PERIODICO di MINERALOGIA
established in 1930

Dipartimento
di Scienze della Terra

Sapienza
Università di Roma

An International Journal of
Mineralogy, Crystallography, Geochemistry,
Ore Deposits, Petrology, Volcanology
and applied topics on Environment, Archaeometry and Cultural Heritage

Separation and purification of Nickel and Cobalt from pregnant leach solution by conventional vs ionic liquid as extractant: an overview

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ARTICLE INFO

Submitted: March 2023
Accepted: September 2023
Available on line: October 2023

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Doi: 10.13133/2239-1002/18026

How to cite this article:
Bahfie F. et al. (2023)
Period. Mineral. 92, 287-306

ABSTRACT

Solvent extraction (SX) is a common method used for nickel extraction, and conventional acidic extractants such as Cyanex 272, PC88A, and D2EHPA are typically employed. The extractant requires multi-step extraction and separating various metal impurities before the cobalt extraction stage. However, strict pH maintenance is needed during extraction, and strong acids must be used in stripping, which can negatively impact the environment and ecosystem. Treatments such as saponification are also required in conventional extractants to control the fall of pH and extraction value. The ionic liquid is a type of extract that is more environmentally friendly, harmless to the ecosystem and does not require further treatment such as saponification to get good results. One type that has been tried to separate cobalt from nickel is Phosphonium ionic liquids (PILs). The extraction value can exceed 95%, the use of acidic solutions is reduced, as well as proven to be more environmentally friendly. The advantages of ionic liquid are based on the lack of release of H^+ ions in the by-product of the solvent extraction process and stripping agents can use deionized water very effectively. Further research on ionic liquid solvents such as PILs could bring us closer to the realization of an economically viable and environmentally friendly extraction process at an industrial scale.

Keywords: purification; solvent extraction; ionic liquid; nickel; cobalt.

INTRODUCTION

Nickel is used in various industries such as stainless steel, non-ferrous alloy, plating, alloy steel, and now the battery is overgrowing (Nickel Institute, 2023). Nickel is a metal that is the primary raw material in the manufacture of electric batteries. Indonesia is one of the countries with the largest laterite nickel reserves in the world. According to the Indonesian Ministry of Energy and Mineral

Resources in 2020, the number of nickel reserves in Indonesia was 72 million tons as primary resources. Nickel extraction can also be obtained from secondary resources from Co-and-Ni-bearing waste such as aerospace waste materials (Xiao et al., 2012), spent catalysts (Le and Lee, 2021), and spent batteries. Lithium-ion batteries (LIBs) have great potential as secondary resources due to their massive usage, starting from computers, phones, and other electronic devices (Hanisch et al., 2015). The demand for nickel will continue to increase along with the need for electric vehicles (EV). In 2050, nickel will become a metal with a high demand compared to cobalt or lithium (Xu et al., 2020). In the hydrometallurgical process to obtain pure nickel, a purification process is carried out on the pregnant leach solution (PLS). Several process options for nickel purification include precipitation, ion exchange, and solvent extraction. Solvent extraction is the most preferred and versatile method, SX was chosen because of its selectiveness, low chemical consumption, and recyclability (Prasetyo and Anderson, 2020) Cu, and Ni from glutamate media as hypothetical product of electric arc furnace dust alkaline leaching was developed, with concentrations being 17.6, 0.35, and 0.14 g/L, respectively. Three extractants were investigated: Cyanex 272, DEHPA, and Acorga M5640 selectively separated Zn, Ni, and Cu from each other. Aside from pH, parameters investigated included O/A ratio, extractant concentration in kerosene as diluent, and sulfuric acid concentration as stripping agent. pH was the most critical factor in determining the separation factor among three metals since pH controlled metal speciation in pregnant leach solution and regulated the interaction between metal ions and extractant. Based on previous studies, a flowsheet for Zn, Cu, and Ni isolation is proposed, which obeys the following sequence: Zn separated from Cu and Ni by Cyanex 272 (in pregnant leach solution at pH 8, log separation factor Zn-Cu 4.78, Zn-Ni 2.51; according Figure 1 (Prasetyo et al., 2020; Prasetyo et al., 2021; Swain et al., 2015; Xu et al., 2020). Cobalt and nickel will play an essential role in the future as the battery industry improves. Given the anticipated demand for cobalt and nickel in the battery industry, it is important to continue researching and developing effective, economical, and environmentally friendly processes for their separation using solvent extraction. In this literature review, we aim to explore the current state of knowledge on cobalt and nickel solvent extraction and identify areas where further research is needed.

SOLVENT EXTRACTION

Solvent extraction (SX) is a well-established method for metal recovery that offers several advantages, including a simple process, short operating time, and the ability to reuse chemicals. The process involves two phases: the organic phase (extractant) and the aqueous phase, aqueous can be a pregnant leach solution (PLS) or a synthetic

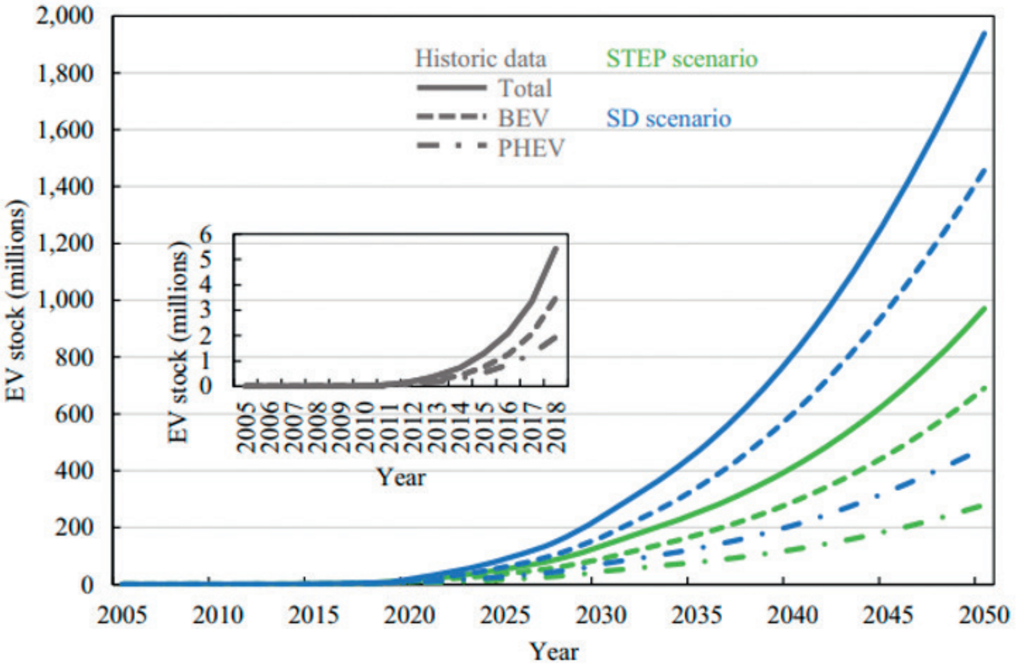

Figure 1. Global EV stock development projected until 2050, modified from Xu et al., 2020.

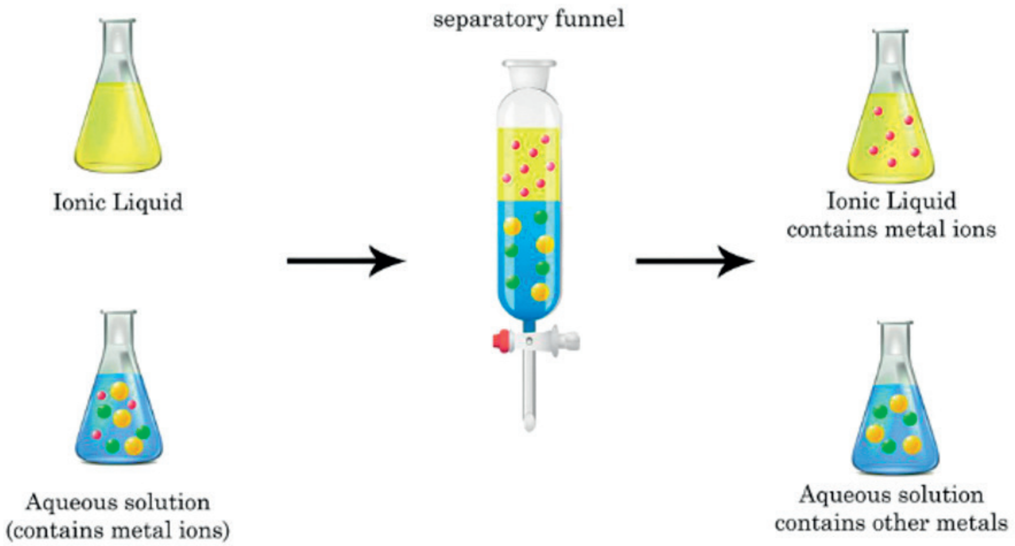

Figure 2. Schematic of solvent extraction process modified from Ali Akbari et al., 2020.

solution (Kislik, 2012). To better understand the solvent extraction process, please refer to the schematic diagram shown in Figure 2.

