CHAPTER 4

Recovery of Copper and Zinc from Spent Brass Pickle Liquors

The recovery of copper and zinc from spent pickle liquor obtained from a brass processing industry using solvent extraction is discussed in this Chapter. The extractants were regenerated by reclaiming copper and zinc as oxalate precipitates using the precipitation-stripping technique. Subsequently the oxalates were calcined to form copper oxide and zinc oxide that have considerable commercial potential. A processing scheme for recovery of metals from pickle liquors is developed.

4.1 Introduction

Brass, an alloy of copper and zinc finds wide application due to its unique combination of properties such as strength, malleability, and high thermal conductivity. It can be easily cast to shape and used for costume jewellery, decorative trims and other similar applications because of its bright gold like appearance. There are over 60 different types of brass specified by European Norm (EN) Standards with varying compositions depending upon the properties required for a particular application. (Skogsberg and Kanannathan 2017)

The amount of copper in brass varies between 55% (w) and 95% (w) depending on the type of brass and its intended use. Zinc content can vary between 10% (w) to about 45% (w). Brasses with higher percentages of zinc are stronger and harder. Brass also contains small percentages of other materials to improve certain properties. Iron, 1 to 3% (w) makes the brass harder and makes the internal grain structure smaller so that the metal can be shaped by repeated impacts in forging. Up to 3% (w) aluminium is added in brass to form a protective oxide film to keep the molten metal clean and corrosion free. Tin 1% (w) is included to provide improved corrosion resistance against water. Nickel is added in brass to have superior tarnish resistance and resistance to stress corrosion (Figure 4.1).

India is well known for its brass jewellery, artefacts and industrial components. In India

Haryana (Jagadhari and Rewari), Orissa (Mayurbhanj, Dhenkanal, Keonjhar and Sundargarh), Assam (Hazo and Sarthebar) Uttar Pradesh (Moradabad, Aligarh, Hathras and Varanasi), Jammu & Kashmir (Samba), West Bengal (Purulia, Bankura, Birbhum, Murshidabad) and Rajasthan (Jaipur) (Winrock International India).

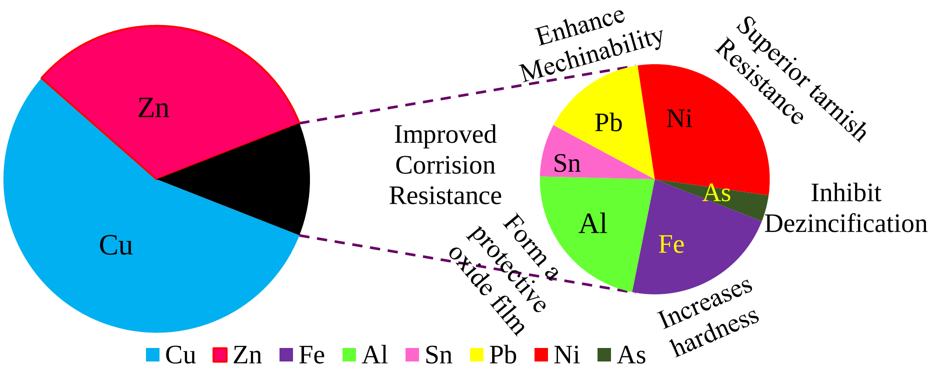

Fig. 4.1: Constituents of brass (Davis 2001)

From the point of view of its application or usage pattern, the products manufactured in most of the states are consumer products and are used as gift, utility or decorative items, whereas, the products manufactured in Gujarat can be classified as industrial products and consumed by industries as a part/component of their final product. Table 4.1 lists the composition and the major usage of brass in industrial components and artefacts.

Table 4.1: Applications of brass (Gupta et al., 2014)

Sr. No.	Brass component	Composition in percentage						
		Cu	Zn	Sn	Pb	Al	As	Fe
1	Tube	71.6	26.7	1.1	-	-	-	-
2	Heat exchanger tube	77.5	20	-	-	2	0.1	-
3	Connector	58	39-40	-	2-3	-	-	-
4	Valve	62-63	38-39	-	0.33	-	-	-
5	Cooler tube	76-77	20	-	-	2.06	0.04	-
6	Ornaments	69	29	0.8	-	-	-	1.1
7	Plumbing fittings	60	38	0.81	-	-	-	1.2

(Minor components are approximate values)

The brass parts cluster at Jamnagar has over 5,000 small units and meets almost 70% of the entire requirement for brass parts in India (Gujarat State Report - March 2017). Majority of the raw material requirement in Jamnagar brass cluster is met through imports. The countries from which brass is imported are USA, Singapore, Gulf and European countries. Brass also has an advantage over other materials that the products made from brass can be recycled or reused, rather than being discarded in a landfill, this reduces pollution (GLE scrap metal 2018).

Brass on exposure to atmosphere undergoes surface discolouration, called tarnish, due to formation of a thin oxide layer that needs to be removed to impart its lustrous look. Cleaning and finishing process to remove tarnish and oxide layer formed on industrial brass components subjected to heat treatment process involves stages of acid wash and water rinse (Davis 2001). Acid wash with H_2SO_4 is more common but many processors prefer to use HCl since it reacts quickly, preferentially attacks the oxide layer, prevents pitting and the pickling baths can be operated at ambient temperatures. The pickling bath is used till the acid concentration declines to such a low value that the time required for tarnish removal becomes large and uneconomical for operation, resulting in a substantial metal build up in the pickle liquor.

The metal loaded pickle liquor and rinse waters are often discharged to sewers without any treatment. Heavy metals in discharge waters pose considerable threat as they enter the aquatic ecosystem where they bio-accumulate and bio-magnify in the food chain and become toxic for living organisms at higher tropic levels in nature (Singh, 2014). Although copper and zinc are essential nutrients for various enzymatic reactions, but at high concentrations both aquatic as well as human life are adversely affected. Hence, recovery of these metals is not only important from the point of view of pollution abatement but also results in profit by recycling of the metals.

A continuous research effort is focussed on developing options for the recovery of metals from aqueous waste streams (Fu and Wang, 2011). Most commonly used technique for the processing of spent pickling solution is the precipitation neutralization process with lime. This process generates huge quantity of sludge which is either disposed as landfill or stored for further processing. The loss of metal values during the precipitation makes this process inappropriate in both economic and environmental aspects.

The hydrometallurgical route using Solvent Extraction (SX) is often advantageous over other methods due to its high selectivity, versatility and its ability to produce highly pure products while handling of large amount of solutions (Sinha 2012). This route generates value added products and mitigates the problem, which would arise from the direct disposal of the waste pickle liquor. A comprehensive review of copper and zinc recovery from brass components, brass ash, brass dross and slag, brass flue dust, soil contaminated from brass industry and brass pickle liquors using different techniques is presented in Table 4.2.

Table 4.2: Recovery of copper and zinc from brass components/pickle liquors

<table>
<tr><th>Sr. No.</th><th>Brass component</th><th colspan="8">Composition</th><th>Treatment technique</th><th>Operating parameters</th><th>Recovered as</th><th>Reference</th></tr>
<tr><td rowspan="8">1.</td><td rowspan="8">Brass ash</td><td>E</td><td>Zn</td><td>Cu</td><td>Ca</td><td>Al</td><td>Mg</td><td>Na</td><td>K</td><td rowspan="2">Leaching with Ionic liquid</td><td rowspan="2">Leachant:50% [bmim]HSO$_4$ in presence of 50%H$_2$O$_2$ at atm. Press., temp. 70^{0}C, stirring rate 400 r/min, recover 99% of Zn and 82% of Cu</td><td rowspan="2">Copper and zinc solution in Ionic liquid</td><td rowspan="2">Kilicarslan <i>et al.</i>,2014</td></tr>
<tr><td>C (%w)</td><td>53.9</td><td>22</td><td>5.8</td><td>3.</td><td>0.3</td><td>0.3</td><td>0.35</td></tr>
<tr><td>E</td><td>Zn</td><td>Cu</td><td>Pb</td><td colspan="2">SiO$_2$</td><td colspan="2">Cl</td><td rowspan="2">Carbothermal recovery by graphite, treatment of ash in temperature-controlled tube furnace</td><td rowspan="2">Mechanism: diffusion control, Temp. 1200°C, time 60 min, recovery of zinc 92·5%, E= 90·1 kJ mol^{-1}</td><td rowspan="2">Metallic zinc and zinc oxide</td><td rowspan="2">Kahvecioglu <i>et al.</i>, 2003</td></tr>
<tr><td>C (%w)</td><td>59.6</td><td>9.22</td><td>1.45</td><td colspan="2">2.6</td><td colspan="2">0.36</td></tr>
<tr><td>E</td><td>Zn</td><td>Cu</td><td colspan="5"></td><td rowspan="2">Beneficiation by acidic or/ and alkaline leachant</td><td rowspan="2">Treating with H$_2$SO$_4$ or (NH$_4$)$_2$CO$_3$+NH$_4$OH mixtures. Leaching rate :90% of Zn and more than 65% of Cu</td><td rowspan="2">Cement copper and zinc sulfate solution</td><td rowspan="2">Timur <i>et al.</i>,2000</td></tr>
<tr><td>C (%w)</td><td>28.5</td><td>16</td><td colspan="5"></td></tr>
<tr><td>M</td><td>Cu</td><td>Zn</td><td>Ni</td><td colspan="2">Mn</td><td colspan="2">Fe</td><td rowspan="2">Solvent extraction using 20% LIX84 and 0.25M NH$_4$D2EHPA in kerosene</td><td rowspan="2">Cu extraction O:A=2:3, Zn Extraction O:A=4:3, Cu recovery 99.43% at 10.75 pH, Zn recovery 99.3% at 7.1pH</td><td rowspan="2">Copper and zinc pregnant electrolyte</td><td rowspan="2">Nathsarma 2002</td></tr>
<tr><td>C (g/l)</td><td>5.4</td><td>13.76</td><td>0.031</td><td colspan="2">0.00043</td><td colspan="2">0.00169</td></tr>
<tr><td rowspan="2">2.</td><td rowspan="2">Industrial brass dross</td><td>E</td><td>Zn</td><td>Cu</td><td colspan="5"></td><td rowspan="2">Ionic liquid oxidative leaching</td><td rowspan="2">Cu recovery 95%with 20%(HmimHSO4), T=40^{0}C t=2hrs,Zn recovery 100% with 20%(HmimHSO4), T=80^{0}C t=40 mins</td><td rowspan="2">Copper and zinc</td><td rowspan="2">Kiliçarslan and Saridede 2015</td></tr>
<tr><td>C (%w)</td><td>54.5</td><td>22.36</td><td colspan="5"></td></tr>
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<tr><td rowspan="2">3.</td><td rowspan="2">Brass Slag</td><td><table><tr><td>E</td><td>Zn</td><td>Cu</td><td>Fe</td><td>Al</td><td>Si</td><td>Ca</td></tr><tr><td>C (%w)</td><td>69</td><td>13</td><td>1.3</td><td>4.4</td><td>6</td><td>1.7</td></tr></table></td><td>Leaching with sulfuric acid</td><td>30%H_2SO_4,pH-3.5, E=59.0 ± 2.7 kJ mol-1</td><td>Spongy Cu, zinc sulfate crystals</td><td>Ahmed *et al.*,2016</td></tr>
<tr><td><table><tr><td>E</td><td>Cu</td><td>CuO</td><td>ZnO</td><td>PbO</td></tr><tr><td>C(kg)</td><td>6.3</td><td>14.4</td><td>11.35</td><td>1.33</td></tr></table></td><td>Hydrometallurgical treatment using acid or alkali leachant</td><td>Leachant: 6M HCl Solid:aqu=1:8, temp. 90^0C ,t=12 hrs ii)6.5M NH4OH,T=70^0C,t=3hrs</td><td>Copper salts and zinc salts</td><td>Basir and Rabah 1999</td></tr>
<tr><td>4.</td><td>Brass flue dust</td><td></td><td>vaporization and condensation</td><td>T=1100°C, reducing time of 90 min.</td><td>Zinc and zinc oxide</td><td>Saridede and Altuner 2007</td></tr>
<tr><td>5.</td><td>Industrial brass wastes, brass ash and flue dust</td><td><table><tr><td>E</td><td>Zn</td><td>Cu</td><td>Al</td><td>Ca</td><td>Cl</td><td>Na</td><td>S</td></tr><tr><td>Ash</td><td>53.9</td><td>22</td><td>3.4</td><td>5.8</td><td>0.3</td><td>0.3</td><td>12.1</td></tr><tr><td>Dust</td><td>81.8</td><td>1.1</td><td>0.2</td><td>0.3</td><td>3.8</td><td>1.2</td><td>1.2</td></tr></table></td><td>Combined pyro-hydrometallurgical treatment</td><td>leach parameters: 1 M H_2SO_4, 120 min, 60°C, 400 rpm stirring speed, and 1/10 solid liquid ratio. Recovery Zn 99.4% ,Cu 99%</td><td>Copper master alloy, metallic zinc</td><td>Kiliçarslan and Saridede 2015</td></tr>
<tr><td>6.</td><td>Brass filings</td><td><table><tr><td>E</td><td>Cu</td><td>Zn</td></tr><tr><td>C (%w)</td><td>34.1</td><td>16.1</td></tr></table></td><td>Acid leaching with an oxidizing agent</td><td>50% v/v HCl and 125 ml NaClO , t=4hrs, . Cu and Zn recovery 99.7%, 99%</td><td>Copper oxychloride and zinc hydroxide</td><td>Oliveira *et al.*, 2013</td></tr>
<tr><td rowspan="2">7.</td><td rowspan="2">Brass pickle liquor</td><td><table><tr><td>E</td><td>Zn</td><td>Cu</td><td>Cr</td><td>Fe</td><td>Ni</td></tr><tr><td>C (g/L)</td><td>30</td><td>35</td><td>0.03</td><td>0.75</td><td>0.03</td></tr></table></td><td>Solvent extraction using 30% LIX 984N in kerosene</td><td>copper extraction 99.9% at the O:A of 2:1 at 2.5 pH, Zn recovery 99% at pH 5.5 and O:A = 2:1</td><td>Copper and zinc oxide powder</td><td>Sinha *et al.*, 2012</td></tr>
<tr><td><table><tr><td>E</td><td>Zn</td><td>Cu</td><td>Cr</td><td>Fe</td><td>Ni</td></tr><tr><td>C (g/L)</td><td>25</td><td>35</td><td>1.1</td><td>0.2</td><td>0.01</td></tr></table></td><td>Solvent extraction using 30% Versatic acid and 20% Cyanex 272 in kerosene</td><td><table><tr><td></td><td colspan="2">Cu</td><td colspan="2">Zn</td></tr><tr><td>Extr.</td><td>pH</td><td>O:A</td><td>pH</td><td>O:A</td></tr><tr><td>Versatic acid</td><td>3.28 - 4.9</td><td>1.1:1</td><td>5.1 - 7</td><td>1.9:1</td></tr><tr><td>Cyanex 272</td><td>4.6</td><td>1.8:1</td><td>3.5</td><td>1.8:1</td></tr></table></td><td>Copper sulfate solution, zinc sulfate solution</td><td>Sinha *et al.*, 2016</td></tr>
</table>

E = Element, C = Composition

4.2 Solvent extraction of copper from chloride media

There is considerable interest in the extraction of copper and zinc from chloride media, since use of HCl is popular with processers in India. Low cost and ease of availability of HCl coupled with its rapid rate of tarnish removal from brass products contribute to extensive use of HCl as the pickling agent. Although, hydrometallurgical extraction of metals from sulfate media is more prevalent than from chloride media, chloride based leaching in hydrometallurgy is used for the recovery of metals from complex and low-grade bulk sulphidic ore concentrates that cannot be treated easily or economically by other means. HCl solutions used for etching printed circuit boards, hydrochloric acid based pickle liquors and many such instances are there where chloride solutions are extensively encountered.

