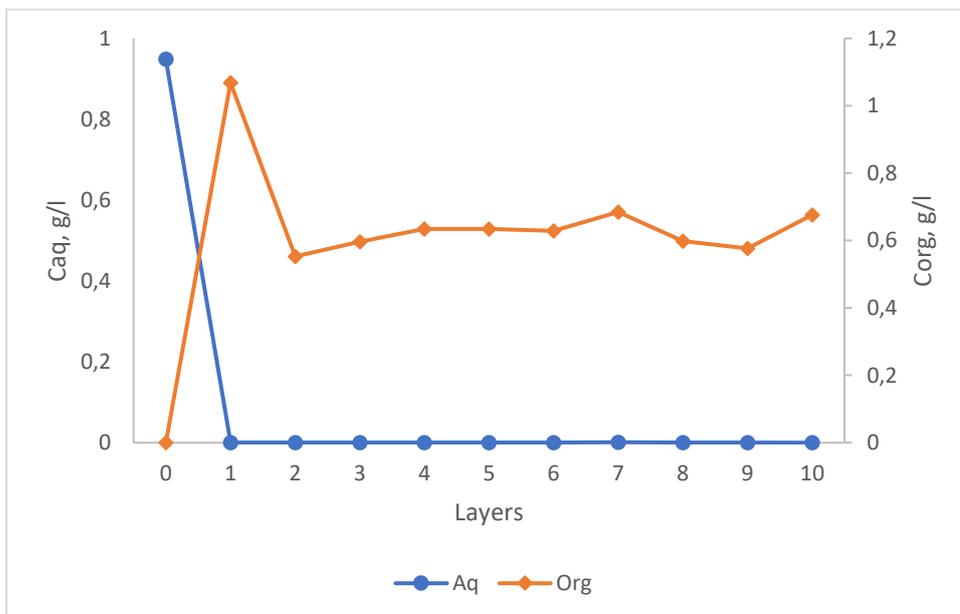


Figure 69. Pseudo c-c loading isotherm for iron (O:A = 5:3)

Iron and aluminum extraction obtained almost 100 and 75 %, respectively, already at first layer. It can be exactly observed from points for initial of Al concentration in aqueous phase (concentration of Al in feed solution) 1.55 g/L and concentration of Al in organic phase at first layer 1.17 g/L (Figure 68). The iron extraction underwent finished transfer of three-valent ions to organic at first layer, which is also clearly observed from the points at first layer of chart, therefore it can be interpreted as satisfactory extraction of that metals.

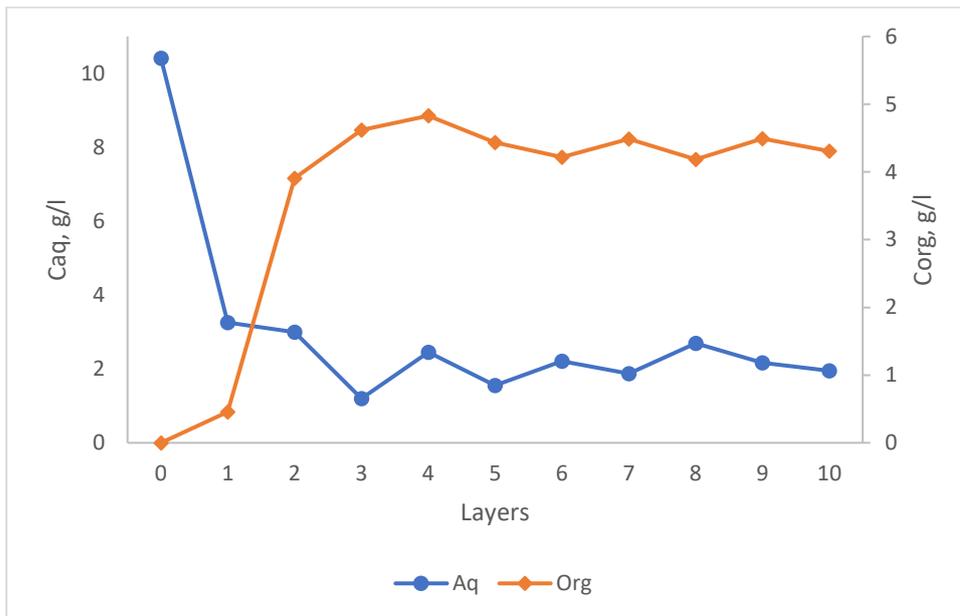


Figure 70. Pseudo c-c loading isotherm for cobalt (O:A = 5:3)

