

용매추출에 의한 코발트 분리 기술

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Extraction/Separation of Cobalt by Solvent Extraction: A Review

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초 록

용매추출에 의한 코발트 분리 기술에 대해 리뷰하였고 특히 다양한 시약을 사용한 코발트의 분리 및 상용 추출용제를 사용하여 스크랩으로부터의 코발트 회수기술에 대하여 분석하였다. 코발트 분리 능력은 phosphinic > phosphonic > phosphoric acid 순으로 정리되며, 이것은 유기상내에 추출용제와 존재하는 코발트의 사면체 배위 화합물의 안정성이 증가하기 때문이다. 용매의 조성에 따라 달라지지만 주로 Cyanex 272, D2EPHA 및 PC 88A와 같은 상용 추출용제 등이 상용 추출 공정에서 우선적으로 사용되어야 하며, 다양한 조합을 효과적으로 관리한다면 코발트 함유 스크랩과 관련한 다양한 분리기술 문제점들을 해결할 수 있을 것이다.

Abstract

Extraction/separation of cobalt by solvent extraction is reviewed. Separation of cobalt using various reagents and also cobalt recovery from scrap using commercial extractant were analyzed. The separation ability for cobalt followed the order of phosphinic > phosphonic > phosphoric acid due to the increasing stabilization of tetrahedral coordination of cobalt complexes with the extractant in the organic phase. Depending upon the solution composition, commercial extractants like Cyanex 272, D2EPHA and PC 88A should primarily be used for commercial extraction processes and also the efficient management of their combination could address various separation issues associated with cobalt bearing scrap.

Keywords: solvent extraction, cobalt, hydrometallurgy, resources recycling, commercial extractant

1. Introduction

Conventionally various methods are being used to separate and purify various metals from primary resources as well as secondary resources[1]. Though various techniques like; ion exchange purification, adsorption with chelating ion exchange resins, zeolite cation exchange, and chromatography have been used for metal separation and purification purpose, the solvent extraction technique is one of the most versatile methods used for the removal, separation and concentration of metallic species from mixed metal aqueous media[2-7]. Upon growing concern over industrial waste treatment, industrial wastewater treatment, urban mining and metal recycling the hydrometallurgy is increas-

ingly gaining attention for research to production during the current decade. Concerning the recovery of valuable metals from waste, separation, purification and concentrate of metals from its mixed solution, the solvent extraction processes are efficient and flexible to a variation in the metal contents in the wastes, compared with other processes. The recycling of industrial wastes bound in cobalt consists of complicated multi-step procedures such as dissolution in mixed acid solution, neutralization and precipitation, filtering and various extraction procedures using different organic solvents. Since solvent extraction technique is one of the most versatile methods used for the removal, separation and concentration of metallic species from mixed metal aqueous media, it has also been successfully applied for recovery of cobalt from various resources[8-11].

2. Solvent Extraction of Metals

Solvent extraction or liquid-liquid extraction is a separation process which is based on the different distribution component to be separated

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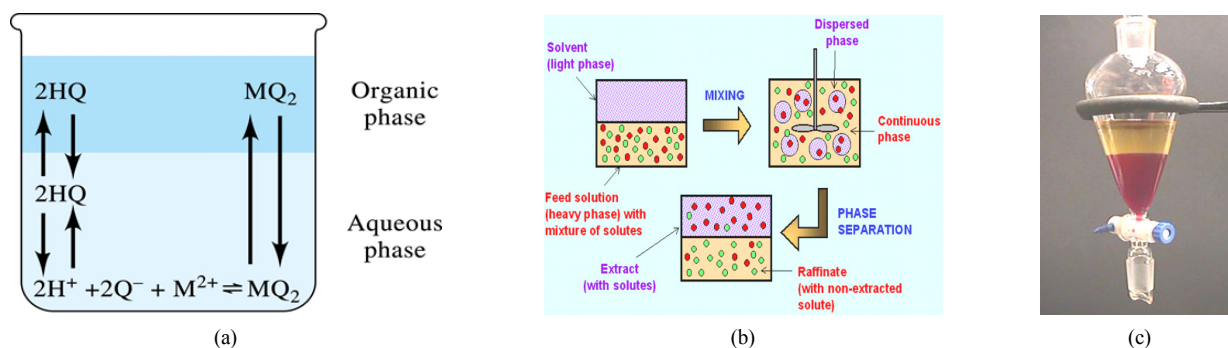