Solvent extraction process, metal ions are exchanged and distributed between the aqueous and organic phases. This process depends on the mass transfer of compounds from one liquid phase to a second liquid phase, because it is often called liquid-liquid extraction (Bohnet and Ullmann, 2002). After shaking, the metal distribution reaches equilibrium due to differences in density and immiscibility between the two phases (Li et al., 2021). Two phases after the SX process produce loaded organic and raffinate which are ready to be separated and carried out further processing. Common solvent extraction reactions can be represented by equation 1, as described by Bard (Bard and Faulkner, 1980). However, other reactions may occur using the solvent extraction method during metal extraction, depending on the extractant and leaching agent used in the aqueous phase. For example, equation 2 shows cobalt extraction using the oxime compound in chloride liquor (Rafighi et al., 2010). Other compounds, such as amine functional groups (Foltova et al., 2018) and phosphonium ionic liquid (Wellens et al., 2013) can be used for metal extraction, as shown in equations 3 and 4.

$$M^{n+} + {}_{n}RH \leftrightarrow MR_{n} + {}_{n}H^{+} \quad (1)$$

$$Co^{2+}(aq) + HL(org) + Cl^{-} \leftrightarrow CoLCl.3H_2O(org) + H^{+}(aq) \quad (2)$$

$$M^{2+} + 2Cl^{-} + 2[A336][Cl] \leftrightarrow [A336]_2[MCl_4] \quad (3)$$

$$[CoCl_4]^{2-} + 2[P_{66614}]Cl \leftrightarrow [P_{66614}]_2[CoCl_4] + 2Cl^{-} \quad (4)$$

Description:
M: Metal ions in the solution phase
n: Number of payloads
H^+: Hydrogen Ion
RH: Extractants
R_nM: Metal in the organic phase
[A336]: Aliquat 336
$[P_{66614}]$: Tri(hexyl)tetradecylphosphonium chloride

After being shaken and left in separate phases, the solution in solvent extraction will distribute itself into the two solvents. The ratio of solute concentrations in the two solvents remains constant at a fixed temperature. The exchange of metal ions from the aqueous phase to the organic phase occurs by exchanging hydrogen ions for cations and chloride ions for anions (Li et al., 2021). In assessing the efficacy of solvent extraction, various parameters are taken into consideration, among which the percentage (%E), distribution ratio (D), and separation factor (α), which can be calculated using the following equations 5, 6, and 7.

$$D = \frac{Co}{Ca} \quad (5)$$

$$\%E = \frac{Co}{F} x100\% \quad (6)$$

$$\alpha = \frac{Da}{Db} \quad (7)$$

Co and Ca represent the organic phase and aqueous phase concentrations, respectively, while Da and Db refer to the distribution of elements a and b. F represents the feed concentration for extraction. The primary goal of solvent extraction is to separate metals from other elements selectively, hence high extraction value and separation factors are desirable. Extractants play a critical role in achieving this, and their modification can increase extraction efficiency. The type of extractant, molarity, and addition of modifiers are some ways to modify extractants (Li et al., 2021). Modifier agents play an essential role in preventing and controlling the formation of unwanted third phases, because they can reduce extraction efficiency and complicate operational activities. TBP and TODGA are included in one of the modifiers that can be used (Swami et al., 2019). The modifier acts by reducing the average aggregate size and increasing the value of the limiting organic concentration by manipulating the chemical chain length (Berthon et al., 2007, 2021). There are also several other factors to consider to achieve optimum extraction, such as the influence of acidity, pre-oxidation, phase ratio, and concentration of extractant (Mubarok and Yunita, 2015).

Solvent extraction of precious metals can be challenging if the extraction process is carried out in only one step. However, multi-stage extraction can address this issue and make the solvent extraction more effective. This method enables near-complete recovery using a limited volume of solvent.

To perform multi-stage extraction, first prepare fresh aqueous and organic phases, and then combine them in the second funnel. Shake the mixture until it reaches equilibrium, and then separate the two phases. After the first extraction is carried out in funnel 2, pour the resulting aqueous (A2) and organic (O2) phases into funnels 1 and 3, respectively. The aqueous phase in funnel 1, which still contains precious metals, can be reacted with fresh organic solution, while in funnel 3, an almost saturated organic solution can be reacted with a fresh aqueous solution (Peng et al., 2021).

Types of Solvent Extraction

Many types of organic solutions can be used to extract nickel from PLS. Some extractant classes are commonly used in cobalt and nickel separation. The following is an extract used for nickel solvent extraction (Alvial, 2021).

The solution mentioned in Table 1 is a type of extract commonly used to separate nickel cobalt in sulfuric acid media and basic extractants, solvating, and ionic liquid can be seen in the list of Table 2. Actually, many other extractants still have the potential to separate nickel and cobalt effectively, they can be classified as acid, alkaline or basic, solvating to ionic liquid extractants (El-Nadi, 2017). Here is additional information on some of the extraction classes.

Acidic extractant

Acidic extractants are a group of extractants that are generally used in refining nickel and cobalt through the solvent extraction method. The reaction that occurs between the organic and aqueous phases is the organic phase forming new complex compounds with metal cations, an example of the reaction is in equation 1. The metal cation Mn^+ will combine with the anionic ligand to form a neutral complex compound A^- to form a neutral complex MAn. Acid extractants such as PC-88A and D2EHPA have instability in monomers and tend to form dimers (Biswas and Begum, 1998) H_2A_2, usually hydrogen-bonded dimer H_2A_2 in non-polar diluents. The extractant must be saponified by neutralization reaction to

Table 1. Extractant used for nickel extraction (Chauhan and Patel, 2014).

No	Extractant	Description	Application
1	D2EHPA	*di(2-ethylhexyl) phosphoric acid*	Separation of cobalt and nickel in various media such as sulfuric and chloride, pH values 3-5 can be used for extraction
2	PC88A	*2-ethylhexyl phosphonic acid mono 2-ethyl hexyl ester*	Separation of cobalt and nickel in various media such as sulfuric media, pH values 4-7 can be used for extraction
3	Cyanex 272	*bis(2,4,4-trimethylpentyl) phosphinic acid*	Separation of cobalt and nickel generally media such as sulfuric acid, pH value 6-7.5 can be used for extraction

Table 2. List of basic extractants, solvating, and ionic liquid (Alvial-Hein et al., 2021).

No	Class	Extractant	Chemical name	Chemical formula
1	Basic	Alamine 308	Tri-n-octylamine	$C_{24}H_{51}N$
2		Alamine 336	N,N-dioctyl-1-octanamine	$C_{24}H_{51}N$
3		Alamine 304	Tri-n-dodecyl amine	$C_{36}H_{75}N$
4	Solvating	Cyanex 923	Mixture of trialkyl-phosphine oxides	
5		1-octanol	1-octanol	$C_8H_{18}O$
6		TBP	Tributyl phosphate	$C_{12}H_{27}O_4P$
7	Ionic Liquid	Cyphos IL 101	Trihexyl(tetradecyl)phosphonium chloride	$C_{32}H_{68}ClP$
8		Cyphos IL 104	Trihexyl(tetradecyl)phosphonium bis-2,4,4-(trimethylpentyl) phosphinate	$C_{48}H_{102}O_2P_2$
9		TOPO	Trioctylphosphine oxide	$C_{24}H_{51}OP$

increase extractability and avoid pH increase (Sun et al., 2019). The number of studies related to acidic extractants on nickel and cobalt extraction solvents, Table 3 shows a summary of several types of acid extractants, leaching media, sources, and composition of feed solutions, extracted metals, and stripping media used (Kihlblom, 2021), an ore derived from the Finnish Boliden mine are leached using sulfuric acid. Feed solution contains metals such as Co, Ni, Mg, Al, Mn, Cu, Fe, Zn and Ca. The pregnant leach solution is carried out precipitation process to remove Fe, Zn, and Cu. Cyanex 272 extractants were modified by adding TBP and naptha as modifiers. Batch simulation 3 cycles were used with a ratio of A/O=1, resulting in 69% and 100% cobalt recovery values at pH 4.5 and 4.8, while nickel recovery values of 0% and 3%. Furthermore, a scrubbing process was carried out using $CoSO_4.7H_2O$ dissolved in distilled water at pH 3.7 to separate nickel from organic solution, after which the stripping process was successfully carried out using 24 g/L sulphuric acid (Oliveira et al., 2019) HPAL process is used to recover nickel and also cobalt. After the leaching step using sulfuric acid, a separation step is required. Ion exchange technique is commonly used, mainly solvent extraction. Cyanex 272 is usually used as an organic extract to separate cobalt from nickel-rich solution. Despite that, the use of more than one organic extract can increase the metals separation and it is not explored. The goal of this work was to study the synergism of Cyanex 272 and Ionquest 290 to separate cobalt from nickel-rich solution. Experiments were performed at pH 5.2 and 65 °C. Results showed that cobalt separation was maximum using 80% of Ionquest 290 and 20% of Cyanex 272 (99.3%). Performs solvent extraction with synergis from two acid extractants: cyanex 272 and ionquest 290. Leach liquor is synthesized to simulate nickel laterite leach solution using a sulphate leach agent. Leach solution, there are nickel and cobalt and other metals such as Mn, Mg, Cu, Zn, and Ca. The experiment was carried out at pH 5.2 at a temperature of 65 ºC with a ratio of A/O which is 2/1 and kerosine was used as a diluent. The best results cobalt extraction was obtained at the synergistic ratio of Ionquest 290 80% and 20% cyanex 272 yielding a value of 99.3%, the synergistic ratio of the extractant can minimize nickel co-extraction up to a value of 4.6%.

(Taylor and Reddy, 2007) copper raffiné was used in nickel cobalt separation studies using saponified Cyanex 272. Composition of copper raffinate Cu: 0.35 g/L, Ni: 16.88 g/L, Co: 1.69 g/L and Fe: 0.07 g/L with a pH of 1.0. Other impurities such as copper and iron are separated through a precipitation process using a pH range of 5.3 to 7.7 using an alkaline solution. The aqueous feed used contains s 1.65 g/L cobalt and 16.42 g/L nickel. The use of 0.13 M Cyanex 272 (60% neutralized with alkali) in two counter-current stages at an aqueous to organic phase ratio of 1.1:1 gives a cobalt extraction yield of up to 99% and Ni co-extraction of only 0.18%. After that, the nickel scrubbing was carried out with a cobalt sulphate solution containing 0.06 to 0.48 g/L Co at pH 3-4.5. Stripping cobalt using synthetic spent electrolyte solution with a ratio of O/A=2.5 at pH 1.5 with two counter-current stages, the result is 98% cobalt can be stripped.

