

水溶液中 코발트와 니켈 分離

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Separation of Cobalt and Nickel from Aqueous Solution

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요 약

코발트와 니켈에 대한 수요가 증가함에 따라 다양한 자원으로부터 순도가 높은 상태로 이 금속들을 회수하는 것은 중요하다. 고순도 코발트와 니켈을 얻기 위해서는 다른 금속이온과의 분리가 필요하다. 본 총설에서는 순수한 코발트와 니켈용액을 얻을 수 있는 용매추출, 이온교환 및 침전법을 소개하고 비교하였다. 특히 용매추출에 대해서는 기존 공정의 장단점과 함께 공정조건을 조사하였다.

주제어 : 코발트, 니켈, 용매추출, 침전, 이온교환

Abstract

Recovery of pure cobalt and nickel from diverse resources is important due to the increased demand for these metals. In order to get cobalt and nickel with high purity, separation of them from other metal ions is necessary. In this review, several methods to obtain pure cobalt or nickel solution, such as solvent extraction, ion exchange, precipitation were introduced and compared. For solvent extraction, the advantage and disadvantage of the separation process together with detailed process conditions were investigated.

Key Word : cobalt, nickel, separation, solvent extraction, precipitation, ion exchange

1. Introduction

The rapid increase in the consumption of cobalt and nickel has made it important to recover these two metals from ores and various secondary resources.¹⁾ The main nickel ores include sulfide(pentlandite, nickel-pyrrhotite, carrollite and linnaeite, etc) and oxide (laterite). Around 1/3 of the nickel consumed is

produced from laterite ores, which occupy 2/3 of the world's nickel resources.²⁾ They also are an important source of cobalt. In secondary resources containing cobalt and nickel are waste batteries, spend electrodes, sludges, and spend catalysts. Hydrometallurgy methods for handling these cobalt-nickel resources include atmospheric acid pressure leaching, high pressure acid leaching, biological leaching and microwave heating.³⁾

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In hydrometallurgical treatment of laterite ore with little Mg content, high-pressure acid leaching (HPAL) has been widely employed due to the in-situ removal of iron by precipitation as hematite from acid solution at high temperature. The leaching of ores and secondary resources can be done in chloride, sulfate and chloride-sulfate systems and led to mixed solution containing cobalt and nickel together with other metal ions. In order to recover cobalt and nickel from these materials, the leaching step is followed by various purification steps.

In treating laterite ore or secondary sources, mixed solutions containing various metal ions, such as manganese, magnesium, aluminum, and iron are obtained. In order to recover cobalt and nickel with high purity from these solutions, separation of them from other metal ions is necessary. It is difficult to obtain pure cobalt and nickel compounds from these leach liquors because of the difficulties in separating cobalt from nickel.

Methods of separating nickel and cobalt from solution can be classified as solvent extraction, ion exchange and precipitation (hydroxide or sulfide). In comparing these methods, the cost of reagents, the efficiency of the processes, and the quality of the products are important.⁴⁾ In this review, the current technology employed in the separation of nickel and cobalt from solution is discussed. For this purpose, various extractants and ion exchange resins used in the separation of the two metals are introduced and their advantage and disadvantage is discussed.

2. Precipitation

2.1. Hydroxide precipitation

Hydroxide precipitation is by far the most widely used process to remove heavy metals from solutions. The reaction of metal hydroxide precipitation can be described as:



The equilibrium constant can be expressed by

$$K = 1/([M^{n+}][OH^{-}]^n) = 1/K_{SP} \quad (2)$$

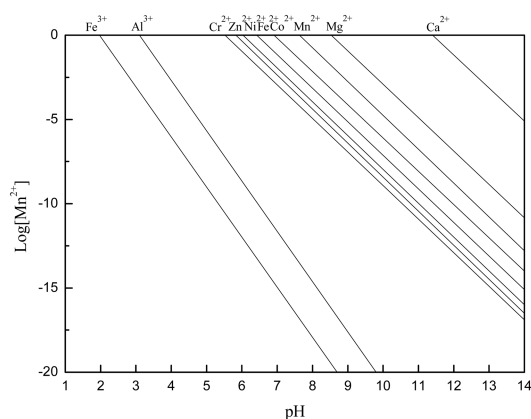


Fig. 1. Solubility diagram for metal hydroxides at 25°C

where K_{SP} is defined as the solubility product.

