AN ASSESSMENT OF THE POTENTIAL FOR WASTE MINIMISATION IN SMALL AND MEDIUM SIZE ENTERPRISES IN SOUTH AFRICA

by

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PREFACE

Against a background of a chemical engineering degree and a few years of industrial experience, I undertook this M.Sc. degree with the conviction that chemical engineering skills have a unique role to play in addressing environmental problems of pollution generated by industrial activity. Moreover, given that, of industrial activity, it is chemical processing industries (CPI) and mining industries which are the major contributors to generation of waste, hazardous waste in particular, it is appropriate that the chemical engineering profession, which populates such industry activities, should assume such responsibility.

In response to increasingly vociferous demands for more stringent environmental control over industrial activity, and regulatory compliance with stricter constraints on emissions of pollutants, there is a tendency to rely on readily available end-of-pipe solutions to resolve environmental management problems. This strategy is embodied in current practices in South Africa at effluent treatment- and landfill disposal facilities. Yet this is a costly solution in the long term, with implications for increasing operating costs, investment costs for development of new facilities, as well as closure and potential liability costs for old facilities. Furthermore this strategy fails to address problems of resource depletion and the potential for resource recovery from materials considered to be "waste". Waste minimisation offers an alternative waste management strategy which seeks to reduce the generation of waste before end-of-pipe management is required, and to recover resources for reuse, thereby reducing resource consumption.

The Department of Environment Affairs in the South African government has recommended that there should be research in the application of waste minimisation. While clearly there is a need for fundamental research into particular technological problems (such research is being undertaken at some institutions), the approach I adopted was to investigate potential for effecting meaningful waste minimisation solutions using procedures and techniques which constitute popular waste minimisation assessment methodologies. I focused specifically on small and medium scale industry operators which traditionally do not employ chemical engineering skills and which need a practical tool to improve in-house environmental management capability.

This investigation has not been confined to technological considerations. Out of interest and necessity socio-economic issues, both international and in South Africa, have been addressed, albeit briefly. This has provided a perspective for a waste minimisation strategy in South Africa. It has also been an important part of my own learning experience.

The work described in this dissertation was undertaken in the Department of Chemical Engineering at the University of Cape Town and at the sites of case study industry members who participated in this investigation. I thank Dr. Jim Petrie for his supervision of my work. I greatly appreciate his philosophy on life, breadth of comprehension and sustained constructive criticism.

I would also like to thank staff and fellow students in the Department of Chemical Engineering for their friendly support and assistance in day-to-day activities, as well as the invaluable assistance of librarians in the science and engineering library.

This study would not have been possible without the co-operation of the Cape Town City Council, who provided funding, Waste-Tech and participating case study industry members. Thanks are due for this financial support and to the various individuals who have provided information on request.

The work reported in chapters 5 and 6 of this dissertation is the direct result of the waste minimisation case studies. Some of the work contained in these chapters and content of chapters 2, 3 and 4 was used by the author in compiling a report on clean technology options for selected industrial sectors as part of a separate collaborative project between UCT Chemical Engineering Department and the Environmental Monitoring Group (EMG) Western Cape[1]. Thanks go to the EMG for their kind permission to include the author's original work as part of this dissertation. This dissertation has not been submitted at any other university .

Finally, for his support and common convictions, I thank my husband Neill .

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[1] *Clean Production: A preliminary assessment of the need and potential for the introduction of clean technology in some industrial sectors in South Africa.* Ed. Environmental Monitoring Group (EMG) Western Cape. November 1993.

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GLOSSARY OF ACRONYMS

AESF	American Electroplaters and Surface Finishers
BATNEEC	Best Available Technology Not Entailing Excessive Cost
BPEO	Best Practicable Environmental Option
CEST	Centre for Exploitation of Science and Technology
CHIEF	Chemical Industries Environmental Forum
CIA	Chemical Industries Association
CMA	Chemical Manufacturers Association
CPI	Chemical Processing Industries
EPA	Environmental Protection Agency
GDP	Gross Domestic Product
HMIP	Her Majestys Inspectorate of Pollution
HSWA	Hazardous and Solid Waste Amendment
ICPIC	International Cleaner Production Information Clearinghouse
IEF	Industry Environmental Forum
IWM	Institute of Waste Management
IPC	Integrated Pollution Control
ISP	Industry Strategy Project
LCA	Life Cycle Analysis
NATSURV	National Industrial Water and Waste-Water Survey
NGO	non-governmental organisation
NIC	newly industrialised country
NPC	National Productivity Council (India)
OECD	Organisation for Economic Co-operation and Development
OTA	Office of Technology Assessment
SANF	South African Nature Foundation
SME	small and medium size enterprises
TRI	Toxic Release Inventory
WCED	World Commission on Environment and Development
WRC	Water Research Commission

CHAPTER 1
INTRODUCTION

1.1 BACKGROUND

Johannson (1992) reports that industrialisation is deemed to have "...created benefits for (only) one fifth of the earth's population..". These benefits include greater personal wealth, higher standards of living and improved quality of life. However poor environmental management of industrial activities has had global consequences in terms of depletion of natural resources and wide spread pollution. Well documented effects include global warming, destruction of the ozone layer, acid rain and contamination of water and land by hazardous wastes.

In *Our Common Future*, the World Commission on Environment and Development (WCED, 1987)) reviews failures of "development" and management of the human environment. In brief, most industrial activity has taken place in developed economies (First World), but with large scale consumption of resources from the less developed and poorer countries. This has resulted in many places in impoverishment of the local resource base, including degradation of soils, water, atmosphere and forests, and loss of an agriculturally based economy. Migration of masses of people from the country side to towns has increased pressures on urban areas and demands for further industrial development to create employment opportunities and economic growth to alleviate socio-economic deprivation. Yet this growth is limited by the loss of resources and the need for costly remediation of polluted environments which threaten human health and safety.

In recognition of these problems there have been a number of studies in recent years which have sought to formulate strategies for more "sustainable development". This is defined broadly as development which "..meets the needs of the present without compromising the ability of future generations to meet their own needs.." (WCED, 1987) i.e. development should provide opportunities for economic growth without destroying the resources necessary to sustain this growth. Waste minimisation favours resource conservation and resource recovery activities which reduce consumption of resources, including raw materials, water, energy and the natural environment, which is used as a repository for waste products. Pearce, Markandya and Barbier (1989) suggest that it is this loss of amenities which is of greatest immediate concern, and the interruption of this flow of wastes, by means of waste minimisation, is perhaps the major feature of sustainable development in economic progress. In the field of hazardous waste management in particular, there is an urgent need to minimise or prevent as much hazardous waste as possible to mitigate environmental impacts of these wastes.

In the interests of encouraging waste minimisation, a number of waste minimisation assessment procedures have been developed as generic methodologies for assessing waste minimisation opportunities. Jackson (1991) considers use of such procedures to be relatively easy and applicable to a range of industry activities. There have also been recent innovative developments in cleaner technologies, which are less waste producing. These are being marketed internationally.

Christiansen and Kryger (1989) warn, however, of the failure of inappropriate transfers of management systems and technology between different countries, particularly from the highly developed to the less developed countries with differences in industrial structure. Given that there is potential for significant industrial growth in South Africa in the near future, with considerable interest from foreign investors, simultaneously with demands for greater environmental responsibility by industry, it is an opportune time to consider the practicability of such information and technology transfer.

The premise for this dissertation has been that established waste minimisation assessment methodologies and waste minimisation measures should be assessed in the local context. Small and medium sized enterprises (SMEs) were selected for case study assessment as, in general, SMEs lack the in-house waste management resources of the larger industry members, many of whom already have internalised environmental management systems. Moreover SMEs experience greater difficulties in managing their wastes cost-effectively and therefore are most threatened by demands for greater environmental responsibility. There is a need to facilitate improved environmental capability in SMEs.

1.2 OBJECTIVES

This research has addressed broadly:-

- applicability of generic waste minimisation assessment methodologies in selected industry activities;
- ease of implementation of waste minimisation opportunities;
- cost-effectiveness of waste minimisation measures.

Specific objectives were identified thus:-

1. to assess the ease of application and relevance of an established methodology for identifying and evaluating opportunities for waste minimisation;
2. to formulate waste minimisation case studies, based on practical on-site assessments of industrial practice using real operating data;
3. in doing so, to identify particular environmental problems associated with activities of the case study industry members and current waste management practices; and
4. to identify potential waste minimisation measures and evaluate these on a technical, environmental and economic basis;
5. where possible, to extrapolate the findings of this investigation in a way that will provide some assistance in the formulation of an environmental policy in South Africa.

1.3 SCOPE OF RESEARCH

This research project has been based on an extensive literature review of waste minimisation practices and two practical case study assessments.

Before conducting the case study assessments international perspectives on waste minimisation were reviewed to identify lessons from the experiences of researchers, industry and government who have already investigated and/or implemented waste minimisation techniques, policies and strategies. In addition to technical literature, reference was made to policy documents which have been written for the governments of the United States, Britain and some European countries. These documents address strategies for environmental management in tandem with economic development in these countries. Cognisance must be taken, however, of the developing component of South Africa's socio-economic climate which would not be reflected in First World economic experiences. Initiatives of the National Productivity Council of India were reviewed as an indication of a developing country's response to waste minimisation.

Environmental performance and waste management practices in South Africa were reviewed to provide an understanding of current attitudes, priorities and potential constraints to implementation of waste minimisation. Reference was made to:-

- the recent Department of Environment Affairs (1992) report on hazardous waste in South Africa;
- local publications; and
- relevant government regulations

Given that the political dispensation in South Africa is moving towards strong regionalisation, with waste management to be vested in regional government, it was deemed appropriate that the case studies should address representative regionally-based industries. This provided an opportunity to identify common problems and potential common solutions with due regard to relevant local legislation, government and industry practices and other regional characteristics. The Western Cape region of South Africa was selected for the practical reason of access to site.

Collaboration of willing local industry members was sought through discussions with the local municipal council (responsible for water supply and effluent treatment plants) and private waste contractors (responsible for landfill disposal sites). Waste streams of principal interest were those containing hazardous chemicals in aqueous and sludge form, which are discharged to these off-site facilities. As these waste types impact on the operation of these facilities, there is an interface of responsibility shared by industrial waste generators and off-site waste managers.

The industrial activities selected for case study assessment were:

SCALE	INDUSTRY MEMBER	INDUSTRY SECTOR
small:	garment dye house	textiles
medium:	metal finishing	metal processing

The case studies were formulated to demonstrate key features of a waste minimisation assessment methodology. This was compiled from existing, popular methodologies and structured in such a way that different levels of assessment could be implemented in the two case studies. The purpose of this approach was to identify the ease of effecting meaningful waste minimisation or extent of useful information which can be ascertained from each level of assessment, with minimum allocation of resources of time and money.

The first case study was based on a preliminary assessment only, and included:-

- site visits to examine operating practices;

- reviews of existing records of water usage and effluent analyses;

- literature reviews of process chemistry and technology involved in processing operations used by the case study companies;

- identification and evaluation of potential waste minimisation measures based on existing records of information and case studies for similar activities reported in published references.

In addition to the above activities, more detailed site specific investigation was conducted for the second case study. This included:-

- monitoring programmes to review processing conditions and to characterise process and waste streams; and

- derivation of material balances.

The information which was obtained was used as a basis for conceptual flow sheet development for a material recycling process. The feasibility of this option was evaluated with respect to site-specific conditions.

1.4 CONSTRAINTS

Whilst co-operation of the local municipal council, waste contractors and case study industry members facilitated this research initiative, there was no participation by these parties in evaluating the practicability of the waste minimisation methodology nor potential waste minimisation measures. The principal constraint was the preoccupation of company management with production priorities and hence a low level of commitment to the assessment objectives.

Local commercial companies were also unwilling (or unable) to provide technical advice and costing information for design proposals. This may reflect disinterest in an academic exercise, coupled with disinterest in small scale industry activities which are perceived to offer limited commercial opportunities. There may also be a lack of experience locally in applications of established technology to alternative process applications.

These constraints have undermined the efficacy of this research initiative. Hence conclusions generated by this research investigation require further evaluation with greater support from industry, local government, waste managers and policy makers.

1.5 LAYOUT OF THESIS

Waste minimisation techniques and assessment methodologies are discussed in Chapter 2. This concludes with a description of the waste minimisation assessment methodology which was followed in the case study assessments.

Chapters 3 and 4 present general reviews of international experiences in waste minimisation and the current situation in relation to waste management in South Africa. These reviews provide a perspective for implementation of a waste minimisation strategy in South Africa.

The case studies themselves are presented in Chapters 5 and 6 respectively. Each chapter comprises literature reviews pertinent to each case study and results of each waste minimisation assessment. Detailed technical information on process chemistry and technology with technical glossaries; tabulated waste minimisation case studies; details of monitoring programmes; material balance calculations and economic evaluation are documented in appendices, but summarised in the main text.

Chapter 7 presents an overall discussion of conclusions, with respect to the objectives of this research initiative, drawn both from the practical experience of conducting the waste minimisation assessments and the literature review of international experiences. Some strategic considerations for regional waste management and national policy for addressing environmental and development concerns in South Africa have been identified.

CHAPTER 2
PRINCIPLES OF WASTE MINIMISATION

2.1 INTRODUCTION

The purpose of this chapter is to describe technical aspects of waste minimisation, i.e. the underlying theory, and methodologies for evaluating waste minimisation opportunities. There is a considerable volume of published literature which expounds the theories of waste minimisation, but with use of different terminology to which different interpretations may be attached. This makes evaluation difficult. The term "waste minimisation" is used consistently in this dissertation in accordance with the definition given in section 2.2 below.

Chapter 1 has indicated that the link between waste minimisation and sustainable development is dependant on the conservation of raw materials and environmental resources (see section 1.1). There are a number of other related concepts in environmental management which cannot be discussed in detail within the scope of this dissertation. However, given that they are increasingly common features of emerging environmental management strategies, they are briefly described in section 2.2.

Section 2.3 describes different waste minimisation techniques. Section 2.4 describes waste minimisation assessment methodologies, outlying typical procedures and considerations for economic evaluation. The structure and content of the waste minimisation assessment proposed for the case studies presented in chapters 5 and 6 is described in the concluding sections, 2.4.3. and 2.4.4.

2.2 WASTE MINIMISATION AND RELATED CONCEPTS

Drabkin (1989) gives the US EPA definition of waste minimisation, applied to hazardous waste, as:

> "The reduction, to the extent feasible, of hazardous waste that is generated or subsequently treated, stored or disposed of. It includes any source reduction or recycling activity undertaken by a generator that results in either:
>
> * the reduction of total volume or quantity of hazardous waste, or
>
> * the reduction of toxicity of hazardous waste, or both
>
> so long as the reduction is consistent with the goal of minimising the present and future threat to human health and the environment."

Source reduction and recycling techniques cannot eliminate waste generation completely. Given fundamental thermodynamic limits to the efficiency of all processes of conversion, production, consumption and recycling (Jackson, 1991), as well as possible technical or economic constraints, the attainment of zero emissions is usually impossible or impracticable. There will always be some residual waste for which appropriate end-of-pipe treatment processes and disposal practices need to be applied in such a way that environmental hazards are minimised. Figure 2.1 illustrates the preferred waste management hierarchy in which waste treatment for pollution control and waste disposal should be considered only after appropriate waste minimisation measures have been taken.

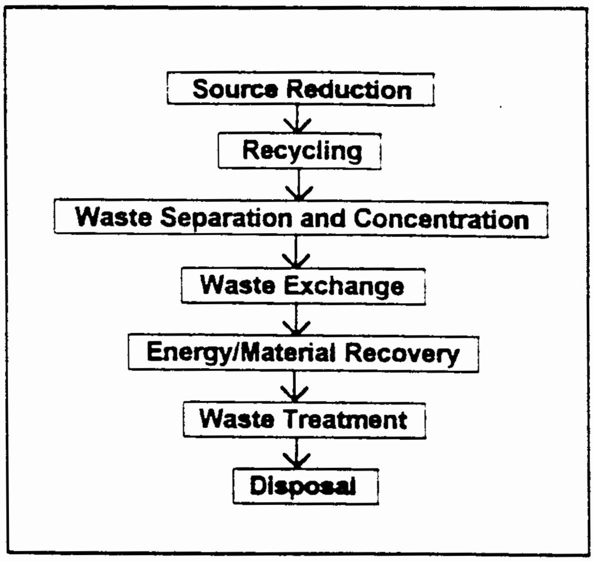


FIGURE 2.1: Waste Management Hierarchy

Clift (1992) describes *"cleaner technology"* as that which provides a service or a product in a way which reduces environmental damage or consumption of resources more efficiently than the use of end-of-pipe (EOP) technologies. In practice, the focus of cleaner technology is on technological and engineering improvements to specific production processes using waste minimisation techniques. *"Life Cycle Analyses"* (LCA) address a broader range of activities encompassing upstream and downstream phases in the life cycle of a product or process. This would include processing of the required raw materials, re-evaluation of product utilisation itself, and final disposal of the spent material, and is therefore known as the "cradle to grave" approach. By considering all associated impacts, LCA helps to ensure that real, rather than superficial, environmental improvements are identified in comparative assessments of alternative processes or products. Thus LCA should enable true cleaner technology, which does minimise environmental hazards, to be identified (Clift, 1992).

Hence successful implementation of true cleaner technology relies not only on developing new technologies and improving operating practices, but also on the willingness of society to accept changes in current consumption and production patterns (De Larderel, 1992). This is the ambit of *"cleaner production"* which, in addition to technological change, requires socio-economic changes e.g. in relation to business practices, use of more durable products and greater support for public transport systems.

2.3 WASTE MINIMISATION TECHNIQUES

Figure 2.2 illustrates the established waste minimisation techniques. The preferred hierarchy for implementation is source reduction before recycling, as this avoids problems of subsequently managing waste after its generation (Ghassemi, 1989). While source reduction is analogous to resource conservation, recycling implies resource recovery activities which themselves consume resources and generate wastes.

2.3.1 Source Reduction

This technique is based on fundamental improvements in thermodynamic efficiency of processes and substitution of problematic materials, processes and activities with alternatives which inherently are less waste producing or less harmful (Jackson, 1991). In the long term, such measures clearly will achieve waste minimisation most successfully. However they are also the most difficult to implement. Proven technology may not be available, or such technology, if it is available, may be deemed to be too expensive. Considerable research effort and expenditure may also be required to investigate and exploit opportunities of this nature.

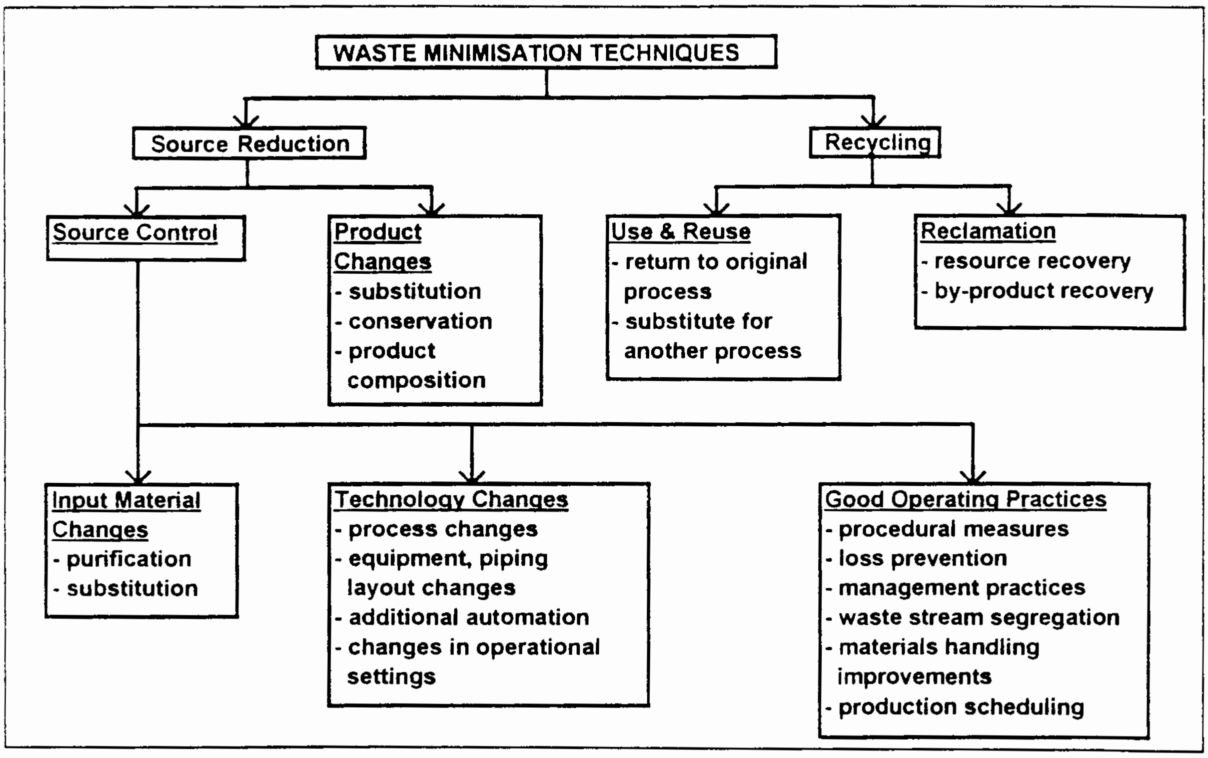


FIGURE 2.2 Waste Minimisation Techniques (Freeman, 1990)

Examples of source reduction measures are described as follows:

2.3.1.1 Input Material Changes

Material changes require use of alternative materials which may be less hazardous, of greater purity, and/or which facilitate easier separation, recycling or treatment of the waste stream (Ghassemi, 1989). Examples of this include replacement of solvent-based solutions (coatings and cleaners) with water-based chemicals, resulting in reduced volatile organic carbon (VOC) emissions and reduced toxicity of wastes generated, as well as safer working conditions. While substituted materials may be more expensive, higher purchase costs may be off-set by potential savings in waste treatment and disposal costs, for example by avoiding the need for air pollution control.

There are potential implications, however, for alternative materials to cause other pollution problems. For example the use of inorganic alkaline chemicals in cleaners will increase levels of dissolved salts in the waste water. These effluents may be less readily recyclable than solvents with current established technologies. Moreover equipment changes may be needed to enable use to be made of alternative materials, e.g. the need for corrosion resistant material with water based solutions.

2.3.1.2 Technology Changes

Technology changes include new process developments based on application of fundamental principles of process design, or may involve alterations to existing process design, including equipment, operating conditions and process control. Modifications should be made with the purpose of eliminating intrinsic wastes - those which are inherent in the fundamental process configuration (Berglund and Lawson, 1991). This may require significant changes involving research and capital expenditure, and normally would be considered only for new investments.

Often successful applications will be process and plant specific, and technology options may not be transferable directly to other operations. Moreover some industry activities may be more amenable to change than others. Berglund and Lawson (1991) identify two advantages of large scale complex facilities. Firstly the greater ease with which material flows from different processes can be integrated to minimise transportation of raw materials, by-products and wastes. Secondly the ability to co-ordinate maintenance activities or process changes in such a way that emissions can be transferred and contained in other process units. Small scale, single product operations lack this flexibility.

However there are some generic techniques which have been applied in numerous published case studies of successful waste minimisation. These include:-

- optimisation of process variables to maximise process performance efficiency;

- use of additional process automation to improve reliability of process control;
- improved equipment design to promote reaction kinetics e.g. improved mixing in a reactor;
- recovery of steam condensate to improve energy efficiency of steam generation.

These should find application in both continuous and batch type operations.

2.3.1.3 Improvements In Operating Practices

Good operating practices (GOP) are important to all types of operations. They have value in reducing extrinsic wastes caused by auxiliary aspects of the operation (Berglund and Lawson, 1991) and offer direct benefits in preventing unnecessary waste generation and reducing production costs, with low levels of expenditure. For example Freeman etal (1992) report that significant decreases in materials used and waste products can be effected by avoiding material redundancy through better inventory management. Other potential measures would include avoiding spillages, leaks and fugitive emissions by means of careful materials handling and scheduled maintenance; greater use of monitoring equipment to detect abnormal processing conditions which may result in unacceptable product quality or process failure; and waste segregation so that separate streams can be managed in the most effective way. Reducing waste generation in this way is usually catered for by in-house loss prevention and control activities and quality management systems. Hence implementation of GOP requires a refocus of management responsibility in addition to technological improvements.

However results of a survey of American companies by the Office of Technology Assessment (OTA, 1986) suggest that there is greater resistance to management improvements than technological change. Drabkin (1988) reports that GOP are often considered trivial - and critical assessments of management performance considered insulting - with limited appreciation of potential cost savings. Yet, to date most reported waste minimisation case studies implementing such GOP techniques have realised payback periods of just months.

Possibly the most difficult GOP to implement is waste stream segregation. Usually this will require some physical re-layout and/or repiping. However this would be a prerequisite for application of appropriate recycling processes to different waste streams (see below) e.g. segregation of scrap metal; recycling of dilute waste water and treatment of concentrated waste waters. For the latter examples, cost savings would be realised through reduced capital and operating costs for smaller waste water treatment plant i.e. with reduced hydraulic load. Moreover treatment processes are, in general, more efficient when used to treat concentrated- rather than dilute waste feed streams. Handling of residual wastes of consistent character is easier, and often safer, than is the case when wastes are mixed and potentially reactive.

2.3.1.4 Product Changes

Berglund and Lawson (1991) advocate that, in a long term waste minimisation programme, consideration should be given to the potential to effect product changes which reduce the environmental impacts of existing products. Freeman etal (1992) and Berglund and Lawson (1991) identify criteria for evaluation of the environmental performance of alternative materials, including:-

- reliability and durability;
- recyclability i.e. potential for material recovery;
- toxicity of waste residues;
- amenity of waste to treatment which reduces hazardous properties;
- stability of waste residues.

Ideally, these criteria should be considered at an early stage in the formulation of new products. It is more difficult to implement product changes for an established product range, particularly where changes in product specifications affect product quality or function. The success of such changes may depend more on marketing skills to overcome resistance to change than technological advances. Industry may also be resistant to change which results in the loss of a profitable product (Hirschhorn and Oldenburg, 1989).

If environmental life cycle impacts are to be minimised, consideration must be given to changes in composition, design, packaging and use patterns of the product (Ghassemi, 1989).

2.3.2 Recycling

Recycling is inherently less efficient than source reduction as it requires input of additional materials and energy to process the waste streams. These additional processing stages would include:-

- separation of wastes;
- conveyance or transport of waste to the processing plant;
- physical or chemical treatment.

Recycling activities may take place on-site, including in-plant recycling and reclamation, or at off-site recovery facilities. The latter option would incur the additional impacts associated with transportation, but such facilities may offer cost-effectiveness of greater economy of scale as well as greater process flexibility in an integrated waste processing facility. Moreover there are advantages in a focused presence of qualified and experienced technical and management staff and heightened responsibility for proper treatment and disposal of hazardous materials, such as waste acids and waste oils, which might otherwise be mishandled. Such facilities are reportedly well established in Western Europe, particularly in Denmark, Sweden, Netherlands, West Germany and France (Skinner, 1988). Combinations of incineration with energy recovery, e.g. for district heating, inorganic waste treatment, waste oil recovery and controlled landfill disposal would appear to be common. The provision of such facilities is usually a more attractive option for small scale industrial operators who may themselves lack appropriate operating skills and capital for on-site investment.

The viability of recycling for reclamation and reuse either on-site or at centralised facilities will depend on:-

- the technical feasibility of waste separation and recovery;
- economy of scale and operability of the waste processing technologies;
- production costs, including that for transportation to off-site destinations;
- quality of recycled material; and
- availability of markets for recycled products.

2.3.2.1 Use and Reuse

Additional utilisation of resources would be minimised by exploiting opportunities for reusing waste streams on-site without any specific treatment. For example dilutely contaminated waste water potentially could be reused in an application where contamination in the water has an insignificant effect. This principle is used in countercurrent rinse systems. As indicated in 2.3.1.3 the ability to exploit such opportunities requires that mixing of waste streams is avoided.

Some waste materials which may be byproducts of reactions, and therefore not recyclable within the process, could be used as feedstocks in other industrial processing operations or processed to recover constituents of value or other marketable products (Ghassemi, 1989). Trading of wastes between companies is facilitated by waste exchange systems which transfer either information concerning the availability or need for waste materials or the waste materials themselves.

2.3.2.2 Reclamation

Reclamation involves processing of waste to recover a valuable material or to make a waste material suitable for subsequent reuse. This may require sophisticated technology, for example processes employing solvent extraction, evaporation, ion exchange or membrane technology. In general, processing of waste materials for material or energy recovery can pose particularly difficult problems for materials handling because of possible reactive properties and cross contamination of different materials. Additional material and energy consumption is involved, and there will always be some waste residual.

Material recycling is usually considered more energy efficient than energy recovery through combustion, and it avoids environmental impacts associated with processing of raw materials (Mournigham, 1987). However recent analyses of the life cycles of different products have indicated that mitigation of total environmental impacts may favour material destruction with beneficial energy recovery, as opposed to additional resource consumption in material recycling processes. One such example is paper recycling. A study by Daae and Clift (1993) has shown that environmental impacts of paper are minimised when waste paper is used as waste derived fuel (WDF) in small-scale incinerators with energy recovery for domestic heating, and pulp resources are replenished from quick rotation crops. Clearly the unique circumstances of different products, processes and use patterns in different countries need to be accounted for in such studies.

Other wastes with a suitable calorific value, typically solvents, plastics or tyres, can also be used as fuel substitutes, such as are being used for firing cement kilns. This practice has been driven by a desire to reduce energy costs in cement production (Mournigham, 1987). In terms of waste minimisation, the benefits include energy recovery, conservation of fossil fuels such as coal and oil, reduction of waste volumes for management by other means, and potentially a reduction in toxicity by altering physical and chemical properties of materials which are emitted as atmospheric discharges, solid residues or effluent. Effective air pollution control and measures for safe disposal of combustion residues are required.

> Extraction and reuse of methane generated by anaerobic digestion in reactors or engineered landfill sites could also be considered an energy recovery process. Landfill gas has been exploited as a replacement fuel in kilns and boilers in the U.K. (Brown and Maunder, 1994). However to date, methane extraction has been practised principally as a safety measure. Apart from odour caused by gaseous emissions, methane also has explosive properties. Explosions at locations some distance from landfill sites have been caused following migration of landfill gas through ground fissures (Brown and Maunder, 1994).

The above examples demonstrate the need for an objective and comprehensive approach to evaluating potential waste minimisation opportunities, to identify those which optimally will reduce total environmental impacts. In order to apply this principle to processes, methodical assessment procedures have been formulated to ensure that alternative options are rigorously evaluated in terms of technical, environmental and economic acceptability. This approach is described in the following section.

2.4 WASTE MINIMISATION ASSESSMENT METHODOLOGY

2.4.1 A Management Tool

A waste minimisation assessment is analogous to an audit, and the words are used in the same sense by some authors, while others differentiate between the objectives of these as management procedures. Hadley (1991) considers auditing strictly as an activity of verification i.e. a comparison of outcomes against expectations The International Chamber of Commerce defines environmental auditing as:-

> " a management tool comprising a systematic, documented, periodic and objective evaluation of how well environmental organisation, management and equipment are performing with the aim of helping to safeguard the environment by:
>
> - facilitating management control of environmental practices;

> - assessing compliance with company policies which would include regulatory requirements.."

Thus auditing is an information and data gathering activity which results in identification of problem areas requiring investigation and/or recommendations for necessary action to correct potential problems, but excludes the actual measures and mechanisms by which these problems should be addressed.

In comparison, Drabkin (1989) describes a waste minimisation assessment as:-

> " ...a value management activity with a primary objective to reduce the quantity and/or toxicity of production wastes....", which

> "...does not seek to determine or improve the regulatory compliance status of a facility. Rather it is primarily oriented toward producing a set of effective measures to reduce waste generation."

So while auditing is an integral part of a waste minimisation assessment, such an assessment would include additionally the technical evaluation of proposed potential solutions to achieve specific objectives of cost-effectively reducing quantities of waste which are generated and require treatment and disposal. It is these activities which are defined by the methodology discussed below.

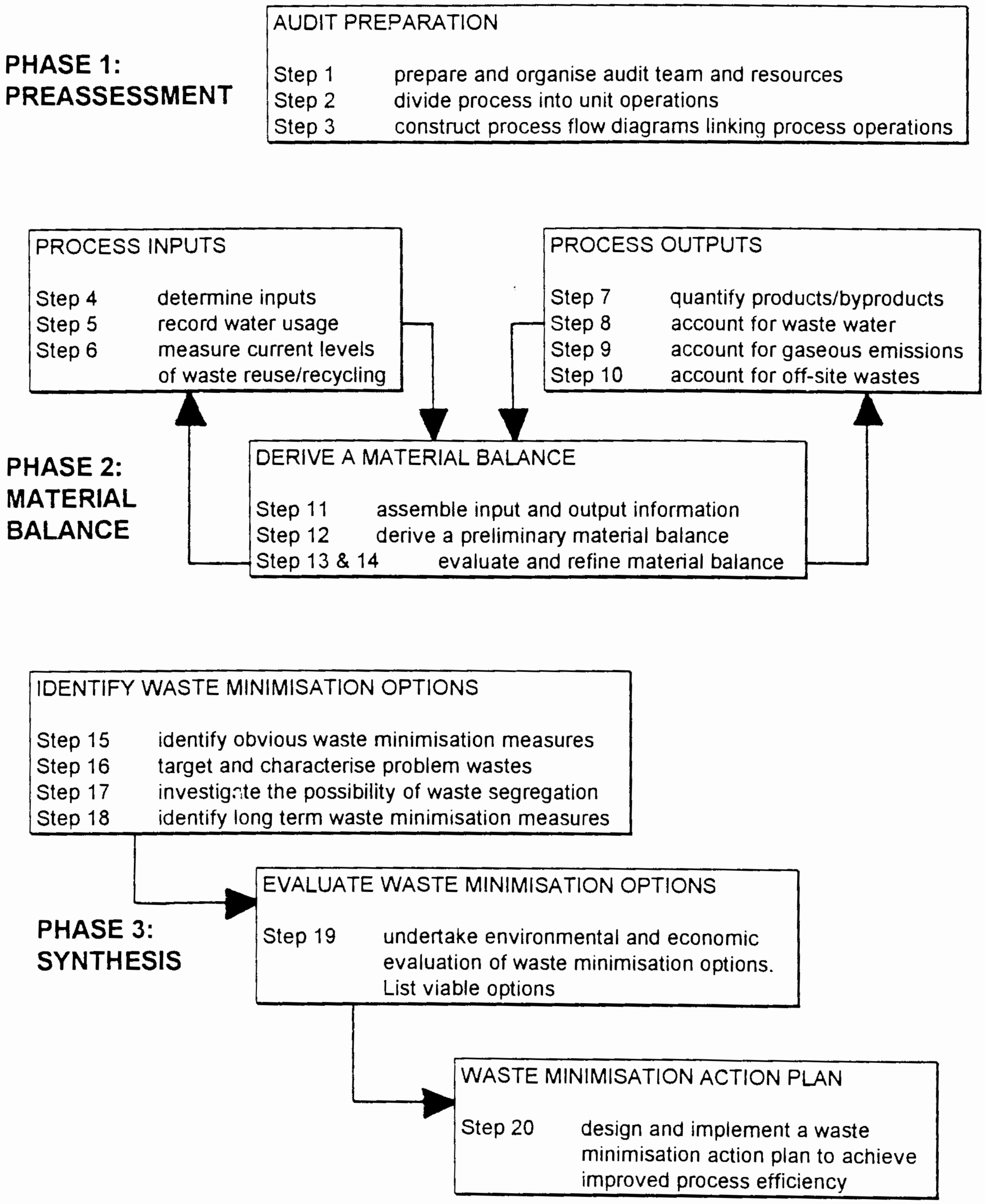
2.4.2 Review of Alternative Methodologies

The components of a waste minimisation assessment programme are described in various references in the form of generic methodologies designed to ensure a comprehensive, efficient and consistent review of all applicable process operations. Drabkin (1989) reviews "The EPA Manual for Waste Minimisation Opportunity Assessments" which prescribes a set of worksheets. These are formulated as a predefined set of data requirements e.g. as checklists of material types, consumption and production rates, unit costs, management practices and related details (see Appendix A). As such they provide a template for data and information input which would facilitate standardisation of information for compilation and reporting. The worksheets define a scope for waste minimisation assessment, but by themselves do not explain how to conduct an assessment. The original EPA manual was not reviewed, but it is assumed that these worksheets are supplemented by a more qualitative description of actual procedures. This methodology has been used in a series of publications by the US EPA entitled Guides To Pollution Prevention e.g. (EPA, 1992).. Each such publication addresses a particular industrial activity for which the worksheets have been customised to apply specifically to process operations characteristic of the selected industry activities. These guides are intended to assist companies in performing waste minimisation self-assessments. However their structure may be too inflexible to accommodate process and plant specific characteristics, and may inhibit identification of potential solutions which could be unique to site-specific processing conditions.

Freeman etal (1992) describe a less prescriptive procedure, referred to as a "descriptive" approach. This avoids standardised forms and encourages greater understanding of the source of wastes and the interrelationship between waste generating processes. In this way it is the process rather than the waste stream which is the focus of assessment. A similar approach is used in UNEP's "Audit and Reduction Manual for Industrial Emissions and Wastes" (UNEP, 1991) which gives a qualitative description of data and procedural requirements in a waste minimisation assessment (described as an "audit"). This provides a guide to a logical progression of activities, interpretation and presentation of relevant information. The summary guide is shown in Figure 2.3.

Missing from this guide procedure is a distinct initial 'planning and organisation' stage which Drabkin (1989) recommends for securing management commitment, setting goals and timescales and establishing an assessment team. Published case studies and other literature references stress that the effectiveness of any assessment procedure is reliant on sustained management commitment to ensure that appropriate resources are provided and reliable data can be accessed.

Involvement of production staff, who are most familiar with operations, in the assessment procedure would be important in reviewing existing operating conditions and operability of proposed waste minimisation measures. Over and above the co-operation of production staff an understanding of fundamental process chemistry and technology may be needed to identify factors that affect



PHASE 1: PREASSESSMENT

AUDIT PREPARATION

Step 1 prepare and organise audit team and resources
Step 2 divide process into unit operations
Step 3 construct process flow diagrams linking process operations

PHASE 2: MATERIAL BALANCE

PROCESS INPUTS

Step 4 determine inputs
Step 5 record water usage
Step 6 measure current levels of waste reuse/recycling

PROCESS OUTPUTS

Step 7 quantify products/byproducts
Step 8 account for waste water
Step 9 account for gaseous emissions
Step 10 account for off-site wastes

DERIVE A MATERIAL BALANCE

Step 11 assemble input and output information
Step 12 derive a preliminary material balance
Step 13 & 14 evaluate and refine material balance

PHASE 3: SYNTHESIS

IDENTIFY WASTE MINIMISATION OPTIONS

Step 15 identify obvious waste minimisation measures
Step 16 target and characterise problem wastes
Step 17 investigate the possibility of waste segregation
Step 18 identify long term waste minimisation measures

EVALUATE WASTE MINIMISATION OPTIONS

Step 19 undertake environmental and economic evaluation of waste minimisation options. List viable options

WASTE MINIMISATION ACTION PLAN

Step 20 design and implement a waste minimisation action plan to achieve improved process efficiency

FIGURE 2.3: Summary Audit Guide To Waste Minimisation Assessment Activities (reproduced from UNEP (1991))

volumes and composition of waste streams and so to clarify causes of waste (Van Berkel and Kortman, 1993). This knowledge may exceed the experience of production staff who may not be aware of alternatives. Obtaining such knowledge may require extensive information gathering and/or consultation with technology experts. Potential waste minimisation opportunities should be assessed against this background, together with an appreciation of site-specific conditions.

It is also not clear from the guide procedure that the assessment may be organised to focus on a selected process rather than an entire operating facility. Prioritisation of waste streams or production sources may be made on the basis of costs, environmental concerns, occupational health and safety, production constraints (Elliot, 1991) or the perceived potential for minimisation. Each such assessment would be an iteration in a repeated process, which eventually would investigate all operations in a facility wide waste minimisation programme. The difficulty in this approach is that potential opportunities to integrate flows from different process operations may not be identified at an early stage.

Conventional techniques for economic evaluation rely on the parameters of payback, net present value or internal rate of return to quantify the viability of investment needs. However these do not take account of other potential long term costs. These include the avoidance of potential regulatory costs and potential liability costs for site remediation, damage to property or natural resources or injury to people (Freeman etal, 1992). Other less tangible cost benefits may be improved worker morale, corporate image, community relations and product acceptance (Karam, St. Chin and Tilly, 1988). Both Freeman etal and Karam etal recommend an approach to economic evaluation which uses a hierarchy of analytical techniques comprising three stages:

Stage 1	evaluation of conventional costs which are based on certain, quantifiable cash flows;
Stage 2	probability analysis of potential regulatory and liability costs, based on compliance and permit requirements and penalties;
Stage 3	sensitivity analysis of the effects of non-quantifiable cashflows referred to above as the less tangible costs.

Each successive stage is only used if the results of the previous stage do not indicate feasibility. By addressing all stages it is reasoned that the true value of capital investment in waste minimisation will be fully accounted for. It is not clear to what extent these analytical tools have been used in practice, although they are available as both software systems and hard copy worksheet methodologies (Freeman etal, 1992)

2.4.3 Methodology Selected For Case Study Assessments

A hybrid methodology combining worksheets of the EPA methodology and the descriptive approach of the UNEP methodology was compiled for the case study assessments in this investigation. The intention was to assess both:-

- ease of collating information, particularly by company personnel themselves with minimum interface with external inspectors or auditors; and

- the logical problem-solving approach offered by the UNEP procedure.

Moreover, the methodology was structured in such a way that different levels of assessment could be implemented in each case study. The purpose of this distinction was to identify ease with which information can be developed into meaningful solutions without expending considerable effort and cost.

A summary version of procedures is shown in Figure 2.4. Appendix A presents a more detailed version. The assessment procedure itself is described in section 2.4.4.

2.4.4 The Assessment Procedure

The Phase 1/Preparation period of the UNEP methodology has been divided into two stages to distinguish between requirements for securing management commitment (stage 1), and a preliminary information gathering stage. This in turn identifies two stages of activities:-

ASSESSMENT METHODOLOGY
1. PREPARATION – to identify the needs and methodology for conducting the assessment
2. PROCESS OPERATION – to compile background information on process operations; waste types and sources; process technology; waste management practices; and environmental impacts – site survey and possible literature/technical reviews
3. TECHNICAL REVIEWS – to compile information on waste management alternatives and cleaner technologies – literature/technical reviews
4. MATERIAL & ENERGY BALANCES – to resolve material balances. – on-site monitoring
5. IDENTIFICATION OF OPTIONS – to identify & evaluate WM opportunities – to identify other waste management requirements
6. FEASIBILITY ASSESSMENT – more detailed evaluation of selected options

FIGURE 2.4: Summary Of Waste Minimisation Assessment Methodology

stage 2: compilation of information relating to the existing process operations, material and energy use, emissions and waste streams. Information may be obtained from one or more of stock inventories, process control records, waste manifests, permits and previous environmental audits and site observations. This is principally an auditing exercise for which the EPA worksheets should facilitate rigorous and consistent recording of process inputs and outputs.

stage 3: a broader technical review of the process technology and alternatives both for technical innovation and waste management techniques. This activity is intended to increase current awareness and knowledge of potential alternatives, on the basis of which the identification and evaluation stage should take place. It may also be necessary to investigate basic process chemistry and design principles to identify opportunities and/or process constraints which may not be obvious.

These stages provide a preliminary level of assessment. Information from this should at least enable simple, low cost waste minimisation measures to be identified. These could be implemented with limited formality. Other measures may be less obvious, less well established, require greater capital expenditure, or have possible implications for other processing operations. Depending on the potential extent of environmental and economic benefit which could be effected by these measures, a decision can be made whether to proceed with further assessment.

The material and energy balance stage (stage 4) is analogous to the Phase 2/Material Balance of the UNEP methodology. Again, the worksheets should be useful here. However while some information may be readily available, specific monitoring programmes may need to be undertaken to provide missing data or to improve the accuracy of estimated material and energy flows. Data is required for the resolution of material and energy balances, to assess all sources of wastes and emissions and to develop flowsheets which can be used to investigate the effect of waste minimisation options on material and energy flows. Costs associated with these flows need to be ascertained.

Evaluation in stages 5 and 6 would address typically (Drabkin, 1988):-

- waste minimisation effectiveness in terms of reduced waste quantities, hazard and management costs;

- extent of current use in the facility;

- industrial precedence;

- technical soundness;

- effect on product quality;

- effect on plant operations;

- implementation period;

- availability and requirement for other resources;

- capital and operating costs.

At the simplest level, economic evaluation will determine potential savings, required investment and operating costs associated with a waste minimisation option, using the conventional techniques referred to in section 2.4.2. As no published case studies on the use of the comprehensive analytical approach to feasibility assessment, advocated by Freeman etal (1992) and Karam etal (1988), have been reviewed, no attempt is made in this dissertation to utilise this approach.

Before describing the case study assessments, in which this methodology has been applied, international perspectives on waste minimisation are reviewed in chapter 3 to identify lessons from experiences elsewhere in the implementation of waste minimisation techniques, policies and strategies. Following this review, chapter 4 presents an overview of the current situation in industrial waste management in South Africa to provide a local perspective for the case study assessments.

CHAPTER 3
INTERNATIONAL WASTE MINIMISATION PRACTICES

3.1 INTRODUCTION

This chapter presents a review of trends in environmental management and waste minimisation practices in other countries so as to demonstrate the success or otherwise of particular waste minimisation techniques and strategies for implementation of waste minimisation by industry. The purpose of this is to provide perspective for a waste minimisation strategy applicable to South Africa.

Most relevant literature pertains to activity in developed countries, but the experiences of the National Productivity Council (NPC) of India have been reviewed as indicative of a developing country's response to industrial waste management concerns. This is important in formulating a strategy for South Africa in which conditions of both developed and developing status are represented. In reviewing industry experiences distinction has been made between that of large scale industry members and small and medium size enterprises (SMEs).

As chapter 2 has reviewed technical aspects of waste minimisation, economic and regulatory issues relating to waste minimisation are addressed in this chapter. These are reviewed briefly in section 3.2. Responses to these issues of developed and developing countries in formulating national policies, are discussed in section 3.3, while section 3.4 summarises constraints to implementation of waste minimisation. Section 3.5 describes international collaborative initiatives which seek to overcome these constraints. Chapter conclusions are given in section 3.6.

3.2 EXPERIENCES IN WASTE MINIMISATION

3.2.1 Corporate Economic Benefits

There are numerous literature references which describe the benefits of waste minimisation in mitigating costs of addressing pollution control by reducing waste emissions and hence costs for end-of-pipe treatment and disposal, and of potential pollution related liabilities. Moreover benefits are gained from reductions in raw material costs, elimination of inefficient practices, lower production costs and improved public image.

Companies, such as 3M (Minnesota Mining and Manufacturers), have realised these benefits as a consequence of a long standing established waste minimisation programme, "Pollution Prevention Pays (3P). This was initiated in 1975 (Patterson, 1989). Table 3.1 shows some reported waste reductions and cost-savings, but the information given excludes expenditure which was incurred and times for implementation. Clearly investment in equipment and new technology developments has been required for many of the waste minimisation projects.

TABLE 3.1: Reported Waste Minimisation Success Achieved By 3M (Hirschhorn, 1988)

Techniques	% use
housekeeping	10%
equipment & technology changes	31%
in-process recycling	35%
raw material changes	6%
product redesign	1%
Achievements	
savings (1975-1985)	$300 million
waste reduction	50%
reduction in air pollution:	110 000 tonnes
reduction in sludges/solid waste	290 000 tonnes
reduction in water-borne pollution	13 000 tonnes
reduction in waste-water	billion gallons
energy savings	equivalent to 250 000 barrels of oil p.a.

Thayer (1992) reports results of a study of source reduction activities by chemical industries in the U.S.. These activities are described as relatively minor alterations in processes, equipment changes or additions or operational changes. Reportedly most of these changes were implemented in periods of less than six months. However members of the chemical industry itself assert that there are limited opportunities for economically viable projects which can effect meaningful waste reduction, without continued dependence on recycling (Thayer, 1992). Increasingly costly investment is required with reduced savings - though this would depend on the value placed on the material itself and emission charges.

However not all waste minimisation options require costly capital investment. Many case studies report implementation of relatively simple, low cost measures with favourable returns on investment (ROI's). For example Hirschorn (1988) describes results of a US EPA study of U.S. firms which have implemented waste minimisation measures, showing that 54% of cases achieved ROI's in less than one year; 21% took one - two years; and only 7% took more than four years. A survey by the Office of Technology Assessment (OTA, 1986) of broader industrial activity in the U.S. revealed a slightly different picture, showing that the most frequently used technique for waste management was in-process recycling, followed by equipment and technology changes, and only then improvements in house keeping. Experience in Europe indicates that presently most improvements in waste minimisation are based on cost-effective measures which are easiest to implement, i.e. improved operating practices and simple process changes (Huisingh, 1992).

3.2.2 National Economies

An international study by the Organisation for Economic Co-operation and Development (OECD) is reported to have estimated that OECD nations spend about 1 - 1.5% of GDP on environmental protection. This investment has been measured as having only a small effect on GDP, based on conventional economics (Pearce, Markandya & Barbier. 1989). Furthermore this figure excludes environmental benefits associated with mitigation of future environmental costs which would be incurred if no action is taken to improve environmental performance of industry activities. These future costs would arise from more costly end-of-pipe treatment requirements, increasing raw material costs, pollution related liabilities and loss of competitiveness with businesses which are able to operate more efficiently with lower production costs.

The OECD survey also indicated that, in general, investment in environmental programmes such as waste minimisation has stimulated growth and created employment by increasing output of economies operating at less than full capacity, with benefits exceeding the investment costs (WCED, 1987). OTA (1986) reported that American companies did not expect requirements for waste minimisation to reduce employment needs, but to increase opportunities for skills training in waste management. The economic growth in the pollution control industry demonstrates this, with opportunities for investment, sale and exports in a growing market for pollution control systems, equipment and services. Australia, for example, reportedly is realising the advantages of a committed research programme in minerals processing which has included developments in environmental control (Petrie, 1993). Technologies and expertise which have been developed are now being used world wide. Similar services are expected to be required in practically all industrialised countries, including newly industrialised countries (NIC) (WCED, 1987).

More recently, expenditure on environmental protection by companies world wide is reported to be increasing as an urgent necessity, resulting in increased production costs (ACOST, 1992). U.S. costs for environmental protection are expected to rise to over 3% of GNP by the year 2000, while similar estimates in the Netherlands are given as 3-4% of GNP. In order to protect companies commercial advantage, there is a trend towards harmonisation of environmental standards internationally. Compliance with these standards is motivated by potential trade restrictions against companies or countries which do not conform.

3.2.3 Effect of Legislation

The OTA (1986) survey indicated that regulatory compliance has been an important factor in driving implementation of greater pollution control measures. However rapid imposition of constraints may force companies to rely on end-of-pipe treatment technologies (ACOST, 1992), which, ultimately, are more expensive. Such a response is perceived to have retarded economic growth in the U.S. as a result of environmental regulations introduced in the 1970s (Barbera and McConnell, 1990), with reduced investment for growth and reduced competitiveness of U.S. firms in the international market (OTA, 1986). Hirschhorn (1988) reports that U.S. expenditure of GDP for environmental protection in 1980 was four times greater than in Japan and France, and three times greater than in

West Germany. OTA (1986) acknowledges that most European governments devoted more money to waste minimisation that the U.S., without as extensive environmental regulatory control as in the U.S.. It is suggested that the absence of a pollution control culture may have helped to facilitate interest and investment by Europeans in waste minimisation. It is also possible that the time lag between the introduction of legislation in the U.S. and similar legislation in Europe may have resulted in improved ability in Europe to view the process as a whole and to develop an alternative, more cost-effective response.

3.3 NATIONAL POLICIES

3.3.1 Developed Countries

Developed economies, represented by countries such as the USA and most of Western Europe, may be described as possessing a relatively uniform industry base with sophisticated technology and established trading links. Policy mechanisms which have been proposed to encourage waste minimisation in these countries include the following:-

- national waste management strategies which prioritise waste minimisation

- more rigorous and comprehensive legislation

- technical information and assistance programmes

- voluntary industry initiatives

- education and training

- economic incentives

- long term national development strategies

Following are examples of these policy mechanisms.

(i) waste management strategies

The Commission of the European Communities has formulated a waste management strategy for the European Community which promotes waste minimisation (Commission of the European Communities, 1989). Features of this strategy include provision by national governments of appropriate legislative or financial measures as mechanisms to encourage industry responsibility for source reduction of their manufacturing wastes.

Public education programmes and ecologically-based constraints on product specifications are to be used to achieve changes in products and consumer behaviour so as to reduce consumer waste.

Opportunities for recycling are to be encouraged by:-

- optimising collection and transport systems;

- promoting research and development in recycling technologies and applications;

- reducing external costs; and

- creating markets for recycled products.

Disposal practices and landfill site management are to be improved by promoting alternative treatment technologies which reduce the volume and/or hazardous nature of these wastes. The problem of existing pollution and contamination is to be addressed by remediation of polluted areas and research and development of clean-up techniques.

The U.S. has also prioritised waste minimisation as a national policy in the U.S. Hazardous and Solid Waste Amendment Act (HSWA) of 1984 (Stephan & Atcheson, 1989). This Act requires all generators of hazardous waste to certify on waste manifests that a waste minimisation programme is in place as far as is economically practicable. Similar certification is required for any permit issued for the treatment and disposal of hazardous waste. The implementation of these provisions is policed by the U.S. Environmental Protection Agency (US EPA).

(ii) regulatory control

In many countries the severity of environmental degradation caused by industrial activity has driven rapid introduction of increasingly stringent constraints on industry emissions. Environmentally related legislation reported in literature may be summarised as follows:

- imposition of more stringent discharge constraints for specific dangerous substances in waste water, for example the UK Red List substances and monitoring and control standards specified by the UK Water Act 1989 (Butwell, 1990);

- a move towards environmental quality objectives (EQO) and standards (EQS) rather than uniform effluent standards (Butwell, 1990). The EQO is defined as the use identified for a body of water, while an equivalent EQS defines the minimum quality allowable for the water to retain its intended purpose;

- more stringent control standards for the emission of volatile organic carbons (VOCs), for example as regulated by the U.S. Clean Air Act (Lipton, 1992);

- occupational health legislation such as Control of Substances Hazardous to Health (COSHH), enacted in the UK and the Occupational Safety and Health Act (OSHA) in the U.S.;

- more rigorous leachate tests which are designed to assess the leachability of metal-containing sludges under aggressive site soil conditions (Isham, 1988a);

- the imposition of a regulatory demand for regular waste minimisation assessments with annual reporting on waste generation and waste reduction (Jackson, 1991; Stephan & Atcheson, 1989);

- requirement for Integrated Pollution Control (IPC) and Best Practicable Environmental Option (BPEO) (HMSO, 1988).

Jackson (1991) also recommends certification of new facilities to verify that the lowest waste-generating process is being used and that clean technology options have been evaluated

In Germany, in particular, comprehensive legislation targets specific materials, industrial processes and waste management activities. There is legislation governing more stringent discharge constraints and compulsory substitution of listed toxic chemicals; the banning of certain processing technologies; prescribing waste treatment technologies; and mandating recycling levels for priority wastes such as packaging. For example, the 1986 Waste Avoidance , Recycling and Disposal Act seeks to enforce use of low-waste technologies and recycling in preference to customary waste disposal, unless this is economically unreasonable (Sutter, 1989a). There is considerable resistance to the increased costs of environmental protection, which are deemed to threaten the international competitiveness of German industry (Ondrey, 1992). Laser (1992) reports that the government is aware of these difficulties, but the strategy of strong regulations is intended to encourage development of new processes and to change the behaviour of people. Larger companies, principally the CPI and power industry, which have the financial and skills resources to apply to research and development are doing so, developing material substitutes, recycling technologies and more energy efficient processes (Ondrey, 1992). Reported benefits include the realisation of significant reductions in energy costs and increased export of new cleaner technologies.

The U.S. government too, in the interests of pollution control, rapidly introduced legislation with pre-determined time scales for compliance. This includes a "land ban" programme which restricts the land disposal of several hundred materials which must be treated to strict standards prior to disposal (Parkinson, 1990). Restricted wastes include those with metal, cyanide and solvent contamination e.g. waste-water, catalysts, solution and sludges from chemical, petroleum and metallurgical industries (Skinner, 1990). In addition, the Pollution Prevention Act of 1990 mandates compulsory reporting of toxic chemical emissions to the US EPA. U.S. companies are required to report annually quantities of toxic waste which are generated, methods which are used for treatment and disposal, and company efforts in waste minimisation. This information is compiled in a national database, known as the Toxic Release Inventory (TRI), to which there is public access (Rittmeyer, 1991). Companies have objected to this reporting of information on the grounds of commercial interest and concern that government regulators or public pressure groups may use the information against them (Hirschhorn, 1988). Freeman etal (1992) acknowledge that there have been difficulties with a lack of uniformity in methods for reporting data, making assessment of annual results difficult. Nevertheless, reportedly there has been an overall downward trend in reported waste emissions even while production has increased (anon, 1991).

Isham (1988b) reports that industry deems such a regulatory system to be costly and ineffective. Restrictive legislation is considered to have been a disincentive to recycling, reclamation and material reuse activities. For example waste types designated as hazardous under the 1976 Resource Conservation and Recovery Act (RCRA) are subject to such stringent permitting requirements for processing that some companies prefer to use accepted end-of-pipe treatment processes and disposal options rather than seek alternative recycling options (Thayer, 1992). As in Germany, costs incurred in complying with ever increasing regulations are blamed for competitive disadvantages for U.S. firms (Isham, 1988b).

More recently there has been greater interest in a less regulated approach based on incentives including assistance programmes and economic mechanisms. These are discussed below.

In the U.K. a system of Integrated Pollution Control (IPC) is being introduced as part of the government's Environmental Protection Act 1990, administered by Her Majesty's Inspectorate of Pollution (HMIP). Companies are obligated to apply to HMIP for authorisation to operate, to comply with prescribed conditions about operating conditions and monitoring conditions and to use Best Practicable Environmental Option (BPEO) (HMSO, 1988). The principle of this is that all the different forms of environmental pollution from a process as well as all reasonable technical possibilities for dealing with total pollution effects should be considered in developing a pollution control strategy (HMSO, 1988). The selected BPEO must be justified on the basis of an evaluation of available alternative options, with reasons and value judgements clearly identified (HMSO, 1988). These requirements are being phased in over a period of about five years.

(iii) assistance programmes

The expense of developing and enforcing regulations in the U.S. as well as the inability of existing regulatory approaches to effectively address some of the diffuse and complex pollution problems, has motivated a shift away from a strong regulatory approach towards one based on assistance programmes which encourage voluntary action by industry. The OTA (1986) study investigated industrial efficiency in U.S. industry, and identified the need for programmes which offer technical support to help companies improve their ability to implement cost-effective and meaningful waste minimisation efforts. Direct financial assistance to individual companies for specific waste minimisation projects was not deemed appropriate or feasible, largely due to the difficulties in controlling expenditure. It was considered that the most cost-effective allocation of funds is that which increases knowledge, institutional support and technology transfer for as widespread benefit as possible. Accordingly the U.S. government has tended to favour on-site technical assistance programmes, many of which are co-ordinated by government departments and university based technology centres. Funding for such programmes is provided partly by pollution fees and emission taxes charged to industry generators (Freeman etal, 1992).

OTA (1986) reports that most governments in Western Europe initiated programmes to encourage waste minimisation and cleaner technology developments much earlier than the U.S., in the 1970s. The European strategy would appear to have favoured economic measures in the form of grants for research and development in technology and tax incentives and disincentives, with limited on-site assistance. These early initiatives are considered to have achieved improvements in industrial efficiency and economic growth as well as competitive gains in expertise, experience and technology development which can be marketed world wide (OTA, 1986).

Brief descriptions of specific assistance programmes in different countries are given in Appendix B, demonstrating the above differences in approach. Listed too are some U.K. initiatives which have been introduced only in recent years. In function these are akin to the approach of Western Europe and some programmes specifically target collaborative work between U.K. and European companies. Government funding may subsidise initiatives by industry, but companies are expected to conduct their efforts on a commercial basis as collaborative projects between suppliers and users.

(iv) voluntary industry initiatives

The Canadian chemical industry initiated a Responsible Care programme intended to demonstrate that the chemical industry is committed to responsibility towards community and occupational health and safety and to environmental protection (Hart, 1992). Similar programmes have been adopted by chemical industry associations in most developed countries as a corporate ethic. There are no prescribed objectives; these are defined as codes of practice by each national chemical industry association which has adopted Responsible Care (Hart, 1992). For example, the US CMA has adopted a specific Waste and Release Reduction and Management Code containing ten management practices for reducing waste generation and releases to the environment (Freeman etal, 1992), but this code may not be present in the formal codes of other national chemical associations or industry subscribers.

(v) education and training

It is generally acknowledged that a significant constraint to implementation of waste minimisation is lack of knowledge, information and experience. There are a number of private consultancies or trade associations which offer training programmes in environmental management issues e.g. Integrated Environmental Management. Generally these programmes target top management in existing positions of responsibility. Undergraduate and postgraduate education courses in cleaner production concepts have been introduced very recently at some universities (Jnl. Cleaner Production, 1993). Public education is facilitated by activities of non-governmental organisations (ngos) and local voluntary initiatives such as recycling groups.

(vi) economic incentives

The effectiveness of various economic mechanisms in waste management was assessed in a survey of U.S. business opinion (OTA, 1986). The survey results indicated that economic factors relating to production costs, productivity, product quality and liabilities were deemed by U.S. industry to rank with regulatory compliance as the most important factors affecting waste management. Economic constraints were rated the most significant barrier to implementation of waste minimisation.

Large scale industries rated tax credits for capital spending as the most effective economic incentive for implementation of waste minimisation programmes. This preference suggests a reliance on capital plant for achieving waste minimisation, probably using proven technology in recycling applications. Large scale industries would be more accustomed to large scale capital investment projects.

Smaller scale industry members who have lesser capital resources were shown to favour federal grants and direct in-house assistance, with a focus on lower cost, easily implementable waste minimisation measures.

(vii) development strategies

Both the U.S. government (EPA, 1991a) and the U.K. government (P.A.Consulting Group, 1991 and CEST, 1991) commissioned studies to review the environmental impacts of industrial activities and initiatives world wide in waste minimisation, particularly developments in cleaner technology. The purpose of these studies was to identify:-

- scale of environmental problems associated with different industry activities;

- status of work being undertaken by industry in cleaner technologies;

- potential for technological improvements to be realised in each sector;

- extent of benefit which can be derived; and

- economic importance of the sector to national economy.

This approach is intended to identify key technology opportunities and to prioritise research needs so that limited resources, i.e. expertise and finance, can be used in addressing those problems which have greatest potential for success and maximum environmental and economic benefit. These benefits include commercial opportunities in the international market for services in environmental protection i.e. export of technology and expertise. Currently these are areas in which Western European industry is considered to have the commercial advantage (OTA, 1986). The need to be competitive is a goal for economic development strategies.

3.3.2 Developing Countries

Developing countries such as India tend to have a more disparate industry base than developed countries, comprising numerous small scale enterprises. In India, for example, these are reported to make up 90% of total industry (NPC, 1991). These are characterised by :-

- minimum capital investment;

- use of inherently inefficient and wasteful technologies; and

- low level of technological skills and environmental awareness.

Moreover, an infrastructure for dissemination of information and technology transfer is often not available (NPC, 1991). Hence adoption of advanced pollution control systems usually would not be considered feasible or appropriate.

As part of their productivity initiative, the NPC have published case studies of waste minimisation efforts in a number of different industry sectors, including cement, pulp and paper and various food manufacturing units. Many of these studies report successful waste minimisation, of up to 50% in quantity, using simple and inexpensive measures to increase production efficiency, improve product quality and reduce raw material and energy consumption. Use of waste minimisation techniques is still very limited however (Selvam and Chandak, 1992). Reasons for this are discussed in section 3.4.2. To encourage waste minimisation, the NPC has recommended a national strategy based on:-

- phased implementation of successive reductions in emission levels of pollutants;

- technical assistance offered at affordable costs with the help of international organisations such as the United Nations or existing professional bodies in India;

- fiscal incentives;

- gradual up-take of cleaner technologies via investment in new processes.

3.4 CONSTRAINTS TO IMPLEMENTATION OF WASTE MINIMISATION

The fundamental constraint to waste minimisation probably is the fact that it is still a relatively unfamiliar form of waste management and there is inertia in responding to the need to change existing attitudes, administrative systems, accounting practices, regulations and environmental technologies and services. For example, Hirschhorn and Oldenburg (1989) cite reluctance of existing pollution control businesses to encourage waste minimisation in the face of perceived loss of commercial opportunities for established technology. Larger scale companies are expected to adopt new waste management practices more easily than SMEs who are often disadvantaged by reduced economy of scale, lesser in-house skills, experience and financial resources and lack of institutional support. Hence, while there are impediments to waste minimisation which are common to all scales of industry, there are certain constraints which are particular to large scale operations and SMEs. These are discussed below in sections 3.4.1 and 3.4.2.

