CHAPTER 1
INTRODUCTION

1.1 General Introduction

Heavy metals in aqueous streams pose severe health hazard to all life forms due to their inherent toxicity coupled with carcinogenicity and mutagenicity. Ironically many of these heavy metals are essential nutrients and their absence in ecosystem would also pose serious problems, but their excess in the ecosystem could lead to disastrous consequences. The tendency to bio accumulate makes their presence in aqueous streams all the more hazardous. Some disasters involving heavy metal pollution encountered by humankind in the last century are Minamata mercury pollution in Japan in 1932, Sandoz mercury pollution of Rhine in 1986, Coto de Donana dam burst releasing millions of tons of mud containing copper, zinc, lead, cadmium in Spain in 1998. The consequences of these disasters are still being faced in those geographical regions. Hence, it is imperative from ecological, environmental and economical point of view to address the issue of heavy metal damage to the environment.

Heavy metals find their way in aqueous streams from mine run waters and wastewaters from various industrial processes such as smelting, electroplating, metal processing and finishing, fertilizers, rayon, paints and pigments etc. Many of these manufacturing activities are in very small scale and it is futile to expect elaborate treatment processes for the mitigation of these streams. Even in industrial clusters and Special Economic Zones (SEZ's) the effluent treatment plants deal with conventional techniques that can cater to mixed nature of the wastes as a result the economic advantage of the recovery of metal values is not achieved. A lot of metal ends up as sludge that finds its way to land fill sites where seeping water of rains leaches metal ions and brings the metals back in ground waters, aquifers and water bodies where they bioaccumulate and eventually show results of their toxicity.

Metal laden waste water treatment can be successful only when the three R's are fulfilled i.e recovery, recycle and reuse. As it is recycle and reuse of metal values is quite prevalent, steel and aluminium are most recycled metals, copper is recycled to the extent of 40%, zinc 30% and precious metals almost 100%, but most of this recycle is from scrap. Recycling of metal values from aqueous streams is not uncommon but more complex and challenging.

Particularly with metals, environmental sustenance could get high emphasis if the economic aspects are worked out properly since there is tremendous potential of harnessing wealth from waste.

1.2 Background of the work

India is known for its craftsmanship of brass articles and artefacts, there are numerous centres in India where brass jewellery, decorative trims, statutes and artefacts are produced. However, machined and industrial articles made of brass are largely manufactured in Gujarat near Jamnagar which is designated the brass city of India. There are more than five thousand small units in the Jamnagar brass cluster that meets more than 70% of the brass part requirements in India.

Brass on atmospheric oxidation loses its lustre due to formation of an oxide layer called tarnish and as part of final finishing operation the tarnish is removed by acid wash. This leaches out the tarnish and releases the metal components of brass i.e. copper and zinc in the acid solution, the acid is continuously used till its acid strength is depleted and then the metal loaded acid is discarded, in many cases without any treatment into sewers thereby increasing the copper and zinc loading in the aqueous streams. The recovery of copper and zinc from such acid solutions by solvent extraction would give immense boost to environmental sustenance and at the same time reclamation of these metal values would contribute to substantial economic advantage to the processors.

Gujarat is also home to major Printed Circuit Board manufacturers, although Indian contribution to PCB manufacturing is less than 1% of the global capacity at present but there is tremendous potential for growth in this sector. The domestic market will grow at a rate of 20.56 % CAGR and is expected to reach over $ 6 billion by 2020 from the current $ 3.8 billion. The current market size of the bare board is $ 1.2 billion out of which only 30% is met by local manufacturers and the remaining 70% is imported. With the growth of the industry these figures will certainly be modified. Currently there are about 200 PCB manufacturers in India – more than 60% of them are very small and unorganized.

The key process in PCB manufacturing is etching of the copper clad laminate to remove the excess copper. Etching is done predominantly by either a chloride solution or an ammoniacal solution, the later being more common these days. As the etching process proceeds the copper concentration in the etch solution increases and the rate of etching drops to maintain

stable operation, replenishment of a part of the etch solution by fresh solution is necessary. It is imperative to recover the copper from the etch solution for both economic and environmental purposes and for copper reclamation from the spent etch solution solvent extraction and electrowinning operations are practised. On the whole almost 1.5 to 3.5 litre of waste etchant is produced per square meter of PCB produced that figures out to be almost one billion cubic meters of waste etchant being generated annually accounting for more than 70,000 tonnes of copper being lost if not reclaimed.