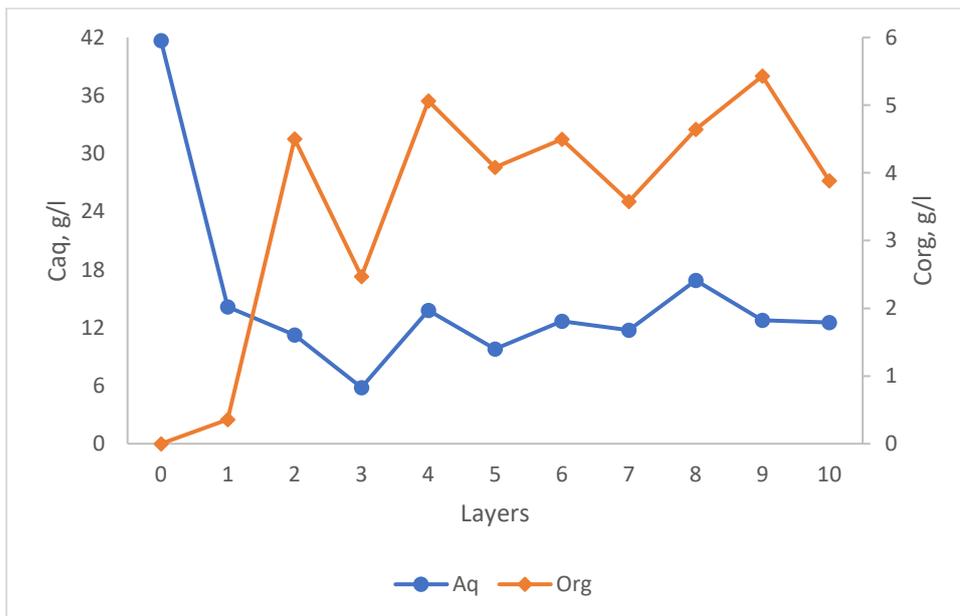


Figure 71. Pseudo c-c loading isotherm for nickel (O:A = 5:3)

Considering Co co-extraction during impurities removal, Co extraction rose significantly at third layer reaching 4 g/L with subsequent leading to steady state at 4.2 g/L of Co presence in organic.

Ni extraction remained between 4 and 5 g/L as steady state, while it also jumped thereafter third layer to 4.5 g/L as Co.

Another pseudo c-c loading experiments were performed trying another parameters of phase ratios: $O/A = 2:1$ and $pH_{\text{feed}} = 3.5$. Feed solution contained following ions concentrations: $Ni^{2+} = 29.62$ g/L, $Co^{2+} = 7.58$ g/L, $Mn^{2+} = 7.67$ g/L, $Fe^{3+} = 0.61$ g/L and $Al^{2+} = 1.15$ g/L. The order of experiments remained the same number of stages and layers. Manganese pseudo c-c extraction is represented in Figure 72, others – in Figures 73-76.

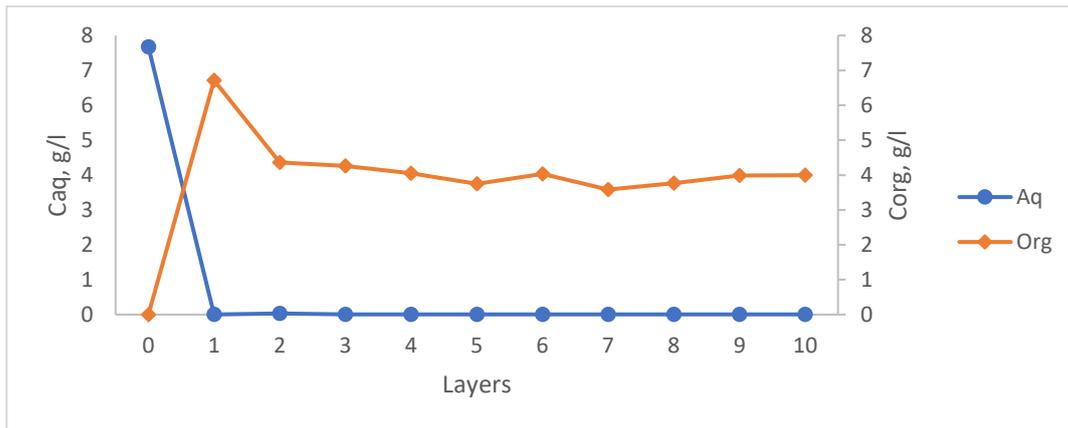


Figure 72. Pseudo c-c loading isotherm for Mn (O:A = 2:1)