The review of experiences in waste minimisation and of national policies has already identified certain constraints which may be summarised as:-

- resistance to change;

- inflexible regulatory control;

- competing production priorities;

- lack of awareness of true costs of waste management;

- incomplete data on sources and amounts of waste;

- unwillingness to share information.

Sections 3.2.3 and 3.3.1(ii) have indicated that, faced with more stringent restrictions on waste emissions, industry tends to favour the established waste treatment technologies which are designed to meet specific emission standards. Resources expended on complying with existing regulations detract from opportunities to explore waste minimisation alternatives. Furthermore existing regulations themselves are also considered to impede waste minimisation. For example the complex, costly and time consuming procedures involved in permit applications for handling hazardous materials in the U.S. is considered to discourage changes to existing approved processes (Ghassemi, 1989). This would also apply in the case of establishing new emission control standards.

The cost-effectiveness of waste minimisation alternatives is often not recognised as commonly used cost-benefit analyses seldom account for savings from future liability costs, improved efficiency and potential benefits from public approval for a product which has lesser environmental impacts. However changes in product specifications may not necessarily be accepted by the public (see section 2.3.1.4) and companies may be concerned about the loss of a profitable product range (Hirschhorn and Oldenburg, 1989).

In the absence of reliable information, it is also difficult to formulate appropriate strategies for effecting waste minimisation. Companies are unwilling to disclose waste related data for fear of attracting attention to their operations. Furthermore there is concern that mandatory waste reduction levels may be imposed which do not take account of the diverse nature of industrial processes (Ghassemi, 1989).

Given that waste minimisation is not yet widely implemented, there is a lack of useful data on its progress in pollution prevention and on clearly defined economic benefits. Although there are a variety of case studies reported in literature, the information given is often incomplete or vague. For commercial reasons, companies are reticent about revealing production details and transferring their knowledge and experience for competitive advantage to other companies. For these same reasons companies with successful waste minimisation programmes are unlikely to support a government programme that would assist other companies in reducing their waste generation (Hirschhorn and Oldenburg, 1989).

3.4.1 Large Scale Companies

The voluntary industry initiatives such as "Responsible Care", referred to in section 3.3.1(iv), are collaborative efforts by large scale industry to preempt imposition of government regulations and to promote the efficiency of self-regulation. In this way these companies form a defensive barrier behind which each company can implement, to the best of its ability, those measures which are considered appropriate and affordable. Conceivably this strategy does help to ensure a consistent standard in environmental management practices and ethics, but it may be that higher standards could be motivated by stricter regulations and greater economic incentives.

3.4.2 Small and Medium Size Enterprises

In general, SMEs lack the institutional support that exists between large scale companies, although they may be supported by trade associations and labour unions. These would not necessarily have a co-ordinated response to environmental issues. Selvam and Chandak (1992) suggest that the value placed on SMEs as employment generators, retards incentives to improve efficiency and productivity implicit in some waste minimisation practices, such as those described as Good Operating Practices (see section 2.3.1.3). Moreover where use is made of casual labour and wages are production related, there would be no vested worker interest in effecting waste minimisation through improved operating practices (Selvam and Chandak, 1992).

In developing countries where regulations are seldom strictly enforced the low costs of waste disposal discourage waste minimisation Even where there are regulatory demands and economic incentives for waste minimisation, SMEs may lack the in-house skills and infrastructure to identify and implement waste minimisation measures. The lesser financial resources of SMEs and smaller scales of operation do not attract the commercial interest of consultants and equipment suppliers or commercial research and development (Selvam and Chandak, 1992). Consequently access to appropriate technical information is difficult and environmental services and technology are often unaffordable.

While it should be possible for large scale companies to assist SMEs by providing technical assistance, such exchanges are limited by:-

- possible conflict of commercial interests;

- technology and management systems which may not be appropriate for SMEs;

- resistance to financial support over and above internal costs incurred for environmental management.

3.5 CO-OPERATIVE INTERNATIONAL INITIATIVES

The assistance programmes referred to in section 3.3.1(iii) generally are country specific. There is also a major international co-operative effort which has been launched by the United Nations' Industry And Environment Programme Activity Centre (UNEP IE/PAC) as The Cleaner Production Programme. This seeks to overcome constraints to waste minimisation. Initiatives include:-

- an international database, the International Cleaner Production Information Clearinghouse (ICPIC);

- specific industry working groups - currently for leather tanning, textiles, solvents, metal finishing, pulp and paper, petroleum and biotechnology;

- publications on cleaner technologies, products and development initiatives (this includes the UNEP audit manual described in section 2.3.2);

- training activities to help implement waste minimisation and cleaner production practices;

- technical assistance, particularly for developing countries.

Technical assistance is facilitated by the working groups who solicit expert membership, compile case studies for dissemination through ICPIC and organise workshops and conferences. There is also a "Working Group on Policies, Strategies and Instruments" to promote cleaner production. This was initiated in recognition that without appropriate market forces, companies cannot respond competitively or easily to changing environmental trends. Issues which are addressed include auditing, labelling, product acceptability, changes in taxation systems, the use of financial instruments and environmental risk assessment techniques (Cleaner Production, 1991).

3.6 CONCLUSIONS

The review of international trends has shown that:-

1. Waste minimisation is accepted generally as the most rational approach to managing industrial wastes safely and cost-effectively as well as conserving resources for sustainable development.

2. Developing countries such as India are actively encouraging pollution prevention in their numerous small scale industry units.

3. Waste minimisation is not expected to be a cause for unemployment, but is considered to offer opportunities to revitalise industry and encourage economic growth.

4. Yet waste minimisation is still not practised widely, particularly in SMEs which lack the skills, resources and infrastructure to identify and implement waste minimisation measures.

5. There is growing international co-operation in efforts to stimulate the uptake of waste minimisation opportunities in the drive for cleaner production and more sustainable development.

6. There are international market opportunities for skills and technology in the field of environmental protection - an economic growth area.

7. Attempts are being made to standardise environmental responsibility at an international level, in order to protect the commercial interests of companies and countries which incur higher costs for compliance with environmental control regulations.

CHAPTER 4
SOUTH AFRICAN INDUSTRY AND THE ENVIRONMENT

4.1 INTRODUCTION

Against the background provided by the review of international practices and experiences in waste minimisation, this chapter presents a brief review of the current situation in waste management in South Africa in order to gain an understanding of local attitudes, priorities, and potential constraints to implementation of waste minimisation.

Existing legislation was not included in this review. The issue of dispersed and sometimes conflicting regulatory control of pollution and conservation matters between different government departments is addressed in a number of publications (CSIR, 1991; PC, 1991; Department of Environment Affairs, 1992b). A detailed compilation of legislation relating to the environment has been published by the Department of Environment Affairs (1993).

Recent developments in environmental management, based largely on voluntary action, are identified in section 4.2. The greater part of this chapter presents a summary of current published data on industry waste quantities, given in section 4.3, as an example of South Africa's attempt at waste evaluation, and reported waste management policy and practices of industry and local government, given in sections 4.4. and 4.5. Section 4.6 presents brief conclusions.

4.2 BACKGROUND

In 1989 the Environment Conservation Act No. 73 was enacted to "provide for effective protection and controlled utilisation of the environment". In terms of this act, the Minister of environment affairs, in consultation with other affected government departments i.e. Finance and Economic Affairs and Technology, is empowered to make regulations concerning activities which have potentially detrimental environmental effects, including waste management. The minister may for example specify requirements for waste minimisation by source reduction measures or waste processing for recovery. No such regulations have yet been made.

More recent developments in environmental management in South Africa have addressed three broad areas:

1. Integrated Environmental Management (IEM) procedures for assessing environmental impacts of new development proposals (Department of Environment Affairs, 1992a);

2. framework for a National Environmental Management System based on recommendations given by the Presidents Council (PC, 1991) and addressed most recently in the government white paper;

3. investigations into the situation of waste management and pollution control in South Africa (CSIR, 1992) and the hazardous waste situation (Department of Environment Affairs, 1992b).

The IEM procedures are not designed to address existing situations associated with previously accepted impacts (Van Lingen, 1991). Many larger scale companies have however developed environmental management systems based on these procedures to formalise company specific environmental objectives.

The latter investigations have made recommendations for a national policy for waste minimisation, which require that the feasibility of waste minimisation should be further researched as a basis for formulation of appropriate action plans (PC, 1991). As yet there has been limited encouragement for waste minimisation. The Department of Environment Affairs (1992b) proposals for a hazardous waste management strategy for South Africa continue to emphasise use of end-of-pipe treatment technologies and disposal techniques. Estimates have been made of quantities of total- and hazardous waste generated by identified industry sectors in South Africa, and these estimates have been allocated to regional areas to indicate "scale of the market in each" to be served by "waste treatment and disposal facilities" (Department Environment Affairs, 1992b). This approach may be of commercial benefit to the environmental technology and consultancy field, but international experience has shown that, in the longer term, it is a costly one for industries whose production costs are increased by installation and operation of expensive waste treatment technologies and by higher disposal charges. In addition there are social opportunity costs associated with the failure to minimise waste generation at source, including, for example, the additional cost implications for existing municipal waste treatment facilities. Waste minimisation should be promoted before major commitments are made for treatment and disposal facilities.

The only known published study to date of the potential for waste minimisation in South Africa is that undertaken by the Environmental Monitoring Group (EMG, 1993a). The report is based on a preliminary assessment of clean technology opportunities reported in literature for a variety of industrial sector activities. Detailed assessments of selected industry activities are to commence in 1994 (EMG, 1993b).

4.3 INDUSTRIAL WASTE GENERATION

The South African government has attempted to evaluate the extent of waste generation by South African industry in order to facilitate development of a hazardous waste management strategy for South Africa (Department of Environment Affairs, 1992b). The scope of this study included estimation of quantities of total- and hazardous waste generated by identified industry sectors, formulation of an appropriate classification system to prioritise hazardous wastes which require treatment and recommendations for specific waste management options and legislative options.

Estimates made of total and hazardous waste quantities from different industrial sectors are summarised and discussed below, as national estimates and those allocated to the Western Cape region which is the location of the selected case study industry members.

4.3.1 National Estimates

Total estimated waste emissions are represented in Figure 4.1 to illustrate the estimated scale of reported waste discharges to each media. Clearly there will be cross media transfer of pollutants, which changes net pollution effects on different environmental media.

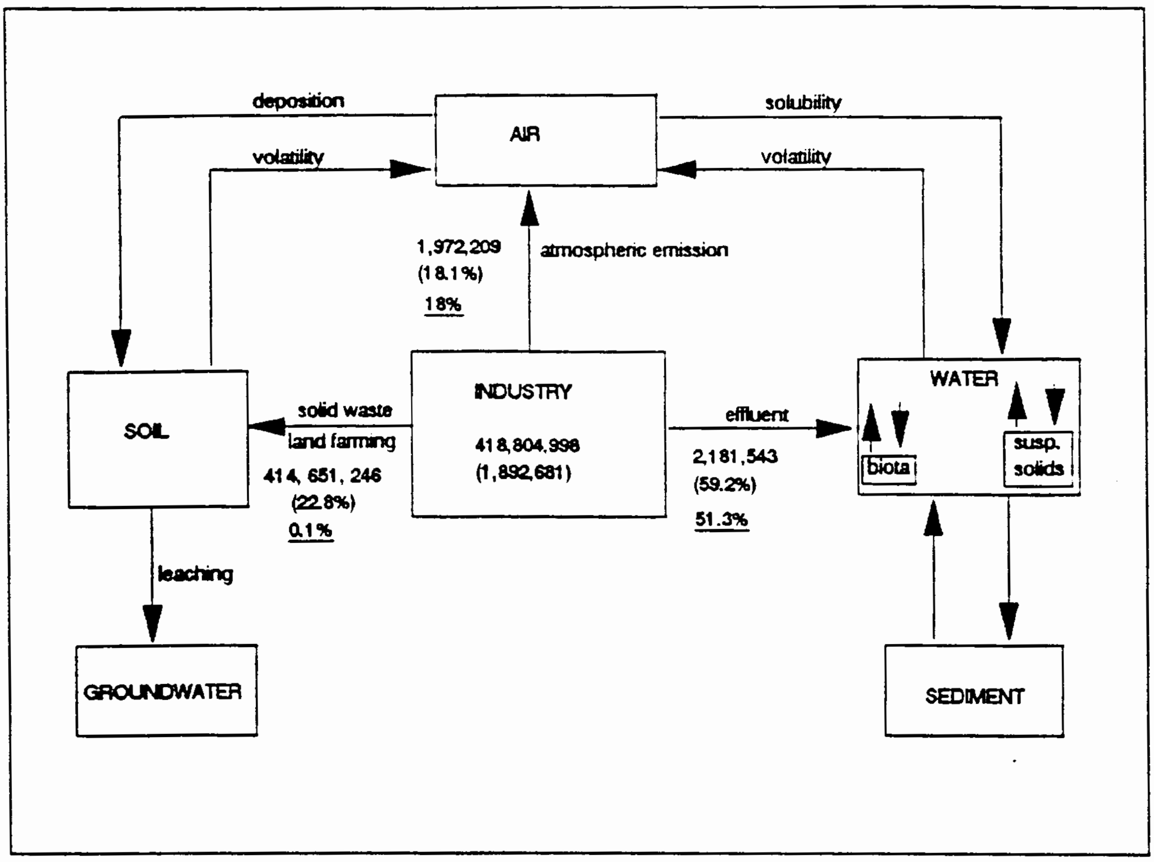


FIGURE 4.1: Model of Industrial Waste Emissions, Based On Department of Environment Affairs (1992b) Estimates

Data given as:

a) TPA *total* waste, excluding water;

b) figures in brackets indicate *hazardous* waste TPA, or % of the industry *total* discharged to each media;

c) figures underlined indicate the *hazardous* % by weight of the total waste discharged to each media.

Excluded from these waste flows are waste emissions due to domestic and commercial use of products and from secondary generation of wastes such as vehicle emissions, organic solvent vapours, combustion products from domestic burning and use of pesticides in agriculture and elsewhere (Department of Environment Affairs, 1992b). Furthermore actual quantities of waste water are not given; only the waste which is discharged as part of a waste water stream. Thus these estimates do not fully quantify the scale of waste generation.

Figure 4.1 illustrates the predominance of total waste discharged to land, but the predominance of hazardous waste which is discharged to water. Industrial waste discharges to both land and water are dominated by mining wastes which account for 90% of total estimated waste generated by industrial sources. Most solid waste from mining is considered to be relatively inert tailings, overburden and spoil with only 0.28% deemed to be hazardous, although this still translates to the greatest single source of hazardous waste. Moreover there is also an estimated 12 million tonnes backlog of overburden and 30,000 tonnes of semi-purified concentrate (Department of Environment Affairs, 1992b).

Mining waste aside, the most significant contributor to waste which is disposed to land is the metallurgical industry, of which waste about 6.6% is deemed to be hazardous. The highest concentration of hazardous waste is that generated by the metal processing industry (86.5%), although net quantities are comparatively small. Concerns about land disposal of hazardous waste include the impact of wind-blown dusts, containing toxic contaminants, and of leaching of toxic materials from soil into water courses.

Most of the waste water from the mining industry is generated by gold mining, and is contaminated with toxic cyanide from gold leaching operations (Department of Environment Affairs, 1992b). Excluding the mining industry, it is food processing, pulp and paper manufacture and the textile industry which are the major contributors to water pollution. Of these the most significant source of hazardous aqueous waste is the textile industry on account of the presence of dyes, detergents and salts in process waste water.

The major source of air pollution is the power generating industry which, reportedly, is responsible for approximately 80% of total estimated atmospheric discharges (Department of Environment Affairs, 1992b). The power stations are concentrated in the Transvaal, lower Vaal and Eastern Highveld areas, close to principal coal sources, but where climatic conditions are highly unfavourable for dispersion of air borne pollution (Tyson, Kruger and Louw, 1988). Consequently there is significant localised air pollution in those areas. An inventory of overall emissions in the *Eastern Transvaal Highveld* (ETH) for 1984 has been reported as a total of 2,383,570 tpa, excluding carbon dioxide (Tyson, Kruger and Louw, 1988). However the *national* estimate given in the Department Environment Affairs (1992b) report is only 1,972,209 tpa, also excluding carbon dioxide. This comparison suggests that the Department of Environment Affairs' estimates may be significant underestimates of actual atmospheric emissions from industry sources.

As indicated above, the Department of Environment Affairs' estimates exclude vehicle emissions and particulates from domestic fires. It is these sources which can be expected to have a much greater impact on suburban areas.

With the exclusion of the mining industry, and service industries (including power generation), Figure 4.2 illustrates comparative total estimated waste quantities generated by industry sub-sectors included in the Department of Environment Affairs' study. Figure 4.3 likewise compares hazardous waste quantities from these sub-sectors.

Comparison of these diagrams demonstrates:-

- the predominance of total and hazardous waste generated by the chemical processing industries and metallurgical industry sectors;

- the significant percentage of total waste which is hazardous from the chemical products manufacturing sector;

- similarly, the significant percentage of total waste which is hazardous from metal processing operations and from the textile manufacturing sector;

- the significant generation of total waste in the building sector, but the low level of hazardous waste content.

Clearly the larger scale industry members, although fewer in number, produce the greatest proportion of total and hazardous waste. There are many more small and medium size enterprises (SMEs) which may be classified as small quantity generators (SQGs) of hazardous waste. Despite the comparatively lesser total quantities, the variability and often high toxicity of waste generated by such activities can result in considerable environmental problems (Baldwin & Van Laum, 1991). Thus although the greatest reduction in industrial waste would be realised by applying waste minimisation strategies in the larger scale industries - the rationale to regulate these activities first (Baldwin & Van Laum,1991) - there is a specific need to implement practicable waste minimisation measures appropriate to SMEs.

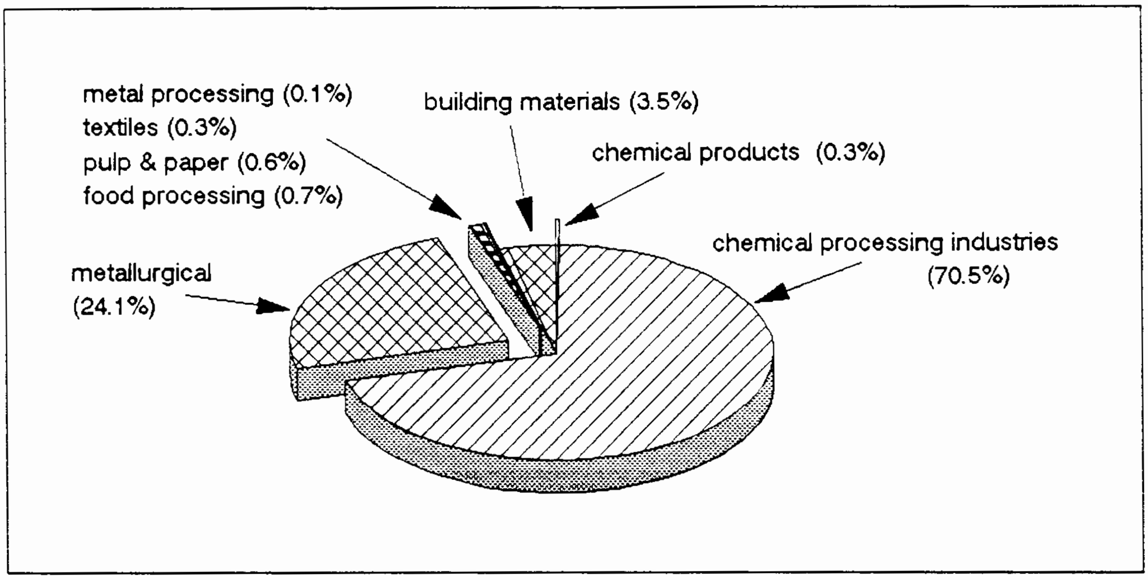


FIGURE 4.2: Comparative Contribution To Total Industry Waste By The Major Manufacturing And Chemical Processing Industries In South Africa, Based On Department of Environment Affairs (1992b) Estimates

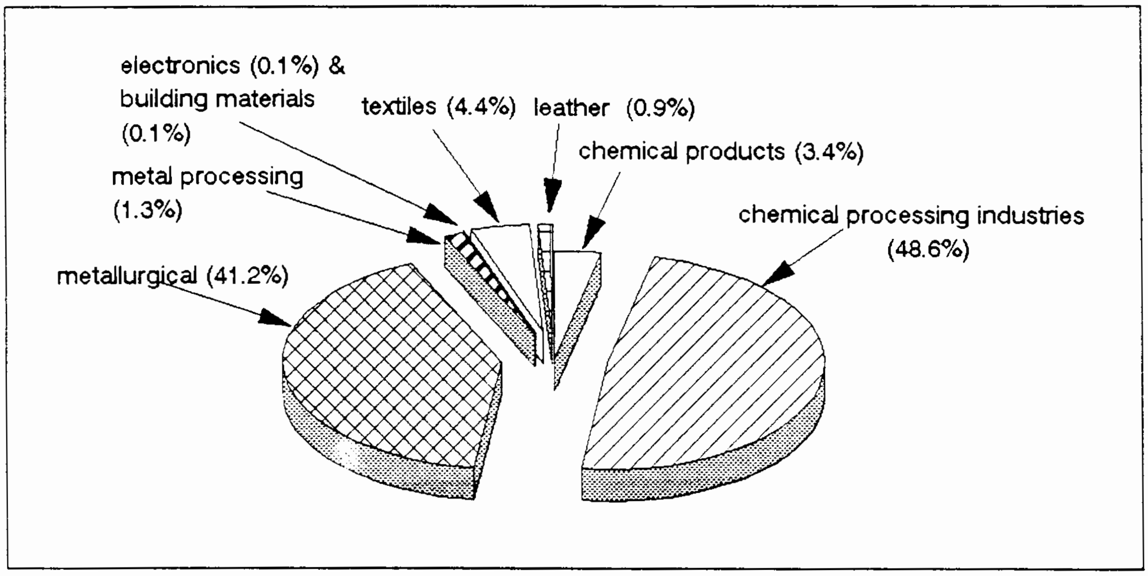


FIGURE 4.3: Comparative Contribution To Hazardous Industry Waste By The Major Manufacturing And Chemical Processing Industries In South Africa, Based On Department of Environment Affairs (1992b) Estimates

4.3.2 Western Cape Figures

The Western Cape region has a limited presence of large scale chemical processing and metallurgical industry operations, and is characterised instead by many more SMEs. This is reflected in the estimated waste quantities attributed to industry in the Western Cape region in the Department of Environment Affairs study (1992b). These waste estimates, compared in Figures 4.4 and 4.5, clearly indicate the predominant presence of the food processing industry and the textile industry. In terms of hazardous waste generation, the industries of primary concern for regional government would be the textile and leather manufacturing companies, chemical products manufacturing and metal processing.

With reference specifically to the selected case study industry members, it is apparent that the textile sector as a whole generates the greatest quantities of hazardous waste. Waste from the metal processing sector is lesser in total quantity, but has the highest content of hazardous material (86.5% by weight).

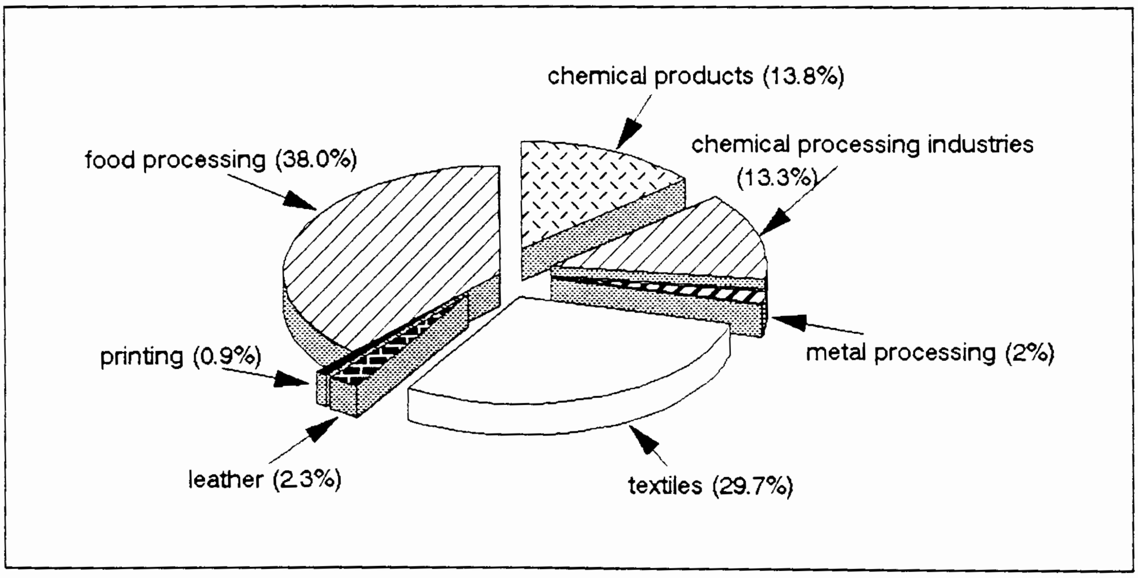


FIGURE 4.4: Comparative Contribution To Total Waste Generation In The Western Cape Region By Regional Industries, Based On Department of Environment Affairs (1992b) Estimates

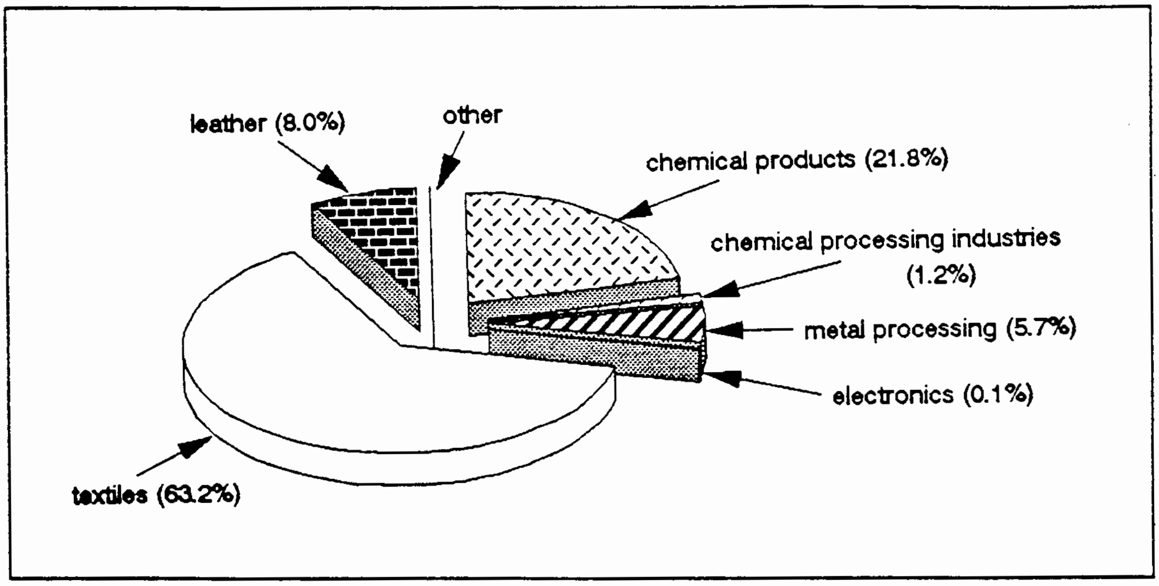


FIGURE 4.5: Comparative Contribution To Hazardous Waste Generation In The Western Cape Region By Regional Industries, Based On Department of Environment Affairs (1992b) Estimates

4.4 INDUSTRY PERCEPTIONS

While larger scale industries are responsive to international pressures, there is resistance to imposition of more rigorous and stringent pollution control legislation. It is considered that South Africa cannot afford to increase costs of environmental protection when there is a priority need for increased expenditure on social infrastructure and economic programmes to create employment opportunities, increase exports and raise GDP earnings.

There are a number of industry initiatives which are intended to help improve the environmental performance of industry and/or to develop an industry response to growing environmental pressures e.g.

- the Industrial Environmental Forum (IEF);
- Chemical Industries Environmental Forum (CHIEF): this was established by the Chemical Manufacturers Association (CMA)[1] in 1991 (anon, 1992);

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[1] more recently reformed as Chemical and Allied Industries Association (CAIA).

- adoption of 'Responsible Care' (Hart, 1992) referred to in section 3.3.1(iv);
- education and training programmes such as the Integrated Strategic Environmental Management Plan (ISEMP) (Odendal, 1992); and
- a considerable number of annual conferences which address various environmental issues.

These initiatives are targeted principally at larger scale industries and are promoted in such a way as to preempt imposition of more rigorous external monitoring and regulations to preserve a self-regulatory mode of operation (Fogel, 1992). This is deemed to be the most cost-effective way of sustaining economic progress which is needed to acquire the resources with which to improve quality of life in South Africa, while improving environmental performance (Fogel, 1992). There would appear to be little practical assistance for smaller industry members, who look to local government to offer them technical advice which can help them comply with legislation. However local government themselves may lack the qualifications and experience to offer appropriate assistance. Presumably there would also be concerns about professional liabilities.

4.5 WASTE MANAGEMENT PRACTICES

The Department of Environment Affairs study (1992b) indicated that little waste minimisation is practised by South African industry. Reportedly there is little appreciation of benefits of waste minimisation which have been identified as savings in raw material, utility and waste management costs, with other benefits in improved occupational health and safety, employee relationships and public image. Waste minimisation efforts which are reported include backfilling of mining overburden, reprocessing of metallurgical waste for recovery of valuable materials and recycling of tar and pitch wastes from petrochemical operations (Department of Environment Affairs, 1992b). These activities are associated with large scale industry members which have economy of scale and technological and financial resources to operate on-site waste treatment and disposal facilities.

SMEs are more dependant on off-site waste treatment and disposal facilities. Typically liquid effluent is discharged to a municipal sewage system and solid waste to landfill sites managed by local municipalities or private contractors. Cumulatively there may be significant quantities of waste from SMEs, including toxic waste, and there are concerns about a shortfall in treatment and disposal capacity at these off-site facilities and costs which will be incurred for treatment upgrades, disposal site remediation and development of new landfill sites.

Given that, at least in the short- to medium term, there will be continued dependence on these facilities and shared responsibility for wastes which are discharged to these facilities, it is appropriate to discuss these waste management practices.

4.5.1 Effluent Treatment

Effluent treatment is integral to control of water pollution and water quality management which are governed by legislation in terms of the Water Act, no. 54 of 1956. This act defines general and special effluent standards as the minimum acceptable effluent standards, referred to as uniform effluent standards (UES). These were set originally as achievable standards using 'best available technology not entailing excessive costs' (BATNEEC) (DWF, 1991).

These standards are legally binding on municipal treatment facilities which receive and treat industrial discharges. Each municipality establishes its own effluent standards for industrial discharges based on the treatment capacity of the facility. Municipal staff are responsible for monitoring effluent quality. Grab samples are taken approximately every six weeks, i.e. eight samples per annum, and analysed for parameters specified in terms of local bye-laws. Analytical results are used as a basis for determining effluent treatment costs which are payable on a six monthly basis by the waste generator and for policing compliance with specified standards. Table 4.1 shows discharge standards and costing formulae which are applicable to the case study industry members.

The treatment charge comprises a standard treatment cost which is calculated from the estimated effluent volume and the average chemical oxygen demand (COD) of the four samples taken in the preceding six months, plus applicable surcharges for transgression of discharge constraints e.g. for metals and salts. These costs are also computed on the basis of an average value of the measured parameters. Clearly these measures cannot accurately account for total discharges to the sewer system, particularly where effluent characteristics are variable in quantity and composition.

TABLE 4.1: Summary Of Effluent Discharge Standards And Treatment Costs Of Cape Town Municipality

ANNUAL PERIOD		88- 89	89- 90	90- 91	91- 92	92- 93	93- 94
Water supply (i)	Cost Unit R/kL		0.70	0.91	1.10	1.27	1.4
Annual % increase				30.0	20.9	15.5	10.2
Effluent discharge: (ii) V*(S+T*(1/3+(COD-75)/1350))							
Effluent conveyance (S)	R/kL	0.1894	0.2031	0.2636	0.2880	0.3197	0.3417
Annual % increase			7.2	29.8	9.3	11.0	6.9
Effluent treatment (T)	R/kL	0.3980	0.4011	0.4533	0.4888	0.5595	0.6015
Annual % increase			0.8	13.0	7.8	14.5	7.5

surcharges calculated based on following formulae: (iii)
Sulphates: S/15 for every 100 mg/L above 500 mg/L
Conductivity: T/30 for every 100 mS/m above 500 mS/m
TDIS: (S+T)/45 for every 100 mg/L above 500 mg/L
Cyanide: (S+T)/45 for every 5 mg/l above 20 mg/l
Heavy metals: T/30 for every 10 mg/l above 50 mg/l
pH: (S+T)/45 for every unit of 1.0 calculated as $(6\text{-pH})^2$ for pH below 5.5

Notes:
(i) charges in effect from 1 April of each year
(ii) charges in effect from 1 June of each year; V = total effluent volume
(iii) ref. Drainage & Sewage By-Law P.N.397/1987

Municipal sewage treatment operations typically comprise biological aerobic and anaerobic systems. These systems are not suitable for high levels of heavy metals or inorganic salts. Lime is usually added to precipitate heavy metals and salts so as to reduce dissolved concentrations to a tolerable limit for bacterial activity. Metal hydroxide sludges and inorganic salts accumulate in the biological treatment sludges. These must be analysed and categorised for disposal according to recommended guidelines for safe waste disposal. Hence local municipalities themselves incur expense and liabilities for management of hazardous waste.

Despite these treatment and disposal problems, discharge constraints are not always strictly enforced, reportedly in recognition of economic difficulties in treating certain "intractable" wastes cost-effectively e.g. inorganic salts (Cape Town City Council, 1992). It is feared that enforcement of stringent discharge limits will threaten the economic viability of small scale operations. There are cases where companies, which do not consider it economically feasible to implement changes needed to comply with local legislation, have threatened to close or relocate to another area where local legislation is less strict (Cape Town City Council, 1992 and Smuts and Hobbs, 1990). The social costs to the community of lost employment opportunities, and the implications for other local infrastructure reduces the leverage of local authorities to enforce or even encourage greater pollution control. Effective enforcement is also inhibited by a lack of sufficient manpower to carry out inspections (Lusher & Ramsden, 1992).

The Water Research Commission (WRC) has sought to encourage improved water management practices by industry. A number of investigations have been carried out addressing environmental problems associated with water management and effluent treatment by, among others, the textile industry (WRC, 1987a & 1990) and the metal finishing industry (WRC, 1984) i.e. industry sectors of which the case study companies included in this research project are members.

The Department of Water Affairs and Forestry (DWF) has also sought to improve water quality management by formulating a new approach based on Best Practicable Environmental Option (BPEO) considerations as defined by HMSO (1988). A policy document has been published (DWF, 1991) which describes the revised hierarchy of water management goals:

1. source reduction, recycling, detoxifying - promoted as a voluntary action;

2. discharged effluent to meet minimum general or special standards if these are acceptable for the receiving water:

3. application of stricter standards in accordance with a Receiving Water Quality Objectives (RWQO) approach to maintain fitness of use of the receiving water; this is similar to the UK's quality objectives approach (see section 3.3.1(ii));

4. exemptions to be allowed only when justified by technological, physical, economical and socio-political considerations.

Application of the RWQO approach requires that the use of water bodies be defined; that the assimilative capacity of the water be specified in terms of water quality requirements for its designated use; and that site specific investigations be carried out to ascertain allowable waste loads for permitted sites (Lusher & Ramsden, 1992). Clearly implementation of this strategy is more complicated than the UES approach, and requires greater skills and manpower. Consequently UES continues to be applied while the new standards are introduced gradually.

Lusher & Ramsden (1992) suggest that the advantages of the RWQO approach are that it is more cost-effective, given that only that level of control which ensures adequate protection of water uses is required i.e. avoids over specification; and provides an incentive for industry to locate in areas where receiving waters are less sensitive to pollution effects. Moreover conservation and more efficient use of water resources should help to avoid the need for additional investment in new resource management projects. This would include effluent treatment facilities and landfill sites.

DWF (1991) reports that it is intended that the RWQO strategy should be implemented with a co-operative relationship between government and industry. Industry initiatives are to be driven by application of the 'polluter pays principle' and economic incentives. However there is no stated intention to provide a sponsored technical advisory service to industry as has been adopted in the U.S. and elsewhere. This is due presumably to lack of sufficient technical staff and financial resources to support such a scheme.

4.5.2 Waste Disposal

There are a large number of poorly managed disposal sites from which leachate may pollute groundwater and surface water. Although regulatory control of landfill sites has been tightened by terms of the Environment Conservation Act No. 73 of

1989, with stricter provisions for permitting and operation of waste disposal sites, Howard and McGee (1991) report significant environmental hazards emanating from most of the regional waste disposal sites in the Durban-Pietermaritzburg area. A similar situation can be expected in other regional areas in South Africa.

In an attempt to standardise management of hazardous waste transportation and disposal systems, the Institute of Waste Management (IWM) and South African Nature Foundation (SANF) have published self-regulatory guidelines (IWM & SANF publication). In accordance with these guidelines waste materials for disposal, including sludges from effluent treatment, are categorised for disposal to different classes of landfill sites depending on their properties. Pollutant limits for hazardous components are prescribed. Implementation of these measures places greater restriction on alternative end uses of sludge, such as landfarming and composting.

4.6 CONCLUSIONS

1. South Africa has no national policy in relation to waste minimisation, although the need to investigate such a strategy has been acknowledged.

2. Recent efforts have been made to address the problems of hazardous waste generation by industry, but there is continued dependence on the technology of end-of-pipe treatment and disposal to manage these wastes.

3. The total waste inventory identified by the Department of Environment Affairs (1992b) study does not itself define the full extent of environmental degradation associated with these wastes.

4. The greatest net quantities of total and hazardous waste are generated by the large scale heavy industries and the CPI. However in the Western Cape, smaller scale operations, notably food processing and textile manufacturing, are the source of most industry waste. Textile processing also accounts for the greatest contribution by weight to hazardous waste generation in the region. Although the metal finishing industry sector is much smaller, it is noted for the high hazardous content (almost 87% by weight) of associated waste. These

differences in waste profiles represent different problems for waste management.

5. Most hazardous waste is discharged to water. New water quality standards are being introduced gradually.

6. The greatest quantities of total waste are discharged to landfill sites, which generally have been poorly managed. Guidelines for improved management have been developed recently to facilitate compliance with stricter regulations governing operation of waste disposal sites.

7. Larger scale industry operators are addressing environmental problems, principally through voluntary initiatives and self-regulation.

8. There is limited practical assistance for smaller scale industry operators. Local government lack the skills and resources to provide an assistance service.

9. Legislation is not always strictly enforced, partly in recognition of economic hardships which such action would cause to small scale industry operators whose economic viability may be threatened.

10. Government seeks a co-operative relationship with industry in addressing waste management concerns.

The reviews of the international and local situation in industrial waste management have reinforced the premise that problems of effective waste management by SMEs require specific attention. In this dissertation, having defined a generic waste minimisation assessment methodology in chapter 2, the potential for effecting waste minimisation using this approach is explored in the case studies which follow.

CHAPTER 5
CASE STUDY: A GARMENT DYE HOUSE

5.1 INTRODUCTION

This chapter describes the activities and results of a preliminary waste minimisation assessment undertaken at a small scale garment dye house.

Monitoring by the municipal council of effluent which is discharged from this operation to the sewer has recorded consistently high levels of sulphates and inorganic salts in excess of discharge constraints prescribed in the relevant local bye-laws. Currently only the surcharge for sulphate is being charged to this company. Surcharges for excess conductivity and TDIS (total dissolved inorganic solids) are not being enforced because of a perceived lack of viable small scale techniques for the removal of inorganic salts, making it economically difficult for small scale operators of this nature to treat such wastes cost-effectively. However local council authorities would like to encourage greater responsibility for on-site waste management to alleviate the waste load on existing off-site facilities. Given the water intensive nature of textile dyeing, water consumption is also an issue for concern.

The case study company is a small scale cotton dyeing operation, employing approximately 20 operators. It is a privately owned business, managed by the owner who has complete authority for all aspects of the business. Interest was expressed in identifying measures by which the efficiency of operations in general could be improved, to improve the working environment and, specifically, by which transgressions of the effluent quality constraints could be avoided. Given the small scale of this company and the lack of a formal organisational structure which could support detailed on-site investigation, only a preliminary level of assessment was carried out, as described in section 2.4.4. This assessment was based on initial site observations and information available from literature sources which report on experiences elsewhere. The work included:-

- compilation of readily available information about the process operations and material flows;

- a site visit to review operating and waste management practices;
- a literature review of dyeing technology;
- a literature review of waste minimisation opportunities reported in published literature;
- identification and preliminary evaluation of potential options to effect waste minimisation.

Background information on process operations, waste characteristics, current waste management practices and environmental impacts of wastes from this dyeing operation are given in section 5.2. Section 5.3 reviews international and local initiatives in promoting waste minimisation, and identifies some reported potential waste minimisation options. Section 5.4 addresses the actual site assessment, while section 5.5 identifies and discusses waste minimisation measures which could be considered for implementation or further evaluation by this company. Conclusions are summarised in section 5.6.

5.2 BACKGROUND

5.2.1 Process Description

Figure 5.1 (on page 65) illustrates the process operations in use at this dye house. These are also summarised in Table 5.1 and described below.

The cotton textile garments may be processed by application of one of three dyeing techniques known as direct dyeing, reactive dyeing and pigment dyeing. Associated wet-processes include desizing, scouring, bleaching and the finishing processes of dye fixing and softening. Each process, with the exception of softening, is followed by a rinse stage to remove unused dyes and chemicals. Figure 5.2 (on page 65) illustrates these wet-processing operations. Appendix C presents a brief review of the chemistry and process technology associated with these processes; a glossary is also given for reference.

TABLE 5.1 Summary Of Process Operations

PROCESS OPERATION	FUNCTION	EQUIPMENT/AREA
Desizing	enzyme treatment to remove starch by conversion to glucose	dye machine
Scouring	detergent washing of garments after desizing	dye machine
Bleaching	chlorine treatment for colour removal	dye machine
Dyeing	bonding of coloured compound to fabric	dye machine
Fixing	cationic surface active treatment to improve dye fastness	dye machine
Softening	cationic surface active treatment to provide fabric softness	dye machine
Rinsing	removal of trace chemicals and dye compounds between processing steps	dye machine
Dye stripping	removal of bonded dye compounds	dye machine
Centrifugation	extraction of bulk water from wet garments	hydro-extractor
Tumble drying	complete drying of garments	tumble drier
Materials handling	sorting and packing of raw and finished garments	sorting tables
Steam generation	heating supply for dye machines and tumble dryers	boiler; HFO storage and transfer pumps; steam header; water softening system
Water supply	supply of process and utility water	storage tank and transfer pumps
Effluent treatment	equalisation and solids settlement prior to sewer discharge	drainage system; equalisation tank and sampling chamber

All of these processes take place batchwise and consecutively in a single reactor (dye machine) of which there are several with capacities ranging from 2.5 L to 2500 L. This structure provides the company with the flexibility to process reasonably large batches of garments on a contract basis and also offer unique customised processing solutions to achieve specific textile dyeing effects for small garment batches.

The raw garments are loaded manually into the reactor, which is then filled with water directly from municipal mains. Required chemicals are added manually as a liquid or dry powder, using simple fixed volume containers which are filled from chemical storage drums. These are located in designated areas in the vicinity of the reactors. The reactors are heated using steam which, in most of the reactors, is injected directly into the process solution. Steam coils are fitted only in the newer reactors. Each processing stage is operated to recommended chemical concentrations, solution temperature, liquor ratios and reaction times, but there is no rigorous process control. For example, the process solution temperature is controlled by manual adjustment of steam valves, with temperature displayed on gauges which are fitted to the reactors. The sequence of process operations may vary for different batches of garments. Some of the garments will have had no prior finishing treatment whereas others may have been previously treated and will require chemical stripping to "undo" treatment effects before they can be subjected to further processing.

On completion of the dye cycle wet garments are transferred to an electrically driven centrifuge which removes the bulk of the water, and then to a convection drier (tumble drier) for complete drying. Heating is achieved using steam coils within the drier.

Plant steam requirement is generated by a boiler fired with heavy fuel oil (HFO) using softened municipal water and return condensate from the dryers and newer dye reactors.

All liquid effluent from the batch reactors, centrifuges, general wash water and boiler blowdown are combined in a single equalisation tank prior to discharge to the municipal sewer.

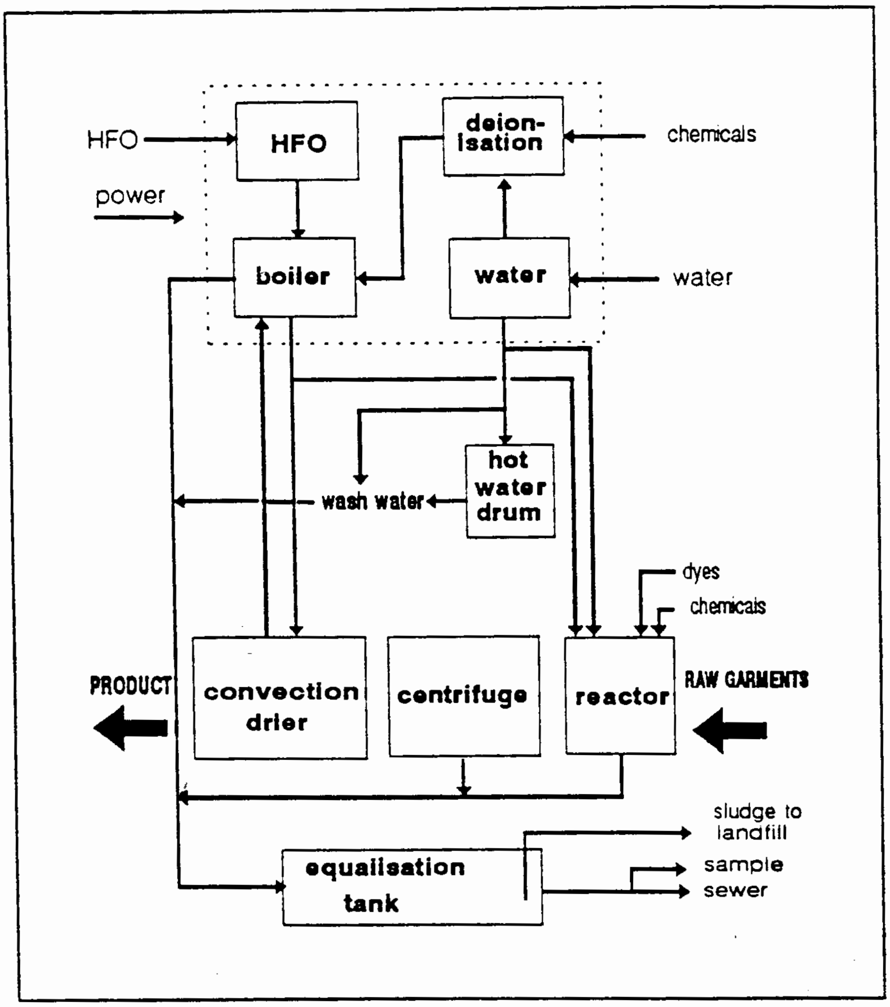

FIGURE 5.1: Flow Diagram Of Process Operations In Garment Dyeing

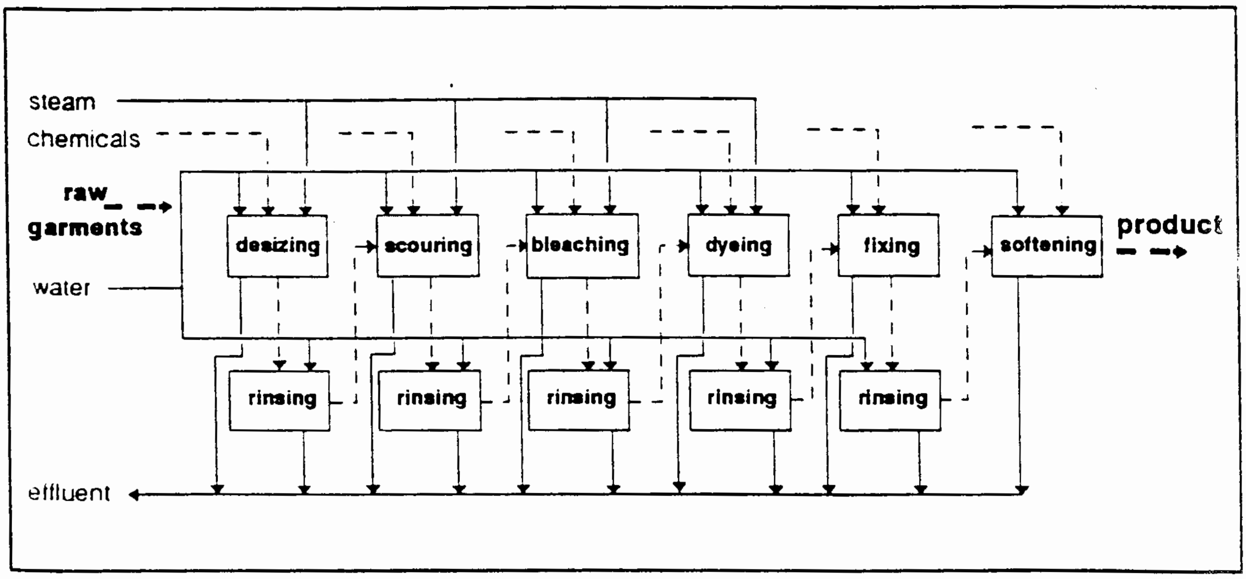

FIGURE 5.2: Diagram Of Wet-Processing Operations

5.2.2 Overview Of Waste Generation

The source, type and characteristics of wastes typically generated by the textile processing operations used by this company are summarised in Table 5.2. The bulk of the waste is generated as liquid effluent which is extremely variable in flow and composition. The polluting compounds are natural impurities extracted from the fibre, and spent processing chemicals. Consequently these effluents are characterised by:-

- high oxygen demand;
- high sulphates;
- high levels of dissolved inorganic salts
- colour and turbidity; and
- heavy metal contamination, which may include chromium, copper and cobalt (Netzer, 1975).

TABLE 5.2: Waste Sources And Types Generated By Garment Dyeing (Nemerow, 1971)

SOURCE	WASTE TYPE	CHARACTERISTICS
Desizing	waste enzyme solution	high BOD; neutral pH; high total solids
Scouring	waste detergent solution	high BOD; high alkalinity; high total solids; high temperature
Bleaching	waste bleach solution	high BOD; alkaline; high solids
Dyeing	waste dye solution	high BOD; high solids; neutral to alkaline; heavy metal content; coloured
Fixing	waste fixing solution	high BOD
Softening	waste softening solution	high BOD
Rinsing	waste water	variable dilute contamination
Equalisation of effluent	waste water water treatment chemicals	variable pollutant load: high BOD; high conductivity; high solids; colour and turbidity inorganic sludges
Boiler	waste gas blowdown	CO, CO_2, H_2, H_2O, NOx, SOx; high salt content
Materials handling	waste packaging & residue chemicals	cardboard; plastic bags; plastic & steel drums; general solid refuse

Given the absence of on-site waste related records, other than effluent treatment and sludge disposal accounts, reference was made to textile effluent characterisation data which had been published in a report by the Water Research Commission (WRC) in South Africa. This data may be used for predicting expected effluent characteristics of a selected process or series of processes. By way of example, Table 5.3 gives a typical effluent composition for a woven fabric finishing operation, although the type of fabric has not been identified. This composition could vary from plant-to-plant even for the same particular operation on a specific fabric depending on impurities in the raw fibre, type and configuration of equipment, mode of operation, chemical concentrations, liquor ratios and general operating practices.

TABLE 5.3: Typical Effluent Characteristics For Woven Fabric Finishing (WRC, 1987a & 1990)

Water Use	297 l/kg	**Heavy Metal**	**(mg/l)**
pH	7-11	Cr (i)	0.3-2.3
sulphide	3 mg/l	Cu	0.12-1.6
COD	850 mg/l	Fe	0.4-3.78
BOD	550 mg/l	Zn	0.13-1.22

Notes

(i) form of heavy metal ion not reported.

Table 5.4 compares typical characteristics of effluents generated by direct dyeing and reactive dyeing. Pigment dyeing uses much less water than either of direct or reactive dyeing, approximately 2.7 l/kg (WRC, 1987a), as this process does not require equivalent quantities of rinse water.

TABLE 5.4: Typical Characteristics For Direct And Reactive Dyeing Effluent (WRC, 1987a)

PROCESS	DIRECT DYEING	REACTIVE DYEING
water usage l/kg	40-80	70-100
pH	6.5-7.5	>11
temperature (c)	60-100	60-100
colour	low	fairly high
TDS - g/kg	200	>900
- mg/l	2500	9000

TABLE 5.5: Relative Pollution Load By Various Wet Processes (WRC,1990)

PROCESS	EFFLUENT VOLUME	COD MASS	TS MASS	OA MASS	TC MASS
desizing	1.5	9.7	6.1	3.6	18.7
scouring	1.0	4.3	5.1	1.9	8.1
bleaching	1.0	1.0	1.0	1.0	1.0

Notes:

COD = chemical oxygen demand
TS = total solids
OA = oxygen absorbed
TC = total carbon

Table 5.5 indicates the relative contribution of other wet-processing operations to the pollution load (WRC, 1990). This indicates that desizing and scouring contribute the greatest load of organic pollutants, derived from removal of glucose/starch and natural impurities. Sulphates, inorganic salts and heavy metal contamination would arise from the many varied chemicals used in dyeing and finishing stages.

Other forms of chemical waste which are generated include sludges containing dye and chemical compounds, which settle in the equalisation tank, and potential atmospheric emissions from bleaching and from volatile organic components contained in some dye compounds and binding agents. However this effect is more applicable at high temperature operations associated with wet-processing of synthetic fabrics. These are not processed at this dye house.

5.2.3 Current Waste Management Practices

(i) on-site treatment

On-site, there is a single equalisation tank which is used to blend and dilute the various liquid waste streams and to allow settlement of solids (see Figure 5.1). The settled solids form a sludge which is removed periodically by a waste contractor for off-site disposal at a Class 1 landfill site. The effluent still contains high levels of inorganic suspended and dissolved solids, as well as soluble sulphates

Local municipal authorities would prefer the solids content in the dye house effluent to be reduced further prior to sewer discharge. Alum (aluminium sulphate) has been used previously as a flocculating agent which reduces the settling time of suspended solids, thereby retaining more of the solids in the equalisation tank. (Goldman etal (1977) describes the sludge product as high volume with low solids content (about 1%) and poor dewaterability properties.) This treatment was stopped owing to the disruption caused to processing operations and loss of production time due to the need for more frequent tank cleaning by a waste contractor. Differences in costs for dosing chemicals and sludge removal versus higher effluent treatment costs were considered to be insignificant[1].

(ii) local council responsibility

In terms of local bye-laws, the local municipal council monitors the effluent discharge by means of grab samples from the effluent sampling trap which is fitted in the discharge line from the equalisation tank. These samples are analysed for sulphates, conductivity, total dissolved inorganic solids (TDIS) and pH. Heavy metal concentration apparently is no longer analysed after initial testing showed detectable concentrations to be below the discharge constraint of 50 ppm.

As explained in section 5.1, only payment of the sulphate surcharge is enforced. This charge is related to estimated costs which would be incurred by the council for repair of structural damage to the sewer system, caused by sulphuric acid attack (see section 5.2.4). The original discharge constraint of 500 mg/l has or will be increased to 1800 mg/l, being the solubility limit of calcium sulphate ($CaSO_4$), the precipitation product of lime dosing[2].

The council themselves dose the influent to the sewage treatment plant with lime, for pH control and to lower the levels of sulphates and heavy metals salts. The resultant sludge must be managed in accordance with guidelines for waste disposal, referred to in section 4.5.2.

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[1] communication with company management.

[2] communication with local council.

(iii) sludge disposal

Sludge removed by the waste contractor is checked for pH and flammability and co-disposed with dry domestic waste. Reportedly, this is the lowest cost disposal option. Sludge from this dye house has been described as being consistently alkaline and, on the understanding that heavy metals are stabilised as hydroxides in alkaline conditions, heavy metal analyses normally are not carried out. Such analyses are conducted only on waste for which a low pH is measured. If the detected heavy metal concentration exceeded 10 ppm, the waste would be treated with lime to precipitate the metals as hydroxides[3]. The basis for the 10 ppm limit on heavy metals is not known.

5.2.4 Environmental Impacts

The principle concern relating to waste generation by dyeing operations is the high level of sulphates and other inorganic salts and heavy metal-bearing dye chemicals in process effluents and sludge wastes. The environmental impacts discussed below have been reviewed with respect to the implications of these waste characteristics for existing waste treatment and disposal systems, and the effect of waste emissions on water bodies and land (as a result of waste disposal).

(i) sulphates

Table 5.2 has identified typical waste materials. Of these, sulphates are biodegradable, but have a high oxygen demand. Where excessive sulphates are present in the effluent released to the sewer, oxygen supply in the sewer may become depleted with reduction of sulphates to sulphides by anaerobic bacteria. At low pH conditions hydrogen sulphide (H_2S) can form. This is considered toxic to the human respiratory system (Meyer, 1988). The hydrogen sulphide reacts with moisture forming sulphuric acid (H_2SO_4) which attacks construction materials in the sewage treatment plant. This acidity can also solubilise metals such as zinc, aluminium, cadmium, iron, nickel, arsenic, copper and chromium, which potentially could reach toxic levels (Duffus, 1980).

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[3] communication with waste contractor.

(ii) heavy metals

Heavy metals are classified as toxic on account of properties such as carcinogenicity, but degree of toxicity depends on the form and mobility of metal ions, water soluble salts being the most toxic. In natural environments these can be absorbed by many organisms with varying accumulative effects. Metal ions in textile effluents are discharged as water soluble compounds e.g. chromate ions. These are often complexed with chelating agents which stabilise the metal ions in solution and moreover may mask heavy metal detection by standard analytical procedures. This creates potential for inadequate treatment of contaminated water which could lead to accumulation of heavy metals in the receiving water system. While heavy metal concentrations in textile effluents are not monitored locally, in Germany it is acknowledged that heavy metal content in effluent containing dyestuffs poses an environmental problem (Mohr, 1992). A more detailed review of the potential environmental effects of the heavy metal, chromium, is given in Chapter 6.

(iii) inorganic salts

Inorganic salts are not biologically treatable and may inhibit aerobic and anaerobic activity in the sewage treatment plant. Persistence of the salt contributes to an increased salt loading in the receiving waters and accumulation in the treatment sludges. If land farmed, these sludges may cause salination of soil and groundwater.

(iv) colour

The coloured dye compounds are not readily biodegradable, resulting in persistent colour and high chemical oxygen demand (COD).

5.3 WASTE MINIMISATION OPTIONS

5.3.1 International Research

Internationally, waste minimisation initiatives in the textile industry are being driven principally by:

- concerns about availability of water of required quality; and
- increasing costs of water and of waste handling and treatment.

Much of current reported research effort in waste minimisation is being carried out in Asia where there is significant textile industry activity, largely based on labour intensive practices with generally lower standards of pollution control. In comparison, more rigorous legislation in First World environments enforces strict discharge constraints which are necessitating more on-site pre-treatment, including sophisticated mechanical, biological and chemical technologies.

A Working Group for Textile Industry has been initiated by the Industry and Environment Office (IEO) of UNEP to promote waste minimisation by disseminating information on research and development efforts throughout the world (Modak, 1991). Examples of typical projects are listed in Appendix D. In general these research efforts seek to conserve water and recover chemicals where possible. Potential opportunities are discussed in the following sections in terms of the waste minimisation techniques reviewed in chapter 2.

5.3.2 Source Reduction

5.3.2.1 Changes In Input Materials

Examples of chemical substitution include replacement of acetic acid (a solubilising agent) with an inorganic salt such as ammonium sulphate or chloride (Nemerow, 1971). In Germany, legislation enforces compulsory replacement of chemicals identified as toxic, such as chlorinated hydrocarbons, and re-specification of auxiliary chemical formulations to possess 90% biological primary decomposition (Mohr, 1992). Research in the U.K. is attempting to reduce usage of salt based chemicals in reactive dyeing by development of alternative processing conditions, including use of enzymes (PA Consulting Group, 1990). A number of literature references report research efforts to improve dye biodegradability, but results repeatedly show the difficulty of generalising dye effluent treatment due to unpredictability of dye wastes from different sources and different processes (Netzer, 975; Shriver & Daque, 1977; Weeter & Hodgeson, 1977; Yang & Pescod, 1977).

Hence changes in textile processing chemicals require long term research. The complexity of surface chemistry in textile processing may require fundamental changes in applied wet-processing methods.

5.3.2.2 Technology Developments

In the interests of water conservation there have been developments in single stage desizing, scouring and bleaching (WRC, 1990). This option reduces wash water requirements, but has a greater chemical demand. Net benefits would require evaluation.

5.3.3 Recycling

5.3.3.1 Direct Reuse

A more common technique for water conservation is direct reuse of rinse water containing low concentrations of chemicals in other processes which are more polluted, and in which the small content of chemicals present in the waste water should make little difference to the process. For example, rinse waters from washing after bleaching could be used potentially for rinsing off after scouring (WRC, 1990).

Another technique is dye bath reuse: reuse of 15 to 30 batches has been reported, with significant reductions in consumption of dyes, auxiliary chemicals and energy (Energy Pathways Inc. and Pollution Probe Foundation, 1987). This technique requires that bath solutions are analysed between uses and reconstituted by addition of chemicals as required.

5.3.2.2 Recycling Technologies

In most recycling applications effluent requires appropriate treatment which will either recover chemicals in a condition suitable for reuse, recover and purify water to a quality suitable for reuse or achieve both. Depending on the end use of recycled water simple filtration or more sophisticated technology may be required.

WRC (1990) identify treatment-for-reuse technology which has been proposed and in some cases successfully applied, including:-

- evaporation to recover chemicals and water;
- flotation to remove impurities from water;
- combustion and chemical conversion to recover sodium hydroxide;
- electrolytic- and membrane technology for water purification and sodium hydroxide recovery.

To date membrane separation processes would appear to have been used most extensively in textile processing. These have been shown to be cost-effective as a result of cost savings from water and chemical conservation and reduced waste management costs (WRC, 1987a & 1990).

5.3.4 Initiatives In South Africa

Locally, potential for waste minimisation by textile industry members has been demonstrated in research work done by the Pollution Research Group at Natal University (WRC, 1987a & 1990). Their work indicates that recycling of water and recovery of caustic chemicals from textile process effluent is technically feasible. For example they have proposed a closed loop treatment system incorporating reverse osmosis (hyperfiltration) with microfiltration as a pre-treatment stage (WRC, 1987a). It is acknowledged that economic viability of this operation is sensitive to many factors inherent in the nature of the processing operations and locality of different plants. It is not known whether such a system is in use.

Currently, emphasis would appear to be on development of cost effective biological treatment technology for textile dye house effluent. This includes on-going research by the Pollution Research Group (Carliell, 1992),and at Rhodes University where yeast is being used as an organism for heavy metal accumulation (Academic Std., 1992). This may offer potential for detoxification of heavy metals such as chromium in industrial effluents and for recovery of heavy metals. The scale of systems using these technologies is unlikely to be appropriate for on-site implementation by small scale dyeing operations, but may find application at centralised regional facilities.

5.4 WASTE MINIMISATION ASSESSMENT

5.4.1 Scope Of Assessment

Given the general interest by the management of this case study company in improving operating performance in the dye house, and the local council concerns about the waste load discharged from the site, the complete operating facility was reviewed with a focus on sources of effluent and sludge wastes which are discharged from site. The overall objective of this assessment was to review technology and production practices, including waste management practices, used by this dye house, so as to identify potential opportunities for reducing these waste quantities.

As this assessment was of a preliminary level only, no attempt was made to resolve material balances. Instead expected material flows were estimated from existing records and reported literature values for similar type operations, such as the data given in Tables 5.3 - 5.5. These material flows are discussed in section 5.4.2 in the order of the step-wise procedure of the UNEP assessment methodology (shown as steps 4 - 11 in Figure 2.3). Against the background of information obtained from site observations, these estimated material flows, and the literature reviews, potential measures are reviewed in section 5.5

It was not possible to complete the EPA-type worksheets to any useful extent as most of the information which was needed was unobtainable. A complete revision of existing record keeping by the case study company would be required to address these data requirements. This was not practicable for this assessment.

5.4.2 Site Observations And Estimation Of Material Flows

(i) <u>material inputs</u>

The raw materials are the garments, dyes and process chemicals which are used to treat the surface of the garment fabric to promote wet-processing reactions.

