

**CRANFIELD UNIVERSITY**

**SCHOOL OF INDUSTRIAL AND MANUFACTURING  
SCIENCE**

Department of Advanced Materials

**PhD THESIS**

Academic Year 1998/9

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**MEASUREMENT AND REDUCTION OF THE  
ENVIRONMENTAL IMPACT OF INDUSTRIAL  
PHOTOCHEMICAL MACHINING**

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October 1998

This thesis is submitted in fulfilment of the requirements for the  
degree of Doctor of Philosophy

## **Abstract**

This thesis concerns research into the environmental aspects of the photochemical machining (PCM) industry, involving measurement, analysis, benchmarking, and reducing adverse environmental impacts.

The environmental audit of a PCM company found that the likely significant environmental impacts are the use of ferric chloride etchant, solvents and water. A comparison of the environmental performance of two UK PCM companies showed that there were big contrasts in etchant utilisation and solvent and water consumption, indicating that steps could be taken to reduce these impacts.

A study to assess the feasibility of using laser direct imaging (LDI), a cleaner technology in photoresist imaging, found that LDI could meet the technical requirements of the PCM industry. For LDI to be economically feasible, the reliability has to be high and maintenance cost has to be low.

Audit surveys of PCM companies world-wide regarding etchant utilisation and solvent consumption indicated that:

- (1) There is a vast difference between the performance of companies and companies that regenerate etchants were more efficient in their  $\text{FeCl}_3$  utilisation. The industrial best practice for  $\text{FeCl}_3$  utilisation is 837%.
- (2) Chlorination was the most popular regeneration method but most companies would use a more environment-friendly system at a higher overall cost. Regarding waste disposal, most companies sent liquid waste etchant for reclaim or recycle.
- (3) Half of the PCM companies no longer use solvents, and with the development of liquid aqueous-based resists, it is envisaged that PCM practitioners could eliminate the use of solvents in the near future.

Lastly, an investigation into the feasibility of using oxygen gas in regenerating  $\text{FeCl}_3$  showed that the regenerated etchant could produce good quality etchings. This system is also the second cheapest. Therefore, it is a good option for the PCM companies as the cost of regeneration is not too expensive and it is environment-friendly.

## **Acknowledgements**

I wish to express my highest appreciation to the Government of Malaysia and SIRIM Bhd. (Malaysia) for the sponsorship and support throughout my research at Cranfield. I am also indebted to Professor David M. Allen for his supervision, guidance, help and support.

This research has received a great deal of support from many external parties. Special thanks to Mr Paul Cane, the Managing Director of *Tecan Components Ltd.*, and his staff for the use of the equipment on oxygen regeneration experiment, assistance, support and the hospitality extended during my trips to the company. I also wish to thank *Company E and Company F* for providing information during the data collection exercise, and the members of the Photo Chemical Machining Institute (PCMI) for providing various information and data during the course of the research.

I would like also to express my gratitude to all colleagues and fellow students at Cranfield who are from the various parts of the world for the help and assistance in carrying out my work.

To my family, all my Love. Thank you for the patience and constant encouragement.

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## **Symbols**

[ $a_{\text{ferric ion}}$ ] – Activity of oxidizing ion (ferric ion)

[ $a_{\text{ferrous ion}}$ ] – Activity of reducing ion (ferrous ion)

bar – Measurement of pressure, 1 bar =  $10^5$  N/m<sup>2</sup>

<sup>0</sup>Bé – Baumé, the measurement of the concentration of fresh ferric chloride in terms of specific gravity

C – Coulomb, the unit of electric charge

E – ORP (oxidation reduction potential) of a system

$E^0$  – Standard electrode potential, in volts

F – Faraday constant

K – Kelvin, the measurement of absolute temperature

kg – Kilogramme

KWh – Kilowatt hour

l – Litre

l/m<sup>2</sup> – Litre per metre square

m<sup>2</sup> – Square metre

m<sup>3</sup> – Cubic metre

ml – Millilitre

mV – Millivolt

M – Molarity or moles/litre

n – Number of electrons change in the Redox reaction

R – Gas Constant

Ra – Measurement of surface roughness in  $\mu\text{m}$

R<sup>x</sup> – x times of regeneration

T – Temperature

V – Volts

$\mu\text{m}$  – Micron or one millionth of a metre

% - Percentage

## Chemical Symbols

Al – Aluminium metal

Co – Cobalt metal

CO<sub>2</sub> – Carbon Dioxide

Cr – Chromium ion

Cu – Copper metal

Cu<sup>2+</sup> – Cupric ion

Fe – Ferrous metal or iron

FeCl<sub>2</sub> – Ferrous Chloride

FeCl<sub>3</sub> – Ferric Chloride

Fe<sup>2+</sup> – Ferrous ion

Fe<sup>3+</sup> – Ferric ion

H<sub>2</sub>O – Water

HCl – Hydrochloric Acid

Ni – Nickel metal

Ni<sup>2+</sup> – Nickel ion

NO<sub>x</sub> – Oxides of nitrogen

O<sub>2</sub> – Oxygen gas

pH – Acidity

Sn – Tin metal

SO<sub>2</sub> – Sulphur Dioxide

Zn – Zinc metal

Zn<sup>2+</sup> – Zinc ion

## **Acronyms and Abbreviations**

ABC – Activity Based Costing

APC – Air Pollution Control

BATNEEC – Best Available Techniques Not Entailing Excessive Cost

BPEO – Best Practical Environmental Option

BPM – Best Practicable Means

BSI – British Standards Institution

CAD – Computer Aided Design

CAM – Computer Aided Manufacturing

CNC – Computer Numerical Control

COSHH – Control of Substances Hazardous to Health

EA – Environment Agency

EC – European Community

EMAS – Eco-Management Audit Scheme

EMS – Environmental management System

ENDS – Environmental Data Services

EPA – Environmental Protection Agency

ETBPP – Environmental Technology Best Practice Programme

EU – European Union

IEM – Institute of Environmental Management

ISO – International Organization for Standardization

IPC – Integrated Pollution Control

LDI – Laser Direct Imaging

NGO – Non-governmental Organisation

OECD – Organisation for Economic Co-operation and Development

PCB – Printed Circuit Boards

PCM – Photochemical machining

QMS – Quality Management System

SEA – Single European Act



## **Acronyms and Abbreviations** *(continue)*

TCA – Total Cost Assessment

UK – United Kingdom

UN – United Nations

UNCED – United Nations Conference on Environment and Development

US – United States

UV – Ultra Violet

VOC – Volatile organic compound

## **Chapter 1**

# **General Introduction**

### **1.1 Introduction**

Scientific and engineering advances in the 19th and 20th centuries pose new demands and challenges to the materials processing industry. The advancements have resulted in the development of high strength, heat resistant materials which are harder, tougher and stronger [Snoeys *et al*, 1986]. In addition, these advanced materials often have to be cut to a geometrically complex shape and high precision to meet the requirements of the intended use [McGeough, 1988; Taniguchi, 1983].

As a result of these developments, traditional machining processes such as turning, milling, drilling, grinding etc. are either uneconomical in processing these advanced materials due to the very slow rate of machining [De Barr and Olivier, 1968] or no longer adequate to meet the manufacturing requirements of the advanced materials as these processes have reached their capability limits [McGeough, 1988; Rajurkar *et al*, 1992]. To overcome the limitations of the tradition machining processes, the ensuing result is the development of new manufacturing processes known as non-traditional machining processes, where extensive research is being carried out to develop new manufacturing methods and improve existing techniques which are capable of economically fabricating advanced materials [Rajurkar *et al*, 1992; Springborn, 1967].

The development of manufacturing technologies has also created some unexpected problems. One of the most important considerations is the adverse environment effects generated by the non-traditional machining processes as the manufacturing methods are rather different from the traditional machining processes.

In the past, it was possible to use land, air and water as media for dumping waste and treat the earth as a natural 'sink'. However, the continuing ability of the environment to supply raw materials and absorb waste products generated and at the same time maintain bio-diversity and a quality of life is being increasingly threatened. This has resulted in public awareness and concern for the natural environment that began more than a quarter of a century ago.

The trend of national surveys conducted in the United States (US) between 1965 and 1970 indicated a dramatic increase in public concern regarding environmental quality. Although this trend showed ups and downs in the next two decades, generally public awareness remained extremely high, even higher than two decades ago [Dunlap, 1991]. Strong and developing awareness to the cause and effects of environmental damage has put increasing pressure on commercial and, in particular, manufacturing and industrial organizations to improve their environmental standards. In addition, the soaring costs of treatment and disposal of industrial waste, increasing scarcity of landfill sites and promulgation of new, and tightening of, environmental legislation have forced both the manufacturing industries and research centres to find effective solutions to reduce the adverse environmental effects of manufacturing technologies through 'development of environmentally self-contained processes which generate a non-toxic waste stream' [Rajurkar, 1994].

## 1.2 Photochemical machining

Photochemical machining (PCM) is a typical non-traditional machining method that employs photoresist and chemical etching techniques. PCM, which is sometimes called photoetching, photofabrication or photochemical milling, is especially economical for the production of thin, flat, complex metal parts in comparison with the rival processes of precision stamping, wire electrodischarge machining and laser beam machining [Allen, 1986b; Allen *et al.*, 1989].

The metal to be etched is first cleaned and coated with a layer of photoresist. The resist is then selectively removed through the action of masking ultraviolet radiation by phototooling. Etching of parts is achieved by dissolving the surface of the metal showing through apertures in the resist stencil. The most commonly used etching chemical is an aqueous solution of ferric chloride ( $\text{FeCl}_3$ ), used at a temperature of over  $50^\circ\text{C}$ .

Advantages of PCM processing [Allen, 1986b] are:

- The finished products are burr-free thus no further treatment is required.
- Chemical and physical properties of the parts remain unchanged by the process (there is no heat-affected zone at the cut edges as with laser-cutting or problems such as loss of magnetic permeability or stress caused by stamping).
- Low tooling cost and short lead times make the machining process excellent for small and medium production and prototyping.
- Excellent for production of complex shapes (e.g. lead frames) and the only manufacturing method for components of extreme complexity (e.g. colour TV receiver tube aperture masks)

- Wide range of materials can be machined (although PCM is often used for metal components, non-metallic materials such as glass and ceramics can also be machined in the same way).

### 1.3 History of Photochemical Machining

Etching of metals was a well-known machining method in ancient Egypt. The Egyptians used organic acid for the etching of metals [Harris, 1974]. This machining process was widely used for producing decorative items until the 19th century. The development of photography provided a new dimension to chemical machining and in 1826 J.N. Niepce was the first to use a photoresist made from bitumen of Judea asphalt for etching pewter. In mid 1950s, Kodak successfully marketed a type of photoresist name KPR and the development of further photoresists followed. These developments, together with the efforts of equipment manufacturers, converted PCM into an advanced non-traditional machining process which found wide applications in industry world-wide [Allen, 1986a]. Over the past 30 years, PCM use has grown considerably in the field of electronics (particularly in the production of printed circuit boards and lead frames for mounting integrated circuits), precision engineering and decorative industries. Almost all the commonly used metals and alloys are suitable for PCM and the process has no effect on the physical and chemical properties of the material.

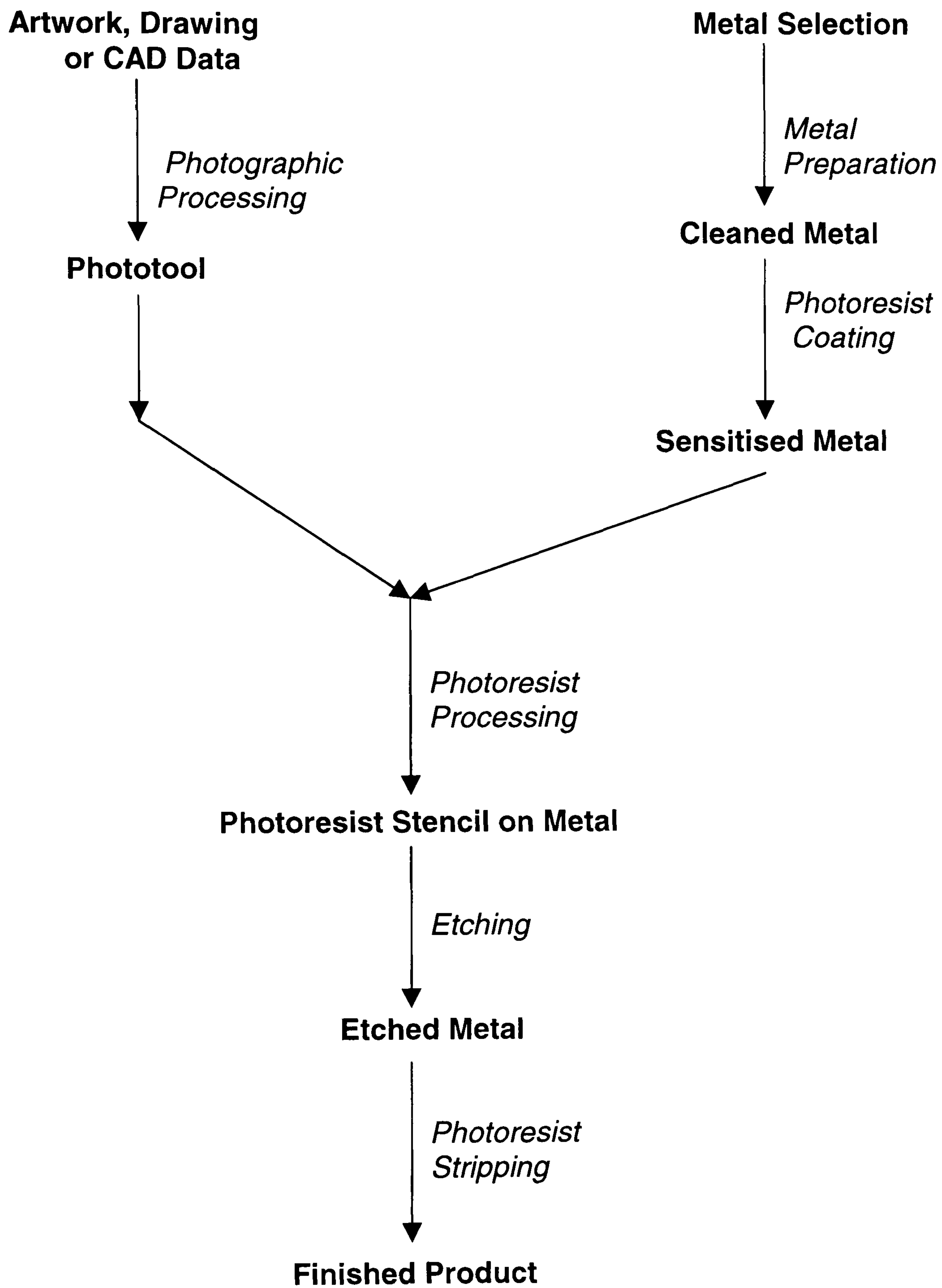
### 1.4 Environmental Impacts of PCM Process

The environmental impacts of the PCM process can be appreciable in view of the nature of the industry whereby various chemicals are used in the preparation and cleaning of metal surfaces, photographic processing of phototooling, coating and selective removal (development) of photoresists, etching through apertures in the resist stencils and finally, stripping of resist after etching [Allen, 1993]. The PCM process can be summarised in *Figure 1*.

#### 1.4.1 Metal preparation

Metal foils and sheets for PCM are formed by rolling with an organic lubricant. During the rolling process, high temperature and pressure cause metal oxides on the surface to react with and form organo-metallic substances [Sedlak, 1997]. The other surface contaminants include dirt, wax, grease, oil, in transit corrosion preventive additives and surface oxides [Abate, 1997].

The purpose of metal preparation is to produce a clean metal surface suitable for obtaining good adhesion with photoresist. Thus all unwanted foreign materials on the surface of the metal substrates have to be removed. Metal preparation and cleaning may involve the techniques below:



**Figure 1.1: Current PCM process**

- Conversion coating
- Pre-etching or microetching
- Chemical cleaning
- Physical cleaning by abrasion of the metal surface.

Of the above, chemical cleaning and pre-etching are the most commonly used methods for PCM companies. Chemical cleaning involves the use of volatile organic compounds (VOCs), some of which are chlorinated hydrocarbons, and proprietary biodegradable aqueous solutions which are either acidic or alkaline-based [Gifford, 1989; Abate, 1997]. Pre-etching is carried out using conventional PCM etchants or special formulations where the etching rate is relatively slow. The process is carried out when photoresist adhesion has to be exceptionally good. The drawback is that matt, non-reflective surfaces are produced which may be cosmetically or functionally undesirable. The use of cleaning chemicals, especially solvents and VOCs, and etching solutions cause adverse effects to the environment.

#### 1.4.2 Image production

PCM uses many methods to produce images in the photoresist which include:

- Production of phototools from master artwork
- Production of phototools from computer-aided-design (CAD) data and
- Direct imaging of photoresist from CAD data.

The first two methods above involve the use of phototools for the imaging of photoresist. Currently, conventional photographic processing method is used to make phototools from master artwork or CAD data. This method generates chemical wastes such as photographic films, developer and fixer solutions.

Direct imaging of photoresist from CAD data is a recent commercial development and utilises an UV or visible light laser source [Arnham, 1993]. This method of photoresist imaging eliminates the use of phototools and thus no photographic processing waste is generated. However, this method is not widely used by the PCM companies due to economic and technical reasons [Miles, 1989; Murray, 1995].

#### 1.4.3 Photoresist processing

Currently PCM companies use three main types of photoresists, namely liquid organic solvent-based, liquid aqueous-based and dry film aqueous-based photoresist.

The use of solvent photoresist causes much environmental concern as various types of solvents and VOCs are used for subsequent processing of photoresist, i.e. in the development and stripping of photoresist. Aqueous-based liquid and dry film resists are more environment-friendly as dilute

solutions (1-5%) of sodium/potassium carbonate and sodium/potassium hydroxides are used in the development and stripping of photoresist [Lott, 1993; Bird and Kapp-Schworer, 1997]. The developer and stripper waste streams contain relevant chemicals used, and traces of metals and resist components, which are relatively easy to treat.

#### 1.4.4 Etching

The most commonly used etchant is an aqueous solution of ferric chloride ( $\text{FeCl}_3$ ), used at a temperature of over  $50^\circ\text{C}$ . It is relatively cheap, comparatively innocuous and versatile, attacking aluminium, copper, iron, nickel and their alloys. Other etchants being used are copper chloride solution for etching copper, potassium ferricyanide-sodium hydroxide-sodium oxalate for etching molybdenum. Hydrochloric, nitric, sulphuric and hydrofluoric acids are also used but they possess the disadvantage of being more dangerous.

In an etching system, the spent etchant and its rinse water is highly acidic and contains dangerous heavy metal ions which are hazardous to the environment and most difficult to render harmless [Kajiwara and Ueda, 1989; Carreiro, 1989].

Methods that can be employed to minimise the wastes generated by the etching system include prolonging the life of etchant, i.e. to increase the degree of 'exhaustion' of etchant before disposal with the drawback of reduced etch rate, and regenerating the spent etchant by oxidation, thus maintaining a constant etch rate. In the most commonly used ferric chloride etching system, suitable oxidation systems of regeneration or rejuvenation of etchants currently used by the industry include the following:

- Chlorine gas
- Sodium chlorate/Hydrochloric acid
- Electrolysis/Hydrochloric acid
- Ozone/Hydrochloric acid

The greatest drawback of the existing regeneration systems is the adverse environmental effects, and health and safety hazards caused by the use of the chemicals as listed in *Table 1.1* [Allen, 1991; Allen and White 1992].

A US patent [Lubert and McGarigle, 1993] and previous research [Ler, 1993; Allen and Ler, 1995] which utilises oxygen for ferric chloride etchant regeneration indicated that this is a much better alternative compared to the other regeneration systems as described above.

#### 1.4.5 Consumption of water and alkalis

Of all the utilities consumed by the PCM process, water consumption poses the greatest adverse environmental effects as it is consumed in rather large

quantities and the waste water generated is highly acidic and contains dangerous heavy metals [Kajiwara and Ueda, 1989; Nowak, 1989]. The majority of the water is used in metal cleaning, rinsing of metal parts, stripping of photoresist and cleaning of final products. In most cases, sodium hydroxide is used to treat (neutralise) the acidic waste water generated.

**Table 1.1: Various problems with different regeneration methods [Allen, 1991]**

Method of regeneration	Environmental, health and safety concerns
Chlorine gas	Hazardous material (short term exposure limit* of 3 ppm) requiring bulk storage.
Sodium chlorate/HCl	Sodium chlorate solution can evaporate and then pose a fire hazard when in contact with organic materials.
Electrolysis/HCl	Large current required. Generation of flammable hydrogen gas. Hydrogen releases are environmentally undesirable.
Ozone/HCl	Hazardous material (short term exposure limit* of 0.3 ppm) but only generated when required. Explosive in concentration of >20%.

\*10 minutes reference period taken from Health and Safety Executive Guidance Note Environmental Hygiene 40/89 (HNSO, January 1989).

## 1.5 Objective and Scope of the Thesis

Manufacturing industries and research centres have conducted much research to find effective solutions to reduce the adverse environment effects of the PCM process. There was, however, no attempt to quantify the environmental impacts of the PCM process to provide a baseline for PCM companies to improve their environmental performance. This thesis is therefore set out to achieve the following objectives:

1. To conduct an environmental audit of a PCM company and provide a preliminary environmental performance measurement of two PCM companies in the UK.
2. To analyse quantitatively the materials consumption and waste generation in the PCM industry in order to determine
  - The efficiency of materials consumption among PCM companies
  - The best practice of PCM industry



The information above can then be used by PCM companies to benchmark and improve their environmental performance.

3. To study the technical feasibility of applying cleaner and more environment-friendly technologies such as laser direct imaging and oxygen regeneration of ferric chloride etchant to reduce the environmental impacts of PCM process.

The research work is focused at looking into the following aspects of the environmental management of PCM process, where no reported research has been carried out yet:

1. This research project started with an environmental review of a PCM company in the UK. One of the latest additions in the field of environmental management in the 1990's was the development of environmental management systems (EMS) at international level and the compliance by companies to these standards to show their commitment. Although most photochemical machining companies have complied with ISO 9000 Quality Management System, none has yet registered to ISO 14001 Environmental Management System. The first step in working towards an integrated EMS is to conduct an environmental review so as to provide a broad picture of the environmental impact of the company's activities and an initial assessment of the environmental performance of the company.
2. The environmental effects of the PCM process can be considerable as reflected in Section 1.4 of this Chapter. Hence the next attempt was to compare and quantify the consumption of materials and generation of wastes, so as to draw up an environment performance measurement of two PCM companies in the UK to provide a preliminary environmental performance measurement of the PCM industry in the UK.
3. From the literature survey, it is known that the ferric chloride waste posed significant adverse environmental effects in PCM. The environmental performance measurement of the two companies showed that the consumption of solvents and VOCs is another area of environmental concern [Allen and Ler 1997a]. As such, further study carried out on a wide range of PCM companies world-wide was focused on the consumption of ferric chloride and VOCs.
4. The world-wide survey in (3) has indicated that the use of regeneration has greatly reduced the ferric chloride consumption [Allen and Ler 1997b; Allen and Ler 1997c]. Hence a study was conducted to determine quantitatively various aspects of etchant regeneration and disposal that include: how widely it is used, methods used, reasons for not regenerating and the future trend of regeneration.

5. The feedback from the PCM industry has indicated that a large number of companies preferred a more environment-friendly regeneration system at a higher cost. Although there are various ferric chloride regeneration systems available commercially, each of them poses adverse environmental effects, and health and safety hazards caused by the use of the chemicals. Recent research [Lubert and McGarigle 1993; Ler, 1993; Allen and Ler 1995] has indicated a more environment-friendly method of regeneration was by using oxygen as the oxidising agent. However, this technology was only used by the patent owner (IBM) to regenerate etching solutions in etching printbands for business forms printing [Lubert, 1997]. Furthermore, oxygen regeneration was not included in the study on the economical aspects of various regeneration systems conducted by Allen and White [1992]. Thus, a study was carried out to determine the suitable operating parameters for efficient regeneration of ferric chloride in PCM industry. Based on the results obtained from this study, it was possible to ascertain the commercial viability of applying this new and more environment-friendly etchant regeneration technology.
6. It was highlighted in the literature survey that the laser direct imaging system is a cleaner technology compared to conventional methods of imaging photoresist as it does not involve the use of conventional photographic processing and thus no photographic waste is generated. Hence, a case study was conducted to ascertain whether this technology is economically and technically feasible at this stage of development.

## **Chapter 2**

# **Environmental Management of PCM Companies**

### **2.1 Introduction**

Public concern for the well being of environmental quality began over a quarter of a century ago. Initially, issues such as wilderness protection and air pollution received the attention of relatively small numbers of conservationists and public health officers. However, in mid 1960s, a wide range of threats to the natural environment began to attract the attention of media, policy makers and the general public. Rachel Carson's *Silent Spring* [1962] is among the most widely known of a number of books which brought public attention to the adverse effects on the environment by human activities and the indiscriminate use of technology. In the book *Limits to Growth* [Meadows *et al*, 1972], the authors further concluded that 'even under the most optimistic assumptions about advances in technology, the world cannot support present rates of economic and population growth for more than a few decades from now.' From computer simulations, the authors also showed that 'only by a concerted attack on all the major problems at once can man achieve the state of equilibrium necessary to his survival'.

Advances in environmental science have brought environmentalism to a new dimension. Scientific investigations in atmospheric, soil science, oceanography, environmental toxicology and ecology provide the public an opportunity to understand the causes and effects of the environmental impacts of human activities, especially those carried out by commercial, and in particular, manufacturing and industrial organisations. At the global level, the green house effect, depletion of the ozone layer, acid rain and pollution of oceans represent a serious threat to the continual viability of ecosystems. At a more local level, the decline in urban air quality, pollution of water courses, degradation of soil quality, loss of habitat and species, and consumption and contamination of natural resources pose threats to the local environment.

### **2.2 Global Development of Environmentalism**

The above developments have led to a surge in public awareness and concern for the quality of the natural environment, and the sustainability of the

environment to withstand future development, in view of the rising industrial output to satisfy the global economic and population growth. A comprehensive review by Dunlap [1991] on the national surveys carried out in the US regarding public opinion toward environmental issues showed that there was a dramatic increase in environmental concern in the late 1960s, reaching a peak with the first Earth Day in 1970. Although this trend showed fluctuations in the 1970s and 1980s, public concern for the environment reached an unprecedented level by the twentieth anniversary of Earth Day. Public opinion towards environment in Europe showed similar concerns. For example, 93 percent of respondents in a survey conducted in Britain, Germany and France in late 1991 stated that environment was one of the most worrying problems facing society [McCann-Erikson and Harris, 1992].

A series of highly publicised environmental disasters such as the escape of toxic gas at Bhopal (India, 1984), the diffusion of radioactive materials from a nuclear reactor at Chernobyl (Ukraine, 1986), a massive chemical spill into the River Rhine from a chemical plant (Switzerland, 1986) and the rupture of the oil tanker Exxon Valdez off the coast of Alaska (USA, 1989) further intensified the global environmental movement. More scientific findings regarding threats and damages to the natural environment like global climate change (notably global warming), disintegration of the stratospheric ozone layer, and transboundary transport of hazardous wastes have also led to the demand by the public for international action to be taken to ensure future economic and industrial development will be environmentally sustainable.

Parallel with the rising public concern towards environmental issues is the formation of organised pressure groups or environment non-governmental organisations (NGOs). In the 1960s and 1970s, realising that governments and private corporate organisations seldom act in the absence of organised public demand, the formation of mainly volunteer, environmental non-government organisations in nearly every developed country, especially in Western Europe and North America was encouraged. The global dimension of environmental problems and the need for counterpart organisations in countries where they work led to the branching out of memberships to other nations for nearly all major environment NGOs. With the developments in globalising popular concern over environmental issues, 'the gap between countries over environment or development priorities has narrowed as the concept of environmental sustainable development has gained adherents' [Caldwell, 1991].

### **2.3 Environmental Legislation and Regulations**

In order to address the concerns raised by the general public and NGOs, various national governments have taken steps to enact legislation and regulations to prevent further degradation of the environment. Strict environmental legislation has been introduced in the more-developed countries such as the USA, Japan, UK, Germany, Denmark and France whereas in the less-developed countries, environmental concerns in general and hazardous waste management in

particular are not high on the political agenda [LaGrega *et al*, 1994; Wallace, 1995].

The United Kingdom (UK) was one of the first industrial countries to introduce environmental legislation by passing the Alkali Act (1863), legislation to protect birds (1869), the Public Health Act (1875) and the River Pollution Prevention Act (1876) [Ball and Bell, 1995a]. Being part of the European Union (EU), the UK environmental legislation is governed by EU environmental laws. This was contained in the 1987 Single European Act (SEA) which confirmed the ability of the EU to legislate in the environmental area and laid down specific powers to act. EU regulations and directives have total control on the environmental issues within all the EU countries. However, member states have the right to maintain or introduce more stringent protection measures [Scherer, 1994]. The Secretary of State for the Environment is empowered to co-ordinate and regulate variances of environmental regulations between UK and EU [Ball and Bell, 1995c; Leeson, 1995].

The basic principles of EU environmental law and policy as laid down in the SEA are [Scherer, 1994; Salter, 1997]:

1. Preventative action is preferred.
2. Environmental damage should be rectified at source.
3. Polluter should pay the cost of measures taken.
4. Environmental policies should form a component of other EC policies.

The USA environmental laws are generally more severe and strict and are administrated by the Environmental Protection Agency (EPA, established in 1970) [Vogel, 1986; Elkington *et al*, 1991; Ball and Bell, 1995d]. The Pollution Prevention Act (1990) established a strategic approach to waste elimination and/or minimisation. This Act set up a criteria of prevention of waste that was symbolised as "Prevent before Recycle before Treatment before Disposal before Release" [Owen, 1995; Valenti, 1994]. The hazardous waste legislation, Comprehensive Environmental Response, Compensation and Liability Act 1986 (CERCLA), the infamous Superfund, imposed cradle to grave liability on waste generators for the wastes they generated or disposed of.

One of the major international initiatives in environmental consideration came from the United Nations (UN) who hosted the EARTH SUMMIT in Rio de Janeiro, Brazil in June 1992. This summit brought together representatives of 178 countries. The decision to hold this international summit in a less-developed country had an enormous political significance and symbolism: it illustrated the extent of the environmental pollution and the need of both the more developed countries and less-developed countries to take collective action to address this problem. Far-reaching environmental problems such as climate change, threats to bio-diversity and sustainable development were discussed and an agenda produced for the UN Conference on Environment and Development (UNCED). The agenda included an 'Earth Chapter' for the next century and was titled 'Agenda 21'. This is an action plan for sustainable

development by integrating the goals of environmental protection and economic development, and based on local community and free market principles. The resolutions in the 'Earth Chapter' strongly emphasised the environmental impact of hazardous waste and set up criteria for their elimination/minimisation [Report of the UNCED, 1992]. Many environmentalists criticised the EARTH SUMMIT as a public relation exercise by national governments and international agencies to address the environmental problems. However, McCormick [1995] noted that 'there has been a marked trend away from the notion of environment as divorced from humanity and towards a new focus on the human costs of environmental deterioration and mismanagement' after Rio.

Further efforts to address global environmental issues after the Rio Summit was the meeting at Kyoto, Japan in December 1997. The global community took its biggest step on agreeing a Protocol to limit greenhouse gas emissions in responding to the threat of climate change. The agreement, known as The Kyoto Protocol, set specific emission targets for 35 member countries of the OECD and former Soviet bloc. The Kyoto Protocol is hailed as the most notable achievement in three decade of international environmental diplomacy, as a framework is now in place to begin addressing one of the world's most intractable environmental problems [ENDS, 1997].

With all these developments, it is difficult to disentangle national policies from global and regional ones, as environment damage does not confine itself to national boundaries. Moreover, global environmental policy has to influence and guide the behaviour of free market and capitalism, as exploring the environmental issue from a purely business and/or consumer perspective is not enough to attain sustainable development [O'Connor, 1996]. Taking all the above development into consideration, the future environment legislation promotes the following broad trends [Ball and Bell, 1995b; Higgins, 1995; Leeson, 1995]:

1. An emphasis on prevention rather than reactive or curative measures of solving environmental problems.
2. Tightening and enforcing environmental regulations more strictly, which include increase in fines, sanctions of custodian sentences for responsible individuals and making polluters pay for all the clean-up costs related to the environmental damage.
3. Setting basic rules for environmental performance reporting to ensure the information is accurate and compatible. Focused and clear goals would be set , leaving it to countries/organisations to achieve them.
4. Increasing cost of waste disposal, especially hazardous waste to make organisations implement well-managed waste minimisation programmes. This will make companies that use resources inefficiently uneconomic or less profitable.

### 2.3.1 Cost of not complying with environmental legislation

The development of environmental legislation is one of the most important factors influencing the behaviour of businesses, especially manufacturing industry in the field of the environment. While striving to achieve competitiveness and efficiency, businesses, in particular the small and medium sized enterprise sector, seldom initiate proactive strategic responses to the environmental issues. Indeed, many proactive responses are themselves driven by environmental legislation, seeking to minimise the cost of future legislation or to exploit the new opportunities offered by the advance of environmental policy [Welford and Gouldson, 1993].

It has been the attitude for most businesses that investment on cleaner technology and waste minimisation is a drain on company profits, implying that the offsetting return is insignificant and certainly lower than the cost of implementation. This may be so as it does not take into account the overall cost of environmental damage. Contravention of environmental legislation can result in the following tangible and intangible costs:

- Cost of litigation
- Compensation and damage cost to third parties.
- Clean-up costs of contaminated sources
- Damage to corporate image and employees' morale
- Loss of sales and fall in stock price
- Higher bank interest on borrowing and insurance premiums.

For example, under the Duty of Care in Section 34, Part 2 of the Environmental Protection Act 1990 (EPA 1990), any person who imports, produces, carries, treats or disposes of controlled waste or who, as a broker, has control of it, has to ensure that it is dealt with properly. Failure to comply is a criminal offence with a statutory maximum fine of £20,000 and a prison term of up to six months if prosecution is brought in a Magistrates Court, or an unlimited fine and prison sentence of up to five years if brought in the Crown Court.

However, such fines are nothing compared to the potential liability for clean up cost and claims for damages from third parties after environmental damage has been done. For example, the Scottish knitwear firm 'Pringle' faced a fine of £5,000 for a pollution offence. In addition, civil damages and claims from a factory nearby were expected to reach £100,000 and clean-up costs could exceed £1,000,000 [Clabon, 1994]. The damage to the corporate image, loss of sales and other intangibles were rather difficult to quantify. When all these are taken into account, the total cost could be enormous.

### 2.3.2 Environmental legislation and regulations in the UK

There are a wealth of publications, reports and articles on environmental legislation. The following legislation and regulations in the United Kingdom that directly or indirectly affect the PCM industry are summarised from various publications [Ball and Bell, 1995; Leeson, 1995; Garbutt, 1995; Scherer, 1994].

#### 2.3.2.1 Integrated Pollution Control (IPC)

The IPC system aims to integrate the control of environmental pollution as a whole, rather than on a compartmental basis. Legislation aimed solely at controlling emissions to a single medium provides incentive for polluters to transfer pollution from one medium to another. The fragmented approach of pollution control by different enforcement bodies also created problems, thus the IPC system provides a more factory-based approach towards pollution control.

IPC is provided for under the Environmental Protection Act 1990. It superseded much former pollution control legislation and introduces new requirements. These include:

- The need to minimise pollution with regard to Best Practical Environmental Option (BPEO).
- The need to control emissions using Best Available Techniques Not Entailing Excessive Cost (BATNEEC). Initially, the requirement of 'best practicable means' (BPM) was applied to control the substances harmful to the environment and formed the basis of environmental regulation of industrial emissions until replaced by the similar concept of BATNEEC within the 1990 Environmental Protection Act.
- An increase in the maximum fine, from £2,000 to £20,000, for a pollution offence which can be imposed in a Magistrates Court.
- The ability of the Environment Agency (EA) to seek, in the High Court, enforcement orders against persistent polluters.
- The empowerment of EA to issue prohibition notices for a prescribed process in certain circumstances.

The operators of the processes that are prescribed under the IPC system need to apply for an authorisation to operate. Only one process consent for emissions to the different environment compartments (air, water, land) is required. The consent is issued by EA in consultation with the Health and Safety Executive, and with consultation from the other relevant statutory consultees.

An application for a variation to the existing authorisation is required should the operator wish to make changes to the nature of the prescribed process. Conversely, EA has the power to vary conditions of an authorisation as and when necessary. Authorisation conditions shall in any case be reviewed every four years.



The IPC system incorporates provisions for public access to the information prior to issuance of authorisation. Further public consultation is required for applications relating to substantial changes to the process.

PCM is currently *not* a process scheduled under the IPC system. However, since the production and use of halogens (which includes chlorine gas) is prescribed under Part A of Schedule 1 in the Environmental Protection (Prescribed Processes and Substances) Regulations 1991, the use of chlorine gas in the regeneration of etchants in PCM needs an authorisation from the EA.

#### 2.3.2.2 Air

Public interest in clean air has a long history leading to the Clean Air Act in the 1950s and increasingly stringent emissions standards for industry to meet across the globe. Global warming, acid rain, depletion of the ozone layer and fear of associated health risks are recent strong drivers for these increasing standards.

Local authorities regulate the Air Pollution Control (APC) of processes scheduled under Part 1 of EPA 1990. The EPA 1990 provides for improved control of atmospheric pollution not otherwise controlled but constitutes a statutory nuisance. Other air pollution control is furnished by the Clean Air Act 1993, in the cases of processes that are not prescribed under the EPA 1990.

The same basic duties and procedures apply under Local Authority Air Pollution Control as under IPC, with local authorities (typically district councils and London borough councils) rather than EA acting as regulatory agencies.

#### 2.3.2.3 Water

Environmental legislation pertaining to water is contained within the Water Industry Act 1991 and the Water Resources Act 1991, which consolidated much of the legislation relating to water pollution control. The EA has the regulatory responsibility for pollution control of discharge to waters.

Under the Water Resources Act 1991, it is a criminal offence to cause or knowingly permit the entry into controlled waters, of any poisonous, noxious or polluting matter or any solid waste matter, trade or sewage effluent, without a consent. In addition, accidental spillage and unconsented discharges of such material constitute the basis of an offence. Controlled waters include territorial waters, coastal waters, inland waters and ground waters. Application for consents to discharge is made to the EA.

Under the Water Industry Act 1991, the water services plcs, which provide water supply and sewerage services, have the responsibility for controlling discharges to sewer through the granting of trade effluent consents. The

discharges of treated effluent to controlled waters are in turn consented by the EA. The Act also makes it an offence to discharge any matter into a public sewer which is likely to damage the sewer or treatment process, or endanger the staff of the water service plc.

Effluents of PCM companies are usually pre-treated to meet the conditions as specified in the consents issued by the water services plcs, prior to discharge to their treatment plants.

#### 2.3.2.4 Waste Management

The EPA 1990 that regulates waste management in the UK defines:

The responsibilities of agencies or authorities involved in regulation and provision of waste collection disposal. The agencies or authorities are usually county councils, whereas the waste disposal contracting services are carried out by local authority waste disposal companies or private companies, through arrangements with authorities responsible for regulating waste disposal. The authorities for waste regulation, collection and disposal are functionally different.

- The requirements for licensing for those involved in waste disposal. Waste Management Licences, issued by Waste Regulation Authorities, authorise the licensee to deposit, treat, keep and dispose waste under specified conditions.
- A 'Duty of Care' on all disposers, carriers, holders, importers and producers of waste not to permit the waste to be deposited, released to the environment or be transported in an illegal manner.

Wastes generated by PCM practitioners are usually handled by the waste management licensees. The services provided include transport, storage, treatment and disposal of waste. For wastes containing chemicals such as heavy metals, specified conditions are imposed in the consents issued by the Waste Management licensees.

## 2.4 Environmental Management Systems

As the ability of the environment to supply raw materials and accept waste is diminished, the costs of these services to industry will increase. Moreover, increasingly stringent legislation which increases the cost of waste management is forcing industry to minimise the utilisation of natural resources to stay competitive. As a result, more efficient raw material utilisation and a decrease in the amount of waste generated are key factors that will encourage industry to minimise its environmental impacts. Waste should be viewed both in terms of physical waste generated and the less tangible loss experienced through an

inefficient use of resources. Avoiding these losses improves both the business and environmental performance of a company.

In an effort to increase the efficiency of their operations, many companies have to develop an integrated environmental management system (EMS) [Hunt and Johnson, 1995a; O'Callaghan, 1994]. The need to develop an appropriate EMS to ensure that environmental issues are under control is vital for business survival [Sunderland, 1996]. The implementation of an EMS can help organisations to reduce inefficiencies and the likelihood of errors, and enhance the achievement of environmental objectives and targets.

British Standards Institution (BSI) responded to the needs of industry, business and other interested parties in having a recognised system in place for managing environmental compliance and performance by developing the first environmental management standard in 1992, known as BS 7750. This standard was subsequently revised in 1994. The European Union developed a similar regulation, Eco-Management and Audit Scheme (EMAS), in June 1993, which incorporated much of the management system requirements of BS 7750. In September 1996, International Organisation for Standardisation (ISO) approved a similar standard namely ISO 14001 which acts as a global standard for the management of environmental compliance and performance for industry, business and other organisations. The purpose of ISO 14001 and EMAS is to provide organisations with a universal framework within which to manage environmental compliance and performance, and an opportunity via certification, to demonstrate their responsibility, in respect of the environment, to other interested parties.

ISO 14001 requires that an organisation formulates an environmental policy. The Policy must be available publicly and the organization must be open to communication with third parties, including the general public. From this, objectives and targets for environmental performances are to be set. An organisation must put in place a procedure for the identification of environmental aspects and evaluation of associated environmental impacts. It must evaluate the significance of such impacts, in which the adverse impacts that are deemed to be significant shall be documented in the Register. Management programmes and operation controls are then put in place to improve the performance of adverse significant environmental impacts.

The standard also requires a procedure to identify and realise access to legislation and regulations to show that the organisation is managing compliance to legal requirements. The legislation and regulations relevant to the organization's operation shall be documented and updated as and when necessary to show that it is managing compliance.

The organisation shall audit the system periodically to ensure compliance of the system. A management review is to be carried out from time to time to review the performance of the whole environmental management system,

including the audit findings to ensure their continuing efficiency in managing environmental performance.

ISO 14001 is similar to the requirements of ISO 9001 Quality Management System (QMS) in many respects. The main differences are in respect of determination of environmental aspects and evaluation of environmental impacts, identification of and access to legal requirements, and to ensure environmental performance improvement.

#### **2.4.1 Evaluation of Environmental Impacts under EMS**

In establishing an EMS, it is important to identify and provide information on the organisation's significant interactions with the environment. As such, identification of environmental 'aspects' and evaluation of environmental 'impacts' form part of both the initial review and the routine operation of an established EMS. Such information is required for setting sound environmental objectives and targets, and for maintaining operation and control of an EMS.

ISO 14001 is a generic international standards specification as it does not specify detailed performance standards to be achieved. Indeed, it is simply not feasible to specify any performance standard in view of the diverse range of organisations to which the EMS is applicable. Therefore, identification of environmental aspects and evaluation of impacts that provide a baseline information for organisations to set goals and targets for environmental improvement is therefore especially important. This would enable public and interested parties to scrutinise the environmental performance so as to provide the basis of credibility.

#### **2.4.2 Environmental Aspects and Impacts**

ISO 14001 defines environmental aspects as 'Element of an organisation's activities, products or services which can interact with the environment' and environmental impacts as 'Any change to the environment, whether adverse or beneficial, wholly or partially resulting from an organisation's activities, products or services'. The scope of evaluation includes the activities, products or services that it can control, and over which it can be expected to have an influence.

In evaluating impacts, ISO 14001 requires that communications and complaints from external interested parties be considered. However, information will also need to be gathered from a wide range of sources, such as government departments, regulatory agencies, environmental NGOs, trade associations, consultants, research organisations, local residents, conservation bodies and environmental journals.

### 2.4.3 Judgement of Significance

Regarding the judgement of significance, impacts that are subject to regulatory control are automatically 'significant'. One of the primary objectives of environmental management is the achievement of compliance with legislation and regulatory requirements. Indeed, an early step in the establishment of an environmental management system is the development of a mechanism by which the organisation can maintain an awareness of the current and projected environmental legislation with which it must, or may in future need to, comply.

It is difficult to evaluate impacts which are not subject to regulatory control, but appear to be potentially significant, because there is no standard performance measure for comparing widely differing impacts [IEM 1997]. The evaluation of these impacts can be made as consistent as possible by establishing a framework of rules and procedures, based on benchmarking data or using an informed group for the final evaluation of significance.

A proposed method for 'impacts' evaluation and judgement of significance formulated for the PCM industry is attached in Appendix A of this thesis.

### 2.5 Benefits of Pollution Prevention

A successful pollution prevention programme can benefit organisations in the following ways:

- Improve global competitiveness through lowering the cost of operation and improving product quality

The famous voluntary waste reduction Pollution Prevention Pays (3P) programme initiated by the US company, 3M, is a good example. It was reported by ENDS [1989] that 3M saved a total of \$482 million in 2,450 projects implemented world-wide since 1975. In PCM, past investigation has shown that ferric chloride etchant regeneration is cost-effective if the annual amount of iron etched exceeds 200 kg, assuming that the etchant is 50% exhausted before disposal [Allen, 1991].

Waste reduction and product quality are inter-related; in PCM, the use of laser direct imaging in photoresist processing eliminates photographic wastes and at the same time improves product quality [Van Arnem, 1993].

- Enhance consumer acceptance of products

The environmental movement and the growing affluence of population especially in the more developed countries have resulted in consumers preparing to pay more for green products [Ford, 1992; McCann-Erikson and Harris, 1992]. Furthermore, being green is perceived to command certain respectability in Western society [Ford, 1992]. Consuming greener products also subjects the consumers to less exposure to hazardous materials as

they are produced or manufactured by using more environment-friendly methods.

- Reduce environmental impacts enabling organisations to comply with legislation and enhance corporate image

A pollution prevention programme can help to prevent the enormous cost of infringing environment legislation as illustrated in Section 2.3.1 of this Chapter. Investment in pollution prevention can also result in reduction in future costs if regulations are made more stringent (which is quite likely). This is because retrofitting modifications or additional end-of-pipe treatment that are required to comply with future legislation is generally much more expensive [Hockley, Walters and Goodall, 1989].

Being green and environment-friendly can also help to improve corporate image and enhance community relations.

- Improve working conditions

A better environment reduces a worker's exposure to toxic materials, which means better working conditions and reduced sick leave. All these would lead to better productivity.

- Waste minimisation can act as a catalyst for innovation and technological change that would bring long term benefits to companies [Hockley, Walters and Goodall,, 1989].

Organisations are reluctant to take proactive pollution prevention measures as they perceived the investments as unprofitable and unjustified. This is because most business accounting systems do not track the operations that cause the greatest environmental expenditures or the products most responsible for waste production; only the direct costs of waste treatment and disposal are taken as the potential benefits for investment in pollution prevention.

'Total Cost Assessment' (TCA) is an investment analysis tool advocated by the US EPA. TCA includes four elements in assessing pollution prevention investments in which full accounting is made of expanded cost inventory (direct cost, indirect cost, potential liabilities and less tangibles), longer term financial indicator, extended time horizon and direct allocation of cost to processes and products. Spitzer [1992] reported that from two case studies conducted in the paper and pulp industry, a TCA approach made the pollution prevention projects far better investments than conventional financial analysis would indicate.

In another analysis known as Activity Based Costing (ABC), this tracks and traces the costs of pollution prevention to the actual products and processes, and waste treatment and disposal. Schaltegger [1997] reported that the first

empirical studies have demonstrated that between six and ten times higher savings could be realised when compared to a conventional accounting system.

## **2.6 Environmental management of PCM Companies**

Taking into consideration the global environmental movement and development, it is obvious that environmental issues are real business issues that no industry can afford to avoid. In addition, the benefits of pollution prevention and waste minimisation can be beneficial instead of burdening the industry. Therefore, the PCM companies should be working towards greener management practice to remain competitive in future.

## **Chapter 3**

# **Environmental Audit of a PCM Company**

### **3.1 Introduction**

Environmental audit is an initial assessment of the environmental performance of an organisation. The first step in working towards an integrated EMS is to conduct an environmental audit so as to provide a broad picture of the environmental impacts of the organisation's activities and to provide a baseline information regarding the environmental performance of an organisation. The information obtained will enable the organisation to decide exactly what environmental concerns need to be addressed, so that a plan of action can be established, with priorities and targets clearly identified and subsequently a system can be put in place. This will provide a framework for effective environmental management.

The information to be gathered by the environmental audit should consist of the following [Hunt and Johnson, 1995b]:

- Legislative and regulatory requirements,
- Evaluation and registration of significant environmental impacts,
- Examination of all existing environmental management practices and procedures, and
- Assessment of feedback from investigation of previous accidents and non-compliances.

From the literature survey carried out, it was found that environmental impacts of PCM were reported in various papers. These include impacts of PCM process as a whole [Allen, 1993], ferric chloride wastes [Allen and White, 1992; Kajiwara and Ueda, 1989], waste-water [Nowak, 1989; Wilk, 1994] and use of VOCs [Lott, 1993; Ryder, 1995]. There was, however, no reported environmental audits conducted on a PCM company to show the quantitative environmental impacts and relevant performance indicators. Furthermore, a planned audit can minimise the risk of overlooking important environmental concerns. As such, an environmental audit was conducted on a typical PCM company located in the UK. This was done with the cooperation and assistance rendered by the company personnel. As the information obtained is



highly confidential in nature, the name of the company is known as F in the audit, and the names of towns and places of interests have also been disguised.

### **3.2 Method of Information Gathering**

Apart from interviewing the relevant personnel and observing various processes and operations of the plant, the information for this environmental audit was mainly gathered from the following sources:

- Information and data stored in the Company's computer system such as annual consumption of metals and chemicals from invoices.
- Information like underlying geology, wind direction, rainfall, boreholes and sites of special scientific interests from the town library.
- Aerial picture of surrounding areas.

It should be pointed out that the scope of this environmental audit has been confined to the photochemical machining operation of the company.

### **3.3 Environmental Audit of a Typical PCM Company**

Established in 1970, Company F is involved in the research & development, design and manufacture of various products, which includes parts and components, tools and fixtures, mainly for the electronics industry, using PCM, electroforming, metal finishing and computer numerical control (CNC) routing processes.

Company F is among the first companies in the UK and the first PCM practitioner to be granted BS 5750 Pt 2, ISO 9002 registration.

#### **3.3.1 Existing EMS of Company F**

The top management of Company F has committed to the setting up of an EMS to comply with ISO 14001. The Personnel and Training Manager, who is also responsible for the Health & Safety issues of the company, was entrusted with the responsibility of coordinating the establishment of an EMS.

It is understood that a combined Health, Safety and Environmental Management System is to be developed as the company was currently revising and updating Control of Substances Hazardous to Health (COSHH) requirements, although ISO 14001 explicitly excludes health and safety from its scope.

The company did not have a formal and documented EMS although it has a corporate Environmental Policy that appeared in at least one of its product brochures. This Environmental Policy was, however, not effectively communicated to the staff. One of the strengths of the company was that it

has a documented QMS that complied and registered to BS 5750. The documented QMS could be used as a basis for EMS documentation.

Another strength of the company was that the key personnel had an awareness of the environmental impacts of the main operations of the company, although the identification of environmental aspects and evaluation of impacts had not been carried out formally. The same applied to the requirements of legal compliance.

Apart from establishing a documented EMS, Company F needed to train the staff to implement and audit the system to ensure compliance with the requirements of ISO 14001.

### **3.3.2 Site environmental setting**

The purpose of the site environmental setting analysis is to determine the susceptibility of the site and its environs to environmental quality change (positive as well as negative) as a result of activities on and related to the site.

Company F is part of G Industrial Estate. The present location was known as C Airfield prior to the granting of planning permission to turn it into an industrial estate in 1961. Originally only 21 acres of the disused airfield was granted for industrial development. In 1966, a further 26 acres of adjoining land were allocated for industrial use, thus giving a total industrial estate area of approximately 47 acres.

Company F moved to the present site in 1979/80. The site occupies approximately 1.5 acres; the built-up area of the plant was 5,000 square feet (sq. ft.) originally and expanded to 28,500 sq. ft. (0.65 acres) gradually over the years due to the growth in business.

The area between west and northwest to the site adjoined other light industrial areas. Several residential areas immediately adjacent to the site were found to the east and the north. The nearest house, located to the east of the Unit B of the plant, was only approximately 2.5 metres away. A few buildings that belonged to the Social Services Department were located at the south of the site.

The underlying geology of the site was composed of Oxford Clay about 250 m thick. According to the contour of the site location published by the Geologist Association of London, 1989, storm water and drainage discharged water to River W, which in turn flows to R Lake. R Lake was a bird reserve area owned by the Royal Society for the Protection of Birds. The domestic and treated industrial effluents were discharged to the treatment plants operated by W Water Plc., a private water company.

There is no borehole within one kilometre radius of the site. It was also unlikely that the surface water would permeate through to the boreholes nearby due to the composition of the underlying geology.

The prevailing wind direction was predominantly westerly and southwesterly. Odours carried by the prevailing winds would impact upon the residential areas to the east and northeast. The annual rainfall in the area was between 666 mm (1990) and 853 mm (1993).

Apart from the R Lake, another nature reserve was located to the south of the plant, which lay between Ctown and Fbridge. The area was used for breeding by rare insects, nesting of birds, oyster farming and a host of other outdoor activities.

