



UNIVERSITY OF KWAZULU-NATAL

**CHEMICAL MONITORING AND WASTE
MINIMISATION AUDIT IN THE
ELECTROPLATING INDUSTRY**

By

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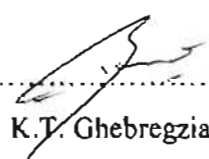
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ABSTRACT

Theoretical waste minimisation opportunities and options for electroplating were sought from the literature. Their suitability under the specific site conditions of a chromium electroplating plant were evaluated using the results of a waste minimisation audit (audit). The audit showed that many waste minimisation practices were already in place. These included counter current flowing rinse systems, multiple use of rinses and recycling of the drag-out solution back into the plating solution. Two types of information were collected during the audit, namely new chemical monitoring (concentration levels of sodium, iron, zinc, copper, lead, chromium and nickel and conductivity, total dissolved solids and pH) and flow rate data and existing data (composition of the process solutions, products and waste outputs, and raw materials, workpieces and utility inputs). The data were analysed using four established waste minimisation techniques. The Scoping Audit and the Water Economy Assessment results were determined using empirically derived models while the Mass Balancing and the True Cost of Waste results were obtained through more detailed calculations. The results of the audit showed that the three most important areas for waste minimisation were water usage, effluent from rinse water waste streams and nickel consumption. Water usage has the highest waste minimisation potential followed by nickel. Draggd-out process chemicals and rinse water consumption contribute to ranking the effluent stream the most important waste minimisation opportunity identified by the True Cost of Waste Analysis. Potential financial savings were roughly estimated to be in the order of R19949 and R126603 for water and nickel respectively. Intervention using only "low cost-no-cost" waste minimisation measures was recommended as a first step before contemplating further focus areas or technical or economical feasibility studies.

DECLARATION

I hereby certify that this research is the result of my own investigation which has not already been accepted in substance for any degree and is not being submitted in candidature for any other degree.

Signed.....

K.T. Ghebregziabher (BSc)

We hereby certify that this statement is correct.

Signed.....

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June 2004

DEDICATION

This study is dedicated to my father Tesfamariam Ghebregziabher, my mother

Silas Weldetinsae, my brothers and sisters.

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LIST OF ABBREVIATION

BT	Bottom tank
> DL	Above detection limit
< DL	Below detection limit
E	Evaporation
EC	Electrical conductivity
EDTA	Ethylenediaminetetraacetic acid
HEDP	1-hydroxyethylenediamine-1,1-diphosphoric acid
HEEDTA	Hydroxyethylenediaminetriacetic acid
HEEF	High energy efficiency formulations
ICP-OES	Inductively coupled plasma optical emission spectrophotometer
IE	Ion exchange
MDCPL	Manual decorative chromium plating line
MF	Micro-filtration
MSDS	Material safety data sheets
NM	Not measured
NTA	Nitilotriacetic acid
PVC	Polyvinyl chloride
RO	Reverse osmosis
SME's	Small and medium scale enterprises
SREP	Standard reduction electrode potential
SRHS	Self regulating high speed
ST	Surface tank
TDS	Total dissolved solids
UV	Ultraviolet

LIST OF UNITS OF MEASUREMENTS

A/dm²	ampere/ square decimeter
°Bé	degree Baumé
°C	degree Centigrade
C/mol	Coulomb/mole
cm	centimeter
g/L	gram/litre
J/Kmol	Joule/degree Kelvin mole
kHz	kiloHertz
kPa	kiloPascal
kW	kiloWatt
L/min	litre/minute
M	molarity
m³/hr	cubic meter/hour
MHz	megaHertz
ML	megalitre
mL	millilitre
mm	millimeter
mol/L	mole/litre
nm	nanometer
rpm	revolution per minute
V	Volt
μm	micrometer
μS/cm	microSiemen/centimeter
μg/L	microgram/litre

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CHAPTER 1

INTRODUCTION TO THE ELECTROPLATING PROCESS

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INTRODUCTION TO THE ELECTROPLATING PROCESS

Electroplating is a process of coating a conducting surface with a metal using electrolysis.^{1, 2, 3} The metal referred to in this definition is a thin 10^{-5} - 10^{-1} mm layer (coating or plate) which is deposited on the surface of the object (workpiece, substrate or base metal item) which is undergoing electroplating.⁴ The workpiece can be made of metal throughout or merely have a conducting outer surface. Special coating techniques, using a metallic loaded paint or silver reduced spray, can be utilised to make non-conducting surfaces, such as plastic and glass, electrically conductive for electroplating.⁵ The electrolysis reaction involved in plating takes place at the surface of the workpiece which is made the cathode in an electrolytic cell. Electricity is used to reduce metal ions, usually from the solution, onto the workpieces.

There are three main reasons for electroplating: for decoration, to slow or prevent chemical corrosion and for functional purposes.^{6, 7, 8, 9} Electroplating is therefore used to change the properties of the surface of a workpiece, for example its strength, resistance to abrasion, chemical resistance, size, hardness, solderability, electrical conductivity and reflectivity.¹⁰

The process has been used successfully in coating objects of many different sizes, shapes and composition. These include solid objects such as jewellery, screws, nuts and bolts, wire products such as shelving, grilles and baskets and sheet (steel) objects such as shelving, car bumpers and hubcaps.

A literature survey was carried out to characterise the electroplating process in terms of the chemicals, equipment, operating conditions and the electrochemical principles used in the industry. The results are presented and discussed in this chapter from the point of view of waste minimisation. Section 1.1 outlines the chemical and electrochemical stages found in electroplating. In Section 1.2 and 1.3, some of these stages are discussed in greater depth. The manual (jigs, barrel and basket), mechanised (jigs and barrels) and automatic (mainly barrels) means by which the workpieces are contained and moved down the electroplating line and other equipment (tanks, cathodes, anodes and power supply) will be discussed in the context of

how the (electro)chemical demands of industrial electroplating can be characterised using a waste minimisation approach. Section 1.4 looks at how these issues affect chromium plating specifically.

1.1 BREAKDOWN OF THE ELECTROPLATING PROCESS

A typical electroplating process is made up of three surface treatment stages namely pre-treatment (cleaning and activation of the workpiece surface), the metal deposition (plating) step and the post-treatment (passivation, neutralisation and/or sealing) of the plate (see Figure 1.1). These can be chemical (degreasing, cleaning, pickling, etching, coating and electroless plating) or electrochemical (plating, electrocleaning, electropolishing and anodising) processes.^{11, 12} Electroplating uses a number of hazardous inorganic such as cyanides and chromates and to a lesser extent organic chemicals such as halogenated hydrocarbons in these cleaning, metal deposition and passivation steps. These chemicals are used in aqueous solutions, usually contained in a dip tank. They are commonly called process solutions.¹² The workpieces are immersed (dipped) in the process solutions one after the other, starting with the cleaning solution (usually alkaline then acid), then the plating solution and finally the passivation solution. The cleaning solutions remove grease, oils, metal oxides and scales which have accumulated on the surface during the manufacturing process or from rusting. Depending on its end purpose, a strike may be applied to the workpiece after acid cleaning but before final plating. A strike is a solution used to quickly produce an initial thin layer of plate which completely covers the workpiece. This has been found to improve the adhesion of the subsequent plates and the quality of the final plate.¹³ Typical examples include a copper strike followed by a nickel layer on zinc based die-castings before chromium plating, a nickel strike or a copper strike followed by a nickel layer on steel before chromium plating, a cadmium or tin strike on cast iron before zinc plating.^{14, 15} In some plating processes, such as hard chromium plating, strikes are not used and the final plate is deposited directly on the workpiece after acid dipping. After final plating, generally the workpiece is treated with passivating solution to reduce corrosion of the plate and prevent discoloration.¹⁴

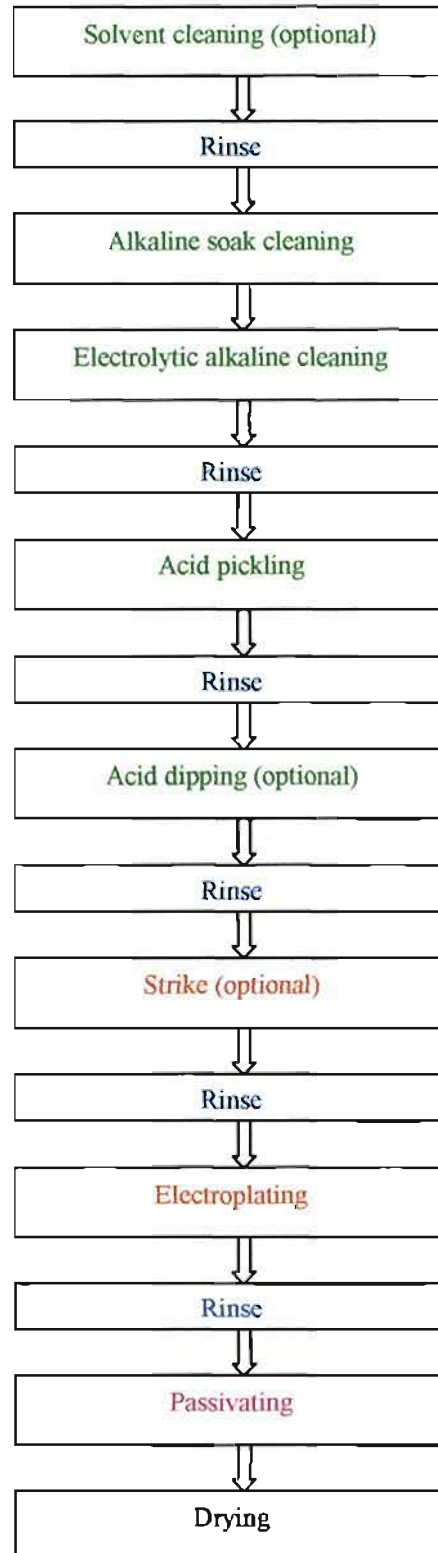


Figure 1.1 Simple process flow diagram of the stages in electroplating operation^{11, 13, 14, 16}

The loss of chemicals from the process solution arises mainly from their consumption in the chemical reactions which make up the surface treatment process. However, process solutions can also be lost from the tank by drag-out. Drag-out occurs when solution is pulled out of a processing tank on the surface of the work being transferred.¹⁵ This happens when the workpieces are manually or automatically moved from one dip tank to another down the electroplating line.

An electroplating line is the layout of the process tank solutions in which one (or more) metal finishing treatment is applied to workpieces.¹¹ It may or may not be in the same order as the dipping sequence used to treat the workpieces. Drag-out has been reported as a significant cause of contamination of one process solution by another.^{12, 14, 17, 18} This can be reduced by having rinse tanks between the process tanks (see Figure 1.1). The rinse water washes the process solution covering the workpiece into the rinse tank where it mixes with the rinse water. This also stops the chemical reactions on the surface associated with the cleaning, electroplating and passivating and limits chemicals coming out of solution and depositing as a stain on the surface.^{18, 19, 20} The drop in chemical content of a process solution can be measured and the appropriate amount added to restore it to its original value. This is known as topping-up.^{14, 21} However when the solution eventually becomes ineffective, through contamination for example, it is termed "spent".¹² The solution is then thrown out (dumped) and replaced with a fresh solution (make-up). Post-treatment solutions are generally replaced more frequently (every few days, weeks or even months) than pre-treatment solution. Well maintained (filtered and/or chemically treated) plating solutions should last for years or decades.³ The chemistry of the process solutions will be discussed in Section 1.3.

There are two basic types of rinsing used in electroplating, namely spray and immersion.^{14, 18} The most common of these is immersion which involves dipping the workpieces in a tank of water. Immersion rinsing leaves a thin liquid film on the surface of the item which has the same concentration as the rinse tank solution. There are a variety of ways in which to carry out immersion rinsing. These include single or multiple static rinsing, single or multiple running rinses and cascade countercurrent rinsing.¹⁸

A static rinse, also called a still recovery or stagnant rinse, is a rinse tank with no water inlet or outlet for continually changing the water used for rinsing.¹⁸ This rinsing system is usually used when a high quality rinse is not required. A static rinse is generally placed directly after the process tanks. The water from this rinse solution is often used to top up the process bath in order to replace the volume lost by drag-out and by evaporation. Static rinses produce the smallest volume of wastewaters but at higher concentrations than found for flowing rinses.¹⁸

A flowing rinse has an inlet and outlet in the tank which allows water to flow into the filled tank from the water supply and exit from the tank into the effluent treatment plant then the sewer. The water is added continuously to wash out the contaminants from the rinse water. The rinse water usually enters from the bottom of the tank and leaves from the top of the opposite side. In a multiple system there are several tanks lined up one after the other. Cascade counter current rinsing has the rinse water moving through a series of tanks as shown in Figure 1.2 below. This water flows in the opposite direction to that in which the workpieces are travelling down the line. This means the water coming out of the last rinse tank (which is the cleanest) is piped into the tank before it on the line and so on down the line. These rinse systems are usually found together with the drag-out (static rinse tank) immediately after the plating tank, after the acid cleaners and after the post-treatment passivation and are named after each process i.e. plating rinse, acid rinse and passivation rinse.

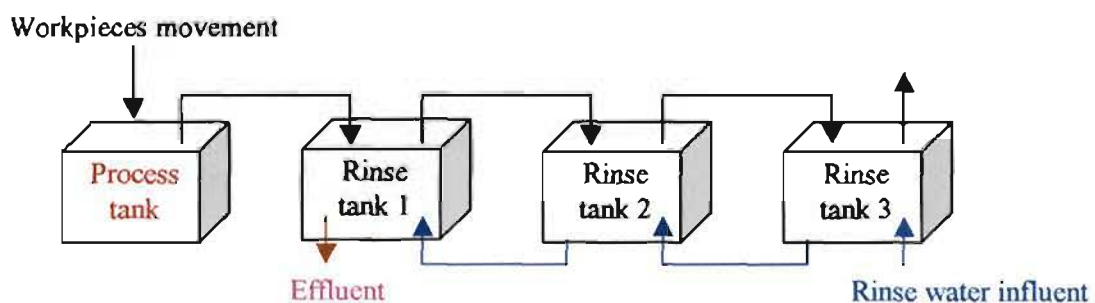


Figure 1.2 Three stage cascading rinse systems^{11, 12}

The quantitative aspects of rinsing pertaining to waste minimisation will be discussed in Section 2.4.2 of Chapter 2.

1.2 CHEMICALS USED IN THE PRE-TREATMENT STAGE

The surface of the workpiece must undergo preparation or pre-treatment before a metallic plate can be successfully applied to it. This is done to remove any contaminants from the surface and, in some cases, to activate the surface for plating or further treatment.^{11, 14, 15}

A number of cleaning methods have been developed in order to remove the contaminants without damaging the workpiece. These include chemical, mechanical and other specialised cleaning methods such as ultrasonic cleaning.²² Chemical cleaning is the most widely used industrially and various preparations have been developed to deal with the range of surface contaminants found on the workpieces. The selection of a suitable cleaning material for chemical cleaning is influenced by the surface to be cleaned (see Section 1.2.2), the dirt or soil to be removed, the degree of cleanliness required (see Section 1.2.4), the methods of application of the cleaning materials, the impact of disposal of the spent (waste) solution on the environment and overall cost of the operation (see Section 6.1 in Chapter 6).^{23, 24}

Contamination of the surface can cause poor adhesion of the plate to the workpiece. This has been observed as bare patches on the workpiece and lifting of the plate away from the surface (forming a bubble or a blister). In extreme cases this has been known to prevent deposition. It also affects the quality of the plate itself. It is well established that poor cleaning causes rough, porous, flaky and patchy coatings.^{3, 14} The main sources of such surface contamination are the manufacturing process and the exposure to the environment. The manufacturing process leaves organics such as oil or grease and inorganics such as mineral dusts and scales on the surface. Exposure to the atmosphere can cause rust and tarnish to form on the surface. These have been termed extrinsic and intrinsic contaminants respectively.⁷

Cleaners can be applied to the surface by immersion (soak or electrolytic) in a chemical bath and by spraying cleaners from nozzles mounted close to the tank lip or on a series of upright pipes or risers in a tunnel. Spray and electrolytic methods have been shown to be more effective.¹¹ This has been put down to the combined mechanical and chemical cleaning which takes place in such cases. However, there are application problems such as ensuring that the spray reaches all parts of the surface and of excessive foaming of the detergents during

spraying. This has raised concerns in the industry that spraying may lessen the solution concentration of the detergent and reduce the cleanliness of the workpiece compared to that obtained by immersion cleaning.^{11, 12}

In chemical cleaning, contaminants are removed by active reagents and additives dissolved or emulsified in the cleaning solution. Chemical cleaning covers both solvent cleaning and aqueous cleaning.²⁵ With safety, health and the environment (SHE) considerations to take into account, aqueous cleaners including alkaline soak cleaners, acid soak cleaners and electrolytic cleaners have become the more widely used in industry.^{25, 26, 27, 28} These will be discussed in Sections 1.2.2 to 1.2.4. Solvent cleaners will be discussed in Section 1.2.1 and non-chemical based cleaning methods will be described briefly in Section 1.2.5.

1.2.1 SOLVENT CLEANING

Solvent cleaning is a surface pre-treatment process that has been developed for removing organic compounds such as grease or oil from the surface of a workpiece. The organic compounds are dissolved off the surface of the workpiece by the solvent. There are two principal types of solvent cleaning, namely cold solvent cleaning and vapour degreasing.²⁹

Cold solvent cleaning is carried out at room temperature. It is used most often for low production applications where time spent cleaning is not central to process efficiency and in situations where initial equipment costs must be kept down and so inexpensive cleaning is essential.²⁹ After cleaning, workpieces may be dried at room or elevated temperatures by centrifugation or air blowing usually with a compressed air line. Some common examples of cleaners used in this process are aliphatic hydrocarbons such as kerosene, petrol and naphtha; chlorinated hydrocarbons such as methylene chloride (CH_2Cl_2), 1,1,1-trichloroethane (CH_3CCl_3); alcohols such as ethanol ($\text{C}_2\text{H}_5\text{OH}$) or isopropanol ($\text{CH}_3(\text{COH})\text{CH}_3$); and other solvents such as acetone ($\text{CH}_3(\text{CO})\text{CH}_3$).^{23, 29}

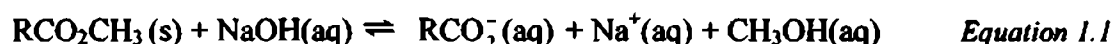
Vapour degreasing is a cleaning process which uses hot vapour of non-flammable solvents to remove oils, grease and waxes from the workpieces. Workpieces are placed in the bottom of what is known as a vapour degreasing unit. The unit consists of a tank with a heated solvent

sump at the bottom and a cooling zone at the top. Heat applied into the sump boils the solvent and generates hot solvent vapour. When this hot vapour reaches the cool workpieces in the cooling zone the vapour condenses on the workpieces and dissolves the dirt. There are two main benefits of vapour degreasing.²³ Firstly, because the workpieces are heated by the condensation of the solvent vapours onto the workpieces surfaces, workpieces dry immediately as they are withdrawn from the vapour zone. Secondly the solvent vapour that carries out the cleaning is not polluted with oil and grease removed from the surface. These are left behind in the bottom of the tank when the liquid solvent vapourises again.

The most commonly used vapour degreasing solvents are trichlorethylene (CHClCCl₂), perchloroethylene (C₂Cl₄), 1,1,1-trichloroethane (CCl₃CH₃), methylene chloride (CH₂Cl₂) and trichloro-trifluoroethane (CCl₃CF₃).³⁰ These are viewed as detrimental to the environment and their use is being phased out or discouraged.³¹

1.2.2 SOAK ALKALINE CLEANING

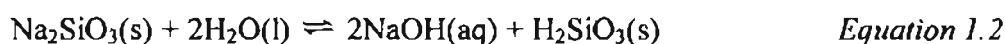
Alkaline cleaners are specifically formulated chemical blends composed of alkaline builders, buffers, water softeners, surfactants as wetting agents or emulsifiers, and chelating agents.^{23, 32, 33} Alkaline builders cover a broad group of chemicals such as sodium hydroxide (caustic soda, NaOH), potassium hydroxide (caustic potash, KOH), phosphates {trisodium orthophosphate (Na₃PO₄), disodium orthophosphate (Na₂HPO₄), monosodium orthophosphates (NaH₂PO₄) and sodium tripolyphosphate (Na₅P₃O₁₀)}, silicates {sodium orthosilicate (Na₄SiO₄) and sodium metasilicate (Na₂SiO₃)} and sodium carbonate (soda ash, Na₂CO₃).^{3, 7, 32} The cleaning action of the builders is largely carried out by the saponification of oil and grease (see Equation 1.1). The alkali metal hydroxides in particular, and to a lesser extent the other builders, provide hydroxide ions to saponify oils and grease (carboxylate esters) and release long chain (10-18 carbon atoms) carboxylates (soaps) into the solution.



R = Hydrocarbon chain

Sodium and potassium hydroxide produce highly alkaline solutions of pH values ranging from 12-14.³² However, these compounds have low cleaning ability for non-saponifiable soils. The soaps produced when alkalis are used on saponifiable compounds in the grease film can improve the cleaning by their surface activity and the soil carrying capacity of the cleaners (see Equation 1.1).³³ The other builders also have a surface active cleaning effect which allows the cleaners to remove non-saponifiable dirt.

Sodium orthosilicate and sodium metasilicate are the main silicates used in alkaline cleaners. They develop their alkalinity through hydrolysis. Hydrolysis is a process in which a salt reacts with water to produce an acid and a base.³⁴ In this case the silicates hydrolyse to form hydroxide and silicic acid (see Equation 1.2).



This silicic acid, present in a colloidal state, assists in emulsification and suspension of the surface soils. Silicates are known to adsorb on metals such as zinc and steel forming a thin film during the cleaning process. This protective coating can reduce oxidation by the alkaline solution.³³ Chemicals which protect the exposed metal of the substrate are called inhibitors.²⁹

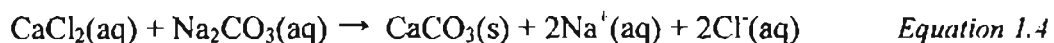
Equations 1.2, 1.3 and 1.5 show how salt hydrolyses of silicates, phosphates and carbonates form alkaline solutions. The hydroxide ions produced in the equilibrium can participate in the reaction shown in Equation 1.1.

Carbonates are a cheap source of alkalinity like silicates and phosphates.³² They have a buffering effect that helps to stabilise (keep down) the pH of the solution during the cleaning process (see Table 1.1).



Carbonates and phosphates are also used for softening hard water which contains chlorides, sulfates and bicarbonates salts of magnesium, calcium and iron. They react with the

magnesium, calcium or iron cations which are responsible for the hardness of the water to remove them as an insoluble precipitate.^{3, 35}



Phosphates are used in alkaline cleaners in the form of orthophosphate (PO_4^{3-}), pyrophosphate ($\text{P}_2\text{O}_7^{4-}$) or tripolyphosphates ($\text{P}_3\text{O}_{10}^{5-}$). In aqueous solutions phosphates help to provide an alkaline environment required for effective cleaning.³⁵



Proprietary surfactants provide the wetting and emulsification properties that lower the surface and interfacial tensions of the water in the solution and prevent soil re-deposition onto the workpieces being cleaned. Surfactants frequently used in aqueous based cleaners are either fatty acid soaps (as formed in Equation 1.1) or synthetic organic surfactants.²⁶ These surfactants are classified as anionic, cationic, non-ionic or amphoteric.^{26, 36} Anionic surfactants like alcohol ether sulfonates {for example isopropanolamine dodecylbenzenesulfonate, $\text{NH}_2\text{CH}_2\text{C}(\text{OH})(\text{CH}_2)_{12}\text{C}_6\text{H}_4\text{SO}_3\text{Na}^+$ } and non-ionic surfactants like alkyl phenol ethoxylates {for example nonylphenol ethoxylate, $\text{C}_9\text{H}_{19}\text{C}_6\text{H}_4(\text{OCH}_2\text{CH}_2)_n\text{OH}$ } are the most widely used compounds in the electroplating industry for cleaning.³² Non-ionic surfactants remove oils from the surfaces of the workpieces but are not as good as anionic surfactants at keeping dirt particles in suspension. These are however the preferred type for addition to electroplating solutions where they do not become involved in electrochemical reduction or oxidation.³⁶

Complexing agents are used in alkaline cleaners to soften water and complex metal ions that form undesirable products such as hard water soap scum. Some widely used chelating agents are sodium gluconate, ethylenediaminetetraacetic acid (EDTA), sodium tripolyphosphate, sodium citrate, nitrilotriacetic acid (NTA), hydroxyethylenediaminetriacetic acid (HEEDTA), triethanolamine and 1-hydroxyethylenediamine-1,1-diphosphoric acid (HEDP).^{23, 26, 33}

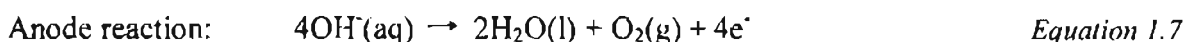
Solution composition and concentration have been used to divide alkaline cleaners into three main groups: heavy, medium and light-duty cleaners (see Table 1.1). Heavy-duty cleaners are usually used to remove soils like grease and oil from iron or steel workpieces. They are not used industrially on brass, zinc or aluminum substrates.³³ The hydroxide ions attack the zinc in zinc die-casting, aluminum and brass forming zincate and aluminate ions in solution. Medium-duty cleaners are applied to clean steel and in certain cases for brass. Light-duty cleaners are utilised to provide a final clean to brass or zinc die-castings and to wet their surfaces ready for electroplating.

Table 1.1 Formulation of alkaline cleaners solution³⁷

<i>Solution composition</i>	<i>Concentration of chemicals in the cleaners (g/l.)</i>		
	<i>Heavy-duty</i>	<i>Medium-duty</i>	<i>Light-duty</i>
Sodium hydroxide, NaOH	37.5	12.5	-
Sodium carbonate, Na ₂ CO ₃	25	25	-
Tribasic sodium phosphate, Na ₃ PO ₄ .12H ₂ O	6.2	12.5	25
Sodium metasilicate, Na ₂ SiO ₃ .5H ₂ O	-	12.5	25
Wetting agents	1.5	0.75	0.75
Operating temperature (°C)	80-95	80-90	80-90

1.2.3 ELECTROLYTIC CLEANING

In electrolytic cleaning (electrocleaning) the workpiece is made the anode or cathode in a specially prepared alkaline cleaning solution. The method is used after alkaline soak cleaning for the final removal of any residual soil from the workpieces prior to acid dipping. As such, electrocleaning solutions are not primarily formulated to chemically remove large amounts of oil or grease from the workpiece's surface. During cleaning a direct current is applied through the solution at a current density of 1–15 A/dm².²³ It is the scouring or scrubbing of the workpiece surface by the gas bubbles produced from the reaction that takes place during electrolysis of water and hydroxide ions (see Equations 1.6 and 1.7) that loosens and removes any remaining surface contamination.^{11, 38}



The two main methods of electrocleaning used industrially are cathodic (direct) and anodic (reverse) electrocleaning.¹³ In cathodic cleaning the workpiece is used as a cathode (see Equation 1.6) and the anode is made of steel or more commonly (and incorrectly) the tank walls. During the process hydrogen ions are discharged to produce hydrogen gas on the surface of the workpiece.

Equations 1.6 and 1.7 show that, on a mole basis, twice as much hydrogen is evolved at the cathode when compared to oxygen at the anode at the same current density. This means stronger agitation for lifting soil off the surface and better surface cleanliness is obtained in cathodic compared to anodic electrocleaning.^{13, 23} However, exposure to hydrogen produced during electrolysis can have a detrimental effect on the integrity of the hardened workpieces. This is known as hydrogen embrittlement.^{14, 15, 39, 40} This occurs when atomic hydrogen, liberated on the metal part, penetrates the metal surface to become absorbed inside the bulk metal. The hydrogen can then form chemical compounds (hydrides) with the metal or can diffuse into the base metal and form hydrogen gas which leads to rupture and cracking of the part.⁴⁰ Hydrogen embrittlement is frequently encountered in steel, aluminum, copper, nickel, titanium and zirconium substrates.^{39, 41} Hydrogen embrittlement can be reduced by using anodic cleaning, keeping the cathodic cleaning time to a minimum or baking the workpieces at high temperature (about 200 °C) for a period of time (about 2-3 hours) after cleaning to drive off the hydrogen held inside the workpieces.^{23, 42, 43} The negative charge on the workpieces has been found to attract positively charged species such as metallic ion impurities and some colloidal materials causing them to plate-out as a loose smut on the metal surface.

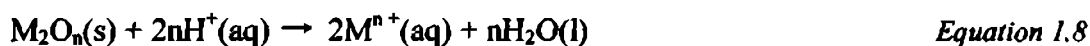
The disadvantages associated with the use of direct electrocleaning have led to anodic cleaning becoming more widely used.¹³ In anodic electrocleaning (reverse current cleaning) the workpiece is made the anode. Electrons are discharged by the hydroxide ions to the metal resulting in the liberation of oxygen gas. A higher current density must be used for anodic electrocleaning in order to produce an equivalent volume of oxygen to maintain good scouring action.⁴⁴ Exposure to the oxygen evolved has been observed to passivate the surface by creating oxide films on the anode surface. Dissolved oxygen generated at the anode has been known to also oxidise organic additives in the cleaner.^{13, 23} However the oxides can be removed

in the next stage (acid cleaning). The metal surface does not absorb oxygen because the oxygen atoms are too large to penetrate the structural packing of the metal workpiece.⁴⁴

Electrocleaning is often carried out using cathodic and anodic electrocleaning together.¹⁴ This is called periodic reverse cleaning and the polarity of the workpieces is switched every few seconds between negative and positive potentials. Anodic electrocleaning is preferred as a final step in the preplate cycle because it removes any bath contaminants that have plated onto the workpiece surface.^{13, 23}

1.2.4 ACID CLEANING

Treatment of the surface of workpieces with acid solutions is undertaken to remove oxides and to neutralise residual alkaline films dragged out from the rinse. Acid cleaning includes pickling and bright dipping. Pickling is the removal of thick oxides, scales and tarnish by chemical reaction with acids (see Equation 1.8).¹⁴ It also includes a light etch of the surface of the metal workpiece by the acid (see Equation 1.9) for better adhesion.⁴⁵



Pickling is usually performed as a preparatory step before plating. Natural inhibitors such as coal tar, gelatin and glue or synthetic inhibitors such as aldehydes, amines (triethanolamine) and pyridines can be used in the pickling solution.⁴³ Inhibitors minimise acid consumption, production of smut, hydrogen embrittlement and over etching of the metal workpieces (see Equation 1.9).⁴⁰

Bright dipping, as its name suggests, is a cleaning process used to produce a clean and lustrous surface after pickling.¹³ This is usually the final step in the cleaning process and removes thin oxides or tarnish films to activate the surface without significant etching of the metal workpiece.

Depending upon the workpieces, and the type and thickness of the oxides involved, many acids and combinations of acids can be used for acid dipping. The most widely used acid dips are solutions of sulfuric acid (H_2SO_4) and of hydrochloric acid (HCl).^{45, 46} Sulfuric acid is most often used because it is the least expensive. The pickling rates can be enhanced by increasing the acid concentration, temperature and degree of agitation of the solution. The optimum concentration range for H_2SO_4 is 20-30% by mass of the concentrated acid.⁴⁰ Like alkaline soak cleaners, H_2SO_4 baths can be operated hot up to 95°C .⁴ On the other hand HCl solutions give off acid fumes at high temperatures and cannot be operated above 40°C .⁴⁰ The optimum concentration of HCl used for the pickling process is 1-10% of the concentrated acid by mass.⁴ It has been found that HCl is faster and more economical on a large scale where recovery and regeneration is practical. Its disadvantage compared with H_2SO_4 is its higher cost for the acid waste sludge disposal and its greater acid consumption.^{4, 40, 45, 47}

1.2.5 NON-CHEMICAL CLEANING

Mechanical and ultrasonic cleaning do not use chemicals to remove dirt. The former is a dry abrasive method used either as the only cleaning step to obtain a specific kind of surface on the workpieces or as a preparatory step to remove heavy solid deposits before chemical cleaning or coating. The method includes blasting, polishing, buffing, grinding and deburring where the surface of the workpiece is cut or worked by abrasives.^{9, 11, 48, 49} These abrasives are moved over the surface of the workpiece on rotating wheels or moving belts or they strike the surface when sprayed in air or water.¹¹ Mechanical cleaning is useful for removing surface roughness, scales, burrs, scratches and irregularity of edges resulting from the primary production stage. It is not very good for precision cleaning. However, for large prefabricated structures such as bridge girders and hulls of ships, it may be the only feasible method available.⁴

Ultrasonic cleaning involves the use of high frequency ultrasonic sound waves, usually in the range of 20-40 kHz in a tank of cleaning solution.^{7, 50, 51} Ultrasonic sound waves are waves which have a frequency above 18000 Hz.^{42, 51, 52} These waves are transmitted into the cleaning solution by a transducer. A transducer is an instrument that converts electrical energy into mechanical energy. The cleaning solution can be trichlorethylene or any alkaline metal cleaner usually heated to 60°C .⁴³ The pressure front created as the sound waves pass through the

cleaning solution produces millions of microscopic bubbles at the surface of the metal workpiece. When these bubbles implode, the shock waves produced enhance cleaning by stripping away contaminants from the workpiece.⁵³ This phenomenon is known as cavitation.⁵⁴ Ultrasonic cleaning action can penetrate cracks, concealed holes and crevices of workpieces making it suitable for precision and general cleaning. The main application of ultrasonic cleaning in industry is in the manufacture of small precision components, such as watch parts and intricate jewellery.¹⁴

1.3 THE ELECTROPLATING STAGE

In basic terms electroplating is an electrochemical reduction process in which a dissolved metal is precipitated out of solution, usually onto a metallic surface. The workpiece to be plated is made the cathode in an electrolytic cell (see Figure 1.3). A plating cell is an electrolytic cell which uses electrical energy from a direct current source to make a non-spontaneous reduction reaction proceed at the surface of the cathode during electrolysis.⁵⁵ The cathode, a negatively charged electrode, is the workpiece at which positive ions are discharged as a deposit of metal when there is a flow of current.^{7, 56} An electrolyte is a solution that contains ions of the plating metal.⁵⁷ The anode is the positive electrode and is usually made of the plating material. When a current passes, the plating metal is dissolved from the anode into the solution (oxidation of the solid metal). The dissolved ions of the plating metal move through the solution to the cathode. The plating metal is then deposited from the solution onto the surface of the cathode (reduction of the aquated or complexed ions). However in some cases like chromium, a salt of the plating metal is dissolved in the solution. This has proved a better way of getting the required amount of metal (plate) ions into the solution when oxidation of the solid anode to aqueous ions is problematic. In such cases a “dummy” lead alloy anode is used to complete the circuit and let current flow through the cell.¹¹

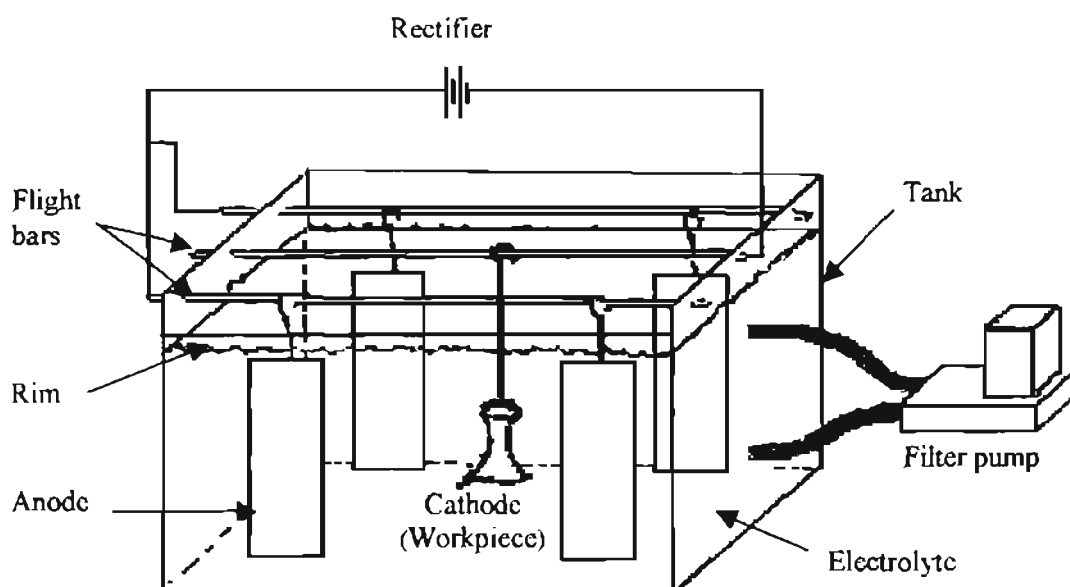


Figure 1.3 A typical electroplating tank⁵⁶

Figure 1.3 above shows an electroplating tank together with the anode and cathode bars (flight bars) from which the anode and cathode are hung. The cathode is connected to the negative terminal of a rectifier and the anode to the positive terminal. A rectifier is a device that converts an alternating current into a direct current by permitting flow of current in one direction and providing a high resistance in the opposite direction.^{58, 59} It also reduces the incoming voltage from thousands of volts from the power station to 220 V (single phase) and 380 V (three phase) on the rectifiers. Single phase rectifiers are used for small scale and experimental operations of electroplating and other electrolytic processes that require a current up to about 150 A.^{14, 58} However for chromium plating three phase rectifiers are required.⁵⁸ Current from the rectifiers is supplied to the electroplating tank by means of flight bars. These are made from high conducting metals such as copper rods or brass tubes or tin-plated aluminum.^{14, 58} Workpieces are hung in the centre of the bath and the anodes symmetrically on the outside as shown in Figure 1.3.

Electroplating tanks (vats) are used to hold rinse waters and process solutions in the electroplating line. There are different kinds of tanks used in an electroplating line. These tanks can be used bare or lined with rubber, plastics or lead depending on the composition and the type of solution employed in the process. The most commonly used tanks are made of mild steel, stainless steel and plastics. Due to their low cost, good mechanical strength and

convenience in construction, mild steel tanks are widely used in most electroplating plants.^{44, 58} These tanks are employed without protection for alkaline solutions and cyanide containing solutions. When lined with plastics, they are used to handle acids and acid plating solutions. Stainless steel tanks are the second most widely used after mild steel. They are employed for holding hot rinses, alkaline cleaners, pickling solutions such as nitric acid, chromic acid or sulfuric acid, fluoride free acid dips and plating solutions. Commonly used plastic tanks include polyvinyl chloride (PVC), polyethylene, polypropylene, fibre re-inforced polyester and Perspex.

During the electroplating process, workpieces are manually or automatically moved from one dip (immersion) tank to another down the electroplating line. They are either contained in barrels or baskets or alternatively are mounted on frames called jigs or racks. Barrels are used for the bulk processing at one time of many small to medium sized workpieces such as screws, nuts, bolts, washers, small fasteners and certain electronic contacts.^{25, 29} They are generally made of polypropylene. There are two common types of barrels used in electroplating: horizontal and oblique (see Figure 1.4 and 1.5).



Figure 1.4 Perforated horizontal barrel

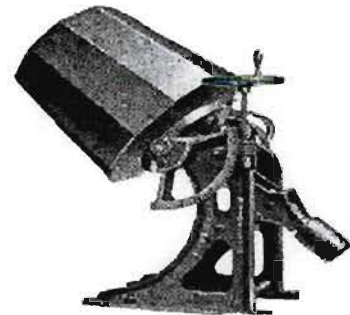


Figure 1.5 Oblique barrel³⁷

Horizontal barrels are by far the most widely used in industry for handling large loads and a variety of workpieces. These barrels have a hexagonal cylindrical shape and a diameter ranging from 15-75 cm.¹¹ One of the barrel walls contains an opening with a removal panel through which workpieces can be loaded and unloaded. They are fitted with a handle for lifting the barrel in and out of the solution by hand or hoist. Horizontal barrels containing the workpieces are dipped into the solution of the plating line. The anode is positioned outside the barrel as

shown in Figure 1.4. This means that barrels and jigs can use the same tank set-up. These barrels can be rotated to tumble and mix the workpieces with the plating solution and bring them in contact with the cathode. The cathode is a flexible cable with a metal tip on the free end commonly referred to as a “dangler”.⁶⁰ It enters the barrel through openings in the two end walls. Depending on the diameter of the barrel and the nature of the article to be plated, barrels can be rotated at variable speeds. Big barrels are operated between 6-12 revolutions per minute and small ones at 10-15 revolutions per minute.⁵⁸ The plating solution enters and leaves the barrel through cylindrical holes in the sides and door. The total number of holes is usually under 30% of the barrel surface area in order to optimise the barrel strength and maintain good plating performance.⁶⁰

The barrel is effectively a resistance to current flow in the solution (see Equation 1.13). This has resulted in platers using voltages higher than, and getting current density lower than, that used in rack plating.⁶¹ Current density is the rate of current flow per unit area of the electrode in the solution.^{15, 44} In many cases, the chemical supplier advises the electroplaters on what current density should be used with a particular plating solution at a given temperature. This is so that plating is carried out at current densities below that which causes burning or roughness but above that which would give no coverage. The barrel plating process does not require solution agitation, wiring (i.e. jiggging) of workpieces or special (conforming) anodes for different shapes of workpieces as with rack plating.⁶² Although barrels have been widely used in industry, there are some problems with their use. The surface of the barrelled workpieces can be scratched during tumbling, the parts can get caught up and stuck in each other and with the danglers.³⁷ Other problems with barreling are electrochemical in nature. For example barrel processing requires a higher voltage than jig plating due to the resistance added by the barrel walls. This will be discussed in Section 1.3.1.

