

Review

Review on the Comparison of the Chemical Reactivity of Cyanex 272, Cyanex 301 and Cyanex 302 for Their Application to Metal Separation from Acid Media

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Abstract: Cyanex extractants, such as Cyanex 272, Cyanex 301, and Cyanex 302 have been commercialized and widely used in the extraction and separation of metal ions in hydrometallurgy. Since Cyanex 301 and Cyanex 302 are the derivatives of Cyanex 272, these extractants have similar functional groups. In order to understand the different extraction behaviors of these extractants, an understanding of the relationship between their structure and reactivity is important. We reviewed the physicochemical properties of these extractants, such as their solubility in water, polymerization degree, acidity strength, extraction performance of metal ions, and the interaction with diluent and other extractants on the basis of their chemical structure. Synthetic methods for these extractants were also introduced. This information is of great value in the synthesis of new kinds of extractants for the extraction of metals from a diverse medium. From the literature, the extraction and stripping characteristics of metals by Cyanex 272 and its derivatives from inorganic acids such as HCl, H₂SO₄, and HNO₃ were also reviewed. The replacement of oxygen with sulfur in the functional groups (P = O to P = S group) has two opposing effects. One is to enhance their acidity and extractability due to an increase in the stability of metal complexes, and the other is to make the stripping of metals from the loaded Cyanex 301 difficult.

Keywords: Cyanex 272; Cyanex 301; Cyanex 302; synthesis; reactivity

1. Introduction

Dialkylphosphinic acid and its thio derivatives with the formula R₂PX₂H (where R is an alkyl group, X is an O or S atom) are phosphorus (V) compounds with tetrahedral molecular geometry. Under the brand names Cyanex, these chelating extractants are widely used in the extraction and separation of metal ions from aqueous solutions [1]. The advantages of Cyanex extractants over other extractants are a high loading capacity and selectivity from diverse aqueous medium. For example, the bis (2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272) is effective in the selective extraction of cobalt and nickel from sulfate and chloride media as well as gold and rare earth elements [2–4]. Cyanex 301 (the main constituent is bis(2,4,4-trimethylpentyl) dithiophosphinic acid) is suitable for extracting zinc and other heavy metals, including platinum group metals [2,5,6].

The replacement of oxygen atoms in di (2,4,4-trimethylpentyl) phosphinic acid by sulfur atoms leads to a change in their physicochemical properties and chemical characteristics [5]. Since the acidity of Cyanex 301 and Cyanex 302 is stronger than that of Cyanex 272, they can extract metal ions at a lower pH. Besides, Cyanex 302 can selectively extract Co(II) over Mn(II), while their separation by Cyanex 272 is difficult [6]. However, the degradation of mono- and dithiophosphinic acids limits their industrial application compared to Cyanex 272.

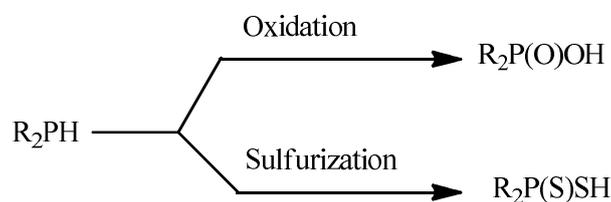
With such useful applications, the synthesis of potential extractants is of importance in the field of analytical chemistry and the separation of metal ions. However, little information has been reported on the synthesis conditions of the extractants. Moreover, an analysis of the chemical reactivity on the basis of chemical structure is valuable in developing new kinds of extractants which can be employed for the extraction of metals. The strong interaction of extractants and diluents leads to a lower performance in the extraction of metal ions [7]. Therefore, the clarification of these issues is extremely useful to upgrade the solvent extraction process.

In this manuscript, we reviewed the synthesis methods and the chemistry of Cyanex 272, Cyanex 301 and Cyanex 302 based on their structures. This can provide important information on the chemical reactivity and extraction characteristics of the above mentioned Cyanex extractants which are employed in hydrometallurgy for the extraction and separation of metal ions. Subsequently, the extraction and stripping behaviour of Cyanex 272 and its derivatives in inorganic acids such as HCl, H₂SO₄, HNO₃ were also reviewed. Particularly, the characteristics, efficiency, and feasibility of these extractants in each case were compared.

2. Synthesis Method

2.1. Synthesis Methods of Phosphinic Acids and Their Derivatives

There are many paths to synthesize organophosphinic acids and their derivatives such as the hydrolysis of halophosphines, the Michaelis–Arbusov reaction, treatment of tertiary phosphine oxides with alkali-metal hydroxides, addition to double bonds with organophosphinates RHP(=O)OH and the oxidation of secondary phosphines, phosphine oxides, and halophosphines with oxygen, sulfur, halogens, or other oxidizing agents [1]. Among these synthesis methods, the oxidation and sulfurization of secondary phosphines are the most important industrial processes and the reaction paths are shown in Scheme 1 [8].



where R is alkyl group

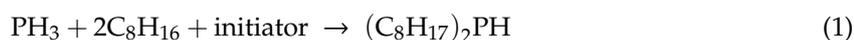
Scheme 1. Oxidation reaction of secondary phosphines.

2.2. Synthesis of Dialkylphosphinic Acids and Thio Derivatives

2.2.1. Cyanex 272

Reaction of phosphine: The treatment of red phosphorus with steam under pressure results in the production of phosphines which can be a raw material for the synthesis of most organophosphorus compounds. Phosphinic acid and its derivatives are synthesized by the reaction of phosphine with α -olefins, and the subsequent oxidation of the products to acids. Among the three derivatives, namely, mono-, di- and trialkylphosphines, dialkylphosphines are preferred for two main reasons: (i) it may not be practical to synthesize mono-derivatives because the reaction is too fast; (ii) it is difficult to make trialkylphosphines owing to its steric hindrance [9].

Cyanex 272 is manufactured by the reaction between phosphine (PH₃) and 2,4,4-trimethylpent-1-ene (C₈H₁₆). In this reaction, the intermediate bis(2,4,4-trimethylpentyl) phosphine (C₈H₁₇)₂PH is oxidized by hydrogen peroxide to form Cyanex 272 ((C₈H₁₇)₂P(O)OH) [10].





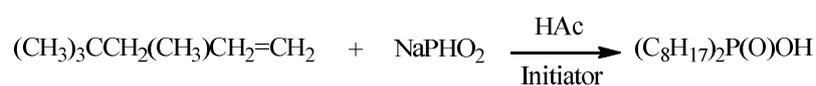
Denote: C_8H_{16} is $(\text{CH}_3)_3\text{CCH}_2\text{C}(\text{CH}_3)=\text{CH}_2$.

The byproducts formed in the first step of Reaction (1) are the trialkylphosphine, $(\text{C}_8\text{H}_{17})_3\text{P}$ and the monoalkylphosphine, $\text{C}_8\text{H}_{17}\text{PH}_2$. They can be separated from $(\text{C}_8\text{H}_{17})_2\text{PH}$ by distillation. The major impurities present in the product are trialkylphosphine oxide, $(\text{C}_8\text{H}_{17})_3\text{PO}$ and the diacid species, $\text{C}_8\text{H}_{17}\text{P}(\text{O})(\text{OH})_2$ and $(\text{C}_8\text{H}_{17})_2\text{P}(\text{OH})_2$.

However, the synthetic process has some disadvantages such as the treatment of highly toxic phosphine, pressure conditions and olefinic polymerization. Thus, hypophosphorous acid seems to be a better alternative as a phosphorous resource in the synthesis of Cyanex 272.