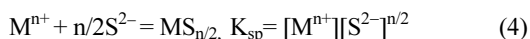
The difference in the solubility product of metal hydroxide offers the possibility to separate them by adjusting the pH. The solubility-pH diagram is shown in Fig. 1.⁵⁾ It is predicted that Fe^{3+} , Al^{3+} and Ca^{2+} can be separated from Co^{2+} and Ni^{2+} , while separation of Co^{2+} from Ni^{2+} is difficult by using hydroxide precipitation method. After removing some impurities by neutralization at low pH, nickel and cobalt refining could be carried out in a high pH range of about 5-7 with ammonia or sodium hydroxide as neutralization reagents.⁶⁾ Precise control of pH in neutralization is essential because higher pH results in the loss of cobalt and nickel to the precipitate owing to adsorption, while lower pH leads to insufficient precipitation of the metal ions.⁷⁾

Zhu⁷⁾ found cobalt and nickel were present in the precipitate even at a low pH of 4, which was much lower than their precipitation pH of 7.0. That was ascribed to two chemical forms, one as sulphate resulting from chemical adsorption (below pH 5.7); and also as the hydroxide which resulted from coprecipitation (above pH 5.7).

However, metal hydroxides are of amphoteric nature and the pH value corresponding to the minimum solubility varies for each heavy metal. Thus, it may be difficult to adjust to optimum pH for the treatment of solutions containing a mixture of several heavy metals. Further, the metal hydroxides tend to redissolve when the optimum pH value is changed, which could result in the dissolution of heavy metals into the environment.⁸⁾

2.2. Sulfide precipitation

Other treatment methods such as sulfidation treatment have been tried. The reactions involved in the sulfide precipitation are:



where X_2S represents sulfidation agents, and K_{sp} is the solubility product of metal sulfide.

In the sulfidation treatment, the sulfidation agents can be classified as solid (FeS, CaS), aqueous (Na_2S , NaHS, $(NH_4)_2S$) or gaseous sulfide sources (H_2S). Precise pH control is of great importance if high precipitation selectivity is to be achieved. The main advantages of sulfide precipitation are lower solubility of metal sulfide precipitates, potential for selective removal of metal, fast reaction rates, better settling properties, reuse of sulfide precipitates by smelting and finally higher dewaterability of metal sulfide sludges compared to metal hydroxide sludges.⁹⁾

Fukuta¹⁰⁾ reported the possibility of separation of Cu, Zn and Ni by precipitation with Na_2S at different pH. They reported as high as 94.5% for Cu (pH 1.5), 75.9% for Zn (pH 2.5) and 65.9% for Ni (pH 5.5 - 6.0) was achieved. Kondo¹¹⁾ studied the precipitation of Cu, Zn and Ni from mixed plating wastewater with H_2S and reported that higher precipitation selectivity can be achieved with H_2S compared to Na_2S . The precipitation selectivity was 95.5% for Cu (pH 1.5), 87.4% for Zn (pH 4.5) and 94.7% for Ni (pH 6.7 ± 0.2).

Because the toxicity, corrosiveness of excess sulfide and the difficulty in controlling the dosage of the sulfide, sulfide precipitation is not widely used.¹²⁾

Precipitation provides a useful means to separate cobalt and nickel from other metals. In general, precipitation in separation of cobalt and nickel is used together with other methods like solvent extraction.

3. Solvent extraction

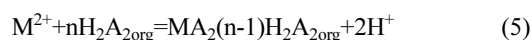
Leaching of either laterite or secondary sources usually results in a mixed solution of cobalt and nickel with some impurities such as iron, manganese, copper and zinc. The recovery of cobalt and nickel from the

leach solution through solvent extraction is one of the versatile methods. A lot of work has been performed to develop extractants which are selective for one of the metal ions.

Although there are some kinds of extractants which have been used to separate cobalt and nickel from various aqueous solutions, in most cases cobalt is extracted while nickel remains in the raffinate. In this review, cationic exchange reagents, amine reagents and synergistic extractants system are introduced.

