A Review on Solvent Extraction of Nickel

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Abstract-- **Nickel in waste streams causes environmental problems and due to its wide applications apart from extracting from primary sources it is required to be recovered from secondary sources. It is available in both leach liquors from ores and in secondary sources at lower pH. Most of the work in hydrometallyrgy is related to extract metals at pH as low as possible. Nickel extractions with different extractants are facing one or another problem. Along with pH other factors to be considered for examining suitability of extractant are distribution coefficients, selectivity, extraction and stripping, selectivity, effect of additives, effect of temperature, maximum loading capacities etc. This paper discusses extractants and approaches for nickel extraction considering all above factors.**

Key words: Nickel, Extraction, organophosphorus acids, chelating oximes, nickel sources

I INTRODUCTION

Presence of heavy metals in waste streams resulted in many environmental problems and sometimes deterioration of many ecosystems. Accumulation of such pollutants is due to improper management resources and increased industrial activities. Hence removal of these metals from waste water streams is unavoidable [1]. Compared to conventional waste water treatments use of separation processes provide the means for creating valuable product streams suitable for recycle or re-use from such waste streams.

The wastewater stream is fractionated into two or more liquid phases that are either process recyclable, saleable, or waste [2]. Solvent extraction (SX), membrane-based processes adsorption and ion-exchange technology are the main separation technologies those can be utilized for such purpose. Solvent extraction is a suitable process for reducing solute concentrations in aqueous streams [2].

From viewpoint of environmental protection and resource saving effective recycling and reusing of the heavy metal is strongly acceptable.

Nickel is a hard, silvery-white metal which can be combined with other metals, such as iron, copper, chromium, and zinc, to form alloys. These alloys are used to make coins, jewelry, and items such as valves and heat exchangers. Most nickel is used to make stainless steel [3]. Other uses of nickel are in electroplating and batteries and as a catalyst [4]. Nickel can combine with other elements such as chlorine, sulfur, and oxygen to form nickel compounds. Many nickel compounds dissolve fairly easy in water and have a green color.

II SOURCES OF NICKEL

Primarily nickel can be obtained from leaching of nickel laterite ores and sulfide ores [5-6]. The leach liquors obtained by leaching of ores contains significant amount of nickel along with copper and other metallic impurities. Laterite ores contains about 0.5-1.5% nickel [5] and sulfide ores contains about 0.3-1% nickel. Due to rapid depletion of primary resources and ever increasing demand for nickel, secondary resources have gained recent attention. These secondary resources are spent catalysts, alloy scrap, sludge, waste streams from plating plants, metal finishing industries, spent metallic batteries and dust that can be utilized for cobalt / nickel production [7-12].

Apart from these secondary resources, manganese nodules found in the North and South Atlantic Ocean, the Indian Ocean, and the South Pacific Ocean are considered potential future resources for nickel and cobalt [13-15]. A comprehensive compilation of the various sources of nickel is shown in Fig. 1. Table I and Table II list the various secondary and future resources of nickel.
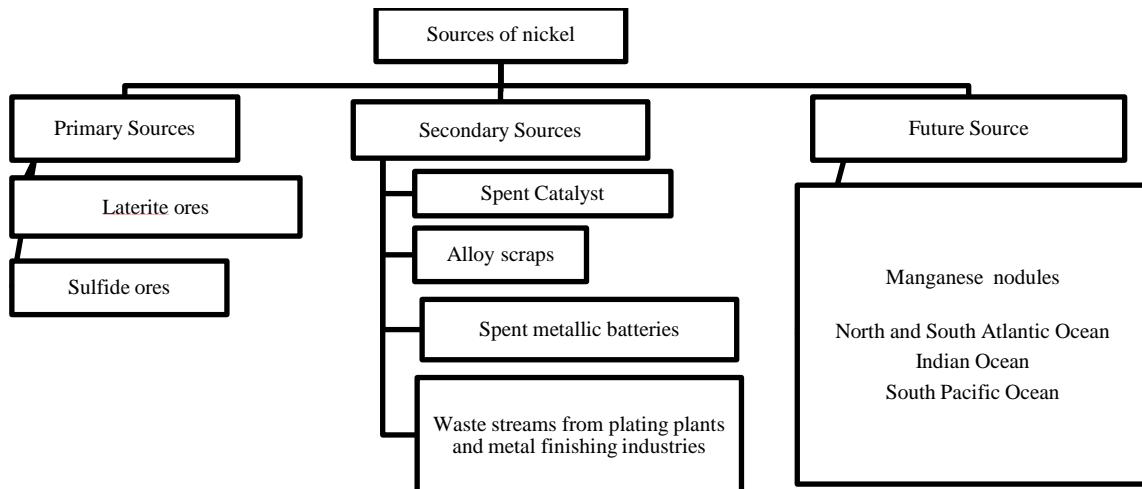
Fig. 1 Sources of nickel