Reaction of hypophosphorous acid: Dialkylphosphinic acids can be produced by a Grignard reaction and free radical addition reaction. The latter is preferred to the former because a Grignard reaction has its own disadvantages such as rigorous reaction conditions, a low yield, and use of CCl_4 which restricts its industrial application owing to its high toxicity [11].

Di-2, 4, 4-trimethylpentylphosphinic acid (main ingredient of Cyanex 272) is synthesized by free radical addition reaction methods (Figure 1). Under the initiation of peroxides or azocompounds, α -olefin is far more active than the β -type [12]. A number of technical measures have been taken to improve the reaction efficiency and to limit the formation of byproducts. Optimum conditions, such as temperature ($130\text{ }^\circ\text{C}$) and reaction time (15 h), have been reported and centrifuges are employed after the alkali-washing step to eliminate polyene byproducts through mechanical separation processes. Cyanex 272 is synthesized from olefins with a branched-chain which prevents polymerization due to steric hindrance. Therefore, the synthetic yield of Cyanex 272 is very high. Notably, the high temperature is a key requirement for this reaction. Owing to the strong affinity between the double-bond oxygen and hydroxyl in H_3PO_2 , the breakage of the two P-H bonds is more difficult than that in the PH_3 molecule [12]. Hence, a higher energy is necessary for the formation of the P-containing free radical with $\text{P}=\text{O}$ and $-\text{OH}$. That means the reaction between α -olefin and H_3PO_2 needs a higher starting temperature ($130\text{ }^\circ\text{C}$). Moreover, Cyanex 272 must be synthesized in a sealed autoclave because the boiling point of diisobutylene is much lower than $130\text{ }^\circ\text{C}$.

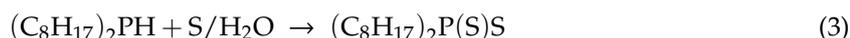


where C_8H_{17} is 2,2,4-trimethylpentyl group

Figure 1. Synthetic route for dialkyl phosphinic acids [12].

2.2.2. Cyanex 301

Under suitable conditions, sulfur can be substituted for peroxide in reactions with $(\text{C}_8\text{H}_{17})_2\text{PH}$ to form the dithioacid, which is the major component of Cyanex 301 [2,8]. The major impurities in this reaction are $(\text{C}_8\text{H}_{17})_3\text{PS}$ which results from the $(\text{C}_8\text{H}_{17})_3\text{P}$ byproduct of Reaction (1) and $(\text{C}_8\text{H}_{17})_2\text{P}(\text{S})\text{OH}$ (monothioacid). After the completion of the reaction, unreacted sulfur remains in Cyanex 301.

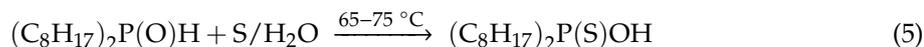


2.2.3. Cyanex 302

The reaction of $(\text{C}_8\text{H}_{17})_2\text{PH}$ with hydrogen peroxide under less severe conditions than Reaction (2) produces dialkylphosphine oxide [8].



The next reaction of $(C_8H_{17})_2P(O)H$ with sulfur in the presence of water at an elevated temperature leads to the formation of monothioacid:



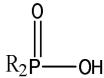
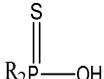
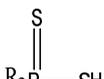
In this case, the product contains dialkyldithioacid, $(C_8H_{17})_2P(S)SH$ (Cyanex 302) whose potential impurities are $(C_8H_{17})_3PO$ (byproduct of Reaction (2)) and dialkyl phosphines sulfide, $(C_8H_{17})_2P(S)H$.

3. Chemical Reactivity Analysis of Cyanex Extractants Based on Chemical Structure

3.1. Solubility and Self-Association Form

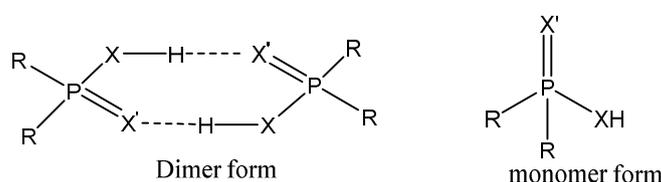
The replacement of oxygen atoms in di (2,4,4-trimethylpentyl) phosphinic acid with sulfur atoms causes an increase in the water solubility and acidity of the resulting products. Therefore, the water solubility increases in the following order: Cyanex 272 < Cyanex 302 < Cyanex 301 (respective values at 25 °C are 4.58×10^{-5} mol/L, 5.41×10^{-5} mol/L, and 28.4×10^{-5} mol/L) [5]. However, the very small water solubility of these extractants can be attributed to the presence of the long alkyl branch which decreases the tendency to be hydrolyzed. Thus, Cyanex 272 and its derivatives might be a good choice for extractants in terms of aqueous solubility. The structure and properties of these three acids are shown in Table 1.

Table 1. Structure and properties of Cyanex 272, Cyanex 302 and Cyanex 301 at 24 °C [10,13].

Extractant	Structure	Density (g cm ⁻³)	Viscosity (cP)	pK _a	Molecular Weight
Cyanex 272		0.91	142	6.37	290
Cyanex 302		0.93	195	5.63	306
Cyanex 301		0.95	78	2.61	322

Denote. R is the 2,4,4-trimethylpentyl group.

Tait (1993) reported that sulfur is weaker than oxygen as a proton acceptor in the extraction [14]. Therefore, Cyanex 301 is monomeric in low polarity solvents due to the poor proton donor properties of the S-H group, whereas Cyanex 272 and Cyanex 302 exist as a dimer. The accepted structure is:



where; X, X' = O/S

Based on the analysis of the titration data, NMR spectra (Nuclear magnetic resonance spectroscopy), gas chromatograms, and mass-spectral data, the composition of these commercial extractants can be represented as Table 2 [6].

Table 2. Components of Cyanex 272, Cyanex 302 and Cyanex 301 [6].

Extractant	Species	Concentration (%)
Cyanex 272	R ₂ PO ₂ H	87–88
	R ₃ PO	10
	Unknown	~2
	R ₂ PSOH	78–80
Cyanex 302	R ₃ PO	10–12
	R ₂ PO ₂ H	2–3
	R ₂ PS ₂ H	2
	Unknown	~8
Cyanex 301	R ₂ PS ₂ H	75–83
	P ₃ PS	5–8
	R ₂ PSOH	3–6
	Unknown	~2

3.2. Acidity and Extraction Potential

Although the carbon chains of Cyanex 272, Cyanex 301 and Cyanex 302 are the same, their functional groups are different and thus there is some difference in their acidity. Cyanex 301 and Cyanex 302 contain a sulfur atom in their acidic groups, which can enhance their extraction capacity. Based on the Brønsted–Lowry theory, the acidity strength of phosphinic acids is related to the stability of the conjugate bases. The more stable its conjugate base is, the more acidic a compound is. This is explained by the stability of the negative charge on the conjugate base of the phosphinic acid. However, the acidity of the extractants is not a unique factor in determining their stability [13]. The extractability of Cyanex 272, Cyanex 301 and Cyanex 302 also depends on the presence of a phosphoryl group (P = O) and thiophosphoryl group (P = S). The extraction power of the extractants containing P = O and P = S is due to either the ionic character or a shift from P = O to P⁺–O[–] and from P = S to P⁺–S[–] configuration. The extraction properties of compounds with P = S bonds are higher than those with P = O bonds owing to the possibility of increasing the ionic character by proper substituents [15]. The stability of complexes formed with the sulfur-containing extractants is stronger than that of the oxygen-containing ones owing to π bonding between the d orbitals of the metal and the donor atoms. This also agrees with the HSAB (hard soft acid base) principle. Molecular orbitals between metals and oxygen involve only sigma bonds, while the overlap of the d metal orbitals with the π orbitals of sulfur occurs. Sulfur atoms are sp³ hybridized to form a sigma bond, with an electron density transferred onto the positively charged metal center. Since the dipole moment of the P = S is relatively small, the delocalization of electrons over the (P–S–metal–S) four-membered ring further increases the stability of the dithio complexes [13].