### 3.3.3 Air

The company utilised solvents and volatile organic compounds (VOCs) in its operations. Apart from solvents and VOCs, other fugitive emissions were mainly from the plating shop and etching room. The fume extractors removed most of the emissions in the plant before these fumes were emitted to the atmosphere.

Of the 12,000 litres (approximately) of solvents and VOCs used annually, 180 litres were 1,1,1-Trichloroethane (Genklene), which is classified as an ozone layer depletion substance. Not all VOCs used were emitted to the air as certain proportions were treated and reclaimed by outside contractors.

It should be pointed out that the EC Regulation 3093/94 implementing the Montreal Protocol 1987 specified that 1,1,1-Trichloroethane shall be phased out by 1 January 1996. The company personnel were also unsure whether its PCM and electroplating process were listed as Part B processes of Environmental Protection Act 1990 (EPA 1990), which are controlled by the Local Authority for Air Pollution Control.

According to a survey (see Chapter 5 and 7 and Allen and Ler, 1997a) on the usage of ferric chloride and VOCs by PCM industry recently, Company F was found to be using extremely large quantities of solvents due to the nature of the photoresist used. It was noted that the company was studying the feasibility of using aqueous liquid photoresist in the PCM process. The success of the trial would greatly reduce the consumption of VOCs by 10,000 litres per annum.

An alternative for 1,1,1-Trichloroethane, which was mainly used as a degreasing agent in the electroplating process, is Trichloroethylene. However, negative feedback from the shop-floor operatives due to the health risks posed by the latter had forced the management to defer its usage. The company was in the midst of finding a more acceptable alternative.

In terms of quantifying the usage of VOCs and other emissions, a computerised monthly purchase report was available. This could be used to monitor the progress of VOC consumption for performance improvement in implementing the EMS in future.

Apart from VOC emissions, it is important to control and monitor the smoke, fumes, odour and noise levels in the plant as the nearest residential building is located very near to unit B of the plant. These emissions are classified as statutory nuisances under EPA 1990 and Clean Air Act 1993. It was reported that the residents nearby had lodged a complaint previously regarding air emissions. ISO 14001 specifies that complaints from the public have to be dealt with and investigated in an appropriate manner.

### 3.3.4 Water

Water supply, treatment and drainage costs contributed a large proportion of the total utility cost of the company. It is estimated that 41,040 m<sup>3</sup> of water was consumed annually. The water was supplied on the site by W Water Services. A plan outlining the water supply, drainage of sewer and surface water was available in the company's computer system.

#### 3.3.4.1 Discharge to Public Sewer

The majority of the water was treated prior to discharge to the public sewer through a written consent that specified control levels of various components permitted on the discharge. The domestic effluents and effluents from the photoresist developing and stripping areas (which use about 12% of total water consumption) were discharged directly to the sewer without further treatment. The above arrangements were regulated by the Water Industry Act 1991.

The company consumed a total of 41,500 litres of 42 °Bé ferric chloride which was used to etch an estimated 14,500 kg of metals with an area of 5,000 m<sup>2</sup>. The ferric chloride waste and wastewater generated were treated by the in-house effluents treatment plant. Caustic soda was used to treat the effluent produced by neutralising its acid content, and solids in the effluent are precipitated by flocculation and compacted into cakes before going to landfill via a waste management contractor.

The quality of treated water was monitored by an in-house pH control and a monthly analysis by W Water Services to ensure that it was within the permitted level. The effluent treatment plant was well under control from the results of monthly analysis and pH print outs. It was also understood that no formal enforcement action had been taken by the water company against violation of consent to date.

Currently regeneration/rejuvenation of ferric chloride was only carried out at one of the etching machines, although sodium chlorate and hydrochloric acid (BEAC) regeneration facilities were available at the main etching operation of

Company F. It was also noted that the excess ferric chloride regenerated was drained to the effluent treatment plant instead of being collected and re-used. The company's performance was ranked as medium according to the survey [Allen and Ler, 1997b; Allen and Ler, 1997c]. As such, there was room for improvement in this area.

Private water companies were under pressure in relation to their own sewage treatment work to produce a higher quality discharge in response to the enforcement of the Helsinki Agreement which banned the ocean dumping of treated water. This agreement has been written into the EU Directive on urban wastewater, to be enforced from 31 December 1998 [Kiely, 1997]. This will enable the water companies to place higher restriction on volume and content of trade effluent discharges. The restriction is especially applicable for discharges from the photoresist developing and stripping areas, as evident by a recent discussion between Company F and W Water Services. All these developments are likely to be reflected by significant cost increases. These pressures meant that there was an added incentive for the company to minimise effluent discharges whenever possible and to remove as much polluting material as practicable. The top management was also looking into ways of reducing the water usage as the cost was escalating.

#### 3.3.4.2 Discharge to surface waters

The rainwater run-off in the plant was discharged into the surface water surrounding the area (rivers and lakes). Discharges to surface waters (or controlled waters) are regulated by a system of consents under Water Resources Act 1991. Under Section 85 of the above act, it is an offence to cause or knowingly permit any poisonous, noxious or polluting matter to enter any controlled waters. Contravention of this or of conditions attached to the consent of discharge given under the Act may result in a fine to a maximum of £20,000.

Contamination of surface water could be caused by the lack of adequate bunding in certain areas of the plant. For example, accidental spillage of ferric chloride at the filling point would cause the chemicals to enter the surface waters via the storm drains as there was no spill containment at the filling area. Solvents and chemicals at the storage area could also enter the storm drains as run-off due to lack of bunding as pointed out by the Environment Agency during their recent visit.

#### 3.3.5 Storage

Materials and chemicals are stored in different locations of the site. The containers used were:

- Tanks/drums for ferric chloride, caustic soda, Genklene, anti-freezes, waste effluents.

- Plastic containers for acids, alkalis, resist, strippers, cleaning agents.
- Skip for storage of waste metal cake.
- Other plastic containers of chemicals at the plating shop.

Some storage tanks were observed to have no bunding (110% containment of volume stored) around the perimeter of the tank, e.g. the Genklene tank in the flammable chemical store and various tanks in the effluent treatment plant. Some of the drums were kept in the open air and found to be in poor condition, e.g. two drums of anti-freeze kept outside the effluent treatment area were found to have rusty tops and caps. It is understood that the two underground tanks used for effluent treatment were not tested for leakage (or integrity test) after the installation. Leakage of untreated effluent from these tanks would contaminate the surrounding waters as the immediate underlying geology of the site is Oxford Clay. There were, however, no past incidents of chemical spillage at the site.

Chemicals and solvents in the plastic containers were well labelled and stored in three areas, the main store, the chemical store and the flammable chemicals store outside Unit B. However, there were a few containers of unidentified waste chemicals found near the skip and in the backyard (scrap-yard).

The skip used to contain waste metal cake was functioning well as there was no sign of spillage of waste outside it. But the request by the Environmental Agency to put a layer of water-proof material on the skip was valid, as seepage of rainwater through the skip which contained dissolved metals could be poisonous to wild life in surrounding waters.

The staff was aware of some unidentified chemicals in the plating area, but this area was generally well managed. The cyanides (gold, silver and potassium cyanide) were stored separately and only trained and competent personnel were allowed to handle them.

The regulations governing spillage and discharges are Water Resources Act 1991 and EU Directive on Toxic and Dangerous Waste (78/319/EEC). Section 85 of Water Resources Act 1991 states that it is an offence to cause or knowingly permit any poisonous, noxious or polluting matter to enter any controlled waters, and EU Directive on Toxic and Dangerous Waste requires good practice and a Register of Spillages. Therefore, good management practice involves sound containment of any such substances to prevent dispersion or diffusion via ground, or such potential.

### **3.3.6 Solid, liquid and special waste**

The processes in the plant of Company F generated a range of wastes. These wastes were collected and disposed of by contractors. The types of wastes and the areas where they originated from is summarised in *Table 3.1* below. It should be noted that the inventories above were not exhaustive.

The general awareness on segregation and management of wastes at the plant was good, except the few unlabelled and unidentified containers of waste (believed to be used chemicals).

Waste management is controlled mainly through Duty of Care provisions of the EPA 1990 although there are other regulations of importance such as Control of Pollution (Special Waste) Regulations 1995 and Environmental Act (1995).

**Table 3.1: Types of waste generated**

Type of waste	Sources
<u>Solid Waste</u>	
Household waste (including waste papers, films)	All areas
Scrap metals/defective components	All areas
Disused machinery/equipment	Backyard
<u>Liquid waste</u>	
Solvent resist/thinners	Unit B
Lubricating oil	Unit A
Coolant	Unit A
<u>Special Waste</u>	
Genklene	Unit B
Plating chemicals	Unit B
Waste metal cake	Effluent treatment plant

Under the Duty of Care, Company F is responsible for the waste they produced although these wastes are transported and disposed of by various contractors eventually. The company has to ensure that the contractors have the proper Waste Management Licences for the category of waste that they deal with. In this case, the identification of types of waste was important.

Due to the size of operation, it is perhaps not economically feasible for Company F to carry out audits of the waste disposal contractors' operations. However, Company F shall ensure that the contractors are qualified and shall retain and update copy(ies) of the waste management licences, contracts and waste transfer notes.

### 3.3.7 Energy

Electricity was the main source of energy used for the processing and manufacture of final products whereas gas was only used for central heating. It

was estimated that about 594,398 KWh of electricity and 422,535 KWh of gas are utilised annually.

Energy production and consumption leads either directly or indirectly to emissions of CO<sub>2</sub>, SO<sub>2</sub> and NO<sub>x</sub> which contribute to global warming and acid rain. Reduction in energy consumption will help to address these problems and cost reduction.

### **3.3.8 Transport**

Road transport accounts for approximately 85% of carbon monoxide, 45% of nitrous oxide and 30% of hydrocarbon atmospheric emissions in Britain. Despite its environmental impact, little attention was given to transport by industry when considering its environmental impact.

The main vehicular movement at Company F was relatively small, mainly the deliveries of materials and chemicals and loading of finished products, and the staff who drive to work (approximately 60 cars). Due to the proximity of the residential houses, this might cause a potential effect on the air quality and nuisance to the residents living nearby if it is not handled properly. There were no vehicle maintenance and refueling activities at the site.

### **3.3.9 Paper**

Approximately 10.2 tons of paper was used annually. Paper is used mainly for three purposes i.e. documentation, handling/drying of parts, and packaging. The finished products of the PCM process are thin and flat, and usually in small pieces. As such, the use of paper and packaging materials is not significant in PCM.

### **3.3.10 Strength and weakness analysis**

An analysis of the strengths and weaknesses of Company F to summarise the findings of the environmental audit is as follows:

#### **3.3.10.1 Strengths**

- Has a documented QMS that could be used as a basis for EMS documentation.
- Key personnel have a good knowledge and awareness of environmental impacts of the company's processes.
- Top management has committed to improve on environmental performance by initiating environmental programmes.
- As the underlying geology is composed of Oxford Clay, it is unlikely that any accidental spillage would permeate and contaminate the underground water source.



- Usage of chemicals that are affecting safety and health is closely tracked. A computer-generated monthly chemicals purchase report is forwarded to the person in charge of health and safety for monitoring.
- Quality of treated water is being monitored continuously by pH control and monthly analysis.
- Good management practice at the storage area e.g. chemicals containers were well-labelled.
- Good management of hazardous materials e.g. cyanides were stored and locked up and only competent personnel were allowed to handle them.

### 3.3.10.2 Weaknesses

- Lack of training in environmental management for the staff in general.
- The prevailing westerly and southwesterly winds could cause nuisance (e.g. odours) to the residential areas due to the closeness of residential houses to the company's operation.
- High consumption of VOCs, especially 1,1,1-Trichloroethane, an ozone depleting substance which should have been phased out in 1996.
- High water consumption and thus the effluent treatment, which is of concern to the company.
- Treatment of effluents from the photoresist development and stripping area (which is currently not treated) is required in future due to the tightening of existing regulations.
- Inadequate bunding at the chemical storage and ferric chloride loading area may cause accidents that would contaminate the surface water.
- No regular leakage test of the underground tanks which may cause contamination of land and surrounding surface water.
- Some waste chemicals were unidentifiable.

### 3.3.11 Recommendations

From the analysis above, it is obvious that Company F has both strengths and weaknesses in managing the environmental issues, which give rise to opportunities for the company to take actions to further consolidate its environmental management:

#### 3.3.11.1 Short term actions

- Substitute 1,1,1-Trichloroethane with a suitable degreasing agent.
- Collect and re-use the excess ferric chloride generated from the regeneration facility instead of draining away.
- Carry out leakage test for underground tanks at fixed intervals.
- Install adequate bunding at the chemical storage and ferric chloride loading area.
- Dispose of unidentified chemicals found in the plants.

### 3.3.11.2 Long term actions

- Substituting organic solvent-based materials such as solvent photoresist with aqueous-based materials that could both save costs and reduce environmental impacts.
- Research into ways of water minimisation and recycling, and method of effluent treatment to reduce the escalating costs of water consumption.
- Conduct research in environment-friendly ferric chloride regeneration system and install more regeneration facilities.
- Control or reduce emissions to atmosphere to foster good relationship with the local community.
- Set up and implement an integrated EMS.

## 3.4 Conclusion

The environmental audit conducted includes all aspects of the company's operation but it merely presents a general scenario of a typical PCM company in the UK. More information regarding the consumption of materials and generation of wastes of other PCM companies would be invaluable to be able to make a comparison of the environmental performance with that of other PCM companies by drawing up a set of performance indicators. Chapter 4 details the work on comparing the environmental performance measurement of two PCM companies in the UK.

## **Chapter 4**

# **Environmental Performance Measurement of Two UK PCM Companies**

### **4.1 Introduction**

If you can't measure it, you can't manage it' is an old maxim. Thus, appropriate measures are needed for effective environmental management. Environmental performance measurement is fundamental to the successful implementation of environmental policy and strategy because it provides an indication for environmental improvement. Furthermore, environmental performance reports that are not quantified are unacceptable. The demand for quantified information comes from all parties: regulators, shareholders, customers, investors, insurers, pressure groups and the general public. Environmental performance is also becoming increasingly important as an indicator of business health. Elkington, Knight and Hailes [1991] predicted that 'environmental performance indicators will in due course become as common as the traditional financial indicators now used by analysts to judge the investment potential of companies'. Lastly, both ISO 14001 and EMAS also required quantified performance measurement to show improvement in managing EMS.

Environmental performance measurement is a relatively new area with little guidance available on what companies should measure and how to go about it [BiE, 1992]. This is especially relevant to the PCM industry. Moreover, there is no absolute rule on what constitutes good performance. This Chapter is thus aimed at defining a set of environmental performance indicators for PCM companies. It is hoped that the environmental indicators developed could provide a preliminary benchmarking of the environmental performance of the PCM industry in the UK.

In defining environmental performance indicators, Azzone *et al* [1996] proposed to segregate the indicators into three categories, namely physical, financial and qualitative for ease of analysis. In developing the performance of the two PCM companies, physical indicators were used as these indicators are quantitative and have direct impacts on the environment. As such, it is an efficient tool to

measure the environmental performance of companies. These indicators are also suitable for external reporting as they are of interest to the stakeholders and the general public. Furthermore, in order to provide a level of information to judge the environmental acceptability of company activities, Bullough and Johnson [1995] envisaged that companies are increasingly likely to produce more sophisticated quantitative environmental performance reports in the future.

## 4.2 Waste Minimisation and Cleaner Technology

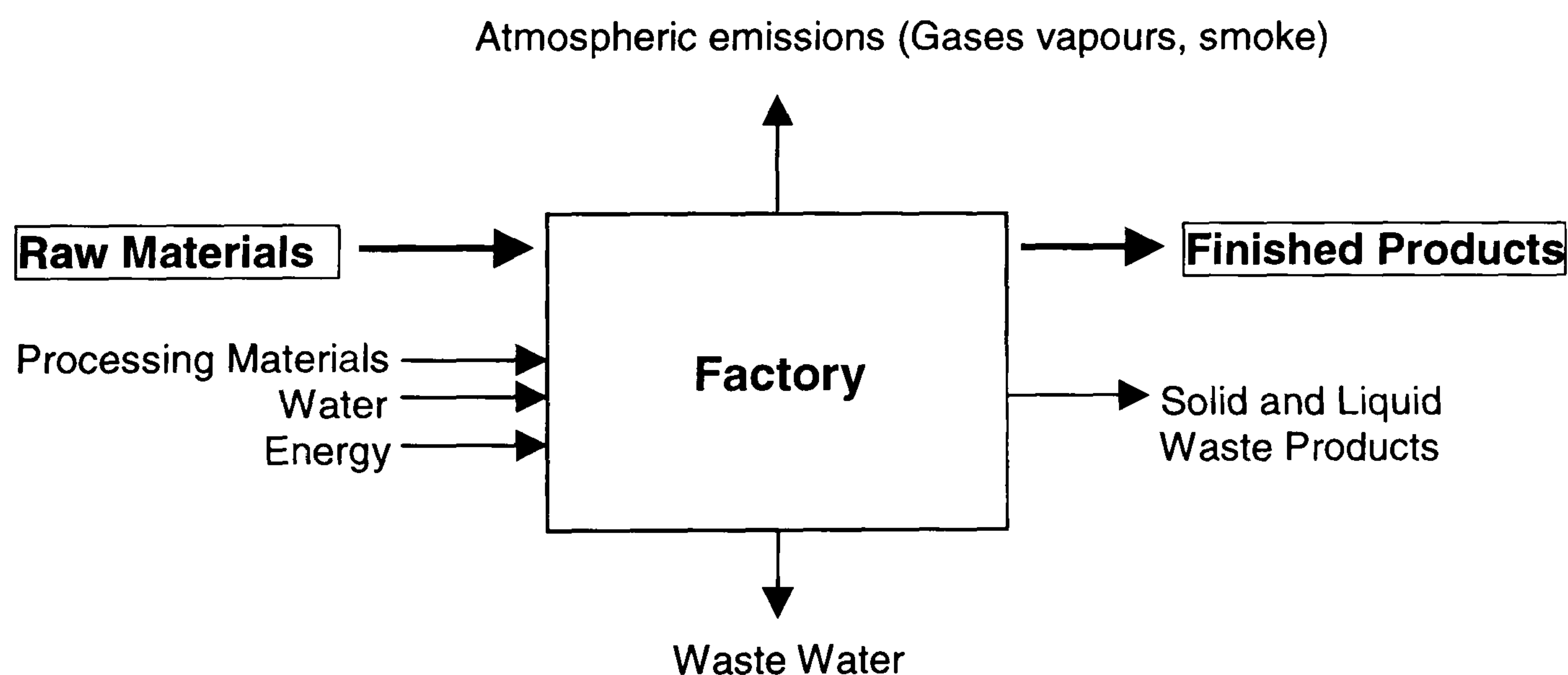
The most effective way to improve environmental performance or to minimise waste generation is through the application of cleaner technology. The philosophy behind cleaner technology is the prevention of waste generation rather than the treatment and disposal. This involves every aspect of a process to be optimized to minimize the usage of materials and generation of waste in any form. The basic options to achieve waste minimisation and management are relatively few and can be summarized in order of preference as [Allen, 1994; Slater, 1996]:

- *Reduction at Source* - The most effective way to prevent a material from entering the environment is to stop using or making it.
- *Product Changes* - A process should only be operated if the products can not be made in a cleaner way. Suitable alternative materials may perform the same function with less environmental consequences.
- *Process Changes* - A process should be designed or changed in such a way that potentially polluting materials are not made or isolated, minimizing the possibility of a release.
- *Re-use* - Re-use of a material is an alternative way of preventing release to the environment.
- *On-site Recycling* - Using a by-product of one process as a raw material for another disposes of it without an environmental impact.
- *Off-site Recycling* - Sending a by-product of a process to be used elsewhere is similar to on-site recycling, but the pollution and cost of transport and handling makes this less desirable.
- *Treatment and Disposal* - Treating the waste by chemical, physical and biological methods to render the waste harmless or less harmful. It is then disposed of to air, water or land in compliance with the law. This is the least favoured option as it is an end-of-pipe treatment and does not contribute to waste reduction.

Cleaner technology is achieved by good engineering design, good management practices, and innovative process design. Because cleaner technology is about innovative ideas for processes and proper management of people and equipment, it is not necessarily expensive technology. In other words, the advantages of using cleaner technology are as much financial as environmental [Slater, 1996; see also Benefits of Pollution Prevention in Section 2.4 of Chapter 2].

### 4.3 Objective and Method of Data Collection

The measurement involves input of materials such as raw materials, utilities and output such as product and the waste streams as shown by *Fig. 4.1*. In PCM, the final product consists of etched metal pieces (refer to *Fig. 1.1, Chapter One*). The other inputs are turned into waste materials, either as emissions to the atmosphere or liquid and solid wastes. As a result, it is assumed that all the materials, other than metal sheets consumed by the PCM process ended up as waste materials. The waste generated is therefore equivalent to the processing materials and utilities consumed, and a certain percentage of metal materials that is etched away.



**Fig. 4.1: Inputs and outputs to a company [Allen, 1994a].**

An exercise to collect quantitative data regarding pollutants/effluents generated by two PCM companies, namely Company E and Company F was carried out. This was done through visits to the above companies and data was collected via personal interviews of the companies' staff, vetting of documents such as purchase orders and data stored in the computer systems of the companies.

The objective of the exercise was to identify the environmental impacts of the PCM companies in the UK. From the impacts identified, it is then possible to formulate a set of environmental performance indicators. The scope of environmental performance measurement has been confined to the direct

effects of the photochemical machining operation that is also the focus of this project. The other processes such as CNC machining and electroplating, which may form part of the factory operations, are not being considered in this performance measurement.

#### 4.4 Consumption of Materials and Generation of Waste

A comparison of the consumption of materials of Company E and Company F is shown in *Table 4.1*. The amount of materials/utilities consumed is for one whole year of operation (the whole of 1995 for Company E and the calendar year 1 July 1995 to 30 June 1996 for Company F). The details of the data collected for this analysis is attached in Appendix B (Company E) and Appendix C (Company F).

#### 4.5 Environmental Performance Indicators

In determining the performance indicators for phototool making, the measurement is based on the amount of developers and fixers consumed against the area of photographic film used instead of raw materials (metals). This is because the use of photographic films may not be directly proportional to the amount of raw materials consumed. It is dependent on the production pattern, i.e. whether the plant is doing mass production or producing customised items. For example, in mass production plants, the use of photographic films for phototool making is much less than producing customised items as the same phototool can be used repeatedly until it develops a defect or is damaged.

In metal cleaning, the chemicals used are a mixture of acids, alkalis, proprietary chemicals of unspecified formulation (which can be acidic or alkaline) and VOCs. The total chemicals consumed are used in measuring the performance since only a rather small amount of individual chemicals are consumed. Moreover, some of the acids and alkalis would neutralise each other in the effluent treatment plant. As the usage of solvents in the metal cleaning process is rather insignificant, it is decided to include these solvents under photoresist processing.

In photoresist processing, the following performance indicators used were related to the consumption of solvents and VOCs.

- Amount of photoresist/area of metal
- Volume of solvents (thinners, developers and strippers) used to process photoresist and
- Total solvents/area of metal.

**Table 4.1: Consumption of materials and utilities**

<b>Materials used or waste generated</b>	<b>Company E</b>	<b>Company F</b>
<b>1.) Phototool making</b>		
Area of film, m <sup>2</sup>	1,640	7,081
Volume of developer, litres	240	1,050
Volume of fixers, litres	60	540
<b>2.) Metal cleaning</b>		
Acids, kg	1,680	510
Alkalis, kg	382	300
Other chemicals, kg	284	1,150
Total chemicals, kg	<u>2,346</u>	<u>1,960</u>
Solvents, litres	6	180
<b>3.) Photoresist Processing*</b>		
Photoresist, litres	480	360
Thinners, litres	500	600
Developers, litres	2,700	2,160
Strippers, litres	3,750	8,750
Other solvents, litres	275	-
<b>Total solvents (2+3), litres</b>	<u>7711</u>	<u>12,050</u>
<b>4.) Etching</b>		
Ferric chloride etchant (48°Be), litres	80,537	-
Ferric chloride etchant (43°Be), litres	-	41,500
Weight of metal etched, kg	3,360	16,100
Area of metal etched, m <sup>2</sup>	10,930	5,000
<b>5.) Effluent treatment plant**</b>		
Sodium hydroxide (32%), kg	5,182	-
Sodium hydroxide (46%), kg	-	21,000
<b>6.) Utilities</b>		
Water, m <sup>3</sup>	12,142	41,040
Electricity, KWh	402,818	594,398
<b>7.) Paper and packaging, kg</b>	-	10,183

**Note:**

\*Company E uses more dry film aqueous based photoresist that does not consume VOCs.

\*\*Company F uses sodium hydroxide for the treatment of spent ferric chloride etchant prior to disposal. Company E does not treat the spent etchant, sodium hydroxide is mainly used for neutralising waste-water.

As both liquid solvent and aqueous dry film photoresist (which is more environment-friendly) are used by Company E and F, the amount of solvent photoresist used to process per unit area of metal can gauge the relative percentage of solvent photoresist with respect to aqueous photoresist. A higher value means that a bigger proportion of the products is processed by solvent resist.

The volume of solvents such as thinners, developers and strippers consumed to process solvent photoresist is a measurement of the efficient use of solvents. The lower the value, the more efficient is the usage. The most important indicator is the total consumption of solvents and VOCs in the PCM process with regard to unit area of metal processed. This includes the solvents used in the metal preparation process. This measurement can determine the overall efficient use of solvent in the plant.

The spent ferric chloride etchant poses the most significant adverse environmental impact in the PCM process due to its acidity and the dangerous heavy metal content. As such, the efficient use of ferric chloride etchant is an important parameter in measuring the performance of PCM companies. In determining the percentage efficiency of etchant utilisation, factors that have to be taken into consideration are etchant consumed, total weight of metal processed and percentage of metal etched out (refer to Appendix B and C for details of calculations). Utilisation efficiency of more than 100% can be achieved if regeneration is used.

The waste water generated from the PCM process is acidic because of the high acid content of ferric chloride etchant. Alkalis are used to neutralise the wastewater prior to discharge to the sewage treatment plants. The consumption of alkalis can be reduced if the volume of etchant carried over the edge of the etching machine is lowered. Therefore, the consumption of alkalis is a measurement of efficiency in the conservation of etchant.

Water and electricity are the two main utilities used in the PCM process as gas is only used for heating the office and factory buildings. The main bulk of the water consumed in the PCM process is used in metal preparation, rinsing of work pieces during etching and stripping of resist after etching. The volume of water consumed per unit area of metal etched provides an indication of efficient use of the utilities. The consumption of electricity and gas have insignificant impacts on the environment as PCM is not considered as an energy intensive process.

Paper is used in documentation, packaging and drying (for some companies). The finished products of the PCM process are thin and flat, and usually in small pieces. As such, the use of packaging materials is not significant.

The environmental performance measurement indicators for Company E and Company F are shown in *Table 4.2*.



**Table 4.2: Environmental performance indicators of PCM companies**

Performance Indicator	Company E	Company F
<b>1.) Phototool Making</b> Developer/area of films, litre/m <sup>2</sup> Fixer /area of films, litre/m <sup>2</sup>	0.146 0.037	0.148 0.076
<b>2.) Metal Cleaning</b> Total chemicals/area of metal, kg/m <sup>2</sup>	0.214	0.392
<b>3.) Photoresist Processing *</b> Photoresist/area of metal, litre/m <sup>2</sup> Volume of solvents (thinners, developers and strippers) used to process photoresist, litre/litre Total solvents/area of metal, litre/m <sup>2</sup>	0.044 14.79 0.705	0.072 31.97 2.410
<b>4.) Etching***</b> % efficiency of ferric chloride utilisation	6.2	36.8
<b>5.) Alkalis**</b> Wt. of alkalis/wt. of metals, kg-NaOH /kg-metal	0.517	1.316
<b>6.) Utilities</b> Volume of water/area of metal, m <sup>3</sup> /m <sup>2</sup>	1.110	8.208

Note :

\*Company E uses more dry film aqueous based photoresist that does not consume VOCs.

\*\*Company F uses sodium hydroxide for the treatment of spent ferric chloride etchant prior to disposal. Company E does not treat the spent etchant, sodium hydroxide is mainly used for neutralising waste-water.

\*\*\*Company E has an average % etch out of 17.5% whereas Company F has only 10%.

## 4.6 Discussions

### 4.6.1 Image production/phototool making

The consumption of developer for both companies is rather similar whereas the consumption of fixer varies by more than a factor of two. Thus, Company F can improve on the usage of fixer. The scope for waste minimisation in phototool making is rather limited due to the nature of the conventional photographic process in which fixed proportion of developers and fixers are used in processing. One of the solutions to eliminate the photographic processing chemicals generated by the PCM practitioners is to use a different type of photographic product known as 'dry process phototool film' [see for example, Polaroid, 1995]. This process does not require chemical processing

or dark room environment but it merely transfers the waste generation from PCM practitioners to the suppliers of films. A better solution is to eliminate the phototool making process totally by direct imaging of the photoresist from CAD data with a laser source. This clean technology eliminates the use of photographic processing and its associated wastes. In view of the predicted increase in the cost of raw materials (photographic films and chemicals) and waste disposal, this laser direct imaging (LDI) technology breakthrough may be viable in the near future. It is thus decided to carry out a case study on the technical and economical viability of using LDI in PCM and details of this study is reported in Chapter 6 of this thesis.

#### **4.6.2 Metal preparation**

In the metal cleaning area, Company F consumed nearly twice the weight of chemicals per unit area of metal processed. Thus Company F can make some improvement in this area. The trend for metal cleaning in PCM is the use of semi-aqueous and aqueous cleaning agents [Wilk, 1994]. As such, VOCs were only used for metals contaminated with highly organic materials. In terms of process changes, reverse current and conveyorised electrolytic cleaning [Melonas, 1992] are the other alternatives for reducing environmental impacts. Allen [1993] proposed a solution to eliminate the metal cleaning processing altogether. The proposal is to have all the metals cleaned and laminated with strippable, recycled plastic films by the rolling mill prior to dispatch to the PCM companies. These additional processes would entail extra cost but may be viable in view of the costs associated with metal preparation and waste disposal that can be dispensed with by the PCM companies

#### **4.6.3 Solvent and VOC consumption**

Company F had a higher total consumption (more than 3 times) of solvents. This is because Company F uses a comparatively smaller percentage of aqueous dry film photoresist for masking and consumed much more solvent in processing the solvent resist, especially in the stripping process after etching. It is understood that both companies were in the midst of conducting technical studies to determine the suitability of using aqueous resists in their operations. The success of the research would greatly reduce the consumption of VOCs in the plant, as the use of aqueous resist means the subsequent processes, i.e. developing and stripping, would be VOC-free. As the environmental impacts of VOCs cause much concern, it was decided that a more detailed study into this issue was necessary. Thus a survey of PCM companies worldwide was carried out to gather additional data for further analysis. Details of the survey are reported in Chapter 5 and 7 of this thesis.

#### **4.6.4 Efficiency of ferric chloride utilisation**

Although Company F etched more metals in terms of weight, its usage of ferric chloride etchant was much lower. The performance indicator showed that

Company F was more than 5 times more efficient in terms of utilising ferric chloride etchant. This could be due to two reasons. First, relatively fresh etchants were disposed of by Company E, and partial regeneration facility is used at Company F. However, the % utilisation of 6.2% and 36.8% respectively are considered low by PCM industrial utilisation average. Allen [1991] estimated that the % utilisation should be between 25% and 50% without regeneration. A survey carried out later by the author showed that the industrial average is 51.1% for companies without regeneration and 340.8% for companies with regeneration [see Chapter 8; Allen and Ler, 1998].

In view of the environmental concern regarding spent ferric chloride etchant, more effort should be put into this area to reduce the environmental impacts of the etching process. Reducing the usage of ferric chloride would also reduce the consumption of alkalis used for the treatment of spent etchants. A study into the industrial utilisation efficiency of ferric chloride would enhance good environmental practice by providing a benchmark for PCM companies to make improvements. Details of this study in this benchmarking exercise are reported in Chapter 5 and 8.

The best way to increase the efficient utilisation of etchant is to use regeneration. However, the current regeneration systems have the setbacks of causing environment, health and safety hazards [Allen, 1991; Allen and White, 1992]. It was thus proposed to conduct research into oxygen regeneration, which is a more environment-friendly method and has proven to be efficient and cost-effective in regenerating ferric chloride etching print-bands. Details of this research are reported in Chapter 10 and 11.

Another alternative but less efficient method is to increase the etchant life by controlling the level of hydrochloric acid in the etching bath. Scarpellino *et al* [1996] reported that the metal loading of ferric chloride etchants can be greatly increased by maintaining the HCl or 'free acid' concentration at between 0.4% and 1.0%. Replenishment of free acid during the etching of stainless steels and copper alloys rejuvenates ferric chloride etchant in several ways. Free acid helps to solubilise the metal that is etched during the etching process. It also prevents ferrous chloride from precipitating out of solution and participates in the oxidation of this material back to ferric chloride using oxygen in the air [Allen and Ler 1995].

Controlling the order of the metals processed can also increase etchant life. For example, stainless steel is sensitive to copper by-products, as it causes a poor, rough and pitted surface finish on steel products. Thus the consumption of ferric chloride can be reduced by etching stainless steel first, followed by nickel-iron alloys, and carbon steels, with copper last [Allen, 1986c].

#### **4.6.5 Consumption of alkalis**

Company F had a higher alkalis consumption because its highly acidic etchant was treated in-house whereas Company E sent the spent etchant for treatment

and disposal by the waste contractor. As such, it is difficult to gauge the efficiency in conserving etchants between the two companies.

Reducing the volume of etchants carried over the edge of an etching machine by emerging work pieces has a few benefits. Apart from reducing the consumption of alkalis in the effluent treatment plant, it also helps to conserve etchants and minimise the quantity of rinse water required to clean a work piece before subsequent processing. Mabbett *et al* [1992] suggested a few ways to reduce the drag out of etchants. These include maintaining the etchant concentration at the lower end of the optimum operating range (thereby reducing the total amount of chemicals utilised), operating the etcher at the highest possible temperature to lower solution viscosity, allowing for sufficient solution drainage when drawing work pieces from etching tanks, and maintaining wipes in the etcher to maximise etchant capture.

#### **4.6.6 Consumption of water**

Company F consumed nearly 8 times more water to process one unit area of metal. Thus, much improvement can be made in this area. As a result of the environmental review carried out, Company F has embarked on a research programme to look into ways of conserving water. Currently in the UK, waste water generated by the PCM process is either partially treated by neutralising the acid content, or treated by a more in-depth process to neutralise the pH and precipitate the sludge (which includes heavy metals) by adding flocculating agent prior to disposal to sewage drains. The method of treatment used depends on the consents issued by the water companies. Methods that can be used to reduce water consumption include recycling the water after treatment and carrying water minimisation programmes in the plant.

#### **4.7 Conclusions**

The performance indicators in *Table 4.2* showed that there were big contrasts in terms of usage of materials and generation of waste by the PCM companies. For examples, Company E was more efficient in terms of solvent consumption whereas Company F fared better in etchant utilisation. It is evident that there is room for improvement to reduce the environmental impacts of the PCM process in the UK.

If the industrial best practices for various environmental performance indicators are available, then PCM companies can use the best practices to benchmark against their operations for environmental improvements.

## **Chapter 5**

# **Surveys of PCM Companies**

### **5.1 Introduction**

From the environmental review (see Chapter 3) and the environmental performance measurement (see Chapter 4) of the PCM companies carried out. It was shown that consumption of VOCs and ferric chloride etchants posed the most significant effects in PCM. Thus, there is a need to conduct further study into the consumption patterns of the two materials so as to establish an industrial best practice for PCM companies to benchmark.

From the literature survey carried out, only one survey has been carried out in PCM. The PCM Survey [1996] touched on more general issues such as sale, types of industries served, types of materials used, problems faced by the industry, cost of production and legal compliance. So far, there has been no study conducted to assess quantitatively, the consumption of materials such as ferric chloride and solvents.

### **5.2 Environmental Effects of Solvent and VOC**

The use of solvents and VOCs is a sensitive issue. It has been known for years that some solvents and VOCs can harm human health as they are toxic or carcinogenic [Albert, 1987]. VOCs or solvent-containing wastes are usually classified as special waste due to their toxicity and/or flammability [ETBPP and ECOTEC 1996]. Although the materials safety data sheets [see, for example, Cassio Chemicals, 1995] specified that the solvents used in PCM are not considered as a carcinogen, overexposure over a prolonged period can cause health problems such as narcosis and respiratory tract inflammation. Moreover, prolonged overexposure to xylene, used as thinner in diluting solvent photoresists, can lead to kidney damage. These solvents and VOCs are also moderately toxic to mammals, fish and bacteria.

Scientific investigations have shown that VOCs contribute to the destruction of the stratospheric ozone layer and act as global warming gases. VOCs also

take part in photochemical reactions with other substances in the air to produce photochemical smog that can potentially damage the human respiratory system, crops and natural vegetation.

The intensity of the problem has called for international joint actions. In 1987, a major initiative to reduce the substances that deplete the ozone layer was reached, which resulted in the signing of the Montreal Protocol by over 60 countries that include the UK and the rest of the EU. This Protocol was subsequently amended at the London and Copenhagen meetings of the Parties to the Protocol, requiring the manufacture and use of certain stratospheric ozone-depleting solvent to be phased out. The phase out schedule as legislated in EC Regulation 3093/94 implementing the Montreal Protocol is given in Appendix D.

Further efforts to reduce solvent and VOC consumption were reached at the meeting in Kyoto, Japan in December 1997 to limit greenhouse gas emissions in response to the threat of climate change. The agreement, known as The Kyoto Protocol, set specific emission targets for 35 member countries of the OECD and former Soviet bloc. Although carbon dioxide emission is the main contributor to the greenhouse effects, solvents and VOCs do play a secondary role.

With all these developments, it is envisaged that current legislation will be further tightened in order to reduce the solvent and VOC emissions to meet the targets set by the Protocols above. This in turn will lead to an increase in prices of solvents and VOCs. Thus, PCM companies should look into ways of reducing the consumption of the above materials.

### **5.3 Environmental Effects of Ferric Chloride Etchant**

Fresh ferric chloride etchant at a concentration of 3.37M (or 43 °Bé) is commonly used in PCM due to the high etch rate and good quality of finish. Ferric chloride etchant acts as a strong acid at this concentration. Typical pH readings are in the region of -1.0 [Kortelahti, 1996]. This is because of the presence of free acid (HCl) and the dissociation products of ferric chloride into varying species like  $\text{FeCl}_4^-$  and  $\text{Fe}(\text{H}_2\text{O})_4\text{Cl}_2^+$  [Murata and Irish, 1988; Apted, Waychunas and Brown, 1985; Wertz and Luter, 1981]. The spent ferric chloride is also strongly acidic and contains heavy metal ions. Thus, it is classified as a special waste.

The effects of ferric chloride on human bodies is equally hazardous compared to solvents used in PCM. It is a corrosive material and can cause irritation after inhalation, skin contact or eye contact according to the materials safety data sheets [See, for example, Merck, 1996; UEI, 1994]. Absorption of large quantities can cause more severe problems such as cardiovascular disorders and toxic effects on liver and kidneys. However, the effects of strong acids and

heavy metals content of ferric chloride waste on the ecosystem are more serious. In summarising two decades or more of research activity on the effects of acids on surface waters and soils, Howells [1990] concluded that

- Most fish species do not survive at pH below 4.0, whereas at higher pH (5.0-5.5), the presence of aluminium and other heavy metals act as more effective toxic agents. Moreover, the upper limit of iron content for fish life is 50 mg/litre [Merck, 1996]
- Fewer species of other aquatic life are present in acidic waters.
- Vegetation and foliar canopies are damaged if pH in the soil is below 3.0.

In addition, the findings of field experiments on restoration of acid waters and lakes also concluded that

- Reversing the acidity of waters can be achieved by reducing or stopping the emissions. However, the problem is that it is difficult to know what the pristine state of the affected environment is.
- Biological recovery or response is slow, and the recovered communities are likely to be unstable.

Thus, if the spent ferric chloride is not handled and treated properly before disposal at suitable landfill sites, the environmental consequences can be serious.

The responsibility and liability for the owner (or generator) of wastes, especially special wastes like spent ferric chloride, have increased with the imposition of Duty of Care in the EPA 1990. As such, the owner of waste has to ensure that all the waste generated is dealt with and disposed of properly by licensed waste contractors. Otherwise the owner of wastes will be responsible for any breach of regulations that includes all costs incurred in remedial works to restore the land, controlled waters and groundwater contaminated with the waste under the legislation related to contaminated land in Environmental Act 1995. The tightening of legislation coupled with the increase in landfill tax and growing scarcity of suitable landfill sites for special waste has increased the cost of ferric chloride waste disposal tremendously. It is therefore in the interest of the PCM industry to reduce the environmental effects by increasing the efficiency of ferric chloride utilisation.

#### **5.4 Objectives and Background of the World-wide Survey**

In order to gather more information regarding the environmental performance on VOC and ferric chloride utilisation, it was decided to carry out surveys of PCM companies in various countries, especially those located in the EU and

the US. A questionnaire survey was used for this information-gathering exercise as it was the most convenient and efficient method. If the information provided by the companies surveyed was incomplete, the issue could then be clarified through telephone conversation with the personnel responsible. Altogether two surveys were conducted by using questionnaires which were sent to PCM companies throughout the world which were affiliated to the Photo Chemical Machining Institute (PCMI).

#### 5.4.1 Survey on VOC and Ferric Chloride Utilisation

The objectives of this survey were to determine the environmental performance measurement and the prevailing best practice of the PCM industry regarding the

- efficiency of solvents and VOCs consumption with respect to the area of metal etched.
- efficiency of  $\text{FeCl}_3$  utilisation with respect to the weight of metal etched, taking into consideration etchant regeneration if used.

It was hoped that once the best practice of the industry was determined, the other PCM companies could use this information to benchmark against their operations.

In this survey, the companies were asked the amount of metals used, which are classified under ferrous, copper and other materials, total area of metals etched, the total consumption of ferric chloride etchant, whether regeneration of ferric chloride is used and finally, the total consumption of solvents and VOCs. A copy of the questionnaire is attached in Appendix E.

The questionnaire was designed to be in a simple format in order to get as much feedback as possible. As such, only a few vital questions regarding the consumption of materials were asked. Regarding the use of metals, companies were requested to provide data on ferrous, copper and other materials instead of a complete breakdown of materials consumed. On the solvent and VOC usage, companies were asked to provide total solvents used instead of individual items such as solvents used in metal cleaning, resist coating, developing and stripping.

As a lot of detailed information was required from the PCM companies for them to respond to this survey, the return rate was rather low. Altogether, 18 companies responded to this survey, out of 65 questionnaires sent, which represents a return rate of 27.7%.



#### 5.4.2 Survey on Regeneration and Disposal of Ferric Chloride Etchant

The objectives of this survey were as follows:

- to determine various aspects of etchant regeneration in the PCM industry. The aspects include how widely the regeneration is being used, methods of regeneration used and reasons for not regenerating etchants if it is not being used.
- to determine the current methods employed by the PCM companies in disposing of the waste  $\text{FeCl}_3$ ,
- to gauge the response of PCM companies regarding environmental protection, with respect to the use of 'cleaner' regeneration methods.

The PCM companies were asked if regeneration was used, and methods of disposing spent ferric chloride. This survey also asked for reasons for not regenerating and priorities to consider if the company intended to use regeneration in future. Lastly, the companies were asked whether they would use a more environment-friendly regeneration system at a higher overall cost. A copy of the questionnaire is attached in Appendix F. Again, a simple format was used in this questionnaire.

Altogether, 39 companies responded to this survey, out of 65 questionnaires sent, which represents a return rate of 60.0%. The rate of return in this survey was higher because only qualitative questions were asked.

#### 5.5 Reporting of Survey Findings

The results and discussions regarding survey findings on the efficiency of solvent and VOC consumption are reported in Chapter 7 of this thesis.

The theoretical consideration of ferric chloride etching reactions, the factors influencing etchant utilisation and the methodology used in calculating etchant utilisation, the results and discussions regarding the efficiency of  $\text{FeCl}_3$  utilisation and regeneration are reported in Chapter 8 of this thesis.

The results and discussions regarding the survey findings on the regeneration and disposal of ferric chloride etchant are reported in Chapter 9 of this thesis.

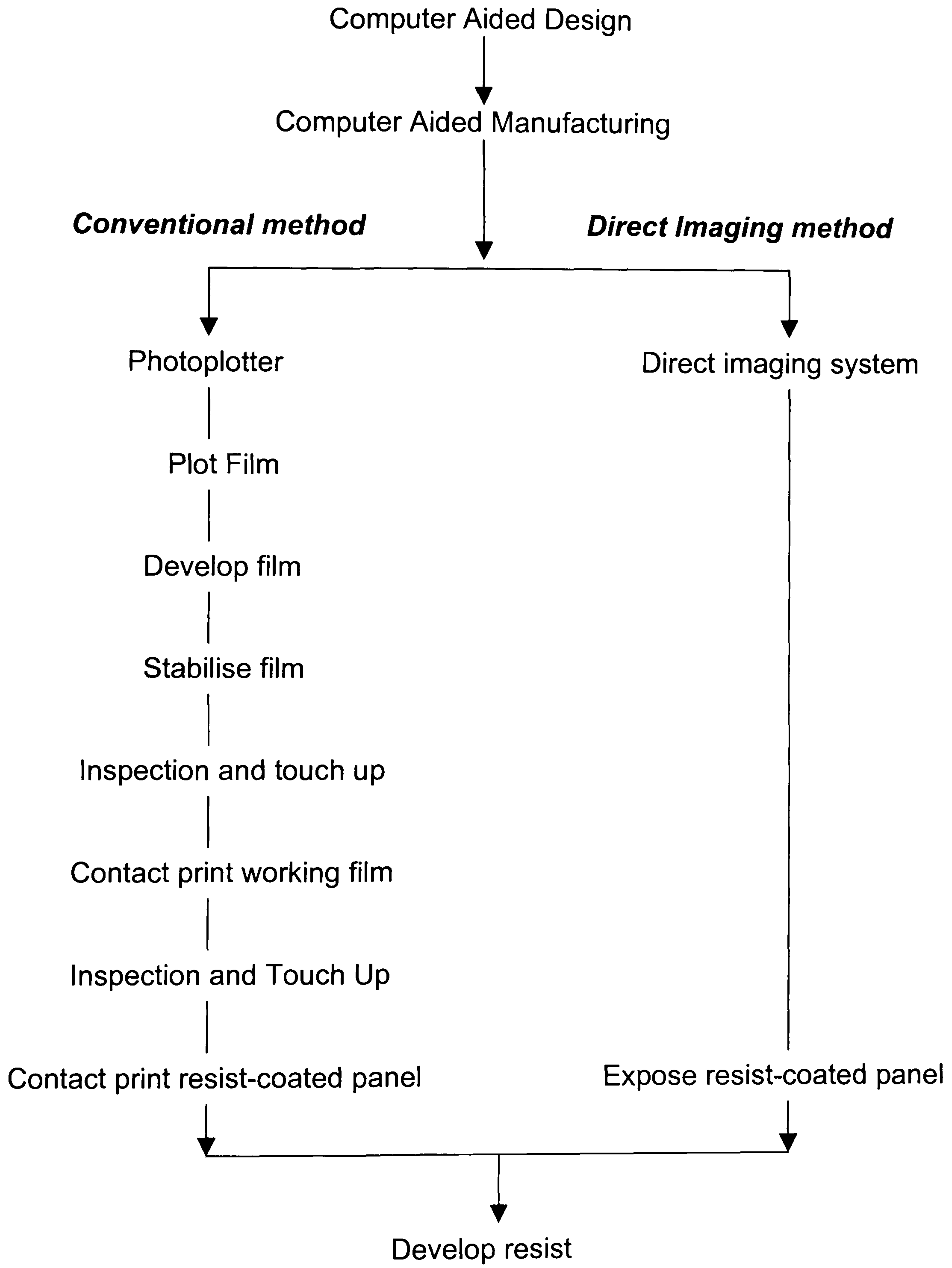
## Chapter 6

# Feasibility Study of Laser Direct Imaging of Photoresist

### 6.1 Introduction

Traditionally, phototools are used for the imaging of photoresists in PCM. Phototools are produced either from master artwork or directly from Computer-Aided Design (CAD) data [Allen 1986d]. The master artwork is produced manually or by computer-aided artwork generators and converted to a phototool by standard photographic reduction, step and repeat and contact printing techniques. In the other case, CAD data is used to drive a photoplotter or laser photoplotter to produce a phototool directly. The two methods above required the use of conventional photographic processing and thus generate waste photographic developer and fixer solutions, along with waste photographic films. As the silver metal in the waste fixer solutions is a valuable material, it is normally recovered, by cementation or electrolytic process.

In order to eliminate the use of conventional photographic processing and its associated wastes, a cleaner technology that has emerged is laser direct imaging (LDI) of photoresist. In LDI, CAD or computer-aided manufacturing (CAM) data is written directly onto resist-coated substrates employing a raster-scanned laser beam without the need of phototooling. Apart from getting rid of photographic wastes, LDI also minimises many of the problems associated with the traditional imaging process by reducing many process steps compared to the conventional imaging method as shown in *Figure 6.1*. Thus, the application of LDI could improve yields by eliminating the quality problems associated with phototool defects and operator errors [van Arnam, 1993]. The use of LDI for imaging could also enhance resolution as the laser beam has a higher degree of purity, intensity and collimation compared to the conventional UV source [Waterstreet, Inoue and Ishi, 1989; Allen and Buck, 1990; Choi, 1995].



**Figure 6.1: Comparison of imaging steps in LDI and conventional photographic processing**

## 6.2 Laser Direct Imaging System

The typical LDI system operates in a raster-scanning manner very similar in operation to a laser photoplotter used in making phototools. A LDI system creates the image on a panel by scanning a laser beam across the panel, turning the beam on and off, and moving the panel perpendicular to the beam scanning axis. Important parameters in producing image quality and resolution are pixel size, laser spot size and laser power. Pixel size refers to the size of the individual elements of the grid, whereas laser spot size refers to its diameter as defined at a certain energy level. Thus the pixel size must be large enough to cover the grid points to achieve an accurate image. Theoretically the laser spot size must be 1.4 times the pixel size for proper coverage of the pixel area. In practice, a spot size of 2 times the pixel size is often used to yield an equally sized positive and negative image [Waterstreet, Inoue and Ishi, 1989].

As the beam scans across the panel, the effective time of exposure at any one location is a fraction of a millionth of a second. Thus, the resists used for LDI have to be highly sensitive to respond to a very short exposure time. However, if a less sensitive resist is used, the system must be slowed down to provide enough energy for the resist to cure.

## 6.3 Historical Development of LDI System

Interest in LDI started in mid 1970s with the introduction of lasers and CAD/CAM into the circuit fabrication industries. Some of the early efforts towards the development of LDI systems were initiated by Bob Hines of Western Electric (US) in 1975. During the research and development period from 1975 to 1979, alternative methods for imaging were investigated, and a raster-scanning argon UV laser approach was settled upon by consensus [Twaalfhoven, 1985]. The first commercial LDI using a UV laser was developed in 1979. In mid 1980s, although ten of the Excellon Automation's second generation LDI systems were sold world-wide, it was not judged as viable due to the weak, unreliable laser source and long exposure time [Miles, 1989]. This was followed by a few unsuccessful commercial visible LDI systems. As a result, many big capital equipment suppliers subsequently decided to withdraw from this window of opportunity, citing that the LDI system was too slow and costly to be viable commercially. Currently a company, Polyscan (Tuscan, AZ, US), is known to be actively involved in improving the LDI technology [Murray, 1995]. Polyscan is now renamed ETEC Polyscan after a French party bought over the company.

## 6.4 Laser Characteristics and Advantages of LDI System

Important features of a laser which distinguish it from a conventional source are its high degree of chromatic purity, beam intensity and collimation [Choi, 1995].

- **Chromatic Purity** - High chromatic purity allows photoresist formulations to attain optimum resist absorption at a particular wavelength and minimises side reactions. For example, typical UV resists are formulated to have an absorption maximum at 365 nm, hence no new UV sensitizers need to be introduced into the photoresist for the UV LDI application.
- **Beam Intensity** - The high intensity of a laser beam in a LDI system rapidly cures the resist while minimising the negative effects of oxygen inhibition and migration of inhibitors and photopolymer components during slow exposures. In conventional UV flood type contact exposure, the lower intensity of UV beam hardens the upper resist surface quickly while the resist at the metal surface remains soft. The result is a resist which is difficult to strip or remove since the top is very hard and impervious to stripping solutions [van Arnem, 1993].
- **Collimation** - Since the shape of resist sidewall is determined by the light path, any non-collimation of the beams will produce a sidewall other than a desirable vertical geometry. Also, collimated beams minimise the line broadening due to beam spread and multiple reflections. When the resist absorption is partial, the transmitted light beam is reflected from the metal surface and reabsorbed by the resist and this reflection-reabsorption process is repeated until the beam intensity dies. This causes undesirable sidewall formation.

More advantages of a LDI system were realised during evaluation of this system which include the elimination of phototools and associated costs, high production yields (which are affected by phototool defects and operator errors), and improved process flexibility with rapid pattern manipulation using CAD/CAM data. It has been reported that IBM-Endicott and several other printed circuit board (PCB) fabricators were using Polyscan's LDI system for manufacturing products with fine-line features [Murray, 1995]. The advantages of imaging photoresist in PCM using LDI system are summarised in *Table 6.1*.