The processing throughput of garments is not known as no records of this are kept and batch processing quantities can be very variable. An estimate of at least 12,000 garments per month has been made by company management. An estimate of 103.5 tonnes of garments per annum has been made, based on prescribed chemical compositions for specific dyeing processes and approximate annual consumption of selected chemicals as indicated in lists of chemical orders which had been placed during the preceeding 12 month period.

These records, provided by management, illustrated the variety of chemicals required and the high consumption, particularly of salt based chemicals. Commodity chemicals generally are of consistent specification and are used regularly in most of the wet-processing operations. There is a more varied range of auxiliary chemical types, with use of alternative brands to achieve specific desired quality or dye effects.

Total chemical consumption of these varied chemicals was shown to be approximately 83 tpa, but this excludes dye chemicals for which no information was made available. Moreover, during the site visit, note was taken of chemical brands which are present on site, but for which there were no recorded order placements during the preceeding 12 months. Hence the accuracy of the above estimate is not known. It may be that there are obsolete chemicals on-site, and hence potential for spoilage of chemicals which are stored for a long time, with the need ultimately to dispose of this material. Inevitably there will also be some spillage and potential contamination of chemicals from containers located close to the processing equipment (for ease of manual chemical additions). The extent of unnecessary chemical wastage cannot be determined easily.

(ii) water usage

The major water uses in the dye house are wet-processing, steam generation, plant washing, general cleaning and domestic use. Information on total plant water consumption was obtained from the local municipal records for the period 1988-1991. For accounting purposes a fixed percentage of 13.5% of total metered water is assumed to be attributable to domestic usage and evaporative losses, with the balance of 86.5% attributed to process usage and hence effluent volume. Although water consumption more than doubled (approximately 250%) in 1991, following installation and operation of two new large capacity dye reactors, this ratio of process to domestic water usage has not been re-evaluated. Consequently the assumed effluent discharge volume would be an underestimate of actual quantities.

Tables 5.6a and 5.6b show estimated water usage by each wet-processing operation in a 750 L and in a 1000 L reactor. These values were derived on the basis of known machine capacities, liquor rates and processing steps, as used by this dye house, and estimated unit quantities as given in Tables 5.3, 5.4 and 5.5. The 1000 L dye machines are fitted with steam coils and hence do not consume steam directly. Water make-up to replace boiler blowdown has not been included.

The estimated unit consumption of 66 l/kg for direct dyeing and 80 l/kg for reactive dyeing (Table 5.6a) with a liquor ratio of 1:10 falls within the ranges suggested in Table 5.4. Excluding steam, process water usage is doubled in the 1000 L reactors (Table 5.6b) as these are operated at a higher liquor ratio. The estimates for the 750 l reactor (Table 5.6a) include 16 l/kg and 10 l/kg of steam respectively, the quantity for reactive dyeing being less as dyeing temperature is lower. The estimates show that, excluding steam, rinse water accounts for between 40% and almost 70% of the process water in individual operations.

Comparative usage of reactors of different capacities and their associated contribution to water utilisation and effluent generation is not known.

TABLE 5.6a: Estimate Of Water Usage (inferred) For 750 L Reactor

UNIT OPERATION	PROCESS WATER (L)	RINSE WATER (L)	%	STEAM (L)	%	TOTAL (L)	L/KG (i)
desizing	750	1500	67	n/a		2250	30
scouring	750	750	50	n/a		1500	20
direct dyeing	2250	1500	30	1200	24	4950	66
reactive dyeing	2250	3000	50	730	12	5980	80
peroxide bleach	750	750	50	n/a		1500	20

Notes:

(i) - per kg garments; liquor ratio =1:10

n/a - not available or not known

TABLE 5.6b: Estimate of Water Usage (inferred) For 1000 L Reactor

UNIT OPERATION	PROCESS WATER (L)	RINSE WATER (L)	%	STEAM (L)	TOTAL (L)	L/KG (i)
desizing	1000	2000	67	none	3000	60
scouring	1000	1000	50	none	2000	40
direct dyeing	3000	2000	40	none	5000	100
reactive dyeing	3000	4000	57	none	7000	140
peroxide bleach	1000	1000	50	none	2000	40

Notes:

(i) - per kg garments; liquor ratio =1:20

(iii) energy usage

Energy sources are the heavy fuel oil burned in the boiler for steam generation and electrical power for operation of electrically driven equipment including pumps, centrifuges and tumble dryers. Information on annual fuel and electricity consumption has not been reviewed. This information should be available from account records held by company management.

(iv) current levels of waste reuse/recycling

No wastes are reused or recycled at this facility.

(v) quantifying process outputs

Effluents and settleable sludge containing waste residue and unreacted chemicals were the waste flows of primary interest. Only these have been quantified, in subsections (vi) and (viii) below.

(vi) waste water

Average effluent flows and characteristics determined from monitoring records held by the municipal council for the three year period 1989-1991 are summarised in Table 5.7.

TABLE 5.7: Average Effluent Characteristics For Period 89-91 Inclusive, Based On Council Analyses

EFFLUENT PARAMETER	MEDIAN	HIGHEST	LOWEST	DISCHARGE CONSTRAINT
Flow kL/quarter	10976	23313	6207	-
COD mg/L	623	960	340	-
Sulphate mg/L (i)	3298	5643	1261	500
TDIS mg/L (ii)	5787	9542	3040	500
Conductivity ms/m (ii)	781	1317	514	500
pH	10	11.1	9.3	5.5 min

Notes:

(i) 1800 mg/l proposed as new constraint

(ii) monitored, but surcharges are not applied

The data shown in Table 5.7 illustrates the variability of effluent characteristics. Generally highest flows and pollutant concentrations arise during the first six months of the year when winter garments, typically with darker colours, are processed, chiefly by reactive dyeing. Lesser flows and pollutant loads are generated during the second six months when summer garments and lighter dye colours are processed. Clearly pollutant concentrations consistently exceed standards specified in local bye-laws (see Table 4.1).

Given that 86.5% of metered water is rated to be for process usage, this same volume is assumed to be effluent discharged from the site. On this basis effluent rates are shown to vary between 4,000 kL and almost 14,000 kL per quarter. Based on an average of 65 working days per quarter and a 12 hour working day, hourly flows could be between 5 m^3/hr and 18 m^3/hr. Thus retention times in the equalisation tank, of 60m^3 capacity, could be between 12 hours and just three hours. Surges of process effluent may pass through the tank with little hold-up, dilution or settling time for solids. Possibly these surges may carry sludge from the base of the tank over into the sewer discharge.

(vii) gaseous emissions

Process sources of gaseous emissions would be the bleaching solutions and volatile organics. At the relatively low temperature operations used for cotton processing such emissions are not expected to be significant. There was no obvious odour detectable during the site visit and there are no complaints known of to date about off-site emissions. Hence gaseous emissions from the processing operations were not investigated.

Boiler stack emissions would be hydrocarbon combustion products.

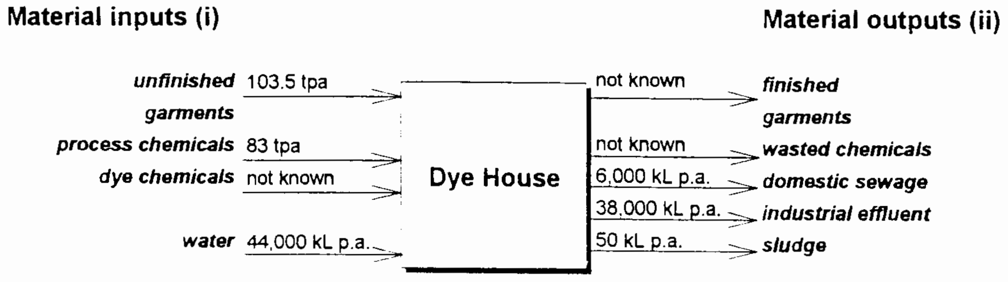
(viii) off-site wastes

Sludge from the settlement of solids in the equalisation tank is removed every two months, and amounts to approximately 50 kL p.a.

Other solid waste comprises discarded packaging from garments, empty chemical containers, and general office waste. It is understood that some of the plastic chemical containers are returnable on a refund basis, but that the bulk of this waste is removed by the municipality for disposal at a landfill site.

(ix) assembling input and output information

Estimated water and effluent flows have been compiled in Appendix E, and are summarised in Figure 5.3 together with other material flows which have been discussed above.



notes:

(i) excludes utility chemicals

(ii) excludes chemical content in garments, effluent and sludge

FIGURE 5.3: Estimated Material Flows In Garment Dye House

A balance of input and output material flows cannot be resolved without detailed site investigation. However the estimates shown are indicative of the consumption of water and generation of waste as effluent and sludge. Based on the estimate of 103.5 tpa of garments, approximately 365 l water per garments (including steam) or 330 l/kg (excluding steam) are consumed. This is slightly higher than the value of 300 l/kg reported by WRC (1990) for a typical woven fabric finishing operation. This may reflect greater inefficiency of batch processing.

5.5 EVALUATION OF POTENTIAL WASTE MINIMISATION MEASURES

Potential waste minimisation opportunities which may be appropriate for this case study company are summarised in Table 5.8. These proposals are based on reported experiences in published literature. Possible technical, environmental and economic implications of these options are discussed below, but no attempt has been to determine specific costs associated with each option.

5.5.1 Short-Term Measures

(i) operating practices

Improved house-keeping and management practices could be applied generally. With minimal expenditure, there are benefits in reducing wastage and associated costs arising from equipment failure and process downtime, superfluous chemical inventory and spoilage and impaired product quality.

(ii) improved process control

Automated process control could be used, for example, for temperature monitoring and control of steam supply; pH monitoring and chemical dosing. These are generally proven control strategies which can help to optimise processing conditions, thereby improving efficiencies, reducing wasteful use of resources such as chemicals and water and improving quality control with resultant cost savings. Such control equipment is readily available commercially. At the simplest level, flow meters could be installed to monitor and record all relevant material flows for information and assessment purposes.

TABLE 5.8: Potential Waste Minimisation Measures

OPTION	TECHNICAL	ENVIRONMENTAL	ECONOMIC
inventory control	simple technique	minimises waste from excess chemicals & spoilage	low cost - savings in chemicals and waste discharges
temperature, pH & flow monitors and controllers	proven techniques to optimise process conditions and improve quality control	minimises wastage of materials and unnecessary waste discharges	initial capital investment offset by reduced rework costs
waste stream segregation	requires modifications to pipework, floor drainage & sump arrangement; requires changes in control &/or operating procedures	facilitates reuse and effective treatment for reuse	capital investment in pipework, control and civils
installation of steam coils for condensate recovery	requires equipment replacement or retrofit and modifications to pipework	water & energy conservation; effluent reduction; reduced water softening chemicals	potentially significant capital investment offset by savings in water, chemical and energy costs
heat exchange between hot effluent and cold water	requires installation of heat exchangers	energy conservation	initial capital investment & increased maintenance costs offset by savings in energy costs
reuse of bleaching rinse water as scouring rinse water	proven technique; requires additional equipment & pipework	reduces water usage & effluent generation	moderate cost, offset by savings in water and effluent conveyance

5.5.2 Longer-Term Measures

Waste stream segregation would be required for implementation of any of the options discussed below. This would necessitate alternative pipework and drainage arrangements which may not be easy to implement with the existing site layout. However consideration should be given to this strategy in any future site development.

(i) equipment changes

Between 12% and 24% of water consumption is accounted for in condensate losses from the use of direct steam injection (see Table 5.6a). Hence there is potential for significant water and energy savings by installing steam coils to allow return of condensate to the boiler. This would also reduce proportionately effluent volume and the load on the water softening plant, with reduced consumption of softening chemical. Retrofitting of steam coils, if these can be accommodated within the existing reactors, or replacement of existing reactors with new reactors fitted with such coils, may require potentially significant capital expense. This would be off-set by savings in operational costs, including energy costs for steam generation.

Further energy conservation conceivably could be achieved by exchange of heat from hot process effluents to cold feed water. This would require modifications to install a pumped effluent system and heat exchangers. There could be operational problems due to the nature of the effluent, e.g. scaling and solids deposition in the pipelines and equipment, and potentially high maintenance requirements. Hence this option requires careful technical consideration. By default, reducing the plant heat load reduces steam consumption, boiler blowdown, consumption of boiler feed water softening chemicals and boiler stack emissions.

(ii) direct recycling

Dilutely contaminated rinse water potentially could be reused without pre-treatment e.g. scouring rinse water reused as desizing rinse water. With the batch mode of operation in use at the dye house, implementation of this operation would require at least additional pipework, storage tanks and transfer pumps, with associated instrumentation and control features.

Savings in water and chemicals could also be achieved if it is possible to reuse dye bath solutions for successive batches. This option would also require additional equipment, pipework and associated control, including analytical and chemical dosing procedures to reconstitute the dye solution to a composition acceptable for dyeing, and more rigorous scheduling of similar dye batches. Trial implementation could be considered to determine the number of reuse cycles before effluent becomes too contaminated for further reuse. This test work would require installation of a temporary collection and storage system for the waste water and evaluation of the effect of repetitive uses on the characteristics of waste water and on product quality.

The effluent rate is directly proportional to water consumption, so any reduction in water usage will achieve a proportionately equivalent reduction in effluent discharge volume. The pollution load will be unchanged however with a more concentrated effluent. This will increase the discharge surcharge unless suitable treatment is applied to the effluent to specifically reduce the polluting load. It should be noted that most treatment technologies do in fact operate more efficiently with a concentrated feed.

(iii) remediation for reuse

Conceivably a closed loop treatment system similar to that proposed by the Pollution Research Group (WRC, 1987a) could be designed for this dye house. The economics of such an operation would be affected by the required scale of equipment, and costs for equipment, utilities and other waste management needs such as disposal of residual concentrates. To explore the cost-effectiveness of such a system, without detailed design or economic analyses, cost data given in WRC (1987a) for a hyperfiltration treatment plant was extrapolated to suit a design basis defined for conditions at this case study company. Assumptions used to derive this design basis and cost calculations which have been made for this evaluation are summarised in Appendix E. The results are discussed below.

5.5.3. Preliminary Economic Evaluation Of A Hyperfiltration Treatment Plant

The design basis assumed that general improvements in water management practices could first reduce water use in each dye operation and for plant washing by 10% of current estimated water use in these activities. The hyperfiltration plant was assumed to recover 80% of water for reuse. Together with implementation of direct reuse of bleaching rinse water for scouring, there would be a net water reduction of 40% of total current water consumption. This reduction would achieve savings from reduced water costs and effluent conveyance costs.

However sulphate surcharges would increase, unless additional measures are taken to reduce the residual level of sulphates in the effluent discharged to sewer. To do so, requires additional chemical dosing in the equalisation tank. Higher costs would be incurred for treatment chemicals (lime) and for sludge disposal. The cost implications of these alternative management actions have been examined. Results of the economic evaluation are summarised in Table 5.9.

TABLE 5.9: Summary Of Economic Evaluation Of Water Recycling Scheme

Cost Component	Value of Cost (R)	
Capital Cost	48,000- 89,200	
on-site treatment option for sulphates	none, i.e. no lime dosing: savings reduced by higher sulphate surcharge	lime dosing to avoid sulphate surcharge
operating cost for hyperfiltration plant	23,000	23,000
lime cost for dosing	-	64,600
disposal cost for $CaSO_4$	-	4,700 (i)
Total Operating Cost	23,000	92,300
Cost Savings	26,000	45,000
Net Savings	3,000	-47,300
Pay Back	> 16 years	

note:

(i) assumes that slurry is dewatered in filterpress to reduce sludge volume before disposal

This simple economic assessment clearly indicates that it would not be economically viable for the case study company to operate an on-site hyperfiltration plant for treatment of water for recycling. Without being able to cost-effectively reduce sulphate concentration in the balance of the effluent, the higher surcharges which would be incurred reduce the potential operational cost savings. This penalty is incurred even though the actual load of sulphate in the effluent is unchanged - it is just less diluted. Excluding this surcharge, net cost savings of approximately R22,000 could be realised. On this basis, the estimated pay back would be between two and four years, reflecting much more favourable economic viability for on-site water treatment and recovery.

5.5.4 Company Response

Water conservation was not a priority for company management who were concerned about the potential effect of such measures on product quality. Use of a water treatment and recycling plant by a major textile operation in Natal (where drought conditions motivated higher water supply costs as a means of encouraging water conservation) was believed to have been unsuccessful due to product quality problems[4] . It has not been possible to ascertain the actual situation.

There was also resistance to any process changes which would make an inherently simple operation more complicated.

5.6 CONCLUSIONS

The objective of this case study has been to assess the potential for waste minimisation at a small garment dye house from a preliminary review only of current operations, waste generation and available literature on waste minimisation opportunities in the textile industry. The small-scale and informal organisational structure of this case study operation precluded detailed site investigation for resolution of material balances. Furthermore a lack of formal record keeping rendered completion of the EPA worksheets impracticable.

Nevertheless this assessment has revealed useful information which can be used as a basis for deciding whether to continue with more detailed assessment, and the direction in which such assessment should be focused for achieving meaningful and cost-effective waste minimisation.

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[4] communication with company management

It is apparent that current waste management practices and treatment technologies are unable to treat dye house (and, by association, textile processing) effluents to a consistent and acceptable quality for reuse or for discharge. Moreover, they fail to address potential for water conservation and chemical recovery. To date there has been a leniency in the enforcement of effluent standards. This is due partly to the perceived difficulties of cost-effectively treating inorganic wastes generated by small scale operators. Coupled with lower cost options for off-site effluent treatment and waste disposal, there is limited incentive to improve environmental performance.

There is some long-term, university based research which is addressing ways of improving the efficiency of textile processing reactions, thereby reducing waste at source, but as yet there would appear to be no proven cleaner technology alternatives to current applications of the surface chemistry and processing technology. However reduction in the discharge of waste from textile processing is being achieved elsewhere as part of waste minimisation programmes, driven principally by concerns about availability of water of adequate quality and increasing costs of water supply and waste handling and treatment.

Based on reported waste minimisation successes, there are a number of water conservation measures which conceivably could be implemented at this dye house. These include procedural changes and, more expensive, treatment technology for recycling of water. The viability of these measures will depend on the required quality of process water, raw material costs, cost-effectiveness of an appropriate system, and willingness of the operator to adopt new techniques. At present, there is resistance to change and the perceived complication and expense associated with on-site effluent management.

A preliminary evaluation of a hyperfiltration plant for water treatment has indicated that it would not be economically viable as a consequence of higher surcharge penalties for concentrated sulphate containing effluent. On-site lime dosing for maximum removal of sulphates would not be cost-effective due to the high lime requirements. However there are other opportunities for improving the efficiency of existing process operations, for example through greater use of process control, recovery of steam condensate, direct recycling of rinse water and general improvements in operating practices. These options should be investigated and evaluated further.

CHAPTER 6

CASE STUDY: A METAL FINISHING FACILITY

6.1 INTRODUCTION

This chapter describes the activities and results of a waste minimisation assessment undertaken at a metal finishing facility. Of the manufacturing wastes generated by this case study operation, it is heavy metal contamination, consisting principally of chromium, in effluent discharged to municipal facilities which is of greatest concern to local authorities. As shown in section 4.3.2. this waste type, although small in volume, has a high hazardous content (almost 87% by weight). Periodically penalties have been imposed on the company for discharge of higher than permitted levels of heavy metals, principally chromium, to the sewer. These penalties, which are in addition to standard effluent discharge costs and sludge management costs, motivated willingness by the company to participate in this waste minimisation assessment to identify measures by which this loss can be avoided.

For the purposes of this dissertation, the scales of operation and infrastructure have been categorised as "medium" scale. The company employs approximately 200 employees, including process operators, professionally qualified engineers and a designated management hierarchy. However there is no clearly defined responsibility for waste management, and no apparent accounting for waste management costs or allocation to production centres. There is limited on-site equipment and facilities for monitoring of waste streams. sampling and analytical procedures which are carried out are used for process control purposes only. There is no metering of point uses of water and sources of waste.

In contrast with the case study reported in chapter 5, this company has structured and distinct process operations, more orderly production scheduling and higher level of operating and engineering skills on-site. Hence it was appropriate and possible to conduct more detailed site specific investigations than were carried out in the first case study. The complete waste minimisation methodology, depicted in Figure 2.4, was implemented for this assessment. The programme of work included:-

- discussions with company personnel;
- a review of water and effluent records (site records and those of the local municipality);
- site visits and a review of plant drawings and operating records;
- literature reviews of process technology and waste management options in relation to hard chrome plating and chromium containing wastes;
- a monitoring programme for the chrome plating plant;
- a monitoring programme for the effluent treatment plant;
- preliminary evaluation of proposed waste minimisation options.

Background information on process operations, waste characteristics, current waste management practices and environmental impacts of chromium is summarised in section 6.2. The review of process technology and chemistry is given in Appendix F. Section 6.3 reviews proven waste minimisation measures and related waste management concepts reported in published literature. Against this background of information, the waste minimisation assessment was carried out. This is described in section 6.4, while detailed results and material balance calculations are reported in Appendices H, I and J. The findings of a preliminary evaluation and feasibility analysis are discussed in section 6.5.

6.2 BACKGROUND

6.2.1 Process Description

Figure 6.1 illustrates the principle process operations in use at this case study company. These include metal component fabrication stages and surface treatment processes (metal finishing), of which the most important are hard chrome plating, phosphating and painting. Generally with each of these is associated cleaning, stripping and rinsing stages. Utility operations include provision of hot oil for heating; cooling water systems and lubricating oils and solutions. Pollution control operations include the effluent treatment plant; a vacuum filtration system for recycling of machining fluids; extract ventilation systems; and water scrubbing systems for control of gaseous emissions. Unit operations are summarised and briefly described in Table 6.1.

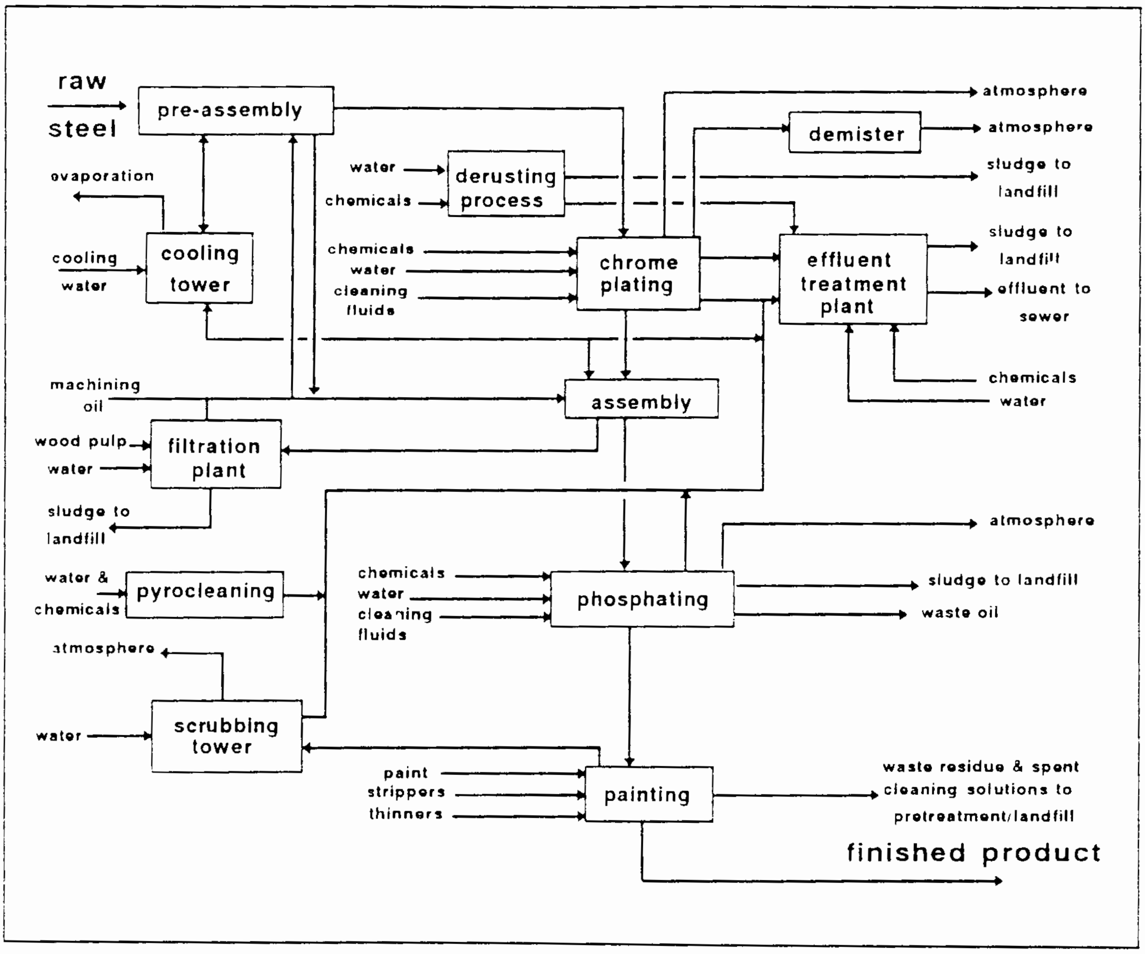

FIGURE 6.1: Flow Diagram Of Metal Fabrication And Finishing Operations

TABLE 6.1: Summary of Process Operations

PROCESS OPERATION	FUNCTION
Fabrication metal cutting, drilling	
grinding, polishing & buffing	improve surface appearance, cutting characteristics and wear ability
Heat Treatment: annealing	stress relief and to improve machinability of the metal work piece
mechanical cleaning: abrasive blasting	cleaning & surface finishing
Chemical Cleaning: vapour degreasing	to remove soil soluble in solvent
pyrocleaning	clean swathe out of tubes prior to complete assembly
Chrome plating plant: soak cleaning	to remove gross soil, oil & metal oxide
electrolytic cleaning	to remove remaining soil after chemical cleaning & to activate metal surface
water rinsing	to rinse alkaline solution and surface soil from work pieces
etching	to activate metal surface
chrome plating	to deposit different metal surface coating with different properties to base metal: corrosion or wear resistance; improved appearance
chemical rinsing (neutralisation)	to reduce hexavalent chromium (adhering to work pieces) to trivalent, to improve rinse-ability
water rinsing	to rinse plating solution from work pieces
metal stripping	to salvage product rejects
Phosphating plant:	to improve corrosion resistance under paint; provide suitable bonding surface for waxes & oils; improve metal forming capability (extrusions); base for lubricants
a) degreasing	to remove surface grease
b) water rinse	
c) zinc phosphating	to impart corrosion resistance
d) water rinse	
e) passivating	to impart anti-rust properties
mercedes phosphating	phosphate treatment for mercedes components
painting:	final surface coating

TABLE 6.1/cont.: Summary of Process Operations

PROCESS OPERATION	FUNCTION
derusting	to remove rust from rusted work pieces (incl. static water rinse and rust-proofing)
Utilities: hot oil	tank heating
cooling water	tank cooling
blower	tank agitation using air
filtration plant	to filter lubrication fluids for recycling
Pollution control: effluent treatment	to reduce hexavalent chromium to trivalent; neutralise effluent & precipitate hydroxide metals from solution; remove & dewater sludge
air cleaning: - wet scrubbers	remove polluting contaminants from atmospheric discharges
extract ventilation	work place safety - to dilute & remove hazardous contaminants

Figure 6.2 illustrates in greater detail the processing stages in one of two parallel chrome plating lines, Line 1. This is identical to the alternative line, Line 2, except that different chromic acid solutions are used in each line; all entrained chromic acid condensate from the scrubbing system, which is common to both lines, is returned to Line 1; Line 1 is used generally to treat the larger work-pieces; and Line 2 is used for the smaller work-pieces.

Chromium-containing effluents from both plating lines are discharged from process tanks downstream of plating to a dedicated sump, designated S1, from which effluent is delivered to the chromium reduction stage in the effluent treatment plant. This is illustrated in Figure 6.3.

The effluent treatment plant is designed to neutralise acidic and caustic effluent, to reduce hexavalent chromium (Cr(VI) and to precipitate chromium and other heavy metals as hydroxide sludges. These sludges are separated from the bulk effluent in a plate separator and thickened by gravity settlement prior to removal from site by contracted waste hauliers for disposal at a Class 1 landfill site. A

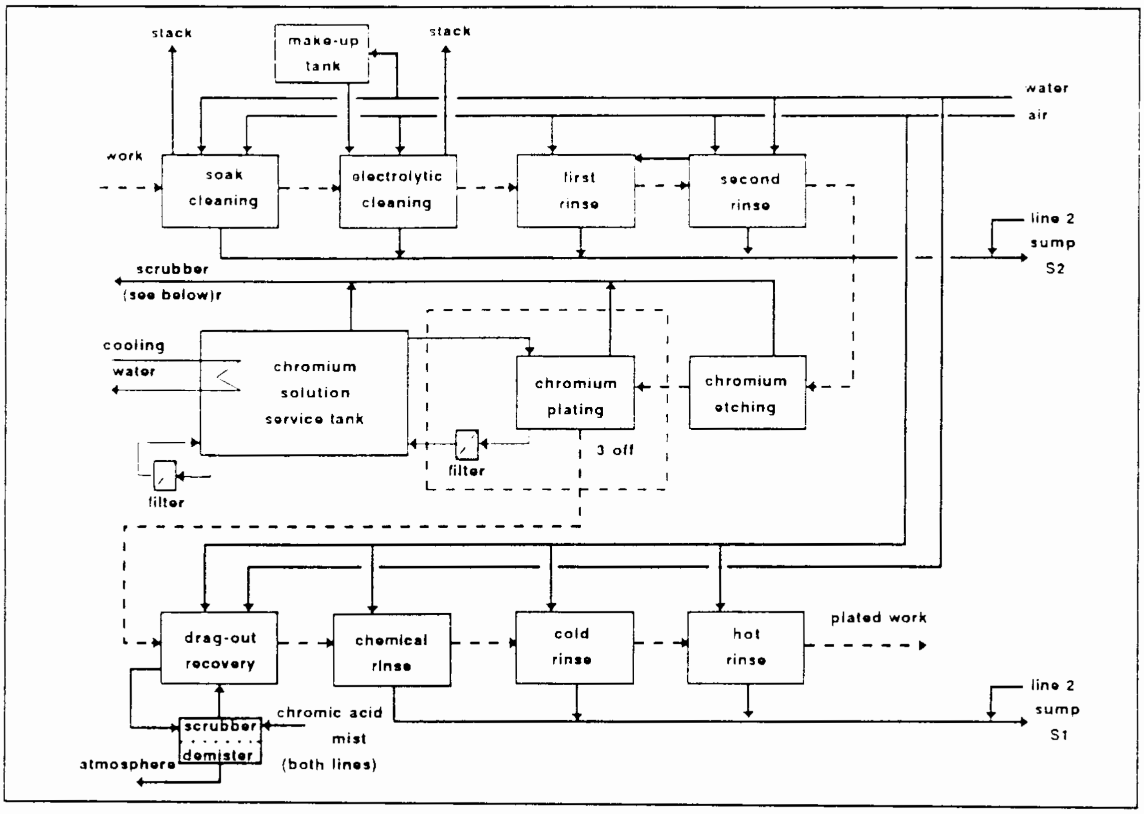

FIGURE 6.2: Flow Diagram Of The Chrome Plating Plant (one of two plating lines)

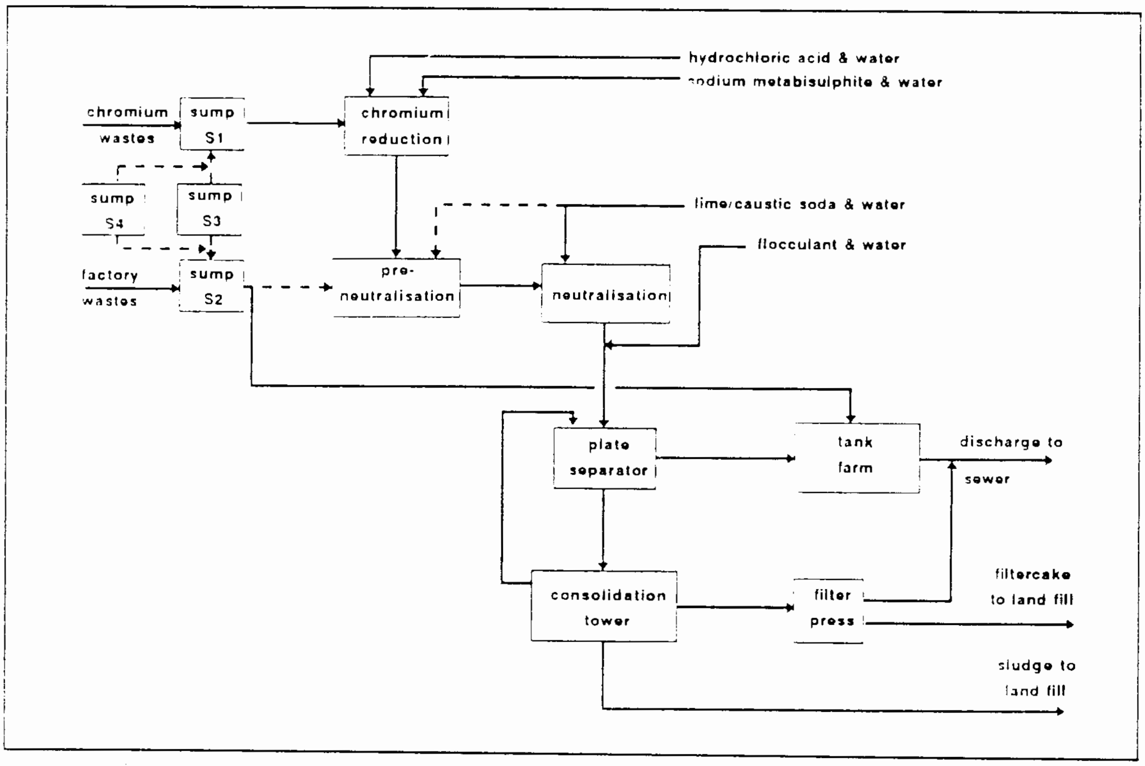

FIGURE 6.3: Flow Diagram Of The Effluent Treatment Plant

small sludge flow is dewatered in a filter press yielding filter cake for disposal. All other effluent from the processing stages upstream of the plating tanks and from other production areas in the facility are pumped directly to the tank farm. Treated and untreated effluents are blended prior to discharge to the sewer.

6.2.2 Overview Of Waste Generation

Waste types and characteristics typical of these metal finishing operations are summarised in Table 6.2. The wastes comprise largely organic material, acids, alkalis and heavy metals, principally chromium and zinc. These are classified as hazardous wastes. The Department of Environment Affairs (1992b) study has categorised 84% of wastes from the metal products sector as hazardous, most of which (99%) is allocated to solid and liquid waste, such as that present as constituents of process solutions. This excludes waste water for which estimates are not given. Yet metal finishing processes such as electroplating and phosphating are water intensive (WRC, 1987b). Significant quantities of water are used in rinsing operations to remove residues of cleaning or plating chemicals. This generates significant quantities of contaminated effluent. For this assessment, it is the chromium contamination of effluent and sludges which is of principal concern in terms of waste management practices and environmental impacts.

6.2.3 Current Waste Management Practices

(i) <u>on-site treatment</u>

The effluent treatment plant, described in section 6.2.1 and shown in Figure 6.3, pretreats liquid effluent prior to discharge to the municipal sewer system. In terms of local by-laws, effluent quality is expected to comply with a discharge constraint of 50 ppm for total metals; no distinction is made between different metal species. No monitoring is carried out on-site.

(ii) <u>local council responsibility</u>

It is the responsibility of the municipality to monitor effluent discharges from the effluent treatment plant. Grab samples are analysed for chemical oxygen demand, pH, conductivity, cyanide (Cn) and heavy metals, including copper(Cu), total chromium (Total Cr), zinc (Zn), cadmium (Cd), nickel (Ni) and lead (Pb). Analytical results are used to compute effluent treatment costs and surcharges for exceeding discharge constraints.

TABLE 6.2: Summary Of Expected Waste Types

PROCESS OPERATION	ASSOCIATED WASTES
Fabrication metal cutting, drilling	metal dusts, grindings & cuttings; spent abrasives; waste lubricants & coolants
grinding, polishing & buffing	lubricants containing abrasive & metal grit e.g. aluminium oxides & silicon carbide.
Heat Treatment: annealing	combustion gases
mechanical cleaning: abrasive blasting	spent blasting material - sand, steel, shot, slag products, aluminium oxide, silicon carbide
Chemical Cleaning: vapour degreasing	residual waste: solvents (trichloroethylene; perchloroethylene: methylene chloride); sludges; volatile emissions
pyrocleaning	spent solution
Chrome plating plant: soak cleaning	waste inorganic alkaline solution: inorganic & organic sludges containing abrasives & chemicals (wetting agents, rust inhibitors, anti-settling agents)
electrolytic cleaning	waste alkaline solution with sludge waste (as above)
water rinsing	alkaline waste water, dilutely contaminated with inorganics (phosphates, silicates, sodium)
etching	spent bath solution with high concentration of hexavalent chromium in acid medium; may contain fluorides, organic compounds, sulphates, inorganics, chlorides
chrome plating	as above; filtered sludges; spent filter cartridges
chemical rinsing (neutralisation)	spent alkaline bath solution, containing soluble chromium and other contaminants from plating & heavy metal contaminated sludge

TABLE 6.2/cont.: Summary Of Expected Waste Types

PROCESS OPERATION	ASSOCIATED WASTES
water rinsing	waste water dilutely contaminated with chromium and other contaminants from plating
metal stripping	waste stripping acid, with metal contamination
Phosphating plant:	
a) degreasing	oil and grease
b) water rinse	alkaline contaminated rinse water
c) zinc phosphating d) water rinse e) passivating	iron- & zinc phosphates & phosphoric acid acidic contaminated rinse water
mercedes phosphating	acidic effluent; zinc phosphates; steel wool
painting:	waste solvents and organics, with heavy metal content; volatile organic emissions empty paint containers
derusting	waste acid effluent & sludge containing heavy metals
Utilities:	
hot oil	combustion gases
cooling water	mineralised effluent
filtration plant	spent wood pulp; oily water effluent
Pollution control:	
effluent treatment	semi-treated effluent (to sewer) and metal hydroxide sludge (to landfill)
air cleaning: - wet scrubbers	waste slurry for disposal? waste scrubbing water contaminated with organics & heavy metals
extract ventilation	atmospheric discharges

The municipal treatment facility itself must comply with a discharge constraint of 0.5 mg/l for total chromium and 0.05 mg/l for hexavalent chromium[1]. The treatment sludges moreover must be analysed and disposed of in accordance with guidelines for land disposal of wastes (see section 4.5.2).

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[1] Ordinance No. R.553.5 April 1962

(iii) waste contractor responsibility

Sludge and solid wastes from this metal finishing process are managed by a specialist waste hauling- and disposal company. Consignments are sampled and analysed to determine pretreatment requirements prior to land disposal within a Class 1 site. Chromium wastes are chemically treated to reduce Cr(VI) and to precipitate Cr(III) hydroxide. Acidic wastes are neutralised. Treated effluents and sludge wastes are trenched with lime to maintain alkaline soil conditions. Oily wastes are usually discharged into lagoons at the waste disposal site, although some work is being done on oil recycling.

6.2.4 Environmental Impacts Of Chromium

Chromium waste discharged from typical metal finishing operations has implications for:-

- the immediate environment, including the work place and plant vicinity as a consequence of spills and atmospheric discharges;
- municipal sewage treatment facilities, which utilise biological treatment systems;
- landfill management, responsible for safe treatment and disposal of liquid-, sludge- and solid wastes.
- the biosystem; and
- risk to humans.

(i) occupational risks

Hexavalent chromium is a recognised toxic material with carcinogenic properties. The primary causes of human contamination are absorption through the skin and inhalation. Effects of these are described by Raghu & Hsieh (1989) as follows:

> " Respiratory effects caused by chromium include ulceration and perforation of the nasal septum, respiratory cancer, irritation of mucous membranes, sneezing, irritation and redness of the throat and generalised bronchospasm. Chromium also causes skin effects such as primary irritant dermatoses and allergic eczematous contact dermatitus."

Despite concern about these effects, acute systematic poisoning is reported as being rare (Raghu & Hsieh, 1989). In an operating environment proper design of ventilation systems and use of appropriate protective clothing and safe operating practices should minimise potential for such health effects. However it is clearly important that there should be an understanding of these health risks to motivate compliance with safe practices.

(ii) impact on sewage treatment systems

Biological waste water treatment systems are not suitable generally for the heavy metals contained in chromium laden waste. The metals may poison the bacteria, though activated sludge reportedly can tolerate up to about 50 ppm of chromium without undue inhibition of the bacterial activity (Kirk-Othmer, 1979). Hickey etal (1989) report that heavy metals upset anaerobic digestion of municipal sludges, seemingly by inhibition of biological degradation. Clearly this would also impact on landfill reactions.

Imai and Gloyna (1990) have investigated experimentally the chemistry of chromium in the activated sludge process. Their work showed trivalent chromium Cr(III) to be removed more efficiently than hexavalent chromium Cr(VI), principally by adsorption to activated sludge floc. Lesser amounts of chromium precipitate as metal hydroxides. Whereas higher pH enhanced removal of Cr(III), it had the opposite effect on Cr(VI) removal. However toxic effects of Cr(VI) were observed only at pH 7. Imai and Gloyna (1990) suggest this may be due to changes in Cr(VI) speciation and predominant bacterial species with varying pH.

These results demonstrate the greater difficulties in removing Cr(VI), particularly at the higher pH values which are preferred for effluent discharged to the sewer system. While Cr(III) can be removed more readily, accumulation of chromium in biological treatment sludges contaminates the wasted sludges, which themselves may be classified as hazardous. This creates a difficult sludge management problem for the municipality, adding to problems of water quality management.

(iii) impact on landfill management

Conventionally Cr(VI) is removed from a soluble state in waste solutions by reduction to Cr(III) and precipitation as an insoluble chromium hydroxide. This is deemed to be non-toxic and inert (Kirk-Othmer, 1979), and is the form in which chromium is disposed to landfill sites with addition of lime to maintain alkaline soil conditions.

There is some concern however about long-term stability of chromium wastes in landfill sites. Acid deposition from acidic precipitation, itself an environmental pollution problem, may result in acidic soil conditions. Below a pH of 5 (Raghu & Hsieh, 1989) the chromium hydroxide is soluble and therefore can be transported in leachate solution and migrate through the soil. Hence there is potential for spread of contamination beyond the designated landfill area and moreover potential for contamination of surface water (from lateral migration) and ground water (from downwards migration). Furthermore, without reviewing in depth the chemistry of chromium in soil[2], it should be noted that thermodynamically it is possible for Cr(III) to reoxidise to Cr(VI) with its associated higher toxicity[3]. Hence the behaviour of chromium in soil has implications for long term liabilities associated with on-going management of landfill sites, beyond the useful life of the landfill itself.

(iv) impact on the biosystem

Being soluble in water Cr(VI) can be absorbed by aquatic plants and animals, with toxic effects. Excessive concentrations of Cr(III) are also reported to have toxic effects particularly on fish (Raghu & Hsieh, 1989). Biological growth in aquatic environments and plant growth on land may be inhibited. This has implications for revegetation of closed landfill sites.

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[2] Current research being done in the Department of Chemical Engineering at UCT is specifically addressing this.

[3] The rate of the oxidation reaction is a complicated function of conditions within the landfill, and is beyond the scope of this study.

Soluble salts contained in treatment chemicals which are used to treat chromium wastes may also be harmful to aquatic life. For example, sodium (Na) increases salinity, possibly changing osmotic pressure in the water (Sax, 1974). As described in section 5.2.4, sulphates have a high oxygen demand which may deplete the natural oxygen supply, resulting in localised anaerobic conditions. Some inorganic sulphates are insoluble. The particulate matter may increase turbidity of the water or deposit on the bottom of stream beds. This deposited layer may interfere with the passage of light and oxygen needed for natural biological activity.

(v) human risk

Risk to people away from operating sites is a consequence of emissions from these sites as atmospheric discharges or as a result of accidents, typically during transportation of waste materials, or pollution of water bodies and soil. Concern about environmental effects and risks to the public from contaminated ground water supplies has driven moves in the U.S. to ban land disposal of spent wastes specifically from metal finishing operations, including metal hydroxide sludges (Isham, 1988a).

6.3 PROVEN WASTE MINIMISATION OPTIONS

A literature review was undertaken to identify waste minimisation measures which have been implemented successfully in other metal plating operations, as well as recent developments in cleaner technology and other waste management practices in relation to chrome plating operations. Some specific case study examples are summarised in Appendix G. A more general discussion of generic type measures is given as follows:

6.3.1 Source Reduction

Chapter 2 has described good house keeping techniques as general measures designed to avoid material losses from faulty operations or careless practices. Such techniques would be applicable to metal plating operations. Process specific examples of source reduction opportunities for metal plating operations in general and for chrome plating technology are discussed below.

6.3.1.1 Changes In Input Materials

(i) replacement of solvent-based cleaners

Alkaline cleaning solutions are available as alternatives to chlorinated solvents for some cleaning applications, but require high alkalinity and operating temperatures. The high temperature is necessary to allow the cleaner to react with organic materials. Greases and oils are saponified and react with the alkaline components to form water soluble species which can be rinsed from the work-pieces (Borruso, 1992). In some applications ultrasonic baths may be required to provide greater agitation, as a mechanical cleaning action (P.A.Consulting Group, 1991), to help in removing material from the cleaned surfaces and maintaining a uniform cleaner concentration. (In chlorinated solvent cleaning it is the chemical and vapour phase properties of solvents themselves which provide 90% of the cleaning effect, with only 10% due to mechanical action (Dalton, 1991).

Environmental advantages of this material substitution include reduced toxicity of the cleaner chemicals, and elimination of volatile organic vapours and organic sludges. However use of aqueous-based solutions also increases effluent treatment requirements and/or may be a less treatable waste material due to use of chelating compounds as stabilisers in the cleaner formulation. These compounds are used to form complexes with metal ions, thereby inhibiting precipitation of metal hydrous oxides in the alkaline conditions of the cleaning solutions. Consequently they also inhibit conventional metal-precipitation treatment. Different pH conditions and excess chemicals are usually required to dissociate the complexes and precipitate the metal (Eilbeck and Mattock, 1987).

There are reported efforts to extend the life of cleaning solutions using ultrafiltration to remove organic waste constituents. In one case study, a life of at least one year, at the time of reporting, had been effected (Dalton, 1991). No details of the cleaner formulation were given. With the presence of chelated metal compounds, recycling may result in a buildup of dissolved metal contaminants which impact on the quality of rinsing. The success of this technique will clearly be process and application specific.

(ii) substitution of metals with less toxic alternatives

There is great interest in the potential to plate chromium from the trivalent form (Cr(III)), rather than the hexavalent form (Cr(VI)). This would avoid the need for the pre-treatment stage in a conventional effluent treatment plant in which Cr(VI) is reduced to Cr(III). Hence there are associated savings in effluent treatment costs. Moreover there are productivity and operational advantages. Trivalent chrome plating is a more efficient process as the charge requirement per unit of metal deposited is half that of hexavalent chromium. Trivalent chromium is reported to have a higher conductivity than hexavalent chromium, such that a more dilute solution can be used (5-7 g/l instead of 200-250 g/l) (DOE[4]). Consequently the drag-out concentration of chromium will be lower, thereby reducing rinse water requirements. Clearly there is significant associated potential for cost savings due to reductions in chemical, power and waste treatment requirements as well as reduced capital costs for smaller baths (DOE[4]). Environmental advantages include a less hazardous working environment and reduced emissions.

There are a considerable number of literature references describing trivalent electroplating baths, but this process would appear to be have been used only for decorative applications i.e. thin deposits. Benaben (1989) explains that thicker deposits, which are required for hard chrome applications, tend to be microporous and to exhibit declining cathodic efficiency. In terms of the plating mechanism (see Appendix F), it is deemed impossible to deposit chromium from the trivalent ion which forms a stable complex, $Cr(H_2O)_6^{3-}$, in solution. Kasaain & Dash (1984) report that research work continues to investigate alternative catalysts which would modify the chemical deposition reaction to enhance efficiency, e.g. by the use of methanol and formic acid. Benaben (1989) describes a process, investigated in a pilot plant study, which uses an aqueous solution of trivalent chromium and hydrochloric acid. Experimental work reportedly has demonstrated deposit characteristics similar to those obtained by conventional hard chrome plating. Graphite anodes are used instead of lead, and chlorine is evolved, necessitating a good ventilation

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[4] UK Department of Environment booklet.

system for operator safety. Hence there are implications for improved design and operating practices.

Recent developments in membrane technology have also facilitated developments in trivalent chrome plating. A company in the U.K. is marketing a system which uses an ion exchange membrane casing around the anodes to separate hexavalent ions (oxidised from trivalent ions at the anodes) and trivalent ions in the bulk solution (DOE[4]). The required equipment modifications can be retrofitted to existing plating configurations. However no successful applications for hard chrome plating are known (Reeve, 1993). Even for decorative applications successful trivalent chrome plating has been limited. The process is reported to be very sensitive, requiring tight control parameters and a complexity of additives (Reeve, 1993).

(iii) use of low concentration baths

New process developments favour use of lower concentration baths in the interests of conserving raw materials. However there are implications for more rapid contamination of the plating baths and/or greater sensitivity to contaminants, and hence the need for more frequent analyses and chemical addition (Altmayer, 1992).

6.3.1.2 Simple Process Modifications

(i) water conservation and drag-out reduction

Water conservation is interrelated with, and largely dependant on, measures which reduce loss of plating chemicals from the plating baths such that water usage for rinsing can be reduced. Savings are effected from reduced water consumption and effluent treatment costs. Waste minimisation techniques in relation to water conservation in plating operations include:

- provision of increased drain times to reduce the carry-over of process solution which adheres to the work-pieces (referred to as drag-out) (EPA, 1987);

- providing a second drag-out tank. On the basis that each such plating tank is reported to recover approximately 50% of the plating solution adhering to the work (UNEP, 1989), one plating tank may be expected to recover 50% of solution lost from the plating tank, while two drag-out tanks used in series potentially could recover approximately 70% of the drag-out solution. The practicable number of drag-out tanks will depend on a cost-benefit analysis of productivity, capital costs for hardware and operating costs for rinse water supply, effluent treatment and chromium recovery.

- using countercurrent rinse systems by which water flows in the opposite direction to the work. Thus work-pieces are rinsed first in a "dirtier" solution followed by a clean water rinse. Assuming that flow rates are matched, each such arrangement would reduce water usage by 50%.

- using conductivity control for rinse water flow. This is used commonly to automatically adjust rinse water flow rates to the minimum required to maintain a quality of rinse water which still provides effective rinsing of the work-pieces.

- optimising rinse tank design and flow configuration to ensure complete mixing and utilisation of the whole tank volume. Hunt (1988) considers this an important activity in a water conservation programme which requires consideration of factors such as water distribution, rinse water flow control and rinse bath agitation to improve rinsing efficiency. Improved rinsing techniques are reported to have been implemented in the development of low-waste plating technology discussed below.

(ii) increased use of process control, automation and optimisation techniques

Automated process control is usually considered a more efficient, reliable and safer mode of operation than manual control, minimising worker interface with potentially hazardous conditions. However the acknowledged complexity of controlling batch processes provides a need for manual control such as ability to adjust operating conditions to unique circumstances or to ensure completeness of reaction.

Process optimisation offers a technique for improving efficiency of process operations by systematically evaluating the effect of different operating conditions on process performance, so as to identify those conditions which are optimum. Improvements may be implemented by monitoring the effects of gradual process adjustments, e.g. rinsing effectiveness with changes in rinse water rates. There are implications arising from disturbances to process conditions, such as loss of product quality. Increasing use is being made of computer models to optimise process operations without disturbing the process. Wilk and Capaccio (1992) report application of such techniques to chrome plating in relation to pollution prevention by specifically optimising conditions, such as rinse rates, which minimise waste generation. Such techniques are unlikely to be practicable for direct use on site, but would be useful in new design developments.

6.3.1.3 New Technology Developments

(i) alternative processes for hard chrome plating

Alternative methods which have been developed for electrodeposition of chromium include plasma spraying, physical vapour deposition and chemical vapour deposition, sputter deposition, ion-plating and ion-beam assisted deposition. In vapour deposition processes the material is vaporised from its source and transported as a vapour through a vacuum or low pressure gas environment to condense on the substrate work-piece. These processes reduce wastage of plating chemicals, rinse water requirements and emission of volatiles as waste, although chromium dusts may be given off. The technology is still very expensive, and not considered viable for most applications.

6.3.2 Recycling

6.3.2.1 Direct Reuse

Countercurrent rinsing, described in section 6.3.1.2(iv), is an example of slightly contaminated water being reused directly in a process. An extension of this principle is that of reactive rinsing, whereby rinse water is also reused to take advantage of its chemical nature. For example, rinse water containing acids could be used to rinse work-pieces carrying adherent films of alkaline liquid. A neutralisation reaction would take place. Conceivably there is potential for deposition of salts of reaction on surfaces of the work-pieces. Rinsing efficiency as discussed in section 6.3.1.2(iv) would need to be evaluated carefully.

6.3.2.2 Reclamation Technologies

Most of the successful waste minimisation case studies which are reported in literature sources have used recovery systems to either decontaminate spent process solutions and rinse water for reuse in the process, or to recover chromium for use elsewhere. These are being integrated into closed-loop processes which are the subject of research work in Germany and Denmark for development of low effluent and effluent-free production methods for electroplating and metal finishing (Sutter, 1989a; Christiansen & Kryger,1989). The principle of a closed loop process is illustrated in Figure 6.4.

Specific case study examples of reclamation technologies are included in Appendix G. Brief descriptions of those technologies commonly reported for both water and chemical recycling follow.

(i) evaporation

Evaporation can be used to recover concentrated plating solution from contaminated rinse water, with the distillate reused as rinse water. It is deemed to be a relatively simple operation, but there are high energy costs and it is not considered cost effective for treatment of dilute rinse waters. Moreover contaminants are not removed, but are retained within the concentrate resulting in the buildup of contamination which will impair the quality of the plating solution. However evaporation is sometimes used in conjunction with other recovery technology such as reverse osmosis, from which the treated product stream may be too dilute for direct reuse.

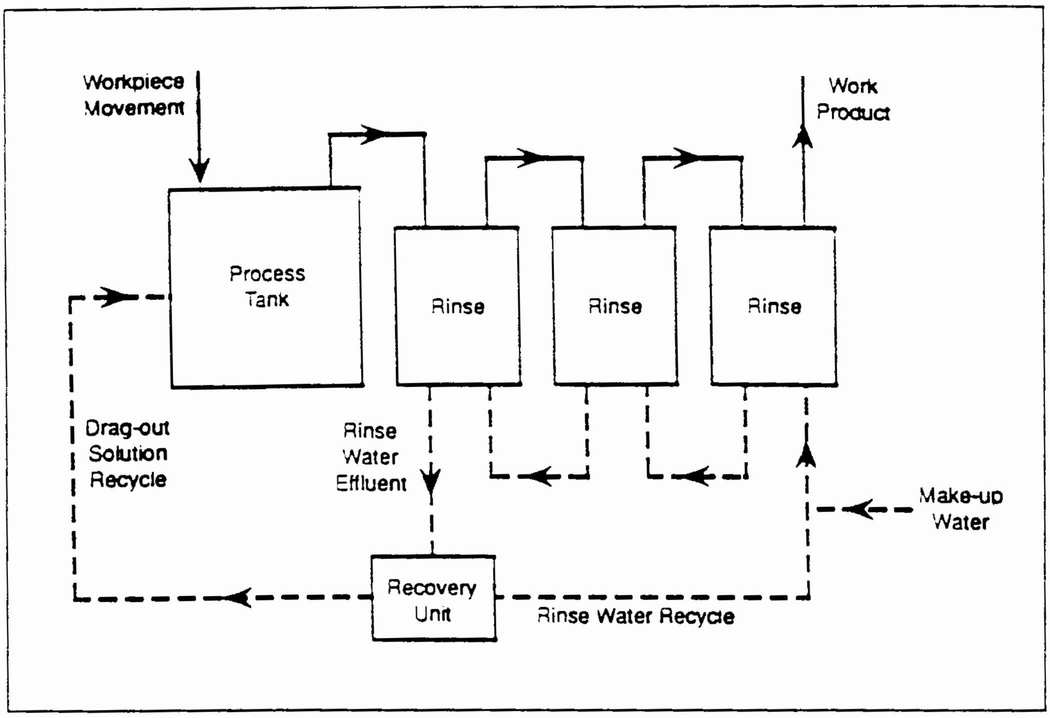

FIGURE 6.4: Schematic Of Closed Loop Electroplating Line (EPA, 1992)

(ii) reverse osmosis (RO)

RO, as a membrane separation process, has been used reportedly successfully for processing of chromium and mixed metal wastes, among others, with reported pay back periods of between 8-36 months. However most of these applications would appear to have been commercial demonstrations, and actual use by industry is unclear. Pre-treatment, including filtration, pH adjustment (depending on the membrane characteristic), and the removal of dissolved organics, colloidal matter and low solubility salts is usually required to protect the membrane. Organics are not removed effectively by RO and aggravate the problem of membrane fouling. Where organics are present pretreatment such as carbon adsorption may be required. This is costly and spent carbon creates a solid waste stream. Regular cleaning of RO membranes with flushing solutions is usually required. It is the associated maintenance and cost of membrane replacement which render this technology unattractive for many applications. Further treatment stages may also be required depending on product quality requirements, for example polishing using carbon adsorption or ion-exchange to remove effectively all of the heavy metals from the water stream (Warnke, Thomas & Creason, 1977), or evaporation of the concentrate stream for reuse in a plating bath.

(iii) ultrafiltration (UF)

Alternatively UF can be used for applications in which complete water purification is not warranted. This may also find use as a pretreatment step prior to RO, removing organic solutes while allowing passage of most inorganic salts (De Renzo, 1981). UF may also be used as a polishing step after precipitation of metal solids.

(iv) ion exchange (IX)

Conventional IX, using a variety of resins, has been demonstrated commercially for recovery of chrome plating chemicals and purification of plating solutions for longer service life (WRC, 1984). Operational advantages of this technology are given as the compact size of the unit; ease of automation compared to precipitation systems; good performance over a broad range of loading conditions; durable resins resistant to severe chemical environments; and effective removal of metal complexes which would not be precipitated as metal hydroxides. This unit operation is reported to be used most frequently as the final or polishing step after other techniques such as RO or precipitation (De Renzo, 1981). Principal operational disadvantages are the need to periodically regenerate spent resins and to manage waste regenerant which will itself be a hazardous material, with associated environmental risks.

(v) electrochemical deposition

Electrochemical techniques include cathodic deposition of dissolved metals; precipitation of metals by means of anodically generated ferrous iron (Fe^{2+}); and electrodialysis (ED) (Pletcher, Walsh & Whyte, 1990). Cathodic deposition processes enable direct recovery of pure metal, which may be valuable for resale, and is termed electrowinning. This process completely eliminates the generation of a metal bearing sludge, but is not suitable for dilute solutions which are characterised by low mass transfer rates (EPA, 1991b).

Metal hydroxide precipitation can be used to remove reduced chromium in the interests of purifying an effluent or to remove cationic contaminants to purify chromate solutions.

(vi) electrodialysis (ED)

ED uses an IX membrane under the influence of an electric field to selectively separate ionic species into segregated product streams, an enriched stream and a depleted stream. These streams may be further treated and/or recycled. Such electrolytic processes have an ease of control facilitated by monitoring of direct electrical signals (Pletcher, Walsh & Whyte, 1990), but this technology is not suitable for varying load conditions and aggressive media. As for RO, pre-filtration, pH adjustment and organics removal may be required. Furthermore iron (Fe) is reported to degrade most common membranes at concentrations greater than about 0.3 mg/l (De Renzo, 1981).

Generally electrolysis is also not economic for treatment of dilute streams which have a high electrical resistance resulting in a high operating cost for electrical power. However electrochemical techniques have been integrated successfully with other recovery operations, such as IX, in closed-loop systems. For example Pletcher, Walsh & Whyte (1990) review such a process in which scrubber water and waste rinse water are treated in a two stage ED unit to purify the water for reuse. This process is illustrated schematically in Figure 6.5.

Metal cations (contaminants) are removed in the first stage by migration through a cation exchange membrane and formation of metal sulphates in reaction with a circulating solution of sulphuric acid. Chromate anions are removed in the second stage through an anion selective membrane with the formation of sodium chromate in reaction with a circulating solution of sodium hydroxide. The sulphuric acid and sodium hydroxide are regenerated in separate ion exchange units with discharge of metal hydroxide sludge as a waste stream and recycle of recovered chromic acid to the plating bath.

WRC (1984) report that, compared with RO, ED can achieve higher concentrations ratios (50 to 100 times compared with 20 times) avoiding the need for evaporation of the concentrate stream containing recovered chemicals. Compared with conventional IX, the combined IX/ED process is a continuous one which requires no regeneration of IX material and associated waste management.

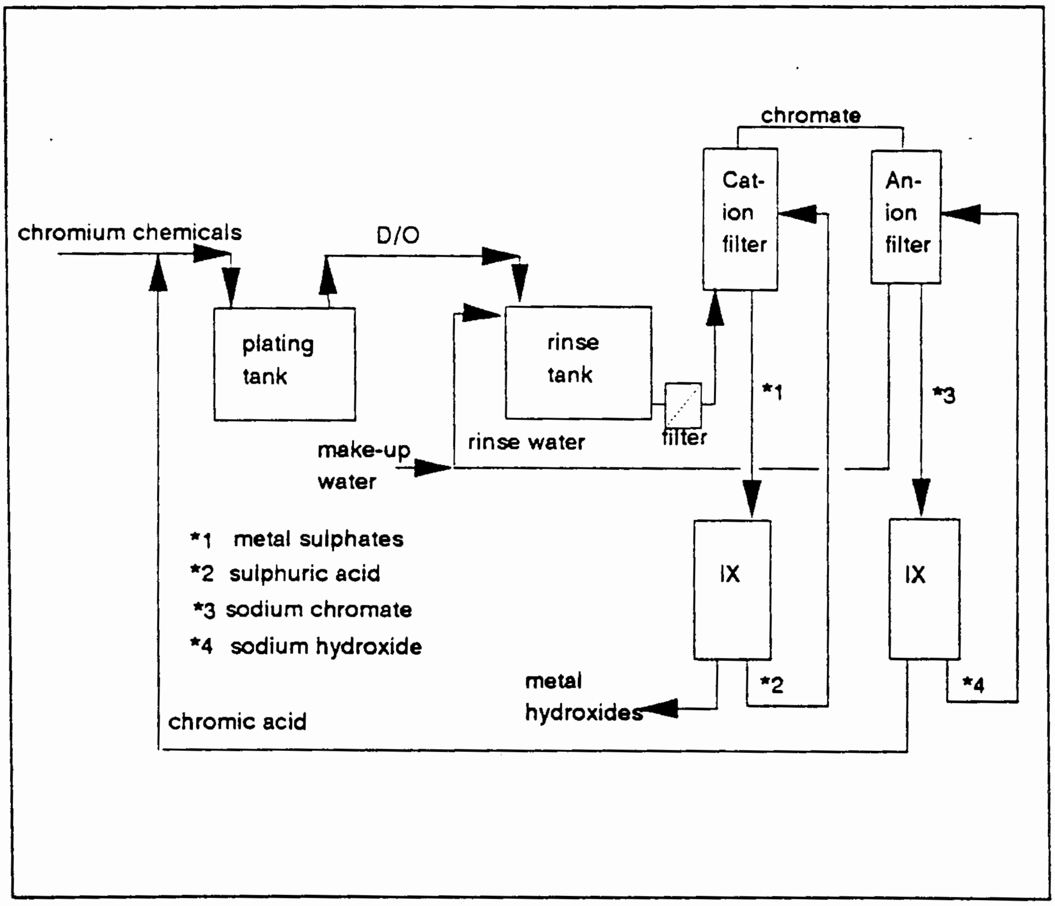

FIGURE 6.5: Schematic Of Combined Ion Exchange And Electrodialysis Treatment (Pletcher, Walsh and Whyte, 1990)

To summarise the above alternative reclamation processes, evaporation is considered costly because of the capital cost of equipment and high operating costs for thermal energy. The more sophisticated technologies are more compact unit operations, but typically incur increased operational costs as a result of the need for specific treatment chemicals, higher maintenance requirements, and a higher level of operational skills. Table 6.2 shows some comparative economics, based on U.S. costs, for the above mentioned technologies. EC is described as being economically more attractive than evaporation (WRC, 1984).

TABLE 6.3: Reported Pay Back Periods For Alternative Chromium Recovery Systems (WRC, 1984)

TECHNOLOGY	PAY BACK (years)
evaporation	4.9
reverse osmosis	4.3
ion exchange	5.2

Specific case study examples, listed in Appendix G, of closed-loop process developments demonstrate payback periods of between 18 months and about three years for large- and small scale operators.