3.3. Diluent Interaction

The diluent is used for the purpose of reducing the viscosity, adjusting concentration and decreasing the emulsion-forming tendency of the extractants. Although there seems to be very little research on the strength and interaction between Cyanex extractants and diluents, they are indirectly inferred through the effect of diluents on the interaction of extractants in the binary system. Specifically, the interaction of Cyanex 272 with hexane, xylene, and toluene is implied by their effect on the interaction between Cyanex 272 and Alamine 336 in the mixture [16]. It is difficult to accurately determine the nature of the bond-forming in the three-component system including Cyanex 272, Alamine 336 and the diluent using only viscosity data. However, the appearance and disappearance of the OH bands in the infrared spectrum of Cyanex 272 in the presence of different diluents can be attributed to the intermolecular hydrogen bond formation between components. The interaction between the diluent and acidic extractant is proportional to the polarity of the diluent molecule [16,17]. A consideration of the interaction of diluents with acid extractants such as Cyanex 272 and its derivatives is important in

metal separation by single as well as mixed extractants. Once the interaction between the extractants in the system weakens, the synergistic effect is enhanced.

3.4. Interaction in Binary Mixtures

Cyanex 272 and its derivatives readily react with organic bases to form organic salts in extractant mixtures. For instance, interactions can occur in the following synergistic extraction systems, such as Cyanex 272 and Alamine 336/tertiary amine (TEHA, tris-2-ethylhexylamine) for the separation of rare earth elements, Cyanex 301 and TOA for the extraction of Co(II) and Ni(II), Cyanex 302 and Alamine 308 for the separation of Nd(III) and Zn(II) [16,18–21].

The corresponding interactions between these Cyanex extractants and tertiary amine (TEHA) are clarified from the measurement of some of the physical properties of the mixtures, like the viscosity and dielectric constant [22]. The data show that the order of interaction between the mixtures is Cyanex 301 + TEHA > Cyanex 272 + TEHA. In these binary mixtures, Cyanex 301 and Cyanex 272 act as a proton donor, while the tertiary amine has a nitrogen atom containing a free electron pair. The reaction can be represented as:



where HA and R₃N represent Cyanex extractants and the tertiary amine, respectively.

As the acidity of an extractant becomes stronger, its proton donor capacity increases. This might be one of the reasons for the higher interaction of Cyanex 301 with tertiary amines. A stable salt (R₃NHA) may form through the ion-pair bonding between the P = O (Cyanex 272) or P = S (Cyanex 301) group of organophosphorus acid and free ion pair in the nitrogen atom of tertiary amines (TEHA) [22]. These results provide some guidance for selecting an appropriate mixture for the synergistic solvent extraction of metal ions.

On the contrary, when Cyanex 301 and Cyanex 302 are mixed with Aliquat 336, their extraction power is decreased and even in some cases could be appreciably suppressed. The high stability of the undissociated acid–base pair is responsible for this suppression [13]. The formation of the acid–base couple can be expressed as:



Although, there is no manifest evidence about the interaction between Cyanex 301/Cyanex 302 with Aliquat 336, these suppressions should be considered in designing metal separation systems and effective stripping processes.

In a binary extractant mixture, the loss of extractants due to the formation of undesirable species is also of interest. Another reason is that it may adversely affect processes such as the increase in the acidity of the organic phase [23]. In the Murrin Murrin solvent extraction circuits, an impurity species, butyl bis(2,4,4-trimethylpentyl) phosphinate (“butyl phosphinate”), is produced by direct reactions between tributyl phosphate (TBP) and the phosphinic acid, which is the principal component (85%) of Cyanex 272 at 70 °C. The hydroxyl group of phosphinic acid is the main active center. The nucleophilic substitution which controls the formation of butyl phosphinate can be proposed in two distinct types of processes as shown in Figure 2. This figure shows the attack of a nucleophile (phosphinic acid anion) to the P-O-C linkage (substrate TBP) leading to the cleavage of the P-O bond or C-O bond and to the ejection of a dibutyl phosphate anion.

Cyanex 301 and Cyanex 302 also react with TBP to form the corresponding butyl esters, and dibutyl phosphate at 65 °C under anhydrous conditions and the rate order is Cyanex 301 > Cyanex 302 > Cyanex 272. Namely, the loss of dithiophosphinic acid in Cyanex 301 is so fast that only 10% remain after six weeks of operation. Besides, some Cyanex 301 also degrades to thiophosphinic (Cyanex 302) and phosphinic acid (Cyanex 272) analogs, which in turn also undergo reactions with TBP. However, there is no information about the mechanism of this degradation in each case. Therefore, more fundamental research in this regard should be investigated in the future [24].

