CHAPTER 7

CONCLUSIONS

7.1 General outline

Heavy metals in aqueous streams and water bodies poses considerable health hazard to humankind and it is imperative to treat the wastes to mitigate the hazard. Since metal values are highly recyclable it also provides a good opportunity to earn revenue while cleaning up the environment.

In this investigation the focus is primarily on reclaiming the metal values from acidic pickle liquor and rinse liquor of brass articles manufacturing processes. Gujarat is well known for manufacturing of brass artefacts as well as industrial components. Almost 70% of brass industrial components manufactured in India come from the Jamnagar brass cluster in Gujarat where 5000 manufacturers' are located. Most of the industrial component manufacturers are small scale producers and the decorative artefacts and articles are mostly produced in cottage industries. Such producers are handicapped by ignorance, lack of awareness and lack of resources to effectively treat the wastes. This investigation was undertaken with a hope that if appropriate technologies are made available then they could be implemented in years to come.

The third stream from which metal was recovered was ammoniacal etch solution of PCB manufacturing. Currently we produce less than 1% of global requirements of PCB while China produces more than 40%. It is foreseen that the growth of PCB industry in India in coming years is likely to be explosive. Hence, the need for regeneration of etch solution is going to be of very large volume. However, like in brass processing even in PCB manufacturing there are a very large number of small scale producers, who need appropriate technologies to be able to process their streams and recover the metal values from them.

The hydrometallurgical route was adopted in this study to recover the metal values from the three streams. Liquid extraction using appropriate metal extractants, extracted the metal from the aqueous streams in to organic phase and subsequently metal values were stripped using PS technique to obtain metal oxalate precipitates that were thermally decomposed to get the valuable metal oxides.

7.2 Recovery of copper and zinc from brass pickle liquor

Solvent extraction using two commercial extractants LIX 84-I and D2EHPA were used to recover copper and zinc respectively. Brass pickle liquor contained 20g/l copper and 12.6 g/l of zinc along with small amount of other metals. Speciation diagrams were developed for both copper and zinc that revealed bivalent cationic specie and small amount of the monovalent chloride specie in the working range of concentration and pH. 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. The maximum loading capacity of the hydroxyoxime LIX 84-IC at an equilibrium pH value of 2 was found to be 0.9 g/L per 1% (v/v) of extractant. There was a good 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.

After copper extraction at equilibrium pH of 2.5, zinc was extracted using 15% (v/v) D2EHPA at an equilibrium pH of 3.0. IR studies revealed that D2EHPA was fully complexed with zinc and free extractant was not present in the organic phase. Slope analysis revealed two extractant molecules participated 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 insoluble oxalate precipitates. Solubility diagrams developed in this investigation could predict the yield of Cu and Zn precipitated as oxalates with high degree of accuracy (99%). 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 their corresponding oxides. Copper was recovered as pure copper oxide, while zinc oxide was obtained with a purity of 99.1%. The unextracted residual copper had slipped into the zinc circuit and was extracted by D2EHPA as a result copper manifested as an impurity in Zn oxide.

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, removing it from the process mainstream.

Copper and zinc are recovered as pure oxalates that are converted as their oxides with very high purity. This process introduces the possibility of generating wealth from the waste. A detailed processing scheme is developed wherein after recovery of copper and zinc to the extent of 98.8% and 98.2% by extraction the residual metals and other trace elements in the aqueous stream was subjected to flocculation and coagulation to obtain a sludge containing the residual metal values and the treated water free of metals could be discharged into municipal water bodies.

7.3 Recovery of copper from spent PCB etch solutions

Ammoniacal etchants-ammonium chloride or ammonium sulfate are the most widely used etchants in the PCB industry. Spent etching solutions obtained from the PCB industry contain a large amount of copper, which can be recovered and recycled for further reuse. Almost one billion cubic meter of waste etchant is being generated annually from the PCB industry worldwide accounting for more than 70,000 tons of copper being lost if unclaimed. An extraction-stripping scheme was developed to recover copper from spent ammoniacal etching solution collected from a PCB manufacturing industry in Vadodara containing 50 g/L copper having an initial pH value of 8.5 using LIX 84-I as the extractant in kerosene. PS technique was used for regenerating the extractant and simultaneously producing copper oxalate particles. The copper oxalate thus obtained was calcined to obtain copper oxide that has considerable commercial potential.

Effect of pH on copper extraction was investigated and a maximum extraction was obtained at a pH value of 8.9. Extraction using 20% (v/v) and 50% (v/v) were investigated at organic to aqueous ratios of 4.5:1 and 1.5:1 respectively. In both the cases three equilibrium stages are required as indicated by McCabe -Thiele plots. Stripping of the fully loaded organic phase containing 50% extractant using 1M oxalic acid was achieved in two contacts with use of fresh acid at each time.