There are opportunities to develop technologies for the extraction of metals from chloride media and apply them in practice for metal recovery and reclamation from chloride solutions. However, extraction from chloride leach solutions with high metal concentration and very low pH, poses problems related to compatibility of metal extractants because very low pH value renders many reagents unsuitable for such solutions.

4.2.1 Extraction of copper

Solvent extraction is the dominant hydrometallurgical process to recover copper from ores in an enriched form as well as secondary sources. Almost all extractants are used to extract copper from chloride media at appropriate pH range. However, selection of the extractant depends on the copper concentration and the chloride concentration.

Copper (II) cations are hydrated with six water molecules (Figure 4.2). The equatorial molecules are bound strongly to the central copper cation and are replaced by the chloride ion forming the monochloro complex (Equation 4.1). When the other strongly bound water molecules are replaced by chloride anions higher chlorocomplexes form (Equation 4.2-2.4).

Depending on the chloride concentration positive, neutral and negative chlorocomplexes are present in solution. Copper hydrometallurgy and extraction from chloride media is discussed in detail by Szymanowski (1996). He observed that as the chloride concentration increases, the reaction equilibria favour the formation of higher chlorocomplexes.

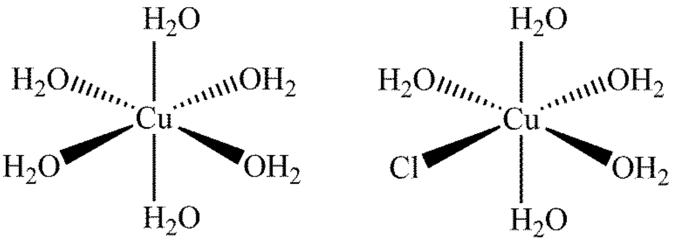

Fig. 4.2: Structure of hydrated copper cation (Szymanowski, 1996)

$$Cu(H_2O)_4^{2+} + Cl^- \rightarrow Cu(H_2O)_3Cl^+ + H_2O \quad 4.1$$

$$Cu(H_2O)_3Cl^+ + Cl^- \rightarrow Cu(H_2O)_2Cl_2 + H_2O \quad 4.2$$

$$Cu(H_2O)_2Cl_2 + Cl^- \rightarrow Cu(H_2O)Cl_3^- + H_2O \quad 4.3$$

$$Cu(H_2O)Cl_3^- + Cl^- \rightarrow CuCl_4^{2-} + H_2O \quad 4.4$$

4.2.2 Extraction using hydroxyoximes

Oxime reagents are strong copper extractants and commercially a number of them are available (Table 2.5). In chloride solutions, hydroxyoximes displace both water of hydration and coordinated chloride ions to form stable complexes. Copper extraction with hydroxyoximes are easier to accomplish from chloride solutions in comparison with sulfate solutions, the isotherms are steeper in chloride media which result in a more complete removal of metal ions. Extraction takes place at a lower pH value however; the presence of chlorocomplexes increases the $pH_{0.5}$. (Szymanowski, 1996)

In the last four decades, the chelating extractants LIX 70 (Lakshmanan and Lawson, 1975), LIX 64N (Christe *et al.*, 1976; Eccles *et al.*, 1976; Cognet *et al.*, 1977), LIX 63 (Sato *et al.*, 1987), LIX 65 N-HS (Zhou *et al.*,1988), LIX 54 (Cierpiszewski and Szymanowski, 2001), LIX 860N-IC and LIX 84-IC (Navaroo and Ruiz 2001; Ruiz *et al.*, 2017), LIX 84-I, LIX 612 N-LV, XI 04003, LIX 984N (Lu and Dreisinger, 2014) were used for copper extraction from chloride media.

Lakshmanan and Lawson (1975) used LIX 70 to extract copper from highly acidic chloride media and showed that extraction is readily achieved in presence of high concentration of chloride ions and is unaffected by the presence of Fe (III).

In the extraction of iron and copper from chloride and sulfate solutions using LIX 64N in kerosene, Eccles *et al.* (1976) reported that extraction was enhanced for both iron and copper in chloride media but separation of iron from copper is low in chloride media. Cognet (1977) used LIX 64N and compared copper extraction from chloride and sulfate solutions and reported that at the same pH copper extraction was higher in chloride solutions.

Christe *et al.* (1976) reported that LIX 64N extracts chloride anion which could be due to the presence of a minor component of LIX 63 in LIX 64N. LIX 63 extracts both iron and copper in the form of neutral chlorocomplexes that involves the chloride anion of the form $CuCl_2.HCl$ or $CuCl_2.2HCl$ at low pH values and extracts the metal ion directly at higher pH value. Extraction of copper from hydrochloric acid solutions in the pH range of 1-5 using LIX 63 was investigated by Sato *et al.* (1987). They used Electron Spin Resonance (ESR) technique for the measurement of copper (II) complexes formed and reported that extracted species vary with the aqueous phase pH.

Zhou *et al.* (1988) studied the effect of chloride concentration on the extraction of copper using LIX 65N-HS diluted in ESCAID 100 and found that extraction rates was maximum at an intermediate chloride concentration. They adopted an interfacial mechanism and postulated that both $CuCl^{+}$ and Cu^{2+} are involved in the complexation process.

Cierpiszewski and Szymanowski (2001) used the chelating extractant LIX 54 as well as the solvating ACORGA CLX-50 to extract copper from chloride solutions. They also used mixtures of these extractants and found that solvating agents had high ability for copper extraction and the extraction ability also depended on the chloride concentration.

Navaroo and Ruiz (2001) in their study on extraction of copper from chloride solutions using hydroxyoximes LIX 860N-IC and LIX 84-IC, reported that both the extractants extract the cationic complex $CuCl^{+}$. The presence of chloride in the aqueous solution has a deleterious effect on the extraction equilibria for both the extractants, particularly the ketoxime LIX 84-IC. The increase in chloride concentration decreased copper extraction due to formation of chlorocomplexes. This aspect was also observed earlier by Laxmanan and Lawson when using LIX 70. In general, as the chloride ion concentration increases, an efficient use of the extractant becomes more difficult (Ruiz *et al.*, 2017).

4.2.3 Extractants other than hydroxyoximes

Anionic extractants extract chlorocomplexes wherein all the hydrated water molecules are replaced by chloride ions. Miller and Fuerstenau (1970) used Aliquat 336 to extract copper from chloride solutions and reported that unhydrated complex copper ion is extracted. Sato *et al.* (1981) also used Aliquat 336 to study the correlation between the distribution coefficient and physicochemical properties of diluent. Copper extraction with trialkyl amines increases when the acidity of the aqueous phase and the chloride content increases (Szymanowski, 1996).

Devi and Mishra (2012) investigated extraction of copper from hydrochloric acid solutions using Cyanex reagents and reported that extraction efficiency for Cyanex 923 was higher than Cyanex 921 in chloride media. Copper extraction increased till a chloride concentration of 6.5 M and thereafter decreased.

Esters and amides of pyridine carboxylic acids are also used for copper extraction from concentrated chloride solutions. Commercial ACOROGA–CLX 50 by ZENECA has been used to recover copper from high tenor chloride solutions via solvation mechanism. Copper extracted depends on chloride concentration, the number and positions of the ester and amide groups, the extractant concentration, water activity and pH (Borowiak-Resterna and Szymanowski 2000). Due to its high selectivity for Cu (II) in comparison with Fe (II), Fe(III) and Zn(II) the extractant was used commercially (Szymanowski, 1996). Copper was extracted from sodium chloride solutions using a pyridine carboxylate ester, n-octyl-3-pyridine carboxylate by Soldenhoff (1987). Extraction mechanism was by solvation and was mainly dependent on the chloride concentration.

Copper extraction from chloride media from two families of thiourea derivatives, N-(thiocarbamoyl) benzamidine derivatives and N-benzoylthiourea derivatives was investigated by Aamrani *et al.* (1998). They reported that N-benzoylthioureas perform better than N-thiocarbomoyl benzamidines.

Hydrophobic pyridine ketoximes have been used to extract copper from chloride solutions (Wieszczycka *et al.*, 2009), chloride and sulfate solutions (Wieszczycka,*et al.*, 2012a) and ammonium chloride and hydrocholoric acid solutions (Wieszczycka *et al.*, 2012b). Wieszczycka and co investigators proposed that the ability to extract copper (II) depends on extractant structure, diluent and feed composition. Their results show that 2-Pyridyl ketone oximes are strong solvating extractants in comparison to amides of pyridine carboxylic acids and can extract copper even at low chloride concentrations. Similarly, 4-Pyridyl ketone oximes similar to esters of pyridine carboxylic acids are weaker extractants and degree of extraction increases with increase in chloride concentration. The extraction ability of pyridine ketoximes with branched alkyl chain towards copper (II) ions depends significantly on the position of oxime group in the pyridine ring (Parus *et al.,* 2015). However, they have a tendency to precipitate and transport hydrogen chloride to the organic phase which results in decreased extraction (Wieszczycka *et al.*, 2009).

Recently, Wojciechowska *et al.* (2017) synthesized pyridine extractants (oxime and ketones) and their quartenary pyridium salts for copper extraction from chloride solutions. They reported that 3-[1-(hydroxyimine) undecyl]-propyl pyridinium bromide could effectively extract copper from solutions obtained from chloride leaching of copper sulphides. The extractants with oxime group exhibited stronger extraction property than with the ketone group.

4.2.4 Mixed extractants

Extraction from chloride medium and change of the system from chloride to sulfate in the extraction-stripping process for subsequent electrowinning can be achieved using mixed extractants: a basic and a chelating reagent, TOA and LIX 54 (Kyuchoukov and Mihaylov, 1991), Alamine 336 and LIX 54 (Kyuchoukov and Mihaylov, 1993), solvating and chelating, ACORGA CLX-50 and LIX 860 (Fletcher *et al.*, 1991) or a bifunctional extractant Kelex 100 (Kyuchoukov and Kounev, 1994). Lu and Dreisinger (2013) recovered copper from copper sulphide concentrates by chloride leaching and cupric solvent extraction to transfer copper to sulfate electrowinning circuit and utilized the advantage of chloride leaching system using four hydroxyoximes LIX 84-I, LIX 984N, LIX 612N-LV, XI 04003.

4.3 Solvent extraction of zinc from chloride media

Solvent extraction is widely used for upgrading and purification of zinc streams. Around 30% of zinc produced in the world arises from recycling of secondary sources (Cole and Sole, 2003). Brass scrap and galvanising residue account for almost 70% of the recycled zinc. Pickle liquors are a source of zinc in chloride solutions. Chloride leaching is used for digesting sulphides and secondary materials. Typical SX processes for zinc extraction from chloride media are the Canmet process, the Cuprex process, the Zincex process, the Minemet process, and the Intec process. Zincex and the modified Zincex process originally used for the extraction of zinc from sulfate media are also suited for recovery of zinc from secondary sources such as zinc ash and brass ash (Koppiker, 2002). The modified Zincex process developed by Técnicas Reunidas (TR) is an adaptation of their Zincex process originally developed to extract zinc from impure chloride leach solutions.

The CENIM-LNETI process uses a low temperature pressure leach in an ammonium chloride solution followed by zinc extraction using D2EHPA modified with isodecanol (Cole and Sole, 2003). Zinclor process was developed by TR, for zinc recovery from chloride media for the treatment of pickle liquors and effluents from surface treatment plants (Frias *et al.*, 2002).

Cole and Sole (2003) and Deep and Carvalho (2008) have reviewed the industrial applications and extractants used for solvent extraction of zinc from different acidic media. Extraction of zinc using acidic, basic, solvating and mixed extractants from chloride solutions is reviewed by Jha *et al.* (2002). They concluded that a combination of two or more suitable extractants such as basic and acidic or basic and solvating can be used to improve extraction, stripping and the selectivity for the recovery of zinc from complex leach solutions.

4.3.1 Extractant types and effects

Over the last four decades investigators have preferred to use both basic and neutral extractants for zinc extraction from chloride solutions. However, selection of an extractant from chloride media depends largely on the zinc species formed in solution. Below 1M concentration the cationic specie Zn^{2+} is dominant and above 1M chloride concentration $ZnCl_4^{2-}$ and $ZnCl_3^{-}$ are formed which are extractable using secondary or tertiary amines by forming neutral chloride complexes (Cole and Sole, 2003).

Amongst the phosphoric group of extractants (TBP, DPPP, and DBBP) for zinc extraction from chloride solutions, TBP is the most widely studied extractant. Extraction follows the solvation mechanism. The oxygen of the phosphoryl group is responsible for the formation of co-ordination bond with metals (Jha *et al.*, 2002). Reports in the early years on the extraction of zinc from chloride solutions using extractants of the phosphoric group include TBP (Rice and Smith, 1975; Ritcey *et al.*, 1980; Ritcey *et al.*, 1982; Preston and du Preez, 1985; Preston and du Preez, 1986), TOPO (Preston and du Preez, 1986), DPPP (Nogueira and Cosmen 1983; Nogueira *et al.*, 1983) and DBBP (Lin, 1993; Alguacil *et al.*, 1999).

Algucil *et al.* (1992) reported Cyanex 302 to be a stronger extractant than D2EHPA and that zinc is extracted preferentially to Fe (III) particularly at low pH values which is an advantage over other organophosphorous reagents. Kirschling *et al.* (2001) studied the recovery of Zn (II) with TBP and CYANEX 923 from HCl solutions and reported that CYANEX 923 was a strong extractant and stripping efficiency of CYANEX 923 in three consecutive strips was below 20% even when hot water was used.

ACORGA ZNX-50 developed by ICI particularly to recover zinc from halide solutions. Dalton *et al.* (1992) used ACORGA ZNX-50 to recover the zinc from chloride-containing effluent streams and solutions produced by the chloride leaching of zinc-bearing wastes. The extractant extracted zinc forming neutral chlorocomplexes from solutions containing 4-8 molar chloride ions. Jakubiak and Szymanowski (1998) and Kyuchoukov *et al.* (1997), (1998) reported that the extraction of zinc from chloride solutions follows an ion exchange mechanism. These investigators also studied zinc extraction from chloride media followed by transfer of zinc to sulfate media using KELEX 100 to facilitate electrowinning of zinc.

With the objective to select an appropriate reagent for zinc extraction from spent pickling solutions, Regel *et al.* (2001) used TBP, CYANEX 921, CYANEX 923, and ALAMINE 336 as extractants. TBP was selected as a suitable extractant as it permitted effective extraction and stripping using water. Though CYANEX reagents and ALAMINE 336 extracted Zn (II) strongly but stripping was not effective with water. All the extractants extracted Fe (III). It was reported that CYANEX 302 could not be used for extraction of zinc from spent pickling hydrochloric acid liquors.

In an attempt to select the most appropriate extractant to recover zinc from spent pickling solutions from hot-dip galvanising plants, Cierpiszewski *et al.* (2002) used TBP and its mixtures with DEHPA, HOE F 2562, ALIQUAT 336, ALAMINE 304, ALAMINE 308, ALAMINE 310, ALAMINE 336, and CYANEX 301. TBP and HOE F 2562 were found to be the most suitable extractants as they could efficiently extract zinc from chloride solutions and could be easily stripped using water. However, ALAMINE 336 and ALIQUAT 336 induced the oxidation of Fe (II) to Fe (III), enhancing the co-extraction of iron with zinc.