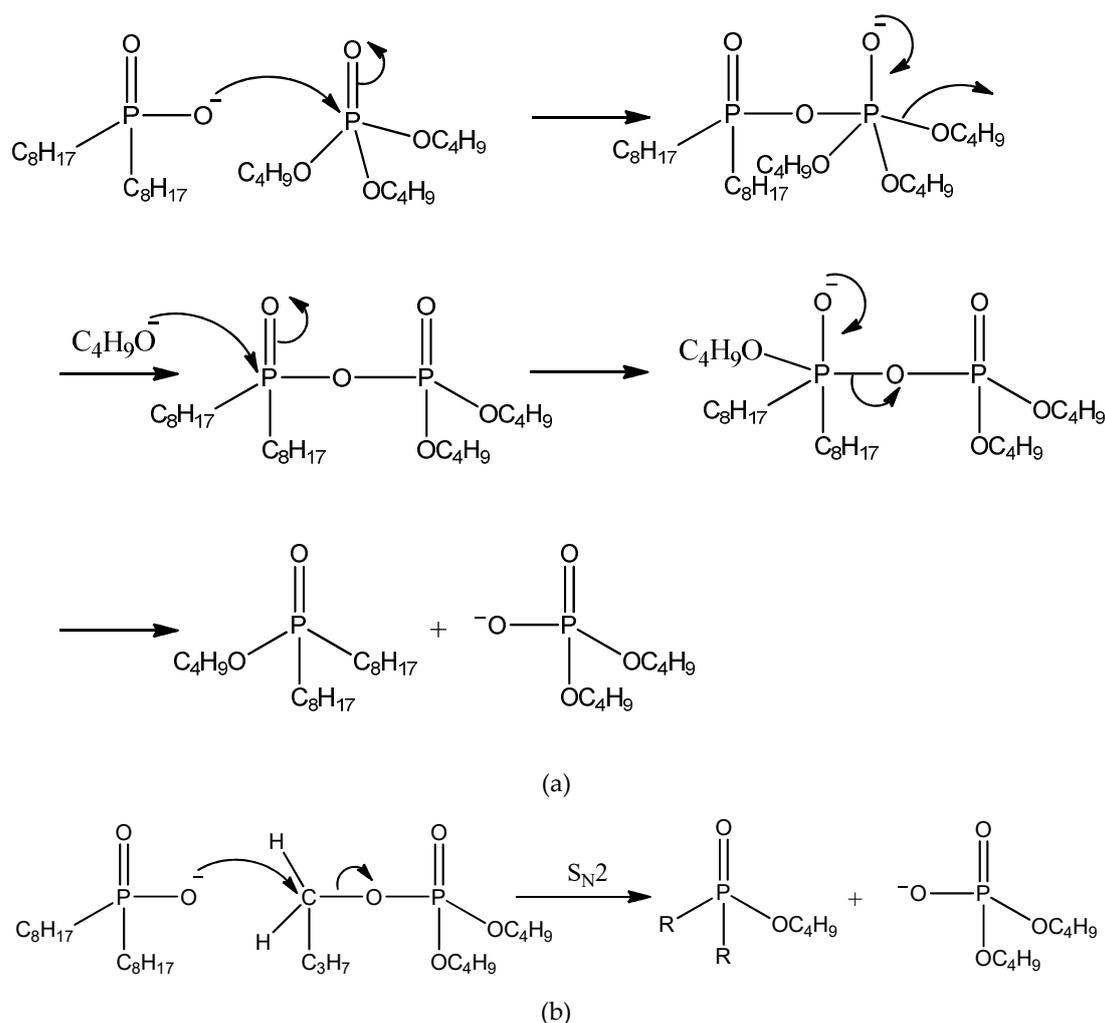


Figure 2. The formation mechanism of butyl phosphinate [23], (a) Mechanism 1, (b) Mechanism 2. Denote. C8H17 is a 2,4,4-trimethylpentyl group.

4. Extraction and Stripping Characteristics of Cyanex 272 and Its Derivatives

4.1. Extraction Behavior of Cyanex for Some Metal Ions from Inorganic Acid Solutions

4.1.1. From Hydrochloric Acid Solutions

It has been reported that Cyanex 301/302 is better than Cyanex 272 in Cu(II) extractions from hydrochloric acid solutions in terms of loading capacity and solution pH. For instance, Cu(II) was selectively extracted (96.3%) over other metals such as Pb(II), Zn(II), a low trace of Mn(II), Fe(III), Co(II) and Cd(II) by 0.2 M Cyanex 272 at an equilibrium pH of 5.0, while the same performance was obtained by 0.08 M Cyanex 301 at an equilibrium pH of 3.8 [25,26]. Between HCl and H₂SO₄ solutions, the separation of Cu(II) by Cyanex 302 from a HCl solution was more efficient than from H₂SO₄ solution because Cu(II) exists as the hydrated copper species ([Cu₂(OH)₂]²⁺) in the sulfate medium which would not be well extracted [26].

Adekola et al. discovered that Cyanex 272 is effective for the selective extraction of Co(II) over Ni(II) in chloride solutions at pH 4 [27]. Moreover, the addition of amine extractants like Alamine 308 into Cyanex 272 enhanced the extraction efficiency and the selectivity of Co(II) over Ni(II) [28]. This could be ascribed to the fact that amine can extract hydrogen ions which are released during extraction, whereby the equilibrium pH can be controlled and thus Co(II) extraction is improved. Compared to

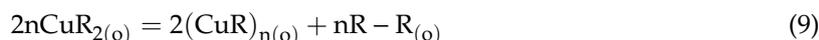
Cyanex 272, Cyanex 301 showed a higher extraction efficiency for Co(II) from the synthetic leach liquor of spent lithium-ion batteries [7]. The advantage of Cyanex 301 lies in its higher loading capacity for Co(II) from dilute chloride solution with pH 6 than Cyanex 272. This can be related to the structural characteristics of Cyanex 301 which contains only sulfur donor atoms in its functional group compared to Cyanex 302 and Cyanex 272. However, the extraction efficiency depends on the temperature and the polarity of the diluents. In general, the strong interaction between polar diluents and extractants leads to a decrease in the extraction efficiency of Co(II) [7,29]. Therefore, a diluent with low dielectric constants like kerosene is appropriate for Cyanex 301 and Cyanex 272.

A high loading capacity of Cyanex 302 for Fe(III) (29.41 g Fe(III)/100 g Cyanex 302) was obtained from a 1 M HCl solution [29]. Additionally, Cyanex 301 and Cyanex 302 are considered to have a high affinity for the silver and palladium present in concentrated HCl solutions owing to the strong interactions between soft bases (extractants) and soft acids (metal ions) [30–32]. By contrast, Cyanex 272 contains oxygen which is considered to be a hard base and thus is less attractive to Pd(II). Au(III) was selectively extracted by Cyanex 272 in the HCl concentration range of 0.5 to 9 M, whereas Pd(II), Pt(IV), Rh(III) and Ir(IV) are not extracted at all [3]. Cyanex 301 was employed to separate Pd(II) over Pt(IV) from hydrochloric acid solutions [33]. This result is consistent with a previous study [31] showing that Cyanex 301 is an effective extractant for Pd(II). Cyanex 301 can completely extract Pd(II) in the HCl concentration range of 1 to 9 M, while Cyanex 272 is not effective.

Cyanex 272 is also used to extract rare earth elements in industrial operations [34,35]. Xie et al. highlighted that Cyanex 272 and its derivatives have the ability to extract rare earth elements [36]. Notably, the saponification of Cyanex 272 is necessary to maintain a high extraction efficiency of rare earth elements [35,37]. When the solution pH is controlled, the use of Cyanex 272 is better than that of Cyanex 301 for the separation of Pr(III) and Nd(III) over La(III) owing to its good extraction capacity and high separation factor. Compared to hydrogen ions, the sodium ions in saponified Cyanex 272 can be better replaced by the rare earth element ions. Therefore, the solution pH can be controlled and thus the extraction efficiency can be maintained. Besides, the appreciable differences in the extraction behavior of Pr(III), Nd(III), and La(III) between Cyanex 301 and Cyanex 272 may be attributed to the acidity of the metal ions which is related to their ionic radii. This is because Pr(III) and Nd(III) ions (hard acids) with smaller ionic radii would prefer to bind to the saponified-Cyanex 272 (hard bases) than Cyanex 301 (soft base). Secondly, the separation factor for Pr(III)/Nd(III) and La(III) was low in the use of Cyanex 301 due to the increase in the co-extraction of La(III) as the Cyanex 301 concentration increased [35].

4.1.2. From Sulfuric Acid Solutions

It has been reported that Cyanex 272 is the most suitable extractant for the separation of Co(II) and Ni(II) from sulfate solutions due to the stability it provides conventional oxidants, good physical and chemical properties, and the ability to avoid the crystallization of gypsum in electrochemical circuits [38]. In practice, the use of Cyanex series extractants for the separation of Co(II) can be achieved under various experimental conditions. However, very high pH conditions should not be taken to avoid the formation of some precipitates. In addition, the replacement of sulfur in functional groups increases the acidity of Cyanex 301/302 and leads to a more efficient extraction of Cu(II), Co(II), and Ni(II). Table 3 lists the equilibrium constants for the extraction reactions of Cu(II), Co(II) and Ni(II) with Cyanex series extractants [39]. As expected, the extraction order of Cu(II) follows Cyanex 301 >> Cyanex 302 > Cyanex 272 and a complete extraction of Cu(II) by Cyanex 301 and 302 was obtained at a low pH. Cyanex 272 reacts with Cu(II) to form a square planar mononuclear complex such as $\text{Cu}(\text{HA}_2)_2$, while the solvent extraction of Cu(II) by Cyanex 301 and Cyanex 302 is accompanied by a redox reaction in the organic phase: (i) reduction in Cu(II) to Cu(I) and (ii) the oxidation of extractants to disulfides (R-R) [14]. Namely, CuR_2 (extracted complex of Cu(II) with Cyanex 301/Cyanex 302) is further polymerized in the organic phase to form oligomeric multinuclear copper complexes. The extraction reactions of Cu(II) and sulfur-containing ligands are presented as Equations (8) and (9) [40].



where HR = Cyanex 301/Cyanex 302.