TABLE I. NICKEL IN SECONDARY SOURCES

Source	Stream	Composition	pH	Reference
Secondary aqueous streams				
Electroplating	First and second Rinse bath solutions	0.3-22.9 g/L	1.40 - 7.51	[2]
	First rinse bath solution	0.3-22.9 g/L	1.9- 7.08	[7]
	Second rinse bath solution	1.6-2.5 g/L	1.42- 6.66	
Copper Plant	Copper bleed solutions	10-20 g/L	(Highly acidic)	[8]
Secondary solid sources (Leached with acids)				
Spent Catalysts	Spent hydrogenation catalyst	8% by weight	<1*	[11]
Electroplating	Electroplating bath residue	27% by weight	<1*	
Nickel Metal hydride batteries	NiMH batteries	~50% by weight	0.03-0.05*	[9]
	NiMH rechargeable batteries	10.6 g/L* Ni and 0.85 g/L* Co	~0.4*	[12]
Alloy scraps	Alloy scraps	28.76% Ni and 40.10% Co by weight, 12.55g/L *Ni and 24.85 g/L *Co	<1*	[10]
		* Data shown are for leach liquors obtained by acid leaching of the material		

TABLE II. NICKEL IN FUTURE RESOURCES

Source	Stream	Composition	pH	Reference
Sea nodules	SW pacific	0.35% Ni and 0.44% Co by weight	~1*	[13]
	Samoan	0.23% Ni and 0.23% Co by weight		
	C-C FZ	1.29% Ni and 0.23% Co by weight		
	Peru	1.4% Ni and 0.09% Co by weight		
	Pacific Ocean nodule	16.78 g/L* Ni and 1.78 g/L* Co	1*	[14-15]
		* Data shown are for leach liquors obtained by acid leaching of materials		

III SOLVENT EXTRACTION

Solvent extraction (SX) is one of the most important separation processes in hydrometallurgy. Solvent or liquid-liquid extraction is based on the principle that solute can distribute itself in a certain ratio between two immiscible solvents [16].

Solvent extraction becomes a popular separation technique to recover metals because of its elegance, simplicity, speed and applicability to both trace and macro amounts of metal ions. Recovery of Cu, Co, Zn, U, Mo, W, V, Zr, Hf, Nb, Ta, rare earths, Ga, Ge, the platinum group of metals (PGMs) utilizes SX in hydrometallurgical processing.

Solvent extraction (SX) in hydrometallurgy was first utilized in1942 in the Manhattan project where ether was used as the extracting solvent for the recovery and purification of uranium [17]. Then for recovering uranium in 1950s alkyl amines and di (2-ethylhexyl) phosphoric acid (DEHPA) were used. The process of SX was then applied to the separation and recovery of metals such as Zr/Hf and Nb/Ta. After development of the hydroxyoxime extractants in 1960s the major breakthrough came in the application of the SX process in large scale hydrometallurgical processing of various metals [17]. At present a large varieties of extractants are explored for extraction of different metals in hydrometallurgy.

