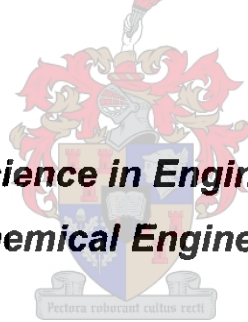


**THE DEVELOPMENT OF AN AUDIT PROCEDURE AND
TREATMENT TECHNOLOGIES FOR RUPERT AND
ROTHSCHILD VIGNERONS' WINERY WASTEWATER**

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Thesis presented in partial fulfilment of the requirements for the degree

***Master of Science in Engineering Science
(Chemical Engineering)***



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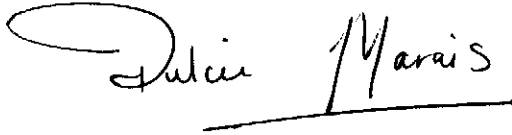
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Stellenbosch

March 2001

DECLARATION

I, the undersigned, hereby declare that the work contained in this thesis is my own original work, except where specifically acknowledged in the text. It has not previously in its entirety or in part been submitted at any university for a degree.

A handwritten signature in cursive script that reads "Dulcie Marais". The signature is written in black ink and is positioned above a horizontal line.

Dulcie Marais

February 2001

SYNOPSIS

Ecosystems and natural water sources are constantly under threat from pollutants and all efforts should be made to minimise polluting factors. In the last decade growing concern has been expressed with regard to the environmental threat posed by wastewater produced by wineries and distilleries. Research into winery wastewater commenced in the early nineties mainly in Australia and France. These investigations characterised winery wastewater, indicating a large diversity in quality and quantity between wastewaters emanating from wineries. Owing to changes in South African legislation, in conjunction with an augmented environmental awareness, the need for an environmental assessment of wineries became apparent. In South Africa, research of this nature had not yet been conducted. Previous research on winery wastewater treatment employed mostly biological technologies, with success but also shortfalls.

In South Africa the majority of wineries are located in the Western Cape Province, several within the same water catchment area. Wineries may produce approximately 1 to 10 litres of wastewater per litre of wine produced, which are turbid and acidic and typically contain high levels of organic compounds (thus oxygen deficient), and suspended material. Usually these wastewaters are irrigated onto land, in close proximity to natural water resources. The pollution of water tables and down-stream water sources may occur. The quantification, qualification and treatment of this type of wastewater are addressed in this study.

Winery wastewater produced from the predominantly red wine producing Rupert and Rothschild Vignerons, served as case study for a two-year wastewater audit strategy. The most common analyses performed on winery wastewater include the Chemical Oxygen Demand (COD), suspended solids (SS), pH and turbidity. A thorough analysis in the form of a comprehensive audit was performed on the water and vinification processes. This allowed for an accurate determination of contamination sources and properties. The audit

entailed a designed sampling protocol, the format of which was tailored as an initial environmental assessment for the development of an Environmental Management System (EMS) unique to Rupert and Rothschild Vignerons. The EMS includes projected future objectives for wastewater quality (COD, SS, pH, turbidity), as well as an environmental policy. In order to reach the proposed quality objectives, a suitable wastewater treatment system must be installed.

The efficiency of the treatment system present at Rupert and Rothschild Vignerons was evaluated and piloted the investigation of physico-chemical treatment technologies. Research into the applicability of induced sedimentation (coagulation) and chemical oxidation (ozone) was the first of its kind for winery wastewater as substrate, and provided an interesting dimension in the sense of pragmatic and economic feasibility.

Dissolved and suspended particles present in winery wastewater do not settle by gravity alone, thus requiring sedimentation agents (coagulants). Bench-scale experiments were conducted employing four types of pre-polymerised metal salt coagulants (polyaluminium chloride). Successful sedimentation of turbidity inducing compounds (up to 98 %) and suspended solid fractions (up to 92%) was achieved. These coagulants are highly suitable for the treatment of winery wastewater since the investigation showed that they are effective over a broad pH and dosage range. In addition, rapid sedimentation rates were observed, favouring thickener design economy.

Ozone is a potent oxidising agent, and has been reported to increase the biodegradability of dissolved organic compounds and result in the decolouring of wastewaters. Ozonation is highly pH dependent, with hydroxyl radical activity dominating at alkaline pH. In the majority of gas-liquid contacting systems, the kinetics of the heterogeneous reaction is not limited by the chemical reaction rate, but by the transport of ozone to the liquid phase. To compensate, the ozone concentration in the gas phase is increased. Coupled to the primary investigation on the applicability of ozone treatment for winery wastewater, thus emerged a secondary investigation into an enhanced mass

transfer system, realised by the use of impinging stream technology. The ozone transfer in a conventional bubble-column was compared to that of an impinging-stream jet-reactor. The latter significantly improved the ozone transfer to the winery wastewater, resulting in the rate-limiting step being the chemical reaction rate. Ozonation resulted in the increased biodegradability of the winery wastewater, and complete colour and odour elimination. Concerning jet-reactors, the principal importance lies in the substantial reduction in the initial ozone concentration requirement, thereby rendering the process more economically feasible.

Following the investigation of the wastewater dynamics, the determination of eco-toxicology during irrigation should be conducted in future. When considering induced sedimentation, further studies should be directed towards ascertaining the most economic yet efficient dosage of the coagulant. Similarly, a study concerning the economic viability of ozone efficiency should be realised in terms of the energy requirements for both ozone generation and the operation of jet-reactors. Although the jet reactor poses a benefit for enhanced mass transfer, the essential criterion concerning residence time in the reactor must be addressed for positive results.

Since no single solution exists for the treatment of winery wastewaters, the application of the considered technology must be carefully selected and incorporated in a treatment design; the two foremost criteria for selection being efficiency and economy.

OPSOMMING

Ekologiese stelsels en natuurlike waterbronne word gedurig bedreig deur besoedeling, dus moet ten alle tye gepoog word om besoedeling te minimiseer of te voorkom. Gedurende die laaste dekade is al hoe meer kommer uitgespreek oor die besoedeling van afloop water afkomstig van wyn en spiritueel-vervaardiging. Navorsing aangaande wynafloopwater het ontstaan in die vroeë negentigs, hoofsaaklik in Australie en Frankryk. Hierdie navorsing het gelei tot die karakterisering van wynafloopwater, en die uiteenlopendheid van hierdie water aangaande die kwaliteit en kwantiteit tussen kelders, is aangetoon. As gevolg van veranderinge in die Suid-Afrikaanse wetgewing, asook 'n groeiende bewuswording van omgewingsake, het die noodsaaklikheid van omgewings impak-studies vir wynkelders na vore getree. Tot op hede is navorsing van hierdie aard nog nie in Suid Afrika gedoen nie. Vorige navorsing op die behandeling van wynafloopwater het meestal biologiese tegnologieë behels, met 'n mate van sukses maar ook met tekortkominge.

Die meederheid wynkelders in Suid Afrika is in die Wes-Kaap geleë, baie binne dieselfde opvanggebied. Wynkelders kan tussen 1 tot 10 liter afloop water produseer per liter wyn geproduseer. Hierdie afloop het tipies 'n hoë konsentrasie organiese stowwe (is dus arm aan suurstof), is troebel en suur, en bevat gesuspendeerde materiaal. Gewoonlik word die wynafloop water besproei in die nabyheid van natuurlike waterbronne. Die besoedeling van watertafels en waterbronne kan dus plaasvind. Die kwantifisering, kwalifisering en behandeling van wynafloopwater word ondersoek in hierdie tesis.

Die wynafloopwater van die hoofsaaklik rooiwyn produserende Rupert en Rothschild Vignerons, het gedien as proefstudie tydens 'n twee-jaar wynafloopwateraudit. 'n Deeglike analise in die formaat van 'n veelomvattende oudit is uitgevoer op die wynmaakproses en die waterafvoerstrome. 'n Akkurate bepaling van die oorsprong van

waterkontaminasie, asook die eienskappe daarvan is bewerkstellig. Die oudit behels 'n spesifiek ontwerpte monsternemingprotokol, waarvan die formaat geformuleer is om te dien as 'n beginpunt vir die ontwikkeling van 'n Omgewingsbestuurstelsel (OBS), uniek vir Rupert en Rothschild Vignerons. Hierdie OBS sluit toekomstige doelstellings vir die kwaliteit (chemiese suurstofbehoefte, gesuspendeerde vaste stowwe, pH, turbiditeit) van wynafloopwater in, asook 'n omgewingsbeleid. Die installering van 'n waterbehandelingsstelsel moet geskied om te voldoen aan hierdie voorgestelde doelstellings.

Die effektiwiteit van die huidige behandeling stelsel teenwoordig by Rupert en Rothschild Vignerons is geëvalueer en het gelei tot navorsing oor fisies-chemiese behandelingstechnologieë. Navorsing aangaande die toepassing van geïnduseerde sedimentasie (koagulasie) en chemiese oksidasie (osoon), is vir die eerste keer toegepas op wynafloopwater, en het interessante gevolge in 'n pragmatiese en ekonomiese sin.

Opgeloste en gesuspendeerde partikels teenwoordig in wynafloopwater sak nie onder normale gravitasie uit nie, en dus word die toediening van sedimentasie-induserende middels benodig. Eksperimente is in die laboratorium uitgevoer met vier verskillende gepolimeriseerde metaalsoutkoagulante (poli-aluminiumchloriedes). Dit het gelei tot die effektiewe sedimentering van stowwe wat troebelheid (turbiditeit) veroorsaak (tot 98 %) en ook gesuspendeerde stowwe (tot 92 %). Dit is gevind dat hierdie tipe koagulante hoogs geskik is vir die behandeling van wynafloopwater, aangesien hulle effektief is by 'n wye pH- en doseringsreeks. Die uitsaktempo is vinnig, wat dus die ontwerp van 'n uitsaktenk (verdikker) ekonomies maak.

Osoon is 'n sterk oksideermiddel, terwyl talle verslae aandui dat dit die biologiese ontbinding van opgeloste stowwe verhoog en die ontkleuring van afloopwaters tot gevolg het. Osonering is pH afhanklik; by alkaliese pH oorheers die werking van hidroksielradikale. In die meerderheid gas-vloeistofkontakstelsels word die kinetika van die heterogene chemiese

reaksie nie beperk deur die intrinsieke reaksietempo nie, maar deur die vervoer van osoon na die vloeistoffase. Om te kompenseer hiervoor, word die osoon konsentrasie in die gasfase verhoog. Gekoppel aan die primêre ondersoek aangaande die toepasbaarheid van osoonbehandeling op wynafloopwater, het 'n tweede ondersoek ontstaan aangaande verhoogde massa-oordragstelsels deur die gebruik van hoëintensiteit spuitreaktore. Die osoonoordrag in konvensionele borrelkolomme is vergelyk met die van 'n hoë intensiteit spuitreaktor. Laasgenoemde het die osoonoordrag na die wynafloopwater aansienlik verhoog, met die gevolg dat die chemiese reaksie die beperking op die reaksie tempo geplaas het. Osonering het die biodegradasie van die wynafloop water verhoog, asook die kleur en reuk verwyder. By die spuit-reaktor lê die belangrikheid daarin by die aansienlike verlaging in die aanvanklike behoefte aan osoonkonsentrasie, derhalwe is hierdie oordragstelsel meer ekonomies.

Na afloop van die ondersoek op die dinamika van wynafloopwater, moet die ekotoksisiteit gedurende besproeiing bepaal word vir toekomstige doeleindes. Indien geïnduseerde sedimentasie verlang word, kan verdere studie gedoen word om die mees ekonomiese dosis van die koagulant te bepaal. Ooreenstemmend, moet die ekonomiese lewensvatbaarheid van die osoon effektiwiteit bepaal word ten opsigte van die energiebehoefte van beide die osoongenerasie en die werking van die hoë-intensiteit spuitreaktor. Alhoewel die spuitreaktor verhoogde massa-oordrag bewerkstellig, moet die effek van die residensityd in die reaktor inag geneem word ten einde positiewe resultate te verkry.

Geen enkele oplossing bestaan vir die behandeling van wynafloop water nie, derhalwe moet die toepassing van die beoogde stelsel versigtig gekies word en ingesluit word in die ontwerp van 'n behandelingsstelsel; die twee vernaamste maatstawwe is ondermeer effektiwiteit en ekonomiese aspekte.

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My Heavenly Father, for saving me by showing me the way.

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I dedicate this thesis to my outstanding parents, Ria and Etienne, whom I love and treasure. Thank you for your eternal faith, support and love. Even a poetic dissertation could not explain the infinity of my appreciation.

Vivez Les Marais!

"Nothing goes by luck in composition. It allows of no tricks. The best you can write will be the best you are."

Thoreau

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NOMENCLATURE

<i>BOD</i>	Biological Oxygen Demand	mg/L
<i>COD</i>	Chemical Oxygen Demand	mg/L
<i>DOC</i>	Dissolved Organic Carbon	mg/L
<i>EC</i>	Electrical Conductivity	mS/m
k_L	Liquid film mass transfer coefficient	m/s
k_{La}	Mass transfer coefficient	s ⁻¹
<i>SS</i>	Suspended Solids	mg/L
<i>SAR</i>	Sodium Absorption Ratio	
<i>TDS</i>	Total Dissolved Solids	mg/L
<i>EMS</i>	Environmental Management System	
<i>NWA</i>	National Water Act	
<i>PPA</i>	Potential Problem Analysis	

CHAPTER 1

INTRODUCTION

It is the aim of this chapter to motivate the study of winery wastewater and treatment thereof. Furthermore, it is endeavoured to convey the strategy that was employed to investigate and evaluate the water processes at Rupert and Rothschild Vignerons. The role of an environmental management system and the development of sustainable treatment technologies will also be revealed. The objectives of this study will be illustrated and the framework of the thesis presented.

1.1 MOTIVATION FOR THIS STUDY

In recent years environmental regulations have become increasingly stringent. The activities of the Wine Industry in South Africa represent a very important sector in the economy and culture of this country. As in any Agricultural Industry, the winery activity leads, unavoidably, to the production of wastewater. With the advent of the National Water Act (*Muller, 1998*), new regulations are imposed on producers in terms of wastewater quality and quantity. Authorities now also require data pertaining to the consumption of water and discharge of wastewater.

Research has been conducted in several other vinification countries pertaining to the production of wastewater and subsequent treatment thereof. However, in South Africa, no research had been conducted, prior to the commence of this project.

Owing to the environmental awareness of Rupert and Rothschild Vignerons, and their interest in ISO 14000 accreditation, an investigation was launched with Rupert and Rothschild Vignerons as case study. No winery in South Africa has been accredited with ISO 14000 status to date.

1.2 AUDITING THE WASTEWATER PROCESS

A comprehensive literature review provided insight into the properties of the wastewater. The 2nd International Conference on Winery Wastewater was presented in 1998, containing the most recent advances made internationally. The findings are discussed in *Chapter 2*.

Due to the seasonal attribute, the wine industry's most significant production of wastewater occurs during the grape harvesting period from January to March. However, cellar operations are conducted throughout the year to produce the final product. The evaluation of the wastewater production was segregated into two divisions: firstly the harvest period (crushing and fermentation); and secondly the year-round activities imposed by racking, blending and bottling.

A sampling strategy allowed for an accurate portrayal of the wastewater characteristics, finding that winery wastewaters exhibit extreme fluctuations in component concentration on a daily basis. *Chapter 3* illustrates the cellar dynamics and the audit procedure. Winery wastewater originating from red wine production is highly turbid. These waters are also oxygen deficient, measured in terms of the chemical oxygen demand (COD). The turbidity is principally ascribed to the presence of anthocyanin molecules, originating from red grapes. The evaluation of the contamination matrix indicates that cellar sanitising agents, lees (yeast cells), grape solids and wine constituents (alcohol) are the major contaminating agents. The results of the component concentrations are discussed in *Chapter 4*.

Of equal importance is the quantity of water consumption by the cellar. Wastewater mainly originates from cleaning activities. Since wine is a beverage for human consumption, extensive sanitary conditions must be maintained. Water consumption for cleaning activities varies according the vinification methodology. The use of small fermentation vessels, increase the consumption of water. The National Water Act (*Muller, 1998*) defines two regulations for the irrigation of biodegradable wastewater: i) up to 50 m² on

any given day, and ii) up to 500 m² on any given day. The wastewater production of Rupert and Rothschild Vignerons generally falls within the first definition, although peaks of more than 50 m² were produced occasionally.

1.3 ENVIRONMENTAL MANAGEMENT SYSTEM

The wastewater audit is considered as the initial environmental review. This review determines the objectives that the winery in question must reach in order to obtain ISO 14000 accreditation. This is encompassed in an Environmental Management System, the principal of which is to illustrate that the cellar is controlling its affect on the environment based on system of continual improvement. *Chapter 5* illustrates the future objectives and environmental policy of Rupert and Rothschild Vignerons.

1.4 PHYSICO-CHEMICAL TREATMENT TECHNOLOGIES FOR WINERY WASTEWATER

The achievement of the objectives determined by the Environmental Management System, rely on the implementation of a suitable treatment technology. Biological treatment (e.g. aerobic and anaerobic ponds, biological reactors and woodlots) is most frequently employed for winery wastewater treatment. Literature reviews indicated that several problems are associated with these systems, i.e.:

- Requirement of large areas,
- High maintenance implications,
- Production of offensive odours,
- Deposition of sludge, and
- High operating costs.

It was thus decided to embark on the investigation of induced sedimentation and ozonation as alternatives. Moreover, no past studies had been conducted on these physico-chemical technologies for the treatment of winery wastewater. Also, induced settling was considered, since the presence of suspended solids and colour compounds are required to be removed by law,

and gravity did not cause their settling. A previous study on the use of chitosan addition had, however, been conducted. Although efficacious, this coagulant is exceedingly costly, thus the efficiency of polyaluminium chloride coagulants was investigated, indicating an extremely viable alternative. The sustainability of coagulation to induce sedimentation of colloidal compounds is illustrated in *Chapter 6*.

Ozonation is commonly employed for the treatment of tannery, pulp mill, olive de-bittering and textile wastewaters. The most commonly used ozone contactors are bubble columns. However, researchers have found that the true efficiency of ozonation is not realised due to limited mass transfer rates of conventional contacting systems. According to *Zhou and Smith (1997)*: "Improving the performance of ozonation should be directed to create gas bubbles the smallest as practical." Research in the field of impinging stream jet reactors provided the means to accomplish high mass transfer rates. Winery wastewaters are highly susceptible to oxidation by ozonation. Intensive investigations showed that pH and wastewater composition directly influence ozonation efficiency. *Chapter 7* provides a detailed report on the sustainability of ozone treatment, indicating operation and design considerations.

1.5 OBJECTIVES OF THIS STUDY

The specific objectives set out for this project were:

- i. Determine the origin of wastewater and the subsequent contamination produced by Rupert and Rothschild Vignerons.
- ii. Quantify and characterise the production of the wastewater from Rupert and Rothschild Vignerons.
- iii. Investigate the potential of induced sedimentation on the quality enhancement of these wastewaters.
- iv. Evaluate the sustainability of ozone treatment on winery wastewater.

The thesis framework is depicted in *Figure 1.1*.

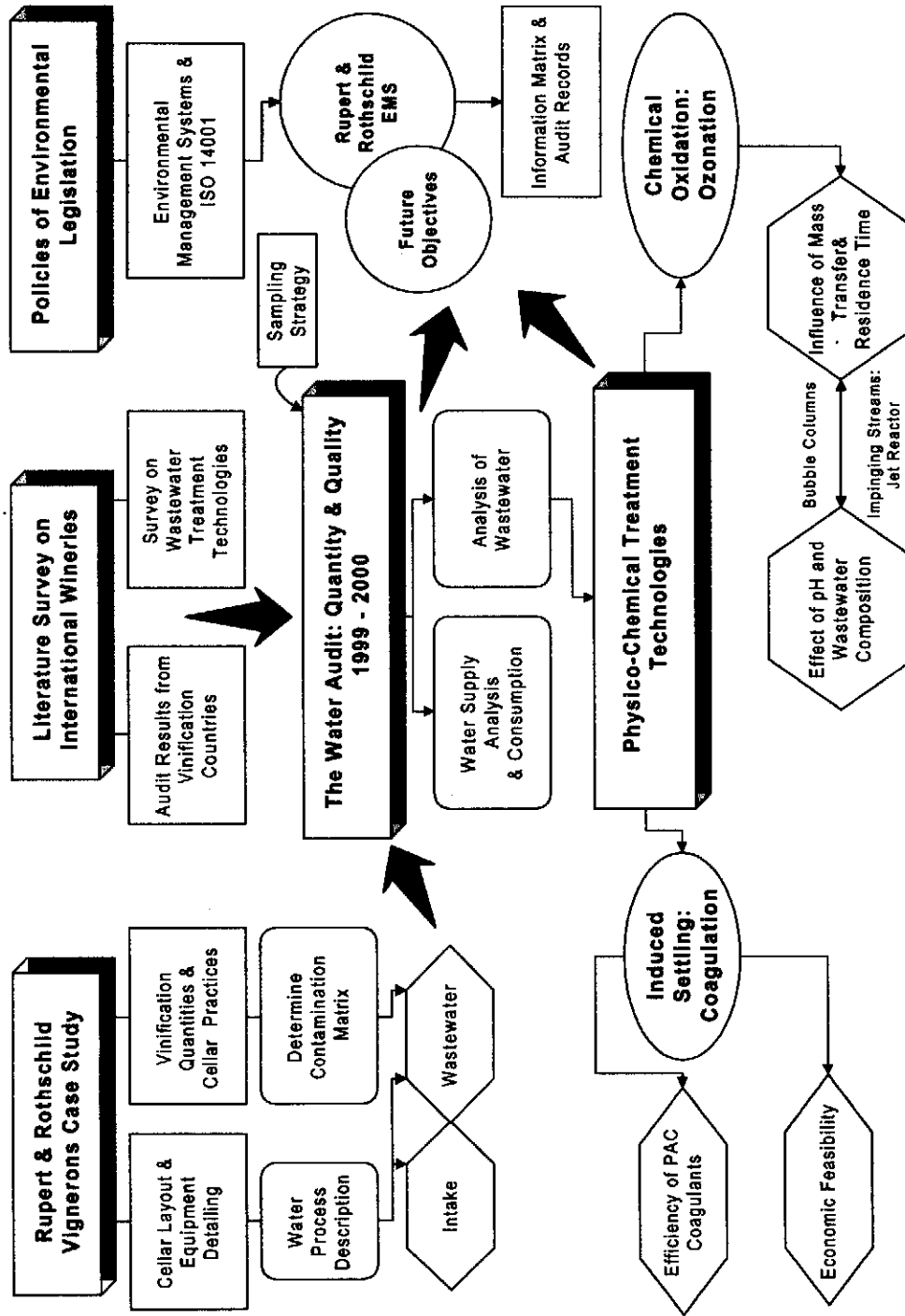


Figure 1.1 Thesis Framework

CHAPTER 2

INVESTIGATION INTO THE ORIGIN OF WINERY WASTEWATER & LITERATURE REVIEW FROM OTHER VINIFICATION COUNTRIES

The various processes of vinification all play a role in the pollution of the natural water source in a winery. The different operations comprising the crushing of grapes, cold-settling of particulate matter (*débourbage*), yeast addition (*levurage*), racking (lees removal), and cleaning of tanks, all uniquely contribute to the pollution of water. Each process also contributes to the total water consumption of the winery. In order to assess the pollution status of wastewater, several chemical properties must be analysed. The aim of this chapter is four-fold, i.e. firstly to provide background information into the winemaking practice; secondly to describe the properties to be analysed in the wastewater; thirdly to review international wastewater audits; and fourthly to review current winery wastewater treatment technologies.

2.1 THE COMPOSITION AND PROPERTIES OF GRAPES

There are several cultivars from which wine is made; Pinotage, Cabernet Sauvignon, Merlot, Shiraz, Cabernet Franc, Chardonnay, Chenin Blanc, to name a few. Each cultivar has a unique composition and structure. The properties of the cultivars ultimately influence the composition of the wastewater. The different parts of the grape berry contain different components and depending on the cellar design and practices, parts of the grape berry may enter the wastewater streams.

Although it is not possible to accurately define by weight the different parts of a grape bunch due to great variety between cultivars, *Rankine* (1989) generalised the following distribution:

- Stems: 2-8 % w/w
- Skin: 5-20 % w/w
- Flesh: 74-90 % w/w
- Pips: 0-6 % w/w

The main properties and components of grape berries are (*Rankine, 1989*):

- i. **Stalks:** The stalks contain a high concentration of potassium and acid. There is very little sugar in the stalks (± 1 %). The other component present is polyphenols that makes up between 0.5 and 3.5 percent of the stalks' weight. These polyphenols are leuco-anthocyanins and catechins and are responsible for 20 % of the tannins in the grapes
- ii. **Seeds:** The seeds contain bitter grape-seed oil. The same tannins that are present in the stalks are present in the seeds. The seed contains 50 % tannins by weight.
- iii. **Skins:** The skins contain a large concentration of sugar; mainly glucose and fructose. The concentration differs according to the cultivar and degree of ripeness. Chenin Blanc is an example of a high glucose containing cultivar, while Chardonnay contains a higher concentration of fructose. The sugar in the skin is 80 % of the sugar level in the flesh of the berry. Red and white grapes contain similar concentrations of non-pigmented tannins. Due to the presence of pigmented anthocyanins in red grapes, red cultivars contain about twice the amount of phenolics. The largest concentration of potassium is found in the skins.
- iv. **Flesh:** The flesh is the main provider of must and occupies most of the volume of the berry. The sap of the berry is mainly contained in the large fragile cells under the hypodermis. The flesh contains a high free acid to potassium ratio. In ripe grapes, the main acids are tartaric (between 5 and 10 g/L) and malic (between 2 and 4 g/L), which together constitute 90 % of the total acidity. Citric acid is hardly ever present in concentrations of more than 0.07 %. The flesh contains less than 5 % phenolics.

The indicator for ripeness is indicated by the content of soluble solids in the grape berry. Soluble solids are expressed in °Balling, with more than 90 % constituted of sugars (*Amerine and Ough, 1980*). The other constituents are organic acids, sulphate, potassium, pectins and protein. The must (non-fermented juice) contains potassium, calcium, magnesium, sodium and iron. According to *Boulton (1980)*, 1-3 g/L amino acids are present (mostly arginine and proline). Between 25-80 % of the iron naturally present in the grape berry is lost during alcoholic fermentation. The loss depends on aeration and presence of polyphenolic compounds and yeast activity. Two types of precipitation can take place: "white casse" is the precipitation of colloidal ferric phosphate, while ferric polyphenol compounds precipitate as blue film termed "blue casse" (*Amerine and Ough, 1980*).

Depending on the passage of the above components and the winemaking practices, one may gain insight into the origins of wastewater contamination (See *Section 3.3*).

2.2 THE WINE MAKING PROCESS AND THE CHEMICALS INVOLVED

Although the exact art of winemaking differs from winemaker to winemaker, and region to region, a brief description will be given to demonstrate the process flow. Since Rupert and Rothschild Vignerons produce both red and white wines, these two processes will be explained. Please note that the techniques explained are general oenology, and are not necessarily employed by Rupert and Rothschild Vignerons.

2.2.1 White Wine Making

Figure 2.1 illustrates the white winemaking procedure. Upon harvesting, grapes should be cool with a 19-24 °Balling, depending on the cultivar and desired style. Approximately 50-75 mg/L of sulphur dioxide as potassium or sodium metabisulphite is added to prevent oxidation. The grapes are destemmed and crushed. On occasion they may be pressed without de-

stemming. Tartaric acid may be added to ensure that the pH is between 3-3.4. Pectin splitting enzymes may also be added to hasten the yield of drained juice. The grapes are then passed through a mass cooler and pressed in bag filters. Sulphur dioxide is usually added (20-50 mg/L). Free-run juice refers to the unpressed juice, which is of higher quality than the juice from the pressings. This is due to the release of astringent phenolics from the skins upon pressing. Depending on the winemaking, free-run juice is separated from pressings. The juice may be clarified by means of cold-settling. However, some winemakers prefer not to clarify the juice and commence fermentation immediately. Cold settling (*débourbage*) results in a concentration of 1-2 % suspended solids in the must (thus, more than 95 % of suspended solids are settled). This step is carried out in either stainless steel tanks, epoxy coated tanks or cement tanks. The relevance of the type of tanks used lies in the required cleaning operation; certain materials need more intensive cleaning procedures, thus increasing the use of water and cleaning aids. The juice is now racked off the suspended solid sediment and alcoholic fermentation commences. Suspended material is frequently directed into wastewater streams.

Alcoholic fermentation may be natural or induced. Juice is inoculated with a yeast culture under aerobic conditions. Upon the decision to allow nature to take its course, the juice is exposed to ambient temperatures and oxygen conditions to promote the growth of natural yeasts found in the vineyard to conduct fermentation. Several ecosystems populate the grapes, ranging between yeasts, bacteria, fungi and viruses; some beneficial to the fermentation process, others detrimental. White wine fermentation is usually conducted at 10-16 °C, but certain strategies allow for even lower temperatures. The temperature of the tank is controlled either manually (as water spray on top of the tank), or by means of an external jacket containing glycol. Modern wineries install probes to measure the temperature inside the tanks. A cooling plant provides the necessary cooling, thus a source of water consumption. Fermentation may be conducted in stainless steel tanks, or barrels, depending on the cultivar and winemaker. The important role of the cultivar range is emphasised by this point. Chardonnay is a cultivar, which

may be either tank or barrel fermented, or both systems may be utilised, thus increasing the water requirement for the cleaning operation. A nitrogen source is added during fermentation (usually as di-ammonium phosphate) to ensure yeast metabolism. The sugars in the must are metabolised to several products, mainly ethanol. Once the yeast cell has performed its function, it dies and settles to the bottom of the barrel or tank, which is termed lees. Autolysis of the yeast cells release amino acids into the wine. Depending on the cultivar and style of wine, the wine may now either be racked off the gross lees, or left on the lees. The secondary settling of yeast cells is termed fine lees, and the wine must also eventually be racked. Should the passage of the lees enter the wastewater streams, it causes extensive contamination.

It is important to realise that the juice and wine is transferred between tanks and barrels regularly, directly influencing the water consumption due to the washing needs after each transfer. The wine is cold stabilised and usually fined (several fining agents exist) to prevent potassium bitartrate deposition and proteinaceous haze formation in the bottle. Young wine is saturated with potassium bitartrate and upon cooling it precipitates on the walls and floor of the storage vessels as argols (impure crystals of potassium bitartrate with wine pigment). Bentonite fining may be used to stabilise the wine against the precipitation of proteins. Bentonite is an impure hydrated aluminium silicate - usually about 90 percent montmorillonite and the other 10 percent consists of feldspar, gypsum, calcium carbonate, quartz, and traces of heavy metals. The presence of especially iron contamination of wastewater may originate from the use of bentonite. Other fining agents include gelatin, casein, insinglass, albumen, polyvinyl-polyrrolidone (PVPP) and silica soil (*Rankine, 1998*).