6.3.3 Sludge Management

Management of sludge once it has been generated as a waste is not part of waste minimisation. However given the concerns about leachability of metals from hydroxide sludges (see 6.2.4(iii)), means of minimising this impact should be considered as part of waste management responsibility. One option may be use of phosphates instead of hydroxides for metal precipitation, given the correct pH conditions and presence of insoluble ionic phosphate species. Solubility of metal phosphates reportedly is lower than metal hydroxides, resulting in improved precipitation and reduced leachability (anon, 1988). Sulphide precipitation may be another suitable alternative. Sulphides are described as being more reactive with metal ions than the hydroxyl ion, and therefore more effective in removing metal ions stabilised in solution by chelating compounds (Anderson & Weiss, 1974). These are often present in alkaline cleaning solutions as well as plating chemicals. Heavy metal sulphides are also insoluble over a broader range of pH conditions (WRC, 1984).

Alternatively solidification, in which mixtures of fly ash and lime are added to the sludge to limit mobility of toxic components, may be required (Isham, 1988a). This clearly does not constitute waste minimisation. but rather risk minimisation. Research in metal waste solidification is currently being carried out in the Department of Chemical Engineering at the University of Cape Town.

Metal-bearing sludges are also potential sources of raw materials i.e. as metal repositories. The potential recovery of these metals requires that the sludges be kept separate from other wastes (Hepworth & Beckstead, 1989). This has implications for current sludge management practices.

Sittig (1980) describes technology for recovery of metals from sludges, even mixed plating sludges, including successive liquid extraction processes using acid leaching and organic extractants, and selective precipitation. The viability of these processes would depend on economy of scale, quality of recovered metal and market availability for recovered products. Use of such technology is considered appropriate in off-site centralised recovery facilities as discussed below.

6.3.4 Centralised Recovery Facilities

Centralised recovery facilities (CRF) have been proposed to cater specifically for the types of waste generated by metal processing type operations. In this way the most appropriate technology or combination of technologies can be used for treatment of metal and organic containing waste-waters and sludges, for recycling and resource recovery; the treatment problem is removed from the local municipal sewage treatment facilities. Technologies reportedly used include chemical precipitation, leaching, electrowinning and evaporation (EPA, 1991b).

Generalised studies in the U.S. have demonstrated that substantial savings can be attained when more than 10 facilities are combined (WRC, 1984). Reinhardt (1985) reports the establishment of a CRF which services 60 plating companies. Rinse water is purified and metals reclaimed using IX technology. The feasibility of a large scale operation using phosphate precipitation for selective separation of metal values from mixed metal sludges has also been verified by the Hazardous Waste Engineering Research Laboratory of the US EPA (EPA, 1988). Residues quantities are reduced and the quality of metal products is reported to be suitable for use as feedstock or for conversion to other products. In Germany there have been investigations into large scale centralised waste paint processing plants (Sutter, 1989a).

6.3.5 Initiatives In South Africa

In a similar way to the investigation of the textile industry, the Water Research Commission (WRC) has reviewed the situation in water and effluent management in the local metal finishing industry. WRC (1984) presents the results of a water and effluent survey amongst industry members and a literature review of technology, waste minimisation opportunities and approximate costs of alternative waste water management systems. General recommendations are made about the need to encourage waste minimisation and resource recovery, but there is no specific technical or economic evaluation of potential technologies. The report identifies the need for research, development and demonstration in innovative technology.

This work was followed by a further study as part of a National Industrial Water and Waste-Water Survey (NATSURV). Based on these survey results WRC (1987b) has defined targets for water use which are deemed to be practicable. Target reductions are not given for waste loads, other than to recommend that dumping of cleaning and process solutions should be controlled.

These studies are intended to be guides to industry. As a broad-based literature review, the information can be used for preliminary assessment of the availability of opportunities for implementing waste minimisation. This parallels the literature review stage undertaken for both case studies in this investigation. On its own this information is of limited practical use unless the effectiveness of perceived opportunities can be assessed within the site specific environment. Such practical assessment is the objective of the waste minimisation assessment which follows.

6.4 WASTE MINIMISATION ASSESSMENT

Given the concern about chromium contamination in the effluent discharged to the sewage treatment facilities, and costly penalties incurred for transgressions of the discharge constraint for chromium, the chrome plating plant, as the principal source of chromium waste, was selected as a focus for assessment. The objectives of this assessment were:-

1. to identify measures by which waste discharges from the chrome plating plant (CPP) and hence the treatment load in the effluent treatment plant (ETP), could be reduced to minimise the need (and associated costs) for end-of-pipe treatment inherent in the ETP, and

2. to evaluate these measures technically, environmentally and economically.

While theoretical waste minimisation opportunities have been identified from the literature review, an attempt to assess applicability and cost-effectiveness of selected options for specific site conditions has been made using the results of on-site monitoring programmes. These were carried out with the following objectives:

1. to assess the performance of the CPP and ETP;

2. to confirm current effluent flows and characteristics and to identify point sources of particular contaminants of concern;

3. to derive material balances;

4. to identify and assess where possible the impact on the performance of the effluent treatment operation of up-stream waste minimisation measures;

5. to identify preliminary design conditions for alternative waste treatment or processing options.

Material balances for overall plant water usage, chromium in the CPP and chemical usage in the ETP have been estimated and used as the basis for the development of alternative flowsheets which incorporate waste minimisation measures. Evaluation of these measures is discussed in section 6.5.

6.4.1 Monitoring Programmes

6.4.1.1 Performance Of The Chrome Plating Plant

Two separate four-week monitoring programmes were carried out in the CPP over an interval of six months. During this time changes in operating practices and equipment design were implemented with the aims of:-

1. increasing production throughput, and
2. reducing the hydraulic load on the ETP which was underdesigned for the volumetric throughput

New jigs which had been designed for higher carrying capacities and faster loading and unloading were installed, and rinse water rates were adjusted manually to reduce to a minimum the volume of effluent discharged to the ETP. Based on results demonstrated by the monitoring programmes, these actions compounded a number of effects as a result of which performance efficiency in the CPP is surmised to have deteriorated. Appendix H presents detailed results and discussion from which the following conclusions have been made, as summarised in Table 6.4.

The new jig designs entrapped greater quantities of process fluid, resulting in increased drag-out effects and greater contamination of all tank solutions. This was demonstrated by significantly higher chromium concentrations both upstream of plating, in the alkaline cleaning solutions, and in the downstream chemical and water rinse solutions. pH of these solutions was also lowered due to the acidity of the chromic acid drag-out. This contamination would have altered the solution characteristics of the alkaline cleaners resulting in off-specification chemical composition. This was detected by routine process control analyses carried out by operating personnel, who consequently added greater quantities of chemical to increase the cleaner concentration and raise the pH. This in turn would have increased solution viscosity, thereby aggravating drag-out effects.

TABLE 6.4: Performance Characteristics Of Operations In The Chrome Plating Plant

CAUSE	EFFECT
new jig design	poor drainage: - higher drag-out losses; - increased contamination of all tank solutions; - increased occupational risks from toxic materials.
Chromium contamination of alkaline solutions	untreated chromium discharges to sewer; chromium content in sludge waste to landfill.
Iron contamination of plating solution	possible impact on plating quality.
excessive drag-out to chemical rinse solution	pH too low for effective reaction; overloading of treatment capacity: - higher drag-out of Cr(VI) to rinse tanks; - increased treatment load in ETP - shock loads; - increased Cr(VI) in all tanks.
rinse water flows too low and/or routine tank cleaning not carried out	rapid contamination of rinse water: - poor rinse water quality; - higher drag-out losses from final rinse; - downstream contamination; - unstable performance in the ETP due to shock loads.
more concentrated caustic chemical solutions being used	wastage of chemicals; increased occupational risk from high pH solutions; higher solution viscosity: - increased drag-out losses - higher rinse water requirements
inoperative conductivity controllers	poor manual control of water flow: - either too high or too low.
spray rinsing of work-pieces withdrawn from cold rinse tank	carryover into hot rinse tank of chromic acid residue: - increased contamination of hot rinse water.

The rinse water flowrate was significantly higher than had been the case during the monitoring period six months earlier. This was probably necessary in order to remove effectively the more viscous adherent cleaner solution. Thus chemical and water usage was increased, wastefully. Moreover the waste process and rinse water, upstream of plating, was discharged directly to the tank farm, prior to sewer discharge, with no treatment for the chromium removal. There was also significant chromium content in the waste sludge removed from the soak cleaner tanks.

Due to increased drag-out of acidic plating solution to the chemical rinse tanks, the pH of these tank solutions was reduced considerably, to as low as 2.3. This condition is not favourable for reduction of Cr(VI) by sodium hydrosulphite (see Appendix F:3.2). Consequently the chemical reaction probably was ineffective, with negligible reduction of Cr(VI) to Cr(III). This would have resulted in higher drag-out of Cr(VI) to the water rinse tanks which became significantly contaminated. The treatment load in the ETP, from both batch and continuous discharges of effluent, was increased, possibly resulting in "shock" loads which the reduction and precipitation stages were unable to treat effectively. Thus there was significant wastage of chemicals both in the chemical rinse tank and in the ETP (see below).

The cut-back of the rinse water flowrates through the hot and cold tanks may have reduced the hydraulic load on the ETP, but this action resulted in much more concentrated chromium contamination in the rinse water. Not only does this have implications for "shock loading" in the ETP, but the rinse water quality may have been too poor for effective rinsing. Drag-out of chromium from the final hot water rinse tank would have been higher, with greater potential for chromium contamination in downstream processes. It was acknowledged that such contamination has been detected in other processing areas of the plant, though it was not possible to track this contamination or to quantify this chemical loss as part of this assessment.

Poor operating practices which have contributed to unnecessary waste generation include reliance on manual adjustment of rinse water valves rather than automatic conductivity control, resulting in poor water flow control, and irregular tank cleaning, with greater solution contamination.

Possibly a design fault of the current plating configuration is the position of the spray rinse nozzles above the cold rinse tank. It may be that drag-out is being washed into the final hot rinse tank which has been shown to contain higher chromium contamination than the preceding cold rinse tank.

6.4.1.2 Performance Of The Effluent Treatment Plant

The monitoring programme in the ETP was conducted over a one week period, a week after the second monitoring programme in the CPP had been completed. During this week a PLC control system in the ETP was commissioned by site engineers. This enabled at least an initial assessment to be made of comparative performance of the ETP under manual control and under automatic control, although the period of monitoring was too short for results to be conclusive. Details of the activities and results of this monitoring programme are given in Appendix I. The findings are summarised in Table 6.5., and discussed as follows:

In the absence of PLC control, effluent flowrates to the chromium reduction stage were controlled by manual adjustment of pumping rates and rinse water rates in the CPP. Significant operator attendance was required in the ETP to check availability of treatment chemicals in the reagent tanks, to manually adjust influent and chemical feed rates and to monitor the visible quality of the effluent. Performance efficiency was poor, measured as high chemical consumption in excess of stoichiometric requirements. pH conditions deviated significantly from values which are needed for effective chemical reaction. Although no highly contaminated effluent was processed at times when the responsible operator could not be in attendance, there were overnight discharges of chromium containing effluent from the countercurrent rinse tanks in the CPP, resulting in detectable hexavalent chromium in the effluent discharged to sewer.

There were continual problems with blockages in the lime supply pipework, resulting in inadequate lime ($Ca(OH)_2$) addition and hence a pH condition which was too low for Cr(III) hydroxide precipitation. Caustic soda (NaOH) was used as a supplementary neutralising chemical. This increased the pH to 11, which might be expected to improve precipitation. However with NaOH, Cr(III) redissolves at pH greater than about 7.5 (see

Appendix F:3.3). It should also be noted that zinc increases in solubility with all common precipitants above pH 9-10, inhibiting its removal as a precipitate. Moreover NaOH-induced precipitation has poorer settling characteristics than $Ca(OH)_2$, lacking the natural crystalline structure of $Ca(OH)_2$ which itself provides attachment points for floc formation. Consequently floc formation may have been inhibited. In consequence of these effects, there would have been greater carry-over of chromium in the effluent discharged to the tank farm and hence to sewer.

TABLE 6.5: Performance Characteristics Of Operations In the Effluent Treatment Plant

CAUSE	EFFECT
no flow balancing	shock loads: - unstable performance; - incomplete treatment.
no flow monitoring	inaccurate accounting
absence for automatic control for chemical dosing	inefficient performance: - either inadequate chemical addition or - chemical and water wastage· - discharge constraints exceeded (high metals or high conductivity).
hydraulic loading too high	short-circuiting of flow in treatment tanks; poor mixing and limited reaction: - potential untreated discharge.
inadequate lime addition due to pumping problems or blockages in pipe lines	pH too low for hydroxide precipitation: - chromium remains in solution.
neutralisation with caustic soda	less effective flocculation: - reduced removal of chromium from solution; pH may be too high: - poor settleability; - poor removal of zinc.
poor maintenance	equipment failure; process failure: - discharge constraints exceeded; dirty equipment: - contamination of treated effluent.
chromium contamination of factory effluents	untreated chromium discharge direct to tank farm and sewer.

Once the PLC had been commissioned towards the end of the week, concentrated chromium containing effluent, which had been stored in a sump awaiting treatment, was added to the influent to the ETP so as to clear this backlog of untreated waste-water. Both the hydraulic load and the net treatment load on the ETP were increased. Preliminary results for the one day period of monitoring, following this addition, indicated that PLC control improved performance as demonstrated by reduced consumption of treatment chemicals i.e. less wastage of excess treatment chemicals. However the hydraulic loading was too high. There was short-circuiting of flow out of the reduction stage tank with incomplete reaction as evidenced by the yellow colour of hexavalent chromium in the neutralisation stage.

In general, it is the extreme variations in treatment load delivered to the ETP which result in ineffective performance. During the week the passage of untreated chromium-containing effluents may be mitigated by dilution with other effluents, termed factory effluents. These are not treated other than by blending in the tank farm. Based on average monthly flows determined by this assessment, chromium-containing effluents are diluted by approximately 60%. However this effect is achieved only when there is simultaneous discharge of effluents. Lower factory effluents are discharged at weekends when the greatest quantities of chromium containing effluents are discharged. It is at these times when effluent quality is at its worst.

These "causes and effects" suggest that it is principally operability problems which need to be addressed to improve the operating performance of the ETP as it is presently configured. However the design criteria for the ETP may need to be re-evaluated to enable other waste components, which are presently untreated, to be removed. These are discussed briefly in section 6.4.1.3 below.

6.4.1.3 Other Problem Wastes

It is suspected that caustic cleaning chemicals used in the CPP may contain cyanide, added to improve cleaning efficiency. Information on chemical characteristics of these chemicals has not been readily available from the chemical suppliers, who have indicated that no cyanide is used in the chemical formulations. However cyanide has been detected by both the local council and waste contractor in samples of effluent and sludge. Cyanide analyses of selected samples should be undertaken to track the source of cyanide.

Chelating compounds are used in the caustic cleaning solutions. These compounds inhibit chromium reduction and precipitation, and removal by filtration of metal contaminants from the cleaning solutions (see section 6.3.3.1(i)). Given the difficulties in removing this contamination, measures to reduce the extent of contamination should be examined.

Effluent from the phosphating plant also contains significant quantities of zinc (Zn). Presently Zn concentration levels are diluted by the total plant effluent (by approximately 70%) to levels which generally comply with discharge constraints. A reduction in effluent flow from the chrome plant will result in higher Zn concentration levels which may exceed the prescribed limits. Therefore this effluent may need to be treated more effectively in the ETP, or similarly assessed in terms of waste minimisation.

6.4.2 Material Balances

Material flows for total plant water, chromium in the CPP and chemical usage in the ETP were derived following the structured procedure of the UNEP methodology, incorporated in Stage 4 of the assessment procedure (described in chapter 2). These derivations required much greater detail and computation than the estimates made for the case study described in Chapter 5. Hence the details of this procedure are documented separately in Appendix J. Only the results of the material balance computations are discussed below.

6.4.2.1 Derivation Of Material Balances

Given the changes to production practices that had occurred between the two monitoring programmes, including the variability in production throughput and process conditions, it was not possible to resolve material balances based on normal annual quantities. Instead balances and/or material flows for chromium, water and effluent treatment chemicals were estimated for the period of the second monitoring programme in the CPP. These flows are depicted in Figure 6.6 based on total combined material flows around the two plating lines.

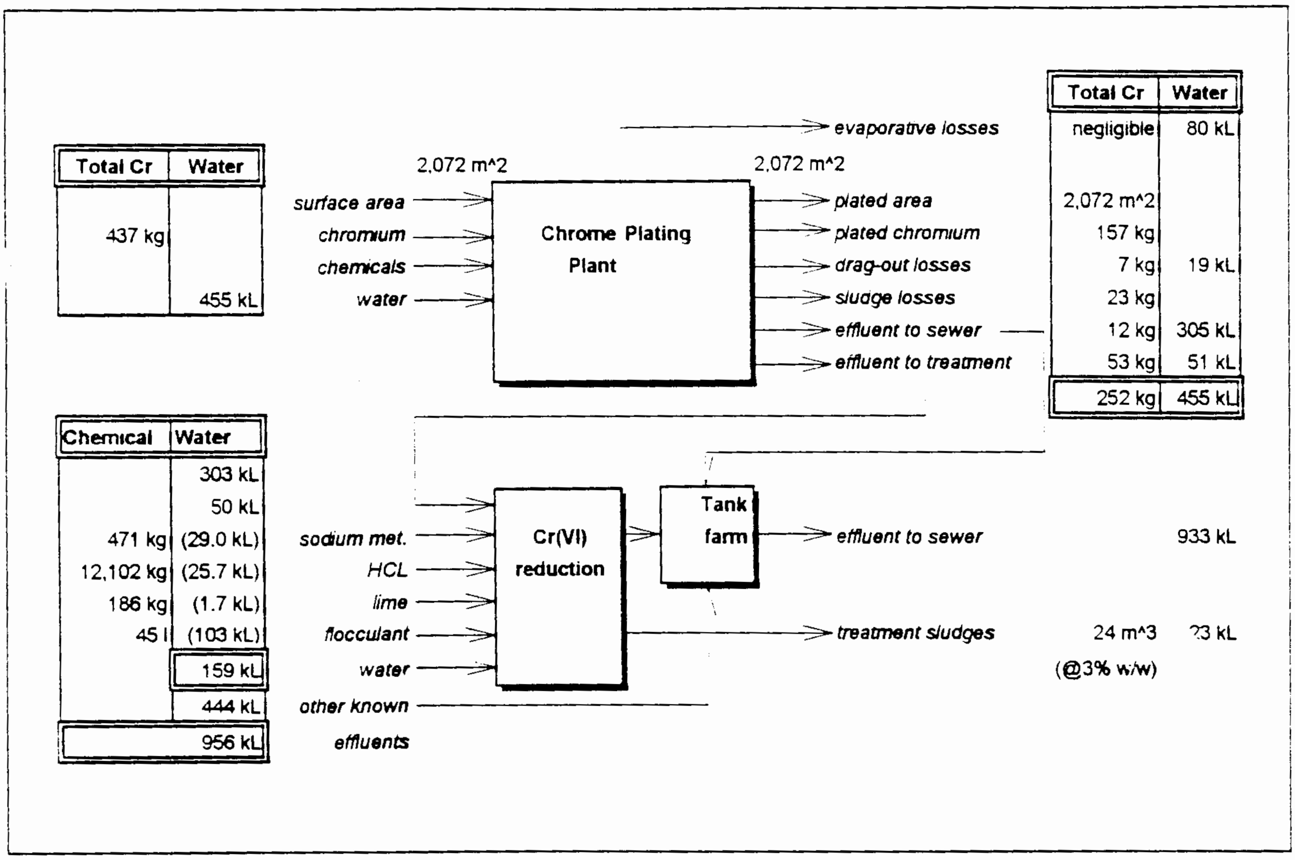

FIGURE 6.6: Estimated Material Flows In The Chrome Plating And Effluent Treatment Plants

As a result of use of different chromium chemicals and operating conditions and different work-piece characteristics in each plating line, solution characteristics were not consistent. Consequently chromium balances for each plating line show different results.

6.4.2.2 Evaluating The Material Balances

(i) chromium balance

Figure 6.7 illustrates the estimated chromium balances for each plating line[2]. Overall only approximately 58% of chromium input has been accounted for as plated surface, drag-out, evaporation and sludge and effluent contamination. While the balance for Line 1 was within 10%, that for Line 2 showed a discrepancy of approximately 68%. Part of this discrepancy may be attributed to the practice whereby all entrained condensate from the common extraction system, connected to both plating lines, is returned to Line 1. This transfer of chromium was not accounted for in the balance. This in turn implies that the balance for Line 1 is inaccurate. Furthermore net entrained loss of chromium in chromic acid mist in the scrubbing system has not been evaluated. Given that company monitoring with Drager tubes reportedly has measured no detectable chromic acid in the emissions from the scrubber system, this potential loss is perceived by the company to be negligible. However the effectiveness of the existing scrubbing action is questioned if drag-out solution with a concentration of approximately 70 g/l of chromium is being used as the scrubbing liquor. The scrubber operation requires more rigorous evaluation.

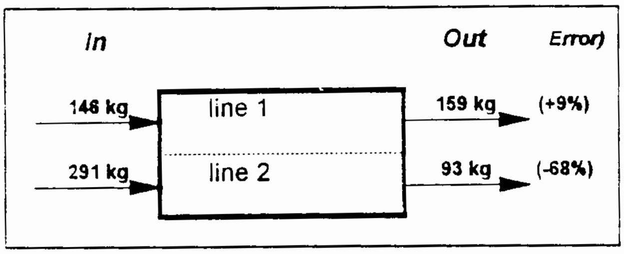

FIGURE 6.7: Chromium Balance for Each Plating Line

Other losses from Line 2 may be due to higher over-plating losses and higher drag-out associated with smaller size work-pieces which were

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[2] Inventory records for purchases made of chromic acid used in Line 1 suggest a much higher apparent usage than reflected in process control records of actual chemical additions. This discrepancy is presumed to be due to the substitution of the chromic acid chemical in Line 2 with a new proprietary chemical, resulting in excess stock of the older chemical. The inventory records and process control records of chromic acid consumption in Line 2 were compatible.

processed exclusively in Line 2 during the period of the monitoring programme.

Over-plating refers to the application of a chromium deposit in excess of the specified thickness to ensure complete plating. The excess chromium is removed in down stream grinding operations. There was much greater variability in the work-piece dimensions and plating thicknesses applied in Line 2 and the effect of over-plating would have been greater than for Line 1. Over-plating losses could not be accounted for.

Higher drag-out effects in Line 2 compared to Line 1 were demonstrated by the analytical results from which estimates of drag-out were made (see Appendix J:3.2(iii)). However, given the non-steady state conditions and the variability in drag-out , the same fixed drag-out rate was assumed for both plating lines in deriving the material balances for each. This may have been a significant underestimate for Line 2. Other unaccounted "losses" from both plating lines include residues on plating equipment.

Within the resolution of the chromium balance, approximately 26% of chromium was detected as losses in effluent and 9% in sludges.

Clearly an improved resolution of the chromium balance is needed to confirm the causes of these losses and to track chromium contamination elsewhere in the plant.

(ii) water balance

Figure 6.8 illustrates the estimated total plant water flows.

Estimated consumption of water by identified process operations and other uses accounts for about 50% of total metered plant water use, and about 74% of assumed effluent flow. Other water flows (50% of total) are attributed to domestic use, evaporative losses from the cooling system and cleaning activities, all of which are non-metered flows. There is no monitoring of wash water usage or automatic shut-off of water supply valves, which, if left unattended, may result in overfilling of tanks. These may account for significant water use, which also contributes to effluent flow. Such water usage conceivably could exceed the apparent 26% shortfall in effluent flow. This would imply that the water rate allocated to domestic use and evaporative duty is too high. This has implications for costs payable for effluent conveyance. While existing accounting parameters may favour lower effluent charges, it should be appreciated that water conservation measures will not reflect associated cost savings in municipal accounts unless actual water and effluent flows are measured.

It was not possible to derive a water balance for the chrome plating plant itself. Water used to fill rinse water tanks is unmetered, and it is not known to what extent these tanks were partially or completely emptied and refilled on a weekly basis.

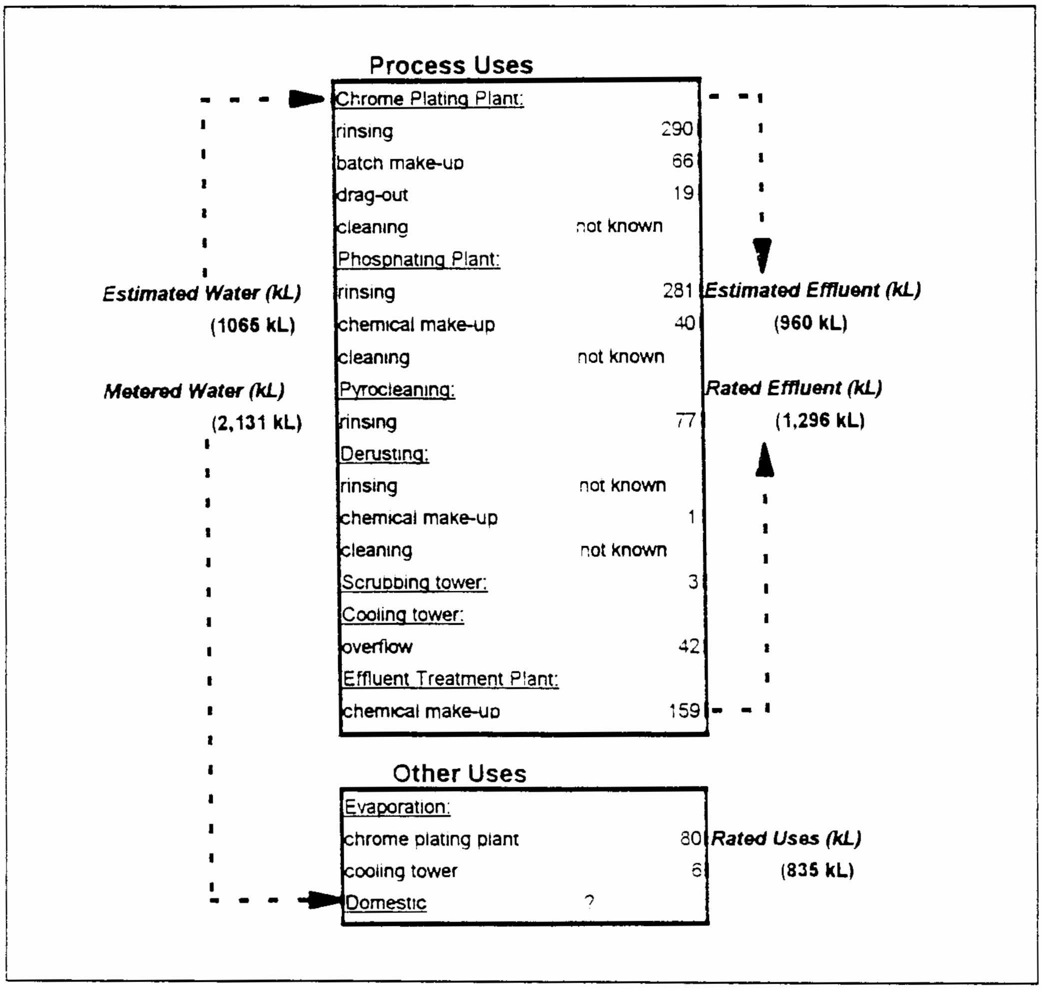


FIGURE 6.8: Estimated Plant Water Balance

Water usage in the different chemical reagent tanks in the effluent treatment plant was estimated by measuring tank level changes where these were filled on a batch basis. This estimation could not be made for lime slurry which is continuously topped up through a float-actuated valve. This flow was unmetered. The estimate made for water use in lime slurry was based on assumed ideal conditions and is likely to be an underestimate (see Table 6.6). Seemingly, the most significant use of water in the ETP was in consumption of flocculant solution.

Of the estimated process water uses, rinsing accounted for about 60% of total water use. Approximately 45% of this rinse water was used in the CPP. Chrome plant rinse water flows have been shown to vary widely during different periods of time, ranging between 200 - 400 kL in a 4-week period. This amounts to 30-36% of plant raw water consumption.

(iii) treatment chemical consumption

Actual consumption of treatment chemicals in the ETP was significantly higher than stoichiometric requirements, as shown in Table 6.6.

TABLE 6.6: Chemical And Water Usage In The Effluent Treatment Plant

Chemical	Stoichiometric Requirement per kg Cr(VI)/ Total Cr	Estimated Consumption per kg Cr(VI)/ Total Cr
sodium metabisulphite	chemical: 2.73 water: not known	10.75 kg 662 l
hydrochloric acid	chemical: 3.36 water: not known	276 kg 587 l
lime	chemical: 3.78 water: 34 l	not known not known
flocculant	chemical: not known	(45 l per 4 weeks) (103 kL per 4 weeks)

This was due conceivably to inefficiencies in processing including poor mixing, inadequate dosing and poor control as discussed above in section 6.4.1.2. Subsequently, efficiency, measured as reduced excess chemical consumption, appeared to improve with PLC control, although the period of monitoring was too short for results to be conclusive.

(iv) sludge production

It was not possible to validate estimates of expected sludge production with actual quantities produced. Slurry from the consolidation tower, at about 5% w/w, is removed in tankers for disposal in evaporation ponds at the landfill site. These disposal records were not made available. Some slurry is dewatered in the filterpress on a batch basis, but this operation is irregular and the throughput could not be ascertained. Available disposal records reflected total sludge volumes without identifying sources or characteristics.

6.4.2.3 Refining The Material Balances

More rigorous record keeping and process monitoring is required to collect accurate and reliable information, which can be used to improve current estimates of material flows and balances. Such action requires significant commitment of effort which exceeds the scope of this assessment, and requires further collaborative work with the company.

Nevertheless the estimates of material flows which were obtained from this assessment have identified specific process conditions which are responsible for unnecessary waste generation. There are opportunities to implement appropriate waste minimisation measures to reduce this waste generation, and to effect cost savings.

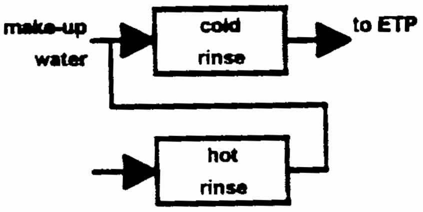
6.5. IDENTIFICATION AND EVALUATION OF WASTE MINIMISATION MEASURES

The measures which are described below are initial proposals which are based on proven techniques and practices which have been implemented elsewhere. It is suggested that these measures could be implemented relatively easily in the case-study operation, though further site-specific evaluation is required.

6.5.1 Short-Term Measures

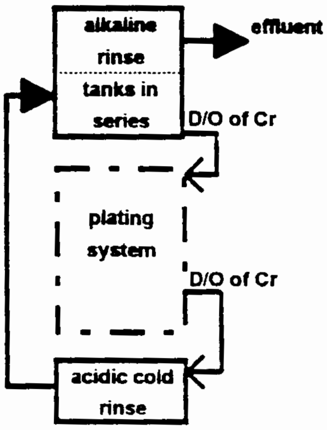
Table 6.7 presents a summary of technical, environmental and economic considerations for measures which conceivably could be implemented in the short-term.

The re-introduction of conductivity control would be the first essential measure, so that appropriate rinse rates can be determined and controlled to maintain a minimum acceptable quality of rinse water. These flowrates would form the design basis for downstream waste-water treatment. While rinse rates would increase to reduce the contamination levels in the water, total water consumption could be reduced by introducing a countercurrent flow configuration from the hot to cold rinse tanks. Increased flow through the hot rinse tank would incur a higher energy penalty for the heating duty, but this cost should be off-set by optimising the flow configuration.



countercurrent flow

Some of the measures require further specific technical evaluation to verify their efficacy. In particular, the potential for reactive rinsing requires technical evaluation. This option would help to retain chromium in the plating system by recycling chromium-containing water to a stage upstream of the plating process to which the chromium would be returned as drag-out. As it is Cr(VI) which is the ionic form required for plating, and Cr(III) is a contaminant, the chemical rinse stage would need to be eliminated to prevent the reduction of Cr(VI) to Cr(III). Potential effects on rinsing performance in the alkaline rinse tanks and in the final water rinse tanks need to be investigated. The



reactive rinsing

TABLE 6.7: Potential Short-Term Waste Minimisation Measures

OPTION	TECHNICAL	ENVIRONMENTAL	ECONOMIC
conductivity control	proven - optimises rinsing rate	balanced water/waste load - improved performance in ETP	low cost
countercurrent flow from hot to cold rinse tanks	proven minor modifications to pipework	water conservation reduced hydraulic load on ETP	low cost
reactive rinsing - recycle acidic chromium rinse water to alkaline rinse tanks	may impact on effectiveness of rinsing and product quality: requires testwork; must ensure there is no cyanide in the alkaline solutions; requires removal of chemical rinse stage	water conservation; reduced effluent; increased chromium recovery; reduced treatment load in the ETP	moderate cost for pipework modifications; reduced water and chemical treatment costs.
waste segregation	may require extensive modifications to pipework, floor drainage and sump arrangement	facilitates improved waste management of separated waste materials	capital costs for civil modifications and pipework
more rigorous maintenance	existing	minimises material losses	low cost: may require higher working capital, but savings from reduced downtime and process failure
pressurised water system for plant cleaning water	packaged equipment available	water conservation	capital costs for tanks, booster pumps, filters, pipework and instrumentation
filtration of cleaning solutions	may not remove chelated metals effectively: requires evaluation	water and chemical conservation	capital costs for filter, pump & pipework savings in water and chemical costs

possible presence of cyanide in the cleaner solutions and cyanide contamination in the rinse water must also be investigated as cyanide may react with acid in the recycled rinse water.

The potential to filter and reuse alkaline cleaning solutions depends on the effect of chelating chemicals in the cleaner formulations. Conceivably quite simple bench top treatability tests could be performed to assess the ability to remove contaminants from recycled cleaning solutions, or site testing of the effectiveness of filtration could be undertaken.

The modification of drainage, sumps and pipework for waste segregation would require the greatest expense for civils work, but there would be long-term benefits in the ability to manage separately distinct waste streams. Practicably, it should be possible to isolate chrome plant effluents from other factory effluents. The greatest difficulty will be imposition of controls and operating practices which minimise transfer of chromium residues on plated work-pieces to other working areas of the plant.

Clearly any reduction in the amount of Cr(VI) which requires treatment will have associated cost savings from reduced water and chemical treatment costs in the ETP. It should also be possible to reduce chemical requirements by utilising the reactivity of waste components in other effluent streams. For example, phosphates in effluent from the phosphating plant could be used to improve flocculation of metal hydroxides. This effluent also contains significant quantities of zinc (Zn) which at present are not treated for removal. This could be done by means of precipitation using lime, but a higher pH is required than that for precipitation of chromium hydroxide. This would increase lime chemical requirements, but could prevent exceeding the heavy metals discharge constraint based on Zn concentration.

6.5.2 Longer Term Measures

In the longer term consideration could be given to the potential to treat chromium containing effluents such that both treated water and recovered chemicals can be returned to process. On the basis that ion-exchange (IX) is proven technology for chrome plating systems and is available as commercialised package equipment.

the decision was made to investigate the suitability of IX for the case study operation.

A design basis was derived for a modified process configuration which incorporates the waste minimisation measures proposed in 6.5.1 above and a chromic acid recovery unit (CRU) which is based on ion exchange technology. The modified process is depicted in Figure 6.9.

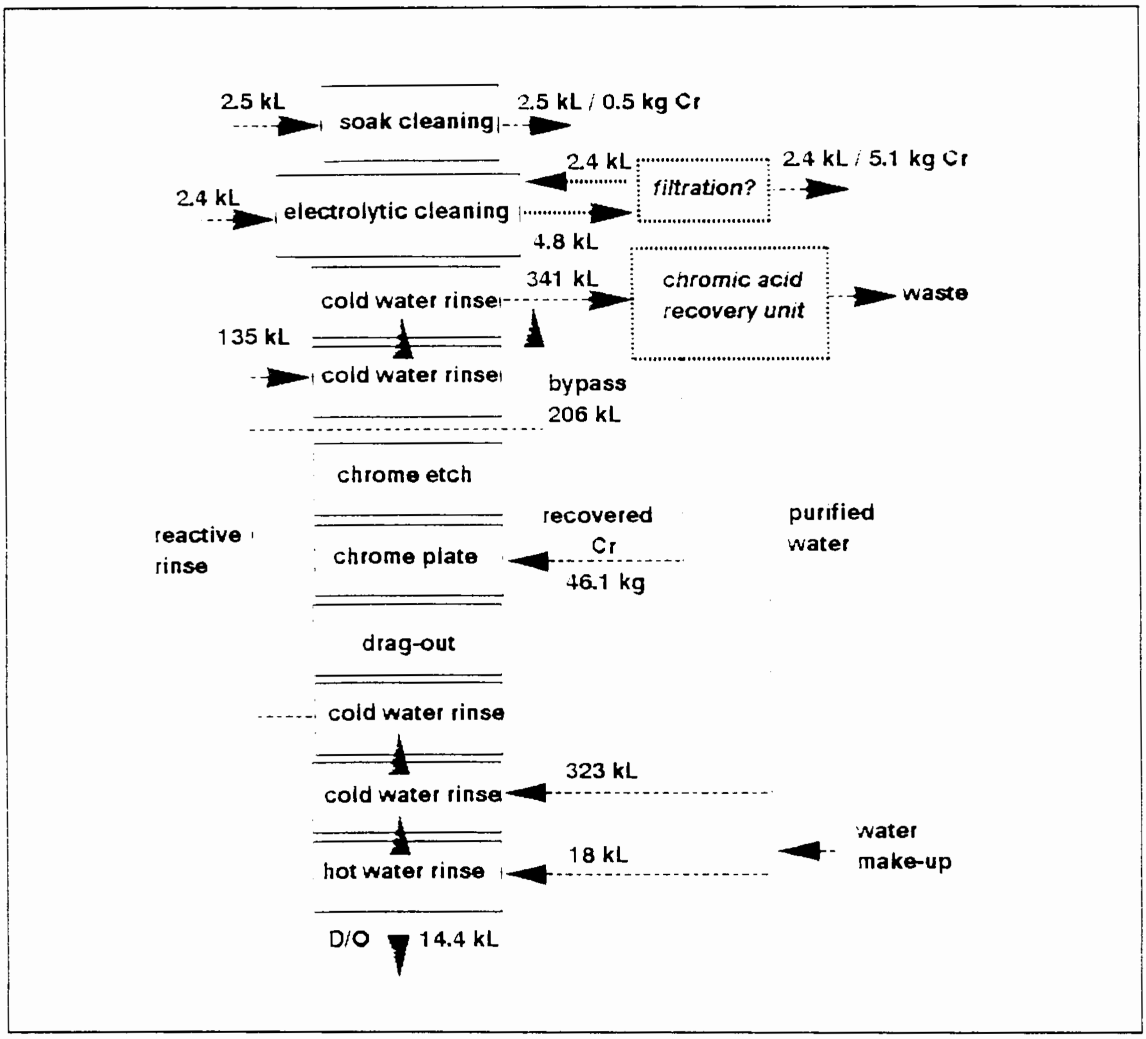


FIGURE 6.9: Modified Process Configuration With Chromic Acid Recovery And Water Recycling

A budget cost for the CRU was obtained by enquiry to an established supplier in the U.K. Local commercial companies who were contacted were unable to provide such equipment or information without detailed process design for which there was insufficient design information and time for such effort. This constraint probably reflects a lack of experience and availability locally of knowledge and technology for such specialised application.

The development of the design basis and budget cost is described in Appendix K.

6.6 EVALUATION OF ION EXCHANGE-BASED CHROMIC ACID RECOVERY

6.6.1 Design Basis

The design flow is based on the combined flow of waste rinse water from both plating lines, estimated as 14.2 m^3/day during 9 hours of daily operation. This effluent was characterised as containing 260 mg/l of chromic acid with 5 mg/l iron and 1 mg/l zinc as contaminants.

This design basis assumes that the chromic acid chemical used in the two plating lines is compatible, in the expectation that the plating bath chemicals will be standardised at some future time. Presently the different plating formulations used in each plating line reportedly are incompatible and each would require a dedicated chromic acid recovery system.

6.6.2 Process Description

The operation of the CRU is illustrated schematically in Figure 6.10.

The CRU itself comprises three ion-exchange beds in sequence. Cationic contaminants are removed in the first cation exchanger (strong acid cation resin) while the anionic chromates (CrO_4^{2-}) are removed in the second anion exchanger (strong or weak base anion resins[3]) producing a purified water stream which can be recycled for process reuse. This forms a closed loop for water. The chromates are recovered from the resin during a regeneration stage in which sodium hydroxide (NaOH) resolubilises chromate as sodium chromate (Na_2CrO_4). This is passed to the final cation exchanger (weak acid cation resin). Sodium ions are

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[3] The choice of strong or weak base resins in an economic decision: strong base resins require greater quantities of sodium hydroxide for regeneration i.e. higher chemical costs; weak base resins are more susceptible to oxidative attack by chromic acid resulting in higher resin replacement costs.

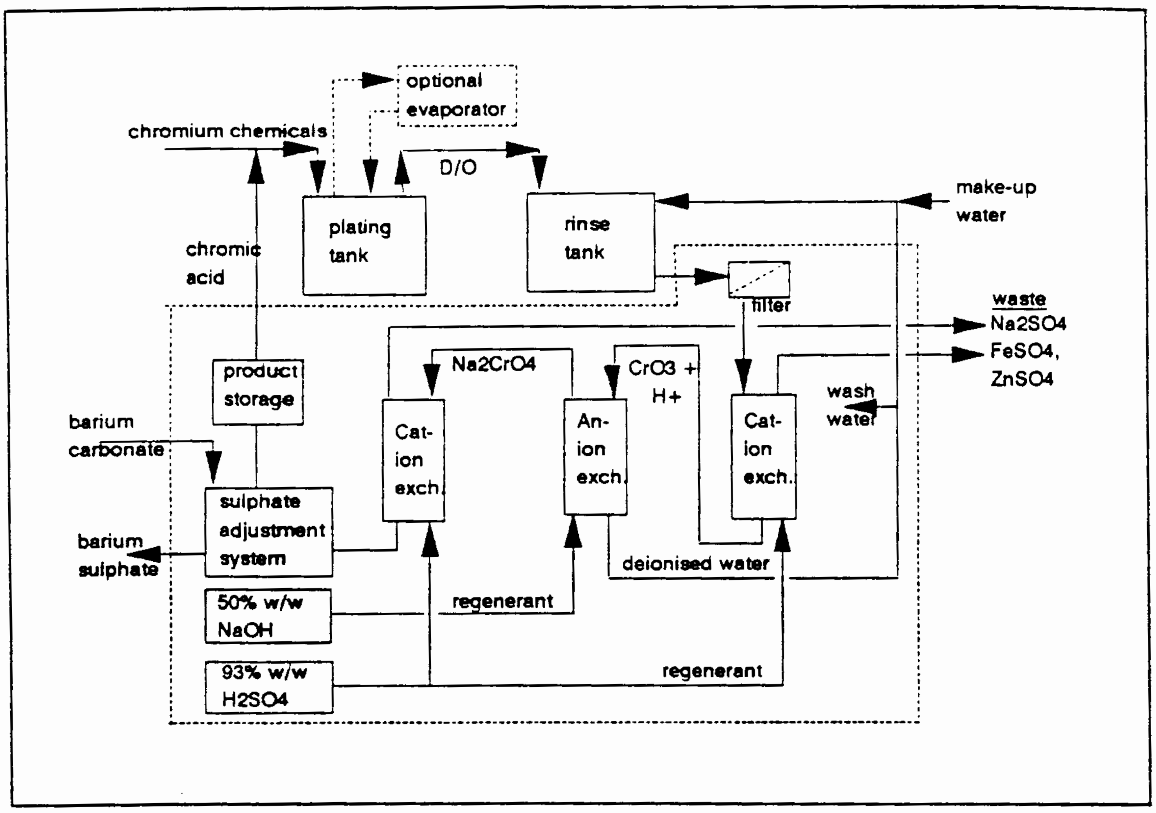

FIGURE 6.10: Chromic Acid Recovery Process Schematic

replaced by hydrogen ions regenerating chromic acid. This is transferred to a sulphate adjustment system where excess sulphuric acid from regeneration is removed from the chromic acid product by addition of barium carbonate ($BaCO_3$) in a batch treatment system (Leatherdale and Dejak, 1991). The chromic acid can then be returned to process. Recovery rates are reported to exceed 99%. The product concentration is approximately 75 g/l (Leatherdale and Dejak, 1991). Natural evaporation from the plating system usually concentrates the chromic acid to that required for plating, failing which supplementary evaporation can be achieved using small evaporators.

Excluding evaporation, the CRU is designed as a skid mounted packaged system with a space requirement of approximately $6m^3$. The operation of the system is completely automated and reportedly requires minimum operator supervision other than a daily inspection and routine analyses of the recovered chromic acid.

Waste streams from the process comprise metal sulphates from the regeneration of the first cationic exchanger, sodium sulphate from the regeneration of the final cation exchanger and barium sulphate ($BaSO_4$) from the sulphate adjustment system. These streams require appropriate treatment. Resins must also be replaced periodically as a consequence of damage caused by oxidative attack by chromic acid. Typical replacement needs are given as 1-2 ft^3 per annum. These resins require disposal.

6.6.3 Technical Evaluation

(i) status of technology

Based on information made available by the equipment supplier, the IX technology which is the basis of this process has been used extensively in the metal finishing industry for more than a decade and has a proven track record in chrome plating applications.

(ii) equipment modifications

For installation at the case-study facility, modifications would be required to existing pipework to allow the counter-current flow of rinse water, as shown in Figure 6.9, and to segregate the rinse water discharge from the common pipework which discharges effluent to the existing effluent treatment plant. In order to accommodate the combined waste rinse flow from both plating lines and to recycle water to both plating lines, a feed water tank and purified water tank with associated transfer pumps and controls would be required in addition to the basic equipment. An evaporation unit should not be required as the concentration of recovered chromic acid is similar to the concentration in the drag-out tank, solution from which is presently returned directly to plating. Hence it may be concluded that natural evaporation is sufficient to concentrate the recovered solution to that required for plating (approximately 250 mg/l chromic acid).

Deionised water or mains water is required for backwashing of the IX resins after regeneration. A portion of the treated water from the purified water storage tank could be used for this purpose, with mains water used to make-up a short-fall in rinse water requirements. Process control requirements for this arrangement require evaluation.

The need to investigate the performance of the scrubber in chromic acid service and the potential loss of chromic acid mist to atmosphere has been identified (see section 6.4.2.2). If it is necessary to replace the existing scrubbing liquor with a cleaner scrubber water make-up, the scrubber waters could also be treated in the CRU and maintained at a low chromic acid concentration. This would improve the scrubbing action, thereby reducing potential atmospheric discharges, for environmental advantage, and recovering chromic acid, for economic advantage. This treatment load would change the current estimated design basis.

(iii) modifications to waste treatment

The elimination of rinse water as influent to the effluent treatment plant removes most of the need for chromium waste treatment. Although there is chromium contamination in process tanks in the chrome plating plant, from which waste is discharged on a batch basis, and in effluent discharged from other processing areas in the facility, chromium levels in these discharges normally would be diluted in the total plant effluent such that concentration levels in the final discharge comply with discharge constraints. Hence treatment normally would not be required. Moreover the presence of chelating chemicals in these process solutions renders treatment of these effluents more difficult (see sections 6.3.1.1(i) and 6.4.1.3). Chromium contamination should be minimised by reducing as far as practicably possible the transfer of chromium contamination e.g. by drag-out effects.

Given the potential for process upsets which generate excess chromium contaminated waste, some provision for chromium waste treatment may need to be retained to avoid incurring penalties for excessive discharges of chromium to the sewer. Furthermore it would be useful to retain a backup system to the CRU. For the reduced, periodic and variable flows which would require such treatment, a batch operated treatment system would probably be more cost-effective than the existing continuous operation. A chromium waste storage tank would need to be provided.

The elimination of chrome plant rinse effluent also reduces the dilution effect for zinc-containing effluent from the phosphating plant. Material flow estimates have shown that the zinc concentration would exceed discharge constraints, thereby incurring surcharge penalties. Hence there is a need for improved management of these wastes. The potential for minimising the discharge of these wastes from the phosphating plant itself should be investigated as part of a waste minimisation strategy. This requires a new and separate assessment. In terms of treatment, zinc could be removed by precipitation with lime in a treatment stage similar to that used presently for chromium precipitation and solids separation. pH conditions will need to be adjusted to conditions favourable for zinc precipitation chemistry. The phosphate content in the zinc-containing effluent may improve flocculation effects. To minimise the hydraulic load on this treatment stage, the phosphating plant effluent should be segregated from other plant effluents.

In order to reduce the quantity of sludge which requires off-site disposal, the capacity for sludge concentration should be matched to the load requirements. This requires a re-evaluation of material flows and duty specifications for the filterpress. The benefit would be cost savings from reduced volumes of sludge which require disposal.

Treated effluents and the balance of plant effluents would be blended in the tank farm prior to discharge to sewer to effect overall dilution of waste constituents.

6.6.4 Environmental Evaluation

(i) extent of waste reduction

Estimates of modified material flows have indicated that the proposed waste minimisation measures would reduce water use in the chrome plating plant by approximately 78%. The overall reduction in total estimated plant water use would be 48%, including the water savings from elimination of chemical treatment in the effluent treatment plant. Chromium discharges to the sewer would be reduced by approximately 70% by weight. The associated saving in chromic acid consumption is approximately 88 kg in a four week period, or 10% of current use.

The potential to reduce chromium loss further depends on the effectiveness of measures which reduce contamination of process solutions which are discharged from the chrome plating plant on a batch basis and drag-out of contamination to processing areas downstream of the chrome plating plant. As these discharges normally would not be treated for chromium removal, the environmental benefit would arise at the downstream sewage treatment plant whose own treatment requirements and sludge waste production would be reduced.

The generation of metal hydroxide sludges (estimated as 24 kL per month) would also virtually be eliminated. However approximately 34 kL per month of effluent, containing 7.5 g/l sodium sulphate (Na_2SO_4) and 45 mg/l chromic acid (CrO_3) would be produced by the CRU (Leatherdale and Dejak, 1991). Under normal conditions these concentrations would be diluted in the total plant effluent to levels below existing discharge constraints for sulphates and chromium. The alternative of lime treatment for removal of sulphate as calcium sulphate ($CaSO_4$) would increase lime consumption considerably, and $CaSO_4$ would require disposal.

(ii) <u>other potential waste problems</u>

Ion exchange resins generate a hazardous waste which requires appropriate safe disposal. The need to address problems of zinc waste also has potential environmental implications which require investigation.

(iii) <u>safety concerns</u>

Concentrated sulphuric acid is an extremely hazardous chemical for which special handling and safety procedures are required. Consequently there are also implications for maintenance activities where there is potential for contact with the acid, including handling of spent resins.

6.6.5 Economic Evaluation

Table 6.8 summarises the results of the economic evaluation presented in Appendix K. The different results shown are due to a difference in the unit cost of the proprietary chromic acid plating chemical. only one of which - it has been assumed - will be used in the future, common to both plating lines. At present there is a cost differential between the two proprietary chemicals of about R30 per kg. Should the more costly chemical be selected for future use, net chemical costs for chromic acid would increase despite the reduction in consumption. This would reduce potential costs savings, compared with current costs. The pay back period is calculated as 5.4 years. Alternatively, assuming future use of the lower cost chemical, potential savings would clearly be much higher. On this basis, the pay back period would be less than two years. (The selection of proprietary chemical is influenced by factors relating to its plating efficiency and plating quality, and thus is an economic decision made by the company concerned.)

TABLE 6.8: Summary Of Economic Evaluation For The Chromic Acid Recovery Unit

COST COMPONENT	VALUE OF	COST (R)
Capital Cost of CRU	726,000	726,000
Operating Costs	18,000	18,000
<u>Cost Savings</u> R per 4-weeks)	using X200 as future chromic acid chemical	using new proprietary chromic acid chemical
water	722	722
treatment chemicals	14,845	14,845
chromic acid	19,983	-2,770
sewer discharge	463	463
Cost Savings (R/p.a)	414,200	152,500
Net Savings (R/p.a)	396,200	134,500
Pay Back (years)	1.8	5.4

The actual value of recovered chromic acid (at the higher purchase cost) amounts to approximately R5,700. In comparison, the cost saving realised by the reduction in utilisation of effluent treatment chemicals is notably more significant. Water supply costs and effluent treatment costs are shown to be, comparatively, insignificant. Savings in disposal costs, from the elimination of chromium hydroxide slurry and filtercake, would be about R3,000 p.a.. This has been assumed to be offset by disposal costs payable for occasional disposal of ion exchange resins and barium carbonate/chromic acid slurry which is generated by the sulphate adjustment system.

These results demonstrate the high cost of chemicals, and, that in order to effect any meaningful cost savings, investment in systems which attenuate the need for end-of-pipe waste treatment must be made. Other cost savings from simple water conservation measures and reductions in sludge disposal requirements would not be significant in the short-term. However, in the light of future increases in costs for water supply and waste disposal, such measures may be cost-effective in the medium to long term. In general, as a "point-in-time" estimate, pay back does not account for such increases in costs. Nor does it reflect potential savings from the avoidance of potential regulatory and liability costs. The need to consider these issues has been addressed in section 2.4.3. However given the inherent inaccuracies in the information and estimations used to derive material flows and costs, more detailed feasibility analysis was not considered justified for this case study.

The principal operating costs associated with the operation of the CRU are those which are incurred for the consumption of chemicals for the regeneration of IX resins. Consideration could be given to alternative chromic acid recovery options which do not require the hazardous and costly regeneration stage involved in ion exchange, e.g. application of the process using both ion exchange and electrodialysis as described in section 6.3.2.2(vi). This process requires no regeneration of ion exchange material and associated waste management, and the economics were indicated as being more favourable than conventional ion exchange. It is not known to what extent this process has been proven commercially[4].

6.7 CONCLUSIONS

This assessment was conducted with the aim of identifying potential waste minimisation measures and evaluating the effectiveness of selected measures in the light of site-specific processing conditions. In this case-study specific on-site investigation was appropriate as the company has structured and distinct process operations, more orderly production scheduling and a higher level of operating and engineering skills than those encountered in the dye house. Consequently it was possible to facilitate monitoring programmes and to designate specific processing areas for investigation. It was not possible to encompass a facility-wide assessment in this initial investigation. However, as a single iteration, this case-study has demonstrated all key features of the waste minimisation

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[4] No response was received to an enquiry for information sent to the registered US supplier of this technology.

assessment methodology, with the exception of formal commitment of company management to the objectives of this assessment.

There was limited involvement by production staff in the assessment procedures and it was not possible to complete the EPA type work sheets to any useful extent due to a lack of rigor in maintaining site records or absence of process related information. These constraints, as well as the limited resources for repeated monitoring activities, did not allow material balances to be resolved accurately.

Nevertheless the estimates of material flows which were obtained from this assessment have identified specific process conditions which are responsible for unnecessary waste generation. This directed attention to opportunities to implement appropriate waste minimisation measures to reduce this waste generation. This is a valuable outcome of such investigation, particularly as correction to such deviant conditions should not require costly expenditure, and should improve processing efficiencies and product quality control, with associated cost benefits.

Results of initial monitoring accounted only for about 58% of apparent chromium use. Possible causes of unaccounted loss include excessive drag-out of chromium from the chrome plating process operation with transfer of contamination to downstream processing areas and higher-than-expected emissions of chromic acid from the scrubbing system. The estimates assumed for these losses may have been too low. More detailed and accurate monitoring is required to verify these losses and improve the known material balance.

Within the resolution of the chromium balance, about 26 % of chromium input is discharged to the effluent treatment plant directly from the chrome plating plant. As a result of poor operation of the effluent treatment plant, this was unable to treat the influent wastes effectively. There was considerable wastage of effluent treatment chemicals. The cost of these chemicals has been shown to be the most significant, compared with the cost of "lost" chromium (in effluent), water usage, effluent discharge to sewer and sludge disposal. Hence any meaningful cost savings require that the consumption of these chemicals should be attenuated. To avoid this end-of-pipe treatment, capital investment in upstream process changes is required.

The literature review of proven waste minimisation measures showed that reclamation techniques for metal-contaminated aqueous wastes, such as plating rinse water, are commercially available. Pay back periods of 4-5 years commonly are reported. In this case study, an initial economic evaluation of an ion-exchange based chromic acid recovery system has indicated a pay back period of either 1.8 or 5.4 years. The difference in results depends on the cost of the proprietary chromic acid plating chemical which would be used in both plating lines in the future.

Operating costs of the chromic acid recovery system are chiefly chemical and waste management costs associated with the regenerating chemicals. The potential to use alternative technology options, which do not require the hazardous and costly regeneration stage involved in ion exchange, could be considered.

This initial assessment of a component part of the complete facility operations has identified measures which can mitigate waste problems associated with the process operation concerned, but which may create other problems. The waste minimisation measures change the remaining waste profile and require other changes to be made to waste management practices. In this case study, reduction in waste discharges from the chrome plating plant would result in higher zinc concentrations in the remaining effluent as the dilution effect of blended effluent would be reduced. In order to avoid transgressions of the effluent discharge constraint for zinc, the processing plant which is the source of this waste, would require investigation in terms of waste minimisation and other improved waste management practices. This requires a new assessment.

CHAPTER 7
CONCLUDING DISCUSSION

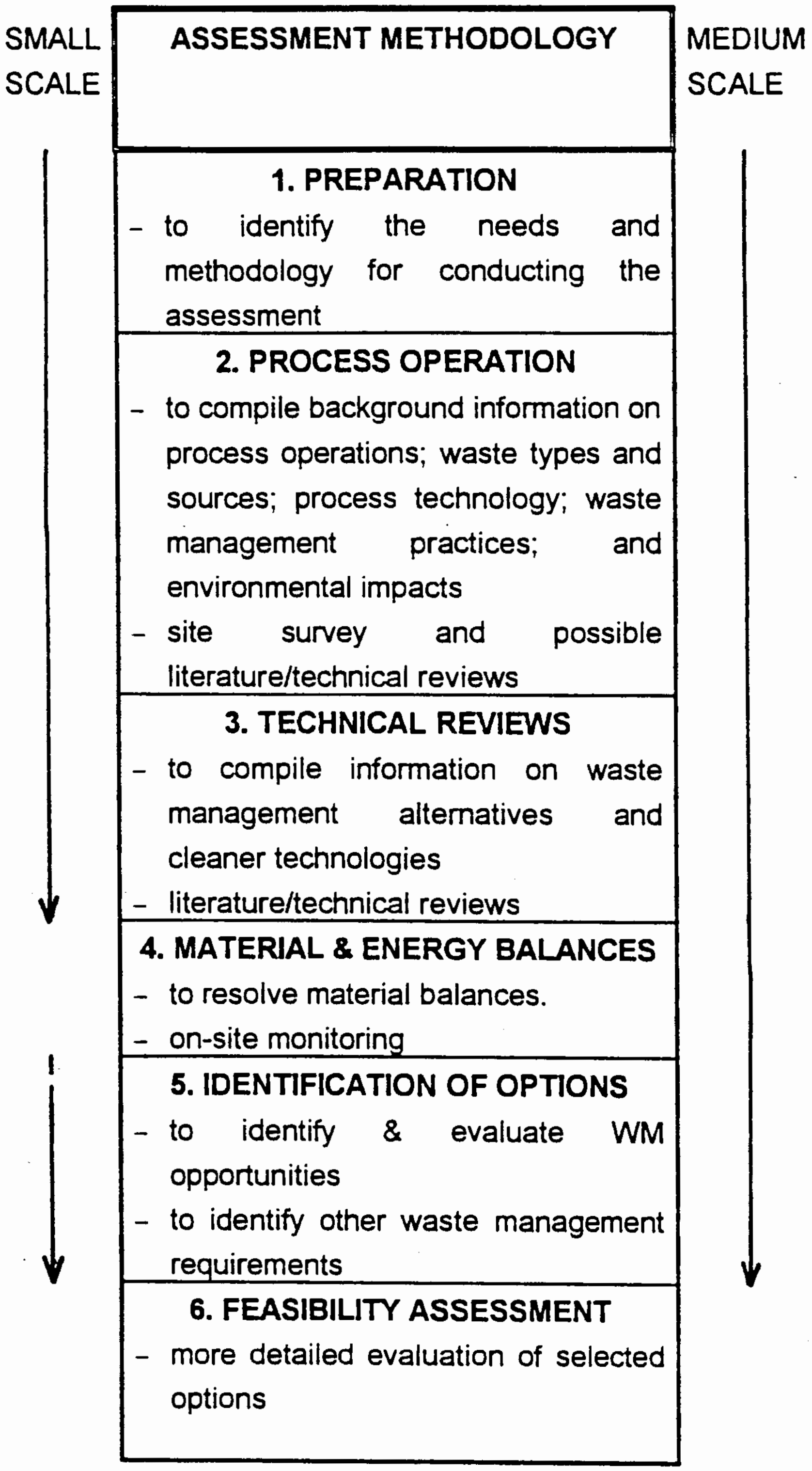
7.1 APPLICABILITY OF THE WASTE MINIMISATION ASSESSMENT METHODOLOGY

7.1.1 Levels Of Assessment

The waste minimisation assessment methodology adopted for the case study assessments of the previous chapters was a hybrid of worksheets proposed by the US EPA and a more descriptive procedure advocated by the UNEP IE/PAC. The methodology was compiled in such a way that different levels of detail could be accommodated in each of the two case studies which addressed, respectively, small and medium scale industry operations. The stages of assessment are summarised in Figure 7.1, with specific reference to the levels of detail included in each case study. The premise for this differentiation was the perceived ability of the companies concerned to conduct assessments, as discussed below.

The small scale company was a garment dye house characterised by an informal organisational structure, irregular and changing production schedules and simple operating procedures which did not require any specific engineering expertise. There was no provision on site for monitoring of process conditions and material flows, and no process records were kept. In an operating environment such as this, it would be difficult to conduct detailed on-site monitoring activities, for the purposes of compiling accurate information on material flows, without considerable time, effort and possible disruption of processing operations. Hence the assessment adopted for this case study was based largely on information derived from readily available site records and from published literature which reported waste minimisation experiences at other textile processing facilities. Thus this assessment sought to identify waste minimisation measures from an analysis of literature, without the need for detailed site evaluation. The level of activity included stages 1 - 3, and stage 5 of the methodology as shown in Figure 7.1, and is deemed to constitute a preliminary level of assessment.

Without accounting for site-specific conditions any information and action obtained from literature sources, generally, is limited to broad-based technology



ASSESSMENT METHODOLOGY

1. PREPARATION
- to identify the needs and methodology for conducting the assessment

2. PROCESS OPERATION
- to compile background information on process operations; waste types and sources; process technology; waste management practices; and environmental impacts
- site survey and possible literature/technical reviews

3. TECHNICAL REVIEWS
- to compile information on waste management alternatives and cleaner technologies
- literature/technical reviews

4. MATERIAL & ENERGY BALANCES
- to resolve material balances.
- on-site monitoring

5. IDENTIFICATION OF OPTIONS
- to identify & evaluate WM opportunities
- to identify other waste management requirements

6. FEASIBILITY ASSESSMENT
- more detailed evaluation of selected options

FIGURE 7.1: Levels Of Activity For Waste Minimisation Assessment

changes in process flow sheets and their operability. Moreover such changes tend to focus on utility usage, changes to which would have lesser impact on processing conditions and product quality. The impact of deviations to process conditions is less predictable. Site-specific conditions more often need to be taken into account in assessing process related changes.

The preliminary assessment also provides for initial screening of potential waste minimisation options prior to a more detailed level of investigation. Depending on the results of such preliminary assessment, a decision can be made whether to commit company resources to more detailed assessment.

This was the case for the second case study of a medium scale metal finishing operation. The literature review directed attention to proven measures for reducing the generation of process waste by means of changes to both the process flow sheet and processing conditions. This encouraged a more detailed site-specific investigation which sought to verify waste quantities and characteristics through a detailed material balance. The improved accuracy of process-related information so acquired provided a working model of actual process conditions. With such information it was possible to assess alternative flow sheets and to evaluate, in greater detail and with greater accuracy, operating cost savings associated with waste minimisation.

The implementation of this level of assessment requires greater effort and collaboration with company staff. This was more practicable in the second case study in which the process technology itself was more sophisticated and required more rigorous process control procedures. Hence the level of technical skills was higher than that employed in the dye house. Operating staff were accustomed to certain monitoring and analytical control techniques and some sampling and analytical equipment was available on site. There was a more structured hierarchy of operating responsibility and, generally, operators had a greater understanding of processing conditions. Consequently it was easier both to plan a monitoring programme and to secure collaboration of operating personnel who assisted in carrying out certain monitoring activities.

The site-specific evaluation is necessary to provide a greater understanding of actual causes and sources of waste which often are symptomatic of particular processing conditions. The latter case study demonstrated that attenuation of one waste related problem can create or aggravate other waste related problems as a result of changes in the process flowsheet or operating conditions. In general there will seldom be a single solution to effecting meaningful waste minimisation.

