

# **METAL RECYCLE AND RECOVERY**

*A Thesis Submitted for the Degree of Doctor of Philosophy*

*by*

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*This thesis is dedicated to my parents,  
my brother, Intizar and my sister, Jehan Afza  
with love.*

## DECLARATION

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A handwritten signature in black ink, appearing to read 'Zaid Hussain', written in a cursive style.

**Z. Hussain**

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*Finally to my young nephew, Hassan - work hard and be dedicated because, "It's your turn next".*

## ABSTRACT

The development of techniques for the removal and recovery of metals from industrial effluent taking account of the consequences of the definition of waste in the Basel Convention on transfrontier shipment of waste is reported.

The use of fluidised bed cell electrolysis in the recovery of metals from dilute solutions is investigated, and the conditions for recovery optimised. For the first time the application of a novel activated carbon cloth concentrator cell to recover metals from effluent solutions is reported and the conditions for its use optimised. Comparative studies using conventional mesh and plate electrodes, and novel activated carbon cloth electrode for the recovery of cobalt from dilute solution, and copper from three different hydrometallurgical solutions *viz* (i) Cu/Zn, (ii) Cu/Zn/Fe and (iii) Cu/Zn/Cd containing effluents were carried out.

Application of concentrator cell technology including activated carbon cloth and ion exchange resin to the recovery of metals, including precious group metals, from industrial as-supplied samples is reported. Optimisation leads to successful recovery of iridium and palladium from very dilute solutions. The alternative recovery of metal as added-value chemicals is also investigated.

The Basel Convention is concerned with transfrontier shipment of waste from developed to developing countries and has produced a need to investigate the leachability of metals in various forms. In this work the leachability of copper and zinc is studied under various conditions that model environmental situations and the results have been used to develop a methodology to determine whether a metal containing material would be subject to a shipment ban under the Convention.

As part of the development of the methodology, leaching studies were also carried out on single chemical compounds of copper, zinc, cadmium and lead, and their bioavailability determined.

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**CHAPTER ONE**  
**INTRODUCTION**

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# **1. INTRODUCTION**

## **1.1 BACKGROUND TO PRESENT WORK**

The polluting of water is an introduction by man into the environment of substances which may cause hazards to human health and harm to any living resources and ecological systems. Organisms living in a water body are sensitive to any changes in their environment caused by man<sup>[1,2]</sup>. Clearly water pollution is a serious environmental problem and the need to clean up effluent is important on this ground alone.

Recent extensive changes in UK environmental legislation have resulted in the setting of much lower discharge consent levels for heavy metals in aqueous effluent and has aroused an increasing awareness of the need for maximum recycle and minimum discharge. Not only has the increase in water charges and legislation covering pollution created a driving force for the recent increased interest in recovery of metals from effluents, but also the removal of metals is important.

Industrialised nations have now begun to acknowledge the problems posed by environmental hazards arising from industrial processes. One consequence of public awareness has been the implementation of evermore stringent legislation which includes The Environmental Protection Act (1990) in the UK and amendments to the Clean Air (1990) and Water Acts (1987) in the US. Industry is now trying to develop methods for reducing its atmospheric emissions, discharges to local water systems and disposal of solids into landfill sites, as well as the recycling of process materials.

The Environment Agency (EA) took over the responsibilities of the National Rivers Authority (NRA), the Waste Regulation Authorities (WRAs) and Her Majesty's Inspectorate of Pollution (HMIP) on 1 April 1996. The principal aim of the Agency is to ensure that industry with the greatest pollution potential is controlled<sup>[3]</sup>.

Many of the metals studied in this research are referred to under the Dangerous Substances Directive (76/464/EEC). This framework directive is divided into two lists, List I which is referred to as the "Black List", and identifies 129 substances selected mainly on the basis of



their toxicity, persistence and bioaccumulation in the environment that priority should be given to eliminating pollution by them. Included are organohalogens, organophosphorus, cadmium and mercury and their compounds. Control of these substances is largely achieved by the setting of limit values or environmental quality standards in subsequent “daughter” directives. From this original list of 129 substances, daughter directives have been adopted for such substances which include carbon tetrachloride, hexachlorobenzene and chloroform.

Metals like copper, lead, nickel, arsenic, chromium and various biocides and substances such as ammonia and cyanide, are contained in List II known as the “Grey List” which covers those substances from the priority list of 129 substances which have not yet been given formal List I status in a daughter directive. The list covers those substances considered to be less harmful when discharged to water. In the UK, the *Environmental Protection Regulations 1991* list a number of Black List substances whose releases to water are prescribed for *Integrated Pollution Control (IPC)* which covers all major solid, liquid and gaseous emissions to air, land and water from the most polluting and complex industrial processes. The same substances, together with carbon tetrachloride, are also prescribed substances under the *Trade Effluents Regulations 1989*. All processes producing these substances, and are sometimes referred to as Red List substances in the UK, must use **BATNEEC** (Best Available Techniques Not Entailing Excessive Costs) to control polluting releases<sup>[4,5]</sup>.

## **1.2 EFFLUENT TREATMENT**

Effluent treatment needs to become an essential part of the total production process, whether it is for the recovery of metals for use as raw materials or to comply with the requirements of the water authorities as to the acceptable level of metals which can be discharged to water. Precious metals such as silver have been recovered for a long time due to their commercial value, whilst the discharge of other metals such as cadmium have been controlled due to high toxicity and interference with sewage treatment works.

A variety of techniques is available for rendering toxic effluents harmless. Some of these processes combine the removal of harmful metals and recovery of valuable metals, thereby making them more attractive to the industrialist. Effluents containing metals in solution

frequently occur in industry and they arise from various sources such as plating, pickling and photographic processes.

Nowadays there are many possible methods of effluent treatment which can be used. In order for a process to become attractive to industry, it needs to be compatible, cost effective, efficient, flexible, reliable, robust, selective and simple. The process that best satisfies these requirements will have the greatest scope for implementation. What follows is a review of the traditional metal recovery techniques.

### **1.3 METAL RECOVERY TECHNIQUES**

Established methods for removal and recovery are still being researched but the main techniques which are used include:- Evaporation, Solvent Extraction, Ion-Exchange, Adsorption, Reverse Osmosis, Electrodialysis, Biological Treatment, Chemical Precipitation, Cementation and Electrowinning; each of these will now be discussed briefly.

#### **1.3.1 Evaporation**

This technique involves liquids being slowly converted into vapours at temperatures below their boiling points. The process of evaporation, which involves concentrating waste streams by evaporation of water, is high in operating costs. Energy efficient evaporators are available, but one of the major drawbacks of this technique is that the concentrate will contain secondary non-volatile contaminants that will deteriorate the product quality.

#### **1.3.2 Solvent Extraction**

The recovery of metals from solution by solvent extraction has been used extensively to achieve analytical separations, and more recently in the treatment of wastewaters to remove soluble metals<sup>[6]</sup>. It is also a widely used technique in hydrometallurgy. The concept involves leaching of the metal from the solid matrix, followed by the recovery stage such as precipitation, crystallisation or electrolysis. Solvent extraction is a technique that can be easily fouled by suspended solids and is intolerant of organic molecules which limits its applications. The metal ion working range is from 1 to 300 g dm<sup>-3</sup>[7].

### **1.3.3 Ion-Exchange**

Ion-exchange can be regarded as the interchange of ions between a solid and a liquid phase, in which there is no permanent change in the structure of the solid. Ion-exchange systems use resins that contain functional groups that act as exchange sites. The exchange sites are initially located with an easily displaced ion, which can be replaced by ions that will bond more strongly to the exchange sites. There are two basic types of resin which possess ion exchange properties. The resins interact with mobile ions in the solution and are either cation or anion exchange resins. The loosely bound ion in the cationic exchange resins is usually either hydrogen or sodium. As wastewater is passed over the resin, the hydrogen or sodium in the resin is replaced by the metal ions present in the wastewater. For anion exchange resins, the loosely bound ion is usually either a sulphate or chloride.

During treatment, the resin exchanges its ions for those in the wastewater. The process continues until the solution being treated exhausts the resin exchange capacity. At this point the exhausted resin must be regenerated by another chemical which replaces the ions given up in the ion-exchange operation, thus converting the resin back to its original composition. The need for regeneration, however, is one of the drawbacks of this technique<sup>[8]</sup>.

### **1.3.4 Adsorption**

Chemical and physical adsorption of metals from dilute aqueous solutions may prove to be an attractive clean-up process. Such treatment can either use a prepared sorption media which can be re-used, or a low cost single use material. The most widely used adsorbent in water treatment is activated carbon. Other materials include starch xanthate as well as discarded agricultural products such as bark, peat moss and straw<sup>[9]</sup>. One of the drawbacks of this technique is the necessary treatment or disposal of the contaminated adsorption material.

### **1.3.5 Reverse Osmosis**

In reverse osmosis (RO) the natural osmotic pressure is overcome by the application of an opposing pressure so that the net result is transfer of the water from the strong solution to the weak solution through the membrane. The stronger solution can be made more concentrated without it going through a phase change. It has been reported that reverse osmosis is well

suited to the recovery of large polyvalent metal ions and is tolerant to limited pH changes, with moderate metal ion selectivity. It is fouled by suspended solids, and is intolerant of organic molecules<sup>[10]</sup>. The metal ion working range is between 0.01 to 1.0 g dm<sup>-3</sup>.

### **1.3.6 Electrodialysis**

Electrodialysis is a membrane-based separation technique that is capable of deionizing one water stream while concentrating the electrolyte in another stream. In this way, electrodialysis produces a purified stream which can be discharged or reused, and a concentrated electrolyte stream that can be disposed of or processed for reclamation of the dissolved salt.

An electrodialysis cell consists of a sandwich of alternate cation-exchange and anion-exchange membranes that are placed between an anode and cathode. The membranes are sheet-like barriers made out of a highly cross-linked polymer matrix to which positive functional groups (for anion transfer) or negative functional groups (for cation exchange transfer) have been chemically bonded. When a voltage is applied to the electrodes, this causes the cations to pass through cation-exchange membranes en route to the negative cathode. The cations are repulsed when they encounter an anion-exchange membrane. In the same way, anions migrate towards the positive anode and are able to pass through anion-exchange membranes, but are prohibited from passing through cation-exchange membranes<sup>[11,12]</sup>.

### **1.3.7 Biological Treatment**

Certain microorganisms have the ability to accumulate heavy metals from their external environment, and therefore can be used as a means of removing heavy metals from water and wastewaters. The uptake of metal ions by micro-organisms can be through both adsorption onto cell surfaces of dead and living organisms and by the active uptake within cells of living organisms.

There are a number of microbial processes that exist which can be applied to metal removal. These are generally divided into two types of processes. **Biosorption** can be regarded as the 'passive' sorption and complexation of metal ions by microbial biomass. The biomass has a high metal affinity, and the uptake of metals is usually rapid, depending on the pH and the presence

of anions. **Bioaccumulation** is the uptake of metals that can be tailored to be more selective than biosorption by the choice of microorganism used. These techniques have a very limited pH tolerance, but can display high metal selectivity. The metal ion working range is from 100 to  $0.1 \text{ mg dm}^{-3}$ .

### **1.3.8 Chemical Precipitation**

In this process the metal is transferred from the soluble ionic state into an insoluble precipitate. Advantage is taken of the fact that many heavy metal hydroxides are insoluble in aqueous solution, particularly at moderately high pH. By adjusting the pH to an appropriate value which varies with the metal, the metal can be precipitated. It has been reported that lime generally gives denser precipitates that are more amenable to direct sedimentation than those produced using caustic soda<sup>[13]</sup>. This technique is very tolerant of pH changes, suspended solids and organic molecules. It has the disadvantage of being non-selective of heavy metal ions, but has a metal ion working range of  $> 10.0 \text{ mg dm}^{-3}$ .

### **1.3.9 Cementation**

Cementation is a form of precipitation in which there is an electrochemical reaction. A metal with a more positive oxidation potential will pass into solution to replace a metal with a less positive potential<sup>[14]</sup>. Copper is most commonly separated by cementation as are Cd, Ni and Co<sup>[15-17]</sup>. Also the precious metals, such as Ag and Au have also been separated<sup>[18,19]</sup>. The metals of greater positive potential used, usually in the form of scrap or waste powders are aluminium, copper, iron, magnesium or zinc.

### **1.3.10 Electrowinning**

Electrowinning is a well established technology and has been used extensively for separation and recovery of metals from solution. Chemical precipitation, solvent extraction and reverse osmosis recover metals as concentrated sludge, but electrolysis has the potential to directly reuse metals like powder and cathode sheet. The great advantage of this technique is that it does not generate additional waste, requiring no chemical additives and producing metal in a useful form. Electrowinning is tolerant of pH fluctuations with moderate metal ion selectivity often dependent on pH. The metal ions are removed from wastewaters by plating the metal

onto the cathode by means of an electrochemical cell.

#### **1.4 COMPARISON OF METAL RECOVERY TECHNIQUES**

Chemical precipitation and solvent extraction are methods which produce good quality treated effluent but continued addition of treatment chemicals is required which increases the amount of contaminants in the discharges and complicates disposal.

With evaporation, a higher concentration of the metal ions is recovered in solution when compared to reverse osmosis or ion exchange. With this technique there is a smaller effluent problem and evaporated water can also be recycled. However, high capital and maintenance costs are needed and there is also concentration of undesirable contaminants taking place.

Reverse osmosis and electrodialysis both produce high quality treated effluent and enable large scale continuous processing to be carried out, however, the disadvantages are high capital and operating costs, non-selective separation processes and irreversible metal fouling.

Ion exchange is a method in which good quality treated effluent is produced and a further advantage is that the resins can be regenerated many times. The disadvantages are non-selective, irreversible resin reaction fouling, limited capacity and high capital costs.

Cementation is a very costly method but the main disadvantages are that oil-laden wastewaters are difficult to treat because the oil wets and blinds the metal scrap used and ultimately reduces the effectiveness of recovery.

Of those described the most desirable techniques are electrowinning / electrolysis because they are primarily recovery methods. The major disadvantage of this technique, however, is that when the wastewater contains high concentrations of cyanide and acid, the effluent still needs to be treated after the recovery of the metal, therefore 100 % recovery is unlikely.

For the majority of the recovery / removal work presented in this thesis, modified electrolytic methods have been used.

## **1.5 THEORY OF ELECTROLYSIS**

The process of electrolysis is one in which a substance is being decomposed due to the passage of an electric current across an electrolyte.

The electrolyte, which is at least partly composed of ions rather than molecules, is the medium which carries the current. The ability of the solvent, especially water, to ionise substances dissolved in it, i.e. to split them into components that carry positive and negative charges, makes electrolysis possible. The current is carried across the electrolyte by the charged ions and products of electrolysis deposit at the electrodes. This is a result of the cations migrating to the negatively charged cathode (where reduction takes place) while the anions travel toward the positively charged anode (where oxidation takes place).

The charges of the ions are neutralised by the charges on the electrodes and so the products of electrolysis appear at the electrodes<sup>[20]</sup>.

The process of electrolysis requires the transportation of ions from the bulk of the solution to the surface of the electrode. In normal electroplating solutions this does not cause a problem because of the high concentration of the metal ions. In dilute solutions, however, the shortage of ions in solution to be plated out causes problems.

As metal is deposited upon a cathode, the solution in its immediate vicinity is depleted of metal ions. If plating is to continue, these ions must be replenished.

There are three possible methods in which ion transportation can be accomplished:

- (a) **Migration**, effect of the applied electric field
- (b) **Convection**, effect of hydrodynamic flow
- (c) **Diffusion**, effect of downward gradient in the bulk of the solution

If the concentration of ions reaching the electrode is small, like in dilute solutions, the effect of ionic migration is negligible.

Convection is very effective in bringing fresh solution, and thus a fresh supply of ions, to the vicinity of the electrodes. At the surface of the electrode itself, and for a very short distance away from the surface, convection is negligible, and the final distance from the bulk of the solution to the actual face of the electrode is negotiated through the forces of diffusion.

Diffusion is a result of the random motion of the ions or molecules; this motion tends to produce more uniform distribution of the various species throughout the solution. Thus the depletion of a species next to the cathode results in a movement of that species from the bulk of the solution toward the cathode [Figure. 1.1].

This region next to the electrode, where the concentration of any chemical species differs from its concentration in the bulk of the solution, is called the boundary or diffusion layer. This boundary layer has a gradient of ionic concentration in it, which is zero at limiting current density.

In order for electrolysis to be viable in the effective removal of metal ions from dilute solutions, the boundary layer needs to be broken down or reduced. If the thickness of the boundary layer is not reduced and the current is increased beyond that which brings the ion concentration at the electrode surface to zero, then other competing reactions such as the evolution of hydrogen will take place and so the current efficiency of the reaction will be reduced.

Hence, migration and convection are not effective, in dilute solutions, for the transportation of ions, because the force of adhesion between the surface of the electrodes and the layer of the solution (the boundary layer), reduce the hydrodynamic flow in the immediate vicinity of the electrodes to zero. Migration, by itself is not sufficient to transport ions through the barriers of the boundary layer to the surface of the electrode. Therefore the only method by which ions can be transported through the boundary layer to the electrode surface is by diffusion.

Graham's law states that the rate of diffusion in an electrolyte is directly proportional to the concentration of the dissolved substances and Fick's law states that the rate of diffusion in any given direction is directly proportional to the rate at which the concentration diminishes in that



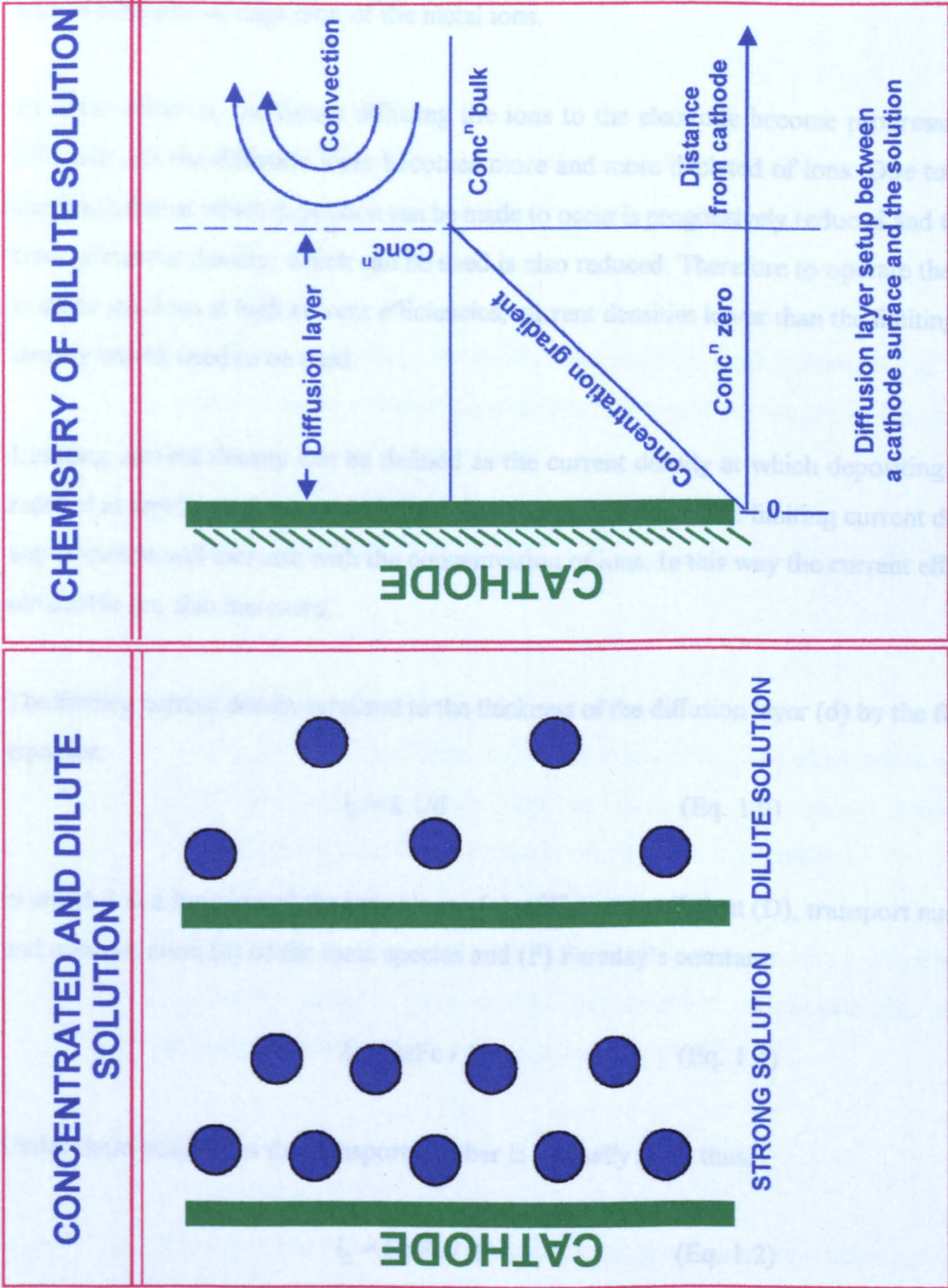


Figure. 1.1:- Diffusion layer set-up between the bulk solution and the surface of the cathode

direction. The operation of these two laws, in normal (non-dilute) electrolyte solutions, ensures that as metal ions are removed from solution at the cathode surface, they are replaced by metal ions from the bulk solution. At these concentrations, the boundary layer has no effect on the rate of diffusion or migration of the metal ions.

In dilute solution, the forces diffusing the ions to the electrode become progressively less effective and the diffusion layer becomes more and more depleted of ions. Due to this, the maximum rate at which deposition can be made to occur is progressively reduced and the upper limit of current density, which can be used is also reduced. Therefore to operate the process in dilute solutions at high current efficiencies, current densities lower than the limiting current density would need to be used.

Limiting current density can be defined as the current density at which depositing ions are reduced as rapidly as they can diffuse to the electrode surface. The limiting current density of any electrode will increase with the concentration of ions. In this way the current efficiencies obtainable are also increased.

The limiting current density is related to the thickness of the diffusion layer ( $d$ ) by the following equation:

$$i_L = k \cdot l/d \quad (\text{Eq. 1.0})$$

in which  $k$  is a function of the ion valency ( $z$ ), diffusion coefficient ( $D$ ), transport number ( $t$ ) and concentration ( $c$ ) of the ionic species and ( $F$ ) Faraday's constant:

$$k = DzFc / 1-t \quad (\text{Eq. 1.1})$$

Under these conditions the transport number is normally zero, thus:

$$i_L = DzFc / d \quad (\text{Eq. 1.2})$$

If the diffusion layer thickness is constant, then a decrease in ionic concentration will produce

a proportional decrease in limiting current density. Similarly by decreasing the diffusion layer thickness, it is possible to increase the limiting current density, thereby increasing recovery rates. All methods of reducing the boundary layer thickness involve mechanical agitation of either the solution or electrodes<sup>[21]</sup>.

## **1.6 THEORY OF ADSORPTION**

Adsorption is a surface phenomenon that is defined as the increase in concentration of a particular component at the surface or interface between two phases. There are two types of adsorption:

- (a) **physical adsorption** - involving only relatively weak intermolecular forces
- (b) **chemisorption** - formation of a chemical bond between the sorbate molecule and the surface of the adsorbent

Physical adsorption can be distinguished from chemisorption according to the following criteria:

- (a) physical adsorption does not involve sharing or transfer of electrons and so individuality of interacting species is maintained. The interactions are fully reversible, enabling desorption to occur at the same temperature. Chemisorption involves chemical bonding and is irreversible.
- (b) physical adsorption is not site-specific; the adsorbed molecules are free to cover the entire surface. In contrast, chemisorption is site-specific, whereby chemisorbed molecules are fixed at specific sites<sup>[22]</sup>.

The basic phenomena of adsorption and desorption are shown in Figure. 1.2.

The solid on which adsorption occurs is the adsorbent and it comprises of so-called active sites, which can bind molecules from the gaseous or solid phase. The molecule to be adsorbed is called adsorptive and, when adsorbed, it forms the adsorbate. The interface consisting of a thin

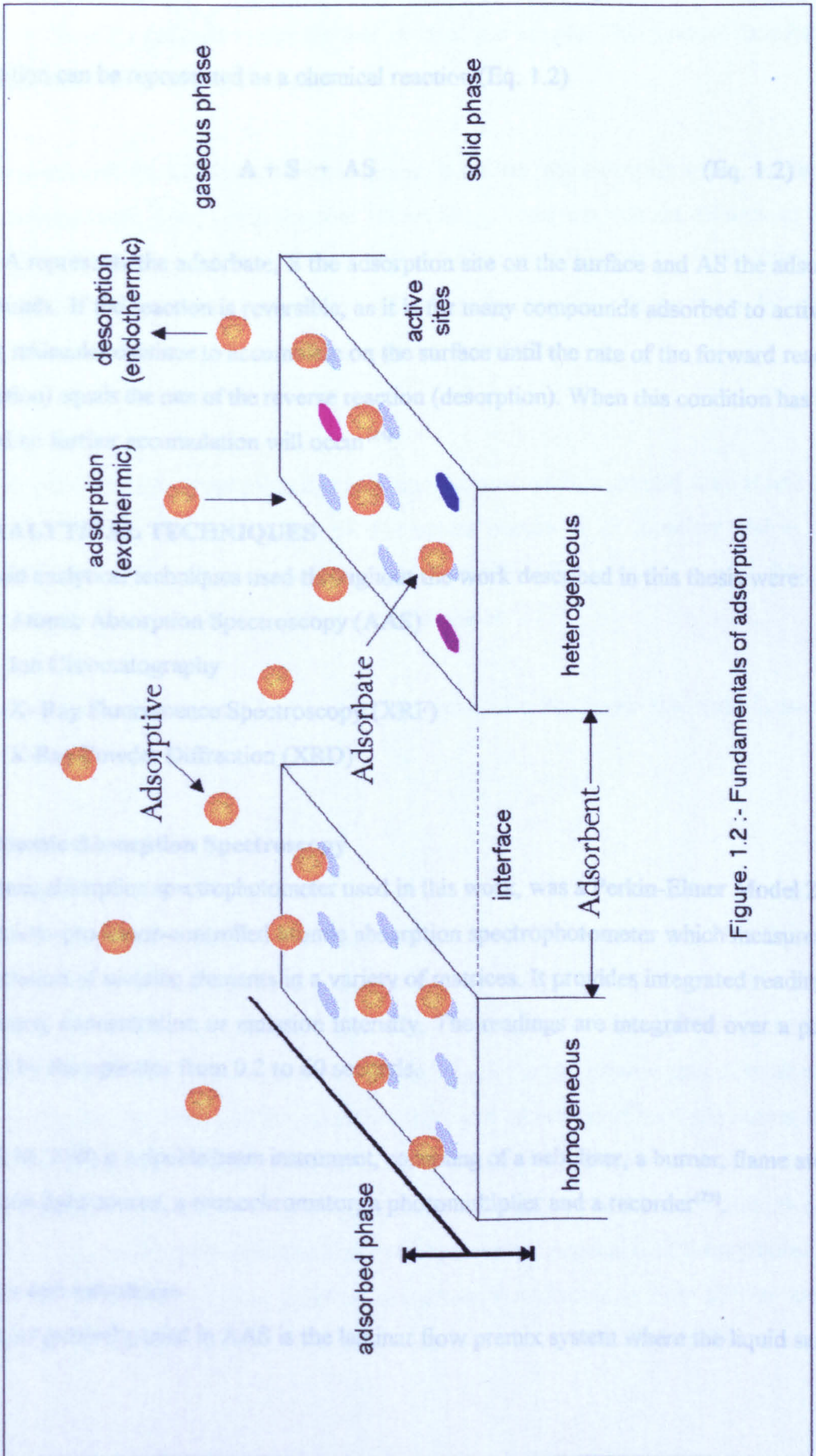


Figure. 1.2 :- Fundamentals of adsorption

layer of adsorbent and adsorbed molecules is called the adsorbed phase<sup>[23]</sup>.

Adsorption can be represented as a chemical reaction (Eq. 1.2)



where A represents the adsorbate, S the adsorption site on the surface and AS the adsorbed compounds. If the reaction is reversible, as it is for many compounds adsorbed to activated carbon, molecules continue to accumulate on the surface until the rate of the forward reaction (adsorption) equals the rate of the reverse reaction (desorption). When this condition has been reached no further accumulation will occur<sup>[24]</sup>.

## 1.7 ANALYTICAL TECHNIQUES

The main analytical techniques used throughout the work described in this thesis were:-

- (a) Atomic Absorption Spectroscopy (AAS)
- (b) Ion Chromatography
- (c) X-Ray Fluorescence Spectroscopy (XRF)
- (d) X-Ray Powder Diffraction (XRD)

### 1.7.1 Atomic Absorption Spectroscopy

The atomic absorption spectrophotometer used in this work, was a Perkin-Elmer Model 2380. It is a micro-processor-controlled atomic absorption spectrophotometer which measures the concentration of metallic elements in a variety of matrices. It provides integrated readings in absorbance, concentration or emission intensity. The readings are integrated over a period selected by the operator from 0.2 to 60 seconds.

The P.E.M. 2380 is a double beam instrument, consisting of a nebulizer, a burner, flame atomic absorption light source, a monochromator, a photomultiplier and a recorder<sup>[25]</sup>.

#### Burners and nebulizers

The burner generally used in AAS is the laminar flow premix system where the liquid sample

is introduced into a burner through the nebulizer by the venturi action of the nebulizer oxidant. Premix chambers are designed to mix the fuel, oxidant and sample. This mixture then flows to the burner head where atomisation occurs.

In passage through the nebulizer the liquid stream is broken into a droplet spray, mixing with the oxidant and fuel. The premix chamber allows large droplets which are deleterious to the adsorption process, to condense and pass out of the chamber through the liquid drain tube. Rejection of these large drops helps minimise light-scattering effects in the flame. Figure. 1.3 shows a cross-section of a nebulizer premix burner assembly.

### **Atomisation**

In order to have atomic absorption, it is necessary to produce free ground state atoms of the element of interest. The production of free atoms occurs in an atomiser and is called atomisation. A variety of commercial atomisers is available for use with atomic absorption equipment, the most common being flames and furnaces.

The most commonly employed flames in atomic absorption are the air-acetylene flame or the nitrous oxide flame.

### **Radiation sources**

#### **Hollow cathode lamp**

Hollow cathode spectral lamps are the most common radiation sources for AAS. Figure. 1.4 shows the essential components of a hollow cathode lamp. The hollow cathode lamp is comprised of a hollow cup cathode made from the metal or an alloy of the element being determined and a tungsten anode filled with about 2 torr of argon or neon gas. A small current is passed between the anode and the cathode resulting in ionisation of inert-gas atoms, as ions and electrons migrate to the electrodes. If there is sufficient potential, the gaseous cations acquire enough kinetic energy to dislodge some of the metal atoms from the cathode surface producing an atomic cloud in a process known as 'sputtering'. A portion of the sputtered metal atoms will be in excited states, emitting characteristic radiation as they diffuse back and redeposit on the cathode surface or the glass walls of the lamp tube. The cylindrical design of

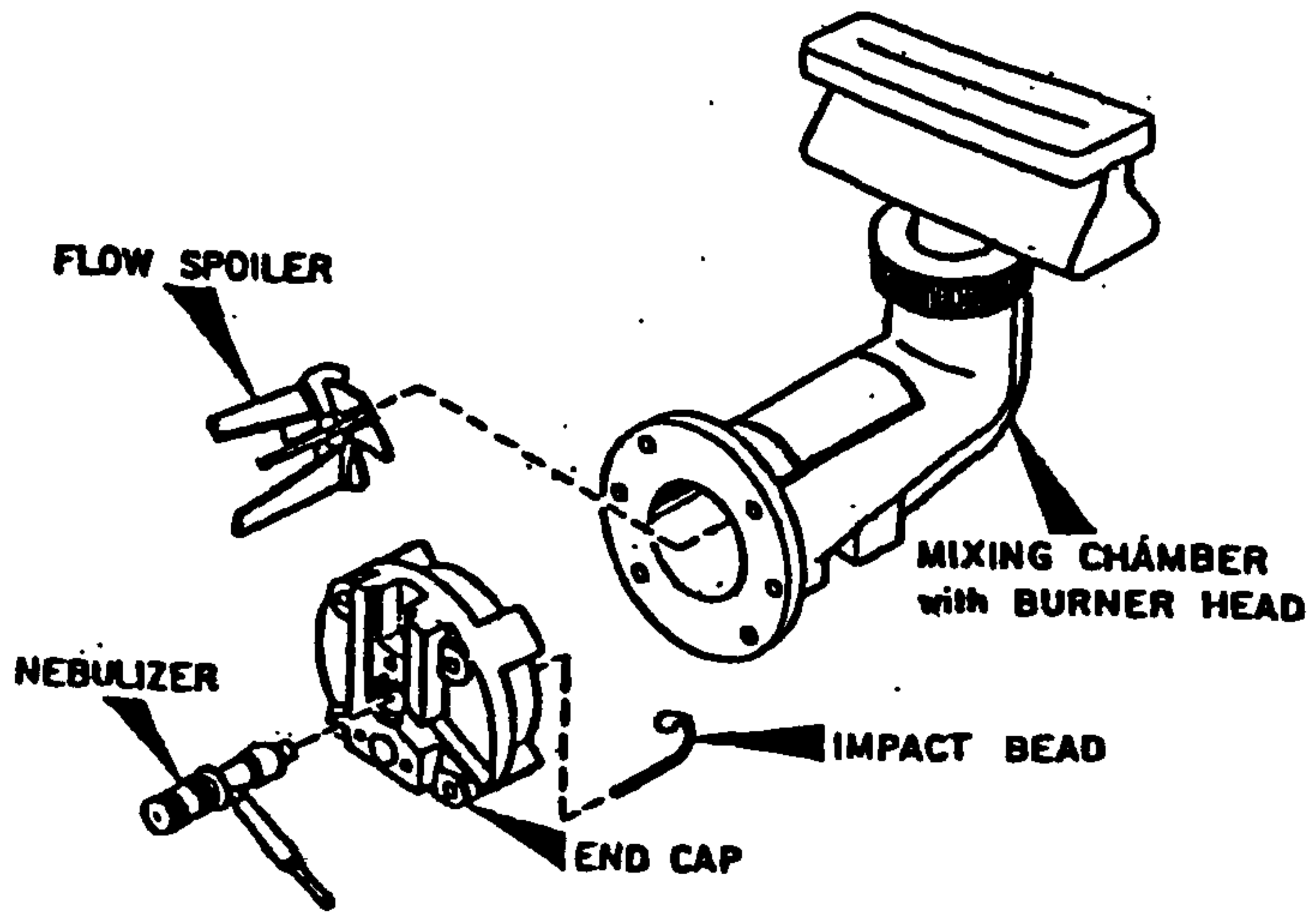


Figure. 1.3:- Diagram of a dual-option burner system

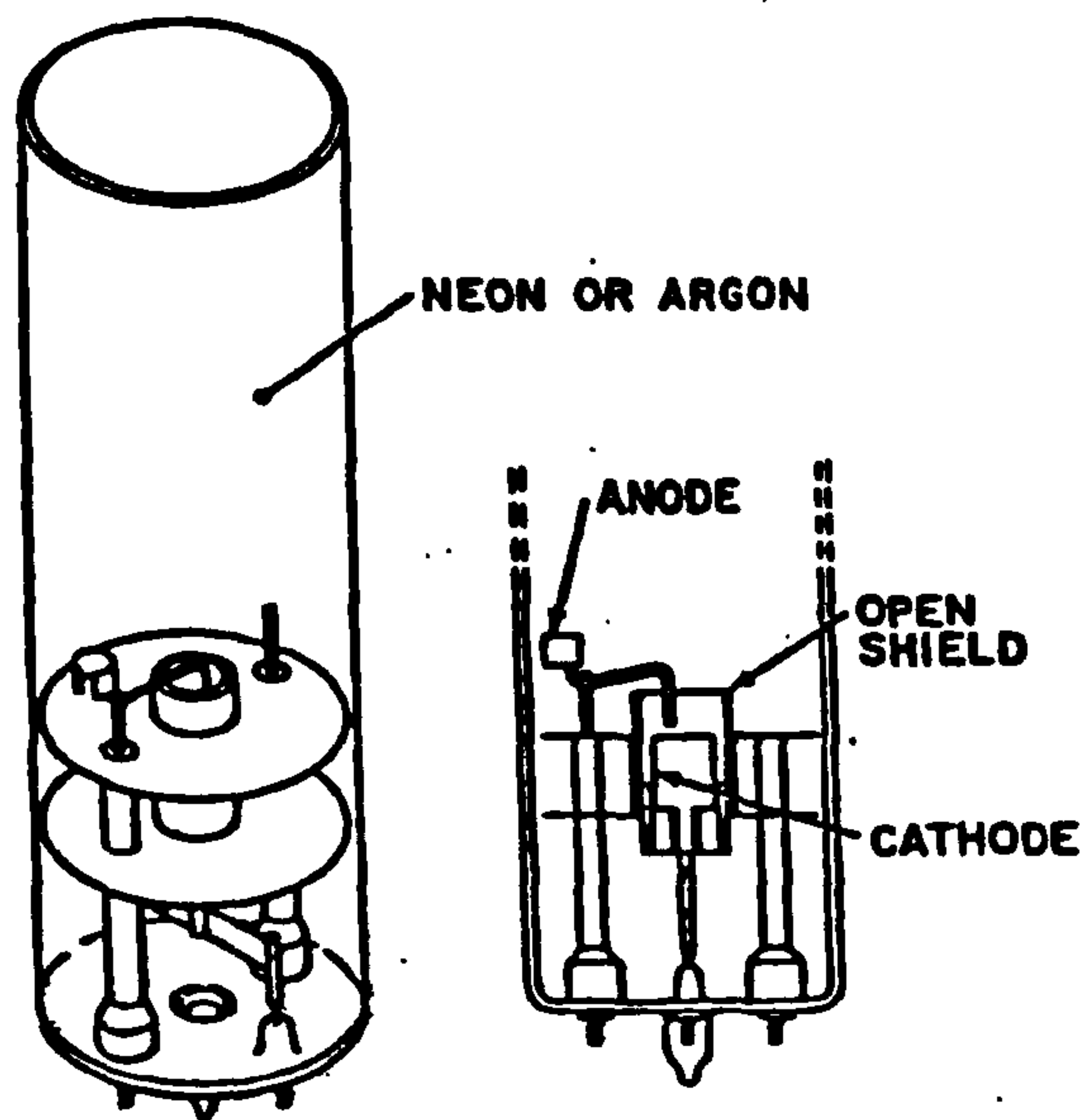


Figure. 1.4:- Diagram of a hollow cathode lamp

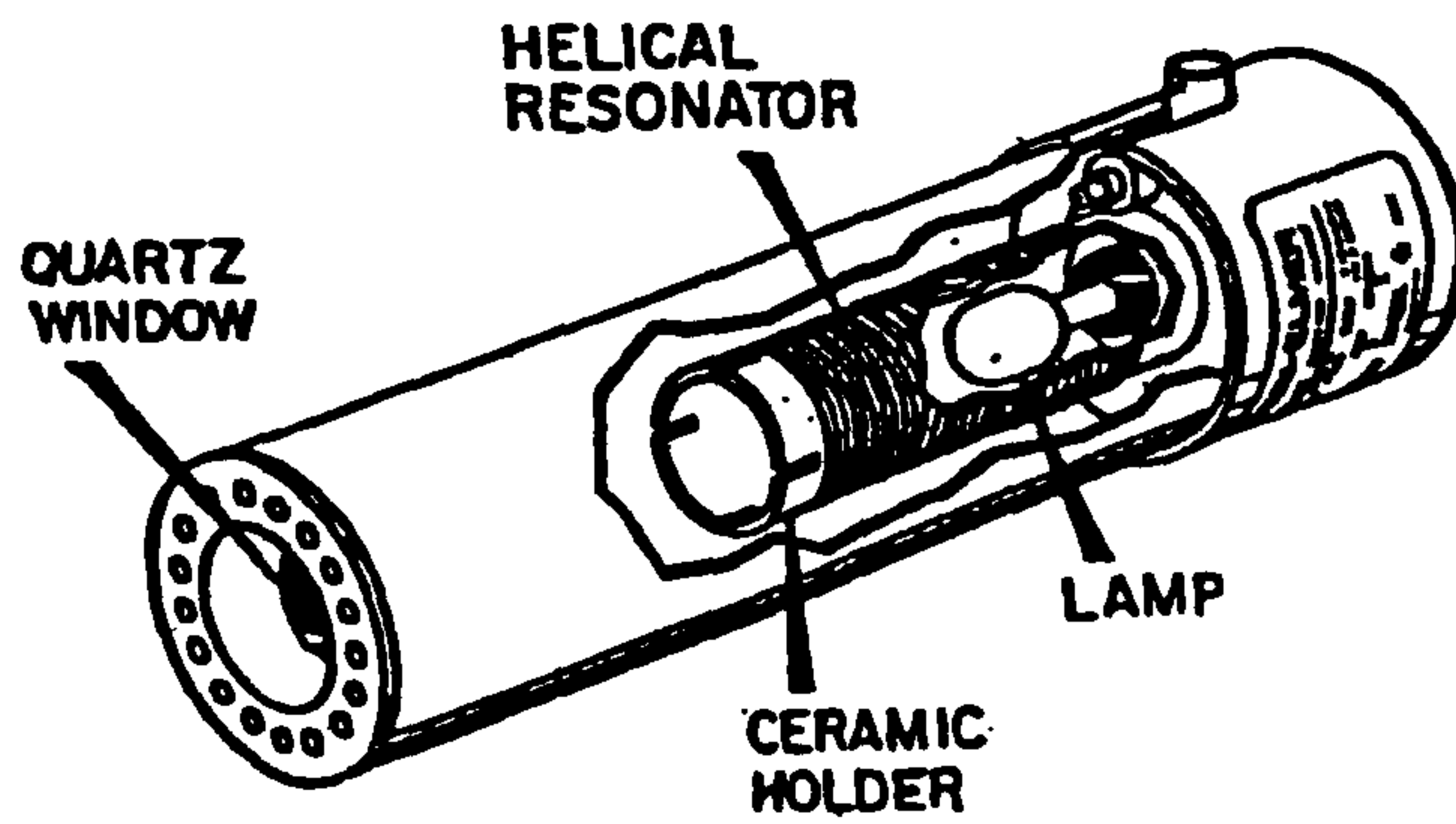


Figure. 1.5:- Diagram of an electrodeless discharge lamp

the cathode tends to concentrate the radiation in a limited region of the tube, thus enhancing the probability that redeposition will occur at the cathode rather than on the glass walls of the tube. This helps to prolong the life of the lamp. The light emitted is then passed through a monochromator, usually a grating or a prism, to separate the resonance lines from the spectral lines<sup>[26]</sup>.

### **Electrodeless discharge lamps**

Electrodeless discharge lamps are constructed by sealing a small amount of the pure metal or pure metal salt of the element of interest inside a quartz bulb together with an inert gas at low pressure. The bulb is placed inside a ceramic cylinder on which a helical, radio frequency resonator, is coiled [Figure. 1.5]. When a radio frequency field is applied, the energy ionises the inert gas and excites the metal atoms inside the bulb into emitting their characteristic spectrum<sup>[27,28]</sup>.

### **Optics**

A diagram of the layout of single and double beam AAS instruments is given in Figure. 1.6. The monochromator is placed after the atom reservoir to help diminish light flux on the phototube. The purpose of the monochromator is to isolate the resonance line and to decrease the emission intensity from the atomiser. The Perkin Elmer Model 2380 AAS is a double beam instrument, in which the light emitted from the hollow cathode lamp is split by a mirrored chopper, one half going through the flame and the other half by-passing it. The two beams are then recombined using a beam splitting mirror and pass into a grating monochromator, with a photomultiplier tube serving as the transducer. As a result of this process, double beam instruments lose a factor of two, but the system can beneficially correct fluctuations in the lamp output.

The output from the transducer is fed to a lock-in amplifier that is synchronised with the chopper drive. The ratio obtained between the sample and reference signal is amplified and then fed to a digital readout and printer giving a readout in absorbance.

### **Sensitivity**

Sensitivity in atomic absorption is defined as the concentration of a solution (typically in ppm)



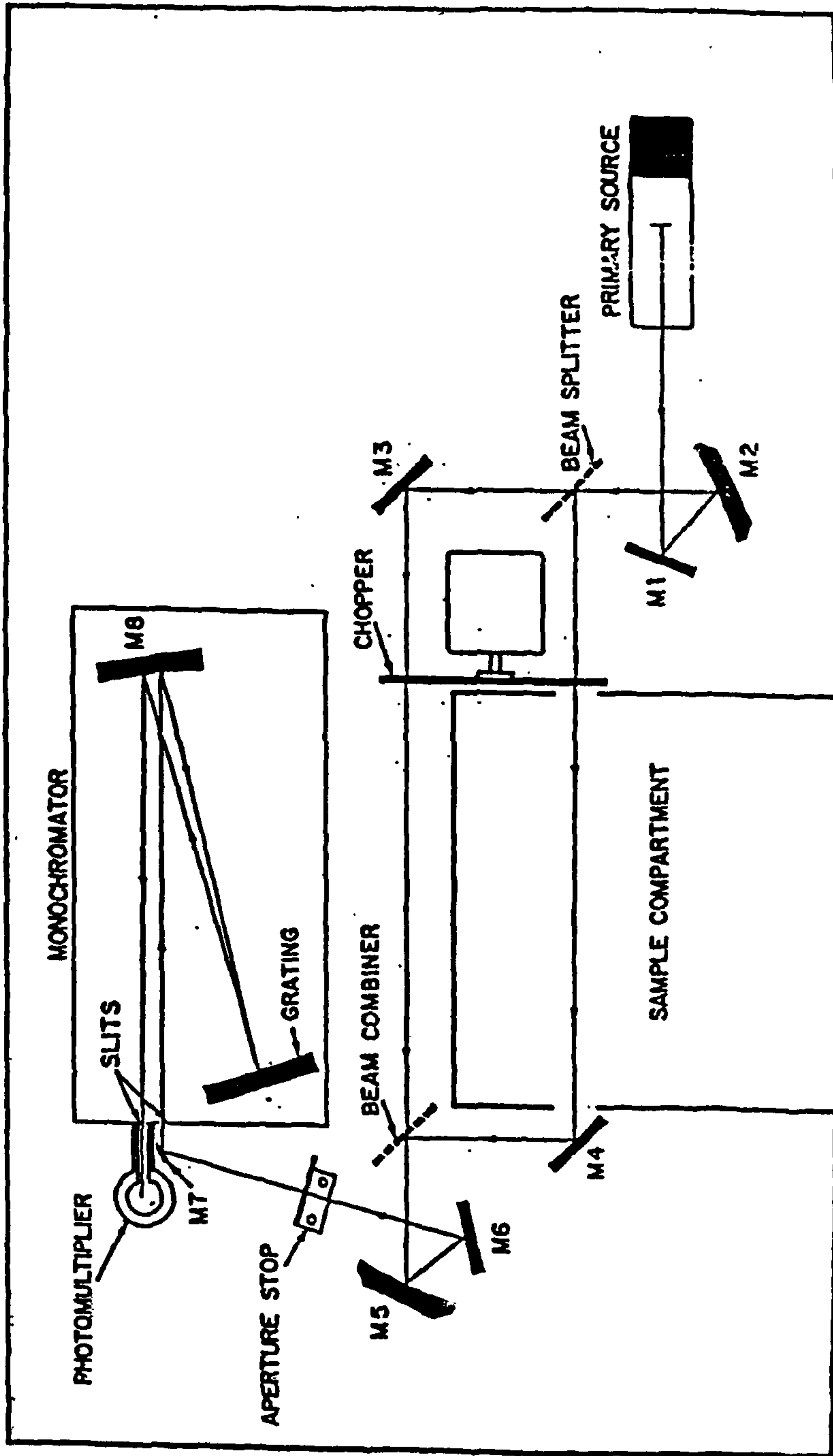


Figure. 1.6:- Schematic layout of a double beam atomic absorption spectrometer

of an element needed to produce a signal of 0.0044 absorbance units (1% absorption). The sensitivity figure is a useful performance index in that it gives the operator information about how well the machine has been optimised. As long as measurements are made in the linear range, the sensitivity of an element can be determined by reading the absorbance produced by a known concentration of the element, and putting it into the following equation (Eq. 1.3):

$$\frac{\text{Concentration of standard}}{\text{Measured absorbance}} = \frac{\text{Sensitivity}}{0.0044} \quad (\text{Eq. 1.3})$$

Knowing the expected sensitivity allows the prediction of the absorbance range that will be observed for a known concentration range of the element of interest.

### **1.7.2 Ion Chromatography**

Since its introduction in the mid-1970's, Ion Chromatography (IC) has become a widely used analytical technique for the determination of all types of ions. Ion chromatography is a liquid chromatographic technique using ion exchange mechanisms and suppressed conductivity detection for the separation and determination of anions and cations.

Chromatography basically involves separation due to differences in the equilibrium distribution of sample components between two different phases. One of these phases is a moving or mobile phase and the other is a stationary phase. The sample components migrate through the chromatographic system only when they are in the mobile phase. The velocity of migration of a component is a function of the equilibrium distribution. The components having distributions favouring the stationary phase migrate slower than those having distributions favouring the mobile phase. Separation then results from different velocities of migration as a consequence of difference in equilibrium distributions.

Ion chromatography is based on the distribution of solutes between a mobile phase and a stationary phase where component separation occurs through the mass transfer effects.

## **High Performance Ion Chromatography (HPIC)**

This involves ion exchange between the mobile phase and ion-exchange groups covalently bound to the stationary phase. The stationary phase is a polystyrene based resin which has been crosslinked with divinyl benzene. For the analysis of anions, the exchange function is usually a quaternary ammonium group, whereas for the analysis of cations, a sulphonate group is most often employed [Figure. 1.7].

### **Instrumentation**

The ion chromatograph used was the Dionex 2010 i. Figure. 1.8 shows the schematic diagram of such a chromatograph. The parts in contact with the mobile phase are constructed from inert non-metallic materials to prevent metallic contamination.

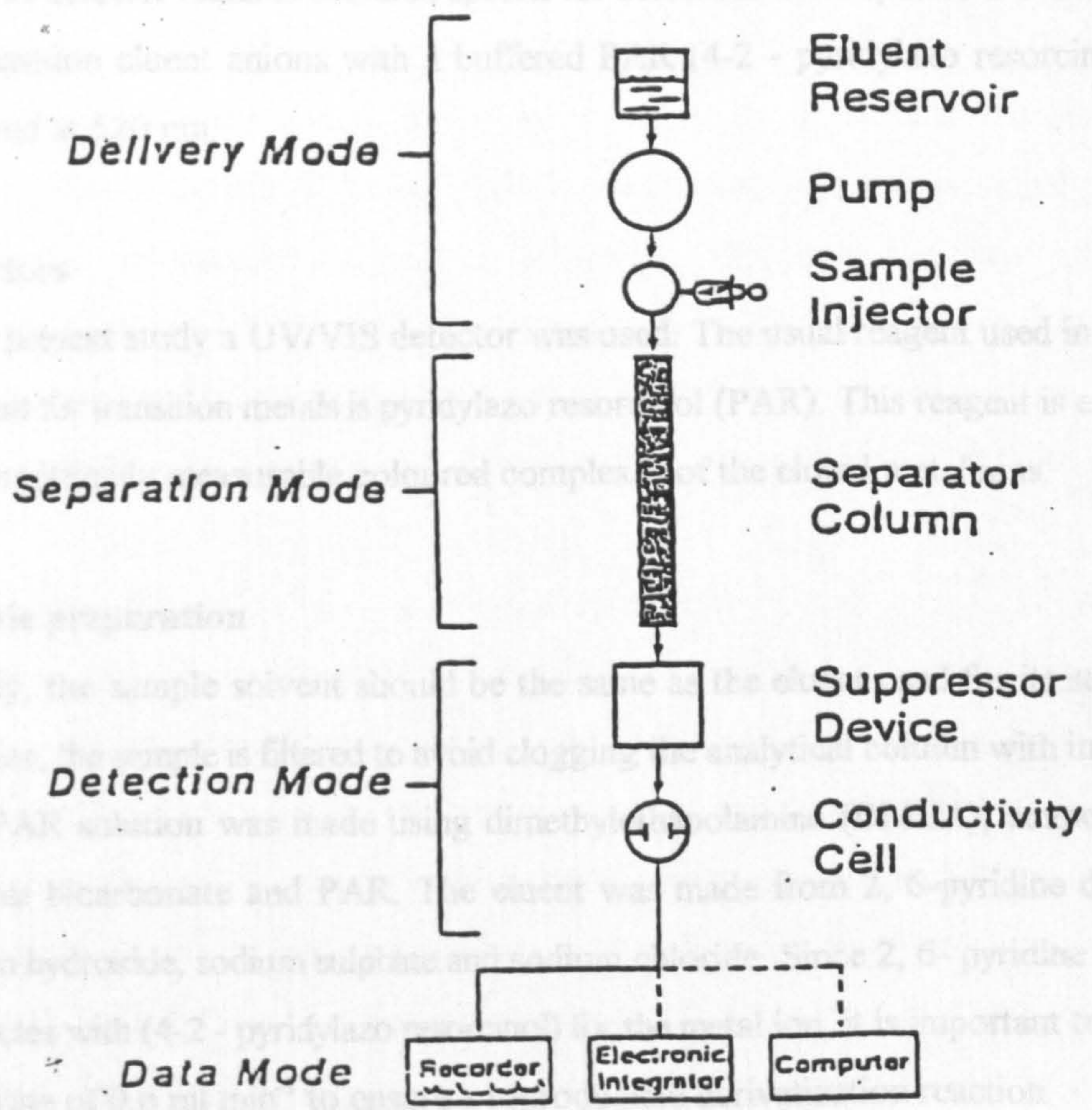
The mobile phase is pumped through the chromatographic system by a double reciprocating pump. A double piston pump gives the constant flow rate which is essential for reproducible analysis. Flow rates between 0.1 and 9.9 cm<sup>3</sup> min<sup>-1</sup> in steps of 0.1 cm<sup>3</sup> min<sup>-1</sup> can be selected with a maximum optimum pressure of 2000 psi. A pulse-free flow, necessary for the UV/VIS detector, is ensured by an electronic controller. Samples are introduced into the system via a 50 µl loop injector.

The two outlets of the sample loop are joined by a three-way valve, through which the sample is transported onto the column by the eluent.

The most important part of the chromatograph is the analytical column. The quality of analysis is determined by the stationary phase and the chromatographic parameters. The column is made of an inert plastic and operated at room temperature. Separator columns vary in size and crosslinking.

Ideally the eluent should have a similar affinity for the stationary phase as the ions to be analysed. A mixture of sodium carbonate and sodium bicarbonate is used for anion separation, because relative sensitivity can be altered by varying the proportion of carbonate and bicarbonate. Basically an eluent consists of a mixture of ionic species which act as a “pusher”





**Figure. 1.8:- A typical Dionex Ion Chromatograph configuration**

Transition metals are separated on ionex using chelating or complexing eluents. The ability of metals to form neutral and anionic complexes with anionic organic chelating agents permits the separation of the metals by cation and/or anion exchangers. A variety of transition metal separations can be obtained by simply changing the eluents.

### 1.2.3 X-ray Fluorescence Spectroscopy

X-ray fluorescence analysis is a rapid, non-destructive, qualitative and quantitative method of

of the analyte species. The analyte species migrate differentially down the column. For various separations the eluent is directed to the detector. Transition metal detection comprises a sensitive and selective postcolumn derivatization with a visible absorbance detector. The UV/VIS detector requires coloured species for detection. Such species are formed by chelation of transition eluent anions with a buffered PAR (4-2 - pyridylazo resorcinol) solution and detected at 520 nm.

### **Detectors**

In the present study a UV/VIS detector was used. The usual reagent used in the post-column reaction for transition metals is pyridylazo resorcinol (PAR). This reagent is employed to form photometrically measurable coloured complexes of the eluted metal ions.

### **Sample preparation**

Ideally, the sample solvent should be the same as the eluent used for its separation. Before injection, the sample is filtered to avoid clogging the analytical column with insoluble particles. The PAR solution was made using dimethylethanolamine (DMEA), ammonium hydroxide, sodium bicarbonate and PAR. The eluent was made from 2, 6-pyridine dicarboxylic acid, lithium hydroxide, sodium sulphate and sodium chloride. Since 2, 6- pyridine dicarboxylic acid competes with (4-2 - pyridylazo resorcinol) for the metal ion, it is important to maintain a PAR flow rate of  $0.6 \text{ ml min}^{-1}$  to ensure a reproducible derivatization reaction.

All reagents used were of analar grade. The standard solutions were prepared by diluting an appropriate AAS standard solution.

Transition metals are separated on resins using chelating or complexing eluents. The ability of metals to form neutral and anionic complexes with anionic organic chelating agents permits the separation of the metals by cation and/or anion exchangers. A variety of transition metal separations can be obtained by simply changing the eluents<sup>[29]</sup>.

### **1.7.3 X-ray Fluorescence Spectroscopy**

X-ray fluorescence analysis is a rapid, non-destructive, qualitative and quantitative method of

determining elements in solids and liquids. The principle of the technique is based on the measurement of wavelengths and intensities of x-rays emitted by a sample, when excited by the rays from a primary x-ray tube. An Oxford Instruments XR 300 X-Ray Fluorescence Spectrometer was used.

If an atom consists of a nucleus surrounded by a system of electrons contained in shells called K, L, M, the electrons in K, L and M shells are the electrons with principal quantum numbers 1, 2 and 3 respectively. An electron bombarding the target may have sufficient energy to completely displace a K electron from the target atom. This produces an unstable ion, and  $10^{-4}$  seconds later an electron from an outer shell drops into the vacant position. This transition is accompanied by the emission of a characteristic x-ray: a photon of definite wavelength.

The relationship between mass absorption coefficient and x-ray wavelength shows that absorption generally increases with increasing wavelength. This is to be expected since x-rays having long wavelengths have less energy than those having short ones. Thus the longer wavelengths have less penetrating power and are more readily absorbed. However, there are a number of vertical discontinuities called absorption edges. These occur at definite wavelengths for specific absorbing materials. If the K-absorption edge of tungsten, for example, occurs at  $0.178 \text{ \AA}$  then x-rays of wavelength  $0.178 \text{ \AA}$  have just enough energy to displace K-electrons from tungsten atoms, whereas x-rays having longer wavelengths have insufficient energy to do so. When high speed electrons dislodge K electrons from atoms, electrons from outer levels fill the vacancies, and characteristic x-rays are emitted. Similarly, x-rays having wavelengths less than or equal to the K absorption edge of an atom, will displace K electrons, so characteristic x-rays will again be emitted. This phenomenon is called x-ray fluorescence. Subsequent movement of electrons from outer levels into these vacant positions gives rise to the emission of characteristic radiation x-rays of definite wavelengths.

### **Detection**

The resultant secondary x-rays are analysed by an Energy Dispersive (ED) system, which consists of devices to detect the X-rays, measure their energy and compute the data. X-rays pass through a thin beryllium window into a cooled, reverse biased, lithium drifted silicon

crystal. The crystal converts the X-ray energy into a pulse of electrical charge. The charge is converted into a voltage pulse by a pre-amplifier, which also amplifies the pulse to a high enough level to be passed along cables to the pulse processor. The pulse is then converted to a digital signal and put into a multi-channel analyser, from where it can be viewed and analysed<sup>[30]</sup>.

#### **1.7.4 X-ray Powder Diffraction**

X-rays are electromagnetic radiation of wavelength approximately 1 Å, that lie between gamma-rays and ultra-violet rays in the electromagnetic spectrum. They are produced by high energy collisions of charged particles with matter. Usually a beam of accelerated electrons is allowed to strike a metal target such as copper. Because the separation of the atoms in a crystal sample is of the same order of magnitude as the wavelength of x-radiation, then the radiation will be diffracted by the sample in the same way that light is diffracted by an optical grating<sup>[31]</sup>.

X-ray diffraction is a powerful physical technique which has been used since the early twentieth century for the identification of crystalline materials and the determination of crystal structure<sup>[32,33]</sup>. Each atom in a crystal has the power of scattering an x-ray beam incident on it. The sum of all the scattered waves in the crystal results in the x-ray beam being, in effect, diffracted from each allowed crystal plane. Every crystalline substance scatters the x-rays in its own unique diffraction pattern producing a 'fingerprint' of its atomic and molecular structure.

Crystals may be regarded as being built of layers or planes, that function like semi-transparent mirrors. When a monochromatic x-ray beam strikes a plane, some of the x-rays are reflected off the plane, where the angle of incidence is equal to the angle of reflection. The rest are transmitted to be subsequently reflected by succeeding planes [Figure. 1.9].

It is only when Bragg's Law is obeyed that the reflected beams are in phase and interfere constructively. At angles of incidence other than the Bragg angle, the reflected beams are out of phase and interfere destructively.

a) Parallel rays are reflected from different points of a plane and are in phase after



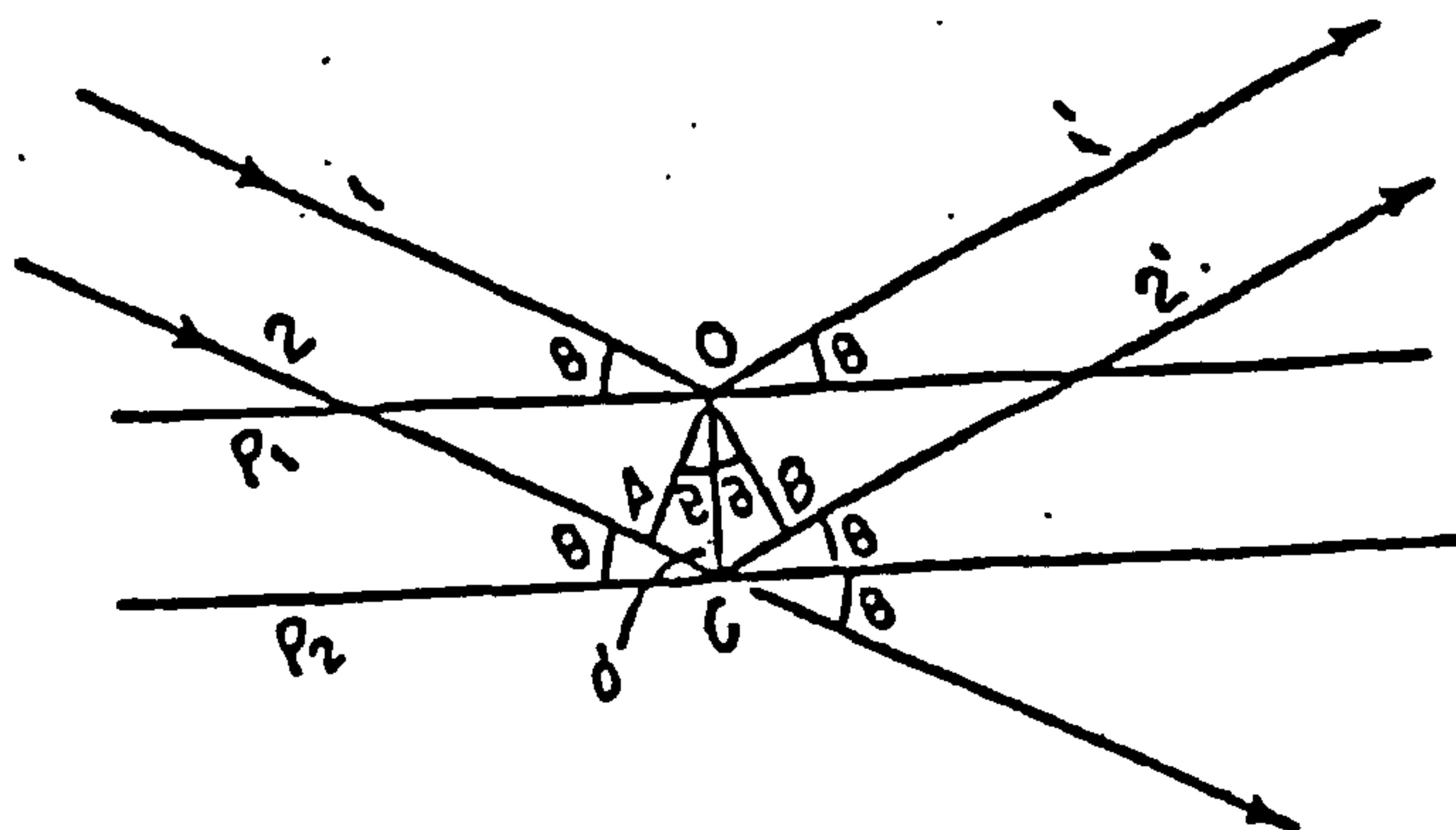


Figure. 1.9:- Construction showing conditions of diffraction

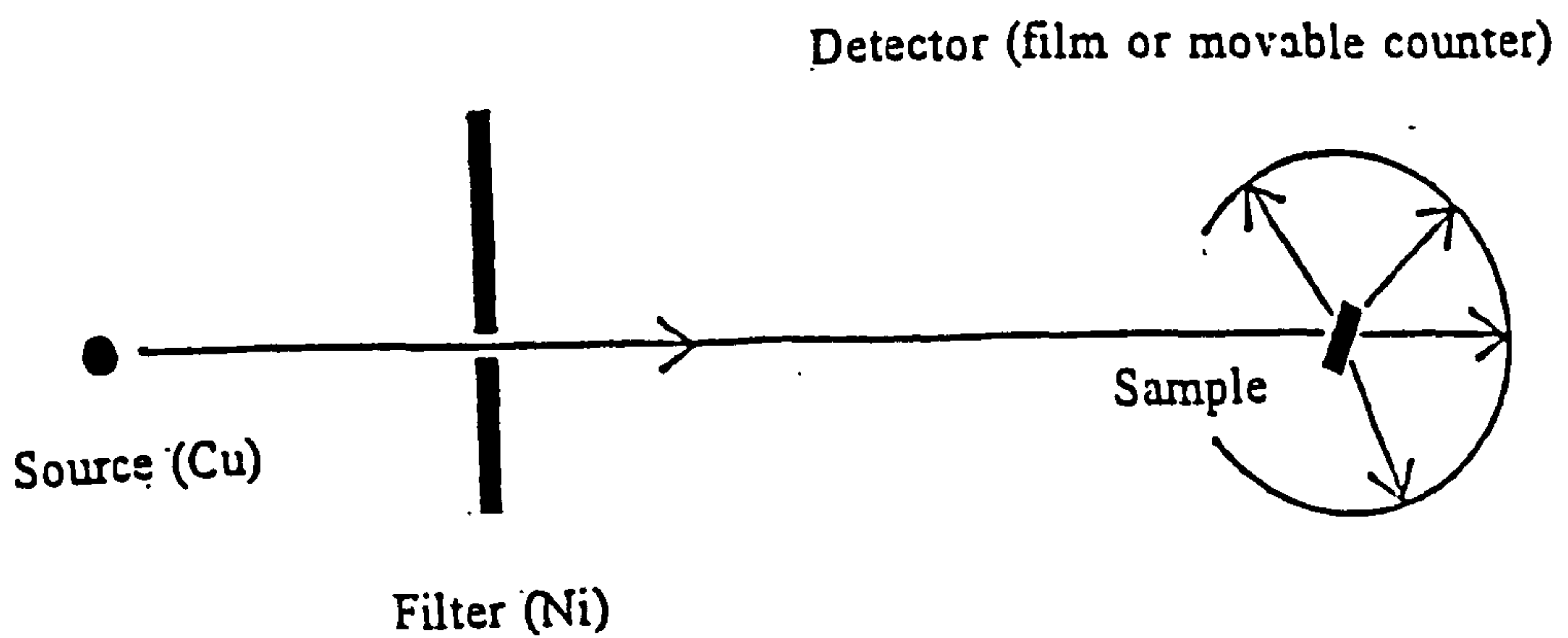


Figure. 1.10:- A simplified diffractometer arrangement

reflection.

- b) Parallel rays reflected from points on neighbouring partially-reflecting planes are in phase when Bragg's law is obeyed.

From b) it can be seen that

$$CB = AC = d\sin\theta \quad \text{giving}$$

$$2d\sin\theta = n\lambda$$

This expression is known as Bragg's law and it gives the permitted angles of reflection,  $\theta$ , in terms of  $\lambda$  and the spacing of the reflecting planes,  $d$ .

The basic information required in crystal structure determination may be obtained from the intensity of each reflection. The relative scattering of different atoms varies due to their having a different number of electrons. Thus the crystal structure dictates the intensity and position of the diffracted beam. Even when two crystals have identical lattices, the kinds of atoms comprising them may be different. Hence, each crystal species diffracts X-rays in a characteristically different way. Figure. 1.10 shows a simplistic diagram of an X-ray powder diffractometer.

### **Instrumentation**

In this work, the instrument used for collecting the X-ray powder data was a Phillips PW1729 X-ray generator using Cu  $K\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) in conjunction with a Phillips PW 1710/00 diffraction control unit. The sample is spun in its own plane and, at the same time, a counter rotates with twice the angular velocity of the sample. The intensity of the diffracted radiation beam is detected using a movable detector (i.e. a scintillation counter) connected to a chart recorder (diffractometer) and is recorded both continuously on a chart as a trace of intensity versus  $2\theta$  and stepwise on a digital printer<sup>[34]</sup>.

## **1.8 AIMS AND OBJECTIVES OF THE RESEARCH WORK**

The aim of the work described in this thesis is to develop techniques for the removal and recovery of metals from industrial effluent taking account of the consequences of the definition of waste in the Basel Convention on transfrontier shipment of waste.

The specific objectives are:-

- (i) to develop and optimise technology for the recovery of cobalt from dilute aqueous solutions
- (ii) to develop and optimise recovery of primarily copper from mixed metal solutions
- (iii) to apply novel concentrator technology to the recovery and recycle of metals from industrial waste streams
- (iv) to investigate the leachability of copper and zinc from metallurgical wastes, as a means of determining bioavailability
- (v) to develop a methodology to assess the classification of wastes under the Basel Convention based on characterisation by leachability and speciation, and
- (vi) to obtain for selected metals subject to the Basel ban, data to be used in the methodology in conjunction with speciation data.

## **1.9 LAYOUT OF THESIS**

This introductory chapter contains descriptions of the background and the research carried out and the analytical techniques used throughout the work and is followed by chapters dealing with the following topics.

Chapter two describes work carried out on the recovery of cobalt from dilute solutions using existing fluidised bed electrochemical cell technology and new techniques, developed in this work that extend the range of applicability of the fluidised bed cell using concentrator methods.

This work is extended to consider the recovery of copper from three different hydrometallurgical solutions *viz* i) Cu/Zn, ii) Cu/Zn /Fe and iii) Cu/Zn/Cd containing effluents and the results are described in chapter three.

The use of different concentrator techniques to recover and separate metal values from industrial effluent samples are described in chapter four including work on the separation of heavy metals from mixed effluent streams and the preparation of added-value chemicals from the recovered metals.

The leaching of metals from industrial materials and pure chemicals is the subject of the studies reported in chapters five and six. Different leach liquors are used to model different environmental conditions. The Basel Convention has changed the requirements for materials being shipped to developing countries for treatment and recycle. As it stands, the Convention attempts to impose a ban on any material containing any of the intrinsically hazardous substances listed in an Annex. Some metals such as cadmium, lead, copper and zinc are included in the list. The results from the leaching studies in this work have been used to interpret the availability of the metals thus representing real risk rather than intrinsic hazard in the context of the Basel Convention.

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## CHAPTER TWO

### THE USE OF A FLUIDISED BED CELL IN THE RECOVERY OF COBALT FROM DILUTE AQUEOUS SOLUTION

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## **2 INTRODUCTION**

The chapter begins with a description of the chemistry of cobalt and its uses before summarising studies on the recovery of cobalt using electrolytic methods. The work presented in this chapter describes for the first time the use of activated carbon cloth (ACC) as a concentrator cell for recovery of cobalt and the use of MgO as an alternative pH controller.

### **2.1 COBALT**

Cobalt (Co) is a metallic metal. Along with iron and nickel it is one of the first row transition metal members of group VIII of the periodic table. Its electronic configuration is  $4s^23d^7$  beyond the argon core giving it an atomic number of 27. The atomic weight of cobalt is 58.93.

In bulk form, cobalt is resistant to many mild corrosive agents but it is more readily attacked when it is in powder or finely divided form. Cobalt is strongly attacked by concentrated nitric acid at ambient temperatures and the metal dissolves slowly in dilute mineral acids.

Cobalt is harder than iron or nickel but more brittle. It is not corroded by air or water, is resistant to alkalis but soluble in acids. Its most important properties are its magnetic powers, its capacity to form alloys, as an essential trace element in the formation of vitamin B<sub>12</sub> and as a radioactive source. Only one of its isotopes, <sup>59</sup>Co, is stable and naturally occurring - the other 12 known isotopes are radioactive.

Cobalt is normally bivalent (cobaltous) but trivalent (cobaltic) compounds also occur. Cobaltous salts tend to be pink in colour in the cationic state and blue in the anionic state. The complex cobaltamines formed with ammonia are of importance in the separation of cobalt from nickel, especially in the preparation of pure metallic cobalt for wire - making and for the manufacture of radioactive sources.

Cobalt metal is used extensively in commercial and military aircraft engines and in aerospace equipment. Cobalt is recovered mainly by hydrometallurgical processes. Metallic cobalt is produced either by chemical or electrochemical reduction of cobalt sulphate. The latter route is more commonly used since most of the virgin cobalt metal now produced is obtained by

electrowinning from a solution of its salt, commonly in the form of sulphate. Cobalt may be electrowon from either a pure sulphate bath, or from a sulphate bath containing additives such as  $\text{Na}_2\text{SO}_4$ ,  $\text{H}_3\text{BO}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NaF}^{(1)}$ .

As cobalt is ferromagnetic ( i.e. it can be magnetised permanently) one fifth of its production is used in the manufacture of magnetic alloys such as AlNiCo (containing aluminium, nickel and cobalt). These alloys form the basis for magnets that are 20 - 30 times more powerful than iron - based magnets.

The production of the metal is also used in the manufacture of pigments for the paint, ceramic and glass industries. Historically cobalt oxide was used to give a blue colour to ceramics, and is currently used in the production of blue glass, although its major current use in this field is to overcome the yellow colour of iron to give a white colour.

### 2.1.1 Chemistry of Cobalt

In the case of cobalt recovery, the very different chemical behaviour of the element in its two most important oxidation states (II and III), provides convenient methods of achieving both the dissolution of cobalt and its separation from other metals present.

In acidic solutions and in the presence of complexing agents Co (II) is the stable oxidation state and oxidation to Co (III) is difficult. The oxidation can be achieved by electrolytic or ozone oxidation but the Co (III) is very unstable and rapidly reduces to Co (II). The differences in behaviour of Co (II) and Co (III) in solution are summarised in Table 2.1.

Table 2.1:- Differences in behaviour of Co (II) and Co (III)		
SOLUTION	REACTION	E (V)
Acid Solution	$\text{Co}(\text{H}_2\text{O})_6^{3+} + e^- \rightarrow \text{Co}(\text{H}_2\text{O})_6^{2+}$	1.84
Alkali Solution	$\text{CoO}(\text{OH}) + \text{H}_2\text{O} + e^- \rightarrow \text{Co}(\text{OH})_2 + \text{OH}^-$	0.17
Solutions of Donor Ligands	$\text{Co}(\text{NH}_3)_6^{3+} + e^- \rightarrow \text{Co}(\text{NH}_3)_6^{2+}$	0.10
	$\text{Co}(\text{C}_2\text{O}_4)_3^{3-} + e^- \rightarrow \text{Co}(\text{C}_2\text{O}_4)_3^{4-}$	0.57

In the absence of complexing agents, the solution chemistry of cobalt in acidic solutions is

dominated by Co (II). The most common species present is  $\text{Co}(\text{H}_2\text{O})_6^{2+}$ .

In alkali conditions Co (II) is more readily oxidised to Co (III), while in the presence of complexing agents, in any solution, oxidation to Co (III) is very easy.

Cobalt in its (II+) oxidation state forms a variety of complexes most of which have either tetrahedral or octahedral cobalt environments. The element is more favourable to form tetrahedral complexes than any other transition metal. This is because the difference between the crystal field stabilisation energies for tetrahedral and octahedral complexes formed with high spin  $d^7$  electronic configurations is very small<sup>[2]</sup>.

### **2.1.2 Uses of Cobalt**

In the pottery industry cobalt oxide was used in the clay body and in glazes to remove discolouration caused by iron and titanium oxides, and a yellow tinge which may occur when the lead oxide present is not fully converted to a silicate. However because the quantities of cobalt required are very small and control is difficult, it has tended to be replaced by selenium for this purpose. The black pigment, cobalt oxide, is used in the glaze for manufacture of jet ware, and also in combination with other pigments for a variety of other colours such as violet ( $\text{CoO}/\text{P}_2\text{O}_5$ ), green ( $\text{CoO}/\text{ZnO}$ ) and pink ( $\text{CoO}/\text{MgO}$ ). Cobalt oxides are also used in the manufacture of coloured pigments in concentrations of as little as 0.1% to 2%.

Cobalt compounds are used widely in paints, but more specifically in oil paints. Cobalt has been used in hair dyes and to a greater extent in tattoo formulations and preparations. For industrial paints, cobalt is used in gloss paints based on white spirit but not in the popular water-based emulsions.

Other uses for cobalt have been in cemented tungsten carbides, high-speed steels and as an important catalyst source for the petroleum industry. Another catalytic use has been in the after-burners of internal combustion engines to reduce atmospheric pollution<sup>[3]</sup>.

The main uses of cobalt are summarised in Table 2.2.

<b>Table 2.2:- Main uses of cobalt</b>	
Metallurgical	Superalloys, Wear resistant coatings, High speed steels, Prosthetics, Low expansion alloys, Steels, Corrosion resistant alloys
Magnetic Alloys	AlNiCo's, Rare earths, Soft magnetic Materials
Chemicals	Catalysts, Adhesives-cobalt soaps, Specialist Chemicals : Driers, Pigments, Colours, Electroplating, Agriculture and Medicine, Electro-magnetic recording
Electronics	Recording material, Matched expansion alloys, Leads
Ceramics and Enamels	Colours in glass, enamels, pottery and china

### 2.1.3 Cobalt in the Environment

Cobalt is released into the environment from various sources which are summarised in Table 2.3.

<b>Table 2.3:- Sources of cobalt</b>	
Natural Sources	Volcanic Emissions
	Extraction by plants
	Weathering of rocks and soils
Anthropogenic Emission into Air, Water and Soil	From ore and metal production
	From metal use
	From fossil fuels

Cobalt is an essential component for all animal life and is the central constituent of Vitamin B<sub>12</sub>. Grazing animals obtain cobalt from plants. However, in soils containing < 5 µg/g plant uptake is low. Ruminants fed on plants with cobalt levels below 0.08 µg Co/g show deficiency symptoms - pernicious anaemia and staggers. In some cases, cobalt is added to feedstuffs as cobalt sulphate and to pastures to counteract this. Humans take up cobalt from Vitamin B<sub>12</sub> in their diet, the source being animal protein.

Cobalt is essential to human health. In the form of Vitamin B<sub>12</sub>, it catalyses the regeneration of red blood cells. Without Vitamin B<sub>12</sub>, or if cobalt is not retained in the body, pernicious anaemia can result with fatal consequences<sup>[4]</sup>.

On the other hand, cobalt can be toxic and occupational exposure can have harmful effects such as “hardmetal pneumoconiosis”, or hardmetal disease, which is reported<sup>[5,6]</sup> to have occurred in workers continuously exposed over several years to the metal in the hardmetal/tungsten carbide/cobalt and diamond polishing industries.

Cobalt can cause allergic reactions which can take the form of dermatitis or a form of asthma which is usually reversible when exposure ceases. The lethal dose of cobalt by injection has been determined experimentally<sup>[4]</sup> to be of the order of 100-500 mg Co/kg of body weight, and been shown to be two to three times less for intake by mouth.

In humans the treatment of anaemia with excessive doses up to 500 mg by mouth of cobalt compounds has led to vomiting, diarrhoea and flushing, and by injection, deafness, palpitations and hypertension. Cobalt is well - recognised as the cause for other illnesses such as lung fibrosis<sup>[7,8]</sup>, polycythemia and heart disease<sup>[9]</sup>.

In large doses, cobalt and its salts can be toxic, but the greatest risk in occupational exposure is from the irritant/allergic effects of cobalt and its compounds. Recently<sup>[10]</sup> the E. U. provisionally classified most metals, including cobalt, and its compounds as R50/53 (where R50 refers to being very toxic to aquatic organisms and R53 refers to causing long term adverse effects in the aquatic environment). This classification procedure was adopted because the effect of a substance is now determined by the amount of a substance which dissolves and not the amount which is added. Strict exposure levels of cobalt are set world-wide at 0.1 and 0.05 mg/m<sup>3</sup> to reduce any risk. The maximum allowable exposure of cobalt to man over an 8 hour average is summarised in Table 2.4<sup>[10]</sup>.

#### **2.1.4 Extraction of Cobalt**

Cobalt can be extracted from ore concentrates or direct from the ore by hydrometallurgical, pyrometallurgical and electrometallurgical processes. Although most methods of extraction are based on hydrometallurgy, cobalt concentrates, mattes and alloys have been reduced to metal by pyrometallurgical methods.

The hydrometallurgical processes for cobalt extraction involve : (i) leaching of concentrates to give a cobalt-containing solution (ii) separation of cobalt from other metal ions in solution and (iii) reduction of cobalt ions to metal. Electrometallurgical and chemical reduction processes are used in releasing the metal from leach solutions and in refining the cobalt that has been extracted by hydrometallurgical or pyrometallurgical methods<sup>[11]</sup>.

Australia	0.05	Netherlands	0.1
Belgium	0.05	Norway	0.05
Bulgaria	0.5	Poland	0.05
Czech Republic	0.05	Russia	0.5
Finland	0.05	Sweden	0.05
France	0.05	Switzerland	0.1
Germany	0.1-0.5	South Africa	0.1
Italy	0.05	U. K.	0.1
Japan	0.05	U. S. A.	0.1

## 2.2 ELECTROLYSIS OF COBALT

Many industrial effluents contain metal ions, which must be treated, if for no other reason but their toxicity. However, the removal of metal may not be simple as the concentration of metal may be very low and may coexist with other metals and other organic species. In many applications residues containing cobalt in dilute solutions are obtained. These dilute solutions give rise to two problems: (i) effluent control regulations often limit the levels of cobalt that can be discharged, (ii) the value of the cobalt present even in dilute solutions could lead to considerable financial losses if the residue is simply dumped. It is therefore important to look at a means of recovering the cobalt from dilute solutions. Situations in which weak solutions could arise are acid treatment of alloys, electroplating rinse solutions and leach and effluent solutions from the manufacture of chemicals<sup>[12]</sup>.

The circumstances in which it can be desirable to recover metals from dilute solutions and the incentives for undertaking such recoveries are listed in Table 2.5<sup>[13]</sup>.

Table 2.5:- Incentives for recovering metals from dilute solutions	
SOURCES OF METAL IN DILUTE SOLUTION	MOTIVES FOR METAL RECOVERY
Primary ore leachings	Financial (for metal value)
Mine dump leachings	Financial (for solution value)
Naturally occurring streams	Effluent for legislation compliance.
Industrial effluents	
Liberator cells in metal-recovery	

The normal method for treatment of metalliferous effluent was chemical precipitation using the cheapest alkali available, usually soda ash or lime.

Electrolysis is a common method for metal removal but effluent tends to have low metal concentration and hence the process of electrolysis must overcome difficulties such as the diffusion layer. The *chemelec* cell is an alternative form of electrowinning technology for the recovery of metals from effluent streams. This cell can be used to increase the limiting current density in the electrolytic process, by decreasing the thickness of the diffusion layer and so increase the concentration gradient to the electrode.

An investigation carried out by Das and Subbaiah<sup>[14]</sup> looked at bath pH and temperature to examine what effect these parameters had on the current efficiency and the nature of the deposit. It was concluded that bath pH and temperature played a major role in the deposition of cobalt. A high current efficiency was achieved at a relatively low temperature and high bath pH (>4.0). At a relatively low bath pH and high temperature (~60°C), a high current efficiency can also be obtained. However, in the former case the cobalt metal deposited was dull, brittle and malleable in nature.

The research work at Brunel has optimised the recovery of cobalt from dilute solutions using the *chemelec* cell. The adjustment of different parameters such as current density, pH, buffer control, acid concentration, cobalt concentration and agitation was studied in order to establish optimum conditions for the removal of cobalt<sup>[15, 16]</sup>.

Many of the methods used for reducing the thickness of the diffusion layer involve agitation in the form of rotating electrodes, mechanical stirring, air agitation, turbulence promoters, slurry or fluidised beds<sup>[17]</sup>.

The development of electrolytic cells has led to their use in metal recovery from dilute effluent streams<sup>[18, 19]</sup>. However, their use is mostly as concentrators where further stages of purification are required to obtain the metal in directly re-usable form. Other systems which are being studied include membrane<sup>[20,21]</sup> and applied field technology<sup>[22]</sup>.

The relative positions of cobalt and hydrogen in the electrochemical series show that the major interfering cathode reaction that occurs during cobalt deposition is the evolution of hydrogen. Since the rate of hydrogen evolution decreases with increasing pH, the current efficiency for the deposition of cobalt would be expected to rise with increasing pH. From previous work it has been shown that the deposition of cobalt can only be achieved when the pH is greater than 4.0<sup>[16]</sup>. When the pH decreases the amount of cobalt recovered decreases rapidly and as the pH falls continuously during the course of electrolysis, there is a corresponding decrease in current efficiency. This is due to the following electrochemical reactions which take place during electrowinning.



The  $\text{Co}^{2+}$  is deposited at the cathode with acid being simultaneously produced at the anode.

### 2.3 CHEMELEC CELL

The *chemelec* cell is a fluidised bed cell [Figure 2.0], developed by Lopez Cacicedo at the Electricity Council Research Centre, Capenhurst<sup>[23]</sup>. It is an electrolytic reactor which has been specifically designed to provide higher ion-transfer conditions during electrolysis, by breaking up the barrier layer at the cathode, thus enabling metals to be removed efficiently from dilute solutions. It provides a means of increasing the limiting current density and therefore current



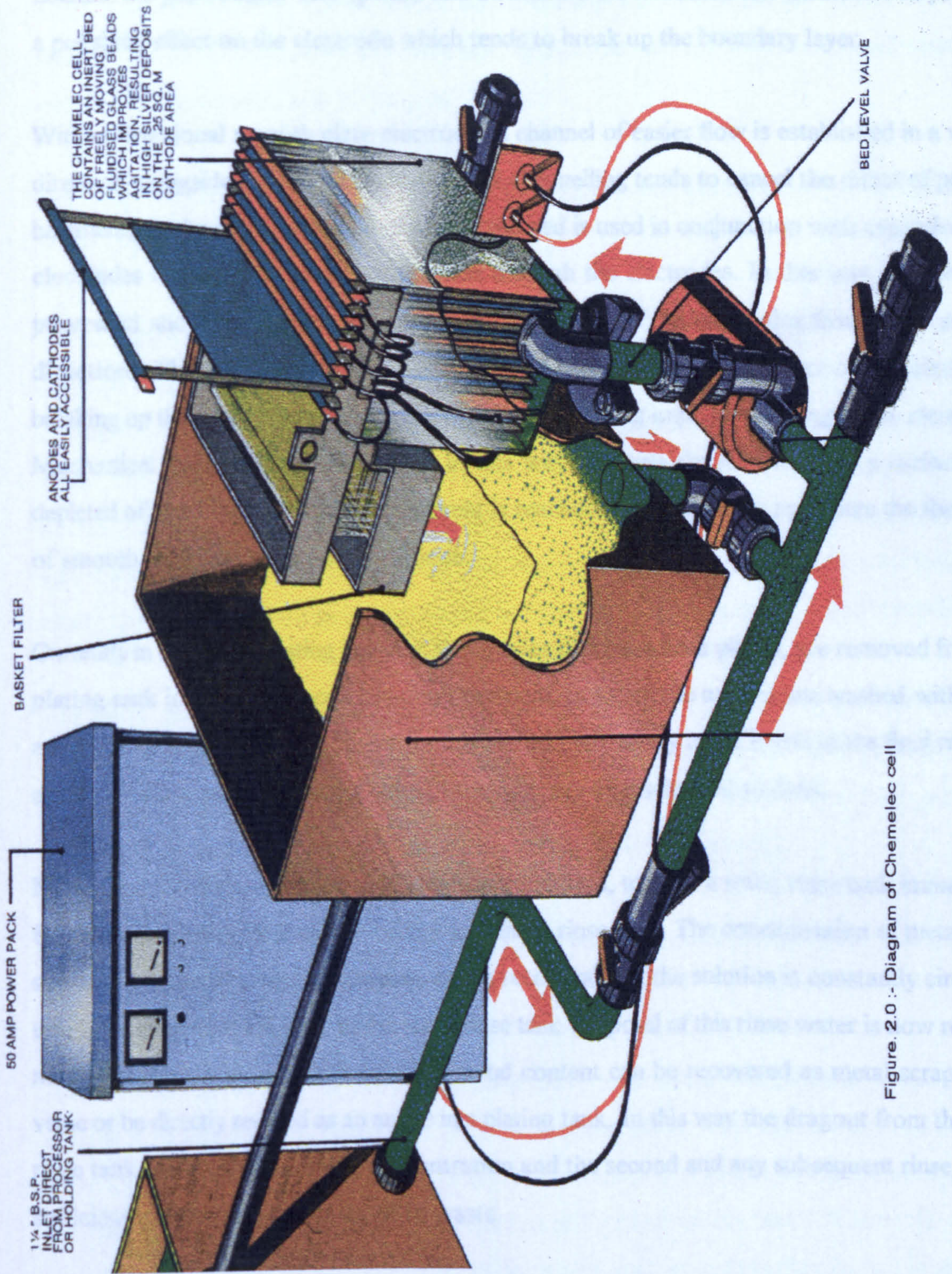


Figure. 2.0 :- Diagram of Chemelec cell

efficiency. The system comprises a fluidised bed of inert glass beads in which expanded mesh electrodes are immersed. When the *chemelec* cell is in operation, the metal-bearing electrolyte is pumped into the lower chamber and passes upwards through a porous flow distributor and fluidises the glass beads. The upward and downward movement of this fluidised bed produces a polishing effect on the electrode which tends to break up the boundary layer.

With conventional smooth plate electrodes a channel of easier flow is established in a vertical direction alongside the boundary layer. This channelling tends to cancel the effect of particles hammering at the electrode. When the fluidised bed is used in conjunction with expanded mesh electrodes the fluidised particles can pass through the electrodes. In this way channelling is prevented and the particles can approach the surface of the electrodes from many possible directions. This movement of the electrolyte enhances the polishing effect on the electrodes, breaking up the surface layer of the electrolyte and causing improved mixing of the electrolyte. Mechanical mixing of the electrolyte in this way prevents the formation of a surface layer depleted of ions until a much higher current is reached, and in addition promotes the formation of smooth metal deposits on the cathode.

Currently in the electroplating industry, the articles that have been plated, are removed from the plating tank into a continuous running rinse tank, in which the articles are washed with water and the rinse is removed as effluent. In this method, the heavy metal levels in the final rinse are above the acceptable limits and valuable metals may be discharged to drain.

Nowadays, it is common practice in electroplating lines, to have a static rinse tank immediately following the plating tank and preceding a running rinse tank. The concentration of metal in the static rinse tanks is always increasing, and is recoverable if the solution is constantly circulated through a *chemelec* cell back to the static rinse tank. Disposal of this rinse water is now required much less frequently, and the valuable metal content can be recovered as metal scrap for its value or be directly re-used as an anode in a plating tank. In this way the dragout from the static rinse tank can be kept at a low concentration and the second and any subsequent rinse will be sufficiently dilute to be discharged to waste.

Since the introduction of the *chemelec* cell in the early 70's, legislation has tightened making processes such as the fluidised bed cell electrolysis, characteristic of the *chemelec* cell, inadequate to cope with removal of metals to acceptable concentrations below the consent levels. Therefore research<sup>[24]</sup> has focussed on the development of technology capable of reaching these low levels. In almost all cases there is a need to combine the fluidised bed cell electrolysis with other single membrane techniques.

One of the techniques investigated in this part of work required the use of activated carbon cloth which is now described.

## **2.4 ACTIVATED CARBON**

Activated carbon is a non-crystalline solid exhibiting a large internal surface area and pore volume<sup>[25]</sup>. These characteristics are responsible for its adsorptive properties, which are used in many different liquid and gas phase applications in water treatment. Activated carbon is an exceptionally versatile adsorbent since the surface charge and pore dimension can be altered for application to meet the needs of current and emerging markets. It can be produced in the form of powders, granules and shaped products according to requirements of specific applications.

The major applications for active carbon involve its excellent properties as an adsorbent. They are used for solvent recovery, gas refining, air purification, exhaust desulphurisation, gas separation and recovery and desulphurization. Active carbons are also used extensively for decolourisation of solutions, and collection and recovery of solutes<sup>[26]</sup>.

The raw materials for active carbons are principally sawdust, coconut shells, black ash, charcoal and petroleum coke.

Another starting material for making charcoals is viscose rayon. This material, in the form of a woven cloth, can be converted into activated carbon cloth, retaining the form of the rayon (although not as strong as the parent precursor material). The rayon is carbonised in a furnace by heating with nitrogen gas at a temperature of 850°C (heating rate 10°C min<sup>-1</sup>), and then activated by changing the gas flow to an oxidising gas, such as carbon dioxide, at the same flow

rate<sup>[27]</sup>. The effect of activation on carbonised rayon is to produce a vast porous network within the volume of the solid. The carbonisation<sup>[28]</sup> and activation of the rayon results in the production of a highly microporous (pore width <2nm) material with very little mesoporosity (pore width 2-50nm)<sup>[29]</sup>. For certain applications the narrowness of the pores limits the usefulness of the material for the removal of large molecules from gaseous<sup>[30,31]</sup> and liquid media<sup>[32]</sup>, and as a support for catalysts<sup>[33]</sup>.

Work has been done on increasing the pore size of the ACC by altering the nature of the activating gas (carbon dioxide) used in the process, by changes in the carbonisation procedure or by pre-treatment of the rayon cloth before carbonisation and activation<sup>[34-38]</sup>.

Activated charcoal cloth is a pure carbon adsorbent with the appearance of cloth. Since ACC has no binder or other support it does not deteriorate with time in storage. The great advantage of this is that it provides the properties of charcoal on an inert support with the ability to conduct electricity, a property which the granules (from coconut or coal) do not possess. This means that the uptake of metals from solution appears to be a combination of both electroadsorption and more predominantly electrolytic deposition of metal ions<sup>[39]</sup>.

The unusual physical form of ACC allows it to be co-pleated or bagged with particulate filtration media for inclusion in filter units where granular or powder charcoal cannot be used. ACC has certain advantages over most powdered and granular forms of activated carbon, offering a potentially higher adsorption capacity and rate of adsorption and also a higher adsorption affinity<sup>[40,41]</sup>.

ACC is already in use in odour - adsorbing products including respiratory masks, wound dressings, ostomy filters, janitorial air-cleaning and mortuary air conditioning filters<sup>[42]</sup>.

The applications of active carbons are of interest to most economic sectors and concern areas as diverse as the food, pharmaceutical, chemical, petroleum, mining, nuclear, automobile and vacuum industries as well as the treatment of drinking water, industrial and urban wastewater, and air and gas<sup>[43]</sup>. Some aspects of the current work involved the use of the *chemelec* cell with

activated carbon cloth cathodes as a novel adsorption technique for the recovery of cobalt.

## 2.5 PARAMETERS INVESTIGATED

To establish the effectiveness of the electrolysis process, the following parameters were investigated:-

- (a) the percentage removal of cobalt ( $\alpha_{Co}$ )
- (b) the current efficiency for cobalt removal ( $\eta_{Co}$ ) and
- (c) the energy consumption, ( $W_{Co}$ ), for each kilogram of cobalt deposited.

### 2.5.1 Degree of purification ( $\alpha$ )

The percentage removal ( $\alpha_{Co}$ ), that is the degree of purification, is the cathodic deposit achieved during the electrolysis process and can be calculated by the following equation:

$$\alpha (\%) = \frac{\text{Initial Weight (g)}}{\text{Actual Deposit (g)}} \times 100 \quad (\text{Eq. 2.2})$$

### 2.5.2 Current Efficiency ( $\eta$ )

In the usual electroplating situation, attention is focused on the quantity of metal deposited at the cathode or dissolved at the anode, and any hydrogen evolved at the cathode or oxygen at the anode. This would represent a waste of energy and so a reduction in the current efficiency of the process. Current efficiency can be calculated by the following equation:

$$\eta (\%) = \frac{\text{Actual Deposit (g)}}{\text{Theoretical Deposit (g)}} \times 100 \quad (\text{Eq. 1.2})$$

where  $\eta$  is current efficiency in percent, actual deposit is the weight of metal deposited and theoretical deposit is the corresponding weight to be expected if there were no side reactions. The current efficiency is a measure of how effectively each amp of current is used during the electrolysis process. In order to calculate current efficiency the electrochemical equivalent based

on 100 % current efficiency (Table 2.6)<sup>[44]</sup> for each metal is used in the above equation.

<b>Table 2.6:- Electrochemical equivalents for various metals</b>		
<b>Metal</b>	<b>Valency</b>	<b>Weight of deposit (g) (ampere hour)</b>
Cadmium	2+	2.100
Cobalt	2+	1.100
Copper (cuprous)	1+	2.370
(cupric)	2+	1.190
Gold (aurous)	1+	7.350
(auric)	3+	2.450
Iron (ferrous)	2+	1.042
(ferric)	3+	0.695
Nickel	2+	1.095
Silver	1+	4.025
Tin (stannous)	2+	2.214
(stannic)	4+	1.107
Zinc	2+	1.220

### 2.5.3 Energy Consumption (W)

The energy consumption determines the power used to deposit 1 kg of metal and can be calculated by Equation 2.3:

$$W \text{ (kWh/kg}^{-1}\text{)} = \frac{I \times V \times T}{\text{Weight Deposited (g)}} \quad \text{(Eq. 2.3)}$$

The most important parameters to be considered with effluent disposal and treatment are the degree of purification and the percentage of metal that can eventually be removed. The energy consumption is not a significant percentage of the overall cost of the process<sup>[45]</sup>.

However because cobalt is a valuable metal - at the time of writing £29,520/ tonne - an economic assessment using the energy data will be presented.

## 2.6 EXPERIMENTAL

In this work a *chemelec* fluidised bed electrochemical precious metal recovery (PMR) cell (supplied by Bewt Environmental Services Ltd), of 10dm<sup>3</sup> capacity was used for the electrodeposition of cobalt from dilute solutions. Two titanium mesh cathodes (surface area 0.050m<sup>2</sup> or stainless steel plate cathodes (total surface area 0.044m<sup>2</sup>) and three mixed metal oxide anodes were alternatively placed in the electrolysis chamber. Each electrolysis was normally run for up to 8 hours and during electrolysis, samples of the solution were taken every hour and analysed by atomic absorption spectroscopy (AAS). Electrolyte solutions were prepared from reagent grade cobalt sulphate crystals (CoSO<sub>4</sub>·7H<sub>2</sub>O) and 55.5ml sulphuric acid, made up to 10 litres. Reagent grade ammonium hydroxide and sulphuric acid were normally used to maintain the pH of the solution between 4-5. A pH of 4-5 was used because:-

- (i) a smaller amount of NH<sub>4</sub>OH is required to maintain the pH.
- (ii) a brighter cathodic deposit is obtained.

The effects of the following parameters were investigated:-

- Effect of cathode current density.
- Effect of concentration of cobalt using mesh and plate electrodes.
- Effect of using MgO or NH<sub>4</sub>OH for controlling the pH of the solution.
- Effect of the number and spacing of electrodes used.
- Effect of using activated carbon cloth (with industrial sample) under the following conditions:-
  - (a) use of NH<sub>4</sub>OH.
  - (b) use of MgO.
  - (c) different cobalt concentrations.
  - (d) different current densities.

## 2.7 RESULTS AND DISCUSSION

The results are presented graphically and error bars have been calculated for the data points in Figure. 2.1. Each data point is representative of the sample taken.

### 2.7.1 Effect of cathode current density

The effect of current density on the deposition morphology, current efficiency, and the power consumption was studied using  $10 \text{ Am}^{-2}$ ,  $15 \text{ A m}^{-2}$  and  $20 \text{ Am}^{-2}$ . In all experiments carried out, the cobalt concentration was  $0.5 \text{ g dm}^{-3}$ . The best value of current efficiency, after 2 h of electrolysis, was 47.73% when a current density of  $20 \text{ Am}^{-2}$  was used. This value then decreased to 31.59% after 8 h of electrolysis. When current densities of  $10 \text{ Am}^{-2}$  and  $15 \text{ Am}^{-2}$  were used, the corresponding values for  $\eta_{\text{Co}}$  were 40.91% and 39.39% respectively after a 2 h electrolysis period. These values, after 8 h, were then 42.05% and 33.56% [Figure. 2.1a].

When a current density of  $10 \text{ Am}^{-2}$  was used, the current efficiency was steady throughout the whole experiment since, after 7 h of electrolysis the  $\eta_{\text{Co}}$  was still 40.92% but this value increased to 42.06% after 8 h [Figure. 2.1b]. As the current density was increased to 15 and  $20 \text{ Am}^{-2}$ , the current efficiency gradually decreased with time.

The  $\alpha_{\text{Co}}$  values for solutions, containing  $0.5 \text{ g dm}^{-3}$  of cobalt, at current densities of  $10 \text{ Am}^{-2}$ ,  $15 \text{ Am}^{-2}$  and  $20 \text{ Am}^{-2}$  were found to increase with increasing current density. Optimum recovery was achieved at a current density of  $20 \text{ Am}^{-2}$  where the  $\alpha_{\text{Co}}$  value after 2 h of electrolysis was 36.84% and 97.54% after 8 h [Figure. 2.1a].

For experiments where current densities of  $10 \text{ Am}^{-2}$  and  $15 \text{ Am}^{-2}$  were used the corresponding values for  $\alpha_{\text{Co}}$  were 16.67% and 27.66% respectively after a 2 h electrolysis period, and after 8 hours the values increased to 68.52% and 94.26% respectively [Figure. 2.1b].

As the current density was increased the energy consumed ( $W_{\text{Co}}$ ) increased after 8 h of electrolysis. The values for  $W_{\text{Co}}$  when using current densities of  $10 \text{ A m}^{-2}$ ,  $15 \text{ Am}^{-2}$  and  $20 \text{ Am}^{-2}$  were 4.76, 6.50 and  $7.48 \text{ kWh kg}^{-1}$  respectively [Figure 2.1c].

In all experiments carried out, it was found that the higher the current density applied, the greater was the percentage of metal removed. The metal deposit was shiny but hard to remove from the cathodes.



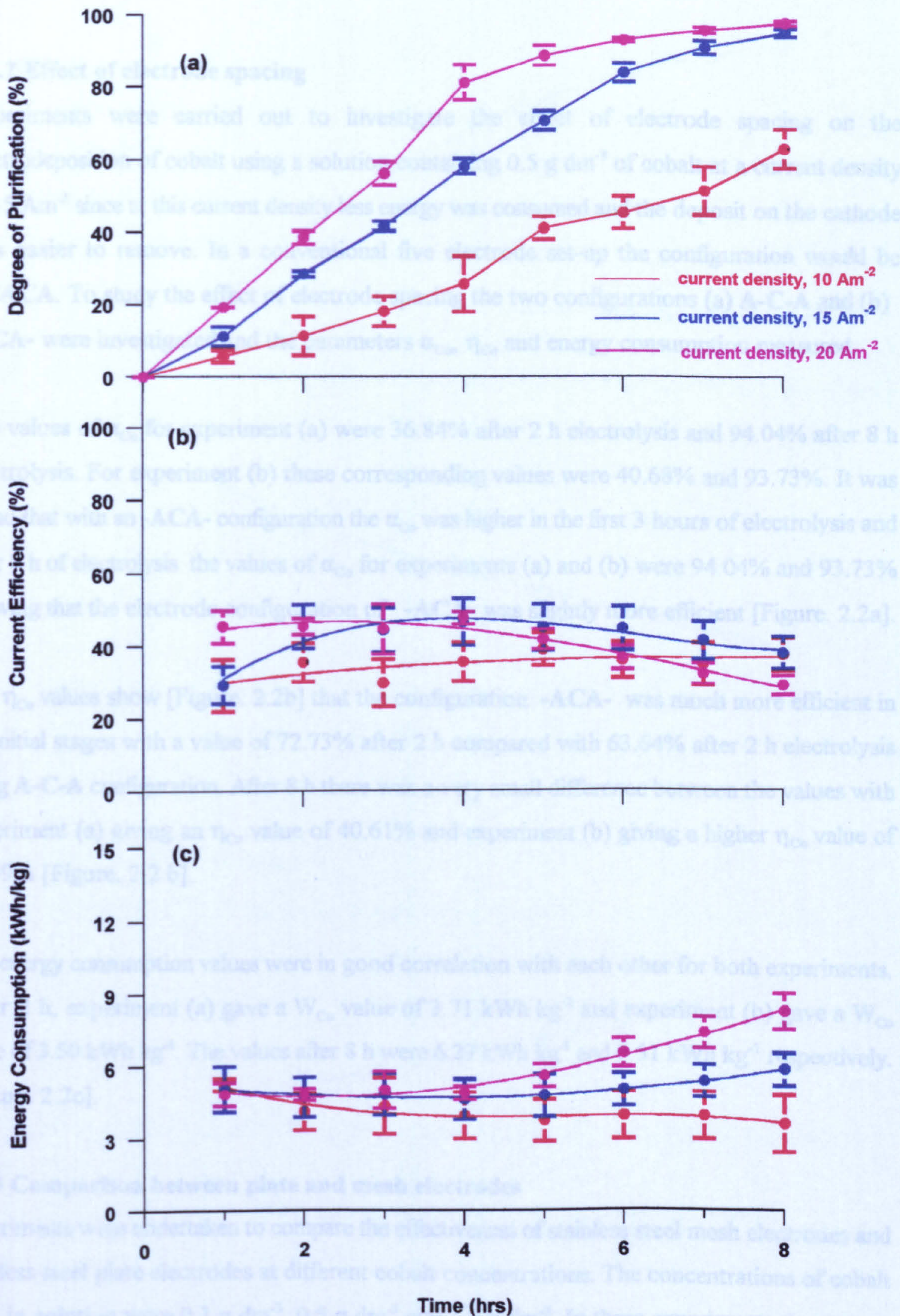


Figure. 2.1: Effect of current density to recover cobalt from a 0.5 g dm<sup>-3</sup> sulphate solution.

### 2.7.2 Effect of electrode spacing

Experiments were carried out to investigate the effect of electrode spacing on the electrodeposition of cobalt using a solution containing  $0.5 \text{ g dm}^{-3}$  of cobalt at a current density of  $15 \text{ Am}^{-2}$  since at this current density less energy was consumed and the deposit on the cathode was easier to remove. In a conventional five electrode set-up the configuration would be ACACA. To study the effect of electrode spacing the two configurations (a) A-C-A and (b) -ACA- were investigated and the parameters  $\alpha_{\text{Co}}$ ,  $\eta_{\text{Co}}$  and energy consumption measured.

The values of  $\alpha_{\text{Co}}$  for experiment (a) were 36.84% after 2 h electrolysis and 94.04% after 8 h electrolysis. For experiment (b) these corresponding values were 40.68% and 93.73%. It was found that with an -ACA- configuration the  $\alpha_{\text{Co}}$  was higher in the first 3 hours of electrolysis and after 8 h of electrolysis the values of  $\alpha_{\text{Co}}$  for experiments (a) and (b) were 94.04% and 93.73% showing that the electrode configuration of -ACA- was slightly more efficient [Figure. 2.2a].

The  $\eta_{\text{Co}}$  values show [Figure. 2.2b] that the configuration -ACA- was much more efficient in the initial stages with a value of 72.73% after 2 h compared with 63.64% after 2 h electrolysis using A-C-A configuration. After 8 h there was a very small difference between the values with experiment (a) giving an  $\eta_{\text{Co}}$  value of 40.61% and experiment (b) giving a higher  $\eta_{\text{Co}}$  value of 41.89% [Figure. 2.2 b].

The energy consumption values were in good correlation with each other for both experiments. After 2 h, experiment (a) gave a  $W_{\text{Co}}$  value of  $3.71 \text{ kWh kg}^{-1}$  and experiment (b) gave a  $W_{\text{Co}}$  value of  $3.50 \text{ kWh kg}^{-1}$ . The values after 8 h were  $6.27 \text{ kWh kg}^{-1}$  and  $6.51 \text{ kWh kg}^{-1}$  respectively. [Figure. 2.2c].

### 2.7.3 Comparison between plate and mesh electrodes

Experiments were undertaken to compare the effectiveness of stainless steel mesh electrodes and stainless steel plate electrodes at different cobalt concentrations. The concentrations of cobalt used in solution were  $0.1 \text{ g dm}^{-3}$ ,  $0.5 \text{ g dm}^{-3}$  and  $1.0 \text{ g dm}^{-3}$ . In these experiments the current density was kept constant at  $15 \text{ Am}^{-2}$ .

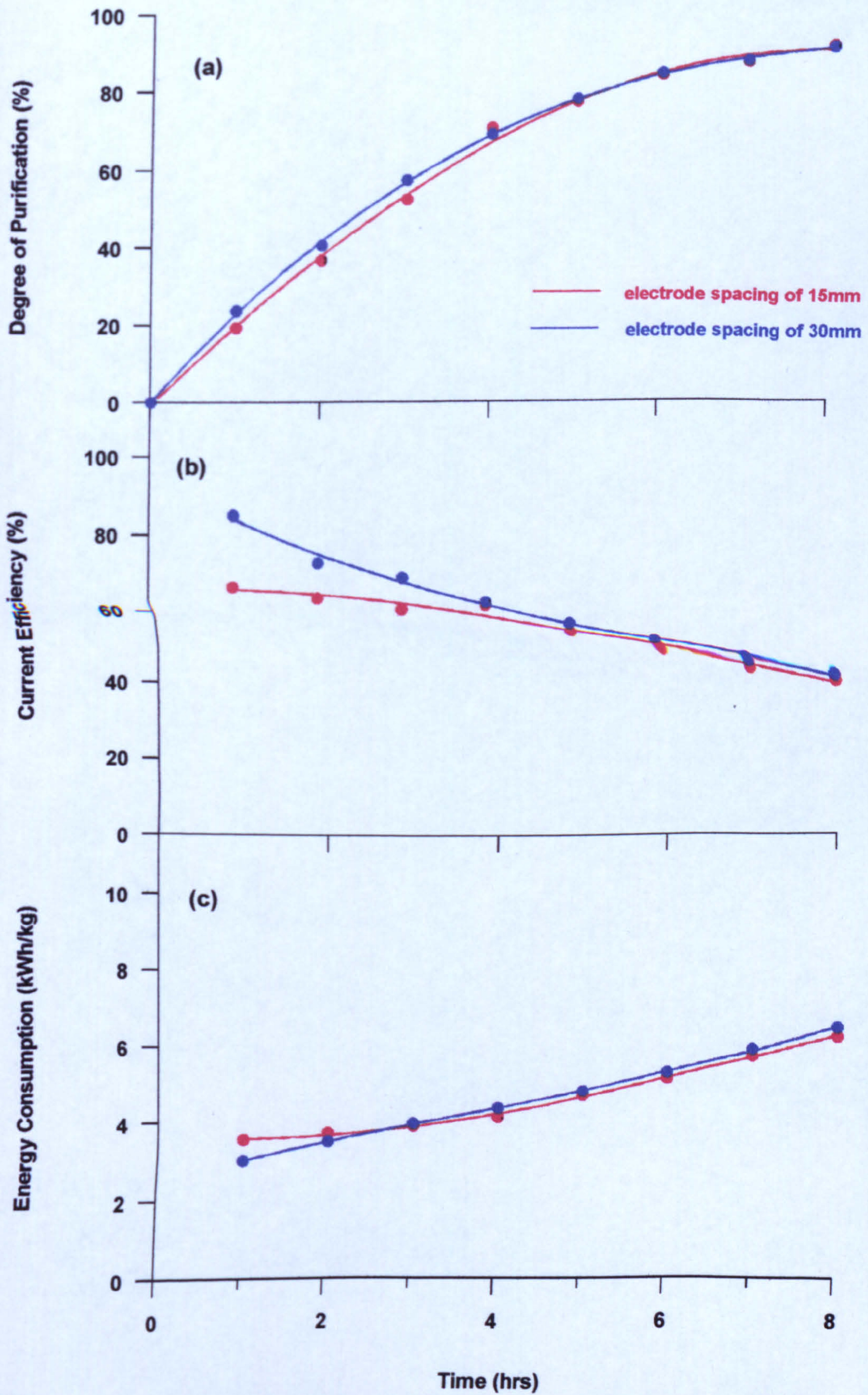


Figure 2.2:- Effect of electrode spacing on the recovery of cobalt from a  $0.5 \text{ g dm}^{-3}$  sulphate solution.

### **2.7.3.1 0.1 g dm<sup>-3</sup> of Co at 15 Am<sup>-2</sup>**

The percentage removal of cobalt,  $\alpha_{\text{Co}}$  using mesh electrodes, after 2 h of electrolysis at a cobalt concentration of 0.1 g dm<sup>-3</sup>, was found to be 48.78%. After 8 h the mesh cathodes still proved to be more efficient giving an  $\alpha_{\text{Co}}$  value of 96.68% whereas with the plate cathodes a value of 95.91% was obtained [Figure. 2.3a].

In terms of current efficiency both mesh and plate electrodes gave a value of 15.15% after 2 h electrolysis. After 8 h there was a difference in this value with the plate electrodes giving slightly more efficient removal at 8.36% than 7.51% for the mesh electrodes [Figure. 2.3b].

The values for  $W_{\text{Co}}$  were 14.4 and 30.27 kWh kg<sup>-1</sup> after 2 h and 8 h electrolysis respectively for mesh cathodes. With plate cathodes less energy was consumed giving values of 13.50 and 26.11 kWh kg<sup>-1</sup> after 2 h and 8 h respectively [Figure. 2.3c].

At this concentration of cobalt in solution it was seen that mesh cathodes proved to be more efficient in terms of degree of purification, but plate cathodes showed a greater efficiency in terms of current efficiency and energy consumption.

### **2.7.3.2 0.5 g dm<sup>-3</sup> of Co at 15 Am<sup>-2</sup>**

At a higher concentration of Co the mesh cathodes proved to be more efficient with  $\alpha_{\text{Co}}$  after 2h and 8 h of electrolysis, of 27.66% and 94.26% respectively. The plate cathodes were less efficient after 2 h with  $\alpha_{\text{Co}}$  equal to 18.75% but after 8 h this value increased to 86.46% [Figure. 2.4a].

The mesh electrodes performed more efficiently than the plate electrodes [Figure. 2.4b] with  $\eta_{\text{Co}}$  giving a value of 39.39% after 2 h electrolysis for mesh electrodes and 27.27% for plate electrodes. Even though there was a noticeable difference after 2 h of electrolysis, the values for  $\eta_{\text{Co}}$  were comparable after 8 h, with mesh electrodes at 33.56% and plate electrodes at 31.44%.

The energy consumption values were greater for mesh electrodes than for plate electrodes.  $W_{\text{Co}}$  for mesh electrodes after 2 h and 8 h electrolysis was 5.54 and 6.50 kWh kg<sup>-1</sup> whereas, for plate

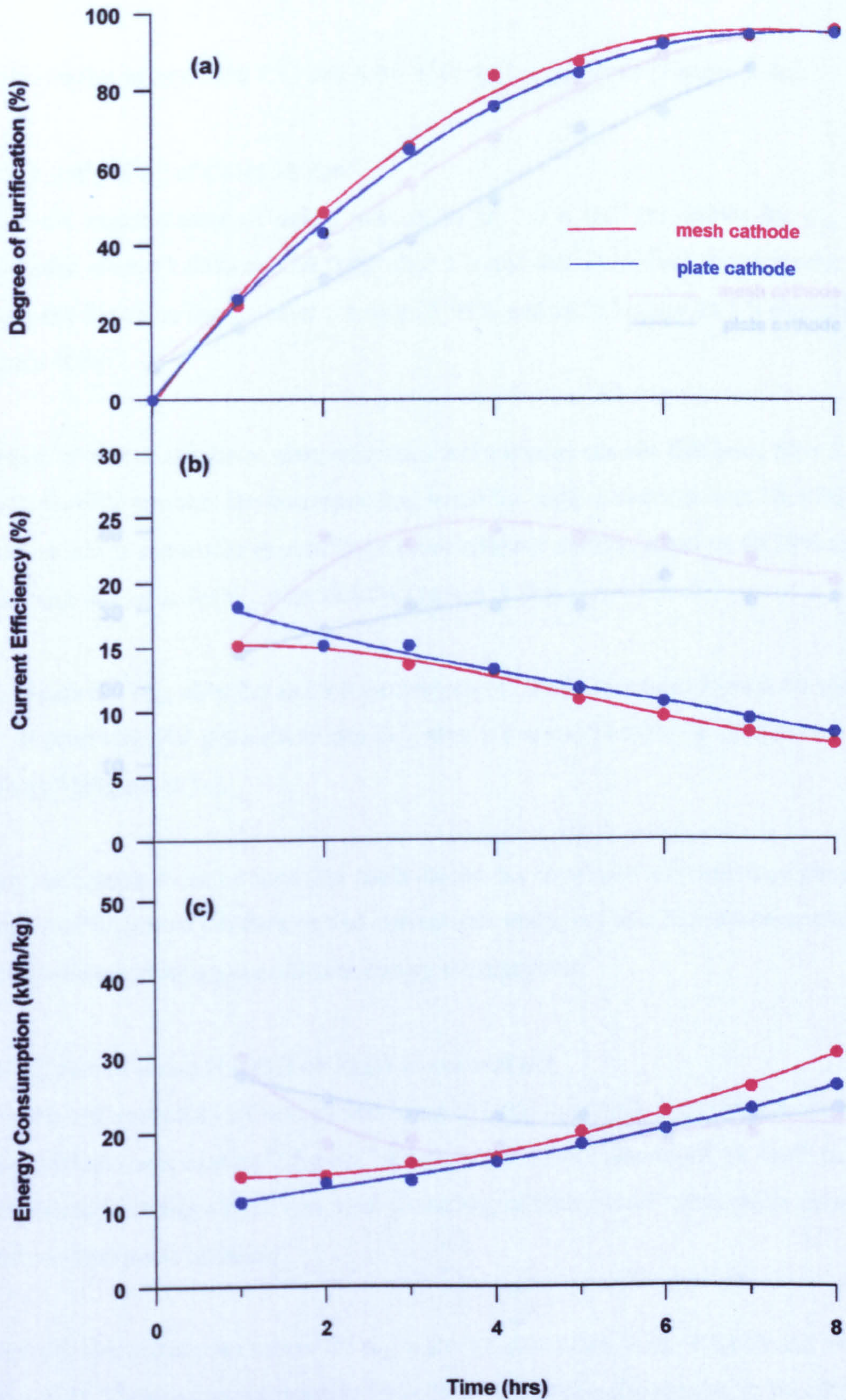


Figure 2.3:- Effect of plate and mesh electrodes on the recovery of cobalt from a  $0.1 \text{ g dm}^{-3}$  sulphate solution.