Different solvent extraction reagents used in hydrometallurgy are acidic extractants (carboxylic acids, alkyl phosphoric acids, alkyl phosphonic acids, aryl sulphonic acids), acidic chelating oximes (hydroxyoximes, beta diketones, hydroxamic acids), basic extractants (Primary amines, Secondary amines, Tertiary amines, Quaternary amines, Mono N-substituted amine, Trialkyl guanidine) and solvating extractants (phosphoric, phosphonic and phosphinic acid esters and thio analogue, various alcohols, esters, ethers, alkyl and aryl sulphides)

IV NICKEL EXTRACTION USING SINGLE EXTRACTANTS

Varieties of extractants have been employed by different investigators to extract nickel because there is no single extractant designed which can extract nickel efficiently at lower pH values. Nickel has been extracted from sulphate, chloride, nitrate, ammonical and phosphoric acid media.

Nickel extraction extractants include organophosphorus acids, chelating oximes (or hydroxyoximes), carboxylic acids and high molecular weight amines (HMWA), among them the organophosphorus acids and chelating oximes are most widely used and commercially acceptable. Table III lists different extractants, their chemical structures and their pH range for nickel extraction.

Among these extractants HMWA and D2EHPA failed due to their emulsion forming tendency. Additionally DEHPA and D2EHPA require a strict control of pH for separation and phase separation becomes poor due to presence of carboxylic acids into them. Applications of Carboxylic acids are limited by high solubility in water. In case of oximes the extractant gets degenerated due to oxidation and regeneration requires an additional step of treatment with hydroxylamine suphuric acid salt [17].
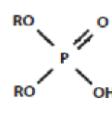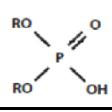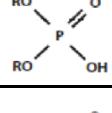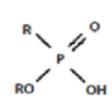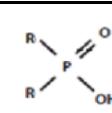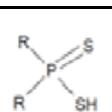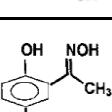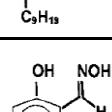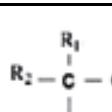
The alkyl phosphonic acidic extractants compared to alkyl phosphoric acids are stable but extracts nickel at higher pH values with faster extraction and stripping kinetics. Equilibrium time for PC 88 is less than 5 minutes but it extracts nickel at pH >4.

The alkylphosphinic acids are most widely used for extraction and separation of nickel. Most of the work reported is related with Cyanex 272 as it has been proven an efficient extractant with faster kinetics and higher loading capacities. Separation using CYANEX 272 is achieved mainly by the control of pH [11]. The main problem associated with CYANEX 272 is it requires high amount of alkali to maintain pH. CYANEX 301 and CYANEX 302 both extract nickel at very lower pH but are not stable and decompose.

Hydroxyoximes extractants exhibits slower nickel extraction kinetics but explored for nickel extraction mainly due to ability of extraction at lower pH values efficiently. LIX 84 IC, LIX 860 and LIX 984 NC extract nickel at lower pH. Among them LIX 984 NC is having emulsion forming tendency.

Use of mixed extractants is now gaining attention to overcome the problems arises when utilizing single extractants. Most widely used and commercially acceptable extractants are organophosphorous acids and hydroxy oximes (chelating oximes).

TABLE III EXTRACTANTS USED FOR NICKEL EXTRACTION

Class of extractant	Extractant	Description	pH	Chemical Structure	
Organophosphorus acid	DEHPA	Di ethyl hexyl phosphoric acid	3-5		Where R= C_9H_{17}
	HDEHP	bis-(2-ethylhexyl) phosphoric acid	3.5-5		
	D2EHPA	di(2-ethylhexyl) phosphoric acid	3-5		Where R= C_8H_{17}
	PC88	2-ethylhexyl phosphonic acid mono 2-ethyl hexyl ester	4-7		Where R = C_8H_{17}
	Cyanex 272	bis(2,4,4-trimethylpentyl) phosphinic acid	6-7.5		Where R = C_8H_{18}
	Cyanex 301	bis (2,4,4-trimethylpentyl) dithiophosphinic acid	1-3		Where R= C_8H_{17}
Chelating Oximes (or hydroxyoximes)	LIX 84I	2-hydroxy-5-nonylacetophenoneoxime	5-6.5		C_9H_{19} can be replaced by $C_{12}H_{25}$
	LIX860	5-dodecyl- salicylaldoxime	2.75-4.25		C_9H_{19} can be replaced by $C_{12}H_{25}$
	LIX 984 NC	1:1 volume blend of LIX84IC and LIX860 N-IC	2.5-5	1:1 volume blend of LIX84IC and LIX860N-IC	
Carboxylic acid	Versatic 10	Neodecanoic acid	6-7		

