UNIVERSITY OF KWAZULU-NATAL

APPLICATION OF ANALYTICAL CHEMISTRY TO WASTE MINIMISATION IN THE POWDER COATING INDUSTRY

By

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Submitted in fulfillment of the academic requirements for the degree of

Master of Science (Chemical Technology)

School of Chemistry
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Pietermaritzburg

2005

ABSTRACT

A local company instituted a new chemical procedure in their spray phosphating system used in the pretreatment of large components for industrial racking systems. An inorganic conversion coating is deposited on the workpiece surface during phosphating and this prepares the surface to receive an organic top-coat. The organic coating is applied to the workpiece surface in the form of a powder and cured to form a continuous film about 80 μm thick.

The solution chemistry of the phosphating system was monitored by sampling and chemical analysis and taking direct reading instrumental measurements on the process and rinse solutions. The process was also evaluated using the results of a waste minimisation audit. This involved gathering data on composition, flow rates and costs of inputs and outputs of the process. Two types of information were collected and used during the audit, namely chemical monitoring (concentration levels of Na, Fe, Zn, Mo, Mn and Cr and measurements of conductivity, TDS, SS and pH) and water usage data on the Phosphating Line and existing data (raw materials, workpieces and utility inputs as well as domestic waste, factory waste and scrap metal outputs). 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. The Mass Balance and the True Cost of Waste findings were obtained through more detailed calculations using the results of the chemical analysis.

The results of the audit showed that the most important area for waste minimsation in the Phosphating Line was the (dragged-out phosphating chemicals present in) wastewater stream. According to the scoping audit, water usage had the third highest waste minimisation potential behind powder and steel consumption for the entire powder coating process. While the scoping audit and the specific water intake value showed that water consumption for the process was not excessive, it did not indicate that the pollution level in the rinse waters was high. Further, drag-out calculations showed that drag-out volumes were typical of those found in the metal finishing industry. However the presence of high levels of metal species in the rinse waters was highlighted through the chemical monitoring of the Phosphating Line. The True Cost of Waste Analysis estimated potential financial savings for the effluent stream at about R8000 for a period of 105 days. However this does not take into consideration the cost of the liability associated with this stream when exceeding effluent discharge limits (given in the Trade Effluent Bylaws) or of the chemical treatment necessary to render this stream suitable for discharge to sewer. Intervention using only "low-cost-no-cost" waste minimisation measures was recommended as a first step before contemplating further areas for technical or economic feasibility studies. However, a further study involving monitoring the sludge was recommended in order to establish the potential financial savings offered by this waste stream.

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...KMoodley..........
K. Moodley

I hereby certify that this statement is correct.

Signed.......SSpankie.....
Dr Sally Spankie
(Supervisor)

Pietermaritzburg
2004

ACKNOWLEDGEMENTS

First and foremost, I would like to thank my parents, **Lovey** and **Leela Moodley**, and sister, **Shuvani Moodley** for their love, support and guidance over the past twenty-four years of my life.

Special thanks must be given to my supervisor, **Dr Sally Spankie**. She was not just my supervisor but my friend, confidant and role model throughout the duration of this project. Her endurance, patience and caring nature will forever be remembered and cherished. I couldn't have asked for a better supervisor.

To my support system, which include all my family and my three special friends: **Avisha Neerahoo**, **Manjeetha Jaggernath** and **Benitha Naidoo**. I would like to thank them for their willingness to listen when times were tough and for their persistent encouragement throughout the course of our friendship. I hope that these friendships will last a lifetime.

To my co-supervisor **Dr Colin Southway** for his advice, incredible assistance with the laboratory work and for lending a sympathetic ear whenever it was needed. Special thanks must be given to **Eloise Marie**, a fellow Masters student for her contribution to this project and to **Sandra Joubert** (PHD) for always giving up her time to lend a helping hand.

I would like to thank the members of **staff** at the Chemistry Department at UKZN (PMB), which includes lecturers, technicians and all other fellow postgraduate students who have assisted me in some way with this project. Your help will be remembered.

Thanks must finally be given to the staff at **Southlands Manufacturing** for giving me the opportunity to do this project with them, for their help and assistance throughout the course of this project

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CHAPTER 1

THESIS STRUCTURE

This thesis begins with an introduction into the process employed at a Pietermaritzburg based Powder Coating Company. A detailed description is given in Chapter 2 on the stages involved in powder coating, the chemicals used, any pre-treatment and post-treatment steps used and the techniques employed during the different stages.

An extensive literature review performed on the waste minimisation programme is presented in Chapter 3. This consists of a waste audit, as well as the presentation of waste minimisation options and opportunities that exist in the powder coating industry. Four assessment techniques were used in the waste audit section of this programme. These were then used later in the implementation of the waste minimisation options.

Chapter 4 consists of a detailed description of the company on which this waste audit was performed. This includes both general information and specific details on the powder coating process. General information includes the products manufactured, equipment used in the manufacture, staff and the company's working hours. Specific details are given on the manufacture of products and the techniques used in the coating.

In the Chapter 5 the scopes and aims of this project are outlined.

The following four chapters all deal with the research aspect of this project. Chapter 6 describes the methods used in the investigation of the process. This includes elemental and sludge analysis, as well as suspended solids and total dissolved solid analysis. The results of these analyses are presented in Chapter 7. A discussion of these results is given in Chapter 8. Finally, conclusions are drawn and recommendations are made in Chapter 9.

CHAPTER 2

INTRODUCTION TO POWDER COATING

The surface (solution and powder) treatment, processes, application techniques and coating chemistry involved in powder coating the surface of steel items are presented in this chapter. Section 2.1, presents an overview of the entire industrial powder coating process. This includes the function of the under (inorganic conversion) and top (cured organic powder, commonly referred to as paint) coat and describes the respective wet and dry processes by which these coatings are formed. The undercoat is applied in the form of an aqueous solution. The deposition of the conversion coating onto the surface of an item has thus become known as a 'wet' process. A 'dry' process, as the name suggests, is carried out without using a liquid medium such as an aqueous solution. In Section 2.2, a description is given of the cleaning of the surface prior to the application of the conversion coat. This includes both chemical and mechanical cleaning methods used industrially. In Section 2.3, the important characteristics of the phosphating solution and of the conversion coat are presented. This section describes the different types of conversion coatings available to the powder coater, the chemistry involved in their formation and the control parameters and systems used to monitor the processes. In Section 2.4 the different types of powders used to make the powder coating are compared in terms of their chemistry and composition. The application techniques used to apply both the undercoat and topcoat can be viewed as being similar and are described in detail in Section 2.5.

2.1 Breakdown of the Powder Coating Process

Organic and inorganic coatings have been applied to the surfaces of commercial products manufactured in light and heavy industries since the late 1800s.[1,2,3] Solvent- then aqueous-borne paints were the first types of organic coatings used industrially. Powder coating came onto the market in the 1950s.[4] The major suppliers to the powder coating industry, in South Africa, today are Akzo Nobel[5], Powder-Lak[6] and Dupont.[7] Powder coating has proved to be very versatile. It can be used to coat small items such as seat frames, garden tools and household appliances as well as larger items such as furniture, shelving systems and architectural profiles.[4,8]

In the surface finishing industry, items for coating are traditionally known as 'workpieces'.[9] These are commonly made from mild steel, aluminum or zinc-based alloys and are also referred to as the 'substrate'[9] or the 'base metal'.[10] Mild steel, commonly referred to as low-carbon steel, is composed of iron, small amounts of manganese and approximately 0.30% carbon.[11] The workpiece is often covered with oils, lubricants, metal fines, dirt, carbides, corrosion products, mildews and scale when it leaves manufacturing or storage. These are generically referred to as 'soils'. This means that the surface must be prepared before the powder is applied. Surface preparation involves cleaning the surface to remove these contaminants followed by an immediate pre-treatment with a conversion coating solution. The latter wet step in the coating process was developed to ensure the powder would adhere well to the workpiece and to give corrosion resistance to the surface. The industrial application of the pre-treatment solution to the workpiece is most commonly carried out by either spray or immersion techniques. Immersion is also known as 'soaking' and 'dipping' in the surface finishing industry.[1,2,3] The next step involves application of the powder using similar techniques as found in the wet pre-treatment process but uses different equipment. Immersion of the workpiece in powder, which is forced to flow over the surface in a fluidized bed, is however less commonly used than manually spraying the powder directly onto the surface of a moving workpiece. This use of fluidized bed application is largely confined to small items for example car battery brackets and shelves. The final step in the process is curing of the powder. This converts the powder particulate deposit into a continuous film and seals the coating onto the workpiece surface.[6,12, 13, 14]

2.2 Surface Preparation - The Cleaning Step

Both the manufacturing process and contact with the environment deposit oils and other contaminants onto the surface of the workpiece. These must be removed prior to treatment with the conversion solution in order to ensure the integrity and effectiveness of this undercoat. The weight and structure of the coating can also depend on the extent and type of cleaning used. Such cleaning of the surface can be carried out either chemically or mechanically. Mechanical cleaning, however, is really necessary only in cases of extreme surface contamination for example after foundry processes. Chemical cleaning has become the essential first step in wet processing. It can be carried out using either aqueous or organic solvent formulations. Today, wet chemical cleaning is increasingly being carried out using aqueous cleaner systems.[1,2,3] Aqueous cleaning is carried out using alkali- and acid-based solutions.[15] These are applied either by spraying the cleaner solution onto the workpiece or by dipping the workpiece into a bath containing the solution[1]. Electrolytic cleaning may be used to chemically and mechanically the remove more stubborn contaminants after the workpiece is cleaned with an alkaline solution[1]. However, this method is most often used in the electroplating industry where electricity is an input into the coating process. It is seldom used prior to the non-electrolytic conversion coating. Aqueous cleaners have replaced much of the solvent and emulsion cleaning in the last thirty years.[15] The exact chemistry, composition and choice of the cleaner used depends upon the following characteristics:

- the type of contaminant present on the surface
- the type of undercoat (for example iron or zinc phosphates) to be applied
- the composition of the substrate.

Different cleaners have been designed to remove different contaminants. Therefore, it is important to know the type of contaminant present on the metal surface in order to select an effective cleaner system. The substrate surface may react with the cleaner and the contaminant must react with or dissolve in the cleaner. However, it is important that these reactions do not seriously alter the composition of the base metal or form any undesirable products with the undercoat.

Aqueous cleaning methods are discussed in Sections 2.2.1, 2.2.2 and 2.2.3. Section 2.2.4 contains a discussion on non-solvent abrasive cleaning methods found in dry mechanical cleaning. Passivation (or sealing) is sometimes still used as a final pre-treatment step in the powder coating industry and is discussed in Section 2.2.5.

2.2.1 Alkaline Cleaning

Alkaline cleaners are relatively cheap and remove a higher proportion of contaminants compared to acid cleaners[12]. This is why they are used first in surface preparation. The major use of these cleaners is the removal of fatty acids and oils. According to the literature, industrial alkaline cleaners are classified as either heavy duty or light duty cleaners largely based on their pH values.[15] The three pH ranges which have also been used to categorize these cleaners, are given below[15]:

- mild, pH 9 –10.5
- medium, pH 10.5 – 11.5
- high, pH > 11.5

Light duty cleaners are typically used to clean steel surfaces and zinc-based alloys and plates. Heavy duty cleaners are reserved for cleaning heavily contaminated steel substrates. The properties of these cleaners are given in Table 2.1. Very little information has been reported in literature on the more detailed chemical composition of such cleaners. For example material safety data sheets (MSDS)[16] name only the major component, normally the builder, but not its exact quantity. Instead the percentage composition of the builder is given often as a range of values in the MSDS. These values are summarized in Table 2.1. Weak alkaline degreasing solutions usually contain some phosphates, carbonates and silicates as well as surface active agents. Hydroxide is usually present to a lesser extent than in other cleaners. As will be mentioned in Section 2.3.1 the degreasing solutions may also include titanium compounds at a concentration of less than 0.0001% by mass.

Table 2.1 Properties of light and heavy duty cleaners[17-20]

Cleaner Type	**Type of Substrate**	**Temperature**	**Composition**	**pH**
Light Duty	Zinc and Zinc Plate	< 66°C	$NaOH$ – 10% Na_2CO_3 – 34% $NaSiO_3$ – 40% Surfactants – NQ	8 - 10
	Steel	NQ	Na_2CO_3 – 45% $NaSiO_3$ – 25% $Na_5P_3O_{10}$ – 25% Surfactants – NQ	11 to 12
Heavy Duty	Steel	50 – 100°C	$NaOH$ – 40% Na_2CO_3 – 22% Na_2SiO3 – 20% Surfactants – NQ Buffer – 10%	10 - 13

NQ – Not Quoted. The percentage of surfactants present are not quoted in this paper but are known to be significantly less than 5%.[2]

Builders have been used to provide alkalinity for the cleaner. The most common builders found in commercial cleaners are hydroxides (NaOH and KOH). It is the hydroxides which are responsible for the saponification of fats and vegetable oils (see Equation 2.1). Its other important surface reaction is to help neutralize and remove acidic soils. Saponification is the breakdown of these fats and oils into soluble soaps which can be easily removed by rinsing the workpiece with water. The vegetable oils and grease are usually carboxylate esters which are converted into long carbon chain carboxylate salts called soaps (see Equation 2.1).[21,22]

$$C_3H_5(C_{17}H_{35}COO)_3\,(s) + 3KOH(aq) \rightleftharpoons 3C_{17}H_{35}COOK(aq) + C_3H_5(OH)_3(aq) \qquad \text{Equation 2.1}$$

Other more multifunctional builders present at lower concentrations include silicates, carbonates and phosphates. Silicates make up a significant part of all cleaners with their percentage composition ranging from 20% (heavy duty) to 40%. This is because, as well as providing alkalinity, they act as dispersing agents and inhibitors. The main silicates present in alkaline cleaners are sodium metasilicate and orthosilicate. The hydrolysis of the silicates with water forms silicic acid and sodium hydroxide which provides alkalinity to the cleaner (see Equation 2.2).[23] Silicic acid is a weak acid with a pKa value of 9.82 at room temperature and thus does not tend to ionize easily.

Silicates have been successfully used to disperse the oils released from the surface in the solution and to act as corrosion inhibitors for the substrate surface.[12,17] The acid precipitates out of solution in a colloidal state. The soils released from the substrate surface attach themselves to the colloidal suspension and this prevents the soils from redepositing on the surface. A silicic acid derived film is also adsorbed on the surfaces of the cleaned aluminum, zinc and steel workpieces. This film protects the base metals from corrosion in such an alkaline solution after the cleaning has removed all the contaminants.[24]

$$Na_2SiO_3(aq) + 2H_2O(l) \rightleftharpoons 2NaOH(aq) + H_2SiO_3(aq)$$

Equation 2.2

Carbonates and phosphates provide alkalinity in a similar manner as silicates, that is through a hydrolysis reaction. These reactions are given in Equations 2.3 and 2.4.

$$Na_2CO_3(aq) + 2H_2O(l) \rightleftharpoons 2NaOH(aq) + H_2CO_3(aq)$$

Equation 2.3

$$Na_3PO_4(aq) + 3H_2O(l) \rightleftharpoons 3NaOH(aq) + H_3PO_4(aq)$$

Equation 2.4

Carbonates are present in mild cleaners and are regarded as a cheap source of alkalinity, together with silicates and phosphates.[25] Mildly alkaline carbonates have a pKa ranging between 9 and 9.5[25] and are useful buffers as they help to maintain the pH of the cleaning solution. Phosphates are present in the form of pyrophosphate ($P_2O_7^{4-}$), orthophosphate (PO_4^{3-}) and polyphosphates ($M_{(n+2)}P_nO_{(3n+1)}$). M can be H^+ or a monovalent metal cation.[26] Phosphates are often used to soften water, and they remove metal oxides and hydroxides from the surface of the workpiece. These agents form complexes with such metals preventing them from reacting further and forming products that will be difficult to remove after the cleaning process.[27] However, this can mean that metallic contaminants become difficult to precipitate out of the waste water.

Alkaline cleaners also contain surfactants, also known as surface active or wetting agents. These are used to reduce the surface tension of the cleaning solution and help it flow over and off the surface of the workpiece. This is important as it allows the cleaner to spread over the surface and to get around and under the contaminant and so remove it from the metal surface.[25] Alkaline cleaners also prevent soils from redepositing on the surface of the workpiece by forming an emulsion with the contaminant.[24, 28] Common types of surfactants used industrially are anionic and non-ionic. Typical examples of these include sodium lauryl sulfate and lauryl alcohol ethoxylate.[29]

2.2.2 Acid Cleaning

There are three main functions of acid cleaning namely:

- the neutralization of any alkali solution remaining on the surface from the previous step
- the removal of the contaminant layer which may contain scale and rust
- the removal of surface layer after severe alkali cleaning to 'activate' or prepare the base metal for the next step.[21]

Scale consists of several oxides and is formed by the action of atmospheric oxygen on iron or steel surfaces at high temperatures[2]. Rust is a product of atmospheric corrosion which consists mainly of a mixture of iron(II) and iron(III) hydroxides.[2,30]

Acid cleaners are usually strong acids such as hydrochloric, sulfuric and nitric. [21] Acid cleaning employs strong acids or a mixture of strong acids depending on what metal needs to be cleaned. Steel sheets are treated with sulfuric acid while brass workpieces, except for lead brass, are treated with a mixture of nitric and sulfuric acid. Like alkaline cleaners, acid cleaners also contain many additives. The main additives required for acid cleaning are inhibitors.[2] These suppress acid attack on the base metal once the oxide layer has been removed. This reduces the evolution of hydrogen (see Equation 2.5) which would otherwise lead to hydrogen embrittlement.[21,31] Hydrogen embrittlement occurs when the gas bubbles produced are absorbed through the surface and into the bulk of the steel. This has been known to cause cracking in the workpiece and reduces the steel's strength.[1,32] Inhibitors also prolong the life of the acid solution as the chemical reaction between cleaner and metal surface ceases once the scale has been removed.[31]

$$Fe(s) + H_2SO_4(aq) \rightleftharpoons FeSO_4(aq) + H_2(g) \qquad \text{Equation 2.5}$$

Acid treatment is often divided into two processes, acid dipping and pickling. Dipping removes any traces of alkalinity from the previous cleaning step by neutralizing the alkaline solution[21] using dilute sulfuric or hydrochloric acid.[31] Acid pickling or etching is more commonly used as a cleaning step to remove scale and dirt (see Equation 2.6) but is also used to remove a layer of the substrate surface which may have been oxidized during the cleaning process itself. For example, atmospheric oxidation of a freshly cleaned surface can occur during transfer from one tank solution to another[30]. Etching has a particular meaning in the phosphating step itself. It refers to the first step in the phosphating process i.e release of iron ions into the solution from the solid substrate (see Equation 2.5).

$$FeO(s) + H_2SO_4(aq) \rightleftharpoons FeSO_4(s) + H_2O(l) \qquad \text{Equation 2.6}$$

Phosphoric acid is more expensive than hydrochloric or sulfuric acid and is important in phosphating when the cleaning and phosphating steps are combined and carried out in one solution.[21]

2.2.3 Organic Solvent Cleaning

Organic cleaners are used to remove contaminants such as oil or grease from the surface by dissolving them in organic solvents. There are two main types of solvent cleaning, cold and hot solvent cleaning. The latter has been traditionally done by vapour degreasing.[21, 33]

In cold solvent cleaning the most common solvents used are trichloroethylene ($CHClCCl_2$), perchloroethylene (CCl_2CCl_2) and 1,1,1-trichloroethane (CCl_3CH_3).[21,31] These are applied by hand wiping or dipping small workpieces in the solvent. Even though all three solvents are non-flammable, only trichloroethane is used as it is safe enough to be used for hand wiping applications.[21] These solvents are volatile organic compounds (VOCs) and thus release vapours which can cause serious health and environmental effects. It is a labour intensive operation and regular exposure to solvents can cause dermatitis and narcosis; many organic solvents are toxic and can cause effluent problems if released into the drain.[31] Both trichloroethylene and perchloroethylene are classified as carcinogens by the U.S. Environmental Protection Agency (EPA)[24] while trichloroethane is an ozone depletor and was phased out on the 1st of January 1996[34] in compliance with the American Clean Air Act Amendments. Thus handling and disposal of these solvents is more expensive than in other cleaning chemicals. For the reasons, given above solvent cleaning is no longer widely used in industry.

Vapour degreasing is a process which uses hot vapour of a solvent to remove oil and grease from the workpiece surface. It has typically used trichloroethylene, dichloromethane and perchloroethylene solvents. The cleaning process takes place in a degreasing unit which consists of a heating element at the bottom of the unit and cooling coils at the top of the unit (see Figure 2.1).

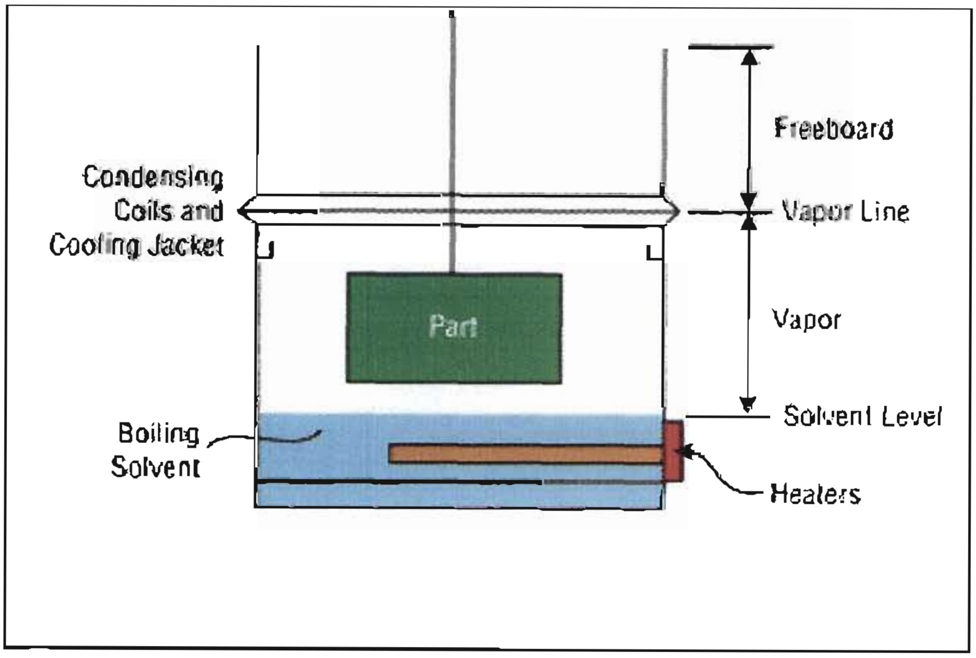


Figure 2.1 Typical degreasing unit[33]

The solvent sits at the bottom of the tank in a sump and is heated. The unit is closed by a lid and the workpieces are hung near the top. The vapours from the solvent are cooled by the cooling coils and condense on the workpiece surface. These condensed vapours wash off the oils and grease which are then carried into the sump. This cycle of distillation and condensation continues once the workpiece reaches the temperature of the solvent. The workpiece then leaves the unit as a clean, dry part. An additional advantage of vapour degreasing is that the contaminants are not re-deposited onto the workpiece as they are contained within the sump and not dissolved in the solvent.

2.2.4 Mechanical Cleaning

Mechanical cleaning is used to remove oil, grease and rust and to provide a good (roughened) surface for powder adhesion.[1,12,35] Typical mechanical methods include abrasive blasting, wire brushing, grinding and sanding. Electrolytic cleaning using bubbles of gas can also be classified as a mechanical method of cleaning. Abrasive blasting is the most widely used. The blasting media used are sand, steel shot, grit and glass beads. Abrasive blasting is carried out by delivering the media onto the surface of the steel workpiece at high speed. Upon impact with the surface, the media release the contaminants by knocking them off. Abrasive cleaning can also be a wet process in which the abrasive is dispersed in water. This can be carried out using handheld equipment or blast cabinets. Wire brushing is less forceful than abrasive blasting. In wire brushing, brushes are attached to a wheel which moves in a circular motion to dislodge casting sand and loose scale. The main function of wire brushing is not only to clean but also to brighten the surface without removing a significant amount of the metal.[31, 36] Grinding, with a rotating stone or disc, is used to grind down the hardest and most difficult materials. Sanding uses a fibre: typically paper, plastic or cloth which is embedded with sand.

Electrolytic cleaning is a technique widely use today in eletroplating and generally follows a soak cleaning step. In electrocleaning the workpiece is made either the cathode or the anode. There are two electrocleaning methods used industrially namely cathodic (direct) and anodic (reverse). In these cleaning method gas bubbles of hydrogen and oxygen are generated at the cathode and anode, respectively. The reactions leading to the formation of these two gases are given in Equations 2.7 and 2.8.[17]

Anode Reaction: $4OH^-(aq) \rightleftharpoons 4e^- + 2H_2O(l) + O_2(g)$

Equation 2.7

Cathode Reaction: $2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$

Equation 2.8

The surface of the workpiece is cleaned by the scrubbing or scouring action of the gas bubbles against the surface. This loosens the contaminant and releases it from the surface. In cathodic cleaning the volume of hydrogen formed at the cathode (Equation 2.7) is twice the volume of oxygen that is formed at the anode (Equation 2.8). As a result, more scrubbing is achieved at the cathode than the anode. During anodic cleaning the surface is dissolved slightly and a current is generated at the anode which creates fresh oxides which form a film on the surface and can oxidize organic additives. Both methods use the same equipment, voltage (3-12 volts) and current density (1-15 A/m^2).

Ultrasonic cleaning is also a type of mechanical cleaning in which high frequency sound waves at frequencies above 20 000 Hz are generated in a cleaning solvent.. This is an immersion technique used for the cleaning of small items such as jewellery and watch parts. The sound waves form cavities that collapse in the solvent and produce a powerful scrubbing action to remove stubborn soils. Ultrasonic cleaning can be applied using solvent cleaners, aqueous detergents and acid cleaners.[1,21,31]

2.2.5 Passivating

The process of passivating has become synonymous with the formation of a protective layer on the metal of a plated workpiece or of a bare (uncoated) substrate surface. This includes metal plates such as zinc or cadmium and substrate surfaces such as aluminium and stainless steel. Passivation is a pre-dip process, in addition to rinses, which is used to modify the weight and structure of the phosphate coating. It is carried out using oxidizing agents such as chromic acid. The application of sodium dichromate or chromate has been traditionally used for improving the corrosion resistance and reducing the tendency of the phosphate coating to blister under the organic coating. Phosphoric acid has also been used as a substitute for chromium (in the form of chromic acid) in the neutralization of the hard water alkalinity and the absorption of the chromium by the phosphate coating. Passivation results in the formation of a thin transparent mixed (chromium and the plate or substrate metal) oxide layer on the surface.[37] This is called the passive layer and consists mainly of insoluble iron chromates which form in the pores of the phosphate coating. In the case of a metal which has been phosphated, the chromium(VI) is applied as a rinse or a seal. This is because the phosphate layer is porous and the use of the acid will dissolve the iron and leave behind a surface that is enriched with chromium. This is a redox reaction resulting in the formation of an oxidized layer containing trivalent chromium, oxygen and the metal species. Chromate coatings have the ability to protect the metal in areas where some of the coating has been removed due to scratching or by abrasion or is absent because of the porous structure of the coating.[1,3]

2.3 Surface Treatment – The Phosphate Conversion Coat

The composition of the commercial phosphating formulation, for making up a phosphating bath, and of the conversion coating as deposited on the workpiece will be discussed in this section. The chemical species in Figures 2.2 to 2.4[1] will be referred to in the discussion of the chemistry of the phosphating solution and conversion coating in Sections 2.3.1 and 2.3.2.

MH_2PO_4	M_2HPO_4	M_3PO_4
(A)	(B)	(C)

Figure 2.2 Phosphate derivatives of the univalent metal M

$M(H_2PO_4)_2$	$MHPO_4$	$M_3(PO_4)_2$
(D)	(E)	(F)

Figure 2.3 Phosphate derivatives of the divalent metal

$M(H_2PO_4)_3$ (G) $M_2(HPO_4)_3$ (H) MPO_4 (I)

Figure 2.4 Phosphate derivatives of the trivalent metal

Quantitative examples for the composition of the bath solution and the conversion coating are presented in Tables 2.2 and 2.3 respectively. Structures (A), (B) and (C) correspond to the primary, secondary and tertiary univalent metal phosphate derivatives. Structures (D), (E) and (F) correspond to the respective phosphate derivatives of the divalent metals while structures (G), (H) and (I) correspond to the phosphate derivatives of trivalent metals. Species containing the PO_4^{3-} and HPO_4^{2-} are known to be water insoluble except for those of the alkali metals and the ammonium ion while those containing the $H_2PO_4^-$ tend to be more soluble. This means that zinc derivatives of structure (F), manganese derivatives of (F) and iron derivatives of (E), (H) and (I), represent species found as constituents of the coating while zinc derivatives of structure (D), manganese derivatives of (D) and iron derivatives of (D) and (G) represent solution species.

2.3.1 An Overview of the Chemistry of Phosphating Solutions

The commercial, proprietary or trade formulation refers to the composition of the commercial solution as it is purchased from the supplier. In this text the commercial solution is also described as the 'neat' solution. The solution in the bath is made up of the neat solution diluted with mains water to give a specific concentration of the (formulation) ingredients in the working phosphating bath. During the phosphating process many reactions take place, both at the workpiece surface and in the bulk of the solution, and consequently various equilibria involving the structures in Figures 2.2 to 2.4 are established. As a result there are many species present in the solution and on the surface simultaneously. Insoluble metal phosphate species formed during the surface reactions have been found to deposit as the phosphate layer. In less balanced systems, insoluble metal phosphates have been observed to precipitate out of the bulk solution as sludge.

Phosphating has been routinely carried out using two different solution formulations[2,3]:

- non-coating producing, conversion phosphating or iron phosphating systems
- coating producing or pseudo-conversion phosphating systems.

In non-coating phosphating, the workpiece is treated with a solution of the sodium, potassium or ammonium derivatives of (A) containing molybdenum salts. As the names (of the processes) suggest, the alkali metal is not incorporated into the coating but the iron from the steel substrate is. This process has also been referred to as alkali metal and lightweight iron phosphating. Such solutions have been known to have zinc and manganese derivatives of (D) and zinc derivatives of (E) present as minor constituents, with levels of metals originating from species (D) being comparable to those of molybdenum. However no iron phosphates are present in these formulations. These solutions can be used at pH values as high as 6. This is because alkali metal phosphates are all soluble in water and the sodium derivative of structure (A) will ionize completely to release all the dihydrogen phosphate ions into solution as opposed to being generated at equilibrium concentration levels (see Equation 2.16). However, the presence of this weak acid causes the alkalinity of the bath to rise as it does not readily ionize in solution. When using a pseudo-conversion phosphating solution, the workpiece is treated with what is essentially a zinc (or manganese) derivative of (D) in phosphoric acid. The mechanisms of coating the workpiece with an insoluble phosphate are different in each case and this will be discussed in Section 2.3.4. However the initial etching step is similar. In the literature the reactions that take place are frequently described as occuring at 'cathodic' and 'anodic' sites on the workpiece surface. This is because the surface reactions are electrochemical in nature and the substrate can thus be thought of in terms of a number of small galvanic cells. The process begins with the oxidation of iron in steel to iron(II) (see Equation 2.9). This takes place at an anodic site. The reduction of hydrogen is the first step, in a sequence of reaction steps, that leads to the formation of the insoluble secondary or tertiary iron phosphate coat on the workpiece. This essentially involves the reaction between the substrate and the coating solution. This reaction is the basis of the coating process and is also the reaction that causes hydrogen embrittlement.

$$2H^{+}(aq) + Fe(s) \rightleftharpoons Fe^{2+}(aq) + H_2(g) \qquad \text{Equation 2.9}$$

In the early days of the process, phosphating baths were operated at high (near boiling point) temperatures and over long periods of time. This is because the phosphating reactions were found to be slow and it took well over an hour to coat a workpiece. Additives, known as accelerators, have been successfully used to reduce the phosphating time to a few minutes. Accelerators were first introduced in 1929 by the Bonderizing process which involved the use of a small amount of copper to accelerate the process.[1-3,38-39] Three categories of accelerators have been identified from the literature. These are chemical (based on redox reactions), electrochemical (based on galvanic coupling) and mechanical accelerators. Although chemical accelerators are the most widely used, in practice all or two of the methods are often used together. Chemical accelerators in general use oxidizing agents such as nitrates, chlorates, peroxides and organonitro compounds such as ntiroguanidine and sodium metanitrobenzenesulfonate. Alkali metal, zinc and manganese nitrates are examples of accelerators, used independently and as mixtures of each other. Three interpretations of chemical acceleration is given in the literature. These are:

- oxidation of hydrogen gas formed on the workpiece surface to water (see Equation 2.10)
- conversion of the hydrogen ions in solution into a water soluble or miscible species[2] (see Equations 2.11 and 2.12) instead of into hydrogen gas
- increase of the overpotential of the reduction of hydrogen ions to hydrogen gas.

$$H_2(g) + [O](aq) \rightarrow 2H_2O(l) \qquad \text{Equation 2.10}$$

[O] = oxygen supplied by an oxidizing agent

$$4Fe(s) + NaNO_3(aq) + 10H^+(aq) \rightarrow 4Fe^{2+}(aq) + NH_4^+(aq) + Na^+(aq) + 3H_2O(l) \qquad \text{Equation 2.11}$$

$$2H^+ + Fe(s) + \tfrac{1}{2}O_2(g) \rightarrow Fe^{2+}(aq) + H_2O(l) \qquad \text{Equation 2.12}$$

The latter has been referred to as hydrogen depolarization or depolarizing the cathodic reaction.[3] This influences the kinetics of the multi-step reduction of aqueous hydrogen ions to hydrogen gas. This results in the electrode potential for the reduction of the hydrogen ions being lowered by the oxidizers, by an amount known as the overpotential and the reaction becomes slower. This makes it more difficult for this reaction to take place with the result that very little hydrogen gas is evolved. Accelerators can also oxidize iron(II) ions in the bulk solution to iron(III) phosphate (see Equation 2.13) which is precipitated as sludge.

$$Fe^{2+}(aq) + 2H^{+}(aq) + NaNO_2(aq) \rightarrow Fe^{3+}(aq) + NO(g) + H_2O(l) + Na^{+}(aq)$$

Equation 2.13

With certain accelerators like nitrite this effect is limited and the accelerator acts to control the build up of iron levels in solution. Nitrates have also been added to commercial phosphating solutions as sodium nitrate or as the *in situ* product of the reaction of zinc oxide (or manganese) with a phosphoric or nitric blend. The level of iron, released into solution, as iron(II), is much lower from this method as compared to that from the electrochemical acceleration.

The action of electrochemical acceleration promotes the oxidation of elemental iron in the substrate to iron(II) in solution by increasing the potential difference between the anodic and the cathodic reaction sites on the substrate surface.[40] This is achieved chemically by depositing a metal with a lower standard reduction electrode onto the substrate surface which acts as a cathodic site (see Equation 2.14). It also serves to increase the number of dedicated cathodic sites for phosphate deposition. Copper salts, and to a lesser extent nickel salts, have been used to achieve this usually along with nitrate accelerators. Electrochemical acceleration can be achieved also by using an external potential.[2] However, anodic methods have been proven to be more appropriate because they promote metal dissolution and passivity.[1]

$$Cu^{2+}(aq) + Fe(s) \rightarrow Fe^{2+}(aq) + Cu(s)$$

Equation 2.14

Mechanical accelerators accelerate the process by dislodging bubbles of hydrogen gas from the substrate surface. This prevents hydrogen from accumulating at the cathodic site and from covering over the surface. Mechanical acceleration can be achieved in two ways: agitation of the immersed workpiece in the solution or spraying of the solution onto the workpiece. However, it is the spraying operation that is more effective. When the solution is sprayed forcibly onto the workpiece surface, the coating forms faster than when the workpiece is immersed in the same solution. Spraying also eliminates the delay due to diffusion of the constituents onto the surface of the workpiece. The action of brushes and rollers on the workpiece surface during phosphating is another means of mechanical acceleration.

It has been found that surface activation (conditioning or pre-rinsing) is required after severe cleaning with concentrated alkali and acid cleaners. Before zinc phosphating of zinc and steel workpieces, titanium phosphate has been found to give a superior performance compared to that from pre-rinsing with oxalic acid, sodium nitrate or copper salts. This treatment stops the organic coating from blistering and from lifting away from the surface. The conditioner sets up a network of uniform acceptor sites onto which the zinc phosphate can be deposited. This has been found to improve the quality of the coating as smaller crystals are formed and gives a more uniform and even coating than the iron phosphate coatings. Calcium additives have been used in zinc phosphating as structural modifiers for the phosphate layer.[41]

Other additives are used in iron phosphating when cleaning and coating steps are combined. This will be discussed in Section 2.5.

2.3.2 The Composition of Phosphating Solutions

The literature search revealed that very little information is available on the detailed chemical composition of the commercial solution. This would appear to be because such products are patented by chemical supply companies and detailed formulations are withheld from the public. Chemical suppliers are legally obliged to supply material and safety data sheets (MSDS) with all their commercial products. These data sheets have to include the composition of the product. However, these data sheets are frequently vague and incomplete.[42-53] Journal articles tend to report experimental bath compositions for new phosphating systems that are under development. Further, as monitoring of the bath chemistry rarely includes elemental analysis, there is little incentive for suppliers to report compositional data on solutions. As will be discussed in Section 2.3.5, analysis relies on pH and titrimetric analysis. In one document, produced by the Organisation of Economic Co-operation and Development (OECD), detailed concentration and speciation data on bath compositions (see Table 2.2) were presented. The OECD is an organization made up of representatives from developed countries.[54] It supports and funds many areas of industrial research in for example the metal finishing sector in those developing countries with an elected government and a market economy.

Table 2.2 Composition of different phosphating solutions[31,54]

Phosphating Solution	Composition	Concentration of Solution (mg/L)	Molar Fractions (α)
Iron Phosphate	Na_2HPO_4	1 100 000	0.94
	NaH_2PO_4	40 000	0.03
	$(NH_2OH)_2(H_2SO_4)$	10 000	0.008
	$MgSiF_6.6H_2O$	10 000	0.008
	H_3PO_4	5 000	0.004
	Wetting agent	11.65	9×10^{-6}
Zinc Phosphate	ZnO	150 000	0.17
	HNO_3	300 000	0.34
	H_3PO_4	400 000	0.46
	$(NH_4)H_2PO_4$	20 000	0.03

Table 2.2 shows that the main constituents of phosphating solutions are phosphoric acid and its derivatives {for example (A) and (B) in Figure 2.2}. The species and their concentrations, as reported in the literature, are presented in column two and column three of Table 2.2. These concentration values were then used to calculate the molar fraction (see Equation 2.15) of each of the species present in the solution. These results are shown in column 4 of Table 2.2.

$$\alpha = \frac{\text{Molar Concentration of species}}{\text{Total molar concentration of all related species}} \qquad \text{Equation 2.15}$$

The phosphating solution is often referred to as the phosphoric acid bath or the phosphate bath. These terms have a vague link with the chemistry of the solution. Orthophosphoric {phosphoric(V)} acid, H_3PO_4, is a tribasic acid which contains three hydrogen atoms. In principle these three hydrogens can be replaced and can thus give rise to a series of three phosphate salts {(A), (B) and (C) in Figure 2.2}. The pKa values given in Equations 2.16, 2.17 and 2.18[55], show that phosphoric acid is a weak acid. The equilibria in Equation 2.16 to 2.18 can be better described by examining the alpha plot for phosphoric acid (see Figure 2.5). This plot can also help to determine the fraction of each of the above species in solution at any given pH. At the low pH values of the phosphating bath the chemistry of the phosphating process will be based largely on the equilibrium in Equation 2.16. In forming the conversion coating, alkali metals of structure (A) will undergo an acidic reaction and structure (B) will undergo a slightly alkaline reaction.

$H_3PO_4(aq) \rightleftharpoons H_2PO_4^-(aq) + H^+(aq)$ $pKa_1 = 2.15$ Equation 2.16

$H_2PO_4^-(aq) \rightleftharpoons HPO_4^{2-}(aq) + H^+(aq)$ $pKa_2 = 7.20$ Equation 2.17

$HPO_4^{2-}(aq) \rightleftharpoons PO_4^{3-}(aq) + H^+(aq)$ $pKa_3 = 12.3$ Equation 2.18

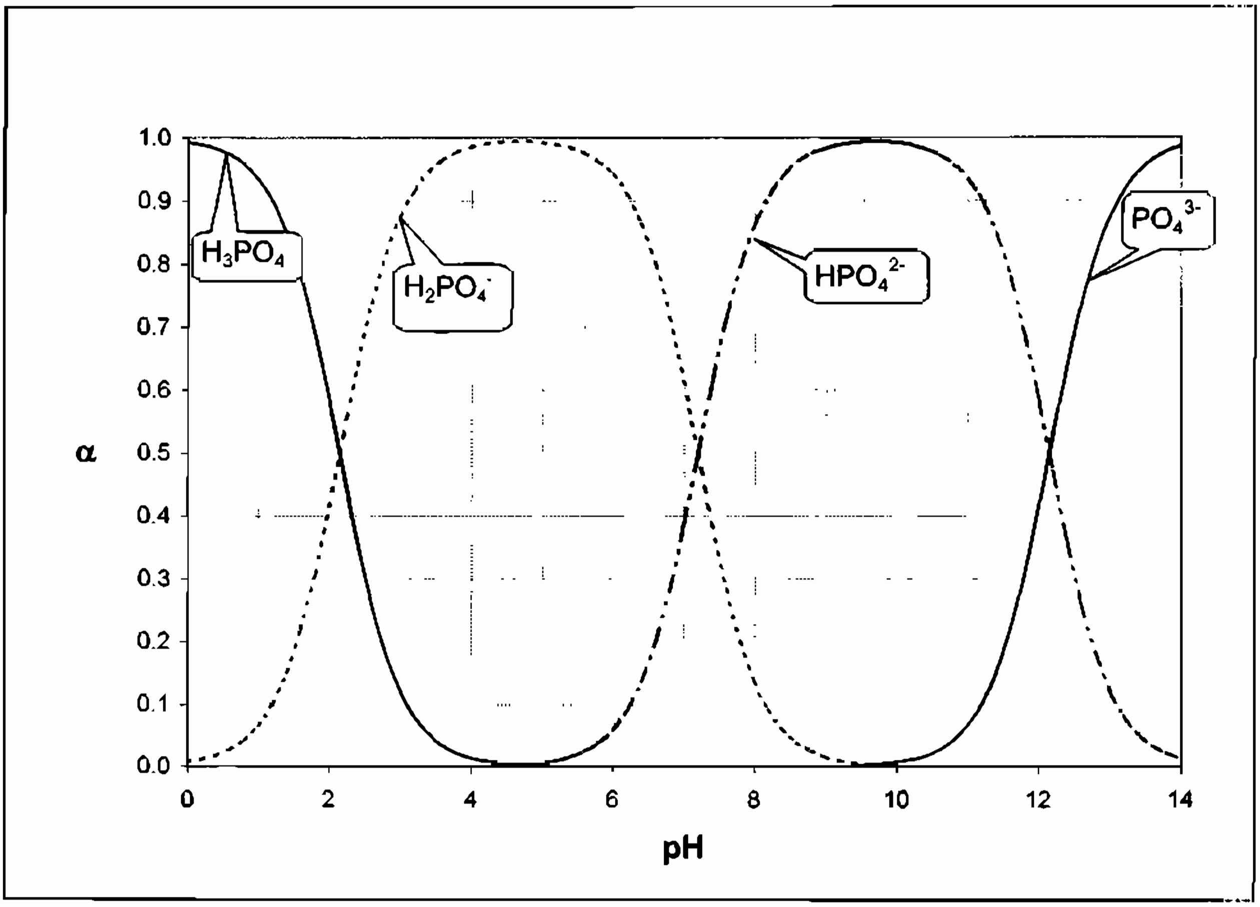


Figure 2.5 Fractional composition of phosphoric acid solution as a function of pH[55]

According to the literature the bath is operated at a pH of 4.8.[54]. Thus only $H_2PO_4^-$ (as indicated by Figure 2.5) should be present in solution as this is the first equivalence point in which all of the H_3PO_4 is converted into $H_2PO_4^-$. However, the fractions in

Table 2.2 show that HPO_4^{2-} is present in the solution. Table 2.2 also shows that there is no iron present in the commercial iron phosphating solution. Conversely zinc, as zinc oxide, is a constituent for the make-up of the commercial zinc phosphating solution. The iron for the phosphate coating typically comes from the substrate and not the phosphating solution. Once the phosphate solution has been applied to the workpiece the conversion coat will form on the surface.

2.3.3 The Chemistry of the Phosphate Conversion Coatings

Analyses of the phosphate coating have been more widely reported in the literature than those of the phosphating solution. The chemical composition and structure of the coating have been established using X-ray diffraction and scanning electron micrsoscopy (SEM).[3] The coating formed on the substrate is made up of insoluble phosphate compounds. These are deposited on the surface as products from reactions of the bath ingredients i.e the substrate and the phosphates. However, in many cases these coatings have not been fully chemically characterised. The coatings arising from zinc phosphating of zinc have been fully documented. However, in most cases there is more than one potential coating metal in solution and the resulting phosphating reactions become more complicated. The proportions of the various coating constituents have been studied under various conditions for example solution agitation, presence of chemical additives and temperature. The findings will not be discussed in this document. However the coating constituents are presented in Table 2.3. The result of a literature survey concerning conversion coatings have shown that there are two main types of phosphate coatings used industrially. These are based on zinc and iron phosphating systems (see Table 2.3). Iron phosphates are typically used to coat steel; while zinc is used for steel, aluminium, zinc and calcium surfaces.[40] Zinc phosphating is also carried out on zinc plate that has been applied to steel electrochemically or by galvanizing.[31] It has not been as widely reported as a surface treatment for zinc workpieces. This discussion will focus on the phosphating of steel substrates.