This difficulty demonstrates the need for an integrated assessment of all material flows to identify meaningful waste minimisation opportunities. At the feasibility stage (stage 6), analysis of environmental and economic benefits of selected waste minimisation options may dictate clearly what measures should be implemented. Alternatively evaluation of other options for addressing the original objective and/or additional processing problems may need to be considered, in an iterative application of the evaluation procedures. The objective of this comprehensive assessment would be to maximise environmental and economic benefits. This exceeds the scope of the levels of assessment implemented in these case studies.

The process of obtaining an integrated solution to waste management is analogous to that of process optimisation where an objective function of environmental quality is defined, and operating constraints are identified. However conventional optimisation techniques are more readily applied at the process design stage at which a process design basis can be formulated. When a waste minimisation assessment is applied in retrospect, there clearly are additional practical constraints within existing processes which result in extra costs to effect the most comprehensive solution. The extent to which this can be achieved, depends on both the capability and willingness of the company concerned to apply skills and resources to address environmental management problems.

Given the need to address certain discrete problems and to respond to changing constraints on discharges of waste to the environment the ability to progressively identify and implement measures which can reduce specific causes of waste is an important one, even though it may not be possible to achieve the optimum solution.

7.1.2 Value Of Existing Methodologies

The value of a waste minimisation assessment methodology, as defined in chapter 2, needs to be reviewed in terms of its ability to produce a set of effective measures to reduce waste generation.

Effective waste minimisation measures are those which result in a net reduction in waste, for both environmental and economic benefit. There may be simple solutions for discrete sources of waste which can be implemented easily. Other proposals may create or aggravate waste problems, or affect operability or product quality. There are no a priori guidelines to assess the effectiveness of waste minimisation measures or their ease of implementation. This difficulty is not apparent in the worksheet methodology advocated by the US EPA. The worksheets are structured as summary sheets for prescribed information relating to material flows and characteristics, and associated costs. This information does not confer an understanding of the interrelationship between waste generating processes and waste streams, and thus an ability to identify actual causes of waste. Nor is the accuracy of information substantiated. In this respect, the "descriptive" approach employed in the UNEP methodology has greater value. Attempts to resolve material balances encourage a greater understanding of processes, material and energy flows, and provide a check whereby the accuracy of information can be defined. This is a more sophisticated approach which requires an appreciation of the principles of chemical processing, skills which conventionally are not employed in the smaller scale manufacturing businesses. Given these skills, this more holistic approach to waste minimisation should have greater benefit in identifying and evaluating meaningful opportunities for waste minimisation than the more constrained approach characterised by the worksheets.

At the time of reviewing these two methodologies, it was felt that the main advantage of the worksheets was the standardised format for compiling and reporting information. This should facilitate comprehensive and consistent auditing practices for the purposes of the information gathering stage in a waste minimisation assessment. Given that the appropriate information is available, in-house staff should be able to carry out this activity with relative ease. Regrettably, in neither case study, was it possible to secure the collaboration of company staff in utilising the worksheets, owing to production priorities which distracted company attention from this waste minimisation initiative. Hence the perceptions of each company of the practical utility of these worksheets is not known. Moreover, in the absence of rigorous record keeping and restrictions on access to certain inventory and cost information, it was not possible to complete these worksheets. It may be that the format of these worksheets is too rigid to be applied generically to different operations. It would probably be more useful to customise relevant worksheets to reflect site specific operations and material flows which are directly familiar to operating staff. This approach has been adopted by the US EPA in their pollution prevention programme. In conclusion, the value of a worksheet methodology requires further evaluation, but this can only be done through collaboration with interested industry users.

7.1.3 Ease Of Implementation

The principle difficulties encountered in conducting the case study waste minimisation assessments may be summarised as:-

- a low level of company commitment;
- poor record-keeping and incomplete process- and waste related information;
- restrictions on the release of information deemed to be confidential;
- lack of in-house monitoring equipment and analytical facilities;
- a lack of understanding by company staff of chemical processes from a chemical engineering perspective and hence a lack of insight into the causes of, and potential solutions to, waste problems;

These conditions reflect a lack of environmental management capability, and a lack of awareness of the benefits of systematic process reviews in identifying process inefficiencies which can be addressed for both environmental and economic advantages. To date companies which are similar in profile to the case study companies investigated for this dissertation have tended to rely on information and advice from outside sources, and to absolve themselves from responsibility for addressing waste related problems. Successful implementation of waste minimisation assessments requires a company culture which proactively accepts this responsibility and is prepared to commit the appropriate resources to addressing environmental problems.

7.2 REVIEW OF WASTE MINIMISATION CASE STUDIES

7.2 1 Small Scale Garment Dyeing

For the reasons identified in section 7.1.1 only a preliminary level of assessment was conducted in this case study. This addressed chiefly liquid effluent and sludge waste which are discharged for off-site treatment and disposal. Wastes from the textile industry sector, of which this dye house is a member, have been shown to account for the greatest contribution by weight to hazardous waste generation in the Western Cape region. Textile processing is also waste intensive. Hence there is a real need to reduce as far as practicably possible discharges of such waste, and consumption of water.

The literature review revealed reports of waste minimisation in textile processing based on water conservation measures, and chemical and water recycling technology. However it is not clear how successfully or widespread these practices have been implemented.

Against this background of information, the preliminary review of site processing conditions identified potential opportunities for changing operating practices to achieve significant reductions in water consumption, resulting in direct cost savings from reduced water use and effluent discharge volume. Some of these changes conceivably could be implemented in-house with existing available resources. These options should be considered in a first phase of activity, given a commitment to waste minimisation. Other potential measures required greater technical and economic evaluation to test the effects of changes to process operations on product quality and economic viability.

Among these options is the potential to treat process effluent for purposes of recycling water. A preliminary evaluation of a hyperfiltration treatment plant clearly indicated that it would not be economically viable for the company concerned to operate such a process. Without implementing any other changes to existing waste management practices (for treating the balance of the effluent) higher surcharges would be incurred for discharge of more concentrated sulphate containing effluent to the sewer. These penalties would eliminate most of the potential cost savings from water conservation and effluent volume reduction by using the recycling process. The alternative of on-site lime dosing for maximum removal of sulphates would not be cost effective due to the high lime requirements.

Given that there are other potential waste minimisation measures which would be less costly to implement, these options merit more detailed investigation.

Small scale companies, such as this dye house, lack in-house resources to undertake such an evaluation. There may also be resistance to implementation of more sophisticated operating procedures or expensive technology which would make an inherently simple process more difficult (and costly) to operate. Increased production costs are perceived to threaten competitiveness in the short-term over those companies who do not take similar action. Consequently, coupled with poorly enforced legislation and the relatively low costs for services such as water and waste disposal within this region of South Africa, there is little incentive to pursue opportunities for waste minimisation.

7.2.2 Medium Scale Metal Finishing

A more detailed, site-specific assessment was carried out in this case study. The larger scale of operation precluded investigation of all process operations. Given the concern about discharges of chromium contaminated waste, the assessment focused on the chrome plating plant, as the principal source of chromium, and the effluent treatment plant, from which the effluent and sludge wastes were discharged to off-site facilities.

The 'material balance' stage of the assessment methodology was implemented to the extent of initial monitoring of operating and process conditions in these plants. Without further monitoring, the information obtained was not sufficiently accurate to resolve material balances completely. However the information so acquired revealed process problems of which operations management had been unaware, and which resulted in the generation of unnecessary waste. Hence this information made it possible to address these problems.

Within the resolution of the material balances, material flows could be estimated to reflect actual processing conditions and operating costs associated with chemical and water consumption, in both the chrome plating plant and the effluent treatment plant, discharge of effluent to the sewer and disposal of treatment sludges. Of these cost components, costs payable for effluent treatment chemicals were, by far, the most significant. Thus meaningful cost savings would clearly only be realised by eliminating, or reducing as far as practicably possible, the need for end-of-pipe chromium waste treatment by minimising the discharge of chromium waste directly from process.

The literature review had revealed the availability of a number of waste minimisation measures which reportedly have been implemented widely in metal finishing operations. These included improvements in operating practices and fairly simple process changes to implement water conservation measures. Some measures require specific technical evaluation to assess possible impacts on processing conditions. The impact of potential cost-savings achieved by these measures would be less significant than that of similar measures proposed for the first case study as a consequence of the relatively higher costs which are incurred for chemical waste treatment at this metal finishing facility.

Most successful waste minimisation in the metal plating industry has required the use of reclamation technology to recover both plating chemicals and water for reuse, e.g. ion exchange (IX). On the basis that IX is available as commercialised package equipment for such applications, the suitability of IX for the case study operation was investigated. A preliminary site-specific design basis was derived for a closed-loop process configuration in which the IX plant would treat rinse water effluent from both plating lines, and recover chromic acid and purified water for reuse in both plating lines. Some equipment modifications would be required for installation and operation of this process. This included pipework changes, provision of buffer and storage tanks for feed and product streams, and some additional process control features. Budget capital and operating costs for the IX plant were determined from commercial sources. Including allowance for installation costs and contingency, pay back was estimated as either 1.8 or 5.4 years. The different results reflect different costs of alternative proprietary chromic acid plating chemicals. At present, two different chemicals are used in separate plating systems. It is not known which chemical would be used in the future. This selection depends on the performance efficiency and quality of plating achieved by each chemical, and would be an economic decision made by the company concerned.

The preliminary evaluation also identified that it is the chemical cost for the regeneration of IX resins which is the principal operating cost component for this technology option. Given that there are alternative technologies available to effect similar recovery with lesser chemical requirements, further evaluation of these options should be undertaken.

In conclusion, the existing high costs for chemical treatment of chromium waste and penalties incurred for high levels of chromium in effluent which is discharged off-site should provide adequate incentive to improve on-site waste management practices. In doing so there are opportunities to improve the efficiency of processing operations for both environmental and economic benefit.

7.2.3 Value Of Waste Minimisation

The practical experience of conducting the case study reviews of chapters 5 and 6, demonstrated the ability to obtain useful information from these assessments before a commitment to lengthy and more costly activity need be considered. To summarise, an initial screening level can identity potential opportunities for cost-effective waste minimisation. At least one iteration of a more detailed level of assessment can provide site-specific process information for practical evaluation of selected waste minimisation measures. Further iterations invariably are required to approach an optimal solution in terms of workability, cost effectiveness and environmental enhancement.

The implementation of any waste minimisation measure will be dependent on management commitment and financial circumstances, for which long term planning may be required. However, even where it may not be deemed possible to effect improvements in the short term, there are at least specific advantages to be gained from undertaking systematic process reviews as part of a waste minimisation assessment. These are enumerated as:

1. directing attention to problem areas which require investigation;

2. identifying necessary actions to correct potential problems;

3. providing a focus for a comprehensive review whereby in-house knowledge and awareness is increased;

4. encouraging improved record-keeping as a consequence of realising the value of access to up-to-date process information;
5. increasing general awareness of issues relating to production- and waste management.

The knowledge and experience gained from conducting such reviews should improve the ability of SMEs to respond effectively to waste management problems. In recognition of particular difficulties characteristic of SMEs there is, however, a need to provide further assistance and appropriate incentives to encourage such initiatives. These constraints are discussed in more detail in the following section.

7.3 Constraints To Waste Minimisation In Small And Medium Size Enterprises

Over and above the specific difficulties identified in section 7.1.3, with respect to applying waste minimisation assessment procedures, generic constraints to the practical implementation of a waste minimisation policy at SMEs have been identified from the literature review and from the practical reality of local case studies. These are discussed as follows:

There is a low level of environmental competence at SMEs where production and operating skills are a priority. Furthermore there is a lack of knowledge about environmental hazards of certain materials, with respect to occupational risks and pollution potential, and a lack of awareness of global trends in legislation and technological alternatives for effecting improved environmental performance. Without appreciating the costs associated with waste generation, SMEs may perceive requirements for waste management, necessitated by environmental legislation, to be too costly and unaffordable within their operating margins. Companies which do not consider it economically viable to implement changes needed to comply with such legislation, have been known to threaten to close, or to relocate to other areas where environmental legislation is less strict. In the face of social costs to the community of lost employment, the leverage of local authorities to enforce environmental laws strictly or even encourage greater pollution control is reduced. This situation reflects a perception that waste management entails costly investment in capital for which smaller scale operations have less resources than large scale industry operators. Linked to this is the often cited disadvantage of poor economy of scale for operations with lower production capacities. Again, this reflects a preoccupation with solutions offered by end-of-pipe techniques which require capital investment. It may be that readily available equipment is not sized appropriately for small scale throughputs. Resistance of SMEs to address waste management issues has limited market demand for such process development with concomitant lack of commercial interest from consultants and equipment suppliers. This self-perpetuating problem needs to be resolved by greater collaboration between industry, legislators and technology experts.

While there has been growing awareness among some SMEs of the need to address their waste management problems more responsibly, the infrastructure which is needed to facilitate an improved management strategy for SMEs is not yet developed in many industrial economies. It is often difficult for SMEs to access appropriate information and secure affordable expert assistance; seminars and training programmes are often too costly; institutional support e.g. that of trade associations, is limited; and SMEs lack the facilities or resources to undertake their own development work. There is a need for greater collaboration between industry members themselves in addressing common problems and transferring knowledge, and between industry and research institutions which can offer cost-effective research and development services.

These are issues which need to be addressed in developing regional and national strategies for industrial waste management.

7.4 Strategic Regional Waste Management Considerations

The industrial infrastructure of the Western Cape region of South Africa is characterised by many more SMEs than larger manufacturing and chemical processing industry members. Specifically, Western Cape industry is dominated by food processing and textile processing operations which have been shown, by the Department of Environment Affairs (1992) study, to generate the greatest quantities of total waste. Textile processing also accounts for the greatest contribution by weight to hazardous waste generation in the region. Although the metal finishing industry sector is much smaller, it is notable for the high hazardous content (almost 87% by weight) of associated waste. Water usage by these industry sectors was not estimated in the Department of Environment Affairs (1992) study, but other literature references have highlighted the water intensive nature of both textile processing and metal finishing operations.

Members of these two industry sectors have been represented by the case studies reviewed in this dissertation, and are referred to above simply to illustrate the nature of industrial activity in the Western Cape. In general SMEs tend to be disproportionately large users of water and similarly producers of waste. As water supply and land for disposal purposes are regional resources, it is appropriate that waste (and resource) management should be considered a regional issue for which an appropriate regional strategy is required.

Given the current constraints to on-site waste management by these smaller operations, there will be a continued dependence on off-site waste processing facilities in the short to medium term. Hence two goals for long term regional waste management can be identified:

1. waste minimisation at source, and

2. optimum regional waste management.

Successful attainment of these goals depends on the availability of skills, experience, cost-effective technology, financial resources and willingness to make changes. These preconditions require the development of an integrated waste management strategy which will facilitate:-

1. the adoption of waste auditing practices and the evaluation of waste minimisation opportunities in waste management systems at different companies;

2. the development of a regional waste arisings database which can be used in strategic waste management planning;

3. training and education to encourage more responsible waste management and to improve current skills;
4. the provision of cost effective technical assistance to help identify, evaluate and implement opportunities for waste minimisation;
5. the development of centralised treatment facilities which can provide economies of scale to cost-effectively process specific waste types using the most appropriate technology in the interests of efficiency, resource recovery and/or detoxification of wastes prior to disposal.

7.5 General Lessons For South Africa

The review of international trends in environmental management has shown that waste management needs to be addressed as part of a broader environmental strategy which accommodates the needs for economic growth, including industrial development and socio-economic benefits, while protecting the environment. Waste minimisation is generally acknowledged to be the only viable long term waste management strategy which will allow such development to be sustained by conserving natural resources and minimising pollution.

In terms of pollution prevention waste minimisation should be the most efficient strategy as operating costs for end-of-pipe treatment will incur considerably greater expense in the long term than reducing generation of waste at source. Moreover a waste minimisation strategy will avoid potential environmental liabilities and costly expenditure for remediation of environmental damage, as witnessed by the Superfund project in the USA. Clearly it is important that environmental concerns be addressed at as early a stage of industrial development as possible. Given current interest in re-investment in South Africa, and possible industrial restructuring, there is now the ideal opportunity to implement an improved environmental management strategy.

In the development of new industrial activities, the adoption of cleaner technologies at the start of an investment cycle should be encouraged to avoid costs of later retrofits for improved pollution control. For existing activities, or where proven cleaner technology alternatives are not available, the use of more rigorous house keeping practices and of treatment technologies for recycling offers the most potential for improved waste management in the short and near term. Where on-site recycling is not practicable for small scale industry operations, consideration should be given to the development of centralised treatment and resource recovery facilities which can process specific waste materials cost-effectively.

Currently the South African industry and economy fall between developed and developing status. As part of the developed sector, large scale manufacturing and chemical processing industries represent a fairly uniform industry base with established international trading links. Increasingly, the environmental management practices of these industry members are influenced by environmental policies of overseas parent companies or business partners. For example, some companies audit prospective trade partners to ensure satisfactory environmental performance, in compliance with standards in their home countries. This has implications for all businesses who wish to trade with countries with such legislation.

Regulatory control to date has focused principally on larger scale industry operations which tend to have well defined point source emissions, and thus are easier to regulate. Yet these industries prefer to preserve a self-regulatory mode of operation through voluntary initiatives such as the "Responsible Care" programme of the chemical industries associations in a number of countries, including South Africa. Arguably, such an approach should achieve harmonisation of standards internationally, among participating industry members, more efficiently than legislation which evolves separately in different countries. Greater attention should be paid to addressing the environmental problems caused by smaller scale SME type activities which tend to be more disparate, particularly in the developing industrial sector.

With respect to SME operations, there has been a leniency in enforcing compliance with environmental legislation. This situation prevails in recognition of perceived problems facing SMEs with respect to cost-effective waste management and the desire to sustain these operations given their value as employment generators. Coupled with low cost disposal options, there has been no incentive for SMEs to improve their environmental performance. Yet this situation cannot be allowed to continue with the associated environmental problems unabated, particularly as a proliferation of SMEs is expected in future industrial development in South Africa. This reinforces the significance of addressing these environmental problems. There is a need to provide a formal education and training structure for tertiary education and industry supported training schemes to raise environmental awareness, and to provide an improved skills base by which SMEs can address environmental problems. In particular, the benefits of waste minimisation, and the availability of opportunities to realise cost-effective improvements in environmental performance, need to be promoted.

Even the larger scale industry operations which generally do have the financial and skills resources to address environmental problems, may lack a comprehensive understanding of integrated environmental issues. Only with an understanding of total environmental impacts associated with the formulation of particular products and their usage, can the environmental impacts of industrial activity be minimised. This is the ambit of environmental Life Cycle Analysis (LCA) in which additional skills training is needed.

Accompanying education is a need for commitment to appropriate research and development to enable South African industry to become more competitive through the use of its technological skills. The experience of developed economies has shown that investment in environmental programmes has stimulated trade opportunities and created employment opportunities in the pollution control service industry and in provision of innovative technologies. Hence forcing a re-evaluation of environmental issues through research and development can create opportunities to become market leaders in particular sectors of industrial activity.

Research needs should be prioritised to identify those areas of economic activity which would be of greatest benefit in terms of mitigating environmental impacts while providing for socio-economic development. Such a strategy requires a reliable information base which can be used to identify the scale of environmental problems and the potential for technological improvements to be realised.

These conclusions are not unique ideas. They are policies which are being incorporated into waste management strategies in other countries, with both developed and developing economies.

The primary perspective of this discussion is in relation to the pivotal role played by SMEs in waste generation and their apparent inability to take on-board responsibility for waste management and new developments in cleaner technology. This dissertation asserts that the tool of waste minimisation assessments can be used by all scales of industry operations to improve their capability to address waste management problems. However a national policy of waste minimisation is needed to create the infrastructure which can support such initiatives, particularly in SMEs.

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APPENDIX A:
WASTE MINIMISATION ASSESSMENT PROCEDURE

CONTENTS:

- tabulated procedure, with reference to work sheet numbers;
- EPA type work sheets (Drabkin (1989)

DATA SOURCE/ TECHNIQUE	WORK SHEET	PROCEDURE	INFORMATION OUTPUT	TABLE/ FIGURE
		1. Preparation		
consultation	S2	secure management commitment	policy statement	
		appoint audit team	audit team	
		identify goals	*review if necessary*	
		identify resource needs	defined goals	
		develop a work programme	defined needs	
company records	S3	review availability of site information & documentation	audit time table/programme	
		2. Process Operation		
layout drawings		initial site survey		
process drawings		identify unit operations	summary of unit operations	Table
process descriptions		identify operating conditions		
equipment specifications		identify expected waste types	summary of expected wastes	Table
process control records		confirm focus for assessment	defined goals/need/programme	
effluent records		construct process flow diagrams	process flow diagrams	
waste disposal records				Figures (as required)
monitoring records				
literature references:		**3. Technical Reviews**		
technical; journals; databases;		process technology	review summary/reports	
exhibitions; expert advice		waste management technology		
		4. Material & Energy Balances		
inventories	S4	determine inputs	raw material inventory	Table
operating procedures	S4	determine water usage	summary of water usage	Table
process control records	S4	determine energy usage	summary of energy usage	Table
water accounts		measure current recycling levels		
site records	S5	determine outputs	summary of outputs	Table
operating procedures	S6	account for waste water	summary of waste flows & characteristics	Table
equipment specifications	S6	account for gaseous emissions	summary of gaseous emissions	Table
estimation	S6	account for off-site wastes	summary of off-site wastes	Table
monitoring		assemble information	summary of inputs & outputs	Table/ Flow Diagram
effluent accounts		derive preliminary balances	comparison of inputs & outputs	
waste manifests		evaluate material/energy balances		
disposal records		refine material/energy balances	*repeat if necessary*	
high treatment costs		identify problem wastes		
operational source				
causes & influences				
sampling & analyses				
reduction priorities				
		5. Identification of Options		
in-house review				
consultation/expert advice	S7/S8	preliminary evaluation of potential waste minimisation measures:	summary/reports:	
test work; demonstration		– short term	– technical	
volume/toxicity reduction		– longer term	– environmental	
cross media effects			– economic	
degradability of wastes				
treatability of wastes				
resource consumption				
energy usage				
cost savings				
operating costs	S9			
capital costs				
		6. Feasibility Analyses		
long term costs		more comprehensive economic analyses of selected options	summary/reports	
regulatory fees				
liability costs			*review if necessary*	
non-quantifiable				
cash flow analyses				
viability			RECOMMENDATIONS	

Firm ________	**Waste Minimization Assessment** Simplified Worksheets	Prepared By ________
Site ________		Checked By ________
Date ________	Proj. No. ________	Sheet 1 of 1 Page __ of __

WORKSHEET
S2

SITE DESCRIPTION

EPA

Firm:

Plant:

Department:

Area:

Street Address:

City:

State/ZIP Code:

Telephone: (   )

Major Products:

SIC Codes:

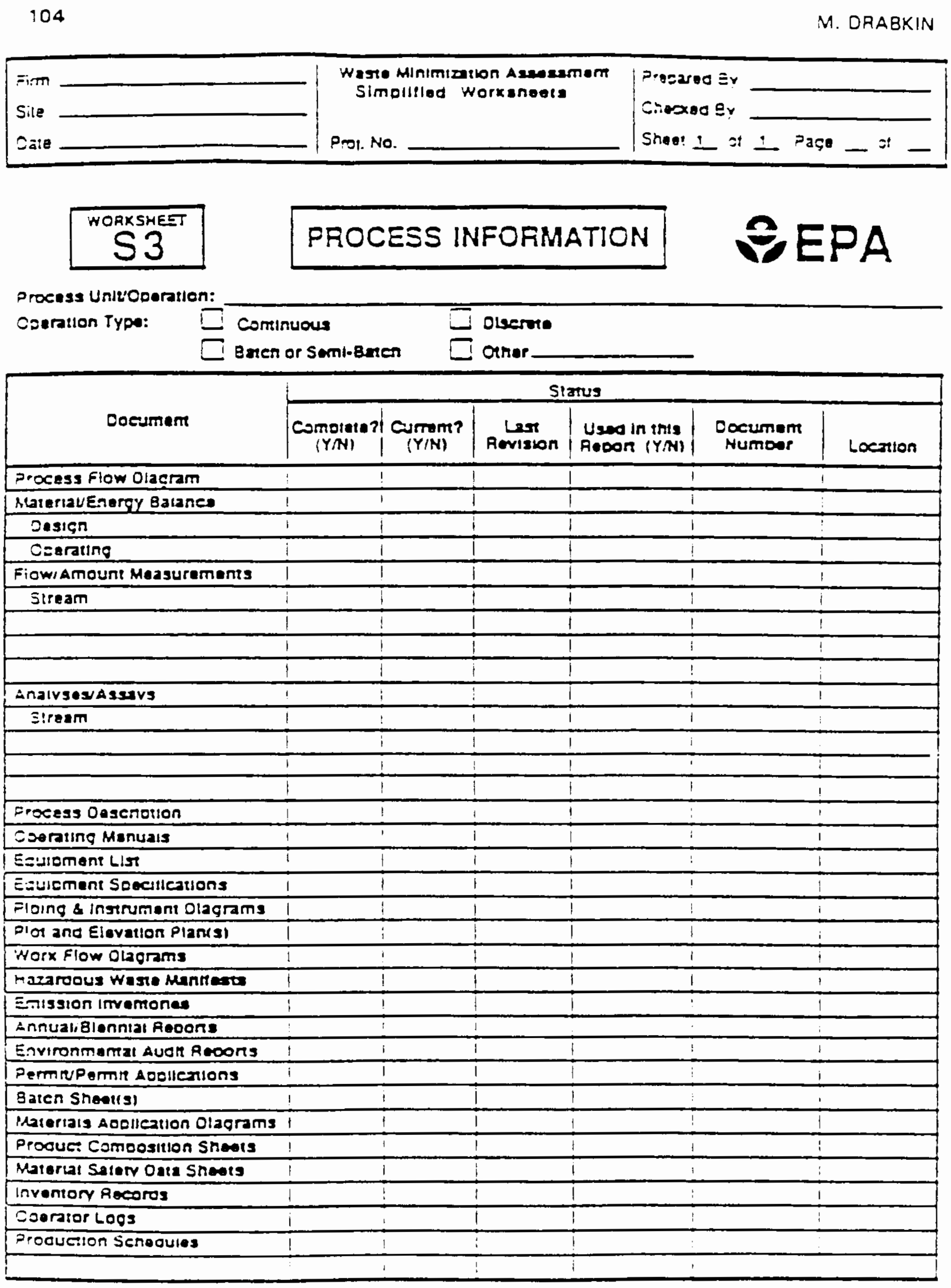
EPA Generator Number:

Major Unit or:

Product or:

Operations:

Facilities/Equipment Age:



Firm __________	**Waste Minimization Assessment** **Simplified Worksheets**	Prepared By __________
Site __________		Checked By __________
Date __________	Proj. No. __________	Sheet 1 of 1 Page __ of __

WORKSHEET
S3

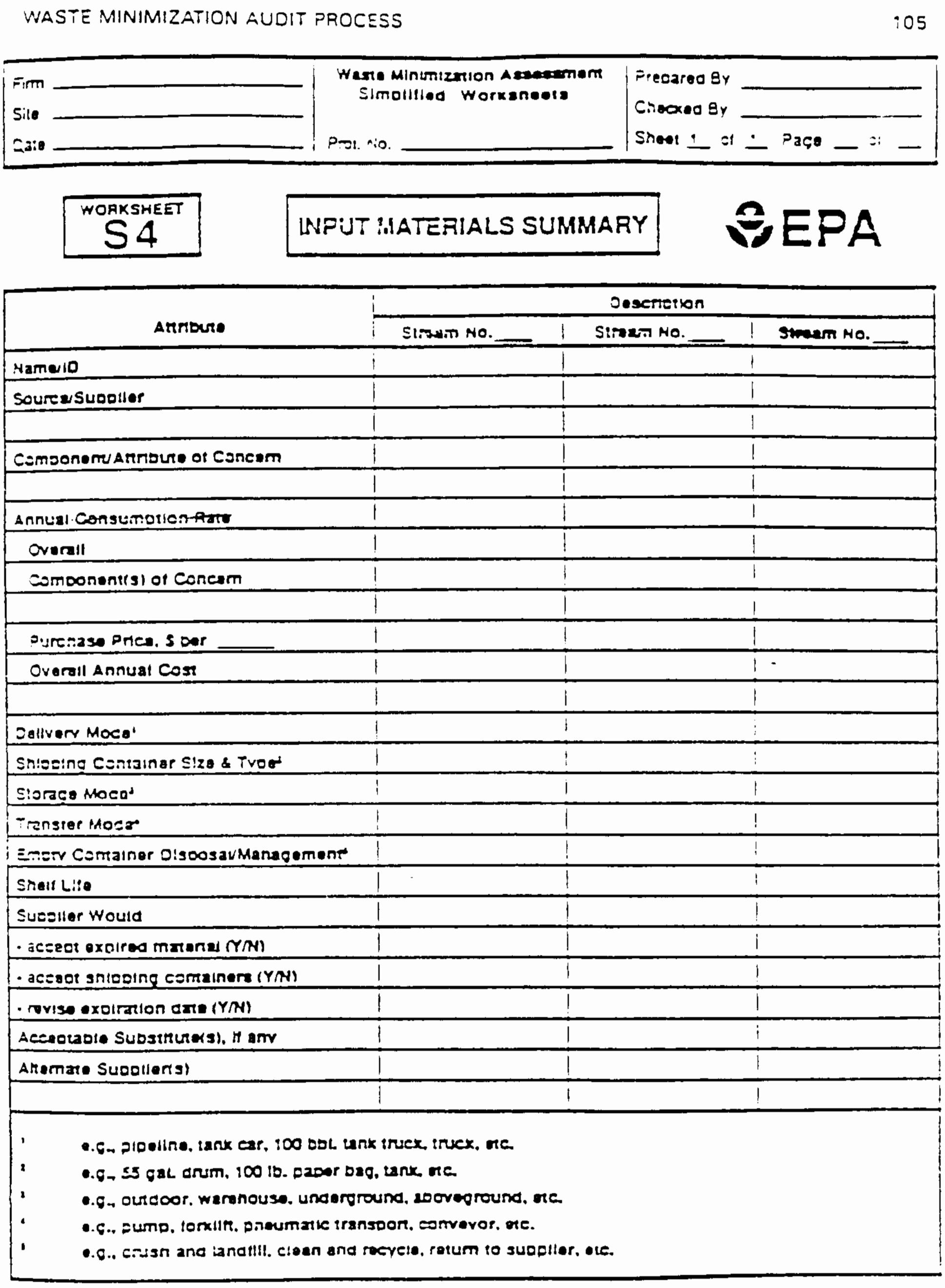
PROCESS INFORMATION

EPA

Process Unit/Operation: ____________________

Operation Type:
☐ **Continuous** ☐ **Discrete**
☐ **Batch or Semi-Batch** ☐ **Other** __________

Document	Status					
	Complete? (Y/N)	Current? (Y/N)	Last Revision	Used in this Report (Y/N)	Document Number	Location
Process Flow Diagram						
Material/Energy Balance						
Design						
Operating						
Flow/Amount Measurements						
Stream						
Analyses/Assays						
Stream						
Process Description						
Operating Manuals						
Equipment List						
Equipment Specifications						
Piping & Instrument Diagrams						
Plot and Elevation Plan(s)						
Work Flow Diagrams						
Hazardous Waste Manifests						
Emission Inventories						
Annual/Biennial Reports						
Environmental Audit Reports						
Permit/Permit Applications						
Batch Sheet(s)						
Materials Application Diagrams						
Product Composition Sheets						
Material Safety Data Sheets						
Inventory Records						
Operator Logs						
Production Schedules						



WASTE MINIMIZATION AUDIT PROCESS 105

Firm ______________________
Site ______________________
Date ______________________

Waste Minimization Assessment
Simplified Worksheets

Proj. No. ______________________

Prepared By ______________________
Checked By ______________________
Sheet 1 of 1 Page ___ of ___

WORKSHEET
S4

INPUT MATERIALS SUMMARY

EPA

Attribute	Description		
	Stream No. ____	Stream No. ____	**Stream No. ____**
Name/ID			
Source/Supplier			
Component/Attribute of Concern			
Annual ~~Consumption Rate~~			
Overall			
Component(s) of Concern			
Purchase Price, $ per ______			
Overall Annual Cost			
Delivery Mode[1]			
Shipping Container Size & Type[2]			
Storage Mode[3]			
Transfer Mode[4]			
Empty Container Disposal/Management[5]			
Shelf Life			
Supplier Would			
- accept expired material (Y/N)			
- accept shipping containers (Y/N)			
- revise expiration date (Y/N)			
Acceptable Substitute(s), if any			
Alternate Supplier(s)			

[1] e.g., pipeline, tank car, 100 bbl. tank truck, truck, etc.

[2] e.g., 55 gal. drum, 100 lb. paper bag, tank, etc.

[3] e.g., outdoor, warehouse, underground, aboveground, etc.

[4] e.g., pump, forklift, pneumatic transport, conveyor, etc.

[5] e.g., crush and landfill, clean and recycle, return to supplier, etc.

Firm ____________	Waste Minimization Assessment Simplified Worksheets	Prepared By ____________
Site ____________		Checked By ____________
Date ____________	Proj. No. ____________	Sheet 1 of 1 Page __ of __

WORKSHEET
S5

PRODUCTS SUMMARY

EPA

Attribute	Description		
	Stream No.___	Stream No.___	Stream No.___
Name/ID			
Component/Attribute of Concern			
Annual Production Rate			
Overall			
Component(s) of Concern			
Annual Revenues, $ ______			
Shipping Mode			
Shipping Container Size & Type			
Onsite Storage Mode			
Containers Returnable (Y/N)			
Shelf Life			
Rework Possible (Y/N)			
Customer Would			
- relax specification (Y/N)			
- accept larger containers (Y/N)			

Firm ______________	**Waste Minimization Assessment Simplified Worksheets**	Prepared By ______________
Site ______________	Proc. Unit/Oper. ______________	Checked By ______________
Date ______________	Proj. No. ______________	Sheet 1 of 1 Page __ of __

WORKSHEET S6

WASTE STREAM SUMMARY

EPA

Attribute	Description		
	Stream No. ___	Stream No. ___	Stream No. ___
Waste ID/Name:			
Source/Origin			
Component/or Property of Concern			
Annual Generation Rate (units ________)			
Overall			
Component(s) of Concern			
Cost of Disposal			
Unit Cost ($ per: ________)			
Overall (per year)			
Method of Management[1]			

Priority Rating Criteria[2]	Relative Wt (W)	Rating (R)	R x W	Rating (R)	R x W	Rating (R)	R x W
Regulatory Compliance							
Treatment/Disposal Cost							
Potential Liability							
Waste Quantity Generated							
Waste Hazard							
Safety Hazard							
Minimization Potential							
Potential to Remove Bottleneck							
Potential By-product Recovery							
Sum of Priority Rating Scores		$\Sigma(R \times W)$		$\Sigma(R \times W)$		$\Sigma(R \times W)$	
Priority Rank							

Notes:

[1] For example, sanitary landfill, hazardous waste landfill, onsite recycle, incineration, combustion with heat recovery, distillation, dewatering, etc.

[2] Rate each stream in each category on a scale from 0 (none) to 10 (high).

Firm ______	**Waste Minimization Assessment** Simplified Worksheets	Prepared By ______
Site ______	Proc. Unit/Oper. ______	Checked By ______
Date ______	Proj. No. ______	Sheet 1 of 1 Page __ of __

WORKSHEET S7

OPTION GENERATION

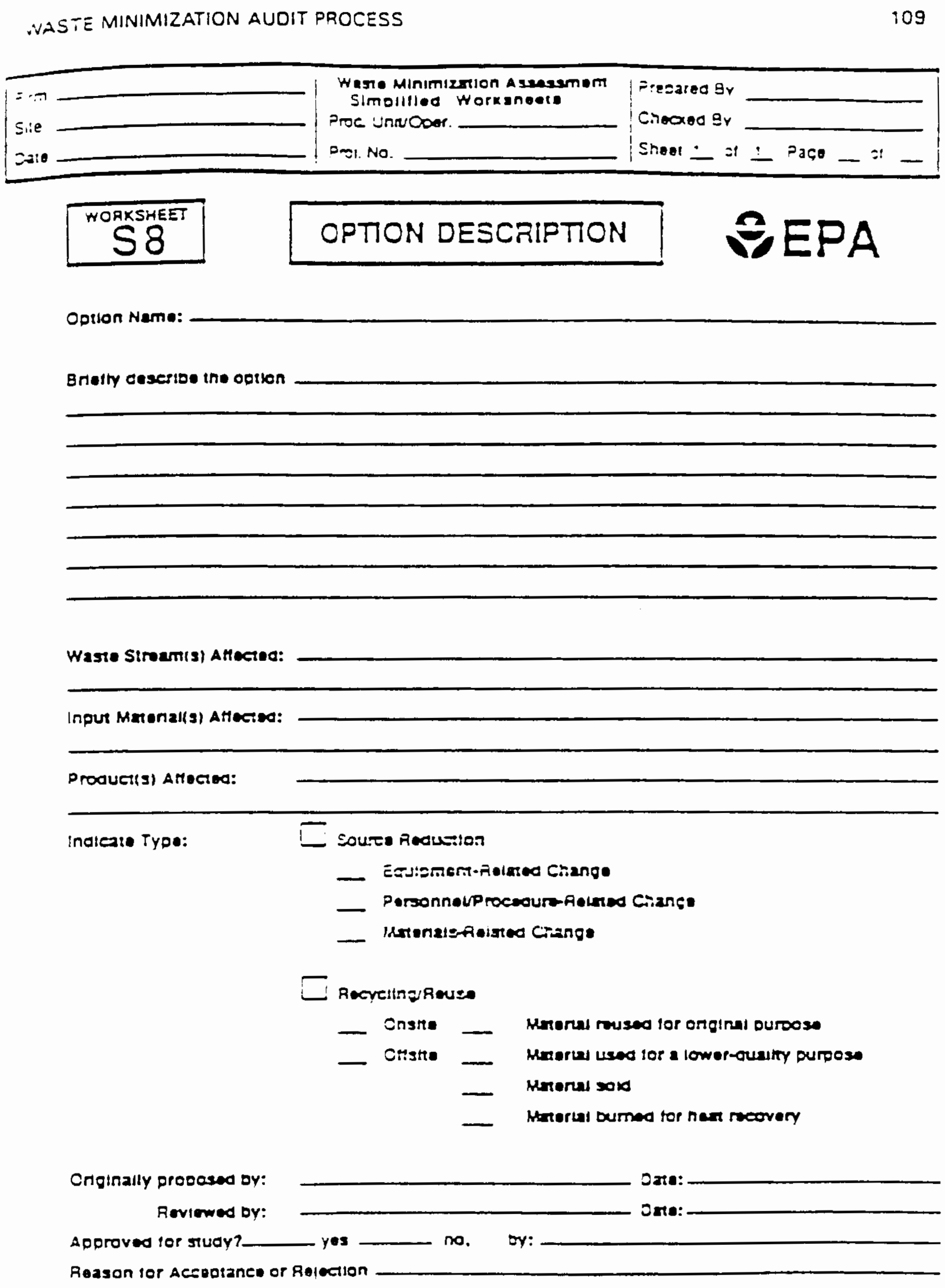
EPA

Meeting format (e.g., brainstorming, nominal group technique) ______

Meeting Coordinator ______

Meeting Participants ______

List Suggested Options	Rationale/Remarks on Option



WASTE MINIMIZATION AUDIT PROCESS 109

Firm ________	**Waste Minimization Assessment Simplified Worksheets**	Prepared By ________
Site ________	Proc. Unit/Oper. ________	Checked By ________
Date ________	Proj. No. ________	Sheet 1 of 1 Page __ of __

WORKSHEET S8

OPTION DESCRIPTION

EPA

Option Name: ________

Briefly describe the option ________

Waste Stream(s) Affected: ________

Input Material(s) Affected: ________

Product(s) Affected: ________

Indicate Type: ☐ Source Reduction
- __ Equipment-Related Change
- __ Personnel/Procedure-Related Change
- __ Materials-Related Change

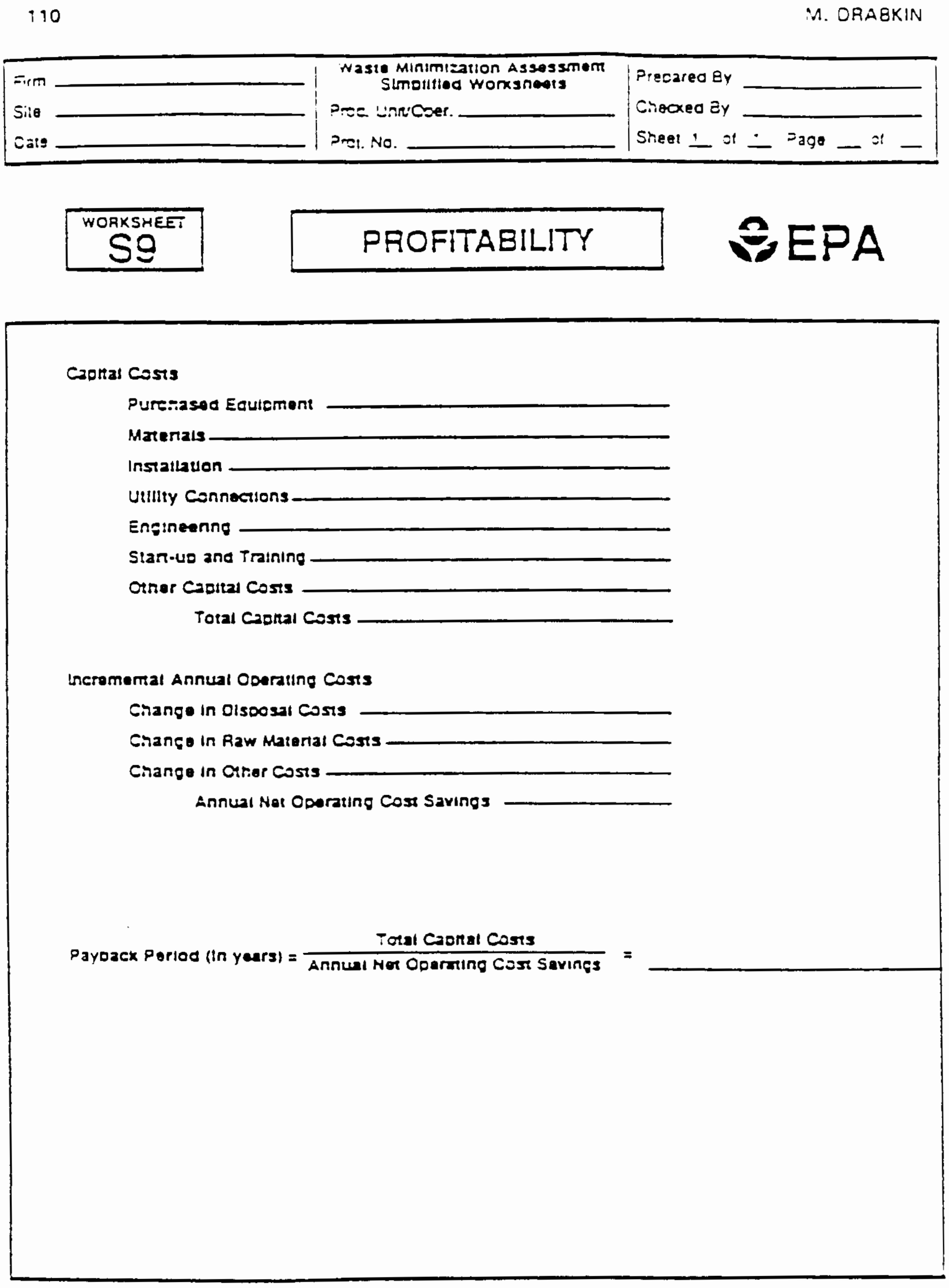
☐ Recycling/Reuse
- __ Onsite
- __ Offsite
- __ Material reused for original purpose
- __ Material used for a lower-quality purpose
- __ Material sold
- __ Material burned for heat recovery

Originally proposed by: ________ Date: ________

Reviewed by: ________ Date: ________

Approved for study? ________ yes ________ no, by: ________

Reason for Acceptance or Rejection ________



Firm ____________	Waste Minimization Assessment Simplified Worksheets	Prepared By ____________
Site ____________	Proc. Unit/Oper. ____________	Checked By ____________
Date ____________	Proj. No. ____________	Sheet 1 of 1 Page __ of __

WORKSHEET S9

PROFITABILITY

EPA

Capital Costs

Purchased Equipment ____________

Materials ____________

Installation ____________

Utility Connections ____________

Engineering ____________

Start-up and Training ____________

Other Capital Costs ____________

Total Capital Costs ____________

Incremental Annual Operating Costs

Change in Disposal Costs ____________

Change in Raw Material Costs ____________

Change in Other Costs ____________

Annual Net Operating Cost Savings ____________

$$\text{Payback Period (in years)} = \frac{\text{Total Capital Costs}}{\text{Annual Net Operating Cost Savings}} = \underline{\qquad\qquad}$$

APPENDIX B
INTERNATIONAL CLEAN TECHNOLOGY INITIATIVES

COUNTRY	ORGAN.	NAME	ACTIVITIES
	UNEP	IE/PAC Industry & Environment Programme Activity Centre ICPIC International Cleaner Production Information Clearing-house	promotes the exchange of information & transfer of technology to achieve Clean Production and sustainable industrial development.
Canada	PAPRICAN	Pulp And Paper Research Institute of Canada	optimisation of combustion & composting of deinked sludge generated by paper recycling
Denmark	Ministry of Environment	Cleaner Technology Action Plan	A framework for maintaining and expanding efforts in Clean Technologies.
Europe	EC	STEP	supports research in Clean Technologies (recycling & EOP), with priority given to energy & raw material issues.
Europe	EC Commission	NETT Network for Environmental Technology Transfer	
Europe	EC Commission	ACE Action by the Community on the Environment	provides financial support for demonstration projects.
Europe	EC Commission	LIFE	provides financing for a) priority environmental action b) technical assistance c) regional or global environmental actions
Germany	government	BMFT Ministry for Science & Technology	provides up to 50% funding for collaborative environmental projects, targeting SMEs, for research, development & demonstration.
India	National Productivity Council	Productivity initiative	promotes waste minimisation in small scale industries and provides information on cost-effective methods of waste treatment & pollution control.
Japan	MITI	Ministry for International Trade & Industry	environmental technology research initiative: 60 major corporations, including financial companies, to ease commercialisation of promising new technologies.
Netherlands	NOTA	Netherlands Organisation of Technology Assessment	PRISMA project: to demonstrate industrial case-studies of pollution prevention
Netherlands	local government	PROGRES: Prevention at Enterprises in Gelderland Reduction of Emissions and Wastes	provincial project, with collaboration between industry, researchers and private companies
UK	DOE	EPTS Environmental Protection Technology Scheme	supports new technologies for environmental improvement in specific priority areas
UK	DTI	ETIS Environmental Technology Innovation Scheme	improves environmental standards; supports research into innovative technologies & promotes commercialisation for equipment suppliers, for whole range of environmental applications.
UK	AFRC/ SERC	CTU Clean Technology Unit	supports primarily fundamental redesign of existing processes as Clean Technology, as well as new technologies for pollution control incl. retrofits & EOP technologies; .
UK	DTI	DEMOS DTI's Environmental Management Option Scheme	promotes widespread adoption of technologies with broad potential for environmental benefits
UK	DTI	SPUR support for products under research	supports process and product development for single companies with less than 500 employees
UK	DTI	EUROENVIRON	mechanism for collaborative R&D with European environmental management industry.

COUNTRY	ORGAN.	NAME	ACTIVITIES
UK	private consultancy	CEST Centre for Exploitation of Science and Technology	Industry & Environment Project reviews current & possible future environmental issues & their implications for industrial opportunities; provides UK Industry with an assessment of priority areas for key technology opportunities. Manages a co-operative waste minimisation project with industry participation; case studies disseminated through local chambers of commerce and trade bodies such as CIA
UK	government	LINK	provides a framework & funding for collaborative research programmes in science, technology and engineering.
UK	private consultancy	R&D Clearing House	seeks products and processes for subscribing members; assists in new product development; facilitates financial & technical support for R&D in chemical & allied industries.
UK	University Bath	Centre for Environmental Process Technology	research & teaching in environmental process technology and management
USA	EPA	WRITE Waste Reduction Innovative Technology Evaluation	identifies & evaluates innovative pollution prevention applications to promote use of effective technologies
USA	EPA	WREAFS Waste Reduction Evaluation At Federal Site Program	demonstration & evaluation projects with collaboration between EPA, Dept. Defence, Dept. of Energy & other federal agencies
USA	EPA	WRAP Waste Reduction Assessment Program	encourages industrial use of waste minimisation assessments; has developed the EPA "Manual For Waste Minimisation Opportunity Assessments"
USA	EPA	WRISE Waste Reduction Institute for Scientists and Engineers	facilitates liaison between researchers and industry by advising on generic technologies & practical application problems; co-ordinates demonstration projects; encourages education & training in waste minimisation concepts.

APPENDIX C
CHEMISTRY AND PROCESS TECHNOLOGY: TEXTILE DYEING

Chemistry and process technology has been reviewed largely from Trotman (1970), and is summarised as follows:

1. COTTON DYEING

Woven cotton fabric consists of cellulose fibres which are polymers of glucose in a linear configuration, as illustrated in Figure C1. The fibres consist mainly of glucose (88-96%) with the balance being impurities of inorganics, pectins, waxes, proteins and other organic compounds (WRC, 1987). In water, cellulose acquires a negative potential giving rise to ionic interactions as described below.

Garment dyeing involves bonding of coloured compounds to the receiving fabric so as to impart a colour change to the fabric. Bonding forces are not well understood, but are attributed to one or more of Van Der Waals forces, hydrogen bonding and covalent bonding with chemical reaction. Pigment dyeing is a printing process which uses a resin to bind coloured pigment to the fabric without chemical reactions at the molecular level. Van Der Waals forces and hydrogen bonding forces are intermolecular forces and are inherently weaker than chemical bonds. Hence the type of bonding influences the nature of dyeing reactions and associated wastes.

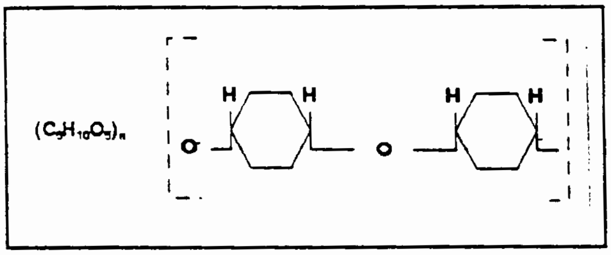


FIGURE C1: Structural Configuration Of Glucose In Cellulose Cotton Fibres

Coloured dye compounds consist of organic molecules attached to chromophore groups such as nitro-, nitroso-, azo- and carbonyl groups. These provide colour by selective absorption and reflection of different wavelengths of light falling onto chromophores in the dyed fabric. These chromophore molecules are insoluble, and to render the dye compound soluble, it must be modified by an amino-, substituted amino-, hydroxyl-, sulphonic- or carboxyl group (referred to as an auxochrome). An example of a direct dye compound is given in Figure C2.

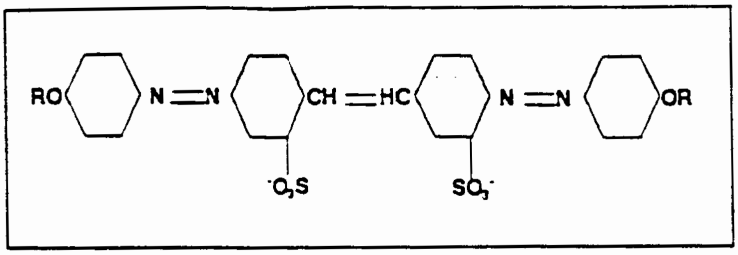


FIGURE C2: Structure Of Chrysophenine G (direct yellow): An Example Of A Direct Dye

Dyes in solution are either molecular (and partially ionised) or exist as ionic micelles, which are spherical aggregates of long chained anions with a smaller number of detached cations in adjacent positions, so there is a net negative charge. Hence dye reactions are affected by electrostatic interaction between charged dyes in solution and the negatively charged cellulose fibre surface. Surface active compounds must be used to modify these surface characteristics. For example an electrolyte, such as the cation surface active compound illustrated in Figure C3, is required to reduce the surface charge to enable dye molecules to approach within the range of the bonding forces. Other auxiliary chemicals are used to similarly modify fibre surface characteristics to impart favourable properties such as wet-fastness and fabric softness.

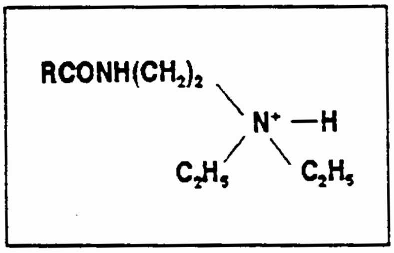


FIGURE C3: Structure Of Diethylethylene Diamine: An Example Of A Surface Active Compound

Once solubilised, transfer of dye takes place by migration of dye molecules from dye solution to the solution/fabric interface and adsorption at the fibre surface, diffusion through the fibre and finally bonding.

The diffusion stage is governed by diffusivity of the dye, permeability of the fibre and concentration of dye molecules in the interfacial layer. Hence operating parameters in wet-processing are temperature, pH, liquor ratio and chemical concentrations. Kinetically, higher temperatures are favourable for promoting vibrational activity of dye molecules. This facilitates closer movement to the fibre surface and increases rate of dye transfer, i.e. rate at which equilibrium is attained. Thermodynamically, however, higher temperatures inhibit the bonding process as separation of hydrogen bonds between water soluble groups and insoluble organic structures within dye compounds is accompanied by a decrease in free energy of the system, with energy release, i.e. an exothermic process. Thus higher temperatures decrease equilibrium dye adsorption resulting in reduced uptake of dye by the fabric.

Consequently operating temperature is a compromise between these two effects in the interests of economy in process time and of chemicals consumption.

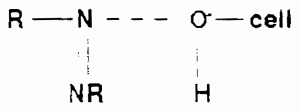
Dyestuff consumption is more economical in baths with short liquor ratios, i.e. with lower water to garment loading and higher solution concentration. Bath solutions potentially can be reused by fortifying dye liquor by small additions of make-up dye. However it may be difficult to ensure reproducibility of colour and dyeing quality as this requires a constant liquor ratio.

2. DYEING PROCESSES

2.1 Direct Dyeing

Direct dyes are based on sodium salts of sulphonic acids, usually sulphonated azo compounds, such as that illustrated in Figure C2. Such compounds have a direct affinity for cellulosic fibres. The azo groups form the hydrogen bonds with hydroxyl groups of cellulosic fibres, as shown in Figure C4.

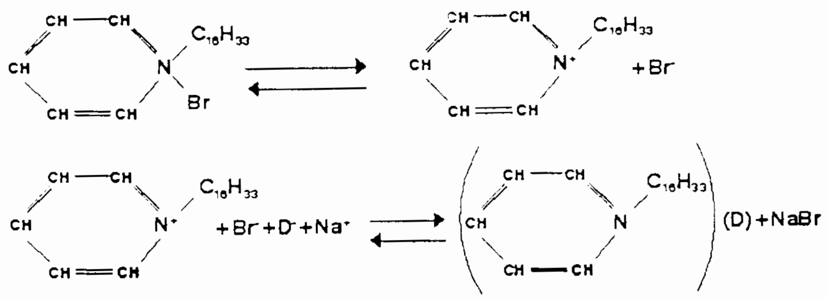
FIGURE C4: Mechanism Of Hydrogen Bonding



$$\begin{array}{ccccccc} R & — & N & - - - & O & — & \text{cell} \\ & & \vdots & & | & & \\ & & NR & & H & & \end{array}$$

The dyeing temperature which achieves maximum exhaustion, i.e. maximum dye take-up, varies from 20°C to 100°C for different dye compounds, with reduced dye exhaustion occurring at higher temperatures. Dye exhaustion is promoted by addition of sodium sulphate (Glaubers salt) or sodium chloride which reduces the fibre surface negative charge, thereby facilitating uptake of dye. Solutions are usually neutral, or may be slightly alkaline if, for example, soda ash is added to soften the water or to improve solubility of certain dyestuffs.

Direct dyes do not possess good wet-fastness, as hydrogen bonds are easily broken, and some form of after-treatment is required to increase molecular weight of the dye so as to render it less soluble in water. One such method is treatment with a cationic fixing agent such as cetyl pyridium bromide, which forms the "insoluble" complex with the anion as follows:



Small amounts of acetic acid are used to bring the cationic compound into solution.

2.2 Reactive Dyeing

Reactive dyes are those which fix onto cellulosic fibres with covalent bonds by reacting with hydroxyl groups of cellulose, for example the reaction with Cl atoms of chlorotriazinyl and chloropyrimidyl compounds, as illustrated in Figure D5. This covalent bonding requires addition of an alkaline fixing agent, normally sodium bicarbonate and soda ash, to absorb the electronegative atom.

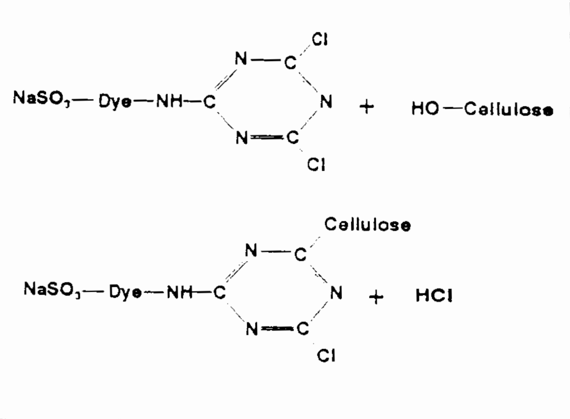


FIGURE C5: Reactive Dye Bonding With Cellulose

Covalent bonding imparts good wet-fastness to these dyes. However reactive dyes undergo hydrolysis with water, as shown in Figure C6. This reduces colour yield and produces a mono or dihydroxy compound, which interacts with the fibre through hydrogen bonding, with its associated reduced wet-fastness. Hence reactive dye solutions cannot be stored for more than a few hours without loss of potential colour and impaired quality.

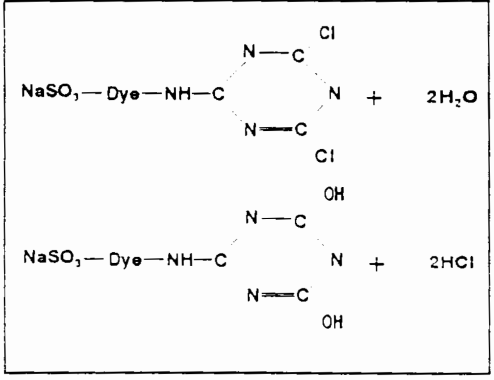


FIGURE C6: Hydrolysis Of Reactive Dyes

Application of heat promotes rapid fixation by removing carbon dioxide (CO_2) from the bicarbonate, forming the more alkaline sodium carbonate. However higher pH values and higher temperatures aggravate hydrolysis. So again operating temperature and pH are a compromise between process time and chemical efficiency. The temperature is generally kept below 40°C, and as much dye as possible is allowed to penetrate the fibre while the solution is still neutral, before alkaline fixing agents are added.

2.3 Pigment Dyeing

Pigment dyeing involves a different application method. Pigment dyes are water insoluble and, having no affinity for textile dyes, cannot enter into chemical or physical reactions with the fabric. Instead a synthetic, latex type binding agent is incorporated in the print paste. This has film forming properties and thus "prints" embedded pigment onto the fibre surface. Prints are fixed by heat treatment.

The binding agent is a dispersion or solution of polymers such as polyacrylic acid derivatives and butadiene-styrene co-polymers. A cross-linking agent consisting of synthetic resin types such as melamine-formaldehyde derivatives is added for extra wet-fastness. The pigment- and binding dispersions are incorporated in a clear emulsion with auxiliary chemicals such as dispersing agents, emulsifiers, lubricants, protective colloids and synthetic thickening agents (Kirk-Othmer, 1979). As no interaction with the fibre is required, this method can be used with a great variety of fabrics.

3. ASSOCIATED WET PROCESSES

Associated with garment dyeing are pre- and post-dyeing processes, including desizing, scouring, washing, bleaching and dye stripping.

3.1 Desizing

Sizing starch is applied to yarns as a gelatinous film which protects and strengthens yarns for weaving purposes. This starch must be removed by desizing which uses an enzyme to convert insoluble starch to soluble glucose. Alternatively oxidising agents such as persulphate and hydrogen peroxide can be used, though starch solubilisation is reduced.

Steeping in a hydrochloric acid solution (0.5%) may be used to dissolve mineral impurities and open up the fibres to render them more amenable to subsequent processes.

3.2 Scouring

Scouring is a treatment process for removing impurities of natural oils and waxes, proteins, pectic substances, natural colouring matter and adventitious dirt. Fatty substances are removed by saponification, emulsification or solvent extraction. In saponification fats are hydrolysed by sodium or potassium hydroxide into glycerol and sodium or potassium alkali salts of fatty acid. This acts as a soap, a surface active compound, which in turn lowers the surface tension between water and air or oily substances thereby allowing oil to form a comparatively stable emulsion and facilitating removal of oil and retention of dirt particles in suspension.

3.3 Bleaching

Bleaching is a treatment process which improves whiteness of the fabric by removing natural colouring by reaction with oxidising chemicals such as sodium hypochlorite and hydrogen peroxide. Various wetting, softening and stabilising agents may be added.

The bleaching agent is active oxygen, which in sodium hypochlorite solutions is formed from hypochlorous acid:

$$NaOCl + H_2O \text{ —— } NaOH + HOCl$$
$$HOCl \text{ —— } HCl + O^-$$

Alternatively active oxygen can be derived from hydrogen peroxide in alkaline solution:

$$H_2O_2 + OH^- \text{ —— } H_2O + HO_2^-$$
$$HO_2^- \text{ —— } OH^- + O^-$$

Sodium carbonate is added as a buffering agent for pH control to prevent excessive release of oxygen which would escape into the atmosphere before acting on the cotton. However it is difficult to maintain an optimum pH with alkali alone, and stabilisers such as sodium silicate are added for better control.

3.4 Dye Stripping

Direct dyes which have not been fixated can be removed by boiling with a sodium hydrosulphite solution or simply by bleaching. Direct dyes which have been treated for wet-fastness and reactive dyes must first be treated by boiling with dilute acetic or formic acid to remove the fixing agent, followed by thorough washing, boiling with sodium hydrosulphite and bleaching.

4. AUXILIARY CHEMICAL FUNCTIONS

Auxiliary chemicals are cationic or anionic surface active compounds which modify surface characteristics of the fibre.

Anionic compounds are typically sulphonic acid and sulphuric esters such as those contained in Teepol and are useful wetting agents and detergents.

Cationic compounds are able to deposit on negatively charged cotton fibre surface to provide properties such as softness, wet-fastness and water-proofing. Softening agents are usually quaternary ammonium or pyridine derivatives, such as diethylethylene hydrochloride. Wet-fastness agents, for example cetyl pyridinium bromide, are cations which form a complex with dyestuff anions to produce a larger, more complex and less soluble molecule. Water-proofing agents, e.g. stearoamidomethyl pyridium chloride, are polymerised by application of heat, reacting with hydroxyl groups in cellulose or condensing with itself to form a hydrophobic compound.

5. WATER QUALITY

Garment dyeing requires a good quality of process water, low in impurities. Raw municipal water can contain dissolved salts such as iron (Fe), which can cause discoloration of whites in bleaching and dulling of colours, and calcium (Ca)and magnesium (Mg), which are responsible for water hardness. Ca and Mg salts displace sodium salts of soap and form insoluble precipitates of fatty acid salts which cause turbidity in water and form a sticky deposit on the fibre, interfering with dye distribution. Loss in effective detergent also requires additional soap, in excess of total hardness, to achieve the cleaning lather. Hence where there is a high level of salination, raw water must be treated before it can be used in textile processing.

Textile wet-processing in general uses large quantities of water in make-up of various chemical processing solutions, and particularly for rinse operations between different process stages. This is necessary to remove trace chemicals which might interfere in the chemistry of subsequent processes resulting in reduced efficiency, loss of chemical effectiveness and impaired product quality. Specifically, anionic and cationic compounds cannot be used together. With their opposite charges, these compounds would tend to combine and either precipitate or mutually destroy their effectiveness, e.g. traces of soap, an anionic compound from scouring, will combine with a cationic reagent used in dyeing to form a scum which adheres to the fibre. Hence even rinse waters with low contamination levels usually require treatment to render quality of water suitable for reuse.