Table 3. Equilibrium constants for the extraction reaction [39].

Extractant	Metal Ion	pH	Metal:Ligand Ratio	log K
Cyanex 272	Co(II)	4.78	1:2	-7.17
	Ni(II)	4.78	-	-
	Cu(II)	3.00	1:2	-6.39 ^a
Cyanex 302	Co(II)	4.78	1:4	-2.40
	Ni(II)	4.78	1:4	-7.01 ^a
	Cu(II) ^b	2.00	1:2	-5.27
Cyanex 301	Co(II)	4.78	1:2	-5.61
	Ni(II)	4.78	1:4	1.56
	Cu(II) ^c	2.00	1:2	0.92
	Cu(II) ^d	-	1:4	2.30

^a Calculations based on data for which $D < 0.11$. ^b Calculations based on the assumption of metal:ligand ratio of 1:2.

^c Calculations based on the results of the absorbance measurements of organic phases. ^d Calculations based on the mass balance data of copper concentrations.

However, Cyanex 302 is considered to be more efficient at extracting Co(II) and Ni(II) in the presence of Mg(II) than Cyanex 272 [41,42]. Indeed, both Cyanex 272 and Cyanex 302 show good performances for Co(II), and Cyanex 302 shows selectivity for Co(II) over Mg(II) from sulfate solutions [43]. In sulfate solutions containing Co(II), Ni(II) and Mg(II), Co(II) separation can be achieved by two steps: (i) the separation of Co(II) and Mg(II) over Ni(II) by Cyanex 272; (ii) the separation of Co(II) from Mg(II) by Cyanex 302. In particular, the control of the solution pH has a significant influence on the extraction percentage of the metal ions. The extracted complexes by Cyanex 272 and Cyanex 302 are proposed to be $[\text{Co}(\text{HA}_2)_2]$ and $[\text{Co}(\text{HA}_2)_2(\text{H}_2\text{A}_2)_2]$, respectively.

Cyanex 272 can selectively extract Fe(III) from sulfate solutions over Cr(III) and Zn(II) or Co(II), Ni(II), Mn(II) in the solution pH range of 1.8 to 2.5, while Cyanex 302 could only separate Fe(III) over Co(II) and Ni(II) [6,44,45]. In contrast, metal ions such as Cu(II), Zn(II), Fe(III), Co(II) and Ni(II) can be extracted from sulfate solutions in the pH range of zero to 2.5 by Cyanex 301 [6].

4.1.3. From Nitric Acid Solutions

The nature of the anionic complexes plays an important role in the extraction of metal ions such as Th(IV), Ag(I), Zr(IV) and La(III) from strong mineral acid media [46–48]. According to the HSAB principle, the hard Th(IV) strongly interacts with a hard base like the oxygen atom in the functional group of Cyanex 272. The replacement of oxygen with sulfur in organophosphorus acids such as Cyanex 301 and Cyanex 302 increases the soft character. The extraction efficiency of Th(IV) from HNO_3 and HCl solutions is in the order Cyanex 272 > Cyanex 302 > Cyanex 301, while the efficiency of the sulfuric acid solution is reversed. This can be attributed to the strong tendency of Th(IV) to form complexes with sulfates, which results in a decrease in its hard character. Thus, the extraction of Th(IV) from a sulfate medium by Cyanex 301 is better than from other mediums. Based on slope analyses, the extracted species are proposed to be $\text{Th}(\text{NO}_3)_2\text{R}_2$ and ThSO_4R_2 (with R denoting the anion of organophosphorus acids) [47].

When oxygen atoms of the functional group of organophosphorus acids like Cyanex 272 are replaced by sulfur atoms, the Ag(I) extraction efficiency from nitric media is enhanced. Cyanex 301/302 can extract Ag(I) in a complex form of $\text{Ag}(\text{HA}_2)$ ($\text{HA} = \text{Cyanex 301/302}$). The increase in the extraction percentage of Ag(I) could be explained by the formation of durable complexes due to the high affinity between soft Lewis acids (Ag(I)) and soft Lewis bases (Cyanex 301/302). In addition, the replacement

of sulfur atoms increases the acidity of the extractants, resulting in the shift of the metal extraction to a lower pH in the ligand order: $R_2PO_2^- > R_2PSO^- > R_2PS_2^-$ [46]. However, the durable complexes of Ag(I) with Cyanex 301 may make stripping difficult and thus a very high concentration of HNO_3 (16 M) was employed for complete stripping [46].

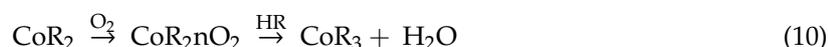
Zr(IV) from 3 M nitric acid was effectively extracted by Cyanex extractants, and the extraction order follows Cyanex 301 < Cyanex 302 < Cyanex 272. One of the advantages of these extractants lies in the fact that nitric acid is not extracted, leading to the complete removal of zirconium from radioactive waste solutions [48].

Generally, the selection of leaching solution has a great effect on the extraction behavior of the extractants due to the formation of diverse metal complexes. The extraction efficiency of some metals from chloride, sulfate and nitrate media by Cyanex 272/301/302 is displayed in Table 4.

4.1.4. Stripping Characteristics

The extraction of metal ions by Cyanex 272, Cyanex 301 and Cyanex 302 is generally carried out in weak acidic media. Therefore, higher acid conditions are favorable to affect stripping [13]. It was reported that many metal ions in the loaded phases of Cyanex extractants can be stripped by acidic agents such as HCl, H_2SO_4 , HNO_3 , and $HClO_4$ [7,27,31]. For example, Co(II) from the loaded Cyanex 272 can be effectively stripped by a 1.0 M HCl solution [27]. Depending on the soft–hardness of the desired metal ion, suitable stripping agents can be selected. The stripping of Pd(II) from a Cyanex 302 system requires the use of a soft ligand such as thiourea in HCl, $HClO_4$, and HNO_3 [31]. Along with these inorganic solutions, a mixture of ammonia and ammonium chloride was employed to strip Ni(II) from the loaded Cyanex 301 by utilizing the complex formation tendency between Ni(II) and ammonia [49]. The addition of ammonium chloride to ammonia could enhance the phase transfer rate and lead to a good separation of the two phases. The optimum composition for the stripping of Ni(II) was reported to be the mixture of 5% NH_4Cl and 75% ammonia [49].