Table 2.3 Characteristics of phosphate coatings[3,31, 56]

Phosphating system	**Composition**	**Mass density (g/m^2)**	**Thickness (µm)**	**Structure**
Iron phosphating using lightweight iron phosphating	$FePO_4$ $Fe_3(PO_4)_2.8H_2O$ (vivianite) FeO $Fe(OH)_3$ (minor component)	0.1-0.7	< 1	Amorphous and porous
Zinc phosphating of a zinc substrate	$Zn_3(PO_4)_2.4H_2O$ (hopetite) $Zn_2Fe(PO_4)_2.4H_2O$ (phosphophyllite) $Fe_5H_2(PO_4)_4.4H_2O$ (hureaulite, minor component)	1.0-4.5 (lightweight)	2 -5	Crystalline and porous
		4.5 –10 (Medium weight)	Not Given	
		10-30 (Heavyweight)	25 – 75	

Table 2.3 shows that there is one main iron phosphating system used in conversion coating. This is referred to in the literature as lightweight iron phosphating (see Section 2.3.4). However there are three other zinc phosphating systems used industrially. Reports on zinc phosphating appear more often than iron phosphating in the literature. However mixed metal phosphating has become a considerably popular coating process in South Africa. Table 2.3 shows the three main parameters used in industry to characterise these coatings. These are:

- mass density in grams per square metre
- thickness in microns
- structure.

The thickness of phosphate coatings has been found to depend on the size of the tertiary phosphate crystals. This in turn depends on the phosphating system, presence of additives, temperature, exposure time of workpiece to the solution and substrate composition and preparation. Thickness values can reach up to 100 µm but the normal lies between 1 and 20 µm.[3] The thickness is more often quoted in literature as a mass density, with units of g/m^2 and less commonly in simple microns. The mass density, also known as the average area density, is equivalent to taking the mass of coating and dividing it by the area it covers.[57] Zinc phosphates give much thicker coatings than iron phosphates and as a result require more powder to cover the workpiece surface. The coating structure is defined as being either amorphous or crystalline. The type of structure obtained is also very significant in the adhesion of the organic coat to the workpiece and quality of the coat achieved. Amorphous coatings do not have a regular or ordered arrangement and thus have no definite shape or form. As a result, the topcoat does not have a uniform consistency throughout the surface. The molecules in a crystalline structure are arranged is an orderly fashion and thus give a more uniform coat of powder on the surface.

The coating formed on the substrate surface is present as an inorganic layer which:

- provides a new surface free from oils and grease
- promotes adhesion of the powder to the substrate by roughening the surface
- provides a stable, insulating layer that inhibits corrosion on the surface.[58]

2.3.4 The Chemistry of Zinc and Iron Phosphating

The surface reactions leading to the formation of insoluble phosphate layers on steel surfaces have not been fully characterised for industrial phosphating baths. This is evident in the literature where unbalanced chemical equations, equations not describing reactions in keeping with the overall bath chemistry as well as confusion over the order of the chemical reactions have been reported. However, this has not stopped zinc and iron phosphating from becoming a popular and successful pre-treatment step for paint and powder coating in the metal finishing industry. [1,40]

Many reactions have been put forward to describe zinc and iron phosphating of steel in simple and accelerated solutions. These are based on the oxidation of the substrate at anodic sites (see Equation 2.19) and the formation (or inhibition) of hydrogen gas followed by the formation and precipitation of the tertiary phosphates largely at cathodic sites. Equation 2.20 represents a coating forming in a zinc phosphating system. The removal of hydrogen ions from the solution causes the pH at the surface-solution interface to rise and the acid soluble tertiary phosphates to precipitate out of solution as the hydrogen ion concentration falls.

$$Fe(s) + 2H_3PO_4(aq) \rightleftharpoons Fe(H_2PO_4)(aq) + H_2(g) \qquad \text{Equation 2.19}$$

$$3Zn^{2+}(aq) + 6H_2PO_4^-(aq) \rightleftharpoons Zn_3(PO_4)_2(s) + 4H_3PO_4(aq) \qquad \text{Equation 2.20}$$

The phosphoric acid generated from the reaction of the zinc derivative (D) is theoretically consumed in the etching or oxidation of iron. However, only some of the hydrogen ions are used up in this direct reaction with the iron in the substrate. In practice, surveillance and control of the rise in the solution pH is necessary, usually through chemical additions to maintain the pH at around 4.

Many equations representing the overall process have been proposed, based on a combination of the surface reactions represented in Equations 2.19 and 2.20. The most important of these reactions are given in Equations 2.21 to 2.25 below.

$$2Fe(s) + 3Zn(H_2PO_4)_2\,(aq) \rightleftharpoons Zn_3(PO_4)_2\,(s) + 2Fe(H_2PO_4)_2\,(s) + H_2\,(g)$$

Equation 2.21[1]

$$Fe\,(s) + Fe(H_2PO_4)_2\,(aq) + 2O\,(aq) \rightleftharpoons 2FePO_4\,(s) + 2H_2O\,(l)$$

Equation 2.22[3]

$$Fe\,(s) + 2Zn^{2+}\,(aq) + 4H_2PO_4^-\,(aq) \rightleftharpoons Zn_2Fe(PO_4)_2\,(s) + H_2\,(g) + 2H^+\,(aq) + 2H_2PO_4^-\,(aq)$$

Equation 2.23[2]

$$Fe(s) + 3Zn(H_2PO_4)_2(aq) + 4H_2O(l) \rightleftharpoons Zn_3(PO_4)_2.4H_2O(s) + FeHPO_4(s) + 3H_3PO_4(aq) + H_2(g)$$

Equation 2.24

$$4M^{2+}(aq) + 3H_2PO_4^-(aq) \rightleftharpoons MHPO_4(s) + M_3(PO_4)_2(s) + 5H^+(aq)$$

Equation 2.25[3]

(M = Fe, Zn or Mn)

Reactions for phosphating of zinc on zinc surfaces have been well defined. However, today most phosphating solutions are multi-metal systems. Phosphating reactions become increasingly complex and difficult to characterise because of the opportunity for the formation of mixed metal phosphates and for a range of competing reactions in solution. Phosphating has been observed to produce sludge containing largely iron(III) phosphates and the iron(II) derivative of (E) but also containing valuable products like zinc phosphate.

Iron phosphate solutions have been used since 1906[2,40]to coat steel surfaces. The formulation of these iron phosphating systems do not contain the iron(II) derivative of (D). The first step in the coating formation is basically the same as that seen with zinc phosphating (see Equation 2.19). This takes place at the anodic site and brings the iron(II) species into solution. The solution must be balanced so that the iron(III) derivative of (F) is near saturation in the acidic solution and the equilibrium in Equation 2.26 lies on the right.

$$4Fe(s) + 4NaH_2PO_4(aq) + 2O_2(g) \rightleftharpoons Fe_3(PO_4)_2(s) + FeO(s) + 2Na_2HPO_4(aq) + 3H_2O(l)$$
Equation 2.26

No liberation of free acid occurs in this reaction. This means that the pH of the solution is higher than those of the zinc phosphating systems. Chemical additions of phosphoric acid are made to aid the etching step. Iron(II) in solution can then be further oxidized to iron(III) by atmospheric oxygen or through the action of oxidizing agents (see Equation 2.26). The oxygen represents acceleration of the process and for alkali phosphate solutions this can also be achieved by using molybdates.[2] Sludge may be formed directly from this iron(III) generated in solution (see Equation 2.27).

$$3Fe^{2+}(aq) + 2PO_4^{3-}(aq) \rightarrow Fe_3(PO_4)_2(s)$$
Equation 2.27

Iron oxide (see Equation 2.26) and iron hydroxide have also been identified as constituents of the coating. However, according to the literature this process should produce very little sludge as the insoluble phosphates should be deposited as the coating. This of course relies on good process control and a sound knowledge of the mechanisms and stoichiometry of the reactions. The latter, amongst other things, has not been fully established and desludging or filtering of iron phosphating solutions is still carried out routinely in industry.

2.3.5 Control of Iron Phosphating Solutions

The phosphating solutions operate at a specified pH and the baths have been described as having a number of 'points'. As the pH of the solution rises during workpiece processing, so the phosphating solution has to be added to restore the pH to the original value. According to the literature, if the pH of the solution is too low (below pH 3) the parts will be cleaned and pickled but will not be coated, since this pH is too low for the formation of insoluble phosphates. Also at lower pH values, the acid attack on the metal is more aggressive and insoluble phosphates making up the coating may not form. If the pH is too high (above 6) the workpieces will not get enough coating and may rust as a result of the thin coat.[12,40]

Monitoring and control of phosphate baths are essential in phosphating operations as they ensure that the acid is replenished timeously and that the process operates efficiently. Parameters that govern the operation of the baths include temperature, concentration of phosphoric acid and the pH of the bath. The latter two parameters are used in industry to maintain chemical control of the bath. This is achieved by means of titrimetric analysis and uses what is referred to in industry as a 'pointage' system as an expression of acidity. The value of a 'point' is assigned to the volume (in mL) of 0.1 M NaOH required to neutralize 10 mL of the phosphate solution, using phenolphthalein as an indicator. This analysis may be carried out by a line operator but is frequently a service offered by the chemical suppliers to the company. Phosphoric acid should ideally show three different end-points corresponding to the dissociation of each proton. However, there are only two different end-points observed in practice: one at a pH of 4.5 and one at a pH of 9.5 (see Figure 2.5). The products formed from the reactions shown in Equations 2.28 and 2.29 are consistent with the structures (A) and (B) given in Figure 2.2. The end-point reached at pH 4.5 is a measure of the 'free acid', 'free acidity of the bath' or 'free acid pointage'. This is said to be the acid that is present in the solution to initiate attack on the metal. When titrated with NaOH, using methyl orange as an indicator, the reaction produces monosodium phosphate as shown in Equation 2.28.[59]

$$H_3PO_4\,(aq) + NaOH\,(aq) \rightleftharpoons NaH_2PO_4\,(aq) + H_2O\,(l) \qquad \text{Equation 2.28}$$

The second end-point reached at a pH 9.5 represents the conversion of phosphoric acid to disodium phosphate using phenolphthalein as the indicator and is shown by Equation 2.24. This is the most commonly used titrimetric analysis used in industry for establishing the concentration of the phosphate bath.

$$H_3PO_4\,(aq) + 2NaOH\,(aq) \rightleftharpoons Na_2HPO_4\,(aq) + 2H_2O\,(l) \qquad \text{Equation 2.29}$$

The pointage obtained here is a measure of the total strength of the bath and is known as either the 'total acidity', 'total acid pointage or points' or 'pointage'.[1,3,59]

2.4 An Overview of the Chemistry of Powders

Powder coatings are derived from finely ground plastic particles and are used for protective and decorative purposes.[6,12] The word 'plastic' is synonymous with the chemical term 'polymer'. Put simply a polymer is a large molecule made from many smaller ones, monomers, which have become linked together through chemical reaction. The word 'plastic' has tended to be used when referring to a class of polymers known as thermoplastics. Thermoplastics are one of two basic types of plastics found in powder coatings the other one being thermosetting. The major difference between these two powders lies in their structure and their response when exposed to heat. The polymer molecules in thermoplastics are one-dimensional, chain or linear in structure. Thermosets have a three-dimensional structure in which polymer chains are cross-linked together through branches or reactive groups in the chain. When heated, thermoplastics melt and resolidify on cooling, while thermosets do not melt. According to the literature thermoset powders are used more in industrial applications than thermoplastics.[5] This is due to the fact that thermoplastics have poor adhesion properties and, unlike thermosets, are thermally unstable. There are four main types of thermosetting powders used industrially: epoxies, polyesters, polyurethanes and acrylics.[4,5,12,60-62] The first three will be discussed below. A summary of the properties and processing of both powder types is given in Table 2.4, which shows that three polymer systems have been used in the formation of thermoplastic powders namely vinyls, nylons and linear polyesters.

Table 2.4 Properties of thermoplastic and thermosetting powders[5,63]

Property	Thermoplastic	Thermosetting
Corrosion resistance	Excellent	Excellent
Structure	Linear	Cross-linked
Thermal stability	Unstable	Heat stable
Operational requirements	Workpiece must be pre-heated and post-heated	Powder is heated and cured after spraying
Thickness	250 μm	20-80 μm
Application	Fluidised Bed	Electrostatic Spray
Composition	Vinyls, nylons and linear polyesters	Polyester, polyurethane and acrylic resins and cross-linkers
Adhesion	Average	Excellent
Uses	Protection	Decoration and Protection

As can been seen from Table 2.4, thermoplastic powders give much thicker coatings than thermoset powders. It is for this reason that thermoplastics are used on outdoor equipment for protection against harsh weather conditions.

Since its introduction, powder coating has becoming a popular alternative to coating with paint. Powders are used because they produce thick coatings that are hard, resistant to abrasion and tough. According to the literature, powder coating is used because it gives consumers and industry one of the most economical, longest-lasting and colour-durable quality finishes available.[64] Powder has been found to offer several advantages over paint:

- powder coatings do not give rise to runs or sags
- the film layer tends to be more even
- the skills required to apply powder are considered to be fewer than those which are required by a painter applying on a wet spray
- powder is less of a fire, environmental and health hazard as it does not involve the use of solvents
- powder application requires simpler equipment
- equipment maintenance and running costs are lower
- wastage is low because theoretically almost 100% of the powder can be utilized during coating.[5]

Powders are comprised of four basic components: resins, pigments, extenders and additives. The specific functions of each are discussed briefly below.

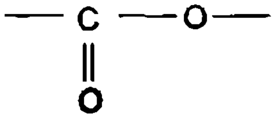
Resins are the primary components which polymerize during film formation. They bind the powder to the workpiece surface and form the continuous structure of the coating. Thermoset powders are made from high molecular weight resins and a cross-linker. Pigments are used to provide colour for decorative purposes. Extenders are used to 'stretch' the powder over the workpiece surface by acting as a filler. This helps to keep powder costs low by reducing the amount of resin used.[4,5] Both pigments and extenders must be chemically inert and heat resistant. Additives used in powders include curing agents, catalysts and flow agents. They are used to modify flow and film properties to suit different application and curing conditions. Curing agents are also known as 'hardeners' and are used to cross-link the resins at a temperature between 100 °C and 180 °C. These agents determine the gloss level, and the structure and texture of the coating. Examples of curing agents used include amines and anhydrides. Sometimes catalysts are also used to speed up the curing time.[5] Flow agents can be used to give a smooth finish to the final coat.

The properties of the three most commonly used powders are shown in Table 2.5. They are described on a four-point performance scale where 'excellent' represents the best and 'poor' represents the worst performance rating.

Table 2.5 Main properties of the different thermosetting powders[5,12]

Property	Polyester	Polyurethane	Epoxy Resins
Weatherability	Excellent	Good	Poor
Corrosion Resistance	Very Good	Very Good	Excellent
Chemical Resistance	Very Good	Very Good	Excellent
Heat Resistance	Good	Very Good	Very Good
Impact Resistance	Good	Very Good	Excellent
Flexibility	Very Good	Very Good	Excellent
Adhesion	Excellent	Very Good	Excellent
Thickness (μm)	25 – 100	75	12.5 - 75

Polyesters are defined as being all polymers which contain repeating units of the ester group (Figure 2.6) in the polymer chain. These polymers can be cross-linked or linear in nature. Cross-linked polyesters are produced by the polymerization reaction between a polyhydric alcohol and a mixture of saturated and unsaturated polycarboxylic acids. The unsaturated polymers are then mixed with a liquid monomer which improves the application characteristics by lowering the viscosity of the polymer and allowing for cross-linking to take place.



$$-\underset{\underset{O}{\|}}{C}-O-$$

Figure 2.6 Ester group present in the polymer chain[65]

Mixed polyester resins have become widely used in powder coating. For example urethane polyesters such polyester triglydyl isocyanurate (TGIC) (see Figure 2.7) employ an epoxy functional as a cross-linker in the TGIC. However, most polyester powders now operate TGIC-free as these are believed to cause sensitization of the skin and respiratory system, when inhaled.[5,65]

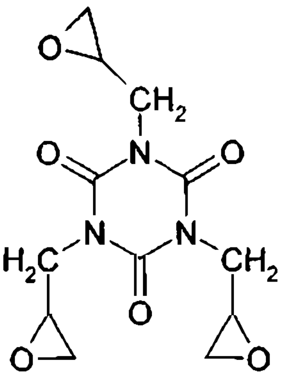


Figure 2.7 Structure of triglydyl isocyanurate

Polyurethanes (PUR) are formed by an addition reaction between polyisocyanates and polyalcohols. These polyurethanes contain the common urethane group shown in Figure 2.8. Powder coatings consist of a combination of a solid polyol (mostly polyester and polyacrylate) and a solid blocked polyisocyanate, which acts as a cross-linker. This reagent contains a blocking agent which is thermally decomposable. It keeps the similar monomer groups, present in the polyisocyanate, together[5,66]

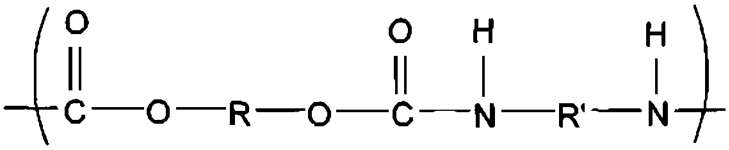


Figure 2.8 Common urethane group found in all polyurethanes[65]

As can be seen from Table 2.5 polyurethanes have excellent heat resistant properties. However, it has been reported in the literature that they burn easily and release toxic fumes.[67] Polyurethane coatings are hard, tough and durable, making them suitable for a wide range of industrial applications.[68,69]

Epoxy resins are derived from polyether prepolymers that contain two or more epoxide groups per molecule. The structure of the epoxide group is shown in Figure 2.9.

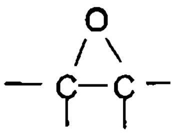


Figure 2.9 Epoxide group[65]

When these resins react with curing agents it results in cross-linking through the expoxy group. A large number of epoxy coatings are based on the diglycidyl ether of bisphenol A (see Figure 2.10). These account for 75% of the epoxy resins, which are sold worldwide. One problem, highlighted under weatherablility in Table 2.5, is the tendency to turn yellow and degrade on exposure to sunlight. Epoxy-polyester hybrids have been developed. These are less expensive than epoxy based powder coatings and have a better resistance to yellowing (discolouration over time). However, they tend to degrade in the sunlight. [5,6,12, 70]

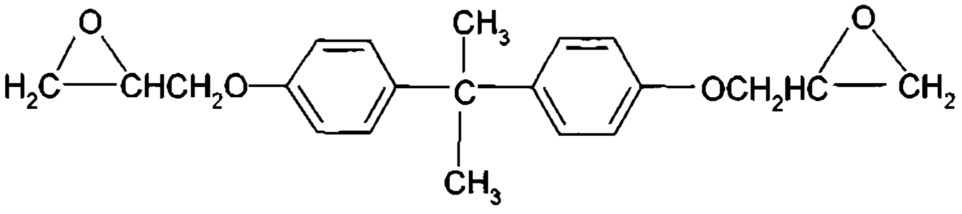


Figure 2.10 Diglycidyl ether of bisphenol A (DGEBA)[71]

2.5 Application Principles and Techniques

The practice of surface finishing i.e. cleaning, phosphating, powder coating and rinsing of the surface, uses variations of the same fundamental application techniques. Wet and dry processes employ both immersion and spraying systems. The alternative wet and dry processes, however, differ with respect to the number of stages required for phosphating. This is dependent on the type of phosphating (iron or zinc) and on the chemistry of the process solution. The total number of stages is equated to the number of degreasing, pickling and phosphating stages plus the number of rinsing (fresh water and activated) which make up the pre-treatment stage. Recent developments have resulted in the pre-treatment process being carried out in one step.

2.5.1 The Phosphating Process

The phosphating process is made up of a number of chemical treatment steps which are shown in Figure 2.11 in the order in which they take place in industry.

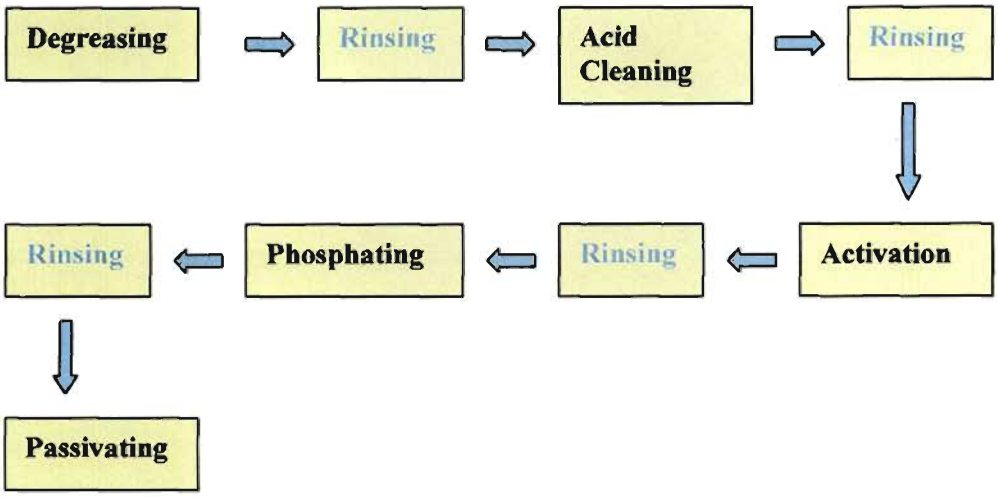


Figure 2.11 Typical immersion system for a zinc phosphating pre-treament process

The first process step typically involves cleaning of the substrate using an alkaline cleaner (see Section 2.2.1). The third step in the process is an acid clean (see Section 2.2.2) with a rinsing stage before and after this treatment. Rinsing the substrate surface with clean water is used to remove any excess process solution or any undesirable products that may form during the pre-treatment process. As the workpiece passes through the rinse system, the solution carried over from the previous treatment is washed off the surface, becomes dispersed and diluted in the rinse water. This film of solution covering the surface of the workpiece is commonly referred to as 'drag-in'.[72,73] Rinsing therefore removes any chemicals that have not reacted and rinsing also stops the surface reaction.[5] This results in the rinse water becoming contaminated with the process solution and this is commonly referred to as 'cross contamination'.

The fifth step in the treatment process (see Figure 2.11) is to activate the workpiece surface (see Section 2.3.1). In step seven the workpiece is phosphated using a zinc or iron solution (see Sections 2.3.1 and 2.3.4). This results in the formation of the conversion coat on the workpiece surface. A sealing treatment is often the final step in the process (see Section 2.2.5). This is commonly referred to as a 'seal rinse' in industry. There is normally a rinse step between each of the above process steps, except between the activating and phosphating steps.

In practice some of these steps can be optional and on occasions two or more of these steps can be combined into one. Three important examples have been found in the literature.[1,2,3] An example of an optional step is pickling. This can be omitted if the workpiece surface is not rusty. Corrosion products can be removed from the substrate surface in alkaline cleaning by incorporating complexing agents such as ethylenediaminetetraacetic acid (EDTA) and gluconate into the formulation and operating the solution at elevated temperatures.[2] However this has been found to require a longer processing time. These complexing agents have the advantage of not reacting with the bare substrate and of preventing hydrogen embrittlement. In the case of iron phosphating the activation step has been found to be unnecessary and workpieces go directly from cleaning to phosphating. However, recently cleaner-coaters have become available in which the cleaning (degreasing and acid cleaning) and the coating (phosphating) are carried out in a single step. In practice two cleaner-coater stages are used in a spray system, one immediately after the other. This is followed by at least one rinsing step. This has resulted in the process shown in Figure 2.12 being preferred for spray application of iron phosphating of solutions. This means that there is traditionally a maximum of eight stages in zinc phosphating and seven stages in iron phosphating.

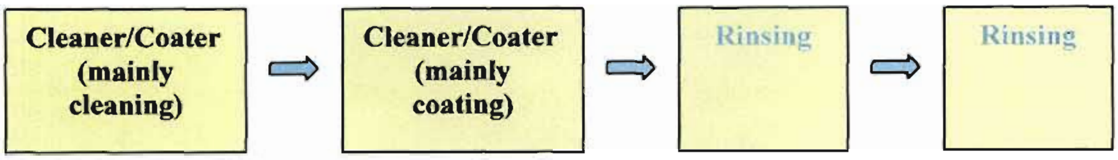


Figure 2.12 Typical spray pre-treatment process

This formulation has been made possible by the comparatively low acidity of iron phosphating solutions. This has allowed the use of non-ionic and anionic surface active and complexing agents in the sodium or ammonium dihydrogen phosphating solutions. Chromate sealing has also been carried out in the cleaner-coater solution. Zinc phosphating has traditionally required more steps than iron phosphating.

Recent developments have shown that the pre-treatment process can take place in one step. This type of process is commonly referred to as 'plaforization' in which cleaning, phopshating and application of an inhibiting sealant all occur in one step. It can be carried out using a dip or spray process. This process must be carried out at very low pressures and requires an exhaust system because it produces organic vapours which are much denser than air. [74,75]

2.5.2 The Immersion Operation

In immersion phosphating plants the process and rinse solutions, called 'baths' are contained in tanks which are arranged one after the other in what is known as a (processing) 'line'. The workpieces are then moved through each of the solutions in the prescribed order using a conveyor system. The workpieces may be loaded onto jigs or placed in baskets or barrels which are secured on an overhead hoist. Immersion operations are used to coat smaller items. These workpieces are then immersed in a series of dip tanks which are situated below the hoists.[1,31] The time the workpiece spends in each tank can be varied in immersion systems and thus the coating weight and thickness can be varied. Typical immersion times for different steps are[2]:

- degreasing – 5-10 minutes
- rinsing – 0.5 -1.5 minutes
- acid cleaning – 10-20 minutes
- activation – 0.5 -1.5 minutes

- phosphating – 3 -10 minutes and
- passivation – 0.5 minutes.

Immersion rinses can be classified into one of two categories: nonflowing or flowing.[72] Nonflowing immersion rinses contain water that is stagnant. As a result there is a contaminant build-up in the tank as the process proceeds until a maximum tolerance level is reached. Once this level is reached the rinse water is no longer effective and the water from the tank must be dumped and the tank refilled with clean water. Flowing immersion rinses consist of water that constantly flows through the tank. This rinse tank is fitted with an inlet (which brings clean water into the tank) and an overflow pipe or weir (which provides an outlet for contaminated water to be sent to a waste stream). Running or flowing the rinse has been used to keep the concentration of contaminants at low levels for longer so as to extend the lifetime of the rinse solution. This is possible due to the continuous dilution and discharge of the tank's contents as effluent. Flowing rinses can be emptied using a single rinse tank or multiple rinse tanks placed in series. According to the literature the latter is most effective when the water is fed into the last tank and allowed to run or cascade from one tank to another in the direction opposite to that in which the workpieces move down the line.[72,76,77] This is referred to as 'counterflow' or 'countercurrent flow'.[72,73,78] In contrast, each tank can be arranged so that the tanks are not linked. In such cases each rinse solution operates individually with its own water supply.

Sludge build-up in immersion systems has been found to give poor quality coatings on the workpieces. This occurs when the sludge can reach a level at which it becomes deposited on the workpiece. In large plants, sludge removal systems are usually fitted into the process to continuously remove the sludge and recycle the phosphating solution to the process tank. These systems are present in the process tanks where the sludge normally forms. Thus the tanks are designed in a specific way to facilitate sludge removal. Some tanks have sloping floors at an angle ranging from 45° to 60°. Other tanks, with horizontal floors, are fitted with a sludge box. Another method of removal involves agitating the sludge to keep it suspended while continuously removing it with a tilted plate separator or filter unit.[2] In small plants the solutions are decanted and the tanks desludged at regular intervals. Decanting may be partial or total. Partial decanting involves draining the solution from the tank and discarding the solution as effluent. The sludge left at the bottom of the tank is then pumped or manually bailed out in a separate step. No literature has been published on the composition of the sludge.

Immersion is also used to apply the organic coat to the surface of the workpiece, and it is carried out using a fluidized bed (see Figure 2.13) [79,80] and is considered to be the dry equivalent to the immersion of the workpieces in the phosphating solution. The powder is placed in a holding container called a 'hopper' and is made to flow like a fluid by passing compressed air through it. The bottom of this container contains air chambers on the sides and there is a porous plate placed at the top. The powder is placed on top of this plate. Compressed air is fed through the bottom of the container and passes through the plate. This breaks up the powder particles, removes any moisture from the powder and provides a lightweight texture that makes it easier to transport the powder. The powder is said to become 'fluidized' and electrically charged. This is achieved by applying a high voltage to the fluidized bed. The workpiece is either heated and dipped into the fluidized bed or hung above in the cloud of powder which becomes deposited on its surface as a continuous film[5,6,12]. According to the literature, fluidized beds are used mainly for the application of thermoplastic powders.[5] Fluidized bed systems should be sufficiently insulated to ensure that the powder does not easily escape into the atmosphere.

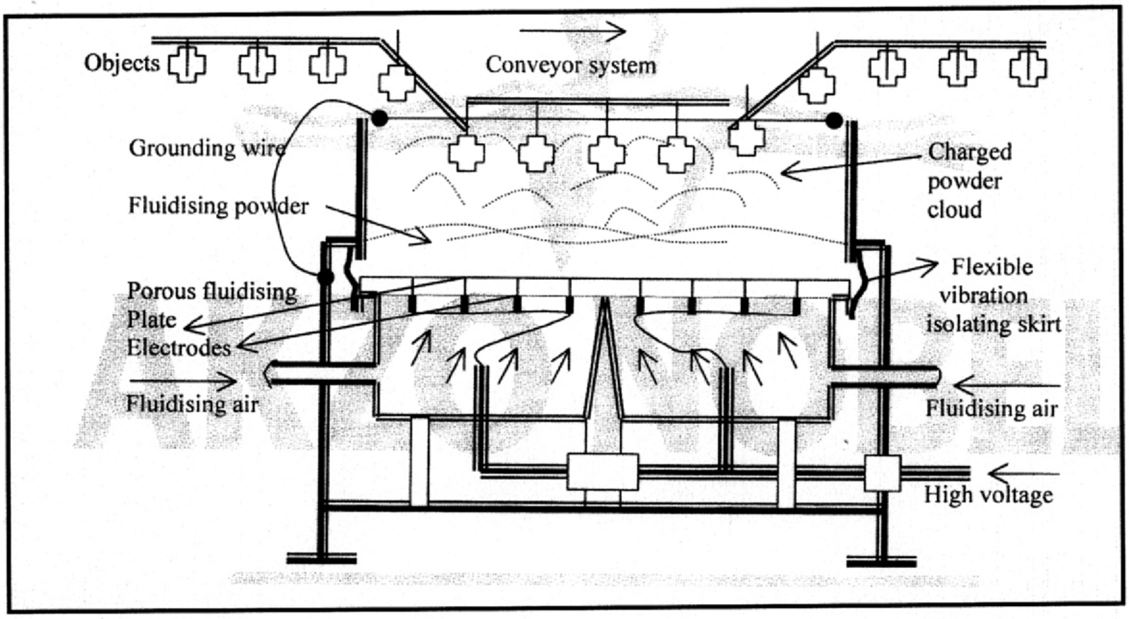


Figure 2.13 Typical electrostatic fluidized bed[5]

2.5.3 The Spraying Operation

Spray phosphating has been considered to be a more effective application process than the immersion treatment. It gives a finer film with a lower coating weight than that achieved by immersion. Spray phosphating uses an enclosed system. The enclosure is known as a 'tunnel'. The items to be coated are mounted onto jigs or are hung individually on a conveyor belt. They are then transported by the conveyor system through the tunnel where the spraying is carried out. The tunnel is above storage tanks which hold the cleaning and phosphate solutions and rinse waters. The tunnel floor is laid with stand pipes, called 'risers', through which the solution from the storage tank is pumped up and sprayed through spray jets or nozzles onto the workpieces. When the solution is sprayed on, some of it forms the coating while the unused solution simply flows off the workpiece. This solution runs through a grating or channel on the tunnel floor and returns to the storage tank. As a result the solution is continuously recirculated and recycled[3,31] through the process. In spraying operations the distance between the different stages and the presence of drainage zones are critical in avoiding cross contamination. Adjustable spray jets (see Figure 2.14) are arranged on the risers and these then determine the type of spray pattern achieved and also prevents overspray while giving a complete cover of the surface.

Spray plants are either fully or partially automated. In spraying operations, especially in the application of zinc phosphates, sludge build up can cause the nozzles to become clogged.

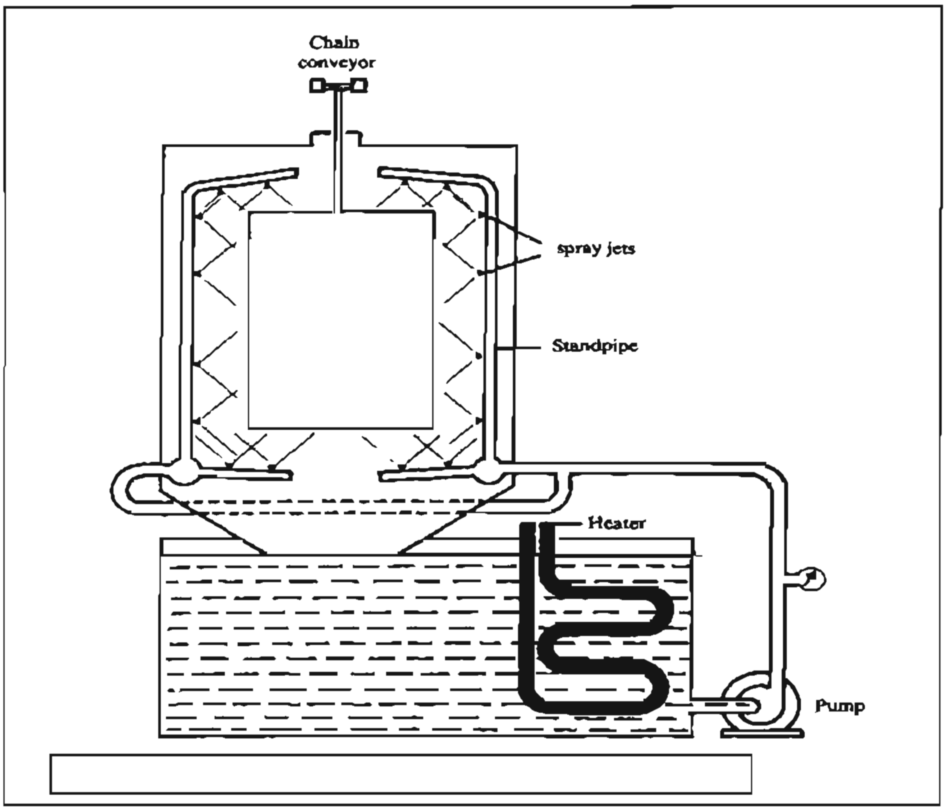


Figure 2.14 Cross-section of a spray phosphating installation[31]

The organic coat can also be applied using a spray application method. Unlike the wet application technique it is carried out using an electrostatic spray gun. Electrostatic spray systems are used more widely in industry than fluidized beds in powder applications.[81] The powder is contained in a hopper in a fluidized form. It is then pumped and transported by an airflow system to an electrostatic spray gun. The particles become charged when they are released from the gun and are transported in one direction by the air transport system. The workpiece is grounded and the charged powder particles move towards the workpiece and become deposited on the surface. The powder particles are charged using one of two methods: the corona charging or the Tribo method. [5,6,12] The Corona method uses a voltage generator to bring an electrostatic charge (negative) onto the surface of the powder particles. The gun is connected to the generator via an electrode situated at the gun tip. In the Tribo method, no high voltage generator is used instead the particles become 'friction' charged (positively) as they move through the spray gun. This is achieved because the spray gun is lined with a specially selected material and as the particles move through they rub against this material at a high velocity. In practice, several advantages and disadvantages have been encountered when using the corona and tribo methods methods. The advantages of the corona method include:

- they give variable film thickness
- it accepts all powder types and particle sizes
- the prescence of the strong electrostatic field has shown to give effective charging and high deposition of powder.

The disadvantages reported include:

- irregular coating
- poor coverage of corners and cracks.

The Tribo method, on the other hand, offers several advantages:

- it gives a uniform coating
- there is better charging effect without a generator
- it gives better coverage of corners, cracks and hollow spaces and
- it uses less powder than the Corona method.

However disadvantages of this method have been reported and include:

- the need to use special types of powder
- a longer time is spent charging the particles
- there is more wear and tear on the gun due to constant rubbing of particles along the inner walls and thus the gun has a relatively short lifespan.[5]

There is a wide variety of spray guns used industrially. These include automatic guns, electrostatic spray guns and airless spray guns.[82] Powder spraying can generate a large amount of waste because not all the powder is deposited on the workpiece surface. As a result, this application must be carried out in an enclosed unit, which is commonly referred to as a spray booth. The purpose of the spray booth is to contain any overspray powder so that it can be recycled and reused.[5,6,12,81] The booth is usually fitted with an extractor fan which is attached to a recovery system. The fan extracts the contaminated air from the booth into the recovery system preventing the contaminated air from escaping into the atmosphere. The powder extracted from the booth is recovered by cyclones and bag filters. Cyclones consist of a simple circular chamber, tapered at the bottom. The contaminated air is fed tangentially into the top of the cyclone and swirls around the chamber.[5,12] The larger powder particles are thrown outwards by a centrifugal force and fall into a collection hopper at the bottom of the cyclone. The lighter particles remain in the air stream and pass through a central outlet in the top of the chamber to the bag filters. These filter out the fine powder particles which then become stored in these bags. The powder recovered from the cyclone is further cleaned and passed through a sieve which removes any foreign matter. This purified powder is then mixed with the clean, unused (virgin) powder and reused in the process. Cyclones are effective industrial collection systems as they have recovery efficiencies as high as 95%.[5]

Once the powder has been applied, it is then cured in order to achieve a smooth coating finish.

2.6 Curing of Powder

Powder curing is the final step in the powder coating process.[83] It involves heating the powder to high temperatures (around 200 °C) which causes it to 'melt', flow and adhere onto the workpiece surface. As a result a smooth, continuous organic film forms on the surface of the workpiece. Curing is commonly carried out using convection or infrared ovens.[5,12, 84] Ultraviolet (UV) curing has recently received a lot of attention in the literature and has been used industrially for curing powders.[84] In South Africa infrared and UV curing is rarely used.

Two oven designs have been in industrial service for curing powder coating, namely the box and tunnel (continuous) types. Box ovens are basically heated chambers with a door through which the workpieces are loaded and unloaded. These ovens have been traditionally used with batch processing of workpieces. The introduction of conveyor systems for transferring the workpieces through the process and the short (powder) curing times has led to tunnel ovens becoming widely used. These are fitted with overhead or floor conveyor systems. The usual method of heating such ovens is by convection i.e. hot air.[6]

Convection ovens use a gas burner as a heat source and operate at temperatures of between 177 °C and 204 °C.[12] The air temperature in the oven is maintained by continuously recirculating the air withdrawn from the heating space inside the oven through the heater and back into the oven through distribution ducting running throughout the tunnel. Air seals are used on the entrance and exit ports of the oven to blow the hot air back into the oven and prevent the outward flow of heated air. The substrate is heated by the air in the oven and in turn conducts heat to the coating. The time needed for curing depends on the mass of the substrate and the type of powder being cured. Typical times for convection curing processes range between 10 and 30 minutes. A major advantage found with convection curing is that the workpiece can be heated for longer than the prescribed time without having an adverse effect on the colour, gloss or quality of the coating.[5,6]

Infrared ovens use light energy, produced from an emitter, to heat the workpiece. Some of the energy is absorbed into the coating and transferred to the workpiece, while the rest is reflected off the workpiece. Polymerization begins immediately upon absorption and operating temperatures range from 600 °C to 2000 °C[12]. As a result infrared curing is much faster than convection curing. Infrared curing is suitable for heating large workpieces which have a consistent shape. The major disadvantage experienced with this process is that there is an uneven distribution of energy as the parts of a workpiece directly exposed to the emitter are heated first.[5,6]

Another method used to cure powder is by means of UV light where the light source is typically a UV lamp. The powder cured by UV light has a lower melt temperature than conventional powders and contains photo-initiators instead of cross-linkers. These compounds initiate chemical reactions upon exposure to light. There is a pre-curing step, known in the trade as 'melting'and 'flowing'. This is carried out using infrared energy in a separate oven from the one where curing takes place. Curing then occurs upon exposure to UV light which causes cross-linking to occur through the photo-initiators..[85,86,87] This method of coating has been found to offer many advantages in the powder coating industry some of which are listed below:

- it cures heat sensitive substrates with operating temperatures ranging from 93 °C to 116 °C
- it requires less energy, due to its low operating temperatures thus reducing the operating costs
- it allows for low temperature powders to be more easily manufactured
- it gives a coating which is an extremely durable and stable polymeric system
- it takes place at high speeds, almost instantaneously, thus reducing the operating times
- it offers a competitive advantage, enhances product quality, simplifies production and complies with environmental legislation.[85,86,87]

The major disadvantage associated with this method is that there are a limited amount of the required resins and photo-initiators available because it is a newly developed technique.

After curing, the workpiece is usually cooled so it can be easily handled for packaging. The finished product is then ready for dispatch and distribution to the customer.

CHAPTER 3

WASTE MINIMISATION AND THE POWDER COATING INDUSTRY

In this chapter, waste minimisation is defined in terms of a waste management approach for sustainable industrial development conceptually (Sections 3.1 and 3.2), strategically (Section 3.2) and practically (Section 3.3, 3.4 and 3.5). In Section 3.2, various definitions, (which have evolved since its inception in 1987[88]) of waste minimisation are discussed as in the established approach used to achieve waste minimisation. A detailed review of the preliminary stage in the assessment of the waste minimisation programme is given in Section 3.3. In this section, four established analysis techniques recommended for use in the initial assessment (and on occasion beyond) are considered in detail. In Section 3.4 the methods of prioritizing the options that are generated from the waste minimisation analyses and selecting suitable options for the feasibility assessment stage are reviewed. In Section 3.5, the two components of the final feasibility analysis are briefly reviewed. Lastly, some waste minimization opportunities and options which have been used in the surface finishing and powder coating industries are reported in Section 3.6.

3.1 Waste and Waste Management

Industrial processes have become synonymous with the production of waste. The term 'waste' as cited in the literature tends to fall into one of three catergories of meaning shown below:

1) undesirable process outputs which are assumed to be relatively benign or not and are considered to cause damage to the environment or to humans
2) undesirable process outputs which are hazardous and present a risk to public health and the environment
3) a useful item which is no longer serviceable because it is damaged beyond repair or is obsolete.

This shows that industrial waste is not the only kind of waste that needs to be managed. Waste has been termed 'established' (also termed 'obvious'[89]and 'controlled'[90]) where the source is known and the quantity can usually be measured. Alternatively waste has been described as being 'less obvious'[89] or 'uncontrolled.'[90] In this case waste is often released, knowingly or unknowingly, directly into the environment and it is difficult to determine its origin.

There is extensive UK legislation which covers waste production and management. The UK Environmental Protection Act 1990[91] defines waste as being " any substance which constitutes a scrap material, effluent or any other surplus substance that arises from any process." This is consistent with definitions of waste given in points 1) and 3) above. Point 2) is covered not only by the Environmental Protection Act but also by other pieces of legislation including The List of Wastes Regulations 2005.[92] This document clearly and extensively defines hazardous waste in terms of its toxicity and concentration, and lists waste according to the relevant industrial sector that generates it. The UK Environment Agency has classified waste into the two types namely controlled and non-controlled waste. Controlled waste consists of household, industrial and commercial waste. This has also been termed municipal solid waste[90] where the industrial waste comes from light industry. Non-controlled waste consists of agricultural waste and waste produced in mines and quarries.[90] These are not normally sent through a treatment process prior to disposal but are discharged or disappear directly into the environment. This has meant it has been very difficult to institute legislative control over the release of these wastes into the environment.

According to documentation published by the SA Department of Water Affairs and Forestry[93] waste is defined as being "any undesirable or superfluous by-product, emission, residue or remainder of any process or activity, any matter, gaseous liquid or solid or any combination thereof." Although this definition is consistent with that given in point 1) above, this document does go on to give a detailed classification of hazardous waste. It defines hazardous waste as being any waste that can cause severe harm to public health and the environment due to its inherent toxicological, chemical and physical characteristics. This definition is consistent with point 3) above. Such solid waste is usually uplifted by private contractors and can be disposed of in one of two ways, either in a hazardous waste landfill site or by incineration. Recently, incineration of hazardous waste has come under criticism both locally and internationally as the method releases heavy metals and other hazardous chemicals like dioxin into the atmosphere.[93] Landfill sites are given a hazard rating on a four point scale (see Table 3.1) which differentiates among the fairly, moderately, very or extremely hazardous waste. This determines what type of landfill site in which the waste must be deposited at.

Table 3.1 Ratings of hazardous waste[93]

Hazard Rating	Risk Factor	Type of Landfill
1	Extremely High	H:H
2	High	H:H
3	Moderate	H:H or H:h
4	Low	Landfill

There are two types of landfill sites that accept hazardous wastes which are **H:H** (High Hazardous) and **H:h** (Low Hazardous). The **H:H** landfills can accept wastes of all hazard ratings that are destined for landfill. However **H:h** landfills accept only wastes with hazard ratings 3 and 4. In Natal there are two low hazardous landfill sites and they are situated in Shongweni and Bulbul Drive in Durban. There are three high hazardous sites in SA: one in Holfontein, East London and Visserhok. Often hazardous waste has to be treated or encapsulated before disposal in a landfill site. This treatment is dependent upon the chemical composition of the waste.

The Department of Environment Affairs and Tourism[94] in SA has begun to publish documentation along the lines of the UK concerning waste. In 1999 the National Waste Management Strategies and Action Plans South Africa were published. In the national waste management strategy, waste and waste management are very thoroughly defined and waste treatment is categorized under seven headings. This includes hazardous waste, both domestic and industrial and covered by points 1) and 2).

In the South African National Water Act of 1998[95] a water-borne waste is defined as being “any solid material or material that is suspended, dissolved or transported in water (including sediment) and which is spilled or deposited on land or into a water resource in such volume, composition or manner as to cause, or to be reasonably likely to cause, the water resource to be polluted.”[95]

There is a general instruction under the National Environmental Management Act (NEMA) No.107 of 1998 not to damage the natural environment. It states “that any individual that causes, has caused or may cause significant pollution or degradation of the environment must take reasonable measures to prevent this from occurring, continuing or recurring”.[96] This will apply to waste especially when it is hazardous.

There are many general definitions of waste in the literature. For example Manahan defines waste as being “all kinds of solids, semisolids, sludges, liquids, contaminated soils, sediments and other kinds of materials that are either wastes themselves or are contaminated by wastes.”[97] This definition agrees with that given in points 1) and 3) above.