Rozenblat *et al.* (2004) used TBP to recover zinc from pickling solutions with high concentration of 100 g/L zinc. Niemczewska *et al.* (2004) studied the extraction of zinc from HCl solution in a Lewis cell and reported the extraction of $ZnCl_2.2TBP$ and $H_2ZnCl_4.2TBP$ complexes. Regel-Rosocka *et al.* (2005) investigated DBBP as an extractant using Exxsol D 220/230 as a diluent and compared DBBP and TBP as extractants and reported that the effectiveness of DBBP was higher than TBP. The extraction ability of zinc chlorocomplexes from HCl solutions decreased with decreasing DBBP concentration.

Daud and Cattrall (1982a) reported the equilibrium constants for extraction of zinc from 1 and 6 M HCl solutions using methyltrioctyl ammonium and methyl tridecyl ammonium chloride in different diluents and compared the same using Aliquat 336. For different diluents used, the order of extraction was isobutyl methyl ketone > cyclohexane > *o*-xylene > chloroform. They also used the single drop technique to explain the mechanism of transfer of zinc into chloroform solutions using methyltrioctylammonium chloride and suggested that interfacial complexes are formed by fast ion-exchange reactions. Interfacial tension measurements showed that the interface was saturated with reagent over the range of concentrations studied (Daud and Cattrall, 1982b).

Thermodynamic analysis of zinc extraction from hydrochloride solutions using TOMAC in different organic diluents benzene, chlorobenzene, o-dichlorobenzene, toluene, m -xylene, nitrobenzene, carbon tetrachloride and 2, 2-dichloroethane is discussed by Sato *et al.* (1983). Further, they examined the heat change associated during the uptake of zinc using TOAHCl and TOMAC as extractants in various organic solvents and concluded that dependence of apparent molar heat change on the aqueous chloride concentration could be attributed to the change in the distribution of zinc (II) chloride species in the aqueous phase (Sato *et al.*, 1984).

Sayar *et al.* (2007) recovered zinc (3, 7, 15 g/L) from hydrochloric acid solutions using Alamine 336 with acid molarities up to 10 M/L and observed an increase in zinc extraction with increasing molarity. They developed model equations simulating metal extractability in terms of organic phase, Alamine volume content, aqueous phase acidic molarity and initial metal concentration. Lee and Nam (2009) used the data reported by Sayar *et al.* (2007) to identify the solvent extraction reaction mechanism and estimated the equilibrium constant considering the activity coefficients of solutes present in the aqueous phase using Bromley equation.

Parus *et al.* (2012) synthesized hydrophobic alkyl pyridyl ketoximes and studied the influence of chloride and zinc ion concentration on extraction. Maximum extraction was observed at 1.0–1.5 M chloride concentration. At higher chloride concentrations the complex-forming power of the extractant slowly decreased. Results obtained from lab scale experiments for zinc removal from acidic chloride solution using hydrophobic 3- pyridine ketoxmie, Wieszczycka (2013) reported that the extractant was efficient and highly selective to zinc extraction and can be used for zinc removal from real spent pickling solutions.Parus *et al.* (2013) used hydrophobic quaternary 3-pyridinium ketoximes and proposed that the Zn(II) extraction proceeded via an ion-exchange mechanism. They showed that at 4 M chloride concentration, regardless of the acidity of the aqueous chloride solutions and type of anions attached to pyridinium ring, extraction of Zn (II) increased with increasing length of the alkyl chain.

4.3.2 Mixed extractants and mixed solutes

Mixed extractants, solvating/acidic, basic/ acidic are also reported for zinc extraction from chloride media. Synergistic and antagonistic effects during extraction of Zn(II) with 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester and primary amine, N 1923 in n-heptane was studied by Han *et al.* (1991). Synergistic enhancement of zinc (II) extraction and formation of mixed complex $ZnX_2.(RH)_2$ have been reported with mixtures of Versatic 911 in Kelex 100 (Harrison *et al.,* 1976). Sekine *et al.* (1994) used mixed TBA- TOPO with 1-naphthoic acid diluted in chloroform, during the solvent extraction of Zn(II) from 0.1 mol /dm^3 NaCl solutions. Azizitorghabeh *et al.* (2017) reported the synergistic effect during separation of iron and zinc using D2EHPA and TBP and showed that these mixtures were more efficient than D2EHPA alone.

Both copper and zinc have also been extracted from chloride media using alkyl-8-hydroxyquinoline (Kyuchoukov, 2000), Kelex 100 (Bogacki *et al.,* 2000; Kyuchoukov and Zhivkova, 2000) and mixed extractants (Mishonov and Kyuchoukov, 1996; Kyuchoukov and Szymanowski, 2000; Resterna and Szymanowski 2000; Szymanowski and Kyuchoukov 2002; Pospiech and Changes 2015).

Copper, iron and zinc often co-exist in chloride leach solutions from industrial effluents. Pyridine ketoximes can extract copper, zinc and iron from single element solutions. However, when all the three ions are present it shows selectivity towards zinc. Recently Zhivkova (2017) used the bifunctional extractant KELEX 100 and proposed a stage wise method to separate copper, iron and zinc.

4.4 Summary of copper and zinc extraction from chloride media

Survey of the literature of copper and zinc extraction from chloride solutions indicates that while the chelating hydroxyoxime extractants are highly selective to copper extraction they are unable to extract higher chlorocomplexes. Thus, extraction using hydroxyoxime from high tenor of copper and high chloride concentrations tends to become uneconomical due to the formation of higher chlorocomplexes resulting in decreased extraction.

Selection of an extractant for zinc from chloride media depends on the zinc species formed in solution. Most of the work reported in literature using SX to selectively extract zinc from chloride solutions has focused on extracting zinc from secondary sources such as spent pickling solutions from hot-dip galvanising plants wherein iron is present. Co-extraction of Fe (III) from chloride solutions is an issue when using D2EHPA, TBP, and CYANEX 923 as extractants.

4.5 Experimental

4.5.1 Extraction

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) analysis was carried out to determine the different metals present in the pickle liquor to develop a strategy to extract and reclaim the major metal components copper and zinc. The chloride, sulfate and nitrate content in the pickle liquor were also determined by methods discussed in Chapter 3. Extraction was carried out in shake flasks at equal organic and aqueous volumes (100 ml each) on a rotary shaker at 30 ± 2^0C and 150 rpm. The organic phase for copper extraction consisted of extractant LIX 84-IC (7.5- 30% v/v) in kerosene as diluent while, for zinc extraction the organic phase was D2EHPA (5-15% v/v) in kerosene. During extraction experiments, the pH of the aqueous phase was controlled using 2N NaOH solution. The aqueous phase metal concentration was determined using AAS as discussed in Chapter 3.

4.5.2 Precipitation-Stripping

After extraction, the organic phase was separated from the aqueous phase and scrubbed with water. Stripping was also carried out in shake flasks using aqueous oxalic acid solutions at equal volume of organic and aqueous phase (100 ml each) on a rotary shaker at 30 ± 2^0C at 150 rpm. Oxalic acid concentration was varied from 0.3M to 1.5 M. Since stripping resulted in metal oxalate precipitation this mode of stripping is denoted as precipitation-stripping (PS). Post stripping the aqueous phase containing the precipitate was separated from the organic phase. The aqueous phase was centrifuged at 5000 rpm to separate the oxalate particles. Stripping was carried out in stages by using fresh acid in each stage. The organic phase was finally stripped with 1.5M sulfuric acid to recover any residual metal present and the stripped organic phase was again contacted with fresh pickle liquor in second cycle this procedure was repeated a number of times to evaluate the efficacy of extraction/stripping cycles and the reusability of the organic solvent.

The precipitates obtained from each stage were washed with ethanol to remove the adhering organic phase and finally washed with water. The oxalate precipitates were dried in an air oven at 60^0C for 1 h and weighed to determine the amount of copper and zinc recovered as oxalate and further calcined under controlled conditions in a tube furnace at a heating rate of 5^0C/min to obtain the respective metal oxide particles. After attaining the desired temperature, the material was soaked for three hours. Copper oxalate calcinations were carried out at 400^0C while zinc oxalate calcinations were performed at 440^0C.

4.5.3 Characterization of particles

Oxalate and oxide particles were characterized by X-Ray Diffraction (XRD) analysis. Infrared Spectroscopy analysis of the organic phase before and after extraction and as well as oxalate and oxide particles was carried out. Thermogravimetric Analysis (TGA) of the oxalates was performed at a heating rate of 20 °C/min in an oxygen atmosphere. • Energy-dispersive X-ray spectroscopy (EDX) analysis was performed to detect the metals present in the precipitates formed. Field Emission Scanning Electron Microscopy (FESEM) was used to study the morphology of the particles obtained. The Particle Size Distributions (PSD) of the oxalate particles was recorded. All the analysis was carried out as per standard operating procedures.

4.6 Results and Discussion

Metal extraction in multi-solute systems depends on the physicochemical properties and the nature of the metal species present in the solution; these factors influence the selection of metal extractants and design of the processing scheme. Spent pickle liquor used in this investigation had an initial pH value of 0.25. The chloride, sulfate, nitrate content and the initial metal composition determined by ICP analysis is shown in Table 4.3.

Table 4.3: Composition of brass pickle liquor

Component	Concentration (g/L)
Cu	20
Zn	12.6
Fe	0.131
Ni	0.1
Na	7.4
Ca	0.226
Mg	0.099
Al	0.118
Sn	0.124
Chlorides	10.968
Sulfates	0.009
Nitrates	<0.1mg/L
pH	0.25

4.6.1 Copper and zinc speciation in chloride media

Extraction of metals from solutions containing chloride ions is complex. Both zinc (II) and copper (II) can form various chlorocomplexes with the relative content dependent on the concentration of chloride ions in the aqueous phase. Equation 4.5 is the general expression for the formation of chlorocomplexes based on the chloride concentration in aqueous solutions (Bogacki *et al.,* 2000).

$$M^{2+} + nCl^{-} \rightarrow MCl_n^{2-n} \tag{4.5}$$

The stability constant (β_n) of the chlorocomplex is given by Equation 4.6

$$\beta_n = \frac{[MCl_n^{2-n}]}{[M^{2+}][Cl^-]^n}\ ,\ n = 1-4 \tag{4.6}$$

Figure 4.3 shows the chlorocomplexes of copper and zinc present in the pickle liquor. Theoretically it is possible to determine the percentage of species present in the aqueous solution based on the formation constants. The speciation of the pickle liquor having copper concentration 20 g/L (0.314M) and zinc concentration 12.6 g/L (0.192M) at varying chloride concentrations was evaluated using *Visual MINTEQ 3.1* operating platform.

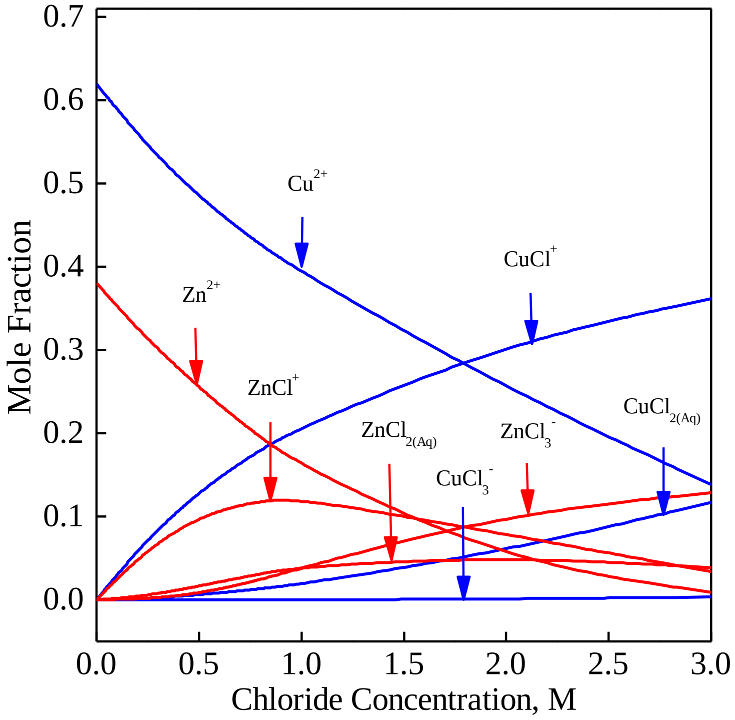

Fig.4.3: Speciation diagram of copper and zinc in pickle liquor as a function of chloride concentration

At initial chloride concentration of 10.968g/L (0.308M) both copper and zinc exist largely as the bivalent cationic species (Cu^{2+}, Zn^{2+}) followed by the monovalent specie ($CuCl^+$ and $ZnCl^+$) and a very small fraction as the neutral specie $CuCl_2$ and $ZnCl_2$. The monovalent specie ($CuCl^+$) is the first chlorocomplex formed in solutions containing low chloride concentrations (~1M) and is capable of cation exchange (Lawson, 1975), higher chloride concentrations in solutions lead to formation of trivalent and higher chlorocomplexes of the metals. Zinc chlorocomplexes are more stable than copper as observed from their higher stability constants (Bogacki *et al.*, 2000).

4.6.2 Strategy of separation

Speciation diagram revealed that both copper and zinc exist predominantly as the bivalent cationic specie, the monovalent chloride specie of copper and zinc is also present in measurable amount in the spent pickle liquor. Under these conditions hydroxyoximes will be appropriate reagents particularly LIX 84-I that selectively extracts copper over other metal ions with maximum extraction at pH 2-2.5 (MCT Red book 1998).

Selection of an extractant for zinc from chloride media depends largely on the zinc specie formed in solution as well as the physicochemical properties of the solution. Below 1M concentration the cationic specie Zn^{2+} is dominant which is extractable by LIX 84 and acidic extractants D2EHPA, and CYANEX 302. The speciation diagram (Figure 4.3) shows that dominant zinc specie present in the pickle liquor was $Zn^{2+}$and $ZnCl^{+}$. While LIX 84-IC could be used for extraction but it would require substantial pH balancing since Zn^{2+} is significantly extracted only above pH 5. Moreover, maintaining same extractant in the process has the possibility of impurity carryover from zinc to copper stream and vice-versa. Hence, it is prudent to use different extractants for copper and zinc recovery and keep both the streams separate. This strategy has been adopted by Sinha *et al.* (2012) for metal recovery from sulfate media from model brass pickle liquor

The extraction cycle was designed to initially selectively extract copper using hydroxyoxime LIX 84-IC a concentrated form of LIX 84-I with a molar concentration of active component 2.2 M in comparison to 1.5M of LIX 84-I. After copper extraction, the pH of the pickle liquor was around 2.5. Since, D2EHPA extracts zinc in the pH range 2-2.5 (Deep and Carvalaho, 2008) pickle liquor could be directly subjected to zinc extraction using D2EHPA. Extraction of zinc with D2EHPA would require very little pH adjustment and a single stage zinc transfer could be achieved by using a high extractant concentration (Cole and Sole, 2003).

4.6.3 Extraction of copper from spent pickle liquor using LIX 84-IC

Extraction of copper using hydroxyoximes is represented by Equation 4.7.

$$Cu^{2+} + 2RH \leftrightarrow CuR_2 + 2H^{+} \tag{4.7}$$

Extraction by chelation is an acid-base reaction wherein the oxime molecules donate protons in exchange for copper ions and the reaction takes place at the oil-water interface. The unpaired d orbital of copper is primarily responsible for complexation through electron pair of O and N atoms of the extractant molecules (Figure 4.4). The strength and the selectivity for Cu^{2+} over other base-metal cations arise in part from the pseudo-macrocyclic structure of the copper complex (Jun et al., 2016).

The strong inter-ligand H-bonds between the oxime hydrogen and the phenolic oxygen atoms define a planar donor set and a cavity which is a particularly good fit for Cu(II) (Wilson et al., 2014). However, the formation of chlorocomplexes can affect the extraction of copper with hydroxyoximes in two ways; by reducing the concentration of the bivalent Cu^{2+} cationic species and by the possibility of extracting the monovalent cationic complex$CuCl^{+}$, or even the neutral $CuCl_2$ complex (Navaroo and Ruiz, 2001).

