

University of KwaZulu-Natal

**APPLICATION OF ANALYTICAL CHEMISTRY
AND WASTE MINIMISATION TECHNIQUES IN A
PAINT DRIER PLANT**

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APPLICATION OF ANALYTICAL CHEMISTRY AND WASTE MINIMISATION TECHNIQUES IN A PAINT DRIER PLANT

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By

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Abstract

Environmental sustainability, strict Municipal bylaws, ever-increasing waste disposal costs and scarcity of natural resources e.g. freshwater, are but a few aspects that necessitate companies to incorporate Waste Minimisation Techniques (WMT) and Pollution Prevention Strategies (PPS) into industrial processes. In a chemical industry expense alone is no longer the defining factor when it comes to cutting down the amount of effluent wastes generated; it is now largely dictated by waste regulations.

Metallica Chemicals (Pty) Ltd (the company) like any other company engaged in the production of speciality chemicals, is not immune to waste production. The company's core business is in the production of speciality textile products and metal soaps known as ***Paint Driers (PD)***. During production of paint driers, (cobalt and manganese processes in particular) it was established that the technology in use results in a release of high quantities of wastewater that contain a high concentration of sulfate ions and traces of these heavy metals, and the result is that the wastewater generated is not useable in the same or other production processes.

The total amount of wastewater produced from these two processes is more than 435 tonnes per annum. The company spends substantial financial resources (an average of more than R236 000 per year) for disposal only. The company management decided to implement a waste management audit and waste minimization strategies or techniques to solve the problem. This meant,

- a change to cleaner production processes and/or
- better ways to manage the waste at reduced costs.

In order to fully understand the extent of the situation, wastewater samples were collected from the company for analysis. Analysis of wastewater samples was carried out using appropriate analytical technique, namely inductively coupled plasma optical

emission spectrometry (ICP-OES), to establish the amount of heavy metals, sulfate ions and any other metal traces. Results were used to make informed decisions for the WMT to apply in order to eliminate/reduce the problems identified by the company.

It was deduced that if WMT and PPS are applied to processes such as, water audit, reuse and regenerative recycling of wastewater, pinch technology, turning waste generated into commercialized product, etc, this could result in the company achieving both financial and environmental goals.

Careful consideration of recommendations made will put the company's environmental standing on a far sounder footing. The rewards on the production capacity, efficiency and financial savings will by far exceed the current volumes and revenues.

Declaration

I, Muvhango Rasalanavho, hereby certify that this research work was independently carried out and written by me. It has not already been accepted in substance for any degree or been submitted in candidature for any other degree. Unless otherwise stated, figures, tables and pictures belong to me.

Signed:

Muvhango Rasalanavho

I hereby certify that this statement is true and correct.

Signed:

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“Ndi a livhuwa”.

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List of Abbreviations

| | |
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| PD | Paint driers |
| SAPMA | South African Paint Manufacturers Association |
| VOCs | volatile organic compounds |
| DMR | Direct metal reaction process |
| 2-EH | 2-ethyl hexanoic acid |
| US EPA | United States Environmental Protection Agency |
| DEAT | Department of Environmental Affairs and Tourism |
| WM | Waste Minimization |
| SEPA | Scottish Environment Protection Agency |
| ROI | Return on Investment |
| EA | Environment Agency |
| SHE | Safety, Health and Environmental |
| M&T | Monitoring and targeting |
| W/S | White spirit |
| SMFD | Standard Manufacturing Formulation Document |
| R5 | Reactor number 5 |
| R6 | Reactor number 6 |
| EDTA | ethylenediaminetetra-acetic acid |
| PAN | 1-pyridyl-2-azonaphthol(2) |
| SANS | South African National Standards |
| ICP-OES | Inductively Coupled Plasma Optical Emission Spectrometry |
| MSDS | Material Safety Data Sheets |
| HDPE | high density polyethylene |
| AAS | absorption spectrometry |
| ETAAS | electrothermal atomic absorption spectrometry |
| LEAFS | laser-excited atomic fluorescence spectrometry |
| FAPES | furnace atomization plasma excitation spectrometry |
| CCD | Charge coupled device |
| USN | ultrasonic nebulizer |

List of Abbreviations

| | |
|------|--|
| PHZ | preheating zone |
| IRZ | initial radiation zone |
| NAZ | normal analytical zone |
| BOD | biochemical oxygen demand |
| MDGs | Millennium Development Goals |
| OHNP | Occupational Health Nurse Practitioner |

Chapter 1

Thesis structure

Industrial manufacturing companies are now faced with a daunting task of taking care of their employee's health and the environment while striving to maintain their core business. The current mushrooming of unions at each and every industry sector makes it practically impossible for companies to carry on with their business as they did 50 plus years ago. Unless the management of companies embodies clean production in their business, they will always be prone to liabilities that can run into millions of Rands and lose substantial amounts of the company's financial resources. Liabilities can either be initiated by unions on behalf of the employees' or by government while enforcing Municipal bylaws for incorrect disposal of waste generated.

Metallica Chemicals initiated a waste minimization project for their paint drier (PD) production section of the company. Their objective was to reduce both wastewater generated as well as disposal costs. The project was more concerned with two production processes of metal PD, cobalt and manganese.

Chapter 2 looks at the need for PD as an additive in the paint industry. Several PDs which are currently available on the market and knowledge of how they interact with the paint system or surface coating were explored. Production technologies practiced by companies involved with manufacturing PD were looked at in detail.

Chapter 3 describes types of production processes available for Speciality manufacturing companies. It was noted that each industrial company, one way or the other, produces some form of waste while busy transforming raw material into useful products. Wastes produced can pose a danger to those handling them, and in

some cases can cause adverse, irreversible damage to the environment. This calls for ways in which waste can be eliminated or reduced at source. It is currently known that waste minimisation programmes can inevitably assist in solving the problems of waste generated, while at the same time affording the company many benefits.

Chapter 4 gives a description of the company where the project took place. Their core production business was looked at in detail. Two waste streams, cobalt and manganese, were investigated in order to identify points in the process where waste minimisation could be targeted. Details of product formulation, from the point of charging raw materials until packaging of final product is made were closely scrutinized.

Information gathered from chapters 3 and 4 were used to determine the scope and aims of the project. This was communicated to the company management in a detailed report.

In chapter 6, the monitoring methodology of both old company data and new data was carried out. Monitoring was done through sampling, measuring samples using laboratory instruments and finally, characterizing samples collected. Sampling and analytical methods were optimized in order to validate and determine the reliability of all the results. A preliminary report was prepared and sent to the company.

Results from old data and new data were all tabulated in chapter 7. Results were extracted from company documents, utility invoices, private company invoices and from analysis of samples

In chapter 8, all results were carefully discussed in order to see how the information gathered fitted together. A comparison was made of results obtained from company documents with analytical results based on sample analysis.

Results were also used to formulate new possible commercialized products derived from wastewater under investigation.

Finally, in chapter 9 conclusions and recommendations based on results were made. A brief of current problem(s) followed by a series of recommendations were made. The situations were based on raw material and wastewater generated from both streams. It was demonstrated beyond reasonable doubt that recommendations made will produce a number of benefits to the company.

Chapter 2

2. Introduction to Paint and Paint Driers

Most items that we use daily are to a large extent coated with paint. The primary uses of paint on surface of substances are to provide protection and also for decoration. Other uses include reflection of lighting, safety promotion, electrical insulation and fire retardation.^[1, 2] Once applied to the surface of the substance, for it to serve its primary purpose, it undergoes both physical and chemical changes from liquid form to solid state. For the drying process to occur rapidly within hours of application, additives called “Paint Driers” (PD) are added during paint formulation. The focus point of this research project is on wastewater management and minimization during manufacturing of two widely used paint driers, cobalt and manganese octoates.

2.1 Short History of Paint, South African Perspective

Archeological excavation obtained from Zambia has so far revealed that paint was used as far back as 350 000 to 400 000 years.^[3, 4] Paintings on stones at caves around the world are testimony enough that paint was used during nomadic times.^[5-8] There is a cave at Giant’s Castle in the Ukhahlamba Drakensberg Park in KwaZulu-Natal which has great paintings depicting animals and people who once inhabited the area. Figure 2.1 shows some of the beautiful pictures portrayed at the main cave of Giant’s Castle.



Figure 2.1 The Bushman or San's rock painting at Giant's Castle, Ukhahlamba Drakensberg Park

According to the tour guide at Giant's Castle, the paint was prepared using a mixture of red or yellow ochre, clay and charcoal. The three ingredients were crushed into fine powder before being mixed with water, egg yolk, animal blood and animal fats. Egyptians are credited for their ingenious creation of a variety of pigments, such as blue, lapis lazuli, azurite, malachite green, etc. between 3000 and 600 BC.^[5-8, 12]

The word "Paint" or "Surface Coating" as it is sometimes referred to, can be described as any fluid substance that will spread over a solid surface (substrate) and dry or harden to an adherent (i.e. using a primer) skin or film.^[4, 5] Nowadays it generally refers to alkyd & water based paints, varnishes, enamels and lacquers. These fluids are differentiated from each other in their composition. Alkyd or water based paint is an inorganic pigment dispersed in three major components, namely, vehicle, filler and additives. Varnish is a non-pigmented product based on oil and natural resin in a solvent, whereas enamel is pigmented varnish. Unlike the preceding three types of paint, lacquer represents a film that can be re-dissolved even after the solvent has evaporated.^[2, 5, 7, 8]

2.2 Paint producers in South Africa

With the advancement of technology and demands for paint, the formulation of paint has greatly improved. This is largely influenced by

- methods of application (by spreading, spraying, flow coating or electrodepositing)
- cure or dry (through atmospheric oxidation, evaporation of diluent, use of heat or other forms of radiation)
- nature of substrate (wood, household, metal, plastics etc.) and
- conditions of use (mechanical properties, durability and chemical properties).

Paint manufacturing is one of the largest industry sectors in the world and South Africa (SA) has seen a major growth of this industry.^[9] The South African Paint Manufacturers Association (SAPMA), has in excess of 45 membership companies involved in the manufacturing of paint or paint related products, and some of the well known manufacturers and distributors are given in Table 2.1.

Table 2.1 Some paint and paint related products manufacturing companies in South Africa^[9]

| Name of company | Company's business focus | Main products |
|---|---|---|
| Dulux (Pty) Ltd | Decorative paint product sales to retailers, wholesalers & contractors | Painting accessories and wood-care products |
| Barloworld Plascon (Pty) Ltd | Production, marketing and distribution of paint and allied products | Paint, inks, solvents and allied products |
| BASF Coatings (Pty) Ltd | Manufacture and marketing of industrial and automotive coatings | Colour matching, mixing, blending, tinting, letting down and QC testing of coatings |
| Duram Products (Pty) Ltd | Manufacturer of specialized coatings | Paint, sealants and waterproofing |
| Bio Schnell (Pty) Ltd T/A Randcon Paint Centre | Manufacturer | Water & solvent based coatings, waterproofing compounds, cleaning chemicals |
| Libra Paints (Pty) Ltd | Manufacturer of putties & paint | Industrial & decorative paint, waterproofing compounds and glazing putty |
| International Paint (Pty) Ltd | Manufacturer of industrial coatings | Marine, heavy duty and powder coatings |
| Dekro Paints | Manufacturer of automotive, decorative, hygiene, industrial, marine, water proofing and other specialist coatings | Automotive, decorative, hygiene, industrial, marine, water proofing and other specialist coatings |

2.3 Paint formulation and Ingredients/constituent of paints

Contrary to the simple way nomadic people used to make paint, nowadays the process is far more complicated and uses a variety of ingredients, each with a specific, crucial purpose that takes into account important requirements described below. Of the many ingredients used, some are potentially harmful [e.g. volatile organic solvents (VOCs)]. With tight environmental laws and legislations, research is constantly carried out to see the impact some of these ingredients pose to manufactures, users and the environment.

Paint systems are grouped under two categories, liquid and powder paint systems.^[2] Liquid paint systems differ from powder systems in the sense that they contain solvent, whereas the latter is prepared from dry ingredients only. Liquid systems are further divided into two types, solvent and water based paint. Solvent based or non-aqueous paints are flammable, have strong primary odours and exposure limits that may not be exceeded in confined areas. On the one hand, water-based emulsion paints are non-flammable, non-toxic but on the other hand they are susceptible to freezing. There has been a gradual increase in the use of water-based emulsion paints due to their being environmentally friendly.

During paint formulation, the four main ingredients given in Table 2.2 and Figure 2.2, film formers, pigments, solvents and additives are mixed in different proportions by mass. Table 2.2 gives a general composition of liquid paint system.

Table 2.2 General composition of paint (surface coating) mixture [1, 3, 6, 22, 45]

| Component | Weight Percent approximation | |
|---------------------|------------------------------|-------------------|
| | Alkyd paint | Water-based paint |
| Film former/binder* | 30 – 60 | 30 – 55 |
| Solvent | 27 – 41 | |
| Pigment | 19 – 30 | 25 – 37 |
| Water | | 6 – 27 |
| Additives | 2 – 4 | 2 – 4 |

*In water-based paint the binder is called an alkyd emulsion.

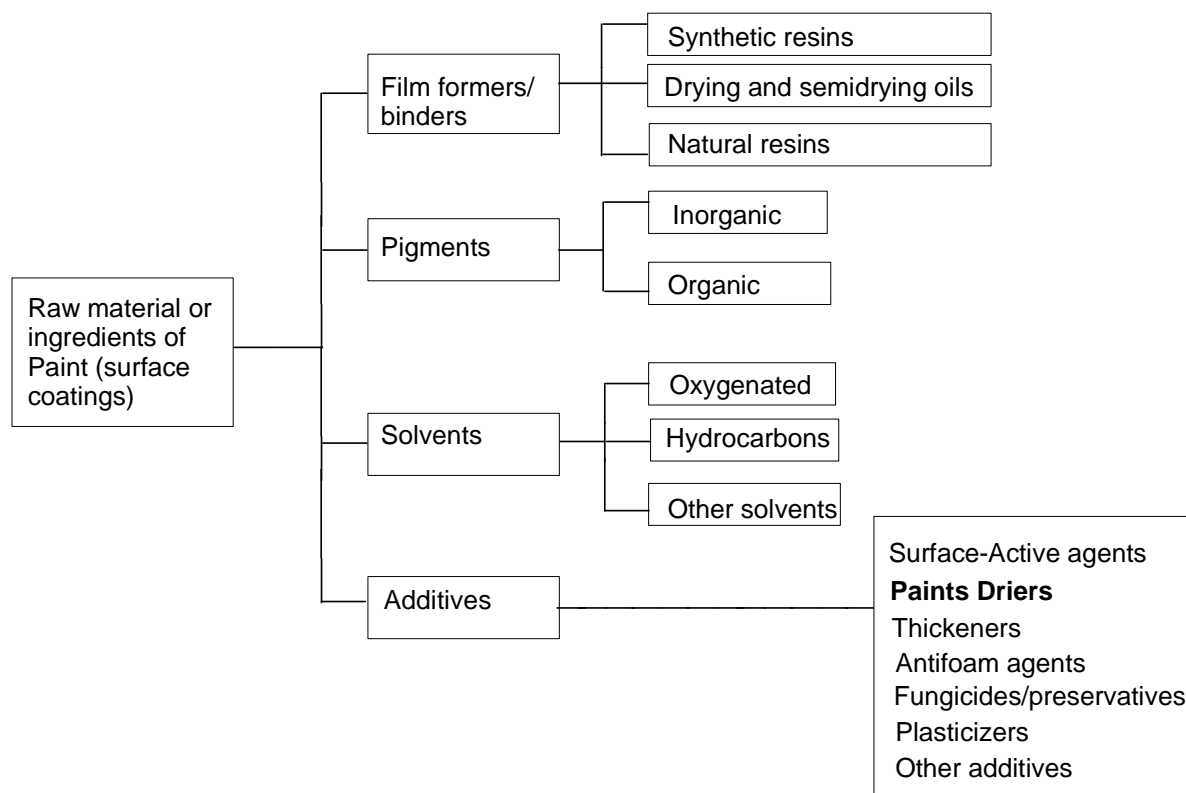


Figure 2.2 Main ingredients of paint or surface coatings ^[2, 5, 47, 51]

The major constituent of all surface coatings (see Table 2.2) is the film former/binder with an average weight percent of more than 30 %. Binders are mostly made of natural or synthetic resins and they include acrylic, alkyd, amino epoxy, phenolic, polurethane, vinyl, butyl acrylate and many more.^[2] In solvent-based paints, alkyd resins (see Figure 2.3) are the ones which are mostly used. Other ingredients are added depending on various factors, hence not all these ingredients will be found in all types of paint formulation. The most widely used component type for each main ingredient of paint systems is given in Table 2.3.

Table 2.3 Ingredients which are widely used during formulation of each paint system ^[1-2, 51]

| Main ingredient | Type of Paint system | | |
|--------------------|----------------------|----------------------|-------------------|
| | Solvent-based | Water-based | Powder |
| Binder/Film former | Alkyd resin* | Epoxy resin emulsion | Epoxy resin** |
| Pigment | Titanium dioxide | Titanium dioxide | Titanium dioxide |
| Solvent | Aliphatic | Water | None |
| Additives | Driers | Driers | Calcium carbonate |

* See example of an alkyd resin given in Figure 2.3

** See chemical structure given in Figure A1

2.4 Paint Additives

Although additives contribute a small percentage, (see Table 2.2) they nevertheless play a crucial role in film formation after application of paint on a substrate. During paint formulation the total level of all additives is usually less than 5% of the total paint product.^[1] A number of additives and the function they play in the paint are given in Table 2.4. With the exception of paint driers, not all these additives are included in all paint types; hence the choice depends entirely on a particular formulation and purpose of paint. As mentioned earlier, the paint drier is of paramount importance to this research project and hence a detailed description of this category of additives is given in the Sub-sections 2.4.1 and 2.4.2. Sub-section 2.4.1 gives a description of types of driers available and how they influence the drying of paint systems. A detailed example illustrating the drying of alkyd resin (Figure 2.3) is shown in Figure A2 under Appendix A. Technologies applied during driers manufacturing and the final form of the drier product are dealt with under Sub-section 2.4.2.

Table 2.4 Some paint additives and their use on paint systems^[1, 5, 8]

| Type of Paint Additives | Function on the paint |
|---|---|
| Antifoams | Reduce formation of foam by lowering surface tension on adjacent bubbles during manufacturing, filling, tinting, shaking and application of the paint. |
| Antisettling agents | They reduce the settling of pigments during storage, e.g. thixotropes. |
| Anti-corrosive pigment enhancers | Used to prevent corrosion on metal substrate. Examples include zinc dust, red lead, zinc chromate etc. |
| Antiskinning agents | Prevention of skin formation while stored in the can e.g. methyl ethyl ketoxime, cyclohexanoneoxime, butyraldoxime and phenols. |
| Can-corrosion inhibitors | To prevent aqueous paints corroding the can e.g. sodium nitrite and sodium benzoate. |
| Dehydrators/antigassing additives | To prevent formation of moisture from pigments at the dispersion stage |
| Dispersion aids | They break down the pigment agglomerate so that particles can be wetted uniformly by the liquid vehicle |
| Driers | For promoting oxygen intake and decomposition of hydroperoxides during oxidative cross-linking process |
| Floating and flooding additives | Reduce separation of pigments by using Ricinoleic acid, silicones etc. |
| Ultraviolet absorbers | Reduce rate of degradation when exposed to sunlight |
| Antistatic agents | They are added mostly to paints used for painting machine and this prevent the machine from gathering dust particles |
| Deodorants | Added in order to eliminate odours from some alkyd paints |
| Antilivering agents | Additives such as 2-amino-2-methylpropane are added to stabilize the paint components so that pigments will not react with the binder |
| Flatting agents | Metallic soaps such as aluminum stearate, zinc stearate and zinc tungate are needed so that the surface of the film can be finely rough rather than smooth, so that it can reflect light diffusely rather than spectrally |
| Viscosity control agents | Used to enhance the rheology or viscosity of paint system |
| Anti-oxidants | Used to prevent skinning or drying out of dispersion during storage |
| Preservatives such as Mildew inhibitors or fungicides | Prevent growth of and flourishing of microorganisms that can damage some components of paint, e.g. vehicle which is a source of food to most fungi |
| Emulsifiers | In order for stable mixtures of immiscible liquids like water and oil to be produced, surfactants are used. The surfactants used are mostly anionic, cationic or nonionic |

2.4.1 Paint Driers

Paint driers fall under a category called additives, (see Table 2.4) which forms an integral part of paint formulation. A paint drier, also called siccatives when in solution, can be described as a metal soap/salt formed from the reaction of a long-chain fatty acid with a metal (mostly transition metals) that accelerates the drying of the paint film after being applied on the substrate. The acid portion of the drier gives solubility in the oil medium. They speed up the oxidative cross-linking and/or polymerization of the film formers or paint resins.^[3, 10-34] Their main role in paint systems is two-fold:

- to catalyse the uptake of oxygen from the atmosphere and
- to enhance the decomposition of stable hydroperoxides to free radicals.

If the driers are not added to paint systems the resins/film undergo a slow autoxidation process which is commercially unacceptable. Paint driers are generally classified under three major categories,^[26, 31, 35-37, 40-44] namely:

- **Primary driers (or active driers)** are sometimes referred to as catalytic, oxidative, surface, top or skin driers. These names originate from the sense that when used alone they accelerate the hardening of the film surface before the underlying film reaches the state of oxidization. Primary driers contain metal of variable valency and examples of this category are given in Table 2.5 below. Their main function in paint is to promote oxygen uptake and breakdown of hydroperoxides (formed by the reaction of oxygen in the air with the film/resin) to free radicals since most of them have two accessible valence states that differ by one electron.
- **Secondary driers (or through-driers)** which are also called cross-linking, polymerization or coordination driers. They provide a through dry of the paint film by forming oxygen-metal-oxygen bridges or cross-links between polymers; hence prevent surface wrinkling that occurs when primary driers are used alone.
- **Auxiliary driers or promoters** enhance the appearance and quality of the total paint film.

Table 2.5 Metal type in each drier category ^[40, 44, 46]

| Primary driers | Secondary driers | Auxiliary driers |
|----------------|------------------|------------------|
| Cobalt | Lead | Calcium |
| Manganese | Zirconium | Potassium |
| Vanadium | Barium | Lithium |
| Cerium | Strontium | Zinc |
| Iron | Aluminum | |
| | Bismuth | |
| | Neodymium | |

Many studies on the action of paint driers in paint systems have been carried out. Research papers on the action of paint driers are mostly based on alkyd resins shown in Figure 2.3.

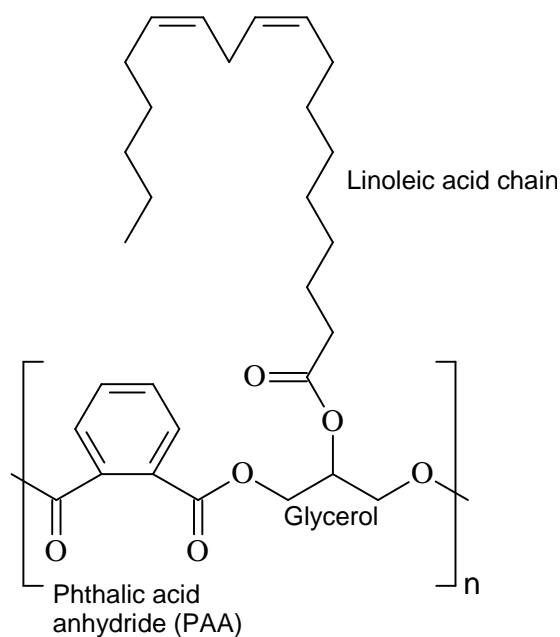
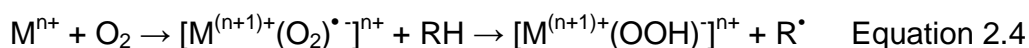
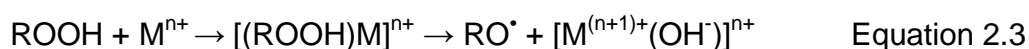


Figure 2.3 Structure of an alkyd resin formed from the reaction of linoleic acid, glycerol and phthalic acid anhydride through monoglyceride process ^[29, 48]

Upon application on the substrate both physical and chemical changes takes place in the paint. The solvent used {volatile organic compounds (VOCs) in the case of

solvent paint or water in the case of water-based emulsion} evaporates upon application. This leaves the binder which should ultimately change from liquid form to a hard solid that finally protects or decorates the substrate. The hardening of the binder follows an oxidative chemical reaction through which a resin interacts with atmospheric oxygen, a process called autoxidation. Studies carried out on the drying of alkyd resin binder has revealed that the addition of certain metal soaps of carboxylic acid, called driers, enhances the speed at which oxygen interacts with the resin.^[50] It is now accepted that this interaction happens on the non-conjugated (isolated) C – C double bonds of the acid chain (see Figure 2.3). It is strongly believed that the driers activate the decomposition of stable hydroperoxides to form free radicals which then cross-link to form a solid dry film. Research literature^[42-43, 56] shows that the drying of paint systems follows five general steps which are briefly described below and represented in Figure A2.

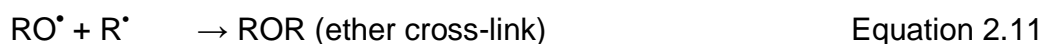
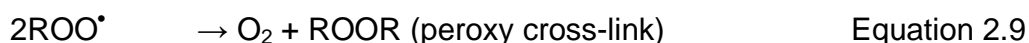
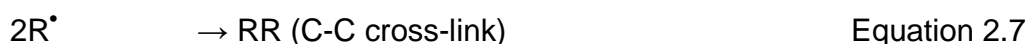
- **Induction period:** This is the period at which the paint is applied to the substrate and oxygen begins to migrate into the liquid paint. Due to natural inhibitors that are present in most alkyd resins, no drying occurs at this stage until all inhibitors are no longer available. Research papers^[53-56] have shown that the induction period is greatly reduced by addition of primary driers. This is enough evidence to support the fact that they activate the intake of oxygen from the atmosphere.
- **Initiation:** This is believed to be caused by either an unknown initiator on the substrate that abstracts allylic hydrogen of the doubly activated methylene group on the acid chain (Equation 2.1), by thermal homolytic decomposition of the hydroperoxides (Equation 2.2) or by the action of metal drier (Equations 2.3, 2.4 and 2.5). Research papers^[53-54] show that the presence of metal drier(s) in the paint system increases radical formations; hence oxidation reactions will by far exceed saturation reactions. Equation 2.4 shows that the multivalent metal in the drier system act as an oxygen carrier.



- **Peroxides formation:** The pentadienyl radicals formed will combine with oxygen molecules to form peroxy radicals which latter abstracts allylic hydrogen to form hydroperoxides (Equation 2.6). This process is known as autoxidation.



- **Peroxide decomposition or propagation:** This occurs when hydroperoxides break down to form alkoxy (RO^\bullet) and peroxy (ROO^\bullet) radicals (see Equations 2.2, 2.3 and 2.6) shown above.
- **Radicals cross-linking (polymerization) or termination:** Cross-linking or polymerization occurs when radicals combine. This yields the formation of peroxy, ethers and carbon-carbon cross-links resulting in the hardening of paint film (see Equations 2.7, 2.8, 2.9, 2.10 and 2.11). Physical changes that occur on the paint during oxidative cross linking include specific gravity and refractive index of the paint.



A number of literatures^[3, 11, 18-25] show that alternative routes on the autoxidative cross-linking of linoleate is currently receiving a lot of attention.

2.4.2 Manufacturing Methods

The amount of paint drier added during formulation is mostly less than 1 % by mass of the total paint. Though it is an important component of paint systems, the relatively minute amount required during formulation puts a limit on drier production quantities. In most cases, driers are sold as blends (see Table 4.1) instead of a single type. Three known companies in South Africa are actively involved in the manufacturing and distribution of paint driers. These are Metallica Chemicals Ltd (where sampling was carried out) and COMAR Chemicals (that supplied literature on the manufacturing of paint driers) which is based in Cape Town. The third company called Chemiphos is situated in Gauteng province but has its production sites at PATCHAM Ltd which is located outside the country in United Arab Emirates (UAE). Besides the use in paint formulation, other manufacturing industries ^[44, 52] such as printing inks, automotive fuel additive, grease and gear oils, and rubber industry utilize driers. They are commercially sold based on the metal concentration (content) as shown in Table 2.6 and this is referred to as the metal specification of the paint drier. The activity of and efficiency of driers in paint systems is a subject of many studies in the field of coating technology.^[36, 40, 42] It has been established that chelating agents such as 1,10-phenanthroline (commercially known as ACTIV-8) or 2,2'-bipyridyl (Bipy) (see Figure 2.4. a and b) accelerates the activity of metal paint drier. The complex formed is usually referred to as non-emulsifiable and are coded as "FS".

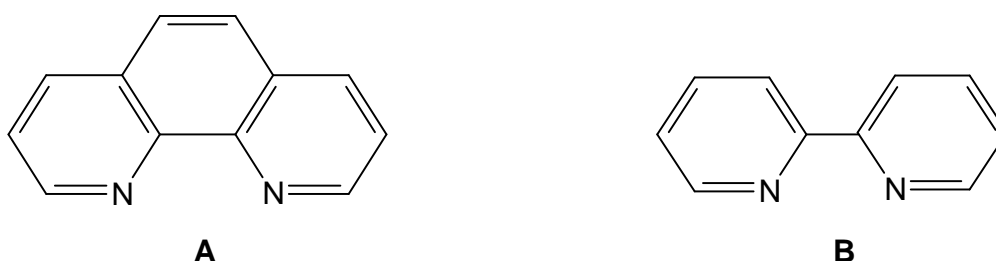


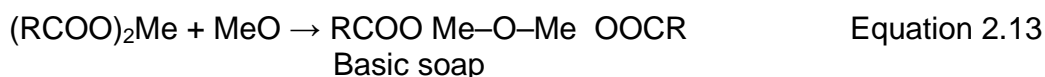
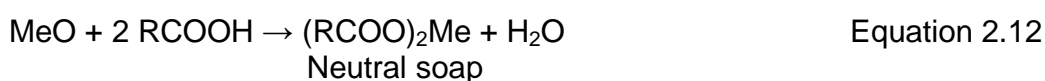
Figure 2.4 Structure A represents 1,10-phenanthroline and B is 2,2'-bipyridyl and both are transition metal (e.g. Co and Mn) chelating ligands

Table 2.6 Characteristics of some commercially available metal octoate driers ^[57]

| Metal | Metal content % | Viscosity at 25 °C, cP | Specific Gravity at 25 °C, g/cm ³ | Appearance |
|-----------|-----------------|------------------------|--|-----------------------------|
| Cobalt | 12 ± 0.2 | 500 | 1.020 | Clear blue violet liquid |
| | 10 ± 0.2 | 175 | 0.975 | |
| | 6 ± 0.2 | 50 | 0.870 | |
| | 3 ± 0.2 | < 15 | 0.830 | |
| | 1 ± 0.2 | <15 | 0.790 | |
| Manganese | 10 ± 0.2 | 1000 | 1.000 | Clear brown liquid |
| | 6 ± 0.2 | 200 | 0.900 | |
| Calcium | 10 ± 0.2 | 500 | 0.975 | Clear liquid |
| | 5 ± 0.2 | 175 | 0.860 | |
| | 4 ± 0.2 | 50 | 0.840 | |
| Lead | 36 ± 0.2 | 1300 | 1.380 | Clear liquid |
| | 33 ± 0.2 | 300 | 1.280 | |
| | 30 ± 0.2 | 150 | 1.230 | |
| | 24 ± 0.2 | 50 | 1.110 | |
| Zinc | 22 ± 0.2 | Not applicable | 1.150 | Clear liquid |
| | 12 ± 0.2 | 50 | 0.930 | |
| | 10 ± 0.2 | 30 | 0.890 | |
| | 8 ± 0.2 | <15 | 0.870 | |
| Zirconium | 18 ± 0.2 | 50 | 1.100 | Clear liquid |
| | 12 ± 0.2 | 25 | 0.960 | |
| | 10 ± 0.2 | 25 | 0.940 | |
| | 6 ± 0.2 | 20 | 0.870 | |
| Barium | 12.5 ± 0.2 | 100 | 0.960 | Clear liquid |

Paint drier manufacturing processes or technologies are based on three basic chemical reactions ^[17, 22], namely:

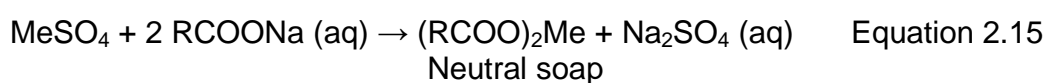
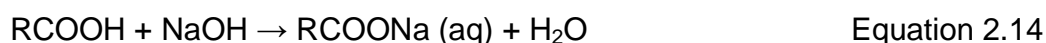
- **Direct fusion (“dry”) process:** This process utilizes a metal oxide (MeO), carbonate or hydroxide which reacts with the carboxylic acid (between 150 and 200 °C) resulting in the formation of a neutral soap (see Equation 2.12). There is no production of wastewater as a byproduct, hence this is mostly seen as an advantage at this point where disposal costs and company liability is of major concern to the industrial manufacturing sector. It is however important to use raw materials of highest purity in order to get driers of good quality. In most instances this tends to be a drawback to most companies as pure, raw materials are very costly. Direct fusion process is the only process that can produce both neutral and basic soap, as illustrated by Equations 2.12 and 2.13 respectively. For the reaction that yields a basic soap, there is less amount of acid required which translates to financial savings.^[52]



Where “Me” and “R” represent a metal and a alkyl group respectively.

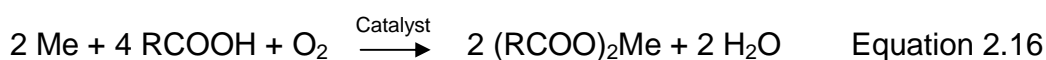
- **Precipitation process:** The process is sometimes called a double decomposition (“wet”) process which begins by alkali metal (sodium) soap formation from carboxylic acid and sodium hydroxide. Salts of heavy metals (e.g. cobalt sulfate, manganese sulfate, etc.) are then added under controlled pH and temperature to the aqueous alkali metal soap. The desired product is easily influenced by keeping the pH and temperature at optimal level. Hence, compared to direct fusion process, the purity of the ingredients is of less importance, implying that raw materials are often obtained at low cost. The disadvantage of precipitation process is the amount of wastewater produced with high level of sulfates. The product is dissolved in an organic solvent, white

spirit, so that the wastewater layer is separated from the product. Depending on the quantity manufactured per annum, disposal costs can run into millions of rands. With current environmental legislations, companies spend valuable time making certain that the wastewater generated is disposed of properly. General equations that illustrate the precipitation process are given below.



- **Direct metal reaction (DMR) process**

The finely ground or melted metal reacts with the carboxylic acid directly to form a metal soap of choice. The reaction takes place in the presence of a catalyst that activates the intake of oxygen from the atmosphere. This method produces an appreciable amount of wastewater as byproduct as shown in Equation 2.16.

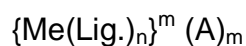


The choice of carboxylate or organic acid is very important when manufacturing driers that can efficiently meet the minimum drying requirements.^[17, 22, 39] The properties will in most cases include:

- Good solubility and high stability in various kinds of binders, hence branched acids are used as they enhance solubility of metal soaps.
- Drier must not form skins, sediment and gel, or interact with pigment which implies that it should have high stability.
- Its catalytic activity after paint application should be of high efficiency at optimal metal content.
- Low viscosity to make the handling of driers easier.
- The size of the acid molecule is important as it will afford adequate metal concentration

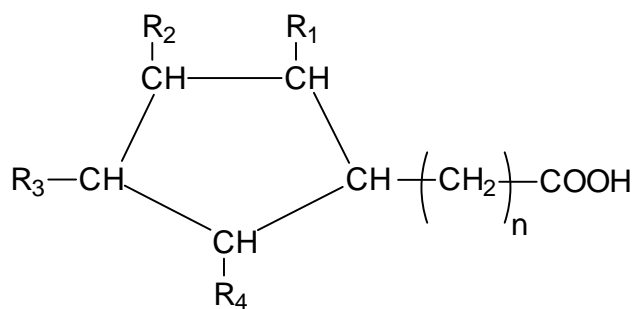
Driers used in paint industry are mostly naphthenates, octoates or neo decanoates.^[38] These are salts of naphthenic acid, 2-ethyl hexanoic acid (2-EH) and neo-decanoic acid respectively (see Figure 2.5). Refined tall oil fatty acids such as oleic acid and linoleic acid are seldom used and are not favoured compared to the first three types. Octoates are the ones which are mostly used because they yield driers of high metal concentrations with low viscosity. The solubility and stability of drier soaps is to a large extent influenced by the position of the substitute on the acid structure. Those that have substitutes adjacent to the carbonyl group are frequently used, e.g. 2-EH and neo- decanoic acid.

In water-based paint, the driers used are pre-complexed^[40] using a ligand and this provides two advantages, namely optimization of their performance and compatibility improvement with the water-borne coating. They are mostly coded as “WEB” (water emulsifiable). The general structure of pre-complexed driers is



Where:

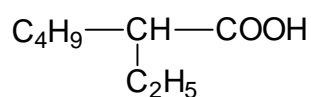
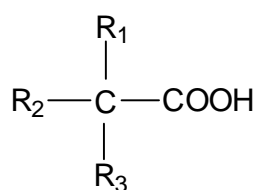
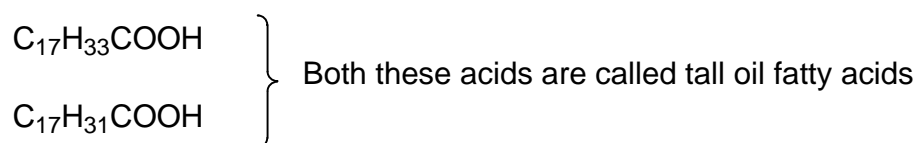
| | |
|------|--|
| Me | = Metal cation |
| Lig. | = Ligand |
| n | = Valency, usually 1, 2, 3 or 4 |
| m | = Valency metal-ion |
| A | = Acid-anion, usually RCOO^- , RPO_3^- , RSO_3^- , R_2PO_4^- , and $(\text{RPO}_4^{2-})^{1/2}$ |

**Naphthenic acid**

Where

R₁, R₂, R₃ and R₄ are short
alkyl chains or hydrogens

n = 1 to 3

**2-ethylhexanoic acid**Where R₁, R₂ and R₃ are
alkyl chains with a total of
eight carbons**Neo-decanoic acid****Oleic and linoleic acid respectively**Figure 2.5 Examples of organic acids used for drier production^[1]

Chapter 3

3. Industrial Processes and Paint Drier Production

It is public knowledge that industrial companies that are involved in manufacturing specialty chemicals are faced with strict environmental regulations with regard to managing waste generated during each production process. Community members, environmental scientists, lawyers and organizations are constantly on the lookout as to how companies conduct themselves when it comes to waste disposal.^[58] In order to adhere to acceptable legislation, chemical manufacturing companies find themselves channeling more financial resources into waste disposal than they would do if only they could eliminate generations of waste. Industrial chemical processes are grouped under three categories^[59] which are:

- **Batch process:** Raw materials (inputs) are added into a reactor and do not leave the reactor until the end product (output) is formed. This shows that they are time-dependent as they require proper planning of production before manufacturing occurs. At the end of the process products and by-products are removed from the reactor to enable it to be used again. Between the start time, $t = t_0$ and end time, $t = t_f$ nothing leaves the reactor boundaries, so for these processes the general mass balance equation^[59] is derived from:

$$\text{Accumulation} = \text{final output} - \text{initial input} \quad \text{Equation 3.1}$$

$$\text{Accumulation} = \text{generation} - \text{consumption} \quad \text{Equation 3.2}$$

Equations 3.1 and 3.2 put together yields the following general equation for a batch process.

$$\text{Initial input} + \text{generation} = \text{final output} + \text{consumption} \quad \text{Equation 3.3}$$

- **Continuous process:** Products and raw material are continuously moving between the reacting vessels. For this type of process there is no accumulation as nothing changes with time, and hence it is usually represented by the following general equation:

$$\text{Input} + \text{generation} = \text{output} + \text{consumption} \quad \text{Equation 3.4}$$

- **Semibatch process:** This is a process which is neither classified as a batch process nor a continuous process.

As described under Sub-section 2.4.2, the three drier production processes follow the batch process described above. The second production process, “precipitation process” as described, generates large amounts of wastewater. With current stringent environmental legislation & laws and disposal costs, it is important for an industry to look at ways of minimizing and managing the production of waste that accompanies this technology during paint drier production.

3.1 Waste minimisation and management at a Paint Drier Plant

Literature that could shed light on waste minimization at a paint drier plant production is unavailable in the public arena. Research carried out on paint driers is mostly based on two areas, i.e. drier interaction with paint and new environmental friendly drier types, rather than on waste minimisation during production processes. It was important to look at other industrial processes that generate waste during production, in order to mimic strategies employed by others when dealing with waste minimisation and management.

3.2 What is Waste and Waste Minimization?

Waste can be described as an unwanted substance or by-product that is produced during the production of an important commercialized product. ^[60-63, 67] This usually includes liquid or solid residues from a process, contaminated materials, off-

specification products, accidental spillage, machine/finishing residues, fugitive emissions and gaseous discharges. Waste can be grouped under three categories, namely process wastes, utility wastes and other wastes. If left unattended these can be a health hazard to humans and usually cause a long-lasting effect on the environment, i.e. to both flora and fauna. Industrial waste should always be handled with care as most are hazardous. Therefore, the type of waste, and harmful effects it is capable of inflicting should be adequately known. Sources of waste during production processes are best described using Figure 3.1 shown below.^[73, 77, 94]

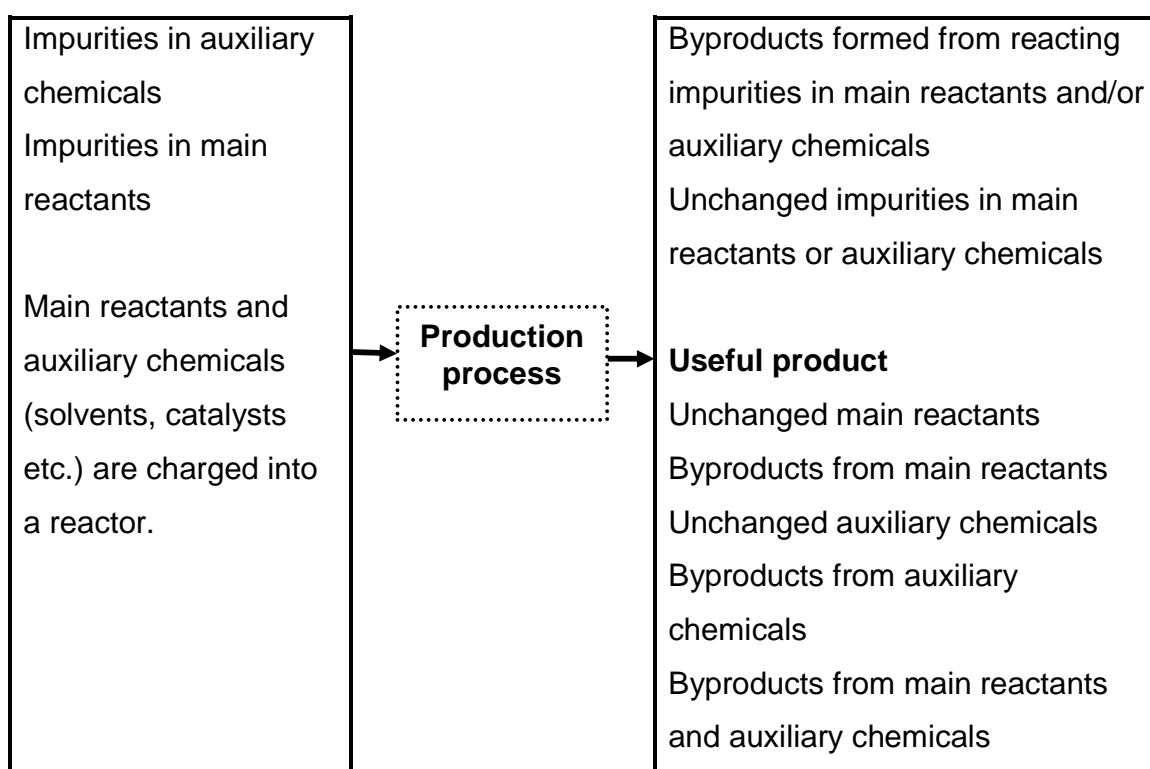


Figure 3.1 Waste generation sources at an industrial production process

Most environmental organizations have offered encompassing descriptions of Waste Minimization (WM). To name but a few organizations, the United States Environmental Protection Agency (US EPA), the Institution of Chemical Engineers' Waste Minimization Guide,^[60, 68] and the Department of Environmental Affairs and

Tourism (DEAT) of South Africa ^[78, 84] describe WM as the reduction, to the extent feasible, of hazardous waste that is generated or subsequently treated, sorted, or disposed of at predetermined zoned sites.^[77-83] Activities that are carried out with the sole aim of avoiding waste creation or applying cleaner production technologies, elimination or reduction of waste at its source, allowing reuse or recycling qualify to be described as WM. The Scottish Environment Protection Agency (SEPA)^[81] on their website describes the procedures that need to be followed when carrying out WM. Industrial manufacturing companies should follow preplanned procedures (methodology of waste minimization) made up of stages or phases. These stages can be revisited whenever the need arises and are described in Figure 3.2 below.