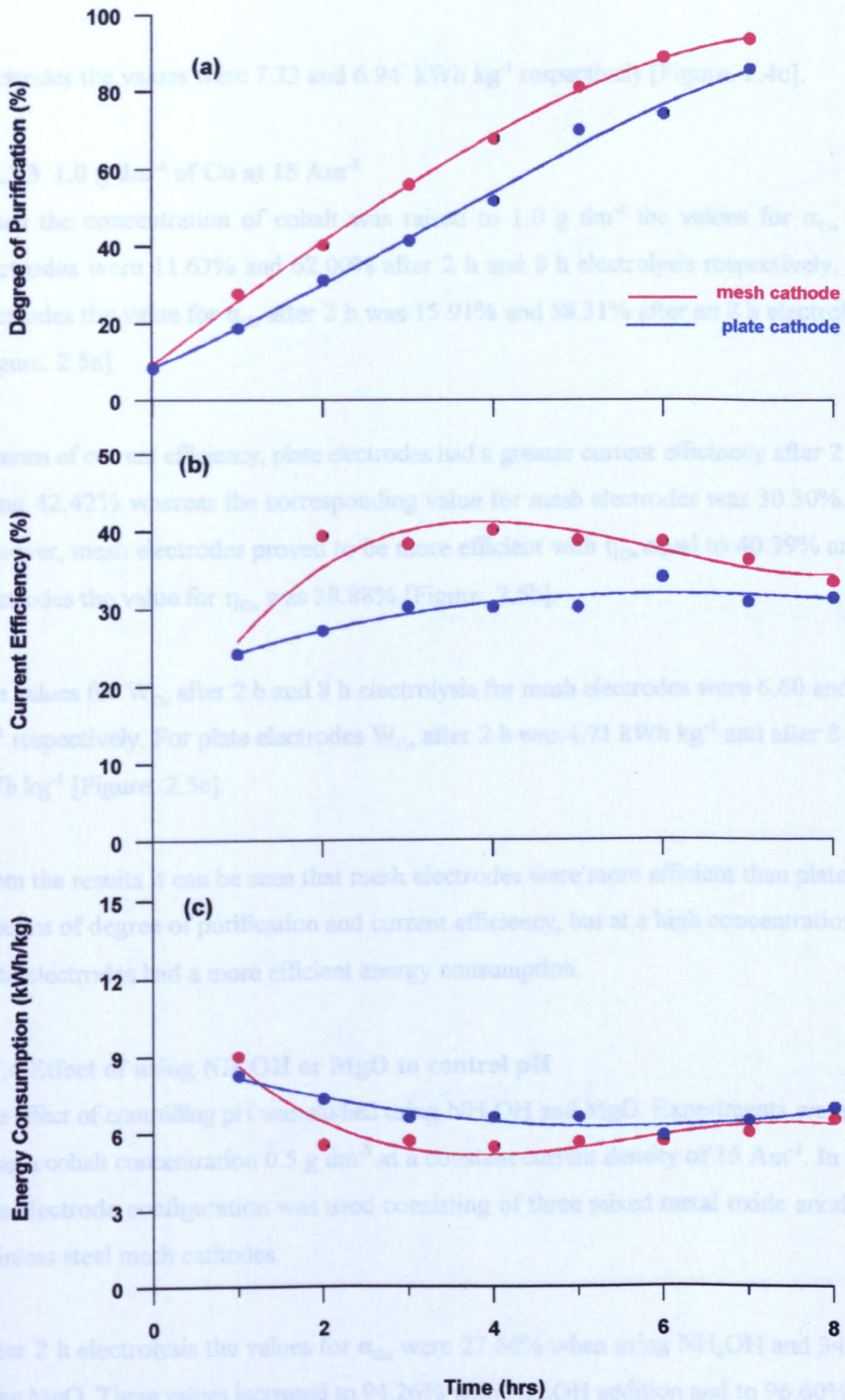


Figure 2.4:- Effect of using plate and mesh electrodes to remove cobalt from a  $0.5 \text{ g dm}^{-3}$  sulphate solution.

electrodes the values were 7.33 and 6.94 kWh kg<sup>-1</sup> respectively [Figure. 2.4c].

### **2.7.3.3 1.0 g dm<sup>-3</sup> of Co at 15 Am<sup>-2</sup>**

When the concentration of cobalt was raised to 1.0 g dm<sup>-3</sup> the values for  $\alpha_{Co}$  with mesh electrodes were 11.63% and 62.00% after 2 h and 8 h electrolysis respectively. With plate electrodes the value for  $\alpha_{Co}$  after 2 h was 15.91% and 58.31% after an 8 h electrolysis period [Figure. 2.5a].

In terms of current efficiency, plate electrodes had a greater current efficiency after 2 h with  $\eta_{Co}$  being 42.42% whereas the corresponding value for mesh electrodes was 30.30%. After 8 h, however, mesh electrodes proved to be more efficient with  $\eta_{Co}$  equal to 40.39% and for plate electrodes the value for  $\eta_{Co}$  was 38.88% [Figure. 2.5b].

The values for  $W_{Co}$  after 2 h and 8 h electrolysis for mesh electrodes were 6.60 and 4.95 kWh kg<sup>-1</sup> respectively. For plate electrodes  $W_{Co}$  after 2 h was 4.71 kWh kg<sup>-1</sup> and after 8 h was 5.38 kWh kg<sup>-1</sup> [Figure. 2.5c].

From the results it can be seen that mesh electrodes were more efficient than plate electrodes in terms of degree of purification and current efficiency, but at a high concentration of cobalt, plate electrodes had a more efficient energy consumption.

### **2.7.4 Effect of using NH<sub>4</sub>OH or MgO to control pH**

The effect of controlling pH was studied using NH<sub>4</sub>OH and MgO. Experiments were conducted using a cobalt concentration 0.5 g dm<sup>-3</sup> at a constant current density of 15 Am<sup>-2</sup>. In each case a five electrode configuration was used consisting of three mixed metal oxide anodes and two stainless steel mesh cathodes.

After 2 h electrolysis the values for  $\alpha_{Co}$  were 27.66% when using NH<sub>4</sub>OH and 34.04% when using MgO. These values increased to 94.26% with NH<sub>4</sub>OH addition and to 96.60% with MgO addition after 8 h of electrolysis [Figure. 2.6a].

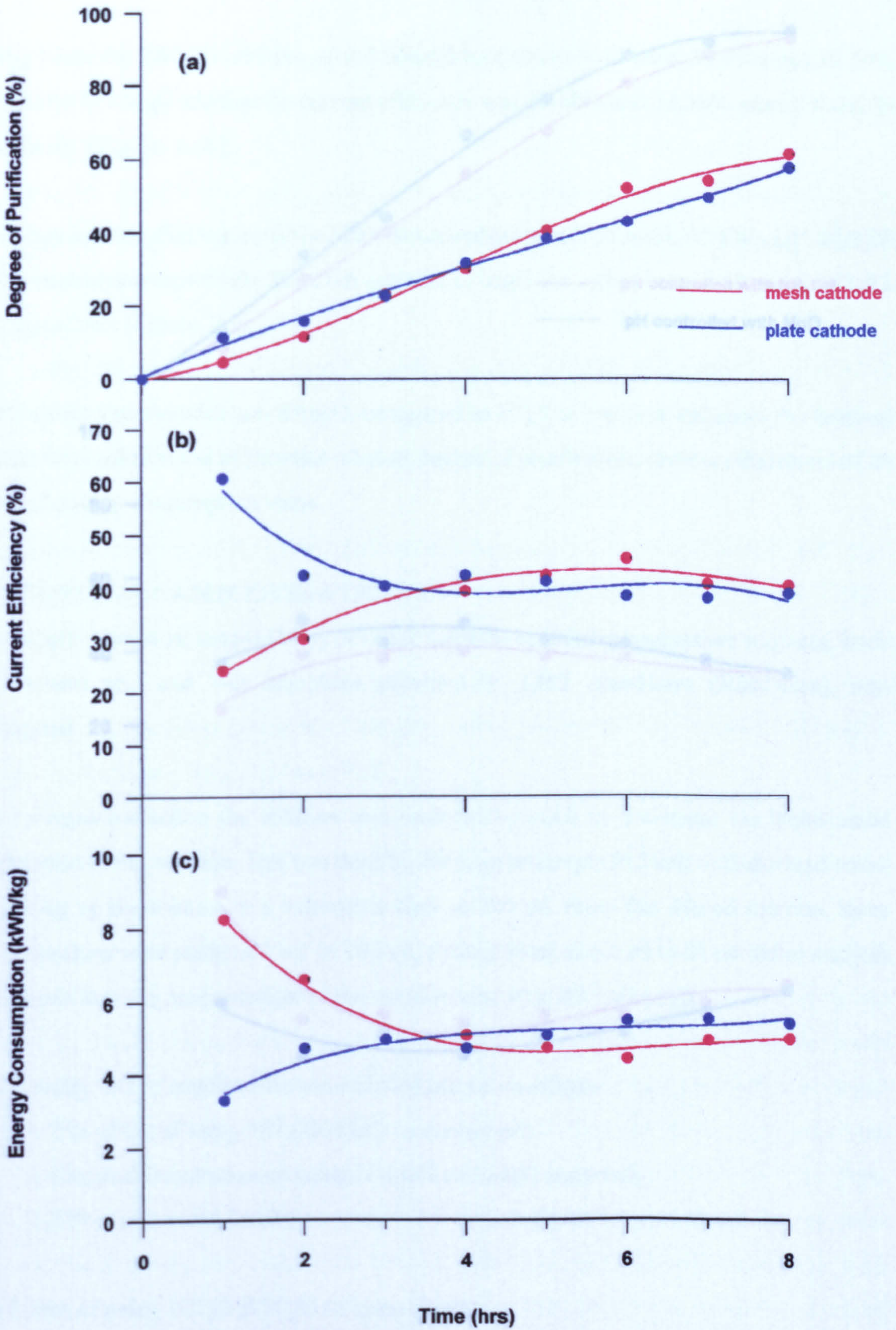


Figure 2.5:- Effect of using plate and mesh electrodes to remove cobalt from a  $1.0 \text{ g dm}^{-3}$  sulphate solution.



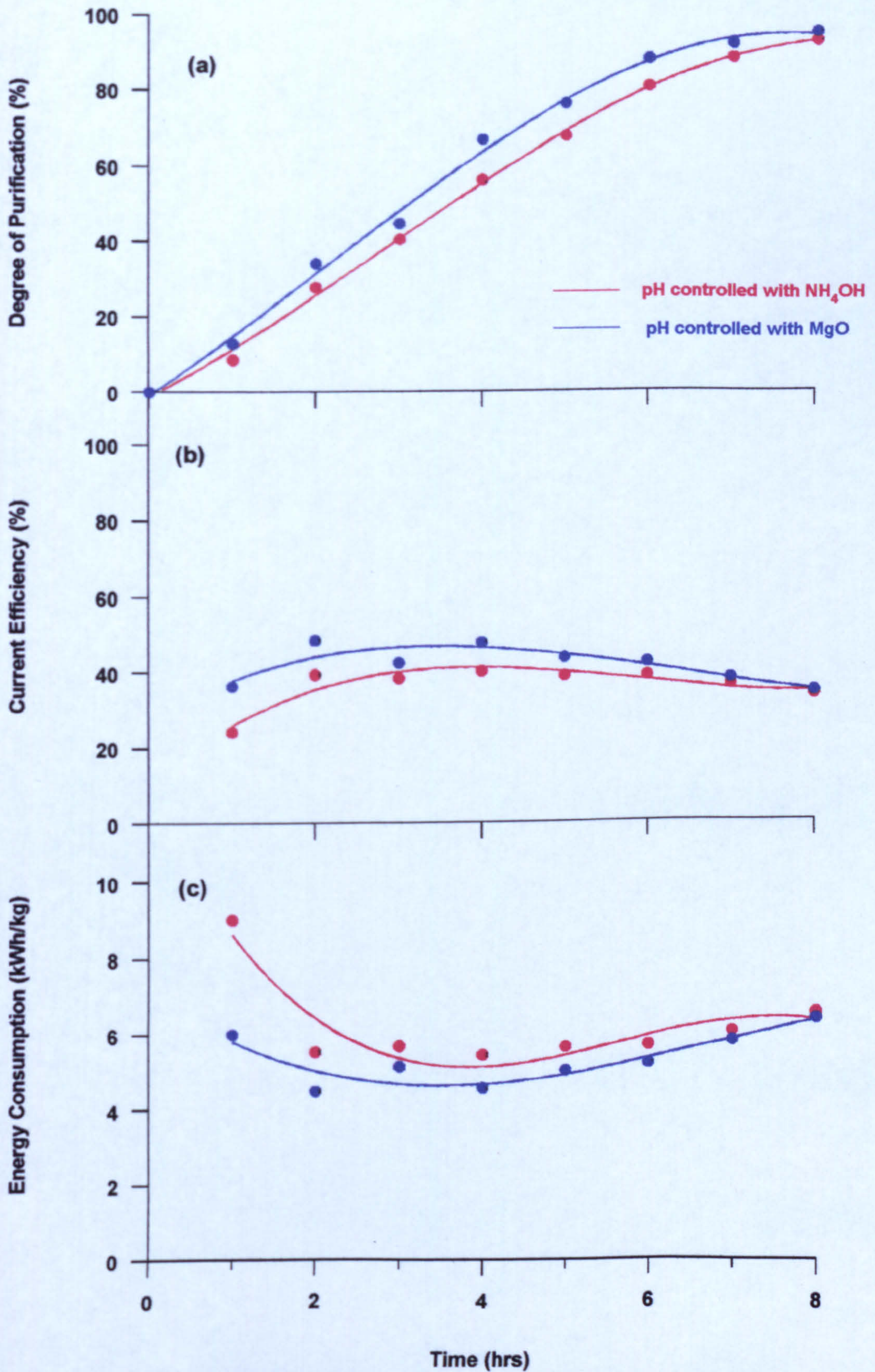


Figure 2.6:- Effect of using NH<sub>4</sub>OH and MgO to control pH when recovering cobalt from a 0.5 g dm<sup>-3</sup> sulphate solution.

The  $\eta_{Co}$  values for  $NH_4OH$  addition, after 2 h and 8 h of electrolysis were, 39.39% and 33.56% respectively. For  $MgO$  addition the current efficiency was 48.48% and 34.39% after 2 h and 8h respectively. [Figure. 2.6b].

The energy consumption values when  $NH_4OH$  was added was 5.54 and 6.50 kWh  $kg^{-1}$  after 2h and 8 h electrolysis respectively. With the addition of  $MgO$  the values were 4.50 and 6.34 kWh  $kg^{-1}$  respectively [Figure. 2.6c].

It can be seen that the addition of  $MgO$ , compared to  $NH_4OH$  addition, enhances the removal of cobalt from solution and so provides a better degree of purification, current efficiency and an improved energy consumption value.

## **2.8 INDUSTRIAL SAMPLE TREATMENT**

An as-supplied industrial sample (10 L) of cobalt sulphate containing magnesium sulphate, boric acid, tartaric acid and iron impurities provided by **LHT Anodisers (Middlesex)**, was investigated.

Prior to experimentation the solution was analysed by AAS to determine the initial metal concentration of the solution. This was done by diluting the sample (0.5 ml) with distilled water and making up the solution in a volumetric flask to 500 ml. From this diluted solution, three further dilutions were made of 1 ml in 100 ml, 1 ml in 50 ml and 1 ml in 25 ml. After analysis it was found that the concentration of the solution was 30 g  $dm^{-3}$  of cobalt.

The following sets of experiments were carried out to investigate:-

1. The effect of using  $NH_4OH/MgO$  to control pH
2. Electrode separation on using  $NH_4OH$  and  $MgO$  separately
3. Effect of current density

### **2.8.1 Effect of using $NH_4OH/MgO$ to control pH**

In these experiments solutions containing 0.5 g  $dm^{-3}$  of Co were studied using three mixed metal oxide electrodes (anodes) and two stainless steel mesh electrodes (cathodes) along with the use

of  $\text{NH}_4\text{OH}$  or  $\text{MgO}$  to control the pH (4-5) of the solution. The current density was kept constant at  $15 \text{ Am}^{-2}$ .

When using  $\text{NH}_4\text{OH}$  the value of  $\alpha_{\text{Co}}$  after a 2 h electrolysis period was 32.61% and this value increased to 91.96%. The  $\alpha_{\text{Co}}$  values for  $\text{MgO}$  addition were 32.65% and 95.31% after 2 h and 8 h electrolysis respectively [Figure. 2.7a].

The  $\eta_{\text{Co}}$  value for  $\text{NH}_4\text{OH}$  addition after 2 h electrolysis was 45.45%. This value then decreased to 32.05% after an 8 h electrolysis period. For  $\text{MgO}$  addition, the  $\eta_{\text{Co}}$  value was 48.48% after 2 h of electrolysis. This value then decreased to 35.38% after 8 h electrolysis [Figure. 2.7b].

The energy consumption was best with  $\text{MgO}$  addition whereby  $W_{\text{Co}}$  was 6.00 and 8.22  $\text{kWh kg}^{-1}$  after 2 h and 8 h respectively. With  $\text{NH}_4\text{OH}$  addition the values were 7.50 and 8.45  $\text{kWh kg}^{-1}$  after 2 h and 8 h electrolysis respectively [Figure. 2.7c].

Hence, with  $\text{MgO}$  addition there is a better degree of purification and current efficiency is obtained with a lower energy consumption.

### **2.8.2 Experiments involving ACC, using $\text{NH}_4\text{OH}/\text{MgO}$ to control pH at different current densities**

In these experiments the effect of  $\text{NH}_4\text{OH}$  and  $\text{MgO}$  to control pH (4-5) was studied at a cobalt concentration of  $0.5 \text{ g dm}^{-3}$  and three different current densities of 15, 20 and  $25 \text{ Am}^{-2}$  using two mixed metal oxide electrodes (anodes) and one activated carbon cloth (ACC) electrode (cathode). The ACC cathode consisted of a stainless steel plate cathode covered with activated carbon cloth obtained from Charcoal Cloth International (UK). Four plastic clips were then secured onto the edges of the carbon cloth covered plate to keep the cloth taut over the plate. The reason for this was to prevent short circuiting with the neighbouring anodes in the *chemelec* cell once the electrode was placed into solution. The two anodes in each experiment were positioned at maximum spacing ( each 27 mm from the cathode) whilst the cathode was placed in between the two anodes to give a configuration of A-C-A.

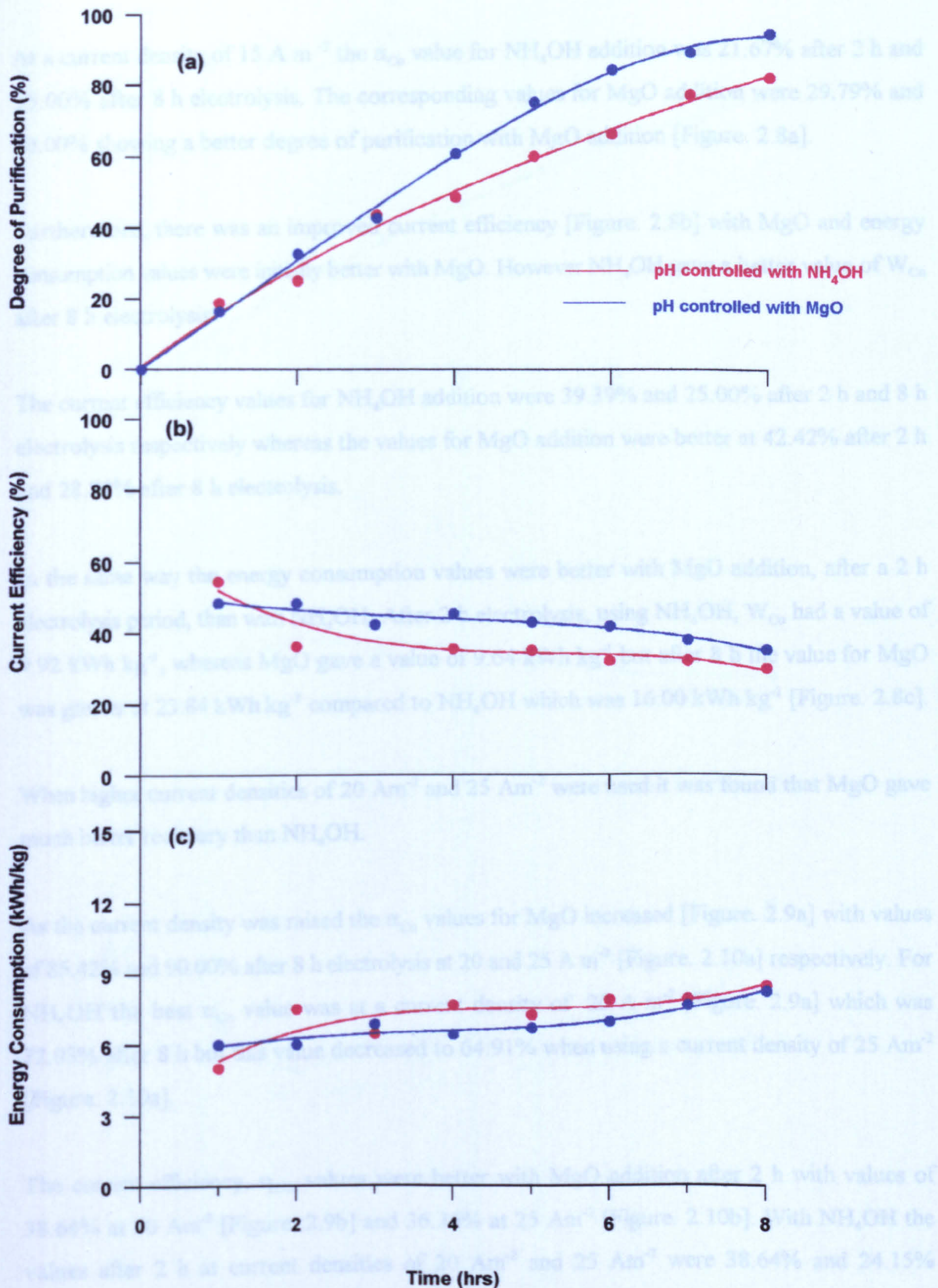


Figure 2.7:- Effect of using NH<sub>4</sub>OH and MgO to control pH when recovering cobalt from a 0.5 g dm<sup>-3</sup> industrial sulphate sample.

At a current density of  $15 \text{ A m}^{-2}$  the  $\alpha_{\text{Co}}$  value for  $\text{NH}_4\text{OH}$  addition was 21.67% after 2 h and 55.00% after 8 h electrolysis. The corresponding values for MgO addition were 29.79% and 80.00% showing a better degree of purification with MgO addition [Figure. 2.8a].

Furthermore, there was an improved current efficiency [Figure. 2.8b] with MgO and energy consumption values were initially better with MgO. However  $\text{NH}_4\text{OH}$  gave a better value of  $W_{\text{Co}}$  after 8 h electrolysis.

The current efficiency values for  $\text{NH}_4\text{OH}$  addition were 39.39% and 25.00% after 2 h and 8 h electrolysis respectively whereas the values for MgO addition were better at 42.42% after 2 h and 28.22% after 8 h electrolysis.

In the same way the energy consumption values were better with MgO addition, after a 2 h electrolysis period, than with  $\text{NH}_4\text{OH}$ . After 2 h electrolysis, using  $\text{NH}_4\text{OH}$ ,  $W_{\text{Co}}$  had a value of  $9.92 \text{ kWh kg}^{-1}$ , whereas MgO gave a value of  $9.64 \text{ kWh kg}^{-1}$  but after 8 h the value for MgO was greater at  $23.84 \text{ kWh kg}^{-1}$  compared to  $\text{NH}_4\text{OH}$  which was  $16.00 \text{ kWh kg}^{-1}$  [Figure. 2.8c].

When higher current densities of  $20 \text{ Am}^{-2}$  and  $25 \text{ Am}^{-2}$  were used it was found that MgO gave much better recovery than  $\text{NH}_4\text{OH}$ .

As the current density was raised the  $\alpha_{\text{Co}}$  values for MgO increased [Figure. 2.9a] with values of 85.42% and 90.00% after 8 h electrolysis at  $20$  and  $25 \text{ A m}^{-2}$  [Figure. 2.10a] respectively. For  $\text{NH}_4\text{OH}$  the best  $\alpha_{\text{Co}}$  value was at a current density of  $20 \text{ A m}^{-2}$  [Figure. 2.9a] which was 72.03% after 8 h but this value decreased to 64.91% when using a current density of  $25 \text{ Am}^{-2}$  [Figure. 2.10a].

The current efficiency,  $\eta_{\text{Co}}$ , values were better with MgO addition after 2 h with values of 38.64% at  $20 \text{ Am}^{-2}$  [Figure. 2.9b] and 36.36% at  $25 \text{ Am}^{-2}$  [Figure. 2.10b]. With  $\text{NH}_4\text{OH}$  the values after 2 h at current densities of  $20 \text{ Am}^{-2}$  and  $25 \text{ Am}^{-2}$  were 38.64% and 24.15% respectively.

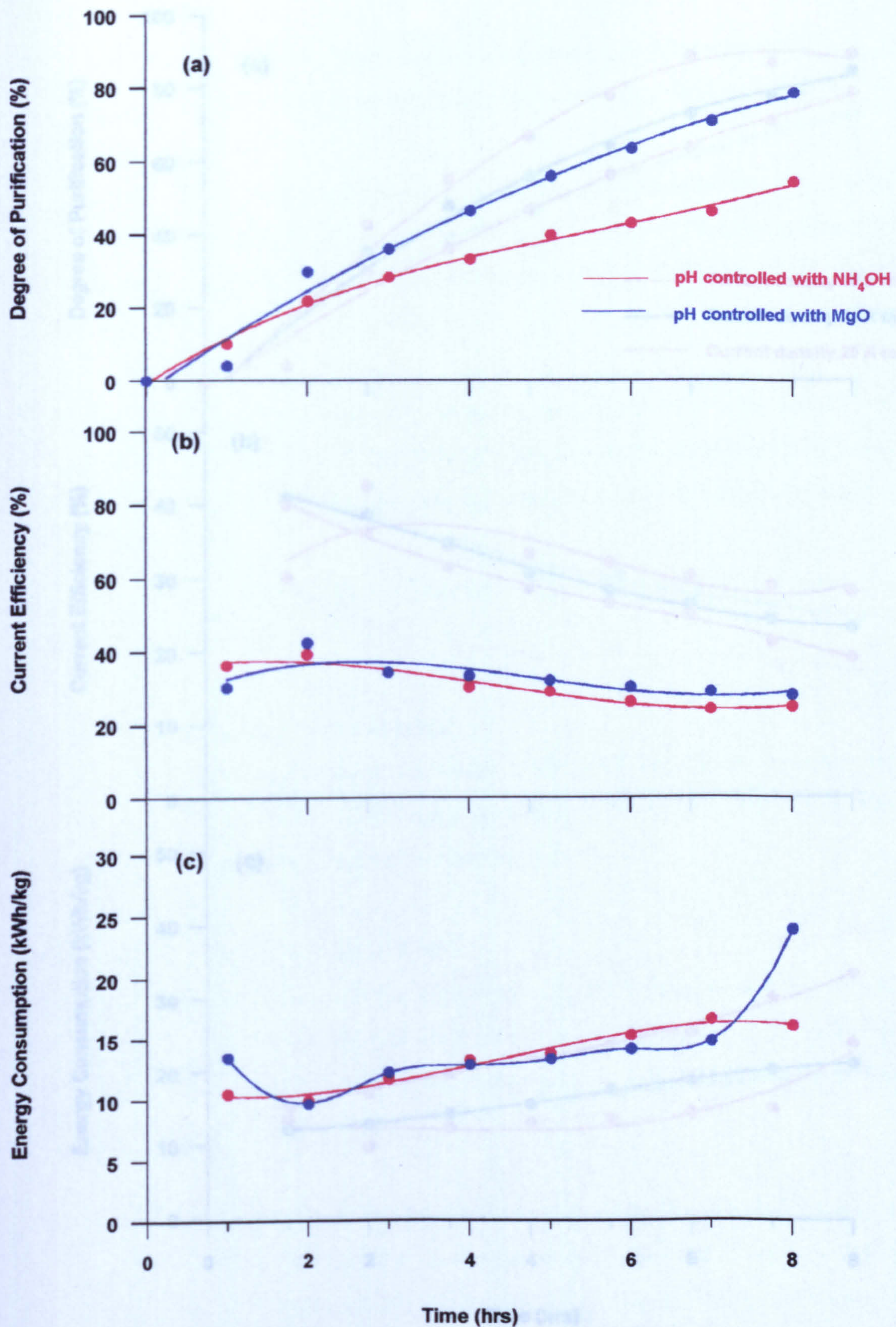


Figure 2.8:- Effect of using NH<sub>4</sub>OH and MgO to control pH when recovering cobalt from a 0.5 g dm<sup>-3</sup> industrial sulphate sample.

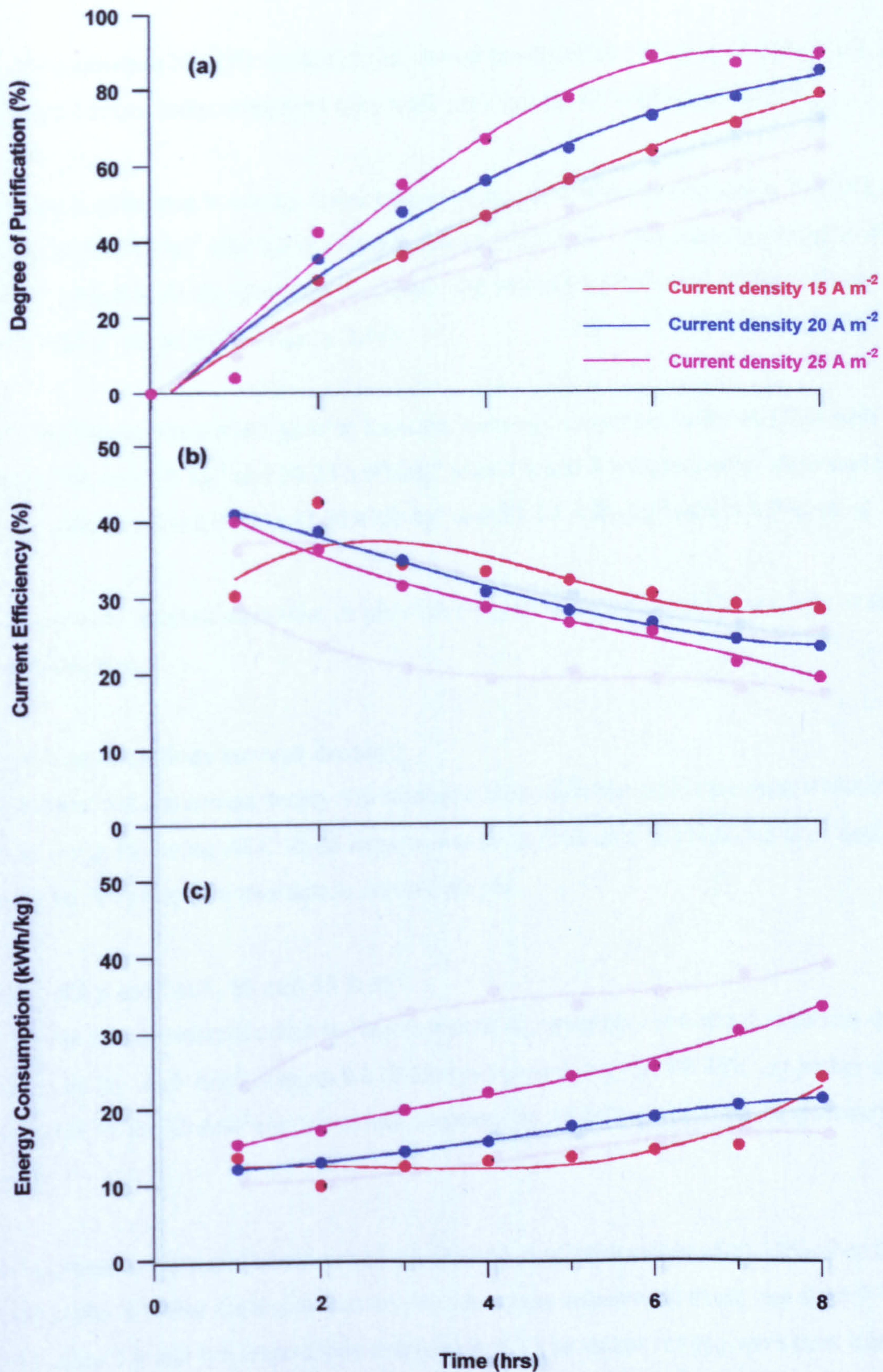


Figure 2.9:- Effect of current density using MgO to control pH when recovering cobalt from a 0.5 g dm<sup>-3</sup> sulphate solution.

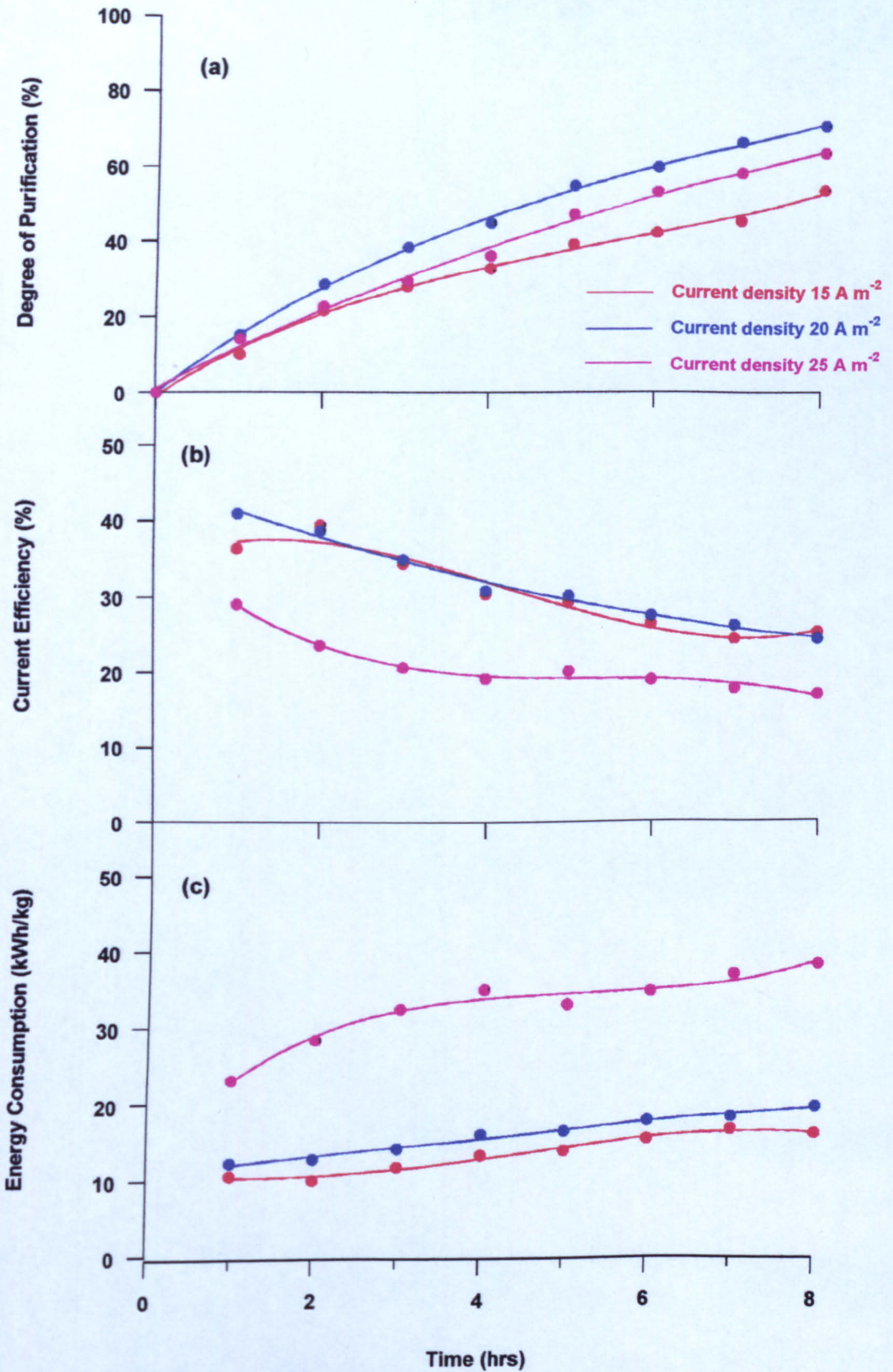


Figure 2.10:- Effect of current density using  $\text{NH}_4\text{OH}$  to control pH when recovering cobalt from a  $0.5 \text{ g dm}^{-3}$  sulphate solution.



After 8 h electrolysis  $\text{NH}_4\text{OH}$  yielded slightly better results of 24.15% and 16.82% at  $20 \text{ Am}^{-2}$  and  $25 \text{ Am}^{-2}$  respectively, compared with  $\text{MgO}$  with values of 23.30% and 19.23%.

There was a difference in energy consumption values at both current densities. For  $\text{NH}_4\text{OH}$ ,  $W_{\text{Co}}$  was  $12.71 \text{ kWh kg}^{-1}$  after 2 h at a current density of  $20 \text{ A m}^{-2}$ . This value increased to  $19.58 \text{ kWh kg}^{-1}$  after 8 h. At the same current density the values for  $\text{MgO}$  were  $12.71 \text{ kWh kg}^{-1}$  and  $21.07 \text{ kWh kg}^{-1}$  respectively [Figure. 2.9c].

At  $25 \text{ Am}^{-2}$  there was a much greater increase in energy consumption for  $\text{NH}_4\text{OH}$  with  $W_{\text{Co}}$  values of  $28.46 \text{ kWh kg}^{-1}$  and  $38.38 \text{ kWh kg}^{-1}$  after 2 h and 8 h respectively.  $\text{MgO}$  was more efficient with  $W_{\text{Co}}$  after 2 h being  $17.00 \text{ kWh kg}^{-1}$  and  $33.10 \text{ kWh kg}^{-1}$  after 8 h [Figure. 2.10c].

$\text{MgO}$  is a more efficient controller of pH than  $\text{NH}_4\text{OH}$  when using ACC especially at higher current densities.

### **2.8.3 Effect of cathode current density**

The effect of cathode current density was studied at three different cobalt concentrations of 0.1, 0.5 and  $1.0 \text{ g dm}^{-3}$  using ACC. In all experiments an A-C-A configuration was used and  $\text{MgO}$  was added at appropriate intervals to control the pH.

#### **2.8.3.1 $0.1 \text{ g dm}^{-3}$ at 5, 10 and $15 \text{ A m}^{-2}$**

At this low concentration of cobalt the best values of  $\alpha_{\text{Co}}$  were obtained at a low current density [Figure. 2.11a]. At  $5 \text{ Am}^{-2}$ , after an 8 h electrolysis period,  $\alpha_{\text{Co}}$  was 86.32%. At higher current densities of 10 and  $15 \text{ Am}^{-2}$  the values had decreased to 84.44% and 75.48% respectively after 8 h.

The  $\eta_{\text{Co}}$  values were best at a low current density of  $5 \text{ Am}^{-2}$  with values of 43.18% after 2 h and 18.64% after 8 h. For the higher current densities these values were much less at 15.91% and 8.64% after 2 h and 8 h respectively using  $10 \text{ Am}^{-2}$ . The values for  $\eta_{\text{Co}}$  were even less using  $15 \text{ Am}^{-2}$  where, after 2 h,  $\eta_{\text{Co}}$  was 9.85% and 4.43% after 8 h [Figure. 2.11b].

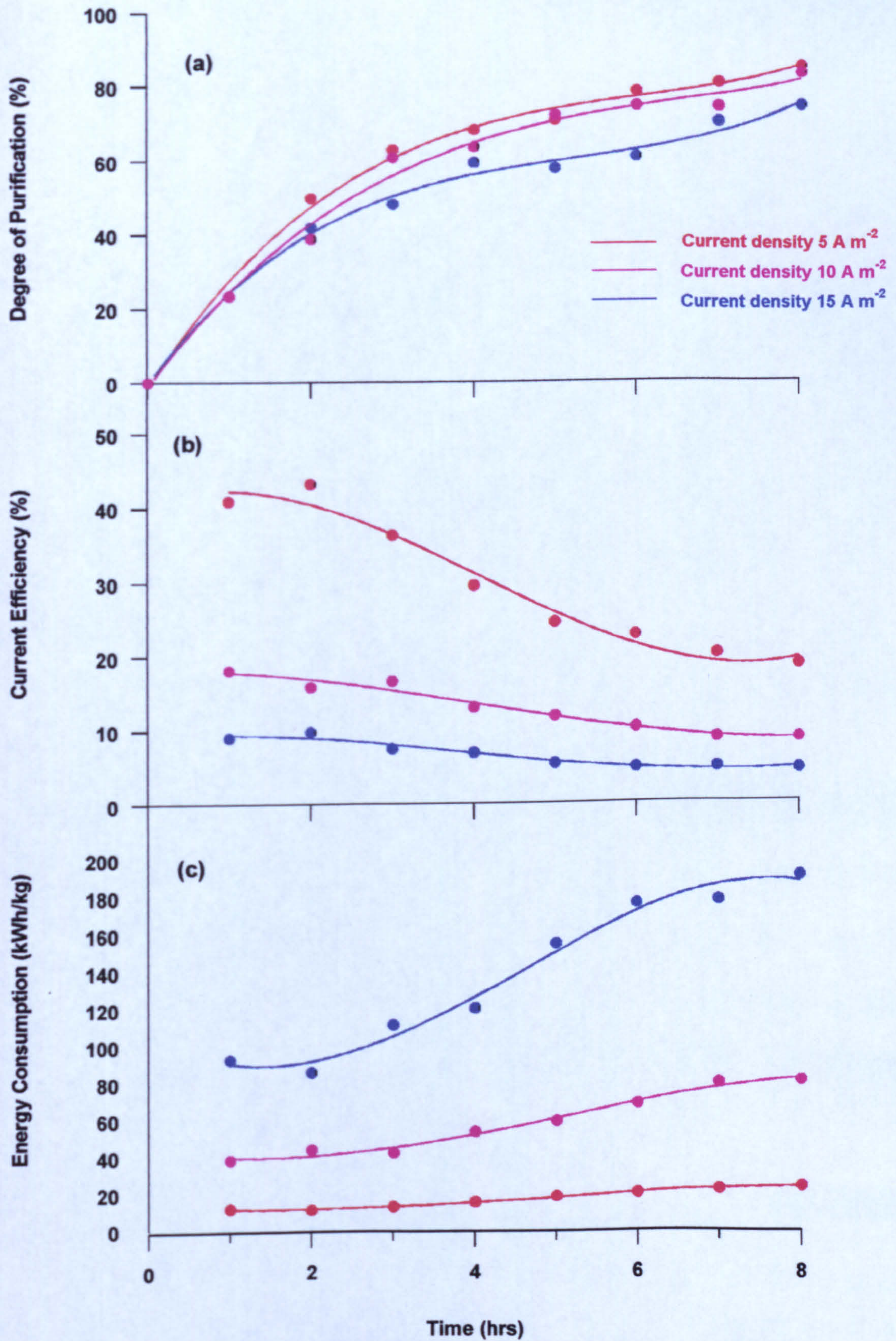


Figure 2.11:- Effect of current density when recovering cobalt from a 0.1 g dm<sup>-3</sup> sulphate solution.

In terms of energy consumption the best values were at a low current density where  $W_{Co}$ , after 8 h for 5, 10 and 15  $A m^{-2}$ , was 21.95, 78.95 and 188.72  $kWh kg^{-1}$  respectively, indicating that as the current density is raised the energy consumption increases [Figure. 2.11c].

At low concentration of cobalt ( $0.1 g dm^{-3}$ ) a low current density yields the best results because it gives a greater degree of purification, better current efficiency and it is more economical in energy terms.

### **2.8.3.2 1.0 $g dm^{-3}$ at 15, 20 and 25 $A m^{-2}$**

At the higher concentration of cobalt ( $1.0 g dm^{-3}$ ), it was found that as the current density was increased the values for  $\alpha_{Co}$  increased. After 8 h of electrolysis, using current densities of 15, 20 and 25  $A m^{-2}$ ,  $\alpha_{Co}$  was 72.09%, 73.13% and 85.81% respectively [Figure. 2.12a].

In terms of current efficiency the best values obtained were at a current density of 15  $A m^{-2}$  with  $\eta_{Co}$  giving a value of 53.53% after 8 h. The corresponding values for 20  $A m^{-2}$  and 25  $A m^{-2}$  were 29.92% and 36.66% respectively [Figure. 2.12b].

Energy consumption was lowest with a current density of 15  $A m^{-2}$  with  $W_{Co}$  of 2.92  $kWh kg^{-1}$  and 6.62  $kWh kg^{-1}$  after 2 and 8 h respectively. At current densities of 20 and 25  $A m^{-2}$  the values for  $W_{Co}$  were 13.07 and 12.40  $kWh kg^{-1}$  respectively [Figure. 2.12c].

At a current density of 20  $A m^{-2}$  the degree of purification is better than at lower current densities of 15 and 20  $A m^{-2}$ . However the lower current density gave lower values for energy consumption and overall better current efficiency, therefore the optimum current density to use at a concentration of cobalt up to  $1.0 g dm^{-3}$  would be 15  $A m^{-2}$ .

## **2.9 ECONOMIC EVALUATION OF COBALT RECOVERY**

The economic evaluation of the recovery of cobalt was calculated for the experiments conducted using the industrial sample provided by LHT Anodisers. The calculations are based on the treatment of a 100 litre solution per day containing 2000  $\mu g/ml$  of cobalt, using a standard electrochemical system. At the time of calculation the value of 1 kg of cobalt (Cobalt

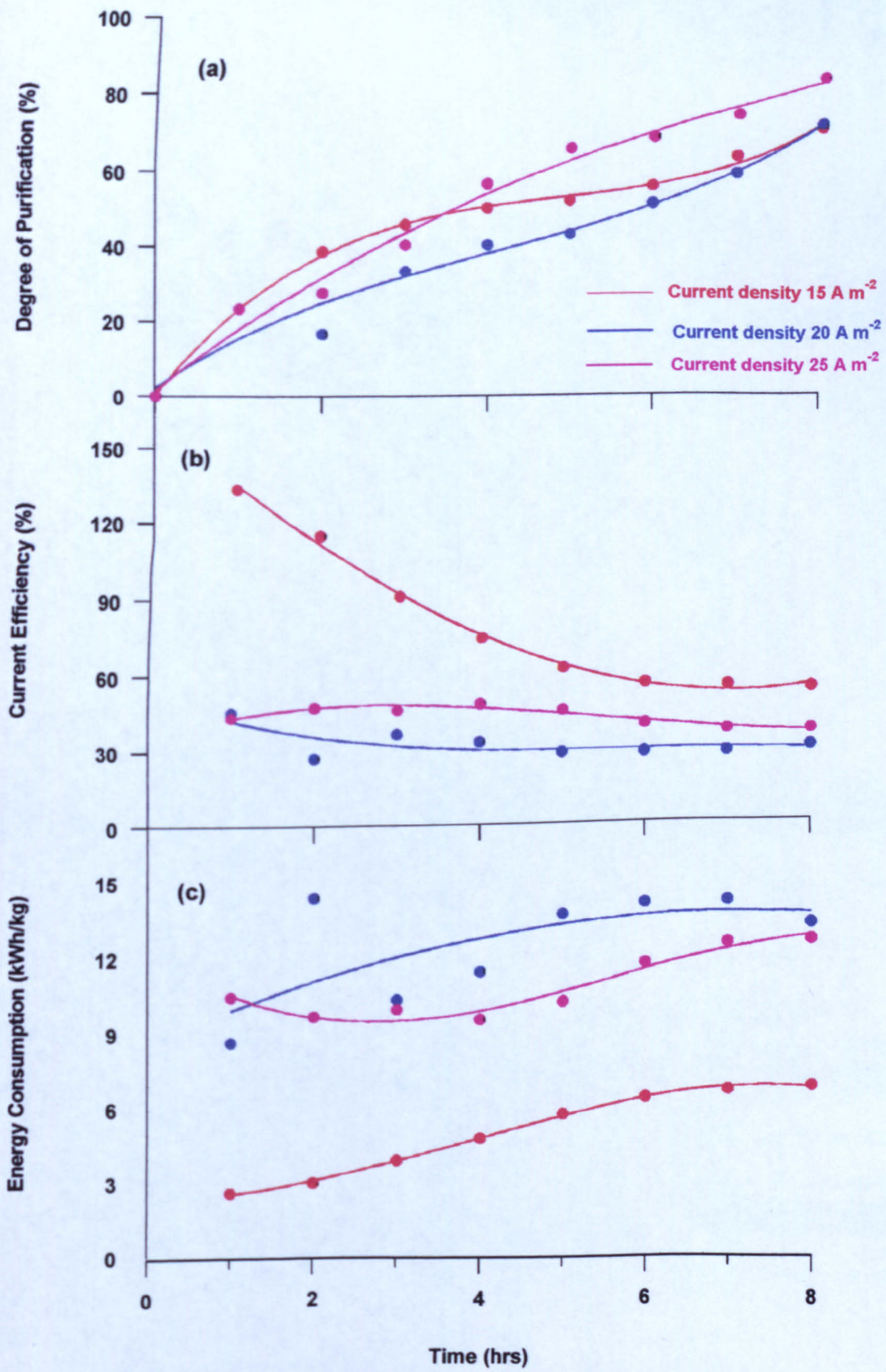


Figure 2.12:- Effect of current density on the recovery of cobalt from a 1.0 g dm<sup>-3</sup> sulphate solution.

Development Institute) was £29.52.

The value of contained cobalt in 100 L (0.2 kg) is  $(0.2 \times £29.52)$  **£5.90**

The energy consumption to recover 99.9% of cobalt is  $\sim 33.0 \text{ kWh kg}^{-1}$ . The energy consumption to recover 0.2 kg of cobalt is  $6.6 \text{ kWh kg}^{-1}$ . The cost of electricity per unit is £0.06.

The total energy cost to recover 0.2 kg of cobalt is  $(6.6 \times 0.06)$  **£0.40**

The volume of  $\text{NH}_4\text{OH}$  required to adjust the pH for a 100 L solution, during the recovery process would be  $\sim 200 - 250 \text{ ml}$  at a cost of £9.70 for 2.5 L of  $\text{NH}_4\text{OH}$ .

Total cost of chemicals (250 ml of  $\text{NH}_4\text{OH}$ ) to adjust the pH **£0.97**

Energy consumption of the pump to circulate the solution in the cell **£0.30**

Total cost for previous 3 stages **£1.67**

Total saving for the company  $(£5.90 - £1.67)$  **£4.23**

Total saving for the company per month  $(£4.23 \times 30)$  **£127**

Cost of the electrochemical cell

(Maximum £15,000) written off per annum  $(£127 \times 12)$  **£1524**

---

The company's priority is not in recovering the cobalt metal but to comply with environmental legislation and also to improve the Environmental Quality Standards (EQS) and Environmental Quality Objectives (EQO). The environmental benefits for the company to meet the discharge limits is important since no extra cost will be made to water authorities for treatment and disposal of the effluent. However in the economic calculation the reduction and cost of on-site treatment and transportation of off-site treatment facilities has not been taken into account.

## **CONCLUSION**

**It has been confirmed that the fluidised bed electrolysis cell is an effective method of removing heavy metals from dilute solutions.**

**In this chapter the effect of different electrodes, current densities, cobalt concentrations and pH modifier has been investigated.**

**Comparative recovery rates are achieved with plate and mesh electrodes, although the same degree of purification can be achieved with a lower current density when mesh electrodes are used.**

**A new concentrator cell technology developed during a WMR3 project in Brunel led to the development of concentrator cells and in this work the effectiveness of activated carbon cloth concentrator electrodes are used. The benefits of this are that the concentration of metal in solution is recovered effectively at high current densities by ACC to meet discharge consent levels. Moreover the recovery rate is accelerated with the use of ACC.**

**The use of MgO as a pH modifier under each electrode type investigated increases the degree of purification and recovery of cobalt.**

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## CHAPTER THREE

### THE USE OF A FLUIDISED BED CELL FOR THE RECOVERY OF COPPER FROM DILUTE AQUEOUS MIXED METAL ION SOLUTIONS

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### **3 INTRODUCTION**

Copper, zinc and cadmium can be recovered from single solutions of their salts using fluidised bed cells under appropriate conditions. The purpose of the work carried out in this chapter is to study the removal of primarily copper from Cu/Zn, Cu/Zn/Cd and Cu/Zn/Fe solutions. Before considering the results for this investigation under different experimental conditions, a description of the chemistry, toxicity and electrodeposition of zinc, copper and cadmium is given.

#### **3.1 ZINC**

##### **3.1.1 Introduction**

Zinc is a bluish white metal with an atomic weight of 65.37. Its physical properties are as follows: density, 7.13 g cm<sup>-3</sup> at 25°C, melting point; 419.6°C and boiling point; 907°C.

Zinc is an important industrial metal. It ranks fourth among metals of the world in terms of annual consumption, being surpassed only by steel, aluminium and copper. Zinc is mined primarily from sulphide ores (sphalerite, ZnS), often associated with ores of copper and/or lead. The automobile industry accounts for almost one third of U.S. slab zinc consumption.

Zinc is used in industry predominantly in its metallic form although there are examples of its use in chemical compound form. Important uses include its role as a major alloying ingredient in brass, as a protective coating for steel and as a chemical compound in rubber and plants<sup>[1]</sup>. Zinc is moderately toxic in some forms but it is not regarded as one of the more toxic heavy metals. The major environmental problem of zinc is that in many cases cadmium (along with arsenic, copper and lead) exists as a co-product of zinc.

The single most important zinc chemical is zinc oxide (ZnO). Zinc oxide (ZnO), 'zinc white' is a white, insoluble powder that was once widely used as a pigment for paints. Today it is mainly used as an accelerator/activator for hardening rubber products (e. g. tyres). Zinc oxide is dispersed to the environment by tyre wear at the rate of 25 kg per million vehicle miles. Since it is made directly

from the ore, the coexistence of cadmium results in cadmium contamination of the ore and the cadmium may not be removed but will accompany the zinc. As a consequence, tyre wear is a significant source of cadmium dispersion into the environment<sup>[2]</sup>.

### 3.1.2 Chemistry of Zinc

Zinc usually occurs as Zn (II) because removal of more electrons would destroy the symmetry of a completed d shell. Since the d shell of zinc is complete, and is not available for bonding, this element shows few properties associated with typical transition elements. It does not show variable valency, and since it has a  $d^{10}$  configuration it cannot produce d-d spectra and hence many of its compounds are white.

When zinc forms complexes its co-ordination number increases 4, 5 or 6. Addition of a base to a solution of the salts of zinc precipitates  $Zn(OH)_2$ . Zinc salts are usually hydrated and when dissolved in water  $[Zn(H_2O)_6]^{2+}$  ions are formed. Solutions of zinc and cadmium are acidic due to hydrolysis and are represented thus:-



### 3.1.3 Toxicity of Zinc

Zinc and many of its compounds are very toxic and can cause both acute and chronic poisoning. Zinc is an essential element for life and is found bound in amino acid complexes. As a result zinc is vital for human growth and must be consumed in the daily diet.

However in industrial settings, considerable hazards are presented by fumes containing finely divided particles of  $ZnO$  which, when inhaled in high concentration, cause an acute illness for a short period of time, known as zinc fume fever. This metal fume fever tends to occur on repeated exposure and is more common than those fevers caused by fumes of other metals.

Zinc fume fever causes a loss of appetite with the onset of thirst, fatigue, tightness and constrictive

pains in the chest, drowsiness and a dry cough. The condition usually clears within 24 hours but may last 2-3 days longer.

Inhalation of  $\text{ZnCl}_2$  fume, for 5-30 mins, causes coughing, nausea and occasionally vomiting. Inflammation in the lungs is also possible. Ingestion of  $\text{ZnSO}_4$  can result in nausea, vomiting, diarrhoea and abdominal cramps<sup>[3]</sup>.

### **3.1.4 Electrodeposition of Zinc**

The equilibrium potential for zinc in contact with a solution containing zinc ions is  $-0.763\text{V}$ . This means that the electrodeposition of zinc from an acid sulphate solution is rendered difficult by the tendency to generate hydrogen instead of depositing zinc. The deposition of zinc from commercial acidic electrolytes with a high acid concentration, would appear even more unlikely. The acid content has a very strong influence on the current efficiency and the power consumption since the current efficiency falls rapidly with increased acid content.

Goodridge and Vance<sup>[4]</sup> carried out a study for the electrowinning of zinc using a circulating bed electrode. It was shown that current efficiencies of 80-90% could be achieved at very high current densities using this system. In another study, it was demonstrated by Scott et al<sup>[5]</sup>, who used a 10L cell with Al cathodes and Ag/Pb anodes, that zinc and acid concentration affected current efficiency and energy consumption. As the zinc concentration was increased the current efficiency also increased because there was an increase in the number of zinc ions in solution. The increase in current efficiency caused a decrease in energy consumption. However, with increasing acidity, current efficiency decreases as the concentration of hydrogen ions increases, so the rate of hydrogen evolution becomes greater and because hydrogen evolution and zinc deposition are both competing reactions it was found that the rate of zinc deposition decreased with increasing acidity. The other variables studied included temperature, impurities and additive levels<sup>[5]</sup>. The authors have considered the effect of additives such as animal glue and antimony and these are found to have a positive effect on the morphology of zinc which is electrodeposited. It was found that additives have no effect on the current efficiency, only the morphology of the deposit<sup>[5]</sup>.

Trivedi<sup>[6]</sup> also found that zinc deposits obtained, using a fluidised bed *chemelec* cell, which had been contaminated with lead were found to have morphologies which were affected by the amount of lead present in the zinc deposits. It was found that the lead content in the zinc deposit was greater for a dilute zinc bath than for a more concentrated zinc bath.

Jirincy and Evans<sup>[7]</sup> carried out a study using a fluidised bed cathode to deposit zinc from acidic sulphate solutions. Their results were in agreement with those obtained by Scott et al<sup>[5]</sup> and they also concluded that the addition of additives, such as glue, positively influenced the mobility of the fluidised bed.

The fact that zinc is electrowon on an industrial scale from such electrolytes is due to the large overpotential for hydrogen deposition on zinc. This overpotential is sensitive to any impurities which may be present in the solution. In a commercial process a highly purified electrolyte must be employed<sup>[8]</sup>. Impurities such as  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  or  $\text{Al}^{3+}$ , which are ions of metals more electropositive than zinc, increase energy consumption because there is an increase in voltage. The current efficiency is found to decrease due to the accumulation of foreign ions at the cathode<sup>[9]</sup>.

Many of the impurities that are likely to codeposit with zinc lower the hydrogen overvoltage and so there will be an increase in the rate of hydrogen evolution which in turn will lower the current efficiency. This has also been found in a study carried out by Dubrovsky and Evans<sup>[8]</sup> where cobalt and nickel impurities were added to a zinc sulphate electrolyte. Since zinc is sensitive to impurities it was found<sup>[8]</sup> that the current efficiency decreased with the addition of these impurities.

The quality of zinc metal can be affected if other metals are codeposited with it. Copper is one metal which will co-deposit with zinc and thus reduce the metal quality of the zinc. The copper content of any electrodeposited zinc will increase as the copper concentration of the electrolyte increases. The presence of impurities in the electrolyte such as antimony and copper decrease the current efficiency for zinc deposition but increase the copper content for zinc deposits. This effect of Cu-Sb interaction on zinc deposition can be counteracted by the presence of glue<sup>[10]</sup>.

The best results obtained with fluidised bed cells are with solutions containing only one metal ion in solution<sup>[11, 12]</sup>, however, with hydrometallurgical leach solutions, particularly those from zinc and cadmium recovery, the presence of other ions such as Cu, Zn, Cd, Fe, Co and Ni affects the efficiency of the electrodeposition<sup>[13]</sup>.

## 3.2 COPPER

### 3.2.1 Introduction

Copper is an abundant trace element found in a variety of rocks and minerals. It is a soft reddish metal and because it is ductile and malleable, it is readily fashioned into wire, tubing and sheets. The pure metal is used extensively in electrical equipment, as well as in alloys such as brass and bronze. Copper is the best electrical conductor among the cheaper metals, but when used for this purpose it must be quite pure, because small amounts of impurities greatly reduce its conductivity<sup>[14]</sup>. Copper is known to be an essential element for land and marine organisms<sup>[15]</sup>.

### 3.2.2 Chemistry of Copper

Copper forms two groups of compounds, in which it has the oxidation states of +1 and +2. Copper (I) forms compounds with the anions of both strong and weak acids. Many of these compounds are stable and insoluble in water. There is a very strong tendency for copper (I) to disproportionate in aqueous solutions into Cu (II) and metallic copper.



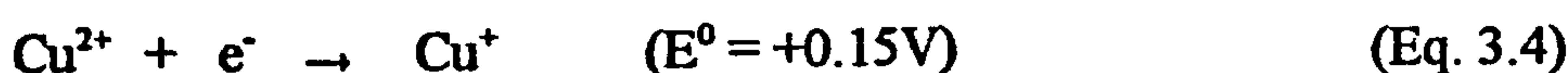
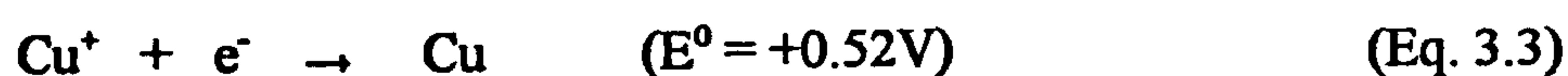
The properties of copper (II) are quite different. Ligands that form strong co-ordinate bonds bind copper (II) readily to form complexes in which the copper has co-ordination numbers of 4 or 6, such as tetraammine copper (II),  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ , and hexaaqua copper(II),  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ . Formation of copper (II) complexes in aqueous solution depends on the ability of the ligands to compete with water for coordination sites. Most copper (II) complexes are coloured<sup>[16]</sup>.



In air the metal oxidises at red-heat to CuO, in this case the Cu<sup>2+</sup> ion is formed - at higher temperatures Cu<sub>2</sub>O is formed with the Cu<sup>+</sup>. Copper dissolves in oxidising acids such as HNO<sub>3</sub>, concentrated H<sub>2</sub>SO<sub>4</sub> or dilute H<sub>2</sub>SO<sub>4</sub> in the presence of air but is resistant to reducing acids such as dilute HCl.

### 3.2.2.1 Chemistry of Cu (I) - d<sup>10</sup>

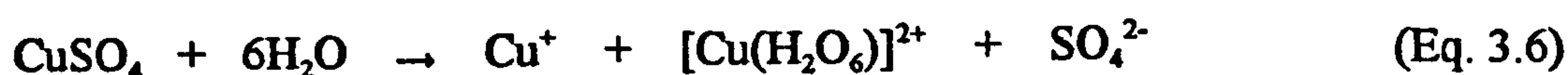
Cu (I) has the closed-shell 3d<sup>10</sup> configuration. If the potentials of Cu (I) and Cu (II) are compared:-



then it can be seen that the Cu<sup>+</sup> ion (Eq. 3.3) is capable of oxidising the Cu<sup>+</sup> in (Eq. 3.4) according to:-



This shows that disproportionation of Cu (I) aquo-ion occurs. Only insoluble salts of Cu (I) are stable in water e.g. CuCl, CuI and CuCN. Those that dissolve undergo disproportionation; CuSO<sub>4</sub> is an example of a soluble salt which undergoes disproportionation since it reacts immediately with water as is illustrated by the following equation:-



### 3.2.2.2 Chemistry of Cu(II) - d<sup>9</sup>

The most stable state of copper in solution is the Cu (II) state. The d<sup>9</sup> configuration of Cu(II) gives rise to Jahn-Teller effects. When Cu (II) salts are dissolved in an excess of water the blue aquo-ion [Cu(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> is formed. Substitution reactions of [Cu(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> with added ligands gives rise to a large number of co-ordination compounds. With concentrated aqueous ammonia, for example, the substitution proceeds as far as [Cu (NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup>.

### 3.2.2.3 Chemistry of Cu(III) - d<sup>8</sup>

Copper (III) is isoelectronic with nickel. Oxidation of Cu(OH)<sub>2</sub> in alkaline solution with chlorine gives a strongly oxidising solution which evolves oxygen on acidification. The solid cuprates (III) can be obtained by heating mixtures of CuO and alkali metal superoxides in oxygen<sup>[17]</sup>.

### 3.2.3 Toxicity of Copper

Although copper is essential to humans and living organisms, at elevated levels, copper becomes toxic; therefore, copper levels in natural environments, and its biological availability are important. To be available to biological systems, copper must be present in a readily soluble form. Some toxic elements are biologically unavailable because they are rare (e.g. Os) or highly insoluble (e.g. Al) in the environment. Copper, however, is relatively abundant in the earth's crust and moderately soluble. The form taken by the metal and hence its bioavailability depends on environmental factors such as pH, redox potential, soil and sediment type, water hardness and organic content. These factors vary in the environment, giving rise to possible conditions of copper deficiency or toxicity<sup>[18]</sup>.

### 3.2.4 Electrodeposition of Copper

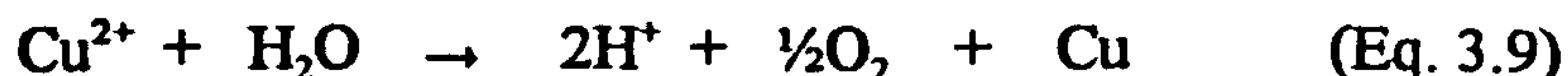
In electrowinning the cathode reaction is:-



However, because of the use of insoluble anodes, oxygen is released at the anode:-



and the overall net reaction is:-



A previous investigation<sup>[19]</sup> carried out on the electrodeposition of copper studied the effect which parameters such as temperature and acid concentration have on current efficiency and energy consumption. It was determined that as the current density was increased the current efficiency also increased. The same was true when copper was deposited from a copper(II)ammine sulphate solution<sup>[20]</sup> where it was found that as the current density was increased, the current efficiency also increased. The current density was also seen to affect the deposit in that higher current densities formed spongy copper deposits which flaked back into solution and hence caused a decrease in current efficiency. It has also been established that pH does not affect the deposition of copper from a chloride or sulphate solution<sup>[21]</sup>.

The electrodeposition of a mixed metal ion solution containing copper, cadmium and nickel has been studied with the use of the *chemelec* cell in conjunction with the use of an in-situ ion exchange resin<sup>[22]</sup>.

### **3.2.5 Effect of Fe (II) and Fe (III) on Copper Electrodeposition**

During the hydrometallurgical extraction of copper-bearing ores, it is found that the leach liquors often contain a substantial amount of iron. Recovery of copper from these solutions is generally achieved by cementation or electrolysis. Since the copper produced by cementation is of low purity, the electrolytic method tends to be more widely practiced.

Dew and Phillips<sup>[23]</sup> studied the electrodeposition of Cu in the presence of Fe using a sulphate solution and found that during the process of electrolysis it is the Fe (II) which is oxidised at the anode and Fe (III) is reduced at the cathode. As more base is added to the sulphate solution the Fe (II) oxidises to Fe (III). However, the Fe (III) is cathodically reduced to Fe (II) which results in a mixed potential at the cathode during copper electrowinning. The presence of Fe (III) in the electrolyte causes a loss in current efficiency and often produces poor quality cathode copper.

In an investigation carried out by Das and Gopala Krishna<sup>[24]</sup> on the effect of Fe(III) during Cu electrowinning at high current densities, it was found that current efficiency decreased and the

power consumption increased with an increase in Fe (III) concentration. The addition of Fe (II) to a solution containing Cu-Fe (III) helped to reduce this effect. It was also concluded that if the ratio of Fe(III)/Fe (II) is maintained at less than or equal to 1 then 90% current efficiency of copper removal can be achieved.

If a solution does contain Fe (III) ions then the major reactions at the cathode are:-



The electrode potential of Fe (III)/Fe (II) is 0.773V and that of Cu (II)/Cu is 0.34V. Since Fe (III)/Fe (II) is more positive it shows that the Fe (III), if present during copper electrowinning, will consume all the current first as Fe (III) is reduced prior to the reduction of Cu (II)/Cu.

### **3.3 CADMIUM**

#### **3.3.1 Introduction**

Cadmium is a very scarce element since its concentration in the earth's crust is 0.1-0.2 ppm and is generally found to coexist, as a contaminant in zinc ores. Cadmium is a soft ductile material which retains its lustre even when exposed to air. Its melting point is 320.9°C and its boiling point is 765°C which makes it useful for incorporation in many low melting point alloys and solders.

Natural processes dispersing cadmium throughout the environment include volcanic action and the weathering of crustal materials. Subsequent atmospheric movements and sedimentation lead to further dispersion.

Cadmium has been used in the past mainly because of its low cost as a by-product of zinc smelting and refining. Cadmium and its salts are used in numerous and varied industrial processes. Electroplating is the major use of the metal itself.

The use of cadmium for metal plating and in pigments has declined sharply in recent years because of environmental restrictions on the use of cadmium. Usage of cadmium varies from country to country, but the major uses at present are for rechargeable batteries, pigments, electroplating, stabilisers for plastic (PVC) and special alloys<sup>[2]</sup> (Table 1). Cadmium can be used to plate metals to prevent corrosion. The advantages of this include good resistance to alkalis and water. The high ductility of cadmium allows parts to be further shaped without peeling off the protective layer.

The disadvantages of this include the high cost and low resistance of cadmium to acid atmospheres. This resistance to acid atmospheres was apparent when during, World War II, outbreaks of 'food poisoning' due to cadmium occurred frequently. The acidic foods and beverages solubilised the cadmium plating<sup>[16]</sup>.

Cadmium is a constituent of alloys and is utilized in many different applications such as amalgam in dentistry and Ni-Cd storage batteries. In recent years cadmium has been used extensively for rechargeable batteries. These batteries are becoming smaller in size and so can be used in small appliances. Eventually these batteries find their way into household and municipal wastes, and may be incinerated, which poses legitimate environmental cause for concern.

**Table 1:- Cadmium Consumption Patterns (MT/year)**

Use	West Germany	United States		Market Economy
	1989	1991	1993	1988
Ni-Cd batteries	427 (48%)	1450 (45%)	(65%)	10,175 (55%)
Pigments	282 (32%)	520 (16%)	(15%)	3,700 (20%)
Stabilisers	94 (11%)	390 (12%)	(12%)	1,850 (10%)
Electroplating	35 (4%)	650 (20%)	(7%)	1,850 (10%)
Glass manufacturing	26 (3%)			
Alloys	21 (2%)		(5%)	555 (5%)
Other	1 (0%)	230 (7%)		

### **3.3.2 Toxicity of Cadmium**

Whenever the metal cadmium or any of its compounds are mentioned today, the topics invariably discussed are the environmental and health considerations. Whilst zinc has been shown to be an essential element cadmium is a highly toxic metal with no known function in animal metabolism. Industrial exposures to humans of cadmium in industrial operations has led to the inhalation of cadmium via the respiratory tract, although bad hygienic practices may result in some gastrointestinal absorption.

Inhalation of fumes or dusts containing cadmium and its compounds primarily affects the respiratory tract. Cigarette smoking is an additional source of cadmium because much of the cadmium present in tobacco is absorbed.

Water and soil pollution by cadmium is often observed in the proximity of lead and zinc smelters. The wastewaters of these industries are treated by conventional methods and then discharged into water streams. The cadmium levels in these streams have then been shown to increase considerably. Also wastewaters from metallurgical works and from factories manufacturing dyes, cadmium-nickel storage batteries or mineral fertilizers sometimes contain cadmium in substantial amounts<sup>[3]</sup>.

### **3.3.3 Electrodeposition of Cadmium**

The introduction of stringent wastewater guidelines is emphasizing the fact that improved processes for the recovery of cadmium from dilute aqueous solutions are required. Much research effort has been devoted towards removal of cadmium metal from aqueous solutions, in particular using electrolytic reduction processes<sup>[25,26]</sup>.

Based on this, the *chemelec* cell is used for the first time in this work to recover cadmium from dilute mixed metal ion solutions under a variety of conditions. Studies<sup>[27]</sup> have been carried out involving the removal of cadmium from a mixed metal ion solution containing cobalt and nickel using a stainless steel and cadmium rotating disc electrode. Scott and Paton<sup>[28]</sup> reported on the

electrodeposition of cadmium from electrolyte solution containing ferric ( $\text{Fe}^{3+}$ ) and cadmium ions ( $\text{Cd}^{2+}$ ) using a batch cell consisting of Pt and Cu foil anodes and cathodes respectively and a flow cell consisting of an anode and cathode separated by a membrane. It was found that the efficiency of the electrodeposition was limited by the concentration of ferric and cadmium ions present in the solution. This was because the ferric ion was readily reduced to  $\text{Fe}^{2+}$  and this caused an immediate reduction in efficiency.

Boyanov et al<sup>[13]</sup> studied the effects of cathode density, pH, time, type of electrode, distance between electrodes and the presence of other ions, such as  $\text{Fe}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Co}^{2+}$ , in solution for the removal of Cu and Cd from dilute solutions. The study was carried out using a *chemelec* cell and fluidised glass beads. It was found that at high concentrations of Cu, the Cu metal would deposit first and then Cd would begin to deposit once the Cu concentration in solution had decreased from  $2.0 \text{ g dm}^{-3}$  to  $0.2 \text{ g dm}^{-3}$ . The influence of other ions showed that Co and Zn did not have any significant effect on the deposition of Cu, whereas  $\text{Fe}^{2+}$  affected the deposition because  $\alpha_{\text{Cu}}$  and  $\eta_{\text{Cu}}$  were low and  $W_{\text{Cu}}$  was high with the presence of Fe in solution.

For the first time, the use of fluidised bed electrolysis has been applied to the recovery of cadmium from dilute Cu/Zn/Cd solutions.

### 3.4 EXPERIMENTAL

In this work a *Chemelec* fluidised bed electrochemical precious metal recovery (PMR) cell supplied by (Bewt Water Engineers Ltd), of  $10 \text{ dm}^{-3}$  capacity was used. Two stainless steel mesh cathodes and three mixed metal oxide anodes were alternately placed in the electrolysis chamber. During electrolysis, samples were collected from the reservoir tank every hour to be analysed by Atomic Absorption Spectroscopy (AAS).

The electrolyte solutions used in these experiments were prepared from reagent grade copper sulphate crystals ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ), zinc sulphate crystals ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ), cadmium sulphate crystals ( $\text{CdSO}_4$ ) and iron sulphate crystals ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) and the required amount of 18 M sulphuric acid

to dissolve the materials was used. Three different mixed electrolyte solutions of composition:-

- (A)  $\text{Cu}^{2+}$  in combination with  $\text{Zn}^{2+}$  controlled at a pH of 4.8 - 5.2 with  $\text{NH}_4\text{OH}$
- (B)  $\text{Cu}^{2+}$  in combination with  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  controlled at a pH of 3.0 with  $\text{NaOH}$
- (C)  $\text{Cu}^{2+}$  in combination with  $\text{Zn}^{2+}$  and  $\text{Fe}^{2+}/\text{Fe}^{3+}$  controlled at a pH of 2.0 with  $\text{NH}_4\text{OH}$

were investigated. The pH was controlled by the addition of either  $\text{NH}_4\text{OH}$  or  $\text{NaOH}$ .

For each set of experiments the following effects were investigated:-

- Effect of current density using mesh electrodes
- Effect of current density using plate electrodes
- Effect of current density using ACC

### 3.4.1 Methodology

#### Combination (A)

For this suite of experiments the concentration of copper in solution was  $1.0 \text{ g dm}^{-3}$  and the corresponding concentration of zinc in solution was also  $1.0 \text{ g dm}^{-3}$ . The pH of the solution was maintained between 4.8 - 5.2 using  $\text{NH}_4\text{OH}$ .

#### Combination (B)

For this suite of experiments the solution contained a copper concentration of  $1.0 \text{ g dm}^{-3}$ ,  $1.0 \text{ g dm}^{-3}$  of zinc and  $0.1 \text{ g dm}^{-3}$  of cadmium. The concentration of sulphuric acid in the solution was 0.1 M. During electrolysis, the pH of the solution was monitored constantly and maintained at 3.0 using  $\text{NaOH}$ . This was used instead of  $\text{NH}_4\text{OH}$  because high concentrations of ammonia form complexes with cadmium to give  $[\text{Cd}(\text{NH}_3)]^{2+}$ , whereas the sodium ions do not interfere with AAS analysis of cadmium<sup>[29]</sup>.



## **Combination (C)**

The following suite of experiments contained a copper concentration of  $1.0 \text{ g dm}^{-3}$ ,  $0.5 \text{ g dm}^{-3}$  of zinc and  $1.0 \text{ g dm}^{-3}$  of iron. The concentration of  $\text{H}_2\text{SO}_4$  in the solution was  $0.1\text{M}$  and the pH was kept constant at  $2.0$  using  $\text{NH}_4\text{OH}$ . Samples were taken every hour for analysis by AAS.

The current and voltage were monitored throughout the experiments and the parameters determined for each experiment were:-

- Degree of purification ( $\alpha$ )
- Current efficiency ( $\eta$ )
- Energy consumption (W)

## **3.5 RESULTS AND DISCUSSION**

The results are presented graphically and error bars have been calculated for each data point. This is represented in Figure. 3.1.

### **3.5.1 Effect of current density using mesh, plate and ACC for recovery of Cu from a Cu/Zn solution**

The effect of current density on the recovery of copper using mesh, plate and ACC electrode configurations are described. The current densities studied with this combination were  $15 \text{ Am}^{-2}$ ,  $20 \text{ Am}^{-2}$  and  $25 \text{ Am}^{-2}$ .

#### **3.5.1.1 Effect of current density using mesh electrodes**

When using mesh electrodes at current densities of  $15$ ,  $20$  and  $25 \text{ Am}^{-2}$  it was found that after a  $2 \text{ h}$  electrolysis period the degree of purification was  $26.67$ ,  $42.22$  and  $58.70\%$  respectively and after  $8 \text{ h}$  the values increased to  $98.06$ ,  $98.33$  and  $98.18\%$  respectively [Figure. 3.1a].

The current efficiency decreased as the electrolysis proceeded using current densities of  $15$ ,  $20$  and  $25 \text{ Am}^{-2}$  from  $88.00$ ,  $83.00$  and  $79.00\%$  respectively after  $2 \text{ h}$  of electrolysis to  $62.01$ ,  $46.64$  and  $38.47\%$  respectively after  $8 \text{ h}$  of electrolysis [Figure. 3.1b].

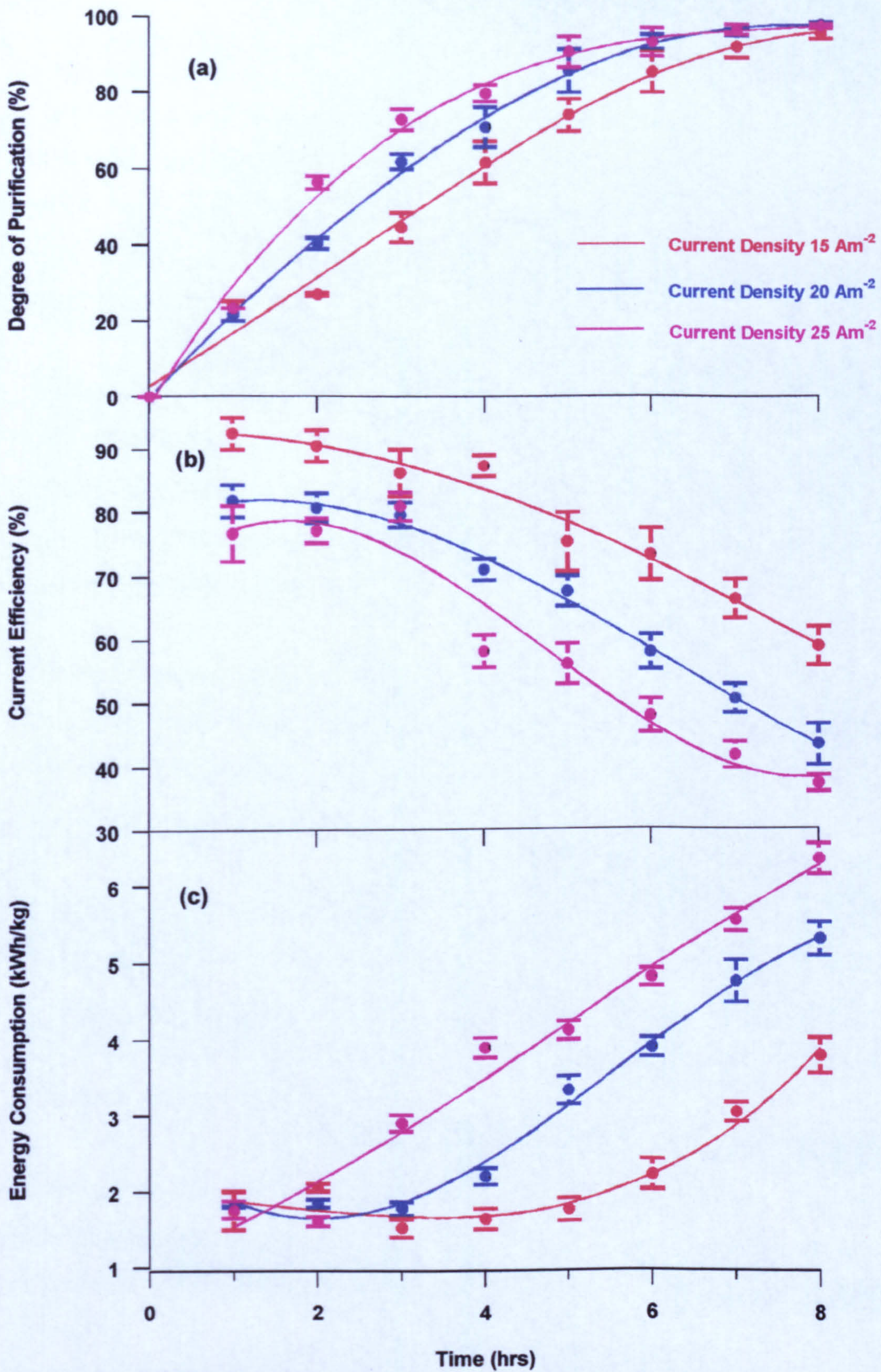


Figure 3.1:- Effect of current density for the recovery of copper using mesh electrodes from a  $1.0 \text{ g dm}^{-3}$  solution of  $\text{CuSO}_4$  and  $\text{ZnSO}_4$  in  $0.1\text{M H}_2\text{SO}_4$ .

The energy consumption at each current density applied followed a general trend of increasing as the electrolysis proceeded. However, it was observed that when a current density of  $15 \text{ Am}^{-2}$  was used, the energy consumption increased from  $1.50 \text{ kWh kg}^{-1}$  after the first hour to  $2.00 \text{ kWh kg}^{-1}$  after the second hour of electrolysis. The energy consumption then decreased to  $1.64 \text{ kWh kg}^{-1}$  following another hour of electrolysis but from the fifth hour onwards the energy consumption rose steadily to  $3.53 \text{ kWh kg}^{-1}$  after 8 h of electrolysis [Figure. 3.1c].

The effect of current density was to optimise the degree of purification in the presence of mesh electrodes when a high current density of  $25 \text{ Am}^{-2}$  was used. Although at a lower current density of  $15 \text{ Am}^{-2}$  current efficiency was maintained throughout the whole electrolysis process. In terms of energy consumption, the optimum current density was  $15 \text{ Am}^{-2}$  giving the lowest value of energy consumption after 8 h of electrolysis.

#### **3.5.1.2 Effect of current density using plate electrodes**

When using plate electrodes in place of stainless steel mesh electrodes at current densities of 15, 20 and  $25 \text{ Am}^{-2}$ , it was found that the degree of purification,  $\alpha_{\text{Cu}}$  increased over the 8 h electrolysis period as the current density was raised.

After the first hour of electrolysis the value of  $\alpha_{\text{Cu}}$  using a current density of  $15 \text{ Am}^{-2}$  was 7.50%. This value, at the end of 4 h electrolysis, increased to 48.75% and after 8 h to 97.19%. Under higher current densities, at 20 and  $25 \text{ Am}^{-2}$ ,  $\alpha_{\text{Cu}}$  increased from 23.81% and 25.58% respectively after the initial hour of electrolysis to 98.81% and 98.84% respectively after a full 8 hour electrolysis period [Figure. 3.2a].

In terms of current efficiency it can be seen that at a low current density of  $15 \text{ Am}^{-2}$  the current efficiency increases from a value of 33.73% after the first hour of electrolysis to a value of 54.63% following an 8 hour period of electrolysis [Figure. 3.2b].

As the current density was increased to  $20 \text{ Am}^{-2}$  and  $25 \text{ Am}^{-2}$  it was found that the current

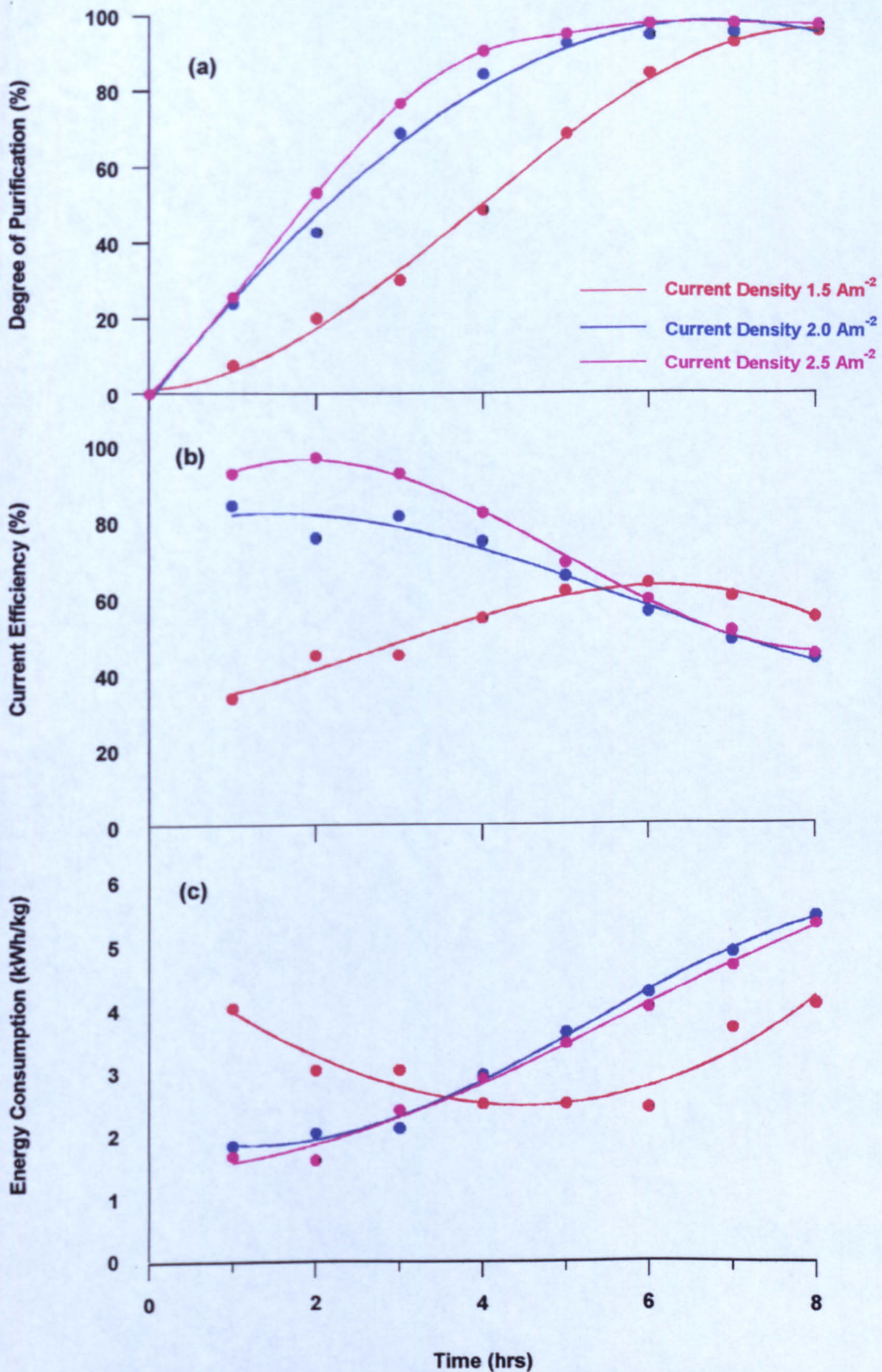


Figure 3.2:- Effect of current density on the recovery of copper using plate electrodes from a  $1.0 \text{ g dm}^{-3}$  solution of  $\text{CuSO}_4$  and  $\text{ZnSO}_4$  in  $0.1\text{M H}_2\text{SO}_4$

efficiency values decreased as the reaction proceeded. In the initial hours of electrolysis  $\eta_{Cu}$  dropped in value from 75.88% and 96.96% respectively after 2h of electrolysis and falling to 43.74% and 44.79% respectively at the end of the 8 h electrolysis period.

At the lower current density of 15 Am<sup>-2</sup> the energy consumption was observed to decrease from a value of 4.00 kWh kg<sup>-1</sup> at the end of the first hour of electrolysis to 2.3 kWh kg<sup>-1</sup> after 6 h of electrolysis. Following this the values for  $\eta_{Cu}$  increased after the final 8 h of electrolysis to 4.01 kWhkg<sup>-1</sup>.

When the current density was raised to 20 Am<sup>-2</sup> and 25 Am<sup>-2</sup> it was noted that the energy consumption increased throughout the 8 h electrolysis period. The value for  $W_{Cu}$  after 2h electrolysis was 2.00 kWh kg<sup>-1</sup> and 1.57 kWh kg<sup>-1</sup>. This value then increased steadily over the electrolysis period to give a value of 5.40 kWh kg<sup>-1</sup> and 5.27 kWh kg<sup>-1</sup> after 8 h [Figure. 3.2c].

From this study of the effect of current density using plate electrodes it is shown that optimum recovery was achieved with a current density of 25 Am<sup>-2</sup>. The optimum conditions for current efficiency and energy consumption were obtained when a current density 15 Am<sup>-2</sup> was used.

### **3.5.1.3 Effect of current density using ACC**

When using ACC in place of mesh / plate electrodes it was seen that the degree of purification increased as the current density was raised. After 5 h of electrolysis, using a current density of 15 Am<sup>-2</sup>,  $\alpha_{Cu}$  was 60.64% and then increased to 86.44% after 8 h. The corresponding values for  $\alpha_{Cu}$  when using current densities of 20 and 25 Am<sup>-2</sup> were 76.25% and 92.50% respectively after 5 h of electrolysis and after 8 h electrolysis these values increased to 92.50% and 99.38% respectively [Figure. 3.3a].

The current efficiency followed a different trend for each of the current densities studied. After the initial hour of electrolysis, the value for  $\eta_{Cu}$  was 89.94% when a current density of 15 Am<sup>-2</sup> was utilized. This value then decreased steadily to 57.62% after a 4 h period of electrolysis. During the

next hour, the current efficiency rose to 64.08% but then fell to 61.83% after 6 h. Following this, the current efficiency gradually declined in value to 57.09% after the 8 h electrolysis period.

With the use of 20 Am<sup>-2</sup> it was found that  $\eta_{Cu}$  increased from 33.73%, after the initial hour of electrolysis, to 67.45% following 3 h of electrolysis.  $\eta_{Cu}$  then fell to a value of 39.90% when the 8 h period of electrolysis was completed. The current efficiency followed the same trend at a current density of 25 Am<sup>-2</sup> but in this case  $\eta_{Cu}$  increased from 75.88% after 1 h electrolysis to 92.75% after 2 h electrolysis and after 8 h electrolysis a current efficiency of 41.89% was achieved [Figure. 3.3b].

At a low current density of 15 Am<sup>-2</sup>, there was a large increase in energy consumed between the first and third hour of electrolysis; the values being 2.34 and 4.95 kWh kg<sup>-1</sup> respectively. From the fourth hour to the seventh hour the energy consumption decreased from 4.83 kWh kg<sup>-1</sup> to 4.87 kWh kg<sup>-1</sup> respectively but then increased to a value of 4.87 kWh kg<sup>-1</sup> for the final eighth hour of electrolysis.

The energy consumption, when using a current density of 20 Am<sup>-2</sup>, following 1 h of electrolysis was 5.00 kWh kg<sup>-1</sup> but this value then declined to 4.59 kWh kg<sup>-1</sup> at the end of 5 h electrolysis. The energy consumption then increased to 6.27 kWh kg<sup>-1</sup> when the 8 h electrolysis period was completed.

The use of 25 A m<sup>-2</sup> showed a decrease in the energy consumption between hours 1 and 2. From the third hour onwards there was a steady increase from 2.00 kWh kg<sup>-1</sup> to 5.84 kWh kg<sup>-1</sup> after 8h of electrolysis [Figure. 3.3c].

With ACC the optimum recovery is achieved at high current density, 25 Am<sup>-2</sup>. The current efficiency is best maintained throughout the whole reaction when a low current density of 15Am<sup>-2</sup> was used but it should be noted that as a higher current density is used, 25 Am<sup>-2</sup> a greater value for  $\alpha_{Cu}$  is achieved in the initial stages of electrolysis when the current efficiency is also high.

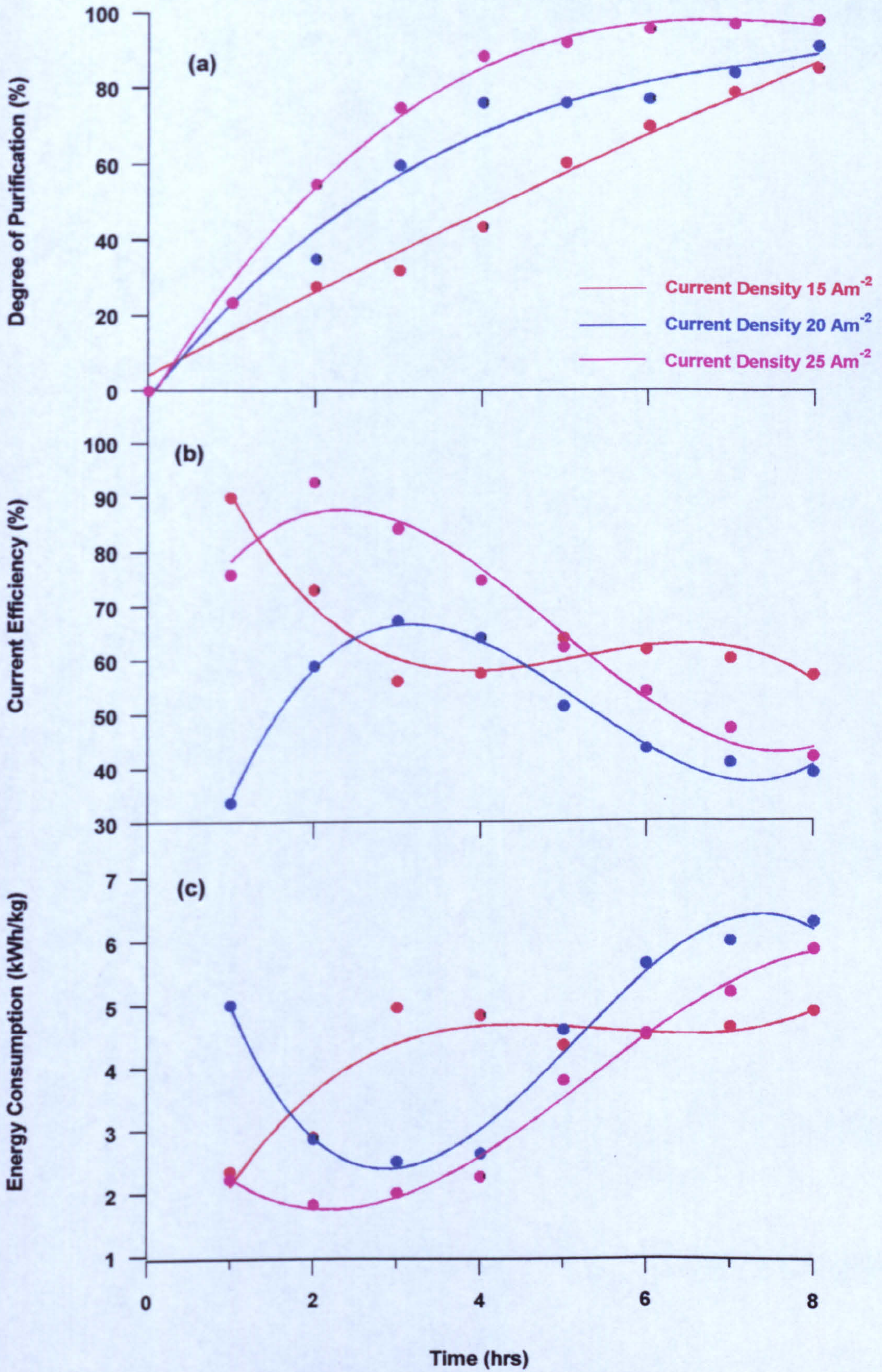


Figure. 3.3:- Effect of current density on the recovery of copper using ACC electrode from a 1.0 g dm<sup>-3</sup> solution of CuSO<sub>4</sub> and ZnSO<sub>4</sub> in 0.1 M H<sub>2</sub>SO<sub>4</sub>.

#### **3.5.1.4 Comparison between mesh, plate and ACC for combination (A)**

This suite of experiments was carried out to investigate the effect of current density on the recovery of Cu from a Cu/Zn solution using different electrode configurations. Comparing the three types of electrodes mesh, plate and ACC, it was found that plate electrodes, when used at  $25 \text{ Am}^{-2}$ , gave a better degree of purification in a shorter period of time. This was illustrated by the fact that  $\alpha_{\text{Cu}} > 90\%$  was achieved after 4 h of electrolysis whereas with the other electrodes such recovery values were obtained only after 5 h or 7 h of electrolysis depending on which current density was employed. The current efficiency in the early stages of electrolysis was also better for plate electrodes compared to the other types of electrodes used. However, if the comparison of the three electrodes is made over the full 8 h of electrolysis, then ACC proved to be the best with the greatest degree of purification being maximised after the 8 h electrolysis period.

In conclusion, if the recovery of the metal is important, then ACC is the best option, but if the time for recovery is the limiting factor then a plate electrode should be used with a cathode current density of  $25 \text{ Am}^{-2}$ .

#### **3.5.2 Effect of current density using mesh, plate and ACC for recovery of Cu and Cd from a Cu/Zn/Cd solution**

The effect of current density on the recovery of Cu and Cd from a Cu/Zn/Cd solution using mesh, plate and ACC electrode configurations are described.

##### **3.5.2.1 Effect of current density using mesh electrodes**

With the use of mesh electrodes at current densities of 15, 20 and  $25 \text{ Am}^{-2}$  it was found that after a 2 h electrolysis period the degree of purification was 22.00, 50.00 and 61.70% respectively and after 8 h the values increased to 97.25, 99.46 and 99.63% respectively [Figure.3.4a].

The current efficiency followed different trends for each of the current densities studied. With a current density of  $15 \text{ Am}^{-2}$ , the current efficiency decreased from 6.74%, after the first hour of electrolysis, to 6.18% after the second hour of electrolysis. Between the third and fourth hour of



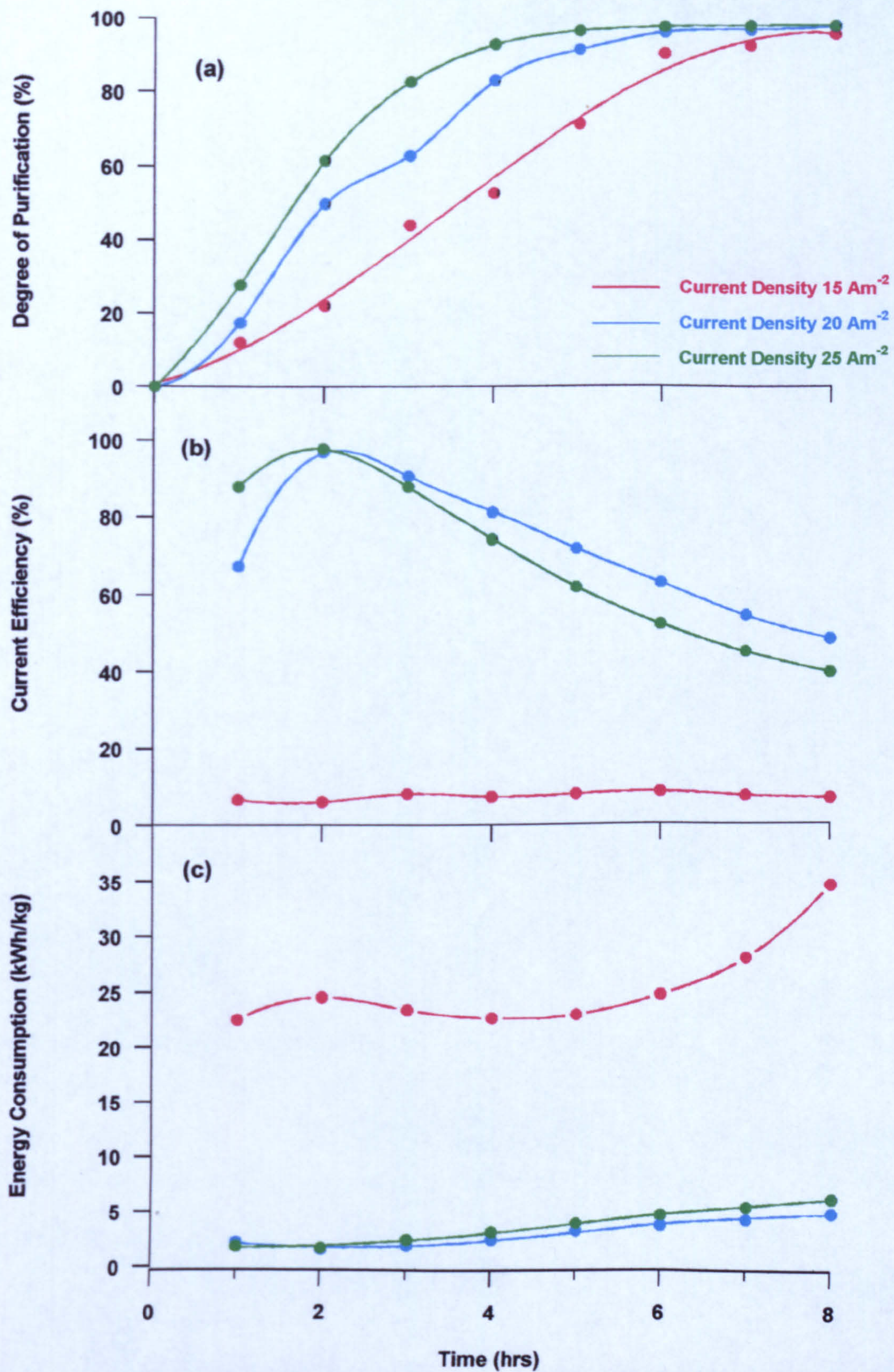


Figure. 3.4:- Effect of current density for the recovery of copper using mesh electrodes from a 1.0gdm<sup>-3</sup> solution of CuSO<sub>4</sub>, ZnSO<sub>4</sub> and 0.1 g dm<sup>-3</sup> of CdSO<sub>4</sub> in 0.1 M H<sub>2</sub>SO<sub>4</sub>

electrolysis the current efficiency decreased from 8.24% to 7.44%. After 6 h,  $\eta_{Ca}$  had increased to 8.57% but then decreased to 6.83% after the 8 h electrolysis period. With a current density of  $20\text{Am}^{-2}$  the current efficiency increased from 67.45% to 96.96% after 2 h of electrolysis but then decreased gradually to 48.22% after 8 hours of electrolysis. When using a current density of  $25\text{Am}^{-2}$  the current efficiency increased from 87.69% to 97.81% in the initial 2 h of electrolysis. The current efficiency was greater in the first hour of electrolysis for  $25\text{ Am}^{-2}$  compared to that of  $20\text{Am}^{-2}$ , due to a 10% increase in  $\alpha_{Ca}$  for  $25\text{ Am}^{-2}$ . After 8 h of electrolysis the current efficiency for  $25\text{ Am}^{-2}$  had decreased to 39.48% [Figure. 3.4b].

The energy consumption was found to increase as the current density was increased. After 8 h the values for  $W_{Ca}$  were 34.55, 4.90 and 6.19 kWh  $\text{kg}^{-1}$  when 15, 20 and  $25\text{ Am}^{-2}$  were used respectively [Figure. 3.4c].

The effect of current density was to optimise the degree of purification in the presence of mesh electrodes. The degree of purification was found to increase as the current density was increased. Also, at a higher current density the value of current efficiency was maintained throughout the entire electrolysis process. In terms of energy consumption, the optimum current density was  $15\text{ Am}^{-2}$  giving the lowest value of energy consumption after 8 h of electrolysis.

### **3.5.2.2 Effect of current density using plate electrodes**

When using plate electrodes at current densities of 15, 20 and  $25\text{ Am}^{-2}$  it was found that after a 3h electrolysis period the degree of purification was 45.83, 63.04 and 74.42% respectively and after 8 h the values increased to 98.18, 99.46 and 99.83% respectively [Figure. 3.5a].

The current efficiency when using a current density of  $15\text{ Am}^{-2}$  decreased from 80.07% after 2 h of electrolysis to 66.22% after 8 h of electrolysis. When higher current densities of 20 and  $25\text{ Am}^{-2}$  were used it was found that the values of current efficiency were 84.32% and 74.20% respectively after 3 h of electrolysis. These values then decreased over the 8 h electrolysis period to 49.27 and 35.94% respectively [Figure. 3.5b].

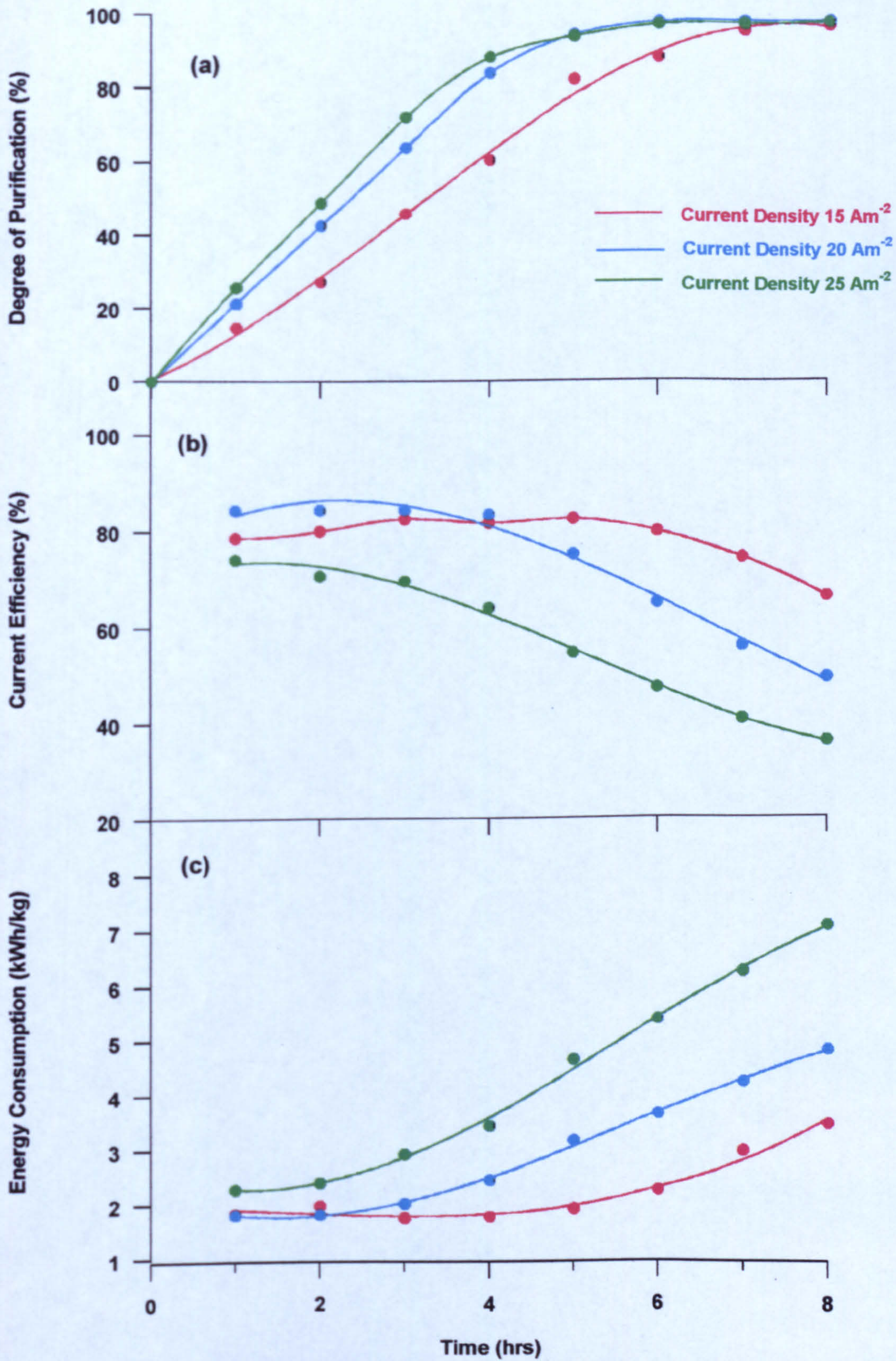


Figure. 3.5:- Effect of current density for the recovery of copper using plate electrodes from a 1.0gdm<sup>-3</sup> solution of CuSO<sub>4</sub>, ZnSO<sub>4</sub> and 0.1 g dm<sup>-3</sup> of CdSO<sub>4</sub> in 0.1 M H<sub>2</sub>SO<sub>4</sub>

The energy consumption at each current density applied followed a general trend of increasing as the electrolysis proceeded. When operating at a current density of  $15 \text{ Am}^{-2}$ , however, the value of  $W_{\text{Cu}}$  increased in the initial 2 h from  $1.82 \text{ kWh kg}^{-1}$  to  $1.96 \text{ kWhkg}^{-1}$ . The following 2 h of electrolysis showed a decrease in  $W_{\text{Cu}}$  to  $1.76 \text{ kWh kg}^{-1}$  after 4 h of electrolysis. The energy consumed after 8 h of electrolysis was  $3.44 \text{ kWh kg}^{-1}$  [Figure. 3.5c].

When using current densities of 20 and  $25 \text{ Am}^{-2}$ , it was found that the values for  $W_{\text{Cu}}$  after a 2 h electrolysis period were 1.80 and  $2.38 \text{ kWh kg}^{-1}$  respectively and these values increased to 4.79 and  $6.99 \text{ kWh kg}^{-1}$  after 8 h of electrolysis respectively.

The optimum current density to utilize when using plate electrodes was found to be  $20 \text{ Am}^{-2}$ . At a low current density of  $15 \text{ Am}^{-2}$ , 80% recovery can be achieved after 5 h electrolysis whereas with 20 and  $25 \text{ Am}^{-2}$ , greater than 90% recovery is obtained after 5 h. Also at a current density of  $20 \text{ Am}^{-2}$ , current efficiency and energy consumption were maintained well throughout the reaction.

### 3.5.2.3 Effect of current density using ACC

When using ACC as opposed to mesh / plate electrodes, it was found that the degree of purification increased as the current density was increased. Where  $15 \text{ Am}^{-2}$  were utilized,  $\alpha_{\text{Cu}}$  increased in value from 20.45% to 59.09% after 2 h and 8 h of electrolysis respectively. When using  $20 \text{ Am}^{-2}$ ,  $\alpha_{\text{Cu}}$  was 23.40% after 2 h of electrolysis and this value then increased to 97.61% after completion of 8 h of electrolysis. Further increasing the current density to  $25 \text{ Am}^{-2}$ ,  $\alpha_{\text{Cu}}$  increased from 57.14% to 91.84% after 5 h of electrolysis giving a final value of 98.98% after 8h of electrolysis [Figure. 3.6a ].

When using a current density of  $15 \text{ Am}^{-2}$ , the value for the current efficiency had decreased in the initial 4 h of electrolysis from 89.94% to 50.59% and after 8 h the current efficiency had decreased further to 36.54%. As the current density was increased to  $20 \text{ Am}^{-2}$  the value of  $\eta_{\text{Cu}}$  increased in the first 4 h of electrolysis, from 33.73% to 55.86%. There was an increase in  $\eta_{\text{Cu}}$  instead of a decrease, as observed with  $15 \text{ Am}^{-2}$ , because at this current density a better degree of purification

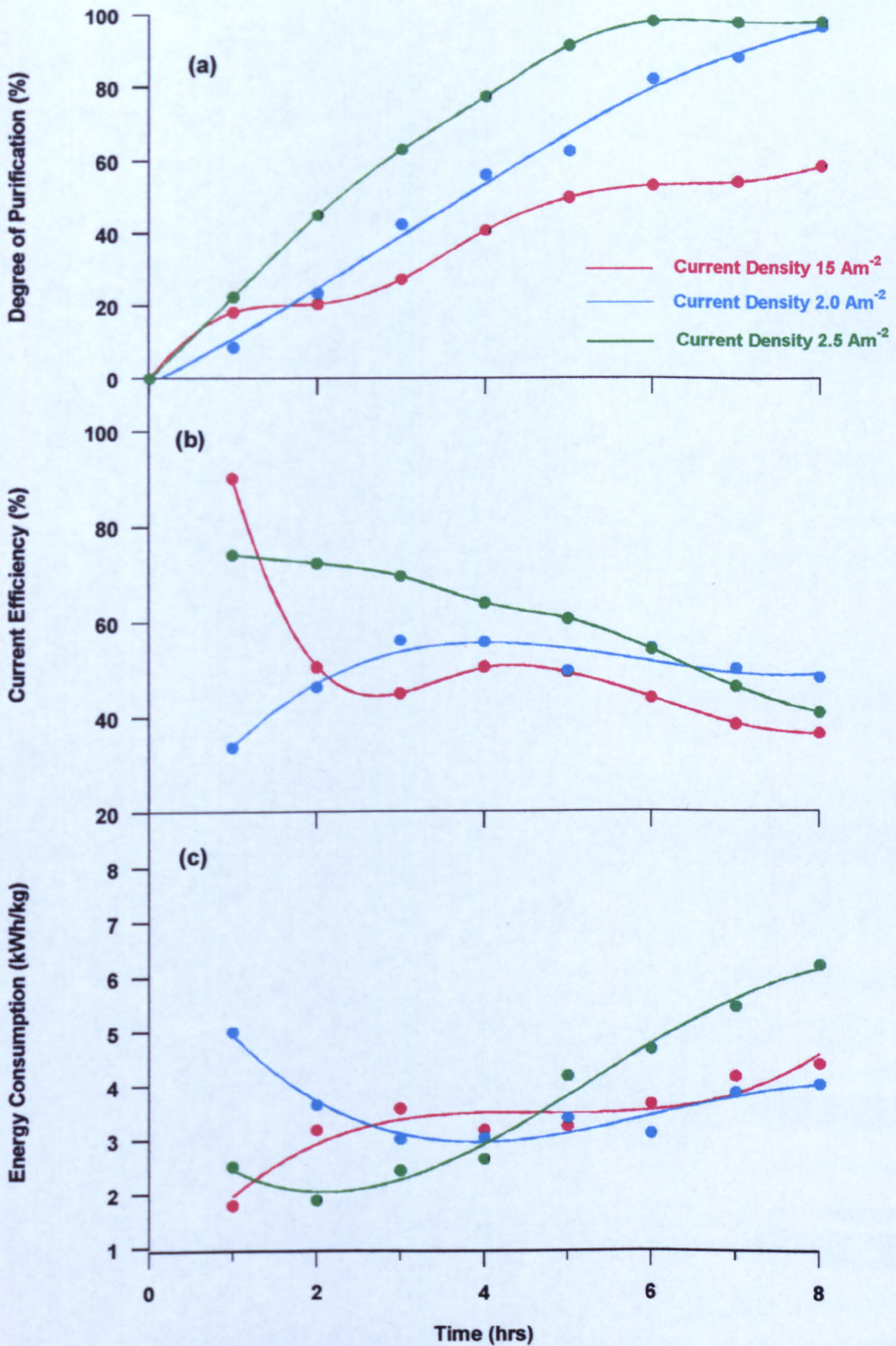


Figure. 3.6:- Effect of current density for the recovery of copper using ACC electrode from a 1.0gdm<sup>-3</sup> solution of CuSO<sub>4</sub>, ZnSO<sub>4</sub> and 0.1 g dm<sup>-3</sup> of CdSO<sub>4</sub> in 0.1 M H<sub>2</sub>SO<sub>4</sub>

was achieved in the initial 4 h of electrolysis. However, at the end of the 8 h electrolysis period,  $\eta_{\text{Cu}}$  had dropped in value to 49.27%. With a current density of 25 Am<sup>-2</sup> the current efficiency was 72.44% and 40.89% after 2 h and 8 h of electrolysis respectively [Figure. 3.6b].

The energy consumption was found to increase over the 8 h electrolysis period for each of the current densities studied. The values of  $W_{\text{Cu}}$  for 15, 20 and 25 Am<sup>-2</sup> were 3.17, 3.64 and 1.88 kWh kg<sup>-1</sup> after 2 h of electrolysis respectively and these values increased to 4.38, 4.01 and 6.18 kWh kg<sup>-1</sup> respectively after 8 h of electrolysis [Figure. 3.6c ].

The best results obtained with ACC were at a current density of 25 Am<sup>-2</sup> where >90%  $\alpha_{\text{Cu}}$  was obtained after only 5 h electrolysis. When this degree of purification was achieved, the current efficiency and energy consumption were also found to be maintained well throughout the period of electrolysis.