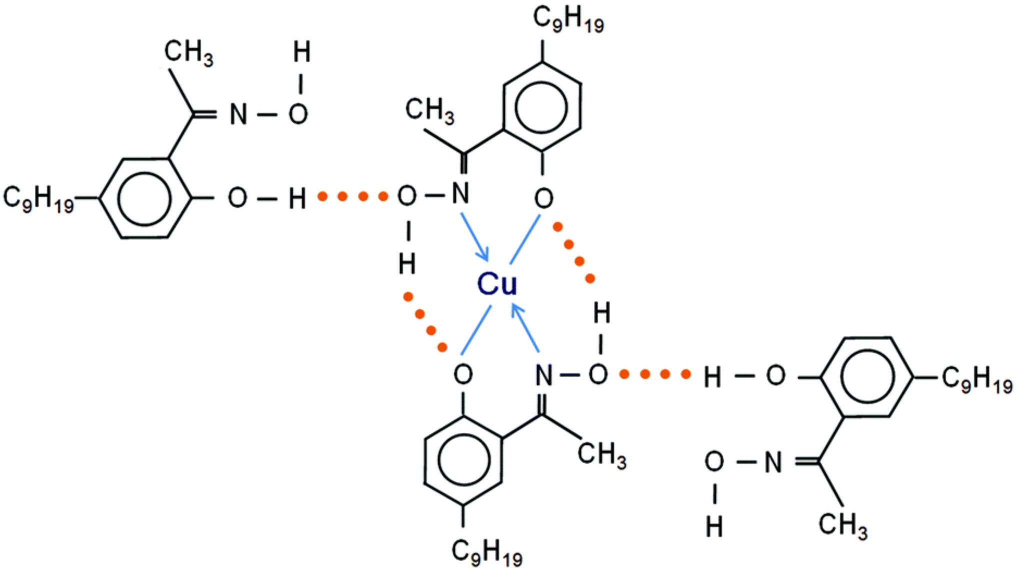

Fig. 4.4: Structure of copper-LIX 84-IC complex (Jun et al., 2016)

Most of the investigations on extraction of metals have been performed under experimental conditions that are deemed to be ideal, considering single metal in very dilute concentration, with extractant concentrations in far excess than stoichiometric requirements. However, in reality situation is quite different. The extraction behaviour, the stoichiometric requirement and the presence of other metals all influence the extraction of metals. In the present study the industrial pickle liquor was used and metal extraction equilibria was determined under prevailing conditions.

4.6.4 Effect of extractant concentration and maximum loading capacity

Copper extraction was carried out using LIX 84-IC at concentrations ranging from 7.5% (v/v) to 30% (v/v). An increase in the extractant concentration resulted in an increase in copper extraction (Figure 4.5) and at 30% (v/v) extractant concentration, 98.8% of initial copper present was extracted at an equilibrium pH of 2.5. Copper remaining unextracted in the pickle liquor was 240 mg/L. It was also observed that of the 131 mg/L iron initially present 77% was extracted. It is well known that Fe^{3+} is moderately extracted by LIX 84-IC in the pH range 2 to 2.5 (MCT Redbook 2007). Other than copper and iron, none of the other metals initially present in the liquor were extracted under the operating conditions.

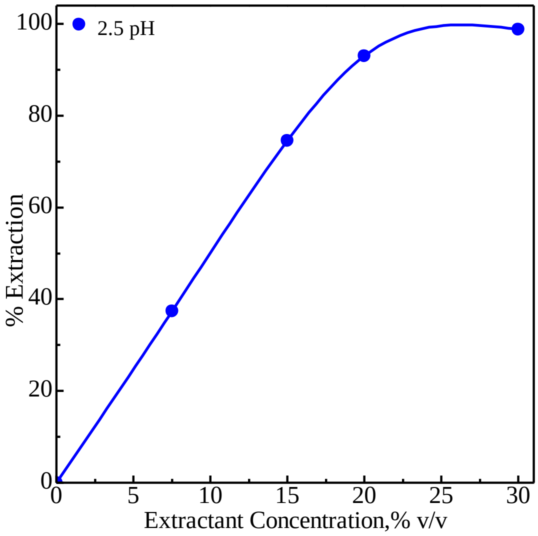

Fig.4.5:Effect of LIX 84-IC concentration on copper extraction (O:A=1)

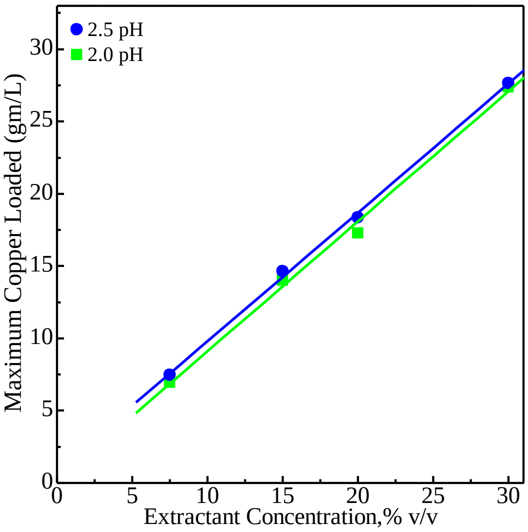

Fig.4.6: Maximum loading capacity of LIX 84-IC (O:A=1)

The maximum loading capacity of LIX 84-IC at an equilibrium pH value of 2 and 2.5 were determined from the extraction data. At an equilibrium pH vaule of 2 maximum loading capacity is 0.9 g/L per 1% (v/v) of extractant as observed from the slope of the linear plot, maximum copper extracted vs extractant concentration as shown in Figure 4.6. This is higher than the value of 0.7 reported for copper extraction from hydrochloride solutions at 2 pH using LIX 84-IC (Navaroo and Ruiz, 2001) and 0.74 for copper removal from electroplating rinse bath solutions with high chloride concentrations in the equilibrium pH range of 1.7-2.1 using LIX 984N-C (Kul and Çetinkaya, 2009).

4.6.5 Effect of equilibrium pH

The effect of pH on extraction for LIX 84-IC concentration ranging from 15% (v/v) to 30% (v/v) is shown in Figure 4.7. An increase in extractant concentration, results in an increase in the percentage extraction and a decrease in $pH_{0.5}$ value. The plots of distribution coefficient vs equilibrium pH (Figure 4.8) is linear at all extractant concentrations, but the slope values are considerably lower than the theoretical value of 2, which is expected if the mechanism of extraction is exclusively governed by Equation 4.7. Slope value of 2 in the plot of log D vs pH indicates binding of two oxime molecules with a single Cu^{2+} ion. Slope value of two is observed under ideal conditions**,** when the concentration of extractant is in considerable excess to that of the metal ion **(**Lakshmanan and Lawson, 1975). Reduction in slope values can also occur due to the transfer of the monovalent ions ($CuCl^{+}$) along with the bivalent ions (Cu^{2+}). Navaroo and Ruiz (2001) reported that low pH value, $CuCl^{+}$competes with Cu^{2+} whereas at higher pH values only Cu^{2+} is extracted.

Further, they showed that LIX 860N-IC and to a lesser extent LIX 84-IC, extract $CuCl^{+}$. Earlier, LIX 63 was shown to transfer chlorocomplexes to organic phase. Lakshmanan and Lawson (1975) reported that LIX 64N and LIX 70 do not transfer $CuCl^{+}$ to the organic phase. The slope of log D vs pH obtained, points to the plausibility that the mechanism of extraction is perhaps not governed exclusively by Equation 4.7 leaving scope for the transfer of $CuCl^{+}$to the oil phase or being adsorbed at the interface after bonding resulting in slope value markedly less than 2.

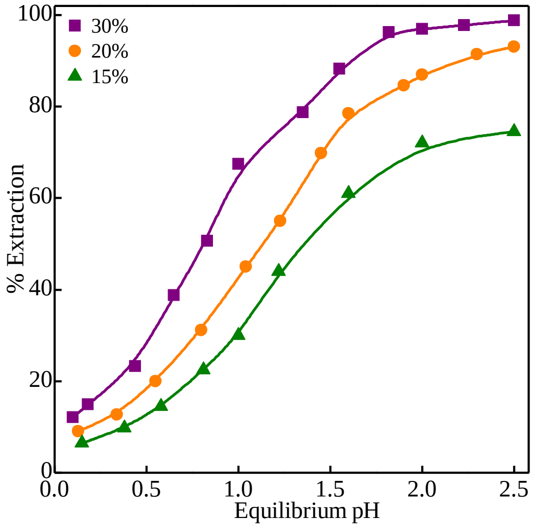

Fig. 4.7: Effect of equilibrium pH on copper extraction at varying extractant concentrations (O:A=1)

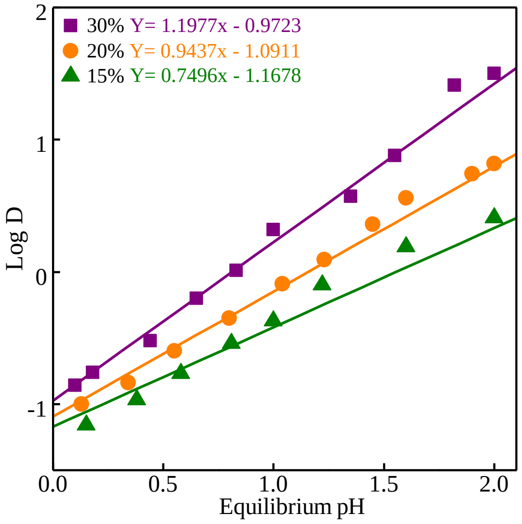

Fig.4.8: Log D vs Equilibrium pH at varying extractant concentrations (O:A=1)

In such a situation less than two hydroxyoxime molecules bind with the copper ions, and consequently would lead to considerably greater extent of copper extraction. However, there is no convincing evidence to suggest that the decline in slope values is due to the transfer of $CuCl^+$except that fairly large amount of copper was extracted. Zhou *et al.* (1988) in their study on extraction of copper using LIX 65N-HS explained the extraction of $CuCl^+$ by two possible mechanisms.

Mechanism (1) $$CuCl_i^+ + RH_{ad} \leftrightarrow CuRCl_{ad} + H_i^+ \quad (4.8)$$

$$CuRCl_{ad} + RH_i \leftrightarrow CuR_{2ad} + H_i^+ + Cl_i^- \quad (4.9)$$

Mechanism (2) $$CuCl_i^+ + RH_{ad} \leftrightarrow CuR_{ad}^+ + H_i^+ + Cl_i^- \quad (4.10)$$

$$CuR_{ad}^+ + RH_i \leftrightarrow CuR_{2ad} + H_i^+ \quad (4.11)$$

Although the two mechanisms primarily differ in their first steps, they eventually lead to the formation of CuR_2 complex.

4.6.6 Study of copper complexation with LIX 84-IC using IR Spectroscopy

The complexation of copper with LIX 84-IC has been investigated by numerous investigators by IR spectroscopy (Komasawa and Otake, 1983; Buketova, 2008). The infrared spectra for oxime in kerosene (organic phase), as well as the maximum copper loaded organic phase with extractant concentrations ranging from 7.5% (v/v) to 30% (v/v) are shown in Figure 4.9.

The band due to N-OH monomeric group and the monomer/dimer band were observed at ~3593 cm^{-1} and ~ 3375 cm^{-1} respectively. The bands associated with stretching vibrations of the C–H bonds in CH_2 and CH_3 groups are in the range of 2960-2850 cm^{-1}. The absorption bands at 1585.53 cm^{-1} and 1620.25 cm^{-1} are assigned to C=N stretching vibrations and at 1494.8 and 1460.1 cm^{-1} assigned to -C=C- stretching vibrations. The absorption band of C-O-H attached to the phenolic structure is at 1383 cm^{-1} and that assigned to nitrogen-oxygen stretching vibrations is observed at 1024 cm^{-1}.

The IR spectrum of LIX84-IC loaded with copper shows absorption band at 1610.61 cm^{-1} assigned to C=N-Cu (II) stretching vibrations and at 1402.96 cm^{-1} assigned to the Cu(II) complex (Inda *et al.,* 2017). A shift in absorption band at 1377.2 cm^{-1} indicates C-O-H whereas stretching vibration, C-O-Cu (II) coordination bond is at 1317.42 cm^{-1}. The absorption band at 1030.02 cm^{-1} is assigned to N-O stretching vibrations.

The maximum copper loaded organic phase at all oxime concentrations studied, show absence of the monomer/dimer peak and peak shift from ~3593 cm^{-1} to ~3616 cm^{-1} corresponding to the monomeric group of the oxime, thereby, indicating that both monomeric and dimeric groups are involved in the complexation process.

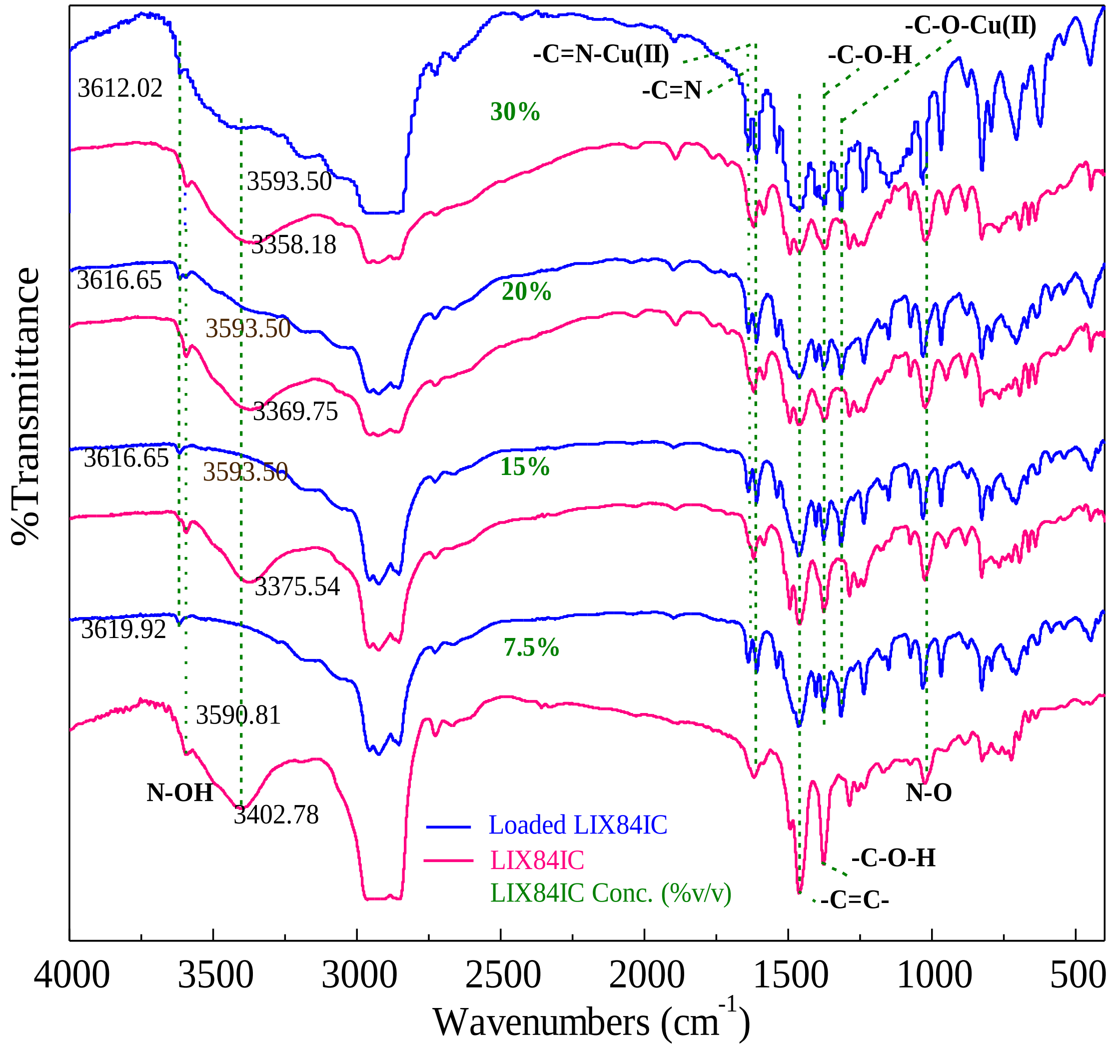

Fig.4.9: FTIR spectra of LIX 84-IC in kerosene and copper loaded organic phase at varying LIX 84-IC concentrations

Szymanowski (1993) also reported that in the IR spectra of 2- hydroxyl 5-alkylbenzaldehyde oxime the monomeric N-OH group manifests at 3580 cm^{-1} and the band at 3420 cm^{-1} is for the associated species and similar values were also observed for other oximes. This finding was corroborated by Albrecht *et al.* (2008) in their study on oximes and clusters by supersonic jet spectroscopy using IR direct absorption and Raman Scattering techniques and reported that for oxime the monomer peaks were at 3657 cm^{-1} and monomer/dimer peaks at 3364 cm^{-1}. This unfolds a very complex picture of molecular association and bonding in chloride media between hydroxyoxime and the copper ions with adsorbed complexes and the two ionic species of copper binding with monomeric, dimeric oximes.