D2EHPA is the first generation of extractants for nickel and cobalt separation. The first cobalt SX plant was commissioned in 1974 at then Matthey Rustenburg Refiners in South Africa using D2EHPA. The use of D2EHPA is done for several reasons, such as laterite leach solution

Table 3. Separation and recovery Co and Ni using acidic reactant.

No	Media	Feed Source	Extractant	Composition g/L	%Separated Metal	Stripping	Reference
1	Sulphate	Ores at Boliden's mine	Cyanex 272	Co: 1.71; Ni: 9.89; Mg: 2.19; Mn: 0.19; Al: 0.36; Ca: 0.13	99% Co	24 g/L sulphuric acid	(Kihlblom, 2021)
2	Sulphate	Synthetic solution	Cyanex 272 and Ionquest	Ni: 88; Co: 2.95; Mn: 0.55; Mg: 3.03; Cu: 0.25; Zn: 0.07; Ca: 0.5	99% Co	-	(Oliveira et al., 2019)
3	Sulphate	Synthetic solution	cyanex 272 and D2EHPA	Cu: 0.35 g/L, Ni: 16.88 g/L, Co: 1.69 g/L, Fe: 0.07 g/L	99% Co	synthetic spent electrolyte (SE) solution	(Taylor and Reddy, 2007)
4	Sulphate	Synthetic solution	D2EHPA	Ni: 1; Co: 1; Fe: 0.5	60.1% Ni and 83.80% Co	2M sulphuric acid	(Arslan et al., 2023)
5	Sulphate	Synthetic solution	D2EHPA	Ni: 3.0, Co: 0.3, Mn: 2.0, Mg: 3.0, Zn: 0.3, Cu: 0.1, Ca: 0.5	99% Mn as impurites	hydrochloric acid	(C.Y. Cheng, 2000)
6	Sulphate	Spent LIB batteries	D2EHPA and Cyanex 272	Co: 20, Li: 2.8, Cu: 1, Ni: 2.4, Mn: 3.9, Al: 0.9	90% impurities extracted; 99% Co extracted using Cyanex 272	3M sulphuric acid	(Pagnanelli et al., 2015)
7	Sulphate	Synthetic solution	Versatic 10	Ni: 3.3, Co: 0.35, Fe: 0.15, Mg: 7.55	94.6% Co and 86% Ni	H_2SO_4 0,1 M	(Ichlas and Purwadaria, 2017)
8	Sulphate	Synthetic solution	Versatic 10 and Cyanex 272	Ca: 0.50; Co: 2.10, Cu: 0.25, Mg: 3.50, Mn: 0.55, Ni: 75.0, Zn: 0.06	Keeping 99.5% Ni on Raffinate	-	(Guimarães et al., 2014)
9	Sulphate	Synthetic solution	PC-88A	Ni: 8.775, Co:0.409	97.21% Co	-	(Dwi et al., 2023)
10	Sulphate	Ni-Cd batteries	D2EHPA	Ni: 12.45, Cd: 7.3, Co: 0.212	98.3% Cd, with co-Extraction Ni and CO	0.2 M H_2SO_4	(Agrawal et al., 2010)

which contains several other metals such as Fe, Zn, Ca, Cd, Mn, Cu, Mg, Co, and Ni (Sole, 2018). D2EHPA has its selectivity against the metal according to pH equilibrium, Co and Ni can be separated effectively at pH 4 (Sole, 2008). Another reason the cobalt-D2EHPA complex is hydrophobic, facilitating its transfer to the organic phase, while the nickel complex can contain one or two water molecules in its inner coordination sphere and is therefore more hydrophilic (Golding and Barclay, 1988).

(Arslan et al., 2023) Solvent extraction is applied for extracting nickel from sulfate solutions containing iron and cobalt ions. This process can also be applied for the cleaning of waste solutions and for increasing solution concentrations after the leaching of low-grade nickel ores. Di-2-Ethylhexyl phosphoric acid (D2EHPA conducted research on synthetic sulfate solutions containing Ni, Fe,

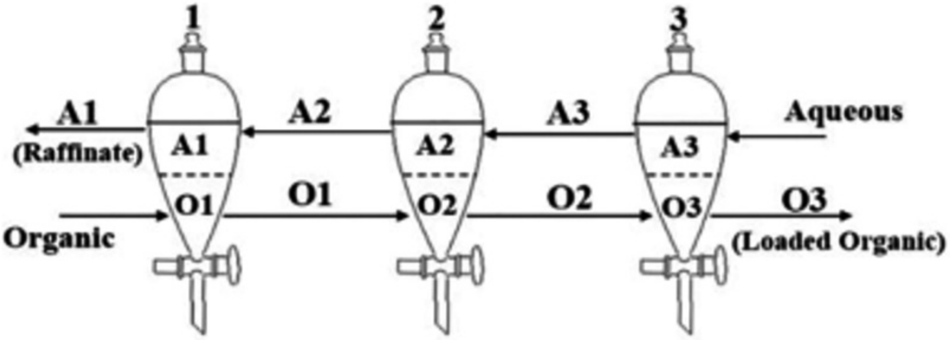

Figure 3. Three-stage continuous countercurrent extraction modified from Peng et al., 2021.

and Co). The study was conducted by considering several factors such as the content of each metal, the ratio of A/0 varied, and steering speed 50 rpm for 15 minutes. Variation in acidity value, with 10 wt% di-2-ethylhexyl phosphoric acid (D2EHPA) extractant diluted using kerosine. pH variations from 1-12 are important in increasing nickel extraction yields, 80% nickel extraction are obtained at pH 12. A/O ratio variation 1/1, 1/2, 1/3, and 1/4 are used, as increasing the ratio will increase the extraction value, but optimum at 1/1. Solvent extraction using D2EHPA will extract the three metals with extraction percent of 60.1% Ni, 99.44% Fe, and 83.8% Co. Iron can be separated during the stripping process using 2 M H_2SO_4 solution, with stripping efficiency values of 53.74% Ni, 0.58% Fe, and 66.67% Co were found.

Nickel laterite leach solution generally has several metal impurities, one of which is Mn (Cheng, 2000). Manganese must be separated from the leach solution to enhance the effectiveness of solvent extraction methods for nickel and cobalt extraction. Synthetic leach liquor contains 3.0 gr/L nickel, 0.3 gr/L cobalt, 2.0 gr/L manganese, 3.0 gr/L magnesium, 0.3 gr/L zinc, 0.1 gr/L copper and 0.5 gr/L calcium to simulate a solution after iron precipitation at pH 4.5. The study explained that acidity, temperature, and multi-stage extraction are important in separating Mn. At pH 3.5 and 40 ºC, two extraction stages can extract 99.9% Mn from leach solution, and only 7 ppm cobalt and 15 ppm nickel are present in the organic solution. A hydrochloric acid stripping is necessary to prevent gypsum precipitation and iron poisoning of D2EHPA. D2EHPA is a frequently employed agent for separating manganese from leach solutions obtained from spent Lithium-Ion Batteries (LIBs). (Pagnanelli et al., 2015), using D2EHPA to remove impurities such as Cu, Al, and Mn. Iron is also categorized as impurities, iron can be removed by precipitation method at pH 3.8, using D2EHPA with D2EHPA/Mn molar ratio=4, with TBP as modifier was done to remove other impurities, using two stages counter current at A/O=1. The reported result is that 90% of impurities were extracted, with co-extraction <20% for Cobalt and Nickel. After that, nickel and cobalt can be separated more effectively using Cyanex 272, with the result that 99.9% of cobalt can be extracted and only 10% of Ni and Li co-extraction is found. The utilization of D2EHPA plays a crucial role in eliminating impurities, thereby enhancing the efficacy of the solvent extraction method for the separation of nickel and cobalt.

The separation of nickel and cobalt from leach solution after Fe precipitation was investigated by (Ichlas and Purwadaria, 2017). A synthetic sulfate solution was created to simulate the pregnant leach solution (PLS) of nickel laterite following iron precipitation through alkali addition. The solution consisted of nickel at a concentration of 3.3 g/l, cobalt at 0.35 g/l, iron at 0.15 g/l, and magnesium at 7.55 g/l. Versatic 10 at a concentration of 20% and TBP (tributyl phosphate) at 5% are diluted with kerosene as the organic phase. The solvent extraction process is conducted at room temperature and pH 7, employing an A/O ratio 1. The extraction yields for nickel, cobalt, iron(II), and magnesium are 96.3%, 94.2%, 98.3%, and 2.7%, according Figure 3, respectively (Peng et al., 2021). Following this, iron in the organic phase can be separated from nickel and cobalt through stripping using 0.1 M H_2SO_4. Stripping efficiency was 86.0% and 94.6% for Ni and Co, while Fe was only 0.8%. (Guimarães et al., 2014) Versatic 10 is also investigated to help solvent extraction under conditions synergize with cyanex-272. The synthesis solution is made to resemble nickel laterite sulphate leach liquor, with each content Ca=0.50; Co=2.10; Cu=0.25; Mg=3.50; Mn=0.55; Ni=75.0; Zn=0.06 in g/l. Cyanex 272 (20% v/v) used at pH 3.9 can separate nickel from other metals, extracted 98% of zinc, 80% of copper, 70% of manganese, 46% of cobalt, and around 10% of calcium and magnesium in a single-stage, thus keeping 99.5% of the nickel in the raffinate stream. Solvent extraction above pH 6.0

is not recommended as it will increase the viscosity of the organic phase to undesirable levels. Afterwards, when Nickel and other metal minorities were left behind in raffinate, a mixture of Cyanex 272 (20% v/v) with Versatic 10 (10% v/v) was used for the separation of calcium and magnesium from nickel sulfate solution at pH 5.1 (Dwi et al., 2023). Research related to Final Separation in Sulphate Leach Solution containing only Ni and Co. Synthesis solution is made for with Nickel (II) sulfate hexahydrate and Cobalt (II) Heptahydrate Sulfate so that it resembles leach solution Ni-Co which has been separated from other impurities. PC-88A with kerosine as diluent is used for the solvent extraction process, with the best conditions at pH 5, shaking speed 60 rpm, and shaking time 90 minutes. A/O ratio=1:4, with PC-88A concentration of 40% to obtain 97.21% cobalt extraction from nickel sulfate solution.