Oblique barrels are generally used to hold small loads of very small workpieces such as screws.⁵⁸ They have an opening in the end wall for loading and unloading workpieces. Oblique barrels are constructed in one of two ways: either with solid walls to contain the plating solution or with porous walls to be contained in the plating solution. In the former case the anode and cathode as well as the workpieces are all inside the barrel. In the latter case the

cathode is inside the barrel and the anode is positioned outside the barrel in the bulk solution of the plating tank.

Jigs are widely used as an alternative means of dipping workpieces in a bath of an electroplating line. They are used to process workpieces that are too heavy, too large or too complex in shape to be barrel processed.^{25, 29} In the process, the workpieces are held in a fixed position on a vertical frame by copper wiring or by hooking them in place. The jigs are then hung vertically from bus bars which lie across the surface of the tank solution. Ideally the top of the jig should be 15 cm below the surface of the solution and the bottom of the jig should be 15-30 cm above the bottom.¹⁵ This practice has been used successfully to prevent disturbance of sludge lying on the tank bottom during transfer of jigs from one solution to another or when shaking the immersed jig to provide agitation.

Jigs are generally constructed from copper because of its high current carrying capacity, ease of fabrication and relatively high strength.⁴⁴ In fact all current in the external circuit is carried by copper or brass cables. Jigs are coated with a suitable insulating material such as polyvinyl chloride, waxes, lacquers or sprayed plastic coatings with only the conducting tips left exposed. The purpose of the insulating coating is to restrict current loss and so prevent metals from plating onto the jig.⁵⁸ It also protects the jig from corrosion and thus keeps the plating solutions free from contamination by the resulting corrosion products.

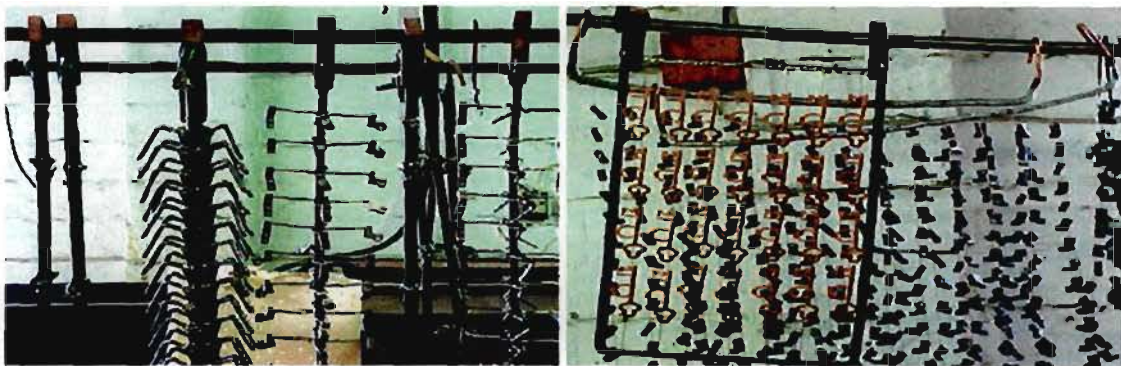
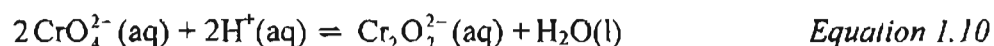


Figure 1.6 Different types of jigs used during cleaning and plating of workpieces

It is often found that during plating the jig tips become coated with an excess of the plated metals. This can entrap the plating solution leading to drag-out which can contaminate the rinse water tank. The plate has been known to reduce the flexibility of the tips causing breakage and so down time in production results. To avoid all these problems the plated metals are usually chemically stripped off the jigs by dipping them in different solutions. Depending on the nature of the plated deposit and the workpieces, the solution used for stripping can be nitric acid, hydrochloric acid, sulfuric acid or phosphoric acid. Sometimes the plated metal can be stripped off the jigs by using electricity. For example the anodic stripping of chromium is accomplished by using electricity in a solution of sodium hydroxide and sodium carbonate.¹⁴ The coated jig made with the anode in an electrolytic cell is oxidised from chromium to chromium(VI), Cr(VI). The resulting Cr(VI) forms the chromate ion, CrO_4^{2-} , in the alkaline solution. Equation 1.10 shows that CrO_4^{2-} ions are predominant in alkaline or dilute aqueous solutions while dichromate ions, $\text{Cr}_2\text{O}_7^{2-}$, are the preferred species in acidic or concentrated solutions.



Baskets (perforated buckets) are used to process very small workpieces such as screws by hand. Generally the baskets are made of plastics such as polyvinyl chloride and polypropylene.



Figure 1.7 Baskets used in the electroplating plant for cleaning workpieces

The electroplating solution is in fact more complex in its chemistry and operation than is described above. A more detailed account of the electrochemistry and chemistry involved in electroplating is presented in Sections 1.3.1 and 1.3.2 respectively.

1.3.1 THE ELECTROCHEMISTRY BEHIND ELECTROPLATING PROCESSES

The voltage or potential for a reduction reaction (for example, Equation 1.11 below) under equilibrium conditions where hydrogen is the reference electrode, is approximately given by the Nernst Equation (see Equation 1.12).³



$$E = E^0 + \frac{RT}{nF} \ln[M^{n+}] \quad \text{Equation 1.12}$$

E^0 = standard reduction electrode potential, V

R = gas constant, 8.314 J/Kmol

T = temperature, K

n = number of electrons per mole of oxidised form

F = Faraday's constant, 96485 C/mol

$[M^{n+}]$ = concentration of the oxidised species, mol/L

In practice the operating voltage (applied, tank or bath voltage) required to deposit a metal plate onto a workpiece in a plating cell is greater than the electrode potential calculated using Equation 1.12. The standard reduction electrode potential for the reduction of Cr(VI)(dichromate) to chromium metal, Cr, has been reported as 0.40 V.³ Most plating and electrocleaning processes use about 8 V.²³ Decorative chromium plating uses between 4-10 V^{3,63} while hard (functional) chromium plating uses around 12 V.^{14, 58} Anodising requires a higher voltage of about 16 V in sulfuric acid and up to 50 V in chromic acid.⁴³

There are a number of inherent causes as well as practical reasons for using voltages of around 8 V.¹³ For example some of the current generated in the plating cell will become unavoidably used up by undesirable electrocleaning reactions. The electrolysis of water, the oxidation of

organic additives (e.g. brighteners) and the reduction of metal impurities (e.g. Fe^{2+} , Cu^{2+} and Pb^{2+}) found in solution are among those side reactions which have been identified as sources of energy wastage in electroplating.^{23, 40, 44, 64} Consequently extra voltage has to be applied in order to carry out the desired plating reaction because of these unnecessary but largely unpreventable processes.⁶⁵ These are often referred to as resistances. Equation 1.13 shows that the applied voltage is largely made up of the potentials (resistances) equivalent to electrode polarisation (η_a and η_c) and the solution resistance (V_s).

$$V = E_a + E_c + V_s + \eta_a + \eta_c + V_0 \quad \text{Equation 1.13}$$

V = applied voltage between cathode and anode

E_c = equilibrium reduction electrode potential for plating reaction
i.e. for the cathode reaction (Equation 1.12)

E_a = equilibrium electrode potential for the anode reaction

V_s = voltage drop across the plating solution

η_a = anode overpotential

η_c = cathode overpotential

V_0 = voltage drop in the external circuit

The cathode, which is the workpiece being plated, is supplied with electrons from the rectifier in the form of current. This means the reactions at each electrode are not at equilibrium. The forward reaction in Equation 1.11, i.e. the reduction or deposition reaction, is taking place at a faster rate than the oxidation or dissolution reaction at the cathode. Cathode polarisation arises only when current is passed through the workpiece. More voltage than E_c has to be supplied in order to deposit the metal at a reasonable rate. This is called the overpotential or overvoltage and is defined as the difference between the potential of the electrode when it is working¹⁵ i.e. carrying a significant current and the “rest” or “reversible” potential when it is not. The electrode is said to become polarised.

The series of standard reduction electrode potentials (SREP) or E^0 values and the derived values from the Nernst Equation are based on the thermodynamics of the reactions at equilibrium. Unlike the E^0 value, the overpotential originates from the kinetics of the reduction

reaction. Such a change in potential on the cathode and anode from the E^0 (and E) value has to do with the concentration gradients and structure of the aqueous layer, the electrode, the type of electrolyte (simple or complex ions), solution agitation and the mechanism of the electrode reaction taking place.⁵⁸ The first of these is thought to contribute to the additional voltage needed to deposit the metal onto the workpiece. As the metal plates onto the workpiece the levels of reducible metal ions in the solution close to the cathode become depleted. This means the conductivity of the solution falls and so the solution resistance next to the electrode increases. This is reflected in the extra voltage required for reduction.

Overpotential is not found to be the same at all points on the surface.⁶⁶ This is a result of the shape of the workpieces influencing the current distribution on their surfaces. At points on the cathode furthest from the anode i.e. holes and recesses, the solution resistance is higher. This is because the path between the anode and the cathode is longer. This means less current will flow through the cavities. Such points are said to have a low current density and have low overpotential or surface polarisation. Conversely projections from the cathode surface including corners, tips, points and edges are high current density areas and have a high overpotential. The variation of current density and polarisation is an established cause of inconsistent deposit thickness on the workpiece surface and of the quality (poor, medium, good) of throwing power of the solution.⁶⁶ Throwing power is the ability of a plating bath to uniformly deposit metal on a cathode surface so plate thickness is the same at all points on the cathode.⁴³ A better throwing power can be obtained by choosing an appropriate bath composition, appropriate operating parameters, use of auxiliary (internal or inside) anodes for coating intricate shapes and use of additional (dummy) cathodes on either side of a workpiece in order to take off excess current from the edges.⁴⁰ A bath with good throwing power is able to decrease the excess deposition at high positions and enhance the deposition at recessed positions. This is due to the evening out effect of the plate thickness caused by cathode polarisation.

Polarisation makes it harder for current from the rectifier to reach the prominent points on the surface. This prevents or reduces the deposition of excess metal at high current density spots

reducing burning. Conversely polarisation promotes deposition on the low current density areas. This results in a more uniform thickness of deposit on irregular shaped workpieces.

The multi-step mechanism of the electrolytic reduction of water to hydrogen gas is considered to be responsible for the hydrogen overpotential (see Equation 1.6).⁵⁸ This is the polarisation which occurs during the formation of hydrogen gas during the electrolysis reaction.^{15, 58} In a mixture such as a plating solution the most easily oxidisable species lying higher in the SREP series (more negative E^0 values) will be oxidised first and the most easily reduced species (more positive E^0 values) will be reduced first. This means hydrogen would be expected to be discharged preferentially at the cathode or concurrently with the plated metal.

The hydrogen overvoltage makes the potential at which hydrogen is reduced more negative. When it falls well below the value for the reduction at the plated metal only the metal is deposited. This is observed for copper and nickel for example. However, in a few cases like zinc and chromium plating the cathodic potential for hydrogen lies close to that for the metal reduction. This causes hydrogen to be discharged along with the metal at the workpiece surface. In certain types of steel this gives rise to hydrogen embrittlement (see Section 1.2.3) and low current efficiency.

It is necessary for the surface area of an anode to be proportional to the area of the cathode (workpiece).⁵⁶ This is because the current flowing through the solution prefers the path of least resistance between the anode and the cathode. This means if the cathode is large, most current will flow towards its centre resulting in burning rather than deposition. This leads to high reject rates and/or the need for rework i.e. stripping and replating. Increasing the size of the anode helps to avoid this but if the cathode is too small more plate will deposit closer to the edges and less in the centre. This may give rise to rejects or wasted raw material by plating more than the specified thickness. This is wasteful of time and uses more plating and stripping chemicals than necessary.

If all of the current passing through the plating bath is not used to deposit the metal plate, the cathode efficiency is said to be low. Cathode current efficiency has been defined as the fraction

or percentage of the total current actually used to deposit the metal plate on the workpiece.^{43, 58} This is represented in Equation 1.14 below. Good current efficiency means the mass of the metal deposited equates with that defined by Faraday's Law.

$$\emptyset = \frac{I_c}{I_t} \quad \text{Equation 1.14}$$

\emptyset = cathode current efficiency

I_c = current passing through cathode associated with deposition reaction

I_t = total current passing through the electrolyte

This can be measured in terms of the actual mass of metal deposited (see Equation 1.15 below) compared to the mass which should be obtained at 100% cathode efficiency. This theoretical quantity of metal deposited is obtained from Faraday's Law (see Equation 1.15). This law states that the mass of the metal produced by electric current is proportional to the quantity, I , of electricity used.¹⁴

$$\emptyset = \frac{\text{Measured mass of the electroplated metal}}{\text{mass of metal calculated using Faraday's Law}}$$

$$\emptyset = \frac{m}{ItM/nF} \quad \text{Equation 1.15}$$

I = current, A

t = time, s

m = mass of the electroplated metal, g

M = molar mass of metal, g/mol

n = number of electrons per mole of oxidised form

F = Faraday's constant, C/mol

This can be simplified to Equation 1.16

$$m = \emptyset \left(\frac{Mit}{nF} \right) \quad \text{Equation 1.16}$$

For nickel plating cathode efficiency is high, hence very little hydrogen is discharged along with the nickel. However, in chromium plating the cathode efficiency is low, reaching a maximum of around 20%.⁷ When the cathode efficiency is poor compared to the anode efficiency the levels of plating metal ions can build up to concentrations over the specified value. This is wasteful of raw materials which have to be removed from the solution to restore the concentration to the specified level. The current efficiency and quality of the plate are known to be affected to a greater or a lesser extent by the bath temperature, current density and bath composition.

The current efficiency of most electroplating baths has been reported as increasing with increasing temperature and as being largely independent of current density.⁶⁷ Increasing the temperature of the bath is consistent with increasing the conductivity of the solution hence the current that may flow through the cathode.⁶⁸ This would give rise to an increased deposition rate. Increasing current density however, would bring about an increase in the overpotential at the electrode surface. The associated increase in resistance would in turn make it more difficult for current carried by the solution to reach the cathode. Therefore there would be no apparent increase in the deposition rate. In conventional chromium plating baths the current efficiency has been found to fall with increasing temperature.⁴⁰ This has been attributed to the different reaction mechanism used in chromium deposition. Compared to other metals Cr(VI) has been shown to deposit from a Cr(VI) containing film formed on the cathode rather than directly from aqueous or complexed Cr(VI) in the electrolyte solution.⁴ The thickness of this film decreases as the temperature rises because the film becomes more soluble and so the Cr(VI) held in the film re-dissolves. This means less Cr(VI) is available in the cathodic film for reduction to chromium metal. High bath temperatures give low deposition rates at a given current density but the plate has good brightness and the bath has good throwing power.

In chromium plating, cathode efficiency has been found to increase with current density for certain solution compositions (see Self Regulating High Speed solution in Section 1.3.4).⁶⁷ The effect of this has been related to the poor throwing power of the bath. On complex shaped workpieces there is heavier deposits on corners, edges and points close to the anode. Normally corrective action has to be taken in order to ensure uniform coverage. Such action is usually

based on increasing the local concentration of Cr(VI) close to the cathode by for example agitation of the solution and use of complexing ions in the electrolytes.^{14, 58} These effectively increase the supply of Cr(VI) to the cathode film and so higher current density can be used without burning occurring at the points on the surface corners and edges. This means low current efficiency in chromium plating can be compensated for by using high current density.⁵⁸ The minimum current density at which deposition takes place is two or three times that of zinc, nickel etc. This in turn requires a high voltage (4-10 V) compared with plating other metals which use less current.⁶³ Rectifier capacity is therefore greater for chromium plating (see Section 1.3).

1.3.2 THE CHEMISTRY AT THE ANODE

Anodes are positive electrodes in a plating bath where oxidation takes place.⁵⁶ They are utilised for two purposes. Firstly, to complete the electrical circuit and secondly, where it is a soluble anode, to enable replenishment of the metal content removed during the plating process of the plating bath.⁵⁸

There are two types of anodes used in electroplating namely soluble and insoluble (inert) anodes.^{4, 68} Soluble anodes are electrodes that can undergo oxidation to release metal ions into the electrolyte during electroplating processes. In most electroplating processes such as the plating of copper, nickel, zinc, cadmium, tin, lead and silver soluble anodes made of the corresponding metals are used. Soluble anodes are selected when metal replenishment in the form of addition of a salt is costlier than in the form of metal. The disadvantages of using soluble anodes are tying up capital in the form of costly anodes, cumulative buildup of impurities (particles on the surface of the anode, sizing from anode bags or sludges resulting from the anode dissolution) derived from the anode material and passivation of the anodes.⁵⁸ Passivation is the formation of coatings such as oxides on the surface of the metal which act as barriers and prevent further chemical action.¹⁴ Passivation can cause a lowering of the metal content of the bath due to metal ions not being released from the anode.

Insoluble (inert) anodes provide current but not metal ions for plating.⁴ The ions used for plating come from metal salts already in the solution thus the bath needs periodically to be replenished by adding more chemicals. Insoluble anodes are generally made of stainless steel or platinum-coated metal or lead and lead alloys. These anodes are often used when the depositing metal is unavailable in fabricated form or when it is too expensive to use pure metal as anodes.^{4, 56}

1.3.3 THE PLATING SOLUTION

The chemistry of the plating solution and the chemicals used in the plating solution will be discussed in this section. Plating solutions used in metal finishing contain both organic and inorganic chemicals in addition to the metal ion precursor to the plate and conducting counter ions. The plating solution is essentially an aqueous solution which contains a mixture of soluble ions of the metal being plated, various electrolytes, complexing agents and additives that ensure the electroplate has the desired structures, properties and quality.⁶⁹ The metal to be plated is generally present as a simple hydrated or as a complex ion in an acid or alkaline solution.^{16, 69} Acidic electrolytes have been used for the deposition of chromium, nickel, copper and zinc.⁷⁰ Alkaline electrolytes contain the metal as hydroxy, cyano or cyanohydroxo mixed complexes and are used for plating copper, zinc, cadmium, gold, silver and brass.¹⁶ Except for the precious metal baths which are low (for instance, some gold baths operate at gold level less than 0.051 mol/L), the metal to be plated is present in the solution in high concentration, typically 1-3 mol/L.⁶⁹ The chemical composition of solutions used to plate nickel and chromium are given in Tables 1.2 and 1.3 respectively.

Table 1.2 Composition and operating parameters of conventional chromium plating baths^{66, 71, 72}

<i>Parameters</i>	<i>Decorative chromium plating</i>	<i>Hard chromium plating</i>
Chromic acid, CrO ₃ (g/L)	200-400	250-400
Mass ratio (CrO ₃ /SO ₄ ²⁻)	80:1-125:1	75:1-100:1
Temperature (°C)	40-43	54-60
Cathode current density (A/dm ²)	7.5-17.5	22-100
Cathode efficiency (%)	6-12	10-15

Table 1.3 Composition and operating parameters of nickel baths^{23, 58, 63, 73}

<i>Parameters</i>	<i>Watts</i>	<i>Sulfamate</i>	<i>Fluoborate</i>	<i>All chloride and high chloride</i>
Nickel sulfate, NiSO ₄ .6H ₂ O (g/L)	225-410	-	-	70-200
Nickel chloride, NiCl ₂ .6H ₂ O (g/L)	30-60	0-30	0-15	100-300
Nickel sulfamate, Ni(SO ₃ NH ₂) ₂ (g/L)	-	263-450	-	-
Nickel fluoborate, Ni(BF ₄) ₂ (g/L)	-	-	225-300	-
Boric acid, H ₃ BO ₃ (g/L)	30-45	30-45	15-30	20-55
pH	3-4	3-5	3-4.5	1-4
Temperature (°C)	46-71	38-60	38-71	38-71
Cathode current density (A/dm ²)	1-10	2.5-30	2.5-30	2.5-30
Cathode current efficiency (%)	95-100	95-100	95-100	95-100
Anode	nickel	nickel	nickel	nickel

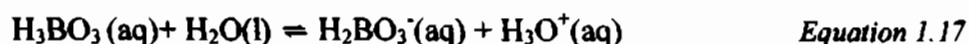
Although the chemistry of industrial plating baths is well established, the chemical composition of some ingredients, organic additives in particular, are often patented by the chemical manufacturers. This means exact and complete qualitative and quantitative composition data on these additives and hence the chemical formulation of the solution is not always available. This has to be borne in mind whenever attempting to quote the specification of an electroplating solution. Available compositional data is often quoted in terms of the metal as the element or as a compound. For example in zinc cyanide plating using sodium cyanide, the concentration of zinc is expressed as zinc ions. When nickel is plated on a workpiece from a Watts bath the nickel levels are expressed in terms of nickel sulfate (300 g/L) and of nickel chloride (60 g/L).⁷³ This in no way reflects the speciation of the metal in solution. However it may show how the metal is added to water at make-up or how much is added to the solution as top-up or merely be a means of expressing concentration but not detailed chemistry. The speciation of zinc in alkaline zinc cyanide plating solution is not simple zinc ions but rather mixed cyanohydro complexes. Similarly the nickel in a nickel plating solution is not added as chloride or sulfate salts. A soluble anode is used to supply nickel ions into an acid solution made up from hydrochloric and sulfuric acids. Alternatively the electroplating specification can be given as a mass ratio of the metal to complexing or counter anion. For example in chromium plating, the ratio by mass of chromic acid to sulfate is maintained within definite limits but preferably at 100:1^{3, 7, 63} and in zinc cyanide plating the mass ratio of zinc to cyanide (expressed as sodium cyanide) is 2.5:1.³

It is an established practice for the chemical suppliers to quote a range of values within which the bath composition must lie for best performance. For instance, during chromium plating using Lumina 34 the operating concentration range for chromic acid is from 125-375 g/L with an optimum concentration of 250 g/L.⁷⁴ Supply houses offer a regular (weekly or monthly) test service when they sample and analyse the bath and recommend “top-up” rates to restore the constituent concentration to the specified level.

1.3.3.1 INORGANIC COMPOUNDS IN THE ELECTROPLATING SOLUTION

The various electrolytes present in the plating bath are used to increase conductivity of the plating solution and improve anode corrosion.⁶⁹ Conductivity is the ability of a solution to carry an electric current.⁷⁵ For example the addition of sulfuric acid to copper sulfate and tin sulfate baths, the addition of sodium hydroxide to cyanide baths, the addition of nickel chloride to nickel baths, the addition of carbonate to silver and gold baths are all used to increase the electrical conductivity of the baths. In chromium plating the chromic acid (CrO₃) concentration of 400 g/L gives the best conductivity.⁶³ Compounds such as carbonates in cyanide copper baths and chloride in nickel baths are used to obtain a proper dissolution of the anodes.

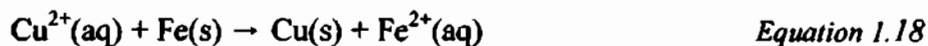
Some electrolytes are also used to buffer the plating solution to give a good quality deposit. A buffer is a solution that resists a change in pH when small amounts of acid or alkali are added or when dilution occurs.⁷⁶ For example boric acid buffers nickel plating solutions (see Table 1.3) by controlling the pH in the cathode film.⁷⁷



Equation 1.17 shows a simplified version of the buffer action of boric acid at the concentration found in a nickel plating solution. It can be seen that the addition of excess acid in the solution (H₃O⁺) shifts the equilibrium to the left side of the reaction to consume the H₃O⁺. Any OH⁻ produced from the electrolysis of water at the cathode (see Equation 1.7) would cause the equilibrium shift to the right side to replace the H₃O⁺ which is removed by OH⁻. For either situation, the equilibrium constant of the buffer solution remains the same. Therefore, the pH remains practically constant to within the operating range.

In some plating solutions, for instance nickel, controlling the pH of a plating bath is essential for achieving good deposits and efficient use of materials and electricity. In nickel plating, if the pH of the bath is higher than the optimum recommended value, the deposit will be rough, burned, dull and brittle due to precipitation of metallic contaminants and increased consumption of brightener components.^{58, 77} On the other hand, low pH causes evolution of hydrogen which consequently results in a decrease in cathode efficiency.⁵⁸ This in turn leads to an accumulation of hydroxide ions in the cathode region and consequent precipitation of basic salts that may get included in the electrodeposits, thereby altering the deposit properties. Therefore, the pH of a bath must be regulated without a significant change in the bath composition. This can be done automatically by the buffer within certain limits or by chemical additions made by the operators. To increase the pH of acidic baths, for example, nickel baths, nickel carbonate or nickel hydroxide can be used. To decrease the pH of chloride or sulfate baths of nickel and acid zinc, dilute acids such as hydrochloric or sulfuric acid may be employed. The pH of alkaline baths containing hydroxides can be increased by adding sodium or ammonium hydroxide. Generally, highly acidic baths such as chromic acid, acid copper sulfate, fluoborate formulation, or alkaline baths such as a stannate tin bath cannot use pH measurements to monitor and control the composition of the plating solution.⁵⁸

Complexing agents are compounds or ions that combine with metallic ions in solution to form complex ions.⁴³ The most common complexing agents used in the electroplating industry are cyanides, hydroxide and the sulfamate ion. Complexing agents have been widely used in plating baths to make the deposition potential more negative when it is necessary to prevent a spontaneous chemical reaction between the cathode and the plating ion e.g. plating of copper onto iron as shown in Equation 1.18.⁶⁹



The E^0 values for the reduction of Cu^{2+} and Fe^{2+} are 0.34 V and -0.44 V respectively (see Equation 1.18).³ The addition of a complexing agent makes the potential of the Cu^{2+}/Cu couple more negative than that for the Fe^{2+}/Fe couple thus Equation 1.18 is no longer thermodynamically favoured.⁶⁹

Complexing agents have also been used to improve the throwing power. This is affected by the electrical conductivity of the solution, the degree to which the cathode polarizes with an increase in current density and the relationship between cathode current efficiency and cathode current density.^{40, 58} The steeper the slope of cathode polarisation and the greater the conductivity of the solution, the more uniform will be the current diffusion at the cathode. The evenness of metal distribution will be higher, the greater the decrease of cathode current efficiency with an increase in current density.⁴⁰

Complexing agents have been used to enhance the solubility of slightly soluble salts added to the plating bath during top-up. For instance, silver cyanide and copper(I) cyanide are slightly soluble in water. However, these dissolve readily in sodium or potassium cyanide solutions to form highly soluble metal cyanide complexes (see Equation 1.19).⁵⁸



Complexing agents also facilitate the dissolution of the anode and in so doing prevent passivation and loss of current efficiency during the oxidation of the anode.⁶⁹

1.3.3.2 ORGANIC COMPOUNDS IN THE ELECTROPLATING SOLUTION

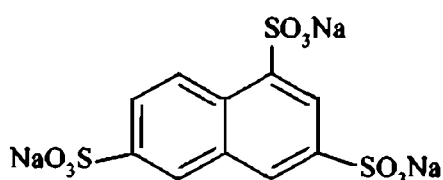
Additives are often high molecular weight organic compounds or colloids added in relatively low concentration, usually from 10^{-4} to 10^{-2} mol/L, to the electroplating bath in order to modify the structure and properties of the cathode deposit.⁷⁸ They are classified into four major categories: brighteners, levellers (dendrites and roughness inhibitors), structural modifiers e.g. stress relievers, and wetting agents.^{69, 78} Some additives belong to more than one category because they perform more than one function.⁶³ The only structural modifiers which will be discussed in this section are stress relievers which also serve as brighteners.

Brighteners usually cause the workpiece to have a bright and shiny look compared to the matte or dull deposits obtained from baths without such additives. This means the surface must be even (not rough) so that a high proportion of the light reflected from them is not scattered.

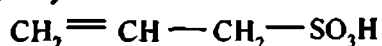
Brighteners usually cause the formation of an even and fine-grained deposit by modifying the deposition processes during plating.⁶⁸

Brighteners are used extensively in nickel plating baths. There are two types of nickel brighteners: class I (primary or maintenance brighteners) and class II brighteners (secondary or carrier brighteners).⁶³

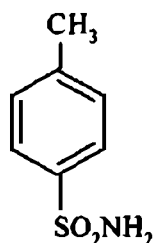
A) Sodium naphthalene trisulfonate



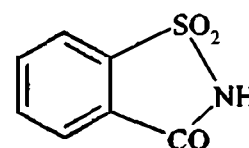
B) Allyl sulfonic acid



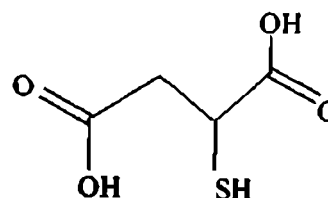
C) p-toluene sulfonamide



D) o-benzoic sulfonimide (saccharin)



E) Thiomalic acid



F) Coumarin

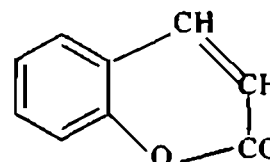


Figure 1.8 A selection of additives used in nickel plating⁶³

Brighteners of the first class are aromatic or unsaturated sulfur-containing compounds which include aromatic sulfonic acids, sulfonamides and sulfonimides (see Figure 1.8).^{63, 79} Saccharin (Structure D, Figure 1.8) is a widely used example of this type of brightener. These brighteners produce very bright plate only if the workpiece surface itself has been prepared to a bright finish. They work by incorporating sulfur into the nickel plate but fail to give high lustre with continued plating. Brighteners of the second class are needed in order to give such a fully bright plate.⁶³ However, class I brighteners, unlike class II brighteners, do not cause brittleness or stress in the deposit which may lead to deformation of the workpiece or rupture of the plate.

This has led to low concentrations (0.005-0.2 g/L) of class II brighteners being used together with higher concentrations (1-10 g/L) of class I brighteners in order to achieve a bright and stress free finish.³ Compounds like saccharin (structure D, Figure 1.8), sodium naphthalene trisulfonate (Structure A, Figure 1.8), allyl sulfonic acid (Structure B, Figure 1.8) and p-toluene sulfonamide (Structure C, Figure 1.8) are among the class I brighteners which are used to reduce stress in nickel plating.⁶³ Depolarisers such as thiocarboxylic acid e.g. thiomalic acid (Structure E, Figure 1.8) are also added to reduce stress in the plate and so allow higher concentrations of these chemicals to be used in the electroplating solution.²³

“Throwing”, “covering” and “levelling” are all terms used to describe the distribution of the plate on the surface of the workpiece.^{63, 66} As such they all deal with plate thickness but in quite different ways. Plate distribution has been traditionally looked at in terms of shapes, both workpiece shape and surface contours. This has been termed the macro- and micro-level approach respectively. The term good “throwing power” has been given to a plating solution which deposits an even thickness of plate over the whole three dimensional form of the workpiece i.e. in protruding (sharp corners and points) and in recessed areas (holes and indentations). This is a macro-level “shape” phenomenon.⁷ Good coverage means that there is no bare areas on the surface of the workpieces i.e. the plate is continuous. Good “levelling” on the other hand has been used to describe a surface where the plate has filled in any scratches or pores on the substrate’s surface, irrespective of that surface being on a protruding or recessed area of the workpiece. Good throwing power means that the measured plate thickness should be the same at every point on an irregularly shaped cathode.⁶⁶ In levelling the thickness is not considered the same for the layer of levelled plate which is effectively the initial layer of atoms deposited directly onto the substrate. This is because levellers put more plate in surface troughs than on the flat surfaces and the peaks. This is thought to occur because more levellers become incorporated into the deposit at the peaks and less in the troughs on the surface. This has been observed to make the deposition reaction occur at a more negative potential and so it is more difficult for the reduction reaction to occur on the peaks than in the troughs. Levellers do not tend to be sulfur based compounds. Coumarin (Structure F, Figure 1.8) for example is used to deposit semi-bright deposits usually as part of a duplex system. But it is also a class II

brightener for fully bright nickel plating.⁶³ Those levellers containing sulfur cannot be used to deposit semi-bright nickel and are found only in bright nickel baths.

Wetting agents or surfactants are used to control pitting (holes developed because of gas bubbles) and to decrease drag-out by reducing the surface and interfacial tension of the plating solution.³² This means that air and hydrogen bubbles do not adhere to the workpieces being plated and neither does much process solution. This is because wetting agents make the process and rinse solution flow off the surface faster. Sodium lauryl sulfate ($C_{12}H_{25}SO_4Na$), sodium lauryl ethoxy sulfate, $CH_3(CH_2)_{11}(OCH_2CH_3)OSO_3Na$, and sodium lauryl sulfonate, $CH_3(CH_2)_{11}SO_3Na$, are some common wetting agents used in nickel plating baths.

The working principle of additives is based on an adsorption mechanism.⁷⁸ The molecules of the compound are adsorbed on the metal nuclei which are depositing. When new ions are discharged, the resultant metal atoms cannot deposit over the previous nuclei covered with the addition agents, but instead, start new nuclei resulting in fine-grained deposit. Very small amounts of additives are usually adequate to produce the desired improvement. If additives are present in excess, the nuclei carry a large amount of the additives and the deposit becomes loose and powdery or brittle.⁶⁶ This explains why the concentration of additive must be kept within a definite range for best results.

1.3.4 CHROMIUM ELECTROPLATING

There are two main types of chromium plating namely decorative and hard chromium plating. A decorative chromium plate is a very thin deposit with a thickness of between 0.25 and 0.8 μm .^{14, 58} Some authors have reported decorative chromium plating thickness of 1.3 μm or more.^{23, 63} Decorative chromium offers a long lasting, bright, lustrous appearance while also providing corrosion resistance, lubricity and durability.⁸⁰

Hard chromium plating, also called heavy industrial, functional or engineering chromium plating has the following characteristics. It is:

- used to build up badly worn or undersized parts and so increasing the service life of the workpieces,^{14, 23, 81}
- usually deposited to a thickness ranging from 2.5 - 500 μm ,^{58, 82}
- generally plated directly on the base metal and only occasionally over other electrodeposits such as nickel.^{14, 58}

The chemistry of both plating baths is broadly similar. However, hard chromium plating has been traditionally carried out using more dilute solutions and over a longer period of time.^{5, 7, 83}

This discussion will look at decorative chromium plating only i.e. bright, porous and cracked.

The chemistry and operating conditions under which decorative plating has been carried out has changed relatively little since the 1920's.⁸⁴ This can be explained in terms of the inherent differences and difficulties of chromium plating compared to that of other metals like nickel and zinc. The important developments which have been made will be highlighted here except for the commercialisation of the trivalent chromium plating (use of chromium(III) plating solutions) system. This has not been widely adopted in South Africa as yet and so is excluded from this discussion.

Chromium plating differs from the other plating systems in several important areas which are related to the electrochemistry of the process.^{3, 40, 63, 66, 67} These include the following:

- low cathode current efficiency;
- poor throwing power;
- tendency of the solution to stratify;
- high current density requirement;
- high bath temperature requirement;
- undercoat requirement;
- insoluble anode requirement.

These characteristics are often interrelated. For example high current densities are used in chromium plating compared to that for other metals because of the poor current efficiency at the cathode.⁴⁰ This in turn improves the throwing power, giving an even thickness of deposit everywhere on the workpiece. This arises because there is less of an increase in polarisation with increasing current density at the low points (recesses) on the cathode surface than there is on the high points (projections). In contrast to most other metal plating, high bath temperatures give bright deposits but this leads to the lowering of current density and hence throwing power.⁶⁷

Chromium is a transition metal with a rich redox chemistry. It exists in an oxidation state from -2 to +6. The -2, -1, 0 and +1 are formal oxidation states displayed by chromium in compounds such as carbonyls (-C=O) and nitrosyls (-N=O) and with organoligands, for instance C_2H_4 . The chromous or chromium(II), Cr(II), species is basic and is very unstable since it oxidises in air or water to give chromic or chromium(III), Cr(III).^{7, 85}



The E^0 for Equation 1.20 is -0.41 V.⁷ Cr(III) is amphoteric and the most stable oxidation state of the element. It forms many compounds which have commercial applications, for example chromic oxide (Cr_2O_3) and basic chromium sulfate $[Cr(OH)(H_2O)_5]SO_4$.⁸⁵ The former compound is used for making pigments and the latter for leather tanning. Cr(VI) has the greatest industrial application due to its acidic and oxidant properties and its ability to form strongly coloured and insoluble salts.⁸⁵ One of the primary and most important uses of Cr(VI) is for electroplating.

During chromium plating different reactions occur at the cathode and anode. The cathode reactions are those reactions that take place at the surface of the workpieces being plated. Even though the exact speciation of Cr(VI) in the plating solution is unknown and there are a number of theories to explain the mechanism of plating, the overall reaction that produces the chromium plate at the cathode is accepted to be the stepwise reduction of Cr(VI) to Cr.⁶⁴ This can be represented by Equation 1.21, i.e. the conversion of the dichromate ion ($Cr_2O_7^{2-}$) to

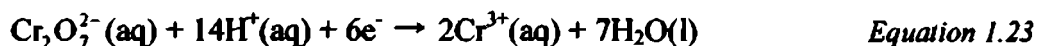
chromium metal atoms. However, as will be mentioned again later, this is not an accurate representation of the reduction reaction leading to the deposition which takes place at the cathode.



The standard redox potential for the reaction given in Equation 1.21 is 0.4 V.³ In the actual electroplating process a higher voltage is used because chromium deposition is characterised by low cathode efficiency (10-20%).^{7, 40, 63} This is because most of the current is consumed on side reactions. A significant side reaction is the electrolysis of water which involves the conversion of hydrogen ions to hydrogen gas molecules (see Equation 1.6) and hydroxide to oxygen gas molecules (see Equation 1.7)⁴⁰. About 80-90% of the power consumed in the chromium electroplating processes is used by this reaction resulting in the evolution of very large quantity of hydrogen gas from the workpieces' surface.⁶⁴



Another side reaction is the reduction of the dichromate ion, $\text{Cr}_2\text{O}_7^{2-}$, to Cr(III).



When chromic acid is dissolved in water, it forms a mixture of species including the chromate ion, CrO_4^{2-} and the dichromate ion, $\text{Cr}_2\text{O}_7^{2-}$. These are in a dynamic equilibrium with each other as shown in Equation 1.10. These polymerise further through oxygen and hydroxo bridges to give extended anions containing Cr(VI).³ When the solution is electrolysed, a strong film of basic chromium(III) chromate (CrOH.CrO_4) is formed at the cathode (see Equation 1.24) that hinders the formation of a metallic deposit.^{3, 40}

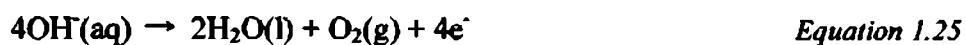


The sulfuric acid in the bath loosens the film by forming a soluble complex with Cr^{3+} and thus prevents formation of the film at the cathode.⁴⁰

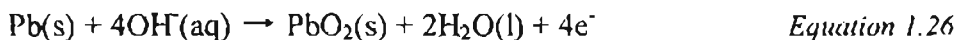
Most decorative chromium plating solutions operate satisfactorily below 3-4 g/L of chromium(III) in the bath.⁶⁴ The maximum concentration of Cr(III) that can be tolerated is 7.5 g/L.⁸⁶ Greater concentrations than the maximum value in the plating bath cause the conductivity of the solution to decrease which leads to chromium plate adhesion problems.

The anodes used in chromium plating are generally made of insoluble lead alloys.^{63, 87} For conventional sulfate baths lead-antimony (6-8% antimony) alloy is preferred, while for fluoride containing baths lead-tin (4-7% tin) alloy is recommended.¹¹ Chromium metal cannot be used as an anode for several reasons. Firstly, it is more economical to use an insoluble anode of some type and keep the concentration of chromium in the solution at the correct value by adding chromic acid than by using chromium anodes.^{7, 83} Secondly, chromium deposits with only about 10-20% efficiency while a chromium anode will dissolve with approximately 85-100% efficiency.⁷ This means that the bath could very soon deviate from the specified Cr(VI) concentration level. If the solution becomes Cr(VI) rich (~ 400 g/L CrO_3), the conductance of the solution will fall and it will become ineffective for plating.⁶³ Thirdly, the use of soluble anodes (chromium anode) is not satisfactory because as they dissolve chemically to give Cr(III) there will be little possibility of re-oxidation to Cr(VI).^{7, 86} The ratio of the anode-to-cathode area used is between 1.5:1 to 2.0:1, in order to control the concentration of chromium(III) and carry sufficient current.^{66, 88}

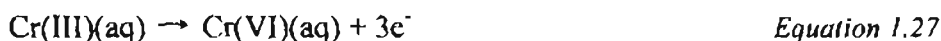
Three reactions are involved at the anode and these are given in Equation 1.25-1.27.⁶⁴ The first reaction is the discharging of hydroxyl ions to give water and oxygen gas.