Figure 1. (a) Molecular solvent extraction mechanism, (b) Schematic for aqueous and organic phase mixing, and (c) Physical separation of Aqueous and organic phase through separatory funnel.

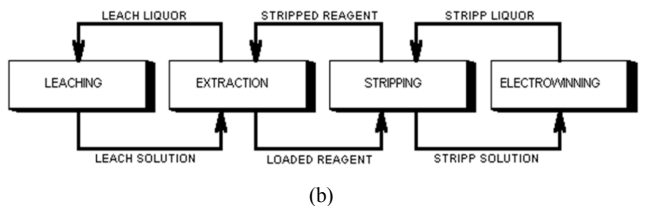
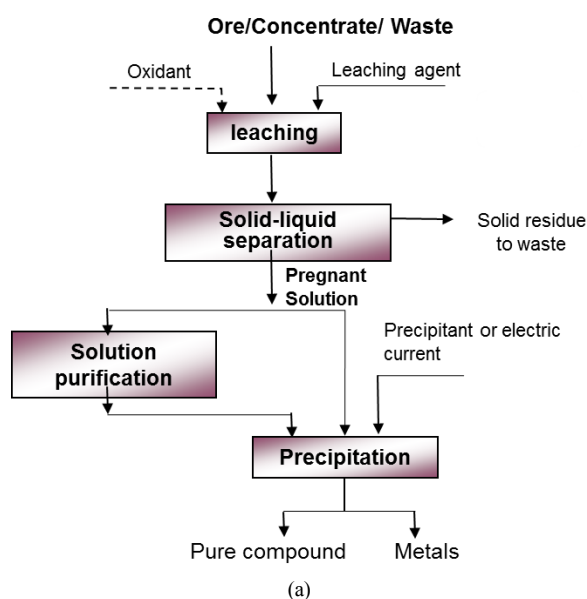


Figure 2. Schematic presentation of industrial solvent extraction process.

from two immiscible liquid phases usually water and an organic solvent. It is an extraction of a substance/molecule/metal atom from one liquid phase into another liquid phase. It depends on the mass transfer of the compound to be extracted from first liquid phase to second liquid phase[12].

3. Principles of Solvent Extraction

The principle of solvent extraction (SX) is illustrated in Figure 1. Figure 1a shows the fundamental molecular mechanism involved in the solvent extraction process. As shown in figure when the metal ion from the aqueous phase comes in contact with the organic phase con-

taining solvent under proper experimental condition, the metal and solvent bonding facilitates, by which the metal gets extracted to the organic phase. The back extraction is exactly the opposite when the reversible reaction facilitates. The Figure 1b shows the mixing of two phases followed by phase separation, which leads to either metal extraction or back extraction and the Figure 1c shows a typical laboratory setup separation process. As shown in Figure 1c, a separatory funnel contains two layers; one is generally water and other generally an organic solvent. The key component which is targeted to be extracted M^{n+} , is extracted by the extraction along with some contaminant C. As shown in Figure 1, solvent extraction is a basic separation and purification technique in chemical laboratories, where it is done in separating funnels, as well as a common process in chemical industry and ore processing.