In the USA, the Resource Conservation and Recovery Act (RCRA) of 1988 covers hazardous wastes and solid wastes only. It also requires that the company responsible for generating the waste must have a programme in place to reduce the volume, quantity and toxicity of the waste to a degree that becomes economically practicable. [98] Other forms of waste for example that are water or air-borne are dealt with in different pieces of legislation. The US Environment Protection Agency defines waste as being “any unwanted product arising from a process which should be discarded irrespective of their impact on the environment.”[99] General waste refers to “any waste that does not fall within the definition of hazardous waste. It is waste that is unlikely to cause significant harm to the public or the environment, provided it is properly managed.”[93] The treatment of this waste has been prioritized according to a waste management hierarchy (See Figure 3.1).

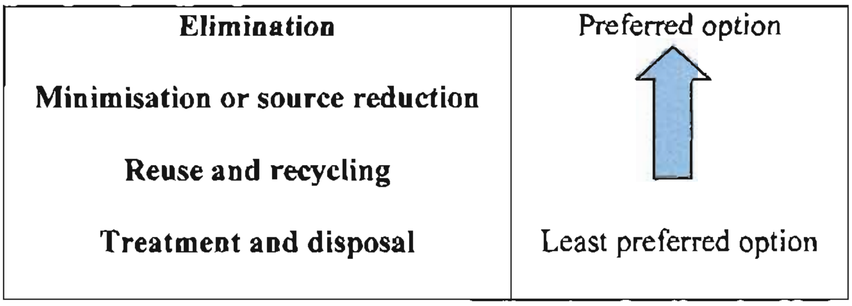


Figure 3.1 The waste management hierarchy [88,99-106]

Waste minimisation deals mainly with the first three levels of the hierarchy namely, elimination, minimization, and recycling and reuse. These are listed in order of decreasing sustainability as shown in Figure 3.1. Sustainability has been defined as "existing and solving today's problems in a responsible and environmentally friendly manner without prejudicing the ability of future generations to exist or solve their own problems."[106] The first option for sustainable waste management is elimination and this involves stopping waste from being formed in the first place. This has led to elimination and waste minimisation being called 'start of pipe' treatments.[107,108] Elimination produces 'zero waste'[109] and the only output from the process is saleable products.[102] However, elimination of all wastes is often unachievable in reality.[99] This means that other waste management options from the waste hierarchy must be sought in order to reduce waste. The second most preferred option in the hierarchy is waste minimisation. Such source reduction techniques have been employed not only to reduce the quantity of waste generated, but also to reduce the amount of toxic chemicals used and released into the environment.[110] According to the EPA[101], waste minimisation includes both source reduction and recycling.

The UK Environment Agency [111,112] describes waste minimisation as being the efficient industrial use of natural resources by understanding and changing processes. This emphasizes the need for an in-depth understanding of the process in terms of inputs so that natural resources can be conserved. This definition given by the agency stresses that less hazardous inputs should be used instead of more toxic ones in the production process. Adoption of these practices leads to a reduction in the amount of waste generated by the process.

Waste minimisation can be achieved through material changes {see points 1) and 3) below} or procedural changes {see points 2) and 4) below}.

1) Raw Materials

A change in the raw materials can involve using one of three options. The most important of these is reducing the amount of raw materials put into the production process. Quite often excess chemicals, rather than the correct amount, are added to a process because it is felt that this will benefit the process. In the production process, if the material is used in a purer form, waste products containing the impurity can be avoided. Substituting the raw material with one that is less environmentally harmful may not alter the amount of the waste, but it will reduce its toxicity and adverse impact on the environment.[111,113-115]

2) Technology

Technological changes can be simple like changing the layout of existing equipment, changing operating conditions and improving process controls. Alternatively they can be more complex and expensive for example adding to existing equipment or using different equipment.[98,114,115]

3) Product Change

Changes in the product which would aid waste minimisation include making the product 'user-friendly' so that it has a longer lifetime or ensuring that it can be recycled more easily. This relies on the acceptance by the consumer of a 're-designed' product, which they reject. This means that this option is rarely used.[98,115]

4) Improved Housekeeping

Housekeeping involves making simple administrative or procedural changes to the process. For example this includes preventing unnecessary spills by fixing leaking taps and pipes, using the correct amount of chemicals in a process and good store keeping. In any of the above ways resources can be conserved and waste management thus made more sustainable.[88,108,114,115]

The third option in the hierarchy is the reutilization of a waste material on site in a manner that will not harm humans or the environment.[110] Reuse is reported to be a form of recycling and can only take place on site. It involves returning the material or workpiece back into the same process from which it originated.[116] This means that a material can be reused as an intermediate in an industrial process to make a product or be used as a substitute for a commercial product.[110] Recycling has been found to take place either on or off site. In onsite use the waste from one process is used as an input into another process. For example water from a cleaning rinse can be used to wash floors. Offsite the waste from one company is sold to another. For example in scrap metal items can be taken and reprocessed by scrap metal dealers. In both these cases the waste is reprocessed using a different operation from the one by which it was first made. This means a new product is formed. [99,100,110,116] The least favourable option on the hierarchy involves the treatment and disposal of the waste. This is considered to be a last resort when production of waste is unavoidable, and is referred to as 'end-of-pipe' treatment.[117],[118] Treatment is any method, technique or process designed to make waste less harmful.[99,110] This includes detoxifying, neutralizing or incinerating the waste so that it can be safer to transport, store or be disposed of into air, water or land in a safe way. Landfill sites are usually used to reduce, contain or monitor the waste. Of course this merely transforms the waste from one form into another. Treatment can never, according to the Law of Conservation of Mass, destroy the waste completely.[100]

3.2 Waste Minimisation and the Waste Minimisation Programme

Waste minimisation involves the systematic reduction or elimination of waste at the source. Complete waste minimization can be regarded as elimination or zero waste. This offers many benefits to industry. These advantages have centred on achieving an increase in profits without increasing outputs. Such benefits include a reduction in the use of raw material, utility consumption, waste treatment and disposal by reducing emissions and the need for landfill. Waste minimisation also assists in the compliance with environmental regulations, in improved process performance and in gains in a competitive advantage for the company concerned.[105] However, the greatest tangible benefits are financial savings made through the reduction of costs for material purchases and for waste management.[110] Waste minimisation can be achieved through the implementation of a systematic waste minimisation programme. The waste programme consists of a number of different steps as illustrated in Figure 3.2.

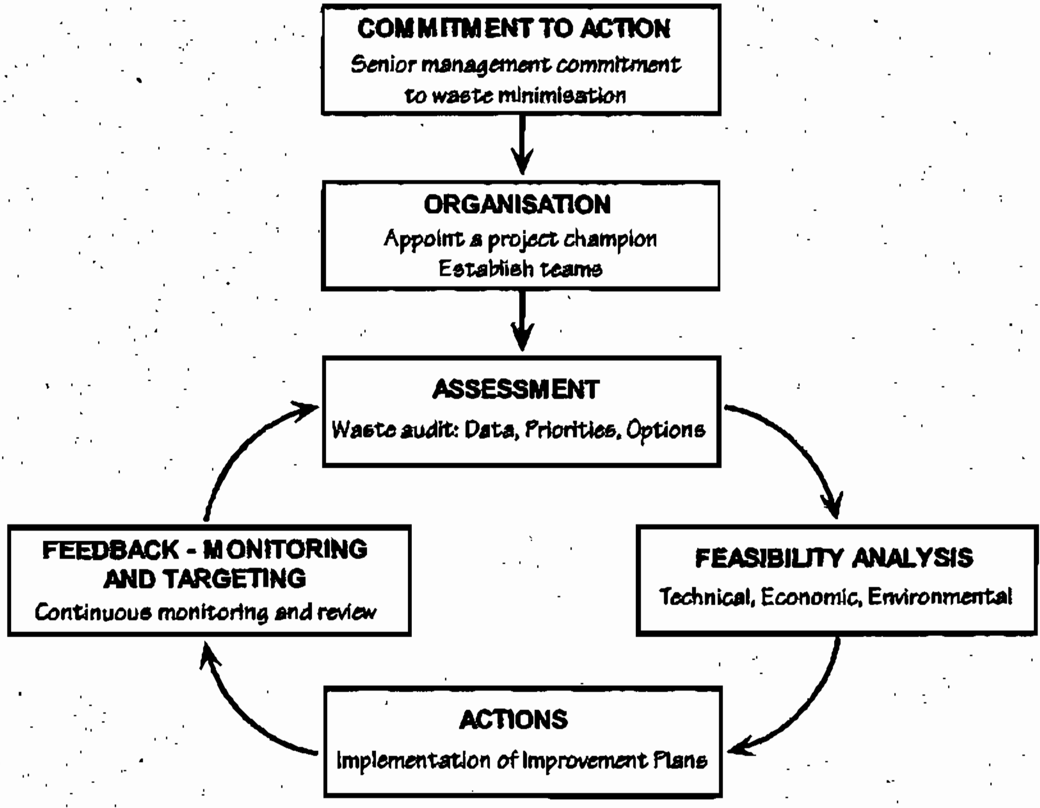


Figure 3.2 Steps in establishing and running a waste minimisation programme[98,100,104,111,119-121]

The success of a waste minimisation programme has become widely regarded as being dependent on the first and second steps which involves making all stakeholders aware of and involved in the programme.[122] This is reported extensively in the literature, but will not be discussed further here.[107,123-126]

Baseline data on each or on selected factory processes is obtained in the next step known as the waste minimisation audit.[101]This involves collecting two types of information, namely existing (historical) or new (live) data for analysis in the next step.[112,127] Existing data include water, chemical usage and costs, production (of finished goods and rejects) levels, and effluent and waste disposal charges. These are usually obtained from consulting documents such as invoices for the purchase of raw materials, for solid waste disposal, for water supply, for effluent removal. Process reports (water meter readings and chemical additions), daily production sheets and sales receipts for products are also consulted. Such data will come to a company from the chemical suppliers and service providers as a matter of course in business. It is often found that the data obtained can be insufficient[128] thus they will have to be obtained through measurement by observing the process and through informal interviews with process operators.[129] This new data must be collected over a period that best represents the process (not during shutdowns or maintenance).[122] Many 'proforma' for gathering data have been developed by many countries worldwide for entering and storing process data required for waste minimisation analysis. However very little of this data has been collected over short time intervals e.g. less than one week and/or consistently for an extended period of time. Therefore limited data has been available for more detailed analytical techniques.[101, 130, 131]

The audit data are then analysed to identify waste minimisation opportunities. Waste minimisation opportunities are the sources or areas of waste in the output stream of the process. The second assessment phase is used to identify specific waste minimisation solutions to these waste problems in the process. These are known as waste minimisation options or measures.[98] The final step involves the implementation and performance monitoring of these options.

3.3 Assessment Techniques Used in the Waste Audit Step

The assessment phase covers two main stages in the programme, namely the waste audit (preliminary or the pre-assessment) phase and the in-depth technical and economic assessment phase (feasibility analysis). The pre-assessment phase may be used to firstly establish the broad focus areas for waste minimisation in a factory or in a process and to secondly make a more detailed assessment of these particular areas. The outcomes of the first assessment are the identification of the sources of waste generated in the process and their quantification using measured or estimated values. This establishes the waste minimisation opportunities for which waste minimization options must be generated.

These waste minimisation options or measures are then ranked in order of preference with which they will be selected for a feasibility assessment. The various means for ranking options are discussed in Section 3.5. In this review, one pre-assessment technique (scoping audit) and three more detailed assessment techniques (mass balancing; true cost of waste analysis and monitoring and targeting) are describe with reference to the metal finishing industry.[134-136]

The first step in the analysis of the data collected during the waste audits is the construction of process flow diagrams (see Figure 3.3). These diagrams are used to identify all the materials that flow into and out of the process boundary.[122] Process flow diagrams provide a good way to understand and summarize a process because they indicate the flow of all input, output and recycle streams involved in a process.[137] Process flow diagrams also serve as the starting point for performing the assessment techniques described in Sections 3.3.1, 3.3.2, 3.3.3 and 3.3.4.

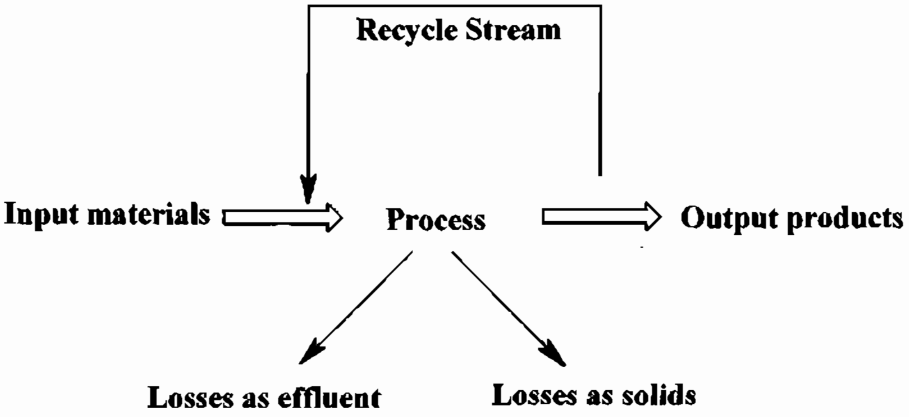


Figure 3.3 A generalized process model[102,127,137]

3.3.1 Scoping Audit

The aim of a scoping audit is to estimate the financial savings that can be obtained through waste minimisation. It involves collecting data on annual costs of materials (raw materials, cleaning agents, packaging), of utilities (electricity, heat, water) and of waste produced (effluent, solid waste). The scope of the savings that can be made in each of these areas is then assessed. Thus the areas that will give the greatest financial savings can be easily identified. The first step of a scoping audit is to determine the amounts and costs of materials, utilities and wastes at each step in the process. This information is filled into a 'waste minimisation cost assessment table' (see Table 3.2). Each resource or service has a 'scope to save' minimum or maximum percentage allocated to it. These percentages were developed by the UK Environment Agency[112] for industries in the UK, and thus may not be completely accurate for South Africa. A 'scope (min)' refers to the minimum savings that can be made through waste minimisation while the 'scope (max)' indicates the maximum savings that can be made. These minimum and maximum values are obtained by multiplying the cost of each input or output stream by its respective 'scope to save' percentage. The 'scope to save' values are ranked in order to identify the area in which the largest savings can be achieved. This allows the industry to focus its waste minimisation efforts on these streams.

Table 3.2 Waste minimization cost assessment table for a scoping audit[112]

Resources & Services	Quantity	Units	Cost/Year	Priority (1=Highest)	Scope to Save %	Scope (min)	Scope (max)
Materials:							
Raw Materials					1-5		
Cleaning Agents					5-20		
Packaging					10-90		
Utilities:							
Electricity					5-20		
Heat					10-30		
Water					20-80		
Waste:							
Effluent					20-80		
Solid waste					10-50		
Total:							

3.3.2 Mass Balance

Mass balancing should ideally be carried out to confirm that the sum of the masses of all the inputs to a system is equal to the sum of all the masses of the outputs from that system. This mass balancing is in accordance with the Law of Conservation of Mass[138], but it relies on having a complete set of quantitative data on everything that goes into and comes out of the process. It is evident from published literature that this is rarely possible. More often than not the 'mass in' does not equate to the 'mass out'. Thus, mass balancing is more often used as a means to calculate for the process missing data that have not been (but the means are there to do so) or cannot be easily measured.[99,122,139] For example it can be used where the exact composition of a fugitive emission (output stream) is unknown and cannot be otherwise quantified.[110]

The literature shows that mass balance can be carried out at a number of different levels. This is based on how the system, generally single or multiple industrial processes, is defined and on the availability of suitably detailed data for mass balancing. The different systems can be defined in terms of the boundaries (size) and the process characteristics (for example open or closed, steady or non-steady state, batch or continuous). A system is defined as being opened or closed according to whether or not the masses cross the system boundary, during the period of time covered by the mass balance analysis.[140] A steady state system is one in which all the variables in a process such as temperature, volume or flow rates effectively do not change with time [140].A continuous process is one in which the inputs and outputs flow continuously throughout the duration of the analysis. A typical example of a continuous process found in the metal finishing industry is the flowing rinse system. This will be discussed later. A batch process can be defined as a process in which the raw materials are added to a reaction vessel (charging) at the beginning of the process, the process or reaction is allowed to run and the contents are removed sometime later. No mass crosses the system's boundary between the time the raw material is charged and the time the product is removed.[140] In metal finishing, a workpiece is moved through a number of steps making up the process. The chemicals dissolved in the process solution, through which the workpiece is moved, are used up during the surface treatment and 'dragged into' the next solution. Continual addition of chemicals (dosing) to these solutions is the preferred top-up method to restore the bath to its specified concentration. However such additions are usually carried out batchwise and manually. They take place at suitable intervals: daily, weekly or monthly as determined by process monitoring through chemical analyses.

Data of sufficient quality and quantity appropriate to the system must be obtained. In continuous processes for example flow rates, composition and operation time of the various streams must be collected. In the case of batch systems the mass or volume (and density) of additions to and outputs from the process must be obtained. The most general mass balances have been calculated based on Equation 3.1 in terms of a single material used across the whole factory process.[137]

$$\text{Inputs} = \text{Outputs} \qquad \text{Equation 3.1}$$

Large scale (macro) mass balancing typically takes the system as being the entire factory site and effectively as being closed and at steady state generally over a one-year period. The literature shows that water has been the most commonly selected single material for most balance analysis in industry.[111,141,142] Examples have been found in chemical,[120] food,[143],[144] and textile [103,123] manufacturing and the metal finishing industries, amongst others.[103,145] The incoming metered volume of water recorded by the service provider should equal the sum of all the water volumes used and lost. Water can be used industrially as a raw material, a solvent in waste treatment, in heat exchangers and cooling towers. It is lost from the process through evaporation, spillage, leaks, effluent discharge and in finished products. The water inputs maybe mains, borehole or on site purified or recycled water.[119,146] However, the literature shows that more studies have focused on characterizing the output waste streams only.[141,145,147-149] This is especially true in the case of inert solid waste, commonly referred to as municipal waste. In South Africa this is also termed refuse and low hazard waste. Examples of this are found in the construction[132], recreational[147] and metal finishing[136,150] industries Such studies seldom provide enough information on inputs in order to devise a mass balance.

The results from this (large) scale mass balancing can be used to indicate areas where waste is generated and where financial savings may be made.[146] A single process, or step(s) in a process, may be selected for micro-mass balance analysis because a deeper understanding of the source of, migration of and sink for waste within the process is desired. Such detailed and focused micro-mass balances have been used to prioritize waste streams within a process for waste minimisation, to provide baseline data for feasibility analyses of waste minimisation options and to set up targets against which to monitor the performance of these waste minimisation options once implemented. Despite these benefits, very few mass balances on individual processes have been reported in the literature. A lack of suitable data[112] has been identified as the main reason for this. Companies seldom gather such information as new data or have them available as existing data.

An appropriate mass balance equation applicable in this case would be Equation 3.2. The mass balance would be carried out over an appropriate operating period or cycle of the process where useful measurements and data could be obtained.

$$\text{Input} + \text{Generation} = \text{Output} + \text{Consumption} + \text{Accumulation} \qquad \text{Equation 3.2}$$

Input = input over boundary
Generation = generated within the system boundary
Output = outputted across boundary
Consumption = consumed within the system boundary
Accumulation = accumulated within the system[137]

If the process were operated under steady state conditions there would be no build up of any material in the system.[140] As already stated, this forms the basis for a factory wide mass balance. In many industrial processes, however, a change in composition of the system would result as a new product is formed. In a continuous process the associated mass increase would continually leave the system in the output stream and so maintain a steady state.[137] In a batch process all raw materials go into the process at the same time and the products and unreacted raw materials are withdrawn at a later stage. This means that all the inputs into the system at the start of the process must be accounted for in the products, waste and unreacted raw materials. In both cases the accumulation term would go to zero. This would also be true for a system where there is no reacting species and no product formation for example in a unit operation. In the non-steady state situation of say a batch reactor or a continuous process where the rate of the product formation is not matched by its withdrawal from the system, the accumulation term would have a finite value. The latter is found in many uncontrolled or non-perfect rinsing operations used in the metal finishing industry.[141] In rinsing there are two types of systems that are used in industry, single tank flow rinsing and multiple tank flow rinsing. Both these systems can use mass balances to determine contamination caused by drag-in and the effectiveness of the rinse. For rinsing to be effective, the amount of contaminant dragged in must equal the amount dragged out to prevent a build up of chemicals in the rinse. This equilibrium is expressed as 'mass in' equals the mass going out (see Equation 3.3) and is a typical example of a general mass balance for a single tank flowing rinse.

$$D \times Cd = F \times Cr \qquad \text{Equation 3.3}$$

D = drag-in Volume to the rinse tank
Cd = concentration in process tank
F = flow through the rinse tank
Cr = concentration in rinse tank

For this system it was assumed that there is complete dispersion of the drag-in in the rinse tank and that this occurs quickly. By measuring or assuming any of the three terms, the fourth term can be determined. Once all four terms are known the effectivity (E) of the rinse tank can be determined using Equation 3.4.

$$E = F \times Cr / (D \times Cd) \qquad \text{Equation 3.4}$$

In the metal finishing industry[150] for example static and flowing rinses are used to wash the cleaning, phosphating, plating and passivating solutions from the surface of the workpieces after the respective treatments. The two main types of flowing rinse described in the literature, namely parallel or individual-feed rinsing and cascade rinsing have been discussed in Section 2.2.5. Mass balance forms the basis on which the rinsing equations were developed and used to estimate flow rate settings for optimal water usage and pollutant concentration.[111,142,151]

3.3.3 Monitoring and Targeting

Monitoring and targeting is a technique which starts with monitoring the consumption of raw materials and utilities by a process and then comparing this data to a measure activity, like production. These data are collected over a number of different monitoring periods of the same duration.[152] Records of data inputs to and outputs from a process are typically kept on a temporal basis. For example, utility bills, which give the volume and cost of the water usage for the factory, are received monthly by the company.[153] The bills also quote the tariffs charged by the City Engineer's department on the collection and disposal of refuse bins on site.[153] Such data can be used to construct a 'trend graph'. Trend analysis starts by measuring the amount of an input used over a number of time periods of equal length. A time interval of a week has been successfully used for this in the electricity industry.[154] In this case the variables measured were energy and time. It shows at what times unusual consumption events for example, seasonal variations, happen. A disadvantage of trend graphs is that they do not show any dependence on production levels, only on time. Monitoring and targeting, however, seeks to establish a relation between a consumption variable and a production variable which gives rise to such events. Such a series of values for two parameters are often presented as points on a graph for comparison. The resulting scatter graphs (see Figure 3.4) will therefore show a set of points, pairing two data variables, and will shows the process inputs such as raw materials, water or chemicals as a function of the outputs. The data situated on both axes must be collected over the same period of time. Once the data has been plotted, a regression line[112] is added, which represents the average consumption for a given level of production.

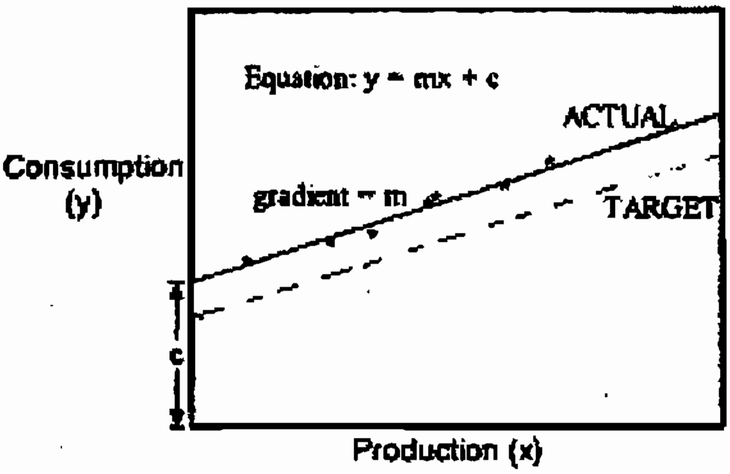


Figure 3.4 An example of an XY scatter graph of consumption versus production[89,155]

The regression line is often used to highlight several features of the process. Firstly, the y-intercept gives the baseload[104] of the process, which is the amount of material consumed at zero production. The slope or gradient indicates the process efficiency[104] of the plant: thus the smaller the slope, the higher the efficiency. Finally, the spread of the points on either side of the line gives a measure of the level of control over the process.[105,156] In this case a plot of the amount of powder used as function of product output, will be plotted, to evaluate the powder consumption. Determining the reasons for poor efficiency, process control and a high baseload enables waste minimisation opportunities to be identified. An ideal graph should have a small slope, an intercept close to zero and the data points should lie as close as possible to the regression line. At this point targeting comes into play. The regression line can be used to set a realistic target, which is the desired consumption of the resource related to production. Once drawn, the target can be set below the actual consumption if reduced consumption is required. The validity and practicality of this target should be verified using a mass balance. This type of analysis identifies the causes of the fluctuations and thus the potential sources of waste. These graphs allow various time periods to be compared. They also show variations in performance. A target level can be included on a trend graph (see Figure 3.5).

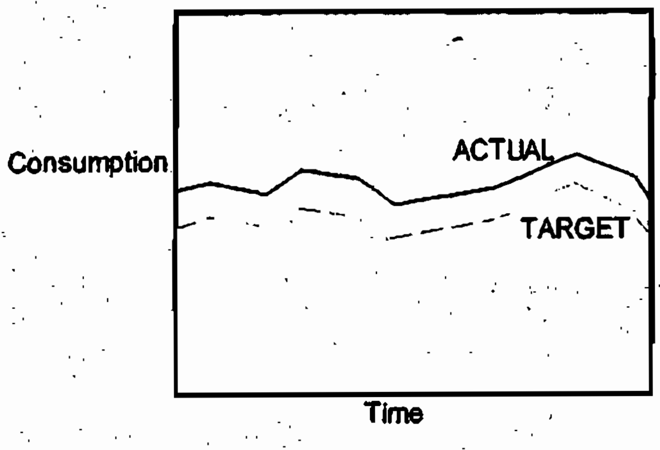


Figure 3.5 An example of a trend graph of consumption versus time[104,155]

Monitoring the amount of water consumed is essential for any company that employs a wet pre-treatment step. A survey was carried out by Envirowise, previously called the Environmental Technology Best Practice Programme, to collect empirical data from metal finishers in the UK as part of one of the few monitoring and targeting exercises to be reported in the literature. This survey can be related to production data using the Water and Paint Economy Diagrams shown in Figures 3.7, 3.8 and 3.9. These diagrams allow companies to establish and manage their water usage more effectively.[157] A line was plotted through the graphed data to represent the average water consumption in relation to the surface area and mass of workpieces processed. This line served as a baseline measure of performance and was referred to as a key performance indicator.[104] Two 'target' lines were drawn on either side of this line, one above and one below. These lines demarcated areas on the graphs where the worst and best performances in water usage were achieved, respectively. In order to use these diagrams a company first has to measure two parameters, namely annual water usage and the number of workpieces processed during the same time period in units of m^2 and tonnes.[157] The values obtained for the above measurements can then be plotted as on Figure 3.7 to establish which of the four performance areas they fall into with respect to their water usage.

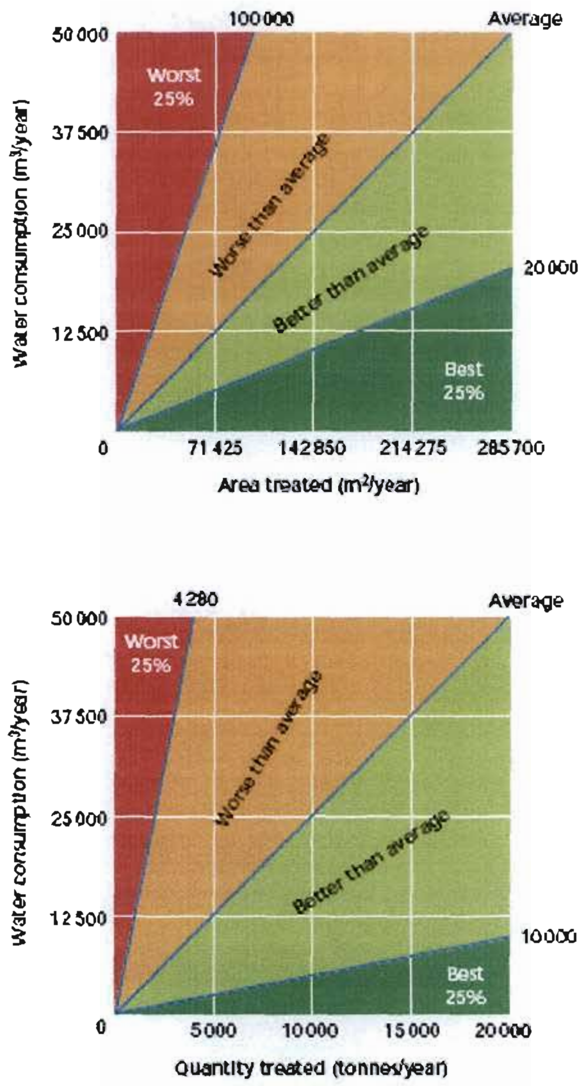
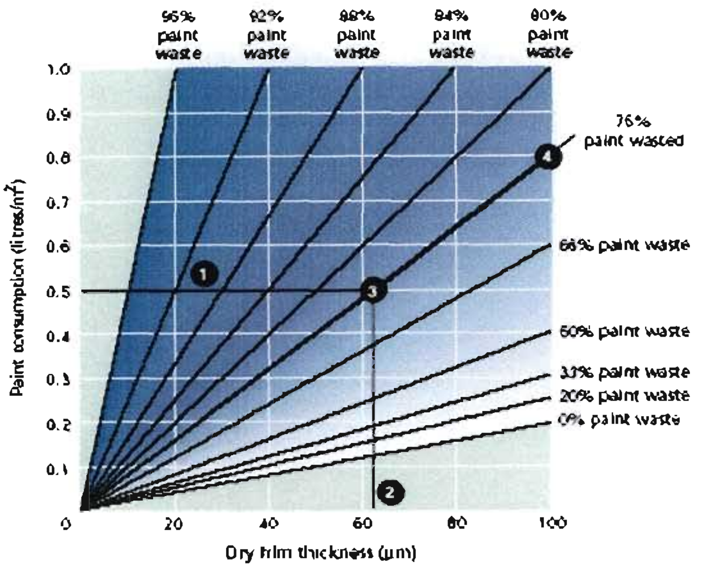


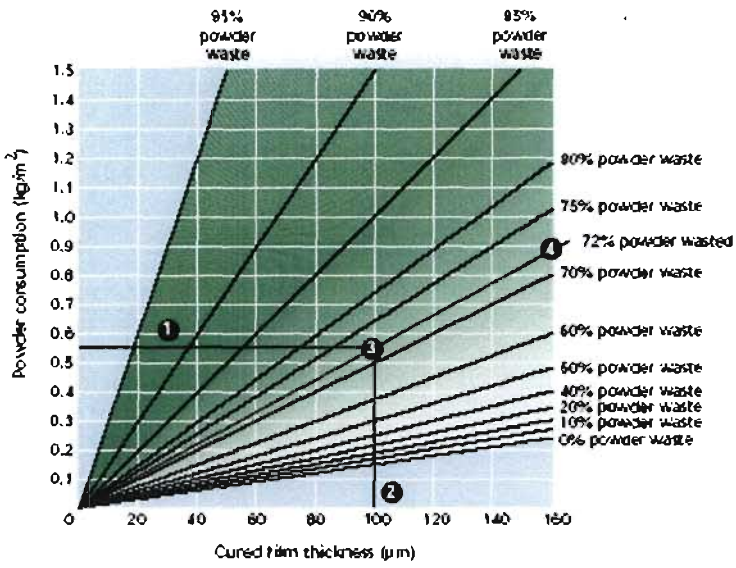
Figure 3.7 Water economy diagrams[157]

A similar approach was used to evaluate how effectively companies were coating their workpieces. The amount of paint and powder consumed in the industry was plotted against thickness of the coating layer as measured after processing.[158] The less powder used to obtain the required thickness, means less powder is wasted and better performance is achieved.



1 Mark your specific paint consumption
2 Mark the coating thickness
3 Mark the intersection
4 The radial shows the amount of paint wasted

Figure 3.8 Paint waste[158]



1 Mark your specific powder consumption
2 Mark the coating thickness
3 Mark the intersection
4 The radial shows the amount of powder wasted

Figure 3.9 Powder waste[158]

Statistical Process Control (SPC) can also be thought of as a form of monitoring and targeting where one of the variables is fixed. Examples in the literature of variables which are constant include the quality of the finished product and effluent.[159] For products this can be specification criteria set by the client buying the finished product, in-house criteria set by the manufacturing company for work in progress,[159] or standards set by an independent watch dog body.[112,159]

Although there are many advantages of monitoring and targeting, these include cost savings of between 5 and 15%,[159] from reducing energy usage and input consumption and pinpointing the source of waste. The literature survey showed this method to be the least widely used waste minimisation technique in both industry and research.

3.3.4 True Cost of Waste

Waste takes up valuable space, production capacity, and represents products which have failed to reach manufacturing specifications and can be in the form of unconverted raw materials. These are termed indirect costs of waste. Direct or visible costs are made up of treatment and disposal costs.[118] These costs are typical of items or services a company would get billed for. These bills for example would include municipal effluent treatment costs and charges for the collection of refuse bins from the site.[153] When the true cost of waste is calculated for each waste stream it must include both direct and indirect costs of producing that volume of waste. Indirect or invisible costs are less obvious than direct costs as shown by Equation 3.5. Any waste produced is a bad reflection on the company and increases the short-term (for example transportation and on-site storage) and long-term (for example landfill disposal) liability costs.[122]

$$\text{Indirect Cost} = \underset{\text{raw materials}}{\text{unconverted}} + \text{rework} + \text{storage} + \underset{\text{time}}{\text{personnel}} + \underset{\text{monitoring}}{\text{process}} + \underset{\text{equipment}}{\text{health and safety}} + \underset{\text{costs}}{\text{liability}}$$

Equation 3.5

The costs of unconverted or unused raw materials, are costs that arise from material that is bought by the company, added to the process but not converted into products. It therefore ends up in the waste stream. Rework costs arise from re-processing an item which has come off the product line but failed to meet the product specification. It has to be prepared to go through the process a second time and both of these steps (preparation and processing) have costs attached to them. Personnel costs consist of operators' and management's time spent in organizing and carrying out the rework. Liability costs include management's time spent complying with regulations, handling of on-site waste and finding the best deal for disposal of wastes and purchase of insurance policies for transport for example.

Direct and indirect costs are represented by what has become known as the Iceberg Model (see Figure 3.10). It clearly illustrates the significant contribution of the invisible costs to the true cost of waste. The results of this analysis can be used to prioritize the waste streams i.e. the waste minimisation opportunities that would benefit from a more thorough assessment.

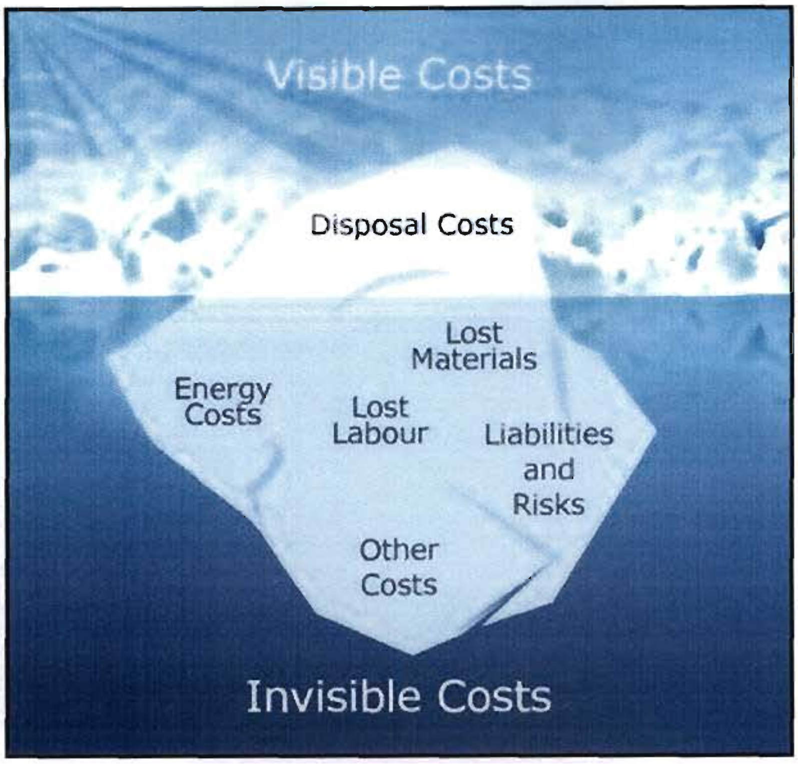


Figure 3.10 Iceberg model of the costs of waste[160]

3.4 Prioritizing Waste Minimisation Options

Several stages are required to gather all the data and information needed to be able to identify waste minimisation opportunities and to determine potential waste minimisation options. Four analytical methods which identify and quantify waste minimization opportunities have been discussed in Section 3.3. Other methods, like pinch analyses,[103,104,161,162] have also been used but these are not discussed here. Once opportunities have been identified they are put in an order of priority for which suitable options will be sought. This requires a more thorough and vigorous assessment. Areas producing most waste are given a high priority for undergoing this feasibility testing on the selected waste minimisation options. The basis for assigning a priority status to each waste minimisation opportunity has traditionally been decided on financial grounds. This means that the greater the potential financial savings that could be made if the waste was not produced, then the higher the priority which would be given to the opportunity.[120]

The true cost of waste analysis for a waste stream has been used for this purpose. However where 'no cost-low cost' waste minimisation measures have been employed to reduce the waste, they are implemented without going through a feasibility study. Such waste minimisation interventions involve making simple changes to the efficiency of the process runs without requiring much expense. Often such wastes are generated in small amounts and are cheap to eliminate. Good housekeeping[163] provides many examples of such waste minimisation options.

More recently, some of the other benefits from waste minimisation have been incorporated into the prioritizing of opportunities (see Table 3.3). One example is the reduction of the environmental impact of the waste. Further, some of these methods have been designed to identify waste minimisation options (see Table 3.3). Some are mathematically based and involve assigning values to weighted variables in an equation or algorithm to calculate the priority value. These are often solved using computer programmes[113]. The opportunities have been rated using variables entered in Table 3.3.

Table 3.3 Variables used in ranking waste minimisation opportunities and in assessing the feasibility of waste minimisation options[98,99,101,164,,165,166]

Opportunities	Options
Cost and amount of disposable waste	Waste management practice (position in waste management hierarchy)
Cost and amount of fugitive waste	Implementation ease
Hazardous nature of waste	Cost and payback period
Future liability of waste e.g. at disposal site	Quality of technical information supporting the option
Current liability of waste e.g. during transportation or during on–site storage	
Personal health and safety risks of waste	

3.5 Feasibility Analysis

This analysis is an in-depth assessment of waste prevention measures which represent a significant cost to the plant. In this evaluation, the impractical options would have already been screened out. The feasibility analysis means, therefore one must cost the selected options and determine if these are technically and economically feasible.

3.5.1 Technical Evaluation

The technical evaluation determines whether a proposed waste minimisation option will work in a specific situation.[98,99] The factors considered when determining the technical feasibility of an option have been categorized into two main groups of factors. These are termed process related or company related factors as shown in Table 3.4 below.

Table 3.4 Factors used in determining an option's technical feasibility

Process Related Factors[110]	**Company Related Factors**[98,99,110]
Maintenance of product quality	Ensuring pollution prevention
Availability and suitability of existing equipment	Making sure no additional labour costs are incurred
Ease of implementation e.g. amount of downtime required to implement changes	Employee training requirements for new procedures
Utility installation requirements	Treatment or disposal costs
Provision of services by the vendor	Time to implement changes
	New equipment and materials requirements

3.5.2 Economic Evaluation

This evaluation starts once the waste prevention project has been deemed to be technically feasible. Information such as start-up expenditure and payback period is needed to determine the economic feasibility of an option. A project is deemed to be economically feasible if it yields a cost savings or if there are no initial costs involved. [41] A common measure used in evaluating economic feasibility is payback period. The payback period is the amount of time it will take to recover the initial cash investment in implementing a particular option.[99] This is given by Equation 3.6.

$$\text{Payback period} = \frac{(\text{initial investment} \times \text{capital}) + \text{startup costs} + \text{other costs}}{\text{average annual savings} + \text{average annual depreciation}}$$

Equation 3.6

3.6 Waste Minimisation Opportunities and Options in the Powder Coating Industry

A great number of waste minimisation opportunities have been recognized in the metal finishing industry. This has led to many options being devised and implemented in order to reduce the volume of water used and of effluent wasted, the amount of process and waste treatment chemicals used and the amount of solid waste stored and/or sent offsite for disposal. These have been widely published in the literature for electroplating and to a lesser extent for powder coating. The literature has been surveyed and the important waste minimisation options are presented here. Points 1 to 4 discuss the waste minimisation options found for the wet process while point 5 looks at the waste minimisation options applicable to the dry process.

1) Chemicals lost in the pretreatment process, due to drag-out and production, result in the chemical contamination of proceeding baths and depletion of the process solutions. This means that the process solutions need to be replenished regularly with raw materials while rinse tanks need to be re-charged with clean fresh water. Drag-out can be reduced in the following ways:
    - lowering the viscosity of the process solution by maximizing the bath operating temperatures and minimising the chemical (raw material) content of the solution
    - using wetting agents in the bath to reduce the surface tension of the solution and increase the flow rate of the drag-out on the surface of the workpiece
    - placing drainage boards between process and rinse tanks so that drag-out can be re-routed into the process tank from which it has been drawn
    - using drag-out (static rinse) tanks after process baths to capture drag-out and prevent it entering subsequent process solutions

- extending the drip time that the workpiece is over the solution (after its withdrawl) in order to give maximum drainage of drag-out back into the process solution. This can be achieved by withdrawing the workpiece slowly from the immersion tank or by slowing down the speed of the workpiece as it moves through a spray system
- using air knives or spray rinses above process tanks to 'power' rinse any excess process solution off the workpiece surface and back into the process solution
- improving the position of the workpiece on the conveyor system i.e securing it at an angle or adding drainage holes, to allow the process solution to flow more easily off the workpiece surface.[77,167,168] However, the latter is rarely used because the workpiece may not usually be approved of by the client.

2) Process solutions in the metal finishing industry can last for years if correctly managed. The life span of process solutions can be extended by proper maintenance treatment and monitoring. Measurements of parameters, such as pH, conductivity and chemical composition, are used to determine the minimum amount of chemical that needs to be added to the bath in order to top it back up to the specified concentration level. This ensures that raw materials are not overused and therefore wasted.[77]

3) The life span of a process solution is shortened as a result of sludge build-up in the tank. Sludge also incurs high disposal costs, especially if needs to be treated prior to disposal. The volume of sludge formed can be reduced by the following methods:

- using treatment chemicals that reduce the generation of sludge such as caustic soda[167] to remove hard water ions that contribute to sludge formation
- using appropriate chemical pre-treatment systems, to coat the metal surface, which are known to be low heavy metal sludge producers. This is especially important in spray operations where sludge tends to block the spray nozzles.

- Pre-treating the mains water or using deionized water to make up the process solution in order to reduce natural contaminants which contribute to the build-up of sludge[138]
- dewatering the sludge, using a filter press or centrifuge, to reduce the water content of the sludge[169,170]
- reducing drag-out from process solutions to reduce the likelihood of chemicals precipitating out and forming sludge[167,171]
- routinely filtering and purifying process solutions to physically remove the sludge.

4) A primary waste reduction option for a wet process like the phosphating process is the reduction of water use. Water use in the surface finishing industry can be kept to a minimum by implementing a number of different practices given below:
    - using a concurrent rinse system to significantly reduce the volume of water required for immersion rinsing[77]
    - using flow restrictors on operations that employ a continuous supply of water. These are placed directly in the rinse water inlet to restrict the water flow rate in the system to an acceptable level[77,171]
    - using immersion and spray rinsing systems in combination rather than as separate operations to make a more economical use of water[157]
    - closing water off to areas of the plant which do not require water continuously so stopping water running constantly into the drain
    - treating rinse water to remove contamination and reusing it for rinsing or in other areas of the plant to clean floors and containers[172]
    - reusing used rinse to dilute process chemicals or directly for other purposes. It needs to be ensured that the quality of the rinse water is suitable, so that any impurities present do not react with the process solution[157]
    - keeping the temperature of the rinse bath low to ensure that water is not lost unnecessarily by evaporation

- installing conductivity meters to automatically control the amount of water added to the rinse tank during operation. These meters can be use to automatically control the volume of the rinse water added to the tank [157]
- using discharge from the acid rinse stream to neutralize the alkali effluent stream if both alkali and acid cleaning systems are used in the process. This has been shown to reduce the amount of clean water required by 50%.[157]
- using alternative, cheaper water supply sources, to mains water, such as borehole water. This reduces the water costs rather than the volume of water used
- checking that nozzles have not been knocked and become misdirected, where there is a large throughput of big workpieces
- checking pipes, valves, tanks and connection for damage in order to prevent water leaks
- segregating waste streams thus making it easier to obtain a level of water quality suitable for water reuse of effluent discharge[77] This can also effluent reduce the discharge volume and treatment.

5) The application of powder to the workpiece can generate solid waste. Powder loss has been described in terms of transfer efficiency. This is a measure of the actual mass of the sprayed powder which reaches the workpiece surface (see Equation 3.8).

$$\text{Transfer efficiency} = \frac{\text{Amount of powder used for coating}}{\text{The total amount of powder used}} \qquad \text{Equation 3.8}$$

High transfer efficiencies can be obtained by adopting the following practices:

- reusing the powder that does not adhere to the workpiece[173]
- selecting a suitable application method to maximise transfer efficiency. Fluidized beds have been quoted as giving a 100% transfer efficiency compared to spray guns which give 65%[105] efficiency. However, fluidized

beds are mostly suitable for large workpieces but the parts to be coated must be pre-heated.[174] The latter requires additional time, space and energy[79]

- maintaining good spray techniques. This includes factors such as speed of delivery by the gun and distance of the gun from the workpiece. Maintaining a steady gun will ensure that a uniform thickness of the coating will be obtained. Since spray losses increase with distance, the gun should be held at between 15 and 20 cm from the workpiece[173]
- selecting a suitable coating material to meet the product specification. For example powders have been found to be environmentally friendly, as they produce no VOCs in comparison to liquid finishes[64]
- capturing and reusing oversprayed powder. This is the excess powder which gets transferred to the workpiece and also becomes deposited on the spraybooth floor. This is collected by an air cleaner system (in the spray booth's local exhaust ventilation system) such as a cyclone. The excess powder deposited on the workpiece is considered to be wasted powder and has been found to result in streaks in the coating.[173] Using cyclones has been found to be the cheapest method of capturing powder. They have few moving parts, a wide choice of materials for construction, can be easily cleaned[174] and have low maintenance costs.[175] In addition, they have recovery efficiencies of between 85 and 95%.