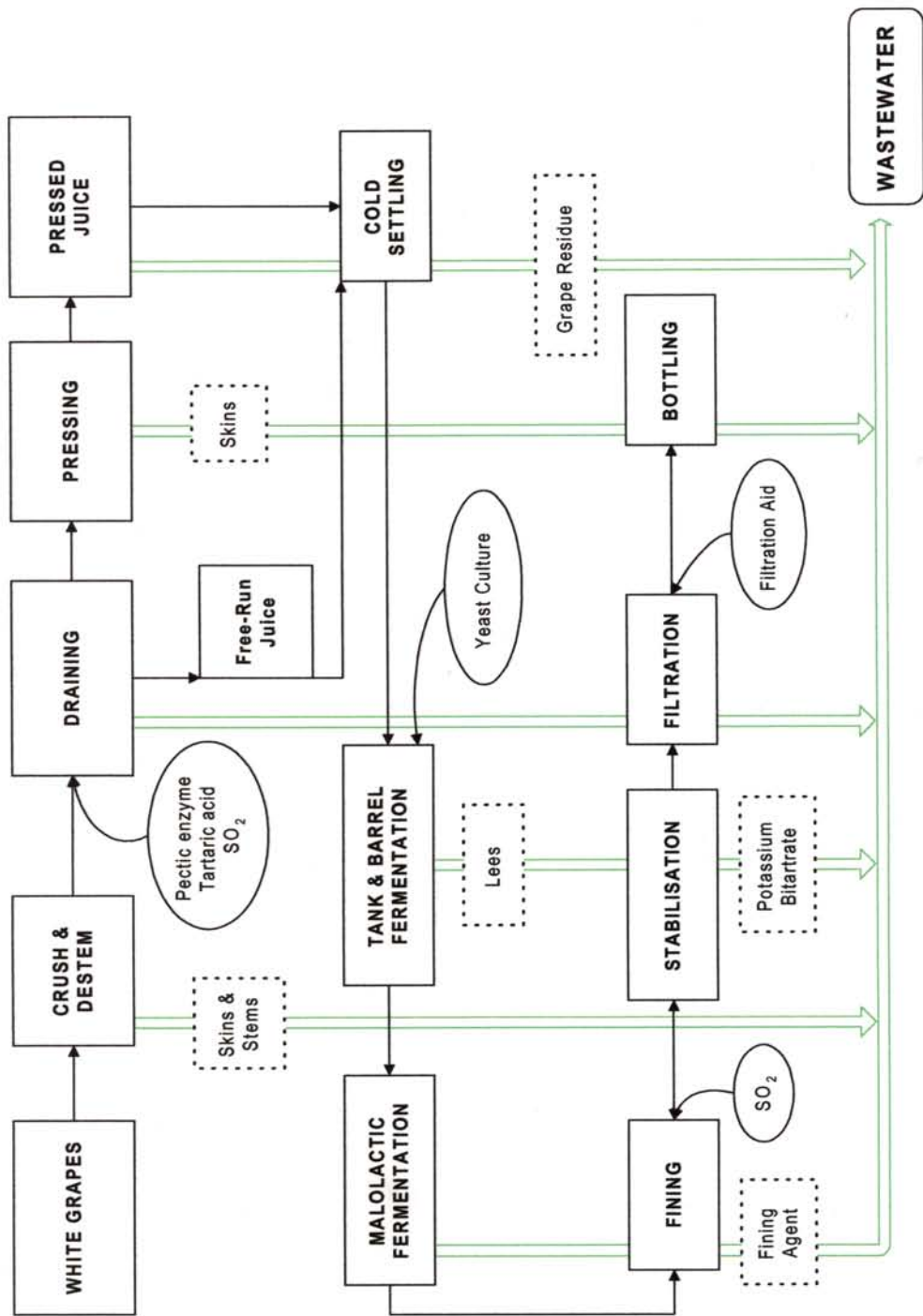


Figure 2.1 Process of White Wine Making and Potential Wastewater Components

2.2.2 Red Wine Making

The main difference between red and white wine making resides on the need for colour extraction from the skins. The colour, which consists of anthocyanins, resides in the vacuoles of the cells just under the skin. Natural pigments in grapes are anthocyanidin monoglucosides (sugar molecule affords greater chemical stability to the anthocyanin molecule). Red grapes are usually harvested between 20-25 °C, resulting in a wine containing 11-14 % alcohol by volume. The grapes are crushed, de-stemmed and pumped to a fermentation vessel. Tartaric acid may be added. Inoculation or natural fermentation on the skins then commences. Two examples of colour extraction are described:

- i. In small fermentation vessels and cement tanks, the cap of floating skins is pressed manually or mechanically at regular intervals.
- ii. Irrigation of the skin-cap occurs by pumping the fermenting must over the cap intermittently. This method is used at Rupert and Rothschild Vignerons and is also called the autofermenter. It consists of a tank with an upper and lower section. The lower section holds the fermenting must under an inert atmosphere of carbon dioxide. The must is then forced to the upper section due to the pressure of carbon dioxide. Upon the opening of a release valve, the juice runs down a central tube and is sprayed on the mass of skins in the lower section.

Pressing takes place once sufficient colour, flavour and tannin extraction have been achieved (1-4 weeks). The wine is then pumped to fermentation vessels (tanks or barrels) and fermented to dryness (between 1-2 g/L reducing sugar). The wine then undergoes malolactic fermentation, and as with alcoholic fermentation, it may be induced or allowed to occur naturally. *Leuconostoc oenos* is the bacterium responsible for malolactic fermentation, causing the decarboxylation of L-malic acid to lactic acid. The wine is thus de-acidified, the stability improved and desirable levels of diacetyl are produced, which adds complexity to the wine and imparts a buttery flavour. It should be noted that white wine may also undergo malolactic fermentation. Racking takes place during both fermentations. The wine is allowed to

age in barrels, and is finally be filtered and/or fined. Filtration is part of the overall process of clarification with diatomaceous earth being the most common medium (*Rankine, 1989*). A general red winemaking process is illustrated in *Figure 2.2*.

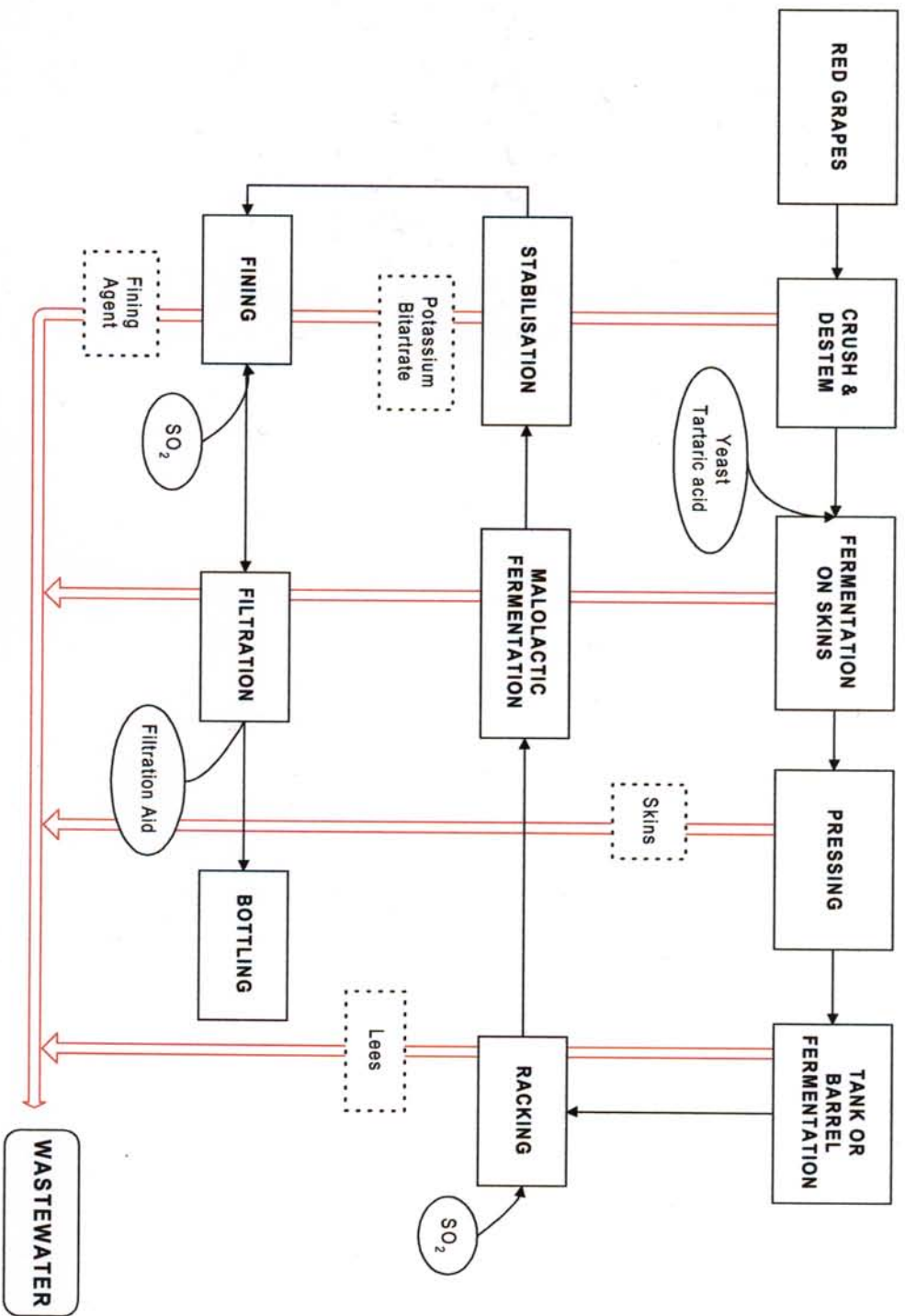


Figure 2.2 Red Winemaking Process and Potential Wastewater Components

2.3 DESCRIPTION OF THE COMPONENTS ANALYSED IN WASTEWATER AND APPLICABLE TREATMENT OPTIONS

Several analyses must be performed to ascertain the quality of the wastewater originating from the winery. The following paragraphs serve to provide significance to the respective analyses performed.

2.3.1 Chemical Oxygen Demand (COD)

Chemical Oxygen Demand (COD) is defined as a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. The COD test is a useful parameter for monitoring pollution and is expressed in mg/L.

Organic matter can be present either in dissolved form, or as particulate organic matter. The presence of organic matter promotes the formation of microbiological slimes, acting as a nutrient source for bacterial growth. Such microbial slimes often contain sulphate-reducing bacteria, which are responsible for extensive damage to heat exchange and cooling systems through microbial induced corrosion (MIC). Fouling of ion-exchange resins may also occur. There are many factors which influence the recommended COD in wastewater: discharge volumes, catchment area, geographical influences, other "polluters" in area and levels of other contaminants. According to the National Water Act (*Muller, 1998*), the COD should be below 5000 mg/L if less than 50 m³ of water is consumed per day (Refer to *Section 4.2.1*).

Particulate organics may be removed by sedimentation or flotation. The removal of dissolved organics will require more complex chemical treatments e.g. ozonation. Several treatment technologies exist to improve wastewater quality and are discussed in *Section 2.4.2*.

2.3.2 Biological Oxygen Demand (BOD)

BOD signifies the concentration of biodegradable organics principally composed of proteins, lipids and carbohydrates. The application of untreated winery wastewater onto land may deplete the soil of oxygen and lead to septic conditions. Prolonged oxygen depletion (anaerobic conditions) reduces the soil micro-population that breaks down the organic matter, thus causing odour problems and contamination of ground and surface waters (Levay, 1999). The soil structure thus also plays an important role and should be investigated. However, this study will only concern the wastewater production.

2.3.3 pH

Winery wastewater characteristically has a very low pH. Neutralisation by means of lime addition may be considered.

2.3.4 Salinity

Winery wastewater that is moderately saline and irrigated must be monitored regularly. Free draining soils should constitute the irrigation area (sandy loam to loam texture) planted with a salt tolerant species. The ground water tables must also be taken into consideration to prevent potential land salination. Consideration must also be made concerning the grapevine. Vines are moderately sensitive to salinity based on yield and foliar symptoms. It has been documented that yield loss may occur due to total dissolved solids concentrations of 600-1200 mg/L. It should also be observed that salinity due to sodium chloride should be distinguished from that due to other dissolved solids, some of which might be beneficial to the soil. Several aspects of salinity are discussed in the following sections.

2.3.4.1 Total Dissolved Solids (TDS) and Electrical Conductivity (EC)

TDS is the measure of various inorganic salts dissolved in water. It is directly proportional to the electrical conductivity (EC). The EC is the ability of water to

conduct an electrical charge. Carbonate, bicarbonate, chloride, sulphate, potassium, calcium, magnesium; all influence EC due to electrical charge. In conjunction with pH, hardness and alkalinity, the TDS play a major role in the determination of the corrosion or scaling potential of water.

$$EC(mS / m @ 25^{\circ}C) \cdot 6.5 = TDS(mg / L) \quad (2.1)$$

2.3.4.2 Sodium

Metabolically sodium interacts with potassium. Sodium interactions in the soil are best described when considering the sodium absorption ratio (SAR).

2.3.4.3 Sodium Adsorption Ratio

The SAR is an index of the potential of the given irrigation water to induce sodic soil conditions. Soil sodicity is usually measured by the percentage of the soil's cation exchange capacity that is occupied by sodium ions. It is calculated from the concentrations of sodium, calcium and magnesium in water, and gives an indication of the level at which the exchangeable sodium percentage (ESP) of the soil will stabilise after prolonged irrigation. SAR is determined on the saturated soil extract. Irrigation water with high bicarbonate/carbonate concentrations gives rise to the precipitation of calcium carbonate in soil. This causes soil to become enriched with sodium, thereby increasing the SAR. Lime decreases the effective SAR and leads to the calculation called the adjusted sodium ratio (adj.RNa).

$$SAR = \frac{Sodium}{(Calcium + Magnesium)^{0.5}} \quad (2.2)$$

where sodium, calcium and magnesium = mmol/L

The SAR only represents problems when its value is high. It is recommended that the level be <3.0 if considering irrigation (Holmes, 1996), while National Water Act (Muller, 1998) requires a value below 5.0 (Refer to Appendix C). The SAR of water can be reduced by decreasing the sodium concentration or by increasing the calcium

and/or magnesium concentrations. Sodium can only be removed by highly sophisticated physico-chemical separation techniques. More cost-effective, however, is the addition of calcium and magnesium salts to the irrigation water; gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is most generally used but has limited solubility. It should be noted that calcium and magnesium could cause plant nutritional imbalances.

2.3.4.4 Chloride

At high concentrations, chlorides interact with metals, which can enhance corrosion by accelerating oxidation. Chloride concentrations should be interpreted in conjunction with the major cations (sodium, potassium, calcium and magnesium) and anions (sulphates and bicarbonates). Depending on the discharge system, chloride values should generally be below 600 mg/L, at a recommended level of 250 mg/L (Holmes, 1996).

2.3.5 Suspended Solids (SS)

Suspended solids (SS) are particulate matter remaining after filtering and drying a sample at 103-105 °C (Holmes, 1996). SS consists of organic and inorganic matter and can lead to the development of sludge deposits and anaerobic conditions. Upon irrigation of high SS containing wastewater on land, drip irrigation systems become clogged, soil surface crusts will form (inhibits water infiltration and seedling emergence), and photosynthetic activity reduction. The target concentration range is 50 mg/L. These levels can be decreased substantially by settling, coagulation or filtration.

2.3.6 Microbiological Examination

Wastewater should also be analysed microbiologically to determine the presence of bacteria. The presence of pathogens may lead to disease transmission. Even though most winery wastewater systems are not connected to the sewage system, contamination by various sources may occur and should be monitored. Faecal coliforms, and more specifically *Escherichia coli*, are the most common bacterial indicators of faecal pollution. The presence of *E.coli* is used to confirm the presence

of faecal pollution by warm-blooded animals (often interpreted as human faecal pollution). Some organisms detected as faecal coliforms may not be of human faecal origin but from warm-blooded animals. Some faecal coliform tests also enumerate *Klebsiella spp.*, which can originate from non-faecal sources. *Klebsiella spp.* are commonly found in soil and waters.

Factors that influence the destruction of their activity include sunlight, temperature, pH, salinity, competition, predation, algae, nutrient deficiencies, toxic substances, and organism density (Holmes, 1996). These organisms may be present in high numbers in winery wastewater and their removal can be achieved by sedimentation and chemical oxidation.

For wastewater audit at Rupert and Rothschild Vignerons, the above components were analysed, and will be discussed in *Section 4.2*.

2.4 LITERATURE REVIEW

Internationally, the subject of winery wastewater has received much attention over the last 8-10 years. In South Africa, however, research has only recently commenced in this field, this study being the first of its kind.

The various vinification regions of the world differ greatly in several aspects regarding the winery environment. The following section is divided into two parts; the first part reviews research that has been done concerning wastewater auditing results from other winemaking regions; and the second part serves to review wastewater treatment research. The case studies serve to provide background on this field of study, demonstrating the problems faced by other wineries and subsequent treatment technologies. It provides a frame of reference, placing some perspective on the South African case study. A discussion on the auditing results will be conducted in *Section 4.5*.

2.4.1 International Auditing

For the purpose of clarification it should be noted that the terms "cellar" and "winery" might be used interchangeably. The same holds true for "harvest" and "vintage". The difference in usage is usually related to the country; Australia and America commonly employ the terms "vintage" and "winery", while Europeans use "cellar" and "harvest". Also, the terms "effluent" and "wastewater" are commonly confused, but in this study have similar meaning. The terms employed by the respective researchers will be similarly employed in the literature reviews, while the remainder of the study will refer to "wastewater", "winery" and "harvest".

2.4.1.1 Case Study: Portugal

An integrated approach for assessing the environmental impacts of winery in Portugal was conducted by *Duarte et al.* (1998) and presented at the 2nd International Specialised Conference on Winery Wastewater in Bordeaux, May 1998.

The study was conducted at Dois Portos, a small winery close to Lisbon. The size (harvest quantity) and production (cultivar range and fermentation techniques) of the winery are extremely important criteria when analysing and evaluating the water processes. The following summary serves to describe the Dois Portos Winery:

- The winery has an area of 720 m².
- The vineyard has an area of 6.8 ha.
- During the 1997 harvest, 47000 kg red grapes and 35390 kg white grapes were harvested.
- The production totalled 305 hL of red wine and 226 hL of white wine (cultivars not listed).
- The harvest period lasted 12 days.

The solid wastes and wastewater from the winery were quantified. *Table 2.1* demonstrates the results from the investigation.

Table 2.1 Results from the Investigation for the Harvest Period of 1997 (Duarte et al. 1998)

Production	Red Wine	White Wine
Grapes Harvested [kg]	47430	35390
Wine [L]	30420	22610
Pomace [kg]	6640	4780
Lees [kg]	1420	1240
Water for cleaning operations [L]		37176
Litres wastewater / litres wine		0.70
Litres wastewater / kg grapes		0.45

Once the quantification strategy had been realised, the analytical characterisation was done. Effluents originating from different periods during the harvest (I, II, III), and one stage during the first racking (IV), were analysed.

- i. Crushing of white grapes.
- ii. Pressing of white grapes.
- iii. Pressing after fermentation on skins in red wine.
- iv. Racking of white and red wine.

Table 2.2 summarises the analyses of the effluent (refer to *Section 2.3* for details on the individual parameters).

Table 2.2 Analyses of Effluent Types I, II, III, IV (Duarte et al.1998)

Parameter	Harvest Period			Harvest Average	1 st Racking	
	I	II	III		IV	
Av. Wastewater (L/day)	550	660	500	570	165	
pH	4.0 -4.5	5.0-5.5	4.5 -5.0	4.0 -5.0	4.0 -4.5	
COD	kg/day	3.0 -4.0	1.0-2	9.0 -10.0	7000 -8000	3.0 -4.0
	[mg/L]	6500 -7000	2000 -2500	19000 -20000		4000 -4500
SS	kg/day	0.05 -0.1	0.5 -0.1	0.2 -0.3	150-200	0.3 -0.4
	[mg/L]	150 -200	50 -100	450 -500		350 -400
TKN	kg/day	9 -10	11-12	30 -35	20 -30	25 -30
	[mg/L]	15 -20	15 -20	60 -70		25 -30
K	kg/day	45 -50	30 -35	240 -250	150 -170	770 -790
	[mg/L]	80 -90	45 -55	450 -500		850 -1000
P	kg/day	8 -9	2 -3	15 -16	20 -25	13 -15
	[mg/L]	12 -17	3 -5	60 -70		15 -18

From *Table 2.2* it can be seen that the daily wastewater production during the harvesting season is considerably higher than during the 1st racking period. This is an important observation when considering a suitable treatment strategy. Low levels of phosphorus (P) and nitrogen (TKN) were present in relation to the organic load. The polyphenols present in the wastewater (isolated on Seppak C₁₈ and identified by RP-HPLC coupled a diode array detector) were identified as anthocyanins, (+)-catechins, (-)-epicatechins and phenolics acids. *Duarte et al.* (1998) considered other phenolic compounds to be present, advocating further research when considering an applicable treatment technology.

2.4.1.2 Case Study: Italy

Rozzi *et al.* (1998), evaluated the pollutant loads in effluents from three wineries in North Italy. During the vintage and racking periods very high levels of organic pollution is generated by oenological industries, and this organic load may be three times higher than that of the domestic sewage. The organic load was measured in terms of grams COD discharged per 100 kilograms grapes harvested (g COD/100 kg grapes), thus enabling comparison between three co-operatives, irrespective of their size.

Merlot and Cabernet Sauvignon are grown in the Pordenone area. Sampling took place from October to December 1996, crushing lasted from the 2nd to the 11th October and the 1st racking from the 4th to the 15th of November. Sampling occurred twice daily and the composite was analysed. The effluent from all three cellars was discharged into a municipal sewer. The sizes and production of the respective wineries are presented in *Table 2.3*.

Table 2.3 Characterisation of Wineries Investigated

	Grapes [Ton]	Equipment and Processes	Lees Treatment
Winery I	18 000	Concrete vessels and bottling	Lees are separated and dried
Winery II	5000	Not described	Lees are separated and dried
Winery III	5000	Not described	Lees discharged down sewer

Table 2.4 and *2.5* present the data of the polluting loads (g COD/ 100 kg grapes) and the water consumption (dm³/ 100 kg grapes) respectively.

Table 2.4 The Pollution Load during the Harvesting and Racking Periods for the Three Wineries (Rozzi et al. 1998)

		I	II	III
		Pollution Load [g COD/ 100 kg grapes]		
Vintage	Minimum	1.10	0.12	11.37
	Average	5.16	3.23	13.50
	Maximum	8.87	9.27	15.16
Racking	Minimum	1.44	0.40	3.24
	Average	5.08	1.74	5.07
	Maximum	11.93	2.93	8.61

Table 2.5 Water Consumption during the Harvesting and Racking Periods for Three Wineries (Rozzi et al. 1998)

		I	II	III
		Water Consumption [dm ³ / 100 kg grapes]		
Vintage	Minimum	0.78	0.28	1.27
	Average	2.08	0.98	1.27
	Maximum	3.19	1.54	1.27
Racking	Minimum	1.17	0.30	0.73
	Average	2.65	0.49	0.73
	Maximum	4.56	0.80	0.73

The large difference in the polluting load of winery III in comparison with wineries I and II was attributed to the discharge of lees in the effluent system. Other researchers confirmed the critical influence of the lees on the pollutant load (Rochard and Viaud, 1996), attributing a 40-50 % reduction in the polluting load by separating the lees. Trends in the wastewater COD concentration are illustrated in Figure 2.3.

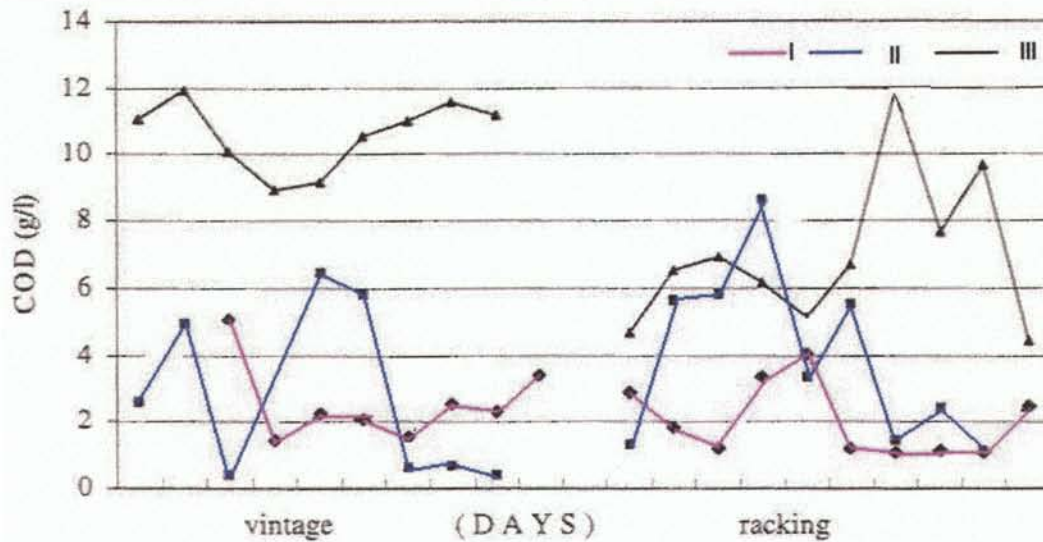


Figure 2.3 COD Concentrations for the Three Wineries during Vintage and Racking Periods (Rozzi et al., 1998)

Table 2.6 summarises the pollutant loads found in wastewaters of cellars in France and Germany.

Table 2.6 Specific Polluting Loads in French and German Wineries (Rozzi et al., 1998)

Winery	Grapes Pressed [x 100 kg/year]	Specific load [g COD/100 kg grapes]
Perrisac	30 000	8
Rauzan	170 000	12
Ville sur Arce	50 000	6
Sallèles	56 120	14
Ornaisons	58 700	4.3
Vendargues	120 000	4.9
Caromb	60 000	6.9
Gau-Bickelheim	100 000	4.3
average		7.2

The data may be divided into 2 categories; the category range from 10-14 g COD/100 kg grapes, refer to wineries where the lees were mostly disposed of in the wastewater; while in the 4-8 g COD/100 kg grapes category, the wastewater was filtered, thus separating the lees (Rozzi et al., 1998).

2.4.1.3 Case Study: France

The effluent characteristics of two wineries in the south of France were measured over two years. The first winery is situated in the Languedoc-Roussillon area (Winery I), and the other in the Provence Aples Côte d'Azur region (Winery II). The periods of vintage and racking produced 65-75 % of the annual effluent volume. *Table 2.7* presents the effluent volumes from the two wineries.

Table 2.7 Annual Volume of Effluent and Contribution of Each Period to the Total Volume (Picot and Cabanis, 1998)

	Winery I		Winery II	
	1994	1995	1994	1995
Wine Production [hL]	98 000	105 000	51 000	56 000
Effluent Volume [m³/year]	2000	2700	2200	2300
Contribution to Total Effluent Volume:				
Harvest	40 %	39%	-	35 %
Racking	25 %	27 %	-	39 %
Remainder of year	35 %	34 %	-	26%
L Water/hL Wine	20	26	43	41

The ratio obtained from winery I (0.20-0.26 L/L wine) was low in comparison to reported average ratio of 1 L/L wine as reported by *Rochard et al. (1995)*. The ratio did, however, correspond to the average ratio of 0.36 L/L wine obtained from twelve wineries in the Languedoc-Roussillon area. The ratio of 0.41-0.43 L/L wine for winery II corresponded to the average value of 0.5 L/L wine calculated for a hundred cellars in the Rhone Valley by *Chastan (1994)*.

According to *Picot and Cabanis (1998)*, it was very difficult to attribute effluent volumes to unit operations due to the great diversity of the operations. The effluent originated mainly from reception bins and washing of the presses and tanks.

Table 2.8 presents data collected from the two wineries. During both periods of harvesting and racking the COD was high, in the order of 20000 mg/L with daily fluctuations between 9000-47000 mg/L. For two wineries in question, the pollutant charge expressed as g COD/hL wine was found to be 250 and 260 g/hL respectively during the harvest, and 320 and 400 g/hL respectively during the racking period. Exceptionally high COD values can be explained by accidental leakage or spillage of wine or chemicals. The effluent generally comprised of a high organic load. In comparison to domestic effluent, the organic load could be 10-50 times higher (Picot and Cabanis, 1998). The effluent also exhibited a high degree of biodegradability as indicated by the Biological and Chemical Oxygen Demand Ratio of 0.5-0.6 (BOD₅/COD). The pH was acidic (pH 4-5), and alkaline peaks were observed occasionally due to the use of chemical products to remove tartrates from tanks. The effluent exhibited low concentrations of nutrients as nitrogen (N) and phosphate (P). High potassium levels were present (300-400 mg/L), as were polyphenolic compounds. These contaminants should be taken into consideration when wastewater is irrigated on land due to the potential toxicity.

Table 2.8 Wastewater Characteristics for the Vintage and Racking Periods (average and extreme values in italics) (Picot and Cabanis, 1998)

	Harvest		Racking	
	Winery I	Winery II	Winery I	Winery II
Wine [hl]	105000	56000	105000	56000
Av. Effluent [m ³ /day]	24 (12-50)	19 (2-38)	7 (0-28)	7 (0-44)
Av. pH	6 (4-10)	4.8 (4.4-5.7)	4.8 (4.4-5.6)	5.8 (5.7-6)
Av. COD [mg/L]	24600	22000	18500	14600
Av. SS [mg/L]	2490	1190	3370	4190
Av. TKN [mg/L]	81	52	185	129
Av. P [mg/L]	31	17	31	26

2.4.1.4 Case Study: Australia

According to *Levay (1999)*, 5 kL of effluent may be produced per tonne of grapes processed, depending on the extent of the wash water recycling. *Table 2.9* illustrates the average effluent production for different winery sizes.

Table 2.9 Relative Effluent Production in Terms of Winery Size (*Levay, 1999*)

Size of Winery	Weight of Grapes [tonnes]	Effluent Quantity [ML]
Small	5000	1-9
Medium	5000-20000	5-100
Large	> 20000	40-240

Upon conducting a survey of effluents arising from Australian wineries, *Levay (1999)* concluded that both solid and liquid wastes are produced by wineries. Solid wastes included stalks, seeds (marc); sediments (lees and grape solids) containing pulp, tartrates and yeasts; and bentonite and diatomaceous earth (which may be processed to recover cream of tartar and tartaric acid). The effluent arised from the rinsing water of tanks, floors and equipment; chemicals (e.g. caustic soda) used to remove tartrates and organic acids deposited in fermentation vessels; earth filtering and ion exchange processes (when present).

The liquid waste typically had the following characteristics (see *Table 2.10*):

- Simple organic acids, sugars, alcohols (causing high COD values).
- Moderate salinity, with proportionally high concentrations of sodium relative to calcium and magnesium.
- Low amounts of nitrogen and phosphorus in comparison to total carbon.
- Inorganic components.