Stripping of the metal loaded organic phase with 1 M ethanolic oxalic acid solution required just one stripping stage when ethanol content was 25% and more (50%). However, when 10% ethanolic oxalic acid solution was used two stripping stages was necessary. The stripping was complete in all cases in one hour contact between oil phase and oxalic acid. The particles produced in aqueous oxalic acid were of wide size distribution and quite aggregated while particles formed in 50% ethanolic oxalic acid were not only very small in size but had a very narrow distribution as well. .

Particles were characterized by XRD, FTIR, FESEM etc. and were identified as pure copper oxalate matching with JCPDS standard. TGA of particles identified the decomposition patterns and copper oxalate, this information was used to get copper oxide by calcinations at 400^0 C for 3 hours in a tube furnace. The oxide particles were also characterized by XRD, EDX, FTIR, the morphology was observed by FESEM, particle size distribution was determined, surface charge zeta potential were measured. CuO particles obtained matched JCPDS standards, no impurities were observed.

The copper oxide prepared was used to catalyze the reduction of nitrobenzene to aniline and the effects of various parameters were investigated. The overall conversion was found to be over 98% with 100% selectivity. The catalyst could be reused a number of times without any loss of activity.

7.4 Particle formation during precipitation-stripping

Brass rinse liquors were used to recover copper and zinc on the same lines as brass pickle liquors for the recovery of these metals. The concentration of the metals in the rinse solution was significantly lower than the concentration of metals in the brass pickle liquor. Hence, the extraction circuits were designed to recover copper using 10% (v/v) LIX 84-IC and subsequently zinc was recovered using 10% (v/v) D2EHPA. The recovery of copper was quantitative at an equilibrium pH of 2.5. While 98.8% zinc was recovered at an equilibrium pH of 3.

The metal values were reclaimed by PS that regenerated the solvent for reuse. The efficacy of PS was explored over a wide range of parametric space and the nature of the particles obtained under different precipitating conditions was investigated. Key parameters varied were rate of agitation, precipitation time, concentration of oxalic acid and initial metal concentration. For all these situations the PSD were obtained and an attempt is made to interpret the precipitation patterns.

Striping mechanism of copper from LIX 84-IC and zinc from D2EHPA are significantly different since copper is held as a chelate while zinc could be bonded as well as solubilized by D2EHPA. Precipitation of particles in Cu -LIX 84-IC system takes place at the interface while in the case of D2EHPA because of its phase transfer behavior stripping also takes place in the aqueous film surrounding the oil phase. It was observed that copper stripping is much better defined than the stripping of zinc. However, in both the cases the precipitation yield consistently increases with concentration of oxalic acid. With an increase in degree of agitation and contact time, the PSD narrows and there is a shift towards smaller particle sizes and more stable size distribution patterns emerge.

The effect of concentration of oxalic acid on copper stripping is not very pronounced although there are differences in particle sizes when oxalic acid concentration is changed from 0.078 to 1M. For the case of zinc oxalate there is a drastic reduction in particle size with increase in oxalic acid concentration. The $d_{0.5}$ shifts from 18.26 mm at 0.057M to 3.07 mm at 1M concentration. A four to five fold increase in concentration of the metal in the organic phase did not make any significant difference in the PSD obtained.

The particles obtained were characterized by XRD, FTIR, EDX and XRF studies and results indicated that pure copper and zinc oxalate were obtained. Morphology of the copper oxalate particles were cushion shaped whereas zinc oxalate particles had sharp edges which were built layer by layer. Controlled calcinations of the oxalate particles at the appropriate temperatures resulted in the formation of copper and zinc oxide. The oxalates on transformation to the oxide did not lose its ordered structure. XRD analysis revealed that pure copper oxide and zinc oxide were obtained. For both copper and zinc oxide the metal- oxygen ratios were in stoichiometric proportions.

The antibacterial activity of copper oxide and zinc oxide were evaluated against four gram negative and one gram positive bacteria. Both the oxides exhibited antibacterial activity when tested against the five organisms. The diameter of the inhibition zone which reflects the susceptibility of the microorganism was higher for copper oxide.

7.5 Concluding Remarks

Processes have been developed to recover copper and zinc from three different industrial waste streams containing copper in the range of 20g/L to 4.38 g/L and zinc 12.6 g/l to 2.78g/L. Almost 99% + recovery was achieved in all the cases and the residual metal values could be precipitated out thereby releasing the aqueous streams free of metals as effluents from the brass units while recirculating the ammoniacal etch solution back to the process in PCB units. Copper and zinc where finally obtained as pure oxides and applications of copper oxide as a catalyst for reduction reactions and both copper and zinc oxide as antibacterial agents were investigated. However, numerous other applications of these oxides as gas sensors, in photovoltaic cells, ceramics, catalysts etc. need to be specifically explored and tailoring of the recovery processes towards specific outcome should be attempted in the future. Developing appropriate technologies to process such metal containing effluent streams gives us an opportunity to fulfill the twin goals of environmental sustainability and economic gain.