CHAPTER 4

COMPANY PROCESS AND PROFILE

Southlands Manufacturing Ltd (Southlands) came was formed in 1948 and has operated in KwaZulu Natal since then. It was originally known as Braziers and later as Dexian. The company fabricates and powder coats items used for constructing industrial and commercial storage systems, shelving and mezzanine flooring. The mezzanine flooring is an intermediate floor constructed in a space between the ceiling and adjacent floor in a building.[176] The shelving and storage systems are intended for storage of large or bulk goods in factories and stores. The surface of the items are finished with a phosphating treatment followed by a plastic coating. The latter is carried out by means of applying and curing a powder coat. Southlands Manufacturing Ltd sells its products both locally and internationally. It supplies local food stores, it provides advice on racking systems and supplies its products to local food stores, vehicle factories, medical supply companies, and chemical companies such as Nestlè, Marathon Logistics, E21 Racking, Toyota, Med Tech and Sasol. The company also supplies retail stores such as Pep, Foshini and Apparel Industries. Its overseas clients include companies situated in the Seychelles, Madagascar and Kenya, and include companies such as ABI and Coke.

Details of the company structure and operations are discussed in Section 4.1. The range of products manufactured and powder coated by the company are given in Section 4.2. Section 4.3 presents an overview of the complete manufacturing process. In Section 4.4 the plant, chemicals, work practices and operations involved in the phosphating and powder coating processes are discussed in more depth.

4.1 Company Description

The company is made up of six divisions namely Administration, the Roll Mill Department, the Welding Shop, the Press Department, the Paint Line, and Stores. Stores is further divided into a section receiving the raw materials from supply houses, i.e. inputs which are not provided by utility companies, and “dispatch” of the finished goods to the customer. Administration is divided into planning, purchasing and wages.

There are approximately 25 people working on the factory floor, 11 working in administration and 1 member of staff involved in cleaning duties. The factory operates for 236 days of the year. No production is carried out during the two-week maintenance shutdown (23rd of December to the 10th of January) and the fourteen public holidays during the year. Employees work a 40-hour week. Working hours are from 7:00 to 16:00, from Monday to Thursday and from 07:00 to 12:00 on Fridays. There is one 15 minute tea break between 10:00 and 10:15 and one 30 minute lunch break between 13:00 and 13:30 Figure 4.1 gives a plan of the factory floor showing the location of all the departments.

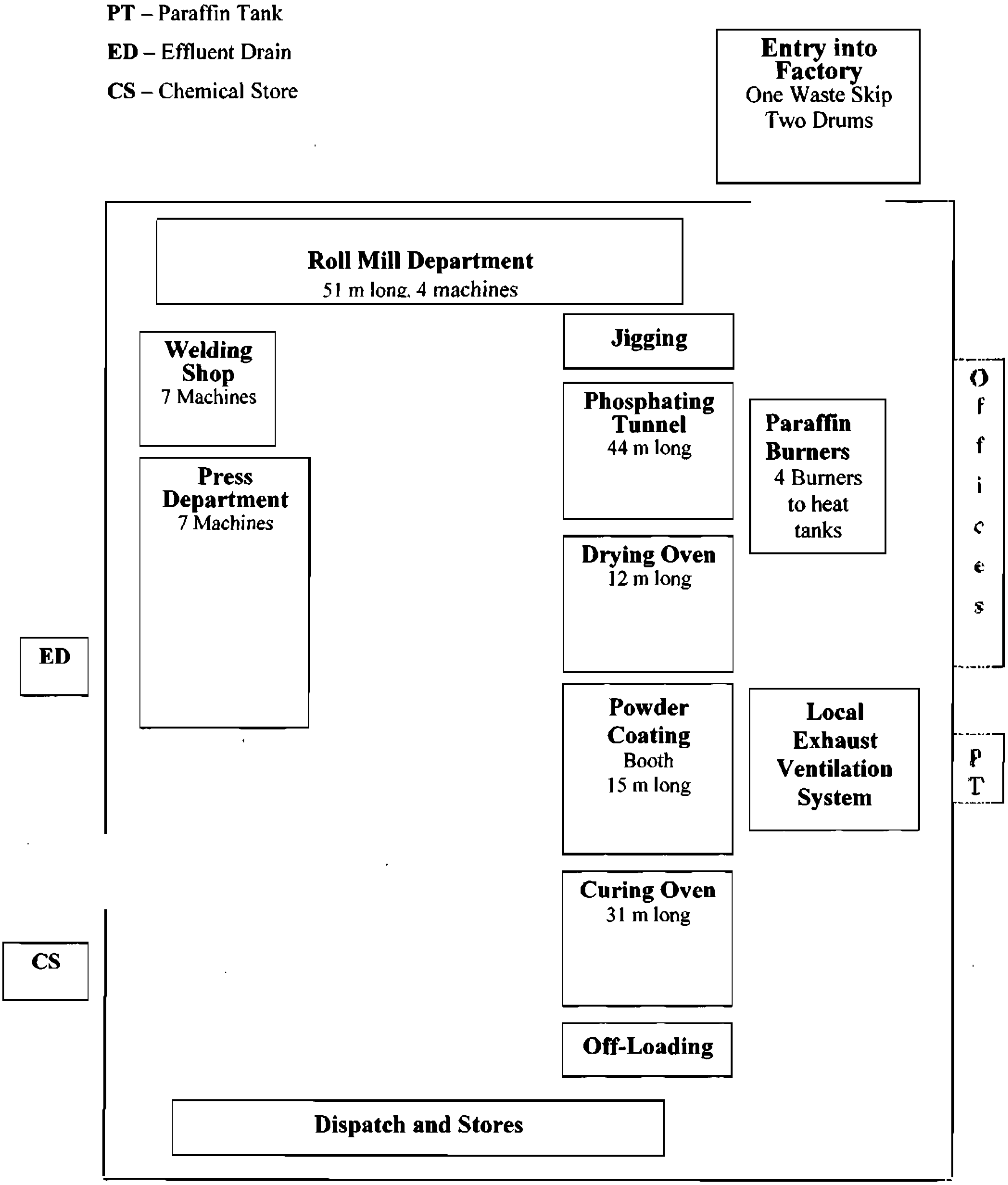


Figure 4.1 Factory floor plan

The Roll Mill Department occupies an area of 1275 m^2 and is situated at the top end of the factory (see Figure 4.2). It houses 4 milling machines. A steel strip is uncoiled and fed into one of four machines where it is cut to size and formed into a profile (see Figure 4.3). One machine is used only to bend and the other three are used to bend and punch the steel parts. The roll mills are referred to as 'roll formers' and are listed below together with the workpieces they produce:

- roll former 1 is used to make beams
- roll former 2 is used to make standard uprights
- roll former 3 is used to make angled uprights and
- roll former 4 is used to make bracings (see Figure 4.3).

Figure 4.2 The roll mill department

Figure 4.3 A milling machine for the manufacture of bracings

The Press Department (see Figure 4.4) is situated opposite the Phosphating Tunnel, which is on the Paint Line. This line is used to bend and punch holes in the flat pieces of steel used to make shelving and flooring. These steel sheets are commonly referred to as 'blanks' in the trade. The Press Line contains five bending machines and seven press machines. The five bending machines consist of one 4 m (12-foot), one 2 m (8-foot), one 2 m (6-foot) and two 1 m (4-foot) machines. These machines for bending are referred to by the length of the bending blades on the machine in empirical units. The seven press machines consist of one 75 000 kg, two 90 000 kg, one 125 000 kg, one 60 000 kg, one 30 000 kg and one 15 000 kg machine. The press machines are categorized according to the pressure they exert on the steel. The pressing is carried out by a blade called a 'die'.

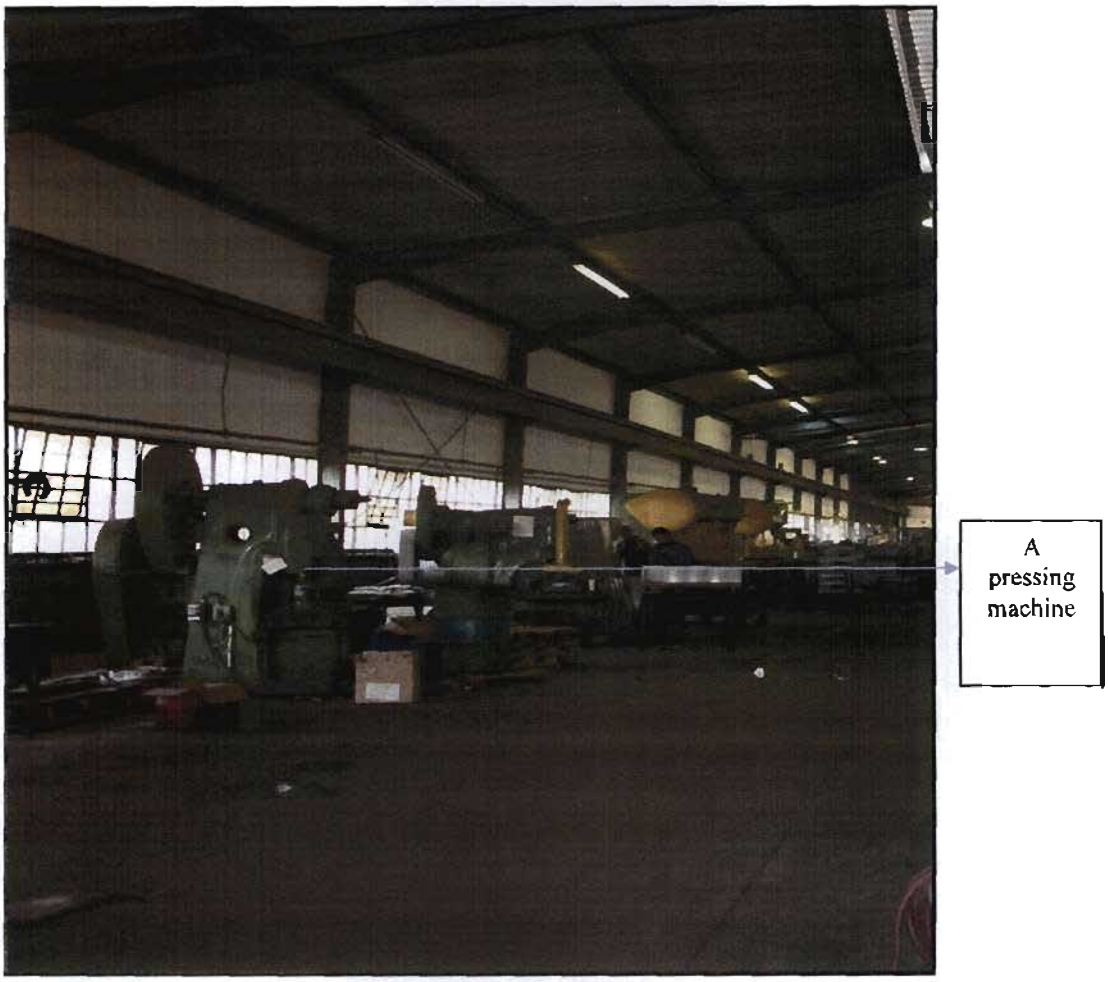


Figure 4.4 Press department, housing five press machines

The Welding Shop is situated between the roll mill Department and the press department. There are seven welding machines namely, six carbon dioxide machines and one arc-welding machine. Certain workpieces are composite pieces made from two or more individual structural elements joined together. These include closed beams, frame-to-wall ties, back-to-back ties and base feet. These are assembled in the Welding Shop from the individual workpieces.

The Paint Line situated opposite the press line, consists of a phosphating tunnel, ovens and a Powder Coating Booth. The Phosphating Tunnel sits above four tanks which contain the process and rinse solutions with which the workpieces are sprayed. Tank 1 (T_1) and Tank 2 (T_2) are process solution tanks which hold the phosphating solution.

Tank 3 (T_3) and Tank 4 (T_4) are rinse tanks which contain municipal water and are used to rinse off excess process solution from the surface of the workpieces. The preparation of these tank solutions will be discussed in Section 4.4.

4.2 Product Description

Workpieces are made from primary and secondary structural elements manufactured by the company. The workpieces are used to make various products which are generically referred to as racking systems. An industrial racking system can be thought of as being made up of three basic structural elements: uprights, beams and shelves.

Uprights are vertical poles which are shaped from strip steel into the following profiles: two-sided (angled uprights) or three-sided (standard uprights). Small (~1 cm diameter) holes are punched at regular intervals along the edges of the long side (13 holes/m). Both types of uprights, angled and standard, are manufactured in two different thicknesses: regular or medium (1.9 mm) and heavy duty (3.55 mm). The steel strip used to make angled uprights is bent once in the center creating a corner with two faces at right angles to each other (see Figure 4.5). The angled uprights have a row of holes punched along both sides of the upright. Standard uprights (see Figure 4.6) have been bent into a three-sided profile which contains an opening leading into an internal channel. The standard uprights have two rows of holes punched on the middle face of the upright, as well as a single row of holes in both of the side faces. The holes punched into the uprights can be one of three shapes: circles, coffin slots and wing slots. These holes allow horizontal beams to be secured between two uprights via bolts or hooks.

Figure 4.5 Racking unit made from angled uprights

Figure 4.6 Racking system made from standard uprights, horizontal and diagonal bracings

A beam is a bar which is transversely fitted in between two uprights that are placed a set distance apart. Beams support large items which rest directly on them or are loaded with pallets which contain stock items. Shelves, on the other hand, are permanently attached to the beams and items to be stored are placed directly on the shelves. Two types of beams are manufactured namely, open beams and closed beams. They are manufactured in different widths ranging from 60 mm to 146 mm. Pallets are platforms onto which goods or large items can be stacked and are designed so they can easily be transported by a forklift (see Figure 4.7). Shelving is used in conjunction with racking that is made from angled uprights. Shelving (see Figure 4.7) is referred to as 'deck panelling' where standard uprights are used to make the racking. Shelving is a fixed unit and cannot be removed from the rack system like the pallets can.

Figure 4.7 Racking system with pallets and shelves

The primary structures made from the three basic racking elements often have attachments fitted to them. These are designed to stabilize the racking system and will be referred to as secondary elements. The most common ones are listed and discussed below:

- bracings
- feet
- back-to-wall ties
- back-to-back ties
- cladding Sheets
- corner Plates
- hooks.

The steel frames, mentioned earlier, are braced with horizontal or diagonal configured straps to increase the load bearing capacity of the frame. Bracings are inserted between two uprights and fit into the internal channel of the standard uprights and thus add support to the structure. There are two types of bracings manufactured: diagonal and horizontal. These two names refer to the orientation of the bracing between the uprights (see Figure 4.6). The bottom of the uprights are often fitted with a foot to help steady the racking system and spread the load at the base. Some structures have fixtures called back-to-wall ties: which allow them to be bolted to the wall. Some structures have back-to-back ties, which are used to secure individual racking systems to one another. Panels, called cladding sheets are made and fitted across the bottom of the racking frame to protect it from damage caused when, for example, forklifts bump into the racks. Corner plates are small inserts between the shelf unit and the upright it is attached to, and these plates enable the shelf to be attached to the upright. Hooks are small units that are used to attach beams to the uprights without bolting and are shown in Figure 4.8.

Figure 4.8 Extended racking system with hooks

Industrial racking systems are made from many uprights that are placed a specific distance apart and are joined together by (horizontal) beams. The beams are attached to the uprights by means of bolts or hooks. The main racking systems manufactured by the company include Mobile, Live Storage, Drive-in and Cantilever. The Mobile Racking systems are made from racking frames that are not in a fixed position. The bottom of the uprights are fitted with wheels which sit in a channel, so that the racking can be easily moved into and out of position, thus closing and opening the aisles between adjacent frames. This type of racking is used mainly to save space when storing items. The frames in the other racking systems are in fixed positions. The Live Storage Racking system is made from racking in which pallets sit on a moving shelf. The pallets are stacked on a roller system which allows the stored items to be automatically moved along the length of the racking. The aisles between the frames are effectively redundant here as the forklift trucks lift items from the short (braced) end of the frame rather than from along its length. The Access Drive-in Racking systems are different from that of Live Storage but similar to Mobile or Drive-in. The forklift trucks moves in between the frames to pick up loads from the length of the racking. The drive-in racking is made from uprights that are 211 m long and 3 mm thick and has a design that creates a very high-density storage for loads that cannot be stacked on top of each other.[177] Cantilever Racking systems are made from uprights and cantilever arms that are place at either a 90° (straight arms) or a 60° angle (inclined arms) to the uprights. Straight arms are used for storing stable loads such as lumber, steel, cartons and skids. Inclined arms are used for cylindrical objects or loads that tend to roll forward.[178] The uprights are present only on one side of the racking system.

4.3 The Manufacturing Process

The company is supplied with steel from a nearby supplier Discount Steel, which delivers mostly cold-rolled, plus some hot-rolled, and galvanized steel. This is supplied in coil, sheet (blanks) or strip form, to the factory. Rolling is a process of flattening metal sheets to a prescribed thickness. The steel is passed between two rollers that revolve at the same peripheral speed but in opposite directions. Cold-rolled steel is steel that is rolled at room temperature and results in a smooth surface finish.[176] The entire cold-rolling operation occurs in a bath of oil which leaves the product smooth, unoxidized and the same colour as the original steel.[179] Hot-rolled steel is rolled at a temperature higher (approximately 1000 °C) than that used in cold-rolling. The steel is again squeezed through rollers in order to reduce the thickness of the metal. The process is long and results in a thick oxidized surface.[179] Galvanized steel is steel that is coated with a thin layer of zinc to provide corrosion resistance. Sheet steel, like that used by the company is cold-rolled prior to the galvanizing stage.[180] It is delivered to the company as cold-rolled steel. The flat pieces of steel are sent to the Press Department so that holes can be punched into them. Most of the workpieces manufactured by the company have holes punched into them so that they can be built into an extended racking system.

The coating process consists of five steps namely phosphating, rinsing, drying (and heating), powder coating and curing (see Figure 4.9).

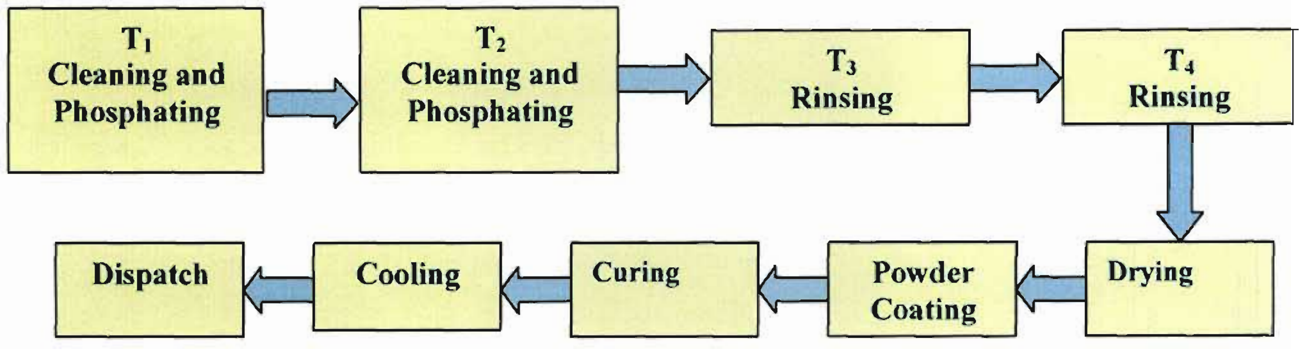


Figure 4.9 Flow diagram of the entire powder coating process

Figure 4.6 illustrates the entire process which the workpiece undergoes from the time it is loaded or 'jigged' onto the line until it is off-loaded and sent to dispatch. The workpieces are first hung by hooks on the conveyor system for transporting through the process. Depending on the size and shape of the workpieces, they are hung either vertically or horizontally (see Figure 4.10). The bigger pieces are hung horizontally and at an angle, while the smaller ones are hung vertically.

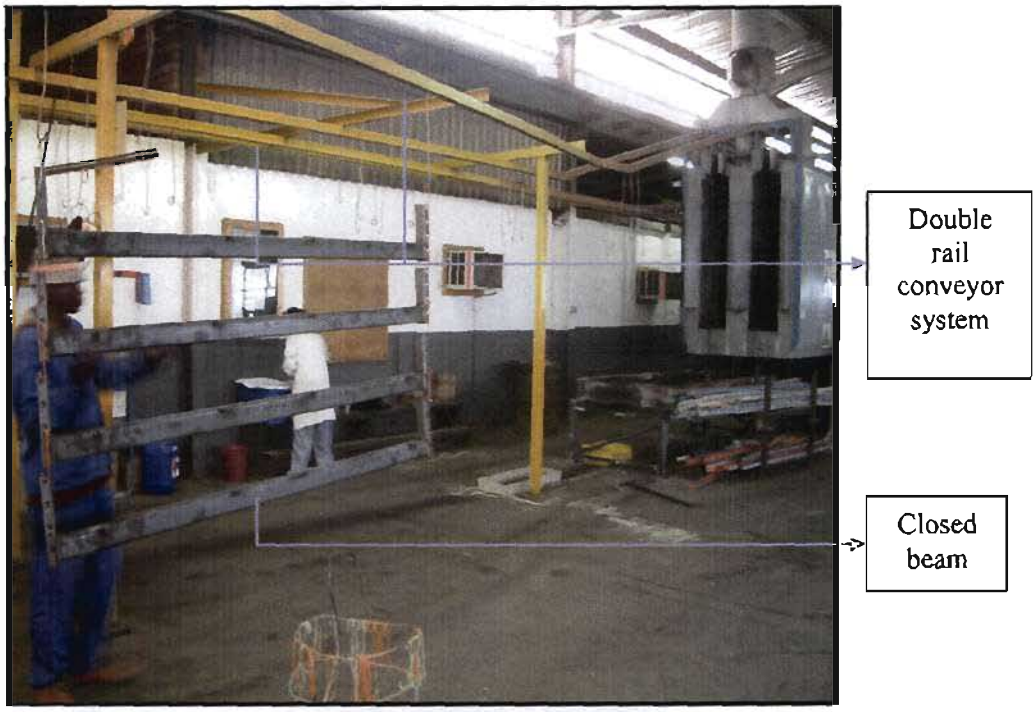


Figure 4.10 A closed beam with hooks hung horizontally onto conveyor system

A twin-conveyor belt (double rails) system runs through the spray tunnel and ends just beyond the curing oven and exits at a speed of approximately 0.0104 m/s. Workpieces are hung onto one rail while the second rail is in use when the line is busy. The workpieces are sent into a 30 m long spray tunnel first where they are phosphated. There is a spillage tray (see Figure 4.11) situated between the tunnel and oven to collect any excess solution that might have accumulated on the workpiece leaving the tunnel.

Figure 4.11 Spillage tray used to collect excess water from the workpiece

The workpieces are then oven dried and transferred by the conveyor system to the powder coating booth. After coating they are sent to the curing oven which converts the powder into a continuous film and seals it to the workpiece. The finished workpieces are then pass over a cooling fan so that they can be offloaded quickly by hand at dispatch. The final step in the process is a quality control inspection before the finished product (see Figure 4.12) is sent to the customer.

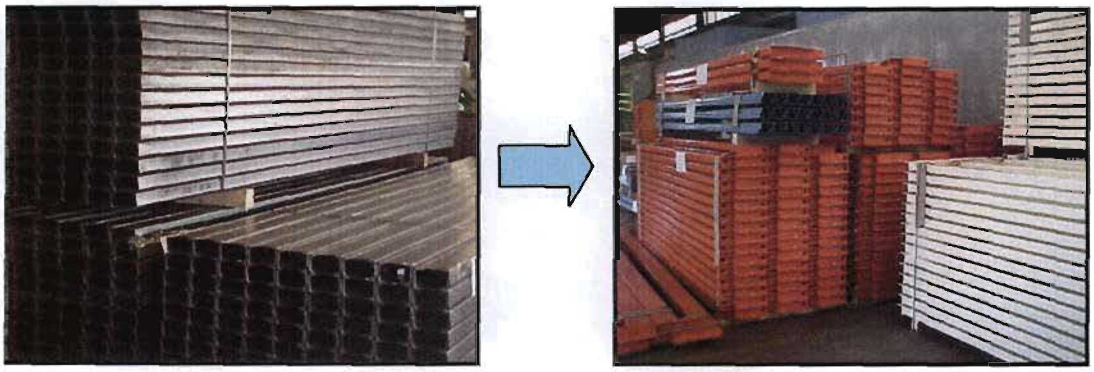


Figure 4.12 From raw materials to finished goods

4.4 The Phosphating Step

This is a wet process and requires the use of water for three purposes. Firstly, water is needed to dilute the process solution and make up the rinse solutions; secondly, to operate the heat exchangers; and thirdly to maintain the tank solution level by restoring the volume to the original working level. The incoming water passes through the only water meter on the phosphating line (see Figure 4.13) and enters the tunnel through pipes in the sides of the tanks. These tanks are situated under the phosphating tunnel and are situated 4.5 m apart from each other. The water flow through this inlet pipe can be manually controlled for filling up the tanks at solution make-up and filling the rinse water tanks. Topping up of the tank solutions is largely automated using a ball-cock system. This lets water into the tanks when the water levels become too low.

Figure 4.13 Piping system coming from the main inlet pipe

The phosphating step takes place in an enclosed spray tunnel. Process and rinse solutions are pumped up into the tunnel from the respective holding tanks. Grills have been laid in the sides of the floor of the spray tunnel. These 30 cm wide grills run along each side of the tunnel and are used to drain the sprayed solutions back into the tanks. The risers run up the sides, across the top, and down the center of the tunnel. These pipes are fitted with nozzles through which the solution is sprayed onto the workpiece surface. There is a gutter on either side of the tunnel in which the solution returns to the tank to begin the re-circulation process again. The number of risers and nozzles situated in the tunnel were counted and recorded in Table 4.1.

Table 4.1 Structure of the spray system

Tank	No. of Risers			No. of Nozzles		
	In the floor pipe	In the centre	In the side	In the floor pipe	In the centre	In the side (per riser)
1	7	8	7 (pairs) x 2	7 x 2	6(pairs) x 2 per riser	6
2	4	4	4 x 2	4 x 2	6 (pairs) x 2	6
3	8	8	8 x 2	8 (riser) x 2	6 (pairs) x 2	6
4	4	4	4 (risers) x 2	4 (risers) x 2	6 x 2 per riser	6

There are two hatches which allow personnel access into the tunnel. One hatch is situated between T_1 and T_2, while the other is situated between T_3 and T_4. The four tanks below the tunnel contain the solutions used in the phosphating step and collect the solution returning from the spraying operation. There are also two local exhaust ventilators system attached to the top of the spray tunnel. One is positioned at the start of the tunnel and one at the end. These ventilators extract the fine mists which are emitted in the tunnel during the spraying operation and transfers it to the outside of the building. There are brushes on either side of the conveyor rail. The bristles of the brushers are there to sweep back the solution escaping from the tunnel via the conveyor system back into spray tunnel. Chemcoater 755 (Chemcoater) is the commercial phosphating solution used to make up the tank solution. This chemical is supplied by the chemical supplier Chemrox Chemicals in 25 L drums. Four 25 L drums are manually emptied into T_1 and two 25 L drums are emptied into T_2 at solution make-up. The contents of T_1 and T_2 are then diluted to volumes of 3.14 m^3 and 1.71 m^3, respectively. T_3 and T_4 are filled up with clean water from the mains supply. No formal records have been kept as to when these tank solutions were disposed of and replaced. Records of the chemical additions made to top up the solutions, replacing the chemicals used and wasted in the pre-treatment process are kept by the line supervisor. The company throws away spent solution as full or partial dumps. A full dump is where the entire contents of the tank are thrown away. In a partial dump only half of the tank's contents are dumped. Only the rinse tanks are partially dumped. Process tanks are usually fully dumped twice a year. There is a drain pipe (see Figure 4.14) situated at the bottom and back of each tank. This pipe is used to empty the contents of the tanks into the main drain which in turn flows to the municipal drain.

Figure 4.14 Main pipe inlet into Tank 2

A crude sludge filter has been fitted inside each of three of the tanks. This filter sits almost vertically in the tank. There is a gap between the bottom of the filter and the base of the tank. This allows the re-circulating process solution to flow through the filter while the sludge drops out and is swept through the gap and collects against the tank wall. The purpose of this filter is to stop any sludge from entering the risers and thus from being deposited onto the workpiece and eventually blocking the nozzles. The sludge is removed manually when the process tanks are fully dumped. Half way along the tunnel, there is a control panel, which is used to operate the spray tunnel, pumps, heat exchangers and extractor fans. There are three heat exchangers which are manually cleaned with soap and water twice a year. One heat exchanger is attached to T_1, one is attached to T_3 and the other is attached to T_4. However, the process solutions were generally run at around 40 °C, the first rinse tank was generally run hot (28 to 57 °C) and the final rinse is run as a cold rinse. Figure 4.15 shows the pipes that enter and leave the heat exchanger. These pipes are approximately 80 cm long and have their ends bent up at a 60° angle. Hot water from the boiler enters the heat exchanger through the bottom and exchanges heat with the solution from the tank. Cold water then exits the heat exchanger through the top. A third pipe, attached at the front of the tank, brings water from the bottom of the tank into the heat exchanger. A fourth pipe then transfers the heated solution back into the tank. The water flowing to the heat exchangers flows through a closed loop system. This water is drained and refilled only during maintenance which takes place once a year.

Figure 4.15 Piping system through the heat exchanger

Each tank has a pressure and temperature gauge attached to it. The pressure gauges are set at 2 bars for heavy items such as uprights and beams, and at 1 bar for small items such as shelving and deck panels. The temperature gauge is set at 40 °C. Each tank has an overflow pipe connected to the main drainage pipe. It has a ball and cock system which automatically opens when the level of solution in the tank becomes too high.The overflow is directed to the drain.

The water feed to the heat exchangers is heated by paraffin from boilers. The paraffin tank is situated underground outside the building (see Figure 4.16).

Figure 4.16 Paraffin tank situated on the outside of the factory

A paraffin cleaner additive, Pyron 7 Industrial Fuel Additive, is added to the tank before the paraffin is put in. This is done because the paraffin must be lubricated in order to be pumped around the factory. This paraffin is piped from the paraffin tank into the building to supply the following seven burners:

- one burner on the drying oven
- two burners on the curing oven
- four burners for the heat exchangers.

The paraffin levels are measured manually using a steel scale (see Figure 4.16) which is calibrated in units of 100 L. The scale starts at 500 L and goes up to 14 038 L.

Once the workpiece passes through the drying oven, it is transported to the powder coating booth.

4.5 The Powder Coating Step

Powder is purchased in 20 kg boxed sacks from a firm called 'Powderlac.' Powder, which have been coloured blue and orange, are used to coat the pieces. The powder is sprayed manually using a spray gun, the Sure Coat Manual Spray Gun System by Nordson. The coating operation is illustrated in Figure 4.17.

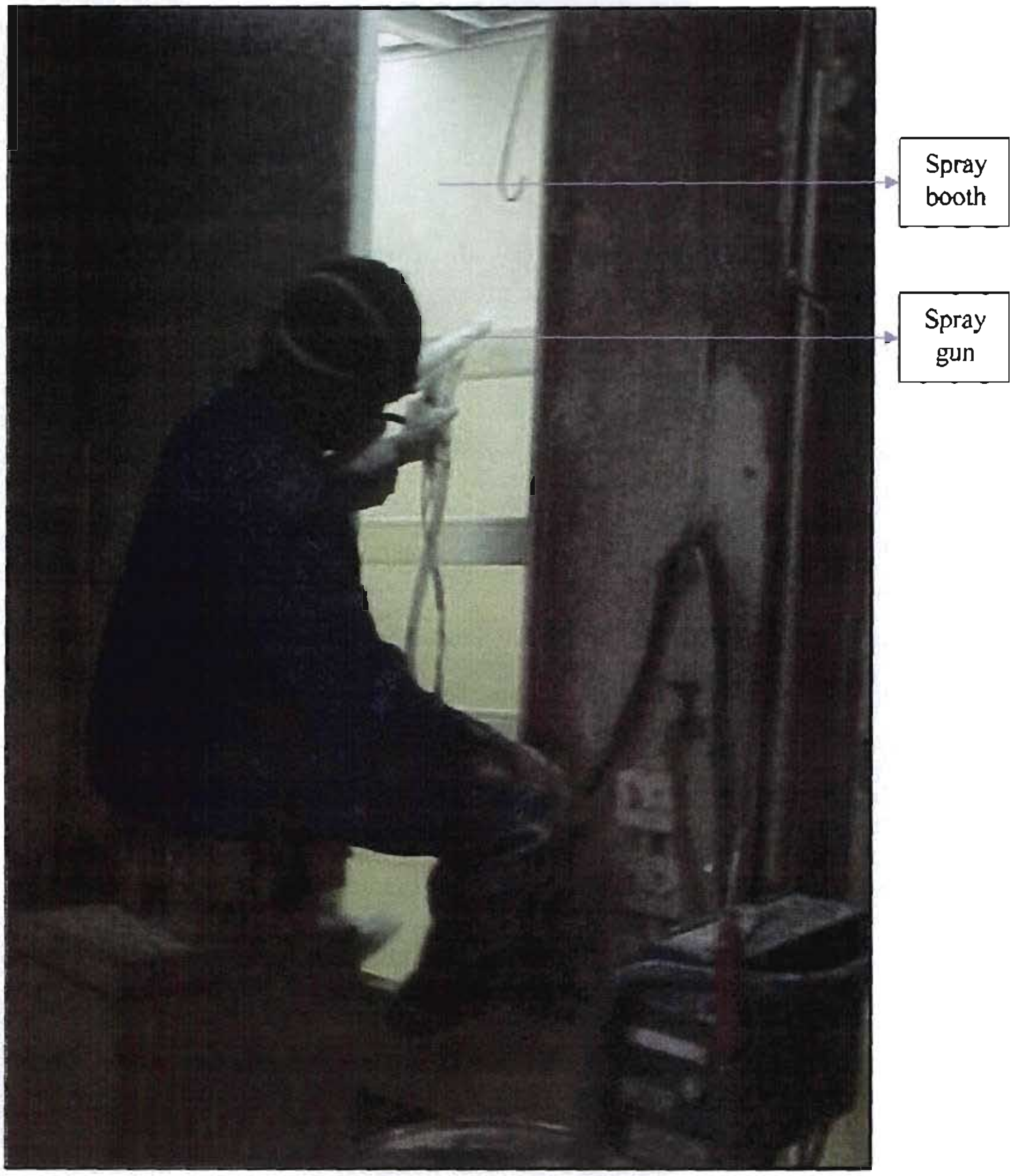


Figure 4.17 Factory worker spraying powder onto a beam

A maximum of four people are stationed in the spray booths. Two are dedicated to spraying one colour and two to another colour. In two separate booths, two individuals spraying one colour operate on opposite sides of the same booth some distance apart and not directly opposite each other. This is to ensure that they do not spray each other and to ensure that both sides of the workpiece are coated properly. There is a local exhaust ventilation system attached to each booth (see Figure 4.18).

Figure 4.18 Powder coating booth illustrating ducting

The air-borne blue powder is recovered by a bag filter unit and one cyclone, while the orange powder passes is recovered by another bag filter unit and two cyclones (see Figure 4.19). The powder first passes through bag filters then through the cyclones. The bag filters filter out the fine particles while the cyclones filter out the larger particles. The powder passing through the cyclones is collected in drums (see Figure 4.19). The powder from the bag filters, the cyclones and the powder collected from the spray booths is filtered further using an Air Vibrating Machine. This machine filters out the larger powder particles so that the fine powder can be reused. Once it is filtered, 30% of this powder is mixed with 70% virgin (unused) powder and reused in the coating process. The powder that falls onto the floor of the spray booth and the recovery booth is disposed of as waste into a skip.

Figure 4.19 Bag filters situated next to cyclones

4.6 The Curing Process

A tunnel oven is used for curing the workpieces after powder coating. The tunnel has two openings, one for entry and one for the exit of the workpiece. It operates at around 200 °C. In the curing oven a smooth coating is formed on the workpiece surface when the chemicals in the powder particles are cross-linked during polymerization. This oven is fitted with a burner and a fan in order to continually reheat and recirculate the air. The workpieces, when they exit the oven, are cooled by means of a cooling fan situated on the factory floor. Cooling helps the surface coating on the workpieces to set and allows for faster offloading of the workpieces.

4.7 Process Control

The quality of both the process and products manufactured must be constantly assessed. This is achieved by quality assurance and quality control. Quality assurance is the criteria that must be met to achieve quality. Quality control is the procedure carried out to measure the quality of a process or product and ensure that it complies with the criteria outlined in quality assurance. The company monitors its phosphating step and evaluates its product quality via quality control.

Quality control performed on the phosphating step of the powder coating process is carried out by the line manager (in-house). It is also done by the chemical supplier twice a week as part of its services. This is done by a simple titration of the tank's solution. The line manager pipette's 10.00 mL of the tank's solution, which contains phosphoric acid, using a graduated pipette. He then adds 5 drops of IND No.2 indicator (essentially phenolphthalein) and titrates the solution against 0.1 M NaOH (see Equation 4.1). The NaOH is supplied by Chemrox Chemicals in a 500 mL bottle, and lasts at least a month and a half. A 50 mL burette is used to standardize the NaOH. The volume of titre used is recorded as points on a daily control sheet. If the points recorded are below 9 then Chemcoater is added to the tank. The typical additions occur as follows:

- for points of approximately 7, ¾ of the 25 L drum is added
- for points of approximately 8, ½ of the 25 L drum is added
- for points of approximately 8.5, ¼ of the 25 L drum is added.

The above titration is performed to determine the phosphoric acid concentration in the tank's solution. The reaction of the above titration corresponds to that given in Equation 4.1 which involves the displacement of one hydrogen. The species present in solution is consistent with that shown in Figure 2.5 in Section 2.3.1.

$$H_3PO_4 + 2NaOH \rightleftharpoons Na_2HPO_4 + 2H_2O \qquad \text{Equation 4.1}$$

Quality control is also carried out on the final product, after it has been powder coated. This is an in-house function carried out using a 'Hatch and Impact Test'.[77] The Hatch test is carried using a Stanley knife to mark out squares on the product surface and then placing a piece of tape over the squares. If the squares are easily removed when the tape is pulled off, then the product is classified as being of poor quality. The Impact Test is carried out using a Ball Pin Hammer which is used to directly hammer the product. If the powder is removed upon impact then the product is deemed to be of poor quality.

CHAPTER 5

SCOPES AND AIMS

A waste audit was undertaken on the Paint Line of a local manufacturer of industrial and commercial racking systems. The Paint Line is made up of two surface treatment processes, firstly a wet pre-treatment phosphating and secondly the dry application of an organic powder coat. The company decided to change the chemicals and the process sequence for the wet phosphating process. During this study, the old phosphating system ran for one week before being replaced by the chemicals for the wet phosphating pretreatment. There are many sources of waste arising during the powder coating of workpieces from both the wet and dry process namely:

- water, chemicals and powder overuse
- wastewater, spent process solutions, sludge, airborne particulate and solid waste production
- overuse and wastage of fuel (paraffin, gas and electricity) for heating ovens and water, compressed air production, cooling of coated workpieces.

This project focused on the material flows into and out of the wet phosphating process and to a much lesser extent on the dry powder application and curing process. Energy is a major input to and concern for the powder coating industry. However it is beyond the scope of this project to consider energy as a potential waste minimisation opportunity here. There are six main objectives to this project. These are listed below:

- to collect accurate quantitative and cost data on material inputs and outputs of the Paint Line and to establish base line data for the chemistry of the new and the previous pre-treatment processes carried out on the phosphating line.

- to measure the concentration profiles of selected elements within tank solutions on the phosphating line during an operating cycle. This will help to characterise pollutants in waste streams, monitor movement of chemicals through the process and identify possible sources of contamination in the tank solutions arising from processing of workpieces.

- to establish to extent to which the concentration data can be used in waste minimisation analyses and whether the concentration results obtained above are a valuable data input to a waste audit (see objective below).

- to compare the results from the application of four waste minimisation analysis techniques on the Paint Line in order to identify and quantify waste minimisation opportunities. These techniques include the following:
    a) scoping audit – performed on the entire Paint Line i.e the wet and dry processes
    b) mass balance – performed on Phosphating Process
    c) monitoring and targeting – performed on for the wet and dry processes
    d) true cost of waste – performed on Phosphating Tunnel
    e) to compare the results obtained from each of the above analyses.

- to express the results from the waste minimisation analysis techniques together with the concentration data in terms of potential environmental and financial savings in order to prioritize waste minimisation opportunities.

- to attempt to cost and prioritize some potential waste minimisation options by considering economic indicators based on simply a financial basis i.e capital and operating costs, and also on a more sophisticated basis using integrated and weighted approaches.

CHAPTER 6

MONITORING METHODOLOGY

The purpose of the waste minimisation audit was to collect and analyse data on the composition, flow rate and cost of the process and waste streams. This was carried out to identify the original causes and levels of waste and the expense to the company. Two types of data were collected, namely, existing (historical) data and new data. The method of collection and reasons for the collection of the specific data are summarized in Table 6.1.

Table 6.1 Data collected for the waste minimisation audit

Data	Data and Data Collection Method
Existing	Consulting company-prepared documents (records of raw material purchasing, departmental requisitions from stores and additions to the process). Consulting service providers' and private contractors' documents (bills for utilities used and receipts for purchases made). Informal discussion with factory operators and management.
New	Detailed and generic solution composition on the Phosphating Line by sampling and chemical analyses and by direct reading instrumental analyses of process and rinse solutions. Monitoring of water consumption on the Phosphating Line using a water meter. Observing work practices and process operations. Estimating surface area of workpieces gone through the line during monitoring period, by consulting daily production sheets and workpiece specifications.

Collection of both numerical and qualitative existing data therefore formed a major task in this research project. This is outlined in Section 6.1. New data is presented from Section 6.2 onwards. In Section 6.2, method are described of obtaining new raw data by using what are effectively on-site monitoring techniques. These include taking readings from *in situ* meters, portable instruments, and measuring the dimensions of workpieces and tanks with a tape measure. In Section 6.3, the sampling protocol used to collect representative samples of the phosphating solutions for laboratory analyses is described. The spectroscopic and gravimetric analytical techniques which were used are described in Sections 6.4, 6.5 and 6.6. The preparation of sludge samples, collected during desludging of the process tanks, for Inductively Coupled Plasma Optical Emission Spectrophotometry (ICP-OES) analysis, is described in Section 6.7.

6.1 Collection of Existing Data

The existing data, specified in Table 6.1, were collected to perform specific waste minimisation analyses. Table 6.2 specifies the type of existing data collected, the source from which they were collected and the analysis for which they were used.

Table 6.2 Existing data collected from Company A

Type of data collected	Source	Reasons for data collection
Throughput, number and type of workpieces processed	Daily production sheets	Monitoring and targeting
Chemical additions of Chemcoater to process tanks	Line supervisor and chemical supplier	Daily control sheets
Workpiece dimensions	Daily production sheets	Monitoring and targeting
Water usage	Water bills (municipality)	Scoping audit
Chemicals Purchased	Administration compilation	Scoping audit
Powder	Administration compilation	Scoping audit
Steel	Administration compilation	Scoping audit
Paraffin	Administration compilation	Scoping audit
Packaging	Administration compilation	Scoping audit

6.2 New Data Collected as derived from Meter Readings and Simple Measurements

The first set of new data collected, the tank measurements were used to calculate the volume of the process and rinse solutions. These volumes were calculated in order to analyse the true cost of waste and to perform mass balances, on the chemicals used on the Phosphating Line.

For monitoring and targeting purposes, the surface area of the workpieces was calculated. This was achieved by consulting the daily production sheets (DPS), measuring items and through communication with the line supervisor. A formula for calculating the surface area was derived for each workpiece and used with the dimensional data to establish the surface area.

Other new data collected included a measurement of the solution volume present in the tank by using a measuring tape to measure the tank dimensions and headspace.

Table 6.3 Tank dimensions

Tank no.	Length (m)	Breadth (m)	Height (m)	Volume (m^3)	Headspace (m)	Volume of Solution (m^3)
1	2.61	2.11	0.80	4.41	0.23	3.14
2	1.25	2.2	0.85	2.34	0.23	1.71
3	2.61	2.11	0.80	4.41	0.23	3.14
4	1.25	2.2	0.85	2.34	0.23	1.71

6.3 Monitoring Strategy Employed for Collecting New Data by Sampling and Chemical Analysis

High density polyethylene (HDPE) bottles were used for the collection of samples from the process and rinse tanks, the effluent stream and water taps. Three samples were taken from each tank on each sampling occasion: two for the ICP-OES, as well as one for total dissolved solids (TDS) and suspended solids (SS) analysis. These bottles were prepared for sampling analyses. They were first washed with soapy water then rinsed with tap water. Thereafter they were washed with 2 M HCl, rinsed again with tap water and finally rinsed with distilled water.

6.3.1 Collection of Samples

The following points describe the terminology and information used and assumptions made during the development of the sampling strategy.

- an operating cycle (OC) runs from recharging to dumping the rinse tanks
- dumping takes place on a Friday and operation with new process and rinse solutions begins on the following Monday
- samples were taken on 29 occasions which will be referred to as sampling points and are represented by the date on which the sample was taken
- the time between successive sampling points is called a monitoring period
- the measured concentration representing a sampling point (SP) is assumed to be the concentration value for that day
- the production output during the monitoring period is taken from the first sampling point (day) to the end of production on the day before the next sampling point
- SP 1-10 (1/3/04 – 22/4/04), SP11-19 (04/5/04 – 02/7/04) and SP20-29 (05/7/04 – 29/7/06) represent operating cycles 1, 2 and 3

The samples were taken from the solution returning into the tank after the product was sprayed. It was assumed that the returning solution would be completely mixed and thus, the sample taken would be representative of the solution in the tank. Further, a layer of foam had built up on the solution surface making it difficult to obtain a consistent set of samples from the bulk tank solution. Two samples were obtained from each tank, one of which was acidified with 65% HNO_3 for the preservation of trace metals. The effluent sample was collected from a single effluent stream, situated outside the powder coating section of the factory. The water blanks were collected from the tap, which is also situated outside the powder coating plant, near the effluent stream. Refer to factory floor plan (Figure 4.1) for sampling points.