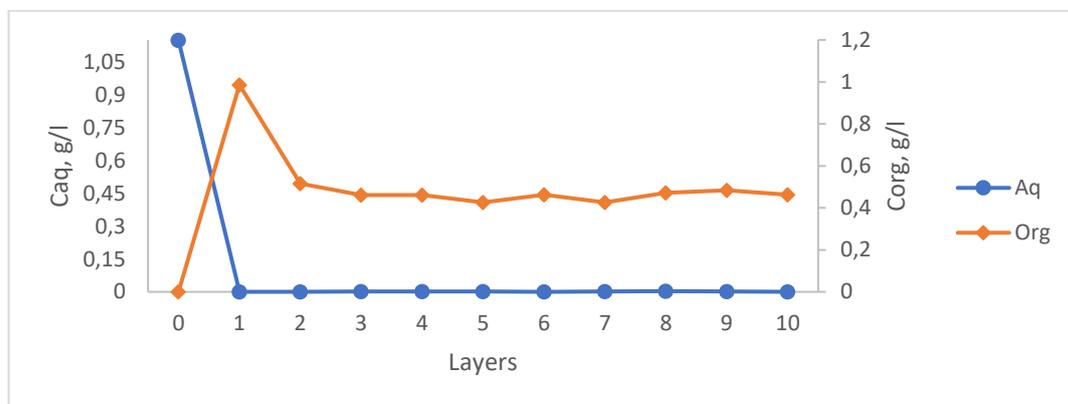


Figure 73. Pseudo c-c loading isotherm for Al (O:A = 2:1)

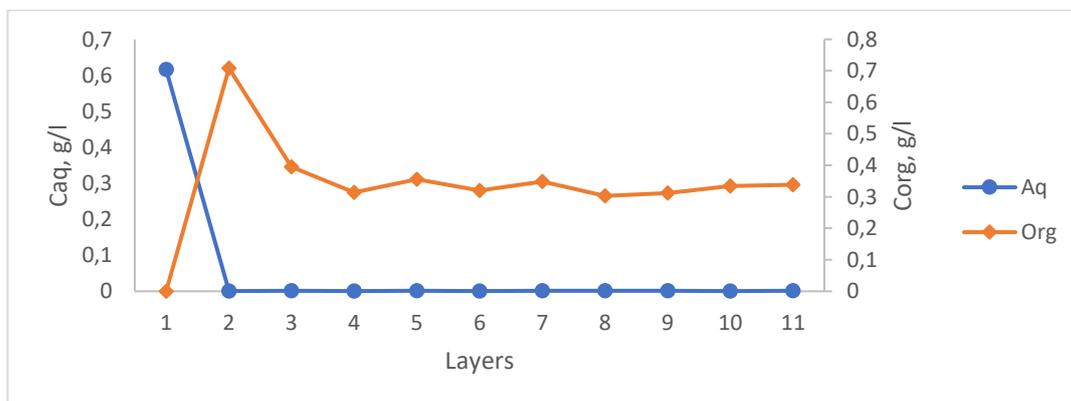


Figure 74. Pseudo c-c loading isotherm for Fe (O:A = 2:1)

Under elevated organic content (O:A = 2:1) Mn was extracted at 7 g/L at first layer forming 91 % of total quantity of Mn ions in feed aqueous solution. Mn extraction achieved steady state at 4 g/L thereafter pick of extraction at first layer as 7 g/L. Mn content in aqueous phase remained at relatively low level as less than 0.1 g/L leading to conclusion, that Mn extraction was carried out effectively.

Al extraction performed high removal percentage of the ions, achieving approximately 1 g/L at first layer of pseudo c-c extraction scheme. The steady state for organic was fixed at 0.5 g/L, while aqueous phase Al content was estimated close to zero and can be even neglected.

Total Fe extraction occurred at first layer of process and reached the steady state at 0.35 g/L for organics. The mutual level of top points for feed concentration of Fe and extraction point level of first layer under almost same scale gives obvious conclusion about 100 % removal of iron from aqueous phase at the most beginning of process.