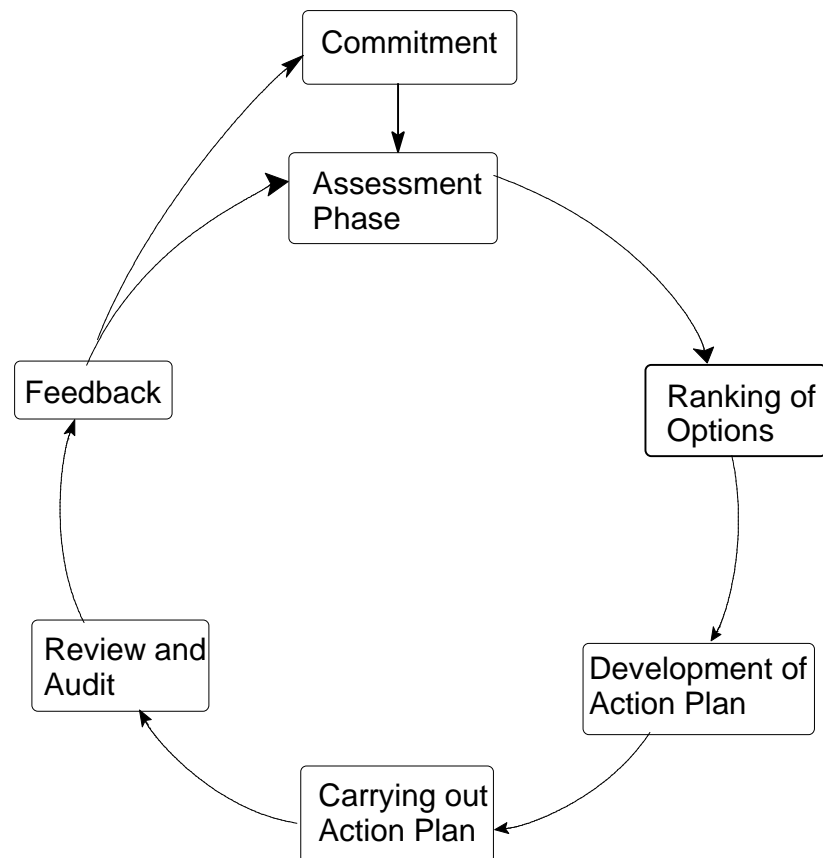


Figure 3.2 An organized and continuous systematic approach to WM^[16, 68-69, 87]

Figure 3.2 shows that the management's commitment to WM is crucial for the company to achieve the desired results.^[81, 84, 86] All other subordinates in the company can only play a major role if the company management prioritize WM in their planning, just as they do when it comes to product quality. The driving team will be able to tackle waste problems faced by the company with great enthusiasm, and be able to involve everyone if the management is supportive.

The next phase is the determination of the extent of the effluent/waste problem. This is usually referred to as the assessment phase and is discussed in more detail in Section 3.3 below. Accurate records of inputs to and outputs from the production process, as well as disposal costs, are needed to build up a strong case. It is important to score each issue while noting the benefit each intervention will provide. Information obtained during assessment is then used to rank the problems so that priorities for WM can be determined. Ranking is usually done after feasibility analysis is carried out and takes into account technical, economic and environmental evaluations and considers the most profitable option.^[64, 92] The profitability of carrying out a WM programme is usually determined during assessment phase or review stage. This is done in order to determine its impact on the benefits (see Section 3.4) the company hopes to achieve. If the company had listed Return on Investment (ROI) as one of the goals to achieve, the percent on ROI can be calculated using Equation 3.5.

$$ROI = \frac{(B - A) - [(C + E + D)/L]}{C + E + D} \times 100 \quad \text{Equation 3.5}$$

Where: A = annual costs after implementing of WM programme

B = annual costs before implementation of WM programme

C = capital investment for WM programme

D = estimated project termination/disassembly cost

E = installation operating expenses

L = number of useful years of the programme

Development of action should take into account the WM practices hierarchy shown in Figure 3.3 shown below. Timeframes should be clearly stipulated at this stage. If a private company is required to carry out the action plan, there should be someone to liaise with the team who makes sure that timeframes are always adhered to.^[16] Though an “outsider” will bring in new ideas and be unbiased as to the production processes, problems with employee openness should be attended to speedily, as withholding vital information can impede the smooth running of the project. In the case where waste streams are expected to be measured, installation of meters to all outlet pipes should be made in order to accurately determine wastes generated. The action should constantly be reviewed in order to identify or make improvements where possible. The findings, improvements and actions or recommendations should be communicated to both the management and employees.^[81] As this is a crucial stage to make everyone buy into the idea, all communications made should also take production quality and quantity into consideration. All role players should receive updates timeously on new findings through company newsletters, weekly meetings or notices on the company notice boards.

Finally, all findings and recommendations should be consolidated in a report that needs to be revisited at a predefined stage. This will help the company to determine the impact of the WM programme on all expected benefits.

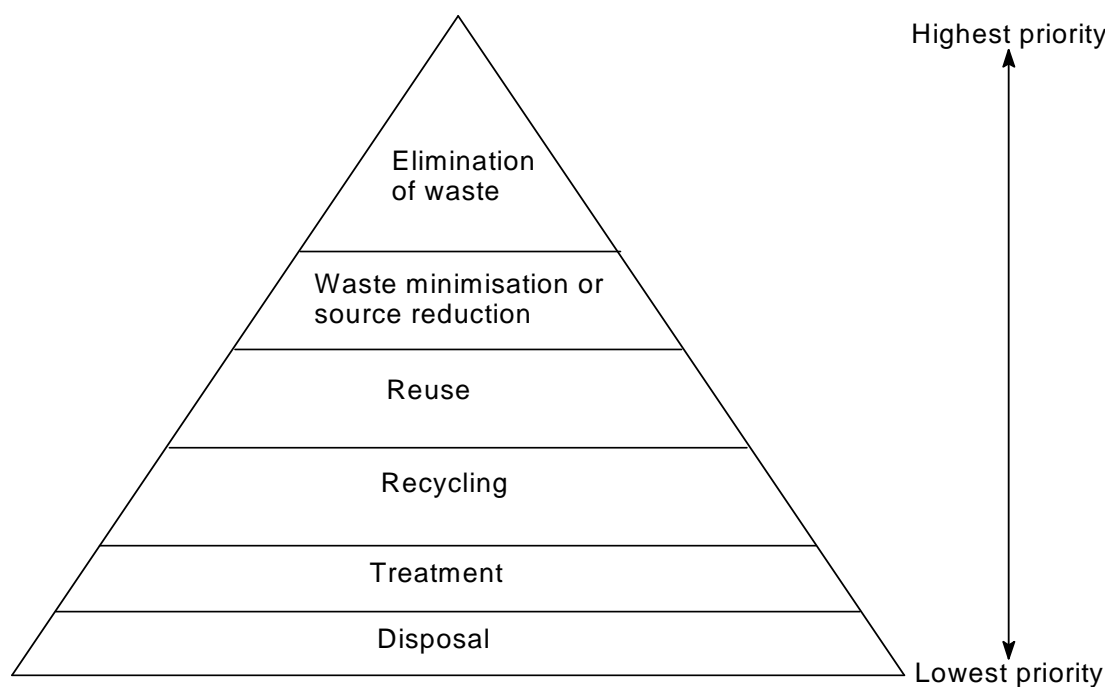


Figure 3.3 Integrated waste management practices hierarchy ^[69-71, 117]

Traditionally, industries never bothered much on waste minimisation and hence missed out on process improvement that could ultimately translate to high profit.^[82] It is currently accepted that while carrying out WM and management, a particular hierarchy, shown in Figure 3.3, that emphasises certain priorities should be borne in mind.

Figure 3.3 shows that elimination of waste should be given highest priority if possible. If this is not possible to achieve, source reduction should be next priority on the line. Source reduction will in most cases focus on the following aspects:^[84, 85]

- **Material substitution:** Main reactants can be replaced, e.g. replacing metal sulfate by metal hydroxide (see Sub-section 2.4.2).

- **Process substitution or elimination:** With regard to the current case study, it will mean changing from precipitation process to direct fusion process or DMR process described under Sub-section 2.4.2.
- **Good housekeeping and equipment maintenance:** This is usually achieved by keeping a proper record of meter reading of the resources (electricity or water) utilized against production amount. Routine maintenance of equipment will surely extend their lifespan, e.g. painting to prevent rust formation.
- **Water and energy conservation:** Water and energy are scarce resources and proper usage is vital.
- **Pollution prevention in design and planning:** Re-engineering process in order to minimize pollution in design will help reduce costs.
- **Training awareness:** Personnel running the plant should be trained and their voices should be heard, as they have more practical knowledge of operation than management.
- **Life-cycle analysis:** This is sometimes referred to as “cradle-to-grave” analysis as waste generators are required to trace the waste from the point it was generated to the final site where it is properly disposed of. This shows that a traceable track record should be made for each waste generated. Therefore all individuals (vendors, customers and contractors) who are directly involved should be co-opted into the pollution prevention team
- **Inventory control:** “Just-in-time” purchases ^[128, 16] of raw material could be implemented for most local materials. Material usage can be traced using barcodes, hence inventory in store is known at all times.

It should be mentioned that successful recycling is only achievable if the waste can be used as a resource for starting materials.^[154] For this to be implemented efficiently, the effect and amounts of contaminants should be known so that production quantities and quality are not compromised. Two recycling categories have been identified as:

- **On-site recycling:** This to a large extent includes in-process recycling, re-use and regeneration re-use. During in-process recycling the starting material is recycled back to the process without firstly collecting it, so this is sometimes not regarded as waste. Reuse of waste is mostly carried out on collected, stored waste that contains appreciable amounts of contaminants. The waste is used as starting material for the same production process from where it originated. Regeneration reuse can be described as using waste that has or has not been treated (depending on the amount of contaminants) in other production processes at the site.
- **Off-site recycling:** Once the purity of waste in hand has been established, the waste can be used for other purposes rather than in production processes.

A summary of information provided above for source reduction and recycling of waste is given in Figure 3.4 below. The figure shows that these two waste management practices hierarchy are usually referred to as “Waste minimization techniques”.

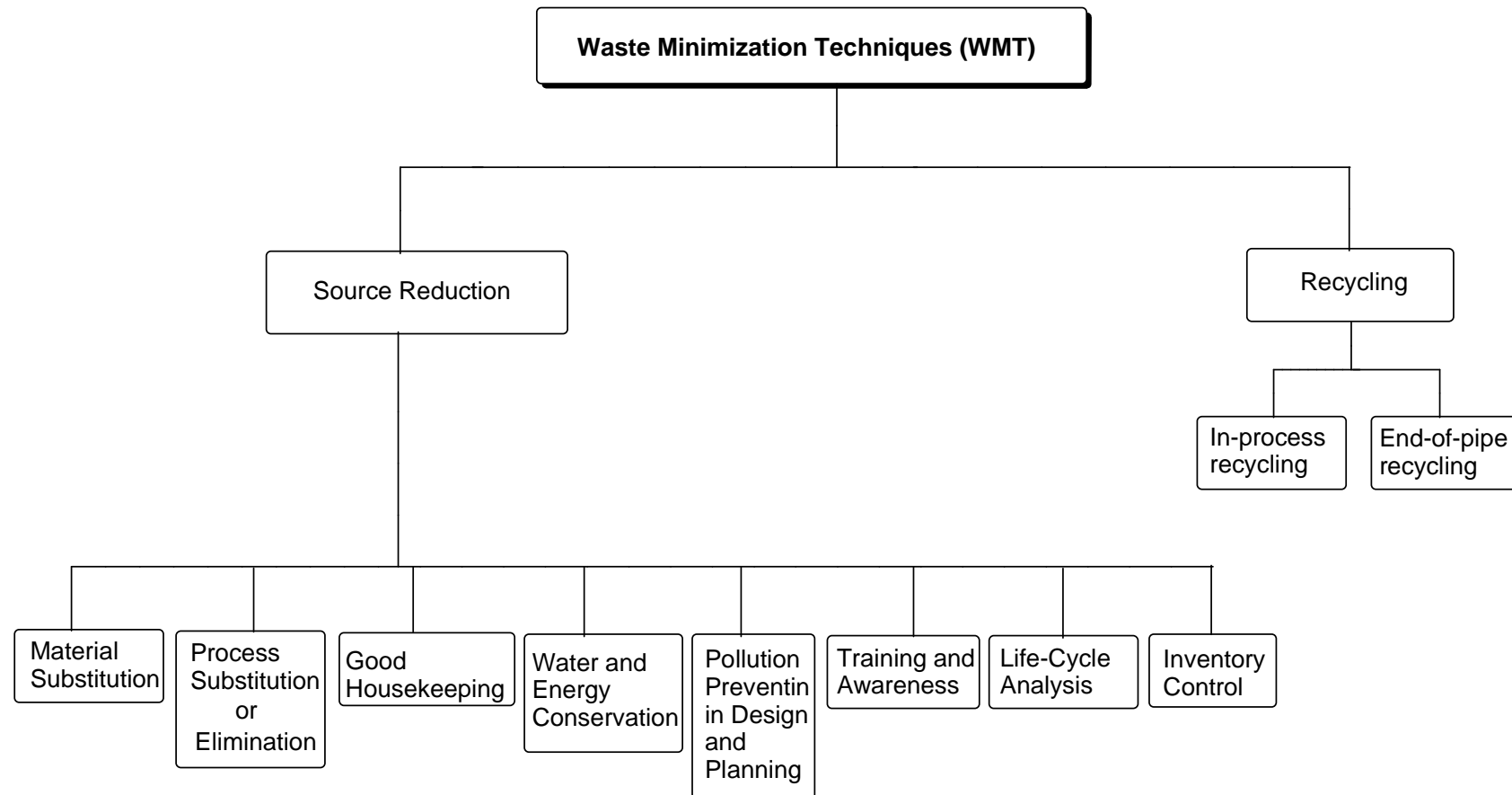


Figure 3.4 Applicable waste minimization techniques for an industrial sector [63, 64, 66]

Treatment using a contractor is applied if the preceding measures cannot be implemented. This will be cost effective if waste streams are segregated as it is easier to treat few contaminants than will normally be the case for mixed waste stream.

Techniques used when treating waste^[84, 95-97, 132] include:

- physical treatment (filtration, ash blending, evaporation, stabilization, and flocculation),
- chemical treatment (oxidation, reduction, and precipitation),
- biological treatment,
- encapsulation,
- special burial,
- neutralization, and
- incineration.

The company's detailed records of waste generated should be readily available and properly archived.

Disposal is usually regarded as the last measure that should be carried out when all other waste management practices cannot be implemented. It should be carried out at designated sites while taking into consideration the impact this will have on the environment if not properly done.^[5, 58] This is usually carried out by a private contractor and the management should ascertain that such an individual or company is properly registered and has a valid permit.^[88] It should be remembered that the generator of waste is responsible throughout the life cycle of the waste and hence should carry out an audit to verify the contractor's compliance with environmental legislations. As it is embodied in the Constitution of South Africa Act 108 of 1996, "Everyone has the right to:^[88]

- An environment that is not harmful to their health or well being; and
- To have the environment protected, for the benefit of present & future generations."

Section 2 of the National Environment Management Act 107 of 1998 lists 18 principles which include; prevention principles, waste hierarchy, precautionary principles, cradle-to-grave principle, and polluter pays principle, to mention just a few.^[88] The emphasis is placed on the generator of waste as opposed to the collector. This means that once the waste leaves the company site, the company is still 100% responsible for any unlawful disposal that can impact on the environment.

3.3 Waste Minimisation Assessment Techniques

During the assessment phase (see Figure 3.2) several techniques can be applied to a particular production process.^[63, 65] Some of the known techniques might not be applicable but the ones which are will surely provide valuable information. Assessment phase is sometimes carried out under two broad categories which are pre-assessment stage and assessment stage.^[66, 74-77] In this project, the techniques discussed below will just be grouped under the broad name “assessment phase”. Waste minimization assessment techniques include:

3.3.1 Scoping Audit

The starting point of WM is looking at what goes into the production process and the business operation.^[65-67, 72] This means that a review of the process flow diagram for each production process in the company should be made.^[69] Identification of potential and actual waste streams (both inputs and outputs) will make it easier for measurements to be taken. The information obtained is then used to establish a WM baseline for a particular process. Basic cost data are collected to determine the main raw material and energy resources.^[62] This is done using a list of all inputs and outputs. This will mean going through company purchase records and invoices. It is important to know that internal stock transfer records are mostly misleading and should be avoided unless purchase and invoices are not available.^[69] Material suppliers could also help with data unavailable at the company. Energy, water and effluent costs are easily obtainable from company invoices. If the required information

is unavailable the service providers should be approached in order to obtain such information. The information obtained can be collated in a table showing the scope to save (see Table 3.1). The estimated scope to save is found by multiplying the estimated cost/year by the scope to save percent. Using Table 3.1, each material is then ranked and the one that shows highest saving margin is given the highest priority. Note that percentages given in Table 3.1 were obtained from UK based industries; they are however applicable globally and South African industries are no exceptions.

Table 3.1 Waste minimisation scope to save for industrial production process ^[65, 77]

| Resources and Services | Quantity | Cost/unit in Rand | Estimate Cost/year in Rand | Scope to save % | Estimate of Scope to Save | | Priority Ranking (1=highest) |
|-------------------------------|----------|-------------------|----------------------------|-----------------|---------------------------|-------------|------------------------------|
| | | | | | Minimum (R) | Maximum (R) | |
| Raw materials | | | | | | | |
| First most used | | | | 1 to 5 | | | |
| Second most used | | | | 1 to 5 | | | |
| Third most used | | | | 1 to 5 | | | |
| All other materials | | | | 1 to 5 | | | |
| Packaging | | | | 10 to 90 | | | |
| Ancillary materials | | | | 5 to 20 | | | |
| Consumables | | | | 10 to 30 | | | |
| Energy: | | | | | | | |
| Electricity | | | | 5 to 20 | | | |
| Heat for the process | | | | 10 to 30 | | | |
| Water | | | | 20 to 80 | | | |
| | | | | | | | |
| Wastewater or effluent | | | | 20 to 80 | | | |
| Solid waste | | | | 10 to 50 | | | |
| | | | | | | | |
| TOTAL | | | | | | | |

3.3.2 Mass Balance for materials

Equations 3.1 through 3.4 give a summary of mass balance which is defined as a “balance sheet” for material use.^[76] This means that any losses or emissions that were previously unaccounted for can be quantified.^[62] Based on Equations 3.1 to 3.4 material balance is usually represented by the mass conservation principle:^[64, 66]

$$\text{Mass in} = \text{Mass out} - \text{Generation} + \text{Consumption} + \text{Mass accumulated}$$

Equation 3.6

Using mass balance for material, the concentration of waste constituents can be determined. This is mostly achievable by drawing a process diagram which shows the system boundaries, streams entering and leaving the process as well as points at which wastes are generated.^[66] An example of a process flow diagram is given in Figure 3.5 below.

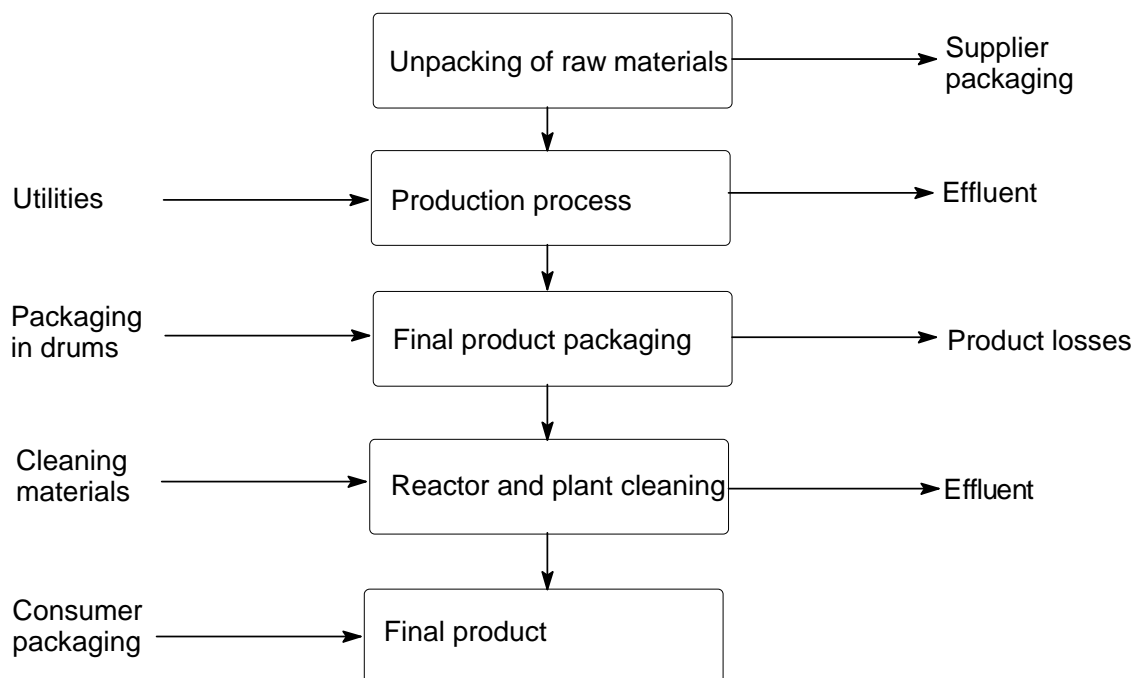


Figure 3.5 General process flow diagram for a manufacturing company^[76, 77]

Table 3.2 shows that using the mass balance, calculation of elemental balances in the raw material and product for a particular process are possible. Any difference can be tracked down in the wastewater produced. Information obtained from analytical results can then be compared with calculations made. When preparing mass balance, the following factors should be taken into account:^[64]

- Precision of analytical data and flow measurements for wide inlet and outlet waste streams
- The time span under which measurements are made
- Complexity of large processes where recycle streams are present
- Need to comply with certain emission regulations

Table 3.2 Mass balance for inputs and outputs for a production process

| Inputs to reactor | | Outputs from reactor | |
|-----------------------------|------------|------------------------------------|------------|
| Substance | Amount, kg | Substance | Amount, kg |
| Metal in raw material | | Metal in the product made | |
| Wasted part of raw material | | Reaction wastewater | |
| | | Wash wastewater | |
| | | Distillate water | |
| | | Wasted part in reaction wastewater | |
| | | Wasted part in wash wastewater | |
| | | Wasted part in distillate water | |
| TOTAL | | TOTAL | |

3.3.3 True Cost of Waste

According to the Environment Agency (EA), a UK based organization, “the cost of your waste is not so much the cost of getting rid of it as the value of what you are getting rid of”.^[65] Most companies underestimate the true cost of waste because they

only pay attention to the disposal cost.^[62, 65] The true cost of waste should be based on:

- *Disposal costs*: Vary from simple disposal to treatment, usually by a private company, which then disposes to landfill.
- *Purchase cost of unreacted raw materials and materials that constitute waste*: The purchase price will include the amount paid for anything that ends up being thrown away resulting in a negative return on investment.
- *Handling/processing costs*: From the moment it is generated, labour and storage facilities are all required to keep it safe.
- *Management time*: Useful time that could be spent on valuable product is spared to deal with waste.
- *Lost revenue*: It is mostly regarded as something that produces a negative return on investment.
- *Any potential liabilities*: Certain waste produced by the company will be subject to Safety, Health and Environmental (SHE) regulations and as such requires special disposal procedures. Companies could be required to alter their production process, hence incur financial loss.

This shows that;

The true cost of waste = disposal costs + purchase cost of materials
 + handling/processing costs
 + Management time
 + lost revenue
 + any potential liabilities
 = much more than the company realize!

Equation 3.7

Table 3.1 can only be utilized once the true cost of waste and potential savings have been established. Equation 3.7 reveals the shocking truth of the cost of waste that can range between 5 to 20 times that of disposal.^[80, 93]

3.3.4 Monitoring and Targeting

Monitoring and targeting (M&T) is sometimes referred to as “measuring to manage” (MtM) which is mostly used to compare consumption with production targets.^[65, 77, 85] In this project, monitoring and targeting will not be applied but is nevertheless worth mentioning. This technique utilizes pictorial representations such as a trend analysis graph, histogram, pie charts, Pareto charts, Sankey diagrams, etc. for data analysis. Since this technique is less important in the current project, details regarding graphs utilized will not be made.

3.4 Benefits of carrying out a Waste Minimisation Programme

The main objective of any industrial manufacturing sector is to make profit while keeping expenses low. Company shareholders could be more than happy if the process is 100% efficient and is able to convert all raw materials to product without generating any waste. Unfortunately this is an ideal situation that is almost impossible to achieve. Even a minor process that takes place in all household kitchens produces waste in one way or the other. Having said this, it is important to seek ways in which waste can be reduced at source. One such way is through implementation of WM at a production facility. There are several benefits for carrying out WM programme^[90, 91, 94-97] and they include:

- **Conservation of scarce resources:** Practicing WM will conserve most resources; including water, which are very scarce and nonrenewable raw materials. Reduction of fresh water usage will affect the amount of waste generated positively.
- **Cost savings:** Improved raw material use will impact positively on the production cost for a particular product. The efficiency of the production process, productivity and profitability will increase. The amount of raw material turned into useful products will increase. Waste management, energy costs and disposal costs will reduce.

- **Environmental Compliance:** Chances of the company being litigated are reduced and less impact on the environment is caused due to waste reduction.
- **Risk or liability reduction:** Shareholder's confidence will be enhanced and the company will receive high accolades from the community it serves. Employees will feel safer as soon as they realize that the management cares about their safety.
- **Company position in the market:** Customer relations will increase once they realize that they are dealing with an eco-friendly company. The image and profile of the company and its competitiveness will strengthen.

3.5 Waste Minimisation Barriers

The implementation of WM is without doubt derailed by many obstacles just as any new programme to be implemented in a company for a particular purpose. Barriers that are associated with WM fall into four categories: economic, technical, regulatory and institutional.^[68, 117] It is strongly believed that regulatory barriers pose more major problems than the other three. This is usually observed while trying to keep within one correct regulatory framework, only to find that the company is itself violating others.

Potential barriers will always be encountered while implementing WM techniques, but the company shouldn't be deterred by them as they are outweighed by benefits mentioned above.

CHAPTER 4

4. COMPANY PROFILE AND PROCESS

Metallica Chemicals (Pty) Ltd (the company) was formed on the 1 July 2000. The company produces specialty chemicals for the paint and textile industries. In the case of the paint industry they produce metal paint drier soaps (PD). The company's production site is situated in the Ebuhleni Industrial Park at Cato Ridge, KwaZulu–Natal, South Africa. Acti-chem is the distribution wing of the organization. Its head offices are situated in Westville, KwaZulu–Natal, South Africa. It operates as the sales agent for both local and export markets of Metallica Chemicals (Pty) Ltd's products.

This chapter consists of five sections. Section 4.1 gives a description of the company structure and operations. In Section 4.2 the PD products manufactured by the company are outlined. A detailed description of the production process for cobalt octoate [cobalt 2-ethylhexanoate, $\text{Co}(\text{C}_7\text{H}_{15}\text{CO}_2)_2$] and manganese octoate [manganese 2-ethylhexanoate, $\text{Mn}(\text{C}_7\text{H}_{15}\text{CO}_2)_2$] is given in Section 4.3. Quality control and efficiency during the production process and the end product is described in Section 4.4. Finally in Section 4.5 the packaging and storage of final product are described.

4.1 Company Description

The company's factory at Cato Ridge consists of two production plants, one for textile auxiliaries and one for paint driers. There is also an administrative department, a laboratory, a workshop, two storage facilities and a clinic run by a full time occupational health & nursing practitioner. The site plan for this factory is shown in Figure 4.1.



Figure 4.1 Site Plan of Metallica Chemicals (Pty) Ltd at Cato Ridge, South Africa

Key to areas highlighted in Figure 4.1

- | | |
|---|--------------------------------------|
| 1. Security Check Point | 21. Redundant Mercury Building |
| 2. Main Administrative Offices | 22. Compressor Room |
| 3. Canteen and Kitchen | 23. Electrical Store |
| 4. Main Laboratory | 24. Water Cooling Tower (below 25) |
| 5. Factory offices and Training Room | 25. Textile Effluent Storage Area |
| 6. Factory Canteen | 26. Boiler House |
| 7. Clinic | 27. Mercury Laundry and Change Rooms |
| 8. Change Rooms | 28. Mercury Laboratory |
| 9. Mercury Warehouse No. 4 | 29. Laundry |
| 10. Mercury Warehouse No. 3 | 30. Effluent Treatment Plant |
| 11. Workshop | 31. Disused Still Room |
| 12. Finished Goods Warehouse | 32. Bulk Tanks |
| 13. Bonded Warehouse | 33. Mercury Recovery Plant |
| 14. Raw Material Warehouse | 34. Storm water Dam |
| 15. New/Reconditioned Drum Store | 35. Ash Dam |
| 16. Mercury Warehouse Intermediate | 36. Outside Solvent Store |
| 17. Textile Production Plant (TPP) | 37. Covered Storage Pad |
| 18. Redundant Catalyst Plant | 38. Covered Storage Pad Dam |
| 19. Metal Paint Drier Production Plant (MPDPP) | 39. Dam No. 3 |
| 20. Storage Shed | 40. Outside Solvent Store |
| L. Boundary line beyond which eating is prohibited. | 41. Sweetwater Dam |

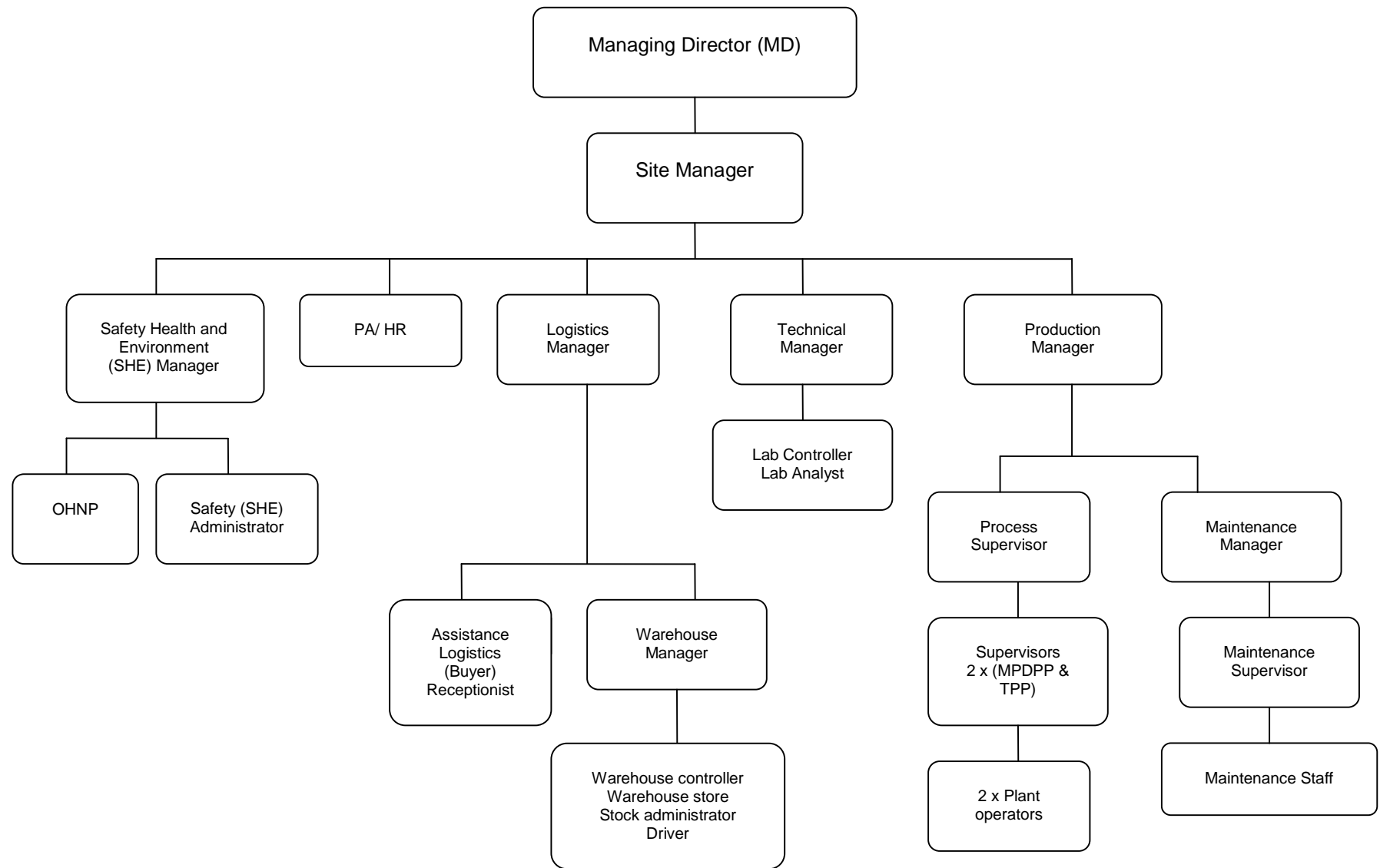


Figure 4.2 The organizational structure of Metallica Chemicals (Pty) Ltd

Figure 4.2 shows the organogram of the company. It has a staff complement of 28 personnel of which 6 have been loaned from Acti-Chem. Two cleaners, three grounds maintenance staff and two security personnel form part of everyday staff, but are hired from two private companies.

The production plant operates continuously from Monday to Friday. From Monday to Thursday it operates for 24 hours a day, with two 12 hours shifts (from 6am to 6pm and from 6pm to 6am). On a Friday it operates until 4.30pm as there is no night shift. The plant supervisors work for 8 hours (from 8am to 4pm). The administration department's working hours are 8am to 4pm. Each 8 hour shift has a 30 minute break and the 12 hour shifts have two 30 minute breaks. Entry to and exit from the company is controlled by a private security guard.

4.2 Product Description

The company has two production plants. One is engaged in the manufacturing of PD and the other makes textile auxiliaries. The following PDs are produced by the company

- Barium nonyl phenate [$\text{Ba}(\text{C}_{15}\text{H}_{23}\text{O})_2$]
- Calcium octoate [calcium 2-ethylhexanoate, $\text{Ca}(\text{C}_7\text{H}_{15}\text{CO}_2)_2$]
- Calcium naphthenate [$\text{Ca}(\text{C}_6\text{H}_5\text{CO}_2)_2$]
- Cobalt octoate [cobalt 2-ethylhexanoate, $\text{Co}(\text{C}_7\text{H}_{15}\text{CO}_2)_2$]
- Manganese octoate [manganese 2-ethylhexanoate, $\text{Mn}(\text{C}_7\text{H}_{15}\text{CO}_2)_2$]
- Copper octoate [copper 2-ethylhexanoate, $\text{Cu}(\text{C}_7\text{H}_{15}\text{CO}_2)_2$]
- Potassium octoate (potassium 2-ethylhexanoate, $\text{C}_7\text{H}_{15}\text{CO}_2\text{K}$)
- Lead octoate [lead 2-ethylhexanoate, $\text{Pb}(\text{C}_7\text{H}_{15}\text{CO}_2)_2$]
- Zinc octoate [zinc 2-ethylhexanoate, $\text{Zn}(\text{C}_7\text{H}_{15}\text{CO}_2)_2$]
- Zinc naphthenate [$\text{Zn}(\text{C}_6\text{H}_5\text{CO}_2)_2$]
- Zirconium octoate [zirconium 2-ethylhexanoate, $\text{Zr}(\text{C}_7\text{H}_{15}\text{CO}_2)_2$]
- Mixed drier blends namely Putty drier LFC, LF7N, LF9N, LF11, D048N and CAL-DRY PLUS N. LF represents lead free in drier blends. The compositions of these drier blends are given in Table 4.1.

Table 4.1 Composition of Mixed Drier Blends

| Drier blend | Metal octoate used | | | | | | Other raw materials added | | | | |
|--------------------|--------------------|----|----|----|----|----|---------------------------|---|----|------|-----|
| | Ca | Co | Mn | Pb | Zn | Zr | W/S | S | BO | DppG | PEp |
| D048N | ✓ | ✓ | | | ✓ | ✓ | ✓ | ✓ | ✓ | | |
| LF7N | ✓ | ✓ | | | ✓ | ✓ | | ✓ | | | |
| LF9N | ✓ | ✓ | | | ✓ | ✓ | ✓ | ✓ | | | |
| LF11 | | ✓ | ✓ | | | ✓ | | | | | ✓ |
| Putty drier LFC | ✓ | | ✓ | | ✓ | ✓ | ✓ | | | | |
| CAL-DRY PLUS N | ✓ | ✓ | | ✓ | | | | | | ✓ | |

W/S white spirit*, ^S Sabutol, ^{BO} Butyl oxitol, ^{DppG} dipropylene Glycol, and ^{PEp} plus Exx print T76A.

* A mixture of saturated aliphatic and alicyclic C₇-C₁₂ hydrocarbons with a content of 15-20% of aromatic C₇-C₁₂ hydrocarbons ^[10]

The main aim of this research was to look at waste minimisation in the drier plant with specific reference to cobalt and manganese driers. The other products will therefore not be discussed any further in this document.

The octoate is a metal compound of 2-ethylhexanoic acid and the cobalt derivative is one of the most commonly used in making commercial PD products. PD as described in Sub-section 2.4.1 is a solution of the metal drier in organic solvents, usually VOCs. The concentration of the commercial PD is expressed as the percentage by mass of the metal content in the mixture. A common PD manufactured by the company is Co(C₇H₁₅CO₂)₂ in white spirit. Table 4.2 shows the % content of cobalt and manganese in the final product. These are the standard concentrations of the PD routinely manufactured by the company. These products are sold to Acti-Chem which then sells them to local, national and international paint manufacturing industries.

Table 4.2 Cobalt and manganese based PD specifications manufactured by the company

| Metal of interest | Percent content of metal |
|--------------------------|---------------------------------|
| Cobalt | 6 % cobalt naphthenate |
| | 6 % cobalt heptanoate |
| | 6, 8, 10 or 12 % cobalt octoate |
| Manganese | 6 % manganese naphthenate |
| | 8 , 9 or 10 % manganese octoate |

However, products can be customized before selling to suit the customer's PD metal content specifications. The company also makes six multi-metal blended driers (see Table 4.1) from a combination of some of the PD. In Section 4.3 the manufacturing process involving the production of cobalt octoate and manganese octoate PD as well as modifications made during the process are described. Each finished product is packaged according the description given in Section 4.5.

4.3 The Manufacturing Process

Cobalt products are usually manufactured once or twice per week while manganese products are made less frequently (once a month or less often). Prior to production starting on the plant, the plant operator collects a ten page Standard Manufacturing Formulation Document (SMFD) which accompanies the batch from the start to the finish of the production process. The contents of this document are described below. The SMFD is prepared by the production manager for a particular batch to be manufactured. Information contained on each page is:

- Page 1 gives the Standard Manufacturing Formulation (SMF). This shows the percentages by mass of all the raw materials to be used and the mass of the product to be made. This can be considered equivalent to a product specification sheet.
- Page 2 gives a summary of the manufacturing method in a maximum of six simple steps, a list of safety precautions to be taken and processing equipment required. It also shows the operator assigned to this batch by their name and signature.

- Pages 3 to 5 give a detailed description of the manufacturing procedure. For example it includes how and when each raw material should be added, safety precautions which should be followed, drumming procedures to be followed while packaging the finished product. The operator has to enter the time when each step in the process has been completed, how much and the source of, each substance which has been added to the batch. This involves having available extensive information on raw material batches, wash wastewater stored in the flow-bins, part drums of previously manufactured batches and ullages (finished product used for flushing out delivery pipes).
- Page 6 is a quality control sheet for intermediate and final product testing. This is completed by the laboratory technician.
- Page 7 is for container and labeling check.
- Page 8 is a batch control form for the operator to record any information on changes made to the production process as instructed by the laboratory analyst, and any problems encountered during production.
- Pages 9 to 10 contain the actual amount of raw and recycled (taken from Pages 3 to 5) material used and products produced. Further, it details packaging information, the yields and actual concentration of the product to three significant figures.

4.3.1 Manufacturing process of cobalt octoate

The 12% cobalt PD makes up about 80% of the cobalt-based drier output from the plant. It is produced as a 3.5 T batch only. The process flow diagram in Figure 4.3 describes the steps involved in the manufacture of cobalt PD at the plant. There are five steps involved in the production of cobalt-based paint driers. The tasks involved in each of the five steps of the process in Figure 4.3 will be discussed in this section in terms of inputs to, output from, control measures in place and operating conditions used in the production of the cobalt octoate. The whole process, from the moment the reactor is charged through to the dilution of the final product (see Figure 4.3), takes about 12 to 16 hours to complete.

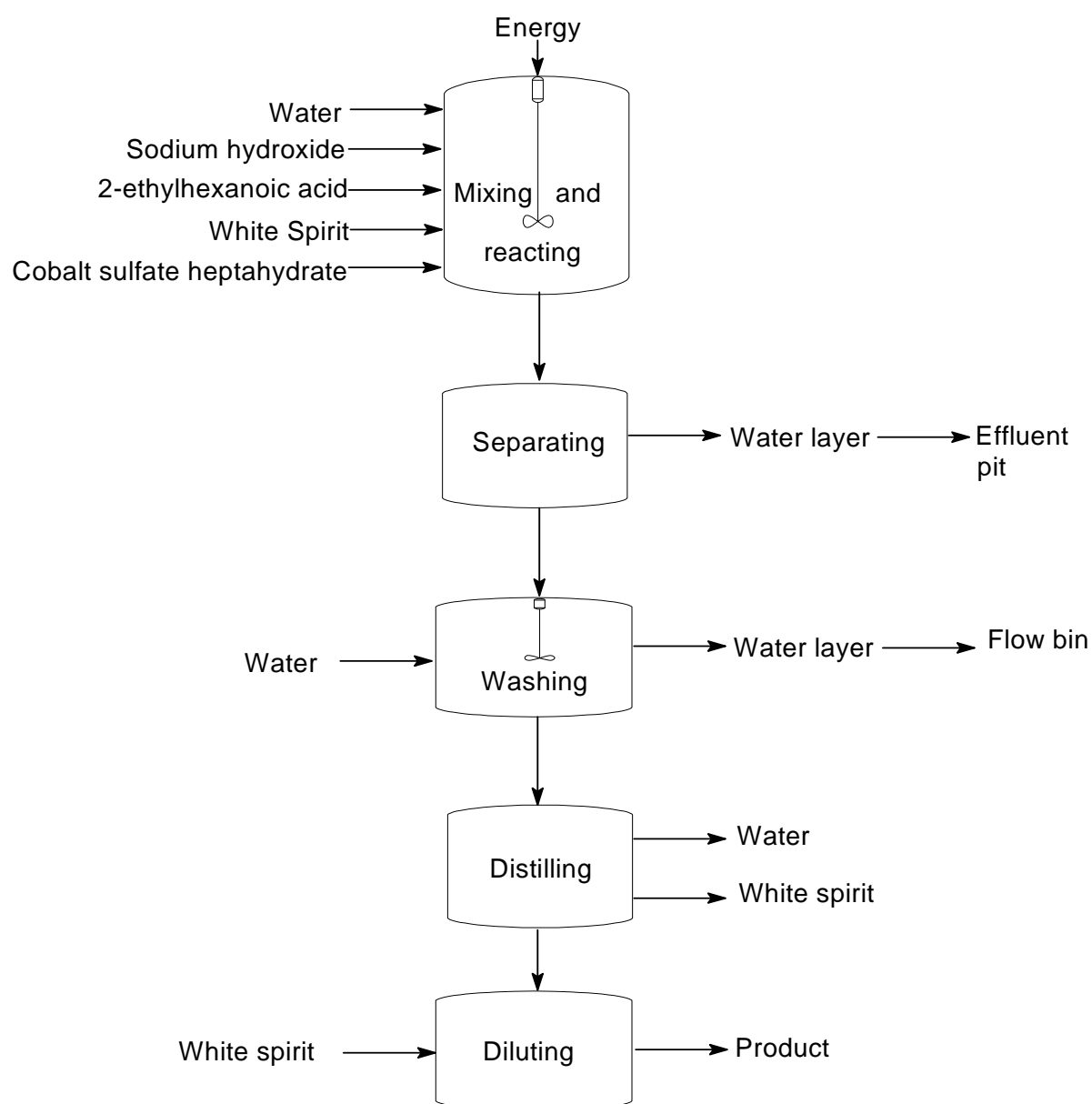


Figure 4.3 Manufacturing process and source of waste during cobalt paint drier production

The reaction takes place in a 4000 L reaction vessel Reactor 6 (R6) in the drier plant. The inside lining of the reactor is stainless steel (see Figure 4.6). The head of this reactor, shown in Figure 4.4 is accessed from the first floor of the PD's production plant. The body and base lie between the first floor and ground level as shown in Figure 4.5.