V. NICKEL EXTRACTION CHEMISTRY USING

ORGANOPHOSPHORUS ACIDS AND CHELATING OXIMES

Both organophosphorous acids and chelating oximes are dimeric extractants. All acidic extractants follow cation exchange mechanism. Chelating oximes also follow cation exchange mechanism. The general reaction for nickel extraction can be given as [14] equation 1,

$$n\,(HR)_{2\,(org)} + Ni^{+2}_{(aq)} \leftrightarrow [NiR_{2n}\,H_{2n-n}]_{(org)} + 2H^+_{(aq)} \qquad (1)$$
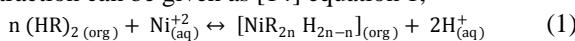
Where,

n = stoichiometric coefficient

R = Hydrocarbon group

aq = aqueous phase

org = organic phase

The equilibrium constant for the reaction is then given by,

$$K = \frac{[(NiR_{2n}\,H_{2n-n})_{org}]\,[H^+]^2}{[Ni^{+2}][HR_2]^n} \qquad (2)$$

The distribution coefficient can be given as,

$$D = \frac{[Ni_{org}]}{[Ni_{aq}]} = \frac{[(NiR_{2n}\,H_{2n-n})_{org}]}{Ni^{+2}} \qquad (3)$$

Therefore:
$$K = \frac{D[H^+]^2}{[(HR)_{2\,(org)}]^n} \qquad (4)$$

and

$$\log K = \log D - 2pH - n\log[(HR)_{2\,(org)}] \qquad (5)$$

At constant extractant concentration, a plot of log D against pH yields a straight line with slope n which gives number of extractant molecules involved in extraction. For nickel extraction with chelating oximes and organophosphorus acids reported values of n are near to 2 when metal concentration is much lower than extractant concentration present. Distribution ratio of metal in organic phase depends on pH and free concentration of extractant. Higher values of n (3 and 4) have also been reported [18] at higher concentrations of extractants.

Generally octahedral metal complexes are formed by with dimeric extractant. The sixth coordination site of nickel complex remains hydrated (Fig. 2). The nature of extracted species proposed using different extractants and organic phase is listed in Table IV.

VI . EFFECT OF PARAMETRIC VARIATIONS ON NICKEL EXTRACTION AND STRIPPING

To determine the feasibility of different extractants most of the investigators have focused their attention on selectivity of extractants, effect of parameters such as phase acidity, temperature, extractant concentrations, diluents, addition of salts, neutralization of extractants, aqueous media, organic phase additives and mixture of extractants, nature of complexes formed, thermodynamic and kinetic aspects of extraction, stripping behavior of extractants and regeneration and maximum loading capacities of extractants.

A. Effect of extraction concentration

At constant pH, metal extraction increases with increasing extractant concentration. Higher concentration of extractant shifts extraction equilibria to lower pH values for both single as well as mixture of extractants [2][14][18][23-25]. An increase in distribution coefficient with increase in extractant concentration has been reported by Singh et al. (1999)[11], Koladkar and Dhadke (2001)[20] and Reddy and Priya (2006)[26]. For mixtures of extractants, generally, concentrations of extractants are varied and effects of varying concentrations are studied [27-29].

B. Effect of diluents

The diluent can influence the selectivity of a solvent extraction process through both chemical and entrainment effects. Diluents used in the solvent extraction of the major metals are usually either de-aromatized hydrocarbons containing less than 0.5% aromatics or diluents containing between 17 and 23% aromatic[30]. Both types of diluents contain about 40% cyclo-paraffins.

Aromatic components in the diluent can have three main effects on the chemistry of solvent extraction.

