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TO MY FAMILY WITH MUCH LOVE

ADDED-VALUE CHEMICALS FROM SECONDARY AND LOW-GRADE PRIMARY SOURCES

A THESIS SUBMITTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN THE
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BY

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ADDED-VALUE CHEMICALS FROM SECONDARY

AND

LOW-GRADE PRIMARY SOURCES

CONTENTS

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DECLARATION

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ABSTRACT

A number of metals have been recovered from a variety of secondary and low-grade primary sources. Processing the leach solution directly to recover metals has the advantage over the conventional metal salt recovery system which usually requires the expensive chemical purification steps to get high added-value chemicals. Metals were recovered from dilute solutions using fluidised bed electrolysis in an easily dissolved form to produce added value-chemicals.

A detailed study on the separation of cobalt and nickel from cobalt-nickel cake by oxidative precipitation using Caro's acid as an oxidant is also reported. Following encouraging laboratory studies the process was successfully tested on pilot scale at a copper nickel smelter. The cobalt level was brought down from 8.6 g/l to 50 ppm with the pH kept above 4. Studies have also been carried out for the recovery of gold along with other metals from computer scrap. Following nitric acid pretreatment the gold was recovered using acidic thiourea leaching method.

The manufacture of arsenic acid from arsenic(III) oxide by nitric acid was also studied. Two reported methods are, (1) standard method (addition of solid arsenic oxide to hot acid) and (2) slurry method (addition of acid to slurried arsenic oxide). The problems associated with the standard method are, (a) Excessive foaming and (b) Evolution of large volume of gases leads to uncontrollable reaction. These problems were avoided by changing the standard route to slurry method. The slurry method was tested successfully on a plant scale production at William Blythe & Co. Ltd., U.K. The company is now producing arsenic acid routinely using slurry method.

The production of aluminium sulphate from clay samples and the purification of quartz for glass industry is also reported. The use of 50% sulphuric acid was found to be the best to extract all the aluminium in the clay samples. The excess of sulphuric acid (23% of stochiometry) is required to leach all the aluminum. The product was found to contain trace level impurities of iron, calcium, potassium, and sodium. The quartz purification step includes the use of sulphide and non-sulphide collectors to remove the undesirable impurities. The final stage involves the acid washing step to dissolve the acid soluble impurities. The acid washed product was pure and suitable for glass industry.

CHAPTER 1

INTRODUCTION

Page

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND TO THE PRESENT WORK

The increasing importance of recovering and recycling metals from secondary sources, as well as from low-grade primary ores, provides the driving force behind the present work. As the reserves of high grade ores are gradually exhausted there is an increasing tendency towards the treatment of higher tonnages of secondary and low-grade primary materials. In order to improve recoveries of metal values investigations have taken place in the use of alternative techniques[1]. Traditionally many metals have been recovered by pyrometallurgical processes but soaring smelting costs and more stringent pollution regulations now combine to make pyrometallurgical methods less and less favourable. Recovery using hydrometallurgical process provides a commercially attractive alternative because of its reduced plant costs and its less obvious pollution problems. In this work hydrometallurgical methods have been studied as means of recovering metals from secondary and low grade primary sources. These recovered metals can be used to manufacture added-value chemicals.

Hydrometallurgy is that branch of extractive metallurgy which normally operates using aqueous solutions in the temperature range of 25-250°C. The processes can operate at pressures of only a few kPa (vacuum) up to about 500 kPa. Hydrometallurgy is readily adaptable to large scale continuous operations and is flexible in the chemical and physical nature of the end products. Hydrometallurgy is not the panacea for extractive metallurgy. It should be treated as a cog in the wheel which includes mineral processing and pyrometallurgy[2-4]. Hydrometallurgical processes generally involve some or all of the following stages:

(a) Pretreatment of the sample under investigation
(b) A leach treatment with a suitable solvent
(c) Purification of the liquor by chemical methods such as selective precipitation under controlled

conditions or by physical methods such solvent extraction, ion-exchange or electrolysis

(d) Recovery of the principal metal by reduction or by precipitation of a salt of the metal

(e) Product precipitation, including washing and drying

(f) Regeneration of reagents and removal by-products.

The use of higher temperatures and/or high pressure hydrometallurgy has several distinct advantages including

(a) The reaction rate may be increased

(b) Thermodynamic equilibria may be shifted in a favourable direction

(c) Some reactions occur which would not be effected at ordinary temperature and pressures so that difficult or impractical ambient dissolutions can sometimes be carried out relatively easily

(d) Gaseous or highly volatile reagents such as ammonia, oxygen and hydrogen may be used.

The leaching and precipitation stages in hydrometallurgical processes usually involve reactions which occur at the solid-liquid phase boundaries in heterogeneous systems. If one reactant is a gas the kinetics become more complex and the use of higher pressure is distinctly advantageous as reaction rates then depend upon the dissolution of gaseous reactants, the transport of dissolved reactants to the solid-liquid interface, the reaction at the interface and the transport of the reaction products away from the solid-liquid interface[5].

The use of chemical methods in metal separation depends upon two factors, a knowledge of the chemistry of the elements being separated and the advantageous use of that chemistry to preferentially recover the element. These factors are described in detail in Chapter 3 where the separation of cobalt from nickel sulphate solution was carried out by using Caro's acid as an oxidant.

The main objectives of hydrometallurgy are to extract metals; to purify and concentrate metal bearing solutions; to recover metals; and to render waste streams acceptable for disposal to repositories and the environment.

1.2 THE NEED FOR RECYCLING

A significant and growing proportion of metals consumed by industry in all industrialised countries is provided by the recycling of waste materials. Conventionally, the quantity of metal produced by recycling is compared to current consumption of the metal, the recycled fraction often being expressed as a percentage of total consumption[6]. Table 1.1 gives typical values for this in the final column:

TABLE 1.1 SECONDARY METALS PRODUCTION AND CONSUMPTION IN THE UK FOR 1977

Metal	Total Consumption $\times 10^3$ tonnes	Secondary Production $\times 10^3$ tonnes	Recycled (%)
Al	589	171	29
Cu	643	207	32
Pb	290	174	60
Sn	15	4	26
Zn	315	70	22

Perhaps of greater importance, however, is the fact that existing deposits of many metals are being consumed at such a rate that some materials are going to be expended by the end of this century or at least early in the 21st century. A recent projection has indicated that the expected life-span of worldwide deposits of many materials is very short[7,8]. The statistics reproduced in Table 1.2 suggest that the recycling of metals must become increasingly important in the future.

TABLE 1.2 THE PROJECTED LIFE-SPAN OF EXISTING METAL DEPOSITS

	APPROXIMATE EXHAUSTION DATE	
Metal	At Current Consumption Rates	At Continued Exponential Growth Rates
Cr	2550	2065
Co	2125	2015
Cu	2010	1995
Fe	2400	2045
Pb	1990	1985
Mn	2150	2015
Ni	2110	2000
Zn	1990	1985

1.3 SCOPE OF THIS WORK

The purpose and objectives of the work described in this thesis and the analytical techniques used throughout the work have been outlined in this introductory chapter. In chapter two the recovery of metals from dilute solutions by fluidised bed electrolysis is described in detail. This work extends research previously carried out in the group on the recovery of metals as chemicals from leach solutions[9]. This is because the deposition of recovered metals in a fluidised bed cell provides pure metal in an easily dissolved form for conversion to high added-value pure chemicals. The separation of cobalt and nickel by oxidative precipitation using Caro's acid as an oxidant is described in chapter three. Chapter four describes the recovery of gold and other metals from computer scrap by acidic thiourea leaching method. The manufacture of arsenic acid from arsenic(III) oxide by nitric acid method is described in chapter five. The final chapter includes the detailed study on the production of aluminium sulphate from Nigerian clay and the purification of quartz for glass industry.

1.4 ANALYTICAL METHODS

The main analytical methods used throughout the work described in this thesis are:

1) Atomic Absorption Spectrophotometry (AAS)
2) Ion-Chromatography (IC)
3) Thermal Methods of analysis
4) X-Ray Methods

A brief description of all the analytical techniques is now given in the following subsections and analytical data obtained using these techniques are given where appropriate.

1.4.1 ATOMIC ABSORPTION SPECTROPHOTOMETRY (AAS)

Atomic absorption spectrophotometry can be used to determine most elements. In this method, a solution containing low concentrations of metallic elements is atomized into a vapour containing free atoms of the elements. A hollow cathode lamp (light source) emits radiation which is characteristic of the element to be determined and this radiation is directed through the vapour. The analyte atoms dispersed throughout the vapour absorb a proportion of the radiation resulting in a decrease in the radiation emerging from the vapour and it is the decrease in radiation which is measured by a detector. A monochromator is included in the system so that energy of the desired wavelength can be isolated from that of neighbouring wavelengths emitted from the light source[10-12].

Sensitivity is defined as that concentration of an element, in ppm, (or µg/ml or mg/l) in agueous solution which gives a 1% absorption signal.

Hollow-Cathode Lamps

Hallow-cathode lamps are the most common radiation sources for AAS. The Hollow-cathode lamp comprises a hollow cup cathode made from the element to be determined and a tungsten anode housed in a glass envelope containing an inert gas at low pressure (Figure 1.1)[10]. Ionization of the inert gas occurs when a potential is applied across the electrodes, and a current of about 5 to 10 mA is generated as ions and electrons migrate to the electrodes. If the potential is sufficiently large, the gaseous cations acquire enough kinetic energy to dislodge some of the metal atoms from the cathode surface and produce an atomic cloud; this process is called sputtering. A portion of the sputtered metal atoms are in excited states and thus emit their characteristic radiation as they return to the ground state. Eventually, the metal atoms diffuse back to the cathode surface or to the glass walls of the tube and are redeposited. The cylindrical configuration of the cathode tends to concentrate the radiation in a limited region of the tube; this design also enhances the probability that redeposition will occur at the cathode rather than on the glass walls. The total light obtained is subsequently passed a monochromator, usually a grating or prism, to separate the resonance line from other nearby spectral lines.

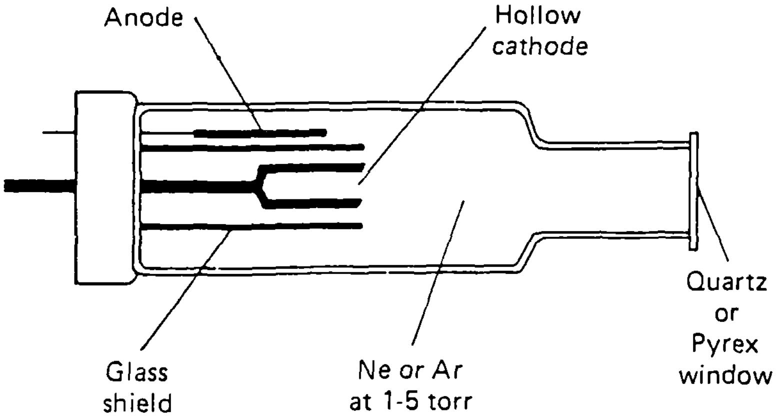


FIGURE 1.1 Schematic cross section of a hallow cathode lamp.

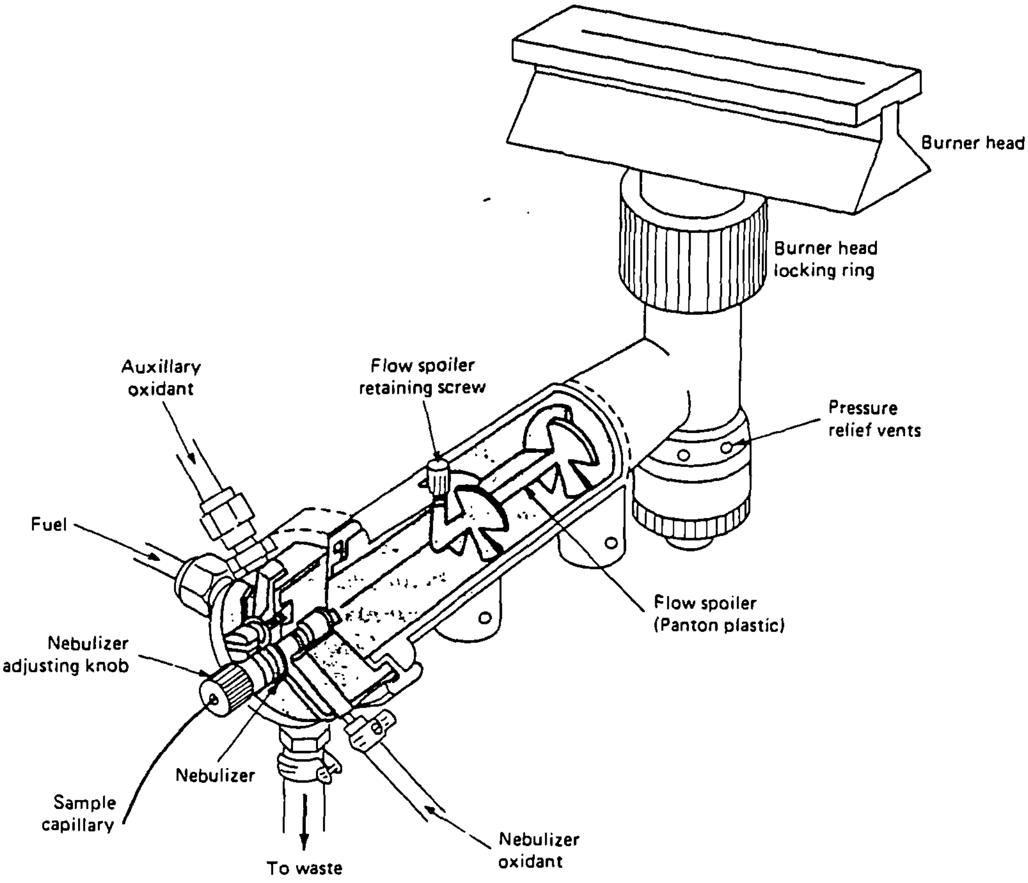


FIGURE 1.2 A laminar flow burner.

Atomisation systems

The gas combination most often used to produce atomisation of the vapours in AAS is air-acetylene and nitrous oxide-acetylene. Other rare combinations include air-hydrogen, argon-hydrogen, air-propane and air-natural gas. These cooler flames are often useful for specific determination but in general they are more susceptible to interference effects. Air-acetylene is the preferred flame for the determination by AAS. Its temperature is approximately 2300°C and it may be used as an oxidising lean blue flame. Nitrous oxide- acetylene has a maximum temperature of about 2900°C and it is used for the determination of elements which form refractory oxides. Light emission from the N_2O/C_2H_2 flame is very strong at certain wavelengths causing fluctuations in the analytical result at those wave lengths. However, it is unlikely to be a problem when using a primary wave lengths of the elements but may occur when using a secondary wavelength.

Burner-Nebulizer system

The laminar flow premix system is the only type of burner in general use for AAS. Liquid sample is introduced into a burner through the nebulizer by venturi-action of the nebulizer oxidant. Figure 1.2 shows a cross-section of a nebulizer premix burner assembly[10]. In passing through the nebulizer, the liquid stream is broken into a droplet spray. Premix burner contains, in addition to a nebulizer, a premix chamber and a burner head. Premix chambers are designed to mix the fuel, oxidant and sample.

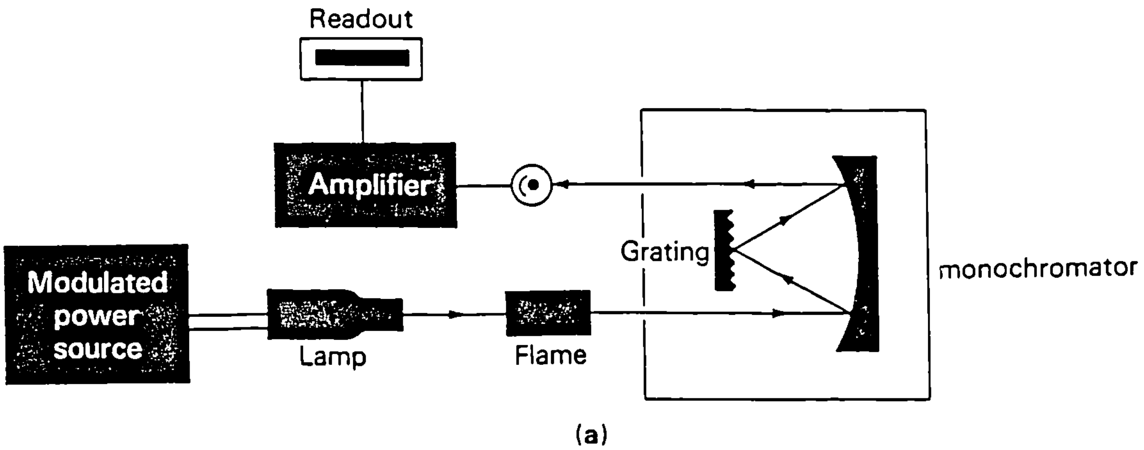
Not all the liquid entering a premix burner passes into the flame. The premix chamber allows large droplets; which are deleterious to the absorption processes to condense (aided by the flow spoiler system) and pass out of the chamber through the liquid drain tube. Rejection of these large drops helps to minimise light scattering effects in the flame.

Optical system

In AAS the monochromator is placed after the atom reservoir to help diminish light-flux on the photo tube. Figure 1.3 is a schematic diagram of a typical single and double-beam instrument[10]. The instrument used throughout the present study was a Perkin-Elmer 370 Atomic Absorpton Spectrophotometer. It is a double beam model, the beam from the hollow cathode source is split by a mirrored chopper, one half passing through the flame and the other half around it. The two beams are then recombined by a half-silvered mirror and passed into a grating monochromator; a photomultiplier tube serves as the transducer. The output from the latter is fed to a lock-in amplifier which is synchronized with the chopper drive. The ratio between the reference and sample signal is then amplified and fed to the readout which may be meter, digital device, or recorder. Double beam instruments lose a factor of 2 in signal, as a result of this process. The main purpose of this system is to cancel instabilities in the source by correcting for fluctuations in lamp output. However, the more complexes the optics, the greater the reduction in signal strength.

1.4.2 CHROMATOGRAPHY

Chromatographic techniques depend principally on the variation in the rate at which different components of a mixture migrate through a stationary phase under the influence of a mobile phase. During a chromatographic separation, solute molecules are continually moving back and froth between the stationary and mobile phases. While they are in the mobile phase, they are carried forward with it but remain virtually stationary during the time spent in the stationary phase. The rate of migration of each solute is therefore determined by the proportion of time it spends in the mobile phase, or in other words, by its distribution ratio. The process whereby a solute is transferred from a mobile to a stationary phase is known as 'sorption'.



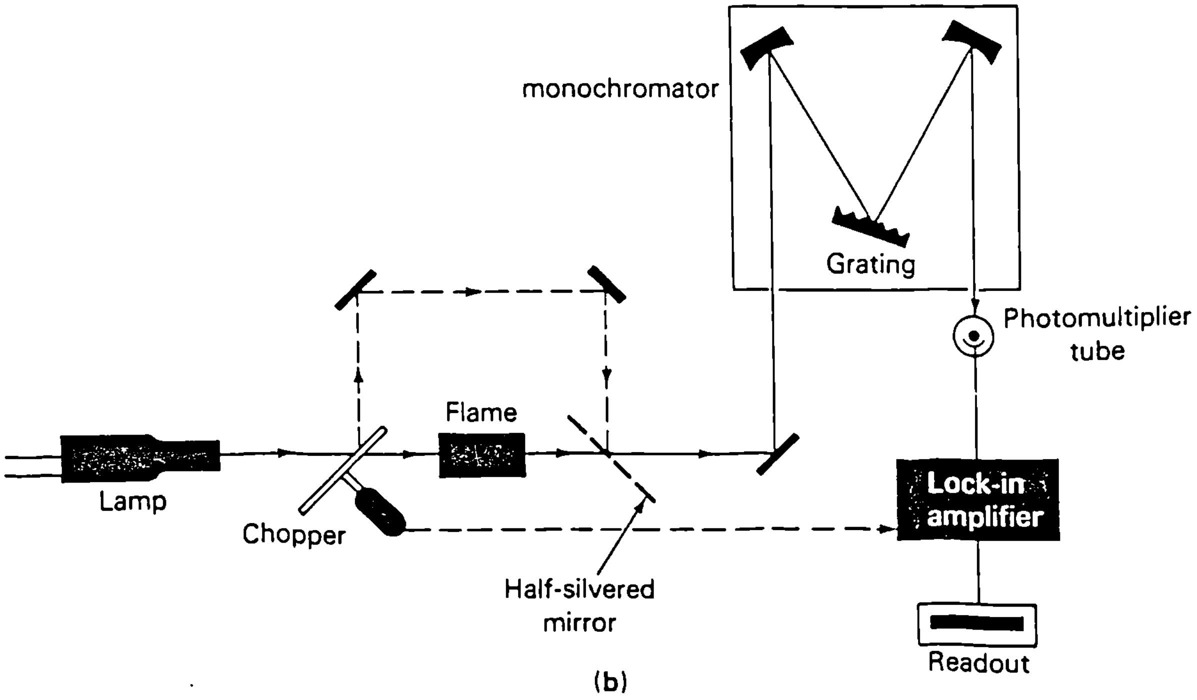


FIGURE 1.3 Typical flame spectrophotometers: (a) single-beam desgn; (b) double-beam design.

Ion-Exchange Chromatography
(High Performance Ion Chromatography - HPIC)

Ion-exchange separations are limited to samples containing ionized or partially ionized solutes; it is used in the separation of anionic and cationic species. The process concerns an interchange of ions like sign between the solution and an essentially insoluble solid in contact with the solution. The stationary phase consists of a polystyrene based resin crosslinked with divinylbenzene (DVB) and contains fixed charged groups and mobile counter-ions which can be reversibly exchanged for those of a solute carrying a like charge, as the mobile phase travels through the system. The proportion of DVB is 2 to 20% and results in a three dimensional cross-linked structure that is rigid, porous and highly insoluble[13]. The extent of cross-linking, expressed as the weight percent of DVB, affects the rigidity of the structure and the pore size. A low degree of cross-linking produces beads which swell appreciably when in contact with a polar solvent and have large pores enabling ions to diffuse into the structure and exchange rapidly. This phenomenon of 'swelling' results from the osmotic pressure set up when a resin bead, which can be considered to be a concentrated electrolyte solution, is surrounded by a more dilute polar solution. Solvent flows into the bead and distends the structure in an attempt to reduce the osmotic pressure by dilution. Resins with a high degree of cross-linking have smaller pores and are more rigid. The degree of cross-linking and thus pore size is controlled by the polymerization process.

For the exchange of cations, the exchange function is usually a sulphonate group; whereas for the analysis of anions, a quaternary ammonium group is commonly employed. The different rates of migration result from variations in the affinity of the stationary phase for different ionic species. The mobile phase contains an ion of low resin affinity, and the separated components collected at the bottom of the column are thus accompanied by a relatively high concentration of this ion. Procedures often adopted in

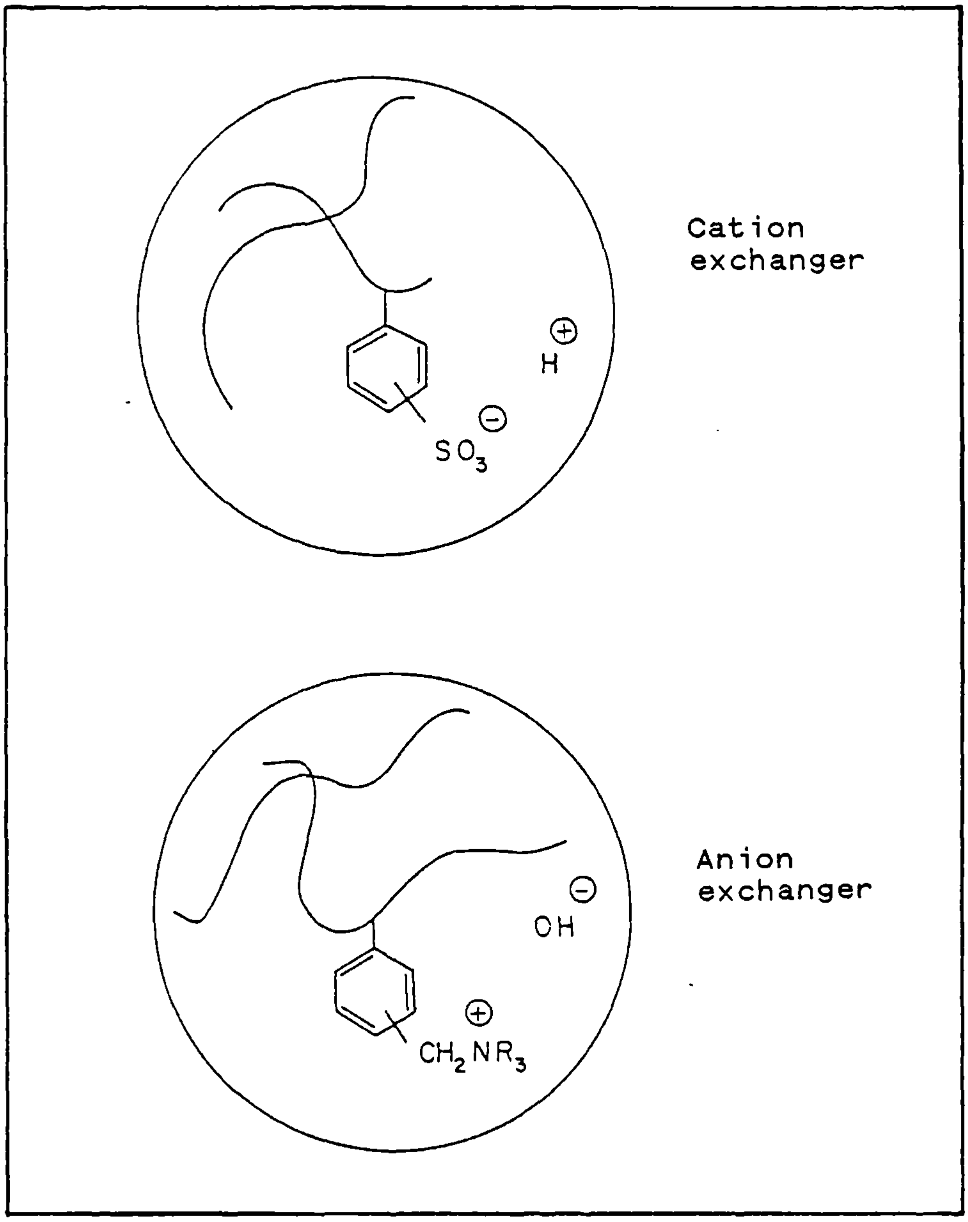


FIGURE 1.4 Representation of common forms of ion-exchanger.

ion-exchange chromatography are 'gradient elution', involving continuous variation in the composition of the eluting agent, 'stepwise elution', in which the composition is altered at specific points during the separation, and 'complexing elution', where a reagent which forms complexes of varying stability with the sample components is included in the solution. Acids, bases and buffers are most widely used as eluting agents.

Instrumentation

The major components of a modern chromatographic instrument, as used in this work and developed by Dionex are illustrated in Figure 1.5.

The mobile phase is pumped through the chromatographic system by a double reciprocating pump[14]. A pulse-free flow, necessary for both UV/Vis and amperometric detectors, is ensured by a complex electronic control of the pump.

The samples are introduced into the system via a loop injector shown schematically in Figure 1.6. The two outlets of the sample loop which is loaded at atmospheric pressure, are joined by a three-way valve. After the valve is switched the sample is transported onto the column by the mobile phase.

The two ion-exchange column are coupled in series and form the most important part of the chromatograph. The selection of a suitable stationary phase as well as of the appropriate chromatographic parameters, determined the quality of the analysis. The column bodies are fabricated with inert materials and are generally operated at room temperature. In some instances, such as in the analysis of carbohydrates and amino acids, it is necessary to thermostat the columns at elevated temperature.

The performance of a detector (which serves to identify and quantify the species being analyzed) depends upon (a) linearity; (b) resolution; and (c) noise.

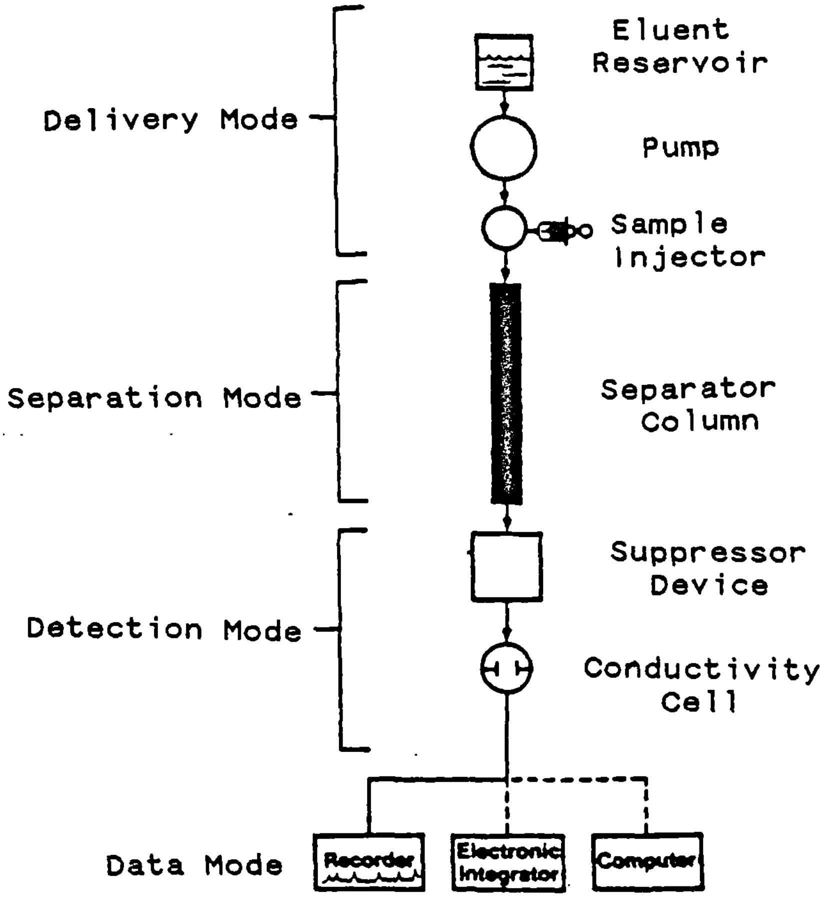


FIGURE 1.5 A typical Dionex Ion Chromatograph configuration.

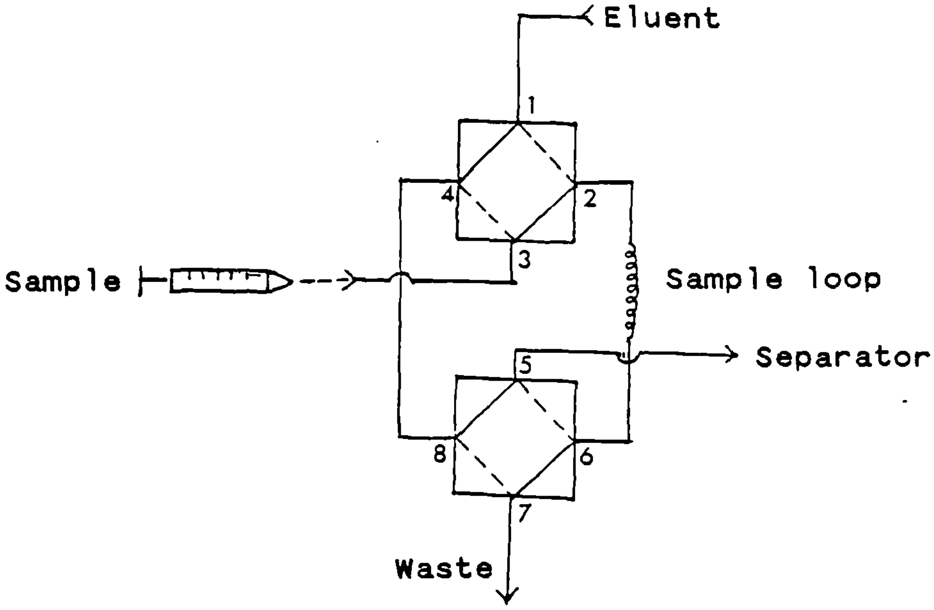


FIGURE 1.6 The loop injector.

The most widely used detector in ion-exchange chromatography is the conductivity detector. This detection system usually incorporates a suppressor device that serves to chemically reduce the background conductivity of the eluent which, simultaneously, converts the species of interest into a more conductive form[15]. UV/Vis, amperometric, and fluorescence detectors are sometimes used in addition to the conductivity detector.

The chromatogram is obtained via a recorded or computer. Quantitative results are derived from a calculation of peak areas, or peak heights, that are proportional to the concentration of the species being determined.

1.4.3 THERMAL ANALYSIS

Thermal analysis is the generic term encompassing a group of related techniques whereby some physical parameter of a system under investigation is determined as a dynamic function of temperature. The main parameter important in methods of thermal analysis is the change in heat content.

Differential Thermal analysis

Differential thermal analysis (DTA) is a technique in which the temperature difference between a test sample and an inert reference sample is recorded as a function of temperature, or time, as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate[16,17]. Any physical or chemically change, evident in the test sample, involving the evolution of heat, will cause the samples's temperature to rise temporarily above that of the reference material, thus engendering an exothermic peak on the DTA plot. Conversely, any process accompanied by the absorption of heat will cause the temperature of the test sample to lag behind that of the reference sample, resulting in an endothermic peak. A hypothetical DTA trace is shown in Figure 1.7.

However, even where no physical or chemical process occurs, a small and steady differential temperature normally

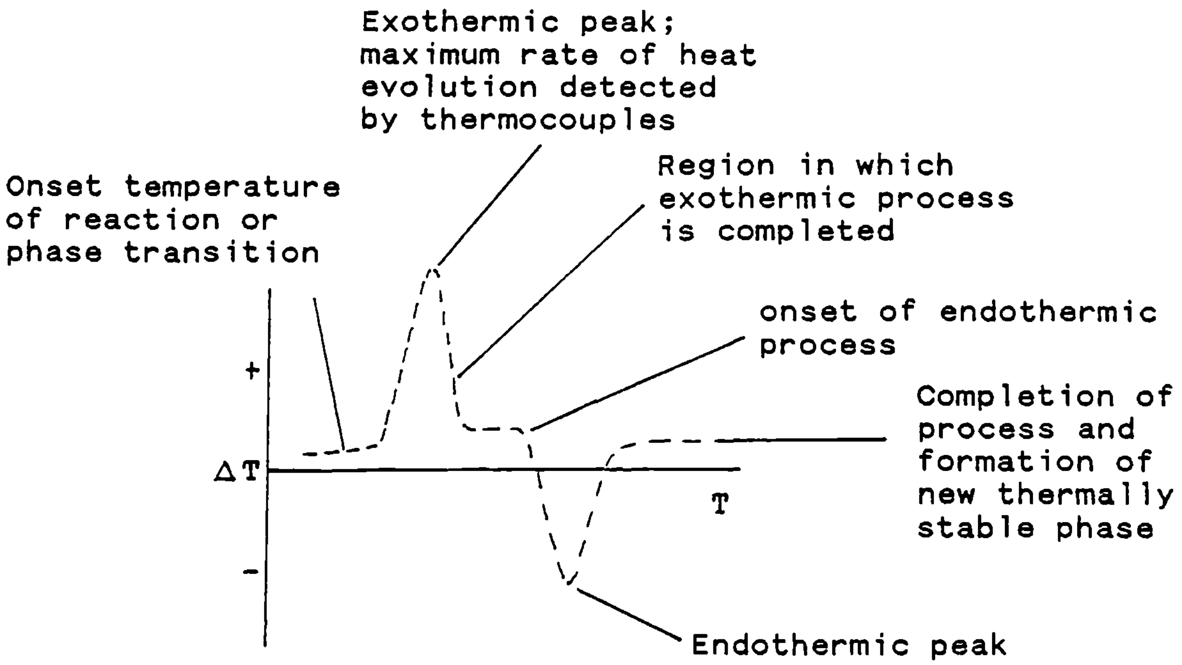


FIGURE 1.7 Hypothetical DTA trace indicating an exothermic and endothermic peak.

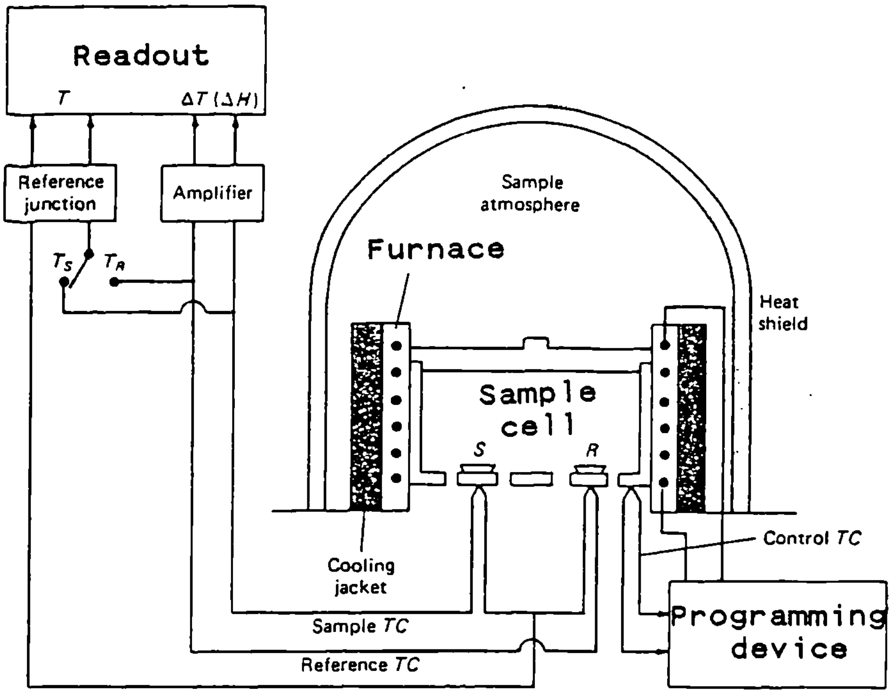


FIGURE 1.8 Schematic diagram of a typical differential thermal analyzer system.

develops between test and reference materials. This is primarily due to differences in the heat capacity and thermal conductivity of the two materials, but is also influenced by other factors, such as sample mass and packing density. Consequently, DTA can be used to study transitions in which no heat is evolved or absorbed by the sample, as may be the case in certain solid-solid phase changes[18]. The difference in the heat capacity of the sample before and after the transition has occurred will then be reflected in a new steady differential temperature being established between the test and reference samples. The base line of the differential curve will accordingly show a sudden discontinuity at the transition temperature, while the gradients of the curve in the regions above and below this temperature will usually differ significantly.

Clearly, the peaks due to chemical changes may ensue not only from reaction of the sample itself, but also from secondary reactions of evolved decomposition products. Such reactions can often occur catalytically on the surface of the residual solid.

To rely entirely on the evidence obtained by DTA in the elucidation of a problem is undesirable. Thus, thermogravimetry (TG) is commonly employed in conjunction with DTA.

Thermogravimetry

In dynamic thermogravimetry, as used in this work, changes in the weight of a sample, subjected to a uniform rate of increase in temperature are recorded. (Static thermogravimetry measures the change in weight of a sample with time at a constant temperature.) This enables any DTA peak due to a chemical reaction involving a weight changes to be identified. If a DTA peak arises at a temperature where the sample weight remains constant, it may be assumed that either a solid state reaction, or a phase transition has occurred. Therefore, the TG curve provides information on the thermal stability and composition of the initial sample, on the intermediate compound that may be formed, and on the composition of any residue.

Differential Thermogravimetry

Differential thermogravimetry is a technique expressing the results of TG by yielding the first derivative of the TG curve with respect to either temperature (T) or time (t):

$$dm/dt = f\ (T \text{ or } t)$$

The area under the curve is proportional to the total change in mass of the sample.

Several advantages may be attributed to DTG, as have been outlined by Erdey et al[19]: DTG curves are more reproducible than DTA curves (the results of the latter indicate even those changes in state that are not accompanied by a loss in mass); DTG measurements reveal the precise temperatures of the onset, the maximum rate and the termination of the change, whereas DTA curves extend over a wider temperature interval owing to subsequent warming of the material after reaction; the effect of rapid changes is to encourage overlapping of TG curves, complete with the difficulties implicit in interpretation, the DTG curves of the same transitions are usually more distinct with prominent peaks.

Instrumentation

In this work, a Stanton Redcroft STA 780 simultaneous Thermal Analyzer was used and samples heated to 600°C unless stated otherwise. The instrument is designed to give temperature, TG, DTA and DTG curves simultaneously, facilitating the correlation of data for the same substance.

The DTA apparatus consists of four major components, as is illustrated in Figure 1.8[16].

1. Sample holder - measuring system. This comprises the thermocouples and sample containers.

2. Furnace - heat source having a large uniform temperature zone.

3. Temperature programme - supplies energy to the furnace in such a manner as to ensure a reproducible (and preferably linear) rate of change of temperature.

4. Recording system - method of indicating and/or recording the e.m.f. (suitably amplified) from the differential- and temperature-measuring thermocouples.

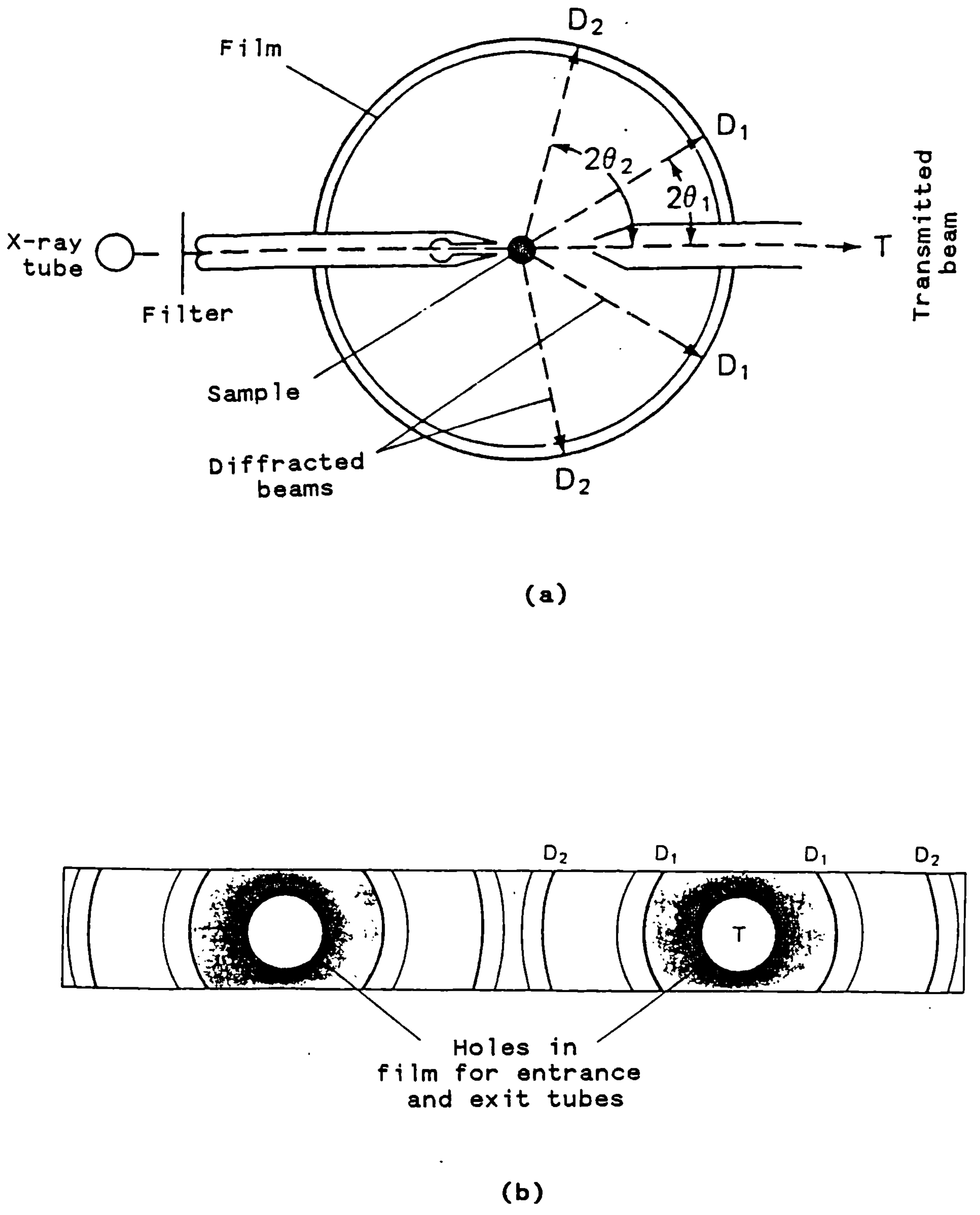
1.4.4 X-RAY METHODS

X-Ray Powder Diffraction

X-ray powder diffraction is a physical technique used in the characterization of solids. It has in use since the early part of this century for the 'fingerprint' identification of crystalline materials and for the determination of crystal structures[20].

The principles of X-ray powder diffraction are illustrated in Figure 1.9. A monochromatic beam of X-ray strikes a finely powdered sample, which, ideally, consists of randomly orientated crystals. In such a sample, the various lattice planes are also randomly orientated. Thus, for each set of planes, at least some crystals must be orientated at the Bragg angle, theta, to the incident beam and so diffraction occurs for these crystals and planes. The diffracted beam may be detected either by surrounding the sample with a strip of photographic film (Debye-Scherrer and Guinier focusing methods) or by using a movable detector, such as a Geiger counter, connected to a chart recorder (diffractometer).

The original powder method, Debye-Scherrer method, is used little nowadays, although its mode of operation is instructive. For a given set of lattice points, the diffracted radiation forms the surface of a cone. The only requirement for diffraction is that the planes must be at the angle, theta, to the incident beam. In finally powdered



(a)

(b)

FIGURE 1.9 Schematic diagram of (a) a powder camera; (b) the film strip after development.

samples, crystals are positioned randomly about the incident beam and the resulting diffracted beams appear to be emitted from the sample as cones of radiation. Since the Bragg angle is θ, The angle between diffracted and undiffracted beams is 2θ, and the angle of the cone is 4θ . Each cone of radiation is produced by a different set of planes. A thin strip of film wrapped around the sample detects the cones which appear as arcs, symmetrical about the two orifices in the film (these allow entry and exit of the incident and undiffracted beams). Finally ground samples produce a continuous line; in coarser samples, relatively few particles are present and so, do not satisfy the assumption that they lie in all possible orientation which may result in the arcs being 'spotty'.

To obtain the d-spacing, the separation, S, between pairs of corresponding arcs is measured and by knowing the radius, R, the following expression is applied:

$$S/2\pi R = 4\theta/360$$

From this, 2θ and therefore d may be obtained for each pair of arcs.

Modern film methods, such as Guinier focusing methods, make use of a convergent, intense incident beam. A bent single crystal of quartz or graphite is placed between the X-ray source and the sample to obtain a convergent beam. The orientation of the bent crystal is adjusted so that it diffracts the incident beam and converts it from a divergent to a convergent one. The beam then strikes the sample and the diffracted beams are arranged to focus at the surface of the film.

Another modern powder technique, as implemented in this work, is diffractometry. Again, a convergent beam is used and the resolution fairly good. Another advantage of this method is the reduction in exposure time (typically 10 minutes to 1 hour). The instrument has a proportional scintillation or Geiger counter as the detector which is connected to a chart recorder. The counter is usually set to scan over a range of 2θ values at the constant velocity. Generally, the range 10 to 80 2θ is sufficient to cover the most useful part of the powder pattern. The output to chart paper consists of a plot of peaks against values of 2θ. A Philips PW051 diffractometer was used in this work.

Interpretation

The principle features of a powder pattern are the d-spacings and intensities. The d-spacings (positions) of the lines in a powder pattern are governed by the values of the unit cell parameters (a, b, c, α, β, γ). The intensities provide information on the types of atoms present in the sample. Intensities are recorded relative to the intensity of the strongest line of the pattern which is arbitrarily assigned 100. For a particular substances, the line positions are essentially fixed and are characteristic of that substance. Intensities may vary somewhat from sample to sample, depending on the method of sample preparation and instrumental conditions.

A important use of the powder method is the qualitative analysis of crystalline phases. For the identification of unknown crystalline materials, an invaluable reference source is "The Powder Diffraction File" (Joint Committee on Powder Diffraction Standards, U.S.A.); (supplementary data are issued annually).

THE ELECTRON MICROPROBE

(Energy Dispersive Analysis of X-Ray (EDAX)

With the electron microprobe method, X-ray emission is stimulated on the surface of the sample by a narrow, focused beam of electrons. The resulting X-ray emission is detected and analysed with wavelength or energy dispersive spectrometer[21,22].

Figure 1.10 is a schematic diagram of an electron microprobe system[23]. The electron beam is produced by a heated tungsten cathode and an accelerating anode. Two electromagnetic lenses focus the beam on the specimen and the fluorescent X-ray produced by the electron beam are collimated, dispersed by a single crystal, and detected by a gas-filled detector. By counting the number of X-ray that correspond to each element of interest it is possible to obtain an elemental analysis of the specimen. A complete sample analysis by EDAX usually takes 5 minutes. Because the sample holder is made of copper, spurious measurements of this element are often obtained.

For EDAX analyses about 10mg of sample was finely ground and fixed to copper sample holder using a double sided adhesive tape and the excess sample shaken off before mounting the sample holder in the electron microscope. When recording EDAX, the electron beam was focused onto the sample and a visual picture of the intensity of the desired elements was acquired.

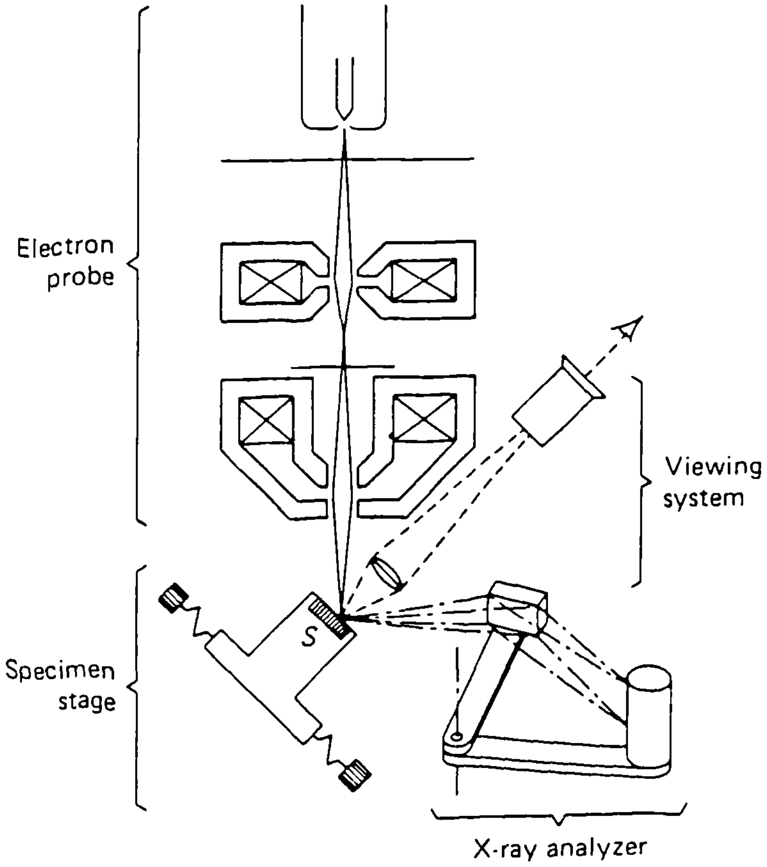


FIGURE 1.10 Schematic view of an electron-microprobe instrument.

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CHAPTER 2

THE RECOVERY OF METALS FROM DILUTE EFFLUENT STREAMS BY FLUIDISED BED ELECTROLYSIS

CHAPTER TWO

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2.1 EFFLUENT

2.1.1 Introduction

Most of the important metal ore deposits are gradually becoming depleted because of the finite nature of the Earth's resources and because man continually seeks further metal resources, over time, these will become of lower and lower grade. Because of this, there is a gradual movement towards the extraction of metal from low grade materials, wastes and industrial effluents. The use of lower grade resources and industrial effluents leads to higher consumption of fuel per unit of metal extracted; it also causes progressively greater loads on the environment due to increasing waste produced per unit of metal extracted. In the past, industries did not want to recover metals from their effluents and wastes due to the high cost of recovery, and simply pumped them to drain, thus losing these important metals and causing a pollution problems. The volume of liquid sludge which is produced at a sewage treatment works only corresponds to 1-2 per cent of the total flow of sewage[1-4]. However, its treatment and disposal is generally a major operation often accounting for as much as 50 per cent of the total running costs of the works.

Since the industrial revolution, regulations have been introduced over many years to protect the air we breath, the water we drink, and the environment of the animals and fish that we eat. The majority of manufacturers discharging effluents containing high metal concentrations, have been required to install pre-treatment plant to enable their discharges to comply with Water Authority discharge limits. Although, the main effects on the environment of most industrial metals and their compounds are now understood, we have not necessarily achieved a satisfactory degree of protection from them in all cases and in all countries. Some of the British Water Authorities discharge limits for different toxic elements in effluents[5] and in sludges[6] are given in Tables 2.1 and 2.2 respectively.

In most treatment plants, the metals are precipitated as hydroxides, usually by the addition of lime and the solids dewatered. The filtrate containing metal levels within the guideline limits is then passed to the pipeline sewer. The dewatered sludge produced is then taken to a suitably licensed site for disposal. This method is satisfactory as far as the Water Authority discharged limit is concerned, but it rules out the recovery of the metals.

2.1.2 Effluent Treatment

In the current economic climate, effluent treatment is an area that must now be given high priority. It should be an essential part of the total production process, either to recover valuable raw materials or to comply with the requirement of the water authorities on the acceptable levels of contaminants in the discharge stream. This is specially true in industries producing effluent streams containing heavy metals. For instance, silver and other precious metals have been recovered by users for many years due to their high intrinsic value. Cadmium, on the other hand, is recovered because its levels in discharge are closely controlled by water authorities due to its toxicity and interference with sewage treatment and disposal.

One of the main sources of metal-bearing effluent is from the electroplating sector of the finishing industry. For instance, in an electroplating shop it is essential, before the objects being plated proceed to the next stage, to remove from them the solution which adheres (dragout) when they are removed from any plating bath. This is usually carried out swilling or spraying the objects with clean water. In many cases the contaminating metal has low value. However, these polluted rinse waters cannot be discharged directly to the sewers without prior treatment.

The earliest form of treatment for this kind of effluent was

TABLE 2.1. DISCHARGE LIMITS OF ELEMENTS IN EFFLUENTS

Element	Concentration, (mg/l)
Ag	5
Cd	2
Cr	5
Cu	5
Hg	0.1
Ni	4
Pb	5
Zn	10
Total non-ferrous metals (excl. alkali & alkaline earths)	30
Soluble non-ferrous metals (excl. alkali & alkaline earths)	10

TABLE 2.2. LIMITING CONCENTRATIONS OF ELEMENTS IN SLUDGE

	Water authority limiting con'c. in Sludge.	E.E.C proposed Limits in sludge (mg/kg dry solids)	
Element	(mg/kg dry solids)	Recommended	Mandatory
Arsenic	130	-	-
Boron	1400	-	-
Cadmium	70	20	40
Chromium	13000	750	-
Copper	-	1000	1500
Fluorine	3500	-	-
Lead	2000	750	1000
Mercury	25	16	-
Molybdenum	50	-	-
Nickel	-	300	400
Selenium	70	-	-
Zinc	-	2500	3000

TABLE 2.3 ELECTROPLATING DATA

		Weight of deposit/ampere hour	
Metal	Valency	Ounce	Grammes
Cadmium	2+	0.074	2.10
Cobalt	2+	0.0388	1.10
Copper (Cyanide)	1+	0.0837	2.37
(Acid)	2+	0.0418	1.19
Gold (Cyanide)	1+	0.260	7.37
Iron	2+	0.0368	1.042
Lead	2+	0.136	3.865
Nickel	2+	0.0386	1.095
Silver	1+	0.142	4.025
Tin (Stannous)	2+	0.078	2.214
(Stannic)	4+	0.039	1.107
Zinc	2+	0.043	1.2

to throw it down the drain and forget about it. The deterioration in the quality of waterways soon forced a review of this practice and the plating industry was required to treat effluent. The first thought was to use the plating process itself to remove the metals from the effluent but the low metal concentration and the mixture of metals defeated this approach for many years[7]. Situations in which such dilute solutions could arise are acid treatment of alloys, electroplating rinse solution, leach and effluent solutions from the manufacture of chemicals. Static rinse tanks in electroplating situation provide good examples of the types of dilute metal containing solutions that are to be considered in this chapter.

There are many possible methods of metal recovery which can be used - these include: electrolysis, chemical treatment, solvent extraction, and ion exchange. The method for the recovery of metals from dilute solutions studied in this work involves the use of a fluidised bed electrolytic cell.

2.2 ELECTROLYTES AND ELECTROLYSIS

Substances that yield electrically conducting solutions are known as electrolytes and they differ from normal conductors in that when current is passed through them it is always associated with the transference of matter. This transportation only occurs in the electrolyte and is stalled or terminated by processes at the electrodes.

Electrolysis can be defined as the chemical decomposition of certain substances by an electric current passed through a liquid (solution or molten state). The process includes transport of charged species towards the oppositely charged electrodes where they react to become uncharged atoms or groups and are either liberated (as gas) or deposited at the electrodes, or react chemically with the electrodes, the solvent, or each other, according to their chemical nature.

2.2.1 Theory of Electrolysis

The process of electrolysis requires the transportation of ions from the bulk of the solution to the surface of the electrodes. 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 to be plated out cause problems[8].

There are three possible methods of ion transportation:

a) **Migration** -due to effect of an electric field
b) **Convection** -due to hydrodynamic flow
c) **Diffusion** -due to the effect of a downward gradient to the electrode, in the concentration of the solution.

Migration and convection are not effective in dilute solution 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 neighbours of the electrodes to zero. Thus there is no mass transport by the convection in this region. Migration by itself is not sufficient to transport ions through the barriers of the boundary layer to the surface of the electrode.

Thus the only way in which the ions can be transported into the boundary layer and so to the electrodes is by diffusion. This boundary layer is known as diffusion layer, and there is a gradient of ionic concentration in it, from that of the bulk of the electrolyte to that at the electrode, which is zero at limiting current density (Figure 2.1). If the diffusion layer is not reduced in thickness and the current density is increased beyond that which brings the ion concentration level at the electrode down to zero, other competing reactions, such as the evolution of hydrogen will take place and the current efficiency will decrease.

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

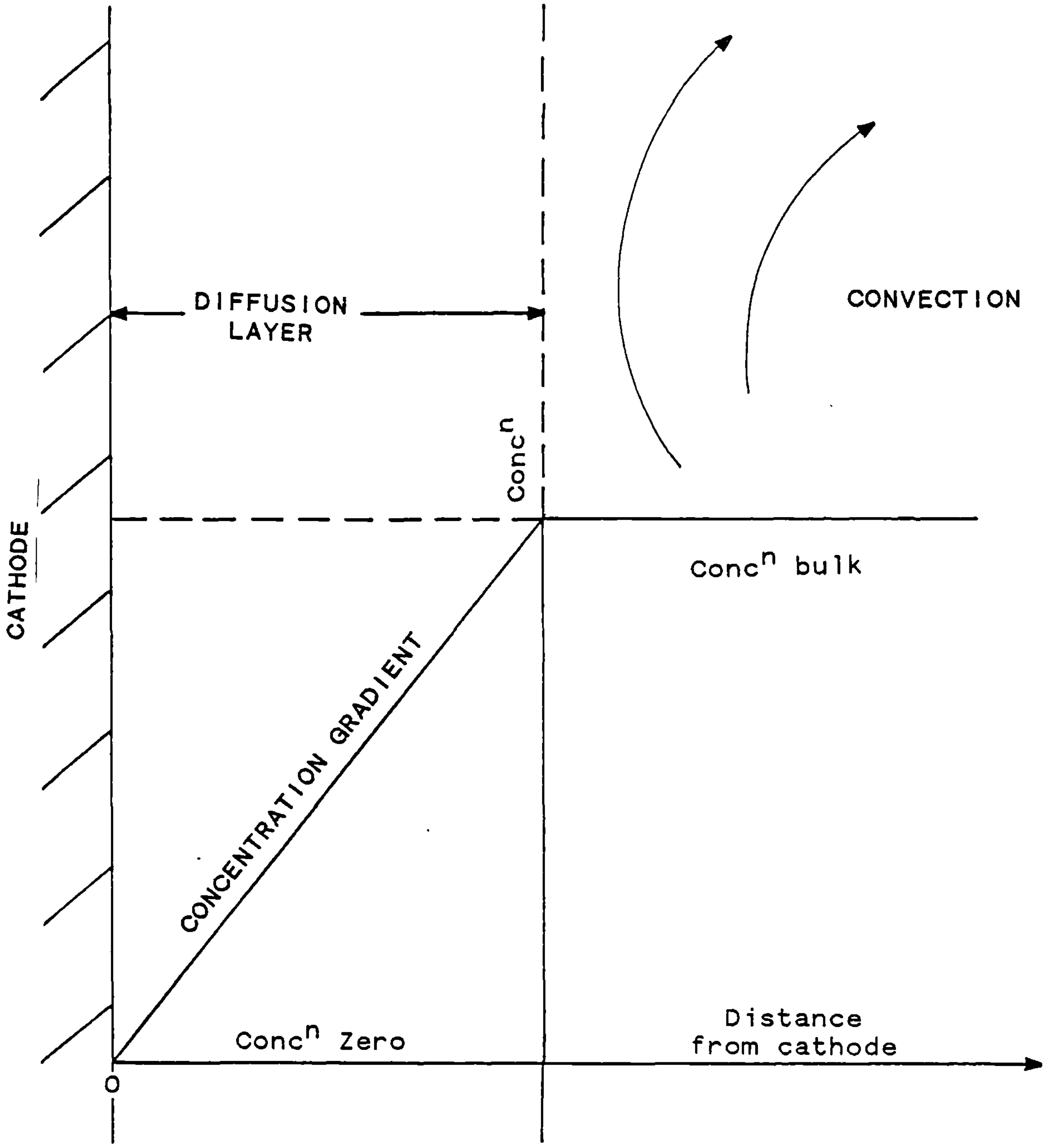

FIGURE 2.1 Diagram illustrating the diffusion layer set up between a cathode surface and the solution.

law). So, in electrolysis, the controlling and the limiting factor is electrolyte concentration. The operation of these laws in normal electrolyte concentrations ensures that the boundary layer does not hinder the performance of the cell. For example in electroplating, there are sufficient ions in solution to achieve high current efficiency with a use of a high current density. The electrowinning of cobalt[9-14], copper[15] and nickel[16] from sulphate solutions containing sufficiently high concentration of metals have been reported in the literature. Besides a pure sulphate bath, electrowinning of cobalt from sulphate bath containing additives such as Na_2SO_4, H_3BO_3, $(NH_4)_2SO_4$, NaF, etc. have also been reported[17-20]. When the concentration of the solution is reduced the forces diffusing the ions to the electrode become progressively less effective and the diffusion layer becomes more and more depleted of ions. So 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 progressively reduced.

Current density = Current applied/Surface area of cathodes

Problems such as these arise when very dilute or low concentration electrolytes are used. The rate of deposition of metal at the cathode is limited by the rate of diffusion of ions into the boundary layer and if an attempt is made to pass a greater current through the cell, hydrogen gas will be liberated which will cause embrittlement or powder formation of the metal. In other words, to operate the process in low concentration solutions at high current efficiencies, low current densities would have to be used. There is however, only one method available to increase the limiting current density in this electrolytic process, and that is to decrease the thickness of the diffusion layer and so increase the concentration gradient to the electrode. This can be achieved by using the fluidised bed cell.

Limiting Current Density

Limiting current density can be defined as the current density at which the metal ions are reduced as rapidly as they diffuse to the electrode surface. The limiting current density of any electrolyte increases with the concentration of solution and the current efficiencies which can be achieved also increase as a result.. The limiting current density (i_l) is related to the thickness of the diffusion layer (d) by an equation of the type:

$$i_l = k.1/d \qquad (1)$$

in which k is a function of the ion valency (z), diffusion coefficient (D), transport number (t) and concentration (c) of the ionic species:

$$k = DzFc/1-t \qquad (2)$$

The transport number (t) is usually zero under these situations thus the limiting current density is:

$$i_l = DzFc/d \qquad (3)$$

where F = Faraday's constant

If the ion concentration is constant a reduction of the thickness of the diffusion layer will produce a proportional increase in the limiting current density.

All the methods of reducing the thickness of the diffusion layer involve agitation, that is rotating electrodes, mechanical stirring, air agitation, turbulence promoters, slurry or fluidised beds[21].

Many electrolytic cells have been proposed for metal recovery from dilute effluent streams. They are used mostly as concentrators where further stages of purification are required to obtain the metal in a directly re-usable form. Some of the most important are the fluidised bed electrodes developed by Newcastle University as described by Vance[22], the carbon particle packed bed studied by Bennion and Newman[23], the Eco-Cell invented and developed by Holland[24], the Du-Ponts' Extended Surface described by Keating[25], and the Swiss-roll cell developed by Robertson[26].

2.3 CHEMELEC CELL

The Chemelec cell is a fluidised bed cell, which is relatively cheap to produce and simple to operate. The cell was developed by Lopez-Cacicedo at the Electricity Council Research Centre, Capenhurst[27]. 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 efficiency. The system involves 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 (Figure 2.2). 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 the conventional smooth plate electrodes this polishing effect does improve performance somewhat but is not particularly effective, as the smooth plate offers less resistance to fluid flow than the fluidised bed itself. A channel of easier flow is established in a vertical direction alongside the boundary layer and this channelling tends to cancel the effect of particles hammering the electrodes.

However, when the fluidised bed cell is used in conjunction with expanded mesh electrodes the fluidised particles can pass through the electrodes (Figure 2.3). In this way channelling is prevented and the particles can approach the

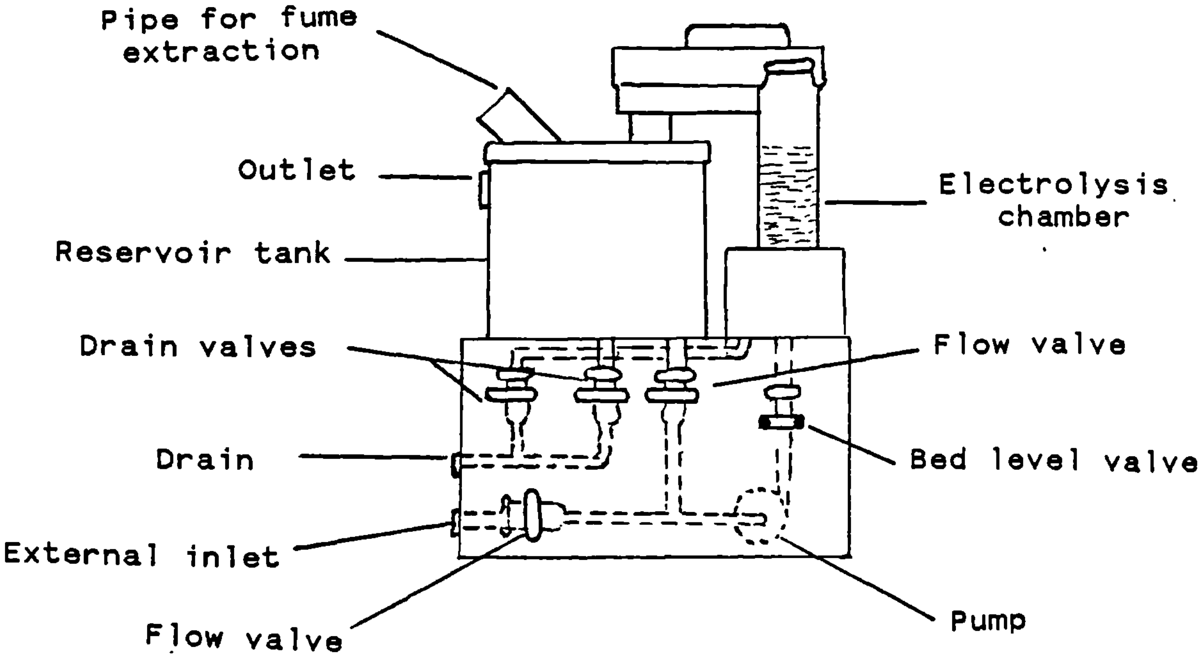

FIGURE 2.2 Chemelec cell.

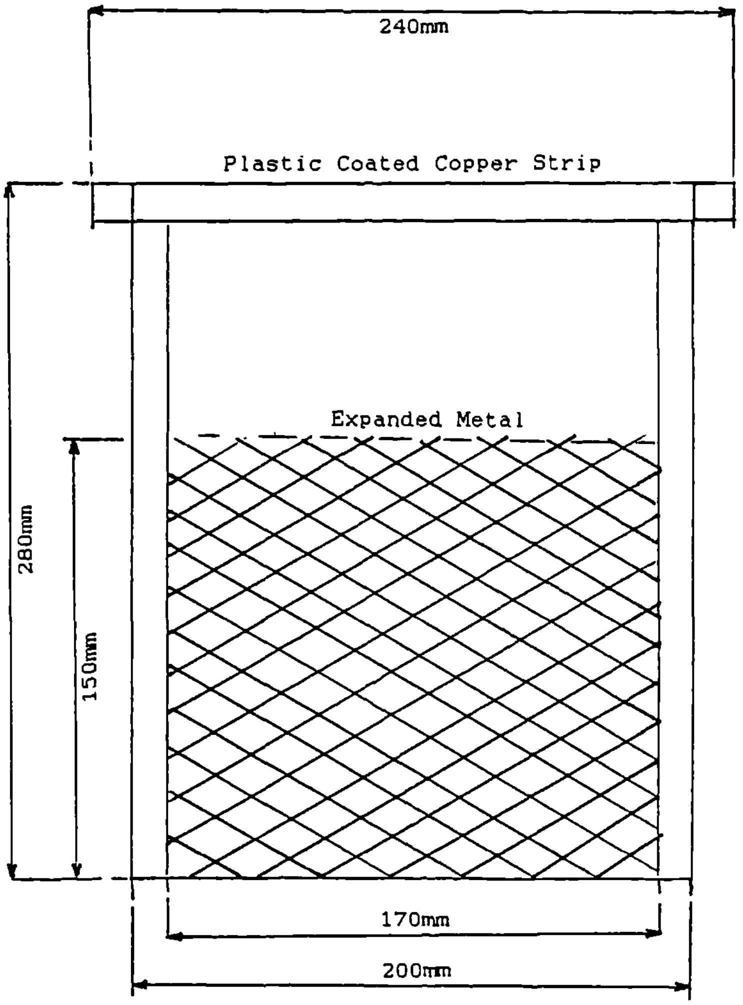

FIGURE 2.3 Mesh electrode for Chemelec cell.

surface of the electrodes from many possible directions. This movement of the liquid 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 deposit on the cathode[28].

Nowadays it is a common practice in electroplating lines to have a static rinse tank immediately following the plating tank and preceding a running tank (Figure 2.4). Metal can be removed from the static rinse tank if its contents are continually circulated through a fluidised bed cell and back to the tank. Circulation through the cell ensure that a low concentration of metal is maintained in the static rinse tank (typically 200-250 mg/l or less) and that very little contamination is carried into the running rinses that normally follow the drag-out and therefore these rinse waters can usually be discharged directly to drain.

Current Efficiency and Degree of Purification

The electroplating data or the electrochemical equivalent based on 100 per cent current efficiency for various metals are given in Table 2.3. These values are commonly used in order to find out the current efficiency (η) of the reaction during the electrolysis process. The current efficiency can be calculate by using the following equation:

$$\text{Current effcy.} = \frac{\text{Actual deposit}}{\text{Theoretical deposit for current passed}} \times 100$$

Degree of purification (α) is a cathodic deposit achieved during the electrolysis process and can be calculated by the following equation:

$$\text{Degree of purification} = \frac{\text{Actual deposit (g)}}{\text{Initial weight (g)}} \times 100$$

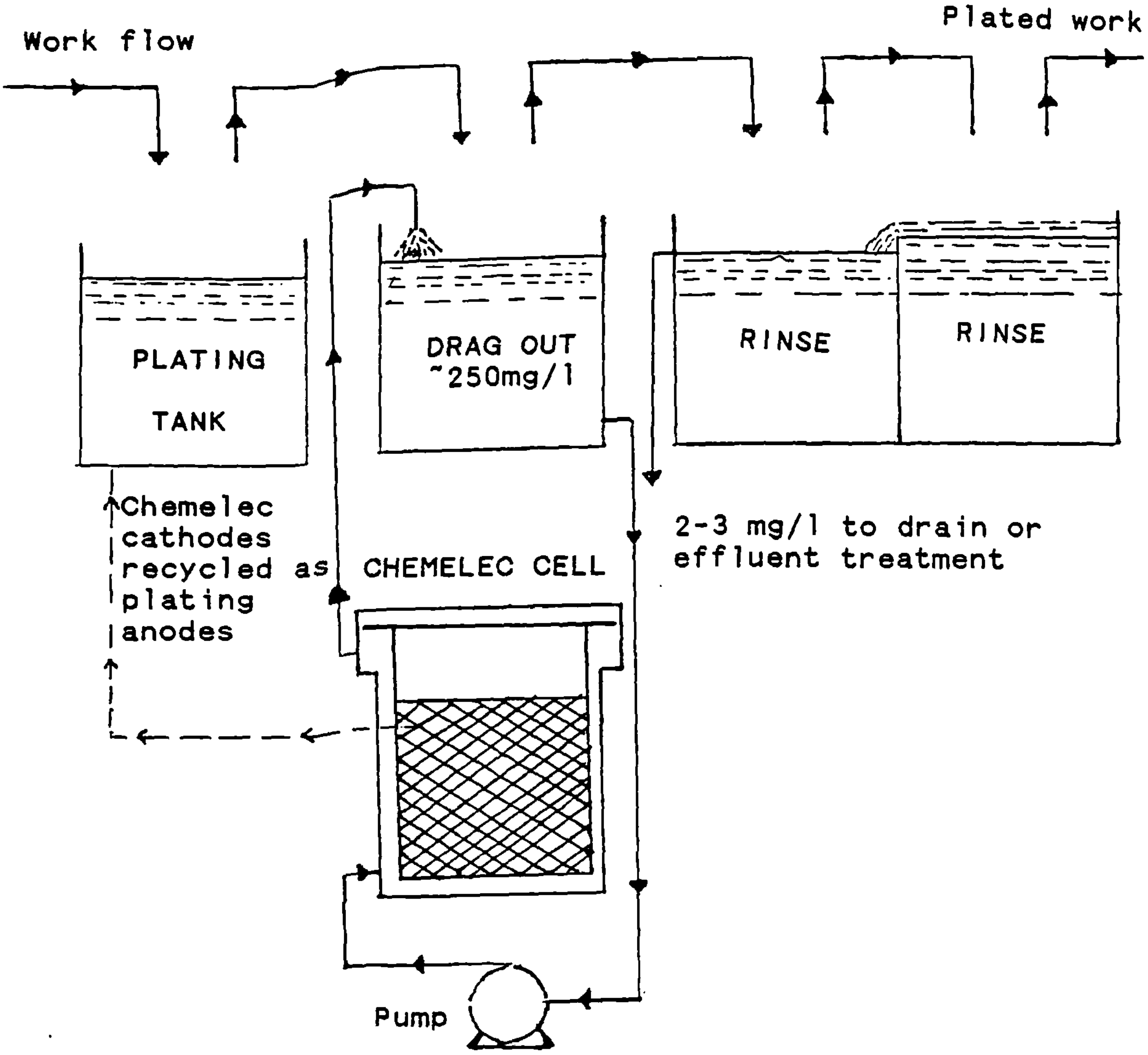

FIGURE 2.4 Operation of Chemelec cell on a plating line.

2.3.1 The Use of Chemelec Cell for the Separation of Metals

The Chemelec cell is used for the recovery of individual metals from the industrial effluents, but it can also be used for those effluents which contain more than one metal. The Chemelec cell will recover, on one cathode, all the metals in a particular solution with the same effectiveness as for a single metal. The different metals deposited will not, however, be laid down homogenously on the cathode but their deposition order will depend upon their standard electrode potential[29-32].

In electrodeposition, a metal is deposited on a electrode from a solution of its ion. By Faraday's law of electrolysis, the amount of metal deposited at the electrode is proportional to the quantity of electricity that is passed through the electrolyte. If the metal is to be deposited quantitatively from the solution, the voltage applied to the cell must be greater than the decomposition potential and the resistance of the cell since the decomposition potential increases as the concentration of the metal ions falls, the applied potential must be large enough to offset this increase. For a unipositive metal ion the increase in potential is about 0.25 volt, and for a dipositive ion about 0.12 volt.

When the decomposition potentials of two metals differ by more than 0.35 volt it is often possible to separate them by electrodeposition. The metal with the most positive reduction potential is deposited first. If a constant current is maintained the reduction potential of the metal will decrease as deposition progresses. When it is complete, the potential will fall again until the next reduction potential is reached and the deposition of second metal will begin.

When the potentials of two metals are similar, these ions in solution cannot be separated by deposition from solution but may be conveniently separated if one of the ions forms a stable complex with a suitable ligand. For example, a solution containing a mixture of bismuth(III) and copper(II) cannot be separated, since the potentials are close together. However, copper forms a stable complex cyanide, $[Cu(CN)_4]^{2-}$ that remains in solution, while the uncomplex bismuth ion is deposited as metal.

2.3.2 Advantages of the Chemelec Cell

The advantages of the Chemelec cell, compared with hydroxide precipitation in effluent treatment in the plating industry can be enumerated as:-

1) Reduction of 99.6% in the amount of sludge generated.
2) A consequently similar reduction in the load on the oxide precipitation tank (or on the ion exchange or other treatment equipment) with the corresponding saving in the labour and transport charges associated with its disposal.
3) A saving in the replacement water or the first rinse tank. Because the metal concentration level is maintained at 200 ppm it only has to be replaced when the other impurities build up to an undesirable level.
4) A large saving in the amount of replacement water required for the second rinse tank which only receives dragout at 200 ppm.
5) The metal recovered can be reused directly as an anode in the plating bath, and the cost of recovery is only a proportion of the cost of the metal recovered.
6) The use of the cell does not add to the labour costs of the plating line.
7) The use of the cell cannot affect the plating tank because it is in a completely isolated, closed circuit.
8) The size of the cell is such that it can always be placed next to the rinse tank - and so becomes part of line.
9) No chemical costs involved.

2.4 EXPERIMENTAL

In this work a small fluidised bed electrochemical cell, supplied by BEWT (Water Engineering) Ltd., of 10 litre capacity was used to study the deposition of metals from dilute sulphate solutions of cobalt, copper and cadmium. It was also used for the electrodeposition of copper from a brass fines leach solution, which also contained zinc and lead. In all electrolysis experiments two titanium mesh cathodes (total surface area 0.1 m^2) and three platinised titanium mesh anodes were used for the electrodeposition. The five electrodes were placed in the electrolysis chamber, anode, cathode, anode, cathode, and anode. The cathodes were weighed before and after electrolysis to determine the amount of metal recovered. After electrolysis, the cathodes were removed and washed thoroughly with tap water followed by distilled water and then let them dry overnight. The deposited metal was brushed off with a wire brush.

2.5 ELECTRODEPOSITION OF COBALT

In all electrolysis experiments a ten litre solution containing different concentrations of cobalt were treated at ambient temperature. Electrolyte solutions were prepared from reagent grade cobalt sulphate crystals ($CoSO_4.5H_2O$) and 400ml of 1M sulphuric acid. The ammonium hydroxide and sulphuric acid used for adjusting the pH of the electrolyte were also of reagent grade. Since pH control is important 100ml of 10% ammonium formate solution was used as a buffer in each case and the solution was made up to 10 litre with distilled water.

The pH of the solution was monitored continuously and kept constant through out the experiment by addition of ammonium hydroxide solution - a continuous dropwise addition of alkali was required especially during the early stages of electrolysis.

Periodically during the electrolysis, samples were collected from the reservoir tank for the AAS analysis of metal ions. The parameters determined for each electrolysis experiment were: the degree of purification of cobalt, α_{Co}; the current efficiency for cobalt, η_{Co}; and the energy consumption for 1 Kg of cobalt deposited, W_{Co}.

The influence of the following factors on the deposition of cobalt were studied: pH, buffer concentration, cobalt concentration, Current density, and agitation. Each of these factors are now considered.

2.5.1 Effects of pH

Solutions containing 1 g/l cobalt were studied at different pH values. All pH values were kept constant through out the experiment by addition of ammonium hydroxide solution. A constant current density of 25 A/m^2 was applied across the electrodes for the electrodeposition of cobalt, results are given in Table 2.4.

2.5.2 Effects of Buffer solutions and concentrations

The effects of different buffers on the electrodeposition of cobalt were studied in three experiments, one without any buffer, one with 100ml of 10% sodium formate solution, and another with 100ml of 10% ammonium formate. The cobalt concentration was 1g/l in each case. The pH of the solution was kept constant at 4-5 and the current density was 25 A/m^2. The results are given in Table 2.5.

In further experiments, three solutions containing 0.5 g/l cobalt along with 100ml of 5%, 10% or 15% solutions of ammonium formate were used to deposit cobalt. Ammonium formate was preferred to sodium formate solution because an excess of sodium ions makes it difficult to analyse the solution by AAS. Although there is little difference between sodium and ammonium formate buffers in use.

Electrolysis experiments were carried out at constant pH (4-5) and at a current density of 15 A/m^2 for 8 hours. The results show that, although, the percentage of cobalt deposition is the same for every experiment the 10% and 15% solutions gave much easier control over the pH value. The

TABLE 2.4 EFFECT OF pH ON THE ELECTRODEPOSITION OF Co

Time (hr)	pH	Concentration (ppm)	Deposition α_{Co}, (%)	Current effy. η_{Co}, (%)
2	3-4	810	19.0	34
	4-5	605	39.5	72
	5-6	611	38.9	71
	6-7	620	38.0	69
4	3-4	586	41.4	37
	4-5	293	70.7	64
	5-6	288	71.2	64
	6-7	260	74.0	67
6	3-4	190	81.0	49
	4-5	82	91.8	56
	5-6	83	91.7	56
	6-7	75	92.5	56
8	3-4	45	95.5	43
	4-5	20	98.0	44
	5-6	16	98.4	44
	6-7	15	98.5	44

Conditions: Initial conc., 1 g/l; Current density, 25 A/m^2.

TABLE 2.5 EFFECT OF BUFFER SOLUTION ON ELECTRODEPOSITION

Buffer	Time (hr)	Concentration (ppm)	Deposition α_{Co}, (%)	Current effy. η_{Co}, (%)
None	2	636	36.4	66
	4	282	71.8	65
	6	74	92.6	56
	8	14	98.6	44
HCOONa	2	621	37.9	69
	4	280	72.0	65
	5	106	89.4	64
	7	29	97.1	50
	8	17	98.3	44
$HCOONH_4$	2	644	35.6	65
	4	287	71.3	65
	6	62	93.8	57
	8	12	98.8	45

Conditions: Initial conc., 1 g/l; Current density, 25 A/m^2.

results for various buffer concentrations are in Table 2.6.