GLOSSARY

auxiliary chemical	Chemical used to modify the fibre surface characteristics
azo compound	Contains the azo group -N=N- which provides the coupling mechanism in formulation of new dye structures and properties
direct dyeing	A dyeing process characterised by surface adsorption bonding forces with compounds which have a direct affinity for cellulose fibres
fixing agent	A surface-active compound which unites with the dye compound to produce a more complex molecule with improved wet-fastness
hydrogen bond	A weak to moderate attractive intermolecular force existing between certain covalently bonded hydrogen atoms and lone electron pairs of another atom
hyperfiltration	A pressure-driven membrane process similar to reverse osmosis
liquor ratio	The ratio of weight of liquor to weight of material in any treatment process
pigment dyeing	A dyeing process in which the colour imparting pigment is pasted onto the fabric with a resin, without chemical bonding forces
reactive dyeing	A dyeing process characterised by covalent bonding between hydroxyl groups and chemical reaction
Van Der Waals forces	Weak attractive intermolecular forces existing between molecules which are polar or can form instantaneous dipoles
wet-fastness	Resistance to removal of colour in washing

APPENDIX D
CASE STUDIES ON CLEANER PRODUCTION IN THE TEXTILE INDUSTRY[1]

Dye Bath Reuse in Textile Industry, Adams-Millis Company, Textile Industry, High point and Franklinton, North Carolina, USA

Conversion of Willow Dust into Biogas at Cotton Textile Processing Mill, Apollo Textile Mills, Bombay, India.

Water Conservation in a Textile Industry, A Textile Mill, Madras, India.

Elimination of problems of Sulphides by Chemical Substitution in Textile Industry, Century Textiles and Industries Limited, Bombay, India.

Heat Recovery in Textile industry, Ellen Knitting Mills, Spruce Pine, USA

Zinc recovery in a Rayon industry in Netherlands, Enka B. V., Velperweg 76, Location Kleefsewaard at Arnhem, Netherlands

Case Study on Dyebath reuse in Textile Industry, Evans and Black Carpets., Dalton, Georgia, USA

Application of Counter-Current Rinsing and Washing in Woolen Industry, Textile Industry in France

Case Studies on Water and Energy Conservation in Textile industries of Rajasthan, India.

Closed Loop Recycle Systems for Textile Effluents, Textile Mills and Pilot Plants at University of Natal, Durban, South Africa.

Ozonation for Recycling Textile Wastewaters for Process Use, Pilot Plant study in Textile Industry, USA

Reduction in Moisture Regain in Fabrics using Machnozzle™ Predryer in Textile Industries, Pilot plant testing, J.P. Stevens Inc, USA

Heat Recuperation and Dyebath Reuse at Russel Corporation USA, Russel Corporation, USA

Reuse of Water in a Woolen mill, Shanghai Woolen Mills, Shanghai, China

Modified Pressure Kiers saves Energy - Case Study on a Textile Mill in India, Shri Ranjitsinghji Mills, Solapur, India

Reclamation of Sewage for Process Use in Textile Industry, Bhutan.

A Case Study on Heat Recovery in a Textile Industry, Russel Corporation, USA

Poly Vinyl Alcohol Recycling, Textile Industry, South Africa.

Recovery of PVA from Desizing Process using Ultra- filtration, Textile Industry, USA

A Case Study on Heat Recovery, Textile Industry, USA

Chemical Substitution in Textile Wet Processing Industry, Textile industries in North Carolina, USA

Recycling of Wastewater in Textile Industry, The Raymond Woolen Mills Ltd., Thane, Maharashtra, India

Heat recovery in the Textile industry, USA.

Dye Waste Treatment and Reuse in Textile industry, Wansona Industries, Wadesbore, North Carolina, USA

Utilization of Solid Waste through Innovative Techniques, Harihar Polyfiber, GRASIM, Karnataka, India.

Heat Recovery in a Synthetic Textile industry, Harihar Polyfibers, GRASIM, Karnataka, India

Reduction in the Oil Consumption in the Synthetic Fibre Industry, Harihar Polyfibers, GRASIM, Karnataka, India

Recycling of Process Waste to Reduce Chemical Requirement in a Synthetic Fibre Industry, Harihar Polyfibers, GRASIM, Karnataka, India

Improved Washing Equipment for Pollution Load Reduction in a Synthetic Fiber Mill, Harihar Polyfibers, GRASIM, Karnataka, India.

Changeover from Peroxide Bleaching to Sodium Hypochlorite Bleaching gives Dividends, Bombay Textile Research Association , Bombay, India

Efficient Recovery and Reuse of Caustic Soda from Mercerizing Washwaters, Bombay Textile Research Association, Bombay, India

Recovery and Reuse of Water in Wet Processing in a Textile Mill in Bombay, India, Bombay Textile Research Association , Bombay, India

Low Wet Pick-up Finishing of Fabric Sorts by Modified Threading on Stenter, Bombay Textile Research Association Member textile Mill, Bombay, India

Recovery of Iso Propyl in the Textile Processing Operations, American Enka Company, USA

Dye-bath Reuse in Carpet Dyeing, Bigelow, USA

Recovery of Toluene from Printing Press Cleanup in a Textile Industry, Rexham Corporation, City of Mathews, Macklenberg County, USA

Reuse of Iso-Propyl-Acetate during Printing Equipment Cleanup in a Textile Industry, Thiele-Engdahl Inc., City of Winston-Salem (Forsyth County), USA

Meeting Effluent Phosphorus Limits via Chemical Substitution in a Textile Industry, United Piece Dye Works, City of Edenton, Chowan County, USA

Recovery and Reuse of Freon and Heat Transfer Fluid in a Textile Industry, Celanese Corporation, City of Green valley, South Carolina, USA

Reutilization of Saw Dust for Energy Recovery at a Textile Mill, Ellen Knitting Mills, Spruce Pipe, North Carolina, USA

Case Studies on Water Reuse in Textile Industries in Bombay, India, Textile Mills under Mill Owner's Association, Bombay, India

Evaluation of Three Clean Technologies for Adoption in Textile Industries in Thailand, Textile Mills in Bangkok, Thailand

Nordic Project on Water Use Reduction in Textile Industries based on Fifteen Textile industries in Denmark, Finland, Norway and Sweden

Wastewater Reuse in a Synthetic Textile Mill in Bombay, India, Orkay Textile Processors, Bombay, India

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[1] entries in MICRO-TEXTBASE compiled by the Working Group for Textile Industry (Modak, 1991)

APPENDIX E

ESTABLISHMENT OF DESIGN BASIS FOR ECONOMIC EVALUATION: DYE HOUSE CASE STUDY

1. CURRENT MATERIAL FLOWS

Table E1 shows estimates of current water and effluent characteristics based on assumptions described below.

TABLE E1: Current Estimated Water and Effluent Characteristics For Annual Flows

Process	Water kL	Steam kL	Effluent kL	COD mg/l
desizing	4150		4150	227
scouring	2641		2641	136
bleaching	2641		2641	23
direct dyeing	7169	2264	9433	238
reactive dyeing	9961	1358	11319	part of above
plant washing	7546		7546	
domestic and evaporation	5889			
TOTALS	39997	3622	37730	623
l/kg	386		365	

1. annual water consumption and effluent discharge volume the same as the total for 1991, i.e.

   water supply volume = 43,620 kL

   effluent discharge volume = 0.865 * 43,620 = 37,730 kL incl. process water and steam

   domestic/evaporation = 0.135 * 43,620 = 5,889 kL

2. unit process contribution to water usage inferred based on data in Table 5.6a of the main text, and adjusted to include 20% contribution from plant wash water.

3. condensate contribution to effluent attributable to direct and reactive dyeing only, as 24% and 12% of total effluent flow from each of these process (based on Table 5.6a of the main text).

4. average total effluent characteristics as in Table 5.7 of the main text and inferred for each process stream based on indicative analyses given in Tables 5.3-5.5 of main text.

2. MODIFIED WATER FLOWS

Table E2 suggests a modified water balance on the basis that various water recovery measures, identified below, are implemented.

TABLE E2: Modified Water Flows

Process	Water kL	Steam kL	Effluent kL	Treatment	Water reuse kL	% reduction in effluent	Conc. kL
desizing	4150		4150	size recovery	3320	(8.8 %)	830
scouring	0		2641	evaporation	2113	(5.6 %)	528
bleaching	2641		0				
direct dyeing	6452		6452	hyperfiltration	5162	(32.7 %)	1290
reactive dyeing	8965		8965	hyperfiltration	7172	(part of above)	1793
plant washing	6791		6791	evaporation	5433	(14.4 %)	1358
domestic and evaporation	5889						
TOTALS	34888	0	29000		23200		5800
l/kg	337		280				56
% Reduction	13 %	100 %	23 %		61.5 %		85

Assumptions:

without treatment

1. recovery of steam condensate = 3,622 kL
2. reuse of bleaching rinse water for scouring = 2,641 kL
3. water management/process control to achieve 10% reduction in each dye operation and in plant washing = 2,468 kL total

Total Savings = 8,730 kL (20% of raw water - process & steam use; 23% of effluent volume)

with treatment

Assuming treatment of each individual effluent/water recycle stream is technically feasible:

4. reuse of recovered sizing agent = 80% water recovery = 3,320 kL
5. evaporation of scouring effluent and plant wash water = 80% water recovery from each
   = 7,546 kL combined
6. hyperfiltration of dye effluents = 80% water recovery = 12,334 kL combined

Total savings = 23,200 kL (a further 61.5% of effluent volume)

(The remaining concentrate could potentially be reused so that there would be no off-site discharge.)

Realistically only options 2, 3 & 6 above are considered to be practical. These would yield a water saving of 17,433 kL p.a. i.e. 40% reduction.

3. WATER AND EFFLUENT COSTS

Tables E3a, -b and -c show the effect of various percentage reductions in water usage on effluent volume and characteristics, associated discharge costs and potential savings. Cost calculations are based on water and effluent charges for the 1991 -1992 period, as shown in Table 4.1 of the main text, i.e.

TABLE E3a: Estimates of Projected Effluent Characteristics With Water Conservation

% Reduction in Water Usage	Water Volume (kL)	Effluent Volume (kL)	COD (mg/L)	Sulphate (mg/L)	TDIS (mg/L)	Conductivity (mS/m)
0	43620	37731	623	3298	5787	781
40	26172	22639	1038	5497	9645	1302
45	23991	20752	1133	5996	10522	1420
50	21810	18866	1246	6596	11574	1562

TABLE E3b: Estimates of Water Supply and Effluent Discharge Costs With Water Conservation

% Reduction in Water Usage	Water Charge (R)	Effluent Charge (R)	Sulphate Surcharge (R)	TDIS Surcharge (R) (i)	Conductivity Surcharge (R) (i)	Total charge (R) (ii)
0	61068	29671	12876	41812	2126	103614
40	36641	21992	19064	43394	3639	77697
45	33587	21032	19838	43592	3828	74457
50	30534	20072	20611	43789	4017	71217

Notes:

(i) these are no longer charged

(ii) includes only sulphate surcharge

TABLE E3c: Estimates of Potential Savings in Water Consumption and Effluent Discharge

% Reduction in Water Usage	% Water cost (i)	%Surcharge cost (i)	Potential Savings (R) (ii)	% Saving	Potential Savings (R) (no surcharges) (iii)	% Savings
0	59	12	-			
40	47	25	25917	25	44982	43
45	45	27	29157	28	48995	47
50	43	29	32397	31	53008	51

Notes:

(i) based on sulphate surcharge only

(ii) including higher sulphate surcharges

(iii) assuming no sulphate surcharge

water supply @ R1.40/kL
effluent conveyance @ R0.3417/kL
effluent treatment @ R0.6015/kL

with the sulphate discharge constraint set at 1,800 mg/l.

@ 40% water reduction, potential savings of either:-

(i) R25,920 including higher sulphate surcharge, or

(ii) R45,000 excluding sulphate surcharge, but costs incurred for chemical treatment and sludge disposal.

4. TREATMENT CHEMICAL AND SLUDGE DISPOSAL COSTS

@ 40% water reduction, precipitation of sulphates to the solubility limit will yield approximately: (5,497- 1,800) mg/l * 22,639 kL = 84 tpa sulphates for disposal.

lime requirements

84 * 74/96/0.85 = 76 tpa $Ca(OH)_2$ (assuming 85% efficiency)
@ R0.85/kg lime[1], cost = R64,600 p.a. i.e. costly

sludge disposal requirements

84*136/96 = 110 tpa $CaSO_4$
Without sludge dewatering, settled solids @ 3% w/w will generate 4,000 tpa slurry @ R23.50 per 2 tonnes[2], disposal cost = R47,000 p.a.
With pressure filtration, filtercake @ 30 % w/w will generate 400 tpa assuming the same unit disposal cost, net cost this will be R4,700 p.a.

Cost saving associated with volume reduction = R42,300/3,600
= approx. R12/tonne

Therefore a 90% reduction of current sludge quantities (of 50kL p.a.) would save approximately 45 kL * R12 = R540 p.a. (assuming sludge S.G. of 1)
i.e. low cost saving potential.

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[1] price quoted by local chemical supplier

[2] price quoted by Cape Town City Council

5. DESIGN BASIS FOR HYPERFILTRATION PLANT

Based on a design example given in WRC (1987a):

Equipment Requirements, inclusive of:-

pipework
pretreatment
intermediate storage
pumping
product and concentrate storage
flow measurement and recording
effluent storage and screening
chemical conditioning
microfiltration
hyperfiltration unit
all associated process controls
product measurement and recording
ancilliaries: electrics, air, water, drains, building, emergency treatment option (in the event of breakdown)

Design Parameters For Case Study

Dye effluent flow = 6,452 + 8,965 = 15,417 kL p.a. (say 15,420 kL)
Operating time: 128 working days per half year (256 p.a.) @ 11 hours per day.
Average daily flow = 60 kL and Maximum daily flow = 1.2 * 60 = 72 kL per day
Design flow = 6.5 kl/hr (approximately 10X smaller than design example)

6. COST ESTIMATE

Plant Capital[3]

given as : 600 - 1,115 per m^3/day (Jan. 1984)
cost index multiplier for 1991 update = 358.2/322.7[4]
666 - 1,238 per m^3/day (1992)
@ 72 m^3/day = R48,000 - R89,200 (1992)

Plant Operating Cost

given as: R0.61 - R0.79 /m^3
10 % inflation p.a. assumed: * $(1.10)^8$ = R1.31 - R1.69 /m^3

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[3] based on imported US equipment, an assumed exchange rate of $1 = R1, and incl. of 20% freight and importation (WRC, 1987a)

[4] US chemical engineering plant cost indices (Chemical Engineering, July 1993)

@ 15,420 m^3 p.a.	R20,200 - R26,060 p.a.	
assume:	R23,000 p.a.	(1992)

Economic Parameters

Given the high chemical cost for lime dosing, compliance with sulphate discharge is not economically possible in this way. Including the higher surcharge:
savings - operating cost = R26,000 - R23,000 = R3,000
payback = 48,000/3,000 = 16 years i.e. not economically viable.

APPENDIX F
PROCESS TECHNOLOGY: HARD CHROME PLATING AND ASSOCIATED PROCESSES

Chrome plating is an electrolytic deposition process whereby chromium metal is cathodically deposited as a coating onto a work surface which has been made conductive. Thin plated deposits are used for decorative purposes, while hard chrome plating refers to deposition of thicker plates which provide hardness, wear resistance and lubricity for engineering applications which are the concern of this manufacturing facility. While the principles of plating are the same, time required for hard chrome plating is much longer.

1. CHROMIUM CHEMISTRY

Chromium exists naturally in the stable oxidation states of Cr(III) and Cr(VI). Thermodynamically Cr(III) is stable at moderate pH (2-8) and redox potential while Cr(VI) is stable in more oxidising environments, pH > 6 (Raghu & Hsieh, 1989).

Cr(VI) exists in oxo species such as chromic acid (CrO_3) which dissolves in water to form acidic solutions of chromate ions, the form of which is pH and concentration dependant. The following dissociation reactions can occur:

$CrO_3 + H_2O$ —— H_2CrO_4 —— $HCrO_4^- + H^+$ —— $CrO_4^{2-} + 2H^+$ chromate

$CrO_3 + CrO_4^{2-}$ —— $Cr_2O_7^{2-}$ or $2HCrO_4^-$ —— $Cr_2O_7^{2-} + H_2O$ dichromate

$CrO_3 + Cr_2O_7^{2-}$ —— $Cr_3O_{10}^{2-}$ trichromate

In most references only the balance between chromate and dichromate is considered. Dichromate predominates under acidic conditions, in which Cr(VI) is strongly oxidising according to:

$Cr_2O_7^{2-} + 14H^+ + 6e^-$ —— $2Cr^{3+} + 7H_2O$

Chromate dominates under basic conditions, with Cr(VI) being less oxidising. The following reaction may then take place:

$$CrO_4^{2-} + 4H_2O + 3e^- — Cr(OH)_3 + 5OH^-$$

Hence at high pH values, metal hydroxide precipitation tends to occur.

Cr(III) forms the stable aqua-complex $Cr(H_2O)_6^{3+}$ in acidic solutions and is kinetically inert to substitution (Hamilton & Wetterhahn, 1988). At higher pH values, hydroxo substitution occurs as:

$$Cr(H_2O)_6^{3+} + OH^- — Cr(OH)(H_2O)_5^{2+} + H_2O$$

with successive substitution to form $Cr(OH)_3(H_2O)_3$. This is insoluble above pH 5 (Raghu & Hsieh, 1989) resulting in precipitate formation.

Chromium hydroxide may also react with hydroxo ions of a strong base to form soluble chromite anions (Ebbing, 1984), as follows:

$$Cr(OH)_3\ (s) + OH^-\ (aq) — Cr(OH)_4^-\ (aq)$$

Both Cr(III) and Cr(VI) are able to form complexes with inorganic (e.g. water, as above) and organic compounds, such that either form can be rendered soluble under conditions where they would otherwise be expected to be removed from solution by precipitation or adsorption (Raghu & Hsieh, 1989). This complexation property is utilised for processing advantages by the use of chelating chemicals.

2. PLATING TECHNOLOGY

2.1 Principles of Plating

Electrolytic processes are based on Faraday's principles:

(i) that the quantity of metal deposited is directly related to the quantity of electricity;

(ii) that the quantity of a specific metal deposited by a given quantity of electricity is directly related to the gram equivalent weight of the metal i.e. the weight in grams that is equivalent to one mole of electrons.

Faraday's constant of 96,489 Coulombs per mole defines the charge required to deposit one mole of electrons. With its valency of 6, Cr(VI) has the highest charge requirement per unit of metal:

$Cr^{6+} + 6e^{-}$ ----- Cr^{0}

1 gmole of Cr^{6+} requires $6e^{-}$ i.e. $6e^{-}$ per 52 g Cr

52/6 * 1gmole/96,489 * 1,000 = 0.08982 mg per C

With a current supply of 1 Ampere-hour i.e. 3,600 C per hour, this equates to:

0.08982 * 3,600/1,000 = 0.323 g/A-h.

Therefore to deposit a thickness of 1 micrometer per m^2 of surface - given S.G. = 7.1 - requires:

$1 * 10^{-6} * 7{,}100 * 1{,}000 = 7.1$ g/m^2, with a charge requirement of 21.98 A-h per m^2 per micrometer of plating thickness

Clearly plating from a Cr(III) would halve the charge requirement.

2.2 Electroplating System

The chrome plating system, as depicted in Figure F1, comprises:

- electrolyte solution containing ions of the metal to be deposited;
- power supply;
- inert lead anodes; and
- cathodes, being the surface which is to be plated.

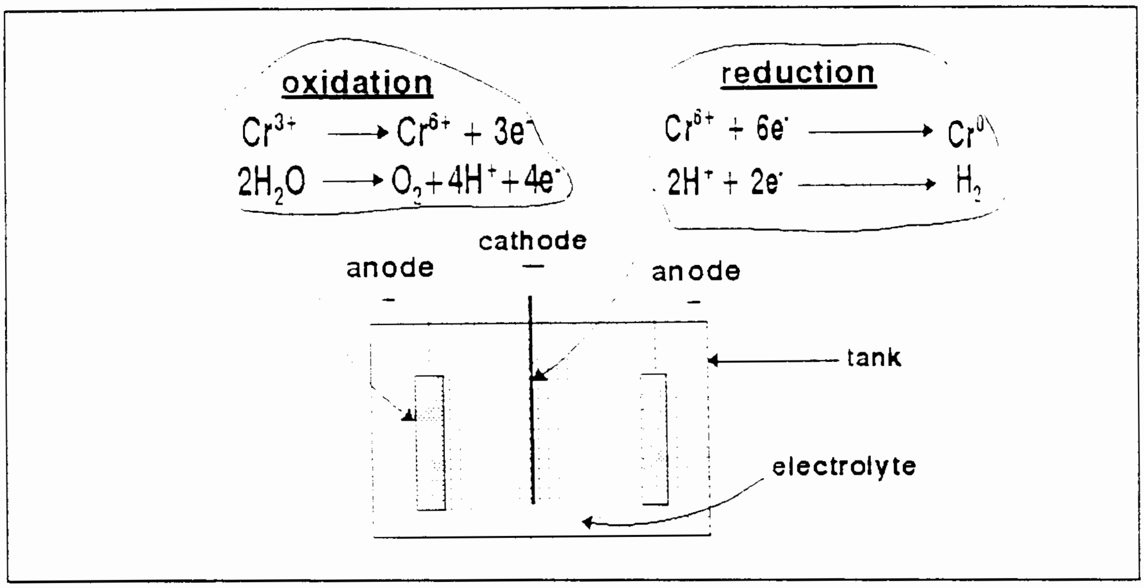


FIGURE F1: Schematic Of Plating Tank

In conventional chrome plating the electrolyte solution contains hexavalent chromate ions derived from chromic acid, in combination with sulphate free acid radicals. These are catalysts in the plating mechanism, reviewed below in section 2.7.

Equilibrium oxidation/reduction reactions take place at the cathode and anode as follows:

cathodic reactions:

Cr^{6+} + $6e^-$ ----- Cr^0
$2H^+$ + $2e^-$ ----- H_2

anodic reactions:

Cr^{3+} ----- Cr^{6+} + $3e^-$
$2H_2O$ ----- O_2 + $4H^+$ + $4e^-$

Hexavalent chromium (Cr(VI)) reduction is not a single step, but passes through successive reduced stages. Final reduction is believed to take place from the chromous ion (Cr(II)). In the bulk solution away from the cathode, chromate presumably is continuously reduced to Cr(III). This is known to inhibit chrome plating at concentrations greater than about 15-20 mg/l (Gabe, 1978). Hence anodic oxidation of Cr(III) helps to maintain a low level of Cr(III).

Hydrogen reduction at the cathode is significant. The consumption of electrons in hydrogen reduction results in a characteristically low plating efficiency, typically 12-16% (Gabe, 1978), where efficiency is defined as:

$$\text{Cathode current efficiency (CEE)} = \frac{\text{no. of Coulombs depositing metal}}{\text{total no of Coulombs passing}}$$

The removal of H^+ from solution would also raise pH at the cathode. Thermodynamically this would promote precipitation of $Cr(OH)_3$ and $Cr(OH)_2$ which may partially passivate the cathode, further inhibiting reaction (Kirk-Othmer, 1979).

Operating efficiency achieved in practice is affected by the nature of the plating solution and additives, plating bath design, flow patterns in the bath, pH conditions and temperature.

2.3 Plating Solution

Plating solutions are proprietary formulations developed not only to provide depositing ions but also:

- to form complexes with these ions so as to control deposition rate;
- to provide conductivity which reduces electrolyte resistance
- to stabilise the solution against decomposition reactions such as hydrolysis;
- to buffer solution pH;
- to regulate the physical form of deposit.

Conventional chrome plating is based on chromic acid and sulphuric acid solutions, with typical chromic acid concentrations of 200 - 400 mg/l. Minimum chromium levels are needed to provide sufficient quantities for plating. However concentration levels which are too high reduce plating efficiency due to higher solution viscosity and increased thickness of the surface film at the cathode. This retards diffusion of plating chemicals (see Plating Mechanism). Experience has shown an optimum chromic acid: sulphuric acid ratio to be 100:1, for greatest deposition. Solution conditions are maintained by replenishment of chromium plated from solution and periodic dosing of the acid chemical to maintain this balance. Although sulphate is not consumed in the plating, drag-in of other sulphates from upstream processing and drag-out of plating solution to downstream processing tend to alter this balance. High sulphates are reported to reduce throwing power.

Newer plating solutions are based on Self-Regulating High Speed (SRHS) formulations in which sulphate has been replaced by silicofluoride compounds. These have limited solubility and therefore can self regulate the dissolved catalyst composition at an optimum value for the plating conditions. Chelating compounds would also be present. These solutions are characterised by higher efficiencies.

Levelling agents may be used to modify surface reactions by, for example, adsorbing preferentially on surface peaks thereby inhibiting further metal growth (Gabe, 1978). This encourages metal deposition in underplated areas.

Electrolytes can become contaminated with metal cations such as Fe, Cu, Zn, Ni, as well as Cr(III) formed by reduction. Metal cations increase resistance of the bath, thereby increasing the voltage requirement for the same current ($I = V/R$). These metal levels should therefore be kept low. Low equilibrium levels of Cr(III) are maintained by pre-conditioning the anodes to form a stable conducting film of brown peroxide (PbO_2). This acts as an oxidant for the reaction: Cr^{3+} ----- CrO_4^{2-}

Chromic acid plating baths have a typical "life" of up to 25 years (WRC, 1984). When plating slows, electrolytic decomposition of water at the anode also slows, resulting in reduced formation of H^+. Therefore pH tends to increase, favouring the chromate ion and rendering Cr(VI) less oxidising. Slow oxidation of the lead anode occurs, with formation of yellow lead chromate as follows:

$Pb^{2+}(aq) + CrO_4^{2-}(aq)$ ----- $PbCrO_4$

This passivates the surface inhibiting further chromium deposition. The solution must then be replaced.

There has been some development of trivalent chromium plating solutions based on a mixture of organic solvents and water. The organic solvents are dipolar aprotic solvents with high dielectric constants which permit ionisation of dissolved metal salts and which readily form complexes with metals (Dennis & Such, 1972). Advantages of trivalent chromium based solutions are:

- lower charge requirement;
- higher conductivity, which enables more dilute solutions to be used;
- this in turn reduces the solution viscosity, with faster deposition;
- improved throwing power.

Current efficiencies are given as 40 - 50% (Dennis & Such, 1972). However the deposits are described as being softer and more ductile than conventional chromium deposits, and therefore not acceptable in engineering applications.

2.4 Plating Bath Design

Chrome plating efficiency increases with current density, which refers to the charge distribution per unit plated area. Consequently there is greater deposition on surfaces exposed to greater current density compared to those in low current density areas. This is known as poor throwing power. Where plating bath configuration interferes with current distribution, causing variations in current density, non-uniform deposition may result.

The cathode/anode area relationship affects the chemical equilibrium of Cr(VI) and Cr(III) ionic species and hence efficiency of the plating process. Larger anode areas are deemed preferable. Alternatively the bath can be run occasionally with only a small cathode area, i.e. small or few work-pieces, to readjust the ion balance (Sulley, 1954).

Flow patterns in the bath alter diffusion behaviour, particularly in the boundary layer from which deposition is considered to take place at the cathode surface. Rate of deposition is considered to be diffusion controlled so that decreasing the boundary layer, i.e. the diffusion path, increases speed of plating. This can be achieved by a high rate of relative motion between the cathode and bulk solution. Therefore agitation caused by evolution of gaseous deposition products, hydrogen and oxygen, is a useful effect.

However this gaseous evolution also generates large quantities of chromic spray. Foam suppressants can be used to minimise this entrainment which constitutes a chemical loss from the bath as well as a potential hazard, but problems with pitting of the plated surface are reported. Extraction and scrubbing systems generally are used for occupational safety and recovery of chromic acid.

2.5 Temperature

Temperature and solution concentration conditions combine in affecting current efficiency. Hoare, LaBoda & Holden (1981) explain that at low temperatures the fraction of ions with enough energy to be discharged is reduced, so that a greater fraction of current is taken up by H^+. Yet, at high temperatures, mobility of H^+ ions is enhanced thereby increasing H^+ activity at the cathode so that H^+ reduction is also favoured. Temperature is also considered to affect solution conductivity and sulphate solubility. As conductivity changes so the current flow for a fixed voltage changes, with potential for under- or overplating. The sulphate balance may also be disturbed. Temperature control is therefore important to maintain near optimum conditions.

2.6 pH

The review of chromium chemistry has shown that the predominant form of chromate is pH dependant as is the ionic form of chromium. Thus pH influences plating efficiency. pH is also reported to affect the general appearance, stress, levelling and hardness of coating, although reasons for these are not clear. pH control is not usually required in solutions containing large amounts of free acid.

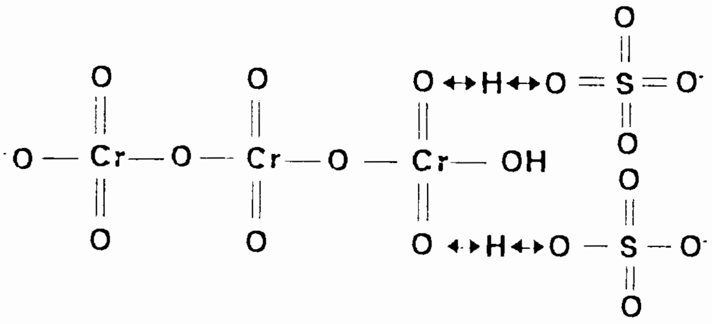
2.7 Plating Mechanism

The actual mechanism of plating is still not completely understood, although the process has been used empirically for decades and research continues in attempts to improve process efficiency. Features of chrome plating which are well established are:

(i) plating occurs from Cr(VI) and not from Cr(III). This was demonstrated, for example, by radioactive tracer techniques used to measure activity of deposits from trivalent and hexavalent chromium solutions (Sulley, 1954).

(ii) Cr(VI) cannot be plated without the presence of a "catalyst" which is a free acid radical. Sulphate, supplied as sulphuric acid, is the conventional catalyst anion. This is commonly described as forming a complex with chromium, which, in its absence, tends otherwise to form a passivating hydroxy layer at the cathode. This presumably is caused by reduction to Cr(III) which precipitates as pH increases with H^+ reduction.

(iii) High sulphate levels cause a reduction in plating efficiency. Earlier researchers have explained this phenomenon in terms of a critical cathode film thickness which is rate controlling. It was thought that if sulphate content is too high, then diffusion resistance retarded deposition, while with insufficient sulphate there is an inadequate reactive layer. More recently Hoare[1] has explained the deposition mechanism by identifying the electroactive species as a trichromate-bisulphate complex which, thermodynamically, is present at its greatest concentration when the ratio of chromic acid/sulphuric acid is 100:1. This complex is depicted as:



Hoare believes that this complex protects the Cr(VI) as it passes through the Cr(III) state thereby preventing formation of the stable complex $Cr(H_2O)_6^{3+}$ which inhibits plating. Once Cr(VI) is reduced to Cr(II), this is believed to form a chromous oxybisulphate complex by acid hydrolysis with a positive end which is adsorbed onto the cathode surface:

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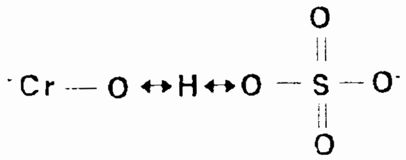
[1] There are numerous reports describing Dr. J. Hoare's work which has been published as a result of his research for General Motors (GN). Many of these are therefore restricted. The information reported here has been obtained from a brief article entitled "The Chromium Mechanism". This reference was made available by management of the case study company, but GM themselves were unable to provide full reference details.



$$ {}^{-}Cr-O \leftrightarrow H \leftrightarrow O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-O^{-} $$

Metallic chromium can then be formed by electron transfer from the cathode. The bisulphate ion (HSO_4^-) is regenerated.

2.8 Surface Preparation

Associated with plating are surface preparation steps, which in this case include soak- and electrolytic cleaning and etching.

Soak cleaning is a pre-cleaning stage designed to remove excess soil and to reduce viscosity of oils which then can be removed more easily in electrolytic cleaning. The soak cleaner is described as a 10-15% solution of sodium salts, including hydroxide, carbonate, phosphates and silicates. Surfactants are also present to facilitate release of soil by lowering surface tension at the soil/metal/solution interface.

Electrolytic cleaning uses a similar chemical, but agitation caused by upward movement of H_2 or O_2 - formed by electrolytic decomposition of water - assists in dislodging the soil. Chelating agents may be used to complex metal ions in solution to prevent precipitation of insoluble hydroxides or carbonates. Examples are given as sodium gluconate or ethylenediaminetetraacetic acid (Gabe, 1978). Cyanide may also be used - e.g. sodium cyanide may be added to alkaline cleaners to enhance the cleaning effect[2].

This complexing of contaminants in solution inhibits removal of these contaminants by filtration which could otherwise be used to extend the effective life of these cleaners. Normal practice is to periodically replace the cleaning solutions with fresh solution.

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[2] Information obtained from operating instruction for proprietary alkaline cleaner.

Electrolytic etching is used prior to plating to reduce surface imperfections. The metal substrate is anodically etched in a solution of chromic and sulphuric acid. Oxidation of surface iron occurs as follows:

$$3Fe + 6H_2SO_4 + 2CrO_3 \text{ —— } 3FeSO_4 + Cr_2(SO_4)_3 + 6H_2O$$

Complexants may also be present in the etch solution.

The acid solution will neutralise any residual alkaline adhering to the work-pieces (cathodes). The same chemical species as used in the plating solution is used in etching, to avoid the drag-in of undesirable contaminants into the plating solution.

2.9 Rinsing

Alkaline cleaning stages need to be followed by good water rinsing to remove alkaline films which adhere to the work-piece surface. Carry-over of such solution would clearly have a deleterious effect on plating. The etch solution provides an acid rinse as discussed above.

Good rinsing is also required after plating to remove acid and chromium residue from the plated surface. Trivalent chromium is more easily removed than hexavalent chromium (EPA, 1973), and a static chemical rinse is often used in which Cr(VI) is chemically reduced to Cr(III) before water rinsing (see 3.2). WRC (1984) report that use of this chemical treatment reduces rinse water usage by up to 80% of the rinse rate which would otherwise be required.

Rinsing efficiency is improved at higher temperature which reduces solution viscosity. However too high a temperature may cause drying of chromium on the surface with undesirable staining. Moreover use of hot water rinsing obviously has a heating energy penalty.

3. CHEMICAL PROCESSES IN WASTE TREATMENT

The text of Eilbeck & Mattock (1987) has been used to review chemical processes involved in effluent treatment operations used at this facility. These include:

- chromate reduction;
- metal precipitation; and
- flocculation;

followed by physical liquid/sludge separation in an inclined settler and a filter press.

3.1 Chromium Reduction

Conventional hexavalent chromium reduction is based on the redox reaction between Cr(VI) ions and sulphur(IV) compounds such as sodium metabisulphite. This hydrolyses in water to form hydrogen sulphite ion, which is readily oxidised to sulphate:

$$Na_2S_2O_5 + H_2O \text{ —— } 2Na^+ + 2HSO_3^-$$

$$SO_3^{2-} + 2OH^- \text{ —— } SO_4^{2-} + H_2O + 2e^-$$

This reaction shows that oxidation is favoured by alkaline conditions. However the Cr(VI) reduction half reaction is favoured by acid conditions, in accordance with the following reaction:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \text{ —— } 2Cr^{3+} + 7H_2O$$

Cr(VI) is reduced with much greater difficulty in alkaline solutions. Hence conventional Cr(VI) reduction is normally carried out in the pH range 2-3.

The overall stoichiometry is represented by one of more of the following reactions, depending on pH conditions and the relative presence of reacting species:

$$2Cr_2O_7^{2-} + 3S_2O_5^{2-} + 16H^+ \text{ —— } 4Cr^{3+} + 6HSO_4^- + 5H_2O \qquad \text{(i)}$$

$$2HCrO_4^- + 4HSO_3^- + 6H^+ \text{ —— } 2Cr^{3+} + 2SO_4^{2-} + S_2O_6^{2-} + 6H_2O \qquad \text{(ii)}$$

$$2HCrO_4^- + 3HSO_3^- + 5H^+ \text{ —— } 2Cr^{3+} + 3SO_4^{2-} + 5H_2O \qquad \text{(iii)}$$

$HCrO_4^-$ will predominate at lower pH values. With excess Cr(VI) reaction (iii) can be expected to predominate, while reaction (ii) will be favoured in the presence of excess HSO_3^-.

These reactions show that acid is consumed in reaction, necessitating pH control as well as redox control to provide fast reaction. Both reaction rate and electrode response are known to slow as pH increases. At pH 2, a minimum reactor residence times of 10 minutes is recommended, with longer residence times at high pH values. Performance characteristics are demonstrated by Figures F2 and F3.

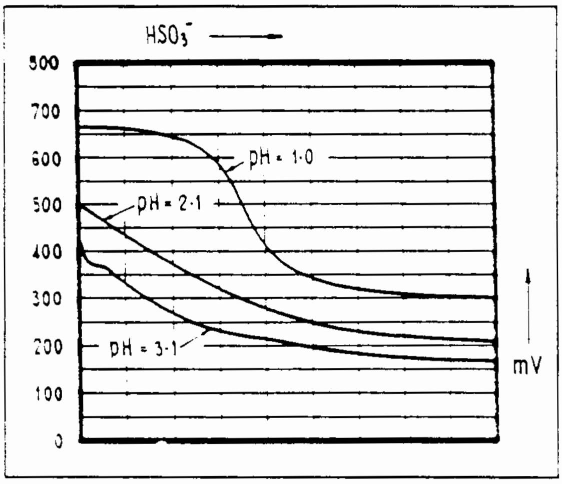

FIGURE F2: Effect Of pH On The Redox Titration Curve*

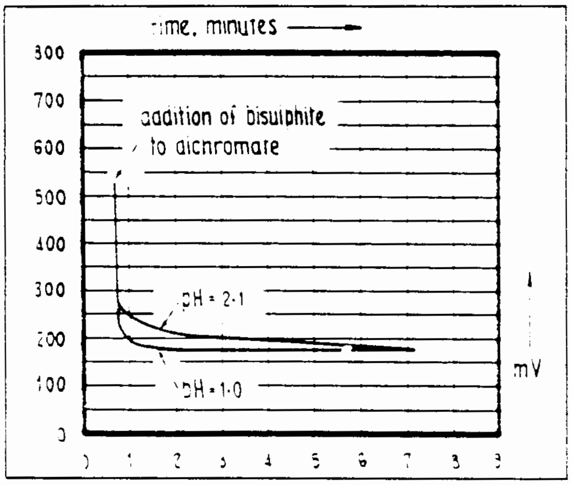

FIGURE F3: Effect Of pH On Speed Of Response Using Excess Bisulphite Reagent*

*Cr(VI)/HSO3- system, using a platinum indicator electrode . Reference electrode saturated KCl calomel (Eilbeck & Mattock, 1989)

Efficiency of reaction is also affected by the mode of reagent dosing and mixing efficiency in contacting reactive species. Oxidation with oxygen also interferes, and may be significant at pH values below 4.

3.2 Alkaline Reducing Media

An alternative Cr(VI) reduction process is that using sodium dithionite, $Na_2S_2O_4$, also known as sodium hydrosulphite. This is the active reagent used in chemical rinsing in the chrome plating plant itself. It is a powerful reducing agent under alkaline conditions, reacting as follows:

$$S_2O_4^{2-} + 4OH^- \text{ ----- } 2SO_3^{2-} + 2H_2O + 2e^-$$

but is less powerful in acid conditions, in which hydrolytic decomposition occurs:

$$2S_2O_4^{2-} + H_2O \text{ ----- } S_2O_3^{2-} + 2HSO_3^-$$

Eilbeck & Mattock (1987) explain that sodium carbonate, Na_2CO_3, is usually added with $Na_2S_2O_4$ to act as a pH buffer to maintain a pH condition of approximately 11.5. The stoichiometry for chemical reduction of Cr(VI) is given as:

$$2CrO_4^{2-} + 3S_2O_4^{2-} + 2OH^- + 2H_2O \text{ ----- } 2Cr(OH)_3 + 6SO_3^{2-}$$

Again, oxygen interference reduces Cr(VI) reduction and produces hydrogen sulphate and sulphite ions:

$$S_2O_4^{2-} + H_2O + O_2 \text{ ----- } HSO_3^- + HSO_4^-$$

The presence of complexing agents may also slow reaction.

It is reported that this process does not completely reduce Cr(VI) even with large excesses of reagent, and the process cannot be monitored by redox potential due to characteristics of the titration curve. Hence, in operation, a large excess of chemical is usually required to ensure reasonable completion of reaction. In the Lancy closed-loop system this is achieved by flowing the chemical rinse solution to a treatment reservoir to which chemicals are added, and the overflow returned to the process tank. The reservoir also acts as a settling tank from which precipitated reaction products can be removed. This minimises carry-over of contaminants into subsequent rinse tanks (EPA, 1973). In the presence of a high excess of treatment chemicals, precipitates are more dense and settle faster than precipitates from dilute rinse water (WRC, 1984).

Incomplete reaction, control difficulties and expense of this chemical make this reduction process impracticable for effluent treatment where more accurate control of effluent quality is generally required. However it may be advantageous to eliminate the need for pH adjustment of neutral or alkaline effluents as required for conventional Cr(VI) reduction. An alternative option for effluent treatment may be reduction using ferrous sulphate. This is a cheaper reagent and effective in both acid and alkaline conditions. In alkaline conditions reduction and precipitation take place in a single operation, according to:

$$CrO_4^{2-} + 3Fe^{2+} + 4OH^- \text{-----} Cr(OH)_3 + 3Fe(OH)_3$$

However the reduction reaction rate is slower, requiring a retention time of at least one hour as instead of 5-10 minutes. This is more practical for batch operations. Settleability of precipitates is higher than achieved by lime treatment, but the quantity of sludge produced clearly is greater due to formation of ferric hydroxide.

3.3 Metal Precipitation

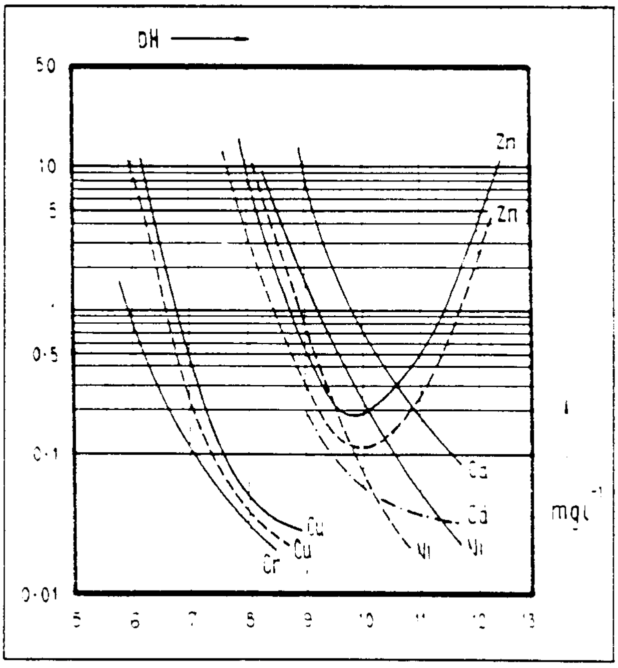

FIGURE F4: Residual soluble metal concentrations as a function of pH using $Ca(OH)_2$ as precipitant.

Solid lines: precipitate stood for 30 minutes before filtration.

Broken lines: precipitate stood for 24 hours before filtration (Eilbeck & Mattock, 1987).

Following reduction of Cr(VI) to Cr(III), the removal of these and other dissolved metal ions from solution is effected by pH adjustment to a condition which is optimum for formation of insoluble hydrous metal oxide precipitates. This pH condition is different for different metals, as illustrated by Figure F4. This indicates a minimum pH of about 8.5 for minimum chromium hydroxide solubility using lime ($Ca(OH)_2$) as the precipitant, but a pH of 10 for maximum zinc removal. Zn is amphoteric, existing as a positive ion at lower pH values, but becoming negative at higher pH values. This results in a changing solubility - with redissolution of hydrous zinc oxide at high pH values.

With other precipitants, sodium carbonate and sodium hydroxide, redissolution of chromium hydroxide occurs at pH greater than 7.5, presumably due to formation of $Cr(OH)_4^-$ (aq) (see chromium chemistry). This effect is illustrated by Figure F5.

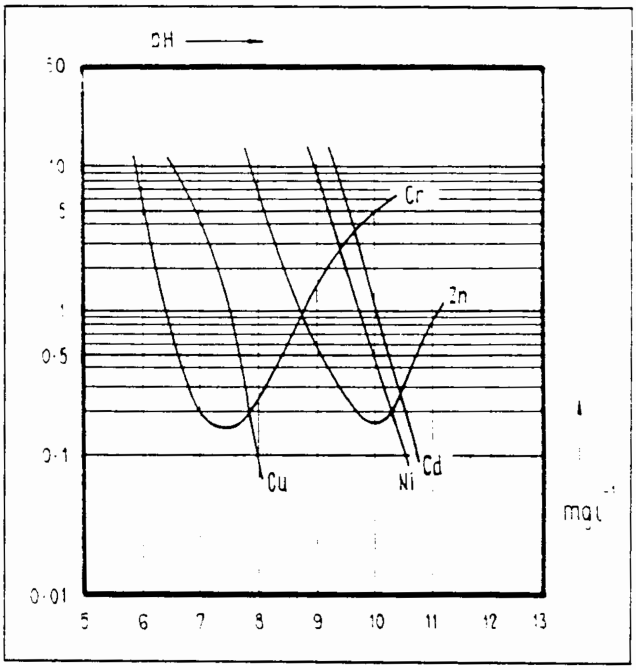

FIGURE F5: Residual soluble metal concentrations as a function of pH using NaOH as precipitant: precipitate stood for 30 minutes before filtration. (Eilbeck & Mattock, 1987).

Kinetically, neutralisation of acids by sodium alkalis is considered to be instantaneous, but precipitation reactions require some time for effective completion depending on:

- rate of solution of lime;
- solution pH;
- temperature; and
- mixing efficiency.

Using lime, residence times of 5-15 minutes are recommended.

Different precipitants provide different equilibrium conditions, with lime considered generally to be the best precipitant. Lime forms more stable precipitates and solid particles, which exist at higher pH values, act as an adsorbent. This provides a second mechanism for metal removal which is more effective for adsorption of metal ions solubilised by complexing agents contained in some process chemical formulations.

Lime is also a relatively cheap reagent, even with reported inefficiencies of 15-25%. It is normally used at a maximum strength of 10 % w/w. Material handling problems are its tendency to crystallise, resulting in difficult pumping and mixing problems at high concentrations.

The nature of precipitant and mode of addition also determine extent of precipitation, as well as character and volume of precipitate. Because equilibrium is pH dependant, approach to the desired pH will alter the relative forms of ionic species. For example, at pH greater than 10, under which conditions zinc is solubilised, a reduction in pH to 10 may not render zinc insoluble due to its presence as an anion. It may be necessary to adjust the pH to below 10, followed by correction to pH 10 from a lower value at which zinc is cationic in form. This example illustrates the complex nature of precipitation, and effluent treatment in general, when processing effluent of mixed character.

Efficiency of metal ion removal is also influenced by the relative concentrations of different metal species and presence of anions. Phosphates, for example, as PO_4^{3-} ions form precipitation products with metals and are considered to be useful for reducing zinc levels. However this benefit is reduced in the presence of lime due to the formation of insoluble calcium phosphates, $CaHPO_4$ and $Ca_3(PO_4)_2$.

Lime produces greater weight of precipitate than sodium hydroxide, but as the precipitate tends to be denser and more readily settleable, the volume of sludge is not necessarily greater than from sodium hydroxide treatment. Use of flocculating agents also promotes settleability and can reduce volumes of precipitate. Recycling of settled slurry to the metal influent before pH adjustment in a pre-conditioning step is reported to facilitate a dense precipitate which results in a sludge close to 10% w/v rather than the usual 2-4% w/v. This phenomenon is explained in terms of ion exchange effects between calcium, hydrogen and metal ions carried in the sludge.

3.4 Flocculation

Polyelectrolyte concentrations in the range 1-10 mg/l are reported to be typical, with correct dosage being application specific, given that performance is affected by solution chemistry and conditions of temperature and pH. While underdosing of flocculant (polyelectrolyte) results in poor flocculation, overdosing can result in the formation of flocs which are too large to agglomerate, and have poor settleability. Two stage dosing is recommended: an initial addition which is mixed vigorously to initiate flocculation, with a residence time of 10-20 minutes, followed by a second dose and mild blending to facilitate floc development. This is expected to develop within a few minutes. It is suggested that flocculant addition be economised by linking delivery to the flow of effluent.

3.5 Liquid/Sludge Separation

Typical sludge concentration achieved by sludge settling is 3% w/w. This can be increased by sludge thickening in which sludge is compacted under the influence of gravity in a cone bottomed tank (UNEP, 1989), and by dewatering. Filterpresses typically produce filter cake of 30 - 35% solids content (UNEP, 1989).

3.6 Process Control

pH and redox control are needed to maintain correct conditions for effective Cr(VI) reduction and precipitation. On-off control is used most commonly in the interests of simplicity, despite poor response times caused by inherent lags in the configuration and operation of control systems. Normally a slight excess of chemicals is delivered to ensure that reasonable treatment is effected.

Poor control problems, which undermine treatment efficiency, may be one or more of:

- inappropriate positioning of sensors which are not exposed to the true bulk solution conditions;
- dirtying of sensors resulting in faulty detection;
- inadequate dosing capability.

GLOSSARY

amphoteric	a compound which can behave either as an acod or a base
anode	the positive electrode of an electrolytic cell, usually composed of the metal to be electro-deposited
aprotic solvent	a type of solvent which does not offer or accept protons
cathode	the negative electrode of an electrolytic cell which, in electroplating receives the metallic deposit
chelation	process of ring formation with inclusion of metal ion within the ring resulting in stable complex formation
chelating or complexing agent	a compound which will combine with metallic ions to form soluble ions
conductivity	refers to the ability to transfer electricity - measured in Siemens (inverse ohms)
coulomb	unit of quantity of electricity
current density	applied current per unit area
dielectric constant	measure of an amount of electric charge that a given substance can withstand - measure of non-conductivity
dipole	a grouping of atoms (or other particles) having equal electric charges of opposite sign separated by a finite distance e.g. H & Cl of HCL
drag-out	volume of solution carried over the edge of a process tank by an emerging piece of work

electric potential	work required to transfer electric charge - measure of ease of electron exchange in chemical oxidation - reduction reactions
electrochemical equivalent	weight of an element, compound, radical or ion involved in a specified electrochemical reaction which passes a unit quantity of electricity
electrochemical techniques	electrically induced chemical processes
electrolysis	production of chemical change by the passage of current through an electrolyte
electrolyte	a solution that conducts an electric current by means of ions contained in the solution.
electrolytic resistance	reciprocal of conductivity - measure of resistance to the transfer of electricity
electroplating	deposition of a metallic coating onto the cathode in an electrolytic cell which contains an electrolyte composed of the metal being deposited.
gram equivalent weight	weight in grams of a substance involved in an oxidation-reduction reaction that is equivalent to one mole of electrons
ion exchange	process by which ions of opposite charges can be exchanged by adsorption onto charged resin materials
levelling action	ability of an electroplated deposit to produce a surface smoother than that of the basis metal
phosphating	a process in which a corrosion-resistant lubricative surface is applied to steels, often before painting. The steel is dipped into a zinc or iron phosphate solution to which phosphoric acid has been added.

pickling	removal of oxides or other compounds from a metal surface by means of an acid, usually hydrochloric or sulphuric.
pyrocleaning	removal of swathe out of tubes or semi-assembled components
reverse osmosis	membrane separation process in which solvents and solutes are separated by the use of pressure to force the solvent through a membrane
throwing power	ability of an electrolyte to minimise the difference in deposit thickness between high and low current density areas
ultrafiltration	filtration process used to remove particles 1 micron (10^{-6} m) or smaller

APPENDIX G

WASTE MINIMISATION CASE STUDIES FOR METAL PLATING

TABLE G1: Waste Minimisation Opportunities For Metal Plating Operations

Technique	Application	Description	Environmental Advantages	Other Implications	Status	Ref.
operational changes	acid pickling	use of temperature control and good agitation to promote pickling reactions	reduced waste pickling liquor volumes; more effective pickling	no significant cost requirements; savings and reduced occupational hazards due to reduced waste handling;	in use	Taviarides (1985)
procedural change	tank cleaning	2-stage rinsing: initial low volume concentrate recycled, followed by low concentrate rinse stream	95% reduction in waste load	savings in raw material	in use	Price (1990)
process change	metal descaling	replacement of acid-dip with mechanical roller-binding and sand blasting	elimination of hot acid - improved safety & reliability & reduced hazardous waste; reduced energy requirements	solid scale waste requires disposal	in use economics not reported	ICPIC[1]
process change	metal cleaning	replacement of chlorinated solvents with a) aqueous solutions b) semi-aqueous solutions c) hydrogenated CFCs	reduced quantities of toxic waste; safer working conditions	not available for all cleaning applications; requires special equipment e.g. ultrasonic	a & b - commercialised; in use; c - under development	P.A. Consulting Group (1991)
process change	acid pickling	use of cascade or counter current rinsing to reduce waste water volumes from rinsing operations	reduced waste water volumes	savings in water and treatment costs	in use	Taviarides (1985)
process change	metal plating	dry plating: metal vapour deposition in vacuum chamber	minimum pollution and worker exposure	very costly - uneconomic for most applications	outstanding technical problems	DOE[2]
process change	chrome plating	replacement of hexavalent chrome with trivalent chrome, using membrane technology	reduced toxicity of wastes - safer working conditions; reduced energy requirements	greater efficiency; savings in raw material, energy and treatment/disposal	commercialised limited use not proven for hard chrome plating	P.A. Consulting Group (1991) UNEP metal finishing[3]
recycling	large scale component manufacturer	closed loop recycling system	waste volume reduced by 87%; raw material consumption reduced by 90%	savings in raw materials, transportation & disposal costs. Example payback: less than 2 years Design principles applicable to most operations.	implementation in progress	ICPIC[1]
recycling: resin adsorption	metal pickling	recovery of acid by adsorption onto resin bed and desorption by water which is recycled to the process - a closed loop recycling system. Acid Purification Unit (APU)	regenerates acid solution for reuse; effluent contains concentrated values which can be recovered; reduced raw material usage and waste generation.	savings in raw materials, waste treatment and sludge disposal; reduced labour requirements for tank cleaning and solution replacement	large scale operation: payback: 18 months small scale operation: payback: 3 years	DTI[4]
recycling: ultrafiltration	metal cleaning	ultra filtration to remove oil contamination from alkaline cleaner, which can be reused on-site; waste oil sent for off-site recycling	reduced waste discharge	savings in raw material (20-50%) and in waste handling (90%). Example payback: less than 12 months	in use	ICPIC[1]

TABLE G1/cont.: Waste Minimisation Opportunities For Metal Plating Operations

Technique	Application	Description	Environmental Advantages	Other Implications	Status	Ref.
recycling: ion exchange	metal plating	ion exchange for treatment of contaminated rinse water to enable water reuse and raw material recovery	reduced water usage and effluent generation; reduced waste load; reduced raw material consumption	generally applicable; higher maintenance requirements Example: payback: 2.5 months	in use	ICPIC[1]
recycling:	metal plating	aluminium displacement process: for recovery of heavy metals from waste streams	metal recovery; reduced waste	reported low equipment cost & simple operation - suitable for smaller scale operations	under development	ICPIC[1]
recycling: evaporation	metal plating	closed loop recycling using evaporation only to recover rinse water for reuse & return of concentrate to plating bath	reduced water usage and effluent generation; reduced waste load; reduced raw material consumption	payback: 4.9 years	in use	WRC(1984)
recycling: evaporation	metal plating	open loop process using evaporation to recover chemicals from D/O only	reduced raw materials consumption and waste load generation	payback: 3.4 years	in use	WRC(1984)
recycling: reverse osmosis	metal plating	open loop process for the purification of rinse water for reuse, with pre-filtration & pH control; RO reject concentrated in ponds prior to disposal	reduced water usage and effluent generation;	3 year membrane life reported; costs n/a	successful demonstration	WRC(1984)
recycling: ultrafiltration	metal plating	2-stage UF to treat 3m^3/hr of rinse water containing 59 mg/l Ni	91% water recovery, with 83% Ni rejection	estimatef \$720/m^3 @ 1979 prices for operating costs	study estimate	WRC(1984)
recycling: electrodialysis	metal plating	recycle of drag-out from Ni plating bath	90% reduction in raw materials & treatment chemicals	estimated payback: 2.8 years	study estimate	WRC(1984)
recycling: electrodialysis	metal plating	regeneration of spent chromic acid solution from brass pickling operation	extended life of bath solution to min. 18 months of previous daily discharge; low sludge production; reduced chemical consumption and effluent generation.	estimated payback: 26 months	study estimate	WRC(1984)
recycling: IONSEP process	chrome plating	closed loop recycling: combination of ED & IX technology to purify rinse water, regenerate chromic acid & remove metal hydroxide precipitates	reduced water usage, chemical consumption & waste generation.	savings in raw materials, water and waste treatment costs.	patented technology	Pletcher, Walsh & Whyte (1990)
remediation: reverse osmosis	metal plating	reverse osmosis for treatment of waste water: with filtration; pH control & polishing stages (carbon adsorption & IX)	removes most of heavy metals	high capital & operating costs; increased maintenance.	long term performance & life not proven	Warnke, Thomas & Creason (1977)
reclamation: solvent extraction	metal plating	use of organic phase to extract Cr(VI) from spent sulphuric acid	faciliates Cr(VI) recovery	in relation to organics	research	Salazar, Inmaculada & Urtiaga (1992)

TABLE G1/cont.: Waste Minimisation Opportunities For Metal Plating Operations

Technique	Application	Description	Environmental Advantages	Other Implications	Status	Ref.
reclamation: metal absorption	metal wastes	absorption of heavy metals using starch based products; nitric acid treatment or incineration required to recover metals	removal of metal pollution from water and potential for metal recovery	not known	not known	Wing & Rayford (1977)
reclamation: electrochemical	metal wastes	often integrated with other unit operations e.g. ion exchange or solvent extraction	clean & effective separation; direct recovery of metals in pure form	ease of control and process monitoring, but reactor performance sensitive to solution composition & throughput	in use	Pletcher, Walsh & Whyte (1990)

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[1] entries under metal finishing in ICPIC database

[2] U.K. Department of Environment "*Clean Technology*" booklet

[3] communication from Mr. D. Reeve - consultant for UNEP metal finishing working group

[4] U.K. Department of Trade and Industry publication "*Cutting Your Losses-A Business Guide To Waste Minimisation*"

APPENDIX H:
RESULTS OF MONITORING PROGRAMME: CHROME PLATING PLANT SEPTEMBER 1992 AND JUNE 1993
PART A: DISCUSSION

1. MONITORING SCHEDULE AND ACTIVITIES

Two separate four-week monitoring programmes have been conducted in the chrome plating plant (CPP). The first programme covered the period from 30 August 1992 til 25 September 1992, and was directed only at one of the two plating lines i.e. Line 2. The rationale for this was the presumption that performance characteristics of the two plating lines should be similar enough to assume common characteristics and, furthermore, the wish to minimise extent of sampling and analytical effort required. Given the limited on-site analytical facilities, arrangements were made with an external laboratory service to undertake the required analyses.

Grab samples were taken from each tank in Line 2 on either a daily or weekly basis over the four week period. The physical characteristics of temperature, pH and conductivity were measured at the same time in-situ using hand-held portable monitoring equipment. The water meter readings were also recorded. The grab samples were bottled, stored in a refrigerator on-site, and transported in bulk to the off-site laboratories. Selected analyses included total and hexavalent chromium (Total Cr & Cr(VI)), iron (Fe) and sulphates (SO_4^{2-}). Given the complexity of the chemical compositions in the process solutions, it was not considered feasible to undertake complete analyses.

This initial monitoring programme had certain shortcomings, which were principally as follows:

1. No account was taken of differences in the operation of the two lines, such as rinse water usage; chemical concentrations e.g. of plating chemicals; return of chromic acid condensate (to Line 1 only); and production throughput.

2. Due to changes in the maintenance and tank cleaning schedule for Line 2 on the week-end of 26 September, no samples could be taken of tank solution

residues (solution or sludges) and it was not possible to review the tank cleaning or chemical make-up practices, for example in relation to water use.

3. There was no direct control over the analytical activities. Some of the analyses which had been requested were not conducted and it was difficult to make direct enquiries about the sample handling, analytical procedures and particular analytical results which were questionable. Finally, the samples were disposed of before these issues could be resolved satisfactorily.

Given the uncertainties and incompleteness of these initial results the second monitoring programme was conducted so as to include both plating lines, and to analyse the samples using laboratory facilities in the Department of Chemical Engineering. This monitoring programme covered the period 4 June 1993 til 25 June 1993. In addition to the previous sampling schedule, samples were also taken from the drained tanks of Line 2 during clean-out activities on Sunday 27 June, on the basis that analytical results of these samples would indicate the lowest quality of effluent discharged to the effluent treatment plant. Samples included those of soak cleaner sludge, electrolytic cleaner solution, alkaline rinse water and water from the cold- and hot rinse water tanks.

The samples were stored in a refrigerator in the Department of Chemical Engineering, and analysed on the 21st, 22nd and 26th of July, with repeat analyses of selected samples on the 28th July i.e. approximately the same time delay between sampling and analyses during the 1992 monitoring programme. No special sample preservation measures were taken other than to use plastic sample bottles (to minimise the potential for chromium adsorption to the glass), and to store the samples at a low temperature.

2. ANALYTICAL PROCEDURES

The analytical procedures undertaken at the private laboratory were described as standard in-house procedures including ultraviolet (UV) spectrophotometric analyses for trivalent chromium (Cr(III)), titrametric analyses for Cr(VI) and Atomic Absorption (AA) spectrophotometric analyses For Total Cr and for iron (Fe). Separate Cr(VI) analyses were not carried out for samples with a Total Cr below 100 mg/l.

The analyses undertaken in the Department of Chemical Engineering consisted, for all liquid samples, of AA analyses for Total Cr and for Fe and colorimetric analyses using the UV spectrophotometer to determine hexavalent chromium concentration based on the diphenyl carbazide (DPC) reaction. This was carried out in accordance with the procedure of Standard Methods (1965). Sample filtering prior to analyses was not necessary as the samples were clear and free of any suspensions. No sample preparation was undertaken to remove potential interfering compounds, which would principally be Fe. However the level of Fe concentration was determined using AA analyses to identify where potential interference effects may have occurred in the DPC reaction.

These procedures were carried out by different analysts working independently of each other, each with their own analytical technique. Some randomly selected samples were analysed a second time using both procedures to verify results and/or detect changes in effluent quality.

Sludge samples were subjected to acid digestion using sulphuric acid, and the digestant analysed as above to ascertain, indicatively only, potential chromium losses to these waste residues.

3. RESULTS AND PRELIMINARY COMMENTS

The results of both monitoring programmes are given in Part B of this Appendix - in summarised tabular format and/or graphs to illustrate, quite clearly, trends in process stream characteristics. Despite the uncertainties about the results of the first monitoring programme they did provide useful indications of trends in carry-over of chromium, acid and alkali contamination as "drag-out" from process solutions into water rinses. In comparison the overall trends illustrated by results of both programmes are similar, but there are significant differences in some analytical results. Reasons for these differences can be traced to changes in operating practices. These are reviewed below.

It should be noted that there are some apparently anomalous results shown by the June 1993 analyses, for example where Cr(VI) concentration is reported as being higher than Total Cr. These discrepancies can be attributed to inherent lack of precision in analytical techniques themselves, instrument sensitivity and operator errors, probably arising most significantly from dilution effects given the need for up to 500 times dilution of some samples. Considering the separate sources of results which indicate similar trends, it is felt that the results are reasonably representative of actual conditions at the time of analyses.

Fe in concentrations greater than 1 mg/l is reported to interfere in the DPC reaction, producing a yellow color, which is described however as "not strong" and no cause for difficulty in the analyses (Standard Methods, 1965). Visible evidence of interference - an orange-red color- was apparent only in the samples of electrolytic cleaning solutions which contained the highest levels of Fe, up to about 60 mg/l. This is taken to demonstrate the presence of ferrous iron (Fe(II)), as Fe(II) forms an orange-red complex with phenanthroline (Standard Methods, 1965), which is an amine compound of similar structure to DPC. Hence it may be presumed that this chemical has reacted with the Fe(II). Analysis for Cr(VI) in these electrolytic cleaning samples was re-attempted a week later, with no visible color interference. It is probable that oxidation of Fe(II) to Fe(III) (ferric iron) has occurred. This would have been accompanied by equivalent reduction of Cr(VI) to Cr(III), with a lower Cr(VI) determination than would have been made a week earlier. Consequently actual concentration levels of Cr(VI) discharged from the electrolytic cleaning tank as part of factory effluent may have been higher than shown by analytical results as there was a time lapse of at least four weeks between sampling and analyses.

Standard Methods (1965) recommend a maximum time lapse of 12 hours between sampling and analyses of polluted waters if no preservation methods are used. The four week delay was selected as explained above. However a consequence of this is that the measured concentration levels of Cr(VI) may be lower in general than the true values at the time of sampling.