Table 2.10 General Characteristics of Winery Effluent in Australia (Levay, 1999)

Property	Vintage	Non-vintage
SS [mg/L]	100-1300	100-1000
pH	4-8	6-10
TDS [mg/l]	<550-2200	<550-850
BOD [mg/L]	1000-8000	<1000-3000
TOC [mg/l]	1000-5000	<1000
TKN [mg/l]	5-70	1-25
Na [mg/l]	110-310	250-160
Total P [mg/l]	1-20	1-10
C:N:P	30-100:4:1	15-30:5:1
Ca [mg/l]	13-40	20-45
Mg [mg/l]	6-50	10-20
SAR [mg/l]	4-8	7-9
K [mg/l]	80-180	40-340

2.4.2 International Research Concerning Wastewater Treatment

Research has been conducted to identify applicable treatment technologies for particular characteristic effluents. From *Section 2.4.1*, it is clear that wastewater differs considerably with respect to the vinification region, winemaking operations, and grape harvesting quantities. The following section reviews the principal treatment systems employed internationally for winery wastewater.

2.4.2.1 Aerobic Biological Treatment - Case Study: France

The main objective of aerobic wastewater treatment is to biologically convert soluble and colloidal organic matter into gaseous products (carbon dioxide) and biological matter (activated sludge). Heterogeneous cultures of micro-organisms (mostly bacteria) acclimatise to the wastewater and are responsible for the degradation of organics and other contaminants. Bacteria reproduce by binary fission and have very short doubling rates (± 20 min, depending on species). Several factors impact the performance of the aerobic treatment system:

Nutrients are required for cell synthesis (nitrogen (N), phosphorus (P) and oxygen (O)). A conservative estimate of the requirements is that the BOD/P/N should be 100/5/1 (*Bridle, 1994*). Wastewaters are often deficient in N and P, and must be added to ensure optimum performance. Oxygen requirement is generally 2 kg O₂/ kg BOD load. Oxygen transfer rates range from 0.8-1.6 kg O₂/ kWh. Temperature is an important factor for doubling rates, every 10°C increase causes the bacterial population to double, up to approximately 35 °C. Enzyme reaction kinetics generally decrease above 40°C. The pH values should ideally be 6.5-8.5. Neutralisation is usually required if organic acids and caustics are present. Toxicity in the form of phenols may inhibit extra-cellular enzyme activities responsible for the breakdown of organics.

Rochard et al. (1998) researched the potential of aerated storage for the treatment of winery wastewater and installed several plants in France (Champagne region). The

studies showed that the purification time varied between 3-8 weeks, according to the standard of the receiving environment. The principal of retaining the effluent in an aerated storage tank was applied. It was found that the quantity of the storage volume contributed to the buffering capacity of the effluent, thus decreasing the organic load and chemical contaminants imposed by hygiene products. The aerated storage of effluents may be realised in concrete ponds, tanks or in the form of lagoons; depending on the winery. In a practical light, organic acids may affect the concrete ponds adversely. Open ponds and lagoons are usually equipped with aerators.

Characterisation of the De-Pollution Cycle

During the investigation, the COD, BOD, pH and SS were monitored regularly to determine the effect of the aerated storage. The concentrations of COD and BOD rapidly decreased within the first 10 days due to the rapid biodegradability of sugars, acids and alcohols. The final stages of the treatment were marked by a significant reduction in biodegradability of the contaminants (probably macromolecules and phenolics compounds). The initial pH increases slowly to reach a value of 8-9 by the end of the treatment process (40 days), due to the progressive degradation of organic acids. The SS concentration increased at a constant rate due to the multiplication of the biomass, and eventually decreased due to sludge deposition (*Rochard et al. 1998*)

Upon microbiological examination the progressive biomass evolution occurred as follows:

- i. The first phase was dominated by yeast populations, which rapidly reduced the COD thereby decreasing the oxygen demand and increasing the temperature.
- ii. The second phase was characterised by the presence of bacteria.
- iii. The diminishing bacterial population and the appearance of protozoa (paramecia) marked the third phase termed the "stabilization phase". The sedimentation of sludge became more effective during this phase.
- iv. The bacterial population decreased constantly due to the decrease of organic substrates and their consumption by protozoa. The bacteria flocculated and

were decantable. The presence of nematodes, vorticelles, amoebas and rotifers were detected.

Although an effective strategy, certain restrictions are placed on the utilisation of this system, notably:

- The location of the winery: urban sites are not suitable for lagoons and ponds.
- This type of treatment system may add to the problematic generation of offensive odours if anaerobic conditions occur.
- Although suitable for small wineries, it is not viable for large volumes of wastewater.
- Very high operating costs due to the requirement of artificial aeration.

2.4.2.2 Constructed Wetland Systems - Case Study: California

Constructed wetlands are widely employed to treat wastewater from different industries. *Shepherd* (1998), designed the pioneer wetland for use in the wine industry, the plant is described and discussed in the following section. Due to the presence of several variables (as discussed in *Section 2.4.1*), one should consider several types of treatment strategies in conjunction with the winery characteristics in order to design a sustainable treatment facility. It should be noted that although the treatment facility discussed in this section has been used for decades, very little work has been done on the application of winery wastewater as the substrate for these facilities.

Constructed wetlands are amongst the most biologically active terrestrial ecosystems. High biological activity enhances wastewater treatment and constructed wetlands may be considered as "natural bioreactors". The chemical and microbiological oxidation-reduction reactions occur within the matrix of the wetland and this system is considered to have low financial implications. Since winery wastewater may contain up to 500 times the organic load compared to municipal water, the design parameters had to be adjusted significantly for the treatment of winery wastewater, also considering that no data was available for this type of

application (Shepherd, 1998). Impact assessments regarding firstly the performance under high and variable organic loads, and secondly the assignment of a rate constant for the removal of COD, were unknown.

Table 2.11 summarises the average wastewater quality and quantity of the winery.

Table 2.11 Water Quality Winery (average values are indicated in brackets) (Shepherd, 1998)

Constituent	Vintage	Non-Vintage
Flow Rate [gpd] ¹	30000 -45000	12000- 26500
pH	3.8-7.8	3.8-7.8
COD [mg/L]	7500-44000 (12400)	750-13000 (2500)
SS [mg/L]	57-3952 (350)	12-400 (200)
TDS [mg/L]	315-1240	214-720
Nitrate [mg/L]	0.63-362	0.23-53
Ammonia [mg/L]	2.25	-

¹1 gallon = 3.78 L

Shepherd (1998), constructed a wetland with the following dimensions:

- Tank with dimensions 6 m (length) by 2.4 m (width) and 1.2 m deep.
- Filled to 0.95 m depth with pea-gravel (0.5-2 cm fractions).
- Planted with bulrush (*scirpus acutus*) and cattails (*typha dominica*).
- The walls of the tank were constructed from 16-gauge corrugated steel and lined with polyethylene (60 mm) to prevent leakage.
- The tank was equipped with 33 sampling ports, constructed from 1.27 cm PVC pipe, extending 30 cm into the tank and fitted with a screen on the inside to prevent gravel entering the port. Rubber gaskets pressed against the liner and were sealed with silicone.

The wastewater was diluted in a holding tank and applied at 500 L per day. A tracer study (potassium bromide) indicated a hydraulic residence time of 9.4 days. Samples were taken at the inlet, after the pre-filter, from the sampling ports and at the outlet, three times weekly and analysed. Table 2.12 presents some of the data

obtained from the constructed wetland experiments with varying input COD concentrations. This system effectively lowered the COD, SS and neutralised the pH.

Table 2.12 Results from Constructed Wetland Treatment

Exp.#	Property	Input	Post-Filter	Output
1	COD [mg/L]	2039	993	21
	pH	5.04	-	6.85
	SS [mg/L]	370	-	32
	TDS [mg/L]	811	-	867
2	COD [mg/L]	4851	4723	51
	pH	5.41	5.36	7.5
	SS [mg/L]	622	316	15
	TDS [mg/L]	920	911	1483

Although efficient, it is highly sensitive and not appropriate for wineries that generate high volumes of wastewater or high COD values.

2.4.2.3 Woodlot Irrigation - Case Study: Australia

The Australian Wine Industry is more comparative to the South African Industry based on the size and area surrounding the wineries. The Berri Estate is located on the Sturt Highway at Glossop in South Australia's Riverland. The Riverland region is part of the Murray-darling Bassin, Australia's foodbowl. The region faces serious problems of environmental degradation and a concerted effort by the producers is needed for a sustainable future. To play its part, the Berri Estates needed to change its wastewater management procedures. The specific guidelines Berri had to meet are listed below:

- Reduce, if not totally eliminate the odour problem from the lagoons.
- Not to contribute to the river salinity or the rise of the water table.

The winery crushes 50000 tonnes of grapes and produces around 200 ML of wastewater per annum, with an average BOD of 2500 mg/L. The option that best

met the requirements of the Estate in terms of cost and environmental objectives was the plantation of Redgums (*Eucalyptus camaldulensis*), using the wastewater from the winery for flood irrigation (Kennedy, 1994). The general guidelines for the disposal of the winery wastewater are described below (Kennedy, 1994):

- The maximum application of wastewater to a depth of 100 mm, employing intermittent irrigation.
- Bi-weekly application.
- Maximum organic loadings of 100 kg BOD per day.

In order to irrigate the wastewater, the removal of suspended solids had to be envisaged. This called for the design of screening, settling and pumping ponds. Several ponds were constructed and mostly diatomaceous earth was settled. The solid waste generated by the ponds was pumped out as a slurry to a landfill. Once screened and settled, the wastewater was pumped to the woodlot. In 1996, 30 hectares comprising 40 000 seedlings were planted and watered by the river until 1988, and ever since wastewater has been applied.

Monitoring showed no negative impacts on the woodlots. Although the low pH could constitute a future problem, no evidence of acidification was reported, and should it occur, horticultural lime was considered a solution. The nutrient concentrations of phosphorus and nitrogen in the soil were noted and not found to be problematic (Kennedy, 1994).

This system has had irrefutable success in Australia and does indeed provide a pragmatic solution for large wineries and co-operatives should there be an available agricultural area for plantation. This system requires physical maintenance of the woodlots (e.g. weed clearance) and removal of sludge from ponds. Diatomaceous earth may enter the pipeline, thus annual flushing or pigging of the pipeline must be done. It should also not be overlooked that this system comprises two treatment units, and that the removal of suspended matter is very important for the Redgum plantation success.

2.4.2.4 Anaerobic Treatment in Hybrid Reactors- Case Study: Italy

Andreotolla et al. (1998) installed a hybrid anaerobic reactor (as a pre-treatment) for the effluent from the Mezzacorona winery, in the north of Italy. The study was aimed at determining the performance and stability of the reactor in terms of the organic load variations.

The Mezzacorona winery has an annual harvest of 28 000 tonnes (53% white and 47% red) and the resulting wastewater was found to be heavily polluted. An aerobic wastewater plant consisting of several tanks (process similar to that described in Section 2.4.2.1) was installed at the winery. However, due to the envisaged increase in production, an alternative solution to the effluent had to be investigated. Consequentially, a pilot test of the hybrid process was carried out. The hybrid up-flow system combined two treatment processes: the lower part consisted of a UASB reactor that carried out the degradation of the organic pollutants; and the upper part, which consisted of an aerobic filter. The advantage of the hybrid configuration was two-fold: firstly it eliminated the hydraulic problems of wastewater distribution; and secondly prevented the clogging of fixed bed up-flow reactors, while maintaining the advantages of anaerobic filters and UASB reactors (*Andreotolla et al.*, 1998)

The pilot plant included a 6 m³ storage tank, a 2 m³ anaerobic Up-flow Hybrid Digester (UHD; D= 0.8 m; H= 4.5 m), feed and recycle pumps, and flow meters. Temperature control was established by means of controlled heat exchangers. The filling material used for the anaerobic filter in the upper part was Flocor R, consisting of PVC rifled cylinders. In the final experimental phase, an aerobic sequencing batch reactor (SBR) tank (5 m³) was installed as a post treatment stage. The UASB in the lower part was started by granular sludge obtained from a full scale UASB reactor.

The feed wastewater was treated with sodium hydroxide and typically comprised a COD concentration of 13000 to 18000 mg/L during vintage, and 4000 to 5000 mg/L during the rest of the year. The influent flow-rate varied between 20 and 120 L/hour, according to the required influent COD loading rate (1.3-14.9 kg COD/m³), while

recycle flow rates varied between 200-600 L/hour. *Table 2.13* summarises the results obtained.

Table 2.13 Summary of Operating Results of UHD Process

Parameter	Run 3	Run 4	Run 5
Temp. [°C]	25.8	25.4	35.8
COD _{in} [mg/L]	4737	10012	11292
COD _{out} [mg/L]	510	706	435
% COD removal	89	93	94
Organic Loading Rate [kg COD/m ³]	3.4	6.0	6.1
pH _{in}	9.37	7.93	6.36
pH _{out}	7.14	7.49	7.33

High COD removal efficiencies were attained (89-96%), with a volumetric flow rate of 10 kg COD/ m³ per day. The plant did, however, show an efficiency drop with sudden organic load variations. Post treatment in the SBR reactor further decreased the COD concentration to below 100 mg/L. The control of daily volumetric loads was a critical factor for success (*Andreotolla, 1998*).

This system offers applicability to large effluent volumes, however, adequate homogenisation volumes must be applied strictly. Continuous monitoring of the system implies a demand on labour. Mechanical problems to recycle pumps, heat exchangers or the pH control system may induce severe efficiency drops.

2.4.2.5 An Alternative to Biological Treatments: A Distillation Process - Case Study: France

Upon analysis of winery wastewaters it was established by *Bories et al.* (1998) that 90 % of the organic load could be ascribed to ethanol (or momentarily to glucose or fructose). The effluent from several cellars in the Languedoc-Roussillon area was analysed. *Table 2.14* depicts the data obtained from the analyses on the cellar effluent.

Table 2.14 Composition of Effluents from Languedoc-Roussillon (*Bories et al.*, 1998)

Property	Beginning of Harvest	Middle Harvest	Vinification	Racking
pH	4.2	4.5	4.7	4.6
COD [g/L]	10	32.75	6.67	18.01
Ethanol [g/L]	0.091	9.33	2.8	8.39
Glucose [g/L]	4.45	6.13	0.118	<0.030
Fructose [g/L]	4.46	6.4	0.208	0.045
Glycerol [mg/L]	32	603	180	713
Acetic Acid [mg/L]	48	170	49	387
Tartaric Acid [mg/L]	942	561	246	1724
Succinic Acid [mg/L]	45	37	15	287

According to *Bories et al.* (1998) the principal contaminants of wastewater were ethanol and sugars. Consideration must be made in that the COD of wine (containing 12 % alcohol) is ± 210 g/L, while must (224 g/L sugar) has a COD of ± 240 g/L. Ethanol was present from vinification to racking, and was considered to maintain high levels. During vinification, the concentration of ethanol in the effluent was 9.33 g/L, equivalent to 1% v/v ($^{\circ}$ alcohol) in the effluent. The presence of glucose and fructose were observed during the initial stages of grape processing and must preparation (± 6 g/L, depending on the effluent). Secondary constituents of the effluent were tartaric acid (<1.7 mg/l), glycerol (<0.7 g/L), succinic acid (<0.3 g/L) and acetic acid (48-387 mg/L).

Due to ethanol being the principal polluting component, several extraction and separation techniques were considered for its recuperation. Fractional distillation combined with thermal concentration (process "ECCF"), allowed the separation of winery wastewaters into three fractions: purified water and by-products for recovery, alcohol and concentrate. This process was selected due to its technico-economical feasibility and compatibility with the problematic effluent. A pilot plant study was conducted and scale-up to a semi-industrial scale to accommodate a flow of 150 L/hour. The semi-industrial scale unit comprised a fractionation column and an evaporator (atmospheric pressure). The operation may be described as follows:

- Alcoholic fermentation of the effluent took place in storage tanks (5-25 hL).
- Yeast addition (5-15 g/L) at an ambient temperature (25 °C) with the addition of nutrients (N and P).
- The pH was not regulated and no agitation was induced.

Figure 2.4 shows the evolutionary cycle of glycerol, ethanol, acetic acid and sugar during the fermentation of the effluent.

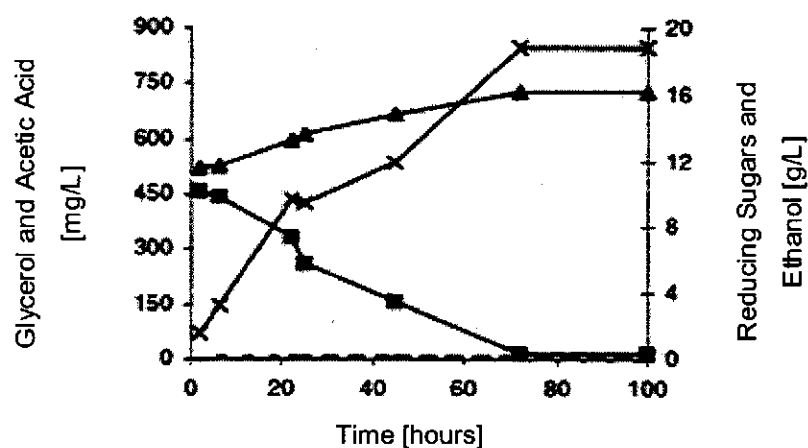


Figure 2.4 Evolution of Compounds during Fermentation (x Glycerol (mg/L); Ethanol (g/L); Reducing Sugars (g/L); --- Acetic Acid (mg/L))

The original effluent contained 10.3 g/L reducing sugars and 11.6 g/L ethanol. The sugar was completely fermented to ethanol with a yield of 0.4 g/L ethanol per g sugar. The production of ethanol was accompanied by the formation of glycerol (0.8 g/L).

The continued fractionation of the effluent on semi-industrial scale (150-200 L/ hour) reduced the COD from a range of 10-55 g/L to between 65-241 mg/L, indicating a reduction of 98.4-99.6 % (see *Table 2.15*).

Table 2.15 Performance of the Fractionated Effluent on a Semi-Industrial Scale (Bories et al., 1998)

	COD initial [mg/L]	COD final [mg/L]	% Reduction
Effluent 1	30 000	241	98.4
Effluent 2	12 000	90	98.5
Effluent 3	10 480	65	98.8
Effluent 4	55 200	120	99.6

A mass-balance on the fractionated effluent is illustrated in *Figures 2.5* and *2.6*. These figures illustrate the volume of each phase and its contribution to the COD.

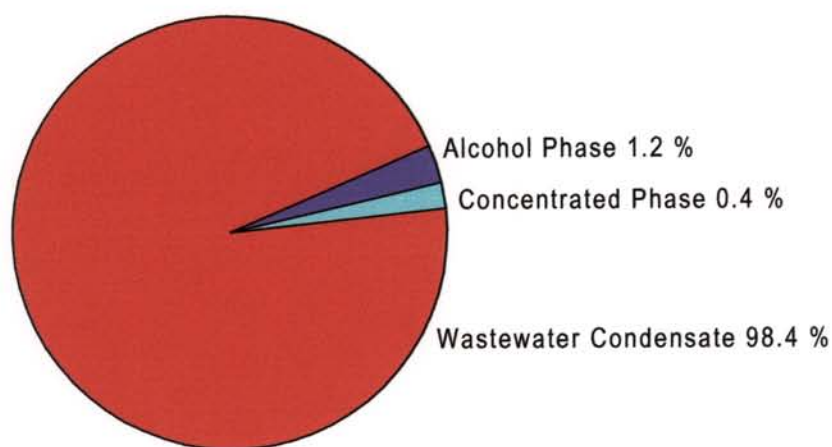


Figure 2.5 Volume Percentage of Effluent Components (Bories et al., 1998)

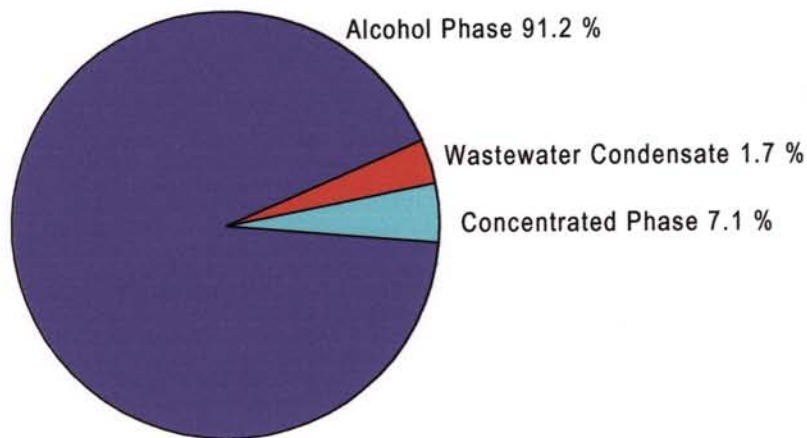


Figure 2.6 COD Contribution Percentages of the Effluent Components (Bories et al., 1998)

The alcoholic phase only represented 1.2 % of the effluent volume, but contributed to 91 % of the initial COD. The concentrated phase (0.4 % of the volume of the effluent) was composed of non-volatile compounds such as tartaric acid (50-80 g/kg liquid concentrate) and glycerol (30-50 g/kg). The wastewater (condensate) represented 98 % of the total volume, and contained no colour compounds, micro-organisms, suspended material or complex organic material. Post-treatment by ECCF, thus rendered the wastewater suitable for re-use or discharge into the environment. Tartrates could be extracted from the concentrated phase or could be used as compost material (Bories et al., 1998)

The Evapo-Concentration Condensation Fractionation process (ECCF) required very modest energy consumption due to the small energy consumption of the mechanic vapour compression. This treatment process was far more feasible in terms of energy requirement (15-20 kWh/t evaporated water) compared to the biological treatments that have an energy requirement in the order of 12-19.5 kWh/m³ for an effluent with a COD of 15g/L. Other advantages of this system included:

- Suitable for seasonal activity.
- Not sensitive to the variations of the pollutant flux.
- Compact installation, thus surface area not needed, in contrast to biological wastewater treatment.
- No generation of offensive odours.

It must, however, be noted that fermentation requires sugar, and that the reported sugar concentrations by *Bories et al.* (1998) is considered to be very high. Thus, in order to consider this type of treatment technology, sugar addition will be required post harvest and for wastewaters containing low concentrations of sugar.

2.5 FINAL REMARKS ON THE LITERATURE REVIEW

The following remarks can be made on the production of wastewater from wineries:

- The type of grapes processed by the winery influence the composition of the wastewater.
- The practices of the winery influence the quality of the wastewater.
- The winery size influences the water consumption; generally lower water consumption in terms of L water/ L wine, is observed for large wineries and co-operatives.
- Large variations in the COD and SS concentrations were reported by respective case studies.

The investigation into the treatment of winery wastewater is relatively new. Mostly biological treatment technologies have been investigated, and although these treatments were generally seen to improve the quality of the wastewaters, several disadvantages were observed, primarily:

- Requirement of large areas of land, preferably in rural areas.
- Large capital costs.
- Labour intensive.
- Sensitivity to fluctuations of compounds in the wastewater.
- Generation of offensive odours.

The following chapter will present the South African case study performed at Rupert and Rothschild Vignerons. In all the case studies described, the strategy involved solely the investigation and monitoring of the wastewater production. The study performed at Rupert and Rothschild Vignerons embraced the form of a complete

water and wastewater audit. The audit is a comprehensive evaluation of all the facets of the water cycle, both incoming and exiting the winery. This methodology lends an interesting dimension to future work of this nature and the shift between the *present* state and the *desired* state is recognized.

CHAPTER 3

SOUTH AFRICAN CASE STUDY: RUPERT AND ROTHSCHILD VIGNERONS AND THE WATER AUDIT PROCEDURE

The problem and system definition phase is very important to derive assumptions and manifest pragmatic solutions unique to the winery concerning the water flux and wastewater production. As portrayed in *Chapter 2*, the cultivar range, winemaking practices, and winery capacity all contribute significantly to the resultant wastewater production. In order to audit the water flux in entirety, not only the wastewater streams were analysed and evaluated, but also the source water. Every winery is unique in design and system function, thus it is essential to describe and understand the plant devise. This chapter serves to firstly describe the Rupert and Rothschild Vignerons layout, illustrate the production values, present the current wastewater treatment design; secondly to define the contamination matrix in the wastewater; and thirdly to present the structure of a complete audit and its significance.

3.1 RUPERT AND ROTHSCHILD VIGNERONS

3.1.1 *Origin and History*

The Rupert & Rothschild Vignerons is a partnership in wine production on the historic French Huguenot farm in South Africa, between Anthonij Rupert (son of Dr. Anton Rupert of South Africa) and Benjamin de Rothschild (son of the late Baron Edmond de Rothschild of France).

Both families have considerable interest in wine. The Rupert family owns two other wine estates in Franschoek: L'Ormarins and La Motte. The Rothschild family owns Chateau Clarke, (a cru bourgeois in Lustrac) as well as Peyre-Lebade and Malmaison, and are partners in first-growth Chateau Lafite-Rothschild in Paillac.

Fredericksburg farm is situated on the slopes of the Simonsberg mountains between Paarl and Franschoek. The farm was founded in 1690 by brothers Jean and Daniel Nortier. When Anthonij Rupert bought the farm in 1984, he inherited a jumble of run down buildings on 90 ha. Replanting of noble varieties started in 1986. Today, 60 ha are under vines. Some grape cultivars are bought in from other estates in South Africa. The cellar was built in 1997. White (Chardonnay) and red varieties (Cabernet Sauvignon, Cabernet Franc, Merlot and Pinotage) are produced.

The love of wine is the common interest between these two deeply rooted cultures - French Huguenot and Cape Dutch- and the Rupert and Rothschild families share one goal: to produce world-class wines.

Winemaker Schalk-Willem Joubert and viticulturist André Pens, together with assistant winemakers Clive Radloff and Yann Buchwalter (from France), form a dynamic progressive team concerned not only with the art and science of wine, but are also conscientious towards environmental affairs.

3.1.2 Harvests 1999 and 2000

Research at the Rupert and Rothschild Vignerons commenced in February 1999. The scope of this project dates until October 2000. As portrayed in the international case studies, the grape processing quantity and variety are of intrinsic importance to the quantity of water consumed and the characteristics of wastewater produced.

The 1999 Vintage

During the 1999 harvest ± 790 t of grapes were harvested; ± 120 t white cultivars and ± 670 t red cultivars. The harvesting period, which lasted from 19 January - 20 April, was exceptionally lengthy. The total amount of white juice and red juice produced totalled 78607 L and 403900 L, respectively. *Table 3.1* indicates the quantities of grapes harvested during this vintage.

Table 3.1 Quantity Grape Cultivars Harvested during 1999

Grape Type	Cultivar	Mass [Kg]	Litres [L]
White	Chardonnay	96203	61925
White	Sauvignon Blanc	24938	11400
Red	Pinotage	63558	45180
Red	Merlot	230473	152576
Red	Cabernet Sauvignon	308195	227969
Red	Ruby Cabernet	10848	8000
Red	Cabernet Franc	44094	30206
Red	Cinsaut	28414	22339

The 2000 Vintage

During the 2000 harvest, ± 865 t of grapes were harvested; ± 125 t of white grapes and ± 740 t of red grapes. The harvesting period dated from 17 January - 23 March. The total amount of white juice and red juice produced totalled 75976 L and 489540 L, respectively. The cellar has a capacity of 1200 t. *Table 3.2* indicates the quantities of cultivars harvested.

Table 3.2 Quantity Grape Cultivars Harvested during 2000

Grape Type	Cultivar	Mass [Kg]	Litres [L]
White	Chardonnay	125867	75976
Red	Pinotage	85104	59702
Red	Merlot	230473	152576
Red	Cabernet Sauvignon	383319	252352
Red	Ruby Cabernet	10632	6910
Red	Cabernet Franc	30282	18000

3.1.3 Cellar Layout and Equipment

3.1.3.1 Cellar Design

The cellar has an area of 4000 m² and is divided into two levels. The ground floor is separated into two main sections; stainless steel fermentation tanks, and the bottling and storage area. The underground cellar hosts a variety of barrel types, which are continuously rearranged with respect to the winemaking process. The whole cellar is tiled.

The water source enters the cellar at a single point (See *Figure 3.1*). All the wastewater that is generated by the different sections in the cellar flows to a common collection pit (F6), which is found outside the cellar. The wastewater is pumped to a delta-settler and irrigated onto a field (F8).

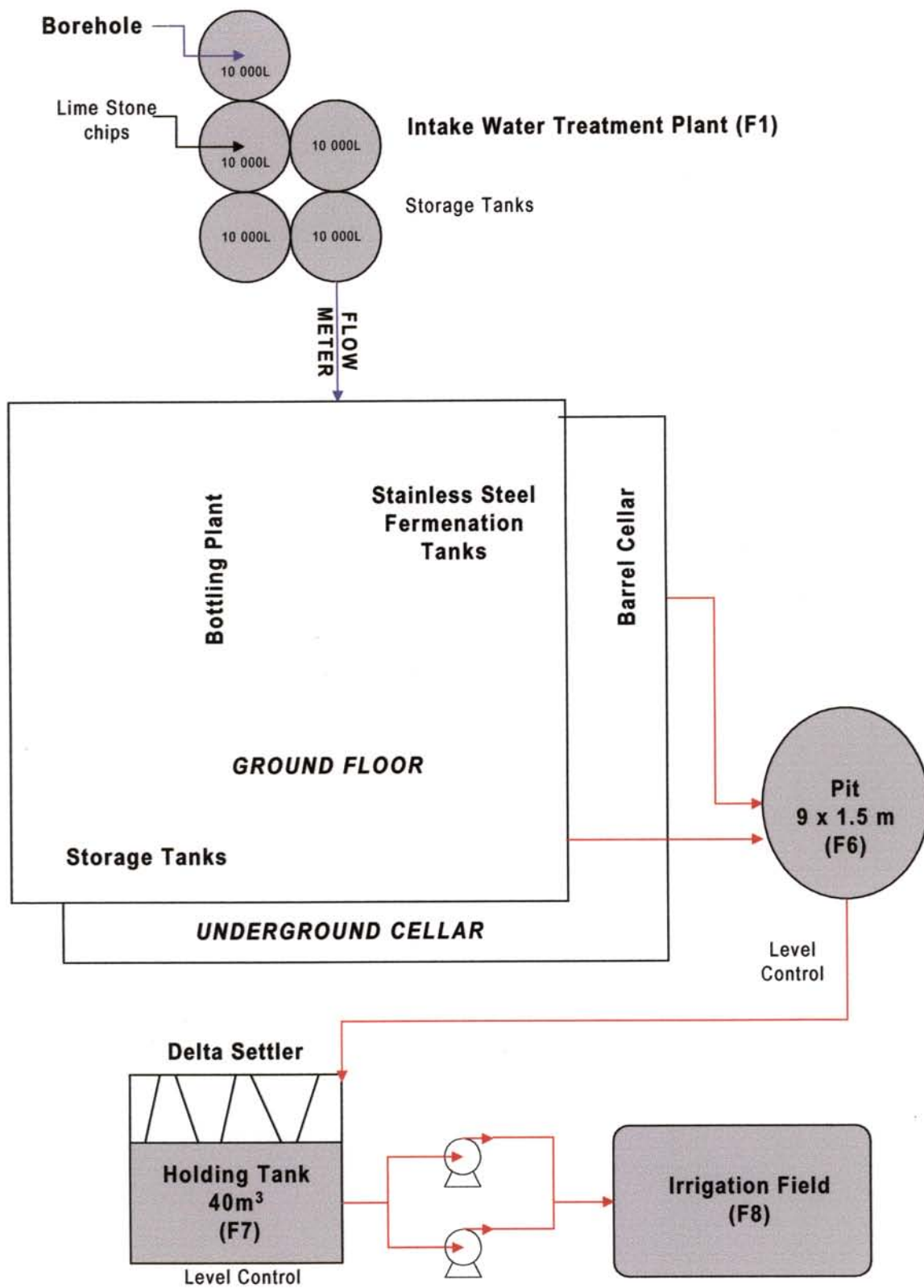


Figure 3.1 Rupert and Rothschild Cellar Layout

3.1.3.2 Equipment

The following equipment is present in the cellar:

- Crusher
- De-stemmer
- Mass Cooler
- 2 Air-Bag- Presses: capacity 8000 t
- Mono-pumps and piston pumps
- Tanks (double-jacketed stainless steel)
- Bulk Filter
- Barrels

The Role of Tank Sizes

As previously mentioned, the ground floor is separated into two divisions: one division contains a series of multi-sized tanks for fermentation purposes; the other side has red-wine storage tanks and the bottling assembly. The size and amount of tanks present in a cellar contributes significantly to the generation of wastewater. Smaller tanks are used to produce top quality wines, and are frequently present in prestigious wineries. No direct relationship can be made between tank capacity/usage and the subsequent water consumption. However, numerous small tanks will require more water for cleaning activities than a few large tanks. The specifications of the tank sizes are presented in *Table 3.3*.