2.5.3 Effects of Cobalt concentration

Five solutions containing cobalt concentration in the range of 0.2-2.0 g/l were used at constant pH 4-5 and at constant current density of 15 A/m^2 for the deposition of cobalt. The results are in Table 2.7.

2.5.4 Effects of Current Density and Cobalt concentration

In the following experiments, solutions containing 0.2, 1.0 and 2.0 g/l cobalt were studied at constant pH (4-5) but at different current densities. The results are in Tables 2.8-2.10.

2.5.5 Effects of Agitation

Experiments were carried out to determine the effects of the agitation due to the upward and downward movement of the glass beads in the electrolysis chamber. Solutions containing 0.2 and 1 g/l cobalt were used at constant pH of 4.0-5.0 with current densities of 15 and 25 A/m^2 respectively. The results are in Tables 2.11-2.12.

2.6 ELECTRODEPOSITION OF CADMIUM

The electrodeposition of cadmium from dilute sulphate solutions (0.5g/l) were carried out in the fluidised bed cell using different current densities. Electrolyte solutions were prepared from reagent grade cadmium sulphate crystals and distilled water. The pH of the electrolyte was adjusted at 3.0 in each case by adding reagent grade sulphuric acid before commencing electrolysis. The results are in Table 2.13.

2.7 ELECTRODEPOSITION OF COPPER

Electrolyte solutions containing 1.0 g/l copper were prepared by using reagent grade copper sulphate and distilled water and adjusted to pH 2.0 with sulphuric acid. The results are in Table 2.14.

TABLE 2.6 EFFECT OF BUFFER CONCENTRATION

Time (hr)	Buffer Conc. (%)	Concentration (ppm)	Deposition α_{Co}, (%)	Current effy. η_{Co}, (%)
2	5	296	40.8	61
	10	298	40.4	61
	15	301	39.8	60
4	5	182	63.6	48
	10	180	64.0	48
	15	174	65.2	49
6	5	30	94.0	47
	10	26	94.8	47
	15	32	93.6	47
8	5	7	98.6	37
	10	5	99.0	37
	15	9	98.2	37

Condition: Initial conc., 0.5 g/l; Current density, 15 A/m^2.

TABLE 2.7 EFFECT OF COBALT CONCENTRATION

Initial Conc. (g/l)	Time (hr)	Concentration (ppm)	Deposition α_{Co}, (%)	Current effy. η_{Co}, (%)
0.2	2	67	66.0	40
0.5		298	40.4	61
1.0		753	24.7	75
1.5		1180	20.8	94
2.0		1680	16.0	96
0.2	4	18	91.0	28
0.5		180	64.0	48
1.0		573	42.7	65
1.5		922	55.2	87
2.0		1375	31.0	94
0.2	6	5	97.5	20
0.5		26	94.8	47
1.0		368	63.2	64
1.5		672	55.2	83
2.0		1180	41.0	83
0.2	8	3	98.9	15
0.5		5	99.0	37
1.0		192	80.8	61
1.5		435	71.0	80
2.0		937	53.0	80

Condition: pH, 4-5; Current density; 15 A/m^2.

TABLE 2.8 EFFECT OF CURRENT DENSITY

Time (hr)	Current density (A/m^2)	Concentration (ppm)	Deposition α_{Co}, (%)	Current effy. η_{Co}, (%)
2	10	132	34.0	31
	15	67	66.0	40
	20	53	73.5	33
4	10	41	79.5	36
	15	18	91.0	28
	20	16	92.0	21
6	10	10	95.0	29
	15	5	97.5	20
	20	4	98.0	14
8	10	4	98.2	25
	15	3	98.9	17
	20	3	98.9	12

Condition: Initial cobalt cocentration, 0.2 g/l.

TABLE 2.9 EFFECT OF CURRENT DENSITY

Time (hr)	Current density (A/m^2)	Concentration (ppm)	Deposition α_{Co}, (%)	Current effy. η_{Co}, (%)
2	15	753	24.7	75
	30	511	48.9	74
	50	275	72.5	66
	75	225	77.5	47
4	15	573	42.7	65
	30	143	85.7	64
	50	63	93.7	43
	75	45	95.5	29
6	15	368	63.2	64
	30	28	97.2	49
	50	14	98.6	30
	75	10	99.0	20
8	15	192	80.8	61
	30	8	99.2	37
	50	6	99.4	23
	75	6	99.4	15

Condition: Initial cobalt concentration, 1.0 g/l.

TABLE 2.10 EFFECT OF CURRENT DENSITY

Time (hr)	Current density (A/m²)	Concentration (ppm)	Deposition α_{Co}, (%)	Current effy. η_{Co}, (%)
2	15	1680	16.0	96
	25	1509	24.5	89
	50	1028	48.6	88
	100	428	78.6	71
4	15	1375	31.0	94
	25	1172	41.4	75
	50	360	82.0	75
	100	126	93.7	43
6	15	1180	41.0	83
	25	805	59.8	72
	50	110	94.5	57
	100	20	99.0	30
8	15	937	53.0	80
	25	470	76.5	70
	50	26	98.7	45
	100	3	99.8	23

Condition: Initial cobalt concentration, 2.0 g/l.

TABLE 2.11 EFFECT OF AGITITION

Agitation	Time (hr)	Concentration (ppm)	Deposition α_{Co}, (%)	Current effy. η_{Co}, (%)
Yes	2	67	66	40
	4	18	91	28
	6	5	97	20
	8	3	98	17
No	2	94	53	32
	4	46	77	23
	6	20	90	18
	8	10	95	14

Conditions: Initial conc., 0.2g/l; Current density, 15 A/m².

TABLE 2.12 EFFECT OF AGITITION

Agitation	Time (hr)	Concentration (ppm)	Deposition α_{Co}, (%)	Current effy. η_{Co}, (%)
Yes	2	631	36.9	67
	4	282	71.8	65
	6	65	93.5	56
	8	11	98.9	45
No	2	682	31.8	58
	4	318	68.2	62
	6	114	88.6	53
	8	35	96.5	44

Conditions: Initial conc., 1 g/l; Current density, 25 A/m².

TABLE 2.13 DEPOSITION OF CADMIUM

Time (hr)	Current density (A/m^2)	Concentration (ppm)	Deposition α_{Cd}, (%)	Current effy. η_{Cd}, (%)
2	12.5	322	35.6	34
	25	148	70.4	33
	50	119	76.2	18
4	12.5	162	67.2	32
	25	24	95.2	23
	50	22	95.6	11
6	12.5	44	91.2	29
	25	5	99.0	16
	50	4	99.2	8
7	12.5	18	96.4	26
	25	3	99.4	14
	50	1	99.8	7

Conditions: Initial conc., 0.5 g/l.

TABLE 2.14 ELECTRODEPOSITION OF COPPER

Time (hr)	Current density (A/m^2)	Concentration (ppm)	Deposition α_{Cu}, (%)	Current effy. η_{Cu}, (%)
2	12.5	711	28.9	97
	25	437	56.3	95
	50	177	82.3	70
4	12.5	433	56.7	95
	25	71	92.9	78
	50	33	96.7	41
6	12.5	175	82.5	92
	25	10	99.0	55
	50	8	99.2	28
7	12.5	42	95.8	92
	25	6	99.4	48
	50	3	99.7	24

Conditions: Initial concentration; 1.0 g/l.

2.7.1 Separation of Cu from Cd

In this experiment sulphate and nitrate solutions containing 1.0 g/l copper and 0.3 g/l cadmium were used to determine the effects of cadmium on Cu electrodeposition. The solution was adjusted to pH 2.0 in each case by addition of the appropriate acid. The results for sulphate and nitrate solutions are in Table 2.15 and 2.16 respectively.

2.8 DISCUSSION

2.8.1 Deposition of Cobalt

Comparing the positions of cobalt and hydrogen in the electrochemical series, it is seen that hydrogen evolution from aqueous solutions will compete with cobalt deposition. Therefore, to maximise efficiency in cobalt electrowinning, the conditions should be such that the hydrogen evolution reaction is suppressed and the cobalt deposition reaction is favoured.

a) Effect of pH control

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 and the data listed in Table 2.4 show that the deposition of cobalt can only be achieved when the pH is >4.0. By decreasing pH the cathodic deposit (purification factor) decreases rapidly. Moreover, as cobalt is electrowon from a sulphate solution, the pH falls continuously during the course of electrolysis with a resultant decrease in current efficiency. This is because the electrochemical reactions taking place during electrowinning are:

$$2Co^{2+} + 4e^- \longrightarrow 2Co$$

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$$

The Co^{2+} is deposited at the cathode simultaneously with the production of acid at the anode.

TABLE 2.15 INFLUENCE OF Cd ON Cu DEPOSITION IN SULPHATE SOL.

Time (hr)	Current density (A/m^2)	Conc. (ppm)		Deposition (%)		Current effy. (%)	
		Cu	Cd	Cu	Cd	Cu	Cd
2	12.5	724	298	27.6	0.6	93	0.4
	25	453	290	54.7	3.3	92	0.9
	50	182	276	81.8	8.0	69	1.1
4	12.5	451	293	54.9	2.3	92	0.6
	25	80	279	92.0	7.0	77	1.0
	50	38	168	96.2	44.0	40	3.1
6	12.5	197	287	80.3	4.3	90	0.8
	25	13	265	98.7	11.6	55	1.1
	50	10	93	99.0	69.0	28	3.2
7	12.5	68	274	93.2	8.6	89	1.4
	25	6	245	99.4	18.3	48	1.5
	50	5	78	99.5	74.0	24	3.0

Conditions: Initial conc., Cu, 1.0; Cd, 0.3 g/l.

TABLE 2.16 INFLUENCE OF Cd ON Cu DEPOSITION IN NITRATE SOL.

Time (hr)	Current density (A/m^2)	Conc. (ppm)		Deposition (%)		Current effy. (%)	
		Cu	Cd	Cu	Cd	Cu	Cd
2	12.5	713	299	28.7	0.3	96	0.2
	25	443	296	55.7	1.3	94	0.4
	50	225	289	77.5	3.7	65	0.5
4	12.5	440	298	56.0	0.6	94	0.2
	25	75	287	92.5	4.3	78	0.6
	50	52	204	94.8	32.0	40	2.2
6	12.5	183	290	81.7	3.3	90	0.6
	25	17	276	98.3	8.0	55	0.7
	50	13	160	98.7	44.0	28	2.2
7	12.5	90	282	91.0	6.0	87	0.9
	25	6	260	99.4	13.3	48	1.0
	50	6	116	99.4	61.3	24	2.5

Conditions: Initial conc., Cu, 1.0; Cd, 0.3 g/l.

The values obtained for the purification factor, α_{Co}, at a cathode current density of 25 A/m^2, and at different pH values are given in Figure 2.5. It is clear from the plot that percentage deposition is relatively low at pH 3-4, while at higher pH values the same degree of purification is found after 8 hours of electrolysis. When the pH value was below 2.5 there was no deposition of cobalt. As the pH value was increased from 2.5 to 3.5, cobalt starts to deposit but at a low rate of deposition especially in the initial stages.

The best pH value for the electrodeposition of cobalt is 4-5, there being no advantage in carrying out the deposition at higher pH. All of the work was carried out at pH 4-5 for two reasons; (1) less ammonium hydroxide is required to maintain this pH; and (2) the nature of cathodic deposit is best at this pH. The deposit is comparatively dull in the higher pH range, and brighter in the more acidic pH range.

During the early stages of an electrolysis process it is difficult to maintain a constant pH without the use of a 10% sodium or ammonium formate buffer solution.

It is clear from Table 2.5 that both ammonium and sodium formate buffer solutions give the same deposition percentage, but ammonium formate is preferred because a high concentration of sodium ions interferes with AAS analysis. The purification factor, α_{Co}, for cobalt is the same over a range of concentrations of ammonium formate. The data in Table 2.6 show that the deposition of cobalt is independent of the buffer concentration.

b) Effect of Cobalt concentration

The influence of cobalt concentration was studied in the range of 0.2-2.0 g/l cobalt, using a current density of 15 A/m^2 for a period of 8 hours at ambient temperature, and pH 4-5. The results are in Figure 2.6. The best values for cobalt efficiency, η_{Co}, are obtained from the most concentrated solutions (Table 2.7). Current efficiency

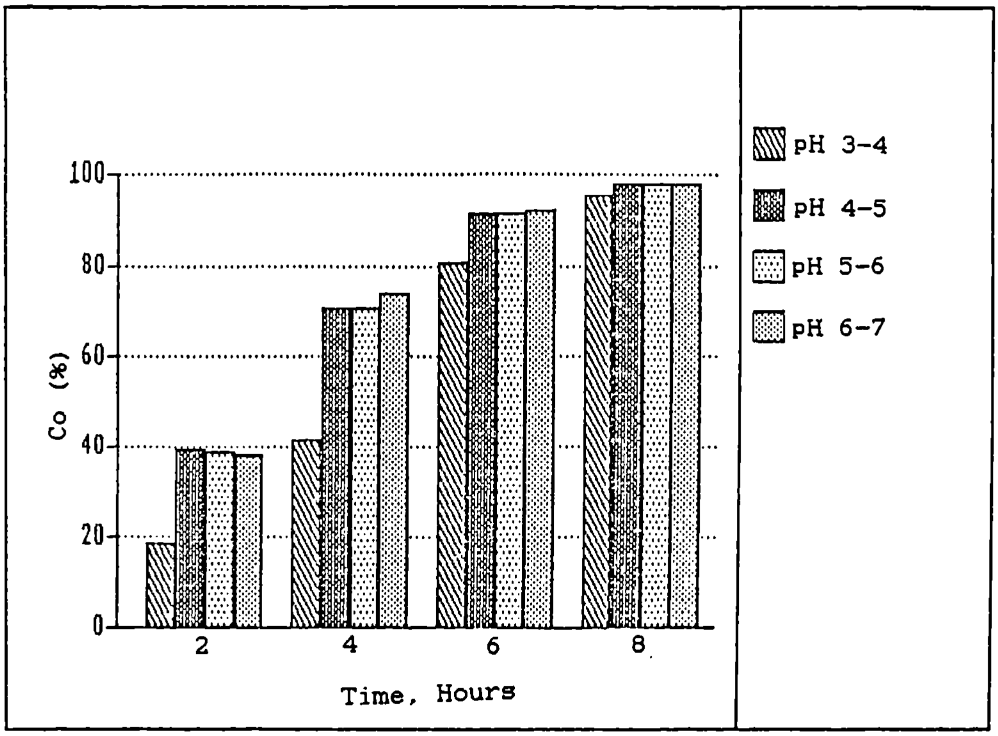

FIGURE 2.5 Effect of pH on cobalt deposition. (Cobalt Concentration. 1 g/l; Current density, 25 A/m^2).

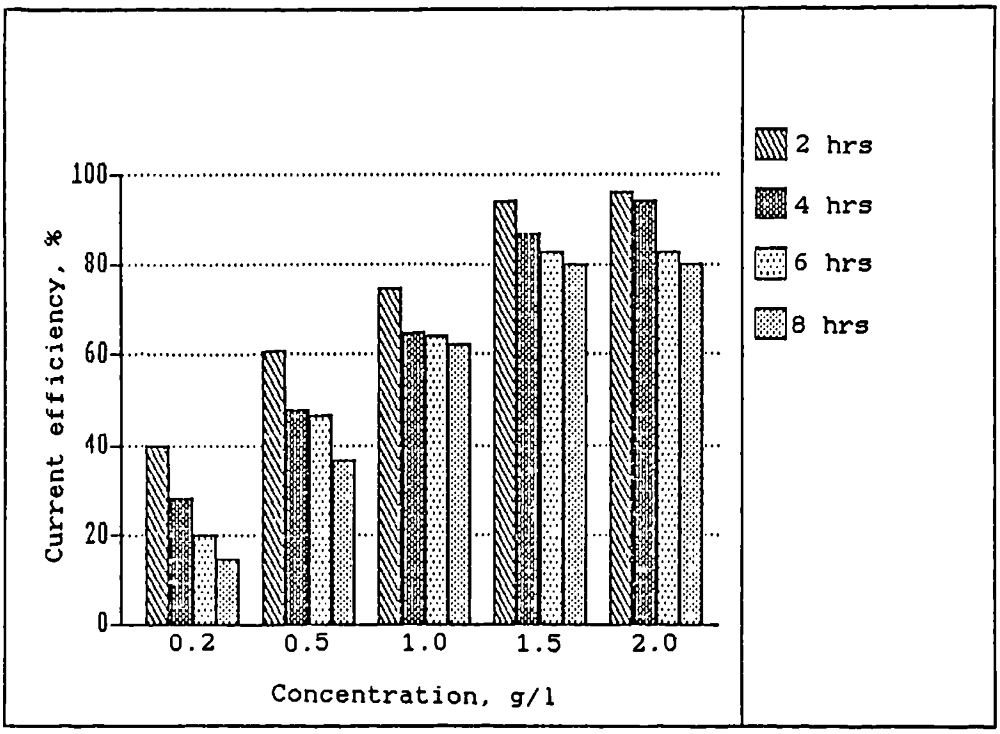

FIGURE 2.6 Effect of cobalt concentration on current efficiency. (current density, 15 A/m^2).

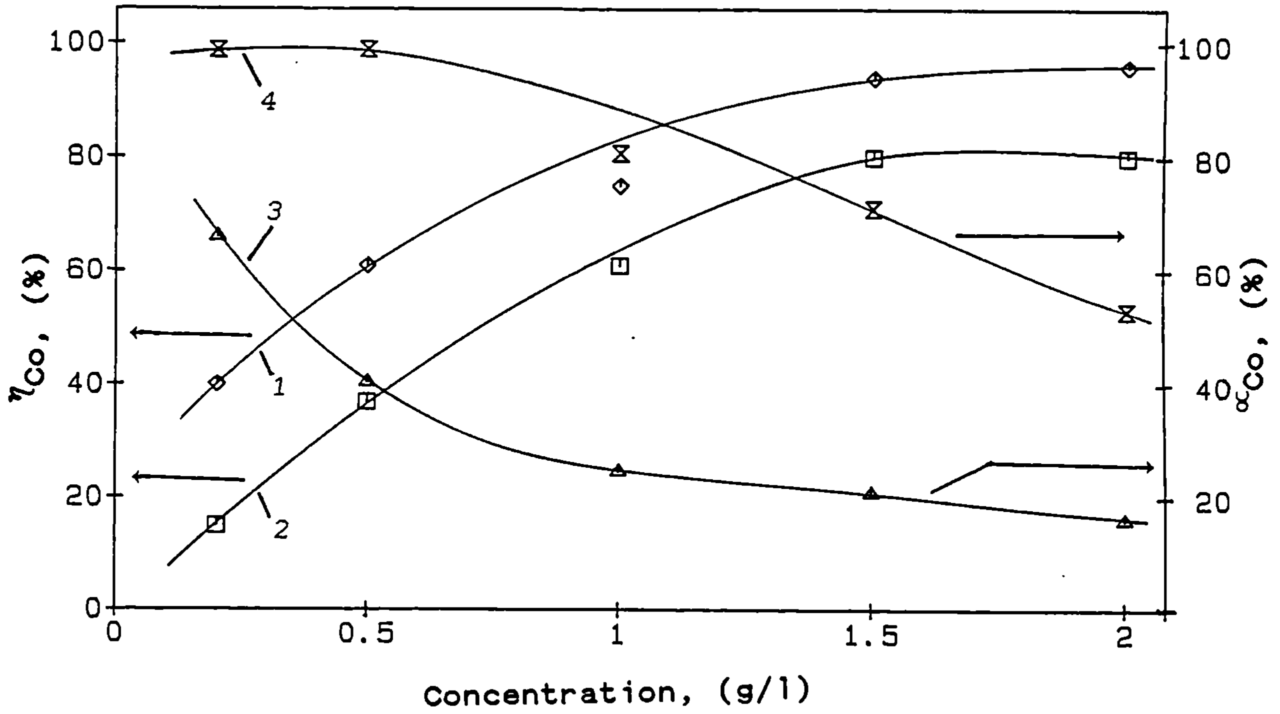

FIGURE 2.7 Effect of cobalt concentration on current efficiency and degree of cobalt purification. (1, 2 hrs; 2, 8 hrs; 3, 2 hrs; 4, 8 hrs; current density, 15 A/m^2).

increases steadily from 40% to 96% as the cobalt concentration is increased from 0.2 to 2.0 g/l after 2 hour electrolysis (Figure 2.7). The highest value of current efficiency is 96% at cobalt concentration of 2.0 g/l after 2 hours of electrolysis time. This value then decreases to 80% after 8 hours.

The degree of purification of cobalt, α_{Co}, decreases as the concentration of cobalt increases at constant current density of 15 A/m² . The purification factor was 66% which decreases to 16% as the cobalt concentration is raised from 0.2 to 2.0 g/l after 2 hours of electrolysis. After 8 hours the purification factor was 98.9% and 53% at cobalt concentrations of 0.2 and 2.0 g/l respectively.

c) Effect of Current Density and Cobalt concentration

The effect of current density on the current efficiency, deposition morphology and the power consumption was also studied (in the range of 10-100 A/m²) using solutions containing 0.2-2 g/l cobalt (Tables 2.8-2.10). The purification factor, α_{Co}, for various concentrations of cobalt increases with increasing cathode current density (Figures 2.8a-2.10a).

The current efficiency decreases as the current density is raised in each case (Figures 2.8b-2.10b). This probably due to a decrease of the effective metal ion concentration (Co^{2+}) in the vicinity of the cathode. At cobalt concentrations of 2.0 g/l the current efficiency is highest (96%) at 15 A/m² after two hours electrolysis period and decreases to 80% after 8 hours. The corresponding values of current efficiency after 2 and 8 hours for current densities 25, 50 and 100 A/m² are 89, 88 and 71% and 70, 45, 23% respectively. At a lower current density (10 A/m²), the metal deposit was shiny but very hard and difficult to remove from the cathode. When the current density was 100 A/m² the deposit was dull and flaky which can easily be lost from the cathode. The best deposit occurred when the current density was 20-50 A/m². The energy consumption (W)

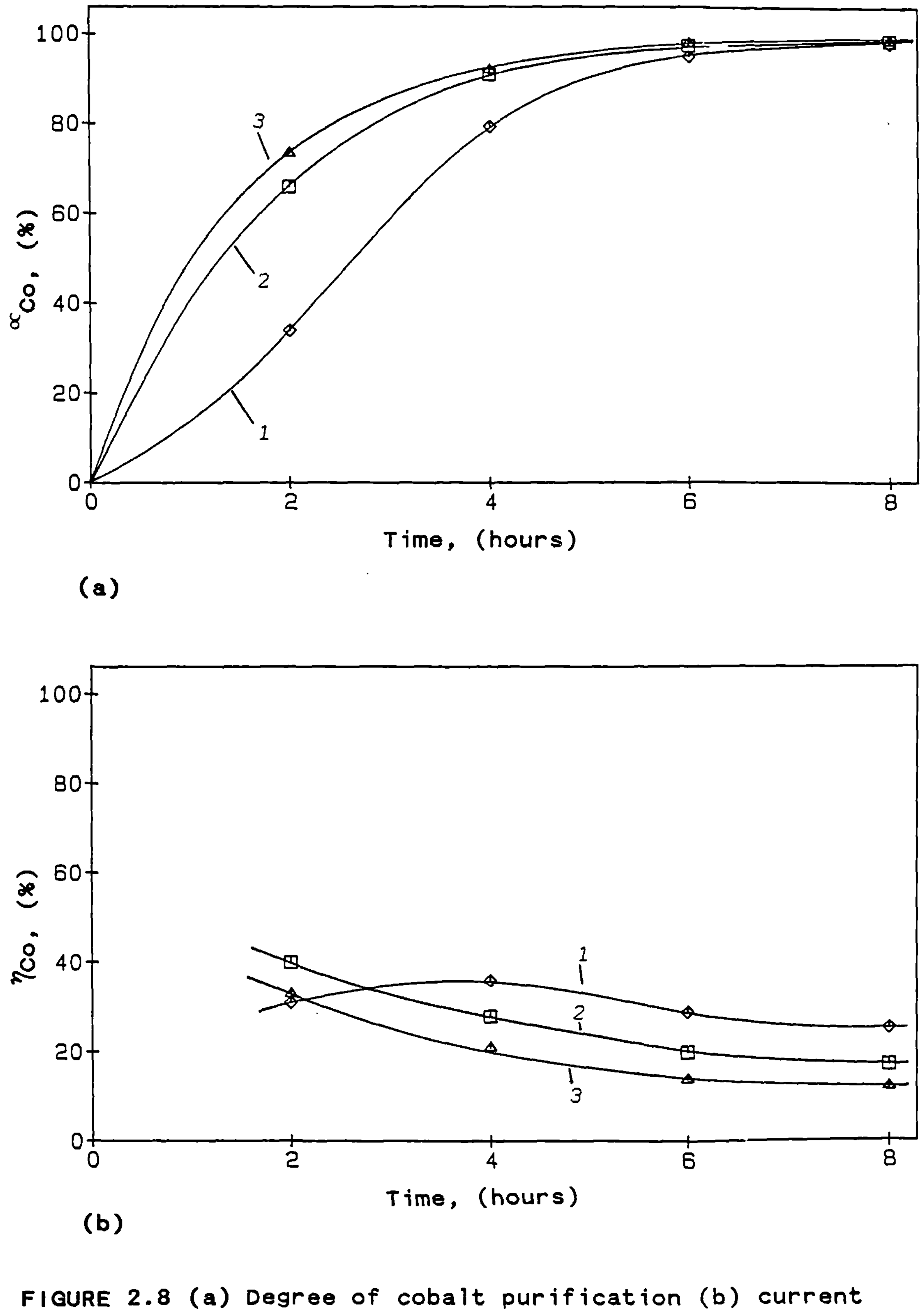

FIGURE 2.8 (a) Degree of cobalt purification (b) current efficiency versus time and current density. (1, 10 A/m^2; 2, 15 A/m^2; 3, 20 A/m^2).

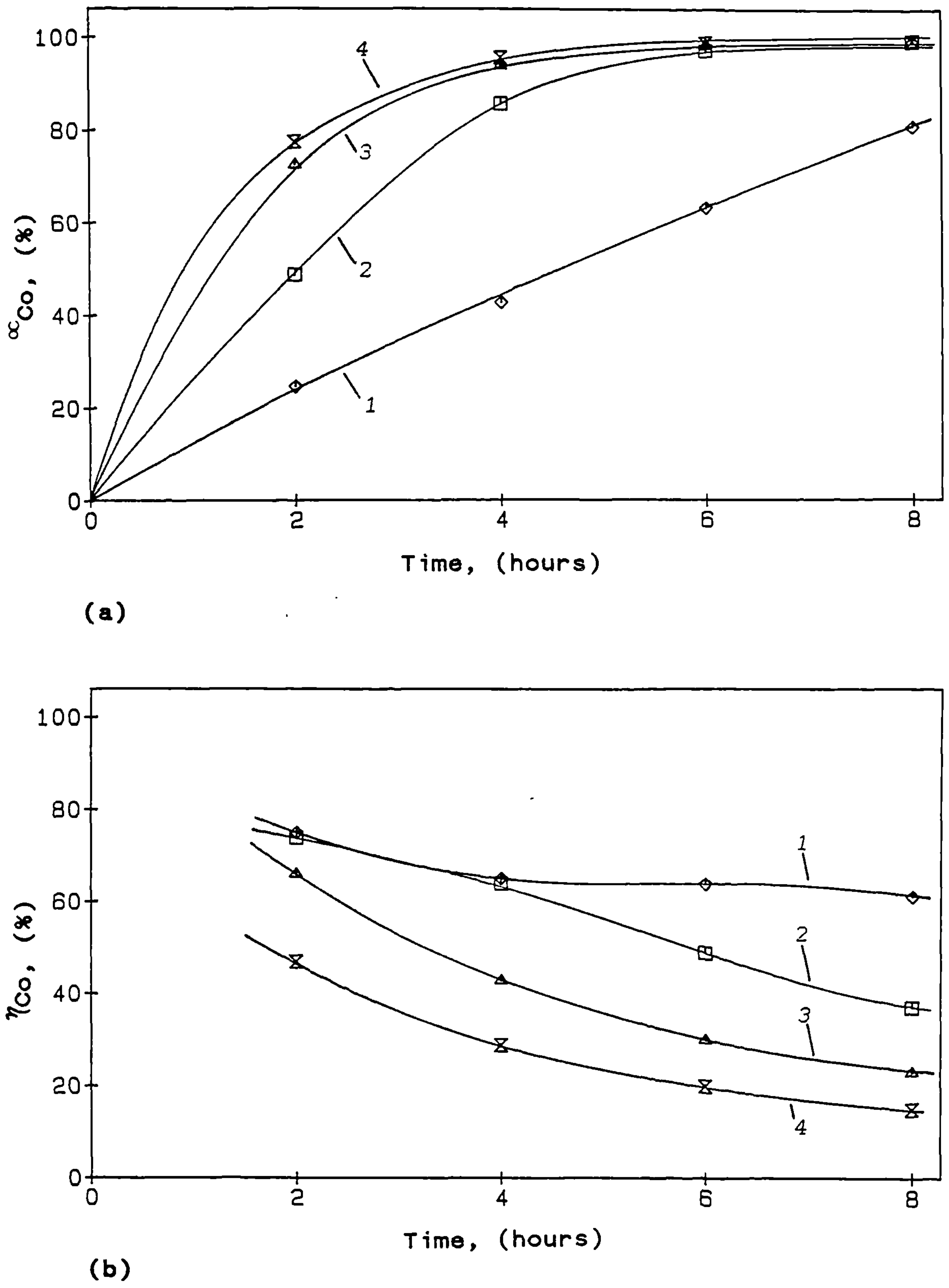

FIGURE 2.9 (a) Degree of cobalt purification (b) current efficiency versus time and current density. (1, 15 A/m^2; 2, 30 A/m^2; 3, 50 A/m^2; 4, 75 A/m^2).

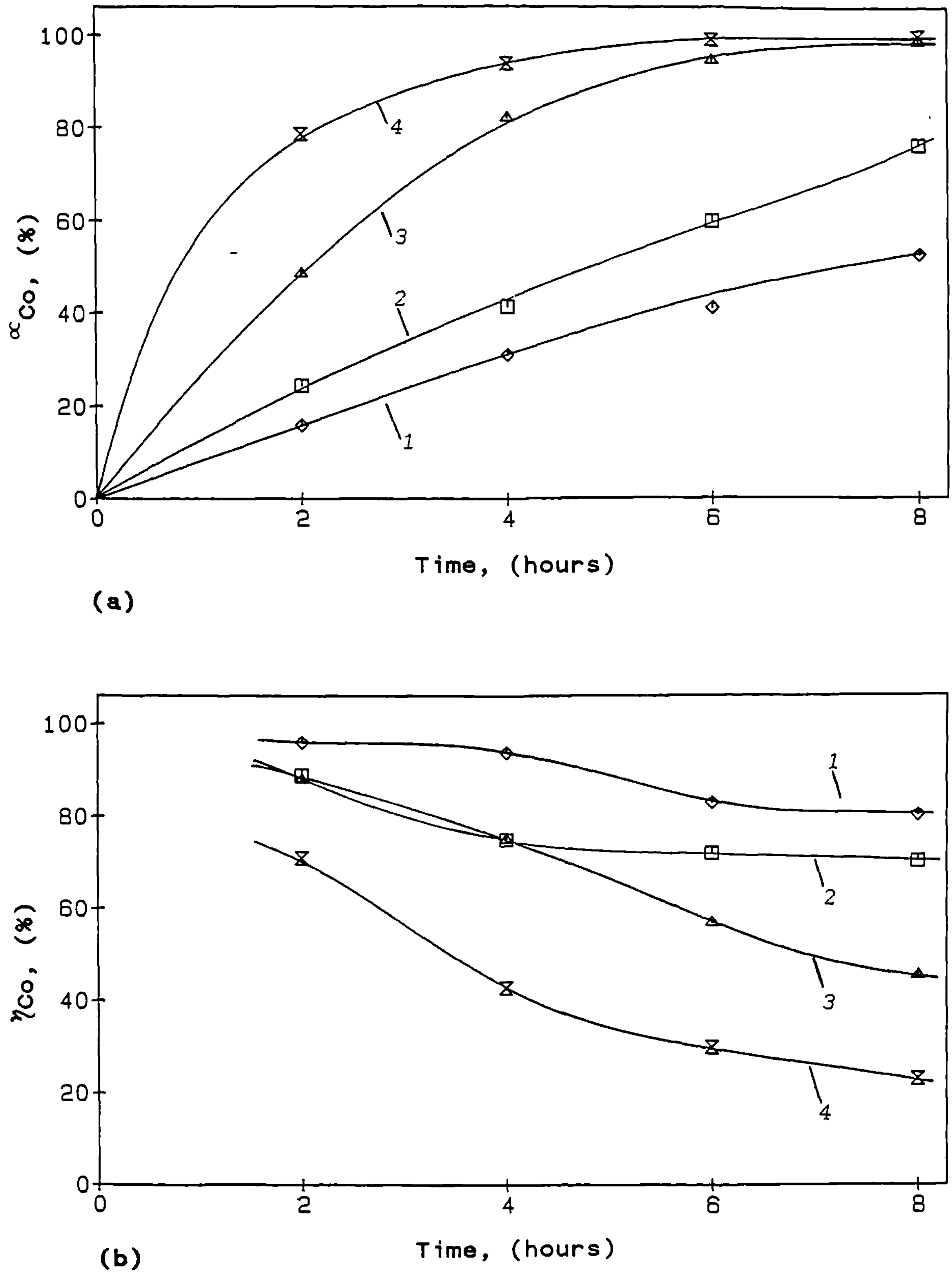

FIGURE 2.10 (a) Degree of cobalt purification; (b) current efficiency versus time and current density. (1, 15 A/m^2; 2, 25 A/m^2; 3, 50 A/m^2; 4, 100 A/m^2).

per kg of Co deposited is lowest at current density of 15 A/m^2, for example, after 8 hours of electrolysis period the values of W_{15}, W_{30}, W_{50} and W_{75} are 5.0, 9.4, 16.9 and 27.1 kWh/kg respectively (Figure 2.11).

d) Effect of Agitation

The effect of agitation due to the upward and downward movement of the glass beads on the electrodeposition was also studied. It was found that agitation plays an important role during electrolysis, especially at low metal concentrations. The purification factor, α_{Co}, with and without agitation for 0.2 g/l cobalt was 66% and 53% respectively after 2 hours electrolysis at current density of 15 A/m^2 (Figure 2.12a). When the cobalt concentration was increased from 0.2 to 1.0 g/l, the purification factor for cobalt with and without agitation was 36% and 31% respectively after 2 hours electrolysis at 25 A/m^2 (Figure 2.13a).

The current efficiency with and without agitation at cobalt concentration of 0.2 g/l was 40% and 32% after 2 hours of electrolysis at current density of 15 A/m^2. After 8 hours this drops to 17% and 14% (Figure 2.12b). When the cobalt concentration was raised to 1.0 g/l, the current efficiency was 67% and 58% for agitation and without agitation experiments after 2 hours of electrolysis at current density of 25 A/m^2. These values drop to 45% and 44% after 8 hours (Figure 2.13b). The plot of current efficiency versus time and current density show that the current efficiency was rather higher with agitation, especially at the initial stages of electrolysis but after 4 hours the two values were very close to each other.

2.8.2 DEPOSITION OF CADMIUM

The results show (Table 2.13) that the purification factor for Cd increases with increasing current density and less time is required to deposit 99% Cd (Figure 2.14a). The highest value of current efficiency at 12.5 A/m^2 is 34% after a 2 hour electrolysis period. This decreases to 26%

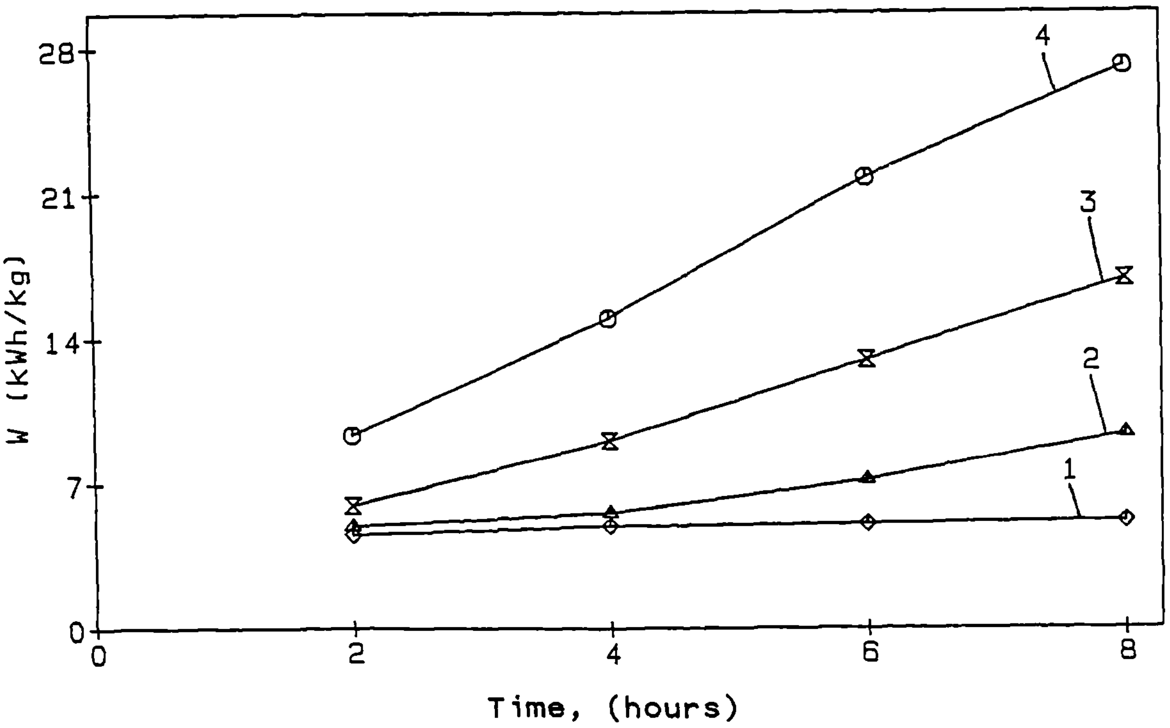

FIGURE 2.11 Energy consumption versus time and current density. (1, 15 A/m^2; 2, 30 A/m^2; 3, 50 A/m^2; 4, 75 A/m^2).

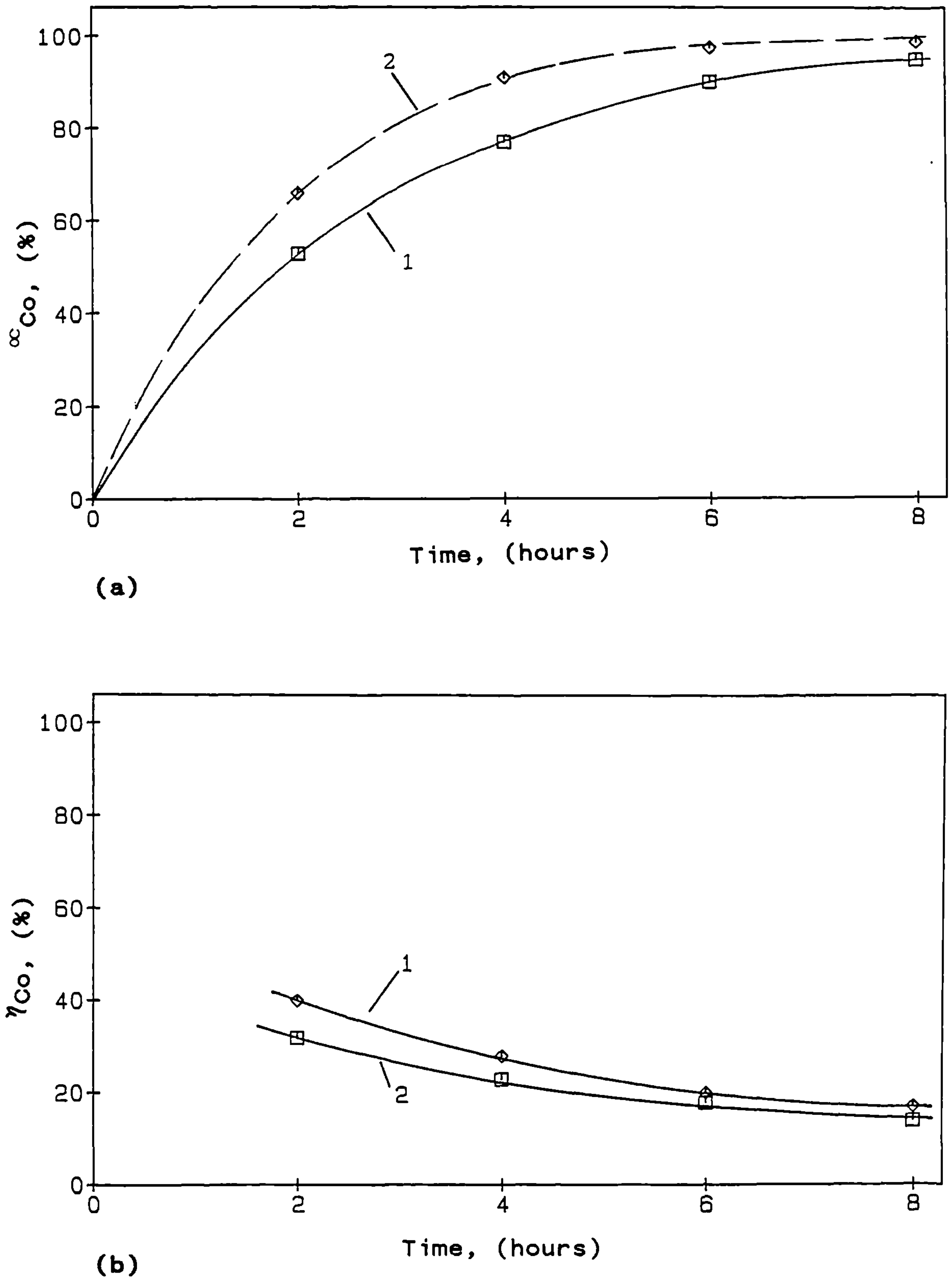

FIGURE 2.12 Effect of agitation on (a) cobalt deposition (b) current efficiency. (1, with agitation; 2, without agitation; Co conc., 0.2 g/l; current density, 15 A/m^2).

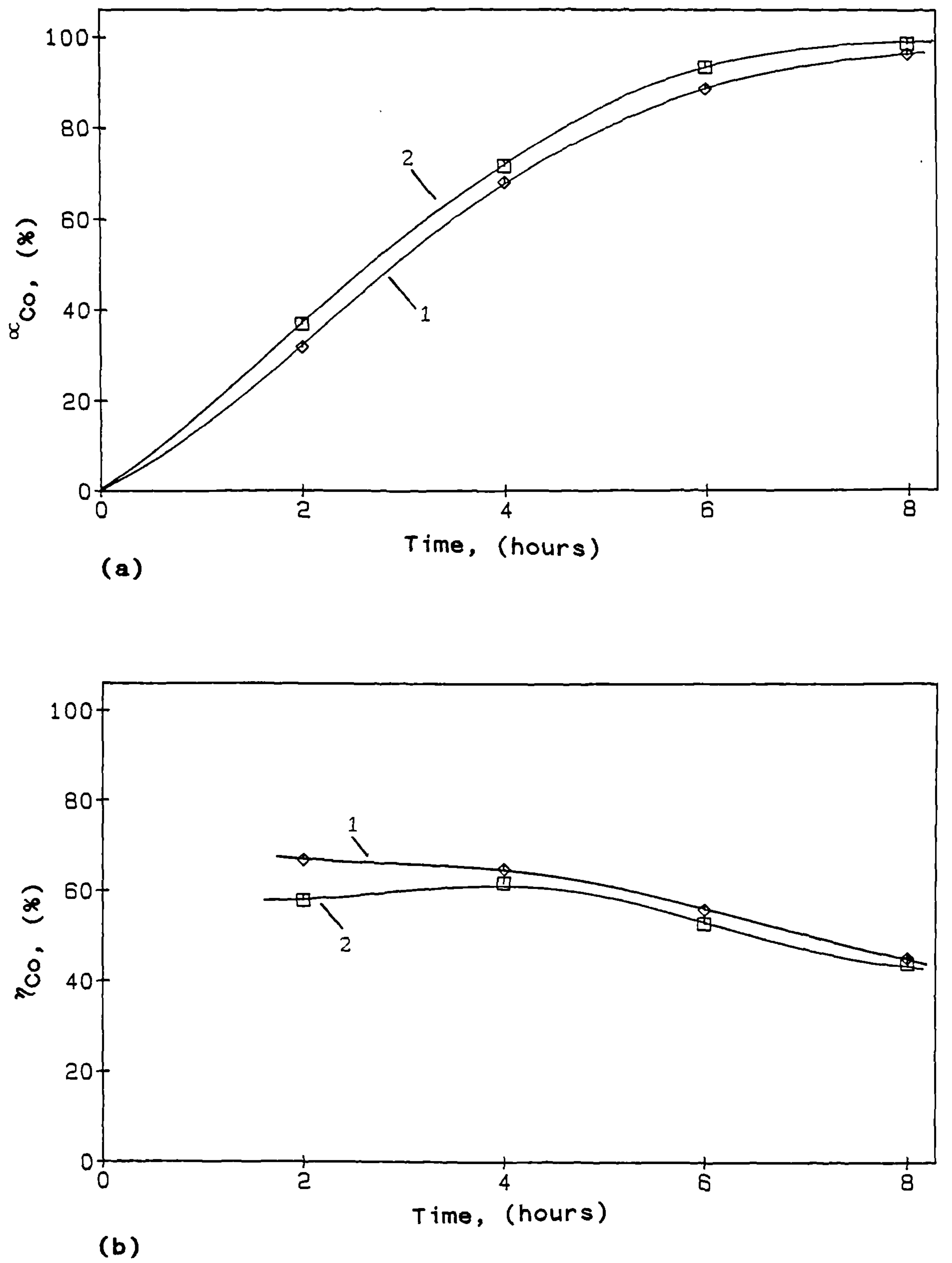

FIGURE 2.13 Effect of agitation on (a) cobalt deposition (b) current efficiency. (1, with agitation; 2, without agitation; Co conc., 1.0 g/l; current density, 25 A/m^2).

after 7 hours. The corresponding values of efficiency after 2 and 7 hours for current densities of 25 A/m² and 50 A/m² are 33 and 18% and 14 and 7% respectively (Figure 2.14b).

2.8.3 DEPOSITION OF COPPER

The data in Table 2.14 show that the purification factor, α_{Cu}, increases with increasing the current density while the current efficiency, η_{Cu}, decreases under the same conditions. Although increasing the current density enhances the rate of copper deposition and less time is required to deposit 99% of the metal, at higher current density the deposit is soft. At a current density of 12.5 A/m² the deposition was 28.9% after 2 hours of electrolysis and 95.8% after 7 hours (Figure 2.15a). The highest value of current efficiency at 12.5 A/m² is 97% after 2 hours this decreases to 92% after 7 hours. The corresponding values of efficiency after 2 and 7 hours for current densities of 25 A/m² and 50 A/m² are 95 and 70% and 48 and 24% respectively (Figure 2.15b).

a) Effect of Cadmium on Copper deposition

The data in Tables 2.15 and 2.16 show that the deposition percentage of Cu in the presence of Cd is less than the values obtained from the pure Cu solutions (Table 2.14). Electrolysis of Cu in the absence of Cd is more efficient and both α_{Cu} and η_{Cu} have higher values. In the presence of 0.3 g/l Cd, the cadmium starts depositing on the cathodes when the concentration of Cu drops during the electrolysis. The deposition of Cd depends upon the Cu:Cd ratio in the solution and the current density. At 12.5 A/m² the deposition of Cd was 0.6 % after 2 hours of electrolysis time and increases to 8.6 % after 7 hours. The corresponding values for purification factor, α_{Cd}, at current density of 25 A/m² and 50 A/m² after 2 and 7 hours of electrolysis time are 3.3 and 8.0 % and 18.3 and 74 % respectively.

The purification factor, α_{Cu}, obtained from sulphate and nitrate solutions at current density of 12.5 A/m² after 2 hours of electrolysis time is 27.6 and 28.7% respectively.

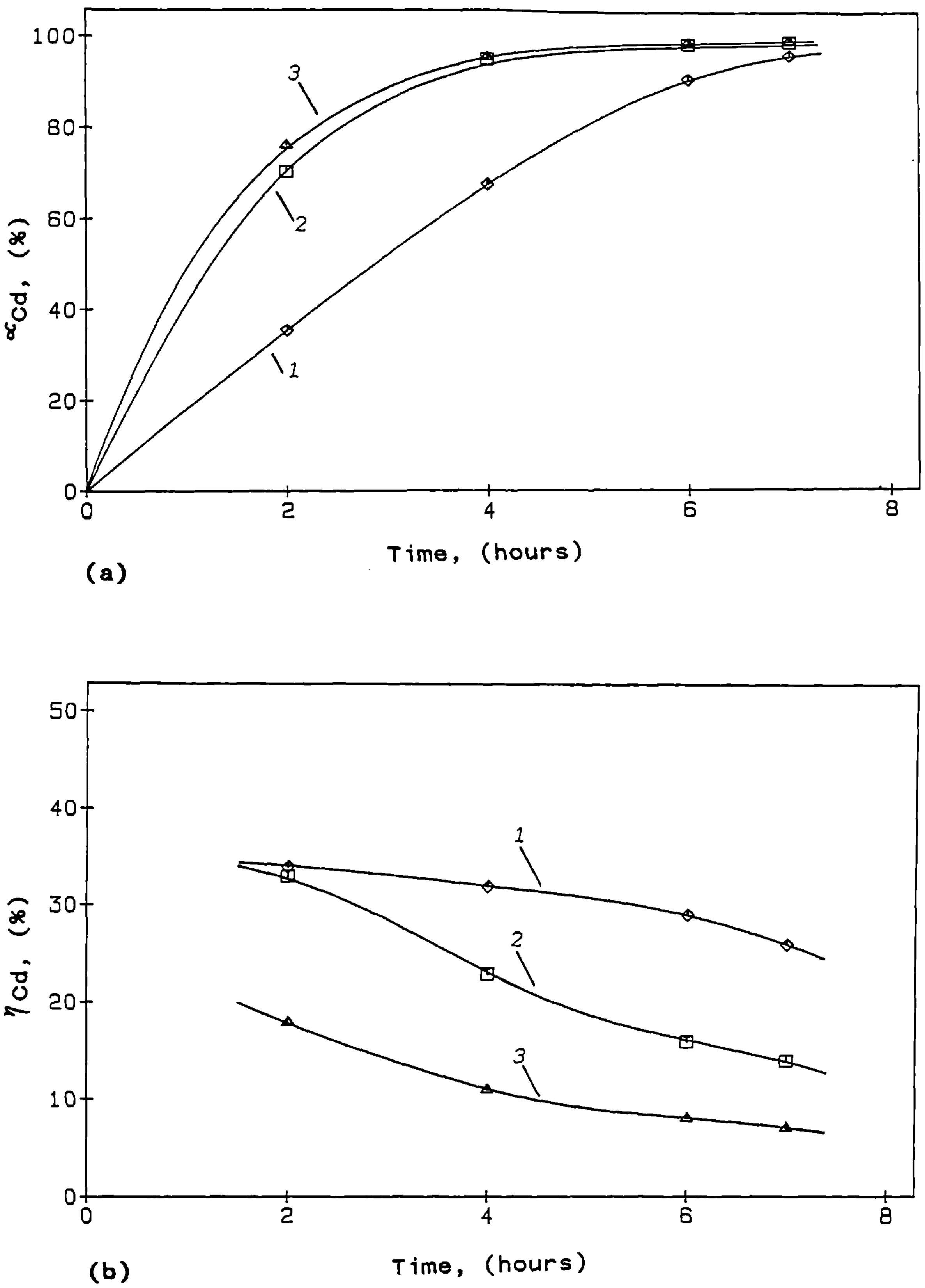

FIGURE 2.14 (a) Degree of cadmium purification (b) current efficiency versus time and current density. (1, 12.5 A/m^2; 2, 25 A/m^2; 3, 50 A/m^2).

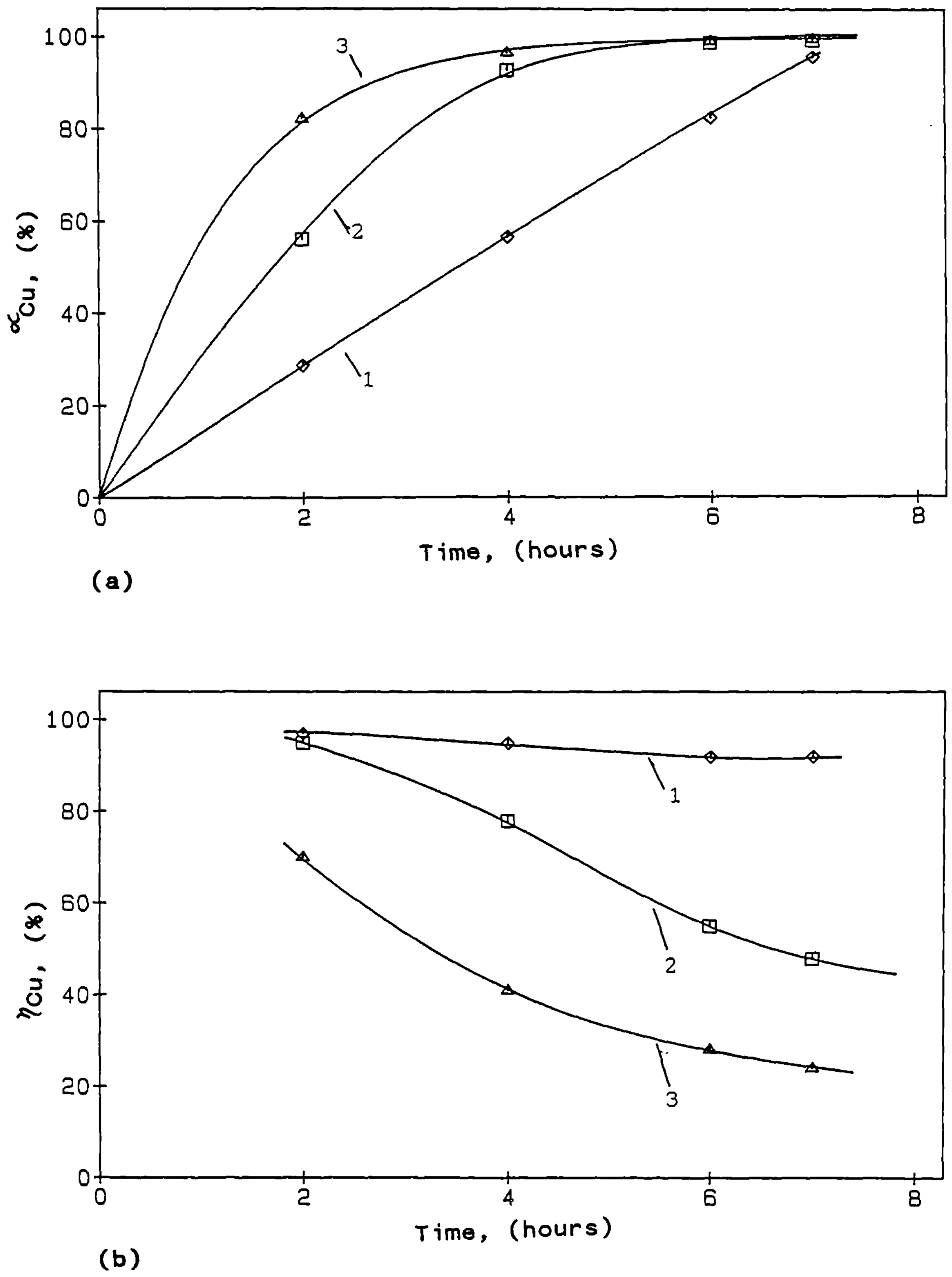

FIGURE 2.15 (a) Degree of copper purification (b) current efficiency versus time and current density. (1, 12.5 A/m^2; 2, 25 A/m^2; 3, 50 A/m^2).

The deposition percentage of Cu obtained from sulphate and nitrate solutions are the same at different current densities but the deposition values for cadmium in sulphate solution is higher than the values obtained in nitrate solution. At 50 A/m^2 the values obtained for Cd deposition after 7 hours are 74% and 61% for sulphate and nitrate solution respectively.

2.9 BRASS FINES

2.9.1 Chemical Analysis

The brass fines sample, C1510, was supplied by William Blythe & Co Ltd. Church, Accrington, U.K. These brass fines are considered as a source of copper and zinc. The sample was analysed and found to contain 47.7% zinc, 20.8% copper and 1.5% lead.

Preliminary studies were carried out on the brass fines supplied to determine the best leach solution. Copper is insoluble in dilute acids other than nitric, but may be attacked by concentrated sulphuric acid. Leaching tests were therefore carried out using nitric and dilute hydrochloric acids. The 50% nitric acid was found to be the best leaching media for this sample. Almost complete dissolution of Zn, Cu and Pb occurred at 70°C in 2 hours.

2.9.2 Nitric Acid Leaching

In these experiments, a 20g and 10g sample, C1510, were leached with 600 and 400ml of 50% nitric acid at 70°C for 2 hours on a magnetic hot plate to form a blue solution. The filtrate was slightly turbid and the residue (12.7%) a grey solid. The filtrate was diluted to 1 litre and 500ml for 20 and 10g respectively. The contents of the leach liquors were analysed by AAS (Table 2.17).

The data in Table 2.17 showed a typical leaching composition of brass fines in 50% nitric acid. The results have shown that ~96% Zn, 99% Cu, and 98% Pb can be extracted in 50% nitric acid solution.

2.9.3 Hydrochloric Acid Leaching

Hydrochloric acid leaching experiments consisted of two steps: a) leaching with dilute hydrochloric acid; and b) subsequent leaching with 50% nitric acid. A 20g of C1510 sample was leached with 800ml of 3M hydrochloric acid at 70°C for two hours on hot plate. In second experiment, a 10g sample was leached with 400ml of 2M hydrochloric acid. During the leaching process the solution was stirred once with a glass rod. The solution was green and when filtered gave a clear filtrate. The remaining residue was washed with distilled water and leached respectively with 400 and 300ml of 50% nitric acid at 70°C for 2 hours with continuous stirring. The leach liquors from both experiments were analysed by AAS and the results for 20 and 10g samples are given in Tables 2.18 and 2.19 respectively.

The purpose of using the hydrochloric acid leach was to extract zinc and lead in chloride solution leaving the copper in residue. This residue can then easily be dissolved in nitric acid followed by the recovery of copper by electrodeposition. Use of dilute hydrochloric acid resulted in the extraction of >70% Zn, >60% Pb and >8% Cu (Tables 2.18-2.19). When the washed residue was treated with nitric acid, the solution was found to contain >5% Zn, >83% Cu and >17% Pb. So the idea of selective extraction of Zn in hydrochloric acid solution was not successful. For the recovery of copper, brass fines were leached with 50% nitric acid followed by deposition by fluidised bed electrolysis.

2.10 ELECTRODEPOSITION OF COPPER

Before using the brass fines leach liquor to deposit copper, some experiments were carried out to determine the key process parameters using a synthetic feed liquor, containing 0.4 g/l copper, 1.0 g/l zinc, and 0.04-0.4 g/l lead. These concentrations were chosen to give the same ratio of these metals as in the brass fines. The concentration of nitric acid was 0.1-0.5M. The fluidised bed cell was operated at different voltages to deposit copper at the cathode and leave a zinc nitrate solution.

TABLE. 2.17 BRASS FINES LEACHING IN NITRIC ACID

	20g sample		(Extraction)		10g sample			
	A		B		C		D	
Metal	(%)	(g)	(%)	(g)	(%)	(g)	(%)	(g)
Zn	94.9	9.06	92.9	8.86	96.0	4.58	91.5	4.36
Cu	98.5	4.10	98.5	4.09	99.2	2.06	98.8	2.05
Pb	97.6	0.29	93.3	0.28	98.3	0.14	88.3	0.13

TABLE. 2.18 BRASS FINES LEACHING

	HCl Extraction		HNO_3 Extraction	
Metal	(%)	(g)	(%)	(g)
Zn	80.7	7.70	5.5	0.53
Cu	8.5	0.35	83.8	3.49
Pb	66.3	0.20	16.6	0.05

TABLE. 2.19 BRASS FINES LEACHING

	HCl Extraction		HNO_3 Extraction	
Metal	(%)	(g)	(%)	(g)
Zn	69.3	3.31	16.3	0.78
Cu	9.1	0.18	88.9	1.86
Pb	60.0	0.09	26.6	0.04

TABLE 2.20 DEPOSITION OF COPPER

Time	Concentration, (ppm)			Deposition, (%)		
(hr)	Zn	Cu	Pb	Zn	Cu	Pb
2	1024	112	0	-	71.8	-
4	1026	23	0	-	94.2	-
6	1022	5	0	-	98.6	-

Conditions: Concentrations, Zn, 1.0; Cu, 0.4; Pb, 0 g/l;
Voltage, 2V; Acid concentration, 0.1M.

It was observed that, during the electrodeposition of copper from a solution containing high concentration of lead (0.4 g/l) in 0.3M nitric acid, the lead starts to deposit on anodes. This is due to the oxidation of lead to the 4+ state in the nitric acid medium, and the subsequent conversion of Pb(IV) ion into hydrated lead dioxide, $PbO_2.xH_2O$, at the anode. In the electrolysis, copper and nitrate ions are reduced more easily than the lead(II) and function as a cathodic depolarisers to maintain the cathodic potential below the value required for the reduction of the lead ion. This anodic deposit was actually detached from the anodes during the upward and downward movement of the glass beads and collected at the bottom of the reservoir tank for easy recovery at the end of the electrolysis process. The actual electrochemical reactions which occur during this deposition can be represented as follow:

$$Cu^{2+} + 2e^- \text{--->} Cu$$
$$NO_3^- + 3H^+ + 2e^- \text{--->} HNO_2 + H_2O$$
$$Pb^{2+} \text{--->} Pb^{4+} + 2e^-$$
$$Pb^{4+} + 2OH^- + 2H_2O \text{--->} Pb(OH)_6^{2-} \text{--->} PbO_2 + 2H_2O$$

For lead deposition as oxide the concentration of lead and nitric acid, which acts as an oxidising agent, must be high to initiate the electrochemical reaction. Periodically during the electrolysis, samples were collected from the reservoir tank for analysis. The results of these electrolysis experiments are given in Tables 2.20- 2.23.

2.10.1 Deposition of Cu from Brass Fines leach solution

20g of brass fines were leached with 600 ml Of 50% nitric acid at 70°C for 2.5 hours. The mixture was filtered and the filtrate diluted to 10 litre with distilled water and analysed for metals. The fluidised bed cell was used for the deposition of copper leaving the zinc nitrate solution in the reservoir tank. Periodically during the electrolysis, samples were collected from the reservoir tank for the analysis of metal ions in the solution. The data are in Table 2.24.

2.10.2 Influence of Lead and acid concentration

Electrolysis of copper in the absence of lead and at acid concentration of 0.1M was more efficient and gave higher values for copper deposition (Table 2.20). The presence of 0.04 g/l of lead has a small effect on the copper deposition. In the absence of lead and at acid concentration of 0.1M the deposition is 71.8 and 98.6 % after 2 and 6 hours of electrolysis time. This decreases to 68.4 and 98.4% after the same electrolysis time when the solution contained 0.04 g/l of lead (Table 2.21).

From the results in Table 2.22 and 2.23 it is clear that the deposition of copper decreases when the concentration of lead and acid is increased. Under these conditions the anodic deposition of lead also starts and up to 38% of lead is deposited after 6 hours of electrolysis. When the concentration of acid was increased from 0.3 to 0.5M keeping the lead concentration constant (0.4 g/l), the deposition of lead on the anodes increased from 38 to 46% after the same electrolysis time. Under these conditions the copper deposition decreased from 95.8 to 94.7% after 6 hours. The presence of zinc (0.9-1.0 g/l) in the electrolyte solution has no effect on the deposition of copper. The parameters which enhance the deposition of lead on anodes are the high acid and lead concentrations, low voltage, and long electrolysis times. The deposition of lead from a solution containing 1.0 g/l zinc, 0.4 g/l copper and 0.4 g/l lead with an acid concentration of 0.5M at voltage of 1.5V was 96% after 17 hours electrolysis period.

The results of the electrolysis of copper from the brass fines solution (Table 2.24) and the synthetic solution show that it is not possible to deposit lead electrochemically, due to the low concentration of lead in the leach solution (0.03 g/l). The deposition of lead on the anodes was achieved at the higher acid and lead concentration in the standard electrolyte solutions (Tables 2.22-2.23).

TABLE 2.21 EFFECT OF LEAD CONCENTRATION ON Cu DEPOSITION

Time	Concentration, (ppm)			Deposition, (%)		
(hr)	Zn	Cu	Pb	Zn	Cu	Pb
2	1000	126	46	-	68.4	-
4	990	26	47	-	93.4	-
6	990	6	40	-	98.4	-
8	980	3	39	-	99.2	-

Conditions: Concentrations, Zn, 1.0; Cu, 0.4; Pb, 0.04 g/l; Voltage, 2V; Acid concentration, 0.1M.

TABLE 2.22 EFFECT OF LEAD AND ACID CONCENTRATION

Time	Concentration, (ppm)			Deposition, (%)		
(hr)	Zn	Cu	Pb	Zn	Cu	Pb
2	1010	131	335	-	67.2	16.2
4	1000	52	275	-	86.7	31.2
6	985	16	247	-	95.8	38.2

Conditions: Concentrations, Zn, 1.0; Cu, 0.4; Pb, 0.4 g/l; Voltage, 2V; Acid concentration, 0.3M.

TABLE 2.23 EFFECT OF ACID CONCENTRATION ON Cu DEPOSITION

Voltage	Time	Concentration, (ppm)			Deposition, (%)		
(V)	(hr)	Zn	Cu	Pb	Zn	Cu	Pb
2	2	1020	135	300	-	66	25
	4	1020	53	257	-	86	35
	6	1015	21	214	-	94	46
	7	1000	10	190	-	97	52
1.5	2	1000	212	320	-	47	20
	4	995	156	276	-	61	31
	6	990	108	232	-	73	42
	17	980	32	13	-	92	96

Conditions: Concentrations, Zn, 1.0; Cu, 0.4; Pb, 0.4 g/l; Acid concentration, 0.5M.

TABLE 2.24 COPPER DEPOSITION FROM BRASS FINES LEACH LIQUOR

Time	Concentration, (ppm)			Deposition, (%)		
(hr)	Zn	Cu	Pb	Zn	Cu	Pb
0	906	407	30	-	-	-
2	904	140	30	-	65.5	-
4	905	48	29	-	88.2	-
6	903	29	27	-	92.8	-
7	900	25	27	-	93.8	-

Conditions:- Concentrations, Zn, 0.9; Cu, 0.4; Pb, 0.03 g/l; Voltage, 2V; Acid concentration, 0.5M.

2.11 SUMMARY

The Chemelec cell combining fluidised beds of inert glass beads and mesh electrodes provides a simple and economic method of recovering in a directly reusable form, metals from dilute effluent streams. Its simplicity allows economic recovery when small quantities of metal solution arise from a process (like rinse waters from electroplating lines). The Chemelec cell can also be used to separate metals from a leach liquors obtained from low grade materials and wastes such as brass fines.

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CHAPTER 3

COBALT AND NICKEL SEPARATION BY OXIDATIVE PRECIPITATION

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3.1 INTRODUCTION

Cobalt occurs in nature in association with nickel, copper and usually also with arsenic. The ores of cobalt contain very low concentration of the metal associated with relatively high concentration of other metals. Relatively little cobalt ore is mined for the cobalt content, and most of the metal is recovered as a by-product of ores treated for their copper or nickel contents. The chief technical source of cobalt are residues called "Speisses" which are obtained in the smelting ores of nickel, copper and lead.

The cobalt content of the earth crust (about 25 ppm) is of the same order of magnitude as that of lead (15 ppm), copper (45 ppm) and zinc (65 ppm). In comparison with these metals mentioned however, the production of cobalt is very modest. The major cobalt (mine out put) producers in 1985 were Zaire(45%), New Caledonia (16%), Australia (14%), Zambia (8%), and Canada (5%). In terms of estimated cobalt metal produced by refining, the largest producers were Zaire, USSR, Zambia, Japan and France. The distribution of worlds refined cobalt metal and or/oxide production in different countries is shown in Figure 3.1.

The copper deposits from Zaire[1,2] and Zambia[3-5] are the most important source of cobalt since these two countries account for more than 70% of the total world production of the metal. Minerals are mostly sulphides although some dolomitic oxides are also processed. Significant deposits of cobalt-arsenides are also located in Canada, USSR and Morocco.

Cobalt can be extracted from concentrates and occasionally directly from the ore itself by hydrometallurgical, pyrometallurgical and electrometallurgical processes. Although most methods of extraction are based on hydrometallurgy, cobalt concentrates, mattes and alloys have

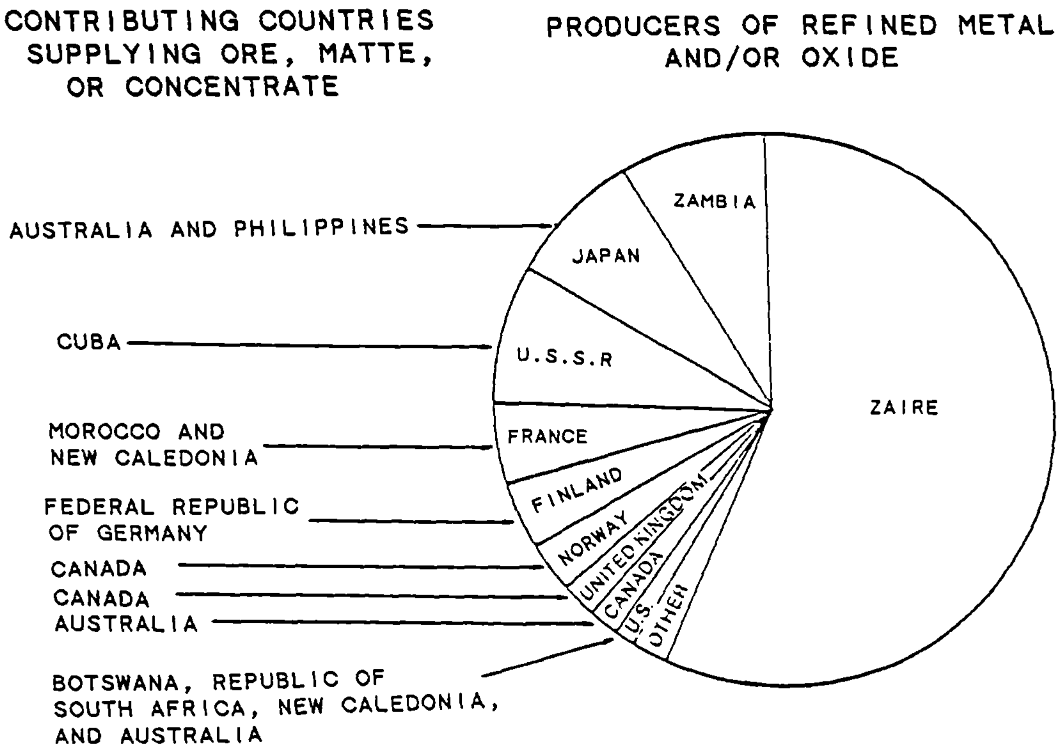


FIGURE 3.1 Distribution of World refined Cobalt metal and Oxide Production.

been reduced to metal by pyrometallurgical methods. The hydrometallurgical processes for cobalt extraction involve: (1) leaching of concentrates to give a cobalt-containing solution; (2) separation of cobalt from the other metal ions in solution; and (3) 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.

3.2 LEACHING OF COBALT ORES AND CONCENTRATES

Cobalt can be leached from its ores and concentrates in both acidic and alkaline media. The commonly used leaching methods include, sulphuric acid, hydrochloric acid and ammonia solutions. But there are some recent reports on the use of nitric acid as a leaching solution. The oxidation of mixed oxide is carried out with the acid by pressure leaching at 11-19 Kg/cm^2 for one hour at 150-250°C and the nitrogen oxide gases formed can be recycled as nitric acid[6].

3.2.1 Acid Sulphate Leaching

Cobalt oxides are soluble in sulphuric acid (particularly in the presence of SO_2 or other reducing agents if Co(III) is present) and this acid has been used to leach oxide ores floatation concentrates. H_2SO_4, H_2SO_3 and SO_2 have also been used with or without preliminary roasting of the concentrates at 550-570°C. Oxidising roast pretreatment of ores particularly of sulphide containing ores can also be used to convert the cobalt present to sulphate.

$$CoS + 2O_2 \text{ -----> } CoSO_4$$

Cobalt ores and secondary materials including those containing sulphide can also be converted into soluble sulphate by a sulphatising roast with sulphuric acid or a metal sulphate.

$$CoS + H_2SO_4 \text{ -----> } CoSO_4 + H_2S$$

This method of pretreatment is used in the *Outokumpu* process[7].

The use of pressure leaching with sulphuric acid is common because it increases the rate of dissolution of cobalt sulphate often in the presence of oxygen. Typical leach conditions use dilute sulphuric acid at 129-180°C and a pressure of 30-50 Kg/cm^2. Sulphate pressure leaching is used by MRR plant in South Africa[8] and also by Nippon Mining Plant at Hitachi in Japan[9,10]. A combination of atmospheric and pressure leaching with sulphuric acid is the process reported in the Amax plant at Port Nickel, Louisiana[11,12].

3.2.2 Acid Chloride Leaching

Hydrochloric acid and chloride solutions have been used as alternatives to sulphuric acid solutions for leaching ores, mattes and secondary cobalt arisings. They are suitable for most materials including oxides, sulphides, arsenides and alloys. Formation of chloride complexes such as $CoCl_3^-$ in these solutions often aids the dissolution of the arising. Chloride solutions are often used in preference to sulphate leaches for the extraction of cobalt in processes where separation of cobalt from nickel by solvent extraction or ion exchange procedures are used.

The *Falconbridge* process involves hydrochloric acid leaching[13], while the *Sumitomo* process involves a mixed hydrochloric sulphuric leach solution[10,14] and solution containing $FeCl_3$ and Cl_2 has been used by *Societe Le Nickel* in france.

3.2.3 Ammoniacal Solution Leaching

Cobalt ores are often found to be soluble in ammoniacal solution because of the formation of cobalt hexamine complex $[Co(NH_3)_6]^{2+}$. Ammoniacal solutions have been used to solubilise cobalt arisings and pressure hydrometallurgy of cobalt with ammonia solutions is important in the *Sherritt*

Gordon process[15].

The Sheritt Gordon technology has also been used by Impala Platinum in South Africa since 1969 to treat a nickel-copper matte and recently they started producing small amounts of Co powder as a by-product of platinum recovery[16]. Near Perth, Australia, Western Mining Corporation's Kwinana Refinery uses the Sheritt Gordon process to treat nickel sulphide concentrates and mattes.

3.3 COBALT SOURCES

The main sources of cobalt are: (1) copper-cobalt ore concentrates; (2) laterite ores; (3) arsenide ores and; and (4) nickel sulphide ores concentrates. A little detail of the chemistry involved in the methods of winning cobalt from these concentrates and mattes is described in the following subsections.

3.3.1 Cobalt from Copper-Cobalt Concentrates

The copper-cobalt ores of Zaire and Zambia undergo a sulphate roast operation in a fluid bed furnace where copper and cobalt are transformed into soluble oxides and iron into insoluble haematite. The calcine is subsequently leached with sulphuric acid from the spent copper recovery electrolyte. Oxide concentrates are also introduced at this leaching step to maintain the acid balance in the circuit. Iron and aluminium are removed from the leach solution and the copper is electrowon on copper cathodes. A part of the copper spent electrolyte is sent to the cobalt recovery circuit. In this circuit the solution is further purified by removal of iron, copper, nickel and zinc prior to precipitation of cobalt as its hydroxide. In the final stage, this cobalt hydroxide is dissolved and the metal is refined by electrolysis. This process is used at the Generale de Carrieres et des Mines (GECAMINES) plant Luilu[2].

In Zambia, cobalt is being recovered from copper-cobalt concentrates by Zambian Consolidated Copper Mines[17-19].

3.3.2 Cobalt from Laterite Ores

The hydrometallurgical processes for laterite ores can involve use of acid or ammonia leach solutions. The process at Moa Bay in Cuba uses a pressure sulphuric acid leach to extract the cobalt along with other metals prior to their precipitation as sulphide for further hydrometallurgical separation[20]. In the alternative ammonia leach process, the ore is subjected to a preliminary reductive roast and then leach in ammoniacal ammonium carbonate solution. This process is used in the Greenvale Mines, Queens land, Australia.

3.3.3 Cobalt from Arsenide Ores

Figure 3.2 shows two possible routes for processing the cobalt arsenides concentrates. The first route is now being used on an industrial scale in France.

First the cobalt-arsenide concentrates are roasted in fluid bed at 600-700°C at Estaque plant of Penarroya near Marseille. This operation remove about 60-70% of the arsenic as saleable trioxide. The roasted concentrates containing 17-18% Co, 17-18% As and 13% Fe are treated at the Metaux Speciaux plant at Plombieres, which has total capacity of 1500 tons of cobalt per year. The roasted concentrates are leached with hydrochloric acid and chlorine and, after several purification steps, the purified solution is electrolysed, producing cobalt cathodes and chlorine which is recycled to the leaching step.

The second route was used some years ago by Metallurgie Hoboken-Overpelt Belgium[21]. The concentrates were smelted to speiss in a Cupola furnace with volatilization of nearly 75% of the arsenic. The resulting speiss at 40% As and 34% Co was then roasted in a fluid bed furnace at 850°C. The calcine with 5% As and 40% Co was leached in sulphuric acid, and after different purification steps, the cobalt was recovered as a pure carbonate.

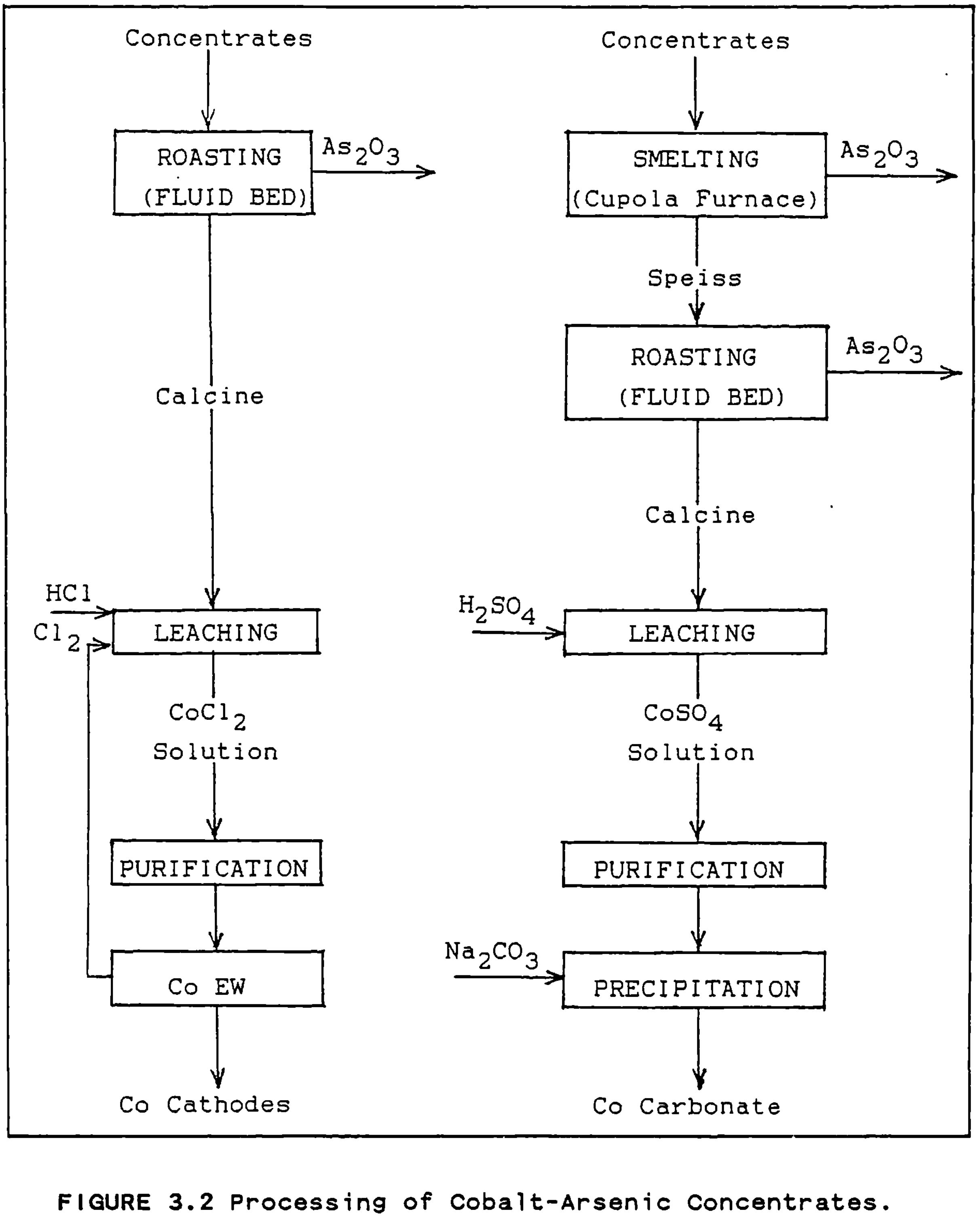


FIGURE 3.2 Processing of Cobalt-Arsenic Concentrates.

3.3.4 Cobalt from Nickel Sulphide Concentrates

Cobalt-nickel sulphide concentrates and secondary arisings (sludge) are the most important source of cobalt and nickel. The three different ways to process nickel sulphide concentrates[22] are shown in Figure 3.3.

In the first method, the concentrates are roasted in a fluid bed reactor, the roasted concentrates are smelted for matte in an electric furnace and the matte is blown in convertors, giving a converted matte with varying amounts of cobalt, nickel and copper depending upon the feed source. The system is used by INCO in Thompson, Manitoba; by Falconbridge in Sudbury, Ontario; by Mathey Rustenburg Refiners Ltd. (MRR) in South Africa by the Russian plants Pechanga and at Monchegorsk and by INCO at Copper Cliff, Ontario although the latter case roasting is done in multi hearth furnaces and matte smelting in reverberatory furnaces.

In the second system, concentrates are dried to less than 1% water and injected in a flash smelting reactor, giving a matte which is blown in convertors. This scheme is used by Outokumpu at Harjavalta in Finland; by Western Mining (WM) at Kalgoorlie in Australia; by Bamangwato Concessions Ltd. (BCL) at Selebi Pikwe in Botswana and in the Russian plant at Norilsk.

A third possibility for processing nickel sulphide concentrates is the Sheritt Gordon Mines Ltd. process which was used by this company at their Fort Saskatchewan plant in Alberta when processing Lynn Lake concentrates[15].

Table 3.1 shows the different ways used in the plant practice for the production of cobalt from nickel matte and mixed nickel-cobalt sulphides.