## 6.5 Problems with Development of LDI

Although LDI technology has been available since 1984 and offers several advantages, PCM practitioners have been reluctant to take advantage because of the high cost and the following technical problems during the initial stage of development [Twaalfhoven, 1985; Miles, 1989; Murray, 1995].

- Speed of machine - Although lasers offer a high scanning speed, it was still much slower than the conventional UV contact film exposure. The laser system should be as fast as conventional film exposure methods in order to be considered as a viable alternative.
- Resist Characteristics - More sensitive photoresists are required for LDI systems so that the exposure time of resists is much shorter than conventional methods of exposure (see also Section 6.2). However, resists that are more sensitive to lasers will also become more sensitive to yellow and white light and hence may require a red light environment for lamination, exposure and development. This in turn may require changes in existing darkroom conditions.

**Table 6.1 : Advantages of LDI [van Arnam 1993]**

1. Elimination of artwork and expensive glass or film phototools
  - eliminate storage requirements
  - no need for environmental 'normalisation' of artwork
  - reduced environmental impact via waste reduction
2. Reduction of additive registration errors.
3. Direct tie to CAD/CAM (electronic image transfer)
4. Rapid design changes and error corrections (reduced lead times)
5. Quick turn around for prototypes.
6. Flexible manufacturing for small lot sizes.
7. Real-time serialisation and board identification marking, including bar codes.
8. Work-in-process/inventory minimised - Compatible with JIT programmes.
9. Same machine can have dual functions - direct imaging and photoplotting.
10. Improved yields and lower costs resulting from :
  - repetitive errors from phototool
  - fewer steps, less handling and less contamination in process
  - no phototool or panel damage resulting from contact exposure
11. Fewer defects reduces
  - product inspection time
  - product repair/rework time
12. Laser imaged resist sidewalls are sharper than conventional exposures.
13. Image pattern size scaling.

- **Data Rate** - Data rate is the time required to convert the data from a vector to a raster format. A large amount of computer memory is needed for raster data and the greater the resolution of the image required, the greater the raster data. Furthermore, problems with modulation (turning the beam on and off) occur as the data rate increases.
- The lasers used in early LDI systems were low-powered, unreliable and had a short laser tube life, thus making cost of operation and maintenance prohibitively high.

Recent developments in LDI technology have resulted in improvements such as expansion of computer memories, more sensitive and faster photoresists at reasonable prices, and more reliable and less expensive key components like laser tubes [Murray, 1995]. New generation LDI machines have benefited from this revolution, thus makes this technology more viable, both technically and economically. It also provides PCM industry an opportunity to improve the environmental performance.

This Chapter is therefore aimed at studying the technical and commercial viability of using LDI in photoresist imaging for the PCM industry, taking into consideration of the developments above.

## 6.6 Specification and Performance Requirements of PCM Industry

The most important criterion for assessing the suitability of a new technology is to test whether its specification meets the current manufacturing requirements. It is thus important to ensure that the quality performance of LDI equals or exceeds that required by the existing PCM industry. *Table 6.2* provides a comparison of the performance requirements of photoresist imaging of the PCM industry and the specification provided by the latest LDI system.

From the figure provided, it is clear that the LDI system has no problem meeting the manufacturing requirements of the PCM industry except the requirement for exposure time, where LDI is much slower. The problem becomes more acute if a slower resist is used, as the exposure time will be longer than 60 seconds. However, on close examination, it was found that the total cycle for resist exposure which includes loading and unloading using a typical UV exposure unit is approximately 90 seconds. Moreover, the bottleneck in resist processing is not during the resist exposure; it is in the development area instead. For example, the development time for resist is approximately twice that of UV exposure time when liquid solvent resist is used and as a result, the UV exposure unit is not utilised most of the time. Since the loading and unloading time is the same for both systems, the slower exposure time of the LDI system can still meet the requirement of the PCM industry.

**Table 6.2: Comparison of specifications of LDI and performance requirements of PCM**

Features	LDI Specification*	PCM Requirement
Minimum line-width ( $\mu\text{m}$ )	12.5	25
Minimum spot size ( $\mu\text{m}$ )	12.5	25
Minimum feature ( $\mu\text{m}$ )	50.0	50.0
Exposure time for a 45 x 60 $\text{cm}^2$ panel (seconds)	60**	20-25
Maximum area of imaging (cm)	61 x 71	47 x 66***
Maximum substrate thickness (mm)	15.87	Rarely exceeds 1.5 mm

\*Source: Polyscan™ 2430 Technical Description – This is the latest LDI system developed by Etec Polyscan, Inc, USA.

\*\*For panel coated with 15  $\text{mJ}/\text{cm}^2$ . A longer exposure time is required when a slower resist is used. Typical resist speed used by PCM industry currently is between 200-300  $\text{mJ}/\text{cm}^2$  (liquid resist) and 70-80  $\text{mJ}/\text{cm}^2$  (dry film).

\*\*\*Except big decorative items where sizes can vary.

It should be pointed out that the current LDI system that meets the technical requirements of PCM has not been tested on the commercial environment. It is thus not able to verify the reliability of its performance.

## 6.7 Qualitative Evaluation of LDI system against Conventional Photographic Processing

Table 6.3 shows the qualitative comparison of the conventional method of photoresist exposure and LDI system.

### 6.7.1 Equipment

Both systems use similar CAD/CAM hardware and software to produce the profiles of the final products. However, a conventional system requires at least a laser photoplotter, photographic development machine and modifier, and UV exposure/curing machine for making phototool whereas CAD/CAM data is fed directly into the LDI system for imaging and curing of photoresist. Photographic processing and modifier is not necessary.



**Table 6.3: Qualitative evaluation of conventional and LDI system**

Item	Conventional Imaging	Laser Direct Imaging
<b>Equipment</b>	<ul style="list-style-type: none"> <li>• CAD/CAM hardware and software</li> <li>• Laser photoplotter</li> <li>• Photographic development machine</li> <li>• Photographic modifier</li> <li>• UV curing machine</li> <li>• Resist coating</li> </ul>	<ul style="list-style-type: none"> <li>• CAD/CAM hardware and software</li> <li>• LDI system</li> <li>• Resist coating</li> </ul>
<b>Space</b>	<ul style="list-style-type: none"> <li>• For equipment and staff</li> </ul>	<ul style="list-style-type: none"> <li>• For equipment and staff</li> </ul>
<b>Operational Cost</b>		
- Labour	<ul style="list-style-type: none"> <li>• Processing of CAD/CAM</li> <li>• Photographic development/modify/touch up</li> <li>• UV imaging</li> </ul>	<ul style="list-style-type: none"> <li>• Processing of CAD/CAM</li> <li>• Photographic processing is not required</li> <li>• LDI imaging</li> </ul>
- Materials	<ul style="list-style-type: none"> <li>• Phototool processing <ul style="list-style-type: none"> <li>- Photographic films</li> <li>- Fixers/developers</li> </ul> </li> </ul>	<ul style="list-style-type: none"> <li>• Not applicable</li> </ul>
- Utility cost	<ul style="list-style-type: none"> <li>• Power</li> <li>• Water</li> </ul>	<ul style="list-style-type: none"> <li>• Power</li> <li>• Water</li> </ul>
- Preventive/ breakdown maintenance	<ul style="list-style-type: none"> <li>• Photoplotter, photographic development, UV curing machine.</li> </ul>	<ul style="list-style-type: none"> <li>• LDI system</li> </ul>
- Waste treatment	<ul style="list-style-type: none"> <li>• Photographic waste</li> <li>• Other waste, development of resist and its rinse water</li> </ul>	<ul style="list-style-type: none"> <li>• Not applicable</li> <li>• Other waste, development of resist and its rinse water</li> </ul>
<b>Quality cost</b>		
- Yield	<ul style="list-style-type: none"> <li>• Lower</li> </ul>	<ul style="list-style-type: none"> <li>• Higher</li> </ul>
- Lead time (quick turnaround)	<ul style="list-style-type: none"> <li>• Longer</li> </ul>	<ul style="list-style-type: none"> <li>• Shorter</li> </ul>
- Quality	<ul style="list-style-type: none"> <li>• Lower</li> </ul>	<ul style="list-style-type: none"> <li>• Higher</li> </ul>

### 6.7.2 Space

Both systems need the same space to house the equipment and staff.

### 6.7.3 Operational cost

The operational cost consists of costs of labour, materials, utilities, maintenance and waste treatment.

#### 6.7.3.1 Labour

The same level of skill and amount of labour is required in the processing of customers' drawings into CAD/CAM data for both systems. However, phototool making, which is a laborious process, is not required in the LDI system. In conventional photographic processing, labour is required to operate the photoplotter, photographic processing unit and lastly, to touch up and modify the phototools as and when necessary as distortions may occur during the image plotting and photographic development process.

#### 6.7.3.2 Materials

Photographic films, developers and fixers solutions are required for the manufacture of phototools in the conventional process whereas all these materials are not required in the LDI system.

#### 6.7.3.3 Utility

The main utility cost for LDI system is the electrical power in running the laser imaging and chilling water system. For the conventional system, electrical power is used to drive the photoplotter, operate the UV exposure machine and photographic processing unit. A small amount of water is also required in the photographic processing area.

#### 6.7.3.4 Preventive/breakdown maintenance

Both systems require preventative and breakdown maintenance although the cost of maintaining the LDI system may be higher as it is more sophisticated.

#### 6.7.3.5 Waste treatment/disposal

Waste developers and fixers solutions have to be treated prior to disposal. The photographic film is disposed of as solid wastes. Both systems are identical in developing the resists. The cost of waste treatment and disposal may not be significant.

### 6.7.4 Quality cost

Choi [1995] reported that the yield loss for conventional photographic processing system is much higher than LDI. The other quality costs such as shorter lead time and higher quality inherited in the LDI system are not tangible and thus is difficult to be quantified in the evaluation.

## 6.8 Economic Evaluation

In evaluating the economics of the two systems, detailed costing of the phototool making and photoresist imaging department of Company F was used. It is based on the qualitative analysis as detailed in *Table 6.3* of Section 6.7. Those areas where similar equipment, materials or labour are required for both systems are omitted in this analysis. The results of analysis are as shown in *Table 6.4*.

Since the space requirements of the two systems were found to be approximately the same, it is not taken into the calculation of cost. The total annual cost of the system is thus made up of annual cost of equipment amortized, total operational cost and quality cost. The total operational cost consists of labour, materials, utility, maintenance and replacement of parts, and cost of waste treatment.

In considering the cost implications of the two systems, it is assumed that:

- (1) The cost of capital equipment can be amortized over a 5-year period.
- (2) As a yield loss of 30% was reported for conventional photographic processing system of resist imaging when compared to the LDI system [Choi, 1995], this value is used as the basis of calculation in imposing the quality cost for Company F.

In the course of data collection, numerous attempts were made to request data from the equipment manufacturer. However, only certain data were made available such as the cost of equipment and life of laser tube. The other data like the cost of maintenance, replacement of parts, utility cost and reliability of the system were not able to be obtained from the equipment supplier. This is because the system has not been tested on the actual production environment [Polyscan, 1997].

## 6.9 Discussion and Conclusion

From the analysis carried out, it was found that the total cost of operating the conventional system of phototool making and photoresist imaging is £154,674 per annum. The total cost of operation for LDI system, excluding maintenance, replacement of parts and utility cost is £120,000 per annum. It is thus not possible to judge the feasibility of applying this more environment-friendly technology to the PCM process at this juncture as a lot of key data is still not available. For the LDI system to be viable economically, the total cost of operation must not exceed that of the conventional system.

**Table 6.4: Cost comparison of conventional photographic processing and LDI system**

Item	Conventional Photographic Processing	Laser Direct Imaging
<b>I. Cost of equipment</b> (Amortized over a 5-year period)	<ul style="list-style-type: none"> <li>Laser photoplotter 1 - £75,000</li> <li>Laser photoplotter 2 - £18,000</li> <li>Photographic development machine -£5,200</li> <li>Photographic modifier - £4,475</li> <li>UV curing machine - £19,000</li> </ul> <b>Total equipment cost: £121,675</b> <b>Cost per annum: £24,335</b>	LDI system - £550,000  <b>Total equipment cost: £550,000</b> <b>Cost per annum: £110,000</b>
<b>II. Space requirement</b>	Approximately 30 m <sup>2</sup>	Approximately 30 m <sup>2</sup>
<b>III. Operational cost (per annum)</b>	<ul style="list-style-type: none"> <li>Labour               <ul style="list-style-type: none"> <li>3 persons in photographic processing = £8,500 x 3 = £25,500</li> <li>One person in UV exposure of resist = £8,500</li> </ul> <b>Cost of labour: £34,000</b> </li> <li>Materials               <ul style="list-style-type: none"> <li>Photographic films £47,126</li> <li>Fixers £882</li> <li>Developers £1,547</li> </ul> <b>Cost of materials: £49,555</b> </li> <li>Utility               <ul style="list-style-type: none"> <li>Power - £350</li> <li>Water - Negligible</li> </ul> </li> <li>Maintenance and replacement of parts               <ul style="list-style-type: none"> <li>Photoplotter - £18,000</li> <li>UV exposure machine - £1,000</li> <li>General maintenance - £1,500</li> </ul> <b>Cost of maintenance: £20,500</b> </li> <li>Cost of waste treatment               <ul style="list-style-type: none"> <li>Waste water and solid waste - £500</li> </ul> </li> </ul> <b>Total operational cost: £104,555</b>	<ul style="list-style-type: none"> <li>Not required</li> <li>Imaging of resist; LDI requires more skilful staff due to the sophistication of equipment. = £10,000</li> <li>Cost of labour: £10,000</li> <li>Not required</li> <li>Not available</li> <li>Not available</li> <li>LDI system - Data not available</li> <li>Not required</li> </ul> <b>Total operational cost: £10,000</b> (excluding maintenance, replacement of parts and utility cost)
<b>IV. Quality cost</b> (30% of total cost of rejects of Company F)	<b>£25,434</b>	Not required
<b>Total cost</b>	<b>£154,674</b>	<b>£120,000</b> (excluding maintenance, replacement of parts and utility cost)

In addition, the following aspects of operation must be fulfilled before LDI can be introduced to the PCM process:

- (1) The system has to withstand the reliability test. Although the LDI system specification provided by the equipment manufacturer can meet the production requirements of PCM, the reliability of the system has not been tested commercially at the time of writing. It is thus not possible to ascertain whether the system can perform reliably in order to meet the PCM requirements.
- (2) The types of resists for LDI must be suitable for the PCM process and cost-effective. Preferably, the existing production environment (dark room condition) should be maintained as far as possible.

## Chapter 7

# Solvent and VOC Consumption of PCM Companies

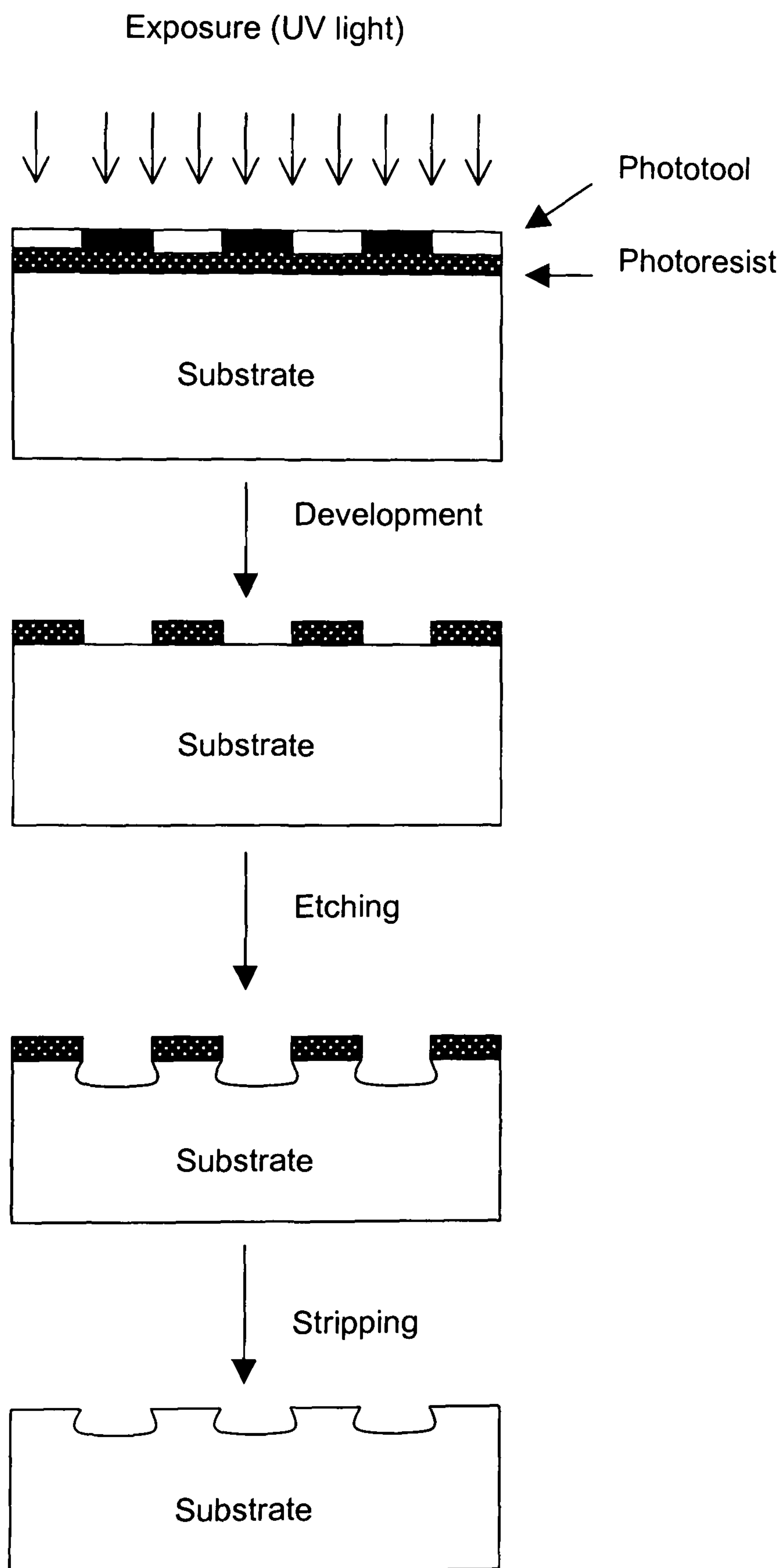
### 7.1 Introduction

In PCM, solvents are mainly used in metal preparation and photoresist processing.

In metal preparation, organic solvents are used as cleaners in removing oil, waxes, greases and other organic materials on the metal surfaces. Although the trend for metal cleaning in PCM is to use more aqueous and semi-aqueous cleaning agents, organic solvents are still used, especially if the company uses a chemical cleaning method in removing the surface contaminants on the metal.

However, the use of solvents in metal preparation is insignificant compared to the amount consumed in photoresist processing. For example, Companies E and F consumed 0.08% (6 litres out of 7700 litres) and 1.46% (180 litres out of 12,370 litres) of the total solvents used respectively in the metal preparation process. The main bulk of solvents consumed in PCM is to process organic solvent-based photoresist, as reflected in *Table 4.1 of Section 4.4* of this thesis. This is because organic solvents and VOCs have to be used in the subsequent processing of solvent-based resist such as the development and stripping process. *Figure 7.1* shows the various steps involved in the processing of a metal substrate coated with negative-working photoresists.

Currently, photoresists used in PCM can be divided into liquid organic solvent-based, liquid aqueous-based and dry film resist. Aqueous-based photoresist is perceived to be more environment-friendly as it eliminates the use of organic solvents. It can be in dry film or liquid form. Dry film resist is now widely used commercially whereas the positive working aqueous photoresist is not used due to some technical reasons such as lack of chemical resistance to survive the long etching times needed, thus it is too fragile to be used in PCM [Moyer and Wagner, 1992].



**Figure 7.1: Processing of metal substrate coated with negative-working photoresist**

Basically, a liquid solvent-based resist consists mainly of resin polymer and solvents with some additives to prevent reactions occurring on contact with metal. The commercial photoresist is usually diluted with thinners, that is made up of xylenes, in order to achieve the desired coating thickness and other qualities such as good adhesion to the metal surface.

The developers used consist of white spirit and xylene whereas the strippers consist mainly of xylene. The composition of organic materials used in solvent-based photoresist processing in PCM is as shown in *Table 7.1*.

**Table 7.1: Typical composition of materials involved in organic solvent based photoresist processing**

Materials	Compositions
Photoresist	Resin polymer, 30-40% Xylenes, 60-70% 2-methoxyethanol <5%
Thinner	Xylenes
Developer	White spirit >90% Xylenes <10%
Stripper*	Formic acid 3% Aromatic hydrocarbon 75%

\*Proprietary chemicals, exact chemical composition is unknown

It can be seen that the solvents used in resist processing consist mainly of VOCs, substances that come under continually scrutiny of government regulators and environmental pressure groups. Thus, if the PCM practitioners can eliminate the use of solvent-based resist in processing, VOC emissions would no longer become an environmental issue for the industry. From the data collected (See Chapter 4) and company visit [Company N, 1997], it was found that liquid solvent-based resist was still widely used by PCM companies in the UK. In order to gather more information regarding the consumption trend of solvents and VOCs in PCM, a world-wide survey of PCM companies was carried out.

## 7.2 Development of Resist Technology

In the early 1960's, the only photoresist available to the PCM companies was liquid-based. Most of these resists were organic solvent-based and thus required solvent systems for developing and stripping. Several liquid aqueous-based photoresists introduced in the mid 1960's were unsuitable for the PCM



industry although they offered some cost savings, because many of these products were too fragile for long etching times required for PCM.

The first dry film photoresist introduced by Du Pont in 1968 was a solvent developable resist. Semi-aqueous (mixture of aqueous solution and organic solvent are required for development) and aqueous systems were introduced later on. However, the earlier aqueous-based dry film resists were developed mainly to improve the production cost, yield and quality of products. Some of the earlier literature on dry film resists mentioned ways to improve resolution and adhesion [Bridges, 1987], and to improve resolution, increase throughput and high etch throughput [Moyer and Wagner, 1992]. Thus, environmental problems caused by the solvent system were not the main reasons for switching to the aqueous systems. However, things began to change after that. In introducing a new aqueous-based system, Lott [1993] strongly emphasized the environment-friendliness of the resist instead of cost, throughput, yield and related issues.

However, more research and development efforts were targeted towards developing a suitable liquid aqueous-based resist as it has better adhesion characteristics [Schwab, 1995]. The dry film resist is also brittle and the overhang cannot be maintained and tended to peel off unevenly especially when etching thicker substrates. Electrophoretic deposition resist is one of the aqueous systems developed to address this window of opportunity [Ryder, 1995; Schwab, 1995; Sakurai and Nishijima, 1995]. However, the system was developed to suit automation needs of resist processing in mass production plants and thus was not suitable for PCM companies that normally cater for various types of products with different order sizes. As a result, many PCM practitioners found difficulties in controlling the production process to meet the operating requirements of electrophoretic coating. Efforts to pursue a better solution for a more suitable resist began to bear fruit lately; recent joint research into liquid aqueous-based negative working resist carried out by the photoresist suppliers and PCM companies have produced some promising results. The initial trial runs showed that such resists are cost effective and suitable for PCM application [Bird and Kapp-Schwoerer, 1997; Striedieck and Albin, 1997]. The success of this research effort would help to solve a crucial environment issue for the PCM industry in the UK.

### **7.3 Analysis of Survey Findings and Discussion**

The results of the 18 companies that have responded to this survey are as shown in *Table 7.2*. There is a big variation in terms of solvent utilisation as some companies used rather big amount of solvents and VOCs whereas the others have totally eliminated the usage of solvents in their process.

The use of solvents is directly proportional to the area instead of the weight of metal etched. Thus, the area of metal is used to calculate the solvent

consumption efficiency. The average consumption of the companies surveyed was found to be 0.106 litre per square metre of metal etched (litre/m<sup>2</sup>). Company F has the highest consumption of solvents at 2.474 litre/m<sup>2</sup>, which is more than twice the amount used by the second highest company.

It is interesting to note that 38.9% (7 out of 18) of the companies that responded have totally eliminated the use of solvents in their process. This shows that these companies were using aqueous-based resist and non-chemical cleaning methods in the metal preparation such as pumice spray, a physical cleaning method. However, only companies located in areas where materials for physical cleaning are readily available can use this method of cleaning. Meanwhile, two companies, namely G and L had a very low solvent consumption. This is probably because these two companies have switched to aqueous-based resist and organic solvents were only used in cleaning the organic matter on the metal surface during the metal preparation process. If these two companies are taken into consideration, then the total percentage of companies that are using only aqueous based photoresist is 50.0% (9 out of 18).

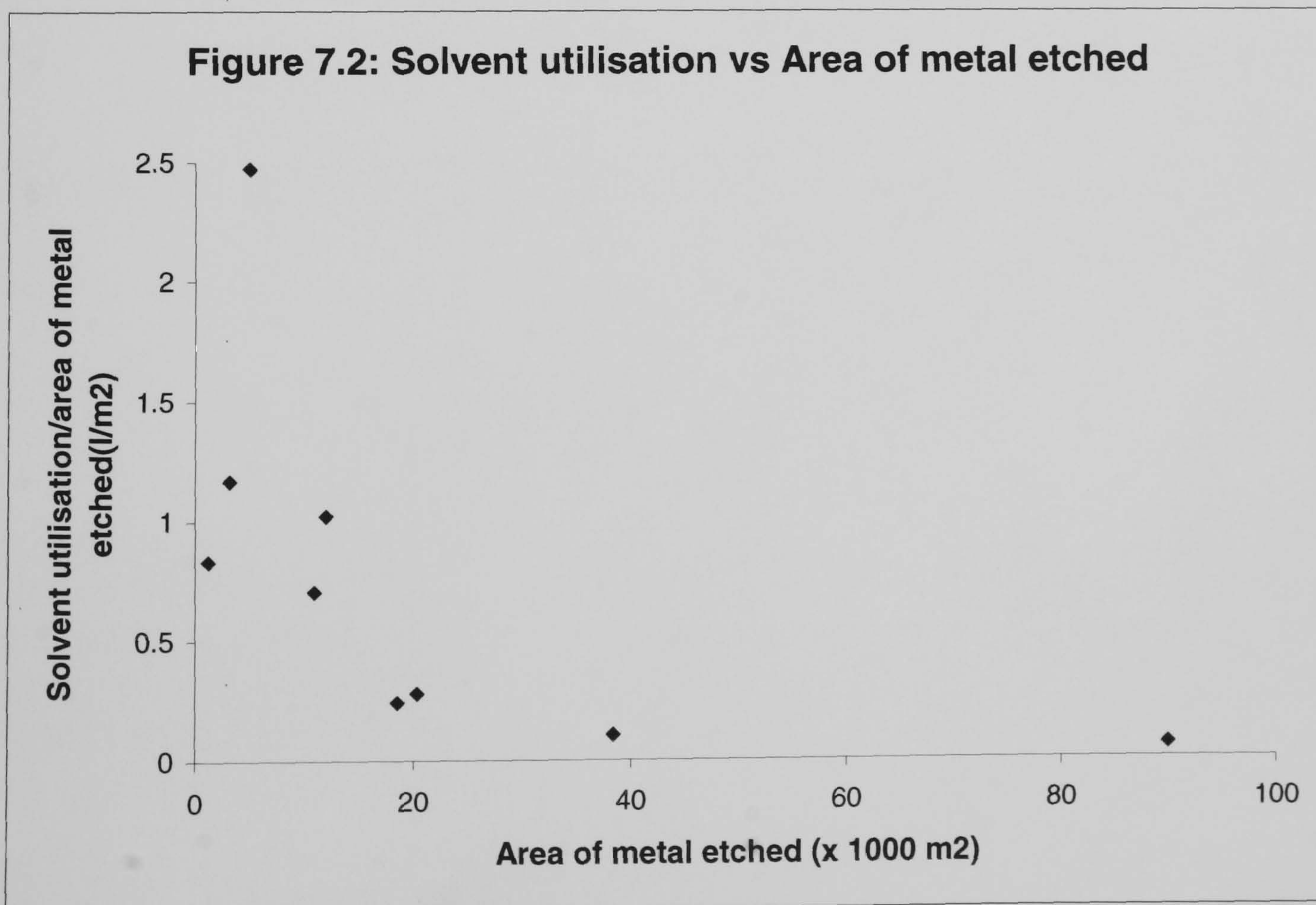
**Table 7.2: Comparison of solvent consumption of PCM companies**

Company	Weight of metal (kg)	Area of metal (m <sup>2</sup> )	Volume of solvent (l)	Volume of solvent /area of metal (l/m <sup>2</sup> )
A	50,000	45,000	0	0
B	11,150	3,150	3,679	1.168
C	9,000	5,100	0	0
D	15,400	18,550	4,513	0.243
E	3,360	10,930	7,700	0.704
F	16,100	5,000	12,370	2.474
G	130,000	45,000	120	0.003
H	8,915	2,925	0	0
J	8,400	1,200	1,000	0.833
K	2,160	2,500	0	0
L	1,611	2,700	50	0.019
M	16,950	7,540	0	0
N	29,270	12,000	12,290	1.024
P	364,729	38,400	4,000	0.104
Q	460,000	216,480	0	0
R	10,758	4,786	0	0
S	33,181	20,345	5,700	0.280
T	30,000	90,000	5,000	0.056
Total	1,200,984	531,606	56,422	Average = 0.106

By omitting companies that have eliminated the use of organic-solvent based photoresist (*Table 7.3*), the solvent utilisation of companies is plotted against the area of metal etched (*Figure 7.2*). The curve indicates a pattern that obeys the law of economics of scale in general; the larger the area of metal etched, the more efficient the solvent is used. This is expected as low volume production plants normally produce a higher ratio of wastage per unit product, especially working with volatile substances that tend to vaporise while they are being used in production.

**Table 7.3: Comparison of solvents consumption of PCM companies**

Company	Area of metal (m <sup>2</sup> )	Volume of solvent (l)	Volume of solvent /area of metal (litre/m <sup>2</sup> )
J	1,200	1,000	0.833
B	3,150	3,679	1.168
P	38,400	4,000	0.104
D	18,550	4,513	0.243
T	90,000	5,000	0.056
S	20,345	5,700	0.280
E	10,930	7,700	0.704
N	12,000	12,290	1.024
F	5,000	12,370	2.474



## 7.4 Conclusion

The survey findings indicated that 50.0% of the responding companies have switched to aqueous-based resist in their operation. This figure coincides with the findings of a separate survey carried out by the Photo Chemical Machining Institute [PCMI, 1996] which showed that 57.4% (27 out of 47) of the companies that responded used aqueous dry film resist in their production process. These two survey findings have shown that the aqueous resists are commercially acceptable, cost effective and suitable for the PCM process.

The literature survey on the development of modern photoresist technology indicated that the search for a suitable liquid aqueous based resist for the PCM industry has been fruitful. One of the companies involved in the research, Tecan Components Ltd., intended to fully convert to the new resist in the near future [Tecan, 1998]. This showed that this newly developed aqueous resist is also viable for commercial production. Thus, it provides another alternative for the PCM industry.

The above study clearly showed that the consumption of solvents and VOCs could be eliminated or reduced in the PCM industry. Since the solvents and VOCs are mainly consumed as a result of using solvent based photoresist and its related processing, those companies that are still using solvent resist should convert to the aqueous based dry film or newly-developed liquid resist to make PCM a more-environment-friendly process.

## Chapter 8

# Quantitative Analysis of Ferric Chloride Etchant Utilisation

### 8.1 Introduction

Ferric chloride etchant is a mixture of ferric chloride, hydrochloric acid and water. Ferric chloride is a red brown, volatile solid that is very hygroscopic and forms a yellow-brown solution. The solution at about 3.37M is a commonly-used etchant in PCM due to the high etch rate and good quality of finish at this concentration. The environmental effects of ferric chloride etchant have been discussed in Chapters 1 and 5. The main aim of this chapter is to present the findings of the survey on the utilisation of ferric chloride etchant in PCM.

### 8.2 Theoretical Considerations in Determining Efficiency of Etchant Consumption

The basic chemistry for etching metals with  $\text{FeCl}_3$  solution is as follows:



for     M = Metals etched such as Fe, Ni, Cu and Al  
           x = Valency of metal etched

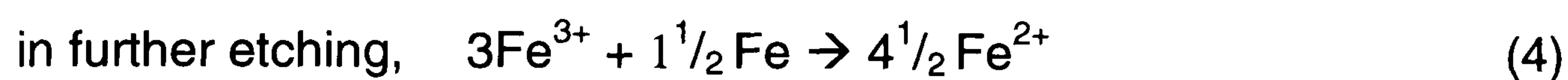
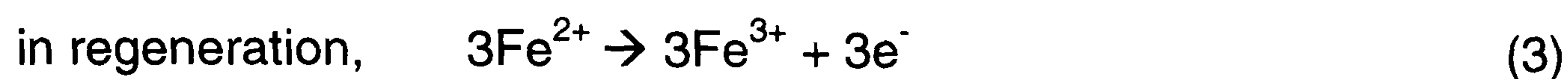
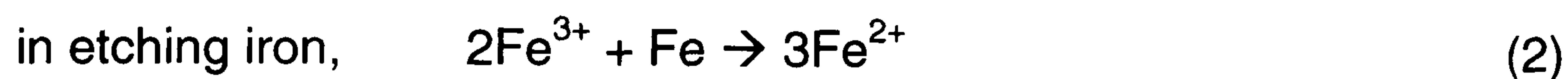
For example, for every mole of iron and copper (which have a valency of 2) that is etched, 2 moles of ferric chloride are consumed. For 100% efficient utilisation of etching solution, the volume of etchant required to dissolve one tonne of iron and copper is given in *Table 8.1* and *Table 8.2* (for detailed calculations, see Appendix G).

## 8.2.1 Regeneration of etchants

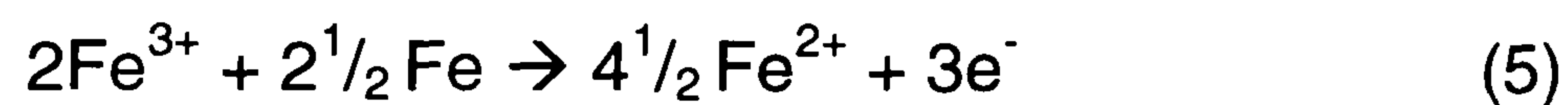
There are various methods that can be employed to reduce the consumption and thus the environmental impacts of ferric chloride. Regenerating the spent ferric chloride etchant by oxidation is one of the methods that can be employed to minimise the wastes generated by the etching system.

### 8.2.1.1 Regeneration of etchants in etching iron

The chemical reactions of regeneration of  $\text{FeCl}_3$  in etching iron are as follows:

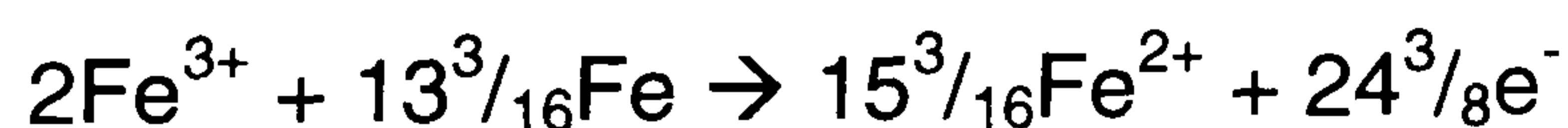
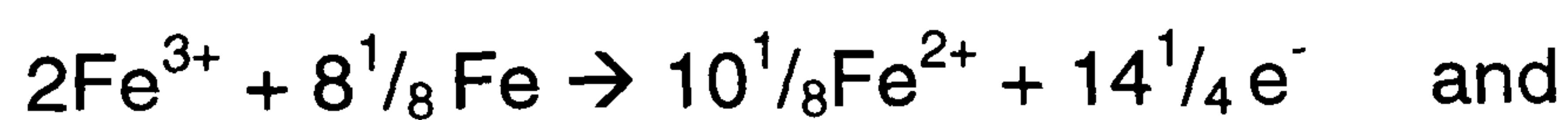
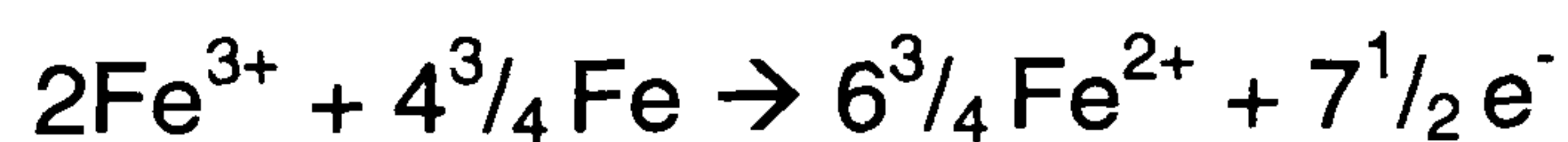


Adding (2), (3) and (4) gives overall



Comparing (2) and (5), it can be seen that  $2\frac{1}{2}$  times the amount of iron can be etched after a single regeneration ( $R^1$ ) cycle than without one. Thus the utilisation is 250%. As such, for companies carrying out regeneration in their operations, more than 100% utilisation of etchants is possible.

Similarly, it can be derived that the percentage utilisation of ferric chloride after two ( $R^2$ ), three ( $R^3$ ) and four ( $R^4$ ) rounds of regeneration are 475% ( $4\frac{3}{4}$  times), 812.5% ( $8\frac{1}{8}$  times) and 1318.75% ( $13\frac{3}{16}$  times) respectively by the following equations:



From the above, it is observed that the percentage (%) utilisation of etchant regeneration follows a regular pattern as below:

$$R^1 = (1 + 1.5^1) \times 100\% = 250\%$$

$$R^2 = (1 + 1.5^1 + 1.5^2) \times 100\% = 475\%$$

$$R^3 = (1 + 1.5^1 + 1.5^2 + 1.5^3) \times 100\% = 812.5\%$$

$$R^4 = (1 + 1.5^1 + 1.5^2 + 1.5^3 + 1.5^4) \times 100\% = 1,318.25\%$$

Thus, the % utilisation of ferric chloride in etching iron when regeneration is used can be expressed mathematically by the following formula:

$$R^n = (1 + 1.5^1 + 1.5^2 + 1.5^3 + \dots + 1.5^{n-2} + 1.5^{n-1} + 1.5^n) \times 100\%$$

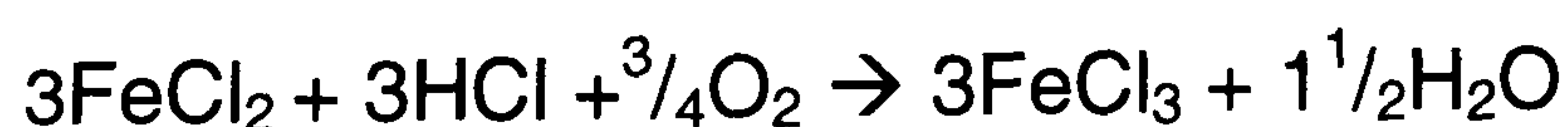
Where n = number of times regeneration is carried out.

**Table 8.1: Relationship between regeneration cycles, % utilisation and volume of etchant required for dissolution of iron**

No. of regeneration of FeCl <sub>3</sub>	% utilisation of FeCl <sub>3</sub>	Vol. (l) of FeCl <sub>3</sub> required for dissolution of 1 tonne of iron
No regeneration	100	10,626
One	250	4,250
Two	475	2,237
Three	812.5	1,318
Four	1318.75	806

Table 8.1 indicates that the volume of ferric chloride etchant required to etch ferrous materials decreases considerably when regeneration is used. For example, after four regenerations, only 806 litres of ferric chloride is required to etch one tonne of iron compared to 10,626 litres required for 100% utilisation when no regeneration is used. As such, apart from reducing environmental impacts, the use of regeneration would reduce the cost of production in view of the price increase of fresh etchant, and the soaring cost of waste etchant disposal due to increasing scarcity of landfill sites and tightening of environmental legislation.

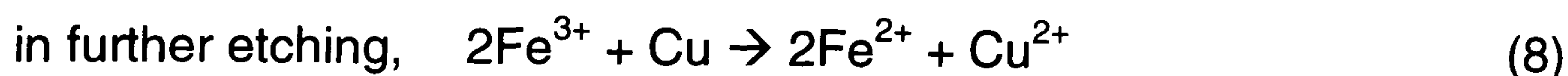
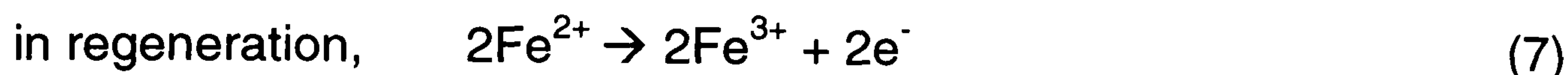
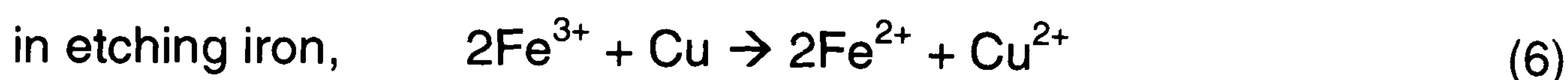
It should be noted that more than 100% utilisation of etchants is possible even in PCM companies that are not regenerating the etchants as the presence of free acid (HCl) and dissolved oxygen in the etching solution can cause 'natural' regeneration to take place according to the equation:



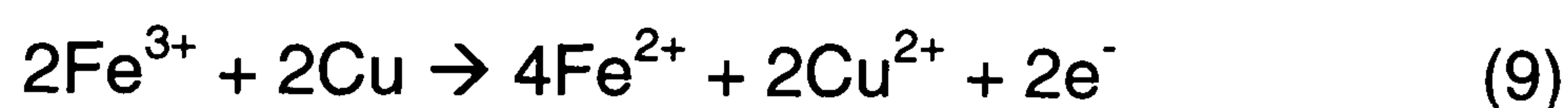
although the aerial oxidation process is not as quick or efficient as using chlorine, sodium chlorate, electrolysis or ozone. Previous research by Scarpellino *et al* [1996] has also shown that if the free acid is replenished and maintained at a certain level in the etching process, the overall metal loading of the etchant can be greatly increased. This is because the presence of free acid allows ferrous ions to stay in solution from which state they can be oxidised by the dissolved oxygen in the solution to ferric ions. This reaction cannot occur if the ferrous ion is in a solid state after precipitation out of solution.

## 8.2.1.2 Regeneration of etchants in etching copper

The chemical reactions of regeneration of  $\text{FeCl}_3$  in etching copper are as follows:



Adding (6), (7) and (8) gives overall



Comparing (6) and (9), it can be seen that twice the amount of copper can be etched after a single regeneration ( $\text{R}^1$ ) cycle than without one. Thus the utilisation is 200%. Similarly, it can be derived that the percentage utilisation of ferric chloride in etching copper after two ( $\text{R}^2$ ), three ( $\text{R}^3$ ) and four ( $\text{R}^4$ ) rounds of regeneration are 300%, 400% and 500% respectively by the following equations:

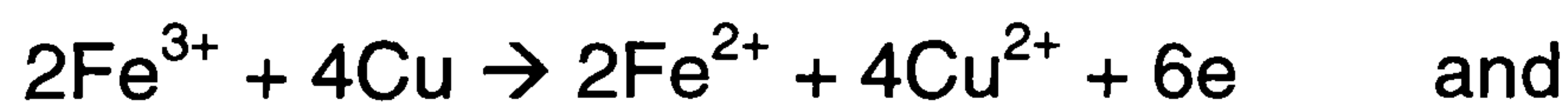


Table 8.2 shows the relationship between regeneration and the volume of ferric chloride etchant required for dissolution of copper.

**Table 8.2: Relationship between regeneration cycles, % utilisation and volume of etchant required for dissolution of copper**

No. of regeneration of $\text{FeCl}_3$	% utilisation of $\text{FeCl}_3$	Vol. (l) of $\text{FeCl}_3$ required for dissolution of 1 tonne of copper
No regeneration	100	9,340
One	200	4,670
Two	300	3,113
Three	400	2,335
Four	500	1,868



### 8.2.2 Percentage (%) etch out of metal processed

Another factor to be considered in determining the efficient use of ferric chloride is the percentage (%) etch out area of the metal sheets processed. This figure varies from company to company, and depends on the geometry of products etched.

Obviously, ferric chloride consumption can be greatly reduced by decreasing the % etch out area. This can be done by using etch bands [Allen, 1986e], which consist of uniform width bands surrounding the whole piece-part, and parts-nesting CAD programs for phototool production.

## 8.3 Efficiency of Etchant Consumption

### 8.3.1 Influence of alloy composition on efficiency of etchant

In PCM, a rather wide variety of metals are used in the etching process. The commonly etched materials are stainless steels, mild steels, copper, brass, nickel and aluminium. As such, it is not easy for the PCM companies to keep the details and up-to-date records for each of the metal alloys consumed. In this survey, it was found that only one company, Company N, was able to supply a complete breakdown of the metal alloys etched over a period of one year. These are shown in *Table 8.3*, together with weights of metallic elements processed according to the elemental composition of the various alloys.

In summary, Company N processed 29.27 tons of metals per year. Ferrous materials (stainless, carbon and mild steels, Kovar and Nilo 42) totalled 6.900 tons, copper and its alloys 22.277 tons and aluminium 0.093 tons. *Table 8.4* shows that 958,689 moles of  $\text{FeCl}_3$  are required to dissolve the metal alloys completely. If, on the other hand, a more detailed analysis is carried out by calculating the number of moles of  $\text{FeCl}_3$  required for the dissolution of all the individual elements contained in the alloys, according to chemical equation (1), then a total of 967,713 moles is required (see *Table 8.5*). The error in the approximation is therefore only 0.93% by the calculation below:

#### Total moles of ferric chloride solution required for dissolution using

- (i) Approximation method = 958,689 moles
- (ii) Individual elements method = 967,713 moles

$$\text{Percentage error} = (967,713 - 958,689)/967,713 \times 100\% = 0.93\%$$

As the vast majority of PCM companies were unable to provide detailed information on the exact breakdown of the metals consumed, the metals used in etching were classified into two main categories, namely ferrous and copper materials for ease of analysis.

**Table 8.3: Actual metals processed in Company N in one year**

<b>Metal</b>	<b>Kg</b>	<b>Fe</b>	<b>Cr</b>	<b>Cu</b>	<b>Ni</b>	<b>Zn</b>	<b>Co</b>	<b>Sn</b>	<b>Al</b>
Stainless steel	3,600	2,664	648	-	288	-	-	-	-
Carbon steel	300	300	-	-	-	-	-	-	-
Mild steel	1,350	1,350	-	-	-	-	-	-	-
Copper	1,700	-	-	1,700	-	-	-	-	-
Copper 194/195	1,250	-	-	1,250	-	-	-	-	-
Brass, 63.5% Cu	13,166	-	-	8,360	-	4,806	-	-	-
Phosphor bronze	1,011	-	-	950	-	-	-	61	-
Beryllium copper	350	-	-	350	-	-	-	-	-
Nickel silver	4,800	-	-	3,120	960	720	-	-	-
Kovar & Nilo 42	1,650	891	-	-	479	-	280	-	-
Aluminium	93	-	-	-	-	-	-	-	93
<b>Total</b>	<b>29,270</b>	<b>5,205</b>	<b>648</b>	<b>15,730</b>	<b>1,727</b>	<b>5,526</b>	<b>280</b>	<b>61</b>	<b>93</b>

Table 8.4: Comparison of calculation of ferric chloride consumption using Approximation Method

Approximation	Atomic Weight	Moles/kg	Weight (kg)	Valency	Moles of FeCl <sub>3</sub> required for dissolution of elements
Fe	55.85	17.91	6,900	2	247,158
Cu	63.54	15.738	22,277	2	701,191
Al	26.98	37.06	93	3	10,340
					<b>Total = 958,689</b>

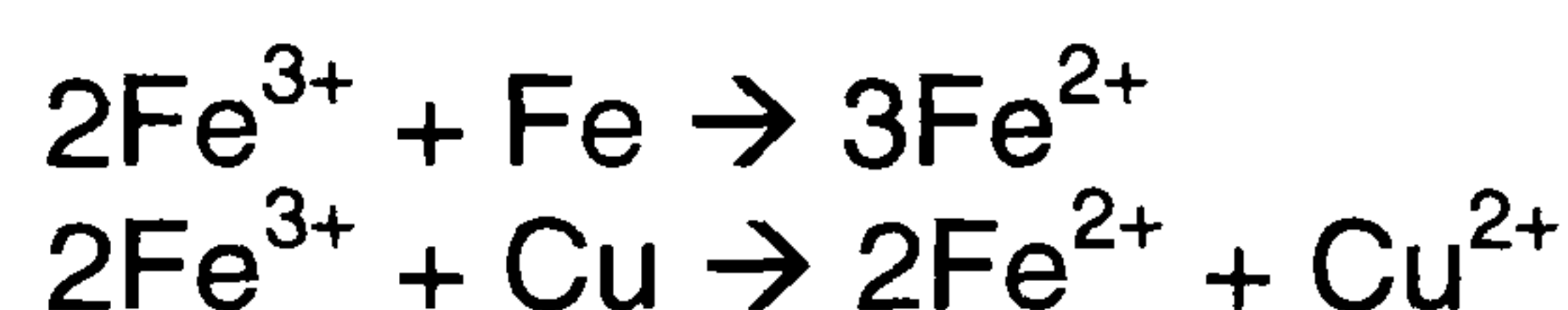
Table 8.5: Comparison of calculation of ferric chloride consumption using Individual Elements Method

Individual element	Atomic Weight	Moles/kg	Weight (kg)	Valency	Moles of FeCl <sub>3</sub> required for dissolution of elements
Fe	55.85	17.91	5,205	2	186,443
Cu	63.54	15.738	15,730	2	495,118
Cr	52.08	19.231	648	3	37,385
Ni	58.69	17.04	1,727	2	58,856
Zn	65.38	15.295	5,526	2	169,040
Co	58.93	16.97	280	2	9,503
Sn	118.69	8,425	61	2	1,028
Al	26.98	37.06	93	3	10,340
					<b>Total = 967,713</b>

### 8.3.2 Methodology used in calculating the % utilisation of ferric chloride etchant

The following methodology was used in the calculation of % utilisation of ferric chloride etchant.

The chemical reactions in etching ferrous and copper materials are:



Total moles of Fe/kg = 17.91 moles/kg (molecular weight of Fe = 55.85)

Total moles of Cu/kg = 15.74 moles/kg (molecular weight of Fe = 63.54)

For **Company A**, the following data were obtained:

- (i.) Consumption of ferrous materials = 10,000 kg/annum  
Consumption of copper materials = 40,000 kg/annum
- (ii.) Average % etch out = 13%.
- (iii.) Consumption of ferric chloride = 100,000 litres.

#### 1. Total moles of ferric chloride required for etching

Total moles of materials etched  
 = (10,000 x 0.13 x 17.91) moles + (40,000 x 0.13 x 15.74) moles  
 = (23,283 + 81,848) moles  
 = 105,131 moles

Total moles of ferric chloride required for dissolution of the above materials = 105,131 x 2 moles  
 = 210,262 moles

#### 2. Total moles of ferric chloride consumed

Total moles in 100,000 litres of ferric chloride consumed in etching  
 = 100,000 litres x 3.37 moles /litre  
 = 337,000 moles

#### 3. % Utilisation

Thus, the % utilisation of ferric chloride  
 = 210,262 moles/337,000 moles x 100%  
 = 63.1%

## 8.4 Results and Discussions

### 8.4.1 Analysis of overall results

The results and analysis of metal processed and ferric chloride consumption of the 18 PCM companies that have responded to the survey are detailed in *Table 8.6*. The minimum and maximum weights of metal processed were 1.61 and 460.00 tonnes per annum respectively, an immense range covering over two orders of magnitude. The average weight of metal processed for the 18 companies is 66.72 tonnes. The area of metal processed ranged from 1,200 to 216,480 m<sup>2</sup> per annum.

By assuming a density of 8.0 for all the metals processed, an approximation of the average thickness of metals processed can be made and this ranged from 0.037 to 1.187 mm with an average of 0.281 mm. This latter figure has been used to calculate the weight of metal processed for Company M and area of metal processed for Company R, who were only able to supply the area and weight of metal processed respectively. The average % etch out of metal processed was 22.7%, with minimum and maximum given as 10% and 42.5% respectively.

*Figure 8.1* shows the status of regeneration of the companies; 8 out of 18 companies (45%) carried out regeneration, 6 companies were not regenerating the etchants and the rest were using partial regeneration.