Based on the analytical results, and awareness of potential reasons for discrepancies and error, the following specific comments are made:

The 1992 results demonstrated variable conductivity and pH value in the alkaline rinse waters, indicating reasonable rinse flow control by the conductivity meter (see Figure H14). Results for the cold and hot chromium rinse water samples indicated less effective control, with an upward trend in conductivity and downward trend in pH value as the rinse solutions became progressively more contaminated (see Figures H8 and H11). Conductivity measurements were not repeated during the 1993 monitoring programme on the assumption that general trends would be similar. However these may have been a useful indication of changes in quantities of chemicals used e.g. alkali cleaning reagents, and chemical losses due to drag-out to rinse tanks. Both chemical usage and drag-out increased subsequent to the monitoring period of 1992, as discussed below.

pH measurements were repeated as a simple indicator of alkali or acid carry-over between tanks. The results (see Figure H15b) indicate that on average the pH in the alkaline cleaning solutions was higher during the monitoring period in 1993 than during the 1992 programme. This suggests that the alkaline solution was more concentrated. Reportedly additional cleaning chemical *was* being used in the make-up of the cleaning tank solutions. The reasons for this are unknown, but this may be unnecessary wastage of chemicals. Moreover increased chemical content increases solution viscosity, drag-out losses are increased and rinsing becomes more difficult. This may be one reason for the higher rinse water rates in 1993 compared with metered readings of 1992 (compare Table H3 with Tables H11a&b). It has also been acknowledged that the rinse rate has been increased of necessity to counter increased drag-out due to greater entrapment of process fluid by jigs of new design. Consequently contamination of all tanks will have increased.

There was significant chromium contamination of alkaline cleaning solutions and subsequent rinse water solutions. This was caused most likely by carry-over of chromium-laden condensate and residue on jigs and on work-pieces. The 1993 results showed the soak cleaning tanks to contain 100's of mg/l, up to 415 mg/l at month end for Line 1 (see Table H8a&b), while the electrolytic cleaning tanks had an even higher concentration, up to 1340 mg/l at month end in Line 1 (see Table H9a&b). Chromium levels in the rinse water were much lower as a consequence of continual through flow of fresh water. Of the Total Cr in each stream, a significant proportion was Cr(VI). All of these waste waters were discharged as part of factory effluent which is not treated for Cr(VI) reduction and removal in the effluent treatment plant. Hence there are implications for untreated Cr discharges to the sewer, and moreover for operator safety given the acknowledged toxicity of Cr(VI). Apart from chromium, the strong alkali concentrations render these solutions hazardous on grounds of corrosivity.

Chromium analysis had not been requested for equivalent samples taken in the 1992 monitoring programme since Cr presence had not been anticipated until the actual operating conditions in the plant had been monitored.

The analytical results from 1992 showed a maximum Total Cr concentration of 70 g/l in the drag-out recovery tank solution of Line 2 (see Table H4). The drag-out recovery tanks were not sampled for analyses in the 1993 programme, which, with hindsight, was an omission. Chromium concentrations in this tank would be expected to be approximately consistent. Even though drag-out effects may have increased since the 1992 programme (due to altered jig design), the greater loss of chromium solution from the plating tanks should be compensated by greater addition of make-up water to maintain tank levels, thereby achieving a similar diluted chromium concentration. However, given that drag-out solution from Line 1 is also used as the scrubbing liquor to remove chromic acid mist from the extraction system, the chromium content in this tank could be higher than that of Line 2. It has not been possible to assess this difference.

Chemical rinsing is intended to reduce Cr(VI) to Cr(III) which is more easily rinseable than Cr(VI) as well as being less toxic. Yet, based on the 1993 analytical results, there were 1000's of mg/l of Total Cr in the chemical rinse tank solution, and almost all of this was present as Cr(VI) (see Tables H12a&b). It is understood that the chemical reagent is sodium hydrosulphite, which requires a pH above 9 to be effective. Due to increased drag-in of acidic plating solution pH of these tank solutions was reduced considerably , to as low as 2.3. Hence there may have been ineffective chemical reaction and/or excessive drag-in of plating solution in excess of treatment capacity of the chemical reagent.

Repeat analyses after a week's interval of two samples from these tanks showed an unchanged Total Cr level, but a significant reduction in Cr(VI) concentration: 93% reduction in one sample and 72% in the other. This would suggest that the chemical *does* reduce the Cr(VI), but not effectively in conditions in the chemical rinse tank. Similar effects were demonstrated by analyses of Cr(VI) contamination in the rinse water tanks, in which almost all of the Total Cr was Cr(VI). Repeat analyses of samples from these tanks also showed decreasing levels of Cr(VI) with time. However the small differences in the Total Cr and Cr(VI) analytical results would suggest that little, if any, chemical reduction took place during the storage time in the sealed bottles.

The equivalent reported analytical results for the 1992 samples showed a maximum Total Cr concentration of 71 mg/l, with pH values in the range 8.7 - 9.0 (see Table H5). These conditions are more favourable for effective reduction. It was not possible to obtain a sample of tank bottoms, which may have been solution or sludge, to examine content of precipitated chromium hydroxide and to assess effectiveness of this treatment stage. Clearly this would be dependant on maintaining correct operating conditions, pH in particular. With incorrect conditions there are implications for chemical wastage, both in the chemical rinse tank and in the effluent treatment plant, higher drag-out and rinse water contamination, and operator safety in the handling of contaminated work-pieces.

It should also be noted that there was a high level of Fe in the chemical rinse tank solution of Line 2 in the period after 14th June 1993 (see Table H12b). This suggests that there was a high level of Fe contamination in the plating solution. This may have had an impact on plating quality.

Rinse water usage in the cold and hot rinse tanks was much lower during the 1993 period than during the 1992 programme (compare Tables H6 and H7 with Tables H14a&b and H16a&b). It is understood that this was due to the perceived need to reduce the treatment load on the effluent treatment plant. A consequence of these lower flows was higher levels of chromium contamination, up to 1000's of mg/l (see Tables H13a&b) compared with reported levels of less than 100 mg/l in the 1992 results (see Tables H6 and H7). The higher chromium content of this rinse water would cause a greater shock load on the effluent treatment plant when tanks are drained during weekend clean-out activities.

The equivalent analytical results from the 1992 programme had clearly shown greater contamination of the hot rinse baths than the cold rinse baths. Two possible reasons for this are condensation on carrying racks of water evaporated at the higher temperature of the hot rinse bath, with return of contaminated condensate to the tank below; and the carryover of chromic acid in spray rinse water which is sprayed onto work-pieces above the cold rinse water tank. This trend is not conclusive based on the 1993 analytical results which showed comparable chromium concentration levels in both tanks. This may be due to the fact that, reportedly, less use is being made of spray rinsing than has been used previously.

The pH trends (see Figures H18b and H20b) suggest that the rinse tanks were not drained and replaced on a regular weekly basis. Low pH values of 2.5-3.0 were measured, with pH values of 5-6 following refilling. Conceivably the low pH values reduce the extent of pH adjustment required in the effluent treatment plant for chromium reduction to take place, but implications of this poor rinse water quality for work-piece surface quality and downstream chromium contamination should be considered.

The analytical results of samples taken on Sunday 27 June 1993 (see Line 2 results) showed slightly higher contaminant levels, following overtime production on Saturday 26 June. This waste quality would define the treatment load on the effluent treatment plant arising from derived from periodic discharge of process solutions.

Analysis of the soak cleaner sludge indicated that there was significant chromium content in the caustic sludge in the soak cleaner tanks (see Table H8b). It was not possible to ascertain the amount of sludge itself, but there was a thick layer in the bottom of the tank in Line 2. This waste is sent for landfill disposal.

APPENDIX H:
RESULTS OF MONITORING PROGRAMME: CHROME PLATING PLANT
SEPTEMBER 1992 AND JUNE 1993
PART B: MONITORING AND ANALYTICAL RESULTS

RESULTS OF MONITORING PROGRAMME: CHROME PLATING PLANT (Sept. 1992)

LINE 2 ONLY:

PROCESS UNIT: Soak Clean TANK VOL.(l): 1650
SAMPLE VOL. 500

TABLE H1

DATE:	pH	CONDUCT (mS/cm)	Fe (ppm)
30-Aug	11.6	22.4	1
04-Sep	11.9	34.4	2
11-Sep	12.4	35.7	2
18-Sep	11.9	37	3
25-Sep	12.3	42	

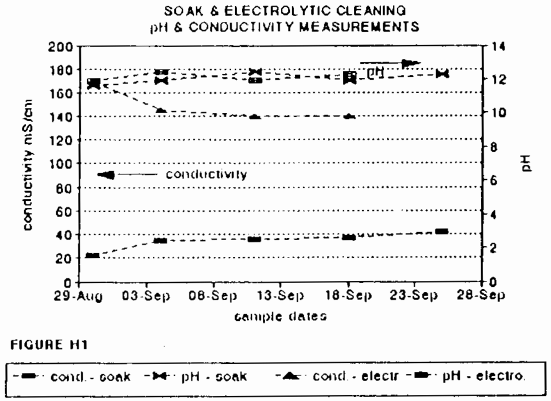

FIGURE H1

PROCESS UNIT: Elect. Clean TANK VOL.(l): 3200
SAMPLE VOL. 500

TABLE H2

DATE:	PH	CONDUCT (mS/cm)	Fe (ppm)
30-Aug			6
04-Sep	11.9	168.7	20
11-Sep	12.4	144.7	25
18-Sep	11.9	140	32
25-Sep	12.3	140.4	

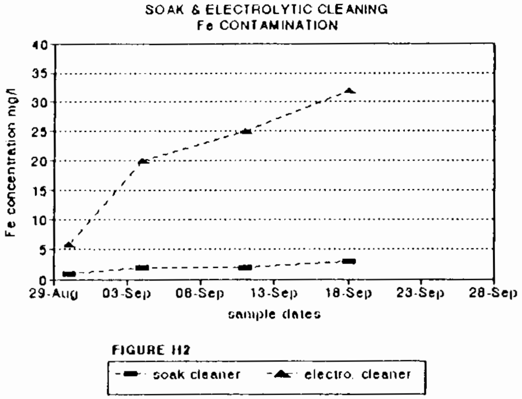

FIGURE H2

PROCESS UNIT: Alkaline Rinse TANK VOL.(l): 1650

TABLE H3

SAMPLE VOL.(ml):

DATE:	2nd Rinse (l)	Diff.	PH	CONDUCT (microS)
30-Aug			6.9	181
31-Aug	18334		9.3	162
01-Sep	21329	2995	11	789
02-Sep	24418	3089	10.9	560
03-Sep	27276	2858	11.3	777
04-Sep	29434	2158	11.3	940
07-Sep	31405	1971	10.8	625
08-Sep	34552	3147	8.2	171
09-Sep	40246	5694	8.7	164
10-Sep	43034	2788	7.8	178
11-Sep			10.9	675
14-Sep	46601	3567	11.1	1478
15-Sep	48594	1993	10.9	1106
16-Sep	51102	2508	10.9	940
17-Sep	53495	2393	10.5	454
18-Sep	56472	2977	9.5	616
21-Sep	57885	1413	11.1	1118
22-Sep	62153	4268	11	709
23-Sep				
24-Sep	69680	7527	11.1	777
25-Sep	70437	757	9.9	498
TOTAL FLOW		52103		
Av. Daily Flow		2004		
Std. Dev.		1546		

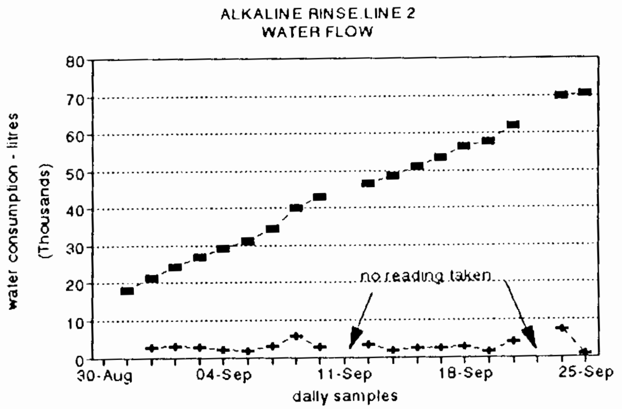

FIGURE H3

- ■ - cummulative total - ✦ - daily variation

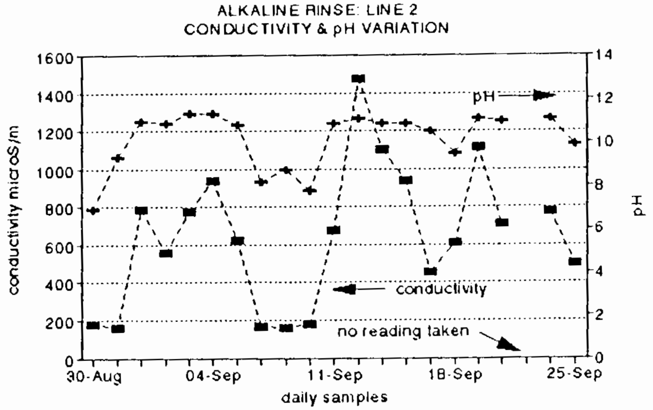

FIGURE H4

- ■ - conductivity - ✦ - pH

RESULTS OF MONITORING PROGRAMME: CHROME PLATING PLANT (Sept. 1992)

LINE 2 ONLY:

PROCESS UNIT: Drag-out Recovery

TANK VOL.(l): 1650

SAMPLE VOL. 500

TABLE H4

DATE:	PH	CONDUCT (mS/cm)	Fe (ppm)	TOT.Cr (ppm)
30-Aug	0.4	73.5	14	70
04-Sep	1.5	8.4	5	69
11-Sep	1.9	3.36	2.5	67
18-Sep	2.1	3.83	3.2	67
25-Sep	2.1	6.09		

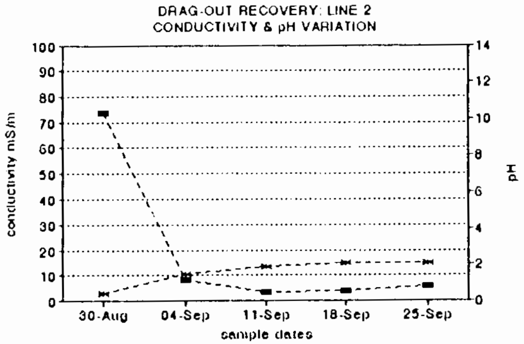

FIGURE H5

PROCESS UNIT: Chemical Rinse

TANK VOL.(l): 1650

SAMPLE VOL. 500

TABLE H5

DATE:	PH	CONDUCT (mS/cm)	TOT.Cr (mg/l)
30-Aug	8.7	34.5	
04-Sep	8.8	28.6	71
11-Sep	8.7	29	66
18-Sep	8.5	25.8	65
25-Sep	6.3	22.5	

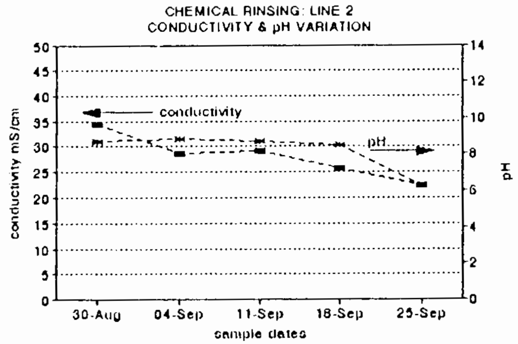

FIGURE H6

PROCESS UNIT: Cold Rinse TANK VOL.(l): 1650

TABLE H6 SAMPLE VOL.(ml): 500

DATE:	Flow (l)	Diff.	PH	CONDUCT (microS)	TOT.Cr (ppm)
30-Aug	assume 0		8	234	nd
31-Aug	4719	4719	8.3	373	4.6
01-Sep	7218	2499	6.6	383	8
02-Sep	11651	4433	7.3	254	5.2
03-Sep	11849	198	7.4	538	9
04-Sep	13144	1295	6.8	500	11
07-Sep	13948	804			7.5
08-Sep	15475	1527	8.1	426	3.2
09-Sep	16386	911	7.9	555	19
10-Sep	16386	0	8.1	861	25
11-Sep			8.2	1041	28
14-Sep	17218	832	8.2	1093	44
15-Sep	17791	673	7.2	1142	45
16-Sep	18603	812	6.7	959	45
17-Sep	19504	901	7.6	1105	31
18-Sep	21808	2304	7.2	572	37
21-Sep	23644	1836	7.2	530	60
22-Sep	24267	643	3.5	830	
23-Sep					60
24-Sep	31044	6757	5.5	896	
25-Sep	34667	3623	6.1	409	
TOTAL FLOW		29948			
Av. Daily Flow		1152			
Std. Dev.		1784			

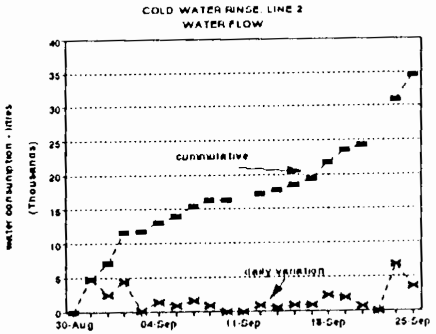

FIGURE H7

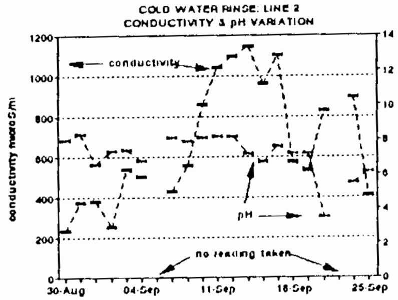

FIGURE H8

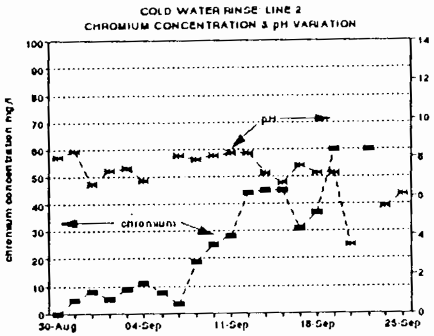

FIGURE H9

PROCESS UNIT: Hot Rinse TANK VOL. (l): 1650

TABLE H7 SAMPLE VOL. (ml): 500

DATE:	Flow (l)	Diff.	PH	CONDUCT (microS)	TOT.Cr (ppm)
30-Aug	assume 0		8.5	162	0.7
31-Aug	1840	1840	6.8	349	5
01-Sep	1840	0	5.9	424	10.5
02-Sep	1901	61	5.6	426	12
03-Sep	1930	29	5.3	447	13.5
04-Sep	1936	6	3.6	646	16
07-Sep	3680	1744	6.6	519	
08-Sep	3748	68	6.3	761	11
09-Sep	3748	0	6.1	719	40
10-Sep	3748	0	5.9	732	44
11-Sep			6.5	770	49
14-Sep	3891	143	5.1	826	54
15-Sep	3891	0	4	871	56
16-Sep	3891	0	3.6	942	57
17-Sep	4045	154	3.2	1320	63
18-Sep	4045	0	4.5	1384	
21-Sep	4103	58	3.5	871	62
22-Sep	4129	26	3.1	1680	67
23-Sep					65
24-Sep	4204	75	2.9	1901	68
25-Sep	4204	0	2.4	953	
TOTAL FLOW		2364			
Av. Daily Flow		91			
Std.Dev.		553			

HOT WATER RINSE: LINE 2
CUMMULATIVE WATER FLOW

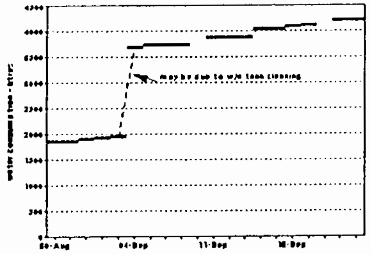

FIGURE H10

HOT WATER RINSE: LINE 2
CONDUCTIVITY & pH VARIATION

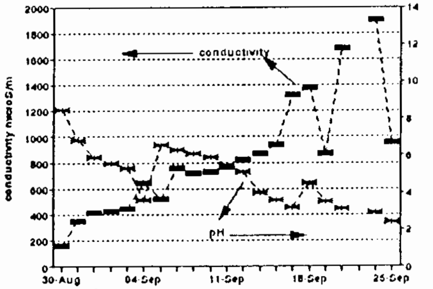

FIGURE H11

HOT WATER RINSING: LINE 2
Cr CONCENTRATION & pH VARIATION

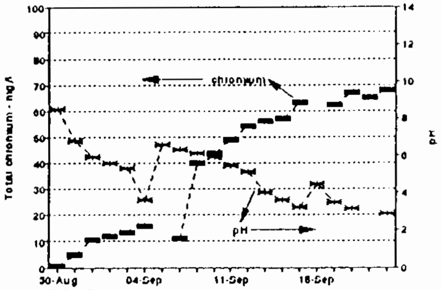

FIGURE H12

RESULTS OF MONITORING PROGRAMME: CHROME PLATING PLANT (June 1993)

PROCESS UNIT: Soak Cleaning TANK VOL.(l): 1650

SAMPLING: twice weekly SAMPLE VOL. 500

TABLE H8a - Line 1 (A1) 22-Jul

DATE:	PH	Fe (mg/l)	Total Cr (mg/l)	Hexa.Cr (mg/l)
04-Jun	12.46	11.4	222.0	66.3
07-Jun	13.2	2.4	40.1	11.7
11-Jun	13.4	3.7	79.9	19.2
14-Jun	12.37	4	74.5	17.2
18-Jun	13.42	5.4	153.0	41.1
21-Jun	13.34	5.8	156.0	43.1
25-Jun	13.33	8.6	233.0	71.2

TABLE H8b - Line 2 (B1) 22-Jul

DATE:	PH	Fe (mg/l)	Total Cr (mg/l)	Hexa.Cr (mg/l)
04-Jun	12.54	3.8	118.0	41.6
07-Jun	13.28	3.9	147.0	56.4
11-Jun	12.96	5.0	190.0	141.7
14-Jun	13.27	5.1	255.0	120.3
18-Jun	13.34	6.3	228.0	184.3
21-Jun	13.41	6.7	368.0	178.0
25-Jun	13.39	9.3	415.0	238.1
27-Jun sludge sample: > 300 mg/l Total Cr in digestate				

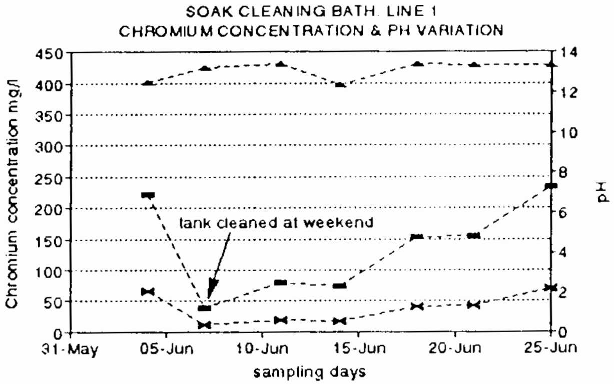

FIGURE H13a

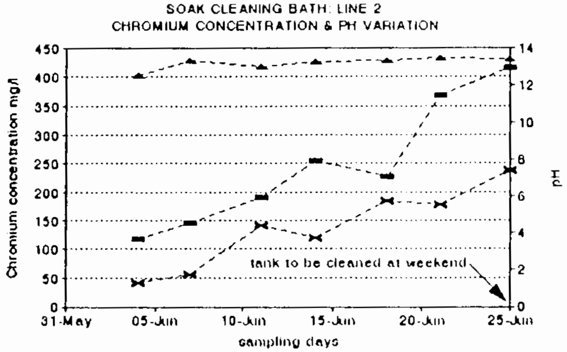

FIGURE H13b

RESULTS OF MONITORING PROGRAMME: CHROME PLATING PLANT (June 1993)

PROCESS UNIT: Elect. Cleaning TANK VOL.(l): 3200

SAMPLING: twice weekly SAMPLE VOL. 500

TABLE H9a - Line 1 (A2)

				22-Jul
DATE:	PH	Fe (mg/l)	Total Cr (mg/l)	Hexa.Cr (mg/l)*1
04-Jun	12.27	57.6	1450.0	n/a
07-Jun	12.88	6.2	41.6	n/a
11-Jun	13.49	23.2	428.0	n/a
14-Jun	12.2	15.8	328.0	n/a
18-Jun	13.52	33.3	777.0	n/a
21-Jun	13.64	32.9	264.0	n/a
25-Jun	13.7	47.8	1460.0	n/a
04-Jun	(28-Jul)	repeat sample	1400.0	122.9

*1: orange interferance

TABLE H9b - Line 2 (B2)

				22-Jul	28-Jul
DATE:	PH	Fe (mg/l)	Total Cr (mg/l)	Hexa.Cr (mg/l)	Hexa.Cr (mg/l)
04-Jun	12.57	11.5	251.0	113	127.8
07-Jun	12.88	14.2	250.0	0	159.8
11-Jun	13.42	24.0	253.0	0	100.8
14-Jun	13.81	21.9	383.0	53	12.3
18-Jun	13.67	38.5	430.0	0	73.7
21-Jun	13.66	40.6	233.0	0	125.4
25-Jun	13.66	58.2	1340.0	366	211.4
27-Jun	-	83.3	1290.0		287.0

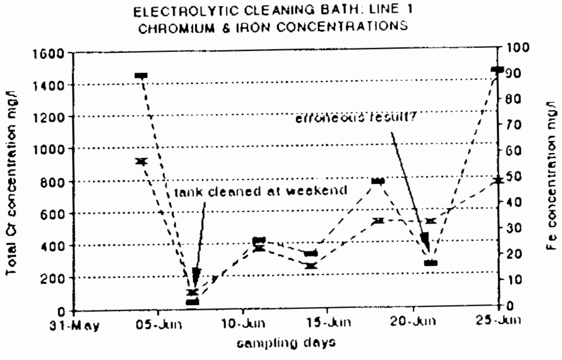

FIGURE H14a

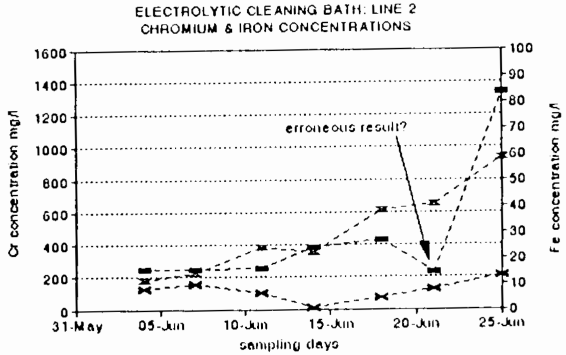

FIGURE H14b

RESULTS OF MONITORING PROGRAMME: CHROME PLATING PLANT (June 1993)

PROCESS UNIT: Alkaline Rinse TANK VOL.(l): 1650*2

SAMPLING: twice weekly SAMPLE VOL. 500

TABLE H10a - Line 1 (A3)

				21-Jul	28-Jul
DATE:	PH	Fe	Total Cr	Hexa.Cr	Hexa.Cr
		(mg/l)	(mg/l)	(mg/l)	(mg/l)
04-Jun	11.71	0.4	3.3	2.3	2.4
07-Jun	12.42	0.3	3.5	1.9	2.4
11-Jun	10.79	0.2	0.9	0.6	0.7
14-Jun	11.1	0.2	10.1	8.9	9.2
18-Jun	12.79	0.6	8.6	6.5	6.5
21-Jun	11.98	0.4	1.9	3.1	2.9
25-Jun	10.83	0.3	4.2	5.4	5.6
14-Jun	(28-Jul)	repeat sample	10.7		

TABLE H10b - Line 2 (B3)

				21-Jul
DATE:	PH	Fe	Total Cr	Hexa.Cr
		(mg/l)	(mg/l)	(mg/l)
04-Jun	12.67	0.4	6.0	3.6
07-Jun	13.28	0.7	15.4	11.0
11-Jun	12.74	0.5	1.1	2.1
14-Jun	12.14	0.5	7.7	4.4
18-Jun	12.54	1.5	8.7	11.3
21-Jun	12.70	2.2	7.5	13.8
25-Jun	11.83	0.9	12.1	9.0
27-Jun		0.4	22.8	20.2

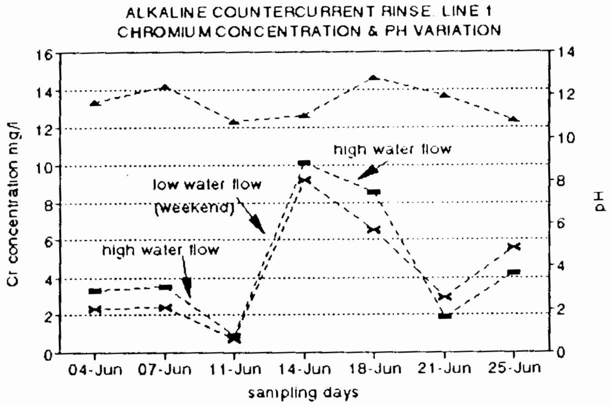

FIGURE H15a

-■- total Cr -✕- Cr6+ -▲- pH

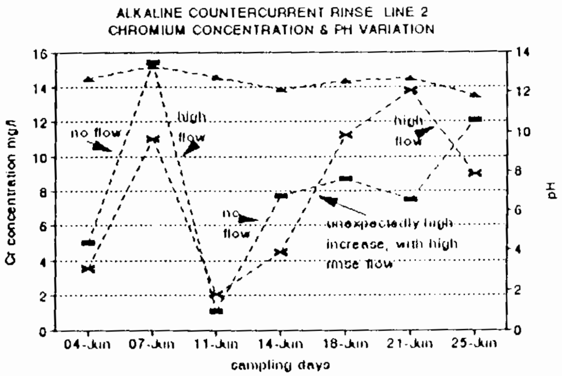

FIGURE H15b

-■- total Cr -✕- Cr6+ -▲- pH

RESULTS OF MONITORING PROGRAMME: CHROME PLATING PLANT (June 1993)

PROCESS UNIT: Alkaline Rinse - meter readings

TABLE H11a - Line 1 (A3)

Date:	1st Rinse	Diff.	Daily	2nd Rinse	Diff.	Daily
04-Jun	42196			943549		
07-Jun	45699	3503		948256	4707	
11-Jun	57721	12022	2404	975413	27157	5431
14-Jun	60404	2683		980630	5217	
18-Jun	66265	5861	1172	995344	14714	2943
21-Jun	66993	728		997752	2408	
25-Jun	70385	3392	678	1022345	24593	4919
Total	28189	28189		78796	78796	
Av. Daily Flow			1418			4431
Std. Dev.			726			

TABLE H11b - Line 2 (B3)

Date:	1st Rinse	Diff.	Daily	2nd Rinse	Diff.	Daily
04-Jun	49204			948020		
07-Jun	49204	0		951280	3260.0	
11-Jun	51338	2134	427	977881	26601.0	5320
14-Jun	51338	0		983365	5484.0	
18-Jun	66700	15362	3072	998864	15499.0	3100
21-Jun	67038	338		998973	109.0	
25-Jun	70318	3280	656	1021945	22972.0	4594
Total	21114	21114		73925	73925	
Av. Daily Flow			1385			4338
Std. Dev.			1197			

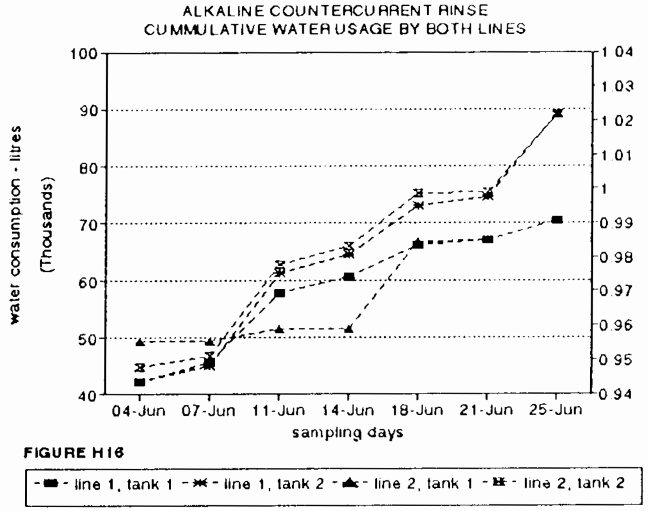

FIGURE H16

RESULTS OF MONITORING PROGRAMME: CHROME PLATING PLANT (June 1993)

PROCESS UNIT: chemical rinse TANK VOL.(l): 1650

SAMPLING: twice weekly SAMPLE VOL. 500

TABLE H12a - Line 1 (A7) 26-Jul

DATE:	PH	Fe (mg/l)	Total Cr (mg/l)	Hexa.Cr (mg/l)
04-Jun	6.31	0.7	5020.0	4649.8
07-Jun	9.11	0.3	1240.0	1335.4
11-Jun	8.9	0.5	1985.0	1918.2
14-Jun	8.49	0.7	2150.0	2209.5
18-Jun	6.87	0.5	3820.0	3508.6
21-Jun	6.73	0.5	4000.0	4091.3
25-Jun	5.53	0.7	5590.0	5621.0
11-Jun	(28-Jul)	repeat sample	1985.0	637.7

TABLE H12b - Line 2 (B7) 26-Jul

DATE:	PH	Fe (mg/l)	Total Cr (mg/l)	Hexa.Cr (mg/l)
04-Jun	8.90	0.3	1210.0	1116.9
07-Jun	9.80	0.6	19.7	0.0
11-Jun	6.29	0.4	2100.0	1918.2
14-Jun	6.31	0.1	2230.0	2209.5
18-Jun	2.91	67.8	3750.0	3217.2
21-Jun	2.75	74.5	4030.0	3447.9
25-Jun	2.29	96.2	4930.0	4103.4
04-Jun	(28-Jul)	repeat sample	1210.0	73.7

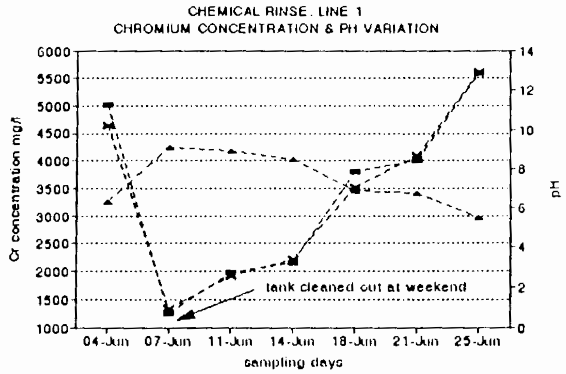

FIGURE H17a

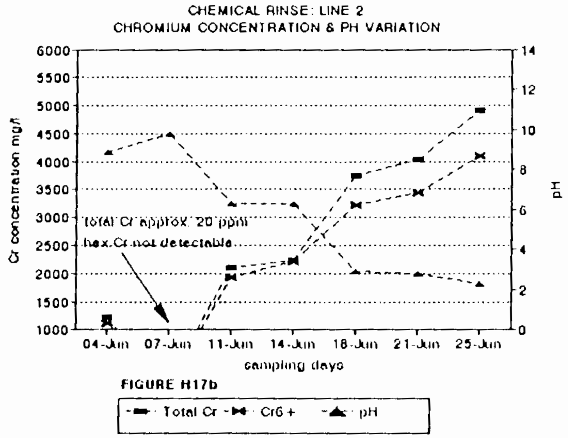

FIGURE H17b

RESULTS OF MONITORING PROGRAMME: CHROME PLATING PLANT (June 1993)

PROCESS UNIT: cold rinse TANK VOL.(l): 1650

SAMPLING: twice weekly SAMPLE VOL. 500

TABLE H13a - Line 1 (A8) 26-Jul

DATE:	PH	Fe (mg/l)	Total Cr (mg/l)	Hexa.Cr (mg/l)
04-Jun	6.31	0.7	4980.0	3906.8
07-Jun	7.72	0.1	650.0	616.7
11-Jun	4.09	0.2	540.0	507.5
14-Jun	4.7	0.3	576.0	624.0
18-Jun	3.2	0.3	310.0	332.6
21-Jun	3.48	4.6	340.0	356.9
25-Jun	2.9	12.9	610.0	643.4
14-Jun	(28-Jul)	repeat sample	576.0	314.7

TABLE H13b - Line 2 (B8) 26-Jul

DATE:	PH	Fe (mg/l)	Total Cr (mg/l)	Hexa.Cr (mg/l)
04-Jun	8.77	0.1	460.0	449.2
07-Jun	5.07	neg	93.2	153.0
11-Jun	6.60	0.4	1020.0	905.7
14-Jun	6.64	0.5	1160.0	1000.4
18-Jun	3.16	6.1	360.0	337.5
21-Jun	2.96	8.4	460.0	439.5
25-Jun	2.46	29.6	1200.0	997.9
27-Jun		32.0	1285.0	1099.0
07-Jun	(28-Jul)	repeat sample	93.2	7.4

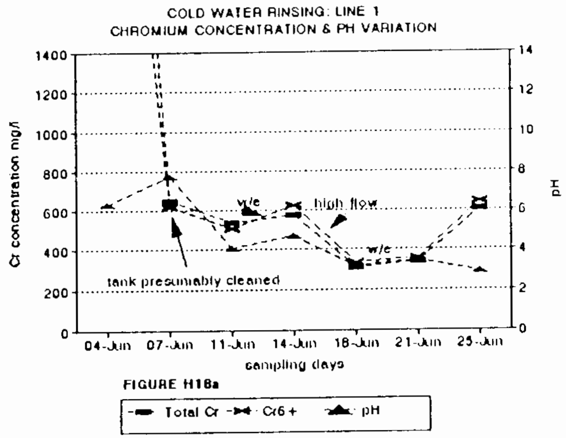

FIGURE H18a

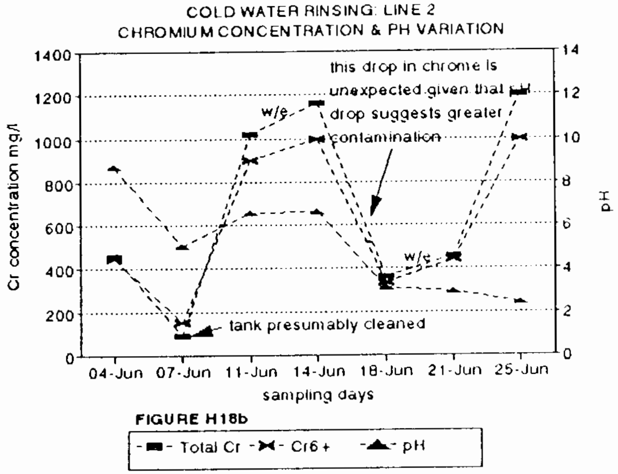

FIGURE H18b

RESULTS OF MONITORING PROGRAMME: CHROME PLATING PLANT (June 1993)

PROCESS UNIT: Cold Rinse - meter readings

TABLE H14a - Line 1 (A8)

Date:	Flow	Diff.	Daily
04-Jun	389082		
07-Jun	390570	1488	
11-Jun	390570	0	0
14-Jun	390570	0	
18-Jun	401229	10659	2132
21-Jun	401229	0	
25-Jun	402335	1106	221
Total	13253	13253	
Av. Daily Flow			784
Std. Dev.			957

TABLE H14b - Line 2 (B8)

Date:	Flow	Diff.	Daily
04-Jun	272552		
07-Jun	272552	0	
11-Jun	272552	0	0
14-Jun	272552	0	
18-Jun	272958	406	81
21-Jun	272958	0	
25-Jun	273064	106	21
Total:	512	512	
Av. Daily Flow			34
Std. Dev.			34

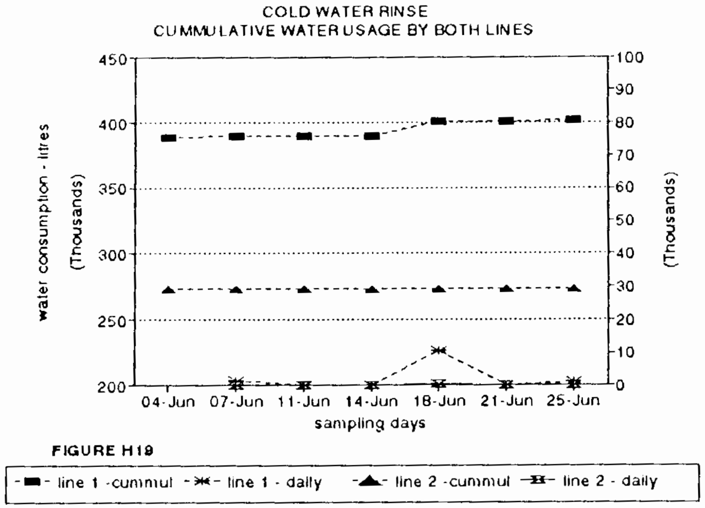

FIGURE H19

RESULTS OF MONITORING PROGRAMME: CHROME PLATING PLANT (June 1993)

PROCESS UNIT: Hot Rinse TANK VOL.(l): 1650

SAMPLING: twice weekly SAMPLE VOL. 500

TABLE H15a - Line 1 (A9) 26-Jul

DATE:	PH	Fe (mg/l)	Total Cr (mg/l)	Hexa.Cr (mg/l)
04-Jun	3.1	2.6	470.0	446.8
07-Jun	5.07	0	153.0	71.3
11-Jun	2.19	1.1	205.0	262.2
14-Jun	3.56	0.2	213.0	257.4
18-Jun	2.9	4.3	460.0	454.0
21-Jun	2.89	4.8	460.0	461.3
25-Jun	2.73	8.5	640.0	607.0
07-Jun	(28-Jul)	**repeat sample**	153.0	71.3

TABLE H15b - Line 2 (B9) 26-Jul

DATE:	PH	Fe (mg/l)	Total Cr (mg/l)	Hexa.Cr (mg/l)
04-Jun	5.56	0.0	160.0	76.2
07-Jun	5.33	0.0	27.8	106.8
11-Jun	5.41	0.1	370.0	354.5
14-Jun	5.79	1.1	370.0	369.1
18-Jun	3.70	0.7	520.0	517.2
21-Jun	3.73	9.8	570.0	522.0
25-Jun	3.00	5.6	680.0	672.6
27-Jul		1.2	745.0	674.6
04-Jun	(28-Jul)	**repeat sample**	160.0	76.2

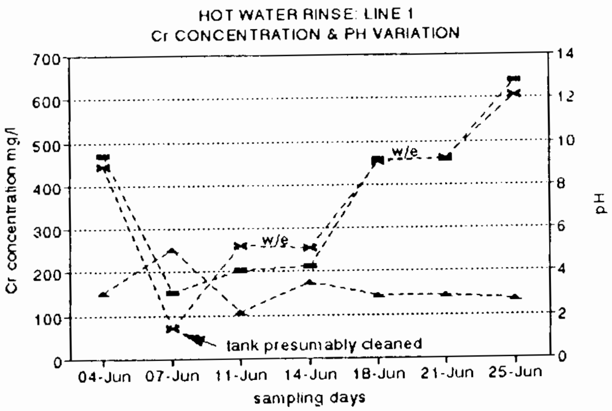

FIGURE H20a

-■- total Cr -⧓- Cr6+ -▲- pH

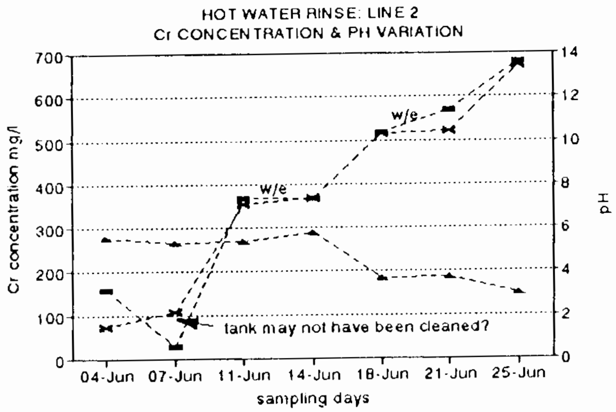

FIGURE H20b

-■- total Cr -⧓- Cr6+ -▲- pH

RESULTS OF MONITORING PROGRAMME: CHROME PLATING PLANT (June 1993)

PROCESS UNIT: HOT RINSE - **meter readings**

TABLE HI6a - Line 1 (A9)

Date:	Flow	Diff.	Daily
04-Jun	28632		
07-Jun	30177	1545	
11-Jun	30280	103	21
14-Jun	30345	65	
18-Jun	30471	126	25
21-Jun	30541	70	
25-Jun	30618	77	15
Total	1986	1986	
Av. Daily Flow			20
Std. Dev.			4

TABLE H16b - Line 2 (B9)

Date:	Flow	Diff.	Daily
04-Jun	19389		
07-Jun	19389	0	
11-Jun	19389	0	0
14-Jun	19389	0	
18-Jun	19389	0	0
21-Jun	19389	0	
25-Jun	19389	0	0
Total	0	0	

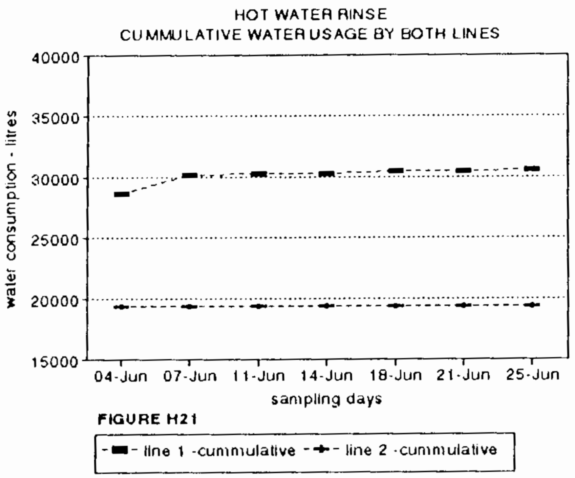

FIGURE H21

APPENDIX I:
RESULTS OF MONITORING PROGRAMME: EFFLUENT TREATMENT PLANT
JULY 1993
PART A: DISCUSSION

1. MONITORING SCHEDULE AND ACTIVITIES

A week long monitoring programme was conducted in the effluent treatment plant (ETP) during the period 3 July 1993 til 9 July 1993. An automatic sampler was hired to enable continual composite samples to be taken of treated effluent discharged to the sewer, for the day-time period (typically 8.30 am til 5 pm) and overnight. The sampler was set-up and tested during the weekend of 3rd and 4th July; samples were taken of untreated and treated streams so as to indicate weekend condition. Automatic sampling was initiated on Sunday evening.

During the early stages of the monitoring period flow rates of influent- and sewer discharge streams were estimated by repeated periodic measurements of time taken to fill containers of known volume. Flowmeter readings were also taken twice daily from the alkaline-, cold- and hot rinse tanks in both plating lines so as to monitor discharge rates. Approximate measurements were taken hourly of levels of treatment reagent solutions in the reagent tanks in the ETP inorder to estimate both treatment chemical consumption and additional use of water in the ETP itself.

During the day-time period of the 5th, 6th and 9th of July hourly grab samples were taken from the following streams (provided they were flowing):

- untreated chromium containing influent (A);
- plate separator/settler feed (B);
- treated discharge to the tank farm (C);
- factory effluent to the tank farm (D);
- discharge to the sewer (E);
- discharge from the filterpress, at the filterpress and at the discharge point to the sewer (F).

Figure I1 illustrates these sampling locations.

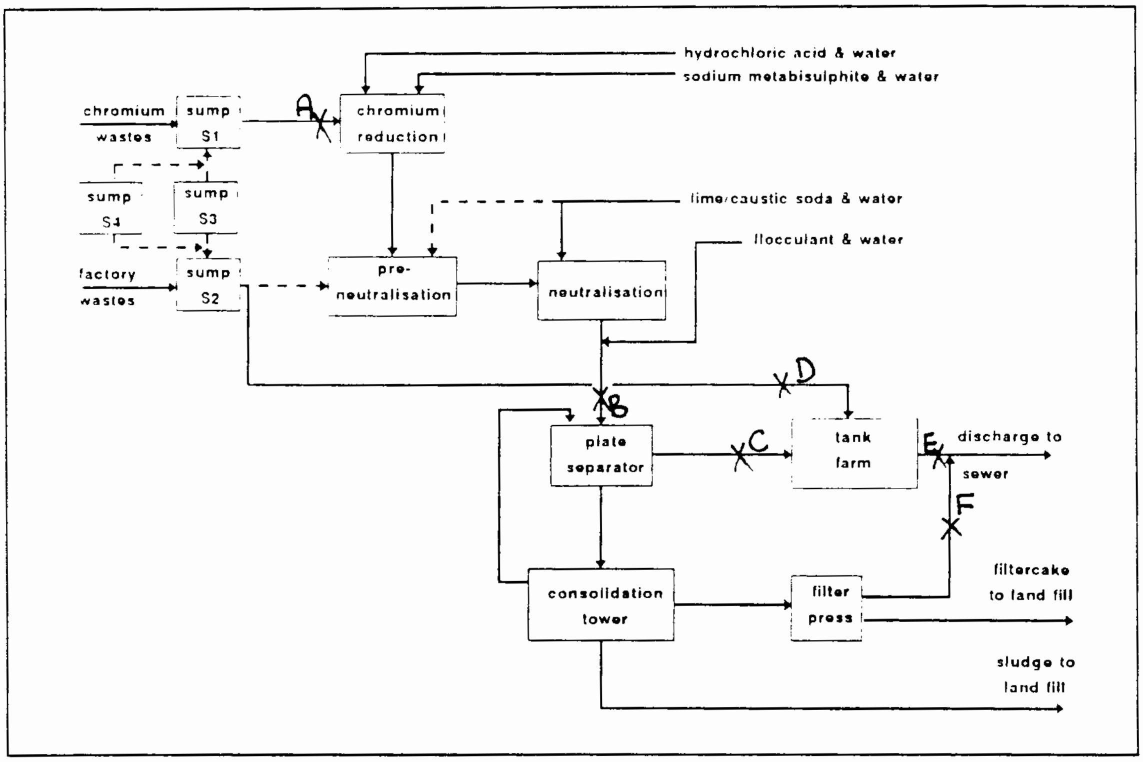

FIGURE I1: Sampling Locations For ETP Monitoring Programme

On the 7th and 8th July these streams were sampled only twice: in the morning and again in the evening, while the automatic sampler collected the composite sewer discharge sample (E). Likewise reagent tank levels were measured only at these times.

pH and conductivity of samples were measured using hand-held portable monitoring equipment and individual samples of each stream were blended to yield a composite sample for each stream for each day. Obviously only the discharge to the sewer (E) could be sampled overnight. The samples were bottled, acidified with nitric acid as a preservation measure and stored in a refrigerator in the Department of Chemical Engineering to await analyses. This took place on 4th and 5th of August, again after a time lapse of about one month.

Other selected samples were also taken during this period. In particular, contents of each of the sumps were sampled, including:

- chromium waste sump (S1)
- factory effluent sump (S2)

- "spare" sump (S3)
- "emergency" sump (S4)

S4 contained waste process solution which had been discharged from the chrome plating plant (CPP) during the tank clean-out activities of Sunday 27 June i.e. following the period of monitoring in the CPP, and was awaiting treatment in the ETP. This waste stream was being stored until the control system in the ETP was commissioned. Processing of this waste commenced overnight on Thursday (8th July) and continued during Friday (9th July) by blending with CPP rinse water discharged from the rinse tanks to S1.

Samples were also taken of the chromium contaminated rinse effluents (hot and cold rinse water discharges) from both plating lines on Wednesday (7th July) to provide an indication of the quality of rinse water being discharged from the CPP itself during that week.

2. ANALYTICAL PROCEDURES

The same procedures described in Appendix H were used (Dept. Chem.Eng only), with the addition of AA analyses for zinc (Zn) Some samples had to be filtered to remove suspensions and precipitates of (presumably) metal hydroxides, or oily surface films. The reappearance with time of particulate material in filtered samples suggested that reactions were still taking place.

3. RESULTS AND PRELIMINARY COMMENTS

The monitoring and analytical results are shown in Part B of this appendix. Some general comments are made as follows:

The individual samples blended into composite samples were not flow proportional: while the sample volume was consistent, stream flowrates were variable and actual discharges were irregular. However the results obtained are considered to be reasonably representative of conditions in the ETP during the week of monitoring.

Conductivity measurements give a general indication of effluent quality in terms of dissolved ion content including, for example, sodium (Na). Hence addition of treatment chemicals increases effluent conductivity which therefore can provide an indication of relative usage of treatment chemicals. High conductivity in the sewer discharge may incur penalties for exceeding the discharge constraint of 500 mS/m. This was not exceeded during the period of the monitoring programme.

For most of the week reagent addition was controlled manually while commissioning work continued on the PLC. Deliberately, therefore, no highly contaminated chromium effluent was processed during night-time while there was no operator in attendance. Cr(VI) was detected in just one overnight composite sample (0.2 mg/l on Tuesday night - see Table I1). Based on water meter readings (see Table I5), it is deduced that rinse water was discharged from the first alkaline rinse tank of both plating lines in the CPP, between Tuesday evening and Wednesday morning and during Wednesday. This could have been the source of Cr(VI) contamination which, as part of factory effluent, is not treated in the Cr(VI) reduction stage.

75% and greater of Total Cr in chromium containing influent (A) was Cr(VI) (Table I1). No detectable Cr(VI) was analysed in settler feed (B) or the treated effluent (C), with the exception of the sample taken on Saturday 3 July (2.3 mg/l). There may have been incomplete treatment of chromium following a shock load of spent process solution or highly contaminated rinse water discharged during weekend tank clean-out activities.

The Total Cr in "C" generally exceeded the 50 mg/l total metals constraint, but after dilution with (comparatively) chromium free factory effluent, Total Cr concentration in tank farm discharge (E) averaged 22 mg/l (excluding Sat. sample) with no detectable Cr(VI).

Cr(VI) would appear to have been effectively reduced, but there was significant retention of Cr(III) in solution; it is the dilution effect which reduced the net concentration value. Neutralisation and precipitation of chromium hydroxide ($Cr(OH)_3$) may have been ineffective as a consequence of inadequate lime addition and too low a pH. The pH of settler feed (B) ranged between 5.2 and 8.2 for most of the monitoring period (Table I1) yet, to be effective, $Cr(OH)_3$ precipitation requires a pH in the range 8.5 - 11 (UNEP, 1992). The addition of caustic lye (NaOH) as a back-up to lime slurry, in the latter part of the week, raised the pH to 11. This should have improved precipitation; certainly a low level of Total Cr was analysed in "C". However NaOH induced precipitation is associated with poor settling characteristics as NaOH lacks the natural crystalline structure of lime which itself provides attachment points for floc formation. The visible clarity of "B" and "C" on Friday indicated absence of floc formation. The UNEP (1992) guide also warns against unnecessarily high pH which may interfere with formation of a good settleable sludge, and recommends a pH only slightly above minimum. This would also minimise unnecessary chemical consumption (see also Appendix F: section 3.3).

Previous site experience reportedly has already demonstrated to company operators the beneficial effect on metal precipitation and flocculation of the addition of phosphate-containing effluent to this neutralisation stage. This is due to lower solubility of metal phosphates compared with metal hydroxides. Leachability is therefore also reduced, thereby reducing potential environmental impacts of metal sludges in landfill sites.

The apparent increase in metals concentration and conductivity, and the lower pH between "B" and "C" (Table I1) suggest that treated effluent becomes re-contaminated to some extent before discharge to sewer - probably by residue from a poorer quality effluent which had previously passed through the pipework between the settler and the tank farm.

Delivery of factory effluent (D) was erratic, with estimated delivery rates between 20 and 50 l/min. This effluent is the primary source of iron (Fe) and zinc (Zn) contamination as a result of discharge of effluent from the phosphating plant. In general, without an inline flow measuring instrument, the variable and inconsistent delivery of influent streams made it impossible to determine normal or average throughput for the ETP. Feed flows have been estimated where possible from the plant water balance.

Factory effluent (D) undergoes no treatment but may contain chromium, a high proportion of which can be Cr(VI). This has been shown by the analytical results for Saturday 3rd July (8.3 mg/l Cr(VI) - a weekend discharge) and for Thursday 8th July (2.5 mg/l) (Table I1). The source of this chromium may have been alkaline rinse waters discharged during weekend tank cleaning in the CPP, and discharged midweek as indicated by increased water meter readings for these tanks between Tuesday afternoon and Wednesday afternoon (see Table I5). This deduction is supported by the lower than normal levels of Fe and Zn which characterise factory effluent derived largely from the phosphating plant.

It should be appreciated that there are also other potential sources of chromium contamination. For example, chromium may be contained in some of the phosphate plant chemicals, although this could not be confirmed from the chemical suppliers as the formulations are proprietary. Furthermore, contamination of water in manufacturing stages downstream of the CPP may occur as a consequence of carry-over of chromium residue on work pieces.

Net heavy metals concentration (based on Fe, Cr and Zn) in the discharge to sewer (E) during the monitoring period ranged from 3.5 (Wednesday overnight) to 228 (Sunday over-night) with a day-time average of about 40 mg/l (Table I1). This demonstrates an extreme variation in treatment load which was (and is) required of the ETP and/or ineffective performance in the ETP.

One difficulty has been poor control of treatment chemical addition which has relied on manual operation. The PLC was operated during Thursday night and Friday while concentrated chromium waste solution was processed through the ETP. Regrettably monitoring could not be continued beyond Friday to investigate performance, with these conditions of operation, of the ETP by tracking effluent quality at specific treatment stages. However one early indicator of improved performance relates to apparent reduced consumption of treatment chemicals (see Appendix J). In the period between Thursday evening and Friday evening the estimated consumption of hydrochloric acid (HCl) and sodium metabisulphite ($Na_2S_2O_5$), in excess of stoichiometric requirements, was significantly lower than during the monitoring period prior to operation of the PLC. This demonstrates the value of PLC control in avoiding wastage of excess chemical, apart from other benefits such as reduced need for process supervision by an operator.

Sumps S1 (chromium) and S4 (emergency) were shown to contain about 1400 mg/l and 1700 mg/l respectively, of which 85-90 % was Cr(VI) (see Table I2). This was similar in quality to chemical rinse and water rinse effluent which would have been discharged to these sumps from the CPP. There would appear to have been only a limited extent of reduction of Cr(VI) in S4 during hold-up in the sump. pH was not measured, but, based on typical pH results measured during the CPP monitoring programme, these effluent streams generally would have been too acidic for effective reduction by the chemical rinse reagent, sodium hydrosulphite (see Appendix F: section 3.2).

Analyses of rinse water samples taken midweek showed comparatively low concentrations of chromium, i.e. relatively clean conditions, ranging from 58 mg/l in the cold rinse bath of Line 1 to 318 mg/l in the hot rinse bath of Line 2 (see Table I3). Contamination of the hot rinse water baths was higher than that of the cold rinse water baths in both the plating lines. The water meter readings recorded during this week (see Table I5) showed that water flow rates used in the cold rinse water baths were approximately ten times the flow rates which had been used during the June 1993 monitoring programme in the CPP (see Appendix H, Tables H11a&b; H14a&b; H16a&b). Likewise these lower chromium concentrations were approximately ten times diluted compared with those of the samples taken during the CPP monitoring programme.

Chromium concentration in influent (A) increased during Friday (see Table I1) due to addition of concentrated effluent from S4, estimated to have contributed 11% of total chromium containing influent flow during Friday (see Appendix J). The monitoring period was too short to take account of periodic dumping of spent process solutions from the CPP and from other process areas in the facility.

During Friday it was noted that the delivery rate of chromium contaminated influent appeared to be too high, hydraulically, resulting in carry-over of "yellow" Cr(VI) solution into the neutralisation tanks. Kinetically the reduction reaction is effectively instantaneous given sufficient quantities of sodium metabisulphite and correct pH conditions of 2-3. Hence constraints to Cr(VI) reduction are rate of addition of chemical reagents and mixing efficiency in the reaction tank. At too high a delivery rate of chromium influent (A) it may not have been possible to effect correct pH adjustment or to add enough sodium metabisulphite. There may also have been short-circuiting of flow out of the tank with limited reduction.

APPENDIX I:

RESULTS OF MONITORING PROGRAMME: EFFLUENT TREATMENT PLANT

JULY 1993

PART B: MONITORING AND ANALYTICAL RESULTS

TABLE I1: Analyses Of Samples From The Effluent Treatment Plant (July 1993)

Stream		Sat.	Sun.	Mon.	Tues.	Wed.	Thurs.	Fri.	average	maximum	minimum
Sample no.		42		D1A	D2A	D3A1/2	D4A	D5A			
chrome influent	Fe mg/l	27.8		4.4	4.6	2.3	2.7	9.0	4.6	9.0	2.3
	Total Cr mg/l	1525.0		291.0	214.0	91.4	261.0	374.0	246.3	374.0	91.4
	Zn mg/l	6.17		0.84	0.92	0.23	1.50	1.43	0.98	1.50	0.23
A	Cr6+ mg/l	1368.9		228.2	159.5	52.8	212.2	299.9	190.5	299.9	52.8
	pH	3.20		5.04	6.88	6.09		3.82	5.46		
	conduct. mS/cm	3.01		0.73	0.81	0.48		0.96	0.74		
Sample no.				D1B	D2B	D3B1/2	D4B	D5B			
settler feed	Fe mg/l			2.2	0.6	4.1	0.1	3.5	2.1	4.1	0.1
	Total Cr mg/l			95.1	15.5	165.5	0.2	91.0	73.5	165.5	0.2
	Zn mg/l			0.92	0.21	0.88	0.00	0.96	0.59	0.96	0.00
B	Cr6+ mg/l			nd	nd	nd	nd	nd			
	pH			8.22	7.76	5.19		11.04	8.05		
	conduct. mS/cm			3.40	2.28	1.90		4.54	3.03		
Sample no.		43		D1C	D2C	D3C1/2	D4C1/2	D5C			
treated chrome effluent	Fe mg/l	2.4		1.8	0.8	1.7	0.8	0.5	1.1	1.8	0.5
	Total Cr mg/l	16.2		143.0	39.7	104.5	46.6	3.4	67.4	143.0	3.4
	Zn mg/l	6.09		3.53	1.41	1.84	0.96	0.67	1.68	3.53	0.67
C	Cr6+ mg/l	2.3		nd	nd	nd	nd	nd			
	pH			4.93	6.78	no measure		10.75	7.49		
	conduct. mS/cm			4.39	2.49	no measure		3.51	3.46		
Sample no.		44		D1D	D2D	D3D1/2	D4D	D5D			
factory effluent	Fe mg/l	1.4		2.9	32.8	20.4	1.4	3.3	12.2	32.8	1.4
	Total Cr mg/l	11.8		2.3	4.9	6.7	3.5	3.9	4.3	6.7	2.3
	Zn mg/l	4.69		10.85	17.70	17.00	8.05	17.65	14.25	17.70	8.05
D	Cr6+ mg/l	8.3		nd	nd	nd	2.5	nd			
	pH	10.50		7.62	7.33	8.83		8.20	7.99		
	conduct. mS/cm	1.05		0.48	0.64	0.70		0.76	0.65		

BLE I1: Analyses Of Samples From The Effluent Treatment Plant (July 1993)

Stream		Sat.	Sun.	Mon.	Tues.	Wed.	Thurs.	Fri.	average	maximum	minimum
mple no.		45/46		D1E	D2E	D3E1/2/3	D4E	D5E			
k farm	Fe mg/l	0.25		1.9	11.4	15.8	0.8	9.3	7.8	15.8	0.8
charge	Total Cr mg/l	41.4		48.4	12.9	18.7	4.7	24.0	21.7	48.4	4.7
	Zn mg/l	9.56		12.60	7.30	14.42	0.44	10.25	9.00	14.42	0.44
E	Cr6+ mg/l	0.5		nd	nd	nd	1.3	nd			
	pH	10.70		6.63	7.43	6.82		9.05	7.48		
	conduct. mS/cm	3.05		2.26	1.24	1.46		1.87	1.71		
mple no.			N0E1	N1E1	N2E1	N3E1					
N composite	Fe mg/l		12.1	1.8	15.7	0.7	no sample	no sample	3.6	15.7	0.0
	Total Cr mg/l		145.0	14.8	14.6	2.2			7.9	14.8	0.0
	Zn mg/l		70.40	3.33	7.80	0.55			2.92	7.80	0.00
E	Cr6+ mg/l				0.2						
	pH		7.25	6.91							
	conduct. mS/cm		1.57	1.44							
mple no.				D1F	D2F1/2/3						
terpress	Fe mg/l			4.7	1.0/0.95	no sample	no sample	no sample	0.9	4.7	0.0
trate/	Total Cr mg/l			124.0	44.7/41.7				62.0	124.0	0.0
wer discharge	Zn mg/l			1.59	1.97/2.07				0.80	1.59	0.00
F	Cr6+ mg/l				nd/0.3						
	pH			7.18	-/6.59						
	conduct. mS/cm			6.45	-/4.26						

BLE I2:Analyses Of Sump Samples: 03-Jul-93

mps	S1	S2	S3	S4
mple no.	51	52	53	54
mg/l	24.7	19.2	9.9	8.0
r mg/l	1380.0	3.0	72.9	1705.0
mg/l	5.26	1.98	8.06	5.15
r6+ mg/l	1234.0	not detect.	40.0	1454.8

TABLE I3: Analyses Of Chrome Plating Plant Rinse Water Samples: 07-Jul-93

Rinses:	line 1/cold	line 1/hot	line 2/cold	line 2/hot
Sample no.	47	48	49	50
Fe mg/l	1.3	1.3	1.3	1.6
Cr mg/l	58.0	127.0	137.0	318.0
Zn mg/l	not analysed			
Cr6+ mg/l	48.5	112.8	103.0	293.2

Table I4: Tank Level Changes During ETP Monitoring Week

chemical	tank	Day/time	Sunday	Monday	Tuesday	Wednesday	Thursday	Friday	Total	Total
	height (cm)	vol (l)/cm	pm	16.00	16.45	16.15	17.25	pm	usage (cm)	usage l
Na2S2O5	184	16.7	full	-28 cm	-46.5 cm	-75 cm	-111.5 cm	- 20 cm (i)	204	3406.8
HCl	184	16.7	full	-34 cm	-48.5 cm	-77.5 cm	- 20 cm (i)	-46 cm	230	3841
flocculant (ii)	168	14	n/a (iii)	-61/-85	-12/-12 (i)	-12/-12	-74/-75	n/a (iii)	both tanks: (v)	
flocculant (ii)		14	n/a (iii)	-69/-10 (i)	-12/-44	-112.5/-125	-75.5/-79.5	n/a (iii)	790	11060
lime (iv)	180	22.7								

notes:

(i) tanks refilled

(ii) measurements shown for morning/evening time

(iii) not measured

(iv) no measurable change as tank is filled continuously via ball level valve

(v) 3 day period

Table I5: Rinse Water Use During ETP Monitoring Week

stream/tank	Day:	Monday		Tuesday		Wednesday		Thursday		Friday		usage
	Time:		14.00	9.00	17.30	10.05	15.45	9.05	16.50	9.05	16.15	(l)
Line 1	alk.rinse 1st	no reading	71,166	71,166	71,166	71,297	71,675	72,011	72,011	72,012	72,012	846
	alk.rinse 2nd	taken	1,036,864	1,038,779	1,042,751	1,044,771	1,046,299	1,048,119	1,050,120	1,050,121	1,050,816	13,952
	cold rinse		405,699	406,281	408,159	409,737	411,696	412,329	414,543	414,543	416,395	10,696
	hot rinse		32,425	32,466	32,466	32,466	32,466	32,520	32,520	32,520	32,531	106
Line 2	alk.rinse 1st		71,699	71,699	71,699	71,899	72,411	72,866	72,866	72,866	72,866	1,167
	alk.rinse 2nd		1,072,004	1,073,046	1,076,870	1,079,030	1,081,054	1,083,537	1,086,350	1,088,032	1,090,303	18,299
	cold rinse		283,255	283,627	285,419	286,911	288,663	289,357	291,747	294,905	296,733	13,478
	hot rinse		19,389	19,389	19,389	19,389	19,389	19,389	19,389	19,389	19,389	0

Total Flows (l)		Daily average (l/day)	
alkaline rinse water	34,264	8,566	
cold rinse water	24,174	6,044	
hot rinse water	106	27	
total (l)	58,544	14,636	
estimate for 4 weeks	409,808		(an overestimate as w/e water use is lower)

APPENDIX J
DERIVATION OF MATERIAL BALANCES: METAL FINISHING CASE STUDY

1. BASIC ASSUMPTIONS:-

- 46 week production per annum
- normally 9 hours operation per day and 5 days operation per week for most activities, with exception of the chrome plating plant (CPP) and effluent treatment plant (ETP):
- 6 days per week for CPP
- 7 days per week for ETP

2. DETERMINING INPUTS

2.1 Chromium Chemicals

Estimates for ***chromium IN*** have been based on:

i) process control records of chromium chemical addition during the period of the monitoring programmes, and
ii) inventory records of the most recent purchases for a period of at least one year.