4. Industrial Application of Solvent Extraction and Practices

Figure 2 indicates general industrial practices used for metal production process. The Figure 2a indicates in a typical industrial practice, the metal purification is an important process, where the solvent extraction plays a vital role for metal purification. The Figure 2b shows, in any hydrometallurgical process the solvent extraction is a vital process. As the solvent extraction process is a versatile, flexible, and easy to scale up, economical and environment friendly process, it is holding determinant position for industrial production of non-ferrous metal. Solvent extraction is a selective separation process for isolating and concentrating the metal values from an aqueous solution with the aid of an organic solution. In the procedure the aqueous solution containing the metal/substance of interest, often at a low concentration and together with other dissolved substances, is mixed (extraction) with an organic solvent containing an extractant/reagent. The substance of interest reacts with the reagent to form a chemical compound, which is more soluble in the organic than in the aqueous solution. As a consequence, the substance of interest is transferred to the organic solution. Subsequently, in order to recover the extracted substance, the organic solution is mixed (stripping) with an aqueous solution whose composition is such that the chemical compound between the substance and the reagent is split and, thus, the substance is recovered in the

“fresh” aqueous solution, in a pure form. The concentration of the substance in the “fresh” aqueous solution may be increased, often to 10-100 times that of the original aqueous solution, through adjustment of the liquid flow rates. Freed from the substance of interest, the organic solution is returned for further extraction, either directly or after a fraction of it has been cleansed of impurities[13].

5. Extraction/Separations of Cobalt by Solvent Extraction

A thorough literature investigation suggests that different techniques has been applied to the separation of cobalt and/or lithium such as ion exchange purification[14,15], adsorption with chelating ion exchange resins[16,17], zeolite cation exchange[18], and chromatography[19], concerning the recovery of valuable metals from waste, separation, purification and concentration of metals from its mixed solution. The solvent extraction (SX) processes are efficient and flexible to a variation in the different metal contents in the wastes, compared with other processes. SX technique is one of the most versatile methods used for the removal, separation and concentration of metallic species from mixed metal aqueous media and has also been used in the extraction of cobalt and lithium[20,21].

Extraction of cobalt(II) has been reported to separate cobalt(II) from nickel(II) by using several complexing reagents such as pyridinecarboxylate esters[21], di(2-ethylhexyl) phosphoric acid (D2EHPA), 2-ethylhexyl phosphonic acid (PC88A), bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272)[22-23], polyoxyethylene nonyl phenyl ether with 10 ethylene oxide units (PONE10), and 2-ethylhexyl phosphonic acid mono 2-ethylhexyl ester (EHPNA)[24]. Other complexation reactions between metals and ligands have been applied to extract Co(II) by using PC88A[25], sodium di(2-ethylhexyl) phosphate (D2EHPNa), and tributyl phosphate (TBP) into cyclohexane; and *n*-dodecane[26-27] and *N*-phenyl-*N'*-(2-butylthiophenyl) thiourea (PBT) into chlorobenzene[28]. Cobalt(II) also has been extracted as ion pair complexes together with other transition metal ions by using *N,N'*-bis(2-pyridylmethylidene)-1,2-diiminoethane (BPIE), *N,N'*-bis [1-(2-pyridyl)ethylidene]-1,2-diiminoethane(BPEE), and *N,N'*-bis (2 pyridylmethylidene)-*trans*-1,2-diimino-cyclo-hexane (BPIC) into nitrobenzene[29], *N,N'*-bis (2-hydroxyphenylmethyl)-*N,N'*-bis(2-pyridylmethyl)-1,2-ethanediamine (BBPEN) into chloroform[30], *N,N'*-dibutyl-*N'*-benzoylthiourea (DBBT) into paraffin[31], mixture of four trialkyl phosphine oxides (Cyanex 923) into toluene[32], and trioctylphosphine oxide (TOPO) into chloroform[33].

Separation of cobalt in the presence of either cobalt or other metals using various extractant as single extractant or synergistic extractants such as Cyanex 302[34-37], Cyanex 272[34-40], Cyanex 923[41,42], Cyanex 301[36,43,44,45], D2EHPA[37,39,46,47,48,49], Versatic acid 10[35,49], PC88A[39,50], Alamine 336[51], Hexaacetatocalix(6) arene[52] has been reported. The separation of cobalt has been investigated either from sulfate media or from chloride media using above extractant individually or from their mixtures.