The second reaction is the combination of the lead anode with hydroxyl ions to give lead(IV) that coats the anode surface.



The film of lead(IV) oxide formed at the anode is very important because it causes the third reaction to take place (see Equation 1.27). That is it oxidises the Cr(III) which is constantly formed in the bath to chromic acid and so maintains the Cr(III) concentration in the bath at the desired level.^{7, 59, 64}



Bright chromium deposits have traditionally been obtained from Cr(VI) plating solutions used as aqueous solutions of chromic acid, CrO₃.²³ Chromium is deposited without the use of brighteners, which have been found to decompose in such strong oxidising conditions, but in the presence of one or more acid radical catalysts.⁷ The chemistry of the solutions must be maintained within the specified concentration values for each constituent (see Table 1.4) to achieve an acceptable deposit. The most commonly used catalyst is sulfate. Developments in chromium electroplating have largely involved making improvements to the catalyst system.³ The exception to this came in the 1970's with the introduction of the first Cr(III) plating solution.²³

The first catalyst used with CrO₃ was sulfuric acid.^{23, 83} It is now thought that the function of the sulfate ion is to complex Cr(VI) in the form of a film on the cathode surface. It is only once the Cr(VI) is present in the cathodic film that reduction to Cr can take place. Many explanations have been put forward to account for the deposition of this reaction.^{4, 7, 63} They usually involve extended species where Cr centres are bridged by oxygens in SO₄²⁻, hydroxy groups, in water and oxygen itself. This means that the reduction of Cr(VI) as a dissolved species in the electrolyte, as shown in Equation 1.21 is not a true reflection of the electrochemical reduction reaction.

The composition of the simple sulfate only and the three different dual-catalysed plating solutions are given in Table 1.4.

Table 1.4 Composition of different types of chromium electroplating baths^{4,7, 63, 83, 89}

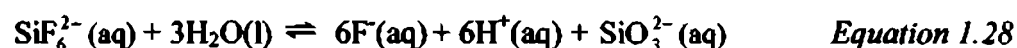
	Single catalyst	Double Catalyst		
		Fluoride	Non-Fluoride	Self Regulating High Speed (SRHS)
CrO ₃ (g/L)	250	250	250	> 250
SO ₄ ²⁻ (g/L)	2.5	1.67	2.5	< 1.5
CrO ₃ /SO ₄ ²⁻ mass ratio	100:1	150:1	100:1	150:1
SiF ₆ ²⁻ (g/L)	-	2	-	6
Sr as SrSO ₄ (g/L)	-	-	-	4
K as K ₂ CrO ₄ (g/L)	-	-	-	14
Alkene sulfonic acid	-	-	1 - 3% of CH ₂ (SO ₃ H) ₂	-
Temperature (°C)	40	45	55	45
Current density (A/dm ²)	10	15	30	15
Cathode efficiency (%)	8	15	25	15

Although one concentration value for the CrO₃ and H₂SO₄ is given in Table 1.4 for each solution, a range of values in fact can be used. For example the highest chromic acid levels which can be used for the single catalyst bath, the fluoride bath, the non-fluoride bath and the Self Regulating High Speed (SRHS) bath are 500 g/L, 400 g/L, 300 g/L and 400 g/L respectively.⁷ However in all cases the CrO₃:SO₄²⁻ is kept at one preferred value. Higher bath concentrations than shown in Table 1.4 result in lower current efficiency. The bath conductance has been observed to drop above 400 g/L and so would require a higher voltage to achieve a particular current density.⁶³

Mixed catalyst baths are similar to conventional sulfate baths in conductivity but have a higher current efficiency than that of the conventional sulfate bath of the same concentration.⁷ In addition the baths can be operated at higher current densities giving a higher deposition rate, producing smoother, harder and brighter deposits than the conventional sulfate baths.^{3, 7, 23, 80} They also exhibit a better ability to activate passive nickel surfaces. Due to their greater current efficiency and ability to operate at higher current densities, mixed catalyst baths have been known to double production over that of conventional sulfate baths.²³ The disadvantage of these baths is their corrosive nature which shortens the life of the plating equipment such as tank liners and heating coils. Besides this, they are more expensive than the conventional sulfate plating baths.^{7, 80}

In chromium plating cathode efficiency has been found to be closely related to bath composition. For any current density, cathode efficiency falls with increasing temperature in a single catalyst system. This is because the solubility of the film increases with temperature. Therefore the film dissolves in the plating solution and the thickness decreases and Cr is released into solution and less is available for reduction. However for a SRHS bath the cathode efficiencies tend to rise with increasing temperature. This is linked to the increased solubility of the secondary catalyst e.g. K_2SiF_6 in this bath.⁷¹

Sulfuric acid has been used together with one of two catalysts, namely fluoride or an organic acid such as methane disulfonic acid, $CH_2(SO_3H)_2$ (see Table 1.4).⁷ These have been commercially available as high energy efficiency formulations (HEEF). Simple fluoride salts are not generally used as a source of the fluoride ion catalyst in the plating solution.³ They are needed in such small amounts that it was found difficult to determine the drag-out losses from the solution and to manually administer the correct amount in order to restore the specified levels. The chemistry of the fluoride system was then developed further giving rise to the SRHS plating solutions. This system uses complex fluorides such as silicon hexafluoride to supply the fluoride ions to the plating solution (see Equation 1.28).



This preserves the useful properties of fluoride catalysed systems, like higher current efficiency at higher temperatures, higher current density and better throwing power, while avoiding etching of the workpiece's surface.^{63, 80, 83} In SRHS baths fluoride compounds of low solubility like potassium silicon hexafluoride (K_2SiF_6) provide the fluoride catalyst while strontium sulfate supplies the sulfate. The CrO_3 to catalyst (SO_4^{2-} and F^-) ratio is kept constant by using the chemistry of the common ion effect.⁶³ The CrO_3 to SO_4^{2-} ratio is controlled by saturating the solution with strontium sulfate (see Equation 1.29).⁷ This means any sulfate lost from the bath may be replenished by dissolution of more of the excess solid strontium sulfate in the bath and thus maintaining the equilibrium situation. Conversely if sulfate levels rise, by adding impure CrO_3 or by drag-in, strontium sulfate would be precipitated out of the solution.⁸³

Additions of slightly soluble strontium chromate have also been used to suppress the dissolution of the strontium sulfate if the levels become too high.



A similar situation is found for the fluoride catalysed system. A desired amount less than the saturated solution concentration of potassium silicon hexafluoride can be kept in solution by the addition of potassium dichromate to a saturated solution.⁶³ The addition of potassium dichromate displaces the equilibrium in Equation 1.30 to the left hand side and automatically precipitates the potassium silicon hexafluoride out of the solution.



Decorative chromium deposits are generally plated over nickel for economic reasons as well as to achieve good corrosion protection and plate brightness.¹⁴ These will be discussed below.

Chromium deposition is characterised by its low cathode efficiency.⁴⁰ Chromium is also a relatively expensive metal to plate.⁹⁰ This is evident from the long deposition time which results in high power usage. So chromium plating directly onto the base metal has not been an economic possibility for decorative plating.

The corrosion protection offered by a plated system depends on the following related points:^{3, 63, 65}

- potential difference between the undercoat and the chromium plate and between the undercoat and the substrate;
- thickness and porosity of the undercoat and of the chromium plate;
- passivity of the top chromium layer.

Decorative electroplated chromium deposits are very chemically stable, thin and porous.⁶³ This means that they do not offer protection to ferrous substrates. In fact, they accelerate corrosion of the base metal at the bottom of the pores or cracks in the deposit. It is the bright nickel

deposit which is used to provide electrochemical (sacrificial) protection to the base metal. Chromium provides protection from the environment through a barrier mechanism by forming a passive surface layer when it is neither cracked nor porous.⁹¹

The E^0 values for the reduction of Ni^{2+} and Fe^{2+} are -0.25 and -0.44 V respectively.⁶⁵ The E^0 of Cr(III)/Cr is lower still at -0.74 V.³ From these E^0 values, it can be seen that nickel ions would be reduced and iron would be oxidised (see Equation 1.31).



This means that thermodynamically chromium should corrode to protect iron and nickel. However, it is nickel which oxidises when a nickel plus chromium coating corrodes. Such E^0 predictions are based however on a single metal substance and a simple neutral aqueous solution. The predictions fail to consider the actuality of the situation which includes the following points.^{58, 63, 65}

- the chromium is co-deposited with additives which lowers its E^0 ;
- the chromium is passive which means the exposed chromium is present in an oxidised form in a clear oxide film;
- the chromium deposits are sometimes discontinuous i.e. cracks and pores occur.

When the chromium coating is breached or is porous or cracked the nickel layer becomes exposed. The sulfur brighteners in the nickel plating solution form a species with the nickel which lowers the E^0 (makes it more negative) below that of iron and probably chromium.⁴⁰ This means that nickel is preferentially oxidised to Ni^{2+} (see Equation 1.32) and supplies electrons to sacrificially protect the exposed iron of the substrate. This is commonly reported as being “anodic” protection in the literature.¹³



The reduction reaction which takes place in the nickel layer while the nickel is oxidised is shown in Equation 1.33.



This principle is well known for causing hydrogen embrittlement in cyanide zinc plating where cyanide lowers the deposition potential for zinc close to that for the hydrogen overpotential. This leads to considerable hydrogen discharge accompanying zinc plating.

Discontinuities are found in most electroplated chromium deposits.⁶³ These are of two types, micro-porous and micro-cracked. Crack free chromium (electro)plate has been obtained largely from a single catalyst chromium plating solution, having low CrO_3 /catalyst ratio and a high CrO_3 concentration. However such coatings tend to rupture under service to form a macro-cracked structure. Obviously this reduces the barrier protection offered by chromium to the nickel undercoat. However, micro-cracked and micro-porous chromium (electro)plate spread the corrosion reaction out over many corrosion points on the surface. This improves the corrosion protection over that obtained from crack free chromium when it ruptures in use. This has been explained in terms of the lowering of potential difference between the two half reactions in Equation 1.32 and Equation 1.33. This occurs because the redox reactions are not located at one point but rather are spread across the entire surface. This slows down the oxidation rate of the nickel and so the effects of corrosion take longer to show up. The high protection comes from chromium with $10\text{-}17 \times 10^3$ pores/cm and 27-50 cracks/mm in the coating.^{71,92}

CHAPTER 2

INTRODUCTION TO WASTE MINIMISATION IN THE ELECTROPLATING INDUSTRY

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2.1 WASTE MINIMISATION AND WASTE MANAGEMENT

An industrial process can be regarded as the conversion of low cost input/s into more valuable output/s using machinery and/or labour (see Figure 2.1).^{93, 94} These input are of two types, energy and matter.

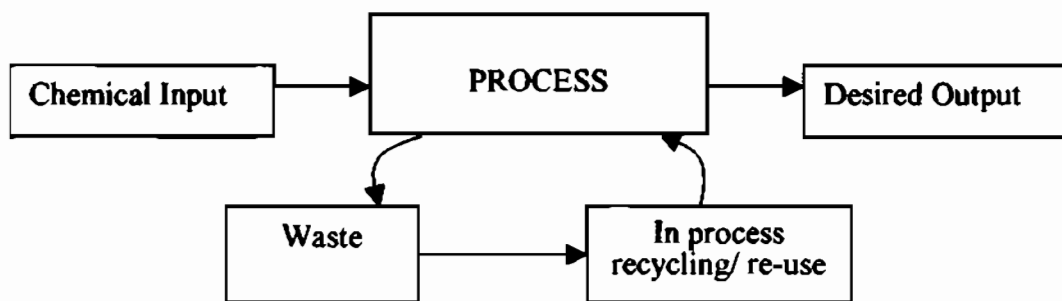


Figure 2.1 Simple industrial process model^{93, 94, 95}

Chemical inputs include primary raw materials which end up in the finished product as well as process, ancillary or secondary raw materials that are not found in the final product but are necessary to run the process.⁹⁴ The latter includes lubricating oils for plant machinery, catalysts to speed up the process, analytical chemicals for process monitoring and control, any personal protective equipment worn by workers and water used as a chemical (raw material), solvent (or carrier) or as a rinse. Output can also be of two types: desirable and undesirable. The desired output is obviously the final product which meets those specifications laid down by the customer or by trade law. Undesired outputs are waste. There are very few industrial plants that do not produce waste when preparing their desired products. Waste is defined as any matter, whether gaseous, liquid or solid or any combination thereof, which is deemed as undesirable or superfluous by-product, emission, residue or remainder of any process or activity.⁹⁶ This means that it exists in material and energy forms, which can be interconverted. Material waste streams include wastewater or liquid effluent discharge, particulate and gaseous atmospheric emissions

and solid waste. These can be conscious and/or accidental emissions. For example the release of chromic acid mist from an electroplating solution into the atmosphere would be an established process waste whereas a vapour leak from a solvent degreaser would be an accidental or fugitive emission. Chemical wastes are often referred to as pollutants and contaminants in the literature.³⁵ In both these cases, the chemicals are present in higher concentration than that found in the natural or ambient environment. This increase is man made through, for example, industrial or agricultural activities. Such waste only becomes a pollutant at these elevated concentrations if it damages the environment whereas it is termed a contaminant if it has no adverse effect on the environment. These wastes are all covered by the National Environmental Management Act No. 107 of 1998 and include the waste produced from metal finishing processes like electroplating and powder coating of workpieces.

Once waste is formed it can be handled in many different ways depending on the amount or volume, its physical form (solid, liquid or gas), its toxicity and its suitability for re-processing. These approaches to handling waste are listed in order of decreasing sustainability in the waste management hierarchy (see Figure 2.2).

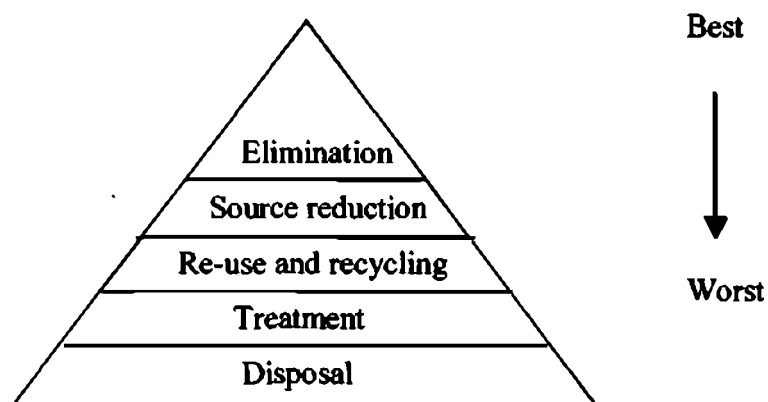


Figure 2.2 The waste management hierarchy^{97, 98, 99, 100}

Waste management looks at using waste minimisation approaches at the upper end of the hierarchy to deal with industrial waste. The ideal approach therefore is to reduce waste at source; that is decrease (minimise) or eliminate (waste avoidance or zero-waste) any waste produced in the process.^{96, 101, 102} This means using less raw materials (which end up in the finished product) and less process chemicals at the start of the process. By not forming waste in

the first place, it means there will be no storage, handling, treatment, disposal or recovery problems of waste. This approach to waste management is termed start of pipe treatment.^{94, 103} The alternative to waste minimisation is the treatment of waste once it has already been produced. This uses waste management approaches from the lower end of the hierarchy to deal with the waste. This means having to re-use or recycle the waste and, where this is not possible, having to treat the waste so that it can be disposed of safely. Re-use and recycling^{104, 105} is concerned with used raw materials (which have been through the process), processed and rejected workpieces and waste. Re-use sends used materials or workpieces through the same process again (in-process recycling which takes place on-site). Recycling looks at re-processing used raw materials etc. in order to make different products or in energy production (waste recycling). Recycling can take place on- or off-site and the selling of waste for recycling can generate income. Such an approach is referred to as end of pipe treatment.^{106, 107}

The hierarchy also defines the order of preference for ranking potential waste minimisation efforts that can be implemented in an industrial process. This is based on achieving the maximum conversion of input to output and the minimum conversion of input and output to waste in a sustainable way. It aims to make high environmental savings or benefits by preventing damage to the environment caused by the creation and disposal of waste. The former involves producing less waste by not using excessive amounts of non-renewable or scarce resources as input to the process.^{94, 96} This avoids depleting raw material stocks by conserving mineral and other non-farmed or cultivated resources. The latter means not placing toxic waste output into the land, water courses or the atmosphere where they can cause damage by migrating, (bio)accumulating or persisting in the environment.^{105, 108} However the hierarchy does not always offer a practical means for enabling industry to prioritise its waste minimisation efforts. The fact that waste minimisation can be expressed in monetary terms as well as by volume or amount of waste can be used to overcome this problem.¹⁰⁴ The cost of producing waste based on raw material consumption has been widely used as a means for selecting suitable waste minimisation options from a range of potential options in order to achieve sustainable waste minimisation.¹⁰² Producing less waste can reduce the economic expenditure on purchasing raw materials (pay for then use), on waste treatment and disposal

and on collecting and transporting both raw and waste material. It also reduces the cost of utilities including water and electricity which, unlike the other raw materials, are used first and paid for later. The waste minimisation audit takes this into account by seeking to identify the most cost effective and viable ways to achieve waste minimisation using established waste minimisation analysis techniques. Other benefits arising from practising waste minimisation include reduced immediate and future criminal risk and liabilities and a better, greener public image.¹⁰⁹ However the financial savings and reduced operating costs which a company can make have been found to be the most significant incentive for the adoption of a waste minimisation approach in industry.¹¹⁰

2.2 WASTE AUDITING IN THE WASTE MINIMISATION PROGRAMME

Waste minimisation is defined as the application of a systematic approach to reducing the generation of wastes at the source.¹¹¹ It applies to all inputs to and outputs from the process. This includes emission to the air, water, or land; utilities consumption; materials used both directly and indirectly in products, processes or operations.

Waste minimisation is accomplished through a Waste Minimisation Programme.^{12, 96} This is a structured, stepwise approach to initiating and sustaining waste minimisation efforts in industry. Many models for such programmes have been published in literature^{94, 97, 105, 108, 112} and one particular example is shown in Figure 2.3 below.

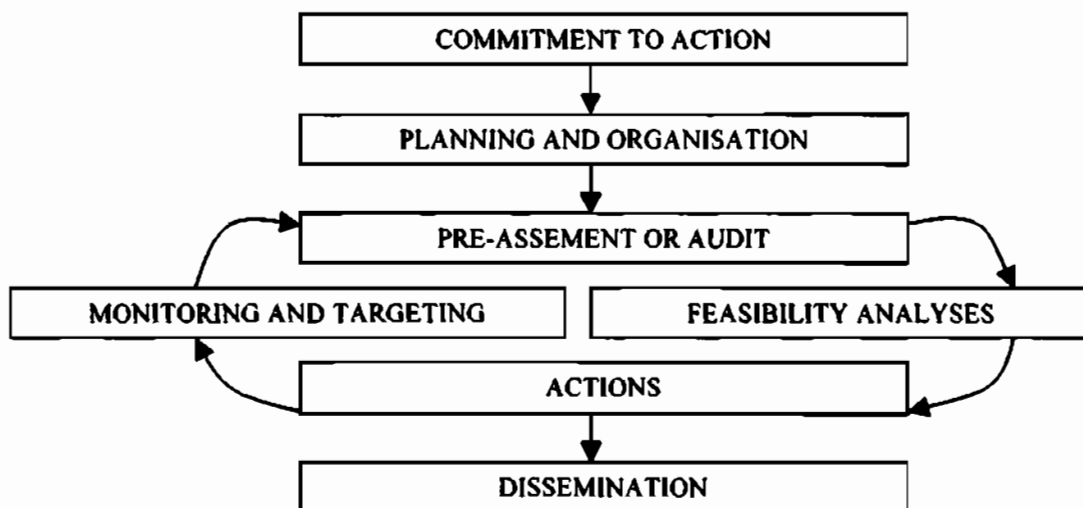


Figure 2.3 The stages for establishing and running a waste minimisation programme¹¹³

The first stage in a waste minimisation programme is to obtain commitment from senior management to run a waste minimisation programme. Once commitment has been obtained the next stage is planning and organisation. The essential elements of this stage are setting overall waste minimisation goals and appointing personnel to carry out the programme. In many cases this has led to establishing an assessment and evaluation task force and appointing a project champion.¹¹⁴ This has been widely reported in the literature and will not be discussed further here.^{105, 108, 114}

The next stage is the waste minimisation audit which deals with data gathering on the composition, flow rate and cost of all process input and output streams for assessment and analysis of the data thus gathered in order to:

- identify waste minimisation opportunities;
- generate waste minimisation options for the opportunities;
- prioritise these opportunities and options for a feasibility analysis.^{105, 114}

The feasibility analysis includes technical, economic and environmental evaluations.

The last stage in the waste minimisation programme is the implementation of the most feasible of the selected waste minimisation options. Once the selected options are implemented, the process is monitored and the performance of the selected options is reviewed. The waste minimisation procedure can be repeated further by putting new options in place to further improve the process.¹¹²

The stage in this programme which will be discussed in detail in this section is the waste audit step (also called the preliminary, initial or pre-assessment step). It is the third stage shown in Figure 2.3. The waste minimisation study reported in this dissertation, involves an audit of an electroplating plant in terms of material wastage and identifies some potential waste minimisation options.

The waste audit identifies, quantifies and prioritises sources of waste and waste streams.¹¹⁴ It also seeks out ways to bring about waste reduction in the process stage. The first step in auditing is to understand the process. This involves establishing all input, output and return

streams in all the stages of the process. This includes waste streams. The waste source is the point in the process where waste is generated. The waste may stay there or may be moved through the process in a waste stream. Such locations of waste generation or accumulation in the process identified by the waste audit represent targets for waste minimisation (reduction).^{94, 108} An established waste problem is known as a waste minimisation opportunity. Waste minimisation options or measures are the (waste reduction) solutions to these waste problems. These have been widely reported in the literature and are discussed in Section 2.3. However some form of waste treatment will always exist until a process produces zero waste. The current waste segregation systems and waste treatment and disposal methods for example chemical treatment, recycling and re-use must therefore be identified for the process.^{21, 94}

Data on composition and flow rate (or loads for a batch process) of these process streams must be collected. This information is then compiled into a Process Description which can be represented in a Process Flow Diagram (see Company and Process Profile in Chapter 3). This data can then be analysed using established waste minimisation audit techniques to determine the composition, quantity and cost of the waste streams. These techniques include a Scoping Audit^{94, 96}, Mass Balance Analysis^{93, 96, 108}, True Cost of Waste Analysis^{93, 94}, Monitoring and Targeting^{93, 94} and Statistical Process Control.^{93, 94, 96} The latter two will not be considered in this study. Cost data must also be gathered for use in the Scoping Audit and the True Cost of Waste Analyses. This is used to charge the cost of the waste directly to the process which generates them and would represent a financial saving which could be made if that waste were not produced.⁹⁴

Some of the required information may already be held in company documents. Such Existing Data can be retrieved for use in the auditing analyses. This is known as a Historical Survey.^{94, 96} Other data will be lacking and will need to be collected as New Data. This is carried out using a Live Audit.⁹³

Data can be collected from various sources which include the company, chemical suppliers, regulators, and trade and research literature.^{94, 96, 114} The data can include raw material purchases and requisition records, utility bills, production records, waste disposal manifests,

process solution and effluent analysis results and articles and publications on the industry. The existing data for this project have been collected from computerised and handwritten company documents, discussions with plant owners and employees, analyses results of plating tanks from chemical suppliers, Material Safety Data Sheets (MSDS) issued by the suppliers and a literature survey. New data has been obtained from on-site measurements made using direct reading instruments, sampling and chemical analyses results of the rinse and drag-out tank solutions and observing work practices.

A Scoping Audit is used to analyse the data using empirically determined percentage savings on raw material, waste and energy streams. To perform a Scoping Audit, it is essential to determine the amounts and costs of raw materials, utilities and wastes. This information is utilised in filling in a waste minimisation cost assessment table (see Table 2.1).

Table 2.1 Waste Minimisation Cost Assessment Table^{93, 103, 115}

<i>Resources and services</i>	<i>Quantity</i>	<i>Cost per year</i>	<i>Scope to save (%)</i>	<i>Scope (min)</i>	<i>Scope (max)</i>	<i>Priority (1=highest)</i>
Materials:						
Raw materials			1-5			
Cleaning agent			5-20			
Packing			10-90			
Utilities:						
Electricity			5-20			
Heat			10-30			
Water			20-80			
Waste:						
Effluent			20-80			
Solid wastes			10-50			
Total						

In the table, each material, utility and waste is allocated an established minimum and maximum scope to save percentage. The scope to save percentages published by Environmental Good Practice Guide for Industry were developed for industries in the United Kingdom. Since no equivalent percentages have been determined for South African industries, these percentages were adopted in this study. Multiplying the cost of each input or output stream by the respective scope to save percentage gives the scope for potential financial saving. Scope (min) is the minimum saving that can be attained and scope (max) is the maximum saving that can be attained through waste minimisation. The scope to save results can be rated to distinguish the

area where the largest savings can be attained. Thus waste minimisation attempts can be focused on those streams.⁹⁶

True Cost of Waste allows the main areas of wastage, which are the most expensive to the company, to be identified. True Cost of Waste is found by adding together the costs of raw materials and utilities which are not converted to product, as well as any other waste-related or associated loss costs.^{93, 96, 116} These include material costs like waste treatment costs, rework costs of rejected products and personal protective equipment. It includes the cost of production time lost through for example process down time during plant repair, setup time for product change over and time taken for reworking items. Potential environmental and financial savings may be calculated for each stream using the True Cost of Waste and the cost of the waste remaining after a waste minimisation option has been put into place. Implementation of waste minimisation options that are considered as “low cost-no cost” measures will bring about financial savings that are very close to the actual cost of the waste.

Put simply, Mass Balance Analysis seeks to fit the collected mass data on material input and output (from composition and flow rate in a continuous process or directly as a mass measurement in a batch process) onto a partial (e.g. a process stream or system therein) or complete process flow diagram. It makes it possible to see quantitatively where the inputs are turned into products and where they are converted to waste. Mass Balance Analysis may be used here to confirm that waste is a real loss and not missing or unmeasured data. This is particularly useful for water usage where (municipality) metered water consumption (input) should equal the sum of the volumes of water calculated as being used in the individual wet steps of the process (output). This can be represented by Equation 2.1.⁹⁶

$$\text{Loss from the process} = \text{Input} - \text{Output} \qquad \text{Equation 2.1}$$

For chemical usage an overall Mass Balance Analysis is carried out using the relationship in Equation 2.2.^{93, 96}

$$\text{Loss from the process} = \text{Input} - \text{Output} - \text{Stock} \qquad \text{Equation 2.2}$$

This means that the volume or mass of purchased raw materials (inputs) should be material not yet used (in the store as stock), or already converted into desired products (outputs) or wasted (loss from the process). This however takes a very broad based view of a process and is often not focused enough to select and rank individual waste streams as potential waste minimisation opportunities.⁹⁶

Equations 2.1 and 2.2 represent Mass Balancing for steady state or equilibrium conditions. As will be discussed in Section 2.3, these principles have formed a basis for setting the water flow rate in running or flowing rinse systems. There are other chemical input examples in the literature where Mass Balance on specific process streams has been carried out. This has involved looking at the significant metal in the plating or passivating solution in order to quantify losses and wastages from the solution. However, there appears to be no similar cases where Mass Balancing analysis has been carried out on organic constituents of the plating solutions. This is probably because such organic chemicals are present in small quantities, their exact chemical identity is unknown (patented by the manufacturer) and they can undergo decomposition mechanisms over time (and/or) at elevated temperature or redox reactions with other chemicals or atmospheric oxygen. In such instances Equation 2.3 gives a more accurate way of quantifying time variable process streams using Mass Balancing.¹¹⁷

$$\text{Loss} = \text{Input} + \text{Generation} - \text{Output} - \text{Consumption} - \text{Accumulation} \quad \text{Equation 2.3}$$

$$\text{Accumulation} = \text{Input} + \text{Generation} - \text{Output} - \text{Consumption} - \text{Loss} \quad \text{Equation 2.4}$$

It takes into account whether or not the inputs are entering the process stream at the same rate as that which the outputs are being removed from the stream. In cases where these are different, a loss or accumulation of a component of the process stream will result. Chemical reactions taking place in a process lead to the generation of new substances through the consumption of raw materials. The migration of raw materials through a process (metal ions in drag-out for example) may also give rise to the presence of loss and accumulation terms (factors) in Equations 2.3 and 2.4. This results in a non-equilibrium or unsteady state condition and presents a more complicated Mass Balancing problem.

Monitoring and Targeting looks at the consumption of input (raw materials, water, gas, electricity or labour {as in hours or number of employees}) and the level of output (product meeting specification, rejects, turnover, solid waste or effluent) arising from that consumption.^{93, 96} This means that both input and output or input alone are potential targets for waste reduction. A linear relationship between the former (plotted on the y axis) and the latter (plotted on the x axis) over the same time point or period is assumed. This involves establishing (by measurement during down time or calculation when the process is running) the quantity of an input consumed at zero production (at $x=0$).⁹⁶ This is termed the base load of the process. By considering the scatter or variability of the data and placing a line of best fit through the data points, a profile of the current situation can be drawn and a target for reduction of consumption can be set. If the new line then falls below the target line then the waste minimisation option which has brought about this improvement has been successful. The environmental performance guides publications from the Environmental Technology Best Practice Programme (Envirowise) have adopted this technique to show graphically the scope to save by indicating the acceptability of levels of waste (water and powder) or output at particular raw material consumption levels.¹¹⁸

Waste minimisation options, generated in Stage 3 of the Waste Minimisation Programme (see Figure 2.3) can apply to any of the stages in the process. This means options can be changes made to the input, to the manufacturing technology or to the output.^{100, 104, 119} The term “process change” has been used in the literature to cover input material changes and technology changes.^{97, 119} Changes in input can be brought about by reducing the amount of the original raw material used in a process to ensure the correct amount, rather than excess, is used and not wasted. Substituting the original raw material with a less toxic one or the same material containing fewer impurities can also effect such changes. Using a less toxic material cuts down on the level of hazardous waste and hence the amount of chemicals required to treat it. Using a better grade of the same material can help to avoid the introduction of impurities into the process and lower the formation of unwanted by-products resulting from the reaction of the impurities. Where the source of the raw material can be replenished then the original raw material can be substituted for a renewable alternative. This means the planet’s stocks can be replaced and not depleted permanently. Changes can also be made to the process technology or

means of production.¹⁰¹ This can take one of two forms – structural changes which include alterations to equipment or to plant layout, or operational changes which include improved operating practices such as changes in the running temperature, pH or time and waste segregation. The latter is normally referred to as “good housekeeping”.¹¹⁹ Good housekeeping applies where human intervention in the manufacturing operation can bring about better management, administration and functioning of the process. This includes for example giving attention to inventory control, production schedules, raw materials (out of date, excess or obsolete chemicals) and product storage, maintenance and material handling and additions to prevent spills and leaks and less downtime on the process. Wastes (waste minimisation opportunities) and the waste minimisation options and measures used to combat the generation of these wastes are well documented in the literature and are reviewed in Sections 2.3 and 2.4 respectively.

It is more difficult to make changes to the product, as this is dependent on the customers' demands. Customers often want a certain product made to certain specifications that will meet their needs. However it may be possible to persuade a customer to look at an alternative especially if it reduces the cost.

Simple “no cost–low cost” options with immediate benefits have been preferred by metal finishers for implementation before the more expensive or time consuming choices. Examples of this in the case of small and medium scale enterprises (SME's) are plentiful in the literature.^{118, 120} They are often found to be achieved by simple housekeeping measures.

New data from chemical analysis can be used to determine the costs of wasted raw materials in wastewater. Concentrations of elements which originate from the raw materials in the wastewater can be measured in the effluent discharge from the electroplating line. The mass of elements in the effluent stream that originate from the raw material can be calculated from the volume of the effluent and the contaminant concentration. This can be expressed as a mass or volume of that raw material if the composition of the raw material is known. This composition can sometimes be obtained from the MSDS or can be sought directly by personal

communication with the supply house or manufacturer. This is determined over a representative time period and then expressed both as a daily and annual amount and cost.

2.3 WASTE MINIMISATION OPPORTUNITIES IN ELECTROPLATING

Common waste types in electroplating may be considered as either 1) unused raw materials for example the constituents of contaminated rinse water, spent process solutions and spent stripping solutions or 2) new undesirable products such as rejects and by-products formed in process solutions and sludge. These waste minimisation opportunities can arise from both chemical and electrochemical reactions in aqueous solution and from chemical mobility within the process. Some waste minimisation opportunities are given below.

- 1) Wastewater which contains unused raw materials e.g. cyanide, metals and impurities from rinsing of process solution dragged-out on the surface of the workpieces or in/on barrels and jigs and in spent process solutions.
- 2) Sludge formed from the chemical treatment of exiting rinse water and the purification of process solutions. It is usually composed of heavy metals in the form of metal hydroxides, sulfides and sulfates.
- 3) Carbonates and organic derivatives formed from the breakdown of chemicals added to plating solutions e.g. cyanide and brighteners respectively.
- 4) Gaseous emissions including hydrogen and oxygen formed at electrodes due to electrolysis of water in plating solutions; and acid and alkali mists resulting from hot or electrolytic cleaners and plating solutions.
- 5) Plating metals and impurities dissolved from the anodes into idle and/or working plating solutions.
- 6) Unsegregated wastewater from rinsing operations.
- 7) Metal pieces including workpieces and wires (used for attaching the workpieces to jigs) that have fallen off jigs and remain at the bottom of tanks. After a period of time the workpieces start to react with the tank solution and contaminate it with iron, zinc or copper impurities.
- 8) Corrosion products from flight bars, racks and tanks.
- 9) Spills and splashes of solutions onto the floor and into adjacent tanks during transfer of workpieces and make-up or top-up of solutions.

- 10) Discarded filters and metal powder in anode bags.
- 11) Solution leaks from faulty tanks, pumps and filters.
- 12) Airborne pollutants entering the solution.
- 13) Substitution of toxic chemicals whose effluent requires chemical treatment prior to discharge to the sewer with a safer chemical e.g. Cr(VI) replaced by Cr(III) or by zinc.

2.4 WASTE MINIMISATION OPTIONS AND MEASURES

Only “low cost–no cost” waste minimisation measures or options will be discussed here. Unlike those options which need capital investment, “low cost-no cost” measures do not always need to undergo a feasibility analysis prior to their implementation into the waste minimisation programme. The literature shows that the important waste minimisation measures are associated with reducing the consumption rate of input e.g. water, materials and waste treatment chemicals into the process (Section 2.4.2) and making simple changes in procedure and administration (Sections 2.4.1 and 2.4.3).^{12, 17, 97}

A literature review of waste minimisation practices used in the electroplating industry has established two main areas in which waste minimisation options and measures can be assessed. These are firstly strict waste source reduction and secondly in-process re-use or recycling.^{100, 101} The latter option does mean waste is generated during the manufacturing process. However because no waste leaves the process, this fact has not been regarded as challenging waste minimisation principles. Rather than being thrown away the waste or a component of it is returned to the process for its intended (re-use) or other (recycling) purposes. Conversely, recovery of the waste for recycling into a different process (on-site or off-site) or for re-use at another site has not been considered as a true waste minimisation option. This makes them important factors in determining the True Cost of Wastes.

Most of the waste minimisation options concerned with source reduction have been directed at preventing pollution of the process solutions, particularly the plating baths. The migration of chemicals from one solution to another and by-product formation from side reactions in the solution have emerged as significant waste minimisation opportunities in electroplating.

Together these have led to the carry-over of raw materials, impurities (by-products) and released surface contaminants in the process solution on the surface of the workpiece into subsequent tank solutions. This is referred to as drag-out in the literature.¹² Conditions that allow neat process solutions to flow freely off the surface of the workpieces and which promote contact between the water in the rinse tanks and the workpieces in order to wash off drag-in and dilute the drag-out have been used to reduce drag-out levels. The body of the literature on drag-out reduction and other waste minimisation techniques is vast but is largely qualitative and generic in nature.^{16, 121} The results of the literature survey show that a lack of specific measurements at a base line level and an approach concentrating on the general overall process rather than on individual process streams, has contributed to little accurate quantitative treatment of waste minimisation opportunities and options. This will be dealt with in Chapter 7. This is especially so with those complex processes. This is understandable for three reasons:- the cost and the effort involved in obtaining reliable chemical analytical data of complex systems, the dynamic and changing nature of the production processes, and scheduling the limited publication of detailed data according to the confidentiality agreements struck between researchers and industrialists. The findings of the literature survey are discussed below.

Three main sources of pollution of process solutions have been identified from the literature and from observation.^{122, 123} These are:

- 1) insufficient drainage of workpieces leaving the process (rinse) solutions
- 2) insufficient rinsing of the solution off the surface of the workpieces
- 3) insufficient maintenance (for example purification and monitoring) of the process solution

The documented waste minimisation options or measures used to tackle each of the above waste minimisation opportunities are discussed in Section 2.4.1 to 2.4.3 and discussed below.

2.4.1 DRAINAGE OF WORKPIECES

Promotion of better drainage of process solution from the workpiece as it leaves the tank and of the return of most to the solution has received much attention in the literature^{17, 121, 122, 123, 124}

Documented ways to improve drainage are listed in Table 2.2 below.

Table 2.2 Waste minimisation measures and options for improving workpiece drainage^{12, 16, 17, 105, 122}

1) drip time	5) positioning of workpieces on the jig
2) drip bars	6) shape of the workpieces
3) rate of withdrawal	7) composition, concentration and temperature of the solution
4) agitation	8) drain board

Drain or dripping time is the length of time in which the workpieces are placed above the process solution tank before being moved to the next tank in the line.^{12, 21} If this time is cut short, then the solution adhering to the workpiece surface will not all have flowed off the surface before the workpiece is sent to the next tank. A drain time of at least 10 seconds has been established as being able to reduce drag-out by up to 40%.^{121, 122, 123, 124} It has been found that the drain time on manual lines is frequently shorter than it should be. This is due to operator fatigue and the need to work fast in order to meet the set production rate. In rack plating, drain time has been successfully extended by fitting above the process solution a drip bar (drain bar) onto which the operator can hang the racks.¹⁰⁵ This relieves the strain associated with holding the racks in position. Programming of delays in automatic process lines has been used to increase drain time and to fix immersion time. On manual lines the time to remove an immersed item is often signalled by a buzzer or a flashing light but there is no such indicator for drip time.

The speed with which workpieces are taken out from a process bath has a major impact on the drag-out volume. The withdrawal speed determines the quantity of solution left on the workpieces. The faster a workpiece is lifted out of a solution the more solution is dragged out on it and the longer it takes to drain off.²¹ Some platers believe that more time should be given to slow withdrawal rather than to extend dripping for maximum drainage.¹²³

Agitation refers to the mechanical movement of the workpieces above the solution. Shaking and tilting of jugged workpieces and rotating of barrels has been carried out above the process solution in order to increase drainage rate.

The careful positioning of workpieces on a jig so as to avoid the trapping of chemicals in hollows and siphoning of solutions up tubes ensures quick and complete drainage of the process solutions.²¹ Racking workpieces so that the hollows or cavities open downward and pipes or tubes are vertically at a slight incline facilitates good drainage. In some instances holes have been made in workpieces as an outlet through which process solution can drain.¹²¹

The inherent resistance of a solution to flow is measured by its viscosity. The volume of drag-out that adheres to the surfaces of workpieces is proportional to the viscosity and surface tension (tendency for a liquid to form droplets instead of a film on a surface) of the solution.¹⁷ By reducing the surface tension and viscosity and by lowering the concentration of the active process chemicals together with the use of surfactants causes the solution to spread and run off the workpieces' surfaces more easily.¹²³ This may be further enhanced by raising the temperature of the solution.¹² However, too high an operating temperature can cause decomposition of additives and give evaporative chemical deposits on the surface after withdrawal from the hot solution. The buildup of chemical pollutants or the presence of excess raw materials in the solution can also increase viscosity and so retard drainage. It is estimated that drag-out could be reduced by 50% by improving run off.¹² Solutions run at the lower end of the specified concentration range and at a suitable temperature to keep the concentration of the dissolved salts to a minimum have been found to result in good drainage.¹⁷

Drain boards are slanting surfaces that bridge the gap between the process and rinse tank.¹²² They are used to collect drag-out from workpieces on racks and direct the solution back into its original tank. Drain boards not only save chemicals and reduce rinse water requirements but also improve housekeeping by keeping the floor dry.¹²⁵

2.4.2 RINSING OF WORKPIECES

Rinsing is used between each wet process step that makes up the metal finishing process e.g. pre-treatment, electroplating and post-treatment. Rinsing is carried out between the pre-treatment steps of alkali and acid cleaning, in chromium plating, in the plating steps of copper cyanide, in acid nickel and chrome plating and in the post treatment step of neutralisation.