3.1. Cationic exchange reagents

Cationic exchange reagents include phosphorus acid, carboxylic acid and thiophosphinic acid extractants. Their chemical structures and some main properties are represented in Table 1. They usually exist as dimer state (H_2A_2) in non-polar organic solvent. The extraction reaction of bivalent metals with organophosphorous acid extractants can be represented.¹³⁾



When the extractant is in excess, the value of n for Co^{2+} and Ni^{2+} is 2 and 3, respectively.¹³⁾ The extracted species of cobalt includes tetrahedral and octahedral structures while nickel only includes octahedral structure. The moisture content of tetrahedral extraction complexes is lower than that in octahedral structure. Therefore, the solubility of octahedral structure complex in organic is higher than that of tetrahedral structure. The fact that cobalt is selectively extracted by organophosphorus extractants can be ascribed to the difference in the chemical structure of extracted species and in the solubility. The ratio of tetrahedral to octahedral is the determining factor for the separation factor between cobalt and nickel. In the same extraction condition, the structures and properties of extractants can influence the separation factor significantly.

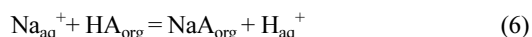
It has been found that the separation factor between cobalt and nickel increased in the following order, phosphinic > phosphonic > phosphoric^{14, 15)} because of the increase in the stability of tetrahedral coordination compound of cobalt with the extractant in the organic phase¹⁶⁾ and the basicity of the extractants increases with the decrease in the distance of the alkyl chain from the central phosphorous atom.¹⁷⁾ Although the

Table 1. Chemical structures and properties of acid exchange reagents

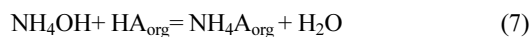
Extractant	Structure	R	pKa	Density /gcm ⁻³	Viscosity (25°C) /mPas	Solubility in water/m ³	Flash point/°C	Ignition point/°C
D2EHPA		CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH(C ₂ H ₅)-CH ₂ -	3.24	0.9699	34	11.8	206	233
PC88A		CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH(C ₂ H ₅)-CH ₂ -	4.51	0.9475	34	10	198	235
Cyanex272		H ₃ C-C(CH ₃) ₂ -CH ₂ -CH(CH ₃)-CH ₂ -	6.37	0.92	14.2	38	108	-
Carboxylic acid (Versatic911)		R = 4-5C, Alkyl groups	-	0.92	42.5	100	103.8	280
Cyanex302		H ₃ C-C(CH ₃) ₂ -CH ₂ -CH(CH ₃)-CH ₂ -	5.63	0.93	19.5	3	96	395
Cyanex301		H ₃ C-C(CH ₃) ₂ -CH ₂ -CH(CH ₃)-CH ₂ -	2.61	0.95	7.8	7	74	-

separation factor of cobalt and nickel by using phosphinic acid is highest among the three extractants, other conditions such as solution pH, ratio of Co-Ni concentration and economics should be considered, in choosing a suitable extractant for application.

During solvent extraction process, acid liberated from acidic extractants affects the metal extraction.¹⁸⁾ The use of saponification with NaOH or NH₄OH was tried to overcome this problem.¹⁹⁾ The saponification reaction can be described^{13,20)}



and



Saponified acidic extractant was prepared by adding a stoichiometric amount of a concentrated base solution to the extractant to form a single phase. The fact that a single phase is formed during the saponification means that water is moved to organic phase and saponified extractants contain water. The consumption of base reagent is a main operation cost of solvent extraction.

3.1.1. D2EHPA

D2EHPA(di-2-ethylhexyl phosphoric acid) was first used to separate cobalt from nickel by Ritcey and Ashbrook.²¹⁾ In sulfate medium, Cheng¹⁾ investigated the potential of D2EHPA in kerosene for separation of impurities like manganese from cobalt and nickel in laterite leach solution. The synthetic leach solution contained Co, Ni, Mg, Mn, Zn and Cu. The extraction order and pH₅₀ for the metals was found to be Zn(1.70) ~ Ca(1.71) > Mn(2.72) ~ Cu(2.80) > Co(3.68) ~ Ni(3.86) > Mg(4.28). It is easy to separate cobalt and nickel from zinc and calcium and possible to separate them from copper and manganese. But it is difficult to separate cobalt from nickel by using D2EHPA.

3.1.2. PC88A

PC88A(2-ethylhexyl phosphinic acid) gives a much higher Co/Ni separation factor than that of D2EHPA.

In sulfate medium, the extraction order and pH₅₀ were found to be Zn(2.2) > Cu(3.8) > Co(4.2) > Ca(4.65) > Mg(5.0) > Ni(5.7).²²⁾ These data show that use of PC88A leads to the separation of zinc from other metals. It is possible to separate cobalt and nickel in sulfate solution by using PC88A. In separation of cobalt and nickel from a sulfate solution containing

1.91 g/L Co and 14.83 g/L Ni,²³⁾ cobalt was quantitatively extracted with 0.2 M PC-88A with 3% co-extraction of nickel, and extraction of Ni from the cobalt-free raffinate was carried out with 0.7 M D2EHPA followed by the stripping of Co and Ni from the loaded organic.