Table 3.3 Tank Capacities and Usages

Tank Capacity [L]	Number of Tanks	Usage
13000	16	Fermentation
10000	22	Fermentation
30000	3	Fermentation
15000	2	Fermentation
18000	5	Fermentation
17000	5	Fermentation
25000	2	Fermentation
12000	2	Fermentation
2500	2	Fermentation
4500	4	Storage
6000	5	Storage
60000	1	Outside Storage
89000	1	Outside Storage

3.1.4 Winery Activities, Procedures and Practices

A generalised description of the annual activities is illustrated in *Table 3.4*.

Table 3.4 Outlined Annual Activity Chart for Rupert and Rothschild Vignerons

January - March	April - May	June - July	August -October	November
Vinification	Racking	Racking of previous vintage	Bottling of previous vintage Blending	Racking of current vintage Blending

For a comprehensive discussion on wine making, refer to *Section 2.2*. At Rupert and Rothschild Vignerons the fermentation process is initiated in the stainless steel tanks and completed in the barrels. Several vinification techniques differ according to vintage, grape quality, winemaker and style of wine desired. Grape skins are used as compost, however, a small percentage find their path into the wastewater streams. Before racking, bentonite may be added to the wine in the tanks to induce adequate settling of

colloidal particles. Racking takes place regularly at Rupert and Rothschild Vignerons, resulting in higher volumes of water consumption. The lees are generally sold for tartrate extraction, or are re-used in winemaking. However, small quantities find their way into the wastewater. Malolactic fermentation only occurs in the barrels. Fining may include the use of gelatine (however, not frequently employed). Upon the requirement of filtration, paper sheeting or filtration powder (diatomite) is used. This material is ploughed into the vineyard.

3.1.4.1 Winery Sanitation

Wine is a beverage for human consumption, and is thus required by law to be made under hygienic conditions. Several washing cycles occur daily in the winery, especially during the harvesting period. All equipment that comes into contact with wine must be maintained in a clean and sanitary condition, using a range of chemicals, which do not affect the wine, processing equipment or storage vessels, but do affect the quality of wastewater. Water is the most important cleaner. Many water-soluble deposits may be cleaned without the use of additional chemicals. Water hardness must be checked regularly to ensure that suitable chemicals are used, since hardness reacts to form complexes, which lower the efficiency of cleaning materials (*Rankine, 1989*). Water hardness can be overcome by using sequestrants (chelating agents); chemicals, which combine with metal ions in solution to form water-soluble complexes. Commonly used chelating agents include EDTA (ethylenediamine-tetra-acetate), sodium hexametaphosphate (calgon) and tetrasodium pyrophosphate (tspp). Potassium bitartrate is deposited in tanks, requiring extensive cleaning. Caustic based cleaning agents such as sodium hydroxide is usually used. Caustic soda dissolves proteins but has poor dispersing, wetting and rinsing properties. The surface material is of importance concerning its cleaning requirement. Caustic soda is too corrosive for use on wood, unlined concrete and certain older lined tanks. Cleaners include sodium carbonate, metasilicates, phosphates and surfactants.

The cleaning process is a multistage operation and is typically conducted as follows:

- Pre-rinse with cold or luke-warm water.
- Detergent wash
- Hot rinse
- Acid rinse
- Water rinse

After cleaning, the surfaces contacting wine are normally sanitised to remove microbial contamination. The principal sanitiser present in cleaners is chlorine. The best sanitiser is steam or hot water (85°C). General cleaning is the biggest user of water in the winery (*Rankine*, 1989). Water is used to clean wine storage and fermentation vessels, grape crushing and handling equipment, and floor areas, and is contaminated with detergents, sanitisers and residual compounds from the vinification procedure (See contaminant matrix, *Section 3.3*)

At Rupert and Rothschild, all pipes are washed daily with detergent-containing (Hygen Q.45) water, and once a week by a solution of caustic soda and citric acid. A weak solution of sulphur dioxide is also used to sanitise the pipe-lines. Tanks are washed with a solution of caustic soda and citric acid, and hot water is used to for sterilisation. Barrels are washed with hot water. During bottling, steam and ozone are used. All wastewater produced by the cellar activities flow to a collection point, however, the washing of off-loading bins and presses frequently take place outside the cellar, leading into a community fresh water stream, thus causing down stream contamination.

3.2 RUPERT AND ROTHSCHILD WATER AND WASTEWATER PROCESS DESCRIPTION

This section serves to describe the water processes of Rupert and Rothschild Vignerons. The analysis and evaluation of each section is discussed in *Chapter 4*.

3.2.1 Incoming Water Plant

A dam (135000 m³) and borehole supply water to Rupert and Rothschild Cellar. The water is pumped to a treatment unit designed with the intention to store and supply water of a high quality. The water resources on Fredericksburg Estate contain varying amounts of iron (0.1-1.0 mg/L). Previously a filtration and ozonation system had been installed in the water treatment unit.

The treatment and storage system at Rupert and Rothschild Vignerons consists of a 10000 L demand tank and four, 10000 L storage tanks. The tanks are interconnected and linked to a treated water supply booster pump. The water treatment system is positioned between the demand and storage tanks. The pH is adjusted by means of limestone addition. A water level detector in the storage tanks controls the system. When the desired water level is reached, re-circulation and simultaneous ozone injection takes place between the first and fourth 10000 L storage tanks.

This system has, however, been bypassed for most of 1999 and 2000. The bag filters clog constantly, causing the supply tanks to overflow, and the ozone unit has subsequently been removed. The water is still subjected to limestone treatment.

In March 2000, a flow meter was installed on the incoming water supply line (see *Figure 3.1*). The data from this flow meter provides the total quantity of water consumed by the cellar, which includes winemaking needs, cooling

plant operation and domestic consumption. It should be noted that the domestic water is discharged separately to municipal sewers.

3.2.2 Collection Pit (F6)

All the wastewater that is produced from the cellar is deferred to a collection pit situated outside the cellar. This pit measures 9 m by 1.5 m and is unlined; lending itself to potential soil contamination (especially by micro-organisms). During the harvest season, a large amount of solid material (mostly grape skins) enters the pit and accumulates. Grape solids ferment and may cause secondary pollution (if not removed frequently) of the fresh wastewater discharged from the cellar. A level control switch controls the volume in the pit. The wastewater is then pumped to a delta-settler.

3.2.3 The Holding Tank (F7)

The original wastewater system at Rupert and Rothschild Vignerons consists of a delta-settler and holding tank (F7). Initially the wastewater was ozonated through venturi-injection. The wastewater is then sprayed onto an irrigation field (5000 m²).

The wastewater pumped from the pit, is passed through the delta-settler in order to reduce the SS concentration. This system relies on gravity to produce the settling of suspended matter (e.g. skins, bentonite, lees, colloidal particles). However, the following aspects were not taken into consideration:

- Peak flow rates (especially common during the harvest period).
- Nature of suspended and colloidal particles.
- Efficiency of gravity to induce settling.
- Secondary contamination of wastewater when flowing over settled matter.
- Maintenance and labour implications.

The efficiency of settling is influenced by the flow rate and the nature of the suspended and colloidal matter. Wastewater containing bentonite settles well, however, colloidal particles (grape must) settle at a much slower rate. Colour compounds (anthocyanins and phenolic compounds) do not settle at all. At peak flow rates, settling is not efficient. Conversely secondary contamination of wastewater may occur at low flow rates, owing to contact with settled matter. Also, the laborious aspect may be tedious and time consuming, since the settled matter has to be shovelled manually to a collection bin for transport with skins or other solid waste material. The advent of induced settling is discussed in *Chapter 6*.

A 40 m³ collection tank is situated beneath the delta-settler. Originally the wastewater was ozonated by means of a venturi system, but this system was not found to be highly effective. However, upon the discontinuance of ozonation, offensive odours were prevalent. Similarly to the pit, the deposition of settling material forms a sludge layer on the bottom of the holding tank. Although ozone is a strong oxidant, it did not produce exceptional results. This may be attributed to several factors and will be discussed at length in *Chapter 7*; one of the principal factors being retention time. A level control switch regulates the discharge of the wastewater to the irrigation field. The irrigation field is situated ± 300 m from the cellar, next to the dam on Fredericksburg Estate. The soil is classified as turf.

3.2.4 Potential Problem Analysis

An operational plant must be investigated to determine whether potential problems may occur. All probable causes should be determined and preventative action must be planned. *Kepner and Tregoe (1981)* formulated a potential problem analysis (PPA), which can be applied to any function. A contingency plan should also be adhered to.

Table 3.5 summarises the potential problems analysis of the water process at the Rupert and Rothschild Cellar.

Table 3.5 Potential Problem Analysis of Water Process at Rupert and Rothschild

Potential Problem	Consequence	Possible Cause	Preventative Action
Iron concentration of incoming water too high	Staining of walls, toxic effects, wine adversely influenced	Inadequate treatment	Design of suitable treatment for iron removal
Presence of pathogens and/or micro-organisms	Epidemic conditions in winery	Contamination of water source	Use biocide (e.g. ozone) to destroy micro-organisms
Scale/ Corrosion of heat exchanger	Expense, serious consequences to cooling operation	Bleed stream not sufficient, incorrect dosage of scale inhibitors	Addition of anti-scaling agents, sufficient bleed stream
Corrosion of pipes and equipment	Expense	Hardness of water not monitored, concentration of cleaning agents	Educated use of chemicals
Generation of offensive odours	Unpleasant	Degradation of sludge deposits in pit and holding tank	Regular removal of residual matter, effective settling unit

Although not in the scope of this project, factors surrounding the irrigation practices must also be mentioned. A complete environmental audit entails not only the water audit, but also the management of soil and land. The discharge of effluent by spray application on land without consideration to hydraulic application rates, pH control and other elements, causes concern. The environmental considerations are (McGregor, 1999). :

- Protection of the vegetative cover and soil biota responsible for nutrient uptake and bioconversion processes.
- Maintenance of the chemical and physical soil structure necessary to support the waste breakdown processes on a sustainable basis.
- Certification that the drainage water is of appropriate quality so as not to contaminate water tables.

3.3 ESTABLISHING CONTAMINATION RATIOS AND A RESULTING MATRIX

Upon having defined the activities of the cellar and the use of chemicals, a contamination matrix may be structured. The rate of contamination by grape skins is also presented.

3.3.1 Rate of Contamination

Preliminary leaching experiments were conducted to determine the rate at which contamination (expressed as COD mg/L) of water occurs by grape skins. Leaching being a process during which the extraction of compounds occur. These experiments were done to assess the impact and rate of contamination due to the presence of pressed grape skins in water. Red and white grapes were pressed at 1 bar. Grape skins were leached in water at 1, 2 and 3 % concentrations (m/m) and COD analyses were performed at regular time intervals. The results are displayed in *Figures 3.2 and 3.3*.

From the figures it is evident that the contamination of water by grape skins occurs very rapidly. Within one hour of contact, COD levels of 870 mg/L (white grape skins) and 949 mg/L (red grape skins) were obtained. After two hours the COD increased to 1150, 2213 and 3320 mg/L for 1, 2 and 3 % m/m red skins, respectively. The white grape skins exhibited a similar trend, with COD concentrations measuring 1100, 1818, 2332 mg/L COD, respectively at 1, 2 and 3 % m/m; the contamination concentration was, however, lower than that of the red skins. Although the contamination increased over a 25 hour time period, the rate of contamination was the highest during the first 1-2 hours. These experiments made it evident that the separation of skins from the wastewater should occur as soon as possible in order to prevent excessive contamination. **Due to these observations, it was recommended that permanent wedge wire screens be fitted on all drain covers to minimise the concentration of skins in the wastewater streams. Particular attention should be paid to the process units of crushing, pressing and fermentation on the skins.**

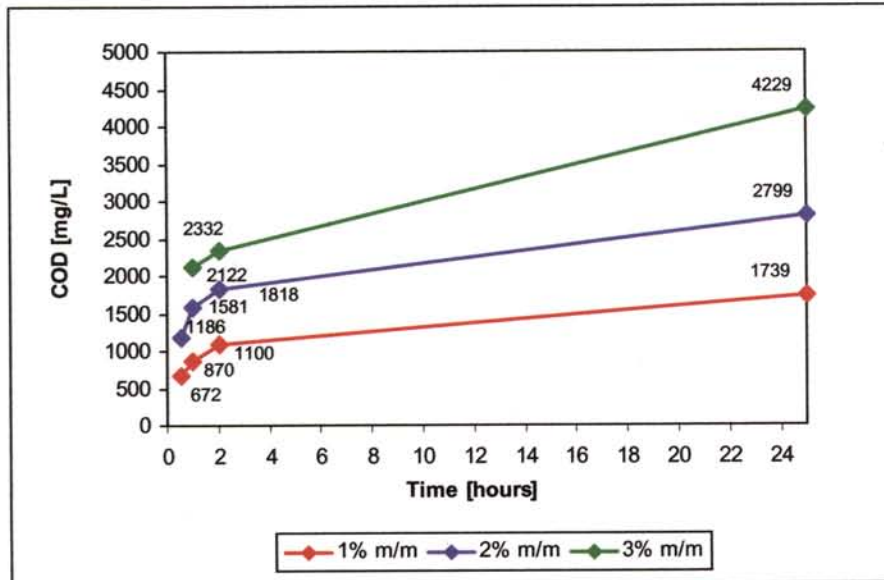


Figure 3.2 Rate of Water Contamination by White Pressed Skins

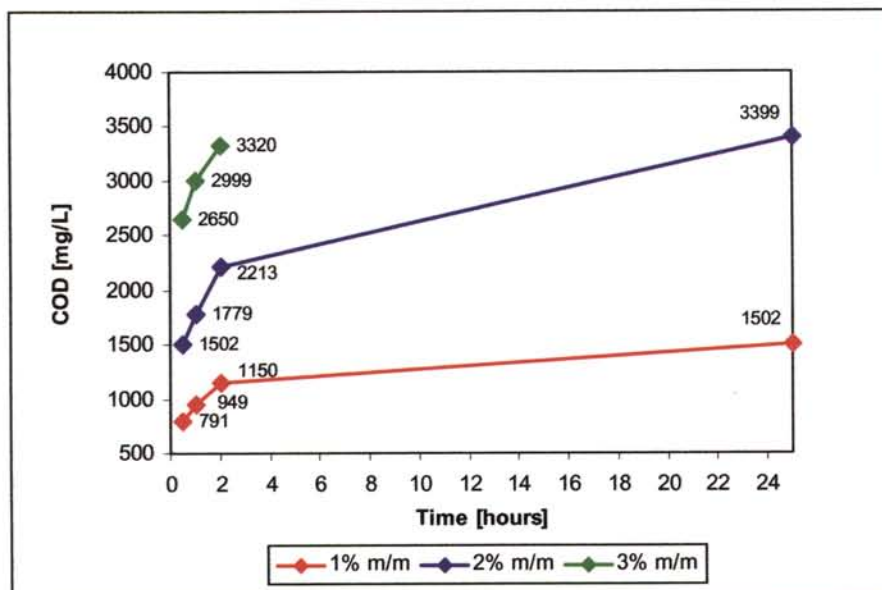


Figure 3.3 Rate of Water Contamination by Red Pressed Skins

3.3.2 The Contaminant Matrix

From *Chapters 2 and 3*, it is apparent that several factors contribute to the quality of wastewater produced by the cellar. Besides cellar practices and harvest dimensions; cultivar, balling, yeast, sulphur dioxide and sanitation chemicals are all factors that contribute uniquely to wastewater contamination. A contamination matrix has been engineered to schematically summarise the contamination dynamics (See *Figure 3.4*). In order to design a successful treatment system, a contamination matrix should ideally be engineered for the particular winery under study.

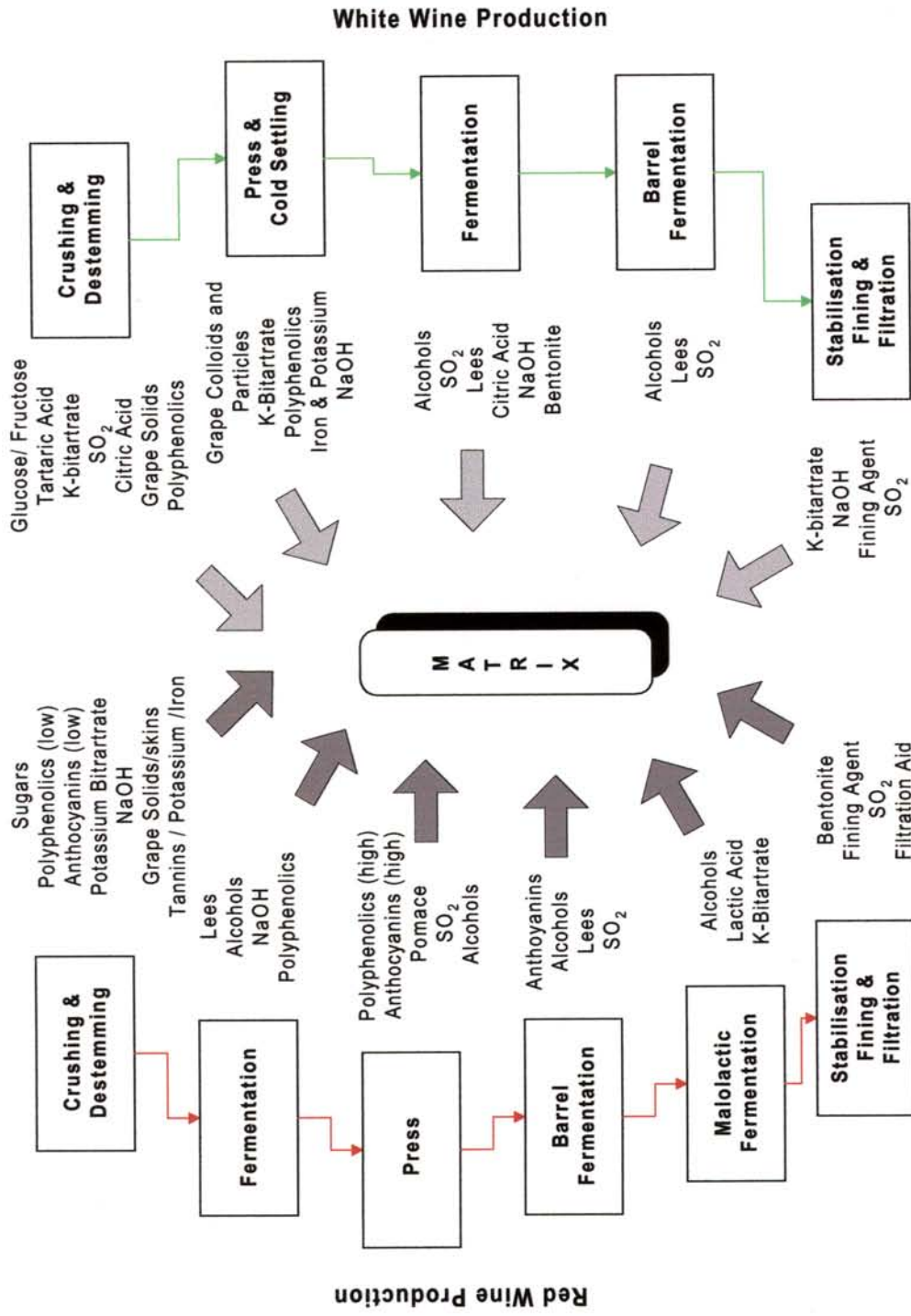


Figure 3.4 Contamination Matrix in Wastewater from Rupert and Rothschild Vignerons

3.4 THE WATER- AUDIT STRUCTURE

The water-audit forms part of the environmental audit. In order to accurately quantify and analyse wastewater, the entire water process should be monitored and evaluated by means of a water audit.

3.4.1 Value and Significance of the Audit

The pollution charge in a winery varies significantly on a daily basis making it difficult to obtain reliable data. A fair evaluation of this charge is necessary to adapt technical management of the winery, as well as to design a suitable treatment unit. "Grab" sampling is referred to when samples are taken in a random fashion, and customarily does not represent an accurate account of the process sampled. A successful water and wastewater auditing procedure should include the following:

- Description of the water processes.
- Data that accurately portrays the characteristics of the incoming water
- Accurate analysis of the wastewater (in terms of the COD, SS, pH and conductivity) resulting from typical operations.

When a water-auditing procedure is evaluated for a specific winery, the following criteria must be addressed and included in the audit to provide a noteworthy study:

- Harvest classification and quantification (grape input ratio).
- Design and layout of the cellar (area, water and wastewater flux).
- Evaluation of the vinification procedure, cellar activities and the chemicals used.
- Presence of other types of operations (e.g. grape-concentrate plant, distillery).
- The volume of water consumed.

3.4.2 Functions of the Water-Audit

A process flow diagram forms the foundation of all material and energy balances. Recording raw material usage, water and chemical usage, waste stream flow rates and compositions are the cornerstones of the water-audit.

In order to collect and evaluate information and data, the process engineering involved in the winemaking at Rupert and Rothschild Cellar was studied (described in *sections 3.1 and 3.2*). A flow meter was installed in the water supply line to the cellar in order to quantify water consumption. The several wastewater streams that manifold into one discharge pit (F6) were mapped. A sampling protocol was designed and is discussed in *Section 3.4.3*. Daily, weekly and monthly samples were analysed during the different operational phases over a two-year period.

3.4.3 Sampling Philosophy

In order to typify a specific system, it is rarely possible to analyse the whole system and all the tributaries. It is, therefore necessary to take representative samples (i.e. samples that reflect the properties of interest in the population) of the system, or in this case, the water and wastewater flux. The principal objective during sample collection is to obtain a small, yet informative portion of the population being scrutinized (quality of the water and wastewater streams). Due to the great expense of sampling and analysis, it is important to establish a sampling protocol to ensure that samples are taken correctly, representatively and accurately to ensure reproducibility. If individual and collective samples cannot provide the required information, analyses are often worthless. Contamination is a common error source in sampling procedures. Planning the sampling procedure must be an integral part of the water-audit.

The following definitions (ISO 6107-2) serve to define the concepts of the sampling protocol:

- Sampler: A device used to obtain a sample of water, either discretely or continuously, for the purpose of evaluation of various defined characteristics.
- Sampling: The process of removing a body of water, intended to be representative, for the purpose of evaluation of various defined characteristics.
- Composite sample: Two or more samples or sub-samples mixed together in appropriate known proportions (either discretely or continuously), from which the average result of a desired characteristic may be obtained. The proportions are usually based on time or flow measurements.
- Periodic samples: Discontinuous sampling.
- Grab sample (also snapshot or spot sample): A discrete sample taken randomly (with regard to time and/or location) from a body of water.

Composite sampling is often used to reduce the cost of analysing a large number of samples. Composite sampling may also reduce inter-sample variance due to the heterogeneity of the sampled material. Because analytical costs are reduced, more samples may be taken and can therefore, lead to a smaller mean square error than by a single grab sample. No samples have to be re-analysed with this approach. The following procedure is recommended to acquire representative samples:

- i. Samples would be drawn from water systems with stainless steel sample cutters.
- ii. Wastewater should be sampled prior to its disposal to land, evaporative lagoons, or sewer. Ideally the exit point of a tank or sump should be of sufficient capacity to store and mix wastewater produced over 24 hours during peak vintage flows.
- iii. Ideally the composite sample should be taken by a proportional sampler, which accounts for variations in flow. The wastewater should

be sampled at the depth at which it is decanted from the storage system, or from the outlet pipe.

- iv. At least 1 L of wastewater should be collected in sterile containers, and preserved by storing at 4°C.
- v. Sampling bottles should be used only once to prevent contamination.
- vi. Wastewater should not be sampled during periods of very low flow, or if excessively diluted by storm water.

Due to the organic content of the samples, analyses should be done preferably within 24 hours after taking the sample. Hence, cooler boxes or portable refrigerators should be used for storing samples. Sampling bottles should be filled to 1 cm from the top, to prevent oxidation due to oxygen contact in the bottles.

The sampling objectives of Rupert and Rothschild Vignerons were:

- Provide information of water quality.
- Provide detail on main sources of contamination within the cellar environment.
- Provide records of water and wastewater quality for future considerations and for authorities.
- Provide (in conjunction with flow measurements) contaminant fluxes, environment impact, and data for treatment, plant sizing and design.

The various water processes and activities at Rupert and Rothschild Vignerons were described and a subsequent sampling procedure was formulated. It should be noted that this procedure is open to much debate and diverse opinions may be expressed. It is therefore, of fundamental importance to tailor the sampling procedure for each winery, the most reliable criterions being observation and familiarity with the plant.

3.4.3.1 Sampling Protocol at the Rupert and Rothschild Cellar

The water from the dam and borehole were analysed to determine the quality of the natural resources on the estate. Due to a general acceptable quality, the resources were monitored periodically. On the date of sampling, several samples were collected in sterile 1 L sampling bottles for the duration of the day and a composite sample was made and analysed. All analyses were performed by Environmentek, CSIR, Stellenbosch. Five to eight samples were taken from different regions in the 135000 m³ dam, and composited. The water used inside the cellar was also collected and analysed. Samples from four random inlet sources were taken and composited.

The water in the sump of the cooling tower (F10) was sampled periodically (cooling unit is only operational during the harvest period). One sample was taken from the sump on two different time intervals on the day of analysis, in conjunction with the incoming water. All samples were marked and stored in an ice-filled cooler bag (the cooling water plant is discussed in *Appendix B*).

Daily, weekly and monthly samples were taken from the pit (F6) and holding tank (F7). Samples were always taken from both collection points in order to determine the following criteria:

- Effect of the pit on the wastewater.
- Effect of the delta-settler on the wastewater.
- Evolution of the wastewater over time.
- Effect of the storage of wastewater in the holding tank.

The ozonator was present in the holding tank during 1999, but removed in 2000. In order to determine the effect of the ozone on the wastewater, the wastewater was sampled in the irrigation pipe (F8).

During the 1999 and 2000 harvest periods, samples were taken according to cellar activities. Since the wastewater is collected before irrigation, less

frequent sampling was possible since automatic compositing took place in the holding tank.

The sampling protocol from both the pit (F6) and the holding tank (F7) is illustrated in *Table 3.6*.

Table 3.6 Sampling Procedure of Wastewater during the 2000 Vintage

Sampling Date	Sampling Points	Total Amount of Samples Taken by 2 L Sampler	Time Intervals between Sampling	Number of Composite Samples Analysed
28/01/2000	F6, F7	3 x 2L	± 2 hours	1 x 1L
09/02/2000	F6, F7	3 x 2L	± 2 hours	1 x 1L
10/02/2000	F6, F7	3 x 2L	± 2 hours	1 x 1L
23/02/2000	F6, F7	3 x 2L	± 2 hours	1 x 1L
25/02/2000	F6, F7	6 x 2L	± 2 hours	3 x 1L
02/03/2000	F6, F7	3 x 2L	± 2 hours	1 x 1L
10/03/2000	F6, F7	(F6) 40 x 2L	± 15 min	12 x 1L
		(F7) 20 x 2L	± 15 min	6 X 1L
15/03/2000	F6, F7	(F6) 9 x 2L	± 1 hour	3 X 1L
		(F7) 6 x 2L	± 1 hour	2 x 1L
22/03/2000	F6, F7	(F6) 6 x 2L	± 1 hour	(F6) 2 x 1L
		(F7) 3 x 2L	± 1 hour	(F7) 1 x 1L

This protocol was sufficient to obtain representative data from the Rupert and Rothschild Vignerons. Sampling at monthly intervals during the rest of the year was sufficient to provide reliable data. Sampling exercises should ideally be formulated around the activities of the cellar (e.g. sampling during bottling, 2nd and 3rd racking, blending). Post-harvest season, five to ten samples may be sufficient to characterise the wastewater.

Having characterised and defined the water process dynamics, the contaminant matrix, and the sampling procedure unique to Rupert and Rothschild Vignerons, the next chapter will present and examine the results from the analyses.

CHAPTER 4

THE WATER-AUDIT: A QUALITY AND QUANTITY ANALYSIS

The water-audit conducted at Rupert and Rothschild Vignerons involved the intake water and wastewater of the cellar. The assessment of the water quality and quantity forms an integral part of the environmental audit. Diverse water and effluent quality criteria and guidelines have been published in international and local literature. Different approaches and methodologies have been used to derive criteria and guidelines, e.g. some guidelines specify maximum concentrations for constituents, whereas others define ideal concentrations for constituents (*Holmes, 1996*). The Department of Water Affairs and Forestry (*Holmes, 1996*) developed Water Quality Guidelines for Irrigation Water, and will be referenced in this study. The analysis of the wastewater will also be discussed in reference to the National Water Act (*Muller, 1998*)

4.1 WATER SOURCE ANALYSIS

Initially the water supply to the cellar was evaluated. The borehole water was analysed when the cellar was built in 1997. The results are illustrated in *Table 4.1*.

Table 4.1 Analysis of Borehole-Water (July 1997)

Property	Concentration	SABS 241 Recommended Limits
pH	5.4	6.0-9.0
EC [mS/m @25°C]	25.8	70
Total Dissolved Solids 180°[mg/L]	168	-
Chloride as Cl [mg/L]	68	250
Alkalinity as CaCO ₃ [mg/L]	42	-
Sulphate as SO ₄ [mg/L]	3	200
Calcium as Ca [mg/L]	3	-
Magnesium as Mg [mg/L]	6	70
Sodium as Na [mg/L]	32	400
Copper as Cu [mg/L]	0.01	1.0
Manganese as Mn [mg/L]	0.04	1.0
Iron as Fe [mg/L]	0.10	1.0
Total Hardness as CaCO ₃ [mg/L]	72	20-300

The borehole water exhibited a low conductivity (25.8 mS/m), low calcium (3 mg/L), low total alkalinity (42 mg/L) and low pH (5.4). These characteristics resulted in the water being corrosive to metals and aggressive to cement type materials (*Mackintosh and De Villiers, 1996*).