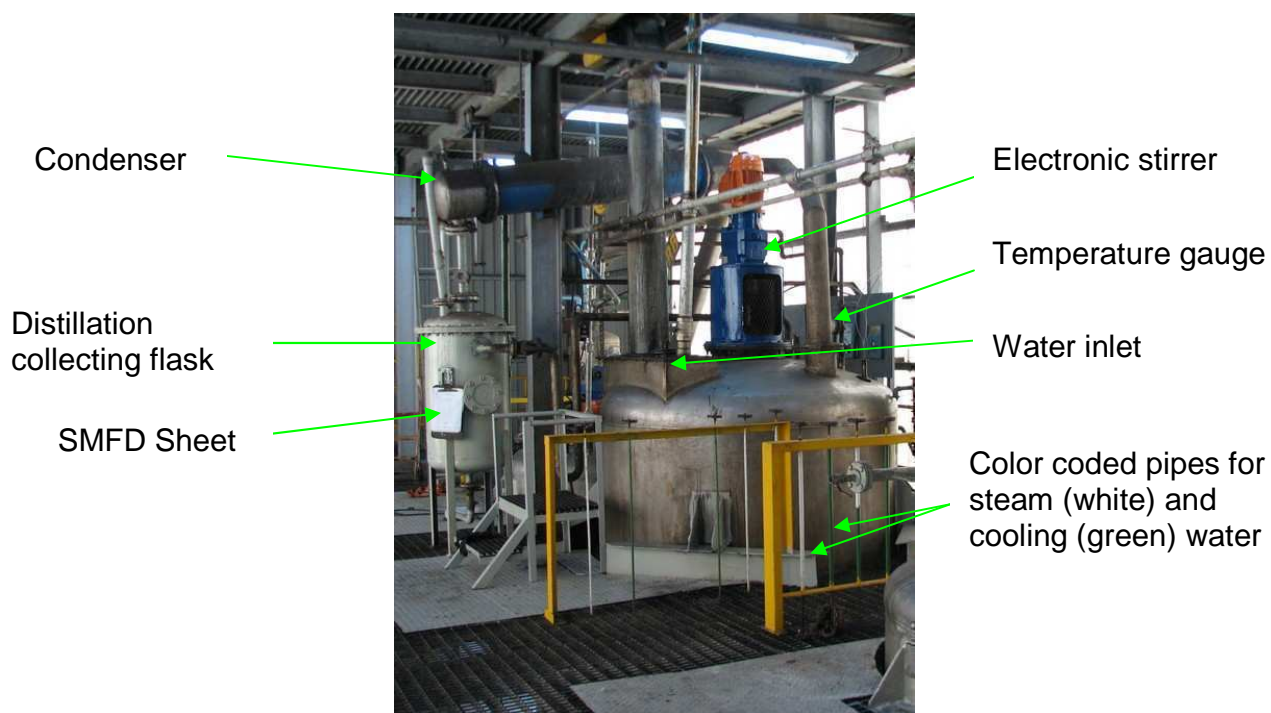


Figure 4.4 Head of Reactor 6

The first step (mixing and reacting in Figure 4.3) involves charging the reactor with the starting materials, sodium hydroxide (NaOH), cobalt sulfate heptahydrate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$), 2-ethyl hexanoic acid (2-EH) and the solvents, water and white spirit.

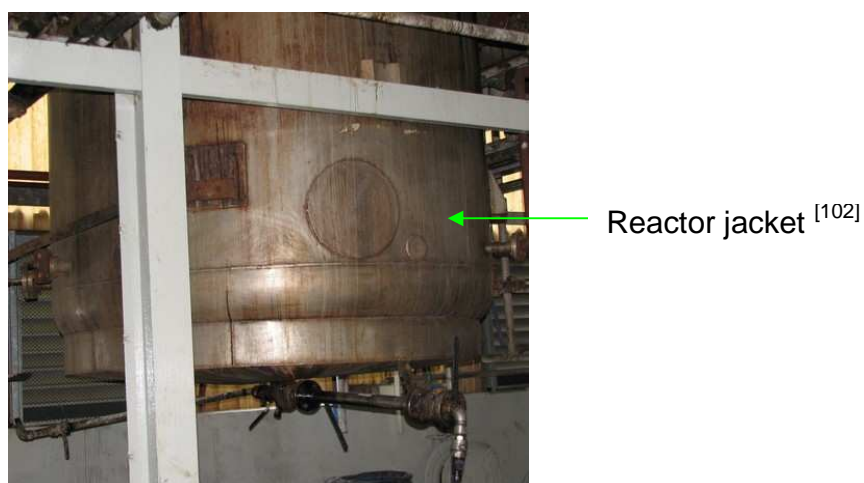


Figure 4.5 The body of R6 as seen from the ground floor

In the first step a measured amount of water is added through an opening on the reactor's head via a hose which is attached to a metered standpipe on the first floor of the building. If wastewater collected in flow-bins is to be used, this is sucked into the reactor using a pressure suction pipe situated at the ground floor of the drier plant. This is closed after additions are completed. This is followed by addition of a measured amount of 2-EH, which is also sucked into the reactor using a pressure suction pipe from metal drums. The reaction mixture is stirred using an agitator (see Figure 4.6 for the cross section of the agitator), while sodium hydroxide is emptied from 25 kg sacks into the reactor through a delivery chute located on the second floor (see Figure 4.7). This transfers the NaOH into the reaction vessel where it reacts with the acidic solution. The reaction is exothermic and the heat released from this process causes the temperature of the reaction mixture to rise to between 80 °C and 90 °C. The temperature is monitored using the temperature gauge located on the first floor adjacent to the reactor head. The temperature can be adjusted by opening the steam or cold taps for heating or cooling the reactor respectively. The steam or cold water circulates in the reactor jacket.^[102] Fumes are also observed coming out through the chute.

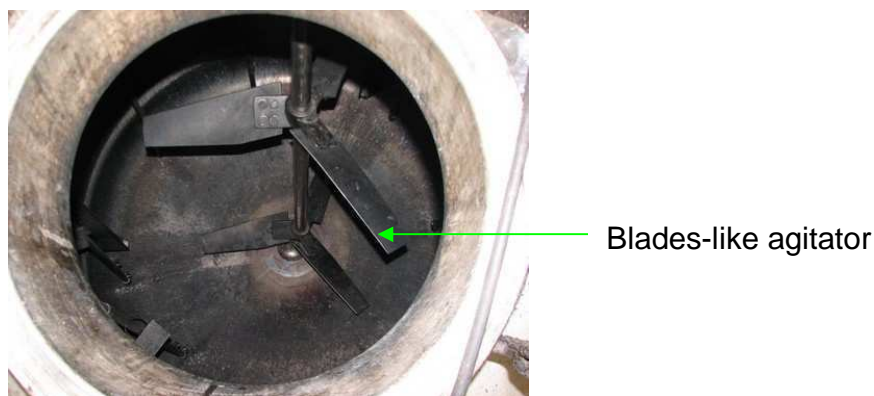


Figure 4.6 The inside of a reactor with blades-like shapes of an agitator

Monitoring of pH to between 7.5 and 8.0 is carried out using phenolphthalein indicator. This is done by dipping a metal stick inside the reactor through the water inlet opening. The metal stick is withdrawn with a few drops of the reaction mixture

which are put on a paper followed by addition of a few drops of phenolphthalein indicator. Any deviation from the required pH is corrected by addition of acid or base until the required pH is obtained. The mixture's temperature is adjusted to 70 °C by opening the cooling or steam water (see Figure 4.4). Once both the pH and temperature have been corrected, a measured amount of fresh white spirit is pumped into the reactor from the flow-bins using a pressure pump located at the ground floor of the production plant. Before addition of cobalt sulfate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$) a sample of the mixture is drawn out of the reactor using a 100 ml sample bottle tied to a string. The sample is taken to the analytical laboratory shown in Figure 4.1 Number 4 for pH check using pH meter. Cobalt sulfate is then slowly added from 25 kg or 500 kg bags to the basic reaction mixture through the chute (see Figure 4.7). The chute is located at the top or second floor. The reaction mixture is stirred for at least 1½ hours after charging with all raw materials. Then stirring is stopped and the organic (cobalt octoate) layer in white spirit is left to separate out as the top layer above the lower aqueous wastewater layer. The aqueous wastewater layer contains the byproduct sodium sulfate (Na_2SO_4) and any unreacted starting material. This bottom layer is the effluent or wastewater that is discharged to the effluent pit by opening the tap as shown in Figure 4.8.



Figure 4.7 Cobalt sulfate added to the reactor through the chute

In the second step (separating in Figure 4.3), the effluent is drained off through a manually operated tap in the base of the reactor. The tap is immediately closed when the purple coloured organic layer containing the desired product is observed leaving

the reactor (see Figure 4.8). This effluent is sent to the sump (effluent pit) situated at the back of the production plant.



Figure 4.8 Effluent collected into the flow bin from the reactor

The organic layer containing the product is then washed (Step 3 in Figure 4.3). A measured amount of mains water is then added into the reactor and stirred together with the white spirit solution of the product for half an hour. Then stirring is stopped and the aqueous and organic layers are left to separate. This takes about one hour to complete. The bottom aqueous layer is then drained off into the flow-bins (1000 L capacity) (see Figure 4.8).

The mixture is then heated to 140 °C (Step 4 in Figure 4.3) in order to distill off any excess water remaining in the white spirit solution of the product. The distillate is collected in a collecting flask adjacent to the head of the reactor (see Figure 4.4) and later into a drum located on the ground floor of the plant. The top layer (white spirit) collected during distillation is baled out and reused as a solvent.

In the final step measured fresh white spirit is added to the product in order to dilute it to the required specification. A sample of the finished product is taken to the laboratory for metal content check, according to the method described in Section 4.4. The concentration can be adjusted to the required percent by adding or distilling white spirit.

4.3.2 Manufacturing process of manganese octoate

The 10% manganese octoate product is produced in two batch sizes namely 2.5 T and 1.8 T. The manganese reactor (R5) has a smaller volume than the cobalt reactor, R6.

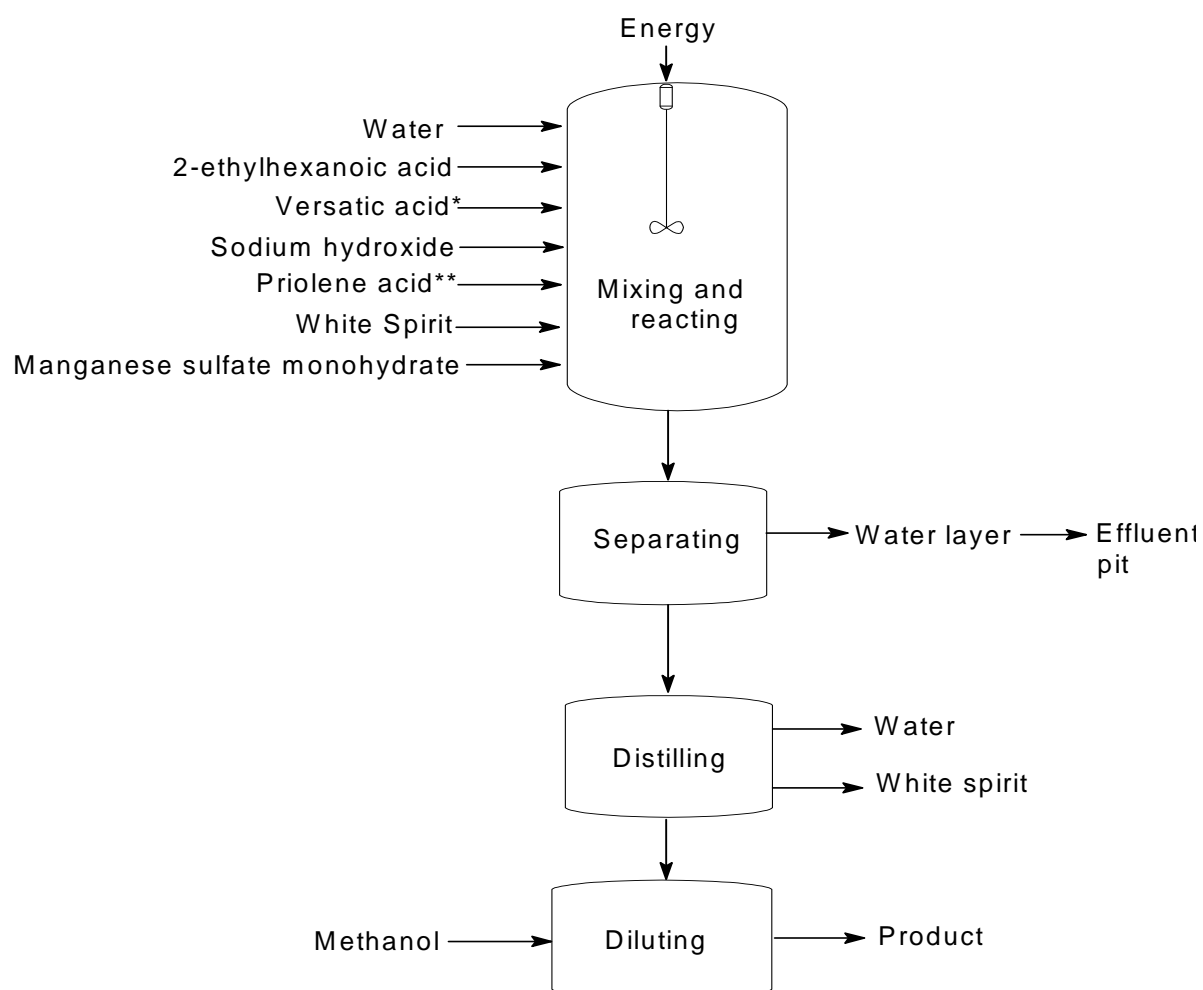


Figure 4.9 Manufacturing process and source of wastewater during manganese octoate paint drier production

Note: *mixture of synthetic carboxylic acid and isomers derived from highly branched C9 and C13 structures

**saturated and unsaturated straight chain aliphatic monocarboxylic acids, Mainly oleic acid

The production of the manganese octoate paint driers follows the same procedure as that described for the cobalt octoate manufacturing process. However, there is no washing of product. As seen from Figure 4.9 the separated product is distilled immediately after draining the aqueous layer. During the final step which is shown in Figure 4.9, methanol is added to the final product instead of white spirit which is added during cobalt octoate production. The entire production process is completed in 6 to 8 hours after which manganese octoate, a brown product is obtained.

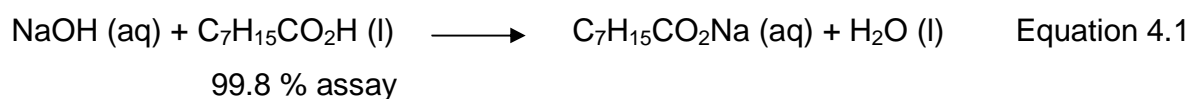
4.3.3 Production modification

The procedures described in Sub-sections 4.3.1 and 4.3.2 are basic manufacturing processes which are stipulated on the SMFD. During production of each batch there are certain modifications which are made. In some batches wash wastewater collected in the flow-bins is added as a starting material. For example, the water used in the reaction can be made up of one third wash wastewater taken from flow-bins and the balance from mains water. The amount and the origin of the water used are recorded on the specified page of the SMFD (see Section 4.3). Sometimes prior to the wash-water being added to the cobalt octoate batch, there is addition of part drums of products made and/or ullages (this is the term used in the company which describes the first drawings used to flush out the pipe before packaging takes place) from earlier batches manufactured. The amount and origin of the product and/or ullages is recorded on the SMFD too.

4.4 Process Control

The chemistry of the PD production process is quite simple. However, the manufacturing process used on the plant is quite complex. This arises from the recycling and reuse of wash wastewater from the flow-bins, part drums and ullages. Each one these enters the process at different times. For example in Figure 4.3 wash wastewater from flow-bins is added in Step 1 as a solvent, ullages are also added in Step 1 just before adding the cobalt sulfate and part drums are added between Step 2 and 3. Because of all these possible variations to the standard procedure formulated, the process has to be monitored very carefully to ensure that the desired product concentration is achieved. It becomes extremely tedious to follow up all these additions while carrying out mass balance. Therefore a number of quality control tests are run throughout the process.

The production of PDs is sensitive to pH and if this is not properly monitored and adjusted the reaction cannot take place. Prior to adding the metal sulfate raw material, the plant operators need to check the pH as well as the temperature of the reaction mixture. After charging with NaOH, the mixture's pH is usually around 13 to 14. This pH range is brought down by adding the 2-EH acid. Both the plant operator and the laboratory carry out checks on the temperature as explained in Sub-section 4.3.1. The value obtained while checking pH helps the controller/analyst to determine the amount of acid that needs to be added to bring the pH to between 7.5 and 8.0. After the addition has been made, another sample is drawn from the mixture and sent back to the laboratory. This is done to ascertain that the correct pH range has been achieved. The plant operator can then continue with addition of the metal sulfate. Sometimes, when the correct pH has not been achieved, the process can warrant the laboratory analyst to carry out an acid/base titration, using 2-EH acid and phenolphthalein according to Equation 4.1.



The amount of acid required is then calculated based on the size of the batch being manufactured and the average titration volume of the acid used according to Equation 4.2.

$$\text{Amount of acid required} = \frac{\text{Batch size (kg)} \times v \times \rho}{\text{Amount of product used for titration (g)}} \quad \text{Equation 4.2}$$

Where: v is average titration volume (cm^3)

ρ (density of 2-ethyl hexanoic acid) = 0.91 g/cm^3

If the reaction wastewater comes out pinkish, it is a problem that needs to be rectified by laboratory analysis. This will mean that not all metal sulfates have reacted due to the shortage of NaOH solution in the reaction mixture. To avoid wasting the sulfate raw material, NaOH solution will need to be prepared outside the reactor and then introduced into the reactor.

If the reaction goes to “completion” a sample of the finished product is drawn from the reactor in a 100 ml bottle for metal specification check. The metal concentration for a 12% cobalt octoate should be between 11.8 and 12.2% while that of 10% manganese octoate is between 9.7 and 10.3%. The adjustment is made by adding more white spirit or methanol for cobalt or manganese drier respectively. To avoid a situation where customers will need to dilute the product, the company always keeps the specification at the lower end 11.8% rather than upper end 12.2% in the case of cobalt octoate.

The metal content in the final PD product is determined by using titration method outlined in most literatures.^[49, 98, 99, 101] A measured mass of the product is dissolved in acetic acid. A measured amount of isopropyl alcohol, distilled water and sodium acetate are added to the mixture. The mixture is subjected to heat until boiling. A known excess of ethylenediaminetetra-acetic acid (EDTA) is added to the boiling mixture in order to complex the cobalt metal. Using copper sulfate (CuSO_4) titre in the

presence of 1-pyridyl-2-azonaphthol(2) [PAN] indicator back titration is then carried out. This method is the most favoured because it takes little time to carry out and so gives a rapid response which is ideal for production control analysis. It is more time and cost effective than other methods that require decomposition of the PD. Based on the titration results, the metal content is calculated using Equation 4.3.

$$\text{Percent metal} = \frac{[(M_1 \times V_1) - (M_2 \times V_2)] \times M_m}{Df \times m_1} \quad \text{Equation 4.3}$$

Where: M_1 and V_1 are the molarity and volume of EDTA respectively

M_2 and V_2 are the molarity and volume of CuSO_4 respectively

m_1 is the grams of metal octoate product used

M_m is the molar mass of the metal.

Df is the dilution factor used when diluting the final product with acetic acid

4.5 Packaging of product

After a sample product has undergone a quality control check by the laboratory analyst and passed the test, (see Section 4.4), it is ready for packaging. This is done after it has cooled down to room temperature. The amount is measured using a calibrated scale (see Figure 4.10). Each scale has a unique identification number which is recorded on the SFMD. The product is packaged in 25 kg, 190 kg or 215 kg drum metal or plastic containers. The drums are labeled with labeling that conforms to South African National Standards (SANS)^[88] and eThekweni Municipality Bylaws. The label must show the extent of hazardous product it contains as shown by Figures 4.10 and 4.11.



Figure 4.10 Packaging process carried out while measuring the amount using a manual mass scale



Figure 4.11 Drum sizes used during packaging of product

Chapter 5

5. Scope and Aims

The management of the company decided to optimise the production of the paint driers (PD) used for surface coatings (paint systems) through waste minimization and management. This meant improving or replacing the existing manufacturing technological processes currently being applied. The company's core business is in the production of textile chemical auxiliaries and paint driers. It has been found that the process used for the former product runs relatively waste-free, and earns more profit for the company than the process used to make paint driers. Consequently, the company wished to look at ways in which to optimise the production of the paint driers, making it more efficient and less wasteful. In doing so they expect to enhance the company's good image with regard to environmental standing, as well as minimizing exorbitant disposal costs.

Two particular processes in the PD plant were identified as creating serious waste problems. These are the production of cobalt and manganese metal driers.

The manganese and cobalt driers are produced according to the metal specification (described under Sub-section 2.4.2). A fraction of the amount produced by the company is used in the manufacture of their multi-metal blended driers shown in Table 4.1.

The products listed in Table 4.2 are manufactured using one of the following methods which are described in Sub-section 2.4.2.

- Double decomposition (Wet process)
- Fusion method (Dry process)
- Direct metal reaction

The company is currently following the double decomposition process. This was chosen after they conducted a comparison study between the wet process and dry process that revealed that the former is cheaper than the latter. In order to achieve objectives set by the company, wastewater samples from each production process were randomly collected. The timing of the sampling was largely dictated by the process and when it was operational. The objectives of the monitoring strategy included:

- measurements of concentration of metals (Co and Mn) and sulfates
- determination of trace metals in wastewater
- checking that wastewater discharged conforms to Municipality bylaws
- provide basis for wastewater minimization.

Monitoring was carried out on mains water, reaction wastewater, wash wastewater, and distillate wastewater. Analytical results were compared with figures calculated based on the information provided on the SMFD described in Section 4.3. Results were further subjected to waste minimization techniques described in Section 3.3 which are:

- scoping audit
- mass balance and
- true cost of waste

Information obtained from these three techniques was used to establish potential environmental priorities and financial savings.

The second part of the project involves a literature study. This involves searching scientific literature for papers, patents and product information on alternative cleaner production processes which do not produce waste; looking at wastewater reuse with or without purification and on reducing or commercialising the sulfate byproduct or using the waste to formulate a new product.

Chapter 6

6. Monitoring Methodology

The monitoring period for the waste minimisation audit carried out at the paint drier (PD) plant ran from January 2006 to March 2007. The monitoring methodology used for this audit is considered under two broad headings, namely “sampling” and “analysis”. Sampling of the industrial process involves two tasks. Firstly it concerns gathering data and information, both existing and new, about the process. Collection of existing data is discussed in Section 6.1. Section 6.2 outlines the development of a sampling strategy for the cobalt and manganese manufacturing processes. The collection of new data is also discussed from this section onwards. Secondly, the monitoring of the process using direct reading instruments to measure pH and conductivity is discussed in Section 6.3. Sections 6.4 through 6.6 describe analysis (preparation of standards, samples preparation and operation of the analytical instrument) of samples of the industrial process for elemental concentrations. This describes chemical analysis, using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES).

6.1 Collection of Existing Data

Data was collected by consulting archived company documents such as the monthly Metro Bill from eThekweni Municipality and the annual Tax Invoice from EnviroServe. eThekweni Municipality is the service provider of utilities (electricity and water supply, and refuse collection). EnviroServe is a private contractor used by the company to remove, transport and dispose wastewater from the effluent pit. Standard Manufacturing Formulation Document (SMFD) and Material Safety Data Sheets (MSDS) on the composition of raw materials and final products were

obtained for all batches manufactured in the DP plant during the monitoring period. Additional information was gathered through informal discussion with company personnel (for example volume of wastewater removed) and by direct observation of the process. Table 6.1 briefly describes information obtained from each document used.

Table 6.1 Existing data collected for developing a monitoring strategy

| Documents consulted | Information obtained | Source |
|---|---|----------------|
| The Metro Bill (eThekweni Municipality) | Water usage rate and cost | Administration |
| Tax Invoice (Enviroserve) | Effluent removal volume and cost | Administration |
| SMFD and MSDS | Raw material usage Product composition Standard control test methods Volume of wastewater removed Safety precautions of each raw material used as well as the products formed | PD plant |
| Certificates of analysis for raw material | Raw material composition | Laboratory |

The amounts of raw materials added and/or part drum or product ullages added were extracted from the SMFD. The amount of reaction wastewater leaving the reactor was only measured once as there is no meter attached to the outlet pipes. The reaction wastewater was collected in flow bins (see Figure 4.8), weighed using a manual scale and thereafter emptied into the effluent pit. This was required in order to ascertain verbal communications made by the plant operators with regard to amount of wastewater released per batch. This procedure was found to be counter productive as it requires the production personnel to collect the wastewater into flow-bins and thereafter measure the mass collected. In so doing they spend valuable time without adding anything to the production quantities or efficiency of the processes. Hence the procedure was only done once on batch number N6 JUN 07 (see Reference Number 10 on Table 6.2).

6.2 Development of a Monitoring Strategy for Data Collection

In the first part of the project industrial monitoring of the production process used for making Co and Mn PDs (see Section 4.3) was carried out. This involved devising and applying a suitable strategy for sampling of wastewater, followed by chemical analysis of the samples using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES).

A total of one hundred and thirty three samples were collected for the sixteen production batches shown in Table 6.2. Thirty one samples (four mains water, twenty five solvent wastewater and two distillate wastewater) were collected from the manganese processes (see Table 6.3). One hundred and two samples (4 mains water, fifty four solvent wastewater, thirty four wash wastewater and ten distillate wastewater) were taken from the cobalt processes (see Table 6.4).

Table 6.2 Paint drier batches manufactured and sampled between January 2006 and March 2007

| Drier | Date | Batch no. | Product composition | Reference Number |
|-------|----------|-----------|---------------------|------------------|
| Mn | 27.01.06 | N6JAN25 | 10 % octoate | 1 |
| | 27.02.06 | N6FEB32 | 10 % octoate | 2 |
| | 01.08.06 | N6JUL31 | 10 % octoate | 3 |
| | 11.10.06 | N6OCT04 | 8 % octoate | 4 |
| | 5.03.07 | N7MAR04 | 10 % octoate | 5 |
| Co | 06.02.06 | N6FEB04 | 12 % octoate | 6 |
| | 06.03.06 | N6MAR06 | 12 % octoate | 7 |
| | 08.03.06 | N6MAR10 | 12 % octoate | 8 |
| | 14.03.06 | N6MAR17 | 12 % octoate | 9 |
| | 06.06.06 | N6JUN07 | 8 % octoate | 10 |
| | 12.06.06 | N6JUN11 | 10 % octoate | 11 |
| | 12.07.06 | N6JUL02 | 12 % octoate | 12 |
| | 17.07.06 | N6JUL12 | 12 % octoate | 13 |
| | 27.07.06 | N6JUL28 | 12 % octoate | 14 |
| | 14.11.06 | N6NOV17 | 12 % octoate | 15 |
| | 23.02.07 | N7FEB22 | 12 % octoate | 16 |

Samples were collected from the plant using the high density polyethylene (HDPE) bottles. The HDPE bottles were washed in the laboratory following a previously

described procedure.^[85, 111-115] At the production plant, each bottle was rinsed twice with the hot (between 75 °C and 85 °C) aqueous wastewater solution being released from the process prior to sampling. Besides samples taken from mains water, three sampling points for cobalt octoate and two sampling points for manganese octoate were identified. A number of samples were taken from each sampling point. The sampling points from which the manganese and the cobalt samples were taken are described in Tables 6.3 and 6.4 respectively.

Table 6.3 Samples collected during the manganese octoate manufacture in Reactor 5

| Sample description | Source of Sample | Date samples taken | Number of samples taken |
|-----------------------|---|--------------------|-------------------------|
| Utility outlet | Fresh mains water from tap | 27.01.06 | 1 |
| | | 01.08.06 | 1 |
| | | 11.10.06 | 1 |
| | | 5.03.07 | 1 |
| Solvent wastewater | Manganese containing solvent wastewater discharged from reactor to effluent pit after reaction complete. Water layer after separation in Figure 4.9 | 27.01.06 | 1 |
| | | 27.02.06 | 3 |
| | | 01.08.06 | 9 |
| | | 11.10.06 | 7 |
| Distillate wastewater | Mixture of wastewater and spirit discharged into a metal drum from reactor during distillation. water collected after distilling in Figure 4.9 | 27.1.06 | 1 |
| | | 27.2.06 | 1 |

At each specified sampling time for each sampling point, three samples were taken. The sampling time refers to the time within the discharge period when samples were taken. Each sample was differentiated from the other using a unique identification number; the date and the sampling time. Samples were taken at each sampling point at 15 minutes intervals while the wastewater was being released. About 3.00 ml of concentrated nitric acid (HNO₃) was added to one of the two 125 ml samples from each sampling point. These samples are called “acidified samples” in this document. The wastewater samples (see Tables 6.3 and 6.4) were taken as soon after it was discharged from the reactor as possible, (see Figure 4.8) and immediately stored in a

cooler box. The distillate for both processes was usually sampled only once. Samples were then transported back to the laboratory for analysis. The conductivity and pH of acidified and non-acidified sample solutions were measured. All samples were then stored in a refrigerator set at 4 °C before further preparation and elemental analysis were carried out.

Table 6.4 Samples collected during cobalt octoate manufacture in Reactor 6

| Sample description | Source of sample | Date samples taken | Number of samples taken |
|-----------------------|---|--------------------|-------------------------|
| Utility outlet | Mains water from tap | 06.02.06 | 1 |
| | | 06.03.06 | 1 |
| | | 27.07.06 | 1 |
| | | 14.11.06 | 1 |
| Solvent wastewater | Co containing solvent wastewater discharged from the bottom of the reactor into the effluent after reaction comes to completion. Water layer after separation shown in Figure 4.3 | 06.02.06 | 8 |
| | | 06.03.06 | 1 |
| | | 08.03.06 | 3 |
| | | 14.03.06 | 2 |
| | | 06.06.06 | 4 |
| | | 12.06.06 | 1 |
| | | 12.07.06 | 3 |
| | | 17.07.06 | 6 |
| | | 27.07.06 | 8 |
| | | 14.11.06 | 7 |
| | | 23.02.07 | 11 |
| Wash wastewater | Co containing wash wastewater discharged from the reactor into the flow-bin. Water layer after washing shown in Figure 4.8 | 06.02.06 | 4 |
| | | 06.03.06 | 1 |
| | | 08.03.06 | 1 |
| | | 14.03.06 | 2 |
| | | 06.06.06 | 1 |
| | | 12.06.06 | 2 |
| | | 12.07.06 | 2 |
| | | 17.07.06 | 5 |
| | | 27.07.06 | 4 |
| | | 14.11.06 | 5 |
| | | 23.02.07 | 7 |
| Distillate wastewater | Reusable wastewater discharged from reactor during distillation into a metal/plastic drum. Water collected after distilling in Figure 4.9 | 06.02.06 | 1 |
| | | 06.03.06 | 1 |
| | | 08.03.06 | 1 |
| | | 14.03.06 | 1 |
| | | 06.06.06 | 1 |
| | | 12.06.06 | 1 |
| | | 12.07.06 | 1 |
| | | 17.07.06 | 1 |
| | | 14.08.06 | 1 |
| | | 23.02.07 | 1 |

6.3 New Data obtained by Direct Reading Instrument

The pH of samples was measured using a pH meter (Model CRISON micropH 2000) shown in Figure 6.1. This pH meter was calibrated prior to making measurements using buffer solution (borate) pH 10.00 ± 0.05 at $20\text{ }^{\circ}\text{C}$ and buffer solutions (phosphate) pH 7.00 ± 0.02 and pH 4.00 ± 0.02 at $20\text{ }^{\circ}\text{C}$. Thereafter the conductivity of the samples was measured using Hanna Instrument HI 9033 multi-range conductivity meter, shown in Figure 6.2. The meter was calibrated using HIL 7030/500 conductivity calibration solution (potassium chloride) $12880\text{ }\mu\text{S/cm}$ at $25\text{ }^{\circ}\text{C}$.



Figure 6.1 The Crison micropH 2000 used when measuring sample pH



Figure 6.2 Conductivity meter measuring the conductivity (mS/cm) of the sample

6.4 Preparation of Standards

Stock standard solutions (100 ml) of Co, Mn and S were prepared from purchased 1000 ppm commercial standard solutions (Fluka) purchased from Sigma-Aldrich. Concentrations were selected in order to cover the high and low sample dilutions made. The concentration for Co was 0.100 to 30.0 ppm, for Mn was 5.00 to 300 ppm and for S was 25.0 to 200 ppm.

Mixed calibration standards for analyzing trace elements (Ca, Co, Mn, Pb, Zn, and Zr) were prepared from a working standard. The working standard was prepared by pipetting 2.5 ml of the commercial standards of each analyte into a 250 ml volumetric flask. The solution was made to the mark using distilled water. The concentration of the working standard was 10.0 ppm for each analyte. The volumes of the working standard used to make the mixed calibration standards and the corresponding concentrations are given in Table 6.5. These standards were all prepared in a 100 ml volumetric flasks. Distilled was included in the calibration as blank.

Table 6.5 Mixed calibration standards used for traces analysis in wastewater

| Standard number | Concentration (ppm) of mixed calibration standards | | | | | | Volume of mixed standard used (ml) |
|-----------------|--|-------|-------|-------|-------|-------|------------------------------------|
| | Ca | Co | Mn | Pb | Zn | Zr | |
| 1 | 0.100 | 0.100 | 0.100 | 0.100 | 0.100 | 0.100 | 1.00 |
| 2 | 0.500 | 0.500 | 0.500 | 0.500 | 0.500 | 0.500 | 5.00 |
| 3 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 10.0 |
| 4 | 5.00 | 5.00 | 5.00 | 5.00 | 5.00 | 5.00 | 50.0 |
| 5 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 | 100 |

6.5 Preparation of Samples

When the samples were released from the reactor and collected in the sampling bottles they were hot, about 75 °C to 85 °C. On cooling, sodium sulfate crystallized out. In order to re-dissolve the sodium sulfate crystals, all samples were reheated prior to dilution on a warm bath as shown in Figure 6.3. This was necessary to maintain the sample condition at the time of sampling. It was not necessary to filter samples since the solutions were homogenous and had no solid particles that could clog the nebulizer. The required sample volume was transferred into a 100 ml volumetric flask using a calibrated Eppendorf pipette. The volume was made up to the mark with distilled water. Few sets of sample dilutions were prepared. These had dilution factors ranging from 4 to 1000.

In order to avoid the problem of the sulfate crystallizing when the samples cooled, an investigation was made into the feasibility of diluting the wastewater samples at the plant, before they cooled. However, this did not prove satisfactorily due to the difficulty of accurately measuring the volume at the plant.



Figure 6.3 Samples reheated before analysis in order to re-dissolve sulfate crystals

6.6 Chemical Analysis of Samples using ICP–OES

Atomic spectrometric techniques^[103] received a lot of attention in the early 20th century through the use of electric arcs and sparks. Several spectrometers are available nowadays and the analyst or researcher is faced with a wide choice to make when analyzing samples. The choice of an instrumental analysis technique depends on various factors, for example

- limitations associated with instrument and
- substance being analysed.

Some of the instruments that are widely used include atomic absorption spectrometry (AAS), electrothermal atomic absorption spectrometry (ETAAS), inductively coupled plasma optical emission spectrometry (ICP-OES), laser-excited atomic fluorescence spectrometry (LEAFS), furnace atomization plasma excitation spectrometry (FAPES), and many more.^[103, 104, 107] All these techniques involve detecting and analyzing electromagnetic radiation absorbed or emitted by ions or atoms in a sample. Quantitative (amount or concentration) or qualitative (type of atoms or ions) properties of samples can be determined. The former depends on the intensity of radiation used to determine the concentration of analyte of interest in the sample. The latter depends on the wavelength associated with a particular radiation from which identity of an analyte is obtained. Analysis of samples in will be carried out using ICP-OES instrument and hence it is important to describe its components and operation.

6.6.1 Operation principles of ICP-OES

The ICP-OES instrument used throughout the entire research project was the Varian 720-ES series ICP Optical Emission spectrometer manufactured by Varian Australia Pty Ltd. Important features of the Varian 720-ES are given in Table 6.6.

Table 6.6 Features of the Varian 720-ES and their use^[105, 106]

| Component | Its use |
|--|---|
| Manual and auto sampler. | For introducing the sample. |
| 3 channel peristaltic pump. | To pump in sample or rinsing solvent into the instrument. |
| Mass flow regulated glass pneumatic Nebulizer gas control. | It changes the liquid sample into aerosol or mist form. |
| Spray chamber | For removing large droplets in the aerosol and to reduce signal pulsation caused the peristaltic pump |
| Torch consisting of three concentric tubes. | For delivering aerosol sample & carrier gas (Ar), coolant gas and auxiliary gas into the plasma |
| Axial plasma | To separate solvent from solute, vaporize, atomize, ionize and excite the analyte(s) of interest |
| Optics (convex lens and concave mirror) | For collecting emitted radiation |
| Reflection diffraction grating and spectrometer | Receiving polychromatic radiation and sort it into a monochromatic light |
| Charge coupled device (CCD) detector | It measures the intensity of the radiation |



Figure 6.4 The set up of the ICP-OES instrument in the research laboratory

Samples were introduced into the ICP-OES instrument using an auto sampler. This was done by pumping samples from the sample tube through a probe and the connecting tube to the nebulizer by means of a 3 channel peristaltic pump shown in Figure 6.5. The probe was rinsed after each sample intake using ultra pure water.

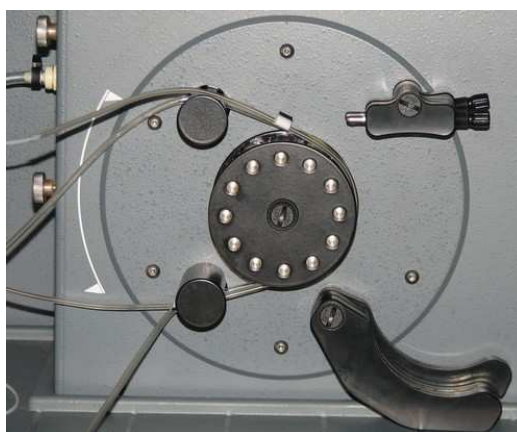


Figure 6.5 Represent a 3 channel peristaltic pump used to pump in samples

The region where the liquid sample is changed into an aerosol or mist-like spray before being swept away by a high pressure flowing argon gas is called a nebulizer. Two types of nebulizers used in ICP-OES instrument are pneumatic and ultrasonic nebulizers (USN).^[103, 118] Pneumatic nebulizers that are most commonly used, include concentric, cross-flow, GMK system, flow focusing, a V-groove etc. The choice is usually dependent on the type of samples being analyzed or one that can produce high sensitivity and low level of matrix effects. The sea spray Cross-flow pneumatic nebulizer was used during sample analysis for this research.

The aerosol-argon carrier gas mixture enters the spray chamber where the larger and finer droplets are separated from each other. Two widely used spray chambers in ICP-OES are the Twister Cyclonic and the Double pass Scott-type spray chamber. For this research, the Twister Cyclonic spray chamber was used, see Figure 6.6. Waste sample leaves the spray chamber through a drain opening at its bottom. The wastes collect in a plastic bottle container that is emptied when full (see figure 6.4).

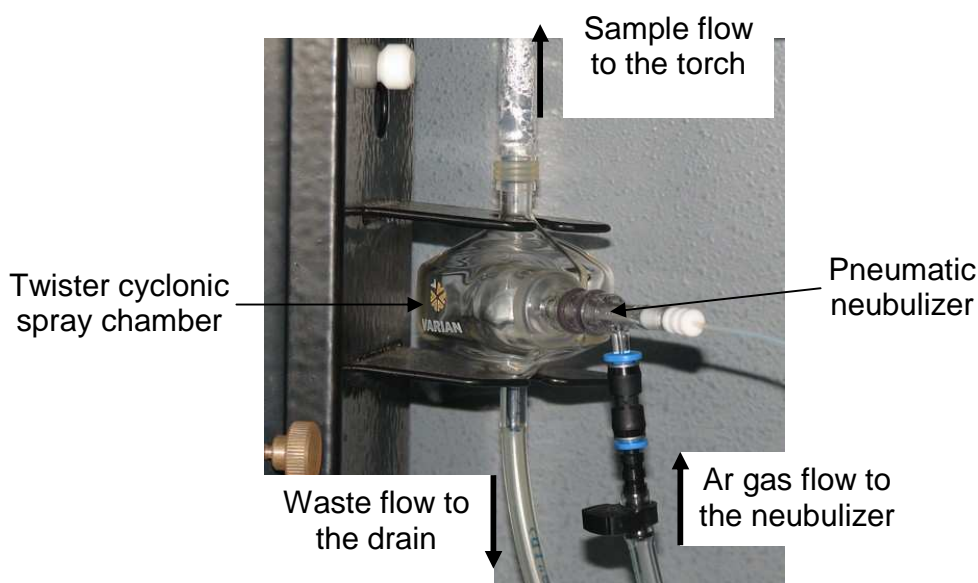
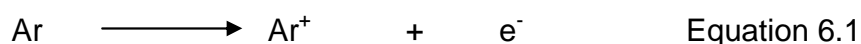


Figure 6.9

Figure 6.6 The Twister Cyclonic spray chamber connected to the nebulizer

During ICP torch ignition stage, i.e. before sample introduction, the RF generator and the copper coil produces “seed electrons” which ionize the argon gas as shown in Equation 6.1. Electrons produced further ionize neutral argon atoms. An intense, brilliant white plasma consisting of argon atoms, electrons and argon ions with temperature ranging from 6 000 to 10 000 K is formed. The plasma discharge can be radially viewed (“side-on”) or axially viewed (“end-on”). In this project, axial view of the plasma was used when analyzing samples.



On entering this high temperature region, the solvent on the aerosol-argon carrier gas is evaporated, particles are vaporized and finally atomised. This is called the preheating zone (PHZ). The atoms are excited and ionized in the region called initial radiation zone (IRZ) and also in the normal analytical zone (NAZ).^[103, 108, 127]

The excited atoms or ions emit energy on returning back to ground state electronic level. The energy emitted is characteristic of the excited atom or ion. For each atom

or ion to be quantified separately, the radiation is dispersed by means of a grating so that an emission spectrum can be obtained and individual wavelength selected. The intensity of radiation was measured by the charge-coupled device (CCD) detector. This is one of the most sensitive and high resolution detector used in spectroscopic applications. The operating conditions under which samples were analysed by ICP-OES are given in Table 6.7.

Table 6.7 Used ICP-OES specifications and instrument operating conditions

| Specification | Condition |
|-----------------------------------|-----------|
| Rf/operating Power (kW) | 1.00 |
| Plasma flow(L/min) | 15.0 |
| Auxiliary flow(L/min) | 1.50 |
| Pump rate (rpm) | 15.0 |
| Pneumatic nebulizer (L/min) | 0.75 |
| Instrument stabilization time (s) | 15 |
| Rinse time (s) | 45 |
| Sample uptake delay (s) | 30 |
| Replicates read time (s) | 1 |
| Replicates | 3 |

Table 6.8 Selected wavelengths for each analyte

| Element | Major analyte in wastewater | | | Traces | | |
|-----------------|-----------------------------|--------|--------|--------|--------|--------|
| | Co | Mn | S | Zn | Pb | Zr |
| Wavelength (nm) | 228.62 | 279.83 | 178.16 | 206.20 | 168.15 | 267.86 |
| | 230.79 | 293.30 | 180.67 | 207.91 | 266.32 | 349.62 |
| | 231.16 | 293.93 | 181.97 | 213.86 | | |
| | 236.38 | 294.92 | 182.56 | | | |
| | 237.86 | | | | | |
| | 238.89 | | | | | |

Note: For each element, intensities at different wavelengths were used to obtain several different estimates of the concentration. The average concentration (see Tables 7.12 through 7.27) of the different estimates for each element used was based on all wavelengths as there were no spectral interferences observed.

6.7 Instrument and parameters optimization

The accuracy and efficiency of any analytical method used while carrying out an analysis depends on many factors. A review of the literature^[108-110, 113, 116, 120-125] shows that factors such as the concentration of the interfering species, instrument variables, the presence of concomitants, the analyte line, sample introduction systems, and many more can greatly compromise the outcomes of the chosen method. It is for these and many other reasons that the instrument sensitivity and its parameters had to be optimized. Preliminary analysis was carried out in order to determine the effect of both instrument parameters and interfering ions on the intensity of analyte of interest. Procedures followed included matrix matching methods, standard addition methods and sample dilutions.^[126, 127] Results from these preliminary procedures showed that the interfering ions and matrix effect had a measurable influence on the sensitivity of the instrument. In order to overcome the matrix effects, samples were diluted in accordance with the description given in Section 6.5.

Chapter 7

7. Introduction

This section deals with the results obtained during the entire period the research was conducted. Results were obtained from two general sources, namely, existing company documents described in Section 6.1 and new collected data sample analysis described in Sections 6.2 through 6.7. Results from company documents are given under Section 7.1 and graphically represented in Appendix B (see Figures B1 through B7). Sections 7.2 and 7.3 describe results obtained from new data. These cover data from reading instruments, water meters and analytical analysis.