3.4 SEPARATION OF COBALT AND NICKEL

All of the processes for extracting cobalt from its ores and secondary arisings described in the previous section show

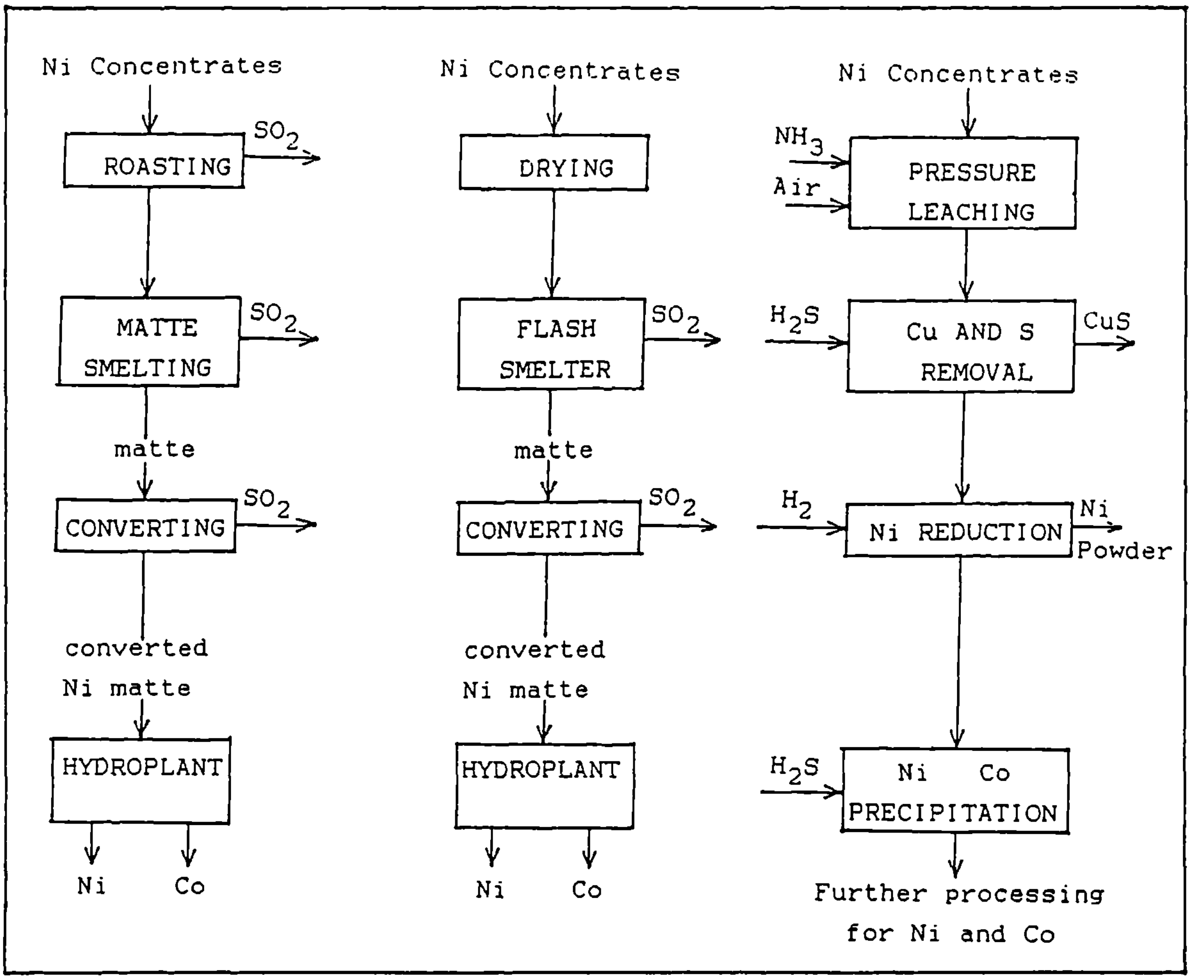


FIGURE 3.3 Processing of Nickel Sulphide Concentrates.

TABLE 3.1 PRODUCTION OF Co FROM Ni MATTE AND MIXED NICKEL-COBALT SULPHIDES

COMPANY	LEACHING		Ni/Co	OUTLET	CAPACITY
	PRESSURE	MEDIA	SEPARATION	Co	t Co/year
AMAX, Port Nickel	atm + pressure	H_2SO_4	AMAX Process	Co Powder	545
MRR, South Africa	yes	H_2SO_4	SX Process	$CoSO_4.7H_2O$	100
NM, Hitachi	yes	H_2SO_4	SX Process	Co cathodes	1300
OUTOKUMPU, Kokkola	yes	H_2SO_4	SHERRITT Process	Co Powder	230
SLN, Le Havre	no	$FeCl_3 + Cl_2$	SX Process	$CoCl_2$ Soln.	600
FALCONBRIDGE, Kristiansand	no	HCl/Cl_2	SX Process	Co Cathodes	2000
SMMC, Niihama	yes	HCl/H_2SO_4	SX Process	Co Cathodes	1410
SHERRITT, Fort Saskatchewan	yes	Ammonia	SHERRITT process	Co Powder	600

that a major part of the recovery processes for cobalt is concerned with its separation from other elements and specially from nickel. As the chemical properties of cobalt and nickel are similar, cobalt which occurs in nickeliferous ores, oxide minerals, sulphide and pyrite concentrates is extracted along with the nickel, during hydrometallurgical processing of the ores and mattes. Most of the cobalt is obtained today as a co-product of copper and as a by-product of nickel extractive metallurgy.

In non-ferrous metallurgy, the separation of Co and Ni is one of the most difficult operations due to very similar behaviour of these elements in most aqueous media. Most of the processes developed involve standard techniques of inorganic chemistry, particularly selective oxidation and precipitation.

There are many possible methods of Co-Ni separation which can be used - these includes : Chemical methods and Physico-chemical methods.

3.4.1 Chemical Methods of Co-Ni Separation

All the chemical methods of Co-Ni separation are based on difference in the solubility or kinetics or thermodynamic stabilities of certain of their compounds[23-25]. The main methods of separation are:

a) hydroxide precipitation
b) carbonates precipitation
c) amine complexes and double ammonium salts
d) sulphides precipitation
e) chlorides fractional crystallisation
f) carbonyles
g) reduction to metal

3.4.2 Physico-Chemical Methods of Co-Ni Separation

Many physico-chemical methods have been used to separate cobalt from nickel but the two most important are ion exchange and solvent extraction.

a) Ion Exchange

Many ion exchange methods have been used to separate cobalt from nickel. The best method of cobalt separation by ion exchange, is the absorption of cobalt from a 9M HCl solution, as a $CoCl_3^-$ complex on an anion exchange resin. Most anion exchange separation of cobalt and nickel rely on the difficulty in forming anionic chloride complexes of Ni(II) - and on a strongly basic anion resin (for example, *de asidite* FF) $CoCl_3^-$ is removed from 9M HCl solution while Ni^{2+} passes through. The cobalt can be eluted from the resin in weaker hydrochloric acid solutions. Other anion exchanger resins that have been used to separate nickel and cobalt include *Dowes* 1, *Dowes* 50 and *Amberlite CG120*. A nickel removal step by ion exchange is included in the Amax cobalt extraction process.

Cobalt and nickel can also be separated by process involving cation exchange resins[26] and resins with complexing exchange groups[27].

b) Solvent Extraction

Liquid-liquid extraction is the most commonly used method for Co/Ni separation. A large number of papers have been published describing the use of solvent extraction for Co/Ni separation from a variety of leach liquors[28-53].

An early approach was based on first forming the anionic chloride complex of cobalt, followed by its separation from nickel[30,31]. This approach is used in *Falconbridge* matt leach process, the *Societe Le Nickel* process[32-33] and the process operated by *Metallurgie Hoboken Overpelt*[34].

The commercial processes which separate cobalt from nickel in sulphate medium have been reviewed recently[28,39]. The *Nippon Mining Co; Hitachi, Japan,* uses alkylphosphonic acid monoalkyl ester *(PC 88 A)* for cobalt extraction[29] while the *Sumitomo Metal Mining Co; Niihama, Japan,* uses Versatic-10 for the simultaneous extraction of cobalt and nickel[36], and then trialkylamine for their separation.

3.4.3 Cobalt/ Nickel Separation by Oxidative Precipitation

Traditionally, cobalt has been separated from nickel in acid sulphate leach solution, by making use of the fact that Co(II) ion is oxidised to Co(III), which then precipitates as the very insoluble hydrous cobalt oxide which is in fact the trihydrate of cobaltic oxide $Co_2O_3.3H_2O$[54].

Oxidation of Co(II) is accompanied by the release of H^+ ions which must be neutralised to precipitate the hydrous cobalt oxide. Careful control of the pH is necessary to maximise the amount of Co precipitated and the Co/Ni ratio in the precipitation. As the pH rises, more Co is precipitated, but the hydrous cobalt oxide also contains more Ni. Precipitation of Ni cannot be avoided, so the precipitation of $Co_2O_3.3H_2O$ is a compromise between maximum Co yield and minimum contamination by Ni.

Fairly powerful oxidants are needed for the oxidation of Co(II) to Co(III). Some of the oxidants which can be applied are, Aqueous chlorine[55] or hypochlorite[56]; Persulphates (NH_4,Na,K)[57]; Ni(III) compound, $Ni(OH)_3$[58] ; Ozone, O_3[59]; and Caro's acid, H_2SO_5[60]. In this work the use of Caro's acid is considered in detail.

3.5 CARO'S ACID

3.5.1 Introduction

Hydrogen peroxide in many ways is the ideal reagent in hydrometallurgy. Its reaction and decomposition products are only water and oxygen, thus making it pollution free and environmentally acceptable. Although most of the applications make use of its oxidising properties, under appropriate conditions hydrogen peroxide will also react as a reducing agent or complexing agent.

A limitation on the efficient use of hydrogen peroxide, as an oxidant for Co-Ni separation, is its tendency to decompose with loss of active oxygen in the presence of transition metal ions, especially at elevated temperatures. In hydrometallurgy, one way of stabilising the peroxygen content from this type of decomposition is by converting hydrogen peroxide to Caro's Acid, H_2SO_5[61].

Caro's acid or peroxymonosulphuric acid is an even more powerful oxidant than hydrogen peroxide and exhibits a greater stability to catalytic decomposition by transition metal ions especially at the elevated temperatures found in most of hydrometallurgical systems. It may be used to complete more difficult oxidations at high redox potential in acid media. The theoretical redox potential for both peroxygens are as follows[62]:

$$H_2O_2 + 2H^+ + 2e^- \text{----->} 2H_2O \qquad E_o = 1.77 \text{ v}$$

$$H_2SO_5 + 2H^+ + 2e^- \text{----->} H_2SO_4 + H_2O \qquad E_o = 1.81 \text{ v}$$

On an industrial scale, Caro's acid is generated by both batch and continuous processes. In industrial use a generator unit should be located at the user's site, with rate of production linked directly to size of demand, and with flexibility to match a fluctuating demand.

Being a liquid, Caro's acid is easily handled on both laboratory and commercial scales. Moreover, since Caro's acid reacts very quickly even at ambient temperatures, processes can be controlled easily at a fixed redox potential thus avoiding any excess of oxidant in subsequent stages. Its decomposition products add only sulphate and water to the reaction system.

3.5.2 Preparation of Caro's Acid for Hydrometallurgy

The method recommended by *INTEROX* for the production of Caro's acid , on any scale, is the controlled addition of hydrogen peroxide (>50%) to strong sulphuric acid (>90%), with cooling to remove the heat of dilution of the acid and the heat of reaction.

$$H_2SO_4 + H_2O_2 \text{------->} H_2SO_5 + H_2O$$

As the above equation shows, that the product solution is an equilibrium mixture which contains the H_2SO_5 along with free sulphuric acid and some traces of hydrogen peroxide[63,64].

Caro's acid is an unstable compound; it is stabilised by dilution of the freshly prepared acid to a strength of 10% (w/w). Decomposition is promoted by high temperature and catalysed by transition metals, especially Co. The formation and dilution of Caro's acid are both exothermic. Cooling of the mixture must be provided, to ensure that the temperature does not rise above 80°C. The diluted acid can be stored at room temperature.

3.5.3 Precipitation of Co(III) Hydroxide by Caro's Acid

Co can be precipitated by Caro's acid, according to the following reaction:

$$2Co^{2+} + H_2SO_5 + 5H_2O \text{ -----> } 2Co(OH)_3 + H_2SO_4 + 4H^+$$

For an optimum separation of cobalt and nickel, the composition of the equilibrium mixture is most important owing to the reducing behaviour of H_2O_2 towards Co(III). Some free hydrogen peroxide can be tolerated in the Caro's acid, but for optimum separation efficiency the $H_2SO_5:H_2O_2$ mole ratio should be 8 or greater. Below this figure both precipitation efficiency and filtration characteristics decline[60].

Oxidation reaction of Caro's acid generates 2 moles of hydrogen ions for every mole of cobalt oxidised, while the free acid of the reagent requires an additional quantity of neutralizing agent. Although the reagents such as NaOH, NH_4OH or nickel, sodium or calcium carbonates can be used, but the best results have been obtained with carbonates. An excess of $NiCO_3$ must however be avoided, as Ni itself is oxidised instead of Co. Ammonia or ammonium salts are less efficient because they decrease the rate of Co precipitation. This is attributed to the formation of cobaltammine complexes and oxidation of NH_3 to NO_3^- by an oxidant, which is catalysed by Co(III).

The optimum pH for almost complete precipitation of Co lies between 3.5 and 5.5, depending on the composition of the starting solution. For partial precipitation of cobalt, the reaction can be carried out at lower pH, between 2.0 and 3.0, at pH value below 3.0 precipitation efficiency is very poor and ceases altogether below pH 2.0[65]. The upper limit of pH is governed by the need to avoid co-precipitation of nickel(II) and Cobalt(II) hydroxide.

3.5.4 Stability and Storage of Caro's Acid

Concentrated Caro's acid and dilute form can be stored for long periods, especially if kept cool. The following storage temperatures are recommended for the different Caro's acid strength.

Concentrated Caro's acid = -10°C
10 % Caro's acid = 0-5°C

At these temperatures storage for several weeks is possible with no detectable change in composition.

At higher temperatures some decomposition occurs due to catalytic impurities in the sulphuric acid, and some self decomposition:

$$H_2SO_5 \text{ ------> } H_2SO_4 + 1/2O_2$$
$$H_2SO_5 + H_2SO_5 \text{ ------> } 2H_2SO_4 + O_2$$

The "half life" or time taken to reach 50% of the original H_2SO_5 concentration for various Caro's acid equilibrium mixtures is shown in Table 3.2 and Figure 3.4.

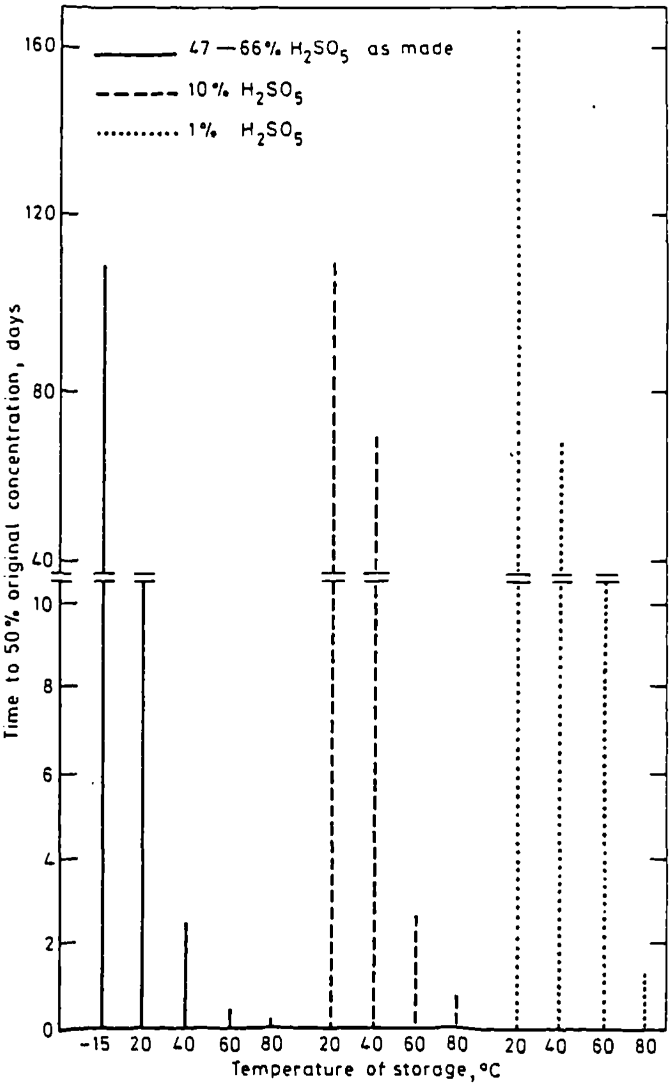


FIGURE 3.4 Stability of Caro's acid.

TABLE 3.2

HALF LIFE OF 26% CARO'S ACID ON STORAGE

Temp. °C	T 1/2
-15	7.5 Years
0	600 days
10	214 "
20	75 "
40	10 "
60	2 "

Starting materials: 98% H_2SO_4, 50% $2H_2O_2$, Mole ratio 3:1

It can be seen that only slight decomposition would be expected over several days at typical ambient temperatures. Despite the decreased stability at high temperatures Caro's acid can still be used in processes at temperatures up to 100°C, as its oxidising reactions are still much faster than its rate of decomposition.

3.6 COBALT-NICKEL SEPARATION FROM MATTE

The aim of the research carried out in this work is to study the use of Caro's acid as a means of separating cobalt from nickel in a cobalt-nickel cake produced as part of a copper-nickel refinery process. The work involved both a laboratory study and an on site trial.

Cobalt-nickel cake arises during the hydrometallurgical treatment of Co-Ni matte which contains about 37% Ni and 0.16% Co and approximately 67% of the matte can be taken into solution. If the cobalt leaching efficiency is the same as that of nickel, a matte leach solution containing 65g/l Ni should contain 280 µg/ml Co. But in actual practice the matte leach solution contains about 120ug/ml Co (Figure 3.5). It has been found that the poor leach efficiency of Co is due to the presence of some Co in the form of insoluble Co(III), but the addition of reducing agent, such as SO_2, makes the process more efficient.

The matte leach solution, containing 65g/l Ni and 120 µg/ml

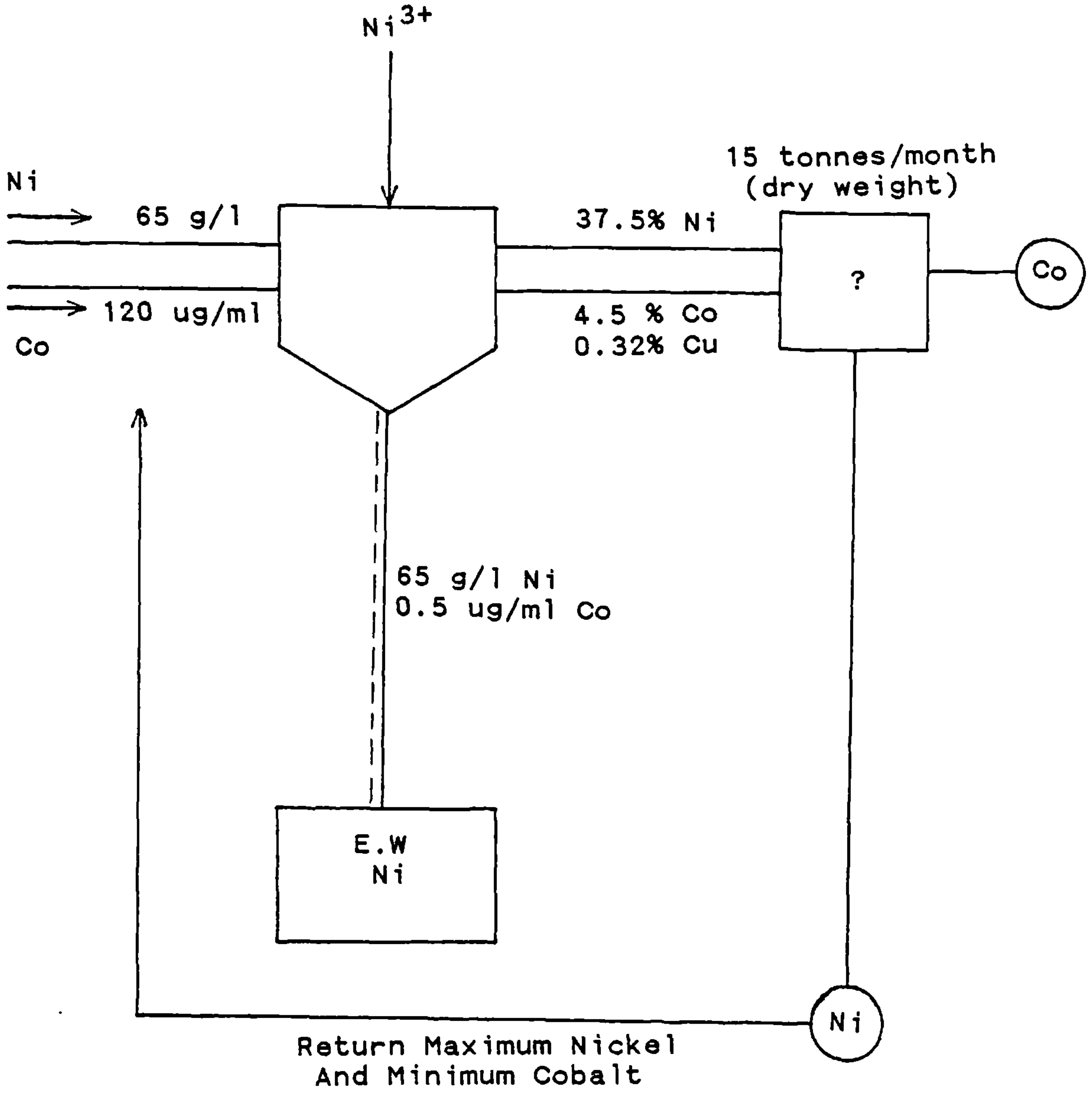


FIGURE 3.5 Origin of the Co - Ni Cake.

Co, is treated with Ni(III) to produce a nickel rich solution. The nickel is recovered from this solution by electrowinning on titanium cathodes. The resulting precipitates contain 37.5% Ni, 4.3% Co and 0.35% Cu. These cobalt-nickel cake precipitates are considered as low grade secondary sources for cobalt metal and are the subject of the work described in this chapter. The main aims of the work are:

(1) To recover the maximum amount of cobalt from Co-Ni cake.
(2) To recover the cobalt as a solid containing the minimum amount of nickel.
(3) To separate the nickel from the cobalt as solution containing the maximum amount of nickel and the minimum amount of cobalt (less than 120 µg/ml to prevent build up).
(4) To reduce the number of filtration stages in the cobalt-nickel separation step.

Preliminary Analysis of Sample

Thermogravimetric analysis indicates that undried Co/Ni cake contains 62 1% moisture (Figure 3.6). The qualitative analysis of dried sample on EDAX indicates the presence of Co, Ni, Cu, Fe, S and Si (Figure 3.7). X-ray diffaraction analysis of oven dried sample did not give any information about the likely nature of the cobalt- and nickel-containing phase. The diffractogram of a cake sample treated in a furnace at 860°C for two hours is shown in Figure 3.8.

In order to find out the weight % of individual metals in Co/Ni cake, a number of experiments were carried out by dissolving the cake in *aqua-regia* and analysing the resultant solutions for each metal by Atomic Absorption Spectrophotometer. The results along with their standard deviations are given in Table 3.3.

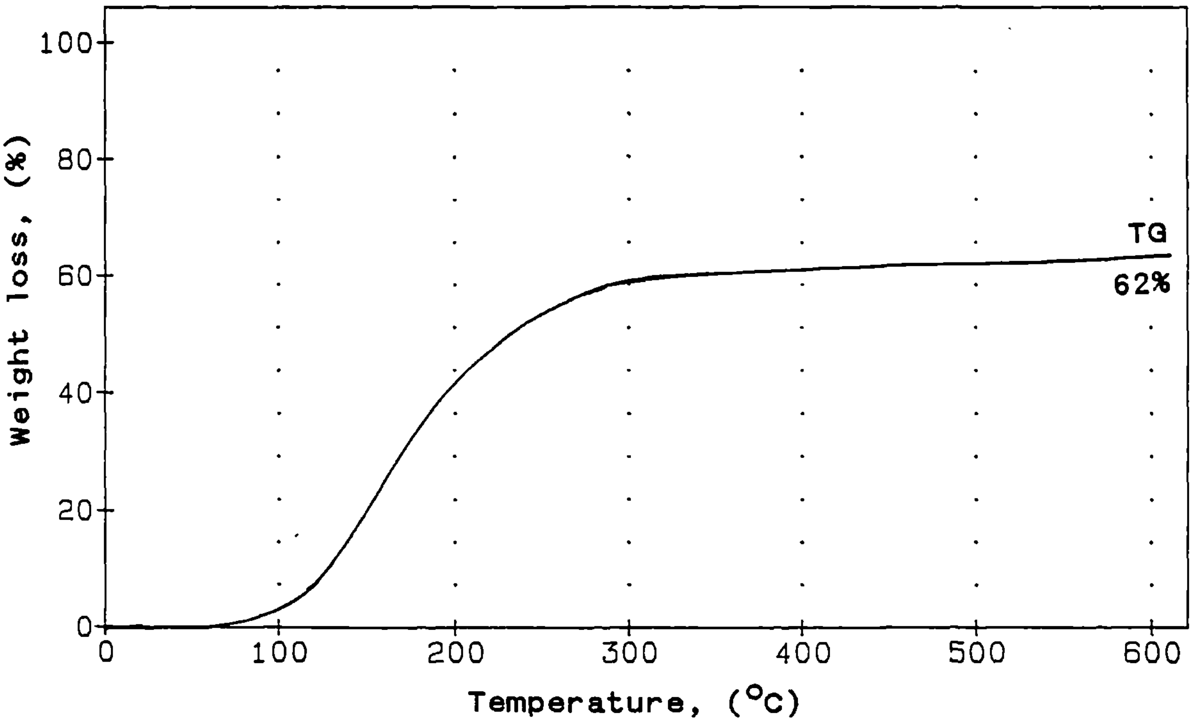


FIGURE 3.6 Thermograph of Co - Ni cake.

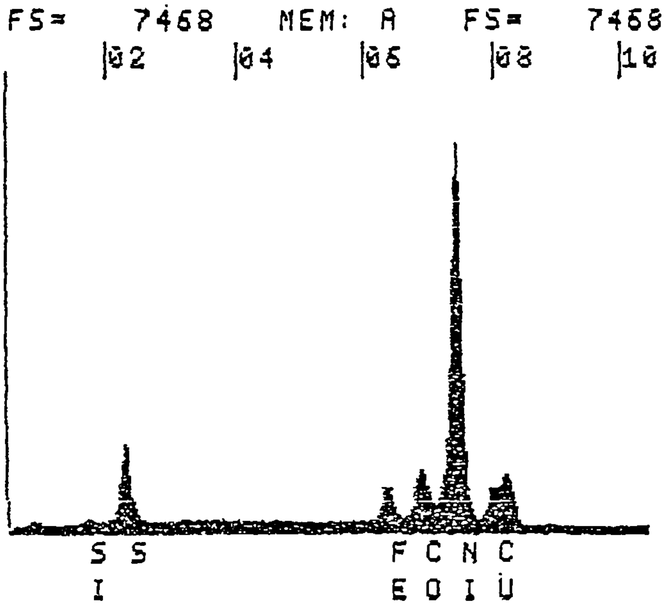
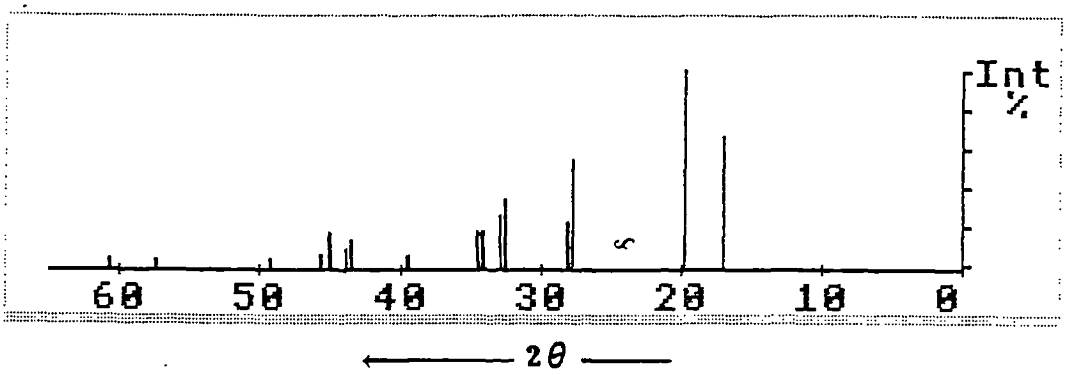


FIGURE 3.7 Electron microprobe analysis of Co - Ni cake.



2θ	d	I
17.0	2.390	68
19.8	2.066	100
27.9	1.474	55
28.0	1.465	19
32.9	1.254	34
33.0	1.251	30
34.4	1.201	19
34.6	1.194	19
39.9	1.041	6
43.6	0.957	13
43.8	0.952	9
44.7	0.935	15
45.0	0.928	6
49.3	0.852	4
57.5	0.738	4
60.7	0.703	4

FIGURE 3.8 X-ray Diffraction pattern for Co - Ni Cake.

TABLE 3.3 Wt. % of Co, Ni and Cu.

Metal	Wt. (%)
Co	4.5 ± 0.1
Ni	38.5 ± 1.0
Cu	0.32 ± 0.01

3.6.1 Solubility of Cobalt/Nickel cake

In this set of experiments, 10 and 20g of undried Co/Ni cake, which contained 62% moisture, was leached in 100 and 200ml of 1, 2 and 3M sulphuric acid at 70°C for two hours with continuous stirring. The residues were filtered off and dried in an oven at 140°C for an hour. The solubility results are in Table 3.4.

3.7 ACID SULPHATE LEACHING

All the leaching experiments were carried in 400 ml glass beaker at 70°C with heating supplied via a hot plate and stirring by a magnetic stirrer. During the leaching period, beaker was covered with a glass dish to minimise the aqueous loss.

3.7.1 Effect of Acid Concentration

(A) In this set of experiments, 5g of dried Co/Ni cake were leached with 200ml of 1, 2 and 3M sulphuric acid at 70°C for two hours. The solution was filtered and the final volume of the filtrate made up to 250ml with distilled water. These solutions were analysed for Co, Ni and Cu by AAS and the results are given in Table 3.5.

(B) In these experiments, 3g of dried Co/Ni cake were leached with 100ml of 1, 2 and 3M sulphuric acid under the same reaction conditions as described in the previous experiment and the results are given in Table 3.6.

The results of this series of experiments indicate that above 85% of Co and Ni can be extracted in 1M H_2SO_4, whereas complete extraction of Co and Ni is achieved in 2 or 3M H_2SO_4 under the same reaction conditions. The extraction of

TABLE. 3.4 SOLUBILITY OF Co/Ni CAKE IN SULPHURIC ACID

Weight of sample (g)	Conc. of acid (M)	Volume of acid (ml)	solubility (%)
10	1	100	87.0
20		200	85.5
10	2	100	90.9
20		200	91.7
10	3	100	93.9
20		200	94.4

TABLE 3.5 EFFECT OF CONCENTRATION OF SULPHURIC ACID ON THE EXTRACTION OF METAL VALUES FROM Co/Ni CAKE

Acid Conc.	Conc. (ppm)			Extraction, (%)		
(M)	Co	Ni	Cu	Co	Ni	Cu
1	765	6850	13	85.0	89	20
2	885	7925	35	98.3	100	55
3	897	7910	40	99.6	100	63

TABLE 3.6 EFFECT OF CONCENTRATION OF SULPHURIC ACID ON THE EXTRACTION OF METAL VALUES FROM Co/Ni CAKE

Acid Conc.	Conc. (ppm)			Extraction, (%)		
(M)	Co	Ni	Cu	Co	Ni	Cu
1	472	4035	9	87	87	23
2	550	4650	12	100	100	31
3	535	4575	28	99	99	73

TABLE 3.7 EFFECT OF LEACHING TIME

Leaching	Co Extracted		Ni Extracted		Co:Ni
time (min)	mg	%	mg	%	in soln.
20	18.7	42	192.7	50	1:10
30	27.5	61	246.0	64	1:9
60	41.2	92	377.5	98	1:9
120	45.0	100	383.7	99	1:9

Cu is also increases with increasing the acid concentration.

3.7.2 Effect of Leaching Time

(A) In this set of experiments, 1g of dried Co/Ni cake were leached with 100ml of 2M H_2SO_4 for 20, 30, 60 and 120 minutes at 70°C. The solution was filtered and the final volume of the filtrate made to 250ml with distilled water. These solutions were analysed by AAS and the results are given in Table 3.7.

(B) In this set of experiments, all the reaction conditions were the same as described in the previous experiment except that 3M H_2SO_4 was used instead of 2M. Results are given in Table 3.8.

Again the results indicate that complete extraction of Co and Ni is achieved in 2M H_2SO_4 at 70°C in 2 hours. In all other experiments leaching was carried out with 2M H_2SO_4 at 70°C.

3.7.3 Effect of Agitation

(A) 3g of dried Co/Ni cake were leached with 100ml of 2M H_2SO_4 at 70°C for 2 hours without stirring. After filtration the final volume of the filtrate was made to 250ml with distilled water.

(B) In this experiment all the reaction conditions were the same as described above except that leaching was carried out with stirring. Both solutions were analysed by AAS and the results are given in Table 3.9.

The results indicate that almost complete extraction of Co and Ni is achieved when the leaching is carried out with stirring. Leaching without stirring extract only 85% Co and 98% Ni.

3.8 LEACHING WITH DISTILLED WATER

(A) 3g of dried Co/Ni cake were leached with 100ml of 2M H_2SO_4 at 70°C for two hours. The cooled solution was

TABLE 3.8 EFFECT OF LEACHING TIME

Leaching	Co Extracted		Ni Extracted		Co:Ni
time (min)	mg	%	mg	%	in soln.
20	24.2	54	236.2	61	1:10
30	30.0	67	270.5	70	1:9
60	42.5	95	373.7	97	1:9
120	44.0	99	381.2	99	1:9

TABLE 3.9 EFFECT OF AGITATION ON THE XTRACTION OF Co/Ni

	Co Extracted		Ni Extracted		Conc. (ppm)		Co:Ni
	mg	%	mg	%	Co	Ni	in soln.
(A)	115	85	1166.0	98	460	4664	1:10
(B)	132	98	1172.5	99	528	4690	1:9

TABLE 3.10 EXTRACTION OF COBALT AND NICKEL

	Co Extracted		Ni Extracted		Conc. (ppm)		Co:Ni
	mg	%	mg	%	Co	Ni	in soln.
H_2SO_4	135	100.0	1168.7	99	540	4675	1:9
H_2O	1	0.8	161.0	14	4	644	1:161

TABLE 3.11 EXTRACTION OF COBALT AND NICKEL

	Co Extracted		Ni Extracted		Conc. (ppm)		Co:Ni
	mg	%	mg	%	Co	Ni	in soln.
H_2SO_4	216.5	96	1880.0	98	864	7520	1:9
H_2O	2.5	1	288.0	15	10	1152	1:115

filtered and the final volume of the filtrate made to 250ml with distilled water.

(B) In this experiment, 3g of dried Co/Ni cake were leached with 200ml of distilled water under the same reaction conditions as described above. Both solution were analysed by AAS and the results are in Table 3.10.

(C) 5g of dried Co/Ni cake were leached with 200ml of 2M H_2SO_4 and 200ml of distilled water under the same reaction conditions as described in previous experiment. The results are in Table 3.11.

The results indicate that by using distilled water leaching it is possible to get Ni rich solution with low Co concentration suggesting that some Ni is present as water soluble sulphate.

3.9 PREPARATION OF CARO'S ACID

As described in Section 3.5.2, the production of Caro's acid, on any scale, is carried out by the controlled addition of hydrogen peroxide to strong sulphuric acid, with cooling to remove the heat of dilution of the acid and the heat of reaction.

$$H_2SO_4 + H_2O_2 \text{ ---> } H_2SO_5 + H_2O$$

As the above equation shows, that the product solution is an equilibrium mixture which contains the H_2SO_5 along with free sulphuric acid and some traces of hydrogen peroxide. The composition of the equilibrium mixture is governed by the concentration and mole ratios of the reactants employed. Typical product compositions are given in Table 3.12.

The laboratory production of Caro's acid was carried out by using 98% of sulphuric acid and 60% of hydrogen peroxide at a molar ratio of 3:1 ($H_2SO_4:H_2O_2$). Some quantities of reagents are given in Table 3.13 for the preparation of four typical Caro's acid, all of which are prepared using a molar

TABLE 3.12 COMPOSITION OF CARO'S ACID EQUILIBRIUM MIXTURE

Starting Materials (% w/w)	H_2SO_4:H_2O_2 Molar Ratio	Composition (% w/w) H_2SO_5	H_2O_2	H_2SO_4
98% H_2SO_4	1:1	42	10	31
70% H_2O_2	2:1	39	2	46
	3:1	29	1	59
98% H_2SO_4	1:1	33	11	35
60% H_2O_2	2:1	35	3	46
	3:1	28	1	58
94% H_2SO_4	1:1	33	12	38
70% H_2O_2	2:1	33	3	49
	3:1	27	1	59
98% H_2SO_4	1:1	23	13	40
50% H_2O_2	2:1	28	4	49
	3:1	26	2	58

TABLE 3.13 REAGENTS Wt. FOR THE PREPARATION OF CARO'S ACID

H_2SO_4 (%)	(g)	H_2O_2 (%)	(g)	% H_2SO_5 in Caro's acid (%)
98	100	70	16.2	29
98	100	60	18.9	28
94	100	70	15.5	27
98	100	50	22.7	26

Molar ratio 3:1 (H_2SO_4:H_2O_2)

TABLE 3.14 REAGENTS WEIGHT FOR THE DILUTION OF CARO'S ACID

Concentrated "as-made" Caro's acid g	% H_2SO_5	Water required g	% H_2SO_5 in dilute Caro's acid
116.2	29	220.8	10
118.9	28	214.0	10
115.5	27	195.5	10
122.7	26	196.3	10

ratio of 3:1 (H_2SO_4:H_2O_2)

The experimental setup for the preparation of Caro's acid is shown in Figure 3.9. The preparation was carried out in a fume hood. 100g of concentrated sulphuric acid (98%) was introduced to a reaction beaker/reactor of 400ml capacity, the reaction beaker also contained PTFE magnetic stirrer bar. The beaker was surrounded by an ice/salt bath. This whole assembly was placed on the magnetic stirrer plate. The reaction beaker was fitted with thermometer (alcohol type) and dropping funnel. Sulphuric acid was allowed to cool with continual stirring.

18.9g of concentrated hydrogen peroxide (60%) was taken into the dropping funnel mounted on the top of the reaction vessel. When the temperature of the sulphuric acid reached to $5^{o}C$, hydrogen peroxide was added very slowly, dropwise, at such a rate that the temperature of the reaction did not exceed $20^{o}C$. After the complete addition of hydrogen peroxide, Caro's acid was allowed to cool with continual stirring to the bath temperature. The reaction product contains 28% (w/w) H_2SO_5, 1% H_2O_2 and 58% H_2SO_4.

3.9.1 Dilution of Caro's Acid

The separation of cobalt from nickel solution was carried out using 10% Caro's acid. The procedure described above produces 28% Caro's acid which was diluted to 10% by adding concentrated "as-made" Caro's acid to known quantity of distilled water. The necessary quantities of distilled water for the dilution of four samples of Caro's acid are given in Table 3.14.

214.0g of distilled water was introduced into a glass beaker of 500ml capacity. This glass beaker was placed in a ice/salt bath. The beaker along with the ice/salt bath was placed on the magnetic stirrer plate and stirred rapidly. Concentrated Caro's acid (28%) was added into a dropping funnel mounted on top of the reaction beaker. The Caro's acid was added, dropwise, into a cold stirred water with

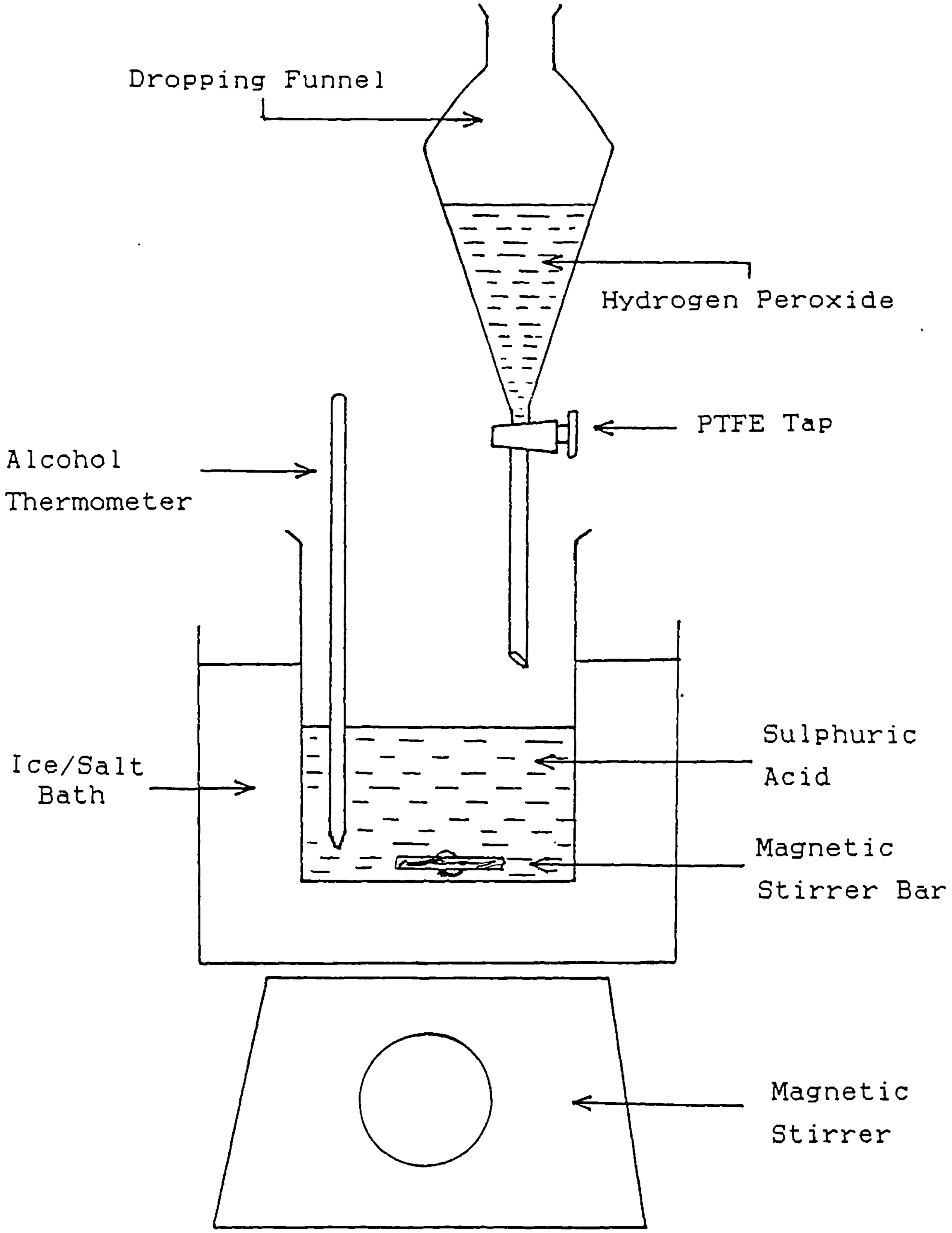


FIGURE 3.9 Setup for laboratory preparation of Caro's acid.

such a rate that the temperature remained below 30°C. After the addition of half Caro's acid, the partially diluted acid was stirred and the temperature was brought down to 10°C. The remaining half of the Caro's acid was added, dropwise, into the partially diluted acid. After all the Caro's acid has been added, the diluted Caro's acid was stirred continuously to ensure that the two liquids were thoroughly mixed before storage. This diluted (10%) Caro's acid was stored in a refrigerator to minimise the risk of its decomposition.

3.10 PRECIPITATION OF Co(III) HYDROXIDE BY CARO'S ACID

In these experiments, 250ml of Co/Ni cake solution containing different concentrations of Co and Ni was placed in a 800ml beaker. The beaker was fitted with a stirrer, a alcoholic type thermometer and a pH electrode. All the precipitation experiments were carried out at an ambient temperature. The pH of the solution was adjusted to the desired value with a saturated solution of sodium carbonate or sodium hydroxide. Caro's acid (10%) was then added drop-wise from a burette such that 15ml of Caro's acid was added in 15 minutes. The pH of the solution was maintained at the desired value by adding a saturated solution of sodium carbonate or sodium hydroxide from a second burette. After the addition of a 2 times stochiometric excess of Caro's acid the solution was allowed to stand for 2 hours to ensure the maximum separation of cobalt. The solution was filtered, and the filtrate was analysed by AAS for residual cobalt. The results are given in Table 3.15-3.17.

The data in Table in 3.15-3.17 indicate that the precipitation efficiency of cobalt from solution is influenced by the choice of neutralizing agent and pH value. For partial precipitation of cobalt, the reaction can be carried out at lower pH values. It was also found that the reaction pH has an important bearing not only on the amount of cobalt precipitated but also on the Co:Ni ratio of the precipitated solid.

TABLE 3.15 SEPARATION OF COBALT USING CARO'S ACID

Test	Feed Solution (ppm) Co	Feed Solution (ppm) Ni	Co in Solution mg	Co in Solution %	Ni in Solution g	Ni in Solution %	Sep^n Effy. %
A	520	4510	32.5	25	1.11	98.5	75
B	460	4690	30.0	26	1.14	97.8	74
C	270	3050	18.7	28	0.74	96.6	72
D	120	770	7.0	23	0.19	98.7	77

Conditions: pH, 3.5; Temperature, Ambient; Neutralizing agent, Saturated solution of sodium carbonate.

TABLE 3.16 SEPARATION OF COBALT USING CARO'S ACID

Test	Feed Solution (ppm) Co	Feed Solution (ppm) Ni	Co in Solution mg	Co in Solution %	Ni in Solution g	Ni in Solution %	Sep^n Effy. %
E	545	4000	17.5	13	0.96	96	87
F	528	4560	19.5	15	1.07	94	85
G	220	2005	8.7	15	0.47	93	85
H	230	1980	8.7	16	0.47	94	84
I	150	2870	7.5	20	0.65	90	80
J	165	1510	6.2	15	0.36	94	85
K	60	400	1.7	12	0.09	95	88

Conditions: pH, 4.0; Temperature, Ambient; Neutralizing agent, Saturated solution of sodium carbonate.

TABLE 3.17 SEPARATION OF COBALT USING CARO'S ACID

Test	Feed Solution (ppm) Co	Feed Solution (ppm) Ni	Co in Solution mg	Co in Solution %	Ni in Solution g	Ni in Solution %	Sep^n Effy. %
L	575	5200	17.5	12	1.20	92	88
M	540	5050	17.5	13	1.16	92	87
N	215	2080	7.5	14	0.47	91	86
O	100	5015	2.5	10	1.13	90	90

Conditions: pH, 4.0; Temperature, Ambient; Neutralizing agent, Sodium hydroxide solution.

The separation efficiency of cobalt is almost the same for both sodium carbonate and hydroxide. But higher co-precipitation of Ni occurs in hydroxide system. The use of carbonate as a neutralizing agent gives high precipitation purity.

By decreasing the pH value the precipitation efficiency decreases but precipitation purity increases. The pH value below 3 gives very low precipitation efficiency and ceases altogether at pH 2.

3.10.1 Precipitation Analysis

The cobaltic hydroxide precipitates, $Co(OH)_3$, were washed at pH 3.0 with sulphuric acid solution. The washing step removes most of the coprecipitated nickel and improves the purity of the cobaltic hydroxide precipitation. The washed precipitates were dissolved in *agua-regia* and the resultant solutions were analysed by AAS. The results are given in Table 3.18.

The analysis of cobalt precipitate obtained from different tests with sodium carbonate addition showed a much lower nickel contents then precipitate samples from sodium hydroxide. The presence of trace level impurities like, Cu and Fe is co-precipitated with the cobalt. It was found that the co-precipitation of Ni and Cu increases with increasing the reaction pH.

3.11 EFFICIENCY OF CARO'S ACID

A stock synthetic solution containing 1g/l of cobalt was prepared from reagent grade cobalt sulphate crystals, $Co(SO)_4.5H_2O$, and 500ml of 1M sulphuric acid. The final volume of the solution was made to one litre with distilled water. Cobalt solutions of 500, 400, 300, 200, 100, and 50 µg/ml were prepared by diluting the cobalt stock solution.

250ml of each diluted solution was treated with a saturated solution of sodium carbonate to raise the pH of the solution to 4.0. The oxidative precipitation of cobalt was then carried out by adding 10% Caro's acid (100% excess) into the stirred solution. The pH of the solution was maintained at 4.0 during the addition of Caro's acid. After the complete addition of Caro's acid, 2 hours additional time was given to complete the precipitation reaction. The solution was filtered, and the filtrate was analysed by AAS for residual cobalt. The results are given in Table 3.19.

The data in Table 3.19 indicate that the efficiency of Caro's acid drops as the concentration of cobalt decreases. The highest precipitation efficiency was achieved with a solution containing high concentration of cobalt. Preliminary studies have shown that the precipitation efficiency can be improved by increasing the pH of the solution.

3.12 RECOVERY OF METAL VALUES

The cobaltic hydroxide precipitation is usually used as a source for the production of various other cobalt chemical compounds. The precipitation purity can be improved by washing at pH 3.0, with a solution of sulphuric acid. It has been found that at this pH value most of the coprecipitated nickel is dissolved with negligible cobalt loses.

Alternatively, the Co(III) hydroxide is dissolved in sulphuric acid in the presence of hydrogen peroxide which acts as a reducing agent in the chemical reaction. The chemical reaction may be represented as follow:

$$2Co(OH)_3 + H_2O_2 + H_2SO_4 \text{ -----> } 2CoSO_4 + O_2 + 6H_2O$$

After adjusting the pH, the electrowining of cobalt is carried out by using Fluidized bed cell on titanium cathodes. The electrowining of cobalt from sulphate solution has already been described in detailed in Chapter 2. The effects of various parameters on the electrowining of cobalt, for example, pH, cobalt concentration, current density and agitation etc. were also studied.

Table 3.18 PRECIPITATION ANALYSIS

Test	pH	Neutralizer	Concentration, (ppm) Co	Ni	Cu	Co:Ni in PPt
A	3.5	Na_2CO_3	370	35	8	11:1
F	4.0	Na_2CO_3	435	85	12	5:1
M	4.0	NaOH	445	110	10	4:1

TABLE 3.19 EFFICIENCY OF CARO'S ACID

Feed Solution (ppm)	Filtrate Conc. (ppm)	Precipitation Effy. (%)
500	20	96.0
400	18	95.5
300	18	94.0
200	15	92.5
100	10	90.0
50	6	88.0

Conditions: pH, 4.0; Neutralizing Agent, Saturated Solution of Sodium Carbonate; Temperature, Ambient.

TABLE 3.20 ELECTROWINNING OF NICKEL

Time (Hour)	Concentration (ppm) Ni	Co	Deposition (%) Ni	Co	Current Effy. for Ni (%)
0	1925	25	-	-	-
2	610	21	68	16	60
4	365	18	81	28	36
6	190	15	90	40	26
8	105	15	95	40	21
10	15	15	99	40	17

Conditions: pH, 4.5-5.0; Neutralizer, ammonium hydroxide solution; Current density, $100A/m^2$.

Recovery of nickel was carried out by electrowinning using Fluidised Bed cell. The design and the operating parameters of the cell has already been described in Chapter 2. Fluidised bed cell consists of mesh electrodes suspended in a fluidised bed of inert glass beads. The metal bearing solution is pumped through distributors at the base of the cell causing fluidisation of the glass beads. The vigorous agitation produced at the cathode surface ensures that the metal is recovered as a hard adherent deposit and at high efficiency.

The purified nickel solutions obtained after the separation of cobalt from different experiments were collected in a 10 litre beaker. To this solution, 100ml of 10% ammonium formate solution was added and the final volume of the solution made to 10 litre with distilled water. The formate solution acts as a buffer and make it lot easier to maintain the pH during the electrolysis process.

The solution was analysed by AAS for Co and Ni concentration and then introduced into the reservoir tank of the Fluidised bed cell. Electrolysis was carried out at an ambient temperature, at current density of 100 A/m^2 on the titanium mesh cathodes. The pH of the solution was maintained at 4-5 during the electrolysis with ammonium hydroxide solution. During the electrolysis, samples were collected and analysed for the residual Ni and Co. The results are given in Table 3.20

The data in Table 3.20 indicate that the purification factor for Ni was 68% after 2 hours of electrolysis time. This was increased to 99% after 10 hours. The Ni deposit was shiny and hard. The highest value of current efficiency is 60% after 2 hour electrolysis period. This decreases to 17% after 10 hours.

3.13 DISCUSSION

The dried Co/Ni cake contains 4.5 ± 0.1% Co and 38.5 ± 1.0% Ni, probably in their oxide form. EDAX qualitative analysis show that Co/Ni cake also contains Si and large weight percentage of S in the dried cake. Si is present as SiO_2 and S as $SO_4^{=}$. The dried cake also contains 0.32 ± 0.1% of Cu and trace quantities of Fe.

A number of experiments were designed to examine the solubility of Co/Ni cake in different concentration of sulphuric acid under various conditions. Data in Table 3.4 show that 86, 91 and 94% of cake can be dissolved in 1, 2 and 3M sulphuric acid at 70°C in two hours (Figure 3.10).

Acid sulphate leaching results indicate that only 87% Co and 89% Ni is extracted when the sample is leached with 1M sulphuric acid at 70°C for 2 hours. These figures can be increased by leaching the sample with 2 or 3M sulphuric acid under the same reaction conditions. In these two sulphuric acid concentrations almost complete extraction of Co and Ni is achieved (Tables 3.5-3.6). Under these leaching conditions some quantity of Cu and traces of Fe is also extracted (Figure 3.11).

The effect of leaching time on the extraction of metal values in different acid concentrations was also studied (Table 3.7 and 3.8). The results show that 61% Co and 64% Ni is extracted in 2M H_2SO_4 at 70°C in 30 minutes leaching time. The values obtained with 3M sulphuric acid under the same leaching conditions were 67% Co and 70% Ni. The complete extraction of Co and Ni (98-99.5%) was achieved when the sample leached with 2 or 3M sulphuric acid at 70°C for 120 minutes. Figure 3.12 and 3.13 represents the percentage extraction of Co and Ni versus time (minutes) for 2 and 3M sulphuric acid respectively.

The extraction of metal values in 2M sulphuric acid depends upon agitation. The experimental results indicate (Table 3.9) that 85% Co and 98% Ni was extracted when the leaching

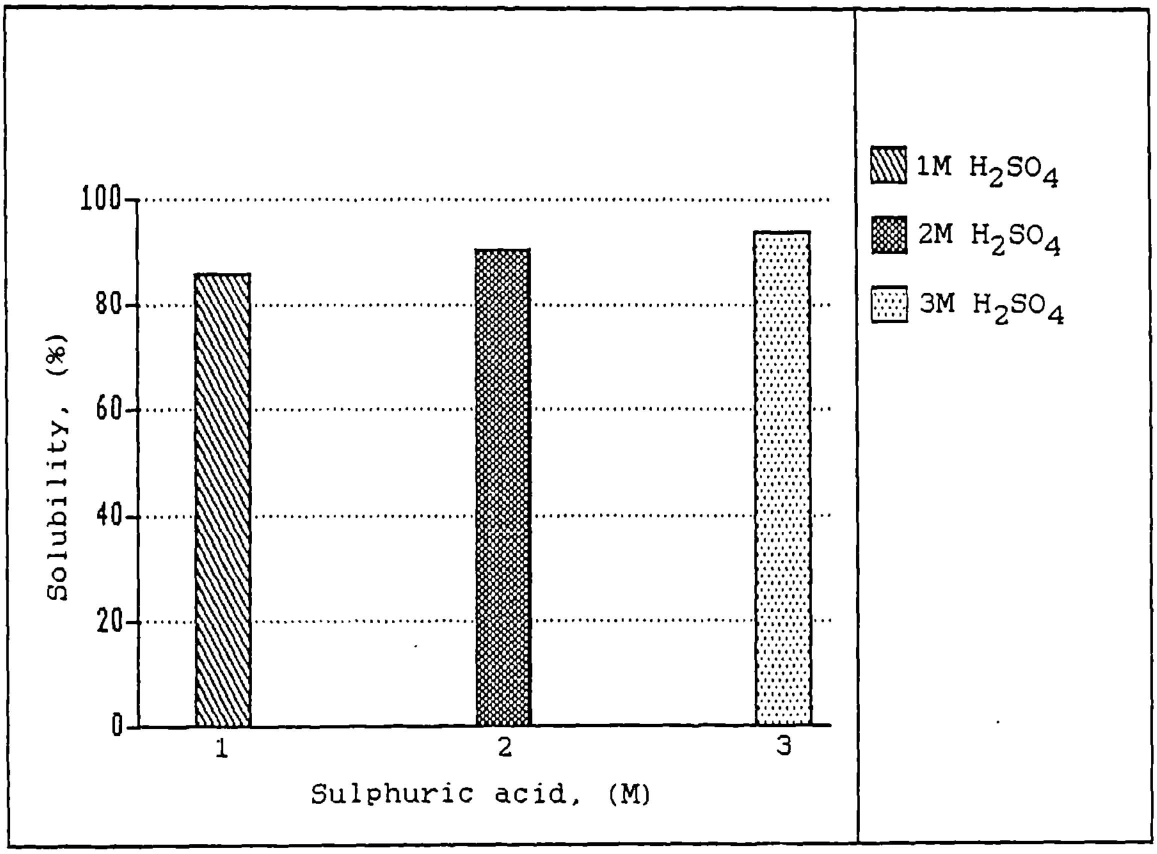


FIGURE 3.10 Solubility of Co - Ni cake in sulphuric acid.

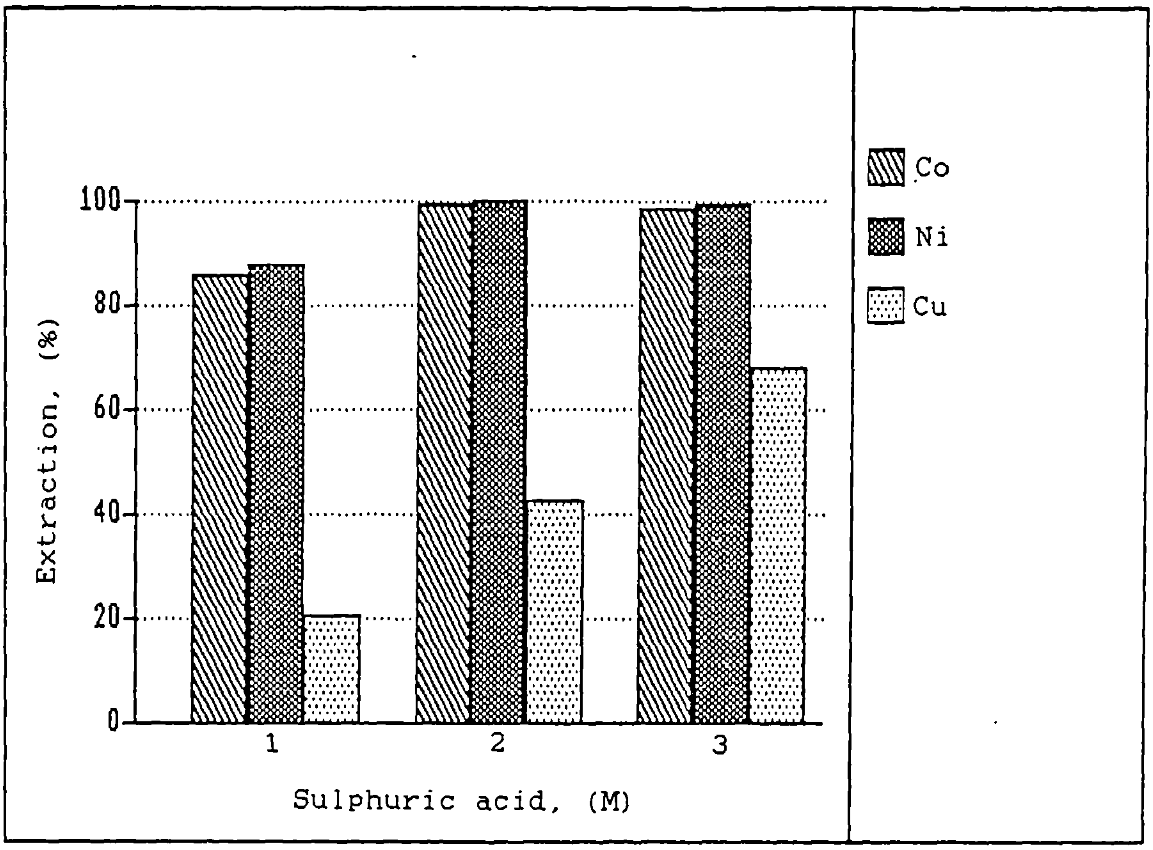


FIGURE 3.11 Effect of acid concentration on the extraction of cobalt, nickel and copper from Co - Ni cake.

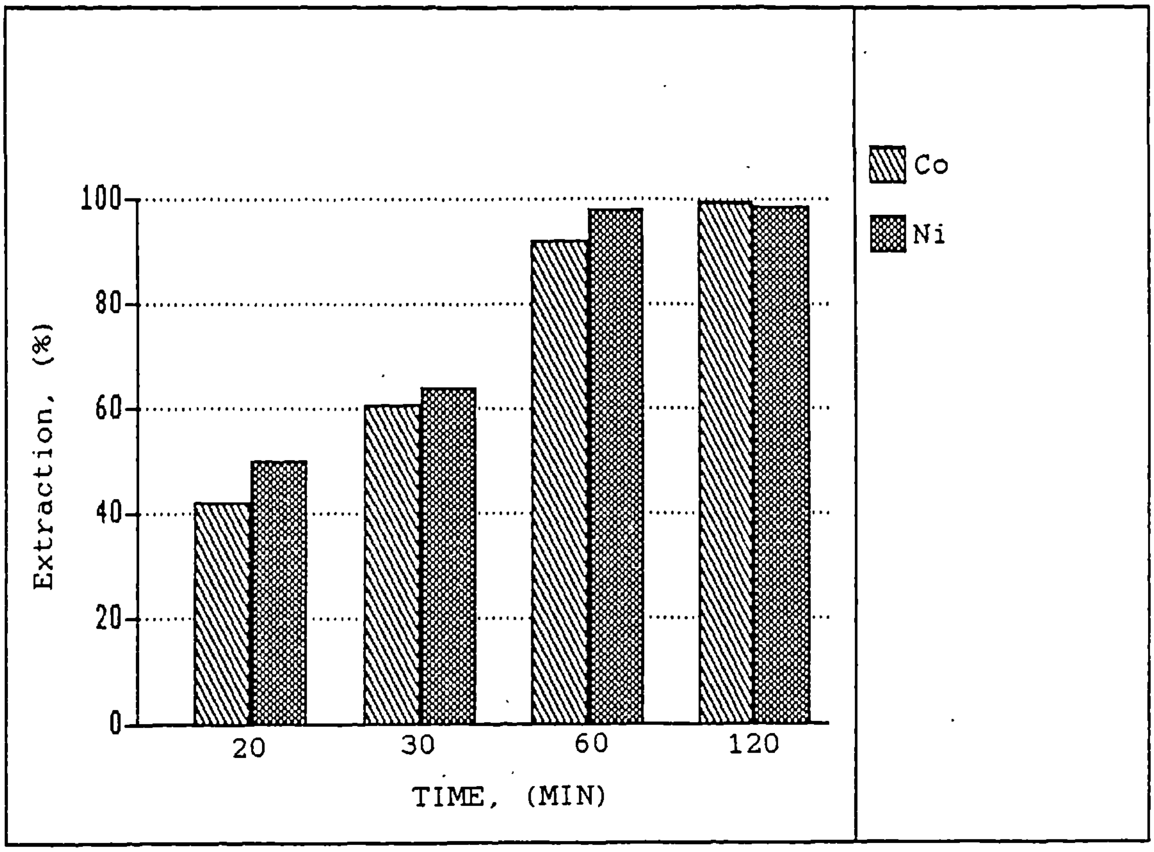


FIGURE 3.12 Effect of leaching time on the extraction of cobalt and nickel. (2M sulphuric acid).

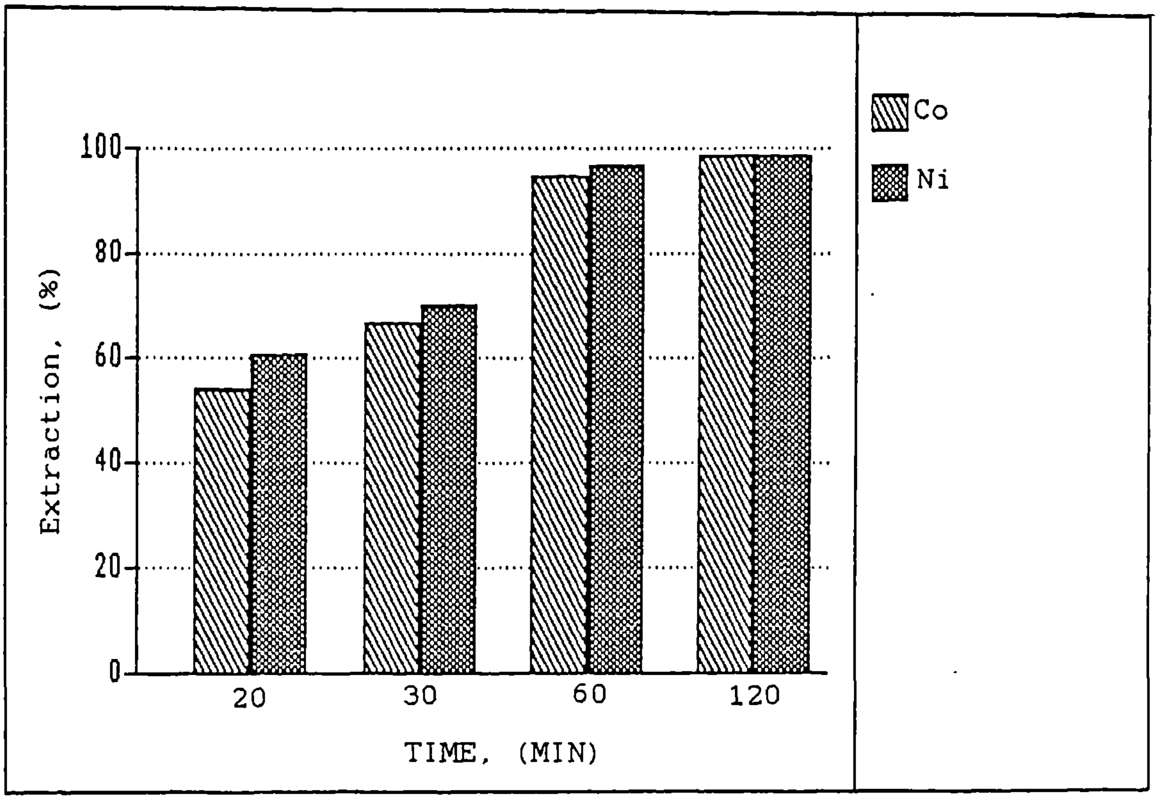


FIGURE 3.13 Effect of leaching time on the extraction of cobalt and nickel. (3M sulphuric acid).

carried out without stirring. The extraction was increased to 98% Co and 99% Ni, when the leaching performed with stirring under the same conditions.

In some experiments leaching was carried out with distilled water at 70°C. The results show that 0.4% of Co and 13% of Ni is extracted in distilled water in 2 hours at 70°C (Table 3.10 and 3.11). These results indicate that some Ni is present in its soluble sulphate form whereas Co is present as insoluble oxide or sulphide. The distilled water leaching can be used to achieved a Ni rich solution.

Co(III) Hydroxide Precipitation

In aqueous solutions containing no comlexing agents the oxidation potential, E_o, for the Co(II)/CO(III) couple is very high.

$$Co(H_2O)_6^{3+} + e^- \text{ -----> } Co(H_2O)_6^{2+} \quad ; \; E_o = 1.8 \text{ V}$$

Theoretically, Caro's acid is just about capable of bringing about such an oxidation at very low pH values (Figure 3.14), but in practice this would be very difficult to achieve with the use of 10% (w/w) Caro's acid, Since the potential generated by the Caro's acid is to some extent influenced by residual hydrogen peroxide[60].

Figure 3.15 indicates that, to separate the cobalt(III) produced, use can be made of the pH-dependence of the two systems Co^{2+}-CoO_2 and Co^{2+} -$Co(OH)_3$[66]. By use of the 10% Caro's acid, an Eh 1.18 V is generated at pH 4.0, this is sufficient to oxidise and cause the hydroxide to precipitate. It may also be concluded from Figure 3.14 that precipitation of $Co(OH)_3$ does not occur below pH 2.0, and this is supported by experimental observation.

A set of experiments was carried out to separate Co from Ni by using Caro's acid as an oxidant over the pH range of 3.5-4.0. The oxidative precipitation were carried out at an ambient temperature. The results show that the separation

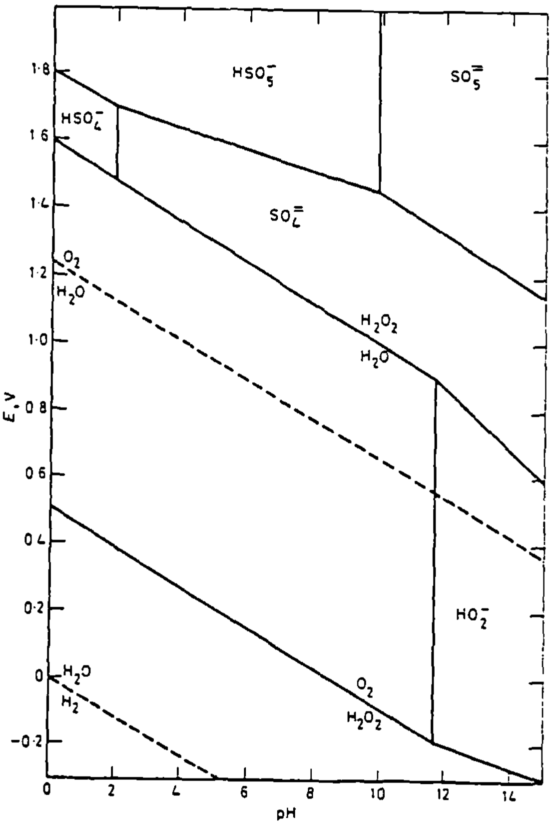


FIGURE 3.14 Potential - pH diagram for system H_2O_2-H_2SO_5-H_2O at 25°C.

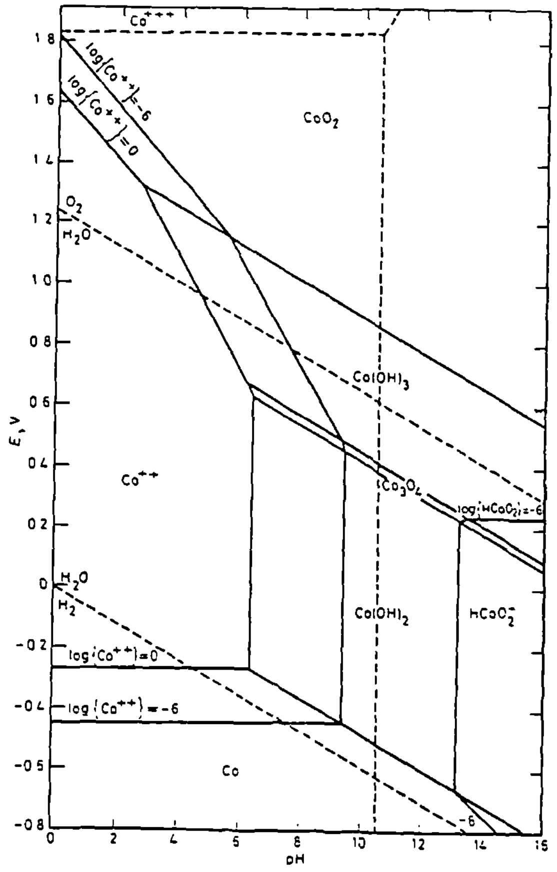


FIGURE 3.15 Potential - pH diagram for system Co-H_2O at 25°C.

process is very effective and it can be used over a wide range of metal concentrations and Co:Ni ratio (Tables 3.15-3.17). The main factor which influences the precipitation rate is pH of the solution. The preferred pH depends upon three factors: (a) The total metal concentration (b) The Co:Ni ratio in the feed solution and (c) the specification requirement for the final product.

Data in Table 3.21 indicate that as the pH is decreased towards 3.5 the cobaltic hydroxide precipitate becomes increasingly pure but precipitation efficiency declines. Conversely as the pH is raised, precipitation efficiency increases at the expense of product purity. Coprecipitation of Ni with $Co(OH)_3$ is influenced by pH and by Ni/Co ratio of the feed solution. At pH 4.0 some co-precipitation of Ni is also achieved. The co-precipitated Ni can be removed by washing the precipitate at pH 3.0 with a solution of H_2SO_4. The complete separation of nickel from the precipitate was very difficult.

The choice of pH regulating agent can also affect the product purity and separation efficiency. Data in Table 3.22 show that sodium hydroxide gives the highest precipitation efficiencies, whereas carbonate solution gives the greatest precipitation purity, probably due to the better buffering action of carbonate.

According to oxidation reaction, one mole of Caro's acid oxidizes two moles of cobalt. But a stoichiometric excess of Caro's acid is usually required to maximise the separation efficiency and also to allow for any decomposition reactions that occur during the separation process. In each experiment 2 times stochiometric excess of Caro's acid was used for the oxidative precipitation of cobalt. In order to achieve a maximum separation efficiency, 2 hours additional time was given after the complete addition of Caro'acid.

Several factors undoubtedly contribute to the need for an

TABLE 3.21 SEPARATION OF COBALT USING CARO'S ACID

Ni:Co Ratio in Feed Solution.	Reaction pH	% Ni Removed	% Co Removed	Ni:Co Ratio in Filtrate
6:1	3.5	1.3	77	27:1
6:1	4.0	5.0	88	54:1
7:1	4.0	4.0	87	55:1
9:1	3.5	1.5	75	34:1
9:1	4.0	6.0	85	55:1
10:1	3.5	2.2	74	38:1
11:1	3.5	3.4	72	39:1
19:1	4.0	10.0	80	86:1

Conditions:- pH Regulating Agent, Sodium Carbonate.

TABLE 3.22 SEPARATION OF COBALT USING CARO'S ACID

Ni:Co Ratio in Feed Solution.	Reaction pH	% Ni Removed	%Co Removed	Ni:Co Ratio in Filtrate
9:1	4.0	8	88	68:1
9:1	4.0	8	87	66:1
9:1	4.0	9	86	63:1
50:1	4.0	10	90	451:1

Conditions:- pH Regulating Agent, Sodium hydroxide.

excess of reagent: three that have been identified are given below.

(1) *Oxidation of nickel* - some Caro's acid is used owing to the reaction:

$$2Ni^{2+} + H_2SO_5 + 3H_2O \text{ -----> } 2NiO(OH) + H_2SO_4 + 4H^+$$

(2) *Catalytic decomposition* - both hydrogen peroxide and peroxymonosulphuric acid are slowly decomposed in the presence of transition metal ions, though the rate of decomposition of peroxymonosulphuric acid is much slower (Figure 3.4).

$$2H_2O_2 \text{ --------> } 2H_2O + O_2$$
$$2H_2SO_5 \text{ --------> } H_2SO_4 + O_2$$

The oxygen released is ineffective as an oxidant in this system. Since cobalt is much more effective catalyst than nickel in the decomposition of peroxide, this mode of decomposition is favoured in solutions with high cobalt concentration, particularly if elevated temperatures are used.

(3) *Reduction by* H_2O_2 - residual H_2O_2 is capable of reducing the cobalt(III) to cobalt(II), which than requires a molar equivalent of H_2SO_5 for re-oxidation.

The advantage of using Caro'acid is that oxidation is carried out at an ambient temperature and also produces a coarser particles of cobaltic hydroxide, which is much more easy to filter. Other oxidants such as Ni(III), chlorine and hypochlorite have also been studied for this oxidation reaction, however they either require the use of elevated temperature or necessitate the handling of chlorine based products and chloride containing effluents. Ni(III) also suffers from the fact that an extensive side stream process is required to generate the oxidant. All these oxidants produce a very fine particles of cobaltic hydroxide which is difficult to filter. Quantitative tests have shown that the filtration rates of cake produced using Caro's acid are some fifty times those obtained by other precipitation techniques.

The optimum conditions for the separation of cobalt from cobalt-nickel cake by Caro's acid are:

a) Complete dissolution of cobalt-nickel cake in sulphuric acid is necessary
b) For maximum cobalt separation the pH of the solution must be above 4 during Caro's acid treatment
c) In order to get maximum cobalt separation excess of Caro's acid (2 of stoichiometry) is required
d) Sodium carbonate or hydroxide can be used as a neutralizing agent.

3.14 INDUSTRIAL TRIAL AND CONCLUSIONS

Following encouraging laboratory studies on the separation of cobalt and nickel from cobalt-nickel cake, series of on-site trials were carried out at a copper-nickel recovery plant using a pilot Caro's acid plant supplied by Interox. A description of some of the tests is given below:

(A) Complete dissolution of primary cobalt-nickel cake was achieved by the addition of sulphuric acid to pH 1 and 20% H_2O_2. The resultant solution was found to be very concentrated (136 g/l). It was diluted with water to 48 g/l Ni and 6.9 g/l Co. This solution was treated with Caro's acid (pH 4) and the changes in composition with time are in Table 3.23.

(B) In this test the conditions were the same as described above except that concentrated solution was used at start. The results are In Table 3.24.

The solution pH was not deliberately altered after 13.05. The mixing of the solution for one hour before filtration increased the pH from 4.0 to 6.4 and hence the nickel content was higher than expected in the cobalt nickel cake.

TABLE 3.23 SEPARATION OF COBALT USING CARO'S ACID

	Time	Ni Conc., (g/l)	Co conc.
Start	11.28	46	3.81 g/l
	11.47	34	3.80 g/l
	12.00	32	1.46 g/l
	12.06	31	836 ppm
Filtrate	12.24	28	436 ppm

Cobalt rich filter cake 7.67% Ni 40.83% Co

TABLE 3.24 SEPARATION OF COBALT USING CARO'S ACID

	Time	pH	Ni Conc., (g/l)	Co conc.
Start	12.00	4.5	68	8.6 g/l
	12.10	4.2	64	4.7 g/l
	12.27	4.0	64	4.1 g/l
	12.40	4.5	64	8.5 g/l
	12.57	4.2	57	757 ppm
	13.05	4.0	59	253 ppm
Filtrate	14.05	6.4	55	49 ppm

Cobalt rich filter cake 16.0% Ni 20.0% Co

TABLE 3.25 WASHING TESTS ON CAKE FROM CARO'S ACID

TEST	TEMP.(°C)	pH	FILTRATE			FILTER CAKE	
			VOL.,ml	Ni, g/l	Co, ppm	Ni%	Co%
A	25	H_2O	830	4.45	33	8.47	45.56
B	25	3	850	7.70	100	5.08	47.14
C	60	H_2O	880	10.00	62	4.74	45.00
D	60	3	850	6.00	61	4.40	40.48
E	25	H_2O	855	8.00	4	11.75	37.20
F	25	3	880	12.00	438	9.17	32.81
G	60	H_2O	900	7.00	3	12.50	32.73
H	60	3	830	12.00	93	7.12	36.46

Tests A to D conducted on cake assaying 7.67% Ni 40.83% Co

Tests E to H conducted on cake assaying 16.0% Ni 20.0% Co

Wash Tests on Cake from Caro's Acid Precipitation

All test were conducted with 200 g of wet cake (35% H_2O) at 2:1, water:solids. The slurry was stirred for 1 hour before filtering. The Filter was further washed with 2 lots of 200ml of cold water whilst on the filter. The results are given in Table 3.25.

A series of six tests were carried out and the conclusions drawn from them were as follows:

1. Direct treatment of the primary cake with Caro's acid does not give satisfactory results.
2. Complete dissolution of the primary cake in sulphuric acid followed by Caro's acid treatment can reduce Co levels in the solution to less than 5 ppm.
3. The level of cobalt in the treated solution can be controlled by pH control. No significant amounts are removed at pH less than 2 while operation at pH 4-5 leads to Co removal to very low levels (few ppm).
4. The cobalt ratio in the solid product from Caro's acid treatment also varies with pH. Low pH treatment (pH 2.5) favours high Co:Ni ratios (>10) while treatment at pH 4-5 gives precipitation with Co:Ni ratios of less than 2:1. In a copper-nickel smelter plant primary cake with the pH kept above 4 a solid product containing 20% Co 16% Ni was obtained at a stage when the Co levels in the filtrate had reduced to 50 ppm. A sample of the cobalt oxide product obtained by treatment of the cake at lower pH and when the filtrate contained 440 ppm Co analysed at 41% Co 8% Ni.
5. The Co:Ni ratio in the solid product can be reduced by washing the product with water. For the two samples of cobalt oxide cake described in 4 above, three water washes (2:1, 1:1 and 1:1 water initial solids) increased the Co:Ni ratios to 5:1 for the 20% Co 16% Ni cake and of 9:1 for the 41% Co 8% Ni cake.
6. Treatment of the primary filter cake to reduce cobalt to acceptable levels can be carried out in four steps:-

A) Dissolution of the primary cake in sulphuric acid or sulphuric acid + SO_2. In laboratory it was found that treatment of 20 g of wet cake (62% moisture) with 100 ml of 4M sulphuric acid at 70°C dissolved more than 97% of the cake. Use of the solution to treatment a further 20 g of wet cake dissolved more than 95% of the second sample of cake. The overall effect was that 100ml of 4M sulphuric acid dissolved more than 96% of 40g of wet cake (about 90% of the solid material present).

These results show counter-current treatment of the cake with sulphuric acid will reduce the quantities of sulphuric acid required. Addition of SO_2 to the acid should also increase the amount of solid dissolved.

B) Filtration to remove any undissolved which should probably be returned to the matte treatment stage.

C) Treatment of primary cake solution with Caro's acid (1.5 of stoichiometry) at pH 3-5 with the choice of pH depending on the desired Co level for this Ni filtrate stream.

D) Filtration to obtain a Ni solution for return to the Ni recovery stage Plus a cobalt oxide cake. Results of the trials at the Cu-Ni smelter showed that the filtration is very easy at this stage and that the resulting cobalt cake is easy to handle.

7. Upgrading the Cobalt Cake

The cobalt cake from the Caro's acid treatment can be upgraded by a combination of a) water washing and b) retreatment of the cake or its solution with Caro's acid at low pH (about 2.5). The filtrate from 7a should be returned to the Ni recovery stream.

The filtrate from 7b can be returned to the first stage Caro's acid treatment or can be treated separately to reduce the cobalt levels. The production of good quality cobalt oxide should be achieved.

8. No difficulties were experienced in the use of the pilot Caro's acid plant on site at a Cu-Ni smelter and installation of a commercial plant with proper safety devices should present no problems and provide a Caro's acid solution that will achieve the desired results.