The stabilisation of this type of water requires the adjustment of the chemical characteristics of the water, i.e.:

- Total alkalinity > 50mg/L as CaCO₃
- 6.5 < pH < 9.5

The borehole water (FB), the dam and the incoming water (F1) of Fredericksburg Estate were analysed during the harvesting season of 1999 and the results are depicted in *Table 4.2*.

Table 4.2 - Water Analysis of Supply Water

Sampling Date	10/03/99	1/03/99	1/03/99	10/03/99	SABS
Source	Dam	FB	F1	F1	241
Potassium as K [mg/L]	4.2		3.3	2.6	
Sodium as Na [mg/L]	19			35	400
Calcium as Ca [mg/L]	9.2	2.8	38	39	
Magnesium as Mg [mg/L]	4.5	6.7	10	8.4	70
Sulphate as SO₄ [mg/L]	7.1			9.1	200
Chloride as Cl [mg/L]	32			60	250
Alkalinity as CaCO₃ [mg/L]	34	8	88	93	
Hardness as CaCO₃	42	35	136	132	20-300
EC [mS/m @25°C]	20	29	49	45	70
pH	7.5	5.5	7.3	7.4	6-9
Copper as Cu [mg/L]				45	1.0
Iron as Fe [mg/L]	1.1	1.0	0.3		1.0
Manganese as Mn [mg/L]				7.4	5.0

Most of the results were in accordance with prescribed health and safety regulations. The following observations were made upon the analysis of the treated water:

- Calcium levels were significantly higher after treatment with limestone (2.8 to 38 mg/L), as was the alkalinity as CaCO₃ (8 to 88 mg/L).
- The pH of the water was adjusted from 5.5 to 7.3, and the conductivity increased from 29 to 49 mS/m.
- A significant reduction in the iron concentration was observed (1.0 to 0.3 mg/L).

The treatment plant achieved a reduction in the corrosivity of the water. Since the bag filters (iron removal) and the ozonation system were bypassed on a regular basis (due to operational error), these analyses may differ considerably. This system should be monitored monthly to ensure continuous water supply that corresponds to an acceptable quality.

The incoming water in the cellar was analysed during the 2000 harvest and the results are presented in *Figures 4.1 to 4.5* (Complete analyses are presented in *Appendix A*). The volume of water consumed by the cellar is discussed in *Section 4.3*.

4.1.1 Alkalinity, pH and Hardness

The alkalinity measurements should be interpreted in conjunction with the pH and total hardness of the water supply. Alkalinity, pH and hardness are important properties to consider during the evaluation of corrosion and scaling. Hardness is a complex quality of water and is governed by the concentrations of calcium and magnesium, expressed as mg CaCO₃/L. Scaling (characteristic of hard waters) is the deposition of insoluble carbonate and sulphate salts of calcium and magnesium, and may result in problematic conditions if heating of water is involved or heat exchange takes place. Soft water in contrast, is aggressive towards concrete surfaces and promote corrosion of unprotected metal surfaces. Hard water is generally softened either by a lime-soda process or ion-exchange.

The operations that take place in a winery can be classed as category I and II type industrial processes (*Holmes, 1996*). These categories have specific ranges of recommendation. Generally the target range is 0-100 mg/L CaCO₃ (alkalinity), pH values between 6.5-8, and hardness as CaCO₃ in the range of 50-100 mg/L. As depicted by *Figures 4.1 to 4.4*, the water supply of Rupert and Rothschild Vignerons falls within these ranges.

However, the saturation pH's (pH's calculated) indicate corrosivity. pH_s is the pH of the water if it was in equilibrium with CaCO₃ at the existing calcium and alkalinity concentrations. Three conditions may arise:

- pH - saturation pH = - value (corrosive potential)
- pH - saturation pH = + value (scaling potential)
- pH - pH_s = 0 (in equilibrium)

Figure 4.3 shows the water to have a corrosive potential. Limestone contact must be regulated to achieve pH values in the range of 8.5 for water of this nature. Classification of the water as category II (water used for cooling and in beverage industry), defines the EC and calculated total dissolved solids (TDS) concentration target ranges to be 0-30 mS/m and 0-200 mg/L, respectively. The analyses showed that the values calculated from Rupert and Rothschild's water supply fall just outside the desired range (EC = 36, 38 and 35 mS/m, with resulting TDS values of 230, 243 and 224 mg/L). This infers the tendency to corrode (See *Figure 4.4*).

From these investigations it may be concluded that the water supply to the cellar is of reasonable quality. The salt balance in the water is of extreme importance, necessitating monthly evaluation of the treatment system.

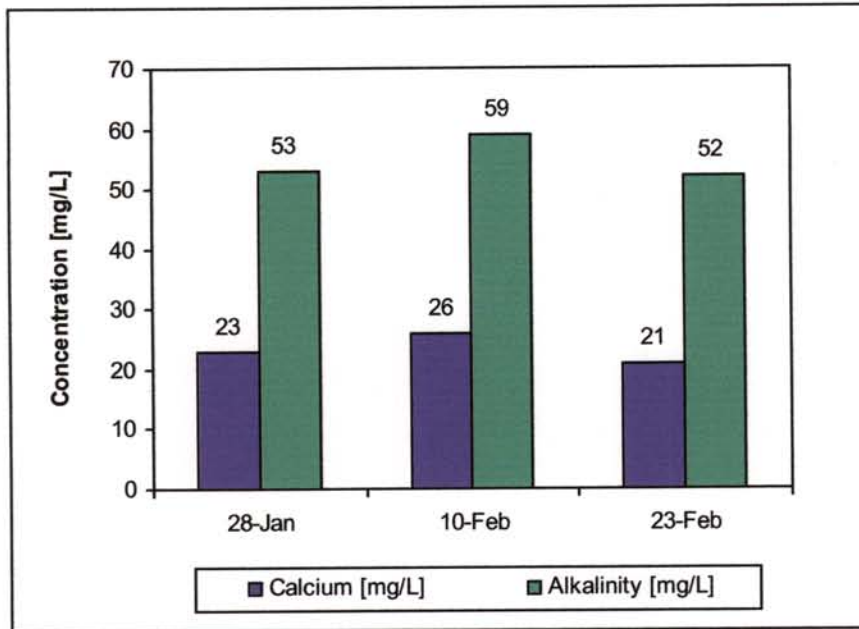


Figure 4.1 Calcium and Alkalinity of Incoming Water (2000)

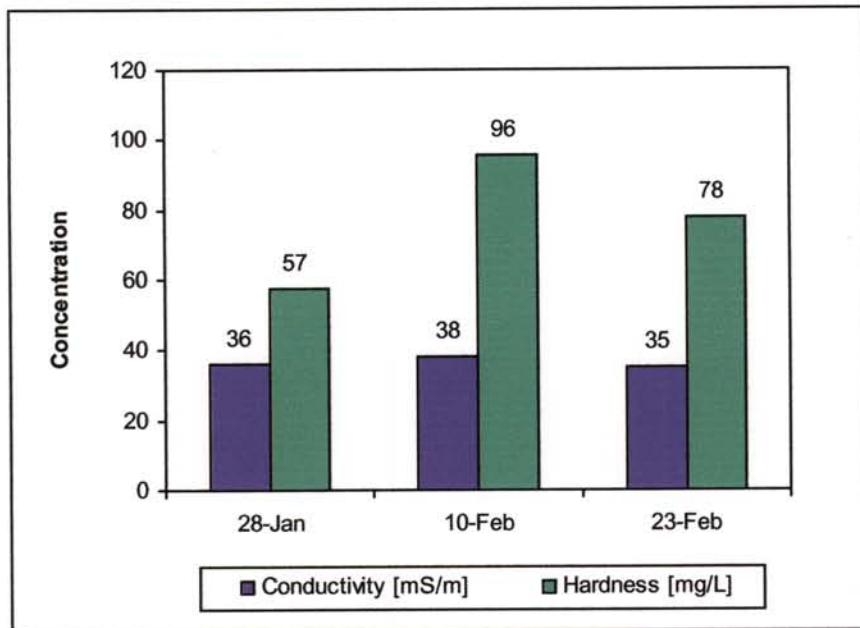


Figure 4.2 Conductivity and Total Hardness of Incoming Water (2000)

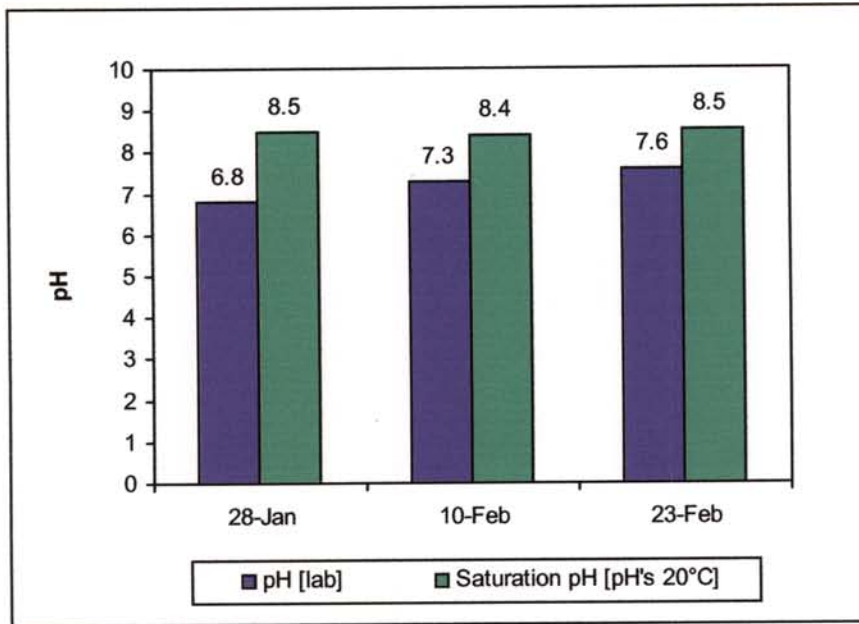


Figure 4.3 The pH and Saturation pH's of Incoming Water (2000)

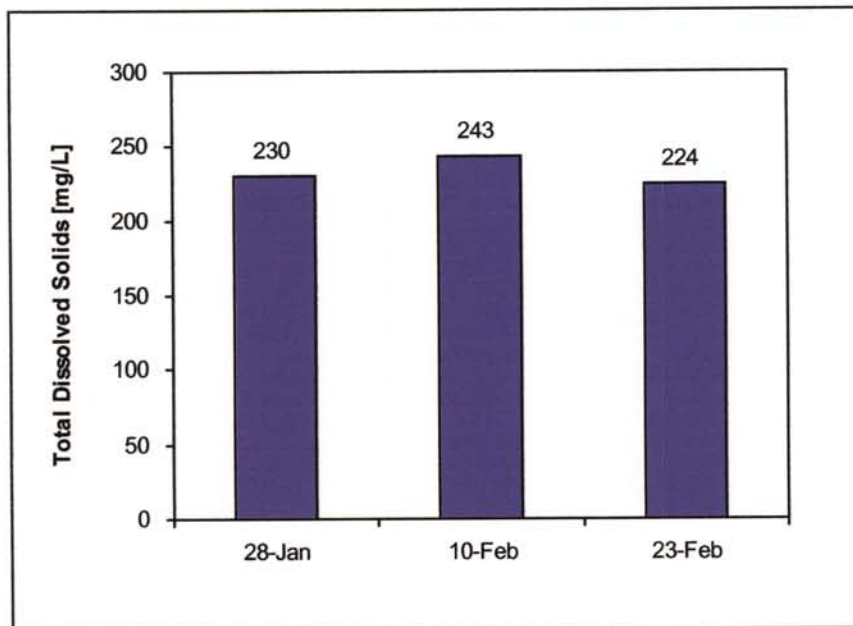


Figure 4.4 Total Dissolved Solids of Incoming Water (2000)

4.1.2 Iron

Turbidity and pH should be taken into account when interpreting iron concentrations in the water supply. Iron may cause damage to equipment as well as health hazards. The presence of even low levels of dissolved iron causes poor taste and the staining of walls (*Mackintosh and De Villiers, 1996*). The desirable range is generally 0.0-0.2 mg/L, depending on the application. Conventionally, iron removal is achieved by lime dosing and chemical oxidation followed by filtration. The iron concentrations may vary considerably depending on whether the bag-filters and ozonation system are operational in the previously designed treatment unit. *Figure 4.5* illustrates the measured levels during 2000.

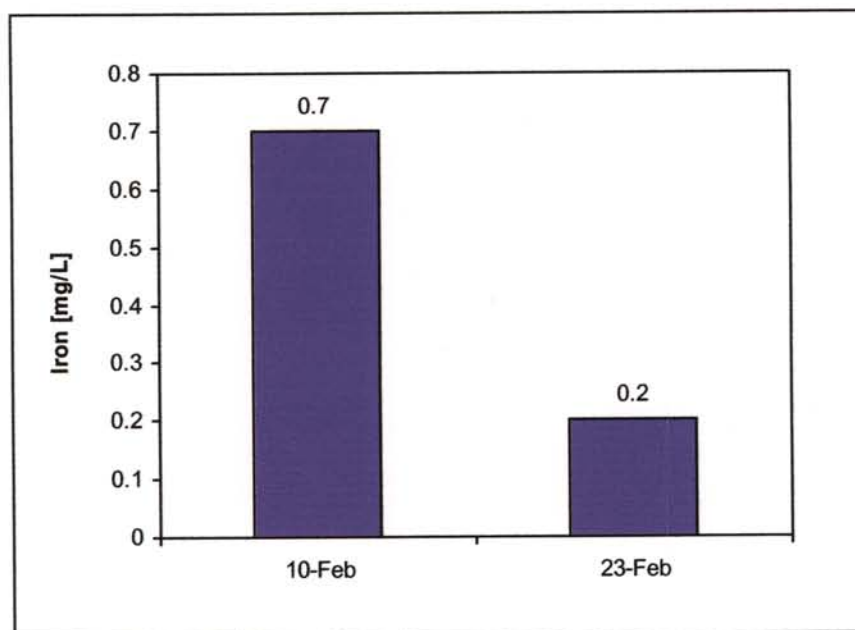


Figure 4.5 Iron in Incoming Water (2000)

To conclude the discussion on the water supply characteristics, *Table 4.3* illustrates potential water-related problems associated with process and utility waters.

Table 4.3 Potential Water-Related Problems Associated with Process Water (Holmes, 1996)

Process	Equipment Damage	Process Problems	Product Problems	Waste Disposal
Process Water	Corrosion/ Scaling	Precipitates	Sediment	SS
	Blockages	Foaming	Foam	Fe/ Mn
	Discolouration	Colour	Taste/odour	TDS
Utility Water	Corrosion/ Scaling		Turbidity	pH
	Fouling		Foam	TDS
			Colour	SS
			Taste/ Odour	Fe/ Mn
			Intestinal irritation	COD
			Health Hazards	

4.2 ANALYSIS OF WASTEWATER FROM RUPERT AND ROTHSCHILD VIGNERONS: AN IMPACT ASSESSMENT

4.2.1 The National Water Act (Act No. 36 of 1998)

Currently, the wastewater from Rupert and Rothschild Vignerons is irrigated onto land. Specific regulations for winery wastewater do not exist as of yet. However, the *National Water Act (Muller, 1998), section 21(e)*, will be used as the determining criterion when considering the quality of the wastewater (See *Appendix C*). The act makes provision for the irrigation of wastewater on land generated by any industrial activity.

Paragraph 2.7.(1) states that the irrigation may take place of up to 500 m³ of biodegradable industrial wastewater on any given day, provided the-

- Electrical conductivity (EC) does not exceed 200 (mS/m).
- pH is not less than 6 or more than 9 pH units.
- Chemical Oxygen Demand (COD) does not exceed 400 mg/L after removal of algae.

- Faecal coliforms do not exceed 100 000 per 100 ml.
- Sodium Adsorption Ratio (SAR) does not exceed 5 for biodegradable industrial wastewater.

Paragraph 2.7.(2) states that the irrigation up to 50 m³ of biodegradable industrial wastewater may take place on any given day, provided the-

- Electrical conductivity (EC) does not exceed 200 mS/m.
- pH is not less than 6 or more than 9 pH units.
- Chemical Oxygen Demand (COD) does not exceed 5 000 mg/L after removal of algae.
- Faecal coliforms do not exceed 100 000 per 100 ml.
- Sodium Adsorption Ratio (SAR) does not exceed 5 for biodegradable industrial wastewater.

Irrigation of more than 10 m³ of wastewater on any given day requires the registration of the water use (*subparagraph 2.8*). Wastewater irrigation is only permitted if the irrigation takes place-

- above the 100 year flood line, or alternatively, more than 100 m from the edge of a water resource or a borehole which is utilised for drinking water or stock watering; and
- on land that does not overlie a Major Aquifer (identification of a Major Aquifer will be provided by the Department, upon written request).

The registered user must ensure the establishment of monitoring programmes to monitor the quantity and quality of the wastewater to be irrigated prior to commencement of irrigation, as follows (*subparagraph 2.10.(1)*):

- the quantity must be measured and the total recorded weekly; and
- the quality must be monitored monthly as at the last day of each month by grab sampling, at the point at which the wastewater enters the irrigation system for all parameters listed in *subparagraph 2.7.(1)*.

In *paragraph 2.11.(1)* it is stated that the registered user must follow acceptable construction, maintenance and operational practices to ensure the consistent, effective and safe performance of the wastewater irrigation system, including the prevention of-

- i. waterlogging of the soil and pooling of wastewater on the surface of the soil;
- ii. nuisance conditions such as flies or mosquitoes, odour or secondary pollution;
- iii. waste, or wastewater, entering any surface water resource;
- iv. the unreasonable chemical or physical deterioration of, or any other damage to, the soil of the irrigation site; and
- v. the unauthorised use of the wastewater by members of the public.

All reasonable measures must be taken for storage of the wastewater used for irrigation when irrigation cannot be undertaken (*paragraph 2.11.(2)*). Suspended solids must be removed from any wastewater, and the resulting sludge disposed of according to the requirements of any relevant law or regulation (*paragraph 2.11.(3)*).

Storm water may be discharged if it does not contain waste or wastewater emanating from industrial activities, into a water resource (*subparagraph 3.7.(2)*). *Table 4.4* defines the general limits and special limits applicable to the discharge of wastewater into a water source.

Table 4.4 Wastewater Limit Values Applicable to the Discharge of Wastewater into a Water Resource (Muller, 1998)

Parameter	General Limit	Special Limit
Faecal Coliforms [per 100 ml]	1 000	0
Chemical Oxygen Demand [mg/L]	75*	30*
pH	5,5-9,5	5,5-7,5
Ammonia as Nitrogen [mg/L]	3	2
Nitrate/Nitrite as Nitrogen [mg/L]	15	1,5
Chlorine as Free Chlorine [mg/L]	0,25	0
Suspended Solids [mg/L]	25	10
Electrical Conductivity [mS/m]	70 mS/m above intake to a maximum of 150 mS/m	50 mS/m above background receiving water, to a maximum of 100 mS/m
Ortho-Phosphate as phosphorous [mg/L]	10	1 (median) and 2,5 (maximum)
Soap, oil or grease [mg/L]	2,5	0
Dissolved Iron [mg/L]	0,3	0,3

* After removal of algae

The reference to the National Water Act places the analyses of the wastewater audit in context with the requirements of the authorities, and should be kept in mind when evaluating the wastewater produced by a winery (the impact assessment).

4.2.2 The South African Water Quality Guidelines for Irrigation Use

The Department of Water Affairs compiled a manual to indicate target levels of properties in water when considering irrigation. *Table 4.5* depicts certain target levels, the crops it affects and the effects of the properties outside these ranges.

Table 4.5 Target Levels of Water Quality for Irrigation

Property	Target Range	Affected Sector	Effects of High Levels
Chloride as Cl [mg/L]	100	Crop yield	Foliar injury
Iron as Fe [mg/L]	5.0 < 0.2	Crop yield Clogging of irrigation equipment	Plant foliage damaged Aeration of soil important
Manganese as Mn [mg/L]	0.02	Crop yield	Manganese toxicity
Nitrogen as N [mg/L]	5	Crop yield and ground water	Contamination of ground water
pH	6.5 - 8.4	Crop yield Soil physical condition	Foliar damage Unavailability of macro- and micro-nutrients in soil
SAR	2.0 1.5	Crop yield Soil physical condition	Toxic to crops Soil hydraulic conductivity reduction
Sodium as Na [mg/L]	70	Crop yield	Foliar injury
SS [mg/L]	50	Equipment	Clogging of drippers

It must be noted that the target ranges of these properties depend on a host of variables including soil type, crop type and the irrigation system; and are subject to variation.

Wastewater analyses were performed throughout 1999 and 2000, with emphasis on the harvesting periods, since most of the wastewater was produced during these periods.

4.2.3 Harvest 1999

The sampling procedure during the 1999 harvest at Rupert and Rothschild Vignerons aimed to establish:

- i. The characteristic levels of contamination of the wastewater.
- ii. The effect of the of delta-settler and ozone system.
- iii. The evolution of the wastewater characteristics (from the point of collection (F6) to irrigation (F8)).

The sampling procedure commenced in March 1999. *Tables 4.6, 4.7 and 4.8* depict selective data from the sampling points (F6, F7, F8) (Refer to *Appendix A* for the complete analyses).

Table 4.6 Characteristics of Wastewater in Pit (F6) 1999

Property	01-Mar	10-Mar	17-Mar	08-Apr
EC [mS/m]	84	109	62	270
pH	4.9	4.6	4.8	3.8
COD [mg/L]	8851	5257	3492	30710
SS [mg/L]	242	329	382	12994

Table 4.7 Characteristics of Wastewater in Holding Tank (F7) 1999

Property	01-Mar	10-Mar	17-Mar	08-Apr
EC [mS/m]	90	90	106	160
pH	6.3	5.2	5.2	4.2
COD [mg/L]	3350	7510	4762	13780
SS [mg/L]	280	2724	497	4278

Table 4.8 Characteristics of Irrigation Wastewater (F8) 1999

Date	01-Mar	10-Mar	17-Mar	08-Apr
EC [mS/m]	88	103	133	126
pH	6.1	5.3	5.4	4.3
COD [mg/L]	3630	3281	5238	7090
SS [mg/L]	332	203	195	729

Higher levels of potassium (127-273 mg/L) and sodium (66-116 mg/L) were present in relation to the cations magnesium (16-18 mg/L) and calcium (48-58 mg/L) measured in the irrigation water (F8) (See *Figure 4.6*). This is due to high levels found in wine. These cations influence the EC of the wastewater. Although a target range of 70 mg/L is suggested by *Holmes* (1996), the sodium levels did not constitute problematic levels. The concentrations of sulphate (23-90 mg/L) and chloride (90-95 mg/L) present in the three sectors (F6, F7, F8) were considered to be within recommended levels.

Iron levels of between 3.5-15 mg/L (See *Figure 4.7*) were present in the wastewater, thus falling outside the target level of 5 mg/L as advised by *Holmes* (1996). However, depending on the soil structure and aeration quality, acceptable iron levels are subject to variation.

As determined by the NWA, the SAR values for irrigation water of up to 50 m³ per day is subject to a limit of 5 units. The SAR of the irrigation water was calculated to be 2.15, 3.70 and 2.06 units on three separate occasions (See *Figure 4.8*).

The EC of the irrigation water was also within the legal limit of 200 mS/m, computing values of 88, 103, 133 and 126 mS/m on four separate dates.

The irrigation water exhibited pH's of 6.1, 5.3, 5.4 and 4.3. The pH values were low in compliance with the required range of 6-9 units (NWA). The pH's in the pit (F6) were exceptionally low (4.9, 4.6, 4.8 and 3.8) on the selective dates of sampling. It may thus be deduced that the pH increases with time.

During the harvesting season of 1999, large differences were observed in the COD values. The COD of the irrigation water was 3630, 3281, 5238 and 7090 mg/L on four separate sampling dates (see *Figure 4.11*). Analysis on 7 April 1999 reflected a COD concentration of 30710 mg/L in the pit and 13780 mg/L in the holding tank. As previously detailed, the COD concentration is influenced fundamentally by the presence of suspended material (lees, skins

and pips), alcohols and cellar chemicals. The high COD concentration in the pit on this date was thus ascribed to the racking process in the barrel cellar (subsequent lees discharge) and the procedure of extensive sanitation. On the respective sampling dates, COD concentrations in the holding tank (F7) were measured at 3350, 7510, 4762 and 13780 mg/L. Although subjected to ozonation, the COD concentrations in the holding tank were not reduced significantly. This was determined to be due to several factors, including the presence of suspended material and insufficient retention time in the holding tank.

According to the NWA, suspended solids (SS) must be removed from the wastewater. *Holmes (1996)* suggests a maximum value of 50 mg/L. The SS concentrations in F8 were 332, 203, 195 and 729 mg/L on the respective sampling dates (See *Figure 4.12*). A value of 12994 mg/L was observed in the pit on 7 April. On two individual dates, the SS concentrations in the holding tank were measured to be 2724 and 4878 mg/L, respectively. These high concentrations were attributed to various cellar procedures of cold settling and racking, resulting in the discharge of grape particles, lees and bentonite to the wastewater.

With regards to nitrogen and phosphorus, concentrations ranged between 24-29 and 3.3-5 mg/L respectively, which were well within target levels. In all samples analysed, the turbidity was high due to the presence of anthocyanins and other colour compounds, thus rendering analysis impossible.