7.1 Results from Existing Data

Results from existing data were obtained from the SMFD sheet, Metro Bills from eThekweni Municipality and the Tax Invoices from EnviroServe. These documents are described in Table 6.1 while a description of SMFD sheet is provided in Section 4.3. Table 7.1 gives percent usage of raw materials for the production of each commercial PDs. Graphic representations of the percent usage of raw materials are given under Appendix B as well as in Figures 8.1 and 8.2. The percent values given in Table 7.1 were calculated using Equation 7.1.

$$\text{Percent of raw material used per year} = \frac{\text{Total amount used by a drier}}{\text{Total amount used by all driers}} \times 100\% \quad \text{Equation 7.1}$$

Raw materials and costs pertaining specifically to cobalt and manganese driers are given in Tables 7.2 through 7.5. Water consumption costs provided in Tables 7.3 and 7.5 were calculated using the unit values obtained from the Metro Bill. The unit price was not constant throughout the entire year and values shown in entries 1, 2 and 3 of column 3 in Tables 7.3 and 7.5 reflects new rates made during the year. Financial losses provided in Tables 7.3 and 7.5 were based on the relationship between metal present in the wastewater and the composition of raw material.

Table 7.1 Total amounts and corresponding percent of raw materials used during production of each Paint Driers in 2006

| Type of metal drier | *Water, m ³ | % water usage | *2-ethylhexanoic acid, kg | % 2-EH usage | *White spirit, L | % W/S usage | *Sodium hydroxide, kg | % NaOH usage | *Versatic acid, L | % V.A usage | *Naphthenic acid, L | % N. A usage | *Methanol, L | % Methanol usage |
|-----------------------------|------------------------|---------------|---------------------------|--------------|------------------|-------------|-----------------------|--------------|-------------------|-------------|---------------------|--------------|--------------|------------------|
| BARIUM | | 0.00 | | 0.00 | | 0.00 | | 0.00 | | 0.00 | | 0.00 | | 0.00 |
| CALCIUM | | 0.00 | | 31.31 | | 35.17 | | 0.00 | | 31.10 | | 0.68 | | 15.2 |
| COBALT | | 84.0 | | 30.80 | | 22.87 | | 86.56 | | 15.13 | | 53.56 | | 0.00 |
| COPPER | | 3.74 | | 0.66 | | 1.39 | | 1.85 | | 0.00 | | 16.57 | | 0.00 |
| LEAD | | 0.00 | | 11.25 | | 11.32 | | 0.00 | | 33.79 | | 7.32 | | 0.00 |
| MANGANESE | | 8.16 | | 3.50 | | 2.41 | | 10.17 | | 3.56 | | 1.86 | | 52.5 |
| POTASSIUM | | 1.13 | | 2.93 | | 1.15 | | 0.00 | | 1.03 | | 0.00 | | 32.3 |
| SODIUM | | 2.81 | | 0.62 | | 0.15 | | 1.42 | | 0.14 | | 0.00 | | 0.00 |
| ZINC | | 0.12 | | 5.23 | | 5.11 | | 0.00 | | 2.33 | | 20.0 | | 0.00 |
| ZIRCONIUM | | 0.00 | | 13.70 | | 12.96 | | 0.00 | | 12.90 | | 0.00 | | 0.00 |
| DRIER BLENDS | | 0.00 | | 0.00 | | 7.48 | | 0.00 | | 0.00 | | 0.00 | | 0.00 |
| Total amount used per annum | | 100 | | 100 | | 100 | | 100 | | 100 | | 100 | | 100 |

*Amounts (values) used to calculate the percent are NOT shown in line with the confidential agreement signed between the researcher and the company where the project took place.

Table 7.2 Raw materials used during cobalt paint drier production in 2006

| Type of Raw material | Amount of each raw material used and cobalt metal lost per month | | | | | | | | | | | | Total amount per year |
|---|--|--------------------|--------------------|--------------------|---------------------|--------------------|--------------------|--------------------|---------------------|--------------------|--------------------|--------------------|-----------------------|
| | JAN ⁽⁴⁾ | FEB ⁽⁵⁾ | MAR ⁽⁷⁾ | APR ⁽³⁾ | MAY ⁽¹²⁾ | JUN ⁽⁶⁾ | JUL ⁽⁷⁾ | AUG ⁽⁸⁾ | SEPT ⁽⁸⁾ | OCT ⁽⁷⁾ | NOV ⁽⁶⁾ | DEC ⁽⁰⁾ | |
| Mains Reaction water, m ³ | 9.28 | 11.4 | 12.8 | 5.83 | 19.6 | 11.9 | 10.6 | 13.5 | 14.5 | 8.74 | 9.48 | 0 | 127.6 |
| Flow Bin recycled water, m ³ | 0 | 0.804 | 1.95 | 0 | 3.06 | 0 | 1.33 | 0 | 2.78 | 3.18 | 2.56 | 0 | 15.7 |
| White spirit, L | 3673 | 5484 | 7420 | 3844 | 10468 | 9387 | 4505 | 7234 | 9078 | 7337 | 5588 | 0 | 74018 |
| NaOH, kg | 2124 | 2867 | 3424 | 1348 | 5235 | 2736 | 2799 | 3150 | 3750 | 2761 | 2689 | 0 | 32883 |
| 2-ethyl hexanoic acid, kg | 7580 | 8951 | 11382 | 4236 | 18158 | 9809 | 10131 | 10997 | 14321 | 9319 | 9119 | 0 | 114003 |
| Versatic acid, kg | 0 | 959 | 888 | 453 | 786 | 170 | 1276 | 1316 | 666 | 444 | 444 | 0 | 7402 |
| L.O.Kerosene, kg | 0 | 0 | 0 | 0 | 7832 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 7832 |
| Cobalt sulfate, kg | 7000 | 9121 | 11000 | 4400 | 17086 | 9000 | 9000 | 10000 | 12000 | 9000 | 8700 | 0 | 106307 |
| Cobalt metal used, kg | | | | | | | | | | | | 0 | 0 |
| Co metal lost, kg | 34 | 55 | 32 | 61 | 240 | 69 | 10 | 26 | 131 | 61 | 16 | 0 | 735 |
| Naphthenic acid, kg | 613 | 1021 | 674 | 605 | 570 | 613 | 646 | 0 | 613 | 613 | 613 | 0 | 6581 |
| Enerflex 81, kg | 1600 | 2200 | 1800 | 1500 | 1430 | 1800 | 1590 | 0 | 1500 | 1972 | 1780 | 0 | 17172 |

Note: Numbers in parenthesis next to each month represents the number of batches manufactured during that particular month.

Table 7.3 Total consumption of raw material and amount spent during cobalt driers production

| Raw Material | Total Consumption | Unit Price, R | | | Total amount Spent on cobalt drier, R per year |
|--|-------------------|---------------|-------|----------|--|
| | | Jan – Jul | Aug | Sept-Dec | |
| Mains/Fresh water for reaction, m ³ | 127.6 | 5.83 | 5.903 | 6.27 | 759 |
| Wastewater used for reaction, m ³ | 15.7 | (41.67) | 0 | (53.42) | (95)* |
| White spirit, L | 74018 | 6.24 | | | 461872 |
| Caustic soda flakes (NaOH), kg | 32883 | 3.65 | | | 120023 |
| 2-ethyl hexanoic acid, kg | 114003 | 12.15 | | | 1385136 |
| Versatic acid, kg | 7402 | 9.26 | | | 68543 |
| Low Order Kerosene, kg | 7832 | Not provided | | | |
| Cobalt sulfate, kg | 106307 | 56.44 | | | 5999967 |
| Cobalt metal lost, kg | 735 [3500]** | 56.44 | | | [197540]** |
| Naphthenic acid, kg | 6581 | Not provided | | | |
| Enerflex 81, kg | 17172 | Not provided | | | |

* Value in parenthesis represents the approximate amount (in Rands) the company saved by using the distillate.

** Value in brackets represents the corresponding amount of cobalt sulfate or the money (in Rands) lost.

Table 7.4 Raw materials used during manganese paint drier production by the company

| Type of Raw material | Amount of each raw material used and manganese metal lost per month | | | | | | | | | | | | Total amount used per year |
|-------------------------|---|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|---------------------|--------------------|--------------------|--------------------|----------------------------|
| | JAN ₍₁₎ | FEB ₍₁₎ | MAR ₍₃₎ | APR ₍₂₎ | MAY ₍₀₎ | JUN ₍₂₎ | JUL ₍₂₎ | AUG ₍₁₎ | SEPT ₍₂₎ | OCT ₍₃₎ | NOV ₍₀₎ | DEC ₍₁₎ | |
| Mains Reaction water, L | 1200 | 937 | 250 | 1200 | 0 | 1612 | 2400 | 0 | 1200 | 3600 | 0 | 0 | 12399 |
| White spirit | 494 | 385 | 857 | 944 | 0 | 861 | 1057 | 122 | 693 | 2378 | 0 | 0 | 7791 |
| NaOH, kg | 375 | 300 | 60 | 375 | 0 | 511 | 742 | 0 | 375 | 1125 | 0 | 0 | 3863 |
| 2EH, kg | 1069 | 1048 | 94 | 1072 | 0 | 1985 | 2547 | 0 | 1478 | 3674 | 0 | 0 | 12967 |
| Versatic, kg | 409 | 107 | 0 | 409 | 0 | 409 | 0 | 0 | 0 | 409 | 0 | 0 | 1743 |
| Mn-sulfate, kg | 800 | 625 | 125 | 800 | 0 | 1075 | 1600 | 0 | 800 | 2400 | 0 | 0 | 8225 |
| Mn metal | 244 | 190.63 | 38.125 | 244 | 0 | 327.88 | 488 | 0 | 244 | 732 | 0 | 0 | 2509 |
| Mn metal lost | 9 | 13 | 0.5 | 20 | 0 | 21 | 6 | 0 | 18 | 50 | 0 | 0 | 138 |
| Methanol | 220 | 172 | 0 | 220 | 0 | 137 | 220 | 0 | 220 | 660 | 0 | 0 | 1849 |
| Priolene acid | 148 | 116 | 0 | 148 | 0 | 201 | 296 | 0 | 148 | 444 | 0 | 0 | 1501 |
| Naphthenic acid, kg | 0 | 0 | 229 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 229 |
| Illuminating paraffin | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 350 | 350 |

Note: Numbers in parenthesis next to each month represents the number of batches manufactured during that particular month

Table 7.5 Total consumption of raw material and amount spent during manganese driers production

| Raw Material | Total Consumption | Unit Price, R | | | Total amount Paid for manganese drier, R per year |
|--------------------------------------|-------------------|---------------|--------------|----------|---|
| | | Jan – Jul | Aug | Sept-Dec | |
| Mains Reaction water, m ³ | 12.4 | 5.83 | 5.903 | 6.27 | 74 |
| White spirit, L | 7791 | | 6.24 | | 48616 |
| Caustic soda flakes (NaOH), kg | 3863 | | 3.65 | | 14100 |
| 2-ethyl hexanoic acid, kg | 12967 | | 12.15 | | 157549 |
| Versatic acid, kg | 1743 | | 9.26 | | 16140 |
| Manganese sulfate, kg | 8225 | | 3.50 | | 28788 |
| Manganese metal lost, kg | 138 [452]* | | [3.50] | | [1582]* |
| Methanol | 1849 | | 3.16 | | 5843 |
| Priolene acid | 1501 | | 9.00 | | 13509 |
| Naphthenic acid, kg | 229 | | Not provided | | |
| Illuminating paraffin | 350 | | Not provided | | |

* Value in brackets represents the corresponding amount of manganese sulfate and the money (in Rands) lost.

The company receives clean water from the eThekweni Municipality which is billed per month according to the unit price used (see Table 7.3 & 7.5). Table 7.6 gives the amount of water used by both the production section including the offices that housed production staff. This information was extracted from the monthly statement the company receives from the Municipality. Amounts of water used in May and June are similar, though the charges differ by almost one hundred rands (R100). This was due to reconnection charges which the company could have avoided by paying the account timeously and also the fact that the fixed charge was lower in June than in May. It was not easy to determine how the basic charge is worked out as it fluctuates from month to month.

Table 7.6 Amount and charges for the use of eThekweni Municipality water

| Month | Meter reading (m ³) | | Water Used (m ³) | Amount Paid, R |
|-------------------------------------|---------------------------------|-------|------------------------------|----------------|
| | Initial | Final | | |
| JANUARY | 37779 | 38144 | 365 | 2661 |
| FEBRUARY | 38144 | 39308 | 1164 | 8420 |
| MARCH | | | | |
| APRIL | 39308 | 39717 | 409 | 3038 |
| MAY | | | | |
| JUNE | 39717 | 40126 | 409 | 2912 |
| JULY | 40126 | 40516 | 390 | 2835 |
| AUGUST | 40516 | 40984 | 468 | 3583 |
| SEPTEMBER | 40984 | 41393 | 409 | 3139 |
| OCTOBER | 41393 | 41815 | 422 | 3286 |
| NOVEMBER | 41815 | 42144 | 329 | 2550 |
| DECEMBER | 42144 | 42565 | 421 | 3217 |
| TOTAL AMOUNT OF WATER USED PER YEAR | | | 4786 | 35641 |

The percent production of each PD and the drier blends (as described in Table 4.1) manufactured by the company are provided in Table 7.7. Appendix C gives graphic representations of the production percentage per annum for each metal drier and blends. Percent values were calculated based on equation 7.2.

$$\text{Percent of each drier produced per year} = \frac{\text{Total amount of PD produced}}{\text{Total amount of all PD manufactured}} \times 100\% \quad \text{Equation 7.2}$$

Table 7.7 Production percents of Paint Driers produced by the company

| Metal Paint Drier | *Amount manufactured in year 2006, kg | % manufactured with respect to all driers Plus blends | % manufactured of drier blends with respect to other drier blends |
|--|--|--|--|
| BARIUM | | 0.202 | |
| CALCIUM | | 22.4 | |
| MANGANESE | | 2.54 | |
| COBALT | | 17.9 | |
| COPPER | | 0.784 | |
| LEAD | | 11.2 | |
| POTASSIUM | | 1.48 | |
| SODIUM | | 0.388 | |
| ZINC | | 4.16 | |
| ZIRCONIUM | | 10.17 | |
| TOTAL AMOUNT OF DRIER BLENDS | | 28.8 | |
| D048N | | 6.09 | 21.10 |
| LF7N | | 8.58 | 29.73 |
| LF9N | | 13.1 | 45.42 |
| LF11 | | 0.292 | 1.01 |
| CAL-DRY PLUS N | | 0.325 | 1.13 |
| PUTTY DRIER LFC | | 0.467 | 1.62 |
| TOTAL AMOUNT OF DRIERS PRODUCED PER ANNUM | | 100 | 100 |

*Actual amounts (masses) used to calculate the percent are NOT shown in line with confidential agreement signed between the research institution and the company.

Total monthly amounts of freshwater used and wastewater removed from the PD section of the company and percent disposal costs are given in Table 7.8. These values were obtained from the SMFD documents and Tax Invoices provided by EnviroServe (described in Table 6.1). A graphic representation of wastewater collected and percent disposal cost is also shown by Figure D1 in Appendix D.

Table 7.8 Freshwater used, wastewater disposed and percent of total cost in the drier plant

| Month | Freshwater Used (tonnes) | Wastewater Collected (tonnes) | Percent Total Cost (%) | |
|-----------|--------------------------|-------------------------------|------------------------|----------|
| | | | Freshwater | Disposal |
| JANUARY | 11.18 | 10.45 | 0.03 | 2.23 |
| FEBRUARY | 13.57 | 33.05 | 0.03 | 6.87 |
| MARCH | 15.36 | 30.50 | 0.04 | 6.59 |
| APRIL | 7.23 | 43.00 | 0.02 | 9.04 |
| MAY | 21.39 | 18.45 | 0.05 | 4.19 |
| JUNE | 13.55 | 65.95 | 0.03 | 13.7 |
| JULY | 14.85 | 43.70 | 0.04 | 9.12 |
| AUGUST | 14.24 | 19.80 | 0.04 | 4.34 |
| SEPTEMBER | 15.70 | 20.90 | 0.04 | 4.46 |
| OCTOBER | 13.78 | 55.90 | 0.04 | 14.7 |
| NOVEMBER | 10.61 | 33.45 | 0.03 | 8.79 |
| DECEMBER | 0.03 | 60.60 | 0.00 | 15.6 |

*Amounts (values) used to calculate the percent are NOT shown in line with confidential agreement signed between the research institution and the company.

7.2 Results from reading instruments and municipality water meter

Characteristics of Co and Mn samples were determined by measuring the pH and the conductivity of the sample at the laboratory. Average pH and conductivity results obtained using measuring instruments shown in Figures 6.1 and 6.2 are tabulated in Tables 7.9 and 7.10.

A Municipal water meter is few meters away from the entrance to the facility and is easily accessible without entering the company premises. Water readings were collected during the first few weeks of the year during weekends when the company was not in operation. Results from the findings are given in Table 7.11. From these figures, it is clear that the company is losing a substantial amount of water during shutdown. The question is, where is the loss occurring and how can it be eliminated? If the amount is lost through leakage, the picture is even worse than is reflected here as it means water is also lost during operation.

Table 7.9 General nature and characteristics of Co wastewater samples, pH and conductivity (mS/cm) at the time of sampling

| Parameters | Reaction wastewater | Wash wastewater | Distillate |
|----------------------|-----------------------------|-------------------------------|-------------------------------|
| Temperature (°C) | 80 – 90 | 50 – 60 | 80 – 90 |
| Colour | Clear – pale pink | Clear | Clear mixed with white spirit |
| pH | 7.10 – 8.05 | 7.20 – 7.55 | 7.00 – 7.10 |
| Conductivity (mS/cm) | 80.0 - 150 | 25.0 – 40.0 | 0 |
| Co metal (ppm) | 100 – 260 | 5.00 – 100 | 0 |
| Sulfate (ppm) | $(1.00 – 11.5) \times 10^4$ | $(0.200 – 0.710) \times 10^4$ | 0 |

Table 7.10 General nature and characteristics of Mn wastewater samples, pH and conductivity (mS/cm) at the time of sampling

| Parameters | Reaction wastewater | Distillate |
|----------------------|------------------------------|-------------------------------|
| Temperature (°C) | 80 – 90 | 80 – 90 |
| Colour | Clear – light brown | Clear mixed with white spirit |
| pH | 6.80 – 7.10 | 7.00 – 7.10 |
| Conductivity (mS/cm) | 90 – 150 | 0 |
| Mn metal (ppm) | $(2.30 – 5.00) \times 10^3$ | 0 |
| Sulfate (ppm) | $(0.900 – 1.20) \times 10^5$ | 0 |

Table 7.11 Amount of water lost during weekends when the plant is not in use

| Weekend of the year | Initial reading, m ³ | Final reading, m ³ | Amount lost, m ³ |
|--|---------------------------------|-------------------------------|-----------------------------|
| 18 - 21 January | 48125 | 48136 | 11 |
| 25 - 28 January | 48227 | 48241 | 14 |
| 1 - 4 February | 48386 | 48393 | 08 |
| 15 - 18 February | 48543 | 48551 | 08 |
| 22 - 25 February | 48633 | 48638 | 05 |
| 7 - 10 March | 48771 | 48777 | 06 |
| 16 - 19 May | 49721 | 49730 | 09 |
| TOTAL AMOUNT OF WATER LOST IN SEVEN WEEKENDS | | | 61 |
| AVERAGE AMOUNT OF WATER LOST PER WEEKEND | | | 8.71 |

7.3 Results from Chemical Analysis

Tables 7.12 through 7.22 and Tables 7.23 through 7.27 give results obtained when analysing cobalt and manganese wastewater respectively using ICP-OES instrument. Instrument operating parameters applied and wavelength lines chosen for analytes are given in Tables 6.7 and 6.8 respectively. Parts per million (ppm) units were used to report the elemental concentration in the wastewater samples. Results for cobalt and manganese wastewater are reported under several dilutions in accordance with the description provided in Sections 6.5 and 6.7. At each sampling point, whilst the wastewater was being discharged, several samples were collected in groups of three. Each group of three was separated in time by 15 minutes. Occasionally, due to operational reasons, a longer period between groups of samples was necessary. Depending on the size of the batch being manufactured, the total time for complete discharge of the reaction wastewater was typically about 2.5 hours. The sample groupings are designated sequentially by T₁, T₂, etc. Group T₁ being collected first, followed (15 minutes later) by T₂, etc. At least two set of results were recorded for each sampling grouping, one for acidified (shaded in Tables 7.12 through 7.27) and another for non-acidified (not shaded) samples. The amount of sulfate in the wastewater from both processes was established through analysis of sulfur concentration. Results for sulfur analyte are given in the last column of each table. The Reference Numbers cited on the table headings for Tables 7.12 through 7.27 correspond to all the batches sampled described in Table 6.2. The abbreviations NM for “not measured” and ND for “not detected” were used where applicable in Tables 7.12 through 7.27. Analytical results given in Tables 7.12 through 7.27 are average concentrations for all wavelengths lines selected which are given in Table 6.8. The superscript “df” represents the dilution factor used when diluting samples.

Trace elements described in Section 6.4 were not detected (see Tables 17 and 18 of Appendix E) in the wastewater for either process and as such were not included when compiling the results. Cobalt or manganese analyte were not detected in the mains water and distillate from either process. Results from these sampling points were not tabulated.

Table 7.12 Average elemental concentrations (ppm) in non-acidified and acidified samples of reference number 6

| Sample Source | Sampling Group | [Co] | | | | | [S] x 10 ⁴ |
|--------------------|-----------------|-----------------|------------------|-------------------|-------------------|-------------------|-----------------------|
| | | 4 ^{df} | 20 ^{df} | 100 ^{df} | 200 ^{df} | 400 ^{df} | |
| Solvent wastewater | T ₁ | 61.7 | NM | 161 | 161 | 159 | 2.03 |
| | | NM | 77.5 | 107 | NM | NM | NM |
| | T ₂ | 64.6 | NM | 163 | 164 | 166 | 1.97 |
| | | NM | 89.1 | 122 | NM | NM | NM |
| | T ₃ | 69.5 | NM | 175 | 181 | 185 | 2.01 |
| | | NM | 103 | 138 | NM | NM | NM |
| | T ₄ | 68.0 | NM | 172 | 175 | 165 | 2.04 |
| | | NM | 103 | 139 | NM | NM | NM |
| | T ₅ | 69.0 | NM | 176 | 180 | 180 | 2.01 |
| | | NM | 104 | 142 | NM | NM | NM |
| | T ₆ | NM | 72.0 | 99.4 | NM | NM | 2.16 |
| | | NM | 39.9 | 55.2 | NM | NM | NM |
| | T ₇ | 65.6 | NM | 170 | 168 | 170 | 2.25 |
| | | NM | NM | NM | NM | NM | NM |
| | T ₈ | 67.2 | NM | 169 | 162 | 168 | 1.95 |
| | | NM | NM | NM | NM | NM | NM |
| Wash wastewater | T ₉ | 56.3 | NM | 83.4 | 81.2 | 74.2 | 0.894 |
| | | NM | NM | NM | NM | NM | NM |
| | T ₁₀ | NM | 57.8 | 62.5 | 52.3 | NM | 0.861 |
| | | NM | 34.6 | 39.1 | 18.3 | NM | 0.842 |
| | T ₁₁ | NM | 62.9 | 68.1 | 43.0 | NM | 0.824 |
| | | NM | NM | 10.7 | 20.5 | NM | 0.903 |
| | T ₁₂ | NM | 56.8 | 62.7 | 52.6 | NM | 0.866 |
| | | NM | NM | 11.4 | 13.5 | NM | 0.805 |

Table 7.13 Average elemental concentrations (ppm) in non-acidified and acidified samples of reference number 7

| Sample source | Sampling Group | [Co] | | | | [S] x 10 ⁴ |
|--------------------|----------------|-----------------|------------------|-------------------|-------------------|-----------------------|
| | | 4 ^{df} | 20 ^{df} | 100 ^{df} | 200 ^{df} | |
| solvent wastewater | T ₁ | 93.0 | NM | 233 | 241 | 2.01 |
| | | NM | 96.6 | 133 | NM | NM |
| Wash wastewater | T ₂ | NM | 85.3 | 49.2 | 47.1 | 0.852 |
| | | NM | 79.0 | 92.6 | 98.1 | 0.898 |

Table 7.14 Average elemental concentrations (ppm) in non-acidified and acidified samples of reference number 8

| Sample source | Sampling Group | [Co] | | | | | [S] x 10 ⁴ | |
|--------------------|----------------|-----------------|------------------|-------------------|-------------------|-------------------|-----------------------|-------------------|
| | | 4 ^{df} | 20 ^{df} | 100 ^{df} | 400 ^{df} | 800 ^{df} | 100 ^{df} | 800 ^{df} |
| solvent wastewater | T ₁ | NM | 80.1 | NM | 107 | NM | NM | NM |
| | | 47.9 | NM | NM | 119 | 132 | NM | 2.63 |
| | | NM | 72.3 | NM | 99.0 | NM | NM | NM |
| | T ₂ | NM | 83.4 | NM | 111 | NM | NM | NM |
| | | 48.0 | NM | NM | 130 | 132 | NM | 2.66 |
| | | NM | 83.1 | NM | 110 | NM | NM | NM |
| | T ₃ | 50.0 | NM | NM | 129 | 144 | NM | 2.71 |
| | | NM | 86.1 | NM | 114 | NM | NM | NM |
| | | NM | 92.3 | NM | 106 | NM | NM | NM |
| Wash wastewater | T ₄ | NM | 161 | 137 | 139 | NM | 0.100 | NM |
| | | NM | 92.6 | 196 | 210 | NM | 0.104 | NM |

Note that with the exception of wash wastewater, samples whose results are listed in Table 7.14 were not acidified

Table 7.15 Average elemental concentrations (ppm) in non-acidified and acidified samples of reference number 9

| Sample source | Sampling Group | [Co] | | | | | [S] x 10 ⁴ | |
|--------------------|----------------|-----------------|------------------|------------------|-------------------|-------------------|-----------------------|-------------------|
| | | 4 ^{df} | 20 ^{df} | 50 ^{df} | 100 ^{df} | 800 ^{df} | 100 ^{df} | 800 ^{df} |
| solvent wastewater | T ₁ | 46.1 | 92.8 | NM | 121 | 133 | NM | 2.77 |
| | | NM | 86.8 | NM | 118 | NM | NM | NM |
| | T ₂ | 50.9 | 91.2 | NM | 132 | 146 | NM | 2.71 |
| | | NM | 149 | NM | 170 | NM | NM | NM |
| Wash wastewater | T ₃ | NM | 37.7 | 151 | 155 | NM | 0.621 | NM |
| | | NM | 61.5 | 48.1 | 50.0 | NM | 0.680 | NM |
| | T ₄ | NM | 65.5 | 75.5 | 76.8 | NM | 0.611 | NM |
| | | NM | 62.3 | 178 | 187 | NM | 0.622 | NM |

Table 7.16 Average elemental concentrations (ppm) in non-acidified and acidified samples of reference number 10

| Sample Source | Sampling Group | [Co] | | | | | [S] x 10 ⁴ |
|--------------------|----------------|-----------------|------------------|-------------------|-------------------|-------------------|-----------------------|
| | | 4 ^{df} | 20 ^{df} | 100 ^{df} | 200 ^{df} | 800 ^{df} | 200 ^{df} |
| Solvent wastewater | T ₁ | 33.6 | 66.5 | 87.4 | NM | 107 | 2.03 |
| | | NM | 63.5 | 82.6 | NM | NM | 2.38 |
| | T ₂ | 36.1 | NM | 89.3 | NM | 116 | 1.97 |
| | | NM | 65.1 | 85.4 | NM | NM | 2.39 |
| | T ₃ | 36.8 | NM | 92.8 | NM | 112 | 2.02 |
| | | 37.0 | 63.6 | 89.5 | NM | 111 | 2.42 |
| Wash wastewater | T ₄ | 30.9 | NM | 76.1 | NM | 76.6 | 4.42 |
| | | 42.5 | 73.9 | 103 | NM | 127 | 2.40 |
| | | NM | 113 | 127 | 119 | NM | 0.150 |
| | | NM | 89.7 | 114 | 109 | NM | 0.165 |

Table 7.17 Average elemental concentrations (ppm) in non-acidified and acidified samples of reference number 11

| Sample Source | Sampling Group | [Co] | | [S] x 10 ⁴ |
|--------------------|----------------|------------------|-------------------|-----------------------|
| | | 20 ^{df} | 100 ^{df} | 100 ^{df} |
| Solvent wastewater | T ₁ | 103 | 144 | 3.49 |
| | | NM | NM | NM |
| Wash wastewater | T ₂ | 59.2 | 85.9 | 0.668 |
| | | 84.2 | 132 | 0.708 |
| | T ₃ | 54.8 | 63.0 | 0.678 |
| | | 163 | 241 | 0.705 |

Table 7.18 Average elemental concentrations (ppm) in non-acidified and acidified samples of reference number 12

| Sample source | Sampling Group | [Co] | | | | | [S] x 10 ⁴ |
|--------------------|----------------|-----------------|------------------|-------------------|-------------------|-------------------|-----------------------|
| | | 4 ^{df} | 20 ^{df} | 100 ^{df} | 400 ^{df} | 800 ^{df} | 100 ^{df} |
| Solvent wastewater | T ₁ | 89.8 | 155 | 219 | NM | 246 | 3.29 |
| | | 91.0 | 163 | 219 | NM | 259 | 6.10 |
| | T ₂ | 73.4 | 161 | 212 | NM | 203 | 5.04 |
| | | 88.4 | 157 | 209 | NM | 250 | 6.18 |
| | T ₃ | 91.1 | NM | 209 | NM | 242 | 4.92 |
| | | 89.9 | 163 | 219 | NM | 259 | 3.43 |
| Wash wastewater | T ₄ | NM | 47.9 | 48.9 | 31.0 | NM | 0.579 |
| | | NM | 93.5 | 102 | NM | NM | 0.626 |
| | T ₅ | NM | 79.6 | 112 | 91.1 | NM | 0.553 |
| | | NM | 41.2 | 90.7 | 100 | NM | 0.607 |

Table 7.19 Average elemental concentrations (ppm) in non-acidified and acidified samples of reference number 13

| Sample Source | Sampling Group | [Co] | | | | | [S] x 10 ⁴ |
|--------------------|-----------------|-----------------|------------------|-------------------|-------------------|-------------------|-----------------------|
| | | 4 ^{df} | 20 ^{df} | 100 ^{df} | 200 ^{df} | 800 ^{df} | 100 ^{df} |
| Solvent wastewater | T ₁ | 75.0 | 171 | 225 | NM | 242 | 2.05 |
| | | 94.2 | 180 | 241 | NM | 291 | 6.07 |
| | T ₂ | 38.4 | 83.3 | 104 | NM | 131 | 1.89 |
| | | 41.7 | 79.8 | 104 | NM | 128 | 6.00 |
| | T ₃ | 33.4 | 82.0 | 109 | NM | 130 | 1.93 |
| | | 41.9 | 82.1 | 109 | NM | 133 | 2.34 |
| | T ₄ | 35.8 | 71.9 | 97.7 | NM | 137 | 2.02 |
| | | 38.9 | 75.7 | 99.9 | NM | 121 | 5.91 |
| | T ₅ | 38.2 | 74.2 | 105 | NM | 141 | 2.16 |
| | | 41.7 | 81.1 | 107 | NM | 136 | 3.67 |
| | T ₆ | 42.0 | 87.9 | 115 | NM | 148 | 1.97 |
| | | 42.4 | 81.0 | 107 | NM | 132 | 5.67 |
| Wash wastewater | T ₇ | NM | 63.6 | 71.2 | 59.4 | NM | 0.284 |
| | | NM | 4.89 | 7.76 | 5.58 | NM | 0.293 |
| | T ₈ | NM | NM | 38.1 | 39.7 | NM | 0.283 |
| | | NM | 2.14 | 6.92 | 6.43 | NM | 0.293 |
| | | NM | 71.9 | 80.6 | 52.4 | NM | 0.274 |
| | T ₉ | NM | 68.6 | 75.4 | 54.2 | NM | 0.282 |
| | | NM | 21.7 | 14.3 | 6.41 | NM | 0.293 |
| | T ₁₀ | NM | 49.9 | 55.4 | 46.3 | NM | 0.289 |
| | | NM | 15.5 | 16.4 | 4.23 | NM | 0.307 |
| | T ₁₁ | NM | 73.0 | 80.5 | 45.4 | NM | 0.293 |
| | | NM | 75.0 | 85.2 | 54.9 | NM | 0.299 |

Table 7.20 Average elemental concentrations (ppm) in non-acidified and acidified samples of reference number 14

| Sample source | Sampling Group | [Co] | | | | | | | | | [S] x 10 ⁴ |
|--------------------|-----------------|-----------------|------------------|------------------|------------------|-------------------|-------------------|-------------------|-------------------|--------------------|-----------------------|
| | | 4 ^{df} | 16 ^{df} | 20 ^{df} | 50 ^{df} | 100 ^{df} | 200 ^{df} | 400 ^{df} | 800 ^{df} | 1000 ^{df} | 100 ^{df} |
| Solvent wastewater | T ₁ | 28.8 | 52.7 | 73.6 | 75.0 | 84.8 | 88.6 | 91 | 83.8 | 102 | 1.81 |
| | | 53.9 | 98.8 | 90.8 | 117 | 132 | 139 | 150 | 160 | 165 | 6.25 |
| | T ₂ | 40.7 | 74.8 | 74.6 | 92.6 | 102 | 110 | 110 | 114 | 116 | 1.63 |
| | | 50.9 | 94.3 | 85.3 | 111 | 125 | 132 | 142 | 151 | 156 | 6.00 |
| | T ₃ | 42.8 | 81.4 | 75.7 | 94.8 | 104 | 108 | 113 | 114 | 118 | 2.00 |
| | | 52.6 | 98.8 | 87.9 | 114 | 126 | 136 | 145 | 156 | 161 | 5.61 |
| | T ₄ | 40.8 | 76.2 | 74.7 | 86.7 | 96.2 | 103 | 107 | 110 | 116 | 2.26 |
| | | 51.9 | 97.1 | 87.6 | 111 | 123 | 135 | 144 | 151 | 157 | 6.06 |
| | T ₅ | 37.2 | 69.1 | 73.5 | 80.0 | 86.9 | 73.1 | 70.7 | 73.3 | 73.8 | 1.66 |
| | | 69.7 | 130 | 114 | 149 | 162 | 160 | 176 | 189 | 190 | 4.98 |
| | T ₆ | 35.1 | 62.9 | 61.6 | 85.4 | 88.7 | 87.1 | 85.2 | 85.3 | 85.1 | 1.71 |
| | | 54.3 | 88.6 | 89.3 | 118 | 129 | 134 | 139 | 150 | 151 | 6.53 |
| | T ₇ | 39.0 | 66.3 | 68.1 | 81.7 | 92.9 | 84.5 | 82.5 | 80.7 | 82.9 | 2.25 |
| | | 48.5 | 77.8 | 81.6 | 116 | 117 | 121 | 128 | 134 | 142 | 6.67 |
| | T ₈ | 46.7 | 75.8 | 57.8 | 101 | 112 | 99.6 | 95.8 | 92.1 | 92.2 | 1.57 |
| | | 224 | 381 | 375 | 489 | 547 | 556 | 593 | 628 | 625 | 2.14 |
| Wash wastewater | T ₉ | NM | 133 | 150 | 143 | 169 | 82.6 | NM | NM | NM | 0.230 |
| | | NM | 18.9 | 13.0 | 23.4 | 18.0 | 15.0 | NM | NM | NM | 0.271 |
| | T ₁₀ | NM | 164 | 192 | 176 | 217 | 104 | NM | NM | NM | 0.273 |
| | | NM | 42.5 | 11.2 | 46.1 | 35.0 | 27.0 | NM | NM | NM | 0.267 |
| | T ₁₁ | NM | 137 | NM | 147 | 123 | 86.6 | NM | NM | NM | 0.231 |
| | | NM | 37.4 | 24.6 | 83.7 | 70.0 | 52.0 | NM | NM | NM | 0.251 |
| | T ₁₂ | NM | 206 | 228 | 223 | 272 | 144 | NM | NM | NM | 0.378 |
| | | NM | 53.9 | 12.5 | 109 | 96.8 | 70.9 | NM | NM | NM | 0.256 |

Table 7.21 Average elemental concentrations (ppm) in non-acidified and acidified samples of reference number 15

| Sample source | Sampling Group | [Co] | | | | | | | [S] x 10 ⁴ | |
|--------------------|-----------------|-----------------|------------------|------------------|-------------------|-------------------|-------------------|-------------------|-----------------------|-------------------|
| | | 4 ^{df} | 20 ^{df} | 40 ^{df} | 100 ^{df} | 200 ^{df} | 400 ^{df} | 800 ^{df} | 200 ^{df} | 400 ^{df} |
| Solvent wastewater | T ₁ | 66.2 | 143 | NM | 196 | NM | 203 | 185 | NM | 2.38 |
| | | 75.0 | 152 | NM | 221 | NM | 268 | 267 | NM | 3.63 |
| | T ₂ | 67.5 | 138 | NM | 199 | NM | 206 | 185 | NM | 2.38 |
| | | 81.5 | 160 | NM | 229 | NM | 263 | 259 | NM | 3.57 |
| | | NM | NM | 177 [#] | 207 [#] | 228 [#] | 245 [#] | 258 [#] | NM | 2.68 [#] |
| | T ₃ | 62.5 | 144 | NM | 188 | NM | 191 | 176 | NM | 2.36 |
| | | 76.4 | 148 | NM | 215 | NM | 246 | 243 | NM | 3.56 |
| | | NM | NM | 176 [#] | 195 [#] | 185 [#] | 184 [#] | 186 [#] | NM | 2.44 [#] |
| | T ₄ | 70.3 | 146 | NM | 196 | NM | 191 | 186 | NM | 2.36 |
| | | 78.1 | 148 | NM | 212 | NM | 235 | 241 | NM | 3.50 |
| | | NM | NM | 184 [#] | 195 [#] | 195 [#] | 215 [#] | 179 [#] | NM | 2.53 [#] |
| | T ₅ | 73.7 | 145 | NM | 194 | NM | 195 | 186 | NM | 2.35 |
| | | 77.7 | 148 | NM | 217 | NM | 229 | 238 | NM | 3.58 |
| | | NM | NM | 176 [#] | 189 [#] | 196 [#] | 194 [#] | 181 [#] | NM | 2.51 [#] |
| | T ₆ | 71.0 | 142 | NM | 196 | NM | 190 | 185 | NM | 2.35 |
| | | 79.8 | 147 | NM | 214 | NM | 227 | 251 | NM | 3.54 |
| | | NM | NM | 180 [#] | 193 [#] | 190 [#] | 182 [#] | 167 [#] | NM | 2.50 [#] |
| | T ₇ | 71.2 | 139 | NM | 189 | NM | 189 | 181 | NM | 2.32 |
| | | 192 | 349 | NM | 523 | NM | 557 | 576 | NM | 3.47 |
| | | NM | NM | 167 [#] | 184 [#] | 185 [#] | 175 [#] | 176 [#] | NM | 2.49 [#] |
| Wash wastewater | T ₈ | 62.2 | 84.4 | NM | 66.7 | 52.8 | NM | NM | 0.453 | NM |
| | | 4.87 | 12.3 | NM | 12.2 | 9.56 | NM | NM | 0.450 | NM |
| | T ₉ | 35.8 | 68.3 | NM | 39.2 | 31.6 | NM | NM | 0.442 | NM |
| | | 5.85 | 9.07 | NM | 8.35 | 8.11 | NM | NM | 0.457 | NM |
| | T ₁₀ | 62.4 | 76.4 | NM | 70.4 | 56.8 | NM | NM | 0.456 | NM |
| | | 8.80 | 5.30 | NM | 16.6 | 18.2 | NM | NM | 0.461 | NM |
| | T ₁₁ | 107 | 125 | NM | 133 | 109 | NM | NM | 0.448 | NM |
| | | 11.6 | 3.66 | NM | 25.1 | 28.4 | NM | NM | 0.459 | NM |
| | T ₁₂ | 145 | 221 | NM | 188 | 160 | NM | NM | 0.457 | NM |
| | | 7.06 | 7.36 | NM | 6.96 | 6.32 | NM | NM | 0.461 | NM |

[#] Samples diluted at the production plant. Note that results from these samples were not used as explained in Section 6.5.