4.6.7 Extraction of zinc using D2EHPA

The pickle liquor after copper extraction contained 12.6 g/L zinc, 240 mg/L copper, 47 mg/L iron along with the other metals initially present as listed in Table 4.3. The pickle liquor was further contacted with an organic phase containing 5-15% (v/v) D2EHPA at equal organic to aqueous ratio. It is observed that at pH 2, using 5% (v/v) extractant, 47.6 % zinc was extracted. Increasing the extractant concentration from 5% (v/v) to 10% (v/v) resulted in an increase in extraction to 73%. Further increase in concentration to 15% (v/v) D2EHPA resulted in 98.25% of zinc was extracted. The iron present was extracted quantitatively. Out of the 240 mg/L copper present 99.99% copper was also extracted resulting in 5 mg/L of copper remaining unextracted in the pickle liquor. None of the other metals present in the pickle liquor were extracted under these conditions. Zinc extraction isotherm using 15% (v/v) D2EHPA is shown in Figure 4.10. The maximum loading capacity of zinc using 15% (v/v) D2EHPA at an equilibrium pH of 2 was 14.38 g/L.

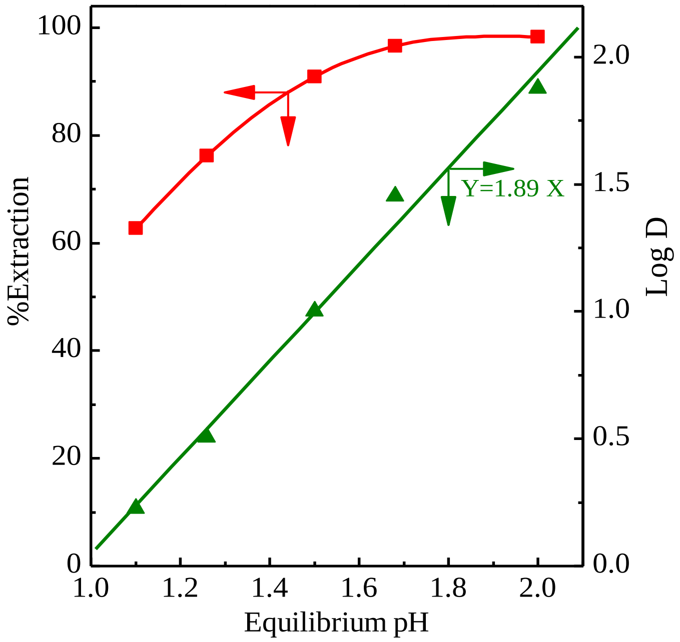

Fig.4.10: Zinc extraction isotherm (D2EHPA 15% (v/v), O:A=1) and log D vs Equilibrium pH

Zinc extraction from chloride media using D2EHPA is well investigated by Li *et al.* (1986). They postulated the extraction equilibria according to Equation 4.12 and 4.13.

$$2HR \leftrightarrow H_2R_2 \tag{4.12}$$

$$Zn^{2+} + (1+x)H_2R_2 = ZnR_2.x\,HR + 2H^+ \tag{4.13}$$

D2EHPA has a strong tendency to form a dimer in organic solutions and subsequent reaction with zinc leads to the formation of Zn complex where x is the number of HR molecules complexed with ZnR_2 , these investigators reported the value of x =1. The effect of dimerization of D2EHPA is apparent only at low metal ion concentration, dimerization effects are eliminated at high metal concentration and extraction occurs according to Equation 4.14 leading to formation of ZnR_2 as extractable species (Ritcey and Ashbrook, 1979).

$$Zn^{2+} + nHR = ZnR_2 + 2H^+ \tag{4.14}$$

The number of extractant molecules participating in the extraction process was determined by the plot of Log D vs pH. A slope value of 1.89 indicates two extractant molecules participating in the complexation process indicating that at high zinc loading the dimerization effect is negligible and the extracted specie is ZnR_2.

The slope analysis technique is generally used when working with low metal concentrations so that the amount of zinc extracted is substantially lower than the initial extractant concentration. Hence, the concentration of free extractant at equilibrium will be nearly equal to the initial concentration. Since zinc concentration in the pickle liquor was high it is unlikely that the free extractant concentration at equilibrium will be equal to the initial extractant concentration. On the contrary it is likely that the extractant is saturated with zinc and there is little or no free extractant after equilibrium. The IR results were testimony to this statement.

4.6.8 Study of zinc complexation with D2EHPA using IR Spectroscopy

The complexation of zinc with D2EHPA in the organic phase was determined by comparing the IR spectra of the extractant in kerosene and the metal loaded organic phase (Figure 4.11). The FTIR spectra of 15% (v/v) D2EHPA in kerosene shows the presence of the main bonds P=O, P –O–C, P–O –H and OH. The characteristic P=O stretching band is at 1232.5 cm^{-1}, P-O-H at 1033.87 cm^{-1}, P-C band at ~ 887 cm^{-1}, OH band at 1655 cm^{-1}. The stretching vibrations of CH bands in CH_2 and CH_3 are observed at 2956.97 cm^{-1} and 2856.67 cm^{-1}.

The bands at 1464 cm^{-1} and 1379.14 cm^{-1} are associated with bending vibrations of P-O bonds.

The IR of loaded organic phase shows that when D2EHPA interacts with zinc, the phosphoryl bond (P=O) is highly affected. The P = O band shift from 1232.5 cm^{-1} to 1201.69 cm^{-1} shows co-ordination of D2EHPA with zinc forming the complex. The *v*(P=O) bands, at 1234 cm^{-1} and 1206 cm^{-1}, correspond to the free D2EHPA molecules and the D2EHPA/Zn complex, respectively. The absence of P=O bond at 1234 and the sharp intensity band at 1206 cm^{-1}confirm that there is no free extractant and all is bound to zinc in the D2EHPA/Zn complex. The IR spectra for zinc extraction using 5 % (v/v) and 10 % (v/v) also shows the absence of P=O bond at 1234 cm^{-1}indicating an absence of free extractant. However, the P=O bonds for the D2EHPA/Zn complex were observed at 1191 cm^{-1} and 1197 cm^{-1} respectively.

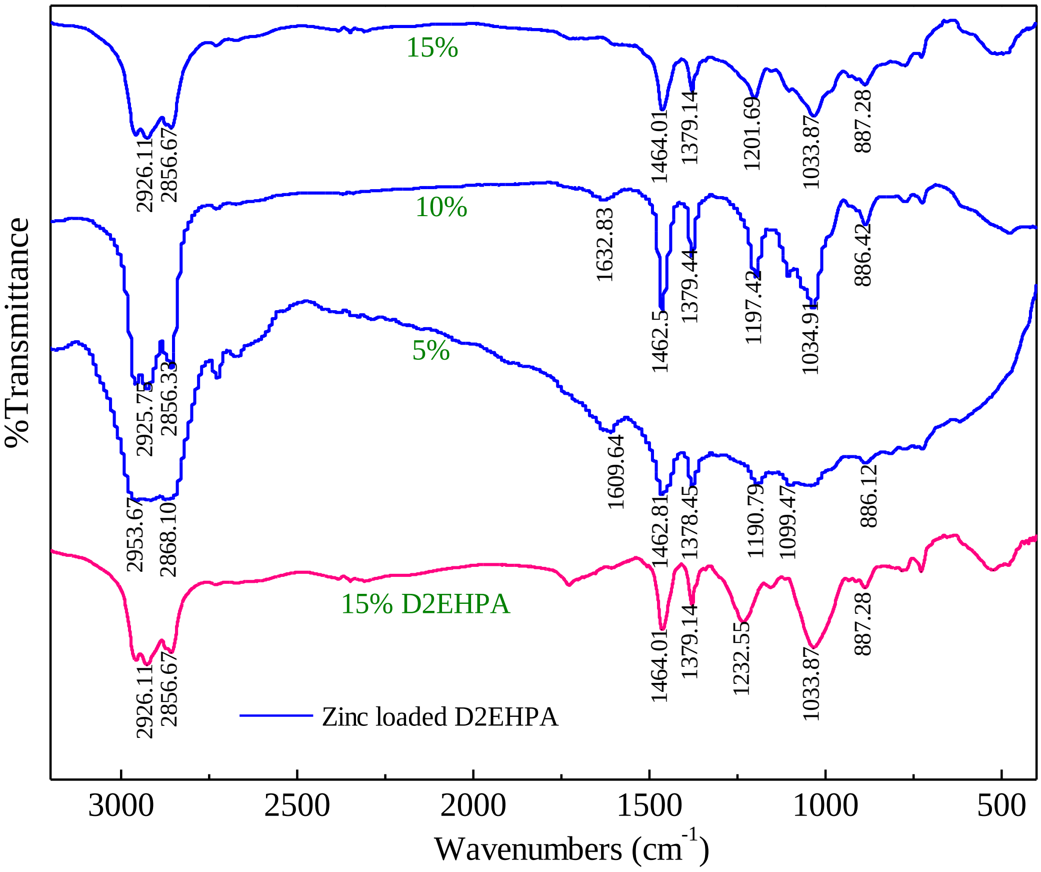

Fig. 4.11: FTIR spectra of 15% (v/v) D2EHPA in kerosene and zinc loaded organic phase at varying D2EHPA concentrations

Interaction between zinc and D2EHPA has been studied by Sainz-Diaz *et al.* (1996). They modelled this interaction in terms of two different molecular arrangements arising out of (1)

PO_2 anion of the Zn/(D2EHPA)$_2$ complex and (2) the P=O bond co-ordinated with the Zn atom of the salt (Figure 4.12). Based on their studies on extraction of zinc, nickel, and copper with D2EHPA they identified the band at 1197 cm^{-1}and attributed it to Zn/(D2EHPA)$_2$ complex resulting from a stoichiometric ratio of 1:2 between zinc and D2EHPA and band at 1202 cm^{-1} as an overlap of P=O of both the of phosphoryl bonds.

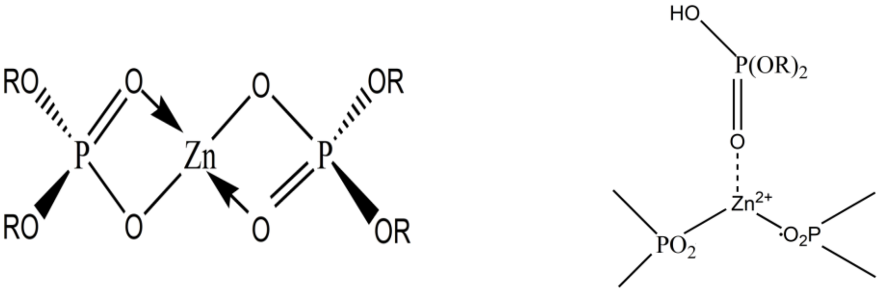

Fig. 4.12: Interactions between the phosphoryl groups and zinc atom in the Zn/D2EHPA complex (Sainz-Daiz *et al.*, 1996)

FTIR studies carried out in this investigation using 10% (v/v) D2EHPA, show the PO_2 anion of the Zn/(D2EHPA)$_2$ complex at 1197 cm^{-1}. Under these conditions 73 % zinc was extracted and the ratio of zinc to D2EHPA in the oil phase was 1:2.06 which is in line with the observation of Sainz-Daiz and co-workers. However, while using 5% (v/v) and 15% (v/v) extractant concentration the P=O bond was observed at 1190 cm^{-1} and 1206 cm^{-1} where the stoichiometric ratios were 1.6 and 2.2 respectively.

4.6.9 Precipitation - Stripping of copper and zinc from loaded organic phase

It is a common practice in extraction from chloride media to scrub the oil phase prior to stripping of metal values to remove chloride ions adsorbed at interface. Kyuchoukov and Szymanowski (2000) reported that when hydroxyoxime is used as a chelating agent, water can be used for scrubbing without any pH adjustment. The metal loaded organic phase was scrubbed with distilled water to remove the adhering chloride ions prior to precipitation-stripping.

Precipitation - stripping of copper from the organic phase involves a reaction between the loaded organic phase with an aqueous solution of oxalic acid. The acid dissociates into hydrogen ions and oxalate anions in the aqueous phase and acts both as a stripping and precipitating agent. Copper ion is released from the copper-oxime complex at the organic aqueous interface by exchange with H^+ ions. The Cu^{2+} cation transfers to the aqueous phase where it undergoes a second reaction with the oxalate anion in the vicinity of the interface to form copper oxalate precipitate.

$$CuR_2 \;+\; 2H^+ \;\rightarrow\; Cu^{2+} \;+\; 2HR \tag{4.15}$$

$$Cu^{2+} \;+\; C_2O_4^{2-} \;\rightarrow\; CuC_2O_4 \tag{4.16}$$

Overall rate of stripping is controlled by the diffusion of the metal complex from the bulk of the organic to the liquid-liquid interface (Konishi *et al.*, 1993). The driving force for mass transfer is high when the organic phase metal concentration is high. Stripping is much faster at high concentration of metal complex in organic phase. The faster rate at which metal ions are supplied to the aqueous solution combined with high stirring, results in production of finer oxalate particles. This is caused by the fast nucleation under the conditions where the aqueous phase copper concentration rises more rapidly to the threshold concentration at which nucleation can occur (Konishi *et al.*, 1998).

4.6.10 Precipitation using oxalic acid: Theoretical considerations

Oxalic acid, is a weak diprotic acid, it dissociates in a stepwise manner in solution. It dissociates into hydrogen ions and oxalate anions depending on the solution pH.

$$H_2C_2O_4 = H^+ + \;HC_2O_4{}^- \tag{4.17}$$

$$HC_2O_4 = H^+ + \;C_2O_4{}^{2-} \tag{4.18}$$

The speciation diagram (Figure 4.13) for 1M oxalic acid was construed as a function of pH. In a solution of oxalic acid, molecules of oxalic acid and its ions $HC_2O_4^-$ and $C_2O_4^{2-}$ co-exist in equilibrium.