Basic Extractant

Many types of base extractants in nickel cobalt extraction solvents are amine, primary, secondary or tertiary amine (Wang and Lee, 2016) solvent extraction experiments were performed by employing the mixture of organophosphorous extractants (D2EHPA, PC 88A and Cyanex 272. The mechanism of distribution of metal ions in the aqueous and organic phases occurs in anions (Lommelen et al., 2019). In equation 3 described (Foltova et al., 2018), chloride media generally reaches better conditions than in sulphide media for cobalt extraction. Cobalt ions will form cobalt chlorocomplex compounds with Cl^- ions, but nickel ions do not form chlorocomplex compounds (Cheng, 2019). These differences in properties make cobalt easier to react with basic extractants. The use of basic extractants began to be developed such as Tri methyl amine (TMA), Tri-n-octylamine (TOA), Tris-2-ethylhexylamine (TEHA), Methyltrioctylammonium chloride (MTOAC), to Alamnie 336. Table 4 provides a comprehensive summary encompassing the fundamental categories of basic extractants, leaching media, sources, and compositions of feed solutions, as well as the extracted metals and stripping media employed. The study was conducted by (Mubeena and Muthuraman, 2015), simulating waste water containing nickel carried out solvent extraction with Tri methyl amine (TMA). Various variations include pH, extractant concentration, process time, A/O ratio, and stripping agent. Optimum extraction can obtain Ni more than 90%, using 1.35 TMA in kerosine solution with a reaction time of 5 minutes, pH 7, A/O ratio 1:1. Stripping had a good result using 2 mol/L HCl and 0.3 mol/L H_3PO_4 with extraction values of 75.3% and 57.8% respectively. This organic phase can be used up to 10 times, with a slight loss of efficiency.

The study of separating cobalt from acid leaching spent Lithium-ion batteries (LIBs) with Alamine 336 as extractant in solvent extraction was studied by Xuan et al., 2022. After leaching spent LIB, cobalt(II) was selectively extracted toward manganese(II) by liquid-liquid extraction with 0.4 mol/L Alamine 336 (tri-octyl/decyl amine) diluted in kerosene modified using 10% (vol) 1-dodecanol at an optimized phase volume ratio between the organic phase and the aqueous phase of OA=1/2. After that, the manganese remaining in raffinate was extracted using 0.7 mol/L Alamine 336 in kerosine modified with 10% (vol) 1-dodecanol at O/A=2. A raffinate containing a high concentration of nickel was obtained in the preceding process. Subsequently, nickel precipitation was performed by adding NaOH at pH 8, forming solid nickel(II) hydroxide. This process can produce an aqueous phase 94.6% cobalt and 5.4% manganese for further precipitation. During the second solvent extraction of the raffinate, a manganese (Mn) purity of 99% was achieved. This process also facilitated the extraction of over 97.0% nickel(II) from the leach solution, which was precipitated as nickel(II) hydroxide.

(Kumbasar and Tutkun, 2008) Study of separation of cobalt from acidic solution by TOA as emulsion liquid membrane. The aqueous feed is prepared from a zinc plant residue leach solution using H_2SO_4. Leach liquor contains Zn, Cu, Fe and Cd, besides Co and Ni. The separation focuses on Ni and Co, so metals other than nickel and cobalt are precipitated by adding reagents and adjusting pH. The study used TOA as an extractant, nonionic polyamine as phase modifier, NH_4SCN as an additional reagent to increase the selectivity of Co over Ni and kerosine as diluent. The phase concentration had a significant effect, the increase in nonionic polyamine from 2% to 3% led to a decrease in cobalt extraction. TOA concentrations did not significantly impact variations from 1.5 to 8% v/v. The increase in pH from 3.8 to 4.5 only slightly increases the extraction of cobalt. 99% cobalt extraction was achieved under optimum conditions under NH_4SCN 0.3 M reagent conditions, feed solution 4.5, ECA 4360J 2% W/W, Tri-octylamine 2% W/W, Treatment ratio (volume ratio of emulsion phase to feed phase): 1/4, and Phase ratio (volume ratio of strip phase to membrane phase): 1.0.

Various methods and research have been carried out to further understand the cobalt separation and purification process from both primary and secondary resources. Tri-n-octylamine (TOA) as an extractant for cobalt in acidic chloride was studied by (Mishra et al., 2021). a synthesis solution is prepared from $COCl_2$ (0.01 M)+1.5 M KCl+ 3 M HCl. The use of 0.1 M TOA in kerosine was able to extract 89.71% Cobalt at a 4:1 O/A ratio. Extractant concentration, salt concentration, HCl concentration, diluent type and O/A ratio significantly influence solvent

Table 4. Separation and recovery Co and Ni using basic reactant.

No	Media	Feed Source	Extractant	Composition g/L	% Separated Metal	Stripping	reference
1	Sulphate	Simulated wastewater	Tri methyl amine (TMA)	Ni: 0.01-0.05	90% Ni	2 mol/L HCl	(Mubeena and Muthuraman, 2015)
2	Acid	Spent (LIBs)	Alamine 336	Ni, Mn, Li	97% Ni		(Xuan et al., 2022)
3	Sulphate	Zinc plant residue	TOA	Co: 1.2, Ni: 1.5	99% Co	6M NH_3	(Kumbasar and Tutkun, 2008)
4	Chloride	Synthetic solution	Tri-n-octylamine (TOA)	$CoCl_2$ (0.01M) + 0.5M KCl+3M HCl	89,7% Co	-	(Mishra et al., 2021)
5	Chloride	Spent Ni-Cd batteries	Trioctylalamine	Cd: 13.5; Ni: 12.15, Co: 0.9	First 92.7% Cd and 26.7% Co, the second 83% Co	0.5 mol/L Ammonia	(Fatemeh et al., 2022)
6	Chloride	Synthetic solution	Tris-2-ethylhexylamine (TEHA)	Co: 1, Li: 0.3	99% Co	0.5 mol/L HCL	(Nguyen et al., 2021)
7	Chloride	Spent LIB	Methyltrioctylammonium chloride (MTOAC)	Co: 10.19, Ni: 0.42, Li: 0.03	98.23% Co	0.01 M HCl	(J. Cheng, 2019)
8	Chloride	Synthetic and real LIB leach solution	Methyl trioctyl ammonium chloride	Li: 1.163; Mn: 3.534, Co: 2.493, Ni: 6.4	99% Co	1.5 mol/L HCL	(Yang et al., 2023)
9	Chloride	Spent Ni-Cd batteries	Tri-n-dodecyl amine (Alamine 304)	Cd: 16.1, Co: 0.85, Ni: 20,8,Zn: 0.02, Mn: 0.02; Fe: 2.71	90.4% Co	0.5 mol/L H_2SO_4	(Fernandes et al., 2012)
10	Chloride	Synthetic Spent Catalyst Solution	Alamine 308	Co: 0.12, Al: 17.9	99% Co	H_2O pH=1.0	(Banda et al., 2012)

extraction. The study may provide a deeper understanding of the use of TOA as an extractant in cobalt recovery from secondary resources.

(Fatemeh et al., 2022) The research was conducted to determine the separation behavior of cadmium and cobalt from spent rechargeable Ni-Cd Batteries hydrocloric leach solution using Trioctylalamine (TOA), so that the purity value of cobalt and nickel can be obtained. Concentration in leach solution Cd: 13500, Ni: 12150, Co: 900 in mg/L. The proposed process has 2 stages, the first stage is carried out 4 successive extraction which produces 92.7% cadmium and 26.7% cobalt extracted in the organic phase. Nickel is not extracted because it does not form metal chlorocomplexes. Cobalt and cadmium in the organic phase form $[TOAH^+]$ $[MCl_3^-]$, M is Cd or Co, which can be stripped with ammonia solution. In the organic phase of the first step extraction, Cd can be separated from Co by stripping using 0.5 mol/L Ammonia. 86.3% of cadmium was extracted on the loaded phase of the aqueous strip. The second stage was performed with five consecutive extractions on raffinate, the total extraction of cobalt accumulated in the organic phase reached 83%. Efficient recovery on stripping using 7M NH_3 can extract 79.3% Co from the organic phase step two. This stage is suitable for separating Cd and Co from the Nickel rich aqueous phase. In their study, Nguyen et al. (2021) examined the application of tris-2-ethylhexylamine (TEHA) as an extraction agent in the synthesis of chloride leach solution from spent lithium-ion batteries. The primary objective was to investigate the separation between cobalt (Co) and nickel (Ni). It was observed that TEHA, when diluted in fatty acid methylesters (FAME), demonstrated the capability to separate nickel from cobalt effectively. Optimum conditions were obtained at 10% TEHA diluted with FAME, with a ratio of A/O=1/2, 97.5% Cobalt can be extracted from the synthesis solution. Stripping with 0.5 mol/L HCL with A/O ratio=3/2 at two stages counter current yields 99% cobalt extracted from the organic phase. Interestingly, the extraction capacity of TEHA that has been regenerated after five cycles has not changed. These results indicate that TEHA and FAME have the potential as renewable extractants. The use of methyltrioctylammonium chloride (MTOAC) to separate cobalt from chloride solution from spent lithium-ion batteries was studied by (Cheng, 2019). Chloride complex compounds can be formed with chelating Co, but not nickel. This difference in complexity is used for chelating complexes by methyltrioctylammonium chloride (MTOAC). Cobalt extraction achieved maximum efficiency with an extraction value of 98.23%, while nickel only lost 0.86%. These optimal results were achieved under single-stage conditions of $[Cl]^{-}aq$= 5.5 M, [MTOAC]org=1.3 M, O/A=1.5, and pH=1.0. The stripping rate of cobalt from Co(II)-MTOAC complexes using 0.01 M hydrochloric acid was 99.95%. The study noted that several factors such as Cl ion, MTOAC concentration and phase ratio have an essential role in the separation of cobalt, but the acidity value does not have a significant effect. The study identified that a chemical reaction governed the extraction of cobalt, that the activation energy and associated kinetic equation were 44.98 kJmol1 and $R_{(Co)}=4.7x10^{3}[MTOAC](org)1^{.85}[Co](aq)^{1.25}$.