Table 7.22 Average elemental concentrations (ppm) in non-acidified and acidified samples of reference number 16

| Sample source | Sampling Group | [Co] | | | | [S] x 10 ⁴ | |
|--------------------|-----------------|-----------------|-------------------|-------------------|-------------------|-----------------------|-------------------|
| | | 4 ^{df} | 100 ^{df} | 400 ^{df} | 800 ^{df} | 100 ^{df} | 800 ^{df} |
| Solvent Wastewater | T ₁ | 31.1 | 68.2 | 69.6 | 74.1 | NM | 2.60 |
| | | NM | NM | NM | NM | NM | NM |
| | T ₂ | 47.4 | 119 | 122 | 124 | NM | 2.57 |
| | | 60.6 | 139 | 163 | 178 | NM | 3.91 |
| | T ₃ | 52.0 | 119 | 129 | 192 | NM | 2.56 |
| | | 55.9 | 134 | 147 | 171 | NM | 3.99 |
| | T ₄ | 53.5 | 122 | 127 | 128 | NM | 2.54 |
| | | 54.5 | 134 | 155 | 168 | NM | 3.95 |
| | T ₅ | 54.5 | 128 | 133 | 138 | NM | 2.58 |
| | | 56.4 | 140 | 162 | 178 | NM | 3.97 |
| | T ₆ | 53.4 | 125 | 130 | 133 | NM | 2.52 |
| | | 55.9 | 137 | 159 | 172 | NM | 3.95 |
| | T ₇ | 50.6 | 121 | 126 | 130 | NM | 2.57 |
| | | 54.1 | 135 | 156 | 169 | NM | 3.93 |
| | T ₈ | 56.7 | 139 | 145 | 211 | NM | 2.57 |
| | | 54.0 | 138 | 161 | 174 | NM | 3.97 |
| | T ₉ | 30.2 | 111 | 115 | 118 | NM | 2.56 |
| | | 50.4 | 128 | 151 | 179 | NM | 3.92 |
| | T ₁₀ | 49.9 | 121 | 128 | 131 | NM | 2.54 |
| | | 55.7 | 143 | 168 | 181 | NM | 3.93 |
| | T ₁₁ | 73.8 | 186 | 198 | 201 | NM | 2.56 |
| | | NM | NM | NM | NM | NM | NM |
| Wash wastewater | T ₁₂ | NM | 95.3 | NM | NM | 0.200 | NM |
| | | NM | 44.8 | NM | NM | 0.201 | NM |
| | T ₁₃ | NM | 89.7 | NM | NM | 0.202 | NM |
| | | NM | 42.5 | NM | NM | 0.202 | NM |
| | T ₁₄ | NM | 94.5 | NM | NM | 0.201 | NM |
| | | NM | 40.8 | NM | NM | 0.200 | NM |
| | T ₁₅ | NM | 259 | NM | NM | 0.197 | NM |
| | | NM | 71.9 | NM | NM | 0.202 | NM |
| | T ₁₆ | NM | 137 | NM | NM | 0.197 | NM |
| | | NM | 66.0 | NM | NM | 0.200 | NM |
| | T ₁₇ | NM | 196 | NM | NM | 0.201 | NM |
| | | NM | 148 | NM | NM | 0.200 | NM |
| | T ₁₈ | NM | 341 | NM | NM | 0.201 | NM |
| | | NM | 321 | NM | NM | 0.202 | NM |

Table 7.23 Average elemental concentrations (ppm) in non-acidified and acidified samples of reference number 1

| Sample source | Sampling Group | [Mn] x 10 ³ | | | | | | [S] x 10 ⁵ | |
|--------------------|----------------|------------------------|-------------------|-------------------|-------------------|-------------------|--------------------|-----------------------|--------------------|
| | | 20 ^{df} | 100 ^{df} | 200 ^{df} | 400 ^{df} | 800 ^{df} | 1000 ^{df} | 800 ^{df} | 1000 ^{df} |
| Solvent wastewater | T ₁ | 3.12 | 3.61 | 4.91 | 4.92 | 4.94 | 4.87 | 1.08 | 1.11 |
| | | 3.33 | 4.54 | NM | | | | NM | |
| | | 4.06 | 5.88 | NM | | | | NM | |

Table 7.24 Average elemental concentrations (ppm) in non-acidified and acidified samples of reference number 2

| Sample source | Sampling Group | [Mn] x 10 ³ | | | | | | [S] x 10 ⁵ | |
|--------------------|----------------|------------------------|-------------------|-------------------|-------------------|-------------------|--------------------|-----------------------|--------------------|
| | | 20 ^{df} | 100 ^{df} | 200 ^{df} | 400 ^{df} | 800 ^{df} | 1000 ^{df} | 800 ^{df} | 1000 ^{df} |
| Solvent wastewater | T ₁ | 1.77 | 2.31 | NM | | | | NM | |
| | | 1.99 | 2.16 | 2.87 | 2.89 | 2.87 | 2.86 | 1.07 | 1.09 |
| | | 1.61 | 1.70 | 2.26 | 2.27 | 2.27 | 2.29 | 1.08 | 1.11 |
| | T ₂ | 1.62 | 2.10 | NM | | | | NM | |
| | | 2.07 | 2.26 | 2.98 | 2.96 | 3.01 | 2.95 | 1.04 | 1.08 |
| | | 1.68 | 2.20 | NM | | | | NM | |
| | T ₃ | 2.07 | 2.73 | NM | | | | NM | |
| | | 1.84 | 1.98 | 2.61 | 2.62 | 2.63 | 2.60 | 1.04 | 1.08 |
| | | 1.66 | 2.13 | NM | | | | NM | |

Table 7.25 Average elemental concentrations (ppm) in non-acidified and acidified samples of reference number 3

| Sample source | Sampling Group | [Mn] x 10 ³ | | | | | | [S] x 10 ⁵ | |
|---------------|----------------|------------------------|-------------------|-------------------|-------------------|-------------------|--------------------|-----------------------|--------------------|
| | | 20 ^{df} | 100 ^{df} | 200 ^{df} | 400 ^{df} | 800 ^{df} | 1000 ^{df} | 800 ^{df} | 1000 ^{df} |
| wastewater | T ₁ | 2.15 | 2.80 | NM | | | | NM | |
| | | 2.73 | 3.64 | NM | | | | NM | |
| | T ₂ | 1.91 | 2.04 | 2.71 | 2.72 | 2.77 | 2.70 | 0.989 | 1.02 |
| | | 1.75 | 1.83 | 2.46 | 2.46 | 2.48 | 2.48 | 1.06 | 1.09 |
| | | 1.98 | 2.65 | NM | | | | NM | |
| | T ₃ | 1.77 | 1.88 | 2.54 | 2.52 | 2.52 | 2.54 | 1.01 | 1.03 |
| | | 1.68 | 1.78 | 2.48 | 2.48 | 2.45 | 2.45 | 1.09 | 1.11 |
| | | 3.16 | 2.38 | NM | | | | NM | |
| | T ₄ | 1.79 | 1.90 | 2.57 | 2.57 | 2.57 | 2.56 | 1.02 | 1.04 |
| | | 1.72 | 1.84 | 2.45 | 2.45 | 2.45 | 2.43 | 1.06 | 1.08 |
| | | 1.74 | 1.83 | 2.45 | 2.45 | 2.49 | 2.49 | 1.10 | 1.14 |
| | T ₅ | 1.77 | 1.88 | 2.54 | 2.54 | 2.56 | 2.56 | 1.02 | 1.03 |
| | | 1.75 | 2.26 | NM | | | | NM | |
| | | 1.85 | 2.40 | NM | | | | NM | |
| | T ₆ | 1.77 | 1.88 | 2.52 | 2.52 | 2.54 | 2.54 | 1.03 | 1.04 |
| | | 1.72 | 1.85 | 2.44 | 2.44 | 2.45 | 2.43 | 1.04 | 1.05 |
| | | 1.76 | 1.84 | 2.51 | 2.51 | 2.55 | 2.54 | 1.06 | 1.09 |
| | T ₇ | 1.78 | 1.89 | 2.52 | 2.52 | 2.54 | 2.53 | 0.992 | 1.01 |
| | | 1.86 | 1.86 | 2.46 | 2.46 | 2.48 | 2.45 | 1.02 | 1.04 |
| | | 1.81 | 1.96 | 2.63 | 2.63 | 2.64 | 2.64 | 1.07 | 1.09 |
| | T ₈ | 1.91 | 1.88 | 2.48 | 2.48 | 2.50 | 2.50 | 1.02 | 1.03 |
| | T ₉ | 1.76 | 1.72 | 2.27 | 2.27 | 2.31 | 2.30 | 1.07 | 1.09 |
| | | 1.65 | 2.08 | NM | | | | NM | |
| | | 1.82 | 2.37 | NM | | | | NM | |

Table 7.26 Average elemental concentrations (ppm) in non-acidified and acidified samples of reference number 4

| Sample source | Sampling Group | [Mn] x 10 ³ | | | | | | [S] x 10 ⁵ | |
|--------------------|----------------|------------------------|-------------------|-------------------|-------------------|-------------------|--------------------|-----------------------|--------------------|
| | | 20 ^{df} | 100 ^{df} | 200 ^{df} | 400 ^{df} | 800 ^{df} | 1000 ^{df} | 800 ^{df} | 1000 ^{df} |
| Mains water | | ND | | | | | | ND | |
| Solvent wastewater | T ₁ | 3.12 | 3.16 | 4.24 | 4.24 | 4.27 | 4.27 | 1.07 | 1.11 |
| | | 3.11 [#] | 3.16 [#] | 4.32 [#] | 4.32 [#] | 4.35 [#] | 4.42 [#] | 1.11 [#] | 1.12 [#] |
| | | 3.18 | 4.28 | NM | | | | NM | |
| | T ₂ | 3.05 | 3.16 | 4.20 | 4.21 | 4.21 | 4.23 | 1.06 | 1.07 |
| | | 3.16 [#] | 3.22 [#] | 4.32 [#] | 4.35 [#] | 4.37 [#] | 4.36 [#] | 1.07 [#] | 1.09 [#] |
| | | 3.10 | 3.18 | 4.29 | 4.29 | 4.37 | 4.40 | 1.08 | 1.09 |
| | T ₃ | 3.07 | 3.14 | 4.20 | 4.20 | 4.24 | 4.20 | 1.06 | 1.08 |
| | | 3.16 [#] | 4.25 [#] | NM | | | | NM | |
| | | 3.16 | 4.22 | NM | | | | NM | |
| | T ₄ | 3.01 | 3.12 | 4.18 | 4.18 | 4.21 | 4.23 | 1.08 | 1.09 |
| | | 3.22 [#] | 4.34 [#] | NM | | | | NM | |
| | | 3.08 | 4.14 | NM | | | | NM | |
| | T ₅ | 3.03 | 3.17 | 4.15 | 4.15 | 4.19 | 4.23 | 1.06 | 1.07 |
| | | 3.11 [#] | 4.23 [#] | NM | | | | NM | |
| | T ₆ | 3.04 | 3.16 | 4.20 | 4.22 | 4.27 | 4.23 | 1.09 | 1.09 |
| | | 3.16 [#] | 4.31 [#] | NM | | | | NM | |
| | | 3.08 | 4.14 | NM | | | | NM | |
| | T ₇ | 3.06 | 3.12 | 4.10 | 4.11 | NM | 4.14 | 0.843 | 1.30 |
| | | 3.09 [#] | 4.19 [#] | NM | | | | NM | |
| | | 3.03 | 4.03 | NM | | | | NM | |

[#] Samples diluted at the production plant. Note that results from these samples were not used as explained in Section 6.5.

Table 7.27 Average elemental concentrations (ppm) in non-acidified and acidified samples of reference number 5

| Sample source | Sampling Group | [Mn] x 10 ³ | | | | | | | [S] x 10 ⁵ | |
|--------------------|----------------|------------------------|-------------------|-------------------|-------------------|-------------------|-------------------|--------------------|-----------------------|--------------------|
| | | 20 ^{df} | 50 ^{df} | 100 ^{df} | 200 ^{df} | 400 ^{df} | 800 ^{df} | 1000 ^{df} | 800 ^{df} | 1000 ^{df} |
| Solvent wastewater | T ₁ | 2.88 | 3.18 | 3.50 | 3.72 | 3.70 | 4.00 | 2.57 | 1.18 | 0.743 |
| | | 2.74 [#] | 3.21 [#] | 3.56 [#] | 3.56 [#] | 3.65 [#] | 3.77 [#] | 3.81 [#] | 1.17 [#] | 1.18 [#] |
| | | 2.95 | 3.24 | 3.53 | 3.73 | 3.70 | 4.05 | 2.58 | 1.17 | 0.726 |
| | T ₂ | 2.90 | 3.20 | 3.55 | 3.74 | 3.89 | 4.00 | 2.55 | 1.15 | 0.706 |
| | | 2.75 [#] | 3.26 [#] | 3.35 [#] | 3.60 [#] | 3.45 [#] | 3.81 [#] | 3.83 [#] | 1.20 [#] | 1.20 [#] |
| | | 2.88 | 3.22 | 3.48 | 3.66 | 3.86 | 3.99 | 2.53 | 1.17 | 0.720 |
| | T ₃ | 2.90 | 3.24 | 3.52 | 3.74 | 3.90 | 4.03 | 4.03 | 1.15 | 1.15 |
| | | 2.72 [#] | 3.21 [#] | 3.36 [#] | 3.56 [#] | 3.70 [#] | 3.79 [#] | 3.80 [#] | 1.18 [#] | 1.20 [#] |
| | | 2.91 | 3.20 | 3.44 | 3.70 | 3.88 | 3.95 | 2.49 | 1.15 | 0.731 |
| | T ₄ | 2.92 | 3.24 | 3.54 | 3.74 | 3.91 | 3.97 | 2.58 | 1.14 | 0.733 |
| | | 2.76 [#] | 3.24 [#] | 3.40 [#] | 3.59 [#] | 3.69 [#] | 3.83 [#] | 3.84 [#] | 1.19 [#] | 1.20 [#] |
| | | 2.94 | 3.21 | 3.50 | 3.70 | 3.90 | 4.00 | 4.00 | 1.15 | 1.16 |
| | T ₅ | 2.86 | 3.15 | 3.49 | 3.66 | 3.87 | 3.19 | 4.98 | 0.912 | 1.42 |
| | | 2.75 [#] | 3.23 [#] | 3.34 [#] | 3.50 [#] | 3.67 [#] | 3.72 [#] | 3.76 [#] | 1.17 [#] | 1.18 [#] |
| | | 2.79 | 2.13 | 2.29 | 2.40 | 2.46 | 2.41 | 2.42 | 1.07 | 1.09 |

[#] Samples diluted at the production plant

Table 7.28 Mass measurements for inputs raw materials and outputs (product and wastewater) for Batch number N6JUN07

| Inputs to reactor | | Outputs from reactor | |
|--------------------------------------|------------|----------------------|------------|
| Substance | Amount, kg | Substance | Amount, kg |
| Reaction water | 2 050 | Product | 4 962 |
| 2EH | 2 255 | Reaction wastewater | 4 088 |
| NaOH | 614 | Wash wastewater | 702 |
| White Spirit | 3 001 | Distillate water | 104 |
| CoSO ₄ .7H ₂ O | 2 000 | Distillate spirit | 163 |
| Wash water | 600 | | |
| TOTAL | 10 520 | TOTAL | 10019 |

The composition of the wastewater includes the reaction water used to dissolve the sodium hydroxide, water from neutralisation of the 2-EH, water from the seven waters of crystallisation of the hydrated cobalt salt and sodium sulfate byproduct (see Section 5 of Appendix E). According to the production personnel, an average of about 4 tonnes (a little more than 4 m³) of wastewater is released as reaction water during production.

Table 7.29 Mass (kg) of cobalt lost during production in each batch sampled with respect to instrumental analysis and SMFD sheets information

| Date Collected | Batch Number | Metal Specification | Ave. Elemental concentration, ppm | | Average amount of unreacted Co according to ICP-OES results, kg | Amount of unreacted Co according to SMFD, kg |
|----------------|--------------|---------------------|-----------------------------------|-----------------|---|--|
| | | | Solvent wastewater | Wash wastewater | | |
| 06.02.06 | N6FEB04 | 12 % octoate | 165 | 40.2 | 0.800 | 7.00 |
| 06.03.06 | N6MAR06 | 12 % octoate | 147 | 76.7 | 0.622 | 4.00 |
| 08.03.06 | N6MAR10 | 12 % octoate | 114 | 116 | 0.625 | 0.00 |
| 14.03.06 | N6MAR17 | 12 % octoate | 148 | 101 | 0.663 | 1.00 |
| 06.06.06 | N6JUN07 | 8 % octoate | 97.1 | 95.4 | 0.475 | 21.00 |
| 12.06.06 | N6JUN11 | 10 % octoate | 135 | 89.2 | 0.602 | 20.00 |
| 12.07.06 | N6JUL02 | 12 % octoate | 238 | 63.2 | 0.956 | -5.00 |
| 17.07.06 | N6JUL12 | 12 % octoate | 168 | 51.5 | 0.692 | -14.00 |
| 27.07.06 | N6JUL28 | 12 % octoate | 106 | 113 | 0.555 | -3.00 |
| 14.11.06 | N6NOV17 | 12 % octoate | 183 | 46.9 | 0.985 | -5.00 |
| 23.02.07 | N7FEB22 | 12 % octoate | 148 | 107 | 0.723 | -33.00 |

Table 7.30 Mass (kg) of manganese lost during production in sampled batches with respect to instrumental analysis and SMFD sheets information

| Date Collected | Batch Number | Metal Specification | Average Elemental concentration, ppm | Average amount of unreacted Mn according to ICP-OES results, kg | Amount of unreacted Mn according to SMFD, kg |
|----------------|--------------|---------------------|--------------------------------------|---|--|
| 27.01.06 | N6JAN25 | 10 % octoate | 5100 | 9.05 | 9.00 |
| 27.02.06 | N6FEB32 | 10 % octoate | 2690 | 3.74 | 13.00 |
| 01.08.06 | N6JUL31 | 10 % octoate | 2590 | 4.60 | 6.00 |
| 11.10.06 | N6OCT04 | 8 % octoate | 4250 | 7.54 | 11.00 |
| 05.03.07 | N7MAR04 | 10 % octoate | 3770 | 6.69 | 27.00 |

Entries given in column 4 and 5 of Tables 7.29 and 7.30 were calculated using Equations 7.3 and 7.4 respectively.

$$\text{Analytical Amount of unreacted metal} = \frac{\text{Average Elemental Concentration}}{\text{Concentration}} \times \text{Estimated Volume of Wastewater}$$

Equation 7.3

$$\text{Theoretical Amount of unreacted metal} = \text{Amount of Metal used} - \text{Amount of Metal in the Product}$$

Equation 7.4

Since results for cobalt solvent wastewater between acidified and non-acidified samples were significantly different (see Figure 8.8), the average elemental concentration was based only on non-acidified samples. Non-acidified samples were considered to better represent the original nature of the wastewater on the time of release than acidified ones (see Figure 8.10). Observation made on the analytical results (see Tables 7.12 through 7.22) shows that suppression of analyte intensity was stable for solutions with dilution factors ranging between 200 and 800 fold. Analytical results used when compiling Table 7.29 were based on one of these dilutions. This was done in line with preliminary investigations that revealed that at more than 100 fold dilutions there was less matrix interference. On the other hand there was no significant difference in the results for acidified and non-acidified for cobalt wash wastewater and for manganese reaction wastewater. Hence, average elemental results reflected for cobalt wash wastewater and manganese reaction wastewater (see Tables 7.29 and 7.30) were based on results for both acidified and non-acidified samples. Results obtained from samples that were diluted in the production plant were not used because of the uncertainty of the measured volume of the hot solution.

7.4 Sodium sulfate by-product purity

The research team was also mandated to identify alternative cleaner production methods or ways to reduce the level of wastewater in the paint drier plant. In order to address this problem, the water going into and leaving the reactor as wastewater was characterized as shown by the results given in Tables 7.12 to 7.28. Another major problem that was faced by the company was the hard labour time it took the wastewater removal company while digging the sulfate that had crystallized out from the effluent pit. This cleaning process, which takes long to complete, translated to more expenses that the company is required to pay. The company wished to determine if they can commercialize the wastewater in its usual state or use it to produce a valuable commercial product. As a way of responding to this problem, the research team carried out experimental tests on the wastewater with the hope of retrieving the sulfate from

wastewater in the form of sodium sulfate. To do this, fourteen samples were randomly selected from a total of hundred and thirty three.

Selected samples were removed from the refrigerator and left on the laboratory bench overnight. This was necessarily in order to loosen the sulfate salt without reheating as the process could re-dissolve most of the sodium sulfate. The mother liquor was carefully decanted into a clean HDPE bottle. The remaining contents were vigorously shaken up to loosen them up again. The contents were then poured onto a No. 1 qualitative filter paper (Whatman®) placed on a white porcelain Buchner funnel which was attached to a vacuum pump set at 400 mmHg. The liquid was filtered and the white crystals were washed three times with about 50.0 ml distilled water. Crystals were carefully removed from the funnel and poured into a clean 250 ml beaker. The beaker and its contents were placed in an oven set at 115 °C for 48 hours in order to remove excess moisture. The dried salt, in its container was cooled and stored in a desiccator until further investigations were carried out.

The salt was checked for its purity by dissolving a measured amount (see column 2 of Tables 7.31 and 7.32) into a clean 100 ml volumetric flask with distilled water. Solutions made from salt obtained from cobalt wastewater were clear whereas solution made using salt from manganese wastewater had a brown-to-colourless like droplets floating. These were separated from the clear solution using of a separating funnel. The solutions were then analysed for the presence of cobalt and manganese from cobalt and manganese wastewater respectively. Section 6.5 shows the need to dilute solutions with high sulfate concentration. However diluting the solutions would have compromised the ability of the instrument to detect the presence of cobalt or manganese at very low concentrations. Therefore, solutions were not diluted in order to reduce analyte intensity suppression by the amount of sulfate.

Analytical results obtained from these randomly selected samples are shown in Tables 7.31 and 7.32. The emphasis of the results was on quality rather than quantity of the sulfate salt obtained. Table 7.31 represents results from cobalt wastewater while Table 7.32 represents results from manganese wastewater. Cobalt reaction wastewater was used for trial purpose as it contains a “large amount” of unreacted metal compared to wash wastewater. Results listed in column three of Tables 7.31 and 7.32 were obtained through analysis using the ICP–OES instrument while values listed in column four were calculated using Equation 7.5.

$$\% \text{ of metal in the amount of Na}_2\text{SO}_4 = \frac{\text{Concentration} \times \text{volume of solution}}{\text{Mass of Na}_2\text{SO}_4 \text{ used}} \times 100 \%$$

Equation 7.5

Table 7.31 Elemental composition from sulfate retrieved from Co wastewater

| Sample ID | Mass of Na ₂ SO ₄ (g) dissolved in 100 ml | [Co] ppm | % of Co in Na ₂ SO ₄ | Corrected % of Co in Na ₂ SO ₄ |
|-----------|--|----------|---|---|
| MV 21 | 6 | 1.07 | 0.0018 | 0.0029 |
| MV 29 | 6 | 0.624 | 0.0010 | 0.0017 |
| MV 101 | 10 | 1.18 | 0.0012 | 0.0020 |
| MV 172 | 10 | 0.849 | 0.00085 | 0.0014 |
| MV 273 | 10 | 0.117 | 0.00012 | 0.00019 |
| MV 292 | 10 | 0.430 | 0.00043 | 0.00071 |
| MV 346 | 10 | 0.294 | 0.00029 | 0.00049 |
| MV 352 | 10 | 0.286 | 0.00029 | 0.00047 |
| MV 360 | 15 | 0.0632 | 0.00004 | 0.00007 |
| | | Average | 0.00067 | 0.0011 |

Table 7.32 Elemental composition from sulfate retrieved from Mn wastewater

| Sample ID | Mass of Na ₂ SO ₄ (g) dissolved in 100 ml | [Mn] ppm | % of Mn in Na ₂ SO ₄ | Corrected % of Mn in Na ₂ SO ₄ |
|-----------|--|----------|---|---|
| MV 276 | 10.0 | 15.3 | 0.015 | 0.019 |
| MV 285 | 10.0 | 16.6 | 0.017 | 0.021 |
| MV 393 | 10.0 | 2.68 | 0.0027 | 0.0034 |
| MV 396 | 10.0 | 7.05 | 0.0071 | 0.0088 |
| MV 402 | 10.0 | 4.89 | 0.0049 | 0.0061 |
| | | Average | 0.0093 | 0.012 |

Results given in Tables 7.12 through 7.22 shows that the cobalt concentrations differ by 65 % i.e. for 4 fold and 800 fold dilution factors. Taking this factor into account, the correct analytical results which are given in Table 7.31 shows that the average elemental percent in sodium sulfate from cobalt wastewater is 0.0011 %. On the other hand, results given in Tables 7.23 through 7.27 shows that manganese concentration differ by 25 %, i.e. for 20 fold and 800 fold dilution factors. The corrected percent of manganese which are given in Table 7.32 shows that the average elemental percent in sodium sulfate from manganese wastewater is 0.012 %.

Chapter 8

8. Introduction to discussion

Every organization involved in a profit making business strives to achieve the highest margin of revenue while keeping expenses at a low level. The aim is to maximize profits. For a business to achieve maximum profits it should:

- Position itself in such a way that customers are kept satisfied through provision of highly competitive products of high quality and standards.^[119]
- Strive to keep financial overheads low.

Like any other profit making organization, in an Industrial environment, expenses are kept at a low level by making sure that raw materials are used properly and accounted for at all times. The proper use of raw materials includes, but is not exclusive to, transforming them to valuable commercialized products and keeping an up-to-date inventory of purchased, used, and available raw materials and products at the company's warehouse.^[128]

Metallica Chemicals is a chemical manufacturing company producing specialty chemicals for industries in South Africa and abroad. The company has two production plants operating at its site in Ebuhleni Industrial Park at Cato Ridge. These plants make raw materials for the textile and paint industries. The production of textile chemical auxiliaries has been found to run relatively waste-free, and waste disposal costs are fairly reasonable compared with costs incurred for the process used to make PD. Consequently, the company wishes to look at ways in which to optimise the production of the paint driers, making it more efficient and less wasteful in terms of effluent production. In doing so the company should easily achieve its primary goal and at the same time keep the environment clean. The company is currently spending a substantial amount (financial resource) on disposal of wastewater generated during PD production processes shown by percent values in Table 7.8 and graphically described by Figure D1 in Appendix D. Financial resources being wasted could either be used to expand the production plants or to create community projects that can uplift the current unacceptable low standard of living in nearby communities.

Two particular processes in the paint drier (PD) plant (organometallic or metal soap plant) have been identified as creating large effluent volumes. They are the production of cobalt and manganese octoate driers (described in Section 4.3). The process used to make cobalt octoate has been found to generate large volumes of wastewater. Depending on the number of production batches they make, an average of 35 m³ of this effluent can be generated per month. The effluent is made up of a saturated solution of sodium sulfate, Na₂SO₄, together with metal contamination from unreacted starting materials.

Cobalt makes up only 21% of the mass of cobalt sulfate (CoSO₄·7H₂O). Thus 79% by mass of the CoSO₄·7H₂O ends up in the wastewater when manufacturing cobalt PD. In terms of masses, this means that for the production of a batch of 12% cobalt octoate, (which is their largest batch manufactured and requiring at most 2000 kg of CoSO₄·7H₂O) at least 1580 kg of the starting material becomes waste. On the other hand, during manganese PD production, 68% by mass of manganese sulfate (MnSO₄·H₂O) is released into the wastewater stream. Because of production quantity and the fact that the company rarely manufactures the manganese drier (see Tables 7.4 and 7.7), relatively low waste of this drier is collected per annum. Though the amount of waste is less compared to that produced during cobalt production, it is nevertheless important to put in place measures that can further reduce its current level.

This project's aim was largely two-fold.

- Firstly, to characterize the wastewater discharged in the two production processes. This should enable the research team to establish the extent of contamination as perceived by the company and provide information on whether the wastewater can be reused, or commercialized, or used to manufacture a more valuable product.
- Secondly, to identify alternative, cleaner, cost effective production methods/processes to the ones currently employed by the company. This includes raw material changes, alternative technologies and improvement of current production practices. Research done on several industrial processes has shown that changing the way the business or process is run can effectively enhance revenue and profits.^[130]

The data obtained from chemical analysis of the water inputs to and outputs from the process were used to define the quality of water desirable for each step in the process. Collectively the data could be used to:

- Determine the processing (e.g. dilution or blending) necessary to allow the available waters (fresh water or mains, water from washing and water from distilling the final product) to be used in selected steps of the process.
- Assess the potential waste minimisation practices, such as recycling, segregating and reducing the concentration of the effluent which is generated by the process (described by Figure 3.3).
- Suggest ways of commercializing the current waste through new product formulation from the waste generated, which could be introduced to the existing process in order to reduce waste.^[130]

Section 8.1 looks at the results obtained from historical audit (existing data) while Section 8.2 gives a description of experimental results obtained from new collected data.

8.1 Analysis of Results from Existing Documents

The documents consulted are fully described in Table 6.1 of Section 6.1. One particular document, the Standard Manufacturing Formulation Document (SMFD) was extensively scrutinized as it contains exact amounts of raw material used, products formed and to some extent, wastewater released to the effluent stream or flow-bin. The information was found to be properly archived by the company.

8.1.1 Major Raw Materials, other than water used in the Drier Plant

The company uses a range of raw material for the production of several metal PDs (see Table 7.1). The commonest raw materials used during paint drier production are 2-ethyl hexanoic acid (2-EH) and white spirit solvent.

With the exception of barium nonyl phenate and drier blends, all driers use 2-EH as a reaction raw material (see Table 7.1). The PD plant uses in excess of 370 tonnes of 2-EH per year. This product is shipped from overseas and hence a lack

of it in the plant can be a major blow to the production of PDs. Calcium paint drier, the major ingredient of all drier blends, uses more of 2-EH as shown in Table 7.1 and Figure 8.1. This is followed by cobalt paint drier, which uses 0.5% less than the amount used for calcium paint drier production.

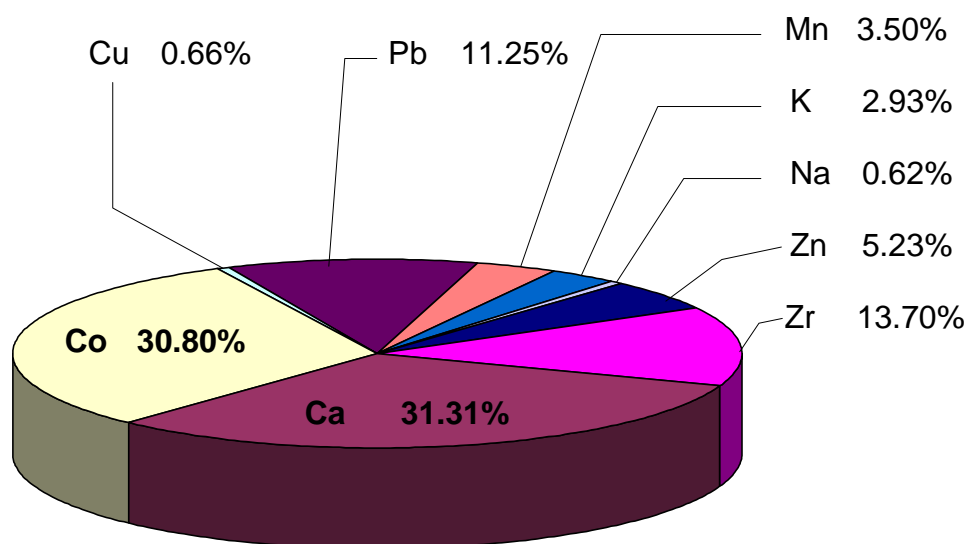


Figure 8.1 2-ethyl hexanoic acid used by each metal paint drier per annum

All but barium nonyl phenate drier uses white spirit, a volatile organic compound (VOC). Though mostly used in paint products, white spirit is also used as a solvent in aerosols, wood preservatives, and asphalt products.^[135] According to the Material Safety Data Sheet (MSDS) provided by the company, white spirit is highly toxic to aquatic organisms and the effect can cause long term damage to the environment. Because of its low density and immiscibility with water, it easily forms a thin layer on the surface of water resulting in poor oxygen transfer between the atmosphere and water. Employees handling this raw material should take reasonable precautions for themselves, their co-workers and the environment at large. On average, the drier plant uses more than 323 m³ of white spirit per year and this excludes the amount used for cleaning that is not easily accounted for. Calcium paint drier uses 12% more white spirit than cobalt paint drier which uses at least 23% of the total amount per year (see Table 7.1). The use of white spirit per drier in the PD plant is illustrated by Figure 8.2 below.

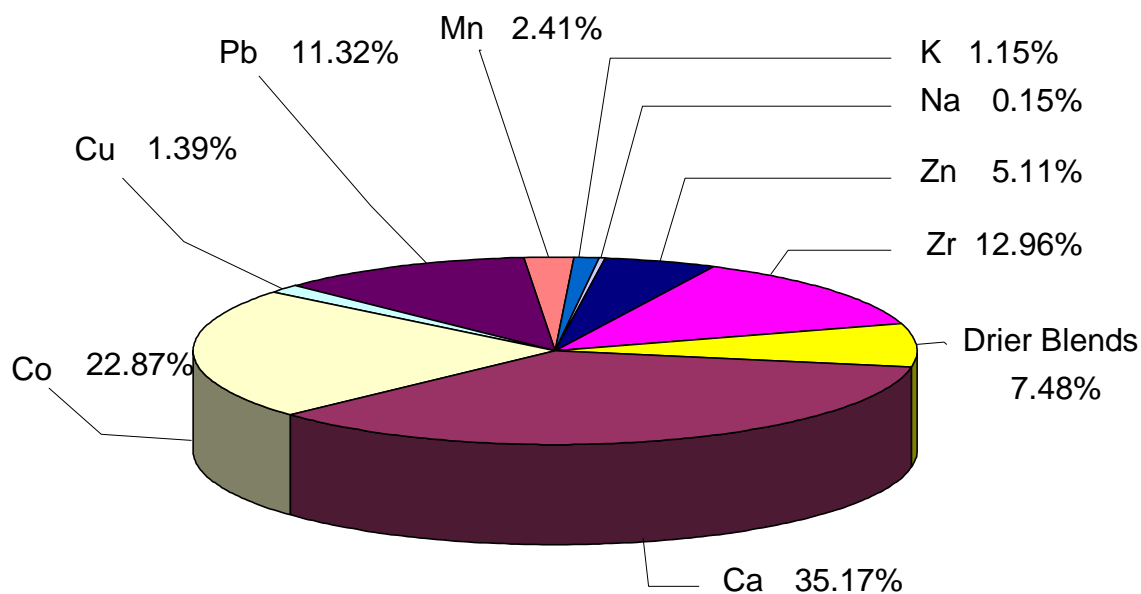


Figure 8.2 White Spirit used for metal paint drier Production per annum

8.1.2 Raw Water Usage and Wastewater Released

Water, a natural resource, is vital to both living organisms and industrial operations.^[102] This shows that safe reliable water use in daily activities is important. For this and other environmental reasons it is important to establish water and wastewater services.^[129, 132, 134] The development of such services can be traced back more than 4000 years. The Romans, to name but one, had a well developed piped water supply, latrines and services. Though these ancient civilized nations showed knowledge and importance of clean water, little is known about whether they ever treated the wastewater generated for reuse or recycling. Without this knowledge, the civilized nations were prone to water-borne diseases such as cholera and typhoid fever which can cause fatal consequences such as the ones recorded in London (Broad Street Pump episode) and in Wheeling, West Virginia.^[129, 133] The 1993, 2005 and 2007 outbreaks of waterborne diseases in Delmas, Mpumalanga, South Africa emphasise the need for clean, renewable water.^[149-153] The “Earth Summit” in Rio de Janeiro in 1992 and the biggest gathering by 189 heads of state in 2000, which came up with the “Millennium Development Goals” (MDGs) are some of the commitments shown by developed and developing countries when it comes to distribution of clean water.^[130, 137]

Though there is a large amount of water on the earth, 96.5% is saline seawater, 2.8% is part of polar icecaps and glaciers leaving only 0.7% fresh water in lakes, rivers and the atmosphere. It is important to note that this freshwater is not evenly distributed. According to the UN World Water Development Report 2, South Africa is regarded as a water stressed country, compared to water rich countries, with only less than $104 \times 10^3 \text{ m}^3$ water available per person per year.^[129, 130]

8.1.2.1 Water usage in the production site of the company

A review of literature^[86] shows that the cooling system, starting raw material and steam production uses more freshwater in an industrial manufacturing sector than any other section of the company. The company uses Municipal water for product manufacturing and in-house cleaning. A large amount of water from the Municipality is used in the textile production plant, the boiler and the cooling tower. For the latter two, no records were available to substantiate this fact. In the PD plant water is mostly used as a reaction starting material and for washing the final product. Apart from these two major uses, it is also used for steam production and cooling the reaction mixture. All but barium, calcium, lead and zirconium PD utilizes water as a starting material. The percent usage of water in the PD Plant is provided in Table 7.1. Since this project was to a larger extent concerned with wastewater minimization and management, water usage became a focus point. From the percentages tabulated in Table 7.1 it was important to picture the usage graphically as shown in Figure 8.3. The figure shows that Co drier consumes almost 80% of freshwater (municipal water) that goes to the PD plant followed by Mn drier that consumes a little less than 8%. Of paramount importance is the fact that every drop of water used and formed as a by-product does not form part of the end product as illustrated by Equations 2.14 and 2.15. This means that whatever amount is used and generated as a by-product from auxiliary reactants ends up in the effluent pit or flow-bin. Hence, limiting the amount of freshwater intake will help to reduce the generation and accumulation of high volume of wastewater.^[133, 140, 141] Freshwater can easily be reduced without sacrificing the quality and amount of product through application of four general approaches, namely process changes, water reuse, regeneration reuse and regeneration recycling.^[129-136, 136]

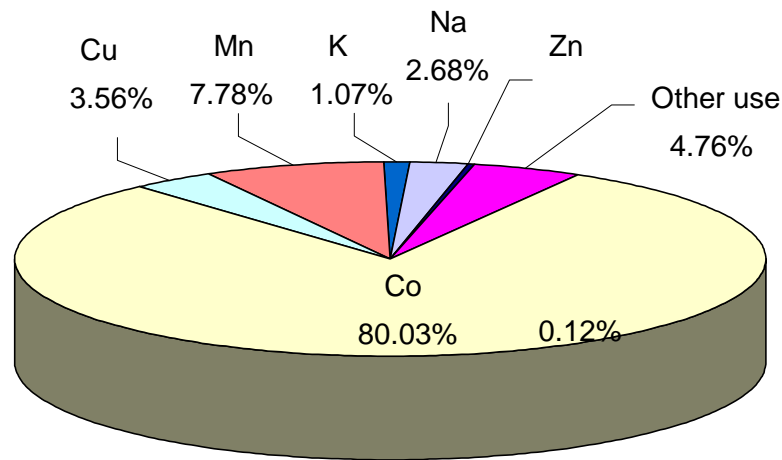


Figure 8.3 Percent of Total Fresh Water that was consumed by each Metal Paint Drier during Production per annum

Although the project's mandate was to look at Co and Mn driers production, in order to get a clear picture of Municipal water usage by these two driers, it was crucial to look at water usage by the two production plants (described in Section 4.1). Table 7.6 gives a month-to-month usage of water in the two production plants. The information provided in the table was extracted from the Municipal Bill statement (described in Table 6.1). Comparing these figures with what is actually used in the PD plant, it is evident that the average volume of water used per month in the PD plant is less than 3.2% of the total amount of water paid for by the company per month. This is clearly illustrated in Figure 8.4 below.

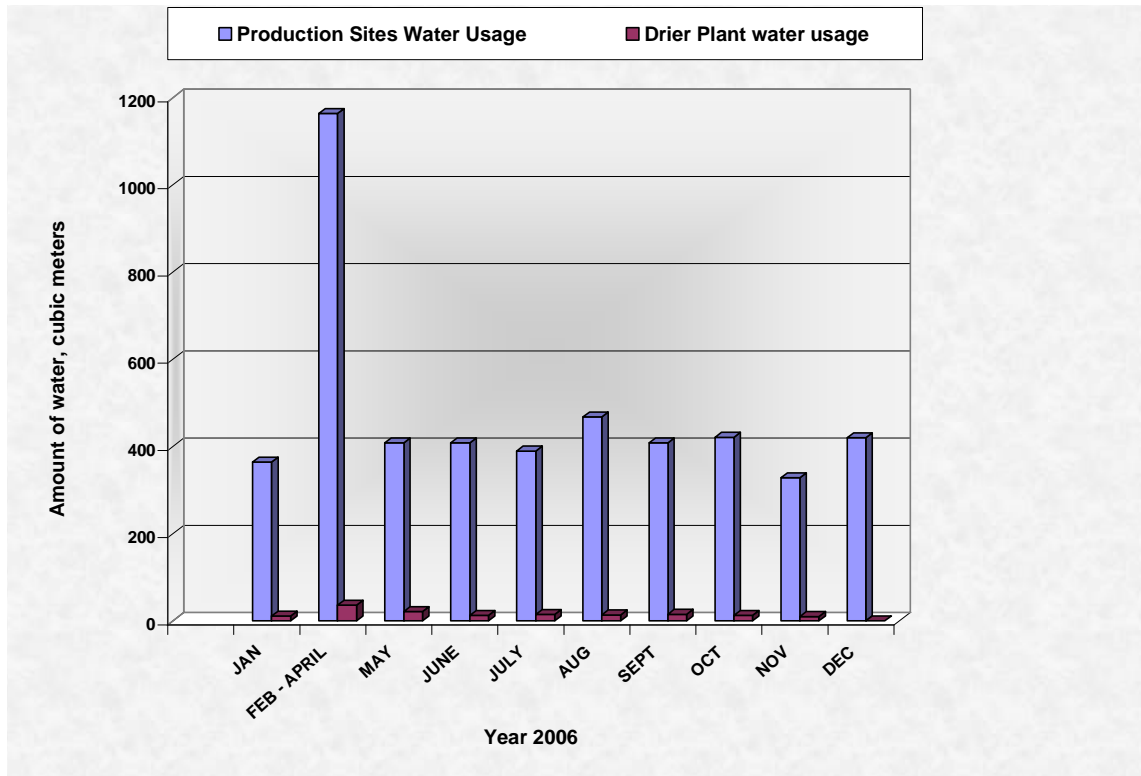


Figure 8.4 Comparison of water used in the Production sites with that used in the PD Plant

Figure 8.4 shows that only a fraction of water is used in the PD plant and a much larger amount is used elsewhere in the production site. It is however important to take note that the fractional amount (3.2%) that is utilized in the PD plant ends up in the wastewater stream. Hence a further reduction on fresh water intake to the PD plant can help when it comes to waste reduction.

It was established through verbal communication with the company management and the plant operators that the textile plant uses a substantial amount of freshwater. Since the water taken forms part of final product less wastewater is generated.

Another portion is spent in the cooling tower and on steam production, which is essential for heating during production processes. Steam and cooling amounts to the PD plant were not easily measured.

Monitoring of Municipal water meters during production site shut-down revealed that the plant was losing freshwater possibly through unnoticed leaks. The results collected over the seven weekends monitoring period are given in Table 7.11 and

graphically represented by Figure 8.5. The Municipality meter reading was taken on each Friday, Saturday, Sunday and Monday morning before production resumed. The results show that on average the company is losing 8.71 m^3 per weekend (60 hours), an amount equivalent to two thirds of what is spent in the production of manganese drier per year. If the flow rate is constant each day and the lost amount is extrapolated, this will mean that the company is losing almost 1271 m^3 of fresh water per year. This according to Table 7.6 is equivalent to 26.6% of the total freshwater the company received from the eThekweni Municipality in 2006. One seriously concerning fact is that this amount is 8.37 times the total amount (151.8 m^3) spent on production in the PD plant per year. This is quite significant for a water stressed country like South Africa.^[130] The lost amount is equivalent to what is received by at least seventeen poor families per annum. These are families receiving free water (72 m^3 per year) according to the South African Free Basic Water Policy promulgated in September 2000.^[147]

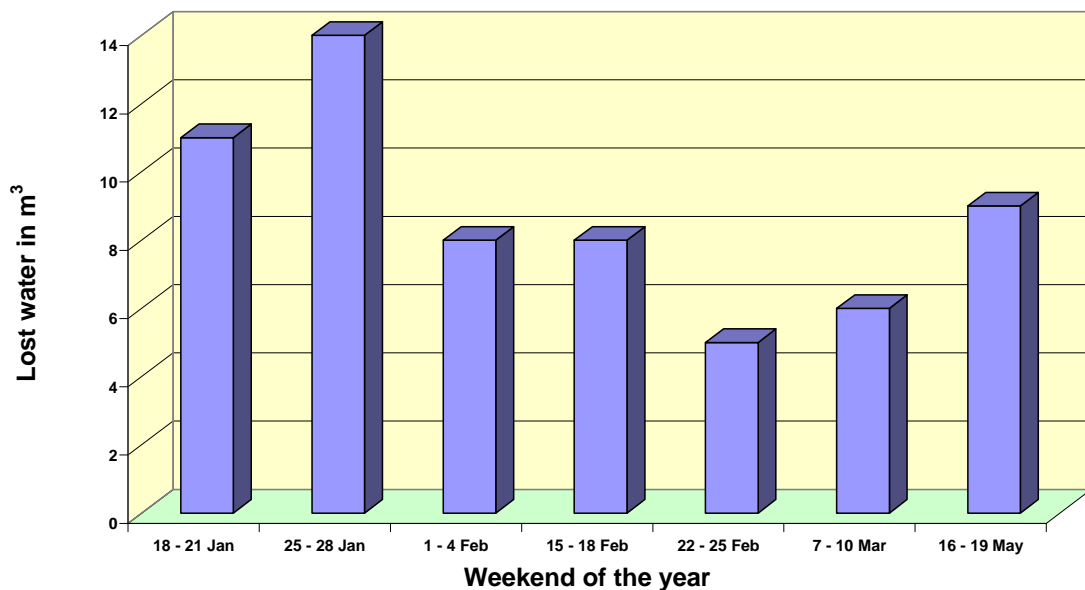


Figure 8.5 Graphical representation of loss of water during production plant shut down

8.1.2.2 Wastewater released at the end of production processes

According to the Water Pollution Control Federation (a US organization)^[139] it is estimated that more than 120 million cubic meters of wastewater will be produced in US alone, which emphasizes the need to limit wastewater generation through wastewater management and minimization. Cost of disposal alone should never be seen as more important than the impact the wastes have on the sustainable environment.

The PD plant alone uses less amount of freshwater but generates vast amounts of wastewater per month as shown in Table 7.8 and graphically represented below in Figure 8.6a.

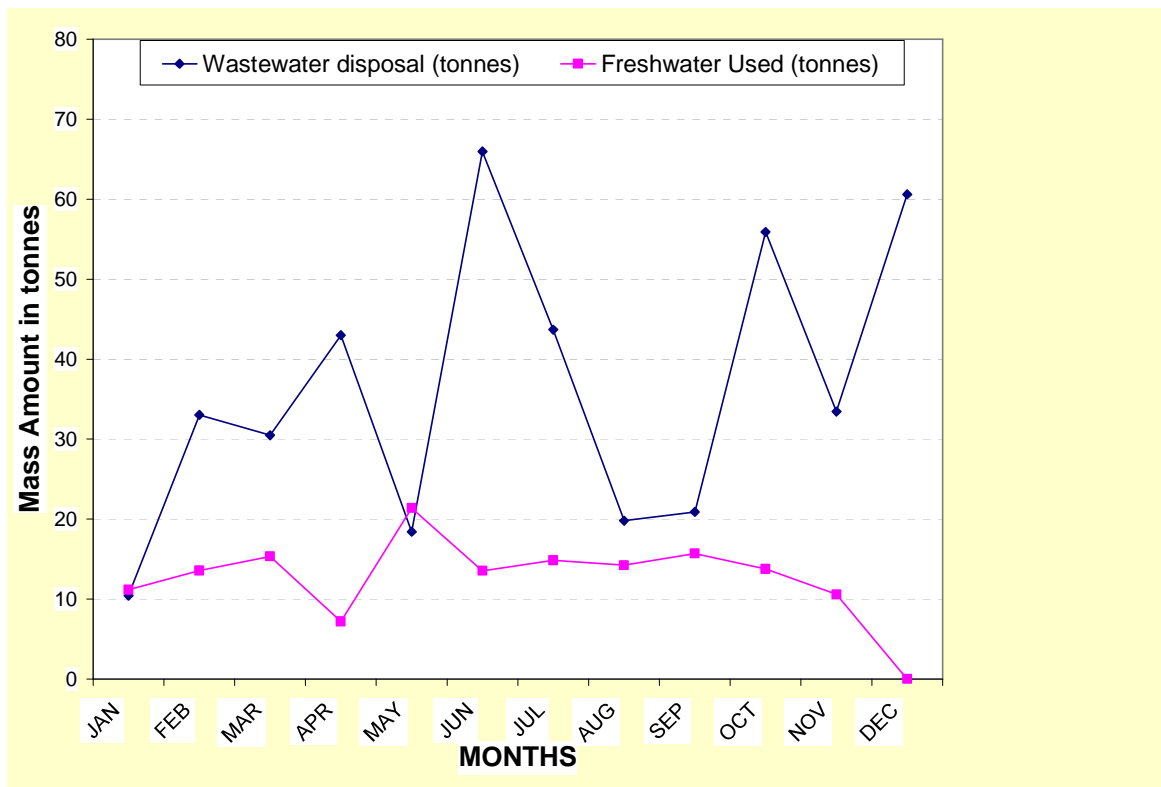


Figure 8.6a Comparison between freshwater intake and end-of-pipe wastewater disposed per month

Figure 8.6a gives a comparison between the amounts of freshwater consumption and the wastewater disposal on a month to month basis. It should be noted that the “mass of wastewater” includes all the solutes (mostly sodium sulfate) in the wastewater stream. There are some discrepancies with regard to the amount of

wastewater recorded per month. This is due to instances where there is a roll-over of effluent from previous months that were not completely removed; hence the figures given in Table 7.8 are based on what was collected by the private company, rather than what was generated in that particular month. For example, Figure 8.6a shows almost equal amounts of freshwater intake and wastewater removed in January and May. The most probable explanation is that not all wastewater was collected and this is supported by high amount collected in February and June respectively. In addition to this, there was large amount of wastewater removed in December when there is virtually no production taking place which indicates that the private company removed wastewater generated in previous month(s). In general, the trend shows that the company's effluent disposal amount far exceeds the amount of freshwater used. This is consistent with what was mentioned earlier on and also supported by values given in Table 7.28. What Figure 8.6a is telling us is that the wastewater is NOT only determined by the amount of freshwater used in an operation (see Table 7.28). For these processes the freshwater used only contributes 0.035% of the total wastewater generated in the PD plant. This is because the wastewater will by nature contains by-products from side reaction (i.e. both liquids and salts formation). Though it is recommendable to reduce freshwater intake it should be noted that merely reducing the use of freshwater will not necessarily translate to a substantial decrease in wastewater as it is observable from Figure 8.6a. This is a strong reason why it is important to measure the wastewater, characterize it and then determine the species that can render a measurable reduction or total elimination of waste in a stream.