Rinsing is used to:^{18, 19, 126}

- stop chemical reactions on the surface of the workpieces by washing away the raw material reactants which come from the process solution;
- remove raw materials and extrinsic chemicals from the surface of the workpieces;
- minimise contamination of the next tank in line;
- avoid salt coatings collecting on the finished workpieces.

Successful rinsing can obviously be carried out using copious amounts of water to flush the surface of the workpieces directly or while they are submerged in a tank of water. However, excessive use of water is not consistent with the principle of waste minimisation. Much research has been done on how best to achieve good rinsing (rinsability) while using as little water as possible.¹ Descriptions of established methods of what is termed drag-out reduction together with water conservation have been found in the literature and are listed below in Table 2.3. Point 12) but will not be discussed here.

Table 2.3 Waste minimisation measures and options for improving rinsing^{17, 105, 127, 128, 129}

1) drag-out tank	7) slow flow rates for flowing rinses
2) drip tank	8) design of flowing rinse tanks
3) drag-in – drag-out rinses	9) dwell (soak) time
4) rinsing over the plating tank	10) agitation
5) flowing (running) rinses	11) barrelling or jiggling of workpieces
6) multiple rinse systems	12) water re-use from air cleaners in local exhaust ventilation systems etc.

The direct return of neat or diluted drag-out back into the plating solution has been achieved by using entries 1) to 4) on the list of methods given in Table 2.3. However, many cases have been reported in the literature where the drag-out must be concentrated or purified in a separate step prior to being put back into the plating solution. Alternatively the plating solution itself undergoes regular or continuous purification which will be discussed in Section 2.4.3. Similar situations have been found for flowing rinse configurations {entries 5) to 8) on the list}. But in these cases the rinse water being returned to the rinse system has always been processed in some way first to remove chemicals. The return of drag-out or rinse water is discussed more fully later in this chapter. However, it is limited to certain processes and can require the use of

specific and expensive waste minimisation options. This is because the solution or water entering or leaving the system must be balanced. For example the volume of water exiting the plating solution as drag-out and evaporation (caused naturally and/or forced by using an atmosphere or vacuum evaporator) must equal the volume of solution coming in as drag-in and top-ups made directly from the drag-out tank solution and/or concentrated and returned drag-out solution. The drag-out (recuperative, static, still, stagnant or recovery rinse) tank solution is a static immersion rinse. The drag-out tank is initially filled with clean fresh water and as workpieces go through it the chemical levels rise. This is because drag-out from the plating solution is washed from the surface of the workpiece and accumulates in this tank. This is preferred over spray rinsing especially when the workpiece has a complicated shape or structure. Making up a decrease in volume of the solution in the plating tank with saved drag-out (recovery rinse) is termed "closing the loop".¹²⁸ This means that the evaporation losses must be high enough to give the tank room for drag-out return (neat or concentrated) without risking the tank overflowing. Where the plating solution temperature is high above 50 °C and the drag-in is low, the plating tank is more able to receive recovered (treated or not) drag-out.^{122, 128} When the concentration of the drag-out tank solution has reached a suitably high level then the neat drag-out can be added to the plating solution without concentrating but may need purification (see Section 2.4.3).

A drip tank is an empty tank which captures drag-out after plating but before rinsing.¹²¹ It is found to be less commonly used than a drag-out tank. It is more suitable for barrelling where the barrel can be rotated to increase drainage from workpieces and can maintain continuous dripping. Once sufficient solution has been collected it is returned to the plating solution. There is no dilution of the drag-out here so this can be used in combination with low temperature plating solutions.

Drag-in drag-out rinsing has been used for plating baths which are not heated. Essentially it involves dipping the workpieces in the drag-out solution before they enter as well as after they leave the plating baths. This is carried out in order to restrict the direct drag-in of the rinse water into the plating bath. Sometimes this means using the drag-out tank twice (double dipping). This usually involves passing the workpieces over the plating solution to reach the

drag-out. However this is not in keeping with good waste minimisation practice. The alternative is to have two static tanks (which may be connected to circulate the solution) either side of the plating tank. This is common for cyanide zinc plating where the volume of the rinse water dragged-in is often in excess of the combined volume drag-out and evaporation.

Rinsing over the plating tanks means that the workpieces are held above the plating solution and flooded (hosed) or sprayed with rinse water. This water washes the process solution covering the surface of the workpiece back into the plating solution. Spray rinses have been found to use less water than hoses and have been used on occasions on low temperature plating baths.^{17, 18} However the workpieces must have a simple structure with no hollows or cavities.

Air flow (air knives) can also be used to blow rather than wash off the solution from workpieces back into the tank.¹²⁷ However, this requires careful operation so as not to dislodge any workpieces from the rack with the force of the air and not to dry and hence stain workpieces. The latter problem has been overcome by using humidified air.

The results of the literature survey shows that a second closed loop system, termed zero discharge, can be applied this time to the flowing rinse system.^{12, 121} In this case as well as recovering and returning chemicals to the plating process, the effluent water from a flowing rinse is treated and can be similarly re-used. These two operations together are referred to as total recycling which means no materials other than products leave the process.^{12, 105}

There are a number of means reported by which a closed loop system can be established.^{12, 105, 121, 128} These have been developed to ensure that impurities from the process solution and rinse systems are not recycled in the process. They fall under three broad categories according to waste minimisation theory and are given below:-

- purification of the plating solution for re-use by removing pollutants and impurities;
- chemical recovery from the static and flowing rinse water: this involves separation; of active plating chemicals from impurities and concentrating the solution to make it viable for re-use or for reclamation;

- water recovery from the flowing rinse for re-use or to comply with effluent standards for discharge or to reduce volume of effluent.

There are many ways for recovering chemicals for potential re-use in the plating solution besides using static rinses.^{11, 12, 18, 124} These include low flow rinsing, multi-static (2 or 3 stage static rinse systems), membrane filtration with micro-filtration (MF) or reverse osmosis (RO), evaporation (E) and ion exchange (IE). MF, RO, E and IE have also been used in the treatment of spent plating solution, obtaining purer rinse water from raw water, the treatment of chemically treated wastewater from an effluent plant and for end of pipe waste treatment.^{12, 17, 121, 128} These are however expensive. Rinsing is less costly, simpler and the benefits can be quickly felt (short payback period).

In chromium plating the solution in the static or drag-out rinse tank placed immediately after the plating solution has been traditionally used to top-up the plating solution. This has been done to make-up the drag-out and the plating losses from hot process solutions and save Cr(VI) usage. But the returned drag-out often requires purification first to prevent the return and buildup of undesirable concentrations of Cr(III), Cu(II), Fe(II), Fe(III) and Zn(II) for example in the plating solution. Other rinsing methods like flowing rinses have been used to avoid the transfer of solutions from one tank to another by lowering drag-out losses and using little water.

Flowing or running rinses supply a (theoretically) constant flow of clean water into an immersion rinse tank full of water. This water washes off and disperses the dragged-in chemicals on the workpiece surface into the bulk rinse solution. This solution flows out of the tank to be discharged to the drain or fed to another tank. After some time the concentration of the dragged-out species reaches a stable level in the rinse water which is less than the concentration in the process solutions. This concentration level is related to the rate at which the water flows through the tank. The volume of solution that must be removed from the rinse tank (D in Equations 2.5-2.8) and replaced with fresh water in order to keep the rinse water concentration in the tank at a fixed level, C_R in Equations 2.5-2.8, therefore depends on the

rate, Q in Equations 2.5-2.8, at which water flows through the tank. This is expressed as a rinsing criterion and is basically a dilution factor (see Equation 2.5).^{130, 131, 132}

$$\frac{Q}{D} = \frac{C_D}{C_R} \quad \text{Equation 2.5}$$

$$\frac{Q}{D} = n \left(\frac{C_D}{C_R} \right)^{\frac{1}{n}} \quad \text{Equation 2.6}$$

$$\frac{Q}{D} = \left(\frac{C_D}{C_R} \right)^{\frac{1}{n}} \quad \text{Equation 2.7}$$

$$Q + D = \frac{C_D}{C_R} \times D \quad \text{Equation 2.8}$$

Q = Rinse water flow rate through the tank solution, m^3/hr

D = Drag-out flow rate into the tank, m^3/hr

C_D = Concentration of the drag-out coming into the tank (drag-in)

C_R = Concentration of the rinse solution in the tank

n = number of stages (tanks) in the rinse system

Equation 2.5 describes the situation at equilibrium when there is a steady state and the solution concentration has ceased rising. In practical terms this arises after between 1000- 10000 rinses (i.e.1000-10000 loads have passed through the rinse tank) or over three holdup times (i.e. residence time of water in the flowing rinse tank) as defined by Equation 2.9.^{18, 126}

$$\text{Holdup time} = \frac{\text{Volume of tank (m}^3\text{)}}{\text{Rinse water flow rate (m}^3\text{/hr)}} \quad \text{Equation 2.9}$$

Equation 2.5 shows that the cleanliness of the workpiece cannot be improved by increasing the dwell (residence) time in the rinse solution. No matter how long the workpiece spends in the rinse solution it will always leave the rinse solution covered with drag-out which has the same concentration as the rinse solution.

Immersion rinsing and cleanliness can be improved by increasing the flow rate (adding more clean water) or by having a series of these flowing rinse tanks, one after the other.¹³² The extension of a single stage rinsing by introducing two or more rinse tanks each with its own supply of fresh clean water is called parallel rinsing or individual feed rinsing.¹³⁰ However, these arrangements use a lot of water. Equation 2.6 shows the volume of water or flow rate, Q , required to achieve a specific rinse water quality, C_R , when n , the number of individual rinse tanks are arranged one after the other. (The rinse water quality in Equations 2.5, 2.6 and 2.7 is not well defined in the literature. It has been quoted empirically and most frequently in terms of conductivity and total dissolved solids and less often in terms of individual elemental concentration. This limits the use of these equations for those pollutants which present a particular operational or disposal effect for rinse solutions).

It is possible to achieve better rinsing by having a number of these flowing rinse tanks placed after the process solution. However, this will use proportionally more water. Where the water exiting the rinse tank becomes the influent water for another tank significant water savings have been reported.^{18, 128, 129} This rinsing technique is called cascade or multiple stage rinsing (see Figure 1.2 in Chapter 1). This happens when two or more rinse tanks are connected so that the fresh rinse water comes into the tank which is furthest away from the process tank (cleanest rinse solution) and flows through any intervening tanks finally to the tank closest to the process tank (dirtiest rinse solution) where it leaves the rinse system as wastewater. Such multi-staged rinsing is termed counter current (counter flow) or co-current rinsing depending on the direction in which the workpieces move down the line. The preferred rinsing setup in industry has been the counter current option in which the workpiece is rinsed first in the dirtiest rinse and finally in the cleanest rinse water. This means it moves in the opposite direction to the flowing rinse water. The flow rate needed to maintain a specific rinse water quality can be calculated using Equation 2.7.¹³¹

It has been shown that to maintain the same rinse water quality (dilution factor) less water is used according to the following rinse system order.¹³⁰

Single rinse > Parallel rinse > Counter current rinse

Further flowing rinse systems, in contrast to static rinses, should not have to be dumped and recharged and so production time is not lost because a tank is out of commission. However, there are restrictions on the application of these equations. These equations (Equations 2.5 to 2.7) do not hold under conditions of low flow rates and incomplete rinsing. It has been found that when the rinse tank volume is under ten times the drag-out volume, Equation 2.8 must be used.¹²⁸ This allows for the dilution effect that the drag-out volume will make at low rinse volumes. Incomplete rinsing is found when the drag-out film on the workpiece surface is not washed off immediately and then well mixed into the bulk rinse water. These equations will be used in the water usage analysis in Chapter 7.

Agitation has been used to ensure equilibrium rinsing i.e. where good mixing of the drag-in and the water in the rinsing tank is achieved quickly. This is carried out either by moving the workpieces in the solution or by moving the solution over the workpieces. The former can be achieved manually or mechanically, by moving the jig backwards and forwards or/and up and down or rotating the barrel in the tank solution. In the latter case, sometimes the natural movement of the water in a flowing rinse system will be adequate. This may be the case when the water enters the tank at the bottom, travels diagonally across the tank and exits at the top of the other side and vice versa. However often pumping is needed over and above gravitational flow. Air agitation is often used. A perforated pipe runs across the bottom of the tank and compressed air is forced through it generating streams of bubbles through the rinse. Barrelling and jiggling will be discussed more fully in Chapter 3.

2.4.3 MAINTENANCE OF PROCESS SOLUTION

The chemicals in process baths are operated within specific concentration ranges recommended by the chemical suppliers. The chemical composition of a bath alters continuously during its use through various mechanisms such as the surface treatment reaction, drag-out, evaporation, side and decomposition reactions. This means there has to be regular addition of chemicals and water to the solution in order to keep the specified concentration level constant. The level of unwanted chemicals in the bath must be minimised. Several common methods used to detect and remove pollutants from process solutions have been identified from the literature and are shown in Table 2.4.

Table 2.4 Methods of detecting and removing pollutants from process solution^{7, 66, 128}

- 1) monitoring of solution chemistry, conductivity levels, pH, temperature and density
- 2) monitoring the current consumed over a specified time period (ampere-hours)
- 3) filtration and carbon treatment of the plating solution
- 4) addition of chemicals to precipitate out impurities
- 5) use of electricity to plate out impurities (dummying)
- 6) removal of the contaminant source e.g. workpieces dropped from racks and left lying on tank bottom

Various solution monitoring techniques have been developed to detect the buildup of impurities in the bath. These include simple measurements like pH, density, conductivity, ampere-hours as well as elemental and other chemical analysis of the process solution and the consumption of active plating and processing chemicals.^{7, 66} Monitoring allows the correct amount of raw materials and treatment chemicals to be added before any plating problems occur.

A conductivity measurement is one of the simplest ways of determining the quantity of inorganic substances present in effluent and flowing rinse water tanks.⁷ Monitoring the conductivity of rinse water helps to maintain chemical concentrations of pollutants at levels that provide adequate rinsing and prevent excessive drag-in to subsequent process tanks.¹³³ By checking conductivity measurements the amount of water used for rinsing can be also reduced using a conductivity based control system to automatically adjust the rinse water flow rate.¹⁴ Chemical changes taking place in the plating solution itself can be monitored by recording specific density (Baumé reading), pH and ampere-hour measurements. The densities of the process solution can be measured directly using a hydrometer. The Baumé hydrometer scale is calibrated in units of degree Baumé (⁰Bé). These readings can be converted to specific density (see Equations 2.10 and 2.11) or to CrO₃ concentration (using conversion tables):⁸⁹

$$D = \frac{144.3}{144.3 - N} \quad \text{Equation 2.10}$$

$$\delta = \frac{144.3}{134.3 - N} \quad \text{Equation 2.11}$$

D = density for liquids heavier than water

δ = density for liquids lighter than water

N = Baume scale reading

The CrO_3 levels range from 10.5 $^{\circ}\text{Bé}$ (specific gravity 1.080) to 32.0 $^{\circ}\text{Bé}$ (specific gravity 1.285) and a reading of 21.5 $^{\circ}\text{Bé}$ is equal to a CrO_3 concentration of 250 g/L.^{23, 134} The presence of impurities including iron and copper can lead to erroneously high Baumé readings.^{7, 23}

Current, like chemicals, is consumed in the plating process. By monitoring the amperes passed through the solution over time, the amount of chemicals used up can be estimated. This has its basis in Faraday's Law (see Equation 1.15). Chemical suppliers quote the values of ampere-hours at which chemical additions should be made. This is particularly useful for monitoring additive levels e.g. brighteners. These substances are present in small amounts and are not easily chemically analysed. This means chemicals can be added to the solutions at the appropriate time to prevent the bath running below the specified level as chemicals are used up in the plating process.

Filtration is one of the common methods used to remove insoluble suspended solids from a plating solution. These substances have been found to enter the tank from many sources e.g. airborne dust, anode corrosion, drag-in on the workpiece and impurities in make-up chemicals. Suspended solids may cause roughness, porosity, poor adhesion and burning on workpieces.^{14, 63} Filtration of some plating solutions is carried out continuously e.g. Ni while for other solutions it is less frequent (annual) e.g. Cr, Cu, Zn. In both cases the solution is usually pumped out of the tank, through the filter into an empty tank, and the cleaned solution pumped back into the tank. Various specialised pieces of equipment have been developed for filtration of electroplating solutions. The most widely used are wound cartridge filters and disc plate or precoat (diatomaceous earth) filters (see Figures 2.4-2.6 and Figure 3.3 in Chapter 3).¹²⁸ Cartridge filters can be utilised for both small and larger tanks while precoat filters are used mostly for large tanks. The filter media are selected depending on the chemical composition of the solution. Size of filtration systems are based on solid loading and flow rate of the plating solution.¹²⁸

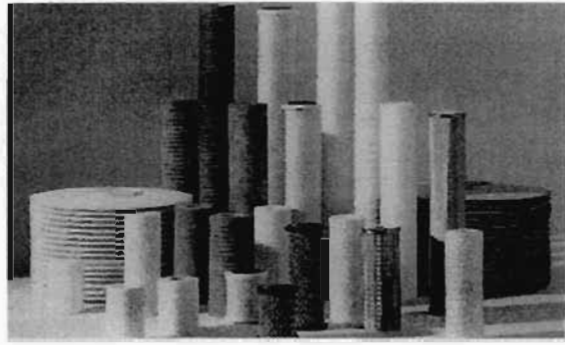


Figure 2.4 Types of filters used in electroplating¹³⁵

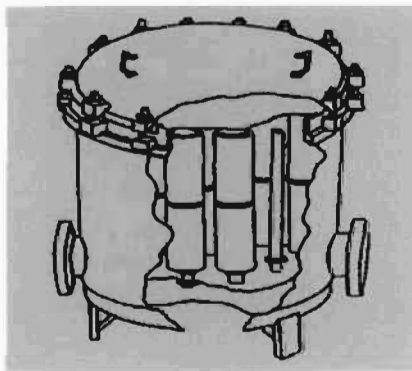


Figure 2.5 Cartridge filter assembly¹³⁵

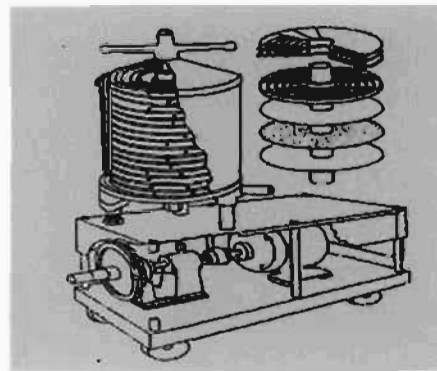
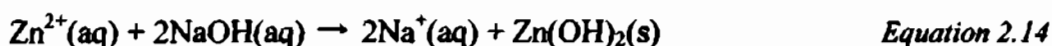
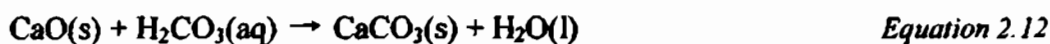
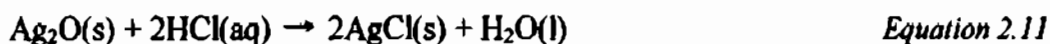


Figure 2.6 Disc and plate clarifying filter assembly¹³⁵

Soluble organic and inorganic bath contaminants cannot be removed by ordinary filtration. The organic contaminants are removed by treatment with activated carbon.^{7, 136} The carbon adsorbs these contaminants and removes them from the solution. Carbon treatment can be applied by various methods such as carbon filtration cartridges, carbon canisters and packing between precoat filters.¹²⁸

The inorganic contaminants, such as dissolved base metals e.g. Fe, Zn and Pb, dragged-in treatment chemicals containing Cr, Ca as well as P and Cu from wiring workpieces are removed by chemical methods such as precipitation or by dummy electroplating.¹³⁶ Precipitation is usually a batch process which is frequently performed by pumping the solution into a spare tank where it is chemically treated and filtered and then pumped through the filter back to its original tank.¹²⁸ The precipitated sludge is left behind in the spare tank for disposal. Chemicals which can be used for the precipitation purpose include barium hydroxide or

carbonate for the removal of sulfate in a chromium bath (see Equation 3.6 and 3.7 in Chapter 3), silver oxide or silver carbonate to remove chlorides from chromium plating baths (see Equation 2.11), lime addition for the removal of carbonate in silver cyanide baths (see Equation 2.12) and nickel carbonate treatment of nickel plating baths to remove metal contaminants such as iron and aluminum (see Equation 2.13).^{66, 128, 137} Iron, zinc and copper can be precipitated out of the solution by treatment with NaOH at high pH (see example Equation 2.14).



Dummy plating is an electrolytic treatment method used to plate out or oxidise metallic ion contaminants from a process solution.¹²⁸ The process uses low current density usually between 0.2-0.5 A/dm² to plate out metallic ion contaminants such as copper, iron and zinc from a process solution onto scrap metal.^{7, 138} This has been found particularly useful for purifying nickel plating baths where hydroxide precipitation leads to loss of nickel as Ni(OH)₂. High current density between 10-30 A/dm² is applied to oxidise Cr(III) to Cr(VI) in chromic acid baths used in chromium plating or chromic acid based anodising operations.¹²⁸

When workpieces hung on a rack move from one tank to the other in the plating line, they may drop into the process solution and dissolve. This may cause Fe or Zn contamination of the solution. Regular removal of these dropped workpieces can help to prevent contamination of the process solution.

Maintenance of process chemical solutions helps to extend their useful lives and improves their operating efficiencies and effectiveness.⁷ The former reduces the dumping frequency and re-charging of process and rinse solutions and the latter reduces reject rates from poor quality plate e.g. those with cracks, inclusions and satins.

CHAPTER 3

COMPANY AND PROCESS PROFILE

CHAPTER 3

COMPANY AND PROCESS PROFILE

3.1 COMPANY DESCRIPTION

Saayman Danks Electroplating operates from premises in Durban and Pinetown. The company is a job shop which means it plates and polishes workpieces brought to the factory by customers such as general engineering companies and government departments. A so called captive shop on the other hand electroplates workpieces manufactured in-house.¹³⁹ The factory was established in 1981 and employs around 70 staff members. The plant operates from Monday to Friday for effectively 234 working days in a year. Many changes have been made to the factory over the years in order to maintain its leading position among the competing companies of KwaZulu-Natal and South Africa. For example, there has been a recent amalgamation with Pinetown Electroplaters and the introduction of automation into the chromium plating shops.

The company carries out a number of different surface finishing processes. These include chromium, nickel, copper, cadmium, silver, gold, tin, brass and zinc plating, irridising, and anodising. The workpieces coming to the factory to be finished are generally made from steel, copper, brass, zinc alloy and aluminum. Both jig and barrel plating are employed.

The factory gets water from the municipality and an on-site borehole. The plating lines excluding chromium generally use borehole water which is metered. There is a dual water supply system to these lines which allows them to be switched from borehole to mains water if the supply dries up. There is also one water meter used to read the total municipality water coming to the factory. The chromium electroplating setup is discussed in Section 3.2. The chemicals used by the factory are purchased from many different suppliers. Some supply houses are used regularly e.g. Orlik, Chemsolve and Protea while other chemical traders are used when they offer the company a competitive price on materials.

The workpieces which are plated range from small items such as electrical components, screwdrivers, bath handles, chains, knobs and bezels (see Figure 3.1) to larger items like

fences, pipes and gates. The plant has developed considerable capacity and flexibility in order to accommodate all varying plating requirements.

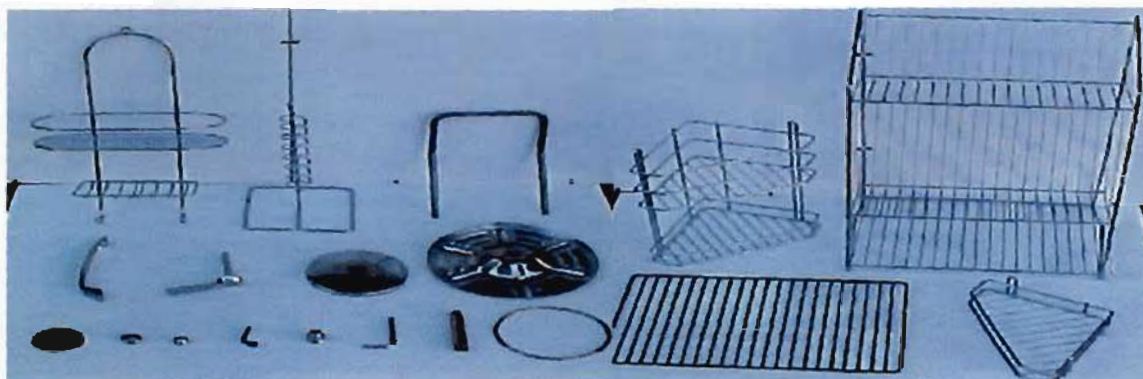


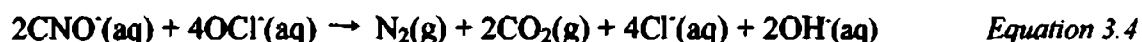
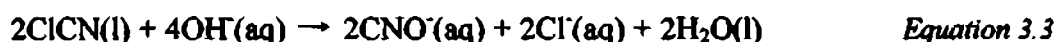
Figure 3.1 Some decorative chromium plated workpieces at Saayman Danks electroplaters

The factory has a mechanical finishing system, a vapour degreaser, an effluent treatment plant and a sludge dewatering unit. The mechanical finishing includes processes such as polishing and blasting. This finishing process is used to remove scales from workpieces through mechanical means. Such finishing eliminates or minimises chemical usage in the pickling process to follow, smut formations and hydrogen embrittlement.^{11, 22} The vapour degreasing unit uses a condensing vapour of a chlorinated hydrocarbon solvent such as trichlorethylene (C_2HCl_3), above a reservoir of boiling solvent to remove heavy oil and grease from the workpieces prior to sending them to each plating line.²³ The vapour degreaser cooling coils are supplied with water from the water exiting the pretreatment rinse systems of the chromium plating line.

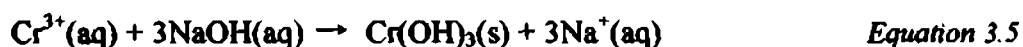
The central effluent treatment plant is used for collecting and treating all the effluents and spent solutions of the electroplating plant. Effluent streams from the various plating lines are not segregated for treatment. However, Cr(VI) in the plating rinse is reduced in an acidic environment (pH between 2-3) to Cr(III) using a sodium metabisulfite treatment (see Equation 3.1).^{132, 140, 141, 142}



Cyanides, used in different plating processes such as zinc, are oxidised in an alkaline environment (pH between 8-11) first to cyanogen chloride (see Equation 3.2) then hydrolysed to cyanates (see Equation 3.3) and finally to carbon dioxide and nitrogen (see Equation 3.4) by the addition of sodium hypochlorite and sodium hydroxide in the plating line.^{143, 144, 145} The solution is then sent to the treatment plant.



The effluents are then chemically treated (by hydroxide precipitation) at pH between 8-9 to precipitate the heavy metals before discharging into the sewer (see example Equation 3.5).¹¹



The sludge from the clarifier in the effluent plant is then piped into a filter press to remove excess water before being loaded into a skip which also acts as a drier. A flocculating agent (Orfloc 4410) is used in the clarifier to help settle any fine particles out of solution.

3.2 THE CHROMIUM PLATING LINES

The plant has four chromium plating lines: two automatic plating lines, a manual decorative chromium plating line (MDCPL) and a second decorative line dedicated to plating screwdrivers. The Chrome Shop and the automatic chromium plating lines use only the municipal water supply. Each plating line has its own water meter. The project focuses on monitoring the rinse tank solutions of the MDCPL. This line was established in 1983. A floor plan of the Chrome Shop showing the tank numbering used in this report is given in Figure 3.2. All tank numbers quoted herein will refer to those given in Figure 3.2. The line shares its soak alkaline cleaner with the copper and brass plating line. All these three lines are housed in what is known as the Chrome Shop. The lines in this shop operate for effectively 24 hours a day from Monday to Friday and are manned by two shifts. On each shift there are five workers. The day shift (5 workers) works from 7:15 to 16:00 and has a 15 minutes tea break in the

morning and a half an hour lunch break at 12:45. The night shift works from 18:00 to 3:00 the next day but often will do overtime which means the shift works on to 6:00.

Decorative chromium is mainly plated onto steel and zinc workpieces. Some chromium plating is also carried out on lead and brass workpieces. Steel is pre-plated with nickel before chromium is applied. Zinc based die-castings, lead and brass are first plated with copper followed by nickel and finally with chromium.

3.3 THE MANUAL DECORATIVE CHROMIUM PLATING LINE

One tap is used to supply water to the line for filling rinse tanks. This is done by means of a piece of hose attached to the tap. This tap is not metered but the water that is piped into the Chrome Shop is metered on the roof. The meter in the main down pipe in the shop feeding the line however was not working at the time of this study. Water flows through the rinse tanks of the plating line continuously for 24 hours for five days a week. Water utilised for process solution make-up, filling drag-out tanks and topping up the plating tanks is performed using buckets. Chemicals are added to the tank using a batch system. Chemical additions are made based on the results from chemical analyses. The process solutions are monitored in-house every day (Tank 3, 4, 9 and 14) and by the chemical suppliers every week (Tank 9 and 14).

There are 21 tanks (Tanks 1-21 in Figure 3.2) for the MDCPL. Tank 3 and 21 are also used by copper and brass plating lines. The copper plating line is made up of eight tanks (Tanks A-H in Figure 3.2) and brass plating has three tanks (Tanks I-III in Figure 3.2) in the line.

There are four surface treatments plus associated rinses which comprise the stages in the MDCPL. These are cleaning (Tanks 1, 3, 4 and 6), striking with nickel (Tank 9 or Tank 9*), plating with chromium (Tank 14) and reducing Cr(VI) and neutralising any acid left on the workpieces (Tank 16). The rinse water tanks are numbered 2, 5, 7, 8, 10, 11, 12, 13, 15, 17, 18 and 19 in Figure 3.2.

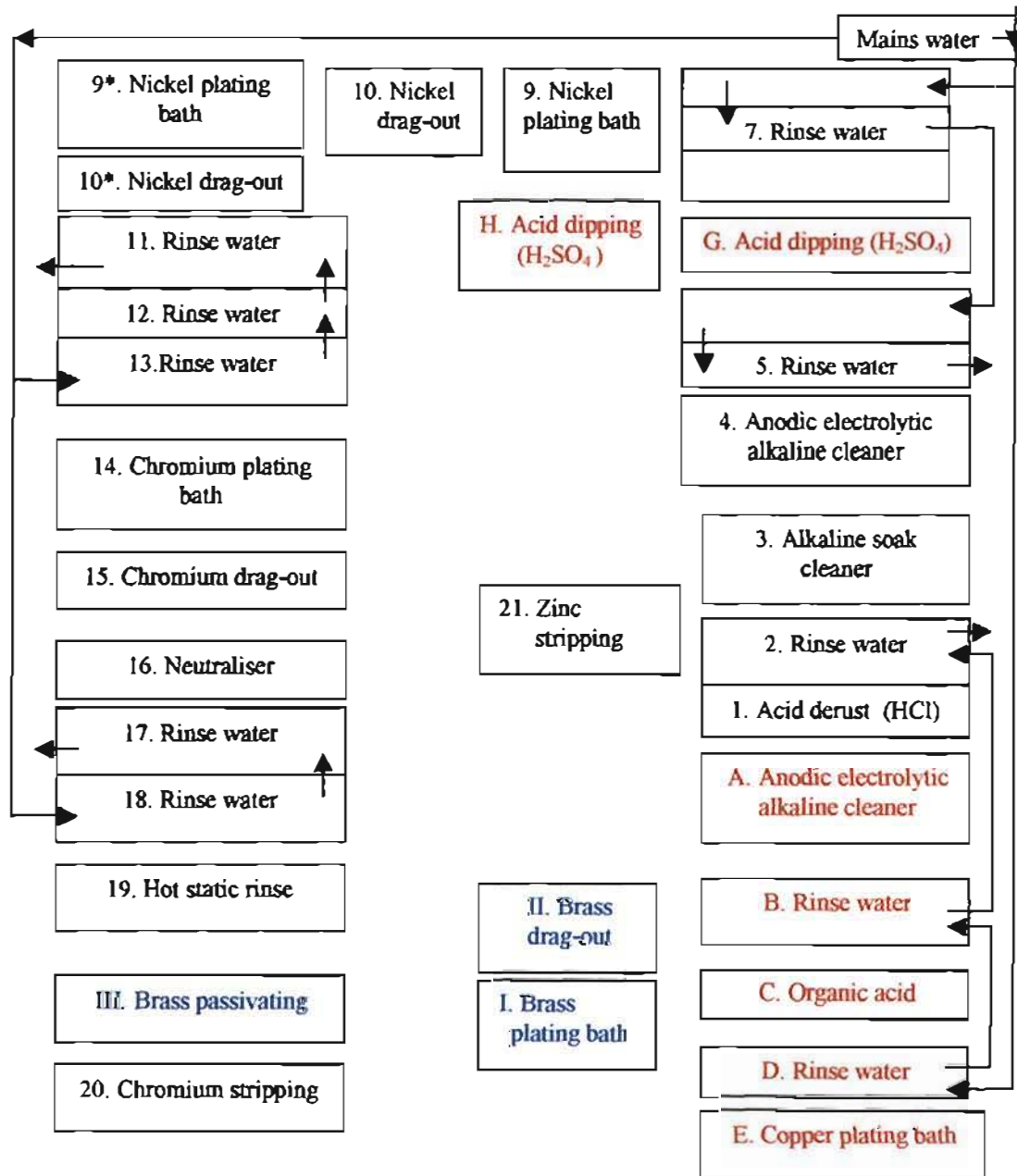


Figure 3.2 Tank arrangement for the chromium, copper, and brass plating lines

The workpieces are loaded into perforated plastic buckets or wired onto jigs for cleaning. They are then transferred onto purpose-made jigs for plating and further treatment. The physical layout of the tanks in the line is not the same as the order in which the workpieces are dipped in the tank solutions. This is because the tanks are not arranged sequentially. They are arranged along three walls of the shop and in a row down the center of the shop. This has made the line unsuitable for automation. Thus loading of jigs and baskets and immersion in the tank is carried out by hand.

In the decorative chromium plating lines the immersion sequence for cleaning, striking, plating and post-plating treatment of steel workpieces, in terms of the tank number system shown in Figure 3.2, is 1, 2, 3, 2, 4, 5, 6, 7, 8, 9(or 9*), 10 (or 10*), 11, 12, 13, 14, 15, 16, 17, 18 and 19. After nickel plating in Tank 9, the workpieces may also be plated with brass in Tank I. The immersion sequence for cleaning and striking the workpieces in the copper plating line is Tanks 3, A, B, C, B, D and E. After this the workpieces are immersed in Tanks D, F, G, 7 and 8 to be plated with any of the following: nickel only, brass only, nickel followed by brass or nickel followed by chromium.

The process solutions used for chromium plating will be discussed in Section 3.3.1 and the rinse systems will be discussed in Section 3.3.2. Solution composition and concentration, dumping and top-up rates are given in Tables 3.1, 3.2 and 3.3. The information presented in the tables is the result of extensive on-site data gathering and compilation. This was not directly available in this, or any written format from the company.

3.3.1 SURFACE TREATMENT ON THE MDCPL

Cleaning of the workpieces is accomplished using both alkaline based and acid based solutions. Two forms of alkaline cleaning are used on the line namely soak alkaline and anodic electrolytic alkaline cleaners. Soak cleaners are used to remove soils from the surface of the metals. The solution in this tank is heated electrically to 50-55 °C to increase its cleaning efficiency. A small rotatory propeller, mounted on the side of the tank, is used to mix the cleaning solution. Oil is skimmed from the solution daily at the beginning of the shift work. The immersion time for the workpieces in the cleaners is between 15 and 20 minutes.

The anodic electrolytic alkaline cleaner is also heated to 50-55 °C. This is used to remove any residual soils that may have been left behind or loosened by the soak cleaners. One bar is suspended across the tank to hold the jig containing workpieces and to pass electric current from the rectifier to the tank during cleaning processes. The immersion time of the workpieces is between 1 and 5 minutes.

Table 3.1 Trade chemicals and their ingredients used in on the MDCPL.¹⁴⁶

Tank	Layout order of tanks	Composition of tank solution		Make-up quantity and specification	Top-up quantities	Dumping frequency	Volume of tank (m ³)	
		Trade chemical	Ingredient					
Acid de-rust	1	30-33% Commercial Hydrochloric acid	HCl	3x28 kg drum (5M HCl)	0	3 months	0.2574	
Flowing rinse water	2		Mains water			Annually	0.3223	
Alkaline cleaners	3	Chemalene 03	NaOH	3x25 kg sack (100 g/L)	3 kg/week	2 month	0.7501	
Anodic Electrolytic cleaners	4	Oxyprep 220	NaOH	3x25 kg sack (90 g/L)	3 kg/week	1 month	0.8303	
Flowing rinse water	5		Mains water			Annually	0.3483	
Acid dipping	6	30-33% commercial Hydrochloric acid	HCl	2.9 M HCl	0	1 month	0.4272	
Flowing rinse water	7		Mains water				0.4381	
Flowing rinse water	8		Mains water				0.4697	
Nickel plating	9 and 9*		NiSO ₄ ·6H ₂ O	300 g/L	0	0	3.000	
			NiCl ₂	60 g/L	0			
			H ₃ BO ₃	40 g/L	5 kg/month			
			Sodium saccharine	Sodium saccharine	30 ml/L			Unknown
			Nichelux-100 plus	Patented	2 ml/L			5 L/day
			Addition agent SA1	Patented	5 ml/L			150 ml/day
			Addition agent NPA	Patented	2.5 ml/L			1 L/week
	Wetting agents AP-7	Patented	4 ml/L	1.5 L/week				
Nickel drag-outs	10 and 10*				70 L/day		0.1945	
Flowing rinse water	11		Mains water			Annually	0.1705	
Flowing rinse water	12		Mains water			Annually	0.3612	
Flowing rinse water	13		Mains water			Annually	0.3822	
Chromium plating	14	Chromic acid	CrO ₃	300 g/L	15 kg/month Cr(VI)	0	1.1201	
			H ₂ SO ₄	2 g/L				
		Fumetrol 140	Patented	2.5 ml/L	1.5 L/week			
Chromium drag-out	15				25 L/day		0.1292	
Neutralizer	16	Sodium metabisulfite	NaS ₂ O ₅	14 kg	0	3 days	0.2143	
		Sodium carbonate	Na ₂ CO ₃	1 kg	0			
Flowing rinse	17		Mains water			Annually	0.2338	
Flowing rinse	18		Mains water			Annually	0.2338	
Hot static rinse	19		Mains water			2 days	0.9308	
Chromium stripping	20	Sodium carbonate	Na ₂ CO ₃	20 g/L	0	10 weeks	0.3216	
		Caustic soda	NaOH	50 g/L				
Zinc stripping	21	Hydrochloric acid	HCl	5 M HCl	0	6 months	0.3367	

Industrial grade hydrochloric acid (32%, 373 g/L, 10 mol/L) and sulfuric acid (98%, 1832 g/L, 18.7 mol/L) are bought in a concentrated form and then made up to the required dilution factor with water. Hydrochloric acid is used to clean and activate steel workpieces and sulfuric acid to activate workpieces after copper plating or chromium stripping (see Equation 1.8 in Chapter 1). Two different acid solutions are made from the hydrochloric acid, HCl. The first HCl acid solution used on the line is a more concentrated (5.0 M HCl) acid de-rust (pre-pickling) solution (Tank 1) and is prepared by adding three 28 kg batches (supplied in 25 L drums) of the industrial grade hydrochloric acid to three 25 L drums of water in a tank. This acid removes oxide films, scales and other contaminants from the surface of the metal. The spent acid from Tank 1 is used to top up the zinc stripping (Tank 21) solution which removes zinc from wire products. Twice a year this acid is taken to the effluent plant which treats rinse effluent from the plating process of the factory. Depending on the amount of rust present, workpieces are immersed in this tank for about 15-20 minutes. The second type of acid dipping (Tank 6) solution (2.9 M HCl) is made by mixing two 28 kg drums industrial grade hydrochloric acid with five 28 kg drums of water. This acid helps to activate the metal for plating. Workpieces are immersed in this tank for about one minute. The sulfuric acid solution of Tank H is prepared by dissolving 4.5 L of the industrial grade acid in a half filled tank of water and topping up with more water. The sulfuric acid solution used in Tank G of the copper plating line is also prepared by mixing the industrial grade sulfuric acid with water in a ratio of 1:3.