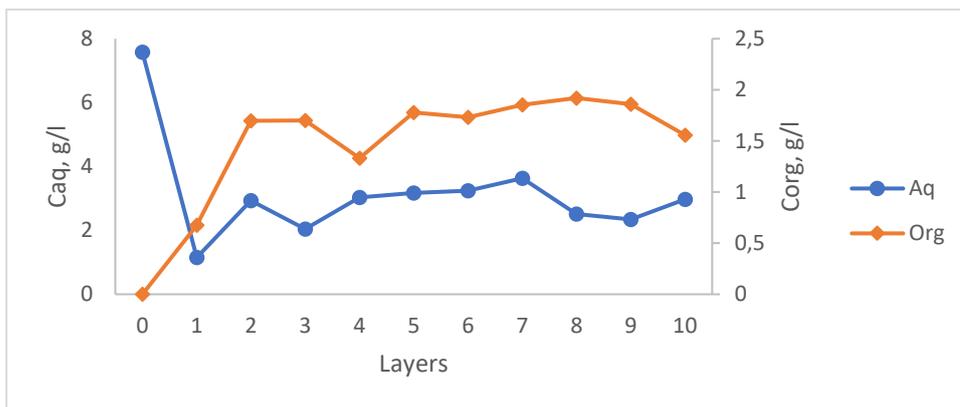


Figure 75. Pseudo c-c loading isotherm for Co (O:A = 2:1)

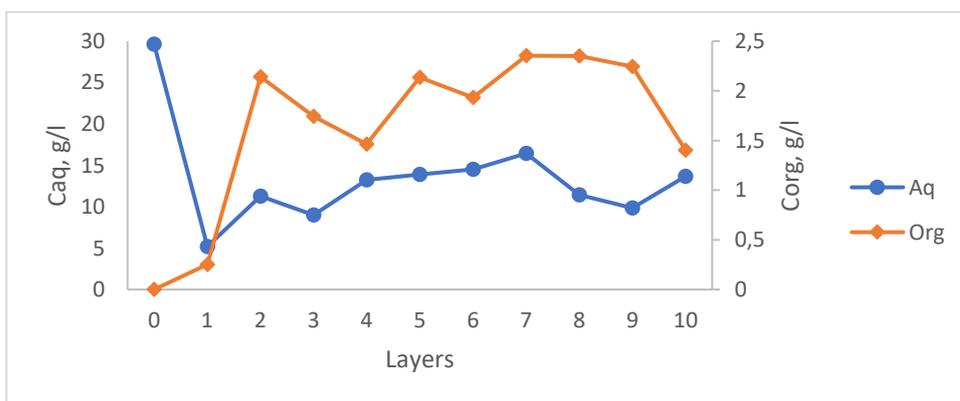


Figure 76. Pseudo c-c loading isotherm for Ni (O:A = 2:1)

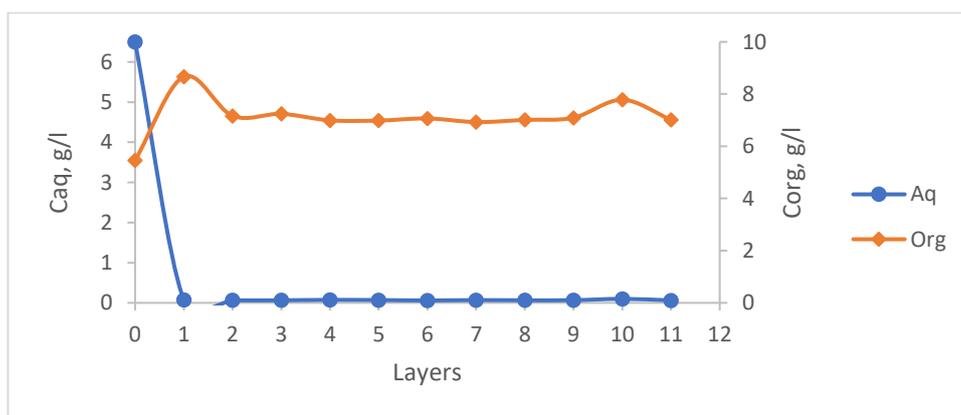
Figures 75-76 illustrate the Co-Ni co-extraction at almost the same quantity as 2 g/L for both. (Ni extraction reaches 2.5 g/L in accurate). In addition, the presence of Co and Ni in aqueous phase is

significantly lower than initial concentration if feed phase Hence, the additional scrubbing is applicable which requires several pseudo c-c tests.