Cost as a percent of the total costs shown in Table 7.8 and graphically represented below in Figure 8.6b show that the disposal cost of wastewater is more than 200 times the cost of freshwater intake per annum. Financially, this is a strong reason companies engage on wastewater management and elimination. Rewards for such an achievement will be felt by the company within a short period of time.

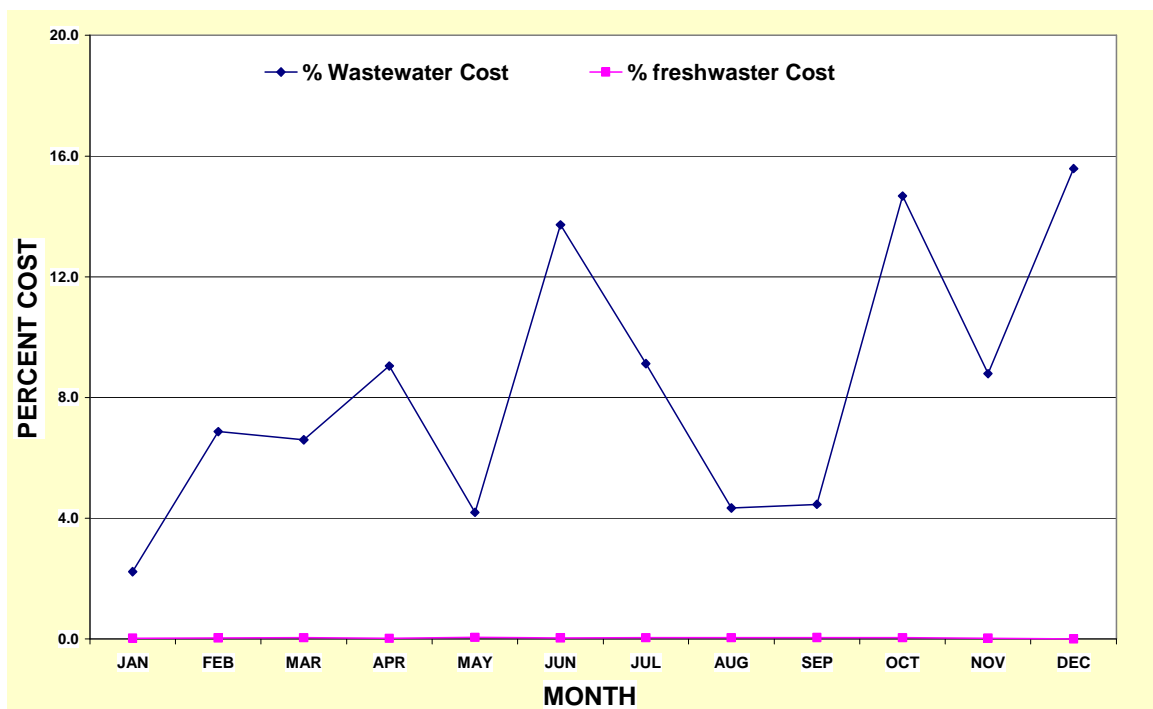


Figure 8.6b Comparison of percent cost between freshwater intake and wastewater collected per month

The company is currently reusing wastewater (distillate), which is the by-product from the zirconium (Zr) and wash wastewater from the Co drier production process. According to the plant operators, at least 1.20 to 1.30 m³ of reusable wastewater is generated during Zr drier production. Together with the wash wastewater amount from Co drier production, both these wastewater streams are reused during the Co drier process as reaction water. Of the thirteen batches that utilized the wastewater as the starting material, the production yield was never compromised. It was pleasing to notice that the company has saved 11% of freshwater through reuse of wastewater from these two processes (see Table 7.3). In terms of effluent disposal cost this is a major saving and according to the United Nations World Water Development Report 2, each cubic meter of water reused or recycled on-site represents one cubic meter that the company will not have to purchase from the Municipality and not worry about disposal.^[130]

8.2 Characterization of the Solvent and Wash Wastewaters

Characteristics of wastewater samples are given in Tables 7.9 and 7.10. In general the samples are slightly alkaline at the time of sampling. Due to high levels of sulfate ions in reaction wastewater, the conductivity is high compared to that of wash wastewater. The distillate from both processes had virtually zero conductivity.

Quantitative and qualitative analysis were carried out on wastewater to determine the extent of contaminants. Results were obtained from company data and analytical results from ICP-OES analyses (see Table 7.12 to 7.27). The results were used to determine whether the wastewater was reusable, recyclable or needed treatment before it could be used.

Tables 7.12 to 7.27 shows elemental concentration obtained for dilutions made on the original sample composition as described in Sections 6.5 and 6.7. Reaction wastewater for both Co and Mn samples contains a high concentration of sodium sulfate (Na_2SO_4) that precipitates on cooling, hence reheating of samples was necessary (see Figure 6.3) before dilution. In order to have approximate chemical nature to that of standards, samples were diluted several times to reduce the effect of physical interference that could compromise the efficiency and proper working condition of the ICP-OES instrument. The efficiency of the nebulizer was greatly enhanced through reduction of original sample concentration. Figures 8.7 to 8.9 shows the effect high concentration of Na_2SO_4 have on the apparent analyte concentration.

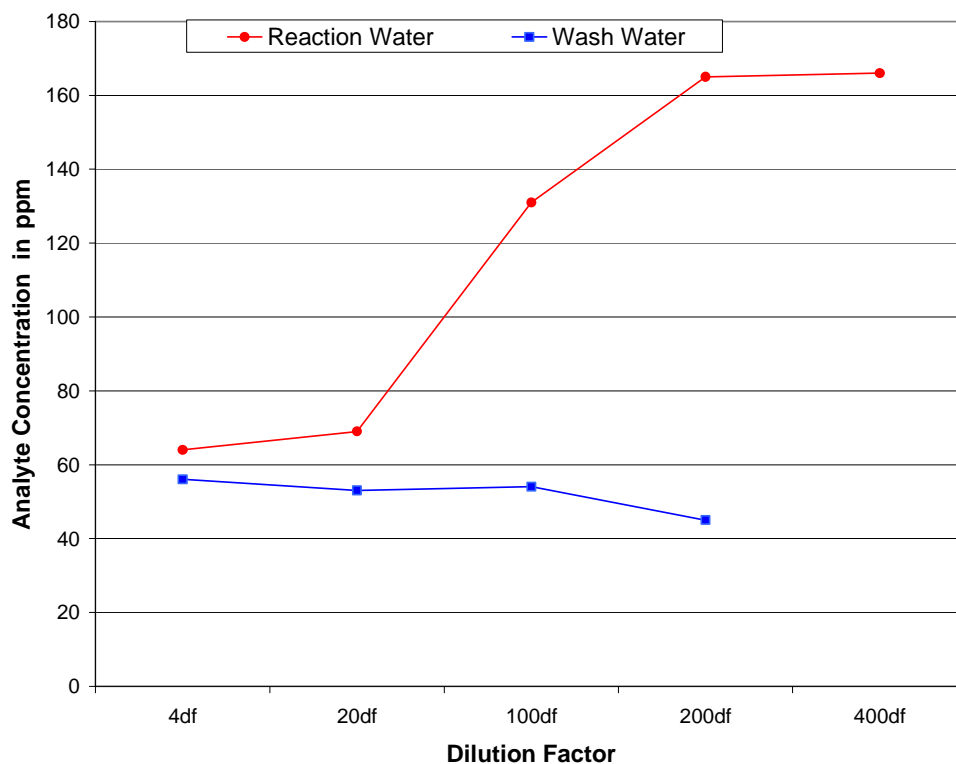


Figure 8.7 Effect of dilution on the concentration for reaction and wash wastewater from Co drier

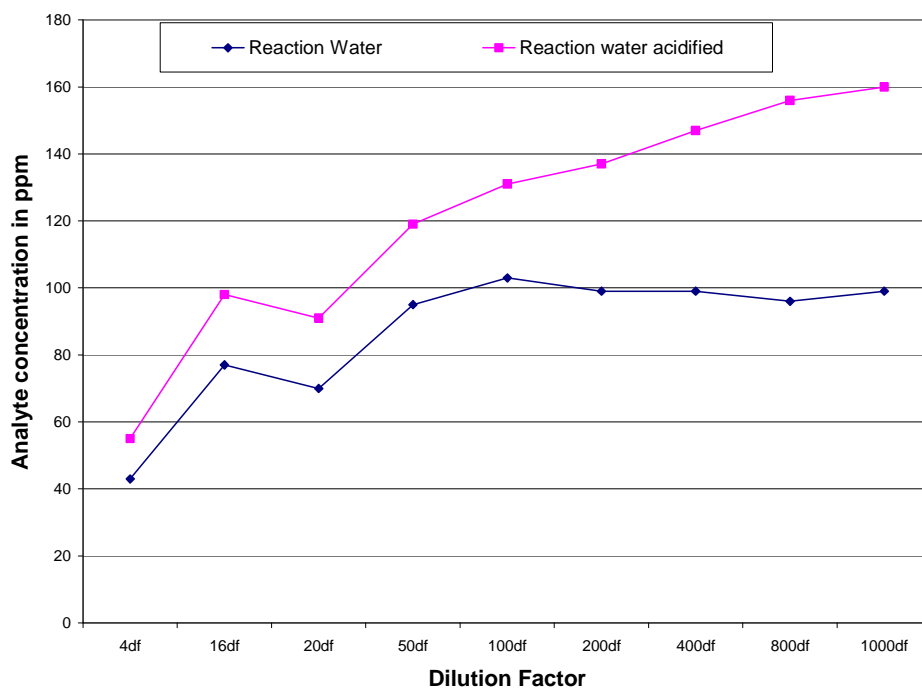


Figure 8.8 Effect of dilution on the analyte concentration for acidified and non-acidified Co reaction wastewater samples

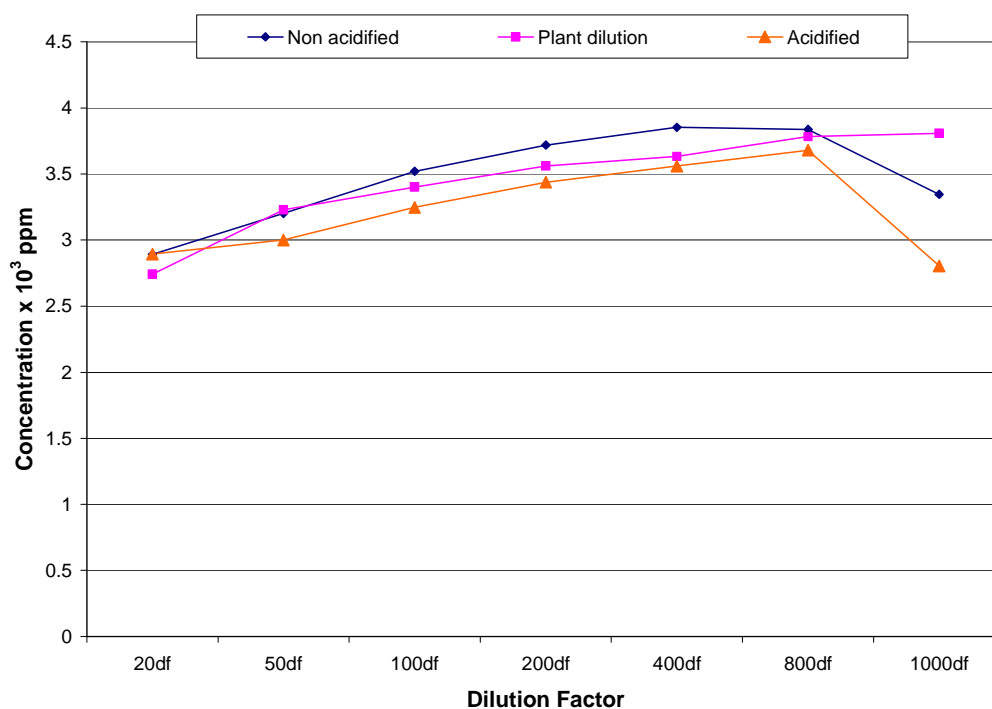


Figure 8.9 Effect of dilution on the analyte concentration for acidified and non-acidified Mn reaction wastewater samples

A sharp increase in the apparent analyte concentration with an increase in dilution factor was observed. The concentration gap between consecutive high dilution factors (e.g. 800 to 1000) was far lower than those at lower dilution factors (20 to 100). This observation was enough evidence to illustrate that the effect had been lowered to acceptable levels and no further dilutions were made beyond 1000 fold. Comparing concentration for lower and higher dilution factors, the difference was enormous and this proved that the concentration of the analyte is heavily affected by matrix interferences in the original sample solution.^[108] The effect was more noticeable in reaction wastewater for Co samples than in wash wastewater (see Figure 8.7). It was noticed (see Figure 8.8) that the analyte concentration in acidified samples appeared to be higher than in non-acidified samples, at least in Co wastewater. However, for Mn wastewater, the analyte concentration appeared to be higher in non-acidified solutions than in acidified ones (see Figure 8.9). This difference was more evident at high dilution factors than at lower dilution factors. A possible reason for the observations made could be due to the effect the high concentration of sulfate have on the analyte's intensity. At lower dilution the effect was more noticeable resulting in concentration of analyte being almost identical. At high dilution factor when suppression was negligible, the intensity of analyte was higher in acidified than in non-acidified samples. One striking observation was the sudden formation of purple-bluish layer-like in Co samples on addition of acid. This showed that the acid was facilitating separation of product like layer from the "homogenous" aqueous layer resulting in a two layered mixture seen here in Figure 8.10. Looking at the first and third samples of Figure 8.10, the top layer resembles the cobalt octoate (the organic layer) while the bottom one is the aqueous layer. On the other hand, the non-acidified, second and fourth samples were homogenous. For acidified samples the mixture was more heterogeneous, meaning that physical and chemical properties of the mixture were different at any given point. After shaking to mix the solution it would rapidly separates out while pipetting out the required volume. This means that it was not possible to thoroughly mix the solution and sampling errors were large. Thus explaining why acidified samples gave rise to high concentration of analyte than non-acidified solutions which were more homogeneous.



Figure 8.10 Acidified (1st and 3rd samples) and non-acidified (2nd and 4th samples) as seen from left to right

8.3 Mass Balance Analysis

According to the SMFD, there is a measurable amount of the major ingredient for these two driers in the wastewater. This is, however, not supported by the production yield at the end of the process whose values range between 90% and 110%. It was therefore necessary to carry out an analysis of the wastewater to determine the validity of the information provided in the SMFD which was subsequently used to calculate unreacted amounts of raw materials.

There are four sets of factory and analytical data on the masses (kg) of Co, Mn and sulfate used and produced in drier production that will be used in mass balance analyses. These are shown in Equations 8.1 to 8.4

These equations show that there is only one input stream in each case. The mass of this stream is obtained from the data contained in the company's SMFD sheet. The mass of the species of interest can be calculated from this using Equation 8.1

$$\begin{array}{lclclcl}
 \text{Total mass of the} & & \text{Amount of} & & \text{percent of Co} & & \text{Amount of Co or Mn} \\
 \text{species of interest} & = & \text{Co or Mn} & \times & \text{or Mn based} & + & \text{from parts added to} \\
 \text{introduced into} & & \text{sulfate used} & & \text{on COA}^* & & \text{the final product} \\
 \text{the reactor} & & & & & &
 \end{array}$$

Equation 8.1

* Represents certificate of analysis indicated on packaging container of the raw material

The output streams are all solutions and the concentrations of the aqueous streams have been determined using ICP-OES instrument. The measured concentration can be used to calculate the mass of the species of interest as shown in Equation 8.2 and 8.3 for cobalt.

$$\text{Mass of Co/Mn in the solvent water (kg)} = \text{Concentration (kg/L)} \times \text{Volume of solution L}$$

Equation 8.2

$$\text{Mass of Co in the rinse water (kg)} = \text{Concentration (kg/L)} \times \text{Volume of solution L}$$

Equation 8.3

Where: Concentration (kg/L) is the calculated value based on analytical concentration of Co/Mn obtained using ICP–OES

Volume of solution is the total volume of aqueous solution released to the effluent pit or flow-bin as indicated in Figure 4.3 and 4.9.

$$\mathbf{I = P + R + S + W} \quad \text{Equation 8.4}$$

- I = Mass of Co in the solid $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ starting material added to reactor
- P = Mass of Co in $\text{Co}(\text{C}_7\text{H}_{15}\text{CO}_2)_2$ in the white spirit stream or finished product
- R = Mass of unreacted Co in aqueous solution of the solvent water
- S = Mass of unreacted Co in aqueous solution of the wash water
- W = Mass of unreacted Co in aqueous solution of distillate water

$$\mathbf{H = M + N + V} \quad \text{Equation 8.5}$$

- H = Mass of Mn in the solid $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ starting material added to reactor
- M = Mass of Mn in $\text{Mn}(\text{C}_7\text{H}_{15}\text{CO}_2)_2$ in the white spirit stream or finished product
- N = Mass of unreacted Mn in aqueous solution of the solvent water
- V = Mass of unreacted Mn in aqueous solution of distillate water

$$J = F + Q + T$$

Equation 8.6

| | | |
|---|---|--|
| J | = | Mass of SO ₄ in the solid CoSO ₄ .7H ₂ O starting material added to reactor |
| F | = | Mass of SO ₄ in aqueous solution of the solvent water |
| Q | = | Mass of SO ₄ in aqueous solution of the wash water |
| T | = | Mass of SO ₄ in aqueous solution of the distillate water |

$$X = Y + Z$$

Equation 8.7

| | | |
|---|---|---|
| X | = | Mass of SO ₄ in the solid MnSO ₄ .H ₂ O starting material added to reactor |
| Y | = | Mass of SO ₄ in aqueous solution of the solvent water |
| Z | = | Mass of SO ₄ in aqueous solution of the distillate water |

Due to time and manpower required to measure the amount of wastewater generated, it was only carried out once. The measurements could only be carried out by firstly transferring the wastewater into flow-bins followed by weighing using a manual scale as shown in Figures 4.8 and 4.10 respectively. The complications created by this shortcoming when it comes to carrying out proper mass balance calculation were enormous. The mass measurement collected while conducting this project were taken during the production of Batch number N6JUN07 (see Table 7.28). Apart from verbal communication from the production personnel, volumes for wastewater released were never measured.

An attempt was made to carry out mass balance calculations using the information provided in Table 7.28 and sulfur concentration given in Tables 7.12 through 7.27. Using the SMFD records and analytical results (see Table 7.29), a comparison of inputs and outputs masses of Co and sulfate were then made. The sulfate amounts, which were based on the measured concentration of sulfur showed some discrepancies in the sense that the input/output values differ significantly with each other within the same batch. This is attributed to the fact that there was no reliable information to carry out proper mass balance calculations.

Apart from this shortcoming, while still stored in the refrigerator, it was observed that in all samples (acidified and non-acidified) the sodium sulfate precipitate was

spreading out of the sample bottle through the process called “crystal creeping”. This was more evident in non-acidified reaction wastewater samples. This phenomenon was not observed in the wash wastewater for both acidified and non-acidified samples. There was also a noticeable amount of sodium sulfate that had crystallized on the disposable tip of the Eppendorf micropipette after dispensing the required volume for dilution. All these could explain the low amount of sulfate found in the wastewater after an attempted mass balance calculation was carried out.

From the mass balance calculation attempt made, the amount of cobalt that was present in the product at the end of the production process was significantly lower than the total amount at the start of the reaction. However, the calculated cobalt outputs values (from wastewater) obtained at each sampling point tells a different story. These values show that about 0.12% cobalt was actually lost during the production process. The conclusion made was that the big difference in the amount is attributed to errors of measurements in the SMFD documents. The significant loss could easily lead one to conclude that the process is inefficient. Apart from the records of effluent collected and disposed of by the private company, no definite records of wastewater generated from each batch are available. This makes it difficult to compare the actual amount of wastewater generated with what was anticipated from each batch process, or with what the private company disposed of. Of paramount importance, any abnormality on the volume of wastewater generated against product yields obtained could not be speedily and easily checked. The information is crucial during instances where low yields are perceived to have occurred.

From the SMFD, amounts of unreacted metal of interest (Co or Mn) were calculated using Equation 8.1 and these were based on the amount added and the actual product yield. Calculated results are given on the last column of Tables 7.29 and 7.30. These values were compared with experimentally determined values (see second column from last of Tables 7.29 and 7.30) calculated using Equations 8.2 and 8.3 for Co and Equation 8.2 for Mn respectively. It should be made clear that the calculations were based on an estimated average volume of wastewater generated, because exact volumes generated from each batch were

unavailable. The estimated volume used was verbally communicated to the research team by the plant operators and this value was verified using measurements from a single batch. The values depend solely on the measurements carried out by the production plant personnel and the accuracy of the analysis carried out by the laboratory analyst (see information on Table 8.1).

Table 8.1 Sources of mass balance calculation errors for inputs and outputs for all batches sampled

| Source of cobalt in the reactor | | | Total amount of cobalt used (4) | Product yield (5) | Percent element in the product (6) | Amount of cobalt in the final product (7) | Cobalt lost (8) |
|--|-----------------------------------|-------------------------------------|---------------------------------|-----------------------------------|------------------------------------|---|-----------------|
| Amount of cobalt from cobalt sulfate (1) | Amount of cobalt from ullages (2) | Amount of cobalt from part drum (3) | | | | | |
| Source value | | | (1)+(2)+(3) | Measured/experimental measurement | | (5) x (6) | (4) – (7) |

Note that:

- (1) depends on the specification indicated by the manufacturer (20.6% to 21.3%), this was randomly checked by the laboratory analyst for each consignment received. For all calculation in this project the value used was 21%.
- (2) depends on the specification errors of the ullage and the amount used.
- (3) depends on the specification errors of the part drum and amount used.
- (4) will incorporate errors mentioned above
- (5) depends on errors of parallax on the scale's pointer since measurement is made using a manual scale
- (6) depends on titration errors which can happen while determining the metal content in the finished product
- (7) will incorporate errors mentioned in (5) and (6)
- (8) all errors mentioned above will form part of the final value.

Due to the complexity of the production process, no estimation of errors was made on the calculated values that were used when producing Figure 8.11, hence it was based solely on reported measurements reflected on the SMFD documents.

It is highly likely that significant errors could have occurred in the SMFD values, hence compromising the validity of results. Comparison of the results (without taking errors into account) is given by Figures 8.11 and 8.12 for Co and Mn paint driers respectively. The ICP–OES instrument results given in Table 7.29 show that on average about 0.200% cobalt metal was lost during production from each batch. This is probably attributed to the fact that this is a batch production process (described in Section 3) that is constantly monitored from the start as soon as raw materials are added to the reactor. Any deviations (i.e. in terms of pH) from well documented reaction procedures and conditions are adjusted after the laboratory analysts have carried out required analyses. On the other hand, results from SMFD sheets were not consistent with the experimental results and Equation 8.1. The last five batches in Figure 8.11 show an increase on the output to input mass percent, which is inconsistent with the Law of Conservation of Mass. The last batch shows an increase of 8% output to input made, which was a serious cause for concern. This shows possibility of calculations flaws which were carried out on the SMFD by the production team. On the basis of the suspected errors, experimentally determined results were accepted and further interrogation and recommendation made depends solely on them.

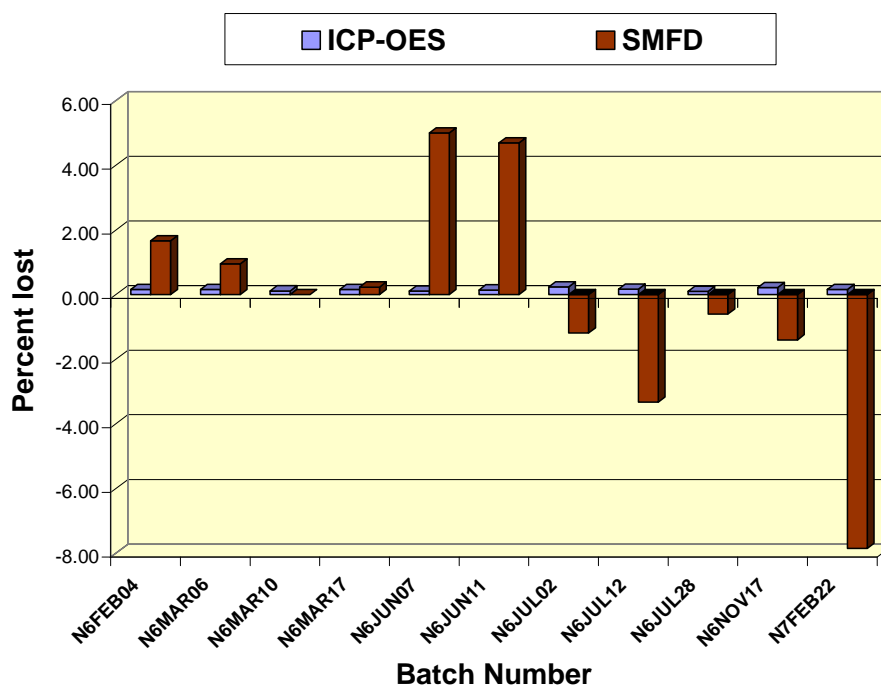


Figure 8.11 Comparison of the percent of cobalt lost during production according to batch sheet information and analytical results

Contrary to the observation made on the cobalt results that were used to generate Figure 8.11, both results (ICP-OES and SMFD) for Mn drier were to some extent comparable even though some SMFD values far exceeded those obtained experimentally (see Figure 8.12). In general, SMFD values imply that a large amount of Mn is lost during production. This difference is again attributed to the way in which product yield or amounts are calculated by the company. ICP-OES results were considered to be more reliable and further investigations were made based on them.

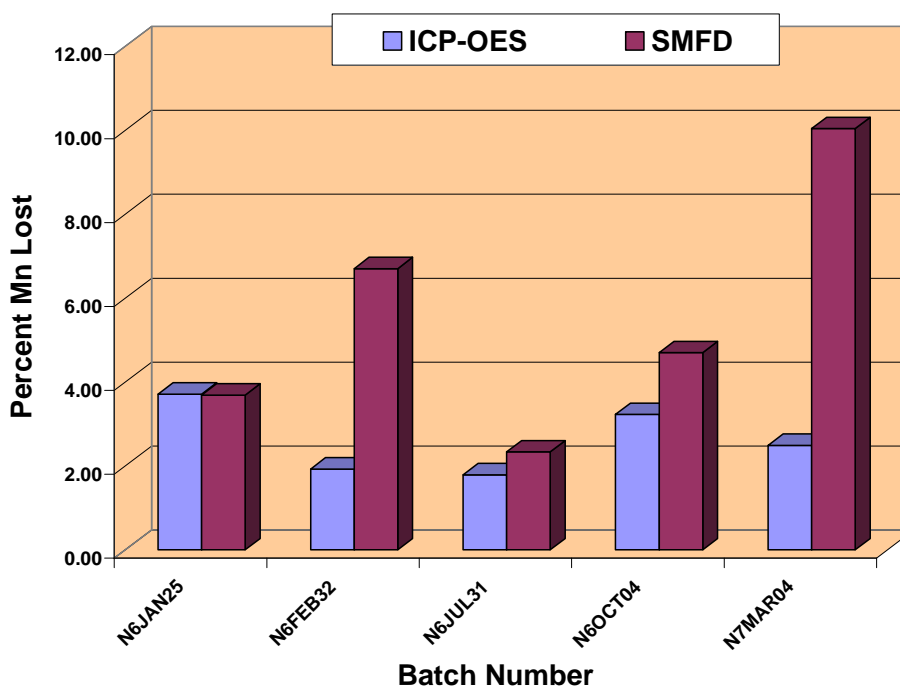


Figure 8.12 Comparison of the mass percent of Mn lost during production according to batch sheet information and analytical results

Figures, 8.11 and 8.12 show that there is a measurable loss of Co and Mn metals respectively with a larger amount lost from Mn drier. It was experimentally deduced that though a loss was indeed occurring, the amount was far less compared to what is predicted by the SFMD, (at least in the Co drier). The average amount of unreacted raw material was less than 0.700 kg (about 0.167% of the amount used) per production batch (see second column from last of Table 7.29). This loss does not warrant treatment for its retrieval as this might turn out to be a costly exercise. On the other hand, the amount of unreacted raw material incurred during Mn drier production was more substantial. This was at an average of 6.32 kg (about 2.63% of the amount used) per production batch (see Table 7.30). The Mn metal lost represents a substantial amount that the company should retrieve from the wastewater.

8.4 Scoping Audit

A feasibility study ^[148] was conducted at the beginning of the project (see Sub-section 3.3.1) in order to determine the following aspects:

- Review of resources usage and cost record
- Walk through the PD plant, identifying all reactors, checking water and steam piping to and from the cooling and boiling tower and meters available.
- Interview operating personnel including the production manager
- Make observations of the warehouse where raw materials and finished
- Check the effluent pit and wastewater storage facilities which are used by the company
- Look at the general layout of the production sites (Textile plant and PD plant)

Information collected was used to fully understand the effluent problems the company was facing. Potential project measures were thought through and, in conjunction with data collected from the company documents, a scoping audit report was compiled and was sent to the Company management as Report 1. The report set out the scope of the project without losing focus of the goals and objectives set by the company management. It also highlighted the expectations and working relationship required amongst all stakeholders (Site manager, Production manager, Laboratory analysts, SHE manager, Plant operators and the Research team). Any information deemed important to the smooth running and speedy completion of the project was to be furnished to the research team.

Raw material usage for each drier tabulated in Tables 7.3 and 7.5 were used to develop a “scope to save” table for Co and Mn PD respectively. Using Table 3.1 as a template, Tables 8.2 and 8.3 were generated for both Co and Mn PD respectively. Total disposal cost contributed by each drier type was calculated on the basis of the percent intake of freshwater during production. According to the Environment Agency (a UK based organization) the scope to save is a tool to help companies identify potential priority areas for waste minimization. ^[119, 138]

Table 8.2 represents the scope to save while manufacturing cobalt octoate paint drier. From this table it is clear that the order of priority the company needs to follow should be the consumption of cobalt sulfate, wastewater, ethyl hexanoic

acid, white spirit and finally caustic soda flakes. An estimated saving of between R123 000 to R572 000 can be achieved and this will in turn reduce the total consumption of freshwater. According to the company records there is a lot of Co that is needed to be saved in order to make substantial saving on the amount spent (see Table 8.2). However, laboratory analysis carried out on wastewater generated show that the amount of Co in wastewater is non-significant and hence it will be pointless to spend valuable financial and human resources trying to obtain it from the effluent stream.

Contrary to Co process, Table 8.3 shows that wastewater generated during Mn production should be given highest priority. This is followed by ethyl hexanoic acid which is heavily used by both Co and Mn PD. A total saving ranging between R7 590 and R33 210 can be realized from this process.

For both processes, if WM is implemented and forms part of day-to-day activity of the company, potential benefits listed under Section 3.4 could be realized.

Table 8.2 Waste minimisation scope to save for Co PD production process

| Resources and Services | Quantity | Cost/unit (R) | Estimate Cost/year (R) | Scope to save % | Estimate of Scope to Save | | Priority Ranking (1=highest) |
|----------------------------------|----------|---------------|------------------------|-----------------|---------------------------|----------------|------------------------------|
| | | | | | Minimum (R) | Maximum (R) | |
| Raw materials | | | | | | | |
| 2-ethyl hexanoic acid, kg | 114 003 | 12.15 | 1 385 130 | 1 to 5 | 13 850 | 69 250 | 3 |
| Cobalt sulfate, kg | 106 307 | 56.44 | 5 999 960 | 1 to 5 | 60 000 | 300 000 | 1 |
| White spirit, L | 74 018 | 6.24 | 461 870 | 1 to 5 | 4 620 | 23 090 | 4 |
| Caustic soda flakes (NaOH), kg | 32 883 | 3.65 | 120 020 | 1 to 5 | 1 200 | 6 000 | 5 |
| Versatic acid, kg | 7 402 | 9.26 | 68 540 | 1 to 5 | 680 | 3 420 | |
| | | | | | | | |
| Water, m³ | 127.6 | 6.27 | 800 | 20 to 80 | 160 | 640 | |
| | | | | | | | |
| Wastewater, m³ | 392 175 | N/A | 212 590 | 20 to 80 | 42 520 | 170 070 | 2 |
| | | | | | | | |
| TOTAL | | | | | 123 030 | 572 470 | |

Table 8.3 Waste minimisation scope to save for Mn PD production process

| Resources and Services | Quantity | Cost/unit in Rand | Estimate Cost/year in Rand | Scope to save % | Estimate of Scope to Save | | Priority Ranking (1=highest) |
|----------------------------------|----------|-------------------|----------------------------|-----------------|---------------------------|---------------|------------------------------|
| | | | | | Minimum (R) | Maximum (R) | |
| Raw materials | | | | | | | |
| 2-ethyl hexanoic acid, kg | 12 967 | 12.15 | 157 550 | 1 to 5 | 1 575 | 7 880 | 2 |
| White spirit, L | 7 791 | 6.24 | 48 615 | 1 to 5 | 490 | 2 430 | 3 |
| Manganese sulfate, kg | 8 225 | 3.50 | 28 780 | 1 to 5 | 290 | 1 450 | 4 |
| Versatic acid, kg | 1 743 | 9.26 | 16 140 | 1 to 5 | 160 | 810 | 5 |
| Caustic soda flakes (NaOH), kg | 3 863 | 3.65 | 14 000 | 1 to 5 | 140 | 700 | |
| Priolene acid, L | 1 501 | 9.00 | 13 510 | 1 to 5 | 135 | 680 | |
| Methanol, L | 1 849 | 3.16 | 5 840 | 1 to 5 | 60 | 300 | |
| | | | | | | | |
| Water, m³ | 12.4 | 6.27 | 80 | 20 to 80 | 16 | 64 | |
| | | | | | | | |
| Wastewater, m³ | 43 575 | N/A | 23 620 | 20 to 80 | 4 720 | 18 900 | 1 |
| | | | | | | | |
| TOTAL | | | | | 7 590 | 33 210 | |

8.5 Production Cost and True Cost of Waste

According to the eThekweni Municipality Bylaws, disposal limits for two types of industrial works which are described by the amount of effluent they produce per day are given in Tables 8.4a and 8.4b. Since the company produces less than 25 ML/day waste, according to the Bylaws, it is classified as a small works industrial manufacturing company. The quality of the wastewater and the high concentration of unreacted metal deemed it unsuitable for disposal in the sewage stream.^[146, 154] The problem is exacerbated by the fact that the wastewater generated during production contains traces of white spirit which is harmful to aquatic animals as described in Sub-section 8.1.1. Table 8.4a and 8.3b, extracted from eThekweni Municipality Bylaws gives guidelines limits on what can and cannot be disposed of into the sewage system.

Results tabulated under Section 7.3 show that Co, Mn and sulfate ions concentration are too high for the company to use sewage disposal. Average cobalt concentration for each batch listed in Table 7.29 shows that the reaction water contains 32 times more Co whereas wash water contains 16 times more Co than the recommended sewage disposal limit of 5 mg/L. With regard to Mn drier, results in Table 7.30 shows that the reaction water contains 736 times more Mn than the prescribed limit allowed by the Municipality.

Table 8.4a Acceptable Concentration of Trade Effluent for discharge into the sewage disposal system^[146]

| General Quality Limits | Large Works >25 ML/d | Small Works <25 ML/d | Units |
|---|-------------------------|-------------------------|----------------|
| 1. Temperature | <44 °C | <44 °C | Degree Celcius |
| 2. pH | 6 < pH < 10 | 6.5 < pH < 10 | pH units |
| 3. Oils, greases, waxes of mineral origin | 50 | 50 | mg/l |
| 4. Vegetable Oils, greases waxes | 250 | 250 | mg/l |
| 5.Total sugar and starch (as glucose) | 1 000 | 500 | mg/l |
| 6. Sulfates in solution (as SO_4^{2-}) | 250 | 250 | mg/l |
| 7. Sulfides, hydrosulfides and polysulfides (as S^{2-}) | 1 | 1 | mg/l |
| 8. Chlorides (as Cl^-) | 1 000 | 500 | mg/l |
| 9. Fluoride (as F^-) | 5 | 5 | mg/l |
| 10. Phenols (as phenols) | 10 | 5 | mg/l |
| 11. Cyanides | 20 | 10 | mg/l |
| 12. Settleable solids | Charge | Charge | mg/l |
| 13. Suspended Solids | 2 000 | 1 000 | mg/l |
| 14. Total dissolved solids | 1 000 | 500 | mg/l |
| 15. Electrical conductivity | - | 400 | mS/m |
| 16. Anionic Surfactants | - | 500 | mg/l |
| 17. C.O.D | Charge | Charge | mg/l |

Table 8.4b Acceptable Concentration of Trade Effluent for discharge into the sewage disposal system^[146]

| General Quality Limits | Large Works >25 ML/d | Small Works <25 ML/d | Units |
|--|-------------------------|-------------------------|-------|
| <u>Heavy Metal and other elements</u> | | | |
| 18. Copper (Cu) | 50 | 5 | mg/l |
| 19. Nickel (Ni) | 50 | 5 | mg/l |
| 20. Zinc (Zn) | 50 | 5 | mg/l |
| 21. Iron (Fe) | 50 | 5 | mg/l |
| 22. Boron (B) | 50 | 5 | mg/l |
| 23. Selenium (Se) | 50 | 5 | mg/l |
| 24. Manganese (Mn) | 50 | 5 | mg/l |
| 25. Lead (Pb) | 20 | 5 | mg/l |
| 26. Cadmium (Cd) | 20 | 5 | mg/l |
| 27. Mercury (Hg) | 1 | 1 | mg/l |
| 28. Total Chromium (Cr) | 20 | 5 | mg/l |
| 29. Arsenic (As) | 20 | 5 | mg/l |
| 30. Titanium (Ti) | 20 | 5 | mg/l |
| 31. Cobalt (Co) | 20 | 5 | mg/l |
| TOTAL METALS | 100 | 20 | mg/l |

Special Limitations

1. No calcium carbide, radio active or isotopes
2. No yeast & yeast wastes, molasses spent or unspent
3. No cyanides or related compound capable of liberating HCN gas or cyanogens
4. No degreasing solvents, petroleum spirit, volatile flammable solvents or any substance which yields a flammable vapour at 21 °C

Guideline limits tabulated above shows that the company can only get rid of waste after treatment with chemicals before landfill at appropriate sites. Proper procedures should be followed in accordance with the South African National Standards document (SANS 10228) put in place in 2006.^[88] The treated waste is then disposed of at designated areas through the use of private waste

management and disposal companies. One big mistake that companies make is to look at disposal costs without carrying analysis on the “True Cost of Waste”. Waste disposal cost is just a fraction of the overall cost incurred by the company (see Sub-section 3.3.3). As mentioned earlier, true cost includes the following:

- Raw material cost
- Treatment cost
- Effect waste has on the productivity
- Time for managing and monitoring the waste
- Environmental liabilities that may arise while storing and disposing the waste.

True cost can be calculated by looking at how much the company spent on acquiring the raw material which forms part of the waste plus disposal costs. The true cost of waste incurred by this company can be calculated using the equation:

$$\text{True Waste Cost} = \text{Disposal Costs} + \text{Total Cost of Raw Material in Wastewater}$$

Equation 8.8

The total cost of raw material is calculated based on the amount a particular raw material contributes to the waste multiplied by the unit cost of the raw material. Communication with EnviroServe (see Section 6.1), revealed that the company is charged for transportation, treatment and disposal of waste. The disposal costs obtained from company records are given in Table 7.8. Using the data collected, a trend curve comparing waste generated to freshwater intake (see Figure 8.6a) shows that the volume of wastewater far exceeds that of freshwater from January to December. Figures 4.3 and 4.9 gives raw materials used during the production of Co and Mn driers manufacturing processes respectively. As mentioned earlier, most of these materials, namely, water, NaOH and sulfates make up the total amount of wastewater generated and do NOT form part of the end product.

8.6 New Product Formulation from Waste

Industrial manufacturing sectors that still consider Waste management and minimization as a problem are probably missing out on cashing in on a possible product waiting to be discovered. This can only be achieved by knowing exactly the quantity and the composition of what is considered to be waste. History^[63] tells us that important products like phenol, benzene and the dyestuffs were all discovered from the waste generated from the production of coke from coal. It is possible that before these products were discovered, many companies lost on the possibility of turning what would have been considered a nuisance to production until very late. This means that it is crucial to evaluate the waste generated to find out hidden useful commercialized product(s) which can ultimately render a reduction in waste generation. In its 2nd Report, The United Nations World Water Development encouraged countries to follow innovations like the one taking place at an Industrial Park in Cape Town, South Africa.^[130, 155] It is an innovation where companies search through the industrial park website database for any waste that has been registered that fits their raw material specification.

Wastewater generated during Co and Mn PD production contains minor amounts of Co metal and Mn metal respectively. The salt in solution is Na_2SO_4 which crystallizes on cooling. Two possible products that the company can formulate from this wastewater are sodium sulfate and calcium sulfate (gypsum). If a market is available for one of these products, the company could commercialize instead of disposing of the wastewater as is happening at the moment. Benefits the company could realize include financial resources (from sales made on the new product and savings on disposal costs) and environmental good standing by saving the limited space they would normally use at a landfill site while disposing the wastewater.

Sodium sulfate was evaluated and found to be the wiser choice the company could invest in as it has advantages that includes:

- Less energy required to get the byproduct from the wastewater
- No other raw materials required for its production
- Requires less amount of water for washing
- Depending on the quality of separation, wastewater generated can be reused for drier production as reaction water, hence solving the problem of retrieving the un-reacted metal.

On the other hand, calcium sulfate requires purchase of raw material which the company has or might need, extra storage facilities, feasibility studies on the expected reaction and disposal cost for the waste generated

In order to demonstrate the quality of solid Na_2SO_4 that can be retrieved from the wastewater a laboratory test (see Section 7.4) was carried out. The results of the test were astonishingly positive as they yielded the salt of high purity, at least from Co wastewater. Results obtained from Co and Mn reaction wastewater are tabulated in Tables 7.31 and 7.32 respectively. Traces of Co in the isolated sulfate crystals contributed an average of less than 0.0011% of sample used. Figure 8.13 shows Na_2SO_4 crystals that were isolated from Co reaction wastewater. The crystals are soft and easily ground into powder.



Figure 8.13 Dried Na_2SO_4 crystals isolated from Co PD reaction wastewater

Na_2SO_4 crystals that were isolated from the Mn wastewater were of lower purity, with manganese contributing an average of about 0.01% by mass. They contained visible traces of manganese octoate drier. The crystals were hard and could not be easily ground into powder as shown in Figure 8.14. It is strongly suggested that if the company wishes to follow this route they should segregate the cobalt and manganese wastewater streams in order to isolate the sulfate for each easily.