#### **3.5.2.4 Comparison between mesh / plate and ACC for electrodeposition of copper using combination (B)**

With this combination it was found that when mesh electrodes were utilized, at a current density of 25 Am<sup>-2</sup>, a greater degree of purification was achieved in a shorter time span. Even though plate and ACC electrodes gave a degree of purification >90% after 8 h of electrolysis, the mesh electrodes proved to be more effective and efficient in removing copper from solution.

In conclusion, if the recovery of metal is important, then all three types of electrodes would be capable of recovering >90% of the metal from solution, but if time is the limiting factor then mesh electrodes should be used.

#### **3.5.2.5 Effect of current density using mesh / plate and ACC for electrodeposition of cadmium using combination (B)**

The effect of current density on the recovery of cadmium using mesh, plate and ACC electrode configurations are described. The current densities studied with this combination were 15 Am<sup>-2</sup>,

20 Am<sup>-2</sup> and 25 Am<sup>-2</sup>.

### **3.5.2.6 Effect of current density using mesh electrodes**

When using mesh electrodes it was found that as the current density was increased the degree of purification increased. At 15 Am<sup>-2</sup>  $\alpha_{Cd}$  was 18.75% after 6 h of electrolysis but this value increased to 62.50% in the next hour of electrolysis. After the final 8 hours of electrolysis  $\alpha_{Cd}$  was 87.50% [Figure. 3.7a]. When the current density was increased to 20 Am<sup>-2</sup>, a 68.75% degree of purification was achieved after 5 h of electrolysis, therefore at the higher current density a better degree of purification was achieved after a shorter period of electrolysis time. After 8 h of electrolysis  $\alpha_{Cd}$  was 93.75% [Figure. 3.7b]. Furthermore, when the current density was increased to 25 Am<sup>-2</sup>  $\alpha_{Cd}$  had reached a value of 62.50% after only 4 h of electrolysis and after 6 h of electrolysis  $\alpha_{Cd}$  was > 90%. When the 8 h of electrolysis was completed,  $\alpha_{Cd}$  was 95.62% [Figure. 3.7c].

It can be concluded that with a high current density a greater degree of purification for cadmium can be achieved with the use of mesh electrodes.

### **3.5.2.7 Effect of current density using plate electrodes**

When plate electrodes were used a high current density gave a better degree of purification. With the use of 15 Am<sup>-2</sup>  $\alpha_{Cd}$  was low in the initial stages of electrolysis but after 7 h of electrolysis a value of 61.11% was obtained. This value was improved further to 72.22% after 8 h of electrolysis [Figure. 3.8a]. Again, in the initial hours of electrolysis a very small amount of cadmium had been deposited when a current density of 20 Am<sup>-2</sup> was employed [Figure. 3.8b]. However, after 5 h of electrolysis  $\alpha_{Cd}$  gave a value of 55.56% and after the 8 h period of electrolysis  $\alpha_{Cd}$  was 93.89%. With a higher current density of 25 Am<sup>-2</sup> a greater degree of purification was achieved over a shorter period of time. The degree of purification was 55.56% after 4 h of electrolysis and this increased to 95.00% after 8 h of electrolysis [Figure. 3.8c].

With plate electrodes it was observed that with a higher current density the degree of purification is significantly increased.

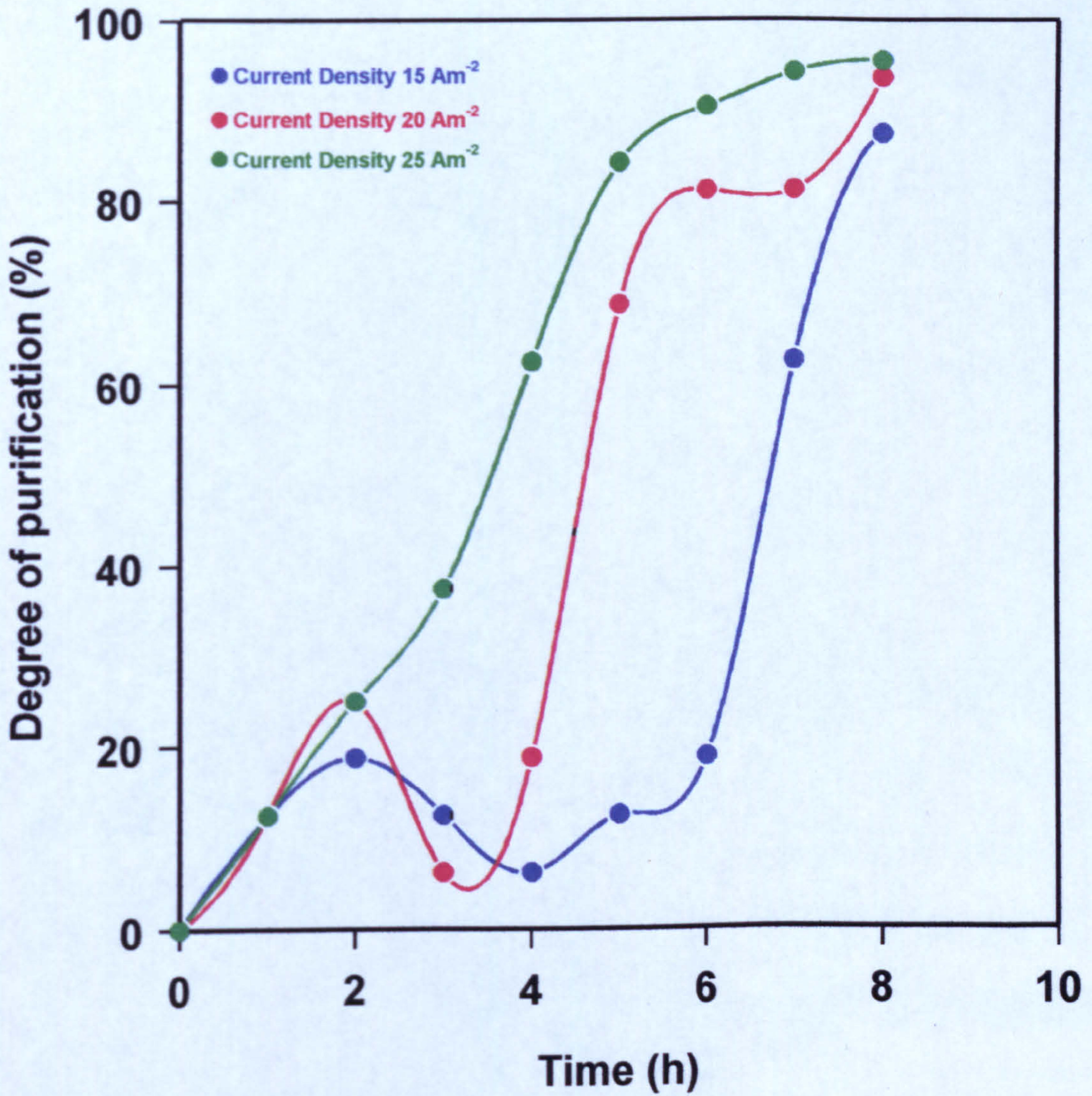


Figure. 3.7:- Effect of current density for the recovery of cadmium using mesh electrodes from a  $1.0 \text{ g dm}^{-3}$  solution of  $\text{CuSO}_4$ ,  $\text{ZnSO}_4$  and  $0.1 \text{ g dm}^{-3}$  of  $\text{CdSO}_4$  in  $0.1\text{M H}_2\text{SO}_4$



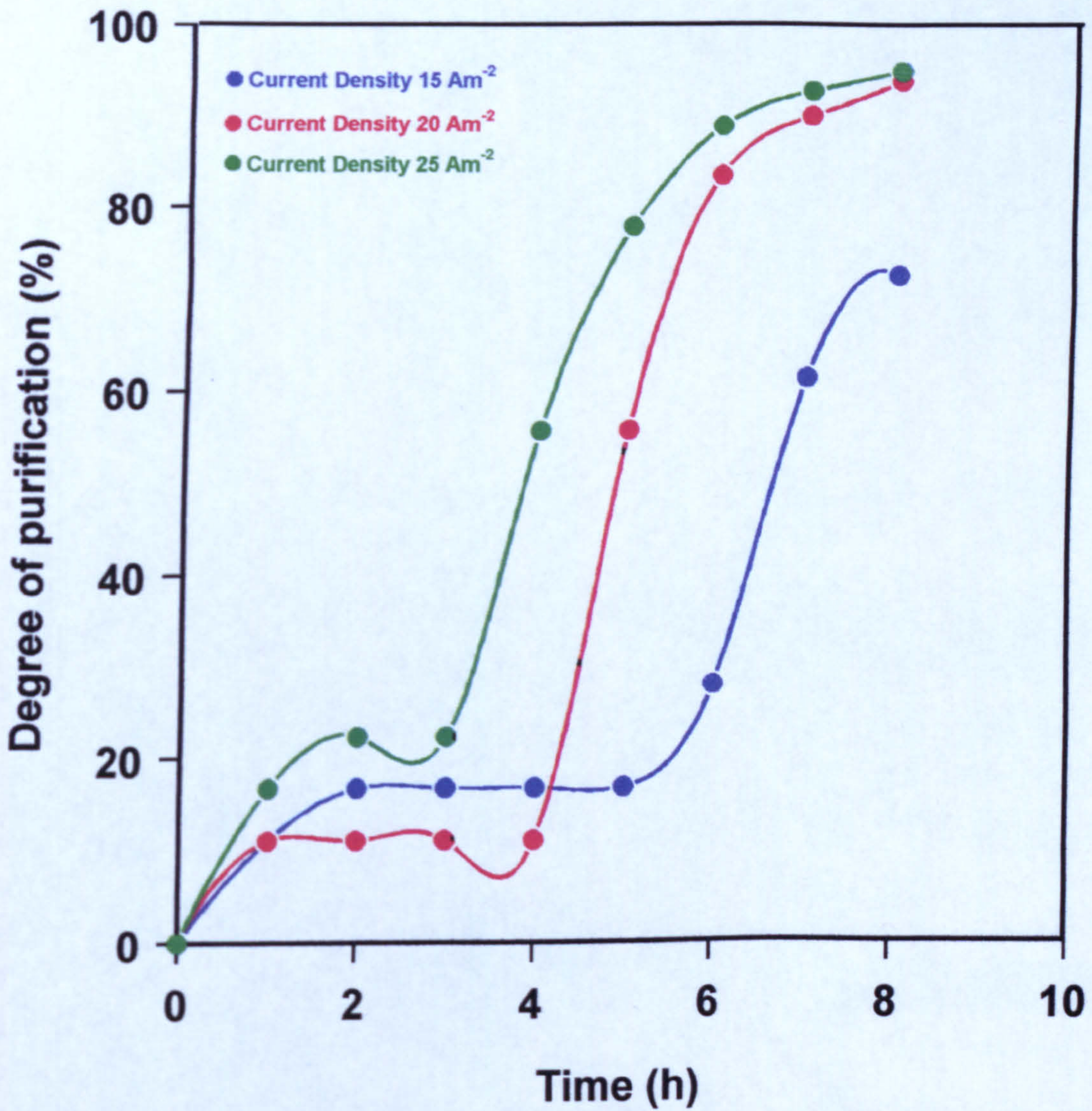


Figure. 3.8:- Effect of current density for the recovery of cadmium using plate electrodes from a  $1.0 \text{ g dm}^{-3}$  solution of  $\text{CuSO}_4$ ,  $\text{ZnSO}_4$  and  $0.1 \text{ g dm}^{-3}$  of  $\text{CdSO}_4$  in  $0.1\text{M H}_2\text{SO}_4$ .

### **3.5.2.8 Effect of current density using ACC**

In experiments where ACC was employed, the percentage removal of cadmium was best when a current density of  $25 \text{ Am}^{-2}$  was utilized. With the lower current densities of 15 and  $20 \text{ Am}^{-2}$  it was seen that cadmium was deposited after a certain period of time, but the deposit was soft and flaked back into solution, hence redissolving. When using  $15 \text{ Am}^{-2}$ , the degree of purification increased from 5.56%, in the initial hour of electrolysis, to 16.67% after 4 h of electrolysis. After this, there was redissolution of the deposit and so  $\alpha_{\text{Cd}}$  decreased in value to 11.11% at the end of the 8 h electrolysis period. This same trend was observed for  $20 \text{ Am}^{-2}$  whereby  $\alpha_{\text{Cd}}$  was 16.67% after 1 h of electrolysis but due to the redissolution of the deposit, this value decreased to 5.00% after 3h of electrolysis.  $\alpha_{\text{Cd}}$  was greatest after 5 h of electrolysis with a value of 33.33% but due to the redissolution of the deposit, this value decreased to 16.67%. When using a current density of  $25 \text{ Am}^{-2}$  it was found that the degree of purification increased from 5.88% after 2 h of electrolysis to 88.23% after 8 h of electrolysis [Figure. 3.9].

### **3.5.2.9 Comparison between mesh / plate and ACC for electrodeposition of cadmium using combination (B)**

Comparing the three types of electrodes for the removal of cadmium, it was found that mesh and plate electrodes, when operated at a high current density of  $25 \text{ Am}^{-2}$ , gave a degree of purification of greater than 90% after the 8 h electrolysis period. However, at a low current density of  $15 \text{ Am}^{-2}$ , mesh electrodes proved to be better. ACC was only effective at a very high current density but it was found that >90% degree of purification could not be achieved after 8 h of electrolysis with the current densities studied [Figure. 3.10].

### **3.5.3 Effect of current density using mesh / plate and ACC for the recovery of Cu from a Cu/Zn/Fe solution**

The current density on the recovery of Cu using mesh, plate and ACC electrode configurations are described. The current densities studied were 15, 20 and  $25 \text{ Am}^{-2}$ .

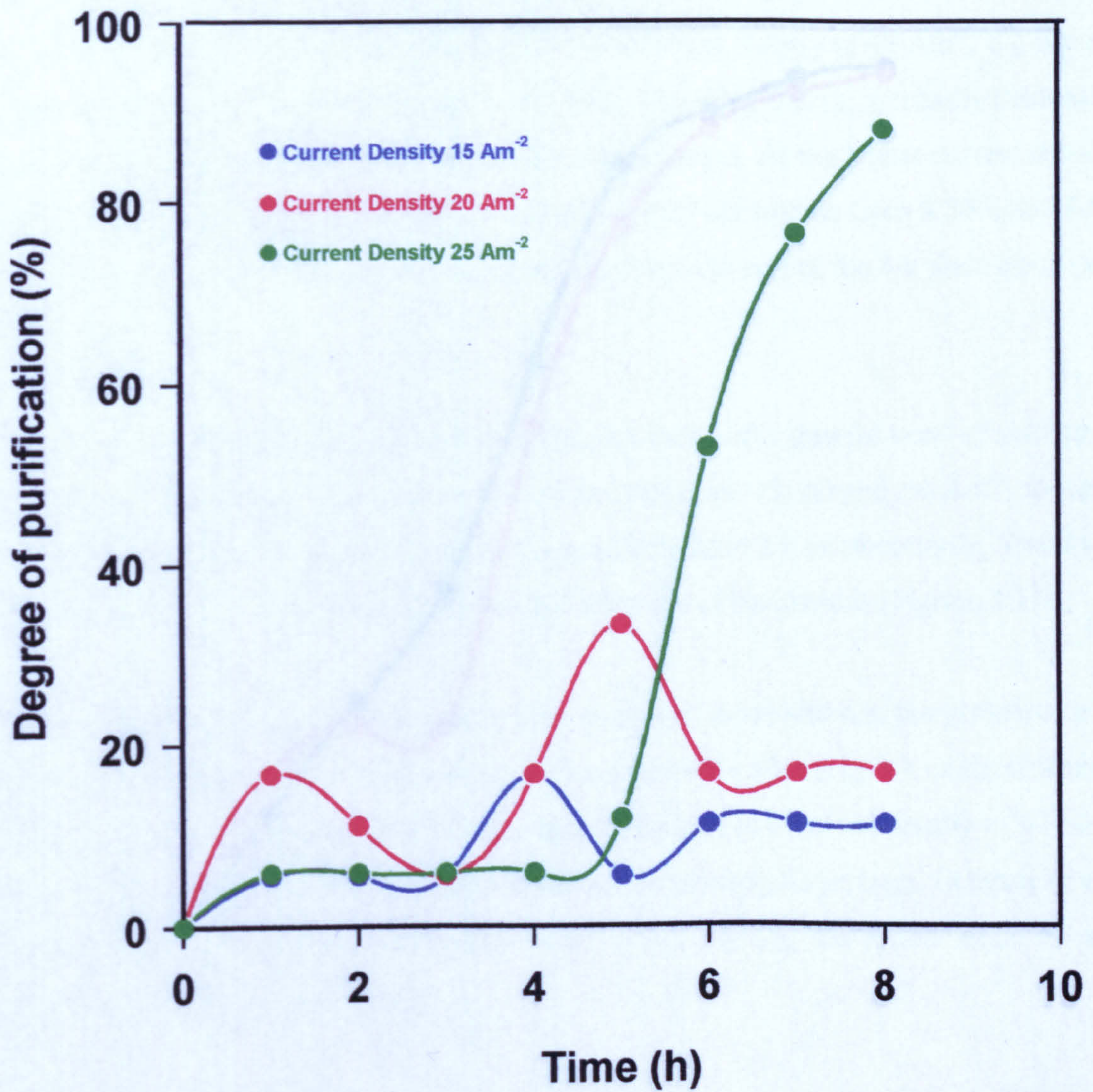


Figure. 3.9:- Effect of current density for the recovery of Cd using ACC electrode from a  $1.0 \text{ g dm}^{-3}$  solution of  $\text{CuSO}_4$ ,  $\text{ZnSO}_4$  and  $0.1 \text{ g dm}^{-3}$  of  $\text{CdSO}_4$  in  $0.1\text{M H}_2\text{SO}_4$

### 3.3.3.1 Effect of current density using mesh electrodes

When using mesh electrodes at current densities of 15, 40 and 50  $\text{Am}^{-2}$  it was found that after a 2 h electrolysis period the degree of purification was 4.08, 52.17 and 85.42% respectively and after 8 h the values increased to 49.20, 99.56 and 99.79% respectively (Figure 3.11a).

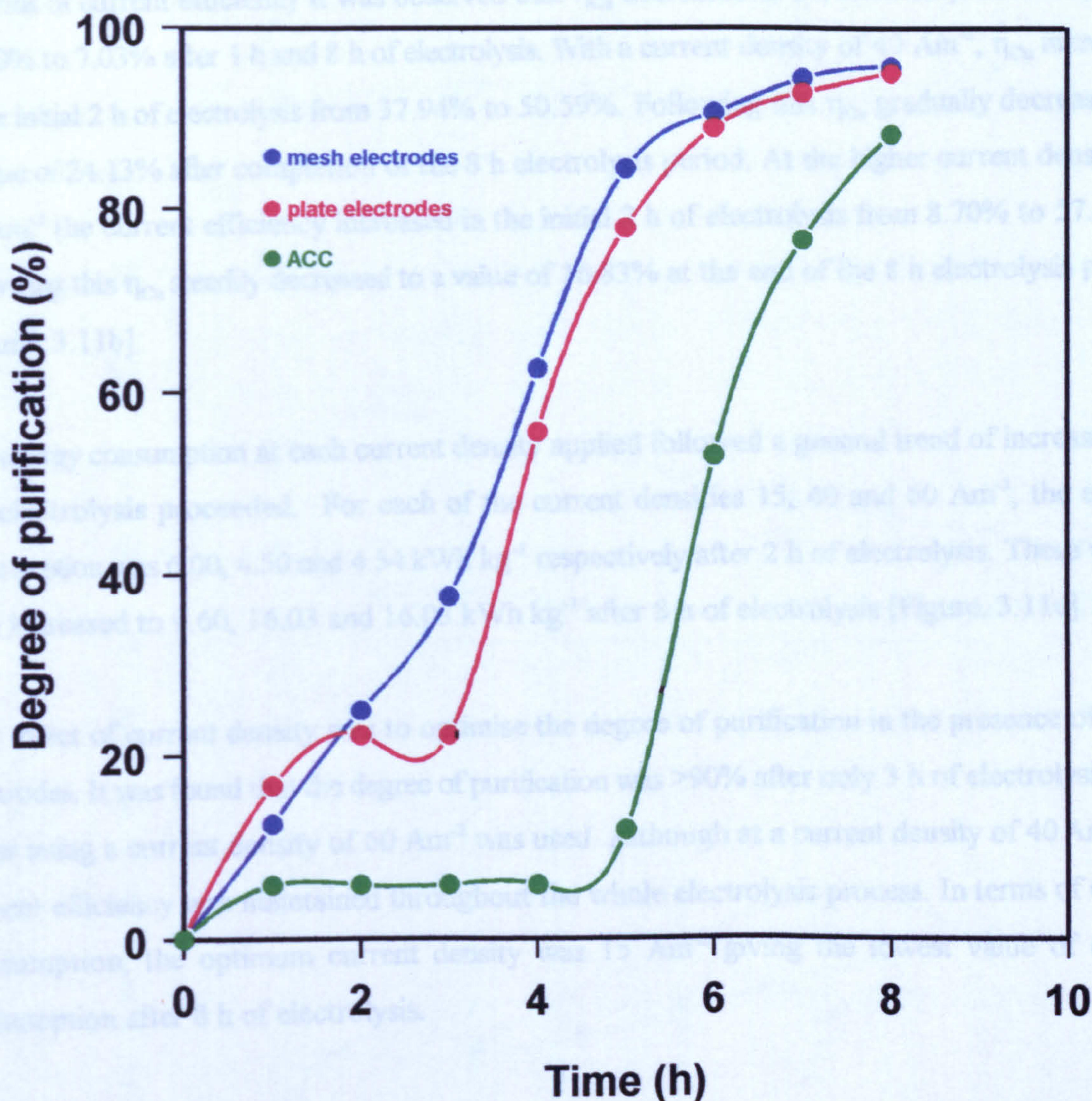


Figure. 3.10:- Comparison between mesh, plate and ACC electrodes for the recovery of cadmium from sulphate solution containing  $1.0 \text{ g dm}^{-3} \text{ CuSO}_4$ ,  $\text{ZnSO}_4$  and  $0.1 \text{ g dm}^{-3}$  of  $\text{CdSO}_4$  in  $0.1 \text{ M H}_2\text{SO}_4$  using a current density of  $25 \text{ Am}^{-2}$ .

### **3.5.3.1 Effect of current density using mesh electrodes**

When using mesh electrodes at current densities of 15, 40 and 60 Am<sup>-2</sup> it was found that after a 2 h electrolysis period the degree of purification was 4.08, 52.17 and 85.42% respectively and after 8 h the values increased to 10.20, 99.56 and 99.79% respectively [Figure. 3.11a].

In terms of current efficiency it was observed that  $\eta_{Cu}$  decreased as the reaction proceeded, from 21.90% to 7.03% after 1 h and 8 h of electrolysis. With a current density of 40 Am<sup>-2</sup>,  $\eta_{Cu}$  increased in the initial 2 h of electrolysis from 37.94% to 50.59%. Following this  $\eta_{Cu}$  gradually decreased to a value of 24.13% after completion of the 8 h electrolysis period. At the higher current density of 60 Am<sup>-2</sup> the current efficiency increased in the initial 2 h of electrolysis from 8.70% to 57.62%. Following this  $\eta_{Cu}$  steadily decreased to a value of 16.83% at the end of the 8 h electrolysis period [Figure. 3.11b].

The energy consumption at each current density applied followed a general trend of increasing as the electrolysis proceeded. For each of the current densities 15, 40 and 60 Am<sup>-2</sup>, the energy consumption was 6.00, 4.50 and 4.54 kWh kg<sup>-1</sup> respectively after 2 h of electrolysis. These values then increased to 9.60, 16.03 and 16.03 kWh kg<sup>-1</sup> after 8 h of electrolysis [Figure. 3.11c].

The effect of current density was to optimise the degree of purification in the presence of mesh electrodes. It was found that the degree of purification was >90% after only 3 h of electrolysis time when using a current density of 60 Am<sup>-2</sup> was used. Although at a current density of 40 Am<sup>-2</sup> the current efficiency was maintained throughout the whole electrolysis process. In terms of energy consumption, the optimum current density was 15 Am<sup>-2</sup> giving the lowest value of energy consumption after 8 h of electrolysis.

### **3.5.3.2 Effect of current density using plate electrodes**

When using plate electrodes it was found that at a low current density the deposit was very soft and flaked back into solution so yielding a very poor degree of purification. After 2 h of electrolysis  $\alpha_{Cu}$  was 8.70% and it was found that after 8 h of electrolysis the value was still 8.70%. At higher

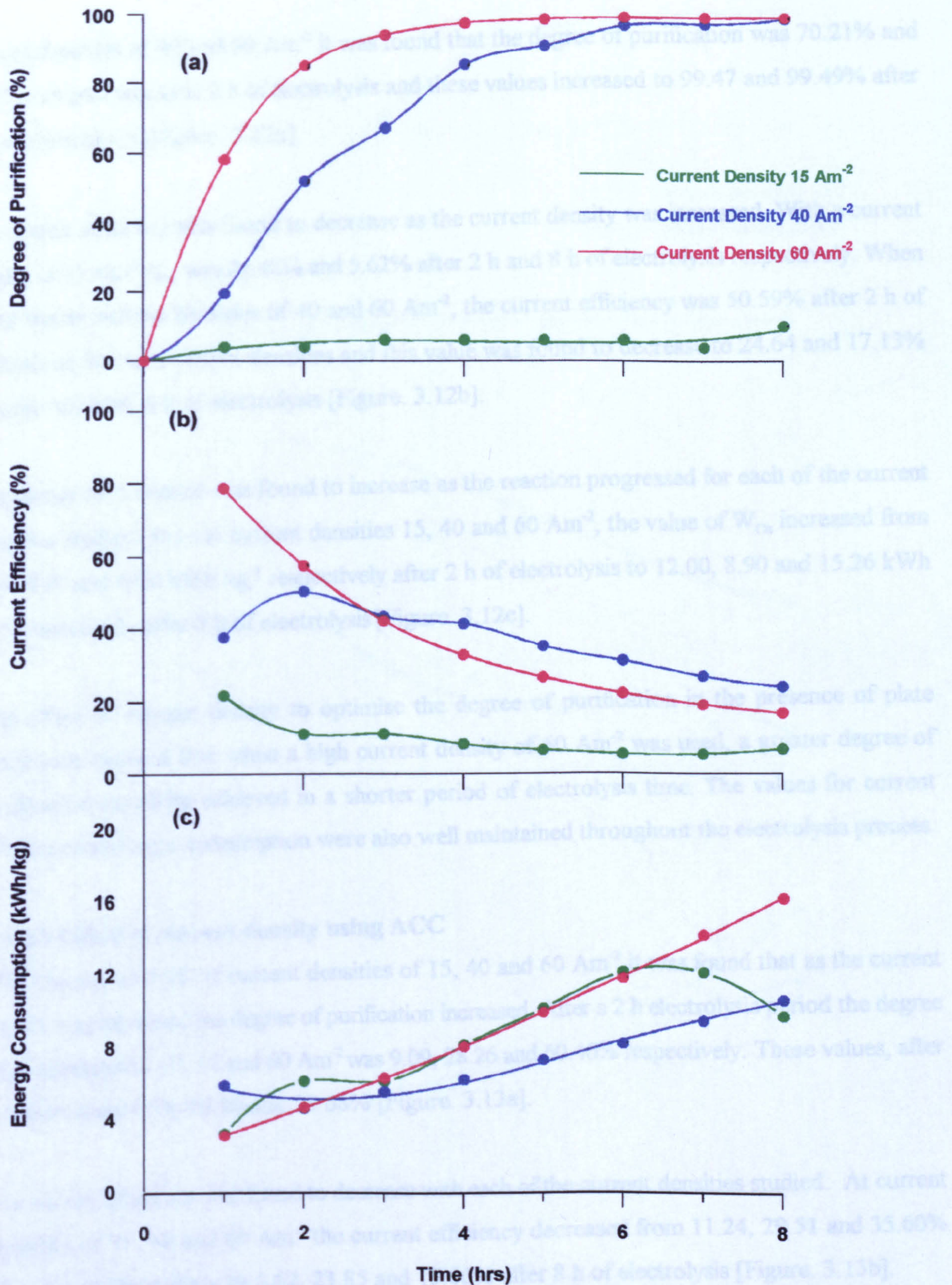


Figure. 3.11:- Effect of current density for the recovery of copper using mesh electrodes from a 1.0 g dm<sup>-3</sup> solution of CuSO<sub>4</sub>, FeSO<sub>4</sub> and 0.5 g dm<sup>-3</sup> of ZnSO<sub>4</sub> in 0.1 M H<sub>2</sub>SO<sub>4</sub>.

current densities of 40 and 60  $\text{Am}^{-2}$  it was found that the degree of purification was 70.21% and 73.47% respectively after 2 h of electrolysis and these values increased to 99.47 and 99.49% after 8 h of electrolysis [Figure. 3.12a].

The current efficiency was found to decrease as the current density was increased. With a current density of 15  $\text{Am}^{-2}$ ,  $\eta_{\text{Cu}}$  was 22.48% and 5.62% after 2 h and 8 h of electrolysis respectively. When using higher current densities of 40 and 60  $\text{Am}^{-2}$ , the current efficiency was 50.59% after 2 h of electrolysis for both current densities and this value was found to decrease to 24.64 and 17.13% respectively after 8 h of electrolysis [Figure. 3.12b].

The energy consumption was found to increase as the reaction progressed for each of the current densities studied. For the current densities 15, 40 and 60  $\text{Am}^{-2}$ , the value of  $W_{\text{Cu}}$  increased from 3.00, 4.00 and 6.00  $\text{kWh kg}^{-1}$  respectively after 2 h of electrolysis to 12.00, 8.90 and 15.26  $\text{kWh kg}^{-1}$  respectively after 8 h of electrolysis [Figure. 3.12c].

The effect of current density to optimise the degree of purification in the presence of plate electrodes showed that when a high current density of 60  $\text{Am}^{-2}$  was used, a greater degree of purification could be achieved in a shorter period of electrolysis time. The values for current efficiency and energy consumption were also well maintained throughout the electrolysis process.

### **3.5.3.3 Effect of current density using ACC**

With the use of ACC at current densities of 15, 40 and 60  $\text{Am}^{-2}$  it was found that as the current density was increased the degree of purification increased. After a 2 h electrolysis period the degree of purification for 15, 40 and 60  $\text{Am}^{-2}$  was 9.09, 28.26 and 60.46% respectively. These values, after 8 h were then 9.09, 99.50 and 99.68% [Figure. 3.13a].

The current efficiency was found to decrease with each of the current densities studied. At current densities of 15, 40 and 60  $\text{Am}^{-2}$  the current efficiency decreased from 11.24, 29.51 and 35.60% after 2 h of electrolysis to 5.62, 23.85 and 15.06% after 8 h of electrolysis [Figure. 3.13b].

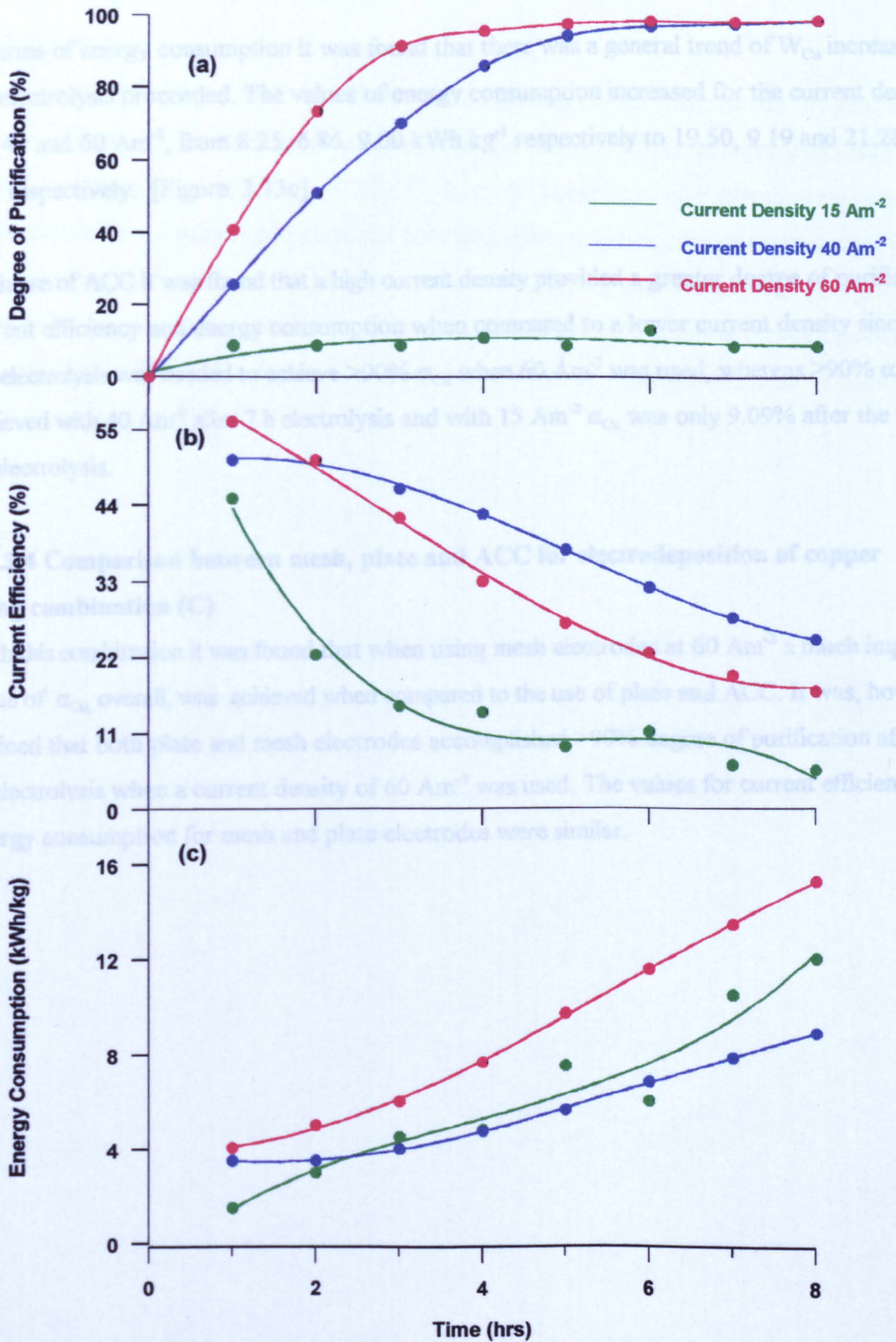


Figure. 3.12:- Effect of current density for the recovery of copper using plate electrodes from a  $1.0 \text{ g dm}^{-3}$  solution of  $\text{CuSO}_4$ ,  $\text{FeSO}_4$  and  $0.5 \text{ g dm}^{-3}$  in  $0.1 \text{ M H}_2\text{SO}_4$ .



In terms of energy consumption it was found that there was a general trend of  $W_{Cu}$  increasing as the electrolysis proceeded. The values of energy consumption increased for the current densities 15, 40 and 60  $Am^{-2}$ , from 8.25, 6.86, 9.00  $kWh\ kg^{-1}$  respectively to 19.50, 9.19 and 21.28  $kWh\ kg^{-1}$  respectively. [Figure. 3.13c].

With use of ACC it was found that a high current density provided a greater degree of purification, current efficiency and energy consumption when compared to a lower current density since only 4 h electrolysis was needed to achieve  $>90\% \alpha_{Cu}$  when 60  $Am^{-2}$  was used, whereas  $>90\% \alpha_{Cu}$  was achieved with 40  $Am^{-2}$  after 7 h electrolysis and with 15  $Am^{-2}$   $\alpha_{Cu}$  was only 9.09% after the full 8h of electrolysis.

#### **3.5.3.4 Comparison between mesh, plate and ACC for electrodeposition of copper using combination (C)**

With this combination it was found that when using mesh electrodes at 60  $Am^{-2}$  a much improved value of  $\alpha_{Cu}$  overall, was achieved when compared to the use of plate and ACC. It was, however, noticed that both plate and mesh electrodes accomplished  $>90\%$  degree of purification after 3 h of electrolysis when a current density of 60  $Am^{-2}$  was used. The values for current efficiency and energy consumption for mesh and plate electrodes were similar.

## **CONCLUSION**

The fluidised bed cell proved to be efficient for recovering copper from the mixed metal solution studied. The results show that copper can be efficiently recovered from all three solutions and that cadmium can be recovered from a Cu/Zn/Cd mixture. Three types of electrode were considered in the processes normally mesh, plate and activated carbon cloth concentrator electrodes and the conditions under which each of these electrodes are effective, were determined. At high current densities it was found that mesh electrodes proved to be the most efficient for each mixed metal ion solution studied except for the Cu/Zn combination where ACC was the most effective.

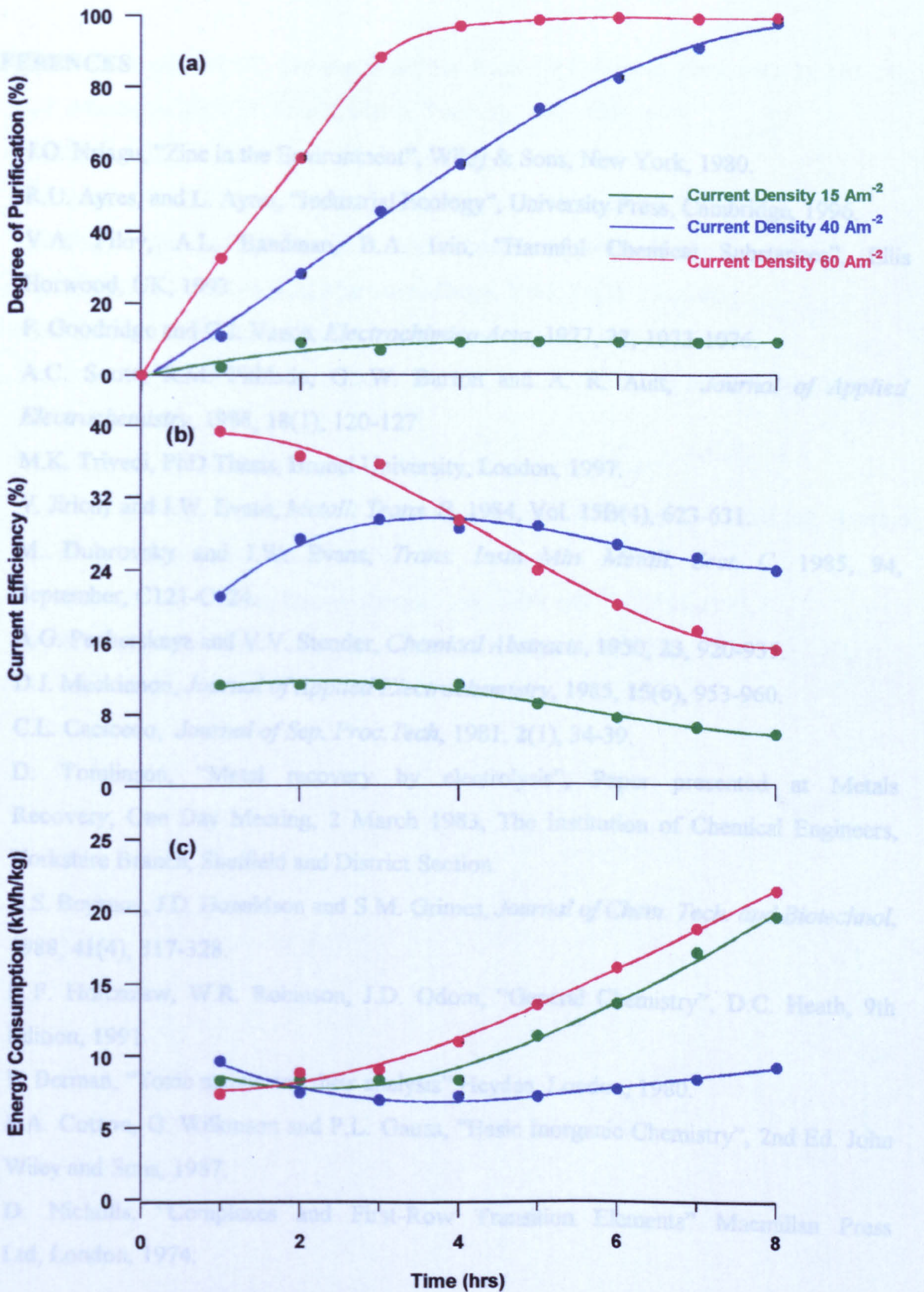


Figure. 3.13:- Effect of current density for the recovery of copper using ACC electrode from a  $1.0 \text{ g dm}^{-3}$  solution of  $\text{CuSO}_4$ ,  $\text{FeSO}_4$  and  $0.5 \text{ g dm}^{-3}$  in  $0.1 \text{ M H}_2\text{SO}_4$ .

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## CHAPTER FOUR

### THE USE OF CONCENTRATOR CELL TECHNOLOGY FOR THE RECOVERY OF METAL VALUE FROM AS-SUPPLIED INDUSTRIAL SAMPLES

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## **4 INTRODUCTION**

Recent work<sup>(1)</sup> in the Centre for Environmental Research (CER) has led to the development of novel concentrator cell electrodes that can be used in conjunction with fluidised bed cell electrolysis to increase the amount of metal recovered (thereby decreasing any residual metal in effluent to very low levels) and providing a technique for in process recovery rather than end-of-pipe recovery and recycle. The concept of the concentrator cell is to effectively concentrate metal ions in a region in front of the cathode.

The work described in this chapter reports for the first time the use of the concentrator cell technology (i) to recover metals from industrial as-supplied samples, and (ii) to extend this application to the recovery of the metal as added-value chemicals.

### **4.1 RECOVERY OF METALS FROM INDUSTRIAL AS-SUPPLIED SAMPLES**

Samples were supplied from a selection of different industries ranging from printed circuit board (PCB) manufacturers to precious metal group refiners and are listed in Table 4.1 along with details of the primary metal to be recovered.

The objective in the first part of this work was to optimise the recovery of the metal for each sample using a concentrator cell. In some cases, preliminary investigations were carried out to establish operating conditions for recovery. For example, the United Distillers sample had a high concentration of Cu, and since the use of this developed technology was primarily for recovery from dilute concentration of metal, it was necessary first to establish if the concentrator cell technology could be used under these conditions. Furthermore, any difficulties specific to the recovery from the as-supplied sample would be highlighted. In the same way, no earlier work on the recovery of the precious metals, Ir and Pd had been undertaken, so preliminary investigations were carried out on synthetic samples to establish appropriate recovery conditions.

<b>Table 4.1:- Samples provided by industry</b>	
<b>Industrial Sample</b>	<b>Metal value</b>
<p><b>VERO</b> PCB manufacturers. This industry provided three different samples.</p> <ol style="list-style-type: none"> <li>1. CuCl<sub>2</sub> etching solution.</li> <li>2. Copper-EDTA solution.</li> <li>3. Tin-palladium solution.</li> </ol>	<ol style="list-style-type: none"> <li>1. Cu</li> <li>2. Cu</li> <li>3. Pd</li> </ol>
<p><b>UNITED DISTILLERS</b> A distilling industry supplying a copper solution</p>	Cu
<p><b>INCO</b> Precious group metal refiners. The solution supplied consisted of many different precious metals including iridium and palladium.</p>	<p>Ir</p> <p>Pd</p>
<p><b>GRAPHIC WASTE SERVICES</b> Five silver bromide solutions, labelled A-E, supplied by a silver plating company.</p>	Ag
<p><b>PENDAR POOLE</b> A silver nitrate solution supplied by a silver plating industry.</p>	Ag
<p><b>PREMINCO</b> A chemical company in India providing a hydrometallurgical cobalt leach solution.</p>	Co



### **4.1.1 Experimental**

All experiments, unless otherwise stated, were carried out in a 10 L concentrator cell with a continuous circulatory motion used to stir the solution. For each of the samples three different electrode configurations were used. In the control experiment two mixed metal oxide anodes and one stainless steel plate cathode were used in the configuration A-C-A and the distance between the anode and cathode was 15mm. A second set-up involved the addition of an ion exchange (IX) resin pocket to give an A-IX-C-IX-A electrode configuration with an A-IX inter distance of 12mm. The third set-up involved the use of an activated carbon cloth electrode in an A-ACC-A configuration. Each of these set ups was used in order to evaluate the optimum conditions for recovery of metal value for each industrial sample.

In each experiment, unless otherwise stated, a constant current of 1.5 A was applied, and the voltage was kept at a maximum. Each experiment was carried out a minimum in duplicate in order to obtain reproducible results. Samples were taken every hour and then analysed by AAS.

#### **4.1.1.1 Vero Industrial Sample**

For this series of experiments, two samples were provided by Vero Electronics Limited, Southampton:-

Sample (A) was a Shipley circuposit 3350, Electroless Copper, 2.5 g l<sup>-1</sup> Cu, EDTA solution. Sample (B) was a Macdermid "High Speed Etchant", Ammoniacal solution, containing 140 - 150g l<sup>-1</sup> of Cu.

Analysis of the as-supplied sample showed sample (A) to contain 1,100 ppm Cu and sample (B) to contain 127,600 ppm Cu.

The as-supplied samples were diluted with distilled water so that an initial concentration of 0.01g dm<sup>-3</sup> of sample (A) could be used and for sample (B) an initial concentration of 0.1g dm<sup>-3</sup> was used. It was observed that when sample (B) was diluted, copper was precipitated after dilution and so the solution was acidified with 0.1M hydrochloric acid in order to dissolve the copper precipitate. A clear blue solution was then obtained at pH 1.5.

### ***In-situ re-use of carbon cloth concentrator cathode***

Two experiments, using sample (B), were carried out to study the in-situ reuse of the activated carbon cloth concentrator cathode for the recovery of copper from the etching solution supplied by Vero Electronics, Southampton. The experiment was repeated twice under identical conditions to compare the efficiency of activated carbon cloth cathode with a stainless steel plate cathode after repeated use. The copper concentration was brought back to 100 ppm after 24 h and the experiment was continued for a further 24 h. Hence, the duration of the experimental procedure was for a total reaction time of 48 h.

### ***Separation of copper from palladium and tin solution***

A single 400 ml sample containing copper, palladium and tin ions was supplied by Vero Electronics, Southampton. The industry uses a chloride solution containing palladium and tin ions as a catalyst solution. During the PCB manufacturing process the concentration of copper is increasing which reduces the efficiency of the catalyst solution. The company is interested in separating copper without affecting the concentration of palladium and tin ions.

#### **4.1.1.2 United Distillers - Scottish Malt Distillers Ltd**

The sample provided by United Distillers, Perth was a sample of a backwash ion exchange solution containing 15% sulphuric acid. Due to the high concentration of copper in solution (in excess of 25,000 ppm) preliminary studies were carried out to investigate the conditions for copper recovery.

### ***Recovery of copper from concentrated 25 g dm<sup>-3</sup> CuCl<sub>2</sub> solution***

For the following experiments a 25 g dm<sup>-3</sup> solution containing copper as chloride, was used. The solution was made from reagent grade CuCl<sub>2</sub>·2H<sub>2</sub>O with an acid concentration of 0.1 M H<sub>2</sub>SO<sub>4</sub> and made up to 10 L volume for use in the cell.

#### **United Distillers As-Supplied Sample**

A 10 L solution of the as-supplied sample was used without further treatment.

#### 4.1.1.3 INCO Sample

Before investigating the as-supplied 'Pd/Ir' solution from INCO, preliminary studies were carried out to optimise the operating conditions of the 'control' electrolytic system for the recovery of (i) Pd from a solution (400 ml) containing 80 ppm Pd in 0.25 M HCl, and (ii) Ir from a solution (400 ml) containing 40 ppm Ir in 0.25 M HCl. Each experiment was carried out under static and agitated conditions to determine the optimum working conditions.

#### 4.1.1.5 Pender Pouch

An INCO as-supplied sample (15 L), which was brown in colour, was provided by the industry and showed an analytical composition (Table 4.2):-

Metal concentration (ppm)														
Pt	Pd	Rh	Ru	Ir	Au	Ag	Fe	Ni	Cu	Zn	As	Sb	Pb	Bi
5.3	2	40	1.2	640	0	30	5	4	22	6	1	2	1739	25

The analysis also showed that the as-supplied sample contained 17% (w/v) HCl.

The company is producing 4 million litres of this effluent each year and were not interested in the separation of each metal but wanted to recover all the metals in the first instance and then using their established process to obtain concentrate. At present the company is capable of removing precious group metals apart from iridium using electrochemical techniques. This industry was interested in alternative techniques for the recovery of iridium.

To study the effect of current density on the recovery of iridium, two separate current densities were used, 20 Am<sup>-2</sup> and 300 Am<sup>-2</sup>. For each run the electrolytic cell volume was 400 ml and different concentrator systems were used: ion exchange resin and activated carbon cloth, and compared with the control.

#### 4.1.1.4 Graphic Waste Services

For this series of experiments, five samples A, B, C, D and E were supplied by Graphic Waste Services to investigate the efficiency of the different concentrator technologies for the recovery

of silver from silver bromide solution. The XRF analyses of as-received samples are presented in Figure 4.1. These results show that each sample apart from sample A contains iron impurities.

A current density of  $300 \text{ Am}^{-2}$  was applied and the voltage was kept at a maximum.

#### **4.1.1.5 Pendar Poole**

A silver drag-out solution, supplied by Pendar Poole was used to optimise the recovery of silver using the two concentrator cells. In this case 400 ml of solution was used.

#### **4.1.1.6 Preminco Industrial Sample**

Model solutions containing cobalt, nickel, copper, zinc and iron were prepared according to the specification supplied by the industry Preminco Ltd. The specification was such that a solution should contain  $20 \text{ g dm}^{-3}$  Co,  $1 \text{ g dm}^{-3}$  Ni,  $0.5 \text{ g dm}^{-3}$  Fe,  $0.5 \text{ g dm}^{-3}$  Cu and  $1 \text{ g dm}^{-3}$  Zn using sulphate salts and the acidity of the solution was 0.5 M using sulphuric acid.

The electrolytic process was carried out using model solutions containing metal ions according to the specifications supplied by Vergi. In one experiment the electrolytic process was carried out containing ferrous ions. In a second experiment hydrogen peroxide was used to oxidise ferrous to ferric ions prior to the electrolytic process. This set of experiments was carried out to optimise the conditions for the oxidation of ferrous to ferric ions using 30 and 60% hydrogen peroxide prior to the electrolytic process.

## **4.2 RECOVERY OF METALS AS ADDED-VALUE CHEMICALS**

Although there is general awareness of the finite nature of the earths resources and a gradual movement towards the extraction of metals from lower grade ores, the recovery of metal values from waste sources is important. Most recovery processes for non-ferrous metals recover the metal itself and in such processes the expensive stage is usually the final one of obtaining the metal. It is however, possible to achieve considerable economic advantages if the elements can be recovered by chemical methods as commercially useful compounds rather than the metal itself<sup>[2]</sup>.

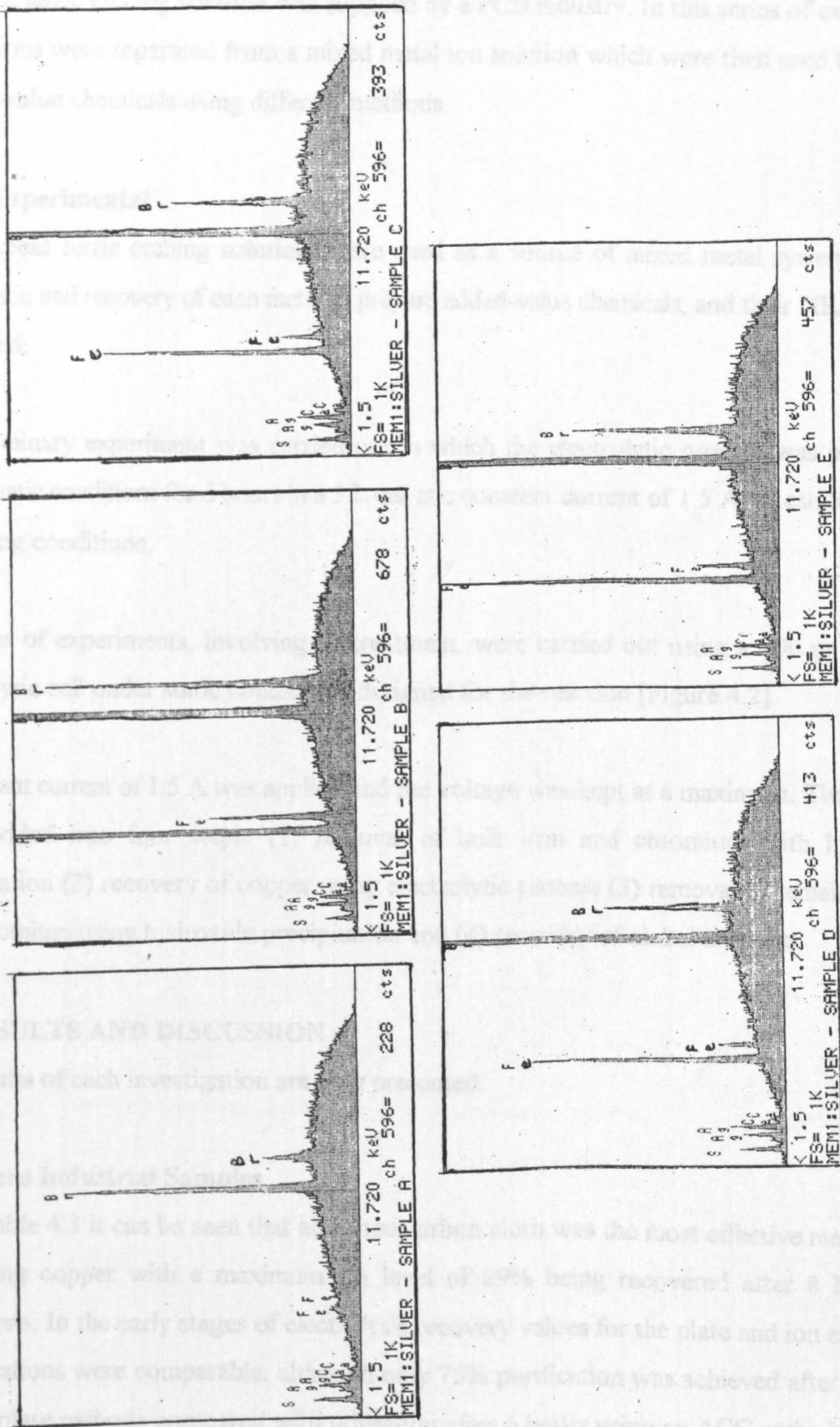


Figure 4.1: XRF analyses of as-supplied Graphic Waste Services samples

A spent ferric etching solution was supplied by a PCB industry. In this series of experiments metal ions were separated from a mixed metal ion solution which were then used to prepare added-value chemicals using different methods.

#### **4.2.1 Experimental**

Four spent ferric etching solutions were used as a source of mixed metal systems for the separation and recovery of each metal to prepare added-value chemicals, and their XRD spectra recorded.

A preliminary experiment was carried out in which the electrolytic process was performed under static conditions for 6 hours in a 5 L cell at a constant current of 1.5 A, to establish basic operating conditions.

A series of experiments, involving pretreatment, were carried out using a 400 ml capacity electrolytic cell under static conditions, designed for the reaction [Figure 4.2].

A constant current of 1.5 A was applied and the voltage was kept at a maximum. The process was divided into four steps: (1) removal of bulk iron and chromium with hydroxide precipitation (2) recovery of copper using electrolytic process (3) removal of remaining iron and chromium using hydroxide precipitation and (4) recovery of nickel and zinc.

### **4.3 RESULTS AND DISCUSSION**

The results of each investigation are now presented.

#### **4.3.1 Vero Industrial Samples**

From Table 4.3 it can be seen that activated carbon cloth was the most effective method for recovering copper with a maximum Cu level of 89% being recovered after 8 hours of electrolysis. In the early stages of electrolysis recovery values for the plate and ion exchange configurations were comparable, although only 75% purification was achieved after 8 hours using a plate cathode compared with utilisation after 6 hours using an ACC cathode. These results are illustrated in Figure 4.3.

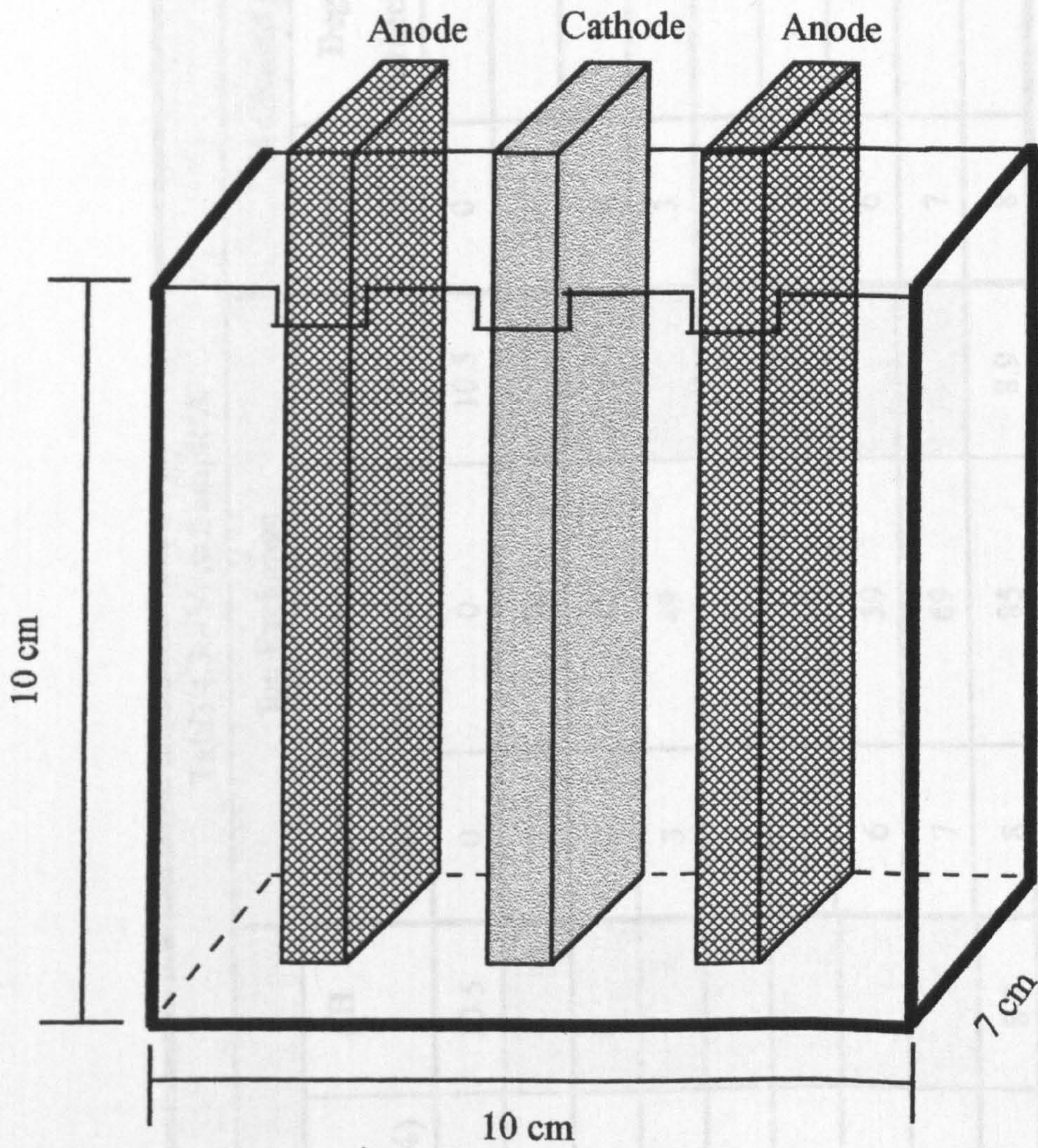


Figure. 4.2:- Layout of the electrolytic cell designed for industrial sample trials

**Table 4.3:- Vero Sample A**

Control			Ion Exchange			Activated Carbon Cloth		
Time (h)	Degree of Purification (%)	pH	Time (h)	Degree of Purification (%)	pH	Time (h)	Degree of Purification (%)	pH
0	0	10.5	0	0	10.5	0	0	10.5
1	12		1	30		1	20	
2	14		2	45		2	50	
3	35		3	49		3	50	
4	51		4	53		4	57	
5	57		5	56		5	69	
6	60		6	59		6	73	
7	65		7	69		7	79	
8	75	8.9	8	85	8.9	8	89	8.9



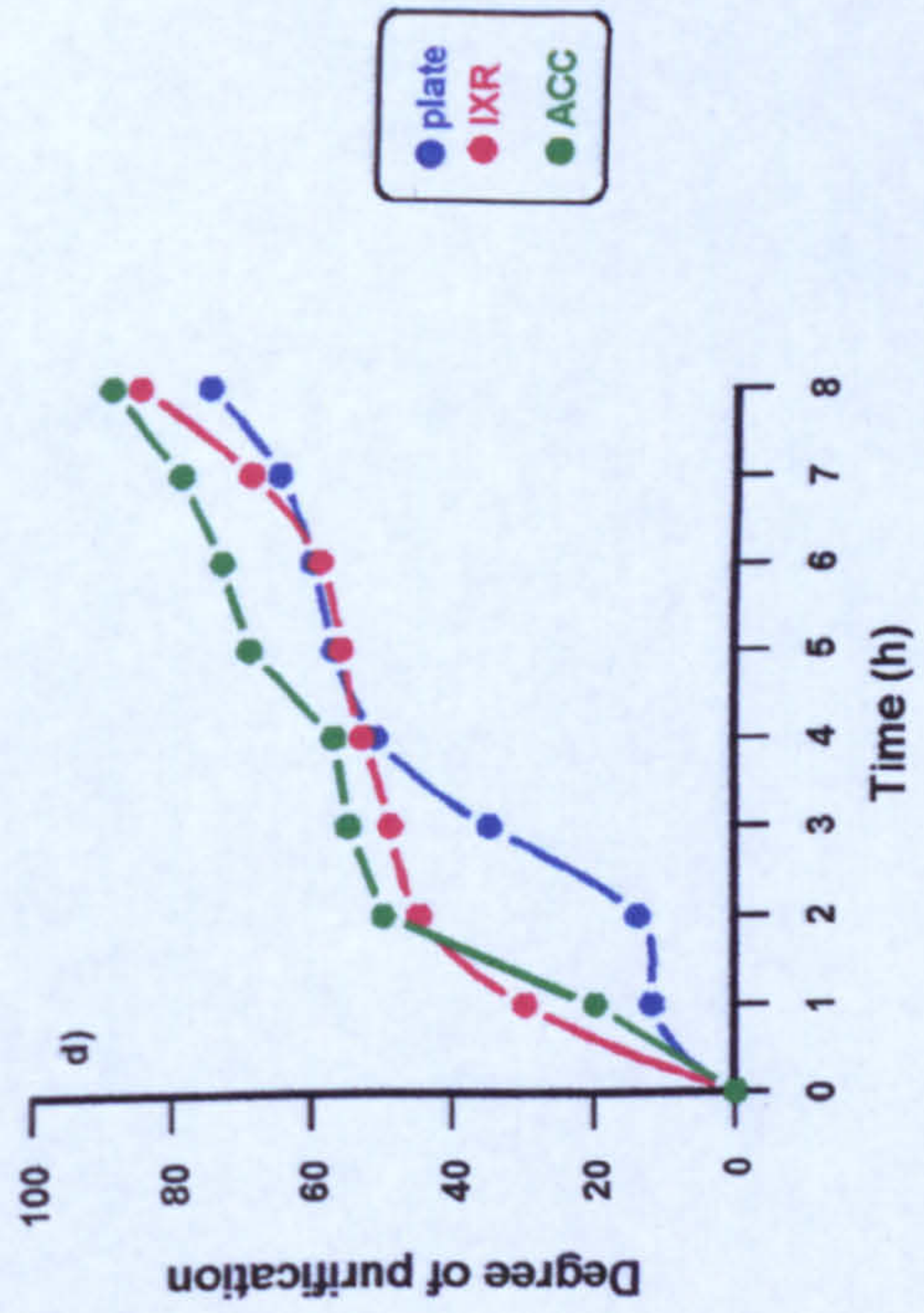
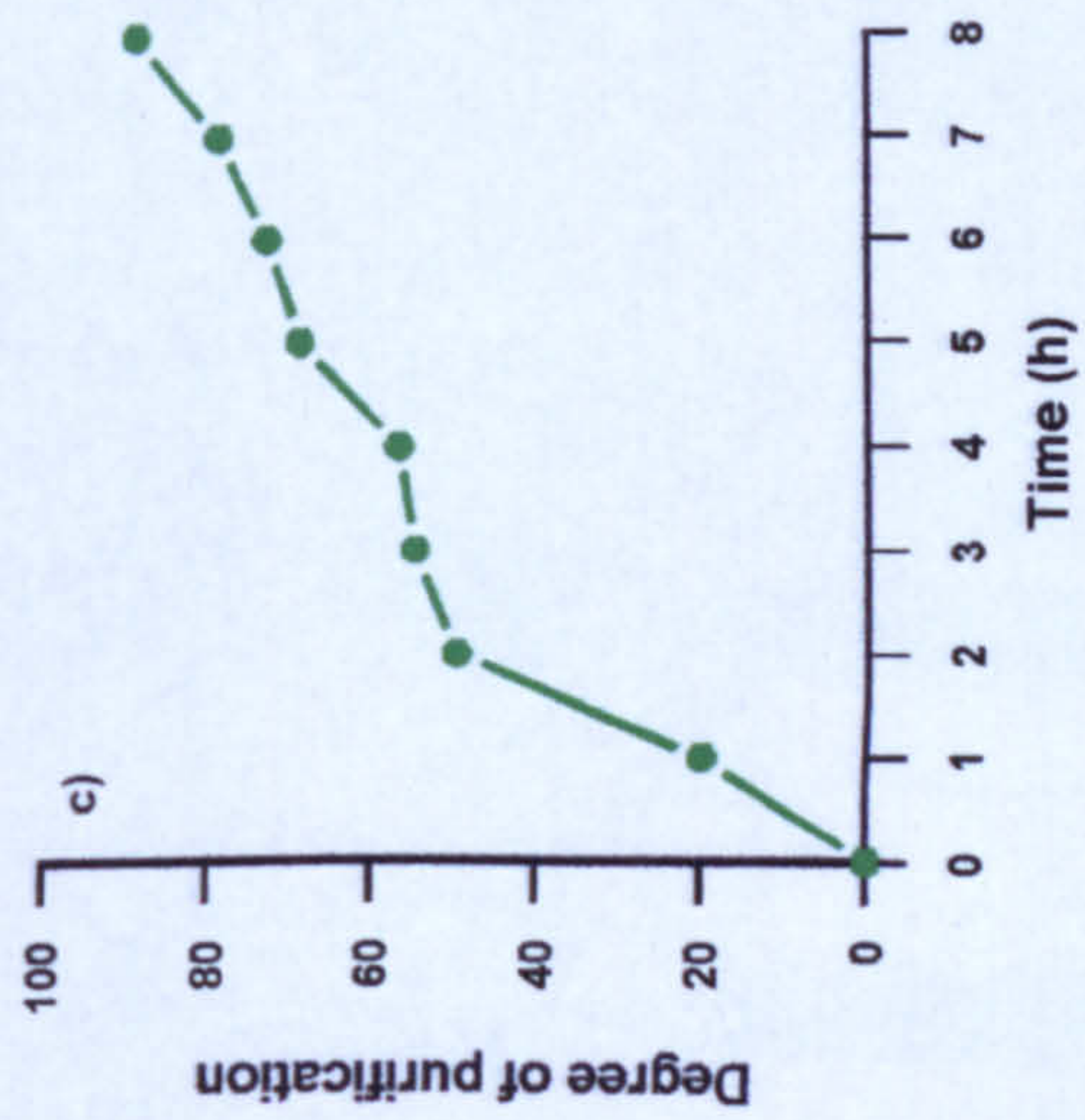
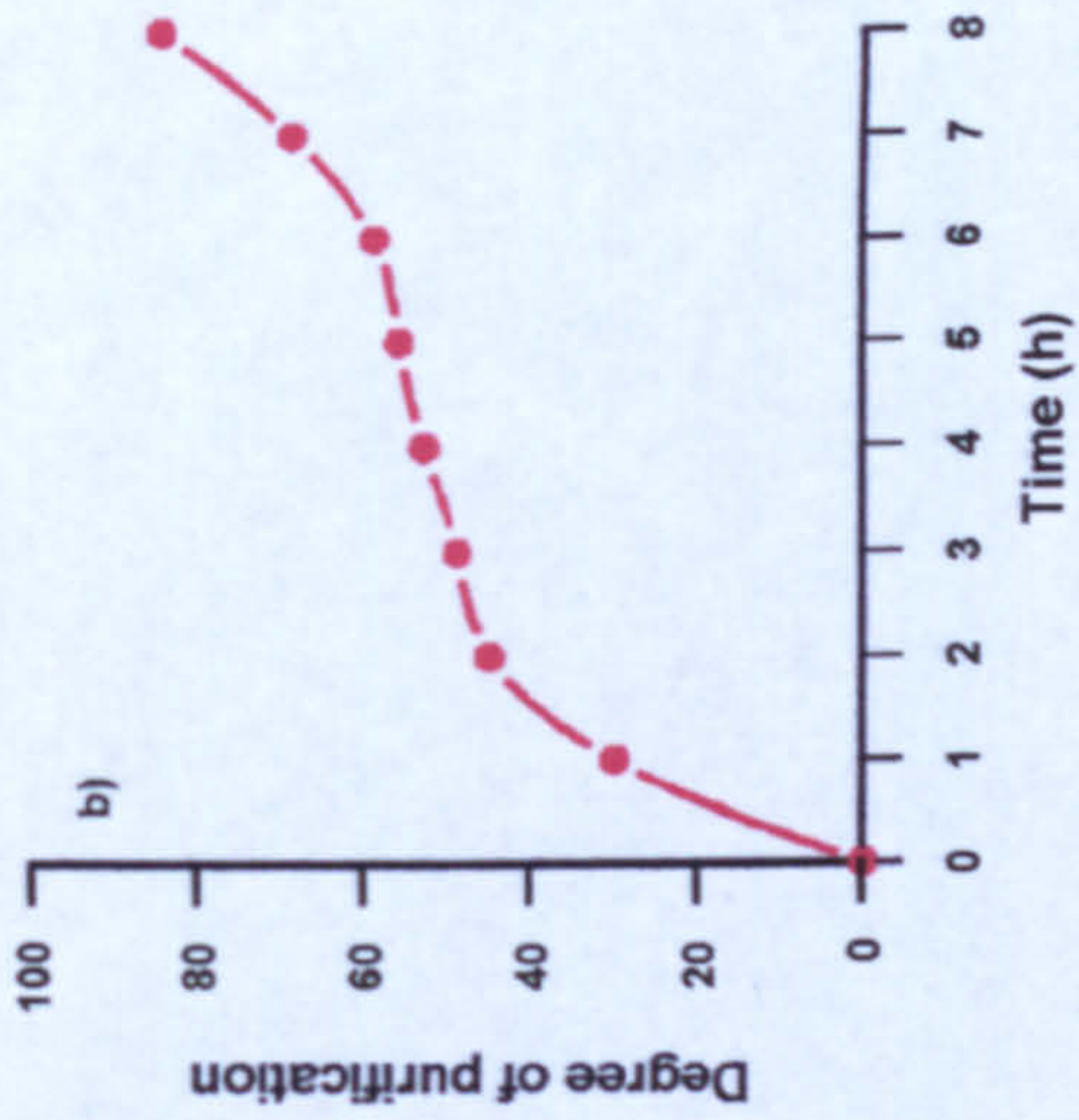
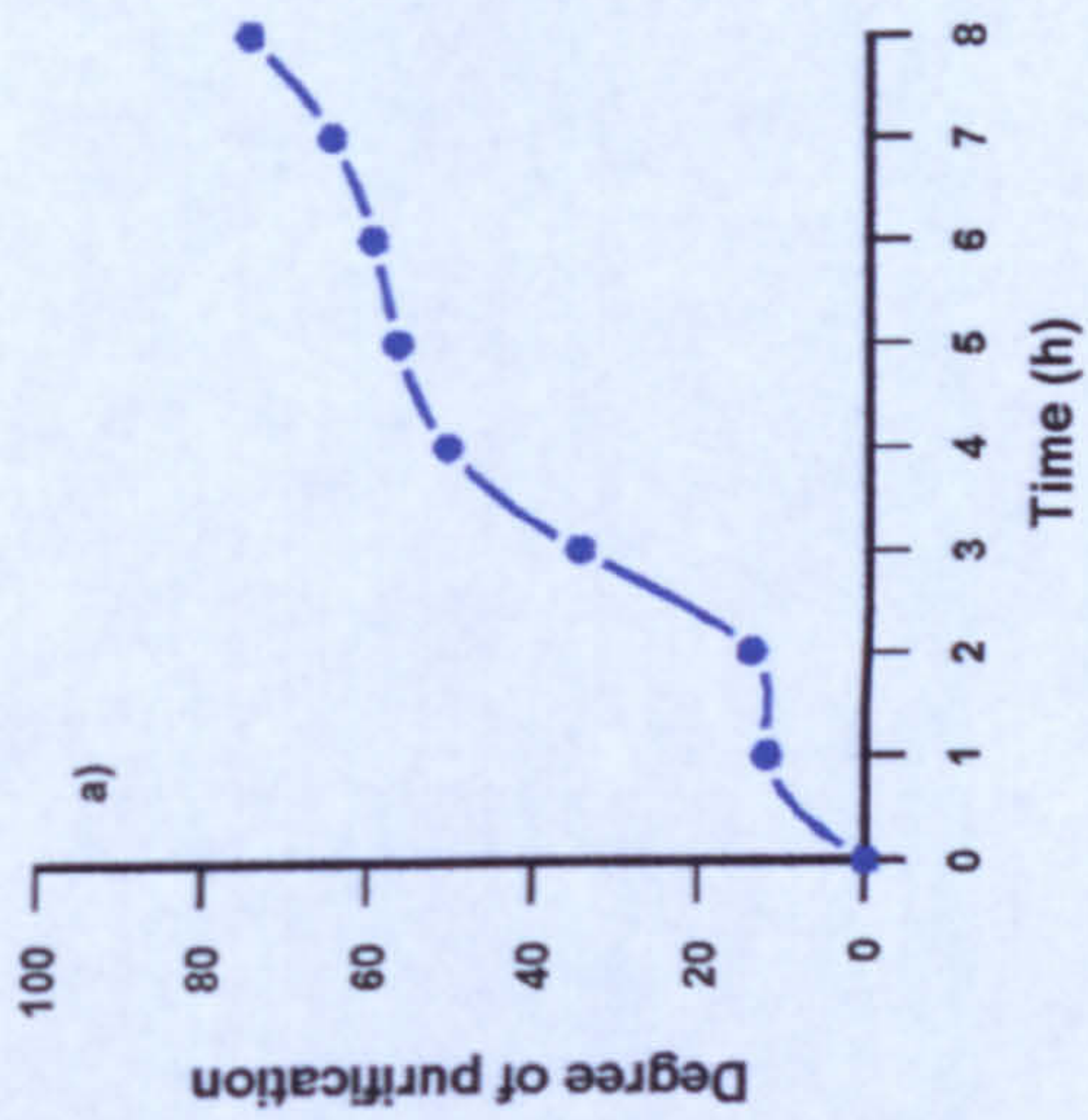


Figure 4.3:- Recovery of copper from Vero sample A using plate, IXR and ACC. A comparison is shown in graph d).

From the results obtained it can be concluded that with the use of activated carbon cloth, a greater degree of purification can be achieved. In each of the experiments conducted the process occurring is that of copper ions being reduced at the cathode surface. This is illustrated by the equation 4.1:-



This is the case both with hydrated copper and a copper-EDTA complex. This is illustrated in Figure 4.4. The diagram on the left shows the case of hydrated  $\text{Cu}^{2+}$  overcoming the activation barrier to become copper metal. The diagram on the right is also illustrating this but here the situation is dealing with a complex. From this section of the diagram it can be seen that the activation barrier is higher for the complex than that of the hydrated copper.

This is due to the fact that water is not bound to copper as strongly as the EDTA. Therefore when the Cu metal is to be deposited onto the cathode surface there is a higher activation energy for the EDTA complex to overcome. The stretching bonds on the diagram also illustrate this phenomenon. Since the EDTA is more tightly bound to the copper than the water, it can be seen from the diagram that bonds for the hydrated complex are not stretched to the same extent as those for the EDTA complex.

Although similar results were obtained when using plate and ion exchange, there is a difference between the two systems. The plate is only allowing electrodeposition to occur, whereas in the case of ion exchange the two processes of electrodeposition and absorption are occurring simultaneously.

With activated carbon cloth the degree of purification is enhanced because electrodeposition and adsorption are occurring simultaneously. The adsorption process for the copper-EDTA complex undergoes a reaction which does not need to overcome the activation barrier, but instead can be adsorbed onto the activated carbon surface. Hence, the increase in recovery when utilising ACC can be attributed to the adsorption of the copper-EDTA complex.

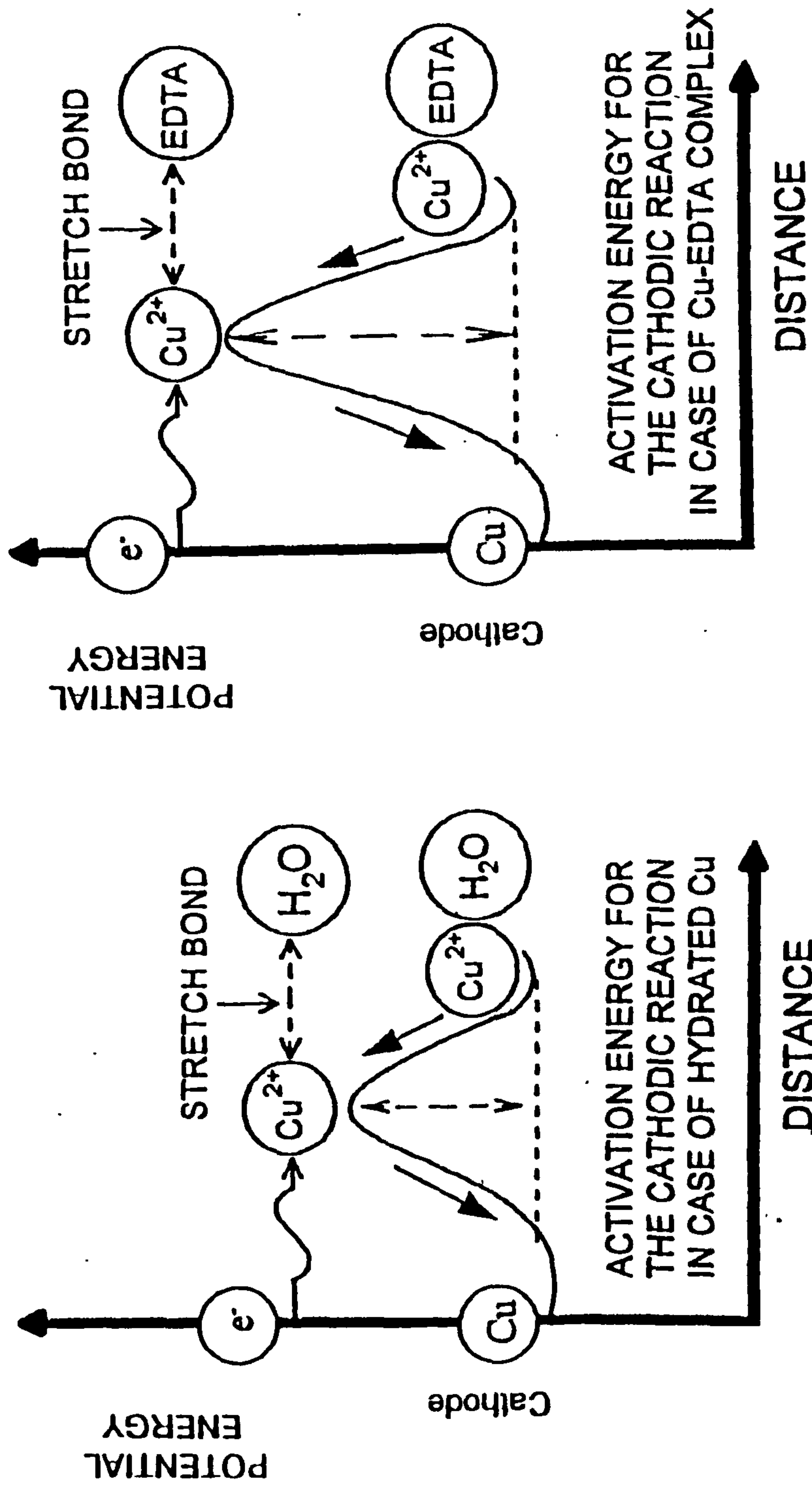


Figure. 4.4:- Activation energy diagrams for the case of hydrated Cu and Cu-EDTA complex

In the case of sample (B) the following results were obtained (Table 4.4).

From the results it can be seen that both concentrators proved to be more efficient than the control. Ion exchange proved to be the most effective with  $\alpha_{Cu}$  being 76% after only the first hour of electrolysis. Activated carbon and control gave values of 69% and 15% respectively after the same time period of electrolysis [Figure 4.5].

As the reaction proceeded both concentrators achieved 90% purification after 4 h of electrolysis compared with 37% recovery with the control during the same electrolysis period.

The low percentage recovery of copper for sample (A) was due to the copper EDTA complex. In the case of a model copper solution there are plenty of hydrated copper ions which absorb on the resin active sites at the initial stages. The saturated resin then begins to discharge these ions to the cathode surface without increasing the solution concentration. In the case of the copper EDTA complex, there are no free copper ions to absorb on the resin active sites. The first reaction is the breakdown of the EDTA complex before the absorption and the deposition takes place. These factors reduce the reaction efficiency.

Studies investigating the in-situ re-use of the carbon cloth concentrator showed that in the case of the activated carbon cloth concentrator the residual copper concentration was 1.3 and 1.7 ppm after the first and second run respectively. In the case of the stainless steel plate cathode the residual copper concentration was 16 and 17 ppm after the first and second run.

The results obtained from copper/palladium/tin solution (Table 4.5) supplied by Vero show that the selective separation of copper from palladium and tin ions is not possible under the conditions studied. However, it was noticed that most of the palladium is recovered as a cathodic deposit whereas most of the copper along with some tin ions were precipitated from solution as powder. The XRF analysis of the solid powder obtained at the end of the experiment is presented in Figure 4.6. The results are illustrated in Figure 4.7.

Table 4.4:- Vero Sample B											
Control			Ion Exchange				Activated Carbon Cloth				
Time (h)	Degree of Purification (%)	pH	Time (h)	Degree of Purification (%)	pH	Time (h)	Degree of Purification (%)	Time (h)	Degree of Purification (%)	pH	
0	0	1.4	0	0	1.4	0	0	0	0	1.46	
1	15		1	76		1	69	1	69		
2	15		2	79		2	59	2	59		
3	20		3	89		3	83	3	83		
4	37		4	93		4	90	4	90		
5	50		5	94		5	93	5	93		
6	56		6	97		6	94	6	94		
7	62		7	98		7	98	7	98		
8	69	1.3	8	99	1.3	8	99	8	99	1.3	



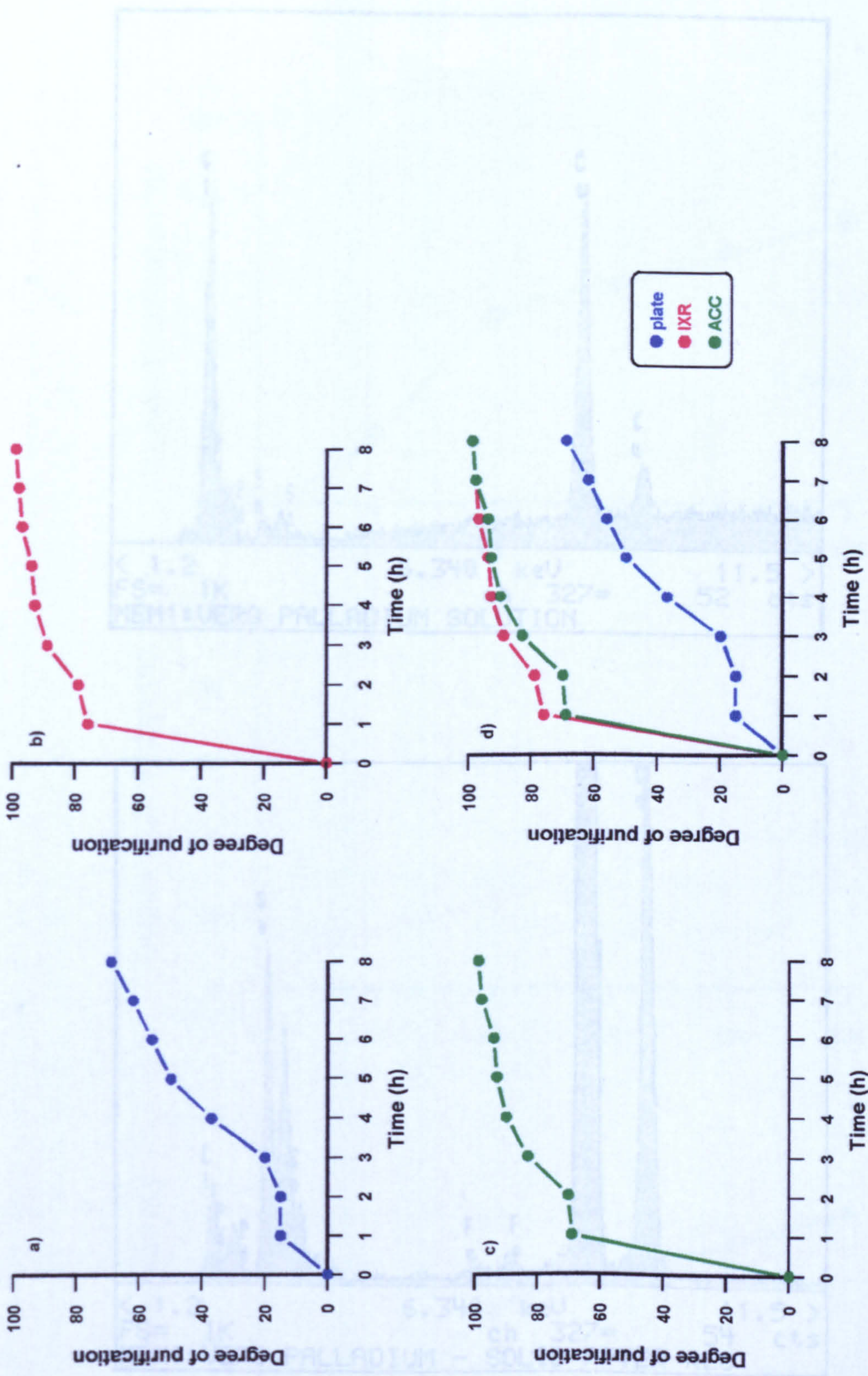


Figure 4.5:- Recovery of copper from Vero sample B using plate, IXR and ACC. A comparison is shown in graph d).

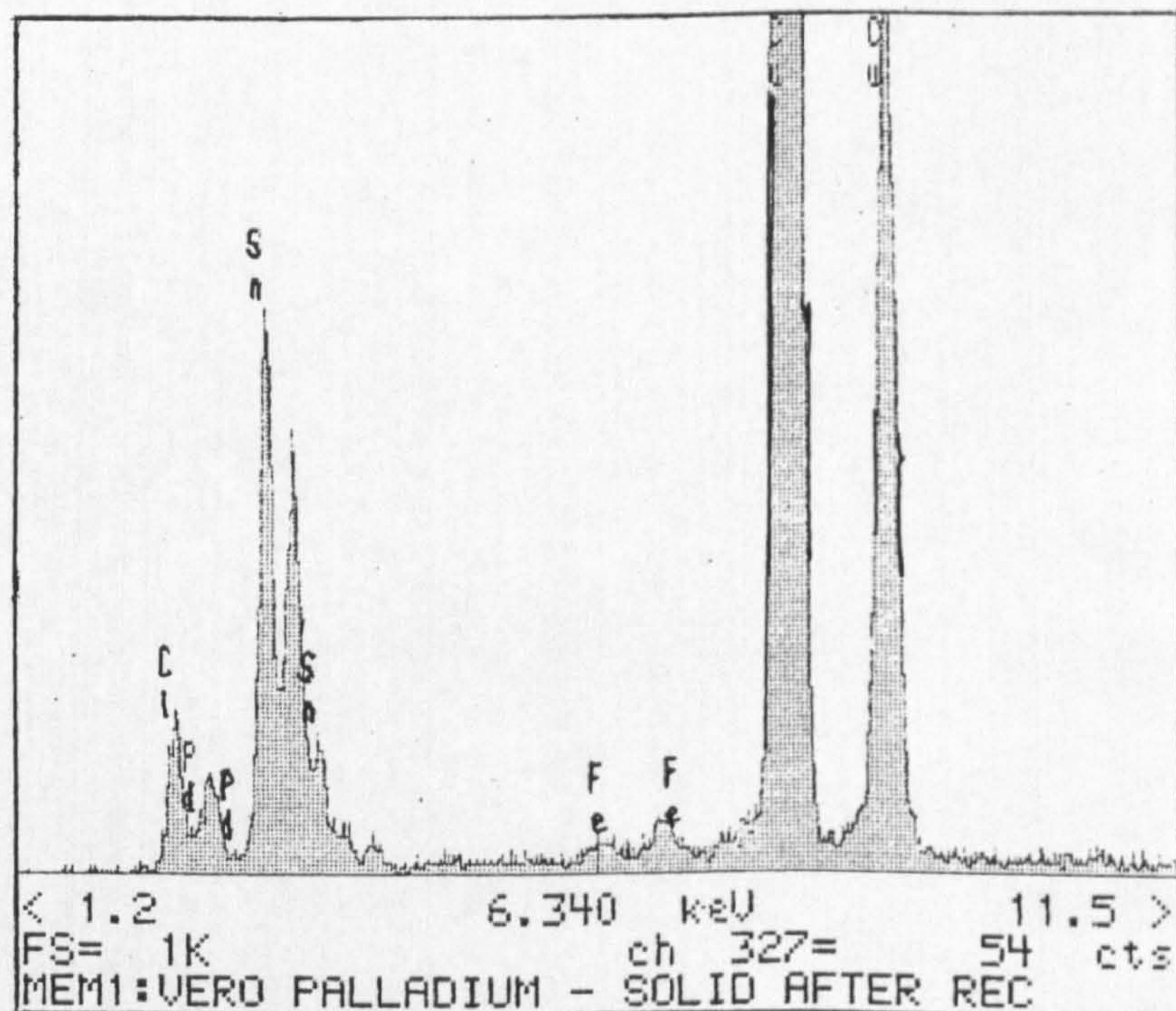
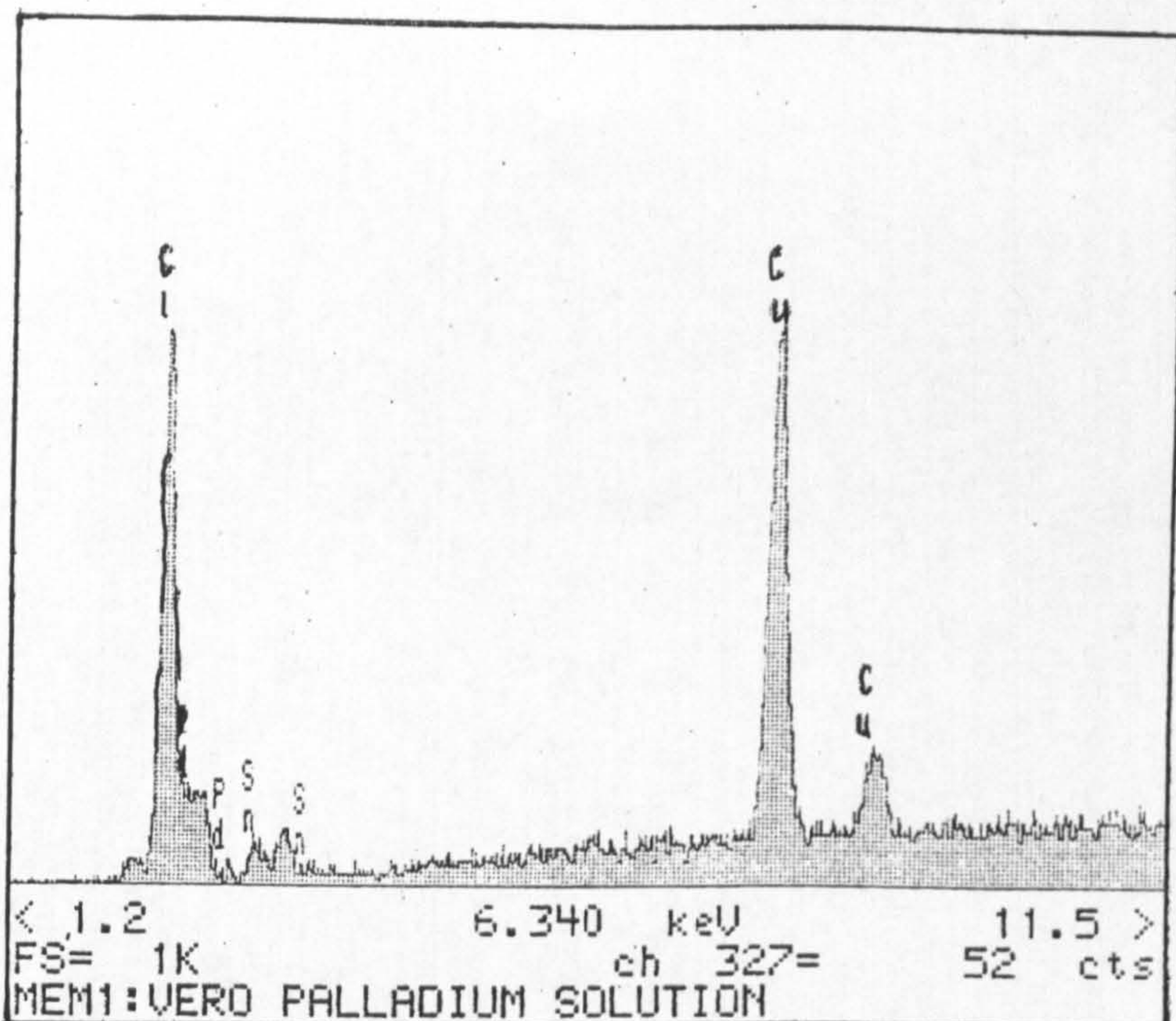


Figure. 4.6: XRF analyses of as-supplied sample and the solid powder

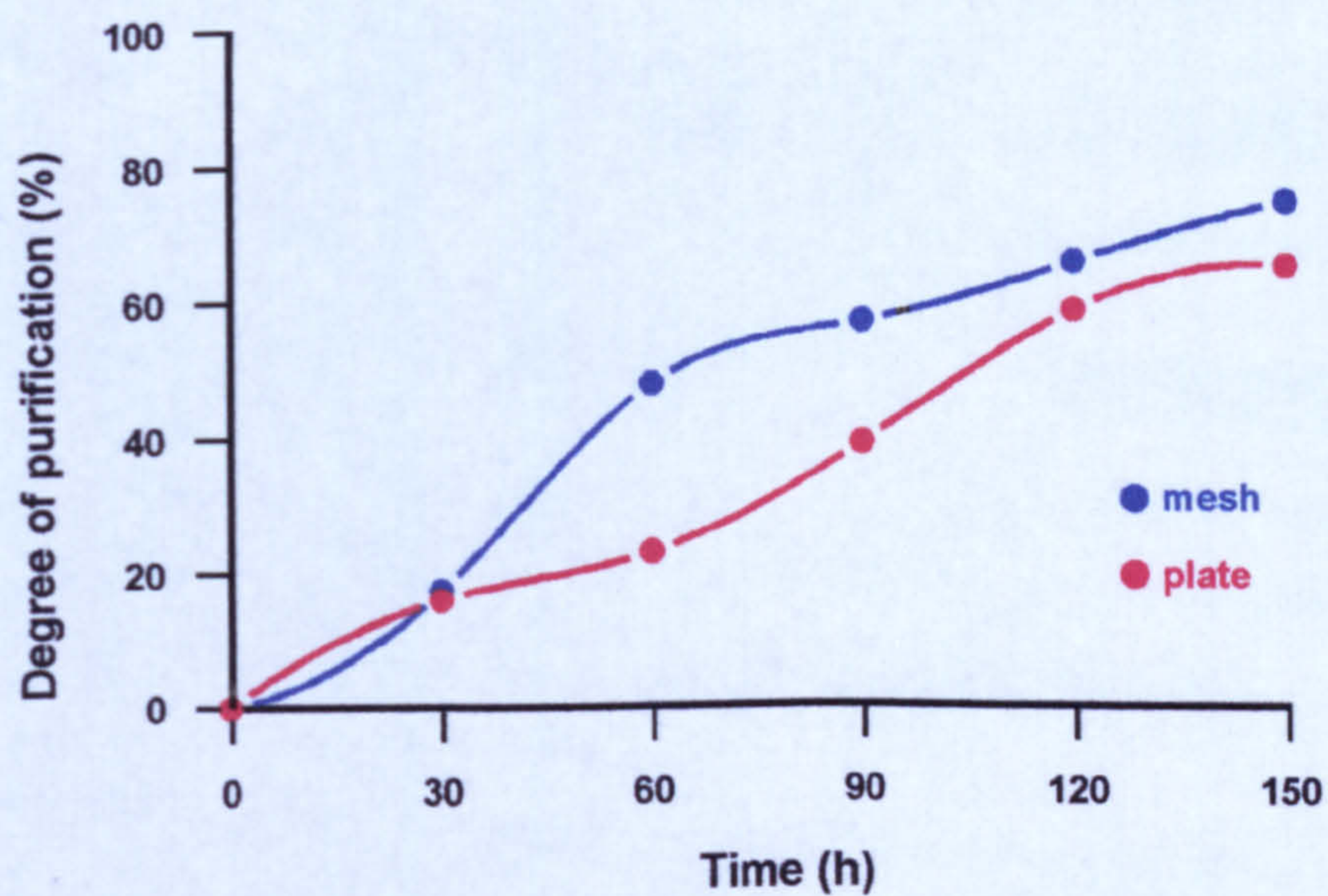
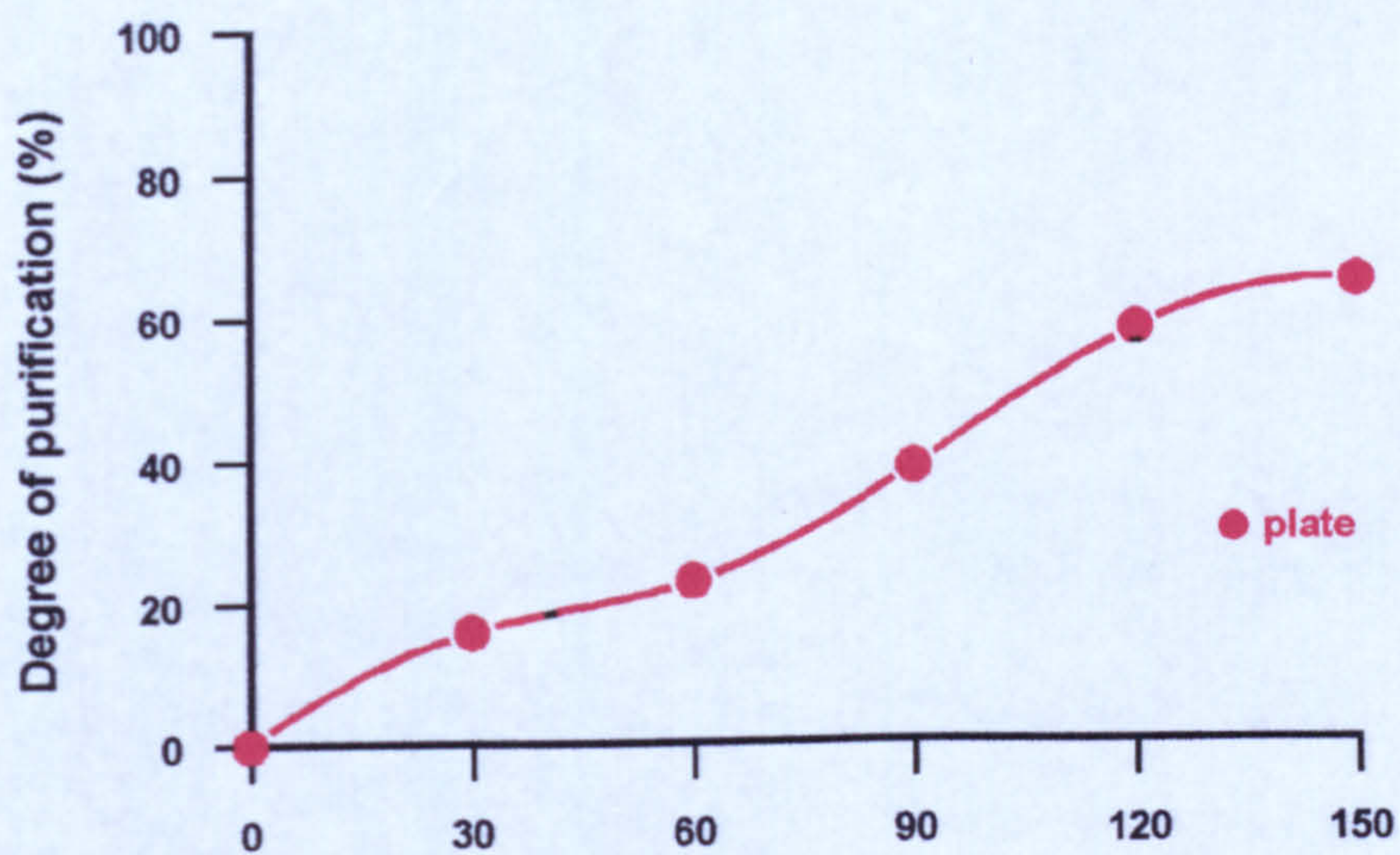
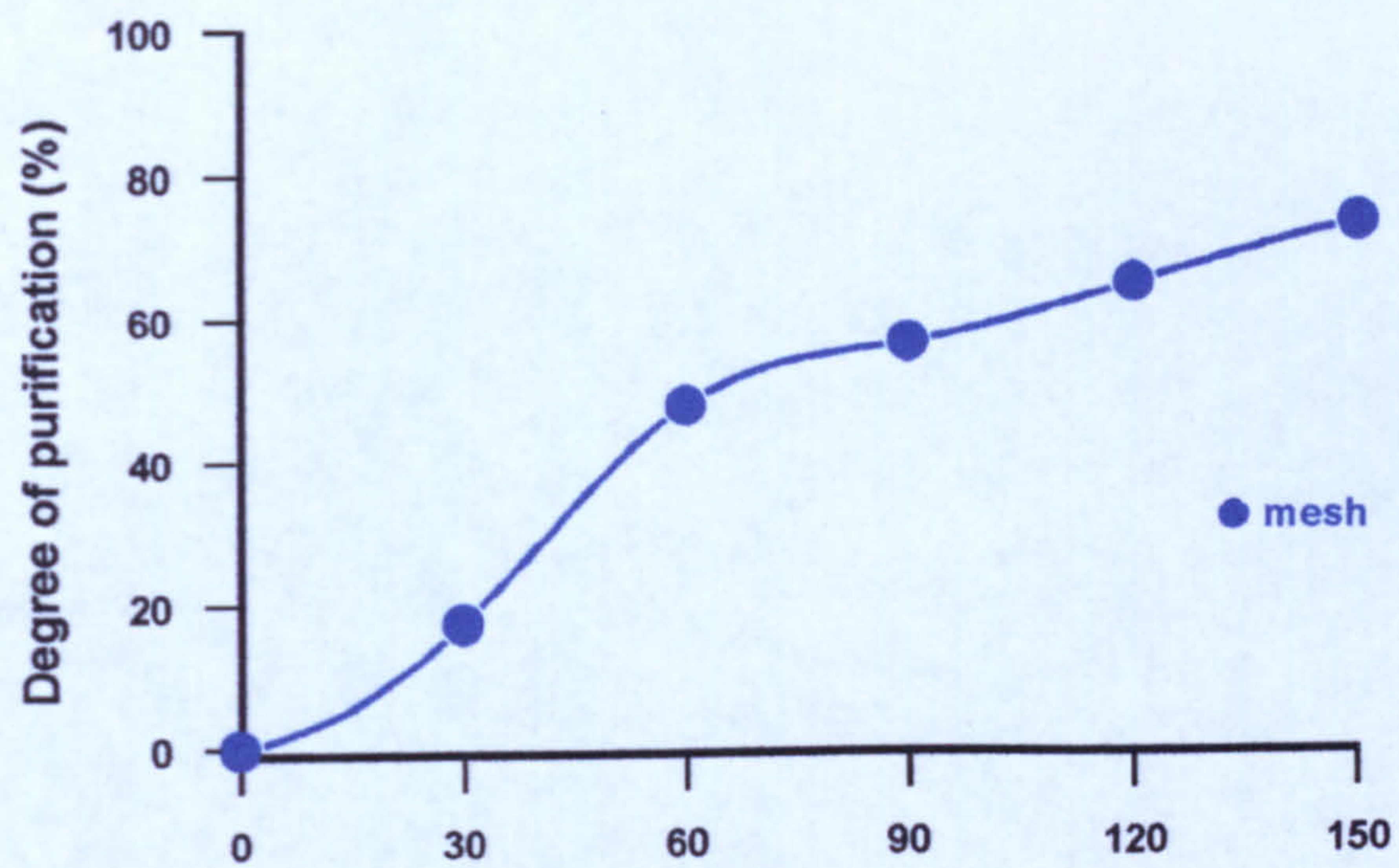


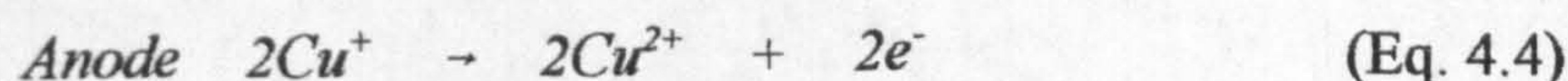
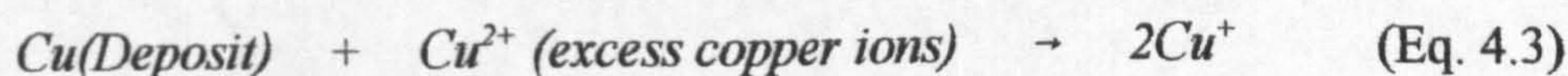
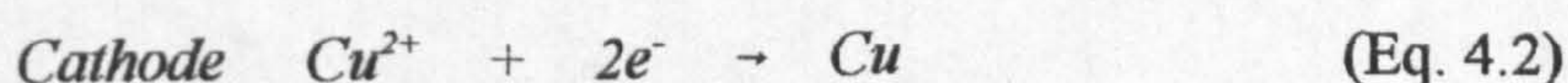
Figure 4.7:- Comparison for the recovery of Cu, Pd and Sn from Vero Shipley Catalyst solution using a mesh and plate electrode.



Table 4.5:- Separation of Pd and Cu from Cu/Pd/Sn solution		
Reaction Time (mins)	Concentration (ppm)	
	Cu	Pd
0	0	0
30	17.4	16
60	47.8	23
90	56.5	38
120	65.2	58.1
150	73.9	64.5

#### 4.3.2 United Distillers

A very low recovery of copper was achieved under the conditions studied for each system. The low copper recovery from this solution is attributed to the etching ability of copper chloride solution at this high concentration (25, 000 ppm) due to the following reactions:



The presence of  $\text{Cu}^{+}$  ions causes a parasitic redox shuttle reaction to occur and therefore the removal of copper is very low in the circulatory system.

In the absence of recirculation it would be expected that the copper ions would reduce as rapidly as they diffuse and there should be no excess ions near the cathode surface. The reaction efficiency should be high because the redox shuttle reaction is suppressed.

The low percentage recovery of copper using both concentrator systems compared to the control system is again explained because of the excess supply of copper ions in the

concentrators near the cathode surface. This effect was observed by a change in colour of solution from blue ( $\text{Cu}^{2+}$ ) to green ( $\text{Cu}^+$ ) near the cathode surface particularly when an ion-exchange concentrator system was used.

A second set of experiments was, therefore, carried out under identical electrolysis conditions without circulation of the electrolyte. For each of these experiments a cell was constructed of 490 cm<sup>3</sup> capacity [Figure 4.2]. A 400 ml solution was used and a constant current of 20 Am<sup>-2</sup> was applied. The results obtained under each condition show a high recovery of copper with best results obtained with the use of a stainless steel plate cathode (Table 4.6) and [Figure 4.8]. Results from the as-supplied samples of backwash ion exchange solution are presented in Table 4.7 and Figure 4.9. It can be seen that in the case of using a stainless steel plate cathode on its own, the degree of purification was 55% after 6 h of electrolysis. For use with an ion-exchange resin it was found that the degree of purification had increased to 67 % but the greatest increase in the amount of copper recovered from the solution was obtained with activated carbon cloth with a value of  $\alpha_{\text{Cu}}$  being 86%.

<b>Table 4.6:- Recovery of copper using a control and concentrator technologies</b>			
<b>Reaction</b>	<b>Degree of purification for copper (%)</b>		
<b>Time (h)</b>	<b>Control (plate)</b>	<b>Activated carbon cloth</b>	<b>Ion-exchange</b>
0	0	0	0
1	56	64	46
2	80	84	66
3	83	88	90
4	95	91	80
5	99	99	82
6	99	99	85

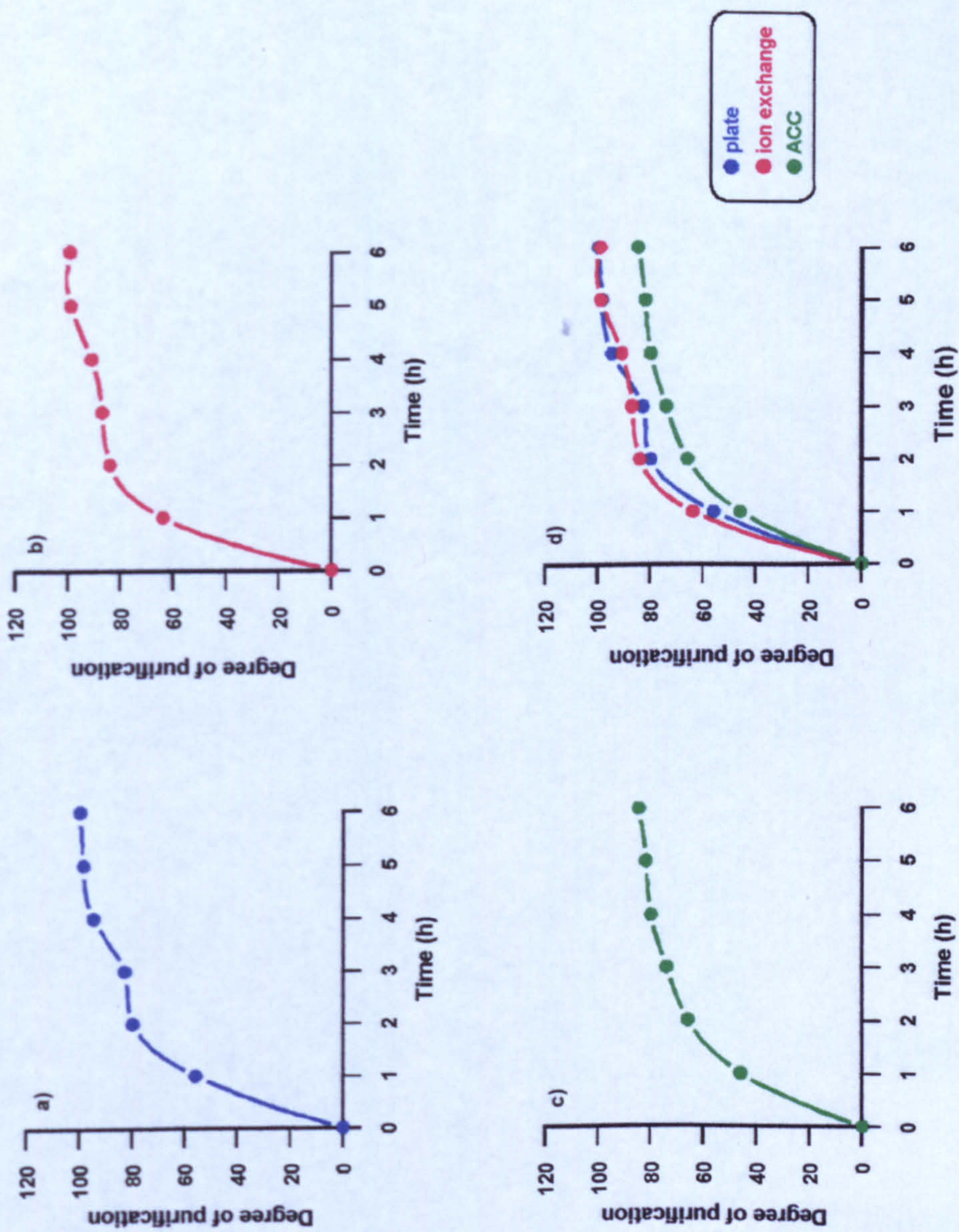


Figure 4.8:- Recovery of Cu from  $\text{CuCl}_2$  solution using plate, ion exchange and ACC. Graph d) shows a comparison between the three systems used.