Lin²⁴⁾ used 60% saponified 20% PC88A in kerosene to recover cobalt and nickel from the purified chloride leach solution. They found the pH_{50} value difference between cobalt and nickel was 1.40 in chloride solution, indicating the possibility of separating cobalt and nickel. After single extraction the separation factor $\beta_{Co/Ni}$ can reach over 350 at equilibrium pH 3.8-4.5 at 70°C. Increase of extractant concentration and temperature is beneficial to the separation of cobalt and nickel.

3.1.3. Cyanex272

Cyanex272 (di(2,4,4-trimethylpentyl)phosphinic acid) was found to be effective in separating cobalt from nickel from sulfate solution. The separation factor between Co and Ni by Cyanex 272 is much higher than that by D2EHPA and PC88A. The extraction order and pH_{50} of metals from sulfate medium with Cyanex272 in kerosene was in the following order, Fe(III)(0.6) > Zn(2.1) > Cu(3.7) > Mn(3.9) > Co(4.2) > Mg(4.7) > Ca(5.3) > Ni(6.2).²²⁾

NaD2EHPA, NaPC-88A and NaCyanex272 were used to separate cobalt and nickel from sulfate solution bearing 0.01 M metal ions each with 0.1 M Na₂SO₄.²⁵⁾ Extraction of metal ions increased with increasing equilibrium pH and extractant concentration, and cobalt was preferentially extracted. When 0.05 M extractant was used, the value of the separation factor of cobalt and nickel was as follows ; D2EHPA ($\beta_{Co/Ni}$ = 6.01, pH = 5.1), PC88A ($\beta_{Co/Ni}$ = 1810, pH = 6.2) and Cyanex272 ($\beta_{Co/Ni}$ = 3936, pH = 6.85). Separation factor with NaCyanex272 was the highest. Extraction of cobalt and nickel was successively carried out with 0.05 M NaPC-88A and NaCyanex 272 in 2 stages at 1:1 phase ratio followed by the stripping of respective loaded organic phases with 0.02 M H₂SO₄.

Rickelton²⁶⁾ has reported the superiority of Cyanex272 for cobalt-nickel selectivity compared to phosphoric and phosphonic acid to obtain high pure cobalt metal from chloride solution in a mini-plant scale continuous

counter-current extraction.

3.1.4. Carboxylic acid extractants

Carboxylic acids are used for the extraction of Co and Ni from sulfate solution by the exchange of its dissociative proton and metal ions. The sequence and pH_{50} of metals extracted by carboxylic acid is Fe(III) (1.9) > Cu(4.05) > Zn(5.5) > Ni(6.3) > Co(6.6) > Mn (6.8) > Ca(7.4) > Mg(8.2).²²⁾ While the separation of cobalt, nickel from manganese is difficult, it is easy to separate them from other metals such as copper and zinc. Although this kind of extractant is not expensive, one of the disadvantage is the high water-solubility.²⁷⁾

A kind of carboxylic acid containing 9-11 carbons (Table 1) can be used to extract Co and Ni because the solubility of these extractants in aqueous is low. They can be used to extract metals from acidic solution as well as alkaline solution with NH₃-(NH₄)SO₄. In acidic solution, Ni is electively extracted prior to the extraction of cobalt.

3.1.5. Thiophosphinic acid extractant

Recently thiophosphinic acids have been successfully used for the extraction of cobalt and nickel in the presence of manganese at low pH. Cyanex301, a dithiophosphinic acid, is very effective in separating nickel and cobalt from manganese, magnesium and calcium from laterite leach solutions.²⁸⁾ Tsakiridis²⁹⁾ studied a simultaneous extraction of cobalt and nickel in the presence of manganese and magnesium from sulfate medium by Cyanex301. They found that Cyanex301 with TBP in Exxsol D-80 can extract Co and Ni 99.9% and 99.7%, respectively. Manganese co-extracted in Cyanex301 can be scrubbed by scrubbing with 1M HCl. After stripping with 5 M HCl the stripping percentage of cobalt and nickel reached 99.6% and 99.2%, respectively.