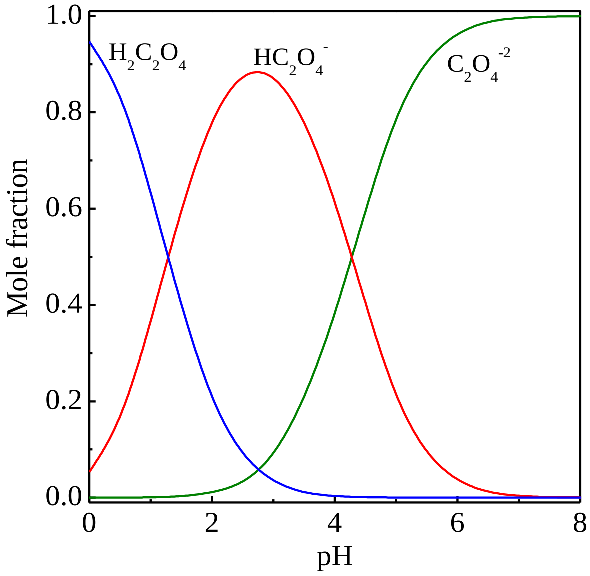

Fig.4.13: Distribution of oxalic acid species

As shown in Figure 4.13, in strong acidic solutions pH< 2, $C_2O_4^{2-}$ concentration is negligible and the dominant species is $C_2O_4^-$. At pH values > 3 complete ionisation is there and both $C_2O_4^{2-}$ and $HC_2O_4^-$ are formed. $C_2O_4^{2-}$ concentration is high in alkaline solutions and low in acidic solutions (Zouaoui *et al.*, 1999). The monoprotonated species $HC_2O_4^-$ dominates at intermediate pH values.

The equilibrium constant for Equation (4.17) and (4.18) are represented as K_1 and K_2 respectively. The oxalate species can be expressed as

$$[C_2O_4{}^-] = \alpha_{C_2O_4}A_T \tag{4.19}$$

The concentration of the complexing $[C_2O_4{}^-]$ ions will be determined by the pH,

$$[C_2O_4{}^{2-}] = [1 + \frac{H^+}{K_1} + \frac{[H^+]^2}{K_1K_2}]A_T \tag{4.20}$$

Where, $A_T = H_2C_2O_4 + HC_2O_4 + C_2O_4{}^{2-}$ is the total concentration of the oxalates and $\alpha_{C_2O_4}$ is the ionisation fraction of oxalate anion $C_2O_4{}^{2-}$. Introducing the equilibrium constants K_1 and K_2 (Table 4.4) and total concentration A_T, gives the concentration of oxalate species ($C_2O_4{}^{2-}$) at different pH values.

Table 4.4: Equilibrium constants of formation reactions of copper oxalate and zinc oxalate complexes.

Equilibrium reactions	**Log of constant**	**Reference**
$HC_2O_4 = H^+ + C_2O_4{}^-$	$K_1 = -4.266$	Martell and Smith, 1977
$H_2C_2O_4 = H^+ + HC_2O_4{}^-$	$K_2 = -1.252$	
$CuC_2O_{4(s)} = Cu^{2+} + C_2O_4{}^{2-}$	$K_{SP} = -9.35$	Lide, 2004
$Cu^{2+} + C_2O_4{}^{2-} = CuC_2O_{4\ (aq)}$	$\beta_1 = 6.23$	Martell and Smith, 1977
$Cu^{2+} + 2C_2O_4{}^{2-} = Cu(C_2O_4)_2^{2-}$	$\beta_2 = 10.27$	
$Cu^{2+} + HC_2O_4{}^{2-} = Cu(HC_2O_4)^+$	$\beta_3 = 7.32$	
$ZnC_2O_{4(s)} = Zn^{2+} + C_2O_4{}^{2-}$	$K_{SP} = -8.86$	Lide, 2004
$Zn^{2+} + C_2O_4{}^{2-} = ZnC_2O_{4\ (aq)}$	$\beta_1 = 4.87$	Martell and Smith, 1977
$Zn^{2+} + 2C_2O_4{}^{2-} = Zn(C_2O_4)_2^{2-}$	$\beta_2 = 7.65$	
$Zn^{2+} + HC_2O_4{}^{2-} = Zn(HC_2O_4)^+$	$\beta_3 = 6.44$	
$Zn^{2+} + 2HC_2O_4{}^{2-} = Zn(HC_2O_4)_2$	$\beta_4 = 12.32$	

4.6.11 Precipitation-stripping of copper from LIX 84-IC: Theoretical aspects

The overall stripping and precipitation of copper with oxalic acid can be represented by Equation 4.21.

$$CuR_2 + H_2C_2O_4 \rightarrow CuC_2O_4 + 2RH \tag{4.21}$$

The oxalate ion gives complex ions with many cations with some neutral complexes of $CuC_2O_{4_{(s)}}$ with certain solubility. This represents the concentration of the metal not included in the oxalate precipitate, i.e. present in the solution based on the solubility. The solubility equilibrium for copper- oxalic acid system can be expressed as,

$$CuC_2O_{4_{(s)}} = Cu^{2+} + C_2{O_4}^{2-} \tag{4.22}$$

taking logarithm and rearranging gives

$$log\ [Cu^{2+}] = log\ K_{SP} - log\ C_2{O_4}^{2-} \tag{4.23}$$

Substituting the value of $C_2{O_4}^{2-}$ and K_{SP} results in Cu^{2+} concentration equilibrated with solid $CuC_2O_{4_{(s)}}$. Figure 4.14a shows the solubility curve, $CuC_2O_{4(S)}$ as a function of pH. Besides the solubility equilibrium, Cu^{2+} complexes with oxalate anion forming various soluble species $CuC_2O_{4\ (aq)}$, $Cu(C_2O_4)_2^{2-}$, $Cu(HC_2O_4)^+$. Since the domain in the current investigation is acidic the hydroxide species are neglected. McAuley and Nancollas (1965) reported that copper oxalate has appreciable solubility in the presence of excess oxalate ions due to the formation of increasing quantities of $(Cu(C_2O_4)_2)^{2-}$.

Oxalate anion reacts with Cu^{2+} cation in aqueous solution to form successively two soluble complexes represented by the equation (4.24) and (4.25). The complexes are characterized by their stability constants β_1 and β_2 respectively.

$$Cu^{2+} + C_2{O_4}^{2-} = CuC_2O_{4\ (aq)} \tag{4.24}$$

$$Cu^{2+} + 2C_2{O_4}^{2-} = Cu(C_2O_4)_2^{2-} \tag{4.25}$$

$$\beta_1 = \frac{[CuC_2O_4\ ]}{[Cu^{2+}][C_2{O_4}^{2-}]} \qquad \beta_2 = \frac{[Cu(C_2O_4)_2^{2-}}{[Cu^{2+}][C_2{O_4}^{2-}]^2} \tag{4.26}$$

Rearranging and taking logarithm of equation (4.24) and (4.25) results in

$$log\ CuC_2O_4\ _{(aq)} = \ log\ Cu^{2+} + \log\beta_1 \ + log\ C_2O_4{}^{2-} \qquad (4.27)$$

$$log\ Cu(C_2O_4)_2^{2-} = \ log\ Cu^{2+} + \log\beta_2 \ + 2log\ C_2O_4{}^{2-} \qquad (4.28)$$

Introducing the values of β_1 and β_2, the concentration of $CuC_2O_4\ _{(aq)}$ and $Cu(C_2O_4)_2^{2-}$ species are obtained. In addition, the 1:1 oxalate complex can also be protonated to form $Cu(HC_2O_4)^+$ specie in acidic media. The resulting acid – base equilibrium is characterized by its ionization constant β_3.

$$Cu^{2+} + \ HC_2O_4{}^{-} = Cu(HC_2O_4)^+ \qquad (4.29)$$

Rearranging and taking logarithm of equation (4.29)

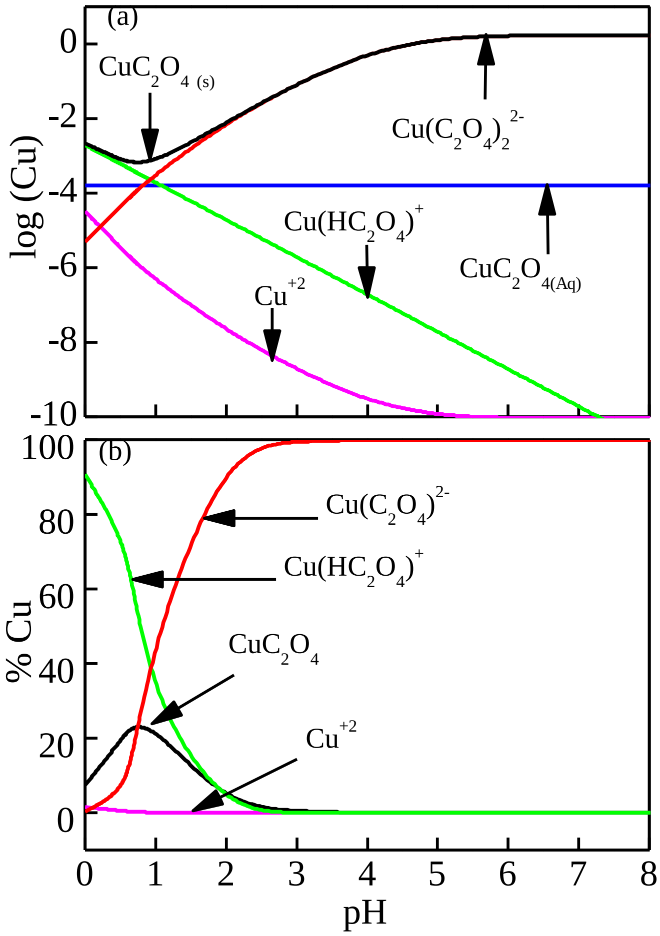

Fig.4.14: (a) Solubility diagram: Copper-oxalic acid system, (b) Distribution curves of soluble copper species

$$log\ Cu(HC_2O_4)^+ = \ log\ Cu^{2+} + \ log\ \beta_3 + log\ HC_2O_4{}^- \tag{4.30}$$

$$\text{Where, } log\ HC_2O_4{}^- = \ log\ H^+ + \log C_2O_4{}^- \tag{4.31}$$

Introducing the values from Table 4.4 enables the $log\ CuC_2O_4\ _{(aq)}$ concentration equilibrated with solid $CuC_2O_{4(s)}$to be plotted vs. pH (Figure 4.14 a). The solubility minima corresponding to the maximum precipitation of copper oxalate occurs in the pH range 0.6 to 0.7. The percentage soluble copper species were calculated by dividing the individual soluble species (Cu^{2+},$CuC_2O_4\ _{(aq)}$, $Cu(C_2O_4)_2^{2-}$, $Cu(HC_2O_4)^+$) by the total soluble species present in the system.

The solubility of oxalates of Cu, Ba, Ca, Bi etc. was investigated by Marta *et al.* (2003) at oxalic acid concentrations ranging from 0.05M-1M. They established the oxalates co-precipitation conditions by considering the formation of hydroxo-complexes and soluble oxalato-complexes. They reported the optimum pH for copper oxalate precipitation to be 0.7- 0.8, further except for Bi all other solubility curves showed a minima which was attributed to two opposing factors, protonation of the oxalate ions in strong acidic media and formation of complex oxalates at high pH values when the available oxalate concentration increases. Zielinski *et al.* (1998) examined precipitation– stripping process for heavy metals using D2EHPA and maximum precipitation of metal oxalates was observed at oxalic acid pH < 1.

4.6.12 Precipitation-stripping of zinc from D2EHPA: Theoretical aspects

The solubility diagram developed theoretically for zinc-oxalic acid system, using appropriate values of constants (Table 4.4) is shown in Figure 4.15(a). Zinc has one ionic species more than that observed for copper. The additional species $Zn(HC_2O_4)_2^{2-}$ forms due to protonation of $Zn(HC_2O_4)^+$ in acidic medium which is not observed in the case of copper because copper oxalate protonates to form the highly stable ($Cu(HC_2O_4)^+$) complex whereas when zinc oxalate gets protonated, it forms an unstable complex ($Zn(HC_2O_4)^+$) that has the capacity of getting protonated again to go to [Ar]3d^{10}4s^2 state to stabilize its energy level.

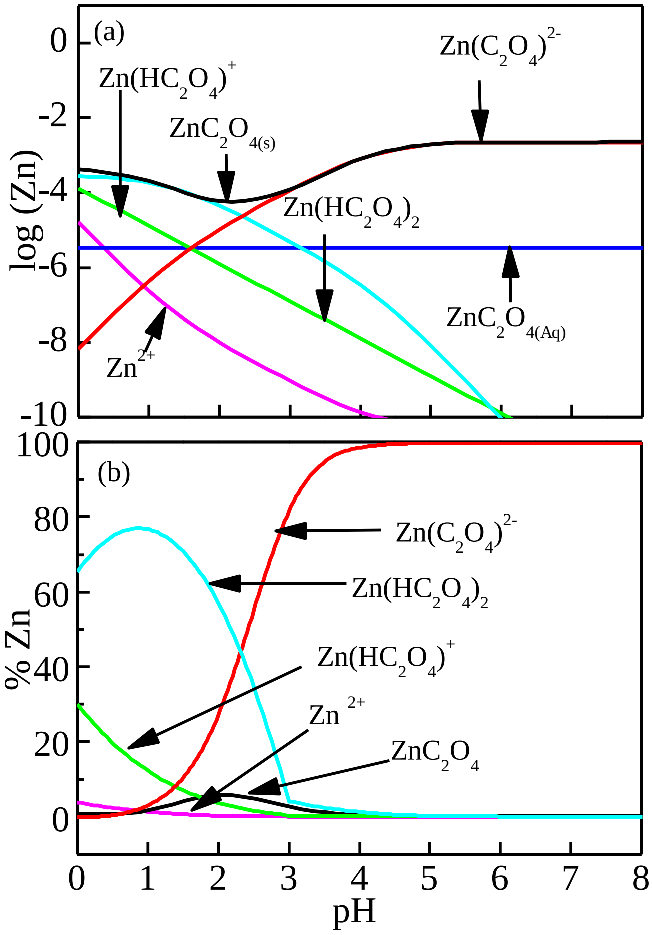

Fig.4.15: (a) Solubility diagram: Zinc-oxalic acid system, (b) Distribution curves of soluble zinc species

4.6.13 Results of Precipitation-stripping of copper and zinc

Precipitation-stripping was carried out using oxalic acid 1 M at equal oil to aqueous volumes for one hour at 150 rpm and 30^0C. Increasing the concentration of oxalic acid from 0.3 M to 1 M resulted in an increase in amount of precipitates obtained. Oxalic acid strengths beyond 1M were not attempted due to solubility constraints at the operating temperature. Stripping of copper was performed using 1M acid in three stages with fresh acid at each stage. The total copper stripped at each stage is the sum of copper present in the precipitate and the copper remaining dissolved in the oxalic acid solution.

Experimental data presented in Table 4.5 show that of the 19.76 gm copper loaded in the organic phase, the amount of copper precipitated as oxalate in stage 1 was 13.17 gm, and 4.06 gm and 2.25 gm of copper was precipitated in stage 2 and stage 3 respectively accounting for a cumulative yield of 98.6%. Copper remaining soluble in oxalic acid after precipitation in each stage was also determined experimentally. The solubility of copper oxalate at the precipitation pH value of 0.67 was determined from the solubility diagram Figure 4.14 (a). The experimental yield and the predicted yield considering dissolved copper obtained from solubility diagram are in close agreement as shown in Table 4.5. Figure 4.14(b) shows the distribution of soluble copper species present in the solution at pH 0.67 based on theoretical consideration.

Stripping of zinc was performed using 1M acid in two stages with fresh acid at each stage. The total zinc stripped at each stage is the sum of zinc present in the precipitate and the zinc remaining dissolved in the oxalic acid solution. Experimental data presented in Table 4.5 show that of the 12.38 gm zinc loaded in the organic phase, the amount of copper precipitated as oxalate in stage 1 was 9.78 gm, and 2.59 gm of zinc was precipitated in stage 2 with a cumulative yield of 99.1% .