1.   To increase the solubility in the organic phase of the metal - extractant complex

2.   To act as an equilibrium modifier

3.   To influence the selectivity of the extractant.
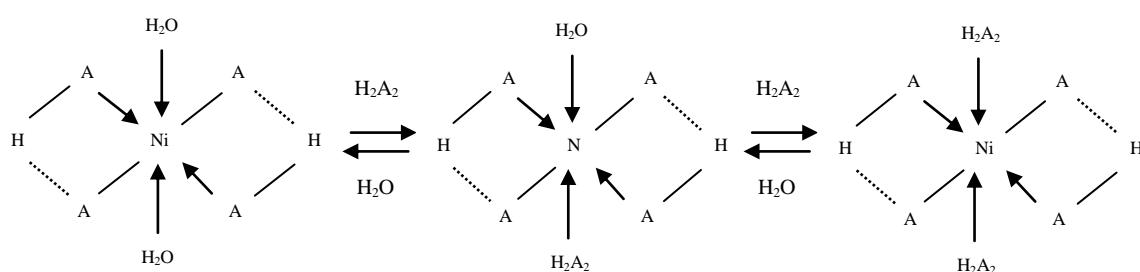
Fig. 2 Structure of nickel octahedral metal complex

TABLE IV. NATURE OF EXTRACTED SPECIES FOR NICKEL EXTRACTION USING SINGLE EXTRACTANTS

Organic phase	Proposed metal complexes/ metal species	Reference
Cyanex 301 in toluene	NiR_2	[11]
Cyanex 301 in nonane	NiR_2	[19]
D2EHPA, RD577 and Cyanex 272 in xylene	$Ni(HR_2)_2(H_2R_2)x(H_2O)_2\text{-}x$ Where, x = 0, 1 or 2	[18]
PIA-8 in toluene	$NiR_2 \cdot 2(HR)_2$	[20]
HDEHP and EHPNA in different diluents	$NiR_2 \cdot 2(HR)_2$	[21]
HDEHP in kerosene	$NiR_2(HR)_3$ and $NiR_2(HR)_4$	[22]

Different diluents used in nickel extraction are n-hexane [4][11], chloroform [4][11], cyclohexane[4][11], xylene[4][11][18][31-32], benzene [4], toluene [11][20][28], kerosene [4][10-11][15][33-34], carbon tetrachloride [4], n-heptane [18], pentane [18], Shellsol D70 [28][35] Shellsol 2046AR [36], nonane [19][37], Escaid 102 [37], dodecane [38], and Exxol D100 [23] etc. By far kerosene is the diluent most commonly used.

Singh et al.(1999) [11] studied extraction behavior of nickel using Cyanex 301 in different diluents n-hexane, chloroform, cyclohexane, xylene, toluene and kerosene and reported that all solvents used can replace each other without any significant change in extraction behavior. With cyclohexane slow phase separation has been observed. Preston (1982) [18] reported shift in extraction to lower pH values with use of aliphatic diluents in place of aromatic diluents. Use of aromatic diluents enhances the extraction of nickel. Reddy and Priya (2004) [4] investigated extraction of nickel using LIX84-I at equilibrium pH 7.5 in various diluents and reported nickel extraction varies with the nature of diluent in order xylene < chloroform < carbon tetrachloride < benzene < cyclohexane < n-hexane < kerosene.

C. Effect of temperature on extraction

Effect of temperature on extraction of nickel has been investigated by various researchers. Temperature has no effect on nickel extraction and stripping rates when LIX 84-I was used as an extractant [4]. Using (PIA-8) Koladkar and Dhadke (2001) [20] and (DP-8R) Cepra and Algucil (2002) [23] also observed a marginal effect of temperature on extraction rates. Using PC88A as an extractant Lin et al. (2006) [39] observed a decrease in nickel extraction with increase in temperature. Using organophosphorus acids mixtures little effect of temperature on extraction was observed by Darvishi et al. (2005) [27]. Sarangi et al., (1999) [24] observed an increase in nickel extraction with increase in temperature using neutralized organophosphorus acidic extractants. In case of synergistic extraction systems, an enhancement in extraction rates were observed at initial time using LIX63 + Versatic 10 [35] and LIX84-IC + Versatic 10 [30], mixtures and later the rates became constant. Preez and Preston (2004) [32] reported that temperature had no effect when mixtures of carboxylic acids were used.