6.4 Chemical Analyses of Samples using ICP-OES

The ICP-OES was used for the analysis of six metals (Mo, Mn, Fe, Na, Zn, P and Cr) present in solution in Company A's phosphating line. The ICP-OES was used for this analysis based on its ability to rapidly analyse several metals simultaneously. It also offers the advantage of low chemical interference, unlike techniques such as atomic absorption spectroscopy.[181] In Section 6.4.1 how the instrument works is described, while in Sections 6.4.2 and 6.4.3 how the standards and samples were prepared for the analysis is described.

6.4.1 Principles of Inductively Coupled Plasma Optical Emission Spectrophotometry (ICP-OES)

The apparatus consists of two main components: an ICP source and a spectrometer. There are two types of spectrometers that can be used: a polychromator or a monochromator. For the purpose of elemental analysis in this project, the sequential type of monochromator was used. The ICP source consists of a radio frequency generator that produces an operating power of at least 1.10 kW. Other components include a torch, coil, nebulizer, spray chamber and a drain, whose operating conditions are specified in Table 6.4. The torch can be mounted in two ways, either in an axial position or in a radial position. The axial position generates a higher light intensity while the radial position requires less maintenance and consumes less argon. The radial position is used for normal analysis and complex materials, while the axial position is used for the analysis elements with lower detection limits.[182] The technique is based upon the ionization of a flowing stream of argon gas by an applied oscillating radio frequency field, which is inductively coupled to the ionized gas by a water-cooled coil. The coil is wound around a quartz torch that confines the plasma. The liquid sample is pumped to the nebulizer and generates aerosols in the spray chamber. This aerosol is then injected into the ICP, at temperatures of between 6000 and 8000 K. These high temperatures perform a dual function: they ionize the atoms, producing an emission spectrum, and they reduce chemical interferences by completely dissociating the molecules of compounds formed. The light emitted is then focused onto the monochromator for detection.

Spectral interferences can occur and may alter the net signal intensity. These interferences are caused by ion-atom recombination, spectral line overlaps, molecular band emission, or stray light. Spectral interferences can be overcome by choosing appropriate analytical wavelengths and by making background corrections. This instrument was the most appropriate to use for this project as it was used for multi-elemental analysis and has the appropriate detection limits required. In this project the concentrations of seven elements were determined and the detection limit of 0.001 mg/L for Fe, Mn and Zn was low enough to measure these concentrations. The operating conditions of the ICP-OES used in this analysis for this project, are summarized in Table 6.4.

Table 6.4 Specifications and operating conditions for ICP-OES

Instrument	Varian Liberty 150AX Turbo
Torch Mounting	Axial
Nebuliser	Pneumatic (Concentric)
Operating Power	1.10 kW
Nebuliser Pressure	240 kPa
Photomultiplier Voltage	800 v
Plasma Argon Flow	15.0 L/min
Auxillary Argon Flow	1.50 L/min
Pump Speed	15.0 rpm

6.4.2 Preparation of Standards

For the ICP-OES analysis, seven calibration standards were prepared from a mixed stock standard solution containing Mo, Mn, Fe, Zn, Na, and P. These standards covered a wide range of concentrations of these six elements. These are represented in Tables 6.5 to 6.6. A second set of standards was prepared, for Cr analysis only and is shown in Table 6.7. The mixed stock solution was prepared from 1000 mg/L Mo, Mn, Fe, Zn and P solutions purchased from Fluka. The Na solution was prepared using NaCl, supplied by

Riedel-de Haën, which was dried overnight in an oven set at 110 °C and left to cool in a dessicator. The mass of NaCl, required to obtain a 1000 mg/L (which equals to mg/L) solution of Na, was calculated.

$$\begin{aligned} C_{Na}\,(\text{required}) &= 1000\ \text{mgL}^{-1} \\ V_{Na} &= 250\ \text{mL} = 0.25\ \text{L} \end{aligned}$$

The concentration of 1000 mgL^{-1} is required. The volume the of the flask used to prepare the standard solution was 250 mL. Then using Equation 6.1, the mass of Na required, was calculated.

$$\begin{aligned} M_{Na} &= C_{Na} \times V_{Na} \\ M_{Na}\,(\text{required}) &= 1000\text{mgL}^{-1} \times 0.25\text{L} \\ M_{Na}\,(\text{required}) &= 1000\text{mgL}^{-1} \times 0.25\text{L} \\ &= 250\text{mg} \end{aligned} \qquad \text{Equation 6.1}$$

Using the molar mass ratios of Na and NaCl, the mass of NaCl required could be calculated. This is shown by equation 6.2.

$$\begin{aligned} M_{NaCl} &= M_{Na} \times \frac{Mr_{NaCl}}{Mr_{Na}} \\ M_{NaCl} &= 250\ \text{mg} \times \frac{58.44}{22.99} \\ M_{NaCl} &= 635.5\ \text{mg} = 0.635\ \text{g} \end{aligned} \qquad \text{Equation 6.2}$$

Table 6.5 Preparation of mixed stock solution from proprietary 1000 mg/L solutions

Metal	Purchased Solution Conc	Mixed Stock Solution Conc
P	1000	400
Na	1000	200
Zn	1000	80
Mo	1000	80
Mn	1000	80
Fe	1000	80

From this mixed stock, seven working calibration standards were prepared. The concentrations of the six elements in each standard are shown in Table 6.6.

Table 6.6 Contents and concentration (mg/L) of the seven working calibration standards

Metal	Concentration						
	Std 1	Std 2	Std 3	Std 4	Std 5	Std 6	Std 7
P	0.8	4	8	20	40	80	200
Na	0.4	2	4	10	20	40	100
Zn	0.16	0.8	1.6	4	8	16	40
Mo	0.16	0.8	1.6	4	8	16	40
Mn	0.16	0.8	1.6	4	8	16	40
Fe	0.16	0.8	1.6	4	8	16	40

Table 6.7 Preparation of Cr stock solution (standard 8) and three working standards

Mixed Stock Solution (Standard 8) Conc (mg/L)	Standard 9	Standard 10	Standard 11
5	1	0.2	0.04

Two calibrations were performed for each analysis: one before the analysis and one after the analysis. These calibration curves are presented in Appendix A.

6.4.3 Preparation of Samples

All samples obtained were filtered for ICP-OES analysis using 20 ml plastic syringes and 0.45 μm nylon filters manufactured by Anatech Instruments (Pty) Ltd. Many samples had to be diluted by an appropriate dilution factor to ensure that the concentrations of the metal ions were within the calibration range. These dilution factors ranged from 4 to 2000. The samples were stored in a refrigerator at a temperature of approximately 8 °C.

6.5 Gravimetric Analyses of Samples

6.5.1 Method for Determination of Total Dissolved Solids(TDS)

A stock standard solution of 5000 mg/L NaCl was made using pure water. A working analytical standard solution of 100 mg/L was then prepared from the stock. This analytical standard solution was freshly prepared every time the analysis was run.

The standard procedure followed for each analysis was to evaporate 250 ml of a well mixed, filtered, solution sample to a constant dry weight in a pre-weighed beaker. The increase in mass (of the beaker) represented the total dissolved solid content of the sample. Beakers were washed and dried in the oven and then stored in the dessicator until needed. The beakers were weighed on a four decimal balance, the Mettler AJ100, before use. Three blanks together with the samples were evaporated to dryness, cooled in a dessicator and reweighed. The drying, cooling, dessicating and weighing cycle was repeated until a constant mass was obtained. The total dissolved solid content was calculated using Equation 6.3. This equation shows that the TDS are calculated by taking the difference between the mass of the beaker after heating and the mass of beaker before heating. This yields the mass of solids which is corrected for the blank. This final mass is then divided by the volume of the sample filtered.

$$\mathrm{TDS(g/L)} = \frac{\left[(\mathrm{M}_2 - \mathrm{M}_1) - \mathrm{Blank}\right]/\mathrm{g}}{\mathrm{V/L}} \qquad \text{Equation 6.3}$$

M_1 is mass of empty beaker after drying (g)

M_2 is the mass of beaker and dry residue after heating (g)

V is the volume of the solution sample (mL)

Blank is the average mass after evaporating three 250 mL samples of ultra pure water. The TDS in a standard solution of NaCl (100 mgL^{-1}) was determined using the above method to check the accuracy of the method.[183]

6.5.2 Method for Determination of Suspended Solids (SS)

A 100 mgL^{-1} cellulose microcrystalline stock standard solution was prepared, using distilled water. Approximately 0.1 g of cellulose microcrystalline stock was accurately weighed out and left overnight to dry at 105 °C.

A standard procedure was followed for each sample and standard solutions. A well mixed 250 ml sample was vacuum filtered through a dried, pre-weighed, 9 mm, glass fibre filters. This was a GF6 Glasfaser Rundfilter type of filter. The filter was dried until all the solution had been evaporated. The residue was then cooled and weighed until a constant mass was obtained. Three blanks, using distilled water only, and the cellulose microcrystalline stock were similarly treated. Suspended solids in the sample were obtained by subtracting from the mass of the filter and the mass of the residue and correcting for the blank.

$$\mathrm{SS(mg/L)} = \frac{[(M_2 - M_1) - \mathrm{Blank}]/\mathrm{g}}{\mathrm{V/L}} \times \frac{1000\,\mathrm{mg}}{\mathrm{g}} \qquad \text{Equation 6.4}$$

M_1 is mass of empty filter paper after drying (g)
M_2 is the mass of filter paper and dry residue after heating (g)
V is the volume of the solution sample (mL)
Blank is the average mass after evaporating three 250 mL samples of distilled water. The expected SS value, based on the mass of solute dissolved in 250 mL of 100 mg/L solution Cellulose Microcrystalline, is 100.[183]

6.6 Sludge Analysis

During cleaning, the tanks were desludged and samples of this sludge were taken. These were first digested and the metals were determined by ICP-OES. The method consists of two parts: determination of density of the liquid sludge and acid digestion of the sludge.

6.6.1 Determination of the Density of Liquid Sludge

The samples were first well shaken and three 10 mL samples were extracted, by means of a pipette, from the liquid. The temperature of the sample was measured with a thermometer. The masses of the samples were measured immediately. The average mass and volumes were then used to measure the density.

6.6.2 Acid Digestion of Sludge

A 1 g sample (triplicate) of solid sludge was dried in an oven for 2 days at 105 °C and then cooled in dessicator and reweighed. The sample was then homogenized and crushed into a fine powder using a sieve. The sample was then transferred into a 100 mL digestion vessel, to which 10 mL of 1:1 HNO_3 was added. This 1:1 HNO_3 was made from an equal mixture of concentrated HNO_3 and ultra pure water. The vessel was then covered with a watch glass and refluxed at approximately 98 °C for 15 minutes on a steam bath. The sample was then cooled to room temperature and thereafter 5 mL of concentrated HNO_3 was added. The sample was then refluxed for a further 30 minutes. After every 30-minute interval, 5 ml of concentrated HNO_3 was added until there were no brown fumes visible. The sample was then refluxed for a further 2 hours without boiling, at 98 °C and then cooled to room temperature. Afterwards, 2 mL ultra pure water and 3 mL H_2O_2 were added. The sample was then allowed to warm until the effervescence subsided. The reaction was constantly monitored to ensure that no solution was lost due to excessively vigorous effervescence. The sample was then cooled to room temperature and H_2O_2 was continually added until the effervescence was minimal. The mixture was then heated until the final volume was reduced to approximately 5 mL. A 10 mL volume of HCl was added and the solution was then refluxed for 15 minutes. Finally, the solution was cooled and then filtered under gravity through a Whatman no.41 filter paper, into a 100 mL volumetric flask, then diluted and mixed well.[184]

CHAPTER 7

RESULTS

The results of the research are reported in this chapter in three sections. In Section 7.1 the results obtained from company documents (written data) and from factory personnel (aural data) are presented. In Section 7.2 the data collected to establish the water flow rate and other new solution characterization data for the Phosphating Line on the Paint Line are shown. The data for the water flowrates were obtained using the existing company water metering system. The data for the new solutions were gathered using hand-held direct reading instruments. Finally, in Section 7.3 the results obtained from elemental analysis of the tank solutions using the spectroscopic techniques described in Section 6.4 are given.

7.1 Results from Existing Data

Company documentation which was consulted for information gathering was of two basic types, namely that containing data on material inputs and on material outputs in the powder coating process. Tables 7.1 to 7.3 show the total surface area of the workpieces treated on the Paint Line during the three operating cycles. The surface areas for these workpieces were calculated by multiplying the number of each type of workpiece by the estimated surface area of each workpiece. These surface areas were calculated from the formulae derived from breaking down the structure of the workpiece into simple shapes. The workpieces' dimensions needed for the calculation were obtained by direct measurement of the workpieces and from specifications given by the factory supervisor. The name and the product code for the workpieces undergoing phosphating were entered in the Daily Production Sheets kept by the line supervisor. The code gives the variable dimensions of the workpiece. The structure and shape of the workpiece were ascertained by observation.

Table 7.1 Workpieces treated on the Paint Line in OC1

Monitoring Period	Number of Days	Number of Workpieces Treated	Total Surface Area of the Workpiece Treated (m^2)
1	2	11304	1667
2	4	8238	1060
3	5	6588	1204
4	6	9802	1204
5	3	3214	435
6	5	3384	690
7	4	3419	2020
Total	**29**	**45949**	**8280**

Table 7.2 Workpieces treated on the Paint Line in OC2

Monitoring Period	Number of Days	Number of Workpieces Treated	Total Surface Area of the Workpiece Treated (m^2)
8	6	5459	2390
9	6	13288	2987
10	3	94	201
11	5	3325	3990
12	6	5087	3117
13	6	3355	816
14	6	4583	3281
15	5	4655	1613
Total	**43**	**39846**	**18395**

Table 7.3 Workpieces treated on the Paint Line in OC3

Monitoring Period	Number of Days	Number of Workpieces Treated	Total Surface Area of the Workpiece Treated (m^2)
16	4	5565	2582
17	7	10801	4493
18	6	3622	4044
19	6	796	1925
Total	**23**	**20784**	**13044**

Another piece of new data collected from existing documentation was the chemical additions made to the process solutions contained in Tanks 1 and 2. Table 7.4 shows the date and the volume of Chemrox's Chemcoater 755 (Chemcoater) addtions made to each process tank. Most of the data were recorded in litres. However, three entries were recorded in fractions of a drum and these data were then converted into litres.

Table 7.4 Chemical additions (litres) made to the process solutions after make-up

Date	Tank 1	Tank 2
1/0304	13	6
2/03/04	50	0
3/04/04	13	19
8/03/04	13	6
9/03/04	13	6
10/03/04	0	20
24/03/04	0	13
25/03/04	13	0
26/03/04	0	20
1/04/04	0	20
19/04/04	0	12
20/04/04	25	12
4/05/04	25	13
12/05/04	10	10
21/05/04	0	5
24/05/04	0	13
25/05/04	8	25
1/06/04	0	13
3/06/04	13	13
7/06/04	0	13
10/06/04	0	13
17/06/04	0	13
24/06/04	0	13
30/06/04	0	19
8/07/04	13	13
13/07/04	13	13
15/07/04	0	13
19/07/04	0	13
22/07/04	13	13
23/07/04	0	13
26/07/04	13	13
27/07/04	13	13
29/07/04	0	13
Total	**261**	**414**

Table 7.5 presents the data on the chemicals purchased by the company and used on the Paint Line for the full monitoring period. These include both the quantity and average unit cost for the water, powder, paraffin and Chemcoater. The volume of water coming into the factory was obtained from the Msunduzi Municipality bills. Factory requisition sheets held by dispatch were consulted for powder purchases and data were compiled by Administration on paraffin, steel, Chemcoater and powder. These data are broken down to show the consumption of these raw materials on the paint line for each of the

Monitoring Periods within an Operating Cycle in Tables 7.6 to 7.8. The steel is supplied in many different forms eg. sheets, coils and strips of varying dimensions. These have been allocated by the company Administration in these terms. However it is impossible to present all these data concisely. Therefore the term 'unit' has been used to describe all forms in which the raw material is supplied.

Table 7.5 Raw material data for the factory for the full monitoring period (01/03/04 to 29/07/04)

Raw material	**Average unit cost/R**	**Into factory from supplier**		**Out of store to the Paint Line**	
		Quantity	**Cost (R)**	**Quantity**	**Cost (R)**
Water (kL)	6.45*	685	5037	Unavailable Data	
	7.10#	99	801		
Chemcoater (L)	8.42	1836 L	15459	Data Not Recorded	
Powder (kg)	31.02	10420	323205	10717 kg	332441
Paraffin (L)	2.59	52350	135399	##31500	81472
Packaging	Unavailable Data				
Steel (unit)	5.62	698814	4051301	Not applicable**	

Table 7.6 Raw materials used on the Paint Line for OC1

Raw materials used	**OC1**							**Total quantity**	**Cost**
	MP1	**MP2**	**MP3**	**MP4**	**MP5**	**MP6**	**MP7**		
Water (kL)	20.7	10.6	11.3	13.1	5.70	9.25	2.90	73.6	499
Chemcoater 755 (L)	68.5	62.25	88.25	88.25	12.5	12.5	49	381.25	3210
Powder (kg)	340	440	500	560	540	540	560	3480	107950
Paraffin (L)	Data Not Recorded								
Packaging	Unavailable Data								
Steel (unit)	13302	8586	9802	9802	3344	3521	5051	53408	300153

*This tariff was charged from the 2nd of February to the 25th of June

#This was the new tariff charged in July

**This data was not available as the steel was delivered directly to the Press Department

This quantity was calculated from an average consumption (300 L) per day by dividing the total quantity recorded for 16 days (4800 L)

Table 7.7 Raw materials used on the paint line from 04/05/04 to 02/07/04 for OC2

Raw materials used	OC2								Total quantity	Cost
	MP 8	MP 9	MP 10	MP 11	MP 12	MP 13	MP 14	MP 15		
Water (kL)	4.52	2.05	2.03	5.46	4.65	5.50	4.32	2.95	31.5	214
Chem-coater 755 (L)	37.5	0	25.5	33	50	12.5	37.5	19	215	1810
Powder (kg)	857	360	280	640	1137	963	660	600	5497	170517
Paraffin (L)	Data Not Recorded							1200	1200	3108
Packaging	Unavailable Data									

Table 7.8 Raw materials used on the paint line for OC3

Raw materials used	OC3				Total quantity	Cost
	MP16	MP17	MP18	MP19		
Water (L)	4.89	7.39	4.71	10.7	27.7	188
Chemcoater 755 (L)	25	50	50	100	225	1895
Powder (kg)	340	680	500	220	1740	53975
Paraffin (L)	1400	2600	2200	Data Not Recorded	6200	16058
Packaging	Unavailable Data					
Steel (unit)	5861	11368	3722	769	21747	122218

Table 7.9 shows the quantity and cost of the solid waste (domestic) removal. These data are obtained from the Msunduzi Municipality bills. Filled skips, containing solid waste from the process, are rented from and uplifted by a private contractor, Wasteman. Invoices reflecting these respective costs were unattainable but the estimated cost, obtained verbally, was R300 per month. The maximum error for this value is likely to be 17 % as this verbal estimate was based on recall. However, after checking with commercial removal companies, this does seem to be a good estimate in this case. The information presented in Table 7.10 was compiled from data given in invoices and receipts from Waynes Scrap Metal.

Table 7.9 Solid waste removed by the municipality

Date	Solid waste uplifted by municipality	
	Volume (kL)	Cost (R)
02/03/04 – 29/03/04	1.75	712.84
29/03/04 – 26/04/04	1.75	712.84
26/04/04 –26/05/04	1.75	712.84
26/05/04 – 25/06/04	1.75	712.84
25/06/04 – 30/07/04	1.75	819.74

Table 7.10 Metal waste sold to private contractor

Product	Date	Weight (kg)	Revenue
Subs	24/02/04	2250	1539
Steel Subs	11/03/04	3220	2203
Punchings	23/03/04	1490	2059
Steel 80 Sub 20	16/04/04	1520	0
Mixed	19/05/04	1260	756
Steel	14/06/04	1410	846
Steel	30/06/04	1480	888
Punchings	01/07/04	3870	2322
	15/07/04	1430	858
Mixed	30/07/04	1300	780
Steel	20/08/04	310	201
Steel / Drum L/	30/08/04	900	540
Steel 50 / Sub 50	30/08/04	1450	870
		Total	**13862**

7.2 Results from On-Site Collectable Data

Tables 7.11 to 7.14 display conductivity, total dissolved solids (TDS) and pH readings taken for process solutions in Tanks 1 and 2, and rinse solutions in Tanks 3 and 4, for the full monitoring period. Table 7.15 shows water meter readings taken during every sampling session and during other visits made to the company. This reflects the water consumption for the Phosphating Line. The amount of water consumed was calculated by taking the difference between water reading 2 and water reading 1. The total consumption over the full monitoring period obtained from the difference between the first reading taken on the first day of the monitoring period and the last reading taken on the last day of the monitoring period. Some of the results in these tables were not detectable (below respectively. The temperature and conductivity have been abbreviated to Temp and Cond in Tables 7.11 to 7.14.

Table 7.11 Readings taken on Tank 1 for the full monitoring period

Date	Temp (°C)	Cond (µS/cm)	SS (mg/L)	TDS (g/L)		pH	
				Direct Reading Instrument	Gravimetric Analysis	pH Meter	pH Paper
1/03/04	29	9650	75	NM	15.00	3.96	4
3/03/04	31	10560	23	4.38	17.24	5.86	6
4/03/04	45	12330	NM	NM	NM	5.90	6
9/03/04	29	14650	47	5.53	19.67	6.00	6
11/03/04	32	12400	38	5.21	20.14	6.08	6
12/03/04	No Sample Taken						
16/03/04	41	14430	131	5.09	17.87	6.19	6
18/03/04	57	14170	260	5.25	21.93	6.33	7
16/04/05	37	13100	230	5.54	18.52	6.40	7
22/04/05	26	13990	408	NM	18.13	6.28	6 - 7
4/05/04	29	11370	53	5.04	15.44	6.24	5 - 6
12/05/04	29	13150	483	6.11	21.31	6.22	6
20/05/04	26	13360	219	6.29	21.33	6.29	6 - 7
25/05/04	24	14740	491	6.01	23.72	6.30	6 - 7
1/06/04	NM	9520	210	4.44	16.16	5.62	5 - 6
9/06/04	NM	10610	382	5.47	17.38	5.93	5 - 6
17/06/04	39	13360	249	6.00	19.83	6.02	6
25/06/04	NM	13910	214	6.26	20.20	6.25	6 - 7
1/07/04	24	14090	247	5.93	20.33	6.23	6
5/07/04	NM	9090	75	4.15	14.54	5.40	5 – 6
6/07/04	NM	9040	138	4.22	13.70	5.76	5 – 6
7/07/04	40	9100	55	4.25	14.26	5.78	5 – 6
8/07/04	37	9590	62	4.23	14.15	5.93	5 – 6
9/07/04	37	10390	97	4.64	15.64	5.81	6
14/07/04	36	11590	128	5.11	16.20	5.95	6
16/07/04	42	11260	172	5.29	15.81	6.04	6
20/07/04	37	10700	148	4.81	17.19	6.10	6
22/07/04	34	11290	156	5.74	16.88	6.01	5 – 6
29/07/04	35	11890	143	5.28	19.30	5.99	6 – 7

Table 7.12 Readings taken on Tank 2 for the full monitoring period

Date	Temp (°C)	Cond (µS/cm)	SS (mg/L)	TDS (g/L)		pH	
				Direct Reading Instrument	Gravimetric Analysis	pH Meter	pH Paper
1/03/04	28	9000	6	NM	14.00	5.24	5
3/03/04	30	10150	18	4.68	14.91	5.50	4 – 5
4/03/04	43	8620	NM	NM	NM	5.60	5 – 6
9/03/04	29	8450	17	NM	13.35	5.69	5
11/03/04	32	8230	21	3.80	13.65	5.62	5
12/03/04	NM	7660	6	2.05	12.04	7.59	5
16/03/04	39	7880	26	3.20	10.61	6.00	5
18/03/04	54	7030	99	3.39	10.43	6.05	5 – 6
16/04/05	32	7580	112	3.48	11.47	6.08	6
22/04/05	26	12390	268	NM	18.52	5.92	6 – 7
4/05/04	29	9150	120	4.20	13.52	5.92	5 – 6
12/05/04	30	10620	190	4.80	17.60	5.86	6
20/05/04	28	7740	109	3.93	12.17	6.14	6
25/05/04	23	11980	2270	5.56	19.68	5.79	5 – 6
1/06/04	NM	7720	62	3.48	12.16	6.95	5 – 6
9/06/04	NM	9400	274	4.44	13.91	5.91	5 – 6
17/06/04	37	9730	233	4.67	14.25	6.00	6 – 7
25/06/04	NM	9610	172	5.14	19.64	6.05	6
1/07/04	NM	11490	103	4.92	16.40	5.97	5 – 6
5/07/04	NM	8640	108	3.85	13.86	4.85	5
6/07/04	NM	7770	179	3.77	11.85	5.77	5
7/07/04	25	8460	121	3.99	13.36	5.63	5
8/07/04	33	8030	44	3.67	11.12	5.81	5 – 6
9/07/04	34	8730	92	4.02	13.06	5.60	5 – 6
14/07/04	33	8790	101	3.97	12.40	5.66	5
16/07/04	42	9420	148	4.52	13.56	5.77	5 – 6
20/07/04	33	9710	114	4.57	14.95	5.84	5 – 6
22/07/04	31	11130	171	5.74	17.22	5.77	5 – 6
29/07/04	32	9300	170	4.11	13.80	6.00	6 – 7

Table 7.13 Readings taken on Tank 3 for the full monitoring period

Date	Temp (°C)	Cond (µS/cm)	SS (mg/L)	TDS (g/L)		pH	
				Direct Reading Instrument	Gravimetric Analysis	pH Meter	pH Paper
1/03/04	25	2230	8	NM	0.21	6.60	6
3/03/04	29	9620	8	NM	1.11	6.06	5
4/03/04	41	2720	NM	NM	NM	5.74	5 – 6
9/03/04	30	3350	9	1.68	4.46	5.10	5
11/03/04	30	3273	21	1.77	4.77	5.75	5
12/03/04	NM	3898	6	NM	6.91	5.74	5
16/03/04	35	4750	64	2.20	6.48	5.73	5 – 6
18/03/04	37	4335	84	2.21	6.23	5.91	6
16/04/05	35	4525	38	2.21	6.94	5.93	6
22/04/05	26	6550	127	NM	8.42	5.94	6
4/05/04	28	1073	5	0.63	1.45	6.49	6
12/05/04	30	3500	118	1.78	5.36	6.11	5 – 6
20/05/04	27	4260	81	2.20	6.37	6.19	6
25/05/04	24	4805	101	2.46	4.30	6.06	6
1/06/04	18	4440	63	2.50	7.08	6.05	6
9/06/04	NM	4975	164	2.39	7.22	6.14	5 – 6
17/06/04	33	5410	163	2.87	8.64	6.12	5 – 6
25/06/04	NM	6030	158	3.23	9.01	6.24	6
1/07/04	NM	6980	157	3.27	9.39	6.16	7
5/07/04	19	210	5	0.13	0.25	6.99	7
6/07/04	NM	1016	17	0.50	1.16	6.49	6
7/07/04	26	1587	18	0.76	1.84	6.33	5 – 6
8/07/04	27	1838	31	0.88	2.10	6.36	5 – 6
9/07/04	27	2058	30	0.98	2.32	6.23	6
14/07/04	27	2313	33	1.12	2.83	6.32	6
16/07/04	NM	2329	38	1.21	2.68	6.26	6
20/07/04	27	2785	22	1.48	3.58	6.23	5 – 6
22/07/04	27	NM	37	1.48	3.75	6.17	5 – 6
29/07/04	25	469	B/D	0.25	0.48	6.69	6 – 7

Table 7.14 Readings taken on Tank 4 for the full monitoring period

Date	Temp (°C)	Cond (µS/cm)	SS (mgL^{-1})	TDS (gL^{-1})		pH	
				Direct Reading Instrument	Gravimetric Analysis	pH Meter	pH Paper
1/03/04	29	120	5	NM	0.07	7.86	6
3/03/04	29	121	2	NM	0.07	7.73	5
4/03/04	40	182	NM	NM	NM	7.52	7
9/03/04	29	252	4	0.13	0.21	7.19	7
11/03/04	30	163	14	0.09	0.15	7.20	6
12/03/04	NM	242	0.5	0.13	0.23	7.09	7
16/03/04	NM	326	8	0.17	0.29	6.91	7
18/03/04	32	545	B/D	0.29	0.61	6.75	6
16/04/05	33	1055	3	0.54	1.20	6.31	6
22/04/05	26	1728	31	NM	1.77	6.47	6 –7
4/05/04	26	138	B/D	0.08	0.14	7.43	6 – 7
12/05/04	26	434	12	0.23	0.45	6.79	6
20/05/04	25	687	10	0.38	0.76	6.67	6
25/05/04	22	841	2	0.48	0.91	6.39	5 – 6
1/06/04	18	897	11	0.54	1.10	6.42	5 – 6
9/06/04	NM	947	32	0.56	1.15	6.78	6
17/06/04	19	1351	43	0.84	1.68	6.69	6 – 7
25/06/04	NM	1416	30	0.79	1.68	6.82	7
1/07/04	24	1475	20	0.74	1.49	6.76	6 – 7
5/07/04	19	84	1	0.05	0.04	7.58	7
6/07/04	NM	215	8	0.12	0.12	7.27	6
7/07/04	21	485	7	0.25	0.48	6.83	6
8/07/04	22	711	13	0.36	0.75	6.72	6
9/07/04	22	830	10	0.41	0.95	6.60	5 – 6
14/07/04	21	1283	23	0.64	1.41	6.54	6
16/07/04	NM	1556	41	0.86	1.69	6.47	5 – 6
20/07/04	23	1824	49	1.01	2.19	6.45	6
22/07/04	29	NM	53	1.15	2.60	6.36	6 – 7
29/07/04	28	201	4	0.01	0.17	7.23	7

Table 7.15 Water meter readings recorded on-site

Date	Water Reading 1 (kL)	Time	Water Reading 2 (kL)	Time	Water Consumed (kL)	Flowrate (kL/hr)	Flowrtae (kL/day)
1/03/04	5838.124	7:43	5839.289	10:42	1.165	0.388	3.110
3/03/20	5858.760	10:13	5858.806	11:45	0.046	0.031	0.250
4/03/04	5863.962	14:24	5864.180	15:31	0.218	0.195	1.560
9/03/04	5869.111	8:45	5869.403	9:58	0.292	0.239	1.910
11/03/04	5875.161	9:13	5875.270	10:11	0.109	0.109	0.870
12/03/04	5877.047	10:00	5877.099	10:20	0.156	0.156	1.250
16/03/04	5880.725	7:55	5880.854	8:55	0.129	0.129	1.030
18/03/04	5884.355	12:00	5884.410	12:30	0.110	0.000	0.000
16/04/04	5906.492	9:27	5906.535	9:45	0.043	0.033	0.260
22/04/04	5909.371	11:19	5909.388	11:32	0.017	0.014	0.110
4/05/04	5927.053	8:55	5927.113	9:20	0.06	0.143	1.140
12/05/04	5931.550	15:00	5931.574	15:20	0.024	0.072	0.580
20/05/04	5933.595	14:24	5933.595	15:00	0	0.000	0.000
25/05/04	5934.620	9:26	5935.620	9:52	1.000	2.326	18.600
1/06/04	5940.044	11:25	5940.080	11:40	0.036	0.144	1.150
8/06/04	5944.630	11:28	5944.690	12:00	0.060	0.113	0.910
17/06/04	5950.107	11:34	5950.126	12:02	0.019	0.026	0.210
25/06/04	5954.153	11:33	5954.427	11:50	0.274	0.979	7.830
1/07/04	5956.972	11:47	5957.106	12:43	0.134	0.134	1.070
5/07/04	5967.794	7:05	5968.881	9:50	1.087	0.395	3.160
6/07/04	5969.686	9:30	5969.716	9:50	0.030	0.091	0.730
7/07/04	5970.562	10:10	5970.620	10:45	0.058	0.100	0.800
8/07/04	5971.633	10:10	5971.682	10:35	0.049	0.117	0.930
9//07/04	5972.641	9:25	5972.678	9:40	0.037	0.148	1.180
14/07/04	5975.114	10:40	5975.180	11:22	0.066	0.094	0.750
16/07/04	5976.834	9:40	5976.869	10:02	0.035	0.105	0.840
20/07/04	5978.303	9:21	5978.321	9:35	0.018	0.078	0.630
22/07/04	5979.795	9:58	5979.820	10:14	0.025	0.100	0.800
29/07/04	5990.468	9:54	5990.471	10:07	0.003	0.014	0.110
Total water consumed for 105 days					**152**		

The powder thickness of the standard upright, diagonal bracing, shelf and deck panel were measured and recorded. This was carried out using the direct reading instrument, the Elcometer 456. The sensor of this instrument was placed directly on the coated surface and readings of thickness in μm were recorded. For each of the above products, the coating thickness was measured on the outer surface of several items. The readings taken on the standard uprights showed that the sides are generally thinner (50 to 90 μm) than the top (100 to 175 μm). The diagonal bracing thicknesses ranged from 80 to 100 μm. The thicknesses recorded on the shelves were found to increase as the shelves became wider. A range of 100 to 175 μm was recorded. The deck panels were found to have thicknesses ranging from 75 to 100 μm. Thus this resulted in a purely qualitative analysis because of the large variation in the readings.

7.3 Results from Chemical Analysis

The average elemental concentrations (P, Na, Mo, Zn, Mn, Fe, Cr) determined by ICP-OES for samples collected from the company for the full monitoring period are given in Tables 7.16 to 7.40. The tabulated results are presented in order of increasing tank number. This order is the same as the order in which the workpieces are conveyed through the process. This means that all the results for Tank 1 appear first. These data are given in Tables 7.16 to 7.21 and are for each of the operating cycles, 1, 2 and 3, respectively. The results for non-acidified samples are given Tables 7.16 to 7.18; and those for acidified samples are given in Tables 7.19 to 7.21. The same format is used to present the results for Tank 2 (Tables 7.22 to 7.27), Tank 3 (Tables 7.28 to 7.33) and Tank 4 (Tables 7.34 to 7.39). Selected samples from Tanks 3 and 4 were analysed for Cr. These data are given in Table 7.40.

All tanks were desludged manually and the sludge was placed in 250 L drums. The volumes of sludge discharged from each tank were estimated from observation of the task. There were approximately 500 L from Tank 1, 160 L from Tank 2 and 120 L from

Tank 3. The sludge samples were prepared for analysis via acid digestion (Section 6.7 in Chapter 6) and then analysed by ICP-OES. These results are shown in Table 7.41.

In Tables 7.42 and 7.43 the results obtained from chemical analysis carried out on Orlik chemicals are shown. The analysis carried out on the effluent (acidified and non-acidifed) and water samples are shown in Tables 7.44 to 7.46. The dates omitted from Tables 7.44 and 7.45 represent days on which no effluent was flowing and thus no effluent sample was obtained.

Table 7.16 Average elemental concentrations (mg/L) in non-acidified samples of Tank 1 for OC1

Date	[Na]	[P]	[Mo]	[Fe]	[Mn]	[Zn]
1/03/04	91	3	0.2	B/D	B/D	B/D
1/03/04	2469	3155	79	0.80	B/D	1.22
3/03/04	3240	3370	82	2.00	0.53	0.43
4/03/04	3670	3578	88	1.60	0.76	0.16
9/03/04	3822	3700	69	0.34	0.53	0.20
11/03/04	4183	4123	86	0.07	0.64	0.67
12/03/04	Sample not taken					
16/03/04	4258	4048	80	B/D	0.37	0.29
18/03/04	4803	4530	88	B/D	0.44	0.33
16/04/04	4348	3752	69	0.27	0.53	0.02
22/04/04	3780	3377	44	0.28	0.28	0.10

Table 7.17 Average elemental concentrations (mg/L) in non-acidified samples of Tank 1 for OC2

Date	[Na]	[P]	[Mo]	[Fe]	[Mn]	[Zn]
4/05/04	3427	3147	40	B/D	1.70	0.22
12/05/04	5130	4100	75	0.50	0.40	0.031
20/05/04	5550	4280	71	0.50	0.47	B/D
25/05/04	5040	4850	87	1.00	0.78	0.32
1/06/04	4220	3630	61	B/D	0.49	B/D
8/06/04	4500	3670	56	B/D	0.29	B/D
17/06/04	5306	4110	57	0.10	0.42	B/D
25/06/04	4170	3150	56	0.40	0.43	B/D
1/07/04	4410	3790	50	0.76	0.54	0.15

Table 7.18 Average elemental concentrations (mg/L) in non-acidified samples of Tank 1 for OC3

Date	[Na]	[P]	[Mo]	[Fe]	[Mn]	[Zn]
5/07/04	3210	3180	84	0.20	0.30	0.17
6/07/04	2840	2990	83	0.17	0.47	B/D
7/07/04	2850	2950	78	0.20	0.51	0.37
8/07/04	2780	2800	74	0.22	0.47	B/D
9/07/04	3140	3210	80	0.16	0.49	B/D
14/07/04	3470	3410	76	0.29	0.52	B/D
16/07/04	3920	3360	63	0.63	0.36	0.20
20/07/04	3590	3020	57	0.69	0.35	0.18
22/07/04	3820	3260	62	0.81	0.40	0.23
29/07/04	4380	3770	68	0.89	0.44	0.23

Table 7.19 Average elemental concentrations (mg/L) in acidified samples of Tank 1 for OC1

Date	[Na]	[P]	[Mo]	[Fe]	[Mn]	[Zn]
1/03/04	3468	2575	91	2.40	0.30	1.20
3/03/04	3103	3758	85	0.05	1.20	0.10
4/03/04	3560	4203	89	1.53	0.75	0.17
9/03/04	4040	4728	94	0.68	0.77	0.28
11/03/04	4078	4540	89	0.34	0.83	0.58
12/03/04	Sample not taken					
16/03/04	3749	4238	76	0.26	0.62	0.21
18/03/04	4308	4945	86	0.15	0.67	0.39
16/04/04	4170	3654	69	0.25	0.43	0.13
22/04/04	4124	3587	52	0.19	0.47	B/D

Table 7.20 Average elemental concentrations (mg/L) in acidified samples of Tank 1 for OC2

Date	[Na]	[P]	[Mo]	[Fe]	[Mn]	[Zn]
4/05/04	3443	3279	42	0.23	0.49	B/D
12/05/04	4650	4250	77	0.74	0.69	0.47
20/05/04	4900	4260	74	0.38	0.30	0.33
25/05/04	5140	4890	82	0.76	0.81	0.33
1/06/04	3330	3160	61	B/D	0.33	0.33
8/06/04	3940	3600	61	B/D	0.10	0.048
17/06/04	4920	4420	59	0.25	0.24	0.17
25/06/04	4810	4210	57	0.50	0.24	0.17
1/07/04	4500	4200	56	0.73	0.57	B/D

Table 7.21 Average elemental concentrations (mg/L) in acidified samples of Tank 1 for OC3

Date	[Na]	[P]	[Mo]	[Fe]	[Mn]	[Zn]
5/07/04	3300	3160	83	1	0.32	0.25
6/07/04	2740	3050	79	16	0.54	0.30
7/07/04	2680	2930	77	9	0.60	0.36
8/07/04	2670	2860	70	17	0.70	0.41
9/07/04	2960	3110	73	14	0.69	0.78
14/07/04	3440	3500	69	17	0.79	0.60
16/07/04	3860	3280	58	17	0.60	0.43
20/07/04	3670	3080	53	12	0.51	0.44
22/07/04	3860	3270	57	11	0.55	0.52
29/07/04	4330	3720	61	19	0.69	0.61

Table 7.22 Average elemental concentrations (mg/L) in non-acidified samples of Tank 2 for OC1

Date	[Na]	[P]	[Mo]	[Fe]	[Mn]	[Zn]
1/03/04	2505	3318	91	0.38	2.60	4.9
3/03/04	2785	3550	96	0.14	3.40	0.71
4/03/04	2316	2578	65	B/D	2.30	0.21
9/03/04	2111	2168	69	B/D	2.30	0.21
11/03/04	1996	2607	57	B/D	2.90	0.73
12/03/04	1794	2283	56	B/D	2.20	0.29
16/03/04	1659	2006	41	B/D	1.70	0.025
18/03/04	1691	2059	40	B/D	1.50	0.24
16/04/04	2420	2269	45	0.066	1.30	B/D
22/04/04	3448	3318	48	0.092	1.50	0.21

Table 7.23 Average elemental concentrations (mg/L) in non-acidified samples of Tank 2 for OC2

Date	[Na]	[P]	[Mo]	[Fe]	[Mn]	[Zn]
4/05/04	2847	2710	37	0.170	1.10	0.24
12/05/04	4050	3360	64	0.690	1.00	0.12
20/05/04	2790	2250	41	B/D	0.80	B/D
25/05/04	3840	3980	93	0.220	1.60	0.47
1/06/04	3010	2470	48	B/D	0.80	B/D
9/06/04	3530	2840	56	0.007	0.40	B/D
17/06/04	3660	2840	56	B/D	0.40	B/D
25/06/04	5480	4040	64	0.051	0.50	B/D
1/07/04	3560	3360	65	0.390	0.80	0.25

Table 7.24 Average elemental concentrations (mg/L) in non-acidified samples of Tank 2 for OC3

Date	[Na]	[P]	[Mo]	[Fe]	[Mn]	[Zn]
5/07/04	2850	2870	83	0.2	0.54	0.680
6/07/04	2370	2480	76	0.9	0.75	0.009
7/07/04	2590	2700	78	0.3	0.82	0.071
8/07/04	2340	2450	69	0.2	0.77	B/D
9/07/04	2600	2740	74	0.2	0.84	0.430
14/07/04	2530	2710	63	0.8	0.87	0.130
16/07/04	3210	2870	61	1.0	0.64	0.300
20/07/04	3300	2890	61	0.7	0.61	0.270
22/07/04	3780	3340	72	1	0.73	0.420
29/07/04	3080	2630	54	0.8	0.47	0.210

Table 7.25 Average elemental concentrations (mg/L) in acidified samples of Tank 2 for OC1

Date	[Na]	[P]	[Mo]	[Fe]	[Mn]	[Zn]
1/03/04	2441	3345	90	0.40	2.60	6.0
3/03/04	2730	3500	87	0.26	3.60	1.5
4/03/04	2151	2752	66	B/D	2.50	0.5
9/03/04	2068	2581	55	0.07	2.40	0.8
11/03/04	2352	2977	59	0.03	3.10	1.5
12/03/04	2116	2605	49	B/D	1.90	B/D
16/03/04	1854	2278	39	B/D	1.80	B/D
18/03/04	1858	2285	40	B/D	1.70	0.09
16/04/04	2356	2192	44	0.03	1.20	0.18
22/04/04	3520	3354	45	B/D	1.60	0.00067

Table 7.26 Average elemental concentrations (mg/L) in acidified samples of Tank 2 for OC2

Date	[Na]	[P]	[Mo]	[Fe]	[Mn]	[Zn]
4/05/04	2530	2438	28	0.05	1.20	0.10
12/05/04	3770	3570	64	0.11	1.40	0.44
20/05/04	2500	2230	44	B/D	0.80	0.25
25/05/04	2500	2230	89	B/D	0.80	0.25
1/06/04	3810	4010	47	0.15	1.60	0.40
9/06/04	2570	2510	58	0.13	1.20	0.36
17/06/04	3040	2860	59	B/D	0.30	0.14
25/06/04	3240	2090	65	B/D	0.20	0.07
1/07/04	3670	3340	63	0.11	0.30	0.12

Table 7.27 Average elemental concentrations (mg/L) in acidified samples of Tank 2 for OC3

Date	[Na]	[P]	[Mo]	[Fe]	[Mn]	[Zn]
5/07/04	3620	3330	63	0.31	0.78	0.30
6/07/04	2880	2960	83	2.1	0.55	0.75
7/07/04	2170	2460	75	29	1.00	1.4
8/07/04	2300	2680	78	7.7	0.88	0.71
9/07/04	2170	2380	67	16	0.92	0.87
14/07/04	2530	2750	70	14	1.10	0.83
16/07/04	3220	2840	60	26	1.00	0.97
20/07/04	3310	2910	60	16	0.90	0.82
22/07/04	3770	3360	70	25	1.20	1.3
29/07/04	3160	2690	51	16	0.98	1.0

Table 7.28 Average elemental concentrations (mg/L) in non-acidified samples of Tank 3 for OC1

Date	[Na]	[P]	[Mo]	[Fe]	[Mn]	[Zn]
1/03/04	50	48	2	0.3	0.40	0.01
3/03/04	15	146	3	0.2	0.50	0.13
4/03/04	665	611	16	1.0	2.00	0.93
9/03/04	75	589	7	0.6	1.40	0.07
11/03/04	78	612	7	0.5	1.40	0.06
12/03/04	95	713	7	0.5	1.40	0.05
16/03/04	116	769	5	0.6	1.50	0.06
18/03/04	108	751	7	0.5	1.20	0.04
16/04/04	552	501	11	B/D	0.10	B/D
22/04/04	737	661	14	0.2	0.80	0.07

Table 7.29 Average elemental concentrations (mg/L) in non-acidified samples of Tank 3 for OC2

Date	[Na]	[P]	[Mo]	[Fe]	[Mn]	[Zn]
4/05/04	295.5	291.9	7.5	0.66	0.32	B/D
12/05/04	1030	1030	22	0.26	0.16	B/D
20/05/04	1630	1240	24	B/D	0.33	B/D
25/05/04	1440	1410	28	B/D	0.32	B/D
1/06/04	1610	1600	31	0.42	0.54	0.096
9/06/04	1730	1500	31	B/D	0.15	B/D
17/06/04	2260	1660	32	0.71	0.19	B/D
25/06/04	2040	1880	36	0.54	0.32	0.003
1/07/04	2080	1950	38	0.88	0.32	0.045

Table 7.30 Average elemental concentrations (mg/L) in non-acidified samples of Tank 3 for OC3