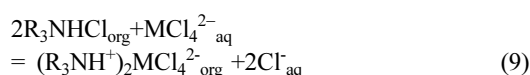
Dhadke³⁰⁾ has extracted manganese (pH 8.5-9.5) and cobalt (pH 7.0-7.5) from sulfate solutions using Cyanex302 (monothiophosphinic) in toluene. Cobalt and manganese were extracted over magnesium by Cyanex302 at pH 5. The loaded organic was stripped with sulfuric acid.³¹⁾

3.2. Amine reagents

In chloride solution, cobalt can form stable anionic

chloride complexes (CoCl_4^{2-}) while nickel only exists as neutral (NiCl_2). The anionic complexes can be extracted from leach solution by amine extractants. Therefore, nickel and cobalt can be separated from chloride solution by using amine extractants. The cobalt anionic complexes can be extracted by tertiary and quaternary extractants. Tertiary amine should react with HCl to form a salt to extract metal.

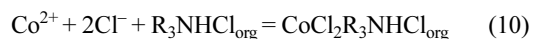
The extraction of cobalt from chloride medium by a tertiary amine can be represented as follows³²⁾



where R denotes an alkyl group or hydrogen.

The separation factor between cobalt and nickel increased with the increase of chloride ion concentration. But in chloride medium, HCl are extracted by amines and competitive reaction occurs between HCl and cobalt complexes.

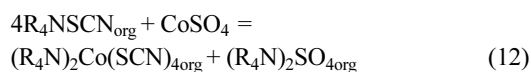
Filiz and Sayer^{33,34)} investigated the extraction of cobalt from single solution and separation of cobalt and nickel from concentrated hydrochloric acid solution by Alamine336. They found the increase in acid concentration significantly improve cobalt extraction. When the acidity was 10 M, the extraction percentage of cobalt reached 100%. While much less improvement was observed for nickel, the increase in acid concentration to 5 M and 10 M dramatically increased separation factor ($\beta_{\text{Co/Ni}}$) value. This denoted a suitable separation possibility of cobalt from nickel. In case of high acid concentration (5-10M) solution, an adduct formation reaction of Alamine336 was investigated³⁵⁾



Quaternary ammonium salts, which exist as stable cation–anion pairs over a wide pH range, are similar with the tertiary amine extractants in separating cobalt and nickel. In general quaternary ammonium salt performs better than tertiary amine in extraction ability when the concentration of chloride is the same. The reaction can be written as³⁶⁾



Cobalt can form a tetrahedron anion coordination complexes $\text{Co}(\text{SCN})_4^{2-}$ with SCN^- while Ni cannot. So the separation factor between Co and Ni in this medium is higher than that in chloride ion solution. It has been found that R_4NSCN can extract Co from sulfate solutions where there is no SCN^- . The reaction can be written as³⁶⁾



3.3. Synergistic solvent extraction

The multi-extraction system consists of two or more than two kinds of extractants. Lots of research has been tried to separate nickel and cobalt from other metals by using synergistic solvent extraction system. Synergetic performances of such combinations in the case of cobalt and nickel extraction in chloride medium were reported by Jackovljevic.³⁷⁾ The synergistic system consisted of the mixture of Cyanex301 with Primene JMT, Amberlite LA-2, Alamine336, Aliquat336. It has been found that the separation of cobalt and nickel from calcium, manganese and magnesium can be accomplished by using Cyanex301-Aliquat336 system. But when the acid concentration increased from 2 to 4 M, cobalt stripping was decreased.

Recently, a number of synergistic solvent extraction systems consisting carboxylic acid and oxime reagents were developed to separate cobalt and nickel from impurities in laterite leach solution.³⁸⁾ Cheng³⁹⁾ used a synergistic solvent extraction system consisting of 0.5 M Versatic 10, 0.45 M LIX63 and 1.0M TBP in Shellsol D70 to separate Co and Ni from laterite leach solution. In this work, 99.6% Ni and 96.9% Co can be extracted after a single contact. In the system, LIX63 and Versatic10 were extractant and synergistic while TBP was added to improve the stripping.