**Figure 8.1: Status of regeneration of companies surveyed**

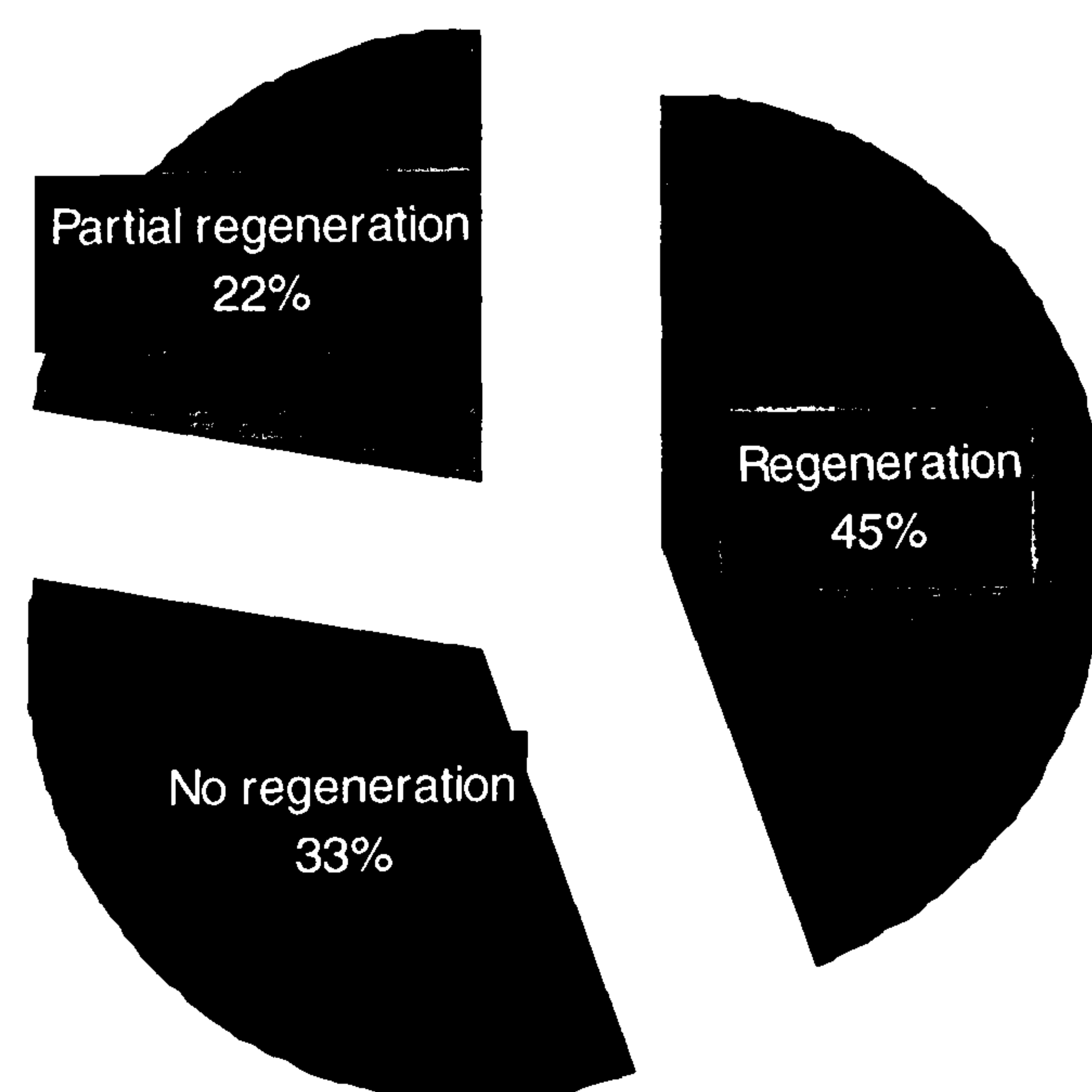


Table 8.6: Metal processed and ferric chloride consumption of PCM companies

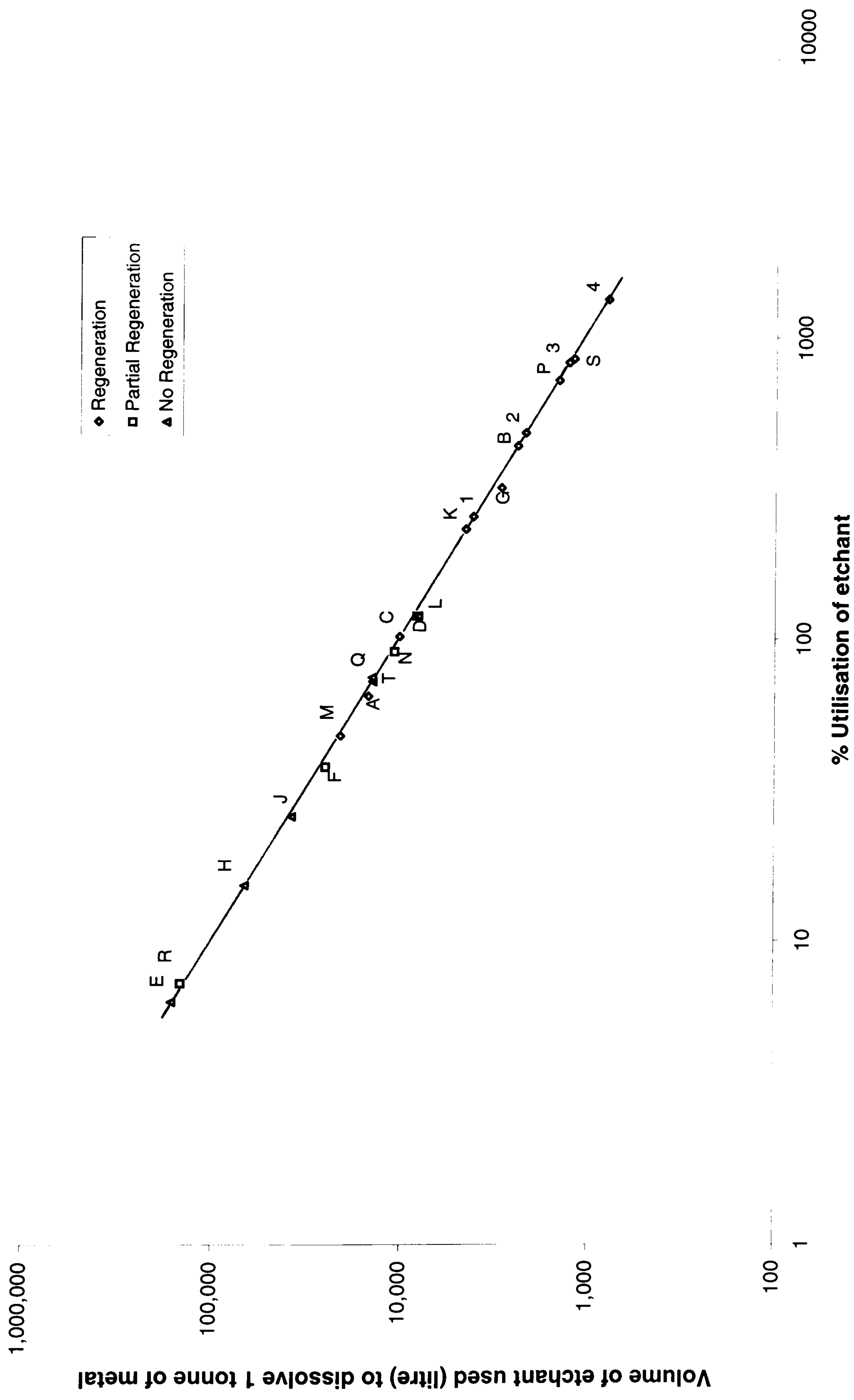
Company	Wt. of metal (kg)	Area of metal (m <sup>2</sup> )	Vol. of etchant (l)	Thickness of metal (mm)	Etch out (%)	Utilisation of FeCl <sub>3</sub> (%)	Vol. of FeCl <sub>3</sub> used in dissolving one tonne of metal (l)
A	50,000	45,000	100,000	0.138	13	63.1	15,230
B	11,150	3,150	8,789	0.442	32	430.0	2,460
C	9,000	5,100	9,600	0.221	10	99.6	10,430
D	15,400	18,550	41,090	0.104	31	117.0	8,450
E	3,360	10,930	80,537	0.037	17.5	6.2	165,860
F	16,100	5,000	41,500	0.363	10	36.8	25,750
G	130,000	45,000	144,300	0.361	37	313	3,000
H	8,915	2,925	61,297	0.381	10	14.9	68,760
J	8,400	1,200	30,000	0.875	10	25.1	38,960
K	2,160	2,500	4,000	0.108	40	227.0	4,650
L	1,611	2,700	4,020	0.075	30	117.0	8,320
M	16,950 <sup>#</sup>	7,540	30,000	0.281 <sup>+</sup>	10	46.6	21,430
N	29,270	12,000	65,000	0.305	20	88.8	11,100
P	364,729	38,400	142,069	1.187	25	710.0	1,480
Q	460,000	216,480	2,000,000	0.266	30	70.5	14,490
R	10,758	4,786 <sup>*</sup>	240,000	0.281 <sup>+</sup>	15	7.14	148,730
S	33,181	20,345	10,202	0.204	25	837.0	1,230
T	30,000	90,000	186,000	0.042	42.5	72.8	14,590
<b>Total</b>	<b>1,200,984</b>	<b>531,606</b>	<b>3,197,867</b>	-	-	-	-
<b>Average</b>	<b>66,721</b>	<b>29,534</b>	<b>177,659</b>	<b>0.281</b>	<b>22.7</b>	<b>182.40</b>	<b>31,380</b>

+ average thickness for companies

# extrapolated from area and average thickness of metal processed

\* extrapolated from weight and average thickness of metal processed

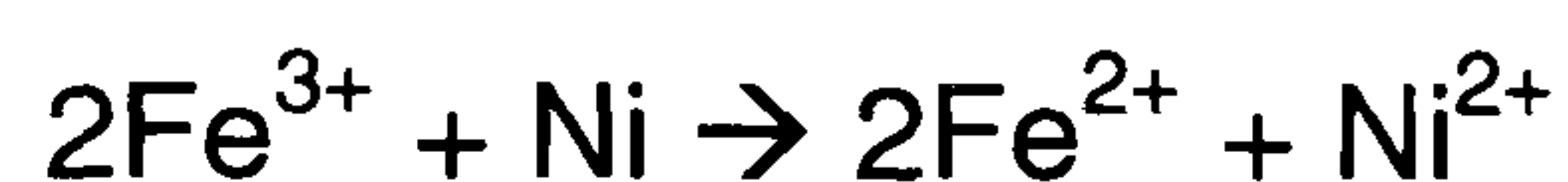
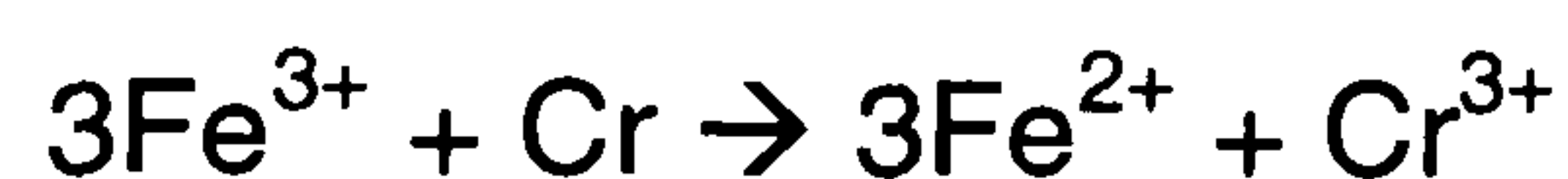
**Figure 8.2: Efficiency of etchant utilisation of PCM companies**



The efficiency of ferric chloride utilisation is shown graphically in *Figure 8.2*, which is a plot of % utilisation of etchant vs volume of etchant used. It was found that:

- (1.) Companies that regenerate ferric chloride etchant were considerably more efficient than companies which do not regenerate. The most efficient company in the survey used 135 times less etchant in etching the same amount of metal compared to the least efficient company.
- (2.) Ferric chloride etchants can be regenerated more than 3 times (see performance of Company S) prior to disposal, which is equivalent to more than 8 times reduction in the usage of ferric chloride for 100% utilisation without regeneration, although it is generally acknowledged that repeated regeneration may affect etch rate and quality of products as a result of impurities build-up in the etching system due to the following:

It is common among the PCM companies to etch different types of materials. In order to minimize the use of etchant, stainless steel is normally etched first, followed by nickel-iron alloys, and carbon steels, with copper last. This is because stainless steel is sensitive to copper by-products, as it causes a poor, rough and pitted surface finish on steel products [Allen, 1986f]. Common grades of stainless steel used in PCM like AISI 302, 304 and 316 have chromium and nickel contents of 16.5-19.0% and 9.0-14.0% respectively apart from other impurities. Therefore, in a system used for etching stainless steel, chromium ( $\text{Cr}^{3+}$ ) and nickel ( $\text{Ni}^{2+}$ ) ions are gradually built up according to the following chemical reactions:



Although the % of  $\text{Ni}^{2+}$  and  $\text{Cr}^{3+}$  will not exceed the % of nickel and chromium in the stainless steel [Allen, 1994b], this can cause undesirable effects and complications. For example, build up of  $\text{Ni}^{2+}$  above 10 g/l has been noted to cause rough surface finish when etching AISI 316 stainless steel [Allen and Li, 1988]. Thus, after certain amount of stainless steel has been dissolved, the regenerated etchant can only be used for etching other materials, if the  $\text{Ni}^{2+}$  in the system is not removed. Fresh etchants have to be used in etching more stainless steels as these are the most sensitive materials to process in PCM.



### 8.4.2 Effects of the use of regeneration

The results and analysis of companies that use regeneration, do not use regeneration and use partial regeneration are shown in *Tables 8.7, 8.8 and 8.9*. It was found that:

- (1.) The average % utilisation of companies that regenerate ferric chloride etchant is approximately 6.7 times (340.8% compared to 51.1%) more efficient than those which do not regenerate. The findings clearly showed the environmental benefits of using regeneration in etching. In addition, past study conducted by Allen [1991] has shown that regeneration is cost-effective if the annual amount of iron etched exceeds 200 kg, assuming that the etchant is 50% exhausted. If the etchant is 25% exhausted, the amount of iron etched is further reduced to 70 kg/annum to be cost effective.

The  $\text{FeCl}_3$  consumption efficiency of companies that carry out partial regeneration fared slightly better than companies not regenerating, with an average of 62.4% compared to 51.1%. The small difference in performance may be because the partial regeneration companies were carrying out regeneration in only a small proportion of the total etching machines. For example, only one out of five etching machines of Company F was carrying out regeneration.

- (2.) Among companies carrying out regeneration, there is a difference of 18 times (837.0% compared to 46.6%) in terms of efficient use of etchant. The same trend is also evident in companies that do not regenerate and carry out partial regeneration. This may be due to the lack of implementation of proper measures in maximising etchant usage, for example, by controlling the order of the metals processed, with etching stainless steel first, followed by nickel-iron alloys, and carbon steels, with copper last [Allen, 1986f].
- (3.) There is, however, no correlation between the use of regeneration and the amount of metal etched as the metal consumption varied vastly within companies that carry out regeneration and no regeneration.

### 8.5 Conclusions

From the survey findings, it is evident that there is a vast difference between the most efficient company and the least efficient company in terms of etchant usage. On average, companies that regenerate ferric chloride etchant are much more efficient compared to companies that do not regenerate.

**Figure 8.7: Metal processed and ferric chloride consumption of PCM companies using regeneration**

Company	Wt. of metal (kg)	Vol. of etchant (l)	Etch out (%)	Utilisation of FeCl <sub>3</sub> (%)	Vol. of FeCl <sub>3</sub> used in etching one tonne of metal (l)
A	50,000	100,000	13	63.1	15,230
B	11,150	8,789	32	430.0	2,460
C	9,000	9,600	10	99.6	10,430
G	130,000	144,300	37	313	3,000
K	2,160	4,000	40	227.0	4,650
M	16,950	30,000	10	46.6	21,430
P	364,729	142,069	25	710.0	1,480
S	33,181	10,202	25	837.0	1,230
<b>Total</b>	<b>617,170</b>	<b>448,960</b>	<b>192</b>	<b>2726.3</b>	<b>59,910</b>
<b>Average</b>	<b>77,146</b>	<b>56,120</b>	<b>24.0</b>	<b>340.79</b>	<b>7,489</b>

**Figure 8.8: Metal processed and ferric chloride consumption of PCM companies not using regeneration**

Company	Wt. of metal (kg)	Vol. of etchant (l)	Etch out (%)	Utilisation of FeCl <sub>3</sub> (%)	Vol. of FeCl <sub>3</sub> used in dissolving one tonne of metal (l)
E	3,360	80,000	17.5	6.2	165,860
H	8,915	61,297	10	14.9	68,760
J	8,400	30,000	10	25.1	38,960
L	1,611	4,020	30	117.0	8,320
Q	460,000	2,000,000	30	70.5	14,490
T	30,000	186,000	42.5	72.8	14,590
<b>Total</b>	<b>512,286</b>	<b>2,361,317</b>	<b>140</b>	<b>306.5</b>	<b>310,980</b>
<b>Average</b>	<b>85,381</b>	<b>393,559</b>	<b>23.3</b>	<b>51.1</b>	<b>51,830</b>

**Figure 8.9: Metal processed and ferric chloride consumption of PCM companies using partial regeneration**

Company	Wt. of metal (kg)	Vol. of etchant (l)	Etch out (%)	Utilisation of FeCl <sub>3</sub> (%)	Vol. of FeCl <sub>3</sub> used in dissolving one tonne of metal (l)
D	15,400	41,090	31	117.0	8,450
F	16,100	41,500	10	36.8	25,750
N	29,270	65,000	20	88.8	11,100
R	10,758	240,000	15	7.14	148,730
<b>Total</b>	<b>71,528</b>	<b>387,590</b>	<b>76</b>	<b>249.74</b>	<b>194,030</b>
<b>Average</b>	<b>17,882</b>	<b>96,898</b>	<b>19.0</b>	<b>62.4</b>	<b>48,507</b>

The other finding is that the most efficient company has regenerated ferric chloride more than 3 times prior to disposal, which is equivalent to more than 8 times reduction in the usage of ferric chloride for 100% utilisation without regeneration.

This showed that the utilisation of ferric chloride in some of the PCM companies could be greatly improved if regeneration is used and waste minimisation programmes are introduced. As a result of the above findings, it is concluded that the environmental performance of PCM companies, especially those less efficient ones, can be further improved to enable the PCM industry to reduce environmental impacts. This can be done by:

- (1.) Installing regeneration facilities in companies that are currently not regenerating.
- (2.) Implementing an effective waste minimisation programme to prolong the usage of etchant.
- (3.) Conducting research into more environment-friendly regeneration methods such as by replacing the existing chemicals used in regeneration with chemicals that have less environmental, health and safety impacts.

## **Chapter 9**

# **Study on Regeneration and Disposal of Ferric Chloride Etchant**

### **9.1 Introduction**

The findings of *Chapter 8* clearly showed that the use of regeneration is very efficient in reducing the consumption of ferric chloride etchants and minimising the related environmental impacts. Currently, various regeneration systems are used commercially by the PCM industry. However, there is a limit to the number of regenerations that can be carried out, thus resulting in spent etchant that has to be recycled or treated prior to disposal. The main objective of this chapter is to present the findings of the survey on the regeneration and disposal of ferric chloride etchant in PCM.

### **9.2 Regeneration Systems**

Apart from the environmental benefits, etching with regeneration is also more economical. Research conducted [Wible, 1981; Allen, 1991; Allen and White, 1992] indicated that significant savings can be realised from regeneration due to the high costs of chemicals and etchant disposal.

Suitable oxidation systems for etchant regeneration currently used by the industry include:

- (1) Chlorine gas,
- (2) Sodium chlorate/Hydrochloric acid (HCl),
- (3) Electrolysis/HCl, and
- (4) Ozone/HCl.

The complete stoichiometry of the etching and regeneration reactions of the above systems is shown in *Figure 9.1*.

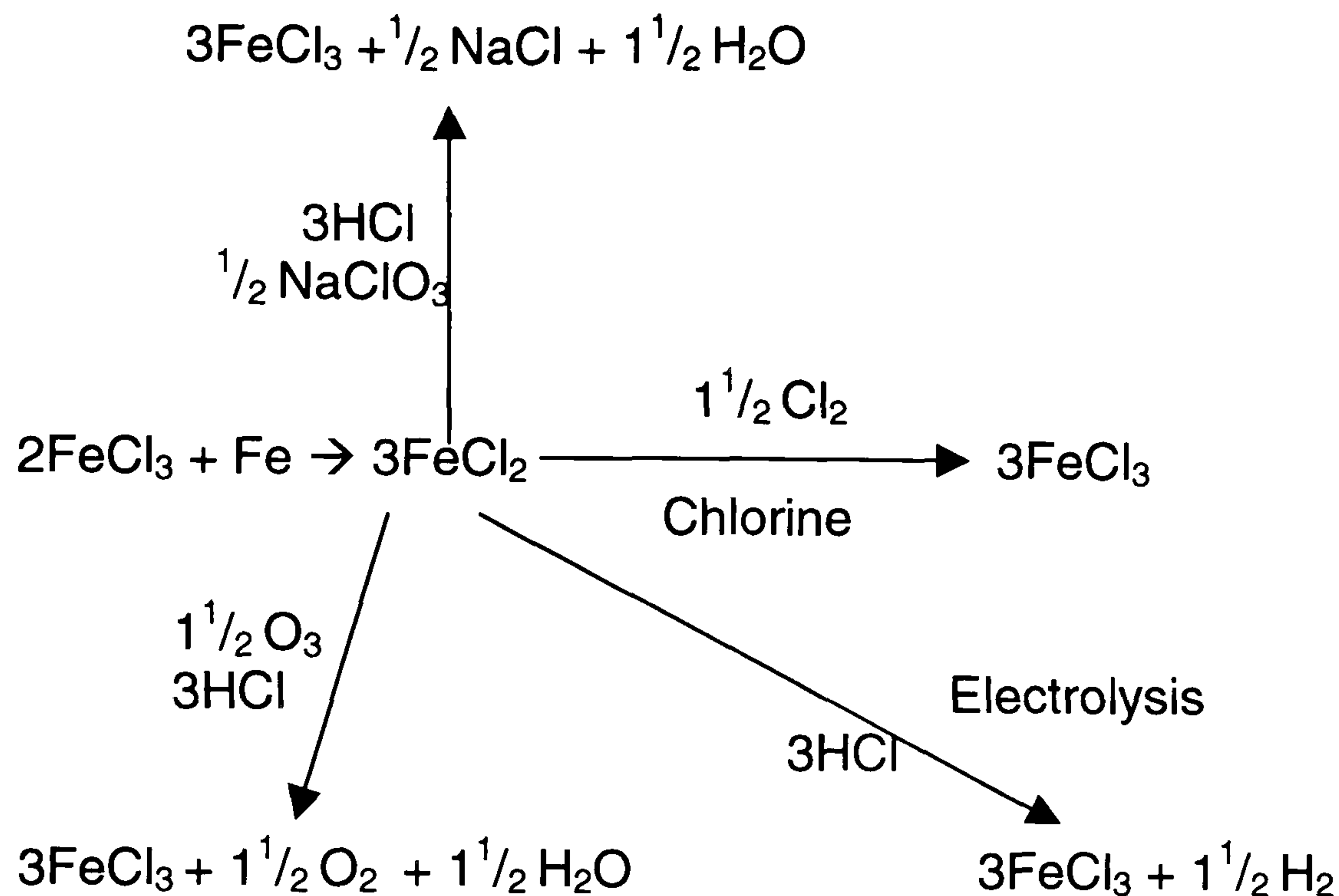
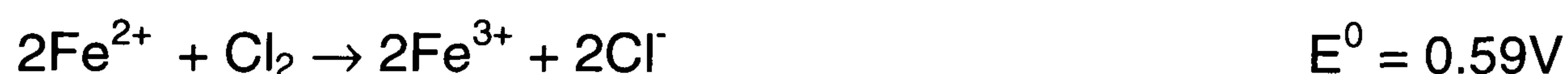


Figure 9.1: Existing regeneration system [Allen, 1991]

### 9.2.1 Chlorine regeneration

This system is based on chlorine oxidation of ferrous ions ( $\text{Fe}^{2+}$ ). The chemical reaction of passing chlorine through a solution containing  $\text{Fe}^{2+}$  is



where  $E^0$  is the standard electrode potential of the reaction. Chlorine regeneration appears to be the best solution in regenerating the spent etchant as chlorine gas is a strong oxidising agent and the reaction does not result in any byproducts or cause any undesirable complications. However, the disadvantage of this method is that chlorine is a green-yellowish poisonous gas with a pungent odour and is classified as a 'toxic or very toxic' substance hazardous to health [BDH, 1996]. Allen and White [1992] showed that due to the need for expensive safety precautions in view of the chlorine manipulation, transport and storage, the use of chlorine is often refused by the relevant authorities in the UK on health and safety grounds. Moreover, the use of chlorine gas is prescribed under Part A of Schedule 1 in the Environmental Protection (Prescribed Processes and Substances) Regulations 1991, which needs an authorisation from the EA.

### 9.2.2 Sodium chlorate and hydrochloric acid regeneration

Acidified chlorate solution is a strong oxidising agent.  $\text{Fe}^{2+}$  is converted to  $\text{Fe}^{3+}$  by the following reaction:



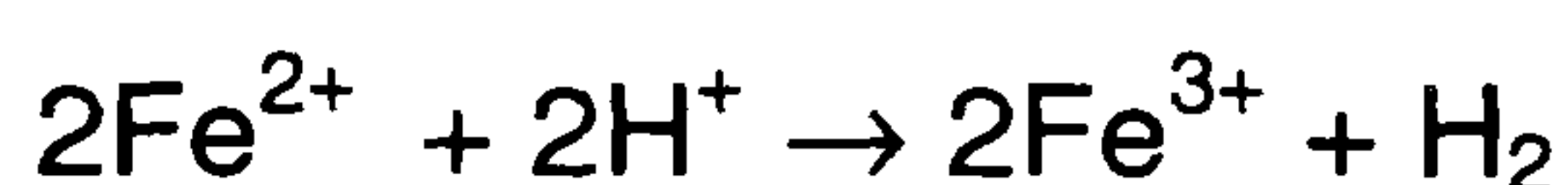
In this reaction, sodium chloride and water are produced as byproducts. The addition of sodium ions ( $\text{Na}^+$ ) to the regenerated etchant is an undesirable complication as its presence may affect the etching rate and quality, although no research has been published in this field. The water produced in this process also results in the dilution of ferric chloride solution. Moreover, the use of sodium chlorate is not encouraged as it can evaporate and pose a fire hazard when in contact with organic materials.

### 9.2.3 Electrolytic regeneration

This system relies on the anodic oxidation of  $\text{Fe}^{2+}$  ion to  $\text{Fe}^{3+}$  ion according to the following reactions:



and

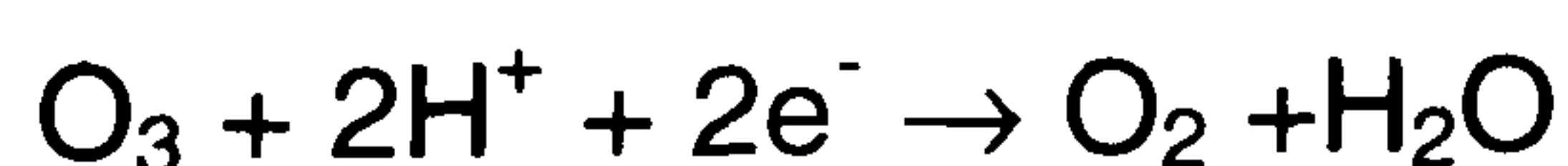


Several patents have been granted based on different techniques of electrolytic regeneration both in the US and UK. The techniques claimed are: organic removal of ferric chloride by Douglas [1968], oxidation of ferrous ion to ferric ion with chlorine gas formed at the anode by Beyer and Lukes [1974], a combination of chlorine oxidation at the anode and controlling the linear speed of the etching solutions by Kucherenko *et al* [1977] and by separating ferric ion formed using two pieces of diaphragm in between anode and cathode by Stehlik [1983].

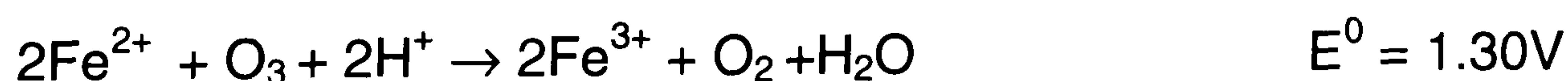
Although electrolytic regeneration has been successfully used in etching metals like stainless steels [Visser and Junker, 1993] that require stringent process control in order to produce good quality products, this system is not desirable to the environment as a large current is required and the flammable hydrogen gas is also liberated.

### 9.2.4 Ozone regeneration

Ozone is another powerful oxidising agent and the oxidation redox half reaction in acidic solution is



In oxidising  $\text{Fe}^{2+}$  back to  $\text{Fe}^{3+}$ , the following reaction occurs:



Only water and oxygen gas are produced as byproducts. Although the formation of water results in the dilution of ferric chloride solution, the oxygen gas liberated can help to regenerate part of the ferrous ions, although the rate

of reaction is slow [Ler, 1993]. This system has been known since the 1970s. A US patent granted to Acocella and David [1988] claimed that for systems with slow etching reaction such as etching nickel, molybdenum, Kovar and INVAR using ferric chloride solutions, the addition of a mixture of ozone and oxygen could simultaneously rejuvenate the etching solution and increase the rate of etching significantly. In addition, David and Kurdziel [1988] also found that in the etching of molybdenum with potassium ferricyanide etchant, apart from the regeneration of spent etchant, ozone re-oxidation has also speeded up the etching rate and improved the etching quality.

However, ozone is a dangerous material and is explosive when the concentration is more than 20%. The advantage of this system is that ozone can be only generated from oxygen as and when required.

### **9.3 Disposal of Waste Ferric Chloride Etchant**

Basically, there are four main methods currently used by the PCM practitioners in disposing of the waste ferric chloride etchant as listed below:

- (1.) Reclaim or recycle of liquid waste etchant
- (2.) Landfilling as a liquid waste
- (3.) Reclaim or recycle of solid waste etchant
- (4.) Landfilling as a solid waste

#### **9.3.1 Reclaim or recycle of liquid waste etchant**

Reclaim or recycle of liquid waste ferric chloride etchant is normally done by the chemical companies, as it is not cost-effective for PCM companies to carry out this task in their own plants. Normally, valuable metals are reclaimed before the waste ferric chloride is recycled to be used as a raw material for another process. For example, in the USA, copper in the waste etchant is first removed by cementation on used tin cans. After oxidation of the resultant ferrous chloride, the ferric chloride solution is then used as a starting material to leach out copper from mined copper ore.

Alternatively, the chemical companies can solidify the liquid waste and then sell to smelters for reclaim using the method as described in *Section 9.3.3*, if the waste etchant contains proportions of valuable metals that are attractive to be smelted.

#### **9.3.2 Landfilling as a liquid waste**

Liquid waste etchant disposed of by this method is done through licensed waste contractors. Landfilling of liquids directly is a practice that is not encouraged as the hazardous heavy metal ions in the waste etchant could escape and subsequently pollute underground waters. The liquid is therefore usually treated by 'stabilisation and solidification' to form sulphides which are

trapped in a solid matrix and cannot be leached out prior to disposal at suitable landfill sites.

### **9.3.3 Reclaim or recycle of solid waste etchant**

PCM companies that use this method of waste disposal have to precipitate out the heavy metals in the waste etchants in-house and after passing through a filter press, the metals present in the solidified waste filter cake are ready to be reclaimed. A third party then combines the solidified waste filter cake with other industrial wastes of a similar composition and sells it as a feedstock to smelters for reclaim.

However, the method of disposal is only viable if the waste etchants contain valuable metals in sufficient concentration that are attractive for reclamation. For example, the minimum content of copper, nickel or tin shall be 5% to be acceptable for reclaim [WRC, 1998].

### **9.3.4 Landfilling as a solid waste**

Alternatively, the solidified waste filter cake can be disposed of at a suitable landfill site by a licensed waste contractor if the metal composition is not economical to be reclaimed. In the UK, solidified waste filter cake is landfilled as the amount generated is insufficient to make reclamation/recycling cost-effective [Willey, 1998; Reynolds, 1998]

## **9.4 Results and Discussions**

Table 9.1 details the results of the survey on regeneration and disposal of ferric chloride etchants. Of the 39 companies that responded to this survey, 51% of the companies are from the US, 36% are European companies and the rest are from Asia.

### **9.4.1 Ferric chloride regeneration**

The response from the survey showed that only slightly more than half of the companies (56%) used regeneration of ferric chloride. Regeneration of spent etchants is not regulated throughout the world. Hence, it is not surprising to note that only 45% of the companies located in the US carried out regeneration compared to 71% in the Europe and 60% in Asia, although it is acknowledged



**Table 9.1: Results of survey on regeneration and disposal of etchants**

Company	Continent	Regeneration	System	Waste	Why not ?	Priority	Friendly
1	USA	N		Liquid reclaim	know-how	cost	Y
2	Asia	N		Liquid reclaim	profit	cost	N
3	USA	Y	Oxygen	Liquid reclaim			Y
4	Europe	Y	Electrolysis	Liquid reclaim			Y
5	Europe	N		Liquid reclaim	profit	cost	N
6	USA	N		Liquid reclaim	Nearby residents	cost	Y*
7	Europe	N		Liquid reclaim	Space	Quality	Y
8	Asia	Y	Chlorine	Solid waste			Y
9	Europe	Y	Electrolysis	Liquid reclaim			Y*
10	USA	N		solid waste	Quality	Technical	N
11	Europe	Y	Electrolysis	Solid reclaim			N
12	USA	Y	Chlorine	Solid waste			Y
13	USA	Y	Chlorine	Liquid waste			Y*
14	USA	N		Liquid reclaim	know-how/low usage	cost	Y
15	USA	N		Liquid reclaim	know-how	cost	Y
16	USA	N		Liquid reclaim	know-how/quality	cost/env.	Y
17	Europe	Y	Electrolysis	Liquid reclaim			N
18	USA	Y	Chlorine	Liquid reclaim			Y
19	USA	Y	Chlorine	Solid reclaim			Y
20	USA	N		Liquid waste	downgrade to aluminium	n/a	n/a
21	Europe	Y	Electrolysis	Liquid reclaim			N
22	Europe	Y	sodium chlorate	Liquid reclaim			N
23	USA	Y	Chlorine	Liquid reclaim/waste			Y
24	USA	N		Liquid reclaim	profit	cost	Y
25	Asia	N		Liquid reclaim	know-how	cost	Y*
26	USA	Y	Chlorine	Liquid reclaim			Y
27	Europe	Y	sodium chlorate	Liquid waste			Y
28	USA	N		Liquid waste	know-how	cost/env.	Y

**Table 9.1: Results of survey on regeneration and disposal of etchants (cont.)**

Company	Continent	Regeneration	System	Waste	Why not ?	Priority	Friendly
29	Asia	Y	unknown	Liquid reclaim	downgrade to aluminium		Y
30	USA	Y	Chlorine	Solid reclaim			Y*
31	Asia	Y	Electrolysis	Solid reclaim			Y
32	USA	N		Liquid reclaim	know-how & small size	cost/env.	Y
33	Europe	N		Solid waste	know-how (technical issues)	cost/env.	N
34	Europe	Y	sodium chlorate	Solid waste	know-how	cost/env.	Y
35	Europe	Y	Chlorine	Liquid waste			N
36	USA	Y	sodium chlorate	Liquid reclaim			Y
37	Europe	Y	Chlorine	Liquid waste			Y
38	USA	N		Liquid reclaim	Chlorine liability	safety/economy.	Y*
39	Europe	N		Liquid waste	others	cost	Y

**Key:**

Why not? – Reasons for not carrying regeneration

Priority – Priority for choosing a regeneration system

Friendly – Whether the company prepares to use a regeneration system at a higher cost.

Cost/Env. – Both cost and environment are priority consideration in choosing a regeneration system in future.

System – Regeneration system used

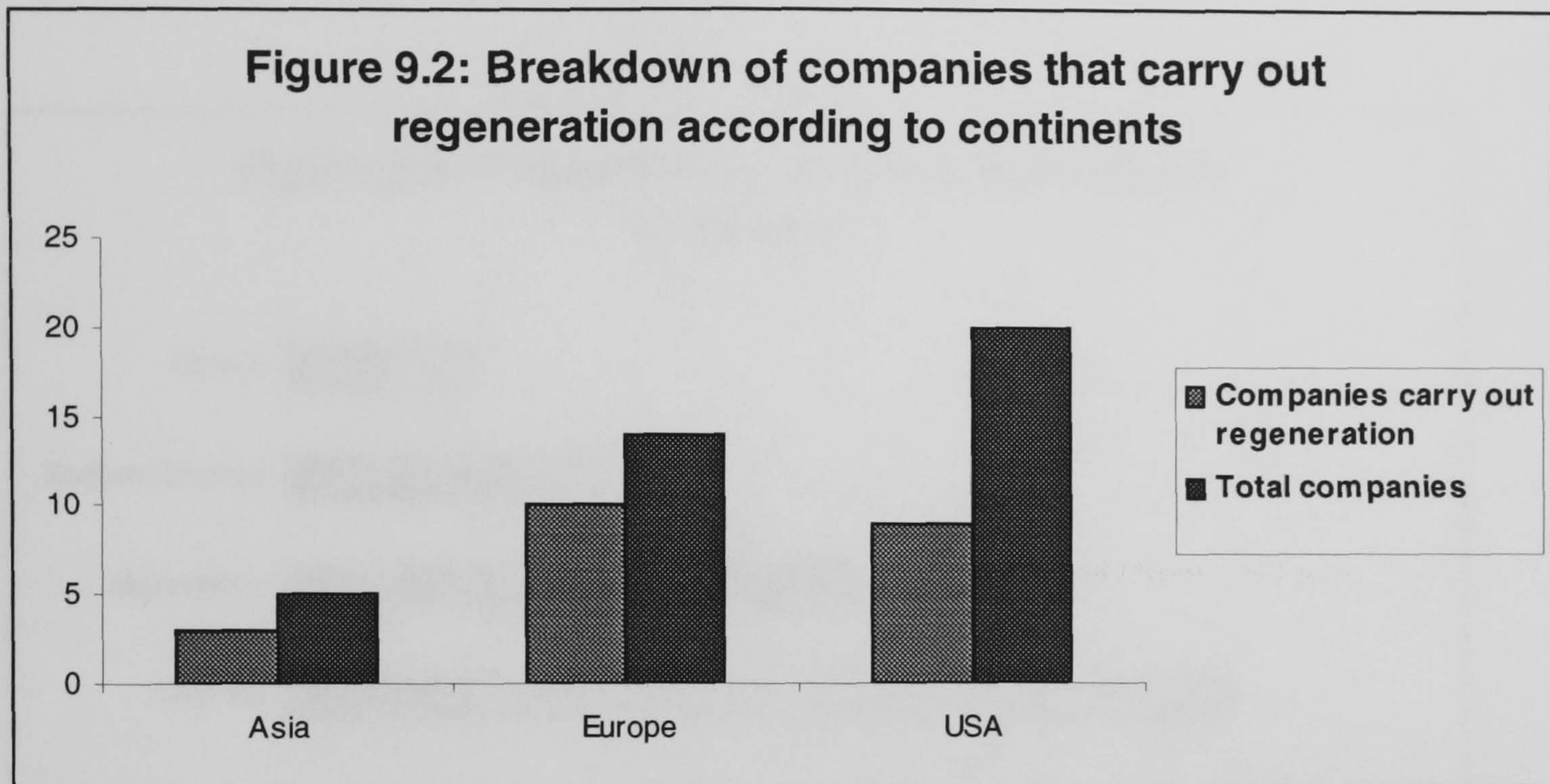
Waste – Method of waste disposal.

Y – Yes

N – No

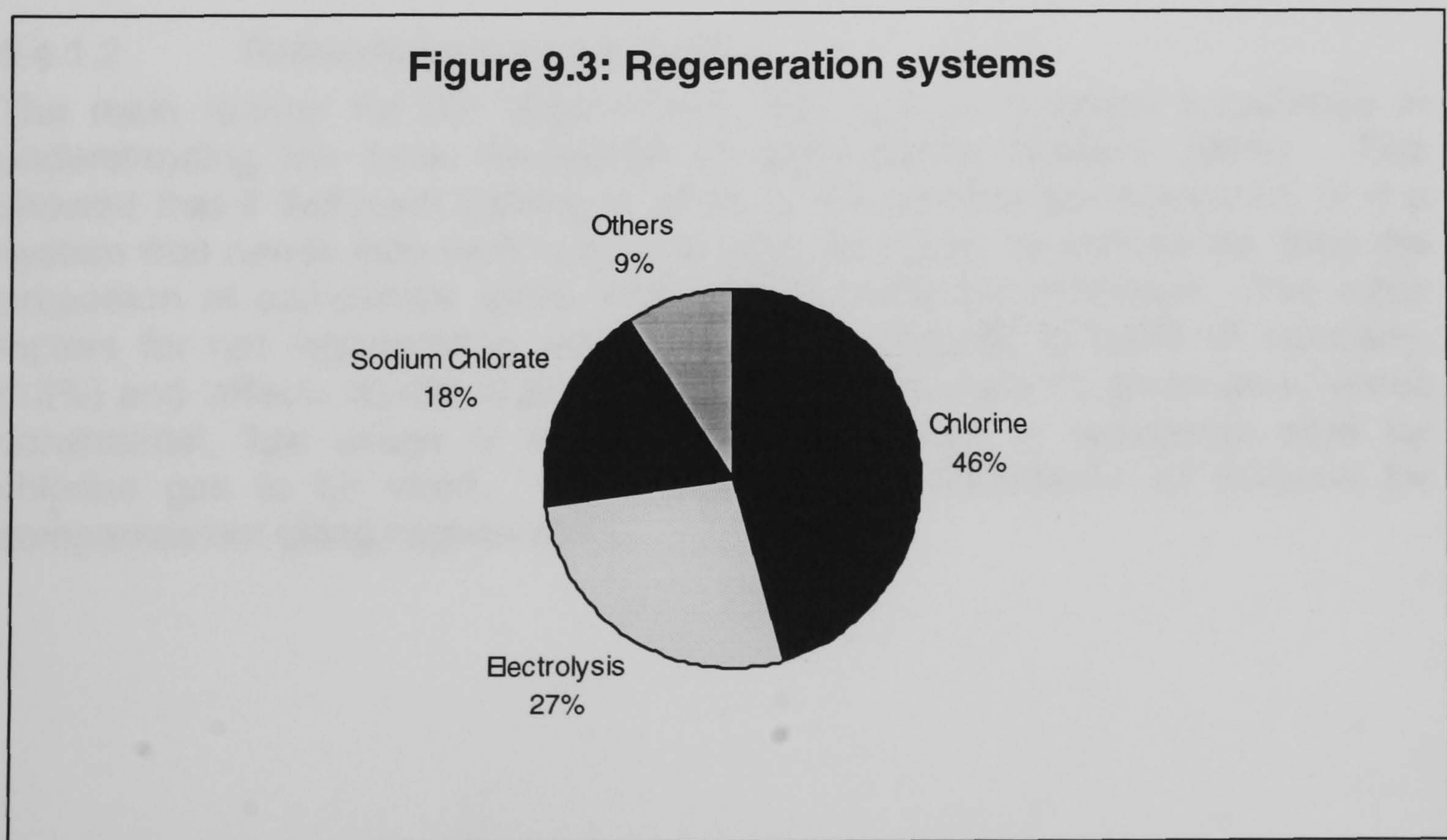
Y\* - Companies prepared to use a more environment-friendly system of regeneration but indicated that the cost should not be too expensive

that the legislation and its enforcement in the US is more stringent. *Figure 9.2* shows a breakdown of companies that carry out regeneration according to continents.

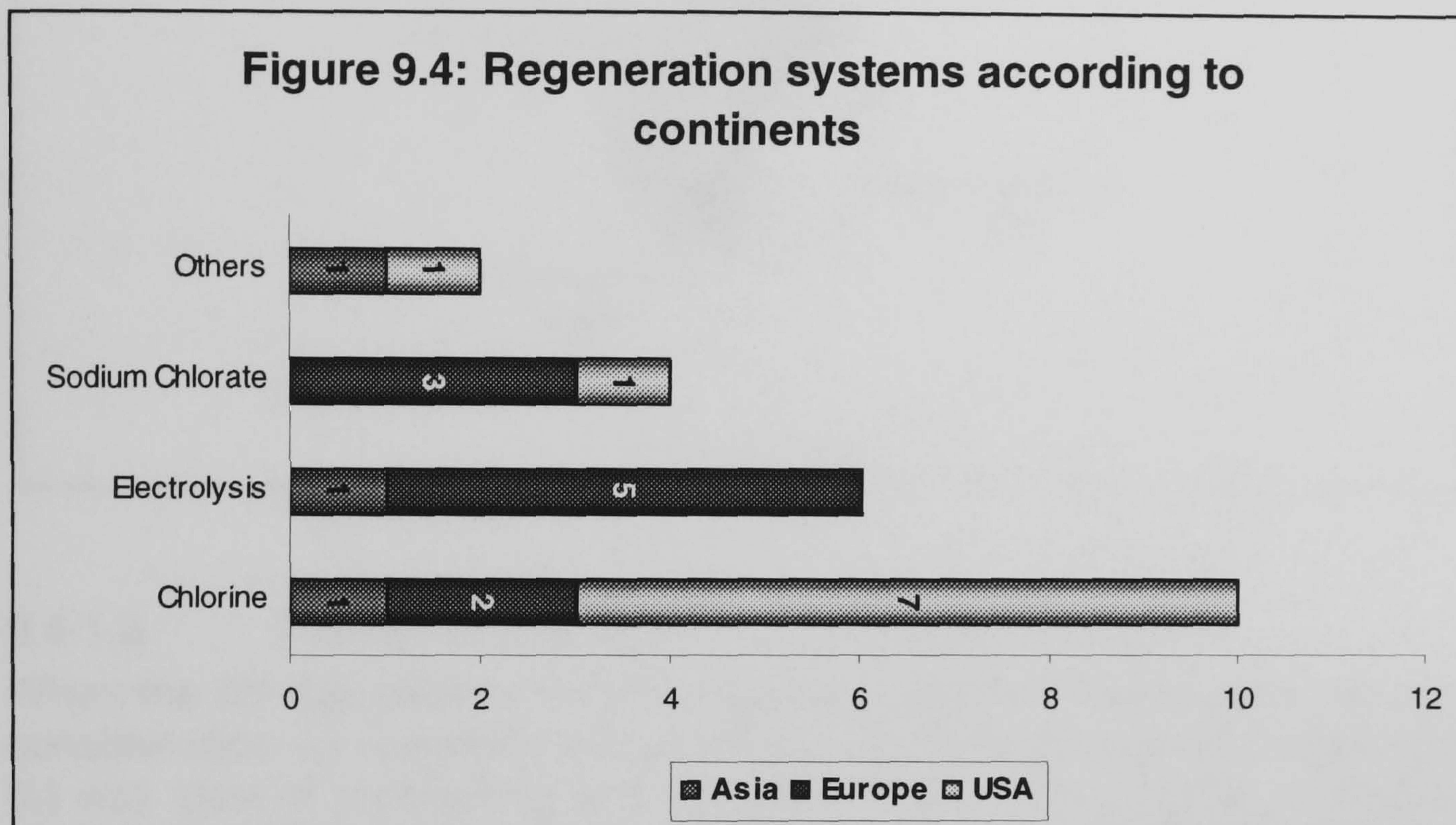


#### 9.4.1.1 Regeneration systems

Of the companies that carry out regeneration, chlorine regeneration was the most popular (46%), followed by electrolysis (27%). The other regeneration systems were sodium chlorate (18%) and others that were not specified (9%). The etchant regeneration systems used are showed in *Figure 9.3*.



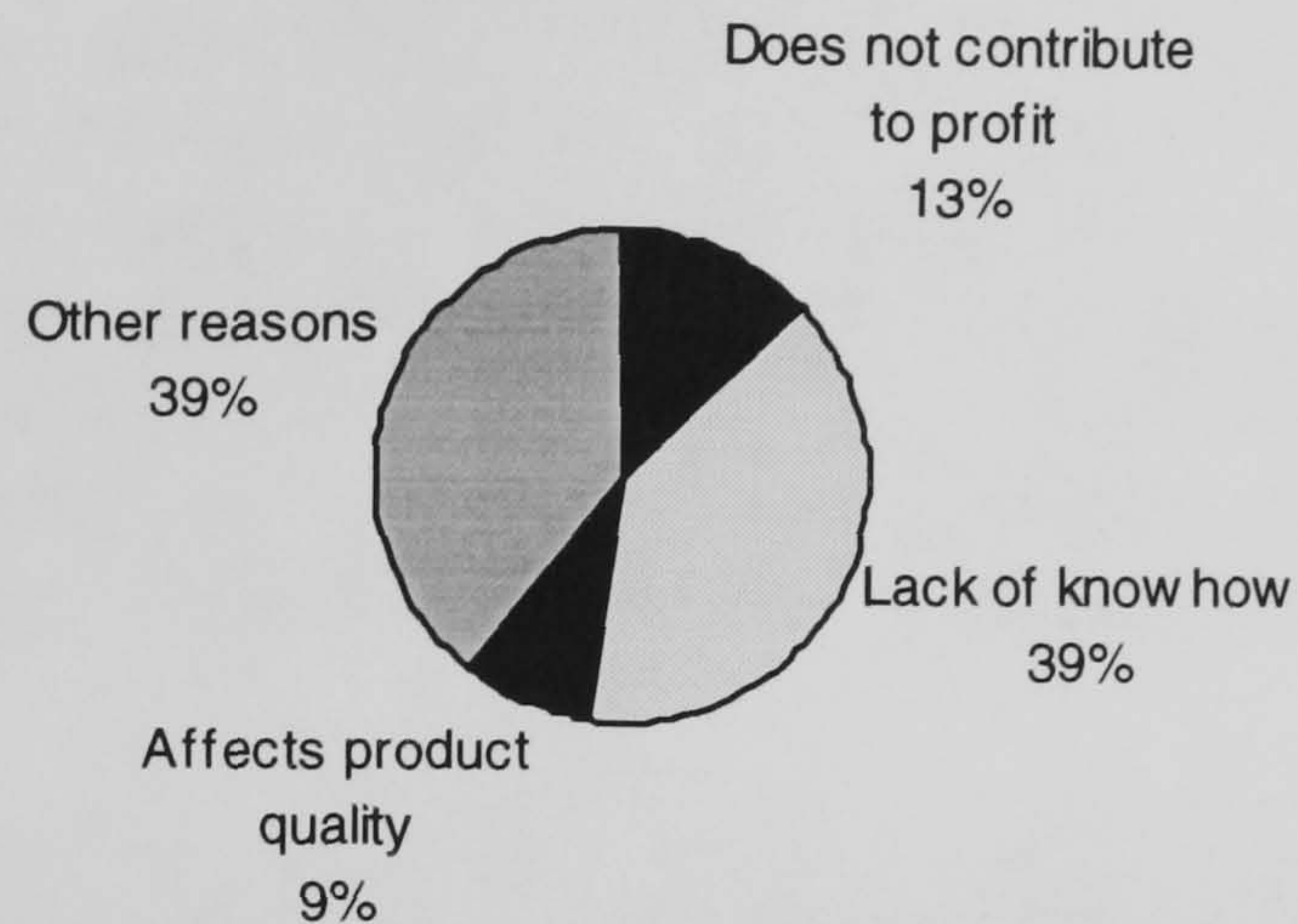
A breakdown to the type of regeneration systems used according to continents is as shown in *Figure 9.4*.



Chlorine gas regeneration system was the most popular among the US companies accounting for 78% (7 out of 9) of the total, whereas 50% of the companies in Europe that carry out regeneration used the electrolysis method.

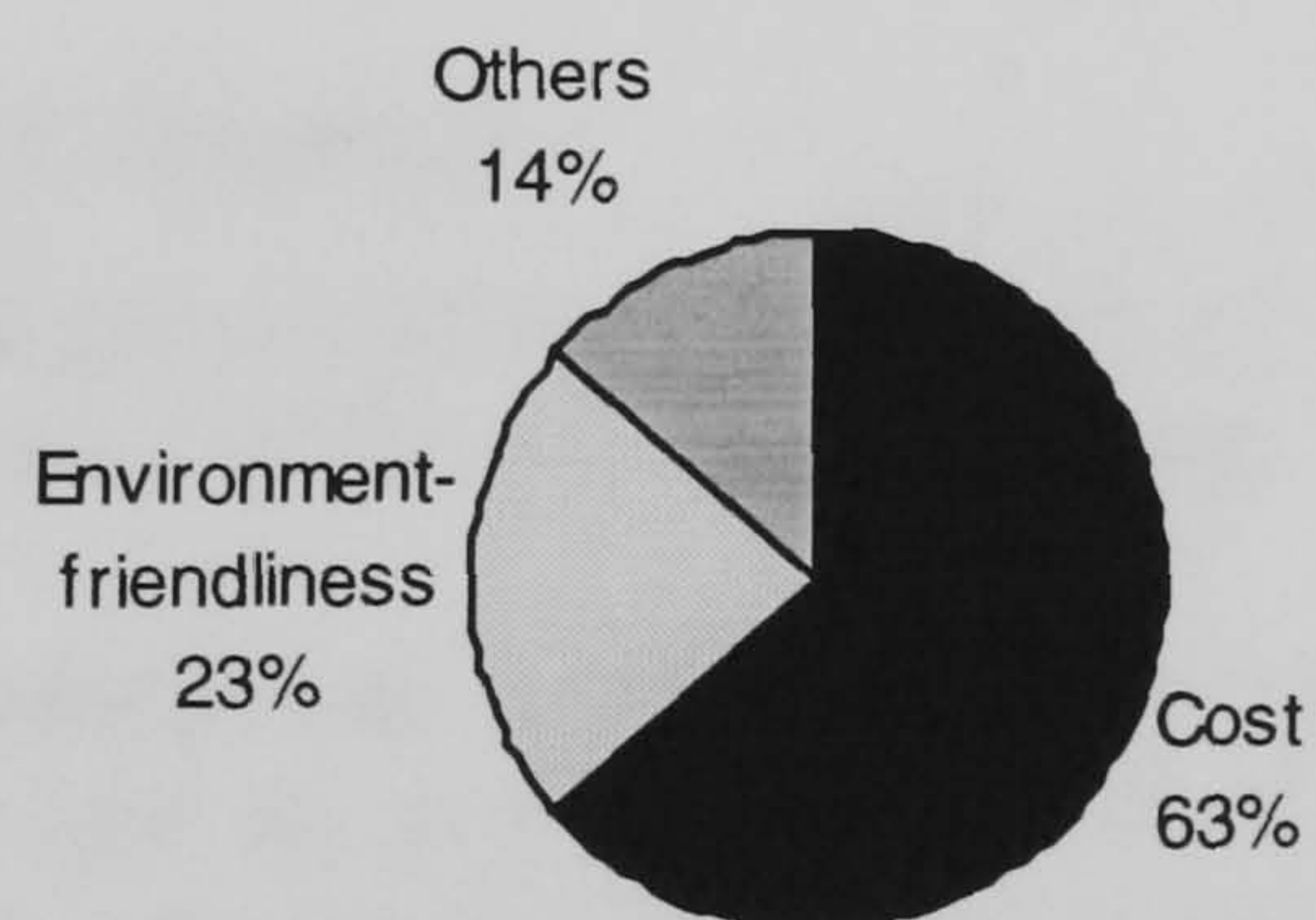
#### 9.4.1.2 Reasons for not regenerating

The main reason for not regenerating was lack of technical knowledge in understanding the basic know-how of regeneration systems (39%). This showed that if technical training is given to the companies concerned, or if a system that needs little technical input to operate can be introduced, then the proportion of companies using regeneration could be increased. The other factors for not regenerating were 'does not contribute to profit of company' (13%) and 'affects quality of products' (9%). Other reasons given were 'space constraints', 'low usage of etchants' and 'too close to residential area for chlorine gas to be used'. *Figure 9.5* gives a breakdown of reasons for companies not using regeneration.