Methyl trioctyl ammonium chloride (N263) as an extractant was investigated (Yang et al., 2023) we investigated solvent extraction with quaternary ammonium salt N263 in the sodium nitrite system. NO2- combines with Co (II to determine the separation of Co ions from cathode materials of lithium batteries nitrate solution. The separation of cobalt is effective with other metals such as Mg, Ni, and Li. The feed of the synthesis solution produces cobalt separation exceeding 99%, under HCL conditions of 1.5 mol/L, the A/O ratio is 1, isopropyl alcohol as the phase modifier and kerosine as diluent. Extraction 92% cobalt can be achieved using 1.5M HCl as a stripping agent. This extractant still has high efficiency when used in five cycles. In the study, several factors that affect SX cobalt using methyl trioctyl ammonium chloride were described. Conditions The concentration of sodium nitrate and acidity in HNO_3, H_2SO_4, or HCL media is important. In terms of increased extraction value, iso-propyl is the best modifier compared to sec-octanol and Iso-Ontanol. After finding the optimum extraction conditions, extraction was carried out on the real of lithium batteries chloride nitrate solution. Extraction efficiency in real leaching solutions exceeding 99% is achieved using three multistage extractions, with stripping can reach 95% with 1.5 mol/L HCl when A/O is 1/1.

(Fernandes et al., 2012) Tri-n-dodecyl amine (Alamine 304) acts as Cobalt extractant against Ni in chloride solution spent Ni-Cd batteries. Cadmium is classified as an impurities in the nickel cobalt separation process, TBP is used as an extractant to separate cadmium. Raffinate rich in nickel and cobalt is carried out as a two stage multi extraction solvent using 0.16 M Alamine 304 to extract Cobalt. 90.4% Co and 23.1% of nickel were extracted under exraktan conditions of 10 vol% in kerosine, ratio A/O=1, and at 25 ºC and the free acidity range of 5-8 mol/L. The acidity value of the solution must be considered because it will affect the formation of cobalt chlorocomplexes. At pH below 2.5 cobalt ions are not in complex compounds as $CoCl_3$ and $CoCl^{2-}{}_4$, but are dominated by Co^{2+} ions.

IONIC LIQUID AS EXTRACTANT

In the hydrometallurgical process of extracting nickel from laterite ores, acid leaching is commonly used. Sulfuric acid is a strong acid widely used in the HPAL process for this purpose (Yuliusman et al., 2018). The leaching process yields several metals, including nickel and cobalt, which need to be separated for further processing. Various extractants, such as Cyanex 272, PC88A, and D2EHPA, are employed. Among these, Cyanex 272, also known as bis (2,4,4-trimethylpentyl) phosphinic acid, exhibits a high capacity for separating nickel and cobalt. In a sulfuric acid medium, Cyanex 272 is known to outperform PC88A and D2EHPA in separating cobalt from pregnant leach solutions (Kursunoglu and Kaya, 2019). However, the use of Cyanex 272 and PC88A is restricted by the narrow pH range in which they are effective. This limitation can be addressed by controlling the pH through saponification, a process in which the extractant is partially converted into its sodium salt (Rodrigues et al., 2022).

Previous studies have also examined the use of saponification in extractants. NaPC88A and NaCyanex 272 at 0.05 M are suitable for cobalt and nickel extraction in sulfuric acid media (Devi et al., 1998). However, stripping requires strong acids such as sulfuric acid or chloride (Kursunoglu and Kaya, 2019). Additional processes and reagents are required to effectively separate cobalt from sulfuric acid media, highlighting the need to switch to alternative extractants that are not pH-dependent and do not require sulfuric acid in the stripping process. The process could lead to a more cost-effective and environmentally friendly extraction process.

The solvent extraction process using conventional organic solutions presents a range of environmental, technical, and human health concerns. To address these issues, a new type of extractant that is environmentally friendly and harmless to the ecosystem has been developed, known as green solvents (Dhiman and Gupta, 2019). In recent years, ionic liquids (ILs) have emerged as a promising alternative in solvent extraction. ILs can be used as a modifier, diluent, or the main extractant, replacing traditional extractants (Chaverra et al., 2020). Ionic liquids (ILs) are liquid salts with a unique ion composition and a melting point below 100 °C. The ions in ionic liquids come from organic cations and inorganic anions. Ionic liquid has several unique physical and chemical properties, such as high flash point value, high heat stability, and the ability to adjust properties relatively easily to be applied to various applications(Caminiti and Gontrani, 2013). Figure 4 below provides additional details on cobalt extraction using the trioctyl(alkyl) phosphonium chloride type of ionic liquids.

The principle of solvent extraction using ionic liquid is almost the same as using organic solutions. Extraction with ionic liquids, chloride ions can generally come from leach agents or chemical reagent added. Then cobalt will form a cobalt chloride complex. After that, complex cobalt compounds will exchange ions in an ionic liquid (Chaverra et al., 2020). The cobalt in Ionic liquid is cobalt chlorocomplexes, which will then be extracted using ionic liquids such as Phosphonium ionic liquids (PILs). The extraction principle of cobalt chlorocomplexes is also utilized in tertiary amine and quaternary amine types of basic extractants. Basic extractant-type quaternary ammonium and phosphonium are efficient for separating Co(II) and Ni(II) aqueous phases of the chloride ion medium. This type of extractant tends to extract cobalt as tetrachlorocobaltate(II) complex, $[CoCl_4]_2$, through the principle of anion exchange mechanism. Some studies have found that this extractant can extract cobalt on sulphate media by adding chloride ions (Onghena et al., 2017). In research conducted by Fernandes, where Co(II) forms chlorocomplexes in HCl concentrations higher than 2.5 mol/L (Fernandes et al., 2013). One tertiary amine compound is N,N-dioctyl-1-octanamine, known as Alamine 336. The following is a reaction between tertiary amine and cobalt chlorocomplexes in equation 8 (Fernandes et al., 2012).

$$R_3N+H^++CoCl_3^-\rightarrow R_3NH^+CoCl_3^- \qquad (8)$$

In the study conducted by Fernandes, Alamine 336 was utilized as an extractant to separate nickel in hydrochloric acid media from Ni-Cd batteries. After two extractant processes, the cobalt content in the leachate decreased from 0.85 g/L to 0.02 g/L with a 97.5% extraction efficiency for cobalt and only a 2.9% extraction efficiency for nickel(Fernandes et al., 2012). Meanwhile, sulfuric acid with low concentration in alkaline extractants has been found to be effective in achieving maximum efficiency (Torkaman et al., 2017) D2EHPA, Cyanex272.

Cobalt can also be extracted from chloride media using quaternary amine type extractants, such as Aliquat 336. As previously mentioned, cobalt tends to form $CoCl_3^-$ and $CoCl_4^{2-}$, while nickel forms Ni^{2+} and $NiCl^+$ (Marcus and Sengupta, 2002). The cobalt chlorocomplex compound is very favorable for reacting with quartenary amine, the reaction equation is as follows equation 9.

$$CoCl_4^{2-}+2R_4NCl_{org}=CoCl_4(R_4N)_2,\ org+2Cl^- \qquad (9)$$

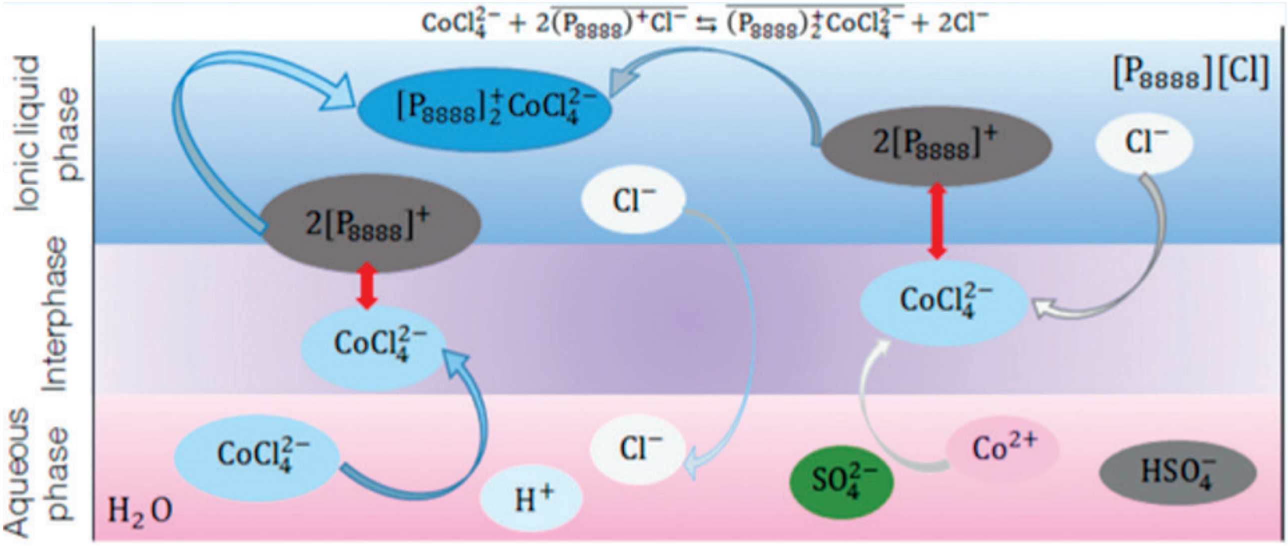

Figure 4. Solvent extraction using ionic liquid modified from Chaverra, 2020.