Figure 8.14 Dried Na_2SO_4 crystals isolated from Mn PD reaction wastewater

Chapter 9

9. Conclusion and Proposed Measures

Environmental sustainability impacts, strict Municipal bylaws, ever increasing waste disposal costs and scarcity of resources e.g. freshwater, are but a few aspects that force companies to incorporate waste management and prevention strategies into industrial processes.^[130, 157-160] In a chemical industry, expense alone is no longer the defining factor in cutting down the amount of effluent wastes generated. Traditionally, end-of-pipe treatment was considered to be the best option when it came to controlling wastes. This is no longer the case and hence cleaner production and eco-efficiency methods are receiving a lot of attention. Reduction or total elimination of environmental hazardous substances can be achieved through:

- Technology modification
- Inputs substitution
- Products modification
- In plant reuse
- Recycling waste or by-products
- New product formulation based on waste
- Treatment of waste and reuse or recycle
- Treatment of waste and the dispose at designated sites

Not only is the reduction or total elimination helping companies to reduce disposal costs and meet acceptable effluent waste levels, the financial position is strengthened, production processes are improved, companies becomes more efficient and profitable.^[161] Since most wastes are contained in the solvent water medium, the reduction or total elimination of pollution also helps to reduce water

consumption. South Africa's industrial sector accounts for 11% of the total water usage and a reduction can assist in attaining the MDGs by 2015.^[130] According to the United Nations World Water Development Report 2, strategies that can save water and increase industrial water productivity include

- water auditing, which shows where the water supplied to the plant is being used, how much is used in each process, and where it ends up
- matching water quality to use requirement which indicates the quality of water that can be used, so that low quality water is utilized in a process rather than high quality water from Municipality
- water recycling and on-site reuse in order to minimize freshwater consumption by maximizing water reuse and recycling, which ultimately lowers/eliminates the production of wastewater
- stream separation which can reduce treatment cost that will not normally be achieved from wastewater containing a variety of contaminants
- raw material and energy recovery from waste which can help recover all unconverted raw material in the wastewater for reuse
- reuse of waste by other companies that might need to utilize the waste for their processes, e.g. forming an Industrial park like that of Cape Town that registers all wastes from local industry^[130]
- wastewater treatment technologies e.g. physical/chemical treatment (settling, filtration, reverse osmosis, adsorption, flocculation, chlorination), biological treatment (aerobic or anaerobic treatment and other specialized processes such as phosphate reduction and sulfate removal)^[130]
- Water Pinch Technology and mathematical programming techniques that can help companies reduce freshwater intake through re-use, regenerative reuse and regenerative recycling.^[142, 143, 145, 146]

9.1 Conclusion

The company produces speciality textile products and organometallic soaps known as paint driers. The production of paint driers produces high volumes of wastewater

and this happens during Co and Mn processes. Wastewater produced requires the company to spend substantial amounts of financial resources for disposal at suitable sites. The company's personnel also spend valuable time in making sure that the wastewater is stored safely at an effluent pit or flow-bins. The company management's decision was to implement a waste management audit and minimization strategies or techniques to solve the problem. This meant a change to cleaner production processes or better ways to manage the waste at reduced costs. Benefits of following a waste minimization programme (see Section 3.4) include reduction of raw material consumption and utility (energy) costs, reduced waste generation and disposal costs, compliance with Municipal regulations, ending up with cleaner production processes, and an increase in revenue and profits.^[117]

9.1.1 Freshwater Intake and other raw material used

Research conducted on water use in various regions of the world has shown that Sub-Sahara Africa spent most of its freshwater on Industry (42%) followed by Agriculture (40%) and lastly domestic (18%).^[130, 155] The report also shows that freshwater withdrawal by industries worldwide is gradually decreasing with an increase in consumption, something that is attributed to water recycling and reuse. A good example given is Denmark that has achieved the highest industrial water productivity world-wide.^[155]

9.1.1.1 Company's Existing Situation

3% of the company's total amount of water received from the municipality forms part of the total wastewater generated in the PD plant (i.e. based on 1st entry of Column 2 of Tables 7.3 & 7.5 and total water used given in Table 7.6). This amount plus other by-products resulted in the generation of 435.8 tonnes of wastewater, which was registered in the PD plant alone (see monthly values in Table 7.8). Another worrying fact was the excess amount of water lost during production shut down which accounted for at least 9.5% of the total municipal water received per year. Added together these amounts shows a loss of R4430 per year, i.e. 12% of the total water

expense (see Table 7.6). The practical ways in which raw materials other than water are charged into the reactor pose a health risk to the plant operators and solid material loss were also observed.

9.1.1.2. Proposed Measures

Water Audit should be carried out in order to determine where the input water is being used. This will help the company to identify the amount of water spent at each area and where possible, if there is an area where it is being unnecessarily wasted.^[130, 155] For water audit to be carried out efficiently and appropriately, installation and use of water metering at each point where municipal water is used should be fitted and should be given the highest priority. This will mean investing in a number of meters for each sectional plant process, including boiler and cooling tower, offices and housekeeping areas. Plant operators or a dedicated employee should be trained to record and analyse meter readings daily or weekly. Workshops or water management meetings should be held weekly or monthly so that everyone is made aware of what the company has embarked on to enable everyone to be involved. To make it formal, a report on the use of water at each section should be compiled and circulated to all employees monthly. Once the report has been disseminated to all employees, a request for inputs and recommendations should be encouraged. Total amounts recorded at each subsection should be checked against the amount registered by the municipal meter. Any deviations, which might reveal leakages, should be attended to speedily. The management should use the results to make correlations between water usage and operating costs/production yield, make any adjustments deemed necessary to alleviate detected problems or modify production processes. Remember “If it can’t be measured, it can’t be managed”.^[87]

Charging of solid raw materials into the reactor during production should be revised by the SHE manager in consultation with Occupational Health Nurse Practitioner (OHNP). A system should be developed whereby the plant operators will have no direct contact with raw material, either in the form of inhalation or skin contact. Ongoing research shows that cobalt/cobalt compound dust poses health risks to

workers.^[100] The company needs to be proactive and invest in machinery that can protect their employees and enhance production capacity.

Re-use and regenerative recycling of water will be beneficial to the company since the levels of contaminants are currently known from results given in Tables 7.12 through 7.27 and moreover, the wastewater contains a single contaminant. The company should enhance the re-use of wastewater generated from the zirconium PD into the Co process that is currently being practiced (reflected in Table 7.3). If properly implemented, the current savings of 11 % on water can easily be improved. The commitment should be demonstrated through the establishment of dedicated storage facilities which are currently not available.

Proposed measure mentioned in this section (wastewater treatment technologies) should be followed as a way of reducing the current levels of the major contaminants (Na_2SO_4). Once the levels have been reduced, the wastewater from both Co and Mn PD can be used as solvent water for the production of Co and Mn driers respectively. This will again yield another saving on both the amount of freshwater withdrawn and the wastewater to be disposed. The schematic diagram illustrating re-use and regeneration recycling^[144, 145] that the company can utilize and modified depending on the level of contaminant for the process is shown below in Figure 9.1.

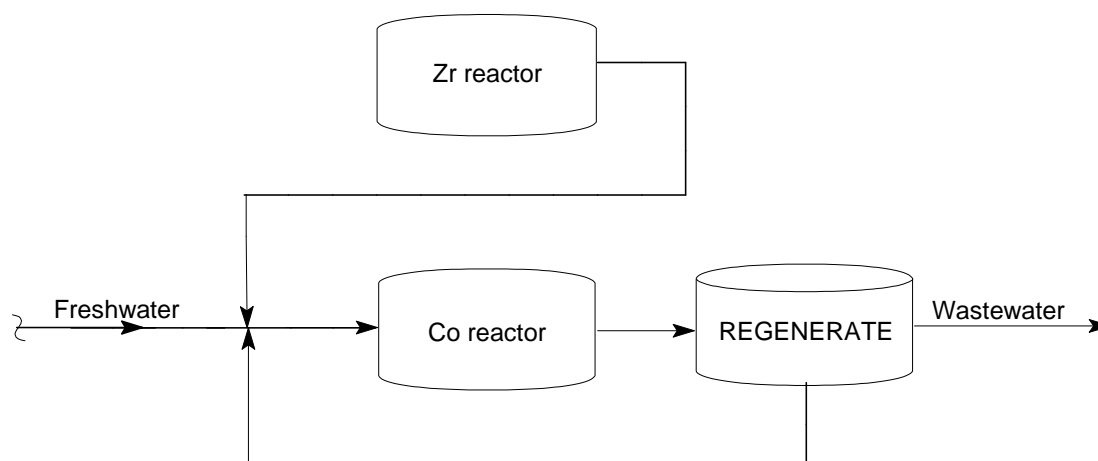


Figure 9.1 Freshwater intake minimization through re-use and regeneration recycling on the Co drier process^[139]

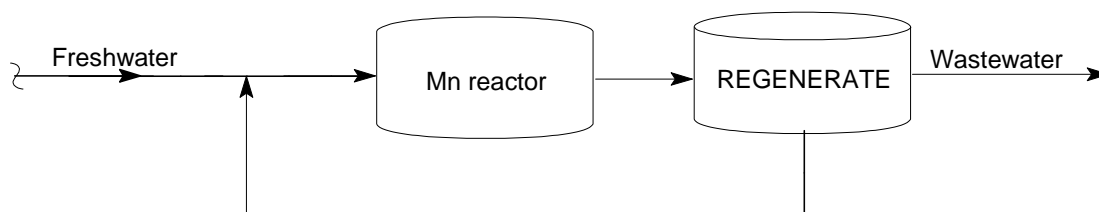


Figure 9.2 Freshwater minimization through regeneration recycling on the Mn drier process^[139]

Depending on the level of contaminants on the distillate from Zr drier process, its water can be utilized during Mn process. Hence Figure 9.1 can be applied to both processes.

Change of production process should be explored in order to reduce the amount of wastewater produced. As explained in Subsection 2.4.2, direct fusion process and direct metal reaction process do not produce any appreciable wastewater. A feasibility study (see Appendix F) was conducted few years back by the company comparing total production costs and production time taken while following the direct fusion process against the precipitation process. Direct fusion process was found to be 60% shorter in terms of production time and a cleaner process. It was established that the precipitation reaction was R3.01 less expensive to produce a kilogram of cobalt octoate than the direct fusion process. This was largely attributed to pure raw materials required for direct fusion process. The cost difference takes into account all factors including labour, energy, costs for both raw materials and waste disposal (see Appendix F). Taking into account current strict environmental legislations and exorbitant disposal costs (see Figure 8.6b), the company should carry out another study in order to determine if the findings made a few years back still hold.

Water Pinch Technology came into existence in 1978 through the work done by Linnhoff and Flower for the optimization of heat exchanger networks.^[144, 145] The technology has recently been extended to freshwater management and optimization.^[141] To date, research investigations on Pinch Technology has been conducted at several industries in South Africa, namely the Sasol Polymers Chlor-

Alkali plant, the Sanachem Agro-Chemicals, the Lethabo Power Station, SA Tioxide, AECI Bioproducts Lysine Plant at Umbogintwini, Ceres Fruit Juices and Mondi Merebank Paper Mill at Merebank^[144, 145] Work carried out at the Sanchem Agro-Chemicals relates much to the company's waste minimization and water management problems. Although pinch technology literature is based on continuous processes, it was easily applied to production that follows batch processes just like that of the company. The implementation of research conducted at Sanchem Agro-chemical was successful in the sense that they were able to reduce freshwater intake by 40% and production capacity increased by 25%.^[145] Application of the technology can also assist the company in determining the amount of water utilized by the cooling tower and the boiler. Instead of allowing steam to evaporate, this can be channeled back into the storage facilities and used as reaction water. Since the research team's expertise does not go beyond Chemistry, the technology mentioned here will require the know-how of a Chemical Engineer and it will be in the company's best interest to initiate such a project.

9.1.2. Wastewater generated during production

Many industrial companies in South Africa are faced with challenges brought about by new environmental legislations requiring everyone to be vigilant when it comes to waste generation and disposal. Most of these companies are beginning to pay more attention to what they are throwing away in the hope of commercializing some or all of the by-products. Sappi Saiccor, the world's largest producer of chemical cellulose is but one good example.^[162] The company generates 5000 m³ effluent per hour, which is then pumped into the sea. The company initiated a research project that looked at characterisation of the wastewater with the hope of obtaining compounds that could be commercialised, while at the same time reducing the impact wastewater generated has on the environment.

9.1.2.1 Company's Existing Situation

Records obtained from the disposal private company shows that the company generates more than 435 tonnes of wastewater per annum in the drier plant section. The major constituent in the wastewater is sodium sulfate (Na_2SO_4) generated as a by-product. One major repeated shortfall highlighted in Section 8.4 is the fact that the company does not have a clue as to the exact volumes of wastewater generated per batch.

The general nature and characteristics of wastewater at the time of release from the reactor is illustrated in Tables 7.9 and 7.10. The Mn wastewater (see Table 7.10) contains a sizeable amount of metal content, more than what it is contained in the Co wastewater as shown in Table 7.9. The sulfate amount in Mn wastewater is 10 times that found in Co wastewater. This is attributed to the volume of water and the amount of reagents used, with Co PD using and generating a lot of water.

9.1.2.2. Proposed Measures

Measuring wastewater generated from each batch should be strictly practiced by the company at each stages of discharge. This will enable the company to become aware of any deviations from expected volumes to be discharged into appropriate catchments. Since the current procedure is time consuming and counter productive, it is suggested that a meter be attached on the outlet pipe. Measurements made should be recorded on the batch sheet. On the one hand, measurements made on the product, using a manual scale, are prone to human error. It will be beneficial to the company to acquire electronic balances as opposed to the use of manual balances that depend entirely on human judgment. Raw material specifications should be carried out for each and every batch purchased instead of waiting until low yields are observed.

Waste segregation according to the type of stream or amount of contaminants it contains should be strictly practiced. From the preceding section the composition of wastewater differs with respect to the process that it originates from, and the

efficiency of treatment will depend on the degree of contamination. Wastewater generated from Mn is on average more concentrated with Na_2SO_4 than the one coming from Co process. Because of low volumes of Mn wastewater generated per year, i.e. based on the freshwater intake, small size batches and number of batches made, it will be less costly to treat it alone than when mixed with Co wastewater. As illustrated in Section 8.6, Co wastewater alone results in pure Na_2SO_4 solid crystals. The purity can be compromised if another stream (other than Co) is combined with wastewater from Co production process.

Turning waste into new product(s) ^[65, 79] should be made the second priority after segregation of streams. Not only will the company achieve reduction in disposal costs, it will generate revenue through commercializing such a by-product. The research team has suggested a potential product in the wastewater that the company might want to explore in the near future (see Section 8.6). The company is fully aware of the amount of heavy metal in each stream. They could also conduct market research to find out whether industries exist that could utilize the current wastewater with its contaminant for other processes.

Wastewater treatment technologies available that the company can implement includes reverse osmosis and biological treatment.^[130-132, 134] The good thing about them is their applicability to wastewater earmarked for recycling or as a form of treatment prior to disposal. Since the idea is the reduction or total elimination of wastewater, the company should apply wastewater treatment technologies for re-use or recycling.

9.2 Final Conclusion

Careful consideration of most of the recommendations made will inevitably put the company's environmental standing on a far sounder footing. The rewards on the production capacity and efficiency will by far exceed the current volumes. Financial rewards in terms of revenue will exceed half a million rand as illustrated in Tables 8.1 and 8.2.

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Appendix A

This section gives the structure of epoxy resin as well as the description of the drying and cross-linking of the binder with special reference to an alkyd resin.

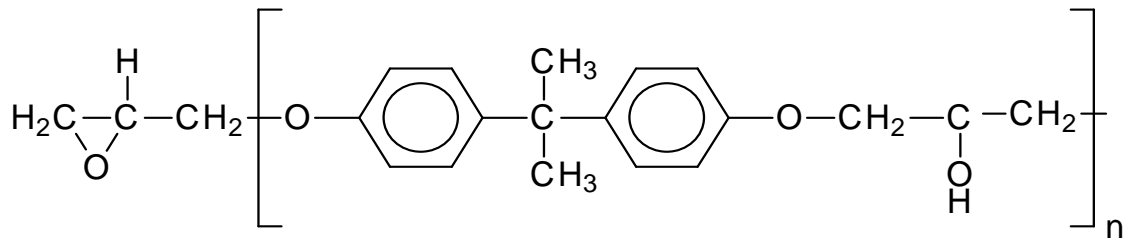


Figure A1 The chemical structure of an epoxy resin

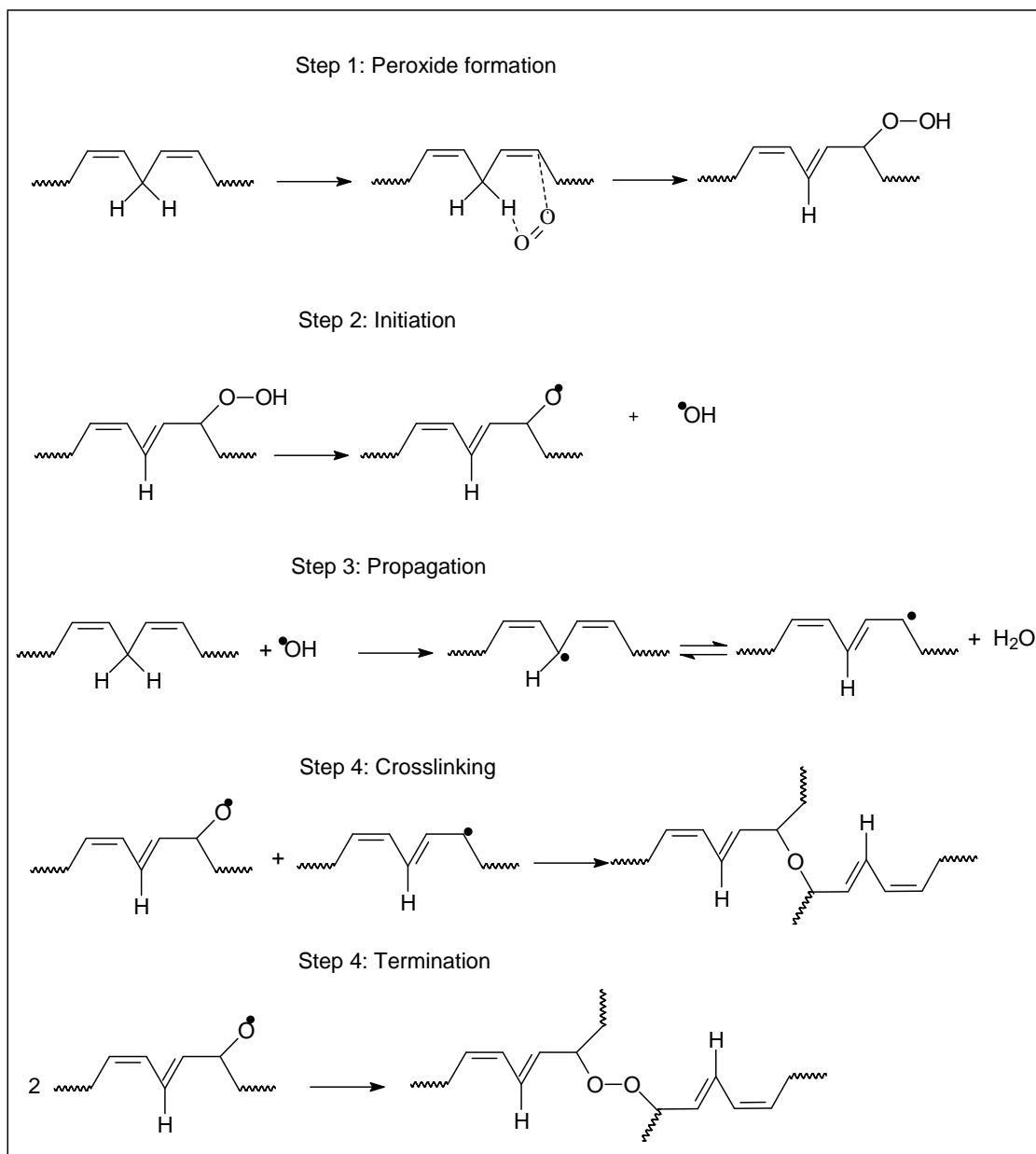


Figure A2 Autoxidation and crosslinking reaction mechanism of the fatty acid part of an alkyd resin^[3, 18-24]

Appendix B

This section gives graphic representations of raw material usage in PD plant. The percent values were calculated from the figures extracted from the SMFD sheets.

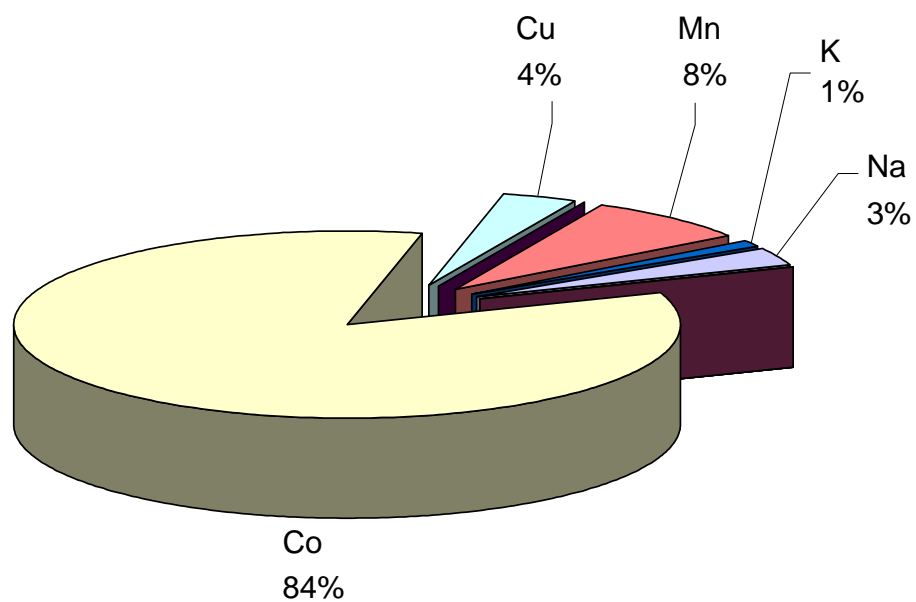


Figure B1 Percent usage of fresh water at the PD plant excluding cleaning

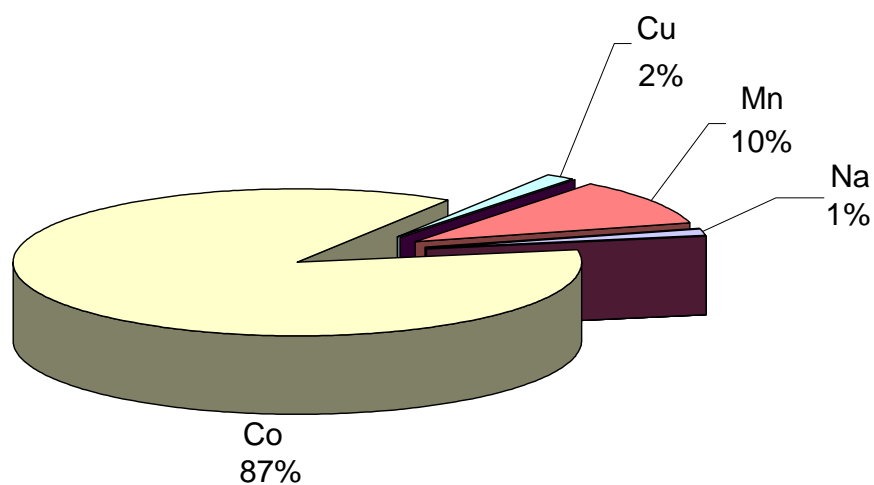


Figure B2

Percent usage of sodium hydroxide at the PD plant

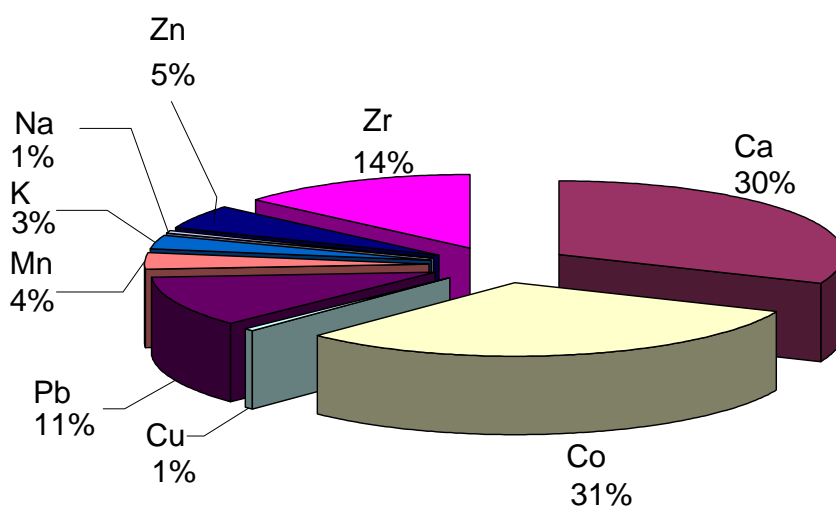


Figure B3

Percent usage of 2-ethyl hexanoic acid at the PD plant

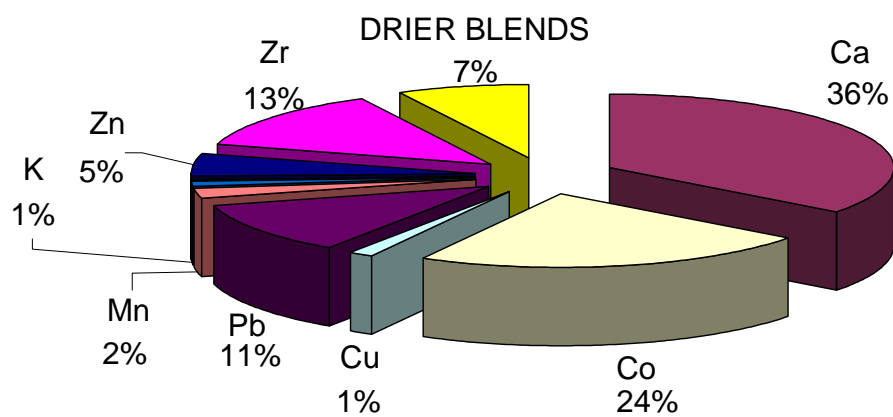


Figure B4 Percent usage of white spirit at the PD plant

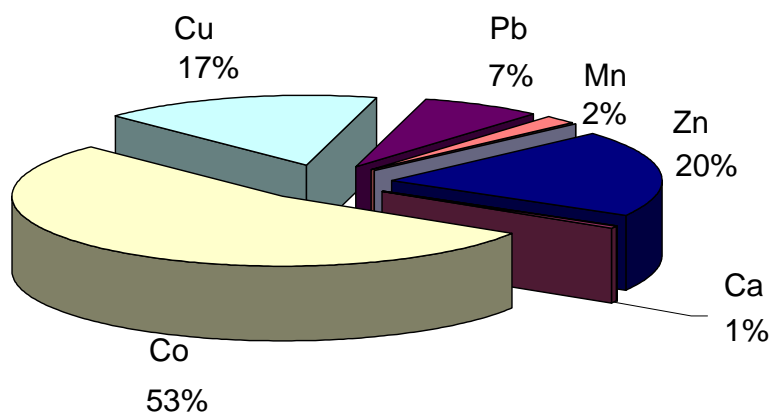


Figure B5 Percent usage of naphthenic acid at the PD plant

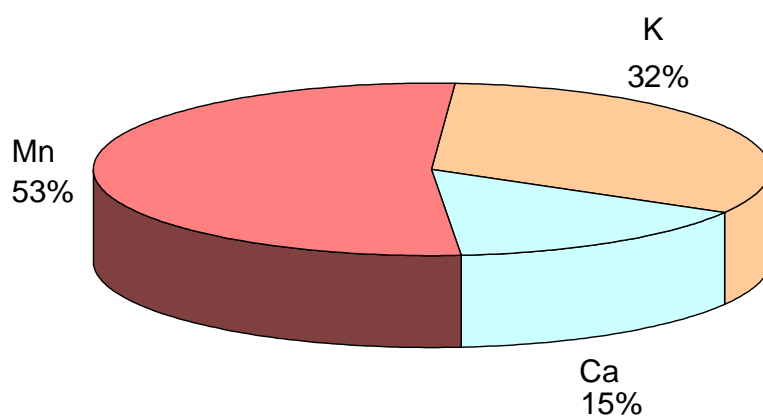


Figure B6

Percent usage of methanol at the PD plant

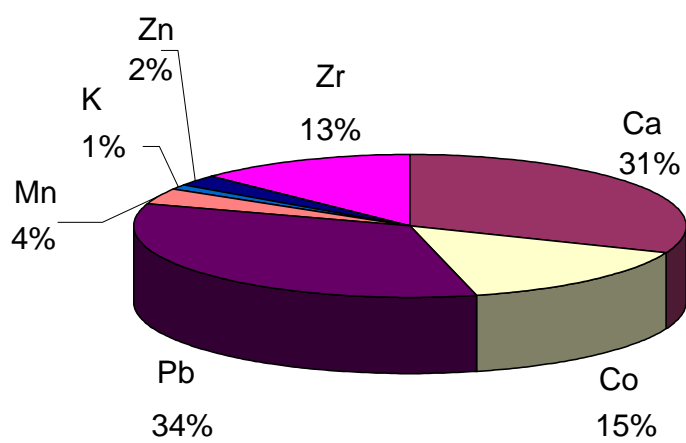


Figure B7

Percent usage of Versatic acid at the PD plant

Appendix C

Three graphic representations of percent production are given in this section. The first graph describes the production of single driers only. Single driers and total blends production per annum are illustrated by the second graph. The final graph represents product percent of drier blends only.

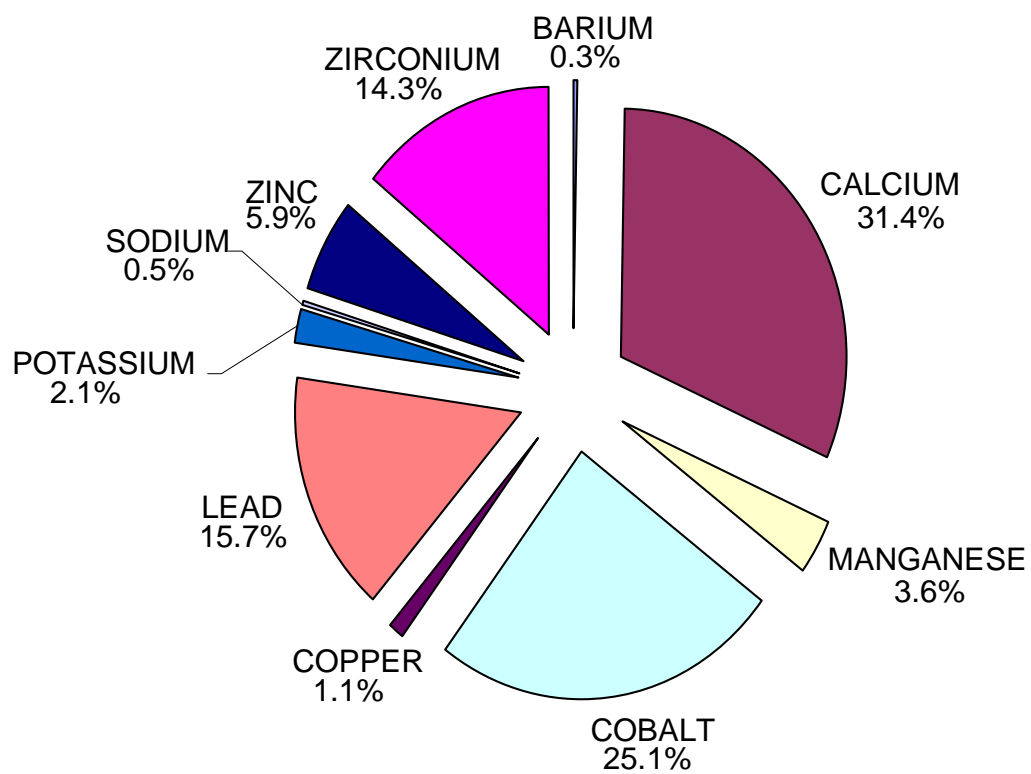


Figure C1 Percent metal PD production per annum excluding drier blends

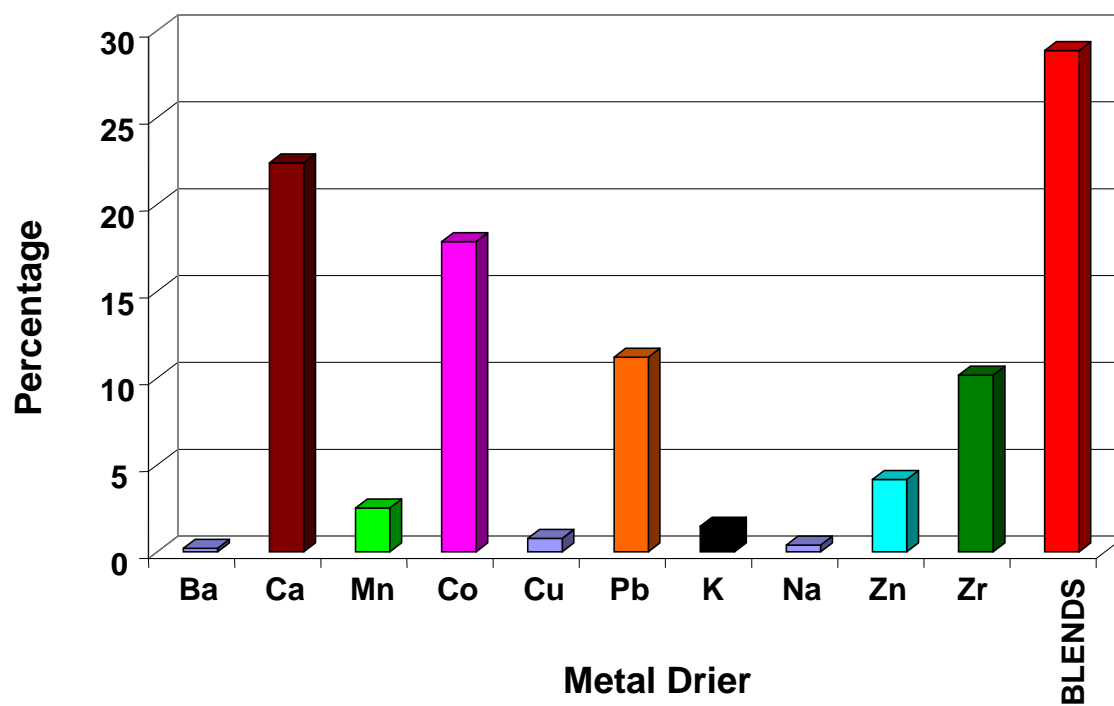


Figure C2

Percent Production including drier blends

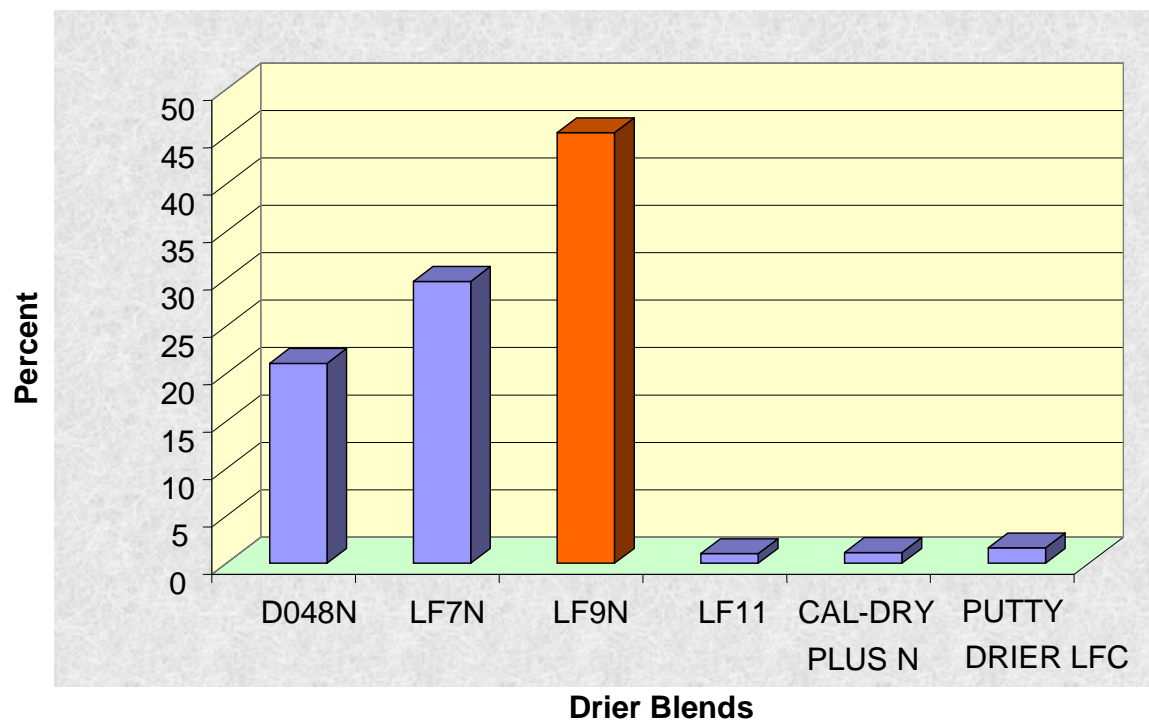


Figure C3 Percent metal drier blends production per annum

Appendix D

Graphic representation of amount of wastewater collected and the disposal costs for each month are given in this section.

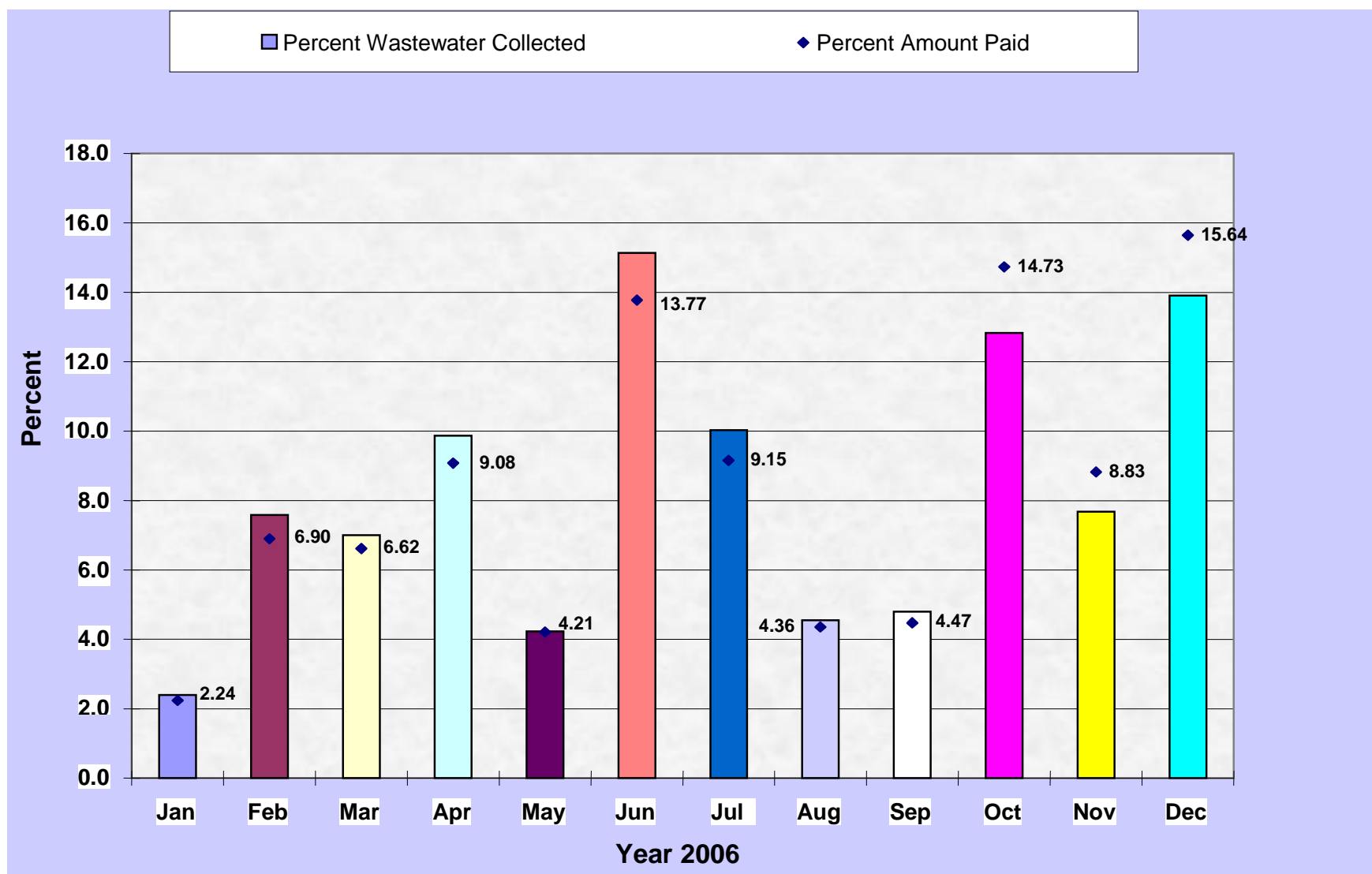


Figure D1 Effluent amount collected and respective disposal costs per month

Appendix E

Two reports and a final presentation were made to the company during the lifespan of this project. The first report, which is not included in this dissertation, looked at the two processes of interest taking place in the paint drier production site. The second report, which is Appendix E in this document, looked at preliminary investigations that were made during the project. The final report, also not part of this dissertation, was in the form of a presentation to the company management personnel. It was during the presentation meeting wherein purified salts from the two streams were also presented.

Pre-assessment Report 28.08.2006

INDUSTRIAL MONITORING AT METALLICA CHEMICALS

1. INTRODUCTION

Metallica Chemicals make cobalt and manganese paint driers and the product range manufactured at their Cato Ridge plant is shown in Table 1.

Table 1 Cobalt and manganese paint driers

| Drier | Product composition |
|-------|---------------------|
| Mn | 6% naphthanate |
| | 10% octoate |
| Co | 6% naphthanate |
| | 6% octoate |
| | 10% octoate |
| | 12% octoate |
| | 6% heptanoate |

The 12% cobalt octoate drier makes up about 80% of the cobalt based drier output from the plant. These products are usually manufactured once a week while manganese driers are made less frequently (once a month or less often).

The manganese 10% octoate product is produced in two batch sizes namely 2.5 T and 1.8 T while the 12% cobalt octoate is made as a 3.5 T batch only. These concentrations (see Table 1 above) are a measure of the mass of the metal species of the drier in the solvent (white spirit).

Preliminary sampling has been undertaken in order to establish four main points concerned with the development of a monitoring strategy. These points seek to determine

- suitable dilution factors for the sample
- suitable concentrations for the calibration standards
- a comparison of the estimates and the experimentally determined concentrations
- instrumental setup

Cobalt and manganese levels were thus determined for six cobalt and manganese paint drier manufacturing processes. The two manganese and the four cobalt production batches that have been sampled and analysed for Mn and Co respectively appear as entries 1 and 2 in Table 2.

Samples were also provided by the company for two particular batches, N6 MAY 48 and N6 JUN 03. These are shown as entry 3 in Table 2. These samples were taken from a cobalt process after a series of low yield runs and analysed in response to a request by Metallichem. These samples were analysed for Co, Mn, Fe, Cu, Ni, Cr, and Zn which were thought to be present in the wastewater released to the effluent. Usually the

solvent wastewater is sent to the effluent pit while the wash wastewater is stored in flow bins for reuse.

It was expected that the levels of Co and Mn present, determined from the wastewater analyses, would be significantly higher than those of the trace metal measured during the multi-metal analysis for Fe, Ni, Zn, Cu and Cr. This is because Co is present in the unreacted raw material $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ while Fe, Ni, Zn, Cu and Cr are thought to be trace impurities in this compound.

Table 2 Paint drier processes sampled during preliminary monitoring

| Drier | Entries | Date | Batch no. | Product composition | Amount of Product (kg) |
|-------|---------|----------|-----------|---------------------|------------------------|
| Mn | 1 | 27.01.06 | N6 JAN 25 | 10 % octoate | 2345 |
| | | 27.02.06 | N6 FEB 32 | 10 % octoate | 1802 |
| Co | 2 | 6.02.06 | N6 FEB 04 | 12 % octoate | 3395 |
| | | 6.03.06 | N6 MAR 06 | 12 % octoate | 3459 |
| | | 8.03.06 | N6 MAR 10 | 12 % octoate | 3876 |
| | | 14.03.06 | N6 MAR 17 | 12 % octoate | 3598 |
| | 3 | 31.05.06 | N6 MAY 48 | 12 % octoate | 3314 |
| | | 2.06.06 | N6 JUN 03 | 6% naphthanate | Unknown |

The sampling procedure used is discussed in Section 2. Cobalt and manganese analysis using inductively coupled plasma optical emission spectroscopy (ICP - OES) has been carried out on all the samples taken during the six processes shown in entries 1 and 2 of Table 2. A multi-element analysis was carried out using samples provided in entry 3 of Table 2. The analytical procedure is discussed in Section 3 and the results and discussion are presented in Section 4 and Section 5 respectively. In conclusion, Section 6 presents a proposed monitoring strategy based on the findings presented in Sections 4 and 5.

2. SAMPLING PROCEDURE

2.1 PRE- AND POST- SAMPLING

Cleaned and labelled (with a unique identification number) sampling bottles (125 ml and 500 ml volume) were taken on-site in a cooler box. Two 125 ml and one 500 ml samples were taken at each sampling point. The solvent wastewater (see Table 3) sample was taken as soon after it was discharged from the reactor as possible. The samples were then immediately stored in the cooler box. Samples were then randomly taken at 15 to 30 minutes intervals while the solvent wastewater was being released. The wash wastewater (see Table 3) was similarly sampled as it was released from the reactor. On the occasions where site personnel took the sample, only one sample was obtained for discharging spent solvents and washings. The distillate (see Table 3) for both processes was sampled only once. Samples were then taken back to the Analytical Chemistry Laboratory at UKZN in Pietermaritzburg. The conductivity of each

solution was measured and one of the two 125 ml samples from each sampling point was acidified with about 5 ml of concentrated nitric acid before storing prior to chemical and gravimetric analyses.

2.2 SAMPLING STRATEGY FOR MONITORING COBALT AND MANGANESE LEVELS

A total of thirty nine samples have been collected for the six processes shown in Table 2 (entries 1 and 2). Nine samples have been collected from the manganese processes and thirty samples have been taken from the cobalt processes. The sampling points from which the manganese and the cobalt samples were taken are described in Tables 3 and 4 respectively. Three samples were collected at each sampling point, two 125 ml samples (one treated with nitric acid and the other one untreated) for ICP-OES analysis and a 500 ml sample for gravimetric analysis. The conductivity of the samples was measured, recorded and all samples were then stored in the refrigerator.