**Figure 9.5: Reasons for not regenerating**

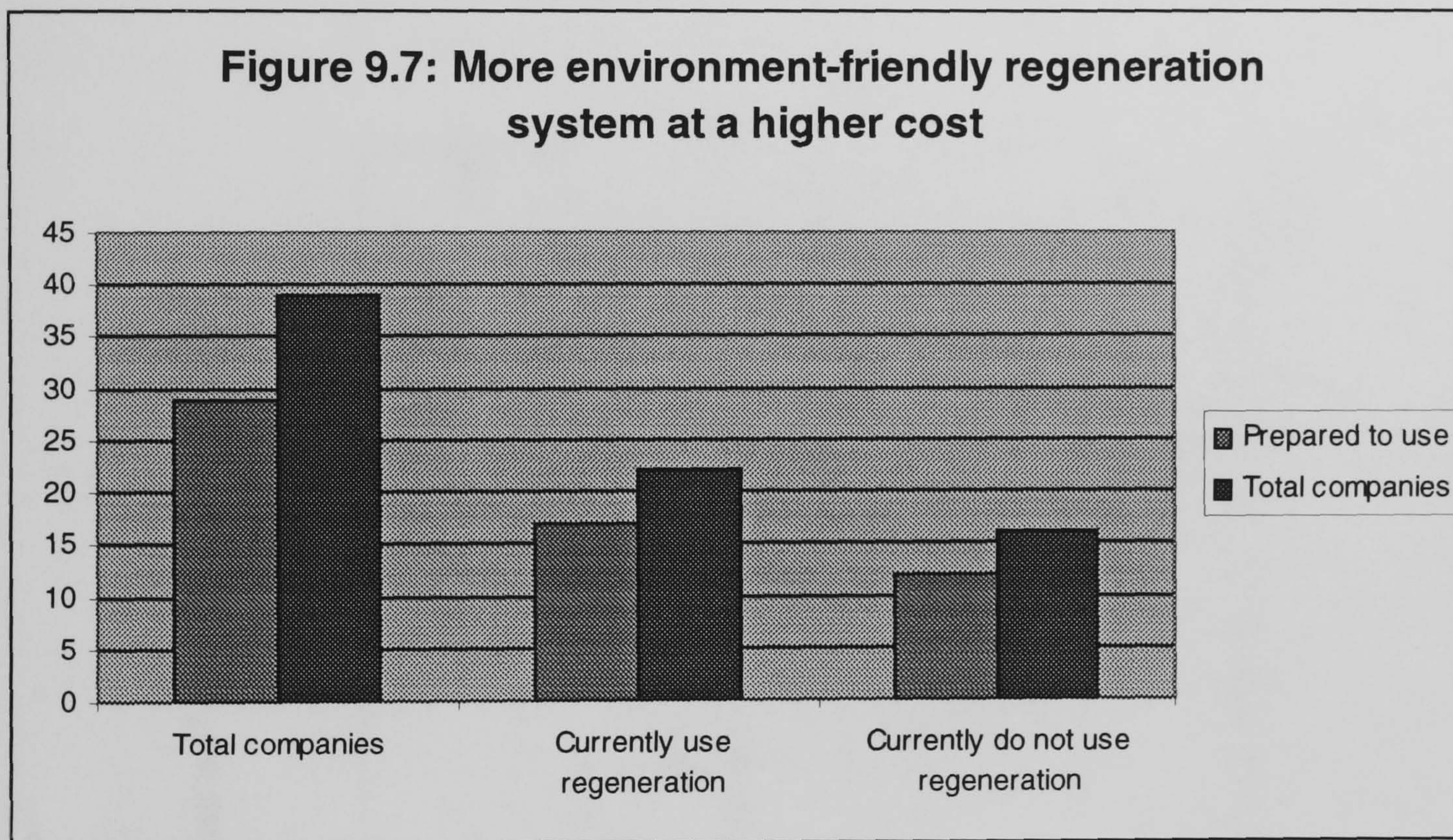
#### 9.4.1.3 Priority consideration for regeneration system

When the companies that do not regenerate etchants were asked about priority consideration for installing a regeneration system in future, the top priority (63%) was 'cost of purchasing and running a regeneration system'. Environment-friendliness of the regeneration system is the next priority consideration that accounts for 23%. This is expected since cost is one of the most important factors to be considered in making investment in capital equipment.

**Figure 9.6: Priority of regeneration system**

#### 9.4.1.4 Environment-friendliness of future regeneration system

Overall, 76% (29 out of 39) of the companies surveyed were prepared to use 'a regeneration system that is more environment-friendly at a higher overall cost'. In addition, only 6 out of these 29 companies further indicated that the cost should not be too expensive. 77% of the companies currently using regeneration in their facilities stated that they would use a more environment-friendly regeneration system at a higher overall cost, compared to 75% of the companies not using regeneration systems. This showed that although those PCM companies currently not regenerating were cost-conscious in choosing a regeneration system (as reflected from *Section 9.4.1.3*), environmental protection was an equally important consideration in making capital investments.



#### 9.4.2 Waste etchant disposal

*Figure 9.8* shows the percentage breakdown of the methods used by the PCM practitioners in disposing of the waste etchants.

Most of the PCM companies (77%) did not treat the waste etchant prior to disposal, as it might not be profitable to do so. 59% of the companies sent liquid waste etchant to the chemical companies for reclaim/recycle. The other 18% of companies engaged the service of licensed waste contractors to get rid of the waste at suitable landfill sites.

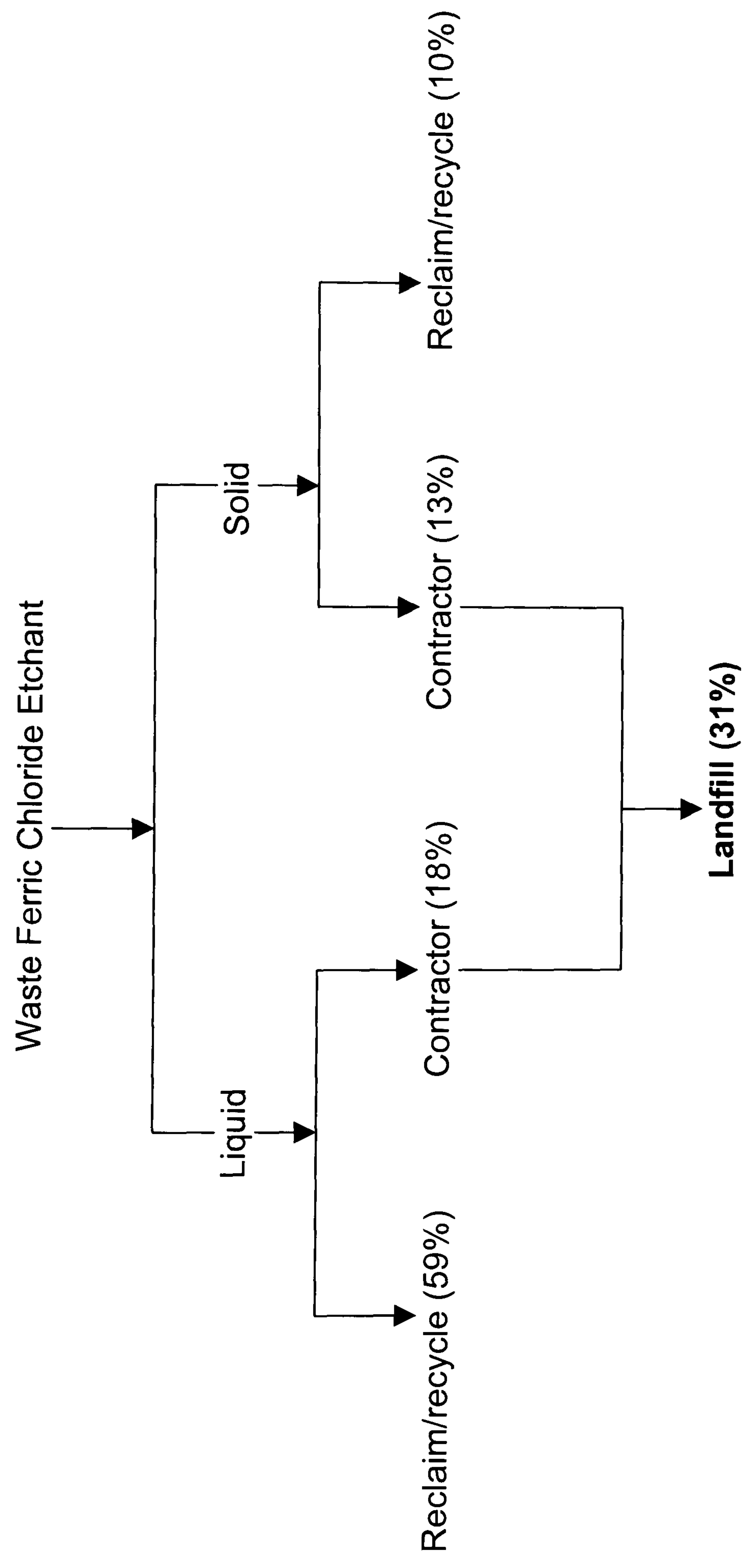
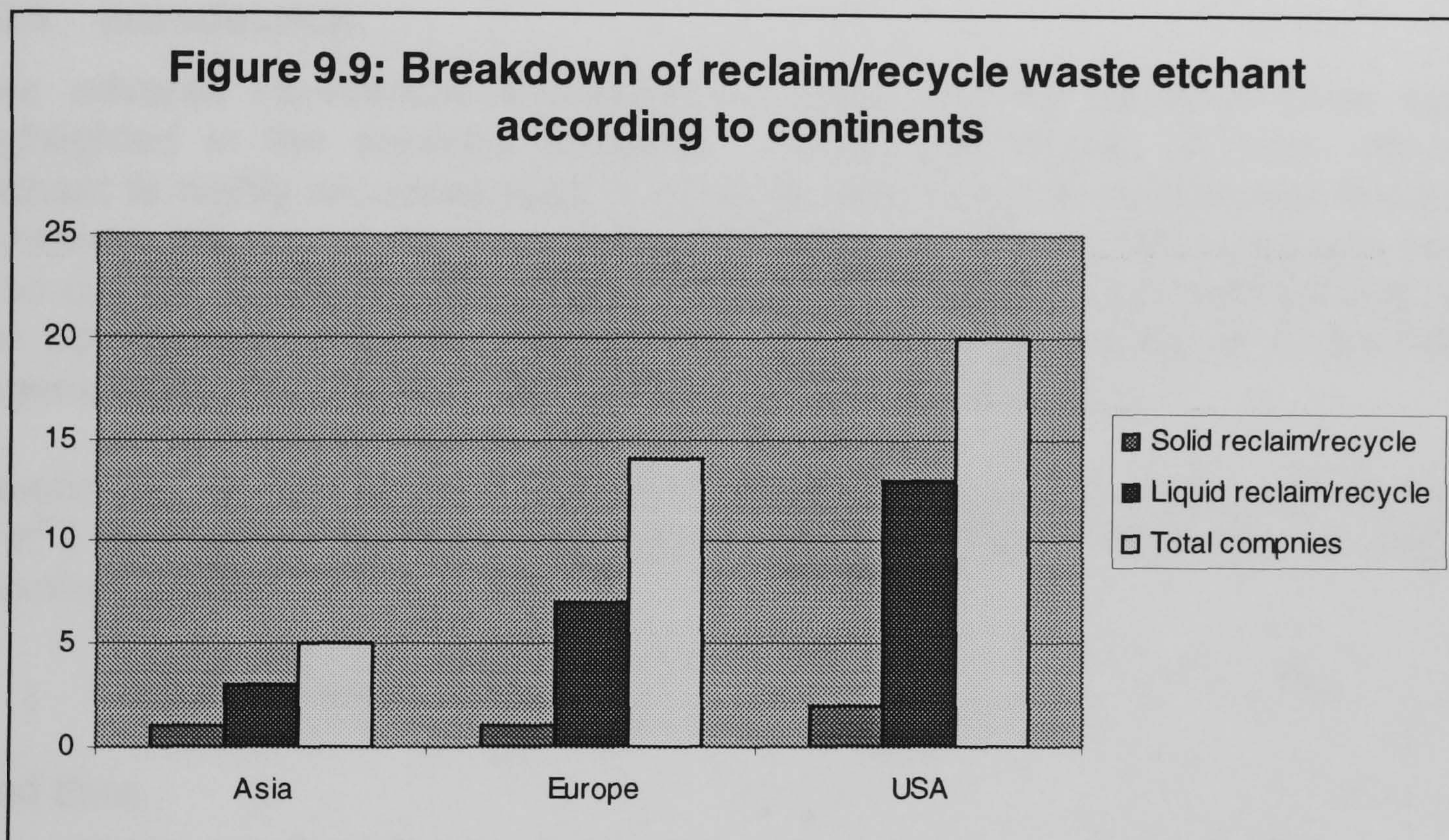


Figure 9.8: Disposal of waste etchant

Only 10% of the companies sent solidified waste etchant for reclaim. This result is expected as only waste etchants that contain relatively high proportion of valuable metals are suitable for this method of disposal. The other solidified waste etchants were disposed at landfill sites. This practice accounts for 13% of the total response.

The proportion of wastes that go to landfill sites (by combining the solid and liquid wastes) is 31% whereas the rest of the spent etchants are reclaimed or recycled.

Figure 9.9 shows a breakdown of the companies that reclaim or recycle the waste etchants according to continents. Asia has the highest percentage of the companies that reclaim/recycle the etchants with 80%, followed closely by US companies with 75%.



## 9.5 Conclusions

More than half of the PCM companies surveyed carried out regeneration, and chlorine regeneration is the most popular, though it has health and safety hazards. The main reason for not regenerating was lack of technical knowledge in understanding the basic know-how of regeneration systems. Hence, if technical training is given to the companies concerned, the proportion of companies using regeneration could be increased. The majority of the companies would use a more environment-friendly regeneration system, even though it may incur a higher overall cost. Regarding waste etchant disposal, most companies sent liquid waste etchant for reclaim or recycle.



## Chapter 10

# Regeneration of Ferric Chloride Solution in Etching AISI 304 Stainless Steel with Oxygen

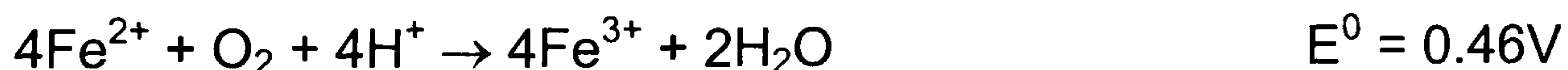
### 10.1 Introduction

The adverse environmental impacts of ferric chloride etchants have been highlighted in the previous chapters. Thus regeneration of ferric chloride etchant is highly recommended in order to reduce the environmental impacts. However, the use of chemicals in existing etchant regeneration systems have also caused environmental, health and safety concerns. One method that has the potential to be an environment-friendly alternative compared to the other regeneration systems is to use oxygen as an oxidising agent.

Kinetically, oxygen is capable of oxidising ferrous ( $\text{Fe}^{2+}$ ) ions back to ferric ( $\text{Fe}^{3+}$ ) ions according to the following redox half reaction although the rate of reaction is slow:



And thus



Indeed, past investigation on the kinetics of copper-ferric chloride reaction by Burrows *et al* [1964] came to the conclusion that dissolved oxygen did not promote regeneration of ferric ions. However, further research conducted showed different results; a laboratory experiment conducted by Ler [1993] showed that ferrous ions could be regenerated back to ferric ions, although the reaction is slow. The investigation indicated that the rate of oxidation is affected by the oxygen flow-rate and the temperature of ferric chloride. Moreover, as the solubility of oxygen in aqueous solution is rather low (see Appendix H), it is necessary to look into a more effective method of retaining the oxygen gas in the ferric chloride solution so that the mixing time is long enough to enhance the rate of chemical reaction. A breakthrough in oxygen regeneration system was achieved by Lubert and McGarigle [1993] with the aid

of a static mixer that prolongs the mixing time of oxygen and ferric chloride etchant, thus increases the rate of reaction. This method of regeneration was implemented in IBM [Lubert, 1997] in etching carbon steel materials for the manufacture of print bands. However, no research has been conducted in regenerating ferric chloride solution in etching other grades of stainless steels commonly used in PCM such as AISI 302, 304 or 316, in which the process control conditions are rather different.

Thus, the primary objective of this project is to study the technical and economical viability of regenerating ferric chloride solution in etching stainless steel grade AISI 304 which is commonly used in PCM, using oxygen as a regeneration chemical. The study was carried out at Tecan Components Ltd., a leading PCM company located in the UK. The study consisted of:

- (1.) To determine suitable operating conditions for oxygen regeneration;
- (2.) To determine the suitability of etching AISI 304 grade of stainless steel using the regenerated ferric chloride solution;
- (3.) To assess the cost effectiveness of oxygen regeneration compared to other existing regeneration systems.

## 10.2 Chemical Reactions of Oxygen Regeneration

From the chemical reaction below,



one mole of oxygen gas is required to regenerate four moles of ferrous chloride solution. Using the Equation of State of an Ideal Gas, it can be derived that one mole of oxygen gas occupies a volume of 24.055 litres by assuming that oxygen gas behaves as an ideal gas at atmospheric pressure and at a temperature of 20<sup>0</sup>C (for calculations, see Appendix J). Thus, 24.055 litres of oxygen is required to regenerate four moles of ferrous chloride if 100% of the oxygen gas is taking part in the regeneration. However, in view of the slow rate of reaction and low solubility of oxygen gas in aqueous solutions, it is envisaged that a much bigger volume of oxygen is required in the regeneration.

According to the collision theory of reaction rate, atoms, ions or molecules must collide before even have a chance of reacting to form one or more new substances. Thus, the more often the reactant particles collide, the faster the reaction should go. This means that the rate of reaction should be dependent on the total number of collisions between reactant particles in a given volume during a given time. The rate of reaction does not depend on collision frequency alone but also on the collision energy. The molecules must collide with enough energy to start a reaction. The minimum energy needed to start a reaction is known as activation energy. So the oxygen molecules must

possess enough activation energy and collide with the ferrous chloride and hydrochloric acid for the regeneration to occur.

### 10.2.1 Factors affecting reaction rate

The rate of reaction is often influenced by some parameters. These parameters can be of different forms; in the regeneration of ferric chloride etchant, the reaction can be affected by the following parameters:

- (1.) Concentration of HCl
- (2.) Flow-rate of oxygen gas
- (3.) Temperature of ferric chloride etchant and
- (4.) Mixing time of oxygen gas with ferric chloride etchant

If the concentration of one or more of the reactants (HCl and dissolved oxygen in this case) in a chemical reaction is increased, a faster reaction would occur. This happens to most chemicals but not all. Earlier investigation by Ler [1993] indicated the reaction rate is independent of HCl concentration whereas the rate of reaction increased with higher flow rates of oxygen.

Most reaction rates increase dramatically with increasing temperature as both the average velocity and kinetic energy of the molecules are increased, which means that the molecules will collide more frequently. The major effect of higher temperatures is the increase in the fraction of reactant molecules that can collide with a kinetic energy equal to or greater than the activation energy. Although the solubility of oxygen gas in aqueous solution decreases with an increase in temperature, the rate of regeneration was much faster (by more than two times) at a temperature of 95<sup>0</sup>C compared to 50<sup>0</sup>C [Ler, 1993]. However, etching of stainless steel is normally maintained at a constant temperature of 52-55<sup>0</sup>C in PCM to maintain the maximum etching rate. This is because most etching machines are made of polyvinyl chloride (PVC) materials that cannot withstand high temperatures. If temperatures higher than 55<sup>0</sup>C are necessary, the machines have to be constructed from titanium sheet [Allen, 1986e], but these machines are very costly. Thus, the parameters that can be varied are the oxygen gas flow-rate and mixing time of oxygen gas with ferric chloride etchant.

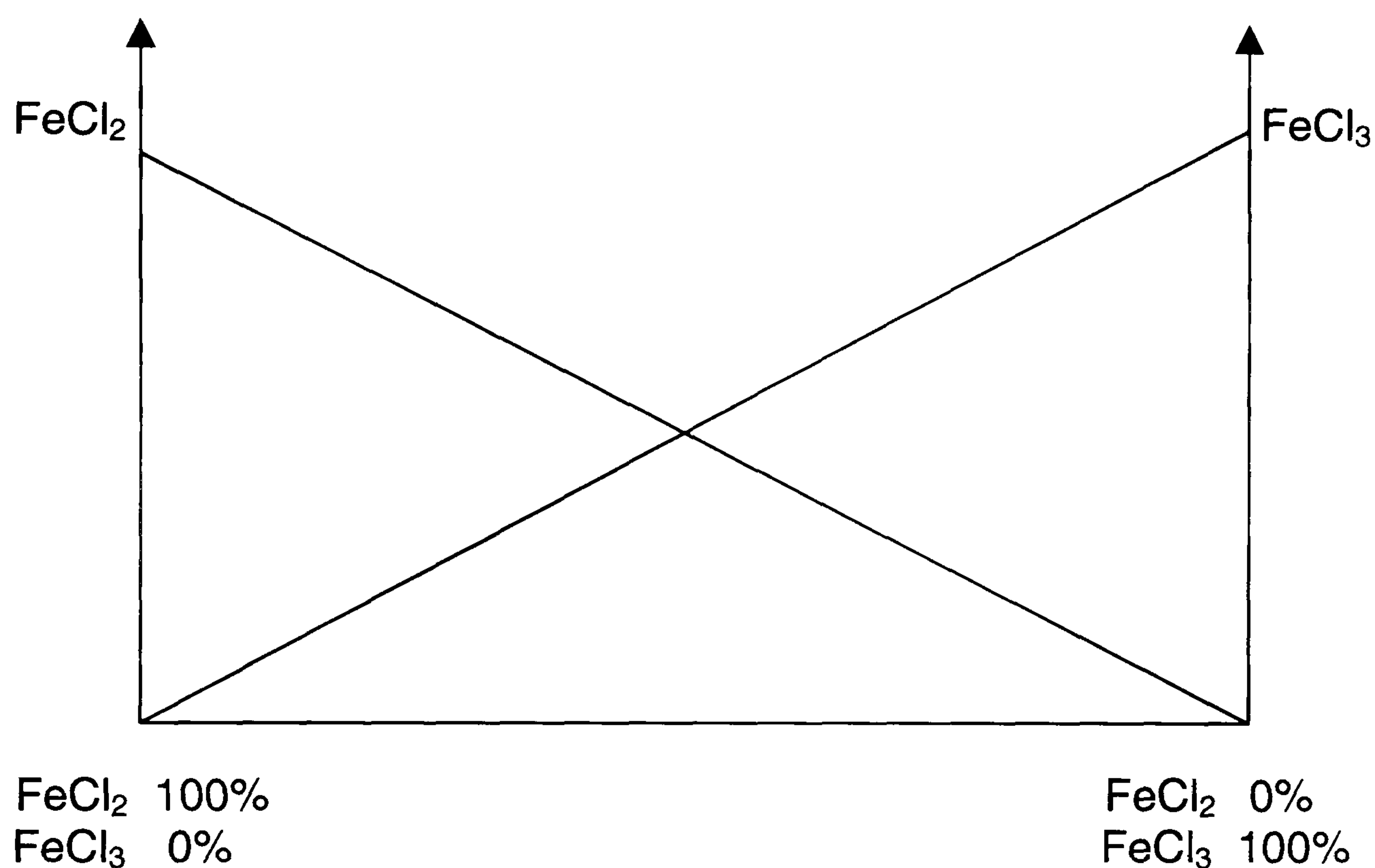
Increasing the mixing time of oxygen gas will provide more opportunity for reacting molecules to collide with each other to start a reaction. Mixing time of the oxygen gas with ferric chloride etchant can be increased by using a static mixer (see Appendix K), and by creating a back pressure downstream to the static mixer. There is, however, no established method of determining the actual mixing time between the oxygen and the etchant.

### 10.2.2 Ferric chloride/ferrous chloride system

In the oxidation of ferrous ions back to ferric ions, the following half reaction occurs:



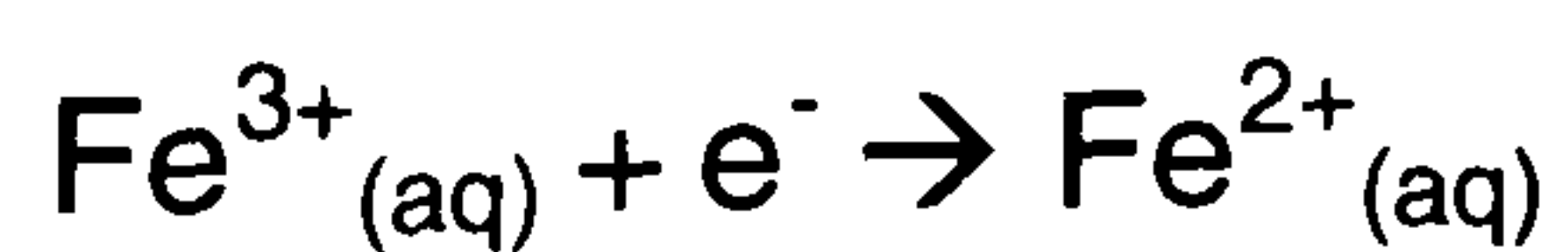
The system can be represented by *Figure 10.1* below:



**Figure 10.1: FeCl<sub>2</sub>/ FeCl<sub>3</sub> system**

### 10.3 Factors Affecting Etching of Stainless Steel

Ferric chloride etchant is a mixture of ferric chloride, hydrochloric acid and water. Ferric chloride is a red brown, volatile solid that is very hygroscopic and forms a yellow-brown solution. An aqueous solution of ferric chloride is acidic due to hydrolysis of the salt and it is also a strong oxidising agent, as shown by the value of the half reaction:



$$E^0 = 0.771 \text{ V}$$

### 10.3.1 Concentration of ferric chloride

The concentration of fresh ferric chloride etchant is often measured in  $^{\circ}\text{Baumé}$  and is a function of specific gravity (sg)

$$^{\circ}\text{Baumé } (^{\circ}\text{Bé}) = 145 \frac{\text{sg} - 1}{\text{sg}}$$

In PCM,  $\text{FeCl}_3$  solution at 43  $^{\circ}\text{Bé}$  (3.37M) is commonly used due to the high etch rate and good quality of finish at this concentration. The concentration of ferric chloride is normally monitored by a hydrometer. As etching proceeds, the ferric ion content decreases with a corresponding increase in the ferrous ion content and thus the strength of the etchant, which is essentially the etching power, decreases. The strength of an etchant can be measured by means of oxidation-reduction potential (ORP).

### 10.3.2 Oxidation-reduction potential (ORP)

Oxidation-reduction potential (ORP), also known as redox potential, is one of the most commonly used analytical methods employed by the PCM industry to measure the strength of etchants. It is often used as a tool for control of continuous etching and rejuvenation/regeneration of etchants. Studies by Allen and Ler [1995] showed that ORP is indeed a function of ferric and ferrous ions in the ferric chloride etching system. The ORP of the half reaction of the ferric/ferrous system can be expressed mathematically by the Nernst equation:

$$E = E^0 + \frac{2.303RT}{nF} \log_{10} \frac{[a_{\text{ferric ion}}]}{[a_{\text{ferrous ion}}]}$$

where

$E$  = ORP of the system

$E^0$  = Standard Electrode Potential

$R$  = Gas constant

$T$  = Absolute temperature (K)

$n$  = Number of electrons changed in the Redox reaction

$F$  = Faraday constant

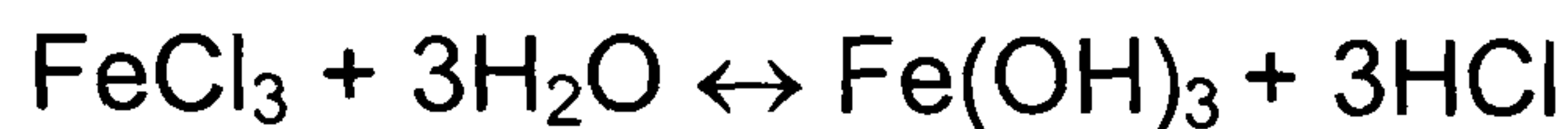
$[a_{\text{ferric ion}}]$  = Activity of oxidizing ion (ferric ion)

$[a_{\text{ferrous ion}}]$  = Activity of reducing ion (ferrous ion)

From the Nernst equation above, it is obvious that the temperature and relative concentrations or activities of ferric and ferrous ions directly affect the ORP of the system.

### 10.3.3 Free acid content

Free acids are present in the etching system in the form of hydrochloric acid (HCl). The presence of free acids in the etching system is due to the hydrolysis of ferric chloride in water that liberates free hydrochloric acid from the following reaction:



If the acid is used up in the oxidation process, the reaction will move to the right and result in further hydrolysis.

Free acids in the etchant affects both the rate of etching and surface finish of the final products [Allen, Hegarty and Horne, 1981; Visser and Junker, 1994b; Allen and Li, 1988; Beaupre, 1987]. Hence, the control of HCl level is important in etching stainless steel, although the regeneration by oxygen is independent of presence of excess free acids [Ler, 1993].

Various manual titration methods have been proposed and studied for the analysis of free acid content in the ferric chloride etchant [Gulbrandsen, 1986; Reyes, 1976; Thayer, 1986; Murski, 1986]. However, these methods give different results even in determining analytically pure  $\text{FeCl}_3$  solutions; in analysing used etchants, these analytical methods are further complicated by contaminant metal ions present in the etching systems. Thus, Allen [1998] proposed the use of pH meters to monitor free acid levels in the etchant in view of the progress in pH probe design. The value of pH is a convenient way of expressing the concentration of hydrogen by the following formula:

$$\text{pH} = -\log_{10} [\text{H}^+]$$

Thus, in the experiment, pH, ORP and temperature are measured simultaneously by using a combination pH meter by means of a pressurised pH probe, and standard ORP and temperature electrodes.

### 10.3.4 Surface finish

Surface finish of etched metal is a measure of etching quality. The surface finish ( $R_a$ ) is measured in terms of  $\mu\text{m}$ , which is the average roughness of etched samples.

## 10.4 Chemicals and Equipment

The following chemicals and equipment were used throughout this investigation. A detailed list is given in Appendix L.

## 10.4.1 Chemicals

### 10.4.1.1 Ferric chloride etchant

Ferric chloride solution, with a maximum 0.6% hydrochloric acid content, was supplied by Hays Chemicals.

### 10.4.1.2 Hydrochloric acid

Concentrated hydrochloric acid (32% volume/weight) was supplied by Hays Chemicals.

### 10.4.1.3 Compressed oxygen and related fittings

Compressed oxygen gas and the related fittings such as regulators and flashback arrestor were supplied by Air Products plc. The oxygen gas was supplied in a cylinder and at a minimum concentration of 99.4% purity. Each cylinder occupies a capacity of 10.05 m<sup>3</sup> at standard temperature and pressure.

## 10.4.2 Equipment

### 10.4.2.1 Etching machine

Chemcut etching machine with a sump capacity of 450 litres was used for this investigation.

### 10.4.2.2 Measurement of pH, ORP and Temperature

Knick Process Unit 73 pH meter, pH, ORP and temperature electrodes were used for the measurement and reading of pH, ORP and temperature simultaneously.

### 10.4.2.3 Measurement of density/concentration of ferric chloride solution

A hydrometer, supplied together with the Chemcut etching machine, was used to measure the density of etching solution in °Bé.

### 10.4.2.4 Oxygen gas flow measurement

Oxygen gas flow meter with a measurement range of 40-400 litre/minute, was supplied by Platon Instrumentation.

### 10.4.2.5 Static mixer

Static mixer for increasing the mixing time of oxygen and used ferric chloride, was supplied by Koch-Glitsch, Inc, USA.

#### 10.4.2.6 Micrometer

Micrometer with accuracy of 0.5  $\mu\text{m}$  was used in measuring the etch rate of samples.

#### 10.4.2.7 Measurement of surface finish

Rank Taylor Hobson 'Talysurf 4' was the instrument used for measuring the surface texture of the etched samples.

#### 10.4.2.8 Scanning electron microscope (SEM)

Scanning electron microscope was used to take the magnified surface texture pictures of the etched samples.

### 10.5. Experimental Set-up

The experimental set-up of the regeneration system is as shown in *Figure 10.2*.

A one-stage Chemcut etching machine **1** with a sump capacity of 450 litres was used to carry out this experiment. The ferric chloride to be regenerated was pumped through a static mixer **3** by a recirculation pump **4** with a pumping capacity of 360 litres per minute and recirculated back to the sump. The ferric chloride solution was conveyed through a polyvinylidene chloride (PVDC) pipe **2** of about 5 cm in diameter. A throttling valve **5** located downstream of the static mixer created a back-pressure of 0.2 bar.

Compressed oxygen gas was introduced into the static mixer via conduit **6**. The oxygen flow-rate was adjusted by valve **7** and monitored by flow meter **8**. The oxygen gas was introduced into the system just upstream of the static mixer. The oxygen gas was supplied by liquified oxygen in cylinders **9**. The process parameters were monitored constantly by a pH meter **10** that also measured the ORP and temperature of the ferric chloride etchant. A specific gravity measuring device **11** was placed at the etching machine to monitor the density of the ferric chloride solution.

### 10.6 Experimental Procedures

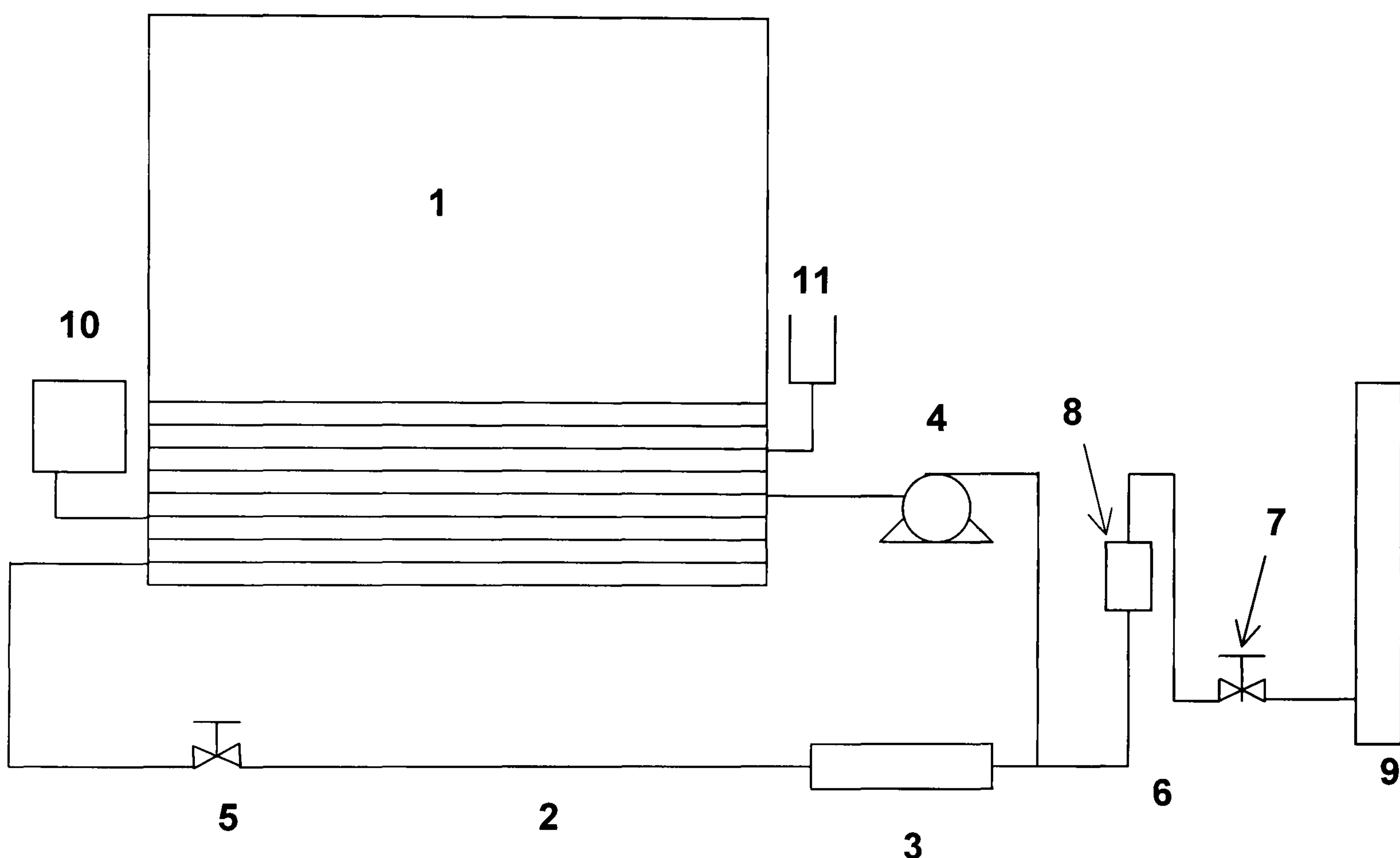
The experimental procedures carried out in this study are as follows:

#### 10.6.1 Dissolution of AISI 304 stainless steel material

450 litres of 43  $^{\circ}\text{Bé}$  (3.37M) fresh ferric chloride solution was used in this investigation. The conveyor speed of the etching machine was maintained at 54 mm/min throughout the experiment. Stainless steel AISI 304 materials were then dissolved in the ferric chloride solution. Initially, blanks of steel materials at about one kg in weight were dissolved in the etching solution and etching quality such as roughness and pitted surfaces were constantly monitored. After



5 kg of AISI 304 materials have been dissolved into the system, or when the ORP was lowered to about 562 mV, the operation parameters like pH, ORP, specific gravity, temperature were closely monitored after each etching cycle. In addition, etching quality such as the etch rate and surface finish were measured and observed. The dissolution of AISI 304 materials were stopped when the etchant showed signs of quality that were deemed to be unacceptable by customers such as roughness and pitted surfaces. At this point, the etchant needed to be regenerated to restore the freshness. Thus, the recirculation pump was switched on and oxygen gas was introduced at the upstream of the pump to start regeneration.



**Figure 10.2: Experimental set-up of oxygen regeneration system**

**Key**

- 1 - Chemcut etching machine
- 2 - Polyvinylidene chloride (PVDC) pipe
- 3 - Static mixer
- 4 - Pump
- 5 - Throttling valve
- 6 - Conduit
- 7 - oxygen flow-regulator
- 8 - Oxygen flow-meter
- 9 - Oxygen cylinders
- 10 - pH, ORP and temperature measuring device
- 11- Specific gravity measuring device/hydrometer

### 10.6.2 Regeneration of spent ferric chloride by oxygen

Three sets of experiments were carried out using oxygen at flow rates of 118, 90 and 60 litres/minute. The main aim of the experiments was to investigate whether the spent etchant could be successfully regenerated. As the free acid level in the etchant affects etching qualities, the experiments were carried out without the addition of HCl. Moreover, it was assumed that HCl could be replenished by the hydrolysis of ferric chloride.

### 10.6.3 Etching of AISI 304 with regenerated etchant

The experiment was carried out to test the suitability of etching AISI 304 materials with the conditions of the regenerated etchant maintained without addition of acids. If the test samples were found to be unacceptable, the operating conditions could then be adjusted. Since the control of free acid level is important, the acid content in the system was adjusted by adding concentrated HCl (32% v/w). Other operating conditions could be adjusted if necessary in order to achieve good surface finish.

### 10.6.4 Effects of varying oxygen flow rate on efficiency of regeneration

Two experiments were carried out with different oxygen flow rates while the pH of the system was maintained at a constant level by adding concentrated HCl. The main aims were to investigate the effects of varying the oxygen flow rates on regeneration and the etching quality of test blanks. Flow rates of oxygen gas at 90 and 120 litres/minute were used in this study and the back pressure of the system was maintained at 0.2 bar. For both the experiments, the ORPs were increased from 577 to 581 mV during regeneration.

## 10.7 Results and Discussions

### 10.7.1 Effects of dissolution of AISI 304 stainless steel on ORP, pH and specific gravity of the system

*Table 10.1* shows the ORP, pH, temperature, specific gravity (in  $^{\circ}$ Bé), etch rate and surface finish of metal substrate after each cycle of etching.

#### 10.7.1.1 ORP

A plot of the ORP against weight of metal dissolved in *Figure 10.3.1* showed that the reduction in ORP is almost directly proportional to the weight of the metal etched. After 5 kg of AISI 304 materials have been dissolved into the system, the ratio of ferric ion against the ferrous ion is approximately 5:1 (See Appendix M). At this ratio, the decrease in ORP should be rather constant as predicted by the Nernst equation and studies conducted by Ler [1993].

**Table 10.1: Dissolution of steel materials against operating parameters and etch quality**

Metal dissolved, cumulative (g)	ORP (mV)	pH	Temp. (°C)	°Bé	Etch rate (mm/min)	Surface finish
5000	562	-0.80	52.8	43	-	-
5085	561	-0.82	53.0	43	39.7	Good
5245	561	-0.84	52.9	43	37.4	Good
5405	560	-0.85	53.1	43	37.4	Good
5565	559	-0.88	52.9	43	37.4	Good
5735	558	-0.89	52.9	43	39.7	Good
5905	557	-0.90	52.8	43	39.7	Good
6075	556	-0.91	52.8	43	39.7	Good
6235	555	-0.92	52.9	43	37.4	Good
6405	554	-0.94	52.8	43	39.7	Good
6575	553	-0.96	52.7	43	39.7	Good
6735	553	-0.97	52.9	43	37.4	Good
6890	552	-0.98	52.9	43	37.4	Good
7030	551	-1.00	52.8	43	37.4	Good
7120	551	-1.01	52.9	43	32.7	Rough

#### 10.7.1.2 pH

A plot of pH against the weight of metal etched as shown in *Figure 10.3.2* showed that pH decreased in proportion to the amount of metal etched. Although the etching of metal does not consume free acid in the system, it is a common belief that the free acid level in the etching system decreases as the etching proceeds, due to the constant evaporation of the acid into the air. This would increase the pH instead of the other way round, as a lower free acid content should produce a higher pH. However, since the ferric chloride/ferrous chloride/water is a complicated system, various complexes might have formed during the course of metal dissolution, resulting in a decrease in pH reading.

#### 10.7.1.3 Temperature

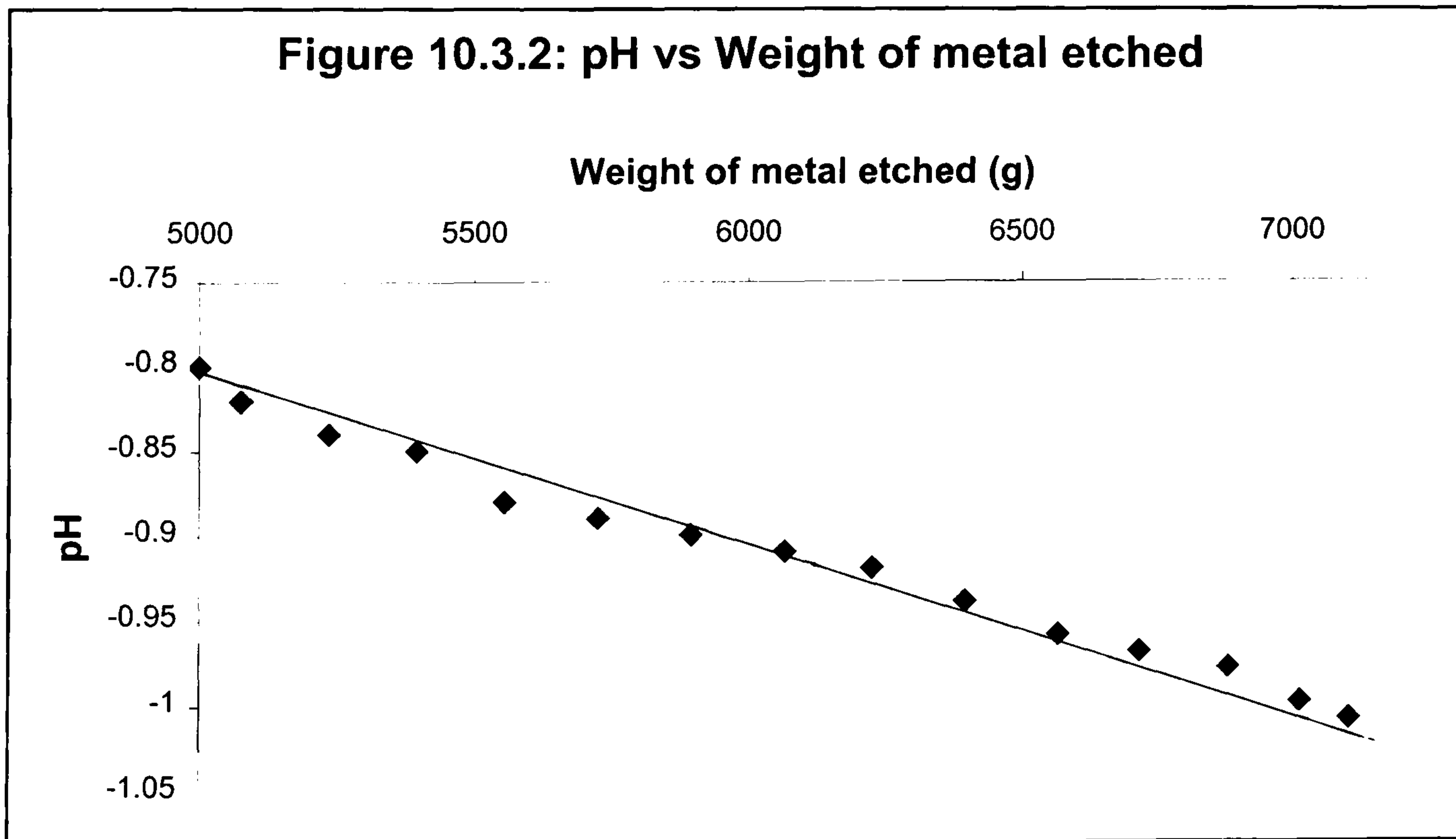
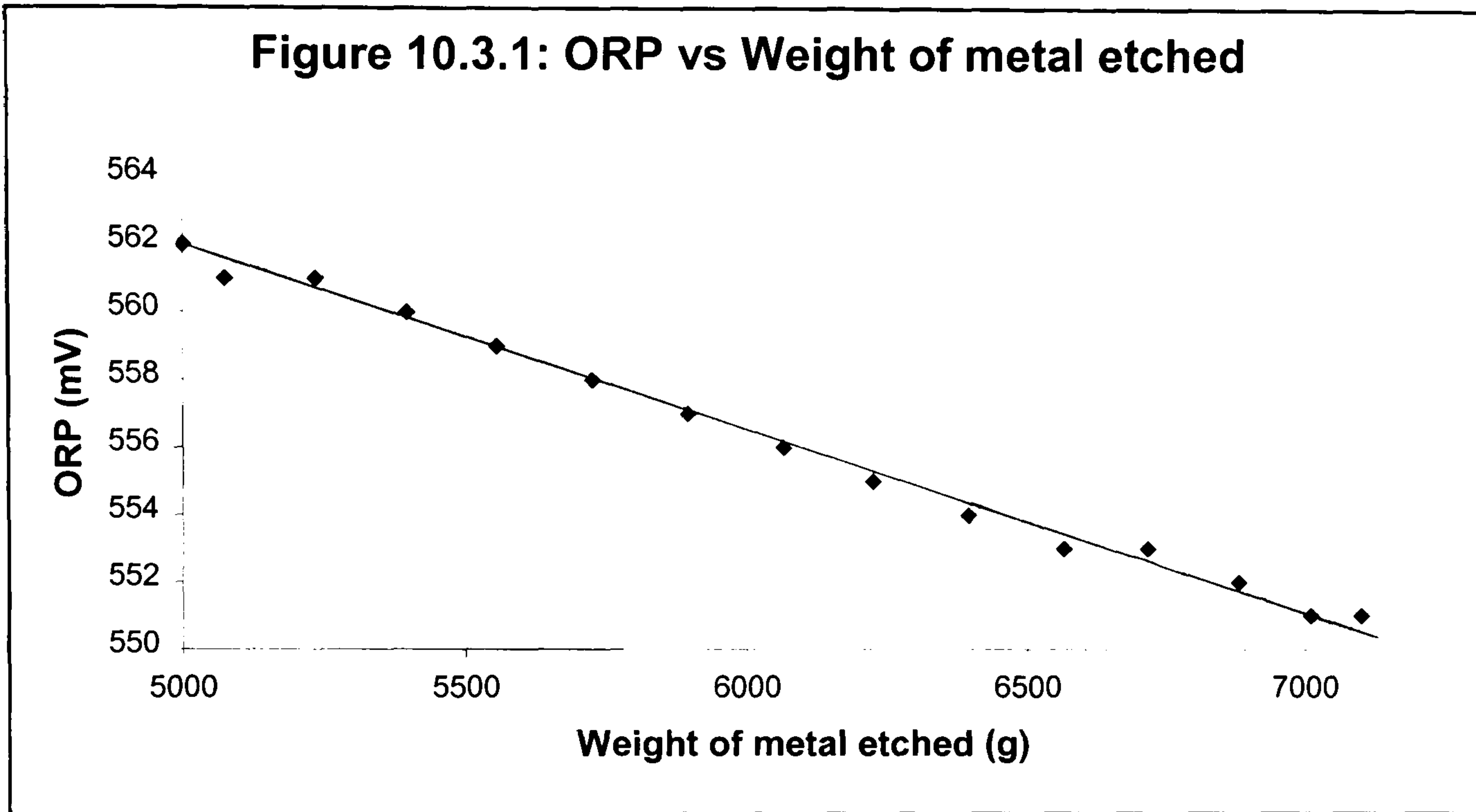
An automatic cooling and heating control system maintained the temperature of the system constantly to 52-54 °C.

#### 10.7.1.4 Specific gravity

The specific gravity of the system remained constant at 43 °Bé.

#### 10.7.1.5 Etch rate and surface finish

Most of the time etch rates were at about 37.4-39.7 mm/min range. The etch rate slowed down and the surface finish began to show rough finish when the ORP was decreased to 551 mV. At this point, the dissolution of metal was stopped as the ferric chloride etchant was no longer suitable for etching AISI 304 materials.



### 10.7.2 Regeneration of spent ferric chloride etchant

The experiments showed that the spent etchant could be regenerated. *Tables 10.2, 10.3 and 10.4* show the results of regeneration of etchant at the oxygen flow rate of 118, 90 and 60 litres/minute respectively.

It should be pointed out that the cooling water system was not functioning properly when the etchant was being regenerated at a oxygen flow rate of 118 litres/minute. Thus, the temperature of the etching solution was not under control and increased to 55.6 °C at the end of the experiment. As a result, the experiment had to be interrupted when the rate of oxygen was lowered to 90 litres/minute.

#### 10.7.2.1 Efficiency of oxygen utilisation in regeneration

*Figures 10.4.1, 10.5.1 and 10.6.1* show the relationship of ORP with time at the oxygen flow rate of 118, 90 and 60 litres/minute respectively. The results indicated that the rate of regeneration is rather constant when the ORP was increased although the volume of oxygen required to regenerate one mV of ORP increases at higher ORPs as shown from the calculations below.

##### (i.) 118 litres/minute (ORP from 551-560 mV)

As the ORP is a function of temperature, the actual ORP should be lower than 561 mV at the end of this set of experiment. From the work carried out by Ler [1993] using analytical grade of ferric/ferrous chloride in the modelling of ORP, a difference of 3 °C would result in approximately one mV of ORP. Thus the actual ORP of the regeneration was 560 instead of 561 mV. Thus the total volume of oxygen used for this set of experiment is 40 minutes x 118 litres/minute = 4720 litres of oxygen

From the Nernst's Equation,

$$E = E^0 + \frac{2.303RT}{nF} \log_{10} \frac{[a_{\text{ferric ion}}]}{[a_{\text{ferrous ion}}]}$$

In which the standard electrode potential,  $E^0$  is 0.771 V.