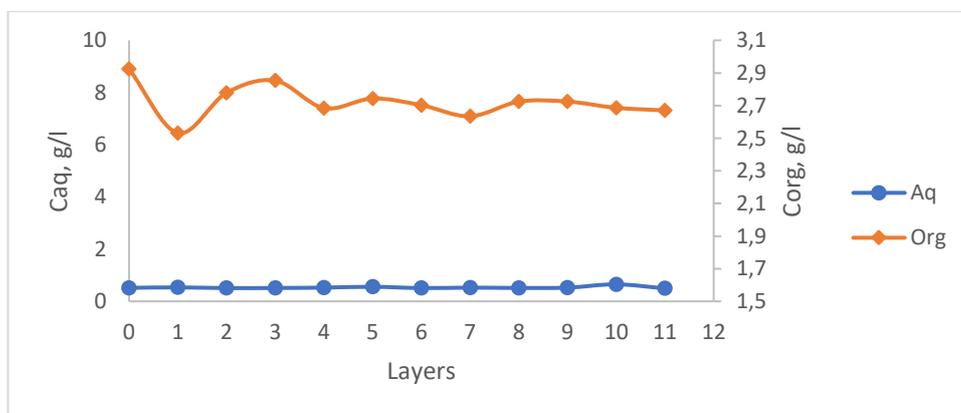
15.2 Scrubbing counter-current experiments

The same counter-current experiments were provided for scrubbing tests. Experiment started from the preparation of loaded organic by one batch in 5:3 O/A ratio (8500 and 5100 ml respectively) and pH adjusted at 4.0. The outcome of preloading for scrubbing pseudo c-c tests was following composition of transferred ions in organics: $\text{Ni}^{2+} = 2.63 \text{ g/l}$, $\text{Co}^{2+} = 0.52 \text{ g/l}$, $\text{Mn}^{2+} = 6.5 \text{ g/l}$. Al and Fe were significantly lower than other metals, hence their initial concentration were negligible.

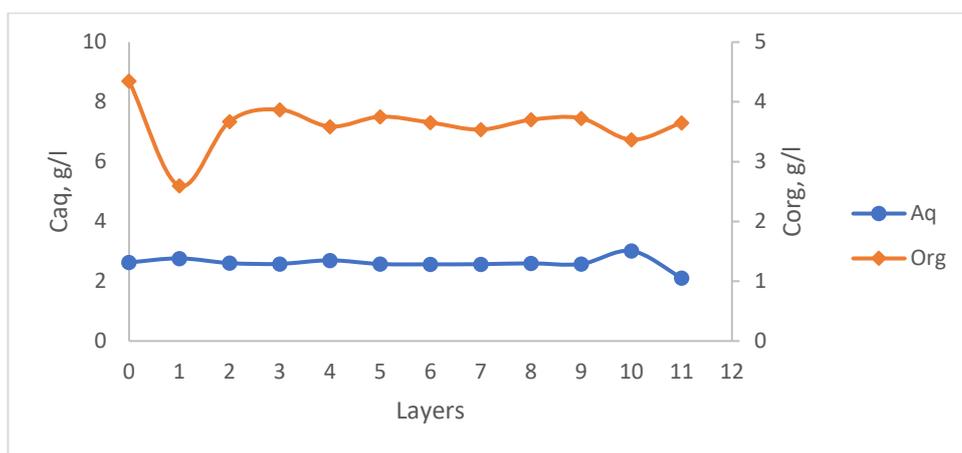
For scrubbing counter-current experiment acidity of scrubbing solution was accomplished to $\text{pH} = 3.5$ and proceeded under $\text{O/A} = 3:1$ (450 and 150 ml respectively). Experiment was stated as two-stage scrubbing with 11 layers. Every batch in counter-current procedure was equilibrated by itself (without addition of the ammonia gas). Aqueous raffinate was equilibrating at 4.3, while fresh aqueous feed was stopping at 4.4-4.6 values. The results were presented for manganese, cobalt and nickel in Figures 77a,b and c.



a)



b)



c)

Figure 77. Pseudo c-c scrubbing isotherm: a) Mn; b) Co; c) Ni

Scrubbing c-c experiment was accompanied by significantly long period of phase separation, which took around one hour. Color change corresponds to abovementioned description of loading isotherm experiments.

Mn presence in organic phase was estimated at steady state as 8 g/L which corresponds to scrubbing ability of Mn-Co exchange. Hence, it was determined that all Mn was transferred to organic phase as its low concentration remained in scrubbing aqueous solution. However, Co content in aqueous phase was not changed and remained at the same level during the carrying out of all layers of pseudo c-c scrubbing. Ni-curve of aqueous phase has behavior of straight line, which also corresponds to the low Ni transfer form organic to scrub solution.