Park et al. reported extraction of cobalt by Cyanex 272 from sulfuric acid solution. The extraction efficiencies of cobalt and nickel were

80% and 1.9%, respectively, with 0.2 M Cyanex and O/A of 1 at equilibrium pH 5.0 has been reported[38]. Similar kind separation using Cyanex 272 in toluene has been studied has been reported by Koladkar et al.[40], Liu et al.[56], Orive et al.[58], Xun et al.[59], Rickelton et al.[60], Chen et al.[61], and Maljkovic et al.[62]. Similar kind of result was also obtained from their study.

Tsakiridis et al. has investigated separation of Co(II) and Mg(II) from nickel sulfate by using the Cyanex 272. Subsequently, cobalt and magnesium separation was achieved by the Cyanex 302. The slope analysis method was used to determine the nature of the cobalt and nickel complexes extracted by both the extractants. The number of stages required for the extraction and stripping processes was also evaluated[34]. The author also studied simultaneously SX of cobalt (II) and nickel (II) from magnesium and calcium synthetic sulfate solution using the carboxylic extractant Versatic 10[35]. Then the two metals were separated by extraction of cobalt using Cyanex 272. Simultaneous SX of cobalt and nickel in the presence of manganese and magnesium from sulfate solutions by Cyanex 301 has also been reported by Tsakiridis et al.[45]. Synergistic separation of nickel and cobalt from calcium, magnesium and manganese by SX using synergistic mixtures of carboxylic acids was studied by Du et al.[43]. The recovery of cobalt can be enhanced employing a slightly higher pH, which also increases the extraction of manganese, calcium and magnesium somewhat. The recovery of nickel was 99.9% and that of cobalt was 84.7%, while the co-extraction of manganese, calcium and magnesium were 2.7, 1.5 and 0.04%, respectively.

Tait et al. reported extraction cobalt(II) and nickel(II) from a sulfate medium and elucidated separation properties these phosphinic acid extractants of Cyanex 301, Cyanex 302 and Cyanex 272[36]. All the extractant extracted cobalt selectively, Cyanex 302 exhibiting better separation characteristics than Cyanex 272, which in turn showed a higher selectivity than did Cyanex 301. Better separation of cobalt and lithium was found for Cyanex 302 at 2.6 pH units, for Cyanex 272 at 1.7 pH and for Cyanex 301 at 1.1 pH. Slope analysis methods were used to determine the nature of the cobalt(II) and nickel(II) complexes behavior. Both Cyanex 272 and Cyanex 302 were existed in dimer and Cyanex 301 exists as a monomer. Darvishi et al. investigated synergistic effects of Cyanex 272 mixed with D2EHPA and Cyanex 302 mixed with D2EHPA for the separation of cobalt and nickel from a dilute sulfate medium with the aim of decreasing the reagent cost[37]. Selectivity in the extraction of cobalt over nickel improved with respect to D2EHPA, but worsened with respect to Cyanex 272. Optimum separation was found with a Cyanex 302 to a D2EHPA ratio of 0.3 : 0.3 when the equilibrium pH 50 was 0.9. The extraction of cobalt was more endothermic than that of nickel. Improved separation factor was hence achieved with a warm mixture.

Sarangi et al. studied the extraction behavior of cobalt and nickel from 1 M chloride solutions using the sodium salt of Cyanex 272 as extractant diluent with kerosene with tri-*n*-butyl phosphate (TBP) employed as a phase modifier. The same extraction study also has been carried out using Cyanex 272, PC88A and D2EHPA. Separation factors were increased about 5.6 times higher in the case of PC88A as extractant and Cyanex

272 as synergist than that for Cyanex 272 alone[39].