Date	[Na]	[P]	[Mo]	[Fe]	[Mn]	[Zn]
5/07/04	52	39	1	0.1	0.06	B/D
6/07/04	230	210	7	0.7	0.07	0.09
7/07/04	330	340	11	3.4	0.12	0.13
8/07/04	380	400	14	3.7	0.14	0.14
9/07/04	430	450	14	7.7	0.22	0.20
14/07/04	540	560	16	6.2	0.22	0.17
16/07/04	520	540	15	4.5	0.20	0.14
20/07/04	700	690	17	3.8	0.22	0.15
22/07/04	700	720	17	2.2	0.23	0.13
29/07/04	110	92	2.2	0.4	0.05	B/D

Table 7.31 Average elemental concentrations (mg/L) in acidified samples of Tank 3 for OC1

Date	[Na]	[P]	[Mo]	[Fe]	[Mn]	[Zn]
1/03/04	42	45	2	0.18	0.39	0.11
3/03/04	15	147	4	0.26	0.32	0.63
4/03/04	668	617	18	0.05	1.50	0.03
9/03/04	75	574	19	0.95	1.10	0.97
11/03/04	79	595	6	B/D	B/D	0.06
12/03/04	98	689	23	1.20	1.30	0.77
16/03/04	116	776	25	0.90	1.30	0.05
18/03/04	1533	1341	28	B/D	B/D	0.07
16/04/04	549	506	11	0.29	0.15	0.07
22/04/04	1566	1805	35	0.11	0.70	0.08

Table 7.32 Average elemental concentrations (mg/L) in acidified samples of Tank 3 for OC2

Date	[Na]	[P]	[Mo]	[Fe]	[Mn]	[Zn]
4/05/04	304	303	5	0.10	0.43	0.37
12/05/04	1050	1010	22	0.25	0.16	B/D
20/05/04	1420	1190	25	2.40	0.36	0.11
25/05/04	1400	1340	27	B/D	0.30	0.03
1/06/04	1680	1530	30	B/D	0.40	B/D
9/06/04	1730	1500	30	B/D	0.15	B/D
17/06/04	2220	1630	30	1.20	0.18	B/D
25/06/04	2020	1940	35	0.66	0.32	0.02
1/07/04	1930	1760	35	0.66	0.33	0.12

Table 7.33 Average elemental concentrations (mg/L) in acidified samples of Tank 3 for OC3

Date	[Na]	[P]	[Mo]	[Fe]	[Mn]	[Zn]
5/07/04	52	39	1	0.4	0.06	B/D
6/07/04	260	270	7	2	0.15	0.051
7/07/04	370	350	10	12	0.23	0.35
8/07/04	450	420	11	17	0.30	0.41
9/07/04	490	490	13	18	0.34	0.45
14/07/04	580	570	14	25	0.39	0.50
16/07/04	620	600	14	28	0.42	0.53
20/07/04	690	720	16	27	0.44	0.61
22/07/04	780	740	16	25	0.46	0.57
29/07/04	110	90	2	3	0.08	B/D

Table 7.34 Average elemental concentrations (mg/L) in non-acidified samples of Tank 4 for OC1

Date	[Na]	[P]	[Mo]	[Fe]	[Mn]	[Zn]
1/03/04	7	1	0.006	B/D	0.120	0.081
3/03/04	14	6	0.3	0.0026	0.004	0.001
4/03/04	22	15	0.8	B/D	0.039	B/D
9/03/04	51	36	1.1	0.6420	0.069	0.250
11/03/04	32	21	0.7	0.0012	0.036	0.014
12/03/04	43	38	1.3	B/D	0.087	B/D
16/03/04	74	58	1.7	0.1720	0.076	0.150
18/03/04	132	124	3.0	0.0035	0.170	0.130
16/04/04	266	221	5.6	0.1144	0.099	0.170
22/04/04	326	269	7.0	0.0494	0.096	0.280

Table 7.35 Average elemental concentrations (mg/L) in non-acidified samples of Tank 4 for OC2

Date	[Na]	[P]	[Mo]	[Fe]	[Mn]	[Zn]
4/05/04	26	17	0.5	B/D	0.06	B/D
12/05/04	96	77	2.4	B/D	B/D	B/D
20/05/04	220	141	3.8	B/D	0.07	B/D
25/05/04	210	170	4.9	B/D	B/D	B/D
1/06/04	280	160	0.2	B/D	B/D	B/D
9/06/04	280	210	6.4	0.2	B/D	B/D
17/06/04	470	300	8.5	2.2	0.07	B/D
25/06/04	380	350	8.3	1.1	0.14	0.008
1/07/04	350	300	7.9	0.4	0.13	B/D

Table 7.36 Average elemental concentrations (mg/L) in non-acidified samples of Tank 4 for OC3

Date	[Na]	[P]	[Mo]	[Fe]	[Mn]	[Zn]
5/07/04	13	4	0.2	0.018	0.05	B/D
6/07/04	51	30	1.6	0.066	0.02	0.07
7/07/04	140	92	3.6	0.13	0.06	0.07
8/07/04	200	150	5.3	0.17	0.09	0.09
9/07/04	190	160	6.0	0.4	0.10	0.10
14/07/04	270	260	9.5	1.4	0.15	0.13
16/07/04	330	330	12.0	1.1	0.16	0.13
20/07/04	390	380	13.0	1.1	0.18	0.15
22/07/04	470	470	16.0	0.47	0.30	0.17
29/07/04	43	24	0.7	0.22	0.05	B/D

Table 7.37 Average elemental concentrations (mg/L) in acidified samples of Tank 4 for OC1

Date	[Na]	[P]	[Mo]	[Fe]	[Mn]	[Zn]
1/03/04	6	1	0.06	0.045	0.170	0.05
3/03/04	11	5	0.27	B/D	0.083	0.24
4/03/04	24	15	0.72	B/D	0.052	0.40
9/03/04	41	35	1.30	B/D	0.090	B/D
11/03/04	2	12	0.30	B/D	B/D	0.00076
12/03/04	3	22	0.31	0.002	B/D	0.0074
16/03/04	65	54	1.40	0.13	B/D	0.30
18/03/04	8	70	2.50	0.14	0.027	0.60
16/04/04	253	216	4.03	0.33	0.230	0.30
22/04/04	423	342	5.90	0.14	0.530	0.35

Table 7.38 Average elemental concentrations (mg/L) in acidified samples of Tank 4 for OC2

Date	[Na]	[P]	[Mo]	[Fe]	[Mn]	[Zn]
4/05/04	26.32	17.59	0.5	B/D	0.075	0.20
12/05/04	97.00	77.00	2.0	0.36	B/D	0.12
20/05/04	200.0	140.0	2.6	0.26	0.130	0.18
25/05/04	201.0	170.0	4.5	0.33	0.005	0.06
1/06/04	280.0	150.0	4.2	0.18	0.057	0.02
9/06/04	280.0	200.0	4.4	0.21	0.059	B/D
17/06/04	480.0	320.0	8.0	0.47	0.130	0.04
25/06/04	430.0	380.0	7.7	0.18	0.230	0.26
1/07/04	350.0	310.0	6.0	1.30	0.200	0.18

Table 7.39 Average elemental concentrations (mg/L) in acidified samples of Tank 4 for OC3

Date	[Na]	[P]	[Mo]	[Fe]	[Mn]	[Zn]
5/07/04	14	5	0.2	0.1	0.05	B/D
6/07/04	46	29	2	0.4	0.12	0.11
7/07/04	120	88	3	5.5	0.15	0.20
8/07/04	170	140	4	7.4	0.19	0.27
9/07/04	220	170	5	8.2	0.20	0.30
14/07/04	280	280	8	13	0.27	0.42
16/07/04	370	360	10	16	0.31	0.58
20/07/04	390	380	11	17	0.34	0.63
22/07/04	550	460	13	14	0.44	0.69
29/07/04	43	25	0.8	2.4	0.09	0.02

Table 7.40 Average elemental concentrations (mg/L) of chromium in selected acidified and non-acidified samples analysed for Cr in Tanks 3 and 4

Date	[Cr]	Date	[Cr]
Tank 3		Tank 4	
1/03/04	0.005	24/02/04	0.0073
	0.004	26/02/04	0.0051
3/03/04	0.004	1/03/04	0.0044
4/03/04	0.024	3/03/04	0.0075
9/03/04	0.032	4/03/04	0.0048
11/03/04	0.034		0.0420
12/03/04	0.039	11/03/04	0.0110
16/03/04	0.043	16/04/04	0.0095
18/03/04	0.042	22/04/04	0.0130
	0.004	4/05/04	0.0075
16/04/04	0.043	12/05/04	0.0076
4/05/04	0.010		
12/05/04	0.033		
20/05/04	0.043		

Table 7.41 Percentage compositions of elements measured in sludge samples

Date	Time	Tank No.	[Na]	[P]	[Mo]	[Fe]	[Mn]	[Zn]
2/07/04	7:50	1	9	11	4	43	2	2
2/07/04	10:00	1	16	24	5	54	6	11
2/07/04	7:50	2	9	18	5	61	6	9
2/07/04	9:00	2	11	16	4	43	5	8
2/07/04	9:00	2	12	20	4	52	6	10
2/07/04	7:50	3	15	26	1	51	6	12
2/07/04	7:50	3	18	28	6	53	2	12
2/07/04	10:05	3	50	79	1	54	1	3

Table 7.42 Average elemental concentrations (mg/L) in the non-acidified samples using Orlik chemicals

Sample.	Date	[Na]	[P]	[Mo]	[Fe]	[Mn]	[Zn]
T_1	24/02/04	6948	423	25	B/D	0.21	B/D
	26/02/04	1475	90	18	B/D	B/D	0.21
T_2	24/02/04	1164	69	0.21	0.6400	0.48	0.23
	26/02/04	52	3	0.01	0.0058	0.02	0.48
T_3	24/02/04	763	1432	30	B/D	43.0	0.08
	26/02/04	1185	2019	42	0.058	49.0	28.0
T_4	24/02/04	44	49	2	B/D	0.19	43.0
	26/02/04	17	12	0.54	B/D	B/D	0.19
Effluent	24/02/04	39	28	0.62	B/D	0.07	B/D
	26/02/04	469	682	15	B/D	10.0	16.0

Table 7.43 Average elemental concentrations (mg/L) in acidified samples using Orlik chemicals

Sample.	Date	[Na]	[P]	[Mo]	[Fe]	[Mn]	[Zn]
T_1	24/2/04	7393	402	1.20	0.10	0.25	B/D
	26/2/04	3258	177	0.20	0.68	0.24	0.25
T_2	24/2/04	44	57	0.25	0.10	0.04	0.02
	26/2/04	44	3	0.04	0.06	0.08	0.04
T_3	24/2/04	886	1688	33.0	1.40	50.0	49.0
	26/2/04	1094	1858	39.0	2.00	43.0	20.0
T_4	24/2/04	44	56	1.59	0.45	0.74	1.10
	26/2/04	19	22	0.54	0.17	0.35	0.74
Effluent	24/2/04	326	269	6.90	0.32	0.40	0.31
	26/2/04	454	699	16.0	16.0	11.0	1.30

Table 7.44 Average elemental concentrations (mg/L) in non-acidified effluent samples

Date	[Na]	[P]	[Mo]	[Fe]	[Mn]	[Zn]
1/03/04	5	18	0.6	B/D	0.068	B/D
3/03/04	2	14	0.6	B/D	0.070	B/D
4/03/04	5	38	0.4	B/D	0.070	B/D
9/03/04	7	49	0.4	B/D	0.070	B/D
11/03/04	10	66	0.4	B/D	0.071	B/D
12/03/04	Suspected bottle contamination					
16/03/04	57	61	1.8	B/D	0.140	B/D
18/03/04	197	190	4.9	B/D	0.490	0.06
4/05/04	1247	1161	20	B/D	0.420	0.30
8/07/04	790	780	22	0.26	0.910	0.59
9/07/04	740	740	20	0.27	0.910	0.60
14/07/04	1560	1580	34	0.14	1.300	0.86
29/07/04	98.00	76.00	1.8	0.26	0.093	B/D

Table 7.45 Average elemental concentrations (mg/L) in acidified effluent samples

Date	[Na]	[P]	[Mo]	[Fe]	[Mn]	[Zn]
1/03/04	65	38	0.4	1.40	0.410	0.17
3/03/04	31	25	0.8	0.10	B/D	0.02
4/03/04	75	66	2.1	0.62	0.004	0.12
9/03/04	92	82	2.6	0.47	0.093	0.28
11/03/04	115	118	3.0	0.46	0.220	0.27
12/03/04	64	54	1.6	0.60	0.099	0.12
16/03/04	Insufficient sample to acidify					
18/03/04	215	207	6.0	1.10	0.390	0.33
4/05/04	1250	1180	22	0.20	0.540	B/D
8/07/04	Insufficient sample to acidify					
9/07/04	Insufficient sample to acidify					
14/07/04	Insufficient sample to acidify					
29/07/04	Insufficient sample to acidify					

Table 7.46 Average elemental concentrations (mg/L) in water samples

Date	[Na]	[P]	[Mo]	[Fe]	[Mn]	[Zn]
24/02/04	0.823	1.575	0.46	B/D	B/D	B/D
26/02/04	0.826	1.580	0.46	B/D	B/D	B/D
1/03/04	0.828	1.573	0.46	B/D	B/D	B/D
3/03/04	0.825	1.586	0.46	B/D	B/D	B/D
4/03/04	0.828	1.603	0.46	B/D	B/D	B/D
9/03/04	0.825	1.587	0.46	B/D	B/D	B/D
11/03/04	0.824	1.596	0.46	B/D	B/D	B/D
12/03/04	0.813	1.591	0.46	B/D	B/D	B/D
16/03/04	3.694	B/D	B/D	B/D	B/D	B/D
18/03/04	0.682	1.604	0.45	B/D	B/D	B/D
16/04/04	3.697	0.044	B/D	B/D	B/D	B/D
22/04/04	3.489	B/D	B/D	B/D	B/D	B/D
4/05/04	B/D	B/D	B/D	B/D	B/D	B/D
12/05/04	4.900	0.370	B/D	B/D	B/D	0.200
20/05/04	4.600	0.180	B/D	B/D	B/D	ND
25/05/04	3.626	B/D	0.15	B/D	B/D	B/D
1/06/04	3.564	B/D	0.08	B/D	B/D	B/D
8/06/04	3.800	0.220	0.09	B/D	B/D	B/D
17/06/04	4.700	0.260	B/D	B/D	B/D	B/D
25/06/04	4.200	0.550	0.22	0.22	0.029	B/D
1/07/04	4.100	0.380	0.22	0.061	0.068	B/D
5/07/04	No sample taken					
6/07/04	4.300	0.250	0.22	0.040	0.063	0.093
7/07/04	4.100	0.140	0.08	B/D	0.019	0.068
8/07/04	4.200	0.130	0.07	B/D	0.012	0.062
9/07/04	4.200	0.150	0.07	0.004	0.068	0.070
14/07/04	4.200	0.170	0.07	B/D	0.009	0.065
16/07/04	4.200	0.170	0.06	B/D	0.009	0.065
20/07/04	4.100	0.140	0.07	B/D	0.009	0.064
22/07/04	4.100	0.130	0.06	0.003	0.010	0.069
29/07/04	4.100	0.520	0.17	0.220	0.022	B/D

CHAPTER 8

DISCUSSION

A waste minimisation audit was performed on the Paint Line at Southlands Manufacturing from the 24th of February to the 29th of July 2004. The Paint Line pretreats a variety of workpieces with a wet phosphating surface pretreatment, then applies an organic powder coating in a dry process. This audit was initiated by the company, as they had changed their in-house process from that shown in Figure 8.1 to that shown in Figure 8.2. On the 1st of March the company changed the chemical supplier for their phosphating process from Orlik to Chemrox Chemicals. This change led to the removal of the first step (cleaning) from their phosphating process. Previously the workpieces had gone through the process in the following sequence: degreasing, rinsing, phosphating and rinsing (see Figure 8.1). This then changed to two cleaning/phosphating steps, followed by two rinses (see Figure 8.2).

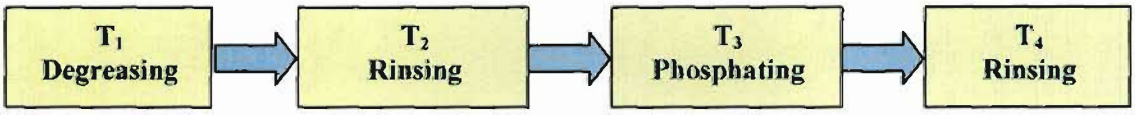


Figure 8.1 Flow chart of the phosphating process using Orlik chemicals

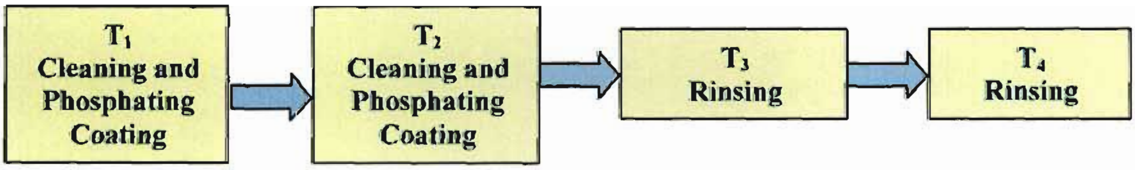


Figure 8.2 Flow chart of the phosphating process using Chemrox chemicals

The company changed its supplier and surface pretreatment method as they believed that it would cost less. Orlik charged R25.83/kg for the ORPREP SP-120 (degreaser) and R13.10/L for the ORPHOS 97-L (phosphator) while Chemrox charges R8.42/L for Chemcoater 755. At this time a complete waste audit was not carried out on the phosphating process using the Orlik Chemicals. The only cost taken into account prior to changing suppliers was the cost of the chemicals purchased. Other raw materials such as water, paraffin and powder, as well as the amount of waste produced by the process were not accounted for. Thus a waste audit was needed to cost all the raw materials and the waste and to fully evaluate the cost efficiency of this new process.

However, comparison of the analytical results obtained for samples taken on the phosphating line for the two different commercial phosphating chemicals (supplied by Orlik and by Chemrox Chemicals) was inconclusive in terms of establishing which is the more efficient system. This is because only two sets of samples were collected on two days of the last week in which the Orlik system was being used. This situation arose because the supplier had already been changed and the Chemrox system was due for introduction on the Paint Line on the 1st of March 2004.

About three 25 L packets of ORPHOS 97-L would have been required to charge T_3 with phosphating chemicals. The analysis results show that the P and Mo levels in the Orlik solution (see Table 7.42) are slightly lower than that in the Chemrox system. However the Mn (and perhaps the Zn) concentrations in the Orlik phosphating solution were observed to be greater than those found in the Chemrox system (see Tables 7.22 to 7.27). As the solutions appear to have different chemistries it is difficult to assume that top-up rates will be the same in both cases. In addition, the Orlik system uses four 25 kg packets of ORPREP SP-120 to make up the degreasing solution used in T_1. The chemical related cost of charging the process solution tanks with Orlik chemicals is estimated at R2583 for T_1 and R983 for T_3. This gives a total cost of R3566. This is much higher than the cost of chemicals for making up T_1 and T_2 with Chemrox's Chemcoater (R1263). The cost of chemical additions and of one chemical dump and recharge of T_1 and T_2 with Chemcoater during the monitoring period is R9136. If the Orlik system required the same number of dumps and top-ups, then it would obviously cost more to run. However there is insufficient monitoring data on which to be able to say how long the Orlik system can run before it needs topping up and/or dumping.

In Section 8.1 of this chapter the chemistry of the process and rinse solutions, the effluent and sludge samples from the laboratory, and the analytical and direct reading instrumental results, are discussed. The scoping audit findings are presented in Section 8.2. This analysis uses both new and existing data. In Section 8.3 mass balances are performed on the water and used for the determination of the average volumes of drag-out for the phosphating line. The results of the true cost waste analysis carried out on the effluent stream of the phosphating process are in Section 8.4. Section 8.5 describes the monitoring and targeting analysis carried out using the consumption variables - water and Chemcoater, and the production variables - effluent quality and surface area treated.

Table 8.1 describes the sampling strategy used in this study, which will be referred to in the discussion on the solution chemistry and the waste minimisation analysis.

Table 8.1 Operating cycles and monitoring periods

Operating Cycle	Monitoring Period	Sampling Points	Date	No.of Working Days
1	**MP1**	SP1 - SP 3	1/03/04 - 03/03/04	2
	MP2	SP 2 - SP 4	03/03/04 - 09/03/04	4
	MP3	SP 3 - SP 5	4/3/2004 - 11/03/04	5
	MP4	SP 3 - SP 6	04/03/04 - 12/03/04	6
	MP5	SP 5 - SP 7	11/03/04 - 16/03/04	3
	MP6	SP 5 - SP 8	11/3/04 - 18/03/04	5
	MP7	SP 9 - SP10	16/04/04 - 22/04/04	4
2	**MP8**	SP 11 - SP 12	04/05/04 - 12/05/04	6
	MP9	SP 12 - SP 13	12/5/04 - 20/05/04	6
	MP10	SP 13 - SP 14	20/05/04 - 25/05/04	3
	MP11	SP 14 - SP 15	25/5/04 - 01/06/07	5
	MP12	SP 15 - SP 16	01/06/04 - 09/06/04	6
	MP13	SP 16 - SP 17	09/06/03 - 17/06/04	6
	MP14	SP 17 - SP 18	17/06/04 - 25/06/04	6
	MP15	SP 18 - SP 19	25/06/04 - 02/07/04	5
3	**MP16**	SP 20 - SP 24	05/07/04 - 09/07/04	4
	MP17	SP 20 - SP 25	05/07/04 - 14/07/04	7
	MP18	SP 25 - SP 28	14/07/04 - 22/07/04	6
	MP19	SP 28 - SP 29	22/07/04 - 29/07/04	6

8.1 Characterisation of the Phosphating Solutions

In this section the results obtained from the analysis of the non-acidified and acidified process and rinse solutions are discussed. The non-acidified samples are a more accurate representation of the (acidified) solutions found on the phosphating process. Acidification of samples is traditionally performed in order to preserve samples while they are stored awaiting analysis. Both types of samples were analysed in order to see how effective and necessary acidification preservation is in analysis of industrial samples. This discussion focuses, therefore, on the non-acidified sample. However, as the analytical results for acidified and non-acidified samples are in good agreement, the acidified results can be used to highlight any inconsistencies in the results.

Concentration profiles for Na, P, Mo and Fe for all three operating cycles have been plotted and presented in Figures 8.3 to 8.14. The profiles for each tank solution have been discussed for all three operating cycles using the results from both the acidified and non-acidified samples (see Tables 7.16 to 7.27). Finally, the profiles of the different tank solutions have been compared. The variations or trends observed in the profiles have been discussed in terms of eight factors listed below:

- chemical additions made to the process tanks
- topping up of the rinse tanks with water additions
- full dumping and desludging of the process tanks
- partial and full dumping of the rinse tanks
- drag-out of chemicals from the process tanks as the workpieces move through the line
- drag-in of chemicals from process tanks into tanks further down line, in particular the rinse tanks
- loss of water due to evaporation and drag-out
- surface area of the workpieces processed.

8.1.1 Characterisation of the Process Solutions

The concentration profiles of the non-acidified samples for the two process tanks (T_1 and T_2) are plotted in Figures 8.3 to 8.14. Figure 8.3 shows the Na and P concentrations and Figure 8.4 shows the Mo and Fe concentrations for OC1. The concentrations of Mn and Zn were found to be much lower than those of the other elements and did not show any significant changes during the full monitoring period. In the first operating cycle their concentration levels were slightly above 1 mg/L in the acidified samples only. In all other samples the Mn and Zn concentrations were below 1 mg/L. Thus the process profile for these two elements have not been plotted.

The results show that the elemental composition of the process solution can be divided into three distinct bands namely those with:

- a high concentration value of around 4000 mg/L for Na and 3400 mg/L for P

- a low concentration value of around 70 mg/L for Mo
- very low concentration values for Mn and Zn of less than 1 mg/L.

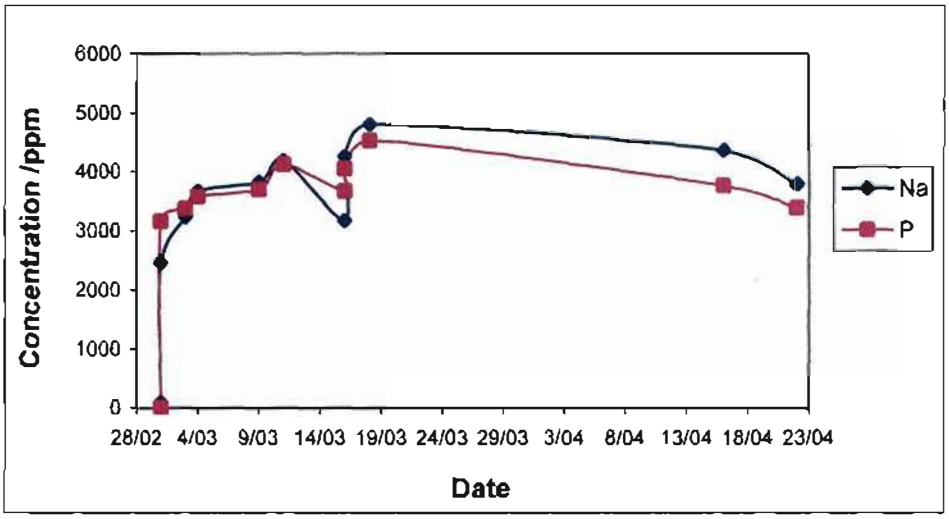


Figure 8.3 Concentration profile of T_1 for OC1

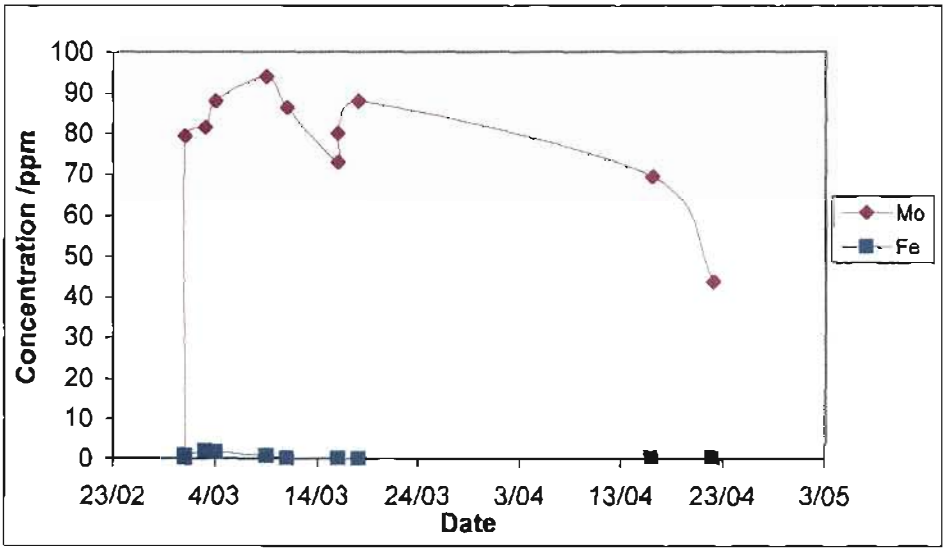


Figure 8.4 Concentration profile of T_1 for OC1

The concentrations for the Na, P and Mo at the start of OC1 were extremely low (Na 91 mg/L, P 3 mg/L and Mo 0.2 mg/L) in T_1. These were observed to increase greatly after a few hours (Na 2469 mg/L, P 3155 mg/L and Mo 79 mg/L). This is consistent with the first sample being taken before the phosphating chemicals were added to the water in the tank and the second sample being taken after solution make-up and mixing. The results for the water sample taken on the same day (Na 0.8279 mg/L, P 1.573 mg/L and Mo 0.46 mg/L, see Table 7.45) show lower Na and P levels and slightly elevated Mo levels compared to this first sample taken from T_1. This may have arisen from contamination of the newly water-filled T_1 by some of the previous process solution remaining after the tank has been emptied and (incompletely) cleaned. The presence of some ORPHOS 97 L may have contributed to the Na and P concentrations in the sample being higher than expected based on the water results. The higher Mo concentration in the water sample is likely to be insignificant at the low concentrations being measured for this element. It should be noted, however, that Mo is not a major constituent in the ORPHOS 97 L whereas it is the third most abundant element in the Chemcoater.

Chemical additions are made in order to maintain a constant concentration level in the solution. The concentration levels drop mainly because of surface reactions and chemical consumption in the coating formation and also because of drag-out. Chemical additions made on the 2nd and the 3rd of March are reflected in the increase in concentration levels measured on the 3rd and 4th of March. The next chemical addition was made on the 8th of March. This is consistent with the continued rise in solution concentration shown by the analytical results for the acidified sample. The average elemental concentrations for this cycle were approximately Na 4000 mg/L, P 3900 mg/L and Mo 70 mg/L.

The concentrations in the acidified samples, during this cycle, were slightly higher than the concentrations in the non-acidified samples. Most results, in the non-acidified samples for this cycle, differed by no more than 15 %.

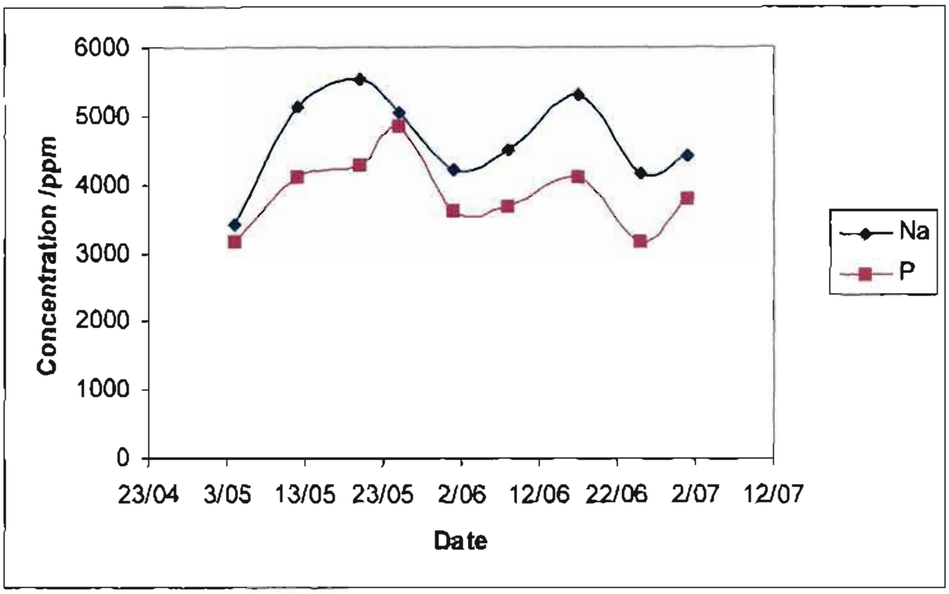


Figure 8.5 Concentration profile of T_1 for OC2

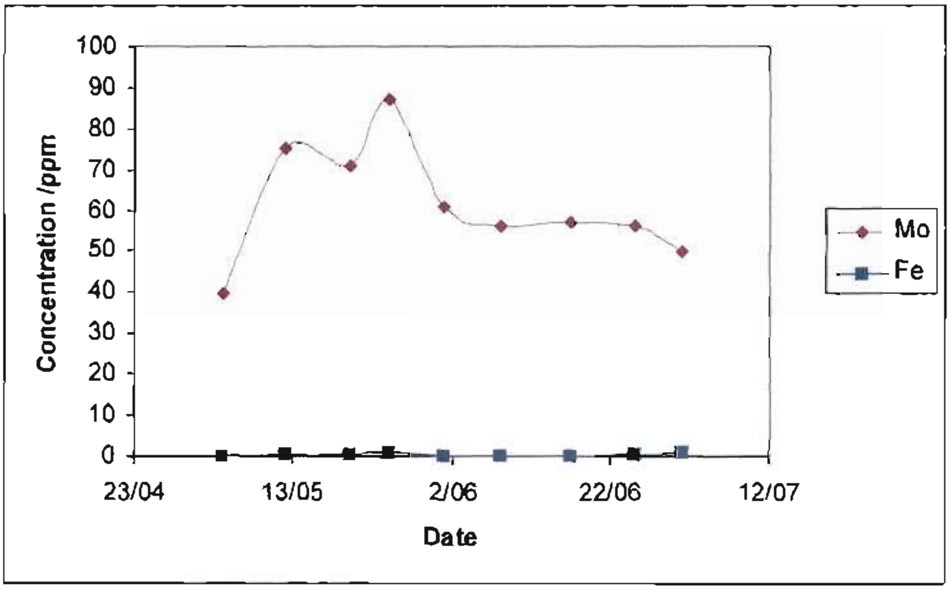


Figure 8.6 Concentration profile of T_1 for OC2

There were only two days in the period between the 23rd of April to the 3rd of May where the Paint Line was working. Therefore no samples were collected during this time. This meant that OC2 started on the 4th of May.

The Mo and P concentrations measured in both the non-acidified and acidified samples are very similar in OC2. The Na concentration would appear to be slightly higher (10%) in the non-acidified samples taken in OC2 than in the acidified samples. The average concentration values for Na, P and Mo in OC2 were approximately 4800 mg/L, 4000 mg/L and 60 mg/L, respectively.

The measured concentrations of Na, P and Mo on the 4th of May were lower than the average values recorded for OC1. On the same day a chemical addition was made to T_1 and this was followed by another addition about a week later. This is reflected in a rise in concentration over the first three sampling points as seen in Figure 8.5. Two more additions were made during this operating cycle, one two weeks later (on the 25th of May) and the next a week and half after that (on the 3rd of June). The first of these two additions was made at this time and is reflected in the highest recorded values for the Na and P concentrations (around 5000 mg/L) of the entire monitoring period. After this last addition, the solution ran for almost four weeks without any phosphating chemicals being added. This is consistent with a larger surface area being treated between SP11 and SP16 (12817 m^2) than between SP17 and SP19 (10462 m^2). The rise in concentration between the 1st and the 8th of June would appear to be consistent with the latter of the two additions made during this time.

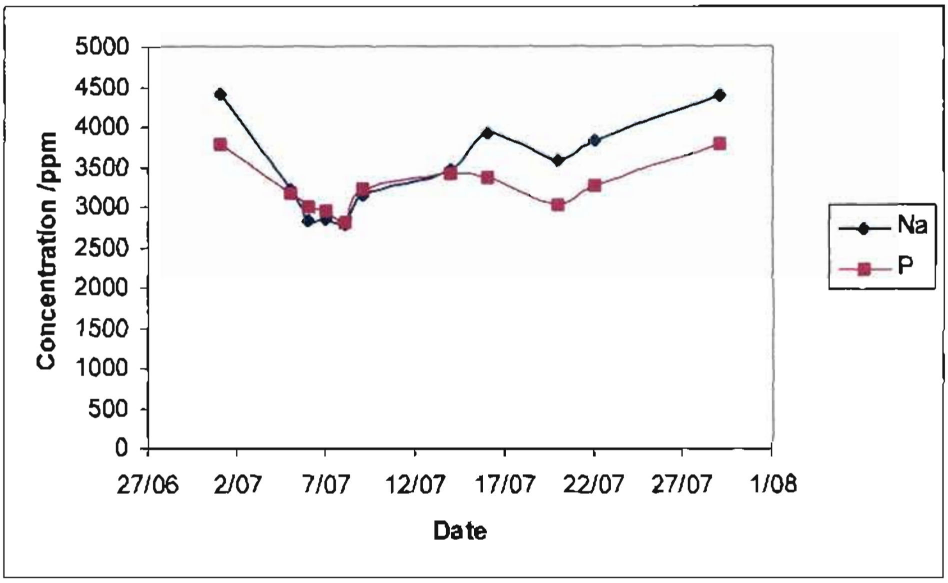


Figure 8.7 Concentration profile of T_1 for OC3

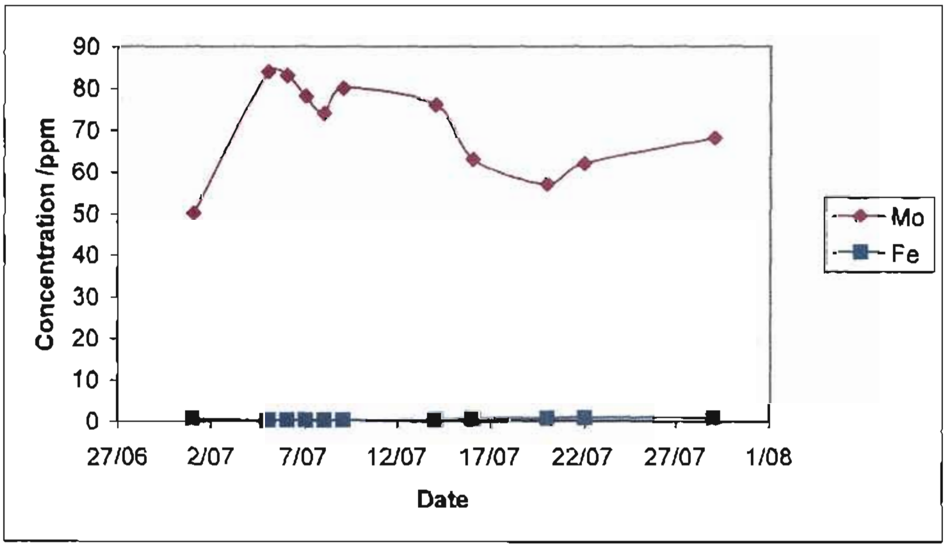


Figure 8.8 Concentration profile of T_1 for OC3

At the start of OC3, the tanks had been fully dumped, desludged and recharged with fresh chemicals and water. Between the 1st and 8th of July there was a drop in both the Na and P concentrations, in both the acidified and non-acidified samples, with the concentrations rising again on the 9th of July. This is consistent with a chemical addition being made on the 8th of July. Another three chemical additions were made during this operating cycle, with the third one being made over two consecutive days. This is consistent with a slight increase in concentration measured on the 14th, the 22nd and the 29th of July.

Between the 20th and the 29th, 37.5 L of chemicals were added to the tank and the surface area treated was 2045 m^2. This surface area was 27% (see Tables 7.2 and 7.3) lower than that treated between the 1st and 7th of July (2787 m^2). However 100% more chemicals were used to treat this lower surface area. The concentration of Na and P rose slightly between the 20th and the 29th of July from 3590 to 4380 mg/L and from 3020 to 3770 mg/L, respectively. This suggests that not all of the chemicals being added were being used to coat the surface. These excess chemicals remain in solution and are effectively wasted at this point in the process. The average concentrations for OC3 were Na 3200 mg/L, P 3100 mg/L and Mo 79 mg/L.

The Fe levels in the non-acidified samples (around pH 6) are below 1 mg/L for all operating cycles. However, for acidified samples (pH 2) the Fe concentrations lie between 8 and 20 mg/L (for most of acidified samples taken during OC3). This suggests that the lower pH causes more of the Fe released from the surface to become dissolved. However, this is not reflected in the acidified samples taken in the first two operating cycles. The highest surface area treated was in OC2 and this cycle would have been expected to show higher Fe concentrations in solution. Therefore there is no simple explanation for the trends in concentration of Fe in solution. Perhaps this is not surprising considering the complex equilibria involved in the coating reaction and the formation of the iron containing sludge. The surface area treated during OC2 was 18395 m^2 and during OC3 was 13044 m^2. These are, respectively, twice and 1.4 times greater than the surface areas treated during OC1.

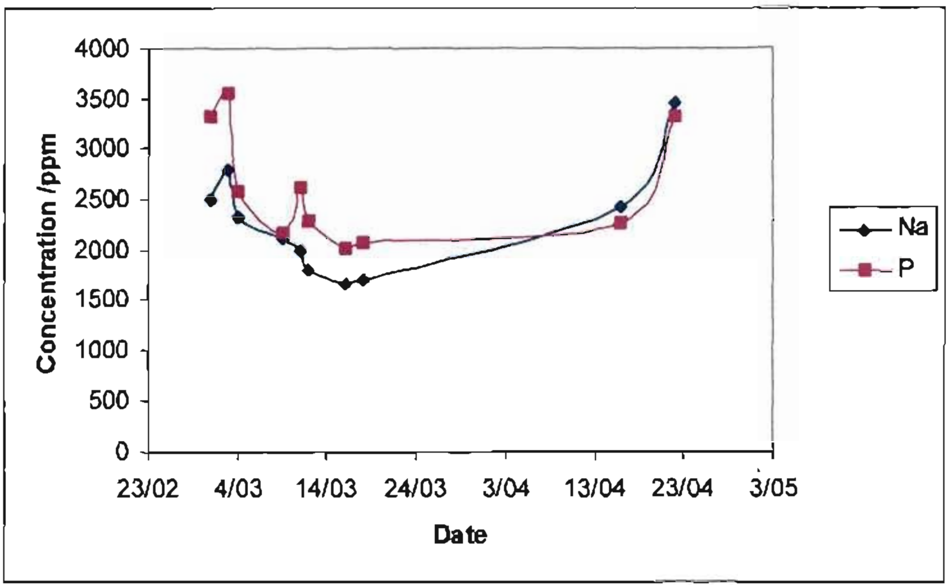


Figure 8.9 Concentration profile of T_2 for OC1

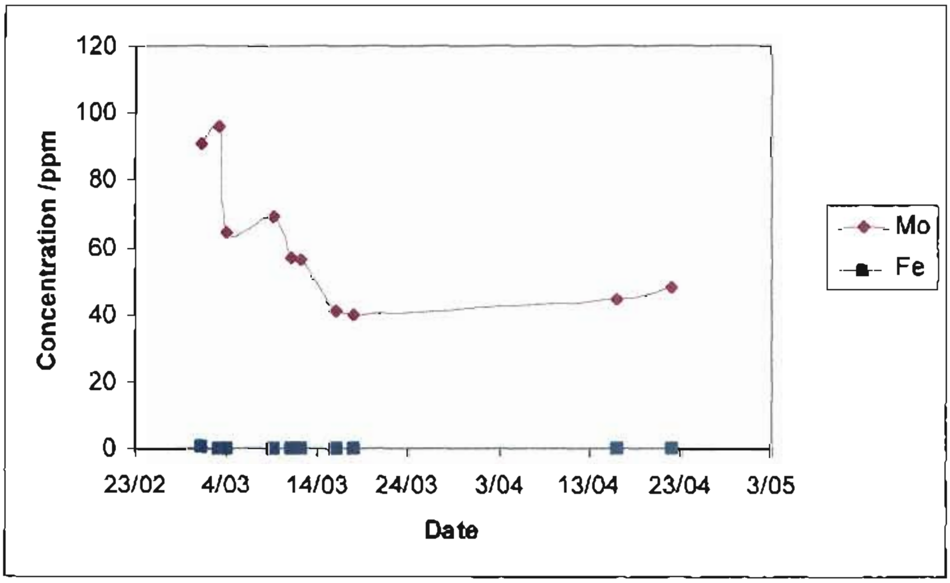


Figure 8.10 Concentration profile of T_2 for OC1

Figures 8.9 and 8.10 show, respectively, the concentration profile for Na and P and Mo and Fe in T_2 during OC1. The tank is made up with fresh phosphating chemicals on the 1st of March, after which the first sample of this second operating cycle was taken. The next addition to T_2 was made on the 3rd of March which is reflected in the rise in concentration levels of the solution constituents. For the next two sampling points (the 4th and the 9th of March) the concentration values fall. During this time a surface area of 936 m^2 was treated. A drop was also observed in SP5 and SP6 for the non-acidified samples. Chemical additions made to T_2 were made on the 8th, 9th and 10th of March, totaling 31 L. This is reflected in a rise in concentration on the 11th in the acidified samples but not in the non-acidified. The concentration continues to fall until the 16th of March when there is a rise. This appears to result from four chemicals additions: two on the 26th of March and 1st of April, and two consecutive additions starting on the 19th of April. However, no samples were taken during that time to show exactly what was happening in the solution. Sampling was not conducted during this time as chemical analysis was being carried out on samples collected for sample points one to eight. The results for the non-acidified samples display slightly lower Na and P levels but slightly higher Mo concentrations than the acidified sample in OC2. This is the reverse of the trend observed for OC1. The average elemental concentrations for this cycle were Na 2400 mg/L, P 2300 mg/L and 48 mg/L. The P concentrations during OC2 were found to be higher than the Na concentrations in both the non-acidified and acidified samples except on the 16th and 22nd of April.

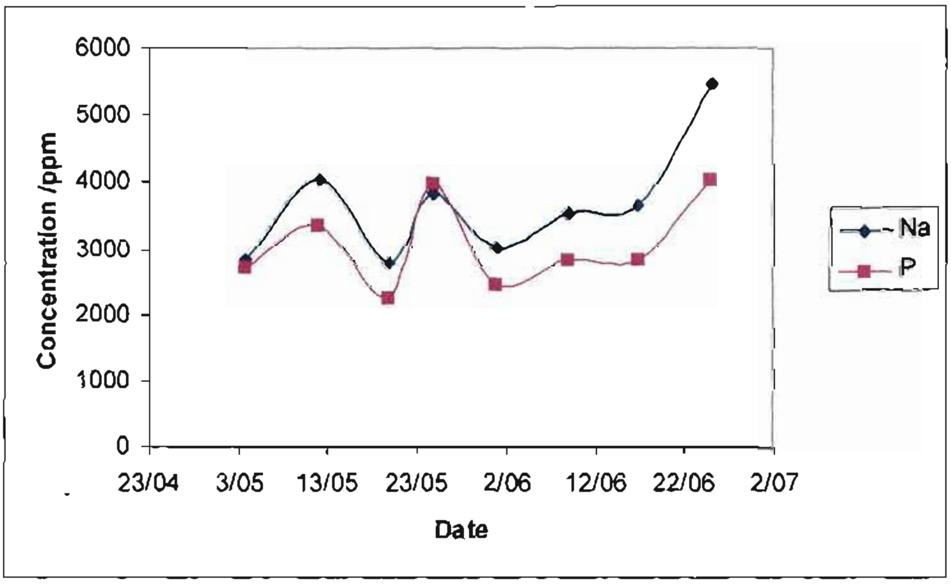


Figure 8.11 Concentration profile of T_2 for OC2

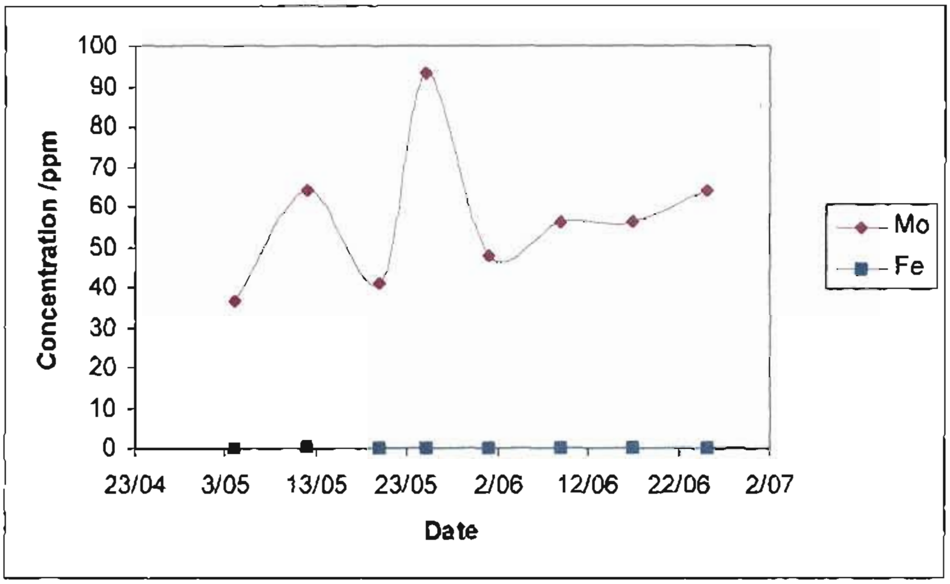


Figure 8.12 Concentration profile of T_2 for OC2

The average concentration values for T_2 during OC2 were Na 3200 mg/L, P 2600 mg/L and 60 mg/L. These values are much higher than the average concentrations calculated for OC1 in T_2, but lower than those calculated for T_1 during this cycle. The average Mo concentration, however, amounted to same value as that seen in T_1. The Na in the non-acidified samples showed slightly higher values than that of the acidified except on the 1st of June. The P concentrations were also slightly higher in the non-acidified samples, except on the 12th of May, 25th of May, 1st, 9th and 17th of June. The highest values for Na, P and Mo in the acidified samples appeared on the 1st of June. This is consistent with the chemical additions made on the 21st, 24th and 25th of May as well as on the first two sampling points of this operating cycle. Chemical additions continued to be made at least once a week thereafter to the end of OC2.