In the research conducted by Liu, a synthesis solution was made to simulate the results of nickel laterite leaching using hydrochloric acid. The composition of synthetic leach solution is Co 0.54g/L, Ni 13.37 g/L, Fe 81.2 g/L, other impurities are Mg, Mn, Ca, and Al as shown in Figure 5 (Fernandes et al., 2012). As seen in Table 5, the best cobalt extraction is at 1 M with a value of 63.7%, while Nickel extraction did not occur. Alamine 336 and Aliquat 336 have similar cobalt extraction capabilities, but Aliquat is superior because there is no nickel co-extraction, according Table 5 (Liu and Lee, 2016).

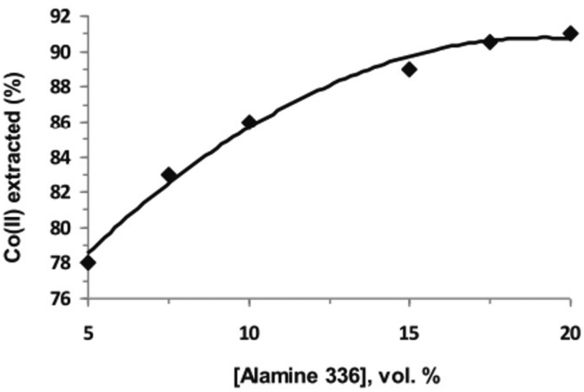

Figure 5. Cobalt extraction on acidic chloride media using Alamine 336 with a variation of extractant dissolved with kerosine modified from Fernandes et al., 2012.

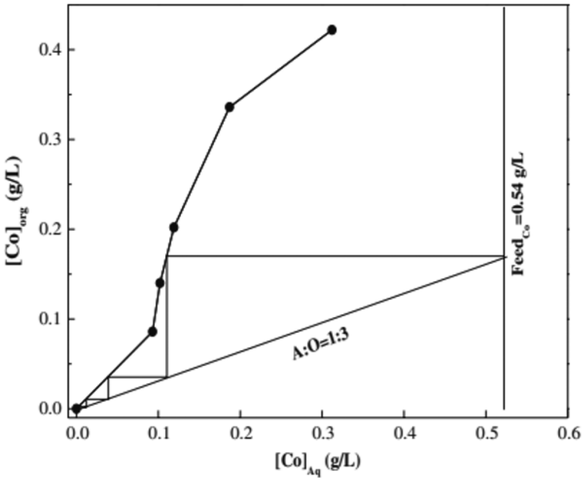

Figure 6. McCabe-Thiele plot for Cobalt extraction using Aliquat 336 modified from Liu and Lee, 2016.

A multi-stage extraction process is required to extract cobalt using aliquat 336 as a single stage is not sufficient. McCabe-Thiele diagrams determine the optimal number of extraction stages required to separate cobalt from nickel effectively. Figure 6 explains that cobalt can be extracted ideally using three stages of counter-current extraction. Hydrochloric acid is used as a stripping agent, with a stripping percentage of 94.4% for cobalt (Liu and Lee, 2016).

The separation of nickel and cobalt in hydrochloric acid solution media can be effectively achieved with tertiary and quaternary amine extractants. However, sulfuric acid is preferred over hydrochloric acid for laterite nickel leaching due to its lower cost and corrosivity (Onghena et al., 2017). Sulfuric acid is commonly used as a leaching agent in the high-pressure acid leaching (HPAL) process to extract nickel and cobalt from limonite ore. The HPAL technology has undergone three generations of development in recent years, making the process more reliable and mature (Gultom and Sianipar, 2020).

When selecting extractants, the widespread use of sulfuric acid as a leaching medium should be considered. The choice of extractant solvent extraction process also depends on the lixiviant used. For example, amine extractants are commonly used in hydrochloric acid as a leaching medium, and their loaded organics require acids such as sulfuric acid or chloride for stripping. Despite its good extraction value, amine extractant heavily relies on hydrochloric acid in the solvent extraction and requires acid during stripping(Fernandes et al., 2012; Liu and Lee, 2016). Therefore, exploring other extractant options with good extraction value in sulfuric acid medium as a lixiviant agent is crucial and does not require acid in the stripping process. One such promising alternative for cobalt solvent extraction is phosphonium ionic liquids (PILs), which have potential for nickel extraction in sulfate media and do not require acid during metal stripping.

Table 5. Effect of Aliquat concentration on metal extraction (Liu and Lee, 2016).

Aliquat 336(M)	Extraction percentage (%)						
	Co	Ni	Mg	Mn	Ca	Al	Fe
0.50	35.7	0	0	6.5	0	0	13.6
0.75	51.8	0	0	9.3	0	0	12.4
1.00	63.7	0	0	16.8	0	0	15.4

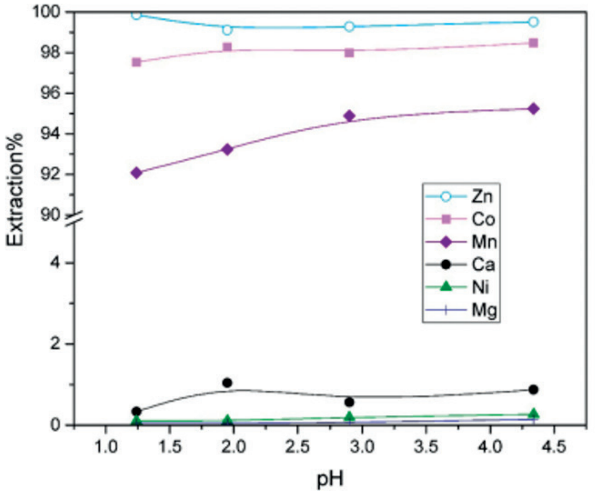

Figure 7. Metal extraction using 0.5 M Cyphos IL 101 at synthesis solution 100 g/L Cl modified from Zhu et al., 2017.

Phosphonium ionic liquids (PILs)

Phosphonium ionic liquids (PILs) have become popular for extracting rare earth and transition metals due to their unique properties. Phosphonium ionic liquid has several special properties compared to other extractants, such as non-flammability, good heat stability, and low vapour pressure(Singh and Savoy, 2020) ionic liquids (ILs). Another advantage of this extract is that it does not release H^+ ions in raffinate, so raffinate tends to be non-acidic and safe for the environment. Therefore, PILs are considered a better alternative to conventional types of extractants.

Tetradecyl-(trihexyl) phosphonium chloride (Cyphos IL 101)

The potential of using Cyphos IL 101 as an extractant has been widely investigated in the recovery process for various metals, and cobalt is one of them. This extractant has been demonstrated to be effective in extracting cobalt from nickel laterite leach solutions (Zhu et al., 2017).

Metal extraction in a solution with chloride ion content using Cyphos IL 101 can extract three primary metals Zn, Co, and Mn. Nickel, magnesium, and calcium are not extracted using Cyphos IL 101; these metal ions do not exchange with chloride ions in the extractant according Figure 7 (Zhu et al., 2017). In stripping experiments using deionized water in an organic solution containing 0.33 g/L Zn, 0.52 g/L Co and 3.31 g/L Mn shown in Figure 8. It is proved that cobalt and manganese can be stripped using water, with extraction yields almost reaching 100%. Once the value of A/0 is less than 1/3, the extraction of both metals decreases. The efficiency of extractant due to the many chloride ions in the aqueous phase. Previous studies have shown that the cobalt and nickel in hydrochloride can be separated using one extraction and three stripping stages. The result obtained is the purity of cobalt up to 99.8% (Wellens and Binnemans, 2012).

Tetradecyl-(trihexyl) phosphonium chloride [C101][Cl] can be modified into the thiocyanate form [C101][SCN] by adding potassium thiocyanate. This modification enhances the separation of cobalt and nickel in sulfuric acid media, resulting in optimal results. In Figure 9, the cobalt extraction almost reaches 100%, while no nickel extraction occurs. The reaction that occurs is an anion exchange, when testing Optical absorption spectroscopy there is a tetrachlorocobaltate (II) complex, $[CoCl_4]^{2-}$, in the IL phase. Interestingly, water can be used for stripping, and the IL can be restored again with $CaCl_2$.