**Table 4.7:- United Distillers**

Control			Ion Exchange			Activated Carbon Cloth		
Time (h)	Degree of Purification (%)	pH	Time (h)	Degree of Purification (%)	pH	Time (h)	Degree of Purification (%)	pH
0	0	1.4	0	0	1.4	0	0	1.4
1	12		1	42		1	14	
2	18		2	50		2	56	
3	22		3	55		3	70	
4	41		4	61		4	68	
5	49		5	63		5	86	
6	55	1.3	6	67	1.3	6	86	1.3

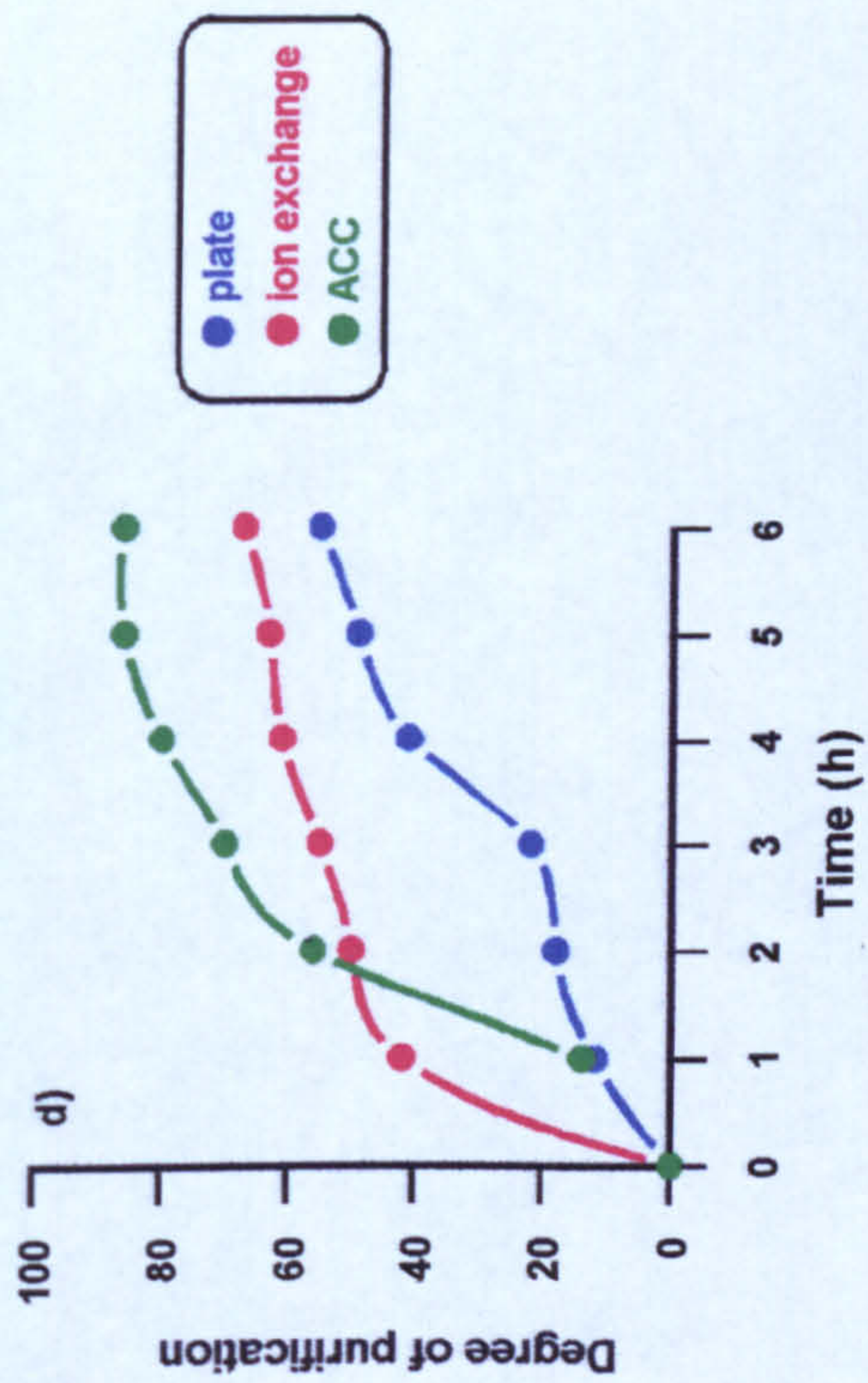
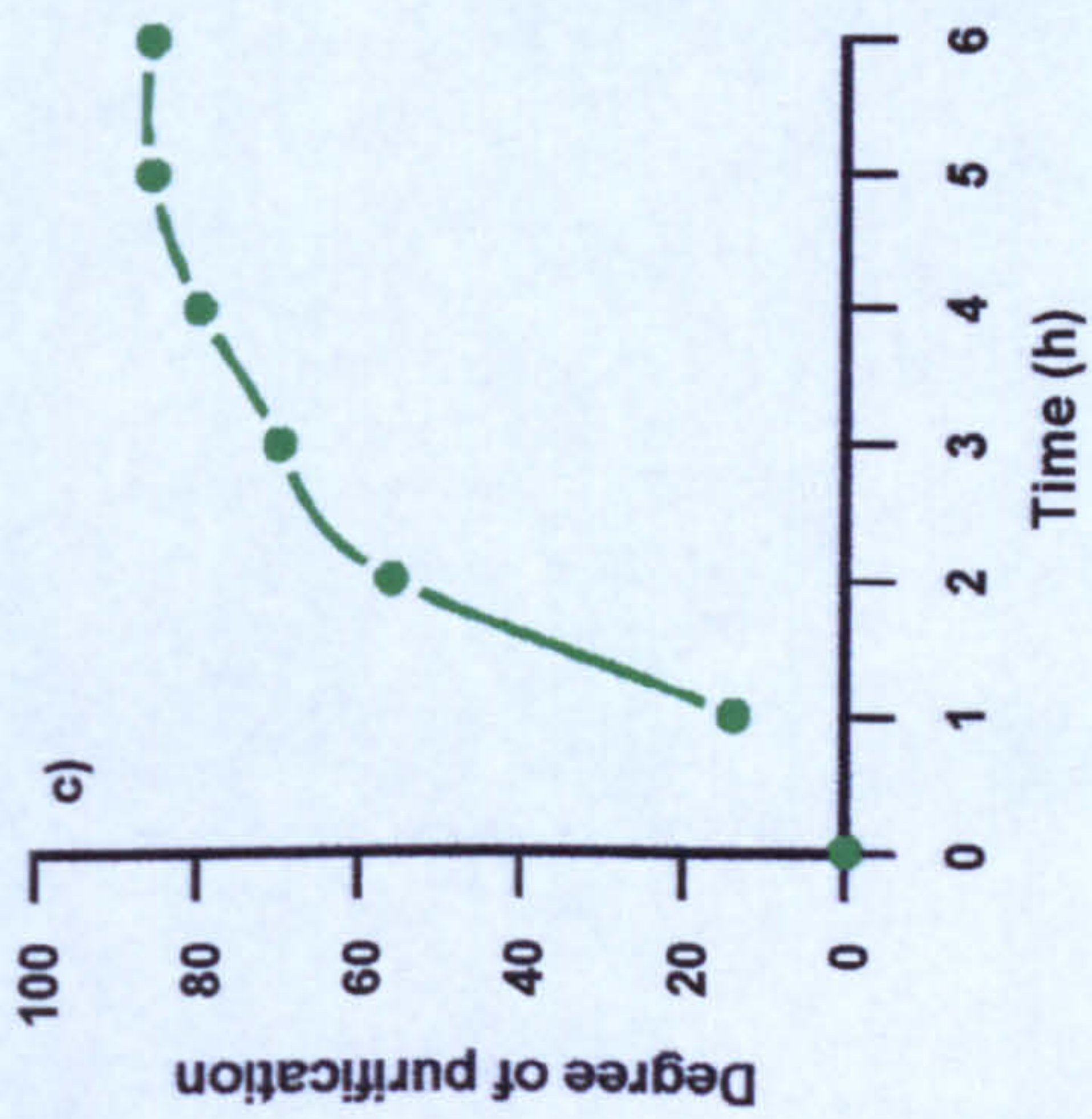
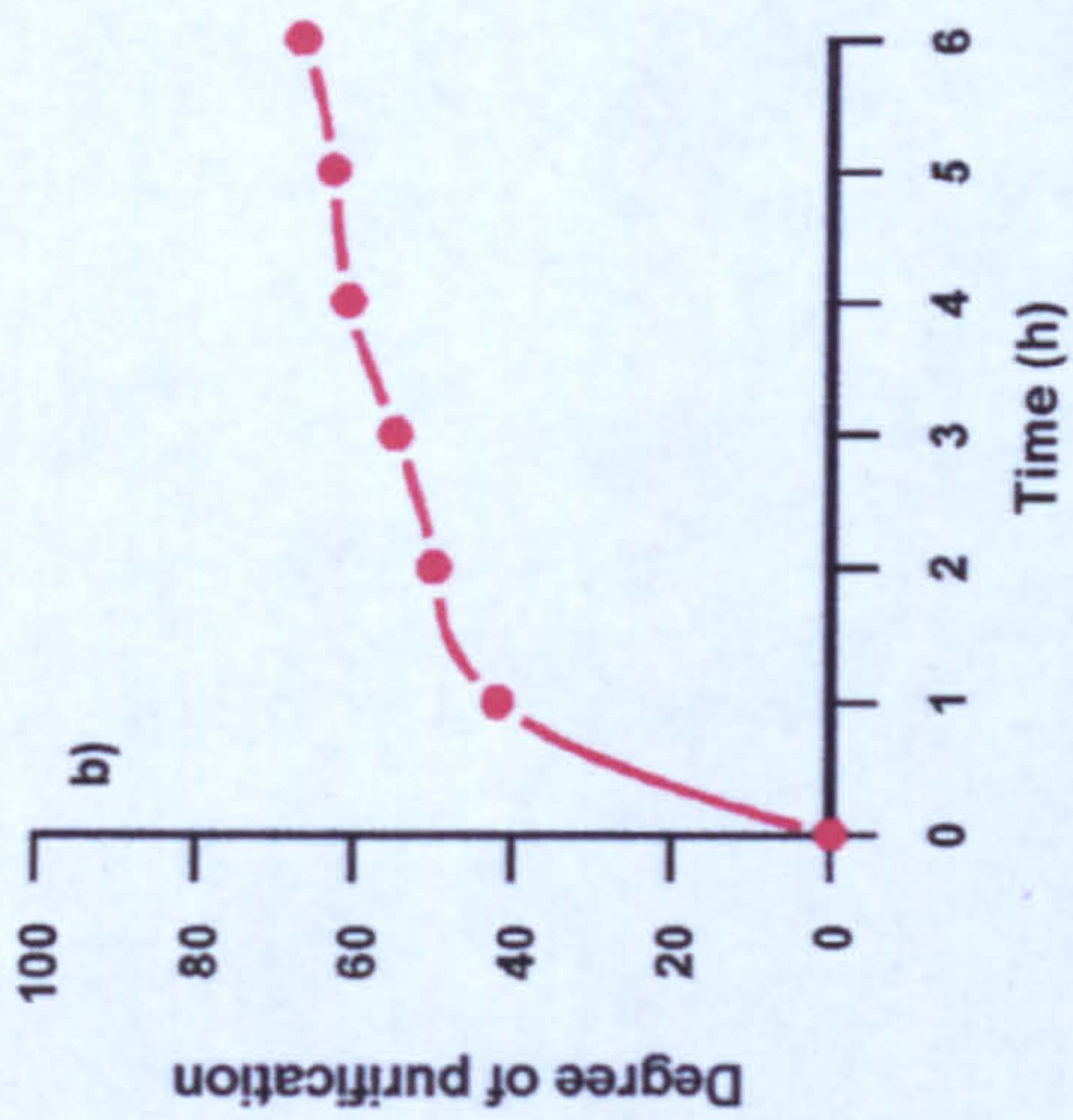
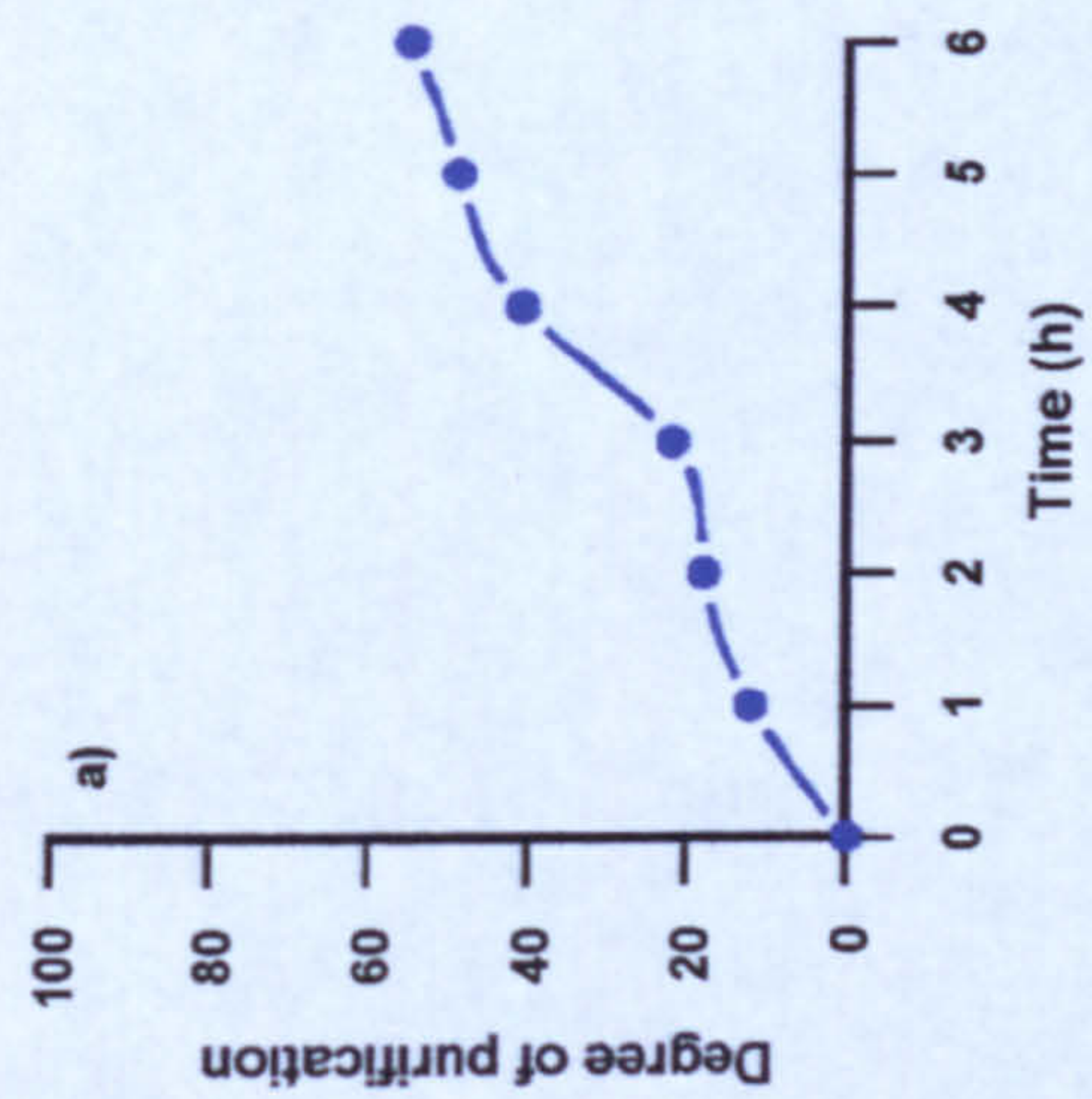
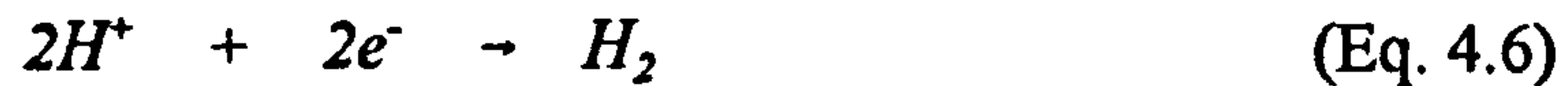


Figure 4.9:- Recovery of Cu from United Distillers sample using plate, ion exchange and ACC. Graph d) shows a comparison between the three systems used.

The major interfering reaction occurring during copper deposition is the evolution of hydrogen gas at the cathode surface. The reactions taking place at the cathode surface are as follows:-



At the anode the following reaction is occurring:-



The oxidation of water at the anode surface produces acid which is being exploited for the in-situ regeneration of ion-exchange resins. In effect, this can be represented by:-

**Deposition of metal ↔ Evolution of hydrogen gas**

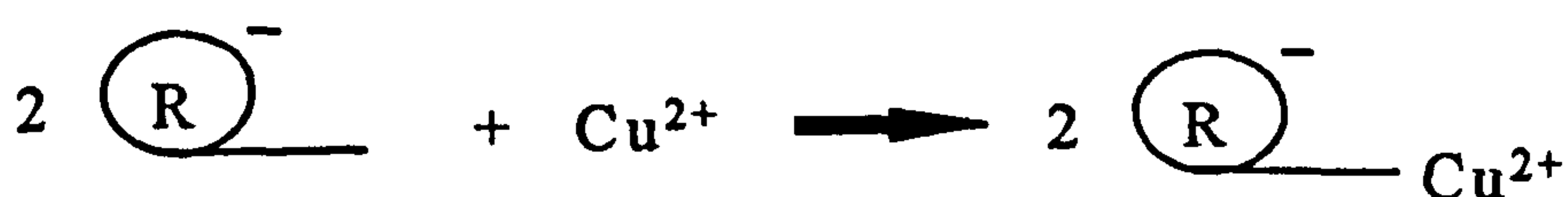
In the presence of ion-exchange resins there are three stages which occur before copper can be deposited onto the cathode surface.

The three step process occurring is represented by the following where  $\text{R}^{-}$  represents the ion-exchange resin.

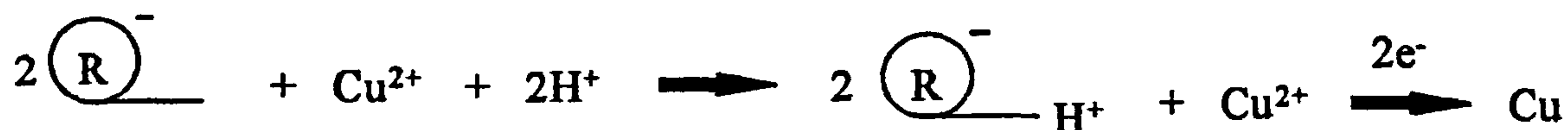
**Stage 1 - Initiation**



**Stage 2 - Absorption**



### Stage 3 - Deposition and Regeneration



The low percentage recovery of copper using the ion-exchange system is mainly due to the following two reasons:-

- a) The initiation step, shown above, does not go to completion.
- b) The regeneration of ion exchange starts at an early stage. Hence activated carbon is more efficient in absorbing the copper metal.

For each of the following experiments a cell was constructed [Figure 4.2] which was 490 cm<sup>3</sup> in volumetric capacity. For each experiment 400 ml of solution was used. Two mixed metal oxide anodes and a stainless steel plate was used for the control set up. With the use of activated carbon cloth the set up was A-ACC-A and for the ion exchange resin the set up was A-IX-C-IX-A. Each electrode had a surface area of 0.01 m<sup>2</sup>. The voltage was kept at a maximum and a constant current of 1.5 A was applied unless stated otherwise.

#### 4.3.3 INCO

##### (1) Recovery of Pd from PdCl<sub>2</sub> solution

The results obtained show that palladium can be recovered using a standard electrochemical cell. The concentration of palladium decreased from 80 ppm to 2.5 and 3.5 ppm with the use of a mesh and plate cathode under identical conditions. These results are true for a static system (Table 4.8). However, when the solution was agitated, the results obtained under these conditions using a mesh and plate cathode show an increase in the recovery of palladium ions. The residual concentration was below 1 ppm after 4 h of electrolysis when using a mesh electrode (Table 4.9) and [Figure 4.10].

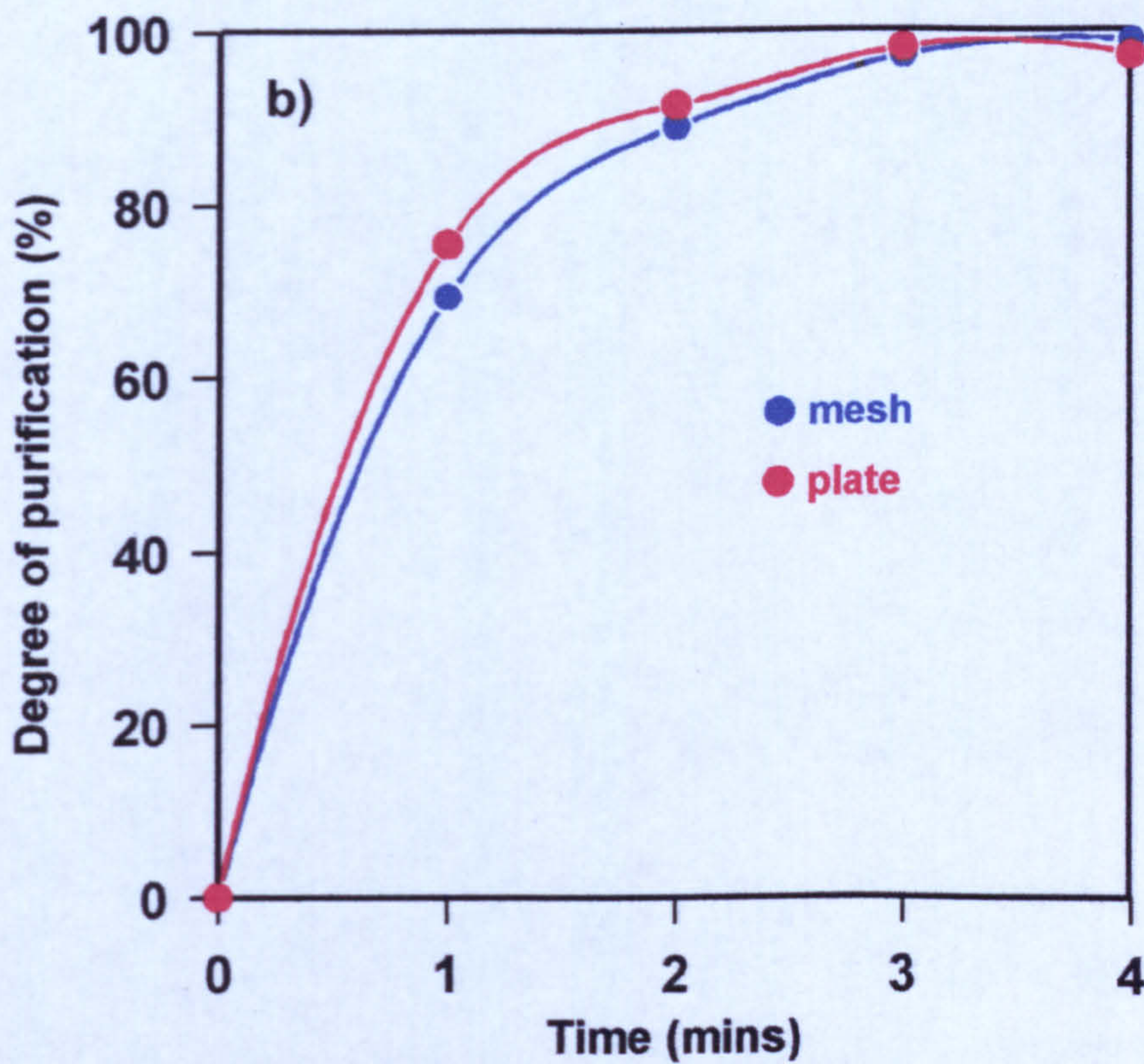
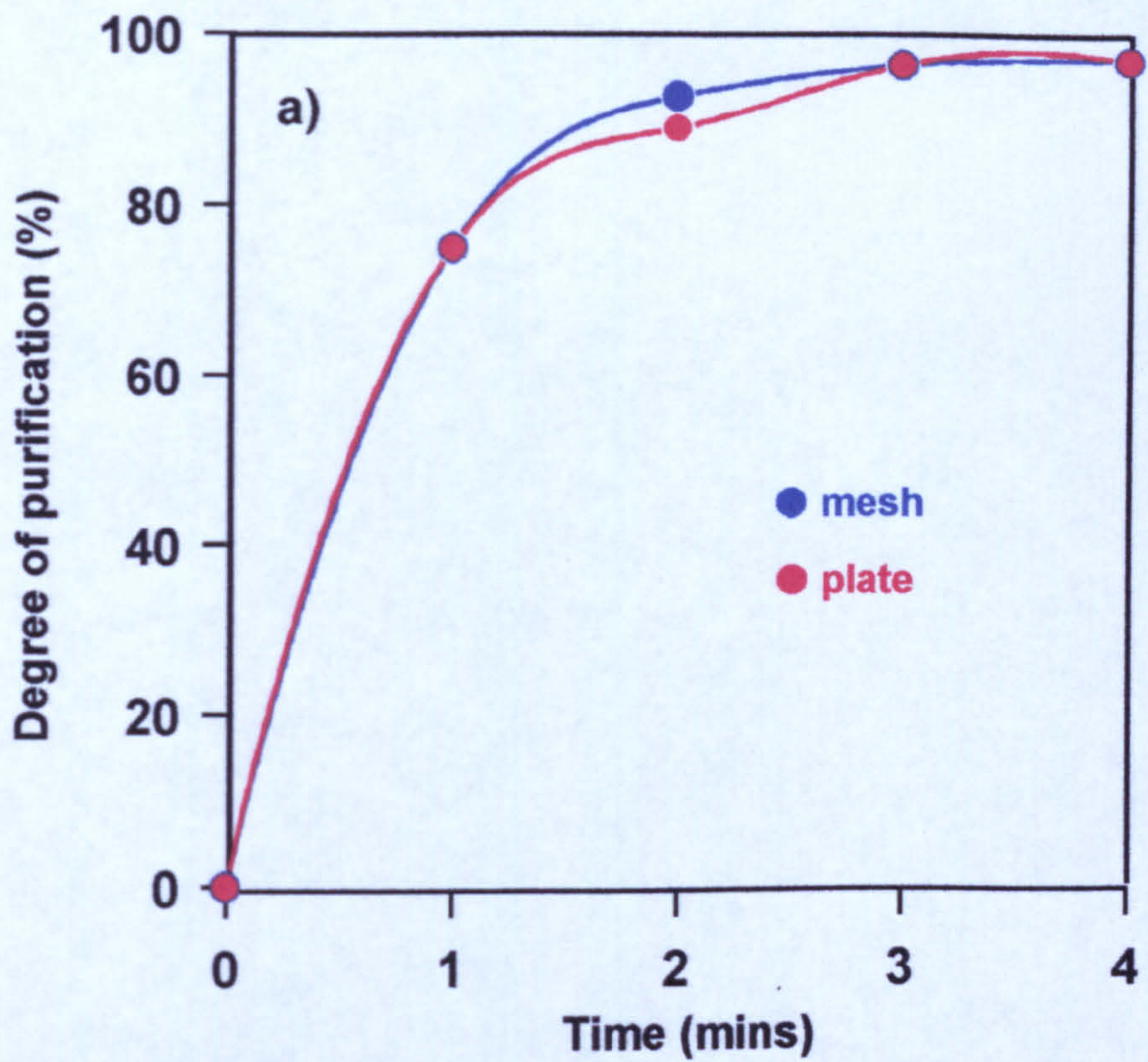


Figure 4.10:- Recovery of Pd from  $0.08 \text{ g dm}^{-3}$   $\text{PdCl}_2$  solution under conditions a) static and b) agitated.



<b>Table 4.8:- Recovery of Pd from PdCl<sub>2</sub> solution under static conditions</b>				
<b>Time (h)</b>	<b>Concentration (ppm)</b>		<b>Degree of Purification (%)</b>	
	<b>mesh</b>	<b>plate</b>	<b>mesh</b>	<b>plate</b>
0	80	80	0	0
1	20	20	14	75
2	6	9	56	89
3	3	3	70	96
4	2.5	2.5	68	97

<b>Table 4.9:- Recovery of Pd from PdCl<sub>2</sub> solution under agitated conditions</b>				
<b>Time (h)</b>	<b>Concentration (ppm)</b>		<b>Degree of Purification (%)</b>	
	<b>mesh</b>	<b>plate</b>	<b>mesh</b>	<b>plate</b>
0	80	80	0	0
1	25	20	69	76
2	9	7	89	92
3	2	2	97	98
4	0.8	2	99	97

## **(2) Recovery of iridium from chloride solution**

The results obtained show that iridium can be recovered using a standard electrochemical cell. The concentration of iridium decreased from 40 ppm to 10 ppm after 6 h of electrolysis with the use of both mesh and plate cathodes under identical conditions. These results are confirmed for a static system (Table 4.10). When the solution was agitated, the results obtained under these conditions using a mesh and plate cathode show an increase in the recovery of iridium ions (Tables 4.11) and [Figure 4.11].

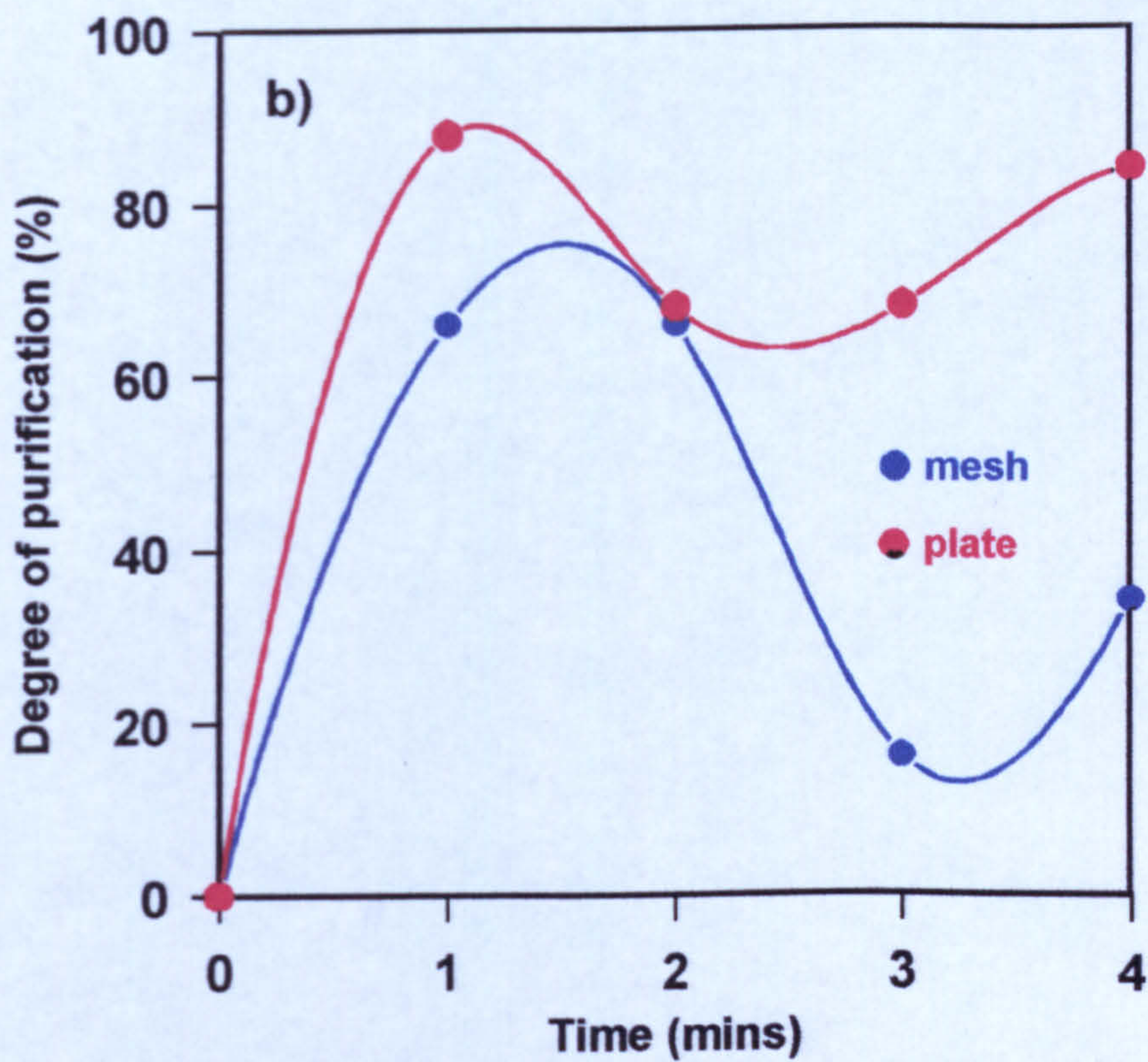
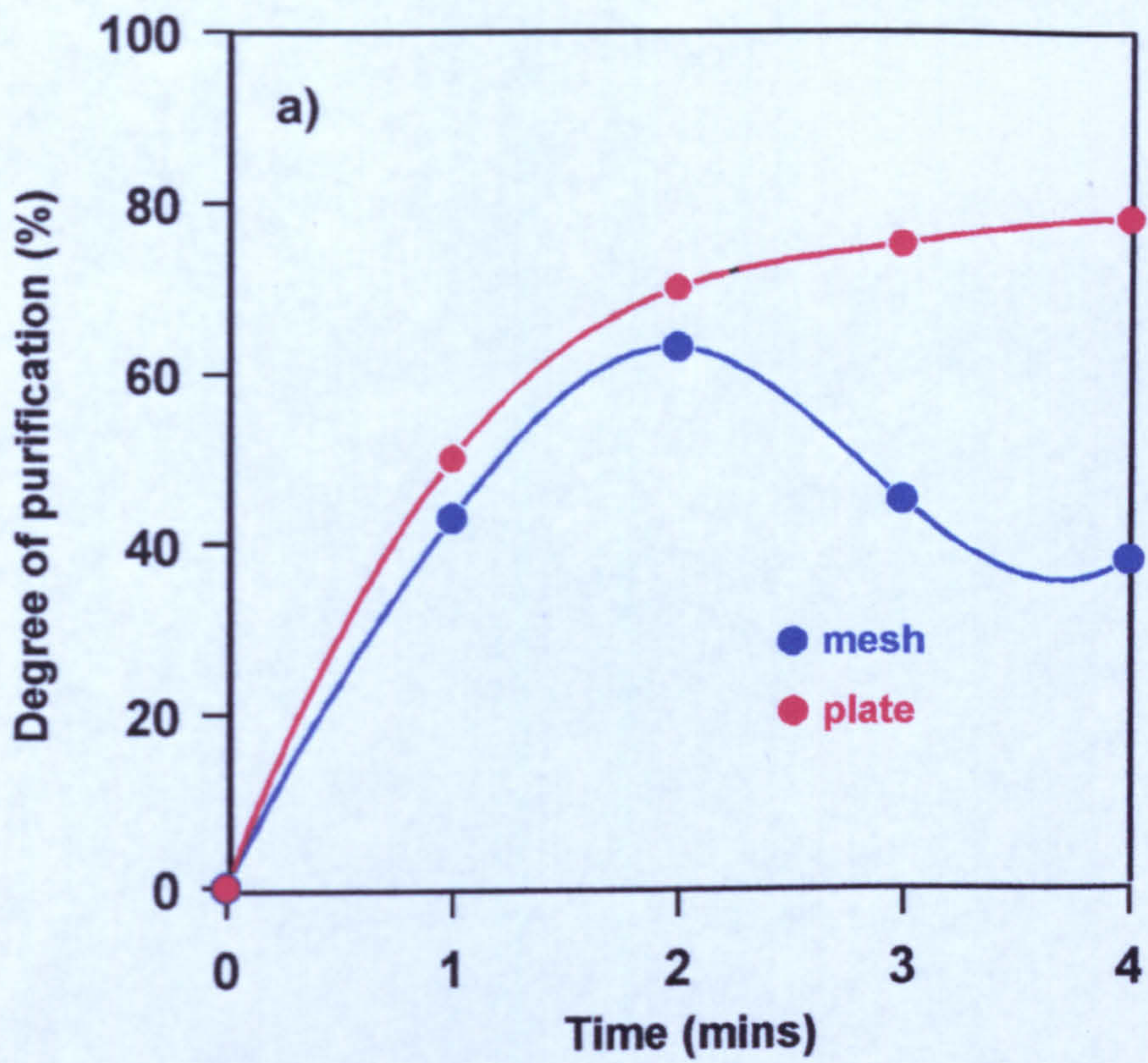


Figure 4.11:- Recovery of Ir from  $0.04 \text{ g dm}^{-3} \text{ IrCl}_2$  solution under conditions a) static and b) agitated.

In both cases the recovery of the metal ions was greater when the solution was agitated due to the high ion-transfer conditions achieved under agitated conditions.

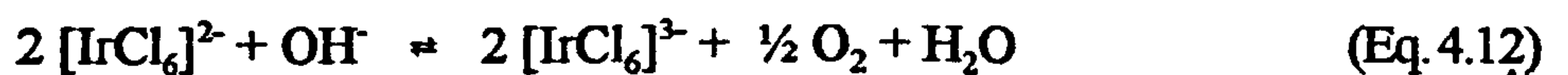
<b>Table 4.10:- Recovery of Ir from IrCl<sub>2</sub> solution under static conditions</b>				
<b>Time (h)</b>	<b>Concentration (ppm)</b>		<b>Degree of Purification (%)</b>	
	<b>mesh</b>	<b>plate</b>	<b>mesh</b>	<b>plate</b>
0	40	40	0	0
1	19	20	53	50
2	15	18	63	55
3	22	16	45	60
4	25	14	38	65
5	12	14	70	65
6	10	15	75	63

<b>Table 4.11:- Recovery of Ir from IrCl<sub>2</sub> solution under agitated conditions</b>				
<b>Time (h)</b>	<b>Concentration (ppm)</b>		<b>Degree of Purification (%)</b>	
	<b>mesh</b>	<b>plate</b>	<b>mesh</b>	<b>plate</b>
0	40	40	0	0
1	17	21	66	58
2	17	16	66	68
3	42	16	16	68
4	33	8	34	84
5	8	11	84	78
6	8	11	84	78

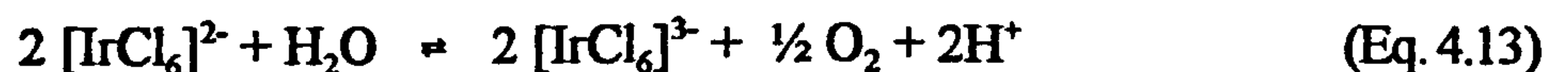
During the electrolysis period, it was found that the colour of the solution changed from dark red-brown to yellow. This can be attributed to the two different oxidation states of Ir<sup>(IV)</sup> and Ir<sup>(III)</sup> which will now be explained.

### Chemistry of iridium

The dark red-brown [Ir<sup>IV</sup>Cl<sub>6</sub>]<sup>2-</sup> ion is rapidly and quantitatively reduced in strong alkaline solution to give the yellow-green [Ir<sup>III</sup>Cl<sub>6</sub>]<sup>3-</sup> complex.



In acidic solutions the principal reaction occurring is:-



Iridium exists in solution in the form of ions in two oxidation states: Ir (IV) and Ir (III). In neutral and weakly acidic aqueous solutions Ir (IV) undergoes spontaneous reduction to Ir (III). Iridium ions form two complexes with the chloride ions. The first complex IrCl<sub>6</sub><sup>2-</sup> is brown in colour and the second complex IrCl<sub>6</sub><sup>3-</sup> is yellowish green.

A study carried out by MacNamara<sup>[3]</sup> investigated the effect of temperature upon the deposition of iridium and the current efficiency. The electrolysis of strongly acidic solutions of iridium at low temperatures can be expected to lead to separation of iridium (IV), which is reduced to iridium (III) and remains in solution. A study by Grushina et al<sup>[4]</sup> demonstrated the possibility of electrochemical separation of iridium and impurities (Au, Pt, Pd, Rh, Cu, Ag and Bi) by electrolysis of chloride solutions using a graphitised fibrous carbon cathode and a cation exchange membrane. Iridium wire was used as the anode.

### *Effect of concentrator at 150 Am<sup>-2</sup>*

In this set of experiments when using the control concentrator it was found that after 15 minutes of electrolysis the concentration of iridium left in solution was 124 ppm (80.6% recovered) indicating that most of the iridium had been recovered in the initial stages of electrolysis. However, some of the deposited iridium flaked back into solution and so there was

some dissolution of iridium. Analysis after 1 h showed that the concentration of iridium in the solution had increased slightly to 138 ppm (78.4%) and there was a further increase since after 2 h of electrolysis the concentration had risen to 151 ppm (76.4%). From the third hour of electrolysis up until the experiment was complete after 6 h of electrolysis the concentration of iridium in the solution had reached stability at 165 ppm (74.2%).

With the use of activated carbon cloth the concentration of iridium in solution, after 15 minutes of electrolysis, had decreased from 640 ppm to 179 ppm (72.0%). As the reaction proceeded, analysis showed that from 30 minutes of electrolysis to 5 h of electrolysis the concentration of iridium in solution remained constant at 119 ppm (81.4%). After 6 h of electrolysis the concentration had risen to 134 ppm (79.1%).

The final concentrator to be used was an ion exchange resin. In this case the concentration of iridium after 15 minutes of electrolysis had decreased to 224 ppm (65%). After 30 minutes to 4h of electrolysis the concentration of iridium remained constant at 115 ppm (82.0%). However, in the remaining 2 h of electrolysis the concentration of iridium had increased to 130 ppm (79.7%).

From these results it can be seen that iridium was best recovered after 15 minutes of electrolysis when using the control system.

#### ***Effect of Concentrator using $10 \text{ Am}^{-2}$***

With the use of the control system at this low current density, it was observed that the concentration of iridium remaining in solution after 15 minutes of electrolysis had decreased from 640 ppm to 126 ppm (80.3%). It was apparent that no more iridium was recovered throughout the duration of the experiment since after 8 h of electrolysis the concentration of iridium in solution was still 126 ppm (80.3%).

With the use of ion exchange resins it was seen that in the first 15 minutes of electrolysis the percentage recovery of iridium was 64.5%. After 30 minutes of electrolysis the recovery of iridium had risen to 81.8% and this figure remained constant until the fourth hour of

electrolysis. However, after 8 h of electrolysis the percentage recovery of iridium had dropped slightly to 79.4%.

The final concentrator to be used was activated carbon cloth. With this concentrator it was found that after 15 minutes of electrolysis  $\alpha_{Ir}$  was 71.7% and this value increased to 81.2%. After 5 h of electrolysis the value of  $\alpha_{Ir}$  was still 81.2%. However, after 8 h of electrolysis,  $\alpha_{Ir}$  had decreased to a value of 76.4%.

During the electrochemical process the following reactions are taking place in the cell:



The iridium is not being recovered as a cathodic deposit because the iridium complexes are negatively charged species. However, the iridium chloride complexes are reduced to iridium metal which drops out of solution at the bottom of the electrolytic chamber from which they can be easily recovered as a powder. The other cationic impurities present such as nickel, iron and copper are deposited on the cathode surface. The XRF analyses of the cathodic deposit and the recovered iridium using three systems are presented in Figures 4.12.

#### 4.3.4 Graphic Waste Services

Preliminary experiments on the silver bromide solutions provided by Graphic Waste Services using the standard electrochemical cell gave the following results presented in Table 4.12 and Figure 4.13.

The results obtained show that not only are silver ions being deposited on the cathode surface but also they are being reduced because of the presence of iron impurities. There are two possible reasons for this:-

(1) The following electrochemical reactions are taking place in the cell:



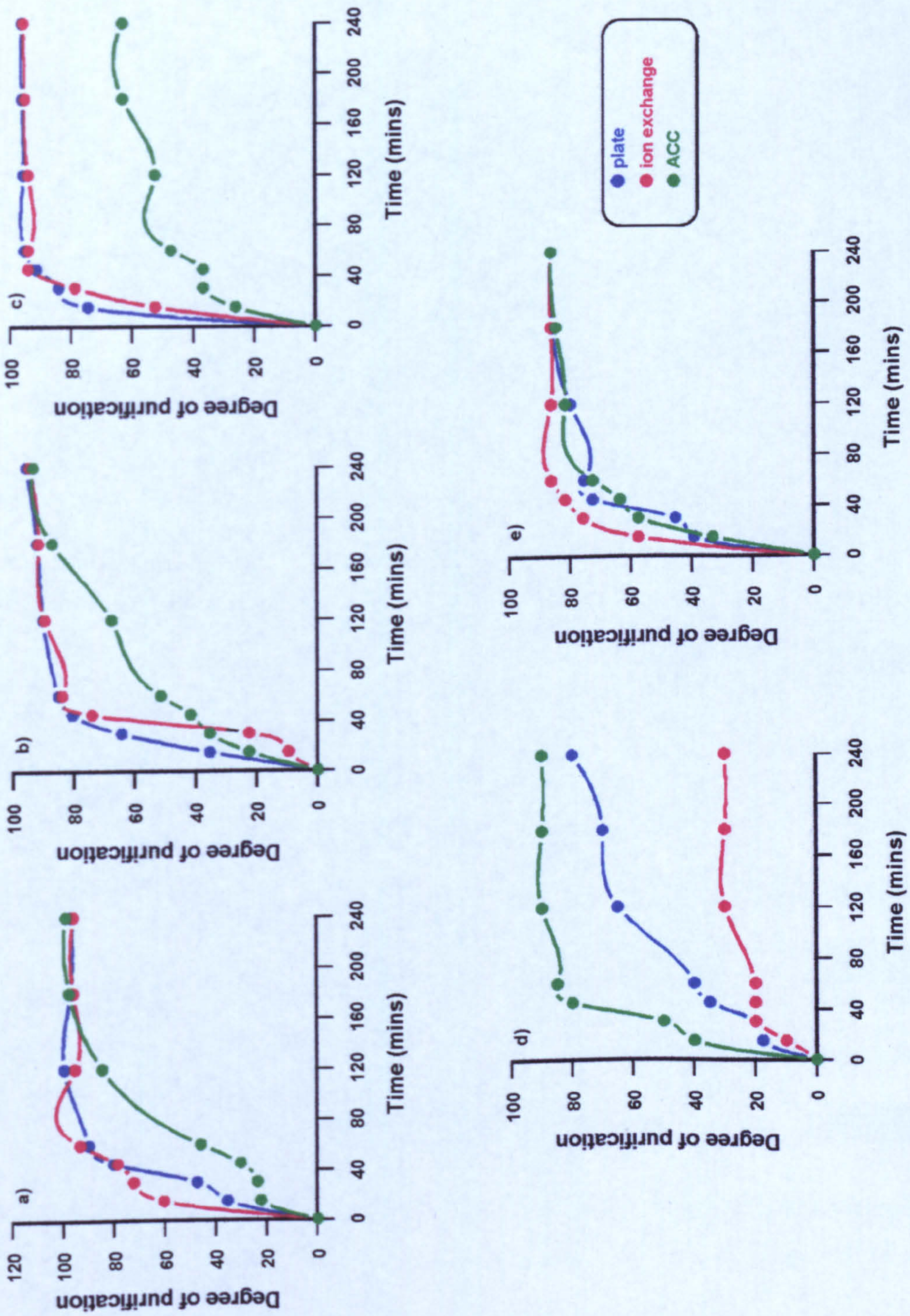


Figure 4.13:- Recovery of Ag from AgBr solution a) sample A, b) sample B, c) sample C, d) sample D and e) sample E using plate, IXR and ACC.



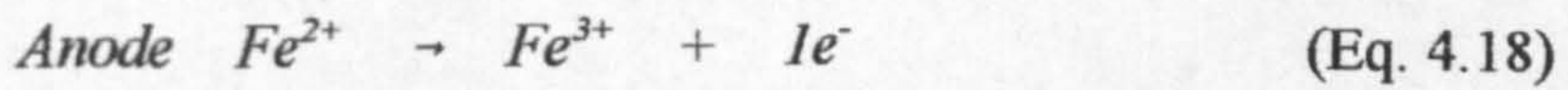
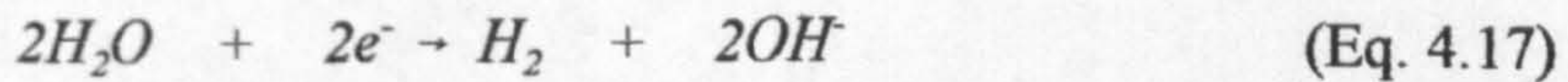
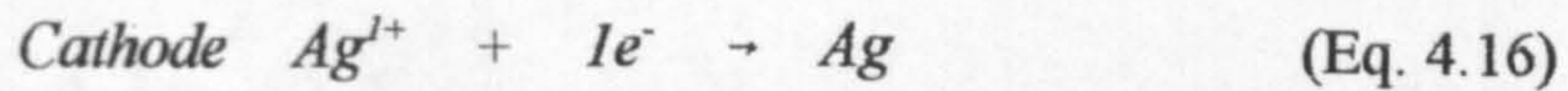
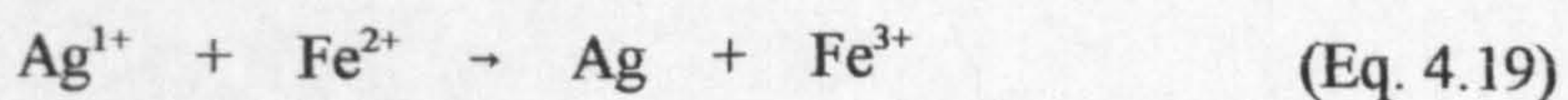


Table 4.12: Graphic Waste Services (Control)					
Reaction Time (min)	Silver Concentration (ppm)				
	Samples				
	A	B	C	D	E
0	7600	3100	1900	20	330
15	4900	2000	480	17	200
30	4000	1100	300	16	180
45	1500	600	160	13	90
60	-	2200	87	12	81
120	40	310	55	7	66
180	210	420	72	6	47
240	250	140	72	4	48

The reduction of silver ions and water molecules on the cathode surface will allow silver to deposit along with the evolution of hydrogen gas and the production of OH<sup>-</sup> ions. The oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup> is taking place at the anode surface. These reactions will allow iron to precipitate as a mixture of Fe(OH)<sub>2</sub> and Fe(OH)<sub>3</sub> from solution. These precipitates are good adsorbents and will adsorb silver bromide from solution.

(2) The presence of Fe<sup>2+</sup> ions in solution along with silver ions, promotes the following reaction to take place:



These two reactions are responsible for the silver ions to precipitate from solution instead of being deposited on the cathode surface. The XRF analyses of the solid obtained at the end of each experiment for each of the different samples are presented in Figure 4.14. The results show that each solid except for sample A, contains silver bromide along with iron impurities. The residue of sample A contains pure silver metal without any iron impurities. This arises because of the high initial silver concentration in solution. This led to a very thick deposit on the cathode surface which was detached from the cathode at the latter stages and during the removal of the cathode at the end of the experiment.

The results obtained in the case of an ion-exchange concentrator system show no improvement (Table 4.13) in silver recovery. The low recovery of silver is attributed to the presence of iron and sodium impurities which compete with silver ions to take over the resin active sites. The percentage recovery of silver from this solution is presented in Figure 4.13.

<b>Reaction Time (min)</b>	<b>Silver Concentration (ppm)</b>				
	<b>Samples</b>				
	<b>A</b>	<b>B</b>	<b>C</b>	<b>D</b>	<b>E</b>
0	7600	3100	1900	20	330
15	3000	2800	900	16	140
30	2100	2400	400	14	80
45	1600	800	110	14	60
60	500	500	110	14	45
120	350	320	110	18	45
180	300	260	90	18	45
240	300	170	80	18	45

With the use of activated carbon cloth, under identical conditions, the recovery of silver compared to a control system had increased [Table 4.14]. This is due to an electrolytic process and an adsorption process occurring at the same time.

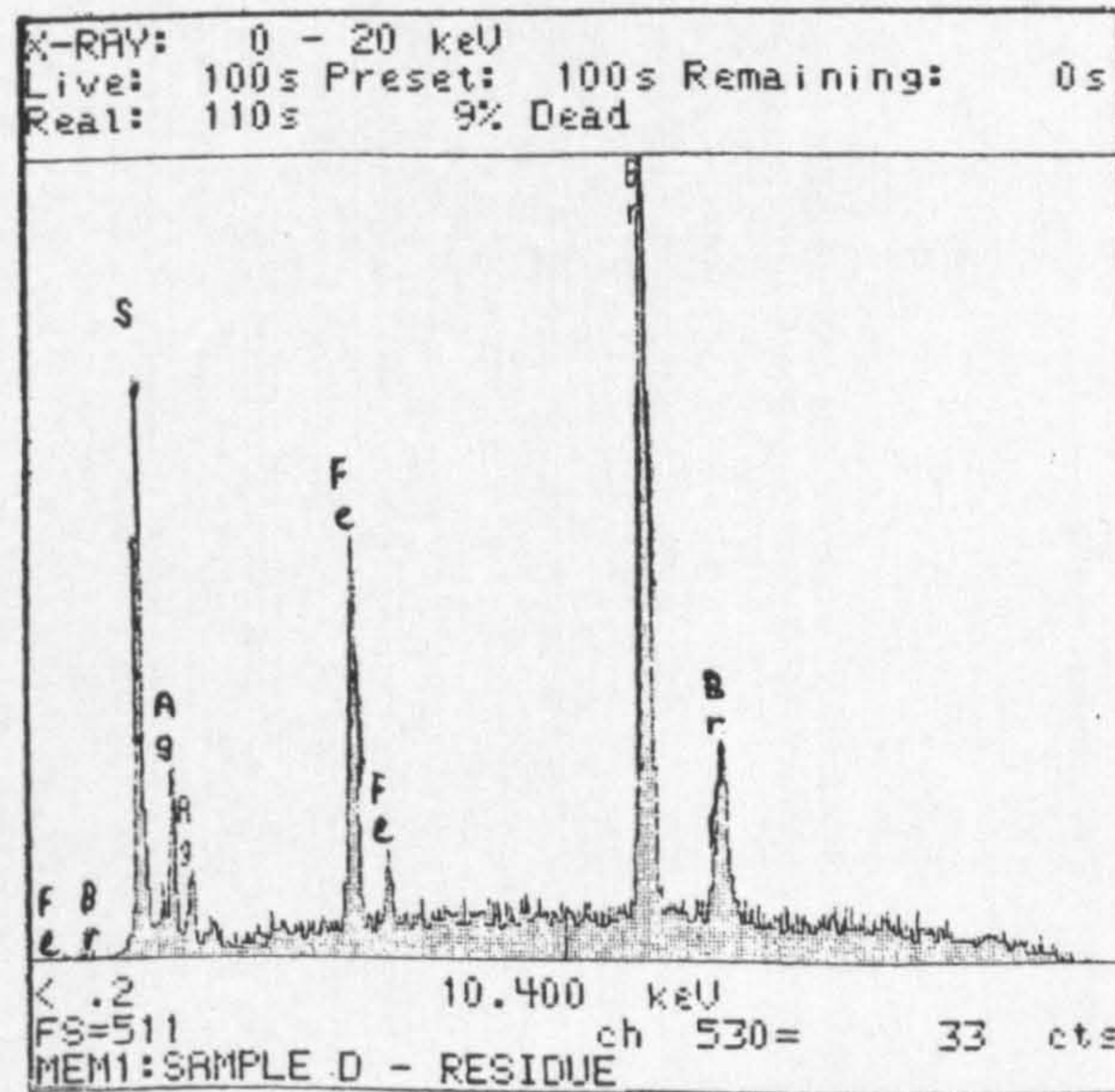
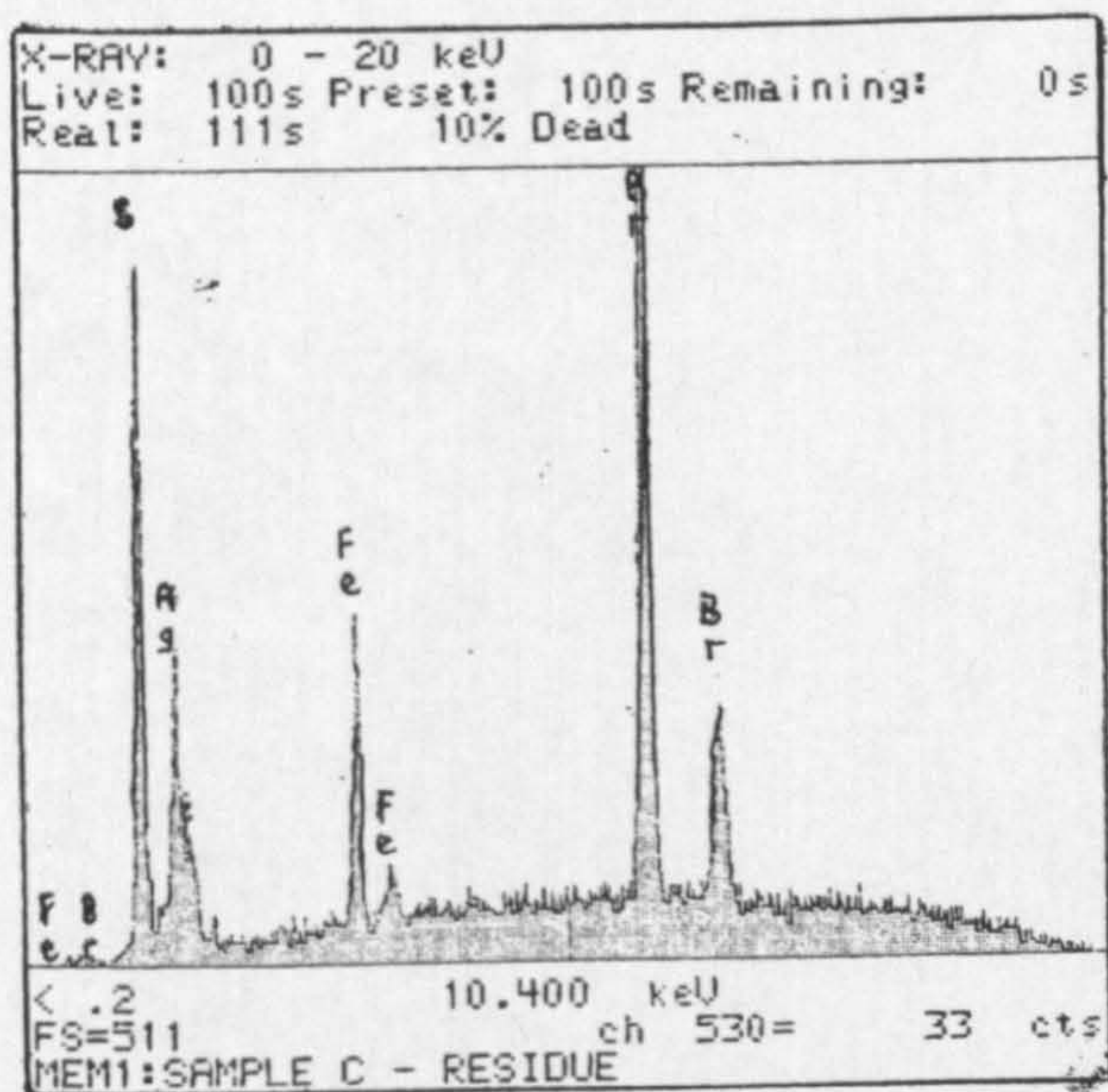
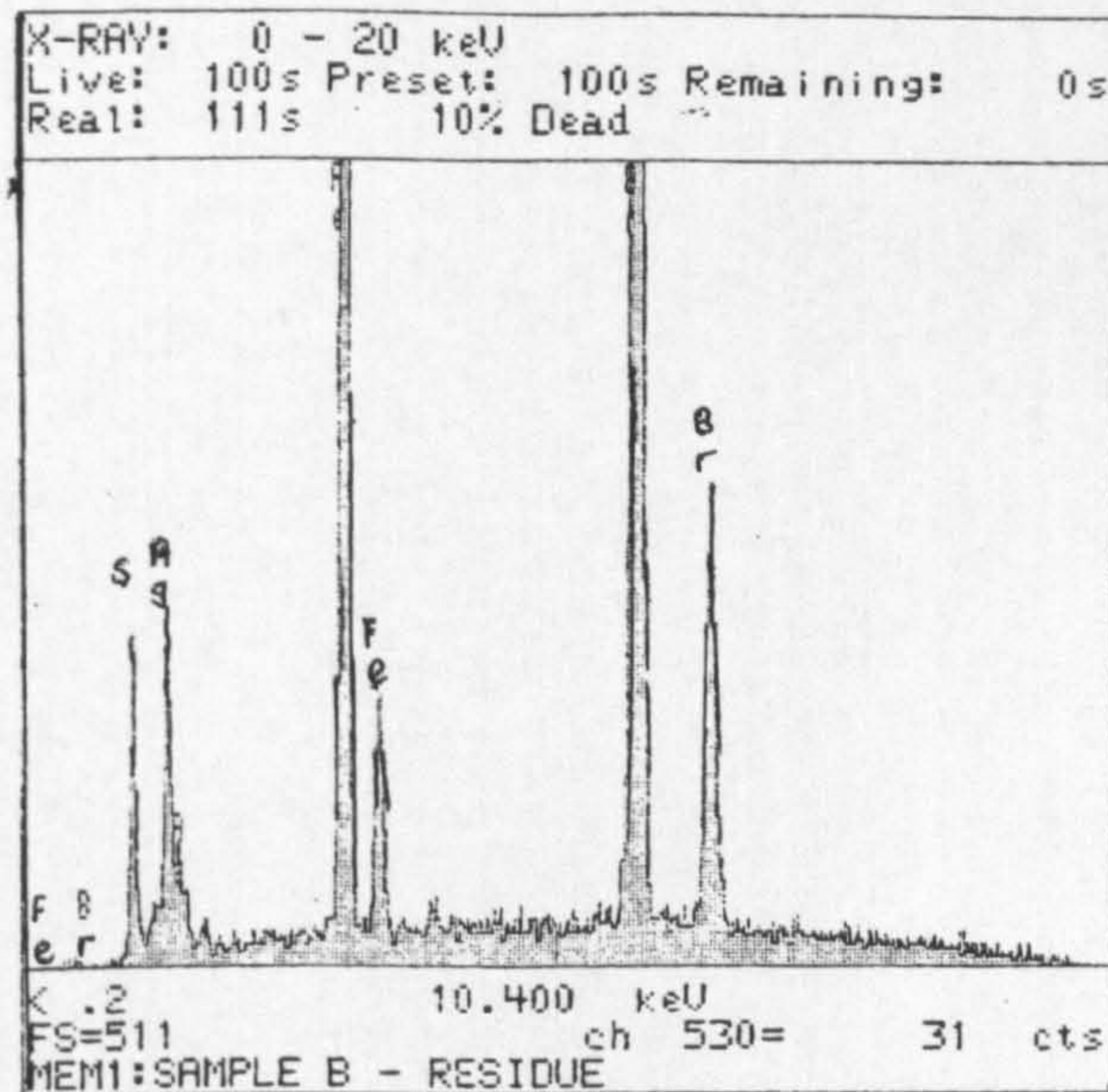
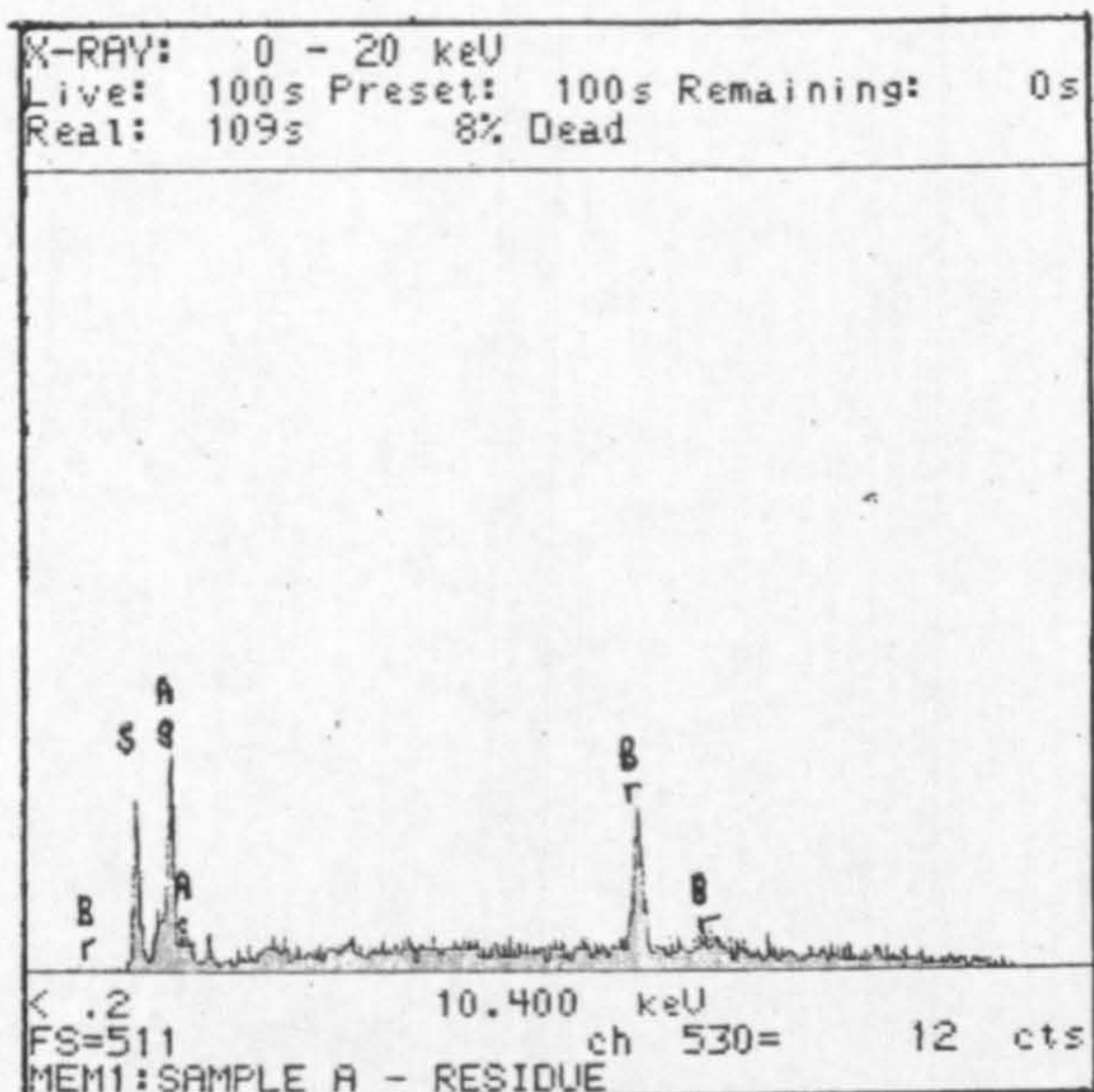


Figure. 4.14 : XRF analyses of silver residues

<b>Table 4.14:- Graphic Waste Services (ACC)</b>					
<b>Reaction Time (min)</b>	<b>Silver Concentration (ppm)</b>				
	<b>Samples</b>				
	<b>A</b>	<b>B</b>	<b>C</b>	<b>D</b>	<b>E</b>
0	7600	3100	1900	20	330
15	5900	2400	1400	12	220
30	5800	2000	1200	10	140
45	5300	1800	1200	4	120
60	4100	1500	1000	3	90
120	1160	1000	900	2	50
180	180	400	700	2	60
240	80	210	700	1	45

#### 4.3.5 Pendar Poole

A second silver containing solution was supplied by Pendar Poole, Dorset, which provided an example of a silver drag-out solution. Three different experiments were conducted. The results for the control set-up were compared with the use of an activated carbon cloth cathode and the use of ion-exchange resins. The results are presented in Tables 4.15 - 4.17.

<b>Table 4.15:- Pendar Poole Silver Sample-Control</b>	
<b>Time (h)</b>	<b>Degree of Purification (%)</b>
0	0
1	95
2	98.5
3	99.6
4	99.9
5	99.96
6	99.98

<b>Time (h)</b>	<b>Degree of Purification (%)</b>
0	0
1	97.4
2	99.7
3	99.8
4	99.9
5	99.97
6	99.98

<b>Time (h)</b>	<b>Degree of Purification (%)</b>
0	0
1	85.7
2	96.1
3	97.8
4	98.4
5	98.9
6	99.6

Since silver has a high positive redox potential, it causes the metal to be reduced very rapidly at the cathode. The results in Tables 4.15 - 4.17, support this showing that the recovery of silver is very rapid even within the first hour of electrolysis when using the different concentrator techniques.

However, looking at the different methods individually, it was calculated that after 1 h of

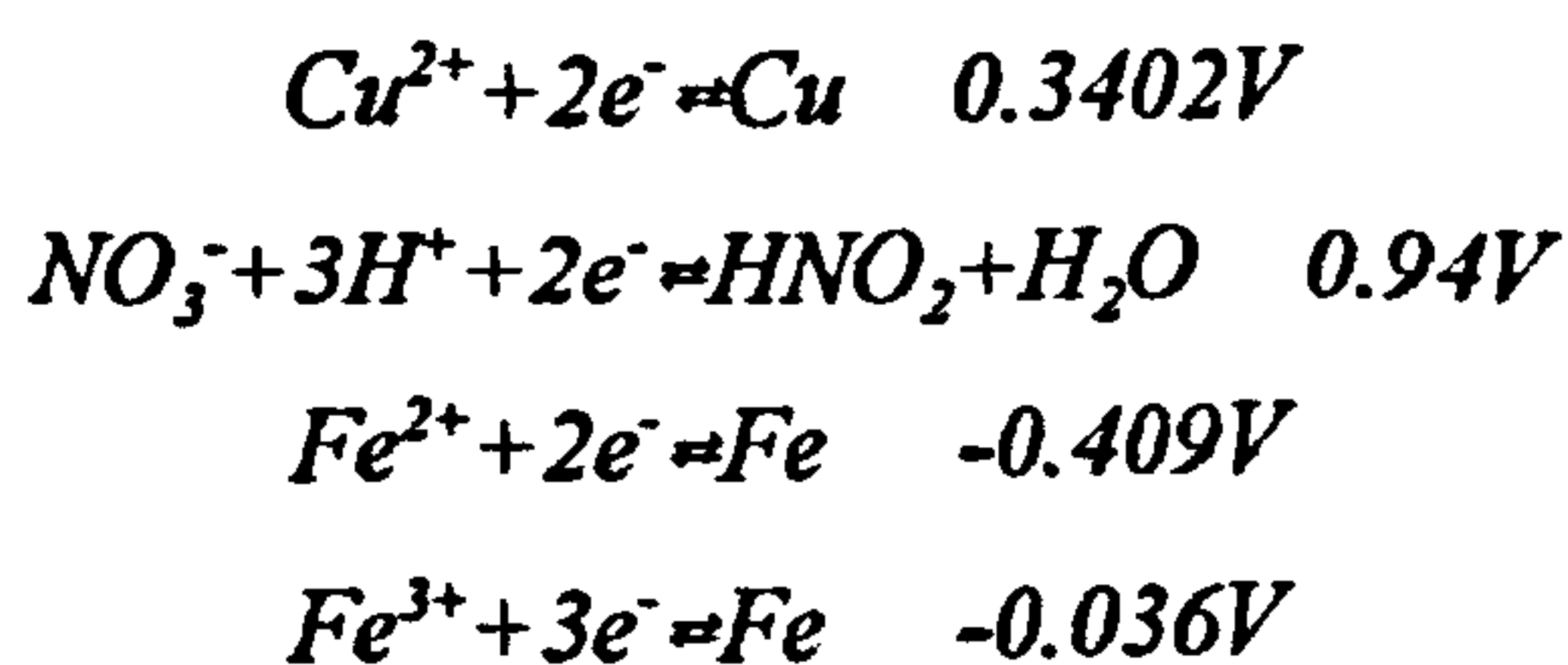
electrolysis the degree of purification achieved with the stainless steel plate cathode and the ion-exchange resins was in excess of 90%. When utilising ACC, the degree of purification was slightly lower at 85.7% after 1 h of electrolysis but this value increased to above 90% within the next hour of the electrolysis period. The results are illustrated in Figure 4.15.

#### 4.3.6 Preminco Industrial Samples

Model solutions containing cobalt, nickel, copper, zinc and iron were prepared according to specifications supplied by Preminco Ltd.

The company is interested in separating metal impurities from cobalt solution to manufacture pure cobalt sulphate. Figure 4.16 represents the present process carried out by Vergi in India for the purification and extraction of cobalt from cobalt bearing residue material of African origin. The removal of iron and copper impurities are carried out by chemical precipitation processes with a total cobalt loss of 30-35% during these two stages. The cobalt purification process was divided into three steps. The first step involved the recovery of copper using a standard electrolytic method.

The Vergi process is based on the leaching of metal values using a strong sulphuric and nitric acid media at an elevated temperature. The presence of nitrate ions along with  $Fe^{2+}$  (ferrous) ions inhibits the removal of copper and iron in a single stage using an electrochemical process. The relevant cathodic electrochemical reactions can be simplified as:



The more positive electrode potential favours the cathodic reaction to occur. These reactions show that nitrate ions are reduced more easily than ferrous and ferric ions. The presence of nitrate and ferrous ions inhibits the co-deposition of copper and iron.

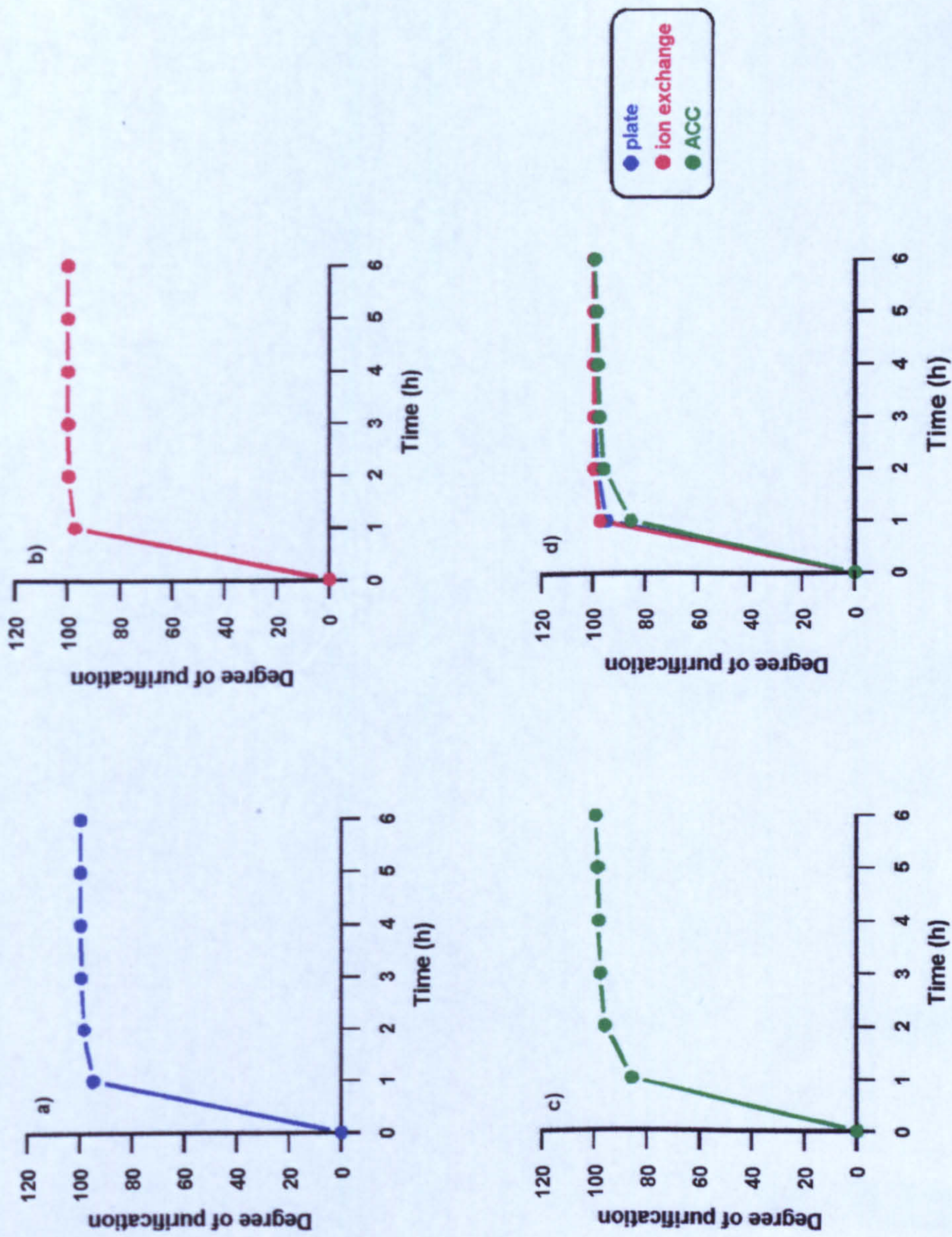
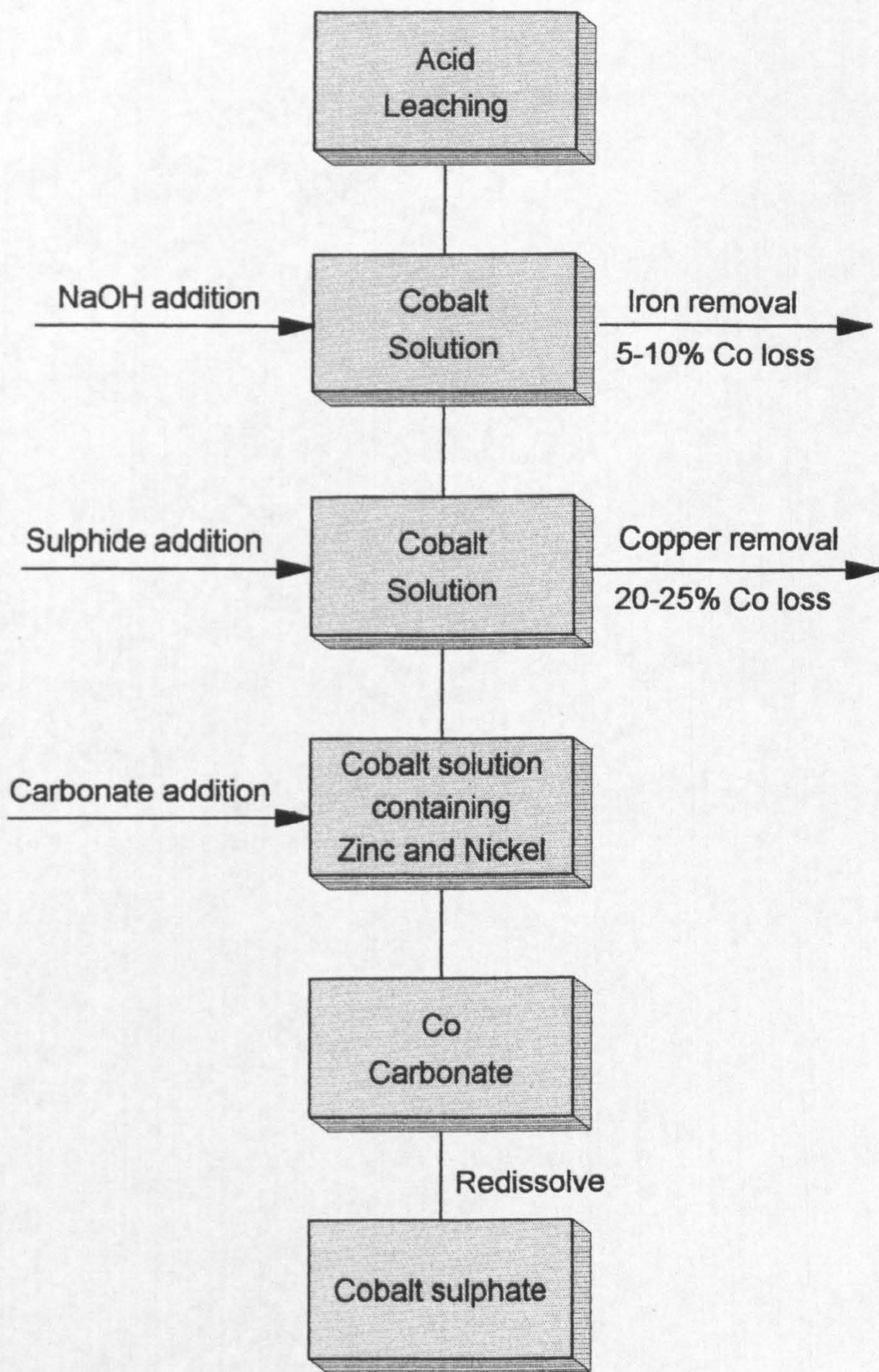


Figure 4.15:- Recovery of Ag from Pendar Pool sample using plate, ion exchange and ACC. Graph d) shows a comparison between the three systems used.



**Figure. 4.16: Current Vergi process for cobalt purification and extraction**



The cobalt leach solution obtained using the existing process at Preminco has the desired conditions for the recovery of copper from rich cobalt solution using an electrolytic process with no loss of cobalt. A single step removal of iron and copper is not possible because of the presence of ferrous and nitrate ions.

A set of experiments designed to achieve a single stage recovery of Cu and Fe by oxidation of ferrous to ferric ions prior to electrolysis was carried out. The results obtained show that 15 and 25% oxidation is achieved using 100 ml/L of 30 and 60% hydrogen peroxide respectively. The decrease in metal ion concentrations during the electrolytic process is presented in Tables 4.18 and 4.19 for solution without oxidation and after oxidation with 60% hydrogen peroxide.

The results obtained show that a standard electrochemical cell can be used to remove copper impurities to a residual concentration of 0.5 ppm corresponding to 99.1% removal.

The optimum conditions for copper recovery using an electrolytic process are:

Cell current	= 1.5A
Cell voltage	= 2.4V
Temperature	= ambient
Solution pH	= acidic solution (0.9 - 1.5)
Cathode material	= stainless steel plate
Anode material	= mixed metal oxide mesh
Cathode surface area	= 0.01 m <sup>2</sup>
Current density	= 150 Am <sup>-2</sup>

During this stage the removal of iron impurities depends on the oxidation state. No removal of iron impurities was achieved in the case of ferrous ions using an electrolytic process and a second stage (hydroxide precipitation) is necessary to remove these impurities (Table 4.18).

In the case of ferric ions, 99.1% copper and 30% iron can be removed using an electrolytic process (Table 4.19). The XRF analyses of the recovered copper from solution containing

ferrous ions show that a pure copper metal deposit is achieved which can be processed further to prepare chemicals [Figure 4.17].

<b>Table 4.18: Purification of cobalt solution containing ferrous ions</b>					
Reaction time (h)	<b>Recovery of copper - electrolytic process</b>				
	Concentration of metal ions (ppm)				
	Cobalt	Nickel	Zinc	Iron	Copper
0	20,000	1000	1000	500	500
6	20,000	1000	1000	500	0.5

<b>Table 4.19: Purification of cobalt solution after the addition of hydrogen peroxide</b>					
Reaction time (h)	<b>Recovery of copper and iron - electrolytic process</b>				
	Concentration of metal ions (ppm)				
	Cobalt	Nickel	Zinc	Iron	Copper
0	20,000	1000	1000	500	500
6	20,000	1000	1000	350	0.6

#### ***Removal of iron impurities using a hydroxide precipitation method***

The removal of iron impurities was carried out by adjusting the pH of the solution between 3-4 with sodium hydroxide. The XRF analysis of the hydroxide precipitate is presented in Figure 4.18(b). To ensure the complete removal of iron impurities with minimum cobalt loss it is recommended that the precipitation should be carried out with continuous air agitation and with the addition of small aliquots of sodium hydroxide.

#### ***Recovery of cobalt using an electrolytic process***

The remaining solution which contained cobalt, nickel and zinc was electrolysed to recover cobalt. After iron removal in the previous stage, it is necessary that the pH of the solution be kept constant (4-5) for the recovery of cobalt. The advantage of using this process instead of carbonate precipitation is that cobalt can be recovered as metal with a minimum level of zinc

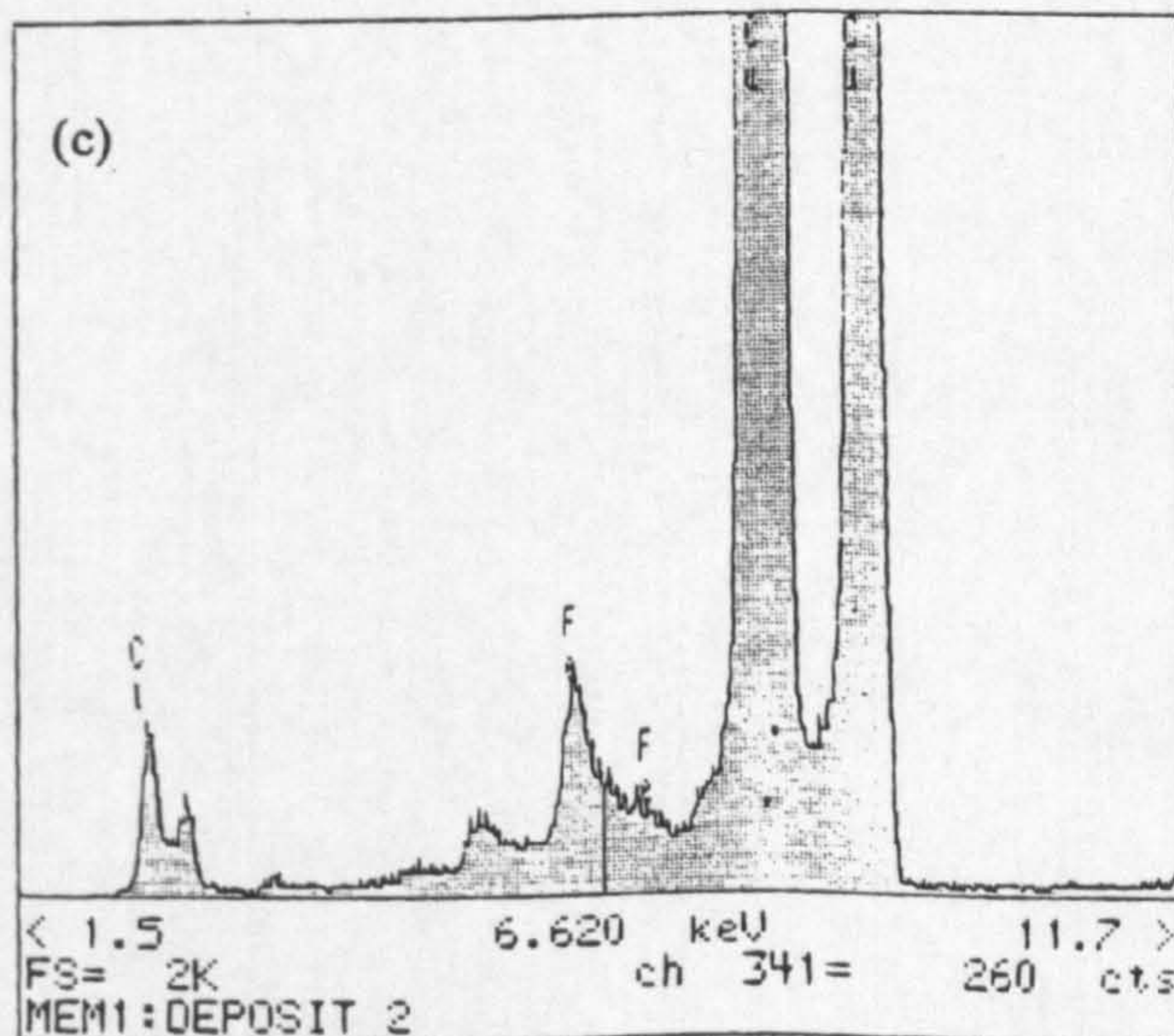
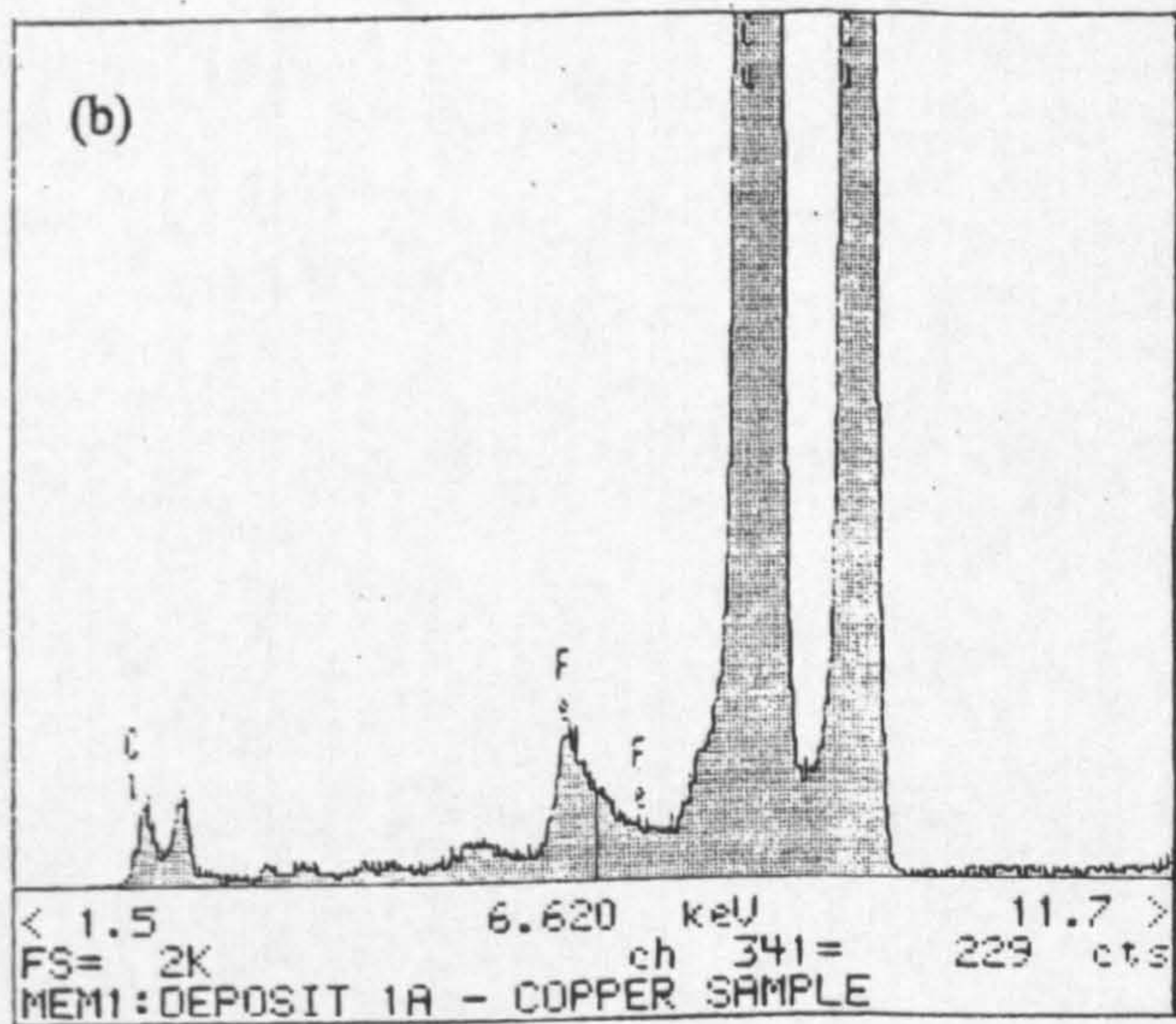
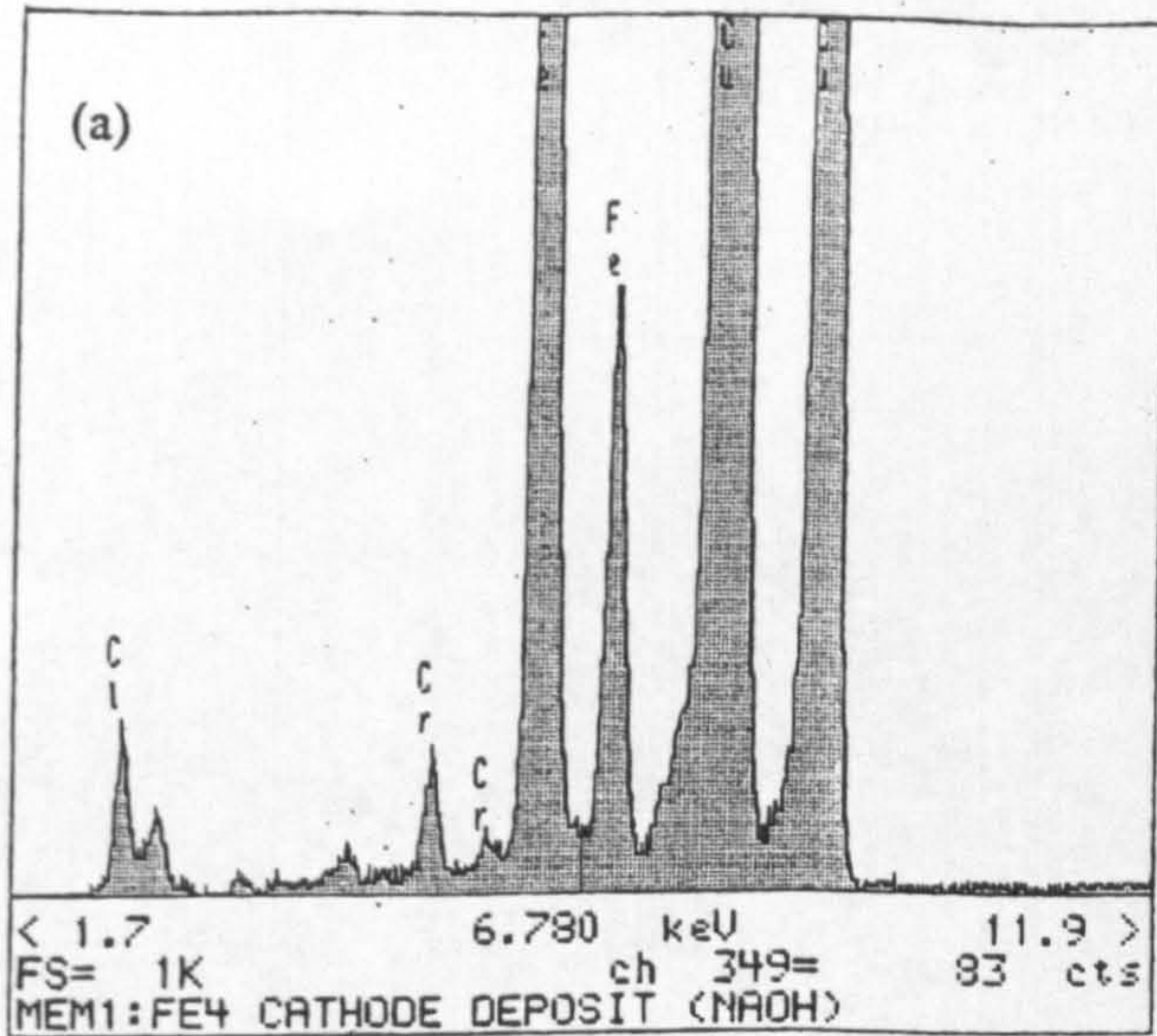


Figure.4.17: XRF analyses of a) first stage cathodic deposit - impure copper b) residue powder - pure copper and c) second stage cathodic deposit - pure copper

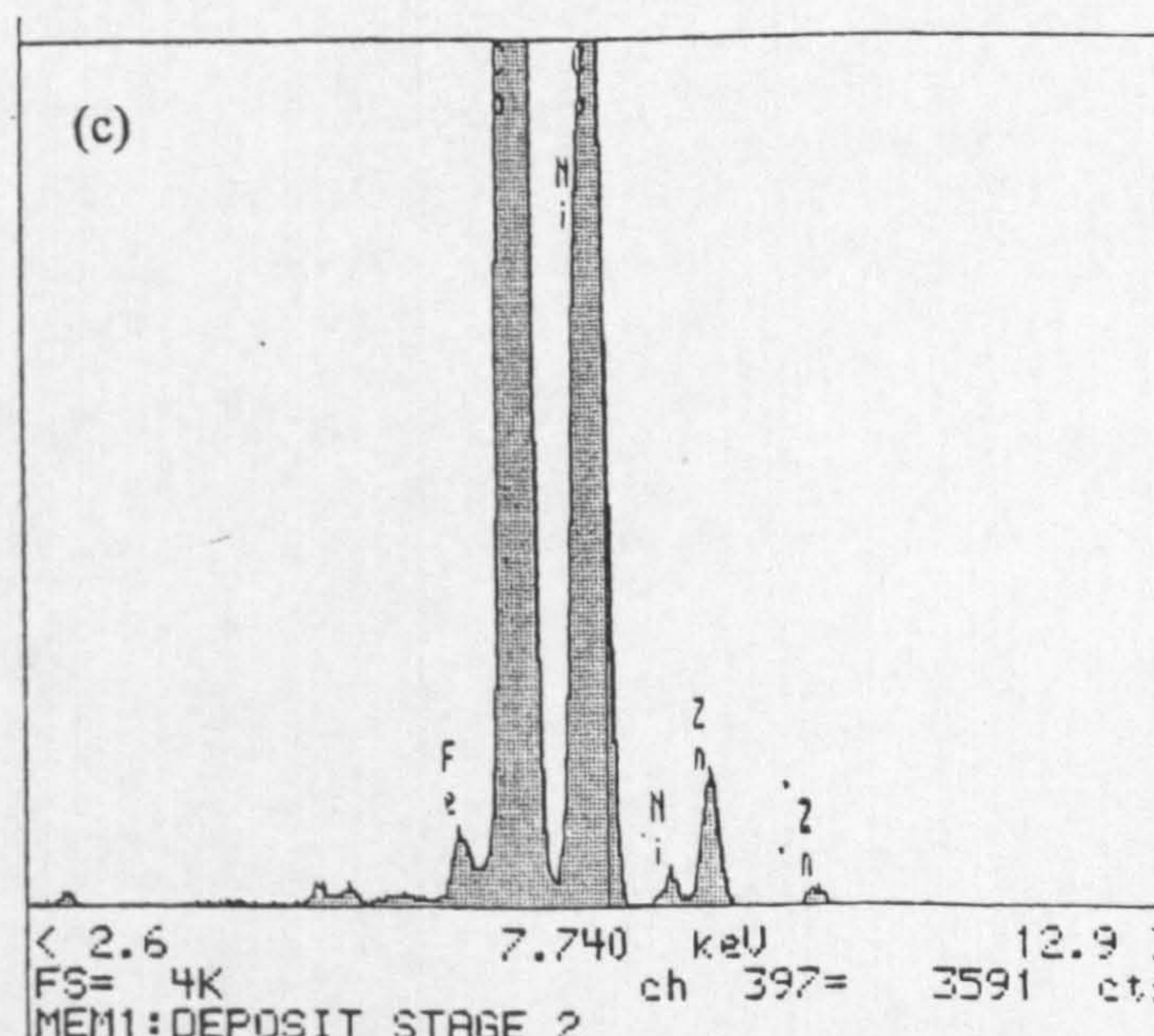
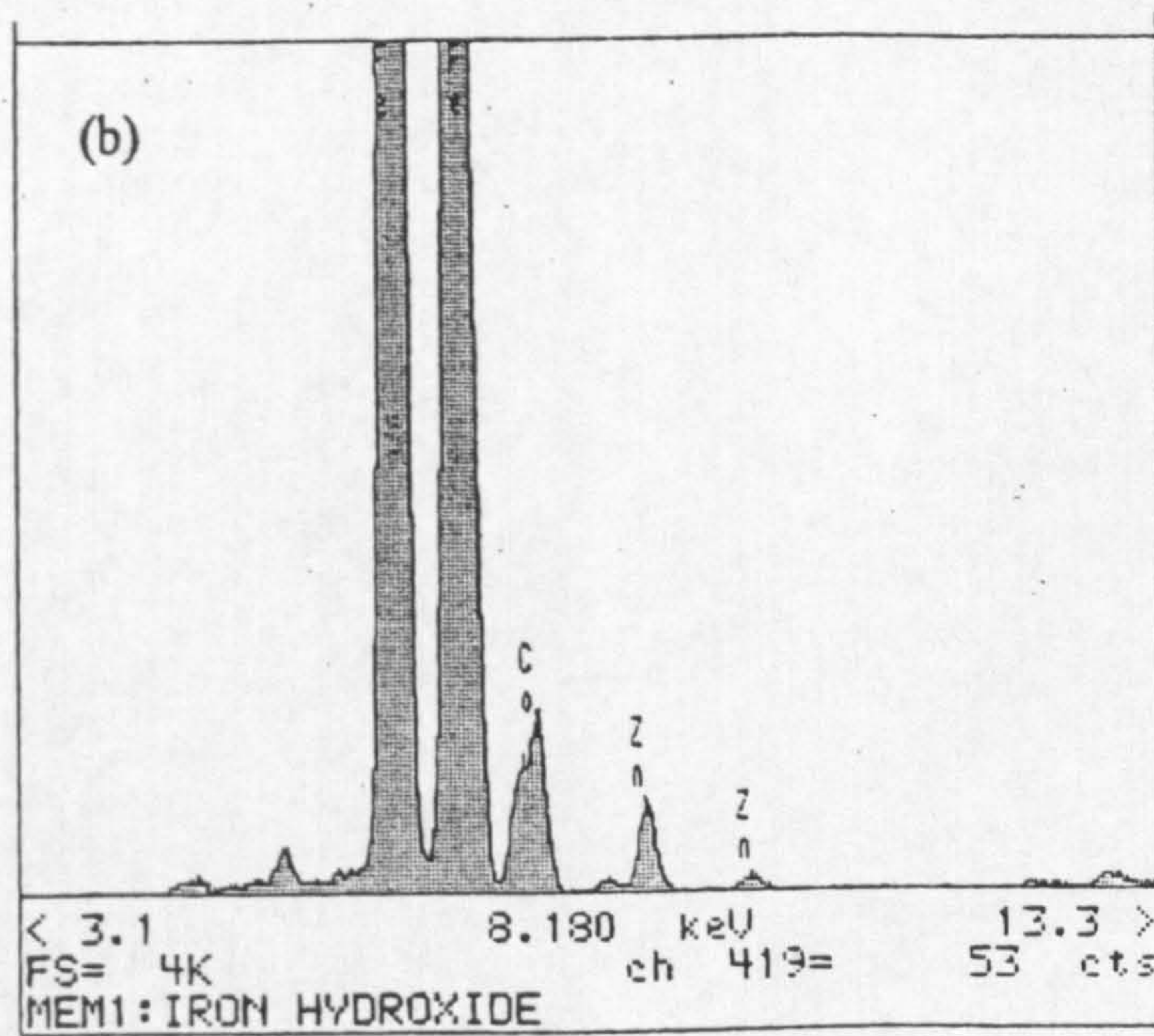
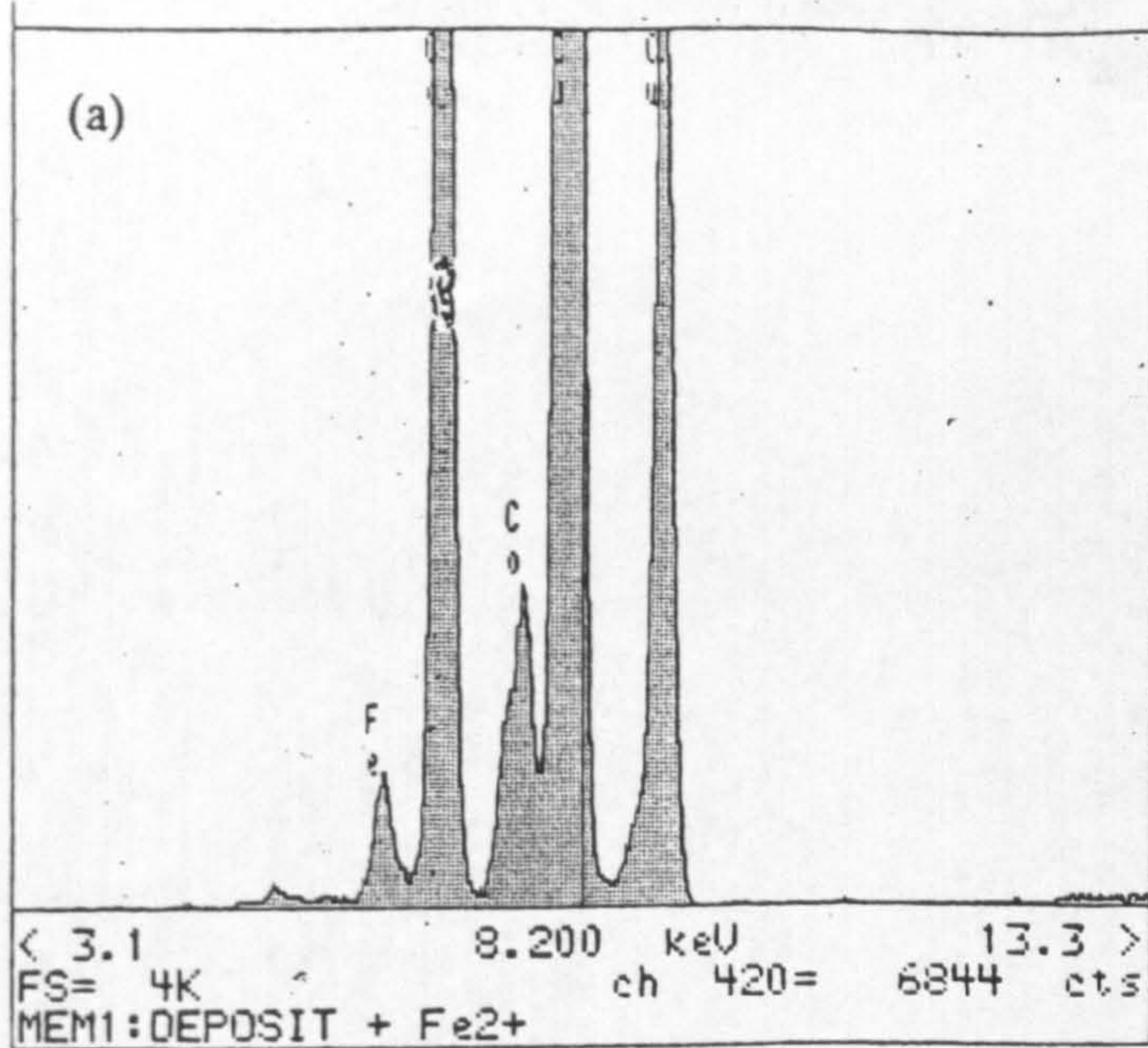


Figure. 4.18: XRF analyses of a) copper - first stage b) iron hydroxide precipitates - second stage and c) cobalt third stage

and nickel contamination. In the case of the Vergi process, a carbonate precipitation method will recover cobalt along with all the nickel and zinc impurities. The recovered cobalt can be used to prepare cobalt sulphate along with other added-value chemicals. The XRF analyses of the recovered cobalt are in Figures 4.18(c) and 4.19(b).

#### ***Separation of zinc with Diethylhexylphosphoric acid (DEHPA)***

The solution obtained after the recovery of copper using an electrolytic process and the removal of iron with hydroxide precipitation was used for the separation of zinc impurities with DEHPA/kerosine (1:1 ratio) mixture. The results are presented in Table 4.20. Preliminary results obtained show that 93% separation of zinc can be achieved and this value can be increased under optimum conditions. The complete stripping of zinc from Zn-DEHPA complex was achieved using 20% sulphuric acid. After zinc stripping DEHPA can be recycled during the process.

<b>Table 4.20: Separation of zinc impurities using DEHPA solvent extraction process</b>		
Zinc concentration (ppm)		
Zn concentration in cobalt solution	Zinc concentration after DEHPA extraction	Zinc concentration in stripping acid
1000	70	930

#### **4.3.7 Ferric Etching Solution**

The preliminary experiment involving recovery of copper without pretreatment destroyed the stainless steel cathode; this was attributed to the etching ability of the ferric chloride solution.

A four-stage recovery process was developed and the results are now described.

#### ***Stage 1 - Removal of bulk iron and chromium***

The removal of iron and chromium was achieved using hydroxide precipitation method. The pH of the solution was adjusted to 3.5 - 4.0 and the precipitates were filtered. The XRF analysis of the precipitates are in Figure 4.20(b). The results show that at this stage some of the copper, nickel and zinc are co-precipitated along with iron and chromium.

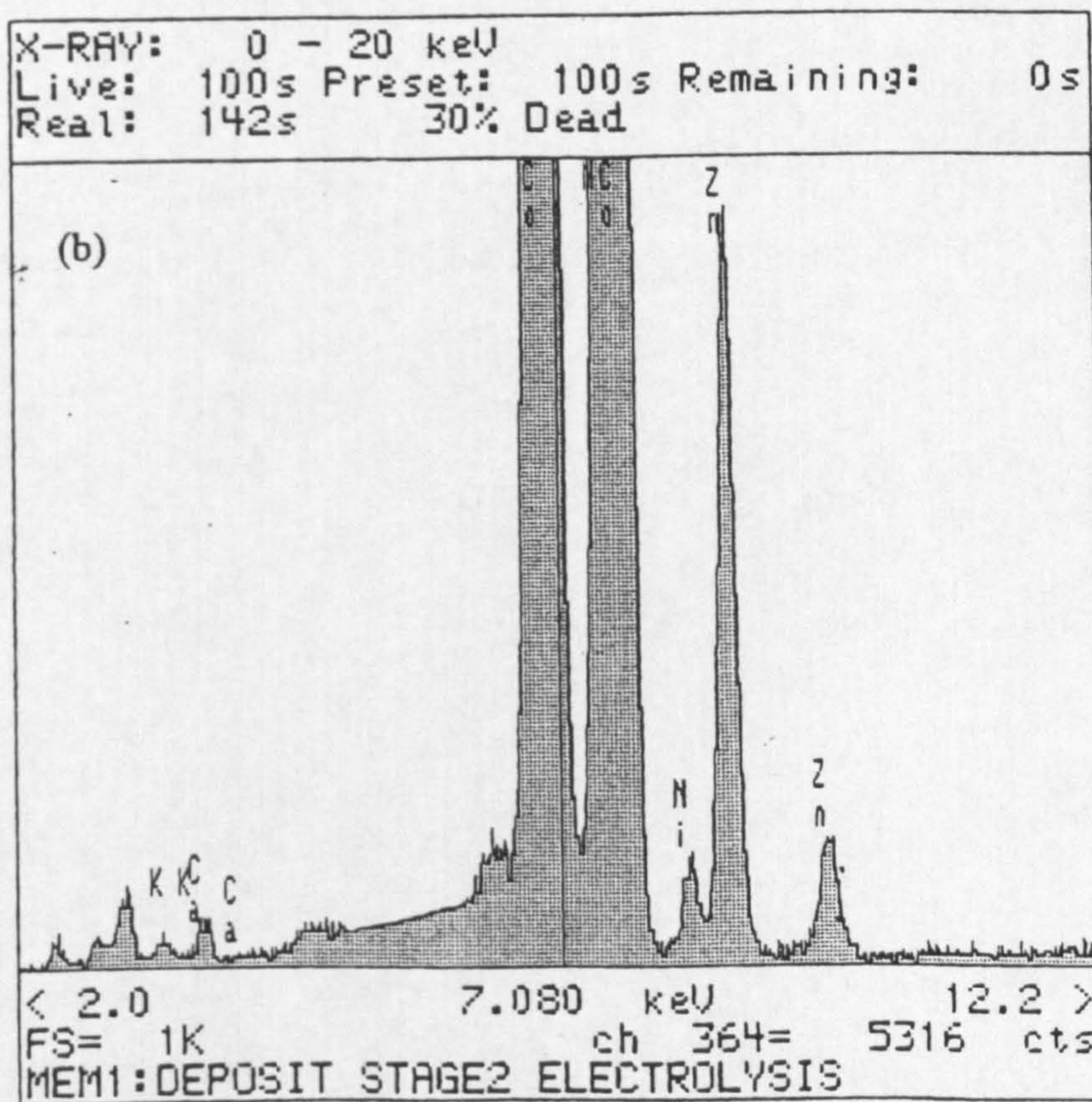
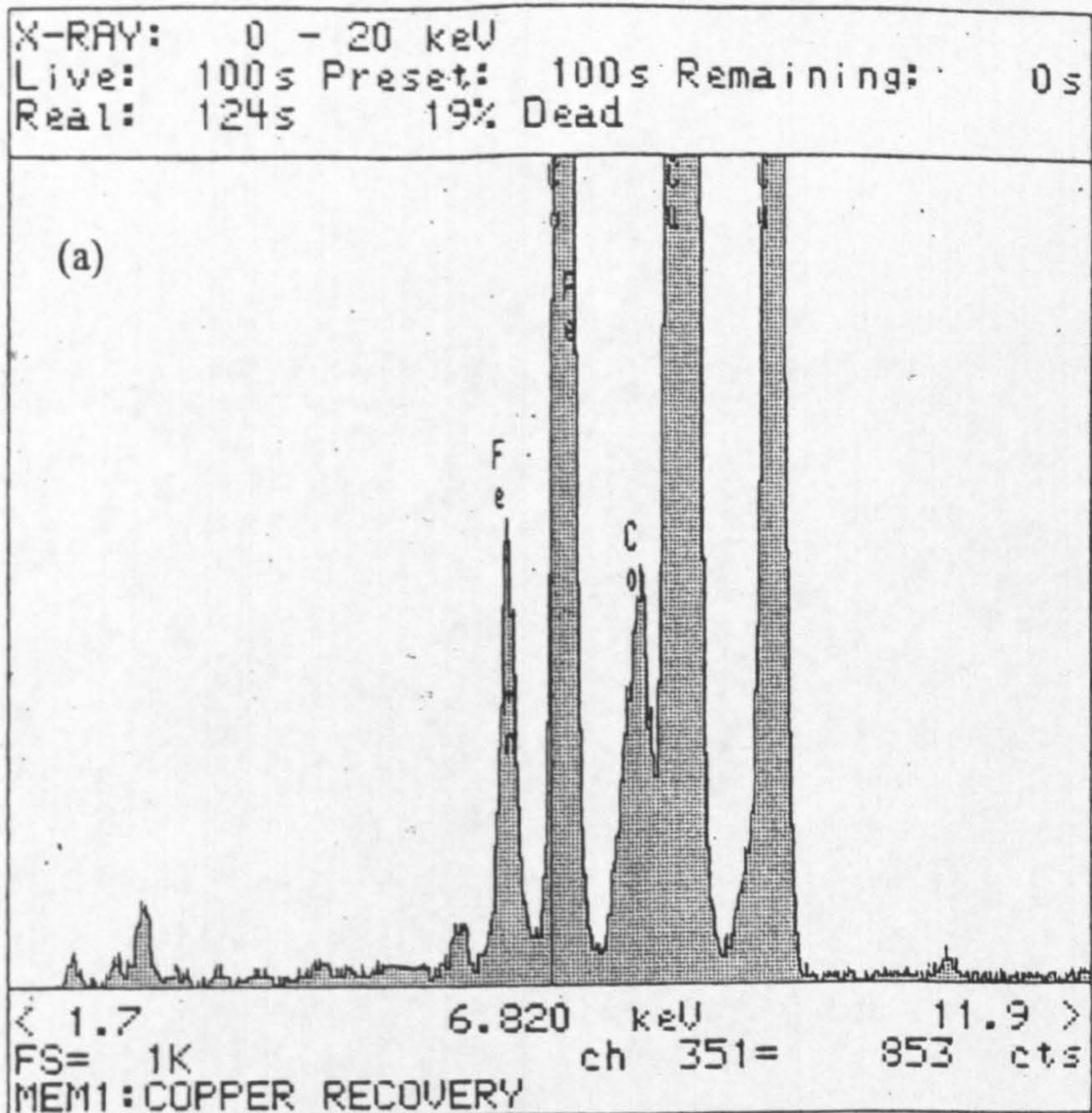


Figure. 4.19: XRF analyses of a) recovered copper and b) recovered cobalt from an industrial sample 169

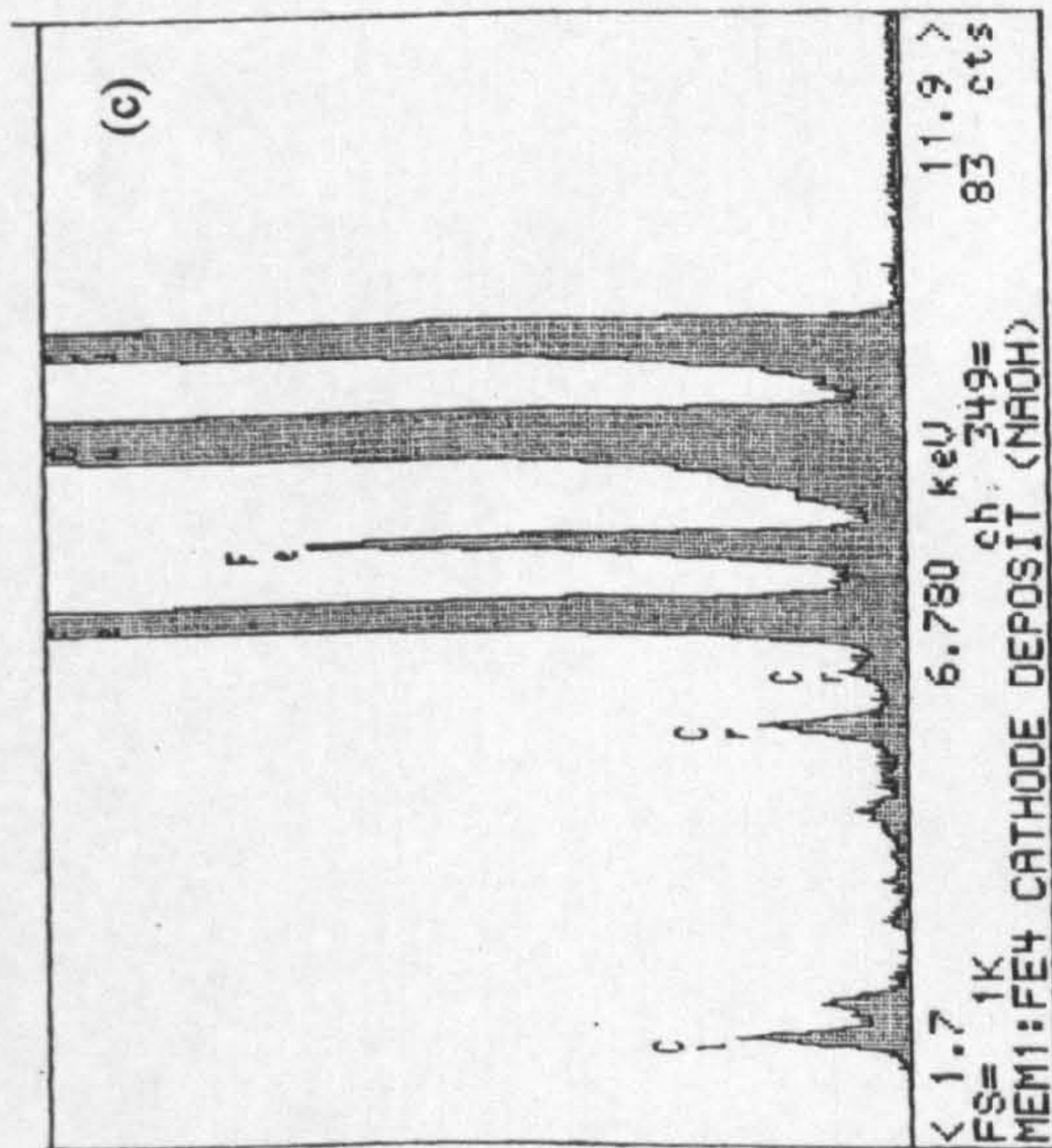
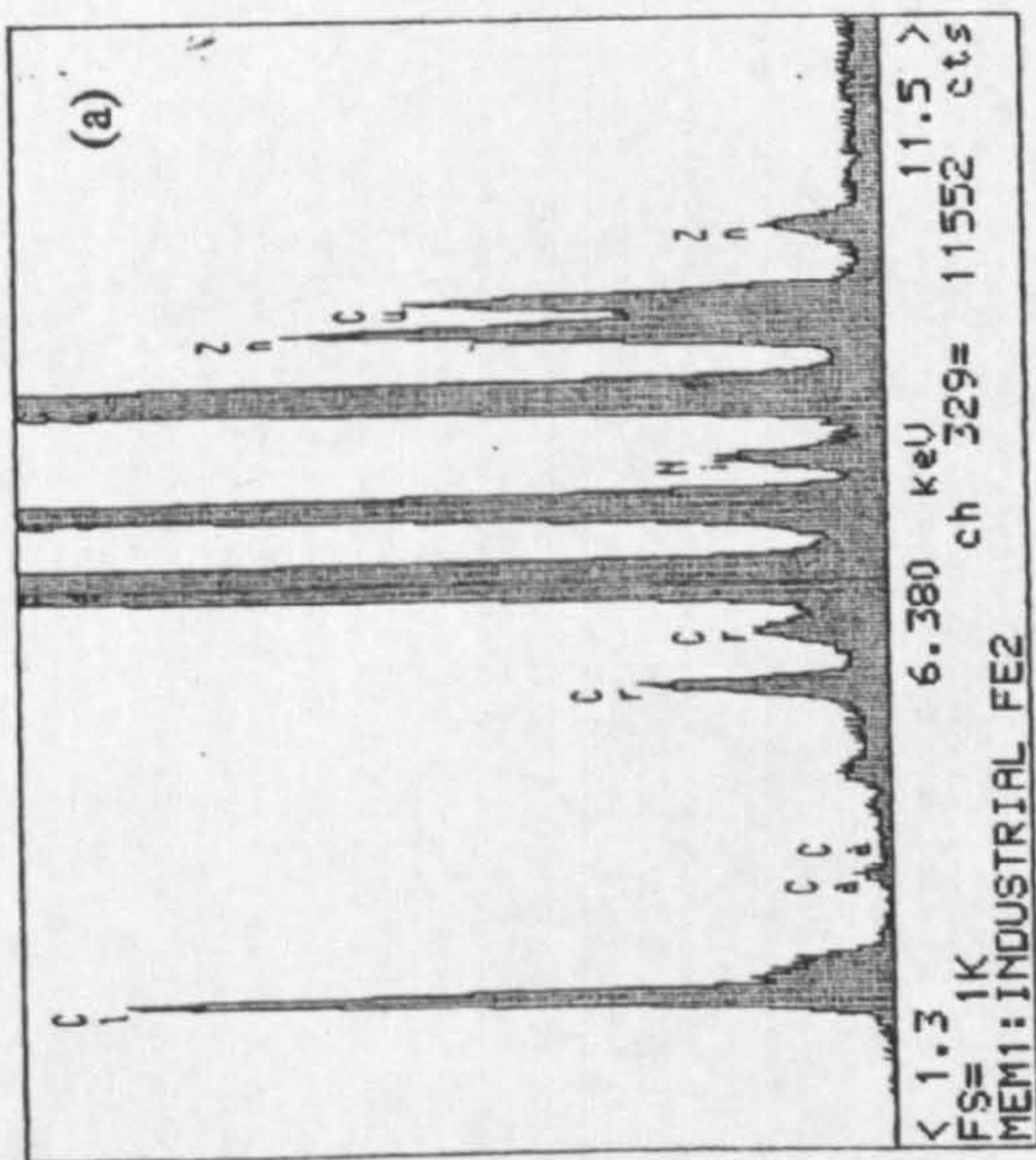
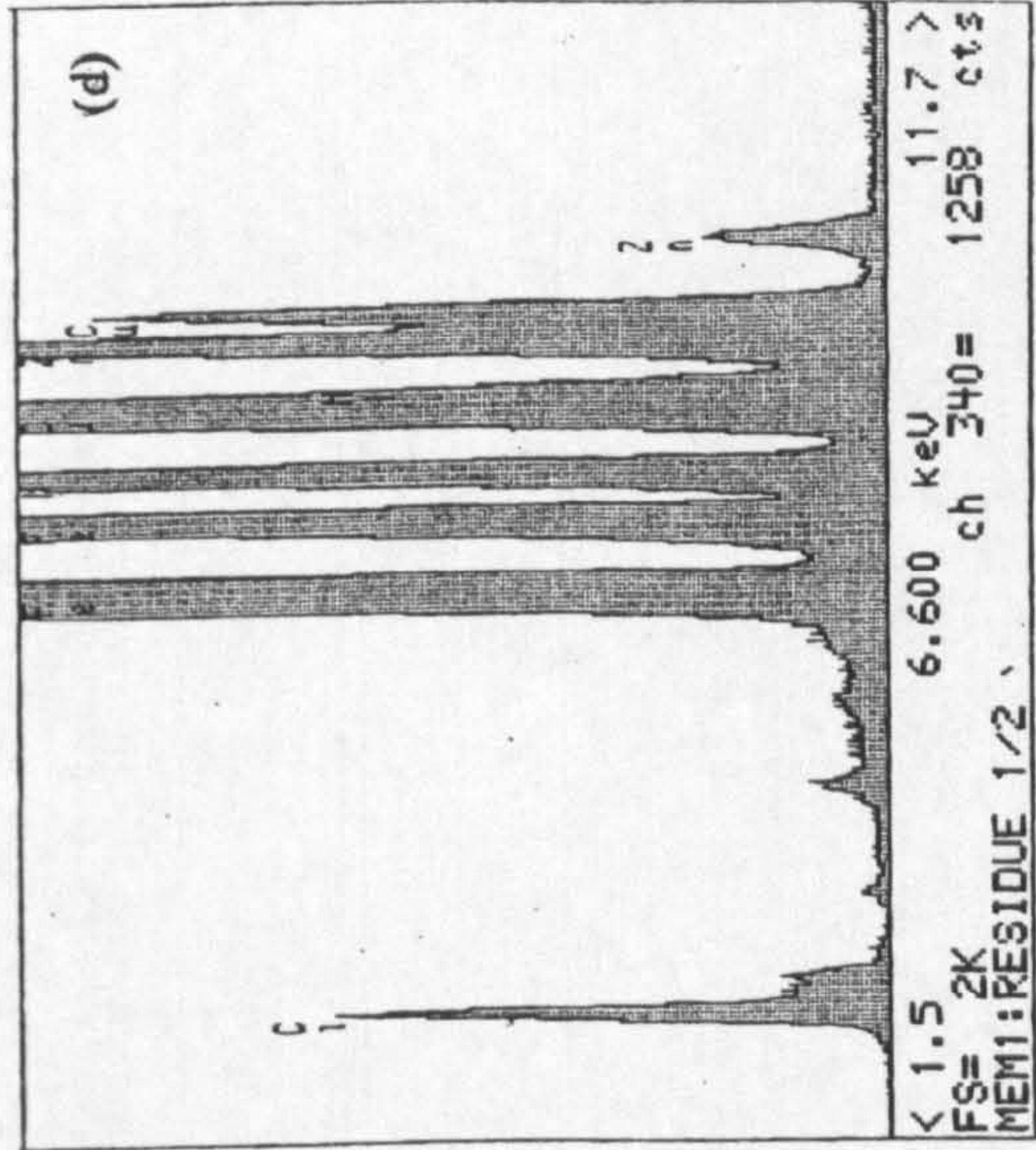
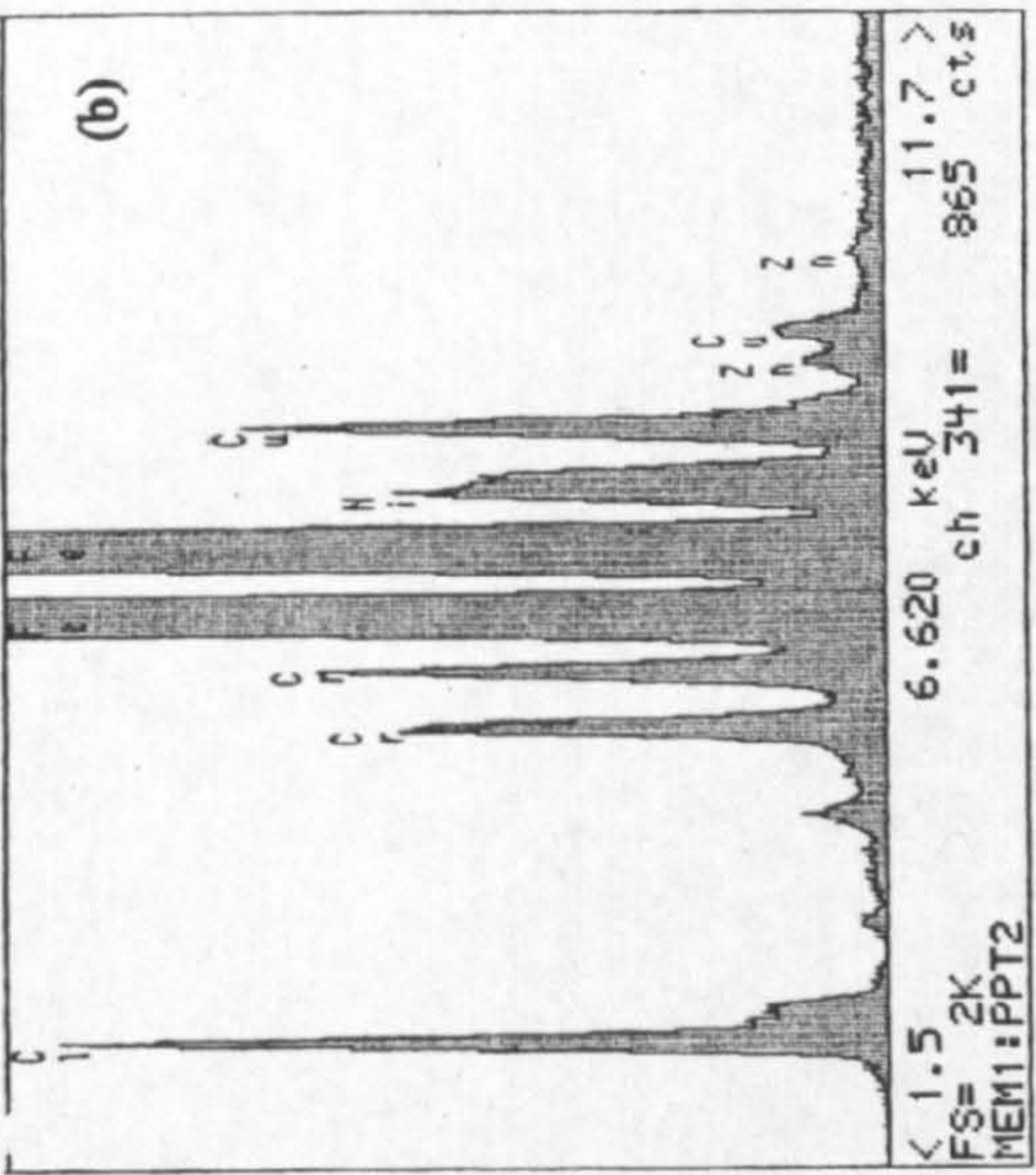


Figure 4.20: XRF analyses of a) as-supplied sample b) removal of bulk iron impurities c) cathodic deposit (copper) and d) *in-situ* production of iron hydroxide

### ***Stage 2 - Recovery of copper using electrolytic process***

The pH of the filtrate obtained from stage 1 was adjusted to 1.5 with hydrochloric acid and a standard electrolytic process was used for the recovery of copper. During the electrolytic process copper is being deposited on the cathode surface along with the production of iron hydroxide precipitates. These hydroxide precipitates are collected at the bottom of the electrolytic chamber. The XRF analyses of these hydroxide precipitates [Figure 4.20(a)] show that the precipitates act as an adsorbent and adsorb copper, nickel and zinc from solution. The cathodic deposit is also contaminated with iron impurities [Figure 4.20(c)]. During this stage approximately 99% of copper was recovered with minimum iron impurities which can be removed to obtain pure copper.