However, the activities of oxidising and reducing species only equate to concentrations in the dilute solutions of 1M or less and therefore have relatively little value when using concentrated solutions such as found in ferric chloride etchant used in this experiment.

When concentration of solutions can be measured, it is simpler to work to the following formula [Allen and Ler, 1995]

$$E = E^0_{\text{formal}} + \frac{2.303RT}{nF} \log_{10} \frac{[a_{\text{ferric ion}}]}{[a_{\text{ferrous ion}}]}$$

From the measurements carried out by Allen and Ler [1995],  $E^0_{\text{formal}}$  for  $\text{FeCl}_3/\text{FeCl}_2$  system at a concentration of 3.7M at  $53^\circ\text{C}$  is estimated to be 0.526 V. This value is thus used for the calculation of oxygen gas utilisation.

The activities of ferric ion to ferrous ion is

$$\log_{10} \frac{[a_{\text{ferric ion}}]}{[a_{\text{ferrous ion}}]} = \frac{nF}{2.303RT} [E - E^0_{\text{formal}}]$$

Where

$$E^0_{\text{formal}} = 0.526 \text{ V}$$

$$n = 1 \text{ (for } \text{FeCl}_3/\text{FeCl}_2 \text{ system)}$$

$$F = 9.6485 \times 10^4 \text{ Cmol}^{-1}$$

$$R = 8.314 \text{ JoulesK}^{-1}\text{mol}^{-1}$$

$$T = (273+53)\text{K} = 326\text{K}$$

At ORP or  $E = 551 \text{ mV}$  or  $0.551 \text{ V}$

$$\log_{10} \frac{[a_{\text{ferric ion}}]}{[a_{\text{ferrous ion}}]} = 0.3864, \text{ and } \frac{[a_{\text{ferric ion}}]}{[a_{\text{ferrous ion}}]} = 2.43$$

Total number of moles of [Ferric ion] in the 450-litre Chemcut etching machine at an ORP of 551 mV

$$= \frac{1}{(1+2.43)} \times 450 \text{ litres} \times 3.37 \text{ moles/litre} = 442.1 \text{ moles}$$

Likewise it can be calculated that at ORP of 560mV or 0.560V,

$$\frac{[a_{\text{ferric ion}}]}{[a_{\text{ferrous ion}}]} = 3.35,$$

Total number of moles of [Ferric ion] in the 450-litre Chemcut etching machine at an ORP of 560 mV

$$= \frac{1}{(1+3.35)} \times 450 \text{ litres} \times 3.37 \text{ moles/litre} = 348.6 \text{ moles}$$

Total number of moles of [Ferric ion] regenerated  
 = (442.1 – 348.6) moles  
 = 93.5 moles

From the chemical reaction below,



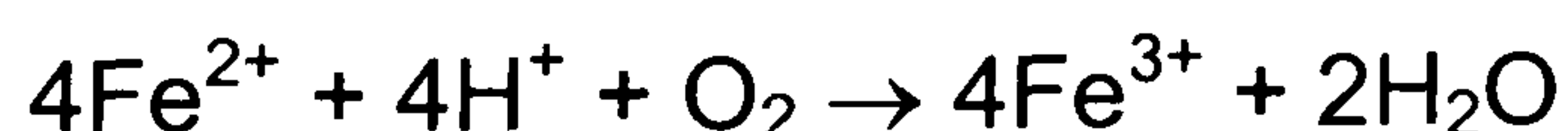
One mole (or 24.055 litres) of oxygen gas is required to regenerate four moles of ferrous chloride solution for 100% efficiency, or 6.014 litres/moles of [Ferric ion]. As 4720 litres of oxygen gas was required to regenerate 93.5 moles of [Ferric ion], the % efficiency of regeneration =  $6.014/4720 \times 93.5 = 11.91\%$

(ii.) At oxygen flow rate of 90 litres/minute (ORP from 560-570 mV) and 60 litres/minute (ORP from 570-575 mV)

The total volume of oxygen gas used in regenerating ORP from 560-570 mV were 5940 litres (66 minutes x 90 litres/minute) and 570-575 mV were 3600 litres (60 minutes x 60 litres/minute) respectively.

Using the calculations above, it can be calculated that the efficiency of regeneration at oxygen flow rate of 90 litres/minute (ORP from 560-570 mV) and 60 litres/minute (ORP from 570-575 mV) was 8.73% and 6.13% respectively (see calculations in Appendix N).

This trend is expected as the ferrous ions, a reactant species, were being used up continuously during the oxidation process below:



and thus the rate of reaction was reduced. Therefore at higher ORPs, more oxygen is required for regeneration.

These % efficiencies were commendable in view of the slow reaction rate as pointed out in the literature survey in Section 10.1. The increase in efficiency was probably due to the use of a static mixer that prolongs the mixing time of oxygen molecules with the ferric chloride solution, thus providing more opportunity for the reactant molecules to react.

#### 10.7.2.2 pH

The pH of the system fluctuated when the oxygen gas was being introduced into the system. This was due to the sudden increase of oxygen gas in the system, both in the form of bubbles and dissolved oxygen. However, the readings showed that the pH was increased at a rate which is directly proportional to the rate of regeneration as shown in *Figures 10.4.2, 10.5.2 and 10.6.2*, although the trend was not very evident at the beginning of the

experiment (see *Figure 10.4.2*). The increase in pH readings is expected due to the depletion of hydrogen ions in the system during the oxidation process.

It was found that there is a change of pH reading whenever the etching solution was cooled overnight and heated up in the next day. For example, when the regeneration was interrupted in the second experiment, the pH was lowered by 0.26 unit, although there was a temperature difference of 3.1 °C (see *Table 10.3*). The pH difference between the second and third experiment was 0.19 unit. It should be pointed out that the ferric chloride/ferrous chloride/water is a complicated system. Although much research has been conducted, the chemical reactions taking place in the system are not fully understood. The possible explanations are:

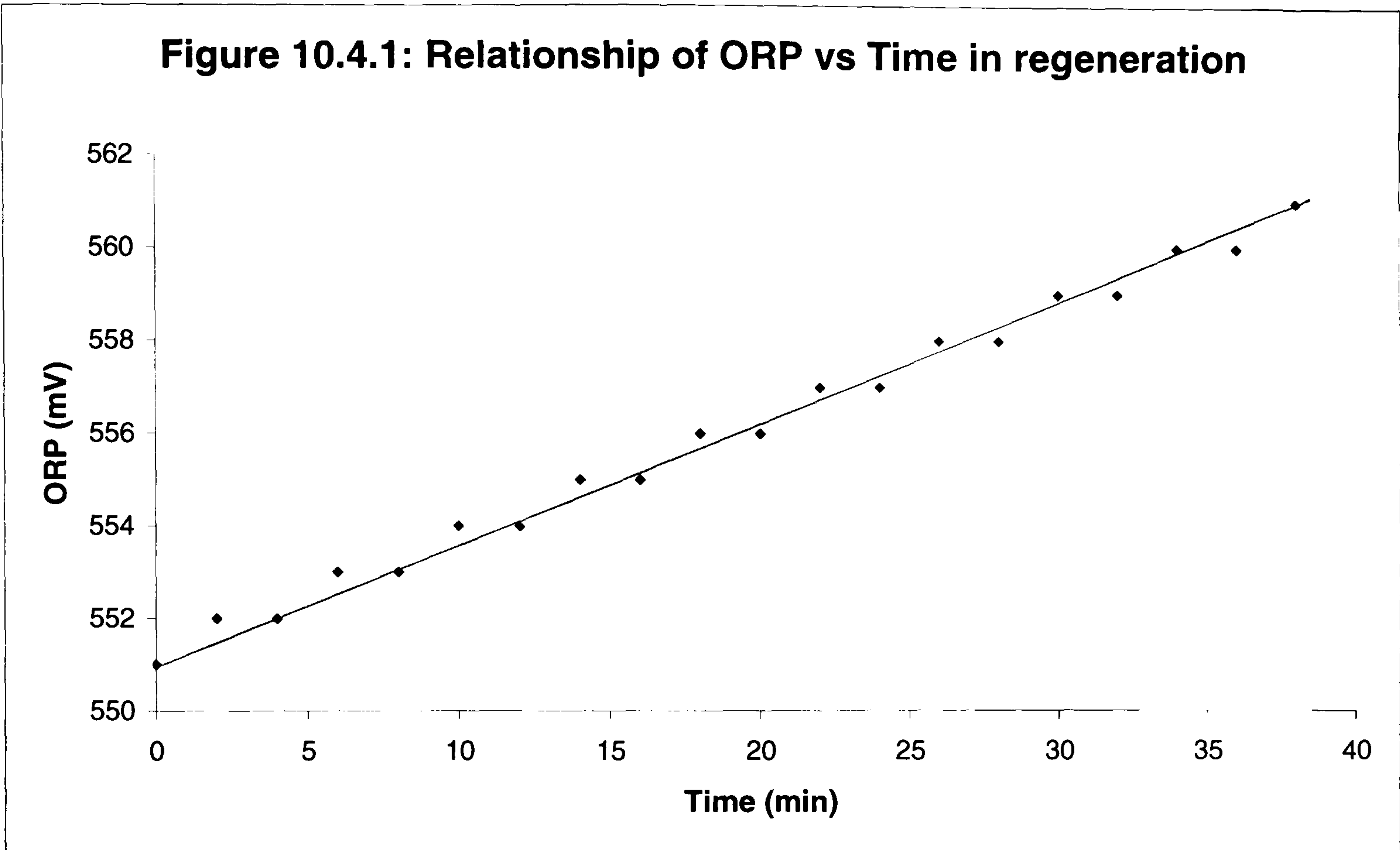
- (1) Certain amount of free acids may have evaporated into the atmosphere when the system is being cooled down and heated up.
- (2) The hydrolysis of ferric ions with water molecules and formation of ferrous/ferric complexes may have decreased the free acid level.

**Table 10.2: Regeneration of etchant at oxygen flow rate of 118 litres/minute**

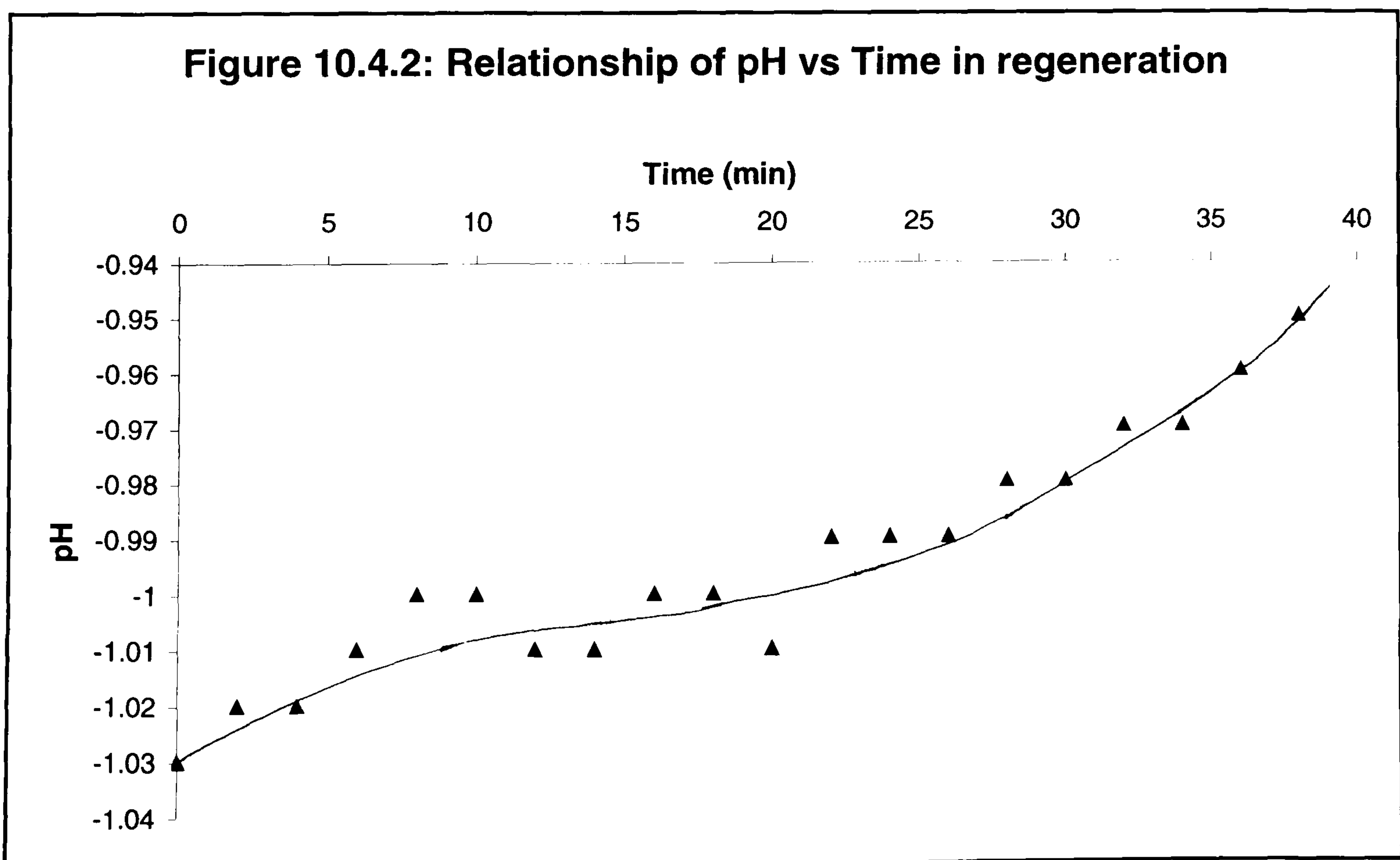
Time (min)	ORP (mV)	pH	Temp. (°C)	°Bé	Observations
0	551	-1.03	52.9	43.0	<ul style="list-style-type: none"> <li>• pH readings were fluctuating.</li> <li>• Cooling water pump was not working.</li> </ul>
2	552	-1.02	53.0	43.0	
4	552	-1.02	53.0	43.0	
6	553	-1.01	53.1	43.0	
8	553	-1.00	53.2	43.0	
10	554	-1.00	53.3	43.0	
12	554	-1.01	53.5	43.0	
14	555	-1.01	53.6	43.0	
16	555	-1.00	53.8	43.0	
18	556	-1.00	53.9	43.0	
20	556	-1.01	54.0	43.0	
22	557	-0.99	54.2	43.0	
24	557	-0.99	54.4	43.0	
26	558	-0.99	54.6	43.0	
28	558	-0.98	54.7	43.0	
30	559	-0.98	54.9	43.0	
32	559	-0.97	55.0	43.0	
34	560	-0.97	55.2	43.0	
36	560	-0.96	55.3	43.0	
38	561	-0.95	55.4	43.0	
40	561	-0.95	55.6	43.0	



**Figure 10.4.1: Relationship of ORP vs Time in regeneration**



**Figure 10.4.2: Relationship of pH vs Time in regeneration**



**Table 10.3: Regeneration of etchant at oxygen flow rate of 90 litres/minute**

Time (min)	ORP (mV)	pH	Temp. (°C)	°Bé	Observations
0	561(560)	-0.95	55.6	43.0	<ul style="list-style-type: none"> <li>pH readings were fluctuating.</li> </ul>
2	562(561)	-0.95	55.7	43.0	
4	562(561)	-0.93	55.8	43.0	
6	563(562)	-0.93	56.0	43.0	
Experiment was interrupted due to malfunctioning of the cooling water pump.					<ul style="list-style-type: none"> <li>Cooling water pump was not working</li> </ul>
8	562	-0.67	52.9	43.0	<ul style="list-style-type: none"> <li>Manual control of cooling system from this stage onwards</li> </ul>
10	563	-0.66	52.8	43.0	
12	563	-0.64	52.7	43.0	
14	563	-0.63	52.3	43.0	
16	563	-0.61	52.0	43.0	
18	563	-0.59	51.8	43.0	
20	564	-0.58	51.8	43.0	
22	564	-0.59	51.7	43.0	
24	564	-0.58	51.8	43.0	
26	565	-0.58	52.0	43.0	
28	565	-0.57	52.0	43.0	
30	565	-0.56	52.0	43.0	
32	565	-0.57	51.7	43.0	
34	566	-0.56	51.5	43.0	
36	566	-0.56	51.5	43.0	
38	566	-0.56	51.6	43.0	
40	567	-0.55	51.8	43.0	
42	567	-0.54	51.8	43.0	
44	567	-0.54	52.0	43.0	
46	568	-0.52	52.1	43.0	
48	568	-0.51	52.2	43.0	
50	568	-0.50	52.1	43.0	
52	568	-0.50	52.0	43.0	
54	568	-0.50	51.8	43.0	
56	569	-0.49	51.8	43.0	
58	569	-0.49	51.9	43.0	
60	569	-0.48	52.0	43.0	
62	570	-0.48	52.1	43.0	
64	570	-0.46	52.3	43.0	
66	570	-0.46	52.2	43.0	

Figure 10.5.1: Relationship of ORP vs Time in regeneration

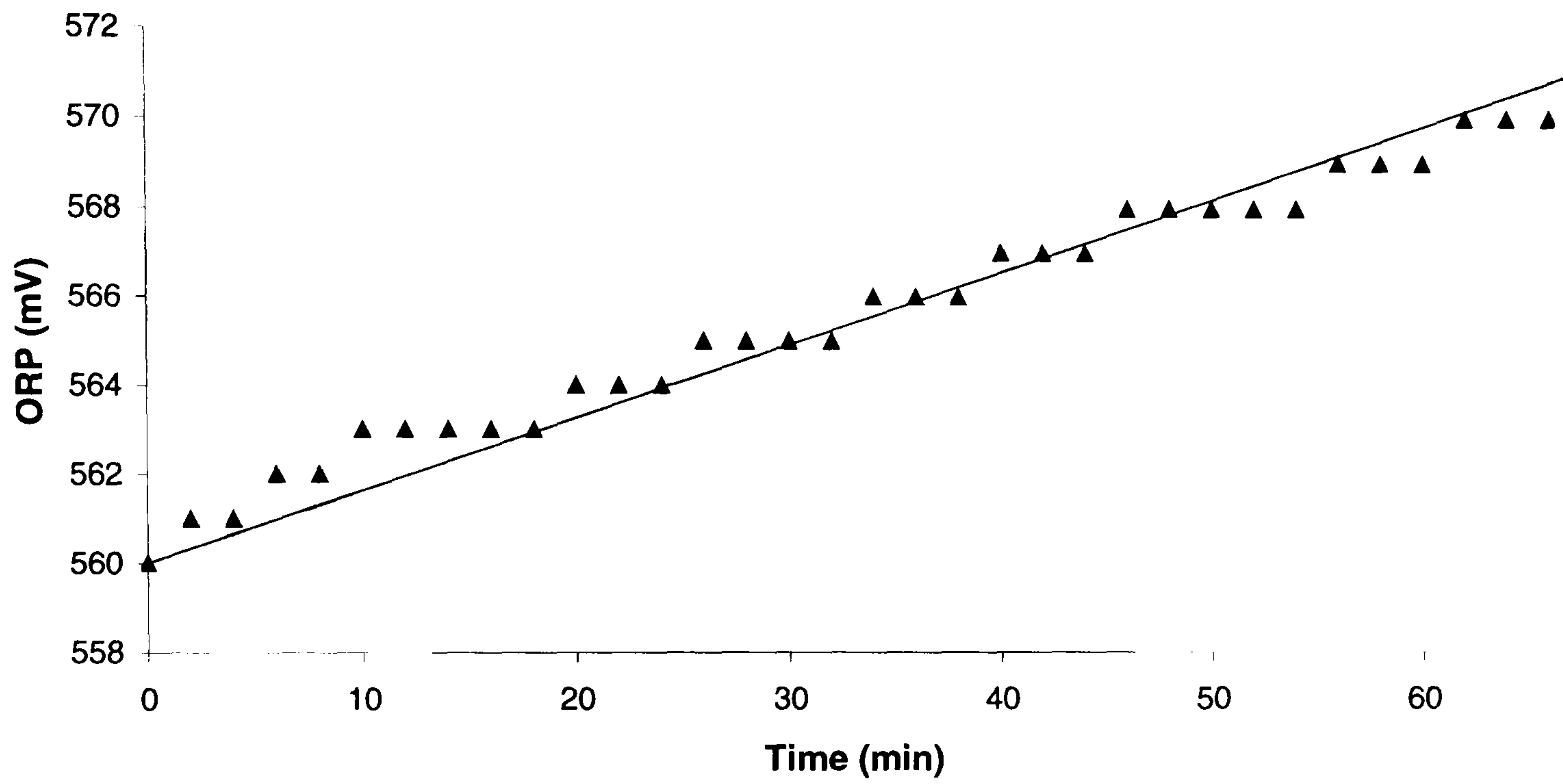
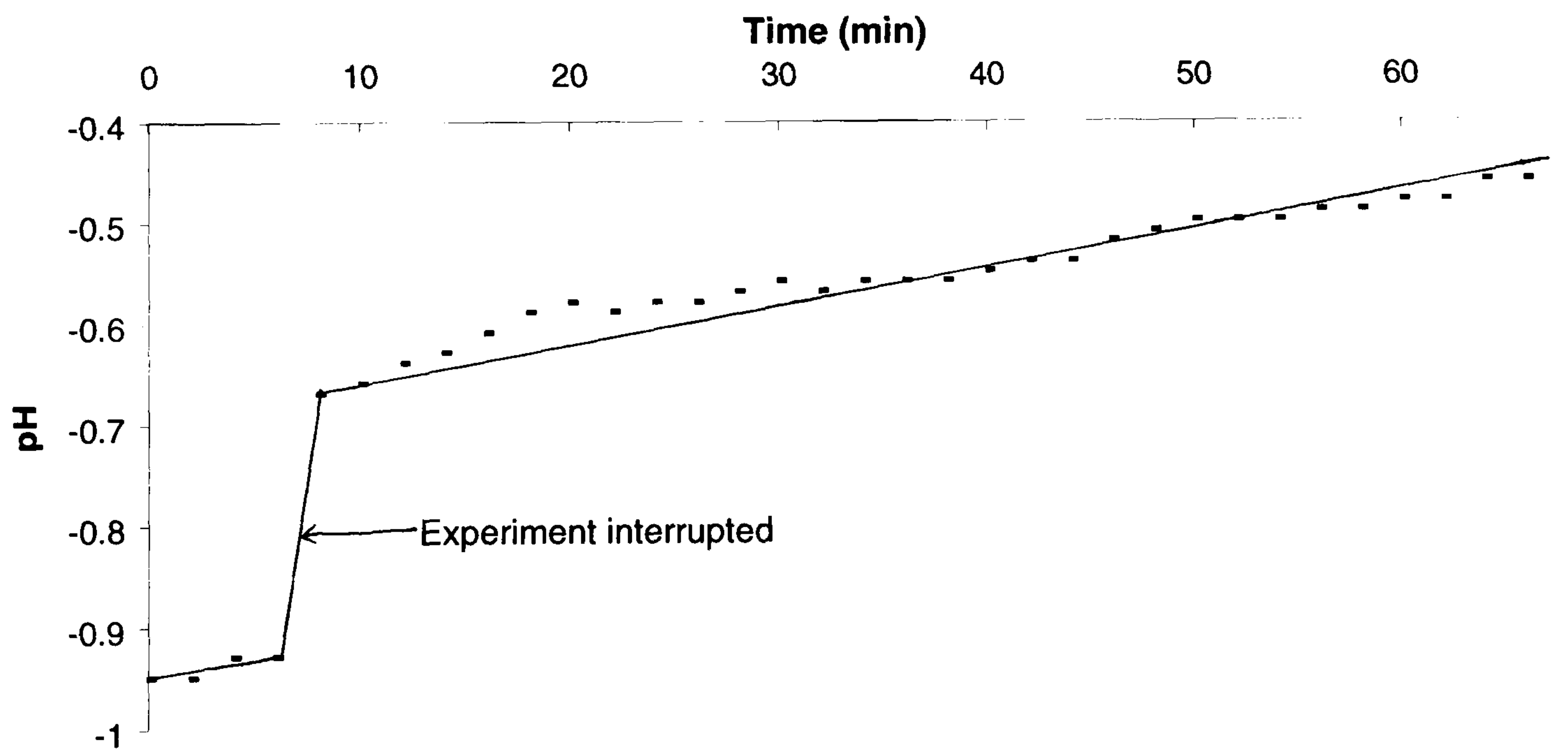


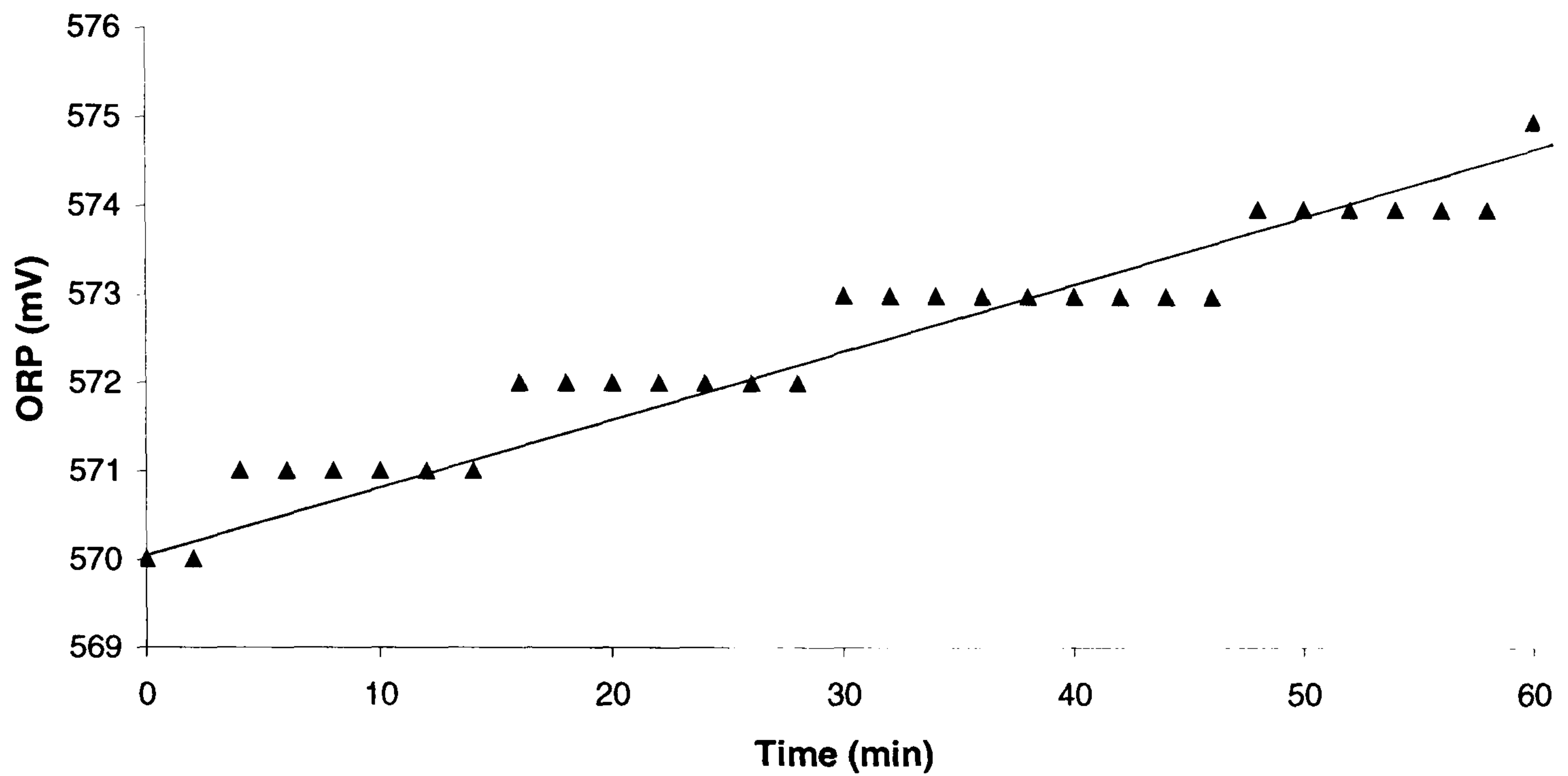
Figure 10.5.2: Relationship of pH vs time in regeneration



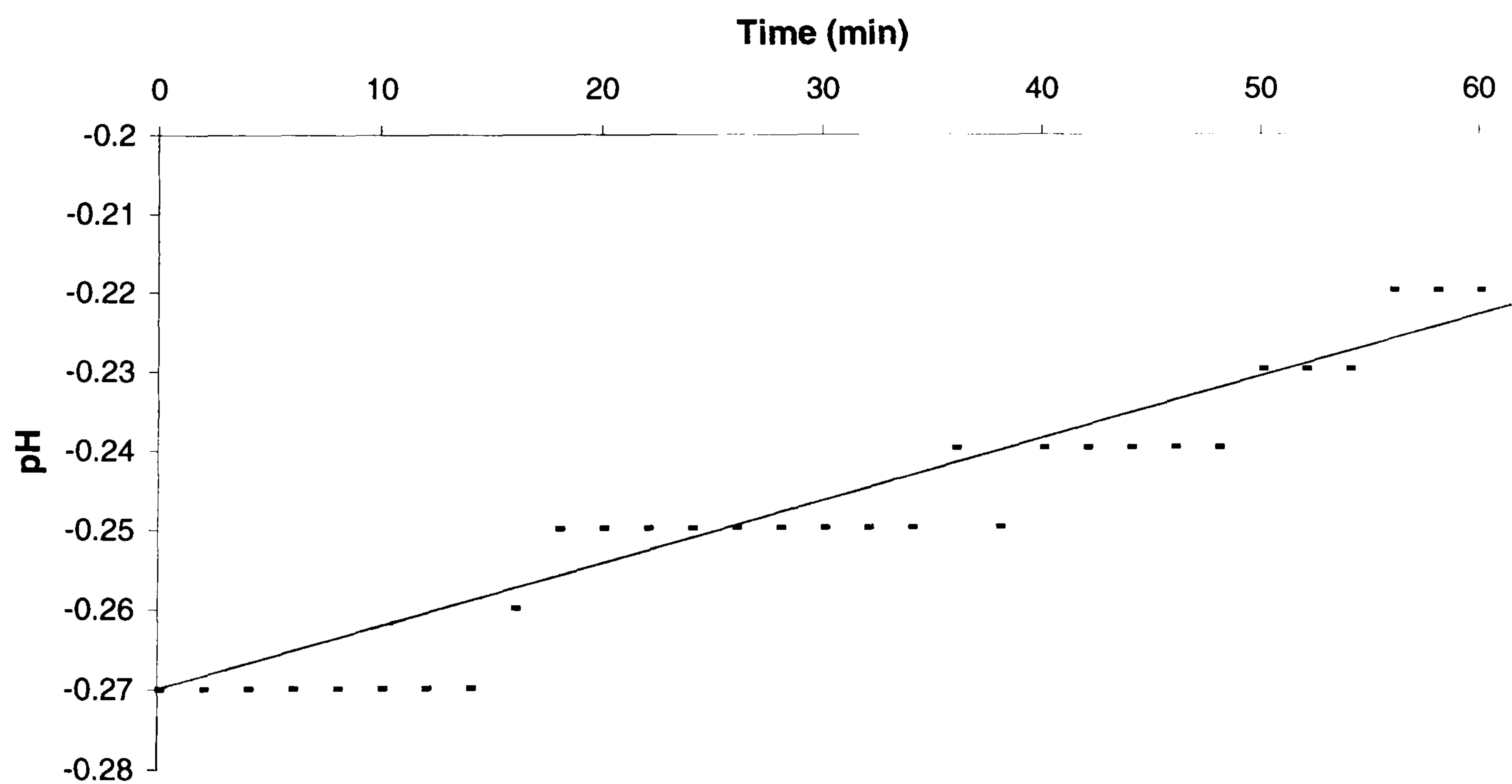
**Table 10.4: Regeneration of etchant at oxygen flow rate of 60 litres/minute**

Time (min)	ORP (mV)	pH	Temp. (°C)	°Bé	Observations
0	570	-0.27	52.8	43.0	<ul style="list-style-type: none"> <li>• pH readings were fluctuating.</li> <li>• Automatic control of cooling system restored.</li> </ul>
2	570	-0.27	52.8	43.0	
4	571	-0.27	52.9	43.0	
6	571	-0.27	53.0	43.0	
8	571	-0.27	53.0	43.0	
10	571	-0.27	52.7	43.0	
12	571	-0.27	52.8	43.0	
14	571	-0.27	52.7	43.0	
16	572	-0.26	52.6	43.0	
18	572	-0.25	52.7	43.0	
20	572	-0.25	52.8	43.0	
22	572	-0.25	52.8	43.0	
24	572	-0.25	52.9	43.0	
26	572	-0.25	53.0	43.0	
28	572	-0.25	52.8	43.0	
30	572	-0.25	52.7	43.0	
32	573	-0.25	52.6	43.0	
34	573	-0.25	52.7	43.0	
36	573	-0.24	52.8	43.0	
38	573	-0.25	52.9	43.0	
40	573	-0.24	53.0	43.0	
42	573	-0.24	53.0	43.0	
44	573	-0.24	52.8	43.0	
46	573	-0.24	52.7	43.0	
48	574	-0.24	52.7	43.0	
50	574	-0.23	52.8	43.0	
52	574	-0.23	52.8	43.0	
54	574	-0.23	52.9	43.0	
56	574	-0.22	53.0	43.0	
58	574	-0.22	53.0	43.0	
60	575	-0.22	53.0	43.0	

**Figure 10.6.1: Relationship of ORP vs Time in regeneration**



**Figure 10.6.2: Relationship of pH vs Time in regeneration**



### 10.7.3 Etching of AISI 304 stainless steel materials with regenerated etchant

#### 10.7.3.1 Etching of AISI 304 with no addition of HCl

Test blanks etched by the regenerated ferric chloride etchant was found to have a very rough and pitted surface. Moreover, there was an accumulation of dark green crystals (suspected to be ferrous chloride) on the test blanks after etching, which indicates acid deficiency. It was thus decided to add in more hydrochloric acid to study the effects of acid on the surface quality of test blanks.

#### 10.7.3.2 Effects of addition of HCl in etching

The etchant conditions and results of etching the test blanks are as shown in *Table 10.5*. Two test blanks of 160 $\mu$ m and 990 $\mu$ m thickness were used in the etching. This was to ensure that the etch quality (surface finish) of both the thin and thick materials were taken into consideration.

The following observations were noted when the acid was added in:

There is an increase in ORP, more evident at the early stage of acid addition, stopped when 1.85 litres of acid was added in. The increase in ORP may be due to the the following reaction:



thus more free  $\text{Fe}^{3+}$  ions were available. However, as the metal was continuously being dissolved into the system, the ORP stopped at 578 mV. The ORP began to decrease when more and more metals were etched as the ferric ions were used up in the etching.

- (1.) There is a decrease in pH, at first rather rapid and then proportional to the amount of acid added in (see *Figure 10.7.1*). This may be because the first 0.45 litre of acids added was mainly used up in freeing the  $\text{Fe}^{3+}$  ions. The ferric chloride formed then reacted with other species in the etching solution to form complexes that caused the steep drop in pH in the initial stage. After that, the equilibrium was reached and the pH decrease was proportional to the volume of acids added.
- (2.) An increase in etchant density ( $^{\circ}\text{Bé}$ ) of the system - When the HCl was being used up in the regeneration earlier, the free acid content in the system was low, and caused a saturation of the etching solution. The solution may contain precipitates such as  $\text{FeCl}_2$ ,  $\text{CrCl}_2$  and oxides of iron.

**Table 10.5: Effects of adding HCl to regenerated etchant and etching results**

Addition of 32% v/w HCl (litres)	ORP (mV)	pH	T (°C)	<sup>0</sup> Bé	Etch rate (µm/min)	Surface finish of 160 µm blank	Surface finish of 990 µm blank	Ra of 990 µm blank (µm)
0	575	0.16	52.7	43.0	37.4	rough*	rough	-
0.25	575	0.05	53.0	43.0	35.0	rough	rough	-
0.45	575	-0.06	53.0	43.0	37.4	rough	rough	-
0.65	576	-0.10	53.0	43.0	32.7	rough	rough	-
0.85	577	-0.13	53.0	43.0	32.7	rough	rough	-
1.05	577	-0.15	53.0	43.0	30.4	rough	rough	-
1.45	577	-0.18	52.9	43.0	30.4	rough	rough	-
1.85	578	-0.21	53.0	43.0	30.4	rough	rough	-
2.85	578	-0.24	53.0	43.5	30.4	rough	rough	2.05
3.85	578	-0.30	52.8	43.5	32.7	good*	rough	1.92
4.85	578	-0.36	52.8	44.0	32.7	good	rough	1.82
5.85	578	-0.43	53.0	44.0	32.7	good	rough	1.00
6.85	578	-0.50	53.0	44.0	32.7	good	rough	0.95
7.85	578	-0.58	53.0	44.0	32.7	good	rough	-
8.85	577	-0.68	53.1	44.0	32.7	good	rough	1.05
9.85	577	-0.79	53.0	44.0	32.7	good	good	0.85

\* An etched surface is classified as 'rough' if it does not meet the surface quality requirements of Tecan Components Ltd., and as 'good' if it is of acceptable quality.

Figure 10.7.1: Relationship of pH vs Addition of HCl

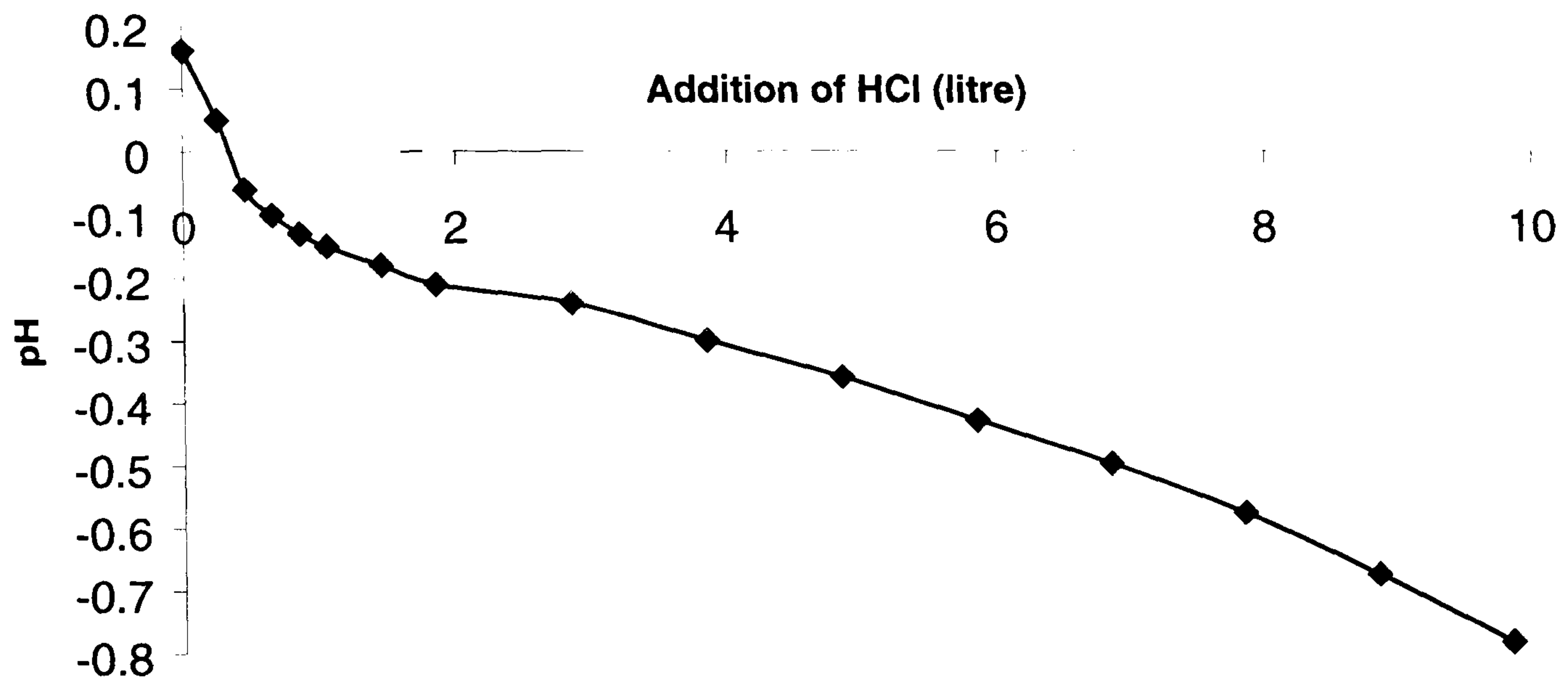
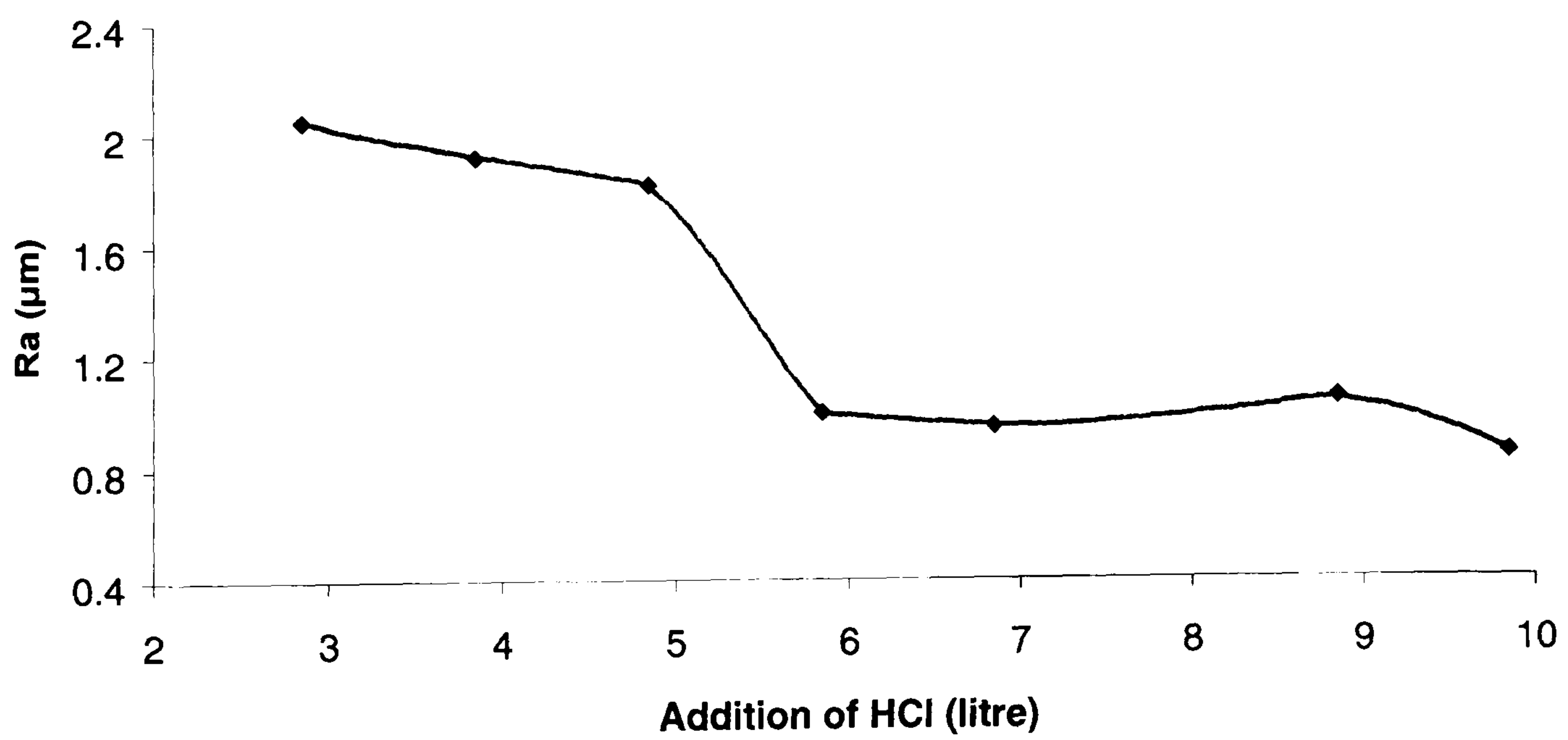


Figure 10.7.2: Relationship of Ra vs Addition of HCl





As a result of an increase in HCl concentration, more precipitates in the etchant were dissolved and this caused an increase in density. The other reason is that more metals were dissolved into the system when test blanks were etched, the etching solution became more concentrated and denser.

- (3.) Good finish for thinner material (160  $\mu\text{m}$ ) was achieved when 3.85 litres of HCl was added in and for thicker material (990  $\mu\text{m}$ ) when 9.85 litres of HCl was added in. This showed that surface roughness is more evident on the thicker materials. Hence the process control parameters for etching thicker materials are tighter.

*Figure 10.7.2* shows a plot of Ra measurement vs addition of HCl. The Ra value of the test samples decreased gradually until the 4.85-litre-HCl level. Then there was a sudden decrease in roughness and the Ra became quite constant at between 5.85-8.85-litre-HCl level. Acceptable surface quality was achieved when the roughness was reduced to 0.85  $\mu\text{m}$

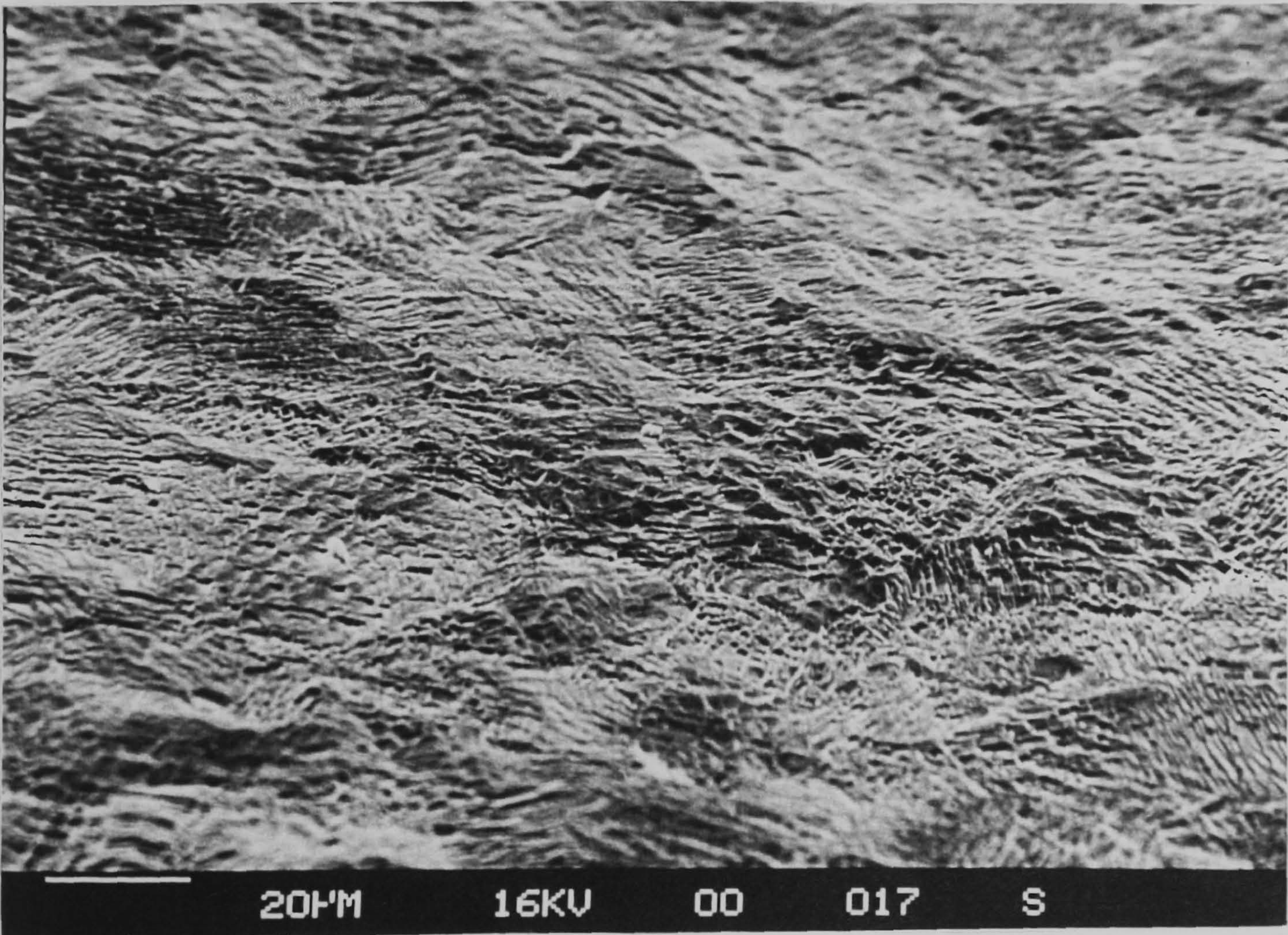
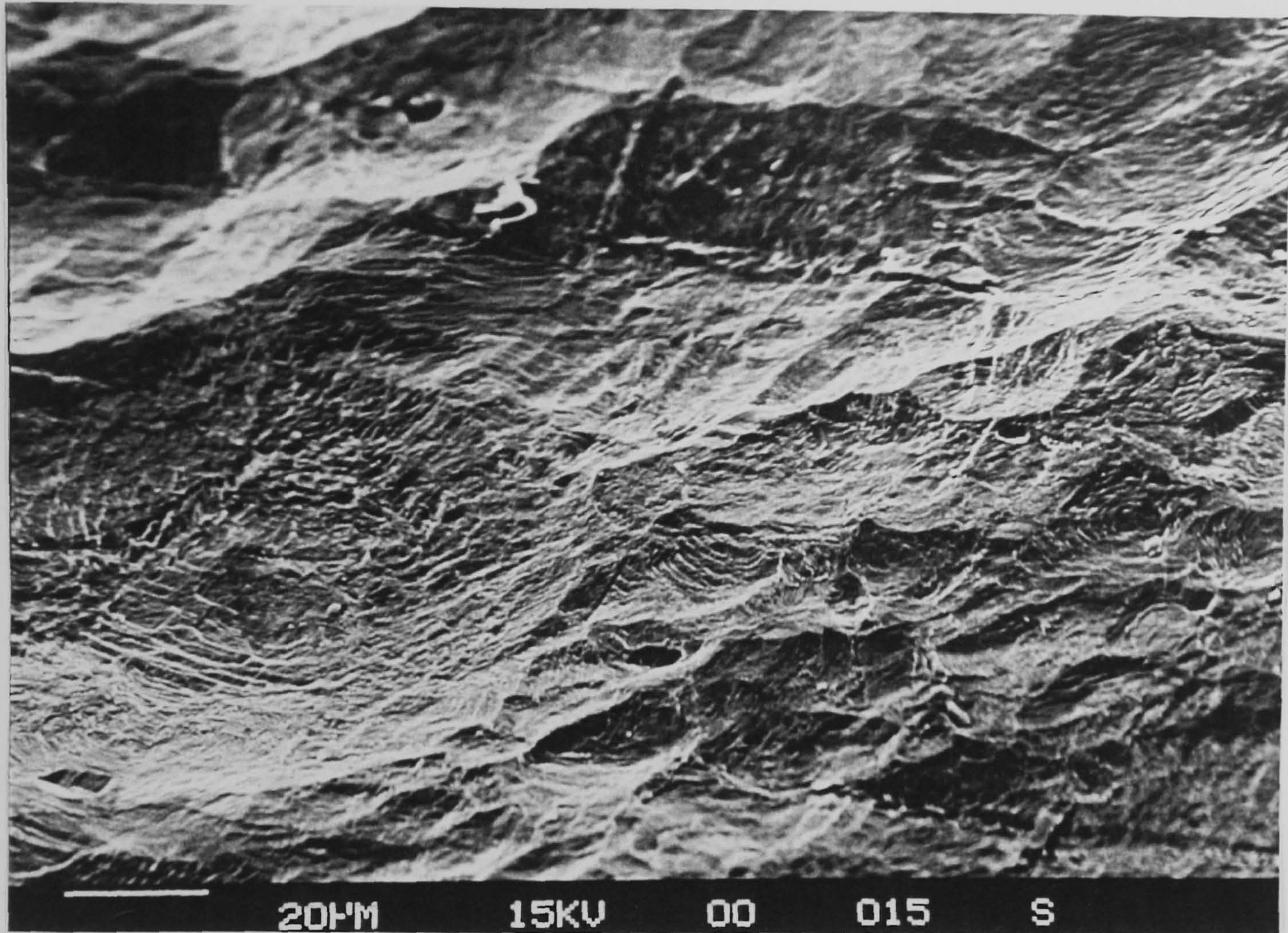
SEM photographs in *Figure 10.7.3* show the difference in surface finish of the 990  $\mu\text{m}$  test samples at 9.85-litre HCl level (good texture) and 2.85-litre HCl level (rough texture).

#### 10.7.4 Effects of varying oxygen flow rate on efficiency of regeneration

The results of the regeneration and etching are shown in *Table 10.6* and *10.7*.