D. Effect of neutralization of extractant

Sodium salts are generally contacted with acidic extractant to neutralize extractant. Other salts are reported in few cases. Presence sodium or other such ions remove free protons and increase pH so no further neutralization is required or amount of alkali required is less depending on percentage neutralization. Neutral form of extractant exists as monomer and acidic form as dimer. Both form take part in extraction. The mechanism by which a metal ion is extracted using partially neutralized cation exchange extractant is reported by Sarangi et al. (1999) [24]. Neutralization releases one proton instead of two as in conventional case.

$$M_{aq}^{2+} + R_{org}^- + 2(HR)_{2\,org} \leftrightarrow MA_2 \cdot 3HR_{org} + H_{aq}^+ \quad (6)$$
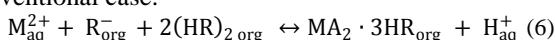
Where,

M = Metal

HR = Acidic extractant

org = Organic phase

aq = Aqueous phase

Extraction of nickel with neutralized acidic extractant has been reported by various researchers [14][24][35][40].

E. Effect of ionic strength

Constant ionic strength is maintained during extraction to minimize effect of activity/concentration difference. Equilibrium constant should be derived using activities instead of concentration, as activity, is not equal to concentration. This assumption is correct using dilute metal solutions as activity increases with increase in metal concentration. Hence, the total ionic strength is maintained at constant value irrespective of metal concentration.

This is usually done by addition of different salts such as Na_2SO_4, NaCl, $NaNO_3$, NH_4Cl, $NHCH_3COONa$, NaSCN, KCl, KNO_3 etc. Addition of salts generally shifts extraction equilibria to higher pH values. These can be partially explained in terms of aqueous phase complex equilibria [25].

$$Na_2SO_4 + H^+ \leftrightarrow Na^+ + HNaSO_4 \quad (7)$$
$$Na_2SO_4 + H^+ \leftrightarrow 2Na^+ + HSO_4 \quad (8)$$
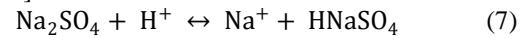
These reactions effectively remove free protons from solution, thereby increasing the pH at which extraction occurs.

Reddy and Priya (2004) [4] observed decrease in nickel extraction in order $NaNO_3 < Na_2SO_4 < NaCl < NaSCN$ using LIX 84I as the extractant. No significant effect of nature or concentration of mineral salts on nickel extraction was observed by Buch et al. (2002) [38] while using mixtures of EHO and D2EHPA.

In order to maintain constant pH during extraction, buffering of aqueous phase using CH_3COOH-CH_3COONa was used by Komasawa et al. (1981) [41] while Pashkov et al. (2008) [19] used $LiSO_4$-H_2SO_4.

F. Effect of phase modifiers and organic phase additives

The commercial use of organic additives in extraction systems are as emulsion inhibitors and as synergists. Chemically there is no distinction between the various types of additives, since; all are capable of interacting with the extractant and the extracted metal complexes to varying degrees. Interaction of an additive B with dimerized organophosphorus extractant has been explained by Preston (1982) [18].

$$H_2R_2 + B = H_2R_2 \cdot B \quad (9)$$
$$H_2R_2 + B = 2HR \cdot B \quad (10)$$
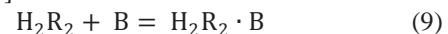
Interaction of an additive with the extracted nickel complex $Ni(HR)_2(H_2R_2)_{2-n}(H_2O)_{2-n}$ can occur by replacement of the coordinated neutral extractant molecules (H_2R_2) and/or water molecules. Various additives used are TBP, TOA, TOP, isooctanol, isodecanol, nonylphenol, TOPO, 2-ethylhexyl alcohol etc. Effect of organic phase additives as synergist were studied by Preston (1982) [18] and Okada et al.(2010) [33]. Effect of additives as emulsion inhibitor or phase modifier were studied by Feng et al.(2008) [10], Cheng et al.(2010) [42] and Komasawa et al.(1984) [43].