However, some complexes of metal ions like Cu(II), Ag(I), Pd(II) and heavy rare earth elements taken in by Cyanex 301 and Cyanex 302 are difficult to strip [13,30,50,51]. This might be related to the strong interaction between the functional group of Cyanex 301/302 and metal ions according to the HSAB principle. Namely, the stability of the complexes of Ag(I) and Cyanex 301/Cyanex 302 in the organic phase is so high that quantitative stripping is only possible by a 16 M HNO_3 solution [46]. Therefore, the nondestructive stripping of the metal ions from these extractants is very complicated [46,52]. Moreover, the difficulty in stripping Cu(II) from Cyanex 301/302 is also attributed to the reduction in Cu(II) to Cu(I). Therefore, mild acid stripping is ineffective because the re-oxidation of the metal ion to its divalent is required for an effective stripping [13,26]. In the other words, Cu(II) is more strongly solvated by water than Cu(I) and thus stripping can be easily performed. In particular, Cu(II) was stripped from the loaded organic phase of Cyanex 302 by using a high concentration of nitric acid (8–10 M) which acts as an oxidizing agent [26,53]. When such concentrated acids are used, there is some significant negative effect on the extractants. These might be a discoloration and increased viscosity of the organic phases, as well as a deterioration of phase separation. The decomposition and long-term stabilities of Cyanex 301 and Cyanex 302 in contact with sulfuric and nitric acids have been investigated because of its serious impact on environmental and economic issues [14]. Besides, the effect of metal oxidation in the loaded Cyanex 301 has been investigated. Some researchers have found metal to oxidize by air during solvent extractions [54,55]. They suggested that Co(II) is possibly oxidized to Co(III) by air in the organic phase. The resulting Co(III) complex is kinetically very inert, leading to the difficulty in stripping. For example, a cobalt oxidation reaction in the presence of Cyanex 301 is proposed as



Denote. HR: Cyanex 301.

Table 4. Results of the solvent extraction of metal ions from inorganic acidic solution by Cyanex 272/302/301.

Concentration of Extractant	Diluent	Aqueous	Selectivity	Extraction Percentage, %	Stripping Agent, %	Ref.
0.2 M Cyanex 272	Kerosene	4 M HCl; 1187.0 mg/L Cu(II), 299.0 mg/L Pb, 165.5 mg/L Zn, Mn(II), Fe(III), Co(II), Cd(II) low trace; pH = 5	Cu(II) over others	96.3	0.1 M HCl: 98	[25]
0.08 M Cyanex 302	Kerosene	0.1 M sodium chloride; 0.063 M Cu(II); pH = 3.8	Cu(II)	complete	3–4 M HCl/HNO ₃ : complete 4 M H ₂ SO ₄ : complete	[26]
1 M Cyanex 272	Kerosene	4 M HCl; 100 mg/L Co(II) and 100 mg/L Ni(II); pH = 4	Co(II) over Ni(II)	93.3	1 M HCl: 99.32	[27]
0.75 M Cyanex 272	Kerosene	HCl; 350 mg/L Li, 1000 mg/L Co, 400 mg/L Cu, 100 mg/L Al and 100 mg/L Ni; pH = 7.2	Co(II) over others	86.15	2 M H ₂ SO ₄ : 96.1	[7]
0.1 M Cyanex 301	Kerosene	As above	Co(II) over others	96.65	2 M H ₂ SO ₄ : 98.0	[7]
0.01 M Cyanex 301	Kerosene	0.5–9 M HCl, 100 mg/L Pd(II)	Pd(II)	>80	-	[33]
3 mM Cyanex 301	n-heptane	1–8 M HCl, 0.5 mM Pd(II)	Pd(II)	almost 100%	thiourea in 1 M HCl, HClO ₄ , HNO ₃ /LiSCN (0.5 M)-1 M HCl: <5.4	[31]
3 mM Cyanex 302	n-heptane	1–8 M HCl, 0.5 mM Pd(II)	Pd(II)	almost 100%	thiourea in 1 M HCl, HClO ₄ , HNO ₃ /LiSCN (0.5 M)-1 M HCl: > 88–99	[31]
0.1 M Cyanex 302	Kerosene	0.083 M Fe(III); 0.02 M H ⁺ and 1 M Cl ⁻	Fe(III)	29.41 g Fe(III)/100 g Cyanex 302	(6 M H ₂ SO ₄ + 1 M Na ₂ C ₂ O ₄):95 (three stages)	[29]
0.05 mM Cyanex 302	Kerosene	1–10 M HCl, 0.037–0.046 mM Ag(I)	Ag(I)	Almost complete	-	[30]
0.05 mM Cyanex 301	Kerosene	As above	Ag(I)	Almost complete	-	[30]
0.2 M Na-Cyanex 272	Kerosene	1 M sodium chloride solution, 0.0066 M Sm(III); pH = 5.1	Sm(III)	-	1 M HCl: 97	[37]
2 M Na-Cyanex 272	Escaid 110	Chloride solution; 781 mg/L La(III), 119 mg/L Pr(III), and 333 mg/L Nd(III); pH = 4.94.	Pr(III) and Nd(III) over La(III)	Pr(III): 96.6; Nd(III): 98.7 La(III): 4.9	1 M HCl: complete	[35]
2 M Cyanex 301	Escaid 110	As above	Pr(III) and Nd(III) over La(III)	Pr(III): > 85; Nd(III): 85 La(III): > 55	-	[35]
0.1 M Cyanex 272	Xylene	H ₂ SO ₄ ; 0.001 M Cu(II), 0.5 M Na ₂ SO ₄ ; pH = 5–6	Cu(II)	Almost complete	From 0 to 8 M H ₂ SO ₄ : 100%	[13]
0.1 M Cyanex 302	Xylene	H ₂ SO ₄ ; 0.001 M Cu(II), 0.5 M Na ₂ SO ₄ ; pH = 0	Cu(II)	complete	13.5 M H ₂ SO ₄ : difficult	[13]
0.1 M Cyanex 301	Xylene	As above	Cu(II)	complete	18 M H ₂ SO ₄ : very difficult	[13]
20% Cyanex 272	Exxsol D-80 with 5% TBP	Sulfate solution; 0.63 g/L of Co(II), 3.8 g/L of Ni(II), 5.75 g/L of Mg(II); pH = 6	Co(II), Mg(II) over Ni(II)	Co(II): 99.7; Mg(II): 99.3	4 M H ₂ SO ₄ : Co(II): 99.6; Mg(II): 99.1	[43]
20% Cyanex 302	Exxsol D-80 with 5% TBP	Sulfate solution; 0.63 g/L of Co(II), 5.75 g/L of Mg(II); pH = 5.0	Co(II) over Mg(II)	99.6	cobalt electrowinning: 99.5	[43]
10% Cyanex 272	Exxsol D-80 with 5% TBP	Sulfate solution of 3.8 g/L Ni(II)	Ni(II)	99.5	nickel electrowinning: 99.4	[43]

Table 4. Cont.