Striking of workpieces is accomplished with nickel using a Watts nickel bath (see Table 1.3 in Chapter 1). There are two nickel plating baths (Tanks 9 and 9*) of equal size serving the chromium plating solution. These baths contain nickel plating electrolytes ($\text{Na}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), a buffering agent (H_3BO_3), a wetting agent Nickelux 100 plus, addition agent SA1, addition agent NPA and an in-house treatment. The wetting agents are added drop-wise into the plating solution from a 25 L plastic container secured on the edge of the plating tank. Metallic contaminants in the plating solution are removed from the bath by electrolytic dummieing twice a year. The solution is heated electrically to 50-60 °C, with constant filtration through activated carbon using a pump (see Figure 3.3).

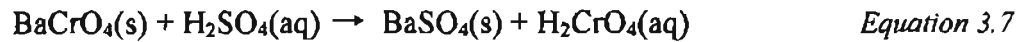
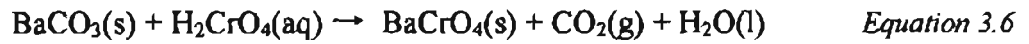


Figure 3.3 Unit for the continuous filtration of the nickel plating solution

This makes the solution well aerated for complete mixing. The carbon in the filtration tank is changed every two weeks. About 300 ml of H_2SO_4 and 400 ml of HCl are added to the tank solution in each shift to maintain the pH around 4.0 and keep the concentration of nickel within the specified values recommended by the chemical suppliers. The optimum concentration of nickel specified by the chemical suppliers is 82.5 g/L. There are two nickel drag-out tanks (tanks 10 and 10*) of equal size in the MDCPL. Each day 70 L of the drag-out solutions are used to top up the process tank. A current density ranging from 1-10 A/dm^2 and a voltage of 5.4-9 V is used during the plating process. Workpieces are plated in these baths with nickel in a time of 15 to 20 minutes and the thickness of the plate is around 10 μm . Five flight bars are used in the plating tank. Three of the bars are used to suspend the soluble nickel anodes and two are cathode bars used to hold the jigs that carry the workpieces. Nickel chips are used to provide anode surface and are arranged in the bath to give as uniform a distribution as possible of the electrodeposits on the work and to maintain the nickel content of the plating solution. The anodes are enclosed in polypropylene bags in order to prevent particles from the surface of the anodes passing into the solution.

The chromium plating bath is made up of chromic oxide (CrO_3) and sulfuric acid that serves as a catalyst along with a proprietary catalyst based on silicon hexafluoride. The mixed catalyst used is Lumina 34 which has been specifically developed for decorative plating where uncatalysed CrO_3 is used in the plating solution (Protea and other suppliers). In the chromium plating bath the ratio of the chromic acid to sulfuric acid is maintained in a fixed ratio, preferably 100:1. The high concentration of sulfate resulting from the buildup of drag-out in

the bath is removed (precipitated) as barium sulfate by adding barium carbonate (see Equation 3.6 and 3.7).^{66, 83, 147}



Low concentration of sulfates is adjusted by adding extra sulfuric acid. The solution is heated electrically to 38–43 °C and a current density ranging from 12–25 A/dm² is used during plating processes. The voltage used during plating ranges from 5.7–10 V and the plating thickness from 0.1–0.8 µm. Workpieces are plated in the bath with chromium in a time ranging from 3 to 5 minutes. Each day, 25 L of the drag-out is transferred to the process tank. A fume suppressant, Orlik Fumetrol 140, is added to reduce emissions of chromic acid mist from the plating tank. An insoluble anode (tin-lead alloy anode) is employed in plating the workpieces. The anode contains 4% tin. Two anode bars are used in the tank to suspend the anodes and one cathode bar is used to hold the jigs that carry the workpieces. Jigs are lifted in and out of the baths by hand except in the case of chrome (see Figure 3.4). Here a gantry is used. Up to four jigs can be plated in the chromium bath at the same time.



Figure 3.4 Gantry used in lifting jigs in and out from chromium plating bath

Chromium plate that does not fulfill the required specification is stripped off the workpieces anodically (see Equation 3.8) in a solution containing 50 g/L caustic soda and 20 g/L sodium carbonate in Tank 20. The Cr(VI) produced is thought to exist as chromate, CrO_4^{2-} in this

alkaline medium(see Equation 1.22 in Section 1.3.4). The voltage required between the anodes and cathode connections is around 6 V. This tank is situated at the far end of the plating line.



Since nickel becomes passive when treated anodically in an alkaline solution, the stripped workpieces are re-activated using the dilute sulfuric acid dip of Tank H. The workpieces are rinsed in Tanks 7 and 8 and then re-plated with nickel and chromium. Customers may also bring steel workpieces plated with zinc to be plated with chromium. In order to avoid contamination of the alkaline cleaning solutions of the chromium plating tanks, the zinc is first stripped off the workpieces by dipping them in the hydrochloric acid solution of Tank 21. This solution is obtained from the acid de-rust tank of the MDCPL.

The post plating so called neutraliser bath contains sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$) and sodium carbonate (Na_2CO_3) to treat the Cr(VI) present. The former compound is used to reduce Cr(VI) to Cr(III) (see Equation 3.1). The sodium carbonate in the solution neutralises any acid left on the workpieces and buffers the solution.

3.3.2 RINSING ON THE MDCPL

After placing the workpieces in the process solution, they are rinsed off in mains water. The plating line has a drag-out for nickel (Tank 10) and for chromium (Tank 15). There is one hot static rinse (Tank 19) used for quick drying of wet workpieces and to dissolve the last traces of the chemicals from the surface of the workpieces. This includes the final flowing rinse stage of the copper pretreatment line (Tank 2, third stage) and the copper and chromium acid pretreatment line (Tank 5, fourth stage), one double-stage counter flowing rinse (Tanks 17 and 18) and one triple-stage counter flow rinse (Tanks 11, 12 and 13).

Water is piped into the rinse systems of the plating line through Tanks 8, 13 and 18. There is no individual metering of water going into any of these flowing rinse systems. The water is piped in half way down the sides of the tank and leaves through an outlet pipe close to the top of the tank and flows into the next rinse tank. In the other tanks of the counter current rinses

the water enters and leaves through a hole close to the top of the tank. All the effluent rinse water that leaves the rinse tanks (as shown in brown line in Figure 3.2) is sent to the central effluent treatment plant for treatment before being discharged into the sewer.

3.3.3 NON-CHROMIUM PLATING IN THE CHROME SHOP

A copper plating line is situated before the pretreatment step of the MDCPL. This line is used to strike zinc, lead, brass and sometimes steel workpieces with copper prior to nickel and chromium plating. Workpieces are cleaned first in the alkaline soak cleaner of Tank 3 of the MDCPL then in the electrolytic cleaner of Tank A and finally in the organic acid (Galtin 140) solution of Tank C of the copper plating line prior to plating with copper. A copper cyanide plating system is used, with copper used as the anode. On each day 10 L of flowing rinse water from Tank D is used to top up the plating tank. This line does not have a drag-out tank. The rinse water of the copper plating line in Tank B flows into rinse Tank 2 and the rinse water of Tank F into Tank 5 of the MDCPL.

Near the copper plating line is a brass plating solution. This solution is used to brass plate workpieces after they have been plated with copper, nickel, or copper and nickel. Workpieces are cleaned in the alkaline soak cleaners of MDCPL and in the pre-treatment tanks of the copper plating line prior to brass plating. Brass is used as the anode. The plating solution is a commercial product called brass salt. After plating, the workpieces are dipped in the drag-out tank. In each week, 10 L of the drag-out is used to top up the brass plating solution. The workpieces are then immersed in a passivating solution of sodium dichromate situated near Tank 19 of the MDCPL. Finally they are dipped in Tanks 16, 17, 18 and 19 of the MDCPL.

Table 3.2 Trade chemicals and their ingredients used on the copper plating line¹⁴⁶

Tank	Layout order of tanks	Composition of tank solution		Make-up quantity and specification	Top-up quantities	Dumping frequency	Volume of tank (m ³)
		Trade chemical	Ingredient				
Electrolytic cleaner	A	Sodium cyanide	NaCN	25 g/L	0	3 months	0.5409
		Sodium carbonate	Na ₂ CO ₃	25 g/L			
Flowing rinse	B		Mains water			Annually	0.2151
Organic acid	C	Galtin 140	Patented	120 g/L	0	1 week	0.1947
Flowing rinse	D		Mains water			Annually	0.1682
Copper plating	E	Copper anode	Cu	30 g/L Cu	2 kg/day	0	1.892
		Potassium cyanide	KCN	20 g/L			
Flowing rinse	F		Mains water			Annually	0.2177
Acid dipping	G	98% commercial sulfuric acid	H ₂ SO ₄	4.7 M H ₂ SO ₄	0	1 month	0.1973
Acid dipping	H	98% commercial sulfuric acid	H ₂ SO ₄		0	3 month	0.1683

Table 3.3 Trade chemicals and their ingredients used on the brass plating line¹⁴⁶

Tank	Layout order of tanks	Composition of tank solution		Make-up quantity and specification	Top-up quantities	Dumping frequency	Volume of tank (m ³)
		Trade chemical	Ingredient				
Brass plating	I	Brass salt	CuCN, Zn(CN) ₂	21 g/L	7 kg/month	0	1.059
Drag-out	II				10 L/week	Annually	0.6854
Brass passivating	III	Orprep MS020	Na ₂ CrO ₄	4 kg/month	0	Monthly	0.1447

3.4 WASTE MINIMISATION OPTIONS USED IN AND WASTE MINIMISATION OPPORTUNITIES FOUND FOR THE MDCPL

A number of waste minimisation options and measures are already in place on the MDCPL. These are entries 1) – 14) in the list below. Some options which appear in other lines in the factory but are not used on the MDCPL and some obvious ones which are missing are listed below from entry 10) onwards.

- 1) There is a gantry on the chromium plating tank to allow good drainage of workpieces over the solution.
- 2) Counter current rinsing has been implemented to keep a low rinse water flow in the running rinses.
- 3) Drag-out tanks follow the nickel and chromium plating line.
- 4) Oil skimming is carried out on the cleaners at the start of every shift.
- 5) Reactive rinsing has been used on the pre-treatment line.
 - Effluent from acid rinse Tanks 7, 8 and F is used as the influent for the rinse in Tank 5 following the alkaline cleaning baths;
 - Effluent from organic acid rinse Tank B is used as an alkali and acid rinse in Tank 2.
- 6) Spent acid from Tank 1 is used in the zinc stripping solution.
- 7) Spent acid from the zinc stripping solution is used for pH adjustment in the central effluent treatment plant.
- 8) Fume suppressant forms a foam blanket on the chromium plating solution to retard acid mist emission.
- 9) The nickel plating solution undergoes continuous filtration.
- 10) Regular analyses of the acid de-rust solution (in-house by titration once a week) takes place.
- 11) Stripping plate off the racks in the chromium stripping solution after each cycle takes place.
- 12) Rinse tanks are small to favour good mixing and interaction of the solution with the workpiece and faster removal of the drag-out.
- 13) Effluent liquid waste is converted to solid waste in the electroplating plant. Sludge de-watering in a filter press and then in sludge dryer.

- 14) Rinse tank design (water is piped in at about half way down the side of the tank and exits from a circular opening in the wall close to the top of the opposite side and flows into next tank and then flows out to the drain from an outlet close to the top of the far side of the tank) favours good mixing in the first (dirtiest) tank.

Some waste minimisation opportunities were observed for the MDCPL and are listed as entries 15) – 18) below. The effect of the water and chemicals from these opportunities will be looked at in this study.

- 15) The water meter on the main pipe into the Chrome Shop is broken.
- 16) There is no agitation of the water in the rinse tanks.
- 17) The rinse systems before and after the nickel process tank are situated opposite to each other on either side of the walkway (aisle) and so are not in line with the process solution. This means racks of workpieces are carried to and from rinse tanks across the walkway, dripping chemicals onto the floor.
- 18) Operators tend to use rinses indiscriminately on occasions and not according to the work practices laid down. For example after stripping off chromium from workpieces, the operators rinse them first in Tank 19 then Tank 18 and finally Tank 17. When workpieces are passivated with brass the operators rinse them in the same way as they do for chromium stripping.

CHAPTER 4

SCOPE AND AIMS

CHAPTER 4

SCOPE AND AIMS

The concept of waste minimisation as a means of tackling the generation of industrial waste is both a simple and obvious waste management approach. If no waste is produced then no waste treatment, handling, transportation or disposal measures are needed. The economic and environmental benefits from waste minimisation extend beyond the manufacturing company creating the waste to include the broader community and the natural environment. By controlling the waste production at the source, the effect of these waste streams on the natural and anthropogenic environment is also reduced. Central to the success of waste minimisation is the waste audit or pre-assessment stage of a waste minimisation programme. Data collection and (waste minimisation) analyses in order to identify waste minimisation opportunities is a fundamental step in waste auditing. The success of this in turn depends on the availability of sufficient and good quality data for the analyses.^{93, 96}

The areas in which waste minimisation can be applied include the inputs to the process such as:-

- utility usage e.g. electricity and water;
- (other) energy usage e.g. petrol, gas and paraffin;
- process or ancillary chemical usage e.g. catalysts, machine oil and dust mask;
- outputs from the process like:-
 - rejected finishing goods,
 - solid wastes e.g. sludge, off-cuts,
 - effluents,
 - dust or gaseous emissions into the atmosphere.³⁵

Reductions in these areas represent the environmental benefits that can be achieved through waste minimisation. This project focuses on data gathering and analyses for a chromium electroplating process in four of these areas. These are water and raw material usage on the input side, and effluent and finished goods on the output side of the chromium electroplating process.

The company hosting the project is a job shop and runs a number of different electroplating processes. The six main aims of the waste audit carried out on one of these processes, the manual decorative chromium electroplating line (MDCPL), are listed below:-

- 1) To obtain baseline data on the chemical composition of the rinse waters in order to characterise the movement through and accumulation of chemicals in the various stages of the electroplating process and to compare the results with effluent discharge limits.
- 2) To investigate the relationship between the concentration levels of metals in the rinse water obtained through sampling and chemical analyses and the pH, conductivity and total dissolved solids readings taken by direct reading instruments.
- 3) To carry out a water (volume) balance and chemical (cleaner, acid, nickel and chromium) mass balance on the manual decorative chromium electroplating line in order to identify and quantify losses.
- 4) To estimate losses as unused raw materials using new chemical monitoring data in waste calculations.
- 5) To compare the waste minimisation opportunities generated from a scoping audit with those arising from the material balances and waste calculations in 3) and 4) respectively.
- 6) To establish the potential of water as an area for waste minimisation using a water economy diagram.¹⁰⁶
- 7) To prioritise the waste minimisation opportunities determined using the waste minimisation analyses techniques used in 4), 5) and 6), and identify some potential waste minimisation measures or options which might be applicable to them.

CHAPTER 5

MONITORING METHODOLOGY

CHAPTER 5

MONITORING METHODOLOGY

Electroplaters use a range of chemicals (see Chapter 1) in aqueous solution some of which become incorporated into the plate and others of which only facilitate the process. Therefore, data has to be collected on chemicals, water and output and organised in a suitable manner for analysis in the waste audit. Three types of data on the process were collected for the waste minimisation audit namely:

- existing data that were collected from the plant, computerised and handwritten records, discussion with the owners and employees of the factory and analysis reports from the chemical suppliers;
- new quantitative data collected on-site using direct reading instruments and measurements made on rinse water flow rate and tank volumes;
- new quantitative data collected from sampling and chemical analysis of samples of rinse water.

5.1 COLLECTION OF EXISTING DATA

The table below shows the documents from which existing data has been collected from the factory for use in waste minimisation and the waste audit.

Table 5.1 Summary of existing data collected

<i>Documents and Data</i>	<i>Source of documents</i>
Material safety data sheet, technical data sheet, certificate of analysis, water accounts, water meter reading to the chrome shop, price of purchased chemicals, chrome and nickel production chart, inventory history (inventory journal and supplier's invoice)	Administration office
Stock requisitions; pH, temperature and Baumé measurement of the process solution	Laboratory
Chemical analysis of chromium plating bath	Chemserve chemical suppliers
Chemical analysis of nickel plating bath	Orlik chemical suppliers

The chrome and nickel production chart (a chart that shows the number of workpieces plated each day in the Chrome Shop) was collected over a two-week period between 09/06/03 and 20/06/03. This time period was used due to the large number (79911) of workpieces plated in this specified period (see Table 6.4 in Chapter 6). The inventory history and store requisitions were collected over a longer time period (March to October 2003) because some chemicals are added to the plating bath only after extended time intervals, which may become shorter if the output rate increases (see Table 3.1 in Chapter 3). The municipal water bill record for the plant was taken from 11/12/02 to 12/12/03 (see Table 6.3 in Chapter 6).

5.2 COLLECTION OF NEW DATA ON-SITE

The new quantitative data collected on-site concerning the chrome shop are listed below:

- rinse water flow rate of the MDCPL using stopwatch and 2000 ml calibrated beaker;
- on-site solution measurements of solution parameters of MDCPL using direct read instruments;
- measurements of tank volumes of the chrome shop using a tape measure;
- measurements of the surface area of workpieces using a vernier caliper and a tape measure;
- Observation of work practices and process operations.

5.2.1 RINSE WATER FLOW RATE

Flow rates can be measured from water meter readings and the time at which they were taken. In the Chrome Shop there was no functioning water meter during the monitoring period. Some pipes used to carry the rinse waters into the tank were fixed to the side walls of the tank (Tanks 2 and 13). In other tanks the rinse water enters and leaves close to the top through an opening in the tank wall, which feeds, into an external pipe. It was possible to measure only the inflow rate of Tanks 8 and 18. The flow rates of Tanks 2 and 13 were measured from the outflow of the rinse water from the tanks. The flow rate was measured using a 2000 ml calibrated plastic container. The process involved timing how long it took to fill up the container and dividing the volume by the time to express the flow rate in L/min (see Equation 5.1). The measurement was repeated until three results were obtained and the average

of these three was used as the flow rate. This was repeated on three different dates. An average of the three days of measurements was assumed to be the flow rate of the mains water into the rinse tanks of the plating line.

$$\text{Flow rate(L/min)} = \frac{\text{Volume of container (L)}}{\text{Time taken to fill container with water (minute)}} \quad \text{Equation 5.1}$$

5.2.2 ON-SITE MEASUREMENTS USING DIRECT READ INSTRUMENTS

Portable direct reading instruments were used to collect quantitative data for the project. These included conductivity, total dissolved solids, temperature and pH measuring instruments. Conductivity, total dissolved solids (TDS) and pH readings were taken on-site for the drag-out and rinse tank solutions using handheld instruments (Hanna HI98311 conductivity and total dissolved solids meter {EC/TDS}, Hanna Dist WP2 total dissolved solids {TDS} meter and HI 98128 pH meter respectively). All instruments were calibrated beforehand using proprietary standards (Hanna conductivity standard HI 7031, Hanna TDS standard HI 7032 and Hanna HIL 7004/500, 7007/500 and 7010/500 buffer calibration standards with pH 4.01, 7.01 and 10.01 respectively). The calibration point for the EC/TDS meter was 1332 $\mu\text{S/cm}$ and 1303 mg/L for Hanna Dist WP2 at 22 $^{\circ}\text{C}$.

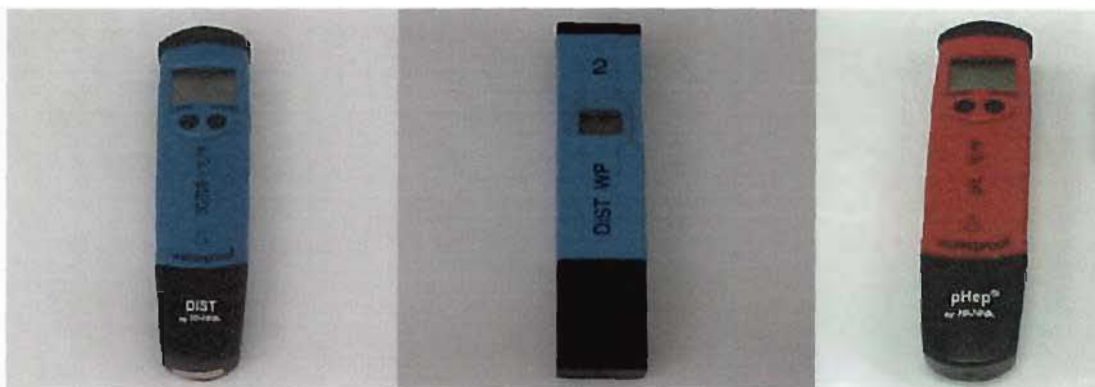


Figure 5.1 On-site measuring instruments (from left to right) HI 98311 waterproof EC/TDS and temperature meters, Dist WP 2 and HI 98128 waterproof pH and temperature meter.

Conductivity is the ability of a solution to carry an electric current.⁷⁵ This ability depends upon the concentration and mobility of all ions present. The mobility of the ions, in turn, depends

upon their size and charge as well as the dielectric constant of the solvent and the solution temperature and viscosity. Conductivity is useful for estimating the total dissolved solids contents in a water sample and, hence, in estimating the volumetric flow rate to be used to achieve a particular rinsing criterion.

TDS refers to the total weight of all solids that are dissolved in a given volume of solution. In general, the total dissolved solids concentration is the sum of the cations and anions plus molecular species in the water generally expressed in milligram per litre or gram per litre.

The pH is one of the most important measurements commonly carried out in natural waters and wastewaters. It is used to express the acidic and alkaline nature of a solution.

5.3 NEW DATA COLLECTED BY SAMPLING AND CHEMICAL ANALYSIS

The flowing rinses, drag-outs and static rinse solutions on the MDCPL were sampled for laboratory analysis of chromium, nickel, iron, sodium, zinc, lead and copper. These elements had been identified as being constituents of the raw materials used in the process solution, and as being constituents of the workpieces and jigging wires that had been dissolved in the line during the plating process and anode impurities. Samples were taken at the start of a working week, then again two weeks later at the end of a working week. This was done to see if there was a buildup of the metal ions in the tank in the specified period of time. Initial sampling was carried out on 31/03/03 and 11/04/03 in order to establish and test a suitable monitoring strategy.

5.3.1 SAMPLING STRATEGY FOR THE MDCPL

Samples were collected and stored in 250 ml high-density polyethylene bottles which had been consecutively washed with diluted Sunlight gel detergent (Lever Ponds), tap water, 0.1 M HNO₃ (Fluka puriss. p.a.) solution, and finally with distilled water. The bottles were left to air dry. When dry, each bottle was assigned the same number as the number assigned to the tanks in the plating line, a date of sampling and a surface (ST) or bottom tank (BT) designation with black ink.

A total of 27 samples were collected from the MDCPL from 9:45 to 10:05 on 9/06/03. One sample was taken from the mains water supply. This was designated the field blank. The remaining samples were collected from two drag-outs, and eleven rinse tank solutions of the plating line. Samples were taken from the surface and bottom of each tank. This strategy of sampling was adopted to see if there was stratification in the tanks that is to determine if a concentration gradient existed between the bottom and surface layers of the tank. Surface samples were taken by hand, just underneath the surface to avoid the collection of any fabrication oils that may have been floating on the surface of the tank solutions. The bottom samples were collected using a depth sampler. Figure 5.2 below, from left to right, shows chromium and nickel drag-out samples collected using the depth sampler and the sampling bottle.

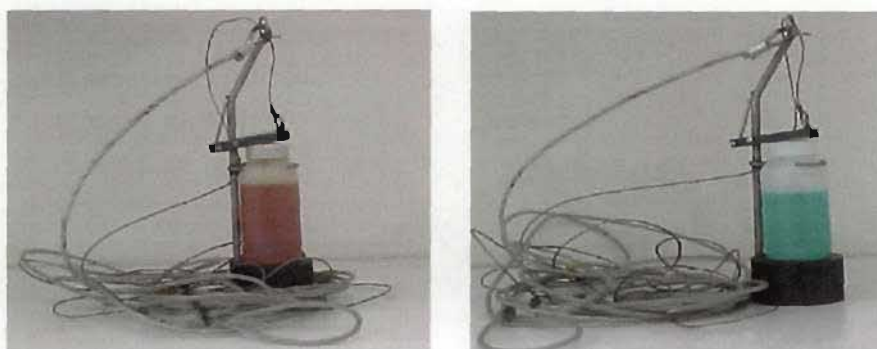


Figure 5.2 A depth sampler used to collect bottom tank samples

Bottom samples were taken after the surface samples as the stream of bubbles released during depth sampling breaks and disturbs the surface integrity. In the flowing rinse system, the clean tank was always sampled first and the dirtier ones last. This was done to limit contamination of the samples and tank solutions during sampling. The depth sampler and the gloves worn during sampling were flushed with water between taking each sample. All the samples were taken from the near side of the tanks where there is a raised duckboard walkway. The far side of each of the rinse tanks is right up against a wall and there is no easy access.

In surface sampling, the bottle was held by its base and its mouth was gently plunged down into the solution to avoid introduction of surface scum into the sample. The sample was taken

with the mouth of the bottle pointing away from the side of the tank and the bottle pointing upwards slightly to allow air to escape and the bottle to fill. After removing the bottle from the tank some air space above the solution sample level was left for proper mixing of the sample before analysis. Finally the bottle was stoppered tightly, and wiped on the outside. Sample location, sampling time, the tank number assigned to the sampling bottles and observations made on the tank solutions during sampling on 9/06/03 and 20/06/03 were recorded and they are given in Table 5.2 below.

Table 5.2 Conditions of the MDCPL on 9/06/03 at 10: 05 and on 20/06/03 at 13:55

Tank	Sample number		Comments and observations on the tank solution
	Surface tank	Bottom tank	
2	ST-2	BT-2	It had a white suspension and oil floating on the surface.
5	ST-5	BT-5	The solution appeared cloudy and had oil floating on its surface.
7	ST-7	BT-7	The solution was clear and the tank contained a lot of tiny workpieces lying on the bottom.
8	ST-8	BT-8	During sampling there was a jig in the tank holding workpieces. The solution was clear with a lot of tiny workpieces lying on the bottom of the tank.
10	ST-10	BT-10	The solution was light green on 9/06/03 and green on 20/06/03.
11	ST-11	BT-11	The solution was clear with tiny workpieces lying at the bottom of the tank.
12	ST-12	BT-12	Tank solution was clear with tiny workpieces lying on the bottom of the tank. There was a jig holding workpieces in the tank on 20/06/03 during sampling.
13	ST-13	BT-13	The solution was clear with a lot of workpieces lying on the bottom of the tank.
15	ST-15	BT-15	The solution was light orange on 9/06/03 and light brown on 20.06/03.
16	ST-16	BT-16	Tank solution was light green on 9/06/03 and green on 20/06/03
17	ST-17	BT-17	Tank solution was cloudy.
18	ST-18	BT-18	The tank contained oil floating with a lot of metal workpieces lying on the bottom.
19	ST-19	BT-19	The rinse water was hot and cloudy. The solution appeared more yellow in colour on 20/06/03 than 9/06/03.
Mains water	S-20		

5.3.1.1 STORAGE OF SAMPLES

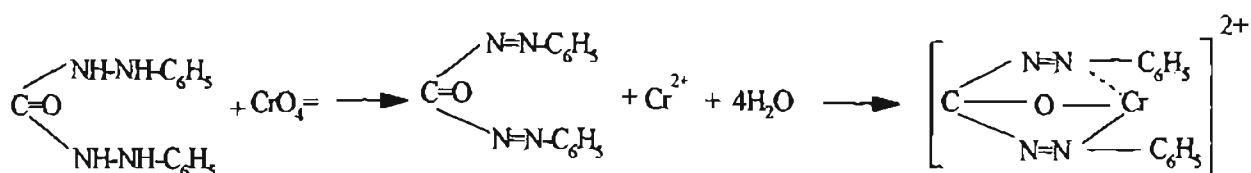
The samples were transported from the sampling site to the laboratory in an icebox for further analysis. Until analysis was performed, the samples were stored in a refrigerator in order to prevent interaction of the samples with the sampling bottles and to prevent chemical reaction of the substances in the samples.

5.3.2 CHEMICAL ANALYSIS OF SAMPLES

Samples collected in the plating line were analysed in the laboratory using ultraviolet visible (UV-visible) spectrophotometry and inductively coupled plasma optical emission spectrophotometry (ICP-OES).

5.3.2.1 DETERMINATION OF Cr(VI) CONCENTRATION BY UV-VISIBLE SPECTROPHOTOMETRY

UV-visible spectrophotometry is the study of how a sample responds to light.¹⁴⁸ It is a widely used technique in quantitative analysis because it is generally accurate, sensitive, selective, widely applicable, easy and convenient to use.¹⁴⁹ This technique uses ultraviolet visible spectrophotometers to measure absorbance in the 200 nm to 1000 nm region.⁷⁵ Simple inorganic ions and their complexes as well as organic molecules which absorb light in this region can be detected and determined successfully. Non-absorbing species can be converted to absorbing derivatives or complexes by chemical reaction with colour forming reagents.¹⁵⁰ For example a hexavalent chromium concentration is determined by reacting the sample containing chromium with 1,5-diphenylcarbazide reagent. During the reaction chromate is reduced to Cr(II) and diphenylcarbazone is formed. These reaction products in turn produce a diphenylcarbazone-chromium(II) complex with the characteristic reddish violet colour.^{151, 152}



Equation 5.2

There are two kinds of ultraviolet visible spectrophotometers: double beam and single beam.¹⁴⁹ In double beam spectrophotometers the light from the source is split into two parallel beams one of which is directed through the blank (or reference) whilst the other is directed through the sample. This instrument has the advantage of removing errors in the sample reading that could result from the intensity fluctuation occurring in the line voltage, the power source, or the light bulb itself.⁷⁵

A single beam spectrophotometer has only one beam of light. The instrument is zeroed with the blank (or reference) in place, the blank is then replaced with the sample and the sample absorbance can then be measured. A single beam instrument was used for sample analysis in this project. The instrument consists basically of a light source, monochromator, cuvette (sample holder), and photomultiplier tube as detector (see Figure 5.3).^{75, 153}



Figure 5.3 Schematic diagram of a single beam spectrophotometric experiment⁷⁶

The light source provides a light to be directed at the sample. Some examples of light sources are the tungsten filament lamp, tungsten iodide cycle lamp, mercury vapour lamp, zinc discharge lamp, deuterium lamp, and xenon lamp. The most common source of light in the ultraviolet region is the deuterium discharge lamp and for the visible region a tungsten filament lamp.⁷⁵ The monochromator is a prism, diffraction grating or filter and has the function of selecting a narrow band of wavelength from the light source. The cuvette is an optically transparent cell where sample solution is irradiated by the light emerging from the monochromator. Cuvettes with a path length of 1 cm are commonly used. Longer cuvettes, for example 5 cm, can be used to increase the sensitivity.¹⁴⁹ The cuvette is made of quartz, glass or plastic. Quartz transmits both visible and ultraviolet light. Since glass and plastic absorb ultraviolet radiation, they are used only for measurement at visible wavelengths.⁷⁶ The detector converts light photons into electrons which can be recorded as an electric signal.

The first step to be followed when using an ultraviolet visible spectrophotometer for the purpose of analysis is to prepare a standard calibration curve. That is, a series of standard solutions of the analyte is prepared, over a specific concentration range, which are then treated with the colour forming reagent, the absorbance of which is then measured. A plot is made of the absorbance against the concentration. The concentration of the analyte in the sample is then assessed from the graph.

The instrument used to determine the concentration of Cr(VI) of the tank samples was a single beam Cary 50 ultraviolet visible spectrophotometer, Varian Australia Pty Ltd (see Figure A.1 in Appendix A). It uses a xenon lamp as a light source.

5.3.2.2 EXPERIMENTAL PROCEDURE

Cr(VI) in the samples was determined using the United States Environmental Protection Agency Method 218 NS.¹⁵⁴ The analysis was done during the day of sampling because Cr(VI) can be slowly converted to Cr(III) on standing. Analysis of the samples was done after calibrating the instrument with working (calibrating) standard solutions. These solutions were prepared from an intermediate standard solution, which was prepared from a stock standard solution.

To prepare a stock standard solution first some amount of 99.5% anhydrous potassium dichromate (Saarchem univAR) was taken on a watch glass and dried in an oven for 1 hour at 105 °C.¹⁵⁵ The dried salt was then allowed to cool in a desiccator over silica gel to prevent absorption of moisture. After cooling, 0.1396 g was weighed using a Mettler AJ100 digital weighing balance. A pre-weighed watch glass was used in weighing the dried analytical reagent salt. The reagent was then dissolved in a 1000 ml volumetric flask using ultra-pure water. This gives a concentration of 49.35 µg hexavalent chromium per 1.00 ml. An intermediate standard solution approximately 1000 µg/L was prepared by taking 2.00 ml of the stock solution and diluting it in a 100 ml volumetric flask using ultra-pure water. To prepare the working standard solutions 1, 5, 10, 15, 20 and 50 ml of the intermediate standard solution were pipetted out into six separate 100 ml volumetric flasks and the volume was made to the

mark with ultra-pure water. The concentration of each of the working standard solutions was 12.3, 55.2, 110, 165, 221 and 552 $\mu\text{g/L}$ respectively.

200 mg of 98% 1,5-diphenylcarbazide reagent (Riedel-de Haën p.a.) was dissolved in 100 ml of 95% (v/v) ethyl alcohol (AnalaR BDH) in a beaker. An acid solution prepared in another beaker from 40 ml of 95-97% sulfuric acid (Pro Analyti Merck) and 360 ml ultra-pure water was added with mixing to the diphenylcarbazide solution. 2.5 ml of this mixed solution was added with thorough mixing to each calibrating standard solution in the volumetric flask. After 15 minutes the absorbance of each solution was measured three times at a wavelength of 544 nm using 1 cm matched optical quartz cells. Ultra-pure water was used as a blank during the calibration of the instrument. From the concentrations and absorbance measurements made by the instrument a calibration graph was plotted. A regression (quadratic) was used to find the equation of the calibration line, which was then used to determine the concentration of Cr(VI) in the samples.

The chromium plating solution is found in Tank 14, hence samples of Tanks 15 to 19 and the field blank were chosen for UV-visible analysis because the plating solution can be dragged by the workpieces into these tanks during plating processes. Before the actual analysis measurements were made, a number of preliminary tests were carried out to check the method, the sensitivity of the instrument and the concentration range over which results could be reliably obtained. To do the analysis, the samples were first filtered through a 25 mm 0.45 μm nylon syringe filter (National Scientific Company) in order to remove insoluble substances which could interfere by scattering the light that passes through the cuvette. Dilutions were made using ultra-pure water to bring the concentration of samples within the concentration range of the calibrating standard solutions, i.e. for samples collected on 9/06/03:

- Tank 15: two successive dilutions were made to give a total dilution factor of 5×10^4 ;
- samples of Tank 19 were diluted 10 times;
- samples of Tanks 16 to 18 were prepared neat without dilution.

Similarly for samples collected on 20/06/03:

- Tank 15: two successive dilutions were made to give a total dilution factor of 7.3×10^4 ;

- samples of Tank 16 and 19 were diluted 10 times;
- samples of Tank 17 and 18 were prepared neat without dilution.

2.5 ml of the acidified 1,5-diphenylcarbazide reagent was added to each sample in the volumetric flask and the contents of the flask were thoroughly mixed. The absorbance was measured in the same way as the standards. Finally the concentration was calculated by substituting the measured absorbance in the calibration equation of the standards.

5.3.2.3 DETERMINATION OF METAL CONCENTRATION BY ICP-OES

ICP-OES is an analytical instrument used for the determination of metals and some non-metals such as phosphorus in various sample matrices. The main advantages of this instrument are its ability to determine the concentration of several elements simultaneously, its good detection limits for most elements, its wide linear dynamic range, its low background emission and relatively low level of chemical interference.¹⁵⁶

The instrument contains a sample introduction system, an inductively coupled plasma source (ICP source) and a spectrophotometer (See Figure 5.4).¹⁵⁰ The sample introduction system consists of a peristaltic pump, a nebuliser, spray chamber and drain. The ICP source consists of a radiofrequency generator, an induction coil and a torch. The spectrophotometer can be a monochromatic or polychromatic type.

In this technique a flowing stream of argon gas is ionized by an applied oscillating radiofrequency field, which is inductively coupled to the ionized gas by a water-cooled coil. The coil surrounds a quartz torch that confines the plasma. A plasma is a conducting gaseous mixture of cations and electrons.¹⁵⁷ The ICP torch consists of three concentric quartz tubes. Argon gas from the outer inlet flows tangentially up the outer tube at a rate of 7-15 L/min and sustains the high temperature plasma and positions the plasma relative to the outer walls and the induction coil, preventing the walls from melting and thus facilitating the observation of emission signals.¹⁵⁸ The argon flowing through the intermediate concentric tube (auxiliary argon gas) flows at a rate of 0-1.5 L/min and helps in aerosol introduction and in keeping the plasma discharge away from the inlet tube.¹⁵⁶

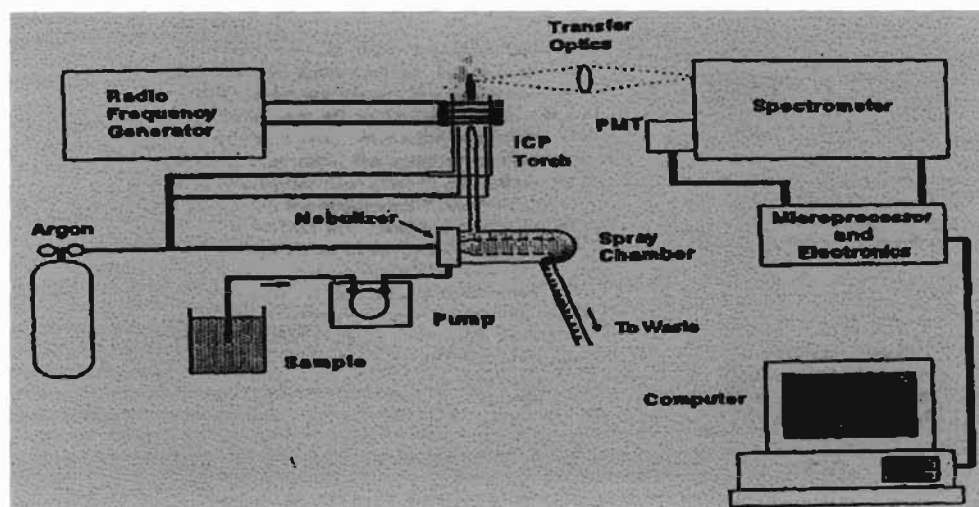


Figure 5.4 Schematic diagram showing the major components in ICP-OES ^{158, 159}

Liquid and gas samples are aspirated via a peristaltic pump to a spray chamber and nebuliser. Solid samples are extracted or acid digested so that the analyte can be in solution form. Two types of nebuliser are used in ICP-OES: pneumatic and ultrasonic. The former nebuliser makes use of high-speed gas flows to create an aerosol and the latter breaks liquid samples into a fine aerosol by the ultrasonic oscillations of a piezoelectric crystal. In this research a pneumatic nebuliser (concentric Meinhard) was used. The sample aerosol generated in the nebuliser is carried by the inner argon gas flowing from the sample inlet and introduced into the central channel of the plasma at a rate between 0.5-1.5 L/min at high temperature up to 10000 K. ¹⁵⁸ These high temperatures liberate analyte elements as free atoms in a gaseous state. Further collisional excitation within the plasma converts some of the atoms into ions and subsequently promotes the neutral atoms and the charged ions into excited states. Relaxation of these excited atomic and ionic species to a lower energy level results in emission spectra. The light emitted is focused onto a simple monochromator for sequential determination of analyte elements or onto a polychromator and an array detector for simultaneous multi-element (for up to 70 elements) determination. ¹⁵⁶

The ICP-OES instrument used in this work was a Liberty 150 AX Turbo, Varian Australia Pty Ltd (see Figure A.2 in Appendix A). The optimum experimental condition used in analysis of the samples is shown in Table 5.3 along with the ICP-OES instrumental specifications. The

metal ions analysed in the samples, the selected wavelengths for each metal and the detection limit of the instrument for the metal ions whose concentrations were to be determined, are given in Table 5.4.