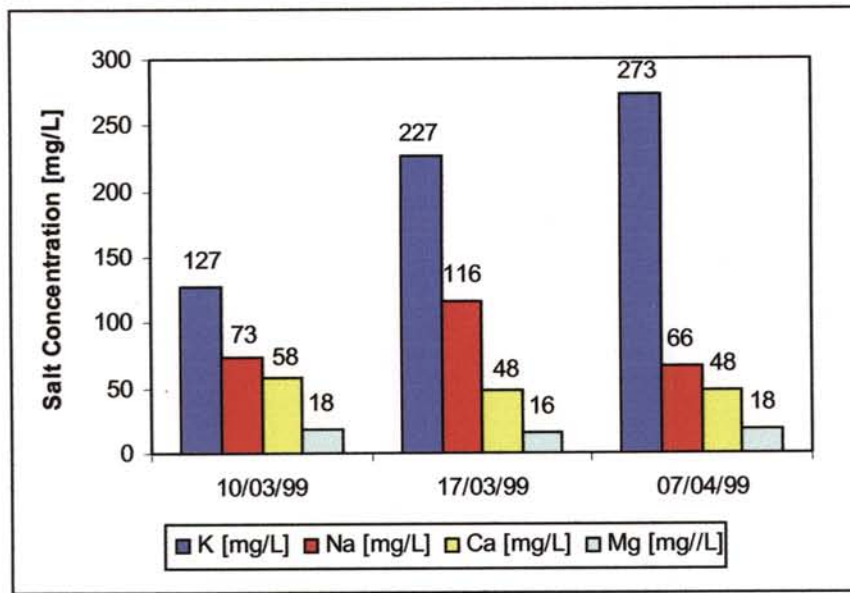


Figure 4.6 Salt Concentrations in Irrigation Water (F8) 1999

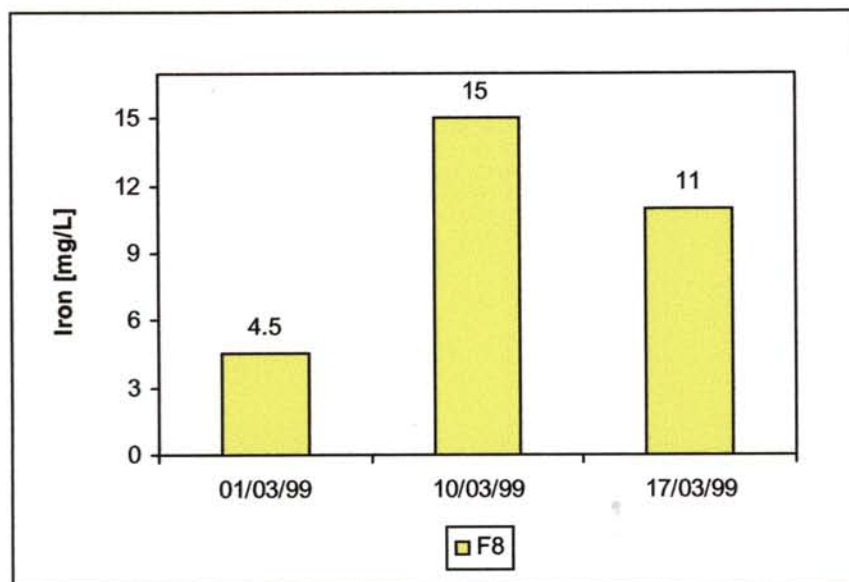


Figure 4.7 Iron in Irrigation Water (F8) 1999

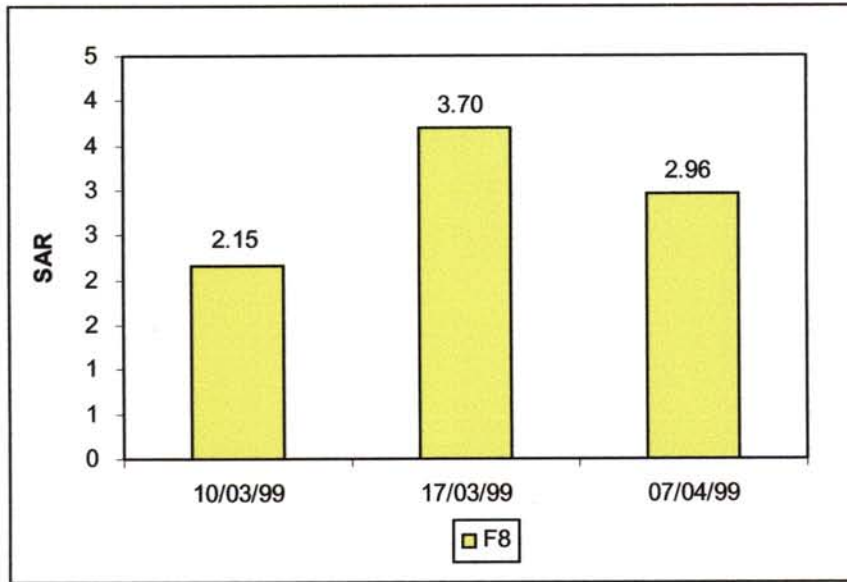


Figure 4.8 SAR in Irrigation Water (F8) 1999

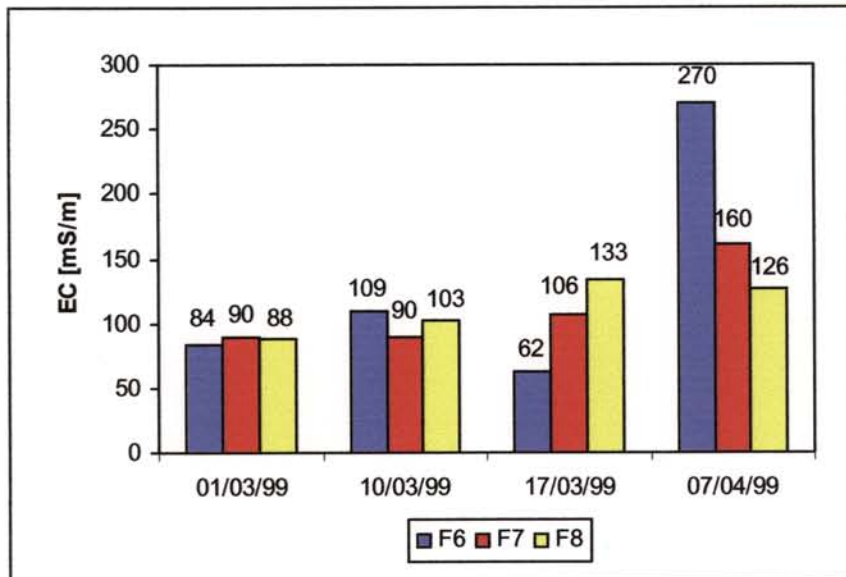


Figure 4.9 EC of Wastewater 1999

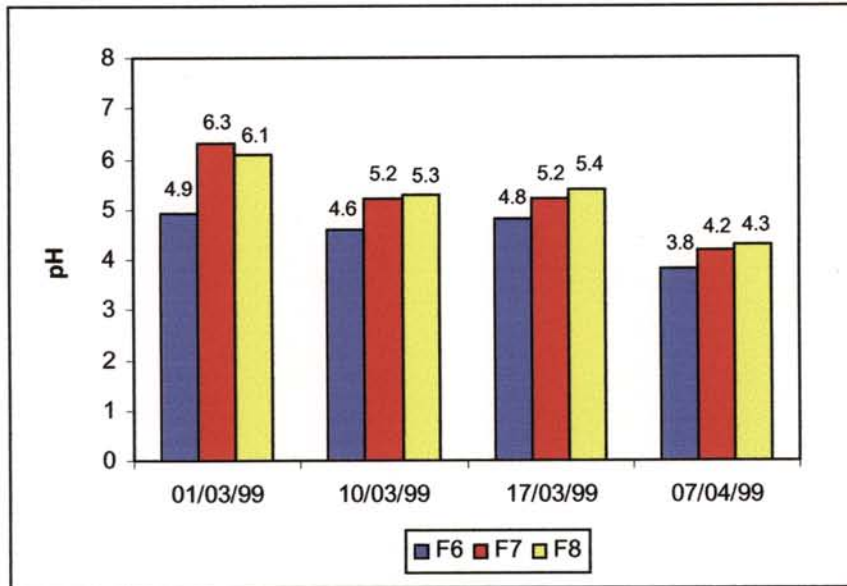


Figure 4.10 pH of Wastewater 1999

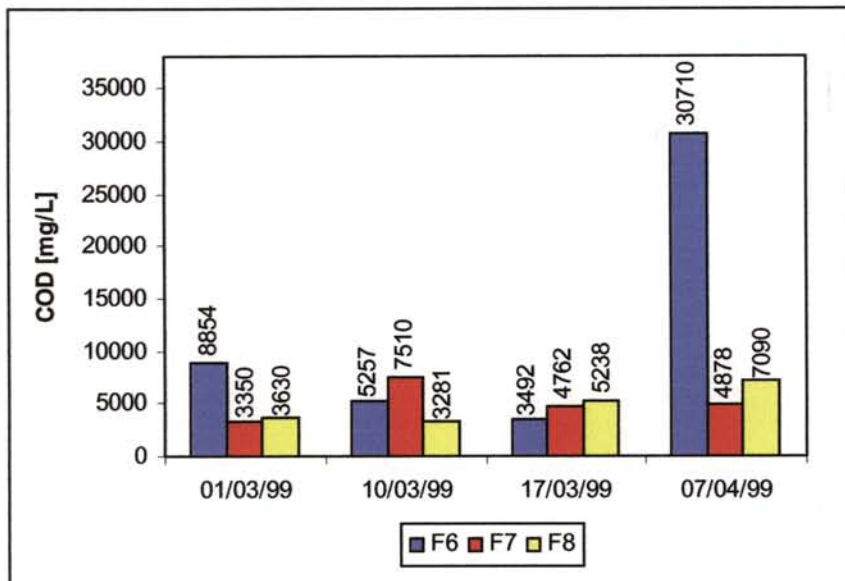


Figure 4.11 COD of Wastewater 1999

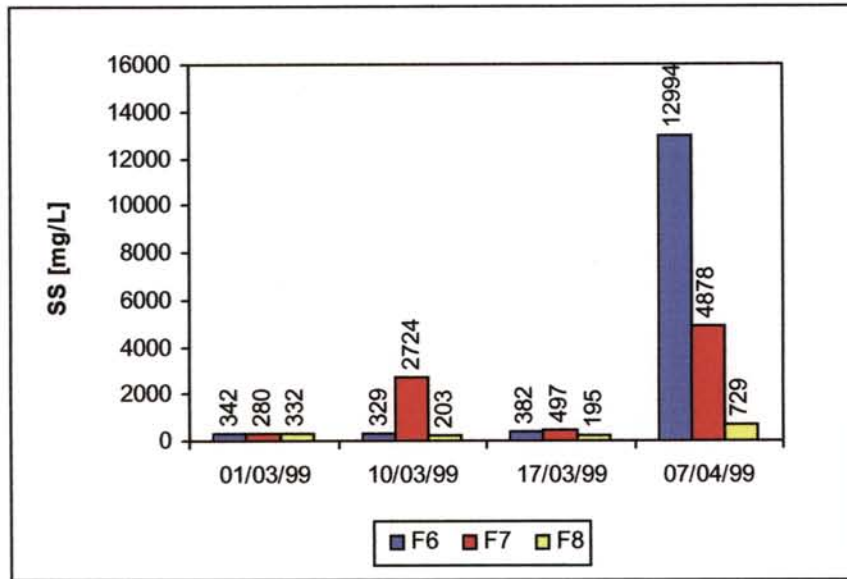


Figure 4.12 SS in Wastewater 1999

Microbiological analyses assessed the presence of microbial populations in the wastewater streams. Winery wastewater contains several nutrient sources providing an ideal environment for micro-organisms. The values are presented in *Table 4.9*.

Table 4.9 Faecal Coliforms Present in Wastewater 1999

Property	Pit	Holding Tank	Final Outflow
Faecal Coliforms [counts/100ml]	1.02×10^7	1.16×10^8	1.16×10^8
<i>Escherichia coli</i> [counts/100ml]	0	0	0

High levels of faecal coli were present in the three sampling points. The presence of these organisms is not acceptable. Certain species of faecal coli e.g. *Klebsiella* spp., may originate from the soil. A biocide is necessary to reduce the number of these micro-organisms.

Conclusions drawn from Analyses from Harvest 1999

The COD concentration was considered the principal criterion when evaluating of the pollution status of the wastewater. Due to the current design of the wastewater system, wastewater is constantly subjected to detrimental conditions. The COD concentrations should decrease as the suspended solids are settled (i.e. in the delta-settler). However, solid matter in the delta-settler was not removed frequently (due to impractical design of delta-settler), and subsequently, the feed stream from the pit was further polluted by the settled solid matter (especially characteristic at low flow rates). Further complications were observed in connection with the holding tank. Since not all particulate matter was settled in delta-settler, a sludge layer was formed in the holding tank. Ozonation efficiency comes into question, as ozone is particularly sensitive to the presence of suspended particles.

Upon the discharge of grape skins, colloidal particles from must, lees, bentonite and cellar chemicals, high peaks of contamination were observed in terms of COD and SS. To prevent these peak pollution loads, suspended matter should be separated from the wastewater as far as possible.

4.2.4 Harvest 2000

The sampling protocol was altered during the 2000 harvest, since ozonation of the wastewater did not take place. For evaluation and cost purposes, the pit and holding tank were sampled at regular intervals. The results from the wastewater in the pit constituted information on raw (untreated) wastewater emanating from the cellar; these analyses are considered to provide data for treatment options. The analyses from the holding tank served to illustrate the general quality of the wastewater produced by Rupert and Rothschild Vignerons during the 2000 harvest.

Selected properties of the wastewater are presented in *Tables 4.10 and 4.11* (see *Appendix A* for complete analytical results).

Table 4.10 Characteristics of Wastewater in pit (F6) 2000

Date	28-Jan	23-Feb	25-Feb	02-Mar	10-Mar	15-Mar	22-Mar
EC [mS/m]	79	80	106	86	158	93.5	83
pH	3.3	4.4	3.6	6	4.88	4.7	5.15
SAR		1.69		7.18	4.66	2.48	2.18
COD [mg/L]	3028	2683	12510	2704	6872	3427	4761
SS [mg/L]	184	565	625	420	599	286	412

Table 4.11 Characteristics of Wastewater from Holding Tank (F7) 2000

Date	28-Jan	10-Feb	23-Feb	25-Feb	10-Mar	15-Mar
EC [mS/m]	80	160	106	89	169	101
pH	4.3	4.7	5.1	4.3	5.9	4.5
SAR	3.17	4.19	4.35	2.35	10.46	2.18
COD [mg/L]	3068	4732	2656	4156	3628	5355
SS [mg/L]	74	159	248	299	218	291

The Pit (F6)

Before commencing the discussion of the wastewater analysis, it should be noted that the data collected on the occasions of 10 and 15 March 2000 is presented as averages from 15-30 min sampling intervals. The significance of this sampling method is discussed in the following section.

As observed during the 1999 harvest, the COD values vary significantly according to the cellar procedures (See *Figure 4.13*). A concentration of 12510 mg/L was observed on 25 February, attributed to the washing of a red grape press. Both particulate organics and dissolved organics contributed to the COD concentration. The dissolved organic carbon (DOC) concentrations are illustrated in *Figure 4.14*. Reductions of these compounds are often expensive and are complicated by the presence of phenolics and tartrates present in the wastewater. The prospect of chemical oxidation is discussed in *Chapter 7*.

Figure 4.15 depicts the measured EC values, which complied with the required maximum value of 200 mS/m.

The SS concentrations in the pit are illustrated in *Figure 4.16*. Values of between 184-625 mg/L were recorded. According to legislation, suspended solids must be removed from wastewater. By reducing the amount of solid particles entering the wastewater, significant reductions in these concentrations may be observed. Induced sedimentation or filtration may be used to remove these suspended particles. *Chapter 6* discusses physico-chemical treatment options for winery wastewater with particular reference to suspended solids removal.

The pH's of the wastewater were well below the legal requirements of 6-9 units (See *Figure 4.17*). The low pH's (3.3-6.0 units) can be attributed to the low pH of grapes and wine. The pH may be adjusted by means of lime addition, which should ideally form part of the design parameters for the treatment of organic compounds.

Figure 4.18 illustrates the sodium:calcium:magnesium concentration ratios measured in the wastewater. Due to the elevated usage of caustic soda (NaOH) in the cellar on 2 March, the resultant sodium concentration was 169 mg/L, explaining the slightly elevated pH of 6 as depicted in Figure 4.18. Figure 4.19 depicts the SAR indices, determining the effect on soil sodicity. These concentrations are relevant when considering soil dynamics, and are presented to illustrate typical levels found in the wastewater.

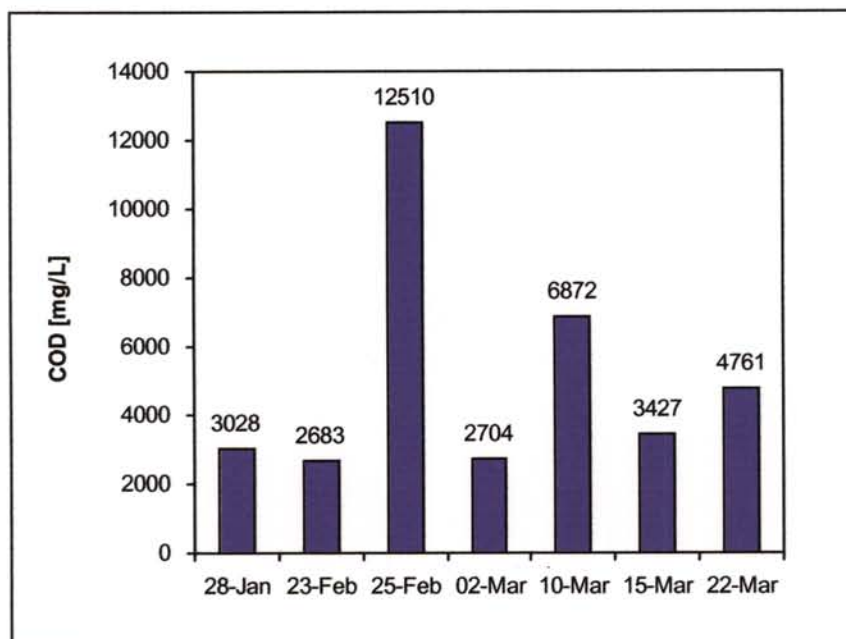


Figure 4.13 COD of Wastewater in Pit (F6) 2000

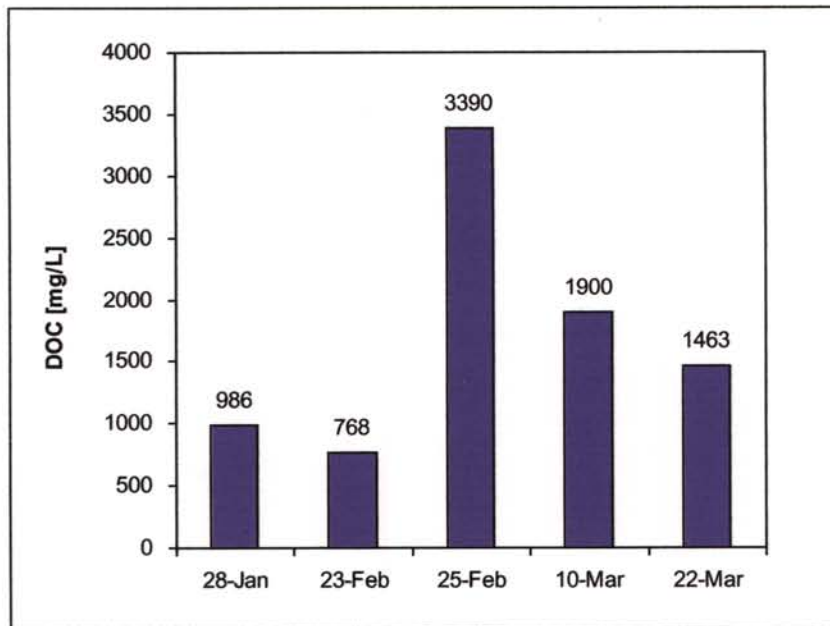


Figure 4.14 DOC of Wastewater in Pit (F6) 2000

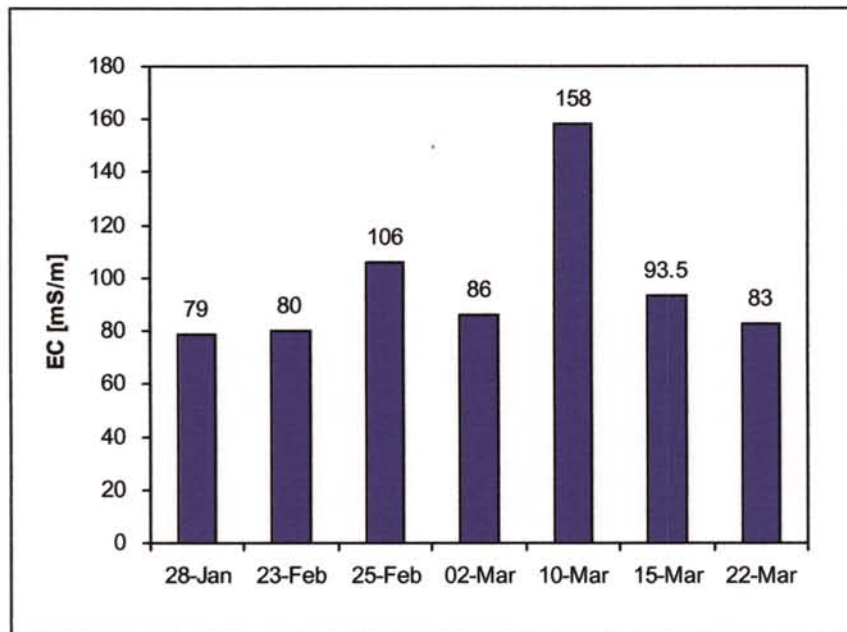


Figure 4.15 EC of Wastewater in Pit (F6) 2000

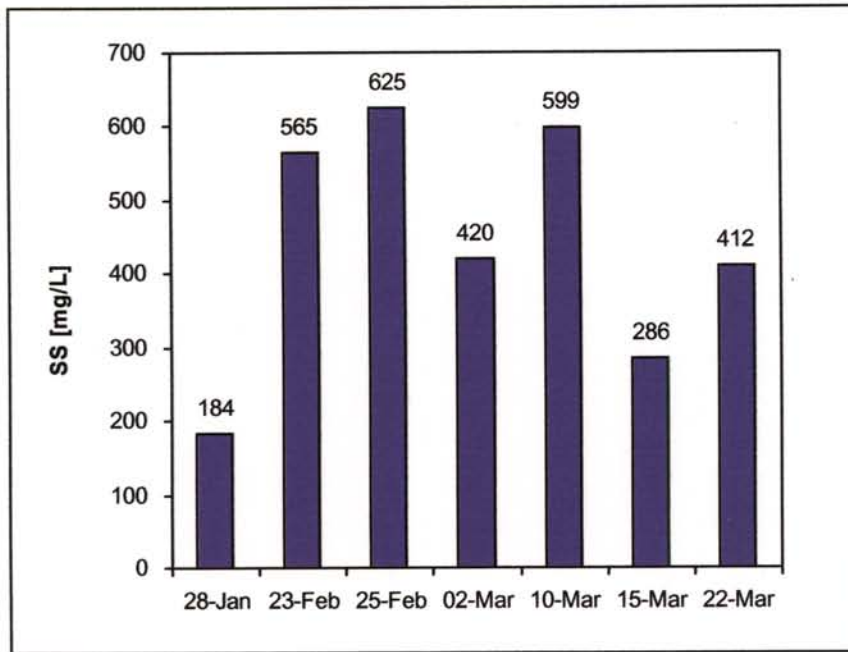


Figure 4.16 SS in Wastewater in Pit (F6) 2000

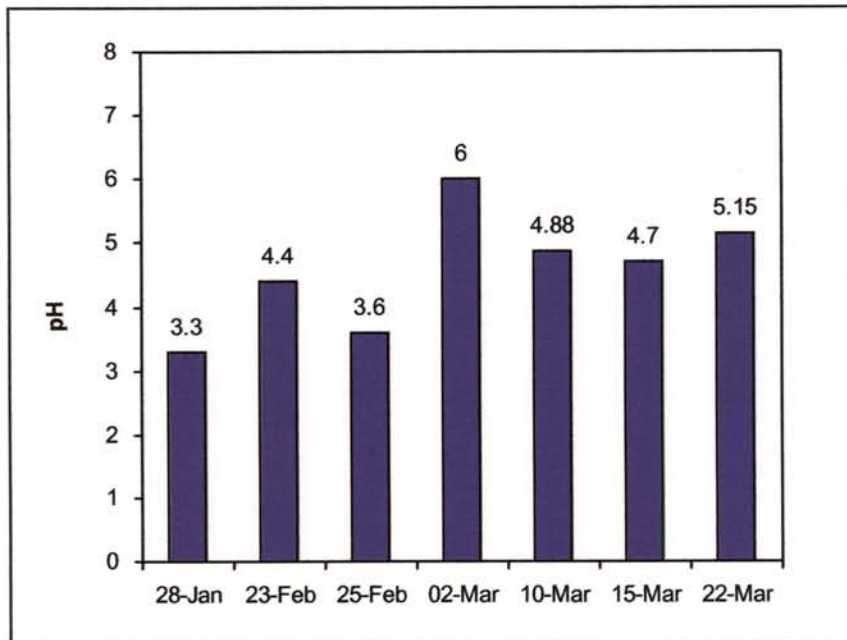


Figure 4.17 pH of Wastewater in Pit (F6) 2000

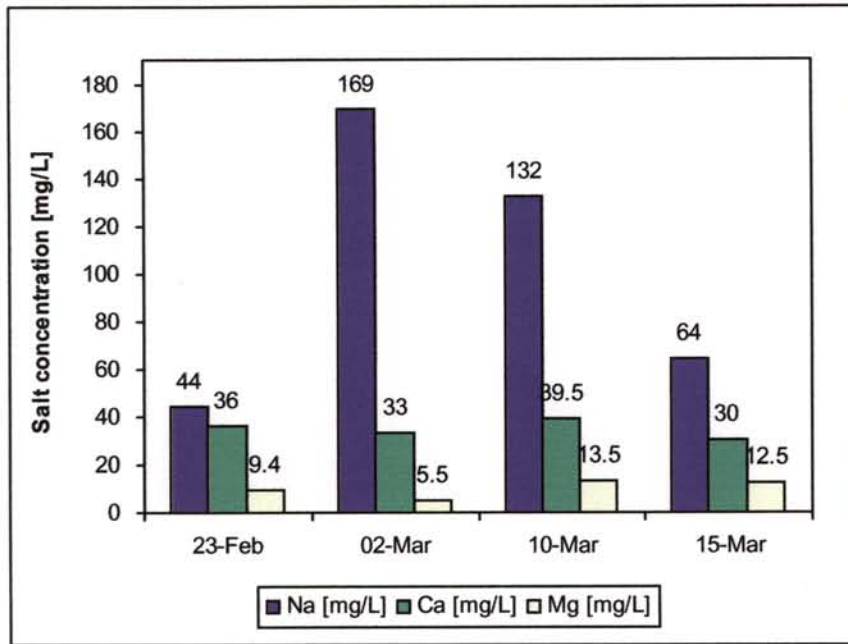


Figure 4.18 Salt Concentrations in Wastewater in Pit (F6) 2000

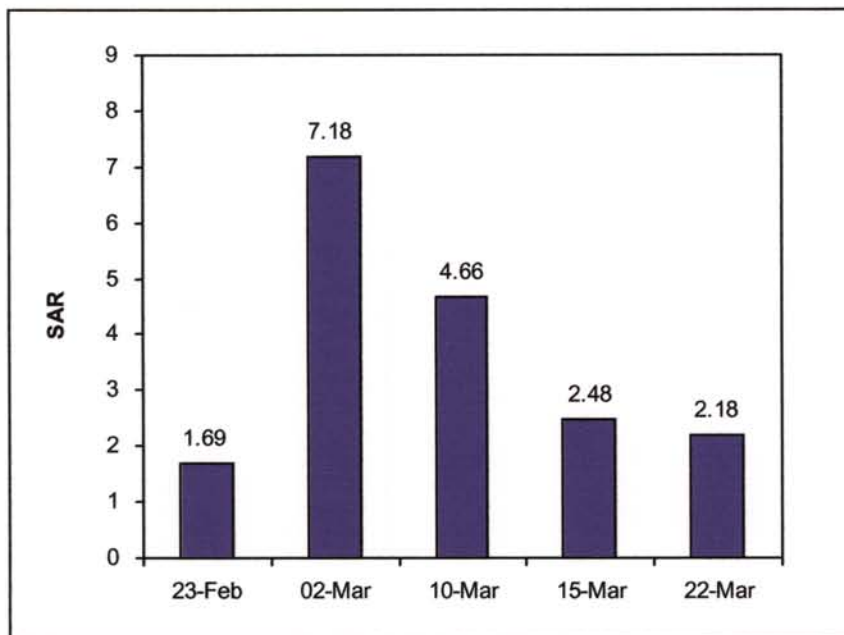


Figure 4.19 SAR of Wastewater in Pit (F6) 2000

The Holding Tank (F7)

The water consumption by Rupert and Rothschild Vignerons generally falls within 50 m³ per day (See *Section 4.3*). A restriction of 5000 mg/L COD is thus placed on the discharged wastewater. As depicted in *Figure 4.20*, the COD ranged from 2656-5355 mg/L. These values were generally lower than observed during the 1999 harvest, being attributed to several improvements of cellar practices and awareness of pollution by staff (considered most significant factor). The DOC content of the wastewater is illustrated in *Figure 4.21*.

The EC was generally within the recommended target range (See *Figure 4.22*). As observed in *Figure 4.23*, pH values were characteristically low (4.3-5.9 units) and must be raised to between 6-9 units.

As previously discussed, the SAR should be below 5 units. Although the values were generally below 5 units (see *Figure 4.24*), a value of 10.46 was measured on 10 March. The use of caustic soda induced this high value, thus an effort should be made to recycle the use of caustic soda for tank and equipment cleaning.

The grass type, soil dynamics and aerobic quality of the irrigation field must be taken into consideration when determining acceptable iron levels, since iron sensitivity varies. The iron levels in wastewater were considered to be within an acceptable range, i.e. below 5 mg/L (See *Figure 4.25*).

Although not below a suggested 50 mg/L, high peaks in SS concentrations were not observed during the 2000 harvest. Great care was taken by the cellar staff to separate lees, bentonite and grape solids from the wastewater. As illustrated in *Figure 4.26*, the concentration ranged from 74-299 mg/L.