16 Removal of magnesium by ion exchange

According to the literature review, magnesium selective extraction over cobalt became quite challenging issue. None of the suggested liquid extractants are able effectively remove magnesium firstly. However, Amberlite IRC 747 shown quite promising results of mg extraction and maintaining Co in aqueous phase. The experiments were done with incremental decrease of acidity of aqueous phase during ion exchange. Prepared aqueous feed fixed at pH = 3.07. Variation of acidity range involve pH decrease from 5.36 to 2.55 by incremental addition of 5 M sulphuric acid to the mixture. For experiment 500 ml volume of aqueous solution was filled to the vessel with 200 g of Amberlite resin. Each change of pH was fixed and sampled. After sample analysis the data was processed and plotted in Figure 78.

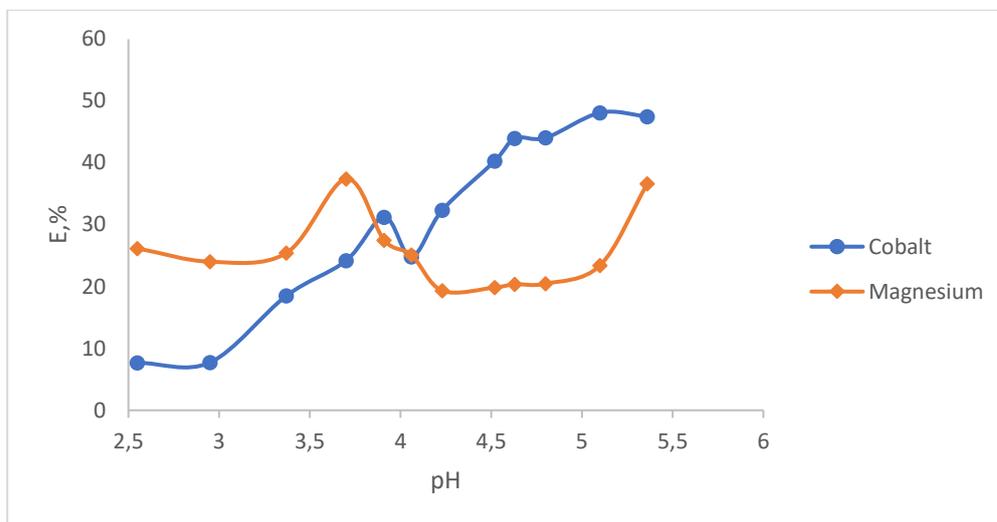


Figure 78. pH isotherm for Mg extraction with ion exchange resin

During the experiment, there were not any significant visual changes of mixture. However, equilibration time of every batch took at least one hour, which is much higher than during liquid-liquid extraction.

Co extraction by ion exchange reached relatively high share and is estimated at 50 % at the end of experimental pH range, while Mg is extracted at 40 % at highest point and under the lowest acidity. It can be concluded that Co-Mg selectivity is noticeably poor and does not appropriate for targets of Mg separation over Co ions in aqueous sulphate solution.

CONCLUSIONS

Purification of nickel-cobalt sulphate solution applying liquid-liquid extraction was studied. Literature review represented the main points of temporary status of applied extraction principles, using organophosphorus extractants, hydroxyoximes, organic acids and ions exchange resins. As a result of investigation, organophosphorus extractants were selected as more effective for removal of metal impurities from based aqueous solutions.

D2EHPA extractant was selected as the most appropriate extractant due to its highest immunity to nickel and cobalt extraction. In addition, D2EHPA demonstrated visible performance of iron, aluminum, zinc and calcium removal, achieved the extraction percentage almost 100 %. During the solvent extraction experiments, provided in current research, D2EHPA extractant managed with purpose of impurities removal and remaining the significant share of Ni and Co ions in aqueous solution. According to the current investigation, D2EHPA is selected as mostly applicable reagent for Mn extraction over Ni-Co, providing enough selectivity for Mn and Co. However, effective Mn extraction is achieved under elevated pH values catching some part of Ni and Co ions, which should be scrubbed subsequently.

During experiments performance and pH curves constructing, it was determined the most effective organic extractant concentration, estimated at 35 % of D2EHPA (1 M). The optimal pH value for maximized impurities removal was selected at 3.5 and used at further experiments.