Table 5.3 ICP-OES specifications and operating conditions

Serial number	95081574
Torch mounting	Axial, low flow
Nebuliser	Pneumatic (concentric)
Radio frequency generator power supply	40.68 MHz
Operating power	1.00 kW
Nebuliser pressure	240 kPa
Photomultiplier voltage	800 V
Plasma argon flow	15.0 L/min
Auxiliary argon flow	1.5 L/min
Pump speed	15 rpm
Pumping flow rate	2.2 ml/min

Table 5.4 Selected wavelengths and the reported instrument detection limit¹⁵⁰

<i>Element</i>	<i>Ni</i>	<i>Fe</i>	<i>Cr</i>	<i>Na</i>	<i>Zn</i>	<i>Cu</i>	<i>Pb</i>
Wavelength (nm)	231.60	259.94	267.72	589.59	213.86	324.75	220.35
Detection limit (µg/L)	15	10	10	25	2	5	50

5.3.2.4 EXPERIMENTAL PROCEDURE

The concentration of each of the metal ions in the samples collected on the two days of sampling was determined using ICP-OES. Analysis of the samples was performed by preparing an intermediate and working calibration standard solutions from 1.000 g/L of stock standard solutions. The nickel stock standard solution was made up from a purchased ampoule (1.00 g) standard concentrate (Fluka) in a 1000 ml volumetric flask. Iron, chromium, sodium, zinc, copper and lead stock standard solutions were ready-to-use purchased standard solutions (Fluka 1.000 g/L). A 50 mg/L mixed intermediate standard solution was prepared by pipetting out 5 ml of each 1.000 g/L standard solution into a 100 ml volumetric flask and filling the remaining volume to the mark with 0.1 M HNO₃ (Fluka puriss. p.a.). The acid was used in order to minimize adsorption onto container walls, a critical factor at trace concentrations. From the mixed intermediate standard solution, seven working standard solutions of 10, 7.5, 5, 2.5, 1.25, 0.25, and 0.05 mg/L were used to calibrate the instrument response with respect to analyte concentration at a selected wavelength for each element. The intensity reading was

recorded three times in order to calculate an average. The calibration procedure included a blank correction using 0.1 M HNO₃. The ICP-OES was programmed for dynamic background correction and to reject any calibration with a correlation coefficient less than 0.995.

Samples were filtered through a 25 mm 0.45 µm nylon syringe filter to prevent interference and clogging of the nebulizer. Concentrated samples were diluted with 0.1 M HNO₃ to make their concentration fall within the range of concentrations of the calibrating standard solutions. The concentration of each metal ion in the sample was then determined using the instrument. In order to get reliable results, a preliminary analysis was done to find the appropriate dilution factors and to ensure that the diluted sample intensities fell within the linear calibration range. The dilution factors made during the actual analyses of the samples are given in Tables 5.8 and 5.9 below. The dashes (-) represent further dilution was not made to determine the concentration of the metal ions in the samples.

Table 5.5 Dilution factor on samples collected on 9/06/03

<i>Tank</i>	<i>Tank name</i>	<i>Ni</i>	<i>Fe</i>	<i>Cr</i>	<i>Na</i>	<i>Zn</i>	<i>Cu</i>	<i>Pb</i>
2	Acid and alkaline flowing rinse	10	10	-	47	47	10	-
5	Anodic electrolytic flowing rinse	-	-	-	47	-	-	-
7	Acid flowing rinse	-	-	-	5	-	-	-
8	Acid flowing rinse	-	-	-	5	-	-	-
10	Nickel drag-out	89	-	-	20	-	-	-
11	Counter current flowing rinse	10	-	-	10	-	-	-
12	Counter current flowing rinse	10	-	-	10	-	-	-
13	Counter current flowing rinse	-	-	-	10	-	-	-
15	Chromium drag-out	89	20	1700	20	20	20	20
16	Neutraliser	-	-	20	1700	-	-	-
17	Counter current flowing rinse	-	-	-	47	-	-	-
18	Counter current flowing rinse	-	-	-	10	-	-	-
19	Hot static rinse	-	-	-	10	-	-	-
20	Mains water	-	-	-	5	-	-	-

Table 5.6 Dilution factor on samples collected on 20/06/03

<i>Tank</i>	<i>Tank name</i>	<i>Ni</i>	<i>Fe</i>	<i>Cr</i>	<i>Na</i>	<i>Zn</i>	<i>Cu</i>	<i>Pb</i>
2	Acid and alkaline flowing rinse	-	10	-	47	10	10	-
5	Anodic electrolytic flowing rinse	5	-	-	47	5	-	-
7	Acid flowing rinse	-	-	-	5	-	-	-
8	Acid flowing rinse	-	-	-	5	-	-	-
10	Nickel drag-out	1700	10	-	460	10	-	-
11	Counter current flowing rinse	20	-	-	10	-	-	-
12	Counter current flowing rinse	10	-	-	10	-	-	-
13	Counter current flowing rinse	-	-	-	10	-	-	-
15	Chromium drag-out	89	20	4350	89	89	89	20
16	Neutraliser	10	10	1700	1700	10	20	10
17	Counter current flowing rinse	-	-	10	47	-	-	-
18	Counter current flowing rinse	-	-	-	10	-	-	-
19	Hot static rinse	-	-	10	20	-	-	-
20	Mains water	-	-	-	5	-	-	-

CHAPTER 6

RESULTS

CHAPTER 6

RESULTS

The results of the project are reported in this chapter in three sections. Section 6.1 presents the results obtained from the collection of existing data. Section 6.2 focuses on flow rate and other new data collected on-site using direct reading instruments. Section 6.3 presents the results obtained from chemical analyses of tank solution samples using spectroscopic techniques and gives the analyses results for the electroplating tanks as reported by the chemical suppliers.

The calibration graph of the chromium working standard solution used in the determination of Cr(VI) in the drag-out and rinse water tanks in the two days of sampling (9/06/03 and 20/06/03) is given in Figures B.1 and B.2 of Appendix B. The calibration graph of the metal standard solutions whose concentration was determined by ICP-OES in the two days of sampling is given in Figures C.1 and C.2 of Appendix C. Two initial sets of chemical analyses results from 30/3/03 and 11/4/03 (Tables D.1 and D.2) for the rinse water solutions are presented in Appendix D.

6.1 RESULTS FROM EXISTING DATA

Results obtained from existing data are tabulated under three headings. Table 6.1 shows the raw materials bought in by the factory for use in chromium and nickel plating and in the MDCPL for 163 days between 1/03/2003 and 25/10/03. Table 6.2 breaks down the chemicals used in the MDCPL from March to October (1/03/03-25/10/03). Table 6.3 presents a breakdown of the costs for mains water used in the factory from 11/12/02 to 12/12/03 as obtained from eThekweni Municipality water bills. Table 6.4 presents the workpieces that were plated between 09/06/03 and 20/06/03 as the number of each type of item and as the surface area plated.

Table 6.1 Raw material data for the factory and for the MDCPL from 1/03/03 to 25/10/03

Raw materials	Average unit cost (R unit)	Into store from supplier		Out of store into				Average Daily Cost (R day)
		Quantity	Cost (R)	Factory		MDCPL		
				Quantity	Cost (R)	Quantity	Cost (R)	
Chemalene 03/kg	11.70	525.0	6143	469.0	5487	459.0	5370	33.00
Oxyprep 220EC/kg	14.34	0.000	0.000	89.00	1276	74.00	1061	7.000
NaOH/kg	3.650	6675	24364	6856	25024	655.0	2391	15.00
HCl/kg	1.640	6272	10286	5936	9735	1942	3185	20.00
H ₂ SO ₄ /kg	1.090	18000	19620	17478	19051	2714	2958	18.00
Nickel chips/kg	67.63	6056	409567	5649	382042	2876	194504	1193
Nickelux 100 plus/L	51.58	1375	70923	1395	71954	814.0	41986	258.0
Brightener/kg	35.50	100.0	3550	120.9	4292	51.20	1818	11.00
Wetting agent/kg	11.46	50.00	573.0	30.50	350.0	14.50	166.0	1.000
Addition agent SA1/kg	34.99	200.0	6998	213.0	7453	101.0	3534	22.00
H ₃ BO ₃ /kg	6.370	863.0	5497	733.0	4669	67.10	427.0	3.000
Filter aid	7.881	0.000	0.000	10.63	84.00	3.100	24.40	0.1500
Filter cartridge	8.400	39.00	328.0	6.000	50.00	2.000	17.00	0.1000
Filter felt 120	45.50	0.000	0.000	5.000	228.0	3.000	137.0	0.8400
Activated carbon/kg	23.00	60.00	1380	55.09	1267	7.700	177.0	1.100
CrO ₃ /kg	15.53	400.0	6212	370.0	5746	139.0	2159	13.00
Lumina 34 make-up	40.40	100.0	4040	90.00	3636	64.00	2586	16.00
Lumina 24	55.00	5.000	275.0	1.600	88.00	0.000	0.000	0.000
Fumetrol 140/L	250.2	25.00	6255	24.50	6130	8.500	2127	13.00
Na ₂ S ₂ O ₅ /kg	2.940	1287.5	3785	1206.5	3547	494.0	1452	9.000
Na ₂ CO ₃ /kg	2.260	1560	3526	1269.5	2869	349.0	789.0	5.000
BaCO ₃ /kg	2.500	20.00	50.00	18.40	46.00	6.480	16.00	0.1000
Lead anode	160.4	12.00	1925	20.00	3208	0.000	0.000	0.000
Copper wire 20 GZ/kg	31.18	2184	68097	1939	60458	1193	37198	228.0
Annual cost of chemicals used in the Chrome Shop (R)							436483	

Table 6.2 Raw materials used in the MDCPL from 1/03/03 to 25/10/03

Chemical used	Unit	March	April	May	June	July	August	September	October	Total
Chemalene 03	kg	29.0	50.0	50.0	35.0	76.0	64.0	60.0	95.0	459
Oxyprep 220EC	kg	74.0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	74.0
NaOH	kg	100	73.0	64.0	99.5	40.5	72.3	130	75.5	655
HCl	kg	112	112	224	224	336	336	234	364	1942
H ₂ SO ₄	kg	240	386	314	253	325	520	320	356	2714
Nickel chips	kg	797	0.000	450	0.000	530	400	382	317	2876
Nickelux 100 plus	L	99.0	110	79.5	94.0	98.0	109	118	106	814
Brightener	kg	4.25	6.55	5.60	7.00	9.30	5.30	6.10	7.10	51.2
Wetting agent air	kg	3.00	1.50	1.00	2.00	4.50	1.00	0.500	1.00	14.5
Addition agent SA1	kg	18.5	17.5	17.5	12.0	10.0	8.00	11.0	6.00	101
H ₃ BO ₃	kg	0.100	15.0	17.0	0.000	25.0	10.0	0.000	0.000	67.1
Filter aid	pack	0.000	0.300	0.600	0.600	1.40	0.000	0.200	0.000	3.10
Filter felt 120	pack	0.000	0.000	0.000	1.00	0.000	0.000	0.000	2.00	3.00
Filter cartridge	pack	0.000	0.000	0.000	0.00	2.00	0.000	0.000	0.000	2.00
Activated carbon powder	kg	0.000	0.700	1.60	1.30	1.00	0.000	2.00	1.10	7.70
CrO ₃	kg	0.000	75.0	20.0	10.0	9.70	0.000	0.000	24.0	139
Lumina 34	kg	0.000	0.000	0.000	0.000	30.0	0.000	24.0	10.0	64.0
Fumetrol 140	L	1.00	0.500	0.750	1.25	1.00	0.500	2.50	1.00	8.50
Na ₂ CO ₃	kg	51.0	26.0	28.3	83.0	28.0	38.0	36.5	58.0	349
Na ₂ S ₂ O ₅	kg	55.0	65.0	50.0	75.0	45.0	74.0	62.0	68.0	494
BaCO ₃	kg	1.88	0.500	0.250	0.000	0.000	2.15	1.00	0.700	6.48
Copper wire 20GG	kg	115	90.0	105	147	174	173	192	197	1193

Table 6.3 Municipality water costs for MDCPL and automatic chromium plating line (at R 4.8/m³)

<i>Month</i>	<i>Volume used (m³)</i>	<i>Cost (R)</i>	<i>Water fixed charge (R)</i>	<i>Trade effluent charge (R)</i>	<i>Trade effluent monitoring charge (R)</i>
11/12/02-15/01/03	368.0	1766.4	166.6	421.1	640.35
15/01/03-13/02/03	1073	5150.4	138.0	1227.8	640.35
13/02/03-14/03/03	1081	5188.8	138.0	1236.95	640.35
14/03/03-14/04/03	1076	5164.8	147.5	1231.2	640.35
14/04/03-16/05/03	1141	5476.8	152.3	1577.2	640.35
16/05/03-13/06/03	1083	5198.4	133.2	1754.8	640.35
13/06/03-30/06/03	535.5	2570	153.6	867.7	640.35
1/07/03-14/07/03	416.5	1999		766.45	691.23
14/07/03-14/08/03	1211	5812.8	162.1	2228.5	691.23
14/08/03-15/09/03	1215	5832	167.3	2235.9	691.23
15/09/03-14/10/03	1464	7027.2	151.7	2694.1	691.23
14/10/03-14/11/03	1296	6220.8	162.1	2384.9	691.23
14/11/03-12/12/03	1375	6600	146.42	2530	691.23
Total	13335	64008	790.0	21157	4788
Estimated volume of water used by the Automatic Plating Line (m ³)					1837
Volume of water used by the Chrome Shop (m ³)					11498
Cost for the volume of rinse water used by the Chrome Shop (R)					55190
Water fixed charge allocated to the Chrome Shop (R)					677.0
Trade effluent charge allocated to the Chrome Shop (R)					18135
Trade effluent monitoring charge allocated to the Chrome Shop (R)					4104
Total water cost for Chrome Shop (R)					55867

The trade effluent charge is calculated based on a volume equal to 96% of the volume of water used in the factory. The trade effluent cost is 119.194 cents/m³ from 11/12/02 to 30/4/03. It has been observed that the cost increased to 168.761 cents/m³ during the billing period April and May. Therefore an average of these two values has been taken in order to estimate the trade effluent charge from 14/04/03 to 16/05/03. From 16/05/03 to 30/06/03, the rate was still 168.761 cents/m³ but from 1/07/03 it increased to 191.69 cents/m³. The company paid R 640.35 for trade effluent monitoring charge from 1/01/03 to 30/06/03 and R 691.23 from 1/07/03 to 30/12/03. The water fixed charge and trade effluent monitoring charges are service costs paid by the company to eThekweni Municipality. Company records were used to estimate the volume of water used by the Automatic Plating Line.

Table 6.4 Workpieces plated in the Chrome Shop from 09/06/03 to 20/06/03

	<i>Workpiece</i>	<i>Workpiece composition</i>	<i>Plating system</i>	<i>Number of workpieces plated</i>	<i>Surface area of a workpiece (cm²)</i>	<i>Total surface area of the workpieces (m²)</i>
1	Wall racks	Steel	Ni-Cr	135	2204	30
2	Spiral	Steel	Ni-Cr	210	189	4.0
3	Grids	Steel	Ni-Cr	620	565	35
4	Toilet roll stores	Steel	Ni-Cr	727	280	20
5	Two tier corners	Steel	Ni-Cr	129	1035	13
6	Table legs	Steel	Ni-Cr	58.0	1433	8.3
7	Axles	Steel	Ni-Cr	7100	31.3	22
8	Cooker tops	Steel	Ni-Cr	909	1398	1.3x10 ²
9	Corner shelves	Steel	Ni-Cr	728	378	28
10	Knobs & bezels	Brass	Ni-Cr	7896	28.7	23
11	Window stays	Brass	Ni-Cr	539	83.1	4.5
12	Heater grids	Steel	Ni-Cr	326	370	12
13	Jewellery (chains)	Brass	Ni-Cr	49.0	4	0.02
14	Chrome pipes	Steel	Ni-Cr	21.0	118	0.25
15	Element support	Steel	Ni-Cr	661	27.2	1.8
16	Cot rods	Steel	Ni-Cr	1258	209	26
17	Domes	Steel	Ni-Cr	128	9.38	0.12
18	Blocks	Steel	Ni-Cr	37.0	665	2.5
19	2 tier shelves	Steel	Ni-Cr	9.00	1.03x10 ³	0.93
20	U arm	Steel	Ni-Cr	123	141	0.85
21	Shower caddies	Steel	Ni-Cr	75.0	627	4.7
22	Copper pipe	Copper	Ni-Cr	6.00	251	0.15
23	Rings	Steel	Ni-Cr	303	70.9	2.1
24	Large basket	Steel	Ni-Cr	18.0	3.38x10 ³	6.1
25	Z.C.C rods	Steel	Ni-Cr	27.0	764	2.1
26	Ni-U arm	Steel	Ni	600	141	8.5
27	Bath plug tops	Steel	Cu-Ni	41.0	804.6	0.080
28	Bath handle	Zinc	Cu-Ni-Cr	1739	106	18
29	Toilet handle	Zinc	Cu-Ni-Cr	7380	75.2	55.0
30	Jewellery (chains)	Zinc/Brass	Cu-Ni-Cr	163	4	7.00x10 ⁻²
31	Jewellery (crosses)	Zinc	Cu-Ni-Cr	400	3.7	0.150
32	Spoons	Zinc	Cu-Ni-Cr	457	42.0	1.90
33	Wheel nuts	Steel	Cu-Ni-Cr	21708	32.2	70.0
34	Generic shafts	Steel	Cu-Ni-Cr	1167	47.0	5.50
35	K. B. rods	Steel/Brass	Cu-Ni-Cr	1140	51.5	5.90
36	K. B. brackets	Zinc	Cu-Ni-Cr	2919	17	5.00
37	Head rest bars	Steel	Cu-Ni-Cr	941	206	19.0
38	G.U.D moulds	Steel	Cu-Ni-Cr	52.0	1.70x10 ³	8.80
39	K.B. arms	Zinc/Brass	Cu-Ni-Cr	6432	13.8	8.90
40	Bracket neck	Zinc	Cu-Ni-Cr	515	14.2	0.730
41	Chrome bracket	Steel	Cu-Ni-Cr	2555	141	36.0
42	Brass motif	Zinc	Cu-Ni-Brass	2852	628	1.80 x 10 ²
43	Brass ring fingers	Zinc	Cu-Ni-Brass	216	0.033	7.10 x 10 ⁻⁴
44	Tie back	Steel	Cu-Ni-Brass	13.0	94.5	0.120
45	Brass motif	Steel	Ni-Brass	1864	628	1.20 x 10 ²
46	Brass U arm	Steel	Ni-Brass	610	141	8.60
47	A/B motif	Zinc	Cu-Brass	3495	628	2.20 x 10 ²
48	Brackets	Steel	Cu-Brass	560	141	7.90
Total number of workpieces plated						79911
Total surface area of workpieces plated (m ²)						1194
Total surface area of workpieces plated with Ni (m ²)						966
Total surface area of workpieces plated with Cr (m ²)						648

6.2 RESULTS FROM ON-SITE COLLECTION OF NEW DATA

Table 6.5 shows the average flow rate of the mains water into flowing rinse tanks of the MDCPL recorded over three different days of measurements. Table 6.6 presents conductivity (EC), total dissolved solids (TDS) and pH readings taken for rinse and drag-out tank solutions on 09/06/03 and 20/06/03.

Table 6.5 Average flow rate of the mains water in to rinse tanks of the MDCPL

Tank	2	8	11	18
Flow rate (m ³ /hr)	0.11±0.01	0.20±0.01	0.20±0.01	0.16±0.01

Table 6.6 Readings taken on 09/06/03 and 20/06/03

Tank	9 06 03			20 06 03		
	EC ($\mu\text{S cm}$)	TDS (g/L)	pH	EC ($\mu\text{S cm}$)	TDS (g/L)	pH
2	> DL	9.2	3.00	> DL	7.5	1.10
5	9.2×10^2	0.56	11.0	1.5×10^3	0.88	8.90
7	8.2×10^2	0.51	2.00	1.3×10^3	0.80	2.20
8	3.0×10^2	0.20	7.00	2.7×10^2	0.15	6.10
10	2.7×10^3	1.5	6.50	> DL	> DL	1.30
11	3.5×10^2	0.22	6.90	1.3×10^3	0.79	2.30
12	2.9×10^2	0.18	6.90	5.5×10^2	0.33	3.10
13	2.6×10^2	0.16	7.20	2.6×10^2	0.16	6.90
15	> DL	> DL	1.00	> DL	> DL	1.30
16	> DL	> DL	4.00	> DL	> DL	6.20
17	5.6×10^2	0.34	5.80	8.9×10^2	0.58	6.50
18	2.6×10^2	0.16	7.10	3.1×10^2	0.19	7.50

> DL = greater than detection limit (10 g/L for TDS)

> DL = greater than detection limit (3999 $\mu\text{S/cm}$ for EC)

The average temperature of all tanks was found to be around 20 °C. Conductivity, total dissolved solids and pH and temperature measurement of Tank 19 were not taken as the tank solution was hot.

6.3 RESULTS FROM CHEMICAL ANALYSES

6.3.1 CONCENTRATION OF Cr(VI) IN THE SAMPLES

Table 6.7 shows the concentration and absorbance of Cr(VI) in the samples collected on 9/06/03. Similarly the concentration and absorbance of Cr(VI) in the samples collected on

20/06/03 is given in Table 6.8. Note that the values given in Tables 6.7 and 6.8 for samples taken from Tank 15 and 19 of 9/06/03 and samples of Tank 15, 16 and 19 of 20/06/03 are of the diluted analytical samples. The dilution factors used for these samples are given in the experimental procedure in Section 5.2.3.1. The actual (tank solution) concentrations are presented in brackets after the measured average concentration of the analytical sample in the fifth column of Tables 6.7 and 6.8. The concentration of Cr(VI) in these original samples, before dilution, are calculated using Equation 6.1.

$$\text{Concentration of Cr(VI)} = \text{Concentration of Cr(VI) after dilution} \times \text{Dilution factor} \quad \text{Equation 6.1}$$

Table 6.7 Average concentration of Cr(VI) for diluted samples collected on 9/06/03

<i>Tank</i>	<i>Concentration ($\mu\text{g L}$)</i>	<i>Absorbance</i>	<i>%RSD</i>	<i>Average concentration ($\mu\text{g L}$)</i>
ST-15	136	0.1092	0.06	139 (6.95×10^6)
BT-15	142	0.1132	0.04	
ST-16	20.4	0.0178	0.3	19.9
BT-16	19.4	0.0170	0.1	
ST-17	6.07	0.0063	0.96	6.13
BT-17	6.19	0.0064	0.56	
ST-18	415	0.3182	0.01	384
BT-18	352	0.2721	0.02	
ST-19	106	0.0854	0.04	101 (1.01×10^3)
BT-19	96.1	0.0778	0.01	
Mains water	2.33	0.0033	1.76	2.33

Table 6.8 Average concentration of Cr(VI) for diluted samples collected on 20/06/03

<i>Tank</i>	<i>Concentration ($\mu\text{g L}$)</i>	<i>Absorbance</i>	<i>%RSD</i>	<i>Average concentration ($\mu\text{g L}$)</i>
ST-15	184	0.1429	0.01	185 (1.35×10^7)
BT-15	186	0.1440	0.02	
ST-16	177	0.1378	0.02	187 (1.87×10^3)
BT-16	196	0.1519	0.01	
ST-17	12.4	0.0114	0.24	13.6
BT-17	14.8	0.0133	0.13	
ST-18	51.1	0.0415	0.12	52.4
BT-18	53.7	0.0435	0.04	
ST-19	137	0.1076	0.02	141 (1.41×10^3)
BT-19	145	0.1132	0.04	
Mains water	3.48	0.0044	0.19	3.48

6.3.2 CONCENTRATION OF METAL IONS IN THE SAMPLES

The average concentration of the metal ions (Ni, Fe, total Cr, Na, Zn, Cu and Pb) determined by ICP-OES for the samples collected on 9/06/03 and 20/06/03 is given in Tables 6.9 and 6.10 respectively. The concentration of Cr(VI) shown in these tables is obtained from the UV-visible analyses results of the samples. On 9/06/03 the concentration of Cr(VI) in Tank 15 was 6.95×10^3 mg/L and in Tank 19 was 1.01 mg/L. On 20/06/03 the concentration of Cr(VI) in Tank 15, 16 and 19 was 1.35×10^4 , 1.87 and 1.41 mg/L respectively. The analyses results of the nickel and chromium plating baths obtained from the chemical suppliers are shown in Tables 6.11 and 6.12.

Table 6.9 Average concentration (mg/L) of metals in the samples collected on 9/06/03

Tank	Ni	Fe	Total Cr	Cr(VI)	Na	Zn	Cu	Pb
2	14.0	69.0	2.30	NM	306	446	28.0	0.510
5	2.60	5.20×10^{-2}	0.640	NM	164	2.60×10^{-2}	0.640	2.20×10^{-2}
7	4.50	1.70	0.300	NM	28.0	0.770	0.190	2.00×10^{-2}
8	1.90	<DL	9.10×10^{-3}	NM	25.0	5.10×10^{-2}	3.90×10^{-2}	1.10×10^{-2}
10	744	5.40×10^{-3}	3.90×10^{-2}	NM	129	3.90	6.20×10^{-2}	0.350
11	24.0	3.80×10^{-3}	9.10×10^{-2}	NM	25.0	0.190	5.00×10^{-2}	2.60×10^{-2}
12	16.0	4.00×10^{-2}	5.70×10^{-2}	NM	23.0	0.150	4.50×10^{-2}	2.20×10^{-2}
13	5.80	0.100	2.00×10^{-2}	NM	21.0	6.80×10^{-2}	4.80×10^{-2}	1.50×10^{-2}
15	180	21.0	8.30×10^3	6.95×10^3	129	82.0	76.0	10.0
16	1.40	0.600	61.0	2.00×10^{-2}	1.38×10^4	0.600	0.870	2.10×10^{-2}
17	0.620	0.110	4.60	6.10×10^{-3}	116	0.290	0.150	1.30×10^{-2}
18	0.200	<DL	0.890	0.384	36.0	5.70×10^{-3}	1.10×10^{-2}	4.50×10^{-3}
19	0.230	<DL	1.30	1.01	23.0	2.70×10^{-2}	2.20×10^{-2}	4.80×10^{-3}
Mains water	<DL	<DL	<DL	2.30×10^{-3}	21.0	<DL	6.10×10^{-4}	<DL

NM = not measured

Table 6.10 Average concentration (mg/L) of metals in the samples collected on 20/06/03

<i>Tank</i>	<i>Ni</i>	<i>Fe</i>	<i>Total Cr</i>	<i>Cr(VI)</i>	<i>Nu</i>	<i>Zn</i>	<i>Cu</i>	<i>Pb</i>
2	12.0	40.0	2.40	NM	168	63.0	50.0	0.600
5	1.80	5.80	1.10	NM	103	9.60	1.00	0.160
7	3.30	3.80	0.230	NM	26.0	4.40	0.480	7.00x10 ⁻³
8	0.930	<DL	<DL	NM	25.0	0.890	0.180	<DL
10	6.44x10 ³	28.0	1.80	NM	1023	70.0	1.70	1.40
11	72.0	1.40	0.510	NM	33.0	0.870	0.350	<DL
12	43.0	0.500	0.300	NM	29.0	0.600	0.150	<DL
13	7.00	<DL	7.70x10 ⁻²	NM	23.0	5.40x10 ⁻²	<DL	<DL
15	450	55.0	2.13x10 ⁴	1.35x10 ⁴	234	178	207	13.0
16	82.0	13.0	3087	1.87	1.17x10 ⁴	22.0	32.0	3.70
17	1.80	0.210	44.0	1.40x10 ⁻²	128	0.680	0.420	2.80x10 ⁻²
18	0.140	<DL	6.40	5.20x10 ⁻²	32.0	5.60x10 ⁻²	1.00x10 ⁻³	<DL
19	6.70	<DL	76.0	1.41	101	0.410	1.40x10 ⁻²	<DL
Mains water	<DL	<DL	<DL	3.50x10 ⁻³	20.0	<DL	<DL	<DL

Table 6.11 Orlik chemical suppliers' analytical results for the nickel plating bath (Tank 9)

<i>Chemicals</i>	<i>Optimum bath concentration</i>	<i>Date</i>			
		<i>03 06 03</i>	<i>10 06 03</i>	<i>18 06 03</i>	<i>24 06 03</i>
Nickel (g/L)	82.50	80.57	78.52	86.44	87.31
Nickel sulfate (g/L)	300.0	272.2	305.86	338.91	346.52
Nickel chloride (g/L)	65.00	97.35	61.36	64.31	61.36
Nickel carrier A5 (ml/L)	40.00	35.20	38.72	39.60	39.60
Addition agent SA1 (ml/L)	4.500	4.320	3.200	1.080	4.300

Table 6.12 Chemserve chemical suppliers' analytical results for the chromium plating bath (Tank 14)

<i>Chemicals</i>	<i>Optimum bath concentration</i>	<i>Date</i>			
		<i>4 06 03</i>	<i>11 06 03</i>	<i>19 03 06</i>	<i>23 06 03</i>
Chrome salt (g/L)	300.0	288.4	288.4	303.4	291.7
Sulfate (g/L)	1.200	2.300	2.300	2.500	1.700
Catalyst X400 (g/L)	3.000	2.700	2.700	2.500	2.700
Baumé reading	21.00	25.00	25.00	26.00	25.00

CHAPTER 7

DISCUSSION

CHAPTER 7

DISCUSSION

In this chapter the results obtained during the data gathering steps of the waste audit of the MDCPL in the Chrome Shop are analysed and discussed. The Chrome Shop is a job shop, like all the plating lines in this factory. This means that many different types of workpieces (in terms of structure e.g. wire or sheet products, flat shapes or indented and substrate composition e.g. zinc, iron and occasionally lead) are cleaned and plated on this line. The Chrome Shop is housed together with a copper cyanide plating line and a brass plating line. It shares some tanks of the pretreatment rinse system with these two lines (see Figure 3.2 in Chapter 3). Therefore the data collected on the Chrome Shop is both diverse and variable. As far as possible, the contributions of other plating processes to the Chrome Shop data have been identified and interferences with the MDCPL results discussed.

A monitoring period of 9 days was reported from 9/06/03 to 20/06/03 in order to simplify collection and analyses of certain data. It was necessary to restrict the monitoring period because the volume of data was high and the content diverse. Data on water and chemical usage, chemical composition of the rinse water and process solutions and product output were obtained over that time period. These data were used in different ways to estimate the water and chemical usage per unit of product surface area and the raw materials wastage for the nickel and chromium lines.

Data on chemical purchases (coming from the suppliers into the factory stores), chemical requisitions (going from the store to all plating lines and to the Chrome Shop) and the water usages for the whole factory were available from the beginning of 2003. Annually adjusted figures for requisitions and water data have been used in the Scoping Audit and daily adjusted figures in the True Cost of Waste Analysis.

7.1 WATER USAGE

Water is an important commodity in any electroplating plant. In the MDCPL mains water is utilised in the process, drag-out and rinse tanks of the electroplating line. Water is used as a solvent in the process tanks. It is utilised in the drag-out tanks as a wash and to replace evaporation and drag-out losses from the process tanks. Water is used in the rinse tanks first for refilling the drained tanks after dumping the contaminated rinse water of the tank. The second use of the water in the rinsing system is as a flowing rinse: that is for continuous flow of clean mains water into the rinse tanks and the outflow of dirty rinse water (wastewater or effluent). Contaminants in the water originate from chemicals such as raw materials, impurities in the raw materials and soils released from the surface of the workpieces.

The total amount of water used in the flowing rinse tank, static rinse tank, drag-out and process tank of the Chrome Shop for a year was calculated based on the following assumptions:-

- The solution volume in all tanks was assumed to be the volume of the individual tanks minus the head space volume.
- The water flow rate entering and leaving each rinse bath was assumed to be equal. There was no water meter on each water inflow rinse tank. The plastic pipes that carry the mains water into rinse Tanks 13 and D ran half way down the sidewall of the tanks and were fixed in position. It was therefore difficult to measure the water entering each of these tanks. Because of this, the flow rate was measured from the rinse water leaving Tank 11 and 2. The flow rate of water into rinse Tank 8 and 18 was measured from the water entering the tanks from the main supply because the pipes that carry the water were not secured to the sidewall of the tanks. This allowed the pipe to be lifted out of the tank and the water flow from this in-pipe to be measured directly.
- The plating line worked effectively for 24 hours from Monday to Friday. The total working days of the electroplating plant in the year of 2003 were 234. Therefore, there were an average of 46.8 (234 days per year excluding weekends and public holidays/5 days per week) working weeks per year and an average of 19.5 (i.e. 234/12) working days per month.

- The rinse tanks solutions were dumped and refilled once a year when the process solution tanks were cleaned out during shut down for annual maintenance.

7.1.1 WATER USED IN THE FLOWING RINSE TANKS

The total volume of water used in the flowing rinse tanks in a year was calculated by adding the total volume of flowing rinse water consumed in the flowing rinse systems per year (see Table 7.1) and the water used to refill the flowing rinse baths in a year (see Table 7.2). The volume of the flowing rinse water consumed was calculated using Equation 7.1

$$\text{Volume of flowing rinse water} = \text{Rinse water flow rate} \times \text{Operating time} \quad \text{Equation 7.1}$$

The operating time in hours is the working days in a year (234) multiplied by 24 hours/day and is equal to 5616 hours.

Table 7.1 Annual volume of flowing rinse water used in flowing rinses

<i>Tank</i>	<i>Flow rate (m³/hr)</i>	<i>Volume of water flow in a year (m³)</i>
D	0.11	618
B	0.11	618
2	0.11	618
5	0.20	1123
F	0.20	1123
7	0.20	1123
8	0.20	1123
11	0.20	1123
12	0.20	1123
13	0.20	1123
17	0.16	899
18	0.16	899
Total volume of water (m ³)		11513

The flowing rinse tanks are dumped and refilled with fresh water once a year during annual maintenance. The refill tank volumes are given in Table 7.2 which are added to the total volume of water used in the flowing rinse to give the total volume of flowing rinse water used. The internal length, breadth and height (minus head space) of the tank were measured on-site and multiplied together to give the volume. These solution volumes are given in Table 3.1.

Table 7.2 Total annual volume of water used in flowing rinse tanks

<i>Tank</i>	<i>Volume of a rinse tank (m³)</i>
D	0.168
B	0.215
2	0.322
5	0.348
F	0.218
7	0.438
8	0.470
11	0.171
12	0.361
13	0.382
17	0.234
18	0.234
Total volume of water used in filling tanks (m ³)	3.60
Total volume of water used in flowing rinse (m ³)*	11513
Total volume of flowing rinse water used (m ³)	11517

* From Table 7.1

7.1.2 WATER USED IN STATIC RINSE TANKS

The total volume of water used in static rinse tanks was estimated from the volume of the rinse baths and the number of dumps of the tank solutions in a given period of time (see Equation 7.2).

Total volume of rinse water = Volume of static solution x Frequency of dumping *Equation 7.2*

Table 7.3 Annual volume of water used in static rinse tanks

<i>Tank</i>	<i>Volume of rinse bath (m³)</i>	<i>Number of dumps per year</i>
19	0.931	117
Total volume of water used (m ³)		109

7.1.3 WATER USED IN THE DRAG-OUT TANKS

The total volume of water used in the drag-out tanks was calculated by adding the volume of water used to fill the drag-out tanks to the volume of water used to top up the drag-out tank after the plating solutions had been topped up from the drag-out tanks. The volume of water added to the drag-out tank in a year is assumed to be the same as the volume of drag-out used to top-up the plating solutions. The volume of drag-out added to the plating solution during the

year is calculated by multiplying the volume added per day (see Tables 3.1, 3.2 and 3.3 in Chapter 3) by the total number of working days in a year (see Table 7.4). The drag-out of the second nickel plating (Tank 10*) is taken to be the same as for Tank 10 based on analyses results obtained on the trials (see Appendix D). Volume of drag-out added to all process solutions (Tank 10,15,D and II) is given in Table 7.4 as 41 m³. Only 1.2 m³ of water was used to fill up the drag-out and so the total volume of water used in the drag-out system was 42 m³.

Table 7.4 Annual volume of water used in drag-out tanks

<i>Tank</i>	<i>Volume of a drag-out tank (m³)</i>	<i>Rate of drag-out additions to a process bath</i>	<i>Frequency of additions per year</i>	<i>Volume of drag-out added to the process bath per year (m³)</i>
10	0.195	70 L/day	234	16
15	0.129	25 L/day	234	5.9
D	No drag-out tank	10 L/day	234	2.3
II	0.685	10 L/week	46.8/week	0.47
Estimated volume of water added to second Ni drag-out (Tank 10*)				16
Volume of drag-out added to a process solution (m ³)				41
Total volume to fill the drag-out tanks (m ³)				1.2
Total volume of water used in drag-out (m ³)				42

7.1.4 WATER USE AS SOLVENT IN THE PROCESS SOLUTIONS

The concentrations of chemicals in the process solutions are operated within a concentration range specified by the chemical suppliers.⁷⁴ Since chemicals and water are lost due to surface treatment reaction, drag-out, evaporation, side and decomposition reactions, regular addition of chemicals and water are made to each solution to restore the concentration back to the specified level. Often the chemical additions are recorded whereas the volume of water added is not recorded. However, the water additions can be roughly calculated using the equation given below if the chemical additions are known and the overall concentration of the process solution is maintained at the specified level.

$$\text{Volume of water addition (L)} = \frac{\text{Mass of chemicals added (kg)}}{\text{Specified concentration (kg/L)}} \quad \text{Equation 7.3}$$

The specified concentration was obtained from the chemical suppliers' MSDS and technical data sheets and the average mass of chemicals added per day was calculated from the total

mass used on the line over the 163 days of the monitoring period (see Table 6.2 in Chapter 6). Table 7.5 shows the annual volume of water used in the process solutions.

Table 7.5 Annual volume of solvent additions made to process solutions ^{160, 161}

<i>Tank</i>	<i>Chemicals</i>	<i>Specified concentration</i>	<i>Average mass of chemicals added/day</i>	<i>Water used as solvent in process tanks per year, m³</i>
3	Chemalene 03	50 g/L	2.8 kg	13
4	Oxyprep 220EC	80g/L	0.45 kg	1.7
9	H ₃ BO ₃	40 g/L	0.41 kg	2.4
	Nickelux-100 Plus	2.0 ml/L	5.0 L	585
	Addition agent SA1	5.0 ml/L	617 ml	28.9
	Addition agent NPA	2.5 ml/L	0.20 L	18.7
	Wetting agents	4.0 ml/L	88.9 ml	5.2
14	CrO ₃	300 g/L	0.85 kg	0.66
	Fumetrol 140	2.5 ml/L	0.052 L	4.9
E	KCN	20 g/L	2.0 kg	23
I	NaCN	21 g/L	0.36 kg	4.0
Estimated volume of solvent water added to second Ni drag-out (Tank 9*)				640
Total volume of water used (m ³)				1328

The process tank solutions such as cleaning, neutralising and stripping are dumped periodically due to a decrease in the activity of the solution and an increase in the concentration of contaminants in the solution. Therefore, a new solution is prepared by dissolving an accurate weight or volume of the chemicals in water to refill the tanks to the specified concentration level. Table 7.6 shows the volume of water used to replace the process tank solutions after dumping (53.5 m³) together with the solvent added to top up the working solution i.e. between dumps (1328 m³ see Table 7.5). The total volume of water used as a solvent in the process solution is the sum of these two values.

Table 7.6 Annual volume of water used in making up the process solution baths

<i>Tank</i>	<i>Water used for solution make-up (m³)</i>	<i>Dumping frequency</i>	<i>Total water used for solution make-up (m³)</i>
1	0.129	4	0.516
3	0.750	6	4.50
4	0.830	12	9.96
6	0.384	12	4.61
9	3.00	0	0
9	3.00	0	0
14	1.12	0	0
16	0.214	78	16.7
20	0.322	4.68	1.51
21	0.337	0	0
A	0.541	4	2.16
C	0.195	46.8	9.13
E	1.892	0	0
G	0.178	12	2.14
H	0.168	3	0.504
I	1.059	0	0
III	0.145	12	1.74
Total volume of water used for solution make-up (m ³)			53.5
Total volume of water additions to the process tanks (m ³)			1328
Total volume of water used as make-up solvent in the process bath (m ³)			1381

7.1.5 TOTAL WATER USAGE

Table 7.7 shows a summary of the estimated water used in the Chrome Shop i.e. the percentage of the total cost of the water used in the respective tanks of the Chrome Shop, the municipal measured water usage and cost and other water related charges (water fixed charge, trade effluent charge and trade effluent monitoring charge).