Bourget et al. and Jakovljevic, studied the SX and stripping behavior of Cyanex 301 binary extractant systems from cobalt and nickel sulfate/chloride solution, respectively[43,44]. The selectivity of Cyanex 301 against calcium, manganese and magnesium was also studied. A large synergistic effect on the stripping kinetics and efficiency of cobalt and nickel was observed. The synergistic Cyanex 301/Alquat 336 was the most promising binary extraction system. Complete extraction of cobalt and nickel was achieved in 2-3 stages while still maintaining a high selectivity against calcium, manganese and magnesium. Complete, stripping of cobalt was also achieved in 2-3 stages, while complete nickel stripping was still difficult. The loading capacity of the binary system for cobalt and nickel was lower than that of Cyanex 301 alone.

Devi et al. reported the recovery and separation of cobalt and nickel ions from sulfate solution using sodium salts of D2EHPA, PC 88A and Cyanex 272 in kerosene[46]. The best recovery of cobalt from cobalt-nickel bearing solution was achieved with 0.05 M Cyanex 272 and PC 88A at an equal phase ratio followed by their stripping with 0.02 M H₂SO₄ at O/A ratio of 2/1. Nickel was extracted from the cobalt-free raffinate in two stages at an equal phase ratio with PC 88A and Cyanex 272 followed by their stripping with 0.02 M H₂SO₄ at O/A ratio of 4/3 and 2/1, respectively. Same author also studied SX of cobalt(II) from an acidic sulfate solution using sodium D2EHPA, PC-88A and Cyanex 272 in benzene[47]. Slope analysis for the study reveals that the extracted species appear to be CoA₂(HA)₂. Synergism has been observed with the binary mixture of all the three extractants used. Of the three extractants, sodium salt of Cyanex 272 has been found to be the best synergist and the sodium salt of D2EHPA the least. The influence of different salts such as NaCl, NaNO₃, Na₂SO₄ and NaSCN on the extraction systems has been investigated.

Nathsarma et al. investigated the SX of cobalt from an ammoniacal sulfate medium using D2EHPA in kerosene[48]. The effect of ammonium chloride and ammonium sulfate on the extraction efficiency was studied. The extracted species in the ammonium chloride and sulfate systems for cobalt and nickel were CoA₂ · 2HA · NH₄Cl and CoA₃ · HA₂(NH₄)₂SO₄, respectively. The ammonium salt of cobalt was obtained after suitable ammoniacal scrubbing and ammoniacal stripping. The kinetics of the SX of cobalt(II) and lead(II) with Versatic 10 acid were studied by Inoue et al. In their study cobalt(II) and lead(II) from aqueous ammonium nitrate was extracted and their kinetic behavior was observed[49]. An interfacial reaction mechanism was proposed in order to give a reasonable interpretation of the observed rate expressions. The extraction of lead was pH dependent at lower pH and it was independent of hydrogen ion concentration at higher pH condition. From this result, it was presumed that only the non-hydrated aquo-cation of lead(II) takes part in complex formation at the interface.

Luo et al. studied extraction studies of cobalt(II) and nickel(II) from chloride solution using PC88A. In their study the pH_{0.5} value difference of 1.40 with PC88A indicates the possible separation of cobalt and nickel. Increase of the concentration of the solvent and temperature enhanced the extraction efficiency for both metal ions[50]. Ahn et al.