Concentration of Extractant	Diluent	Aqueous	Selectivity	Extraction Percentage, %	Stripping Agent, %	Ref.
0.25 M Cyanex 272	Toluene	Sulfate solution; 100 g/L NiSO ₄ ·6H ₂ O and 2 g/L COSO ₄ ·7H ₂ O; pH = 6.5	Co(II) over Ni(II)	Co(II):>80 Ni(II):<10	-	[41]
0.25 M Cyanex 302	Toluene	As above	Co(II) over Ni(II)	Co(II):>90 Ni(II):<10	-	[41]
0.25 M Cyanex 301	Toluene	As above, pH = 1.1	Co(II) over Ni(II)	Co(II): 100 Ni(II):<5	Difficult stripping	[41]
0.2 M Cyanex 272	Escaid 110	Sulfate solution; 300 mg/L Fe(III), 500 mg/L Cr(III), and 6 mg/L Zn(III); pH _{eq} = 1.8	Fe(III) over Cr(III) and Zn(II)	90.0	0.5 M H ₂ SO ₄ : complete	[44]
0.2 M Cyanex 272	Kerosene and TBP as a modifier	Sulfate solution; 7.04 g/L Fe(III), 2.82 g/L Ni(II), 0.184 g/L Co(II), 1.26 g/L Mn(II), 0.05 g/L Zn(II), 0.03 g/L Cu(II); pH = 2.5	Fe(III) over others	95% for two stage of counter current; A/O =1/5	15.0 g/L H ₂ SO ₄ : 78 (one stage)/100 (three counter-current stages at equal phase ratio)	[45]
0.027 M Cyanex 272	TBP/DOSO	0.4 M H ₂ SO ₄ ; 0.001 M Th(IV)	Th(IV)	26.1	-	[47]
0.024 M Cyanex 302	TBP/DOSO	As above	Th(IV)	88.7	-	[47]
0.024 M Cyanex 301	TBP/DOSO	As above	Th(IV)	97.5	-	[47]
0.01 M Cyanex 272	Xylene	Nitrate solution; 0.001 M Ag(I), 0.5 M NaNO ₃ ; pH = 6–8	Ag(I)	Almost complete	-	[46]
0.01 M Cyanex 302	Xylene	1–3 M HNO ₃ ; 0.001 M Ag(I), 0.5 M NaNO ₃	Ag(I)	complete	-	[46]
0.01 M Cyanex 301	Xylene	1–4 M HNO ₃ ; 0.001 M Ag(I), 0.5 M NaNO ₃	Ag(I)	complete	16 M HNO ₃ : very difficult	[46]
0.5% Cyanex 272	Kerosene	3 M HNO ₃ ; 0.0109 M Zr(IV)	Zr(IV)	complete	2.5 M H ₂ SO ₄ : complete	[48]
0.5% Cyanex 302	Kerosene	As above	Zr(IV)	complete	2.5 M H ₂ SO ₄ : 76	[48]
0.5% Cyanex 301	Kerosene	As above	Zr(IV)	>90	2.0 M H ₂ SO ₄ : complete	[48]
0.027 M Cyanex 272	TBP/DOSO	0.2 M HNO ₃ ; 0.001 M Th(IV)	Th(IV)	98.9	-	[47]
0.024 M Cyanex 302	TBP/DOSO	As above	Th(IV)	97.3	-	[47]
0.024 M Cyanex 301	TBP/DOSO	As above	Th(IV)	91.2	-	[47]

The reaction can also occur by an oxidizer, i.e., the disulfide of the dithiophosphinic acid (R – R) present in the Cyanex 301, as follows:



The back reaction, namely the reduction in Co(III) to Co(II) under normal conditions, is very slow due to the inertness of the cobalt(III) complexes [55]. In order to prevent the oxidation of the extracted Co(II) to Co(III), as well as the oxidation of Cyanex 301 to a disulfide by oxygen, the extraction was performed in an inert gas stream (nitrogen or carbon dioxide) [40]. This route can result in an efficient stripping of Co(II) and prevent the oxidation of Cyanex 301. However, the use of concentrated hydrochloric acid for the stripping is a disadvantage of this process [40].

Various stripping agents have been tested to overcome the above-mentioned problems [31,33,56]. The stripping of Pd(II) from Cyanex 302 and some mixtures of Cyanex 301 require the use of a soft ligand like thiourea in HCl, HClO₄, and HNO₃, but not H₂SO₄ because of the protonation of thiourea [31,33]. In this case, thiourea is not a stripping agent and helps to form complexes which makes metal stripping easy with acid. The stripping rate increases with increasing thiourea concentrations owing to the formation of the complexes. The utilization of ligands containing sulfur atoms was also effective in the stripping of Pd(II) with a HCl solution containing LiSCN [31]. In the case of Cu(II), stripping from the loaded phase of Cyanex 301, an aqueous solution of thiourea, hydrazine, and sodium hydroxide was used, resulting in a quantitative stripping as well as the regeneration of the extractant. In this mixture, thiourea acted as the stripping agent, while hydrazine lessened the formation of disulfide. However, the high cost of thiourea and the toxicity of hydrazine limits the commercial application of this method [40]. The stripping performance was enhanced when Y(III) was loaded into an organic mixture of 8-hydroxyquinoline and Cyanex 301 and a mixture of 8-hydroxyquinoline and Cyanex 302. Y(III) in the organic loaded phase was quantitatively stripped by a 0.06 M HNO₃ solution [56]. Since stripping depends on the nature of the metal complexes in the loaded organic phase, the nature and the concentration of acidic stripping solutions affect the stripping efficiency. An important objective is to find the most suitable stripping agent to recover the metal with the highest possible purity. The stripping efficiency of some metal complexes from the loaded phase of Cyanex 272/301/302 is also summarized in Table 4.

4.2. Stability/Degradation of Cyanex 272 and Derivatives in a Solvent Extraction Process

4.2.1. Effect of Acidity

The oxidation and decomposition of sulfur-containing organic compounds are significantly affected by the presence of mineral acids. The amount of phosphorus elements in acidic solutions is a measure of the solubility/degradation of the extractant because phosphorus might be transferred from the organic to aqueous phase [57]. The solubility of Cyanex 272 in acidic solutions increases as the pH values raise from 0 to 5.5 and remains unchanged when the pH reaches the acid dissociation constants. This is ascribed to the suppression of the dissociation of these extractants in the aqueous phase by hydrogen ions [58].

The degradation of Cyanex 301/302 insignificantly occurs after prolonged contact with concentrated H₂SO₄ at an elevated temperature [9]. By contrast, the rapid destruction of these extractants is caused by the strongly oxidizing nature of nitric acid even at low acid strengths and for short periods of time. The degree of decomposition and type of decomposition products of Cyanex 301 depend on the contact time and HNO₃ concentration [59]. Nitrogen oxides present in HNO₃ solutions can act as oxidizing agents, and thus the control of HNO₃ concentration is the key to the extended use of the extractants in operation [59]. Besides the frequent change in the characteristic functional groups on IR spectra data, the formation of a yellow solid (sulfur) at the interface and the evolution of a brown gas (NO₂) through the organic phase are evidence of the degradation of Cyanex 301/302 after contact with 5 M HNO₃ for ten days [60]. Nitric acid, a powerful oxidizing agent, can act as an electron acceptor due to the

highest oxidation state of N (+5), while Cyanex 301 and Cyanex 302 contain S atoms acting as strong donors (see Figure 3). Cyanex 302 and tris (2,4,4-trimethylpentyl) phosphine sulfide are completely oxidized to Cyanex 272 and tris (2,4,4-trimethylpentyl) phosphine oxide. The decomposition of Cyanex 301 results in the formation of Cyanex 302 as an intermediate product which is finally oxidized to Cyanex 272 [60]. Wieszczycka and Tomczyk also agreed that Cyanex 301 decomposed into two stage processes as follows: (i) reversible process—the formation of disulfide and (ii) irreversible process—the decomposition of disulfide to Cyanex 272 and elemental sulfur [61].

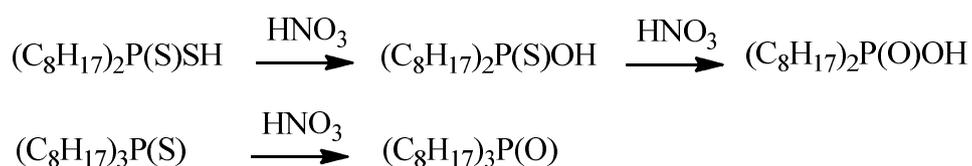


Figure 3. Oxidation of main components in Cyanex 301 and Cyanex 302 by 5 M HNO₃ results in Cyanex 272 and phosphine oxide, respectively. (Shaking time = 15 min and followed 10 days) [60]. Denote. C₈H₁₇ is a 2,4,4-trimethylpentyl group.