### ***Stage 3 - Removal of remaining iron and chromium***

The removal of remaining iron and chromium impurities was achieved by adjusting the pH of the solution between 3 and 4 with sodium hydroxide. The XRF analysis of these precipitates show that during this stage there is minimal loss of nickel and zinc [Figure 4.21(a)].

### ***Stage 4 - Recovery of nickel and zinc***

Again, the electrolytic process was used to recover nickel and zinc on the cathode surface. During the process the remaining iron ions are being precipitated which are responsible for a minimum loss of nickel and zinc [Figure 4.21(b)]. The XRF analysis of the cathodic deposit shows that the recovered nickel and zinc has low levels of iron impurities [Figure 4.21(c)]. Atomic absorption and the XRF analyses of the final effluent show no metal ions in solution which is indicative of total metal recovery [Figure 4.21(d)].

### ***Purification of copper deposit***

Figure 4.22 shows the schematic flow chart for the purification of copper deposit obtained at the first stage of the process. The cathodic deposit was dissolved in 0.1M HCl. All of the iron hydroxide along with minimum copper is dissolved at this stage. Solid - liquid separation was achieved by decantation. The XRF analyses of the solid and the cathodic deposit show only trace levels of iron impurities [Figure 4.23].



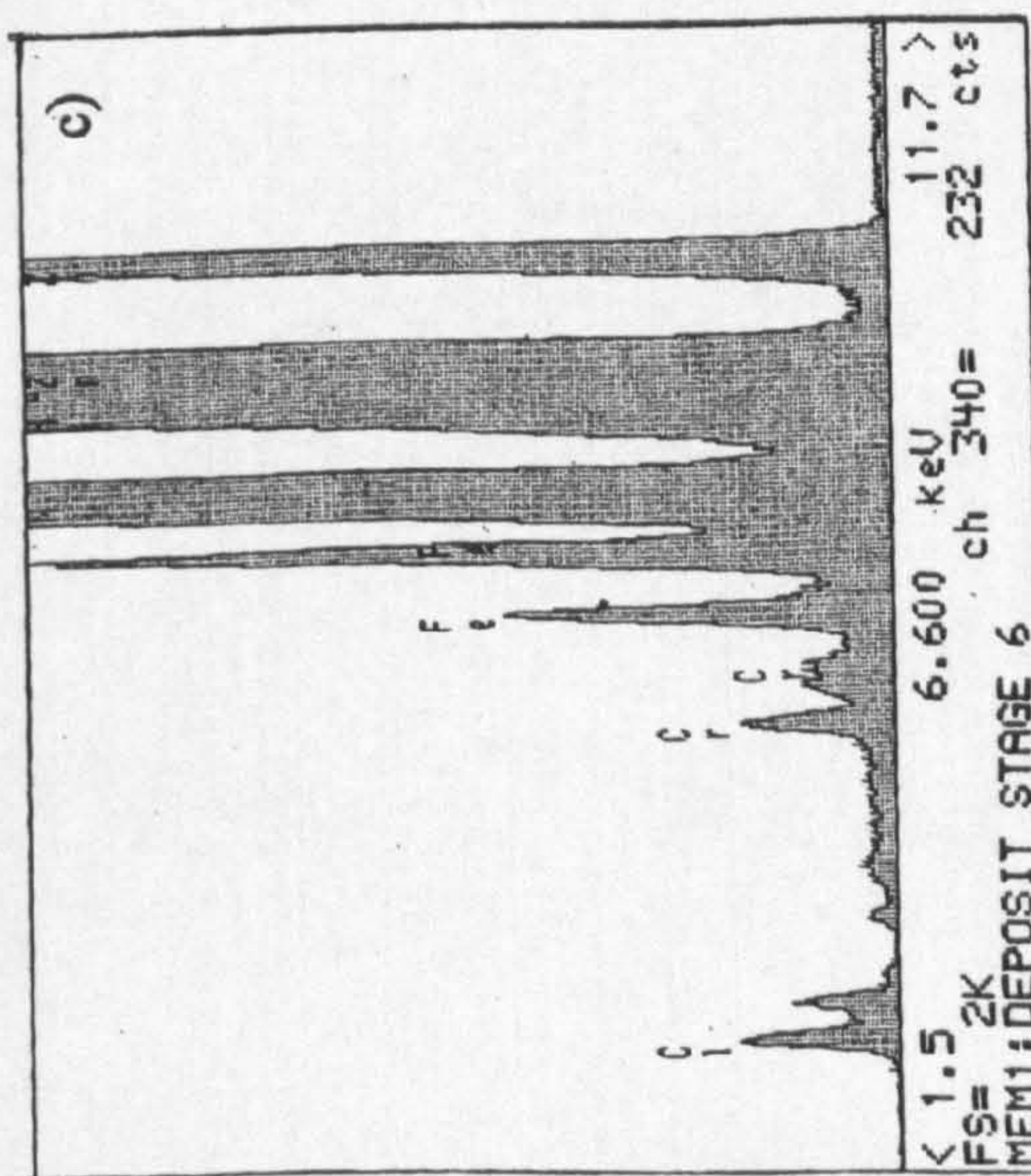
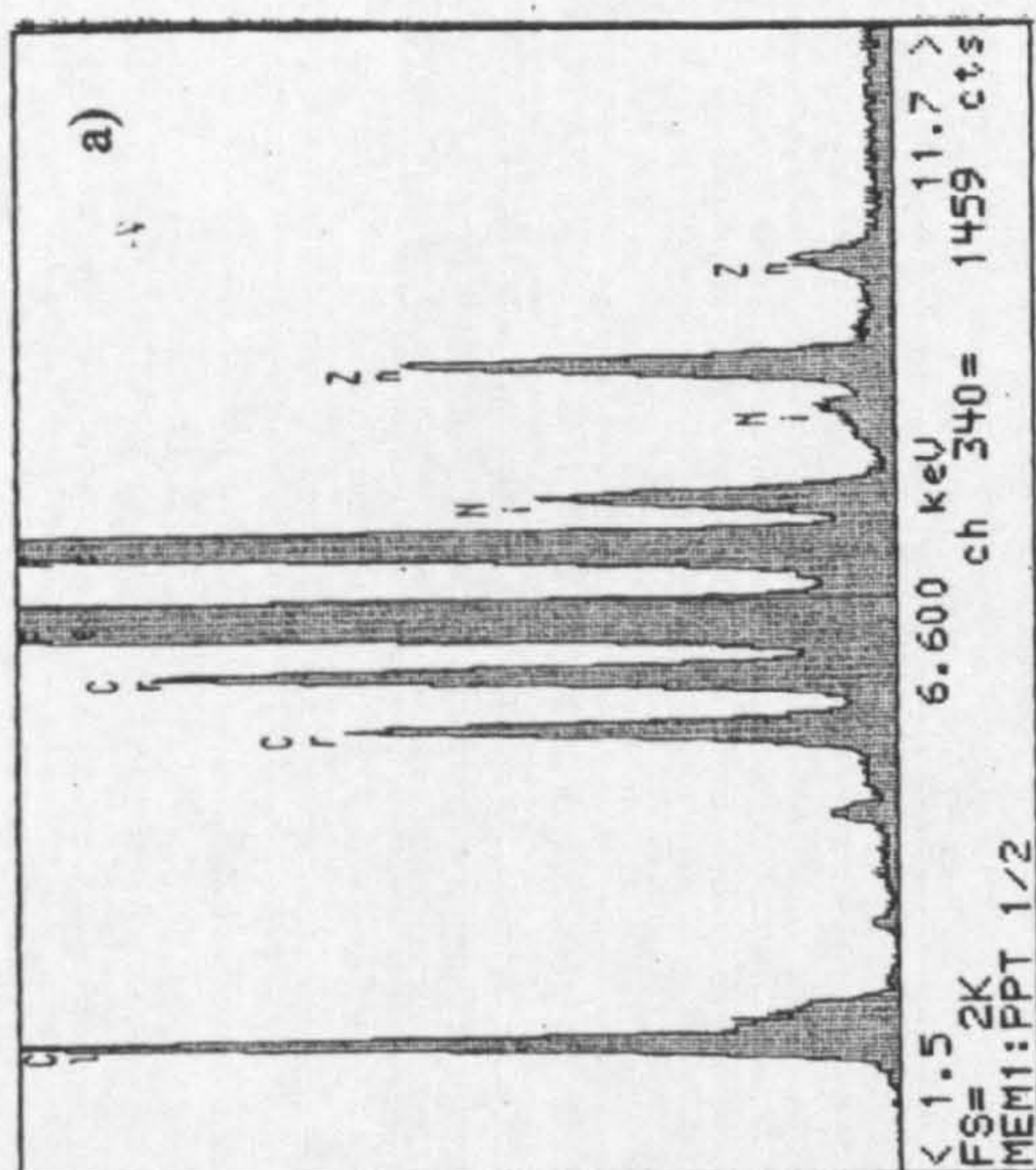
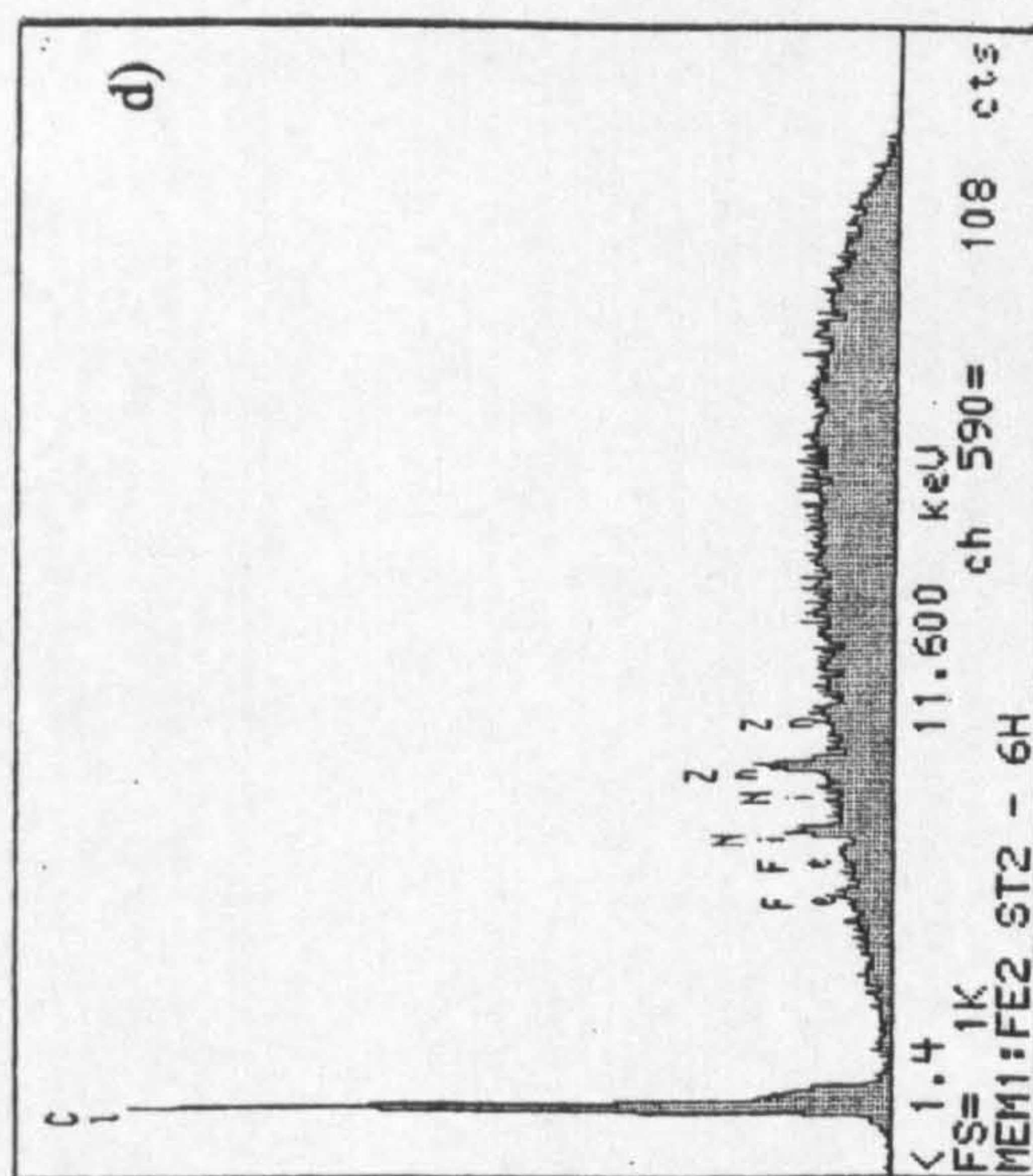
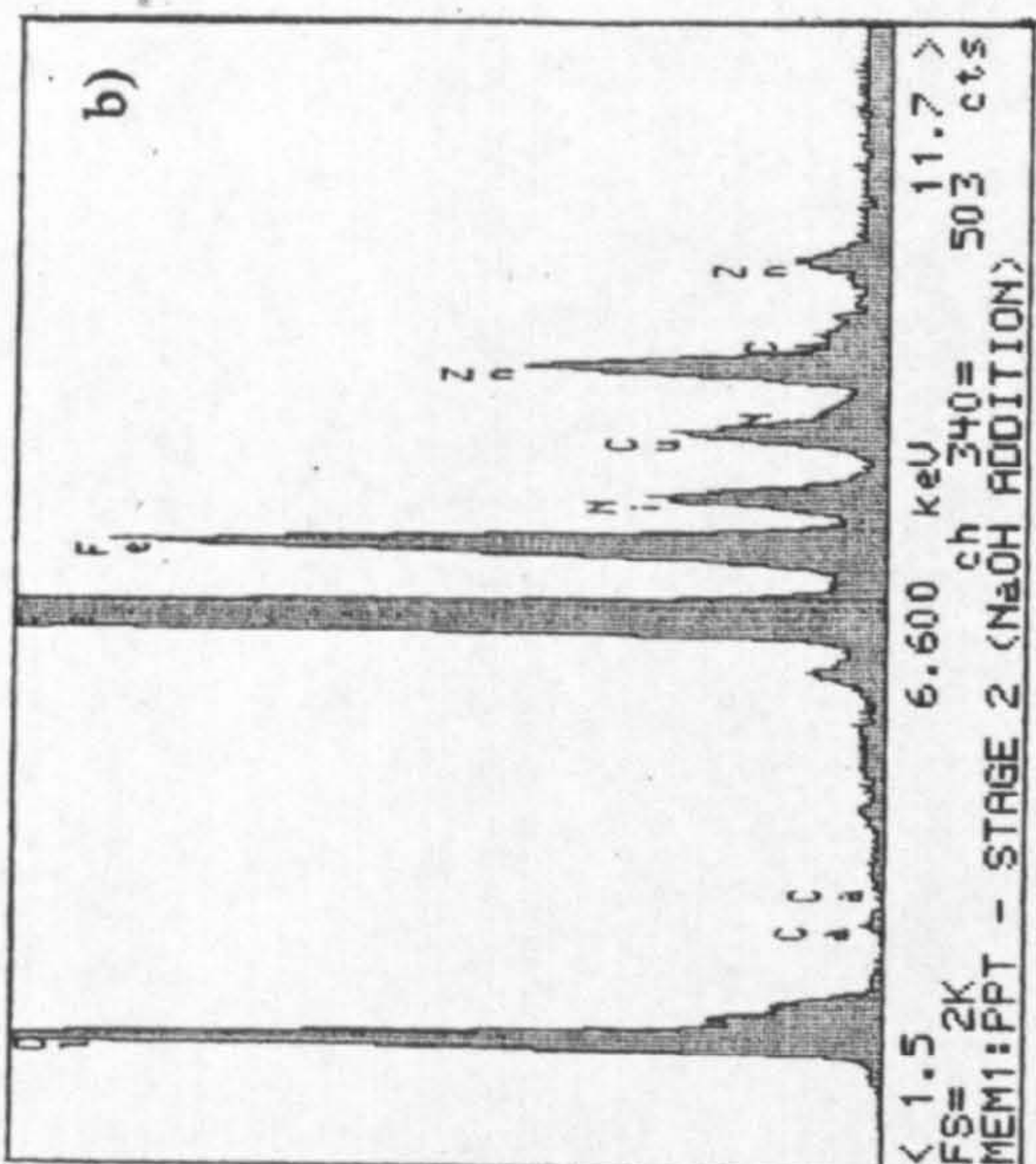


Figure 4.21: XRF analyses of a) removal of remaining iron impurities b) *in-situ* production of iron hydroxide c) cathodic deposit (Ni, Zn) and d) treated solution

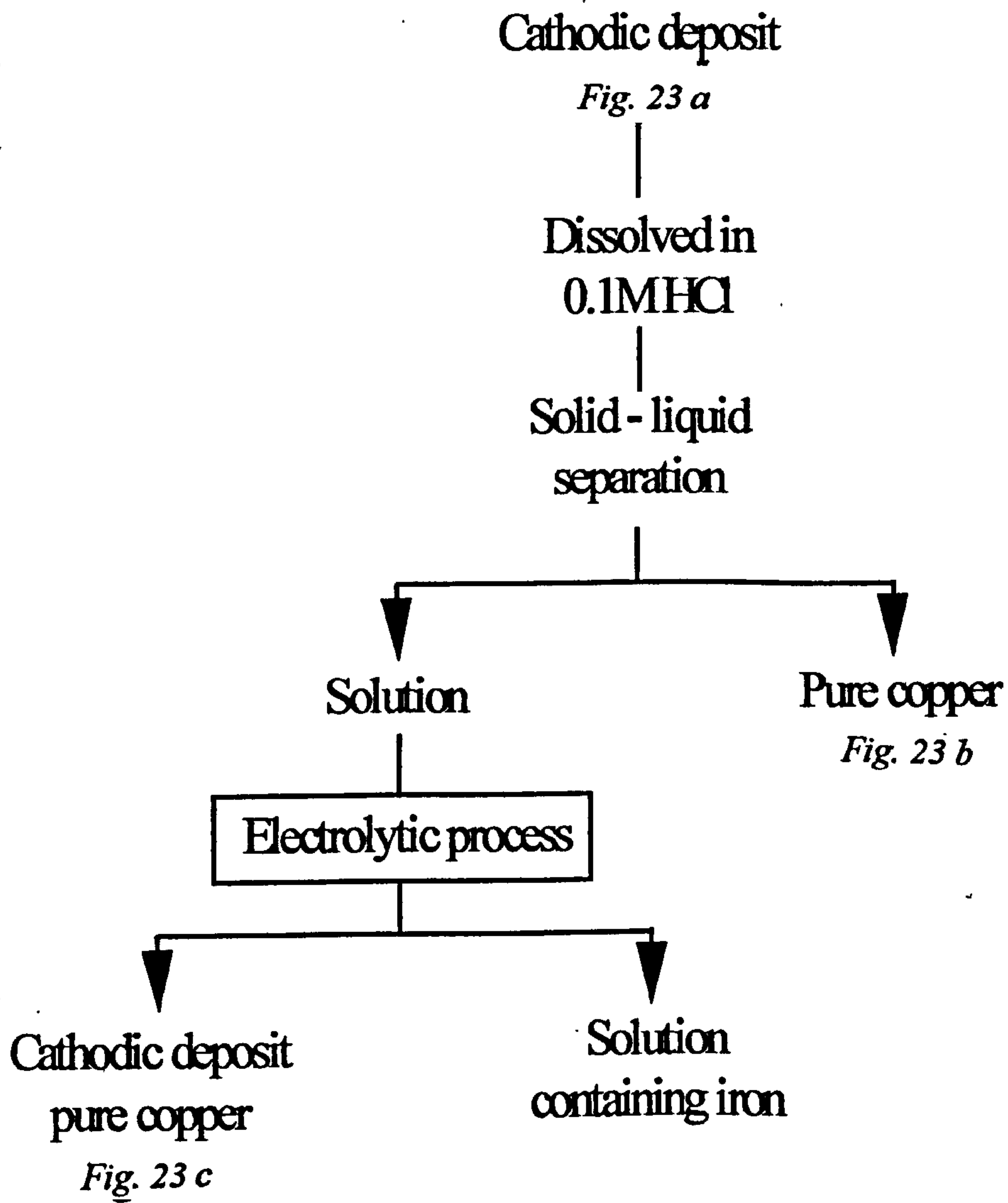


Figure. 4.22:- Purification of cathodic deposit to recover pure copper

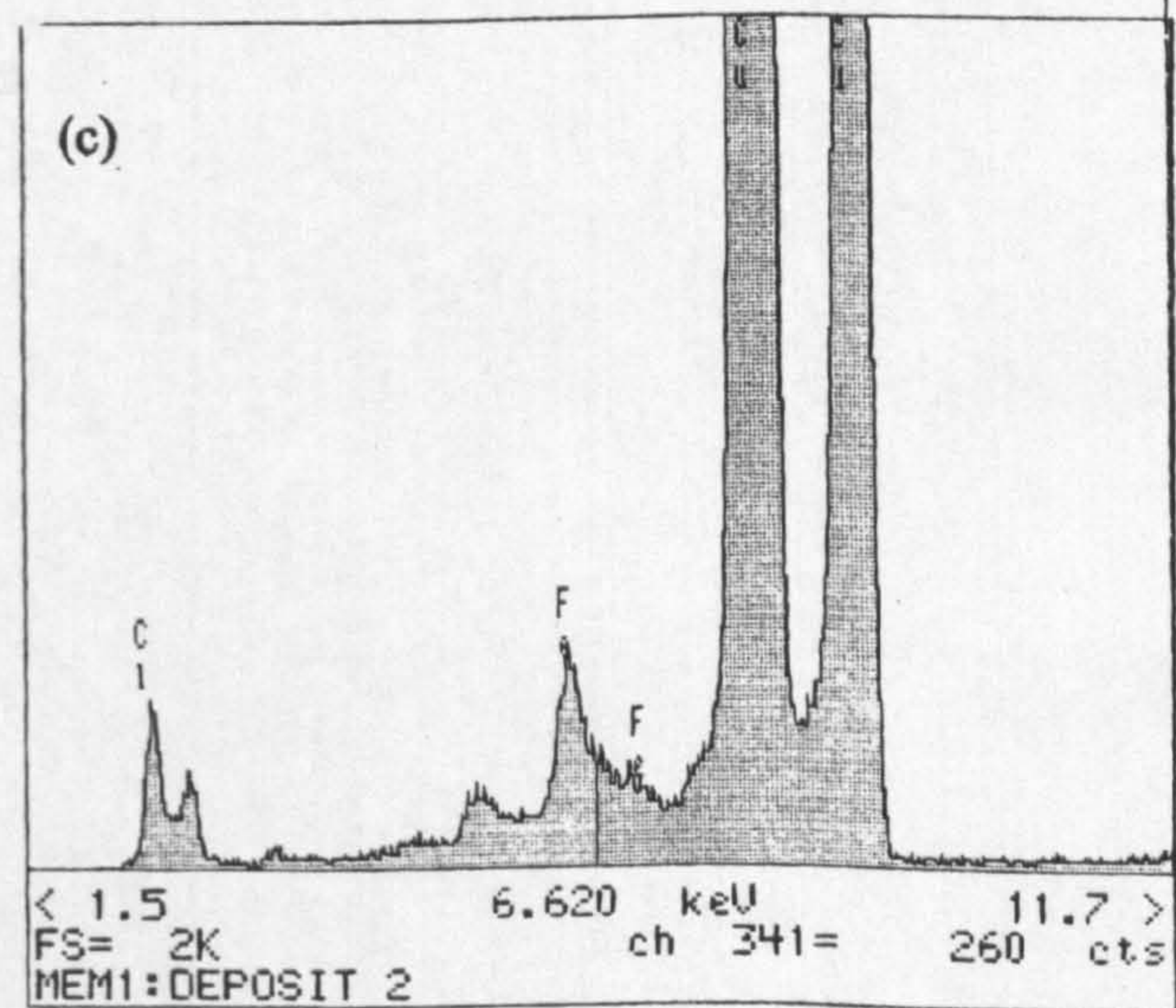
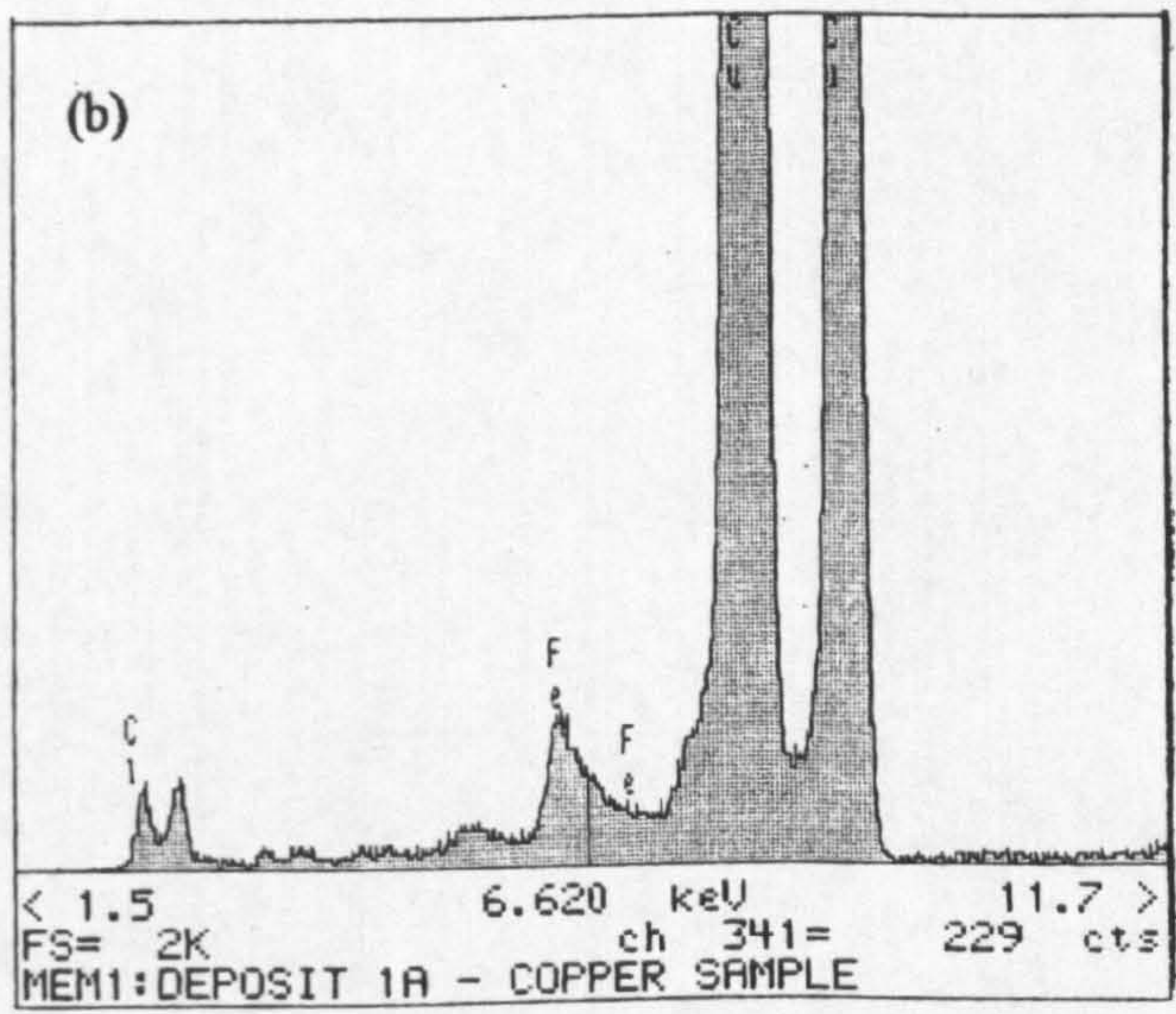
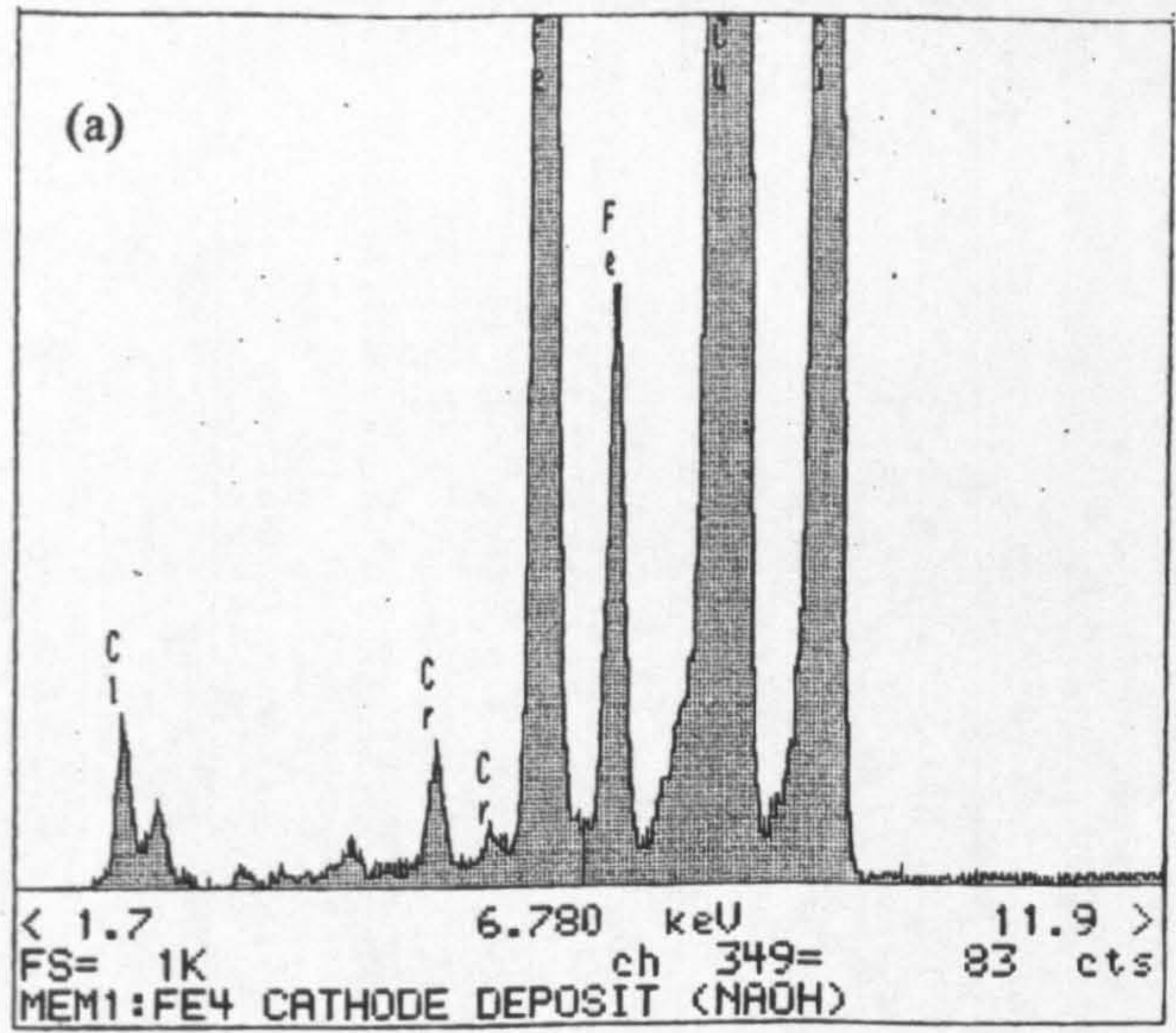


Figure. 4.23: XRF analyses of a) first stage cathodic deposit - impure copper b) residue powder - pure copper and c) second stage cathodic deposit - pure copper

### ***Preparation of added-value chemicals***

The pure copper deposit which was obtained in the previous stage was used to make several different copper compounds. Initially copper nitrate was made by dissolving the copper in a small excess of the stoichiometric amount of nitric acid. The colour of the solution was blue. This solution was then heated at 70°C with continuous stirring using a magnetic hot-plate. The solution was heated to evaporate excess HNO<sub>3</sub> until crystals were obtained. These crystals, which were blue/green in colour, were then dried at 100°C for 24 hours. These crystals were then characterised using XRD.

After characterisation these crystals were dissolved in distilled water to obtain a clear blue solution. The pH of this solution was raised using NaOH solution to obtain copper hydroxide precipitate. The solution was filtered to separate the solid and liquid fraction. The precipitate was dried in the oven for 24 hours.

The precipitate was divided into three fractions to prepare copper sulphate, copper chloride and copper acetate by adding a small excess of the stoichiometric amount of the appropriate acid. Again, each solution was evaporated until a precipitate was obtained, allowed to cool and the product was dried at 100°C for 24 hours.

For each added-value chemical prepared, analysis was carried out using XRD.

### ***XRD analysis of added-value chemicals***

The XRD analysis of each added-value chemical prepared is now presented in Tables 4.22-4.25. For each sample analysed the value of CuK $\alpha$  was 1.5418Å.

<b>Table 4.22:- XRD analysis of prepared copper nitrate</b>		
2θ	Intensity (I)	d spacing
12.78	100.00	6.927
25.725	51.82	3.463
33.52	47.20	2.673
35.448	16.52	2.532
36.46	36.09	2.464
38.228	15.83	2.354
41.879	20.94	2.157
43.556	35.00	2.078
51.336	17.99	1.780
53.516	27.14	1.712
58.029	20.94	1.589

The d spacing values presented in Table 4.22 were comparable with the literature values for copper nitrate of formula  $\text{Cu}_2(\text{OH})_3(\text{NO}_3)$ .

<b>Table 4.23:- XRD analysis of prepared copper sulphate</b>		
2θ	Intensity (I)	d spacing
27.373	100.00	3.258
17.34	79.92	5.114
18.234	53.47	4.865
20.044	141.84	4.430
22.307	61.35	3.985
24.391	87.80	3.649
26.038	79.55	3.422
27.973	59.10	3.190
29.659	63.60	3.012
30.046	39.40	2.974
31.702	84.43	2.822

The d spacing values presented in Table 4.23 were comparable with the literature values for copper sulphate of formula  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ .

<b>Table 4.24:- XRD analysis of prepared copper chloride</b>		
<b>2<math>\theta</math></b>	<b>Intensity (I)</b>	<b>d spacing</b>
28.515	100.00	3.130
16.11	66.90	5.502
21.922	60.99	4.054
28.807	43.26	3.100
32.85	34.04	2.726
33.979	55.08	2.638
34.783	30.02	2.579
35.215	27.90	2.548
40.827	31.91	2.210
43.915	24.11	2.061
45.317	33.10	2.001

The d spacing values presented in Table 4.24 were comparable with the literature values for copper chloride of formula  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ .

The d spacing values presented in Table 4.25 were comparable with the literature values for copper acetate of formula  $(\text{CH}_3\text{COO})_2\text{Cu} \cdot x\text{H}_2\text{O}$ .

<b>Table 4.25:- XRD analysis of prepared copper acetate</b>		
<b>2θ</b>	<b>Intensity (I)</b>	<b>d spacing</b>
11.115	100.00	7.96
11.689	61.17	7.57
12.56	71.09	7.05
16.347	36.20	5.42
21.551	25.55	4.12
25.696	32.41	3.47
29.278	28.18	3.05
32.83	30.66	2.73
35.68	32.70	2.52
37.796	33.43	2.38
38.496	36.35	2.34

## **CONCLUSION**

The results described in this chapter have shown that the novel concentrator techniques developed in this work can be used to recover heavy metals, including precious metals from industrial effluent. In some cases, for example, the recovery of iridium, studies on optimisation led to the development of improved conditions for recovery. The results also show that the final product of recovery can be purified metal or added-value chemicals and that the decrease in the value of the final recovery product will depend on economic as well as technical conditions.



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## CHAPTER FIVE

# LEACHING OF METALS FROM INDUSTRIAL WASTES AND THE DEVELOPMENT OF METHODOLOGY FOR THE CHARACTERISATION OF WASTE

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## **5 INTRODUCTION**

The Basel Convention which is likely to be ratified shortly is concerned with transfrontier shipment of waste from developed to developing countries. The main aim of the convention is to prevent shipment of hazardous waste for treatment and disposal in developing countries. This will be achieved by banning the shipment of any material that is (a) not a primary product and (b) contains any of the components classified in lists of materials with intrinsically hazardous properties. Under the Basel Convention therefore all secondary metal sources, off-cuts (even of precious metals such as gold), slags from refining processes, spent catalysts and end of product life materials would be classified as waste because they are not primary products. The question then arises as to whether they would be subject to the ban if they contain *any* major or trace levels of an intrinsically hazardous component.

Secondary copper and zinc residues that are normally recycled to reduce primary ore requirements, for example, would be considered as wastes even though many developing countries have built up substantial metal recovery industries. The copper and zinc residues could be subject to the ban because they are intrinsically ecotoxic or, more importantly, if they contain other listed hazardous materials such as cadmium.

The Basel Convention has therefore introduced new requirements for (a) complete analysis and speciation of secondary metal sources (b) development of a method of determining whether the secondary materials would be subject to the Basel ban and (c) development of a method for determining the ability of the materials to transfer dissolved metal to the environment, thus making it bioavailable.

In this chapter an outline of the Basel Convention is followed by (1) description of the copper and zinc industries to identify secondary sources (2) leaching studies on copper and zinc containing materials carried out in this work to determine availability and (3) a description of the methodology devised in this work to determine whether any metal containing material could or could not be shipped to a developing country.

## **5.1 THE BASEL CONVENTION**

### ***Introduction***

In recent years a number of incidents in which wastes have been moved clandestinely or under misdescription from one country (usually but not always an industrialised, Annex VII, country) to another (usually but not always a third world, non-Annex VII, country) set a background for the secondary metals industry to preserve its position. As a result of waste being shipped from an Annex VII country to a non-Annex VII country demand grew to regulate the flow of wastes around the world.

Although legal instructions could have been used, these were not implemented and this was then considered to be the prime reason for the fervour and relative haste with which the Basel Convention was negotiated and adopted.

### ***The Basel Convention***

In 1987 the Governing Council of the United Nations Environment Programme (UNEP) convened a working group to provide a global system for environmental control of the transboundary movements of hazardous wastes. On 22 March 1989, in Basel, Switzerland, "The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal" was adopted by the 116 States participating in the Conference of Plenipotentiaries on the Global Convention on the Control of Transboundary Movements of Hazardous Wastes. The Basel Convention came into force on 5 May 1992<sup>[1]</sup>.

Prior to this the Organisation for Economic Co-operation and Development (OECD) Decision on the Control of Transfrontier Movements of Wastes destined for recovery operations was adopted on 30th March 1992 and then amended in July 1993. This Decision (C(92)39/Final) was brought into force so that operation of the Basel Convention would not hinder the movement of waste for recovery between countries belonging to the OECD. The Decision is a multilateral agreement under Article 11 of the Convention.

The Decision divides wastes for recovery into three listings:-

- a green list comprising metal and metal alloy wastes in metallic non-dispersible form
- an amber list of wastes and
- a red list of wastes

The E.U. regulation on the supervision and control of shipments of wastes into and out of the European Union (93/259/EEC) replaces the earlier Council Directive 84/631/EEC. It was introduced to bring the original Directive up to date, to implement the provisions of the Basel Convention throughout the Community, as well as to implement the provisions of the OECD Council Decision<sup>[2]</sup>.

Apart from the provision of a suitable framework for the movement of waste, the Convention called for international co-operation involving the training of technicians, the exchange of information and the transfer of technology on the management of hazardous waste.

The main objectives of the Convention are:

- to reduce transboundary movements of hazardous wastes and other wastes to a minimum consistent with their environmentally sound management
- to treat and dispose of hazardous wastes and other wastes as close as possible to their source of generation in an environmentally sound management
- to minimise the generation of hazardous wastes and other wastes (in terms both of quantity and potential hazard)

One of the primary concerns is to safeguard the environment in countries with less developed technical and regulatory infrastructures against the uncontrolled influx of hazardous wastes originating in industrialised nations.

In 1995, a major modification to the Convention was made. An immediate ban was imposed on the export of waste for disposal from developed countries to developing countries. UNEP had indicated that support for the ban was in the form of a perceived need to protect developing countries from imports of such materials. Potential problems could arise in the prevention of illegal imports and in the monitoring of transboundary movements of hazardous wastes due to the lack of financial, legal, technical and institutional capacity in developing countries.

The third Conference of the Parties, in September 1995, replaced OECD and non-OECD countries with member states of the OECD, the European Union and Liechtenstein (defined as Annex VII countries) so that the export of any wastes, which were considered to be internationally hazardous, was prohibited for final disposal and for recycling or recovery to all countries except those which are members of the Annex VII group<sup>[3]</sup>.

Wastes subject to control under the Basel Convention are classified into two general categories. Annex I of the Convention provides for a list of 45 categories of wastes which are themselves divided into:

- waste streams (e.g. clinical wastes, waste mineral oil, PCB's, etc)
- wastes having as constituents certain enumerated substances (e.g. copper compounds, arsenic, cadmium, lead, organic cyanides, halogenated organic solvent, etc)

The hazard classes of the wastes listed in Annex I (Appendix 1) to the Basel Convention are contained in Annex III (Appendix 2) to that Convention. There are thirteen classes with some of them divided into numbered divisions. The power to recommend the classification of materials as 'hazardous' lies with the Technical Working Group (TWG) of the Convention. The TWG is made up of technical experts from the countries who are Parties to the Convention. TWG listing is inspired by the OECD methodology. Wastes which contain certain constituents and which are shown to exhibit specified hazard properties are prohibited and placed on list A. Wastes which do not fit these criteria are not regulated by the Convention and are placed on list B. Waste types for which insufficient data are available to allow definitive judgement to be made are assigned

to the 'undecided C list. Materials, whether already listed or not, have been assigned to the D list where the TWG has concerns which are beyond the current scope of the convention<sup>[4]</sup>. The classification is summarised in Table 5.1.

<b>Table 5.1:- Classification System</b>		
<b>List A</b>	<b>Banned</b>	<b>Contains Annex I metals and displays Annex III Characteristics</b>
<b>List B</b>	<b>Allowed</b>	<b>Does not contain Annex I metals, or if present, does not display Annex III characteristics</b>
<b>List C</b>	<b>Pending</b>	<b>Scientific evidence required before allocation</b>
<b>List D</b>	<b>Out of Scope</b>	<b>Environmental concerns, but currently outside scope of the Convention</b>

The main issue of this research was concerned with providing scientific data on the content and potential environmental impact of unclassified materials, which would then be designated either, under list A or B.

Developments<sup>[5]</sup> in the Basel Convention were enforced with a ban on the export of hazardous waste for recycling effective from 31st December 1997. This ban takes effect 90 days after ratification and if 65 countries ratify it. At the time of writing, the only countries to have ratified are Norway, Finland, UK, Luxembourg, Spain and the E.U<sup>[6]</sup>.

A prime motivator for the ban was the environmentalist pressure group Green Peace, which argued that industrialised nations often use developing countries, with poor environmental regulations, as dumping grounds for hazardous wastes<sup>[7]</sup>. Other participants see that global trade of non-hazardous recyclables should be further continued and developed as an important source of raw materials and industrial feedstocks for the economies of developing countries<sup>[8]</sup>.

Although the United States was involved in the original negotiations of the Basel Convention and the Senate voted to approve the treaty, there was no legislation put forward for the terms of the treaty to be effective. Thus, as of 1994 the U.S. withdrew support after the 1994 decision of the Conference of the Parties to ban trade in secondary materials between OECD and non OECD countries. The U.S. had a view which saw that implementation of the Convention would seriously disrupt export of secondary metals from the U.S. The U.S. considered that by excluding themselves from the Basel Convention they may continue to export wastes for recovery. Since the U.S. is a member of the OECD, the extent to which export of wastes can occur is questionable.

There has been much criticism in the implementation of this ban. Some see the amendment as 'reckless and misguided' in that the definition of 'waste' and 'hazardous waste' remains vague.

An important feature in the Basel Convention for evaluating the need to consider the banning of materials is the indicator - *trigger guide level* - the purpose of which is now described.

### **5.1.1 TRIGGER GUIDE LEVELS**

#### ***Risk Assessment***

Risk is the probability that an adverse effect would occur during a stated period of time and is often described by the equation (Eq. 5.1):-

$$\text{Risk} = \text{Hazard} \times \text{Exposure} \quad (\text{Eq. 5.1})$$

Risk assessments are required to be carried out under certain legislation, e.g. the Management of Health and Safety at Work Regulations 1992 (SI/1992/2051)<sup>[9]</sup>.

Risk assessment is an estimation of the risk, which includes identifying the hazards, the magnitude of the effects and the probability of an occurrence, and an evaluation of it. This also includes quantifying the significance of the hazards and the consequences for persons and the environment affected.



The determination of the levels of contamination that are acceptable in soil has developed fundamentally by considering the sensitivity of the proposed end use of the site. The International Committee for the Reclamation of Contaminated Land (ICRCL) has introduced the concept of trigger guide concentrations which provide a means by which the significance of contaminants in relation to different land use can be assessed.

The Dutch, German and U.S. Governments have all specified such concentrations for their own national remedial efforts. The U.K. approach will continue to be based upon the concept of trigger concentrations related to end-use as set out within ICRCL guidance note 59/83.

Since some of the waste, which is being generated in industry, is simply dumped on land, this will cause the land and the soil contained in the surrounding area to be contaminated. The sources of soil contamination include a wide range of industrial and waste disposal practices. Hazardous substances in the soil have the potential to cause harm and damage but the risk of harm occurring depends on a great many factors. It is therefore important to develop trigger or guideline values for the assessment of risk from these contaminated lands. The analysis of risk begins with identifying and assessing the various source, pathway and target possibilities and eliminating those which are not significant. The next stage in risk assessment for human targets involves estimating the rate of intake of a contaminant from the various sources and pathways, and then an evaluation is made as to the likely effect which this would have on health. The major concern for human health is usually the effect of chronic exposure to low levels of soil contamination. This would involve predicting levels of exposure over many years from ingestion, inhalation and skin contact<sup>[10, 11]</sup>.

Soil occupies a critical position between the atmosphere and terrestrial water bodies. Any transport or exchange processes, which may occur in this biologically active zone, can exert a huge degree of control over the quality of water that either runs off from, or leaches through soil<sup>[12]</sup>.

Site-specific factors and chemical-specific factors regarding toxicity and mobility are commonly considered in the evaluation of risks posed by contaminated sites. One such factor is solubility

which can have a significant impact on the actual exposure potential for a compound in soils, groundwater or air. Where there is little or no exposure to compounds there will be only a limited risk. Even when exposure does occur, compounds which are not biologically available will pose no risk.

## **5.2 DESCRIPTION OF COPPER AND ZINC INDUSTRIES TO IDENTIFY SECONDARY SOURCES**

In the next section of this thesis a description is given of the copper and zinc industries to identify secondary sources.

### **5.2.1 Copper**

#### ***Introduction***

Copper has always been one of the most important metals used by man. Unfortunately, the processes needed to free the metal from its ores produce pollution. Primary copper production in 1993 was some 5.3 million tonnes annually with a further 3.6 million tonnes from the secondary copper industries. Copper itself is one of a range of elements which is essential to life when present at low levels but is toxic at high levels. The main environmental hazards arising from the copper industry come from the by-products of copper processing.

Copper smelting has been known since predynastic Egypt, about 4000 BC and recent measurements made on Greenland ice cores have provided evidence for large-scale pollution of the atmosphere due to copper production during Roman and medieval times, especially in Europe and China<sup>[13]</sup>. This chapter will examine the waste streams, used for copper production, to identify their environmental hazards and show some ways in which they may be assessed.

The processes involved may be broadly divided into two types, viz pyrometallurgical processes and hydrometallurgical processes. Each process will now be examined in turn.

### ***Pyrometallurgical processes***

Pyrometallurgy accounts for nearly 90% of primary copper production. Copper is most commonly found in the earth's crust as copper-iron-sulphide and copper sulphide minerals such as chalcopyrite ( $\text{CuFeS}_2$ ), bornite ( $\text{Cu}_5\text{FeS}_4$ ) and chalcocite ( $\text{Cu}_2\text{S}$ )<sup>[14]</sup>. The concentrates are smelted to give first *matte* (a mixture of  $\text{Cu}_2\text{S}$  and  $\text{FeS}$ ) and then *blister copper*, which can be sold on for further refining. By-product sulphuric acid from this process can be used for treating copper oxide ores, but if not properly treated will escape into the atmosphere to produce acid rain. Copper concentrates can contain large amounts of lead and zinc which require treatment.

Most of these copper ores contain too little copper to be smelted directly. High copper concentrates are produced by isolating copper-iron-sulphide and copper sulphide ores which can then be smelted economically. The most effective method of isolating the copper minerals is froth flotation. In this method, fine particles of the copper mineral are selectively attached to air bubbles rising through an aqueous pulp of ground ore. Selectivity of flotation is created by the use of reagents which make the copper minerals hydrophobic while the waste minerals are left hydrophilic. The 'floated' mineral particles are held in a temporarily stable froth which overflows the flotation cell to yield a concentrate containing 20-35% copper [Figure. 5.1].

The three main copper smelting methods are:- flash smelting, reverbatory smelting and continuous copper making<sup>[15]</sup>.

### ***Flash smelting***

The most commonly used smelting technology is *flash smelting*, usually by the Outokumpu or Inco process, in which the dried concentrates are blown into a large oxidising furnace (at  $1200^\circ\text{C}$ ) using preheated oxygenated air and reacted before falling into the molten matte. The molten matte and slag are tapped separately from the furnace as they accumulate. The matte which contains about 35-70% copper (typically 60% Cu; 16% Fe; 24% S) is discharged from one end of the furnace and transferred to converters for oxidation to blister copper. The slag (~1% copper) is sent to a copper recovery process and on to a stockpile. The reactions follow equations (Eq. 5.2) like:

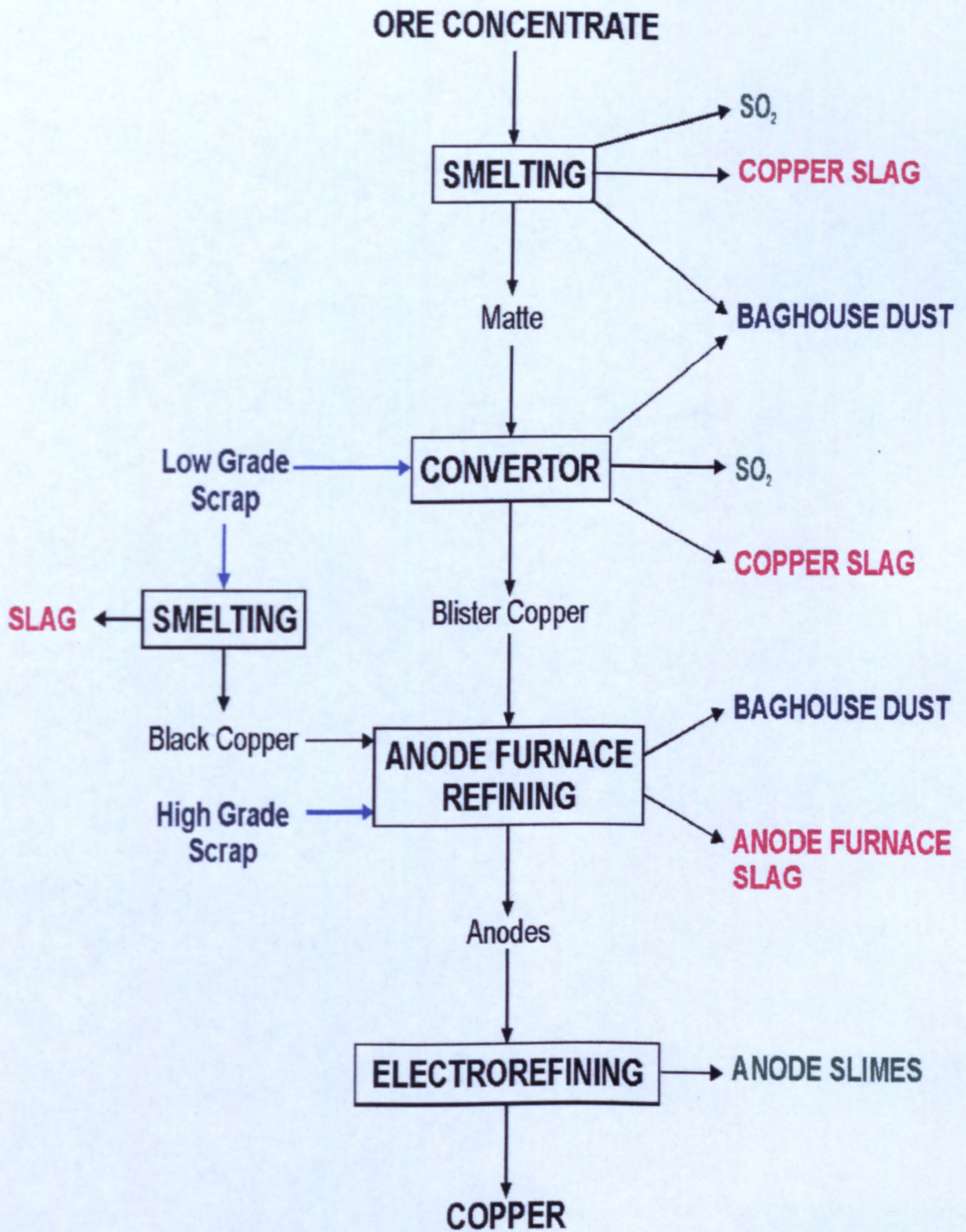
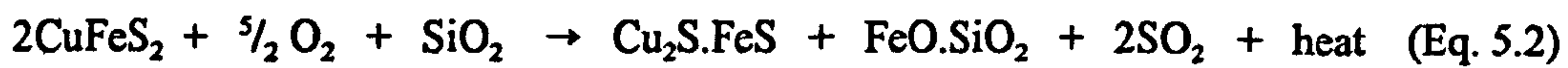


Figure. 5.1:- Copper production by pyrometallurgy



The  $\text{SO}_2$  produced is at a concentration suitable for conversion into sulphuric acid. Flash furnaces accounted for about 40% of the world's copper concentrate smelting in 1994. The distribution of minor elements between the slag and volatilization in the gas phase depends on the amount of oxygen used. Elimination of bismuth and arsenic in the slag, rather than by volatilization, can be greatly affected, followed by that of antimony and lead in decreasing order, and the elimination of zinc is little affected by increased oxygen content in the process gas.

Flash furnace smelting is an oxidation/melting process, whereby oxidation of the iron and sulphur in the concentrate feed provides energy for heating and melting<sup>[14]</sup>.

### ***Reverberatory furnace smelting***

About 25% of the world's copper concentrate smelting is accounted for by the old reverberatory furnace process. The reverberatory furnace is a hearth furnace in which concentrates are melted with a flux by hot gases from burning fossil fuel. The products formed are molten matte (~30-60% Cu) and molten slag (~0.6-0.8% Cu). Since this process is primarily a melting process, compared to flash smelting, it makes little use of the energy from iron and sulphur oxidation from heating and melting.

The sulphur dioxide gas which is given off in large quantities from the fossil fuel is in too low a concentration to be recovered successfully so creating a difficult air pollution problem. It is because of this environmental problem that reverberatory smelting continues to be replaced by flash smelting and other energy and  $\text{SO}_2$  efficient processes such as traditional electric and blast furnace smelting.

### ***Converting***

By far the most widely used technology (1990) for conversion of matte from smelting into blister copper is the Pierce-Smith convertor. The liquid matte is transferred from the smelting furnace and poured into the convertor through a large central mouth. After charging with molten matte, air is blown in and conversion takes place in two stages:

In the first stage the iron(II) sulphide is converted to iron oxides and sulphur dioxide until the matte contains no more than 1% Fe. In the second stage the remaining sulphur associated with the copper is oxidised and blister copper formed. However, oxidation of copper does not occur until the sulphur content of the copper falls below 0.02%. At the sulphur end point, blowing is terminated and the molten copper is sent forward for refining [Figure. 5.2]. The processes follow the equations (Eq. 5.2 and 5.3):



The slags formed are immiscible with the matte and removed by tilting the convertor. The conditions in the convertor are strongly oxidising and agitated so that the convertor slag contains between 2 and 8% copper and is recovered by settling from the molten slag or by froth flotation from slowly, solidified cooled slag. Several impurities, such as lead, arsenic, antimony, cadmium and mercury are evolved during this stage and are collected, usually in electrostatic precipitators or the flues leading to them. Sulphur dioxide can be recovered efficiently from the convertor gas, but there is extensive leakage to the atmosphere during charging and pouring.

A few plants use continuous copper-making but this is restricted because of the large amount of copper oxide formed in the slag which requires further reduction. This process, however, produces less SO<sub>2</sub> than other methods.

The products from the fuming furnace, reverberatory smelting and matte smelting can also be gathered in a baghouse where they are accumulated as 'baghouse' dust [Figure. 5.1]. The impurities can then be recovered using appropriate metal recovery techniques.

The blister copper formed by matte smelting contains almost 99% copper. This, along with some cathode copper, is refined by the almost obsolete fire process or by electrolysis. Blister copper is melted and cast into anodes after deoxygenation. The anodes are then electrorefined using a sulphuric acid electrolyte. From refineries the cathode copper goes to semi-fabricating plants.

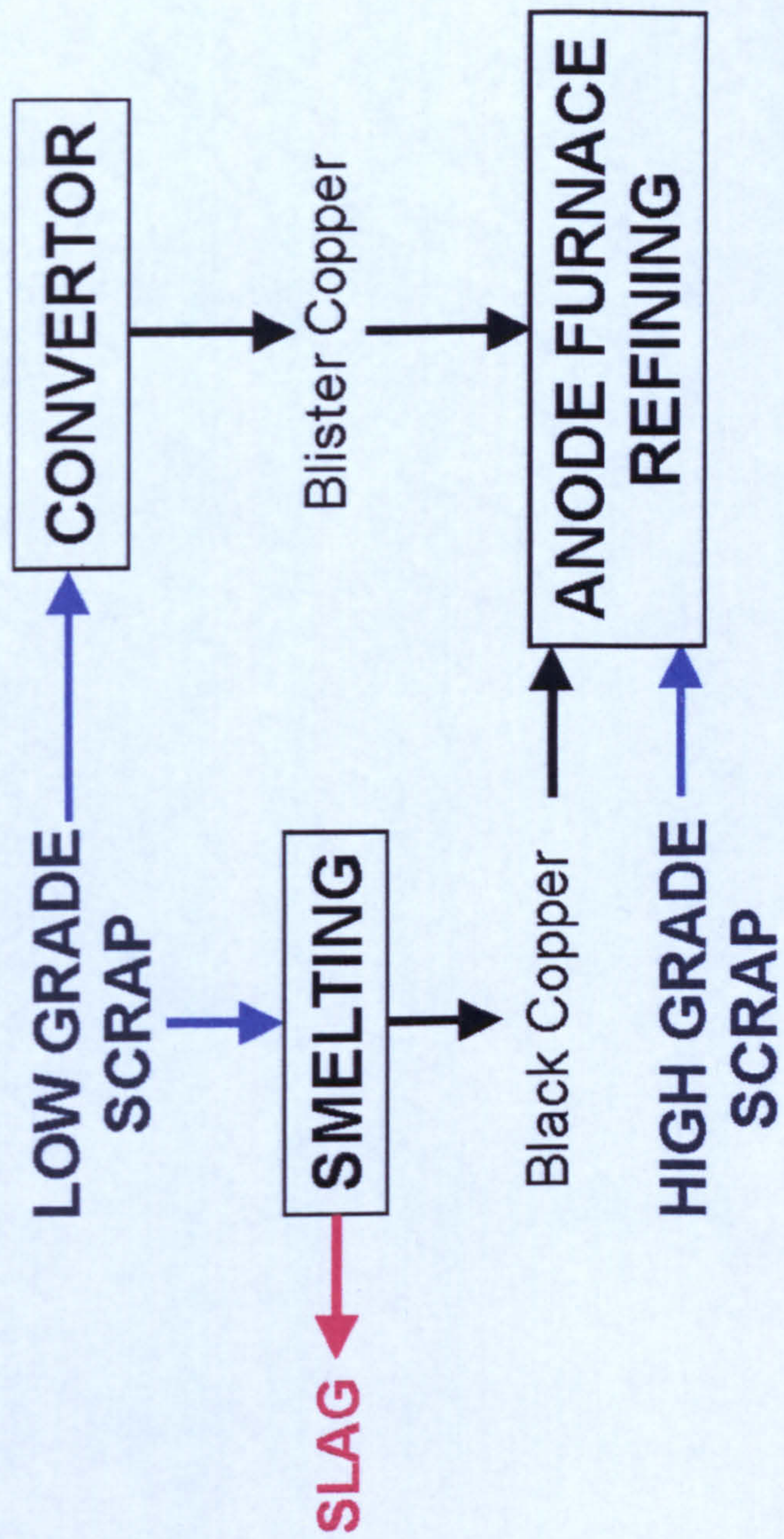


Figure. 5.2 :- Secondary copper production by pyrometallurgy

The remaining impurities in the anode copper, such as the precious metals silver, gold and platinum together with selenium, tellurium and lead, accumulate as a tankhouse slime. This tankhouse slime is removed periodically for further processing. Other impurities in the anode copper include nickel, cobalt, arsenic and bismuth. These metals usually accumulate in the electrolyte from which they are bled and the bleed stream is separately purified [Figure. 5.3].

The main environmental concern of this process is impurity processing, particularly that of arsenic which is a hazard both in-plant and to the environment. Arsenic is present as an impurity in most copper concentrates and requires careful management with respect to hazardous properties related to occupational health and the external environment. The toxic implications of arsenic require copper smelters to operate at extremely low in-plant levels for arsenic compounds. As a result of its toxicity most external uses for arsenic and its compounds have now disappeared apart from the copper-chrome arsenates which are used for timber preservation, yet continued production cannot be avoided. Care also has to be taken during the electrolysis process to avoid formation of the extremely toxic arsine gas. Disposal to permanent, environmentally acceptable waste areas is the ideal. Such preferred disposal areas would be impervious basins which are clay-lined and are remote from any water sources. Products of arsenic which would be favourable for disposal are iron and calcium arsenate since they are inert and relatively easy to make. However, these compounds solubilize slowly if exposed to moist air, therefore clay-clapping and revegetation of such disposal areas is necessary when they are full<sup>[16]</sup>.

### ***Electrorefining of blister to cathode copper***

“Anode slimes” are a by-product which collects in the cells under the anodes after electrolytic refining of copper. This ‘anode slime’ comprises impurities in the copper and is a mixture of elements and compounds which were originally present in the copper or those which may have formed during or after anodic dissolution.

Such slimes are highly variable in composition but, typically contain 5-30 wt% Cu, 5-20 wt% Ag, up to 1 wt% Au, 1-45 wt% Se 2-30 wt% Pb, as well as small amounts of Te, S, As, Bi, Sb and Ni. Since these slimes are a valuable source of precious metals it is important to remove



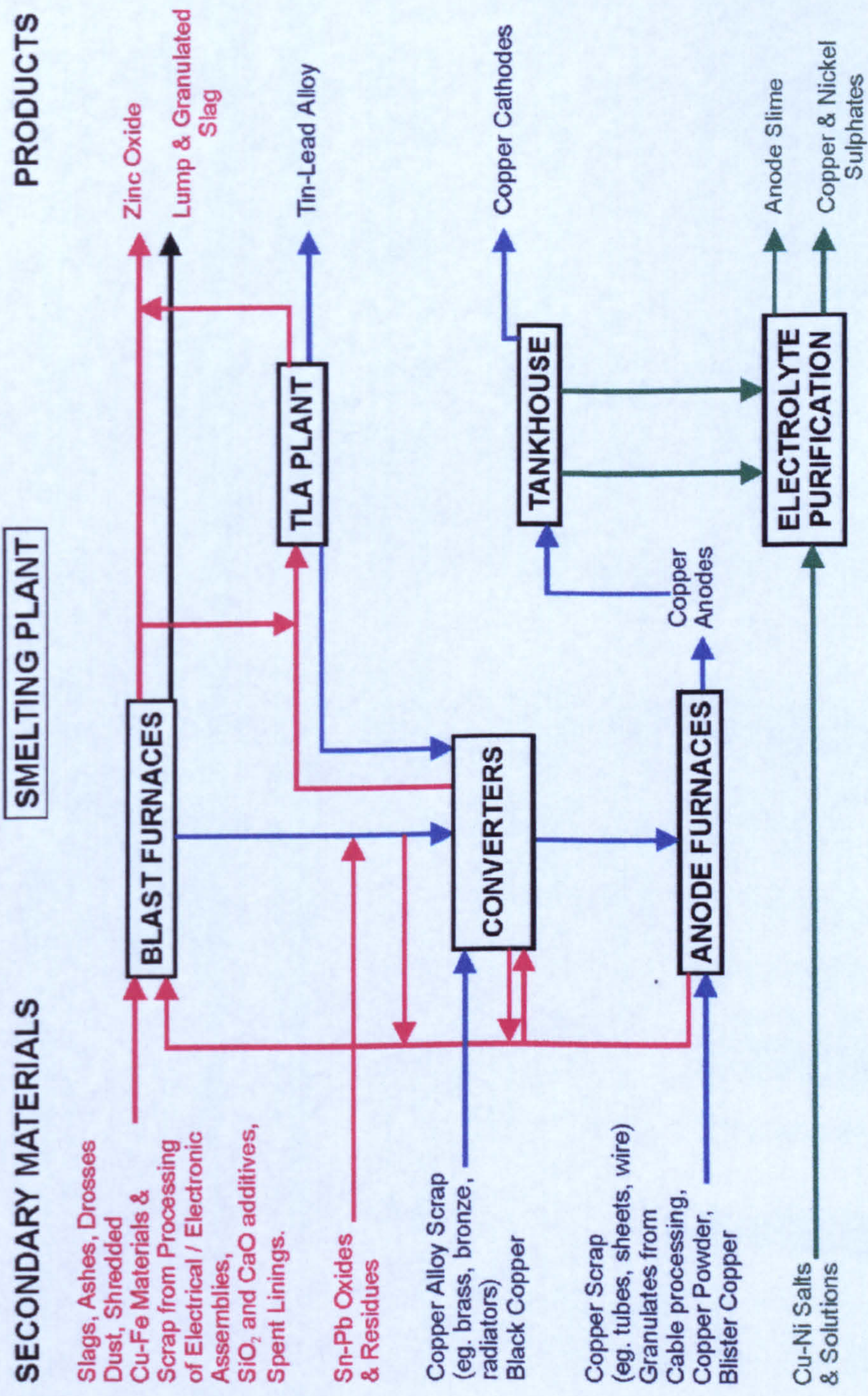


Figure. 5.3 :- Recycling of copper

elements such as Cu, Se, Te using, for example a top blown rotary convertor, to leave behind Ag, Au and the platinum group metals as an alloy called doré which contains 98-99% Ag<sup>[17]</sup>.

The conventional pyrometallurgical treatment for treating slimes involves preliminary leaching of the slimes in sulphuric acid followed by smelting in a reverberatory furnace with fluxes, but it is slow and has many recycle streams. The complexity of the slimes makes it difficult to understand the chemistry occurring in the reactions.

Although 100 varieties of anode slime have been identified, the complex mineralogy of each anode slime causes a high degree of variation from one species to another. However, small generalizations are possible: silver exists in the metallic state, but is predominantly associated with Se as silver selenide ( $\text{Ag}_2\text{Se}$ ) and silver-copper selenide ( $\text{AgCuSe}$ ); copper is found mainly in the metallic state, as the sulphate and is associated with Se as copper selenide ( $\text{Cu}_2\text{Se}$ ) and the silver-copper selenide as before. Lead is present mainly as lead sulphate; tellurium is found substituted for selenium in the selenides and gold, in its entirety is present as the metal<sup>[18]</sup>.

### ***Hydrometallurgical extraction of copper***

As described most copper is recovered by flotation, smelting and refining. However, a significant and growing quantity is recovered hydrometallurgically. Materials most commonly treated in this way are 'oxide' copper minerals such as carbonates, oxides and sulphates and also secondary sulphide minerals such as chalcocite. The copper is dissolved by dilute sulphuric acid during several months of leaching [Figure. 5.4]. The leaching is most commonly carried out by sprinkling dilute sulphuric acid on top of heaps of broken ore and by allowing the acid to trickle through to collection dams. Chalcopyrite bearing mine waste is also leached in this way but many years of recovery are required for efficient copper recovery due to the low concentration of copper in the waste.

The aqueous solution from the leaching process contains 1-5 kg m<sup>-3</sup> copper and 1-10 kg m<sup>-3</sup> sulphuric acid. The copper from these solutions is almost always recovered by preparing a strong, pure electrolyte followed by electroplating. The process by which the electrolytes are most commonly prepared is solvent extraction. In this process the copper is extracted from the

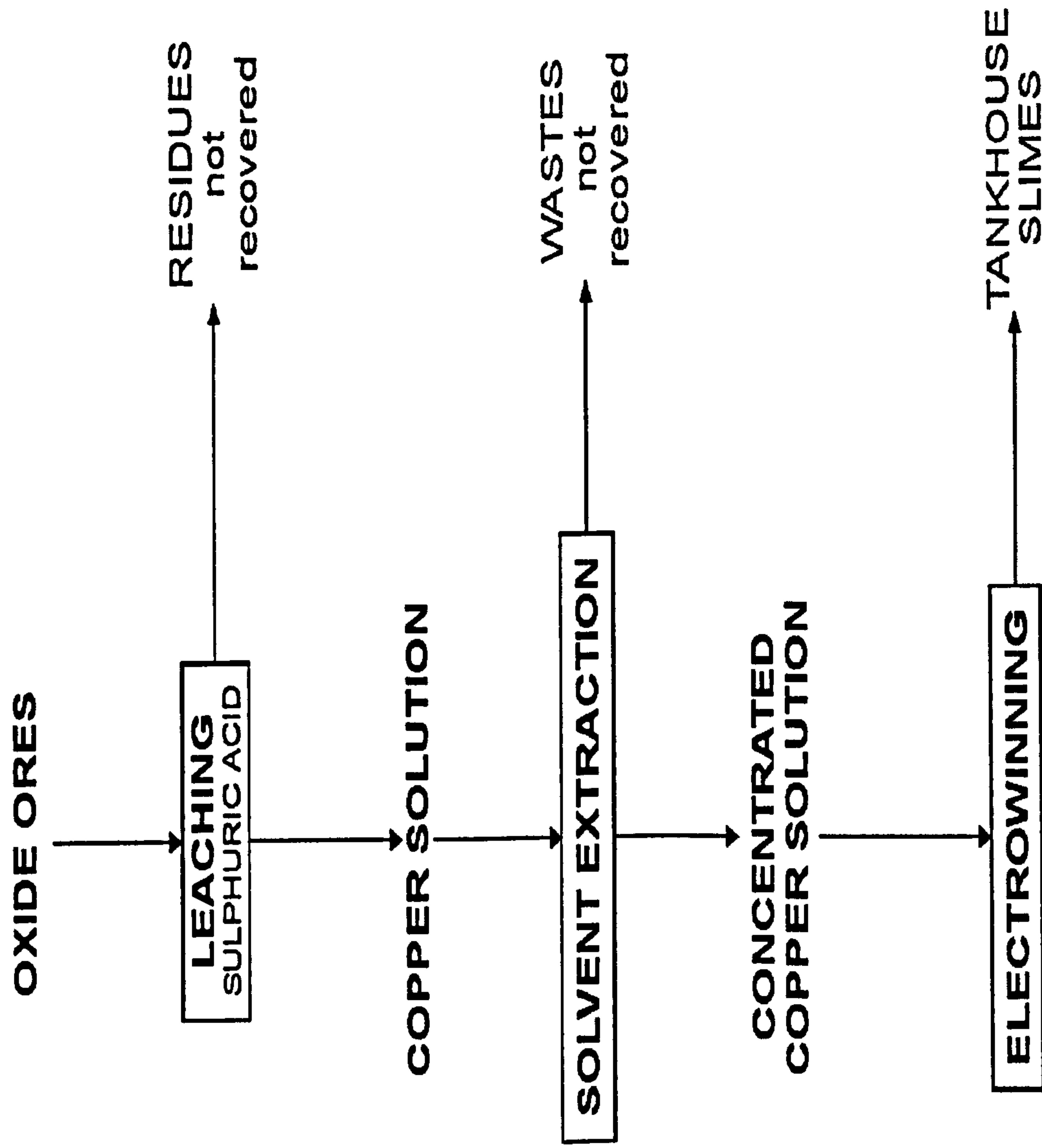
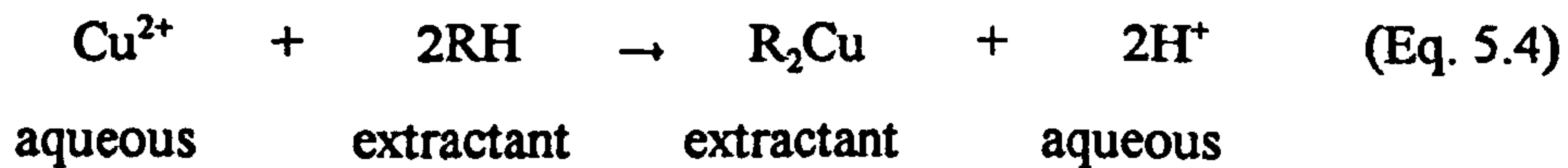


Figure. 5.4:- Copper production by hydrometallurgy

aqueous solution into a copper specific organic extractant, usually a hydroxyphenyl oxime dissolved in petroleum distillate. The copper is then stripped from the loaded organic into a copper depleted strong electrolyte. The process can be represented by the following equation (Eq. 5.4):



The equation shows that a low acid concentration in the aqueous leach solution causes much of the copper to enter the organic extractant phase as  $\text{R}_2\text{Cu}$ , while a high acid concentration has the opposite effect. Thus, when the weak acid leach solution comes into contact with the extractant, the copper is loaded into the organic extractant phase. When, however, the organic extractant is subsequently contacted with concentrated acid electrolyte, the copper stripped from the extractant into the electrolyte at high  $\text{Cu}^{2+}$  concentration, is suitable for electroplating. The extractants which are used in the process absorb considerable copper but almost no impurities and so they produce electrolytes which are concentrated in copper and low in impurities.

### ***Electrowinning***

The copper which is recovered by electroplating is usually as pure metallic cathode copper. The cathode and anode reactions are as follows (Eq. 5.5 and 5.6):-



Copper is produced at the cathode and oxygen at the anode, while sulphuric acid is regenerated for recycle to the solvent extraction phase.

### ***Recycling of copper scrap***

For thousands of years, copper and copper alloys have been recycled. This is because the entire economy of the copper and copper alloy industry is dependent on the economic recycling of any

surplus products. Since there is a wide and varied range of copper based materials for many applications, the most suitable and cheapest feedstock for making the components gives the most economic cost price for the material.

### ***Scrap value copper***

The usual commercial supplies of pure copper are used for electrical applications such as the production of fine and superfine enamelled wires. It is essential that reproducibility is maintained in order to ensure high conductivity, consistent anneability and freedom from breaks during rod production and subsequent wire drawing. It is essential that there are no surface flaws because the applied enamel layers are thin and have to withstand voltage. Primary copper of the best grade is used for producing the rod for this work. Uncontaminated recycled process scrap and other scrap that has been electrolytically refined may also be used.

Copper used for power cables is also drawn from high conductivity rod but to a thicker size than fine wires. The presence of any impurities in the scrap can cause problems and so scrap containing such impurities can only be used if it is well diluted with good quality copper.

Copper is also used to make large quantities of plumbing tube, roofing sheet and heat exchangers for non-electrical purposes. Secondary copper can also be used for the manufacture of these materials, though still within stipulated quality limits for impurities.

### ***Production technology***

Copper deposits vary enormously in size and contain between 0.4 and 6% copper. Depending on many factors such as the size of the deposit, richness of ore grade, type of ore and depth below the surface, the ore can be extracted either by underground or surface mining. Surface mines provide over two thirds of world primary copper and are less costly to operate when compared to underground mines.

An important distinction between ores is that between sulphide and oxide copper ores. Sulphide ores are sometimes mixed with iron sulphides and copper oxide ores include silicates and carbonates. Sulphide ores are usually crushed and ground into a fine powder which is mixed with

water and frothing agents. When air is bubbled through the solution, sulphide ores can be removed by flotation and collected in the form of copper concentrates that usually contain 20 to 35% copper. Oxide ores are usually treated by leaching the ore with dilute sulphuric acid and then collecting the resultant copper-bearing solution which will undergo solvent extraction and then electrowinning.

The solvent extraction process involves the addition of an organic solution to capture copper from the aqueous leach solutions while leaving other materials in the solution. The copper which has been removed is then transferred to an electrolyte suitable for electrowinning. The leach solutions which are sent to solvent extraction and electrowinning plants are usually from mine dumps, constructed ore heaps, mine water or broken up material in mines. Most copper oxides and some sulphide ores are suitable for leaching and the sulphuric acid used in solvent extraction may be obtained as a byproduct of smelting sulphide ores.

Sulphide ores are usually smelted to produce blister copper, which may be sold as such for refining but because it is not of sufficient purity it cannot be used as a final product. There are several types of smelting furnaces, some of which also generate sulphur dioxide in an adequate concentration for it to be converted into sulphuric acid. There are also some hydrometallurgical methods of processing sulphide ores.

The blister copper which is produced from the smelting of sulphide ores requires further refining, either by fire or electrolytic methods to produce refined copper of the required degree of purity. From refineries the finished copper goes to semi-fabricating plants, the most important types of which are wire mills and brass mills.

### ***Semi-fabricating industry***

The semi-fabricating industry is divided into two sectors - the electrical and non-electrical sectors. These two sectors are usually referred to as wire mills and brass mills respectively. The wire mills produce end products of wires and cables and their input as feedstock is high purity primary copper only. This is because the electrical conductivity of copper depends on its purity, so that more current will pass through a higher purity of wire<sup>[19]</sup>.

Brass mills not only manufacture brass semi-fabricated products but also produce copper and copper alloy semi-manufactures such as rods, bars, sheet, strip, tubes in copper, brass, copper-nickel alloys and bronze. The semi-fabricating industry consumes nearly all the output of refined copper with about 2% going to other outlets such as powder plants, foundries or for the manufacture of copper sulphate. Brass mills and other outlets can use large quantities of secondary copper since they have less need of high purity copper [Figure. 5.5].

## **5.2.2 Zinc**

### ***Wastes From The Zinc Industry***

Metallic zinc has been mined for some 200 years since its first commercial extraction in England in 1740. Zinc occurs and is mined from four classes of ore, viz. : in carbonate, shale, volcanic and skarn/manto type deposits. Each contributes about 20% or more of the Western World's supply of primary zinc. In many cases zinc occurs in deposits with a complex mineralogy, usually together with lead, which complicates the production of concentrates<sup>[20]</sup>.

Zinc is obtained from ores and concentrates using horizontal and vertical retorts, electrolysis, overpelt and blast-furnace methods. The hydrometallurgical processes which leach the zinc from the calcine and electrowin to cathode zinc prevent or significantly reduce the emission problems in an electrolytic zinc plant. They do, however, create other problems, particularly with respect to effluent treatment and the disposal of residues. Also the presence of acid mist which collects over the electrowinning cells presents its own hazards.

The residues from dilute acid leaching contain zinc ferrite, entrained zinc sulphate, undissolved zinc oxide, and other values, such as lead, copper, silver and gold. Hot acid leaching improves copper and zinc recovery, but this process is not very widely used because of the difficulty of separating iron which forms a gelatinous precipitate. To obtain higher yields of zinc (>95%), more aggressive leaching is required which solubilizes a significant quantity of iron, which must be precipitated in the form of a residue.

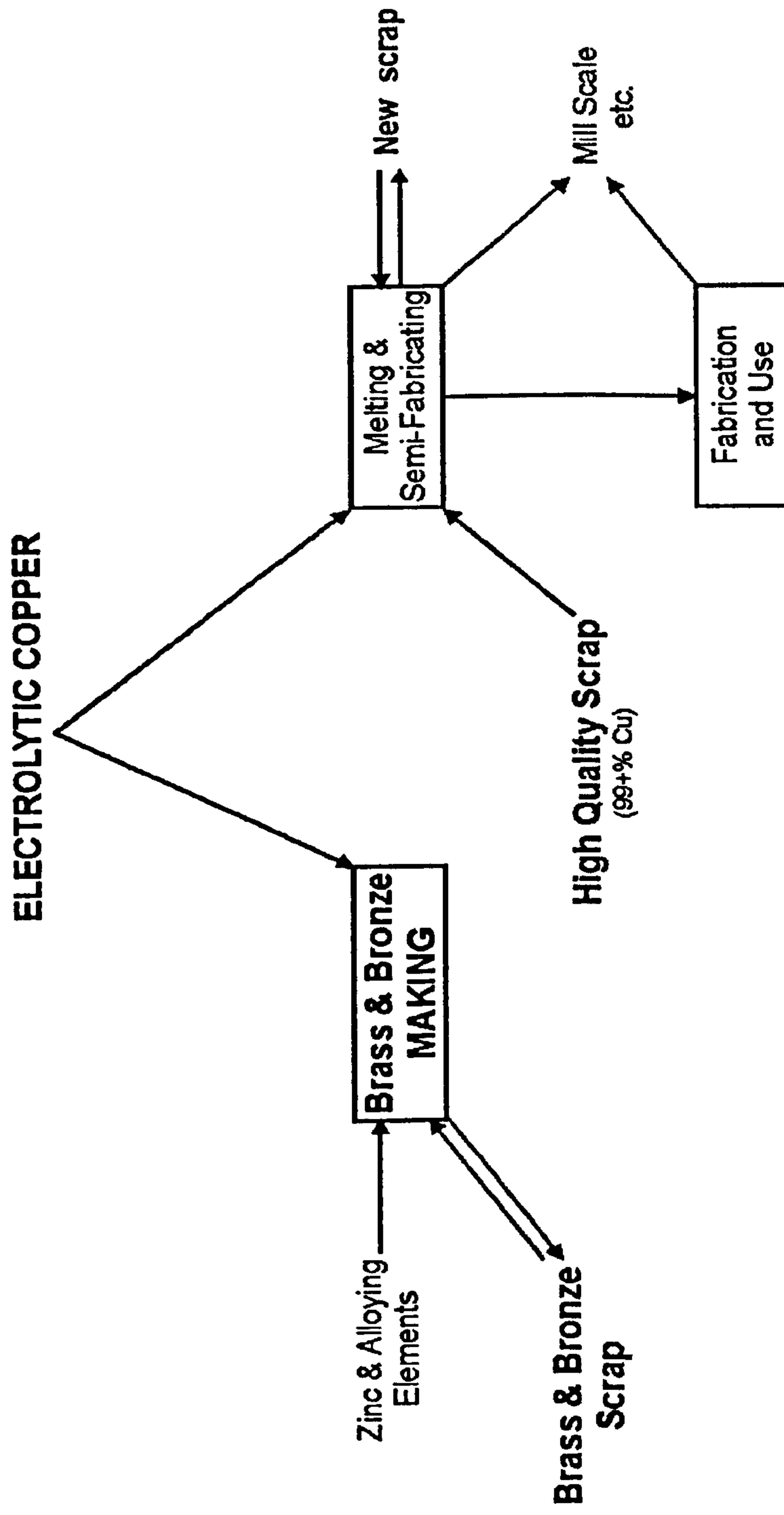


Figure. 5.5:- The copper metal industry



## ***Zinc Production***

Zinc ores generally need to be concentrated before the metal can be extracted. The two processes in use are the wet gravity method and the more commonly used flotation process. The less common wet gravity method relies mainly on the difference in density between mineral particles in the ore and the sandy gangue. The more efficient flotation process deals with the reluctance of water to wet the mineral sulphide particles. In this process the finely crushed ore is agitated with water containing chemicals and a suspension of air bubbles. The mineral particles attach to the air bubbles and float to the surface to form a froth that is skimmed off. The accompanying worthless material sinks to the bottom.

The first stage in the treatment of zinc sulphide concentrates has been roasting. Most of the sulphur removed from the concentrates is converted to SO<sub>2</sub> which can then be used for the production of sulphuric acid. This sulphuric acid can then be used for fertilisers. The crude zinc oxide produced after roasting the concentrate is then treated by either thermal smelting or electrorefining. When, however, acid demand is limited, pressure leaching can be used to produce elemental sulphur which can be stockpiled<sup>[21]</sup>.

Modern zinc production is dominated by two processes, the pyrometallurgical Imperial Smelting (IS) method with about 12% production and the roast-leach electrowin process with about 85% of production.

### ***Pyrometallurgical production of zinc***

The pyrometallurgy of zinc is a carbothermic process which follows the two fundamental equations (Eq. 5.7 and 5.8):-



The old thermal process for zinc production uses horizontal or vertical retorts. The vertical retort process involves mixing the roasted concentrates with coal, briquetted into two stages and heated in an autogenous coker to 700°C before being charged to the retort. The horizontal retort

process produced 90% of total zinc until the electrolytic process was developed in 1917. The horizontal process was used, for many years in this country, to smelt zinc but due to the development of more efficient methods, the last furnace at the Avonmouth plant of the Imperial Smelting Corporation was shut down in 1951. Disadvantages of the horizontal retort process were that a considerable amount of labour was required and also that the energy consumption was very high; in some cases twice as much as that used by modern electrolytic and blast furnace plants.

### ***Imperial Smelting Furnace***

In the Imperial Smelting furnace (IS or ISF) process a blast-furnace is fed with a mixture of roasted lead/zinc concentrates and coke and supplied with hot air blasts. Zinc vapour is removed in a 1000°C stream of gas containing CO<sub>2</sub> and CO and condensed by a spray of molten lead to give liquid zinc of 92-95% purity typically containing 1-2% lead and 0.1 % cadmium. Reflux refining (fractional distillation) at over 900°C can be used to further refine the zinc to 99.995% purity. Both low-grade concentrates and residues from galvanized steel scrap can be treated by this widely used process [Figure. 5.6].

### ***Electrolysis***

Over 80% of the world's zinc is refined by an electrolytic process. For electrolytic zinc production, sulphide concentrates are first roasted, to yield a crude oxide which dissolves easily in dilute sulphuric acid (spent electrolyte) in the leaching plant. During this roasting process, zinc ferrite is formed which is insoluble in the acid. The zinc ferrite residue can be dissolved in hot sulphuric acid and then, with the addition of aqueous ammonia and zinc calcine from the roasting plant, the iron can be precipitated as iron jarosite. However, storage and disposal of the toxic jarosite can cause problems. The iron-reduced solution can be mixed with zinc sulphate solution from the leaching process for further purification. While the leaching process should remove the silica, iron, alumina, antimony and germanium, some of the last three may remain if present in appreciable amounts. The most common impurities remaining in the zinc sulphate solution are copper, cadmium and cobalt. Most of these impurities are precipitated out by stirring zinc dust into the solution. A by-product of this operation is cadmium which is recovered as an oxide fume from the roasters<sup>[21]</sup>.

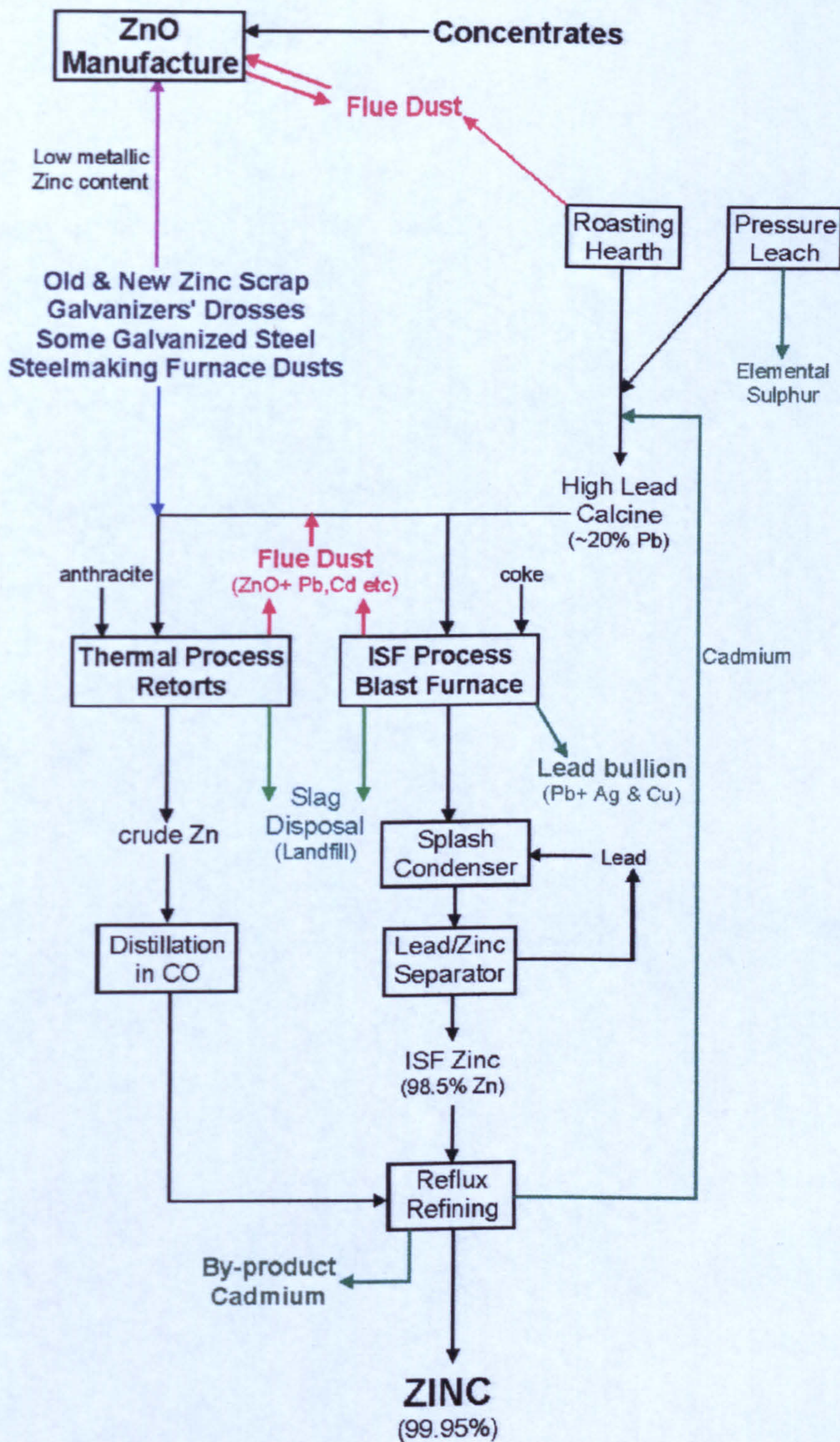


Figure. 5.6 :- Zinc production by pyrometallurgy

The electrolysis generates sulphuric acid which is returned to the leaching plant. Leach and electrolytic tank residues are commonly enriched in lead, gold and silver and are shipped to a lead smelter for recovery. Zinc is electrodeposited from solution onto aluminium cathodes, stripped and melted into slabs with 99.5 or 99.995% purity [Figure. 5.7].

### ***Warner Process***

The Warner process is a recent route in which copper is used to displace zinc from zinc sulphide. The experimental rig, developed by Warner, consists of two blast furnaces where copper sulphide is oxidatively decomposed in one furnace, to liberate pure molten copper, sulphur dioxide and an excess of heat. The hot copper flows by gravity to the lower melting furnace where it combines with more sulphides. The reaction, then, which occurs between the copper and zinc sulphide at 1200°C, releases zinc vapour. This zinc vapour is then sucked into an adjacent condenser where it is collected as molten zinc. The SO<sub>2</sub> which is produced can be drawn off and converted into sulphuric acid<sup>[22]</sup>.

### ***Electrothermic***

In 1926, at the same time as the New Jersey Zinc Company was developing the vertical retort process, The St. Joseph Lead Company also began work on a continuous method of zinc distillation. In both the horizontal and vertical retort processes it was found that when heat was applied externally it had to pass through a retort wall, placing an exacting demand on the refractories. In order to avoid this, attempts were made to supply heat to the charge internally.

The principal adopted by the St. Joseph Company was to produce the heat required by using the electrical resistance of a vertical column of the charge, power being supplied through carbon electrodes. A charge of graded sinter and coke in approximately equal proportions by volume was used, but at this point no attempt was made to condense the zinc vapour leaving the furnace shaft, and it was allowed to burn in an adjoining chamber producing pigmentary zinc oxide. A method was then developed of drawing the vapours from the shaft through a pool of molten zinc. Large quantities of zinc vapour could be condensed to liquid metal<sup>[23]</sup>.

The application of this process, however, is limited since the output of metallic zinc is

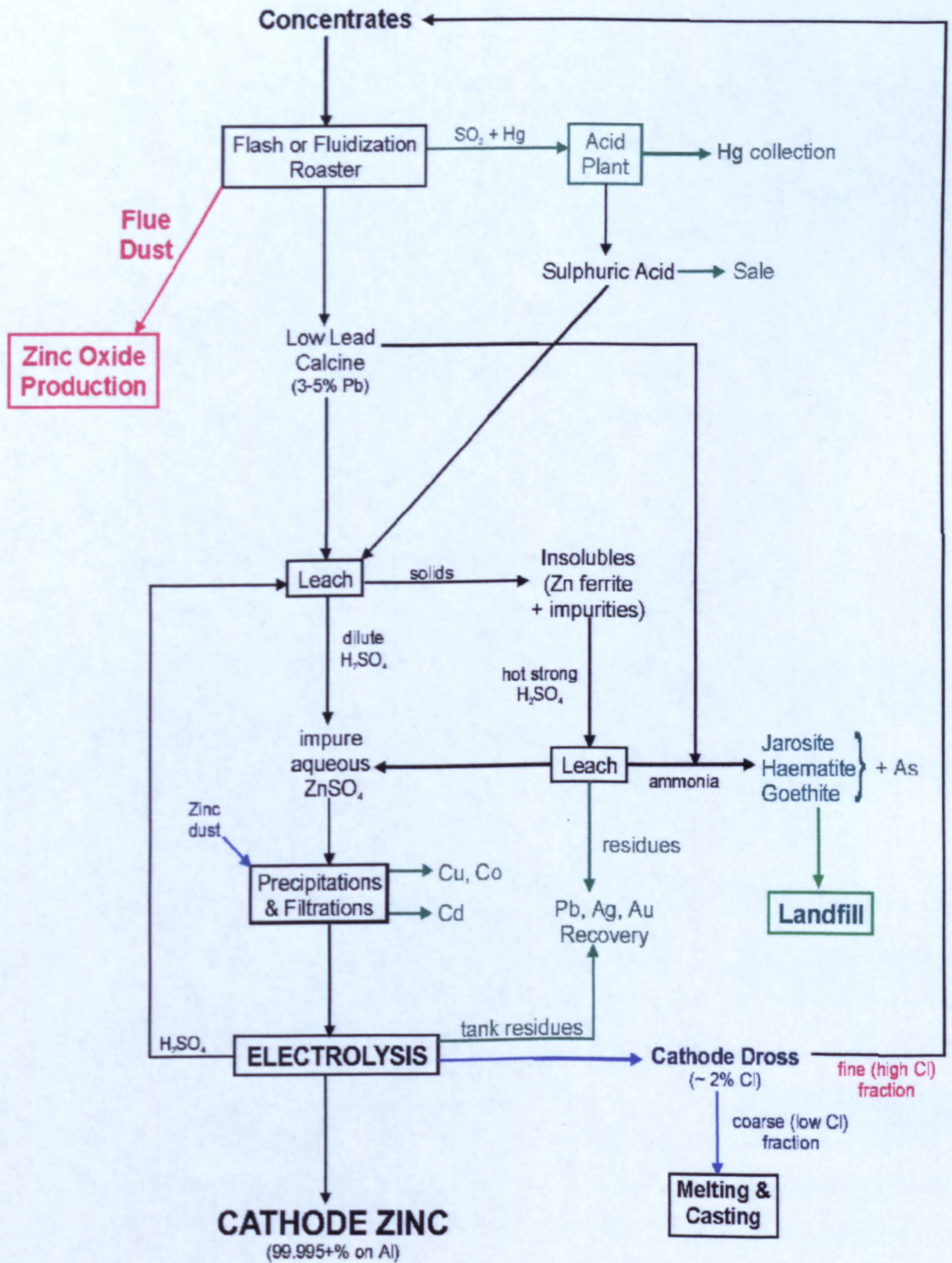


Figure. 5.7 :- Zinc production by electrolysis

considerably less than the output of most zinc-lead blast furnaces.

### ***Overpelt***

A major modification to the horizontal furnaces was carried out at Overpelt in Belgium. A common condensing chamber was formed along each side of the furnace by suspending a removable sheet metal curtain running the length of the furnace and approximately 300m from the retort mouths. The vapours issued from all the retorts on each side of the furnace were collected in two collecting chambers. During distillation heat loss from the sheet was sufficient to cool the vapours and condense most of the zinc, which was collected in a trough from which the liquid metal could be removed<sup>[21]</sup>.

### ***End uses of zinc***

Zinc has five principal areas of application<sup>[20, 21]</sup>:-

- **in coatings** - Zinc can be used as a corrosion resistant coating for steel.
- **in diecasting alloys** - 'New' scrap zinc die castings and zinc casting process scrap are recycled directly. Old scrap, particularly that from shredding of cars and domestic appliances, can be used in the production of zinc dust and zinc oxide. It can also be used as a feed stock for smelters and can be recycled as zinc casting alloys.
- **in rolled and extruded form (e.g. sheet, cladding, coins, batteries)** - This consists largely of old zinc sheet from roofs, cladding, gutters and downpipes. Potential users compete strongly for this form of scrap since it is readily recycled into secondary refined zinc. It is also an ideal material to produce zinc oxide and dust.
- **in brass** - This has a high copper content and brass scrap is recycled almost exclusively by the copper and brass industries. This indicates that any zinc used in brass leaves the zinc recycling circuit forever, and is completely recycled within the brass/copper circuit.
- **in chemicals** - To produce zinc containing chemicals.

The largest single application of zinc is in corrosion protection by galvanising. The methods for protecting ferrous materials with zinc are galvanising, mainly by the hot dip process but also by electrodeposition, metal spraying, sherardizing, the application of zinc dust paints and cathodic means.

### ***Hot Dip Galvanising***

Mild steel is one of the most widely used materials in civil engineering structures. Steel, however has a major disadvantage, in that in most atmospheres it rusts readily and consequently some form of corrosion protection is almost always required. Zinc coatings applied by galvanising or by metal spraying are generally one of the best methods of protecting steel work against corrosion. The two main reasons for this are that zinc itself is resistant to attack in normal atmospheres. The second reason is that because zinc is more electronegative than iron, the zinc tends to dissolve, when the two metals are in contact in an electrolyte, leaving the iron (steel) unattacked<sup>[24]</sup>.

Hot-dip galvanising has been well practised for over a century and the process can be either batch or continuous. The process consists essentially of a pretreatment stage in which the surface of the steel or iron to be galvanised is thoroughly cleaned. This is necessary since the process depends largely on the pretreatment and cleaning of the material before it is immersed into a bath of molten zinc which coats the work with a thin adherent film. In order to obtain uniform and rapid attack on the steel or iron surface by the molten zinc, it is necessary that all oxide and grease is removed so that alloying can take place evenly over all the surface of the steel.

The bath of molten zinc is operated at 450–470°C and since the purity of the zinc is not critical a less pure grade of zinc is used which has a relatively high level of lead. The amount of lead present is beneficial since the solubility of lead in the bath is 1.2% and any excess settles to the bottom of the bath so facilitating dross removal. The solubility of iron in zinc at this temperature is <0.02% so saturating the zinc with iron and any excess forms the zinc dross compound. Also, because of the chemical properties of zinc, the surface of the molten zinc bath used for coating reacts with air and moisture to create a layer of zinc oxide and carbonate. This layer is “skimmed” off, creating a zinc-rich “skim” that is sent for recycling.

Galvanising residues comprise of different materials which include ashes, flux residues, top and bottom drosses (hard zinc). These have a high zinc content (>70%) which is usually entrained zinc metal. These residues may be physically separated which can then be used as feed stock for either primary or secondary zinc metal production. The sources of secondary zinc arisings in the zinc metal industry and the galvanising industry are shown in Figures. 5.8 and 5.9.

### ***Zinc oxide***

Primary zinc oxide is manufactured by oxidising zinc vapour in burners. The concentration of zinc vapour and air flow is controlled in order to develop the desired particle size and shape. The hot gases and fume are passed through tubular coolers and then the zinc oxide is separated in a baghouse<sup>[23]</sup>.

Zinc oxide can be manufactured by two routes; the direct (American) process or by the indirect (French) process. Zinc oxide made by the indirect process is of great purity and about 95% is used in the rubber industry, most of the remainder in paint and a small amount in pharmaceuticals. The purity of this oxide depends on that of the zinc feed. In the direct process, less-pure zinc oxide is manufactured. Secondary Zinc oxide can be produced from zinc scrap, zinc containing sludges and metallurgical slags [Figure. 5.10].

### ***Sherardizing***

Another coating process which can be used for coating small steel articles, such as nuts and bolts with zinc, as an alternative to hot-dip galvanising is sherardizing. The article to be coated is rotated in a drum containing a mixture of metallic zinc and sand. Before the steel parts are to be coated they need to be cleaned in an acid pickling bath, rinsed and dried, and then packed in the drum. The drums are then heated either electrically or by gas to between 370–429°C to ensure a hard, even coating of zinc. The temperature is varied depending on how thick a coating is desired.

### ***Secondary Zinc***

Various kinds of zinc waste materials will arise from various processes using zinc metal, or from the production routes of the metal itself. Zinc-bearing materials in trade are known by names



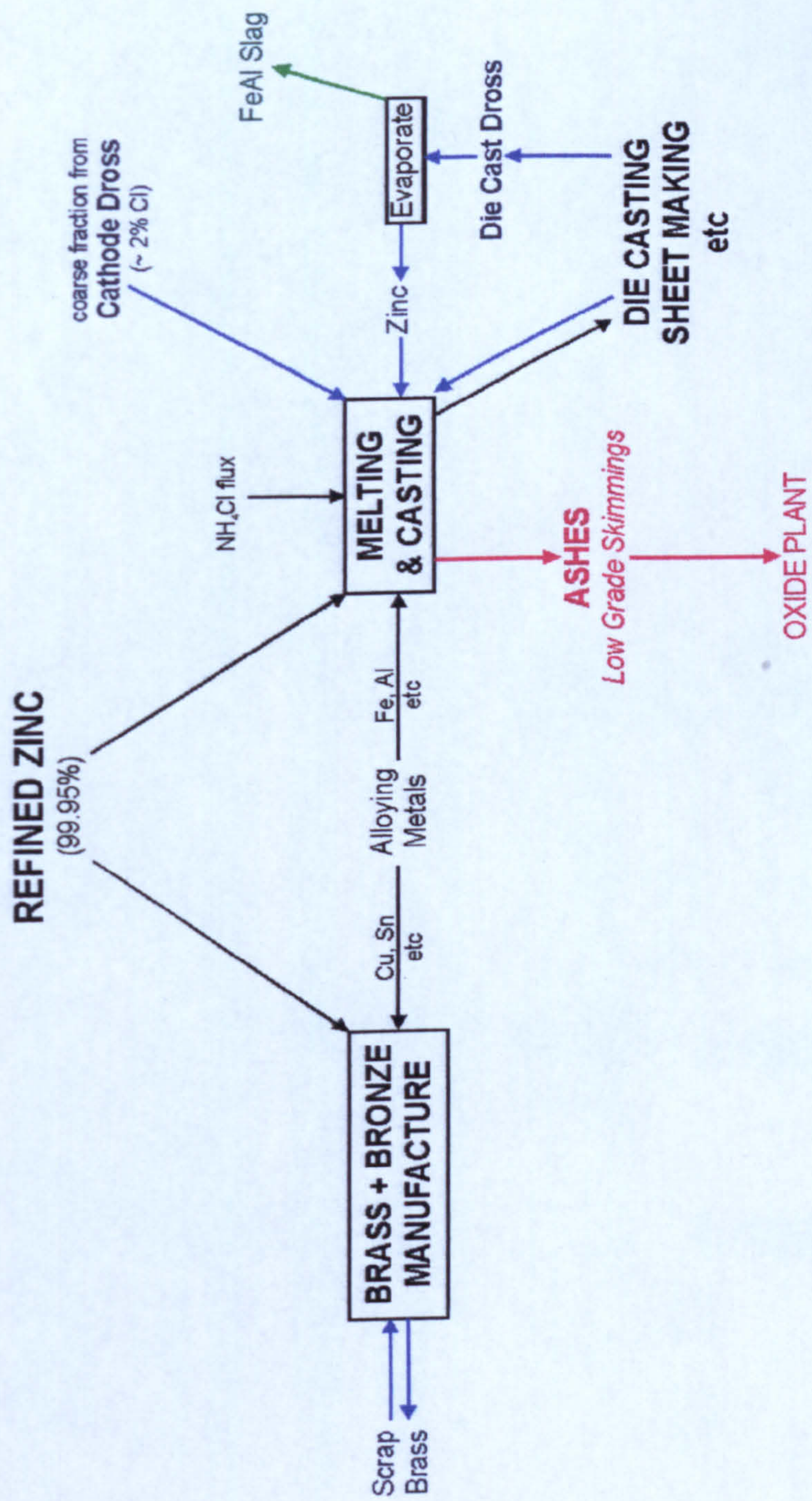


Figure. 5.8 :- The zinc metal industry

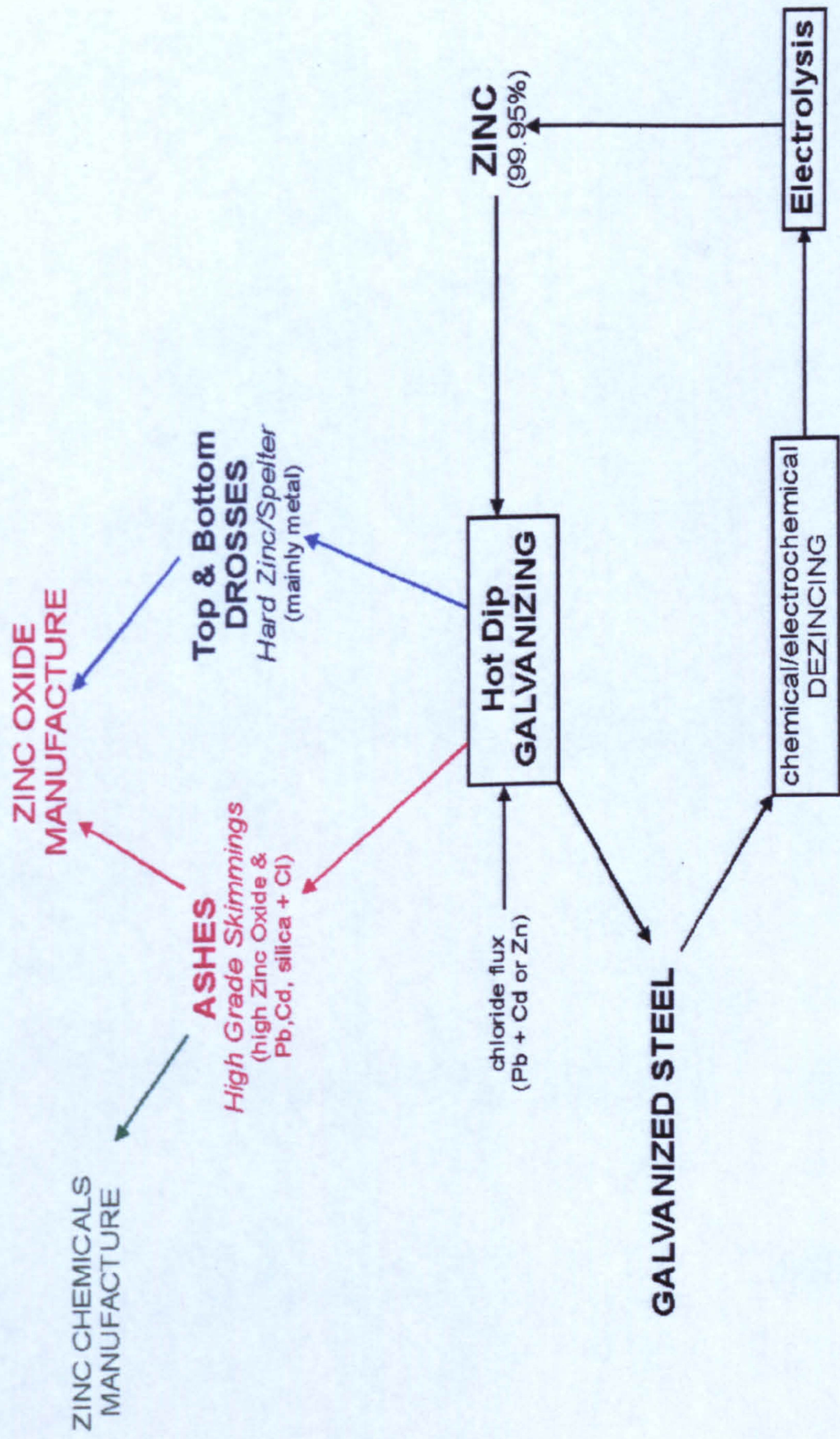


Figure. 5.9 :- Hot dip galvanizing

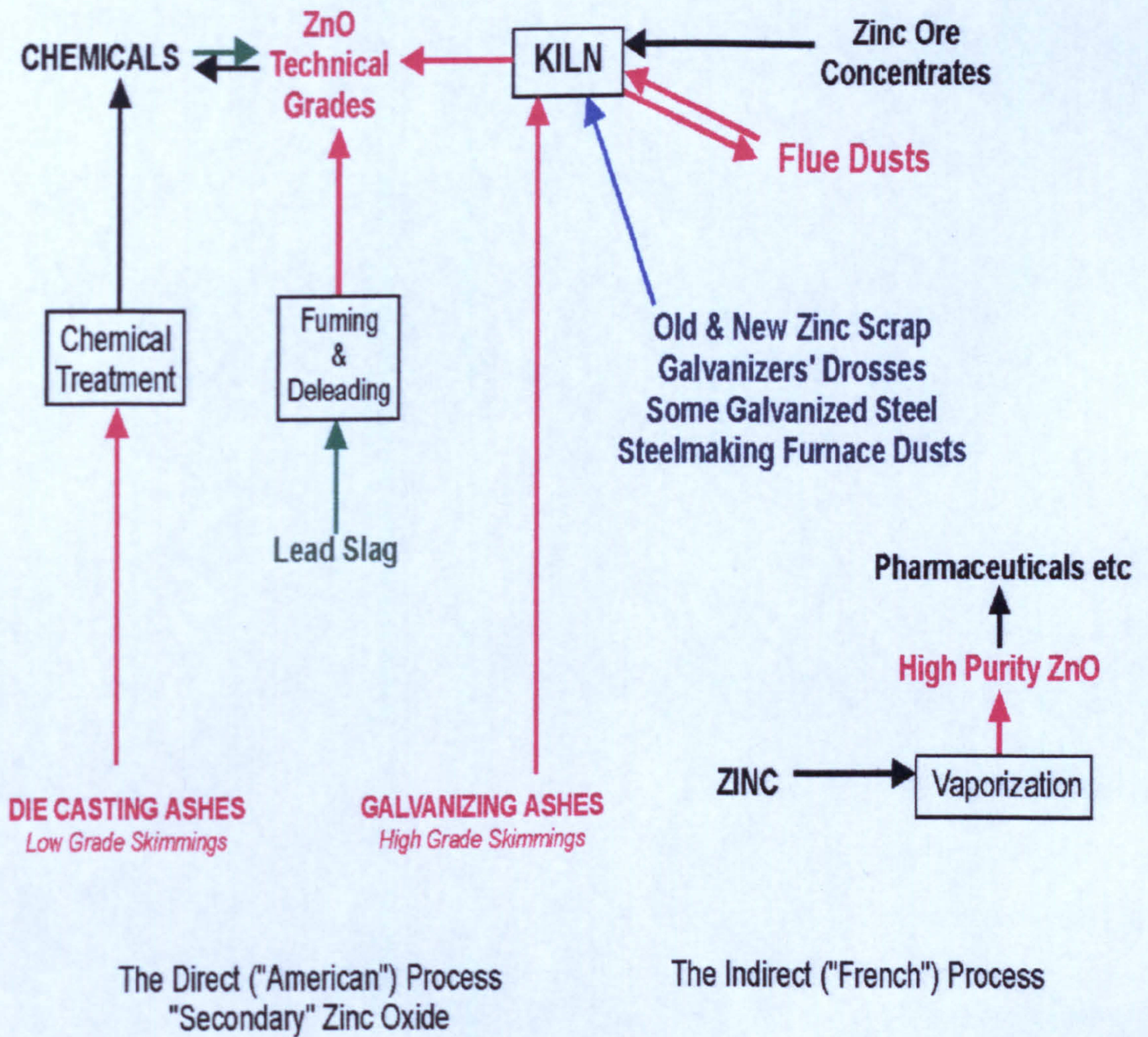


Figure. 5.10 :- Zinc oxide manufacture

such as drosses, skims and ashes. Some of these wastes may be ruled as wastes containing zinc compounds. These materials are of interest because they may contain zinc metal mixed with some compounds such as zinc oxide, carbonate and possibly chloride<sup>[25]</sup>.