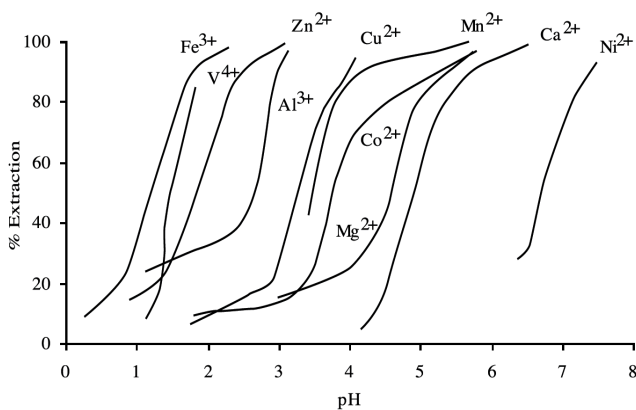
studied the separation of cobalt and nickel by SX with Alamine 336 from chloride solutions iron, manganese and zinc[51]. The extraction behavior in the presence of impurities such as iron, zinc, copper and manganese was also investigated. With the increase of chloride ion concentration cobalt was selectively extracted from nickel. In their study co-extracted metals in the organic phase were effectively separated in the scrubbing using 6.0 M hydrochloric solutions. From the experimental study, the behaviors of impurities in each of operation steps in extraction, scrubbing and stripping processes were investigated. Gupta et al. Proposed new solvent hexaacetatoalix(6)arene in toluene for SX separation of cobalt(II)[52]. Preez et al. reported separation of cobalt from nickel, calcium, magnesium and manganese by solvent extraction by synergistic mixtures of carboxylic acids has added advantage over single carboxylic acid extractant[53]. Zhou et al. has been reported solvent extraction/separation of cobalt from iron and manganese with quaternary ammonium chloride[54]. Although quaternary ammonium chloride extractants are not commonly used for cobalt extraction, but these extractants are available commercially under different brand name. The quaternary ammonium chloride extractants unlikely phosphinic, phosphonic, and phosphoric acid extractant act as anion exchanger, which is otherwise called ion pair extract.

Several hydrometallurgical processes have been reported for the separation and recovery of cobalt, nickel and several other metals from ammoniacal solutions, i.e. solutions of either ammonia/ammonium sulfate or ammonia/ammonium carbonate. The most common process is based upon the dissolution of cobalt and nickel as their ammine complexes, e.g. Ni(NH₃)₆²⁺ or Co(NH₃)₆²⁺ followed by selective precipitation. But such precipitation processes are associated with inherent problems like; solid-liquid separation, high cost slow kinetics, several unit processes and relatively impure products. As explained above several solvent extractants have been investigated as an alternative method to precipitation with the object of improving product purity using both chelating (oximes) and acid extractants (D2EHPA). But using these extractants, it is extremely difficult to strip Co³⁺ from chelating extractants and reagents such as D2EHPA, which exhibit the same low Co-Ni selectivity in alkaline systems as they do in acid media[55]. Rickelton et al. Investigated the separation of cobalt from ammoniacal solutions containing cobalt and nickel in their patent, where commercially available extractant Cyanex 272 has been used as extractant. Cyanex 272 is well known to exhibit high Co/Ni selectivity from sulfate or chloride media [58,59,60]. However, an acid system differs from an ammoniacal aqueous system. At higher pH, it would be expected to promote nickel extraction, and therefore high Co selectivity in an ammoniacal aqueous system would be compromised[55]. Several authors, P. Liu et al.[56], Xun et al.[59], and Rickelton et al.[60] have reported Cyanex 272 can be a comparatively better reagent for selective extraction Cobalt or separation of cobalt from other base metals. Zhu[57], Chen et al.[61], Maljkovic et al.[62], and Kongolo et al.[63] separation of Cobalt from other metals using organophosphorus extractant. Although organophosphorus extractant can extract cobalt but their selectivity is smaller than Cyanex 272.

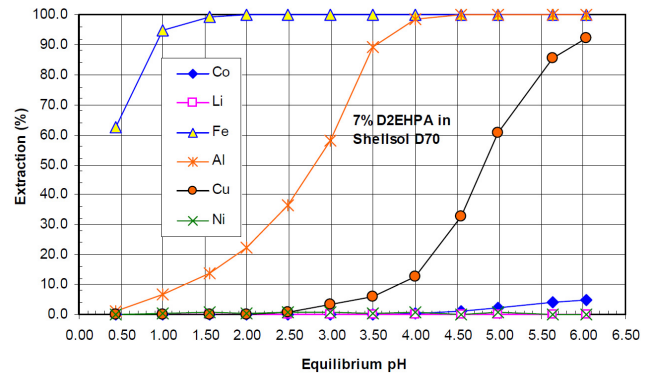
Though several extractants are used for purification purpose, among