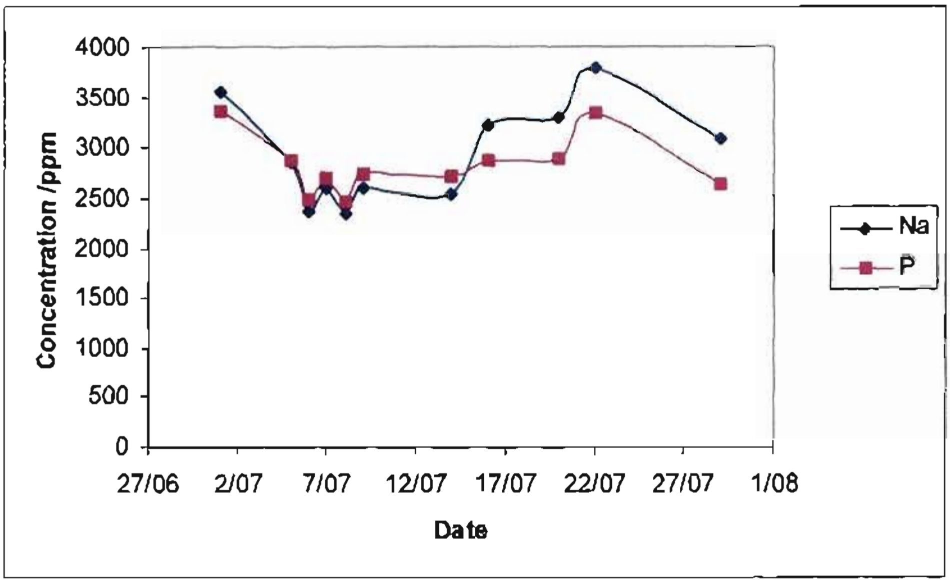


Figure 8.13 Concentration profile of T_2 for OC3

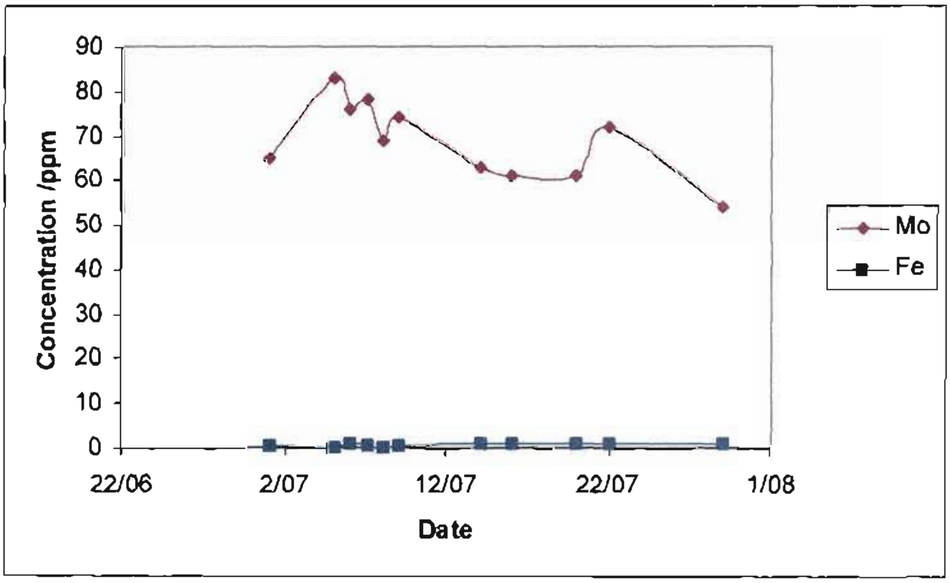


Figure 8.14 Concentration profile of T_2 for OC3

The concentration values for Na, P and Mo during OC3 were similar in both the acidified and non-acidified samples for OC3. The were two exceptions noted on the 5th and 7th of July for the Na and the P, and one noted on the 5th of July for the Mo. Na and P reached their highest concentrations on the 22nd of July. Chemical additions were made throughout this cycle and amounted to a total of 117 L. As a result there were no major fluctuations seen in the concentrations during this cycle. The average concentrations recorded during OC3 were (approximately) Na 2500 mg/L, P 2800 mg/L and Mo 70 mg/L. The P and Mo concentrations were higher those seen for OC2; however, the Na was found to be lower than that obtained in OC2. The average concentrations for T_2 were approximately 17% lower than that of T_1. This is inconsistent with the fact that twice as much chemicals were added to T_2 than T_1 during this cycle.

The Fe levels, in both T_1 and T_2, for the non-acidified samples for all three operating cycles were below 1 mg/L, except for 4 occasions. For the acidified samples the Fe concentrations in the first two cycles were also below 1 mg/L, however, during the OC3 the concentrations ranged from 1 mg/L to 25 mg/L.

The chemical analysis has shown the Chemcoater to be a Mo containing phosphating agent. Derivatives of Mo have been used as accelerators and sealants in phosphating solutions. The iron phosphating solution presented in Table 2.2 is a simple phosphating system. The P and Mo concentrations, recorded for T_1 and T_2 are consistent with that for a multi-metal phosphating solution and as such are qualitatively and quantitative different from the values that are shown in Table 2.2.

8.1.2 Characterisation of the Rinse Solutions

In this section the levels and trends of contamination in the rinse tanks for the three operating cycles (OC1, OC2 and OC3) which occurred between the 26th of February to the 29th of July 2004 will be discussed. The concentration profiles for rinse Tanks 3 and 4 were plotted and are presented in Figures 8.15 to 8.20 and Figures 8.21 to 8.26, respectively.

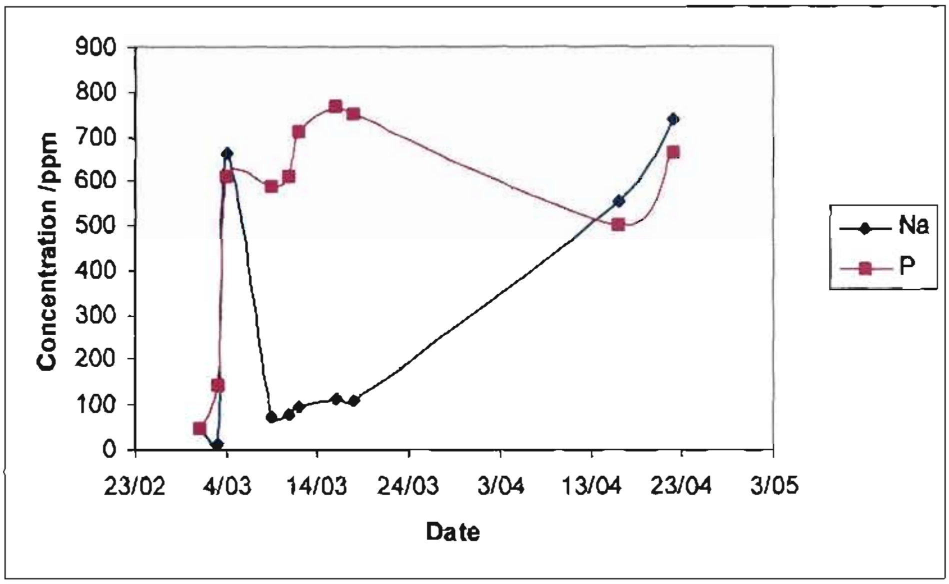


Figure 8.15 Concentration profile of T_3 for OC1

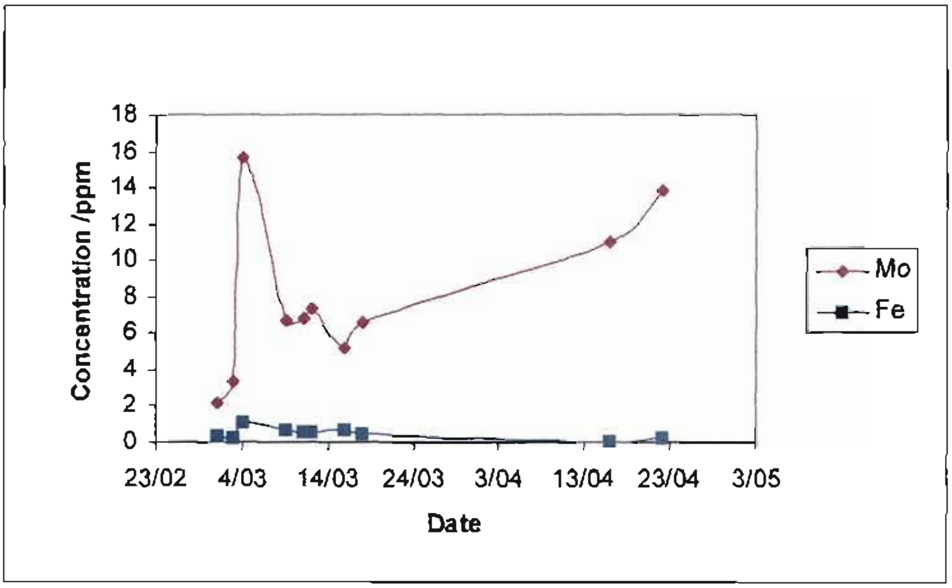


Figure 8.16 Concentration profile of T_3 for OC1

At the start of OC1 all tanks were dumped and T_3 and T_4 were filled with fresh water. The concentrations of Na, P and Mo, in both these tanks, were found to be much higher than the concentrations found in the water sample (Na 0.8 mg/L, P 2 mg/L and Mo 0.5 mg/L). This was consistent with the situation observed for T_1 on that day. No sample, prior to make up was obtained from T_2 on that day. The water in the rinse tanks becomes polluted when phosphating chemicals, by-products and impurities in the rinse solutions are dragged in from the process solutions. The concentrations of Na, P, Mo, Fe, Mn and Zn were expected to rise due to drag-in from T_2.

On the 4th of March a high Na concentration was recorded in both the non-acidified and acidified samples. These concentrations are not in keeping with the observed trend for Na levels in OC1. It is thought that this is not a true reflection of the Na solution concentration on that day and there was some instrumental error in measuring the concentration.

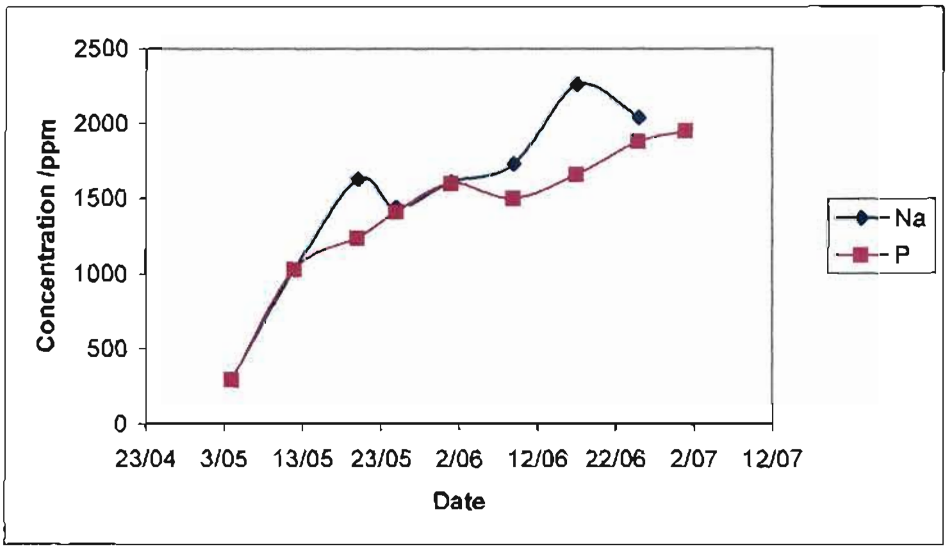


Figure 8.17 Concentration profile of T_3 for OC2

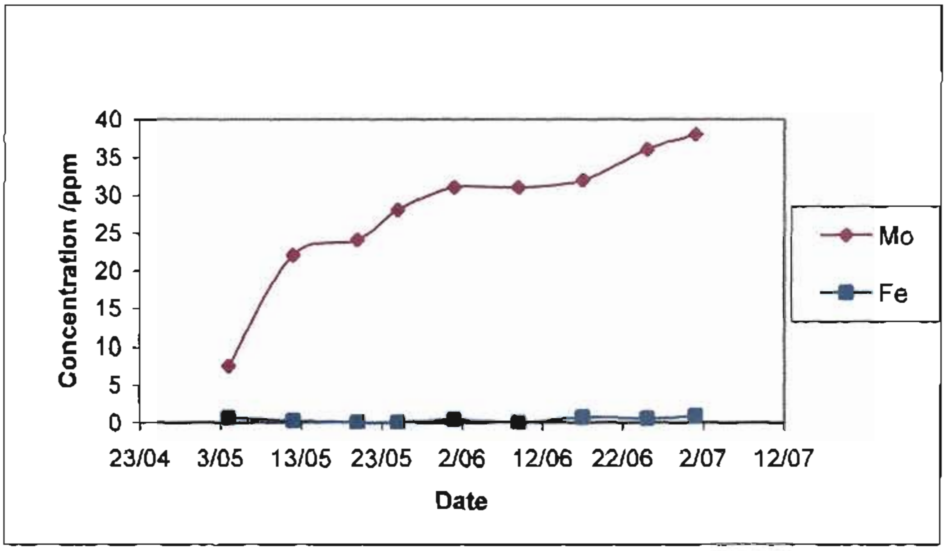


Figure 8.18 Concentration profile of T_3 for OC2

Between the end of OC1 and the start of OC2 the rinse tanks were partially dumped. This is reflected in the concentration levels of Na, P and Mo measured for the first sample taken at SP11 (4th of May). Respective values of 300 mg/L, 300 mg/L and 8 mg/L were recorded at the start of OC2 and were about half of those found at the end OC1. These values rose steadily through the operating cycle, which was expected as the rinses appeared to have a static flow during this cycle. Thus the contamination levels can be attributed to the large surface area processed during this cycle (18395 m^2, see Table 7.2). Both the acidified and non-acidified samples reflected similar concentration values for the Na, P and Mo.

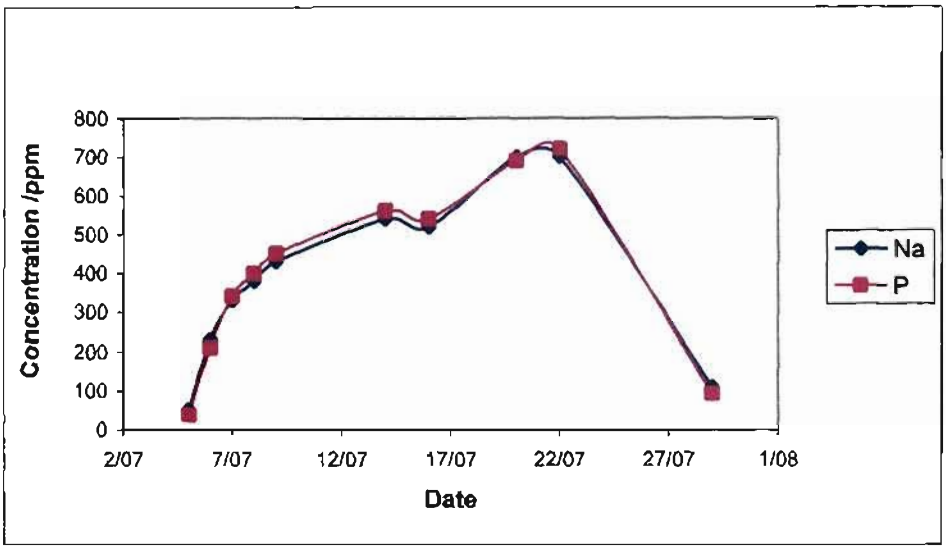


Figure 8.19 Concentration profile of T_3 for OC3

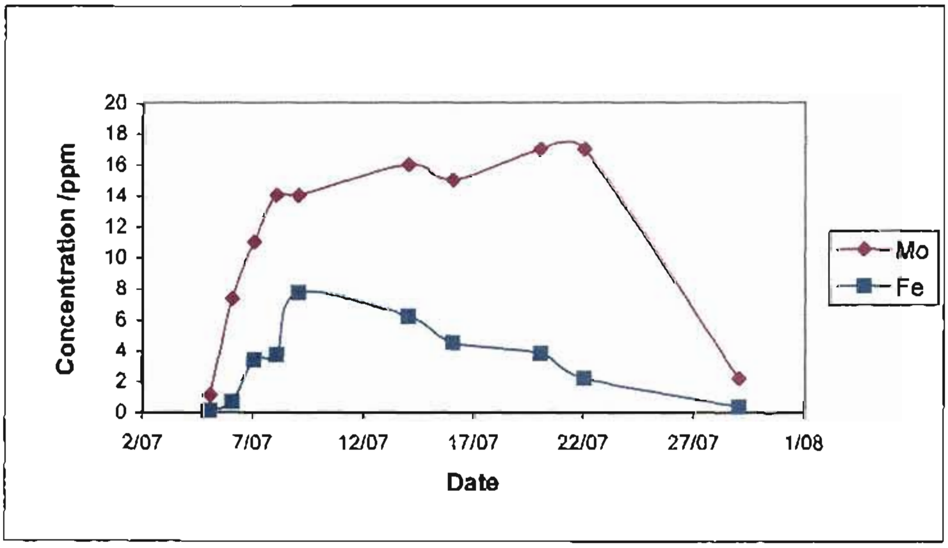


Figure 8.20 Concentration profile of T_3 for OC3

At the beginning of OC3 the tanks were fully dumped and desludged. This is reflected in the steady rise in concentration levels throughout the cycle, before they dropped on the 29th of July the last SP in OC3. The rinses were static during this time, so no flushing of the system took place to dilute the rinse water. The Na and P levels peaked at approximately 800 mg/L, and the Mo level at 17 mg/L, on the 22nd of July, before dropping to 110 mg/L, approximately 90 mg/L, and 2.2 mg/L, respectively. This was attributed to at least a partial dump which took place on the 22nd of July.

The Fe concentrations in T_3 remained below 1.5 mg/L for the first two operating cycles. However in the third cycle these concentrations increased, with irregularities occurring between the non-acidified and acidified samples. This discrepancy could be due to the possibility that the company might have slowed down the conveyor system and the workpieces were spending more time in contact with the process solution, however we have no means of assessing this parameter. There was considerable work going through the line so perhaps more time was needed to load and offload the workpieces from the conveyor system. Hence it was run at a slower speed. Thus more Fe could have been transferred from the substrate to the solution from prolonged contact between the steel substrate and the phosphating solution i.e prolonged contact between the substrate the solution means more Fe in the steel is able to react with the phosphoric acid and form iron(II) complexes in the solution and the sludge.

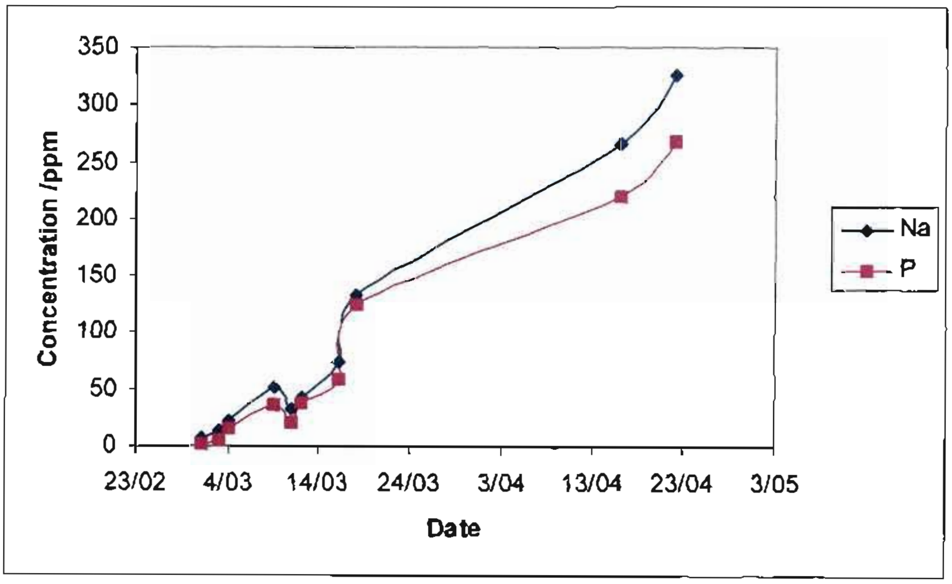


Figure 8.21 Concentration profile of T_4 for OC1

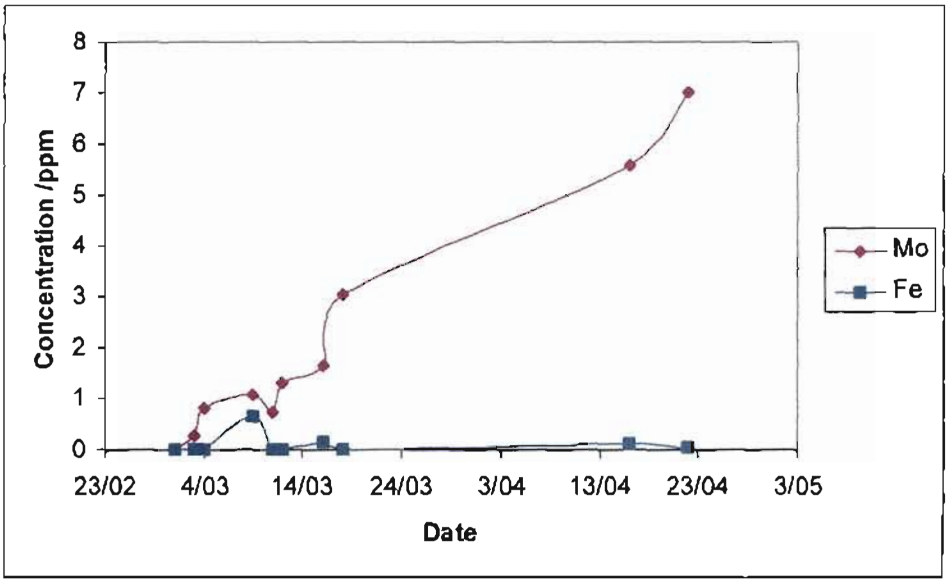


Figure 8.22 Concentration profile of T_4 for OC1

For all three operating cycles the concentration levels in T_4 were lower than those found in T_3. This is because the solution in T_4 is used as a second rinse following T_3 and so most of the rinsing and dilution of the process solution occurs in T_3. This means the drag-in concentration to T_4 is less than for T_3. The solution concentrations measured were 7 mg/L Na, 1 mg/L P and 0.006 mg/L Mo (see Table 7.34) at the start of OC1 and rose steadily through the cycle. These elements reached their maximum values on the 22nd of April at approximately 400 mg/L, 300 mg/L and 8 mg/L (see Table 7.35) respectively, while for OC3 the corresponding values were respectively 550 mg/L, 470 mg/L and 16 mg/L (see Table 7.36). A similar trend was observed for OC2. However the highest concentration levels were observed two weeks before the end of the cycle, after which the concentration levels fell. This is consistent with a surface area of 4894 m^2 which were treated between these two weeks.

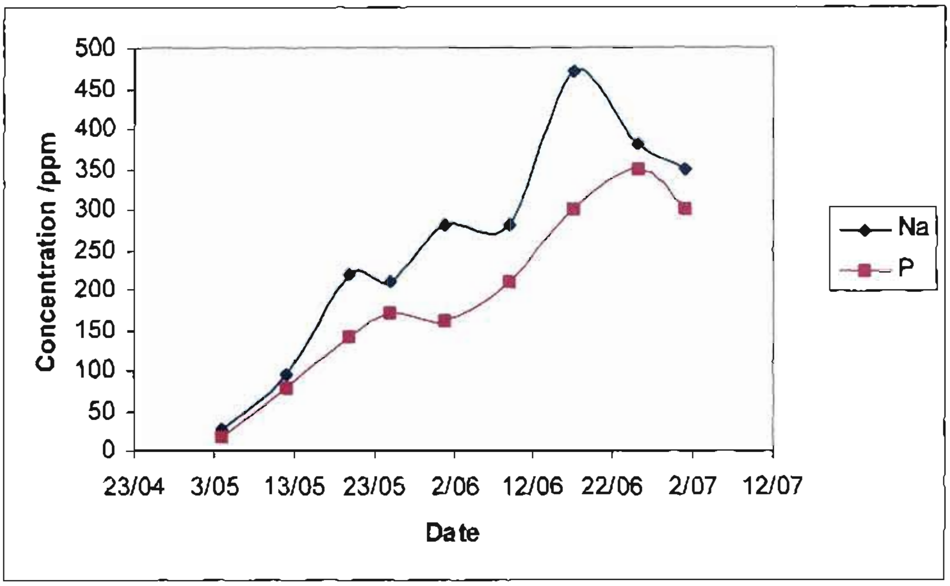


Figure 8.23 Concentration profile of T_4 for OC2

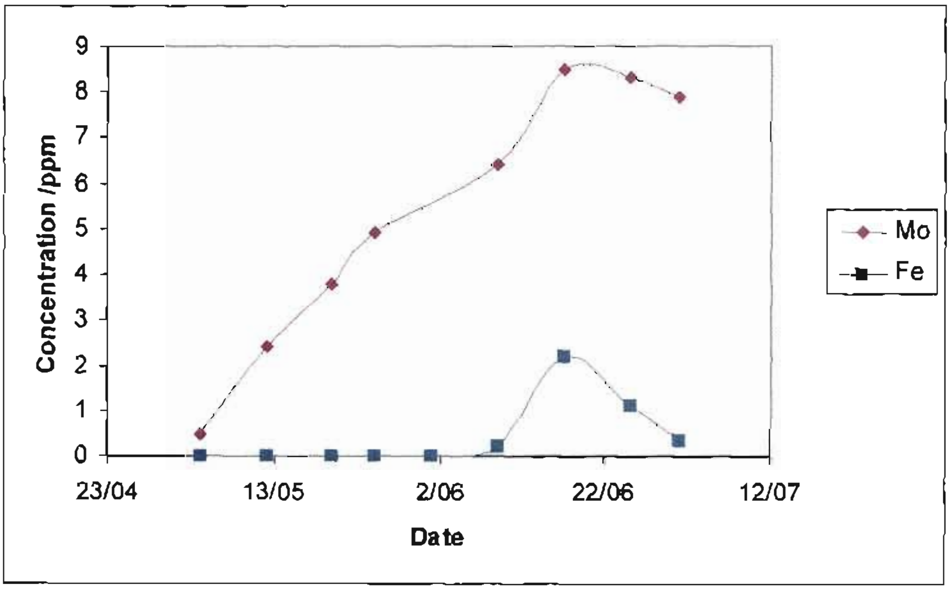


Figure 8.24 Concentration profile of T_4 for OC2

Due to the partial dump at the beginning of OC2 the concentrations of Na, P and Mo were expected to be less than the concentrations found on the 22nd of April (end of OC1). This was observed to be the case and a dilution factor of fifteen was observed between the end of OC1 and the start of OC2 for T_4 (a dilution factor of two was observed in T_3

over the same time period). The concentrations of all three elements rose through the cycle until Na and Mo reached their peaks on the 17th of June and P on the 25th of June.

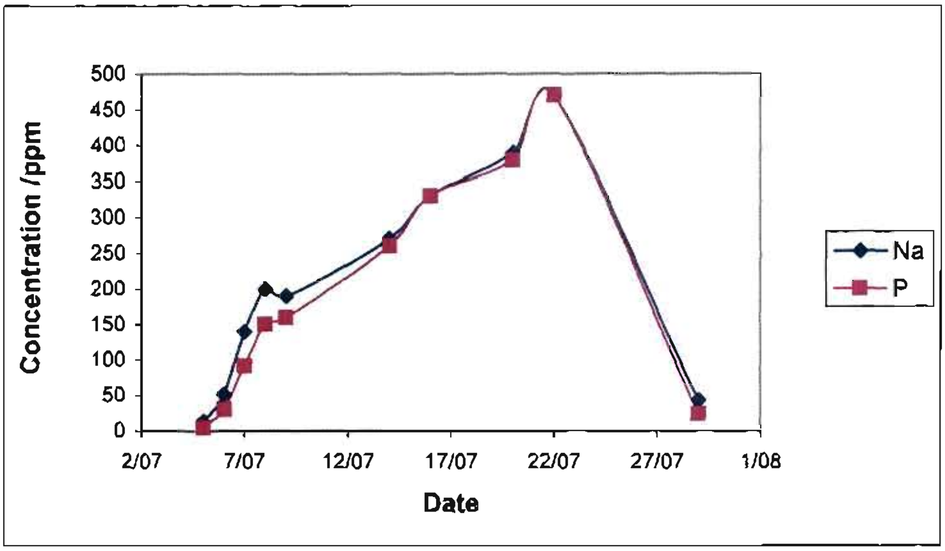


Figure 8.25 Concentration profile of T_4 for OC3

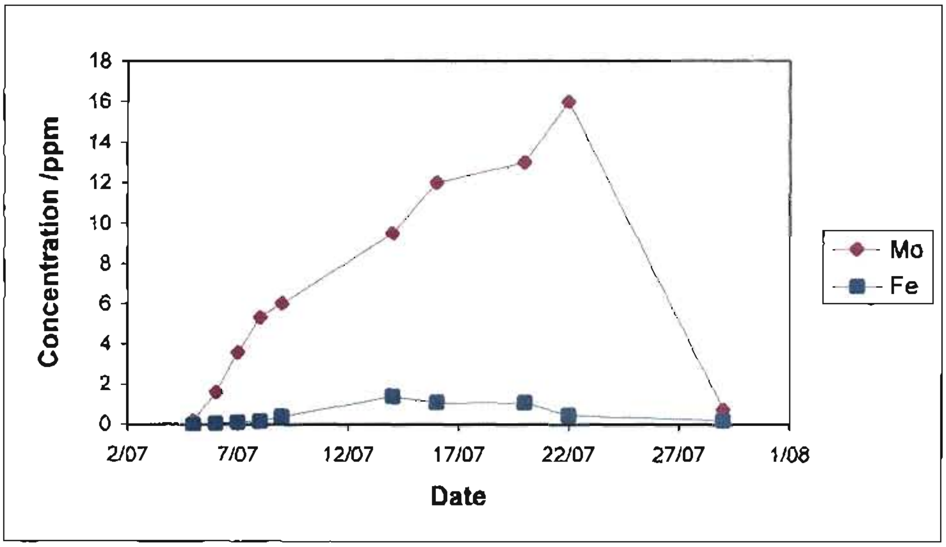


Figure 8.26 Concentration profile of T_4 for OC3

The full dump (which took place on the 2nd of July) was once again reflected in the low concentrations of Na, P and Mo found on the 5th of July, the start of OC3. The concentrations in both the non-acidified and the acidified samples then increased through the cycle until reaching their highest levels on the 22nd of July. This was consistent with the situation found in T_3 during OC3. In T_4 the Fe concentration during OC1 remained below 1 mg/L in both the non-acidified and the acidified samples. The non-acidified concentrations did not compare well with the acidified samples during the OC2. Differences of approximately 80% were noted on the 17th and 25th of June and on the 1st of July. During OC3 the acidified sample concentrations, as in T_3, were found to be between 70% and 95% higher than the non-acidified samples. In addition, the concentration values observed for Fe during this cycle were higher than those for the first two operating cycles. The Fe concentrations reached a value of 17 mg/L in OC3 but never exceeded 1 mg/L in OC1 and OC2.

The elemental Cr concentrations were only measured for T_3 and T_4 (see Table 7.40). In all cases the Cr concentrations were below 0.05 mg/L. These solutions are discharged to the drain as waste water when the rinse water is dumped and maybe considered largely Cr free. However, it is clearly stated in Table 8.2 that no Cr(IV) can be discharged to the sewer. The determination of Cr in these samples was not specific enough to be sure there was no Cr(IV) present at very low levels.

8.1.3 Characterisation of Effluent Samples

According to the 1998 trade effluent by-laws, no individual or industry can discharge substances into the sewerage system in concentrations that exceed limits specified by the Pietermaritzburg – Msunduzi Transitional Local Council. The substances and their corresponding limits are shown in Table 8.2.

Table 8.2 Effluent concentrations limits for substances discharged into the sewer[185]

Substance	**Concentration (mg/L)**
Solids in suspension	400
Grease and mineral oil, tar and tar oils not dissolve in the aqueous phase	50
Animal and vegetable oils, fats or waxes	250
Total Sulfates (SO_4)	250
Sulfides (S)	25
Copper (Cu)	5
Nickel (Ni)	5
Zinc (Zn)	5
Cadmium (Cd)	1
Cobalt (Co)	5
Chromium {Cr(III)}	25
Chromium {(Cr(VI)}	0
Hydrocyanic acid and cyanides or other cyanogens compounds (HCN)	10
Molybdenum (Mo)	1
Lead (Pb)	5
Mercury (Hg)	1
Phosphate (P)	20
Arsenic (As)	1
Boron (B)	5
Fluoride (F)	5
Free and saline Ammonia (N)	80
Selenium (Se)	1
Total Dissolved Solids	5000
Total Sugars and Starch	1000
Total Kjedahl Nitrogen	100

The concentrations of all the elements in the acidified effluent samples were higher than those for the non-acidified effluent samples. This is contrary to what was observed in the rinse solutions where elemental concentrations were very similar. Except for two non-acidified effluent samples that were taken (1st and 3rd of March), the measured P concentrations for all samples exceeded the limit value. These initial low values are consistent with the concentrations of the process solutions still stabilising during this time and T_3 and T_4 being largely operated as flowing rinses. The Mo concentrations in the effluent were observed to be over the limit value in most of the samples and again it is only in samples taken early in OC1 where they were observed to be below the limit.

In all three operating cycles the rinses were dumped at the end of each cycle. Consequently spent rinses can regarded as the main effluent stream from the Phosphating

Line. The recorded concentrations for P and Mo in T_3 solutions exceeded the effluent discharge limits for the full monitoring period. At the end of OC2 time the P concentrations were over 80 times the discharge limits and the Mo concentrations were over 35 times the discharge limit. At the end of OC1 and OC3 the P concentrations were around 35 times the discharge limit and the Mo were around 15 times the discharge limit. These differences are consistent with slow flowing of the rinse water in OC2. Flowing rinses were observed to be used most often in OC1 and to some extent in OC3. This is reflected in the lower P and Mo concentrations in these rinse waters. Similar trends were observed for T_4. The P concentrations exceeded the limit values by a factor of 15, while Mo values were approximately 8 times the limit value.

Umgeni Water monitors the effluent once a month for free. They do measurements including pH and conductivity on-site. Umgeni Water also takes effluent samples on a monthly basis for chemical analysis (which would include phosphate levels). If it is found that the effluent discharge limits are being exceeded, Umgeni Water first gives a warning and then they carry out a second monitoring exercise for which the company is charged around R200. Based on effluent from flowing rinse solutions and waste water from the rinse tanks at dumping it would seem that the company is very likely to incur these costs. Their metal monitoring is limited to six metals, namely Cu, Zn, Pb, Cd, Ni and Cr and takes place every three months. The Zn levels in the effluent and waste rinse water were below the discharge limit and therefore should not be a liability for the company. The sewage charge is based on the formula given in Equation 8.1.

$$C = (V \times X) + V \times 0.357(COD - 350) \times Y \qquad \text{Equation 8.1}$$

Where C = the cost charged on the effluent in R

V = the volume of effluent discharged in kL

X = the rate charged based on the volume of effluent discharged in c/kL

0.357 = the factor for aeration of effluent

COD = the chemical oxygen demand in mg/L

350 = the strength of domestic sewage

Y = the phasing in factor for the implementation of the trade effluent equation, and has increased to a value of 1 from 0.33 since 2001

Inconsistencies in the units used in Equation 8.1 have been noted and questioned but no satisfactory explanation has been given for those e.g. COD and Y.

X is the rate charged as follows: for $0 < V < 400$kL, X= 3.62 c/kL
for $401 < V < 1000$, X = 3.38 c/kL
for V> 1001kL, X = 2.79 c/kL

A maximum charge of R14555.00 is levied for contravening the effluent bylaw discharge limits.

8.1.4 Characterisation of Sludge Samples

Sludge samples were obtained on the 2nd of July when the tanks were dumped at the end of OC2. Sampling was carried out randomly, i.e. when the sludge was made accessible. Further it was impossible to ensure that the sludge was completely mixed prior to sampling. The sludge was being manually bailed out of the tanks into 250 L drums using buckets. Forklift trucks were then used to remove these drums and replace them with empty ones. There was no way of keeping the 250 L drums agitated during lifting. The average Fe concentration in the sludge samples is about 710000 mg/L, showing that the Fe has been precipitated from the solution and ended up in the sludge. The Zn composition of the sludge is about a quarter of the Fe value while the Mo and Mn are about a tenth of the value of the Fe. The P content of the sludge is about half that of the Fe.

The concentrations of P, Fe and Mn in the sludge samples are higher than the acceptable respective concentrations of 0.1 mg/L, 9 mg/L and 0.3 mg/L, published by the Department of Water Affairs and Forestry.[93] These limits are described as the maximum values for which no risk will be caused to the environment.

8.1.5 TDS, SS and Conductivity Determination

TDS is the portion of the total solids in a liquid sample that are soluble in a solution. SS are finely divided particulates in the sample which are not dissolved but remain dispersed in solution.[186] In the laboratory the suspended solids were recovered on a filter after the sample had been filtered. The total dissolved solids were then obtained by evaporating off the water present in the filtrate. Tables 7.11 to 7.14 show that there is an anomaly between the TDS values obtained by gravimetry and those readings obtained on the meter. The results from the gravimetric determination of TDS were found to be about a factor of 4 higher than the values obtained using the direct reading instrument. Conductivity has been related to the TDS by the formula shown in Equation 8.2

$$\mathrm{TDS}\,(\mathrm{mgL^{-1}}) = F \times \mathrm{Conductivity}\,(\mu\mathrm{s/cm}) \qquad \text{Equation 8.2}$$
$$0.55 < F < 0.9^{186}$$

The factor F was calculated for both the gravimetric and direct reading instrument results, and found to be 1.5 and 0.45 respectively. However, Equation 8.2 has traditionally been applied to environmental samples containing Na, Ca and Mg ions rather than to industrial samples containing heavier metals such as Zn, Mn and Mo. Therefore, the accuracy of Equation 8.2 in relating TDS and conductivity is questionable for industrial samples where the mobility of the metal species is likely to be lower than that in environmental samples.

Further more, great care was taken in obtaining these TDS results. For example good agreement was obtained in the laboratory between the expected value of the TDS measurement and that for the standards. A vented oven was used to evaporate off the water and this was in good working order. Mass measurements were taken until concordant results were obtained so it was unlikely that any water was retained in the sample. Gravimetrically determined TDS values for T_3 and T_4 prior to the rinse water dump on the 22nd of April, the full dump on the first of July and the rinse water dump on the 22nd of July were 8.4 g/L and 1.8 g/L, 9.4 g/L and 1.5 g/L, and 3.8 g/L and 2.6 g/L, respectively. These values are considered to be the amount of TDS that would be discharged to the effluent when dumping takes place. The first two values for T_3 (OC1 and OC2) exceed the limit value of 5 g/L in Table 8.6. The other values all fall below the limit value. The TDS values were observed to rise during each operating cycle following the trend shown for elemental composition in solution. The literature shows a range of TDS values for effluent emitted from phosphating processes. The highest value quoted was close to 4 g/L, which is higher than four of the values presented here.

The conductivity in the process solutions ranged between 9000 and 14500 µS/cm for T_1, while for T_2 it ranged between 8000 and 12500 µS/cm. The average conductivity values during the monitoring period were approximately 12000 µS/cm and 9000 µS/cm, respectively (for T_1 and T_2). The conductivity readings recorded for T_3 and T_4 increased during each operating cycle. This parallels the trend seen in the elemental analysis for these two tanks (see Tables 7.28 to 7.39). For T_3 the conductivity values at dumping were close to 7000 µS/cm for OC1 and OC2 and to 3000 µS/cm for OC3. The limit value of 4000 µS/cm[185] has therefore been exceeded by the time T_3 is dumped. For T_4 the conductivity values range between 1500 and 1900 µS/cm at the end of each operating cycle. These values are below the limit value for conductivity. Solutions with pH values less than 6.5 should not be released into the sewerage system. In the case of the process solutions the pH would be too low for dumping without treatment. However, for the rinse solutions this is only a problem for T_3 solutions.

8.2 Scoping Audit

Table 8.3 shows the results obtained from a scoping audit performed on seven quantities consumed and produced over one year.

Table 8.3 Scoping audit

Resources & Services	Quantity	Units	Cost (R)/ Year	Priority (1=Highest)	Scope to Save %	Scope (min)	Scope (max)
Raw Materials							
Steel	1570668	unit	8827154	1	1-5	88272	441358
Powder	24088	kg	825854	2		8259	41293
Paraffin	70800	L	183372	4		1834	9169
Chemcoater	2190	L	18440	8		184	922
Utilities:							
Water	1953	kL	15070	3	20-80	3014	12056
Waste:							
Effluent	1876	kL	6968	5	20-80	1394	5574
Domestic waste	21	kL	9196	6	10-50	920	4598
Factory waste	24	skips	3600	7		360	1800

Each resource in column 1 of Table 8.3 was allocated an annual production or consumption quantity and a costing. These values were obtained using the formula shown in Equation 8.3.

$$\text{Annual quantity} = \text{Quantity for the monitoring period} \times \frac{236\,\text{days}}{\text{Monitoring period}} \qquad \text{Equation 8.3}$$

Only the purchased powder goes into the factory store from which it is requisitioned by the Paint Line. The steel purchased goes straight to the Roll Mill Department. The paraffin is delivered into an underground storage tank and the water is piped straight into Phosphating Line and to four taps situated around the factory.

The steel consumption was calculated from the quantity purchased from the supplier (see Table 7.5). This quantity was obtained for the full monitoring period and was then converted to an annual amount using Equation 8.3.

The powder consumed during the monitoring period was assumed to be the same as the quantity of powder issued from stores to the Paint Line. The mass of powder used over the 236 days was based on that requisitioned by the Paint Line for the full monitoring period and calculated as that used for 236 days using Equation 8.3.

Paraffin readings were only recorded from the 28th of June to the 19th of July (16 days). Thus, the amount used in the process was calculated by converting the quantity used during this time (4800 L) to an average quantity per day. This average was then scaled up to the amount used over 236 days (see Table 7.5).

The amount of Chemcoater used on the Paint Line was calculated from the chemical additions (see Table 7.4) and the amount used in the initial make-up and subsequent recharging of the tanks. Recharging took place once during the full monitoring period and the solution volumes used were equal to that used at the initial make-up. This value was then converted to an annual volume using Equation 8.3.

The water consumption was calculated from the Msunduzi Municipality Tax Invoices. Five of these invoices were collected during the monitoring period. From these invoices a daily water consumption was then calculated. This value was then used to derive volumes that would have appeared in the first month of 2004 and the remaining seven months of the year. This was done because the tariff charged per kL of water increased from R6.45 to R7.10 during the last month of the monitoring period. The annual quantity and cost was based on the period starting from mid December 2003 to mid December 2004. The same procedure was followed for the effluent to account for this tariff rise from R3.16 to R3.38 per kL for the first 400 kL of effluent discharged. The amount of effluent discharged monthly is equivalent to the amount of water consumed.

The company produces three solid waste streams and one liquid waste stream. These are known as:

- factory waste
- domestic waste and scrap metal, and

- an effluent stream.

The factory and domestic waste constitutes the solid waste of the company. The upliftment and removal of the domestic waste is carried out by the City Engineers – Waste Management Department and the charges appear on the invoices. Upliftment is done on a weekly basis and the waste is disposed of at the landfill site situated on New England Road. The City Engineers Department charge a standard weekly tariff for uplifting a 1.75m^3 bin. This tariff had a value of R144.30 for the period from the 1st of July 2003 to 30th of June 2004. On the 1st of July 2004 this tariff increased to R165.94.[187] For invoicing these values are converted to a monthly value (see Equation 8.4) onto which VAT is added.

$$\text{Cost of Removal} = \text{Tariff} \times \frac{52\text{weeks}}{12\text{months}} \qquad \text{Equation 8.4}$$

Thus the annual quantity of solid waste disposed was based on the upliftment of one 1.75 m^3 bin per month. The total cost was calculated using the tariff of R144.30 for the first six months of the year and the tariff of R165.94 for the remaining six months.