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CHAPTER 4

LEACHING OF GOLD FROM COMPUTER SCRAP BY THIOUREA

Page

CHAPTER FOUR

LEACHING OF GOLD FROM COMPUTER SCRAP BY THIOUREA

4.1 INTRODUCTION

Although gold and silver were probably the first metals to be used by man, the use was primarily limited to ornamental purpose and coinage for a very long period in history. Industrial applications have only become significant in recent times but have grown to the point of overshadowing the earlier uses. Although gold occurs in low concentrations in its ores, and other low grade secondary arisings, its high market value justifies full recovery. The improvement in the precious metal extraction has recently begun to contribute to the development of effective recovery techniques.

Due to higher price, the improvement in the technology of leaching and precipitating gold from ore and many sources of gold, that were once considered uneconomic, can now be exploited. The recovery of gold from low-grade resources such as electronic scrap is still very difficult due to the complex nature of the scrap material, which contains an extremely low concentration of gold in the presence of high concentrations of other metals such as copper, lead, tin and iron. Electronic scrap generation is accelerating with the growth of the computer and communications technology. Technological obsolescence of crossbar switching mechanisms in the telecommunications field alone represents an easily segregated scrap source for precious metals recovery with selected high-grade components yielding 200-600 troy ounce gold per ton[1]. The recovery of gold from computer scrap involves the pretreatment of the sample with acid to dissolve all the metal impurities and then subsequent leaching of gold. Recent research efforts have concentrated on more economical and effective approaches to gold recovery from low grade materials. The result of these research efforts include the use of three main leaching processes for the recovery of gold, a) cyanide leach[2], b) thiosulphate leach[3], and c) thiourea leach[4]. Each of these reaction processes are described in the following sections.

4.2 CYANIDE LEACHING (CYANIDATION)

Cyanide based process for the recovery of gold is actually a combination of hydro-, pyro- and electrometalurgical processes[2].

In cyanidation, the gold contents are leached out by an alkaline cyanide solution which is formed by adding lime and sodium or potassium cyanide to the pulp. The consumption of the reagents depend upon the nature of the ore because most of the impurities can consume cyanide solution during the leaching process. The leaching process is normally carried out continuously by passing the leach pulp through a series of agitated vessels. Since oxygen is essential to the dissolution process, air is bubbled into the pulp.

The net result of cyanidation is the solubilization of the gold to form aurocyanide ions, the overall reactions may be represented as follow[5].

$$2Au + 4CN^- + O_2 + 2H_2O \longrightarrow 2Au(CN)_2^- + H_2O_2 + 2OH^-$$

or

$$4Au + 8CN^- + O_2 + 2H_2O \longrightarrow 4Au(CN)_2^- + 4OH^-$$

The above equation show that oxidising conditions are needed in order for cyanidation to proceed. Extra alkali in the form of lime or sodium hydroxide is usually added to keep the system at pH 10-11. This "protective alkalinity" is required to prevent the generation of acid during cyanidation and hence the production of deadly HCN gas. The cyanide may be added as NaCN or KCN. If NaCN is used the addition of less alkali is required but the overall cost is greater. After filtration, the metallic gold can be recovered by either zinc precipitation or electrowinning.

a) Zinc Precipitation

After filtration, the filtrate is then clarified, generally by pre-coated filters, and then vacuum-deaerated, these operations being an essential pre-requisite of zinc precipitation. This process also known as cementation, is a consequence of the relative electropositive nature of zinc in cyanide solution: it dissolves more readily than gold and, when added to gold solution, it displaces the gold from the solution:

$$2Au(CN)_2^- + Zn \text{ -------> } 2Au + Zn(CN)_4^{2-}$$

or

$$2Au(CN)_2^- + Zn + 3OH^- \text{ ----> } 2Au + HZnO_2^- + 4CN^- + H_2O$$

The precipitate is removed by filtration, and the gold slime is then washed by sulphuric acid to remove excess zinc, re-filtered, clarified and finally smelted with various fluxes such as borax and silica to produce bullion for subsequent refining.

b) Electrowinning

For the electrowinning of gold from cyanide solution numerous designs of cells have been proposed (Figure 4.1 and 4.2) the majority of which use steel wool as the cathode because it provides a very large surface area for electrolytic desorption of precious metals. When a cathode is loaded with the required amount of gold, it is removed from the cell and smelted with a flux to produce a high purity bullion.

4.2.1 Activated Carbon for the Adsorption of Gold

The fact that activated carbon has the property of adsorbing precious metals from solutions was first published in 1847[6]. In subsequent years, a great deal of work was carried out to develop an overall recovery process using carbon, but all attempts were uneconomical because the loaded carbon had to be smelted to recover the gold.

It was not until 1950 that Zadra, at the United States Bureau of Mines Research Centre in Reno, Nevada, developed a technique for stripping the loaded carbon using sodium sulphite-sodium hydroxide mixtures and then recovering the

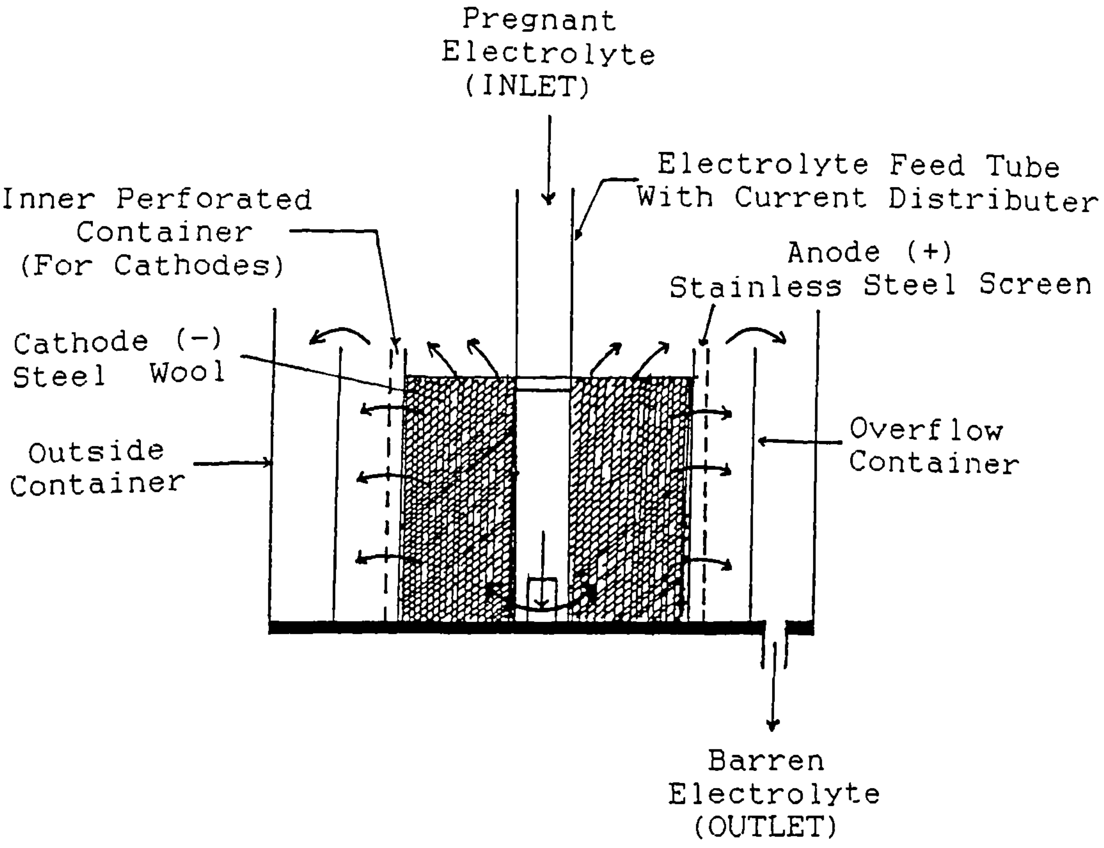


FIGURE 4.1 The circular electrowinning cell.

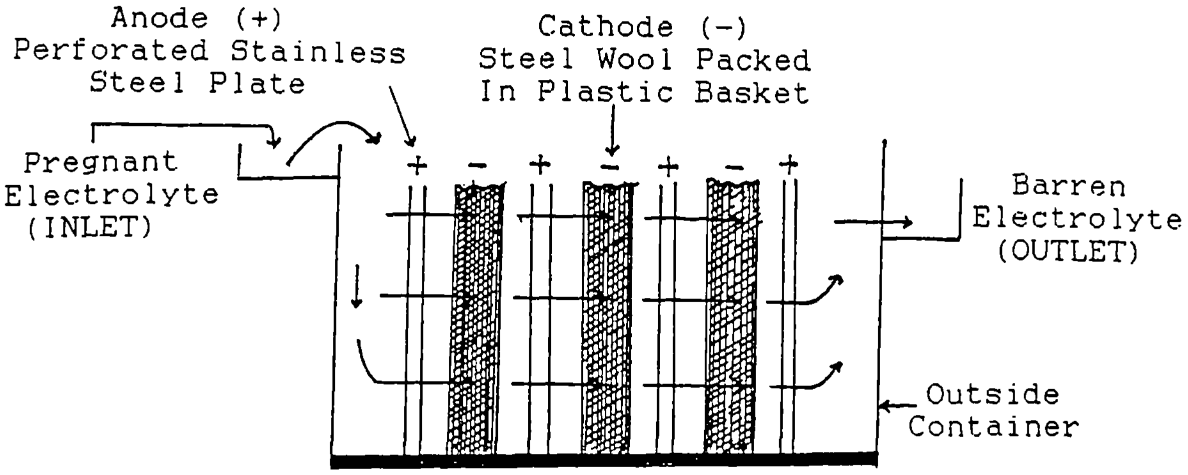


FIGURE 4.2 The rectangular electrowinning cell.

gold from the stripping solution by electrolysis[7]. However, this process was not effective for stripping silver and further test work was carried out on alternative stripping techniques. In 1952, Zadra published another paper describing the use of a hot sodium hydroxide - sodium cyanide stripping technique which was effective in stripping both gold and silver[8].

4.2.2 Carbon based Processes for the Recovery of Gold

The three main processess used for the adsorption of gold on activated carbon are called, carbon-in-pulp (CIP), carbon-in-leach (CIL) and heap leaching. The simplified schematic flowsheet of carbon based processes is shown in Figure 4.3. The flowsheet consists primarily of four operations:

1) **Adsorption** of the gold by activated carbon[9-14].
2) **Elution** of the gold from the loaded carbon[15-23].
3) **Recovery** of the gold from the pregnant solution.
4) **Regeneration** of the eluted carbon.

a) Carbon-in-pulp (CIP)

In 1952, a paper published by Zadra includes a description and flowsheet for CIP process which is essentially the same as is known today[8]. This technique was used in the first major CIP plant constructed and commissioned in 1973 by Homestake Gold Mining Company[24]. Since then there have been numerous CIP plants built in the USA, South Africa, The Philippines, Chile and Australia[25,26]. Thus the CIP process enjoys widespread acceptance as an economical and effective method for precious metal recovery.

In the carbon-in-pulp (CIP) process, dissolved gold is recovered directly by adsorption onto activated carbon. The CIP adsorption circuit is normally designed on the basis of counter current contact between activated carbon and discharged pulp from cyanidation in a series of agitated contactors. The pulp is fed to the first contactor and is continuously transferred from stage to stage until the barren pulp is discharged from the last contactor. The

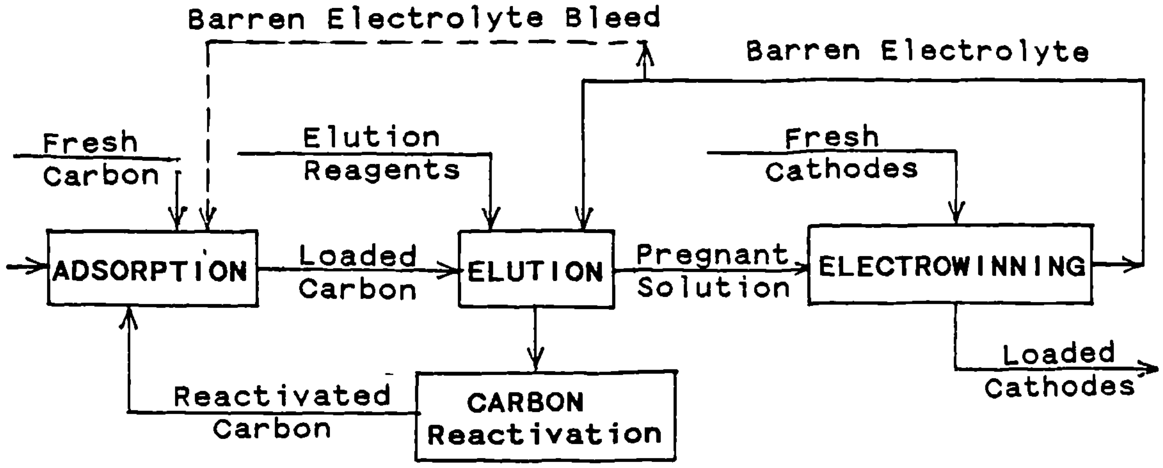


FIGURE 4.3 Schematic flowsheet for Carbon based processes.

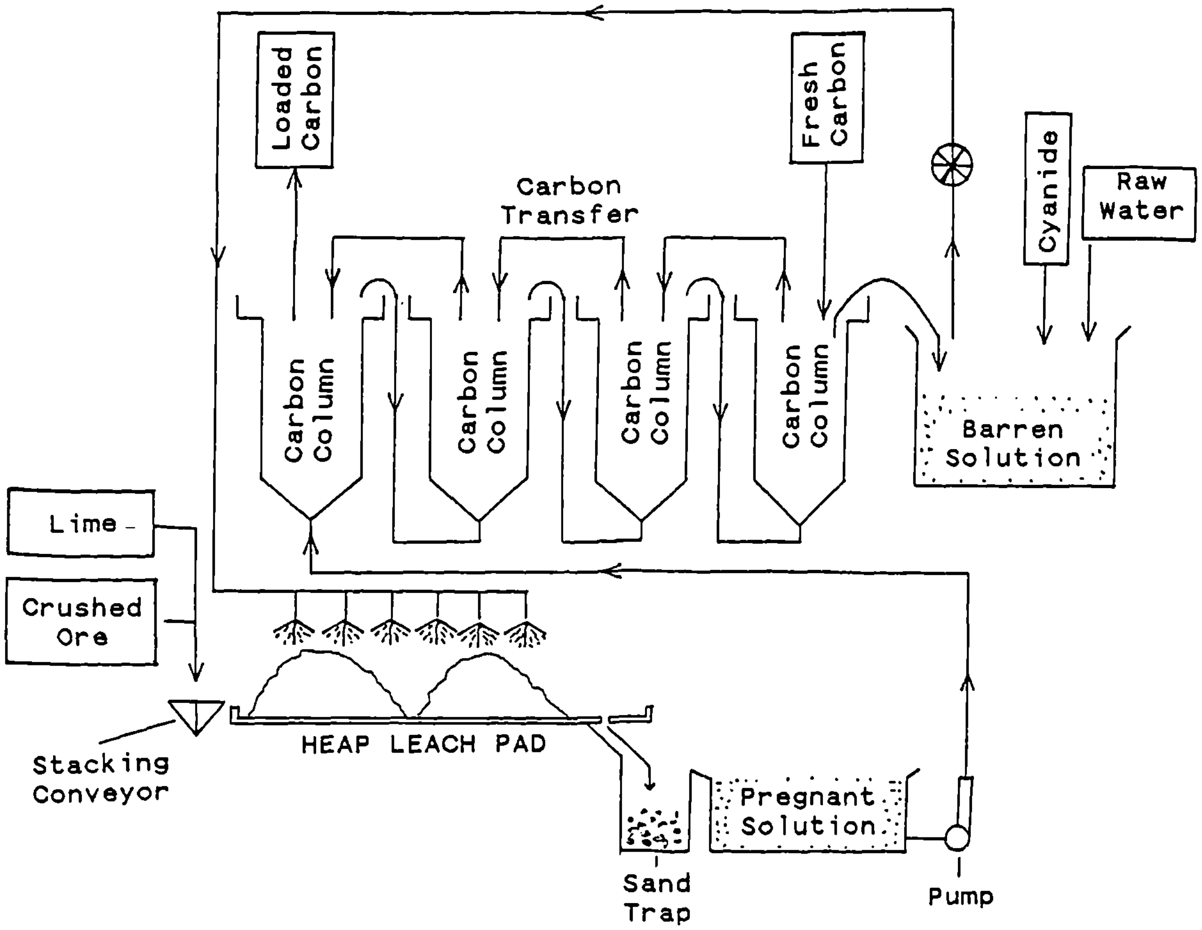


FIGURE 4.4 Heap leach - adsorption circuit.

barren pulp is generally disposed off as tailings. Fresh carbon is added to the last contactor and is progressively loaded with gold as it advances intermittently through the circuit. The loaded carbon from the first stage is screened and washed before transfer to the elution section[27].

b) Carbon-in-leach (CIL)

The carbon-in-leach (CIL) process is basically similar to the carbon-in-pulp (CIP) process except that in CIP the leaching is virtually completed before the adsorption started but in CIL the two occur simultaneously[28]. Cyanidation and carbon adsorption are carried out in the same vessel and the free ions, liberated as a result of gold dissolution by cyanide, migrate to the active carbon surface and are adsorbed. It is postulated that high rate of such transfer improves the rate of gold dissolution.

c) Heap Leaching

Cyanide heap leaching of gold is a relatively recent hydrometallurgical development. It is particularly suitable for recovery from low grade gold ore and deposits. In heap leaching the ore is mixed with lime and stacked on impermeable pads. After the stacking operation the leaching is then carried out spraying cyanide uniformly over the heaps. The cyanide solution percolates through the ore and the pregnant solution runs into perforated pipes at the base of the heap, flowing into a holding pond from which it is pumped through a cascade column unit[29]. The gold in the solution is adsorbed on to the carbon in the columns (Figure 4.4).

4.3 THIOSULPHATE LEACHING

There has been a growing interest in the development of viable alternatives to the cyanide leaching of precious metal ores containing gold and silver. The primary factors responsible for this interest are the concerns regarding the high toxicity of the solutions, the cost of the reagents and the need to decontaminate the effluent. The ability of gold and silver to form stable anionic complexes with thiosulphate has been exploited in the development of alkaline thiosulphate leaching methods for ores and leach tailings containing gold and silver values. Ammonium thiosulphate has been used for many decades as a fertilizer and consequently, from an environmental standpoint, it has a definit advantage over cyanide.

The first reported use of thiosulphate for the precious metal recovery dates back to the early 1900s. In a method known as Patera's process, gold and silver ores were first given a chloridizing roast and then leached with sodium thiosulphate.

The overall chemical reaction during the thiosulphate leaching may be represented as follows:

$$2Au + 4S_2O_3^{2-} + H_2O + 1/2O_2 \text{ ----> } 2Au(S_2O_3)_2^{3-} + 2OH^-$$

After many decades, the interest in the use of thiosulphate was revived by Berezowsky and Sefton[30]. They developed an atmospheric ammoniacal thiosulphate leach process to recover gold and silver from residues of the ammoniacal oxidation leaching of sulphide copper concentrates. They found the thiosulphate leach system to yield higher extractions (92-94% Au, 83-87% Ag) than conventional methods such as cyanidation or brine leaching. They were able to account for 90-95% of the thiosulphate, but did not attempt to identify the degradation products of the thiosulphate. Umetsu and Tozawa[31] investigated the dissolution of pure gold in ammoniacal thiosulphate solutions containing copper ions and arrived at the following conclusion: a) in the absence of $Cu(NH_3)_4^{2+}$ the kinetics of dissolution of gold is very slow, b) at a leaching temperature of 65-100°C, the dissolution of gold is inhibited by the formation of a copper sulphide coating, and c) vigorous stirring and high temperature (>140°C) decrease the dissolution due to excessive oxidation of thiosulphate ions.

Two patents[32,33] were assigned to B. Kerely for the use of sulphite ions to control the stability of solution during leaching. Kerely claimed that sulphite ions complexed sulphide ions in solution, thereby preventing precipitation of metal sulphides.

4.4 THIOUREA LEACHING

Gold is traditionally extracted from its ore and low-grade secondary materials by cyanidation. However, the process is handicapped by its slow rate, being susceptible to interference by other metal ions and poisonous nature of cyanide compounds. A large number of researchers have found that with appropriate oxidants, thiourea can dissolve gold effectively in acidic solution and could thus be a potential substitute for cyanide leached solutions[34-43]. Its overall reaction is

$$Au + 2CS(NH_2)_2 \text{ -----> } Au[2CS(NH_2)_2]_2^+ + e^-$$

The charged complex is positive in contrast with the negatively charged gold complexes formed in most other systems[44-46].

4.4.1 Effect of Oxidant

The effect of various oxidants, including Fe(III)[36], Cu(II)[37], ozone[48], H_2O_2[4], and air[41] on the gold dissolution have been studied and possible mechanism were also investigated. Ferric ions produced the fastest initial rate of gold dissolution[35,36]. Oxidation by ozone gas has been described to gave high dissolution rates[47,48] with large consumption of thiourea. Hydrogen peroxide was found to be better than air and comparable to dissolved oxygen as an oxidant[4]. The choice of acid was also investigated by many workers and sulphuric acid was found to be more effective than nitric or hydrochloric acids. Furthermore it was also accepted that the dissolution of gold by acidothiouration was much faster than by cyanidation[43,49].

In the presence of ferric ions, which are the most commonly used oxidant for the leaching of gold in thiourea solutions, the oxidation and complexing of gold can be represented by the following reaction[50]:

$$2Au + 4CS(NH_2)_2 + 2Fe^{3+} \text{---->} Au[2CS(NH_2)_2]_2^{+} + 2Fe^{2+}$$

in the presence of hydrogen peroxide the following reaction has been proposed[35,50]:

$$2Au + 4CS(NH_2)_2 + H_2O_2 + 2H^{+} \text{---->} 2Au[2CS(NH_2)_2]_2^{+} + 2H_2O$$

The dissolution of gold by thiourea needs to take place in an acidic medium to prevent the rapid conversion of thiourea to urea, $[CO(NH_2)_2]$, and sulphate ions[35] in the presence of oxidants.

In contact with an oxidant such as hydrogen peroxide, thiourea may be oxidised in successive stages to form several products. The first is the formation of formamidine disulphide (FD)[43]:

$$2TU \rightleftharpoons 2FD \text{-->} TU + \text{Sulphinic compound} \text{-->} \text{Cyanamide} + S$$

The first oxidation product of thiourea is formamidine disulphide, FD , in acid solutions, as a result of a reversible reaction. The formation of formamidine disulphide (FD) can act as an oxidant and increase the rate of dissolution of gold in thiourea solution. Formamidine disulphide is formed *in situ* by the action of oxidants, such as hydrogen peroxide, on thiourea according to the following rapid reversible reaction[50]:

$$2CS(NH_2)_2 \text{---->} (NH)_2(NH)CSSC(NH)(NH)_2 + 2H^{+} + 2e^{-}$$

In a second irreversible step, FD undergoes disproportionation to yield thiourea and an unidentified sulphinic compound, which in a third, also irreversible, step finally decomposes to cyanamide (H_2NCN) and elemental sulphur, or to urea and sulphate ions. The rate and extent of these reactions depend on, among other factors, the pH value and the redox potential[35,39]. The elemental sulphur created at the end of this decomposition has a detrimental effect by passivating the leachable gold surface and precipitating some gold from solution.

The study of the effect of oxidizing agents shows that there is an equilibrium between thiourea and formamidine disulphide. The agressiveness and the leaching efficiency of the solution depends on this equilibrium. For the optimum extraction of gold to occur, a redox potential higher than 150 mV and pH value of 1.5, need to be maintained. In addition, as Schulze[39] and Nomvalo[50] have shown, higher redox potentials results in superior dissolution kinetics. However, at redox potentials greater than 250 mV, the irreversible oxidation of thiourea to secondary oxidation products, such as cyanamide and elemental sulphur, leads to the unacceptably rapid consumption of thiourea. Schulze[39] described a procedure in which the consumption of thiourea can be suppressed, at redox potentials as high as 400 mV, by the addition of sulphur dioxide to the solution in the form of gas or as sodium metabisulphite powder. However, efforts by and Nomvalo[50] to reproduce the results obtained by that method were unsuccessful.

Groenewald[35] reported that iron(III) oxidizes thiourea to its secondary oxidation products less rapidly than other oxidants, which retard the dissolution rate of gold. The slow rate of the redox reaction between iron(III) and thiourea is due to the formation of the stable complex in a sulphate medium.

$$Fe^{3+} + CS(NH_2)_2 + SO_4^{2-} \rightleftharpoons [Fe(III)SO_4CS(NH_2)_2]^+$$

The end product of the reduction of iron(III) was identified as the complex $[Fe(II)(CS(NH_2)_2)]SO_4$. Since the passivation of mineral particles is thus decreased by the use of iron(III) as an oxidant, the dissolution rate of gold by fresh acidic solutions of thiourea and iron(III) is higher than that obtained with other oxidants. This phenomenon would obviously also increase the consumption of thiourea. The high consumption of reagents is, in fact, one of the main obstacles to the more common use of thiourea as a lixiviant for gold.

4.4.2 Adsorption of Gold

a) Adsorption on Activated Carbon

The adsorption of gold-cyanide complex on the activated carbon has already been described in detail in cyanide leaching section. Activated carbon can also be used for the adsorption of gold from acidic thiourea solution[51]. The adsorption process is usually carried out by the fluidized bed method. Prior to adsorption, the carbon is washed with water for at least one hour by fluidization of the bed to twice the settled bed height. This process will remove all the carbon fines, which is a major source of gold loss, and also provides rounded shaped activated carbon particles, which have less attrition rate during the adsorption circuit. The adsorption circuit usually consists of a series of columns. In the adsorption step, the pregnant solution is pumped upwards through the columns. The upward flow of the solution in the columns fluidizes the carbon bed to 1.0-1.5 times its settled height. The solution is circulated through each column via fine screen which retained any particles of carbon that has been washed out of the column. The proposed flowsheet of thiourea CIP process is shown in Figure 4.5.

Staden and Laxen[40] have studied the adsorption of gold-thiourea complex on the activated carbon and found that after several hours the decrease in the adsorption rate is not due to the fact that carbon has reached in equilibrium with gold loading. But this decrease in adsorption occurred because the carbon had been contaminated by the oxidation products of thiourea. They concluded that up to 99% adsorption can be achieved by using thiourea solution with

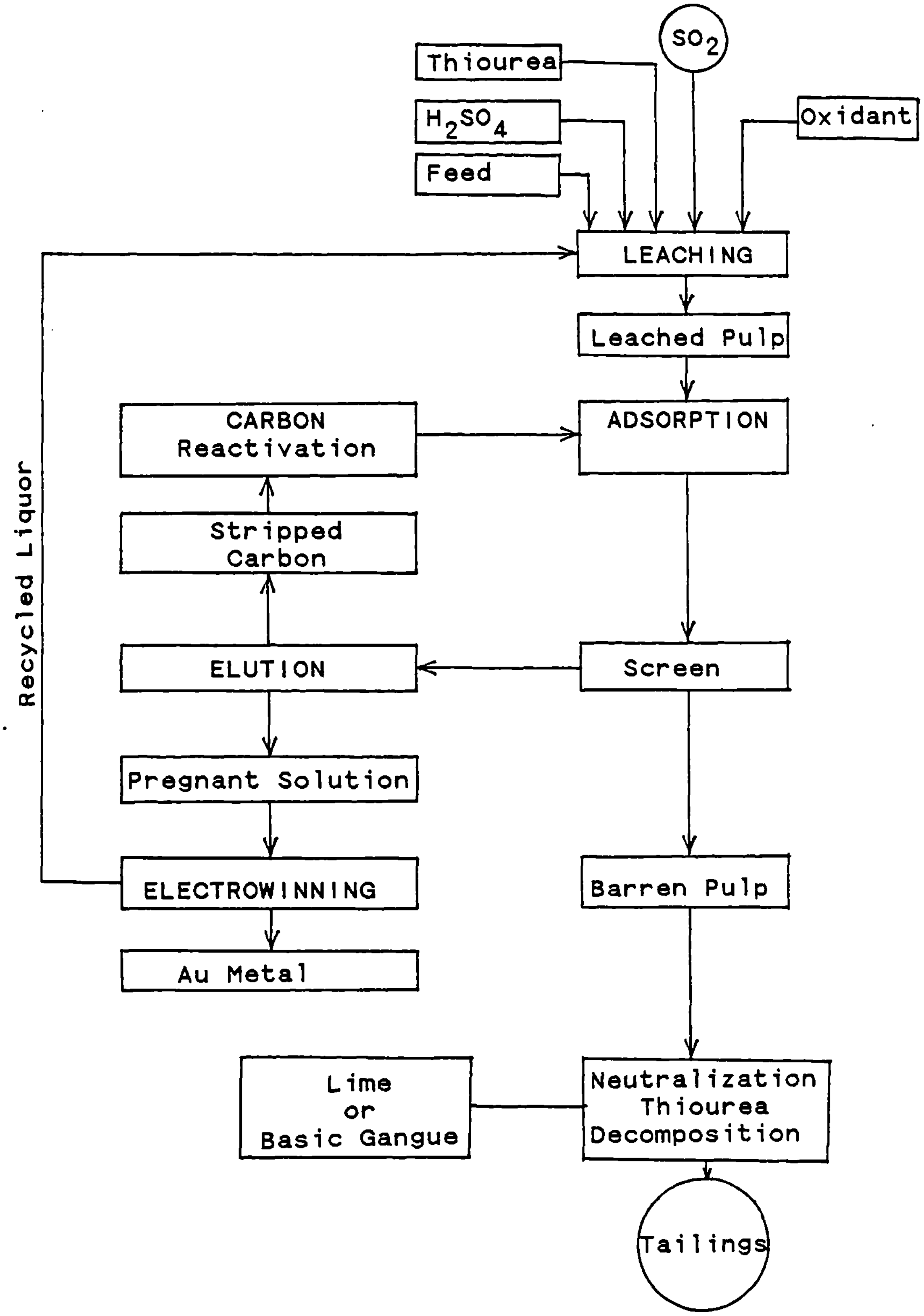


FIGURE 4.5 Thiourea CIP process.

low redox potential and ferric ion concentration.

b) Adsorption on Resin

The thiourea leach solutions contain, besides the gold dissolved as a cationic complex, $Au[CS(NH_2)_2]^+$, considerable amounts of iron (in the form of Fe(III) and Fe(II) compounds). This complex can be extracted with the weak-acid cationite, di-2-ethylhexyl phosphoric acid (D2EHPA), to a limited extent[44], whereas it can be extracted completely with the more strongly acid cationites, dioctyl sodium sulphosuccinate[44] and 100% tributyl phosphate[46].

Becker, Knothe and Lobel[4] have studied the adsorption of gold-thiourea complex along with Fe(II) and Fe(III) compounds by using two solid, strong-acid exchanger, Wofatite gel-type resin KPS and macroporous resin KS10 as well as the liquid exchanger D2EHPA (sodium salt of D2EHPA was used which had shown that the sodium salt, in contrast to free D2EHPA, is a good extractant). The results have shown that the adsorption of gold and iron by cationite takes place purely by means of an ion-exchange mechanism.

From the elution results it has been concluded that the gold complex is bound considerably stronger than the Fe(II) and Fe(III) complexes. The iron complexes (in the absence of gold) occupy virtually all sites of the exchanger, whereas gold species occupy only about 44% (KPS) and about 66% (KS10) of the resin capacity. This may be due to the steric hindrence, because the access of the relatively large ($Au[CS(NH_2)_2]^+$) species to functional groups may be inhibited or blocked. This is supported also by the fact that, on the macroporous resin KS10, higher adsorption rates were obtained than on the gel-type KPS resin.

4.5 PRELIMINARY ANALYSIS OF COMPUTER SCRAP SAMPLE

The computer scrap sample under investigation was supplied by BEWT (Water Engineering) Ltd., for the recovery of gold. This sample contains a very low percentage of gold along with a significantly high percentage of other metals, like copper, iron, lead and tin. Since the scrap material was very complex and contained an extremely low concentration of gold, representative samples for assay were difficult to obtain. Although, a large number of tests were performed to find the weight percentage of each metal present in the sample it was difficult to find out the exact weight percentage of each metal due to the complex nature of the material and the heterogenous distribution of each metal in the sample. After some initial experiments, an attempt was made to homogenise the sample manually and then the sample was divided into different portions. Different weights of sample were then taken from each portion and dissolved in *aqua-regia* and analysed. On the basis of the results of these tests, the weight % of different metals along with their standard deviation is given in Table 4.1.

TABLE.4.1

METAL	WEIGHT, %
Au	0.06 ± 0.02
Cu	18 ± 2
Fe	8 ± 1
Pb	11 ± 1
Sn	11 ± 1

Apart from these five metals some other metal impurities i.e., Zn, Mn, Ni, and Co etc. were also present. Silicon in the form of quartz was also a part of the sample.

Copper and iron were present in the form of very small pieces of wires and coils. Most of these wires were plastic coated. Above 35% of sample consisted of quartz and plastic (total residue).

4.6 THIOUREA LEACHING

The computer scrap sample contains mixture of Cu, Fe, Pb and Sn along with gold, and hence before using the acidic thiourea solution to extract gold, the sample was preleached with nitric, hydrochloric or sulphuric acid. After the pretreatment step, thiourea leaching was carried out in a glass beaker of 500ml capacity connected with a flange lid. Leaching was performed on a hot magnetic plate and mixing was carried out with magnetic stirrer. A reflux condenser was mounted on the top of the leaching beaker to avoid the loss of water (Figure 4.6). Most of the tests were performed using 3g of sample and 250ml of 3% thiourea solution containing 1% sulphuric acid and 0.15% Fe^{3+} or Cu^{2+} (oxidant). The thiourea and oxidizing agent were added and stirred for 3 minutes and then gold containing residue was added. For each test leaching was carried out at 45°C for 1, 1.5 or 2 hours. The choice of temperature was determined by the lower stability of thiourea at high temperatures. A temperature between 35-45°C is considered to be the optimum for the recovery of gold in thiourea solution. The extraction of gold can also be achieved in thiourea solution by leaching the gold sample at room temperature. But extraction at 35-45°C requires short leaching times to extract 90% of gold. The extraction of metal values in preleached acid solution and the subsequent extraction of gold in thiourea solution is described in the following sections.

4.6.1 Preleaching with Nitric Acid (1st. Option)

In the following set of experiments, leaching was carried out in three steps:

a) preleaching with nitric acid
b) subsequent leaching with hydrochloric acid
c) leaching the remaining residue with acidic thiourea solution containing different oxidants, e.g. Cu^{2+}, Fe^{3+} or H_2O_2.

Nitric acid preleaching was carried out by using setup as shown in Figure 4.6. In all experiments, a 3g sample was

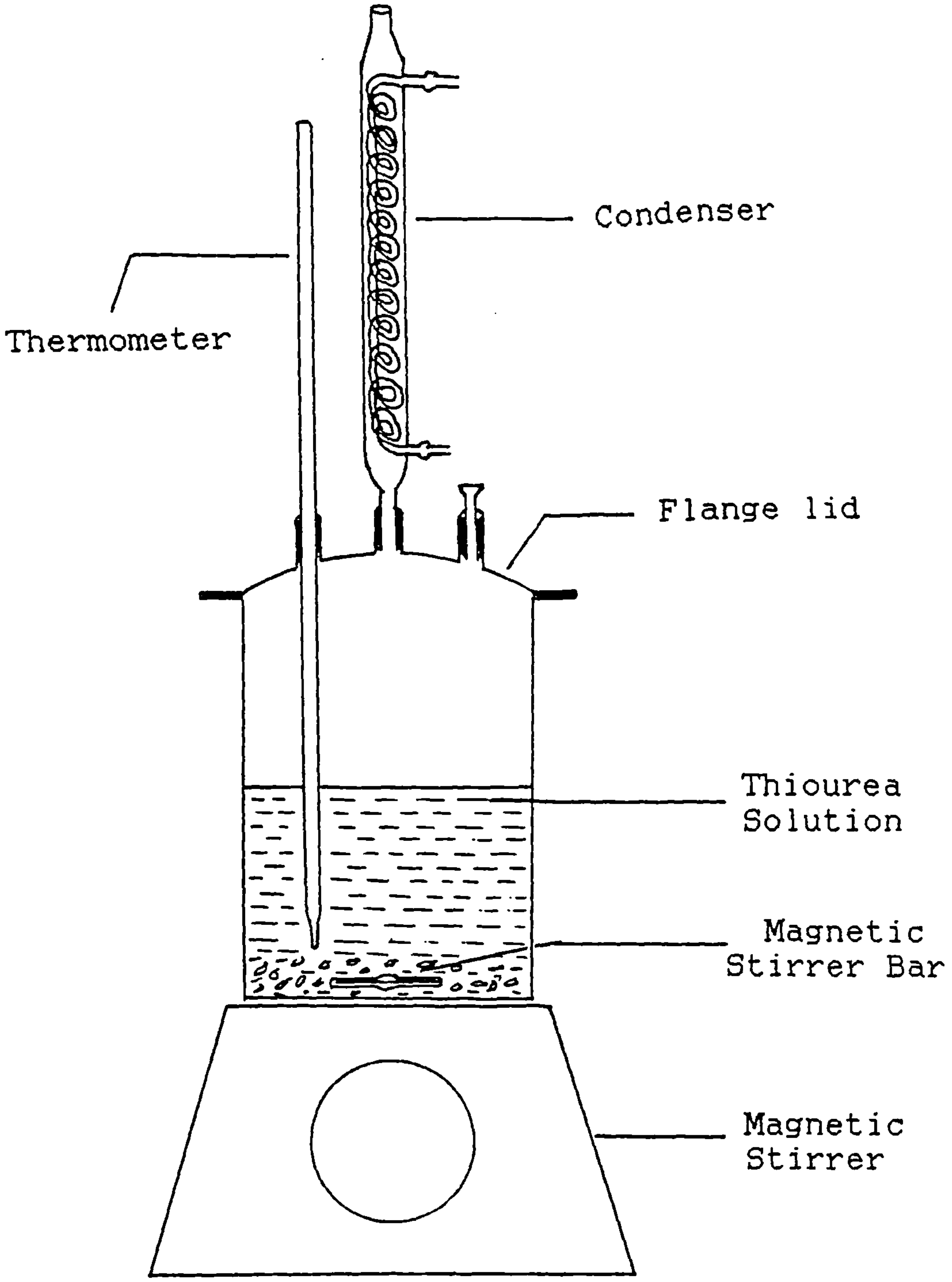


FIGURE 4.6 Experimental setup for Thiourea leaching.

preleached with 250ml of 3M HNO_3 solution. The leached solution was allowed to cool and then filtered under suction. The residue was washed with distilled water and used for second step. The filtrate was diluted to 250ml with distilled water and analysed by AAS. The flow diagram of the leach process is shown in Figure 4.7.

According to first option, the washed residue was leached with 250ml of 3M HCl at different temperatures for 1, 1.5 and 2 hours, while stirring the solution magnetically. The solution was cooled and filtered and the residue was washed with distilled water and used for third step. The filtrate was made up to 250ml with distilled water and analysed by AAS.

The washed residue was leached with 250ml of 3% thiourea solution containing 1% H_2SO_4 and different oxidants at 45°C for different duration of time. The final volume of the filtrate was made to 250ml with distilled water and analysed by AAS.

Three oxidants, $Fe_2(SO_4)_3$, $CuSO_4.5H_2O$ and H_2O_2 were used in different experiments. The oxidant, 0.15% Fe^{3+}, 0.15% Cu^{2+} or 0.25% H_2O_2 was added with thiourea in the leach solution. Experiments with the combinations of Cu^{2+} plus H_2O_2 and Fe^{3+} plus H_2O_2 (0.15% + 0.25%) were also carried out. The results of different tests are given in Tables 4.2-4.9.

In all the above experiments the sample was preleached with HNO_3 which dissolved 95-98% of Cu, and all of the Fe and Pb in 2 hours at 70°C (Figure 4.8). But Sn under the same conditions reacts with nitric acid to form solid hydrous tin(IV) oxide. The chemical reaction may be represented by the following equation:

$$Sn + 4HNO_3 \text{ -------->} SnO_2(H_2O)_n + 4NO_2$$

After the completion of leaching process these off-white precipitates settled on the top of the residue and gave a

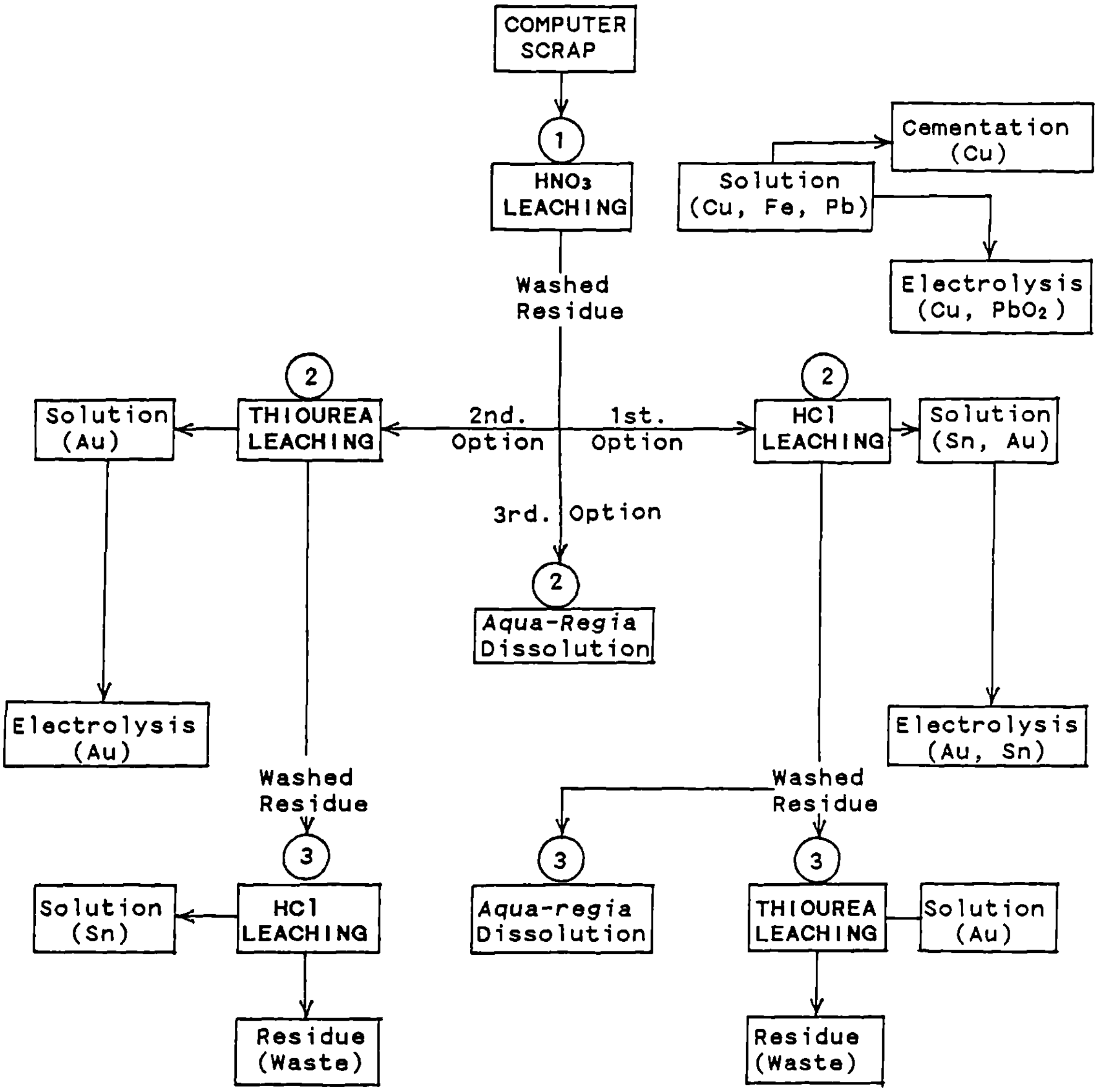


FIGURE 4.7 Schematic flowsheet for the extraction of metals from computer scrap.

(A) TABLE 4.2 EXTRACTION OF METAL VALUES

	HNO_3 Leach Extraction		HCl Leach Extraction		Thiourea Leach Extraction	
Metal	%	mg	%	mg	%	mg
Au	-	-	75	1.25	15.0	0.25
Cu	94	450	1	7.0	-	-
Fe	88	185	5	12.0	0.2	0.5
Pb	97	323	1	4.25	0.8	2.75
Sn	-	-	80	243.0	-	-

Conditions: Leaching time, HNO_3, HCl, and Thiourea, 2 hrs; Temp., HNO_3, and HCl, 70°C; Oxidant, Cu^{2+}.

(B) TABLE 4.3 EXTRACTION OF METAL VALUES

	HCl Leach Extraction		Thiourea Leach Extraction	
Metal	%	mg	%	mg
Au	69	1.25	27.0	0.5
Cu	1	6.75	-	-
Fe	4	8.50	0.2	0.5
Pb	2	7.5	1.1	3.7
Sn	67	202.0	-	-

Conditions: Leaching time, HNO_3, 2 hrs; HCl, 1.5 hrs; Thiourea, 1 hr; Temp., HNO_3, 70°C; HCl, 60°C; Oxidant, Cu^{2+}.

(C) TABLE 4.4 EXTRACTION OF METAL VALUES

	HCl Leach Extraction		Thiourea Leach Extraction	
Metal	%	mg	%	mg
Au	71	1.5	24.0	0.5
Cu	2	12.25	0.3	1.5
Fe	7	16.25	-	-
Pb	2	6.0	0.7	2.25
Sn	80	241.0	-	-

Conditions: Leaching time, HNO_3, 2 hrs; HCl, 1.5 hrs, Thiourea, 1 hr; Temp., HNO_3, 60°C; HCl, 70°C; Oxidant, Fe^{3+}.

(D) TABLE 4.5 EXTRACTION OF METAL VALUES

	HCl Leach Extraction		Thiourea Leach Extraction	
Metal	%	mg	%	mg
Au	41.0	0.75	56.0	1.0
Cu	0.4	2.25	-	-
Fe	2.0	4.5	0.95	2.0
Pb	0.3	1.0	0.75	2.5
Sn	78.0	235.0	-	-

Conditions: Leaching time, HNO_3, 2 hrs; HCl, 1 hrs; Thiourea, 1 hr; Temp., HNO_3, 70°C; HCl, 50°C; Oxidant,Fe^{3+}.

(E)

TABLE 4.6 EXTRACTION OF METAL VALUES

	HCl Leach Extraction		Thiourea Leach Extraction	
Metal	%	mg	%	mg
Au	75	1.25	15.0	0.25
Cu	1	5.5	0.05	0.25
Fe	5	11.0	0.1	0.25
Pb	2	7.5	-	-
Sn	65	196.0	-	-

Conditions: Leaching time, HNO_3, 2 hrs; HCl, 1.5 hrs; Thiourea, 1 hr; Temp., HNO_3, and HCl $70^{\circ}C$; Oxidant, H_2O_2.

(F)

TABLE 4.7 EXTRACTION OF METAL VALUES

	HCl Leach Extraction		Thiourea Leach Extraction	
Metal	%	mg	%	mg
Au	77	1.5	6.4	0.13
Cu	3	17.25	-	-
Fe	9	20.75	0.3	0.5
Pb	3	12.5	0.9	3.25
Sn	85	254.0	-	-

Conditions: Leaching time, HNO_3, and HCl, 1.5 hrs; Thiourea, 1 hr; Temp., HNO_3, HCl, $70^{\circ}C$; Oxidant, Cu^{2+} + H_2O_2.

(G)

TABLE 4.8 EXTRACTION OF METAL VALUES

	HCl Leach Extraction		Thiourea Leach Extraction	
Metal	%	mg	%	mg
Au	82	1.75	6.6	0.15
Cu	4	18.0	0.05	0.25
Fe	13	27.25	-	-
Pb	4	15.0	0.07	0.25
Sn	96	352.0	-	-

Conditions: Leaching time, HNO_3, HCl, 1.5 hrs; Thiourea, 1 hr; Temp., HNO_3, HCl, $70^{\circ}C$; Oxidant, Fe^{3+} + H_2O_2.

(H)

TABLE 4.9 EXTRACTION OF METAL VALUES

	HCl Leach Extraction		*Aqua-Regia* Extraction	
Metal	%	mg	%	mg
Au	76	1.25	18	0.35
Cu	4	22.25	1	5.25
Fe	14	30.0	2	3.25
Pb	5	18.75	1	4.25
Sn	97	293.0	1	3.5

Conditions: Leaching time, HNO_3, HCl, 1.5 hrs; Temp., $70^{\circ}C$.

clear blue solution. After preleaching with HNO_3, the residue containing hydrated stannic oxide (SnO_2) and gold were leached with HCl, this leaching step was intended to dissolve the hydrated stannic oxide from the residue, but above 75% of gold is also extracted during HCl leaching step (Figure 4.8). The extraction of gold in HCl is dependent upon the leaching time and temperature (Table 4.10). The extraction percentage was above 75% in 1.5 and 2 hours leaching time at 70°C. By decresing the temperature to 60 and 50°C the gold extraction was dropped to 69 and 41% in 1.5 and 1 hour respectively.

The extraction percentage of other metals in HCl solution not only depends upon the leaching conditions in the hydrochloric acid but also depends upon the leaching conditions in the nitric acid pretreatment step (Table 4.10)

The results show that with a temperature of 70°C and a leaching period of 2 hours in the preleaching step, only 1% Cu, 1% Pb and 5% Fe is extracted in HCl leaching solution. These figures can further be reduced by carefull filtration and washing of the residue. When the preleaching temperature was dropped from 70°C to 60°C then the extraction of Cu, Pb and Fe in the hydrochloric acid solution increased.

The remaining residue after HCl leaching was leached with acidic thiourea solution containing different oxidants. The effects of these oxidants on the gold extraction are given in Table 4.11.

The results show that in a hour leaching at 45°C, the extraction of gold in thiourea solutions containing Fe^{3+} and Cu^{2+}, as an oxidant, was 24 and 27% respectively. The gold extraction fell to 15% when the thiourea leaching was carried out using 0.25% H_2O_2 as an oxidant. Data in Table 4.11 suggests that the gold extraction efficiency decreases with increasing leaching time from 1 hour to 2 hour. This decrease in extracton could be due to the degradation of gold thiourea complex on long exposure to heat.

TABLE 4.10 EXTRACTION OF METALS IN HCl SOLUTION (2nd. STEP)

Test	HNO_3 leaching Time (hr)	temp. (°C)	HCl leaching Time (hr)	temp. (°C)	Ext. in HCl solution (%) Au	Cu	Fe	Pb	Sn
A	2.0	70	2.0	70	75	1	5	1	80
B	2.0	70	1.5	60	69	1	4	2	67
C	2.0	60	1.5	70	71	2	7	2	80
D	2.0	70	1.0	50	41	.4	2	.3	78
E	2.0	70	1.5	70	75	1	5	2	65
F	1.5	70	1.5	70	77	3	9	3	85
G	1.5	70	1.5	70	82	4	13	4	96
H	1.5	70	1.5	70	76	4	14	5	97

TABLE 4.11 GOLD EXTRACTION IN THIOUREA SOLUTION (3rd. STEP)

Test	Leaching Time (hr)	Oxidant (0.15%)	Gold Extraction (%)
A	2	Cu^{2+}	15.0
B	1	Cu^{2+}	27.0
C	1	Fe^{3+}	24.0
D	1	Fe^{3+}	56.0
E	1	H_2O_2	15.0
F	1	$Cu^{2+} + H_2O_2$	6.4
G	1	$Fe^{3+} + H_2O_2$	6.6

Conditions: Leaching temperature, 45°C

The effect of the combinations of Cu^{2+} plus H_2O_2 and Fe^{3+} plus H_2O_2 as an oxidants on the gold extraction was also studied. The results show that the extraction falls from 27 to 6.4% and 24 to 6.6% respectively. This decrease in level of extraction is due to the reducing properties of H_2O_2 in acidic solution. The presence of transition metal ions in the solution also promotes the reducing behaviour of the hydrogen peroxide and less gold extraction is achieved. The use of hydrogen per oxide as an oxidant promotes the formation of secondary oxidation products of thiourea which actually retard the rate of gold dissolution. This was confirmed by the presence of excessive amount of sulphur in thioure leach solution.

In the experiment H (Table 4.9), after HCl leaching the remaining residue was dissolved in *aqua-regia* instead of leaching with acidic thiourea solution. The result show that all the remaining gold (which is equivalent to 15-18% of the original gold) in the residue could be leached out in *aqua-regia*. The efficiency of gold extraction in *aqua-regia* was compared with that in thiourea extraction. The results show that nearly 3% less extraction of gold is achieved during acidic thiourea leaching step.

4.6.2 Preleaching with Nitric Acid (2nd. Option)

In this set of experiments, 3g, 20g and 50g sample was preleached with 250, 500 and 750ml of 3M HNO_3 at 70°C for 2, 2.5 and 2.5 hours respectively. After preleaching with nitric acid the washed residue was leached with 3% thiourea solution containing 1% H_2SO_4 and 0.15% Cu^{2+} or Fe^{3+} as an oxidant. The third step involved HCl leaching.

The experimental setup was the same as shown in Figure 4.6. Preleaching was carried out with 3M HNO_3 at 70°C for 2 and 2.5 hours. The solution was stirred with magnetic stirrer during the leaching period. After preleaching with HNO_3 the washed residue were leached with acidic thiourea solution containing 0.15% oxidant at 45°C for 1 or 1.5 hours. The final step involved the leaching of washed residue with 3M

HCl at 70°C. All the leach solutions were analysed by AAS and the results are given in Tables 4.12-4.19.

The results of this series of experiments showed that after preleaching with nitric acid, followed by leaching with thiourea solution provides an excellent method for gold extraction (Figure 4.9). The gold extraction in thiourea solutions containing Cu^{2+} and Fe^{3+}, as an oxidant, was 94 and 99% respectively in 1.5 hour leaching time at 45°C. These values were higher than the corresponding recovery levels after only one hour treatment at 45°C (89 and 90% respectively). When a 20 and a 50g sample were used then the extraction of gold in 1.5 and 1 hour, at 45°C, was 87 and 84% and 89 and 80% respectively. The data suggest that almost same extraction of gold is achieved in 1.5 and 1 hour leaching time at 45°C (Table 4.20).

4.6.3 Preleaching with Nitric (3rd. Option)

In these experiments, a 3g, a 20g and a 50g sample were preleached with 250ml, 500ml and 750ml of 3M nitric acid at 70°C for 2, 2.5 and 2.5 hours respectively. After preleaching, the washed residue were dissolved in *aqua-regia*. The solutions were analysed by AAS and the results are given in Table 4.21 (Figure 4.10).

Table 4.22 indicates that the extraction of gold in a thiourea solution is less than that achieved in an *aqua-regia* solution. The preleaching of 3, 20 and 50g samples with nitric acid and then the subsequent extraction of gold in thiourea solutions is 90, 89 and 90% respectively. The recovery levels were higher (99, 97, 92% respectively) after pretreatment in *aqua-regia* (Fig. 4.11).

4.6.4 Preleaching with Hydrochloric Acid

In this experiment, 3g sample was preleached with 3M HCl at 70°C for 2 hours. Solution was stirred magnetically during the leaching process. After preleaching with HCl, the washed residue was leached with 250ml of 3% thiourea solution containing 1% sulphuric acid and 0.15% Fe^{3+} at

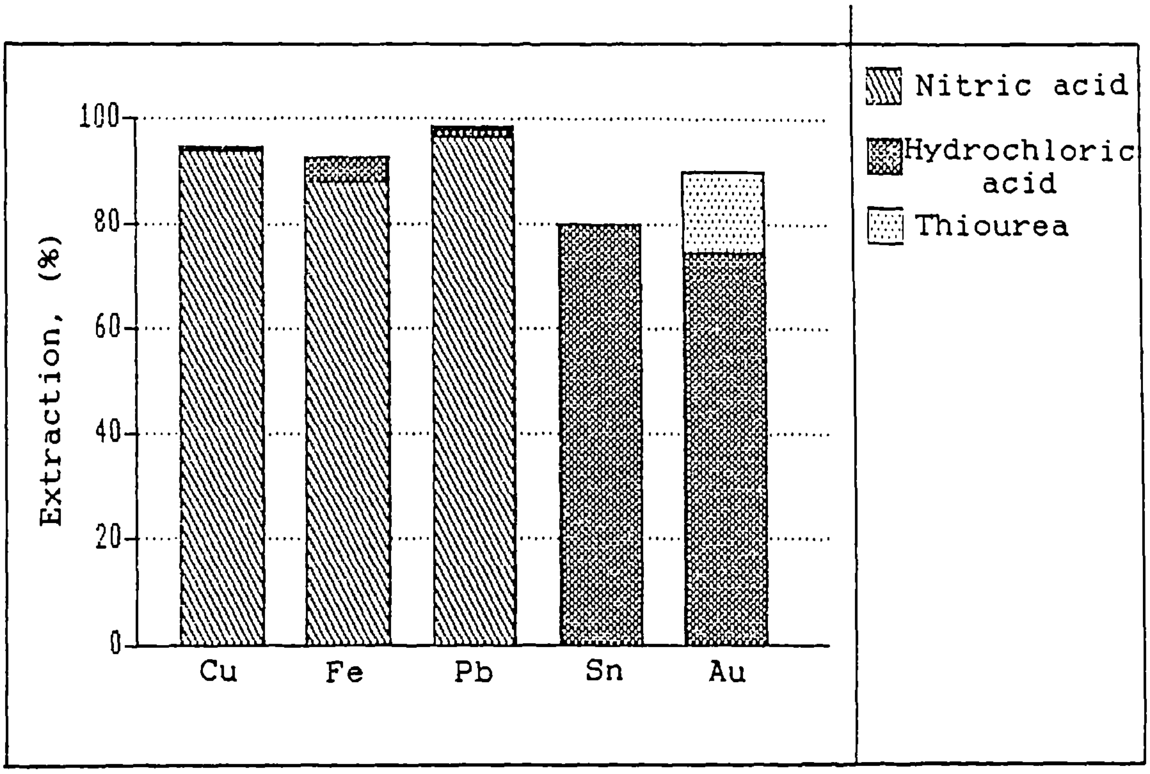


FIGURE 4.8 Pretreatment of computer scrap with HNO_3 followed by HCl leaching.

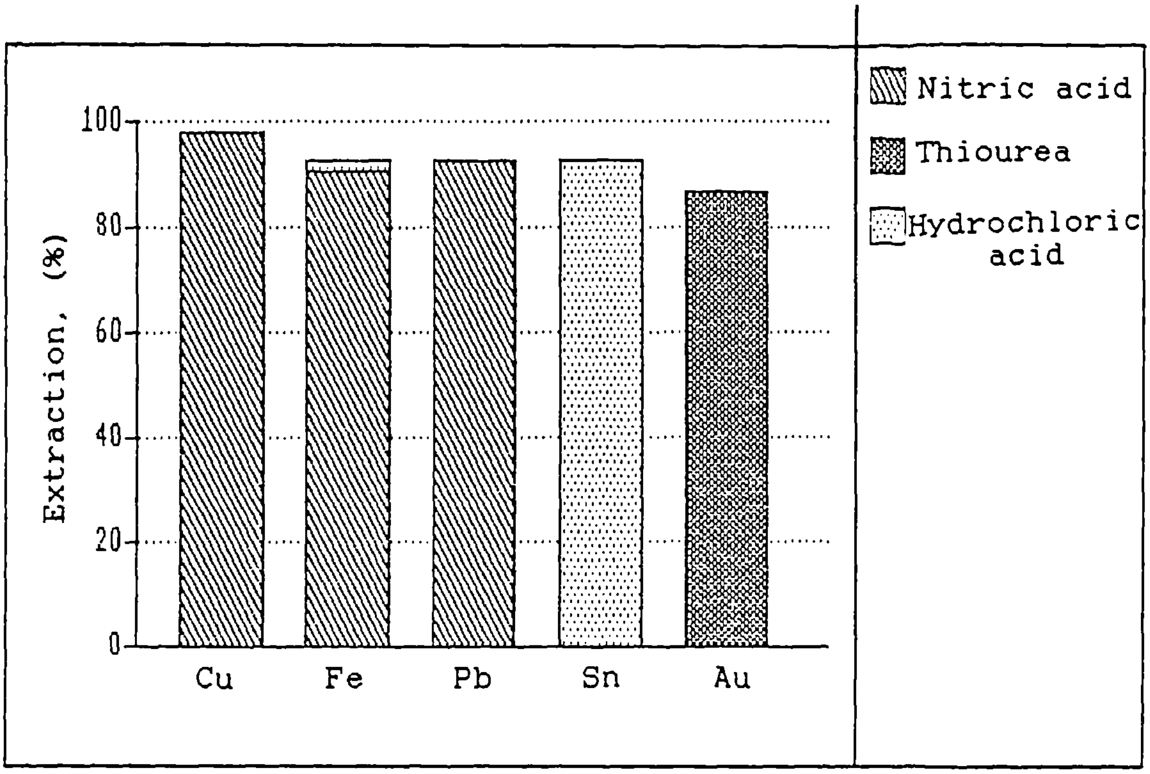


FIGURE 4.9 Pretreatment of computer scrap with HNO_3 followed by Thiourea leaching.

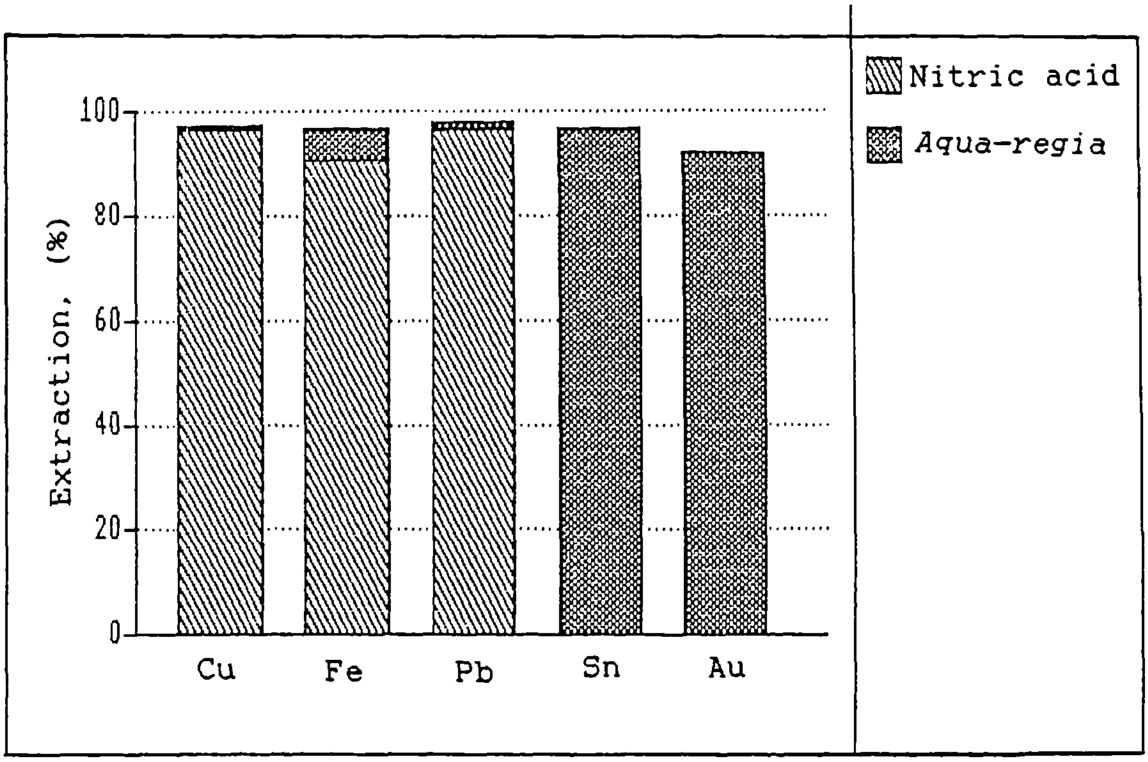


FIGURE 4.10 Pretreatment of computer scrap with HNO_3 followed by dissolution in *aqua-regia*.

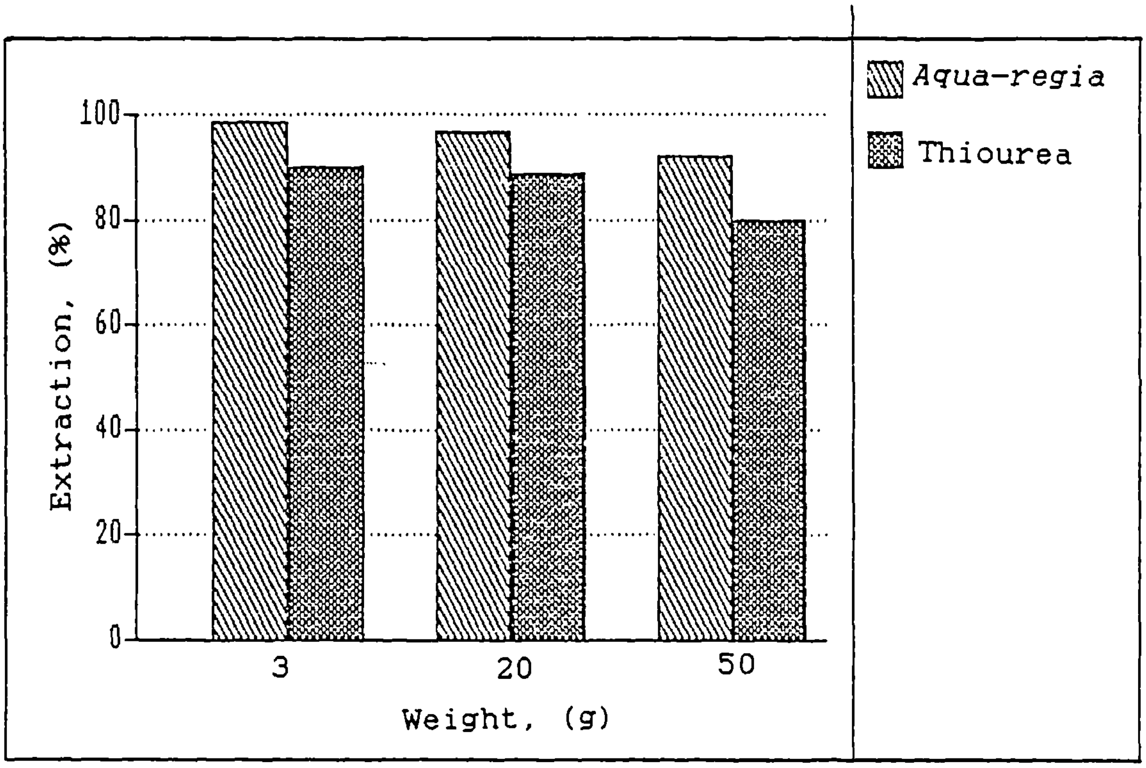


FIGURE 4.11 Comparison extraction of gold from computer scrap in *aqua-regia* and Thiourea solution.

(I) TABLE 4.12 EXTRACTION OF METAL VALUES

	HNO_3 Leach Extraction		Thiourea Leach Extraction		HCl Leach Extraction	
Metal	%	mg	%	mg	%	mg
Au	-	-	94	2.25	-	-
Cu	97	588	-	-	1.5	8.5
Fe	84	176	4	8.5	7.0	14.75
Pb	97	355	1	5.75	0.6	2.5
Sn	-	-	-	-	92.2	277.0

Conditions: Leaching time, HNO_3, 2 hrs; Thiourea, HCl, 1.5 hrs; Temp., HNO_3, and HCl, 70°C; Oxidant, Cu^{2+}.

(J) TABLE 4.13 EXTRACTION OF METAL VALUES

	HNO_3 Leach Extraction		Thiourea Leach Extraction		HCl Leach Extraction	
Metal	%	mg	%	mg	%	mg
Au	-	-	99	2.75	-	-
Cu	93	448	3	14.75	0.2	0.75
Fe	86	181	-	-	7.5	15.75
Pb	88	291	2	9.5	1.1	3.75
Sn	-	-	-	-	68.0	204.0

Conditions: Leaching time, HNO_3, Thiourea, HCl, 1.5 hrs.
Oxidant, Fe^{3+}.

(K) TABLE 4.14 EXTRACTION OF METAL VALUES

	Thiourea Leach Extraction		HCl Leach Extraction	
Metal	%	mg	%	mg
Au	90.0	1.75	-	-
Cu	0.8	4.0	0.1	0.2
Fe	-	-	5.0	13.5
Pb	0.6	2.0	0.3	1.0
Sn	-	-	97.0	350.0

Conditions: Leaching time, HNO_3, 2 hrs; Thiourea, HCl 1 hr;
Oxidant, Fe^{3+}.

(L) TABLE 4.15 EXTRACTION OF METAL VALUES

	Thiourea Leach Extraction		HCl Leach Extraction	
Metal	%	mg	%	mg
Au	89	2.0	-	-
Cu	-	-	0.8	4.0
Fe	3	5.75	2.9	6.25
Pb	1	5.25	0.6	2.25
Sn	-	-	93.0	306.0

Conditions: Leaching time, HNO_3, 2 hrs; Thiourea, HCl, 1 hr;
Oxidant, Cu^{2+}.

(M) TABLE 4.16 EXTRACTION OF METAL VALUES

	HNO_3 Leach Extraction		Thiourea Leach Extraction		HCl Leach Extraction	
Metal	%	g	%	mg	%	mg
Au	-	-	87.0	8.75	-	-
Cu	98	3.55	0.06	2.25	0.03	1.25
Fe	91	1.65	-	-	2.3	41.25
Pb	93	2.25	0.12	3.0	0.2	4.50
Sn	-	-	-	-	93.0	1863.00

Conditions: Leaching time, HNO_3, 2.5 hrs; Thiourea, 1.5 hrs; HCl, 2 hrs; Oxidant, Fe^{3+}.

(N) TABLE 4.17 EXTRACTION OF METAL VALUES

	HNO_3 Leach Extraction		Thiourea Leach Extraction		HCl Leach Extraction	
Metal	%	g	%	mg	%	mg
Au	-	-	84.0	21.0	-	-
Cu	98	8.81	0.05	5.0	1	87
Fe	89	3.98	-	-	6	275
Pb	95	5.70	0.13	7.5	1	60
Sn	-	-	-	-	92	4625

Conditions: Leaching time, HNO_3, 2.5 hrs; Thiourea, 1.5 hrs; HCl, 2 hrs; Oxidant, Fe^{3+}.

(O) TABLE 4.18 EXTRACTION OF METAL VALUES

	Thiourea Leach Extraction		HCl Leach Extraction	
Metal	%	mg	%	mg
Au	89.5	10.75	-	-
Cu	0.3	9.5	0.02	0.75
Fe	-	-	0.3	4.5
Pb	0.2	4.25	2.5	54.75
Sn	-	-	94.0	2244.00

Conditions: Leaching time, HNO_3, 2.5 hrs; Thiourea, 1 hr; HCl, 2 hrs; Oxidant, Fe^{3+}.

(P) TABLE 4.19 EXTRACTION OF METAL VALUES

	Thiourea Leach Extraction		HCl Leach Extraction	
Metal	%	mg	%	mg
Au	80.0	20.0	-	-
Cu	0.04	3.0	1.7	134
Fe	-	-	7.6	345
Pb	0.08	4.5	1.6	90
Sn	-	-	94.5	4727

Conditions: Leaching time, HNO_3, 2.5 hrs; Thiourea, 1 hr; HCl, 2 hrs; Oxidant, Fe^{3+}.

TABLE 4.20 GOLD EXTRACTION IN THIOUREA SOLUTION (2nd. step)

TEST	Sample's Wt. (g)	Time (hr)	Oxidant (0.15%)	Au Ext. (%)
I	3	1.5	Cu^{2+}	94
J	3	1.5	Fe^{3+}	99
K	3	1.0	Fe^{3+}	90
L	3	1.0	Cu^{2+}	89
M	20	1.5	Fe^{3+}	87
N	50	1.5	Fe^{3+}	84
O	20	1.0	Fe^{3+}	89
P	50	1.0	Fe^{3+}	80

Conditions: Leaching temperature, 45°C.

(Q) TABLE 4.21 EXTRACTION OF METAL VALUES

Sample's weight (g)	Leaching Time (hr)	Metal	HNO_3 Leach Extraction %	mg	Aqua-Regia Extraction %	mg
3	2	Au	-	-	99.0	2.5
		Cu	98	0.59	0.7	4.0
		Fe	91	0.20	7.7	16.25
		Pb	97	0.35	1.5	5.25
		Sn	-	-	99.8	360.0
20	2.5	Au	-	-	97.0	9.75
		Cu	98	4.0	0.7	13.75
		Fe	97	1.7	2.5	45.0
		Pb	98	2.5	0.6	13.75
		Sn	-	-	95.5	2293.0
50	2.5	Au	-	-	92.0	23.0
		Cu	97	9.7	0.9	90.0
		Fe	91	4.1	6	275.0
		Pb	97	5.8	1.5	100.0
		Sn	-	-	97.0	5340.0

TABLE 4.22 GOLD EXTRACTION IN *AQUA-REGIA* AND THIOUREA

Sample's Wt. (g)	Ext. in Thiourea (%)	Ext. in Aqua-Regia (%)
3	90	99
20	89	97
50	80	92

Conditions: Thiourea leaching time, 1 hr; Oxidant, Fe^{3+}.

(R) TABLE 4.23 EXTRACTION OF METAL VALUES

Metal	HCl Leach Extraction %	mg	Thiourea Leach Extraction %	mg	HNO_3 Leach Extraction %	mg
Au	-	-	66.6	1.0	-	-
Cu	2	14.0	22.5	135.0	73	443.2
Fe	13	37.5	-	-	78	213.5
Pb	52	187.5	0.4	1.5	32	115.0
Sn	96	343.7	-	-	-	-

Conditions: Leaching time, HCl, 2 hrs; Thiourea, 1 hr;
HNO_3, 2 hrs; Oxidant, Fe^{3+}.

45°C for 1 hour. The last step involved the use of nitric acid (3M) leaching at 70°C. The results are given in Table 4.23 (Figure 4.12).

4.6.5 Preleaching with Sulphuric Acid

In this experiment, the three steps involved were:

(a) preleaching with sulphuric acid

(b) subsequent leaching with acidic thiourea solution

(c) leaching the remaining residue with HCl.

3g sample was preleached with 3M sulphuric acid at 70°C for 1.5 hours. The washed residue was leached with 250ml of acidic thiourea solution at 45°C for 1 hour. The final step involved the use of 250ml of 3M HCl at 70°C for 1.5 hour. The results are given in Table 4.24 (Figure 4.13).

In another experiment, 3g sample was preleached with 250ml of 3M sulphuric acid at 70°C for 2 hour. The remaining residue was dissolved in *agua-regia*. The results are given in Table 4.25.

4.6.6 Extraction of Gold without Preleaching

In this experiment, 2g sample was leached with 100ml of 3% thiourea solution containing 1% concentrated sulphuric acid and Fe^{3+} as an oxidant at 45°C for 1 hour. The results are given in Table 4.26.

The data in Table 4.27 show that the extraction of gold in a thiourea solution without preleaching is very low (40%) and that 34% of the copper is coextracted. Preleaching with HCl and H_2SO_4 also gives low extraction levels of gold along with high concentration of copper in thiourea leaching. Preleaching with nitric acid not only increases the gold extraction but also gives less extraction of copper in thiourea leaching solutions.

Preleaching with nitric acid gives almost complete extraction of copper, iron and lead and leaves the residue with exposed gold particles which are easily leached out in

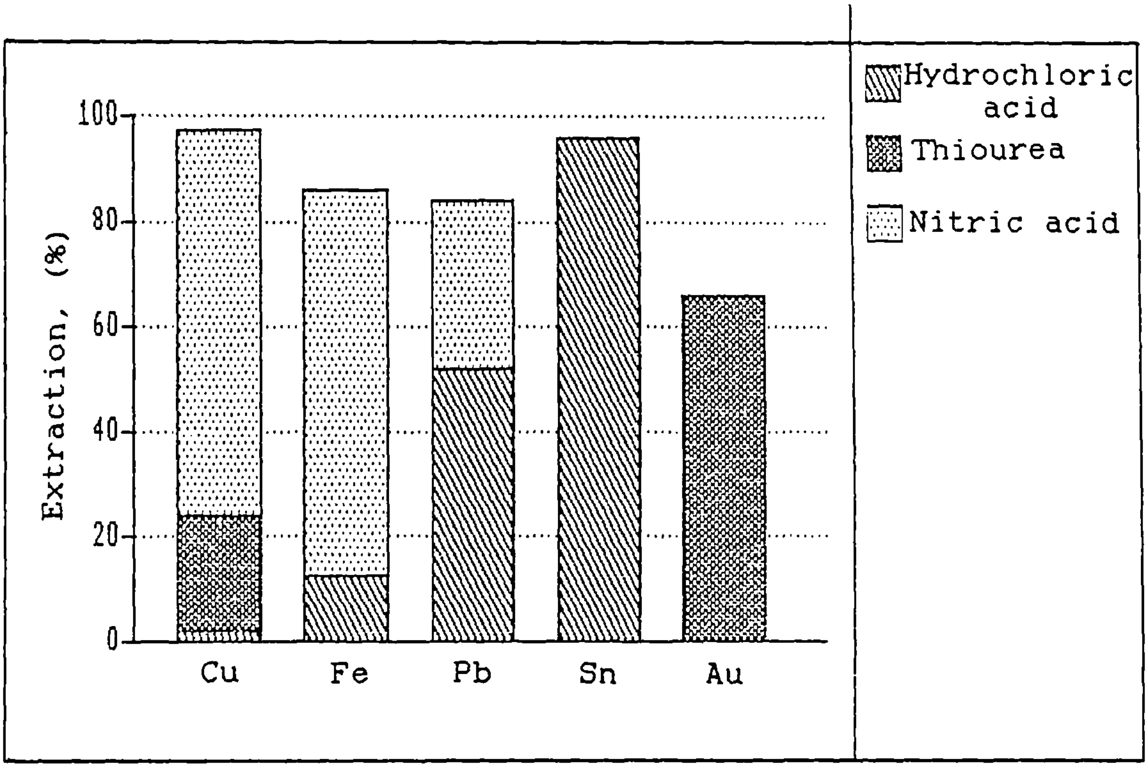


Figure 4.12 Pretreatment of computer scrap with HCl followed by Thiourea leaching.

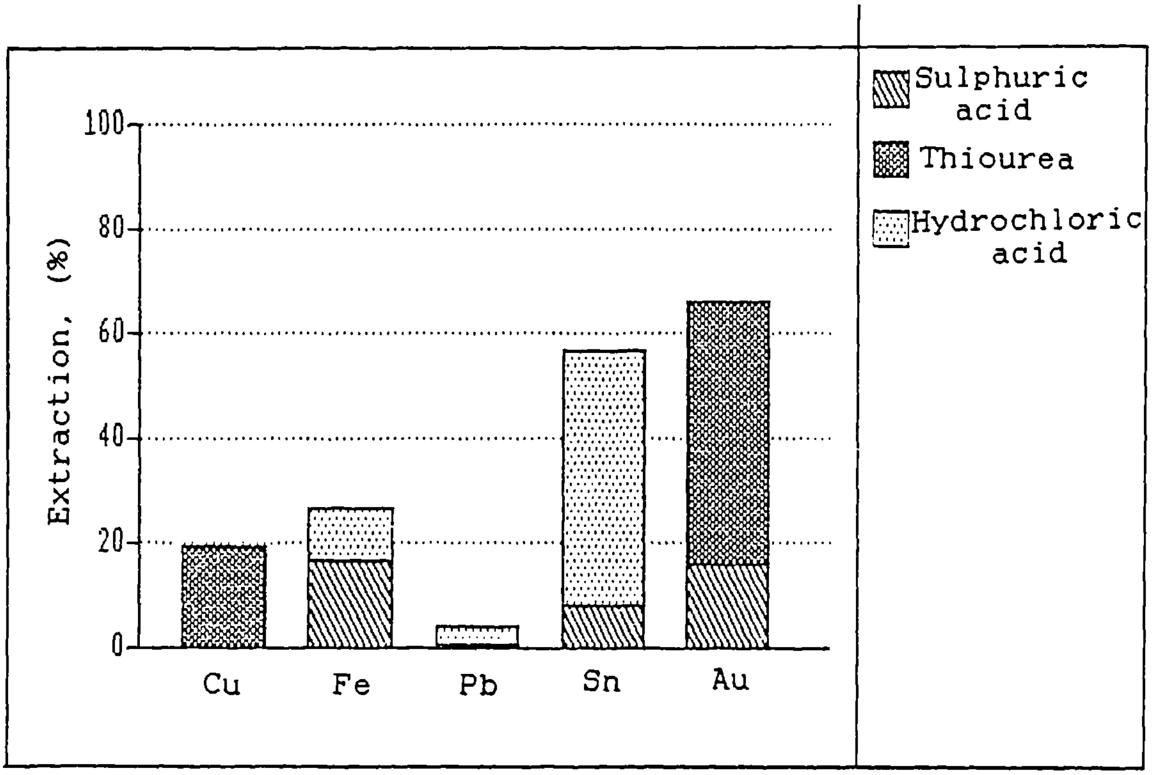


FIGURE 4.13 Pretreatment of computer scrap with H_2SO_4 followed by Thiourea leaching.

(S) TABLE 4.24 EXTRACTION OF METAL VALUES

	H_2SO_4 Leach Extraction		Thiourea Leach Extraction		HCl Leach Extraction	
Metal	%	mg	%	mg	%	mg
Au	16.5	0.2	50.0	0.7	-	-
Cu	0.1	0.5	19.4	105.0	0.2	1
Fe	17.2	46.5	-	-	10.7	27
Pb	0.3	1.0	0.7	2.5	3.4	12
Sn	8.0	24.0	-	-	48.7	146

Conditions: Leaching time, H_2SO_4; Thiourea, 1 hr; HCl, 1.5 hrs; Oxidant, Fe^{3+}.

(T) TABLE 4.25 EXTRACTION OF METAL VALUES

	H_2SO_4 Leach Extraction		*Aqua-Regia* Extraction	
Metal	%	mg	%	mg
Au	16.5	0.2	83	1.25
Cu	0.08	0.5	97	658.25
Fe	20.4	55.0	66	178.00
Pb	0.3	1.0	98	352.25
Sn	6.5	23.5	93	373.50

Conditions: Leaching time, 2 hrs.

(U) TABLE 4.26 EXTRACTION OF METAL VALUES

	Thiourea Leach	
Metal	%	mg
Au	40.0	0.5
Cu	34.0	122.5
Fe	-	-
Pb	0.6	1.6
Sn	-	-

Conditions: Leaching time, 1 hr; Oxidant, Fe^{3+} .

thiourea solution. From the results it is obvious that acid pretreatment has a beneficial effect on the extraction of gold in thiourea solution. The maximum gold extraction was achieved when the sample was preleached with 3M nitric acid. This high extraction is due to the selective leaching of gold with only traces of Cu and Fe. These results confirm that high concentrations of copper and iron have a negative influence on thiourea leaching. In the presence of high concentration of iron the consumption of thiourea increases due to the formation of its complex in sulphate medium according to the following reaction:

$$Fe^{3+} + CS(NH_2)_2 + SO_4^{2-} \rightleftharpoons (FeSO_4(CS(NH_2)_2))^+$$

(the end product is, $[Fe(CS(NH_2)_2)]SO_4$)

The low extraction of gold in thiourea solution without any pretreatment is also attributed mainly to the presence of an excess copper and iron.

It is very difficult to explain the extraction of gold during the acidic pretreatment of the sample with 3M sulphuric acid at 70°C. The only possible explanation is that the gold in the sample may have formed a complex on a colloidal sulphur during the pretreatment.