The zinc ash forms when metallic zinc in a galvanising bath is oxidised on the surface of the bath. The oxidised material floats on top of the bath and is usually removed by skimming. The zinc ash is a mixture of crude zinc oxide and varying quantities of entrained metallic zinc. There are also various contaminants of other metals such as lead, iron and especially chloride compounds from the use of chloride fluxes in the galvanising process.

A zinc ash is not derived from any process of burning, instead it is a substance which forms as a skim on the top of a molten zinc bath when the molten reacts with air. When the “skim” is removed and left to solidify it looks like ash, but in effect is a mixture of zinc and zinc oxide. It arises on galvanising baths from zinc casting and alloy melting.

Steel mills will also produce blast furnace slag which will contain zinc. Zinc and lead from steelworks dust can be removed and enriched in a secondary dust for further treatment via Waelz Kiln operations. The iron content can be recovered as an internal recyclable product either in oxidic or metallic form. From a steel mill the different types of waste obtained are blast furnace slag, steel mill slag, work rubbish, dust and sludges, mill scale and sludges. The reaction conditions of the Waelz process are such that zinc and lead can be volatilized only if most of the iron oxides are reduced to metal. Slags have been re-used for road construction, as fertilisers, or to a lesser extent, as a lime base for the sinter mix.

The flue dust materials are formed in different pyrometallurgical processes such as zinc smelting and Waelz processes. This finely divided material consists mainly of zinc oxide, but also contains different amounts of other metal oxides (lead, tin, copper and iron). The flue dust also contains different amounts of chlorides, mainly as zinc chloride, and in some cases, small amounts of fluorides.

Zinc dross generated during the melting of zinc cathodes contains appreciable amounts of

metallic zinc contaminated with high levels of chlorides, which prevent its direct use in solution purification at hydrometallurgical electrowinning zinc plants. During melting, dross is generated at the top of the molten bath and is removed manually. The zinc dross is sent to a Pontzen Drum for grinding and classification, and is separated into coarse and fine fractions. The coarse fraction is charged back to the melting furnace and the fine fraction to the roaster complex for mixing with zinc concentrates, for the recovery of zinc.

Since ashes and dusts contain substantially different amounts of chlorides, it is important to recover the zinc from the chloride. In one study this was achieved by leaching the waste with a liquid organic phase containing a cation exchanger<sup>[26]</sup>. This process dealt with the recovery of zinc from solid zinc wastes which contain chlorides as a main impurity. As a result of this chloride content the wastes may not be suited for treatment by a direct leach with sulphuric acid since the chloride will enter the resulting sulphate solutions. Electrowinning of the zinc metal will not tolerate chlorides since even a very small amount of chloride in the sulphate electrolyte will interfere with the electrolysis process.

Rabah and El-Sayed<sup>[27]</sup> found that in Egypt several kinds of zinc containing waste materials were available. These included zinc scrap from spent dry cell batteries, zinc dross resulting from the zinc cathode industry and zinc ash which is obtained from galvanizing processes.

Experiments by the authors were carried out to recover zinc metal from these wastes by leaching processes. The factors affecting the performance of the process such as particle size, temperature, concentration of acid leaching and time were studied. It was found that as the particle size increased so to did the zinc content. This was because the concentration of non-metallic inclusions in the fine-powder are increased than when compared to coarser cuts. In the study by Rabah and El-Sayed it was determined that zinc dross was the poorest material with respect to the zinc content as compared to both zinc ash or zinc scrap. However the zinc dross was rich in chloride, silica and iron. Due to the low zinc content the zinc dross would be preferably leached with acidified leachate such as mineral or organic acid solutions<sup>[27]</sup>.

An investigation carried out by Gupta et al<sup>[28]</sup> looked at a method of dechlorinating zinc dross

so that it could be used as a substitute for zinc dust in solution purification within a zinc electrowinning hydrometallurgical plant. The quality of metallic zinc was important so that it can be used effectively for cementation in process solutions. The zinc present in the dross consisted mainly of oxides, oxy-chlorides, chlorides and metallic forms. The analysis of feed zinc dross contained 51.4% of zinc with traces of iron, copper and cadmium. The output zinc dross had a higher value of zinc at 95.95%.

The chemical and metallurgical nature of zinc gives rise to some industrial uses producing residues that fall under Annex I of the Basel Convention: “Y23: Wastes having as constituents zinc compounds”. In order to place such residues under the control system of the Convention it would be necessary to determine whether these residues exhibit an Annex III characteristic. In the research undertaken, zinc scrap in massive form was not of great concern since this has been classified on the B list by the Basel Convention Technical Working Group (TWG). The concern is primarily with Y23: Wastes having as constituents zinc compounds.

The important zinc recovery techniques are:-

- Distillation of galvaniser’s drosses and ashes, diecastings, diecast drosses, rolled zinc to produce slab zinc, zinc oxide and zinc dust.
- Recycling of brass to brass smelters.
- Conversion of galvanisers’ ashes and non-ferrous flue dust to zinc chemicals, particularly zinc chloride and zinc sulphate.
- Refining of diecastings and diecast drosses to produce zinc alloys.

As in primary refining, pre-refining is also needed in secondary refining. This pre-refining can be mechanical where metallics are separated from skimmings by crushing, screening and separating; hydrometallurgical which involves a wet milling process and pyrometallurgical, a sweating operation which is carried out in a kettle, reverberatory or rotary furnace. After pre-

refining, the remaining contaminants are removed by further refining using either “The Retort Distillation Process” or the “Muffle Furnace Distillation Process”.

In the batch retort distillation process graphite or silicon carbide retorts are connected to a condenser. The retort is charged with galvanisers’ dross, molten metal or sweated ingots and heated until the zinc boils. Pressure is used to force the zinc vapour into the condenser where it is collected as liquid zinc or dust. The slag remaining is periodically removed.

The muffle furnace process consists of a distilling furnace or large retort which is fed through a metal seal. The zinc vapour is continuously fed into a condenser. Again slag must be periodically removed.

The ‘Larvik Process’, which was developed in Norway, recovers zinc from scrap by an electrothermic method. Graphite rings are used to allow current to enter for distillation to occur and the zinc vapour produced is collected in condensers as zinc dust<sup>[23]</sup>.

### **5.3 LEACHING STUDIES OF COPPER AND ZINC CONTAINING SECONDARY MATERIALS**

In this chapter, which has highlighted the potential sources of secondary materials for the copper and zinc industries, the leaching of Cu and Zn from these secondary arisings are reported. In chapter 6 this work is extended to include leaching studies of Cu, Zn, Pb and Cd from inorganic compounds.

Standard leach procedures were followed and these are described in the methodology section below.

#### **5.3.1 Experimental methodology**

As mentioned previously the Basel Convention lists materials with intrinsically hazardous properties that would be subject to a ban on transfrontier movement. The list includes wastes containing the following metals and their compounds:- beryllium, arsenic, selenium, cadmium, antimony, tellurium, mercury, thallium and lead and the compounds of copper zinc and

hexavalent chromium. The intrinsic hazardous properties considered include:- explosive, flammability, oxidising, acute poisonous, corrosive, toxic and ecotoxic. For the secondary metal industry most of the problems are concerned with toxicity and a distinction needs to be drawn between the intrinsic toxicity of the metal in a form that is bioavailable and the risks associated with that metal becoming bioavailable in any ecosystem.

It is important for the secondary metals industry to recognise that many scraps and residue traded do contain intrinsically hazardous components that could cause environmental or health damage if released by poor recovery and recycle processes.

The research in this chapter was concerned with the leaching of industrial samples, such as zinc and copper dross, skimmings, slag and ash using different leach liquors which simulate a variety of environmental conditions and scenarios.

The leach liquors used were 0.5 M acetic acid, 0.01 M calcium chloride, 0.1M hydrochloric acid/sodium chloride and 2 M nitric acid. The experimental conditions for each of the leach liquors were as follows:-

#### ***Acetic Acid Extraction***<sup>[29]</sup>

For this leach procedure, a modified version of the Canadian Toxic Characteristic Leaching Procedure (TCLP) method was used. 10g of sample was placed in a 250 ml stoppered conical flask to which 160 ml of de-ionised water was added. The flask was shaken using a mechanical shaker (Griffin) at 10 revs/min After shaking the sample for 15 minutes, the pH of the solution was measured.

If the pH of the solution was greater than 5.2 then sufficient 0.5 M acetic acid was added to reduce and maintain the pH at  $5.0 \pm 0.2$ . The sample was then shaken for 24 hours with the pH being monitored after 1, 3 and 6 hours with a final pH check after 22 hours. The pH was adjusted to 5.2 by addition of drops of 0.5 M acetic acid but, if it was below 4.8 then 40 ml of de-ionised water was added and the pH adjusted. After 24 hours the experiment was stopped, the solution filtered and the filtrate transferred to a 250 ml volumetric flask and sufficient de-



ionised water added to take the volume up to 250 ml. When filtration was slow, solid and liquid phases were separated by centrifugation followed by filtration.

The solid and liquid phases were then separated by centrifuge and filtration to obtain approximately 100 ml of solution for analysis.

### ***Calcium Chloride Extraction***<sup>[30]</sup>

A single extraction with 0.01 M CaCl<sub>2</sub> has been proposed and the procedure followed exactly as a cheap and simple method for the determination of the bioavailability of heavy metals in soils. This method was found to give a better guide to the bioavailability of the metals than a total soil analysis.

In a 250 ml conical flask, 10 g of sample was placed to which 100 ml of 0.01M CaCl<sub>2</sub> was added. The sample was shaken for 2 hours after which the pH was only measured but not adjusted in any way. The solid and liquid fractions were separated by centrifugation and filtration and the filtrate transferred to a 100 ml volumetric flask and sufficient de-ionised water added to take the volume up to 100 ml.

### ***Hydrochloric Acid Extraction***<sup>[31]</sup>

This leach test was carried out by placing 0.5 g of sample into a 250 ml conical flask. To this was added 100 ml of leach solution, a mixture of 0.1 M hydrochloric acid and 0.1 M sodium chloride. The sample was shaken for 1 hour and as previously stated, centrifugation and filtration was used to separate the solid and liquid phases so that ample solution could be obtained for analysis.

### ***Nitric Acid Extraction***<sup>[32, 33, 34]</sup>

This particular test was found to be an aggressive extraction because of the strength of the acid used. After placing 10 g of sample into a stoppered 250 ml conical flask, 100 ml of 2M nitric acid was added. The sample was shaken for 1 hour. Once again, the mixture was centrifuged and filtered and the filtrate was transferred to a 100 ml volumetric flask and sufficient de-ionised water was added to take the volume up to 100 ml.

For each extraction procedure the samples were analysed by ion chromatography using a Dionex 2010i. This is a more efficient method of analysis for identifying a number of elements.

### 5.3.1.2 Samples

The samples of Cu and Zn secondary materials that have been investigated include (Table 5.2),

<b>Table 5.2:- Cu and Zn secondary materials provided by industry</b>		
<b>Sample</b>	<b>Sample name</b>	<b>Supplier</b>
<b>Cu Dross</b>	<b>MHD/BZL BZL Normal</b>	<b>Britannia Refined Metals</b>
<b>Cu Slags</b>	<b>CHG 172/1 CHG 172/2 CHG 343</b>	<b>Hüttenwerke Kayser, AG</b>
<b>Cu Residues</b>	<b>109722/1 104922/1 104922/2a 104922/2b 109059/1</b>	<b>A &amp; H Knight Ltd</b>
<b>Zinc Residues</b>	<b>Leach Residue Steelworks Dust Cu Refinery Bag Filter Dust</b>	<b>Britannia Zinc</b>

## 5.4 RESULTS AND DISCUSSION

The results of these leaching studies are presented both in tabular and graphical form. The tables contain details of the sample, the leach liquor and the source of the concentration of the metal leached. Those coloured in red represent copper and zinc which were the primary metals of concern, along with the other metals which were also leached. The graphical representation show the same information in the form of bar charts.

### 5.4.1 Copper Secondary Materials

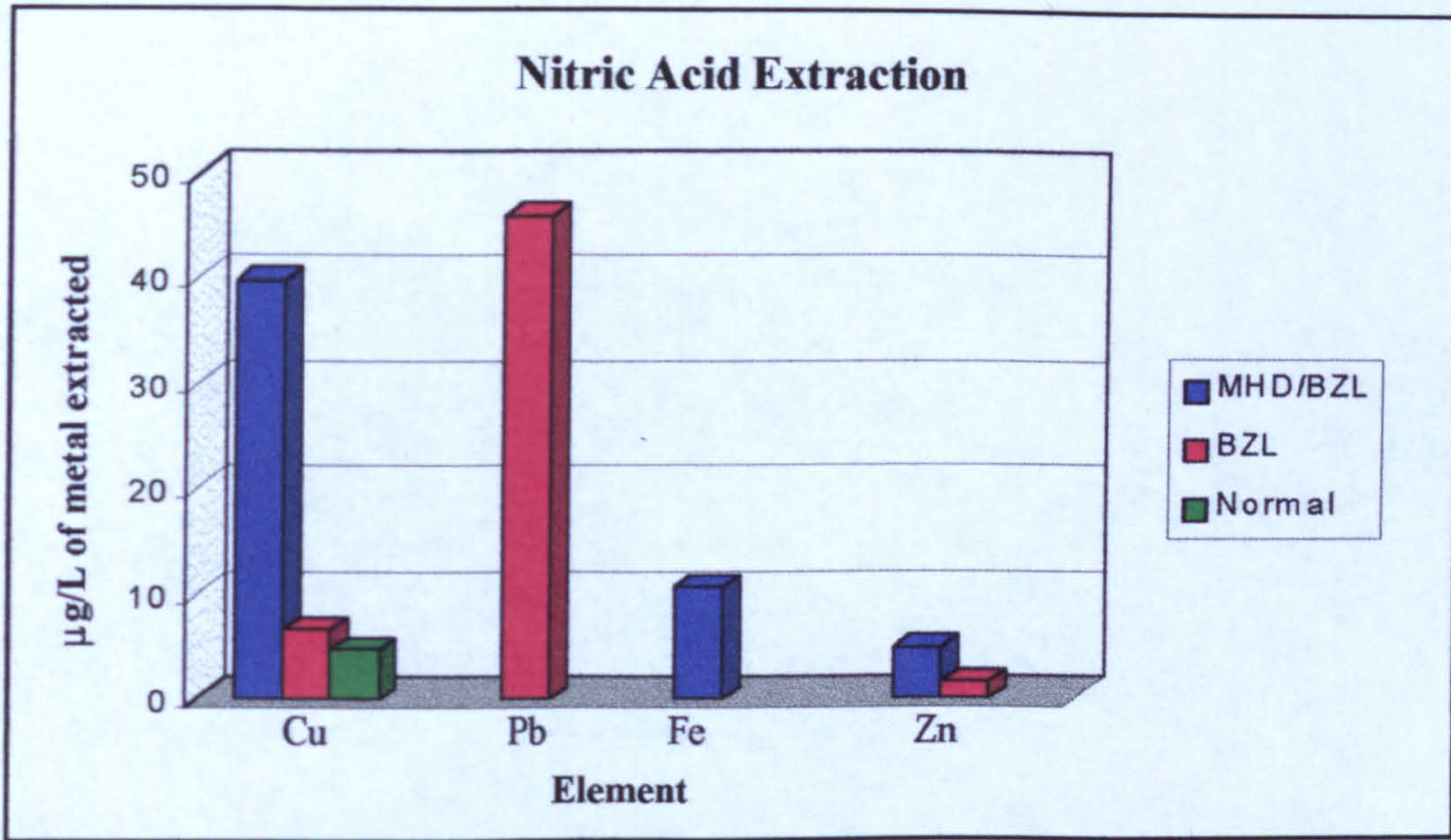
#### *Leaching of Copper Dross Samples*

Three samples of copper dross, MHD/BZL, BZL and Normal, were leached under each of the

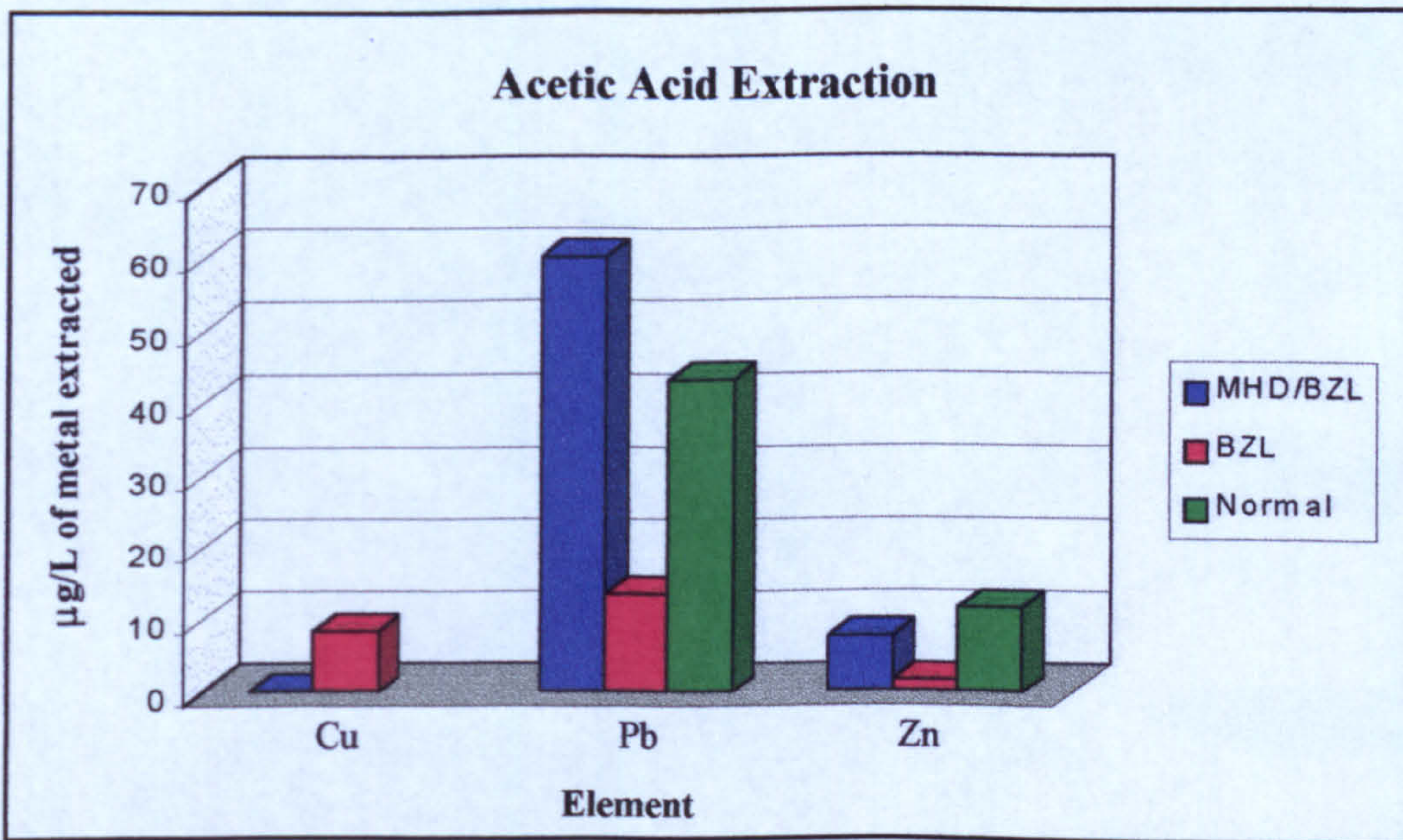
leach conditions described (Table 5.3). The nitric acid extraction test proved to be the most vigorous since high concentrations of Cu and Pb were extracted with this leach test [Figure. 5.11]. However, the acetic acid leach procedure also extracted large amounts of Pb and Zn. A higher concentration of Pb and Zn were extracted by the acetic acid with 60.1  $\mu\text{g/L}$  and 7.9  $\mu\text{g/L}$  respectively for the sample MHD/BZL [Figure. 5.12]. Only 4.9  $\mu\text{g/L}$  of Zn was leached from a sample of MHD/BZL with nitric acid.

**Table 5.3:- Extraction of Copper Dross**

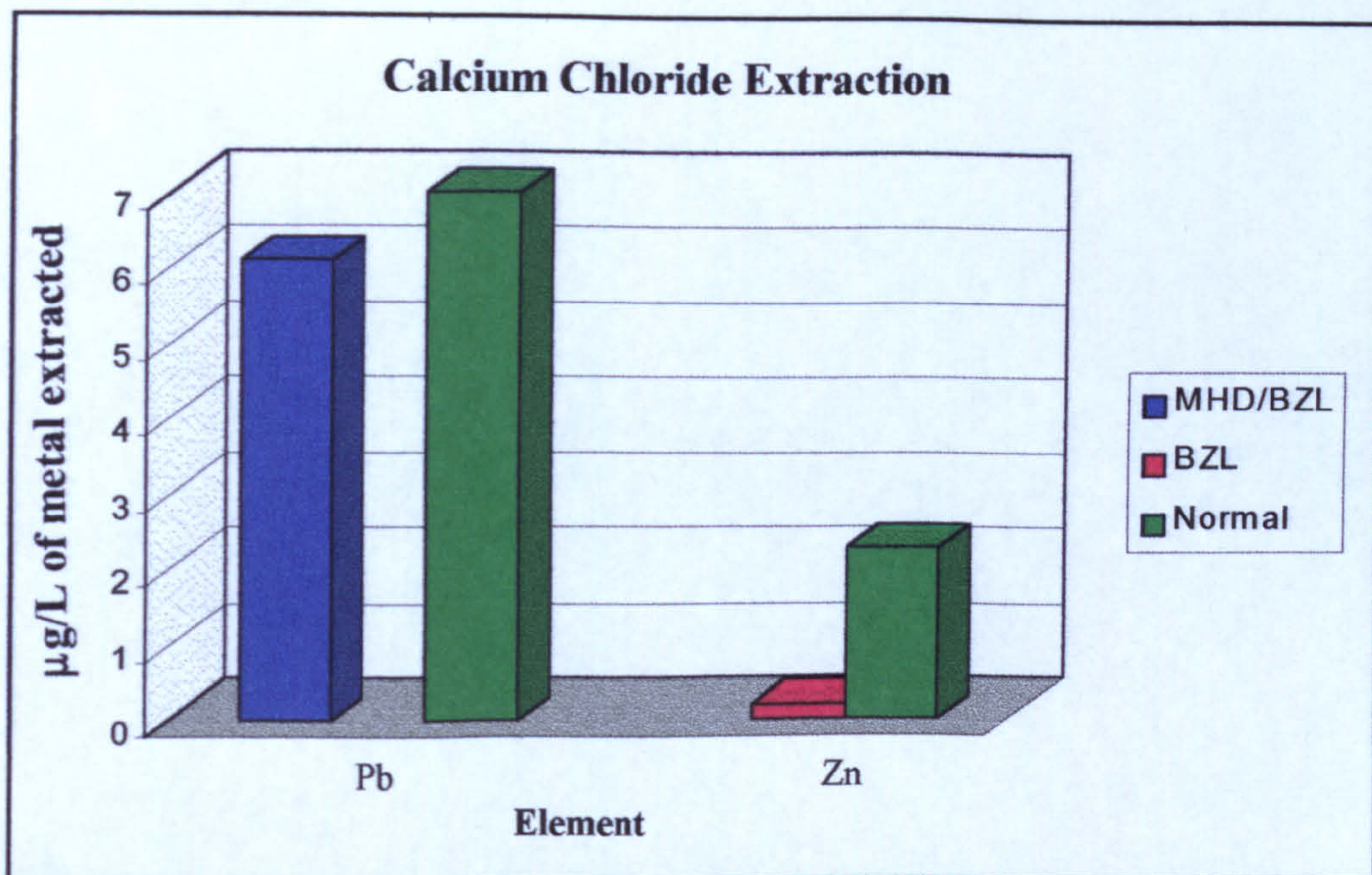
Sample No.	Leach Liquor	Concentration of metal leached, $\mu\text{g/L}$ (Amount of metal extracted, mg/g)			
		Cu	Pb	Fe	Zn
MHD/BZL	CaCl <sub>2</sub>	-	6.1 (0.1)	-	-
BZL		-	-	-	0.2 (trace)
NORMAL		-	7.0 (0.1)	-	2.3 (trace)
		Cu	Pb	Fe	Zn
MHD/BZL	CH <sub>3</sub> COOH	0.1 (0.2)	60.1 (119.0)	-	7.9 (15.6)
BZL		10.1	15.2	-	0.3
NORMAL		-	43.4 (115.0)	-	11.8 (23.3)
		Cu	Pb	Fe	Zn
MHD/BZL	HNO <sub>3</sub>	39.8 (158.8)	-	10.6 (40.5)	4.9 (19.6)
BZL		6.6 (92.2)	46.0 (101.9)	-	1.7 (4.7)
NORMAL		4.7 (137.09)	-	-	-
		Cu	Pb	Fe	Zn
MHD/BZL	HCl/NaCl	1.1 (21.7)	10.3 (201.7)	-	1.9 (36.1)
BZL		5.4 (216.2)	6.3 (251.1)	-	0.9 (34.3)
NORMAL		-	-	-	2.43 (47.6)



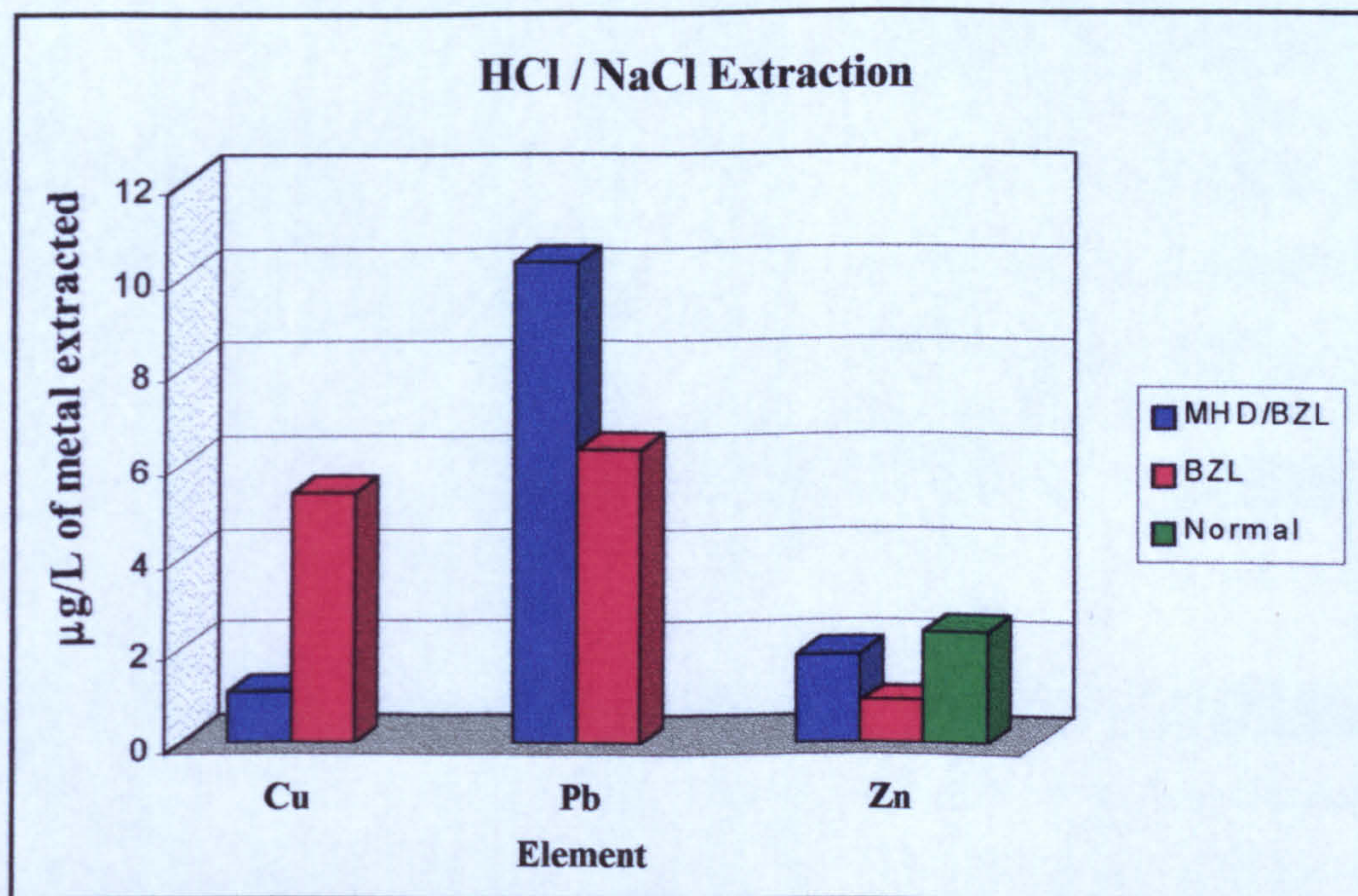
**Figure. 5.11:- Leaching of Copper Dross with nitric acid.**



**Figure. 5.12:- Leaching of Copper Dross with acetic acid.**



**Figure. 5.13:- Leaching of Copper Dross with calcium chloride.**



**Figure. 5.14:- Leaching of Copper Dross with HCl / NaCl.**

The other two leach liquors, calcium chloride [Figure. 5.13] and the HCl/NaCl mixture extracted Pb and Zn, from MHD/BZL, with levels of 6.1 and 10.3  $\mu\text{g/L}$  of Pb respectively and only 1.9  $\mu\text{g/L}$  of Zn extracted using the saline mixture [Figure. 5.14].

### ***Leaching of Copper Slags***

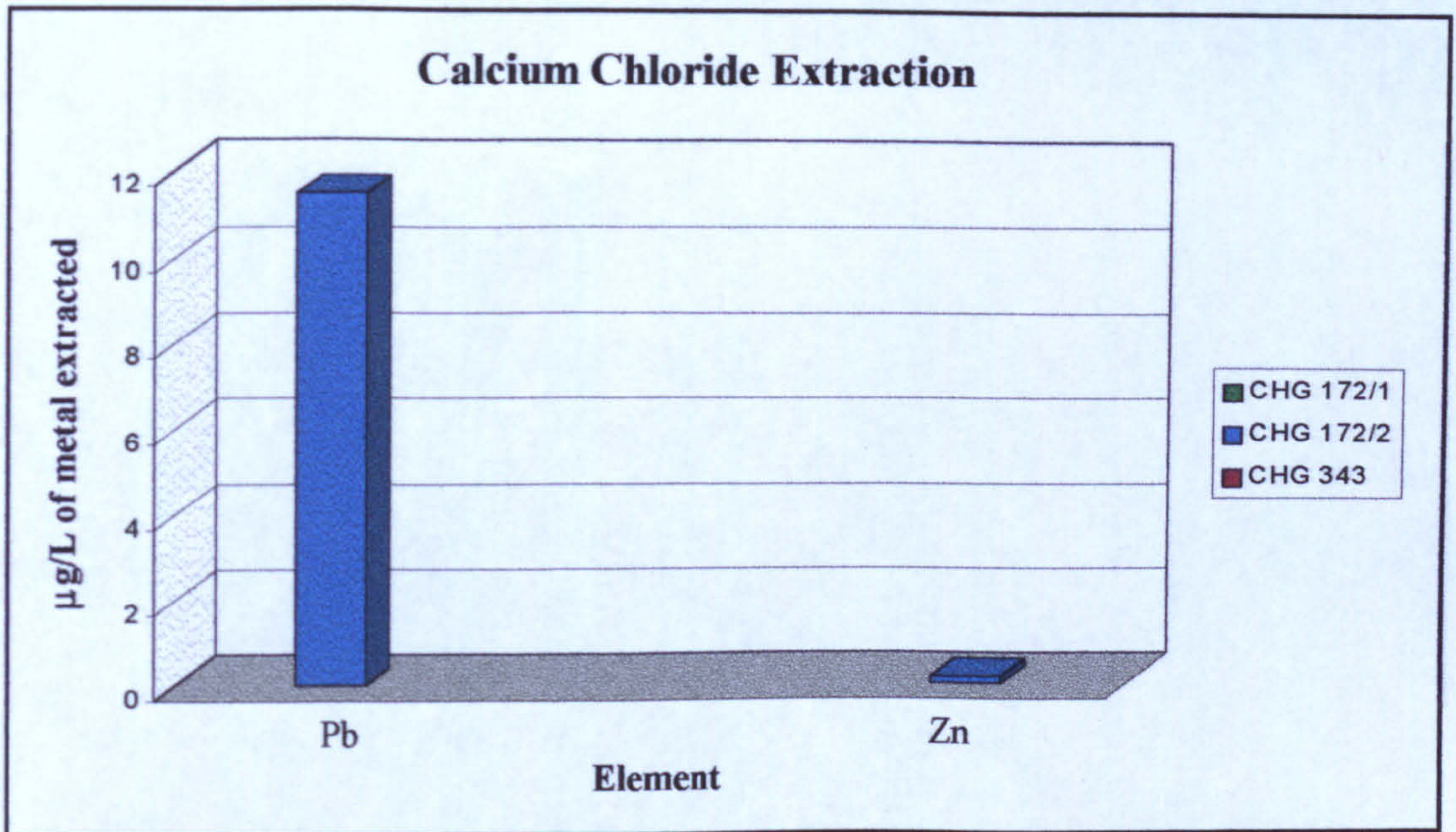
The copper slags which were provided consisted of three different samples, CHG 172/1, CHG 172/2 and CHG 343 (Table 5.4). Each of these three samples was, in turn, leached with the four different leach liquors (Table 5.2). The calcium chloride extraction only leached out two elements, from sample CHG 172/2, Pb at a concentration of 11.5  $\mu\text{g/L}$  and Zn at 0.2  $\mu\text{g/L}$  [Figure. 5.15].

The acetic acid extraction leached out six different elements for sample CHG 172/1, with Pb being the highest at a concentration of 100.7  $\mu\text{g/L}$ . The other two samples also showed high concentrations of Pb compared to other elements such as Cu, Ni, Cd and Mn which were also extracted but in lower concentrations [Figure. 5.16].

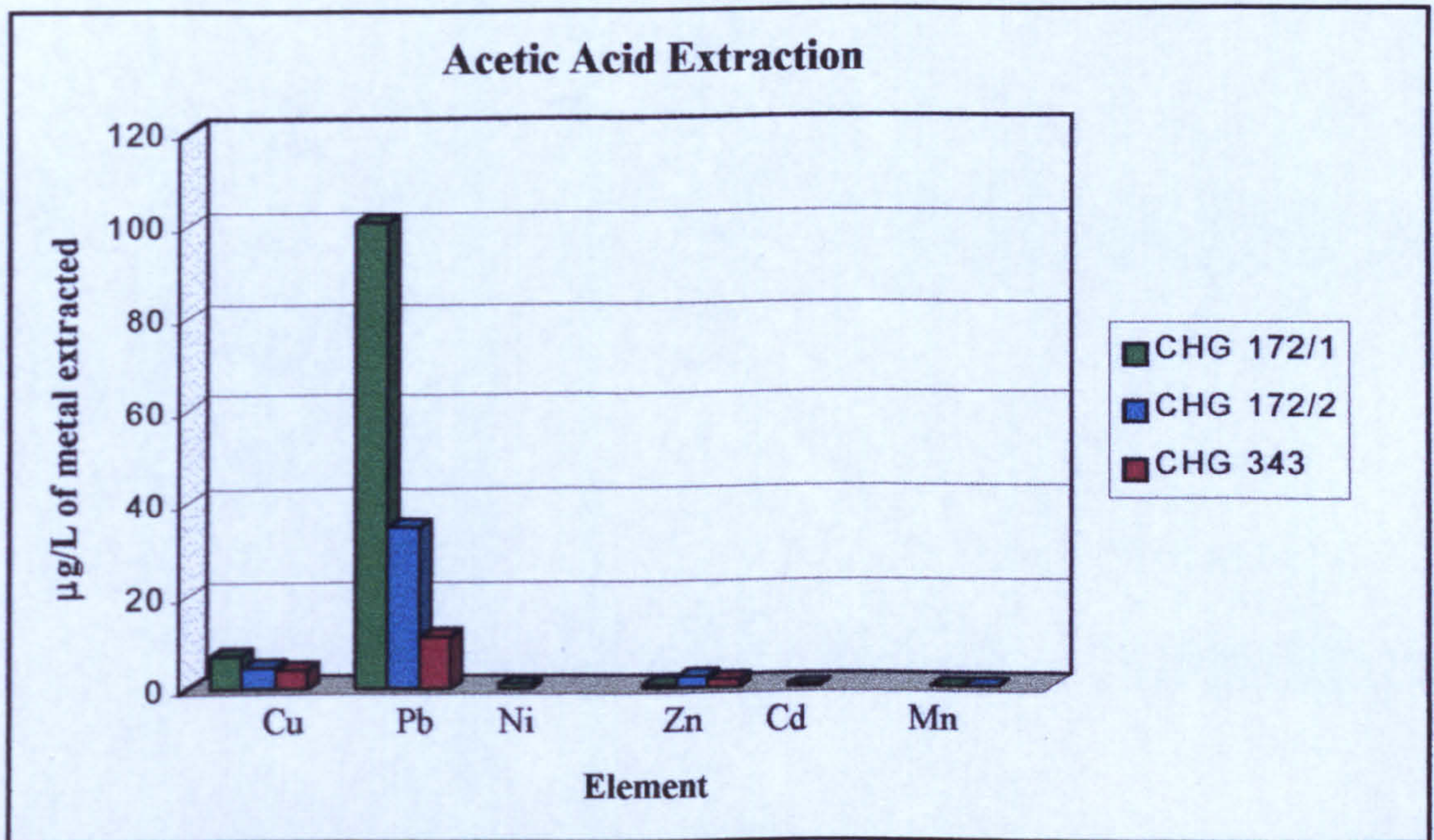
When leaching with nitric acid it was found that the highest concentration of Cu and Zn were leached into solution from sample CHG 343. From this sample, 340.46  $\mu\text{g/L}$  were leached and 3.41 mg/g of Cu were extracted and 54.40  $\mu\text{g/L}$  of Zn were leached into solution and the corresponding amount of zinc extracted from this sample was 0.54 mg/g. Sample CHG 172/1 leached the lowest concentration of Cu at 186.18  $\mu\text{g/L}$  whereas sample CHG 172/2 leached 311.40  $\mu\text{g/L}$  of Cu. A higher concentration of Zn was extracted from sample CHG 172/1 compared to sample CHG 172/2. The amount of Zn extracted from sample CHG 172/1 was 0.36 mg/g and the amount of Zn extracted from sample CHG 172/2 was 0.29 mg/g [Figure. 5.17].

Under leach conditions of HCl/NaCl the majority of the elements, Cu, Pb, Fe, Zn and Mn, were leached for each of the three samples provided. High concentrations of Pb were leached out with 61.2, 13.5 and 28.2  $\mu\text{g/L}$  of Pb being extracted from CHG 172/1, CHG 172/2 and CHG 343 respectively [Figure. 5.18].

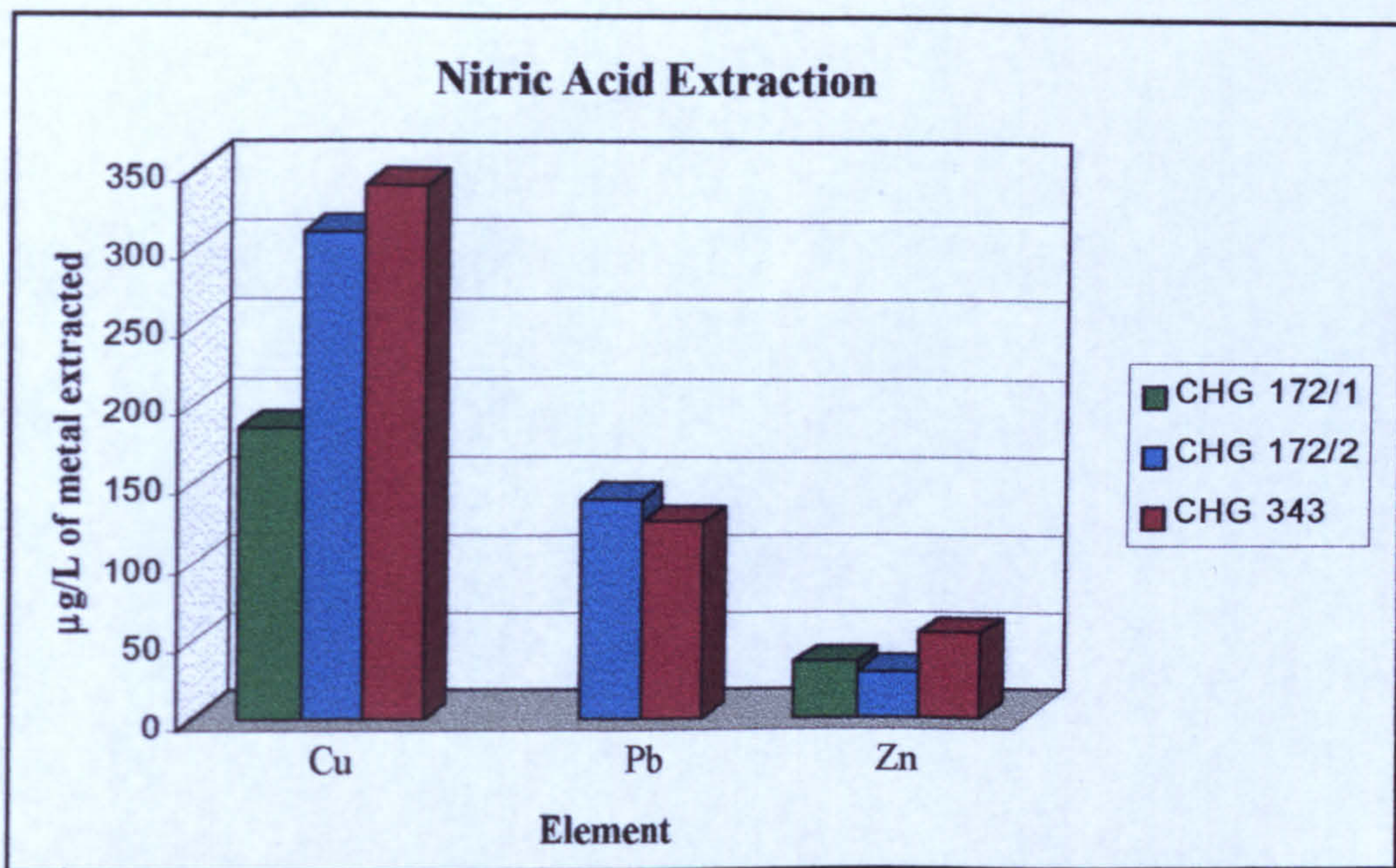
Since the calcium chloride extraction was not a very vigorous test, relatively few elements were



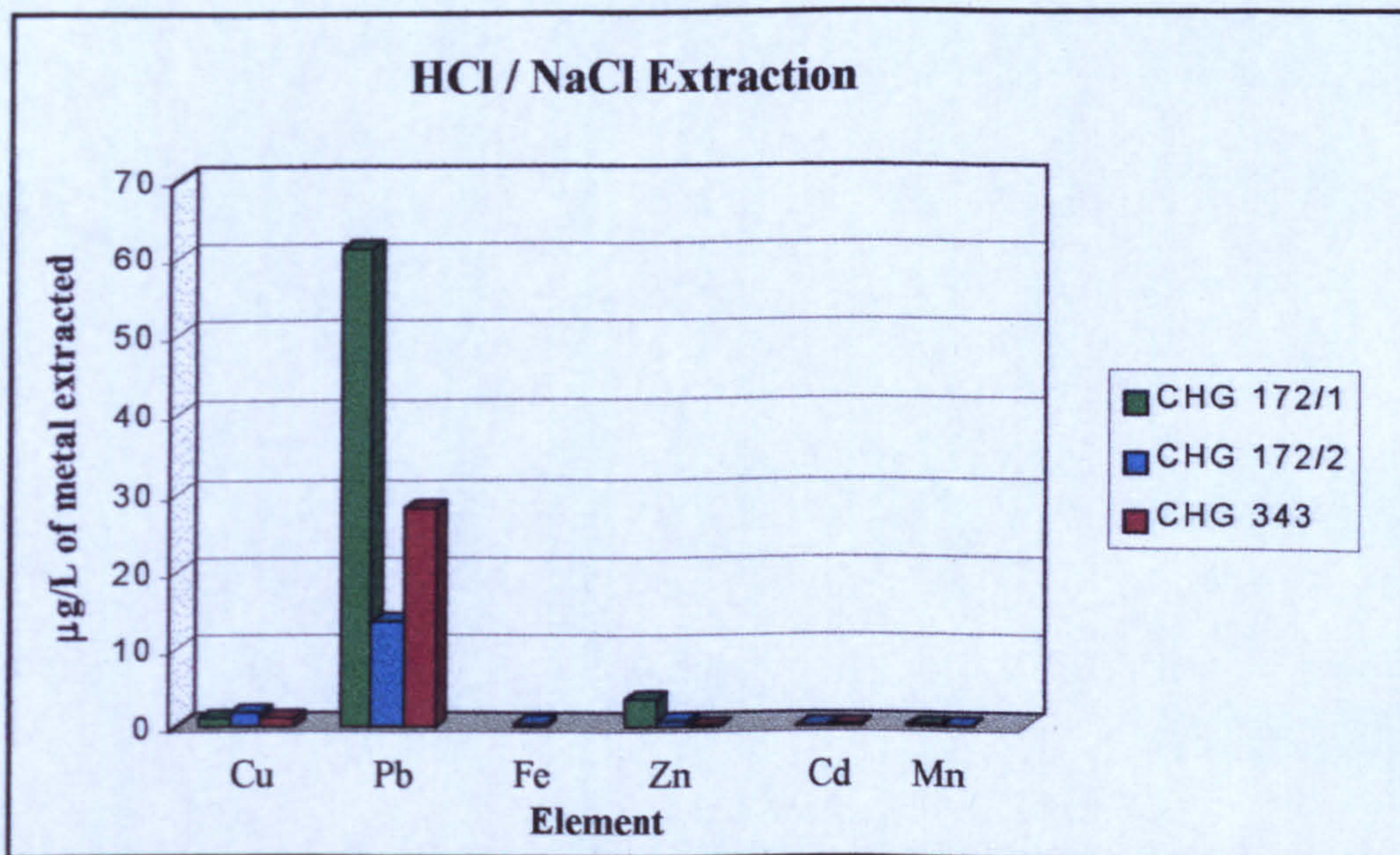
**Figure. 5.15:- Leaching of Copper Slags with calcium chloride.**



**Figure. 5.16:- Leaching of Copper Slags with acetic acid.**



**Figure. 5.17:- Leaching of copper slags with nitric acid.**



**Figure. 5.18:- Leaching of Copper Slags with HCl / NaCl.**



extracted. From the results obtained for leaching the copper dross with  $\text{CaCl}_2$  it was observed that relatively few elements were extracted and so no further leaching studies were carried out using this leach medium.

**Table 5.4:- Extraction of Copper Slags**

Sample No.	Leach Liquor	Concentration of metal leached, $\mu\text{g/L}$ (Amount of metal extracted, mg/g)					
		Cu	Pb	Ni	Zn	Cd	Mn
CHG 172/1	$\text{CaCl}_2$	-	-	-	-	-	-
CHG 172/2		-	11.5 (0.1)	-	0.2 (0)	-	-
CHG 343		-	-	-	-	-	-
		Cu	Pb	Ni	Zn	Cd	Mn
CHG 172/1	$\text{CH}_3\text{COOH}$	6.8 (1.1)	100.7 (16.7)	0.8 (trace)	0.5 (0.1)	0.2 (trace)	0.1 (trace)
CHG 172/2		4.6 (4.6)	34.8 (2.1)	-	2.2 (0.2)	-	0.1 (trace)
CHG 343		4.2 (3.0)	11.2 (0.3)	-	1.8 (0.1)	-	-
		Cu	Pb	Ni	Zn	Cd	Mn
CHG 172/1	$\text{HNO}_3$	186.18 (1.86)	-	-	36.16 (0.36)	-	-
CHG 172/2		311.40 (3.12)	139.57 (1.40)	-	29.48 (0.29)	-	-
CHG 343		340.46 (3.41)	126.33 (1.26)	-	54.40 (0.54)	-	-
		Cu	Pb	Fe	Zn	Cd	Mn
CHG 172/1	$\text{HCl/NaCl}$	1.1 (5.3)	61.2 (294.6)	-	3.5 (16.6)	trace (0.2)	0.2 (0.8)
CHG 172/2		1.8 (217.1)	13.5 (66.9)	0.5 (2.5)	0.8 (3.8)	0.1 (0.7)	0.1 (0.4)
CHG 343		1.1 (138.7)	28.2 (139.0)	-	0.2 (1.0)	0.2 (0.7)	-

### Leaching of Copper Residues

#### Sample 109722/1

The copper residues provided by A & H Knight Ltd were supplied as five batches containing a

different number of samples. The samples within each batch were either mets or fines. The first batch, 109722/1, contained two samples each of which, was extracted with acetic acid, nitric acid and HCl/NaCl (Table 5.5). The saline solution extracted very high concentrations of Cu, Zn and Mn giving values of 39431.9 µg/L of Cu, 7402.6 µg/L of Zn and 316.2 µg/L of Mn [Figure. 5.19]. With the nitric acid extraction, small amounts of Ni were extracted from each of the two samples, with the fines giving almost fourteen times more Ni than the mets. Overall, with the nitric acid leach test it was observed that the fines contained higher concentrations of Cu, Ni, Zn and Mn than those in the mets [Figure. 5.20]. This trend was also observed under acetic acid leach conditions where a large proportion of Zn and Mn of 125.2 µg/L and 105.0 µg/L was extracted respectively [Figure. 5.21].

**Table 5.5: Extraction of copper residues (109722/1)**

Sample No.	Leach Liquor	Concentration of metal leached, µg/L (Amount of metal extracted, mg/g)					
		Cu	Pb	Fe	Zn	Co	Mn
mets 71.17%	CH <sub>3</sub> COOH	3.2 (0.1)	45.2 (1.1)	6.3 (0.2)	4.9 (0.1)	-	2.1 (0.1)
fines 22.57%		4.2 (0.1)	-	38.6 (1.0)	125.2 (3.1)	-	105.0 (2.6)
		Cu	Pb	Ni	Zn	Cd	Mn
mets 71.17%	HNO <sub>3</sub>	4.6 (1.0)	33.7 (6.7)	1.1 (0.2)	2.1 (0.4)	-	0.33 (0.1)
fines 22.57%		98.7 (19.5)	-	14.7 (2.9)	113.1 (22.4)	-	59.6 (11.8)
		Cu	Pb	Fe	Zn	Cd	Mn
mets 71.17%	HCl/NaCl	39431.9 (393.9)	-	-	7402.6 (73.9)	-	316.2 (3.16)
fines 22.57%		34528.8 (344.9)	-	-	6634.1 (66.3)	-	2156.8 (21.5)

### Sample 104922/1

The second batch of copper residues (104922/1) contained three samples of mets each of different composition (mets 1, 2, 3) (Table 5.6). High concentrations of Cu, Fe and Zn were

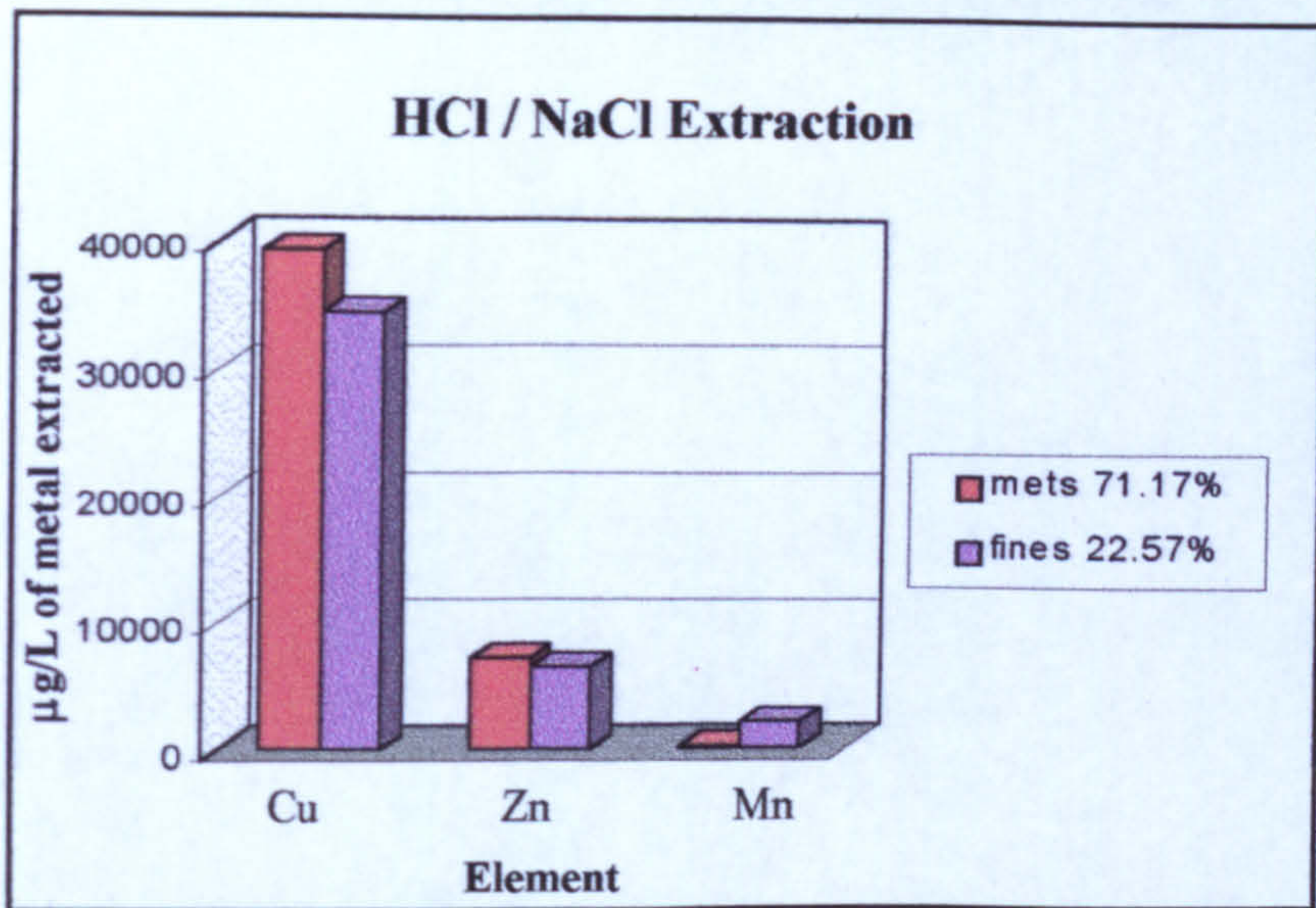


Figure. 5.19:- Leaching of copper residues 109722/1 with HCl / NaCl.

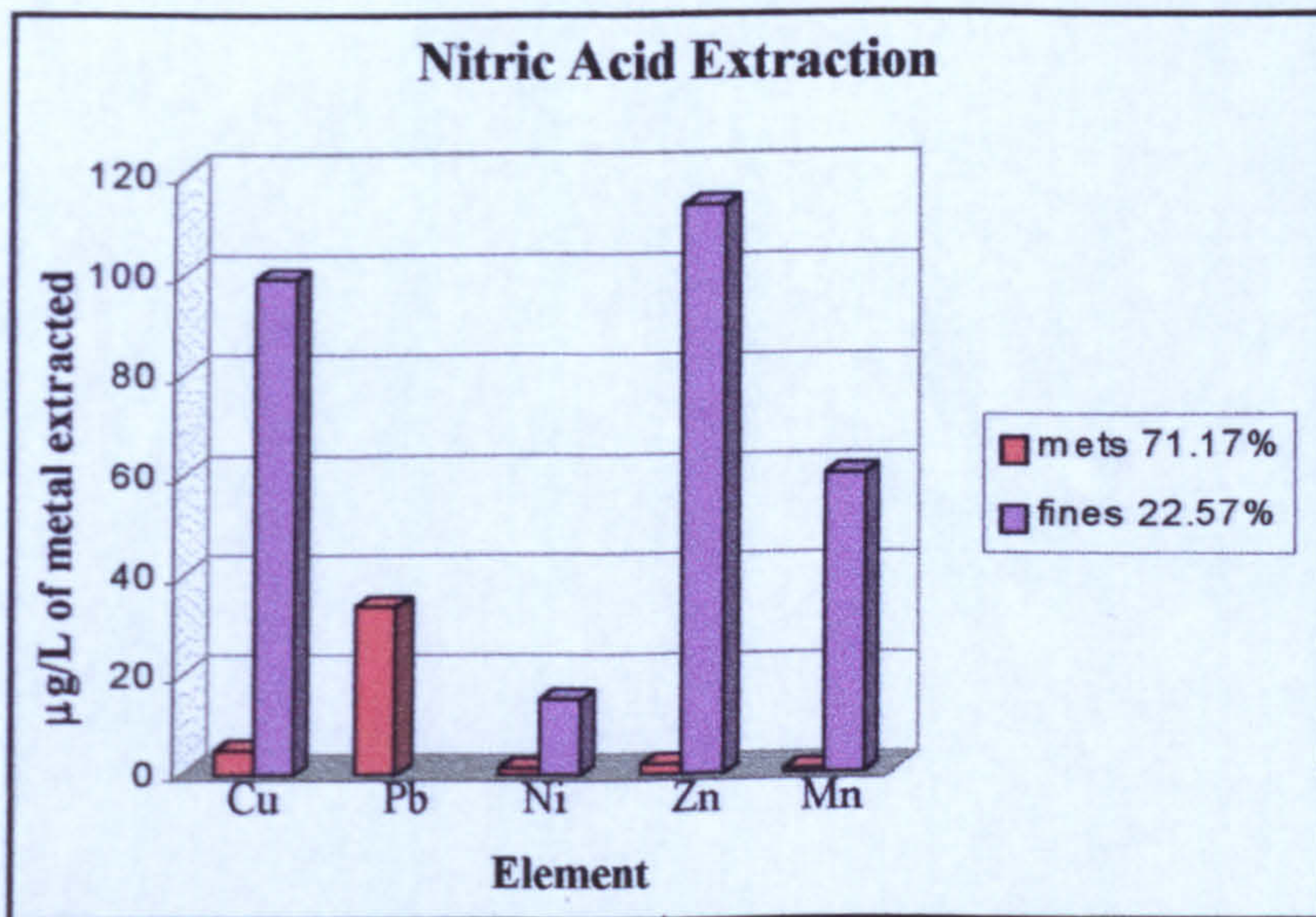


Figure. 5.20:- Leaching of copper residues 109722/1 with nitric acid.

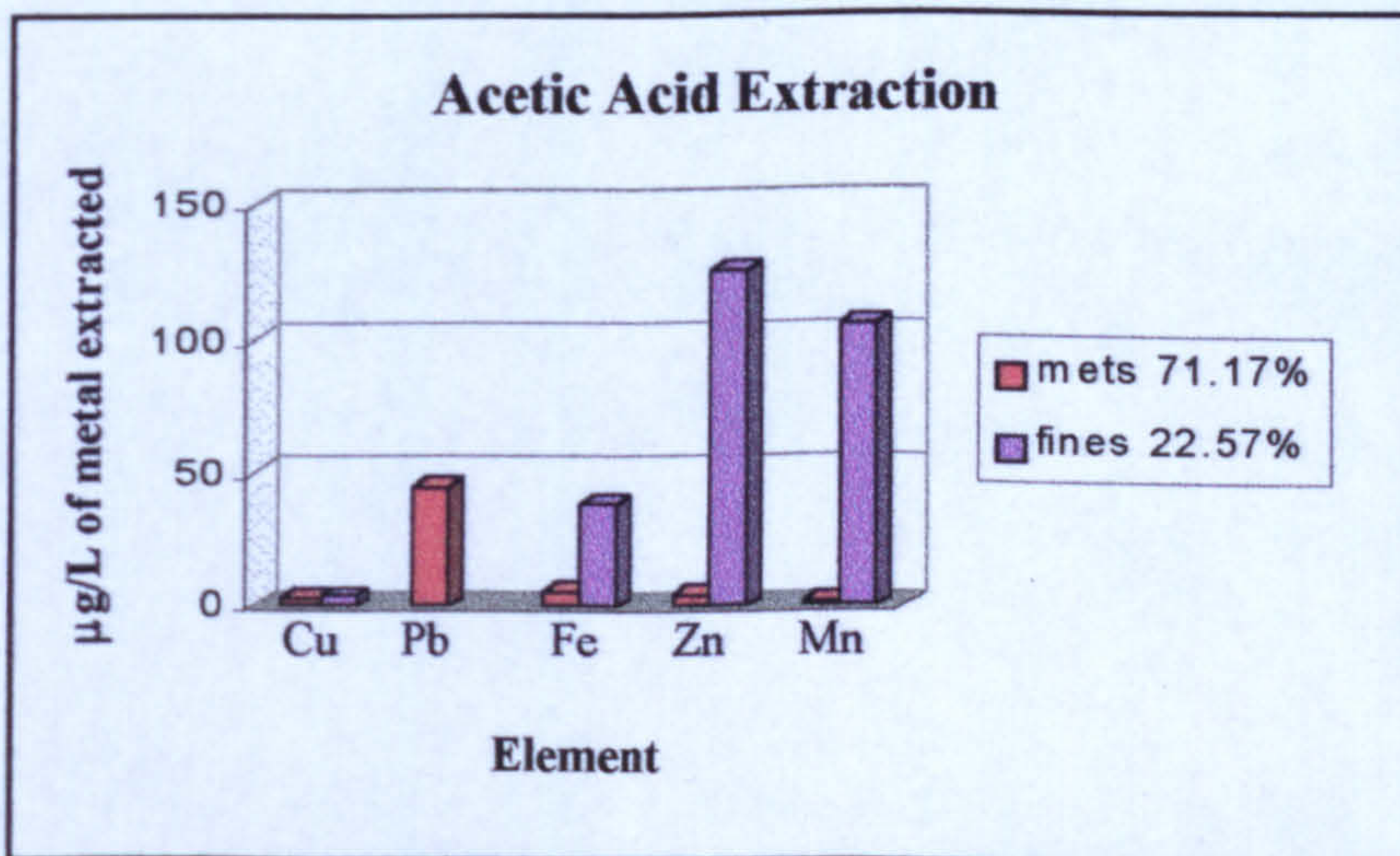


Figure. 5.21:- Leaching of copper residues 109722/1 with acetic acid.

leached using the nitric acid leach test. With this leach test, it was calculated that mets 3 contained the highest concentration of Cu, Fe and Zn compared to the other two samples of mets 1 and mets 2 [Figure 5.22].

When the samples were extracted with acetic acid, the highest concentration of Pb extracted was found in the mets 3 sample. There was a large concentration of iron in the mets 1 and mets 2 samples as was the concentration of Zn where 2.9 µg/L was extracted for mets 1 using this leach test, and subsequently mets 2 and 3 contained 7.5 µg/L and mets 3 consisted of the lowest amount of Zn with 2.1 µg/L [Figure. 5.23].

The final leach test carried out on these samples was the HCl/NaCl procedure and it was found that mets 3 leached a very high fraction of Pb compared to the other two samples. From mets 1 it can be seen that other than Pb, Cu was the next most dominant metal to be leached from the sample, extracting 10.5 µg/L, whereas mets 2 and mets 3 gave Cu concentrations of 3.9 and 1.9 µg/L. All three samples showed the presence of Fe, Zn and Ni, with mets 1 also containing traces of Ni and Mn [Figure. 5.24].

#### ***Sample 104922/2a***

This batch of samples consisted mainly of fines with differing compositions as can be seen from Table 5.7. With the strong, nitric acid leach test large quantities of Cu, Fe and Zn were being leached out. Since fines 2 was of 56.26% composition, the greatest concentration of metals were leached from this sample with the nitric acid leach test. Zinc leached out the most at a concentration of 2,157,502.0 µg/L which was a value well above the trigger guide level of 25 µg/L. Copper was also leached out in a very high concentration from this sample at 171,025.9 µg/L. This was noted to be above the trigger guide level set for Cu according to the Basel Convention. Fines 1 had a composition of 1.77% and fines 3 consisted of 2.22% but from fines 1, 77948.7 µg/L of copper was leached out whereas with fines 3, 7937.2 µg/L of copper was leached out. The same was true of zinc where a higher concentration of this metal was leached from fines 1 compared to fines 2 [Figure. 5.25].

The acetic acid leach test extracted a large concentration of zinc from the fines 3 sample with

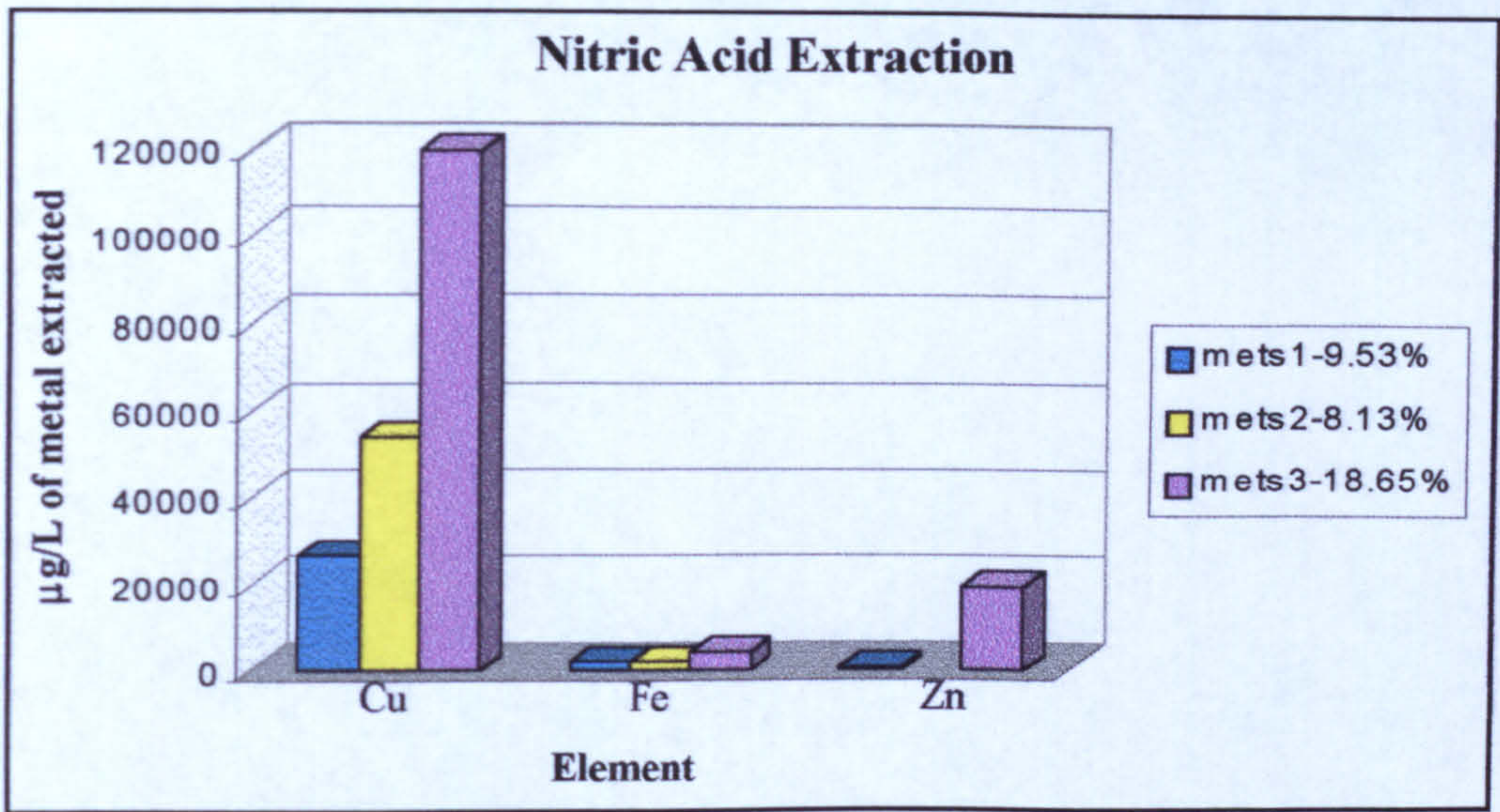


Figure. 5.22:- Leaching of copper residues 104922/1 with nitric acid.

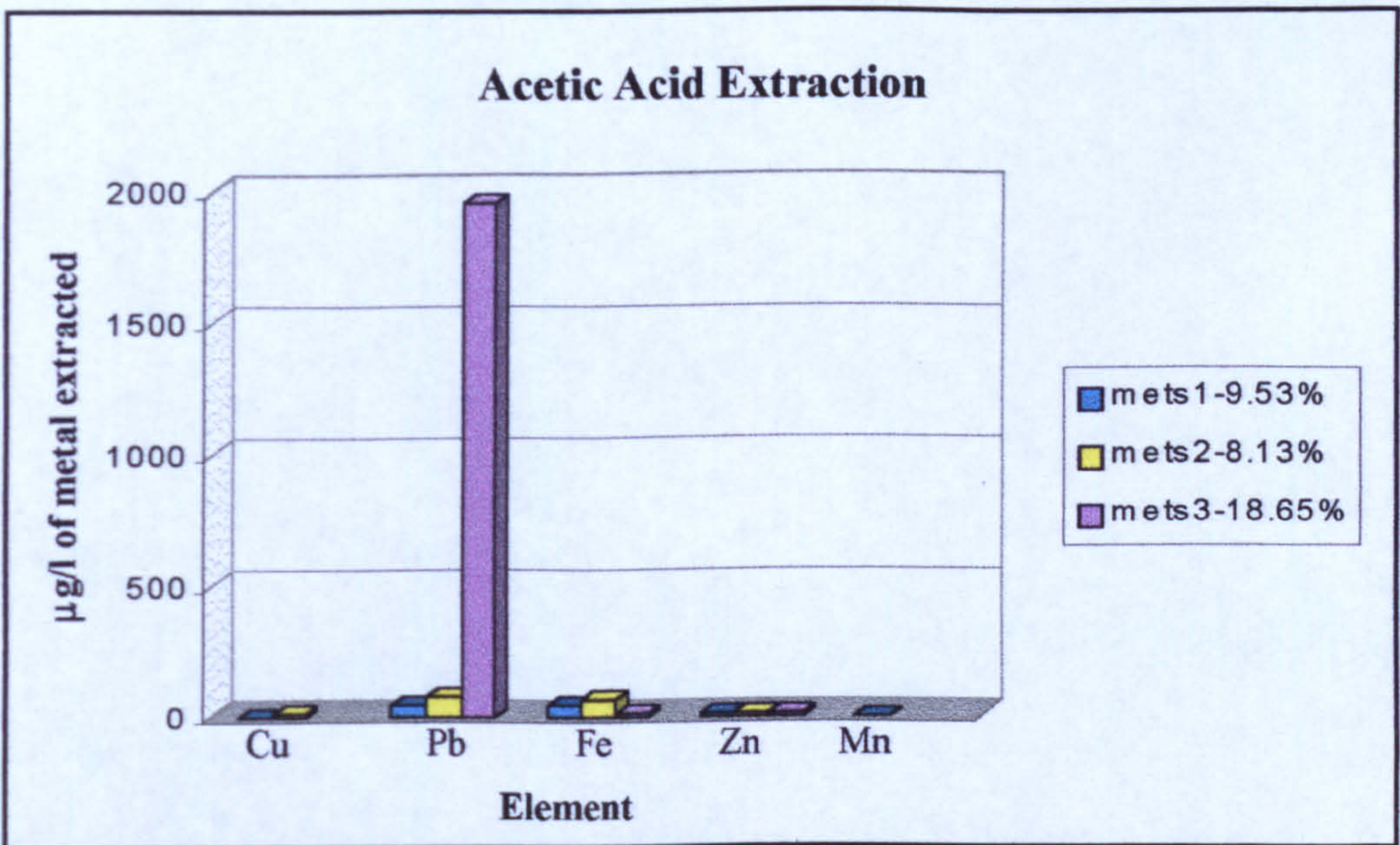


Figure. 5.23:- Leaching of copper residues 104922/1 with acetic acid.

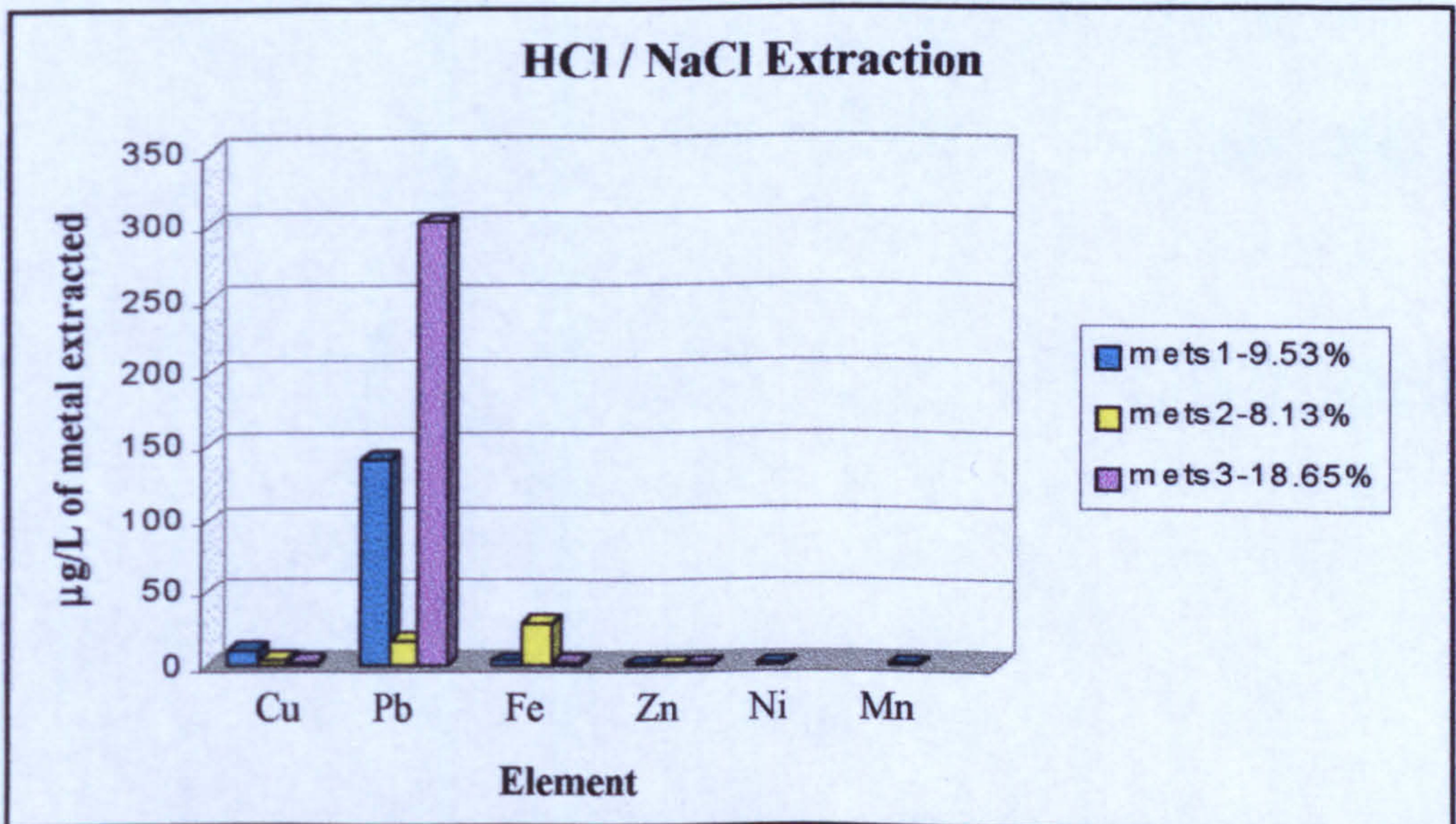


Figure. 5.24:- Leaching of copper residues 104922/1 with HCl / NaCl.

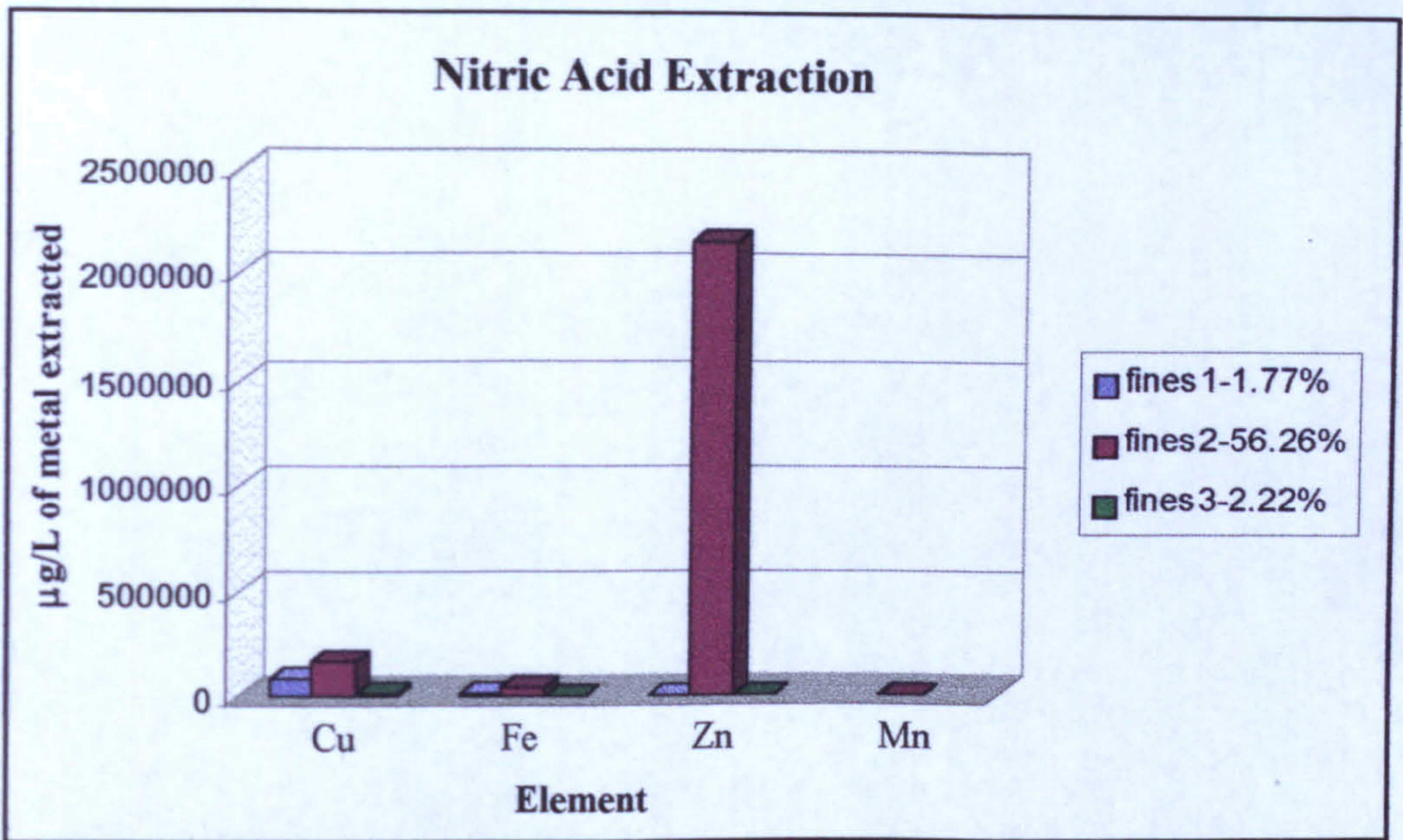


Figure. 5.25:- Leaching of copper residues 104922/2a with nitric acid.

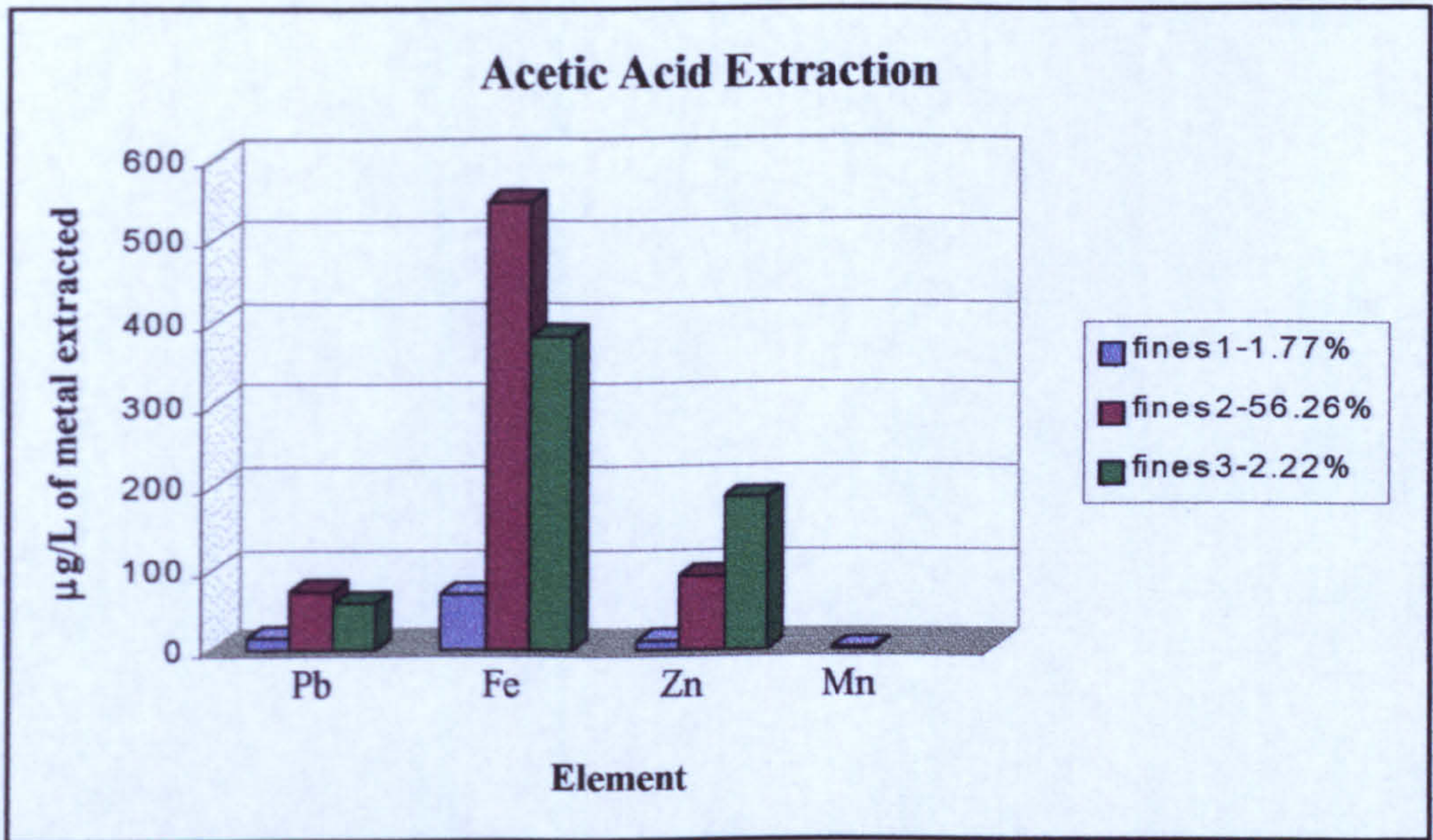


Figure. 5.26:- Leaching of copper residues 104922/2a with acetic acid.

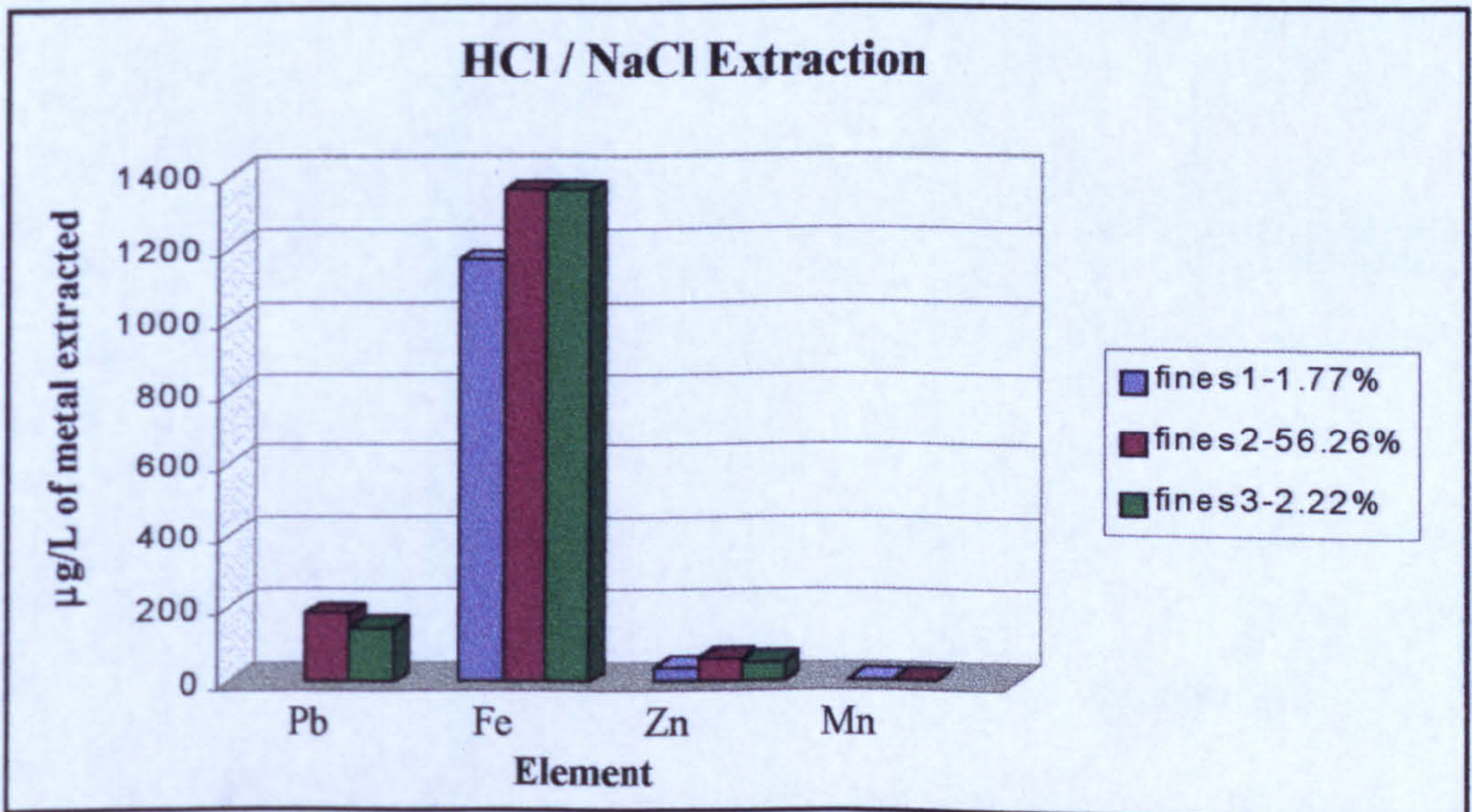


Figure. 5.27:- Leaching of copper residues 104922/2a with HCl / NaCl.

a value of 185.94  $\mu\text{g/L}$ . The other two samples contained zinc in a much lower concentration of 10.2 and 91.0  $\mu\text{g/L}$  for the samples fines 1 and 2 respectively. The concentration of lead extracted was highest in the fines 2 sample at 72.4  $\mu\text{g/L}$  with fines 3 extracting 58.5  $\mu\text{g/L}$ . Only 13.4  $\mu\text{g/L}$  of Pb was extracted for the fines 1 sample [Figure. 5.26].

**Table 5.6: Extraction of copper residues (104922/1)**

Sample No.	Leach Liquor	Concentration of metal leached, $\mu\text{g/L}$ (Amount of metal extracted, mg/g)					
		Cu	Pb	Fe	Zn	Cd	Mn
mets1-9.53%	CH <sub>3</sub> COOH	0.3 (trace)	39.1 (1.0)	34.4 (0.9)	2.9 (0.5)	-	0.1 (trace)
mets2-8.13%		4.2 (3.0)	70.3 (1.4)	57.3 (1.1)	7.5 (0.1)	-	-
mets3-18.65%		-	1945.4 (48.6)	5.8 (0.1)	2.1 (0.1)	-	-
		Cu	Pb	Fe	Zn	Ni	Mn
mets1-9.53%	HNO <sub>3</sub>	26503.6 (260.6)	-	1578.3 (15.5)	221.0 (2.18)	-	-
mets2-8.13%		53582.7 (535.9)	-	1540.2 (15.4)	-	-	-
mets3-18.65%		119301.6 (2180.5)	-	4232.7 (42.3)	19383.9 (193.7)	-	-
		Cu	Pb	Fe	Zn	Ni	Mn
mets1-9.53%	HCl/NaCl	10.5 (2.1)	141.3 (27.3)	3.0 (0.6)	1.2 (0.2)	1.1 (0.2)	0.5 (0.1)
mets2-8.13%		3.9 (0.8)	15.9 (3.2)	28.2 (5.6)	0.8 (0.2)	-	-
mets3-18.65%		1.9 (0.4)	301.9 (56.0)	1.5 (0.3)	0.7 (0.1)	-	-

When using the HCl/NaCl extraction large amounts of Fe were being extracted for all three samples. Lead was found to only leach out in samples 2 and 3 whereby fines 2 contained 183.6  $\mu\text{g/L}$  and fines 3 contained 144.6  $\mu\text{g/L}$ . Zinc was present in all three samples with the highest

concentration contained in fines 2 [Figure. 5.27].

**Table 5.7: Extraction of copper residues (104922/2a)**

Sample No.	Leach Liquor	Concentration of metal leached, $\mu\text{g/L}$ (Amount of metal extracted, mg/g)				
		Cu	Pb	Fe	Zn	Mn
fines1-1.77%	CH <sub>3</sub> COOH	-	13.4 (0.3)	67.7 (1.3)	10.2 (0.2)	1.4 (trace)
fines2-56.26%		-	72.4 (1.4)	547.0 (10.9)	91.0 (1.8)	-
fines3-2.22%		-	58.5 (1.2)	382.8 (7.9)	185.94 (3.83)	-
		Cu	Pb	Fe	Zn	Mn
fines1-1.77%	HNO <sub>3</sub>	77948.7 (778.9)	-	19415.1 (194.0)	2601.7 (26.0)	-
fines2-56.26%		171025.9 (1702.1)	-	35319.7 (351.5)	2157502 (214.6)	3219.5 (32.0)
fines3-2.22%		7937.2 (79.3)	-	4194.5 (41.9)	2158.0 (21.6)	-
		Cu	Pb	Fe	Zn	Mn
fines1-1.77%	HCl/NaCl	-	-	1164.5 (230.3)	36.6 (7.2)	3.4 (0.7)
fines2-56.26%		-	183.6 (36.2)	1357.2 (269.1)	64.6 (12.8)	2.8 (0.6)
fines3-2.22%		-	144.6 (28.7)	1358.8 (267.0)	55.2 (10.9)	-

**Sample 104922/2b**

The samples contained in this batch consisted of two samples which were fines and one sample which was mets (Table 5.8). The fines differed in composition by almost 66%. As expected the highest concentration was extracted when nitric acid was used as the leaching liquor. Large concentrations of Zn, Cu and Mn were extracted for fines of composition 3.95% and 70.80%. However the highest concentration of copper was found to be in the mets sample with a concentration of 47,980  $\mu\text{g/L}$  being extracted. In this sample, zinc was the other metal to be



extracted and this was at a concentration of 15,548.0 µg/L [Figure. 5.28].

It was found with the acetic acid leach test that no copper was extracted from any of the three samples. Pb was extracted from the first sample at a concentration of 447.4 µg/L. Fe, Zn and Mn were also leached from the samples with the greatest amount of Zn being leached from the fines sample of composition 3.95%. Fines 70.80% extracted 1,663.0 µg/L and the mets sample extracted the lowest amount of Zn with only 191.0 µg/L. There was also a high concentration of Fe and Mn present in the fines 3.95% sample [Figure. 5.29].

When mimicking gastric conditions with the HCl/NaCl extraction, Cu was extracted from both the fines samples, but not the mets sample. The concentration of Cu leached out from the fines sample of composition 70.80% was more than double the concentration leached out from the other fines sample. The mets sample, however, contained 16.0 µg/L of Pb but no Zn was found to be extracted. The fines samples leached Zn, and again the fines sample with composition 70.80% leached a higher amount of Zn than the other fines sample [Figure. 5.30].

#### ***Sample 109059/1***

The final batch of samples from A & H Knight consisted of a matte sample of 25.10% composition and a fines sample which had a composition of 89.19%. Cu was found to be extracted only with the acetic acid leach test. The concentration of Cu leached was low in terms of trigger guide levels as can be seen from (Table 5.9). Also using this leach test it was found that Zn was extracted from the matte sample at a concentration of 93.5 µg/L and from the fines sample a concentration of 302.6 µg/L was extracted. A trace of Mn was detected in the fines sample [Figure. 5.31].

With the nitric acid leach test a large proportion of Fe and Zn was mainly leached from the samples with the matte sample extracting 11,646.2 µg/L and the fines sample extracting 1,696.5 µg/L. There was also a trace of Mn present in the fines sample [Figure. 5.32].

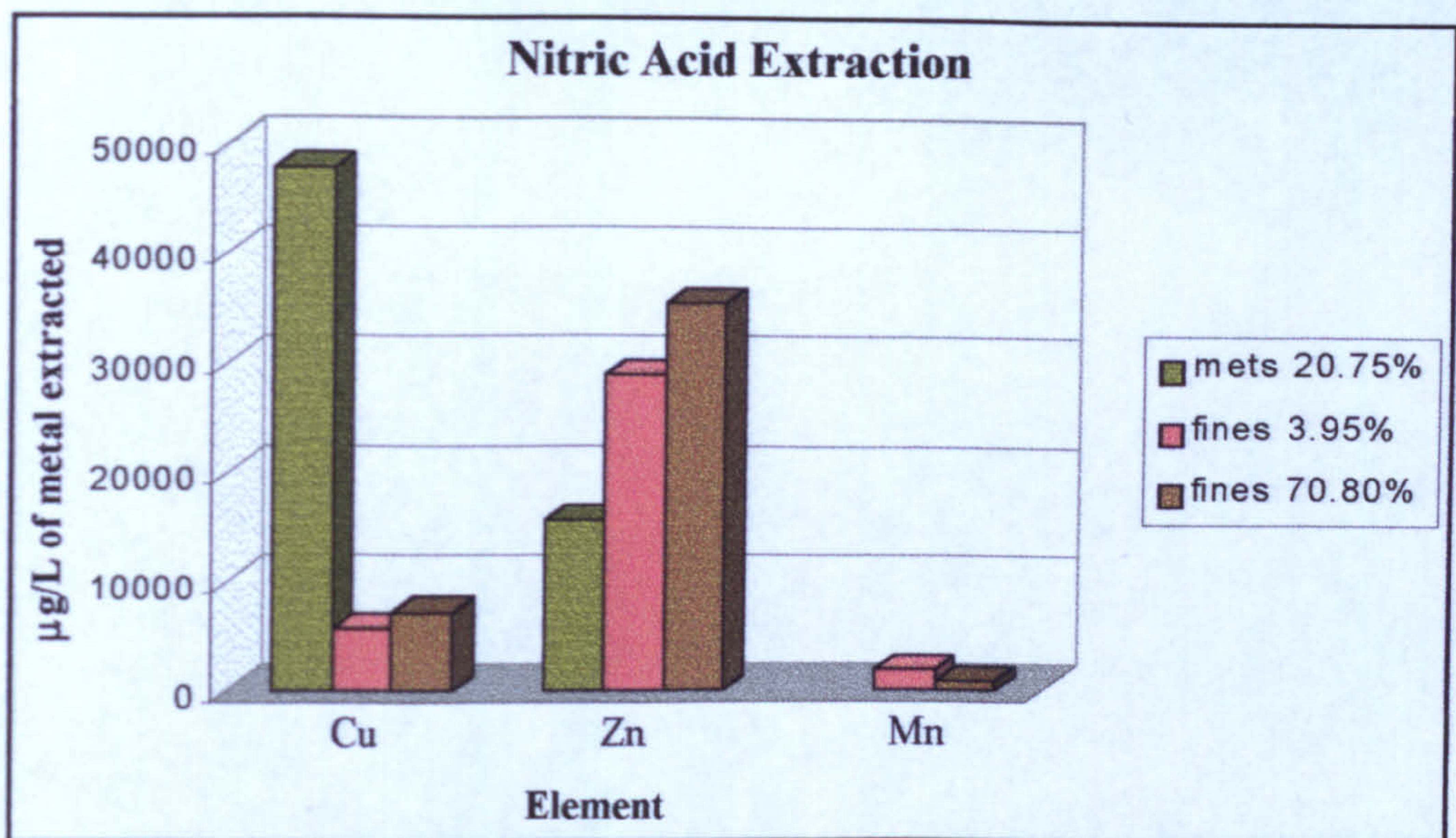


Figure. 5.28:- Leaching of copper residues 104922/2b with nitric acid.

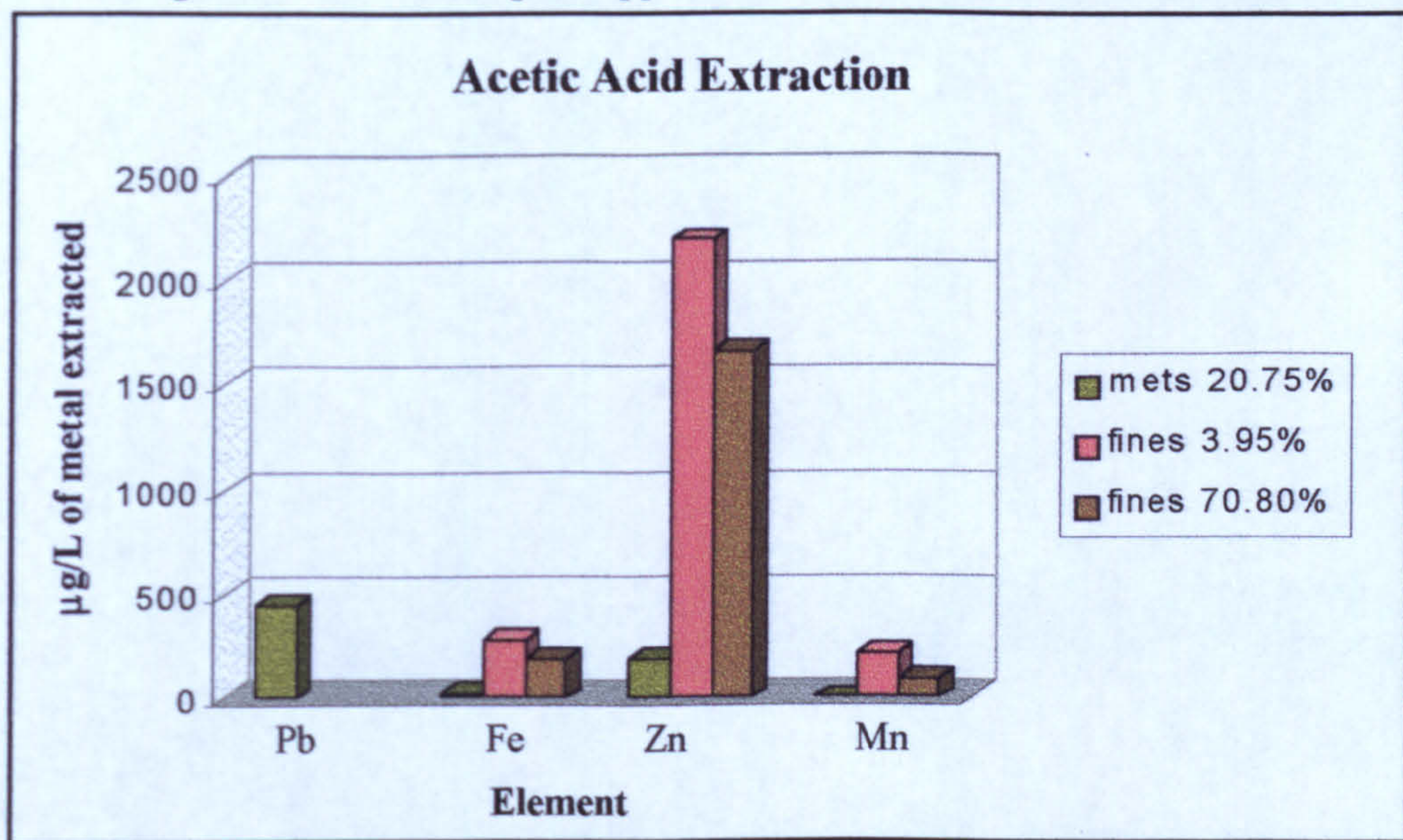


Figure. 5.29:- Leaching of copper residues 104922/2b with acetic acid.

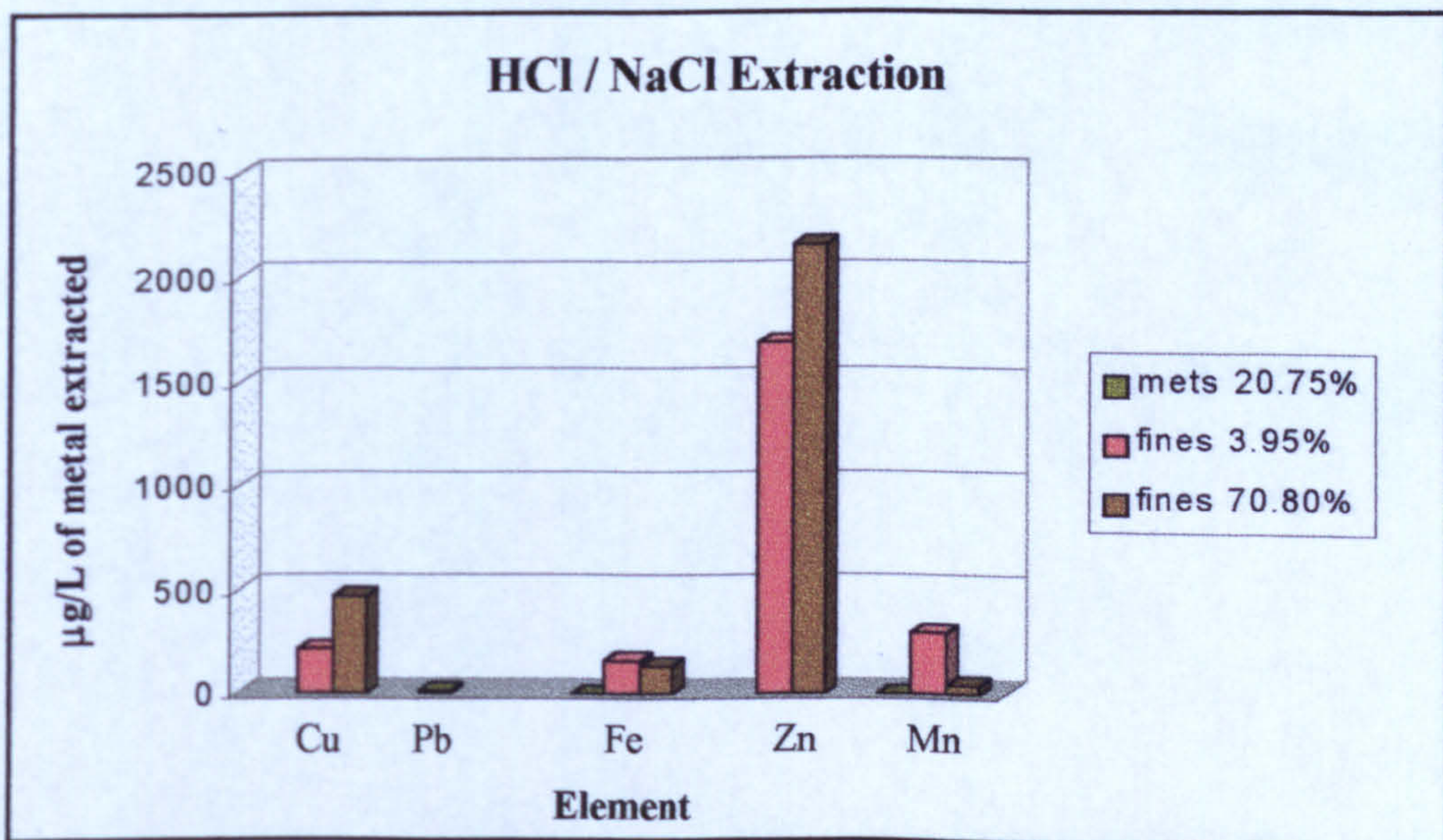


Figure. 5.30:- Leaching of copper residues 104922/2b with HCl / NaCl.

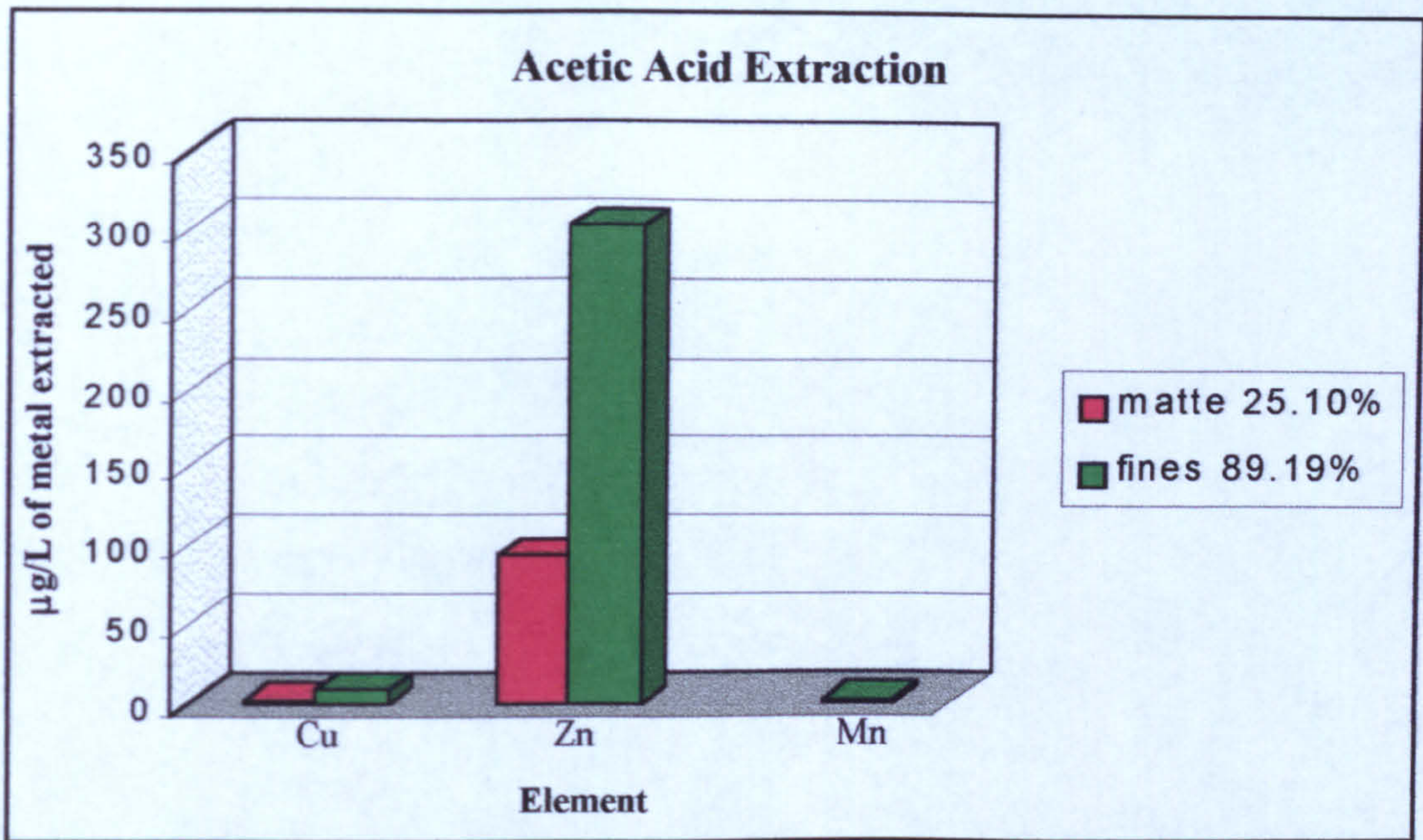


Figure. 5.31:- Leaching of copper residues 109059/1 with acetic acid.

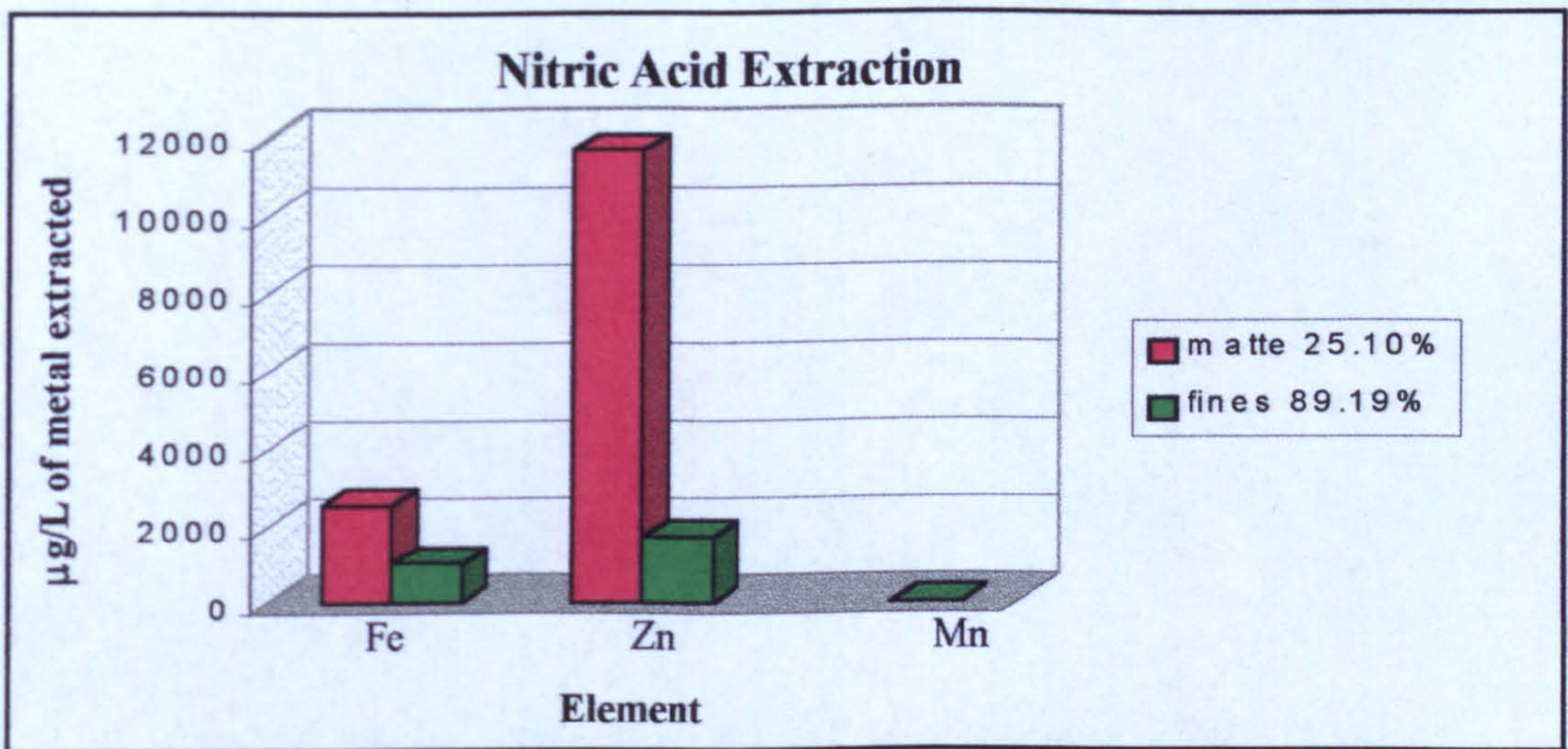


Figure. 5.32:- Leaching of copper residues 109059/1 with nitric acid.

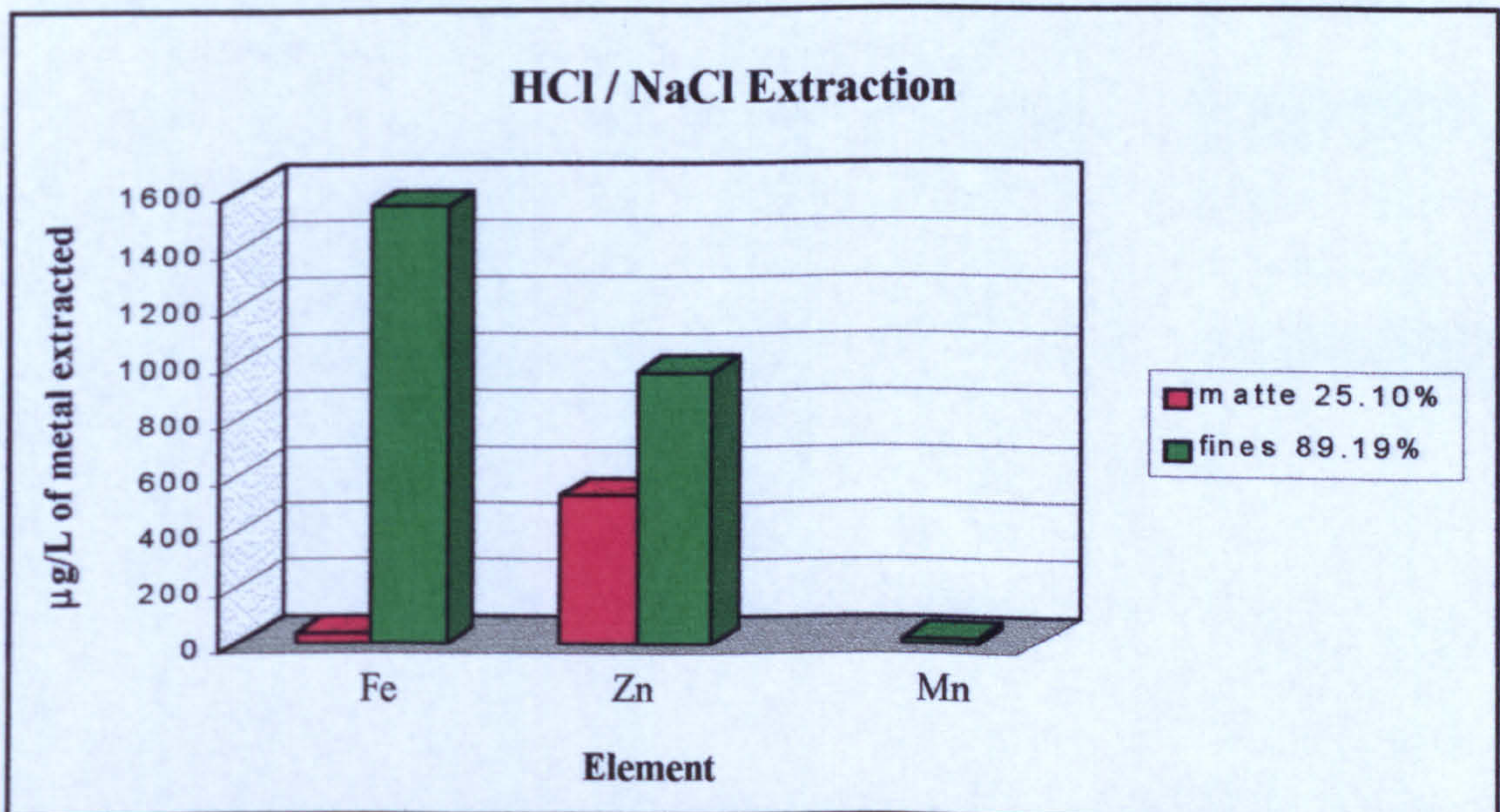


Figure. 5.33:- Leaching of copper residues 109059/1 with HCl / NaCl.