The present work is focussed towards developing processing schemes for the recovery and reclamation of metal values from brass pickle liquors, brass rinse solutions and ammoniacal PCB etch liquors using hydrometallurgical techniques. Focus is also on the use of Precipitation – Stripping (PS) as a tool for metal reclamation from organic solvents as well as a technique for particle synthesis, resulting in the formation of oxalate particles that could be calcined at an appropriate temperature to get the commercially valuable oxide particles.

1.3 Research Objective

The core objective of this study is to recover the metal values from three industrial streams namely brass chloride pickle liquor, PCB ammoniacal etch solutions and post pickling rinse waters from brass processing units. Liquid extraction was adopted as the technique to recover brass components copper and zinc from chloride brass pickle liquors and the rinse solutions and also to recover copper from ammoniacal PCB etch solutions. In view of this the research objectives of this investigation were the following:-

1. Selection of appropriate metal extractant and operating parameters to map the extraction space to search the optimal conditions of extraction. Extraction of a multi-solute system is a challenging task that needs to be explored thoroughly and minutely to avoid impurities in the final products. Extraction of metal values from chloride media is not as prevalent as that from sulfate media and there are unanswered questions related to the transfer of chloride species in the organic phase. Attempts were made to thoroughly explore the extraction domain and provide rational answers.

2. To investigate the use of Precipitation - Stripping technique for the recovery of the metal values from loaded organic phase that precipitates the extracted metals as insoluble oxalates and regenerates the organic solvent for reuse in the next cycle.

This method mitigates the problems posed by release of chlorine during electrowinning.

3. To characterise the particles formed by Precipitation-Stripping in terms of purity and morphology to understand the effects of time, solvent, strippant concentration and metal loading on particle formation behaviour. In case of particles formed from PCB etch solution to get information of surface potential as well.

4. To convert the oxalate particles by thermal decomposition to the more valuable oxide particles and investigate the use of copper oxide as catalyst for reduction reaction. To also study the anti-bacterial properties of copper oxide and zinc oxide to substantiate its uses.

5. To develop processing schemes for metal recovery from the three metal effluents investigated.

6. To model the solubility behaviour, the speciation and precipitation during these processes of metal recover and reclamation.

These research objectives were not always separately addressed but intertwined in a composite whole with the idea to fulfil the core objective of this study.

1.4 Outline of the Thesis

The thesis is presented in seven Chapters, **Chapter 1:** ***Introduction*** discusses the background and defines the objective of the work. **Chapter 2:** ***Heavy Metals in Aqueous Solutions: Sources, Effects and Reclamation*** is a general literature survey that highlights the sources of heavy metals in aqueous streams and their deleterious effects on human health and environment. The treatment methods for removal of metals from aqueous streams, with emphasis on solvent extraction are also discussed. **Chapter 3:** ***Materials and Methods*** discusses the sources of the different aqueous streams collected from industrial sectors and the general methodology for extraction and stripping of metals from such metal bearing streams to prepare fine particles. Instrumental techniques used for the characterization of particles and the instrument details for the same are also listed. **Chapter 4:** ***Recovery of Copper and Zinc from Spent Brass Pickle Liquors*** describes the investigations on recovery of copper and zinc from spent pickle liquor obtained from a brass processing industry using solvent extraction and precipitation-stripping as copper and zinc oxide particles. It also

models the speciation solubility and precipitation and characterises the particles formed. A process flow scheme for their recovery is also developed. **Chapter 5:** ***Reclamation of Copper from Spent Ammoniacal Printed Circuit Board Etch Solutions*** details the investigations on copper recovery from ammoniacal media and discusses the influence of a solvent-alcohol in the precipitation media. Particles were characterised in detail, surface charges were determined and the use of copper oxide particles as a catalyst is also explored. **Chapter 6**: ***Particle Formation during Precipitation-Stripping*** in this Chapter, brass rinse liquors were used as the metal source and precipitation during stripping of metal loaded organic phase is studied over wide range parametric variations to gain insight in particle formation behaviour. The particles synthesized were characterised in detail and antibacterial properties of zinc oxide and copper oxide particles were explored. **Chapter 7:** ***Conclusions*** the summary of the investigation carried out and the scope for future work are listed in this Chapter.