4. Ion exchange

Cobalt and nickel is present as divalent cation in aqueous solution. Therefore, cationic exchange or weakly acidic resins have been suggested and used for the adsorption of cobalt and nickel from hydro-

metallurgical process solutions. It is possible to separate cobalt and nickel in chloride solution due to the formation of stable anionic complexes of cobalt like CoCl_4^- , while nickel cannot form anionic complex with chloride ion. However, when iron, zinc and copper coexist in the chloride solution, these metals can form anionic complexes with chloride ion and it is difficult to separate Co and Ni by ion exchange from these metals.⁴⁰⁾

Ion exchange polymeric resins have found increasing application over the last decade. Zontov⁴¹⁾ pointed out some advantage of ion exchange technology: less water consumption, water recycling opportunity, lower operating and capital cost of equipment and high selectivity for target metals and high separation capabilities. Ion exchange can provide a more effective and straight forward purification compared to purification by precipitation or solvent extraction.

Although the selectivity between cobalt and nickel is low by traditional cationic exchange resins, chelating ion-exchange resins provide opportunities for separation of cobalt and nickel from other metals. Chelating ion-exchange resins are designed to have high specificity for an ion or groups of ions. These types of ion-exchange resins adsorb metal ions through a combination of ionic and coordinating interactions instead of the simple electrostatic interactions in conventional cationic or anionic ion exchange.⁴²⁾

Zaimawati⁴³⁾ investigated a chelating ion-exchange

resin, Amberlite IRC 748, which carries an iminodiacetate acid functional group, to separate cobalt, nickel, manganese and magnesium from sulfate solution. They found the amount of metals adsorbed by the resin increased with increasing pH. Cobalt and nickel can be easily separated from manganese and magnesium at pH 4 and 5.

Mendes⁴⁴⁾ found Dowex M4195R (whose functional group is bis-picolylamine) has good performance both for nickel and cobalt at low pH such as pH = 1.0. While at pH = 4, IRC 748 is selective for copper, nickel and cobalt.

5. A typical process for separation and purification of cobalt and nickel from laterite leach liquor

The flow sheet of Bulong process is shown in Fig. 2.¹⁷⁾ First, Fe, Al, and Cr are removed by hydroxide precipitation. Then cobalt, copper, zinc and manganese are separated from nickel by solvent extraction with Cyanex272. Nickel was extracted by Versatic acid from the raffinate. Mn, Mg and Ca are separated from the stripping solution by precipitation as a sulfide. Zinc is removed by a solvent extraction using D2EHPA and ion exchange is employed to remove copper from the raffinate solution after extraction by D2EHPA. Finally, pure cobalt metal is obtained from the raffinate by electrowinning.

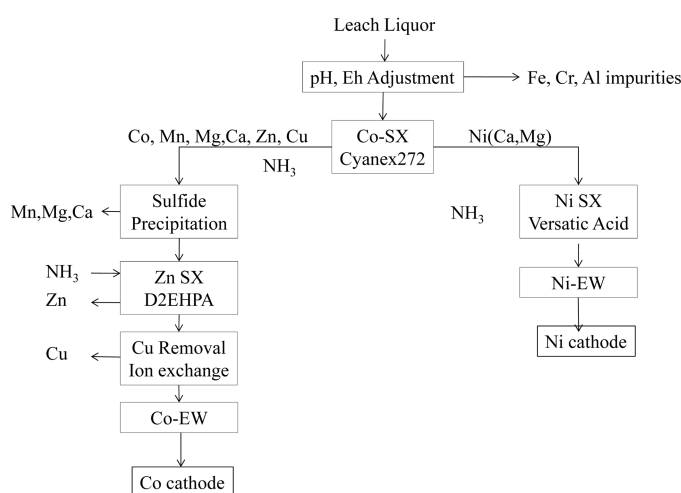


Fig. 2. Bulong flow sheet for purification of nickel and cobalt from laterite leach liquor.

6. Conclusions

Solvent extraction can be applied to separate and recover cobalt and nickel from other metals or separate cobalt over nickel by different extractants. Cyanex272 is the best extractant in separation of cobalt over nickel among the cationic exchange extractants. Amine extractants showed a suitable separation possibility of cobalt from nickel in chloride solution. Recently, synergistic solvent extraction system offers good selectivity for purification of metals in solution.

Precipitation methods provide useful means for purification of impurities from cobalt-nickel solution. Hydroxide precipitation is usually used in removing iron and aluminum from solution before solvent extraction or ion exchange. Zinc and copper can be removed by sulfide precipitation followed by other purification process. But it is less selective for separation of cobalt from nickel.

Compared to solvent extraction and sulfide precipitation, ion exchange is cleaner and easier to control. For the low capacity and low selectivity for cobalt and nickel of resin, ion exchange only can be used in removing small amounts of purities from solution.

감사의 글

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