Trihexyl Tetradecyl Phosphonium bis(2,4,4-trimethylphentyl) Phosphinate

The extractant under consideration is Cyphos IL 104,

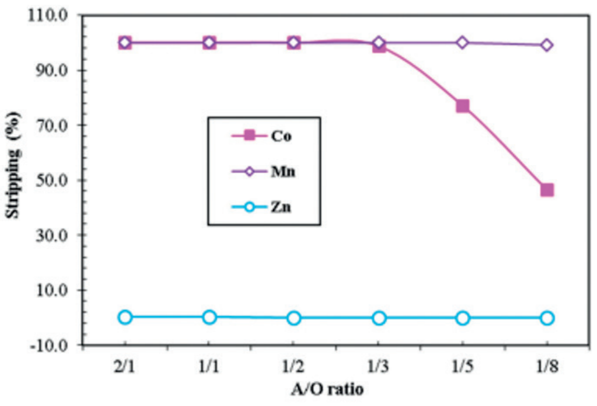

Figure 8. Metal stripping in the organic phase with deionized water modified from Zhu et al., 2017.

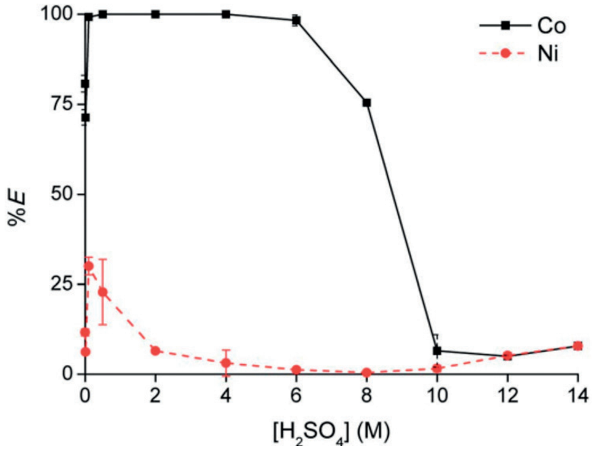

Figure 9. Extraction of CO(II) with [C101][SCN] in sulfate solution modified from Onghena et al., 2017.

which has been shown to be highly efficient (more than 95%) in extracting Co(II) without the presence of HCl. However, the extraction percentage of Co(II) decreases to nearly 3% with increasing concentrations of HCl, with a few exceptions at concentrations of 2 and 5 M HCl where there was an increase of 20% and 70% for cobalt, as shown in Figure 11 and 12, respectively (Rybka and Rgel-Rosocka, 2012; Pospiech and Gega, 2019). Figure 10 shows the effect of HCl concentration on Ni and Co extraction by the extractants of Cyphos IL 101 and Cyphos IL 104.

In another study, the extraction and separation of cobalt and nickel without the use of chloride or HCl were explored using Cyphos IL 104 by Pospiech. The study utilized nickel metal hydride batteries (Ni-MH) as a source of nickel, which was then leached using sulfuric acid, resulting in a leachate containing various metals such as Fe, Ni, Co, La, Ce, Nd, Pr, Gd, Zn, Mn, and K. D2EHPA and Cyanex 272 were used to extract various metals, leaving nickel and cobalt in the leach liquor. After the use of Cyphos IL 104 diluted with toluene to separate cobalt and nickel at O/A=1, it was found that cobalt could be extracted up to 96%, while nickel extraction only reached 18% at a pH of 5.4.

Various stripping media have been investigated for the nickel and cobalt stripping process using Cyphos IL 104. These include deionized water, sulfuric acid at concentrations of 0.25 and 2 M, and hydrochloric acid at 0.5 and 4 M. The most effective stripping medium for cobalt was found to be the aqueous phase containing 2 M sulfuric acid and 0.5 M hydrochloric acid, with more than 90% cobalt extracted in just one stripping stage as shown in Figure 12 (Rybka and Rgel-Rosocka, 2012).

Trioctylphosphine Oxide (TOPO)

The study conducted by Zhang revealed that the combination of Benzoyltrifluoroacetone (HBTA) and Trioctylphosphine Oxide (TOPO) can effectively extract cobalt from sulfuric acid media. Prior to the solvent extraction (SX) process, the extraction saponification was carried out using 2M NaOH until the saponification rate reached 70%, and the experiments were performed at a temperature of 25 °C. TOPO was used as a synergistic extractant as the use of only HBTA did not yield satisfactory results. The addition of TOPO to the organic phase improved the extraction of metal ions while facilitating the separation phase. The selectivity of different metal ions' extraction was affected by varying TOPO concentrations as shown in Figure 13 (Zhang et al., 2021).

Triphenylphosphine Oxide (TPPO)

In the research conducted by Antonio Carlos, he proposed the binary complexes of the general formula CoCl2L2 where L=triphenylphosphine oxide (TPPO). The formation of this complex in an acetone medium at a temperature of 25 °C. The reaction of the formation of cobalt chloride complex with phosphine oxides is in equation 9 (Massabni and Melios, 2019) where L= triphenylphosphine oxide (TPPO). The formation of this complex in an acetone medium at a temperature of 25 °C. The reaction of the formation of cobalt chloride complex with phosphine oxides is in equation 10 (Massabni and Melios, 2019).

$$CoCl_2+2L \rightleftarrows [CoCl_2L_2] \quad (10)$$

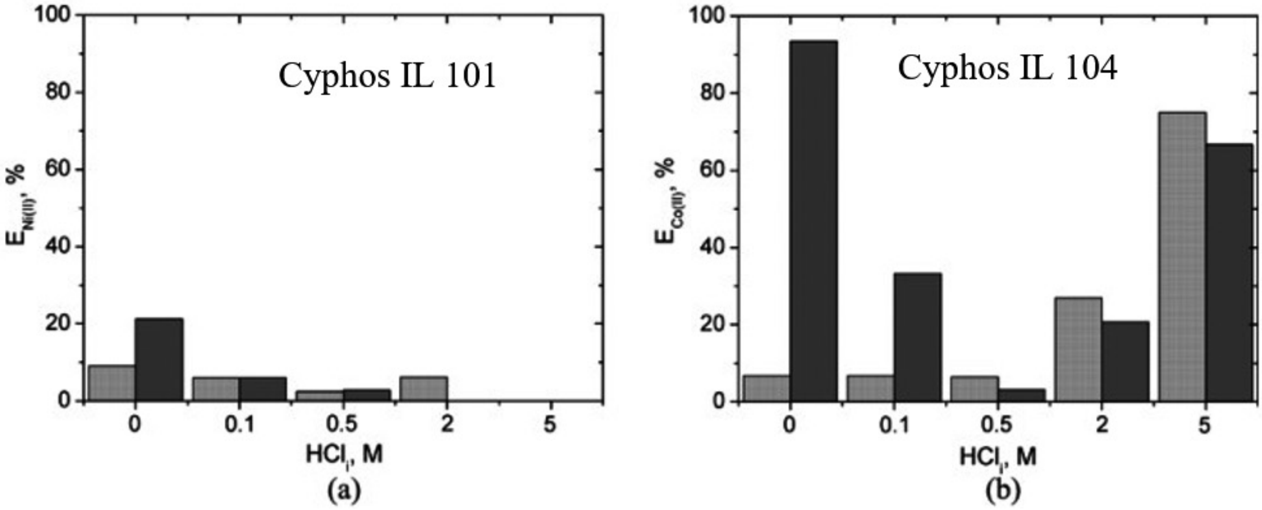

Figure 10. Nickel and cobalt extraction using Cyphos 101 and 104, with the influence of HCl concentration modified from Rybka and Regel-Rosocka, 2012.

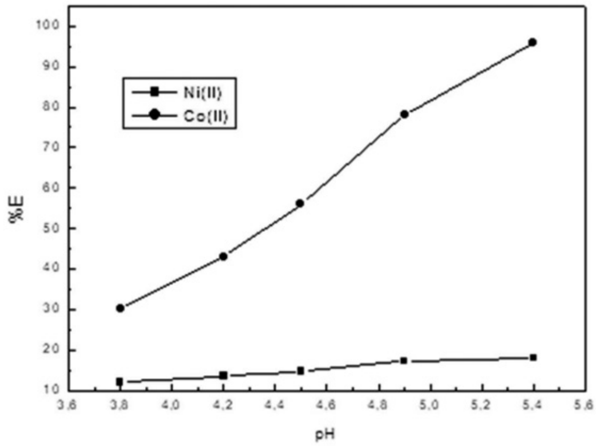

Figure 11. Extraction efficiency (%) of Ni(II) and Co(II) on pH of the aqueous solution with 0.1 M Cyphos IL 104 in toluene at pH=5.4 modified from Pospiech and Gega, 2019.

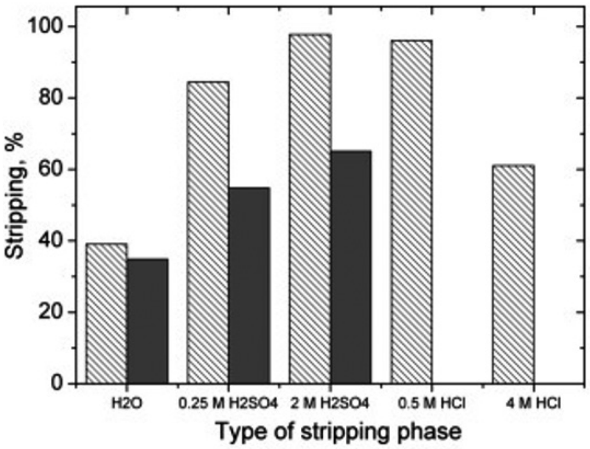

Figure 12. Cyphos IL 104 with various stripping solutions, Co (bright table) and Ni (dark table) of loaded organic 0.2 M modified from Rybka and Regel-Rosocka, 2012.