Factory waste is collected in two skips and removed by a private contractor. No invoices were available for viewing during the monitoring period. However the line supervisor priced this service charge as R300 per month.

The scrap metal is sold on to a dealer and does not appear in the scoping audit.

Table 8.3 shows that the greatest financial savings, represented by the maximum scope to save, can be made through a reduction in the steel consumption. The second most significant waste problem appears to be caused by the powder. The third greatest scope to save can be achieved by reducing water consumption. This lowest scope to save is shown by the Chemcoater consumption. Most of the water and all of the Chemcoater are only used on the Phosphating Line.

8.3 Mass Balance Analysis

There are two sets of data on factory water usage, one new and one existing, which will be considered in this discussion. One comprises the volume and cost of the water used by the whole factory as shown on The Msunduzi Municipality Tax Invoice. This is billed on a monthly basis. This water consumption is made up of water used on the Phosphating Line, domestic water consumption in the ablution block and in the kitchen, water usage in other departments, in heat exchangers and floor washing, and water used outside for gardening (see Equation 8.5).

$$F = PL + D + O + G \qquad \text{Equation 8.5}$$

Where F = Incoming water supply to the factory
PL = Water used on the Phosphating Line
D = Water used in the ablution block and in the kitchen
O = Water used in heat exchangers, floor washing and other departments
G = Water used in gardening

Total water inputs to the Phosphating Line were measured through water meter readings. The breakdown of water usage for the Phosphating Line can be calculated according to Equation 8.6. All water volumes are expressed in units of kL.

$$PL = R + FR + P + AR + AP + S - E - DO \qquad \text{Equation 8.6}$$

Where PL = Volume of water coming into the Phosphating Line
R = Volume of the static rinse water
FR = Volume of the flowing rinses (manual water additions)
P = Volume of the solvent water in the process solution
AR = Volume of the automatic water additions to rinse bath
AP = Volume of the automatic water additions to process solutions
E = Volume of water evaporated from solutions
DO = Volume of drag-out

S = Volume of water contained in recovered sludge

The contributing terms R and P are the make-up volumes used to charge the empty tanks at the start of each operating cycle. The water additions have been classified as manual, FR, or automatic, AR and AP. Designation of these terms is based on water meter readings and effluent flow characteristics discussed in Section 8.4.1. Water additions are made to replace water losses from drag-out and evaporation. Drag-out volumes are discussed in Section 8.4.2. Evaporation losses have been quantified in the literature for hot process solutions such as those found in Cr plating.[149] These have estimated to have a value of around 3% of the inflow rate which in this case would be the water additions namely FR, AR and AP. The moisture content of the sludge which is a byproduct of the coating reaction was estimated during sludge analysis.

Mass balance analysis is carried in Section 8.3.1 to determine the various uses of water in the factory and on the Phosphating Line.

8.3.1 Total Water Usage and Breakdown

Water is an important commodity for the pre-treatment process of any powder coating plant. In the Paint Line mains water is used in the two process tanks and the two rinse tanks of the Phosphating Line. Water is used in these tanks for refilling the emptied tanks after dumping the contaminated and exhausted process solutions and rinse water. Water is used as a solvent in the process tanks in order to dissolve the phosphating chemical. In the case of the rinse tanks, water may also be running through the rinse tank. This is termed a flowing rinse (FR see Equation 8.6). There is a continuous flow of clean mains water into the rinse tanks and an outflow of dirty rinse water (wastewater or effluent) to the drain. Water can be confined to the rinse tank with no continual exchange of dirty for clean water and this is termed a static rinse (R see Equation 8.6). Contaminants in the rinse water originate from chemicals such as raw materials, impurities in the raw materials, by products and soils released from the surface of the workpieces. Water is also used to replace evaporation (E see Equation 8.6) and drag-out losses from the process (DO see Equation 8.6) and rinse tanks.

The process operated with the concentration of chemicals kept within a specified range. The concentrations of chemicals used in the process solutions are operated within a specified range. However, for phosphating solutions the chemical supplier does not specify these in terms of elemental or chemical composition. Since chemicals and/or water are lost due to surface treatment reaction, drag-out, evaporation, sludge precipitation and decomposition reactions, regular addition of chemicals and water (AR and AP in Equation 8.6) are made to each solution to restore the concentration to the specified level. Often the chemical additions are recorded whereas the volume of water added is not. However, the water additions can be roughly calculated using Equation 8.7 given below if the chemical additions are known and the overall concentration of the process solution is maintained at the specified level. The total amount and the function of the water used in the flowing/static rinse tanks and the process tanks of the Phosphating Line in a year were estimated based on the following assumptions:

- the solution volume in all tanks was assumed to be the volume of the individual tanks minus the headspace volume (see Table 6.3 in Section 6.2). The process and rinse solutions are assumed to contain this volume on dumping
- the water flow rate entering and leaving the phosphating line were assumed to be equal. There was no water meter measuring the incoming water to each individual tank. The water pipes supplying each tank were fixed in position. It was therefore impossible to measure the water entering individual tanks directly
- occasions when the rinses were flowing were identified as being when the effluent stream was running and water consumption was significant. This was consistent with water additions being manually controlled through opening of the tap on the tank inlet to the mains supply
- static rinsing was identified as being when no effluent was flowing and water consumption was relatively low (about a factor of 10 less than that for flowing rinses). This was consistent with water additions being made automatically through the ball-cock system

- water additions made to replace the water lost due to drag-out, evaporation and sludge precipitation in the process solution were estimated using Equation 8.7

$$\text{Volume of water added (L)} = \frac{\text{Volume of chemicals added (L)}}{\text{Specified concentration (L/L)}} \qquad \text{Equation 8.7}$$

  The specified concentration in Equation 8.7 is equivalent to the make-up concentration established during charging the tank with the commercial phosphating solution. The make-up concentration was obtained from the Chemrox Work Instruction Sheet.[188] This concentration was quoted as the number of litres of Chemcoater which must be present in the volume of the processing solution used in the tank. For T_1, 100 L of Chemcoater were made up to a volume of 3.14 kL with water. This gives a solution concentration of 0.032 L/L. For T_2 the concentration was 0.030 L/L. This was obtained by taking 50 L of Chemcoater and making it up to a volume of 1.71 kL with water. The chemical additions for each tank were obtained for each operating cycle from the data in Table 7.4 and Equation 8.7

- flowrate indicators (referred to as flowrates) were established for each of flowing and static rinse systems using Equation 8.8

$$\text{Rinse water flowrate} = \frac{\text{Volume of flowing rinse water}}{\text{Time}} \qquad \text{Equation 8.8}$$

  The difference in water meter readings was used to give the volume of the flowing rinse (manually controlled) and the water top-up (automatically controlled). These water volumes were converted into flowrates by dividing them by the time period (in hours) between the initial and final water meter reading. The flowrates referring to static rinses are effectively top-up or addition rates.

- the paint line worked effectively for 40 hours from Monday to Friday. The total working days of the Paint Line plant in the year of 2004 were 236. Therefore, there was an average of 34 (236 days per year excluding weekends and public holidays/5 days per week) working weeks per year and an average of 20 (i.e. 236/12) working days per month

- during the full monitoring period the process solutions were dumped once on the 2nd of July
- during the full monitoring period the rinse solutions were partially or fully dumped between the 22nd of April and the 4th of May (Entry C in Table 8.5) and were fully dumped on the 2nd of July (Entry E in Table 8.5). Partial refill volumes were estimated to be about half of the volume of solution in the tank.
- water usage is calculated based on the monitoring period of 105 days and converted to an annual figure (236 days).

Table 8.5 shows the estimated volume of water used to top-up the process solutions during each operating cycle. These are called water additions and were calculated using Equation 8.7 above. Table 8.5 shows the allocation of metered water used in the Phosphating Line to various functions during the full monitoring period and the corresponding volume of water used in the factory for that time based on the consumption given in the Msunduzi Municipality Tax Invoice. This has been referred to as the invoiced water usage. The water additions made to the static rinse and the process solution are estimated as the difference between the water additions measured by meter readings when no effluent flows to the drain. The water addition to the static rinse only is obtained by subtracting the water additions presented in Table 8.4 from these calculated water volumes. This assumes that water additions are made automatically. The volumes in Table 8.5 recorded for the flowing rinses must also include water additions made to compensate for any losses. These cannot be separated from the volume actually running through the rinse tanks because the tanks are not individually metered.

Table 8.4 Esimation of the volume of solvent additions (kL) made to the process solutions over the Full Monitoring Period

Operating Cycle	Tank 1		Tank 2	
	Chemical Additions	Water Equivalent	Chemical Additions	Water Equivalent
1	140	4	134	5
2	56.0	2	163	6
3	65.0	2	117	4
Total	**261**	**8**	**414**	**15**

Table 8.5 Estimation of annual volume of water (kL) used in Phosphating Line

Entry	OC	Tank	Refill volume	Flowing rinse volume	Top-up only		Total water usage	Invoiced water usage
					Water additions to process	Water additions to static rinses		
A	0-1	1	3	0	0	0	10	0
		2	2					
		3	3					
		4	2					
B	1	1	0	0	9	16	71	194
		2		0				
		3		46				
		4						
C	1-2	1	0	15	0	0	18	0
		2						
		3	2					
		4	1					
D	2	1	0	0	8	22	30	291
		2						
		3						
		4						
E	2-3	1	3	0	0	0	10	0
		2	2					
		3	3					
		4	2					
F	3	1	0	6	6	6	23	77
		2						
		3	3					
		4	2					
Total volume of water used for 105 days							**162**	**562**
Total volume of water used for 236 days							**364**	**1263**

The volume of water used after the dumping of all the tanks on the Paint Line after the 27th of February but before the 1st of March was estimated to be 16 kL (see Entry B in Table 8.5). This is made up of the volume used to refill all four tanks and to clean them prior to filling. Table 8.5 (Entry A) shows that the volume required to fill the tanks totals about 10 kL. This means 6 kL was used to clean the tanks before recharging with the new brand of commercial phosphating chemical.

A flowing rinse system was used on the phosphating line during most of OC1. This is seen from the averaged water flowrate of 0.111 kL/hr, for the period between the 1st and the 18th of March and the ease with which effluent samples could be collected during that time. No effluent samples were collected on the last two SPs of OC1. This means that the manually controlled mains water supply was closed and the tanks were only being filled from the automatic ball-cock system. The rinse tanks were therefore operating as static rinses at the end of the cycle and there was no effluent discharge to the drain.

Between the end of OC1 and the start of OC2 about 18 kL (see Table 7.15) of water was used in 11 days. During this time the Paint Line worked for only 2 days. Communication with the line supervisor established that there had been at least a partial dump of the rinse solutions during this time. This is shown in Entry C in Table 8.5. There is about 15 kL of water consumed that is unaccounted for. This may be attributed to the operation of a flowing rinse during the two days the line was working, or the running of the rinses during dumping.

In OC2 only one effluent sample was obtained and the effluent flowrate was observed to be very slow. The average flowrate from the 12th of May to the 1st of June was found to be 0.02 kL/hr. This is in good agreement with that established for the automatic topping up of solutions found in OC1.

The line was shut down for maintenance between OC2 and OC3. All the tanks were dumped and desludged then recharged with fresh solutions. About 10 kL of water was used for this task (see Entry E in Table 8.5).

The rinsing used in OC3 appears to be randomly switched between flowing and static operation with four effluent samples being obtained from a total of ten sampling points. Three of them were collected in the middle of OC3 and one at the end. Table 8.5 shows 6 kL of water was used to top up the process solution. A total of 23 kL went through the Paint Line. There were 5 kL used to refill the rinse tanks leaving 12 kL for rinsing and additions to the rinse tanks. This is allocated in equal amounts to the flowing and static rinses.

Water is not only used directly in the surface treatment of workpieces going through the phosphating tunnel, but also in the heat exchanger used to warm the solutions in the process tanks and rinse tank T_3. No information was available on the water usage in the heat exchangers as the system had not been cleaned out for some time. Further there are other divisions on and off the factory floor which use water. The water used on the factory floor (excluding the Paint Line consumption) includes washing of heat exchangers (twice a year) and paraffin burners. Water was also lost in sludge produced in the tank. During the monitoring period the tanks were desludged once. Two 250 L drums were obtained from T_1, one 250 L drum from T_2 and one 250 L drum from T_3 and T_4 combined. The sludge was roughly estimated to contain a total of 333 kL of water. Domestic uses include water used in toilets, showers and kitchen facilities. The volume of water used in the toilets was estimated to 12 L/flush[189] and an average of two toilet visits per person per day. The volume of water used in the shower facility was estimated at 15 L/min of water used per person. It was assumed that only the factory staff would shower once a day for an average of 4 minutes. Further water use for refreshment purposes was also calculated. An estimated two cups of tea per day (approximately 250 mL per cup) was consumed by each member of staff. The water used for each of the different purposes (seen in Table 8.6) have been cost at an average (between R6.45 and R7.10 per kL) tariff of R6.78/kL.

Table 8.6 Estimation of total water usage in factory

	Volume during monitoring period (kL)	**Annual volume (kL/year)**	**Cost (R)**	**% of the total**
Refilling of the process solution	10.0	22.5	153	2
Refilling of the rinse solution	18.0	41	278	4
Water additions to the process solutions	23.0	52	353	5
Water additions to the static rinse	44.0	99	671	10
Flowing rinse water	67.0	151	1020	15
Sludge Volume	0.333	79	533	8
Toilets	92	210	1420	20
Showers	164	368	2500	35.6
Refreshments	1.94	4.4	30.0	0.4
	Total	**1027**	**6958**	

The annual volume of water used in the factory was estimated to be 1027 kL from the water mater readings taken during the monitoring period and assumptions made for water used for sanitary and refreshment purposes and the water contained in the sludge. The annual volume of water used on the Paint Line was estimated to be 364 kL (see Table 8.5) which is just over one third of the total annual value. However, most of the water used on the Paint Line (about 30%) was used in the rinses. The lowest amount of water used in production was for refilling the tanks (6%). The projected annual water consumption based on the bills from the municipality water amounted to 1263 kL. The estimated total volume of water used in the Paint Line per year was therefore found to be 17% lower than the value estimated from the water bill. This value is just within the acceptable error range of up to 20%.[190]

Values for specific water intake (m^3/m^2) have been published in the literature for phosphating of workpiece surfaces.[191] This is defined as the volume of water used to process one square metre of a workpiece's surface. An average monthly value had been quoted in the literature of 0.07 m^3/m^2 based on empirical data from a South African study into the metal finishing industry. This value is based on monthly water consumption rates ranging from 500 m^3 to 15900 m^3. A value for the monthly water consumption at the company based on 20 working days per month was estimated using the water consumption over the monitoring period. This gives a value of 31 m^3 for the Paint Line and 107 m^3 for the entire factory based on data in the Mzundusi Municipality Tax Invoice. Both of these volumes for the company's water use are less than the literature values. However it is not made clear in the literature whether this value is for a spray or for an immersion rinse system. It is widely known that spray rinses use less water. They have been used as a means of reducing water consumption in the metal finishing industry. The difference in values may, therefore, be due to the literature value being based on an immersion rinse system while that presented here is for a spray system.

8.3.2 Drag-out Determination

The problems associated with determining drag-out volumes for workpieces undergoing metal finishing is well documented in the literature.[192] Traditional ways of measuring drag-out have used conductivity measurements, capturing and measuring the volume lost during drainage and more complicated methods involving taking solution volume measurements while emptying and refilling tanks between loads of workpieces being processed. Drag-out volumes have been estimated here using the P concentration data for the rinse tanks. This is based on the following relationships and assumptions:

- the change in the concentrations of the P, (and Na, Mo, Mn and Zn) in the rinse solution (T_n) is due to drag-out coming into that solution from the previous one (T_{n-1})
- the P concentration of T_n was taken as the difference between the P concentration at the start of the cycle and at the end of the cycle
- the mass of P dragged into a solution can be calculated using Equation 8.9

$$\text{Mass of P in } T_n = \text{Concentration of P in } T_n \times \text{Solution volume in } T_n \quad \text{Equation 8.9}$$

- the mass of P accumulating in the solution (T_n) is equal to the mass taken out of the preceeding solution (T_{n-1})
- the volume of drag-out coming into a solution is related to the concentration of P in the preceeding solution according to Equation 8.10.

$$\text{Drag - out volume into } T_n = \frac{\text{Mass of P in } T_n}{\text{Concentration of } T_{n-1}} \qquad \text{Equation 8.10}$$

Table 8.7 Estimation of drag-out volumes using analytical results

Solution	Previous solution	OC	Surface area treated (m^2)	Concentration of P (mg/L)	Mass of P in rinse solution at OC end (mg)	Drag out volume (ml/m^2)
T_3	T_2	1	8280	613	1.9×10^6	101
		2	18395	1658	5.3×10^6	108
		3	13044	681	2.2×10^6	58
T_4	T_3	1	8280	267	4.6×10^5	87
		2	18395	333	5.7×10^5	20
		3	13044	466	8.0×10^5	125

Published values for average drag-out rates are quoted on a three-point scale for vertically and horizontally hung workpieces.[193] For vertically hung workpieces an intermediate drag-out rate of 70 – 110 ml/m^2 has been observed for average drainage of this drag-out from the workpiece surface. Good drainage has been found to have a higher drag-out rate and poor drainage has been found to have a lower drag-out rate. For horizontally jigged workpieces a good drag-out rate of 30 – 70 ml/m^2 and a poor drag-out rate of 380 ml/m^2 have been quoted in the literature. The shorter workpieces phosphated by this company were hung vertically on the conveyor system e.g. bracings and shelves. Longer workpieces such as uprights and beams were hung horizontally on the conveyor system. All the drag-out values in Table 8.7 except one are below the intermediate (average drainage) drag-out rate for vertically hung workpieces. For horizontally hung workpieces two of the drag-out values are below the good (drainage) drag-out rate and the other four are under half the value for the poor (drainage) drag-out rate. This would appear to suggest that there is some measure of drag out control in the phosphating tunnel. This is probably a result of hanging the long horizontally mounted workpieces at an angle on the conveyor system.

8.5 True Cost of Effluent Waste

In a Scoping Audit (see Section 8.3) the source and sink for the waste does not have to be established as long as the levels of inputs and/or outputs 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 and sludge allow some materials lost in the wastewater and sludge to be measured directly. 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 phosphating chemicals, suspended sludge as a byproduct and substrate. The bulk of the sludge is deposited in the bottom of the tank. The real cost of waste takes into account the cost of the loss of these chemicals. The concentrations of the elements in the wastewater have been used to determine raw material wastage.

In this section the waste streams produced as a result of the phosphating process have been analysed and allocated a cost. These include water, effluent and sludge. This was carried out to identify opportunities for waste minimization and to prioritise the waste minimisation streams by ranking them from most expensive to least expensive.

The P content of the neat Chemcoater, in the process and rinse solutions was used as the basis for the calculation of the true cost of waste. The P concentration in solution was measured directly using the ICP spectrometry. The P concentration in the neat Chemcoater was obtained in two ways which are outlined below:

1) a value of "10 – 12% P by weight" was quoted for the composition of Chemcoater by a representative of Chemrox Chemicals[194]

2) an estimated P concentration for the neat Chemcoater was derived from the average concentration of P in the process solution in the first operating cycle. The average mass of P in this solution is the same as the mass of P contained in 100 L of the Chemcoater, used to charge the solution. This is obtained using Equation 8.12. Equation 8.13 was used to calculate the percentage composition of P in the Chemcoater and a value of 11% was obtained.

$$\text{Mass of P in the process solution} = \frac{[\text{P}]\text{ in the process solution (mg/L)} \times \text{volume of solution (L)}}{10^3}$$

Equation 8.12

$$\text{\%Composition of P in neat Chemcoater} = \frac{\text{Mass of P in the process solution (g)}}{\text{100 mL of the neat Chemcoater}}$$

Equation 8.13

The mass of the P in the rinse water, which originates from the raw materials, can be calculated from the volume of the rinse water and the measured concentration of the P (see Equation 8.14). The amount of this raw material lost at dumping was estimated using Equations 8.15. This was based on the mass of the P accumulated at the end of OC1, OC2 and OC3 in T_3 and T_4 and the concentration of P in the Chemcoater. The cost of the Chemcoater is R8.42/L. The mass of Chemcoater estimated in each tank was then converted to a volume using the density, measured as 1.2 kg/L, in order to cost the wasted raw material. These values are presented in Table 8.8.

$$\text{Mass of P in the rinse water (kg)} = \text{Measured P concentration (ppm)} \times \text{Volume of rinse water (L)}$$

Equation 8.14

$$\begin{matrix}\text{Mass of raw} \\ \text{material lost}\end{matrix} = \frac{\text{Mass of P in the rinse water}}{\text{\% Compositon}} \times 100$$

Equation 8.15

Table 8.8 Estimation of Chemcoater wasted in rinse waters

OC	T_3		T_4		Total mass of Chemcoater (kg	Total volume of Chemcoater (L)	Cost (R)
	Mass of P (kg)	Mass of Chemcoater (kg)	Mass of P (kg)	Mass of Chemcoater (kg			
1	1.98	18.0	0.537	4.88	23	19	160
2	5.85	53.2	0.600	5.46	59	49	413
3	2.16	19.6	0.940	8.54	28	23	194
		Total for 105 days				91	767
		Total for 236 days				205	1724

The sludge composition is based on too many assumptions for it to be accurately costed in a true cost of waste analysis.

8.6 Monitoring and Targeting

The volume of water used, surface area treated and change in P concentration levels were obtained from the data in Tables 7.6 to 7.7, Tables 7.1 to 7.3 and Tables 7.34 to 7.36 for eight six day periods. This data was used to plot three monitoring and targeting graphs shown in Figures to 8.27 to 8.29.

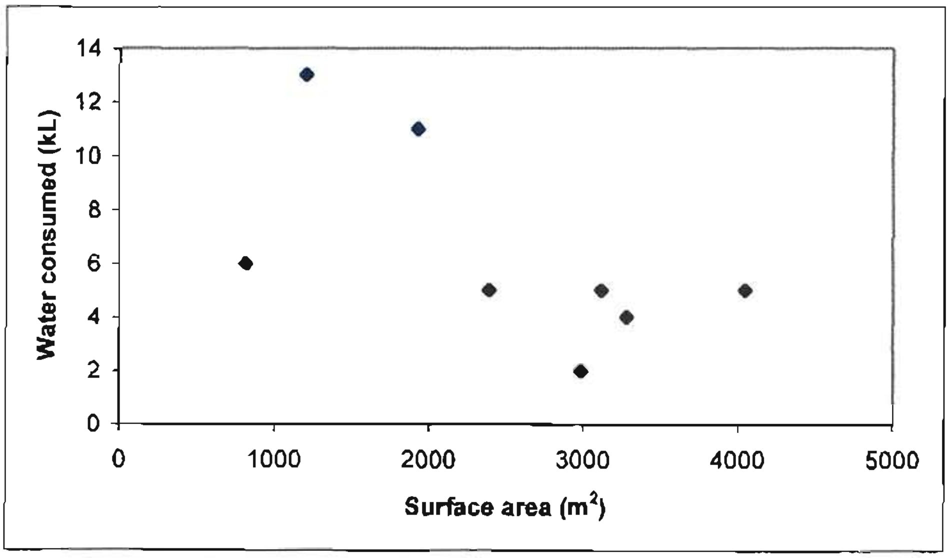


Figure 8.27 Plot of water consumption as a function of surface area produced

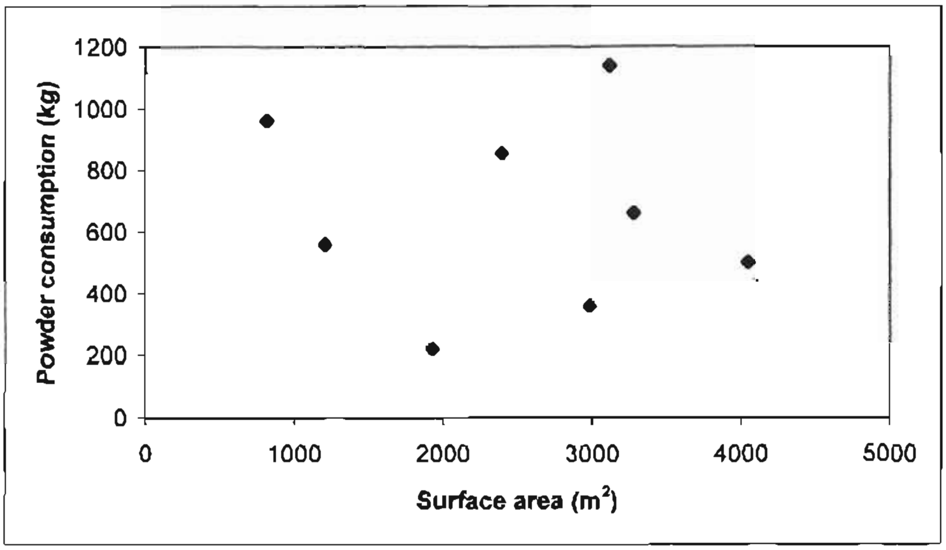


Figure 8.28 Plot of powder consumption as a function of surface area treated

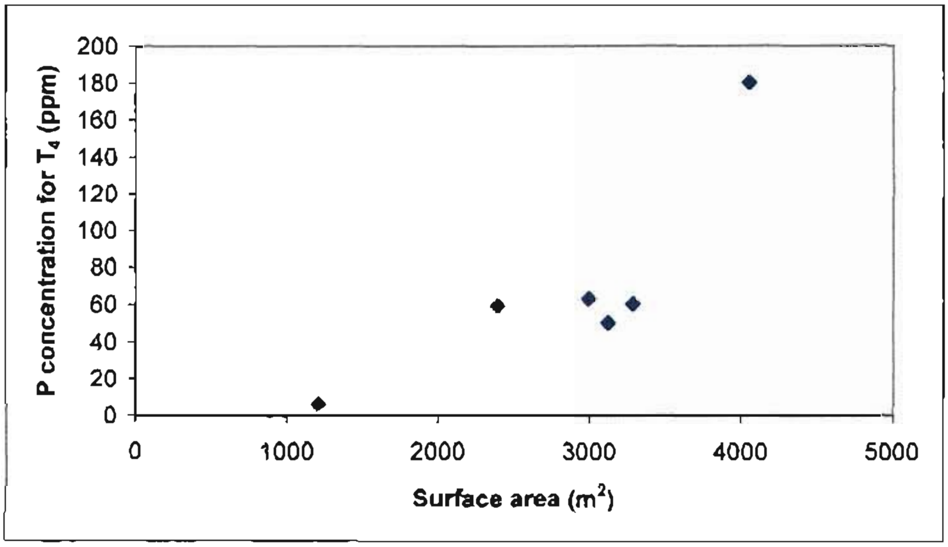


Figure 8.29 Plot of phosphorus consumed as a function of surface area treated

The graphs generally show poor correlation between the consumption and production variables. In the case of water consumption versus surface area treated (see Figure 8.27) this might be explained in terms of the change in the rinsing technique used after OC1. Rinsing changed from flowing to static or was a combination of these two methods. This meant less water was used in OC2 and OC3 but this was not related to a change in any production variable. If the water used by the flowing rinses is excluded from the graph this would remove three highest points which show greatest water consumption for lowest surface are treated. This would reduce the scatter of the points but would not tend to suggest that the process is well controlled.

Figure 8.28 shows very little control on the spray process on the Paint Line. This is consistent with the large variation in coating thickness measured using the direct reading instrument. This confirms the result obtained from the scoping audit where powder was identified as having the second highest maximum scope to save. This means powder consumption it is a significant waste minimisation opportunity.

Figure 8.29 shows the change in the P concentrations for the monitoring periods plotted against surface area treated for those same periods. The one case where the levels of P drops at the end of the monitoring period is clearly identified on the graph as the only negative value. This value results from the rinse water being flowed through the tank solution prior to dumping. This was carried out in order to dilute the solution which would be released into the drain.

The only monitoring and targeting examples found in the literature were published by Envirowise. One publication showed water consumption related to surface area treated in the metal finishing industry and the second one looked at powder consumption related to coating thickness. The estimated annual consumption was 1260 kL and the surface area treated 89000 m^2. When these points are plotted on the water economy diagram in Figure 3.7, the water consumption is in the top category. This category is equivalent to the top 25% of the best performing companies who participated in the study.

The estimated annual powder consumption is 24088 kg and this gives a powder density of 0.3 kg/m^2. The value of the coating thickness as specified by the company is 80 μm. When these values are plotted on the powder waste diagram in Figure 3.9 it shows 60% of the powder used is turned into waste. This again shows that powder wastage presents a greater waste minimisation opportunity than does water.

CHAPTER 9

CONCLUSIONS AND RECOMMENDATIONS

The waste minimisation analyses results from the scoping audit, mass balance analysis and the water economy diagram show that water consumption for the company may be considered reasonable. This is in keeping with the volumes estimated for the specific water intake and the drag-out rate. However the elemental concentrations of the rinse waters in T_3 and T_4 reach up to half and one seventh that of the process solution concentration values and exceeds the effluent discharge limits. Further the P concentration levels in the rinse water, going to the drain, exceed those published in the literature for phosphating processes. This indicates that reduction in drag-out and/or chemical treatment of the discharged wastewater from the rinses and process solutions must be considered in order to help limit the build up of waste in the effluent under the present operating system. However the latter of these two alternatives would not be considered in keeping with good waste minimisation practice. A projected annual figure for the true cost of effluent waste has shown that R1724 (see Table 8.8) is wasted as chemicals and R1969 (derived from Table 8.6) is lost as water from the rinse tank solutions into the effluent stream. The annual cost of chemicals and water lost from the process tank solutions assuming that there were three dumps per year would be R3789 (based on cost of chemcoater and 150 L of chemicals added into tank during each dump) and R506 (derived from Table 8.6), respectively. This gives a total of R7988. The cost of chemicals lost in the sludge, and the cost of treating the effluent and off-site disposal of the sludge would also have to be included in this cost. This would make this value (R7988) considerably higher and identify it as a significant waste minimisation opportunity. It was beyond the scope of this project to establish the true cost of waste for the powder or other material inputs. However it is conceivable that the true cost of waste for the Phosphating Line would be higher than that for powder spraying where there is an informal powder recycling system in place.

A difference between the water consumption estimated from the water meter readings on the phosphating line and domestic use, and that from the Mzundusi Muncipality Tax Invoice was evident from the results. However the contribution of the domestic water use was made on a number of assumptions and observations that may not be typical of the situation, despite best efforts to ensure this. On one on-site visit there was mention of the standpipe behind the building being used by or being on a supply line going into the neighboring company. If this were the case it could mean the company is being billed for water it does not actually use itself.

The drag-out rate was calculated using the analytical results. The drag-out rates expressed as ml/m^2 were in good agreement with those published in the literature. A mass balance performed on the water consumption was carried out for the monitoring period using Equation 8.5 and the values for the water usage quantities therein are shown in Table 9.1

Table 9.1 Water volumes (kL) estimated for water usage quantities

Quantity	PL	R	FR	P	AR	AP	S	E	DO
Volume (kL)	152.3	18	67	10	44	23	0.3	4	7

This showed that the metered volume of water coming into the line (PL in Equation 8.5 and Table 9.1) was 5.5% lower than the estimated value of 151.3 kL. This latter value was estimated using Equation 8.6 and the values for R, FR, P, AR, AP, S, E and DO in Table 9.1. The volumetric drag-out rate (DO in Equation 8.6 and Table 9.1) was calculated using Equation 8.10. There appears to be good agreement between the measured volume of water coming into the line and the estimated value. This suggests that the results of the drag-out calculations and the assumed evaporation rate are reasonably accurate for this process.

The results from the conductivity, TDS and elemental composition analyses for process and rinse solutions showed similar trends over the monitoring period. Not acidifying solution samples, prior to elemental analysis, would not appear to have any adverse effect on the analytical result obtained for these type of samples. Similarly the empirical relationship between conductivity and TDS (Equation 8.2) does not appear to hold for these industrial samples, but are more applicable to environmental samples.

The findings from this waste minimisation audit have been used to make the following recommendations for improving and investigating the process further:

- systematic monitoring of the sludge in order to establish a true cost of waste for this waste stream
- instituting a sludge disposal policy. This may include considering the purchase of a filter press to reduce the volume of sludge and the water content in the sludge for off-site disposal by introducing a filtration system into the process tanks to continuously remove sludge from the process solutions e.g. a band or pressure filters
- checking the plans for the water supply lines coming into the factory to see if there is any supply line going out of the site to other companies nearby
- reducing the drag-out rate by slowing the conveying speed of workpieces through the phosphating tunnel so they have more time to drain and spend in the rinse spray zone, and increase the pressure of the spray system
- using the rinse water to top-up and make-up the process solutions
- instituting and documenting a formal powder recycling system
- employing a meter to measure the thickness of the cured coating on the workpiece in order to introduce stricter control of powder usage
- reducing the concentration levels of P and Mo in the effluent by controlling raw material usage, in keeping with good waste minimisation practice, or by chemically treating (precipitation and neutralization) the effluent stream

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APPENDIX A

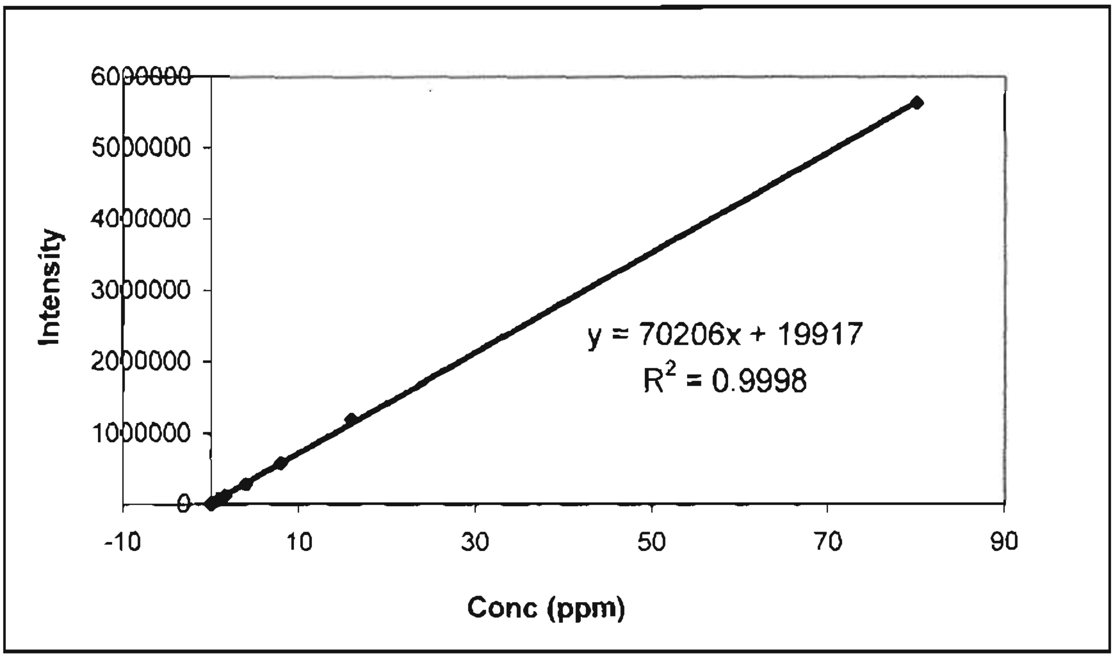
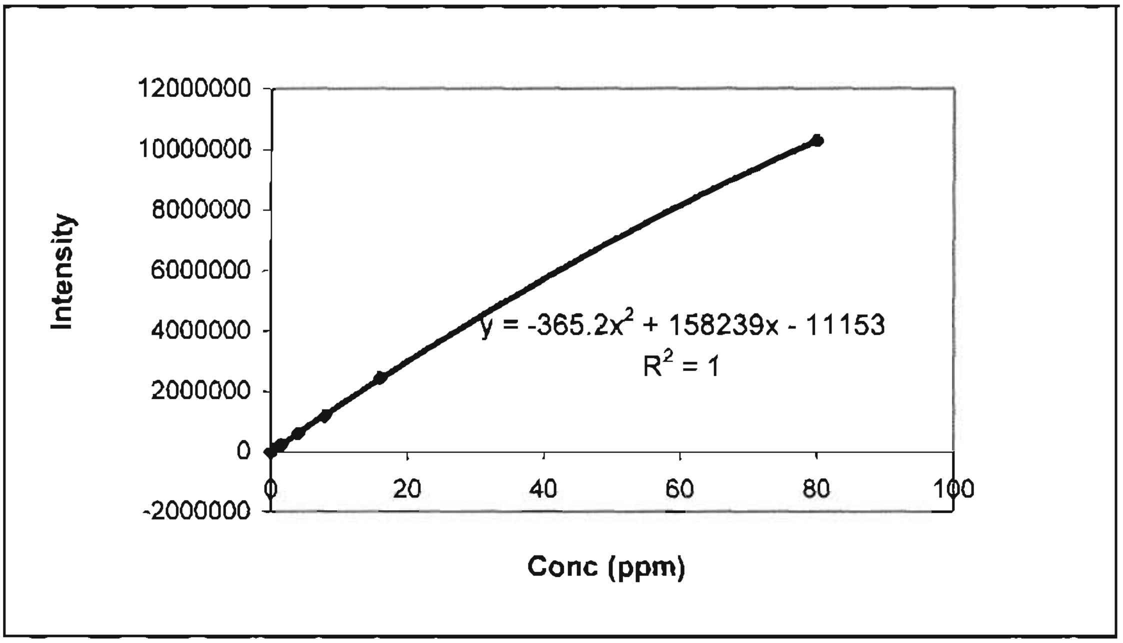


Figure 1: Calibration Curve of Mo



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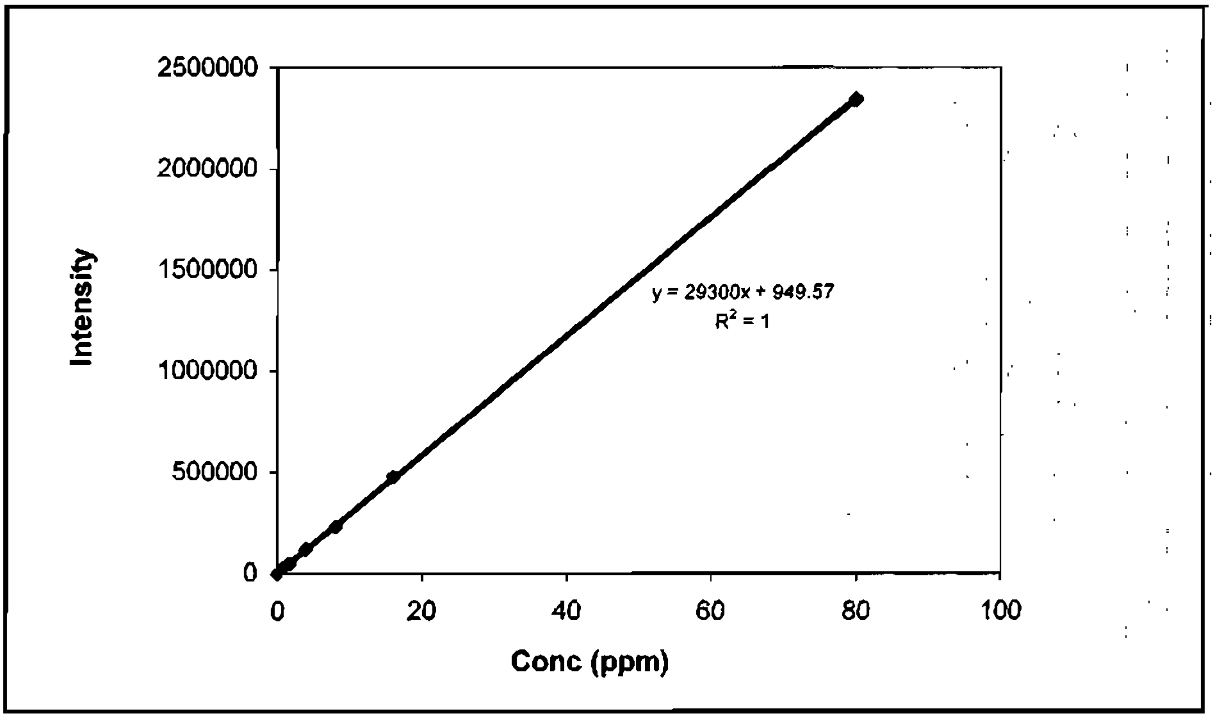

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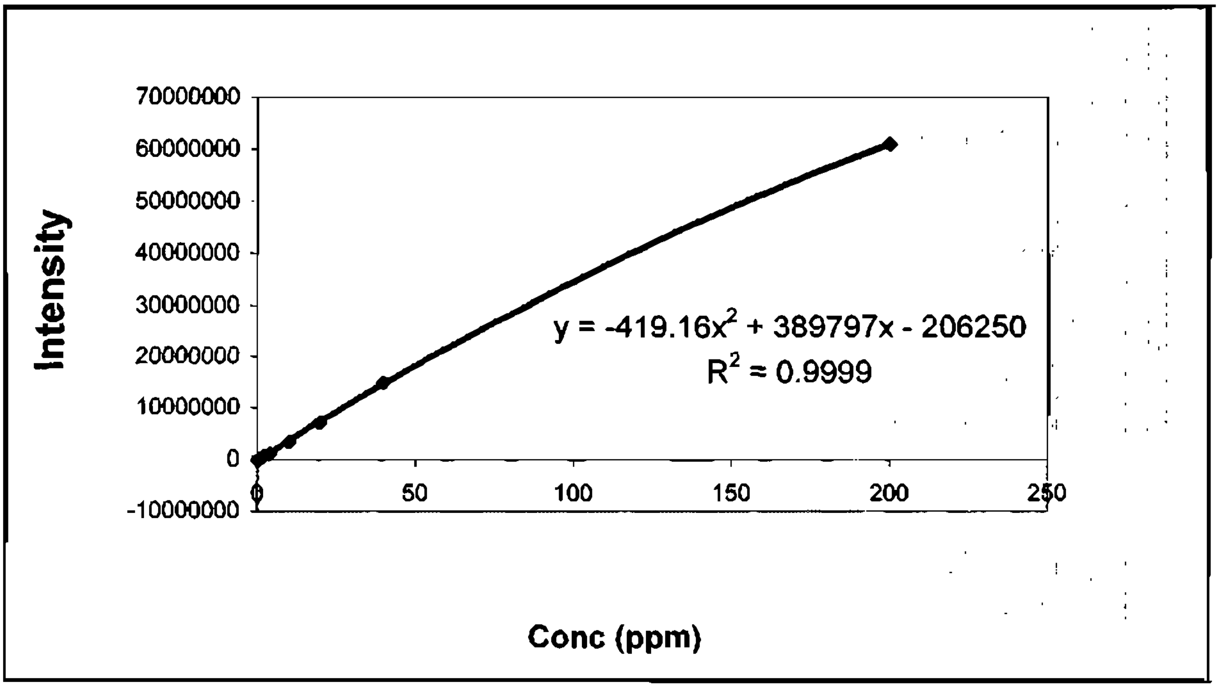

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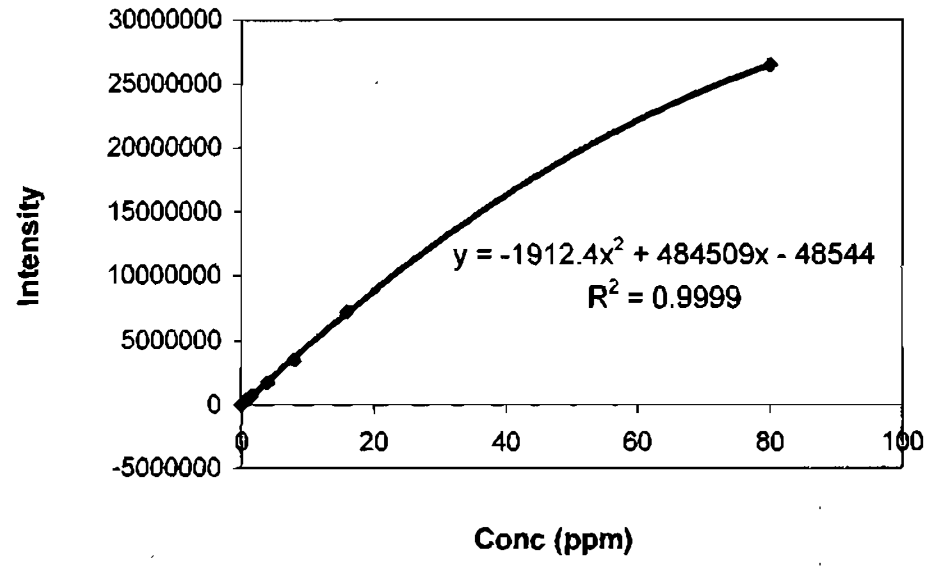

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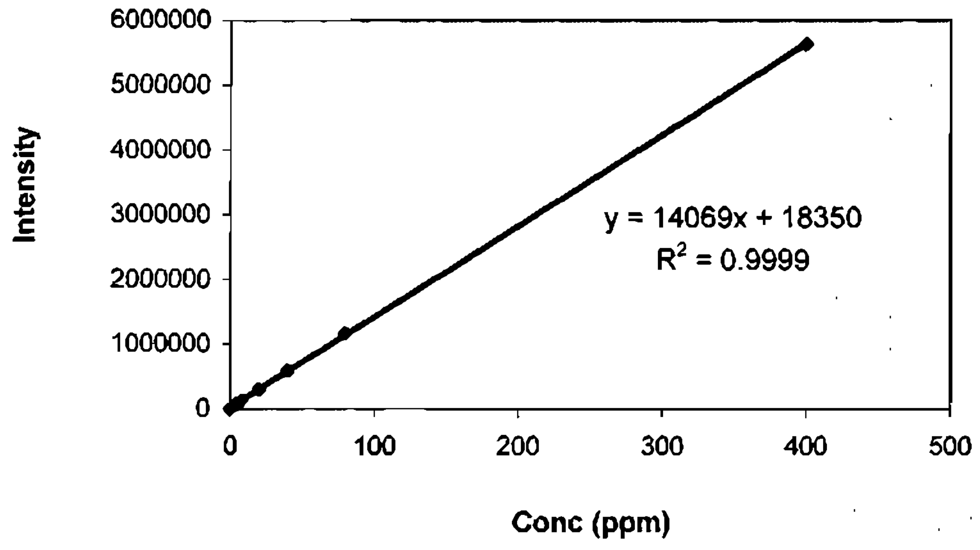

Figure 6: Calibration Curve of P