In acidic solutions, Cyanex 272 is not degraded but it could react with other agents during extraction process [61]. Due to the strong oxidizing nature of the nitrate ion, a solvent extraction with these extractants from a nitric acid medium is not recommended for the extraction of metal ions [9].

4.2.2. Effect of Other Factors

The degradation degree of organophosphorus extractants depends not only on the acidity of the solution, but also other factors such as the nature of metal ions, stripping condition and structure of the extractants [58,61]. The presence of the oxidizing species such as Fe(III), Co(III) and O₂ even in low concentrations during extraction could initiate or accelerate the oxidation of Cyanex 301 and Cyanex 302 to sulfur-sulfur bonded oxidation products over extended periods of time. These products of dithio-phosphorus extractants have significantly reduced metal extraction power. Therefore, the regeneration of dithiophosphorus extractants is carried out using active hydrogen which breaks the sulfur-sulfur bonds in the oxidation products to form the corresponding dithiophosphorus acids [62].

The photodegradation of Cyanex 301 was determined by FT-IR (Fourier-transform infrared spectroscopy) and GC-MS (Gas chromatography–mass spectrometry) methods. Components of Cyanex 301 such as tris (2,4,4-trimethylpentyl) phosphine sulfide, bis (2,4,4-trimethylpentyl) phosphinic acid and dialkylphosphinic acid in toluene or hexane are degraded after exposure to UV light. The photodegradation of Cyanex 301 in diluents is accelerated in the presence of Cu(II) and Co(II) in the aqueous phase. Cu(II), an efficient electron trap, is capable of inhibiting the recombination of radicals, resulting in an increase in the efficiency of photo-oxidation processes. In the presence of Co(II), binuclear peroxobridged species are formed as intermediate products of the catalytic oxidation of Cyanex 301 [61]. The obtained results indicate that Cyanex 301 is more stable in the presence of Co(II) than Cu(II) in terms of the degradation efficiency of its components. In particular, the precipitation of black powder was observed during the irradiation of copper complexes as a result of photodegradation for the formation of CuS and/or CuO molecules. The mechanism of the photodegradation of each compound of Cyanex 301 is shown in Figure 4.

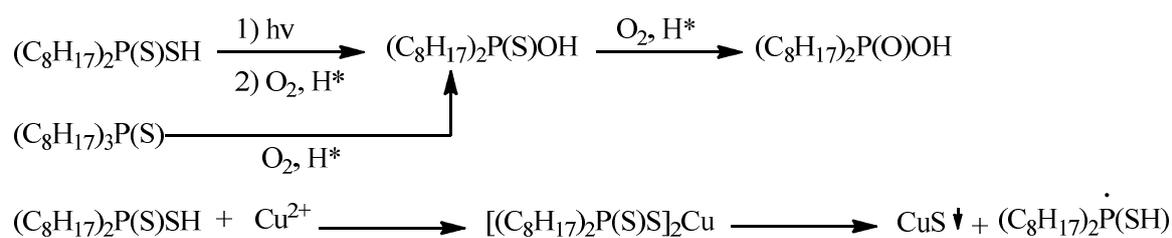


Figure 4. Hypothetical mechanism of the photodegradation of extractant Cyanex 301 [61].

4.3. Recycling of the Extractants

The recycling of Cyanex 272/301/302 is necessary for their economic utilization in the solvent extraction process. In order to investigate the recycling ability of these extractants, consecutive extraction-stripping cycles were employed [49,63–70]. The recycling ability of Cyanex extractants strongly depends on their hydrolytic stability [63]. From the UV-VIS spectra data of the organic phase (before and after extraction as well as after stripping), it was reported that the organic solution of Cyanex 272 could be regenerated for Co(II) extraction [64]. The recycling of Cyanex 272 was confirmed in the closed-loop solvent extraction process for the recovery of Co(II) from the sulfate leachate of a NiMH battery, indicating that the regenerated Cyanex 272 can be efficiently reused for several cycles [65]. In addition, the recycling ability of Cyanex 272 was also studied for Zr(IV) extraction from an acidic chloride solution. The results showed that the extraction and stripping performance of Zr(IV) were kept (over 99.8% for extraction and over 80% for stripping) up to ten cycles of extraction [66]. Similarly, the investigation on the recycling ability of Cyanex 301/302 for the extraction of Hf(IV) from a 0.1 M HCl solution indicated their high stability during extraction and stripping. The organic phase after stripping with 8 M H₂SO₄ was washed with distilled water and then used for further extraction. The results revealed no significant difference in the extraction and stripping efficiency of the extractant within a 10 cycle operation [67,68]. Gupta et al. reported that Cyanex 301 exhibited a good hydrolytic stability, recycling power, and reasonable loading capacity in extraction and separations of Ga(III)/V(IV) from different mineral acid media [69]. The hydrolytic stability and regeneration ability of Cyanex 301 were investigated by contacting Cyanex 301 in toluene with a 5 M HCl/3% H₂O₂ solution for 50 days. The results showed that there was no change in the extraction/stripping of Ga(III) and V(IV) for up to 10 extraction and stripping cycles [69]. In the same way, another study on the successive extraction (from 8 M HCl) by Cyanex 301 and stripping of Ge(IV) by 0.5 M HCl revealed a negligible difference (2 to 3%) in the extraction/stripping percentage of the metal ion up to 15 cycles [70]. Besides, it has been reported that the decrease in the extractability of Cyanex 301 for Ni(II) from 5 M H₂SO₄ was insignificant within 3 days, while after 3 days, a 15% decline was observed [49].

5. Conclusions

Cyanex 272 and its derivatives are employed as extractants for the separation of metal ions in hydrometallurgy. They could be synthesized by employing free radical addition reactions where hypophosphorous acid is used as a phosphorus source. In order to compare the solvent extraction behavior of these extractants, it is necessary to compare their chemical reactivity on the basis of their chemical structure. In fact, these acidic extractants exhibit several chemical properties such as acid–base interactions and interactions with neutral extractants in binary systems and diluents. The use of a polar solvent as a diluent should be considered due to its strong interactions with these extractants which could affect their extraction efficiencies. The interaction of these Cyanex extractants with other extractants in the binary system leads to two opposing phenomena like the loss of extractants and synergistic effects. These extractants can extract metal ions via a cation exchange mechanism from chloride, sulfate and nitrate solutions with low pHs. Cyanex 272 has outstanding physicochemical properties for recovering diverse metals from several acidic environments owing to its effective extraction and stripping characteristics. The substitution of oxygen with sulfur in the functional groups

(P = O to P = S group) enhances the acidity and extractability due to an increase in the stability of metal complexes. Indeed, Cyanex 301 has almost a higher extractability of metal ions compared to Cyanex 272 and Cyanex 302. However, its degradation in the presence of strong oxidizing agents limits the extraction range from nitrate in industrial applications. Moreover, the stripping of metal ions from the loaded phase of Cyanex 301 is difficult. Therefore, it is necessary to find suitable stripping agents for the metals loaded in Cyanex 301, which can improve the applicability of Cyanex 301 to the extraction of metal ions from strong acidic solutions. This review provides important information on the selection of appropriate extractants and improvement measures for the solvent extraction of metal ions by Cyanex 272, Cyanex 301 and Cyanex 302.

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