4.6.7 Separation of Precipitated Stannic Oxide

In this set of experiments, 20g and 50g sample were preleached with 500ml and 750ml of 3M nitric acid at 70°C for 2.5 hour. After this step, the precipitated stannic oxide (off-white) was separated from the residue by filtration. The separated precipitate was dissolved in 3M HCl, and the remaining residue was leached with 3% thiourea solution containing 1% sulphuric acid and 0.15% Fe^{3+} at 45°C for 1 hour. The results are given in Table 4.28.

The data in Table 4.28 indicate that it is very difficult to separate efficiently the stannic oxide formed during the preleaching with nitric acid prior to thiourea leaching.

TABLE 4.27 GOLD AND COPPER EXTRACTION IN THIOUREA SOLUTION WITH AND WITHOUT PRELEACHING

Test	pre-treatment	Au Extraction (%)	Cu Extraction (%)
K	HNO_3	90.0	0.8
O	HNO_3	89.5	0.3
R	HCl	66.6	22.5
S	H_2SO_4	50.0	19.4
U	Nil	40.0	34.0

Conditions: Thiourea leaching time, 1 hr; Oxidant, Fe^{3+};
Temperature, 45°C.

(V) TABLE 4.28 EXTRACTION OF METAL VALUES

Sample's weight (g)	Metal	HCl Leach Extraction %	HCl Leach Extraction mg	Thiourea Leach Extraction %	Thiourea Leach Extraction mg
20	Au	12.5	1.25	67.5	6.75
	Cu	3.9	125.0	2.3	73.75
	Fe	5.6	102.0	-	-
	Pb	3.1	76.75	0.1	2.5
	Sn	77.0	1537.0	-	-
50	Au	16.0	4.0	62.0	15.5
	Cu	1.0	125.0	0.03	1.5
	Fe	11.0	505.0	-	-
	Pb	1.0	82.5	0.2	9.0
	Sn	83.0	4179.0	-	-

Conditions: Leaching time, HNO_3, 2.5 hrs; HCl, 1.5 hrs;
Thiourea, 1 hr; Oxidant, Fe^{3+}.

During separation some very fine gold particles were also removed along with stannic oxide which resulted in gold loss. The best method of overcoming this difficulty is to leach the residue containing the stannic oxide with thiourea solution at 45^{o}C for 1 hour. This step allows extraction of about 90% of gold and the residual stannic oxide can then be dissolved in hydrochloric acid.

4.7 RECOVERY OF GOLD

Computer scrap is a low grade secondary source of gold and copper metal. If the separated scrap is preleached with nitric acid and then with acidic thiourea solution containing an oxidant, the resultant solutions contain very low concentrations of gold along with high levels of iron or copper (oxidants). The main aim in the recovery of metals from computer scrap is to obtain the maximum possible extraction of gold. To do this the thiourea must be retained in the leach solution and the concentrations of other metals must be maintained at levels which will not impair the properties of the thiourea liquor as a solvent for the gold. Because of low concentration of gold in the extract adsorption methods are most suitable. The materials commonly used for adsorbing gold from leach solutions are activated carbon and cation exchange resins. After adsorption the barren thiourea solution can be used for further leaching of gold. Electrolysis is also a promising method of winning gold from thiourea solution. Conventional electrolysis cells will not, however, be able to recover sufficiently high amounts of gold from the weak leach solutions. Different design of electrowinning cells have been introduced for the recovery of metals including gold from low concentration solutions, the most important of these being the fluidised bed cell and two stage electrolysis cell. The working mechanism of fluidised bed cell has already been described in chapter 2.

In this work a study has carried out for the recovery of gold from chloride and thiourea solutions using a mini fluidised bed cell with a single titanium cathode and two platinised titanium anodes. The mini fluidised bed cell of 5 litre capacity was constructed in the laboratory at The City University (Figure 4.14) and consists of a reservoir tank and electrolysis chamber. The electrolysis chamber contains mesh electrodes and inert glass beads. The two containers were fixed on top of the wooden box containing a pump. The gold solution was pumped through the distributors at the base of the electrolysis chamber cell causing fluidisation of the glass beads. The vigorous agitation produced at the cathode surface ensures that the metal is recovered at high efficiency even from a very dilute solution. The fluidised bed cell was used to recover gold from chloride and thiourea solution.

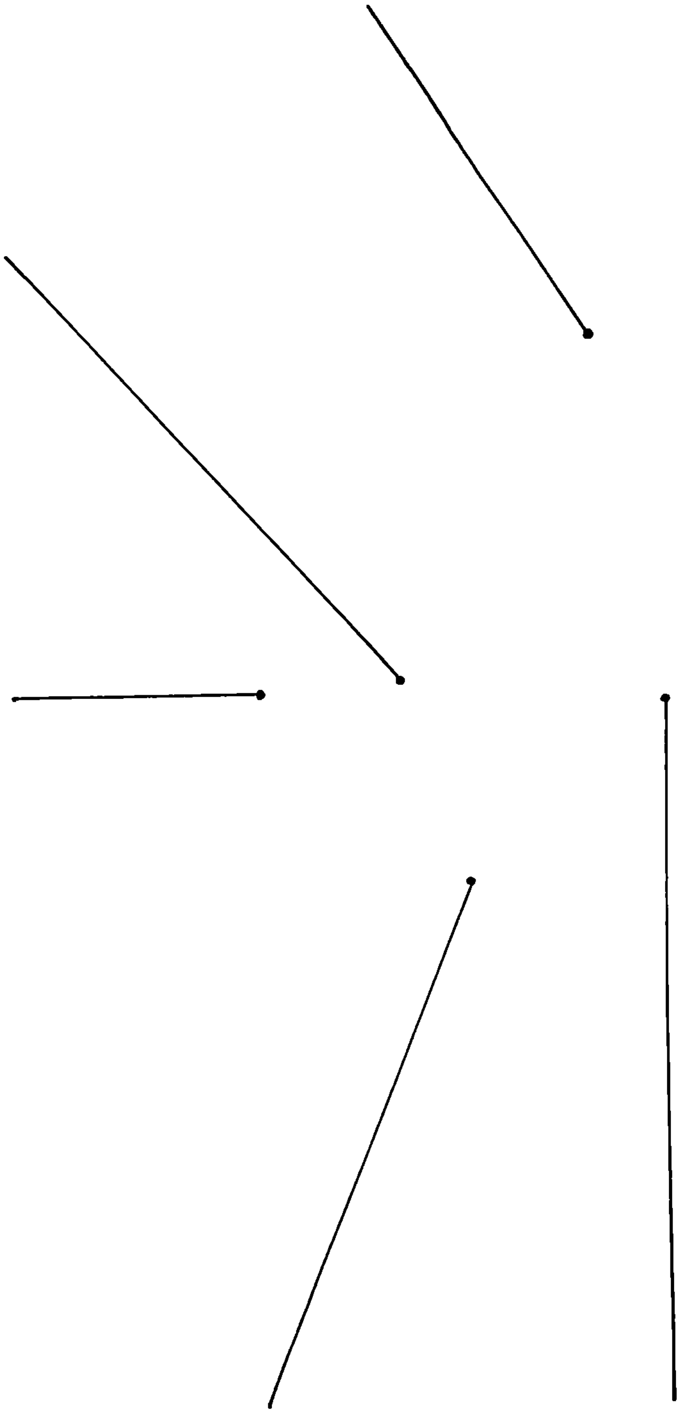
4.7.1 Recovery from Chloride Solution

The chloride solutions containing gold and tin along with traces of copper, iron and lead were collected and diluted up to 5 litre with distilled water. This solution was used for the electrowinning of gold along with other metal on the titanium cathode. The solution was analysed by AAS before starting the electrolysis and after the recovery.

The chloride solution containing gold and tin along with copper, iron and lead was then introduced into the reservoir tank of the mini fluidised bed cell. Electrolysis was carried out at ambient temperature, at current density of 60 A/m^2 on a single titanium mesh cathode.

Periodically during the electrolysis, samples were collected and analysed for the residual metal concentration by AAS. After periods of 2 and 4 hours electrolysis, the cathode was replaced with an unused reserve cathode and the total electrolysis time was 12 hours. The metal content of the cathodic deposit after periods of 0, 2, 4, 6 and 12 hours electrolysis were determined and are given in Table 4.29.

The cathodes were left to dry overnight and the deposited metals were recovered with a wire brush. Most of the metals were removed except some hard deposit. This hard deposit



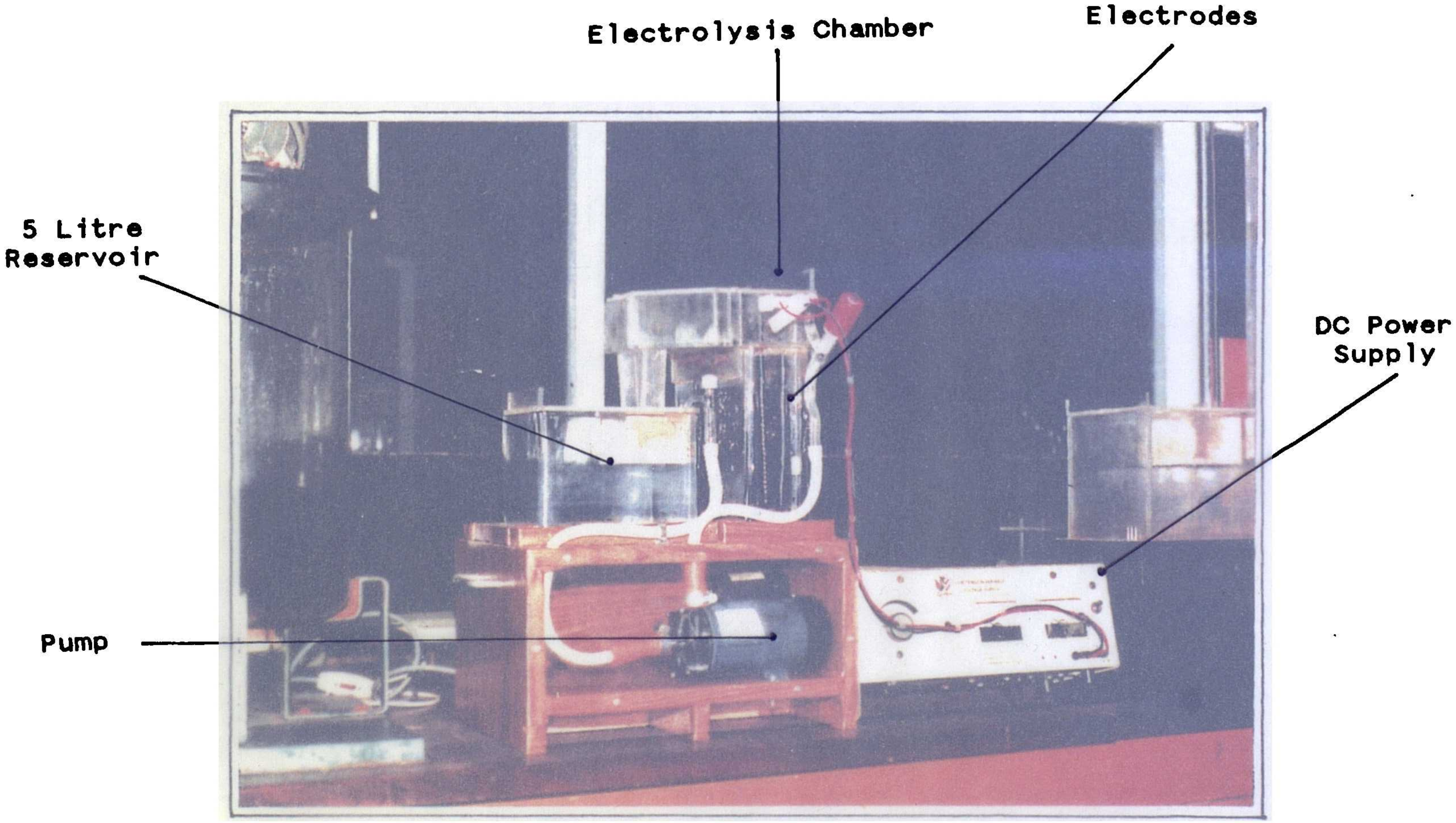


FIGURE 4.14 Mini fluidised bed cell.

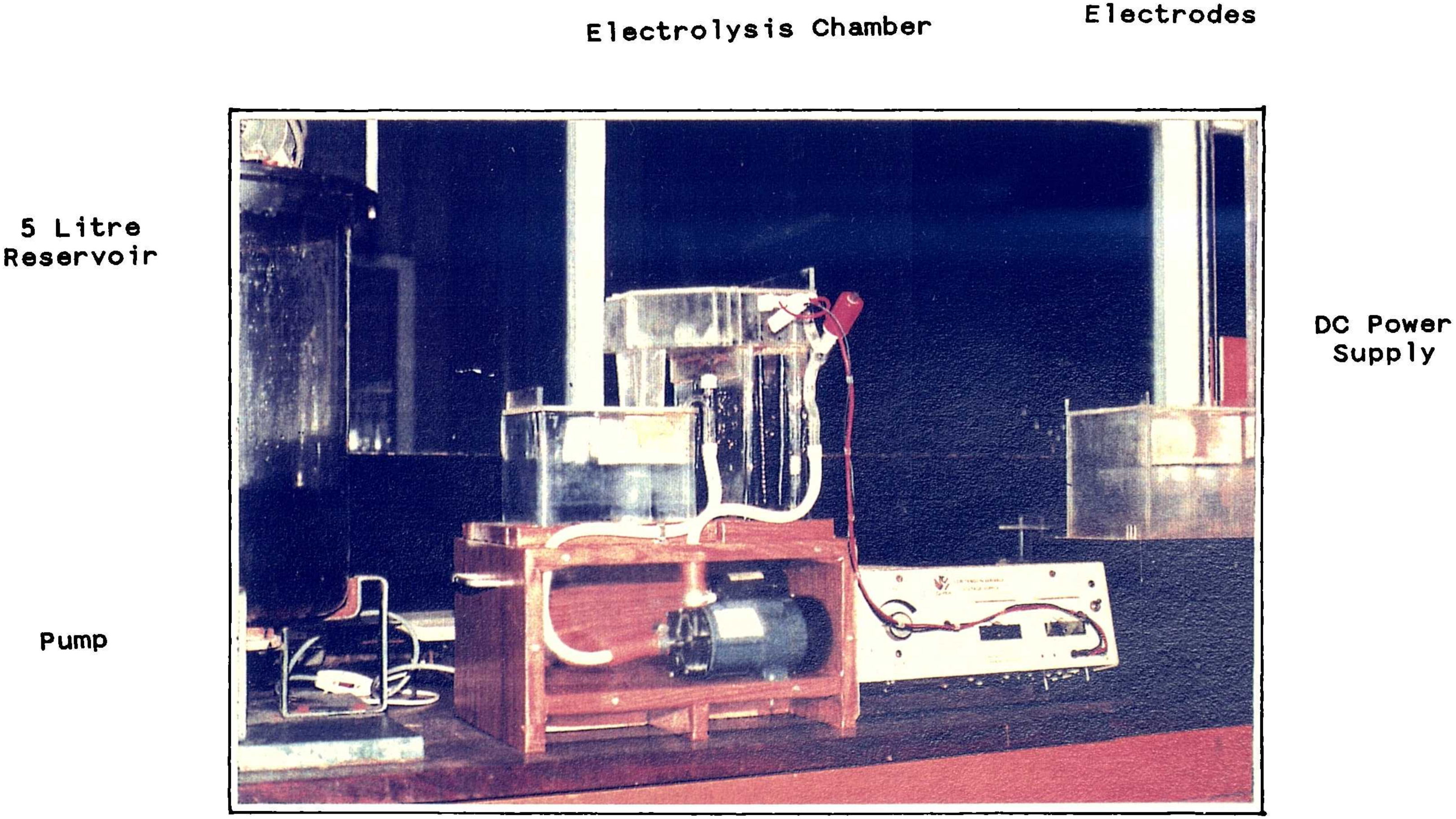


FIGURE 4.14 Mini fluidised bed cell.

was removed by washing the cathodes in a dilute nitric acid solution. The deposit obtained from each cathode was; (a) first cathode (2 hours), 2.2941g; (b) second cathode (4 hours), 2.7140g; and (c) third cathode (12 hours), 4.4990g. Deposit from the first cathode (2.2941g) was dissolved in 2M nitric acid at 60°C for an hour. The solution was filtered and the residue was washed with distilled water and then dissolved in *aqua-regia*. The final volume of both solutions were made upto 250ml and analysed by AAS. The results are given in Table 4.30.

The analysis of cathodic deposit show that it contains 0.8% Au; 7.8% Cu; 1.5% Pb and 82% Sn. By dissolving the deposit in 2M nitric acid all of the copper and lead can be removed whilst the gold in the residue can be extracted by thiourea solution leaving tin as hydrous stannic oxide.

4.7.2 Recovery from Thiourea Solution

It was found that some sulphur precipitates in the thiourea solution after 1-2 weeks. Before the thiourea solution was subjected to electrolysis, the precipitated sulphur was filtered off. The total of 5250ml of thiourea solution was collected for the electrowinning of gold. After analysis the solution was found to be very dilute and the use of elecrolysis method for the recovery of gold is not possible. Just for trial basis the electrolysis was carried out by using a solution of 8ppm at current density of 10 A/m^2. The solution concentration fell to 3ppm after 2 hours of electrolysis. During the electrolysis some sulphur was collected at the bottom of the reservoir tank and electrolysis chamber. This can easily be recoverd by filtration.

4.8 RECOVERY OF COPPER

4.8.1 Cementation

Copper can be recovered selectively from leach solution by cementation reaction using iron powder or filings at low pH values. In this study the cementation of copper was carried out by using both iron powder and coarse iron filings.

TABLE 4.29 DEGREE OF PURIFICATION OF METALS

Time (hr)	Remaining Concentration (ppm)					Cathodic Deposit (%)				
	Au	Cu	Pb	Fe	Sn	Au	Cu	Pb	Fe	Sn
0	9	68	117	225	2152	-	-	-	-	-
2	4	33	104	225	1442	56	51	11	-	33
4	3	21	86	224	966	67	69	27	-	55
6	1	14	77	223	822	88	79	34	-	62
12	1	8	19	220	216	88	88	84	-	90

TABLE 4.30 ANALYSIS OF RECOVERED METALS

Metal	Nitric acid			Aqua-regia		
	%	mg	ppm	%	mg	ppm
Au	-	-	-	0.85	19.5	78
Cu	7.7	186.2	705	0.08	2.0	8
Fe	0.04	1.0	4	0.03	0.7	3
Pb	1.4	32.5	130	0.04	1.0	4
Sn	-	-	-	81.62	1872.5	7490

TABLE 4.31 COPPER CEMENTATION

pH	Time (min)	Concentration, (ppm) Cu	Fe	Pb	Cementation, (%) Cu	Pb
0.38	0	1760	825	1120	-	-
	30	175	2465	1104	90	1.4
	60	52	2800	1096	97	3.0
0.5	0	875	370	645	-	-
	30	45	1245	617	94	4.3
	60	25	1585	59	97	7.7
2.5	0	720	305	510	-	-
	30	75	1195	440	89	13.7
	60	20	1465	40	97	21.5

TABLE 4.32 ELECTROWINNING OF COPPER

Time (hr)	Concentration (ppm) Fe	Cu	Pb	Deposition (%) Cu	Pb
0	370	880	530	-	-
2	370	485	440	44.8	16.9
4	365	160	360	81.8	32.0
6	364	95	305	89.2	42.4
8	360	115	220	86.9	58.4
10	360	160	160	84.0	69.8

Conditions: Current density, 25 A/m^2; Acid concn., 0.3 M

During the cementation reaction the beaker was surrounded by an electromagnet connected with a variac. This variable external magnetic field causes the iron particles to move very quickly with in the solution., thus allowing the deposited copper to become detached, which provides an active site on which other copper ions may deposit.

Cementation is a heterogeneous redox process in which Fe is dissolved at the anodic area of the surface and the electrons that are released serve to reduce copper ions at the cathodic areas. The chemical reactions which are relevant to the cementation reaction are given below:

a) $Cu^{2+} + 2e^- \text{------>} Cu$

b) $Fe \text{------>} Fe^{2+} + 2e^-$

c) $1/2O_2 + H_2O + 2e^- \text{---->} 2OH^-$

d) $Cu^{2+} + 2OH^- \text{------>} Cu(OH)_2$

e) $Fe^{2+} + 2OH^- \text{------>} Fe(OH)_2$

f) $2H^+ + 2e^- \text{------>} 2H$

Reaction (a) and (b) are the principal reactions. During the cementation process copper is deposited at the cathodic sites on an iron surface whilst at separate anodic sites dissolution of iron takes place. Other competing reactions may occur which reduce the efficiency of the reaction. These are dependent upon the pH of the solution. At high pH levels reaction (c) is favoured which may lead to the formation of hydroxides of copper and iron via reactions (d) and (e). These are deposited on the iron surface and form a passive layer preventing further cementation. At low pH values hydrogen evolution (f) becomes the predominant reaction. This implies that there is an optimum pH within which the cementation reaction rate is a maximum.

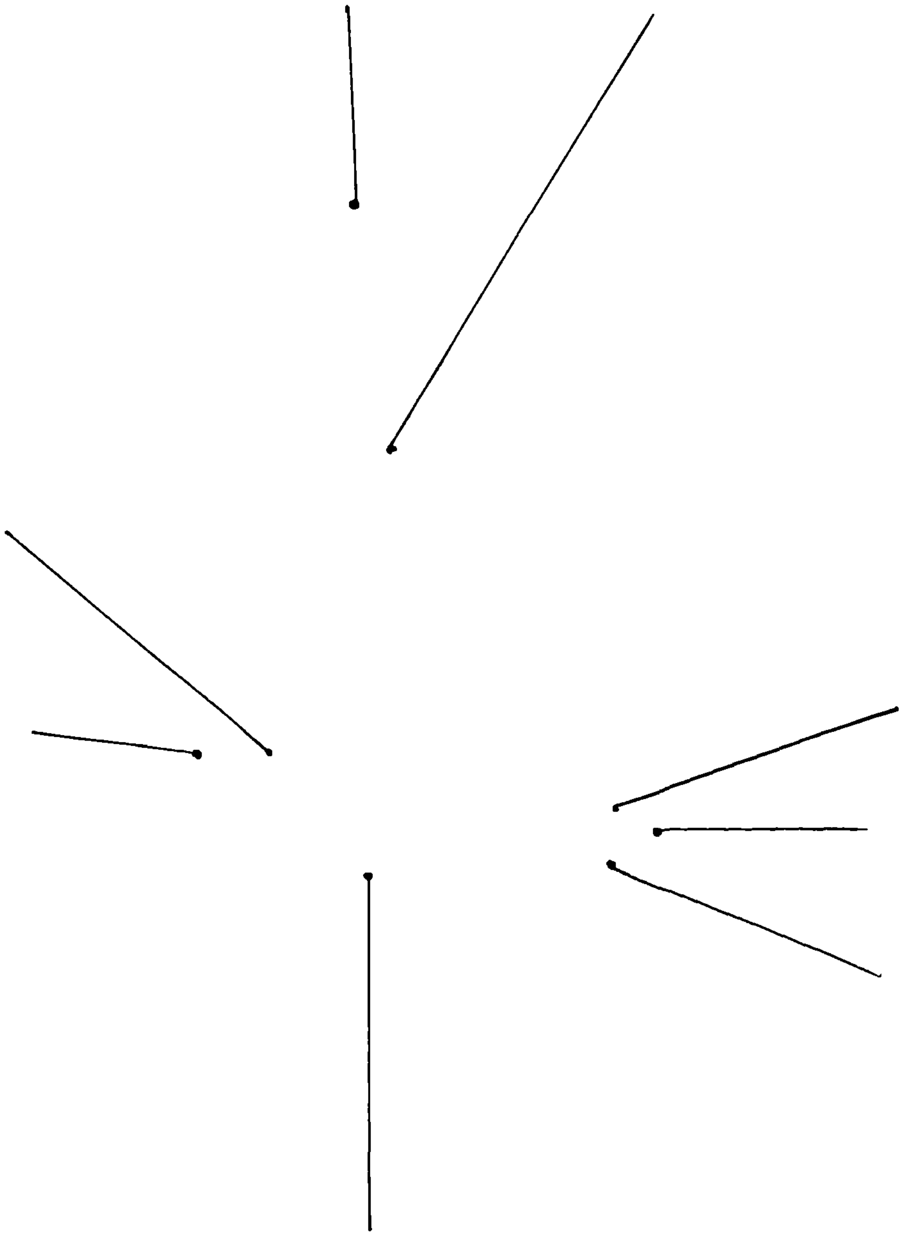
Initial studies of copper cementation were carried out in a glass beaker of 400ml capacity. Preleached nitrate solution (200 ml) containing copper, lead and iron was introduced into the reaction beaker containing 10g of iron powder. The reaction beaker was surrounded by an electromagnet. The solution was stirred with a glass stirrer connected with a overhead motor. At periods of 30 and 60 minutes, samples of the solution were removed and filtered and analysed by AAS for copper, iron and lead contents (Table 4.31).

In another test the pH of the solution was raised to 2.5 from 0.5 by the addition of sodium hydroxide. At this pH value some precipitates appeared in the solution. The solution was filtered and analysed before being subjected to the cementation reaction. No attemt was made to maintain the pH of the solution during the cementation reaction. The samples were collected and analysed by AAS. The results for various pH values are given in Table 4.31.

The results indicate that at the higher pH value of 2.5 not only is copper recovered but also some lead during the cementation reaction. The cementation of lead depends upon the pH value whereas the cementation of copper is independent of the pH of the solution. The percentage of copper recovered after 60 minutes is approximately 97% at each of the three pH values, whereas, only at high pH (2.5) is a lead level of 21% achieved. So in order to recover pure copper the pH of the solution must be low enough to prevent the cementation of lead occuring which is a major interfering reaction during the cementation reaction. The pH must not be too high otherwise the formation of metal hydroxide will begin and the rate of cementation will be reduced. The results obtained showed that at pH 2.5 the cementation of lead was 21% after 1 hour. At low pH values this drops to only 6% after 1 hour cementation reaction.

a) Cementation Cell

After the initial cementation studies, a cementation cell of the type shown in Figure 4.15 was constructed in the laboratory at the City University, U.K. The schematic flow diagram of the cementation cell is shown in Figure 4.16. The cell consisted of a reservoir tank of 5 litre capacity. The solution is pumped from this tank through a cementation tube of 60cm long. This tube was surrounded by an electromagnet.



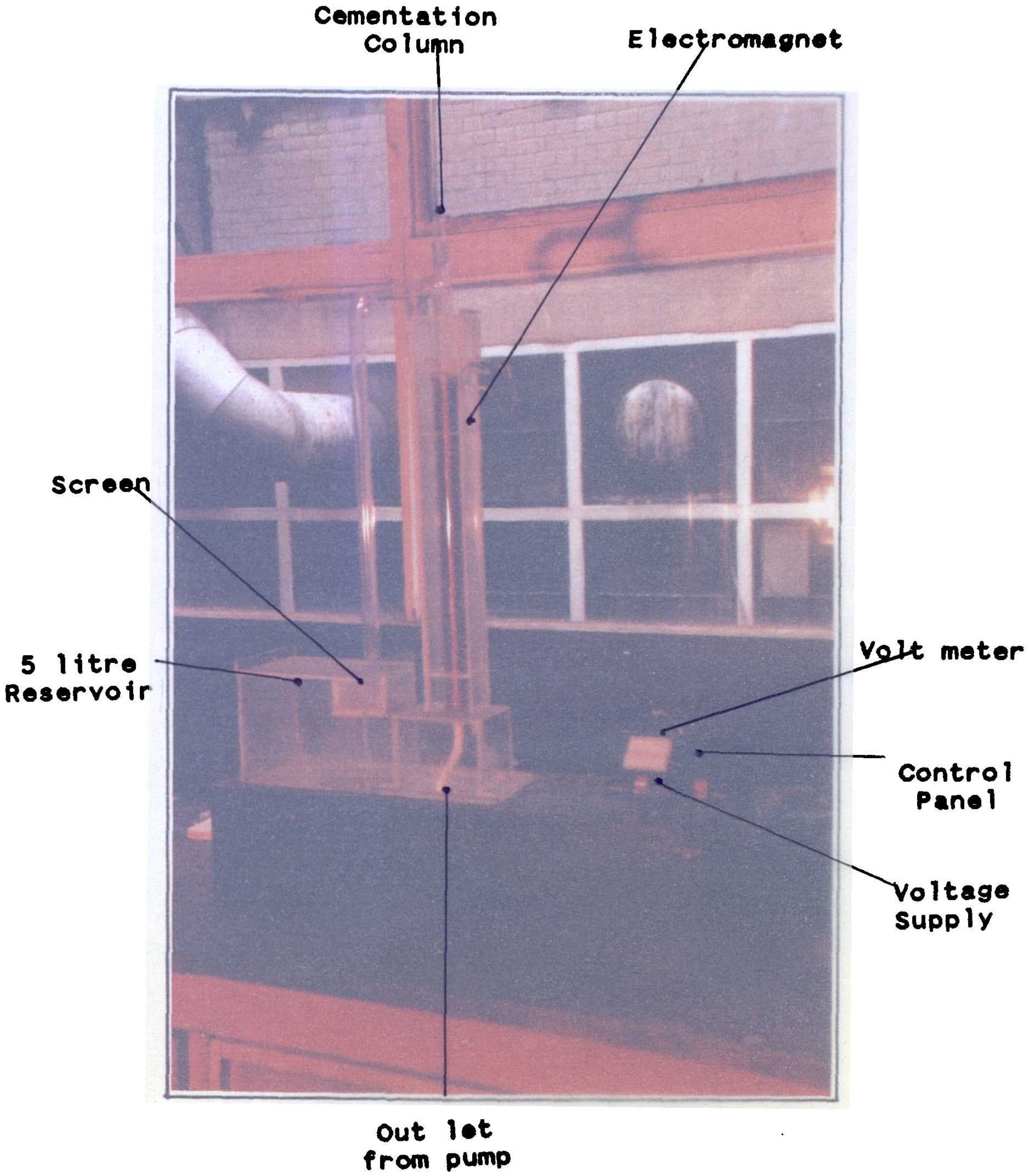


FIGURE 4.15 Cementation cell.

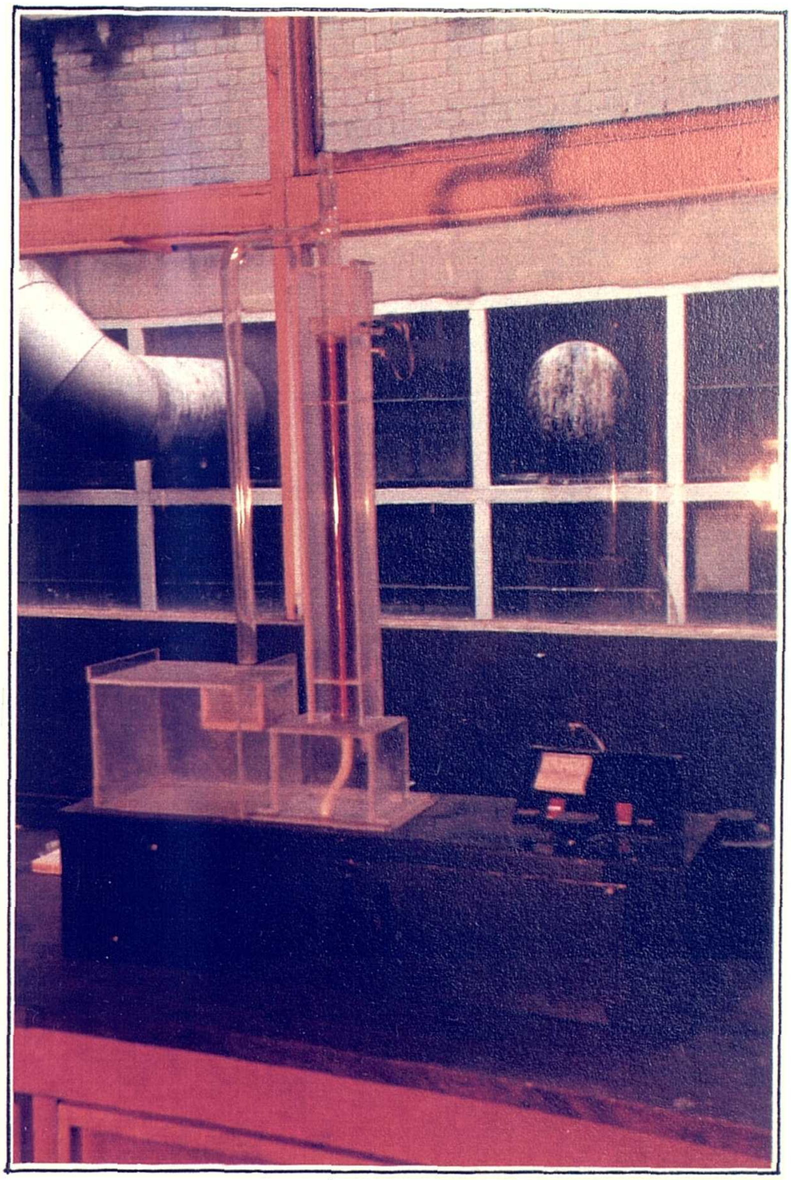


FIGURE 4.15 Cementation cell.

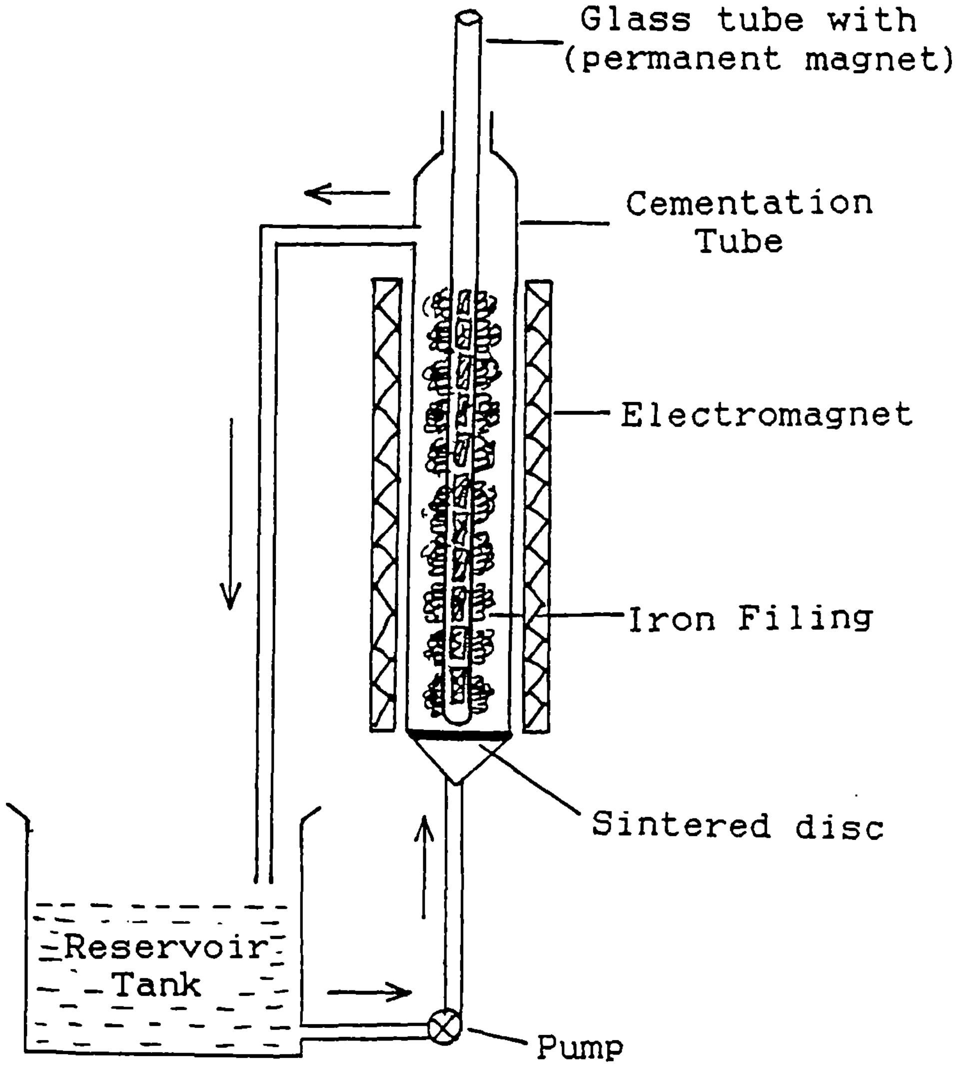


FIGURE 4.16 Schematic flow diagram of the cementation cell.

The cementation tube contained 10 pieces of permanent magnet wraped in a glass tube. The purpose of these permanent magnets was to hold the coarse iron filings inside the system during the cementation reaction. A variable external magnatic field was applied to the iron particles in the main cementation tube. Under the influence of this field the iron particles move with very high velocities relative both to themselves and the surrounding solution. In addition there is a high frequency of collision between the iron particles, and the force of these collisions allows for easy and permanent removal of non-magnetic metals which may cement onto the iron surface, renewing the iron surface for further reactions. The detached metal is easily removed from the processed solution by simply decantation or filtration.

Preleached nitrate solution (5 litre) containing 880ppm copper, 400ppm iron and 570ppm lead was introduced into the reservoir tank of the cementation cell. The pH of the solution was 0.5. This solution was circulated through the cementation chamber, described above. The variable external magnetic field was applied to the iron particles in the cementation chamber. The solution was circulated for two hours with a maximum flow rate of 3 litres per minute. After two hours the solution was analysed for copper, iron and lead concentration. The concentration of copper, iron and lead was 140, 2680 and 540 ppm. This is equivalent to 84% deposition of copper and 5% lead. The low deposition of copper in cementation cell is due to high flow rate of the solution. In order to get maximum deposition of copper this cementation cell needs some minor changes in its design, for example, long cementation chamber and slow flow rate to allow maximum contact time of solution with iron particles.

4.8.2 Electrowinning of Copper

The electrowinning of copper in the presence of lead and zinc has already been studied in detail in chapter 2. It was found that during the electrowinning of copper on cathodes deposition of lead oxide at the anode occured, especially when the nitric acid concentration was high

(0.3-0.5M). The high concentration of nitric acid and the presence of copper ions act as a depolarisers. Copper and nitrate ions are reduced more readily than Pb^{2+}, and thus function as cathodic depolarisers to maintain the cathodic potential below the value required for the reduction of the lead ion. The lead oxide deposition at the anode can be collected at the bottom of the reservoir tank and recovered at the end of the electrolysis process.

In this work a study was carried out for the electrowinning of copper in the presence of lead and iron. The concentration of nitric acid was 0.3M. Preleached nitrate solution (1 litre) was diluted to 10 litre and introduced into reservoir tank of the fluidised bed cell. The electrolysis was carried out at ambient temperature, and a current density of 25 A/m^2 on a titanium cathodes. Periodically during the electrolysis, samples were collected from the reservoir tank and analysed for copper, lead and iron by AAS. The results are given in Table 4.32.

The results obtained showed that 89% of copper is deposited after 6 hours electrolysis time. The subsequent decrease in copper deposition and increase in lead oxide deposition with time is due to the presence of high acid concentration which is produced *in situ* during the electrolysis process.

4.9 CONCLUSIONS OF THE RESULTS OF THIOUREA LEACHING

4.9.1 Effect of Preleaching

The leaching of gold from computer scrap by thiourea solution have been described in this chapter. The analysis of the metal fraction of a computer scrap sample showed that it contained very low concentration of gold along with high concentrations of copper, iron, lead and tin. Before using thiourea solution for the extraction of gold, the sample was preleached with nitric, hydrochloric or sulphuric acid. The results obtained showed that preleaching with 3M nitric acid extracted 95-98 copper, and all of the iron and lead. Leaching the washed residue with acidic thiourea solution then extracted 90-92% gold with very little copper.

Following the thiourea leach stage the washed residue was dissolve in HCl to extract tin.

Experimental results show that pretreatment has a beneficial effect on the extraction of gold in thiourea solution. The maximum gold extraction (90-92%) was achieved when the sample was preleached with 3M nitric acid. The high extraction of gold was due to the presence of less copper and iron (which have a negative influence on the thiourea leaching). Copper and iron compete with gold extraction because they form complexes with the available thiourea and increase the thiourea consumption. The low extraction of gold and high extraction of copper in thiourea solution after pretreatment with HCl, sulphuric acid and without pretreatment was also attributed to the presence of high concentrations of copper and iron in residue.

4.9.2 Effect of Oxidant

The effect of different oxidants on the extraction of gold show that the best extraction achieved when small amounts (0.15%) of Fe^{3+} ion was used as an oxidant. In the presence of an oxidant, thiourea oxidises in successive stages to form several products. The first is the formamidine disulphide which also acts as an oxidant and increase the rate of gold dissolution in thiourea solution.

The low extraction of gold in the presence of hydrogen peroxide alone or in combination with Fe^{3+} as oxidant arises for two reasons: a) hydrogen peroxide can react as a reducing agent in an acidic solution and especially in the presence of transition metals b) the oxidation of thiourea to its secondary product was higher in the presence of hydrogen peroxide. These secondary products of thiourea actually retard the dissolution rate of gold.

4.9.3 Recovery of Gold and Copper

Thiourea leach solutions recover gold in very low concentration and the direct electrowinning by using fluidised bed cell is not economic. The best method of gold extraction from this kind of solution is to use a suitable adsorption system such as activated carbon or resins. After adsorption the barren thiourea solution with some fresh supply can be used for further leaching process. The adsorbed gold can be recovered by using elution method or by burning the adsorption material. After elution, the gold can be recovered by using fluidised bed cell or a two stage electrowinning cell.

The recovery of copper from preleached nitrate solution was carried out by cementation on iron powder and coarse iron filings. The results obtained showed that 97% copper was selectively recovered by cementation at low pH values. At high pH values (2.5) cementation of lead occured along with copper.

The recovery of copper by electrowinning on titanium cathodes using fluidised bed cell was also carried out. The results show that from 0.3M nitic acid it is possible to deposit 89% copper at current density of 25A/m^2 in 6 hours electrolysis time (Table 4.32). The deposition of copper decreased to 87% and 84% after 8 and 10 hours. This decrease was due to excessive acid which produced *in situ* during the electrolysis. Dissolution of some deposited copper occured after 6 hours of electrolysis. At high acid concentration the formation of lead oxide at the anode increased. This increase was due to the presence of copper and nitrate ions which act as depolarisers. Copper and nitrate ions are reduced more easily than pb^{2+} and thus function as a cathodic depolarisers to maintain the cathodic potential below the value required for the reduction of the lead ion. The lead oxide formed at anodes is detached during the upward and downward movement of the fluidiser glass beads and can be recovered easily at the end of electrolysis process and uses in the manufacture of lead chemicals.

4.10 SUMMARY

From the experimental results it can be concluded that the future adoption of acidothiouration to replace traditional cyanidation method looks very promising. Thiourea dissolves gold in the presence of an oxidant from materials with low gold contents. Different oxidants were studied and the best results were found using Fe^{3+} ions. The gold content of leach solution can be recovered by using suitable adsorption material such as activated carbon or cationite resins, and the barren thiourea solution may then be recirculated. The complete removal of gold is necessary when the leaching solution is to be rejected. After elution of the gold from the adsorbed material it is recovered from eluants by electrowinning with a fluidised bed or a two stage cell.

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CHAPTER 5

MANUFACTURE OF ARSENIC ACID FROM ARSENIC(III) OXIDE

CHAPTER FIVE

MANUFACTURE OF ARSENIC ACID FROM ARSENIC(III) OXIDE

5.1 ARSENIC AND ITS OXIDES

5.1.1 Arsenic

Arsenic is a trivalent metalloid of atomic weight 75, density 5.72 and specific gravity 5.725. Arsenic minerals are widely distributed throughout the world and small amounts of the free element have also been found. Common minerals include the sulphides realgar (As_4S_4) and orpiment (As_2S_3), and the oxide form, arsenolite (As_2O_3). The arsenides of Fe, Co, and Ni and the mixed sulphides with these metals form another set of minerals, e.g. loellingite ($FeAs_2$), safforlite (CoAs), niccolite (NiAs), rammelsbergite ($NiAs_2$), arsenopyrite or mispickel (FeAsS), cobaltite (CoAsS), enargite (Cu_3AsS_4) and gerdsorfite (NiAsS)[1]. It is liberated from its ores by heating in enclosed metal retorts, when the element distils over and is condensed to a steel-grey mass of rhombohedral crystals which possess a metallic lustre. Elemental arsenic is obtained on an industrial scale by smelting $FeAs_2$ or FeAsS at 650-700°C in the absence of air and condensing the sublimed element:

$$\text{FeAsS} \xrightarrow{\quad} \text{FeS} + \text{As(g)} \xrightarrow{\quad} \text{As(s)} \qquad (1)$$

Residual arsenic trapped in the sulphide residues can be released by roasting them in air and trapping the sublimed As_2O_3 in the flue system. The oxide can then either be used directly for chemical products or be reduced with charcoal at 700-800°C to give more arsenic[2]. As_2O_3 is also obtained in large quantities as flue dust from the smelting of Cu and Pb concentrates and, because of the huge scale of these operations, secondary arisings represent the most important industrial source of As_2O_3 and can be used in the manufacture of arsenic acid[3].

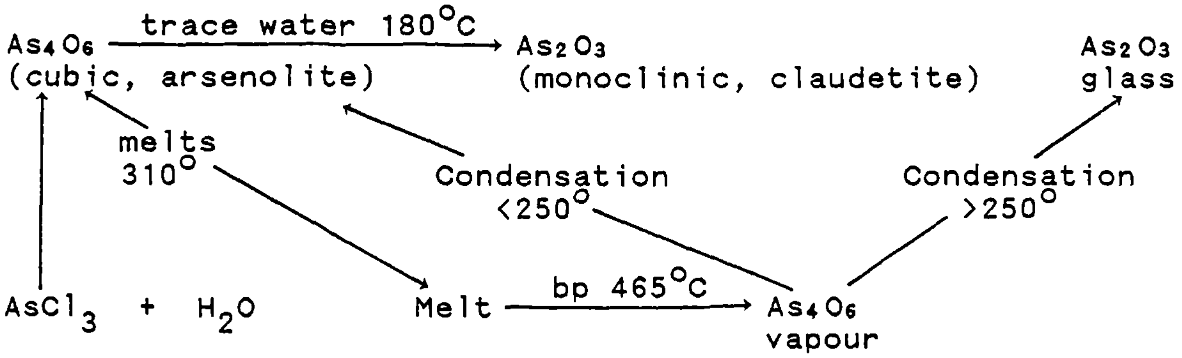
There are three crystalline forms of arsenic. The grey rhombohedral form is the most stable at room temperature and has a structure[4] in which the atoms are linked into sheets which are fitted together so that each atom has six neighbours. Three on one side are at a distance r_1 (2.51 Å), and three on the other side are slightly further away at a distance r_2 (3.12 Å) and the angle As-As-As is 96.7.

5.1.2 Arsenic Trioxide

The most important commercial compound of arsenic is arsenic(III) oxide, As_2O_3. While it occurs naturally, it is usually manufactured by burning arsenic in air, by hydrolysis of $AsCl_3$, or by roasting sulphide ores such as arsenopyrite:

$$2FeAsS + 5O_2 \text{ ------> } Fe_2O_3 + 2SO_2 + As_2O_3 \qquad (2)$$

Arsenic(III) oxide exists in two polymorphic modifications (Scheme 5.1). Both modifications occur in nature - as cubic arsenolite, and monoclinic claudetite[4]. The regular cubic form is the modification of arsenic trioxide stable at ambient temperatures (m.p. 310 , b.p. 465), while the monoclinic modification is stable above 221°.



SCHEME 5.1 Polymorphs of arsenic(III) oxide.

Arsenic(III) oxide vaporizes readily when it is heated. In the vapour phase, As_2O_3 exists as As_4O_6 molecules (Figure 5.1), and this unit also occurs in the cubic crystalline form. The vapours condense in a glassy form of arsenic if the vessel walls are at temperatures above 250°C, and as a mass of cubic crystals at lower temperatures. Above 800°C

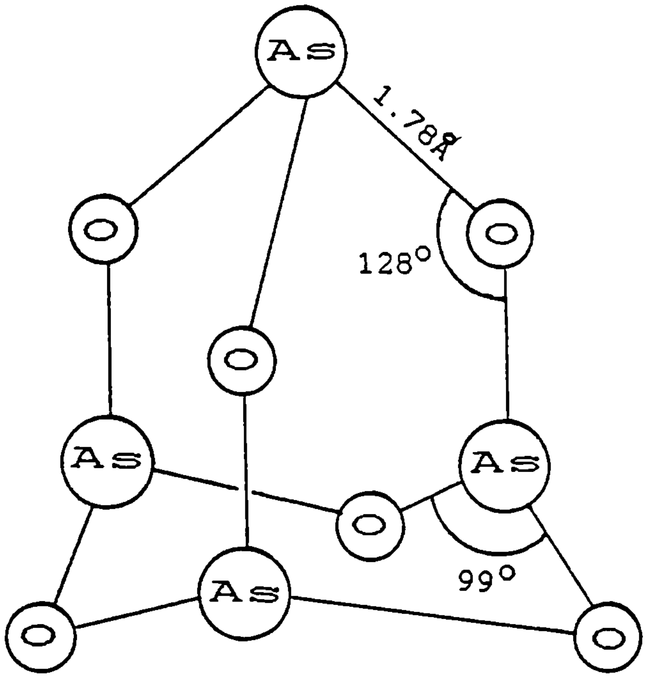
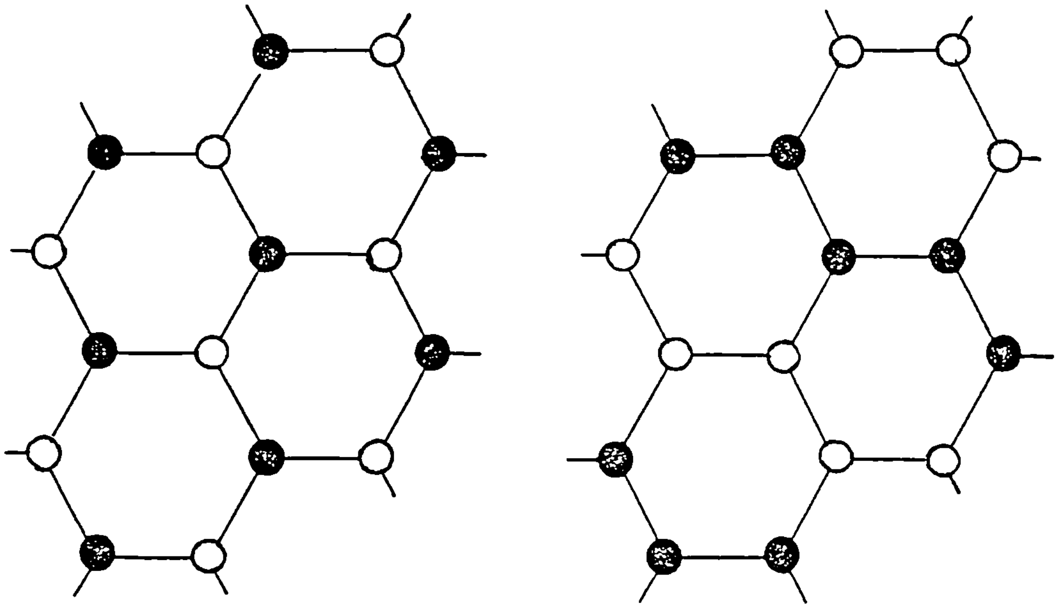


FIGURE 5.1 Molecular structure of As_4O_6.



claudetite-II

claudetite-I

● As atoms above plane of oxygens

○ As atoms below plane of oxygens

FIGURE 5.2 Arrangement of As atoms in the layer structute of monoclinic, As_2O_3 (claudetite).

gaseous As_4O_6 partially dissociates into an equilibrium mixture containing both As_4O_6 and As_2O_3 molecules. This transformation from molecular As_4O_6 units to polymeric As_2O_3 is accompanied by an 8.7% increase in density from 3.8 to 4.2 g/cm^3.

There are two modifications of the monoclinic mineral claudetite. Both have layer structures in which the arsenic atoms are joined through O atoms. The layers are puckered with bond angles of 95.5 (O-As-O) and bond distance of 1.79Å (As-O). The two forms differ in the arrangement of arsenic atoms in the layers. Since each arsenic atom could be either above or below the mean plane of the O atoms there are various possible configurations of the layer differing only in the arrangement of the arsenic atoms (see in Figure 5.2 in which only arsenic atoms are shown).

The solubility of As_2O_3 in water, and the species present in solution, depend markedly on pH. In pure water at 25^{o}C the solubility is 2.1 g per 100 g; this diminishes in dilute HCl to a minimum of 1.5 g per 100 g at about 3M HCl and then increases, presumably due to the formation of chloro-complexes. In neutral or acidic solutions the main species is probably pyramidal $As(OH)_3$, though this compound has never been isolated from solution. The solubility is much greater in basic solutions and spectroscopic evidence points to the presence of anions such as $[AsO(OH)_2]^-$, $[AsO_2(OH)]^{2-}$ and $[AsO_3]^{3-}$. There now seems to be less evidence for other species that were formerly considered to be present in solution, e.g. $HAsO_2$, and $H_3[As(OH)_6]$ or its hydrate, $As(OH)_3(OH_2)_3$[5,6].

Arsenic trioxide is widely used as a pesticide and a wood preservative and, in association with sulphur, in the manufacture of sheep-dips. It is also used in glass manufacture as a clarifying agent and in the manufacture of pigments such as Schweinfurth Green (copper acetoarsenite) and Scheele's Green (copper hydrogen arsenite). Medicinal and veterinary uses are declining, because of concerns about the toxicity of arsenic. The overall pattern of commercial uses of arsenic trioxide in the USA in 1974 is summarized in Table 5.1[5].

TABLE 5.1. SOME USES OF ARSENIC TRIOXIDE

Use	Pesticides	Wood preservatives	Glass	Alloys and electronics	Miscel-laneous
As_2O_3/ton	34000	9500	5000	1500	2000
Percentage	65	18	10	3	4

5.1.3 Arsenic Pentoxide

Arsenic(V) oxide, As_2O_5, is one of the oldest known oxides, but its structure has only been determined very recently because of poor thermal stability, ease of hydrolysis, and the difficulty of growing a single crystal. The structure consists of equal numbers of octahedra and tetrahedra completely linked by corner sharing to give cross-linked strands[7]. As_2O_5 can be prepared either by heating arsenic (or As_2O_3) with O_2 under pressure or by dehydrating crystalline H_3AsO_4 above 200°C. As_2O_5 is deliquescent, very soluble in water, thermally unstable, and an oxidizing agent.

The reaction between As_2O_3 and concentrated nitric acid yields a solution from which two solids may be recrystallized, the product obtained depending on the temperature.

$$As_2O_3 + HNO_3 \longrightarrow \begin{array}{c} 2H_3AsO_4.H_2O\ (\text{recryst. } <30^\circ C) \\ \text{or} \\ 3As_2O_5.5H_2O\ (\text{recryst. } >100^\circ C) \end{array} \xrightarrow{>170^\circ C} As_2O_5$$

$2H_3AsO_4.H_2O$ has a structure in which double sheets of AsO_4 tetrahedra and water molecules are linked by hydrogen bonds. It loses water at 100°C to form $3As_2O_5.5H_2O$ which has a structure in which infinite band-like molecules $(H_5As_3O_{10})_x$ are joined by short hydrogen bonds (O---O, 2.40-2.45 Å) (Figure 5.3). Two of the arsenic atoms in the repeating unit have the usual tetrahedral co-ordination (As-O, 1.69 Å) and

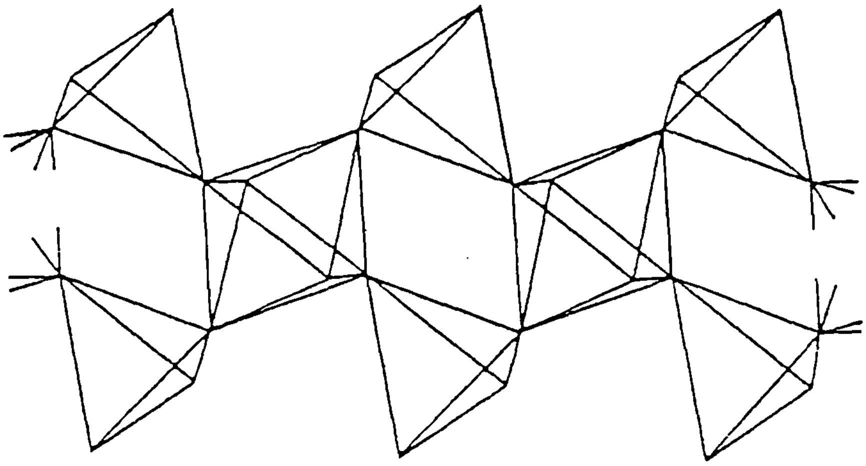


FIGURE 5.3 The linked AsO_4 tetrahedra and AsO_6 octahedra in $As_2O_5.5H_2O$.

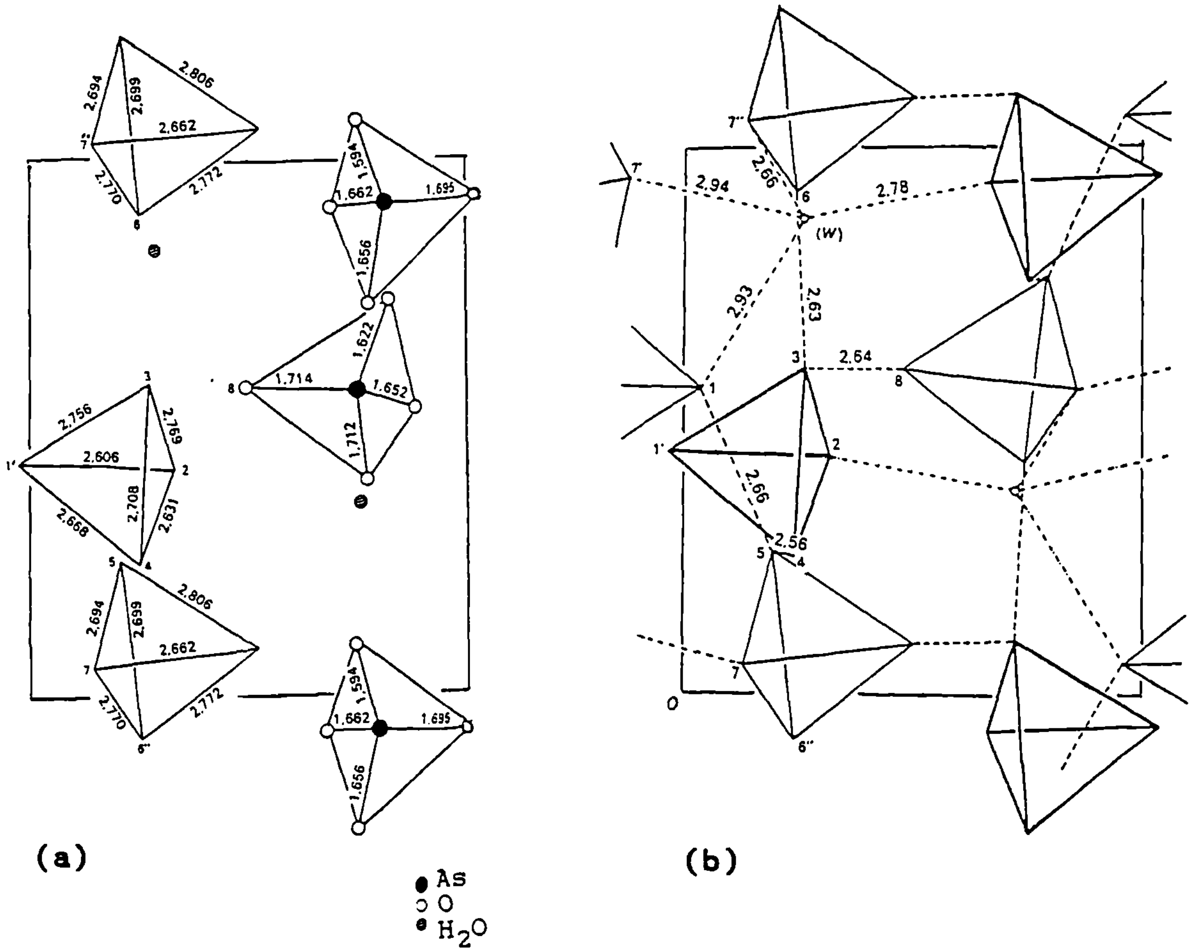


FIGURE 5.4 Structure of $2H_3AsO_4.2H_2O$.

(a) As-O, bond lengths in tetrahedra, AsO_4.

(b) Position of hydrogen bonding, (-----), between tetrahedra, hydrogen bonding, (-·-·-), between tetrahedra and water molecule in double sheet.

the other atom is six-co-ordinated (As-O, 1.82 Å). Both solids yield analytically pure As_2O_5, when heated to constant weight at 350°C.

5.1.4 Arsenic Acid

In aqueous solution, arsenic acid has the formula H_3AsO_4. It is crystallised as a hydrate and can be progressively dehydrated by the stepwise removal of water molecules to form $HAsO_3$ and $H_4As_2O_7$[8].

The crystal structure of $2H_3AsO_4,H_2O$, ($As_2O_5.4H_2O$) has been determined[10]. It contains double sheets of AsO_4 tetrahedra and water molecules linked by hydrogen bonding (Figure 5.4). Arsenic acid and its dehydrated forms have long been used as a pest control agent in insecticides, herbicides and rodenticides, as a component of certain timber preservation products, as a defoliant, and as a desiccant for cotton. It is also used in the manufacture of arsenates for the glass industry.

5.2 PRODUCTION OF ARSENIC ACID

Many methods have been proposed for the industrial manufacture of arsenic acid, the majority of which involve the oxidation of arsenic trioxide, As_2O_3. Oxidising agents that have been proposed for this purpose include chlorine[9-11], sodium or potassium chlorate[12,13], air or oxygen[14-16], hydrogen peroxide[17,18], water/oxygen[19], and nitric acid[20]. Electrolysis oxidation has also been proposed[21,22].

5.2.1 Nitric Acid Method

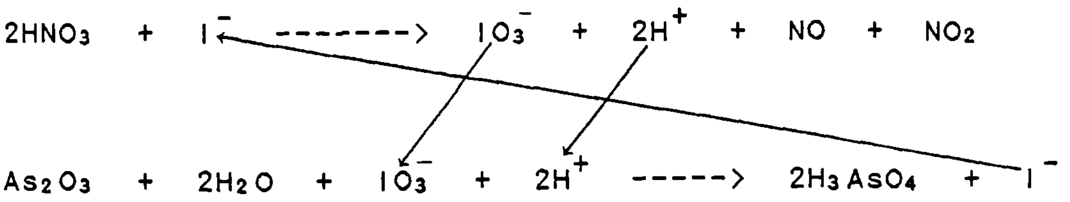
The oxidation of As_2O_3 by nitric acid is the method generally used for the commercial production of arsenic acid. Various catalysts or co-oxidants proposed for use in this reaction include oxygen[23], hydrochloric acid[24,25], air and water[26,27]. The catalysts most commonly used in modern plants are, however, sodium or potassium iodide[28].

The reaction occurring in the manufacture of arsenic acid by nitric acid method may be represented in its simplest form as:

$$As_2O_3 + 2HNO_3 + 2H_2O \longrightarrow 2H_3AsO_4 + NO + NO_2 \quad (4)$$

The process is generally carried out by feeding arsenic trioxide, nitric acid and catalyst (for example, potassium iodide) continuously into a heated reactor at atmospheric pressure, discharging the gaseous nitrogen oxides formed, and running-off the product arsenic acid (Figure 5.5).

It is thought that the nitric acid method using the conventional catalyst (KI) proceeds through a mechanism involving iodate.



$$2HNO_3 + I^- \longrightarrow IO_3^- + 2H^+ + NO + NO_2 \quad (5)$$

$$As_2O_3 + 2H_2O + IO_3^- + 2H^+ \longrightarrow 2H_3AsO_4 + I^- \quad (6)$$

The sum of equations (5) and (6) is equation (4) above.

A number of problems are encountered in operating conventional process based on the nitric acid - As_2O_3 reaction. One of these arises because of the excessive foaming that tends to occur as a result of the large volumes of nitrogen oxides produced. If foaming becomes excessive there is risk of boil-over or blow-out, particularly when there is a build-up in the reactor of large amounts of one or both unreacted starting materials as a result of feed blockage, irregular feeding of one of the reactants, or if the temperature of the reaction mixture should fall too low.

Apart from the problems caused by excessive foaming, the reaction is in any case difficult to control: considerable heat is evolved during the early stages of the process but heat has to be supplied during the later stages. The reactor has to be heated up in advance of mixing the reactants, because there is a risk of sludging, and

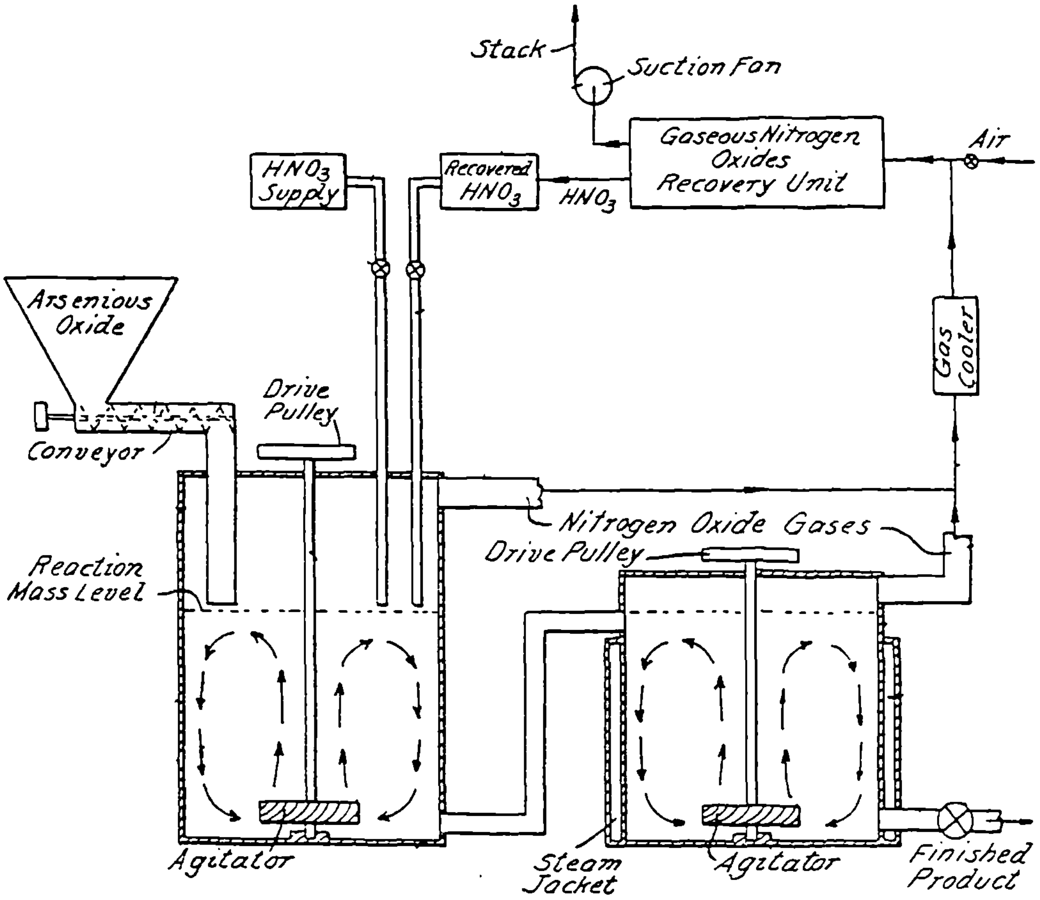


FIGURE 5.5 Industrial production of arsenic acid by reaction of nitric acid and arsenic trioxide, with recovery of nitric acid.

consequent foaming and boil-over because of an initial build-up of unreacted starting materials if the initial temperature is too low. On the other hand, due to its exothermic nature, the process cannot readily be terminated prematurely, if it appears to be getting out of control. Various measures have been proposed for adding and mixing the reactants in a controlled manner in order to overcome such difficulties, but the difficulties still occur even in modern plants[29,30].

The main reason for wishing to retain the nitric acid- As_2O_3 process for commercial purpose is the ease of recycling the oxidant. All plants manufacturing arsenic acid by the nitric acid method therefore include apparatus for recovering the nitric acid. This may be a series of reaction towers connected directly to the main reactor and through which the gaseous nitrogen oxides issuing from the main reactor are admixed with controlled quantities of air and then contacted with suitable oxidant, such as hydrogen peroxide:

$$2NO + 2NO_2 + 2H_2O_2 + O_2 \text{ -----> } 4HNO_3 \qquad (7)$$

or dilute nitric acid:

$$NO + NO_2 + HNO_3 + H_2O + O_2 \text{ -----> } 3HNO_3 \qquad (8)$$

The difficulties associated with the use of nitric acid and arsenic(III) oxide for the production of arsenic acid can, thus, be expressed in term of two problems that must be overcome to achieve an efficient and safe industrial process. These problems stem from 1) difficulty in controlling the rate of the reaction; and 2) the different reactivities of samples of arsenic(III) oxide obtained from different sources and particularly from secondary sources. In spite of these difficulties the nitric acid remains the preferred route for the commercial production of arsenic acid.

The aim of the work described in this chapter is to devise a method to control the rate of reaction and to reduce the effects of the differences in reactivities of arsenic(III) oxide samples from various sources. The next sections describe: (a) the development of experimental methods to follow the reaction; (b) studies on the variable parameters in the reaction; and (c) the specification of new procedure to achieve control over the reaction process.

5.3 STUDY OF THE NITRIC ACID-ARSENIC(III) OXIDE REACTION

Arsenic(III) oxide reacts with nitric acid in the presence of a catalyst to produce arsenic acid according to the chemical reaction given in equation (4). The reaction was carried out by feeding the reactants and catalyst into the heated vessel at ambient pressure.

5.3.1 Experimental Methods to study the Reaction

In spite of the complications involved in the production of arsenic acid by the nitric acid method it is the most commonly used method for the industrial scale manufacture of arsenic acid and is used, for example, by William Blythe & Co Ltd. Church, Accrington, U.K. The William Blythe process was used as the starting point of the studies described here and all suggested developments made as a result of the work described in this chapter were tested on an industrial scale in the William Blythe plant.

The industrial production of arsenic acid by William Blythe & Co is typical and is carried out by the batchwise addition of arsenic trioxide to a large reaction vat containing dilute nitric acid at 70^{o}C (Figure 5.5). The reaction mass is agitated during the addition of raw material and throughout the reaction period. A catalyst (2% KI) is also added dropwise throughout the process from the top of the reaction vat. Over the course of the reaction, and for economic reasons these nitrogen oxides are recovered as nitric acid . The gases with drawn from the reaction chamber mixed with the necessary amount of air, and introduced into a absorption system in which the nitrogen oxide gases are recovered as 27% nitric acid. This nitric acid, together with fresh supply to make up for the amount of acid lost, is reacted with further quantities of arsenic oxide.

This process was subject to the problems described in the previous section. The principal difficulties encountered arose from the inconsistency of nitric acid-arsenic trioxide reaction. In its initial stage, the reaction takes place with great rapidity and large volumes of gaseous nitrogen oxides are evolved often with almost explosive violence. In the later stages reaction velocity drops off rapidly and heat has to be supplied to finish the reaction. The generation of these large volumes of gaseous nitrogen oxide often lead to excessive foaming and, if the foaming becomes excessive, a boil-over can occur when the whole reaction mass bubbles out of the reaction vat along with the reaction gases.

The reaction between nitric acid and arsenic(III) oxide was followed in the present work in a series of experiments using six different samples of commercial arsenic(III) oxide, *viz.*:

(1). TSUMEB (2). LEPANTO (3). HOBOKEN
(4). CHILEAN (5). SALSIGNE-A (6). SALSIGNE-B

Each sample assayed as 98.4-98.9% As_2O_3 with trace impurities of Fe, Pb and Hg.

Two procedures used to follow the course of the reaction between arsenic trioxide and nitric acid namely:

a) chemical analysis of the reaction gases
b) manometric measurement of reaction gases

<u>a) Chemical Analysis of the Reaction Gases</u>

The course of the reaction:

$$As_2O_3 + 2HNO_3 + 2H_2O \text{ -------> } 2H_3AsO_4 + NO + NO_2$$

can be followed by absorbing the nitrogen oxide gases in either water:

$$2NO + 2NO_2 + 2H_2O + O_2 \text{ ----> } 2HNO_3 + 2HNO_2$$

or hydrogen peroxide:

$$2NO + 2NO_2 + 2H_2O_2 + O_2 \text{ ----> } 4HNO_3$$

followed by determination of nitric and nitrous acid by ion chromatography and by pH measurements.

The ion chromatography traces (Figure 5.6) for the gases absorbed in water clearly show the presence of NO_2^- and NO_3^- whereas the H_2O_2 absorbent shows the presence of only NO_3^-. For ease of analysis subsequent monitoring by this route was carried out using hydrogen peroxide as absorbent and determining total nitrogen oxide gases as nitrate. The calibration graph for nitrate concentration against peak height is linear for up to 20ppm (Figure 5.7).

During the reaction of 25g of arsenic trioxide with 500ml of (27%) nitric acid containing 2ml of 2% KI solution, the evolved nitrogen oxides were absorbed in one litre of 40% hydrogen peroxide absorption system. Periodically during the reaction process, 5ml aliquots were taken and diluted to 100ml with the fresh absorbent and then analysed for nitrate by ion chromatography. Results of this type of reaction monitoring (Figure 5.8) show the actual nitrate concentration measured over a period of up to one hour. The amount of nitrate ion absorbed can also be determined indirectly, and inexpensively, but not so accurately, by measuring pH changes. The graph of pH against time measured concurrently with the data shown in Figure 5.6 is shown in Figure 5.9.

The data suggest that large volumes of gases are evolved during the early part of the reaction but, after 20 minutes, the rate slows and less gas evolution occurs. Chemical

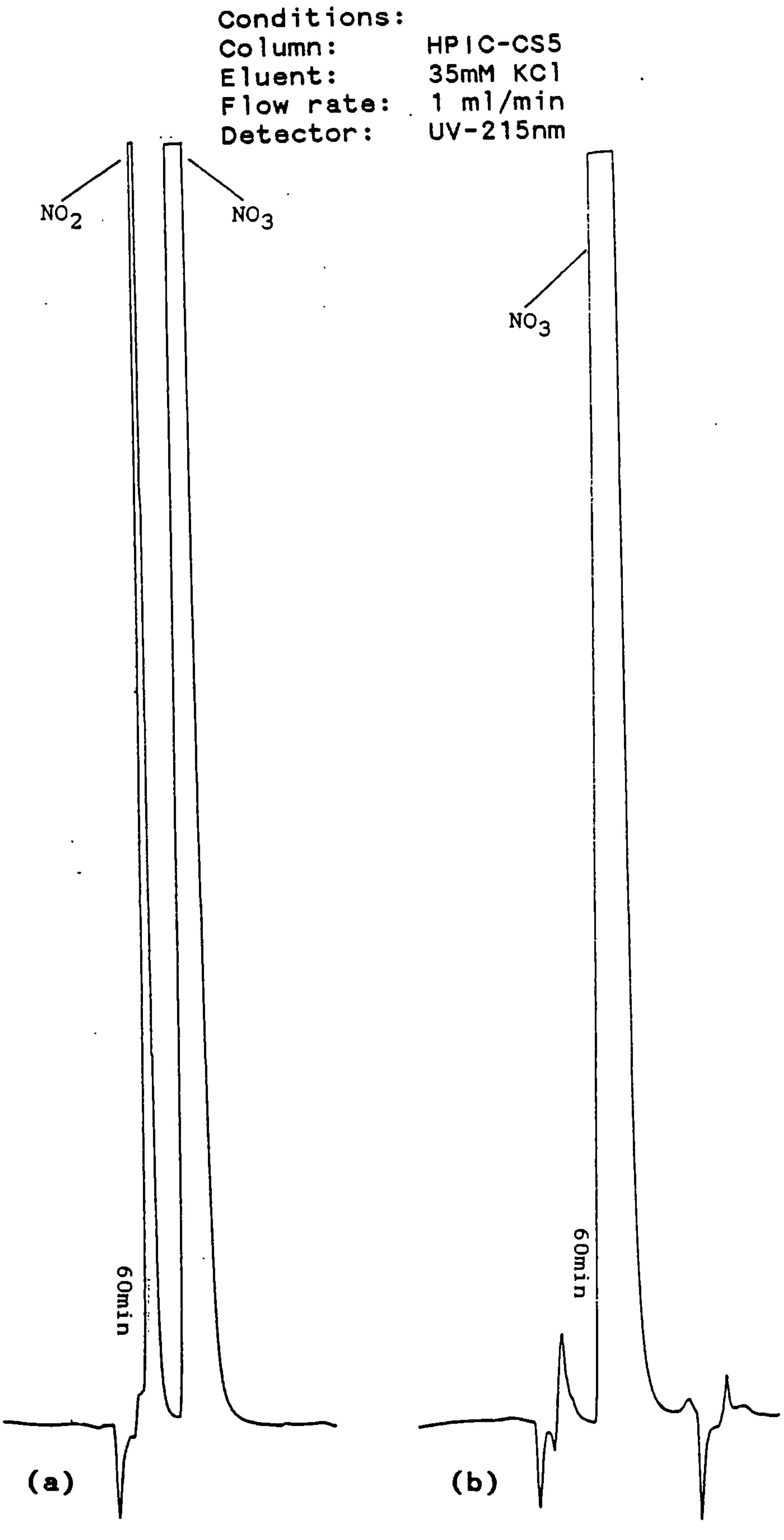
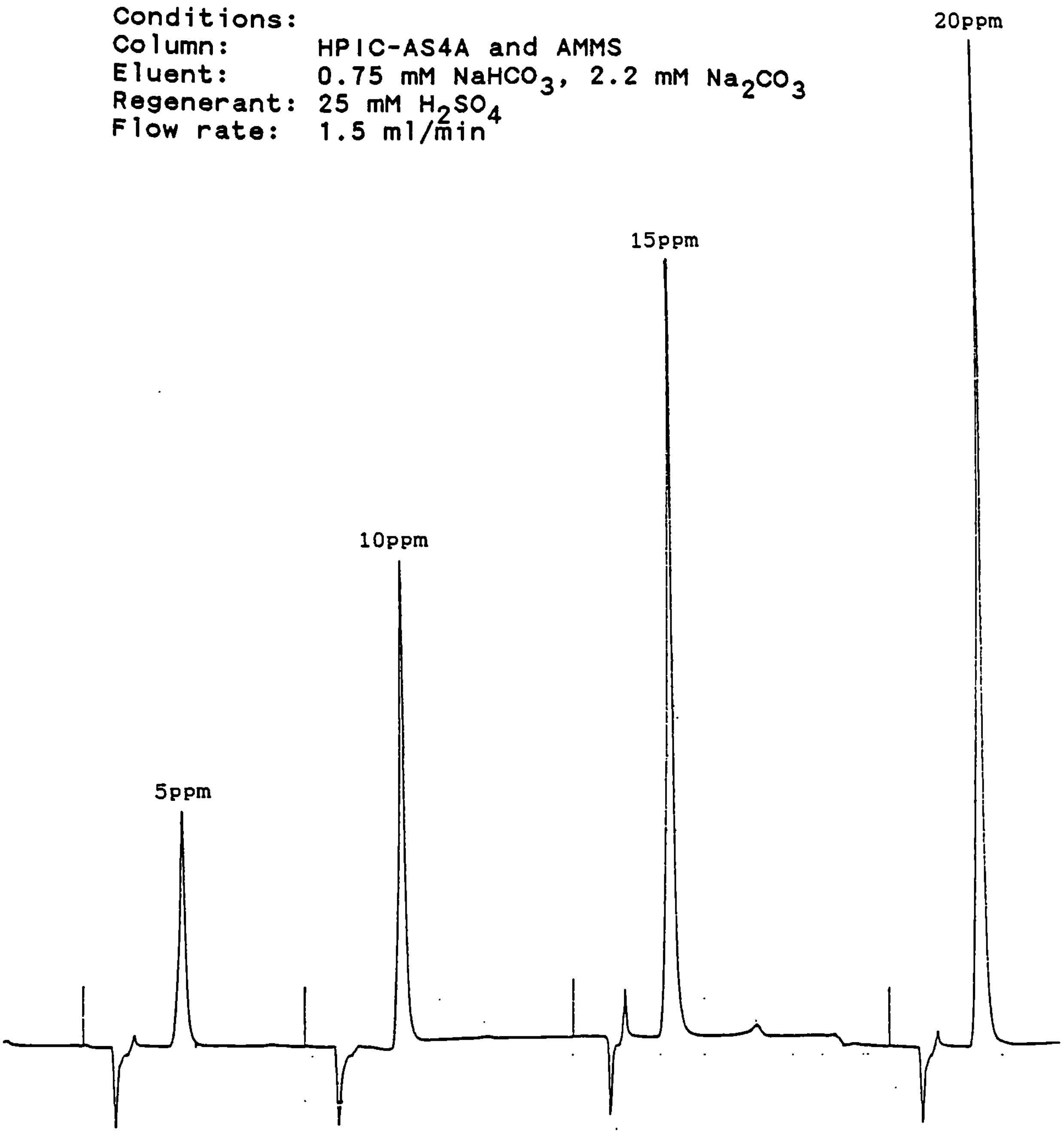


FIGURE 5.6 Chromatographic analysis of (a) distilled water absorption system and (b) H_2O_2 absorption system.



Conditions:
Column: HPIC-AS4A and AMMS
Eluent: 0.75 mM $NaHCO_3$, 2.2 mM Na_2CO_3
Regenerant: 25 mM H_2SO_4
Flow rate: 1.5 ml/min

FIGURE 5.7 Nitrate ion standards for HPIC.