G. Maximum loading capacity of extractant

There are two methods to determine the loading capacity of an extractant. In the first method the O/A ratio

is varied and in the other, the organic phase is loaded several times with fresh aqueous solutions containing metal at previously determined constant pH conditions. The latter process is carried on until the saturation of the oil phase with the metal is obtained and it is the most widely used method. The reported values for maximum loading capacities of extractants are 0.5M D2EHPA- 14.5 g/L [2], 15Vol% LIX 984 N-C- 7.3 g/L [2], 0.01mol/dm^3 LIX 84-I – 0.283 g/L [4], 1M D2EHPA – 17.7 kg/m^3(in sulphate media), 20.74 kg/m^3 (in chloride media) [44], 1M PC 88-18.3 kg/m^3(in sulphate media), 20.75 kg/m^3 (in chloride media)) [44], and 1M Cyanex 272- 18.7 kg/m^3(in sulphate media), 20.35(in chloride media) [44]. For extractant mixtures Cheng et al.(2010) [42] determined maximum loading capacity of 0.5M Versatic 10, 0.45M LIX63 and 1.0M TBP maximum loading capacity was as 2.389 g/L and 0.5M Versatic 10 and 4-pyridine carboxylate as 6.614 g/L.

H. Regeneration or recycling capacity of extractant

For economic utilization of extractant, regeneration of extractant is necessary. Successive extraction-stripping cycles are carried out for determining regeneration capacity of extractant. Regeneration capacity of extractant depends on hydrostatic stability of extractant. Recycling capacity for nickel extraction was determined by Singh et al.(1999) [11] for Cyanex 301and observed no significant decline in extractability of extractant for 3 days and after 3 days 15% decline was observed. LIX 84-I was also reported for having good regeneration capacity by Reddy and Priya (2004) [4]. Extraction efficiencies of fresh and reloaded organic phase for extractant mixture LIX 63 and Versatic 10 were compared by Meyhew et al. (2011) [35]. They observed no significant difference in extraction capacity. .

I. Effect of acid concentration on stripping and stripping kinetics for single extractant

Quantitative stripping of loaded organic phase is as much important as extraction to recover the metal values. Stripping kinetics for nickel is also slower compared to other metals same as in case of extraction. Stripping can be done in several ways depending on stripping has to be done selectively or bulk stripping.

Stripping of organophosphorus acidic extractants loaded with nickel have been performed by many investigators [11][14][39-40][45] and observed that stripping of nickel loaded organophosphorus acids are faster and could be achieved quantitatively even at lower strengths. Stripping kinetics of chelating oximes was observed by Kul and Cetinkaya (2010) [2] using acid strengths ranging from 150-200 g/L. Stripping of 15vol% of LIX984 N-C loaded with 5685 mg/L required 150 minutes. Stripping of nickel loaded LIX84-I was carried out by Reddy and Priya (2004) [4] and they reported 8 mol/dm^3 acid was required to strip 0.01mol/dm^3 of LIX 84-I loaded with 0.283g/L nickel.

J. McCabe-Thiele chart

The number of steps needed in a mixer-settler to reach desired separation can be determined by constructing a McCabe-Thiele chart. The chart is constructed by determining the equilibrium isotherm for extraction or stripping via experiments. The equilibrium isotherm can be obtained by mixing an aqueous solution and organic solution at different phase ratios (organic/aqueous) until equilibrium is reached. McCabe-Thiele charts for nickel extraction [2][14][23][40][42][45] and stripping [2][14][40][45] are plotted by various investigators. Number of stages in both extraction and stripping should be as low as possible for effectiveness of operation. With organophosphorus acidic extractants numbers of stages required are less compared to other class of extractants.

CONCLUSION

Nickel recovery from secondary sources is necessary from view point of both environmental protection and to meet increasing demand of it. Nickel is generally available at lower pH values for extraction. Organophosphorus acids and hydroxyoximes proven efficient for extraction but having one or another problem required to be overcome. Not a single extractant can extract nickel efficiently at lower pH with faster kinetics, with stability and good separation. To increase extraction efficiencies adding large amount of alkali is not advisable approach. Use of mixed extractant system can overcome the problems. Hence mixed extractant systems are required to be explored for extracting nickel at low pH with faster kinetics.

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