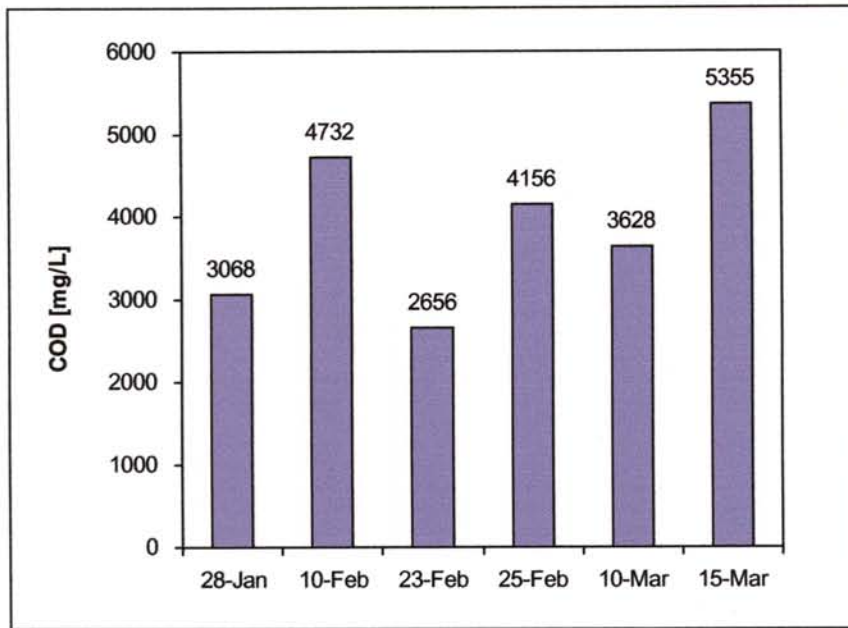


Figure 4.20 COD of Wastewater in Holding Tank (F7) 2000

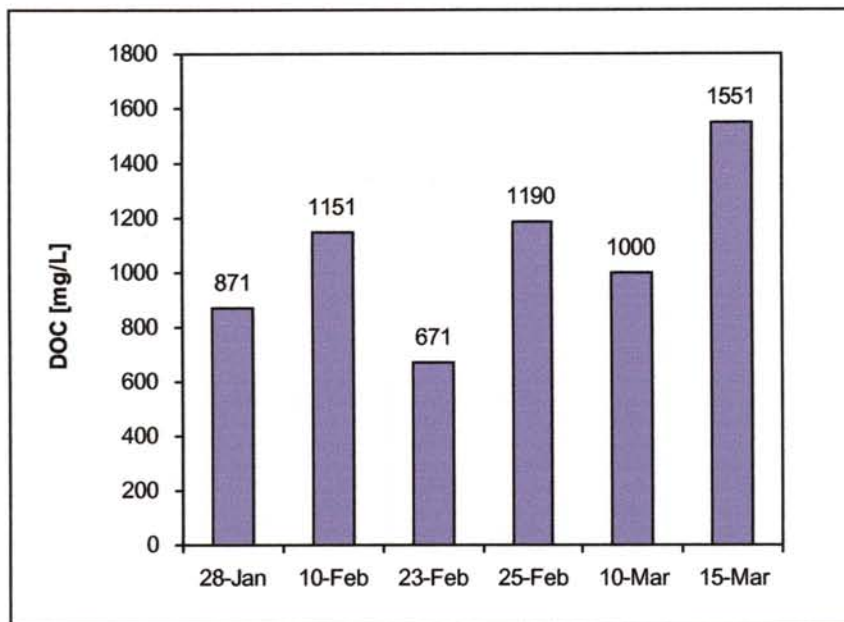


Figure 4.21 DOC in Wastewater in holding Tank (F7) 2000

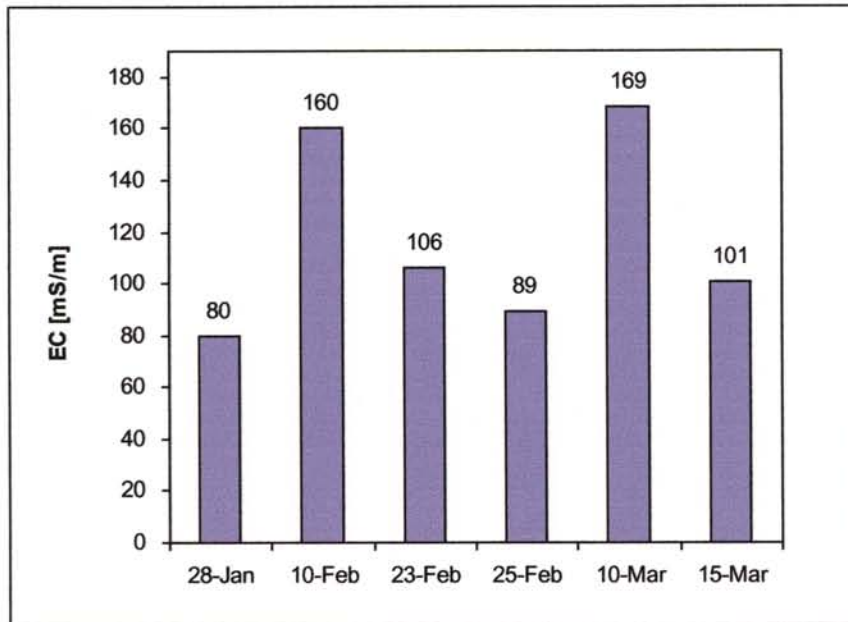


Figure 4.22 EC of Wastewater in Holding Tank (F7) 2000

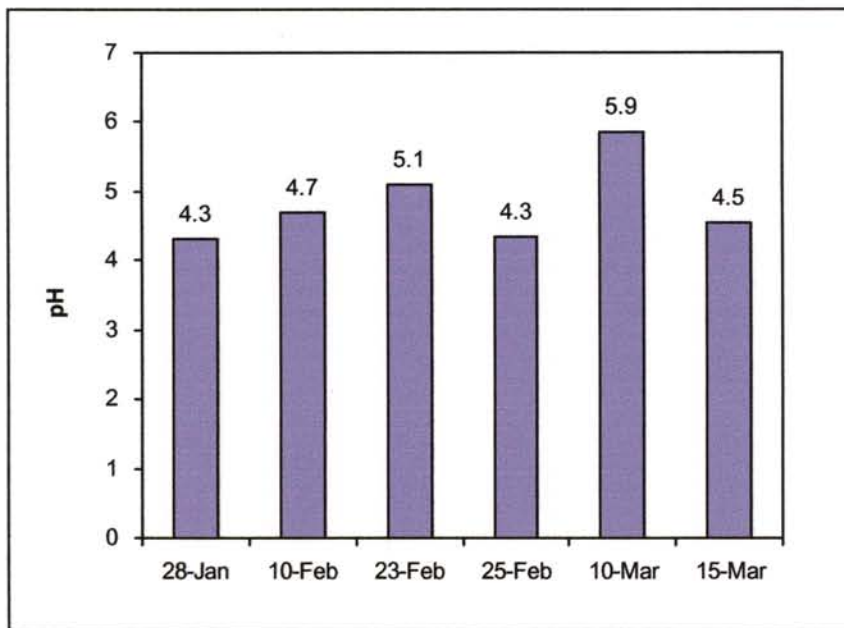


Figure 4.23 pH of Wastewater in Holding Tank (F7) 2000

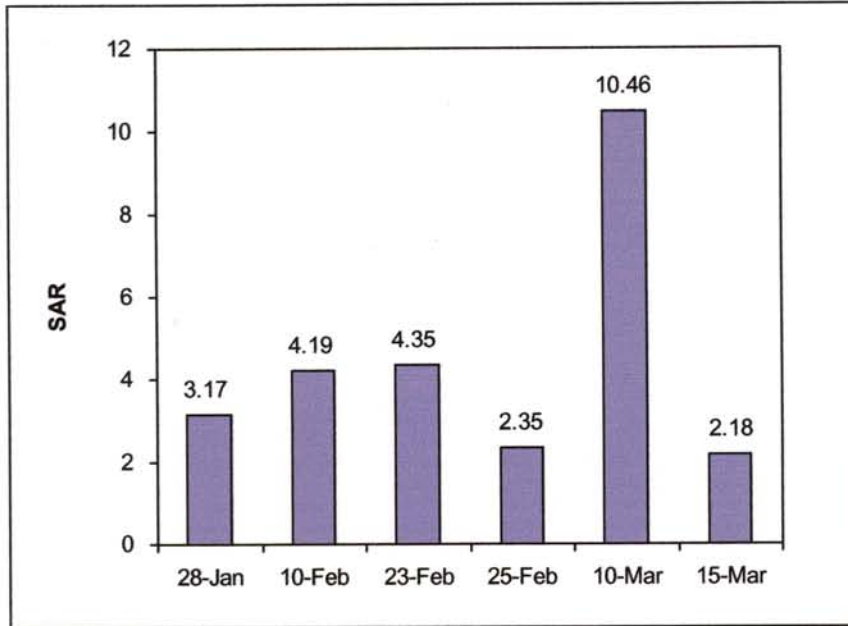


Figure 4.24 SAR of Wastewater in Holding Tank (F7) 2000

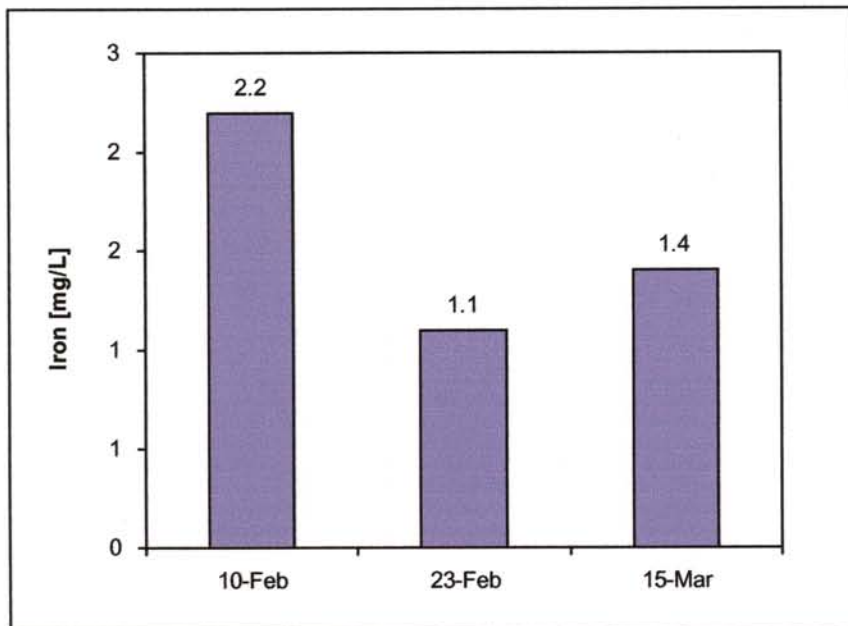


Figure 4.25 Iron in Wastewater in Holding Tank (F7) 2000

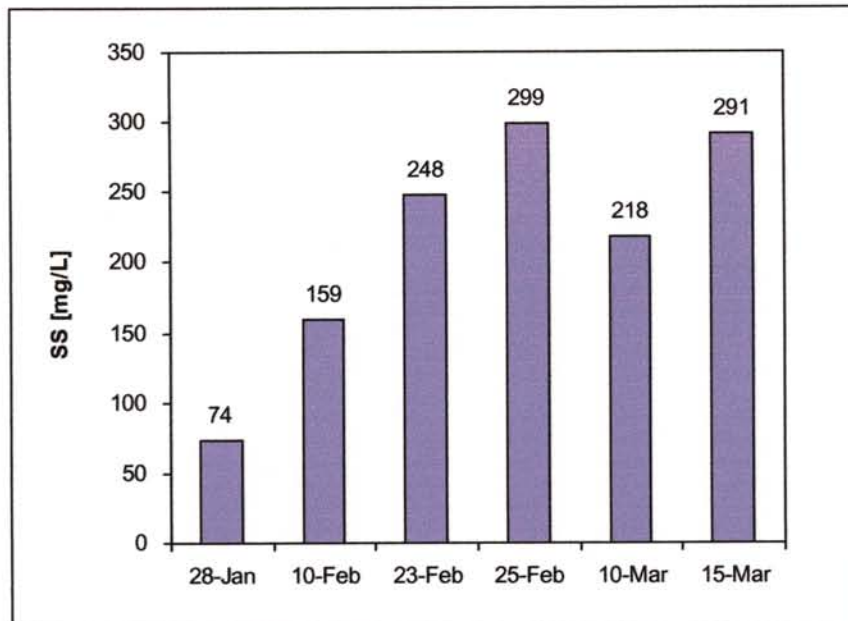


Figure 4.26 SS in Wastewater in Holding Tank (F7) 2000

In order to evaluate the variation of pollution in wastewater in the pit and holding tank on a 12-hour cycle, wastewater samples were analysed at regular intervals on 10 March 2000. This sampling protocol indicated the enormous variations of the components during the daily activities. Cellar procedures were running at full capacity on this date, thus the collected data was considered to illustrate a worse-case scenario for Rupert and Rothschild Vignerons. The pH in the pit (3.8-5.6) was characteristically lower than in the holding tank (5.3-6.2) (See *Figure 4.27*). The EC was measured to deviate between 107-220 in the pit, while it was more constant in the holding tank (165-193 mS/m). Considerable variation was observed in terms of the COD analyses (See *Figure 4.29*). Concentrations of 2584-11508 mg/L were measured in the pit over a 12-hour period. These values prove the inaccuracy of grab sampling. The concentrations measured in the holding tank varied between 3492-4484 mg/L. The smaller variation may be attributed to the mixing of wastewater in the larger capacity of the holding tank (40 m³). A similar trend was observed upon evaluation of the SS concentration (See *Figure 4.30*). Concentrations of 176-913 mg/L were noted in the pit, while the values ranged from 186-305 mg/L in the holding tank.

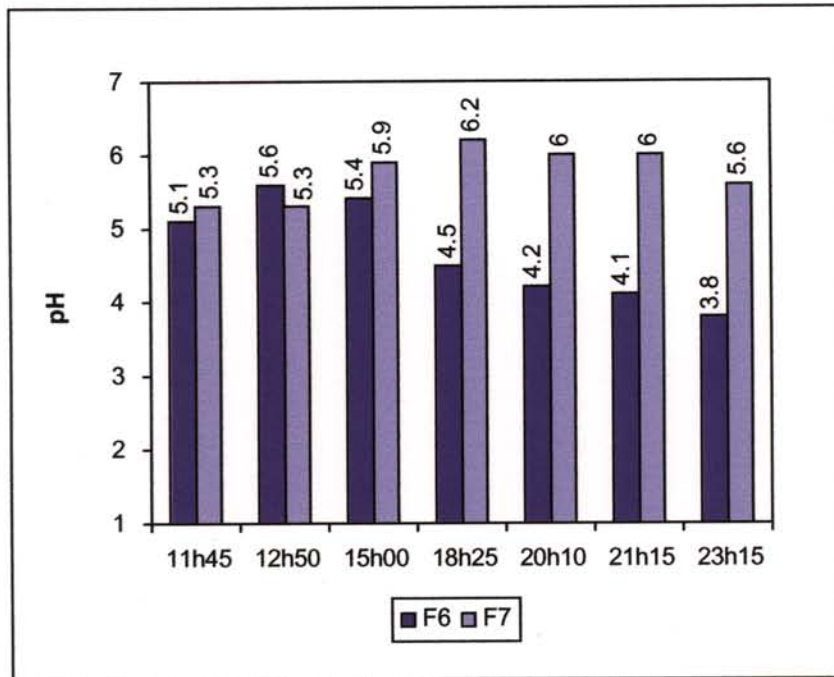


Figure 4.27 pH of Wastewater in Pit (F6) and Holding Tank (F7) on 10 March 2000

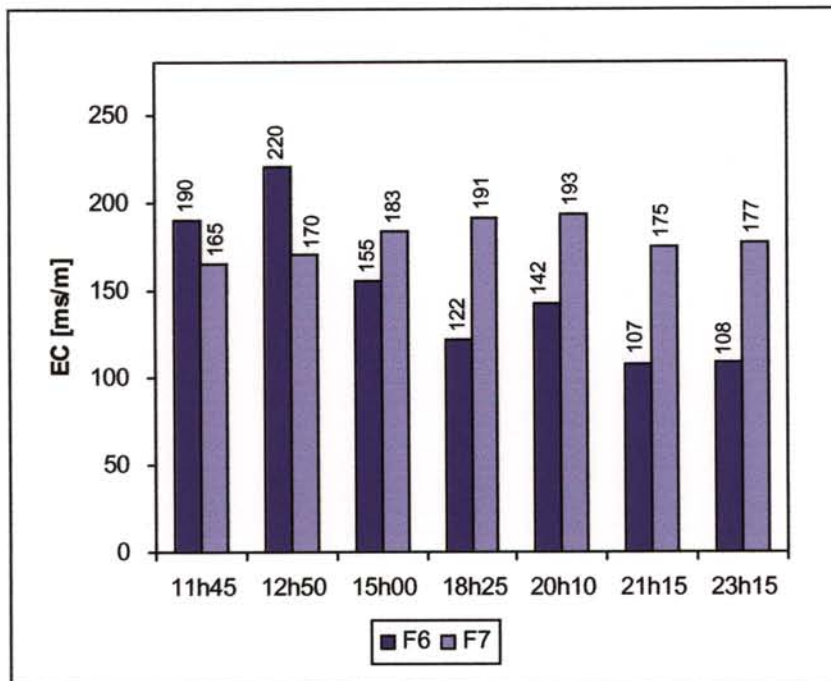


Figure 4.28 EC of Wastewater in Pit (F6) and Holding Tank (F7) on 10 March 2000

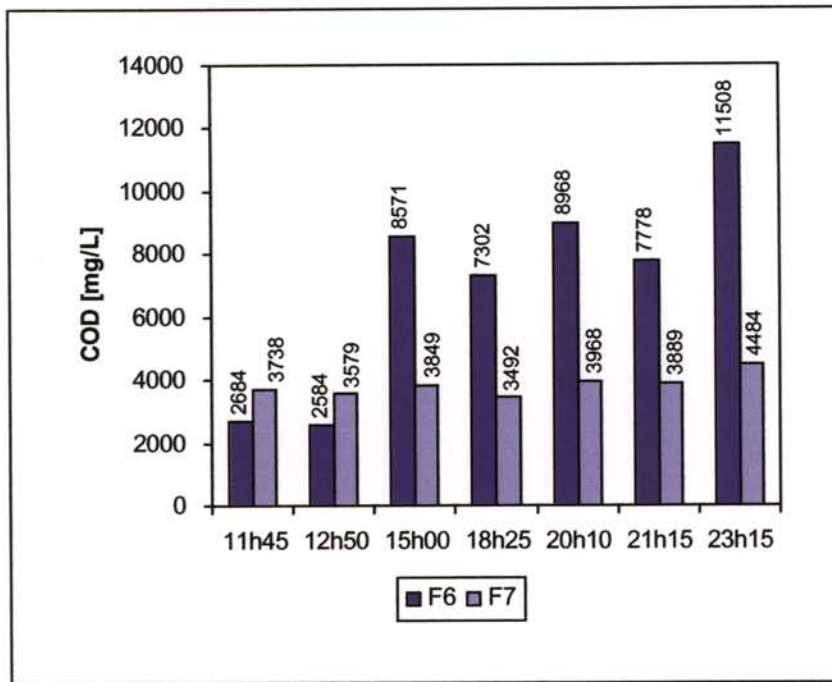


Figure 4.29 COD of Wastewater in Pit (F6) and Holding Tank (F7) on 10 March 2000

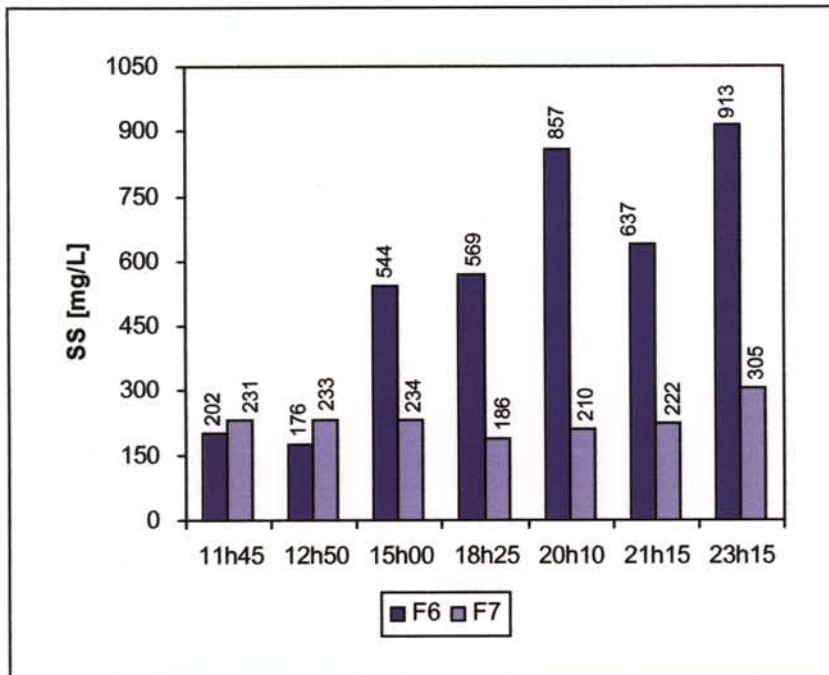


Figure 4.30 SS of Wastewater in Pit (F6) and Holding Tank (F7) on 10 March 2000

4.2.5 Comparison of Averages: Harvest 1999-Harvest 2000

In order to draw comparisons between the two harvest periods, average values for the individual components were calculated. Values from the month of March were selected, since this was the period of peak activity during both harvest seasons. Data from F6 and F7 were used for comparative purposes. The data is portrayed in *Table 4.12*.

Table 4.12 Average Concentrations of Components Determined over Harvest 1999 and 2000

Property	Av. F6 (1999)	Av. F6 (2000)	Av. (F7) 1999	Av. (F7) 2000
EC [mS/m]	85	141	95	150
pH	4.8	4.9	5.5	5.4
COD [mg/L]	5868	6108	5207	4099
SS [mg/L]	351	533	335	236

Although the sampling procedures varied during the two harvests, the average values were shown to be within the same magnitude. It should be noted that these values illustrate only a general impression of the wastewater at Rupert and Rothschild Vignerons. The wastewater was considered to be of better quality during the 2000 harvest.

4.2.6 Post-Harvest Analysis: 1999-2000

Wastewater from the holding tank was analysed throughout 1999 and 2000 in order to determine the pollution status of the water post-harvest.

The pH remained characteristically low, however, during the 1999 post harvest period, pH's were observed to be 5.2, 7.1, 7.3 and 7.7 (See *Figures 4.31 and 4.32*). The EC levels of the wastewater were comparable to those during the harvest period (See *Figures 4.33 and 4.34*). During 1999, the COD measured 3038, 12588, 4504, 8633 mg/L for the respective sampling months, while values of 5180, 5305, 2045 and 4200 mg/L were recorded during 2000

(See *Figures 4.33 and 4.36*). The suspended solid concentrations were also comparable to that of the harvest periods with values of 295, 456 and 636 mg/L during 1999, and 173 and 480 mg/L during 2000 (See *Figures 4.37 and 4.38*).

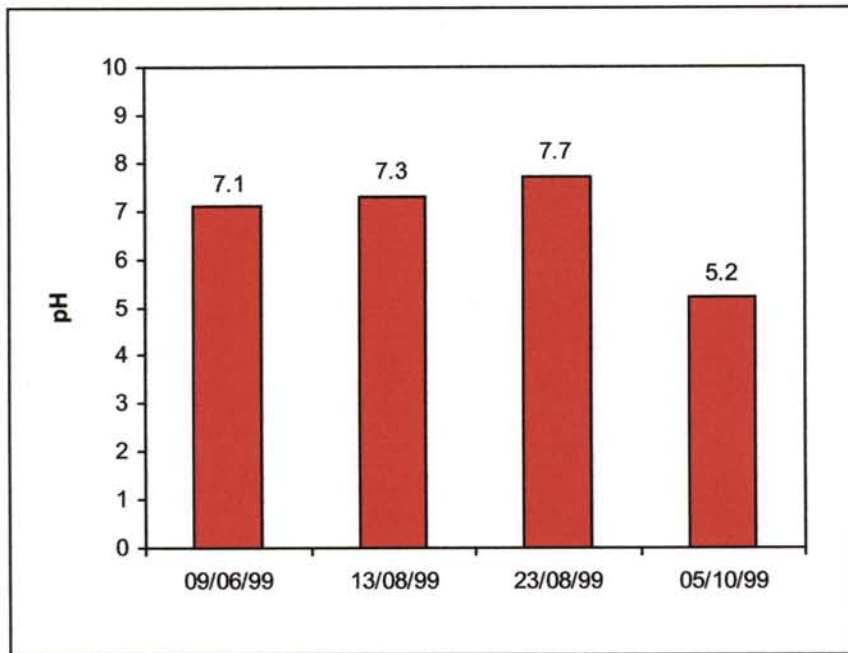


Figure 4.31 pH of Wastewater Post-Harvest 1999

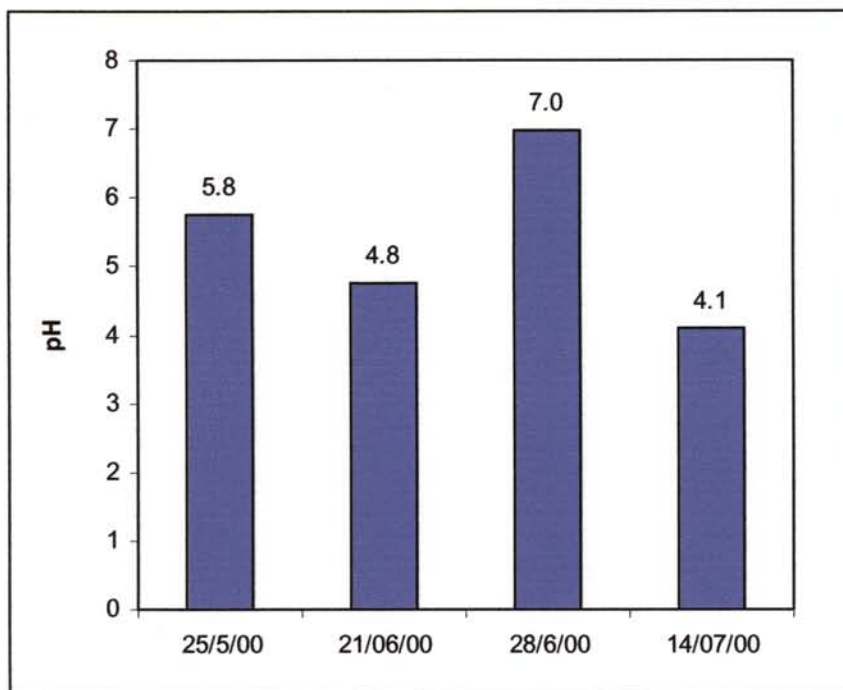


Figure 4.32 pH of Wastewater Post-Harvest 2000

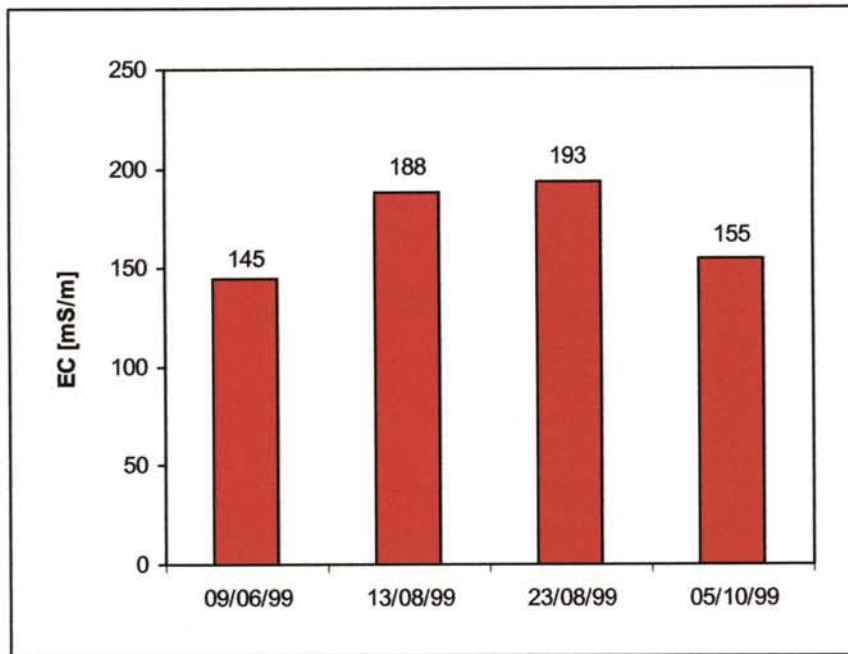


Figure 4.33 EC of Wastewater Post-Harvest 1999

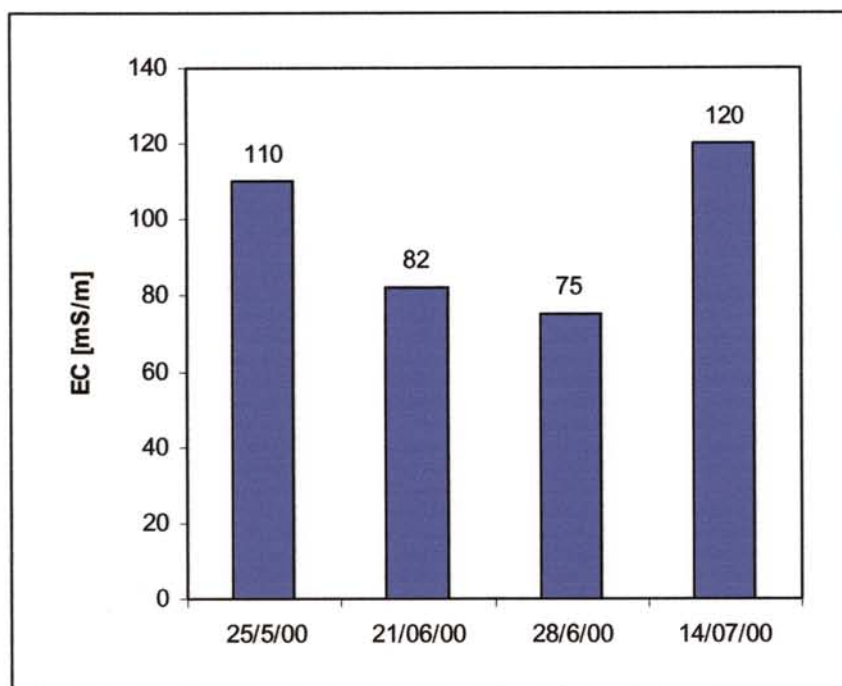


Figure 4.34 EC of Wastewater Post-Harvest 2000

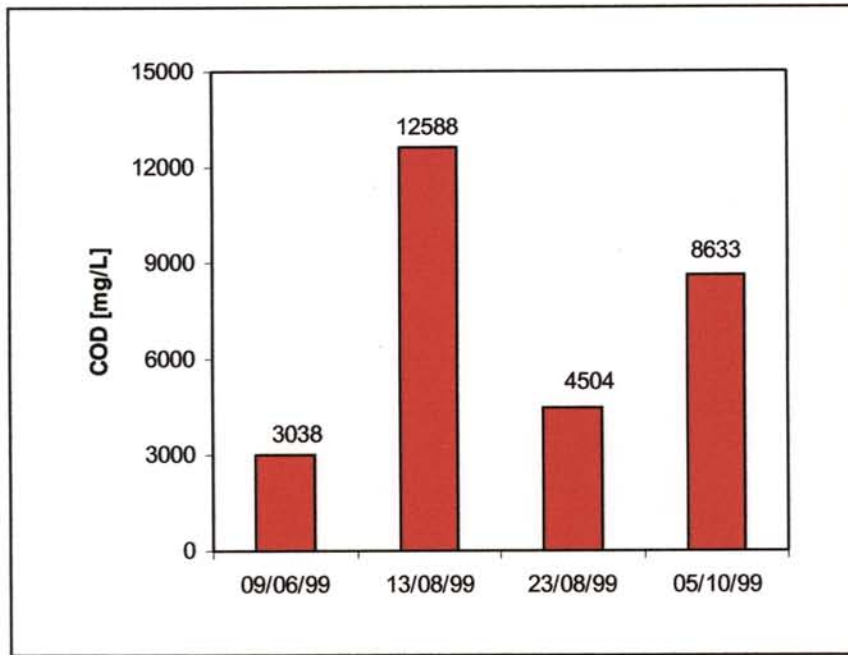


Figure 4.35 COD of Wastewater Post-Harvest 1999

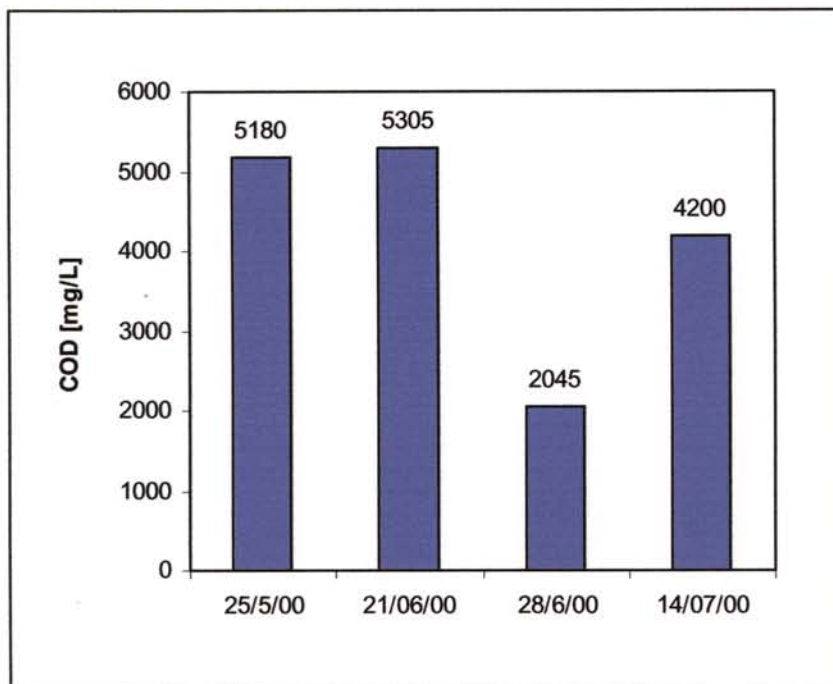


Figure 4.36 COD of Wastewater Post-Harvest 2000

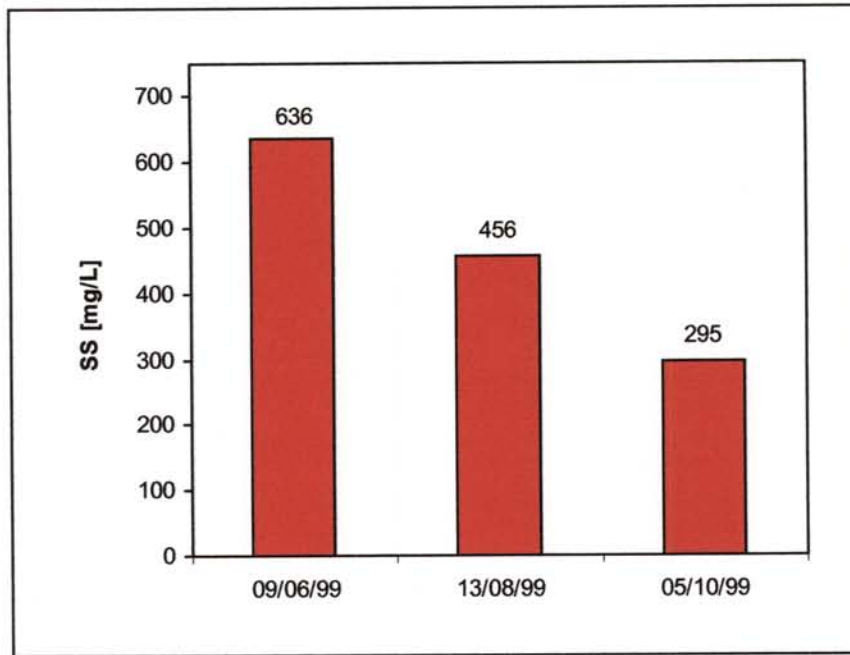


Figure 4.37 SS of Wastewater Post-Harvest 1999

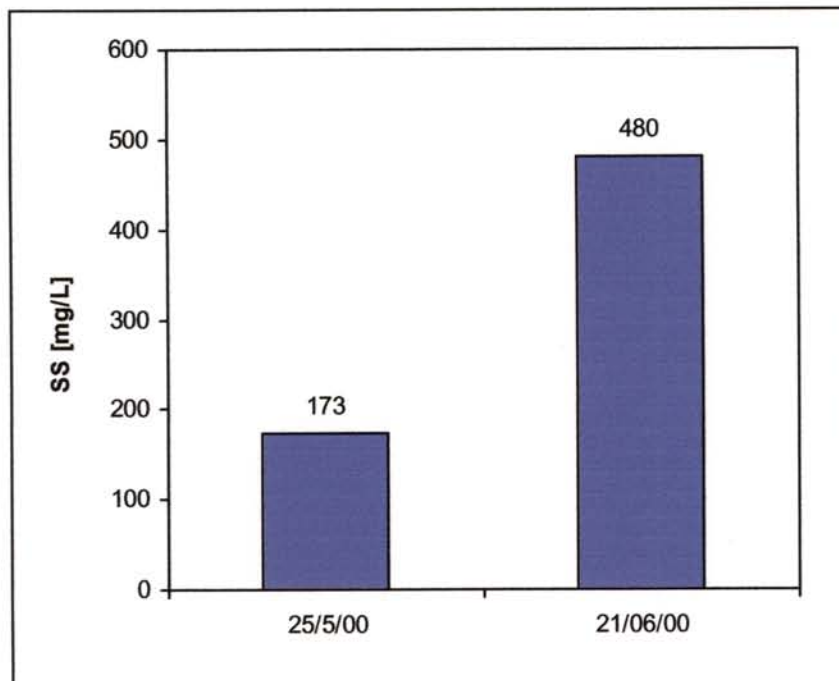


Figure 4.38 SS of Wastewater Post-Harvest 2000

The discussion of the analyses provides insight into the type of wastewater produced by Rupert and Rothschild Vignerons. The analyses on different components provide information on fluxes and any future abnormalities can be traced and compared to this study. Also, it must be emphasised that the analyses done, have a direct influence on the fate of the wastewater, whether concerning a possible treatment option or land application.