Table 5.8: Extraction of copper residues (104922/2b)

Sample No.	Leach Liquor	Concentration of metal leached, $\mu\text{g/L}$ (Amount of metal extracted, mg/g)				
		Cu	Pb	Fe	Zn	Mn
mets 20.75%	CH <sub>3</sub> COOH	-	447.4 (8.9)	19.8 (0.4)	191.0 (3.8)	1.4 (trace)
fines 3.95%		-	-	286.7 (5.7)	2193.9 (43.8)	217.6 (4.3)
fines 70.80%		-	-	189.6 (3.9)	1663.0 (33.2)	89.5 (1.8)
		Cu	Pb	Fe	Zn	Mn
mets 20.75%	HNO <sub>3</sub>	47980.9 (472.7)	-	-	15548.0 (153.2)	-
fines 3.95%		5670.7 (56.3)	-	-	29031.7 (288.4)	1733.9 (17.2)
fines 70.80%		7107.8 (69.8)	-	-	35435.4 (348.6)	607.5 (6.0)
		Cu	Pb	Fe	Zn	Mn
mets 20.75%	HCl/NaCl		16.0 (3.2)	3.8 (0.8)		3.4 (0.7)
fines 3.95%		219.8 (43.2)	-	166.1 (32.6)	1678.5 (329.9)	293.5 (57.5)
fines 70.80%		462.6 (91.1)	-	135.7 (26.7)	2150.9 (423.7)	39.1 (7.7)

Under gastric conditions the same elements which were extracted in the nitric acid test were also extracted in the HCl/NaCl extraction. The concentration of Zn in the fines sample was almost double the amount which was extracted in the matte sample. Again, Mn was found to be present in the fines sample [Figure. 5.33].

**Table 5.9: Extraction of copper residues(109059/1)**

Sample No.	Leach Liquor	Concentration of metal leached, µg/L (Amount of metal extracted, mg/g)			
		Cu	Fe	Zn	Mn
matte 25.10%	CH <sub>3</sub> COOH	1.8 <i>(trace)</i>	-	93.5 <i>(1.9)</i>	-
finer 89.19%		8.4 <i>(0.2)</i>	-	302.6 <i>(6.0)</i>	2.0 <i>(trace)</i>
		Cu	Fe	Zn	Mn
matte 25.10%	HNO <sub>3</sub>	-	2508.1 <i>(25.1)</i>	11646.2 <i>(116.3)</i>	-
finer 89.19%		-	1009.5 <i>(10.1)</i>	1696.5 <i>(16.9)</i>	7.6 <i>(0.1)</i>
		Cu	Fe	Zn	Mn
matte 25.10%	HCl/NaCl	-	33.8 <i>(6.6)</i>	526.5 <i>(103.8)</i>	-
finer 89.19%		-	1541.1 <i>(305.7)</i>	960.1 <i>(190.4)</i>	16.9 <i>(3.4)</i>

#### 5.4.2 Secondary Zinc Materials

A number of zinc residue samples supplied by industry can be classified in terms of their particle size as massive (>1.0 nm), semi-dispersible (>0.1 nm and < 1.0 nm) and dispersible (<0.1 nm) and leaching studies have been carried out on each residue type.

#### *Leaching of Zinc Residues*

##### *Britannia Zinc Ltd*

The samples provided by this company comprised of residues collected during leaching, zinc dross and filter bag dust (Table 5.10). Since the samples originated from various different processes the samples were not homogeneous and so the particle size ranged from dispersible to massive.

With the nitric acid leach test, very high concentrations of Pb, Fe and Zn were extracted with Mn being leached out only from the leach residue and the zinc dross samples. From the leach

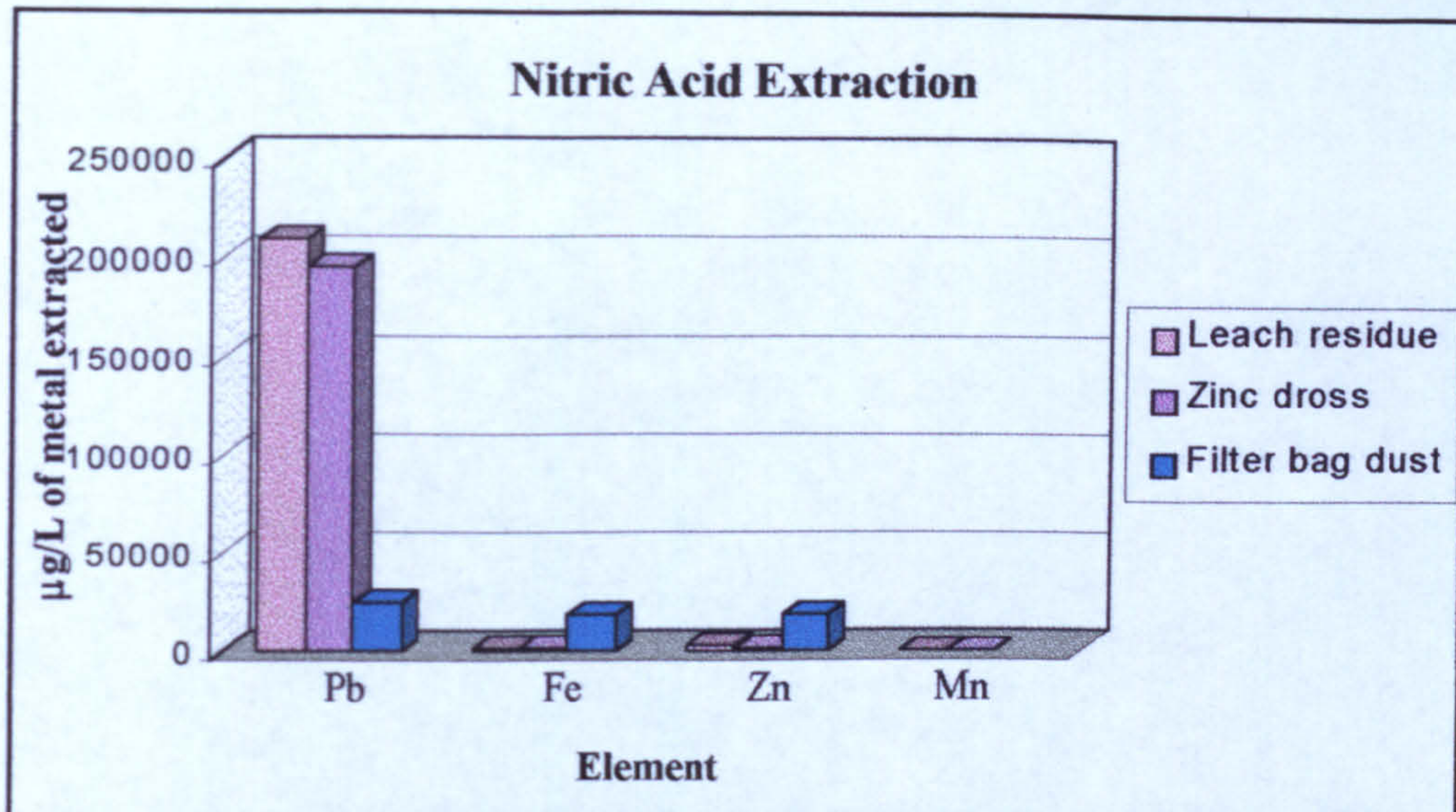


Figure. 5.34:- Leaching of zinc wastes with nitric acid.

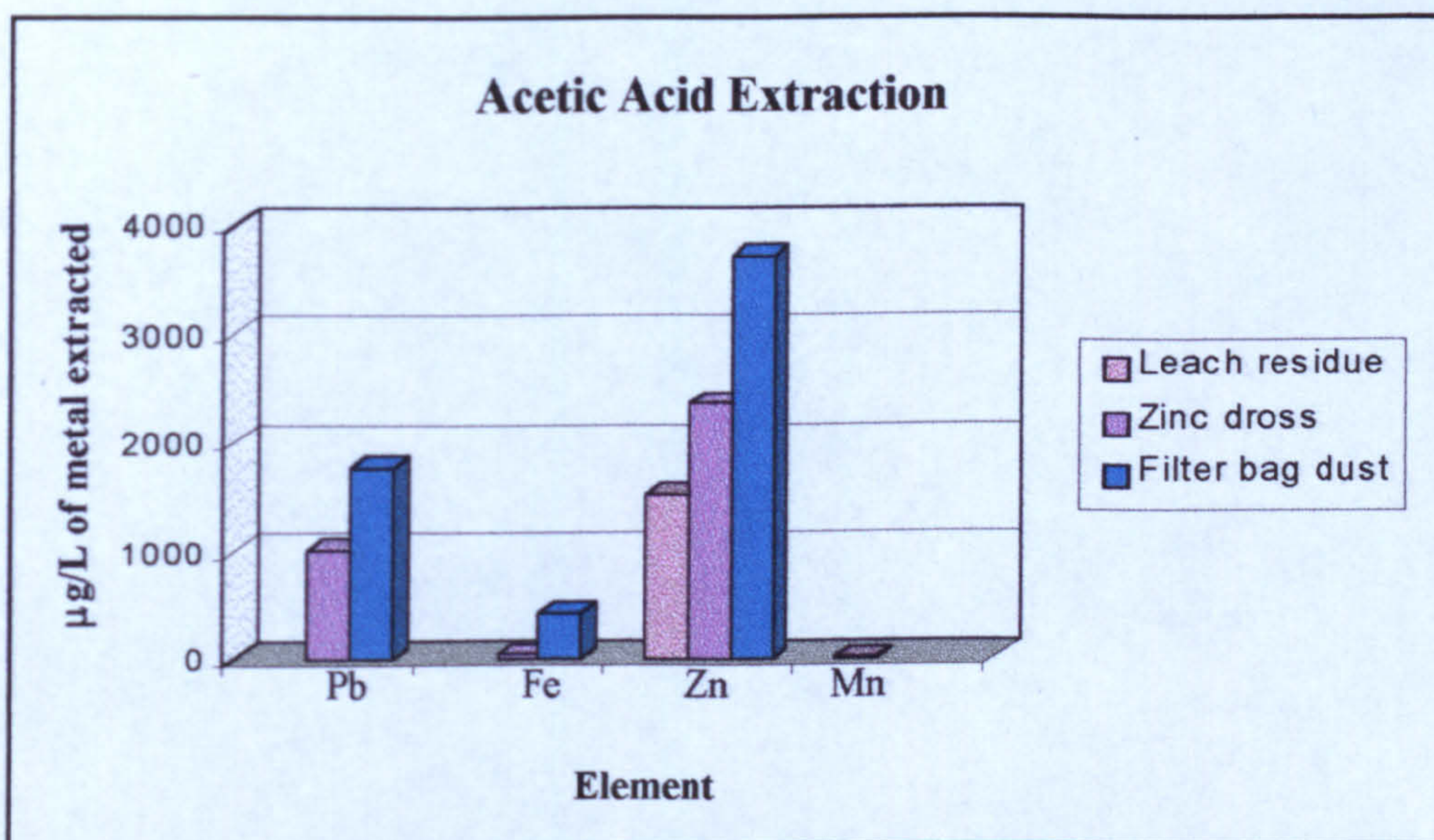


Figure. 5.35:- Leaching of zinc wastes with acetic acid.

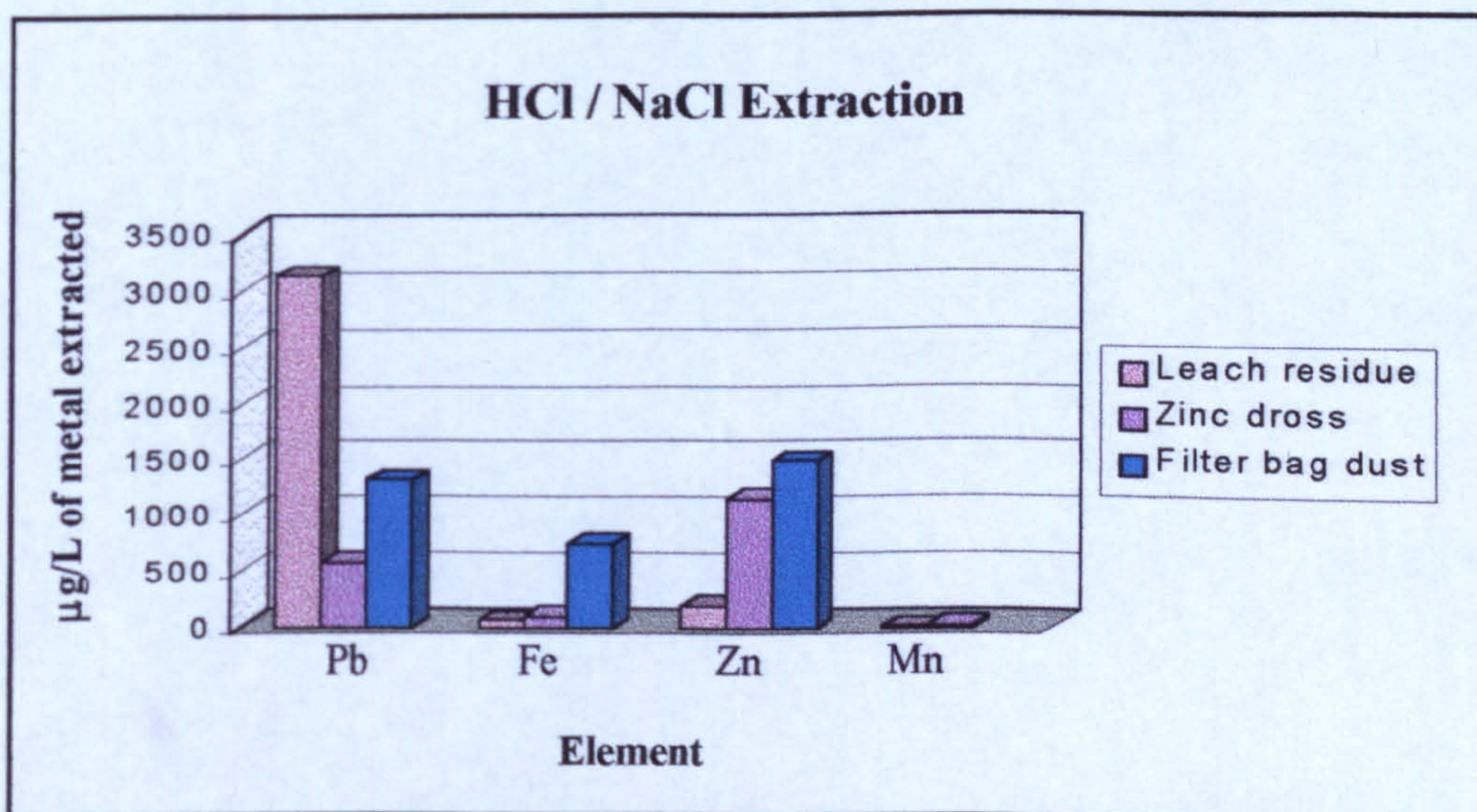


Figure. 5.36:- Leaching of zinc wastes with HCl/NaCl.

residue 209, 040.6  $\mu\text{g/L}$  of Pb were extracted with this test, whereas only 24, 977.9  $\mu\text{g/L}$  were extracted from the copper filter bag dust. The zinc dross leached 23, 697.1  $\mu\text{g/L}$  of Zn but the greatest concentration to be leached out was from the copper refinery bag filter dust with 33, 452.4  $\mu\text{g/L}$  being extracted [Figure. 5.34].

No Pb or Fe was extracted from the leach residue with acetic acid but Zn and Mn was leached out at concentrations of 1514.3 and 12.4  $\mu\text{g/L}$  respectively. There was a large concentration of Fe in the filter bag dust sample as were the concentrations of Pb and Zn in this sample compared to the zinc dross sample [Figure. 5.35].

The final leach test to be carried out was the HCl/NaCl procedure and from this leach test it was found that zinc dross had the lowest concentration of Pb present with only 570.1  $\mu\text{g/L}$  compared to 3119.1 and 1314.0  $\mu\text{g/L}$  being leached from the leach residue and filter bag dust samples respectively. Zinc was present in all three samples with the greatest concentration being leached from the filter bag dust sample. This sample also had the highest quantity of Fe to be extracted [Figure. 5.36].

### ***Particle Size***

In this series of experiments three samples supplied by Hüttenwerke Kayser AG, Germany were used. Once the samples had been separated into the three different categories of particle size range, they were then extracted with each of the leach liquors which have been described previously.

These experiments were undertaken to determine whether the particle size of a sample has any significance on the amount of metal which will be extracted from the sample.

### ***Sample CHG 172/1***

#### ***Dispersible***

This sample was extracted with the three leach tests, acetic acid,  $\text{HNO}_3$  and HCl/NaCl. The first particle size to be studied was dispersible.

In the case of leaching this sample with nitric acid it was determined that Cu was leached out at a concentration of 311.40 µg/L and 3.12 mg/g of Cu were extracted from this sample. The other two metals to be leached from this sample were Pb and Zn. These metals were leached at a concentration of 139.57 µg/L of Pb and 29.48 µg/L of Zn. The amounts of Pb and Zn extracted from this sample were 1.40 mg/g and 0.29 mg/g respectively [Figure. 5.37].

**Table 5.10: Concentration of metal leached from sized fractions of zinc residues**

Sample CHG 172/2	Leach Liquor	Concentration of metal leached, µg/L <i>(Amount of metal extracted, mg/g)</i>				
		Pb	Fe	Zn	Cd	Mn
Leach Residue	CH <sub>3</sub> COOH	-	-	1,514 <i>(23.2)</i>	-	12.4 <i>(1.2)</i>
Zinc Dross		9,050 <i>(67.2)</i>	-	2,490 <i>(63.2)</i>	-	0.1 <i>(trace)</i>
Filter Bag Dust		1,652 <i>(25.4)</i>	300.2 <i>(40.3)</i>	3,750 <i>(72.3)</i>	-	-
		Pb	Fe	Zn	Cd	Mn
Leach Residue	HNO <sub>3</sub>	209,040.6 <i>(200.1)</i>	-	23,697.1 <i>(236.2)</i>	-	0.1 <i>(trace)</i>
Zinc Dross		197,665.6 <i>(160.6)</i>	-	2.5 <i>(trace)</i>	-	0.1 <i>(trace)</i>
Filter Bag Dust		24,977 <i>(250.42)</i>	-	0.15 <i>(trace)</i>	-	-
		Pb	Fe	Zn	Cd	Mn
Leach residue	HCl/NaCl	3,119 <i>(294.6)</i>	25.3 <i>(3.1)</i>	200.1 <i>(16.6)</i>	trace <i>(0.2)</i>	0.2 <i>(0.8)</i>
Zinc Dross		570.1 <i>(71.8)</i>	30.2 <i>(3.6)</i>	1005.2 <i>(189.2)</i>	-	0.2 <i>(0.8-</i>
Filter Bag Dust		1,314 <i>(192.6)</i>	620 <i>(45.2)</i>	1,470 <i>(190.9)</i>	-	-

With the acetic acid leach test it was found that six different elements were leached from the sample. The element which was present in the largest quantity was Pb with 100.7 µg/L leached into solution and 16.7 mg/g being extracted from the sample [Figure. 5.38].



With the saline solution the same elements were extracted when the sample was leached in acetic acid with the exception of Fe. In this case again Pb was found to be present in the largest amount at a concentration of 61.2 µg/L but since only 0.5 g of sample is taken for this leach test, the amount of Pb extracted per gram of sample taken was much higher with a value of 294.6 mg/g [Figure. 5.39].

### ***Semi-dispersible***

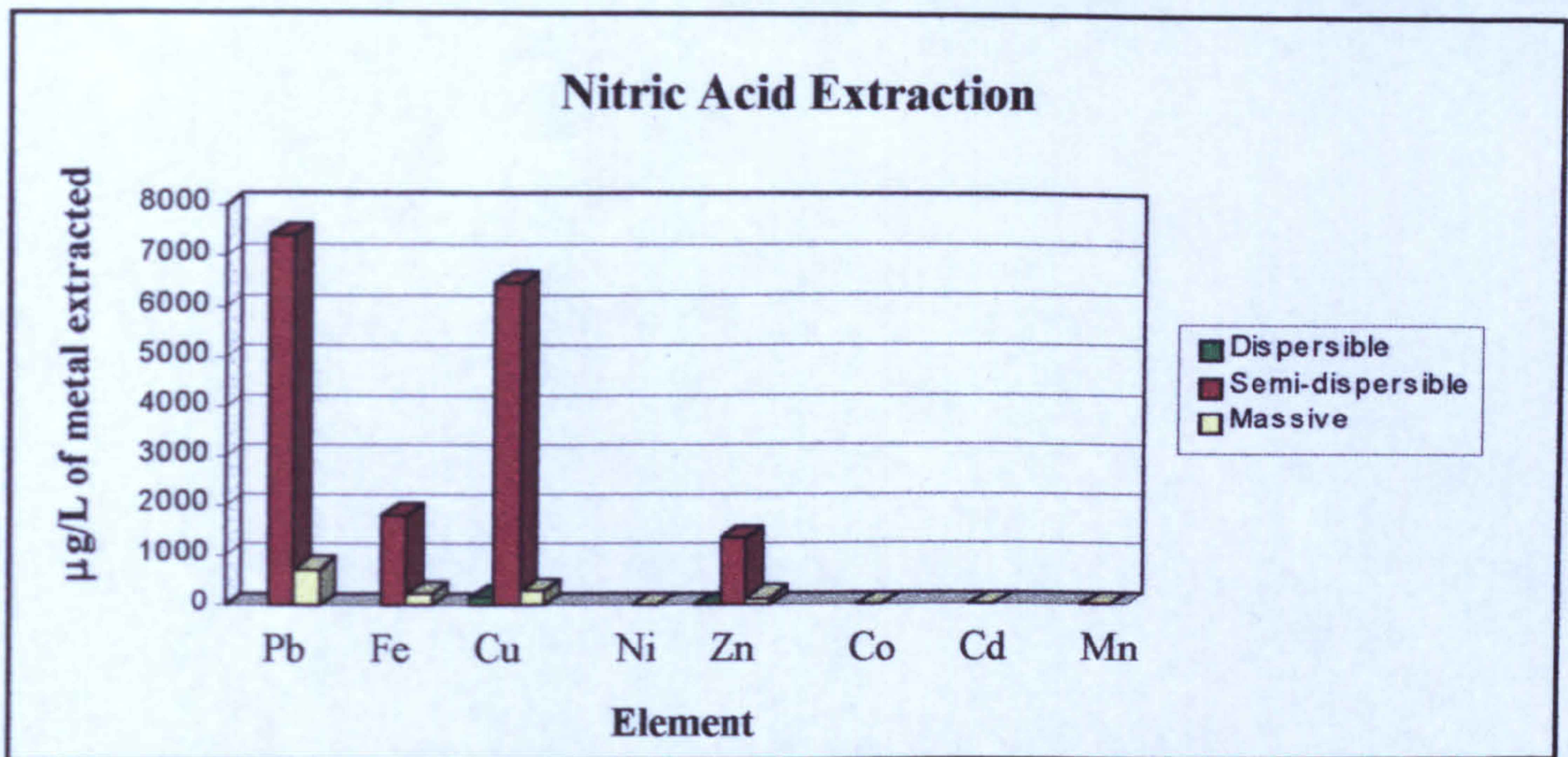
The next particle size range for this sample was semi-dispersible whereby it was found that only two metals were extracted, Pb and Cu. The amounts of Pb and Cu leached into solution with the nitric acid leach test were 7382.05 and 6437.65 µg/L respectively. On comparison with the trigger guide levels it can be seen that the amounts of Pb and Cu extracted were excessive to the values set [Figure. 5.37].

The amount of Pb leached into solution and extracted per gram of sample was 52.73 µg/L and 1.32 mg/g respectively. However, the amount of Cu leached into solution was well above the trigger guide level set for the toxicity of copper in accord with the Basel Convention. This value was 8848.78 µg/L and it was found that 221.11 mg/g were extracted when leached with acetic acid [Figure. 5.38].

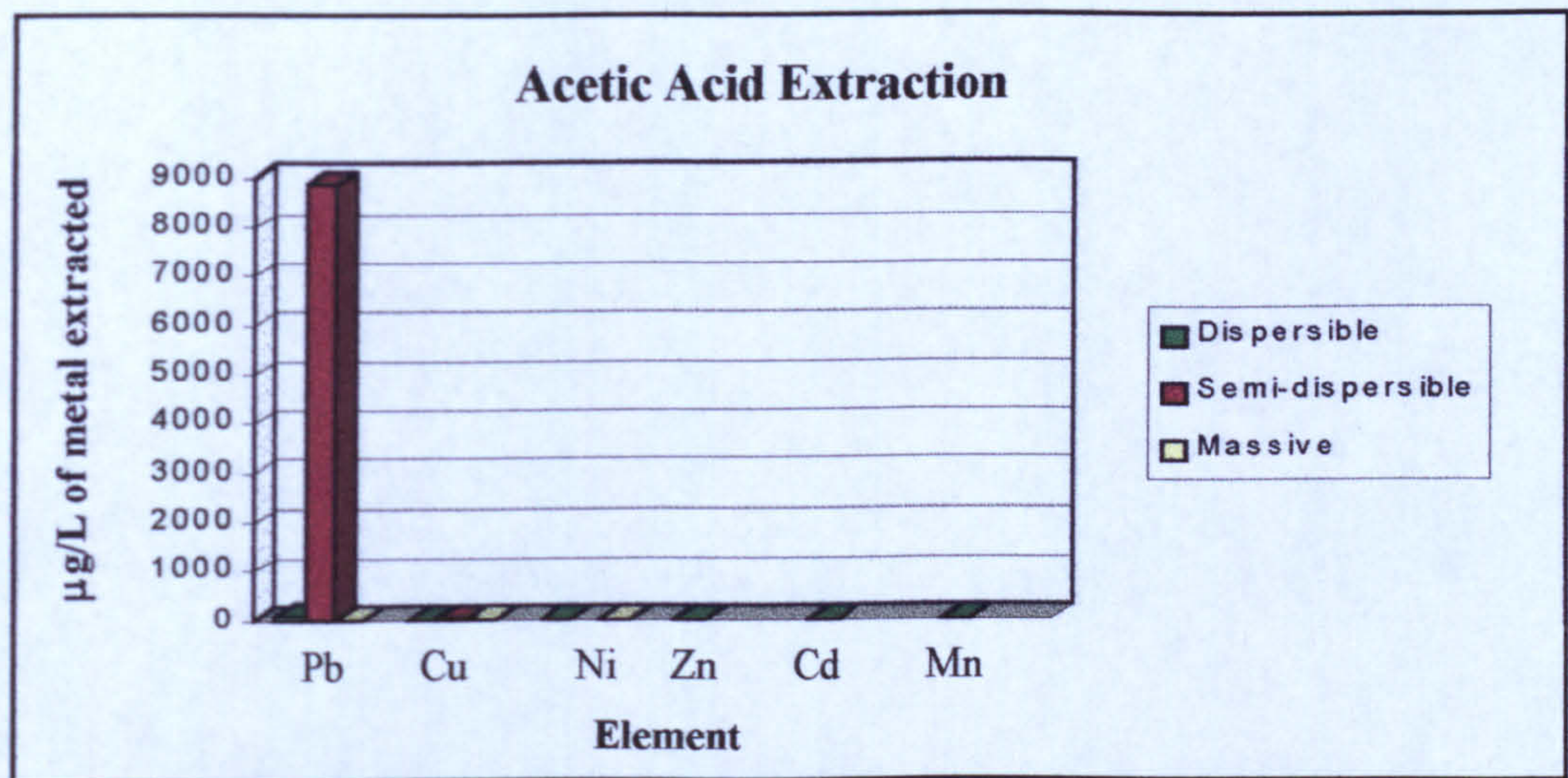
With the saline solution three elements were extracted Pb, Cu and Zn. 1402.98 µg/L of Pb was leached into solution and 271.76 mg/g was extracted from the amount of sample taken. The amount of Cu leached into solution was almost half the amount of Pb leached with a value of 832.66 µg/L and the amount which was extracted was 161.25 mg/g. The metal which was leached out the least was Zn at a concentration of 94.55 µg/L and 18.32 mg/g were extracted [Figure. 5.39].

### ***Massive***

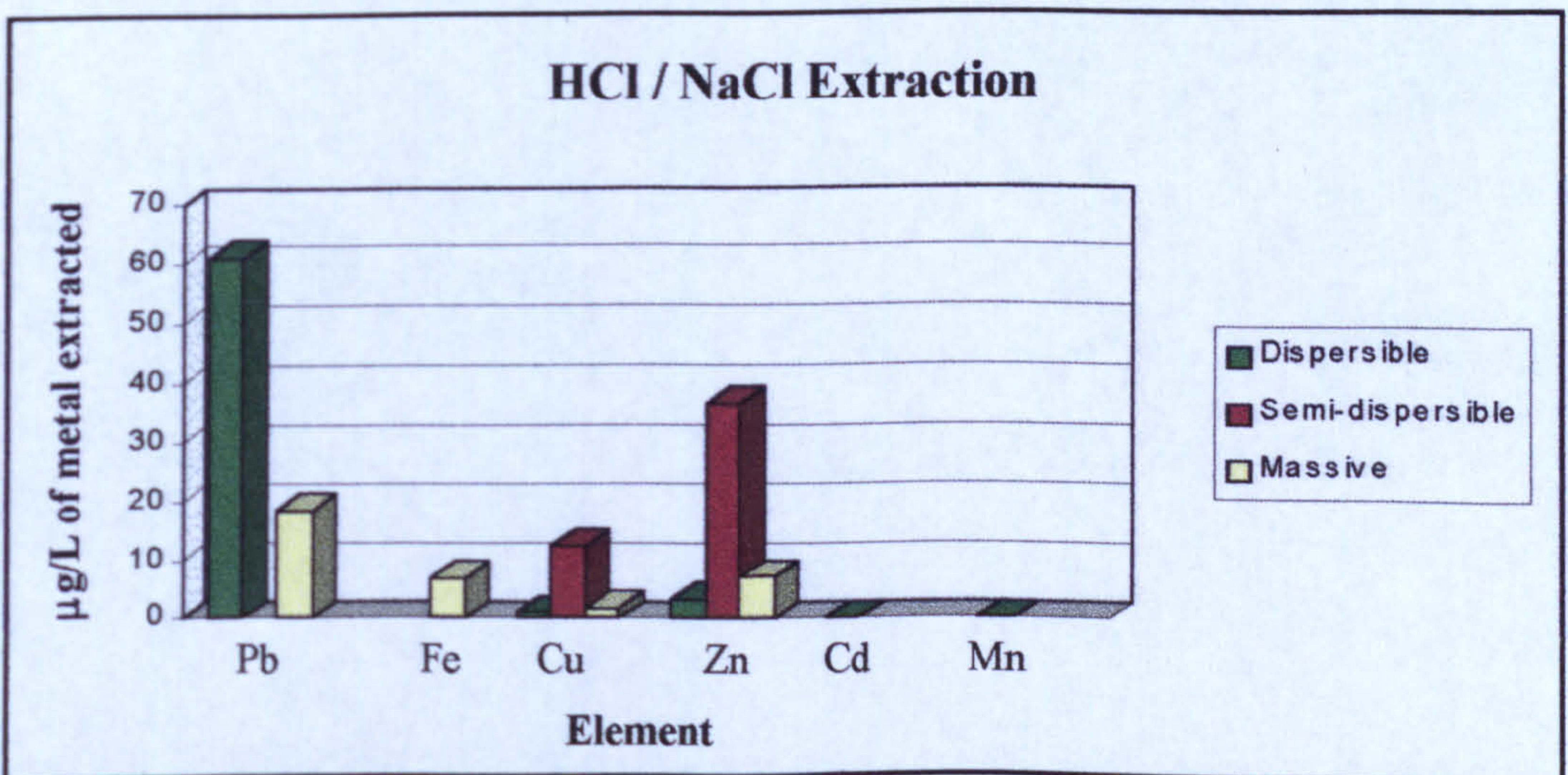
The massive particle size range afforded different metals with each of the different leach tests which were utilised. With acetic acid it was found that the lowest concentration of Pb and Cu were leached into solution when compared to the amounts of Pb and Cu leached into solution with the use of nitric acid and HCl/NaCl.



**Figure. 5.37:- Leaching of copper slag CHG 172/1 with nitric acid.**



**Figure. 5.38:- Leaching of copper slag CHG 172/1 with acetic acid.**



**Figure. 5.39:- Leaching of copper slag CHG 172/1 with HCl / NaCl.**

With acetic acid it was found that 1.44  $\mu\text{g/L}$  of Pb and 0.16  $\mu\text{g/L}$  of Cu were leached into solution [Figure. 5.38] whereas with nitric acid 753.15  $\mu\text{g/L}$  of Pb and 311.30  $\mu\text{g/L}$  of Cu were leached into solution. Also with the nitric acid test it was found that other metals including Fe, Ni, Co, Cd and Zn were also leached into solution [Figure. 5.37].

When HCl/NaCl was used as the leaching liquor the amounts of Pb and Cu leached into solution were 18.40  $\mu\text{g/L}$  of Pb and 1.94  $\mu\text{g/L}$  of Cu. This leach test also leached Fe and Zn into solution [Figure. 5.39].

From this sample it can be concluded that with a smaller particle size a larger amount of metal can be leached into solution and greater amount of metal is extracted per gram of sample than when a larger particle size range is used.

The results for this sample and the different particle size ranges covered are summarised in Table 5.11.

### ***Sample CHG 172/2***

#### ***Dispersible***

With this sample it was found that with acetic acid four elements Cu, Pb, Zn and Mn were leached. The amount of these metals leached into solution was greatest for Pb at 34.8  $\mu\text{g/L}$  being leached and 2.1 mg/g. However, although Cu was leached into solution at a concentration of 4.6  $\mu\text{g/L}$ , a greater amount of Cu was extracted from the sample taken compared to the amount of Pb which was extracted. The amount of Cu extracted from the sample was 4.6 mg/g. The amounts of Zn and Mn extracted and leached were less than that for Cu [Figure. 5.40].

With the nitric acid test it was found that Cu, Pb and Zn were leached into solution at varying concentrations. The metal which leached out the most was Cu at a concentration of 311.40  $\mu\text{g/L}$  and 3.12 mg/g of Cu were extracted from the sample taken. Pb was leached at a concentration of 139.57  $\mu\text{g/L}$  and it was found that 1.40 mg/g were extracted from the sample taken. The lowest concentration of metal leached was Zn at a concentration of 29.48  $\mu\text{g/L}$  and the amount of Zn extracted from the sample taken was 0.29 mg/g [Figure. 5.41].

**Table 5.11: Concentration of metal leached from sized fractions of sample CHG 172/1**

Sample CHG 172/1	Leach Liquor	Concentration of metal leached, $\mu\text{g/L}$ (Amount of metal extracted, mg/g)							
		Pb	Fe	Cu	Ni	Zn	Co	Cd	Mn
Dispersible	CH <sub>3</sub> COOH	100.7 (16.7)	-	6.8 (1.1)	0.8 (trace)	0.5 (0.1)	-	0.2 (trace)	0.1 (trace)
Semi-dispersible		8848.78 (221.11)	-	52.73 (1.32)	-	-	-	-	-
Massive		1.44 (0.04)	-	0.16 (trace)	0.19 (0.01)	-	-	-	-
		Pb	Fe	Cu	Ni	Zn	Co	Cd	Mn
Dispersible	HNO <sub>3</sub>	-	-	186.18 (1.86)	-	36.16 (0.36)	-	-	-
Semi-dispersible		7382.05 (73.81)	1837.85 (18.37)	6437.65 (64.36)	-	1375.20 (13.75)	-	-	-
Massive		753.15 (7.39)	254.4 (2.50)	311.30 (3.06)	15.28 (0.15)	169.26 (1.66)	2.83 (0.03)	18.39 (0.18)	3.7 (0.04)
		Pb	Fe	Cu	Ni	Zn	Co	Cd	Mn
Dispersible	HCl/NaCl	61.2 (294.6)	-	1.1 (5.3)	-	3.5 (16.6)	-	trace (0.2)	0.2 (0.8)
Semi-dispersible		-	-	12.51 (2.42)	-	36.58 (7.08)	-	-	-
Massive		18.40 (3.44)	6.99 (1.40)	1.94 (0.36)	-	7.25 (0.36)	-	-	-

HCl/NaCl leached very low concentrations of Fe, Zn, Cd, Mn and Cu. The highest concentration of metal leached was that for Pb which was leached into solution at a concentration of 13.5  $\mu\text{g/L}$  and 66.9 mg/g were extracted from the amount of sample taken. Although a lower amount of Cu was leached into solution it was found that a higher amount of Cu was extracted from the sample than the amount of Pb which was extracted [Figure. 5.42].

### *Semi-dispersible*

When this sample was used in the particle size range of semi-dispersible it was found that when the sample was leached with acetic acid, two elements were leached into solution. Pb was leached at a concentration of 76.16  $\mu\text{g/L}$  and 1.90 mg/g were extracted from the amount of

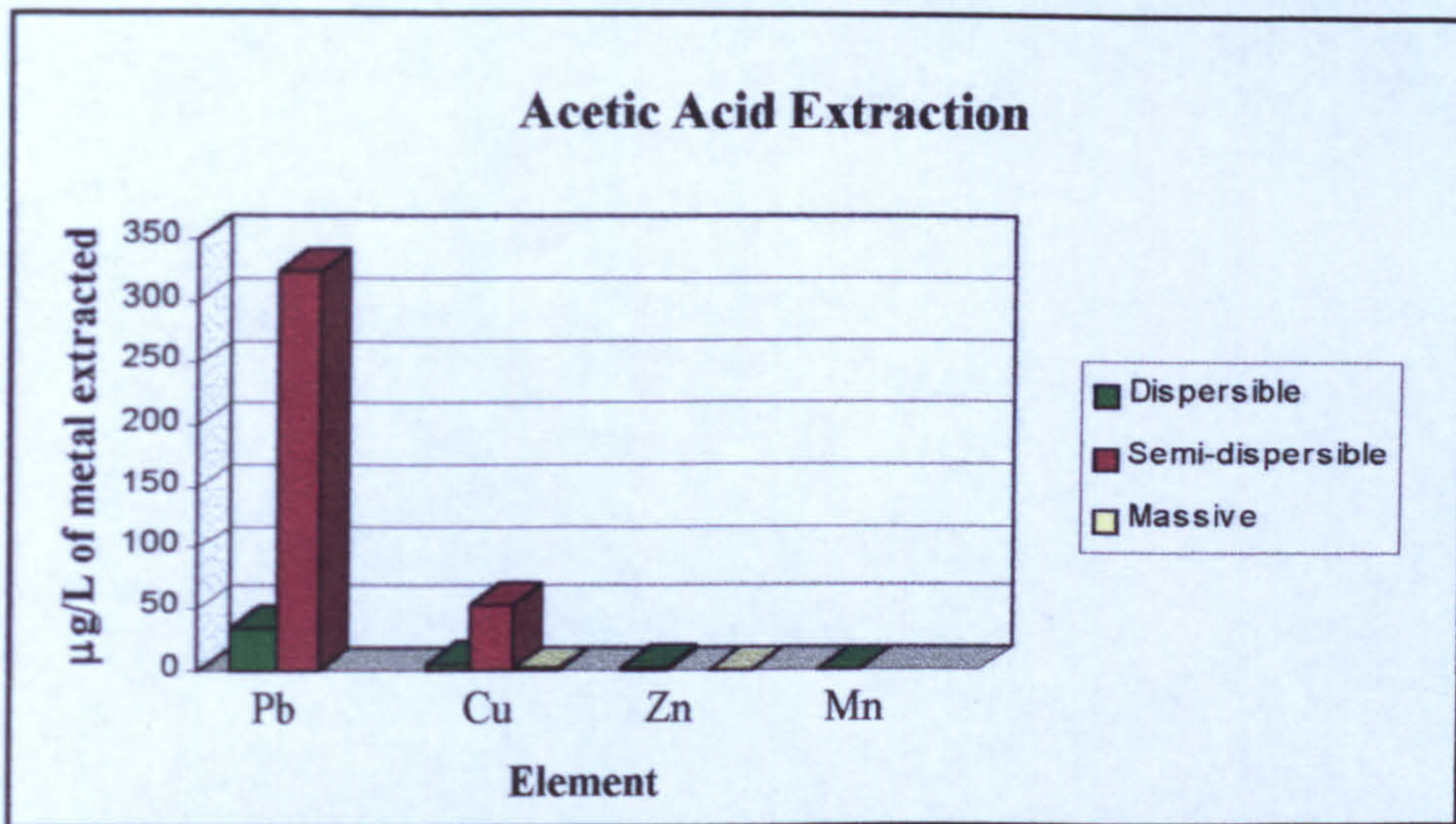


Figure. 5.40:- Leaching of copper slag 172/2 with acetic acid.

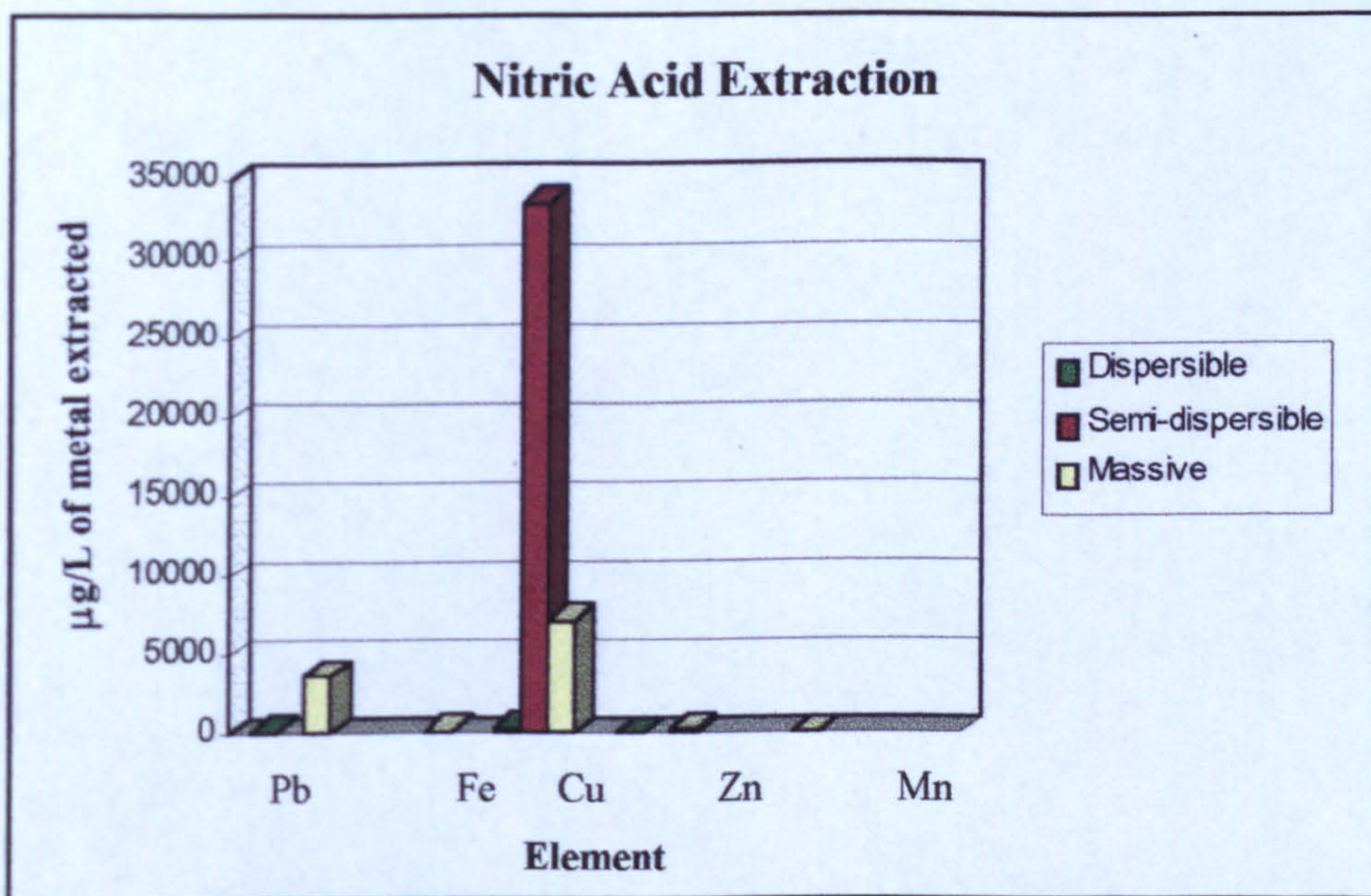


Figure. 5.41:- Leaching of copper slag CHG 172/2 with nitric acid.

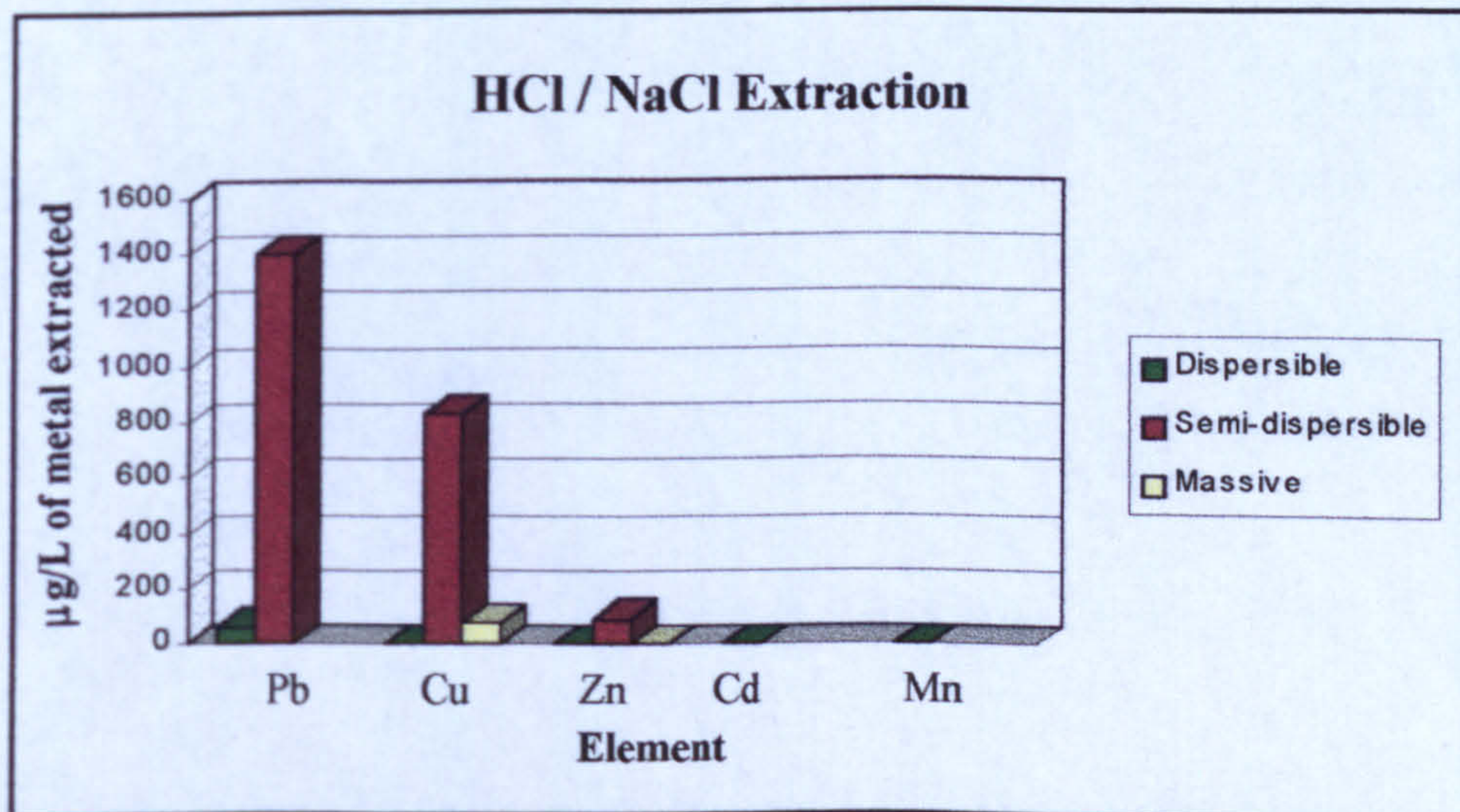


Figure. 5.42:- Leaching of copper slag 172/2 with HCl / NaCl.

sample taken. The concentration of Cu was 50.50 µg/L and 1.26 mg/g [Figure. 5.40].

In the case of nitric acid only one metal, Cu, was found to leach out into solution. The amount extracted from the weight of sample taken was 334.41 mg/g and the amount which leached into solution was 33,457.40 µg/L. From the results it can be seen that the amount of copper which leached into solution was above the trigger guide level [Figure. 5.41].

The final leach test carried out with this sample was the HCl/NaCl extraction and it was found that with this leach test Pb, Fe, Cu and Zn were detected in the analysis. The concentrations of each of these metals in solution was 121.455, 16.81, 12.24 and 33.51 µg/L indicating that the concentration of each of these metals in solution was below the trigger guide level set for the Basel Convention [Figure. 5.42].

### *Massive*

The final particle size range to be used was the massive range and with acetic acid it was found that low concentrations of Cu and Zn were leached into solution. 1.26 µg/L of Cu were leached and 0.03 mg/g were extracted. For Zn, 0.15 µg/L were leached and a trace of Zn was extracted from the sample taken [Figure. 5.40].

With nitric acid Cu was just above the trigger guide level at a concentration of 7,104.25 µg/L leaching into solution and 70.30 mg/g extracted from the sample taken. The amount of Pb leaching out was 3,624.88 µg/L and 35.87 mg/g of Pb were extracted from this sample. Fe and Zn were detected at concentrations of 110.70 and 261.11 µg/L respectively. The corresponding amounts of Fe and Zn extracted from the sample were 1.10 and 2.58 mg/g respectively [Figure. 5.41]. Under gastric conditions Cu and Zn were leached at a concentration of 75.34 µg/L and 1.47 µg/L with 14.62 mg/g of Cu being extracted from the sample and 0.29 mg/g of Zn was extracted from the same sample [Figure. 5.42]. The results for this sample are summarised in Table 5.12.

**Table 5.12: Concentration of metal leached from sized fractions of sample CHG 172/2**

Sample CHG 172/2	Leach Liquor	Concentration of metal leached, $\mu\text{g/L}$ (Amount of metal extracted, mg/g)					
		Pb	Fe	Cu	Zn	Cd	Mn
Dispersible	CH <sub>3</sub> COOH	34.8 (2.1)	-	4.6 (4.6)	2.2 (0.2)	-	0.1 (trace)
Semi-dispersible		322.67 (8.06)	-	52.73 (1.32)	-	-	-
Massive		-	-	1.26 (0.03)	0.15 (trace)	-	-
		Pb	Fe	Cu	Zn	Cd	Mn
Dispersible	HNO <sub>3</sub>	139.57 (1.40)	-	311.40 (3.12)	29.48 (0.29)	-	-
Semi-dispersible		-	-	33,457.40 (334.42)	-	-	-
Massive		3624.88 (35.87)	110.70 (1.10)	7104.25 (71.47)	261.12 (2.58)	-	1.71 (0.02)
		Pb	Fe	Cu	Zn	Cd	Mn
Dispersible	HCl/NaCl	61.2 (294.6)	-	1.1 (5.3)	3.5 (16.6)	trace (0.2)	0.2 (0.8)
Semi-dispersible		1402.98 (271.76)	-	832.66 (161.25)	94.55 (18.32)	-	-
Massive		-	-	75.34 (14.62)	1.47 (0.29)	-	-

**Sample CHG 343**

**Dispersible**

The final sample used to undergo leaching was the copper slag CHG 343. Within this particle size range it was found that with acetic acid Cu, Pb and Zn leached into solution from this sample at concentrations of 4.2, 11.2 and 1.8  $\mu\text{g/L}$  respectively. However, the greatest amount of metal to be extracted from the sample taken was that of Cu which was extracted at a value of 3.0 mg/g whereas Pb and Zn were extracted from the sample at 0.3 and 0.1 mg/g [Figure. 5.43].

The nitric acid leach test afforded three different metals in varying amounts of concentration. Cu was leached at a concentration of 340.46  $\mu\text{g/L}$  and 3.41 mg/g of Cu were extracted from the weight of sample taken. The other two metals, Pb and Zn were leached into solution at concentrations of 126.33 and 54.40  $\mu\text{g/L}$  respectively. The corresponding amounts of Pb and Zn which were extracted from the sample were 1.26 mg/g and 0.54 mg/g respectively [Figure. 5.44].

With HCl/NaCl four metals were detected, Cu, Pb, Zn and Cd. The concentrations of Cu, Zn and Cd leaching into solution was less than the trigger guide level for each of these metals. However Pb leached into solution at a concentration much higher than the other metals. Pb leached at a concentration of 28.2  $\mu\text{g/L}$  and 139.0 mg/g was extracted from the sample taken [Figure. 5.45].

### ***Semi-dispersible***

Within this particle size range it was found that with acetic acid 76.16  $\mu\text{g/L}$  of Pb leached into solution and 1.90 mg/g were extracted from the sample taken. Also 50.50  $\mu\text{g/L}$  and 1.26 mg/g of Cu were extracted from the same sample [Figure. 5.43].

Where nitric acid was used it was found that the two metals which were detected were Cu and Zn at concentrations of 11, 251.73  $\mu\text{g/L}$  and 22.17  $\mu\text{g/L}$  respectively. The amount of these metals extracted from the weight of sample taken was 112.43 mg/g of Cu and 0.23 mg/g of Zn [Figure. 5.44].

In the final leach test for this particular particle size range, it was found that when the sample was leached with HCl/NaCl, 121.46  $\mu\text{g/L}$  of Pb was leached and 23.7 mg/g were extracted. Fe, Cu and Zn were also detected at concentrations of 16.81, 12.24 and 33.51  $\mu\text{g/L}$  respectively. The amount of metal extracted per gram of sample taken was 3.28, 2.39 and 6.54 mg/g [Figure. 5.45].

### ***Massive***

Within this particle size range it was found that leaching with acetic acid afforded very low



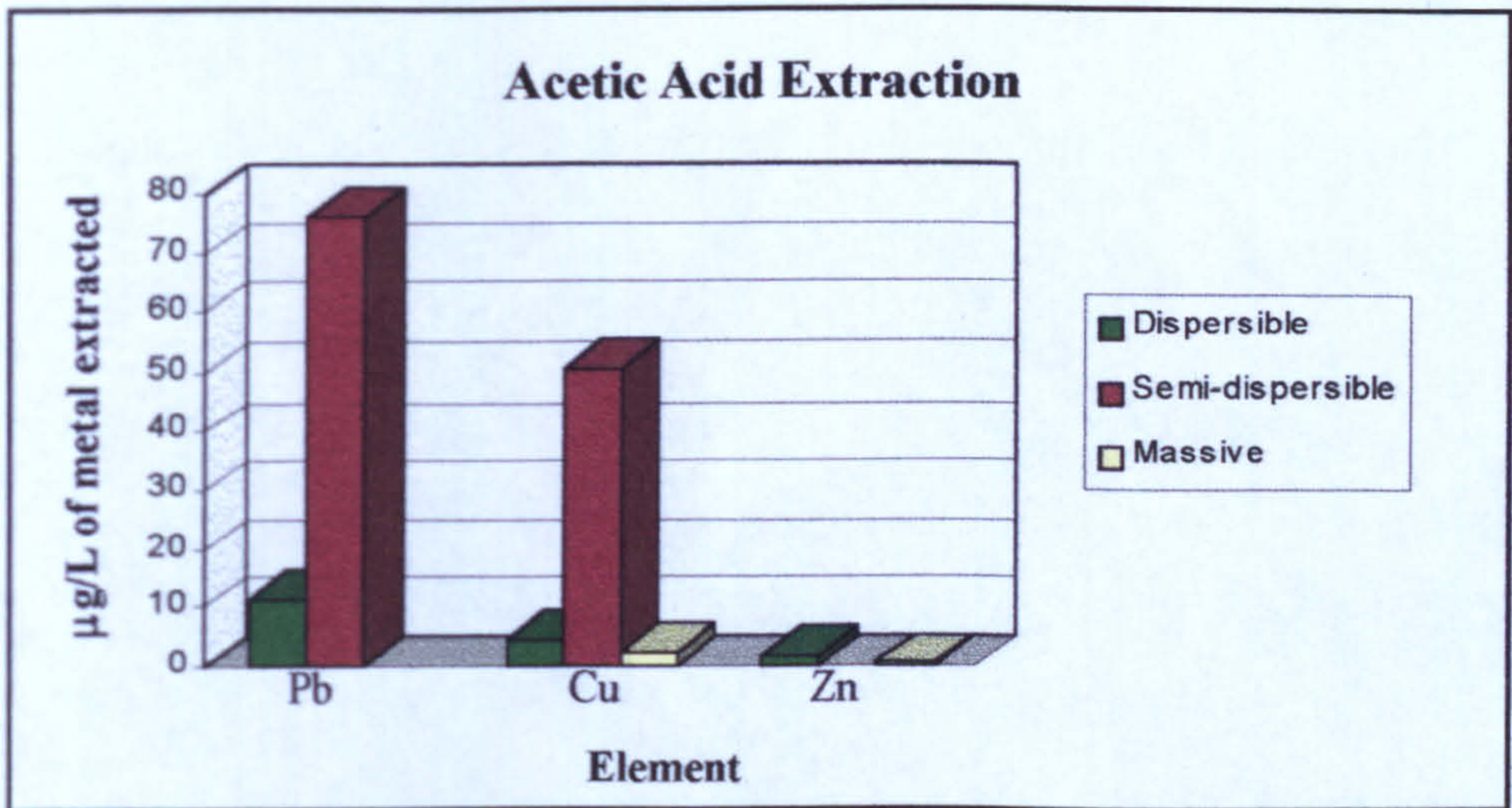


Figure. 5.43:- Leaching of copper slag CHG 343 with acetic acid.

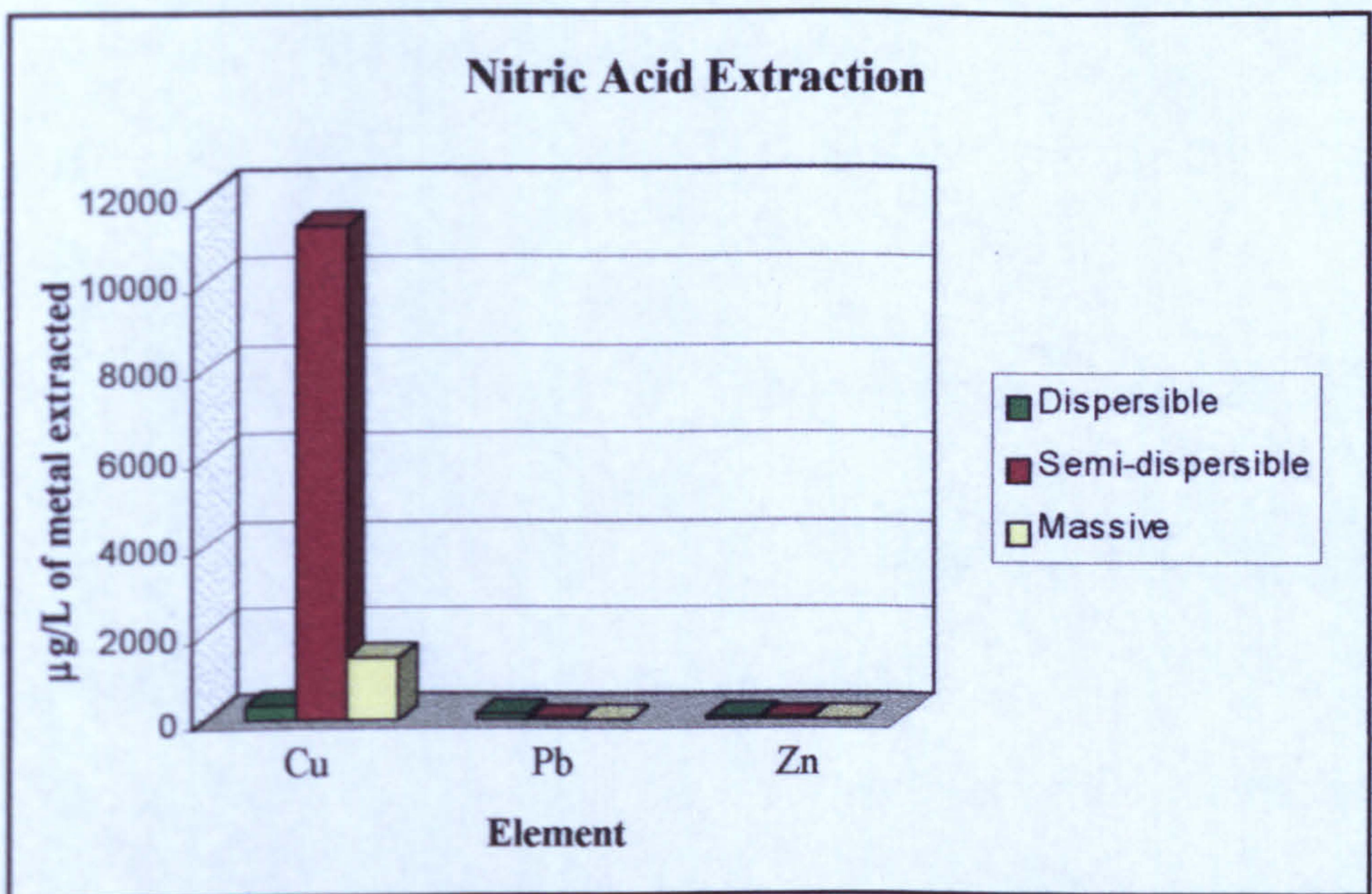


Figure. 5.44:- Leaching of copper slag CHG 343 with nitric acid.

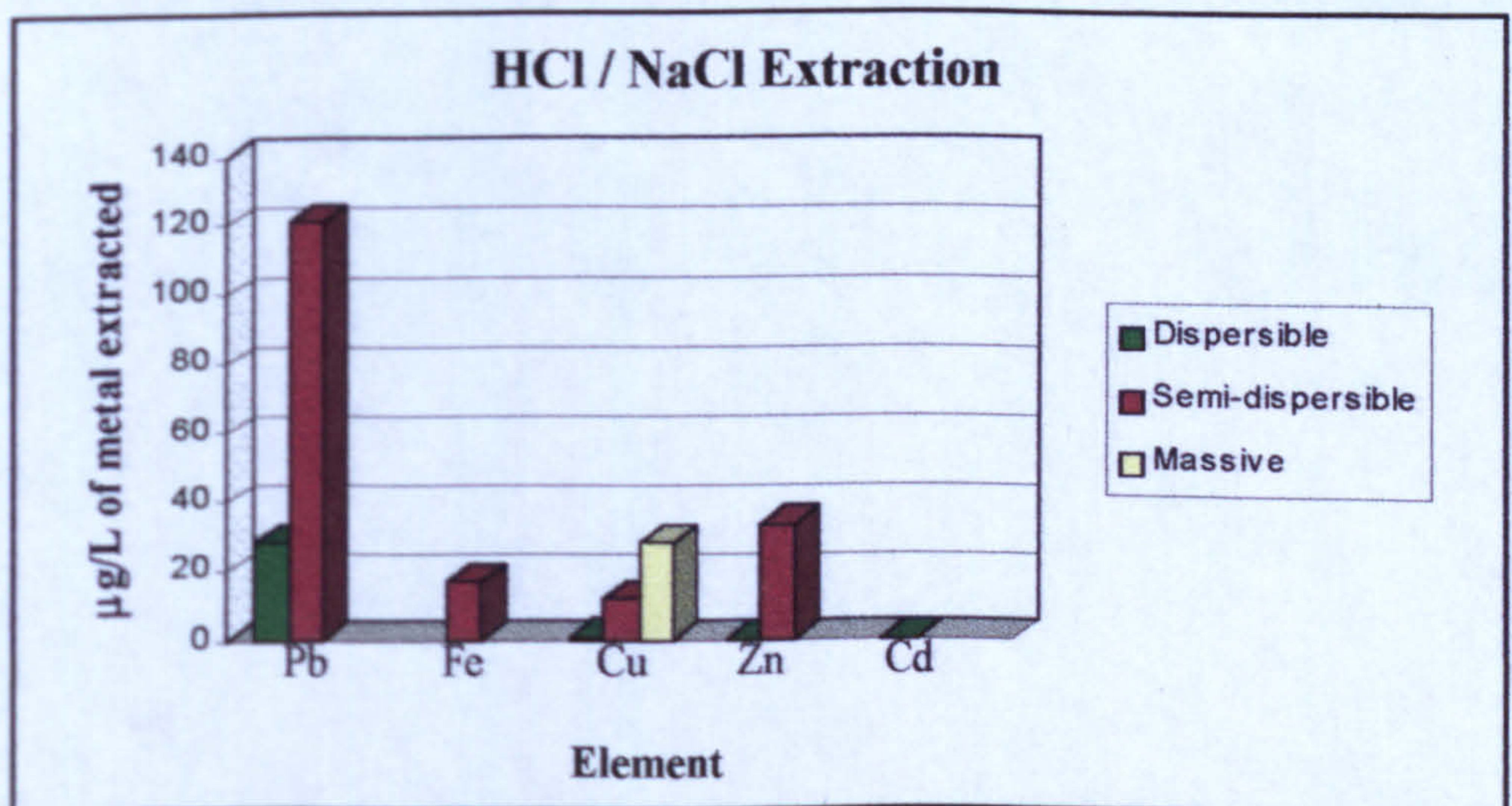


Figure. 5.45:- Leaching of copper slag CHG 343 with HCl / NaCl.

concentrations of Cu and Zn in solution. The concentration of Cu present was 2.01  $\mu\text{g/L}$  and the amount of Cu extracted from the sample was 0.05 mg/g. In the case of Zn, 0.18  $\mu\text{g/L}$  and 0.01 mg/g were extracted [Figure. 5.43].

With the nitric acid leach test, again Cu and Zn were detected but in a higher concentration than the amounts detected with the acetic acid leach test. With this test 1,399.93  $\mu\text{g/L}$  of Cu were leached and 13.94 mg/g was extracted. For Zn the corresponding values were 2.27  $\mu\text{g/L}$  and 0.03 mg/g [Figure. 5.44].

The final test, which was the HCl/NaCl leach test, the only metal to be leached into solution and extracted from the sample was Cu. The concentration of Cu in solution was 28.41  $\mu\text{g/L}$  and it was found that 5.24 mg/g were extracted [Figure. 5.45]. The results are presented in Table 5.13.

### **5.4.3 Solder sample**

Although not a Cu/Zn residue a sample of Sn/Pb solder was supplied by Falcon Metals, Dubai and leaching studies were carried out.

#### ***Leaching of Solder Samples***

##### ***Falcon Metals***

The samples for this part of the study were provided by Falcon Metals Ltd and consisted of solder skimmings, solder dross, solder ash and a sample which was a Sn-Pb-O mix (Table 5.14). After carrying out all three leach tests, it was found that Pb was mainly extracted from the samples in the greatest proportion. The highest concentration of Pb was found in the Sn-Pb-O sample with 9,523.3  $\mu\text{g/L}$  of Pb being extracted from this sample using acetic acid. Between the skimmings, ash and dross samples, the solder ash leached more than double the amount of Pb than the other two samples. [Figure. 5.46].

**Table 5.13: Concentration of metal leached from sized fractions of sample CHG 343**

Sample CHG 343	Leach Liquor	Concentration of metal leached, $\mu\text{g/L}$ (Amount of metal extracted, mg/g)				
		Pb	Fe	Cu	Zn	Cd
Dispersible	CH <sub>3</sub> COOH	11.2 (0.3)	-	4.2 (3.0)	1.8 (0.11)	-
Semi-dispersible		76.16 (1.90)	-	50.50 (1.26)	-	-
Massive		-	-	2.01 (0.05)	0.18 (0.01)	-
		Pb	Fe	Cu	Zn	Cd
Dispersible	HNO <sub>3</sub>	126.33 (1.26)	-	340.46 (3.41)	54.40 (0.54)	-
Semi-dispersible		-	-	11,251.73 (112.43)	22.17 (0.23)	-
Massive		-	-	1399.93 (13.94)	2.27 (0.03)	-
		Pb	Fe	Cu	Zn	Cd
Dispersible	HCl/NaCl	28.2 (139.0)	-	1.1 (138.7)	0.2 (1.0)	0.2 (0.7)
Semi-dispersible		121.46 (23.7)	16.8 (3.28)	12.24 (2.4)	33.5 (6.54)	-
Massive		-	-	28.41 (5.25)	-	-

The nitric acid extraction also leached very high concentrations of Pb from each of the samples, except the solder ash, from which 27.8  $\mu\text{g/L}$  were extracted. Both the solder skimmings and the SnPbO extracted more than 30,000  $\mu\text{g/L}$  of Pb. From the solder dross sample 19,598  $\mu\text{g/L}$  of Pb was extracted. With this extraction other elements which were determined were Fe and Zn. The Zn content was almost the same for the dross and ash but was slightly higher in the solder skimmings [Figure. 5.47].

The HCl/NaCl procedure extracted a much lower concentration of Pb from the solder skimmings than the nitric acid leach test. A concentration of 47.1  $\mu\text{g/L}$  of Pb was extracted from this sample. The greatest concentration of Pb was extracted from the solder ash sample with a concentration of 1387.8  $\mu\text{g/L}$ . This sample also contained the greatest amount of Fe and Zn compared to the other samples which were also leached [Figure. 5.48].

**Table 5.14: Extraction of Falcon metals**

Sample No.	Leach Liquor	Concentration of metal leached, µg/L <i>(Amount of metal extracted, mg/g)</i>				
		Pb	Fe	Zn	Cd	Cu
Solder Skimmings	CH <sub>3</sub> COOH	438.1 <i>(10.9)</i>	0.4 <i>(trace)</i>	1.7 <i>(trace)</i>	-	-
Solder Dross		453.9 <i>(11.3)</i>	1.0 <i>(trace)</i>	2.9 <i>(trace)</i>	0.4 <i>(trace)</i>	-
Solder Ash		1100.3 <i>(27.5)</i>	25.6 <i>(0.6)</i>	491.1 <i>(12.3)</i>	-	-
SnPbO		9523.3 <i>(238.0)</i>	-	-	-	-
		Pb	Fe	Zn	Cd	Cu
Solder Skimmings	HNO <sub>3</sub>	30605.8 <i>(303.0)</i>	107.5 <i>(1.1)</i>	58.9 <i>(0.6)</i>	-	-
Solder Dross		19598.3 <i>(195.6)</i>	124.4 <i>(1.2)</i>	41.3 <i>(0.4)</i>	-	-
Solder Ash		27.8 <i>(0.3)</i>	9.0 <i>(0.1)</i>	41.6 <i>(0.4)</i>	-	-
SnPbO		31645.2 <i>(316.2)</i>				-
		Pb	Fe	Cu	Zn	Cd
Solder Skimmings	HCl/NaCl	47.1 <i>(8.4)</i>	-	-	0.5 <i>(0.1)</i>	-
Solder Dross		167.9 <i>(31.5)</i>	-	0.9 <i>(0.2)</i>	1.3 <i>(0.2)</i>	0.3 <i>(0.1)</i>
Solder Ash		1387.8 <i>(274.4)</i>	148.5 <i>(29.4)</i>	-	725.4 <i>(143.5)</i>	-
SnPbO		1023.1 <i>(200.9)</i>	0.9 <i>(0.2)</i>	-	0.4 <i>(0.1)</i>	-

### 5.5 METHODOLOGY FOR CHARACTERISATION OF WASTE

A description of the methodology developed as part of this work to determine whether any metal-containing material could or could not be shipped is now given in the following flow chart [Figure. 5.49].

The purpose of the flow chart is to provide advice on the status of secondary metal arisings in the context of the Basel Convention and transfrontier shipment of hazardous waste. The flow chart requires the input of characterisation data shown in the brown and blue input boxes in the

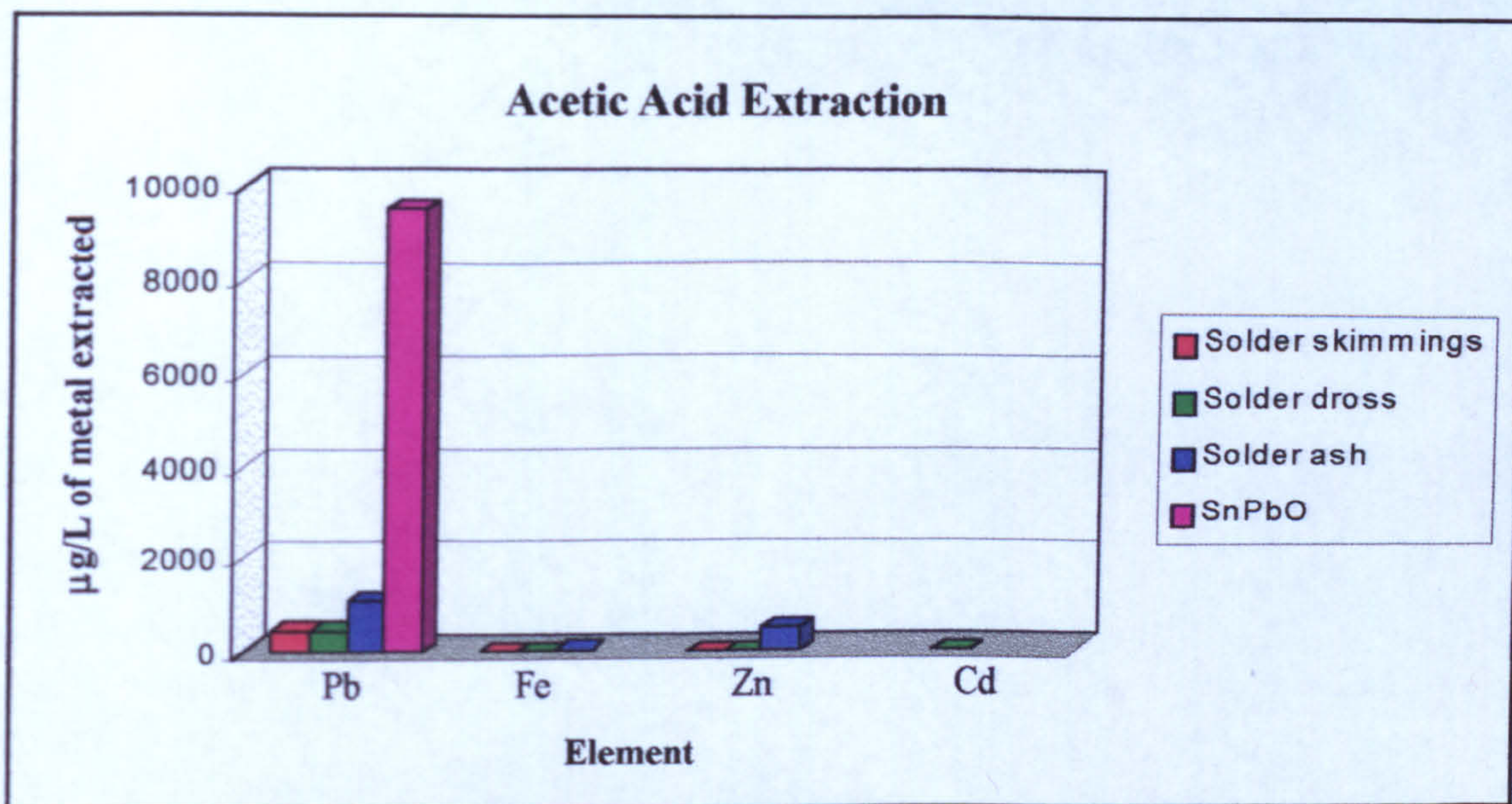


Figure. 5.46:- Leaching of Falcon Metals with acetic acid .

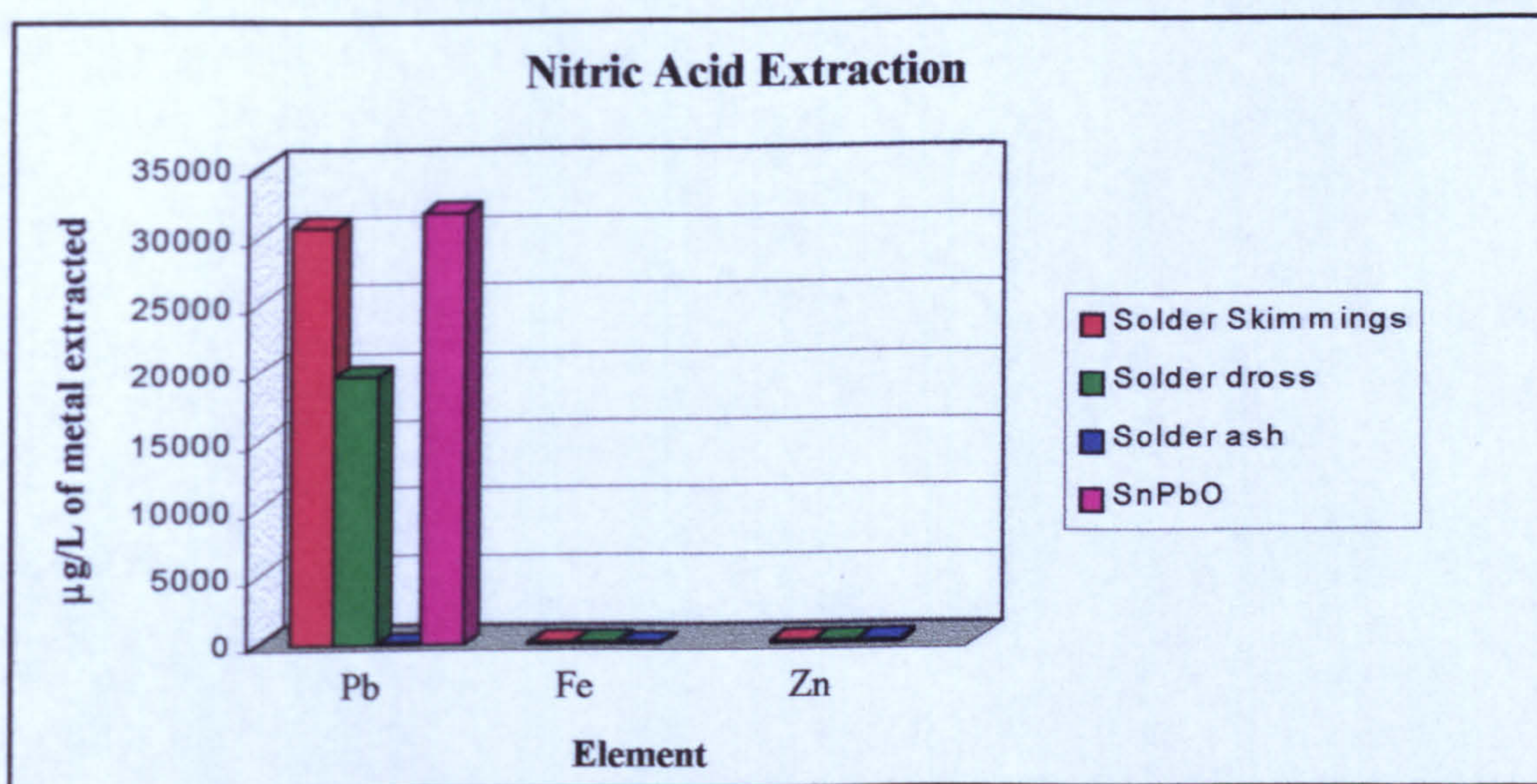


Figure. 5.47:- Leaching of Falcon Metals with nitric acid.

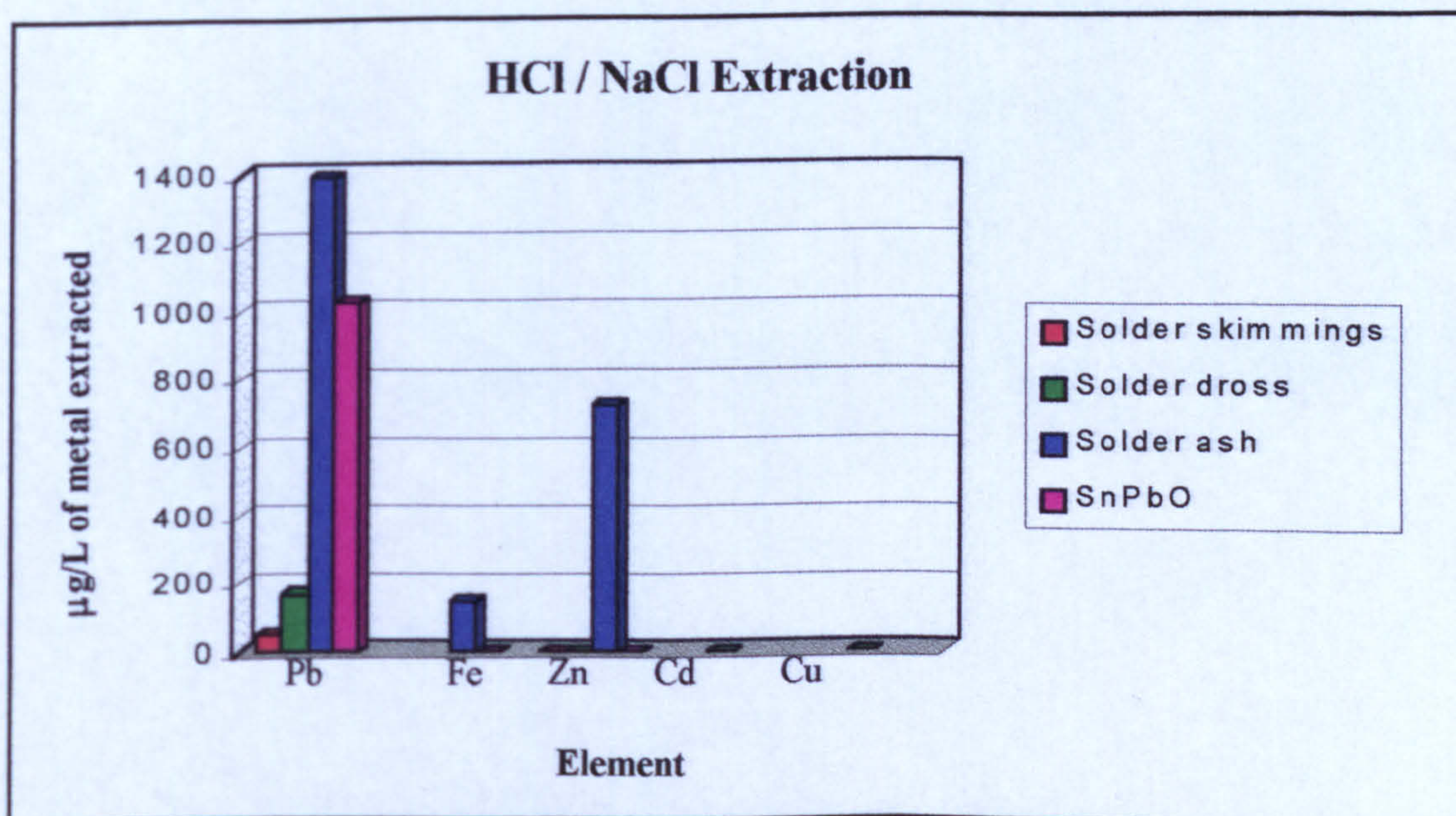


Figure. 5.48:- Leaching of Falcon Metals with HCl / NaCl.

flow chart.

The brown input box requires complete analytical data. Most secondary metal arisings are traded on the basis of main metal content but the Basel ban could be triggered by minor or trace levels of metals or inorganic compounds.

The blue input box requires information that can be used to determine whether a Basel Annex I listed material is present in sufficient quantities to trigger Annex III characteristics. The purpose of the data input at this stage is to determine the real environmental risk associated with the presence of a metal or compound that has an intrinsic hazard. The input at this stage can be of two types:

- (1) Complete speciation data that characterise the exact chemical or alloy phase containing the Basel Annex I metal
- (2) Data from leachability studies

The leachability data are preferred because they give a direct measure of environmental availability of the hazardous metal. Knowledge of solubilities of metal containing compounds and alloys can, however, be used along with speciation data to provide a measure of environmental availability.

The analytical and speciation or leachability data can be used to assess possible triggering of Annex III characteristics. Since many secondary metal arisings are contaminated with organics, it is necessary to determine whether these organics are intrinsically hazardous and if they are, whether they are present in sufficient quantities to trigger Annex III hazard characteristics. These are shown in the green box in the flow chart and this again requires input of complete analytical and speciation data.

**Therefore for a given secondary metal arising, the output for the flowchart is a representation of the indicative legal position with respect to the arising in terms of the Basel Convention.**

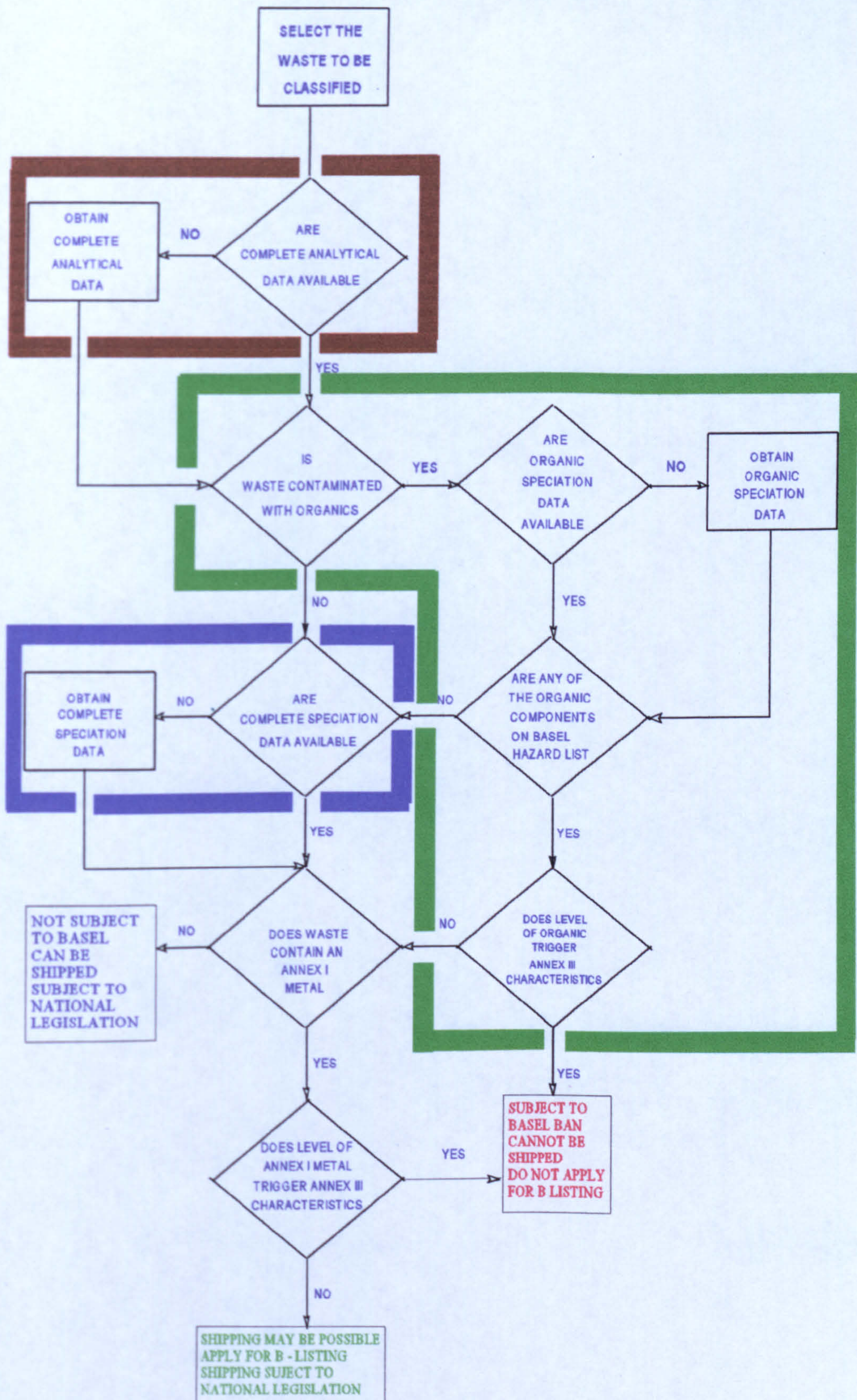


Figure. 5.49 :- Methodology for the characterisation of waste



## **CONCLUSION**

The danger associated with the release of metal-containing species into the environment is associated with the bioavailability of the metal and not solely because of an intrinsically hazardous property. The leachability of primarily copper and zinc from industrial wastes has been determined under various conditions that model environmental situations including acid rain, biological activity in landfill and gastric fluids.

The leaching studies provide information on the bioavailability of copper and zinc in various aqueous solutions and the results can be compared with the ecotoxic properties that represent their intrinsic hazard. The results have been used, along with others in developing a methodology for the characterisation of waste in the context of the Basel Convention. The methodology is represented in terms of a flowchart that can be used to determine whether any metal-containing material would be subject to a shipment ban under the Convention.

As part of the development of the methodology, leaching studies were carried out on single chemical compounds of copper, zinc, cadmium and lead and the results of this work are contained in chapter six.

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**CHAPTER SIX**  
**LEACHING OF CHEMICAL COMPOUNDS**

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## 6 INTRODUCTION

The methodology described in chapter five can be applied either with a knowledge of leachability information or in its absence by speciation that includes the information on the amounts of individual chemical compounds present in the waste. If the information available is speciation data it becomes necessary to obtain data on the leachability of metals from their compounds. In zinc metallurgical wastes, for example, the oxide, ZnO is often a major component of the waste material.

The work presented in this chapter is concerned with the leachability of the metals copper, lead, cadmium and zinc which have been selected as they are examples of Annex I metals of the Basel Convention. Trigger guide levels for metals have been set by The World Health Organisation (WHO) and these values represent the acceptable level of concentration of metal in soils and waters, at which it presents no harm to humans, mammals and fauna. The trigger guide levels for these metals specified for the Basel Convention<sup>[1]</sup> are indicated in Table 6.1.

<b>Element</b>	<b>Trigger level (mg/L)</b>
Cadmium	0.5
Copper	5
Lead	5
Zinc	25

Humans and other animals can be exposed to chemicals through water, air, soils, dusts and their diets. These chemicals can enter the body by several different means such as ingestion, which is mainly in the diet and in water but can also be ingested by dust swallowed in mucus. Other ways in which chemicals can enter the body is by inhalation of air and dusts, and by dermal contact of soil, air and water. In severe cases where highly corrosive chemicals are concerned, these exposure routes can result in localised damage to the cells of the mouth, trachea and digestive system, nasal and respiratory system, the skin and eyes<sup>[2,3]</sup>.

In most cases, the toxic effects of these chemicals occur only after the pollutant has entered the

bloodstream, either by absorption which can take place through the gut, lungs or the skin. Once in the blood stream the chemicals are circulated around the body and are metabolised, usually in the liver, or are stored in various organs. Some of the products from this metabolism can be excreted via the kidneys in urine, the digestive tract, the lungs in exhaled air or sweat from the skin<sup>[4]</sup>.

Toxicology is the study of the effects of poisonous substances on living organisms including the way in which they gain entry into the organisms. Above a certain concentration, the toxicant can have a detrimental effect on some biological functions. Toxicity is commonly categorised on the basis of the duration of the exposure. This can be *acute, chronic and sub-chronic*.

Acute exposure involves a single dose whereas chronic exposure refers to exposure over a long period of time. Sub-chronic exposure is dosing over a shorter period of time which can be a fraction of a life-time.

## 6.1 LEACHING

The removal of materials by dissolving them away from solids is known as *leaching*. The chemical process industries use leaching but the process is usually termed extraction, and organic solvents are often used<sup>[5]</sup>. The theory and practice of leaching are well developed because for many years leaching has been used to separate metals from their ores and to extract sugar from sugar beets.

Environmental engineers have become concerned with leaching more recently because of the multitude of dumps and landfills that contain hazardous and toxic wastes. Occasionally the natural breakdown of a toxic chemical results in another chemical that is even more toxic. Rain that passes through these materials enters ground water, lakes, streams, wells, ponds and the like.

Although many toxic materials have low solubility in water, the concentrations that are deemed hazardous are also very low. Furthermore, many toxic compounds are accumulated by living

cells and can be more concentrated inside than outside a cell, which explains why long-term exposure may be a serious problem.

Countercurrent stagewise processes are frequently used in industrial leaching because they can deliver the highest possible concentration in the extract which is the solvent phase and can minimise the amount of solvent needed. The solvent phase becomes concentrated as it contacts, in a stagewise fashion, the increasingly solute-rich solid. The raffinate, which is the solid material and its adhering solution, becomes less concentrated in soluble material as it moves towards the fresh solvent stage. The solute in the raffinate is in both dissolved and undissolved forms.

“Heap leaching” is a countercurrent process where the solid is in a stationary heap and the solvent percolates through the solid as could be the case in a dump or landfill. This leaching is essentially countercurrent. In industrial leaching, the solvent and the solid are mixed, allowed to approach equilibrium, and then the two phases are separated. Liquids and solvents move countercurrently to the adjacent stages.

Leaching of toxic materials into ground water is a major health concern. Some metals such as lead, cadmium, zinc and copper occur naturally in the environment in the earth’s crust as ores and minerals. Some of these metals such as zinc are essential to human life and plant life and others, such as lead are not. However, regardless of being essential or not, all of these elements can be toxic if ingested in excessive levels.

The metals are released into soils and become available to biological systems through the process of weathering<sup>[6]</sup>. Their mobility and availability are dependant on pH, so the pH of the soil and groundwaters become important. Metal concentrations in the environment above the ‘natural levels’ are cause for concern due to their toxicological effects on humans, mammals and fauna<sup>[7]</sup>.

Heavy metals in the environment can also derive from anthropogenic activity. Sewage sludge spread onto agricultural land, for the dual purposes of disposal and fertilisation, can contain

high concentrations of heavy metals. Other anthropogenic sources include scrap yards and heavy metal industry which can generate airborne pollutants deposited to land as well as solid waste. Waste dumps present a problem with the potential risk of a cocktail of chemical compounds leaching into groundwater.

The next section of this thesis summarises the occurrence of lead, cadmium, copper and zinc.

## **6.2 OCCURRENCE AND TOXICOLOGY OF LEAD, CADMIUM, COPPER AND ZINC**

### **6.2.1 Lead**

Lead is a non-essential, highly toxic heavy metal that has detrimental effects on biological systems. It is a soft and dense ( $11.34\text{g/cm}^3$ ) metal that occurs naturally in the earth's crust at a mean concentration of 12 to 20 ppm making it a relatively rare metal. Lead is present in both organic (Pb-C bonds) and inorganic forms ( $\text{Pb}^{2+}$  and  $\text{Pb}^{4+}$ ) and significantly more inorganic lead is cycled globally than inorganic lead.

Small amounts of lead can be released into the environment by natural processes, including the weathering of rocks, igneous activity and radioactive decay and from Table 6.2 it can be seen that anthropogenic lead emissions have resulted in soil and water lead concentrations several orders of magnitude higher than estimated natural concentration<sup>[8]</sup>.

Lead becomes available in soils and aqueous systems through the natural processes of weathering, leaching, igneous activity and radioactive decay as well as anthropogenic activity. The weathering of lead produces immobile compounds resulting in low concentrations in rivers, streams and oceans. Lead is held strongly in soils by organic matter and so is concentrated in the few top centimetres where it is incorporated by plants and is accumulated in the decomposing humus layer.



Table 6.2:- Lead concentrations in soil, air and water			
Medium	Present day concentration	Estimated natural concentration	Ratio of concentrations
Air Rural/remote Inhabited	0.1-100 ng/m <sup>3</sup> 0.1-10 µg/m <sup>3</sup>	0.10-0.1 ng/m <sup>3</sup> 0.1-1.0 ng/m <sup>3</sup>	10-1,000 100-10,000
Soil Rural/remote Inhabited	5-50 µg/g 10-5,000 µg/g	5-25 µg/g 5-25 µg/g	1-2 2-200
Water Fresh Marine	0.005-10 µg/l 0.05-0.015 µg/l	0.005-10 µl 0.001 µg/l	1 10
Food	0.01-10 µg/g	0.0001-0.1 µg/g	100

Lead occurs naturally in unpolluted waters at a total lead concentration of approximately 0.05-10 mg/L and less than 0.01 mg/L for undissolved lead. Higher levels are indicative of pollution e.g. by wastewaters. Concentrations can be higher where lead piping has been used in sewerage systems. This is the case particularly in soft water areas where pH can be below 5. At a pH of 5 and below, lead is soluble, however in hard water areas pH rarely drops below 7 and consequently the lead is stable and insoluble. Concentrations in soft water areas can be up to 2 mg Pb/L. Elevated concentrations in natural water systems are also the result of leaching from soils containing high concentrations of lead, for example soils which have been treated with sewage sludge, as well as leaching from waste dumps and mine tailings.

#### 6.2.1.2 Exposure to lead in the environment

Today, the major environmental sources of metallic lead and its salts are paint, auto-exhaust, food and water. One of the main modes of exposure to lead in the environment is inhalation of atmospheric lead from vehicle exhausts or in the form of inorganic salts. Once inhaled, the lead can be either exhaled or sneezed out of the nose. Deposition rates in the lungs vary depending upon the size of particles, however an approximation rate is around 50%. From the lungs the majority of lead is absorbed into the blood stream. Ingestion is another significant means of engrossing lead because food which is eaten, may contain lead from the environment or from containers. Acidic foods can leach lead from lead solder in cans and lead glazes used in making

pottery and ceramic objects. Lead can also be ingested with paint and soil. Leaded pipes, soldered plumbing or water coolers are other potential sources of lead exposure<sup>[9]</sup>.

### **6.1.2.2 Toxicity of Lead**

As a toxic agent lead is an accumulative poison. Of the lead retained in the body approximately 90% enters the bones from where it is slowly released into the body. Lead accumulates in the bones where it is stored throughout life however, the amount of lead in the soft tissues stabilises in adult life and may possibly decrease. In an average individual of 70 kg the lead content is approximately 100-440 mg. The World Health Organisation (WHO) recommends that the daily intake should not exceed 3 mg per person per week, whilst the average child intake should be less than 1 mg per week. One study has shown that children living near lead smelters had higher concentrations of lead in their blood compared to those who lived further away from the smelter area. Children exposed chronically to lead were affected in terms of development, co-ordination and IQ<sup>[10]</sup>.

The major routes of entry of lead into the body are the gastrointestinal tract and the lungs. During the time of exposure, lead intake is high and output is low, but once exposure is terminated intake becomes low and excretion of lead increases<sup>[11]</sup>. Once in the lungs, the absorbed lead enters the blood stream where over 90% is bound to red blood cells where it has a mean residence time of one month. The lead is then transported by the blood to organs and tissues within the body. Around 25-40% of the lead in blood enters soft tissues which have a similar residence time to the red blood cells. The remainder of the lead is excreted primarily in faeces but also in urine, sweat and through the hair. From these organs lead is further distributed forming an exchangeable compartment which is primarily the bones. In soft tissues and blood, lead binds to molecules including amino acids, haemoglobin, RNA and DNA. Consequently metabolic pathways are disrupted. This result of the disruption caused by lead poisoning manifests itself in a number of ways. Firstly anaemia results from the disruption of those enzymes that are required to produce haem, a component of haemoglobin and other respiratory pigments. In addition the lead can interfere with uptake of iron by the red blood cells. Secondly, damage to the central nervous system which includes the brain can occur. This is caused by the degeneration of the nerve fibres and interference with capillaries as a result of

intoxication.

Finally, kidney damage has long been known as an effect of lead poisoning. It is associated with heightened levels of amino acids, sugar and phosphates in the urine.

Lead can also be taken up by plants directly through the leaves or by the root system from the soil. However, plants can adapt to an environment which is heavily contaminated with lead in that after the initial stages where lead is toxic, defence processes appear which no longer cause the lead to be poisonous. Animals do not possess these mechanisms and so will be more prone to the adverse effects of lead<sup>[12]</sup>.

### **6.2.2 Cadmium**

Cadmium is a soft, silver-white metal with a faint bluish tinge. As the element is rare, it is usually found as an impurity in ores of other metals, especially zinc. Since cadmium and zinc occur together in nature, they have similar atomic structure and chemical behaviour. Although zinc is an essential element, cadmium is a highly toxic metal with no known function in animal metabolism<sup>[13]</sup>. There are three main routes by which cadmium can enter the environment, *viz*: refining and use of cadmium, copper and nickel smelting and fuel combustion<sup>[14]</sup>

Cadmium is most often encountered in the earth's crust combined with chlorine ( $\text{CdCl}_2$ ), oxygen ( $\text{CdO}$ ) and sulphur ( $\text{CdS}$ ). Cadmium oxide also exists as small particles in air due to the result of smelting, soldering or high temperature industrial processes. Foods are the most important source of cadmium exposure for the general population. Low levels of cadmium can be found in basic foodstuffs, such as grains, cereals and leafy vegetables. These foods readily absorb naturally occurring cadmium or cadmium in soil, which has been contaminated by sewage sludge, fertilizers and polluted groundwater<sup>[15]</sup>.

#### **6.2.2.1 Toxicity of cadmium**

The main routes of exposure of cadmium, for humans, is via respiration and ingestion. The absorption of cadmium is greater for small particles and fumes than for large particle dust. In humans, about 5% of ingested cadmium is absorbed, although a low intake of calcium or iron

increases absorption and gastrointestinal absorption rate may be as high as 20% in individuals with iron deficiency.

Cadmium is mainly transported in the blood bound to the low molecular weight protein metallothionein. As cadmium has a low absorption rate, faecal cadmium is a good indicator of the amount ingested. Most of the cadmium in blood is in the cells, on average about 0.5-1 µg/L and twice as high in smokers.

Any food or drink ingested, which has a high cadmium content, results in acute gastrointestinal effects with diarrhoea and vomiting. Acute inhalation of cadmium from the air can lead to severe chemical pneumonitis and long term exposure to atmospheric Cd may lead to chronic obstructive lung disease and possibly lung cancer. Long term excessive exposure both via air and food leads to renal tubular dysfunction. Other delayed effects of cadmium are anaemia and disturbed liver function.

Animals which have been injected with cadmium compounds often develop sarcoma at the injection site and epidemiological studies carried out on cadmium workers have revealed an increase in lung and prostate cancers. One animal study has shown a clear dose-relationship between lung cancer and cadmium exposure via inhalation.

### **6.2.3 Copper**

Copper in nature is found either in the element form or in several compounds such as oxides, sulphates and carbonates.

#### **6.2.3.1 Toxicity of copper**

Copper is an essential trace element for human beings. In conjunction with Co and Fe it is used in the production of haemoglobin and erythrocytes, and thus in bone and nervous system formation. Some copper compounds can be effective in water treatment to eliminate algae and other micro-organisms. This action is due to the obstructing of the cell walls of the micro-organisms, by copper, which are then incapable of taking up oxygen by themselves.

The chemical inertness of copper allows it to be used in drinking water network systems. Nevertheless, highly oxygenated waters, which can be relatively acidic may contribute to the corrosion of copper pipelines and so increase the copper levels in drinking water<sup>[16]</sup>.

#### **6.2.4 Zinc**

Zinc is generally considered a relatively non-toxic metal. This classification is supported by the fact that zinc is a metal which must be consumed in the diet for optimum health condition and also because the metal is essential for many biological processes. Zinc is relatively abundant in the natural environment and the recommended daily allowance of zinc in the human population is 8-15 mg higher than many other essential metals.

Zinc does not appear to accumulate in the body with age and so there are no known genetic abnormalities which result from excessive accumulation of zinc in the body.

##### **6.2.4.1 Toxicity of zinc**

Zinc is frequently found on industrial waste sites and because of this the industrial use of zinc affects the environmental distribution of this metal. Concern is growing with the realisation of possible increased exposure to zinc through environmental sources such as increases in zinc levels in drinking water particularly through leaching of zinc into ground water surrounding waste sites. Excess exposure to zinc is also potentially a hazard for industrial workers, especially through inhalation of welding fumes and exposure in smelting operations<sup>[17]</sup>.

A number of diseases and dermatological conditions are attributable to zinc deficiency. Zinc is rapidly transported to the skin from the gut and a number of diseases are due to nutritional zinc deficiencies. Ulcers and eczematous skin can occur. The repeated application of zinc chloride to rat and guinea pig skin showed that the metal is absorbed through the skin into the systemic circulation in significant amounts<sup>[18]</sup>.

### **6.3 METHODOLOGY**

The experiments carried out in this study were concerned with the leaching of four different metals cadmium, copper, lead and zinc from inorganic compounds of the same with different

leach liquors designed to simulate a variety of environmental conditions. Different sources of each of these metals have been selected for the leaching studies and these are summarised in Table 6.3 along with a comment on their respective solubilities.

Table 6.3:- Samples and their solubilities							
Sample	Solubility g/100 cm <sup>3</sup>	Sample	Solubility g/100 cm <sup>3</sup>	Sample	Solubility g/100 cm <sup>3</sup>	Sample	Solubility g/100 cm <sup>3</sup>
Copper Turnings	insoluble	Zn*	insoluble	Pb shot	insoluble	Cd*	insoluble
Cu <sub>2</sub> O	insoluble	ZnO	0.0002	PbO	0.0017	CdO	0.00012
CuO	insoluble						
CuS	0.000033	ZnS	insoluble	PbS	0.00009	-	-
CuCO <sub>3</sub>	insoluble	ZnCO <sub>3</sub>	0.001	PbCO <sub>3</sub>	0.00011	CdCO <sub>3</sub>	insoluble
-	-	Zn(PO) <sub>4</sub>	insoluble	-	-	-	-

(Source:- CRC Handbook of Chemistry and Physics, 59th Edition, 1978-1979)

Zn\*- powdered zinc metal      Cd\*- granulated cadmium metal

The various leach liquors (Table 6.4) which were used in the leaching extractions included:-

Table 6.4:- Leach liquors	
Leach liquor	Simulated environmental condition
CH <sub>3</sub> COOH (0.5 M)	Modified Toxic Characteristic Leaching Procedure (TCLP) test
CaCl <sub>2</sub> (0.01 M)	Soil conditions
HCl / NaCl (1:1 mixture, 0.1M)	Gastric conditions
HNO <sub>3</sub> (2 M)	Pseudo total heavy metal fraction analysis for soils
H <sub>2</sub> SO <sub>4</sub> / HNO <sub>3</sub> (60:40 mixture 1 M)	Acid rain
De-ionised water	Water

The procedures for extraction using each of the liquors are now described. All experiments were conducted in duplicate as a minimum to achieve reproducibility and the results presented in Section 6.4 represent averages of the measurements. All experiments were conducted at room temperature. For every metal carbonate which was leached for the individual metals, the experiment was carried out six times with each leach liquor and the standard deviation of the metal carbonate was calculated.

### **6.3.1 Acetic Acid Extraction<sup>[19]</sup>**

For this leach procedure, a modified version of the Canadian, Toxic Characteristic Leaching Procedure, (TCLP) method was used. 10g of sample was placed in a 250 ml stoppered conical flask to which 160 ml of de-ionised water was added. The flask was shaken using a mechanical shaker (Griffin) at 10 revs/min. The pH of the solution was measured after the sample had been shaken for 15 minutes.

If the pH of the solution was greater than 5.2 then sufficient 0.5 M acetic acid was added to reduce and maintain the pH at  $5.0 \pm 0.2$ . The sample was then shaken for 24 hours with the pH being monitored after 1, 3 and 6 hours with a final pH check after 22 hours. The pH was adjusted to 5.2 by addition of drops of 0.5 M acetic acid but, if it was below 4.8 then 40 ml of de-ionised water was added and the pH adjusted. After 24 hours the experiment was stopped, the solution filtered and the filtrate transferred to a 250 ml volumetric flask and sufficient de-ionised water added to take the volume up to 250 ml. When filtration was slow, solid and liquid phases were separated by centrifugation followed by filtration.

The solid and liquid phases were then separated by centrifuge and filtration to obtain approximately 100 ml of solution for analysis.

### **6.3.2 Calcium Chloride Extraction<sup>[20]</sup>**

A single extraction with 0.01 M  $\text{CaCl}_2$  has been proposed and the procedure followed exactly as a cheap and simple method for the determination of the bioavailability of heavy metals in soils. This method was found to give a better guide to the bioavailability of the metals than a total soil analysis.

In a 250 ml conical flask, 10 g of sample was placed to which 100 ml of 0.01M CaCl<sub>2</sub> was added. The sample was shaken for 2 hours after which the pH was only measured but not adjusted in any way. The solid and liquid fractions were separated by centrifugation and filtration and the filtrate transferred to a 100 ml volumetric flask and sufficient de-ionised water added to take the volume up to 100 ml..

### **6.3.3 Hydrochloric Acid Extraction<sup>[21]</sup>**

This leach test was carried out by placing 0.5 g of sample into a 250 ml conical flask. To this was added 100 ml of leach solution, a mixture of 0.1 M hydrochloric acid and 0.1 M sodium chloride. The sample was shaken for 1 hour and as previously stated, centrifugation and filtration was used to separate the solid and liquid phases so that ample solution could be obtained for analysis.

### **6.3.4 Nitric Acid Extraction<sup>[22,23,24]</sup>**

This particular test was found to be an aggressive extraction because of the strength of the acid used. After placing 10 g of sample into a stoppered 250 ml conical flask, 100 ml of 2M nitric acid was added. The sample was shaken for 1 hour. Once again, the mixture was centrifuged and filtered and the filtrate was transferred to a 100 ml volumetric flask and sufficient de-ionised water was added to take the volume up to 100 ml.

### **6.3.5 Sulphuric acid/Nitric acid extraction<sup>[25]</sup>**

This method is based upon US analytical method 1312. The procedure was carried out in the same manner as the acetic acid extraction with the pH being monitored every 1, 3, 6 and 22 hours following an initial pH check after 15 minutes. To adjust the pH to  $5.0 \pm 0.2$  the required amount of a 60/40 mixture of 1M H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> was added.

As previously described in the acetic acid extraction, on completion of the 24 hour extraction the sample was centrifuged and filtered, the filtrate transferred to a volumetric flask and the volume made up to 250 ml.



### **6.3.6 De-ionised water extraction**

10g of sample was leached in a stoppered 250 ml conical flask in 100 ml of de-ionised water for 1 hour. The sample was then centrifuged and filtered and the filtrate transferred to a 100 ml volumetric flask and sufficient de-ionised water was added to make the volume up to 100 ml.

In all cases the samples were analysed using atomic absorption spectroscopy.

## **6.4 RESULTS AND DISCUSSION**

The results of each leaching study are now presented and discussed under the following headings:- lead, cadmium, zinc and copper.

### **6.4.1 Leaching of lead compounds**

The results of this study are presented in tabular and graphical form. The table (Table 6.4) provides a comparative summary of the effectiveness of the leach liquor for each lead compound.

#### ***Lead shot***

Lead shot was extracted with each of the six leach liquors. It was found that de-ionised water extracted the least amount of lead shot both in terms of the concentration of lead in the final solution and the amount of lead extracted per gram of sample taken. The amount of lead extracted for this particular extraction were 1.62 mg/L and 0.02 mg/g [Figure. 6.1].

With the other leach liquors it was concluded that the  $\text{H}_2\text{SO}_4/\text{HNO}_3$  leach liquor extracted the most lead from this sample with values of 14,900 mg/L and 148.81 mg/g [Figure. 6.2].  $\text{CaCl}_2$  extracted 7,900 mg/L and 78.94 mg/g of lead from the lead shot sample [Figure. 6.3]. The  $\text{HCl}/\text{NaCl}$  extraction, extracted the least amount of lead from the lead shot sample with values of 427 mg/L and 84.02 mg/g [Figure. 6.4].

The corresponding values for  $\text{HNO}_3$  were 26,000 mg/L and 259.60 mg/g [Figure. 6.5] and for acetic acid 3540 mg/L and 35.39 mg/g [Figure. 6.6].

Table 6.4:-Leaching of lead compounds

Leach liquor	Lead shot		Lead oxide		Lead sulphide		Lead carbonate		
	Conc. of lead leached (mg/L)	Amount of lead extracted (mg/g)	Conc. of lead leached (mg/L)	Amount of lead extracted (mg/g)	Conc. of lead leached (mg/L)	Amount of lead extracted (mg/g)	Conc. of lead leached (mg/L)	Amount of lead extracted (mg/g)	Standard Deviation (mg/g)
H <sub>2</sub> SO <sub>4</sub> /HNO <sub>3</sub>	14,900	148.81	98.0	0.98	5.35	0.08	3.29	3.3 x 10 <sup>-3</sup>	0.015 ± 0.02
CH <sub>3</sub> COOH	3,540	35.39	7,680	76.78	370	3.70	310	2.40	0.011 ± 0.01
HCl/NaCl	427	84.02	1,959	371.94	1,700	1.70	22,180	4362	4237.4 ± 125.3
DI-water	1.62	0.02	0.23	2.3 x 10 <sup>-3</sup>	5.41	0.01	0.86	8.6 x 10 <sup>-3</sup>	6.6 x 10 <sup>-3</sup> ± 2 x 10 <sup>-3</sup>
HNO <sub>3</sub>	26,000	259.60	86,700	866.63	ppt formed	-	70,450	764.96	734.5 ± 30.4
CaCl <sub>2</sub>	7,900	78.94	15.24	0.15	8.24	0.01	15.24	0.15	0.14 ± 0.01

**Lead Trigger Guide Level - 5 mg/L**

The figures in red exceed the trigger guide level

With this sample it can be seen from Table 6.4 that under acid rain conditions, lead becomes available in a large concentration to the environment.

With this sample the lowest concentration of lead leached into solution and below the trigger guide level was when leaching with de-ionised water was utilised.

### ***Lead Oxide***

In the case of PbO, leaching with HNO<sub>3</sub> proved to be the most vigorous test in extracting lead from the sample used. Values of 86,700 mg/L and 866.63 mg/g were obtained with this particular leach liquor [Figure. 6.5]. When using the Canadian method, the amount of lead extracted was 7680 mg/L and 76.78 mg/g [Figure. 6.6].

Leach liquor simulating gastric conditions leached 1959 mg/L of Pb and 371.94 mg/g of Pb [Figure. 6.4] which is considerably less than the other two leaching liquors which were used. With the use of the acidic rain conditions, only half the amount of lead was extracted compared with that extracted under gastric conditions.

The values for H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> conditions were 98 mg/L and 0.98 mg/g [Figure. 6.2]. However, with the two less aggressive leach tests of CaCl<sub>2</sub> and de-ionised water, a very small amount of lead was extracted as only 15.24 mg/L and 0.15 mg/g was extracted with CaCl<sub>2</sub> [Figure. 6.3] and 0.23 mg/L and 0.0023 mg/g were leached with de-ionised water respectively [Figure. 6.1]. The results for this sample are tabulated in Table 6.4.

The concentration of lead leached into solution, when lead oxide sample was used, was less than the trigger guide level of 5 mg/L only when leached with de-ionised water.

### ***Lead sulphide***

The results for this sample showed a large difference between the values obtained for HCl/NaCl and acetic acid. Almost six times as much lead was extracted under gastric conditions with values of 1,700 mg/L, 1.70 mg/g [Figure. 6.4] and 370 mg/L, 0.37 mg/g with acetic acid [Figure. 6.6].

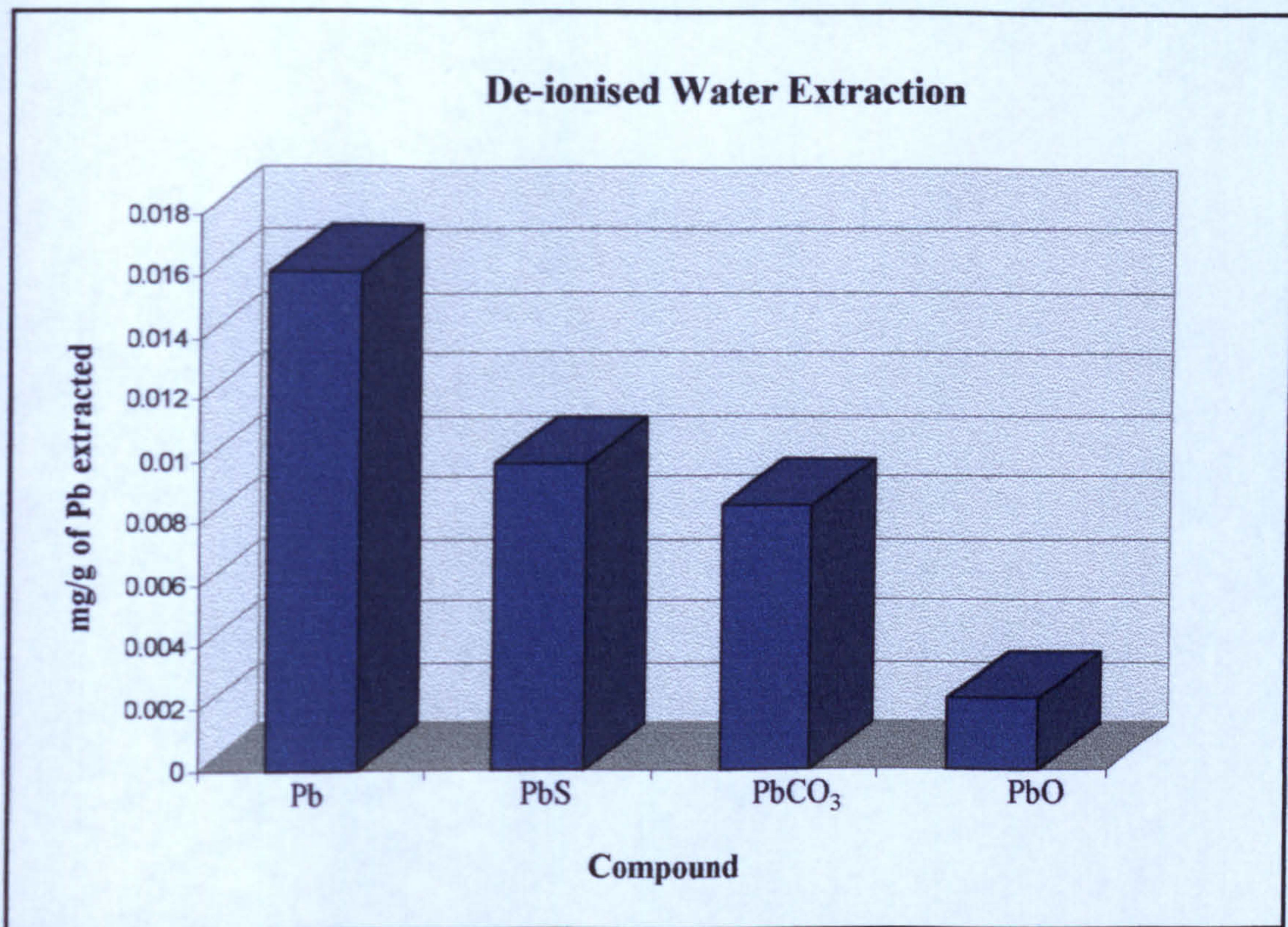


Figure. 6.1:- Leaching of Pb compounds with de-ionised water.