According to loading experiments and plotting of loading isotherms it was determined the required number of stages using for removal of metal ions as Al, Mn and Fe over Ni and Co. Determined stage numbers were equaled 2 and were implemented in performing of pseudo counter-current experiments. In addition, the optimal O:A ratio was found for extraction process which equals 5:3. Selected ratio allows to prevent the waste of extra organic extractant and support the required level of extraction.

The main problem of extraction touched the co-extraction of cobalt and nickel, especially during the attempts to remove manganese due its close pH extraction range to cobalt extraction. In that case, scrubbing process was investigated to exchange manganese and cobalt ions in order to maintain cobalt in aqueous solution. Scrubbing tests demonstrated the satisfactory ability of cobalt maintenance in aqueous phase, however, significant part of cobalt remained in organic.

Stripping tests demonstrated not enough good performance due to the fluctuations of data and possible disability to strip the metals under describe conditions.

Pseudo counter-current experiments proved earlier batch experiments, however it shows less extraction ability of iron and aluminum. During the analysis it was underlined, that co-extraction of cobalt and nickel occurred at pseudo c-c, which obliged to investigate scrubbing in pseudo c-c format as well. Scrubbing process demonstrated high ability of cobalt scrubbing, however its missed significant amount of cobalt which requires further investigation.

The last problem, which was faced was magnesium removal from WP2 solution, which was impossible to do effectively applying liquid-liquid extraction. The ion exchange resin was used as one of possible solutions, however magnesium recovery took only 40 % with cobalt co-extraction reached 25 %. Hence, the received results requires further investigation of the described process.

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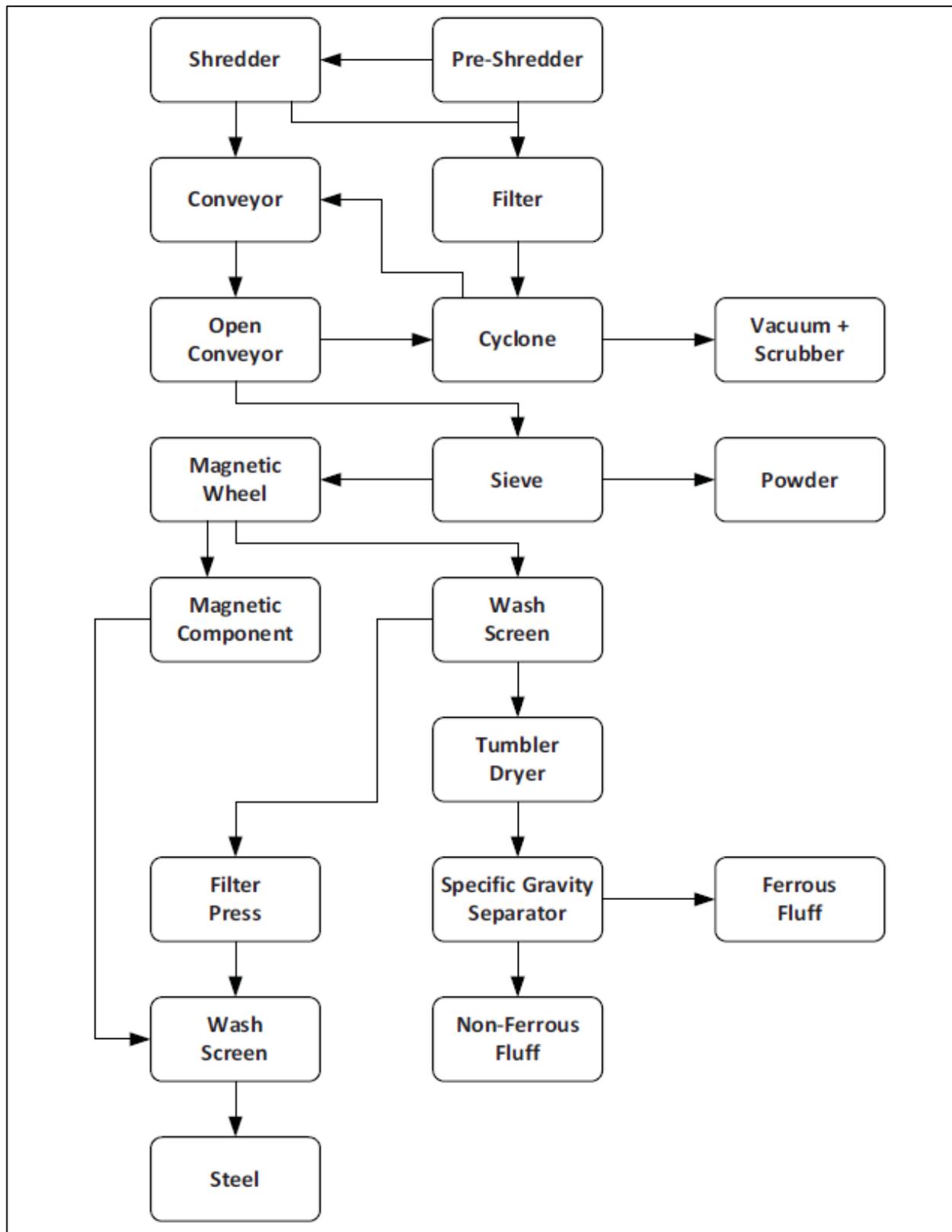
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Appendix 1