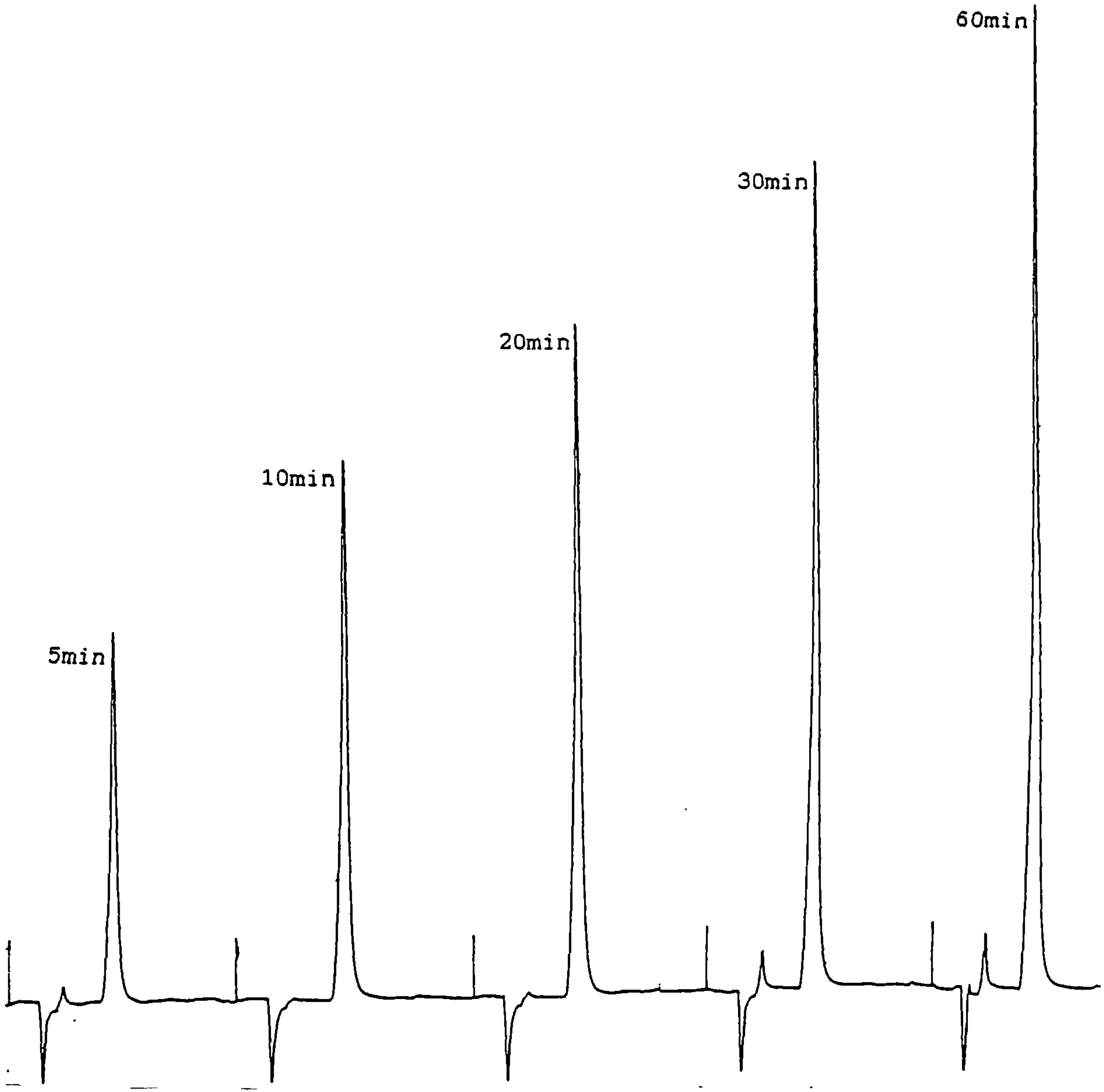


FIGURE 5.8 Concentration of NO_3^- ions in H_2O_2 absorbent.

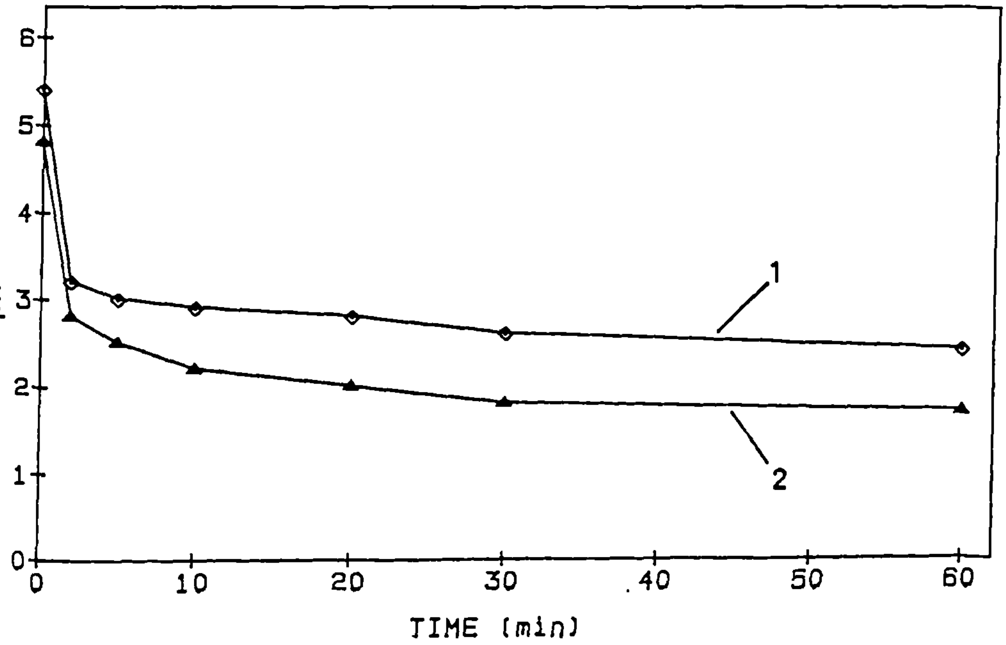


FIGURE 5.9 Decrease in pH versus time:
(1, H_2O absorbent; 2, H_2O_2 absorbent).

analysis of the reaction gases was only possible when a small amount of arsenic trioxide (25g) was used. With larger amounts of arsenic trioxide much greater volumes of peroxide are needed to absorb the gases efficiently to give accurate nitrate analysis.

b) Manometric Measurement of the Reaction Gases

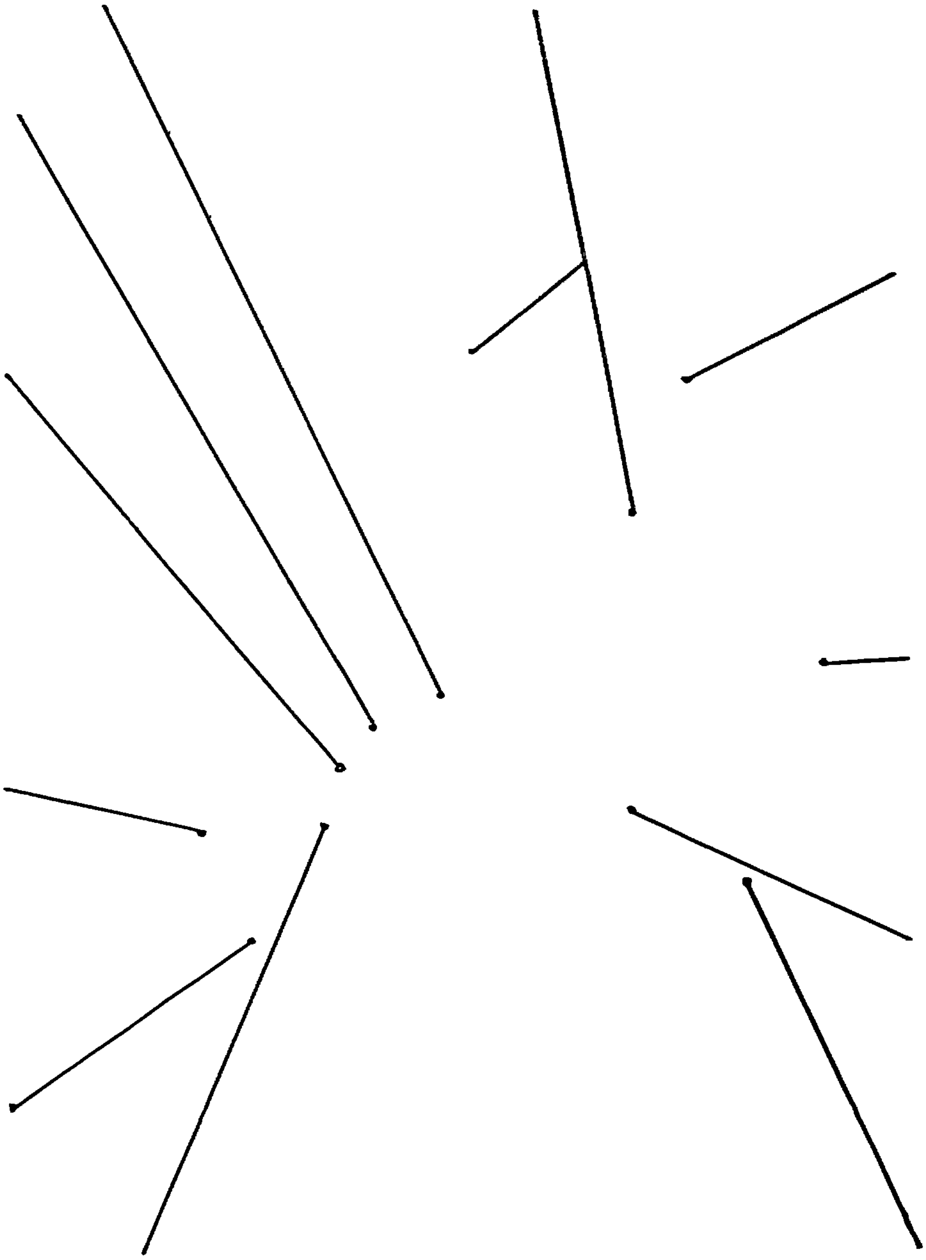
A simple and effective manometer was built for the manometric measurement of the nitrogen oxides gases evolved during the production of arsenic acid. It consists of 225mm long glass tube with an internal diameter of 20mm. One end of this tube was closed and the other end was joined with 24/29 male quickfit socket. A second glass tube with an internal diameter of 6mm was joined at an angle of 45 with the big tube at distance of 60mm away from the closed end. The larger tube was filled with light silicone fluid MS 550 and two marks A and B 250mm apart were etched on the small long tube. The open end of the long glass tube was placed in a flask in order to collect any over flow of silicone fluid.

The manometer was connected via an unreactive silicone tube to the outlet of the reaction flask (Fig. 5.10). During the reaction the gas outlet was closed, usually after every minute (T), and the instantaneous rise in pressure was measured over the silicone fluid manometer. The time (t in sec) taken by the silicone fluid in manometer to travel the 250mm from mark A to B was measured. The results are represented as a plot between T and 1/t.

All the manometric results obtained were represented as a plot between T and 1/t, (where T is the time (in min) from the start of the reaction and 1/t (in sec) is the time taken for the silicone fluid in manometer to travel a measured distance).

5.3.2 Standard Reaction of Arsenic Oxide with Nitric Acid

The standard method of producing arsenic acid involves the addition of solid arsenic(III) oxide to nitric acid. In all



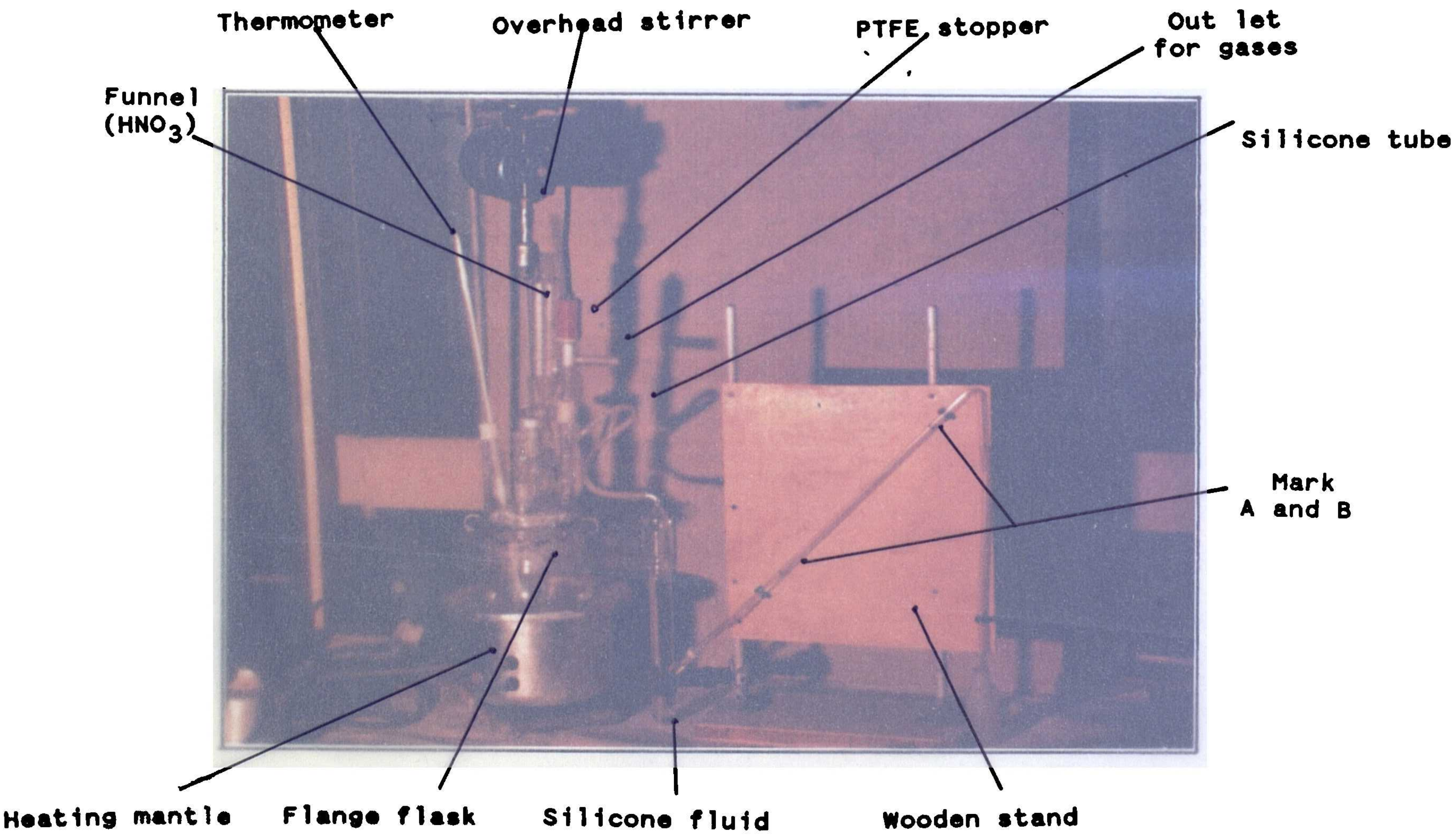


FIGURE 5.10 Experimental setup for the production of arsenic acid and manometric measurement of the reaction gases.

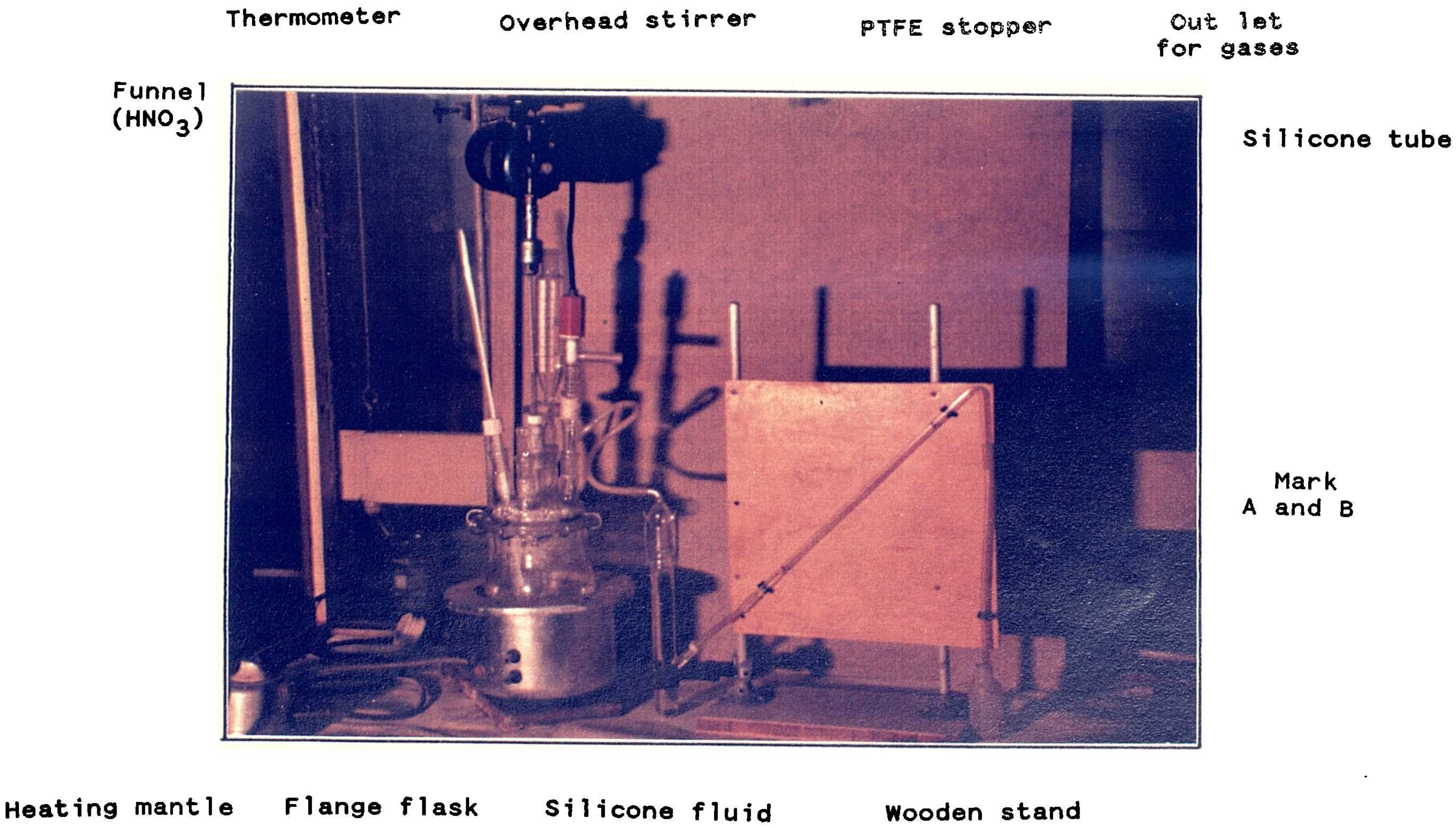
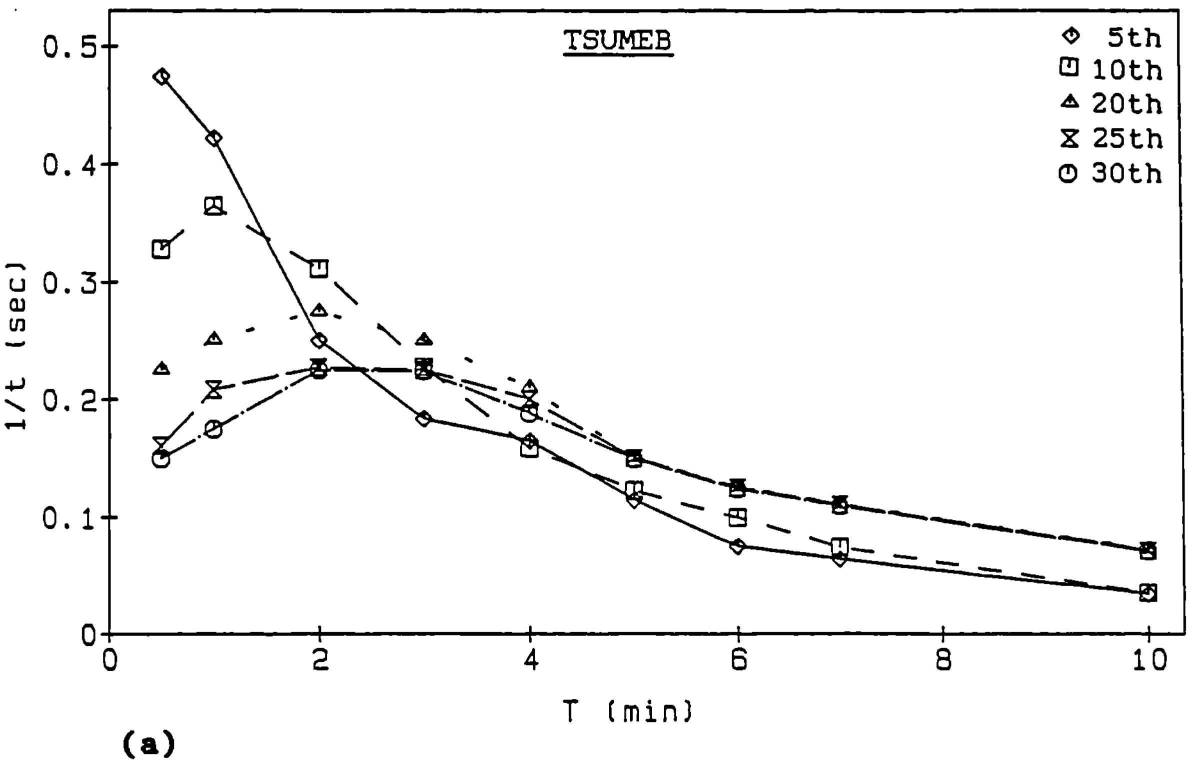


FIGURE 5.10 Experimental setup for the production of arsenic acid and manometric measurement of the reaction gases.

experiments on the standard reaction carried out in this work a 500ml flange flask was used. The flask was charged with 450ml of 27% nitric acid and placed on the heating mantle. An overhead stirrer was used continuously throughout the experiment to slowly agitate the reaction mass. The flask contents were heated to 70°C and 2ml of 2% KI catalyst was added along with the first aliquot of arsenic trioxide powder. A total of 150g of arsenic oxide was added in the form of 5g aliquots at 10 minutes intervals. The reaction generally started after the addition of the 4th aliquot and was marked by a sudden evolution of gas. The instantaneous rise in pressure due to the product gases was monitored on the silicone fluid manometer after the addition of 5th (25g), 10th (50g), 20th (100g), 25th (125g) and 30th (150g) aliquots of arsenic oxides. Control of gas evolution under different conditions is represented in Figures 5.11-5.16, which are graphs of time (T) from the start of the reaction against 1/t. Most of the plots are represented in two forms to give information on effects of addition of individual aliquots of arsenic oxide and the cumulative effect.

The data in Figures 5.11-5.16 represent the reaction of TSUMEB, HOBOKEN and MIXED arsenic(III) oxide samples with nitric acid under different conditions. The same amount of catalyst was used in each experiment (2ml of 2% KI). The graphs show that after the addition of 5th aliquot, the reaction was very rapid especially during the early part (1/t > 0.6). In the later part the reaction substantially flattened off (1/t < 0.1). After the addition of 10th, 20th, 25th and 30th aliquots of arsenic oxide the reaction was fairly rapid but the reaction peaks were low as compared to reaction peak obtained after the addition of 5th aliquot. During the course of reaction, stirring played an important role in control of reaction. If the stirring is very fast then the rate of foaming formation is increased and solid arsenic is carried out of the reaction flask with the reaction gases. The following reaction variables were studied:



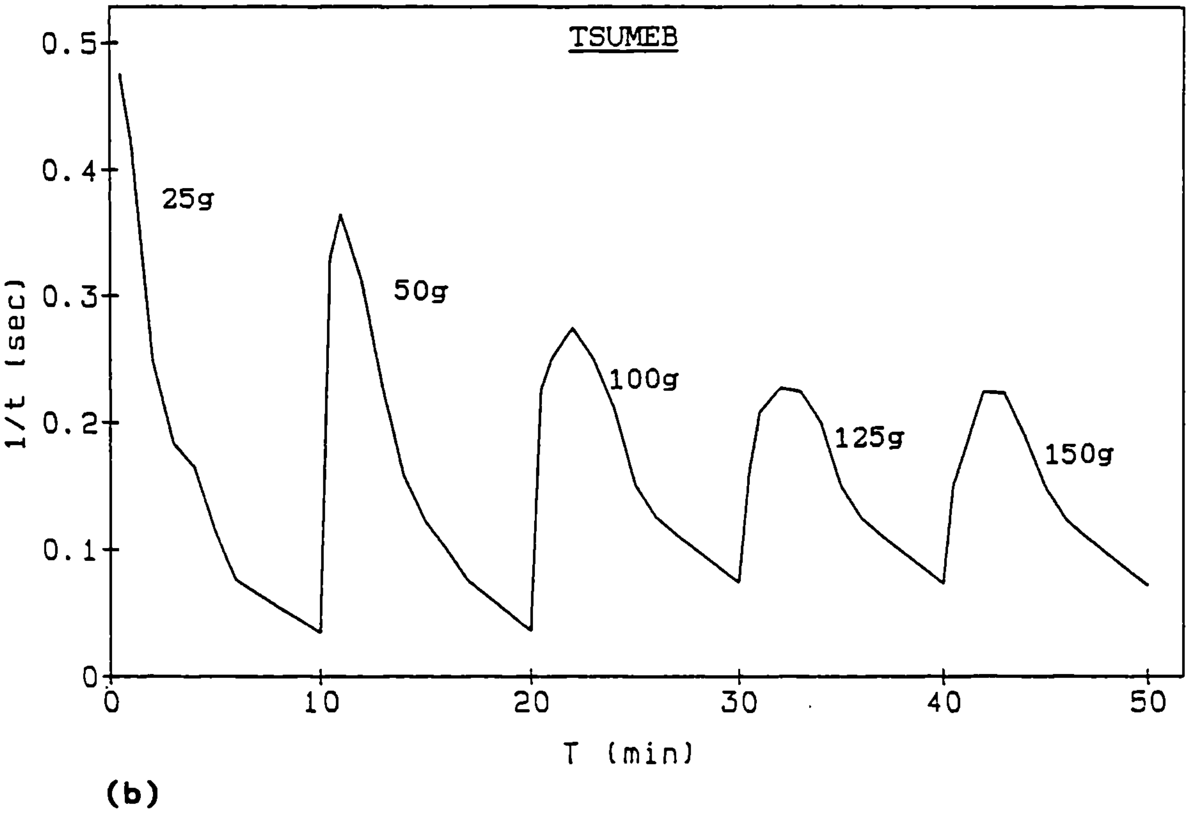
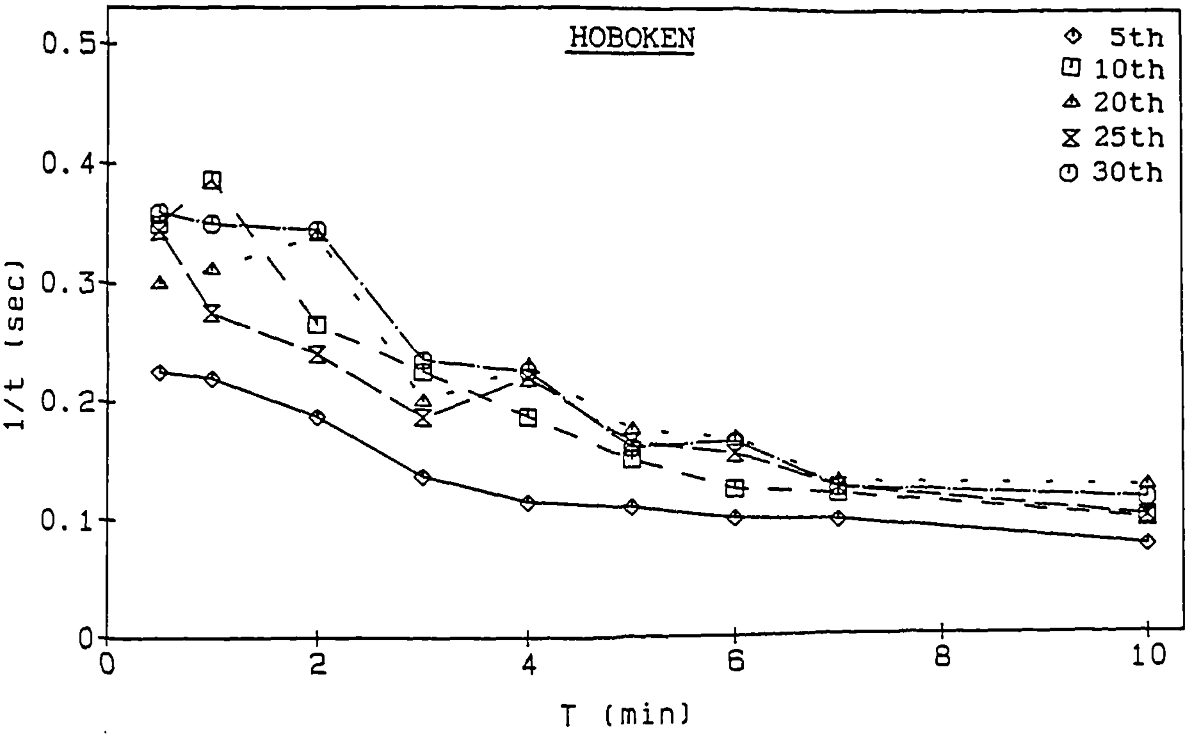
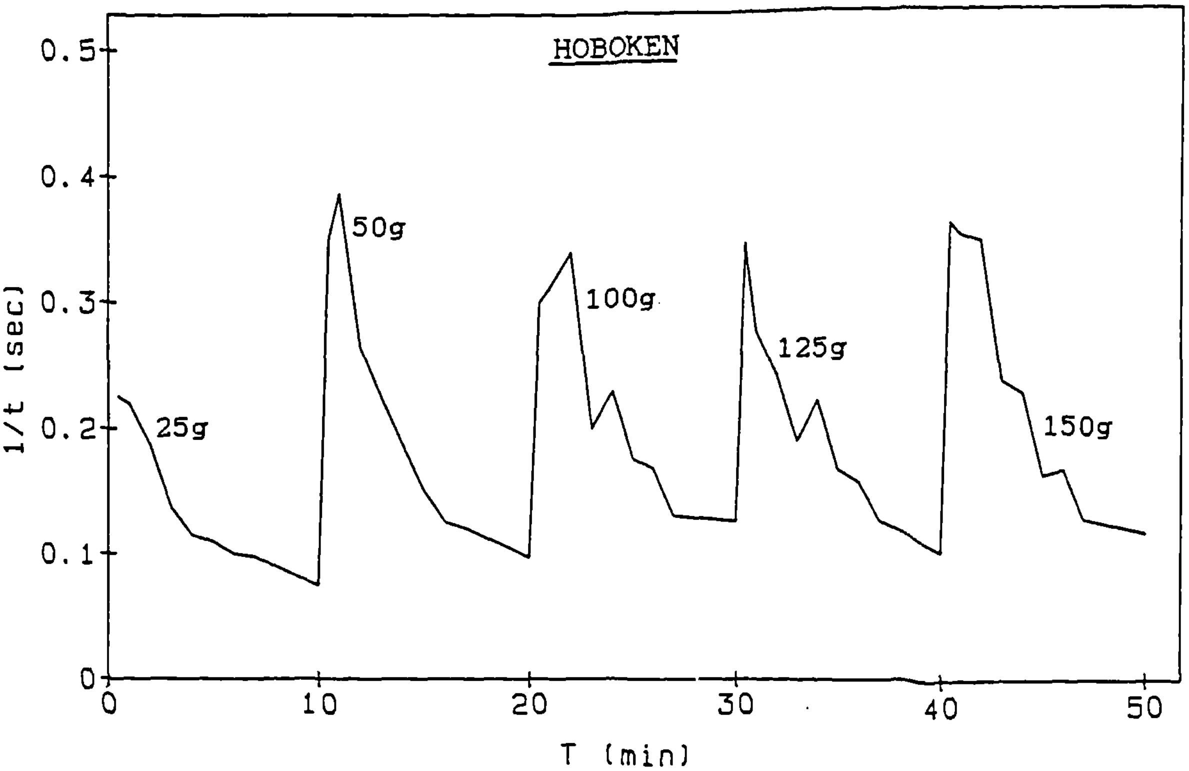


FIGURE 5.11 Reaction behaviour of TSUMEB with 27% nitric acid at 70°C: (a) effect of individual aliquots (b) cumulative effect.

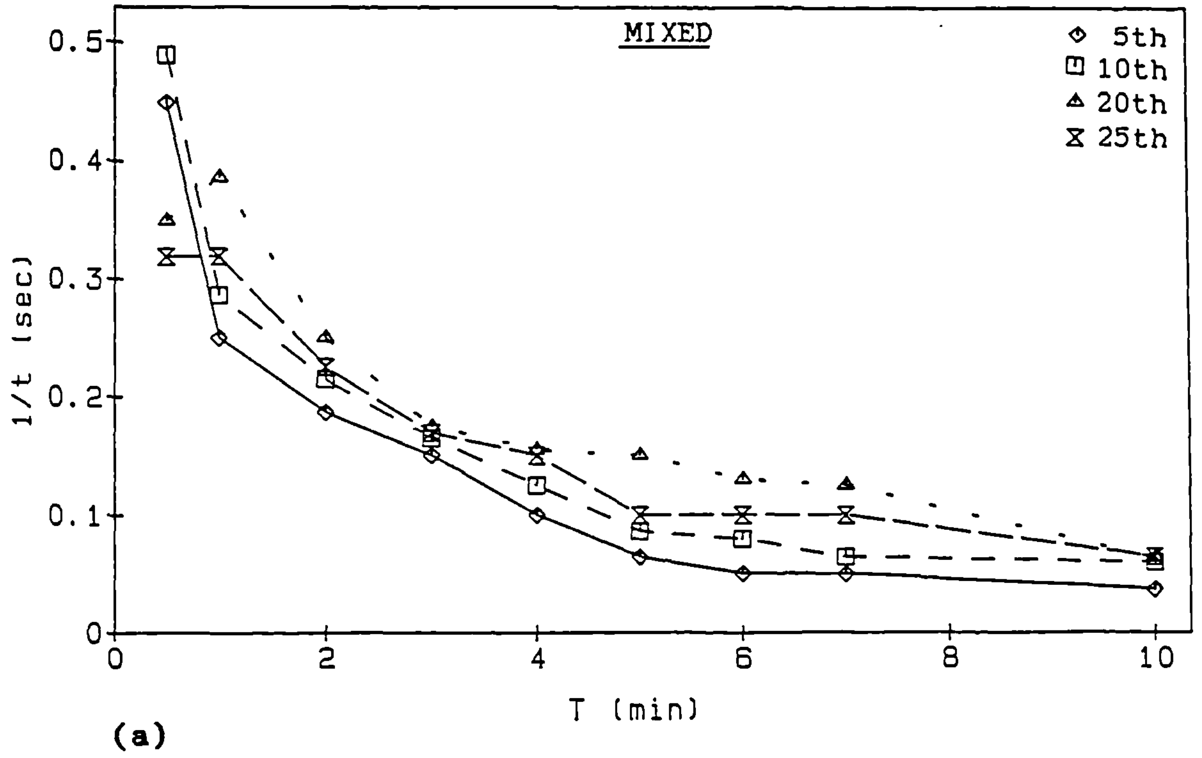


(a)



(b)

FIGURE 5.12 Reaction behaviour of HOBOKEN with 27% nitric acid at 70°C: (a) effect of individual aliquots (b) cumulative effect.



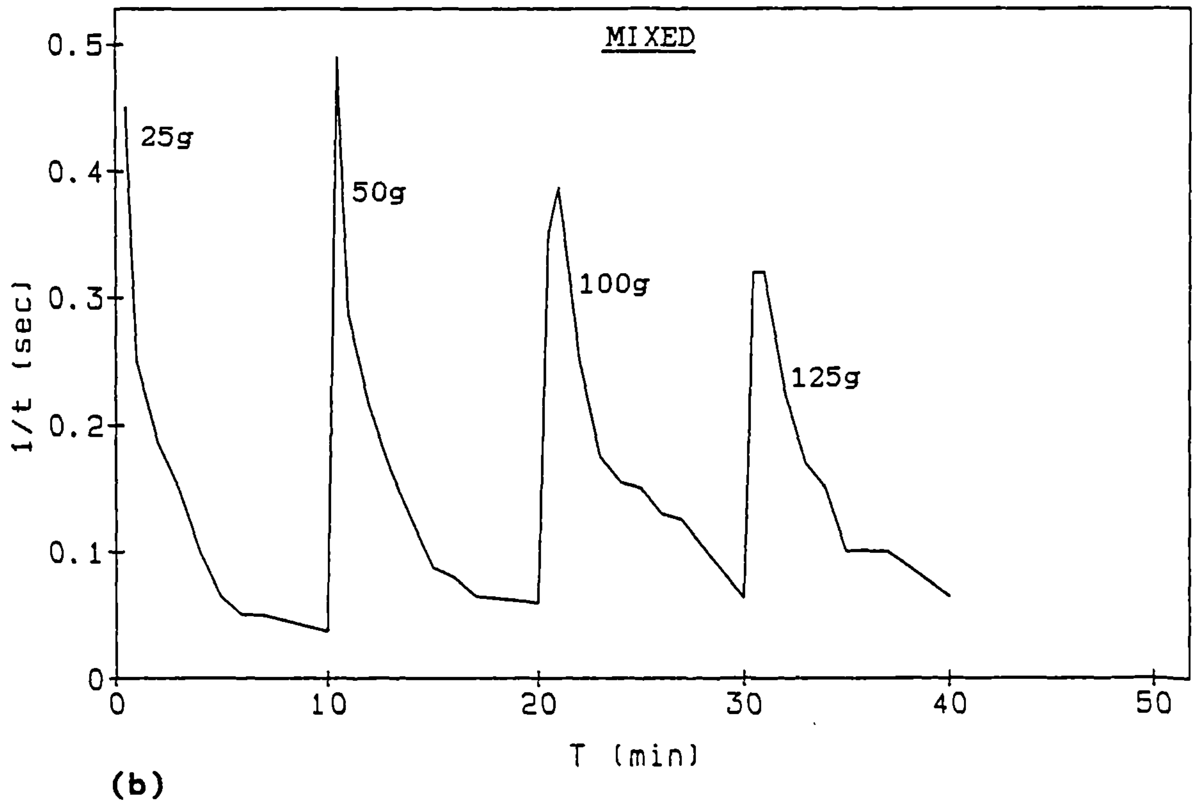


FIGURE 5.13 Reaction behaviour of MIXED with 27% nitric acid at 70°C: (a) effect of individual aliquots (b) cumulative effect.

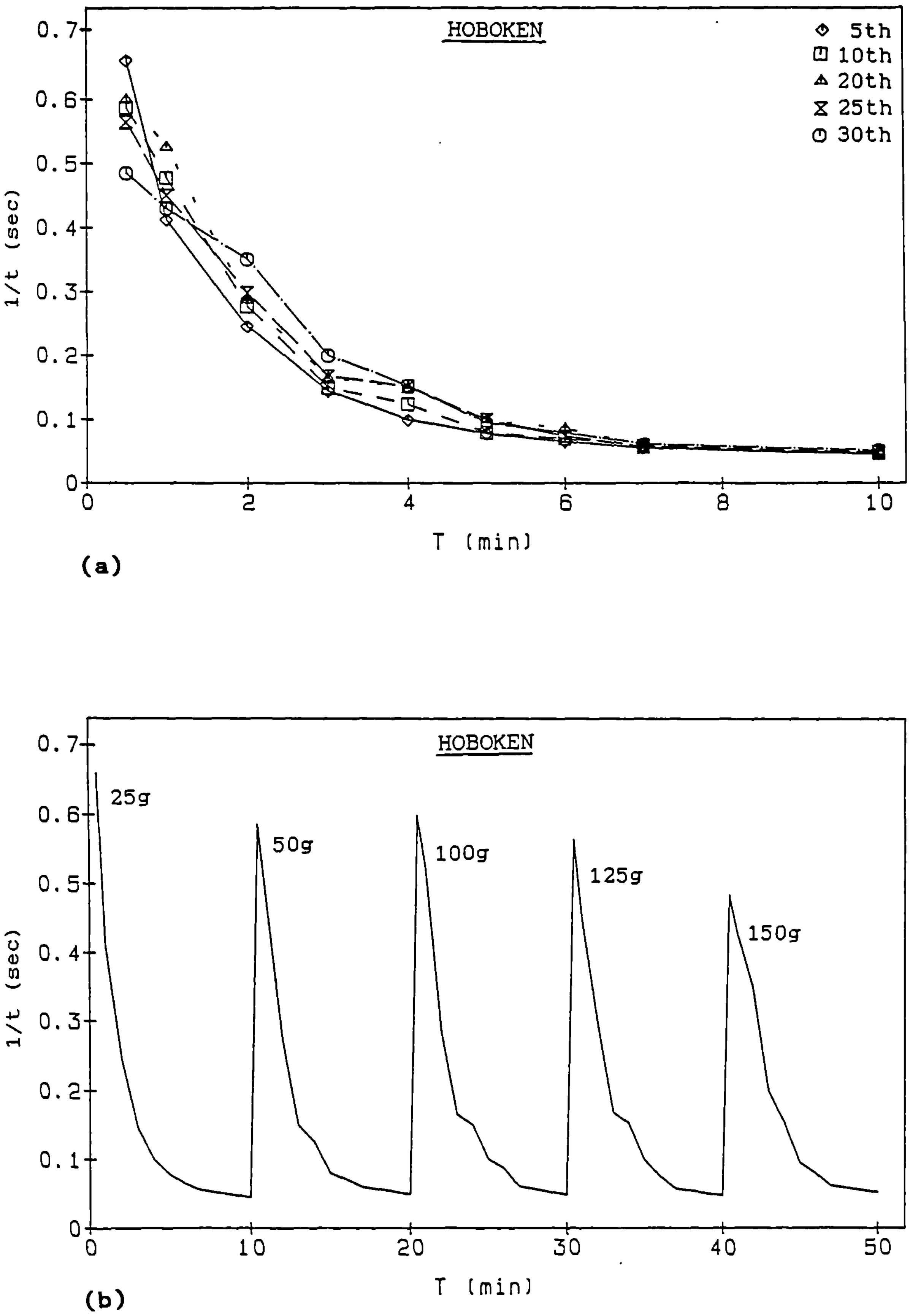
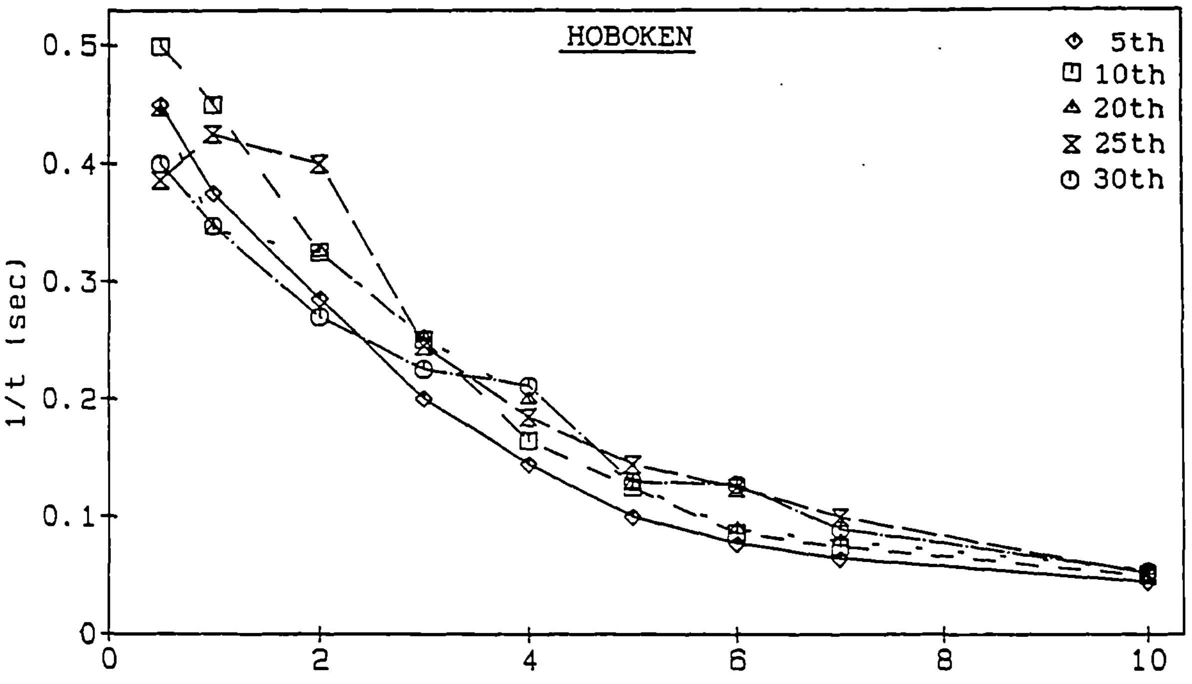
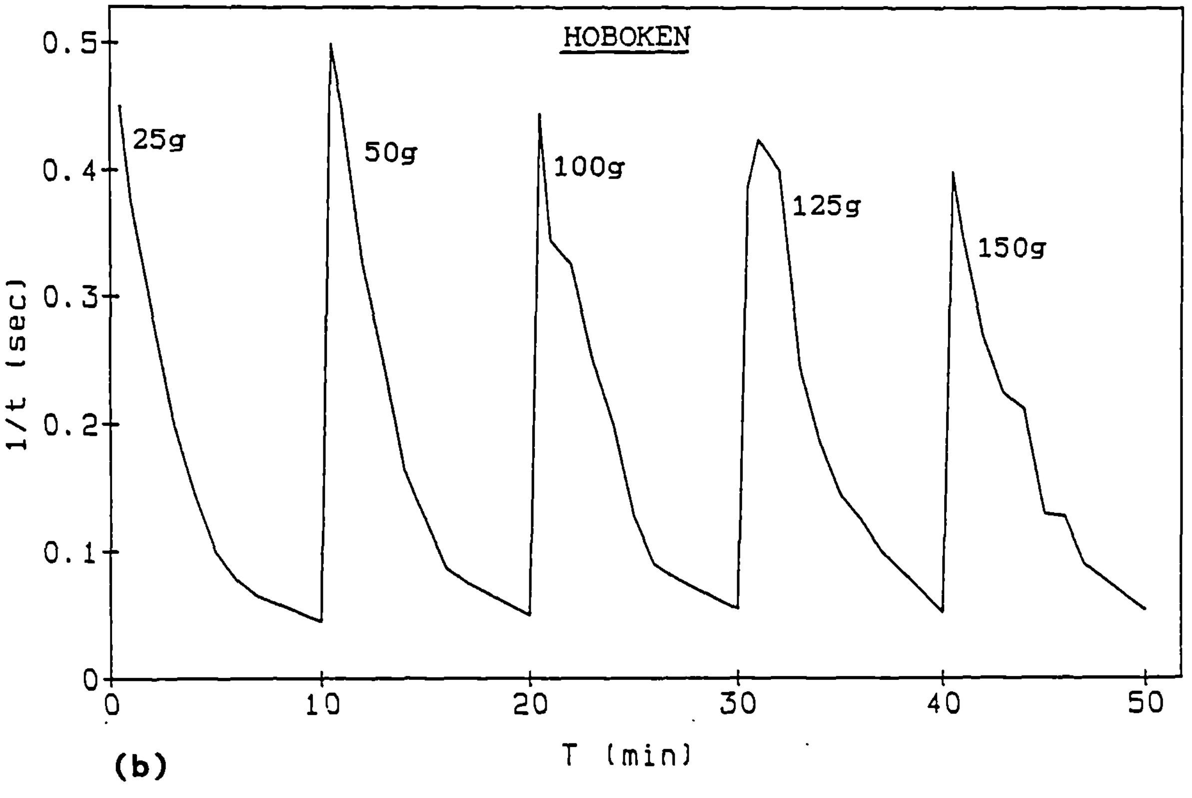


FIGURE 5.14 Reaction behaviour of HOBOKEN with 27% nitric acid at 85°C: (a) effect of individual aliquots (b) cumulative effect.



(a)



(b)

FIGURE 5.15 Reaction behaviour of HOBOKEN with 35% nitric acid at 70°C: (a) effect of individual aliquots (b) cumulative effect.

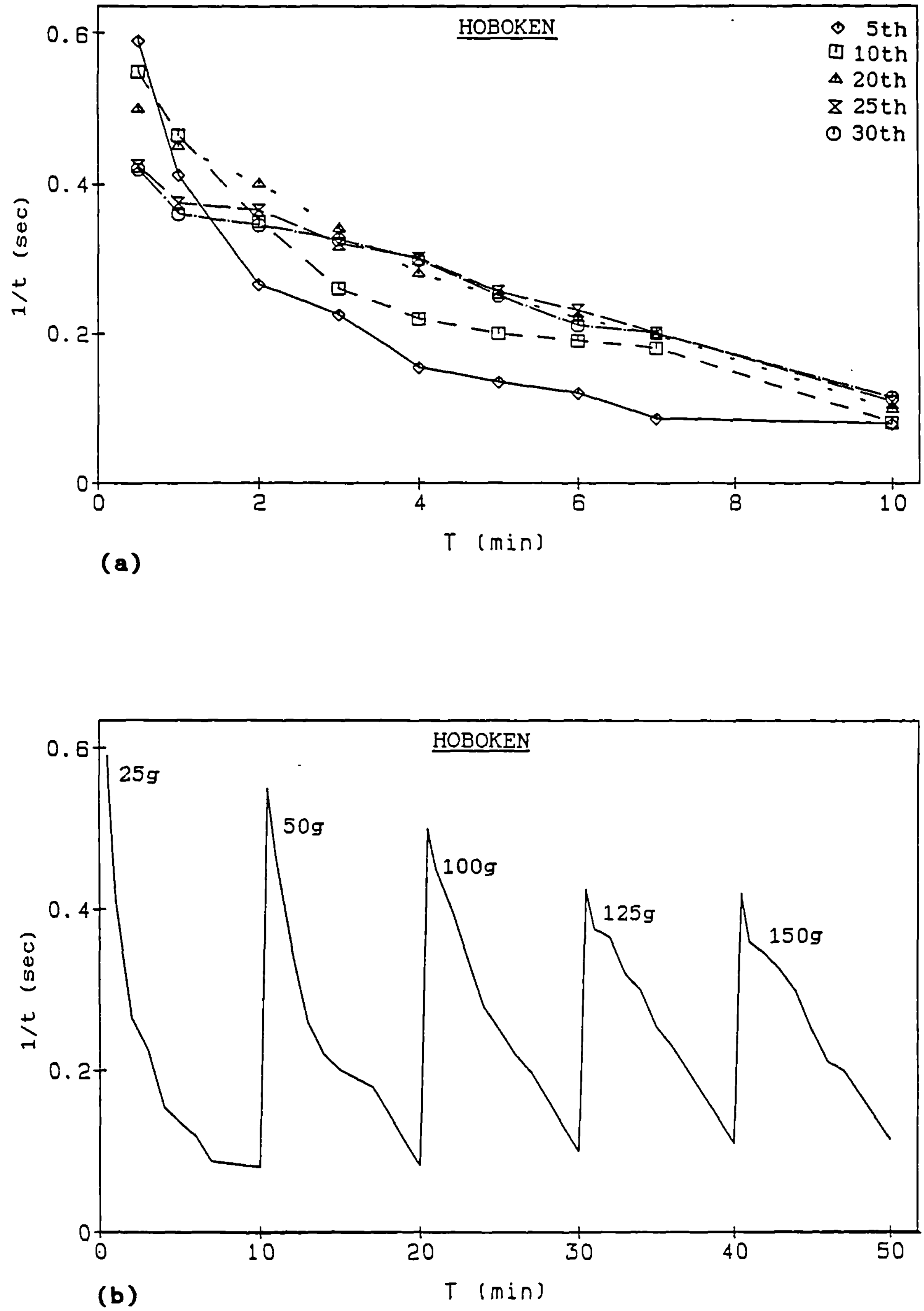


FIGURE 5.16 Reaction behaviour of HOBOKEN with 45% nitric acid at 70°C: (a) effect of individual aliquots (b) cumulative effect.

a) effect of acid concentration
b) effect of temperature
c) behaviour of different arsenic samples

a) Effect of Acid Concentration

In order to determine the effect of acid concentration on the rate of reaction, three experiments were carried, in each experiment a total of 150g of HOBOKEN sample was introduced into the reaction vessel containing 27%, 35% and 45% nitric acid along with 2ml of 2% KI solution at 70°C. The reaction profiles for 5th, 20th, and 25th aliquots are shown in Figures 5.17(a-c), and the cumulative data are given in in Figure 5.17d.

From graphs, in Figures 5.17(a-c), a clear pattern emerges which shows that higher acid concentration produce faster reaction rates, soon after the addition of each aliquot, and the reaction is complete sooner. The reaction was very rapid after the addition of each aliquot of strong acid solution leading to rapid evolution of gases and foaming. The reaction with 27% nitric acid took longer to go to completion. In the reactions with higher acid concentration each aliquot was dissolved completely before the addition of the next aliquot, whereas with 27% nitric acid there was still some unreacted oxide in the reaction vessel. At the lower acid concentration, although the reaction is rapid, the risk of losing control of the reaction is reduced.

b) Effect of Temperature

In this set of experiments aliquots of the HOBOKEN sample were added into the reaction flask containing 27% nitric acid at 70 and 85°C. In each experiment 2ml of 2% KI solution was used as a catalyst. The control of reaction for 5th, 20th, and 25th aliquots are given in Figures 5.18(a-c) and the cumulative data are given in Figure 5.18d. The graphs indicate that the reaction is too rapid at the higher temperature, especially immediately after addition of each aliquot. In the later stages, however, the reaction is more rapid at the lower temperature ($1/t_{85} < 1/t_{70}$). The

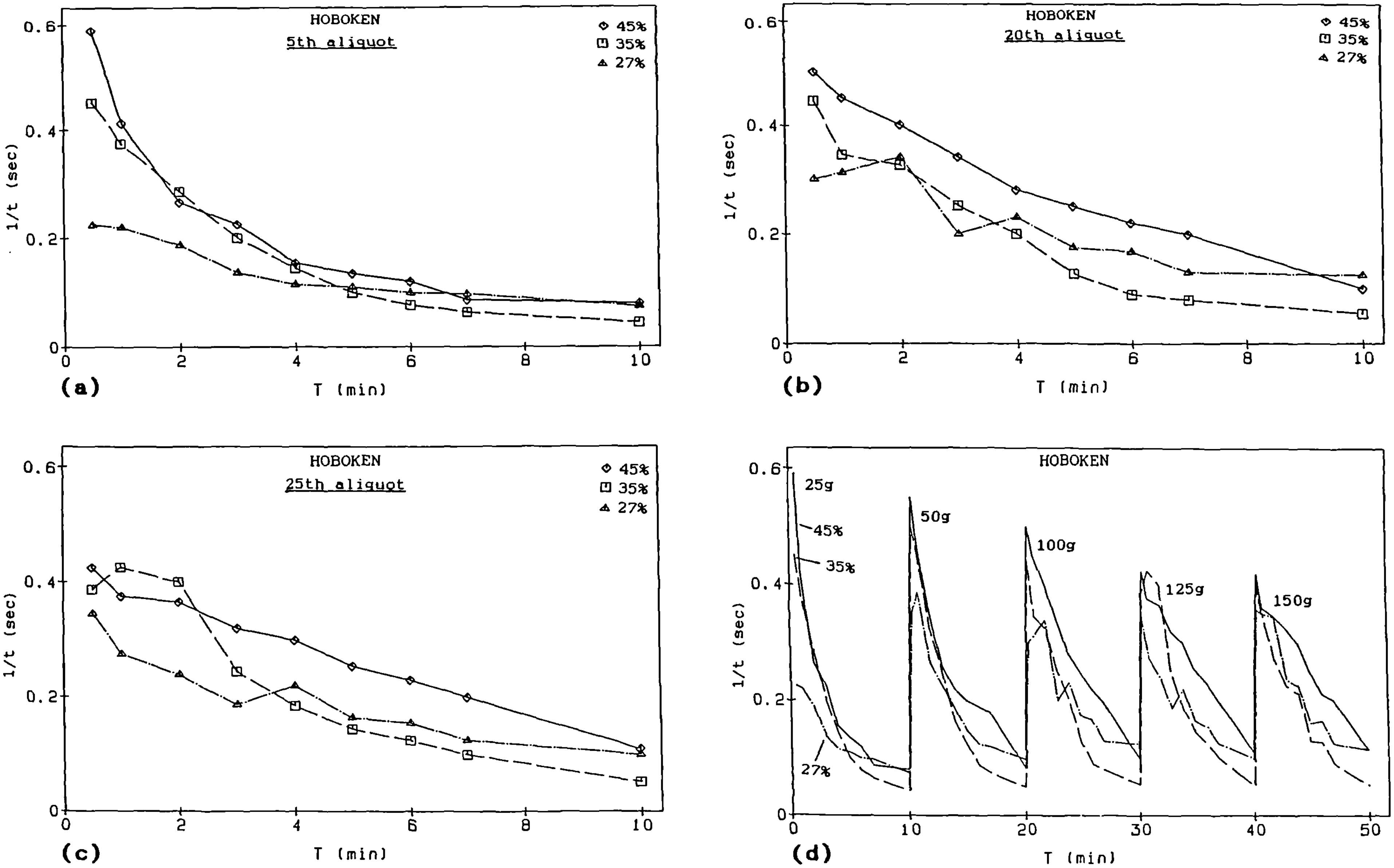


FIGURE 5.17 Effect of acid concentration on the reactivity of HOBOKEN at 70°C after the addition of (a) 5th (b) 20th (c) 25th aliquots and (d) represents the cumulative effect.

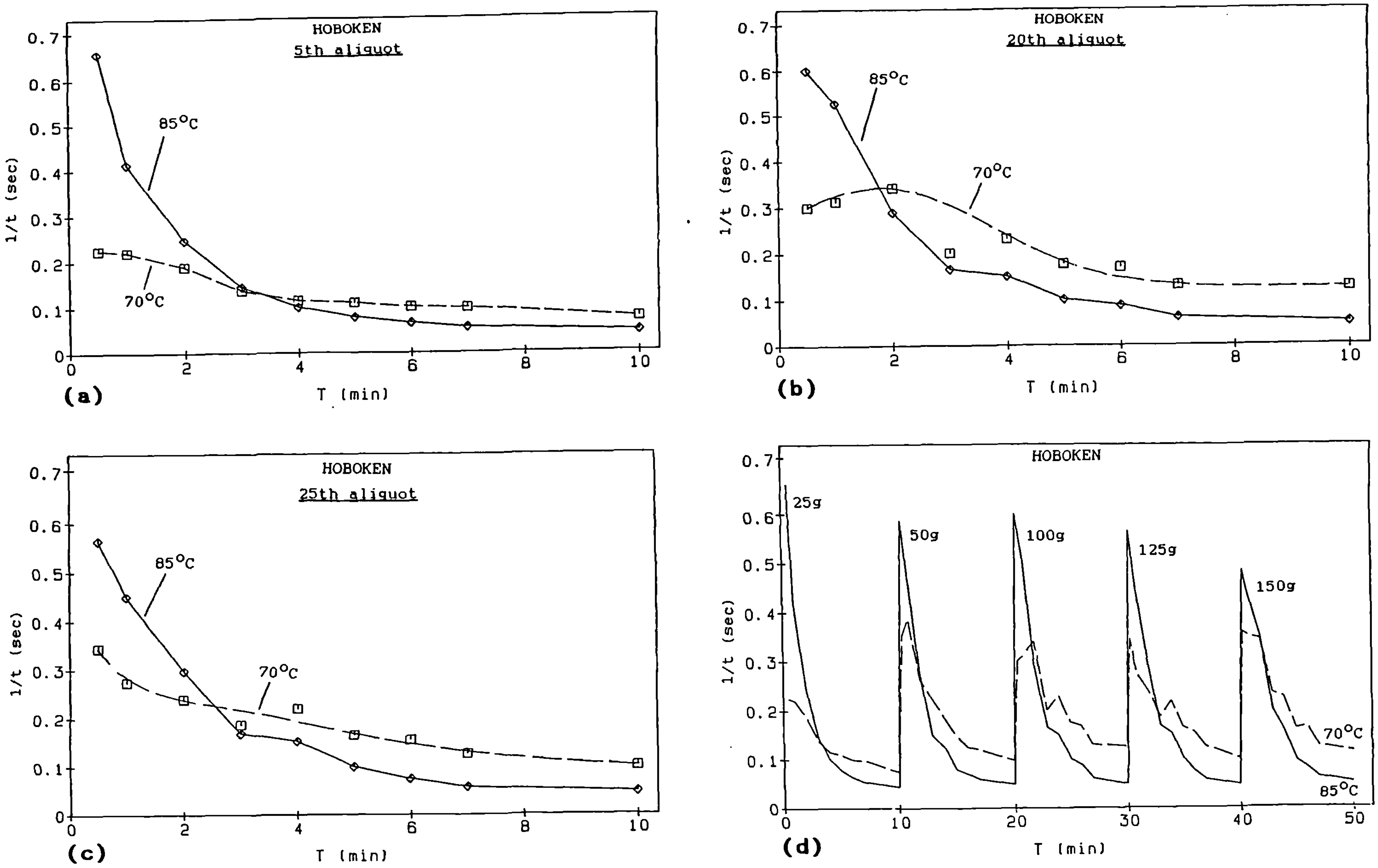


FIGURE 5.18 Effect of temperature on the reactivity of HOBOKEN with 27% nitric acid after the addition of (a) 5th (b) 20th (c) 25th aliquots and (d) represents the cumulative effect.

1/t value after the addition of 30th aliquot for 70 and 85°C was 0.36 and 0.48 in the early part, this drops to to 0.11 and 0.05 in the later part (Figure 5.18d).

c) Behaviour of Different Arsenic Samples

Experiments with TSUMEB, HOBOKEN and MIXED samples in 27% nitric acid containing 2ml of 2% KI at 70°C were carried out. The control of reaction for 5th, and 25th aliquots are given in Figures 5.19(a-b), and the cumulative data are shown in Figure 5.19c. The results have shown that HOBOKEN sample is less reactive than TSUMEB and MIXED sample. Generally all the three samples behave in a similar fashion and the differences observed are probably due to the presence of different concentrations of impurities in each sample.

5.4 REACTION OF NITRIC ACID WITH ARSENIC(III) OXIDE SLURRIES

In most of the experiments described above, a total of 150g of arsenic sample was added into a slowly stirred nitric acid containing 2ml of 2% KI solution at 70°C. The same procedure is being used in William Blythe & Co Ltd., on an industrial scale where there are some difficulties in terms of control of reaction and catalyst requirement. Each aliquot used in this work consisted of 5g of arsenic oxide, and when an attempt was made to increase this amount to 10g the reaction was so fast that suddenly, after the addition of 5th aliquot (50g), the whole sample foamed out of the reaction vessel along with the reaction gases. When the amount of catalyst was reduced with the 10g arsenic oxide aliquot, then the reaction rate was very slow, especially after the addition of the 20th and subsequent aliquots. Addition of one drop of catalyst along with the 25th aliquot however, resulted in an explosive and uncontrollable reaction.

The results obtained showed that the reaction between arsenic(III) oxide and nitric acid when solid arsenic oxide is added to the acid is difficult to control. This arises because of the slow reaction initiation in some stages of

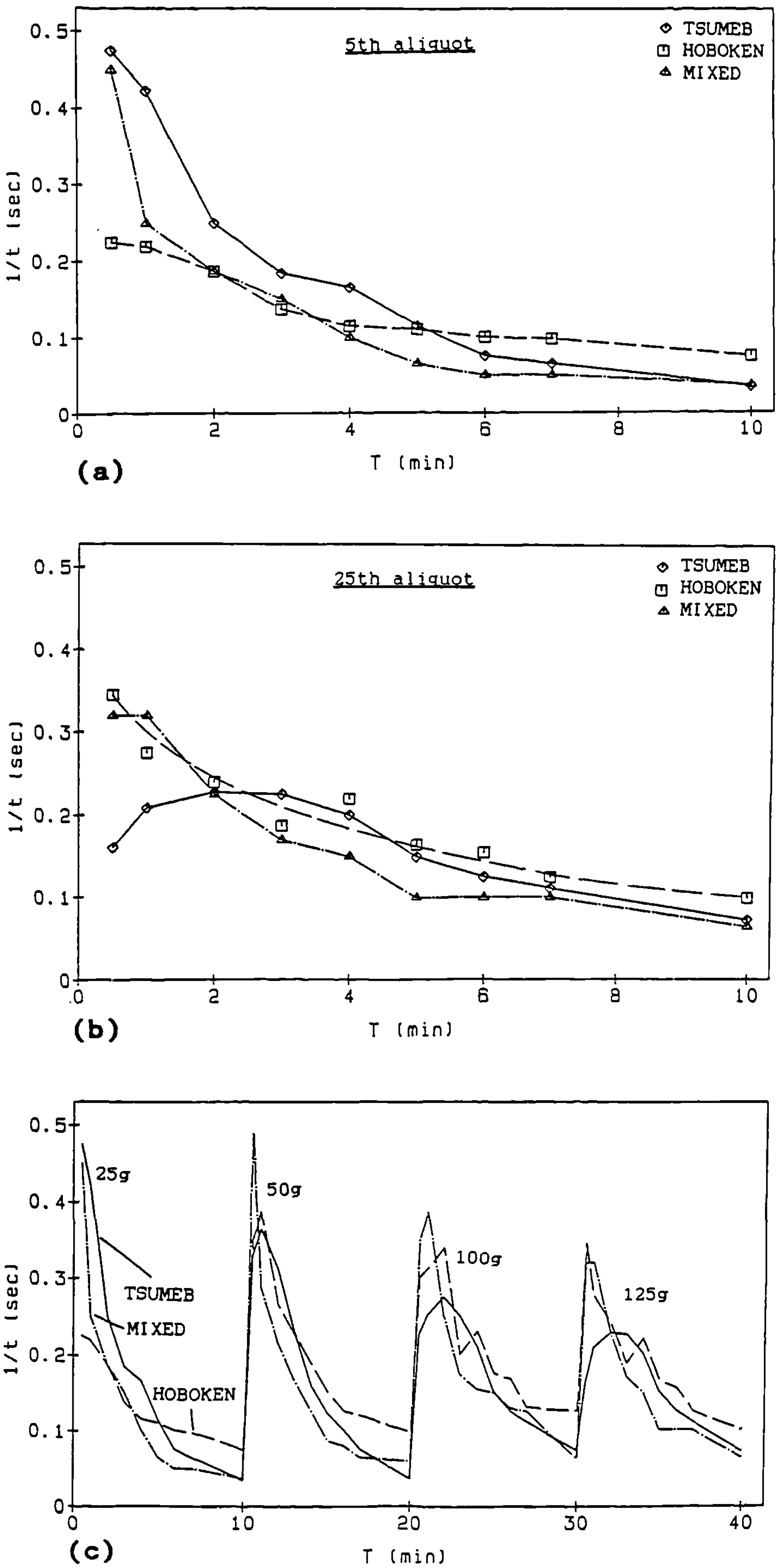


FIGURE 5.19 Reaction behaviour of different arsenic samples after the addition of (a) 5th (b) 25th aliquots and (d) cumulative effect.

the process and the explosively faster reaction that can occur at other stages or when attempts are made to speed up the reaction.

In order to gain more control over the reaction rate and the catalyst requirement, consideration was given to changing the whole procedure. The studies described in this section were carried out on the addition of nitric acid to the slurries of arsenic oxide.

The problems associated with the standard procedure (Section 5.3.2) arise because solid arsenic oxide aliquots of variable reactivity have to be added to a hot nitric acid solution containing catalyst. The work described in this section is based on the assumption that better control of rate of reaction, temperature and catalyst requirement can be achieved by controlled addition of nitric acid to a slurry of arsenic(III) oxide.

In these experiments, arsenic oxide (50, 100, and 250g) was slurried with 325ml of water including 0.5ml of 2% KI solution. The temperature was raised to 60°C. A total of 125ml of concentrated (70%) nitric acid was then added in aliquots of 15-20ml to the very slowly stirred mixture to maintain the temperature at 70°C. The addition of first two aliquots started the process but only maintained the reaction for a few minutes. On the addition of third, fourth, and fifth aliquots, an instantaneous rise in pressure, due to nitrogen oxide gas evolution, was detected on the silicone fluid manometer. By this method, the sudden evolution of nitrogen oxide gases was eliminated and the reaction rate was controlled. The reaction is normally complete for 100 and 250g samples after addition of the 6th and 8th aliquots respectively and resulted in a saving in nitric acid consumption as well as in effective control of reaction rate. Control of gas evolution in experiments with two MIXED, two LEPANTO, two TSUMEB samples, one SALSIGNE-A, and one SALSIGNE-B sample are shown in Figures 5.20(a-d) and 5.21(a-d) which are graphs of time (T) from the start of

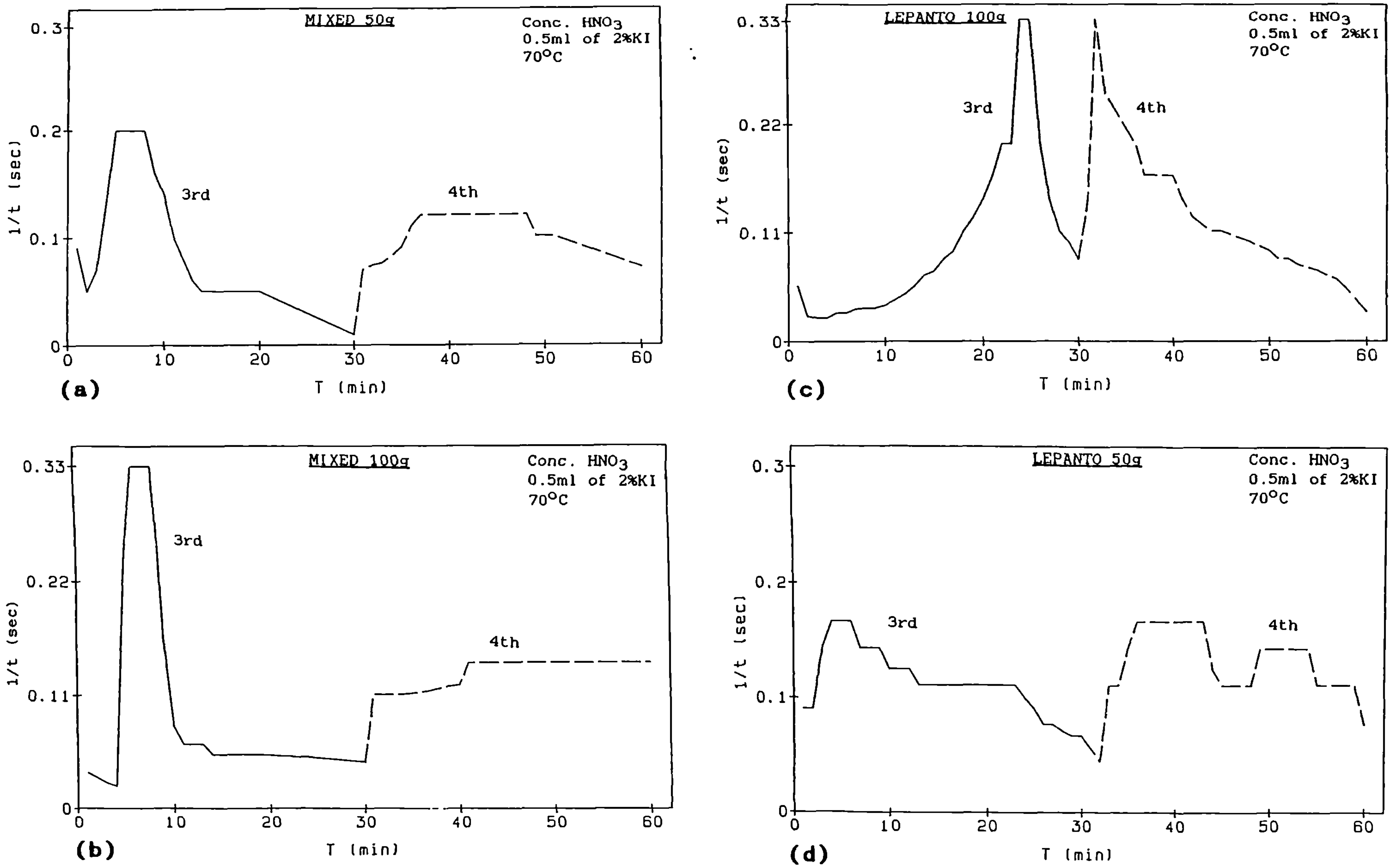


FIGURE 5.20 Arsenic trioxide - nitric acid reactivity: (a, b) MIXED (c, d) LEPANTO.

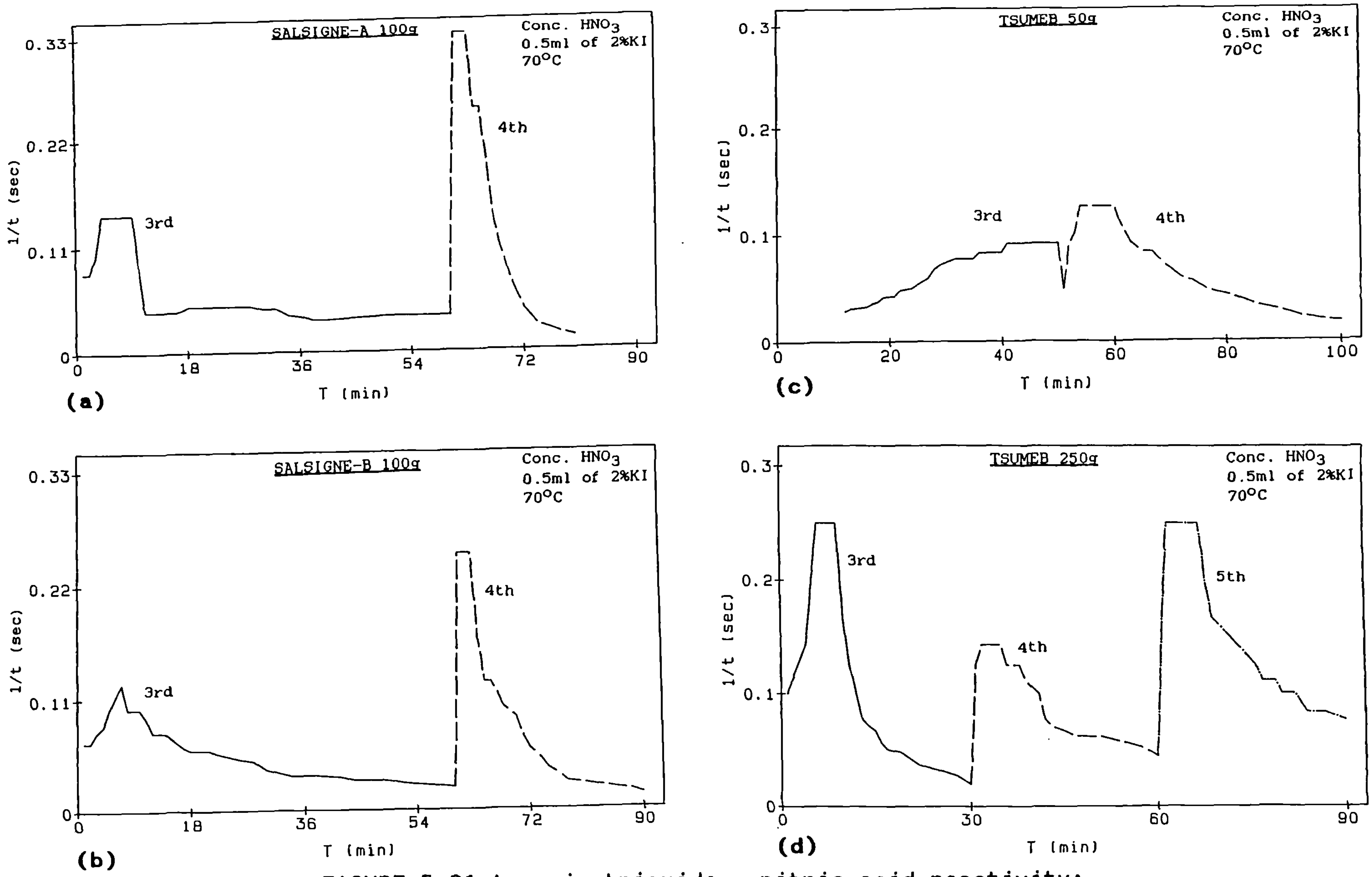


FIGURE 5.21 Arsenic trioxide - nitric acid reactivity:
(a) SALSIGNE-A (b) SALSIGNE-B (c, d) TSUMEB.

the reaction against 1/t (where t is the time taken for the silicone fluid in the manometer to travel a measured distance 250mm. The following reaction variables were studied:

1) arsenic oxide particle size
2) timing of catalyst addition
3) nitric acid concentration
4) slurry thickness - acid concentration
5) arsenic oxide source material
6) ultrasonic agitation
7) catalyst material and concentration

5.4.1 Arsenic Oxide Particle Size

The particle size of the arsenic(III) oxide has an effect on the reaction rate of this process - samples with fine particles being more reactive than larger particles. In the cases of SALSIGNE-A and SALSIGNE-B the particles were so fine that they floated on the liquid surface. With no stirring, at the addition of 3rd aliquot, the oxide was carried out of the reaction system along with the reaction gases. This effect is, however, easily controlled by stirring, slow stirring is always helpful and gives better control over the reaction rate.

5.4.2 Timing of Catalyst Addition

Preliminary experiments of dropwise addition of the catalyst solution to an aqueous arsenic oxide slurry, as an alternative to use of a weak potassium iodide solution to slurry the oxide, suggest that the amount of catalyst required can be reduced. Addition of one drop of 2% KI solution to the reaction mixture along with each of the first two aliquots of nitric acid seems sufficient to initiate and maintain the reaction. Addition of nitric acid to slurries of arsenic trioxide provides an ideal method for controlling the reaction because the rate and extent of reaction can be monitored by measurement of the reaction gas pressure and this, in turn, can be used to control the nitric acid addition. The method also permits more carefully controlled addition of catalyst and the timing of the catalyst addition.

5.4.3 Effect of Acid Concentration

As mentioned in Section 5.2.1 the nitrogen oxides can be recycled as 27% nitric acid. This strength of acid has therefore used in the next batch to produce arsenic acid. In order to determine the effect of acid concentration on the control of gas evolution during the production of arsenic acid, a set of experiments were performed by using 50, 35 and 27% nitric acid.

(a) Addition of 50% Nitric Acid to Arsenic Oxide Slurries

In the first set of experiments, arsenic oxide, (250g), was slurried with 225ml of water containing 0.5ml of 2% KI solution. The temperature was raised to 60°C and a total of 275ml of 50% nitric acid was then added in aliquots of 35-40ml to the very slowly stirred mixture. The temperature was maintained at 70°C. Figures 5.22a and 5.22b show the T vs. 1/t graphs for the HOBOKEN and SALSIGNE-B samples respectively. In both cases all of the remaining nitric acid was added in the fifth aliquot.

The second experiment involved the use of a slurry of mixed arsenic oxide (500g) in 450ml of water containing 1ml Of 2% KI solution. The mixed arsenic oxide consisted of TSUMEB (300g), HOBOKEN (100g), and SALSIGNE-B (100g). The temperature of the slurry was again raised to 60°C and a total of 550ml of 50% nitric acid added in aliquots of 30-40ml to the very slowly stirred mixture to maintain the temperature at 70°C. All of the remaining nitric acid was added in the seventh aliquot. The results are shown in the graph of T vs. 1/t (Figure 5.22c).

The third experiment involved the use of a slurry of mixed arsenic oxide (800g) in 660ml of water containing 1ml of 2% KI solution. The mixture consisted of TSUMEB (200g), SALSIGNE-A (200g), SALSIGNE-B (100g), CHILEAN (100g), and HOBOKEN (200g). The method used was identical to that in the second experiment except that a total of 850ml of nitric

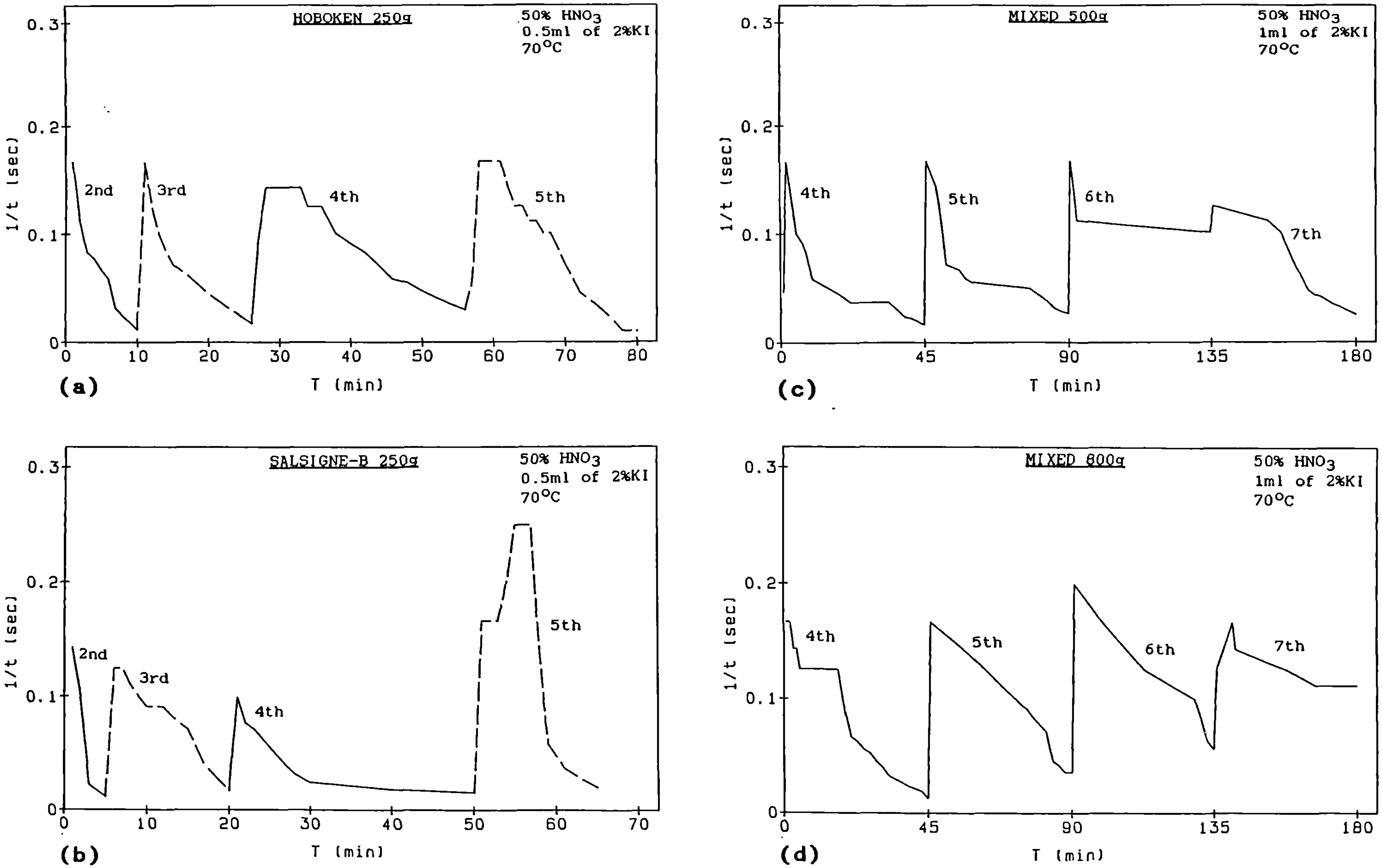


FIGURE 5.22 Arsenic trioxide - nitric acid reactivity:
(a) HOBOKEN (b) SALSIGNE-B (c, d) MIXED.

acid was added. The results are shown in Figure 5.22d.