##### 10.7.4.1 Rate of reaction in regeneration

In both the experiments, the pH, temperature and density of the system were maintained at a constant level as far as possible. *Figure 10.8* shows a plot of ORP vs time at different oxygen flow rates. The rate of reaction is faster at 120 litre/minute, but more oxygen is required to regenerate one mV of ORP at this flow rate. For example, at flow rate of 90 litres/minute, the oxygen consumption efficiency was 2.75% compared to 2.38% at 120 litres/minute (see Appendix N). The regeneration at this level is also much less efficient than the 11.91% achieved at the regeneration at ORP of 551-560mV in *Section 10.7.2*. Moreover, it was difficult to control the pH during the regeneration as there were more dissolved oxygen and air bubbles in the etching solution at 120 litre/minute flow rate. Thus, for more efficient usage of oxygen, regeneration shall be carried out at the lower end of oxygen flow rates, of between 60-90 litres/minute range, and at lower ORPs as there is no obvious improvement in the rate of etching at higher ORPs.



**Figure 10.7.3: SEM Photographs of 990 μm samples at 2.85 litres (above) and 9.85 litres (below) HCl level at 600 times magnification**

#### 10.7.4.2 Etching of AISI 304

Table 10.8 and 10.9 summarise the regeneration conditions of oxygen flow rates of 90 and 120 litres/minute. Good surface textures were obtained using regenerated etchant at oxygen flow rate of 90 litre/minute. A slightly rougher surface finish was obtained when the test samples were etched by regenerated etchant using 120 litres/minute oxygen flow rate. However, after addition of 750 ml of HCl, good surface finish was achieved. This could be due to two reasons:

- (1.) There was no addition of HCl to the etching solution when the ORP of the system was reduced from 581 to 577 mV. Some of the free acids in the system may have evaporated off during the etching process.
- (2.) As the second experiment at 120 litre/minute was conducted the next day, more of the HCl may have evaporated off during the cooling and re-heating of the etchants.

This was evident from the difference of pH readings in the two experiments conducted.

As between 1500 to 2250 ml of HCl were required to regenerate 4 mV of ORP in getting test samples with good surface finish, 400 to 550 ml of HCl shall be added to regenerate one mV of ORP to maintain good process control.

Thus, for a system carrying out regeneration and etching of AISI 304 stainless steel, the following operating conditions shall be maintained:

- (1) The pH of the system should be controlled to the range of -0.65 to -0.85.
- (2) Between 400 and 550 ml of 32% v/w of hydrochloric acid should be added for every millivolt (mV) increase in ORP.
- (3) The temperature of the system shall be maintained at 52-54<sup>0</sup>C to achieve high rate of etching.

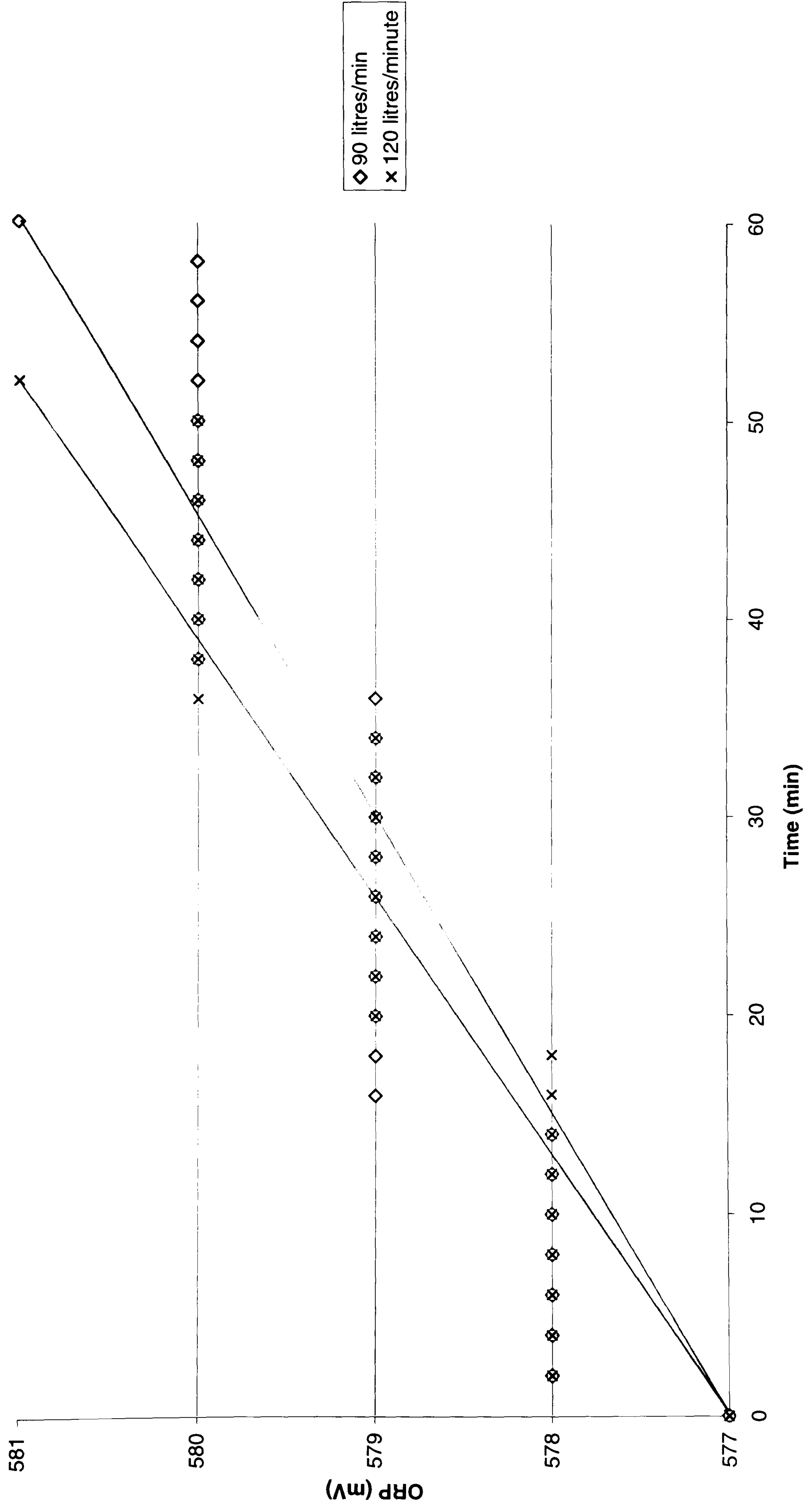
Table 10.6: Regeneration of etchant at oxygen flow rate of 90 litres/minute

Time (min)	ORP (mV)	pH	T (°C)	°Bé	Addition of HCl, 32%, (ml)	Observations
0	577	-0.80	53.1	44.0	-	• pH readings were fluctuating.
2	578	-0.79	53.2	44.0	-	
4	578	-0.79	53.1	44.0	250	
6	578	-0.82	53.2	44.0	-	
8	578	-0.82	53.1	44.0	-	
10	578	-0.81	53.0	44.0	-	
12	578	-0.80	52.8	44.0	-	
14	578	-0.80	52.8	44.0	-	
16	579	-0.79	52.9	44.0	250	
18	579	-0.79	53.0	44.0	-	
20	579	-0.78	53.0	44.0	-	
22	579	-0.79	53.1	44.0	-	
24	579	-0.79	53.2	44.0	-	
26	579	-0.78	52.9	44.0	250	
28	579	-0.80	52.8	44.0	-	
30	579	-0.80	52.8	44.0	-	
32	579	-0.78	52.8	44.0	-	
34	579	-0.80	53.0	44.0	-	
36	579	-0.80	53.0	44.0	-	
38	580	-0.78	53.2	44.0	250	
40	580	-0.79	53.1	44.0	-	
42	580	-0.80	52.8	44.0	-	
44	580	-0.80	52.8	44.0	-	
46	580	-0.79	52.7	44.0	-	
48	580	-0.79	52.9	44.0	-	
50	580	-0.79	52.9	44.0	250	
52	580	-0.80	53.0	44.0	-	
54	580	-0.80	53.0	44.0	-	
56	580	-0.80	53.1	44.0	-	
58	580	-0.80	52.8	44.0	-	
60	581	-0.80	52.8	44.0	250	

**Table 10.7: Regeneration of etchant at oxygen flow rate of 120 litres/minute**

Time (min)	ORP (mV)	pH	T (°C)	°Bé	Addition of HCl, 32% v/w, (ml)	Observations
0	577	-0.49	53.0	44.0	-	<ul style="list-style-type: none"> <li>pH readings were fluctuating.</li> <li>750 ml of HCl was added to the regenerated etchant to achieve good surface finish.</li> </ul>
2	578	-0.48	53.1	44.0	250	
4	578	-0.48	53.2	44.0	-	
6	578	-0.49	53.2	44.0	-	
8	578	-0.47	52.9	44.0	250	
10	578	-0.48	52.8	44.0	-	
12	578	-0.49	52.9	44.0	-	
14	578	-0.48	52.9	44.0	-	
16	578	-0.49	53.0	44.0	-	
18	578	-0.46	53.1	44.0	250	
20	579	-0.45	53.2	44.0	-	
22	579	-0.45	53.1	44.0	-	
24	579	-0.43	53.9	44.0	250	
26	579	-0.45	52.8	44.0	-	
28	579	-0.49	52.8	44.0	-	
30	579	-0.49	52.8	44.0	-	
32	579	-0.49	52.9	44.0	-	
34	579	-0.47	53.0	44.0	-	
36	580	-0.45	53.1	44.0	250	
38	580	-0.47	53.2	44.0	-	
40	580	-0.46	53.0	44.0	-	
42	580	-0.46	52.8	44.0	-	
44	580	-0.45	52.8	44.0	-	
46	580	-0.45	52.8	44.0	-	
48	580	-0.46	52.9	44.0	-	
50	580	-0.47	53.0	44.0	250	
52	581	-0.45	53.1	44.0	-	

**Figure 10.8: ORP vs Time at oxygen flow rate of 90 and 120 litres/minute**



**Table 10.8: Regeneration condition and etching results**

Flow rate of oxygen (l/min)	Time taken (min)	Addition of HCl, 32% v/w (ml/mV)	pH	T (°C)	°Bé	Etch rate (μm/min)	Surface finish
90	60	375	-0.78 to -0.83	52.7 to 53.2	44	33	Good
120	52	375	-0.43 to -0.49	52.7 to 53.2	44	35	Slightly rougher

Note: When the ORP of the regenerated solution was reduced from 581 to 577 mV by dissolving metals, no HCl was added in. The etching solution was also left overnight, thus some free HCl might have evaporated.

**Table 10.9: Regeneration condition and etching results (after addition of 750 ml of HCl)**

Flow rate of oxygen (l/min)	Time taken (min)	Addition of HCl, 32% v/w (ml/mV)	pH	T (°C)	°Bé	Etch rate (μm/min)	Surface finish
120	52	560	-0.63	53.0	44	35	Good

**Table 10.10: Operating conditions for regenerating ferric chloride solution in etching AISI 304 stainless steel materials**

Flowrate of oxygen (l/min)	Addition of HCl (ml/mV)	pH	T (°C)
60 to 90	400 to 550	-0.65 to -0.85	52.0 to 54.0

### 10.8 Conclusion

From the investigations carried out, it can be concluded that:

- (1) Regeneration can occur at different flow rates of oxygen, such as at 118, 90 and 60 litres/minute.
- (2) As the ORP of the system increases, more oxygen is required for regeneration. This is due to the depletion of the ferrous ions in the system, thus resulted in a slower rate of chemical reaction.
- (3) Free acids shall be added in regenerating the etchant to maintain good surface finish, as it is being used up during regeneration. This is because the hydrolysis of ferric chloride solution is insufficient to replenish the free acids consumed.
- (4) Regeneration of ferric chloride shall be carried out at lower flow rates to reduce oxygen consumption.
- (5) Regeneration shall be maintained at conditions as shown in *Table 10.10* to achieve good etching quality.

The overall results showed that ferric chloride etchant can be successfully regenerated and produced quality of etching that is acceptable by the PCM industry.



## **Chapter 11**

# **Economic Model of Regeneration of Ferric Chloride Solution with Oxygen**

### **11.1 Introduction**

The investigation conducted and reported in Chapter 10 clearly showed that it was technically viable to produce good quality etching of low carbon stainless steels such as AISI 304 with oxygen gas regenerated ferric chloride etchants. The other factors to be considered by the PCM practitioners in adapting a new method of regeneration are cost and the associated environmental issues. This chapter is therefore focused on the cost and economical consideration of this more environment-friendly regeneration method.

### **11.2 Cost and Environmental Consideration of Etchant Regeneration Systems**

From the findings of the world-wide survey on regeneration and disposal of ferric chloride etchant (see Chapter 9), it was obvious that the majority of the PCM companies preferred a more environment-friendly method of regeneration even at a higher cost. However, the cost factor cannot be ignored totally as a prohibitively high cost system is not attractive commercially.

On the existing regeneration systems used by PCM companies, investigations by Allen [1991] and Allen and White [1992] showed that the cheapest regeneration method depends on the amount of iron etched per annum. Sodium chlorate/HCl method is the cheapest for low volume production (less than 1.6 tonnes of iron etched per annum) whereas at above 1.6 tonnes iron etched per annum, chlorine gas regeneration is the cheapest method. Both ozonolysis and electrolysis were not competitive at all amounts of iron etched. It was noted that ozonolysis regeneration was cheaper than chlorine gas when the amount of iron etched is small (less than 500kg) and electrolysis regeneration were always more expensive than chlorine gas although both systems have high equipment and power costs.

However, all the methods examined have their drawbacks, due to the adverse environmental effects, and health and safety hazards as detailed in Section 1.4.4 of this thesis. Thus, a cleaner regeneration method using oxygen as an oxidising agent will be attractive commercially if the cost is comparable to, if not lower than other existing systems.

### 11.3 Economical Aspects of Regeneration

In comparing the cost of the oxygen regeneration method with the other methods used by the PCM industry, the following factors are taken into consideration:

- equipment
- maintenance
- power
- chemical
- disposal

It should be pointed out that there is a disposal cost in all the ferric chloride etchant regeneration systems. In the production facility, it may be necessary to dispose of the ferric chloride etchants after repeated regeneration due to the build-up of byproducts, or any excess ferric chloride created in order to maintain constant etching conditions. As waste/excess ferric chloride in the UK is normally disposed of through landfilling, it incurs a disposal cost.

In considering the cost implications of the various regeneration systems, the following assumptions were made:

- (1) The cost of capital equipment can be amortized over a 5-year period (except for housing of a chlorine storage area which was taken over 20 years).
- (2) An annual maintenance cost is required.
- (3) A constant charge of electricity, at the UK business rate.
- (4) Chemicals can be purchased commercially, and costs are proportional to the volume or weight purchased.
- (5) Legislation allows the disposal of waste solution and costs are proportional to the volume disposed.
- (6) The regenerated etchants can produce products with qualities that are acceptable by the PCM industry and its customers.

In addition, it is assumed that all the five regeneration systems require the same amount of labour for the operation of systems, and the space for housing the equipment. Thus, the labour cost and space requirement are not included in the cost analysis.

The costing of the chlorine, sodium chlorate, ozonolysis and electrolysis regeneration systems have been carried out by Allen [1991] and Allen and White [1992]. Since the technology of these regeneration systems has remained the same over the years, the calculations carried out by Allen and White will be used for the economic modelling, by factoring in the inflation rate over this period. UK Retail Price Index (RPI) is used for this purpose.

The RPI figure in 1991 was 133.51 whereas in August 1998, it was 163.70. The price difference is  $(163.70 - 133.51)/133.51 = 0.226$ . This factor is used in calculating the costs of equipment, maintenance and chemicals for the existing regeneration systems. For waste etchant disposal and electricity, the current business rate in the UK is used.

#### 11.4 Costing of Oxygen Regeneration System

The oxygen regeneration system employed by Tecan Components Ltd. as described in Sections 10.4 and 10.5 will form the basis of calculations for this economic model. It should be pointed out that a maximum of 1,800 kgs per year is used in the calculation as it took approximately one hour to regenerate one kg of iron dissolved during the experiment. *Table 11.1* shows the costs of the various items and sub-items involved. The details of the costing aspects of the oxygen regeneration system studied are described below.

##### 11.4.1 Equipment

The oxygen regeneration system consists of the following equipment:

- pH meter, probes and accessories
- Static mixer and the related piping system
- Water pump
- Oxygen flow meter and associated accessories.

The total cost of the above capital equipment is to be amortized over a 5-year period.

##### 11.4.2 Chemicals

Liquid oxygen and hydrochloric acid are the chemicals used in this regeneration system.

In the comparison of cost implications carried out earlier by Allen [1991] and Allen and White [1992], it was assumed that the chemical reactions of chlorine, sodium chlorate/hydrochloric acid, electrolysis and ozonolysis regeneration systems were 100% efficient. This is because the standard electrode potentials of the systems above are higher than oxygen regeneration system, and chlorine gas, sodium chlorate and ozone are strong oxidising agents. In

addition, the low solubility of oxygen gas in aqueous solutions has also resulted in a lower rate of reaction. As such, it is not viable to use 100% chemical reaction efficiency for this method. The investigations, carried out with the aid of a static mixer that prolongs the mixing time of oxygen with the etching solution (see Chapter 10), indicated that the chemical efficiency of oxygen gas in regenerating ferrous ion back to ferric ion was in the range of 2.38-11.91%, depending on the ORP of the system. Thus, an average of 6% is to be used in this evaluation.

It was also found out that between 400-550 ml of hydrochloric acid is required in regenerating one mV of ORP for satisfactory etching of stainless steel materials. Hence an average of 500 ml HCl/mV ORP is used in calculating the volume of HCl required for regeneration.

#### **11.4.3 Maintenance/replacement cost**

It is envisaged that the maintenance and replacement costs of equipment are as follows:

- pH probe has to be replaced twice a year as advised by the supplier.
- Maintenance of other equipment such as water pump and oxygen flow meter as and when breakdown occurs.

#### **11.4.4 Utility**

Power is required to run the water pump during regeneration. The water pump has a power output of 2 horsepower or 2 x 745.5 W.

#### **11.4.5 Waste disposal**

It is assumed that the amount of etchant to be disposed of is the same as ozonolysis as both systems have identical byproducts. The cost of etchant disposal is dependent on the amount of metal etched per annum.

Table 11.1: Costing of oxygen regeneration system

<b>Item</b>	<b>Sub-item</b>	<b>Cost (£)</b>
<i>Equipment</i>	pH meter, probes and accessories	2182.83
	Static mixer	874.67
	Water pump and related piping system	1376.41
	Oxygen flow meter and accessories	1077.91
	<b>Total cost of equipment</b>	<b>5511.82</b>
	Cost of equipment amortized over 5-year	<b>1102.36</b>
Chemicals	Cost of oxygen in regenerating one kg of iron*.	7.40
	Cost of HCl in regenerating one kg of iron*.	0.79
	<b>Total chemical cost/kg of iron etched</b>	<b>8.19</b>
Maintenance	pH probe	303.00
	Other equipment	100.00
	<b>Total maintenance cost/year</b>	<b>403.00</b>
Utility cost	Total cost of electricity/kg of iron iron etched*	<b>0.21</b>
Waste disposal (Same as Ozonolysis)	Total cost of waste disposal/kg of iron etched	<b>0.43</b>

\*See Appendix P for calculations of the costs of chemical and electricity.

**Table 11.2: Cost of various regeneration systems**

Method of regeneration	Equipment	Weight of iron etched per year (kg)	Equipment cost over 5 years (£)	Maintenance per year (£)	Power cost per year (£)	Chemical costs per year (£)	Disposal cost per year (£)	Total costs (£)	Cost of regeneration /kg iron etched (£)
Sodium chlorate + hydrochloric acid	Brent BEAC model (*1)	14	809.16	122.60	0.09	75.77	9.20	1016.82	72.63
	Standard	144	809.16	122.60	0.61	757.67	91.96	1782.00	12.38
	Standard	1440	809.16	122.60	6.13	7576.68	919.60	9434.17	6.55
	Standard	14400	809.16	122.60	61.25	75766.80	9196.00	85955.81	5.97
	Plus	28800	1226.00	122.60	91.00	151489.46	18392.00	171321.06	5.95
	Super	54000	1790.00	122.60	151.38	284082.13	34466.00	320612.11	5.93
Electrolysis	Chempur model (*2)								
	4/1600	100	9317.60	980.80	84.00	103.47	38.90	10524.77	105.25
	4/1600	500	9317.60	980.80	420.00	517.37	194.48	11430.25	22.86
	4/1600	1000	9317.60	980.80	840.00	1034.74	388.96	12562.10	12.56
	4/1600	1999	9317.60	980.80	1679.13	2069.49	777.92	14824.94	7.42
	8/3200	3998	11941.24	1348.60	3358.25	4139.00	1555.84	22342.93	5.58
	12/6000	7497	15692.80	1716.40	6297.38	7763.03	2915.88	34385.49	4.59
Ozonolysis	Polymetrics model (*3)								
	p-10 (air)	26	2452.00	367.80	151.38	26.97	11.44	3009.59	115.73
	p-40 (air)	106	3432.80	367.80	443.63	109.11	45.32	4398.66	41.49
	p-60 (air)	158	3923.20	367.80	665.00	162.28	68.20	5186.48	32.82

**Table 11.2: Cost of various regeneration systems (cont.)**

Method of regeneration	Equipment	Weight of iron etched per year (kg)	Equipment cost over 5 years (£)	Maintenance per year (£)	Power cost per year (*8) (£)	Chemical costs per year (*9) (£)	Disposal cost per year (*10) (£)	Total costs (£)	Cost of regeneration /kg iron etched (£)
Ozonolysis	PCI model (*4)								
	G2	100	2452.00	2338.00	65.63	103.60	42.94	5002.17	50.02
	G21	1000	5884.80	5846.80	656.25	1035.97	429.44	13853.26	13.85
	B250	10000	31,876.00	28445.65	6559.88	10354.80	4294.40	81530.73	8.15
	B800	37700	85820.00	65535.83	24730.13	39038.29	16189.80	231314.05	6.14
Chlorine gas	(*5)	10	5517.00	3065.00	0.06	11.97	4.66	8598.69	859.87
		100	5517.00	3065.00	0.61	119.70	46.60	8748.91	87.49
		1000	5517.00	3065.00	6.13	1197.00	465.96	10251.09	10.25
		10000	5517.00	3065.00	61.25	11970.00	4659.60	25272.85	2.53
		100000	5517.00	3065.00	612.50	119700.00	46596.00	175490.50	1.75
Oxygen gas + hydrochloric acid	(*6)	10	1102.36	403.00	2.10	81.90	4.29	1593.65	159.37
		100	1102.36	403.00	21.00	819.00	42.94	2388.30	23.88
		1000	1102.36	403.00	210.00	8190.00	429.44	10334.80	10.33
		1800 (*7)	1102.36	403.00	378.00	14742.00	772.99	17398.35	9.67

\*1 – Brent Chemicals, UK

\*2 – Chema GmbH, Germany

\*3 – Polymetrics, USA

\*4 - PCI Ozone and Control Systems Inc., USA

\*5 – Based on dosage rate of 5 kg of chlorine gas per 1 kg of HCl (Philips Printed Circuit Board Factory, UK)

\*6 – Based on the equipment used at Tecan Components Ltd.

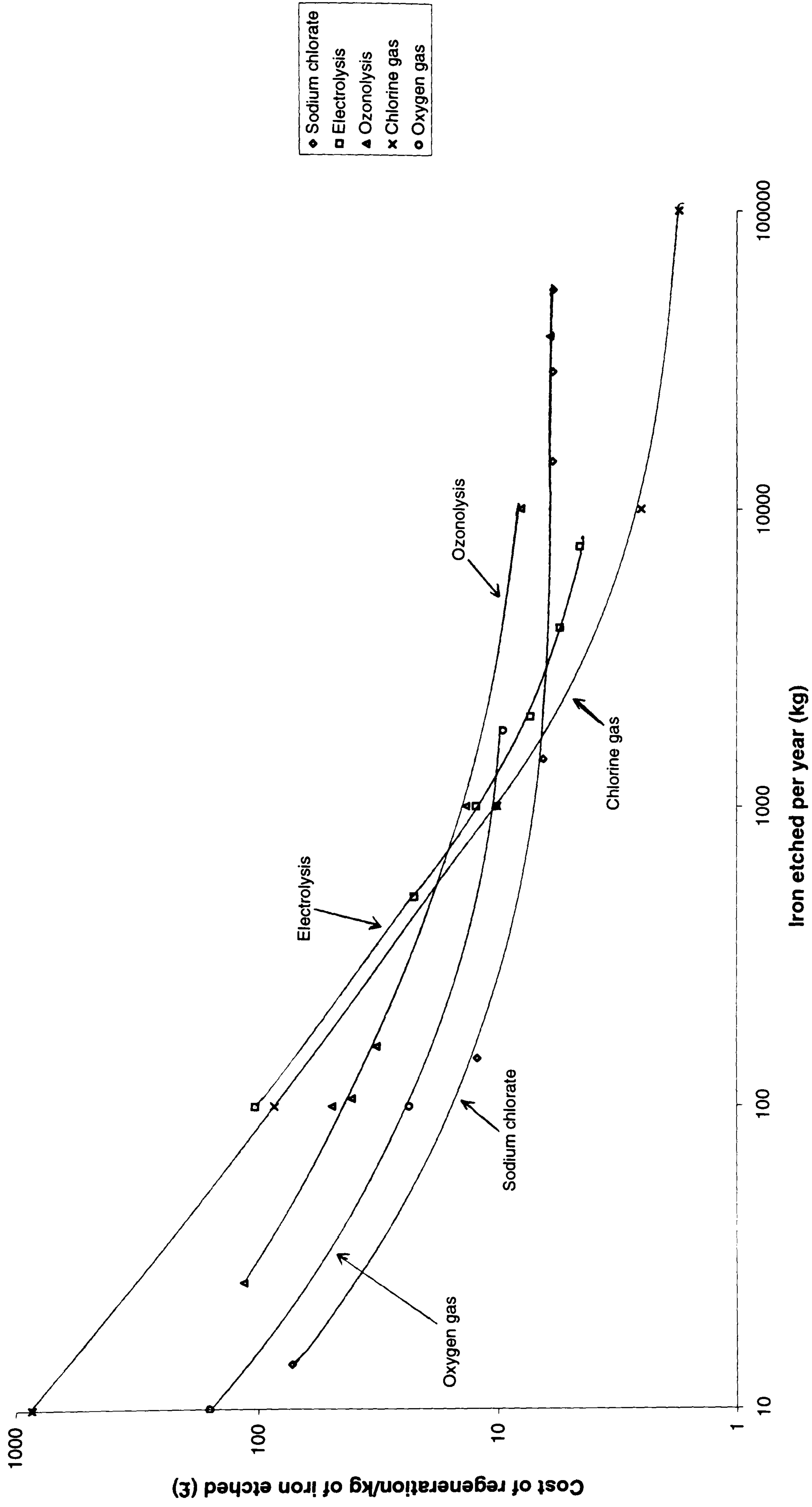
\*7 – For etching machines that etches more than 1800 kg of iron per annum, it is recommended to use an air separation unit as the cost of liquid oxygen supplied in cylinders will be too expensive. However, more study has to be carried out.

\*8 – Power cost at 7p per kWh at UK business rate.

\*9 – Chemical costs: HCl @ 21.8p/l, Sodium chlorate @ £1.86/l, chlorine gas @ 59p/kg

\*10 – Etchant disposal cost at 8.8p/l.

**Figure 11.1: Cost of regeneration Vs Amount of iron etched**





## 11.5 Discussion and Conclusion

The details of the costing of various regeneration systems are shown in *Table 11.2*. When the cost of regenerating one kg of iron is plotted against amount of iron etched per year (*Figure 11.1*).

It was found that sodium chlorate/HCl is still the cheapest method of regeneration for low volume production (less than 1.6 tonnes of iron etched per year). For production facilities with etching capacity of more than 1.6 tonnes of iron etched per year, chlorine gas is the cheapest option.

It is interesting to note that although oxygen gas/HCl system is not the most economical method, it is the second cheapest of all the methods assessed and its cost of regeneration is only slightly higher than the sodium chlorate/HCl method.

From the earlier survey on regeneration (see Chapter 9), one of the findings is that the majority (76%) of the PCM companies was prepared to use 'a regeneration system that is more environment-friendly at a higher overall cost'. Therefore, the oxygen regeneration system is a good option for these companies as the cost of regeneration is not too expensive and it is environment-friendly.

The total amount of stainless and mild steels materials etched by Tecan Components Ltd. was about 1,760 kg per annum in 1995/96, with a 10% etch out, the amount of iron dissolved was only 176 kg. So there is no problem for the company to continue using the existing system.

For the larger users of iron materials, such as Company P and Q, who used 350 and 280 metric tons respectively in 1995, it is proposed to look into the feasibility of using an air separation unit to tap the source of oxygen. This is because the cost of purchasing liquid oxygen in cylinders from the suppliers will be prohibitively expensive at this level, although installing an air separation unit will incur a higher initial plant and equipment cost.

## **Chapter 12**

# **Conclusions, Recommendations and Future Work**

### **12.1 General**

The development and trend of global environmentalism, the enactment of legislation and regulations, the cost of not complying to such regulations, and the demands from NGOs and 'green' consumer groups clearly indicate that companies, especially those involved in manufacturing, can no longer ignore the environmental issues related to their businesses.

In view of the appreciable environmental impacts of PCM due to the nature of the industry whereby various chemicals and materials are used during the manufacturing process, and the environmental pressures from various parties as mentioned above, the PCM companies should be working towards 'greener' management practice to remain competitive in future.

The main thrust of this thesis is to research the environmental aspects of the PCM industry, measure, analyse and benchmark the environmental impacts, and explore ways to reduce the adverse environmental impacts that are deemed to be significant.

It should be pointed out that although the environmental impacts of PCM were highlighted in some of the papers published, no attempt has been made to systematically identify, measure, analyse and benchmark the waste generated by the industry.

### **12.2 Conclusions and Recommendations**

The thesis began with an environmental audit of a PCM company in the UK. It was found that the likely significant environmental impacts are the use of ferric chloride etchant, solvents and VOCs, and water. The audit covered all the environmental aspects of the company's operation but it merely presents a general scenario of a typical PCM company. Moreover, it will be difficult to

judge the performance of a company if no comparison is made with that of other PCM companies.

Thus, an exercise to compare the environmental performance of two UK PCM companies was done by drawing up a set of performance indicators. The results showed that there were big contrasts in terms of etchant utilisation, solvent and water consumption, which are also the likely significant environmental impacts. It is evident that there is room for improvement to reduce the environmental impacts of the PCM process in the UK [Allen and Ler, 1997a].

As such, it was decided to conduct audit surveys of the PCM companies world-wide to find out the industrial best practices for etchant utilisation and solvent consumption. The water consumption of the PCM process is the subject of research carried out by Harris [1998]. Using a combination of proposals comprising of water reuse (wastewater from one operation is suitable for use in another process), partial treatment of wastewater for reuse, and water recycle, Harris concluded that Tecan Components Ltd. could achieve a 52% cost saving in water consumption if the water conservation proposals are implemented in full.

It was also found out during the course of the literature survey that a new and cleaner technology, known as laser direct imaging (LDI) has emerged. LDI eliminates the use of conventional photographic processing and its associated wastes. Thus, a study was conducted to ascertain the technical and economic feasibility of this technology.

The detailed study into the environmental impacts of the PCM manufacturing processes came to the following conclusion:

### **12.2.1 Feasibility study on LDI**

From the information provided by the equipment supplier, it seemed that LDI technology could meet the technical requirements of the PCM industry. However, it is not possible to judge the feasibility of applying LDI to the PCM process at this juncture as a lot of key data is still not available. From the data obtained, a typical operating cost for conventional photographic processing method of exposing photoresists in the UK is £154,674, whereas the cost of operation for LDI system excluding maintenance, replacement of parts and utility cost is £120,000 per annum. For LDI system to be attractive commercially, the total cost of operation must not exceed that of the conventional imaging system. In addition, the system must satisfy the reliability test in the actual production environment before it could be introduced to the PCM industry.

### **12.2.2 Study on consumption of solvent and VOC**

The survey results indicated half of the PCM companies have switched to aqueous-based resist in their operation. This is supported by the findings of a separate survey carried out by the Photo Chemical Machining Institute [PCMI, 1996] which showed that 57.4% (27 out of 47) of the companies that responded used aqueous dry film resist in their production process. Liquid aqueous-based resists suitable for application in the PCM industry have been recently developed. Solvents are also used in the metal preparation process in PCM, but the use is insignificant in the UK companies. Thus, it is envisaged that the PCM practitioners can eliminate the use of solvent-based resist in processing, and VOC emissions would no longer become an environmental issue for the industry in the near future.

### **12.2.3 Ferric chloride utilisation, regeneration and waste disposal**

Due to the significant impact of the ferric chloride etchants pose on the environment, a lot of emphasis was placed in this area during the research. Two world-wide surveys were carried out in this area, to find out the consumption of ferric chloride with respect to the quantities of metals etched, the regeneration methods used, and the method of waste disposal. This is the first time that a quantitative analysis and benchmarking of the ferric chloride utilisation being carried out. The findings of the two audit surveys [Allen and Ler, 1998, 1997b, 1997c] indicated that

- (1) There is a vast difference (135 times) between the most efficient company and the least efficient company in terms of etchant usage. Moreover, companies that regenerate ferric chloride etchant are much more efficient compared to companies that do not regenerate and the main reason for not regenerating was lack of technical knowledge in understanding the basic know-how of regeneration systems. Hence, in order to encourage these companies to use regeneration, technical training should be given to the PCM companies currently not carrying out regeneration.
- (2) There is a vast difference in terms of etchant utilisation among companies that carry out regeneration. It is concluded that having regeneration is not enough to maintain high etchant utilisation; it has to be supplemented by an effective waste minimisation programme.
- (3) In terms of industrial best practice, ferric chloride utilisation of 837% is currently the benchmark for the other PCM companies to emulate.
- (4) Chlorine regeneration was the most popular method of etchant regeneration, though it has environmental, health and safety hazards. However, the majority of the companies (76%) indicated that they would use a more environment-friendly regeneration system, even though it may incur a higher overall cost. Thus, the commercial potential for more environment-friendly methods of etchant regeneration by replacing the

existing chemicals used in regeneration with chemicals that have less environmental, health and safety impacts, is good.

- (5) Regarding waste etchant disposal, most companies sent liquid waste etchant for reclaim or recycle. Overall, about 31% of the total waste etchants ended up in landfill sites. The rest were either reclaimed or recycled.

#### **12.2.4 Technical and economic study of oxygen regeneration**

In response to the demand of the PCM companies in having a more environment-friendly method of etchant regeneration, an investigation into the feasibility of using oxygen gas in regenerating ferric chloride etching AISI 304 stainless steel, a low carbon steel commonly etched by the PCM companies. The research was carried out at Tecan Components Ltd., a leading PCM company in the UK. The results showed that ferric chloride etchant can be successfully regenerated and produced a quality of etching that is acceptable by the company. The following were observed during regeneration and etching:

- (1) Regeneration could occur at different flow rates of oxygen, such as at 118, 90 and 60 litres/minute. However, as the ORP of the system increased, more oxygen was required for regeneration. This is due to the depletion of the ferrous ions in the system, thus resulted in a slower rate of chemical reaction.
- (2) pH of the etching system had to be maintained at a certain level (-0.65 to -0.85) through addition of free acids during regeneration, to achieve good surface finish, as the free acid was constantly being used up during regeneration.
- (3) Regeneration of ferric chloride should be carried out at lower flow rates to reduce oxygen consumption, and the temperature of the system should be maintained as high as technically possible to increase the rate of chemical reaction.
- (4) Oxygen gas/HCl regeneration system is the second cheapest of all the methods assessed and its cost is only slightly higher than the sodium chlorate/HCl method which is the most economical method. Therefore, the oxygen regeneration system is a good option for these companies as the cost of regeneration is not too expensive and it is environment-friendly.

### **12.3 General Recommendation**

The research in this thesis highlights the environmental issues of the PCM manufacturing process and ways to reduce the relevant impacts. However, as the operations of the PCM companies are rather different from each other, for

example, the companies may have other processes such as electroplating, laser cutting or coating in their operation that have different environmental problems. Moreover, as PCM consists of a few manufacturing steps in which different chemicals and materials are used, the environmental impacts of individual companies may not be identical.

Thus, one of the best approaches for PCM practitioners to address the environmental issues that arise is to set up an integrated environmental management system, such as ISO 14001 or EMAS. This approach can ensure the environmental aspects in all areas of the operation are systematically identified and evaluated so that the relevant significant environmental impacts can be reduced or minimised by setting up environmental programmes with clear objectives and targets.

## 12.4 Future Work

The following are recommended for further investigation in the future:

- (1) As the LDI technology can help to reduce environmental impacts and offer other advantages as detailed in Section 6.5, it is suggested to reappraise this technology once all the information and technical and costing data, are available.
- (2) As the environmental performance indicators are increasingly becoming important indicators for judgement of investment potential [Elkington, Knight and Hailes, 1991], and more sophisticated quantitative environmental performance reports are required to judge the acceptability of company activities [Bullough and Johnson 1995]. It is therefore recommended to conduct regular audit surveys and benchmarking of the environmental performance within the PCM industry, especially on the utilisation of ferric chloride, to provide a guideline for PCM companies to judge the individual performance. This work can be carried out jointly by PCMI (to provide liaison and feedback to the members) and Cranfield University (to provide technical expertise).
- (3) To continue with the work below on oxygen regeneration
  - Assess the suitability of using the regenerated etchant in etching other grades of stainless steel, as the etching requirements are different.
  - Assess the viability of using an air separation unit as the source of oxygen supply instead of using highly purified liquid oxygen from cylinders that are rather costly. The air separation unit will be most cost-effective for operations with high metal loading, although it has a high initial capital cost.

- Due to the constraints of the existing equipment, it was not possible to adjust certain operating parameters, such as lowering the oxygen gas flow rate to below 60 litres/minute and increasing the back pressure of the static mixer to above 0.2 bar.

From the experiments conducted, it was evident that reducing the oxygen flow rate promotes higher oxygen utilisation. This could be due to the low solubility of oxygen in aqueous solution. As a result, higher oxygen flow rates cause unnecessary wastage. Therefore, a suitable flow rate can maximize oxygen consumption. In the US patent [Lubert and McGarigle, 1993], it was reported that a back pressure of 0.8 bar was employed in the regeneration. However, only 0.2 bar back pressure could be achieved by the existing system in Tecan due to the high power of the pump used in the experiment.

Thus, more work can be done to improve the process control parameters. This can increase the rate of regeneration, and reduce chemicals (like oxygen gas) and utility consumption. This will lower the cost of regeneration.

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## GLOSSARY OF TERMS

<b>Baumé</b>	Measure of specific gravity (the measure of the density of a substance relative to some other reference substance, generally water).
<b>Cementation</b>	A spontaneous electrochemical reaction also known as reductive precipitation, where a reducing agent is used to displace an ionised metal from solution. The displaced metal is reduced to its elemental state.
<b>Chlorine gas</b>	A poisonous greenish yellow gas (Cl <sub>2</sub> ). Chlorine occurs widely in nature as sodium chloride (as in seawater). It is manufactured by the electrolysis of brine and is a strong oxidising agent. Applications include the chlorination of drinking water, bleaching and in the manufacture of organic chemicals.
<b>Electrolysis</b>	The production of a chemical reaction by the passage of current through an electrolyte. Positive ions migrate to the cathode and undergo reduction and negative ions to the anode and undergo oxidation.
<b>Electroplating</b>	The process of depositing one or more metals on to a cathode by electrolysis.
<b>Environmental Aspect</b>	Element of an organisation's activities, products or services which can interact with the environment.
<b>Environmental Impact</b>	Any change to the environment, whether adverse or beneficial, wholly or partially resulting from an organisation's activities, products or services.
<b>Environmental Management</b>	Parts of the overall management function of an organisation that develop, implement, achieve, review and maintain the environmental policy.
<b>Environmental Management System</b>	Organisational structure, responsibilities, practices, procedures, processes and resources for implementing and maintaining environmental management.

<b>Exhaustion (%)</b>	In the case of a spent $\text{FeCl}_3$ etchant, this refers to the percentage of the $\text{Fe}^{3+}$ ions from the original total $\text{FeCl}_3$ that have been reduced to $\text{Fe}^{2+}$ .
<b>Free acid content</b>	In $\text{FeCl}_3$ , some 'free' acid (HCl) content arises through the reaction between $\text{H}^+$ ions in the aqueous phase and chloride ions from the $\text{FeCl}_3$ . However, more is usually added to provide an extra source of chloride ions during etching and thus prevent dissolved metal species from precipitating out as metal hydroxides.
<b>Hydrolysis</b>	A chemical reaction caused by dissolution of a compound in water.
<b>Ions</b>	An atom or group of atoms that has either lost one or more electrons, making it positively charged (a cation) or gained one or more electrons making it negatively charged (an anion).
<b>Molarity</b>	Measure of gram-molecular weights of a compound present (dissolved) in 1 litre of solution.
<b>Molecular weight</b>	Molar mass of a species in grams per mole.
<b>Oxidation</b>	A chemical reaction involving the loss of electrons.
<b>Ozonolysis</b>	In the context of etchant regeneration, this is an oxidation reaction performed by the bubbling of ozone, through the spent etchant.
<b>Percentage (%) etch out area</b>	The average percentage area of metal processed that are dissolved by ferric chloride etchant
<b>Photochemical machining (PCM)</b>	A multi-stage manufacturing technique involving selective removal of metal by chemical etching.
<b>Photoresist</b>	A photo sensitive coating placed on the metal substrate during the PCM process. Exposure to UV light will cause chemical changes to exposed areas of resist, thus making it either vulnerable to developing solution or inert to it. (This depends on whether the resist is positive or negative-working). The developed resist will protect the substrate against etching.
<b>Phototool</b>	Used in the PCM process. A highly resolution image placed over the photoresist coated substrate, prior to exposure by UV light. The phototool protects selected

areas of the resist from subsequent chemical changes as the result of UV (see photoresist).

<b>pH scale</b>	A logarithmic scale for expressing the acidity or alkalinity of a solution.
<b>Precipitation</b>	The formation of a suspension of small solid particles in a liquid by chemical reaction.
<b>Redox Potential (ORP)</b>	The relationship between the activities of the oxidised and reduced species in a chemical reaction. As an approximation, the respective concentrations of the ionic species can be substituted for their activities. ORP is measured in V (volt) or mV (millivolt).
<b>Reduction</b>	A chemical reaction involving the gain of electrons.
<b>Reducing Agent</b>	A substance that brings about the reduction of other substances (it is oxidised during the process).
<b>Regeneration</b>	A process in which a reduced ionic species is converted back to the oxidised form. For example, in used $\text{FeCl}_3$ , ions from the original total $\text{FeCl}_3$ that have been reduced to $\text{Fe}^{2+}$ ions are oxidised to $\text{Fe}^{3+}$ .
<b>Scanning Electron Microscopy (SEM)</b>	A form of microscope that uses a beam of electrons to scan the surface of a sample, rather than a beam of light. In doing so a large magnification is possible. As the beam scans the surface, those electrons that are reflected, together with any emitted, are collected as a current and used to build up a detailed picture of the surface.
<b>Standard Electrode Potential (<math>E^0</math>)</b>	The potential for a given cell measured when the current flow is essentially zero and all ions and molecules in the solutions are at a concentration of 1M and all gases at a pressure of 1 atmosphere.
<b>Stoichiometry</b>	This describes chemical reactions in which the reactants combine in a simple whole number ratios. A stoichiometric mixture is one that give rise to no excess reactant.
<b>Spent Etchant</b>	Etchant in which the active ionic species has been reduced to such an extent that the rate of etching and surface characteristics of the etched substrates become unacceptable.

**Volatile Organic  
Compounds**

Carbon-containing substances released by natural processes and human activities that readily produce fumes; their reactions with nitrogen oxides in the presence of sunlight produces photochemical smog.





**Table 2: Criteria**

Criteria	1	2	3
Legal	Unlikely to infringe	Infringement could occur	Infringe current legislation
Degree of impact	no or little impact	small impact	large impact
• Scale			
• Severity			
• Duration			
Probability of occurrence	Never or hardly occur	Occasionally	Frequent
Ability to change	Difficult	Could change eventually	Quickly/easily
• Cost			
• Technology			
• Resources			
Concerns of interested parties	Not concern	Little concern	Very concern
Public image	no impact	Little impact	High impact

**Table 3 : Environmental Objectives and Targets**

Item	Activities	Impact	Objectives	Targets
7.1	Gas Turbine operation : Consumption of <ul style="list-style-type: none"> <li>• Natural gas</li> <li>• Distillate</li> <li>• Lube oil</li> </ul>	Depletion of natural resources	To minimise the consumption of natural resources by improving the productivity of the operation for short and long term.	<ol style="list-style-type: none"> <li>1. To improve the use of natural gas and distillate at the operation by increasing the efficiency of gas turbine by year 1998.</li> <li>2. To reduce generation of lube oil waste due to abnormal occurrence by 10% in 1997.</li> </ol>

**Table 4 :Environmental Management Programme**

Target 7.1			
Environmental Program 11 : Natural resources	Control procedure No.	Responsibility	
		By person	End date
1. To study the viability of converting the operation to combined cycle to reduce the impact to environment.	EP 001	Plant Manager	15/12/98
		General Manager	Approval
		Cost	£ 1,000,000.00

## Appendix B

### Usage of materials and utility: Company E

#### B1 Usage of materials and utilities

Process/activity	Type of material/method used	Quantity of materials used in 1995/96
1. Phototool Making/Image Production 1.1 'Cut and peel' artwork	Is cut and peel artwork used in phototool production? <b>Yes/No</b>	If Yes, please specify quantity of cut and peel materials used in 1995/96 <u>80</u> m <sup>2</sup>
1.2 Phototool developing 1.2.1 Processing of line and lith films	Please specify system(s) used by the Company for processing of line and lith films? <u>Photographic processing machine.</u> <u>Most of the original artworks</u> <u>are subcontracted out</u>	a) Please specify types of films used in 1995. <u>Size</u> <u>14" x 18"</u> <u>Quantity</u> <u>1640 m<sup>2</sup></u>  b) Developers <u>240 litres</u> c) Fixers <u>60 litres</u> d) Other materials, please specify  <u>Material</u> <u>Quantity</u> <u>-</u> <u>-</u>
1.2.2 Special processes (e.g. reverse processing, processing of high resolution film, Image Plane Plate, Chrome on Glass)	Please specify special process(es) used, if any. <u>-</u> <u>-</u> <u>-</u>	Please specify types of materials and quantity used in special process, if any. <u>Material</u> <u>Quantity</u> <u>-</u> <u>-</u>

**Usage of materials and utility: Company E**

Process/activity	Type of material/method used	Quantity of materials used in 1995/96															
<p><b>2. Preparation of Metallic Materials</b></p> <p><b>2.1 Cutting metal to required sizes</b></p>	<p>Please specify the composition of incoming metals, in percentage,</p> <p>a) Stainless steel <u>64</u> %            b) Mild steel <u>4</u> %            c) Copper (Cu) <u>2</u> %            d) BeCu <u>6</u> %            e) Cu alloy <u>3</u> %            f) Aluminium <u>4</u> %            g) Brass <u>7</u> %            h) Others, please specify, <u>10</u> %</p>	<p>a) Total weight of incoming metals = <u>3360 kg</u></p> <p>b) Total weight of scrapped metals after cutting =</p> <p>c) Total weight of rejects during production = <u>2.3% of the above</u></p>															
<p><b>2.2 Cleaning of metals</b></p> <p>2.2.1 General cleaning</p>	<p>a) Is conveyer metal cleaning system used? <b>Yes/No</b></p> <p>b) If <b>No</b>, what system is used? Please specify</p>	<p>Please specify quantity of materials used in cleaning.</p> <table border="0"> <thead> <tr> <th><u>Material</u></th> <th><u>Concentration</u></th> <th><u>Quantity</u></th> </tr> </thead> <tbody> <tr> <td>Acids-based</td> <td>-</td> <td><u>1,680 kg</u></td> </tr> <tr> <td>Alkalis-based</td> <td>-</td> <td><u>382 kg</u></td> </tr> <tr> <td>Others, please specify solvent</td> <td></td> <td><u>5 litres</u></td> </tr> <tr> <td><u>Proprietary chemicals</u></td> <td></td> <td><u>284 kg</u></td> </tr> </tbody> </table>	<u>Material</u>	<u>Concentration</u>	<u>Quantity</u>	Acids-based	-	<u>1,680 kg</u>	Alkalis-based	-	<u>382 kg</u>	Others, please specify solvent		<u>5 litres</u>	<u>Proprietary chemicals</u>		<u>284 kg</u>
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Others, please specify solvent		<u>5 litres</u>															
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**Usage of materials and utility: Company E**

<b>Process/activity</b>	<b>Type of material/method used</b>	<b>Quantity of materials used in 1995/96</b>																		
2.2.2 Cleaning of more contaminated metals/special cleaning	What method(s) is(are) used in cleaning more contaminated metal surfaces? Please specify _____ _____ _____	Please specify quantity of materials used in cleaning. <table border="1" data-bbox="690 268 948 1055"> <thead> <tr> <th><u>Material</u></th> <th><u>Concentration</u></th> <th><u>Quantity</u></th> </tr> </thead> <tbody> <tr><td>—</td><td>—</td><td>—</td></tr> <tr><td>_____</td><td>_____</td><td>_____</td></tr> <tr><td>_____</td><td>_____</td><td>_____</td></tr> <tr><td>_____</td><td>_____</td><td>_____</td></tr> <tr><td>_____</td><td>_____</td><td>_____</td></tr> </tbody> </table>	<u>Material</u>	<u>Concentration</u>	<u>Quantity</u>	—	—	—	_____	_____	_____	_____	_____	_____	_____	_____	_____	_____	_____	_____
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2.3 Metal treatment (prior to coating of photoresist)	Are the following methods of metal treatment used in metal preparation prior to photoresist coating? a) Surface abrasion using abrasives <b>Yes/No</b> b) Pre-etching using etchants <b>Yes/No</b> c) Conversion coating using acids <b>Yes/No</b> d) Other methods, please specify _____ _____	Please specify quantity of materials used in metal treatment, if any <table border="1" data-bbox="1120 268 1377 1055"> <thead> <tr> <th><u>Material</u></th> <th><u>Concentration</u></th> <th><u>Quantity</u></th> </tr> </thead> <tbody> <tr><td>—</td><td>—</td><td>—</td></tr> <tr><td>_____</td><td>_____</td><td>_____</td></tr> <tr><td>_____</td><td>_____</td><td>_____</td></tr> <tr><td>_____</td><td>_____</td><td>_____</td></tr> <tr><td>_____</td><td>_____</td><td>_____</td></tr> </tbody> </table>	<u>Material</u>	<u>Concentration</u>	<u>Quantity</u>	—	—	—	_____	_____	_____	_____	_____	_____	_____	_____	_____	_____	_____	_____
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Usage of materials and utility: Company E

Process/activity	Type of material/method used	Quantity of materials used in 1995/96
<p><b>3. Photoresist Processing</b></p> <p><b>3.1 Coating of photoresist</b></p>	<p><b>What are the methods used in coating photoresist ?</b></p> <p>a) Dipping in liquid photoresist <b>Yes/No</b></p> <p>b) Hot laminating of dry film <b>Yes/No</b></p> <p>c) Silk screening application of resist <b>Yes/No</b></p> <p>d) Other method(s), please specify _____</p> <p>_____</p> <p>_____</p>	<p>Please specify quantity of materials used in photoresist coating, if applicable</p> <p><b>Material</b> <b>Quantity</b></p> <p>a) Solvent-based photoresist <u>480 litres</u></p> <p>b) Aqueous photoresist <u>—</u></p> <p>c) Dry film <u>—</u></p> <p>d) Thinners <u>500 litres</u></p> <p>e) Other materials, please specify <u>Screen wash 240 litres</u> <u>resist - 25 litres, thinner - 10 litres</u></p>
<p><b>3.2 Development of photoresist</b></p>		<p>Please specify quantity of materials used in developing photoresist, if applicable</p> <p><b>Materials</b> <b>Quantity</b></p> <p>a) Xylene <u>—</u></p> <p>b) White spirit <u>2,700 litres</u></p> <p>c) Aqueous developer <u>—</u></p> <p>d) Other materials, please specify <u>—</u></p> <p>_____</p> <p>_____</p>

**Usage of materials and utility: Company E**

Process/activity	Type of material/method used	Quantity of materials used in 1995/96
<p><b>3.3 Hardening treatment</b> (applied to certain negative working water soluble photoresists only).</p>	<p>Is hardening treatment used in the production process? <b>Yes/No</b></p>	<p>If <b>Yes</b>, please specify quantity of materials used in the hardening treatment process.</p> <p><b>Materials</b></p> <p>a) Acids _____ <b>Quantity</b> _____</p> <p>b) Solvent _____</p> <p>c) Other materials, please specify _____</p>
<p><b>3.6 Stripping of photoresist</b></p>	<p>-</p>	<p>Please specify quantity of materials used in stripping photoresist, if applicable</p> <p><b>Materials</b></p> <p>a) Solvent stripper _____ <b>Quantity</b> _____</p> <p>b) Aqueous stripper _____</p> <p>c) Other materials, please specify _____</p>
<p><b>3.6.2 Acid dipping</b> (optional)</p>	<p>Is acid dipping used in the production process? <b>Yes/No</b></p>	<p>If <b>Yes</b>, please specify quantity of materials used in the acid dipping process.</p> <p><b>Materials used</b></p> <p>a) Acids _____ <b>Quantity</b> _____</p> <p>b) Other materials, please specify _____</p>

**Usage of materials and utility: Company E**

Process/activity	Type of material/method used	Quantity of materials used in 1995/96
<p><b>4 Etching of metals</b></p>	<p>Are the following systems used in etching metals?</p> <p>a) Ferric chloride etching <b>Yes/No</b></p> <p>b) Cupric chloride etching <b>Yes/No</b></p> <p>c) Ferric nitrate etching <b>Yes/No</b></p> <p>d) Acid etching <b>Yes/No</b></p> <p>e) Alkaline etching <b>Yes/No</b></p> <p>f) Electrolytic etching <b>Yes/No</b></p> <p>g) Other system(s), please specify _____</p>	<p>Please specify quantity of materials used in etching metal, if applicable</p> <p><b>Material</b> <b>Quantity/Concentration</b></p> <p>a) Ferric chloride <u>120,000 kg / 48°C</u></p> <p>b) Cupric chloride <u>Negligible</u></p> <p>c) Ferric nitrate _____</p> <p>d) Acids _____</p> <p>e) Alkalies _____</p> <p>f) Other materials, please specify _____</p>
<p><b>5 Methods of regeneration of spent etchants</b></p>	<p>Are the following systems used in the regeneration of spent etchants?</p> <p>a) Chlorine gas <b>Yes/No</b></p> <p>b) NaClO<sub>3</sub>/HCl (BEAC) <b>Yes/No</b></p> <p>c) H<sub>2</sub>O<sub>2</sub>/HCl <b>Yes/No</b></p> <p>d) Ozone <b>Yes/No</b></p> <p>e) Electrolytic <b>Yes/No</b></p> <p>f) Other system(s), please specify _____</p>	<p>Please specify quantity of materials used in the regeneration of used etchants, if applicable</p> <p><b>Material</b> <b>Quantity/Concentration</b></p> <p>a) Chlorine gas _____</p> <p>b) NaClO<sub>3</sub> _____</p> <p>c) HCl _____</p> <p>d) H<sub>2</sub>O<sub>2</sub> _____</p> <p>e) Ozone _____</p> <p>f) Other materials, please specify _____</p>



**Usage of materials and utility: Company E**

Process/activity	Type of material/method used	Quantity of materials used in 1995/96
<p><b>6 Finishing processes</b></p>	<p>Are the following finishing processes used in production?</p> <p>a) Anodising <span style="float: right;">Yes/No</span></p> <p>b) Electroplating <span style="float: right;">Yes/No</span></p> <p>c) Painting (filling) <span style="float: right;">Yes/No</span></p> <p>d) Other process(es), please specify _____</p>	<p>Please specify quantity of materials used in the finishing processes, if applicable</p> <p><b>Material</b> <span style="float: right;"><b>Quantity/Concentration</b></span></p> <p>a) Chemicals _____</p> <p>b) Paints and solvents <span style="float: right;">300 litres</span></p> <p style="margin-left: 20px;">Paints _____</p> <p>c) Other materials, please specify _____</p>
<p><b>7 Other process not specified above</b></p>	<p>Please specify the process(es), if any</p> <p>_____</p> <p>_____</p> <p>_____</p>	<p>Please specify quantity of materials used.</p> <p><b>Material</b> <span style="float: right;"><b>Quantity Concentration</b></span></p> <p>_____</p> <p>_____</p> <p>_____</p>

**Usage of materials and utility: Company E**

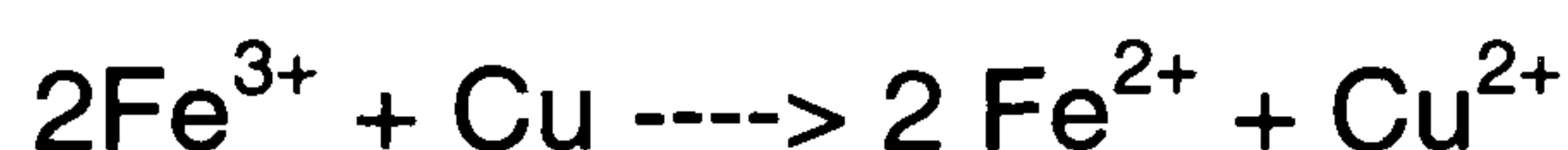
Process/activity	Type of material/method used	Quantity of materials used in 1995/96																		
<p><b>8. Waste/effluent Treatment</b></p>	<p>Are the following waste/effluent treated in-house?</p> <p>a) Spent etchants <span style="float: right;">Yes/No</span></p> <p>b) Effluent/waste water <span style="float: right;">Yes/No</span></p> <p>c) Other waste products, please specify</p> <p>—</p> <p>_____</p> <p>_____</p> <p>_____</p>	<p>Please specify quantity of materials used in waste effluent/treatment.</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="text-align: left;">Material</th> <th style="text-align: left;">Concentration</th> <th style="text-align: left;">Quantity</th> </tr> </thead> <tbody> <tr> <td>NaOH</td> <td>32%</td> <td>4,800 kg</td> </tr> <tr> <td>_____</td> <td>_____</td> <td>_____</td> </tr> <tr> <td>_____</td> <td>_____</td> <td>_____</td> </tr> <tr> <td>_____</td> <td>_____</td> <td>_____</td> </tr> <tr> <td>_____</td> <td>_____</td> <td>_____</td> </tr> </tbody> </table>	Material	Concentration	Quantity	NaOH	32%	4,800 kg	_____	_____	_____	_____	_____	_____	_____	_____	_____	_____	_____	_____
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<p><b>9. Usage Of Other Materials And Services</b></p>		<p>Please specify quantity of material/utility/service used.</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="text-align: left;">Material/utility/service</th> <th style="text-align: left;">Quantity</th> </tr> </thead> <tbody> <tr> <td>a) Electricity</td> <td>402,818 KWh</td> </tr> <tr> <td>b) Gas</td> <td>118,667 KWh</td> </tr> <tr> <td>c) Water</td> <td>12,142 m<sup>3</sup></td> </tr> <tr> <td>d) Packaging materials</td> <td>N/A</td> </tr> <tr> <td>e) Paper</td> <td>N/A</td> </tr> <tr> <td>f) Others, please specify</td> <td>—</td> </tr> </tbody> </table>	Material/utility/service	Quantity	a) Electricity	402,818 KWh	b) Gas	118,667 KWh	c) Water	12,142 m <sup>3</sup>	d) Packaging materials	N/A	e) Paper	N/A	f) Others, please specify	—				
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## B2 Usage of Ferric Chloride in Etching - Percentage Conversion of FeCl<sub>3</sub> to FeCl<sub>2</sub>

In calculating the usage of ferric chloride, the following method is used:

### 1 Chemistry of ferric chloride etching

Assume that metals used are steel and copper and their based metals. From the chemistry of Fe/Cu etching below



2 moles of ferric chloride are required to etch one mole of Fe/Cu metal.