Table 3 Samples taken during the manganese octoate manufacture in Reactor 5

| Sample description | Source of Sample | Date samples taken | Number of samples taken |
|-----------------------|---|--------------------|-------------------------|
| Raw materials | Manganese sulfate from the suppliers packaging | 27.1.06 | 0 |
| | | 27.2.06 | 2 |
| Utility outlet | Fresh mains water from tap | 27.1.06 | 1 |
| | | 27.2.06 | 0 |
| Solvent wastewater | Manganese containing solvent wastewater discharged from reactor to effluent pit after reaction complete | 27.1.06 | 1 |
| | | 27.2.06 | 3 |
| Distillate wastewater | Mixture of wastewater and spirit discharged into a metal drum from reactor during distillation. | 27.1.06 | 1 |
| | | 27.2.06 | 1 |

Table 4 Samples taken during cobalt octoate manufacture in Reactor 6

| Sample description | Source of sample | Date samples taken | Number of samples taken |
|-----------------------|---|--------------------|-------------------------|
| Solid raw materials | Cobalt sulfate & Caustic soda flakes from the supplier's packaging | 6.2.06 | 1 |
| | | 6.3.06 | 1 |
| | | 8.3.06 | 1 |
| | | 14.3.06 | 0 |
| Fresh solvent water | Water added to reactor before any chemical additions were made | 6.2.06 | 1 |
| | | 6.3.06 | 0 |
| | | 8.3.06 | 0 |
| | | 14.3.06 | 0 |
| Utility outlet | Mains water from tap | 6.2.06 | 1 |
| | | 6.3.06 | 1 |
| | | 8.3.06 | 0 |
| | | 14.3.06 | 0 |
| Solvent wastewater | Co containing solvent wastewater discharged from the bottom of the reactor into the effluent after reaction comes to completion | 6.2.06 | 6 |
| | | 6.3.06 | 1 |
| | | 8.3.06 | 3 |
| | | 14.3.06 | 2 |
| Wash wastewater | Co containing wash wastewater discharged from the reactor into the flow bin | 6.2.06 | 4 |
| | | 6.3.06 | 1 |
| | | 8.3.06 | 1 |
| | | 14.3.06 | 2 |
| Distillate wastewater | Reusable wastewater discharged from reactor during distillation into a metal/plastic drum | 6.2.06 | 1 |
| | | 6.3.06 | 1 |
| | | 8.3.06 | 1 |
| | | 14.3.06 | 1 |

2.3 SAMPLING FOR THE MULTI-ELEMENTAL ANALYSIS

Samples from N6 MAY 48 and N6 JUN 03 batches (entry 3 in Table 2) were taken by the staff at Metallichem. They were kept in 100 ml glass bottles. These samples were labelled 1) with a date, 2) batch number and 3) with an indication of whether is the solvent wastewater, wash wastewater or distillate wastewater. Where more than one sample was taken from solvent, wash or distillate wastewater, these were differentiated by numbers (1, 2, 3 and 4) or volume of wastewater which had been released (e.g. 1 L, 800 L or 2000 L). None of the samples collected by the employees of Metallichem had been preserved with nitric acid and all were submitted in glass bottles.

3. SAMPLE ANALYSIS

Section 3.1 describes how samples were prepared for cobalt and manganese analyses, these elements being present as unreacted starting material. Section 3.2 describes the sample preparation used when analysing for impurities in the metal containing raw material.

3.1 PREPARING SAMPLES FOR COBALT AND MANGANESE ANALYSIS

Both acidified and non-acidified samples were filtered and diluted for ICP-OES analysis. About 5 ml of the sample was drawn up into a disposable syringe. It was then released from the syringe, through a 30 mm diameter filter (0.45 µm pore size) fitted to the syringe tip, into a clean 100 ml beaker. Then 200 µl of the filtered sample was pipetted, using an Eppendorf pipette, into a 100 ml volumetric flask and diluted with distilled water up to the mark.

3.2 PREPARING SAMPLES FOR MULTI-ELEMENTS ANALYSIS

About 10 ml of each sample from both batches (N6 MAY 48 and N6 JUN 03) was drawn up into a disposable syringe and filtered into a clean 100 ml beaker using a 30 mm diameter nylon syringe filter (0.45 µm) pore size for ICP-OES analysis. 1.0 ml of the filtered sample was pipetted, using an Eppendorf pipette, into a 50 ml volumetric flask and diluted with distilled water up to the mark and it was then analysed using ICP-OES instrument.

3.3 PREPARATION OF CALIBRATION STANDARDS

Stock standard solutions (100 ml) of Co and of Mn were prepared from purchased 1000 ppm commercial standard solutions (Fluka). The concentrations chosen for these standard solutions (numbered 1 to 6) are given in column 2 of Table 5. These concentrations were selected based on trial and error because no process data was able to be made available by the company at that time. The volume of the commercial standard solution used to prepare these standards was calculated using the dilution factor (see Equations 1 and 2) and is given in column 3 of Table 5.

$$\text{Dilution factor} = \frac{\text{Concentration of commercial standard}}{\text{Concentration of stock standard}} \quad \text{Equation 1}$$

$$\text{Volume of commercial standard} = \frac{\text{Volume of stock standard}}{\text{Dilution factor}} \quad \text{Equation 2}$$

Table 5 Stock standards prepared from 1000 ppm Co & Mn

| Standard solution number | Concentration (ppm) of Co & Mn stock standards | Dilution factor | Volume (ml) taken from 1000 ppm solution |
|--------------------------|--|-----------------|--|
| 1 | 25 | 40 | 2.50 |
| 2 | 50 | 20 | 5.00 |
| 3 | 100 | 10 | 10.00 |
| 4 | 200 | 5 | 20.00 |
| 5 | 400 | 2.5 | 40.00 |
| 6 | 800 | 1.25 | 80.00 |

Preliminary results obtained after analysing few samples using standard solutions given in Table 5 showed that the concentration of the samples were too low compared to the chosen stock standard.

A set of cobalt and manganese mixed calibration standards with concentration ranging from 0.20 ppm to 5.0 ppm and 2.0 ppm to 50 ppm respectively were then prepared. These standards were prepared by further dilution of standard 2 (for cobalt) and standard 3 (for manganese) (see Table 5 above). The volumes of these standards, which were taken to make the calibration standards, (see columns 4 and 5 of Table 6) were calculated using Equations 1 and 2.

Table 6 Mixed calibration standards prepared from 50 ppm Co & 100 ppm Mn

| Standard number | Concentration (ppm) of calibration standards | | Volume (ml) taken of Co solution | Volume (ml) taken of Mn solution |
|-----------------|--|------|----------------------------------|----------------------------------|
| | Co | Mn | | |
| 1 | 5.0 | 50.0 | 10.0 | 50.0 |
| 2 | 2.0 | 20.0 | 4.0 | 20.0 |
| 3 | 1.0 | 10.0 | 2.0 | 10.0 |
| 4 | 0.50 | 5.0 | 1.0 | 5.0 |
| 5 | 0.20 | 2.0 | 0.50 | 2.0 |

Two series of multi-elemental calibration standards, one containing Co, Mn, Fe, Zn, Cu, & Ni and another containing Co, Mn, & Cr, were prepared.

For the first multi-element analysis, a series of Co, Mn, Fe, Zn, Cu and Ni mixed calibration standards were then prepared. The concentration of the five calibration solutions containing Co and Mn and the four trace elements are given in Table 7. A second series of calibration standards containing Co, Mn and Cr, shown in Table 8, were prepared in order to analyse for low levels of chromium.

Table 7 Mixed calibration standards for Co, Mn, Fe, Zn, Cu and Ni analysis

| Standard number | Concentration (ppm) of calibration standards | | | | | |
|-----------------|--|------|------|------|------|------|
| | Co | Mn | Fe | Zn | Cu | Ni |
| 1 | 0.50 | 0.80 | 0.30 | 0.20 | 0.40 | 0.60 |
| 2 | 1.0 | 2.0 | 0.50 | 0.40 | 0.80 | 1.2 |
| 3 | 5.0 | 10 | 1.0 | 0.80 | 1.2 | 2.0 |
| 4 | 10 | 20 | 5.0 | 1.5 | 2.0 | 2.5 |
| 5 | 20 | 30 | 10 | 2.0 | 2.5 | 3.0 |

Table 8 Mixed calibration standards for Co, Mn and Cr analysis

| Standard number | Concentration (ppm) of calibration standards | | |
|-----------------|--|------|------|
| | Co | Mn | Cr |
| 1 | 0.50 | 0.60 | 0.20 |
| 2 | 1.0 | 1.2 | 0.50 |
| 3 | 5.0 | 12 | 1.0 |
| 4 | 10 | 20 | 2.0 |
| 5 | 15 | 25 | 10 |
| 6 | 20 | 30 | 15 |

3.4 SAMPLE ANALYSIS

The ICP-OES instrument was calibrated using standards given in Tables 6, 7 and 8. A good correlation for each of the Co, Mn, Fe, Zn, Cu, Ni and Cr standards was obtained for calibration of the ICP-OES instrument. The conditions under which samples were analysed by ICP-OES are given in Table 9.

Table 9 ICP-OES specifications and operating conditions

| | |
|--------------------|---|
| Power | 1.00 kW |
| Plasma | 15.0 L/min |
| Auxiliary | 1.50 L/min |
| Pump speed | 15.0 rpm |
| Nebulizer | 200 kPa for pneumatic 240 kPa for ultrasonic |
| Stabilization time | 15 s |
| Rinse time | 10 s |
| Sample delay | 30 s |
| Replicates | 3 |

The wavelength used for each metal and theoretical detection limit of the instrument for the metal ions whose concentrations was being determined is given in Table 10.

Table 10 Selected wavelengths and instrument detection limit

| Element | Co | Mn | Fe | Zn | Cu | Ni | Cr |
|------------------------------------|---------------|--------------|--------------|--------------|---------------|---------------|---------------|
| Wavelength (nm) | 237.862 | 260.569 | 259.94 | 213.856 | 324.754 | 231.604 | 267.716 |
| Theoretical detection limit (mg/L) | 0.050 to 2500 | 0.004 to 200 | 0.015 to 750 | 0.009 to 450 | 0.020 to 1000 | 0.060 to 3000 | 0.040 to 2000 |

4. RESULTS

The Co and Mn concentrations obtained from ICP-OES analysis of acidified and non-acidified solution samples (entries 1 and 2 of Table 2) are given in Tables 11 to 16 below. Tables 17 and 18 provide results obtained when carrying out the multi-elements analyses on samples presented as entry 3 in Table 2. Measured concentrations for the analytical samples are given in columns 5 and the calculated concentration values for the original samples appear in column 6 of Tables 11 to 16. With the exception of samples MV002, MV009 and MV069, which were not diluted, the concentration of the original sample, i.e. before dilution, was calculated using Equations 3 and 4. Conductivity (referred to as Cond in Tables 11 to 16) values for the non-acidified samples are also presented in these tables. In Tables 11, 12 and 14 the sampling time is also recorded because more than one solvent and/or wash wastewater samples were taken. The abbreviation “ND” has been used to represent the measured concentration when it was observed to be below the concentration of the lowest calibration standard.

$$\text{Dilution factor} = \frac{\text{Volume of diluted sample}}{\text{Volume of original sample used}} \quad \text{Equation 3}$$

$$\text{Concentration of original sample} = \text{Concentration of dilute sample} \times \text{Dilution factor} \quad \text{Equation 4}$$

Table 11 Average metal concentration (ppm) and solution conductivity (mS/cm) in manganese drier samples collected from Reactor 6 on 27.1.06

| Source of Sample | Cond | Sample number | Sample treatment | Analytical sample | | Original sample | |
|-----------------------|------|---------------|------------------|-------------------|------|-----------------|--------------------|
| | | | | [Co] | [Mn] | [Co] | [Mn] |
| Mains | 0.37 | MV002 | None | ND | 0.56 | ND | 0.56 |
| Solvent wastewater | 126 | MV003 | Acidified | ND | 15.0 | ND | 7.50×10^3 |
| | | MV004 | None | ND | 14.5 | ND | 7.26×10^3 |
| Distillate wastewater | 0.95 | MV005 | None | 0.49 | ND | 245 | ND |
| | | MV006 | Acidified | 0.27 | ND | 136 | ND |

Table 12 Average metal concentration (ppm) and solution conductivity (mS/cm) in manganese drier samples collected from Reactor 5 on 27.2.06

| Sample source | Cond | Sample number | Sample treatment | Analytical sample | | Original sample | |
|--------------------------------------|------|---------------|------------------|-------------------|------|-----------------|--------------------|
| | | | | [Co] | [Mn] | [Co] | [Mn] |
| Solvent wastewater taken at 16:10 | 131 | MV051 | None | ND | 5.57 | ND | 2.78×10^3 |
| | | MV057 | Acidified | ND | 5.25 | ND | 2.62×10^3 |
| Solvent wastewater taken at 16:20 | 134 | MV055 | None | ND | 6.81 | ND | 3.41×10^3 |
| | | MV056 | Acidified | ND | 6.35 | ND | 3.18×10^3 |
| Solvent wastewater taken at 16:40 | 130 | MV060 | None | ND | 5.50 | ND | 2.75×10^3 |
| | | MV061 | Acidified | ND | 5.36 | ND | 2.68×10^3 |
| | | MV062 | None | ND | 5.27 | ND | 2.63×10^3 |
| Distillate wastewater taken at 10:35 | 0.15 | MV066 | None | ND | ND | ND | ND |
| | | MV067 | Acidified | ND | ND | ND | ND |

Table 13 Average metal concentration (ppm) and solution conductivity (mS/cm) in cobalt drier samples collected from Reactor 6 on 6.2.06

| Source of sample | Cond | Sample number | Sample treatment | Analytical sample | | Original sample | |
|-------------------------------------|------|---------------|------------------|-------------------|-------|-----------------|------|
| | | | | [Co] | [Mn] | [Co] | [Mn] |
| Water inside tank | | MV008 | None | 0.226 | ND | 0.226 | ND |
| Mains water | | MV009 | None | ND | ND | ND | ND |
| Solvent wastewater sampled at 15:15 | 125 | MV015 | None | 0.365 | ND | 183 | ND |
| | | MV016 | Acidified | 0.433 | 0.115 | 217 | 57.6 |
| | | MV018 | Acidified | 0.353 | ND | 176 | ND |
| | | MV019 | Acidified | 0.428 | ND | 214 | ND |
| Solvent wastewater sampled at 15:30 | 125 | MV022 | None | 0.435 | ND | 218 | ND |
| | | MV023 | None | 0.427 | ND | 214 | ND |
| Solvent wastewater sampled at 15:45 | 125 | MV025 | Acidified | 0.432 | ND | 216 | ND |
| | | MV026 | None | 0.494 | ND | 247 | ND |
| Solvent wastewater sampled at 16:05 | 126 | MV028 | Acidified | 0.461 | ND | 230 | ND |
| | | MV030 | None | 0.458 | ND | 229 | ND |
| Solvent wastewater sampled at 16:20 | 125 | MV031 | Acidified | 0.455 | ND | 228 | ND |
| | | MV032 | None | 0.448 | ND | 224 | ND |
| Solvent wastewater sampled at 16:50 | 125 | MV034 | None | 0.469 | ND | 235 | ND |
| | | MV035 | Acidified | 0.503 | ND | 252 | ND |
| Wash wastewater sampled at 17:45 | 35 | MV040 | None | 0.311 | ND | 156 | ND |
| | | MV041 | Acidified | 0.3899 | ND | 195 | ND |
| Wash wastewater sampled at 17:55 | 34.7 | MV043 | None | 0.0817 | ND | 40.8 | ND |
| | | MV044 | Acidified | 0.0894 | ND | 44.7 | ND |
| Wash wastewater sampled at 18:05 | 34.8 | MV046 | None | 0.140 | ND | 70.2 | ND |
| | | MV047 | Acidified | ND | ND | ND | ND |
| Wash wastewater sampled at 18:17 | 35 | MV049 | None | ND | ND | ND | ND |
| | | MV050 | Acidified | ND | ND | ND | ND |
| Distillate wastewater | | MV D1 | None | 0.208 | ND | 104 | ND |
| | | MVD2 | Acidified | 0.121 | ND | 60.4 | ND |

Table 14 Average metal concentration (ppm) and solution conductivity (mS/cm)
in cobalt drier samples collected from Reactor 6 on 6.3.06

| Source of sample | Cond | Sample number | Sample treatment | Analytical sample | | Original sample | |
|-----------------------|------|---------------|------------------|-------------------|-------|-----------------|-------|
| | | | | [Co] | [Mn] | [Co] | [Mn] |
| Mains water | | MV069 | None | 0.206 | 0.914 | 0.206 | 0.914 |
| Solvent wastewater | 123 | MV073 | Acidified | 0.348 | ND | 174 | ND |
| | | MV074 | None | 0.468 | ND | 234. | ND |
| Wash wastewater | 36.9 | MV077 | None | 0.118 | ND | 59 | ND |
| | | MV078 | Acidified | ND | 0.127 | ND | 63.4 |
| Distillate wastewater | 0.74 | MV080 | None | ND | ND | ND | ND |
| | | MV081 | Acidified | ND | ND | ND | ND |

Table 15 Average metal concentration (ppm) and solution conductivity (mS/cm)
in cobalt drier samples collected from Reactor 6 on 6.3.06

| Source of sample | Cond | Sample number | Sample treatment | Analytical sample | | Original sample | |
|-------------------------------------|------|---------------|------------------|-------------------|------|-----------------|------|
| | | | | [Co] | [Mn] | [Co] | [Mn] |
| Solvent wastewater sampled at 18:55 | 128 | MV083 | None | 0.208 | ND | 104 | ND |
| | | MV085 | None | 0.171 | ND | 85.5 | ND |
| Solvent wastewater sampled at 19:25 | 102 | MV086 | None | 0.203 | ND | 101.5 | ND |
| | | MV088 | None | 0.173 | ND | 86.5 | ND |
| Solvent wastewater sampled at 20:25 | 111 | MV090 | None | 0.193 | ND | 96.5 | ND |
| | | MV091 | None | 0.234 | ND | 117 | ND |
| Wash wastewater | 40.8 | MV093 | None | ND | ND | ND | ND |
| | | MV094 | Acidified | 0.132 | ND | 66 | ND |
| Distillate wastewater | ND | MV095 | None | ND | ND | ND | ND |
| | | MV097 | Acidified | ND | ND | ND | ND |

Table 16 Average metal concentration (ppm) and solution conductivity (mS/cm)
in cobalt drier samples collected from Reactor 6 on 14.3.06

| Source of sample | Cond | Sample number | Sample treatment | Analytical sample | | Original sample | |
|-----------------------|------|---------------|------------------|-------------------|------|-----------------|------|
| | | | | [Co] | [Mn] | [Co] | [Mn] |
| Solvent wastewater | 128 | MV099 | Acidified | 0.435 | ND | 217.5 | ND |
| | | MV100 | None | 0.548 | ND | 274 | ND |
| | 126 | MV102 | None | 0.569 | ND | 284.5 | ND |
| | | MV103 | Acidified | 0.427 | ND | 213.5 | ND |
| Wash wastewater | 38 | MV104 | None | 0.277 | ND | 138.5 | ND |
| | | MV106 | Acidified | 0.126 | ND | 63 | ND |
| | | MV108 | None | 0.201 | ND | 100.5 | ND |
| | | MV109 | Acidified | 0.412 | ND | 206 | ND |
| | | MV110 | None | 0.205 | ND | 102.5 | ND |
| Distillate wastewater | ND | MV115 | None | ND | ND | ND | ND |
| | | MV116 | Acidified | ND | ND | ND | ND |

Table 17 Average metal concentration (ppm) in cobalt drier samples, (N6 May 48)
collected on 31st May 2006.

| Sample source | Sampling point | Analytical sample | | | | | | | Original sample | | | | | | |
|-----------------------|----------------|-------------------|------|------|-------|------|------|------|-----------------|------|------|-------|------|------|------|
| | | [Co] | [Mn] | [Fe] | [Zn] | [Ni] | [Cu] | [Cr] | [Co] | [Mn] | [Fe] | [Zn] | [Ni] | [Cu] | [Cr] |
| Solvent wastewater | 1 L | 1.86 | ND | ND | ND | ND | ND | ND | 93.1 | ND | ND | ND | ND | ND | ND |
| | 800 L | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| | 2000 L | 1.75 | ND | ND | ND | ND | ND | ND | 87.3 | ND | ND | ND | ND | ND | ND |
| Wash wastewater | 1 | 2.37 | ND | ND | ND | ND | ND | ND | 118 | ND | ND | ND | ND | ND | ND |
| | 2 | 2.33 | ND | ND | ND | ND | ND | ND | 117 | ND | ND | ND | ND | ND | ND |
| | 3 | 1.93 | ND | ND | ND | ND | ND | ND | 96.4 | ND | ND | ND | ND | ND | ND |
| | 4 | 5.55 | ND | ND | ND | ND | ND | ND | 277 | ND | ND | ND | ND | ND | ND |
| Distillate wastewater | 1 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| | 2 | 0.196 | ND | ND | 0.019 | ND | ND | ND | 9.81 | ND | ND | 0.971 | ND | ND | ND |

Table 18 Average metal concentration (ppm) in cobalt drier samples, (N6 JUN 03)
collected on 2nd June 2006

| Sample source | Sampling point | Analytical sample | | | | | | | Original sample | | | | | | |
|--------------------|----------------|-------------------|------|------|------|------|------|------|-----------------|------|------|------|------|------|------|
| | | [Co] | [Mn] | [Fe] | [Zn] | [Ni] | [Cu] | [Cr] | [Co] | [Mn] | [Fe] | [Zn] | [Ni] | [Cu] | [Cr] |
| Solvent wastewater | 1 | 0.632 | ND | ND | ND | ND | ND | ND | 31.6 | ND | ND | ND | ND | ND | ND |
| | 2 | 1.31 | ND | ND | ND | ND | ND | ND | 65.5 | ND | ND | ND | ND | ND | ND |
| | 3 | 2.84 | ND | ND | ND | ND | ND | ND | 142 | ND | ND | ND | ND | ND | ND |
| Wash wastewater | Fast | 2.50 | ND | ND | ND | ND | ND | ND | 125 | ND | ND | ND | ND | ND | ND |
| | Slow | 1.47 | ND | ND | ND | ND | ND | ND | 73.5 | ND | ND | ND | ND | ND | ND |
| | 1L | 2.35 | ND | ND | ND | ND | ND | ND | 117 | ND | ND | ND | ND | ND | ND |
| | No number | 2.53 | ND | ND | ND | ND | ND | ND | 126 | ND | ND | ND | ND | ND | ND |

The entries in the second column of Tables 17 and 18 are described in section 2.3 above.

5. DISCUSSION

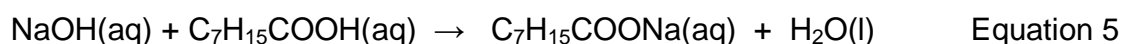
In this section the levels of cobalt, manganese, sodium and sulfate in the solvent water are estimated from the specified quantities. These estimated concentrations are then compared to those measured in solvent wastewater, wash wastewater and distillate wastewater solution and the results expressed as dilution factors where appropriate.

The company produces (an untitled) document that prescribes the specification as the percentage composition of the reaction mixture which goes into the reactor. It also gives a batch size for the output {cobalt octoate in white spirit (w/s)} mass. A second instruction-type document goes out to the operator who is making the batch on the plant. It is entitled the "Standard Manufacturing Formulation", SMF. This quotes the percentage composition (as given in the formulation specification of the first document) and the actual masses (kg) of each raw material which will be used in that particular batch. A rough estimate of the cobalt, sodium and sulfate levels in the solvent wastewater can be obtained from the figures quoted in the SFM. Table 19 shows the masses and moles of three reactants, namely cobalt sulfate heptahydrate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$), ethyl hexanoic acid (2-EH) and sodium hydroxide (NaOH) as well as the solvent which was added to the reactor for the production of 12% cobalt octoate. Water was used to dissolve the solid starting materials and white spirit to extract the cobalt octoate product from the aqueous layer. There follows an example of the calculation of the cobalt, sodium and sulfate levels in the spent solvent water using the SMF data available on-site for the cobalt octoate drier.

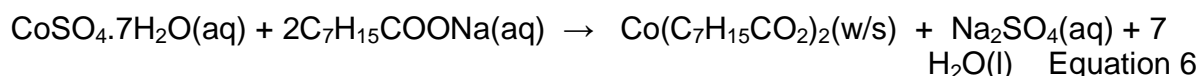
Table 19 Quantities of raw materials used to produce 3395 kg cobalt octoate

| Substance added to reactor | Mass (kg) | Moles |
|---|-----------|--------------------|
| $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ prescribed | 2000 | 7.12×10^3 |
| Co in 2000 kg in $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ | 419 | 7.12×10^3 |
| SO_4 in 2000 kg in $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ | 684 | 7.12×10^3 |
| Ethyl hexanoic acid prescribed | 2256 | 1.56×10^4 |
| NaOH prescribed | 615 | 1.54×10^4 |
| Na in 615 kg NaOH | 353 | 1.54×10^4 |
| Solvent water prescribed | 2050 | |
| White spirit prescribed | 900 | |
| $\text{Co}(\text{C}_7\text{H}_{15}\text{CO}_2)_2$ formed | 2459 | |
| Co in 2459 kg $\text{Co}(\text{C}_7\text{H}_{15}\text{CO}_2)_2$ | 419 | 7.12×10^3 |

Table 19 shows that NaOH and 2-EH are present in a 1:1 mole ratio in the reaction mixture with 2-EH slight excess. This reaction ratio is consistent with that shown in the balanced equation for the conversion of the acid to the sodium salt (see Equation 5). This means that a similar number of moles of water will be formed which is equivalent to a volume of 0.277 m^3 .



The cobalt octoate product is made during the reaction shown in Equation 6 below.



Equation 6 shows that double the number of moles of sodium octanoate are needed in order to convert all the cobalt sulfate heptahydrate into cobalt octoate. The sodium octanoate and cobalt sulfate heptahydrate are present in a 2:1 mole ratio (see Table 19) with the sodium octanoate in excess. This means that no cobalt sulfate heptahydrate should remain unreacted at the end of the run while 1.16×10^3 moles of sodium octanoate should remain unreacted. About 0.898 m^3 of water will be formed and 2459 kg of cobalt octoate will be dissolved in 900 kg of white spirit. Using values given in Table 19 and Equation 7 the percent content of cobalt in the final diluted cobalt octoate product is found to be 12% (w/w) cobalt.

$$\text{Percent of cobalt in the product} = \frac{\text{Mass of cobalt}}{(\text{Mass of cobalt octoate} + \text{Mass of white spirit})} \times 100$$

Equation 7

The mass of sulfate released into the spent solvent water is estimated at 680 kg. Considering this mass to be present in 3.225 m^3 solvent wastewater this gives a concentration of 211 g/l or 21.1%.

The sodium released is estimated to be around 353 kg in 3.225 m^3 water. This gives a concentration of 109 g/l or 10.9%.

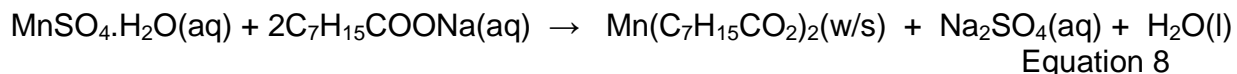
Table 20 shows the masses and moles of the raw materials manganese sulfate monohydrate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$), 2-EH and NaOH. The masses of sulfate and sodium present in the solvent wastewater are also given (see entry three and seven).

Table 20 Quantities of raw materials used to produce manganese octoate

| Substance added to reactor | 1.8 T Batch size | | 2.5 T Batch size | |
|--|------------------|-------------------------|------------------|-------------------------|
| | Mass (kg) | Moles | Mass (kg) | Moles |
| MnSO ₄ .H ₂ O prescribed | 576 | 3.41 x 10 ³ | 800 | 4.73 x 10 ³ |
| Mn in prescribed MnSO ₄ .H ₂ O | 187 | 3.41 x 10 ³ | 260 | 4.73 x 10 ³ |
| SO ₄ in prescribed MnSO ₄ .H ₂ O | 327 | 3.41 x 10 ³ | 451 | 4.73 x 10 ³ |
| Ethyl hexanoic acid prescribed | 1063 | 7.37 x 10 ³ | 1478 | 10.25 x 10 ³ |
| Priolene acid | 106 | 0.375 x 10 ³ | 148 | 0.524 x 10 ³ |
| NaOH prescribed | 270 | 6.75 x 10 ³ | 375 | 9.37 x 10 ³ |
| Na in NaOH | 155 | 6.75 x 10 ³ | 215 | 9.37 x 10 ³ |
| Solvent water prescribed | 863 | | 1200 | |
| White spirit prescribed | 273 | | 380 | |
| Methanol | 158 | | 220 | |
| Mn(C ₇ H ₁₅ CO ₂) ₂ | 1164 | 3.41 x 10 ³ | 1615 | 4.73 x 10 ³ |
| Mn in mass of Mn(C ₇ H ₁₅ CO ₂) ₂ | 187 | | 260 | |

As in the manufacture of cobalt octoate, the specification data shows that NaOH and 2-EH are present in a 1:1 mole ratio for the production of manganese octoate (see Table 20) in this reaction mixture. This is consistent with the balanced equation for the conversion of the acid to the sodium salt as shown in Equation 5. This means that a similar number of moles of water will be formed equivalent to a volume of 0.122 m³ or 0.169 m³ (see Table 20) for 1.8 T and 2.5 T of product respectively.

The manganate octoate product is made during the reaction shown in Equation 8 below.



Equation 8 shows that double the number of moles of sodium octanoate are needed in order to convert all the manganese sulfate monohydrate into manganese octoate. The sodium octanoate and manganese sulfate monohydrate are present in a 2:1 mole ratio (see Table 20) with the sodium octanoate in excess. This means that no manganese sulfate monohydrate should remain unreacted at the end of the run. About 0.0614 m³ and 0.0852 m³ of water for 1.8 T and 2.5 T batch respectively will be formed.

The mass of sulfate released into the spent solvent water is estimated at 327 kg and 451 kg for 1.8 T and 2.5 T of product respectively. Considering this mass to be present in 1.046 m³ and 1.454 m³ water gives a concentration of 313 g/l or 31.3% and 310g/l or 31.0% for 1.8 T and 2.5 T of product respectively.

The sodium released is estimated to be around 155 kg and 215 kg in 1.046 m³ and 1.454 m³ water respectively. This gives a concentration of 148 g/l or 14.8% for both 1.8 T and 2.5 T of product.

A comparison of the analytical results from the acidified and non-acidified sample of all the samples taken showed very similar results for both driers. Some of the results

(about 46%) had the concentrations measured in the acidified sample showing slightly lower values. This has led to the introduction of closer monitoring of the solution samples' pH during sampling.

The levels of manganese leaving the reactor in the wastewater were found to be far greater than those of cobalt. On average, levels of manganese in wastewaters were 27 times greater than those of cobalt.

Results given in Tables 13-16 show that the average cobalt concentration levels in the solvent wastewater are higher than those of the wash wastewater. The approximate average level of cobalt in the solvent wastewater is 192 ppm (0.019%) (see Tables 13 to 16) and in the wash wastewater is 87 ppm (0.0087%).

The concentration of the Co in the solvent water of the reaction mixture is estimated at 2.04×10^5 ppm for the start of the process. This means that after the chemical reaction has taken place, the Co levels in the solvent have been reduced by over 1000 fold. After the product had been washed, the Co levels have been lowered by just over half. This gives a 2 fold dilution of the wastewater by washing the spent solvent.

Some results had been rejected because they were thought to be unreliable and not fully representative of the situation being sampled. Such samples have been rejected on one of two counts. These are 1) the likely contamination of the sample during sampling or when storing the sample and 2) taking an insufficient number of samples from a run. In both these cases the result for the measured concentration of the discharged wastewaters would be considered unreliable. Possible contamination of the distillate sample during taking samples MVD1 MVD2 could have occurred (see Table 13). This could have been so because the distillate was scooped from the bottom of the collecting drum that may not have been thoroughly cleaned.

Manganese levels recorded for two different runs (see Tables 11 and 12) were found to differ by a factor of 3. The average level of manganese in the solvent wastewater for the batch collected on 27.1.06 was 7.38×10^3 ppm (see Tables 11) whereas those of batch collected on the 27.2.06 was 2.86×10^3 ppm (see Tables 12). The latter value was obtained from seven samples taken at three different times during the solvent wastewater release from the reactor. The data in Table 20 show that 2.17×10^5 ppm of Mn was present in both reaction mixtures at the start of each reaction. This means there was about 75 fold decrease in the Mn levels at the end for the batch run on 27.2.06. Only two samples were taken from the batch collected on 27.1.06, both at the same time, during solvent wastewater discharge. The average concentration of manganese was found to be 7.38×10^3 ppm which indicates a 29 fold decrease in manganese levels compared to the starting mixture concentration. However other samples would need to have been taken to make any sensible interpretation of this. The different results from the two different batch sizes is surprising as the reaction ratios were the same. There may have been a production issue unbeknown to us which could have affected either of the results. The batch collected on 27.1.06 showed traces of cobalt whereas batch collected on the 27.2.06 showed nothing in the distillate water. This distillate was

collected by the company's employees and was thought to have been scooped from the collecting drum as explained before.

Results obtained from Mn, Fe, Zn, Ni, Cu and Cr analyses of samples provided by the company showed that none of these trace elements (see Tables 17 and 18) were present at or above respective concentrations 0.80 ppm, 0.30 ppm, 0.20ppm, 0.60 ppm, 0.40 ppm and 0.20ppm. In the 4 cobalt drier processes analysed (see Table 2 entries 2) the solvent wastewater had a higher (about double) concentration than the wash wastewater. The opposite trend is observed with these two batches (see Table 2 entries 3). The average cobalt concentration in the solvent wastewater was lower than that of the wash wastewater by a difference of 35%. The levels were low however so this trend may not be significant. There is no information on the solution pH or how the manufacture of the drier was being carried out to help understand these findings.

6 CONCLUSION

In this section the proposed sampling protocol and analytical procedures which will be used to monitor the Co and Mn drier solutions will be presented. Sampling will be discussed first, then sample and calibration standards preparation.

Sampling would be best done by the researchers. This means that Metallica Chemicals must inform the research team as far in advance as possible as to when they are making batches. On occasions where it is impossible for the research team to get on-site, company staff may take samples. Buckets containing HDPE bottles will be left on site for company personnel to use. It must be insured that at least four samples are taken in 500 ml bottles from the solvent wastewater coming off (the spent reaction solution) with about 15 minutes between each sample and one being taken close to the end of the discharge. The date and time of sampling, the batch number, the wastewater type must be recorded. It would be most helpful if a Standard Manufacturing Formulation sheet used at the processing plant is made available to the research team for each batch samples collected.

Samples have to be diluted prior to measuring their concentrations by ICP-OES. However not all species being measured require dilution by the same factor. Therefore four sets of standards will be prepared and used in the analyses. These are

- cobalt (see Table 21)
- manganese (see Table 22)
- sodium and sulfur (see Table 23) and
- trace elements (see Table 24)

The calibration standards will be prepared in a 100 ml volumetric flask according to the information provided in Tables 21, 22, 23 and 24.

Exactly 1.0 ml of sample will be diluted to 100 ml in order to make the analytical sample for the ICP-OES analyses of cobalt, manganese and trace elements.

Based on the calculations mentioned under Section 5, the concentration of the sulfate and sodium ions in the cobalt solvent wastewater is estimated to be slightly lower than 2.10×10^5 ppm and 1.10×10^5 ppm respectively. This shows that the resulting diluted sample will have concentrations slightly lower than 2100 ppm and 1100 ppm for sulfate and sodium ions respectively. The wash wastewater is assumed to have sulfate and sodium concentration of about 1000 ppm and 500 ppm respectively based on the cobalt dilution factor for washing wastewater. The sulfur concentration in the cobalt solvent wastewater is estimated at 700 ppm and so the wash wastewater would be expected to be approximately half that value.

For manganese drier, the sulfate and sodium levels in the diluted solvent wastewater sample are estimated to be lower than 3150 ppm and 1500 ppm for both batch sizes respectively. The sulfur concentration will be about 900 ppm. The sodium concentrations mentioned above are acceptable in that they should not damage the ICP-OES lamp but are too high to allow preparation of suitable calibration standards (see Table 23). Hence, when measuring the sulfur and the sodium elements, the sample will be diluted by a factor of 1000. This will give a solution with sulfur and sodium concentrations of 70 or 90 ppm and 110 or 150 ppm for cobalt and manganese driers respectively.

Table 21 Calibration standards for Co analysis

| Standard number | Concentration (ppm) of cobalt standard | Volume of Co (25 ppm) standard (ml) |
|-----------------|--|-------------------------------------|
| 1 | 0.050 | 0.20 |
| 2 | 0.10 | 0.40 |
| 3 | 0.20 | 0.80 |
| 4 | 0.50 | 2.0 |
| 5 | 1.0 | 4.0 |
| 6 | 5.0 | 20 |
| 7 | 10 | 40 |
| 8 | 15 | 60 |

Table 22 Calibration standards for Mn analysis

| Standard number | Concentration (ppm) manganese standard | Volume of Mn (50 ppm) standard (ml) |
|-----------------|--|-------------------------------------|
| 1 | 0.010 | 0.020 |
| 2 | 0.10 | 0.20 |
| 3 | 0.50 | 1.0 |
| 4 | 5.0 | 10 |
| 5 | 10 | 20 |
| 6 | 20 | 40 |
| 7 | 30 | 60 |
| 8 | 35 | 70 |

Table 23 Mixed calibration standards for Na and S analysis

| Standard number | Concentration (ppm) sodium standard | Concentration (ppm) sulfur standard | Volume of mixed Na (400 ppm) and S (300 ppm) standard (ml) |
|-----------------|-------------------------------------|-------------------------------------|--|
| 1 | 10 | 7.5 | 2.5 |
| 2 | 20 | 15 | 5.0 |
| 3 | 40 | 30 | 10 |
| 4 | 80 | 60 | 20 |
| 5 | 120 | 90 | 30 |
| 6 | 160 | 120 | 40 |
| 7 | 200 | 150 | 50 |
| 8 | 240 | 180 | 60 |

The mixed standard (see column 3 Table 23) of Na (400 ppm) and S (300 ppm) will be prepared by pipeting 100.0 ml and 75.00 ml respectively of the commercial standards (1000 ppm) in a 250.0 ml flask.

A set of calibration mixed standard for trace elements will be prepared containing the Fe, Zn, Cu, Ni and Cr and separate standard of Co and Mn. Note that when analysing wastewater from a cobalt drier batch, manganese will be treated as a trace element. The opposite will hold when analysing wastewater from manganese drier and so cobalt will be treated as a trace element. Calibration standards for major element, i.e. cobalt and manganese will not be mixed with those for other elements and will be run as a separate standard solution. The lowest calibration standard of Fe, Zn, Cu, Ni and Cr will be 0.005 ppm (see Table 24). This will be used in establishing the detection limit of the instrument.

Table 24 Mixed calibration standards for Co, Mn, Fe, Zn, Cu, Ni and Cr trace elements

| Standard number | Concentration (ppm) of Co, Mn, Fe, Zn, Cu, Ni and Cr standard | Volumes of a 10 ppm mixed standard (ml) |
|-----------------|---|---|
| 1 | 0.0050 | 0.050 |
| 2 | 0.010 | 0.10 |
| 3 | 0.050 | 0.50 |
| 4 | 0.50 | 5.0 |
| 5 | 1.0 | 10 |
| 6 | 1.5 | 15 |
| 7 | 2.0 | 20 |

The mixed standard used (see column 3 Table 24) of 10 ppm Co, Mn, Fe, Zn, Cu, Ni and Cr will be prepared by pipeting 1.0 ml of each commercial standards (1000 ppm) into a 100 ml flask and dilute to the mark.

To check for any instrument drift, standards will randomly be analysed after every ten samples had been analysed. This will help identify any errors that occur from the instrumental analyses as distinct from sampling or sample preparation errors. In all analyses, a water sample collected on site will be run along with the samples.

Appendix F

Feasibility study on cobalt paint drier production routes: Hydroxide versus Sulfate route.

COBALT PRICING, Hydroxide vs. Sulphate

a) Hydroxide Route:



Basis: 1 kg of $\text{Co(RCOO)}_2 = 0.0029\text{kmol}$



Raw Material Costs

$\text{Co(OH)}_2 = \text{R}142/\text{kg} \times 270\text{kg} = \text{R}38\,475$
 $\text{RCOOH} = \text{R}11.62/\text{kg} \times 840\text{kg} = \text{R}9\,760.8$
 $\text{W/Spirits} = \text{R}4.94/\text{kg} \times 395\text{kg} = \text{R}1\,951.3$
R50 187.1 for 1395kg of Co(RCOO)_2

Therefore, RM cost per kg of $\text{Co(RCOO)}_2 = \text{R}35.98$

Labour Costs for Production:

Cost of labour per hour = R53.99

Time taken for a 3400kg batch of $\text{Co(RCOO)}_2 = 8$ hours

Total labour cost per 3400kg batch = R431.92

Therefore, labour cost per kg of $\text{Co(RCOO)}_2 = \text{R}0.13$

Effluent Costs:

No effluent generated from the process, therefore R0.0/kg effluent costs

Energy Costs (Lo10):

Cost of Lo10 = R4/L

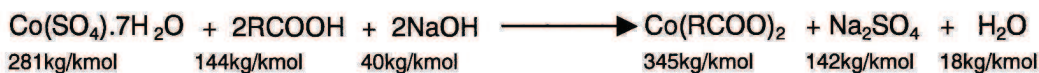
Boiler on for 5 hours at 100L/hr consumption of Lo10

Cost of Lo10 for 3400kg batch = R2000

Therefore, fuel cost per kg of $\text{Co(RCOO)}_2 = \text{R}0.59$

| |
|---|
| Total Cost per kg of Co(RCOO)_2 using $\text{Co(OH)}_2 = \text{R}36.70$ |
|---|

b) Sulphate Route:



Basis: 1 kg of $\text{Co(RCOO)}_2 = 0.0029\text{kmol}$

| | | | | | | |
|--------|----------|----------|---|--------|----------|----------|
| 0.81kg | + 0.84kg | + 0.23kg | → | 1kg | + 0.41kg | + 0.23kg |
| 810kg | + 840kg | + 230kg | → | 1000kg | + 410kg | + 230kg |

Raw Material Costs:

$\text{Co(SO}_4\text{)} \cdot 7\text{H}_2\text{O} = \text{R}38.52 / \text{kg} \times 810\text{kg} = \text{R}31\,202.2$

$\text{RCOOH} = \text{R}11.62 / \text{kg} \times 840\text{kg} = \text{R}9\,760.8$

$\text{NaOH} = \text{R}3.95 / \text{kg} \times 230\text{kg} = \text{R}908.5$

$\text{W/Spirits} = \text{R}4.94 / \text{kg} \times 417\text{kg} = \text{R}2\,060$

R43 930.5 for 1417kg of Co(RCOO)_2

Therefore, RM cost per kg of $\text{Co(RCOO)}_2 = \text{R}31.00$

Labour Costs for Production:

Cost of labour per hour = R53.99

Time taken for a 3400kg batch of $\text{Co(RCOO)}_2 = 20$ hours

Total labour cost per 3400kg batch = R1 079.8

Therefore, labour cost per kg of $\text{Co(RCOO)}_2 = \text{R}0.32$

Effluent Costs:

A batch of 3400kg of Co(RCOO)_2 generates 4000L of effluent

Cost to dispose 4000L of effluent = R2400

Effluent disposal cost per kg of $\text{Co(RCOO)}_2 = \text{R}0.70$

Cost per kg of Co(RCOO)_2 to clean out effluent sumps = $\text{R}35\,000 / 240\,000\text{kg} = \text{R}0.15$

Therefore, total effluent cost per kg of $\text{Co(RCOO)}_2 = \text{R}0.85$

Energy Costs (Lo10):

Cost of Lo10 = R4/L

Boiler on for 13 hours at 100L/hr consumption of Lo10

Cost of Lo10 for 3400kg batch = R5 200

Therefore, fuel cost per kg of $\text{Co(RCOO)}_2 = \text{R}1.52$

| |
|---|
| Total Cost per kg of Co(RCOO)_2 using $\text{CoSO}_4 \cdot 7\text{H}_2\text{O} = \text{R}33.69$ |
|---|

Conclusion and Recommendation

The hydroxide route is 60% shorter and is a cleaner process (no effluent generated). However, it is R3.01 more expensive than the sulphate route.

I believe the R3.01 premium is too expensive taking into account the current demand for Driers and the ongoing need for us to be as price competitive as possible. Also, cobalt production has been very smooth since the Versatic acid substitution has been limited to 10% of 2-EH acid.

However, if at a later stage the demand of Cobalt and Cobalt based driers increases to a

substantial point, resulting in the plants not being able to meet demand (plant capacity constraints), I would recommend producing Cobalt Octoate using the hydroxide route. The increased plant throughput and sales will make it more feasible for the R3.01 premium to be absorbed.

Under the current conditions, I believe we should continue to manufacture Cobalt Octoate via the sulphate route.