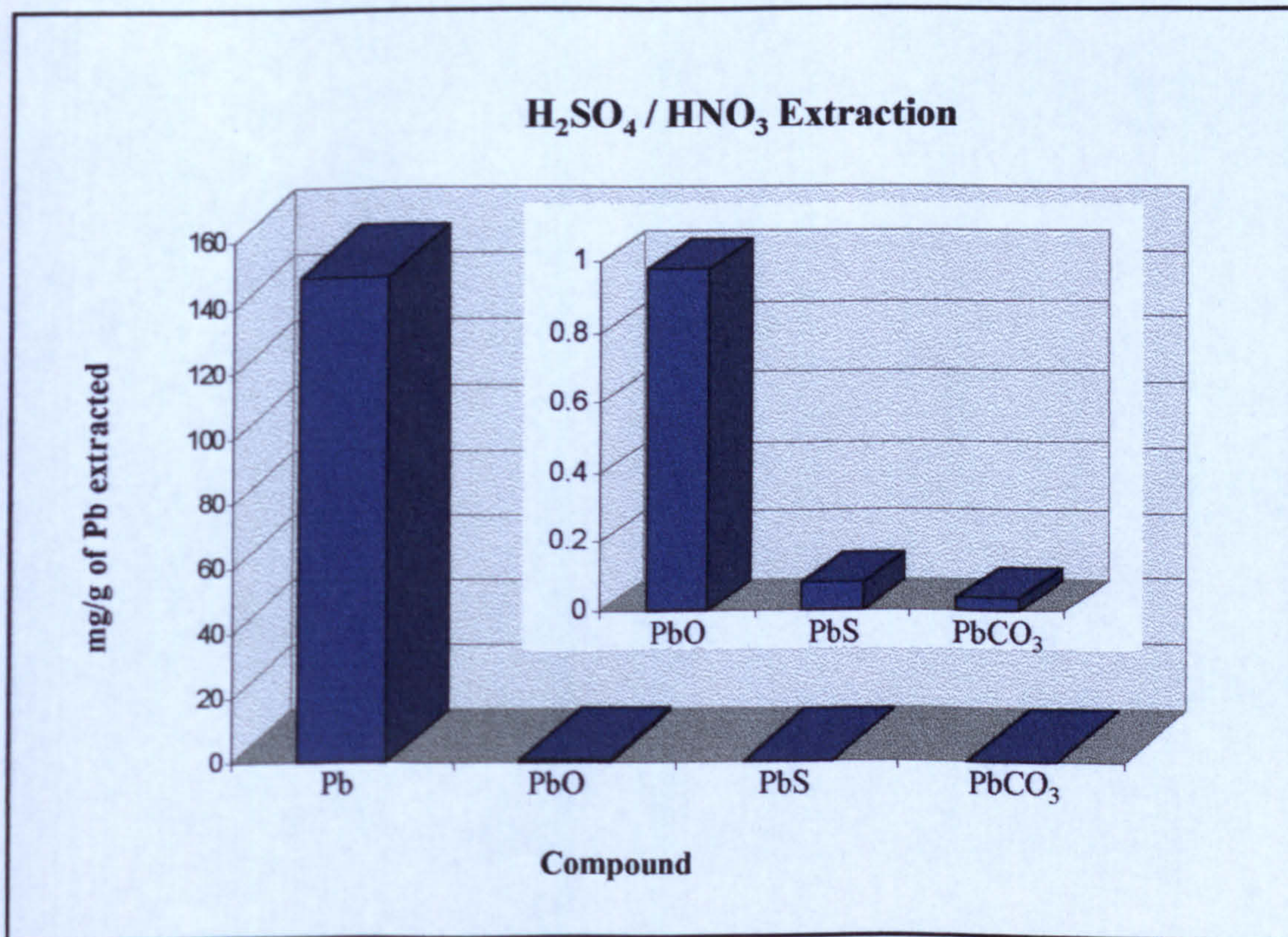
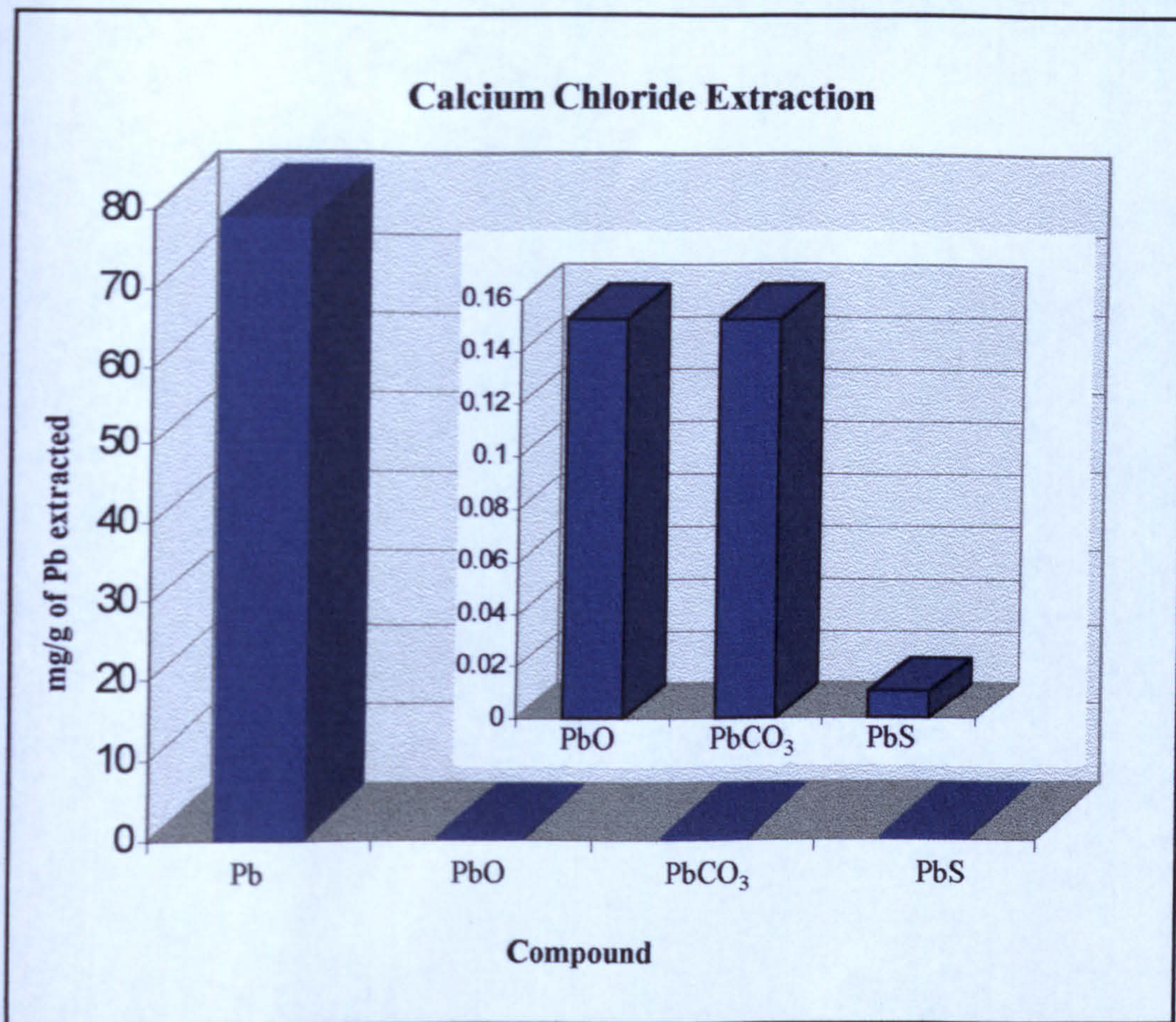
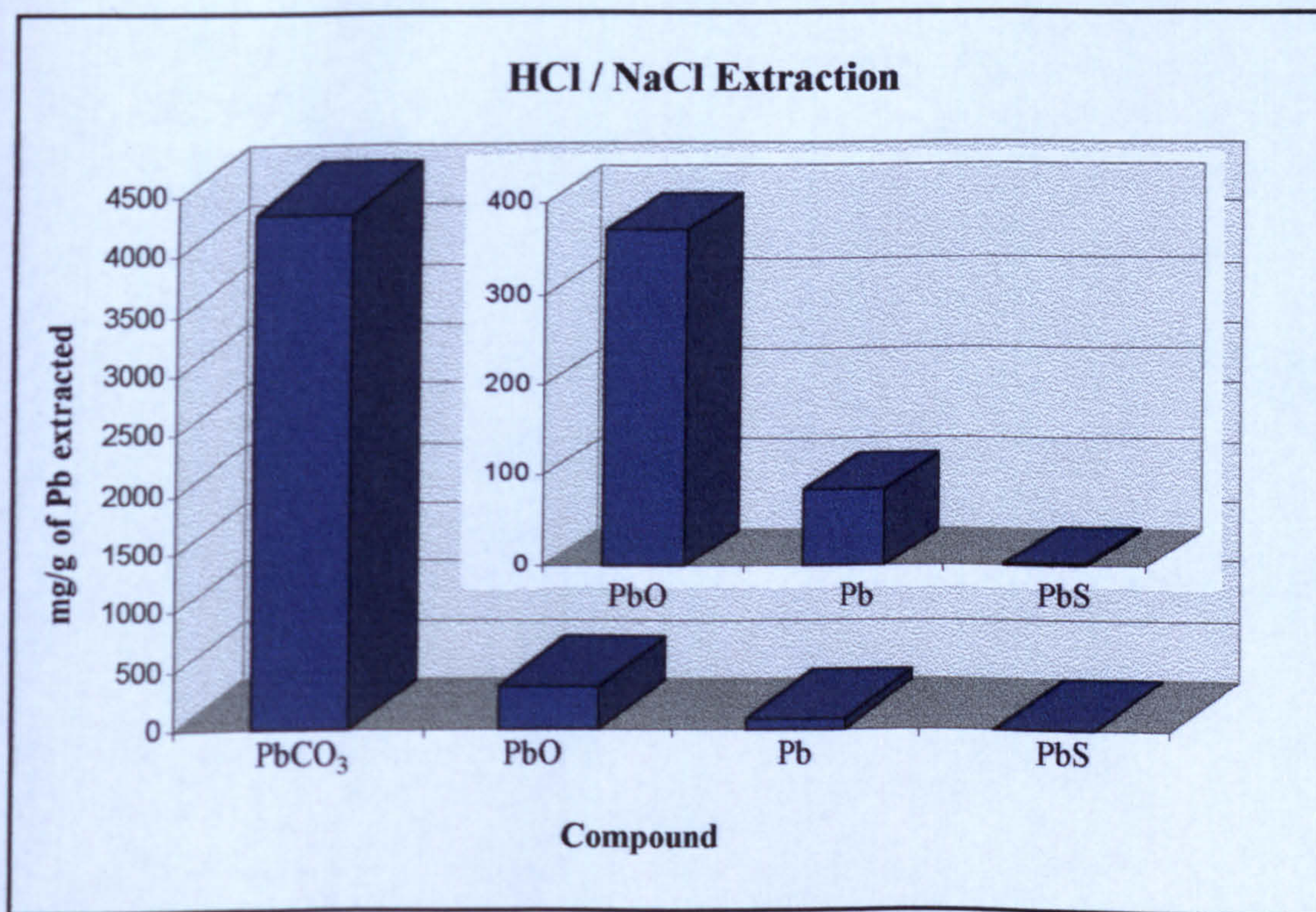


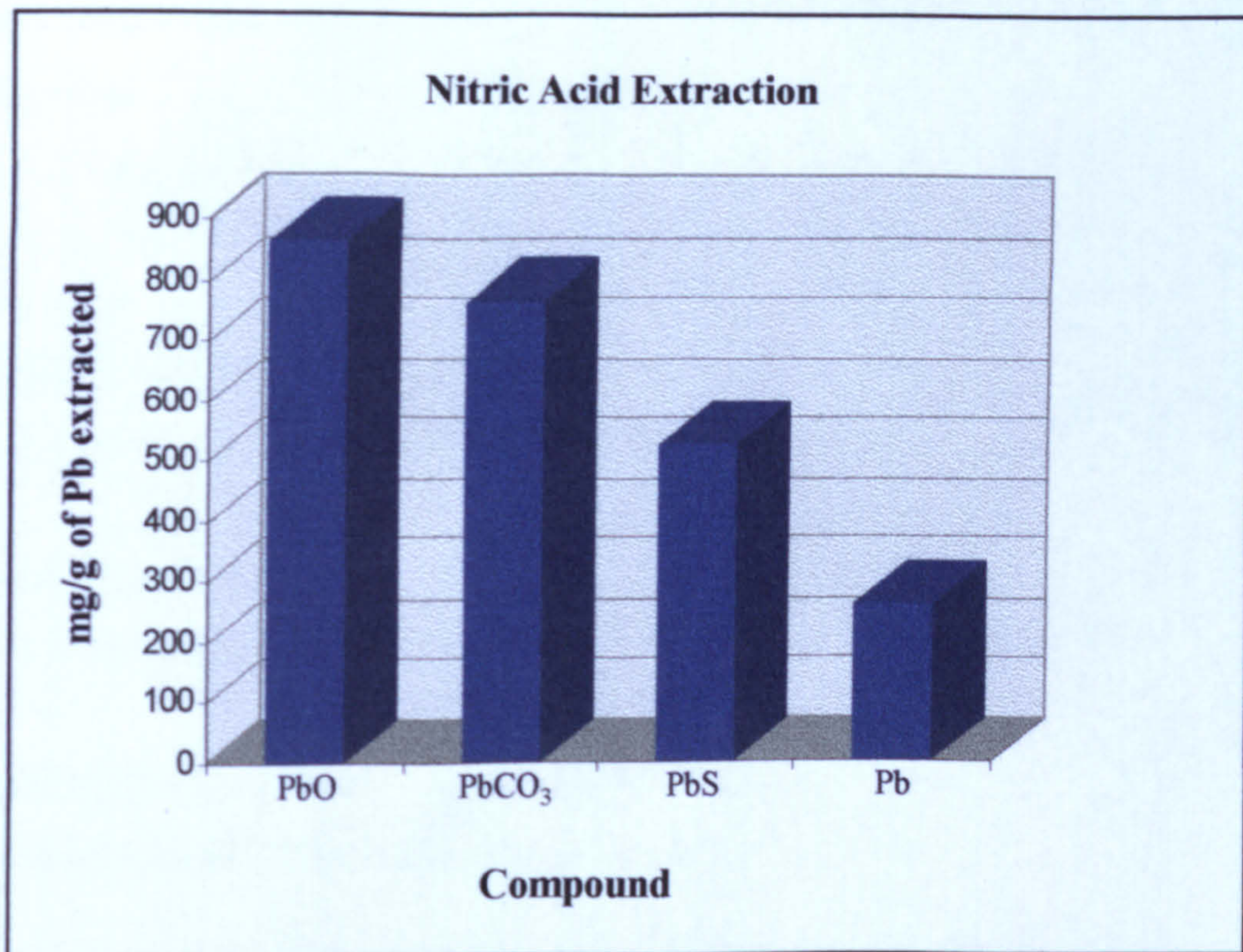
Figure. 6.2:- Leaching of Pb compounds with H<sub>2</sub>SO<sub>4</sub> / HNO<sub>3</sub>.



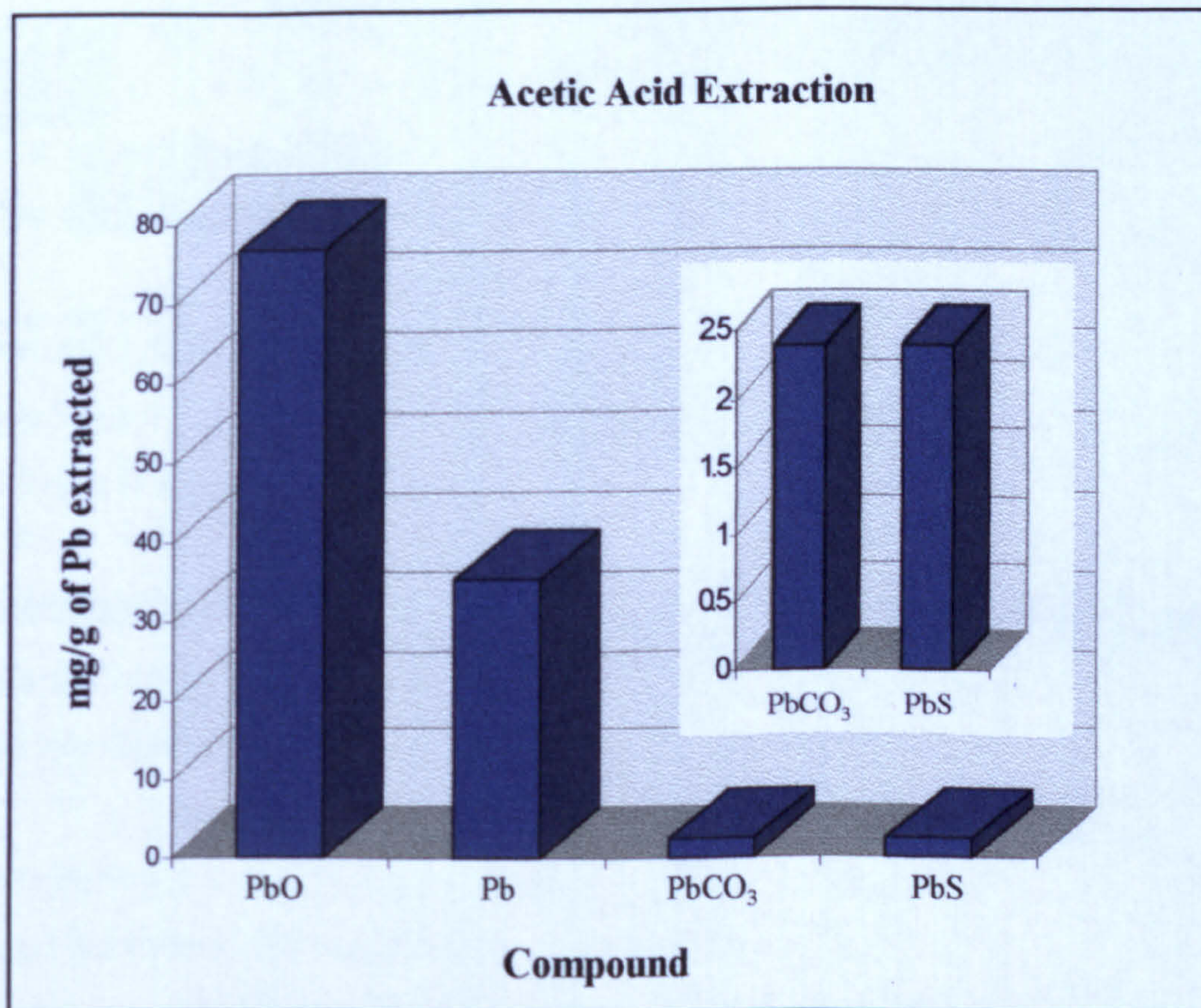
**Figure. 6.3:- Leaching of Pb compounds with calcium chloride.**



**Figure. 6.4:- Leaching of Pb compounds with HCl / NaCl.**



**Figure. 6.5:- Leaching of Pb compounds with nitric acid.**



**Figure. 6.6:- Leaching of Pb compounds with acetic acid.**

The results for the  $\text{CaCl}_2$  [Figure. 6.3],  $\text{H}_2\text{SO}_4/\text{HNO}_3$  [Figure. 6.2] and de-ionised water [Figure. 6.1] extractions did not vary much with values of 8.24, 5.35 and 5.41 mg/L respectively for each and for the amount of lead extracted per gram of sample taken the values were 0.08 mg/g for acidic rain simulation and for soil conditions and de-ionised water the results were 0.01mg/g. When PbS was extracted with  $\text{HNO}_3$  it was not possible to analyse the sample since a precipitate was formed.

From Table 6.4 it can be noted that under simulated gastric conditions, lead can be extracted and so become readily available in high concentrations.

Lead sulphide was found to leach into solution well above the trigger guide level only when it was leached under saline conditions and acetic acid.

### ***Lead carbonate***

When lead carbonate was extracted with each of the six different leach liquors, it was found that the greatest amount of lead was extracted when the sample was leached with nitric acid. In this case 70,450 mg/L was leached in solution and 764.96 mg/g was extracted from the amount of sample taken [Figure. 6.5].  $\text{HCl}/\text{NaCl}$  leached 22,180 mg/L and 4362.0 mg/g of lead when the lead carbonate sample was leached under saline conditions [Figure. 6.4].

The  $\text{H}_2\text{SO}_4/\text{HNO}_3$  test leached 3.29 mg/L of lead from this sample and extracted  $3.3 \times 10^{-3}$  mg/g [Figure. 6.2]. De-ionised water leached the least amount of lead at 0.86 mg/L and  $8.6 \times 10^{-3}$  mg/g [Figure. 6.1].

From the remaining two leach tests 310 mg/L of lead was leached and 2.40 mg/g were extracted with the acetic acid leach test [Figure. 6.6]. With the  $\text{CaCl}_2$  leach test 15.24 mg/L of lead were leached and 0.15 mg/g were extracted [Figure. 6.3].

From Table 6.4 it can be seen that lead carbonate was found to leach into solution below the trigger guide level of 5 mg/L under acidic rain conditions and when leached with de-ionised water.

Table 6.5:-Leaching of cadmium compounds

Leach liquor	Granulated cadmium		Cadmium oxide		Cadmium carbonate		
	Conc. of cadmium leached (mg/L)	Amount of cadmium extracted (mg/g)	Conc. of cadmium leached (mg/L)	Amount of cadmium extracted (mg/g)	Conc. of cadmium leached (mg/L)	Amount of cadmium extracted (mg/g)	Standard Deviation (mg/g)
H <sub>2</sub> SO <sub>4</sub> /HNO <sub>3</sub>	9,000	89.53	2,800	27.97	1.75	0.02	4.9 ± 3.8
CH <sub>3</sub> COOH	370	3.70	5,300	52.98	58.0	0.58	1.6 ± 0.6
HCl/NaCl	14,400	2851.48	19,700	3903.31	1,880	364.06	334.4 ± 214.7
DI-water	16.5	0.16	2.90	0.03	0.10	10 <sup>-4</sup>	4.6 x 10 <sup>-3</sup> ± 4.1 x 10 <sup>-3</sup>
HNO <sub>3</sub>	74,500	739.15	49,000	489.76	33,000	329.72	422.6 ± 78.6
CaCl <sub>2</sub>	900	9.00	1,050	10.49	0.16	1.6 x 10 <sup>-3</sup>	7.2 x 10 <sup>-3</sup> ± 1.2 x 10 <sup>-4</sup>

## Cadmium Trigger Guide Level - 0.5 mg/L

The figures in red exceed the trigger guide level



### **6.4.2 Leaching of cadmium compounds**

The results of this study are presented in tabular and graphical form. Table 6.5 provides a comparative summary of the effectiveness of the leach liquor for each cadmium compound.

#### ***Granulated cadmium***

In these experiments, cadmium metal in granulated form was used. This meant that the particle range covered was “massive” (>1 nm). Cadmium was extracted using the various leach liquors and it was observed that the use of HNO<sub>3</sub> acid provided conditions of maximum extraction of cadmium from this sample with values of 74,500 mg/L and 739.15 mg/g [Figure. 6.7].

Gastric conditions extracted 14,440 mg/L and 2,851.48 mg/g [Figure. 6.8], therefore, in this case more cadmium was extracted per gram of sample taken rather than the amount of cadmium extracted in solution. With H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> cadmium was extracted at concentrations of 1,300 mg/L and 89.54 mg/g [Figure. 6.9]. As expected, de-ionised water gave the lowest concentration of metal extracted at 16.5 mg/L and 0.16 mg/g [Figure. 6.10]. CaCl<sub>2</sub> [Figure. 6.11] and acetic acid [Figure. 6.12] extracted 900 mg/L and 370 mg/L respectively and in terms of metal extracted for the amount of sample taken, the corresponding values were 9.00 mg/g and 3.70 mg/g respectively.

For granulated cadmium, HNO<sub>3</sub> extracted a greater concentration of metal in solution. However, in terms of the weight of sample which was taken, in this case 10 g, H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> was found to extract more cadmium by weight from the sample.

Cadmium metal was found to leach into solution above the 0.5 mg/L level regardless of which leach liquor was used.

#### ***Cadmium oxide***

Cadmium oxide is slightly soluble in nitric acid, therefore it was expected that nitric acid would extract more metal than any of the other leach liquors which were used. The results confirmed this, with HNO<sub>3</sub> extracting more than double the amount of cadmium compared to that achieved using HCl/NaCl.

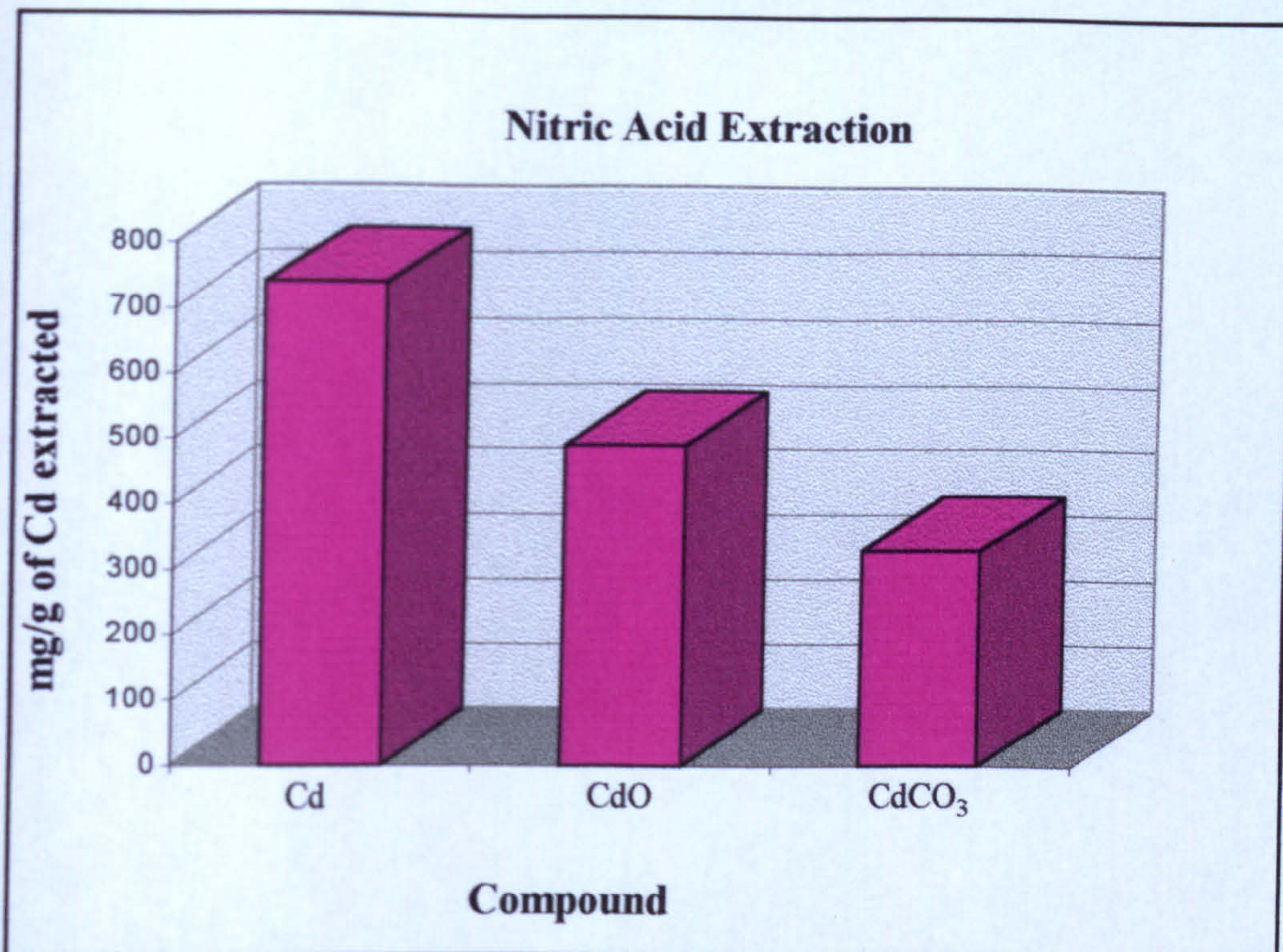


Figure. 6.7:- Leaching of Cd compounds with nitric acid.

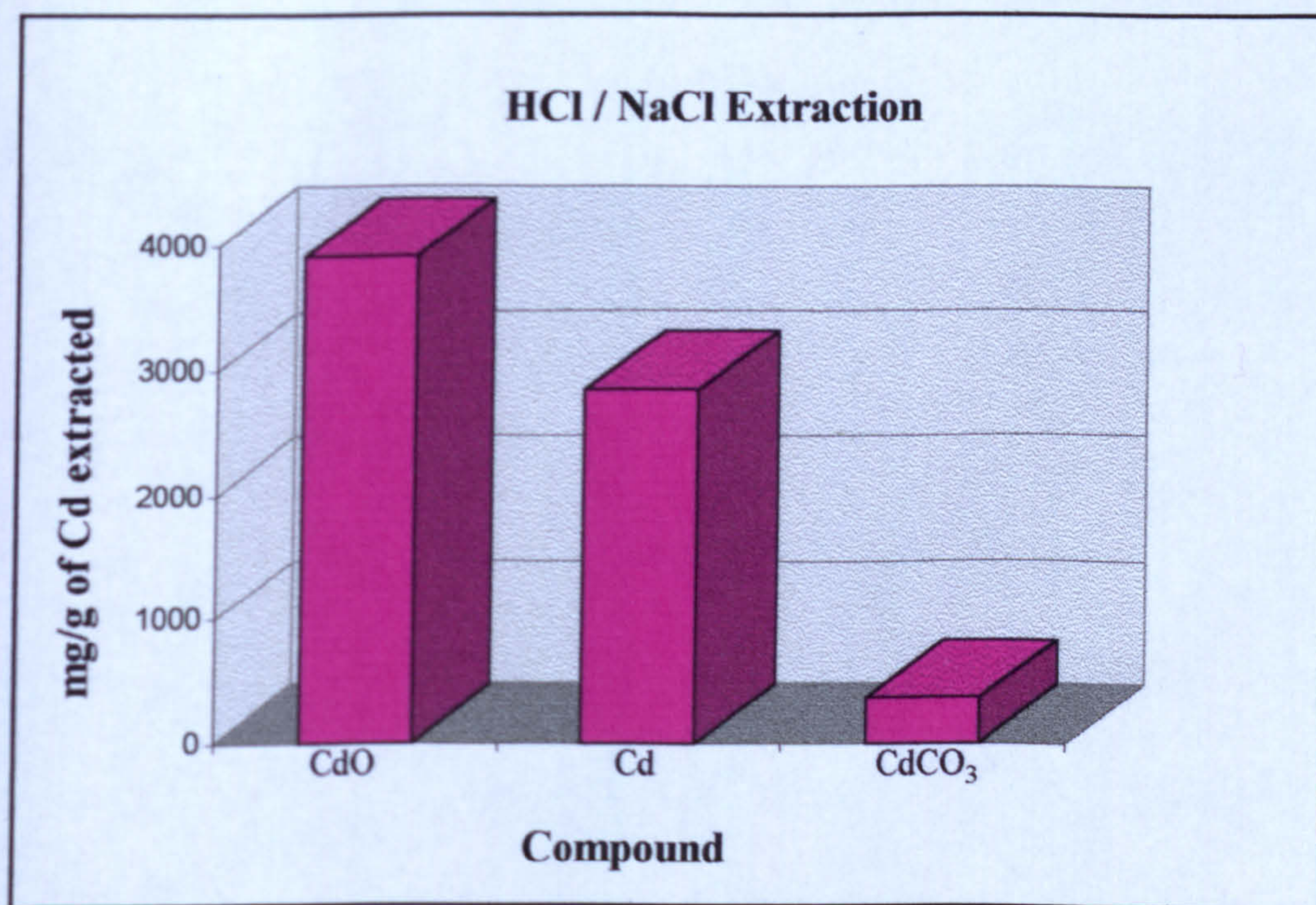


Figure. 6.8:- Leaching of Cd compounds with HCl / NaCl.

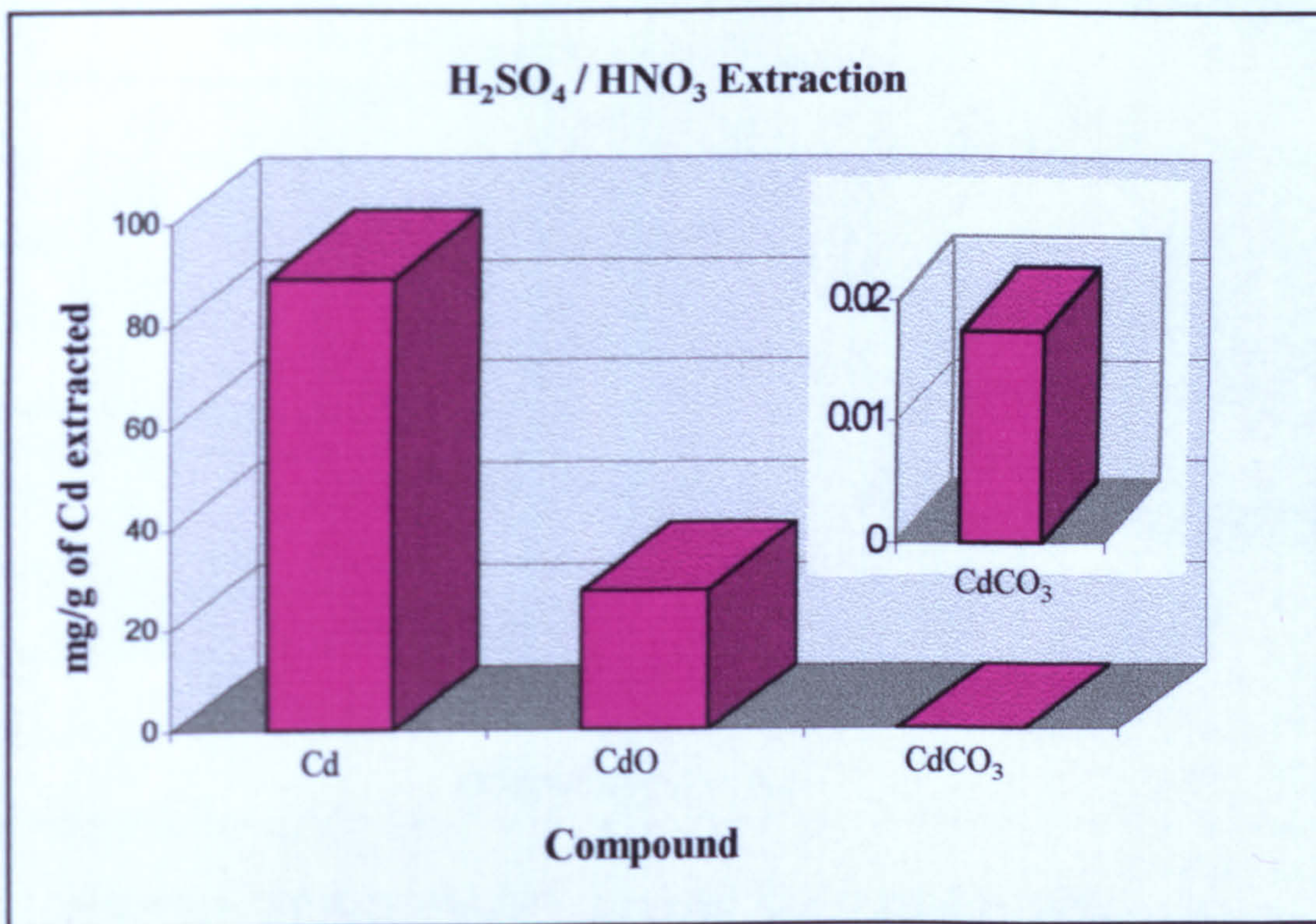


Figure. 6.9:- Leaching of Cd compounds with H<sub>2</sub>SO<sub>4</sub> / HNO<sub>3</sub>.

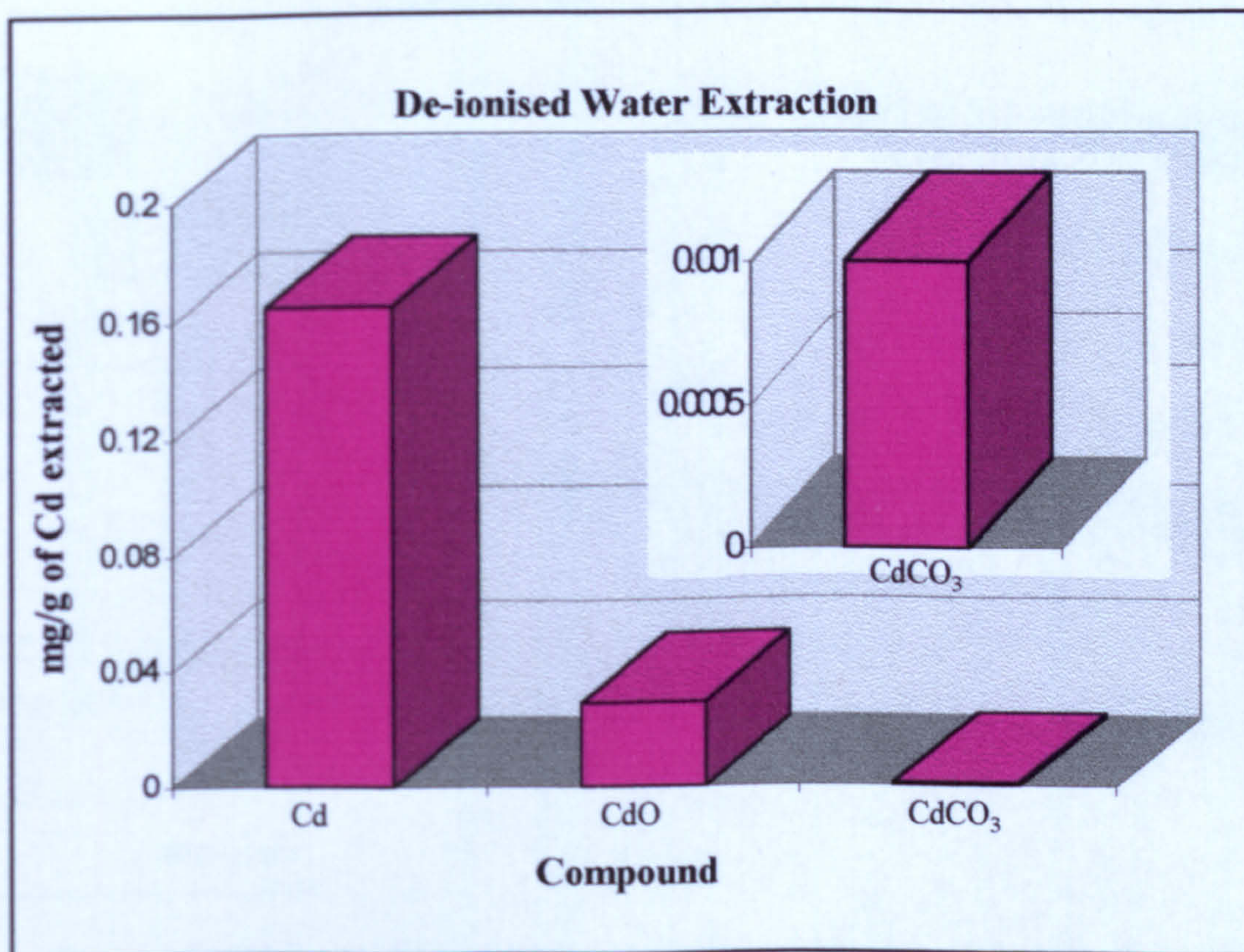


Figure. 6.10:- Leaching of Cd compounds with de-ionised water.

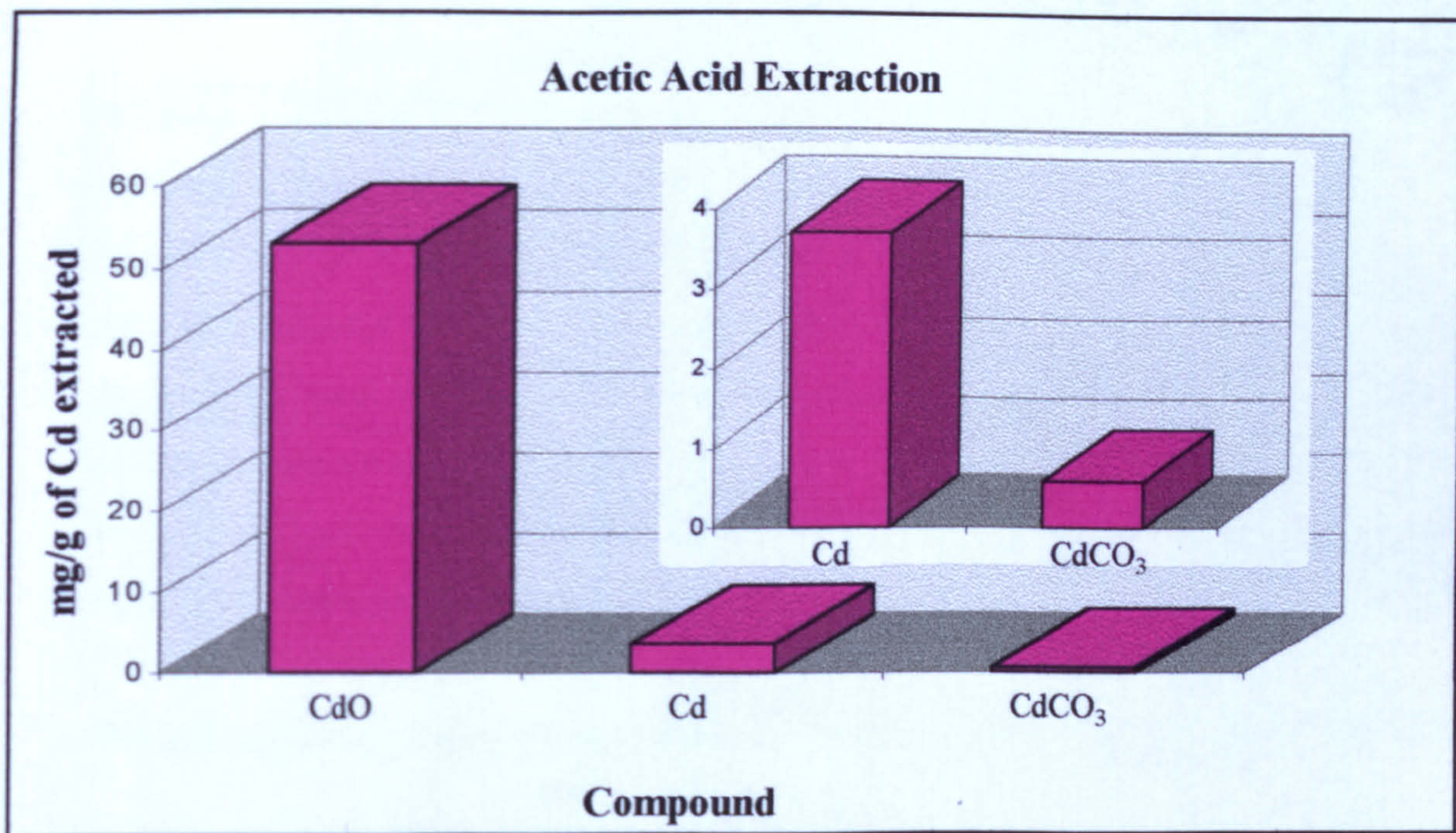


Figure. 6.11:- Leaching of Cd compounds with acetic acid.

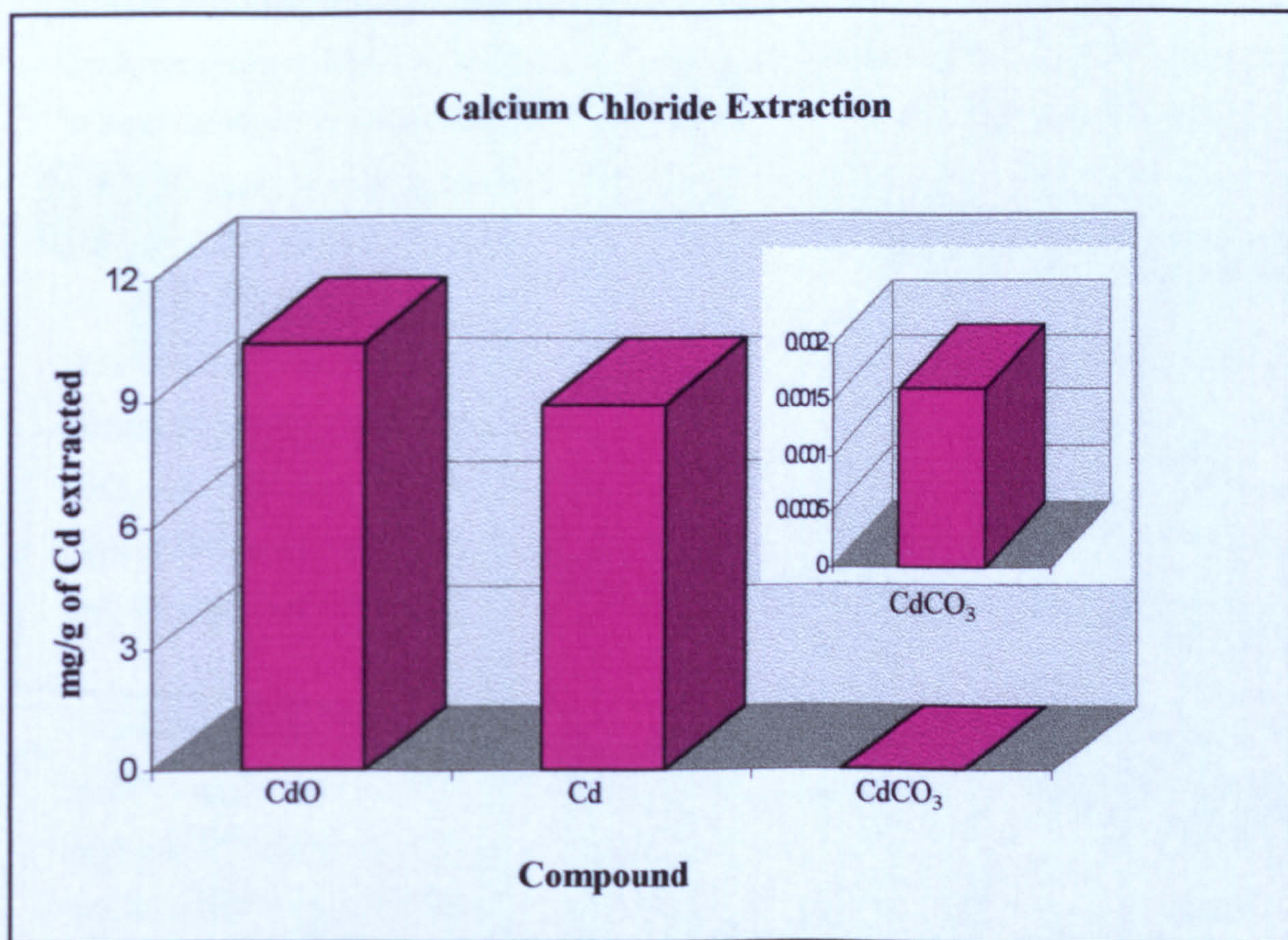


Figure. 6.12:- Leaching of Cd compounds with CaCl<sub>2</sub>.

Cadmium concentrations of 49,000 mg/L and 19,700 mg/L were leached from HNO<sub>3</sub> and HCl/NaCl solution. Once again, HNO<sub>3</sub> extracted a lower amount of metal, 489.76 mg/g [Figure. 6.7], for sample weight taken, compared to 3,903.31 mg/g for HCl/NaCl [Figure. 6.8]. Acetic acid was found to be a reasonably powerful leaching reagent with 5,300 mg/L and 52.98 mg/g [Figure. 6.12] of cadmium extracted whereas H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> extracted 49,000 mg/L and 27.97mg/g of cadmium [Figure. 6.9]. The two weakest leaching liquors were CaCl<sub>2</sub> [Figure. 6.11] and de-ionised water [Figure. 6.10] which gave values of 1,050 mg/L and 2.9 mg/L, and 10.49mg/g and 0.03 mg/g respectively.

The cadmium leached into solution under all conditions was above the trigger guide level.

### ***Cadmium carbonate***

The amount of cadmium leached from the cadmium carbonate sample was much less than the levels of cadmium extracted from granulated cadmium and CdO samples. Although the same trend was observed with HNO<sub>3</sub> [Figure. 6.7] extracting more cadmium (33,000 mg/L) in terms of metal contained in solution compared to any other leach liquor but HCl/NaCl extracts more metal per gram of sample at 364.06 mg/g with less cadmium being leached out in solution (1880 mg/L) [Figure. 6.8].

With acetic acid values of 58 mg/L and 0.58 mg/g were achieved [Figure. 6.12]. Acidic rain conditions extracted cadmium at values of 1.75 mg/L and 0.02 mg/g [Figure. 6.13]. Finally CaCl<sub>2</sub> and de-ionised water were well below the trigger guide level with 0.16 mg/L and 0.0016 mg/g of cadmium being extracted when CaCl<sub>2</sub> [Figure. 6.11] was used as a leaching liquor and only 0.1 mg/L and 0.001mg/g was extracted with de-ionised water [Figure. 6.10].

Cadmium carbonate leached excessive amounts of cadmium in solution above the trigger guide level (0.5 mg/L) when leached with H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> (1.75 mg/L and 0.02 mg/g), acetic acid (58 mg/L and 0.58 mg/g), HCl/NaCl (1,800 mg/L and 364.06 mg/g) and HNO<sub>3</sub> (33,000 mg/L and 329.72 mg/g). When leached with de-ionised water and calcium chloride the concentration of zinc leached into solution was less than the trigger guide level of 0.5 mg/L.

### **6.4.3 Leaching of Zinc Compounds**

In this series of experiments the compounds used were all in the dispersible particle size range since all the compounds were powdered. The results of this study are presented in tabular and graphical form. Table 6.6 provides a comparative summary of the effectiveness of the leach liquor for each zinc compound.

#### ***Zinc sulphide***

When zinc sulphide was leached with the different leach liquors, it was found that the highest concentration of zinc leached out under gastric conditions. Under these conditions, 2,000 mg/L and 391.85 mg/g of sample were extracted [Figure. 6.13].

With the nitric acid extraction a higher concentration of zinc was extracted into solution (7,000 mg/L) compared to the amount extracted per gram of sample taken (69.99 mg/g), under HCl/NaCl leach conditions. [Figure. 6.14].

Acetic acid and  $\text{CaCl}_2$  proved to be weak leach tests for the extraction of zinc from the zinc sulphide sample with only 40 mg/l and 0.40 mg/g being extracted with acetic acid [Figure. 6.15] and  $\text{CaCl}_2$  extracting 60 mg/L and 0.60 mg/g [Figure. 6.16]. However, the zinc sulphide was not very soluble in the other two leach liquors either,  $\text{H}_2\text{SO}_4/\text{HNO}_3$  and de-ionised water, since 130 mg/L and 1.30 mg/g was leached under synthetic rain conditions [Figure. 6.17] whereas 120 mg/L and 1.20 mg/g was extracted with de-ionised water [Figure. 6.18].

Under all leach conditions, concentrations of zinc leached from zinc sulphate solution, were above the trigger guide level of 25 mg/L.

#### ***Zinc metal***

The zinc metal used solubilised quickly in the HCl/NaCl solution and also the  $\text{HNO}_3$  solution. Under gastric conditions 5,000 mg/L and 991.28 mg/g was extracted [Figure. 6.13]. When using  $\text{HNO}_3$  [Figure. 6.14], however, the amount of zinc extracted in solution was greater since 10 g of sample was used instead of the 0.5g which was required for the HCl/NaCl extraction.

Table 6.6:-Leaching of zinc compounds

Leach liquor	Powdered zinc metal		Zinc oxide		Zinc sulphide		Zinc phosphate		Zinc carbonate		
	Conc. of zinc leached (mg/L)	Amount of zinc extracted (mg/g)	Conc. of zinc leached (mg/L)	Amount of zinc extracted (mg/g)	Conc. of zinc leached (mg/L)	Amount of zinc extracted (mg/g)	Conc. of zinc leached (mg/L)	Amount of zinc extracted (mg/g)	Conc. of zinc leached (mg/L)	Amount of zinc extracted (mg/g)	Standard Deviation (mg/g)
H <sub>2</sub> SO <sub>4</sub> /HNO <sub>3</sub>	110	1.10	870	8.69	130	1.30	400	4.00	849	8.69	5.33 ± 1.87
CH <sub>3</sub> COOH	570	5.70	1,170	11.70	40	0.40	5	0.05	1170	11.7	8.01 ± 2.38
HCl/NaCl	5,000	991.28	7,100	887.92	2,000	391.85	5,500	1090.19	1,900	1407.89	796.36 ± 353.81
DI-water	80	0.80	1.00	0.01	120	1.20	110	1.10	0.56	0.01	3.92 x 10 <sup>-3</sup> ± 3.54 x 10 <sup>-3</sup>
HNO <sub>3</sub>	35,500	354.89	32,500	464.79	7,000	69.99	34,000	339.79	39,000	324.90	299.8 ± 25.25
CaCl <sub>2</sub>	40	0.40	90	0.90	60	0.60	70	0.70	190	0.90	0.69 ± 0.12

## Zinc Trigger Guide Level - 25 mg/L

The figures in red exceed the trigger guide level

CaCl<sub>2</sub> leached the least amount of zinc with 40 mg/L being extracted in solution and 0.40 mg/g [Figure. 6.16] was extracted from the amount of sample taken. The de-ionised water extraction leached double the amount of zinc with 0.80 mg/g [Figure. 6.18] and the acetic acid [Figure. 6.15] and H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> [Figure. 6.17] extractions leached 5.70 and 1.10 mg/g respectively.

When zinc metal was leached with the different leach liquors, the concentration of zinc leached into solution was above the trigger guide level.

### ***Zinc Phosphate***

The greatest extraction of zinc from zinc phosphate was achieved with the HCl/NaCl extraction [Figure. 6.13]. With this leach test 5,500 mg/L were extracted and 1,090.19 mg/g of zinc was leached from this sample. The vigorous nitric acid test leached 34, 000 mg/L and 339.79 mg/g [Figure. 6.14].

The weaker leach tests did not extract large amounts of zinc from the sample as 0.05, 4.00, 1.10 and 0.70 mg/g were extracted with the acetic acid [Figure. 6.15], H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> [Figure. 6.17], de-ionised water [Figure. 6.18] and the CaCl<sub>2</sub> leach tests [Figure. 6.16] respectively.

Except under conditions of acetic acid leach, the amount of zinc leached out into solution was above the trigger guide level (25mg/L) under all other leach conditions.

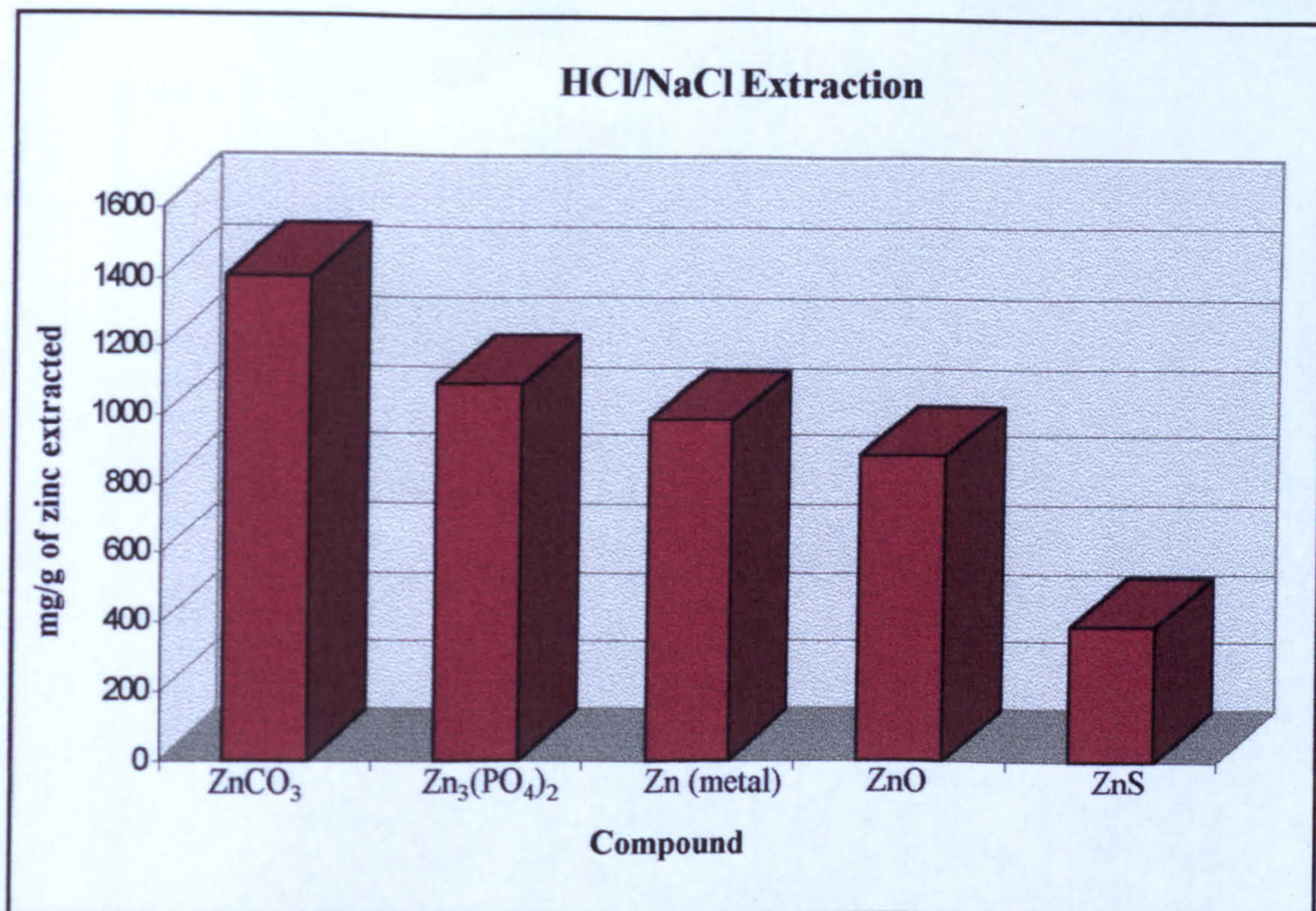
### ***Zinc oxide***

With the zinc oxide sample it was found that the CaCl<sub>2</sub> test extracted the lowest amount of zinc from this sample. 0.30 mg/g and 30 mg/L were extracted [Figure. 6.16].

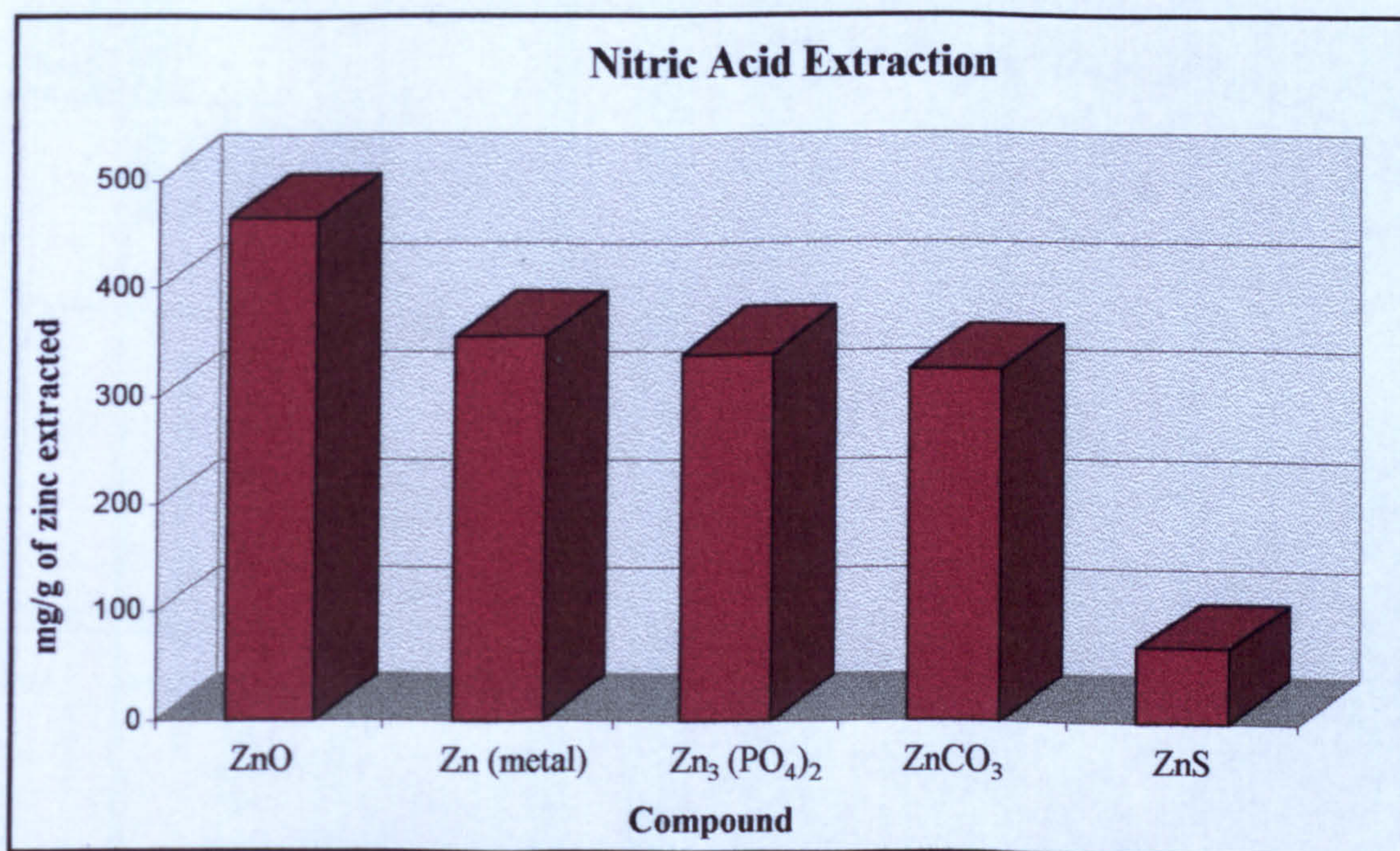
As the strength of the leach liquor was increased the concentration of zinc extracted also increased. With HCl/NaCl the amount of zinc extracted was 887.92 mg/g [Figure. 6.13] whereas with the nitric acid leach test 464.79 mg/g was extracted [Figure. 6.14].

The slightly weaker tests extracted 3.50, 6.00 and 0.60 mg/g from leaching with the acetic acid [Figure. 6.15], H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> [Figure. 6.17] and de-ionised water leach tests [Figure. 6.18]

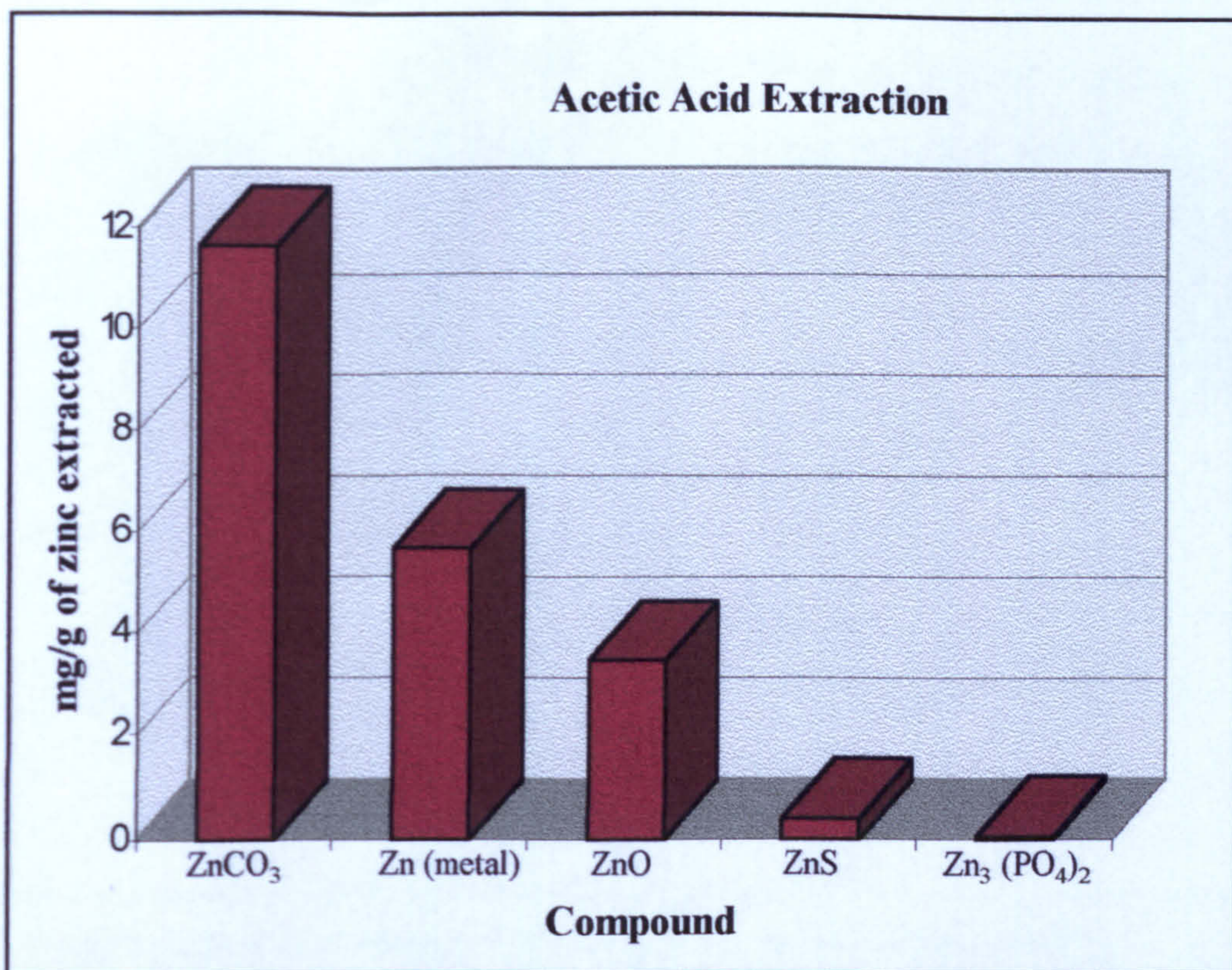




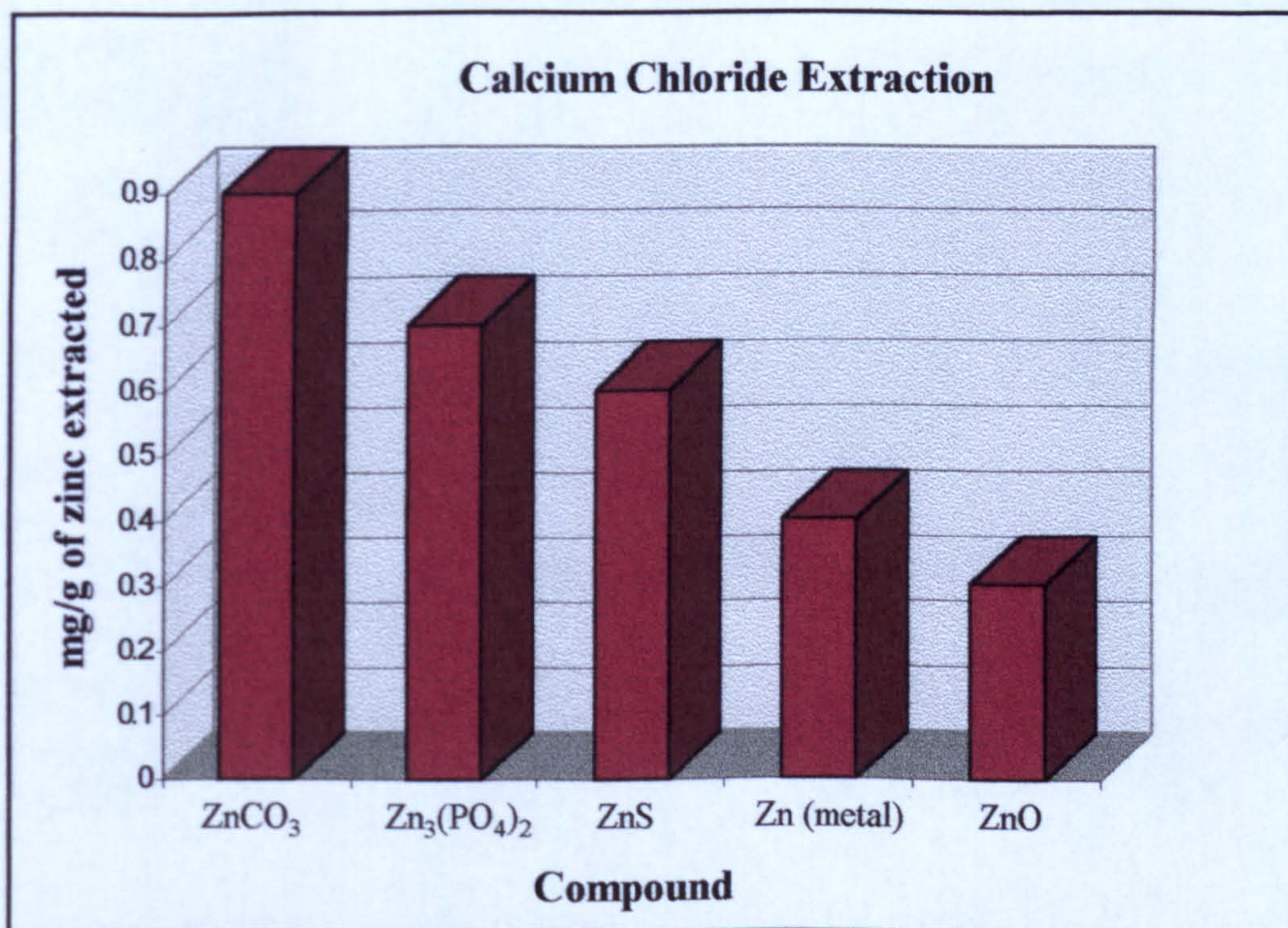
**Figure. 6.13:- Leaching of Zn compounds with HCl / NaCl.**



**Figure. 6.14:- Leaching of Zn compounds with nitric acid.**



**Figure. 6.15:- Leaching of Zn compounds with acetic acid.**



**Figure. 6.16:- Leaching of Zn compounds with CaCl<sub>2</sub>.**

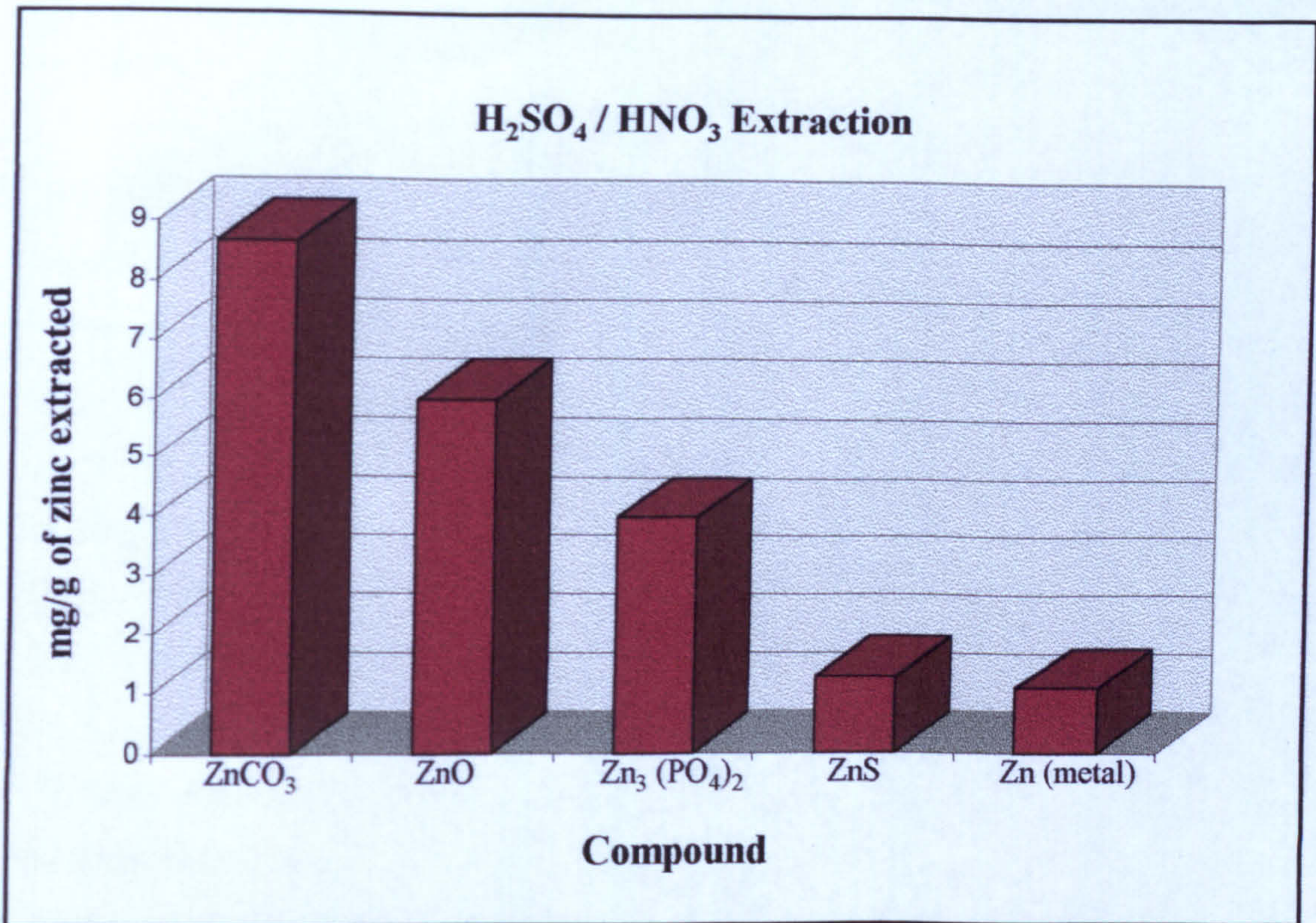


Figure. 6.17:- Leaching of Zn compounds with H<sub>2</sub>SO<sub>4</sub> / HNO<sub>3</sub>.

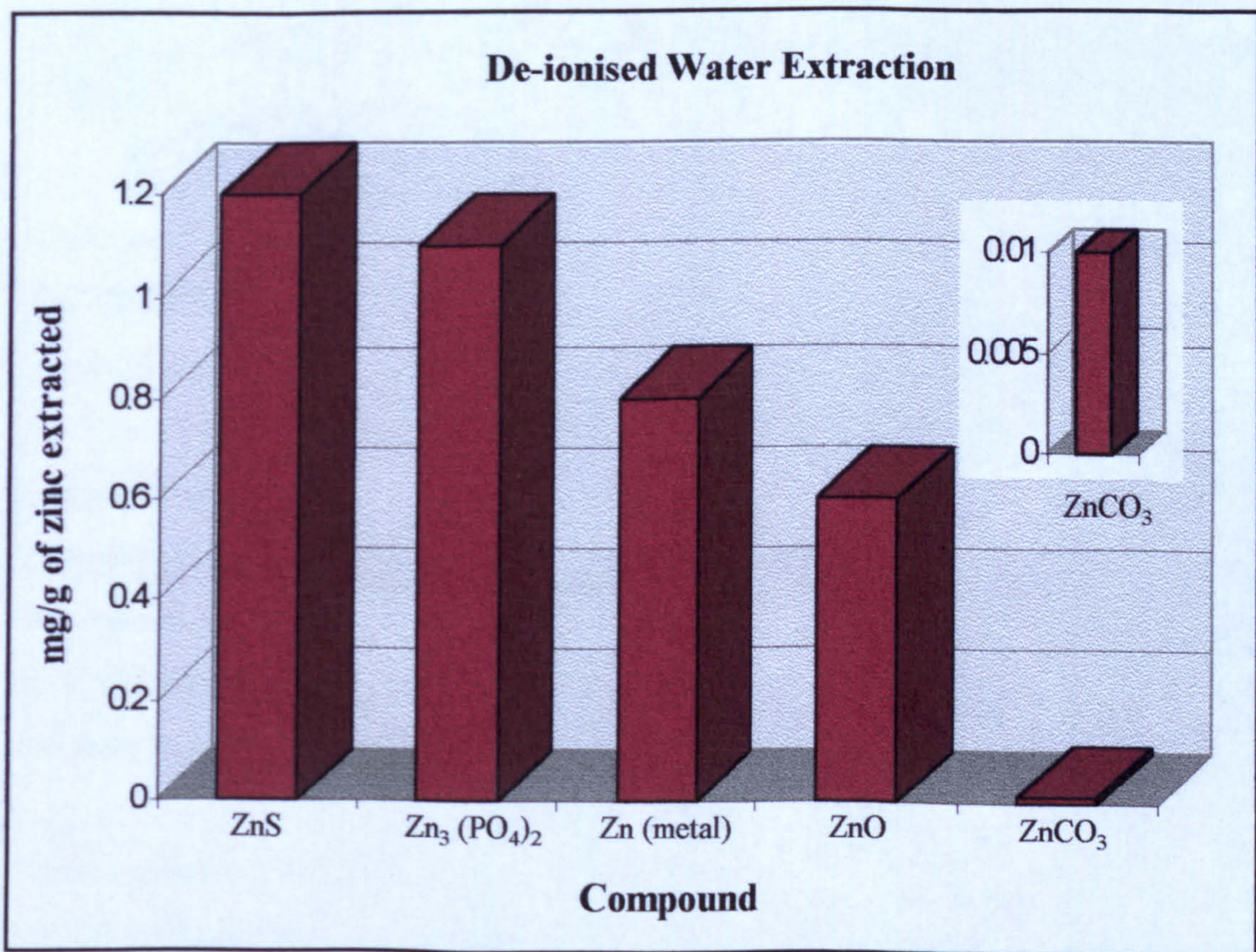


Figure. 6.18: - Leaching of Zn compounds with de-ionised water.

respectively.

The results for this sample show that zinc was leached into solution above the trigger guide level for all the leach liquors except when extraction with de-ionised water was carried out.

### ***Zinc carbonate***

When using this sample it was found that almost three times the amount of zinc was extracted under gastric conditions compared to when the sample was leached in nitric acid. With the use of HCl/NaCl, 1,900 mg/L and 1407.89 mg/g [Figure. 6.13] was extracted whereas with nitric acid 39, 000 mg/L and 324.90 mg/g were extracted [Figure. 6.14].

The least amount of zinc was extracted with de-ionised water with 0.56 mg/l and 0.01 mg/g extracted [Figure. 6.18] with this leach test. The CaCl<sub>2</sub> leached out 190 mg/L and 0.90 mg/g [Figure. 6.16]. The acetic acid [Figure. 6.15] and the H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> leach tests extracted 11.7 and 8.69 mg/g [Figure. 6.17] of zinc respectively.

The zinc in this sample leached into solution above the trigger guide level, when each of the six different leach liquors was used.

### **6.4.4 Leaching of Copper Compounds**

The results of this study are presented in tabular and graphical form. Table 6.7 provides a comparative summary of the effectiveness of the leach liquor for each copper compound.

### ***Copper sulphide***

From the copper sulphide sample used it was found that the amount of copper extracted for four of the leach tests was very similar. The value of copper, in mg/g, extracted from the HCl/NaCl extraction [Figure. 6.19] and the de-ionised water [Figure. 6.20] were very much the same in that 225.23 mg/g and 227.93 mg/g were extracted respectively.

When extracting with nitric acid, a slightly higher concentration of copper was leached with 30,100 mg/L and 292.90 mg/g [Figure. 6.21]. CaCl<sub>2</sub> leached slightly less at 24,800 mg/L Cu

**Table 6.7:-Leaching of copper compounds**

Leach liquor	Copper turnings		Copper oxide (Cu <sub>2</sub> O)		Copper oxide (CuO)		Copper sulphide		Copper carbonate		
	Conc. of copper leached (mg/L)	Amount of copper extracted (mg/g)	Conc. of copper leached (mg/L)	Amount of copper extracted (mg/g)	Conc. of copper leached (mg/L)	Amount of copper extracted (mg/g)	Conc. of copper leached (mg/L)	Amount of copper extracted (mg/g)	Conc. of copper leached (mg/L)	Amount of copper extracted (mg/g)	Standard Deviation (mg/g)
H <sub>2</sub> SO <sub>4</sub> /HNO <sub>3</sub>	68	0.83	21	0.21	50	0.50	7,300	72.99	33	0.33	0.3 ± 0.11
CH <sub>3</sub> COOH	800	8.00	31	0.31	62	0.62	5,500	54.97	321	3.21	3.3 ± 0.81
HCl/NaCl	710	140.43	750	131.42	750	148.25	1,130	225.23	250	49.79	49.1 ± 5.23
DI-water	9	0.09	1.79	0.02	6.29	0.06	22,800	227.93	0.06	0.01	1.83 x 10 <sup>-3</sup> ± 2.34 x 10 <sup>-4</sup>
HNO <sub>3</sub>	9,700	97.0	27,000	269.84	20,000	199.88	30,100	292.90	49,000	489.80	470.5 ± 41.82
CaCl <sub>2</sub>	19	0.19	1.10	0.01	0.38	3.80 x 10 <sup>-3</sup>	24,800	247.90	0.43	4.30 x 10 <sup>-3</sup>	9.0 x 10 <sup>-3</sup> ± 8.2 x 10 <sup>-3</sup>

**Copper Trigger Guide Level - 5 mg/L**

The figures in red exceed the trigger guide level

and 247.90 mg/g being leached [Figure. 6.22].

Significantly lower concentrations of copper were leached from acetic acid and  $\text{H}_2\text{SO}_4/\text{HNO}_3$ , with 5,500 mg/L Cu and 54.97 mg/g Cu [Figure. 6.23] being extracted for acetic acid and 7,300 mg/L and 72.99 mg/g being extracted from  $\text{H}_2\text{SO}_4/\text{HNO}_3$  [Figure. 6.24].

Copper sulphide, when leached with all the leach liquors, was found to leach into solution, in some cases, almost 5,000 times the trigger guide level (5 mg/L).

### ***Copper Turnings***

The sample of copper turnings was classified in the particle size range “massive”. Very little copper was extracted from this sample for four of the leach tests with the minimum being achieved under conditions of de-ionised water leaching. The concentration of copper leached in solution was 9 mg/L and, per gram of sample, the amount of copper leached was 0.09 mg/g [Figure. 6.20]. Twice as much copper was recovered using  $\text{CaCl}_2$  with 19 mg/L being extracted from the sample and 0.19 mg/g [Figure. 6.22].

With  $\text{H}_2\text{SO}_4/\text{HNO}_3$ , 68 mg/L and 0.83 mg/g [Figure. 6.23] of copper were extracted and with the use of acetic acid it was found that 800 mg/L and 8.0 mg/g [Figure. 6.24] of copper was extracted showing that a higher amount of copper is available in solution when using acetic acid, but there is very little difference in the amount of copper extracted from the sample taken.

The greatest amount of copper extracted was when  $\text{HCl}/\text{NaCl}$  was used as the leach liquor. In this test 710 mg/L was extracted and 140.43 mg/g [Figure. 6.19]. The nitric acid leach procedure, resulted in 9,700 mg/L of copper leaching out and consequently 97.0 mg/g was extracted per gram of sample taken [Figure. 6.21].

The copper turnings sample, when leached with the six different leach liquors, gave a concentration of the metal in solution which was well above the trigger guide level.

### ***Copper (I) oxide***

With the  $\text{Cu}_2\text{O}$  sample, there was found to be very little copper leaching out with both de-ionised water and  $\text{CaCl}_2$ . In the de-ionised water test, 1.79 mg/L and 0.02 mg/g [Figure. 6.20] were extracted with 1.10 mg/L and 0.01 mg/g extracted when the leaching liquor was  $\text{CaCl}_2$  [Figure. 6.22].

Little difference was observed in the amount of copper extracted when acetic acid and  $\text{H}_2\text{SO}_4/\text{HNO}_3$  with 31 mg/L and 0.31 mg/g [Figure. 6.24] and 21 mg/L and 0.21 mg/g being extracted respectively [Figure. 6.23].

When  $\text{HCl}/\text{NaCl}$  was used there was a greater amount of copper extracting from the sample with 750 mg/L and 131.42 mg/g [Figure. 6.19] but the highest levels of copper extraction was achieved by leaching with nitric acid where 27,000 mg/L and 269.84 mg/g was extracted [Figure. 6.21].

The copper for this sample leached below the trigger guide level of 5 mg/L under conditions of de-ionised water and calcium chloride leach.

### ***Copper (II) Oxide***

When this sample was used it was found that  $\text{CaCl}_2$  and de-ionised water leached the least amount of copper from the sample.  $\text{CaCl}_2$  leached 0.38 mg/L and  $3.80 \times 10^{-3}$  mg/g [Figure. 6.22] and de-ionised water leached 6.29 mg/L and 0.06 mg/g of copper [Figure. 6.20].

Levels of copper extracted from acetic acid and  $\text{H}_2\text{SO}_4/\text{HNO}_3$  were comparable with 62 mg/L and 0.62 mg/g being leached from acetic acid [Figure. 6.23] and 50 mg/L and 0.50 mg/g being extracted from  $\text{H}_2\text{SO}_4/\text{HNO}_3$  [Figure. 6.24].

As found with the preceding copper compounds, the greatest amount of copper extracted was mainly when the sample was leached with  $\text{HCl}/\text{NaCl}$  or  $\text{HNO}_3$ . The nitric acid extraction leached 20,000 mg/L and 199.88 mg/g [Figure. 6.21]. Under gastric conditions, the concentration of copper extracted from the sample was 750 mg/L and 148.25 mg/g [Figure.

6.19].

The leaching of this sample afforded a concentration of metal in solution below the trigger guide level using calcium chloride only. With the other leach liquors it was found that the concentration of metal in solution was above the trigger guide level.

### ***Copper Carbonate***

The final sample to undergo leaching tests with each of the six leaching liquors was copper carbonate. From this sample the greatest amount of copper was extracted when leached with nitric acid. In this case 0.06 mg/L and 489.80 mg/g were extracted [Figure. 6.19].

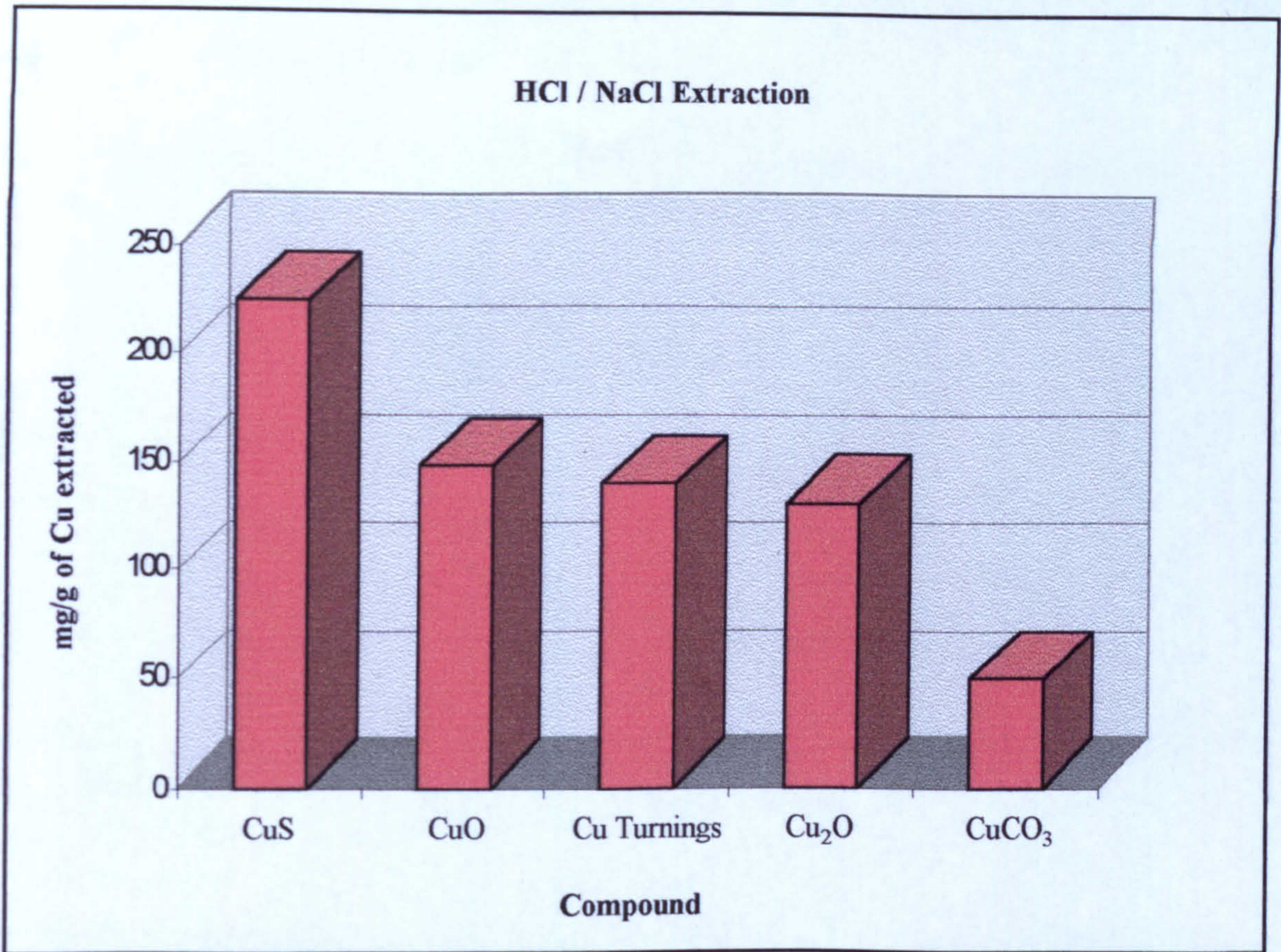
The amount of copper extracted with HCl/NaCl was almost ten times less than the quantity of copper extracted with the nitric acid leach test. With the saline solution 250 mg/L and 49.79 mg/g were extracted [Figure. 6.20].

With de-ionised water and CaCl<sub>2</sub> the respective amounts of copper extracted in solution and per gram of sample taken were 0.01 mg/g [Figure. 6.20] and  $4.30 \times 10^{-3}$  mg/g [Figure. 6.22]. With these two leach liquors it can be seen that there is not much leaching of copper from this sample.

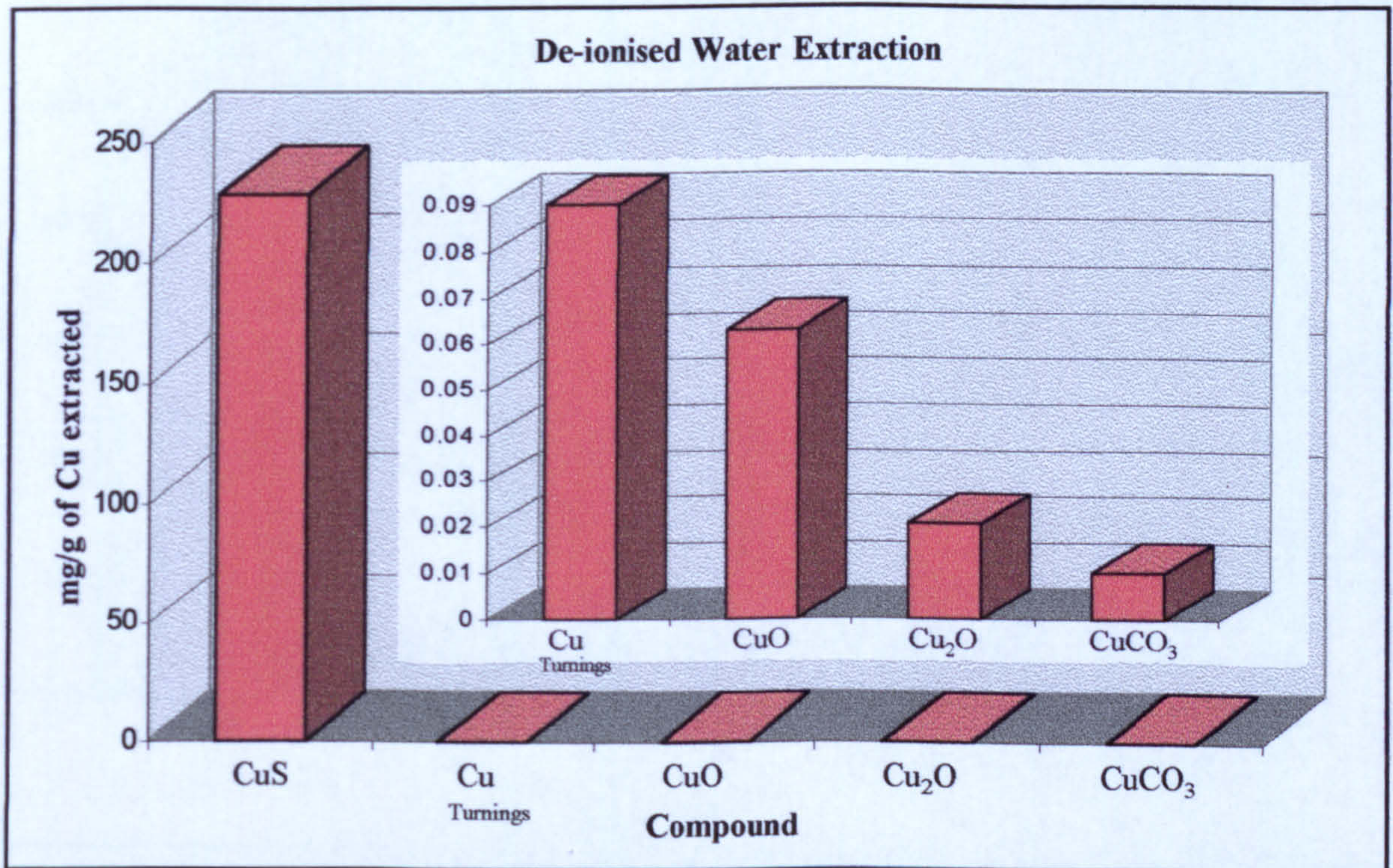
The acetic acid leach test extracted almost ten times more copper from the copper carbonate sample compared to the amount extracted with H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub>, with acetic acid extracting 321 mg/L and 3.21 mg/g [Figure. 6.24] and synthetic rain conditions extracting 33 mg/L and 0.33 mg/g [Figure. 6.23].

The concentration of metal leached from this sample was well above the trigger guide level of 5 mg/L except when the sample was leached with de-ionised water and calcium chloride. With both these leach tests it was found that the concentration of metal leached was below the trigger guide level.





**Figure. 6.19:- Leaching of Cu compounds with HCl / NaCl.**



**Figure. 6.20:- Leaching of Cu compounds with de-ionised water.**

### HNO<sub>3</sub> Extraction

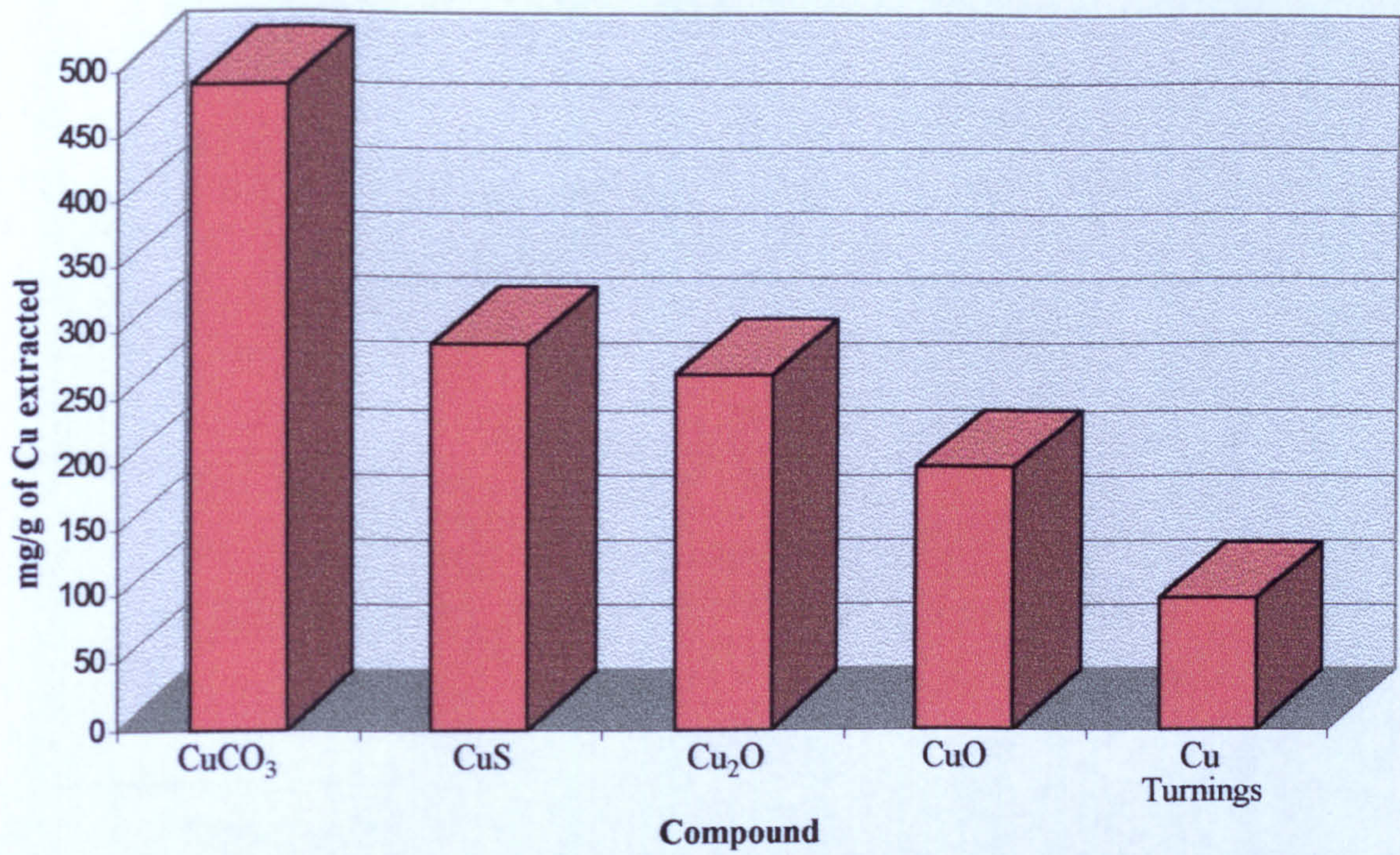


Figure. 6.21:- Leaching of Cu compounds with nitric acid.

### CaCl<sub>2</sub> Extraction

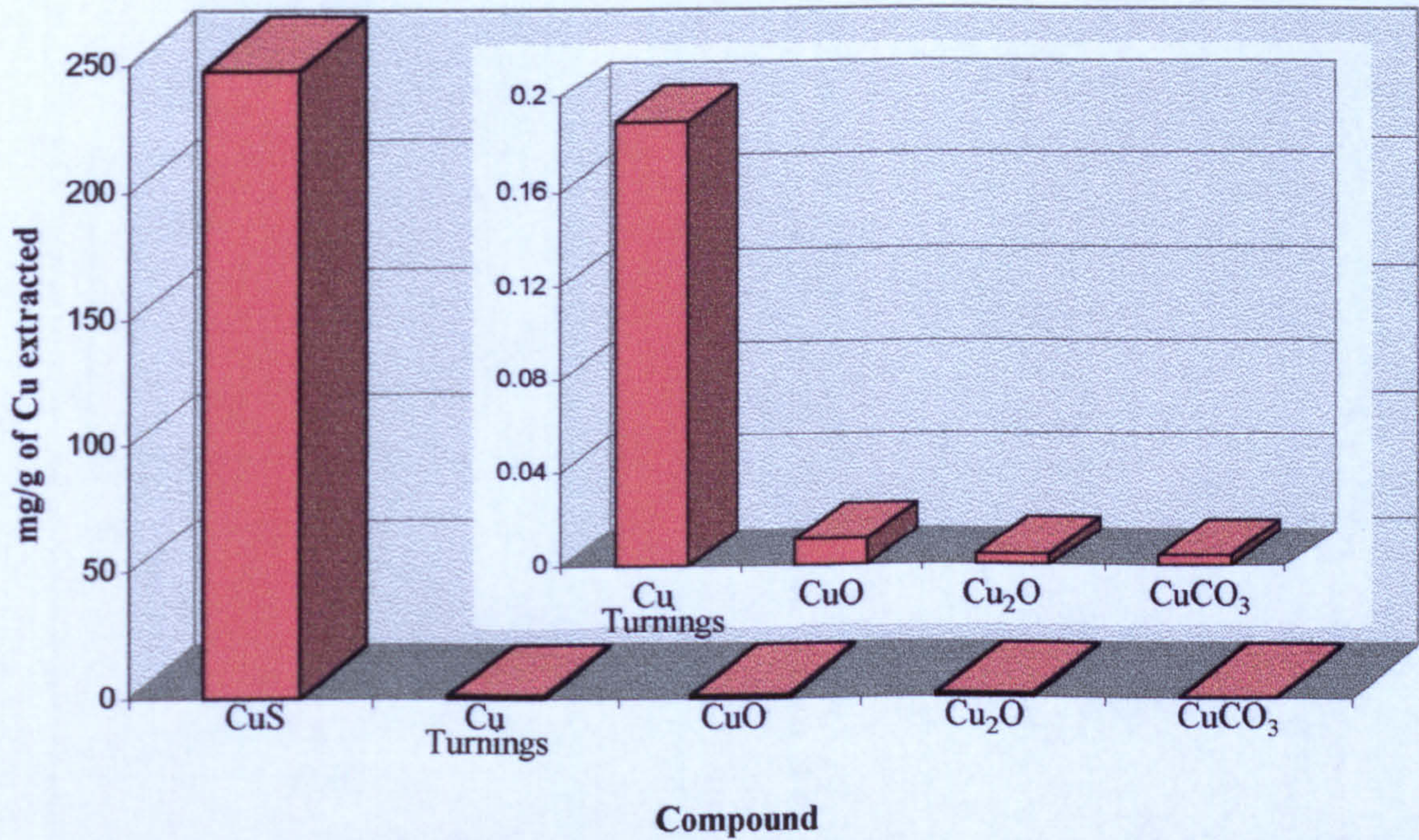
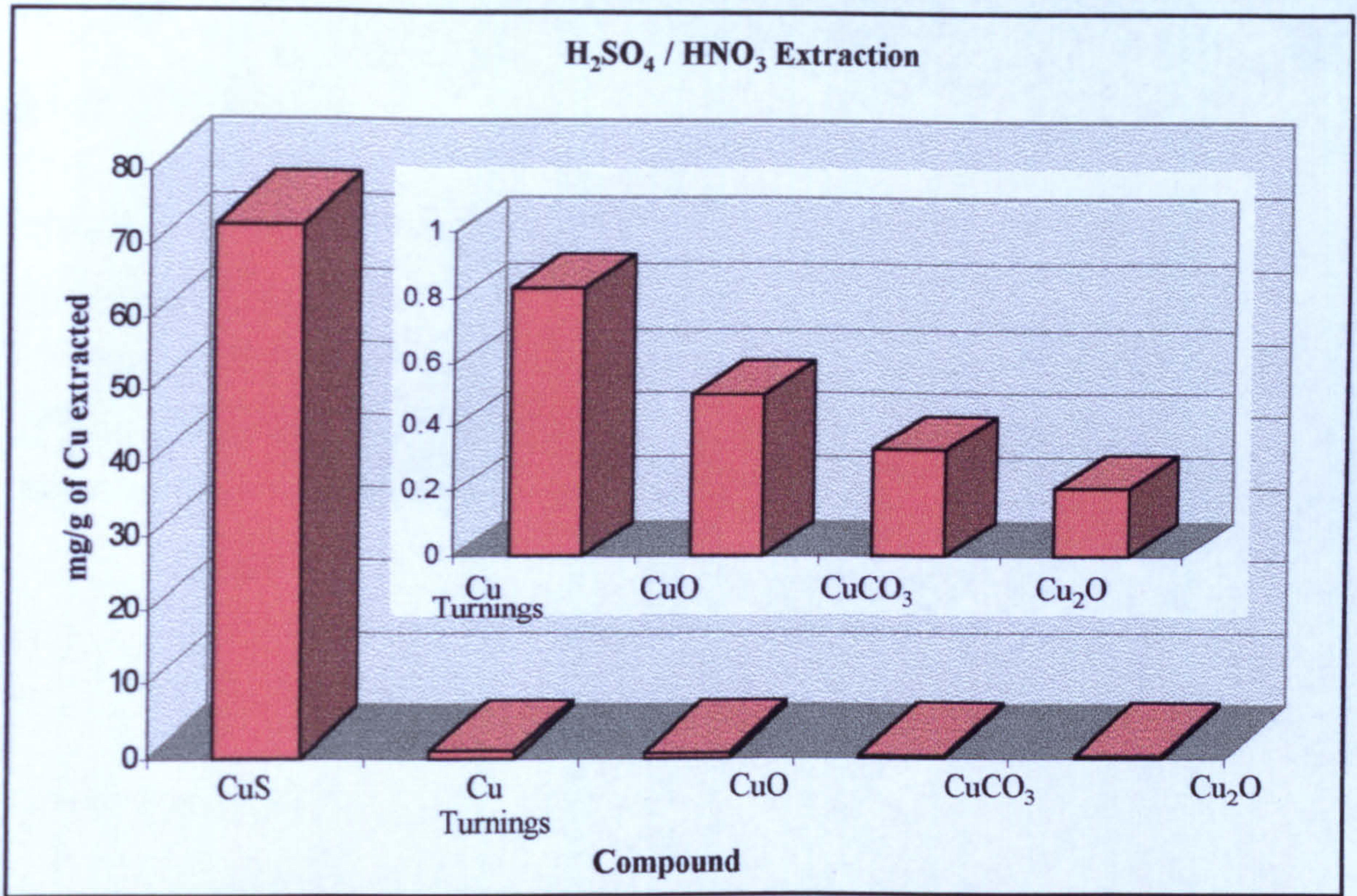
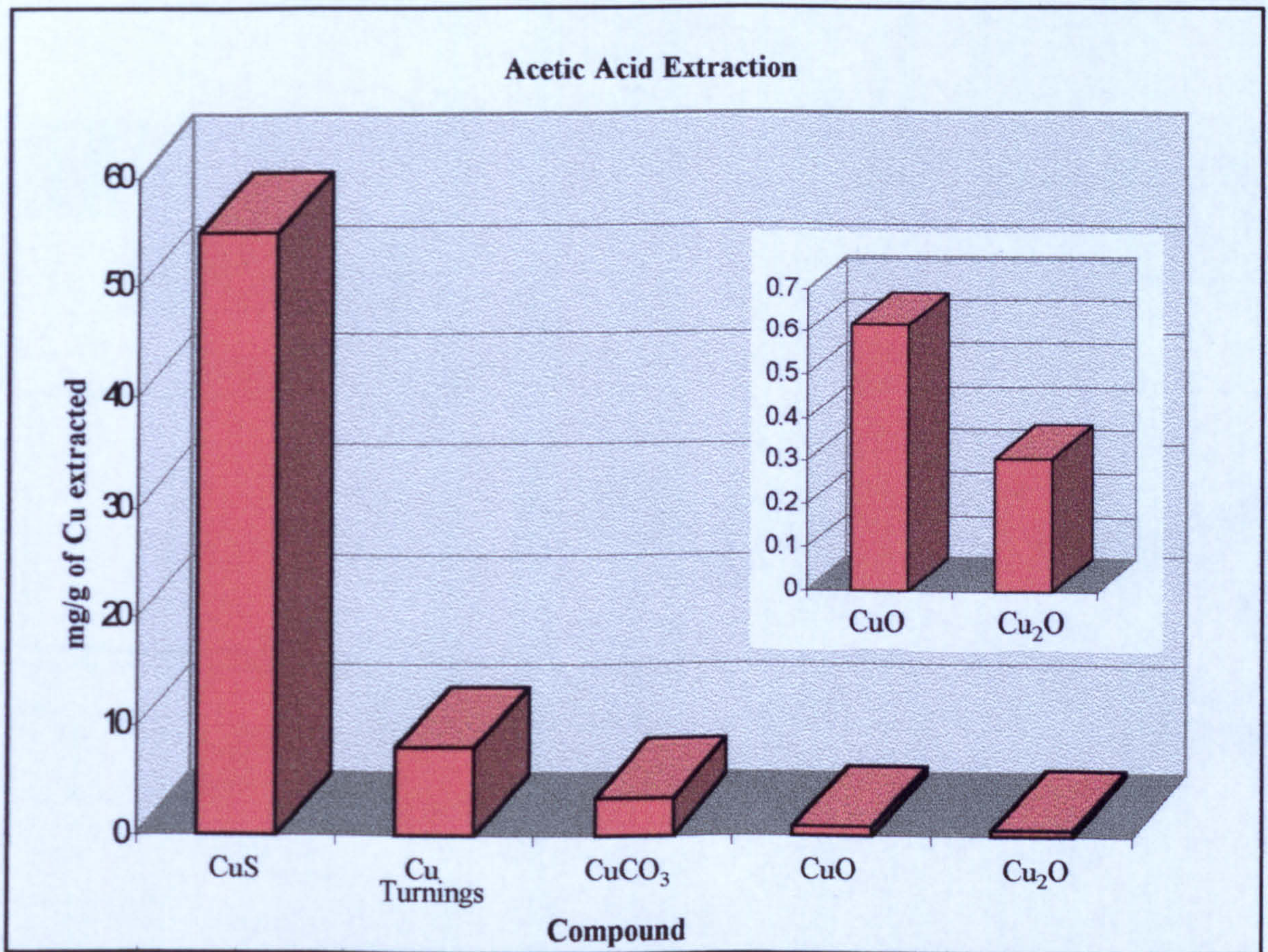


Figure. 6.22:- Leaching of Cu compounds with calcium chloride.



**Figure. 6.23:- Leaching of Cu compounds with H<sub>2</sub>SO<sub>4</sub> / HNO<sub>3</sub>.**



**Figure. 6.24:- Leaching of Cu compounds with acetic acid.**

## **CONCLUSION**

The results of leaching tests show that different concentrations of the same metal can be leached into solution from the chemical compounds of the metal under different environmental conditions. The results of the leaching studies have been used to determine the concentrations of the metal likely to be released and bioavailable under different conditions for comparison with the trigger guide levels which represent a concentration lower than that which would cause toxic effects.

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## **CHAPTER SEVEN**

### **CONCLUSIONS**

Solutions containing dilute metal concentrations arise in many different applications. These dilute solutions can cause two major problems:-

a) The metal present in solution usually exceeds discharge consent levels and so effluent control is important and

b) The value of the metal present in solution may often be of considerable value.

The overall aim of this work was to develop techniques for the removal and recovery of metals from industrial effluent taking account of the consequences of the definition of waste in the Basel Convention on transfrontier shipment of waste and the objectives were:

- (i) to develop and optimise technology for the recovery of cobalt from dilute aqueous solutions
- (ii) to develop and optimise recovery of primarily copper from mixed metal solutions
- (iii) to apply novel concentrator technology to the recovery and recycle of metals from industrial waste streams
- (iv) to investigate the leachability of copper and zinc from hydrometallurgical wastes, as a means of determining bioavailability
- (v) to develop a methodology to assess the classification of wastes under the Basel Convention based on characterisation by leachability and speciation, and
- (vi) to obtain for selected metals subject to the Basel ban, data to be used in the methodology in conjunction with speciation data.

The focus in chapter two was to investigate the effect of different electrode types, cathode current density, pH modifier on the recovery of cobalt and to propose optimised conditions for its recovery.

It has been confirmed that the fluidised bed electrolysis cell is an effective method of removing heavy metals from dilute solutions. Comparative recovery rates for cobalt are achieved with plate and mesh electrodes, although the same degree of purification can be achieved with a lower current density when mesh electrodes are used.

A new concentrator cell technology developed during a WMR3 project in Brunel led to the development of concentrator cells and in this work the effectiveness of activated carbon cloth concentrator electrodes in the recovery of cobalt is investigated. The benefits of this are that the concentration of metal in solution is recovered effectively at high current densities by ACC to meet discharge consent levels. Moreover the recovery rate is accelerated with the use of ACC.

The use of MgO as a pH modifier in the electrolytic recovery of cobalt using plate, mesh or ACC electrode is shown to increase the degree of purification and recovery of cobalt by 30%.

The success of this type of electrode configuration was applied to the recovery of copper from mixed metal solutions and once again the conditions for copper removal were optimised (Table 7.1).

<b>Table 7.1:- Summary and effects for each solution studied</b>						
<b>Solution</b>	<b>Metal Recovered</b>	<b>Current Density</b>	<b><math>\alpha</math> (%)</b>	<b><math>\eta</math> (%)</b>	<b>W (kWh kg<sup>-1</sup>)</b>	<b>Electrode Type</b>
Cu / Zn	Cu	25 Am <sup>-2</sup>	99.38%	41.89%	5.84	ACC
Cu / Zn / Cd	Cu	25 Am <sup>-2</sup>	99.63%	39.48%	6.19	Mesh
Cu / Zn / Fe	Cu	60 Am <sup>-2</sup>	99.79%	16.83%	16.03	Mesh

The results described in chapter four have shown that the novel concentrator techniques developed in this work can be used to recover heavy metals, including precious group metals from industrial effluent. Samples were provided from a number of industries including:-



- Vero
- United Distillers
- INCO
- Graphic Waste Services
- Pendar Poole
- Preminco

Most of the samples provided were of low level metal concentration except for the United Distillers sample which contained a copper concentration of 25,000 ppm in the effluent.

In some cases, optimisation led to the development of improved conditions for recovery, for example iridium and palladium were individually recovered from chloride solution within a 6 h electrolysis period under static and agitated conditions. Furthermore the recovery of copper from a concentrated solution was optimised under static conditions.

The results also show that the final product of recovery can be purified metal or added-value chemicals and that the decrease in the value of the final recovery product will depend on economic as well as technical conditions. The added-value chemicals which were prepared included copper nitrate, copper chloride, copper sulphate, copper acetate and copper hydroxide.

The Basel Convention which is likely to be ratified shortly is concerned with transfrontier shipment of waste from developed to developing countries. The main aim of the convention is to prevent shipment of hazardous waste for treatment and disposal in developing countries. This will be achieved by banning the shipment of any material that is (a) not a primary product and (b) contains any of the components classified in lists of materials with intrinsically hazardous properties. Under the Basel Convention therefore all secondary metal sources, off-cuts (even of precious metals such as gold), slags from refining processes, spent catalysts and end-of-product life materials would be classified as waste because they are not primary products. The question then arises as to whether they would be subject to the ban if they contain *any* major or trace levels of an intrinsically hazardous component.

The Basel Convention has therefore introduced new requirements for (a) complete analysis and speciation of secondary metal sources (b) development of a method of determining whether the secondary materials would be subject to the Basel ban and (c) development of a method for determining the ability of the materials to transfer dissolved metal to the environment, thus making it bioavailable.

In chapter five an outline of the Basel Convention is followed by (1) description of the copper and zinc industries to identify secondary sources (2) leaching studies on copper and zinc containing materials carried out in this work to determine availability and (3) a description of the methodology devised in this work to determine whether any metal containing material could or could not be shipped to a developing country. The leaching studies reported in this chapter provide information on the bioavailability of copper and zinc in various aqueous solutions and the results can be compared with the ecotoxic properties that represent their intrinsic hazard. The results have been used, along with others in developing a methodology for the characterisation of waste in the context of the Basel Convention. The methodology is represented in terms of a flowchart that can be used to determine whether any metal-containing material would be subject to a shipment ban under the Convention.

As part of the development of the methodology, leaching studies were carried out on single chemical compounds of copper, zinc, cadmium and lead and the results of this work are contained in chapter six.

The results of these leaching tests show that different concentrations of the same metal can be leached into solution from the chemical compounds of the metal under different experimental conditions. The results of the leaching studies have been used to determine the concentrations of the metal likely to be released and bioavailable under different conditions for comparison with the trigger guide levels which represent a concentration lower than that which would cause toxic effects.

## APPENDIX 1

### Annex I Wastes having as constituents:

- Y19** Metal carbonyls
- Y20** Beryllium; beryllium compounds
- Y21** Hexavalent chromium compounds
- Y22** Copper compounds
- Y23** Zinc compounds
- Y24** Arsenic; arsenic compounds
- Y25** Selenium; selenium compounds
- Y26** Cadmium; cadmium compounds
- Y27** Antimony; antimony compounds
- Y28** Tellurium; tellurium compounds
- Y29** Mercury; mercury compounds
- Y30** Thallium; thallium compounds
- Y31** Lead; lead compounds

## APPENDIX 2

### Annex III List of Hazardous Characteristics

- H1** Explosive
- H3** Flammable liquids
- H4.1** Flammable solids
- H4.2** Substances or wastes liable to spontaneous combustion
- H4.3** Substances or wastes which, in contact with water emit flammable gases
- H5.1** Oxidising
- H5.2** Organic peroxides
- H6.1** Poisonous (Acute)
- H6.2** Infectious substances
- H8** Corrosives
- H10** Liberation of toxic gases in contact with air or water
- H11** Toxic (delayed or chronic)
- H12** Ecotoxic
- H13** Capable by any means, after disposal, of yielding another material, e.g., leachate, which possesses any of the characteristics listed above.