(b) Addition of 35% Nitric Acid to Arsenic Oxide Slurries

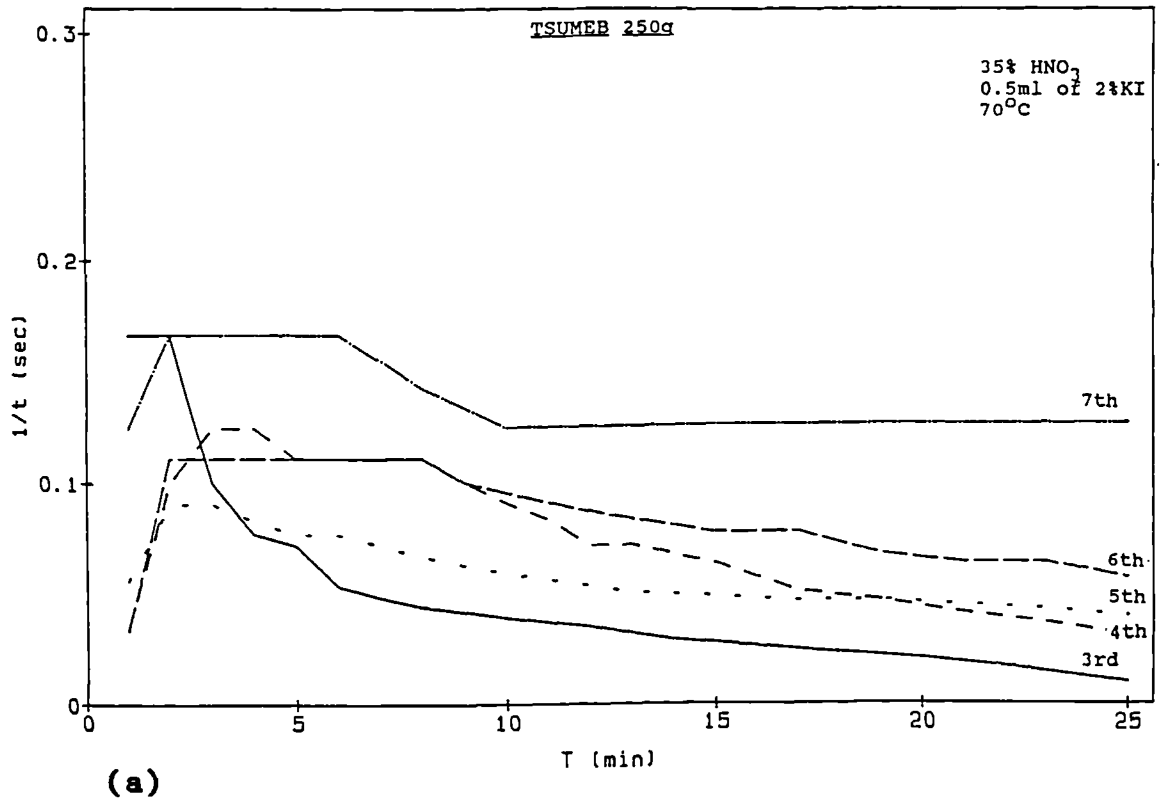
Arsenic oxide, TSUMEB, (250g) was slurried with 100ml of water containing 0.5ml of 2% KI. The temperature was raised to 60°C and a total of 350ml of 35% nitric acid was added in aliqouts of 35-40ml to a very slowly stirred mixture maintaining the temperature at 70°C. The remaining acid was added in the seventh aliquot. The results are shown in Figures 5.23(a-b).

The results of this series of experiments confirm that control of the reaction between arsenic oxide and nitric acid can be achieved by addition of acid in aliquots to the thicker oxide slurries. The data of graph 5.23 show that water can be transferred from the slurry to the acid to permit the use of weaker acids without apparent loss of control or efficiency.

(c) Slurrying with 27% Nitric Acid

In this set of experiments, arsenic oxide, (250g), was slurried with 150ml of 27% nitric acid including 0.5ml of 2% KI solution. When the temperature was raised the reaction starts at 40-50°C but the rate of reaction was very slow, when the temperature reached at 70°C the instantaneous rise in pressure was detected on the silicone fluid manometer. After 20 minutes, the reaction slowed. At this stage, a total of 350ml of 27% nitric acid was added in aliquots (first two aliquots were 35-40ml whereas 3rd and 4th aliquots were 75-80ml). The control of gas evolution for these experiments are shown in Figures 5.24(a-c). In case of MIXED sample, a drop of 2% KI solution was added along with 4th aliquot (Figure 5.24a). The graph indicates that by using dilute nitric acid the reaction is very gentle, slow and well under control. But the rate of reaction can be increased during the course of reaction at any stage by just adding a drop of KI solution into the reaction mixture.

In case of LEPANTO, 0.5ml of 1% KI solution was used and



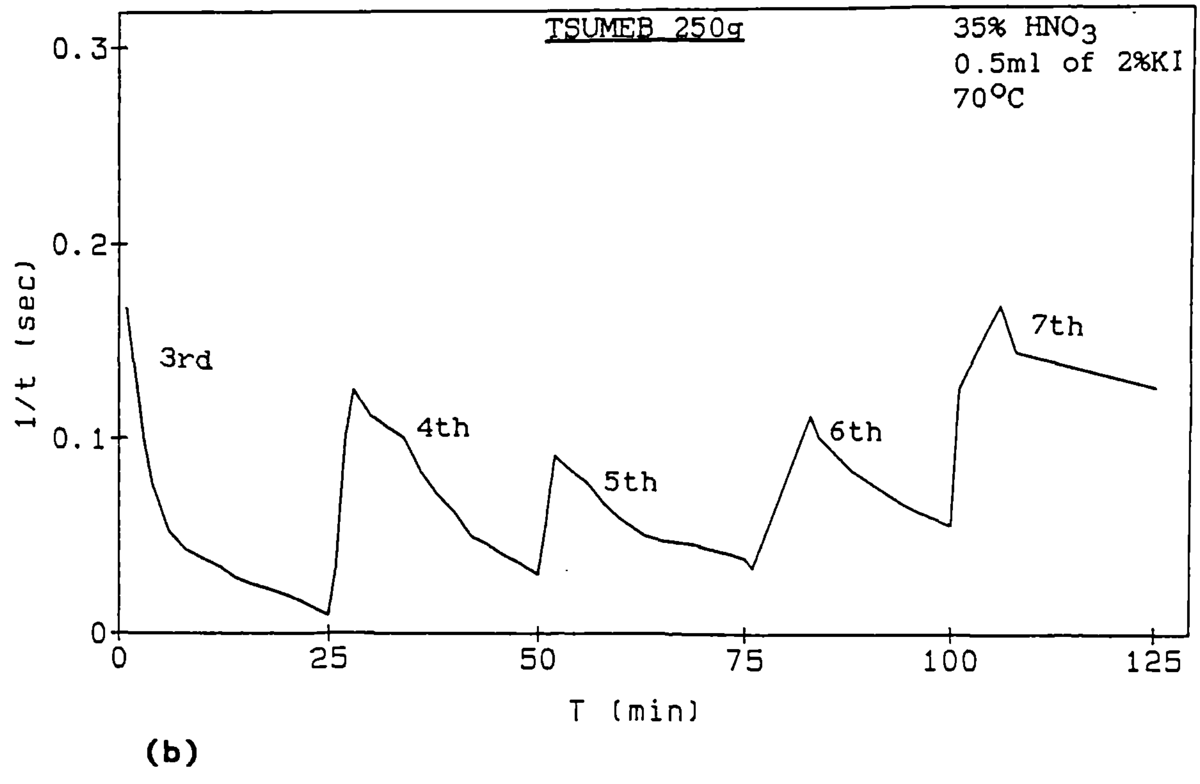


FIGURE 5.23 Reaction behaviour of arsenic trioxide with 35% nitric acid: (a) effect of individual aliquot (b) cumulative effect.

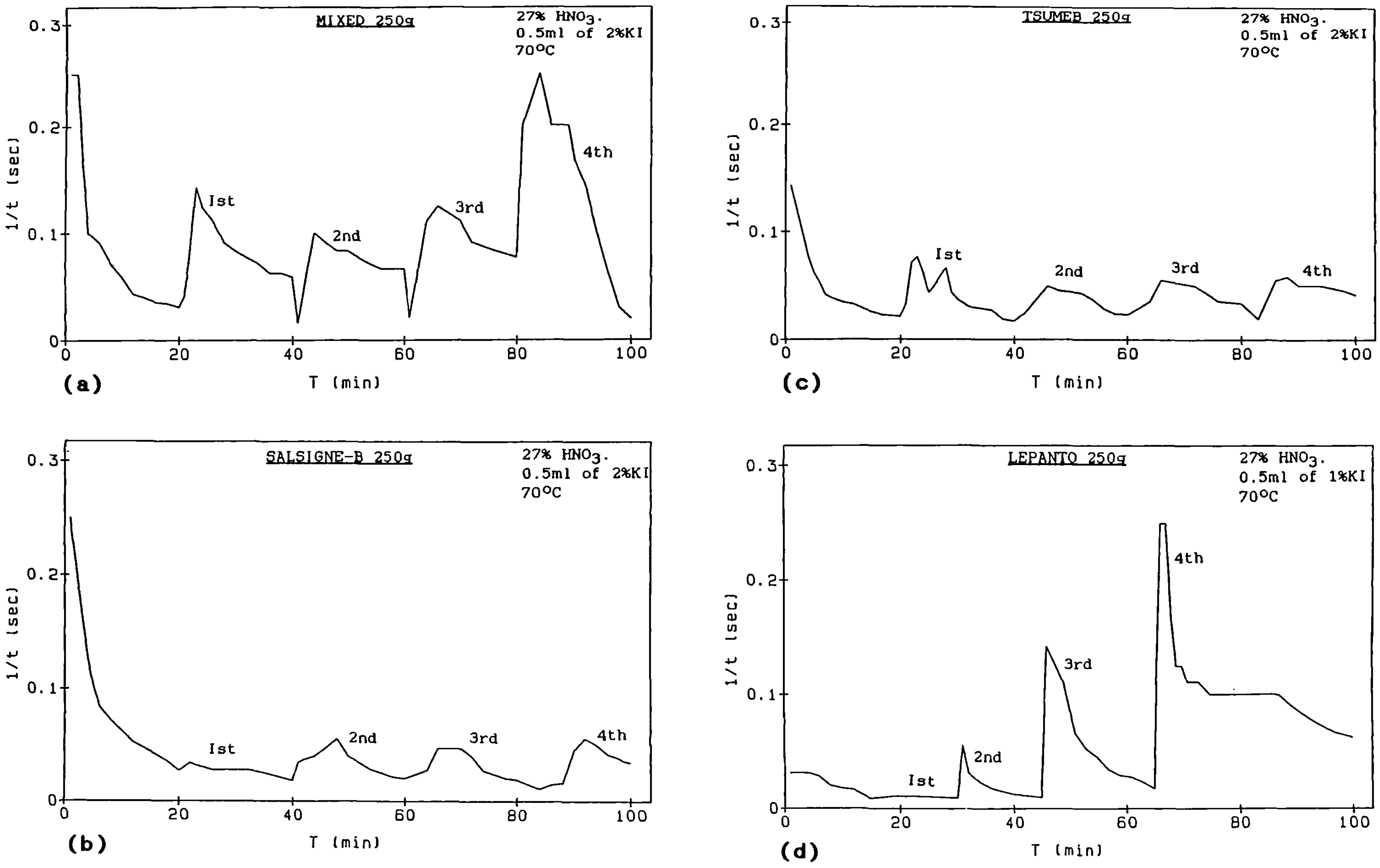


FIGURE 5.24 Arsenic trioxide - nitric acid reactivity:
(a) MIXED (b) SALSIGNE-B (c) TSUMEB (d) LEPANTO.

rest of the conditions were the same as described in the above experiments. Figure 5.24d shows that the reaction was very slow in the initial stage and the addition of 1st and 2nd aliquot has no effect on the rate of reaction. The addition of one drop of 1% KI along with 3rd and two drops with final 4th aliquot increased the rate of reaction. After the addition of final aliquot the reaction was completed and during the entire procedure the reaction was under control and there was no risk of any boil-over.

The results of this series of experiments show that by using 27% nitric acid (strength of acid obtained by recycling the nitrogen oxide gases) for making the oxide slurries gives the best control of the reaction. As the temperature of the slurry was raised a very slow and gentle reaction starts, even at 30°C, and when the slurry temperature reaches to 70°C a lot of arsenic oxide had already been consumed by the nitric acid already present so that, addition of further acid results in a very gentle reaction.

The effect of different acid concentration on the rate of reaction is shown in figures 5.25(a-c) and 5.26(a-c). The graphs show that high acid concentration produce rapid reaction and less time is required to finish the process. On the other hand, dilute acids give slow reaction rate and long time is required to complete the reaction. Dilute acid is exhausted rapidly and further acid addition are needed to trigger the reaction. On the whole, the reaction was under control at all acid concentrations. The choice of acid concentration depending upon the availability of the reactants and the specification of the final product.

5.4.4 Effect of Slurry Thickness and Acid Concentration

The effect of slurry thickness on the rate of reaction for different arsenic samples is shown in Figures 5.27(a-d). The data suggest that the thick slurry always gives high reaction rate throughout the entire process. The graphs, which are T vs 1/t, show that the addition of doses of concentrated (70%) nitric acid into a thick slurry gives

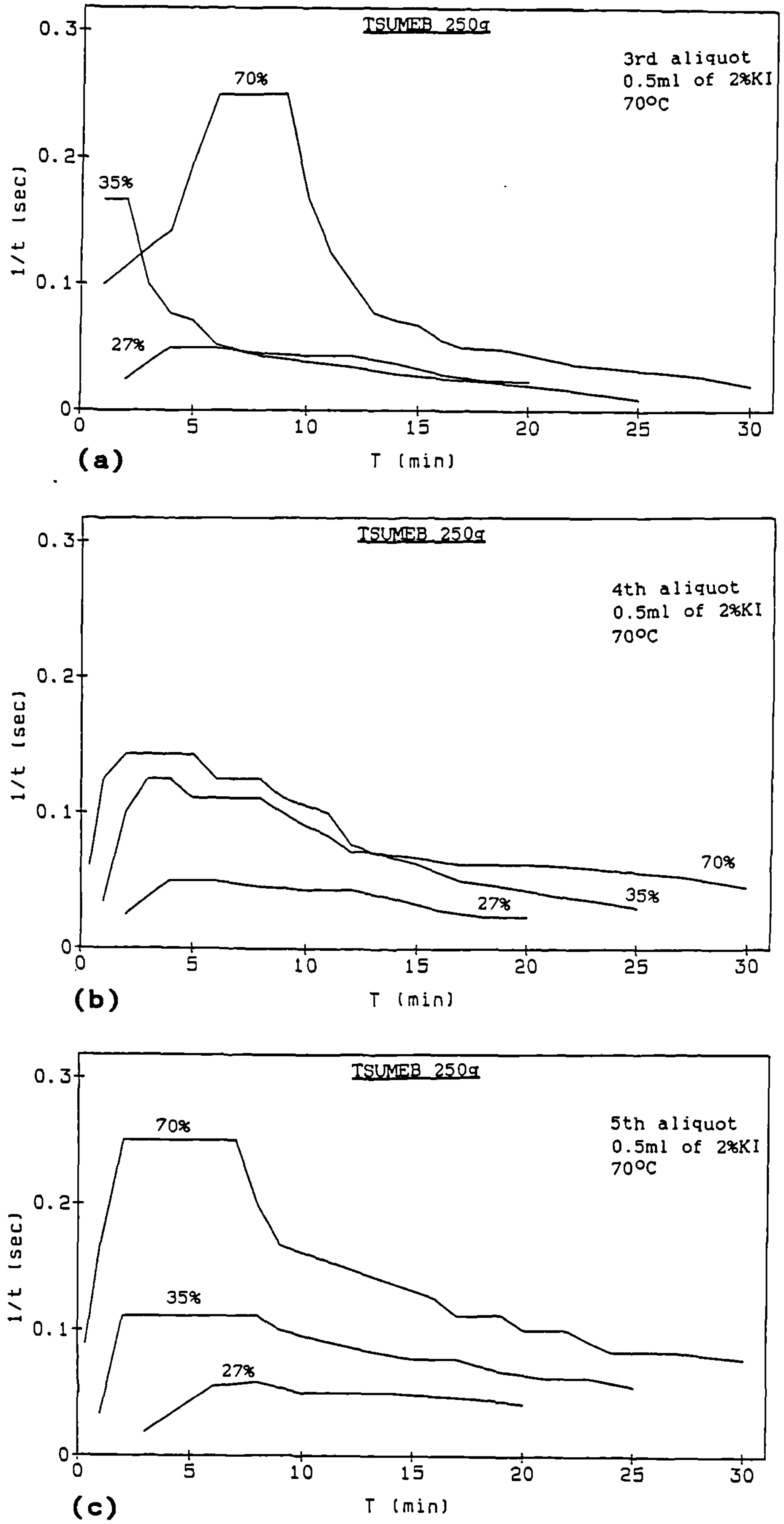


FIGURE 5.25 Effect of acid concentrtion on the rate of reaction after the addition of (a) 3rd (b) 4th and (c) 5th aliquots.

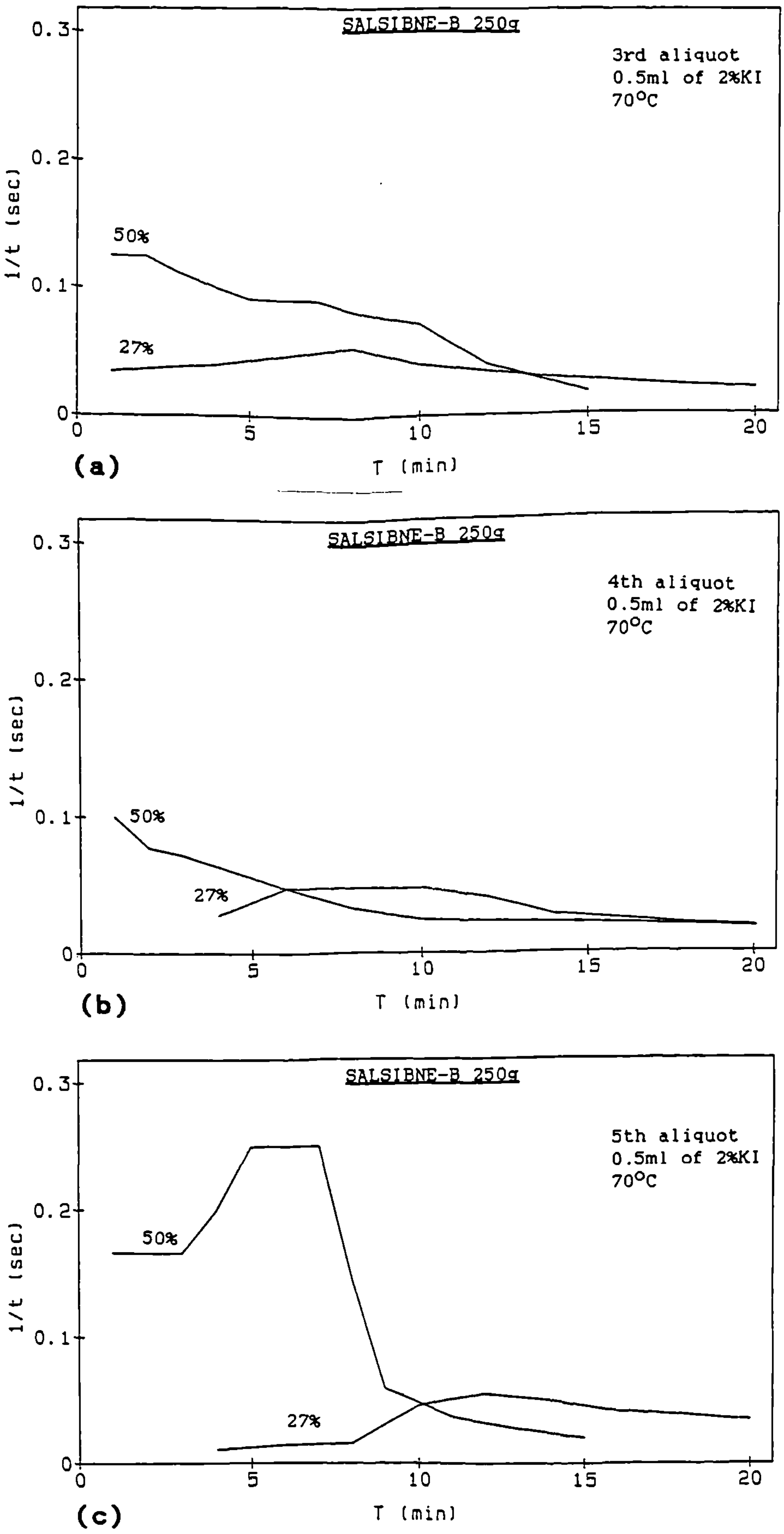


FIGURE 5.26 Effect of acid concentrtion on the rate of reaction after the addition of (a) 3rd (b) 4th and (c) 5th aliquots.

rapid reaction in the initial stages but in later stages the reaction rates are the same for both thick and thin slurries. When the concentrated nitric acid was replaced by 50% acid then the reaction peaks for both thick and thin slurries were equal even in the initial stages (Fig. 5.27d). The only difference is that, for thicker slurries, while the reaction velocity drops very slowly after the addition of each aliquot, for thin slurries the reaction rate drops quickly.

5.4.5 Behaviour of Different Arsenic Samples

In the first set of experiments 100g of SALSIGNE-A and SALSIGNE-B was slurried with 325ml of water containing 0.5ml of 2% KI solution. The temperature was raised to 60°C. Then a total of 125ml of concentrated nitric acid was added in aliquot of 15-20ml into a slowly stirred mixture. The control of gas evolution is shown in Figure 5.28a.

In the second set of experiments 250g of HOBOKEN and SALSIGNE-B was slurried with 225ml of distilled water containing 0.5ml of 2% KI solution. The temperature was raised to 60°C. Then a total of 275ml of 50% nitric acid was added in aliquots of 35-40ml in a very slowly stirred mixture. The control of gas evolution is given Figure 5.28b.

In the third set of experiments 250g of MIXED, TSUMEB and SALSIGNE-B were slurried with 27% nitric acid containing 0.5ml of 2% KI solution. When the temperature raised the reaction started at about 40-45°C but the rate of reaction was very slow. The instantaneous rise in pressure was detected when the reaction temperature reached at 70°C. A total of 350ml of 27% nitric acid was then added in aliquots forms (first two aliquots were 35-40ml where as 3rd and 4th aliquot was 75-80ml). The comparison of the control of gas evolution for each sample is given in Figure 5.28c.

The data suggest that different samples behave similarly under the same conditions. There is very little difference

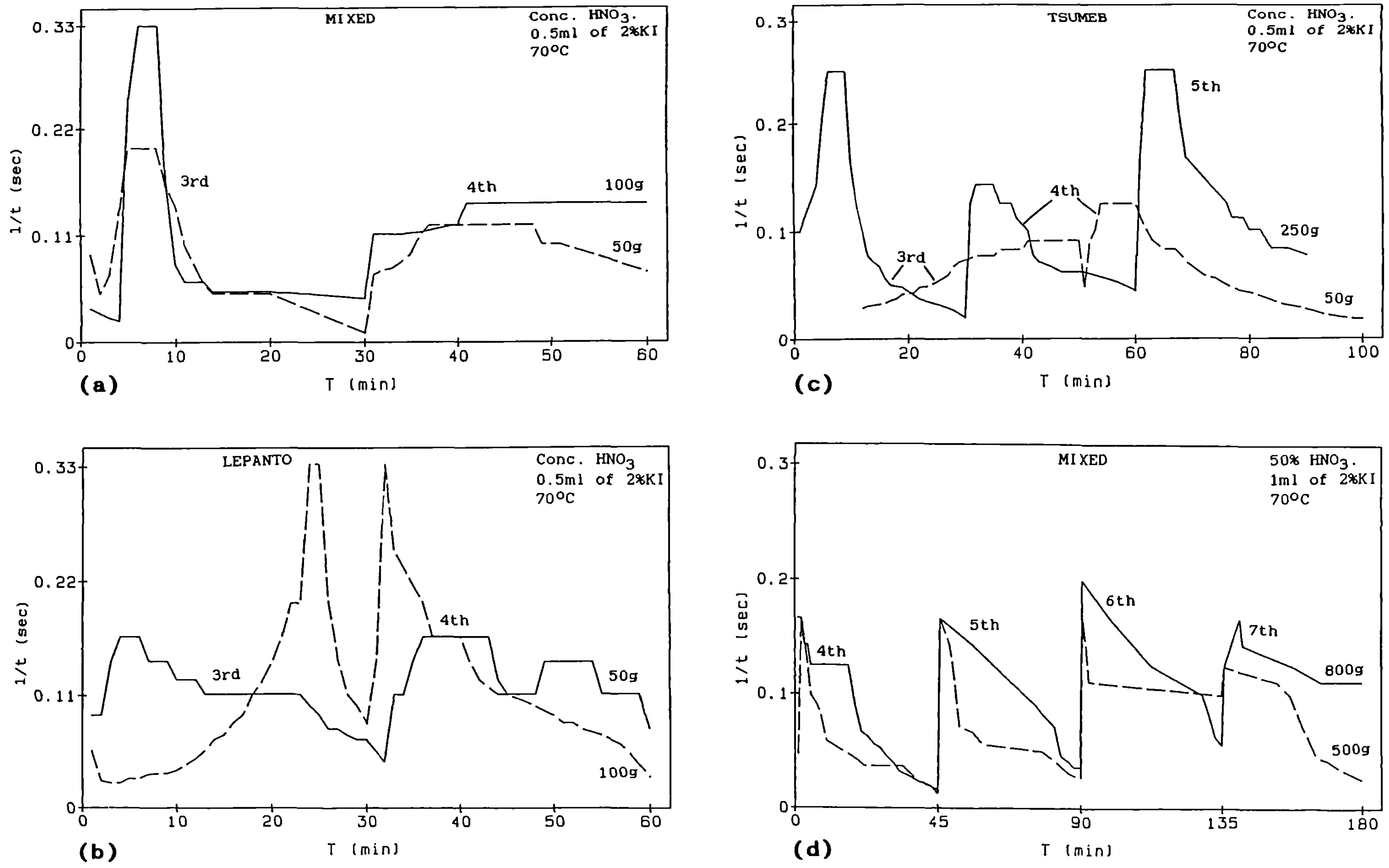


FIGURE 5.27 Effect of slurry thickness on the rate of reaction: (a) MIXED (b) LEPANTO (c) TSUMEB and (d) MIXED.

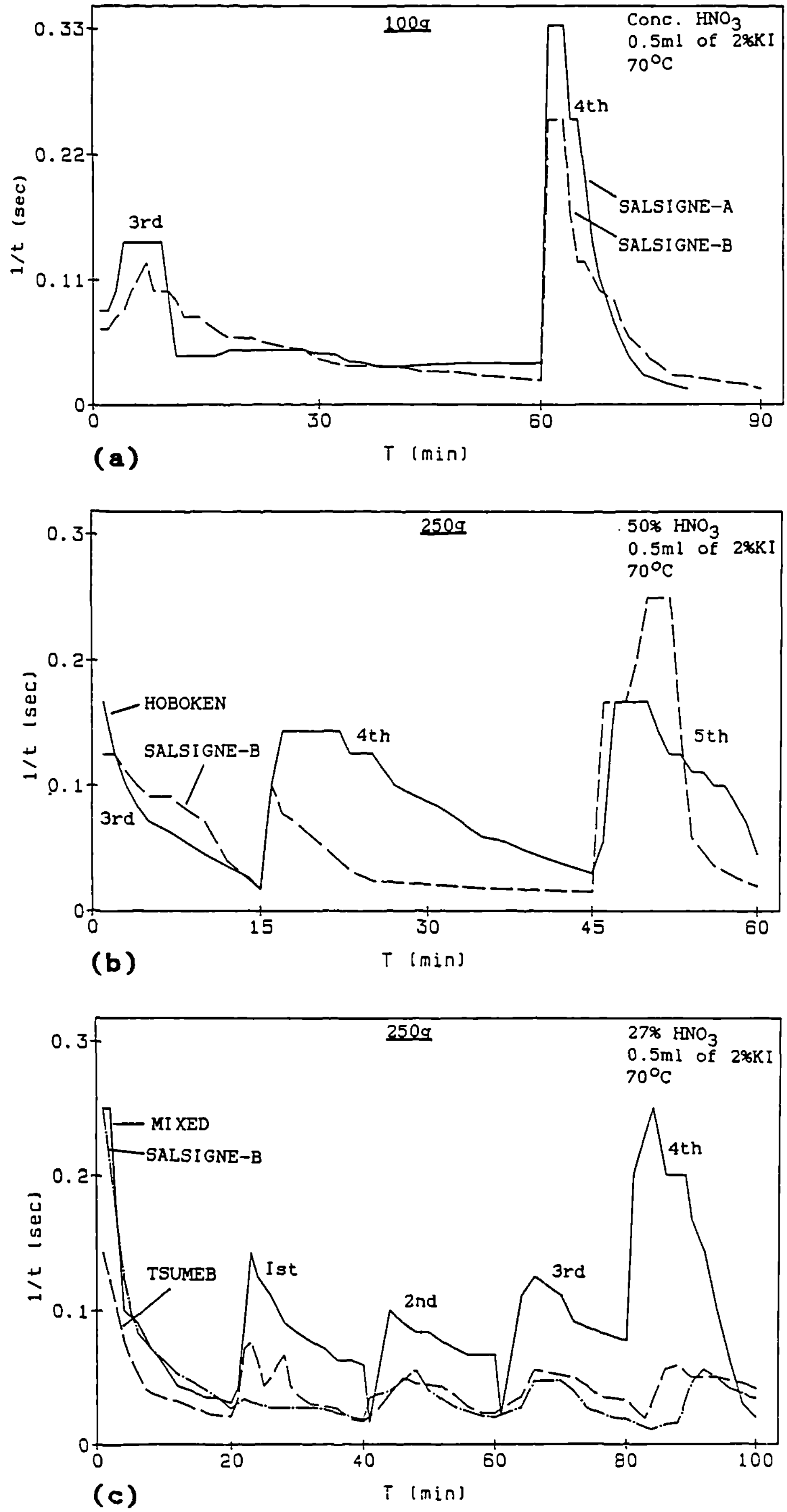


FIGURE 5.28 Reaction behaviour of different arsenic trioxide samples under the same reaction conditions.

in the rate of reaction for TSUMEB and SALSIGNE-B sample where as MIXED sample gives high reaction rate under the same conditions. In case of MIXED sample one drop of 2% KI solution was added along with 4th aliquot (Fig. 5.28c). HOBOKEN and SALSIGNE-B sample behave similarly apart from a little difference in 4th aliquot.

5.4.6 Ultrasonic Agitation instead of Mechanical Stirring

It was noticed during the washing of the glassware that when a dilute solution of potassium iodide (1%) was placed in the ultrasonic bath, brown vapours were liberated at room temperature. So on trial basis ultrasonic agitation was carried out in some experiments. It was found that it does not only initiate the reaction at low temperature (40°C) but the whole process can be carried out at 60-65°C. The ultrasonic agitation helps the reaction in two ways: a) it improve the dissociation reaction of KI to give the active catalyst species and then initiates the reaction at low temperature; b) by decreasing the particle size of the slurry components.

5.4.7 Effects of Catalyst type and Concentration

The ultrasonic experiments were extended to study the effects of KX solution (X = I, Br, Cl) as a catalyst during the reaction process. In each case 200g of HOBOKEN sample was slurried with 150ml of 27% nitric acid containing different volumes (0.25-1.0) of 2% KX (X = I, Br, Cl) solutions. The reaction vessel was immersed up to its neck in a heated ultrasonic bath of SONICLEANER TYPE 6453A (The ultrasonic division, DAWE). The reaction started at 40-50°C. After 20 minutes intervals, a total of 300ml of 27% nitric acid was added into the reaction vessel in aliquots of 35-40ml. The unused nitric acid was added in the 5th aliquot. The manometric data are represented in Figures 5.29-5.35.

a) A comparison of the effects of the addition of 0.25ml 2% KX (X = I, Br, Cl) as catalyst with 27% nitric acid are shown in Figures 5.29(a-c) with the data summarised in

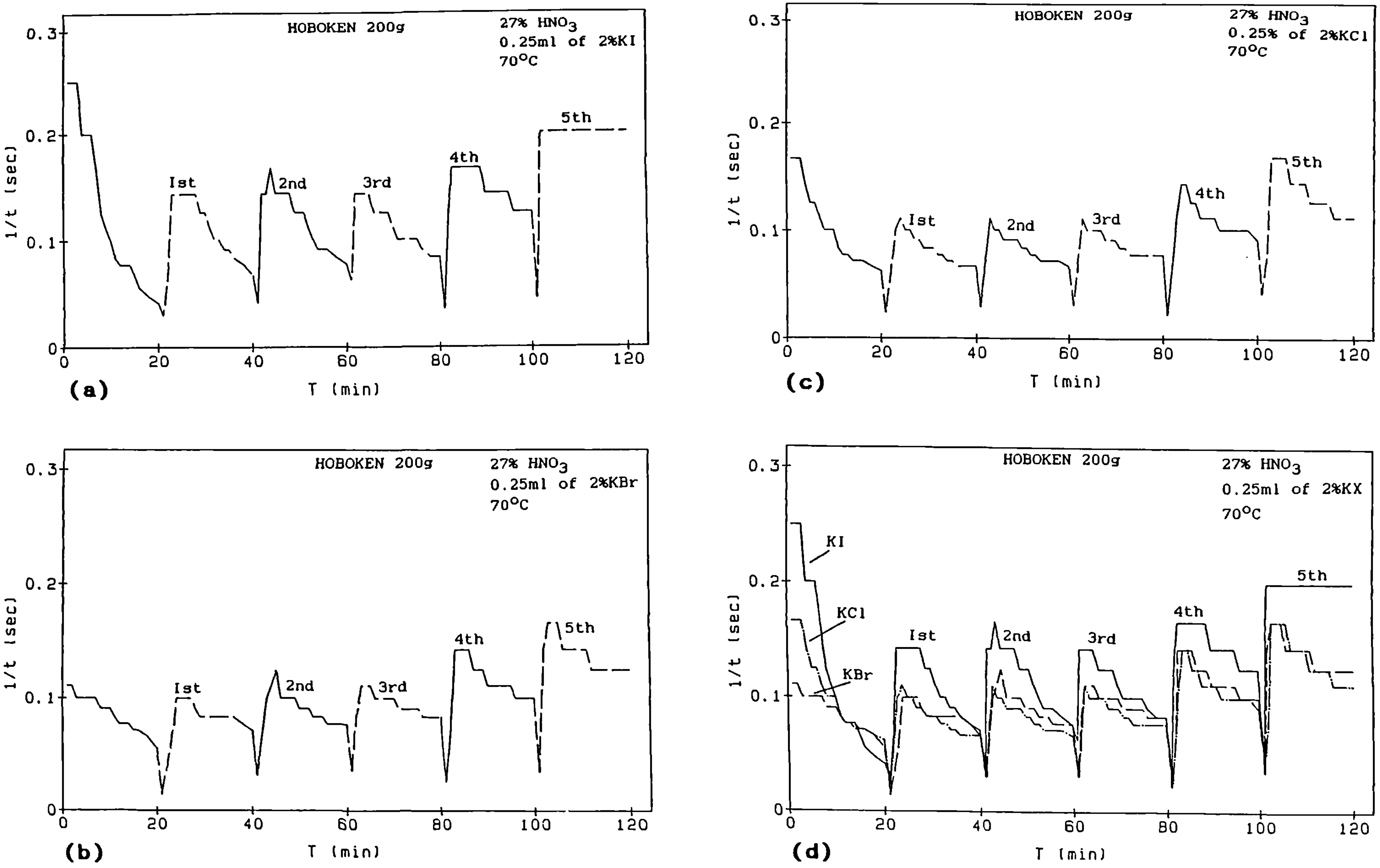


FIGURE 5.29 Effect of different catalyst species on the rate of reaction: (a) KI; (b) KBr; (c) KCl; (d) cumulative.

Figure 5.29d. The data for the individual aliquots are shown in Figures 5.30(a-d). The data in Figure 5.30a show a comparison of the reaction rates for the situation where 200g HOBOKEN oxide are slurried with 27% nitric acid (150ml) containing 0.25ml KX, while 5.30(b-d) show the effects of subsequent aliquots of 40ml (Figures 5.30b-c) and the remainder (Figure 5.30d).

KI is clearly the best catalyst used at this strength. Apart from an initial faster reaction with KCl, there is very little difference between KCl and KBr. KCl would not be an appropriate catalyst in any case because of potential corrosion problems and there is no advantage in using KBr as an alternative to KI.

b) A comparison of the effects of the addition of 0.5ml 2% KX (X = I, Br, Cl) as catalyst with 27% nitric acid are shown in Figures 5.31(a-c) with the data summarised in Figure 5.31d. The data for the individual aliquots are shown in Figures 5.32(a-d), where the data in Figure 5.32a are for slurried oxide in 27% nitric acid containing 0.5ml KX, and Figures 5.32(b-d) show the effects of subsequent aliquots of 40ml (Figures 5.32b-c) and the remainder (Figure 5.32d). Again, KI is clearly the best catalyst at this concentration, and again there is very little difference between KBr and KCl.

c) A comparison of the effects of the addition of 1.0ml 2% KX (X = I, Br, Cl) as catalyst with 27% nitric acid are shown in Figures 5.33(a-c) with the data summarised in Figure 5.33d. The data for the individual aliquots are shown in Figures 5.34(a-d), with the data in Figure 5.34a being those for the slurried oxide in 27% nitric acid containing 1.0ml 2% KX, and Figures 5.46(b-d) show the effect of subsequent aliquots of 40ml (Figures 5.34b-c) and the remainder (Figure 5.34d). The data again show potassium iodide to be the preferred catalyst.

d) A comparison of the effects of the quantity of KI, KBr

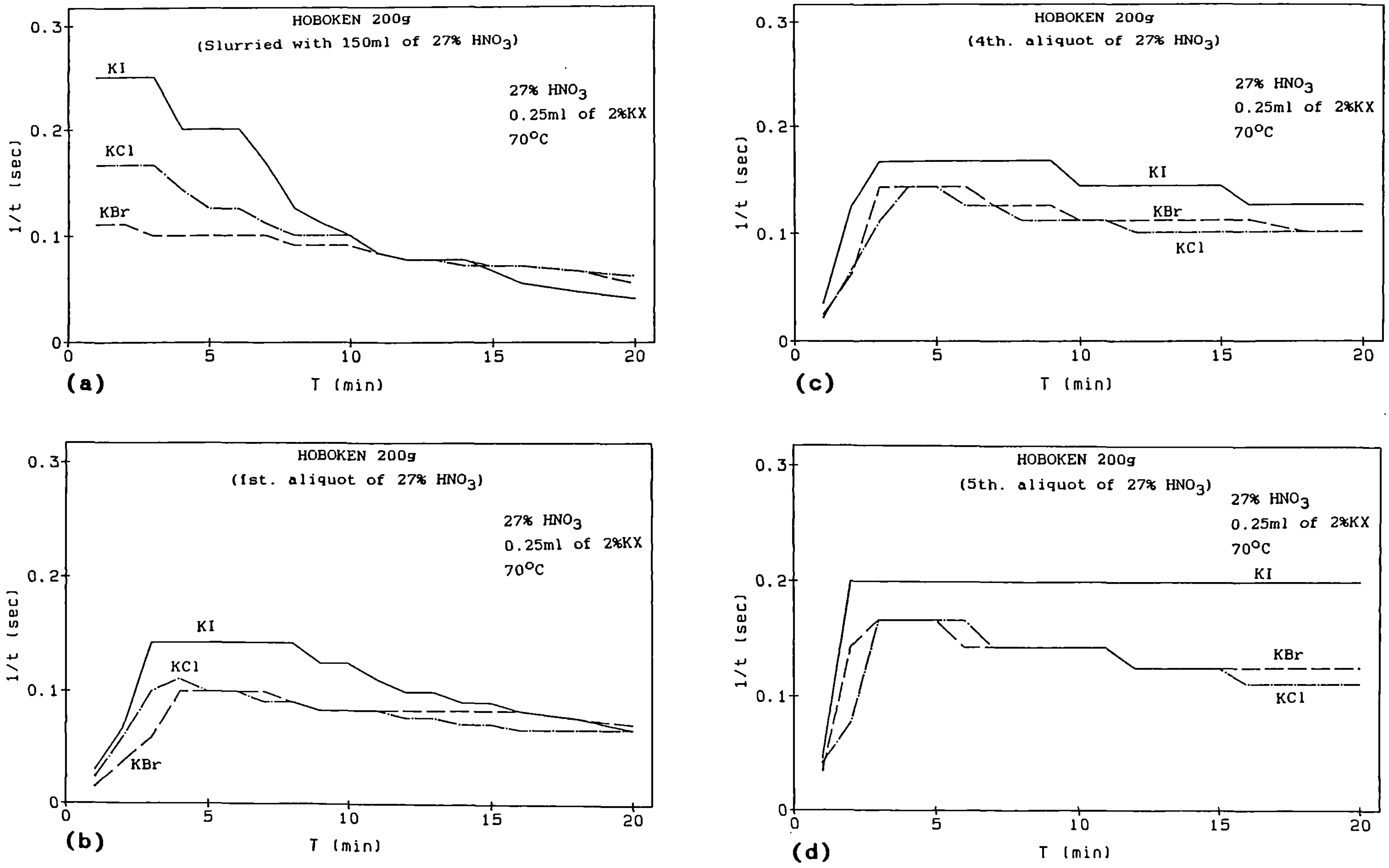


FIGURE 5.30 Effect of individual aliquot of each catalyst solution on the rate of reaction: (a) slurried sample (b) 1st (c) 4th (d) 5th.

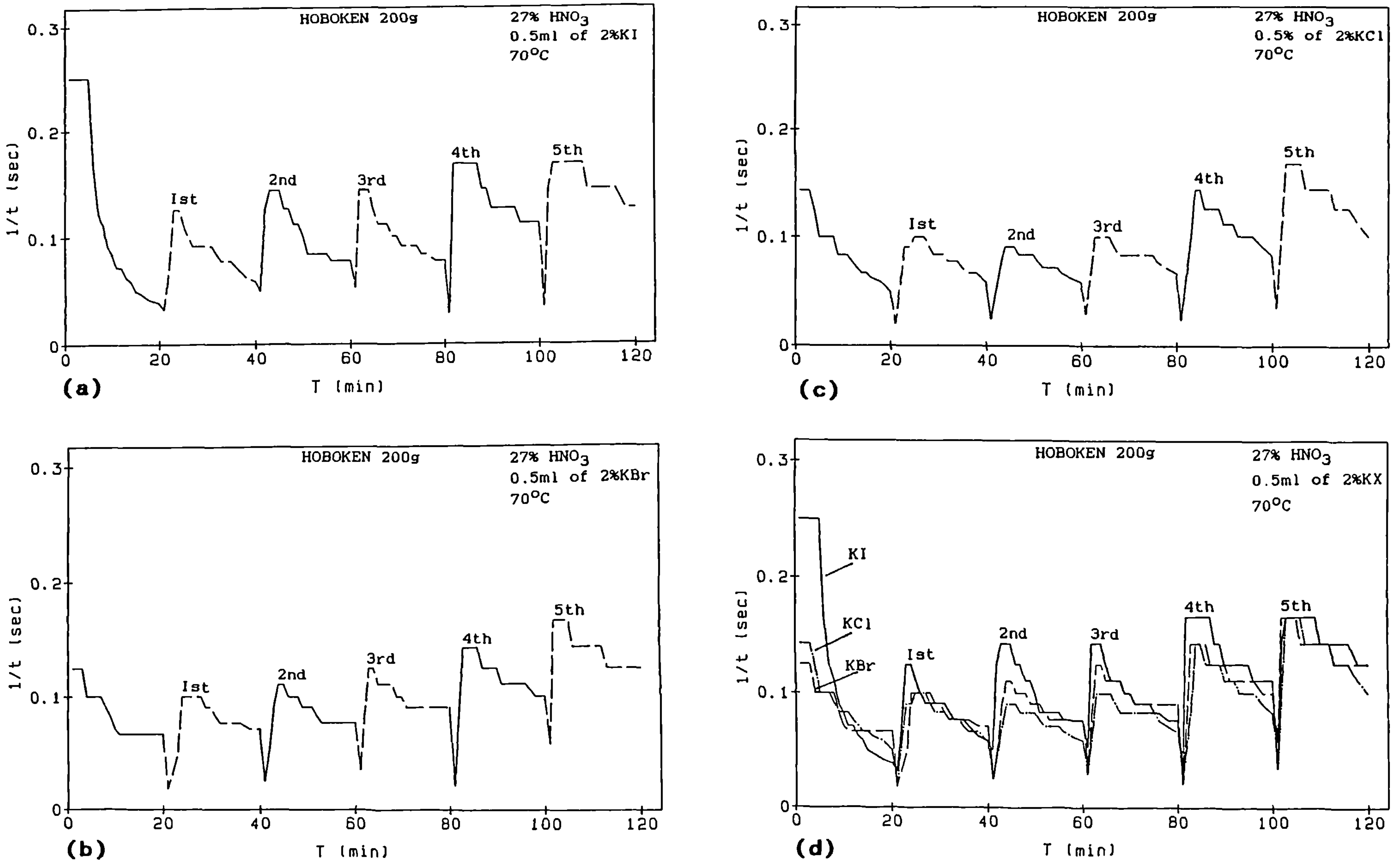


FIGURE 5.31 Effect of different catalyst species on the rate of reaction:
(a) KI; (b) KBr; (c) KCl; (d) cumulative.

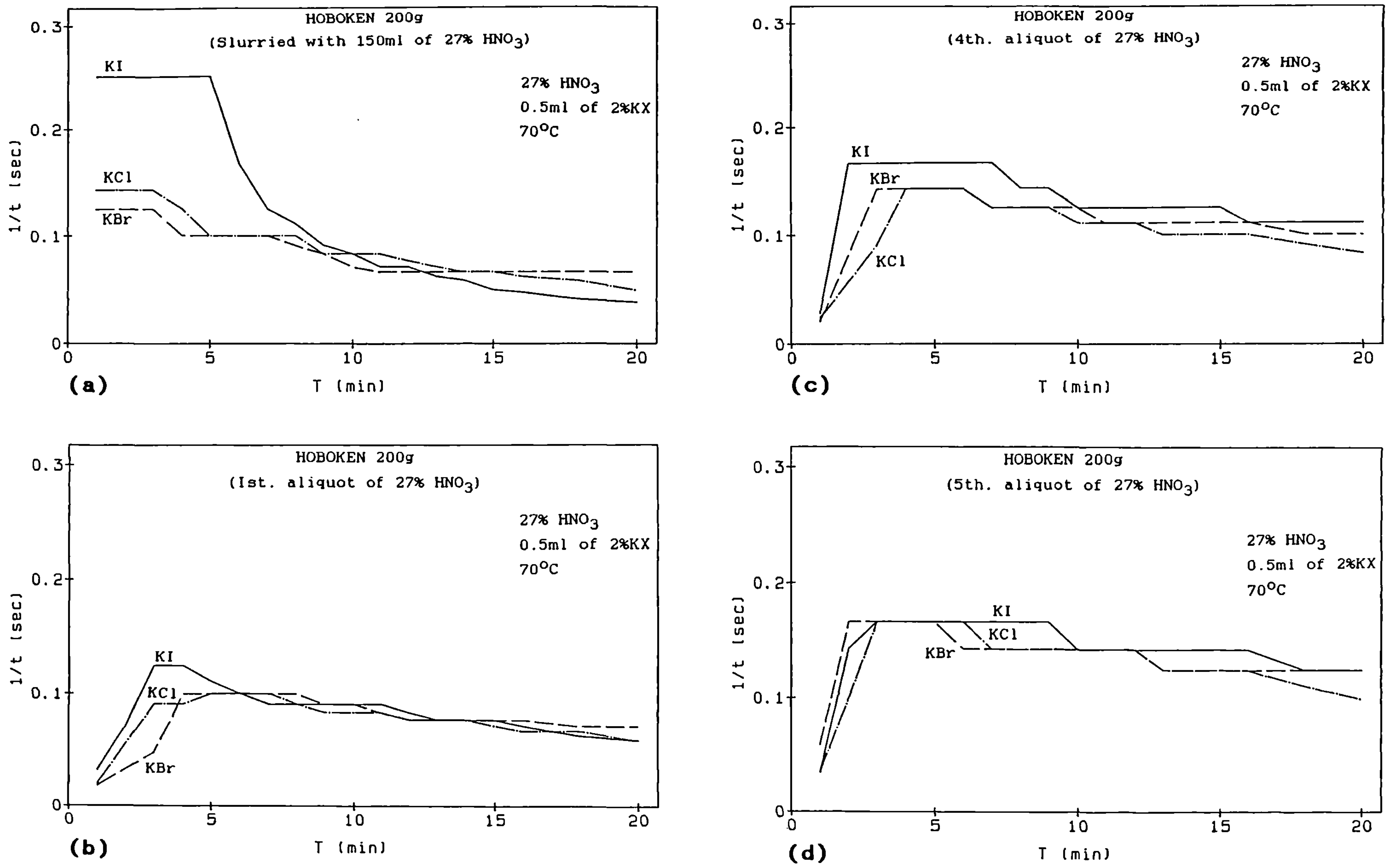


FIGURE 5.32 Effect of individual aliquot of each catalyst solution on the rate of reaction: (a) slurried sample (b) 1st (c) 4th (d) 5th.

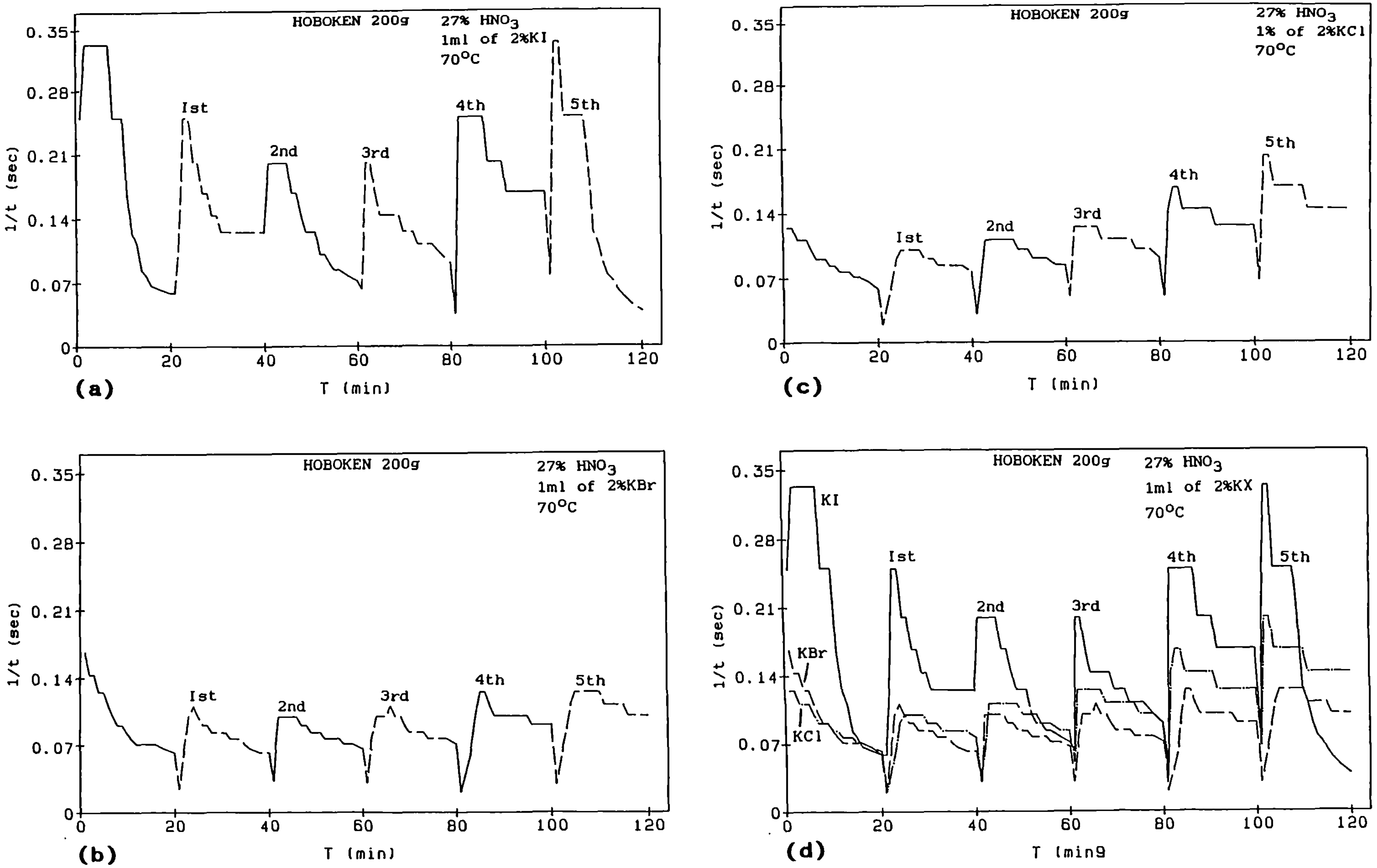


FIGURE 5.33 Effect of different catalyst species on the rate of reaction:
(a) KI; (b) KBr; (c) KCl; (d) cumulative.

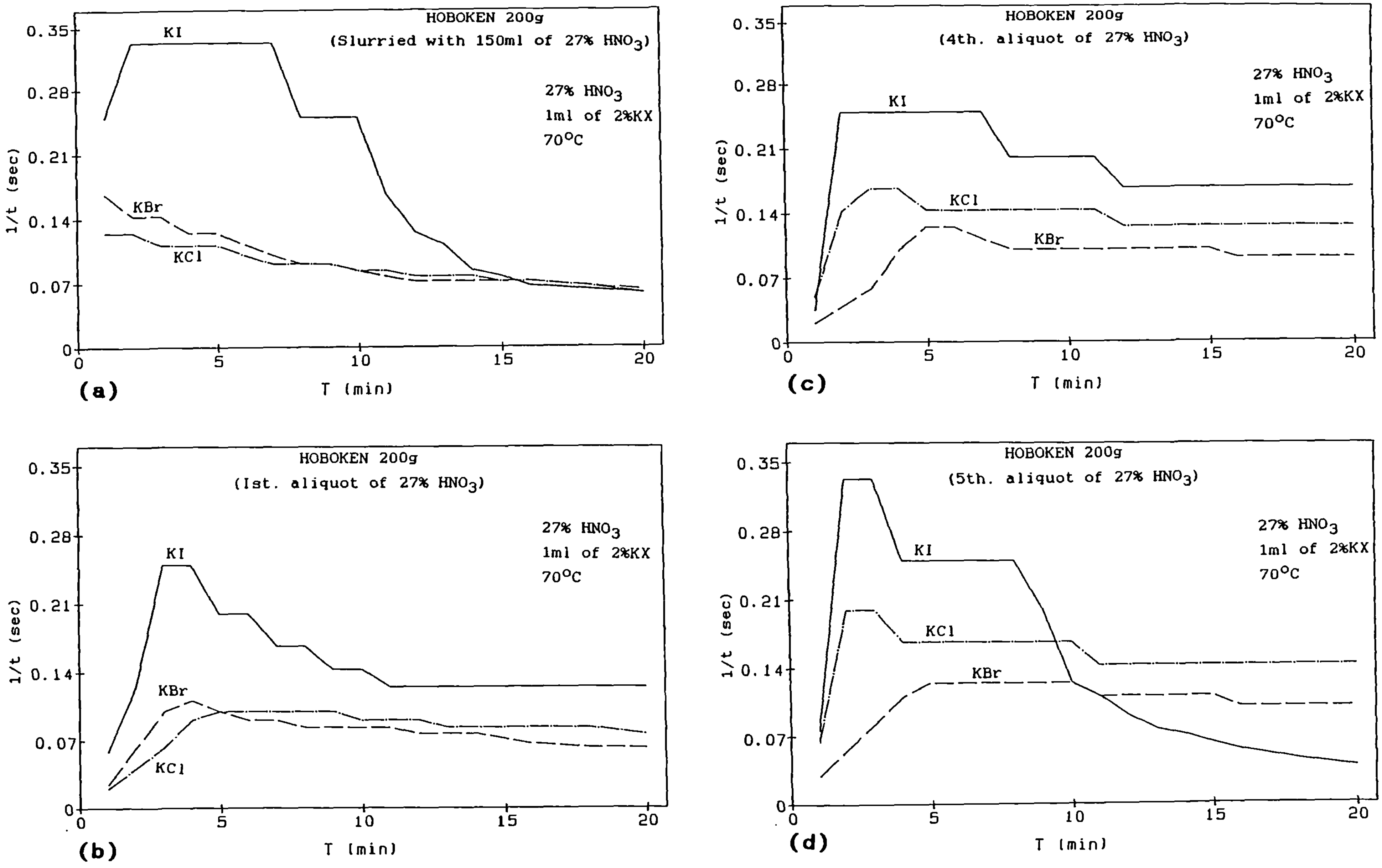


FIGURE 5.34 Effect of individual aliquot of each catalyst solution on the rate of reaction: (a) slurried sample (b) 1st (c) 4th (d) 5th.

and KCl used is given in Figure 5.35(a-c). For KI, (Figure 5.35a), the data show that the reaction of nitric acid with arsenic oxide is complete when 1.0ml of 2%KI is used as catalyst. The reaction although efficient with smaller quantities is not complete at the end of a 120 minute period. These data suggest that the amount of catalyst used in the William Blythe process could be halved without deleterious effects.

The data for KBr and KCl (Figures 5.35b-c) show that not only are they less efficient catalysts but that the reactions are not complete over the 120 minute trial period with the largest amount of acid used.

Ultrasound agitation reduced the temperature required to initiate and complete the reaction by at least 10°C. The quantity of KI catalyst required to achieve similar results with ultrasonic and mechanical mixing is, however, the same. This suggests that the effect of the ultrasound is to improve the dissociation reaction of KI to give the active catalyst species.

5.5 THE ARSENIC(III) OXIDE- NITRIC ACID REACTION CONCLUSIONS

The laboratory results for the standard nitric acid process for the production of arsenic acid showed that the method is handicapped by a lack of control which results in a number of problems, such as excessive foaming; evolution of large volume of gaseous nitrogen oxides, especially in the early part of the reaction; and boil-over. In order to get better control over the reaction rate and to avoid such problems the standard process was reversed and replaced by process based on the addition of acid to arsenic oxide slurries.

The slurry process was carried out by adding aliquots of nitric acid into a slowly stirred slurry of arsenic oxide and water or arsenic oxide and dilute nitric acid (27%). Experiments were carried out by adding 70%, 50%, 35% and 27% nitric acid to an aqueous slurry of arsenic(III) oxide. The results showed that higher acid concentrations produce rapid

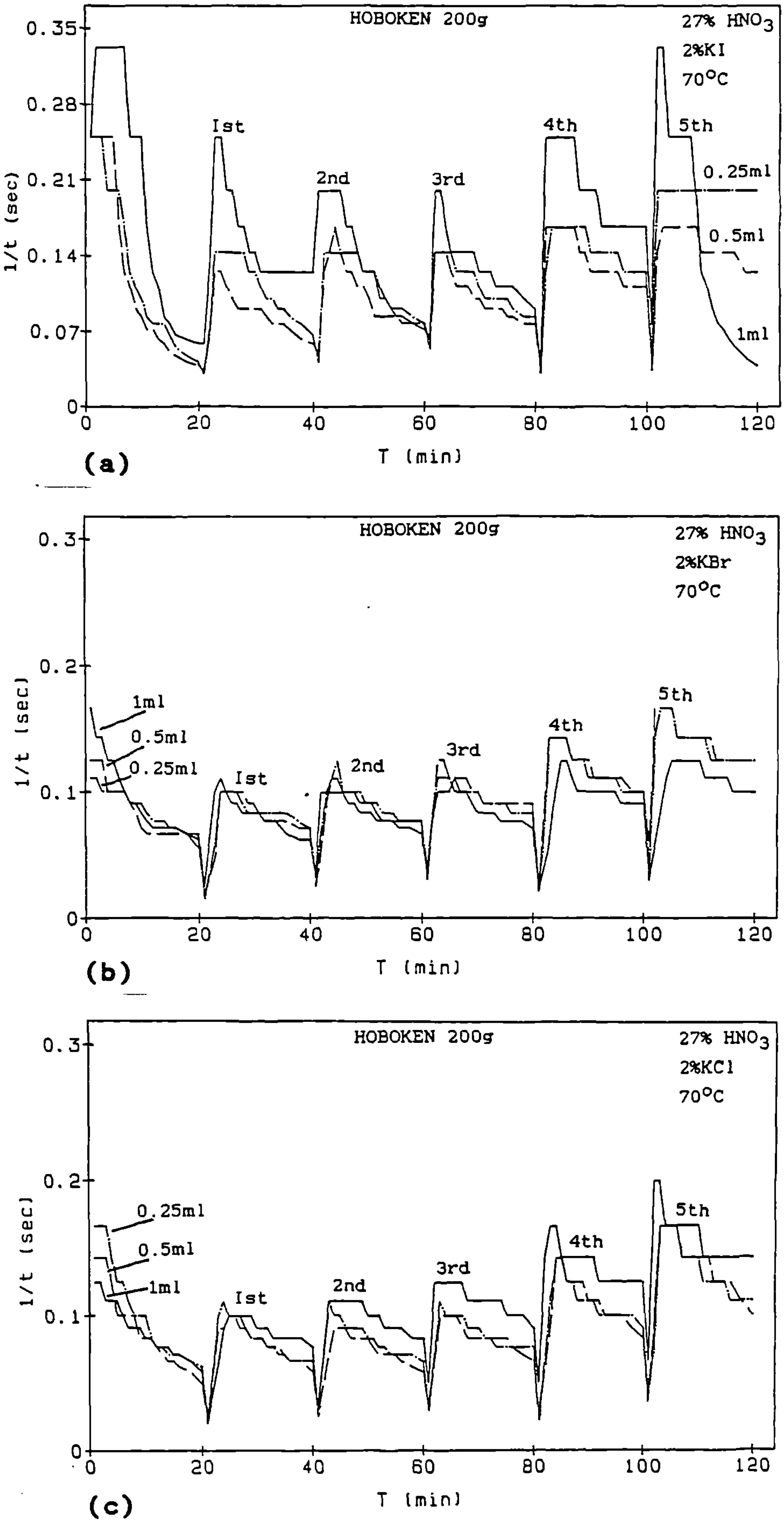


FIGURE 5.35 Comparison effect of different quantity of (a) KI (b) KBr and (c) KCl as a catalyst on the rate of reaction.

reaction and short times are required to finish the process. The use of more dilute acids gives slow reaction rates. In general, the reaction was under control at all these acid concentrations but there are economic and process control advantages in the use of 27% nitric acid. The use of 27% nitric acid rather than water for making the arsenic oxide slurries also gives a gentle reaction, and makes it possible to start the reaction at a lower temperature. Thus when temperature reaches to 70°C, some of the arsenic(III) oxide has already reacted with nitric acid (used for making the slurry) and the addition of subsequent aliquots of 27% nitric acid give a very gentle, controllable, reaction.

The effect of slurry thickness on the rate of reaction was also studied. The results showed that thick slurries give higher initial reaction rates than thin slurries under the same reaction conditions. The reaction rate in the later stages of the process drops slowly in case of thick slurry and rapidly in case of thin until both reach a similar steady reaction rate.

The reaction behaviour of different arsenic(III) oxide samples under the same conditions showed very little difference in their reaction with nitric acid, thus eliminating one of the problems in the old procedure.

A comparison of KI, KBr and KCl as the catalyst show that KI is the most effective catalyst, and apart from an initial faster reaction with KCl there is very little difference between KCl and KBr. The effect of different volumes of 2% KI (0.25, 0.5, and 1ml) show that the reaction is complete when 1.0ml is used as catalyst. The reaction also efficient with smaller quantities is not complete at the end of 120 minute period. The reaction rate can be increased at any stage of the reaction by just adding a drop of catalyst along with the nitric acid aliquot.

The results of ultrasonic agitation instead of mechanical stirring showed that the temperature required to initiate and complete the reaction can be reduced by at least 10°C. The ultrasonic agitation helps the reaction in two ways: 1) by initiating the reaction at low temperature; and 2) by decreasing the particle size of slurried oxide during the reaction.

The results of the slurry process developed in this work show that the reaction rate can be controlled easily by adding the nitric acid at appropriate rates. The reaction can be monitored by measurement of the pressure of the product gases and this, in turn, can be used to control nitric acid/catalyst addition.

5.6 RECOMMENDED INDUSTRIAL PROCEDURE

As a result of the work described in Section 5.4 the following procedure is recommended for the production of arsenic acid by a slurry process.

This process uses the oxidation of slurried arsenic oxide, As_2O_3, by nitric acid together with KI as a catalyst, for the industrial production of arsenic acid. The arsenic oxide is slurried with distilled water or dilute (27%) nitric acid. The slurry temperature is raised to 60°C and nitric acid is added in doses to a very gently stirred mixture. Catalyst may be added to the slurry before heating or may be added with the first nitric acid aliquot. When the reaction slows due to the consumption of most of the available acid, another dose of nitric acid is added to trigger the reaction rate. The rate of reaction can also be increased at any stage by adding a few more drops of catalyst. This procedure has the following advantages:

a) The introduction of nitric acid in aliquot form overcomes the disadvantages inherent in the standard process. Problems such as boil-over, evolution of large volume of gaseous nitrogen oxides and especially the problems associated with foaming can be avoided. The slurry process provides an ideal method of controlling the reaction because the rate and extent of reaction can be varied by the addition of acid or catalyst at an appropriate rate.

b) With the slurry process it is possible to accommodate even high grade arsenic oxides as reagent (SALSIGNE-A and B) without radically altering the reaction conditions.

c) One important feature of the slurry process is the ability to use different concentration of nitric acid without losing control over the reaction. The reaction between nitric acid and arsenic(III) oxide is exothermic in nature. By using a high acid concentration it is possible to control the temperature throughout the reaction period by just adding an aliquot of nitric acid and very little external heating is required. By using concentrated nitric acid the rate of reaction is, however, higher than with a lower acid concentration, and the amount of control is somewhat reduced.

d) Arsenic(III) oxide can be slurried with either distilled water or 27% nitric acid. In order to obtain better control over the initial reaction rate it is suggested that 27% nitric acid rather than distilled water should be used for making the arsenic(III) oxide slurry.

On an industrial scale, the slurry process was tested successfully in William Blythe plant. The company is now producing routinely arsenic acid using the slurry process with both high and low grade arsenic(III) oxides.

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CHAPTER 6

PRODUCTION OF ALUMINIUM SULPHATE FROM NIGERIAN CLAY AND PURIFICATION OF QUARTZ

CHAPTER SIX

PRODUCTION OF ALUMINIUM SULPHATE FROM NIGERIAN CLAY AND QUARTZ PURIFICATION

6.1 CLAY

6.1.1 Introduction

The term clay is applied to a group of substances, derived from the weathering of feldsparthic rocks, which are earthly and soft when dry, but form more or less plastic masses when they are moist. The constituents making up the clays may vary according to the kind of rock from which they were formed by weathering. Purely analytically (without specifying how they are combined), the principal constituents are found to be Al_2O_3, SiO_2 and H_2O. It was formerly assumed that the various clays were all Kaolin, contaminated to a greater or less extent by impurities. According to modern investigations, however, Clay and Kaolin are substances of quite different character, even though they happen to have the same composition. The valuable ceramic clays do, nevertheless, contain considerable amounts of kaolin mixed with them, together with other colloidally dispersed minerals, which also occur on their own as clay forming materials[1].

The chief constituent of Kaolin is Kaolinite[2-4], a compound which is shown by its X-ray pattern to be crystalline, having the composition $Al_2O_3.2SiO_2.2H_2O$ or $Al_2Si_2O_5.(OH)_4$. When heated, Kaolinite loses its chemically bound water. On strong heating, the dehydrated kaolinite (meta-kaolinite) first decomposes into Al_2O_3 and SiO_2; at still higher temperature these form mullite[5-7], $3Al_2O_3.2SiO_2$, together with tridymite. X-ray analysis has also shown that kaolinite is built up from $[Si_2O_5]^{2-}$ sheets, between which are arranged pairs of $[Al(OH)_2]^+$ sheets. The minerals Dickite and Nacrite, occuring in many kaolins, have the same composition as kaolinite. They have different X-ray patterns from kaolinite, but appear to be very similar in structure[8-11]. Pure kaolin is white in colour, and has a relatively low plasticity. Since it is used for the production of ceramics it is also known as china clay. Clay containing much sand as impurity, as well as iron oxide, is called loam and is used primarily for the production of bricks and tiles. Clays contaminated with much calcium and magnesium carbonate are termed marls, and can not be used for ceramic purposes. They are, however, used to some extent in the cement industry.

6.1.2 Formation of Clay

Formation of clay takes place through the weathering of silicate rocks, which is accompanied by a far-reaching mechanical subdivision of the rock. Along with this, a chemical process takes place with hydrolysis of a larger or smaller proportion of the silicate (especially the feldspars) to form amorphous alumina silica gel. These gels, which are known as allophanes, may be mere mixtures of aluminium oxide and silicon dioxide hydrates, or amorphous, hydrated aluminium silicates of the type of the so called 'pro-kaolin'. 'Pro-kaolin' is probably a definite compound of the formula $Al_2O_3.2SiO_2$ containing variable amounts of water which are not chemically combined with it, as they are in kaolinite.

The laboratory formation of kaolin from feldspar, occurs under the special conditions of elevated temperatures and pressures, and is considerably promoted by the presence of strong acids[12]. Kaolinization is a purely chemical reaction, represented by the over-all equation:

$$2K[AlSi_3O_8] + 7H_2O \longrightarrow Al_2Si_2O_5(OH)_4 + 4H_2SiO_3 + 2KOH$$

Kaolinite is also formed naturally by the intensive action of water and weather on the alkaline feldspar, as shown by the following reaction:

$$2K[AlSi_3O_8] + CO_2 + H_2O \longrightarrow Al_2Si_2O_5(OH)_4 + 4SiO_2 + K_2CO_3$$

Kaolin can be formed not only directly from feldspar, but also subsequently from pro-kaolin. Strong acids favour the formation of kaolin because they accelerate the hydrolysis of feldspar, but they are not essential.

6.1.3 Clay Structure

The various clays, are almost entirely composed of silicate minerals and silica. The fundamental unit in all silicate structure is the tetrahedral orthosilicate ion $[SiO_4]^{4-}$ shown in Figure 6.1. The $[SiO_4]^{4-}$ units can exist either as discrete structural entities or can combine by corner sharing of oxygen atoms into larger units. The resulting oxygen lattice is frequently close-packed, or approximately so, and charge balance is achieved by the presence of further cations in tetrahedral, octahedral, or other sites depending on their size.

All the clay minerals have layer/sheet structure in which there is a complete sharing of three oxygen atoms per silicon. The basic unit in layer/sheet structure contains two silicon atoms in combination with three oxygen atoms and sharing a further four oxygen atoms with neighbouring units[5-11]. This gives a total of $3+4(1/2)=5$ oxygen atoms. This yields an empirical formula of $(Si_2O_5)_n{}^{2n-}$. Figure 6.2 represents the structure of kaolinite in which SiO_4 tetrahedra share common oxygen atoms with $Al(OH)_2O$ to give a composite layer of formula $Al_2(OH)_4Si_2O_5$. The double lines and double circles in the tetrahedra indicate bonds to 2 oxygen atoms[13] (one in front and one behind). When heated, Kaolinite loses its chemically bound water. The structure of kaolinite before and after dehydroxylation is shown in Figure 6.3.

6.1.4 Uses of Clay

The total world clay production is about 20 millions tonnes a year, the main producers being the USA (36%), the UK (22%), and the USSR (13%). Nowadays, approximately half of this tonnage is used in the paper manufacturing industry a) as a filler to fill small spaces between the pulp fibres; and b) as a surface coating to produce a smooth, bright, and

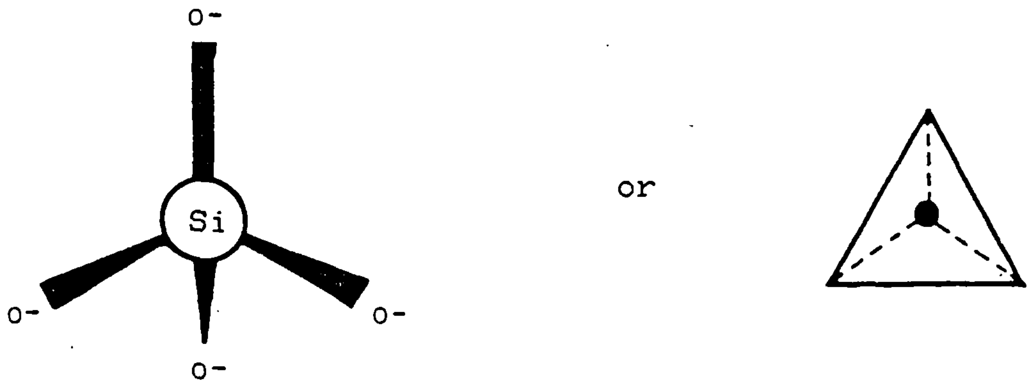
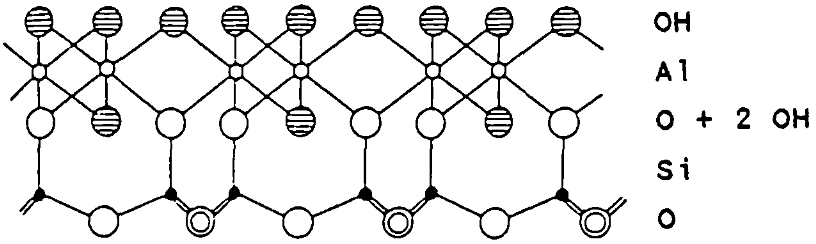
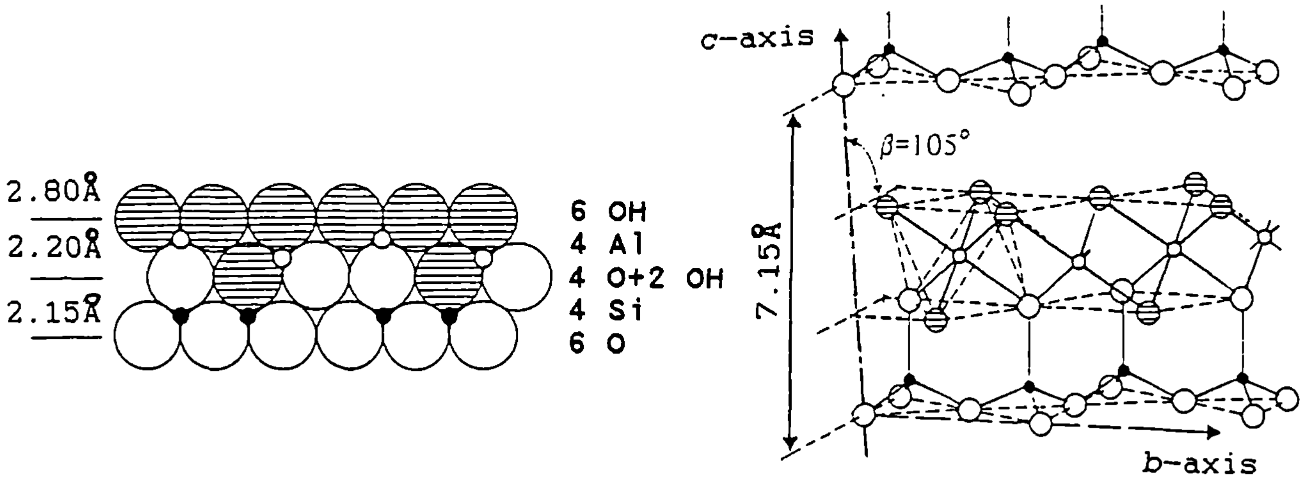


FIGURE 6.1 The orthosilicate ion.



(a) Kaolinite, $Al_2Si_2O_5(OH)_4$



(b) Alternative representations of the layers

FIGURE 6.2 The Structure of Kaolinite.

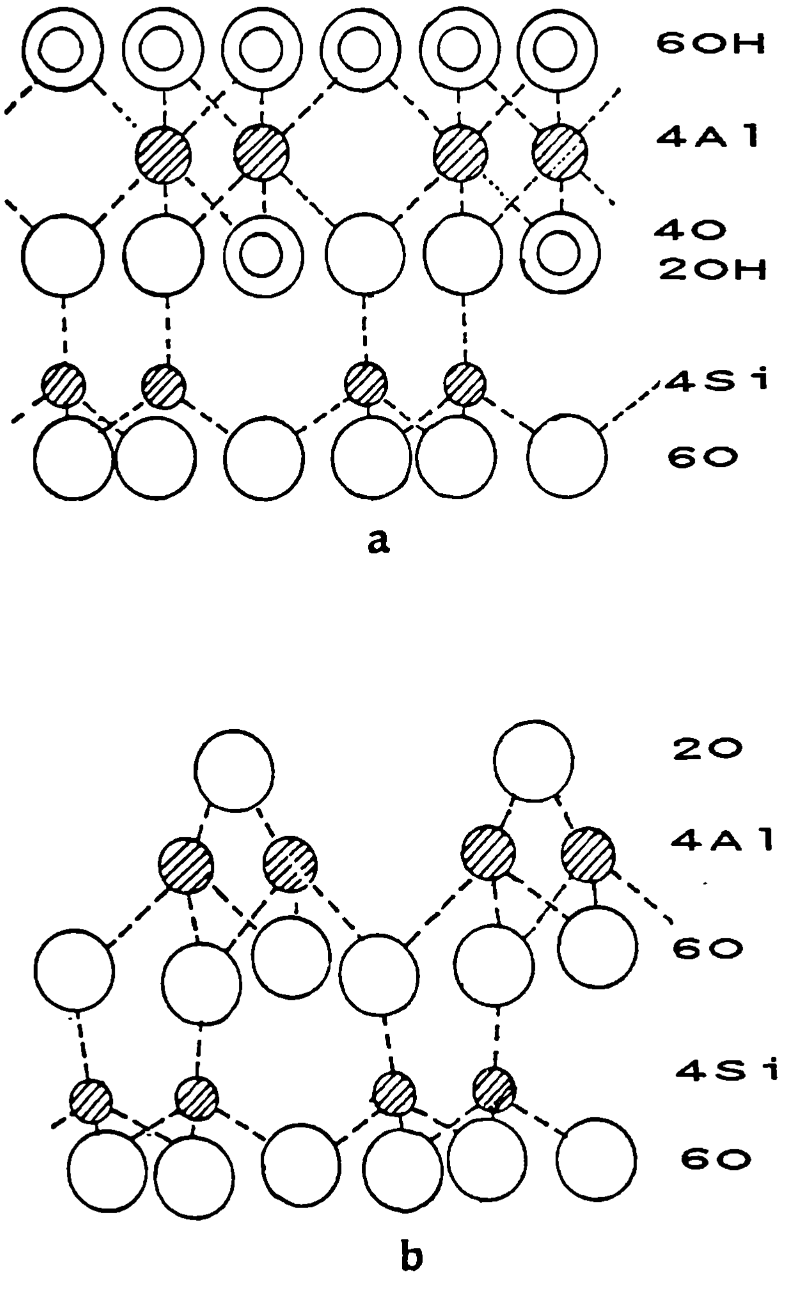


FIGURE 6.3 The Structute of Kaolinite:
(a) Before dehydroxylation
(b) After dehydroxylation

usually white glossy finish. About one-quarter is used for fire bricks and refractories. Only 8200 tonnes is used for china, crockery, and earthenware which is also usually made from ball clay, a particularly fine grained, highly plastic material which is predominantly kaolinite together with clay mica and quartz. Some 800,000 tonnes of ball clay is used annually in USA for white ware, tableware, wall and floor tiles, sanitaryware and electrical porcelain. Articles fabricated from naturally occuring or artificially produced plastic mixtures of clay or kaolin with other substances are known as 'ceramic products'.

Natural clay can also be considered as a low-grade primary source of aluminium. Studies on the use of clay as a source of aluminium sulphate for the chemical industry are described in this chapter. The main solid product of the leaching of clay is silica (α-Quartz). The purification of samples of mineral silica or leaching by-product silica for high quality uses is described in the second half of this chapter.

6.2 SILICON DIOXIDE

Silicon dioxide is found in nature in three different crystalline forms, as quartz, as tridymite, and as cristobalite. These three polymeric form of silica are not readily interconvertable as is shown by the fact that all three are found as minerals, though tridymite and cristobalite are rare in comparison with quartz. Furthermore, each of the three forms exists in low and high temperature transitions as summarised below:

$$\begin{tikzcd}
\beta\text{-quartz} \arrow[r, Rightarrow, "870^{\circ}"] \arrow[d, shift left, "573^{\circ}"] & \beta\text{-tridymite} \arrow[r, Rightarrow, "1470^{\circ}"] \arrow[d, shift left, "120\text{-}160^{\circ}"] & \beta\text{-cristobalite} \arrow[d, shift left, "200\text{-}280^{\circ}"] \\
\alpha\text{-quartz} \arrow[u, shift left] & \alpha\text{-tridymite} \arrow[u, shift left] & \alpha\text{-cristobalite} \arrow[u, shift left]
\end{tikzcd}$$

6.2.1 Quartz Structure

The three main forms, quartz, tridymite, and cristobalite, are all built of SiO_4 tetrahedra linked together so that every oxygen atom is connected to two tetrahedra (thus giving the composition SiO_2), but the arrangement of the linked tetrahedra is quite different in the three crystals. The main crystalline modifications of SiO_2 consist of infinite arrays of corner-shared (SiO_4) tetrahedra. In α-quartz, which is thermodynamically the most stable form at room temperature, the tetrahedra form interlinked helical chains; there are two slightly different Si-O distances (1.59 and 1.61Å) and the angle Si-O-Si is 144°[14]. β-quartz has the same general structure but is somewhat less distorted (Si-O-Si 155°) (Figure 6.4).

6.2.2 Uses of Quartz

The most important use of quartz is as a piezoelectric material; it is used in crystal oscillators and filters for frequency control and modulation, and in electromechanical devices such as transducers and pickups: tens of millions of such devices are made each year. In the form of quartz sand, silicon dioxide has extensive uses. It is used in building, for the preparation of lime mortar, and is also mixed with cement. The purest obtainable quartz sand is also used for the glass and porcelain industries.

6.3 PRODUCTION OF ALUMINIUM SULPHATE

Aluminium sulphate, $Al_2(SO_4)_3$, is a white powder, which is best prepared technically by dissolution of pure aluminium hydroxide or alumina in hot concentrated sulphuric acid:

$$2Al(OH)_3 + 3H_2SO_4 \text{ ------> } Al_2(SO_4)_3 + 6H_2O$$

$$Al_2O_3 + 3H_2SO_4 \text{ ------> } Al_2(SO_4)_3 + 3H_2O$$

In this work, aluminium sulphate was prepared from different clay samples. Aluminium can be directly dissolved from the clay by treatment with sulphuric acid, but a difficulty then arises in removing impurities from the product in a simple manner.