Table 7.7 Estimation of water usage and cost for the Chrome Shop

<i>Water usage</i>	<i>Volume (m³/year)</i>	<i>Cost/year (Rand)</i>	<i>% of total cost</i>
Flowing rinse (see Table 7.2)	11517	55282	88.3
Static rinse (see Table 7.3)	109	523	0.84
Drag-out (see Table 7.4)	42	202	0.32
Process tank (see Table 7.6)	1381	6629	10.6
Total water used in Chrome Shop	13049	62635	
Municipality measured water usage	13335	64008	
Other water related charges	13335	26733.9	

The total volume of water used in the Chrome Shop was estimated to be 13049 m³. Most of the water (88%) was used in the flowing rinses and the lowest amount (0.32%) was used in

topping up the drag-out tanks. The water used in preparing the process solution was about 11% and the water used in the static rinse tank was 0.84% of the total water used in the Chrome Shop. The total billed municipality water used per year for both the Chrome Shop and the automatic plating line was 13335 m³. Factory records showed that the annual volume of water used by the automatic plating line from the municipality water coming to the factory was 1837 m³. This makes the volume of water used by the Chrome Shop to be 11498 m³. The estimated total water used in the Chrome Shop per year was therefore found to be 11.6% greater than the value calculated from the bill and water meter reading taken on the automatic plating line. There are two main reasons for this over-estimate of the Chrome Shop's water consumption by this analysis. Firstly the dumping frequency reported may have been too high. Secondly the water flow rate through the flowing rinse is adjusted manually and the water meter on the MDCPL was not working for the duration of this study. Therefore it was not possible to ensure that the flow rates recorded in this study were the same all year round.

The cost for the water usage for each month in the one year period is given in the results (see Table 6.3 in Chapter 6). The cost of water per m³ was R4.57 from 11/12/02 to 13/6/03. The cost increased from 14/6/03 to 12/12/03 to R5.02. The cost of the consumed water in m³ has therefore been calculated by taking an average (R4.80) of the two values and is R64008 (see Table 7.7). There was also an additional cost for the water fixed charge. Over the one year period, the electroplating plant paid R1819 to fixed water charges. Thus the total cost of the water consumed and the fixed charge was R65892.

7.1.6 REDUCING WATER USAGE

Optimal values for rinse criteria for cleaner, pre- and post plating rinses ¹⁶² (see Table 7.8) as well as concentration levels ^{163, 164, 165} (see Table 7.9) which should not be exceeded in the final (cleanest) rinse solution have been published in the literature. However the rinse criteria are given as a broad range of values while published concentration limits are scarce. Further the concentration of metals in the exiting (flowing rinse) wastewater must be within the local authority's discharge limits.¹⁶³ The metal concentration in the cleanest rinse should also be below the suggested quality criteria for the contaminant limit.¹⁶⁴ The contaminant limit has been defined as the concentration of that metal that is acceptable in the rinse water because it

has no negative effect on the plate.¹⁶² Table 7.9 gives the effluent discharge limits for the metals for which published contaminant limits were also found.

Table 7.8 Optimal values for rinse criteria¹⁶²

<i>Rinsing process</i>	<i>Dilution factor</i>
Post degreasing and pickling	100-1000
Pre electroplating	500-2000
Post electroplating	1000-5000
Post decorative chromium plating	5000-10000

The dilution factor found for the nickel in the plating solution (in terms of its optimal concentration) and the final rinse tank of the nickel rinse system (Tank 13) was 1.2×10^4 and 1.4×10^4 for the two days' analyses results. These values exceed (by a factor of about 2.6) the top of the range literature value for the dilution factor required in post plating rinses (see Table 7.8). Similarly in the final rinse tank of the chromium plating rinse system (Tank 18) the dilution factor for chromium range from 2.3×10^4 to 1.7×10^5 over the monitoring period. The dilution factors measured for the chromium plating operations were found to be greater (by a factor of between 2 and 17) than the literature value for the dilution factor for post decorative chromium plating as given in Table 7.8.

Table 7.9 Effluent discharge and contaminant concentration limits values

<i>Substance</i>	<i>Effluent discharge limit</i> ¹⁶³	<i>Contaminant limit</i> ^{164, 165}
CrO ₃	Not specified	40 mg/L
Calculated as Cr	Not specified	19.2 mg/L
Ni	5 mg/L	8 mg/L
Cl ⁻	500 mg/L	50 mg/L
SO ₄ ²⁻	250 mg/L	200 mg/L
Total metals	20 mg/L	5 mg/L
Zn	5 mg/L	Not specified
Cu	5 mg/L	Not specified
Fe	5 mg/L	Not specified
Pb	5 mg/L	Not specified
Total dissolved solids	500 mg/L	250 mg/L
Conductivity	4000 μ S/cm	200 μS/cm
pH	6.5 to 10	6.0 to 8.0

The Sewage Disposal Bylaws issued by Durban Metro's Department of Waste Management only specifies a total chromium discharge limit {Cr(VI), Cr(III), etc} of 5 mg/L when the

effluent is going into a small sewage works. A small sewage work is defined as a plant which deals with less than 25 ML of effluent per day. The Sewage Disposal Bylaws require that the sum of the concentrations of the individual metal ions does not exceed 20 mg/L for a small sewage works.¹⁶³ All these concentration limits are greater for a large sewage works.

Tables 7.10a and 7.10b presents the data used in estimating the potential financial savings from reducing the volume of water used by the flowing rinses following the nickel and chromium plating solutions. Such calculations could not be performed on the other two rinse systems because these are also used by the other plating processes in the Chrome Shop.

Table 7.10a shows the water volume that can be saved by halving the flow rate in both flowing rinse systems. This (and not the static or reactive rinses) is considered to be the part of the rinsing process where water usage can be reduced. This is based on the finding that the dilution factors calculated using the optimum process solution concentration and the measured concentration in the final rinse solution are about double the top of the range literature value for the dilution factor given in Table 7.8 (dilution factor of 5000 for nickel and 10000 for chromium) for good rinsing. The projected annual water used in the flowing rinse is obtained by multiplying the new flow rate by the number of working hours per year (5616 hours) and the annual volume of water saved is estimated to be (4156m³). The annual water savings (R19949) is equal to the difference between the annual water used in the flowing rinse and the projected annual water used in the flowing rinse.

Table 7.10a An estimate of annual water savings for the plating processes

<i>Rinse system</i>	<i>Annual water used in the flowing rinse (m³)</i>	<i>New flow rate (m³/hr)</i>	<i>Projected annual water used in the flowing rinse</i>	<i>Annual water savings</i>	
				<i>m³</i>	<i>R</i>
Ni	3369	0.1	562	2807	13474
Cr	1798	0.08	449	1349	6475

Table 7.10b considers the rinsing and dilution in two steps namely that taking place in the drag-out and that obtained by the flowing rinse. The first dilution factor describes the situation between the process solution and the drag-out (or reactive rinse in the case of chromium) and the second dilution factor describes the situation between the drag-out and the final solution of

the flowing rinse. The dilution factor between the nickel plating solution and the nickel drag-out was calculated using the average drag-out concentration over the two monitoring days and the specified concentration of 82.5 g/L of nickel in the plating solution. Equation 2.6 given on page 66 in Chapter 2 was used to approximate the value for the average drag-out volume (D in Table 7.10b). The measured flow rate (Q in Table 7.10b), the average concentration in the final rinse (C_{FR} in Table 7.10) and average drag-out concentration (C_D in Table 7.10b) were used in Equation 7.4 to calculate the drag-out volume (D in Table 7.10). The values for Q are given in Table 6.5 in Chapter 6 and the average values C_{FR} and C_D are calculated from the analytical results for nickel and chromium in Tables 6.9 and 6.10. The new flow rate (Q_N in Table 7.10b) was then estimated using the calculated drag-out volume (D) and a dilution factor value calculated for the flowing rinse by dividing 5000 by the dilution value achieved by the static rinse. The volume of water (1291 m³) used in the flowing rinse has been estimated by multiplying the new flow rate by the number of working hours per year (5616 hours). It is assumed in this calculation that the drag-out volume will stay the same despite changes in solution concentration. The symbol “n” in Table 7.10 and in Equation 7.4 represents the number of stages in the flowing rinse system. The nickel rinse system has a three stage flowing rinse and the chromium rinse system has a two stage flowing rinse.

$$\frac{Q_{(N)}}{D} = n \left(\frac{C_D}{C_{FR}} \right)^{\frac{1}{n}} \quad \text{Equation 7.4}$$

Table 7.10b An estimate of annual water savings for the plating processes

Rinse system	Q m ³ /hr	Average C_{FR} (mg/m ³)	Average C_D mg/m ³	D m ³ /hr	Dilution factor	Q_N m ³ /hr	Annual water savings m ³
Ni	0.2	0.0064	3.6	8.1×10^{-3}	217	0.15	842
Cr	0.16	0.0036	1.6	3.8×10^{-3}	105	0.08	449

A comparison of the flow rate results for obtained for the nickel and for the chromium rinses from Table 7.10a and 7.10b show a good correlation for chromium and a higher (by 33%) value for nickel using the method based on Equation 7.4. However as the rates were measured on site using a crude (bucket and stop watch) method this is probably not such a bad result after all.

7.2 CHARACTERISATION OF RINSE WATER SOLUTIONS

The trends in and levels of contaminant concentration in the rinse waters will be discussed here for 13 of the solutions (see Figure 3.2 in Chapter 3 and Table 7.11) in the four counter current rinse systems and the hot static rinse. It must be remembered that there may be numerous reasons for the trend in results which cannot be measured or observed by this study. For example, there may have been fluctuations in the flow rate of the rinse water or differences in the drain time over the rinse tank, in the removal rates of dropped workpieces in the bottom of the tanks, in the amount of copper wire used for jiggling the various workpieces, and in the number and types of workpieces processed on the line. Further, increasing the concentration of the cleaning and of the plating solution increases the viscosity of the solution which is known to lead to an increase in the chemicals dragged-in to the next tank.

Table 7.11 Rinse water tanks in the MDCPL

<i>Tank</i>	<i>Non-MDCPL rinse function</i>	<i>MDCPL rinse function</i>
2	3 rd and last rinse for Cu and brass plating	Soak (acid and alkaline) cleaners' rinse
5	4 th and last rinse after acid dip Ni, Cr, and Cu	Electrolytic alkaline cleaners rinse
7&8	None	Acid dip rinses (1 st and 2 nd rinses after acid dip for Ni and Cr)
10	None	Static Ni plating rinse (Ni drag-out)
11,12 & 13	None	Counter current flowing nickel plating rinse 3 rd (i.e. last), 2 nd and 1 st rinse after drag-out.
15	None	Static Cr plating rinse (Cr drag-out)
16	None	Cr neutraliser
17&18	None	Counter current flowing Cr plating rinse 2 nd (last) and 1 st rinse after drag-out
19	Hot rinse before Tank III	Hot static rinse

In Chapter 6, Tables 6.9 and 6.10 summarise the chemical analyses results obtained for the rinse waters of the MDCPL on 9/06/03 and 20/06/03 respectively. Tables 6.11 and 6.12 show the chemical analyses of the process solutions carried out by the chemical manufacturers for nickel (Orlik) and for chromium (Chemserve). These results will be used to establish the degree of rinsing obtained for the counter current plating rinses and the cost of waste for the nickel and chromium lines.

The first three entries in Table 7.11 can be regarded as the pre-treatment rinse solutions. Of these only the acid dip rinses (third entry in Table 7.11) are exclusive to chromium plating. The other two pretreatment rinses are shared with the copper and brass plating operations. The remaining entries refer to nickel and chromium plating rinse tank solutions. The rinse solutions in Tank 10, 15, 16 and 19 are not flowing rinses. The flowing tank solutions are given in column one of Table 7.11 in order of increasing contamination of rinse water, that is from fresh rinse water entering from the mains to dirtier, used rinse water coming from the previous rinse tank.

The concentration of the metal ions nickel, iron, chromium, sodium, zinc, copper and lead in the mains water and the rinse solution was determined using ICP-OES at the beginning and end of the 9 days monitoring period. The concentration of Cr(VI) in the mains and rinse water was determined by UV-visible spectrophotometry. Tables 6.9 and 6.10 (Chapter 6) show that sodium was the element present in highest concentration in mains water, being at around 20 mg/L. Similar sodium levels were measured for the flowing rinses situated after the acid dip (Tank 6) and after nickel plating (Tank 11, 12 and 13) solutions. The concentrations of all the other metal ions were below the detection limit of the instrument. This indicates that the concentration of these metal in the mains water is negligible in terms of any adverse effect on chromium plating.

7.2.1 SOAK (ACID AND ALKALINE) CLEANER'S RINSE

The flowing rinse water in Tank 2 is used to remove drag-out from solutions in Tank 1 and in Tank 3 from the surface of the workpieces. The water feed into this tank is through two rinse tanks on the copper plating line. Water exiting Tank 2 is piped to the central effluent plant. The analyses results for this tank solution show sodium and zinc to be present in the highest concentrations on both sampling dates. The highest concentrations of sodium and zinc (306 and 446 mg/L) in solution were recorded on the 9/06/03. Iron, copper and nickel levels were more than a third lower by comparison. Even lower concentrations were observed for chromium and lead on this date. The high concentration of sodium in the tank is consistent with the dragged-out alkaline soak cleaners containing NaOH, Na₂SiO₃ and sodium based surfactants from Tank 3 and from the inflow of rinse water containing sodium cyanide from the

copper plating solution (Tank E in Figure 3.2). The pH was around 1.5 making the rinse water very acidic and likely to prevent precipitation of metal ions. The workpieces themselves represent the most likely source of zinc, iron and lead in this acidic solution. The concentration of dissolved zinc would likely originate from the die-cast workpieces such as bath handles, jewellery, toilet handles and brass ring fingers (see Table 6.3 in Chapter 6). The iron in solution could conceivably originate from the iron oxide removed from the workpieces' surfaces in the acid de-rust in Tank 1. The lead is thought to arise from an order of fishing weights plated on this line. Copper is the next most abundant metal found in this solution. On 20/06/03 its concentration was comparable to that of zinc and this solution, excluding the static drag-out, had the highest level of dissolved copper of all the rinse waters. Copper observed in the tank is likely to originate from two sources. Firstly, from the dissolution of the copper wires used in jiggling the workpieces and secondly from the water flowing into the tanks from the copper rinse solutions in Tank D and B of the copper plating line. The traces of nickel and chromium are most likely to be from residual plate which had been dissolved off the jigs themselves. This happens when the plate is not properly stripped off before going back through the process. There is also the possibility that uncontrolled chromic acid mist, produced during chromium plating, may dissolve out from the atmosphere into rinse solutions. The concentrations of these two metals was observed to fall over Tanks 2 and 5 and continue to drop for Cu in Tanks 7 and 8.

A comparison of the results over the two sampling days shows sodium, zinc, and iron levels fall by a factor of 1.8, 7.1 and 1.7 respectively and the copper rises by a factor of 1.8. The addition of chemicals and changes in the daily output can change the concentration of the metals through varying chemical consumption rates. On 17/06/03 17 kg of Chemalene 03 was added to Tank 3. This together with the addition of 25 g/L of caustic soda and 50 g/L of sodium cyanide to the copper plating line on 9/06/03 is one reason why the sodium levels did not fall as much as the zinc levels did. The increased output of the plated zinc workpieces was higher (4131 workpieces on 9/06/03 and 2092 workpieces on 20/06/03) by a factor of 2.0 on 9/06/03 compared to that on 20/06/03. This is consistent with the higher zinc levels found on 9/06/03. However this is not consistent with the iron levels found in the solution on 9/06/03 and on 20/06/03. The iron levels were lower by a factor of 1.7 on 20/06/03 compared to

9/06/03 even though 1513 steel workpieces were plated on 9/06/03 and 2071 on 20/06/03. There are numerous reasons why this was observed. For example, the workpieces cleaned on this day may have been greasy and the iron was not exposed to the solution or there might have been greater number of steel workpieces dropped in the acid de-rust (HCl solution) on 9/06/03 which could have caused an increase in the concentration of iron. The sources of copper are numerous. These include tips of the jig, the wires used for jiggling the workpieces and the dragged-out copper plating solution by the workpieces. This means it is difficult to make any meaningful comparison of the changes in copper levels over the two days.

Cushnie quotes a concentration range of 400 to 1000 mg/L as a “rinse criteria for permissible levels of contamination”.¹²⁸ Mohler gives a value of 750 mg/L as concentration of contaminants in the rinse following cleaning or pickling solutions.¹⁶⁶ Taking these as equivalent to the total dissolved solids levels and comparing them to the values measured for tank 2, 5, 7 and 8, they are all within the acceptable concentration range given by Cushnie. In only one case (Tank 2 on 9/06/03) did this value exceed the 750 mg/L limit value given by Mohler.

7.2.2 ELECTROLYTIC CLEANER'S RINSE

After workpieces are anodically cleaned in Tank 4, they are immersed in Tank 5 to wash off the electrolytic cleaner from the surface. The water feed into this tank comes from acid dipping for nickel, chromium and copper and flows through Tank 8, 7 and F before reaching Tank 5. Water exiting Tank 5 is piped to the central effluent plant. Analyses result for this solution show low concentrations of metals (highest being 9.6 mg/L for zinc) compared to Tank 2 on both monitoring days, except for sodium. The presence of high concentrations of sodium (164 and 103 mg/L) on the two days of analysis is likely to have resulted from the drag-in of the constituents of the electrolytic cleaners solution by the workpieces.

The concentration of iron and zinc was much higher on 20/06/03 than on 09/06/03. This is opposite to the trend observed in Tank 2. The pH in Tank 4 is quite alkaline (8.8) and so may cause these elements to precipitate out of the solution as insoluble hydroxide.

7.2.3 ACID DIP RINSE SYSTEM

Tanks 7 and 8 make up a counter current flowing rinse coming after the acid dipping solution. This rinse system is used to prevent contamination of the nickel plating solution with drag-out from pretreatment solutions. Tank 7 contains the dirtier rinse tank solution because the workpieces from Tank 6 enter this tank before being immersed in Tank 8. The analyses results are consistent with this rinse set-up, showing lower concentrations of all metal ions in Tank 8 compared to those found in the Tank 7 solution. This is because successive rinsing makes the drag-out solutions increasingly more dilute. For example, the dilution factor of the concentration of nickel on the two tanks in the first and second day of sampling was 2.4 and 3.5 respectively. However the concentrations of all the metals in the two days analyses results except sodium were below 5 mg/L.

Analyses results from Tank 7 and 8 solutions gave low concentration results for sodium, iron, and nickel. The sodium concentration was comparable to that found in the mains water supply. The concentrations of chromium, copper and lead metals were under 1 mg/L. This is less than the concentration limit 5 mg/L of nickel, iron, copper, zinc, lead and chromium prescribed in the effluent bylaws.¹⁶³ The different levels found for these metals is again consistent with these being different sources giving rise to the presence of each metal. This has been discussed in previous sections where it has been shown that the changes in each metal's concentration are not in the same proportion to each other. The presence of iron and zinc in this solution is consistent with the dissolution of the substrate metal of those (unplated) workpieces in the acid dip (Tank 6). This is then dragged over into the rinse water on the surface of the workpieces. Surprisingly nickel was observed in these rinse waters. After some investigation this was found to arise from the stripping of the chromium plate which does not fulfill the required specification. After the stripping, the workpieces are dipped in the dilute H₂SO₄ of Tank 22 and then rinsed in Tank 7 and 8 to prepare them for replating with nickel and chromium. Some of the removed nickel plate appears in these tanks because it was washed off the workpieces.

The analyses results of Tanks 5 and 7 show a higher nickel concentration in Tank 7 solution. All other metals show higher concentration in Tank 5 solution. Apart from sodium, all metal concentrations in both solutions are less than 10 mg/L and most are well under this value.

Further, a comparison of the results of Tank 7 of the two sampling days shows nickel, chromium and sodium levels fell by a factor of 1.4, 1.3 and 1.1 respectively. On the other hand, the concentrations of iron, zinc and copper levels were increased by a factor of 0.4, 0.18 and 0.4 respectively.

The analyses results over the two days of sampling for Tank 8 show nickel fell by a factor of 2.0 and the concentration of zinc and copper levels increased by a factor of 17.5 and 4.6 respectively. The concentration fall for nickel could be due to the decrease in stripping of the chromium plated on workpieces on 20/06/03. The increased concentration of zinc and copper in both tanks' solutions may reflect the fact that the dumping of the spent acid and the replacement with fresh acid had not taken place for that week (see Table 3.1).

7.2.4 NICKEL PLATING RINSE SYSTEM

Tank solutions 10, 11, 12 and 13 make up the rinse system used after nickel plating. Tank 10 solution is a static rinse drag-out located immediately after the plating solution. Aliquots of this tank solution are periodically used to top up the nickel plating solution of Tank 9 (see Table 3.1 Section 3.3.2)

Tanks 11, 12 and 13 are counter current flowing rinses used after the drag-out tank after the nickel plating solution. The main reason for using a counter current flowing rinse is to save water and improve the efficiency of rinsing. In the system of rinsing, Tank 11 is the "dirtiest" rinse tank and Tank 13 the "cleanest" rinse solution. This is because workpieces are dipped first in Tank 11 and process chemicals are washed off the workpieces' surfaces into this tank. It also receives the solution exiting from Tanks 12 and 13 which is not a fresh water supply. Water exiting Tank 11 is piped to the central effluent plant.

It is important to rinse the workpieces well after nickel plating in order to remove from the surface of the workpieces any chemicals which might be detrimental to the quality of the chromium plating and to prevent contamination of the chromium plating solution from dragged-in solutions. Iron, zinc, lead and copper concentrations are very low in Tank 13 (less than or equal to 0.1 mg/L) and not likely to present a problem. This is reflected in the limited

chemical treatment carried out on the chromium plating solution. Chlorides and sulfates from the previous tank solution originate from the hydrochloric and sulfuric acid based nickel electrolyte in the plating solution. The concentration of nickel in the plating solution is measured by the suppliers. It is expressed as the total metal, nickel chloride and nickel sulfate concentration. The level of chlorides and sulfates can be established from the values when the nickel is in excess. The levels of chlorides and sulfates in the final rinse have been calculated based on the dilution factor calculated for nickel levels in Tank 9 and Tank 13 and the specified (optimum) sulfate and chloride concentration in the process solution (Tank 9). The sulfate levels in Tank 13 were estimated to be 21 mg/L on 9/06/03 and 25 mg/L on 20/06/03. The chloride levels in Tank 13 were estimated to be 4.6 mg/L on 9/06/03 and 54 mg/L on 20/06/03.

The analyses results show that nickel and sodium are present in the highest concentration in all four solutions. The dissolved nickel species originates from the soluble nickel anode in the acidic nickel plating solution which has been washed off the workpieces into the drag-out. The concentration of sodium is mainly from the brighteners, wetting agents and fume suppressants used in the nickel plating solution. Obviously iron and zinc levels would be expected to be low since progressively less of the substrate is exposed to the solution during plating. The nickel levels are higher in all the rinse solutions than those measured in Tank 8 solutions. The concentration of the other metals are higher in the drag-out, and in many cases in Tanks 11 to 13 solution also, than those found in Tank 8. This is consistent with the drag-out rinse being static and so a buildup of metal ions is observed over time.

A comparison of the results for the Tank 10 solution over the two sampling days shows a higher concentration of all metal ions on 20/06/03. The most significant change was observed for nickel, sodium, iron and zinc. The concentration change of the metals went up by a factor of 8.7, 7.9, 5000 and 18 respectively. The concentration of nickel in the plating solution reported by Orlik chemical suppliers ranged from 78 to 87 g/L from 03/06/03 to 24/06/03 (see Table 6.11 in Chapter 6). The recommended concentration is 82.5 g/L. The measured concentration of nickel in the drag-out from the analysis result was 0.744 g/L on 9/06/03 and 6.44 g/L on 20/06/03. The low concentration of the drag-out compared to the plating solution

was due to the dilution of the dragged-in chemicals by the rinse water in the drag-out tank. About 70 L of mains water is added to the drag-out tank daily when 70 L of the drag-out is transferred to the nickel plating tank. It would be expected that the nickel levels would be highest in a sample of the drag-out solution taken just before transfer and lowest in a sample just after transfer. However assuming the concentration measured on 20/06/03 was prior to top-up i.e. addition of drag-out to process solution and of water to replace drag-out, the concentration expected immediately after top-up would be 4.12 g/L. This is 5.5 times higher than the value recorded on the 9/06/03. This suggests that the selected top-up had not taken place at the correct time or other factors, probably the number of workpieces going down the line had contributed to lower the nickel level in the bath than expected soon after top-up.

The analyses results of the samples of the three counter current rinse tanks of the two experimental days shows a decrease in concentration of the metals from Tanks 11 to 13. When the concentrations of the metals were compared over the two sampling days, higher concentrations were observed for nickel, iron, sodium, zinc and copper on 20/06/03. This is expected based on the concentrations in the drag-out tanks. For example in Tank 11 (the most concentrated), the concentration increased for these metals by a factor of 3, 368, 1.3, 4.6 and 7 respectively. Surprisingly the concentration of iron was observed to increase from Tank 11 to 13 in the samples taken on 9/06/03. During sampling there were around 23 pieces of metal dropped in Tank 13, 11 pieces of metal in Tank 12 and six pieces of metal in Tank 11. It is likely these metals had dissolved and caused deviation from the expected trend in the concentrations.

Over the monitoring period, however it is interesting to note that on both days the concentration of nickel and sodium in Tank 13 was virtually the same. The higher concentration of nickel and sodium in the drag-out on the 20/06/03 means the dilution factor cannot be the same throughout the rinse system on both days. The dilution factor between Tanks 11 and 12 solutions is similar on both days (1.5 and 1.7) whereas it is considerably greater between drag-out and Tank 11 (31 and 89) and between Tanks 12 and 13 (2.8 and 6).

Cushnie's acceptable "rinse criteria for permissible levels of contamination" for rinsing following bright plating ranges from 5 to 40 mg/L.¹²⁸ Mohler quotes an equivalent value of 40 mg/L for this parameter.¹⁶⁶ The values recorded on both sampling dates in all the nickel rinse tanks exceed this value. However during this monitoring period the filtration equipment on the nickel plating solution was not working. This may lead to higher than expected total dissolved solids levels.

7.2.5 CHROMIUM PLATING RINSE SYSTEMS

The chromium plating rinse solutions are found in Tank 15, 16, 17, 18 and 19. Tank 15 is a static rinse that contains solutions dragged-in by the workpieces from the chromium plating solution in Tank 14. The chromium plating tank is topped up with this drag-out solution. Tank 16 is also non-flowing but is drained and replenished regularly. It is a reactive rinse used to convert any dragged-in Cr(VI) into Cr(III) (see Equation 3.1 in Chapter 3) using sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$) and sodium carbonate (Na_2CO_3).

Chromium(VI) is added to the electroplating solution as solid CrO_3 . In acidic solution Cr(VI) is present largely as the dichromate ion, $\text{Cr}_2\text{O}_7^{2-}$, which is in equilibrium with the chromate, CrO_4^{2-} , in alkaline conditions (see Equation 1.10 in Chapter 1). This means that Cr(VI) cannot be precipitated as the hydroxide by raising the pH because the dichromate ion will be turned into the chromate ion. However reduction and precipitation is used for the treatment of wastewater containing Cr(VI). The chromium is reduced to Cr(III) by the addition of a reducing agent, namely sodium metabisulfite in Tank 16 on the line. Precipitation of the reduced chromium as a hydroxide is carried out at the central effluent treatment plant.

Tanks 17 and 18 constitute a two stage counter current rinse. Clean water enters the system through Tank 18 and exits via Tank 17 into the central effluent treatment plant. Tank 19 is a hot static rinse water tank. The main reason for making this tank solution hot is to try to ensure that any remaining chemicals have been removed from the workpiece surface and to dry the washed workpieces quickly in the air.

Analyses results from the two days of sampling shows an increase in the concentration of metals in the drag-out tank on 20/06/03 compared to that on the 9/06/03. The concentrations of chromium, sodium and nickel were highest. For example the concentration of chromium in the sample analysed on 20/06/03 was 21 g/L and nickel was the next highest at 6.44 g/L. The concentration of chromium is caused by the drag-in of the contents of the chromium plating solution of Tank 14 into Tank 15. Chromic acid mist is a well documented side product made when workpieces are plated with chromium.^{5, 14, 16, 38, 72} To prevent the mist from becoming airborne a fume suppressant containing sodium is added to the tank solution. This contributes to the concentration of sodium in the drag-out tank. The nickel present is likely to come from the nickel plate on the workpieces' surfaces which has been dissolved in the acidic Cr(VI) solution. The ratio of zinc to iron was the same on both sampling days. This may indicate that there were the same steel and zinc workpieces immersed in the bottom of the plating tank on both days which were losing iron and zinc at a constant rate. Lead is also dragged-in from the plating solution where lead alloy is used as the anode. Copper is dissolved from the tips of the jigs and the wires used in the jigging process.

The concentration of Cr(VI) in the plating tank (Tank 14) is determined by Chemserve chemical suppliers every week. On 4/06/03 the concentration was reported to be 288 g/L. The same analysis result was reported on 11/06/03. Then 10 kg of CrO₃ was added on 12/09/03. The analyses reported on 19/06/03 were a concentration of 303 g/L and 291 g/L on 23/06/03. The analyses results of the drag-out (Tank 15) were 6.95 g/L on 9/06/03 and 13.5 g/L on 20/06/03. About 25 L of fresh water is added every day to the drag-out tanks when the same amount of drag-out is used to top up the plating tank. It would be expected that the concentration of Cr would be higher in the drag-out solution just before top-up and lower in this solution just after top-up. The concentration measured on 20/06/03 may be assumed to be that prior to the addition of drag-out to the process solution and of water to replace drag-out. The concentration calculated for the drag-out after top-up was 10.9 g/L. This is higher than the value (6.95 g/L) obtained on 9/06/03. However this figure approaches the measured value of 13.5 g/L which is reasonable considering the variations in production rate and product range processed in a job shop.

The analyses results of UV-visible spectroscopy show highest concentration (6.95 and 13.5 g/L) of Cr(VI) concentrations in the drag-out tank (Tank 15) on both sampling days. The same trend is observed for the total chromium (8.3 and 21.3 g/L). The concentration decreased from Tank 15 to Tank 17. This is likely to be due to dilution of the dragged chemicals by each tank solution. The increase in concentration from Tank 18 to Tank 19 is mainly from the drag-in of chemicals from the brass passivation solution Tank III (see Figure 3.2 in Chapter 3) which contains sodium dichromate.

The concentration of Cr(III) in the samples (Tanks 15 to 19) could be calculated by subtracting the concentration of Cr(VI) obtained by UV-visible spectrophotometry (see Section 6.3.1 in Chapter 6) from the total chromium {Cr(VI) and Cr(III)} ICP-OES results. Highest concentrations were recorded in Tank 15 in the two days analyses results. The concentration was 1.35 mg/L on 9/06/03 and 7.5 mg/L on 20/06/03. These concentrations are not greater than the recommended Cr(III) concentration levels in chromium plating baths. In Tanks 16, 17, 18 and 19 low concentrations were recorded due to a decrease in the concentration of total chromium in each tank.

When the samples of Tank 16 were analysed, high concentrations of sodium and chromium were observed. Comparing the Cr(VI) and total Cr concentrations shows that the Cr(VI)-Cr ratio in Tank 15 (0.8) is higher than that in Tank 16 (3.3×10^{-4}). This is consistent with the continuous formation of Cr(III) from Cr(VI) in Tank 16. The obvious reason for this is the presence of sodium metabisulfite and sodium carbonate in Tank 16. However for True Cost of Waste Analysis the total Cr concentration is taken to be the same as Cr(VI) which undergoes reduction when it is dragged into this tank. The concentration of sodium was greater in Tank 16 than in Tank 15 because of the presence of sodium containing reducing and neutralising agents, sodium metabisulfite and sodium carbonate respectively. The concentration of the other metals was understandably less than that in Tank 15. This is because of the washing off of the chemicals in Tank 15 and the further dilution of the dragged-in chemicals by the solution of Tank 16.

The analyses results show that the concentration of the metals in Tank 16 solution on 9/06/03 was less than that on 20/06/03. This is because the solution on 9/06/03 was freshly prepared and the concentration of the metals in Tank 15 was less hence build up of the metal ions by dragged-in was lower compared to that on 20/06/03. However, since 20 kg of sodium metabisulfite was used on 9/06/03 and 14 kg on 19/06/03 to prepare the tank solution, the concentration of sodium in the analysis result was increased by 15% during the first day of sampling.

The concentration of each metal in Tank 18 was less than in Tank 17 of the two days of sampling and it was below 1 mg/L for most of the metals. The metals that showed high concentration levels in both tanks were chromium and sodium. The concentration of chromium is below the range of the effluent discharged by most electroplating industries which is 15-70 mg/L.¹⁶⁷ The concentration of sodium and chromium is mainly from the drag-out of the preceding tank solutions.

The concentration of Cr(VI) in both tank solutions was less than the total chromium determined. The concentration of Cr(VI) was below 1 g/L in all cases and was 0.1% (Tank 17 on 9/06/03) and 43% (Tank 18 on 9/06/03) of the total chromium. It was expected that the concentration of Cr(VI) in Tank 18 would be less than that found in Tank 17. The analyses results for both days showed that the concentration in Tank 18 was greater than that in Tank 17. Tanks 18 and 19 are found at the end of the MDCPL. Their position is close to the brass and copper lines. This enables these tanks to be used for other purposes such as the rinsing of brass plated workpieces after their passivation. In addition to this there is a chromium stripping tank at the far end of the plating line. Therefore after passivation or stripping off the chromium plating, the operators tend to dip the workpieces in these rinse tanks before they plate them again with chromium. The use of these tank solutions for rinsing workpieces after passivation and/or stripping was indicated by the Cr(VI) levels measured in Tank 19 being higher than those measured in Tanks 17 and 18.

The analyses results of Tank 19 show generally a higher concentration of metals than in Tank 18. This is because the tank is hot and static hence there is a buildup of the contents of

the drag-out solution from Tank 18. Analyses results for Tank 19 show that the concentration of nickel, chromium, sodium and zinc increased by a factor of 29, 58.5, 4.4, 15.2 respectively between each sampling day. Tank 19 is changed (dumped) every two days. Buildup of these metals in this tank can increase the concentration of the metals in the tank. The increase in concentration of chromium was highest of all metals. During sampling the colour of Tank 19 solution was yellow. This could be due to drag-in of chemicals mainly the brass passivating solution by brass plated workpieces. The decrease in concentration of copper is due to its low concentration in Tank 18. Thus the dragged-in copper will be low.

Comparison of the total dissolved solids recorded in the chromium rinse solutions show values above Cushnie's acceptable range of values on both dates of sampling periods. The normal range for adequate rinsing after bright plating is given as 5 to 40 mg/L.¹²⁸

7.2.6 THE COMPOSITION OF THE MDCPL RINSE SYSTEMS

The observed drop in the concentration levels for all the metals when comparing Tank 2 results with those of Tank 5, is paralleled by a fall in conductivity and TDS values on both sampling days. The fall in conductivity and TDS on going from Tank 5 to Tank 7 appears to arise from the drop in the sodium concentration in Tank 7 compared to Tank 5. The other metals are present in these tanks at much lower concentrations. For example, the metal with the next highest concentration after sodium on the 9/06/03 is nickel (concentration is about 60 times lower) and on 20/06/03 is zinc (concentration is one tenth that of sodium). The differences observed in their concentrations were small and so would be expected to have little effect on conductivity. The successive lowering of conductivity and TDS in going from Tanks 7 to 8, from Tanks 10 to 11 to 12 to 13 (nickel plating rinse system) and from Tanks 15 to 16 to 17 to 18 (chromium rinse system) and the increase in conductivity and TDS in going from Tanks 8 to 10 and from Tanks 13 to 15 is also consistent with the changing metal concentration trends. In only six cases over both sampling dates has the conductivity exceeded the effluent discharge limit value. The conductivity contaminant limit is quoted in the literature as being 200 $\mu\text{S}/\text{cm}$.¹⁶⁴ The final and cleanest rinse solutions in Tanks 8, 13 and 18 have the lowest conductivity values but these slightly exceed the contaminant limit. However the TDS contaminant limits have not been exceeded by these solutions. The TDS (mg/L) can be

calculated by multiplying the conductivity ($\mu\text{S}/\text{cm}$) by a factor between 0.55 and 0.9.⁷⁵ For the least contaminated rinse solutions in Tanks 8, 13 and 18 this factor was found to be about 0.6 in each case. This suggests that the quoted value (200 $\mu\text{S}/\text{cm}$) for the contaminant limit value of conductivity required for good rinse water quality may not have been set quite correctly.¹⁶⁴ However conductivity relates closely to the sodium and zinc levels in the acid and alkaline cleaner rinses (Tank 2), sodium levels in the electrolytic alkaline cleaners rinse (Tank 5), nickel levels in the nickel drag-out and chromium levels in the chromium drag-out.

The cleanest rinse tank in the MDCPL is Tank 13. Except for Ni, which has an average concentration of 6.4 mg/L, the average concentration of the other metal ions (Fe, Cr, Zn, Cu and Pb) in this tank, sent to the central effluent treatment plant, were below both the contaminant limit and the effluent discharge limit values given in Table 7.9. The highest average concentrations recorded in this tank were for chromium and zinc (0.48 and 0.061 mg/L respectively). The roughly estimated concentration of SO_4^{2-} and Cl^- levels in Tank 13 (see page 129 in Chapter 7) showed that the concentration of these species was below both the effluent discharge limit and the contaminant limit value on both sampling dates. Similarly the pH was within the recommended range while the TDS value was much lower than the effluent discharge limit and the contaminant limit values (see Table 6.6). As mentioned previously the conductivity was less than the effluent discharge limit value but greater than the contaminant limit value.

7.3 CHEMICALS USED AND WASTED

Many waste minimisation analyses techniques such as Scoping Audits, Mass Balancing and True Cost of Waste determinations can be used to quantify waste streams and to identify and prioritise them, with varying degrees of accuracy, as waste minimisation opportunities. This prioritising of potential waste problems for waste minimisation solutions (options or measures) is most frequently based on the expense they incur to the company. The cost of waste includes for example unused raw materials, the treatment and disposal costs of the waste and the utilities used in making the waste. The workpiece is a raw material. In a job shop it may not be viewed as a direct cost to the electroplating company. This study considers the chemical and other material waste but excludes energy beyond the Scoping Audit analysis.

In a Scoping Audit (see Section 7.3.1) the source and sink for the waste does not have to be established as long as the levels of inputs to and/or outputs leaving the process are known. This means little is known about what actually happens to the wasted raw materials during processing i.e. how much of a particular raw material becomes what kind of waste and where it accumulates in or leaves the process. New data from the chemical monitoring of the rinse water allow some materials lost in the wastewater to be measured directly (see Equations 7.5 and 7.6). The movement of this waste in the rinse water waste streams can therefore be tracked, quantified and costed as wasted raw materials in the waste stream. The waste present in the wastewater leaving the line contains unused plating chemicals and substrate. The real cost of wastewater takes into account the cost of the loss of these chemicals. The concentrations of the elements nickel and chromium in the wastewater have been used to determine raw material wastage. The mass of the constituent elements in the wastewater, which originate from the raw materials, can be calculated from the volume of exiting rinse water and the constituents' measured concentrations (see Equation 7.5).

$$\text{Mass in the wastewater} = \text{Measured concentration} \times \text{Volume of rinse water} \quad \text{Equation 7.5}$$

This can be expressed as a mass of that raw material if the composition of the raw material is known.

$$\text{Mass of raw material lost} = \frac{\text{Mass of the constituent elements in the wastewater}}{\% \text{ composition}} \times 100 \quad \text{Equation 7.6}$$

Existing data have been used to estimate the total wastage indirectly (see Section 7.3.2). Material balance calculations based on raw material usage have been carried out to estimate the nickel and chromium losses in the plating process. The losses from other process solutions like the soak cleaners, electrolytic cleaners and acid cleaners have been calculated based on these loss values obtained for chromium. The lack of compositional data on the formulation of the cleaners, together with the multi-use of these pretreatment rinses, made this the best available means of estimating losses to the wastewater stream.

7.3.1 SCOPING AUDIT

A Scoping Audit was prepared for the MDCPL in the Chrome Shop using the material data presented in Table 6.1 and Table 7.12. Chemicals used in the pretreatment stage were classified as “cleaning agents” under the heading Resources and Services in the Waste Minimisation Cost Assessment Table for the MDCPL (Table 7.12). The three most expensive raw materials were entered separately in Table 7.12. Packing is not used by the company and so was not applicable in this case. A category entitled “Treatment agents” (Waste and Process Solution) was created under the heading of Resources and Services with the intention to propose a Scope to Save category (see Conclusion in Chapter 8). It was given a tentative value of 10-40. This value was chosen as it was felt that more could be saved here than on the raw materials. This is because operators would tend to ensure all hazardous waste was completely treated and therefore would add a large excess of the treatment reagents.