### 2 Conversion of FeCl<sub>3</sub> to FeCl<sub>2</sub>

Estimated weight of metals etched is found to be 3360 kg, out of which 2484.4 kg are Fe/Fe-based and 875.6 kg are Cu/Cu-based, and 120,000 kg of FeCl<sub>3</sub> were used in the production in 1995 from the data collected. As an average of 17.5% of the total metals are etched,

#### Total metals etched in terms of moles

Molecular weights of Fe = 55.85, Cu = 63.5

17.5% of 2484.4 kg of Fe = 434.77 kg = 434,770g/55.85g = **7,784.6 moles**

17.5% of 875.6 kg of Cu = 153.23 kg = 153,230/63.5g = **2,413.0 moles**

Total metals etched at 17.5% = **10,197.6 moles**

#### Total ferric chloride used in terms of moles

FeCl<sub>3</sub> at 48 °Be, density = 1.49 kg/litre  
molarity = 4.1 moles/litre

Total ferric chloride used = 120,000 x 1/1.49 x 4.1 moles = **330,201 moles**

% Conversion of FeCl<sub>3</sub> to FeCl<sub>2</sub> at 17.5% metals etched =  
10,197.6x2/330,201 = **6.2%**

## Appendix C

### Usage of materials and utility: Company F

#### C1 Usage of materials and utility

Process/activity	Type of material/method used	Quantity of materials used in 1995/96
1. Phototool Making/Image Production 1.1 'Cut and peel' artwork	Is cut and peel artwork used in phototool production? <b>Yes/No</b>	If Yes, please specify quantity of cut and peel materials used in 1995/96 <u>    </u> m <sup>2</sup>
1.2 Phototool developing 1.2.1 Processing of line and lith films	Please specify system(s) used by the company for processing of line and lith films? <u>Laser pattern generators</u> _____ _____	a) Please specify types of films used in 1995. Size / Type                      Quantity <u>HTU / various sizes</u> <u>6393.44 m<sup>2</sup></u> <u>HTA / various sizes</u> <u>693.7 m<sup>2</sup></u> b) Developers <u>1,050 litres</u> c) Fixers <u>570 litres</u> d) Other materials, please specify  <u>Material</u> <u>Quantity</u> <u>    </u> <u>    </u>
1.2.2 Special processes (e.g. reverse processing, processing of high resolution film, Image Plane Plate, Chrome on Glass)	Please specify special process(es) used, if any. _____ _____ _____	Please specify types of materials and quantity used in special process, if any. <u>Material</u> <u>Quantity</u> <u>    </u> <u>    </u>

**Usage of materials and utility: Company F**

Process/activity	Type of material/method used	Quantity of materials used in 1995/96																		
<p><b>2. Preparation of Metallic Materials</b></p> <p><b>2.1 Cutting metal to required sizes</b></p>	<p>Please specify the composition of incoming metals, in percentage,</p> <p>a) Stainless steel <u>6.5</u> %                      b) Mild steel _____ %                      c) Copper (Cu) _____ % <u>62.77</u>                      d) BeCu _____ %                      e) Cu alloy _____ %                      f) Aluminium _____ %                      g) Brass <u>26.3</u> %                      h) Others, please specify, <u>ms, Al = 4.5%</u></p>	<p>a) Total weight of incoming metals = <u>16,000 kg</u>                      b) Total weight of scrapped metals after cutting = -                      c) Total weight of rejects during production = <u>2-3% of the above</u></p>																		
<p><b>2.2 Cleaning of metals</b></p> <p>2.2.1 General cleaning</p>	<p>a) Is conveyer metal cleaning system used? <b>Yes/No</b></p> <p>b) If <b>No</b>, what system is used? Please specify _____</p>	<p>Please specify quantity of materials used in cleaning.</p> <table border="0"> <thead> <tr> <th><u>Material</u></th> <th><u>Concentration</u></th> <th><u>Quantity</u></th> </tr> </thead> <tbody> <tr> <td>Acids</td> <td>-</td> <td><u>510 kg</u></td> </tr> <tr> <td>Alkalis</td> <td>-</td> <td><u>300 kg</u></td> </tr> <tr> <td>Others, please specify</td> <td></td> <td><u>1,150 kg</u></td> </tr> <tr> <td><u>Proprietary chemicals</u></td> <td></td> <td><u>180 litres</u></td> </tr> <tr> <td><u>Genklene</u></td> <td></td> <td>_____</td> </tr> </tbody> </table>	<u>Material</u>	<u>Concentration</u>	<u>Quantity</u>	Acids	-	<u>510 kg</u>	Alkalis	-	<u>300 kg</u>	Others, please specify		<u>1,150 kg</u>	<u>Proprietary chemicals</u>		<u>180 litres</u>	<u>Genklene</u>		_____
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**Usage of materials and utility: Company F**

Process/activity	Type of material/method used	Quantity of materials used in 1995/96															
2.2.2 Cleaning of more contaminated metals/special cleaning	<p>What method(s) is(are) used in cleaning more contaminated metal surfaces? Please specify</p> <p>_____</p> <p>_____</p>	<p>Please specify quantity of materials used in cleaning.</p> <table border="1"> <thead> <tr> <th>Material</th> <th>Concentration</th> <th>Quantity</th> </tr> </thead> <tbody> <tr> <td>—</td> <td>—</td> <td>_____</td> </tr> <tr> <td>_____</td> <td>_____</td> <td>_____</td> </tr> <tr> <td>_____</td> <td>_____</td> <td>_____</td> </tr> <tr> <td>_____</td> <td>_____</td> <td>_____</td> </tr> </tbody> </table>	Material	Concentration	Quantity	—	—	_____	_____	_____	_____	_____	_____	_____	_____	_____	_____
Material	Concentration	Quantity															
—	—	_____															
_____	_____	_____															
_____	_____	_____															
_____	_____	_____															
2.3 Metal treatment (prior to coating of photoresist)	<p>Are the following methods of metal treatment used in metal preparation prior to photoresist coating?</p> <p>a) Surface abrasion using abrasives <b>Yes/No</b></p> <p>b) Pre-etching using etchants <b>Yes/No</b></p> <p>c) Conversion coating using acids <b>Yes/No</b></p> <p>d) Other methods, please specify _____</p>	<p>Please specify quantity of materials used in metal treatment, if any</p> <table border="1"> <thead> <tr> <th>Material</th> <th>Concentration</th> <th>Quantity</th> </tr> </thead> <tbody> <tr> <td>Acids (ferrous chloride)</td> <td>small</td> <td>quantity</td> </tr> <tr> <td>_____</td> <td>_____</td> <td>_____</td> </tr> <tr> <td>_____</td> <td>_____</td> <td>_____</td> </tr> <tr> <td>_____</td> <td>_____</td> <td>_____</td> </tr> </tbody> </table>	Material	Concentration	Quantity	Acids (ferrous chloride)	small	quantity	_____	_____	_____	_____	_____	_____	_____	_____	_____
Material	Concentration	Quantity															
Acids (ferrous chloride)	small	quantity															
_____	_____	_____															
_____	_____	_____															
_____	_____	_____															

Usage of materials and utility: Company F

Process/activity	Type of material/method used	Quantity of materials used in 1995/96
<p><b>3. Photoresist Processing</b></p> <p><b>3.1 Coating of photoresist</b></p>	<p><b>What are the methods used in coating photoresist ?</b></p> <p>a) Dipping in liquid photoresist <b>Yes/No</b></p> <p>b) Hot laminating of dry film <b>Yes/No</b></p> <p>c) Silk screening application of resist <b>Yes/No</b></p> <p>d) Other method(s), please specify _____</p> <p>_____</p> <p>_____</p>	<p>Please specify quantity of materials used in photoresist coating, if applicable</p> <p><b>Material</b> <b>Quantity</b></p> <p>a) Solvent-based photoresist <u>360 litres</u></p> <p>b) Aqueous photoresist <u>small quantity</u></p> <p>c) Dry film <u>600 litres</u></p> <p>d) Thinners _____</p> <p>e) Other materials, please specify _____</p>
<p><b>3.2 Development of photoresist</b></p>		<p>Please specify quantity of materials used in developing photoresist, if applicable</p> <p><b>Materials</b> <b>Quantity</b></p> <p>a) Xylene <u>2,160 litres</u></p> <p>b) White spirit _____</p> <p>c) Aqueous developer _____</p> <p>d) Other materials, please specify _____</p>

**Usage of materials and utility: Company F**

<b>Process/activity</b>	<b>Type of material/method used</b>	<b>Quantity of materials used in 1995/96</b>
<p><b>3.3 Hardening treatment</b> (applied to certain negative working water soluble photoresists only).</p>	<p>Is hardening treatment used in the production process? <b>Yes/No</b></p>	<p>If <b>Yes</b>, please specify quantity of materials used in the hardening treatment process.</p> <p><b>Materials</b></p> <p>a) Acids _____ <b>Quantity</b> _____</p> <p>b) Solvent _____</p> <p>c) Other materials, please specify _____</p>
<p><b>3.6 Stripping of photoresist</b></p>	<p>-</p>	<p>Please specify quantity of materials used in stripping photoresist, if applicable</p> <p><b>Materials</b></p> <p>a) Solvent stripper _____ <b>Quantity</b> 8,750 litres</p> <p>b) Aqueous stripper _____</p> <p>c) Other materials, please specify _____</p>
<p><b>3.6.2 Acid dipping</b> (optional)</p>	<p>Is acid dipping used in the production process? <b>Yes/No</b></p>	<p>If <b>Yes</b>, please specify quantity of materials used in the acid dipping process.</p> <p><b>Materials used</b></p> <p>a) Acids _____ <b>Quantity</b> _____</p> <p>b) Other materials, please specify _____</p>



**Usage of materials and utility: Company F**

Process/activity	Type of material/method used	Quantity of materials used in 1995/96
<p><b>4 Etching of metals</b></p>	<p>Are the following systems used in etching metals?</p> <p>a) Ferric chloride etching <b>Yes/No</b></p> <p>b) Cupric chloride etching <b>Yes/No</b></p> <p>c) Ferric nitrate etching <b>Yes/No</b></p> <p>d) Acid etching <b>Yes/No</b></p> <p>e) Alkaline etching <b>Yes/No</b></p> <p>f) Electrolytic etching <b>Yes/No</b></p> <p>g) Other system(s), please specify _____</p>	<p>Please specify quantity of materials used in etching metal, if applicable</p> <p><b>Material</b> <b>Quantity/Concentration</b></p> <p>a) Ferric chloride <u>41,500 litres / 42°Bé</u></p> <p>b) Cupric chloride <u>-</u></p> <p>c) Ferric nitrate <u>Negligible</u></p> <p>d) Acids <u>-</u></p> <p>e) Alkalis <u>-</u></p> <p>f) Other materials, please specify _____</p>
<p><b>5 Methods of regeneration of spent etchants</b></p>	<p>Are the following systems used in the regeneration of spent etchants?</p> <p>a) Chlorine gas <b>Yes/No</b></p> <p>b) NaClO<sub>3</sub>/HCl (BEAC) <b>Yes/No</b></p> <p>c) H<sub>2</sub>O<sub>2</sub>/HCl <b>Yes/No</b></p> <p>d) Ozone <b>Yes/No</b></p> <p>e) Electrolytic <b>Yes/No</b></p> <p>f) Other system(s), please specify _____</p>	<p>Please specify quantity of materials used in the regeneration of used etchants, if applicable</p> <p><b>Material</b> <b>Quantity/Concentration</b></p> <p>a) Chlorine gas <u>-</u></p> <p>b) NaClO<sub>3</sub> <u>Negligible</u></p> <p>c) HCl <u>-</u></p> <p>d) H<sub>2</sub>O<sub>2</sub> <u>-</u></p> <p>e) Ozone <u>-</u></p> <p>f) Other materials, please specify _____</p>

**Usage of materials and utility: Company F**

Process/activity	Type of material/method used	Quantity of materials used in 1995/96
<p><b>6 Finishing processes</b></p>	<p>Are the following finishing processes used in production?</p> <p>a) Anodising <span style="float: right;">Yes/No</span></p> <p>b) Electroplating <span style="float: right;">Yes/No</span></p> <p>c) Painting (filling) <span style="float: right;">Yes/No</span></p> <p>d) Other process(es), please specify _____</p>	<p>Please specify quantity of materials used in the finishing processes, if applicable</p> <p><b>Material</b> <span style="float: right;"><b>Quantity/Concentration</b></span></p> <p>a) Chemicals <i>various chemicals are used</i></p> <p>_____</p> <p>_____</p> <p>_____</p> <p>b) Paints and solvents</p> <p>_____</p> <p>_____</p> <p>_____</p> <p>c) Other materials, please specify</p> <p>_____</p> <p>_____</p> <p>_____</p> <p>_____</p>
<p><b>7 Other process not specified above</b></p>	<p>Please specify the process(es), if any</p> <p><i>CNC machining</i></p> <p>_____</p> <p>_____</p> <p>_____</p>	<p>Please specify quantity of materials used.</p> <p><b>Material</b> <span style="float: right;"><b>Quantity Concentration</b></span></p> <p>_____</p> <p>_____</p> <p>_____</p>

**Usage of materials and utility: Company F**

Process/activity	Type of material/method used	Quantity of materials used in 1995/96
<p><b>8. Waste/effluent Treatment</b></p>	<p>Are the following waste/effluent treated in-house?</p> <p>a) Spent etchants <span style="float: right;">Yes/No</span></p> <p>b) Effluent/waste water <span style="float: right;">Yes/No</span></p> <p>c) Other waste products, please specify _____</p> <p>_____</p> <p>_____</p> <p>_____</p>	<p>Please specify quantity of materials used in waste effluent/treatment.</p> <p><b>Material</b> <u>NaOH</u> <b>Concentration</b> <u>46%</u> <b>Quantity</b> <u>21,000 litres</u></p> <p>_____</p> <p>_____</p> <p>_____</p> <p>_____</p>
<p><b>9. Usage Of Other Materials And Services</b></p>		<p>Please specify quantity of material/utility/service used.</p> <p><b>Material/utility/service</b> <b>Quantity</b></p> <p>a) Electricity <u>594,398 kWh</u></p> <p>b) Gas <u>422,535 kWh</u></p> <p>c) Water <u>41,040 m<sup>3</sup></u></p> <p>d) Packaging materials <u>4,134 kg</u></p> <p>e) Paper <u>6,049 kg</u></p> <p>f) Others, please specify _____</p>

## C2 Usage of Ferric Chloride in Etching - Percentage Conversion of FeCl<sub>3</sub> to FeCl<sub>2</sub>

In calculating the usage of ferric chloride, the following method is used:

### 1 Chemistry of ferric chloride etching

Assume that metals used are steel and copper and their based metals. From the chemistry of Fe/Cu etching below



2 moles of ferric chloride are required to etch one mole of Fe/Cu metal.

### 2 Conversion of FeCl<sub>3</sub> to FeCl<sub>2</sub>

Estimated weight of metals etched is found to be 16,100 kg, out of which 1,760 kg are Fe/Fe-based and 14,340 kg are Cu/Cu-based, and 41,500 litres of FeCl<sub>3</sub> were used in the production in 1995 from the data collected.

Total metals etched in terms of moles:

Molecular weights of Fe = 55.85, Cu = 63.5

10% of 1,760 kg of Fe = 176 kg = 176,000g/55.85g = **3,151.3 moles**

10% of 14,340 kg of Cu = 1,434 kg = 1,434,000g/63.5g  
= **22,585.7 moles**

Total metals etched at 10% = **25,734 moles**

Total ferric chloride used in terms of moles

FeCl<sub>3</sub> at 42 °Be', molarity = 3.37 moles/litre

Total ferric chloride used = 41,500 litres x 3.37 moles/litres = **139,855 moles**

% Conversion of FeCl<sub>3</sub> to FeCl<sub>2</sub> at 10% metals etched out  
= (25,734 x 2)/139,855 = **36.8%**

## Appendix D

### Air Emissions – EC Regulation 3093/94 Implementing the Montreal Protocol

## AIR EMISSIONS

### EC REGULATION 3093/4 IMPLEMENTING THE MONTREAL PROTOCOL

SUBSTANCE	PHASE OUT SCHEDULE	
	FOR PRODUCTION	FOR SUPPLY
Halons	Phase out by 1.1.94	Phase out by 1.1.94
CFC's	Phase out by 1.1.95	Phase out by 1.1.95
Carbon Tetrachloride	Phase out by 1.1.95	Phase out by 1.1.95
Hydrobromofluorocarbons	Phase out by 1.1.96	Phase out by 1.1.96
1,1,1 - Trichloroethane	50% cut (on 1989 levels) by 1.1.94	50% cut (on 1989 levels) by 1.1.94
	Phase out by 1.1.96	Phase out by 1.1.96
Methyl Bromide	Freeze at 1991 levels from 1.1.95	Freeze at 1991 levels from 1.1.95
	25% cut (on 1991 levels) by 1.1.98	25% cut (on 1991 levels) by 1.1.98
Hydrochlorofluorocarbons		Freeze at 1989 levels of HCFCs and at 2% of the 1989 levels of CFCs from 1.1.95.
		65% of the quota* by 1.1.05
		40% of the quota* by 1.1.08
		20% of the quota* by 1.1.11
		5% of the quota* by 1.1.14
		Phase out by 1.1.15

\* Quotas for each producer and importer of these substances will be set either when the amount of HCFCs produced reach 80% of the 1989 levels or on 1.1.2000

## **Appendix E**

### **Survey on VOC and Ferric Chloride Utilisation**

From Dr. D.M. Allen & Mr. L.T. Ler

**Data Collection for Evaluation of Environmental Effects of PCM for  
One Year (1995 if possible)**

**1. Please specify composition and weight/area of metallic materials processed.**

- I.) i. Ferrous materials \_\_\_\_\_ kg/year  
 ii. Copper materials \_\_\_\_\_ kg /year  
 iii. Others \_\_\_\_\_ kg/year

II.) Total area of metal processed \_\_\_\_\_ m<sup>2</sup>/year

**2. Please specify quantity of etchants used in the etching process.**

Ferric chloride \_\_\_\_\_ litres/year or \_\_\_\_\_ drums/year

**3. Do you use regeneration of ferric chloride? Yes/No**

**4. Please specify quantity of organic solvents used in the PCM process.**

\_\_\_\_\_ litres/year

***Company Name:***

***Do you wish these details to be kept confidential? Yes/No***

***Signature:***

***Date:***

***Please return to Dr. D.M. Allen***

## **Appendix F**

### **Survey on Regeneration and Disposal of Ferric Chloride**

19 November 1997

**Dear Sir/Madam,**

#### **Survey on Regeneration and Disposal of Ferric Chloride**

I am currently pursuing a PhD degree at Cranfield University under the supervision of Dr. David Allen. My research project is the formulation of a strategy by using cleaner technologies/waste minimisation for the photochemical machining industry to comply with **ISO 14001**.

As it is generally acknowledged that the usage of ferric chloride and disposal of its waste pose the most adverse environmental effects of the photochemical machining process, one of my areas of research is to study the various aspects of regeneration of ferric chloride and its disposal.

I am enclosing a copy of the survey form which consists of some questions on the above subject matter for your completion. Please be informed that all information gathered in this survey will be treated in a strictly confidential manner.

It would be very much appreciated if you could supply the necessary information, and any additional data which you feel would be useful to this study.

Thank you in advance for your co-operation in this matter.

Yours sincerely,

**Leong T. Ler**

From Dr. D.M. Allen & Mr. L.T. Ler

## Survey on Regeneration and Disposal of Ferric Chloride

1. Do you use regeneration of ferric chloride? **Yes/No**  
If the answer is **Yes**, please answer Questions 2,3 and 6.  
If the answer is **No**, please answer Questions 3,4,5 and 6.
  
2. What regeneration system do you use ?
 

a.) Sodium chlorate/hydrochloric acid	b.) Ozone/hydrochloric acid
c.) Electrolysis/hydrochloric acid	d.) Chlorine gas
e.) Oxygen/hydrochloric acid	f.) Others, please specify _____

---
  
3. How do you currently dispose of any waste ferric chloride?
 

a.) As a liquid waste to be reclaimed	b.) As a liquid waste going to landfill
c.) As a 'solid cake' to be reclaimed	d.) As a 'solid cake' going to landfill.
  
4. Please specify reason(s) why regeneration is **not** used.
 

a.) Regeneration does not contribute to profits of company
b.) Lack of technical 'know-how' in company
c.) Regeneration affects quality of products.
d.) Others, please specify _____
  
5. If you intend to use regeneration in the near future, what would be your priority consideration?
 

a.) Cost of purchasing and running a regeneration system
b.) Environment-friendliness of regeneration system
c.) Others, please specify _____
  
6. Would you choose a regeneration system which is more environment-friendly at a higher overall cost? **Yes/No**

**Company Name:**

**Signature:**

**date:**

*Please return to Dr. D.M. Allen at fax no : +44 (0) 1234 752473*



## **Appendix G**

### **Volume of Ferric Chloride required to dissolve one tonne of metal**

#### **G1 Ferric chloride etching iron**

##### **1. No regeneration**



2 moles of ferric chloride is required to etch one mole of iron

Total moles of iron/kg =  $1000/55.85 = 17.905$  moles/kg

Total moles of ferric chloride required to etch one tonne of iron  
=  $17.905 \times 1000 \times 2$  moles

Strength of ferric chloride = 3.37 M

Therefore, the volume of ferric chloride required to etch one tonne of iron  
=  $17905 \times 2/3.37$  litres  
= 10,626 litres

##### **2. With regeneration**

One regeneration, efficiency = 250%

Volume of ferric chloride =  $10,626 \text{ litres}/2.50$   
= 4,250 litres

Two regenerations, efficiency = 475%

Volume of ferric chloride =  $10,626 \text{ litres}/4.75$   
= 2,237 litres

Three regenerations, efficiency = 812.5%

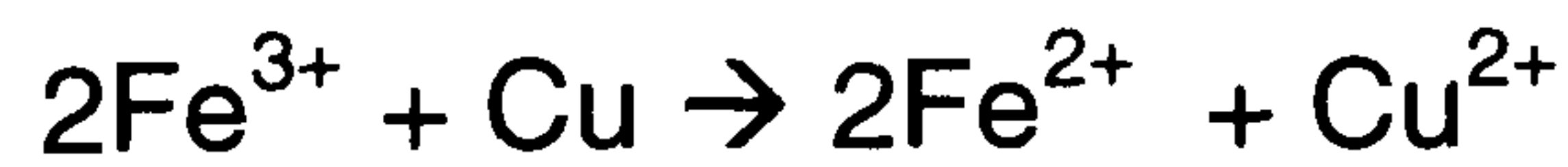
Volume of ferric chloride =  $10,626 \text{ litres}/8.125$   
= 1,307 litres

Four regenerations, efficiency = 1318.75%

Volume of ferric chloride =  $10,626 \text{ litres}/13.1875$   
= 806 litres

## G2 Ferric chloride etching copper

### 1. No regeneration



2 moles of ferric chloride is required to etch one mole of copper

Total moles of copper/kg =  $1000/63.54 = 15.738$  moles/kg

Total moles of ferric chloride required to etch one tonne of copper  
=  $15.738 \times 1000 \times 2$  moles

Strength of ferric chloride = 3.37 M

Therefore, the volume of ferric chloride required to etch one tonne of copper  
=  $15738 \times 2/3.37$  litres  
= 9,340 litres

### 2. With regeneration

One regeneration, efficiency = 200%  
Volume of ferric chloride =  $9,340$  litres/2  
= 4,670 litres

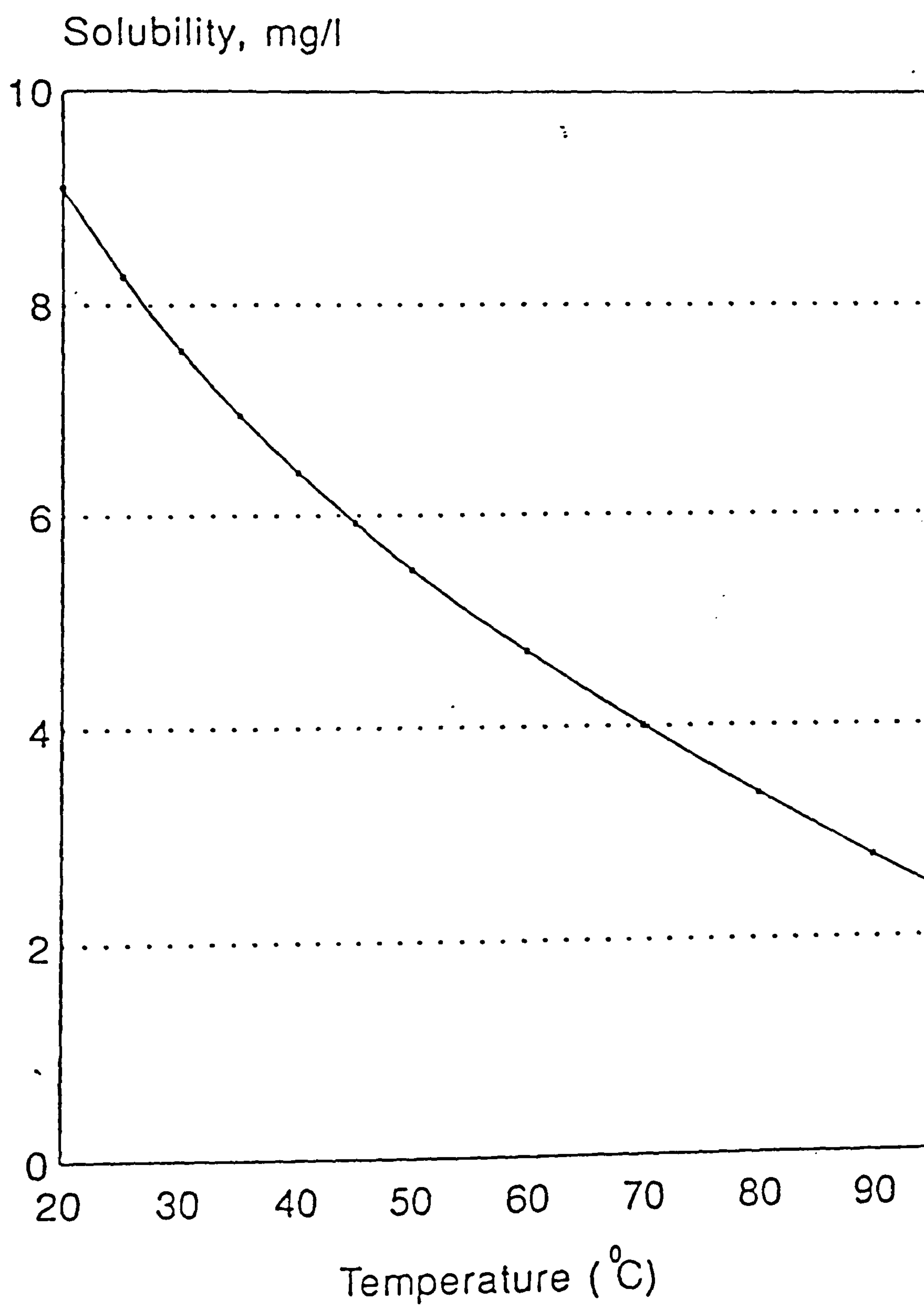
Two regenerations, efficiency = 300%  
Volume of ferric chloride =  $9,340$  litres/3  
= 23,113 litres

Three regenerations, efficiency = 400%  
Volume of ferric chloride =  $9,340$  litres/4  
= 2,335 litres

Four regenerations, efficiency = 500%  
Volume of ferric chloride =  $9,340$  litres/5  
= 1,868 litres

**Appendix H****Solubility of oxygen in aqueous solution****Saturated Oxygen in Aqueous Solution Vs Temperature**

---



## Appendix J

### Volume of one mole of oxygen gas at STP

From the chemical reaction below,



One mole of oxygen gas is required to regenerate four moles of ferrous chloride solution. The volume of oxygen gas required can be calculated from the Equation of State of an Ideal Gas which is expressed as follows:

$$PV = nRT$$

Where

P = pressure of gas

V = volume of gas

n = number of moles

R = Gas constant =  $8.314 \text{ joules } ^\circ\text{K}^{-1} \text{ mole}^{-1} = 82.057 \text{ cc atm } ^\circ\text{K}^{-1} \text{ mole}^{-1}$

T = absolute temperature of gas

Assuming that oxygen behaves as an ideal gas at atmospheric pressure and at room temperature of  $20^\circ\text{C}$ , the volume of one mole of oxygen gas required for the oxidation process of 4 moles of  $\text{FeCl}_3$  is:

$$\begin{aligned} V &= \frac{nRT}{P} \\ &= \frac{(1 \text{ mole}) \times (82.057 \text{ cc atm } ^\circ\text{K}^{-1} \text{ mole}^{-1}) \times (293.15 \text{ } ^\circ\text{K})}{1 \text{ atm}} \\ &= 24,055 \text{ cc} \\ &= 24.055 \text{ litres} \end{aligned}$$

## **Appendix K**

### **Static mixer**

The Koch static mixing unit consists of a series of stationary, rigid elements placed lengthwise in a pipe. These elements form intersecting channels that split, rearrange, and recombine component streams into smaller and smaller layers until one homogeneous stream exists.

Compared to static mixing unit with conventional dynamic agitators, the static mixing unit uses much less power, and since it has no moving parts and no electrical hook-up, the static mixing unit requires no maintenance.

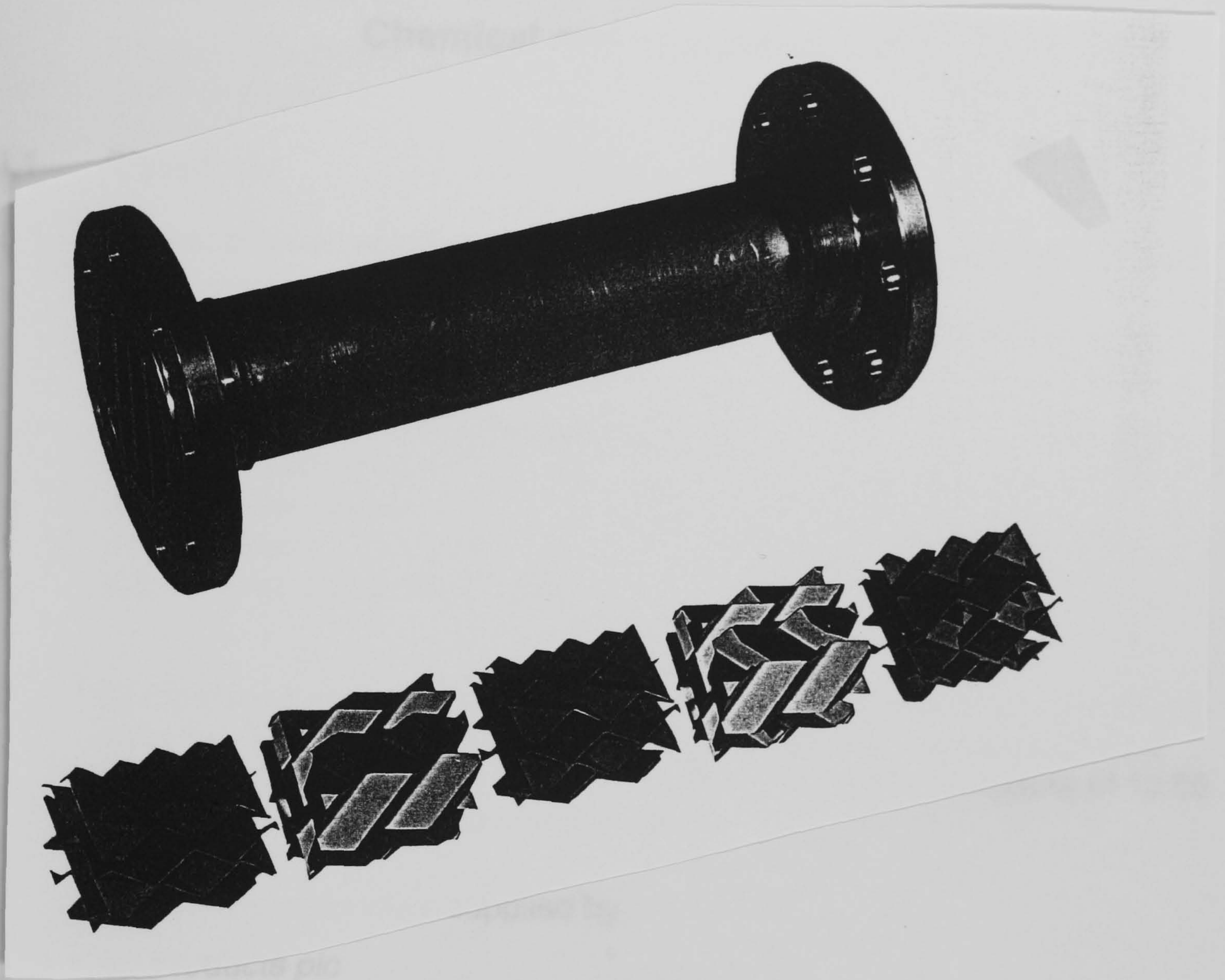
The static mixing elements are made from intersecting bars or corrugated sheets joined together to form open channels. These elements when placed end to end along the length of a section of pipe, form the static mixing unit: a series of open, intersecting channels for fluid flow.

The fluids to be mixed enter the unit and are split into individual streams in the channels. These channels provide strong transversal flow and fluid exchange at the pipe wall. At each channel intersection, a part of the fluid shears off into the crossing channel.

Adjacent mixing elements are positioned 90° relative to each other, so two-dimensional mixing takes place over the first element and three-dimensional mixing over all successive elements. This three dimensional mixing ensures uniformity in composition, concentration, viscosity, and temperature.

Depending on the type of process and the desired characteristics of the final product, any number of elements may be added to form the static mixing unit.

The figure below shows the construction of a Koch static mixer used in the experiment.



(Note: The above information is extracted from a brochure of Koch Engineering Company Inc. on 'Static Mixing Technology')

## **Appendix L**

### **Chemical and equipment list**

#### **L1 Chemicals**

- (1.) - Ferric chloride solution, with a maximum 0.6% hydrochloric acid content.  
- Hydrochloric acid (concentrated, 32% volume/weight)

The above items were supplied by

*Hays Chemicals Distribution Ltd.  
Cogdean Elms Works,  
Higher Merley Lane,  
Corfe Mullen  
Wimbourne, Dorset BH21 3EH*

- (2.) Compressed oxygen and related fittings such as regulators and flashback arrestor. The oxygen gas was supplied in a cylinder and at a minimum concentration of 99.4% purity. Each cylinder occupies a capacity of 10.05 m<sup>3</sup> at standard temperature and pressure.

The above items were supplied by

*Air Products plc  
Hampshire International Business Park,  
Crockford Lane, Chineham  
Basingstoke, Hampshire RG24 8GA*

## L.2 Equipment

- (1.) Chemcut etching machine with a sump capacity of 450 litres with a hydrometer (measurement of density in °Bé).

The above items were supplied by

*Chemcut Corporation,  
State College,  
Pennsylvania, USA*

- (2.) Knick Process Unit 73 pH meter, pH, ORP and temperature electrodes

The above items were supplied by

*Elscolab B.V.  
Zonnebaan 18 – 18  
3606 CB MAARSSENBROEK*

- (3.) Oxygen gas flow meter with a measurement range of 40-400 litre/minute.

The above item were supplied by

*Platon Instrumentation.  
Jays Close, Viables,  
Basingstoke, Hampshire RG22 4BS*

- (4.) Static mixer

The above item were supplied by

*Koch Engineering Company, Inc.  
P.O. Box 8127  
Wichita, Kansas  
USA*



## **Appendix M**

### **Ratio of ferric/ferrous ions in the system**

In etching stainless steel



2 moles of ferric chloride are required to etch one mole of Fe/Cu metal. 3 moles of ferrous ions are produced.

450 litres of 43 °Be' (3.37M) ferric chloride = 3.37 moles/litre x 450 litres = 1516.5 moles of ferric chloride

5 kg of steel has 5,000/55.85 moles = 89.5 moles

Thus the total moles of ferric ions in the system after 5 kg of stainless steel has been dissolved into the system are = 1516.5 – 2 x 89.5 = 1337 moles of ferric ion.

And the total moles of ferrous ions in the system after 5 kg of stainless steel has been dissolved into the system are = 3 x 89.5 = 269.5 moles of ferrous ion.

Therefore, the ratio of ferric: ferrous ion = 1337.0: 269.5 = 4.96: 1

## Appendix N

### Efficiency of oxygen utilisation in regeneration

From the Nernst's Equation,

$$E = E^0_{\text{formal}} + \frac{2.303RT}{nF} \log_{10} \frac{[a_{\text{ferric ion}}]}{[a_{\text{ferrous ion}}]}$$

$$\log_{10} \frac{[a_{\text{ferric ion}}]}{[a_{\text{ferrous ion}}]} = \frac{nF}{2.303RT} [E - E^0_{\text{formal}}]$$

$E^0 = 0.526 \text{ V}$  for ferrous/ferric system

$n = 1$  (for  $\text{FeCl}_3/\text{FeCl}_2$  system)

$F = 9.6485 \times 10^4 \text{ Cmol}^{-1}$

$R = 8.314 \text{ JoulesK}^{-1}\text{mol}^{-1}$

$T = (273+53)\text{K} = 326\text{K}$

**(1.) % utilisation of oxygen in regeneration at oxygen flow rate of 90 litres/minute (ORP from 560-570 mV)**

At ORP or  $E = 560 \text{ mV}$  or  $0.560 \text{ V}$

$$\log_{10} \frac{[a_{\text{ferric ion}}]}{[a_{\text{ferrous ion}}]} = 0.5256, \frac{[a_{\text{ferric ion}}]}{[a_{\text{ferrous ion}}]} = 3.35$$

Total number of moles of [Ferric ion] in the 450-litre Chemcut etching machine at an ORP of 560 mV

$$= \frac{1}{(1+3.35)} \times 450 \text{ litres} \times 3.37 \text{ moles/litre} = 348.6 \text{ moles}$$

At ORP or  $E = 570 \text{ mV}$  or  $0.570 \text{ V}$

$$\log_{10} \frac{[a_{\text{ferric ion}}]}{[a_{\text{ferrous ion}}]} = 0.6801, \frac{[a_{\text{ferric ion}}]}{[a_{\text{ferrous ion}}]} = 4.78$$

Total number of moles of [Ferric ion] in the 450-litre Chemcut etching machine at an ORP of 570 mV

$$= \frac{1}{(1+4.78)} \times 450 \text{ litres} \times 3.37 \text{ moles/litre} = 262.4 \text{ moles}$$

Total number of moles of [Ferric ion] regenerated

$$= (348.6 - 262.4) \text{ moles}$$

$$= 86.2 \text{ moles}$$

From the chemical reaction below,



One mole (or 24.055 litres) of oxygen gas is required to regenerate four moles of ferrous chloride solution for 100% efficiency, or 6.014 litres/moles of [Ferric ion].

As 5920 litres of oxygen gas was required to regenerate 86.2 moles of [Ferric ion], the % efficiency of regeneration =  $6.014/5940 \times 86.2 = 8.73\%$

**(2.) % utilisation of oxygen in regeneration at oxygen flow rate of 60 litres/minute (ORP from 570-575 mV)**

At ORP or E = 575 mV or 0.575 V

$$\log_{10} \frac{[\text{a}_{\text{ferric ion}}]}{[\text{a}_{\text{ferrous ion}}]} = 0.7574, \quad \frac{[\text{a}_{\text{ferric ion}}]}{[\text{a}_{\text{ferrous ion}}]} = 5.72$$

Total number of moles of [Ferric ion] in the 450-litre Chemcut etching machine at an ORP of 575 mV

$$= \frac{1}{(1+5.72)} \times 450 \text{ litres} \times 3.37 \text{ moles/litre} = 225.7 \text{ moles}$$

Total number of moles of [Ferric ion] regenerated

$$= (262.4 - 225.7) \text{ moles}$$

$$= 36.7 \text{ moles}$$

As 3600 litres of oxygen gas was required to regenerate 36.7 moles of [Ferric ion], the % efficiency of regeneration =  $6.014/3600 \times 36.7 = 6.13\%$

**(3.) % utilisation of oxygen in regeneration at oxygen flow rate of 90 litres/minute (ORP 577-581 mV)**

At ORP or E = 577 mV or 0.577 V

$$\log_{10} \frac{[a_{\text{ferric ion}}]}{[a_{\text{ferrous ion}}]} = 0.7883, \frac{[a_{\text{ferric ion}}]}{[a_{\text{ferrous ion}}]} = 6.14$$

Total number of moles of [Ferric ion] in the 450-litre Chemcut etching machine at an ORP of 577 mV

$$= \frac{1}{(1+6.14)} \times 450 \text{ litres} \times 3.37 \text{ moles/litre} = 212.4 \text{ moles}$$

At ORP or E = 581 mV or 0.581 V

$$\log_{10} \frac{[a_{\text{ferric ion}}]}{[a_{\text{ferrous ion}}]} = 0.8502, \frac{[a_{\text{ferric ion}}]}{[a_{\text{ferrous ion}}]} = 7.08$$

Total number of moles of [Ferric ion] in the 450-litre Chemcut etching machine at an ORP of 581 mV

$$= \frac{1}{(1+7.08)} \times 450 \text{ litres} \times 3.37 \text{ moles/litre}$$

$$= 187.7 \text{ moles}$$

Total number of moles of [Ferric ion] regenerated  
 = (212.4 – 187.7) moles  
 = 24.7 moles

As 5400 litres (90 litre/minute x 60 minutes) of oxygen gas was required to regenerate 24.7 moles of [Ferric ion], the % efficiency of regeneration =  
 $6.014/5400 \times 24.7 = 2.75\%$

**(4.) % utilisation of oxygen in regeneration at oxygen flow rate of 120 litres/minute (ORP 577-581 mV)**

At ORP or E = 577 mV or 0.577 V

$$\log_{10} \frac{[a_{\text{ferric ion}}]}{[a_{\text{ferrous ion}}]} = 0.7883, \frac{[a_{\text{ferric ion}}]}{[a_{\text{ferrous ion}}]} = 6.14$$

Total number of moles of [Ferric ion] in the 450-litre Chemcut etching machine at an ORP of 577 mV

$$= \frac{1}{(1+6.14)} \times 450 \text{ litres} \times 3.37 \text{ moles/litre} = 212.4 \text{ moles}$$

At ORP or E = 581 mV or 0.581 V

$$\log_{10} \frac{[a_{\text{ferric ion}}]}{[a_{\text{ferrous ion}}]} = 0.8502, \frac{[a_{\text{ferric ion}}]}{[a_{\text{ferrous ion}}]} = 7.08$$

Total number of moles of [Ferric ion] in the 450-litre Chemcut etching machine at an ORP of 581 mV

$$= \frac{1}{(1+7.08)} \times 450 \text{ litres} \times 3.37 \text{ moles/litre} = 187.7 \text{ moles}$$

Total number of moles of [Ferric ion] regenerated  
 = (212.4 – 187.7) moles  
 = 24.7 moles

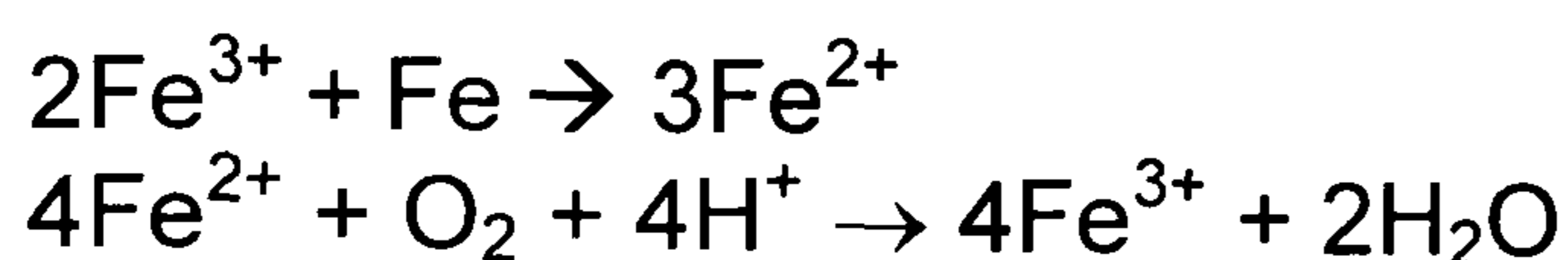
As 6240 litres (120 litre/minute x 52 minutes) of oxygen gas was required to regenerate 24.7 moles of [Ferric ion], the % efficiency of regeneration =  
 $6.014/6240 \times 24.7 = 2.38\%$

## **Appendix P**

### **Cost of chemicals and electricity in regenerating one kg of iron**

#### **P1 Cost of oxygen**

The volume of oxygen required in regeneration can be calculated from the following chemical reactions:



Two moles of ferric chloride are required to etch one moles of ferrous metal and one mole of oxygen is required to regenerate four moles of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ .

Total number of moles of Fe in 1,000g =  $1,000/55.85 = 17.91$  moles

Total number of moles of  $\text{Fe}^{2+}$  produced =  $3 \times 17.91$  moles = 53.73 moles

Total number of moles of oxygen required for 100% efficiency of regeneration =  $(53.73/4)$  moles = 13.43 moles.

As one mole of oxygen occupies a volume of 24.055 litres at standard temperature and pressure (STP), the volume of oxygen required for 100% efficiency

=  $13.43$  moles  $\times$  24.055 litres/mole

= 323.06 litres.

At 6.0% efficiency, the amount of oxygen required in regenerating one kg of iron

=  $323.06 \text{ litres}/0.06$

= 5,384 litres or  $5.384 \text{ m}^3$

One 'L' size oxygen cylinder that has a volume of  $10.05 \text{ m}^3$  cost £13.82.

Therefore, the cost of oxygen in regenerating one kg of iron is

=  $\text{£}13.82 \times 5.384/10.05$

= **£7.40**

## P2 Cost of hydrochloric acid

From *Table 10.1* in Chapter 10, (7,120g – 5000g) or 2,120g of AISI 304 stainless steel materials dissolved in the ferric chloride etchant that resulted in 11 mV reduction of ORP.

Total iron in 2,120g of stainless steel =  $2,120 \times 0.72 = 1,526\text{g}$  iron.

ORP reduction/weight of iron dissolved =  $11\text{ mV}/1,526\text{g}$  iron dissolved  
=  $7.21\text{ mV/kg}$  iron dissolved.

Volume of HCl required for satisfactory regeneration and etching  
=  $500\text{ ml/mV}$

Therefore, total volume of HCl required in regenerating one kg of iron  
=  $500\text{ ml/mV} \times 7.21\text{ mV/kg}$  of iron dissolved.  
=  $3.60\text{ litres/kg}$  of iron dissolved

Total cost of HCl in regenerating one kg of iron  
=  $3.60\text{ litres} \times \text{£}0.218/\text{litre}$   
= **£0.79**

## P3 Cost of electricity

It takes approximately one hour to regenerate one kg of iron etched.  
Therefore, the total electricity consumed  
=  $2 \times$  power of water pump  $\times$  one hour  
=  $2 \times 2$  horsepower  $\times$  one hour  
=  $2 \times 2 \times 745.5 \times$  one hour  
=  $2.982\text{ KWh}$

Cost of electricity in regenerating one kg of iron  
=  $2.982 \times 7\text{p/KWh}$   
= **£0.21**