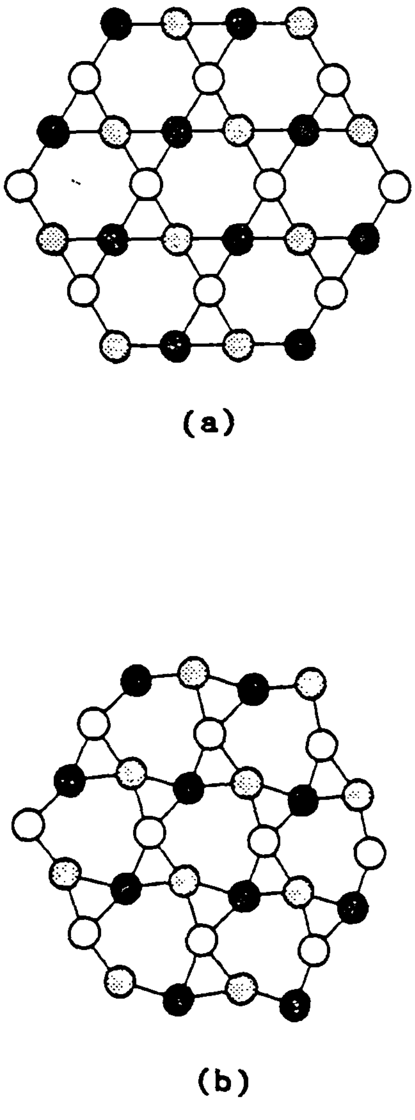


FIGURE 6.4 The arrangement of the Si atoms (in plan) in (a) β-quartz and (b) α-quartz.

$$Al_2Si_2O_5(OH)_4 + 3H_2SO_4 \dashrightarrow Al_2(SO_4)_3 + 5H_2O + 2SiO_2$$

Aluminium sulphate crystalizes in colourless crystals with density 1.62 from aqueous solutions at ambient temperatures as the hydrate, $Al_2(SO_4)_3 \cdot 18H_2O$. From warm solutions of aluminium sulphate, the usual product is $Al_2(SO_4)_3 \cdot 16H_2O$. In addition, hydrates with 27, 10 and 6 water molecules have also been reported. Dehydration is complete if the hydrates are heated above 340°C. Loss of SO_3 commences at about 600°C.

6.3.1 Uses of Aluminium Sulphate

A major consumer of aluminium sulphate is the paper industry where it used to adjust acidity, and to make the paper water resistant. For this application it is important that the aluminium sulphate should be free from iron salts. This applies even more to its use in tanning skins (white tanning), and in dying (wool), where it is used as a mordant.

The use of aluminium sulphate as a mordant depends on the fact that aluminium hydroxide, formed hydrolytically in aqueous solution, is absorbed and retained by the wool fibre. The aluminium hydroxide, in turn can absorb organic dyestuff molecules. Other salts with strong tendency for hydrolysis, such as chromic sulphate and stannic chloride, have a similar action. The wool fibres, previously treated with such salts ("mordanted") can thus be dyed with substances which will not ordinarily take on the fibre.

Cotton, unlike wool, is unable to take up aluminium hydroxide directly from the aluminium sulphate solution. For cotton, therefore, potassium alum, $KAl(SO_4)_2 \cdot 12H_2O$, is used to treat cotton fibre to make them absorb dyes more easily.

Aluminium sulphate is also used in municipal water treatment where it is added to the water along with lime (CaO). The calcium oxide reacts with water to make the solution slightly basic, and cause the precipitation of gelatinous aluminium hydroxide. As the precipitates settle, they carry with them any finely suspended solids and bacteria.

Aluminum sulphate is also used in the chemical industry as the starting material in the preparation of aluminium salts.

6.4 PRELIMINARY ANALYSES OF THE CLAY SAMPLES

Four Nigerian kaolinite samples were supplied, *viz*;

ORIGINAL, CRUDE 1, CRUDE 2, and SDF

All of these clay samples consisted mainly of kaolinite and silica in grey powder form. Thermogravimetric analyses showed that each clay sample has two water molecules which are chemically bound in the silicate structure. The actual weight loss was 11-13% at 600°C which corresponds to 1.7 to 2 molecules of water (Figure 6.5). EDAX analysis indicates the presence of Al, Si, Ti, and Fe (Figure 6.6) while X-ray diffraction data show that each clay sample consists of a mixture of mineral kaolinite, aluminium silicate ($Al_2Si_2O_5(OH)_4$), and quartz, α-SiO_2 (Figure 6.7).

All the clay samples were analysed for aluminium using the sodium carbonate fusion method. The actual Al weight % of each sample is given in Table 6.1.

TABLE 6.1 ANALYSIS OF CLAY SAMPLES

SAMPLE	TOTAL Al (%)
ORIGINAL	12.6 ± 1.1
CRUDE 1	5.5 ± 0.1
CRUDE 2	7.3 ± 0.2
SDF	8.3 ± 0.2

6.5 EXPERIMENTAL METHOD TO STUDY THE REACTION OF CLAY

Aluminium sulphate, $Al_2(SO_4)_3.nH_2O$, can be prepared from Nigerian Kaolinite clay samples by direct reaction with sulphuric acid. The theoretical equation for the reaction is:

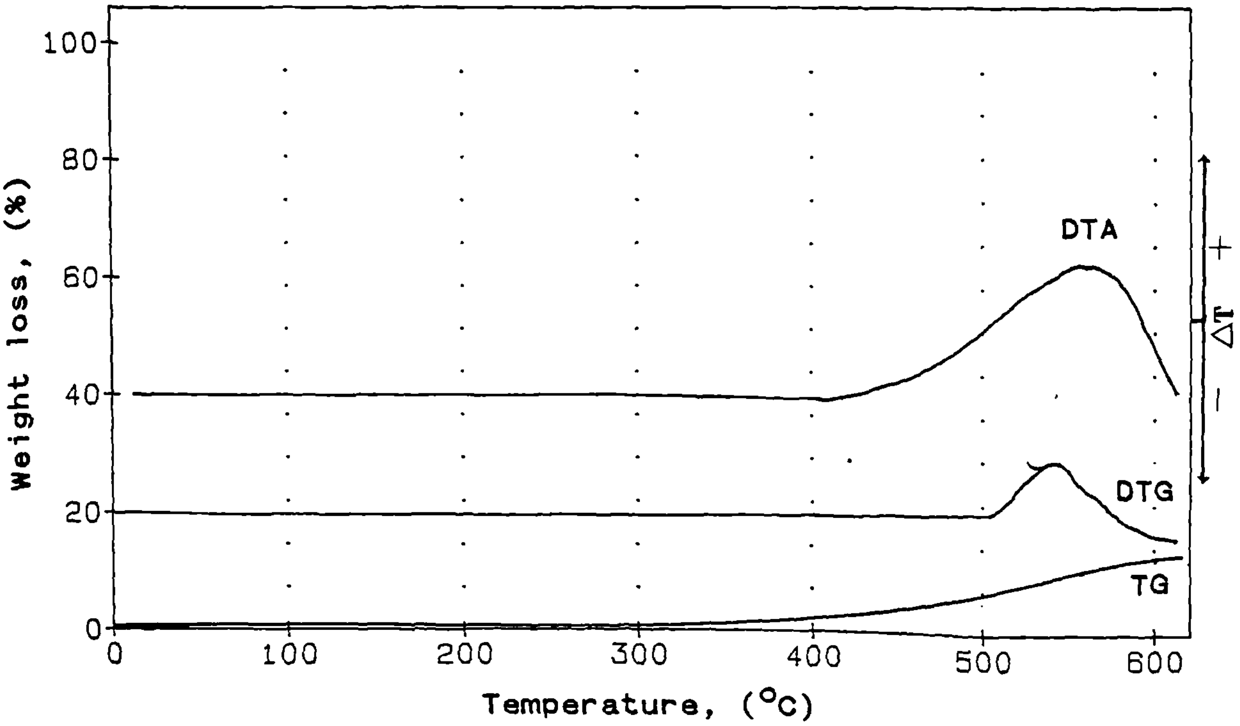


FIGURE 6.5 Thermogram of ORIGINAL clay sample.

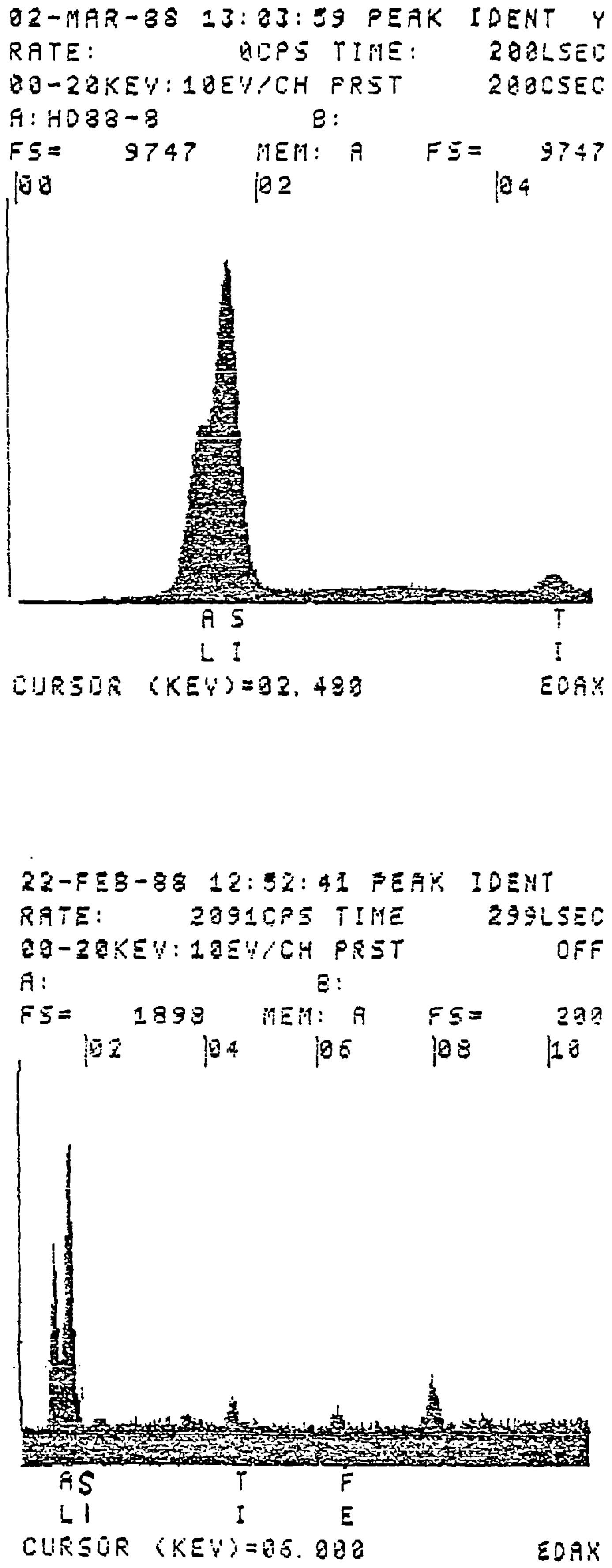
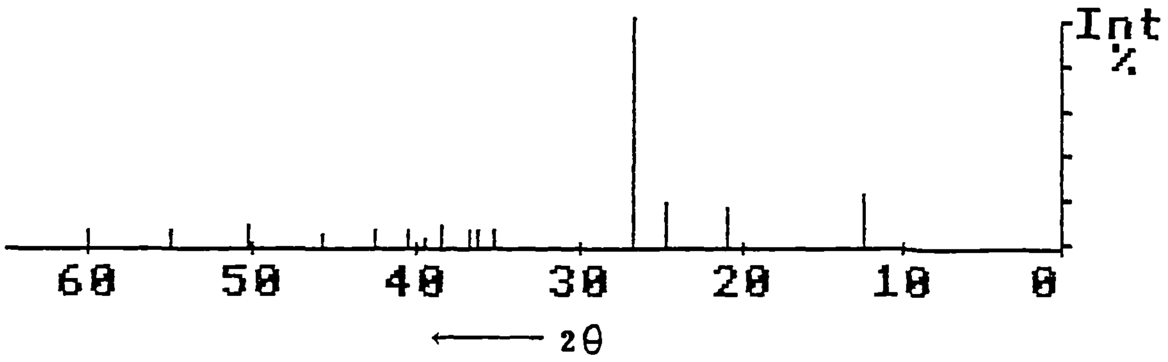


FIGURE 6.6 Electron microprobe analyses of clay sample.



2θ	d	I
12.5	7.081	22
21.0	4.230	17
24.9	3.576	19
26.8	3.326	100
35.3	2.542	7
36.2	2.481	7
36.7	2.449	7
38.6	2.332	9
39.5	2.281	3
40.5	2.227	6
42.5	2.127	6
45.9	1.977	4
50.2	1.817	9
55.0	1.670	6
60.0	1.542	7

FIGURE 6.7 Diffractogram for clay sample.

$$Al_2Si_2O_5(OH)_4 + 3H_2SO_4 \text{------>} Al_2(SO_4)_3 + 5H_2O + 2SiO_2$$

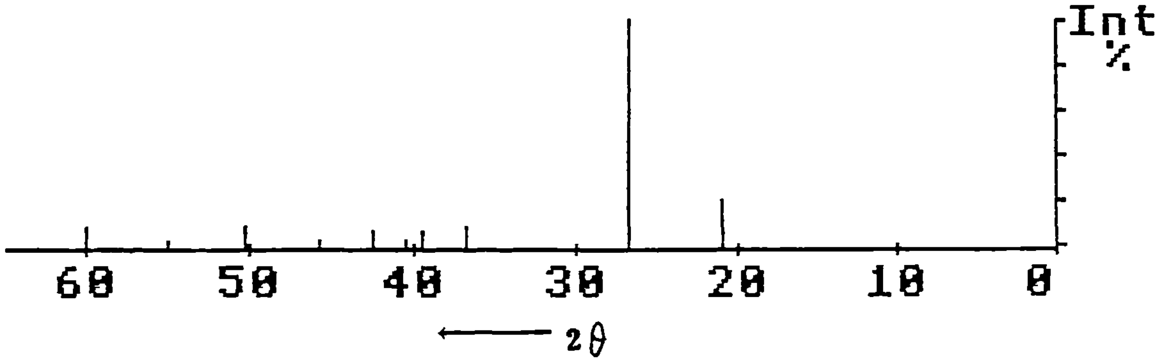
Preliminary analyses showed that ORIGINAL sample was the best sample to study due to its higher Al content. Based on the total aluminum present, the ORIGINAL sample which had a powder density of 1.14 $g.cm^{-3}$ contains approximately 60% aluminium silicate.

Leaching of aluminium sulphate from clay sample was carried out in a 250ml cylindrical flange flask. The flask containing the clay sample was charged with sulphuric acid and mixed with a magnetic stirrer. All experiments were carried out under reflux to avoid the evolution loses. The solution was filtered and the residue was dried in an oven. X-ray examination of the residue showed that it was α-quartz (Figure 6.8), while EDAX showed that it contained some traces of titanium, and iron (Figure 6.9). This residue is suitable for cement and ceramic industries but could be further purified for the use in glass industry. In the following sections the reaction is refined to maximise its efficiency.

6.5.1 Effect of Acid Concentration

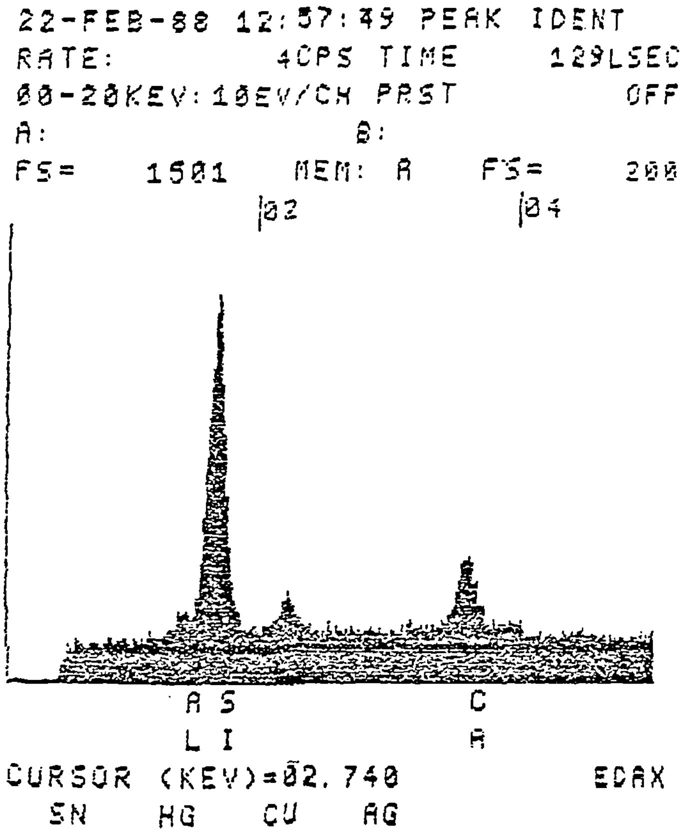
In this set of experiments, 5g of ORIGINAL clay sample was leached by stirring with 100ml of 2, 4.5, 9, 13.5 or 18M sulphuric acid at 120°C for 3 hours. The solution was filtered and the residue was dried in an oven and then weighed. The solubility results are given in Table 6.2.

The results showed that maximum solubility (25%) is achieved with 9M sulphuric acid. The filtrate was analysed by AAS for Al. The results obtained showed that Al can be leached with 100% efficiency from ORIGINAL clay sample to give a residue that is mainly α-quartz. In the case of ORIGINAL sample it is possible to obtain about 795g of aluminium sulphate, $Al_2(SO_4)_3$, from 1 kg of clay.



2θ	d	I
21.0	4.230	21
26.8	3.326	100
36.7	2.449	9
39.5	2.281	7
40.5	2.227	3
42.5	2.127	7
45.9	1.977	3
50.2	1.817	9
55.0	1.670	2
60.0	1.542	9

FIGURE 6.8 Diffractogram for residue obtained after sulphuric acid treatment.



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22-FEB-88 12:57:39 PEAK IDENT
RATE:          4CPS TIME     129LSEC
00-20KEV:10EV/CH PRST            OFF
A:                 B:
FS=    1501    MEM: A    FS=     200
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CURSOR (KEV)=02.740           EDAX
  SN    HG    CU    AG
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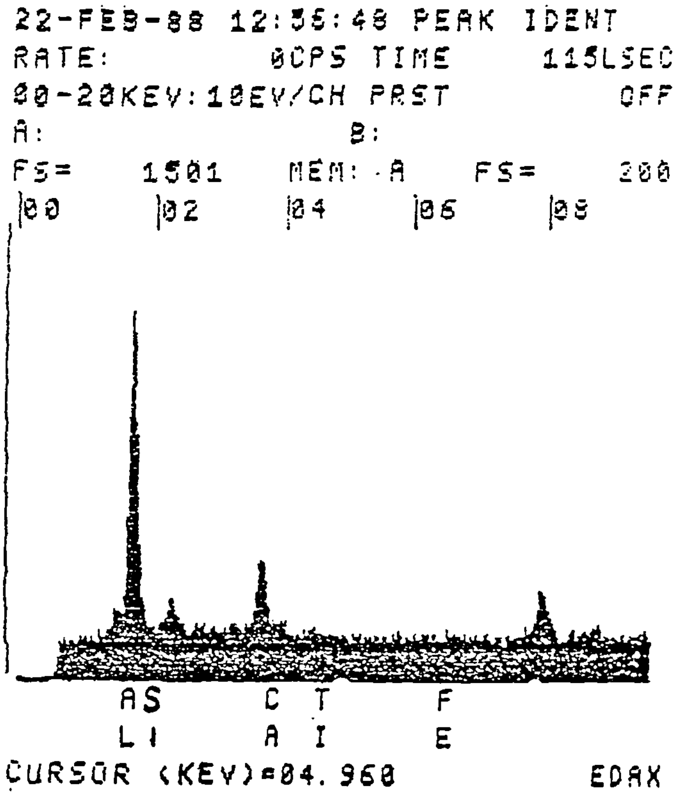

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22-FEB-88 12:55:48 PEAK IDENT
RATE:          0CPS TIME     115LSEC
00-20KEV:10EV/CH PRST            OFF
A:                 B:
FS=    1501    MEM: A    FS=     200
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CURSOR (KEV)=04.960           EDAX
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FIGURE 6.9 Electron microprobe analyses of residue.

6.5.2 Effect of Temperature and Reaction Time

In these set of experiments, 5g of ORIGINAL clay sample was leached with 100ml of 9M sulphuric acid at 60, 80, 120, and 145°C for 1, 2 and 3 hours. The solubility results are given in Table 6.3.

The results obtained showed that a target of 24-25% solubility was achieved when the sample leached with 9M sulphuric acid at 120° or 145°C. Under these reaction conditions complete extraction (11.5-13.6%) of aluminium from ORIGINAL clay sample was achieved.

6.5.3 Solubility of Clay Samples in 9M H_2SO_4

In these experiments, 5g of each clay sample was stirred with 100ml of 9M sulphuric acid at 120°C for 3 hours. The solution was filtered and the residue was dried in an oven for two hours and then weighed. The filtrate was diluted to 250ml with distilled water and analysed by AAS for Al. The results are given in Table 6.4.

6.5.4 Acid Consumption

In all the above experiments, sulphuric acid was used in excess of the theoretical requirement. In theory 20g of ORIGINAL clay sample needs 7.5ml of 98% sulphuric acid. However, experiments showed that it is very difficult to use the theoretical amount for the production of aluminium sulphate because of the presence of some impurities and difficulties in stirring a thick mass. In order to optimise the acid consumption the production of aluminium sulphate was carried out by two routes:

a) addition of acid to slurried sample followed by heating the mixture
b) addition of aliquots of clay to refluxing acid

Addition of acid to slurried sample and heating the mixture

Experiments were carried out by dropwise addition of acid to stirred slurried clay. The evolution of heat in the reaction raised the temperature to 80-100°C (depending on the acid volume) and after the complete addition of acid the slurry

TABLE 6.2 EFFECT OF ACID CONCENTRATION ON CLAY SOLUBILITY

Acid concentration (M)	% Soluble
2.0	5.7
4.5	18.4
9.0	25.5
13.5	14.8
18.0	3.6

TABLE 6.3 EFFECT OF TEMPERATURE AND REACTION TIME

Temperature (^{o}C)	Time (hr) 1	2	3
	% Soluble		
60	-	-	-
80	2.5	6.0	8.0
120	24.4	24.6	25.7
145	24.8	25.3	26.2

TABLE 6.4 SOLUBILITY OF CLAY SAMPLES IN 9M H_2SO_4

Sample	% Soluble	Al Extracted, (mg)
ORIGINAL	25.5	630
CRUDE 1	30.6	280
CRUDE 2	24.5	365
SDF	25.8	420

was refluxed at >120°C for 30-120 minutes. After the leach reaction, the solution was filtered off for aluminium sulphate recovery and the washed residue was dried in an oven and weighed. The results are given in Table 6.5. Results showed that all the aluminium could be extracted by leaching 5g of ORIGINAL clay with 50% H_2SO_4 at 120°C for 30 minutes. After treatment, the leachate was separated from the residue by filtration to leave a fine, slightly off-white, powder which was analysed as almost pure silica (particle size, -75 µm).

The amount of acid required to extract aluminum proved excessive so experiments were carried out to reduce the volume needed. It was found that the acid strength had to be no less than 33% otherwise the reaction temperature could not be maintained high enough to dissolve aluminium present. Vigorous stirring is required to ensure complete mixing of the viscous reaction mixture. Complete reaction has occurred when the silica residue is white and finally divided, an indication of an incomplete reaction was a grey and lumpy residue.

Addition of aliquots of clay to refluxing acid

Calculation shows that the theoretical amount of concentrated H_2SO_4 needed for 20g of kaolinite supplied is 7.5ml. Based on the earlier experiments, a target of 25-29% dissolution was found to correspond to total aluminium extraction. Experiments were carried out by adding 5g aliquot of ORIGINAL clay to refluxing acid at 10 minute intervals. The results of this series of experiments are given in Table 6.6.

The optimum conditions are 15ml acid and 15ml water per 30g kaolinite adding the powder in 5g portion at ten minute intervals to the refluxing acid with vigorous stirring. It may be necessary to add a little extra water with the last aliquot to maintain a fluid mixture. Assuming 60% pure kaolinite and 18M acid, about 3.4ml theoretical excess of acid is needed (23%) for the complete extraction of

TABLE 6.5 ADDITION OF ACID TO SLURRED SAMPLE AND HEATING

Test	Wt. of Kaolinite	Reaction Temp.(°C)	Reaction Time (h)	Acid Vol.	Water Vol.	% Dissolved
1	5	125	0.5	6.6	13.4	12.6
2	5	145	0.5	6.6	13.4	30.6
3	5	125	0.5	7.5	7.5	11.6
4	5	125	0.5	10.0	10.0	29.2
5	5	125	1.0	12.5	12.5	29.6
6	20	>120	18.0	7.5	20.0	5.7
7	20	>120	18.0	9.0	20.0	13.5
8	20	>120	2.0	15.0	15.0	12.9

TABLE 6.6 ADDITION OF CLAY TO REFLUXING SULPHURIC ACID IN 5g PORTIONS AT 10 MIN. INTERVALS.

Test	Wt. of Kaolinite	Reaction Temp.(°C)	Reaction Time (h)	Acid Vol.	Water Vol.	% Dissolved
1	20	>120	2	15	15	27.9
2	30	>120	2	15	15	24.7
3	40	>120	2	15	15	9.6
4	20	>120	2	15	15	27.8
5	30	>120	2	15	15	24.5
6	30	>120	4	15	15	29.9
7	40	>120	2	15	15	9.6
8	40	>120	4	15	15	23.4

aluminium. This can be neutralised by adding powdered alumina (which is easily dissolved) to the reaction mixture near the end of the refluxing period. Water must be added before the leachate can be decanted or filtered off and the aluminium sulphate crystallized out.

Preliminary analyses of aluminium sulphate on EDAX show that it contains Fe, Na, Mg, and Ti. Crystallization at low temperature gives a white product with a much lower iron content. The analyses (AAS) of 2.0360 g of air dried product in 500ml is given in Table 6.7. This product contains 60% water but drying at above 80°C for an hour reduced this figure to 30%. These figures correspond to 28 and 8 water molecules respectively (Figures 6.10 and 6.11). The solid residue was identified as α-quartz. The next sections of this chapter describe a process scheme for the removal of impurities from silica to produce a high quality material for high quality glass and electronic grade material use.

6.6 PURIFICATION OF QUARTZ

The manufacture of aluminium sulphate from clay produced residue which was almost pure α-quartz with some traces of Fe, Ti, Ca and very little Al. This α-quartz can be further purified for use in glass industry. The sand specifications for the glass manufacture are usually quite rigid to particle size distribution with special emphasis on the titanium and iron oxide contents and are specified in Table 6.8[15-18]. Most modern glass manufacturers prefer sand particles between -425 to +90µm with only low ppm levels of Fe(2-3), and Ti(1-2). The α-quartz residue, obtained as a result of clay treatment with sulphuric acid, has particle size -75µm. This fine residue is not acceptable in glass industry but can be used in ceramic production.

The natural quartz sample supplied for the purification study contained the same level of contamination as the α-quartz residue obtained in the previous section but had particles in the range of -25 to +12mm. Natural quartz is usually obtained from siliceous rock such as sandstone or

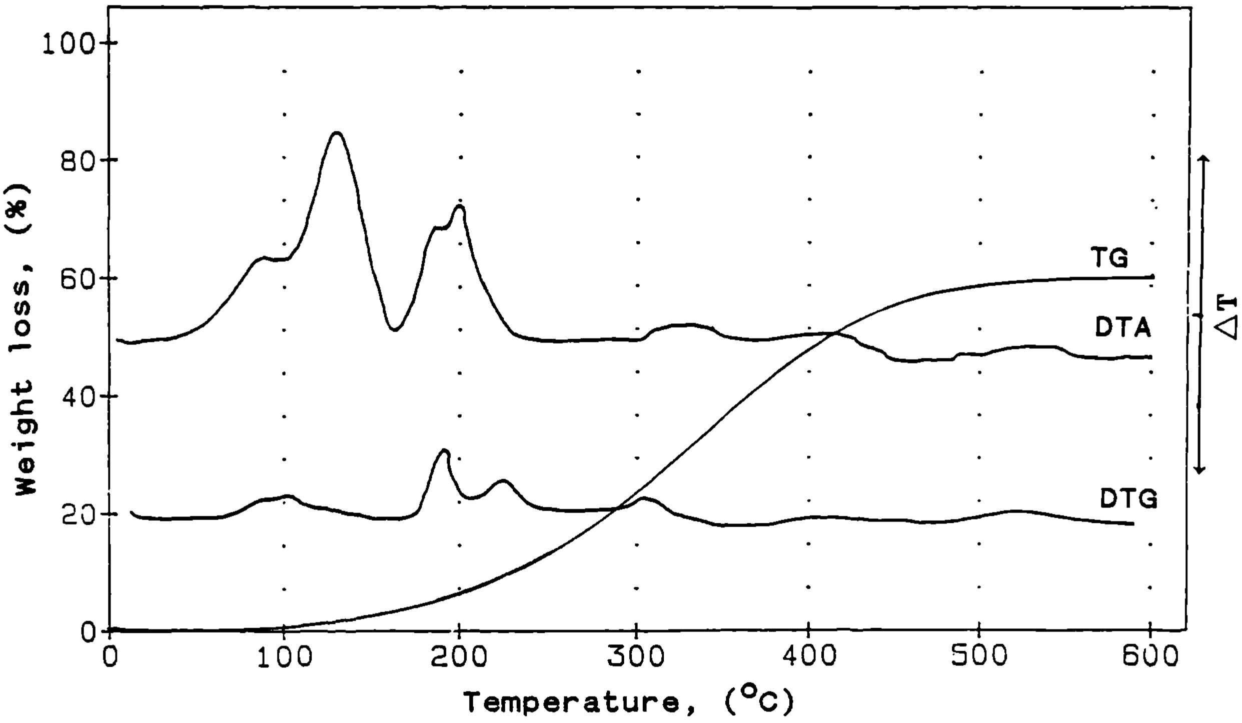


FIGURE 6.10 Thermogram of air dried product. (impure $Al_2(SO_4)_3$).

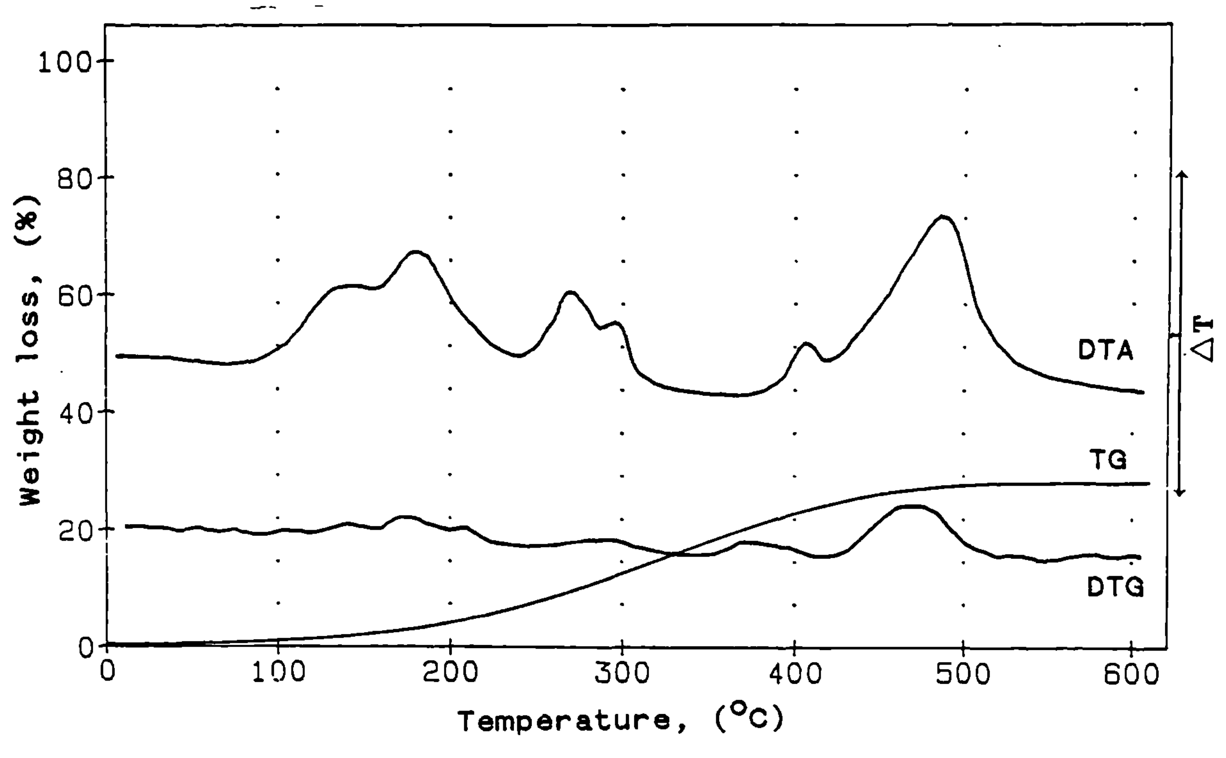


FIGURE 6.11 Thermogram of oven dried product. (impure $Al_2(SO_4)_3$).

TABLE 6.7 ANALYSIS OF ALUMINIUM SULPHATE PRODUCT

Concentration, (ppm)		
Fe	Na	Mg
22	4	3

TABLE 6.8 SPECIFICATIONS OF COMMERCIAL QUARTZ PRODUCTS

Composition and physical characteristics	Quartz sand			
	Foundry		Glass	
	(1)	(2)	(3)	(4)
Total SiO_2, %	95	99	97	99
Quartz, %	90	96	96	98
Al_2O_3, %	0.5		0.3	
K_2O+Na_2O, %	0.3		0.2	
Fe_2O_3, %	NS		0.3	0.03
Loss on ignition, %	0.2		0.5	0.2
Size	-425 +74um and AFS no. 45 to 55			
Shape	Spherical and semi-angular			

(1) Non-ferrous and (2) steel foundry sand; (3) coloured and (4) clear glass sand.

NS, no specifications; AFS no., American foundry Grains Fineness Number.

quartzite. In the natural state, most silica sands contain several iron-bearing minerals. These may occur as surface contaminants, as iron oxides in the form of surface stains or as deposits in the fissures of quartz particles. In any event, the iron contamination must be removed in order to render the quartz suitable for glass production otherwise brown or green product will result.

In addition to iron deposits on the quartz particles, most natural or untreated sands contain a relatively high proportion of heavy mineral particles such as sillimanite, rutile, ilmenite, staurolite, zircon, monazite and garnet. Through the application of cationic flotation, the heavy mineral content of silica sands can be substantially reduced.

The purification process described in this chapter consist of five main steps: a) calcination; b) crushing and milling; c) flotation to separate the sulphide, iron oxide, feldspar and mica minerals; d) magnetic separation to remove the liberated iron and other magnetic species; and e) the acid washing to dissolve the iron species and other impurities coated on the sand grains.

6.6.1 Calcination

The supplied sample has a particle size in the range of -25 to +12mm. As described in Section 6.2, when α-quartz is heated above 573°C, it transforms into β-quartz, which has a similar, but slightly distorted structure. When silica sand is heated above this temperature and quenched in cold water the expansion and contraction causes fracturing at grain boundaries and the quartz lumps become friable and crush easily with minimum formation of fines. Impurities at grain boundaries are either completely liberated or more easily freed by subsequent attrition or milling. A total of 50kg of raw sample, 800g in each batch, was calcined at 850-875°C for 20/25 minute in a fused quartz crucible in a muffle furnace and quenched in cold distilled water. The water was decanted and the calcined quartz kept damp to avoid dusting.

The calcined sample was marked Qz (quartz).

6.6.2 Crushing and Milling

The flowsheet of the crushing and milling process used in this study is given in Figure 6.12. The damp calcined quartz sample was crushed in a single toggle laboratory jaw crusher with closed setting of 2-2.5mm. Ouput was screened on 6 mesh and the oversize material returned to the crusher. The crushed sample was marked Qz-1. A sample of the crushed product was dried in an oven and then split into two parts for sieve analyses. The fractions obtained as a result of sieve analysis were marked Qz-2 to 12 and the percentage of each fraction is given in Table 6.9 and Figure 6.13. The results show that 50% of the crushed material was oversize (+425um).

The total yield of the crushed product was then wet screened on 425µm to derive an on-size, -425µm, and an oversize, +425µm, fractions. The output was:

+425µm = 26.044
-425µm = 25.556
Total = 51.600kg (damp weight)

The on-size material, -425µm, was then wet screened on 90µm with desliming by decantation to achieve the target size. The outturn was:

-425 +90µm = 20.667 (sample Qz-13)
-90µm = 4.074
Slime & loss (by diff.) = 0.815
Total = 25.556kg (damp weight)

The -90µm fraction was dried and weighed (3.177kg) and kept as fines.

The oversize material, +425µm, (26.044kg) was then milled in a roller mill using pure quartz pebbles as the grinding medium. The mill was charged with 2400g of oversize product

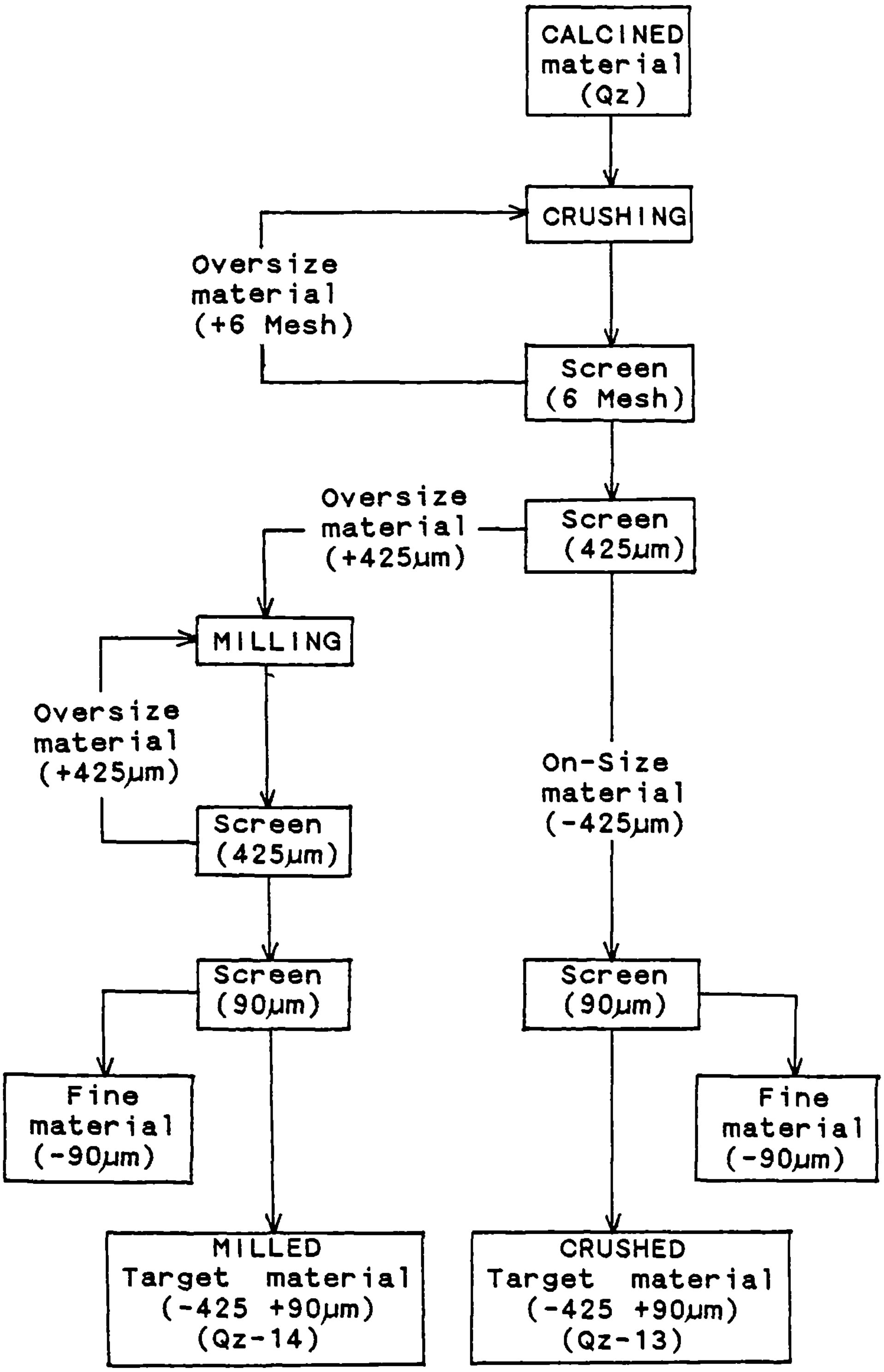


FIGURE 6.12 Schematic flowsheet of crushing and milling.

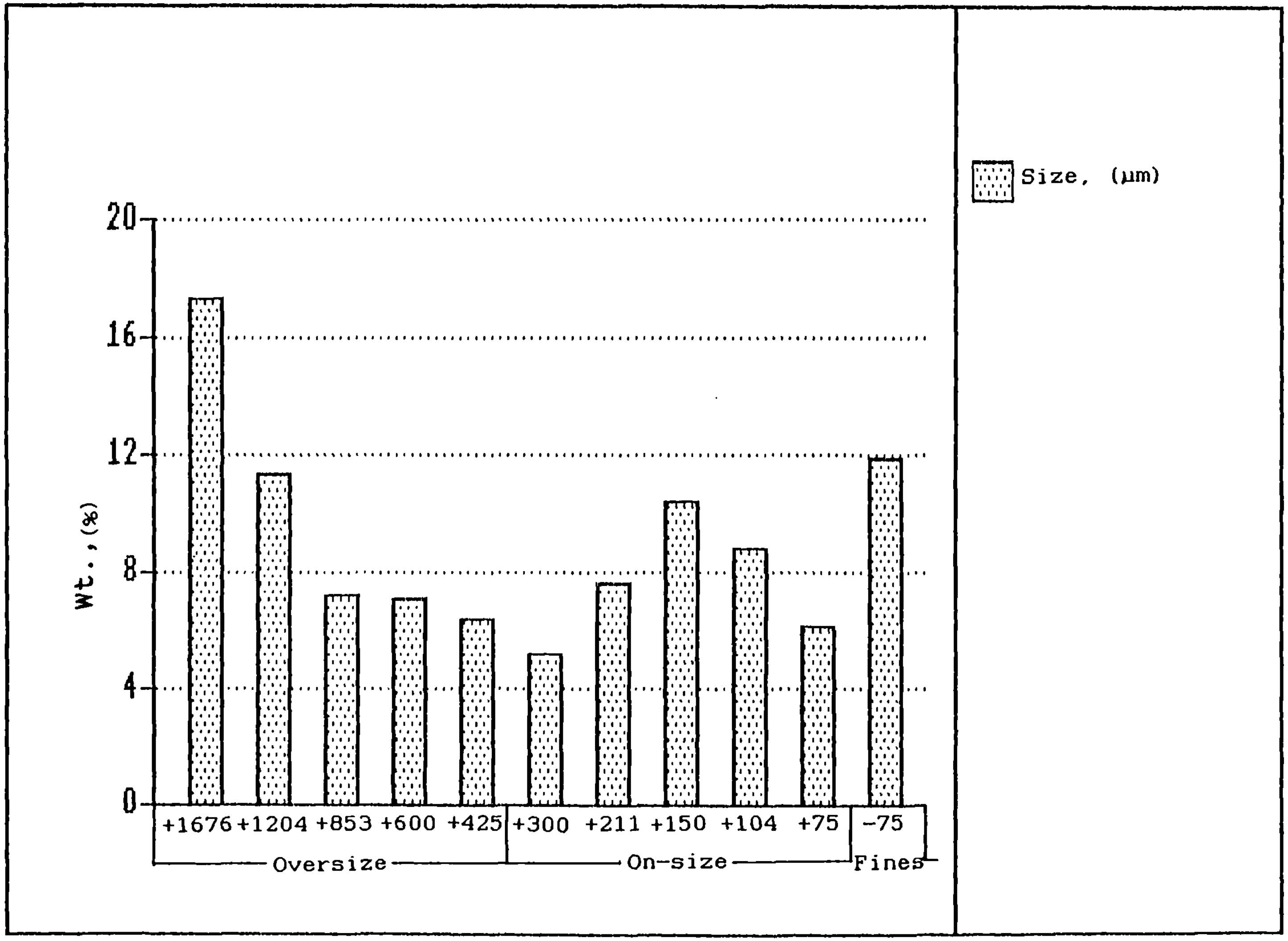


FIGURE 6.13 Sieve analysis of the crushed material.

along with 6250g of rounded quartz pebbles and one litre tap water. The milling was carried out at 52 rpm for 15 minutes. At the end of each batch the output was wet screened first on 600µm and then 425µm. The oversize product returned to milling. This procedure minimised the breakage of already liberated target size particles and prevents the production of excessive amount of very fine material. The on-size product (-425µm) was retained for further screening on 90µm. At the end of complete milling the outturn was:

+425µm = 0.750
-425µm = 23.557
Slime & loss (by diff.) = 1.737
Total = 26.044kg (damp weight)

The on-size material, -425µm, was then wet screened on 90µm with desliming by decantation to achieve the target size. The output was:

-425 +90µm = 20.709 (saple Qz-14)
-90µm = 2.405
slime & loss (by diff.) = 0.443
Total = 23.557kg (damp weight)

The -90µm fraction (fines) was dried and weighed (1.840kg).

a) Sieve analyses of target size material

200g (dried) of crushed and milled material was used for sieve analysis. The results are in Table 6.10.

b) Chemical analyses of crushed material

Quartz samples were sent to British Glass, Northumberland Road, Sheffield, U.K. for chemical analyses. The duplicate analyses of each sample were carried out and the average results are in Tables 6.11 and 6.12. The results obtained showed that impurity concentrations increases as the particles size decreases.

TABLE 6.9 SIEVE ANALYSES OF CRUSHED PRODUCT

		TEST 1 Total Wt. 239.8g		TEST 2 Total Wt. 233.9g		
Sample	Size(µm)	Wt.(g)	%	Wt.(g)	%	Average (%)
Qz-2	+1676	43.4	18.3	38.1	16.4	17.4
Qz-3	+1204	25.9	10.9	27.4	11.8	11.4
Qz-4	+853	15.7	6.6	17.9	7.7	7.2
Qz-5	+600	16.7	7.0	16.8	7.2	7.1
Qz-6	+425	15.4	6.5	15.2	6.5	6.5
Qz-7	+300	12.0	5.1	12.9	5.5	5.3
Qz-8	+211	18.3	7.7	17.7	7.6	7.6
Qz-9	+150	23.8	10.0	25.1	10.8	10.4
Qz-10	+104	22.1	9.3	20.1	8.6	8.9
Qz-11	+75	14.7	6.2	14.6	6.3	6.2
Qz-12	-75	29.1	12.3	26.7	11.5	11.9
Total		237.1	99.9	232.5	99.9	99.9

TABLE 6.10 SIEVE ANALYSES OF TARGET SIZE PRODUCT

	CRUSHED(Qz-13) Total Wt. 200.0g		MILLED(Qz-14) Total Wt. 200.0g			
Size(µm)	Wt.(g)	%	Wt.(g)	%	Aver.(%)	Cumul.(%)
-425 +300	20.1	10.0	17.4	8.7	9.4	9.4
-300 +211	43.3	21.7	38.4	19.2	20.4	29.8
-211 +150	56.3	28.2	57.9	28.9	28.5	58.3
-150 +104	47.8	23.9	50.1	25.1	24.5	82.2
-104 +75	26.2	13.1	28.2	14.1	13.6	96.4
-75	6.1	3.0	7.9	3.9	3.5	99.9
Total	199.8	99.9	199.9	99.9	99.9	

TABLE 6.11 CHEMICAL ANALYSES OF CRUSHED SAMPLE

	Concentration, (ppm)							
Sample	Al	Fe	Ti	Cr	Zr	Li	Na	K
Qz-2 to 6	72	9	8	<1	<1	<1	33	16
Qz-7 to 11	79	22	9	2	<1	<1	32	14

TABLE 6.12 ANALYSES OF EACH FRACTION OF ON-SIZE MATERIAL

	Concentration, (ppm)				
Element	Qz-7	Qz-8	Qz-9	Qz-10	Qz-11
Al	89	78	69	79	83
Fe	17	17	18	29	45

6.6.3 Flotation

Flotation is one of the most important processes used to separate unwanted mineral particles from quartz. The basic principle involved in froth flotation is the capturing of small mineral particles by bubbles and their collection in the form of a froth on the surface in the flotation cell. Flotation was carried out using a Wemco machine which provides vigorous agitation and aeration to the pulp in the flotation cell (Figure 6.14).

There are various chemical reagents which are added to the pulp to separate different minerals during froth flotation. These reagents are commonly known as collectors. The success of the flotation process depends upon the careful selection of the collectors. During the agitation and aeration of the pulp, containing suitable collectors, the air bubbles coming out of the pulp collect the mineral particles and carry them to the top of the separation cell, where they concentrate in a froth which overflows into a launder. The pure materials or tailing are recovered from the bottom of the flotation cell. This process separates mineral particles most efficiently when their particle size is between 10 and 500μm.

There are different types of collectors for sulphide and non-sulphide minerals[19]. Some of the most important sulphide and non-sulphide collectors, which can be used during the purification of quartz are given in Table 6.13. The process described in this chapter made use of both sulphide and non-sulphide collectors.

a) Flotation of Sulphide Minerals

All sulphide minerals are readily wetted by water and are said to be hydrophilic. The collector used in froth flotation process alters the mineral/water interface in such a manner as to reverse this position. Thus the coated minerals now prefers an environment of air rather than water and it is said to have become hydrophobic or aerophilic.

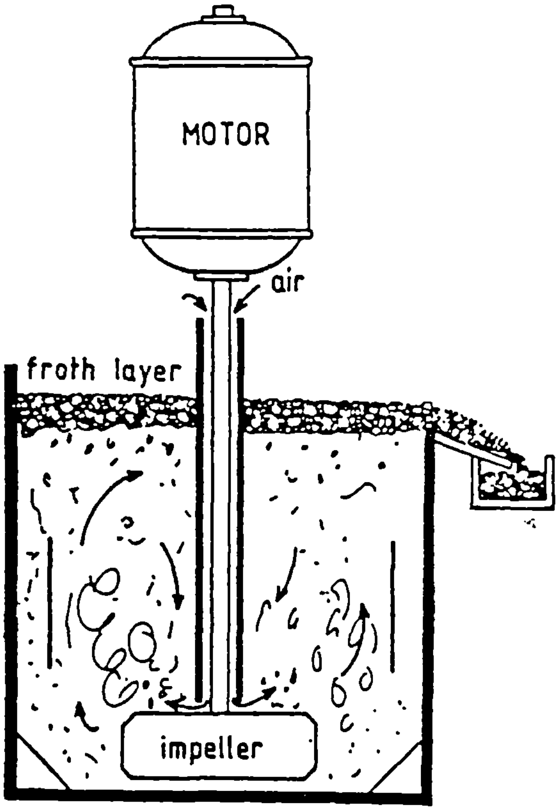
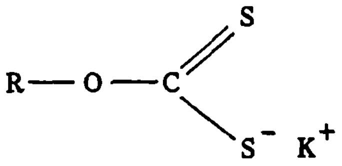
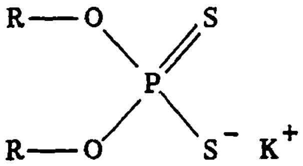
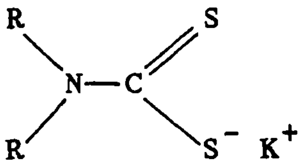
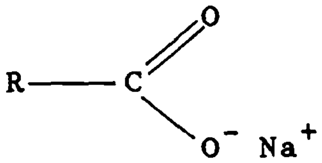
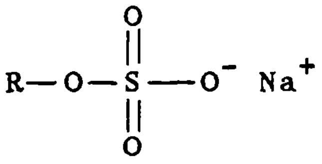
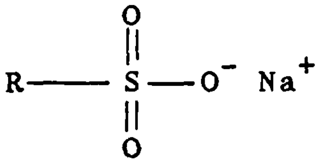
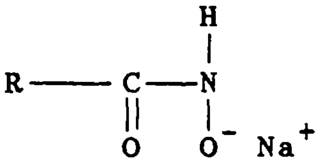


FIGURE 6.14 Schematic diagram of a flotation machine as used for separating minerals.

TABLE 6.13

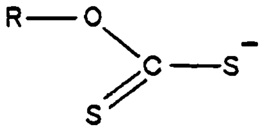
Structure formulae of sulphide and non-sulphide collectors

COLLECTOR	STRUCTURE
Sulphide flotation	
Xanthate	
Dithiophosphate	
Dithiocarbamate	
Non-sulphide flotation	
Carboxylate	
Sulphate	 $R{-}O{-}S(=O)_2{-}O^-\ Na^+$
Sulphonate	 $R{-}S(=O)_2{-}O^-\ Na^+$
Hydroxamate	 $R{-}C(=O){-}N(H){-}O^-\ Na^+$

The requirements of the collector are that part of the molecule is in itself hydrophobic, whilst part will interact selectively with mineral surfaces. This interaction may be purely a physical adsorption or a surface chemical reaction may take place, but commonly a combination of both processes is involved.

In the present investigation, potassium amyl xanthate was used for the flotation of sulphide mineral from quartz. The xanthates have a number of practical merits over dithiophosphates i.e. cheapness, water-solubility, superior selectivity and particularly the improved control they provide when use in conjunction with separate frothers, depressants and activators for differential flotation.

Potassium amyl xanthate ionizes in solution to produce negatively charged xanthate moiety:



This readily interacts with metal sulphide surfaces to give a hydrophobic coating, which is usually carried out during flotation.

b) Flotation of Non-sulphide Minerals

The successful flotation of non-sulphide minerals requires highly specific treatment conditions to achieve adequate selectivity and satisfactory flotation. The separation of non-sulphide minerals depends largely on arranging to get the minerals themselves differently charged by adjustment of pH. Every non-sulphide mineral has one particular pH at which the potential is zero because the density of positive sites is equal to the density of negative sites. This is the so-called p.z.c. (point of zero charge). The pH value corresponds to p.z.c. for different oxide minerals is given in Table 6.14[20].

TABLE 6.14 POINT OF ZERO CHARGE FOR DIFFERENT OXIDE MINERALS

Oxide	SiO_2	MnO_2	TiO_2	Fe_2O_3	Al_2O_3	MgO
pH of p.z.c.	2.5	4	5-6	5-8	7.5-9.1	12

Non-sulphide minerals are generally far more hydrophilic than sulphide minerals. As a consequence, they require a collector that has a proportionally longer hydrocarbon chain in the molecule. The majority of collectors for this type of mineral may be classified into two groups depending on whether they ionize in solution to give negatively or positively charged species and are known respectively as anionic and cationic collectors.

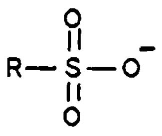
i) Anionic Collectors

This type of collector ionizes in solution to give a negatively charged hydrophobic part which reacts with the mineral surface, and a long hydrophobic tail interacts with the air bubbles in a froth flotation.

The anionic collector used in this work for the flotation of iron oxide minerals was a petroleum sulphonate which belonged to AERO 800 promoters series (AERO 840). Petroleum sulphonates have been used for many years as non-sulphide flotation collectors. Positively charged minerals can be floated with anionic collectors.

The standard 800 series reagents used by the glass industry are AERO 825 and 840 promoters. For this study, the AERO 840 promoter was chosen because it is much more selective than AERO 825, floating less good sand into the waste concentrate; moreover, it is also possible to eliminate the need for an auxiliary fatty acid collector.

AERO 840 ionizes in solution to produce a negatively charged moiety:



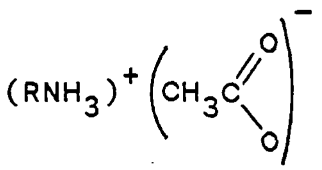
$$R-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O^-$$

This species reacts with positively charged mineral and the long hydrophobic tail rapidly interacts with air bubble in a froth flotation.

ii) Cationic Collectors

This type of collector ionizes in solution to give positively charged hydrophobic ions which react with negatively charged minerals which are carried out with the bubbles during froth flotation.

The cationic collector used in this study for the flotation of feldspar and mica was Tallow Amine Acetate (TAA) with the general formula:



$$(RNH_3)^+ (CH_3COO)^-$$

Where R is an alkyl group derived from Tallow fatty acid[22].

The flotation of feldspar depends upon pH because there is a difference in the values of the point of zero charge (pzc) between quartz and feldspar. Reported mean p.z.c. values are 1.5 for feldspar and 2.5 for quartz, so that with in this pH range it is possible to separate feldspar from quartz. In this work, the flotation of feldspar was carried out between pH 2.0 to 2.2. At this pH range the surface charge of feldspar is negative, since this pH range is above its p.z.c.; quartz now being below its p.z.c. is positively charged and thus unresponsive to cationic collectors.

c) Modifiers

Modifiers are simple chemical reagents which are added to the pulp to modify the response of different minerals to the flotation. A surface modifier that increases the hydrophilic character of a mineral is known as a depressant, and one which increases the hydrophobic character an activator. Some materials can act as either activators or depressants depending on the conditions under which they are used. For example, the fluoride ion behaves as a depressant when used in conjunction with anionic collectors but as an activator when used in conjunction with cationic collectors.

In this work, sodium hydroxide and sulphuric acid were used as modifiers for pH regulation. In the second flotation stage, HF was used as an activator to increase the hydrophobic character of feldspar and mica in conjunction with the cationic collector (TAA).

d) Frother

A frother is a chemical reagent which increases the frothing property to helps in separating unwanted impurities from the quartz product. During the flotation of sulphide and non-sulphide minerals, small quantities of 1% DOWFROTH 1012 were added during each stage. The schematic flowsheet of flotation process used is given in Figure 6.15.

e) Conditions and Reagents Concentration

The reagent concentrations used during flotation to remove the impurities from glass sand were as follow:

Sulphide collector:
Potassium amyl Xantahte = 10%
Non-sulphide collectors:
Sulphonate (AERO 840) = 10%
Tallow Amine Acetate (TAA) = 5%
Modifiers:
NaOH = 10%
H_2SO_4 = 10%
HF = 10%
Frother:
Dowfroth 1012 = 1%

Flotation was carried out batchwise, each batch consisted of 880g (damp weight) portion of target size product. Experiments were carried out by using crushed product (Qz-13), milled product (Qz-14), and 50/50 of crushed and

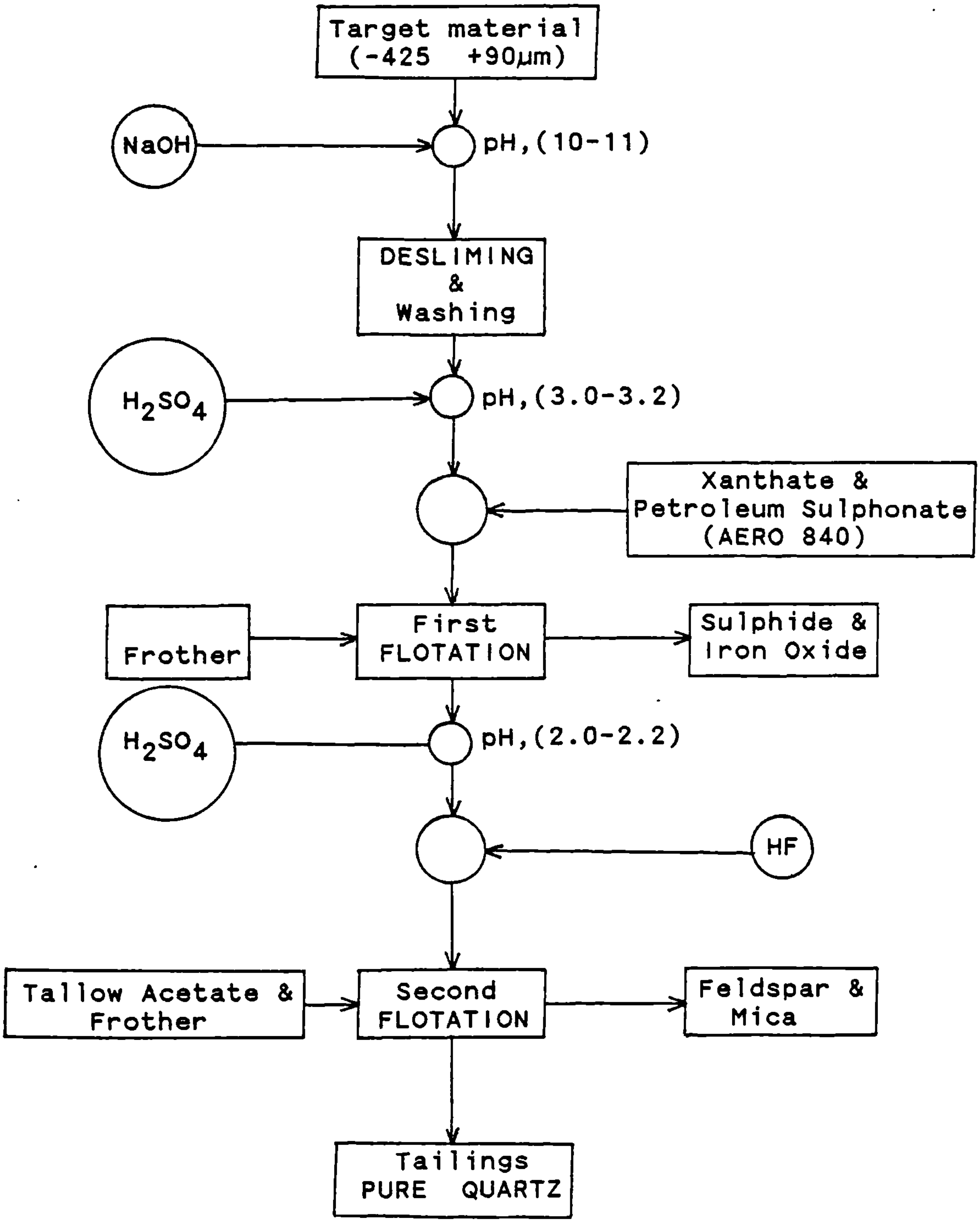


FIGURE 6.15 Schematic flowsheet of flotation process.

milled product (Qz-15). The procedure adopted for removal of impurities consists of three steps: i) desliming; ii) flotation of sulphide and iron oxide; and iii) flotation of alumino-silicate minerals (feldspar and mica). Each stage of flotation was preceded by dewatering step to obtain high solids for conditioning as well as to remove residual reagents and any slimes from the prior float. The remaining tailing was the "pure" silica product.

Desliming was carried out by treatment in the flotation cell for 10 minutes at pulp density of 70-75% solids and at pH 10-11. After desliming, the liquor was decanted off and the quartz washed with distilled water.

Following desliming and washing, the pulp was thickened to 70-75% solids and conditioned in the flotation cell at this density with 5ml of xanthate and 5ml of AERO 840 promoter at pH 3.0 for 5 minutes. Conditioning the pulp with sulphide and non-sulphide collectors in the presence of acid increases the collector selectivity and improves overall purification. Immediately following this step the pulp was reduced to 30-35% solid and 5ml of Dowfroth 1012 added and flotation continued for further 10-15 minutes. In order to ensure the complete flotation of impurity, 1ml of AERO 840 was then added and flotation was carried out for further 5 minutes. The liquid decanted off and the remaining quartz washed with distilled water. The first float was dried and weighed.

In last stage, the pulp was thickened once again to 70-75% solid and conditioned in the flotation cell at this density with 12ml of 10% HF at pH 2.0-2.2 for 5 minutes (10% sulphuric acid was used to adjust the pH in each case). After this stage, the pulp density was reduced to 30-35% solid and 8ml of Tallow amine acetate (TAA) and 3ml of DOWFROTH 1012 were added prior to flotation for a further 10-15 minutes. An extra 2ml of Tallow amine acetate was then added to maximize the separation of feldspar and other negatively charged minerals. The liquor was decanted off and the quartz product was washed with copious amounts of distilled water then filtered, dried, and weighed. The weights of first and second floats and the output of the "pure" quartz products are given in Table 6.15-6.17.

SIEVE AND CHEMICAL ANALYSES - 200g of first and second float and tailings (pure quartz) was used for sieve analyses. The results show that most of the fine particles were floated during the first flotation stage. The sieve and chemical analyses results are given in Tables 6.18-6.20 and 6.21 respectively.

6.6.4 Magnetic Separation

High gradient magnetic separation was carried out to remove the liberated magnetic particles present in the quartz product. Magnetic separation, like many other forms of physical separation, is based on a competition between a number of forces. The principles involved can be best explained by means of the diagram shown in Figure 6.16. A mixture of particles is fed into a separator, and the magnetic forces pull the magnetically susceptible components of the feed in one direction while the competing forces, (i.e. frictional, gravitational and inertial) pull all the other particles in another direction. The result is that the magnetic particles are separated from the non-magnetic ones, so that a magnetic concentrate is produced together with a non-magnetic component. The components are discharged through separate outlets and, in certain cases, a third outlet is also provided for an intermediate fraction. Due to the action of interparticle forces, there are always some non-magnetic particles in the magnetic component and some magnetic particles in the non magnetic component. When the magnetic compound has not been fully liberated before separation, the middle fraction would contain predominantly particles of intermediate effective magnetic properties and these particles would also be found, to lesser extent, in the magnetic and non magnetic fractions.

TABLE 6.15 FLOTATION RESULTS OF SAMPLE Qz-13

	First float	Second float	Product	
	Qz-16	Qz-17	Qz-18	Total
Batch	Dry Wt.(g)	Dry Wt.(g)	Dry Wt.(g)	Dry Wt.(g)
1	66.0	87.8	552	675.8
2	30.5	59.0	580	669.5
3	42.3	102.3	521	665.6
4	38.3	69.9	562	670.2
5	33.2	59.1	586	678.3
6	34.2	40.3	604	678.5
7	35.9	48.4	606	690.3
8	35.2	50.4	628	713.6
9	37.9	54.7	617	709.6
10	39.0	71.0	588	698.0
11	44.7	38.2	606	688.9
12	32.7	76.1	576	684.8
13	44.8	51.7	585	681.5
14	32.2	32.4	609	673.6
15	34.4	52.8	602	689.2
16	80.4	86.1	527	693.5
	661.7	980.2	9319	10960.9

TABLE 6.16 FLOTATION RESULTS OF SAMPLE Qz-14

	First float	Second float	Product	
	Qz-19	Qz-20	Qz-21	Total
Batch	Dry Wt.(g)	Dry Wt.(g)	Dry Wt.(g)	Dry Wt.(g)
1	27.2	30.9	612	670.1
2	56.3	47.8	557	661.1
3	22.7	56.7	578	657.4
4	28.9	69.7	554	652.6
5	18.2	109.1	522	649.3
6	27.4	79.6	576	683.0
7	26.9	107.3	547	681.2
8	53.4	110.1	517	680.5
9	20.4	95.9	584	700.3
10	27.9	137.7	512	677.6
11	27.2	96.8	541	665.0
12	24.1	143.1	495	662.2
13	19.2	78.6	569	666.8
14	20.5	92.1	562	674.6
15	43.7	62.1	570	675.8
16	28.0	68.6	588	684.6
17	20.1	74.8	416	510.9
	492.1	1460.9	9300	11253.0

TABLE 6.17 FLOTATION RESULTS OF SAMPLE Qz-15

	First float Qz-22	Second float Qz-23	Product Qz-24	Total
Batch	Dry Wt.(g)	Dry Wt.(g)	Dry Wt.(g)	Dry Wt.(g)
1	8.7	54.1	647	709.8
2	20.3	52.5	643	715.5
3	52.5	72.1	571	695.6
4	21.6	98.6	589	709.5
5	34.1	66.5	609	709.6
6	37.2	79.2	584	700.4
7	24.7	68.0	582	674.7
8	26.1	119.0	523	668.1
9	32.8	96.7	541	670.5
10	32.9	84.1	557	674.0
11	48.4	130.5	491	669.9
12	28.8	114.9	539	682.7
	368.1	1036.2	6876	8280.3

TABLE 6.18 SIEVE ANALYSES OF FLOATS AND PRODUCT OF Qz-13

Size	First float (Qz-16)		Second float (Qz-17)		Product (Qz-18)	
(μm)	Wt.(g)	%	Wt.(g)	%	Wt.(g)	%
-425 +300	5.9	2.9	9.4	4.7	19.2	9.6
-300 +211	14.3	7.2	28.5	14.3	39.6	19.8
-211 +150	38.5	19.2	58.0	29.0	55.0	27.5
-150 +104	63.6	31.8	57.6	28.8	57.8	28.9
-104 +75	64.7	32.3	38.9	19.5	25.6	12.8
-75	12.8	6.4	7.5	3.7	4.6	2.3

TABLE 6.19 SIEVE ANALYSES OF FLOATS AND PRODUCT OF Qz-14

Size	First float (Qz-19)		Second float (Qz-20)		Product (Qz-21)	
(μm)	Wt.(g)	%	Wt.(g)	%	Wt.(g)	%
-425 +300	4.2	2.1	4.8	2.4	17.2	8.6
-300 +211	11.0	5.5	15.9	8.0	41.1	20.5
-211 +150	32.6	16.2	44.2	22.1	58.0	29.0
-150 +104	55.4	27.7	55.8	27.9	54.4	27.2
-104 +75	73.8	36.9	59.9	30.0	24.3	12.2
-75	22.0	11.0	18.4	9.2	4.8	2.4

TABLE 6.20 SIEVE ANALYSES OF FLOATS AND PRODUCT OF Qz-15

Size	First float (Qz-22)		Second float (Qz-23)		Product (Qz-24)	
(μm)	Wt.(g)	%	Wt.(g)	%	Wt.(g)	%
-425 +300	2.5	1.3	3.3	1.7	16.4	8.2
-300 +211	5.1	2.5	13.3	6.5	38.4	19.2
-211 +150	22.3	11.2	41.7	20.9	57.8	28.9
-150 +104	58.8	29.4	69.3	34.7	54.2	27.1
-104 +75	90.1	45.0	57.7	28.8	27.2	13.6
-75	20.7	10.4	14.5	7.3	5.8	2.9

TABLE 6.21 ANALYSES OF QUARTZ PRODUCT AFTER FLOTATION

	Concentration, (ppm)							
Sample	Al	Fe	Ti	Cr	Zr	Li	Na	K
Qz-21	58	3	2	2	-	<1	23	8

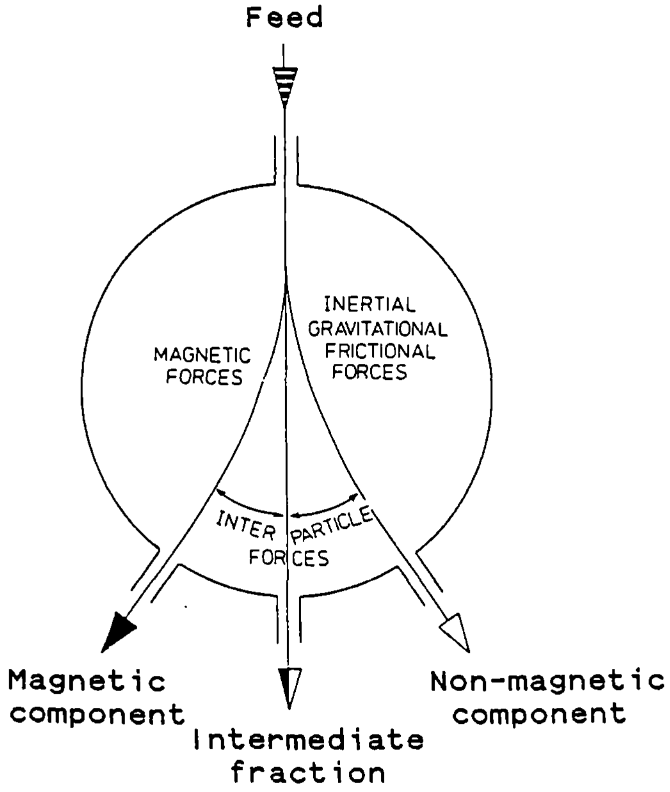


FIGURE 6.16 The principle of magnetic separator.

Magnetic separation was carried out at Cryogenics Ltd., Acton, London, U.K. After flotation, the quartz products, Qz-18, Qz-21, and Qz-24 were subjected to magnetic separation using the high gradient magnetic separator (HGMS). The current rate was set for maximum separation of the magnetic species. The product was analysed and the results are given in Table 6.22. The results obtained showed that the concentration of metal impurities before and after magnetic separation were same, presumably because the magnetic species adhere on the quartz grains.

TABLE 6.22 ANALYSES OF QUARTZ PRODUCT (MAGNETIC SEPARATION)

	Concentration, (ppm)							
Sample	Al	Fe	Ti	Cr	Zr	Li	Na	K
Qz-26	58	2	2	2	-	<1	22	7

6.6.5 Acid Washing

The iron impurities not separated magnetically were, however, removed by acid washing in HCl-HF solutions. Acid washing was carried out in a heavy duty 600ml plastic beaker on a water bath at 60-80°C for 30 to 60 minutes. This step removes any remaining acid soluble impurities still to give pure quartz ready for the glass industry. Mixing was carried out with plastic coated stainless steel overhead stirrer. The stirring rate was same for each batch.

In these experiments, 200g portions of the quartz samples were taken into four separate plastic beakers. Each beaker was charged with a total of 200-300ml mixture of HF and HCl solution. After acid washing, the acid was decanted off and the products were washed thoroughly with distilled water until the decanted liquid was free of chloride. The products were then filtered and re-washed with distilled water dried, and weighed. The average acid washed product output is given in Table 6.23. The chemical analysis of the acid washed sample showed very low concentration of iron and titanium and was suitable for use in glass manufacture (Table 6.24).

6.7 CONCLUSIONS

In this chapter, the first part includes the production of aluminium sulphate by the direct reaction of clay with sulphuric acid. Different variables, for example, acid concentration, leaching temperature, and reaction time were also studied. Two routes used in order to optimise the reaction conditions were, (1) addition of acid to the slurried clay and (2) addition of clay in 5g portions to the refluxing acid after a 10 minute interval.

The results obtained from first route indicated that the acid strength had to be no less than 33% otherwise the reaction temperature could not be maintained high enough to dissolve aluminum - containing component. According to the second route, the optimum reaction conditions are 15ml sulphuric acid and 15ml water per 30g of ORIGINAL clay (23% stochiometry) adding the powder in 5g portions at ten minute intervals to the refluxing acid with vigorous stirring. Under these reaction conditions a complete extraction of aluminium was obtained. The aluminium sulphate crystals contained 60% water but drying at 80°C for an hour reduced water contents to 30%. The largest impurity in the dried product was iron but careful crystallisation at low temperature gives a white product with much lower iron content. The residue obtained as a result of the clay treatment was α-quartz with a particle size -75μm, too fine for use in glass manufacture, the glass industry prefered particle size is -425 +90μm, but can be used in cement and ceramic industry.

In second part, The purification of quartz for the use where high purity is required by industry was carried out on a separate supplied sample. The main object of this work was to develop technically feasible, economic and safe process to produce high purity quartz. The schematic arrangement of principal processes and products are shown in Figure 6.17. Glass industry specifications for high purity solids for optical glass are for example quite rigid and to comply these requirements a purification process was carried out in

TABLE 6.23 ACID WASH OUTPUT

Unwashed sample	Acid Con. HF+HCl(%)	Acid Vol. (ml)	Temp. (°C)	Time (min)	Washed (g)	Recovery (%)
Qz-26	15 + 10	300	80	30	172.9	86.5
Qz-25	15 + 10	200	80	30	176.9	88.5
Qz-26	15 + 10	200	80	30	177.1	88.6
Qz-26	15 + 15	200	60	60	182.4	91.2

TABLE 6.24 ANALYSES OF QUARTZ PRODUCT AFTER ACID WASHING

	Concentration, (ppm)							
Sample	Al	Fe	Ti	Cr	Zr	Li	Na	K
Qz-28	25	<1	2	<1	-	-	18	5

TABLE 6.25 TOTAL OUTPUT MATERIALS AFTER CRUSHING AND MILLING

Material	Damp Wt. (kg)	(%)	
Target size: (-425 +90μm)			
CRUSHED	20.667	40.0	80.1
MILLED	20.709	40.1	
Fines: (-90μm)			
CRUSHED	4.074	7.9	12.6
MILLED	2.405	4.7	
Loss:			
CRUSHED	0.815	1.6	5.6
MILLED	2.180	4.2	
Oversize: (+425μm)	0.750	1.5	1.5
Total	51.600	100.0	100.0

TABLE 6.26 CHEMICAL ANALYSES OF QUARTZ AFTER EACH STAGE

		Concentration, (ppm)							
Stage	Sample	Al	Fe	Ti	Cr	Zr	Li	Na	K
Milling	Qz-14	79	22	9	2	<1	<1	32	14
Flotation	Qz-21	58	3	2	2	-	<1	23	8
Magnetic sep.	Qz-26	58	2	2	2	-	<1	23	7
Acid Washing	Qz-28	25	<1	2	<1	-	-	18	5

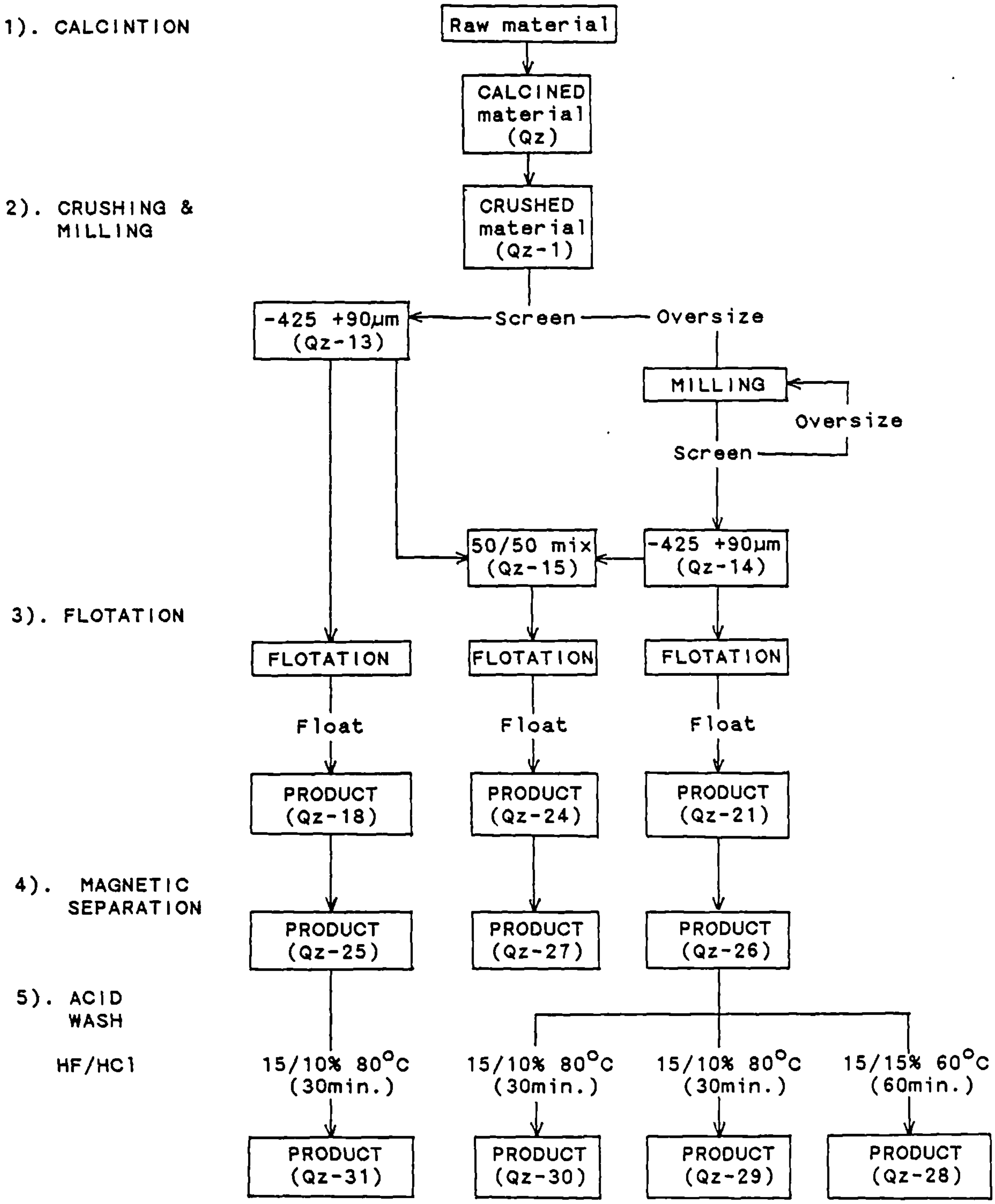


FIGURE 6.17 Schematic arrangement of principal processes and products.

TABLE 6.27 MATERIAL BALANCE AND INVENTORY OF STOCK

Description & sample No	IN	Retained for Reference	OUT Wastage	Sieve test & assay	Product Stock
RAW FEED	50 Kg	1.6			
CALCINED					
Qz			1.0		
CRUSHED			3.4		
Qz-1		0.945		0.474	
SCREENED					
Qz-13 (-425 +90um)		0.622		0.250	
(-90um)		3.177			
MILLED & SCREENED					
Qz-14 (-425 +90um)		0.168		0.250	
(+425um)		0.750			
(-90um)		1.840			
FLOTATION					
(Qz-13)					
1st Float (Qz-16)		0.368		0.200	
2nd Float (Qz-17)		1.024			
Product (Qz-18)		0.530		0.250	
(Qz-14)					
1st Float (Qz-19)		0.492		0.150	
2nd Float (Qz-20)		1.480		0.200	
Product (Qz-21)		0.205		0.050	
(Qz-15)					
1st Float (Qz-22)		0.801			
2nd Float (Qz-23)		1.228			
Product (Qz-24)		0.150			
MAGNETIC SEPARATION		0.158			
Qz-25				0.200	6.260
Qz-26				0.080	4.571
Qz-27				0.120	6.497
ACID WASH					
Qz-28				0.120	0.575
Qz-29					0.602
Qz-30				0.120	2.017
Qz-31				0.120	1.929
TOTAL		15.541	4.4	2.584	22.451
TOTAL ACCOUNTED					44.976
UNACCOUNTED LOSS					5.024
					50.0 Kg

five stages: (1) clacination; (2) crushing and milling; (3) flotation; (4) magnetic separation; and (5) acid washing.

After calcination, 50 kg sample was crushed to produce target size material (-425 +90um) by successive screening. Examination of the crushed product indicated that quartz lumps were reduced to grain size without excessive fracturing of grains and production of waste fines. The sieve analyses of the crushed product showed that bulk of the material was in +425µm range. The oversize material was milled, using quartz pebbles as a grinding medium in a rollar mill, to produce the target size material. The overall recovery of target size material after crushing and milling process was 80% (Table 6.25).

The removal of impurities from target size material was carried out by flotation using sulphide and non-sulphide collectors together with frother at different pH values. For the separation of sulphide and iron oxide minerals potassium amyl xanthate and petroleum sulphonate was used. The results show that both collectors responded well and reduced iron impurities to very low level (few ppm). The collector used for the separation of feldspar was Tallow Amine Acetate. This collector also removed some fine quartz particles during froth flotation.

The results of High Gradient Magnetic Separation show that there is little difference between the iron content of the quartz before and after magnetic separation. This indicates that the iron impurities are not liberated but adhere to the sand grains. Acid washing step was, therefore, carried out to remove these iron impurities. In each case, the level of iron impurities was reduced after acid washing using a mixture of HF and HCl. The recovery of acid washed product depends upon; a) acid concentration; b) acid volume; and c) washing temperature. When 200 and 300ml mixture of HF and HCl (15/10%) was used at 80°C for 30 minutes the recovery of quartz was 88 and 86% respectively. The recovery level was increased to 90% by decreasing the temperature to 60°C. The chemical analyses of the quartz products after each purification stage are in Table 6.26. The results show that the magnetic stage can be omitted. The acid washed product contains very low concentration of iron and titanium and is suitable for use in the optical glass industry. (The material balance and inventory of stock is given in Table 6.27).

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