Table 1. Typical Co/Ni Separation Behavior Using all Three Reagents, has been Reproduced from given Reference[66]

Experimental Condition			Results Obtained		
Solvent (v/o)	20% extractant	Extractant	Co, % Extracted	Ni, % Extracted	Co/Ni Separation Factor
Modifier	5% isodecanol	Cyanex 272	91.5	15.6	58
Diluent	Kermac 470B	PC 88A	91.4	22.0	18
Aqueous (g/L)	0.97 Co ³⁺ , 0.95 Ni ²⁺	D2EPHA	90.4	46.9	7
pH	11.6				
Org/Aq	1				
Time	5 min				
Temperature	50 °C				

**Figure 3. Typical pH extraction Isotherm of Cyanex 272. Experimental condition : 0.6 M Cyanex 272, 0.015 M of metal sulfate, Org/Aq = 1, temperature 50 °C. It has been reproduced from given reference[66].**

them bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272), 2-ethylhexyl phosphonic acid mono-2-ethylhexyl (PC88A), and Bis-(2-ethylhexyl) phosphoric acid (D2EPHA) are more commonly used for separation or purification of cobalt in the industrial separation process. Similar or identical solvent to Bis-(2-ethylhexyl) phosphoric acid, otherwise called as DEPHA, HDEHP, P-204, HDEHPA, TOPS 99, escaid100 are available commercially bring used as substitute of D2EPHA. Similar or identical solvent to bis(2,4,4-trimethylpentyl) phosphinic acid, popularly known as Di-isooctyl phosphinic acid or P229 also fairly common as solvent in the solvent extraction industrial applications. A similar solvent with PC-88A, named as P507 is also being used instead. Separation of cobalt and nickel was a challenge until the discovery of above mentioned phosphoric acid, phosphoric acid, and phosphinic acid. After several decades of research, it has been realized with these acids the extraction/separation of cobalt is a complex function of temperature, activity, concentration, extractant type, medium of solution, phase modifier and even organic diluent. The separation ability for cobalt and nickel challenge follow the order phosphinic > phosphonic > phosphoric acid due to the increasing stabilization of tetrahedral coordination compound of cobalt with the extractant in the organic phase, because the tetrahedral compound is more stable than the octahedral one[50]. The solvent extraction selectivity of phosphinic, phosphonic, phosphoric acid for main group base metals is

**Figure 4. Typical pH extraction Isotherm of D2EPHA. Experimental condition : 7% of D2EPHA, 0.015 M of metal sulfate, Org/Aq = 0.5, temperature 22 °C. Has been reproduced from given reference[67].**

shown below. Hence, the relative position of cobalt and nature of extractant plays a vital and complex role for separation/purification of Cobalt[64].

Cyanex 272 : Fe > Zn > Cu > Co > Mg > Ca > Ni
 PC 88A : Fe > Zn > Cu > Ca > Co > Mg > Ni
 D2EPHA : Fe > Zn > Ca > Cu > Mg > Co > Ni

Table 1 shows typical Co/Ni separation behavior using all three reagents explained below. The table has been reproduced from Cyanex 272 manual[65]. This indicates typically the Cyanex 272 is the best solvent among the three for cobalt and nickel separation. The Table 1 clearly justifies the series explained above hold good for metal separation. The Figure 3 shows a typical pH extraction isotherm using 0.6 M Cyanex 272, 0.015 M of metal sulfate, Org/Aq = 1, temperature 50 °C, which has been reproduced from the given reference[65]. The pH isotherm in Figure 3 clearly indicates that separation of different d-block metals from Cobalt by proper management of aqueous solution pH, Cyanex 272 concentration and temperature. Similarly, Figure 4 shows a typical pH extraction isotherm of D2EPHA at the experimental condition: 7% of D2EPHA, 0.015 M of metal sulfate, Org/Aq = 0.5, temperature 22 °C, which has been reproduced from given reference[66].