The yield of zinc oxalate at the precipitation pH of 0.97 was determined from the solubility diagram Figure 4.15(a) and the values are reported in Table 4.5. Figure 4.15(b) shows the distribution of soluble zinc species present in the solution at pH 0.97 based on theoretical consideration.

Table 4.5: Stage wise recovery of copper and zinc

Stage No.	Copper loaded (19.76 gm)				Zinc loaded (12.38 gm)			
	S (gm)	P (gm)	% Yield		S (gm)	P (gm)	% Yield	
			E	T			E	T
1	13.26	13.17	99.32	99.68	9.78	9.72	99.38	99.83
2	4.15	4.06	97.83	98.96	2.59	2.55	98.45	99.82
3	2.31	2.25	97.4	98.14	-	-		
Total	19.72	19.48			12.37	12.27		

S: Stripped, P: Precipitated, E: Experimental, T: Theoretical.

4.6.14 Characterization of oxalates

The precipitates of copper oxalate and zinc oxalate obtained were characterised by XRD, FTIR and EDX. FESEM analysis was used to study the morphology of oxalate particles.

X-Ray Diffraction analysis

Copper and zinc oxalate particles were characterized by powder X-ray diffraction (XRD) on a PAN Analytical Xpert Pro diffractometer using Cu-Kα radiation at α value of 1.54 Å in Bragg-Brentano geometry. The sharp diffraction peaks of copper oxalate matched with standard data JCPDS 21-297 and that for zinc oxalate were indexed on the basis of monoclinic cell reported for zinc oxalate dihydrate (JCPDS 25-1029) (Figure 4.16).

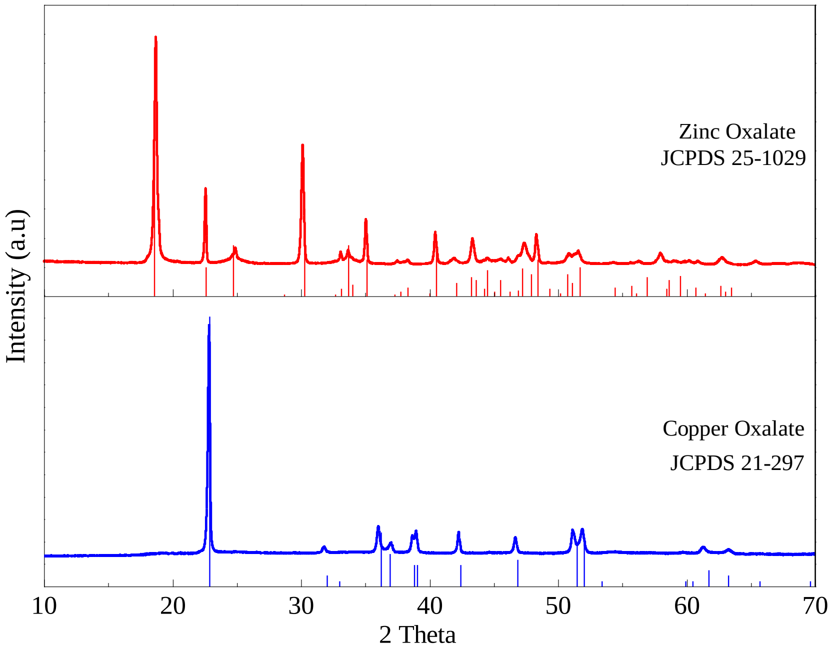

Fig.4.16: XRD spectra of copper oxalate and zinc oxalate

The crystallite size was determined by Debye Scherrer equation

$$Dp = \frac{K\,\lambda}{\beta\ sin\theta} \tag{4.32}$$

Dp = Average diameter of the crystallites (nm)

K= Shape factor related to the crystallite shape which is assumed to be 0.9

λ = Wavelength of the X-ray source, 1.54 Å

β = Line width at half of the maximum intensity (radians)

θ = Diffraction angle

The average crystallite size determined using Debye Scherrer equation were 50.3 nm and 44.3 nm for copper oxalate and zinc oxalate respectively.

Fourier transform infrared spectroscopy analysis

IR spectra of copper and zinc oxalate were recorded in the range of 400 cm^{-1} to 4000 cm^{-1} The spectra of copper oxalate (Figure 4.17) showed a broad band at frequency 3462.06 cm^{-1} corresponding to the OH stretching vibration, peak at 1679.3 cm^{-1} is attributed to the main anti-symmetric carbonyl stretching band ν_{as}(C=O) specific to the oxalate family. Vibration band at 1362.7 cm^{-1} are attributed to σ_s(C-O)+ σ(C-C) while band at 1319.4 cm^{-1} corresponds to σ_s(C-O)+ δ(O–C=O). Bands at 823.1 cm^{-1} and 504.89 cm^{-1} are due to δ(O–C=O) and σ(Cu-O) frequencies of the oxalate moiety.

For zinc oxalate the OH stretching vibration was observed at 3382.38, ν_{as}(C=O) at 1362.85 cm^{-1} , σ_s(C-O)+ σ(C-C) at 1363.6 cm^{-1} , σ_s(C-O)+ δ(O–C=O) at 1317.7 cm^{-1} . Bands at 821.51 cm^{-1}, 494.84 cm^{-1} are due to δ(O–C=O) and σ(Zn-O) frequencies of the oxalate moiety. Similar values were observed by for copper oxalate and zinc oxalate respectively.

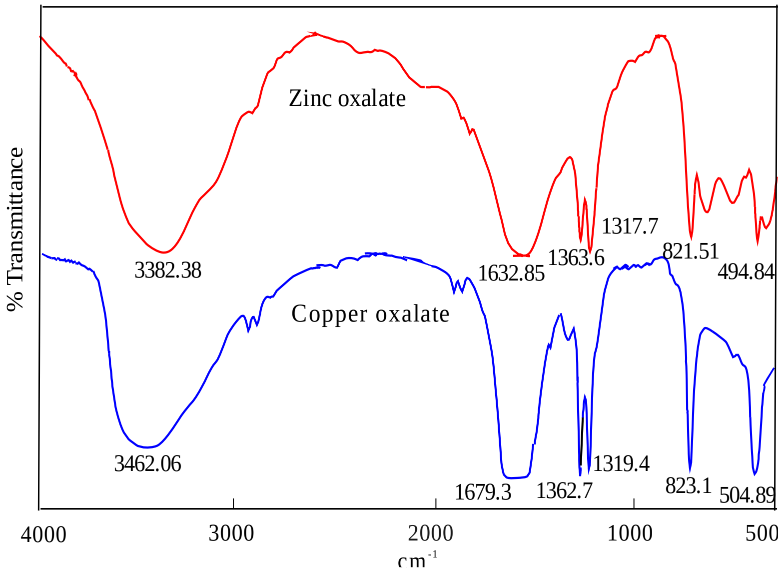

Fig.4.17: FTIR spectra of copper oxalate and zinc oxalate

Energy-dispersive X-ray spectroscopy analysis

The EDX analysis of copper and zinc oxalates is shown in Figure 4.18. EDX of copper oxalate shows that pure copper oxalate produced and there was no other metallic impurity present. The EDX analysis of zinc oxalate reveals the presence of copper as an impurity in the particle. Investigating further it was found that after copper extraction, 240 mg/L of copper remained unextracted in the pickle liquor. This residual copper got extracted by D2EHPA during zinc extraction and was precipitated as copper oxalate along with zinc oxalate. There was no iron detected in copper oxalate and zinc oxalate precipitates. Iron which was co-extracted with copper and with zinc was completely stripped with oxalic acid in two stages during stripping. Ferric ions in oxalic acid form soluble ferric oxalate. Hence, Fe (III) remained in the aqueous phase whereas copper and zinc precipitated as copper oxalate and zinc oxalate. Thus copper ends up as an impurity in zinc oxalate product.

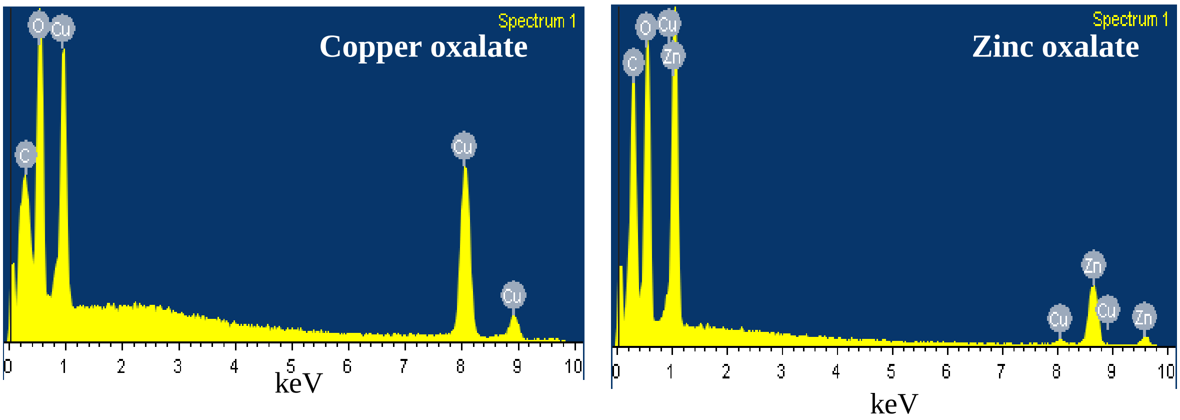

Fig.4.18: EDX of copper oxalate and zinc oxalate

4.6.15 Oxide preparation by thermal decomposition of oxalate and their characterization

Thermogravimetric analysis of copper oxalate and zinc oxalate samples was performed to determine the calcination temperature to convert the oxalates to their respective oxides as discussed in Chapter 3. Based on the results obtained from the thermogravimetric analysis copper oxalate was calcined at 400^0C and zinc oxalate was calcined at 440^0C for three hours to obtain their respective oxides.

X-Ray Diffraction analysis

Figure 4.19 shows the XRD patterns of copper oxide and zinc oxide obtained after calcination. The intensities and positions of peaks are in good agreement with the reported values (JCPDS file No. 05-661) for copper oxide with average crystalline size obtained from the Debye–Scherrer equation as 58.73 nm. For zinc oxide the positions of the peaks were in good agreement with JCPDS 36-1451 with crystallite size 41.68 nm. No oxalate impurities were found in either sample.

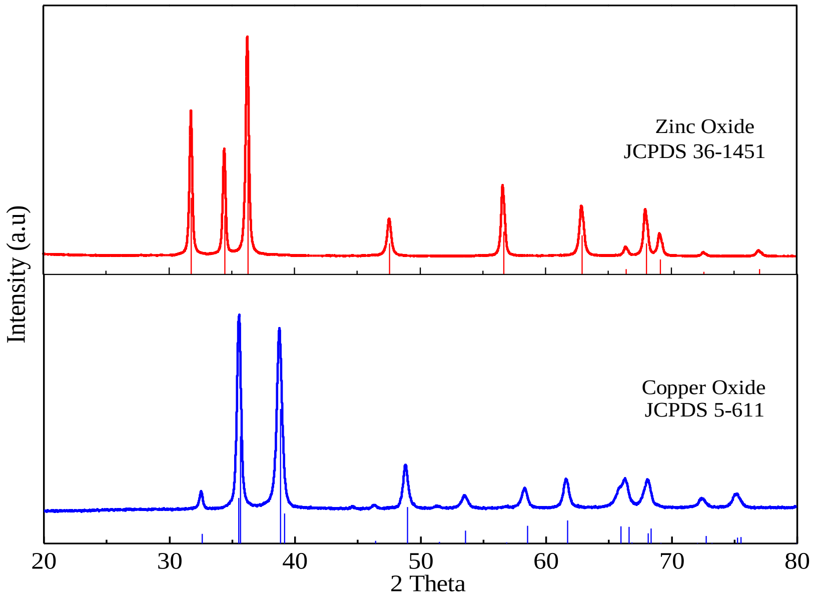

Fig.4.19: XRD spectra of copper oxide and zinc oxide

Fourier transform infrared spectroscopy analysis

The IR spectra of both the oxides (Figure 4.20) show a broad band ~3450 cm^{-1} indicating the presence of surface hydroxyl groups. The sharp peak observed in the IR spectra of copper oxide at around at 531.75 cm^{-1} is due to Cu-O and band at ~1111 cm^{-1} attributed to the OH bending vibrations of Cu-OH, and that at 1383 cm^{-1} is due to CuO stretching. Similarly for zinc oxide the peak at 461 cm^{-1} is due to Zn-O lattice vibrations and that at ~1193 cm^{-1} due to the OH bending vibrations.

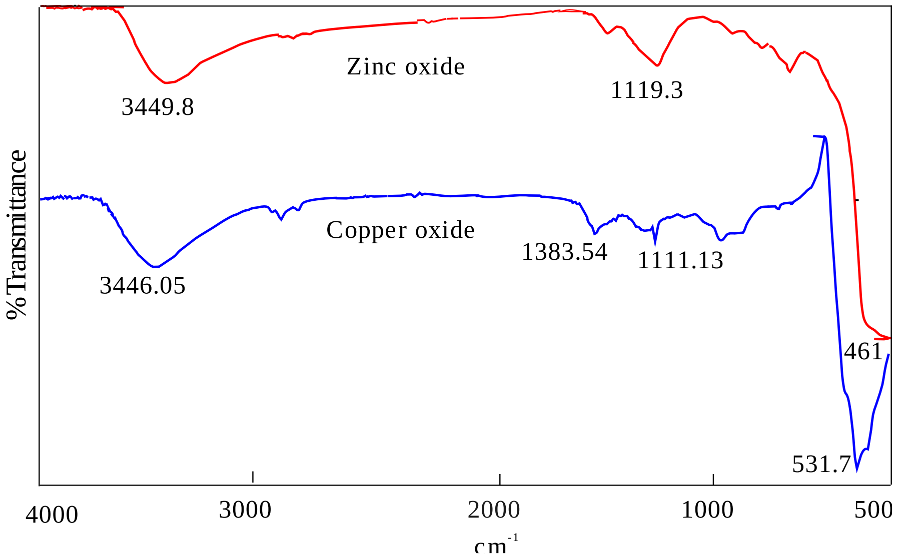

Fig.4.20: FTIR spectra of copper oxide and zinc oxide

Energy-dispersive X-ray spectroscopy analysis

The EDX analysis of copper oxide confirmed pure CuO phase with Cu and O in stoichiometric proportions. The EDX analysis of ZnO shows the presence of copper. (Figure 4.21)

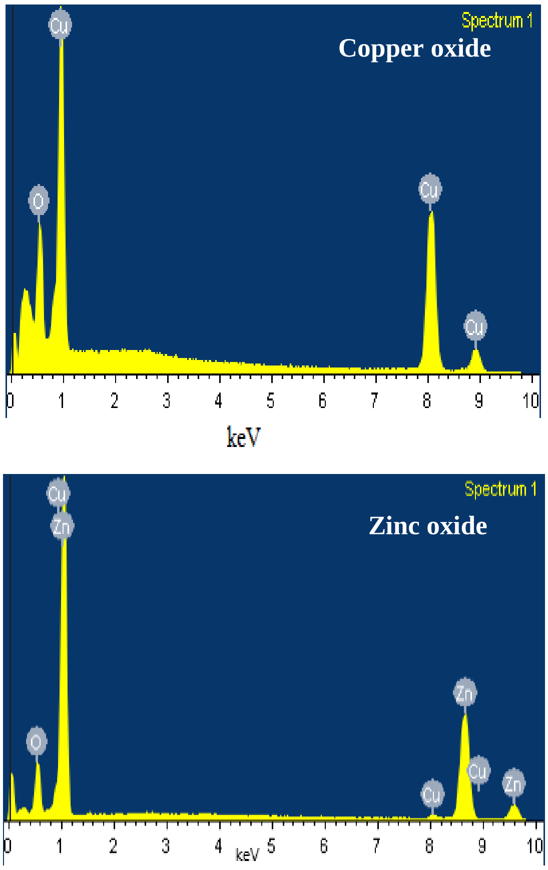

Fig. 4.21:EDX of copper oxide and zinc oxide

The chemical analysis of CuO also confirmed absence of impurity indicating formation of pure copper oxide whereas zinc oxide was 99.1% pure and contained 0.9% of copper oxide as an impurity. However, this did not manifest in the XRD analysis of zinc oxide as copper oxide percentage was very low.