APPLICATIONS IN THE INDUSTRY

Nickel refining with solvent extraction is a vital thing that companies must pay attention to. Solvent extraction in the hydrometallurgical industry generally comes from PLS sulfuric acid medium (Hutton-Ashkenny et al., 2015). Technology in the industry has several options that can usually be used to remove impurities in PLS, such as Al, Fe, Zn, Mn, and Mg. The nickel processing industry not only uses solvent extraction to obtain nickel, but using other processes such as neutralization, precipitation, and scrubbing to increase the extraction value of extraction (Kursunoglu and Kaya, 2019).

Several applications of solvent extraction have been applied on an industrial scale. For instance, Goro mine in New Caledonia utilizes cyanex 301, precipitation are used to remove Fe, Al, and Cr before the primary solvent extraction (Mihaylov et al., 2000). The application of solvent extraction is also present at the Cooperative Research Centre for Hydrometallurgy / CSIRO Minerals. Extraction is carried out by using synergistic extractants containing Versatic 10 and decyl-4-pyridinecarboxylate esters, to extract nickel, cobalt and zinc. Furthermore, it was followed by extraction using Cyanex 272 to obtain purer nickel. The Cadlag mine also uses a solvent extraction process, which starts with extraction using Versatic 10, scrubbing on the loaded organic, then stripping with acidic conditions. The process is then followed by Cyanex 272 extraction to extract cobalt, resulting in nickel-rich raffinate that is ready for nickel electrowinning (Kursunoglu et al., 2017) cobalt 98%. Furthermore, there is also the application of solvent extraction which is carried out in Bulong Mine of Australia.

Bulong Mines employs a unique technology for its hydrometallurgical process to extract nickel. The process involves two main solvent extraction (SX) stages. Solvent extraction first stage uses Cyanex 272 to extract impurities such as Ca, Mg, Zn, Mn and Co. In the second stage, Ni is separated from Co, Ca, and Mg that escape into the raffinate, using Versatic 10 as an extractant, which is then ready for nickel electrowinning. The first extracted organic solution containing Co, Mn, Cu and Zn was sulphide precipitation, re-leaching, and then SX was carried out using D2EHPA to get cobalt and copper as shown in Figure 14 (Zhu et al., 2017). Then the copper is separated using ion exchange.

CONCLUSION

The demand for nickel as a raw material for electric batteries continues to increase, along with the development of electric vehicles that are increasingly massive. Cobalt and nickel will play an important role in the future, as the battery industry improves. The nickel refining process is crucial so that high-purity nickel can be obtained. Solvent extraction was chosen because of its selectiveness, low chemical consumption, and recyclability. Separation cobalt and nickel in solvent extraction is generally performed with acidic extractants of Cyanex 272, PC88A, Versatic 10 and D2EHPA. However, these extractants have environmental, technical process, and human health problems; therefore, further research is needed to replace these extractants. Types of extractants that are environmentally friendly and do not harm to the ecosystem are called green solvents.

Phosphonium ionic liquid (PILs), is one of the friendly extractants for the environmental ecosystem when compared to organophosphorus acid and amines extractant.

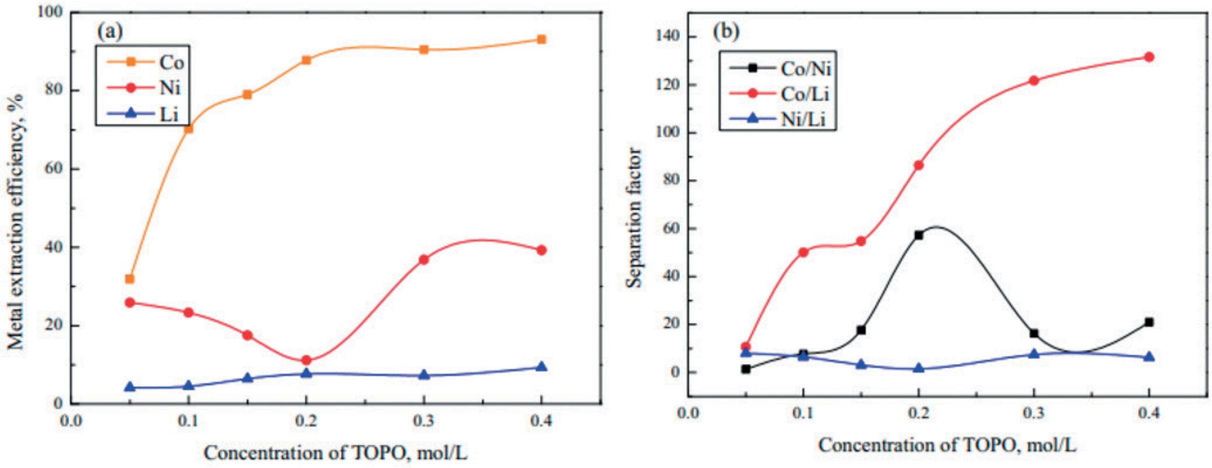

Figure 13. Effect of TOPO concentration on extraction and separation factor modified from Zhang et al., 2021.

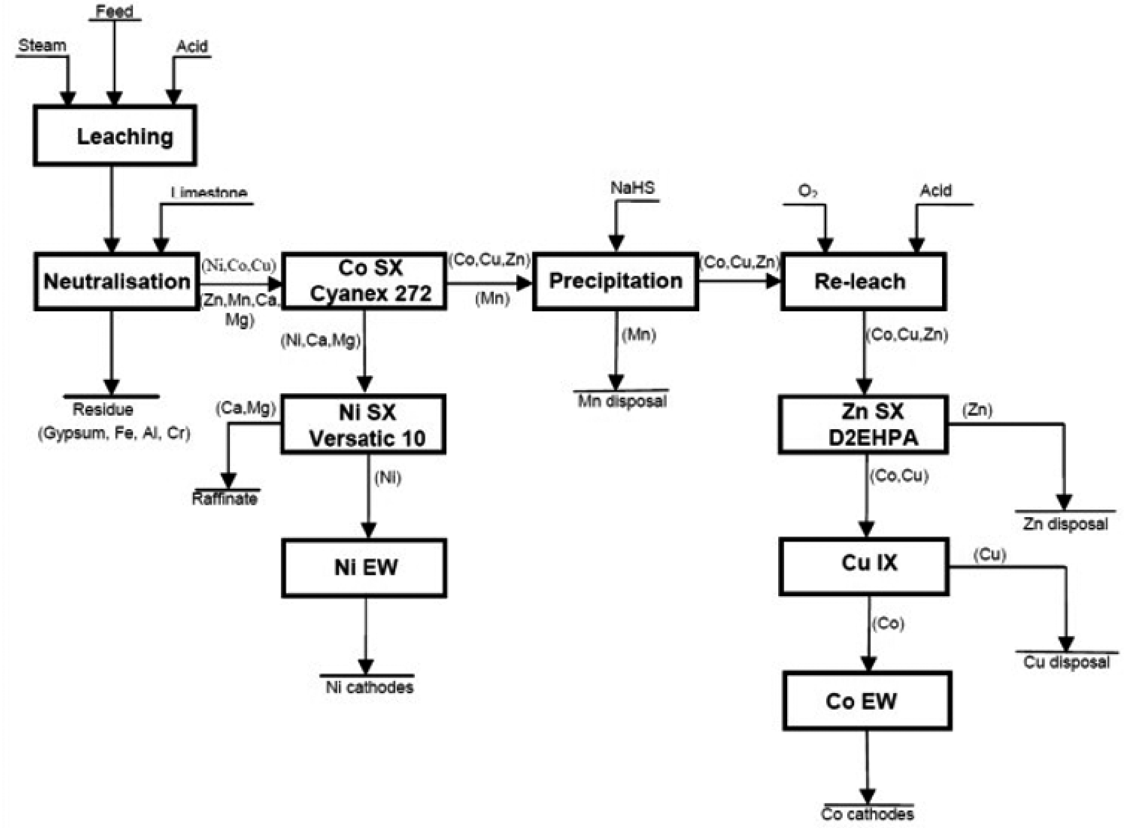

Figure 14. General flowsheet of bulong process modified from Zhu et al., 2017.

PILs offer advantages such as the ability to be used in both sulfide and chloride media, the stripping process can be done with water, and the ability to be reused. PILs have some unique properties compared to other extractants, such as non-flammability, good heat stability and low vapour pressure. Some examples of PILs are tetradecyl-(trihexyl) phosphonium chloride, trihexyl tetradecyl phosphonium bis (2,4,4-trimethylphentyl) phosphinate, and Trioctylphosphine Oxide (TOPO). Despite the potential advantages of PILs, the nickel processing industry still largely relies on conventional solvent extraction, which can have negative environmental and health impacts. Further research related to phosphonium ionic liquids (PILs) is needed to replace conventional solvent extractants in industry. Phosphonium ionic liquids (PILs) have high potential because they have a high extraction value, are environmentally friendly and do not require many chemical reagents.

ACKNOWLEDGEMENTS

We are thankful for the financial support of the Ministry of Education, Culture, Research, and Technology-Directorate of Higher Education, Research, and Technology under research project PDD 2022 and contract no. NKB-968/UN2.RST/HKP.05.00/2022 and Department of Science and Technology (DST), Government of India for funding under ASEAN-India Research and Training Fellowship Scheme with application no. RTF/2022/000219. The authors gratefully acknowledge the support of Materials Science Universitas Indonesia and the Research Center of Mining Technology-National Research and Innovation Agency of Indonesia for the research facilities.

DECLARATION

There is no conflicts of interest associated with this publication, and there has been no significant financial support for this work that could have influenced its outcome. As Corresponding Author, I confirm that the manuscript has been read and approved for submission by all the named authors.

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