Table 7.12 Annual usage and costs of input materials

<i>Input/raw materials</i>	<i>Average annual consumption</i>	<i>% of Total Cost</i>	<i>Consumption/m³</i>
Chemalene	659 kg	1.77	5.51x10 ⁻¹
Oxyprep 220EC	106 kg	0.35	1.10x10 ⁻¹
NaOH	940 kg	0.79	7.87x10 ⁻¹
HCl	2788 kg	1.05	2.89
H ₂ SO ₄	3896 kg	0.97	3.26
Ni chips	4129 kg	63.98	4.27
Nickelux 100 plus	1169 L	13.80	1.21
Brightener	74.0 kg	0.60	7.66x10 ⁻²
Wetting agent	21.0 kg	0.06	2.17x10 ⁻²
Addition agent SA1	145 kg	1.16	1.x5010 ⁻¹
H ₃ BO ₃	96.0 kg	0.14	9.94x10 ⁻²
Filter aid	4.00 pack	0.01	4.14x10 ⁻³
Filter cartridge	3.00 pack	0.01	3.11x10 ⁻³
Filter felt 120	4.00 pack	0.04	4.14x10 ⁻³
Activated carbon	11.0 kg	0.06	1.14x10 ⁻²
CrO ₃	200 kg	0.71	3.09x10 ⁻¹
Lumina 34 make-up	92.0 kg	0.85	1.42x10 ⁻¹
Lumina 24	0	0	0
Fumetrol 140	12.0 L	0.69	185x10 ⁻²
Na ₂ S ₂ O ₅	709 kg	0.48	1.09
Na ₂ CO ₃	501 kg	0.26	0.773
BaCO ₃	9.00 kg	0.01	1.39x10 ⁻²
Lead anode	0	0	0
Copper wire 20GZ	1713 kg	12.24	1.43

Estimates for the electricity used had to be made as no line is individually metered: this is shown in Table 7.13 as NM, not measured. Allocation of electrical consumption to MDCPL was discussed with the manager and a monthly figure of R2880 was considered to be a reasonable approximation of the consumption for the MDCPL. This is made up of the electroplating cells (nickel and chromium), a stirrer on the hot soak cleaner, heaters (for the chromium and nickel plating baths, soak and electrolytic cleaners, and the stripping unit), wall fan and lighting. It has proved impossible to quantify and cost the sludge output from the MDCPL. This is because the wastewater from all the electroplating lines is being continuously fed to the central effluent treatment plant. This means the sludge produced from the effluent coming from each electroplating line is not segregated and so cannot be quantified for individual lines. Therefore sludge has been excluded from the Scoping Audit. The effluent volume is quoted as being 96% of the estimated water used on the MDCPL (see Table 7.13) and the cost is made up of the trade effluent cost and the monitoring cost. The fixed charge is included in the water cost.

The annual average cost obtained by estimating the average daily cost for these chemicals using the data collected for the MDCPL over 8 months (see Table 6.1 in Chapter 6) and multiplying it by the number of working days per year using Equation 7.7. The Scoping Audit calculations were carried out using Equations 7.8 and 7.9.

$$\text{Cost/year} = \text{Cost/day} \times 234 \text{ days/year} \quad \text{Equation 7.7}$$

$$\text{Scope (min)} = \text{Minimum scope to save \%} \times \text{Cost/year} \quad \text{Equation 7.8}$$

$$\text{Scope (max)} = \text{Maximum scope to save \%} \times \text{Cost/year} \quad \text{Equation 7.9}$$

The priority for these resources or waste streams as a waste minimisation opportunity is assigned based on either of these two costs. The greater the scope min or scope max value then the greater is the potential waste problem and the higher the opportunity for waste minimisation. Table 7.13 shows that water and effluent present the company with the most considerable waste problem with the nickel chips being the next likely problem. The higher the waste minimisation opportunity potential of a resource and service, then the smaller the numerical value given to the priority rating in the last column in Table 7.13. The treatment agents for solution maintenance have the lowest priority for waste minimisation in the current

situation. This means opportunities can be ranked simply in terms of the cost they produce or the quantity of the resources they consume. This method fails to consider the hazardous nature of the waste, its treatment prior to disposal and the payback period associated with the institution of a waste minimisation option. Payback period (see Equation 7.10) is basically the time it takes to recoup the money which must be spent in order to put the option into practice i.e. capital investment.

$$\text{Payback period/year} = \frac{\text{Cost of capital investment}}{\text{Annual services} - \text{Annual running costs}} \quad \text{Equation 7.10}$$

Using the priority rating in Table 7.13 means that only “low cost-no cost” waste minimisation options (waste minimisation measures) can be considered as solutions to the waste problems in this case.

Table 7.13 Waste Minimisation Cost Assessment Table for the MDCPL

<i>Resources and services</i>	<i>Quantity</i>	<i>Cost per year (R)</i>	<i>Scope to save (%)</i>	<i>Scope (min)</i>	<i>Scope (max)</i>	<i>Priority</i>
Raw materials:						
Nickel chips	2876 kg	279162	1-5	2792	13958	3
Nickelux 100 plus	814 L	60138	1-5	601	3007	5
Copper wire	1193 kg	53411	1-5	25.7	128.7	8
Cleaning agents:						
HCl	1942 kg	4572	5-20	229	914	6
H ₂ SO ₄	2714 kg	4247	5-20	212	849	7
Treatment agents:						
Filter felt 120	3 pack	196.6	10-40	19.7	78.64	9
Activated carbon	7.7 kg	234	10-40	23.4	93.6	10
Electricity	NM	34560	5-20	1728	6912	4
Water	11498 m ³	55190	20-80	11038	44152	1
Effluent	NM	22239	20-80	4448	17791	2

7.3.2 MASS BALANCE ANALYSIS

The measured concentration values used in Mass Balancing are averaged over the start and the end of a 9 day monitoring period over which detailed output data were collected (see Table 6.4 in Chapter 6). The concentrations were averaged because the concentration levels were assumed to be steady state values. This is indicated by the lack of regular (e.g. weekly) dumping of the flowing rinse water because of the accumulation of metals to levels which adversely affect plating. A daily rate of raw material usage was obtained using the data in

Table 6.2. The consumption after the 9 day monitoring period was based on this figure using Equation 7.11.

$$\left[\begin{array}{l} \text{Average mass of chemicals} \\ \text{used in a given time period} \end{array} \right] = \left[\begin{array}{l} \text{Average mass of} \\ \text{chemicals used/day} \end{array} \right] \times \text{Time period/day} \quad \text{Equation 7.11}$$

The monitoring results for the nickel and chromium plating lines on the 9/06/03 and 20/06/03 show that these metals lost to the rinse system from the plating solution largely end up in the drag-out solutions. From there they are re-used in the plating solution and dragged-out into the flowing rinse system. It was not possible to include chemical treatment of portions of the drag-out for disposal in this study because it is infrequent and not documented.

The final (exiting) rinse water from Tank 2, 5 and 11 contains an average of 13, 2.1 and 48 mg/L Ni respectively which is sent to the effluent treatment plant. Tanks 16 and 19 are static. The solution in Tank 16 is dumped every 3 days. The volume of the tank is 0.214 m³ (see Table 3.1 in Chapter 3). In 9 days the volume of solution discharged is estimated to be 0.64 m³ and the average concentration to be 41.7 mg/L. Tank 19 has a volume of 0.931 m³. The contents are dumped every 2 days. In 9 days the volume of solution discharged will be 4.12 m³ and the average concentration will be 3.47 mg/L. Tables 7.14 and 7.15 show the nickel losses calculated using existing and new (monitoring) data respectively.

Table 7.14 Estimation of Ni waste using existing data

From input data	Mass of Ni anodes used/day	17.6 kg
	Mass of Ni anodes used/9 days	158 kg
From output data	Total area plated/9 days	966 m ²
	Density of nickel ¹³⁴	8.9 g/cm ³
	Thickness of Ni plate ¹⁴⁷	10 µm
	Mass of Ni plated/9 days	86 kg
Mass of Ni lost = Ni anodes used/9 days – Mass of Ni plate/9 days		72 kg
Cost of Ni lost		R4869
% Ni lost = $\frac{\text{Mass of Ni lost /9 days}}{\text{Mass of Ni used/9 days}} \times 100$		45.6

Table 7.15 Estimation of Ni waste using new data

	<i>Tank 2</i>	<i>Tank 5</i>	<i>Tank 11</i>	<i>Tank 16</i>	<i>Tank 19</i>
Average concentration of Ni in exiting rinse water (mg/L)	13	2.1	48	41.7	3.47
Volume of exiting rinse water (m ³)	26.4	48	48	0.64	4.12
Mass of Ni lost in rinse/9 days (g)	343	101	2.30x10 ³	26.7	12.9
Cost of Ni lost in rinse/9 days (R)	23.2	6.82	156	1.80	0.87
Estimated mass of Ni lost in rinse (kg)	2.8				
Estimated mass of Ni lost in the second Ni line (kg)	3.0				
Total cost of Ni lost as drag-out (R)	392				

A comparison of the results of Table 7.14 and 7.15 suggests that very little of the total nickel losses (72 kg) can be ascribed to the drag-out (about 6 kg) over the 9 day period. If the plating thickness were at the lower end of acceptability, 8 μm , the nickel losses would still be high (69 kg). The calculated surface area plated is a very rough estimate which could conceivably be an over-estimate. However, even at half of the value quoted in Table 7.14 the losses would be 43 kg. Anode purity, the mass of the anode stubs and of the suspended nickel removed during filtration or capture in anode bags, over-plating, stripping of nickel with chromium in the chromium stripping bath (Tank 20), dissolving of nickel in the acid dipping tank (Tank H) and dripping of the dragged plating solution onto the floor due to insufficient drain time of the solution from the workpieces when transferred to the drag-out tank and to the flowing rinse system (see Figure 3.2 in Chapter 3) represent some other possible losses not quantified by this study. These results also show that the wetting agent and/or work practices are helping to reduce drag-out from the nickel plating solution. It could be argued that the results obtained on the trial dates (31/03/03 and 11/04/03) are more typical for the system. This means drag-out losses would be higher than those determined here. However job shop operations have an irregular throughput of workpieces which are reliant on the clients' orders and it is felt that the monitored situation reflects such fluctuations in production rate.

The main form of Cr(VI) purchased for use in the plating solution is simple CrO₃ (see Table 6.2). Lumina 34 is used infrequently in the chromium plating solution as a source of Cr(VI). The 8 month consumption rate (see Table 6.2) is therefore taken as being the same as that for the full year for Lumina 34. This means an average of 0.27 kg of Lumina 34 is used per day and 2.5 kg over 9 days. Lumina 34 contains CrO₃ and organic acids. The percentage

composition of CrO₃ in Lumina 34 is assumed to be 100% from the information given in the MSDS. It will in fact be slightly less than this due to the presence of the catalyst(s). This means there are an estimated 1.3 kg of Cr(VI) present in the plating solution originating from Lumina 34.

The exiting rinse water leaving Tanks 2, 5, 16, 17 and 19 (and going to the effluent treatment plant) in the chromium plating line contains an average of 2.35, 0.87, 1574, 24.3, and 38.7 mg/L Cr respectively. Tables 7.16 and 7.17 show the figures for the mass of Cr lost to the effluent streams based on existing and new data respectively.

Table 7.16 Estimation of Cr waste using existing data

From input data	Mass of CrO ₃ used/day	0.85 kg
	Mass of CrO ₃ used/9 days	10.2 kg
	Mass of Cr used/9 days	5.3 kg
From output data	Total area plated/9 days	648m ²
	Density of Cr ¹⁴⁴	7.2 g/cm ³
	Thickness of Cr plate ¹⁴⁷	0.4 μm
	Mass of Cr plated/9 days	1.9 kg
Mass of Cr lost = mass of Cr used/9 days – mass of Cr plated/9 days		3.4
Cost of Cr lost		R90
$\% \text{ Cr lost} = \frac{\text{Mass of Cr lost /9 days}}{\text{Mass of Cr used/9 days}} \times 100$		64

Table 7.17 Estimation of Cr waste using new data

	Tank 2	Tank 5	Tank 16	Tank 17	Tank 19
Concentration of Cr in exiting rinse water (mg/L)	2.35	0.87	1574	24.3	38.7
Volume of exiting rinse water (m ³)	26.4	48	0.64	38.4	4.12
Mass of Cr lost in rinse water/9 days (g)	62.0	41.8	1007	933	159
Cost of CrO ₃ lost in rinse/9 days	0.96	0.65	0.016	14.5	2.47
Total mass of Cr lost in rinse (kg)	2.2				
Total cost of Cr lost as drag-out (R)	34.2				

The results from Tables 7.16 and 7.17 indicate that drag-out (2.2 kg) is responsible for about two third of the Cr losses (3.4 kg). This implies that the release of Cr(VI)-containing acid mist during plating is likely to be significant and the foam blanket (Fumetrol 140) is not stopping all Cr(VI) emissions to the atmosphere. Drag-out control appears to need some improvement. A hoist is used to lift workpieces in and out of the chromium plating solution and hold them

above this solution to allow for good drainage. However perhaps insufficient drain time is allowed and so little of this viscous plating solution is actually returned to the tank. Further, when the line is busy the drain time is likely to become further compromised.

The average Cr losses are around 36 times less than the average Ni losses. This is consistent with much less Cr being used than Ni over the 9 day period.

7.3.3 TRUE COST OF WASTE ANALYSIS

The True Cost of Waste was determined for the raw material wastage and on-site treatment for disposal and for maintenance of process solutions. It was mentioned earlier (Section 7.3.1) that it was not possible to establish the off-site waste treatment and disposal cost associated with MDCPL. For nickel plating there is an additional cost of filtering the plating solution while for chromium plating there is an additional cost for the barium carbonate treatment of the plating solution and the chemical reduction of the waste Cr(VI) in Tank 16. Existing data are used to estimate the maintenance costs for the nickel bath (see Table 7.18) and for the chromium plating solution (see Table 7.19) and the chemical reduction cost for the Cr(VI) (see Table 7.19). The maintenance costs of the nickel plating solution are considered to arise from the materials consumed in purifying the solution by continuous filtration. The results in Table 7.18 can be compared to those entered in Table 7.21 which summarises the calculated True Cost of Waste based on significant aspects of raw material usage and wastage.

Table 7.18 Estimation of maintenance materials used in Ni plating and their costs using existing data

<i>Maintenance material</i>	<i>Quantity used per day</i>	<i>Quantity used per year</i>	<i>Cost (R) per year</i>
Filter aid (pack)	0.019	4	32
Filter felt 120 (pack)	0.018	4	182
Filter cartridge	0.012	3	25
Activated carbon (kg)	0.047	11	253
Annual cost per year (R)			492

Table 7.19 Estimation of maintenance and reactive rinse chemicals used in Cr plating and their costs using existing data

<i>Maintenance material</i>	<i>Quantity used per day</i>	<i>Quantity used per year</i>	<i>Cost (R) per year</i>
Na ₂ S ₂ O ₅ (kg)	3.03	709	2084
Na ₂ CO ₃ (kg)	2.14	501	1132
BaCO ₃ (kg)	0.04	9	23
Annual cost per year (R)			3239

The amount of soak cleaner, electrolytic cleaner and acid cleaner ending up in the wastewater and lost to the sewer as drag-out is derived per year using the loss values obtained for chromium. The nickel plate production is split between two lines each with their own drag-out. However they share the same flowing rinse systems. The drag-out losses from these pre-treatment solutions, which handle all production, is therefore based on chromium percentage value (64%, see Table 7.16 and Tables 7.17). These values were adjusted higher or lower for the process solutions according to the operating conditions i.e. temperature and concentration, (see Table 7.20).

Table 7.20 Estimation of annual drag-out loss using existing data

	<i>Soak cleaners</i>	<i>Electrolytic cleaners</i>	<i>HCl de-rust</i>	<i>HCl dip</i>	<i>H₂SO₄ dip</i>
Average annual quantity (kg)	659	106	340	670	3896
% loss through drag-out	60	50	25	10	25
Average annual drag-out loss (kg)	395	53	85	67	974

The maintenance and treatment costs for chromium and nickel plating have been included in the True Cost of Waste for the effluent stream in Table 7.21. This is because they act to reduce contamination of the rinse solutions. Therefore without these measures in place the concentration of and perhaps the number of species in the drag-out would be greater.

The priority rating of the waste stream as a potential waste minimisation opportunity is assigned in the same way as for the Scoping Audit. This analysis shows the rinse water presents the most significant waste minimisation opportunity. It has about 11 times more potential financial savings {see Table 7.21 column three entitled Total cost (R)} than the second highest waste minimisation opportunity (soak cleaner).

Table 7.21 A True Cost of Waste summary: quantity and cost breakdown

Waste stream	Waste components			Total cost(R)	Priority	
	Chemicals	Quantity	Cost(R)			
Rinse wastewater (effluent)	Soak cleaner	395 kg	4622	85051	1	
	Electrolytic cleaner	53 kg	760			
	HCl (de-rust & dip)	152 kg	249			
	H ₂ SO ₄ cleaner	974 kg	1062			
	CrO ₃	55 kg	854			
	BaCO ₃	9 kg	23			
	Na ₂ S ₂ O ₅	709 kg	2084			
	Na ₂ CO ₃	501 kg	1142			
	Ni	151 kg	10212			
	MM Ni plating	Table 7.18	492			
	Cu	29.4 kg	916			
	Water	11668 m ³	56006			
	Spent process solutions	Soak cleaner	Soak cleaner			659 kg
Water solvent			17.5 m ³	84		
Electrolytic cleaner		Electrolytic cleaner	106 kg	1530	1586	5
		Water solvent	11.66 m ³	56		
Acid dip		HCl	2788 kg	4572	4597	3
		Water solvent	5.13 m ³	25		
Acid dip		H ₂ SO ₄	3896 kg	4247	4260	4
		Water solvent	2.64 m ³	13		

MM Ni plating = Maintenance materials for the Ni plating solution (see Table 7.18)

7.3.4 THE WATER ECONOMY DIAGRAM

The Water Economy Diagram, like the Scoping Audit, is an empirical model specifically designed for analysing water consumption in electroplating plants. It was developed in the United Kingdom based on information supplied by companies in the metal finishing sectors. It allows water usage to be classified into one of four categories using a type of monitoring and targeting matrix. If the water consumption rate falls into either of the two unacceptable categories (Worst and Worse than average) then there is the potential to reduce water usage below the current value.

The Water Economy Diagram shown in Figure 7.1 determines how efficiently water is used in terms of output. Output is expressed as the surface area treated per year. The average annual surface area treated is 31044 m² (see Table 6.4). The estimated annual water consumption is 11498m³ (see Table 6.3). When these are plotted in the water economy diagram, the performance point falls in the “worse than average” sector.

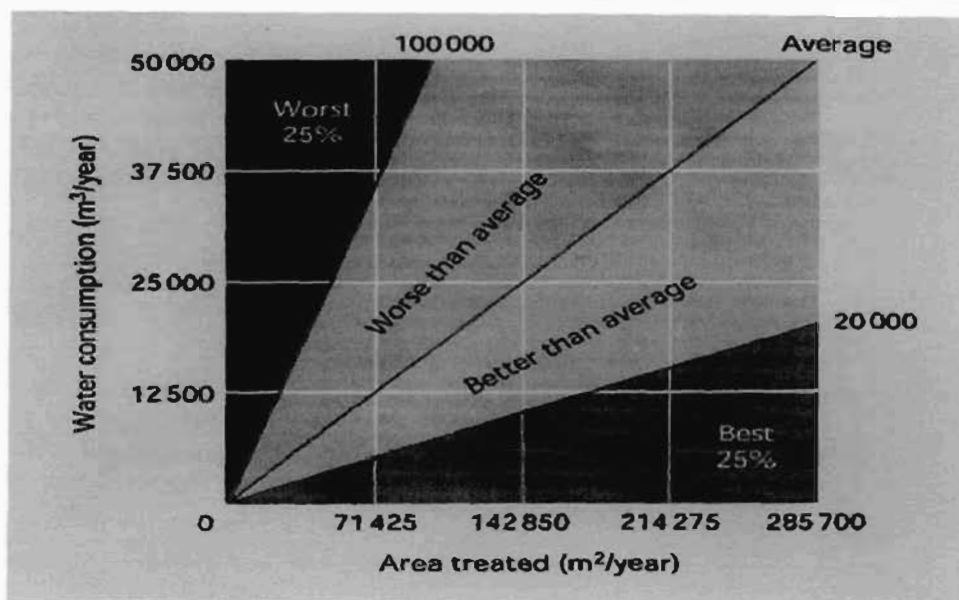


Figure 7.1 Water economy diagram^{106,168}

CHAPTER 8

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8.1 CONCLUSION

The waste minimisation analyses results show that more nickel is lost from the process solution as drag-out than for chromium plating. Therefore nickel is lost from the process by means other than through the flowing rinse system. The opposite appears to be true in the case of the chromium losses. Chromium levels measured in the wastewater make up about one third of the waste in terms of mg/L. From a comparison of the concentration levels measured on 9/06/03 with those measured on 31/03/03, 11/04/03 and 20/06/03 it could be argued that the results from the 9/06/03 are lower than the norm. However fluctuations in incoming workloads and therefore in the rate at which workpieces go down the line are expected in a job shop. This will be reflected in the metal content of the solutions and should be considered as an authentic representation of the situation rather than an artifact. It should also be remembered that a number of assumptions have been made when carrying calculations in this study. Some calculations have used some gross estimates for parameters such as surface area and drag-out losses for pre-treatment solutions. Conversions between daily, 9 days, 163 days (March to October) and 234 days (annual number of working days) have been widely used in calculations. However errors of up to 20 % are not unusual in this type of analysis.¹⁶⁹

The contaminant levels in the exiting rinse water represent a waste minimisation opportunity. This is indicated by the results from the Scoping Audit, the Mass Balancing, the True Cost of Waste Analysis and the Water Economy Diagram.

The chemical consumption data show that the greatest potential financial savings can be made by reducing the nickel losses. The annual total nickel losses have been estimated to be 1872 kg. This represents a potential financial saving of R126603. By reducing annual nickel drag-out from 151 kg to zero would achieve a potential financial saving of R10212.

The Mass Balance and True Cost of Waste analysis were performed for nickel because it was highlighted as a priority area in the Scoping Audit. It was given the third highest value for

scope to save. However the Mass Balance showed that nickel wasted is not ending up in the effluent. This means that reducing drag-out is perhaps not the most significant waste minimisation measure in this case. However preventing spillage on the floor and minimising processing time in the chromium stripping and acid dipping solutions should be looked at. Further it should be ensured that when workpieces are being removed from the nickel plating they must be carried to the drag-out tank over the solution and not over the floor.

The Mass Balancing on chromium shows the loss of two thirds of the chromium to the effluent. The increase in chromium levels in Tank 19 compared to Tank 18 are likely to be the result of the rinsing of workpieces which have been removed from the brass passivation solution (Tank III). This confirms that not all the lost chromium from the chromium plating solution is lost as drag-out and some losses to the atmosphere may occur. Drag-out losses can be minimised by allowing sufficient draining time before transferring workpieces and by using a drain board between the plating and the drag-out tanks. The loss of chromic acid mist to the atmosphere can be reduced by using sufficient and effective fume suppressants in the chromium plating bath and/or by using local exhaust ventilation along the rim of the tank.

Water is used in the electroplating plant for various purposes, the largest volume used being in the flowing rinses and contributing to the effluent waste stream. Minimising the volume of rinse water in a plating line reduces the amount of wastewater discharged to the treatment plant and the cost spent in treating it. In the Scoping Audit (see Tables 7.10) and in the True Cost of Waste Analysis (see Table 7.18) water appears first in the waste minimisation opportunity priority listing. In the True Cost of Waste Analysis (see Table 7.18) nickel lost by drag-out appears second to water in the effluent stream. The "Water Economy Diagram"¹⁶⁸ showed that the use of water in the plating line was "worse than average". Therefore, water and hence effluent, may be considered the most important waste minimisation opportunity in the Chrome Shop from which financial savings can be achieved for the plant.

Water offers the greatest potential financial savings. This is in spite of the fact that countercurrent flowing rinses are operated. However there are no audio or visual alarms on the process solution tanks to indicate when a surface treatment is complete. This together with the

line being manually operated may have led to difficulties in achieving process control. Reducing rinse water consumption by switching off the water supply during idle periods has been estimated to save 950 m³ of water (R4560). By bringing the flow rate down for nickel and chromium plating rinses, in order to achieve a water usage consistent with the literature values for the dilution factors, would save approximately 4156m³ (R19949).

8.2 RECOMMENDATIONS

From the findings of this waste minimisation study, the following waste minimisation measures (focusing mainly on water consumption) of this line are suggested for consideration by Saayman Danks Electroplating for the MDCPL.

- Using water only when necessary. The mains water valve of the Chrome Shop should be closed especially during tea time, lunch time and the time between the two shift changes either manually or by installing activity based control devices. By doing this more than 950 m³ of water at a cost of R4560 can be saved for the plant in a year.
- Reducing the volume of rinse water cautiously in order to approach the literature dilution factors by installing either water flow restrictors or conductivity meters. Based on the estimated water savings for only two of the rinse systems a minimum of 4156m³ (R19949) may be achieved.
- Less use of copper wiring and more use of jigs with suitable hooks for jiggling of workpieces.
- Installing drain board between tanks. The layout of the MDCPL prevents the use of drain boards between tanks which are separated by aisles.
- Increasing the drain time of the solutions by installing drain bars above the process solutions and rinse solutions to hang jigs on. This is especially important before jigs are moved across an aisle when taken from one tank to another.
- Investigating the nickel lost in chromium stripping and acid dipping solutions in order to quantify its contribution to the wastage of nickel.
- Redesigning the structure of the rinse tanks in order to force water entering at the top of a rinse tank to leave from the bottom of the opposite side (and not the top) of that tank or vice versa.

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APPENDIX

APPENDIX A

In this appendix, the instruments used in determining the concentration of metals in the samples are presented. These include UV-visible spectrophotometer used in determining the concentration of Cr(VI) and ICP-OES used in determining the concentration of Ni, Fe, total Cr, Na, Zn, Cu and Pb present in the mains water, drag-out and rinse water tank samples.



Figure A.1 Cary 50 ultraviolet visible spectrophotometer



Figure A.2 Liberty 150 AX Turbo ICP-OES

APPENDIX B

This appendix presents the calibration graphs used in determining the concentration of Cr(VI) in the samples collected on 9/06/03 and 20/06/03.

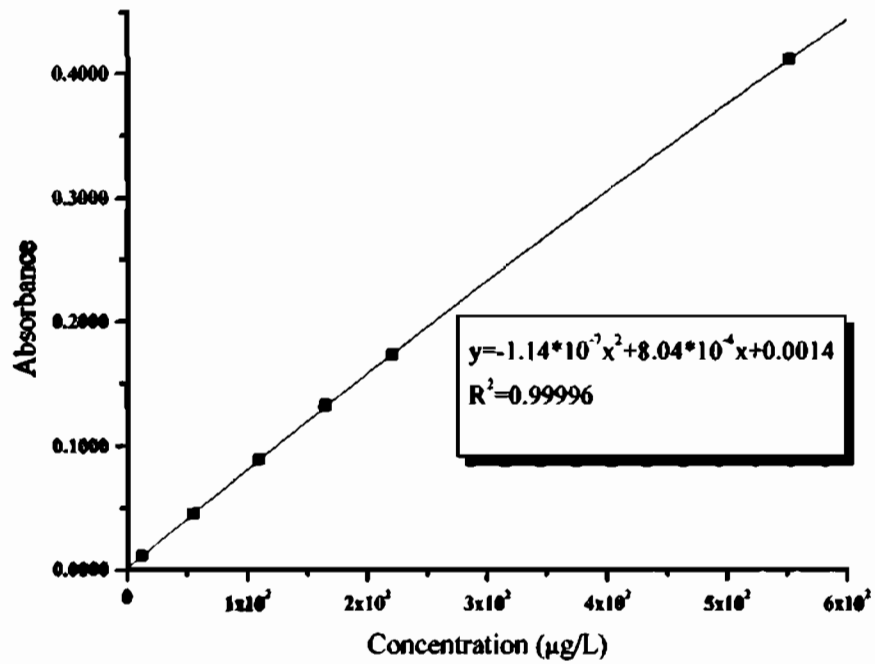


Figure B.1 Calibration graphs of Cr(VI) on 9/6/03

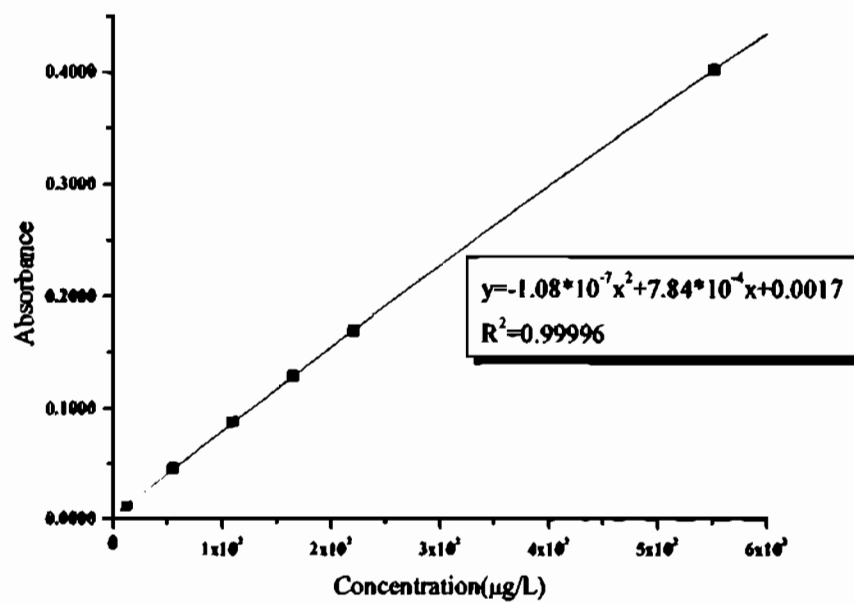


Figure B.2 Calibration graphs of Cr(VI) on 20/06/03

APPENDIX C

This appendix presents the calibration graph of nickel, iron, chromium, sodium, zinc, copper and lead standard solutions for the samples collected on 9/06/03 and 20/06/03. Figures C.1 shows the calibration graph of the metals on 9/06/03 and Figures C.2 show the calibration graph of the metals on 20/06/03.

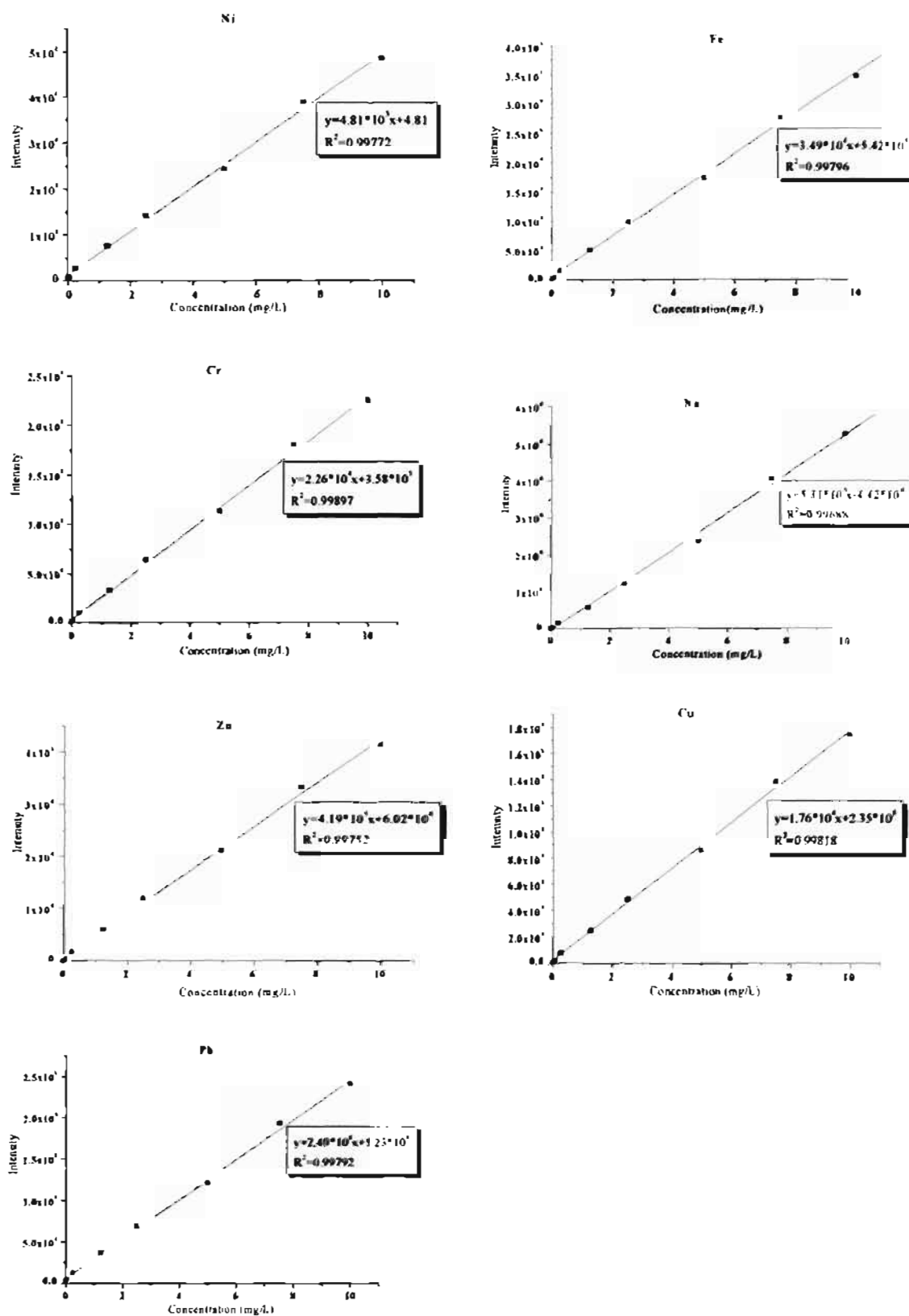


Figure C.1 Calibration graphs of Ni, Fe, Cr, Na, Zn, Cu and Pb on 09/06/03.

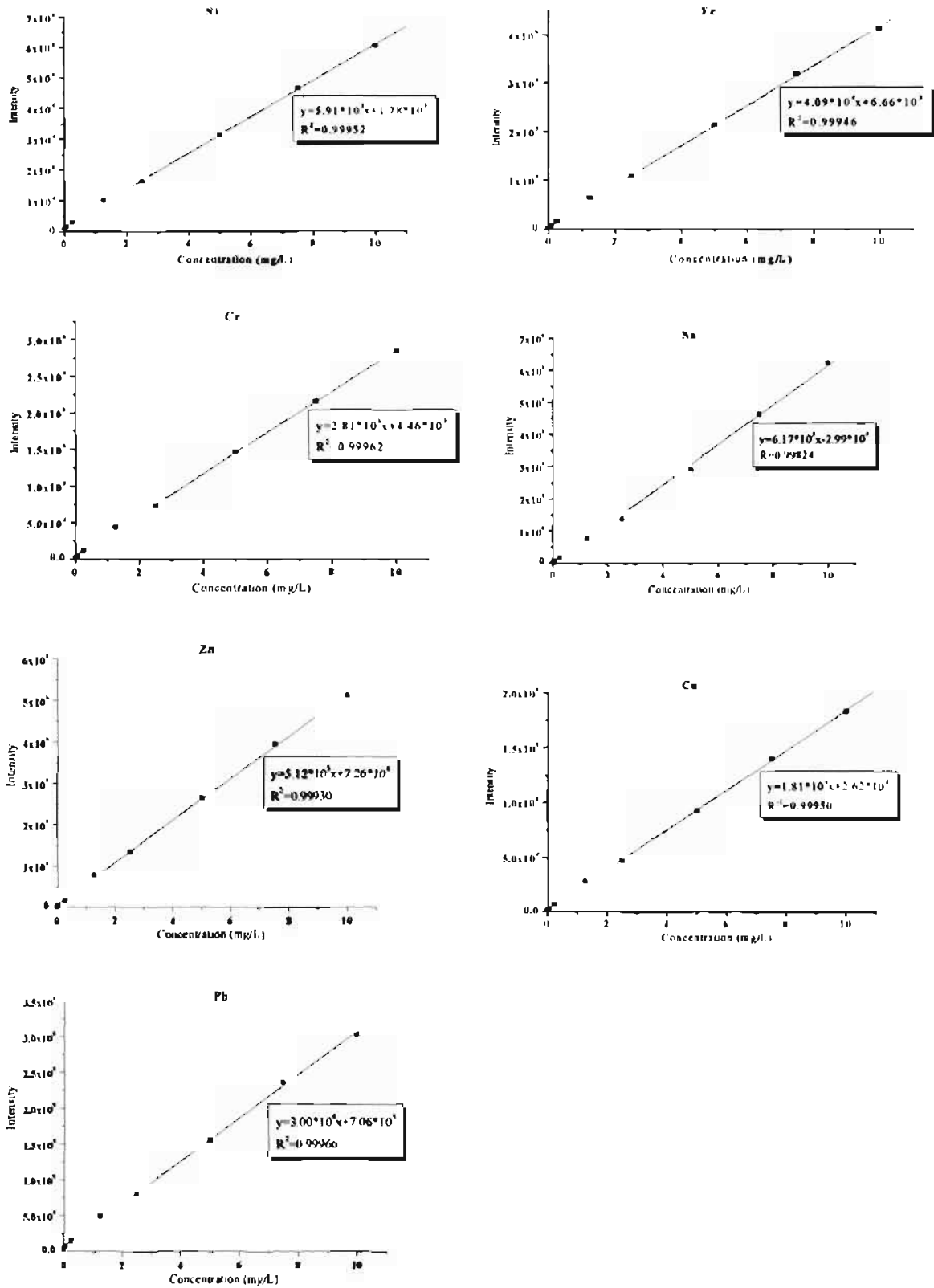


Figure C.2 Calibration graphs of Ni, Fe, Cr, Na, Zn, Cu and Pb on 20/06/03.

APPENDIX D

In this appendix, the analyses results of the samples collected on 31/03/03 and 11/04/03 are presented. Table D.1 presents the average of three concentrations measured on three different samples taken on 31/03/03 from the surface, middle and bottom of the tank at different times between 6:50 and 10:15. Table D.2 shows the average concentrations of the metals measured on two samples taken from the surface and bottom of the tank at one time one after the other on 11/04/03 between 12:55 and 1:15.

Table D.1 Average concentration (mg/L) of metals in the samples collected on 31/03/03

<i>Tank</i>	<i>Ni</i>	<i>Fe</i>	<i>Cr</i>	<i>Na</i>	<i>Zn</i>	<i>Cu</i>	<i>Pb</i>
2	23	57	1.6	1.6x10 ²	62	18	0.18
5	20	10	0.65	1.2x10 ²	4.2	0.97	0.033
7	9.2	17	0.25	35	0.74	0.26	0.063
8	5.6	0.16	0.31	31	0.14	0.042	0.018
10	4.5x10 ⁴	0.11	0.70	7.5x10 ²	18	0.37	3.4
11	22	0.010	0.092	33	0.21	0.026	0.020
12	8.8	0.010	0.054	31	0.069	0.027	0.010
13	1.9	0.010	0.031	30	0.016	0.019	0.0050
15	3.7x10 ²	52	1.3x10 ⁴	1.8x10 ²	90	1.2x10 ²	6.5
16	101	10	3.3x10 ³	6.2x10 ³	17	56	4.2
17	1.5	0.17	17	1.1x10 ²	0.42	0.37	0.13
18	0.11	0.010	3.3	55	< DL	0.056	0.0047
19	0.23	0.065	7.3	57	0.025	0.15	0.014
Mains water	0.21	0.011	0.076	30	< DL	0.016	0.0010

Table D.2 Average concentration (mg/L) of metals in the samples collected on 11/04/03

<i>Tank</i>	<i>Ni</i>	<i>Fe</i>	<i>Cr</i>	<i>Na</i>	<i>Zn</i>	<i>Cu</i>	<i>Pb</i>
2	9.4	14	0.77	2.3x10 ²	1.0x10 ²	63	0.030
5	6.0	2.1	0.29	2.7x10 ²	3.3	1.3	0.0090
7	2.1	0.25	< DL	43	0.97	0.24	0.0050
8	1.2	0.035	0.0090	39	0.26	0.18	0.0040
10	6.0x10 ⁴	0.098	0.41	9.8x10 ²	21	1.1	2.8
11	28	< DL	0.44	41	0.16	0.020	0.030
12	15	< DL	0.29	39	0.090	0.0060	0.013
13	3.4	< DL	0.17	36	0.020	0.030	0.0070
15	5.5x10 ²	76	3.4x10 ⁴	5.5x10 ²	2.1x10 ²	1.7x10 ²	11
16	3.5x10 ²	34	9.7x10 ³	8.4x10 ³	34	2.0x10 ²	19
17	2.4	0.0010	9.0	99	0.84	0.030	0.0080
18	1.4	< DL	6.8	68	2.5	0.030	0.0080
19	0.25	< DL	3.3	39	3.8	0.030	0.0050
Mains water	0.0070	< DL	0.035	36	0.11	0.0070	0.011