LINE 1:

i) approx. 300 kg per (30 day) month of CrO_3 (156 kg of Cr(VI)) giving an estimate of approx. 3,220 kg p.a. (322 days) of CrO_3, of which 1,674 kg is Cr;
ii) approx. 11,480 kg p.a. from inventory records.

LINE 2:

i) approx. 600 kg per (30 day) month of CrO_3 (312 kg Cr(VI)) giving an estimate of approx. 6,440 kg p.a. (322 days) of CrO_3, of which 3,349 kg is Cr(VI);
ii) approx. 6,540 kg p.a. from inventory records.

2.2 Production Throughput

Production throughput, in terms of plated area, for the period 4 June till 25 June (i.e. 22 days) has been estimated from the summation of surface area for different work-pieces recorded by CPP operating staff as having been processed during this time. Details of different work-piece dimensions (and chrome thickness) were obtained from engineering drawings or from information supplied by production staff. Separate estimates were made for the two plating lines, and totals ratioed by 28/22 to yield an estimate for a 4 week period.

<u>LINE 1</u>: 1,185 m <u>LINE 2</u>: 887 m^2 <u>OVERALL</u>: 2,072 m^2

2.3 Effluent Treatment Chemicals

Estimated chemical usage is based on:

- approximate tank capacities calculated from measured dimensions
- reported batch chemical make-up quantities
- tank level changes recorded during the ETP monitoring programme
- treatment loads as determined from the analytical results of the ETP monitoring programme

Tank & chemical make-up details

Tank	Approximate Height (cm)	Approximate Diameter(cm)	Approximate Capacity (l)	Vol./Level Change (l/cm)		Chemical Conc. (kg/l)
Sod.met.	184	146	3080	16.7	(i)	0.01623
HCL	184	146	3080	16.7	(ii)	0.37
Lime	180	170	4086	22.7	(iii)	
Flocculant	168	134	2352	14.0	(iv)	

<u>notes</u>:(i) 50 kg bag per tank

(ii) 32% w/w of HCL, solution density 1.156 g/ml

(iii) approximately 30 kg added to tank per day, but the lime concentration is continuously diluted by the addition of top-up water through a float ball valve

(iv) 1 litre of flocculant added per tank

Results of the ETP monitoring programme have been used to determine the apparent utilisation of chemicals (and water) per unit quantity of chromium discharged to the ETP. Two sets of values have been calculated:

i) a weekly average for conditions under which automatic control (PLC) was *not* operative;

ii) the result achieved with PLC *in* operation - based on one day of monitoring only.

The results are summarised in the following tables, for which sample calculations are shown. (Differences in values calculated and those shown in tables are due to rounding errors). Estimated consumption of effluent treatment chemicals during the period of the CPP monitoring programmes was determined based on these parameters (see section 10).

(i) sodium metabisulphite

Period	**Flow** l	**Total Cr. Conc.** mg/l	**Cr(VI) Conc.** mg/l	**Treatment load** g	**Stoichio. require. (iii)** kg	**Estimated Tank Level Change** cm	**Actual Estimated Usage** kg	**Water Usage** l
Mon. pm till Fri. pm (A) (i)	24,280	214 (average: Mon-Thurs)	163	3,962	10.8	without PLC		
Thurs. pm till Fri. pm (S4) (ii)	821	1,705	1,455	1,195	3.3			
overall:	25,101	246	191	5,157	14.1	204	55.43	3,415
per kg Cr(VI)					2.73		10.75	662
Thurs. pm till Fri. pm (A) (i)	6,849	261	212	1,452	4.0	with PLC		
Thurs. pm till Fri. pm (S4) (ii)	821	1,705	1,455	1,195	3.3			
overall:	7,670	374	300	2,647	7.2	68	18.48	1,138
per kg Cr(VI)					2.73		6.98	430

notes: (i) A designates the chrome plant rinse water as measured during the monitoring programme - see Appendix I:Part B Tables I5 & I1.

(ii) S4 designates the additional flow from the spare sump containing concentrated chromium as estimated from the chromium balance equation shown below.

(iii) see calculation below

chromium balance: (see Appendix I:Part B Tables I1 - I2)

- average chromium influent concentration (Mon-Thurs) = 214 mg/l Total Cr
- chromium influent concentration on Fri. = 374 mg/l
- sump "S4" concentration = 1,705 mg/l
- chromium influent for the period Thurs. pm till Fri. pm = 6,849 l

Hence a chromium balance for the period Thurs. pm. till Fri. pm may be given as:
6,849 * 214 + S4 * 1,705 = (6,849 + S4) * 374 mg/l
S4 = 821 l (approximately 11 % of the total chromium influent flow on Fri.)

stoichiometric chemical requirement:

Excluding competing ions e.g. Fe^{3+} and competing reactions with other forms of the chromate ion, the overall reaction as given by Eilbeck & Mattock (1987) (see Appendix F:section 3.1) is:

$$2\ Cr_2O_7^{2-} + 3\ Na_2S_2O_5 + 16\ H^+ \ ==== \ 4\ Cr^{3+} + 6\ NaHSO_4 + 5\ H_2O$$

i.e. 0.92 g S per g Cr(VI), for which 2.73 g $Na_2S_2O_5$ per g Cr(VI) is required
For example 5,157g * 2.73/1,000 = 14.1 kg

estimated water usage:

approximate tank level change * vol./level change
e.g. 204 cm * 16.7 l/cm = 3,407 l in 4 days

estimated chemical usage:

approximate tank level change * vol./level change * chemical concentration
e.g. 3,407 l * 0.01623 kg/l = 55.3 kg

(ii) hydrochloric acid

Period	Flow	Av. pH	Stoichiometric Requirements (iii)		Estimated Tank Level Change	Actual Estimated Usage		Water Usage
	l		l solution	kg HCL	cm	l	kg HCL	l
Mon. pm till (i) Fri. pm (A)	24,280	6.00 (average: Mon-Wed)	37.61	13.91	without PLC			
Thurs. pm till (ii) Fri. pm (S4)	821	3.15	9.26	3.42				
overall:	25,101	5.46	46.86	17.34	230	3,851	1,424	3,027
per kg Cr(VI)				3.36			276	587
Thurs. pm till (i) Fri. pm (A)	6,849				with PLC			
Thurs. pm till (ii) Fri. pm (S4)	821							
overall:	7,670	3.82	2.26	8.26	26	435	161	342
per kg Cr(VI)				3.12			61	129

notes: as per table (i)

stoichiometric chemical requirement:

Acid is consumed in the reaction, as shown above, i.e. 4 moles H^+ consumed per mole Cr(VI) reduced; and is required for pH adjustment. Assuming:

- the ideal theoretical relationship: $pH = -\log [H^+]$, then $[H^+] = 10^{-pH}$ and
- a desired pH of 2.5

then the required addition of H^+ to achieve this pH can be calculated as $10^{-2.5} - 10^{-pH}$, where pH is the influent pH value, with units in moles/litre of H^+.

The HCL solution is 32% w/w, with a density of 1,156 g/l (molar mass of HCL = 36.46)

e.g. for an influent with pH of 6 and containing 3,962 g Cr(VI), the required HCL addition has been calculated as:

$= ((10^{-2.5} - 10^{-6}) * 24{,}280 + 3{,}962/52*4) * 36.46/0.32/1{,}156 = 37.61$ l solution

or by weight: $= 37.61 * 1{,}156 * 0.32/1{,}000 = 13.91$ kg HCL

estimated chemical usage:

approximate tank level change * vol./level change * chemical concentration
e.g. 230 cm * 16.7 l/cm * (1.156 * 0.32) kg/l = 1,421 kg HCL

estimated water usage:

1,421 kg HCL/0.32 * 0.68/1 kg/l = 3,019 l water

(iii) lime

stoichiometric chemical requirement:

Period	Flow	Av. pH	Total Cr	Stoichiometric Requirements	
	l		g	kg $Ca(OH)_2$	l water
Mon. pm till (i) Fri. pm (A)	24,280	7.06 (average: Mon-Wed)	5,204	2.10	18.89
Thurs. pm till (ii) Fri. pm (S4)	821	not known	1,400		
overall:	25,101	8.05	6,604	25.0	225
per kg Total Cr				3.78	34.0

notes: as per table (i)

Lime is required both for reaction and for neutralisation. Precipitation requirement is assumed to be represented by :
$2Cr^{3+} + 3Ca(OH)_2 ==== 2Cr(OH)_3 + 3Ca^{2+}$.

Neutralisation requirements have been estimated by assuming the ideal relationship H = - log [H^+] such that [H^+] = 10^{-pH} measured in moles per litre. Hence assuming an initial pH of 2.5 and a required pH of 10, the stoichiometric requirement for $Ca(OH)_2$ has been calculated as:

= $((10^{-2.5} - 10^{-10})$ * flow (l)+ Total Cr (g)/52 (g/gmole)*1.5) *molar mass of $Ca(OH)_2$/1,000 = [kg]
= $((10^{-2.5} - 10^{-10})$ * 25,101+6,604/52*1.5) * 74/1,000 = 19.97 kg $Ca(OH)_2$

Assuming an efficiency of 80%[1], the requirement is 19.97/0.8 = 25.0 kg

This represents a minimum chemical requirement, under optimum conditions, of 3.78 kg per kg Total Cr. Actual chemical usage is unknown.

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[1] Eilbeck & Mattock (1987) report inefficiencies of 15-25%

water requirement:

Assuming a 10% w/w as maximum lime solution concentration, make-up water requirements would be: 25.0 * 90/10 = 225 l water.
Actual water usage is unknown, but is likely to be higher and the lime solution of variable dilution as lime is added to the slurry tank only once per day, while water is added continuously through a float-operated valve.

(iv) <u>flocculant</u>

water requirement:

The estimated tank level change (total for 2 tanks) was 790 cm between Monday pm and Thurs. pm i.e. 3 days On the basis of approx. 14 l/cm, estimated usage is:- 790 * 14 =11,060 l in 3 days.
Hence estimate for 4-week period, given by 11,060/3 * 28/1,000 = 103 kL.

estimated chemical usage:

1 l per tank * 103,000/2,300 = 45 l in a 4-week period

3. RECORDING WATER USAGE

3.1 Effluent Account Records

Information on total plant water consumption was obtained from local municipal records of the metered water account for quarterly periods during the four years, 1989-1992:

Average quarterly consumption during 1989 - 1992 = 7,980 kL

1st & 2nd quarter consumption in 1993 given as 6,860 and 6, 850 kL

Based on total metered water of 6,850, average water use in 28 days = 6,850/90 * 28 = 2,131 kL

60.8% attributed to effluent flow = 1,296 kL

39.3% attributed to domestic use and evaporative loss = 835 kL

3.2 Site Assessment

Estimates made of plant water uses are summarised in Table J1, with accompanying notes on methods and/or assumptions which have been used to make these estimates.

(i) CPP rinse water

Estimate based on results for the period 4 June '93 (evening) till 25 June '93 (evening) i.e. 21 days; total ratioed by 28/21. (see Appendix H:Part B Tables H11a&b, H14a&b & H16a&b). Equivalent conditions for September 1992 and the week in July 1993 during which the ETP monitoring programme was conducted are compared in the table below.

Tank	Sept. 1992		June 1993		July 1993	
	usage per 4 weeks	av.daily flow (l/day)	usage per 4 weeks	av. daily flow (l/day)	usage per 4 weeks	average flow (l/day)
alkaline rinse-1st	none, with current operation	counter flow in	65,737	2,804	14,091	503
2nd	116,711	6,040	203,628	8,770	225,757	8,063
cold chrome rinse	67,084	3,523	18,353	409	169,218	6,044
hot final rinse	5,295	39	2,648	10	742	27
TOTAL:(l) per 4 weeks	189,090	-	290,366	-	409,808	-

TABLE J1: Summary Of Estimated Water Balance For 4-Week period: June 1993

Process/Function	Estimated water usage (kL per 4 weeks)	Comment
Chrome plating:		
- rinsing	290.4	see (i) above
- chemical make-up	65.8	see (ii) below
- drag-out	19.2	see (iii) below
- evaporative/entrainment	80.1	see (iv) below
- cleaning	not known	specific water intake = 455.5/2,072 = 0.220 m^3/m^2
sub-total	455.5	43 %
Phosphating:		
- rinsing	281.3	based on average recorded usage April till June 1993
- chemical make-up	40	
- cleaning	not known	according to scheduled make-up
sub-total	321.3	30 %
Pyrocleaning:		
- rinsing	77.2	based on average recorded usage April till June 1993
Derusting:		
- rinsing	not known	
- chemical make-up	0.6	based on reported disposal schedule
- cleaning	not known	
Scrubbing tower:		estimate based on weekly discharge and refill of basin contents
- basin refill (closed circulation)	3.4	
Cooling tower:		
- overflow	42	estimates provided by production staff
- evaporation	5.6	
Mercedes Phosphating:		
- rinsing	not known	
- chemical make-up	assumed negligible	infrequent change of process solution
- cleaning	not known	
Effluent treatment plant:		
- sodium metabisulphite	29.0	from estimates made in sections 2.3 & 11.
- acid	25.7	
- flocculant	103.0	
- lime-	1.7	
sub-total	159.4	15 %
TOTAL (ii)	1.065 kL	

(ii) CPP chemical and rinse water batch make-up

Water usage for chemical make-up has been estimated on the basis of given tank capacities and scheduled process solution discharge and replenishment activities - summarised as follows:

Tank	Capacity (l) (i)	Discharge/repl. Frequency
soak cleaning A	1,650	fortnightly - alternative lines
electrolytic cleaning B	3,200	fortnightly - alternative lines
alkaline rinse (ii) C	1,650 *2	weekly - both lines
chemical rinse D	1,650	fortnightly - alternative lines
cold rinse E	1,650	weekly - both lines
hot rinse F	1,650	weekly - both lines
TOTAL (l) per 4 weeks	65,800 (iii)	

notes: (i) from file records and personal communication with company personnel

(ii) 2 tanks in counter-current arrangement

(iii) calculated as: (A+B+D) *2 + (C+E+F) * 4 * 2

(iii) drag-out (D/O)

Drag-out losses have been estimated on the basis of changes in total chromium concentration in the cold- and hot rinse water tanks. These are "running rinse" tanks with metered water flows. It is assumed that the tank contents are homogenous[2] in concentration and thus the same as the waste rinse water which is discharged to the ETP.

$$D/O = \frac{\{\underset{\text{in rinse tank}}{\text{change in Cr}} * \text{tank volume} + \underset{\text{in rinse tank}}{\text{av. Cr.}} * \text{rinse volume}\}/\text{no.of days}}{\text{av. Cr. in chemical rinse tank}}$$

$$= \frac{[mg/l] *[l] + [mg/l] * [l]\}/[days]}{[mg/l]} = [l/day]$$

tank volume = 1,650 l no. of days = 2 (for weekends) or 5 for weeks

Results of calculations for each line using both 1993 and 1992 data are shown in the tables following.

---

[2] As a result of incomplete mixing, D/O from rinse tanks can be substantially higher resulting in greater contamination of downstream tanks (Eilbeck & Mattock, 1987).

1993 RESULTS:

LINE 1

Period	D/O to cold rinse av. l/day	D/O to hot rinse av. l/day
wk 2	-22.5	35.0
w/e	14.4	24.0
wk 3	287.0	203.1
w/e	6.3	49.5
wk 4	40.5	142.9
per m^2 plated	490 - 5,150 ml/m^2	640 - 3,860 ml/m^2

LINE 2

D/O to cold rinse av. l/day	D/O to hot rinse av. l/day
288.57	202.9
53.35	0
-67.65	65.1
21.21	100.6
58.44	43.7
2,215- 7,390 l/m^2	1,160 - 10,500 l/m^2

1992 RESULTS for LINE 2

Period	D/O to cold rinse l/day	D/O to hot rinse l/day
wk 1	268.6	614.0
wk 2	301.2	533.9
wk 3	665.4	147.3

production throughput unknown

Negative values suggest that tank contents have been diluted, possibly by partial draining and refilling of tanks using water from an unmetered source. 1992 D/O results are considered to be more realistic. For the purposes of this assessment the following D/O values have been used:

- approximately 400 l/day from plating to rinsing and as carry-over from the final rinse (per line).

On this basis net D/O losses of water from the CPP are estimated to be:
(400 l * 2) l/day* 6 days/week * 4 weeks = 19,200 l per 4 weeks

(iv) <u>evaporative & entrainment losses</u>

Simple evaporative losses have been estimated by assuming an air flow rate through each tank, with air saturated at bath solution temperatures. The air flow rate was assumed to be the blower capacity of 4.6 m^3 /min at 300 mBar pressure differential, distributed equally to each of 9 tanks per plating line i.e. 18 tanks. The pressure differential at the inlet to each tank was assumed to be equivalent to a 1 m head of water of density 1,000 kg/m^3 i.e. approx. 0.1 barG. Hence air flow = 4.6 * 1,000/18 * 1.3/1.1 = 302 l/min per tank @ 273 ^{o} C

Summary of Results

Tank	Bath Temp. °C	Air Flow kg/min	Humidity (i) kg H_2O/kg air	Evap. Loss l H_2O/hr
soak cleaner	40	0.34	0.04911	1.00
electrolytic cleaner	55	0.32	0.1116	2.17
alkaline rinse	20	0.36	0.01475	0.32
etching (ii)		none		
plating (ii)		none		
service tank (ii)	55	0.32	0.1116	2.17
drag-out (ii)	25	0.36	0.01948	0.42
chemical rinse	20	0.36	0.01475	0.32
cold rinse	20	0.36	0.01475	0.32
hot rinse	40	0.34	0.04911	1.00
TOTAL (l/day): both lines				139
TOTAL (l/4 weeks)				3,336

notes: (i) Humidity data taken from Perry 5th ed. Table 12.1

(ii) greater losses caused by gas evolution (H_2 & O_2) and entrainment as chromic mist. See below.

Evaporative/entrainment losses from the plating system has been estimated from 1992 results:

- to dilute 260 g/l (from the plating tank, Line 2) to 70 g/l in the D/O recovery tank[3] requires 3.7 l water per l D/O; assume 4 l/l.
- if D/O is 400 l/day per line, water make-up = 400*4 = 1,600 l/day per line, and 3,200 l/day both lines.

  Then 3,200 * 6 days/week * 4 weeks = 76,800 l per 4 weeks

  TOTAL losses to atmosphere = 76.8 + 3.3 = 80.1 kL per 4 weeks

---

[3] Although D/O effects are expected in general to have increased due to the altered jig design, the greater loss of chromium solution from the plating tank should be compensated by greater addition of make-up water to maintain tank levels - hence it is deemed reasonable to assume the 1992 chromium value for the D/O solution.

Excluded from total estimated usage is:-

- water used for washing and laboratory purpose as well as plant cleaning which, typically, is the cause of much wasteful water use
- unmetered water addition to rinse tanks in the CPP
- spray rinse water which is jetted onto work-pieces as they are withdrawn from the cold rinse tank. This has been neglected on the basis that it is a comparatively negligible flow. Such rinses are reported to use between one-eighth and one-fourth the volume of water used by a dip rinse (EPA, 1992) on a continuous operating basis. Infrequent use is made of spray rinsing at this facility.
- domestic water use

Based on the quantified estimates given in Table J1, apparent resolution of water balance is: 1,065/2,131 * 100 = 50 %

4. DETERMINING ENERGY USAGE

Energy sources used in the plant include:-

- electrical power for the operation of electrically driven equipment and, most significantly, for electroplating.
- heavy fuel oil in the burner; and
- welding gases.

Energy usage may be investigated and optimised, if possible, in the interests of energy conservation. This is also a responsibility for pollution control and waste minimisation. However, given the focus on hazardous wastes generated by this facility, no attempt has been made to evaluate an energy balance for the plant.

5. MEASURING CURRENT LEVELS OF WASTE REUSE/RECYCLING

No wastes are reused or recycled at this facility.

6. QUANTIFYING PROCESS OUTPUTS

Chromium related outputs have been quantified from plating records, results of the monitoring programmes and estimated waste quantities based on reported literature parameters. Material flows of interest were plated chromium, chemical losses in process solutions, rinse effluent and drag-out from the final hot rinse water tank, sludge losses, evaporative losses and sludge and filtercake produced in the ETP.

6.1 Plated Chromium

An estimate of ***plated chromium*** has been made on the basis of estimated plated area (see 2.2) and specified chrome thickness given on engineering drawings.

Cr deposited/rod [g] = (Cr. thickness * plated area)* Cr. density
Total Cr deposited expressed as g/m^2 total plated area:

<u>LINE 1</u>: 84.0 g/m^2	<u>LINE 2</u>: 63.7 g/m^2	<u>OVERALL</u>: 75.3 g/m^2
(1,185 m^2)	(887 m^2)	(2,072 m^2)

6.2 Spent Process Solutions

The following tables summarise estimated chemical losses of chromium during the period 7 June till 25 June i.e. 19 days

LINE 1

Tank	Solution Volume Per Tank l	Initial Cr.Conc. mg/l	Final Cr. Conc. mg/l	Cr. Loss To Tank g
soak cleaner (ii)	1,650	40.1	233	318
electrol. cleaner (ii)	3,200	41.6	1,460	4,539
chemical rinse (iii)	1,650	1,240	5,590	7,178
Total Cr (g)	(i)			12,035

LINE 2

Initial Cr.Conc. mg/l	Final Cr. Conc. mg/l	Cr. Loss To Tank g
147	415	442
250	1,340	3,488
19.7	4930	8,102
		12,032

<u>notes</u>: (i) summation of each tank's change in Cr concentration * tank capacity of 1,650 l or 3,200 l (electrolytic tank)

(ii) discharged to sewer without treatment

(iii) discharged to Cr(VI) reduction treatment

6.3 Rinse Water Effluent

LINE 1

Tank	Rinse Water (i)		Batch Accumulation in Tank (ii)	
	Water (l)	Cr Loss (g)	Water (l)	Net Cr Loss (g)
alkaline rinse (2 tanks) (iii)	98,775	458		6.27
cold rinse (iv)	11,765	5,654	13,253	-11.6
hot rinse (iv)	441	158		804
Total				

LINE 2

Rinse Water (i)		Batch Accumulation in Tank (ii)	
Water (l)	Cr Loss (g)	(l)	Net Cr Loss (g)
91,779	917		-10.9
512	397	512	1,868
	-		1,053

notes: (i) calculated as the summation of av. weekly Cr concentration * weekly water flow

(ii) calculated as the difference in Cr concentration measured on 7 & 25 June, * tank capacity of 1,650 l. Partial or complete discharge and replenishment of tank contents during this period has been neglected.

(iii) discharged to sewer without treatment

(iv) discharged to Cr(VI) reduction treatment

Hence **Total Cr losses** = 35,360 g in spent solutions and rinse effluents for the 19 day period 7 - 25 June 1993. Estimate for 4-week period = 52,109 g.

6.4 Total and Hexavalent Chromium Discharge To ETP

The estimated discharge is based on a summation of approximate rinse water loadings and chromium content in tank solutions discharged during month-end cleaning[4]. Continuous rinse water discharge has been estimated by assuming a weekly average chromium concentration. Month-end discharge is based on a chromium concentration the same as that of the last day of production prior to tank cleaning or a specific sample analysis result. Results for the period 4 June till 25 June, i.e. 22 days, are summarised in the following tables:

---

[4] Weekly discharge of some or all of rinse water from rinse tanks has been neglected as it is thought that this was not done during the monitoring programme.

LINE 1			*LINE 2*		*TOTAL*	
Period	**Discharge to sewer g Cr(VI)**	**Total Rinse volume l**	**Discharge to sewer g Cr(VI)**	**Total Rinse volume l**	**Total Cr(VI) Discharge**	**Total Cr Discharge**
w/e	1,028	3,033		0	see below	
wk 2	14	103	0	0		
w/e	14	65	0	0		
wk 3	5,020	10,785	272	406		
w/e	32	70	0	0		
wk 4	566	1,183	76	106		
rinses	6,674 g Cr(VI) 7,015 g Total Cr	15,239 l	348 g Cr(VI) 397 g Total Cr	512 l	7,022 g in 15,752 l av.:446 mg/l	7,412 g in 15,752 l av.:471 mg/l
w/e discharge	(5/6 Jun.) 14,857 g Cr(VI) 17,276 g Total Cr	4,950 l	(26/27 Jun.) 9,697g Cr(VI) 11,484 g Total Cr	4,950 l	5/6 Jun.: 3,000 mg/l 26/27 Jun.: 1,959 mg/l	3,490 mg/l 2,320 mg/l

6.5 Untreated Total Chromium Discharge To Tank Farm

Similar calculations were carried out for the alkaline rinse water and caustic cleaner solutions which are not treated for Cr(VI) reduction.

LINE 1			*LINE 2*		*TOTAL*
Period	**Discharge to sewer g Total Cr**	**Total Rinse volume l**	**Discharge to sewer g Total Cr**	**Total Rinse volume l**	**Total Cr Discharge**
w/e	28	8,210	33	3,260	
wk 2	86	39,179	251	28,735	
w/e	46	7,900	34	5,484	
wk 3	192	20,575	293	30,861	
w/e	47	3,136	43	447	
wk 4	119	27.985	340	26.252	
rinses	519 g Total Cr	106,985 l	995 g Total Cr	95,039 l	1,514 g in 202,024 l av.:7.49 mg/l
w/e discharge	(5/6 Jun.) 5,017 g Total Cr	8,150 l	(26/27 Jun.) 5,048 g Total Cr	8,150 l	5/6 Jun.: 616 mg/l 26/27 Jun.: 619 mg/l

6.6 Drag-Out From Hot Rinse:

Assuming 400 l/day D/O and an average chromium concentration of 423 mg/l, estimated chemical loss = 400 *2 * 6 days/week * 4 weeks * 423/10^6 = 8.12 kg Cr

6.7 Evaporative/entrainment Losses

Entrainment losses from the extraction system were not assessed given that company monitoring with Drager tubes reportedly has measured no detectable chromic acid in the emissions from the scrubber system. (Condensate from the demister and scrubber solution is returned to the drag-out tank of Line 1.) However this operation requires more rigorous assessment. The concentration of chromic acid in the scrubbing liquor which is circulated from the D/O tank is likely to be too high for effective scrubbing action.

6.8 Chromium Losses In Sludge

potential ***sludge losses*** inclusive of:

(i) **electrolyte losses in filtration of plating solution**:

Koziorowski & Kucharshi (1972) indicate an approximate loss of 0.05 - 0.06 l/m^2 surface area. On this basis, estimated loss is:
0.06 * 2,072 = 124.3 l, containing 220 - 260 g/l chromic acid
i.e. 124.3 * 260/1,000 *0.52 = 16.8 kg Cr per 4 week period

(ii) **contaminated sludge in soak cleaner tank.**

Based on:
- sludge analyses of 300 mg/l Total Cr content in 100 ml digestant
- sludge sample weight of 9.9 g
- approximate sludge density of 1.45 kg/l
- approximate sludge volume of 2 X 1.2 X 0.3 = 0.72 m^3 per tank

Estimated sludge Cr content = 300 * 0.1/9.9 *720 *2 *1.45/1,000 = 6.32 kg in one 4 week period (both tanks)

6.9 Sludge Production In Chemical Treatment

Using Figure J1, with an average chromium concentration of 470 mg/l and volume of rinse water = 15, 752/22 * 28 = 20,048 l in 4 weeks, estimated sludge volume @ 26 % = 5.2 m^3 of 3% w/w sludge generated from treatment of rinse effluents with lime neutralisation.

By extrapolation, it may be estimated that treatment of two batch discharges totalling 9,900 l in 4 weeks, with an average total chromium concentration of 2,905 mg/l, would generate approximately 13 m^3 of sludge (131% volume of sludge per volume of effluent).

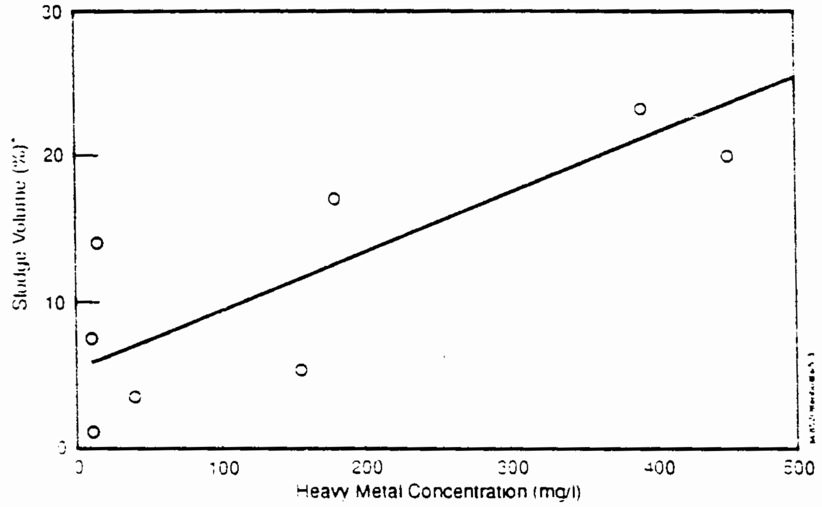

FIGURE J1[5]: Sludge Volume Generation (EPA, 1992)

* i.e. volume of sludge per volume of effluent

It has not been possible to estimate filtercake production. Only a small and occasional portion of treated effluent is dewatered in the filterpress. This flow quantity was not recorded, and details of the design capacity and operating cycles of the filterpress are not known. On the basis of a filtercake quality of 30-35% solids content, use of the filterpress would reduce sludge volume by up to approximately 90 %.

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[5] This graph indicates that treatment of a more concentrated waste stream produces a more concentrated sludge i.e. less sludge volume

7. ACCOUNTING FOR WASTE WATER

Quarterly flows and characteristics of effluent discharged to sewer over the four year period, 1989-1992, are reported in records of the local municipality. Based on the water and effluent account for the 2nd quarter in 1993, the chargeable effluent flow was 1,296 kL (see 3.1). Table J1 shows an estimated effluent flow of 1065-80.1-5.6-19 = 960 kL, equivalent to 74 % of accounted flow.

The shortfall may be partly accounted for by effluent generated by washing and laboratory functions; discharges from the filtration plant; plant cleaning, which, typically uses significant water quantities generating equivalent quantities of effluent; and occasional, non-scheduled discharges of rinse water from the rinse tanks in the CPP.

It should be noted that with the current accounting system, the true volume of discharged effluent is unknown. Costs are being paid twice-over for water:-

i) as part of the effluent volume
ii) as part of the sludge volume removed for disposal

8. ACCOUNTING FOR GASEOUS EMISSIONS

Gaseous emissions may be released as volatile organics from painting and solvent cleaning, acid mists from chrome plating and hydrocarbon combustion gases from the heavy fuel oil burner. Only those emissions required for chromium and water balances in the CPP, i.e. entrainment and evaporative losses, have been considered (see 3.2(iv) and 6.7). Actual chromium losses from the scrubbing system have not been evaluated.

9. ACCOUNTING FOR OFF-SITE WASTES

Quantities of certain process waste removed from site for off-site disposal have been estimated based on reported parameters for sludge production (see 6.8), dumping schedules for spent process solutions (see Table J1) and disposal certificates.

Existing disposal records indicate annual disposal of 2,000 - 3,000 m^3 waste sludges. This far exceeds what would be expected based on above estimates. It is presumed that this recorded quantity reflects a combined total for sludges generated throughout the plant, including sludges from tanks in the CPP and from other process operations.

Other recorded disposals are:

- approximately 20 kL/month of chromic acid
- approximately 0.6 kL/month of derusting acidic effluent
- approximately 6 kL/month oily effluent
- periodic quantities of grinding oil; filtercake; phosphoric acid

Other solid waste includes empty containers, office waste, scrap metal and chemical residues. No attempt has been made to quantify these wastes. Scrap metal is stored on site until removed by a scrap merchant for reprocessing, and company records could be used to quantify this. Estimates of packaging waste could be made from the chemical inventory, or alternatively from accounting records for costs paid for collection and disposal by a waste contractor. Packaging waste generally is not returned to suppliers.

10. ASSEMBLING INPUT AND OUTPUT INFORMATION

Only those material flows of water, chromium, process chemicals and effluent treatment chemicals which are processed in the CPP and the ETP have been compiled.

11. DERIVING A PRELIMINARY MATERIAL BALANCE

Given the batch nature of operations and variability in production throughput and process conditions, it has not been possible to correlate exact inputs and outputs for the periods of the monitoring programmes. Nor is it possible to resolve material balances on a per annum basis. For the purposes of this assessment, approximate balances and/or consumption figures for chromium, water, process chemicals and effluent treatment chemicals have been derived based on the results of the monitoring programmes and the material balance calculations and estimates shown in the preceding sections. These have been compiled as spreadsheets, with separate chromium balances for each of the two plating lines to take account of differences in processing efficiencies (due to use of different chromium chemicals, operating conditions and work-piece characteristics). The spreadsheets are shown as Figures J2, J3 and J4.

Assumptions:

1. Chemical addition is as per process descriptions. (Actual addition is known to have been higher, but no records are kept).

2. The discharge and refill of all rinse water tanks is undertaken weekly. (In practise this was not done).

3. Addition of chromic acid to the etch tank and sulphuric acid to the etch and plating tanks has been excluded; these quantities are not expected to be significant; records are not kept.

4. Total monthly batch quantities are computed as 1.5* the quantities/line as the two plating lines are "serviced" at staggered fortnightly intervals.

5. For the purpose of computing mass of chromium in batch-discharged effluent streams, average concentrations have been calculated for each week. The total estimated discharge of chromium in the total rinse flows and in D/O has been calculated using a weighted average chromium concentration for the 4-week period.

6. Consumption of treatment chemicals in the ETP is based on the estimated usage per kg Cr(VI) or Total Cr determined in 2.3.

7. Estimated generation of waste treatment sludges uses a linear equation derived for the relationship shown in Figure J1:
   i.e. sludge vol. % = 0.0432 * heavy metal conc. + 5.68

8. An estimate for zinc (Zn) concentration in factory effluent has been included to represent *total metals* other than Cr so as to identify the impact on Zn (metals)

concentration in the final effluent of reductions in volume of effluent from the CPP. The estimate for Zn in the final effluent is based on the average of reported *total metals,* excluding Cr, in the effluent account records, for the period 1989 - 1991, i.e. 25 mg/l.

The prorata concentration of Zn in factory effluent, prior to dilution with effluent from chromium reduction in the ETP, has been calculated as:
(25 * 4,852/90 *28)/(673.3 + 74.3) = 50 mg/l
where 4,852 kL is the average assumed quarterly effluent flow during 1989 - 1992 (see 3.1) and where 673.3 kL and 74.3 kL are estimated volumes of effluent contributing to the "other" effluents (not treated in chromium reduction).

9. Implicit to the mass balances is the accuracy of the records of chromic acid addition and of production throughput, from which the plated area and chromium quantity have been estimated.

NOTE: assumptions 2 & 5 differ from those implicit in the preceding computations. The effect of these is to increase the estimated water use and chromium discharge to the ETP, thereby apparently improving these balances slightly. Calculated volumes of waste treatment sludge are also slightly different due to differences in the estimated chromium concentrations in effluent discharged to the ETP.

overall chromium balance:	252/437 * 100 = 58 %
% treated effluent:	51/(51 + 444 + 305) * 100 = 6.4 %
dilution effect of Cr:	approximately 60 % reduction, based on (51 + 305)/956 = 0.37
dilution effect of zinc:	approximately 70 % reduction, based on 321/956 = 0.33

TANK	soak cleaner		electro. cleaner		countercurrent rinse			plating system (iii)		D/O	chemical rinse		cold rinse		hot rinse	
TANK No.	1		2		3	4		5		6	7		8		9	
tank volume (l)	1650		3200		1650	1650				1650	1650		1650		1650	
chemical	cleaner (i)		cleaner (i)		none	none		chromic	sulphu	none	reduction (i)		none		none	
STREAM IN g/l	50		100					240	1-1.25		30					
chemical kg/4 wks	100		300					280	n/a	none	50					
rinse water l/week	n/a		n/a					n/a	n/a		n/a					
wk 1					9396	26265							4418		662	
wk 2					15525	31864							1488		1648	
wk 3					8544	19931							10659		191	
wk 4					4120	27001							1106		147	
TOTAL WATER (kL/4 wks)	1.65		3.20		-	155.85		evap make-up		49.7	1.65		24.27		9.25	
WASTE OUT - analyses	Total Cr	Cr(vi)	Total Cr	Cr(vi)		Total Cr	Cr(vi)				Total Cr	Cr(vi)	Total Cr	Cr(vi)	Total Cr	Cr(vi)
wk 1 - average mg/l	222	66	1450	n/a		3.4	2.1						2815	2262	312	259
wk 2 - average mg/l	80	19	428	n/a		2.2	1.3						595	563	179	167
wk 3 - average mg/l	153	41	777	n/a		9.4	7.7						479	443	356	337
wk 4 - average mg/l	233	71	1460	n/a		3.1	4.3						500	475	550	534
discharge mg/l	233	71	1460	131	wgt. av.	4.5	3.9				5621	5590	1097	936	349	324
effluent rate - batch (kl/4 wks) (ii)	1.65		3.20			13.20					1.65		6.60		6.60	
chrome content (g/4 wks)	384	117	4,672	420		60	51				9,275	9,224	7,242	6,176	2,305	2,140
effluent rate - rinse (kl/4 wks)						142.65							17.67		2.65	
chrome content (g/4 wks)						590	490						18,980	16,078	650	590
TOTAL OUT - per 4 wks																
evaporation - kL										40.1						
drag-out - kL															9.60	
drag-out - g Cr															3,353	
effluent kL	1.65		3.20			155.85					1.65		24.27		9.25	
chrome - g	384		4,672			649					9,275		26,222		2,955	
sludge - g															11,500	

Product Out:	
plated area (m2)	1185
plated mass (g/m2)	84.0
plated mass (kg)	100

Chromium Balance:

IN	OUT	% error
kg Cr	kg Cr	
146	159	-8.9

FIGURE J2 Water And Chemical Flows And Chromium Balance In Plating Line 1: Chrome Plating Plant

TANK	soak		electro.		countercurrent		plating system	D/O	chemical		cold rinse		hot rinse	
	cleaner		cleaner		rinse		(iii)		rinse					
TANK No.	1		2		3	4	5	6	7		8		9	
tank volume (l)	1650		3200		1650	1650		1650	1650		1650		1650	
chemical	cleaner (i)		cleaner (i)		none	none	chromic sulphu	none	reduction (i)		none		none	
STREAM IN g/l	50		100				260 1-1.25		30					
chemical kg/4 wks	100		300				560	none	50					
rinse water l/week	n/a		n/a				n/a	n/a	n/a					
wk 1					7038	24642					171		0	
wk 2					2134	29861					0		0	
wk 3					15362	20983					406		0	
wk 4					3618	23081					106		0	
TOTAL WATER (kL/4 wks)	1.65		3.20		-	139.92	evap.make-up	49.7	1.65		7.28		6.60	
WASTE OUT - analyses	Total Cr	Cr(vi)	Total Cr	Cr(vi)	Total Cr	Cr(vi)			Total Cr	Cr(vi)	Total Cr	Cr(vi)	Total Cr	Cr(vi)
wk 1 - average mg/l	118	42	251	128	10.2	7.3					277	301	94	91.5
wk 2 - average mg/l	190	142	253	101	8.3	6.6					557	530	231	199
wk 3 - average mg/l	228	184	430	74	8.2	7.9					760	669	445	443
wk 4 - average mg/l	415	238	1340	211	9.8	11.4					830	719	625	597
discharge mg/l	415	238	1340	287	wgt. av. 9.1	8.3			4930	4103	606	555	349	333
effluent rate - batch (kl/4 wks) (ii)	1.65		3.20		13.20				1.65		6.60		6.60	
chrome content (g/4 wks)	685	393	4,288	918	120	110			8,135	6,770	4,000	3,661	2,302	2,195
effluent rate - rinse (kl/4 wks)					126.72						0.68		0.00	
chrome content (g/4 wks)					1,148	1,034					444	399	0	0
TOTAL OUT - per 4 wks														
evaporation - kL								40.1						
drag-out - kL													9.60	
drag-out - g Cr													3,348	
effluent kL	1.65		3.20		139.92				1.65		7.28		6.60	
chrome - g	685		4,288		1,269				8,135		4,443		2,302	
sludge - g													11,500	

Product Out:	
plated area (m2)	887
plated mass (g/m2)	63.7
plated mass (kg)	57

Chromium Balance:

IN	OUT	% error
kg Cr	kg Cr	
291	92	68.2

FIGURE J3 Water And Chemical Flows And Chromium Balance In Plating Line 2: Chrome Plating Plant

STREAM	Chrome reduction						Other wastes				TOTALS
	chrome rinses			batch discharge			other rinses		other batch discharges		
Chrome Plant	kL effluent	g Total Cr	g Cr(vi)	kL effluent	g Total Cr	g Cr(vi)	kL effluent	g Total Cr	kL effluent	g Total Cr	
soak									2.5	727	
electr.									4.8	6,816	
alk.rinse							269.4	1,738	26.4	180	
chem.rinse				2.5	13,342	12,608					
cold rinse	18.4	19,424	16,477	13.2	11,241	9,837					
hot rinse	2.6	650	590	13.2	4,607	4,335					
Totals	21	20,074	17,067	29	29,190	26,781		1,738		7,723	
Factory											
phosphate							281.3		40.0		
pyroclean.							77.2				
derusting							not known		0.6		
scrubbing							3.4				
cooling							42.0				
Metal conc. mg/l	Cr	956			1,011		Cr	13	Other (Zn)	50	
ETP	kl water		kg chemical	kl water		kg chemical				**Total Chemicals (kg)**	
sodium meta.	11.3		183	17.7		288				sodium meta.	471
HCl	10.0		4,710	15.7		7,392				HCl	12,102
lime	0.7		76	1.0		110				lime	186
flocc.	part of 103		not known	part of 103		not known				flocc.	
Total Effluent	43.0			63.3			673.3		74.3		957
Estimated sludge (kL)	9.9			14.3							24.1

FIGURE J4: Material Flows InThe Effluent Treatment Plant

APPENDIX K
ESTABLISHMENT OF DESIGN BASIS AND ECONOMIC EVALUATION: METAL FINISHING CASE-STUDY

1. CURRENT MATERIAL FLOWS

Table K1 summarises the current material flows as derived in Appendix J. The CPP flows, combined to represent both plating lines, are shown in a schematic of the current configuration given in Figure K1.

TABLE K1: Estimated Water And Effluent Rates For A 4 Week Period In June 1993

Unit Operation		Water kL	Chemical kg	Effluent kL	Chr. g
soak clean		2.5	150	2.5	727
electrolytic clean		4.8	450	4.8	6,816
alkaline	-batch	26.4		26.4	180
rinse	-rinse	269.4		269.4	1,738
plating	- evaporation	80.1		-	-
chemical rinse		2.5	75	2.5	13,342
cold rinse	-batch	13.2		13.2	11,241
	-rinse	18.4		18.4	19,424
hot rinse	-batch	13.2		13.2	4,607
	-rinse	2.6		2.6	650
	-d/o	19.2		-	6,701
SUB-TOTAL		453	675	353	65,426
other factory uses		450		444	not known
ETP:	sod. bis.	29.0	471	29.0	
	HCL	25.7	12,102	25.7	
	lime	1.7	186	1.7	
	flocculant	103	not known	103	
TOTAL		1,065	13,435	957	65,426

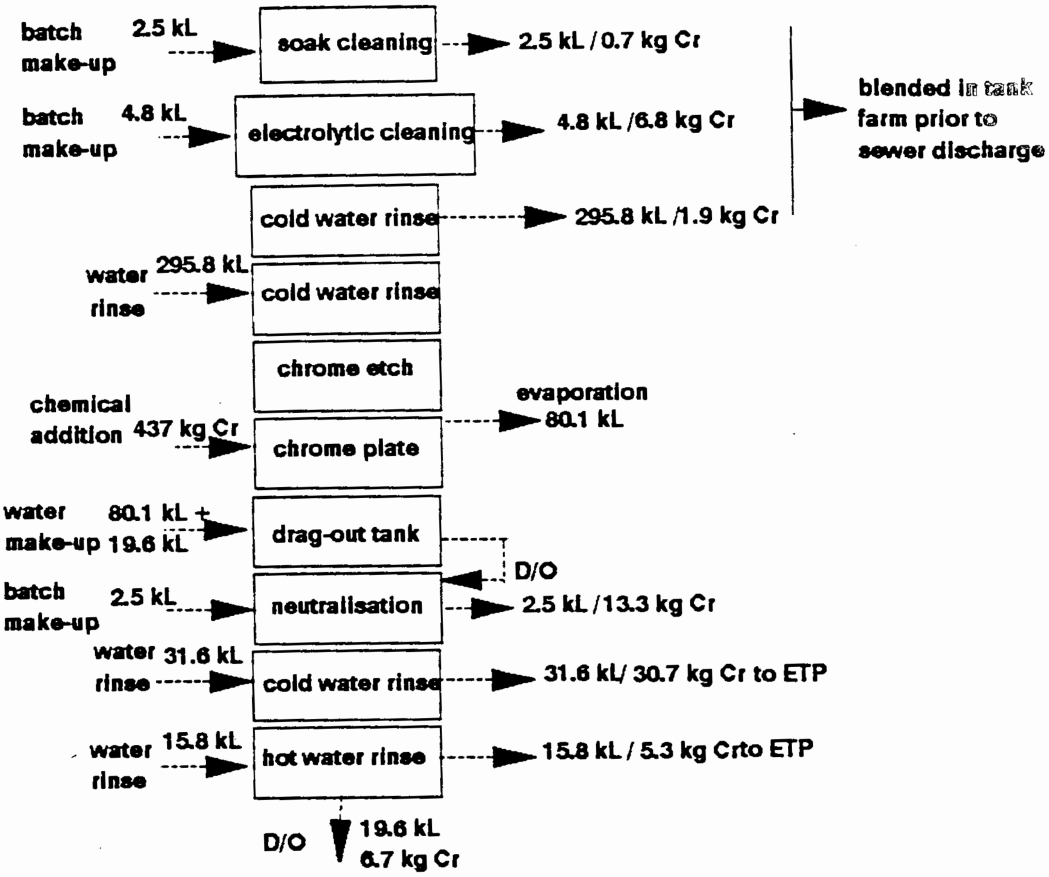

FIGURE K1: Current Process Configuration In The CPP

2. MODIFIED MATERIAL FLOWS

Figure K2 depicts schematically the proposed modified process configuration which employs the principle of reactive rinsing and chromic acid recovery effected by ion exchange technology. Material flows are summarised in Table K2. Again, these flows represent the combination of both plating lines. Modified water and chromium quantities have been derived on the basis that the following various water reduction and chromium recovery measures are implemented.

1. substitution of chemical rinse with cold rinse tank to give two countercurrent cold rinse tanks followed by separate hot rinse tank;
2. with cascade of hot rinse water to cold rinse tanks - new rinse rates estimated as shown:

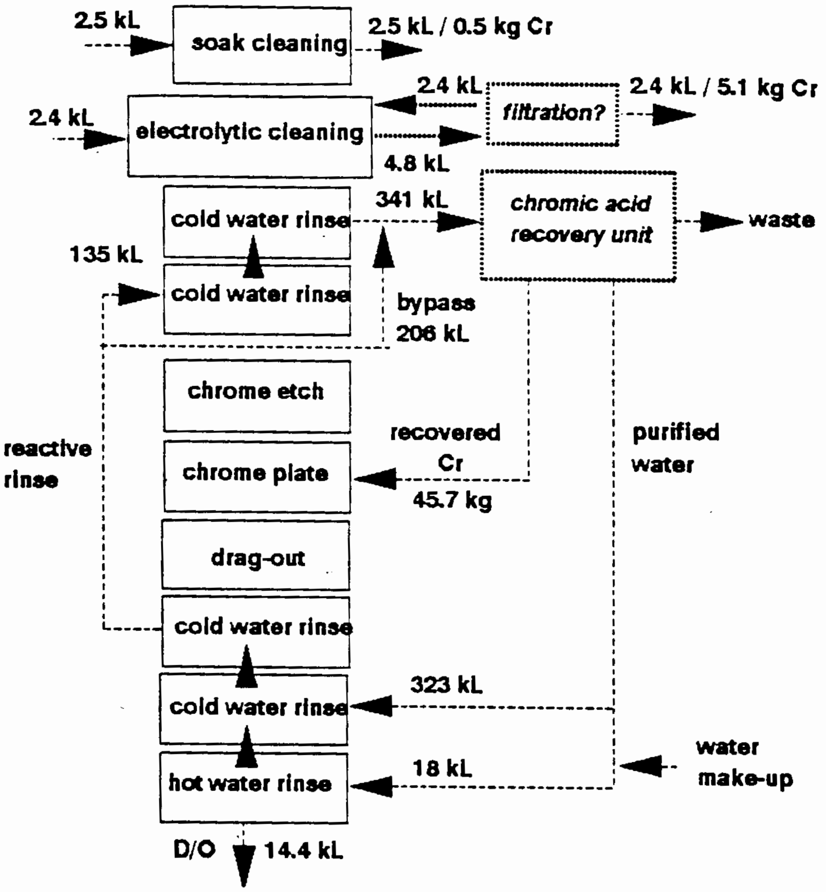

FIGURE K2: Proposed Modified Process Flow For CPP

TABLE K2: Modified Material Flows In The Chrome Plating Plant

Unit Operation (note)			Water kL	Chemical kg	Effluent kL	Treatment	Cr Content g	Water Reuse kL	Cr Rec. g	Discharged Effluent kL
soak clean			2.5	150	2.5		545	0.0		2.5
electro.clean		(5)	2.4	450	2.4	filtration (11)	5,112	0.0		2.4
alkaline	- batch		0.0		0.0	(8)	0	0.0		
rinse	- rinse	(3&6)	(134.7)		incl.below		incl.below	-		
plating	-evap.		80.1							
cold rinse	- batch	(1)	0.0		0.0	(8)		0.0		
cold rinse	-batch		0.0		0.0	(8)		0.0		
	-rinse	(1&2)	(340.8)		340.8	CRU (12)	46,134	340.8	45,672	
hot rinse	-batch		0.0		0.0			0		
	- rinse	(2)	(18.0)		incl.above		incl.above	-		
	- d/o	(4)	14.7				1,444			
SUB-TOTAL			99	600	-		53,231	340.8	45,672	4.9

Calculation of new rinse rates:

Assumptions:

- Total Cr concentration from D/O tank = 70 g/l
- minimum acceptable rinse water quality = 100 mg/l Total Cr
- drag-out rate of 300 l/day

Hence required rinse water rate given by: $D * [C_{in}/C_{out}]^{1/n}$

where D = volumetric rate of drag-out set = 300 l/day

C_{in} = concentration of drag-out from plating system set = 70 g/l

C_{out} = concentration in rinse tank set = 125 mg/l & 100 mg/l

(let cold rinse water quality = 125 mg/l to be reduced to 100 mg/l in hot rinse tank)

n = no. of rinse tanks set = 2 & 1

On this basis, cold rinse rate = $300 * [70 * 1{,}000/125]^{1/2}$ = 7,100 l/day per line and hot rinse rate = 300 * [125/100] = 375 l/day per line hot water

Flow per 4 weeks (both lines) = 7,100/1,000 * 2 * 6 days/week * 4 weeks = 340.8 kL cold water and similarly for hot water, = 18.0 kL

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3. a combination of water management, process control and reduced D/O of caustic cleaner chemicals could conceivably reduce alkaline rinse water by 50% - similar to flow rates of 1992;
4. D/O reduced from 400 to 300 l/day per line;
5. recycling of electrolytic cleaner solution with filtration assumed to reduce water usage by 50%;
6. direct recycle of a portion of cold rinse effluent to the alkaline rinse tanks (reactive rinsing);
7. CRU recycles purified water and chromium for process reuse.

Assumptions:

8. no need for discharge and refill of rinse tanks;
9. there is no cyanide in the chemicals or any other source of cyanide which can react with acid;
10. effluent from both plating lines can be treated together and recovered chromium can be reused in either plating line i.e. chemicals and processing conditions in both plating lines are compatible;

11. filtration is able to remove metal contaminants from solution;
12. IX treatment of chromium containing effluents yields 100% water recovery and 99% chromium recovery as chromic acid

3. DESIGN BASIS FOR CHROMIC ACID RECOVERY SYSTEM

The proposed chromic acid recovery system is illustrated in Figure K3.

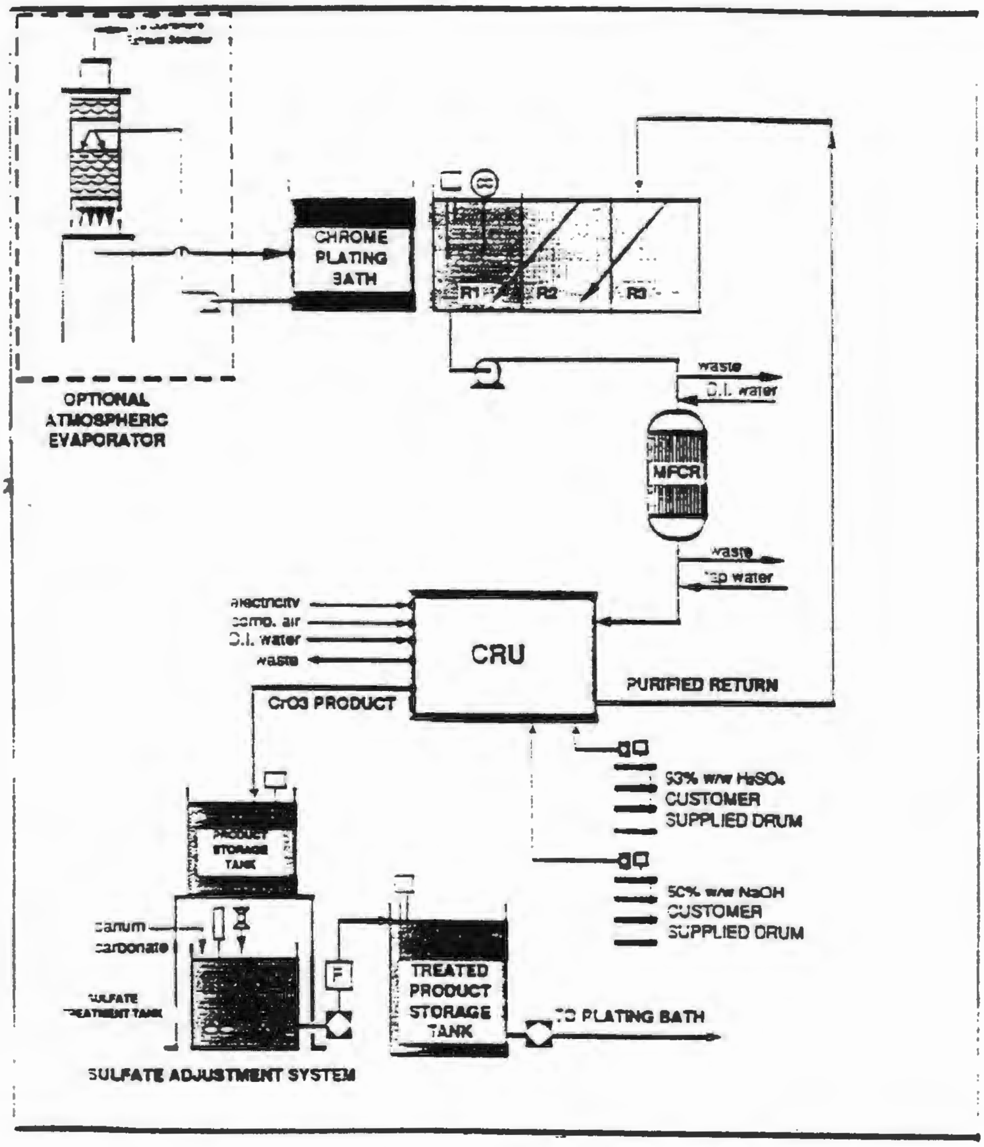

FIGURE K3: Chromic Acid Recovery Process Schematic

Design parameters:

Feed - normal:	14.2 m^3/day of effluent
Composition:	260 mg/l (CrO_3) i.e. 135 mg/l Cr
Contamination:	5 mg/l Fe 1 mg/l Zn
Requirements:	removal of cation contamination regeneration of chromic acid recovery of purified water

Equipment requirements:

- ion exchange units: 2X cation, and 1X anion
- feed buffer tank
- feed filtration
- intermediate storage tanks for treated water, recovered chromic acid, regenerating chemical and waste regenerate
- transfer pumps
- pipework and instrumentation
- all associated process controls

4. COST ESTIMATE

Budget capital cost for packaged plant received from UK supplier

Capital

Item	Budget Cost	Comment
Total Purchased Cost:	R 485,000	assumes an exchange rate of 5:1
surcharge @ 5%	R 24,250	
vat @ 14%	R 71,295	
freight costs	-	neglected
modifications to existing pipework and installation	R 72750	assumes 15% of capital
contingency	R 72750	assumes 15% of capital
TOTAL CAPITAL	R 726,045	

Operating Costs

Item	Unit costs (i)	Unit consumption (ii)	Comment
maintenance			assume no increased requirements
utilities -backwash water		524 l/kg Cr	use portion of treated rinse water or mains water when required - assume no overall increase
labour			assume no increased requirements
process chemicals:			
H2SO4 acid 93% w/w	R2.22/kg	8 kg/kg Cr	R 820 per 4-weeks
NaOH 50 % w/w	R2.58/kg solid	12 kg/kg Cr	R 715 per 4-weeks
barium carbonate	R3.95/kg	0.08 kg/kg Cr	R 15 per 4-weeks
treatment/disposal:			
spent ix resin	not known	approx. 1ft^3 p.a.	see Assumption 3 below
waste stream		100 l/kL treated rinse water, containing 7.5 g/l Na_2SO_4 & 45 mg/l CrO_3	dilution in factory effluent will reduce SO_4 & Cr concentrations to below discharge constraints - assume no increased costs
BaSO4/CrO3 slurry		unknown	see Assumption 3 below
TOTAL			R 17,825 p.a.

notes (i) Chemical costs for regenerant chemicals received from local supplier

(ii) performance parameters derived from Leatherdale & Dejak (1991)

Cost savings

Table K3 illustrates costs associated with current and modified flows, based on the following assumptions:

Assumptions:

1. Water supply and effluent charges are based on current rates for 1993 -1994 as shown in Table 4.2 of Chapter 4.
2. Chemical costs are based on the recorded purchase price at the time the chemical inventory was reviewed (in 1992), inflated by 10%.
3. Savings in sludge and filtercake disposal costs will be attenuated by disposal costs for IX resin and $BaSO_4/CrO_3$ slurry

TABLE K3: Current Processing Costs and Potential Cost Savings

COMPONENT	unit cost		Current Conditions			Modified Conditions	
			consumption per 4 weeks	total cost (R)	cost/m^2 (R)	consumption per 4 weeks	total cost (R)
Chrome Plating Plant							
plated area m^2			2072			2072	
chemicals:							
soak cleaner	6.35	R/kg	150	952.05	0.46	150	952.05
electro.cleaner	6.49	R/kg	450	2,920.50	1.41	450	2,920.50
X200 catalyst	16.06	R/kg	not known	9,702.00	4.68	not known	
X200	34.65	R/kg	280			251	depends on choice of chemical - see below
repl.salt	24.09	R/kg	not known			not known	
repl. solu.	64.90	R/kg	560	36,344.00	17.54	501	depends on choice of chemical - see below
chromic flakes	11.66	R/kg	not known			not known	
chromic acid	11.66	R/kg	not known			not known	
sulphuric acid	5.98	R/l	not known			not known	
sodium hydro.	11.33	R/kg	75	850	0.55	0	0.00
water:	1.40	R/kL					
make-up			65.8	92.12	0.04	4.9	6.83
rinse			290.4	406.51	0.20	0	0.00
evap. + D/O			99.3	139.02	0.07	94.5	132.30
ETP							
chemicals:							
sodium meta.	1.85	R/kg	471	871.08	0.42	0	0.00
HCL	1.05	R/kg	12,102	12,646.55	6.10	0	0.00
lime	0.85	R/kg	186	194.60	0.09	0	0.00
flocculant	not known						
water:			159.4	223.22	0.11	0	0.00
Effluent volume			957			449	
COD		mg/l	602			602	
heavy metals		mg/l	101			84	
conveyance cost	0.3417	R/kL		326.96			156.51
treatment cost	0.6015	R/kL		416.53	0.20		199.38
surcharge				95.92	0.05		27.55
TOTAL COST	(using X200)			66,464.06	32.08		30,450.51
SAVINGS	(per 4 wks)						36,014
SAVINGS	p.a.						414,156
TOTAL COST	(repl. solu.)			66,464.06	32.08		53,203.60
SAVINGS	(per 4 wks)						13,260
SAVINGS	p.a.						152,495
savings in water							722
savings in treat.chemical							14,845
savings in CrO3 as X200							19,983
savings in CrO3 as repl. solu.							- 2,770
savings in sewer costs							463

(estimate for current disposal cost: 24 kL of 3% w/w slurry @ R23.50 per 2kL (Cape Town City Council cost) = R 282 per 4-weeks or R3,242 p.a.)

Economic parameter

pay back = capital / (savings - operating costs)

Alternative chromic acid chemical:

a) X200: = 726,000/(414,200 -18,000) = 1.8 years

b) repl. solu. = 726,000/(152,500 -18,000) = 5.4 years