Adapted from Tanong, et al., (2014)



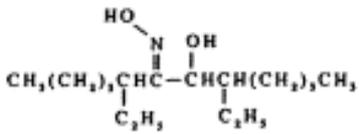
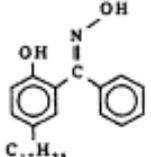
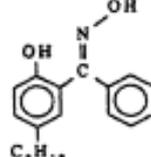
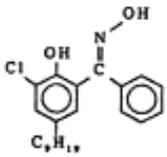
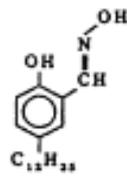
Appendix 2

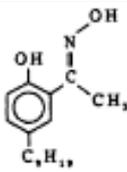
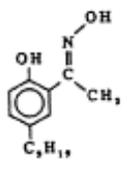
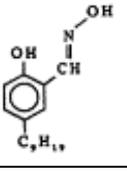
Adapted from Habashi, (1999)

	Group	Example	Abbreviation
Acidic	Dialkyl phosphoric acid	Di (2-ethylhexyl) phosphoric acid	D2EHPA
	Monoalkyl phosphoric acid	Dodecyl phosphoric acid	DDPA
	Alkyl pyrophosphoric acid	Octyl pyrophosphoric acid	OPPA
	Dialkyl phosphinic acid	Bis (2,4,4-trimethyl pentyl) phosphinic acid	Cyanex 272
Neutral	Trialkyl phosphate	Tributyl phosphate	TBP
	Trialkyl phosphine oxide	Trioctyl phosphine oxide	TOPO Cyanex 921
	Alkyl dialkyl phosphinate	-	-
	Dialkyl alkyl phosphinate	-	-

Appendix 3

Adapted from Szymanowski, (1993)

Extractants	Producer	Chemical formula	Industrial application
LIX 63	General Mills Henkel		Catalytic additive to extractive including 2-hydroxybenzophenone oximes derivatives as LIX 65N and LIX 70 (under 40 °C)
LIX 64	General Mills		Ge and Cu extraction. Cu is extracted from sulphate aqueous phase at pH > 1.5
LIX 65N	General Mills Henkel		For copper extraction from sulphate solutions at pH higher 1.5
LIX 64N	General Mills Henkel	LIX 65N + LIX 63 (44:1)	The same application as LIX 65N but under 40 °C
LIX 70	General Mills		Extraction of Cu over sulphate solution up to 100 g/dm ³ of H ₂ SO ₄
LIX 71	General Mills	LIX 70 + LIX 65N	Extraction ability is the average of LIX 70 and LIX 65N
LIX 73	General Mills	LIX 70 + LIX 64N	The same as LIX 71 but under 40 °C
LIX 860	Henkel		Strong extractant with similar properties of P 50 extractant (below)
LIX 622	Henkel	LIX 860 + tridecanol	Similar extraction ability as PT 5050 and higher than LIX 64N
LIX 6022	Henkel	LIX 860 + tridecanol	Similar extraction parameters as LIX 622
LIX 864	Henkel	LIX 64N + LIX 860	Average extraction efficiency between LIX 860 and LIX 64N
LIX 865	Henkel	LIX 65N + LIX 860	The same efficiency as LIX 864 but under 40 °C

SME 529	Shell		CU removal over -SO ₄ solutions including up to 10 g/dm ³ of H ₂ SO ₄
SME 530	Shell	SME 529 + dioxime	The same as SME 529 with upgraded extraction kinetics
LIX 84	Henkel		The same as SME 529 with upgraded extraction efficiency
LIX 984	Henkel	LIX 860 + LIX 84 (1:1)	High Cu extraction ability
P 1	Acorga		
P 50	Acorga		Strong extractants with obligatory addition of modifier

Appendix 4