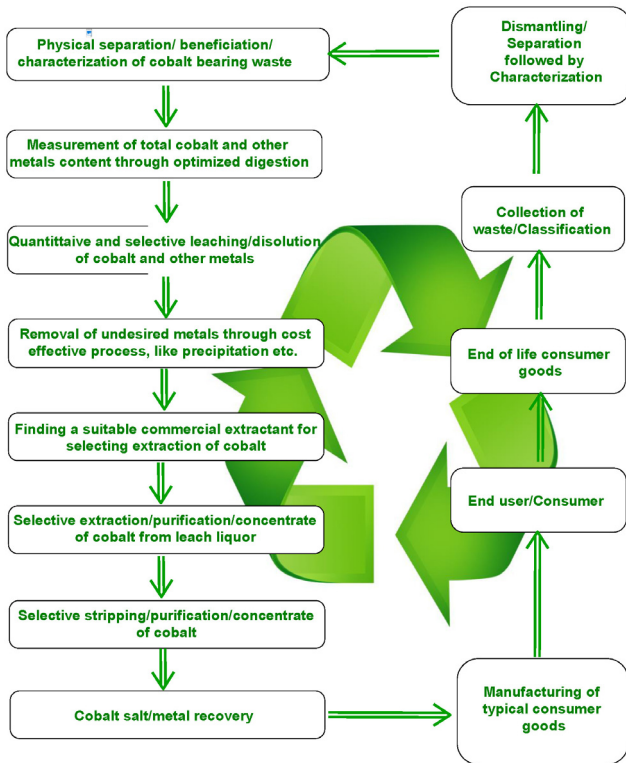


Figure 5. Typical process flow sheet for cobalt bearing waste management and recycling of cobalt bearing scrap through solvent extraction.

6. Cobalt Recovery from Scrap by Solvent Extraction

The recycling of cobalt-bearing scrap and the recovery of cobalt from scrap materials are well-established practices because of the relatively high price of cobalt compared to that of many other metals and the relatively low price of cobalt-bearing scrap compared to that of primary cobalt, make cobalt recycling economical and desirable. Concern over high dependence on imports from uncertain supply sources, potential supply disruptions and global competitiveness has encouraged recycling as a way to diversify the sources of raw materials for the production of cobalt and its end products. Additional factors like, the increasing trend of the waste flux generated, ever increasing energy demand, rapid decrease in primary recourse and strict environmental regulations stimulate the motivation for the waste recycling. The desire to conserve resources and energy, to reduce wastes and the costs of disposing from mining and mineral processing, to reduce levels of such hazardous materials as cadmium in NiCd batteries from the environment, address urban mining notions and to demonstrate an environmentally responsible image; environmental regulations; and periodic increases in the price of cobalt play a role in promoting cobalt recycling and recovery[67]. Recycling of cobalt from various like scrap lithium ion battery[68-75], spent Ni-Cd batteries[76], spent Ni-MH batteries[77-80], spent aerospace material[79], spent Co/Mo/-Al₂O₃ catalysts[80], and Co-based alloy scraps[81] have been reported in the

literature. Among all the lithium ion battery recycling through hydrometallurgy using solvent extraction is quite common and fairly applied in the industries[82-87]. Figure 5 shows a typical process flow sheet for cobalt bearing waste management and recycling of cobalt bearing scrap through solvent extraction.

7. Conclusion

Separation/purification of Cobalt by solvent extraction using commercial extractant is no more a challenge after decades of research in the field. Several commercial cobalt recovery hydrometallurgy plants are now operational. Cheaper and efficient commercial extractants like Cyanex, D2EHPA and PC 88A or its synonymous reagents are added in a sophisticated matter for scrap recycling. Recycling of Cobalt bearing scrap through solvent extraction can be commercially feasible and environmentally friendly process.

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