4.6.16 Morphology of oxalates and oxides

FESEM image of the oxalates (Figure 4.22 a) show that copper oxalate particles were disc shaped, smaller in size and lacked sharp edges whereas zinc oxalate particles were more defined layered structures with sharp edges (Figure 4.22b). In both cases highly agglomerated particles are observed. FESEM images of the oxides (Figure 4.22 c, d) show that on calcination oxalates were transformed to their respective oxides without losing their ordered structure.

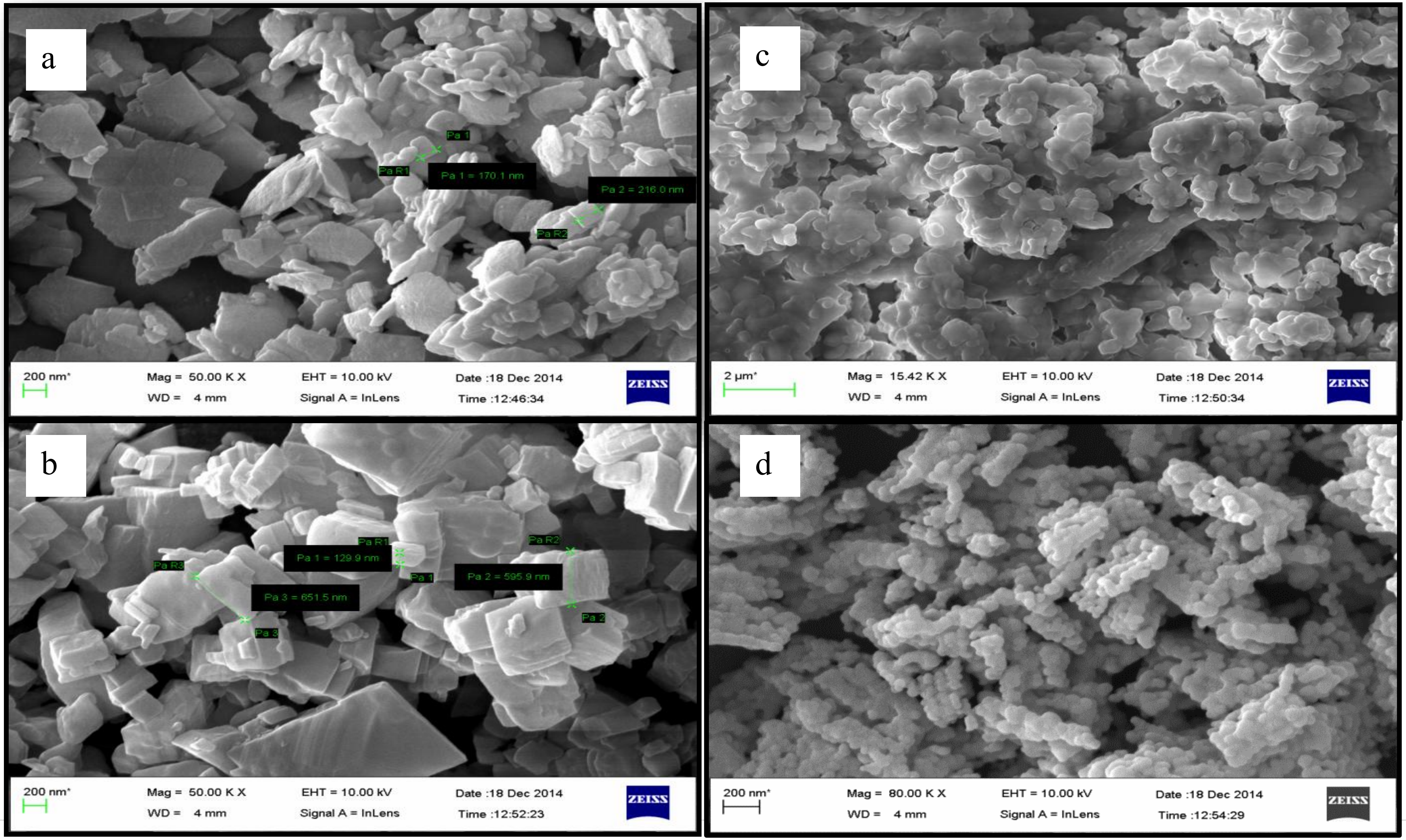

Fig. 4.22 FESEM images of (a) Copper oxalate (b) Zinc oxalate (c) Copper oxide (d) Zinc oxide

4.7 Development of processing scheme

Post PS the organic phase contained traces of copper (40 mg/L) in the copper stream and zinc (10 mg/L) in the zinc stream which were not stripped by oxalic acid. Both organic phases were treated separately with 1.5 M sulfuric acid to strip the residual copper and zinc prior to its recycle. It was found that the organic phase could be reused without any significant decline in the extractability of the metal ion, and even after 5 cycles 98.3% of the copper could be extracted using LIX84-IC at pH 2.5 and 97.7% zinc was extracted by D2EHPA after 5 cycles at pH 2 (Figure 4.23). Since the amount of the metal present in the stripped solution was low the same acid could be reused.

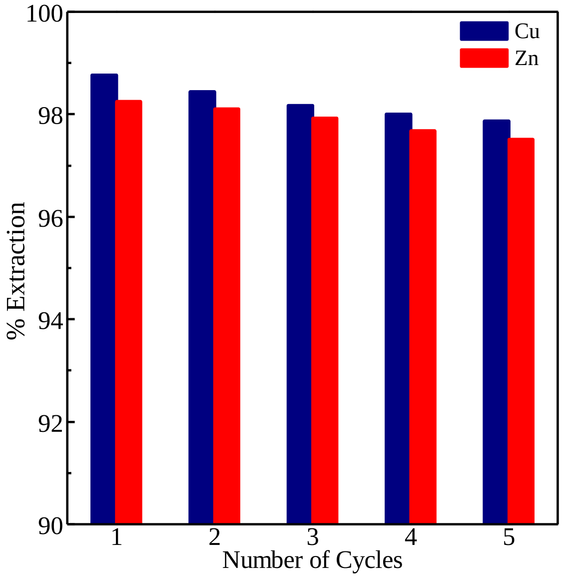

Fig. 4.23: Reusability potential of extractant

The aqueous phase after extraction of zinc contained the other metals present in the pickle liquor. This aqueous stream was mixed with the streams containing soluble oxalates. The combined stream was subjected to coagulation and flocculation to remove the metals present and filtered to separate the solids before disposal of the liquor.

EDX analysis (Figure 4.24) of the sludge generated after processing indicates the presence of the metals originally present in the pickle liquor after copper and zinc extraction. The additional peaks for sulphur in the EDX spectrum are due to the addition of alum during the coagulation and flocculation process. Figure 4.25 shows the process flow diagram for the recovery of copper and zinc from pickle liquors.

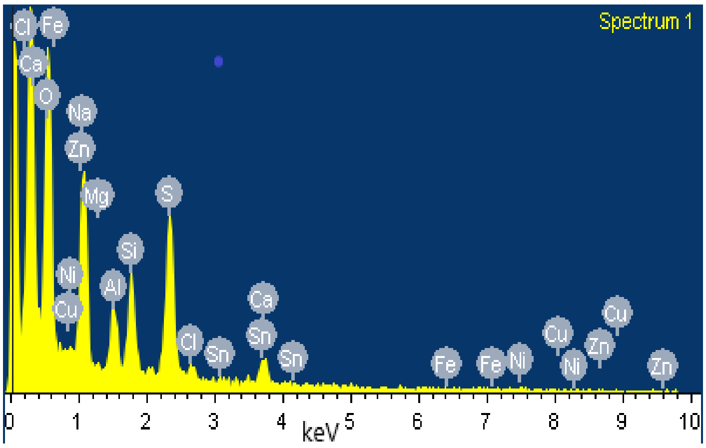

Fig. 4.24: EDX analysis of residual sludge after removal of copper and zinc

4.8 Conclusions

Solvent extraction and precipitation-stripping was used to recover copper and zinc from spent chloride brass pickle liquors. Speciation diagram revealed that both copper and zinc exist predominantly as the bivalent cationic specie, and small amount of the monovalent chloride specie in the range of concentration and pH investigated in this work. Copper was extracted from the pickle liquor using 30% (v/v) LIX 84-IC as an extractant. Small amount of Fe (III) was also co- extracted with copper. High copper loading in the organic phase was observed. The maximum loading capacity of LIX 84-IC at an equilibrium pH value of 2 was found to be 0.9 g/L per 1% (v/v) of extractant which turns out to be more than the case where only bivalent copper specie binds with the extractant, thereby indicating the possibility of transfer of the monovalent ions ($CuCl^{+}$) along with the bivalent ions (Cu^{2+}). IR studies revealed that the oxime extractant in organic phase existed both as a monomer and dimer at the extractant concentrations investigated and both were involved in the complexation process.

Zinc was extracted after the removal of copper using 15% (v/v) D2EHPA as the extractant. IR studies revealed that all the extractant was complexed and there was no free extractant present and zinc to D2EHPA ratio as 1:2. Slope analysis also revealed two extractant molecules participating in the complexation process extracting zinc as the specie ZnR_2.

Precipitation-stripping of the loaded metal using oxalic acid resulted in formation of water sparingly soluble metal oxalates. Solubility diagrams developed in this investigation could predict the yield of Cu and Zn precipitated as oxalates with high degree of accuracy (99%).

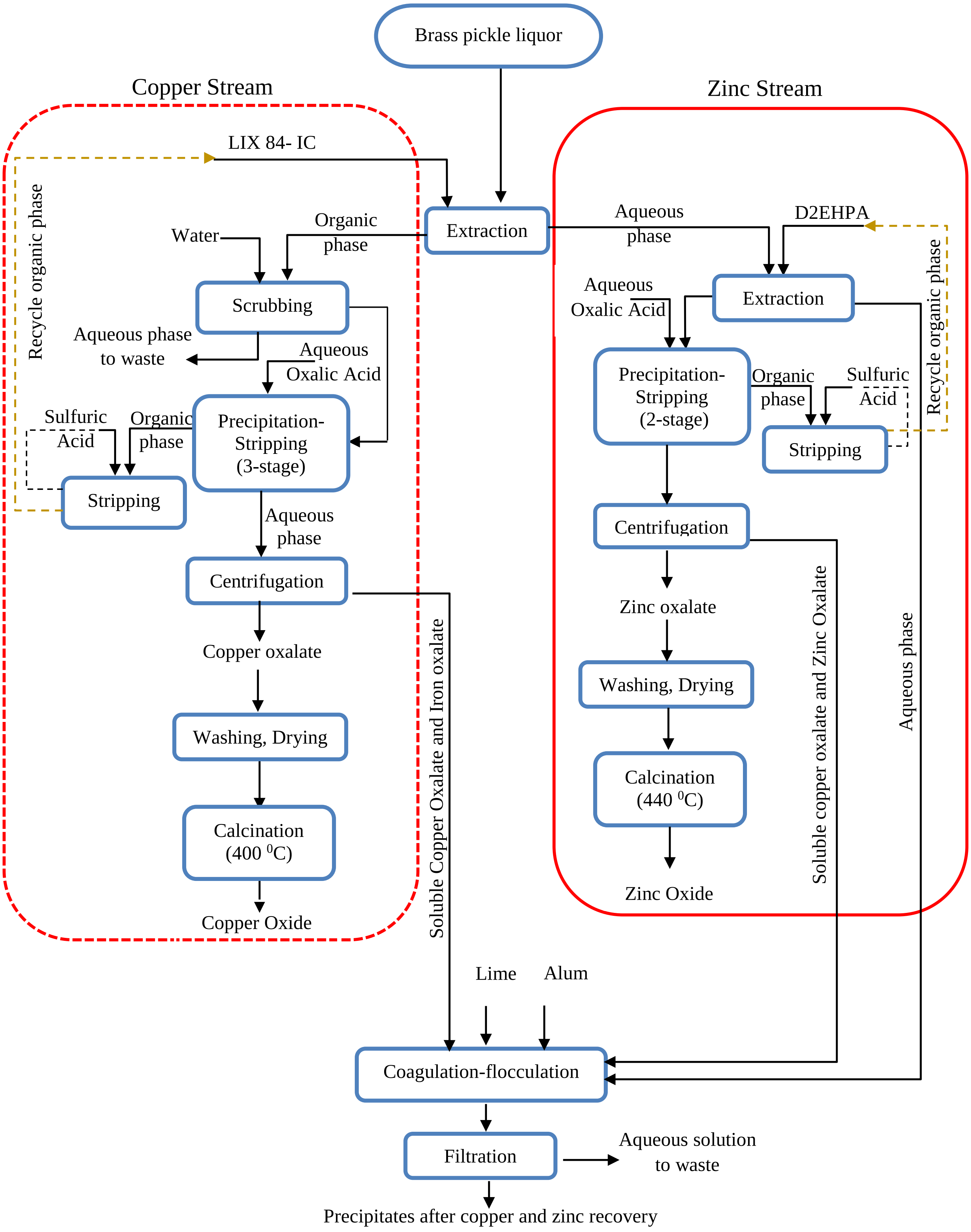

Fig. 4.25: Process scheme for the recovery of copper and zinc from pickle liqour

Iron that got co-extracted with both copper as well as zinc was also stripped as soluble ferric oxalate. It was coincidental that both copper and zinc recovered as copper oxalate and zinc oxalate accounted for 97.3% of the initial copper and zinc present in the pickle liquor.

Calcination of the oxalates under controlled conditions converted them to the corresponding oxides. Copper was recovered as pure copper oxide. The unextracted residual copper that slipped into the zinc circuit was extracted by D2EHPA as a result copper manifested as an impurity in Zn oxide which was obtained with a purity of 99.1%.

Attempts to avoid copper carry over to zinc stream by increasing the extent of extraction or by enhancing extraction pH was not successful, because at higher pH values (> 2.5) LIX 84-I extracted other metals present in the pickle liquor thereby introducing impurities in copper oxide as well. Carryover of copper could be avoided by either increasing the pH during extraction of copper using LIX 84-I or increasing the extractant concentration. However, in both the situations transfer of other metals present in the pickle liquor to organic phase would occur which is undesirable since it would render the copper oxalate impure.

Morphology of the precipitates revealed that zinc oxalate particles were layered structures with sharp edges while copper oxalate particles were disc shaped and lacked sharp edges. In both the cases highly agglomerated particles were observed. Calcinations did not induce any change in the ordered structure observed in oxalates.

Metal reclamation by hydrometallurgical route from chloride media invariably involves transfer of chloride to the stripping phase resulting in chlorine liberation at the anode during electrowinning. Further, copper iron and zinc often coexist in chloride leach solutions from industrial effluents. Separation of iron from the two metals is problematic as iron is co-extracted during extraction with most of the extractants. This problem can be circumvented if precipitation stripping is adopted, since the co-extracted iron gets removed in the form of soluble oxalate. This process leads to recovery of the metals as their oxalates that can be converted as their oxides with high purity thereby generating added value from waste and satisfying the dual goal of environmental sustainability and economic gain in terms of the reclaimed metals.

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