This data is essential when considering potential treatment technologies whether biological, chemical or physical. Also, this data is invaluable when the assessment of soil impacting and discharge is evaluated. It also provides historical records for future reference and when applying for a license with authorities.

4.3 WATER CONSUMPTION OF RUPERT AND ROTHSCHILD VIGNERONS

When considering the environmental impact of winery wastewater, it is of equal importance to consider the water consumption by the winery.

The average daily water consumption was calculated from March 2000 to October 2000. The data is illustrated in *Table 4.13*.

Table 4.13 Water Consumption 2000

Date	Activity	Total Consumption [m ³]	Average Daily Consumption [L]
28 February- 31 March	Harvest	551	16696
4 April- 15 May	Racking	305	6777
16 May- 15 June	Racking	230	7419
19 June- 26 July	Racking	250	6146
1 August- 30 August	Bottling/ Blending	120	4033
4 September- 4 October	Bottling/ Blending	170	5548
Total		1631	

During the harvesting month of March, the water consumption by the Rupert and Rothschild Vignerons varied from $\pm 5 \text{ m}^3$ to $\pm 70 \text{ m}^3$ per day (Refer to *Figure 4.39*). Peak quantities were observed with values of 71, 29, 45, 62, 53 and 30 m^3 . During the last four weeks of harvesting, 551 m^3 of water was consumed, producing a daily average of $\pm 16.7 \text{ m}^3$. During the periods of racking a large decrease in water consumption was observed with a calculated average of $\pm 6-7.5 \text{ m}^3$ per day. Peak levels of water consumption were observed with values of 41, 22, 19, 23, 32, 38 m^3 on individual dates during April, May and June and July (Refer to *Figures 4.40-4.42*). During the periods of bottling and blending, less water was consumed than during the operation of racking. Daily averages were calculated to be $\pm 4.0-5.5 \text{ m}^3$ during this period (Refer to *Figures 4.43 and 4.44*). Peak values of 12, 15, 20 and 22 m^3 were observed in this period.

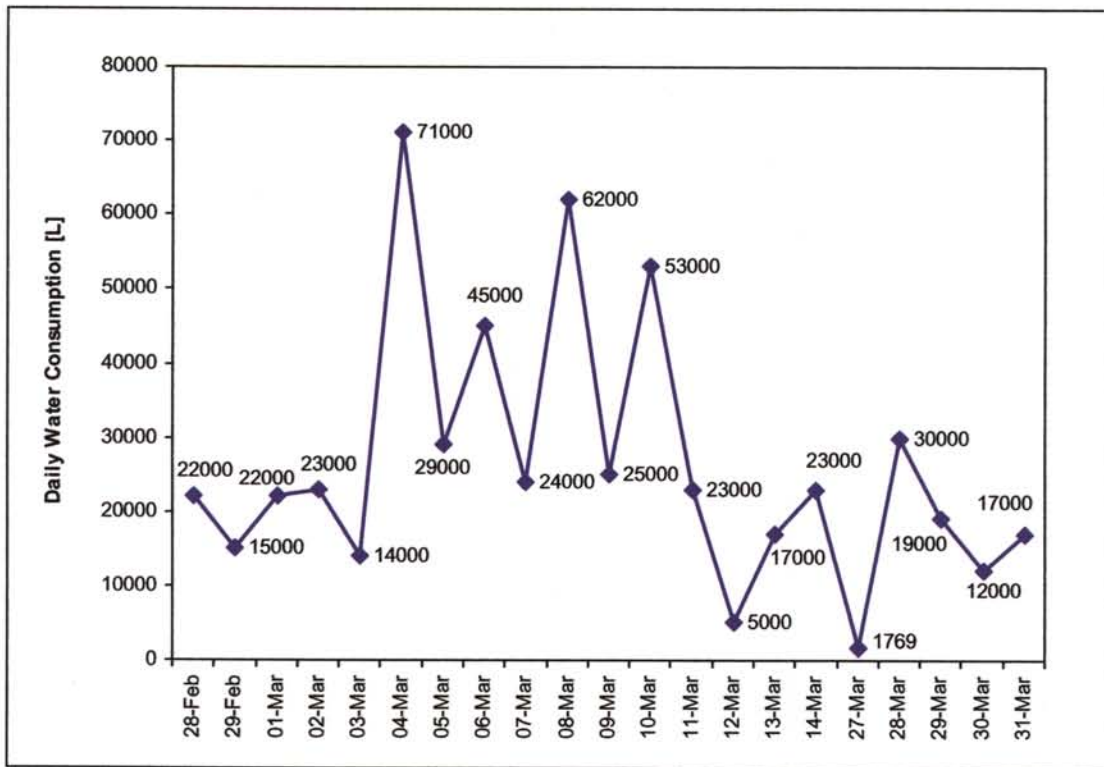


Figure 4.39 Daily Water Consumption (28 February-31 March 2000)

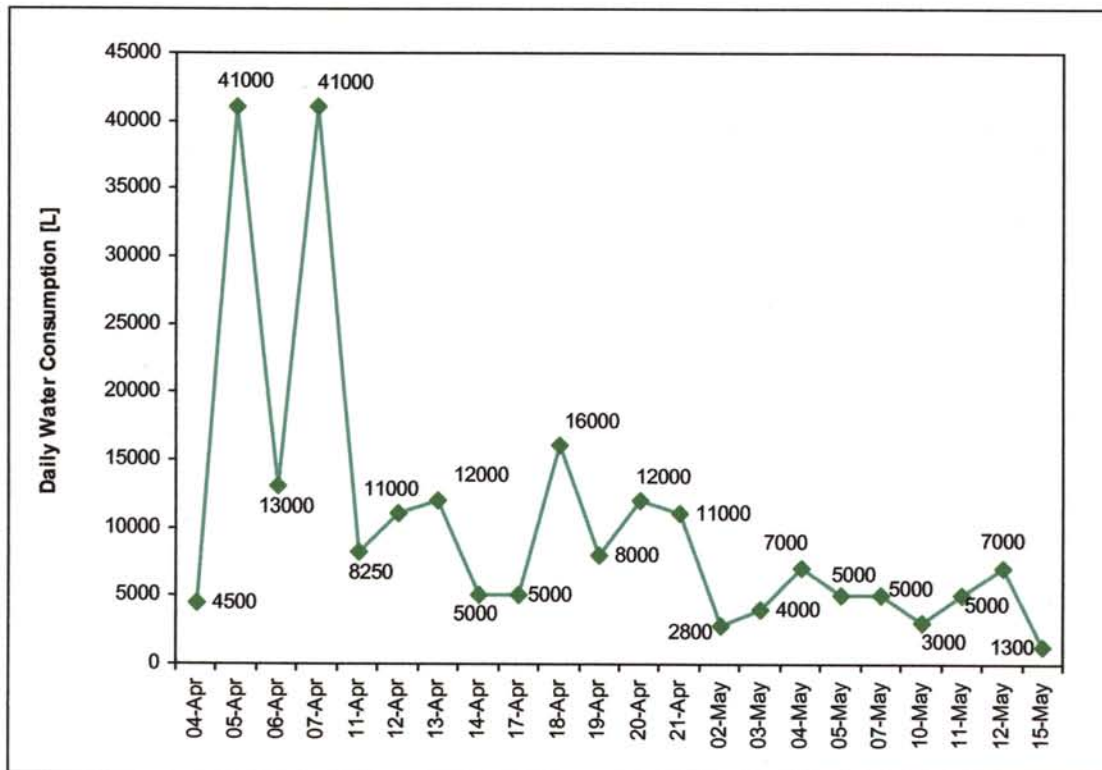


Figure 4.40 Daily Water Consumption (4 April-15 May 2000)

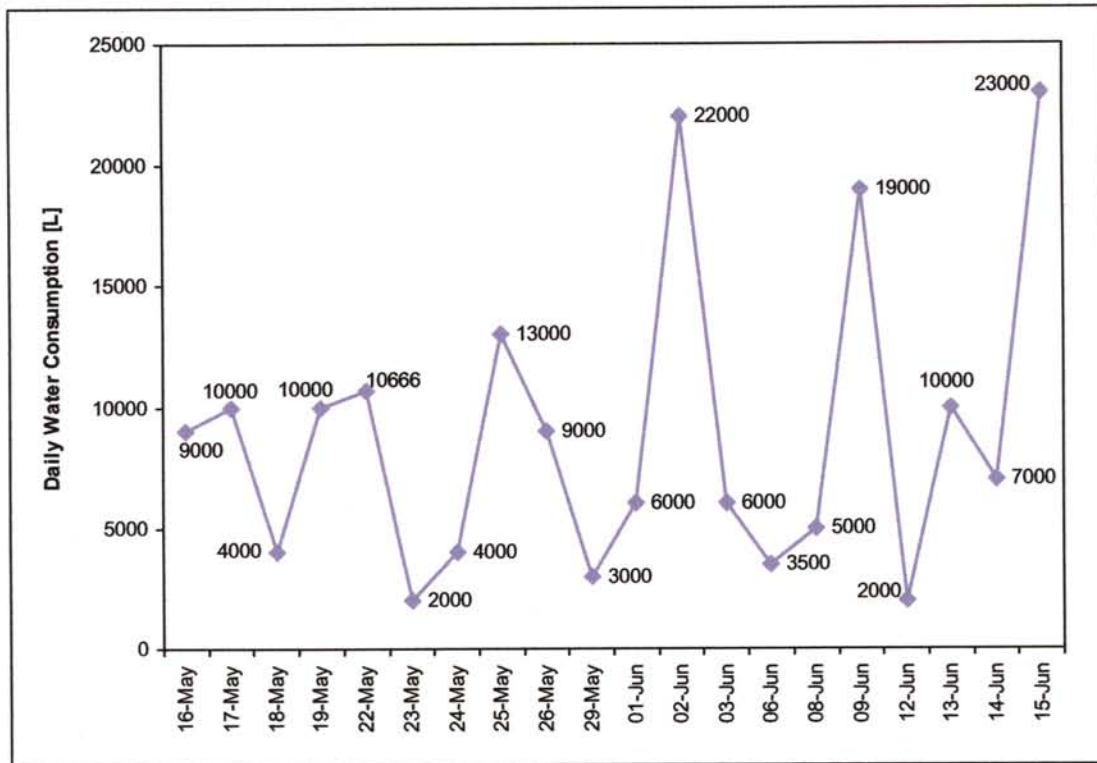


Figure 4.41 Daily Water Consumption (16 May-15 June 2000)

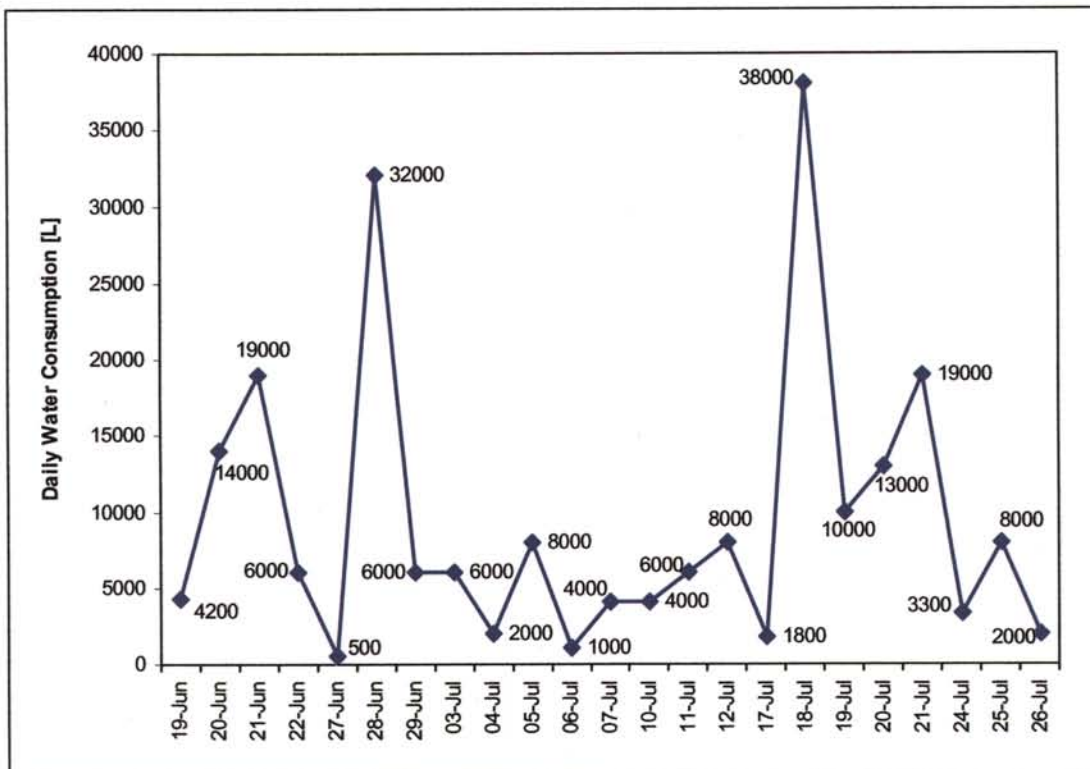


Figure 4.42 Daily Water Consumption (19 June-26 July 2000)

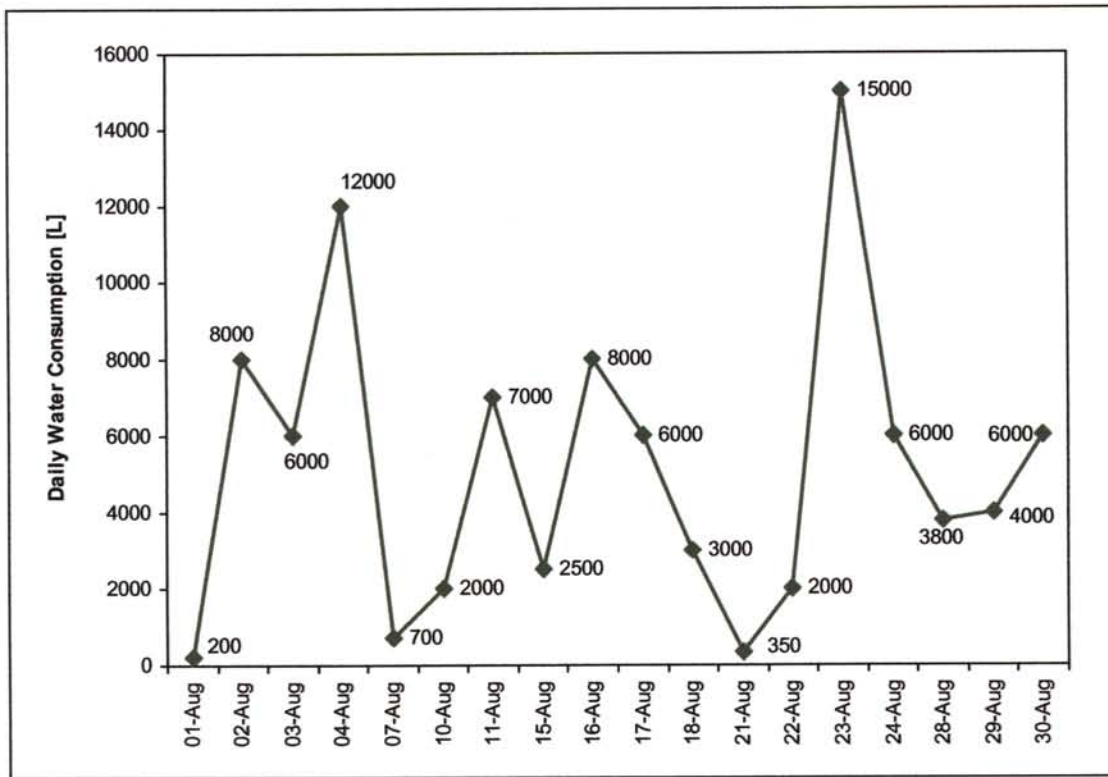


Figure 4.43 Daily Water Consumption (1 August-30 August 2000)

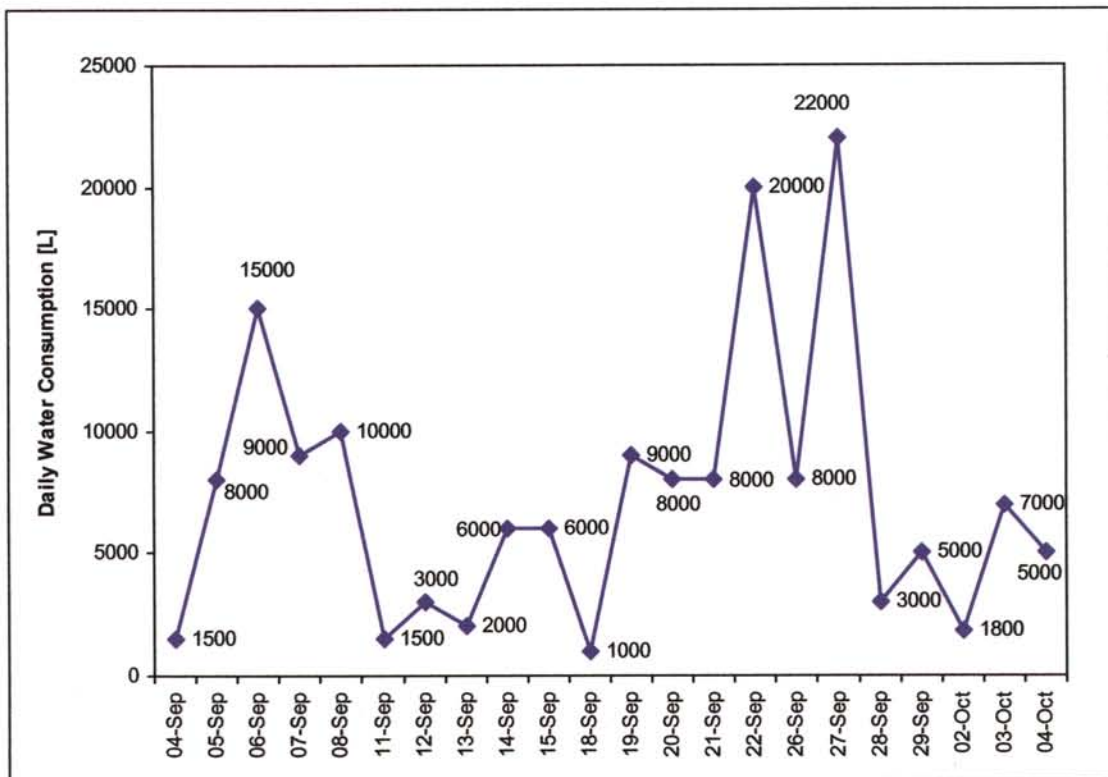


Figure 4.44 Daily Water Consumption (4 September-4 October 2000)

For comparative purposes, the water consumption should ideally have been measured over the complete two-year period. In order to quantitatively ascertain relationships between the water consumption and wine production, an estimated water consumption (ewc) value had to be assigned for the water consumption during the 17 January to 27 February 2000 harvest period (d). By calculating the average water consumption (awc) from 28 February to 31 March 2000 (16696 L), the value of 684 m³ was assigned to this period (See *Equation 4.1*).

$$awc \cdot d = ewc \tag{4.1}$$

This assignment increases the total water consumption by Rupert and Rothschild Vignerons to 2314 m³ (17 January- 4 October 2000).

4.4 QUANTITATIVE ANALYSIS OF WASTEWATER AND WATER CONSUMPTION OF RUPERT AND ROTHSCHILD VIGNERONS

Table 4.14 illustrates the quantitative values between wine production, pollution status and water consumption.

Table 4.14 Quantity and Quality Statistics (2000)

Property	Value	Symbol
Average COD (F7) Harvest [mg/L]	4099	cod
Average Water Consumption (Harvest) [L/day]	16669	awc
Total Water Consumption (Harvest-October) [m ³]	2314	wct
Water Consumption (Harvest Period) [m ³]	1234	wch
Grapes Harvested [kg]	865677	g
Litres Wine Produced [L]	565516	wp
Wastewater/ Wine (Harvest) [L/ L]	2.18	WPW _h
Wastewater/ Wine (Harvest-October) [L/ L]	4.09	WPW _t
Pollution Load [g COD/100 kg grapes]	584	PL _g
Pollution Load [g COD/ hL wine]	895	PL _w
Wastewater Load [L/ 100 kg grapes]	142	WPG

Equations 4.2- 4.6 illustrate the derivations.

$$WPW_h = \frac{wch}{wp} \quad (4.2)$$

$$WPW_t = \frac{wct}{wp} \quad (4.3)$$

$$PL_g = \left(\frac{wch \cdot cod}{g} \right) \cdot 100 \quad (4.4)$$

$$PL_w = \left(\frac{wch \cdot cod}{wp} \right) \cdot 100 \quad (4.5)$$

$$WPG = \left(\frac{wch}{g} \right) \cdot 100 \quad (4.6)$$

4.5 COMPARISON OF RESULTS OF ANALYSES AND WATER CONSUMPTION FROM RUPERT AND ROTHSCHILD VIGNERONS TO INTERNATIONAL CASE STUDIES

Accurate comparison between wineries in terms of quality and quantity of wastewater is not easily accomplished, since harvesting quantities, cultivar range and cellar design vary significantly between the wineries. However, for evaluation purposes, certain parameters and properties pertaining to the wastewater generation were assessed. For qualitative evaluation purposes, the concentration of components in the wastewater produced during 2000, (holding tank) are referenced. When considering the quantitative evaluation of the wastewater production, the values determined in *Section 4.4* were employed. The international wineries are discussed in *Section 2.4.1*.

4.5.1 Rupert and Rothschild Vignerons: Dois Portos Winery (Portugal)

Table 4.15 illustrates the comparison between Rupert and Rothschild Vignerons and the Dois Portos Winery in Portugal.

Table 4.15 Rupert and Rothschild Vignerons: Dois Portos

Property	Rupert and Rothschild Vignerons		Dois Portos	
Winery Area [m ²]	4000		720	
Harvest Quantities [kg]	739810 (Red)		47000 (Red)	
	125867 (White)		35390 (White)	
Wastewater/ Wine [L/ L]	2.18		0.7	
Wastewater/ Grapes [L/100 kg grapes]	142		45	
	Harvest	Racking	Harvest	Racking
Av. Wastewater [L/ Day]	16696	6500	570	165
COD [mg/L]	3000-5500	3000-10000	7000-8000	4000-4500
pH	4.3-5.9	4.1-7.7	4.0-5.0	4.0-4.5
SS [mg/L]	286-625	173-636	150-200	350-400

Rupert and Rothschild Vignerons harvests ± 10 times the amount of grapes compared to Dois Portos Winery, ratio of red to white cultivars of $\pm 5.8:1$ for the respective wineries. As previously mentioned, the cultivar range influences the composition of the wastewater. The water consumption per litre wine produced by Rupert and Rothschild Vignerons is three times that of Dois Portos, and may impart be explained by the larger surface area of the Rupert and Rothschild Cellar (4000 m²: 720 m²). It should also be noted that the harvesting period at Dois Portos lasted only 12 days in comparison to the two-month harvesting period at Rupert and Rothschild Vignerons. Comparison between daily water consumption is inconclusive since the winemaking procedure and tank capacities are not similar. The pH's of the wastewater during the harvesting and racking seasons were similar upon comparison, however, during the racking period at Rupert and Rothschild Vignerons, pH's in the range of 7 were observed. The difference may be attributed to the use of cellar chemicals. Although there is a large variation in terms of size and harvest capacities, the pH, COD and SS are observed to fall within the same order of magnitude.

4.5.2 Rupert and Rothschild Vignerons: Italy

Rozzi et al. (1998) investigated the pollution load from a winery with a harvest capacity of 5000 t. *Table 4.16* illustrates the comparison of this winery to Rupert and Rothschild Vignerons.

Table 4.16 Rupert and Rothschild Vignerons: Italian Winery

Property	Rupert and Rothschild Vignerons	Italian Winery
Harvest Quantity [t]	865 (Red and White)	5000 (Red)
Pollution Load [g COD/ 100 kg grapes]	584	13.5
Wastewater Load [L/ 100 kg grapes]	142	1.27
COD [mg/L]	3000-5500	9000-12000

As illustrated, considerable differences in the pollution loads from the two wineries were observed. The harvest capacity of the Italian Winery (co-operative) is six times that of Rupert and Rothschild Vignerons. Furthermore only red grapes are processed at the Italian winery, decreasing the need for equipment cleaning after each process. Although the COD range during the harvest period is 9000-12000 mg/L recorded at the Italian winery (in comparison to 3000-5500 mg/L at Rupert and Rothschild Vignerons), the pollution load is 43 times that of the load of the Italian Winery. The determination of the pollutant load is directly proportional to the water consumption, and it is due to this factor that the pollution load is considerable higher at Rupert and Rothschild Vignerons. Also, although not described, it is assumed that large fermentation vessels (\pm 100 000-150 000 L) are used by the Italian winery, in comparison to the use of small vessels (\pm 10000 L tanks and barrels). This comparison indicates the dimensions of variability, which may influence the audit procedure, necessitating individual performance and impact assessments.

4.5.3 Rupert and Rothschild Vignerons: France (Languedoc and Provence)

The comparison between Rupert and Rothschild Vignerons and two French Wineries is depicted in *Table 4.17*.

Table 4.17 Rupert and Rothschild: Languedoc and Provence Wineries

Property	Rupert and Rothschild Vignerons	Languedoc Winery	Provence Winery
Wine Production [hL]	5655	105000	56000
Wastewater / Wine [L/ L]	2.18	0.26	0.41
Pollutant Charge [g COD/ hL wine]	895	250	260
Av. Water Consumption [m³/day]	16	24	19
Av. pH	5.4	4.8	5.8
Av. COD [mg/L]	4099	24600	22000

The Languedoc winery processed 18 times the amount of grapes, and the Provence winery 10 times that of the South African winery. The French wineries process red grapes, consuming 23 and 42 litres of water per hectolitre of wine produced respectively, in comparison to the 218 L/ hL by Rupert and Rothschild Vignerons. It may be concluded that co-operative wineries use less water since their equipment differs significantly to that utilised by Estate and Boutique Wineries.

Although a higher pollutant charge was measured for Rupert and Rothschild Vignerons, this value cannot be considered to indicate that the wastewater from this cellar is of worse quality. As previously defined, the pollutant charge is derived from the average COD and total water consumption values. The principal factor attributing to the large variation in the pollutant charge is the

amount of wastewater produced by Rupert and Rothschild Vignerons. The COD of the wastewater produced by the French Wineries is ± 5 times that of the COD produced by Rupert and Rothschild Vignerons, but the pollution load (g COD/hL wine) of Rupert and Rothschild Vignerons is ± 3.5 times that of the French wineries. When considering treatment options, the high COD values exhibited by the French Wineries will require sophisticated treatment, substantially elevating the treatment cost.

It is thus concluded that the pollution load is only relevant when comparing wineries with similar production capacities. The pollution load should be considered as a cellar performance indicator, and must be considered in unison with the average COD of the wastewater.

4.5.4 Rupert and Rothschild Vignerons: Australia

Table 4.18 illustrates the comparison to an Australian survey assessed from several wineries (Levay, 1999).

Table 4.18 Rupert and Rothschild: Australian Survey

Property	Rupert and Rothschild Vignerons		Australian Winery	
	Vintage	Non-Vintage	Vintage	Non-Vintage
pH	4.2-6.3	4.1-7.7	4-8	6-10
SS [mg/L]	74-4278	173-636	100-1300	100-1000
SAR	2.18-10.46		4-8	7-9
Na [mg/L]	44-169		110-310	160-250
Ca [mg/L]	33-58	17	13-40	20-45
Mg [mg/L]	5.5-18	9.5	6-50	10-20
K [mg/L]	127-273		80-180	40-340

It is interesting to note that the component concentrations in the wastewater are largely similar as indicated in Table 4.18.

4.6 CONCLUDING REMARKS ON THE AUDIT ANALYSES

The focus of researchers differs greatly between countries when evaluating wastewaters emanating from wineries. This may be partly attributed to the variation in the fate of the wastewater; subject to land availability and technological trends. Australian researchers refer to the biological oxygen demand (BOD) rather than the chemical oxygen demand (COD) as referred to by the South Africa and European Countries. This is due to their preference of land application treatment technology. Also, Australian literature makes no reference to pollution load, probably since water is a less restricting component as compared to Europe.

In conclusion, it has been shown how the criteria of quantity and quality interact and are interpreted. Once the wastewater from a particular winery has been characterised and evaluated, an Environmental Management System (EMS) and suitable treatment option can be designed. The significance of the wastewater audit for goal setting in an EMS will be demonstrated in *Chapter 5*.

CHAPTER 5

AN ENVIRONMENTAL MANAGEMENT SYSTEM FOR RUPERT AND ROTHSCHILD VIGNERONS

The principal aim of the Environmental Management System is to illustrate that Rupert and Rothschild Vignerons is controlling their effects on the environment based on a system of continual improvement. The ISO 14001 Environmental Management System incorporates environmental concerns into the mainstream of business operations by providing an integrated framework balancing environmental and economic aspects (*Schiffman et al.* 1997). Having conducted an environmental review in the form of a two-year water-audit, an environmental policy specific to Rupert and Rothschild Vignerons may now be developed. This chapter serves to describe an Environmental Management System for Rupert and Rothschild Vignerons based on the information matrix derived from the water-audit.

It must be noted that a detailed project surrounding an ISO 14001 EMS for Rupert and Rothschild Vignerons is being conducted by a private consultant, Dr. N. Barnardt, in conjunction with the Centre of Process Engineering (CPE).

5.1 ISO 14001 ENVIRONMENTAL MANAGEMENT

ISO 14000 is a set of international standards for improving the environmental performance of an organisation (*Haklik*, 1998). This includes the 1996 ISO 14001 Environmental Management System (EMS).

5.1.1 The Benefits of an Environmental Management System (EMS)

The benefits of an EMS are divided into five categories:

- i. Increased Profits: An EMS may reduce the quantities of materials and energy used in the manufacture of products when the management system analyses the raw materials, by-products and waste. In the wine industry sustainable recycling and reuse of cellar chemicals, water, potassium bitartrate and yeast should be considered.
- ii. Operations: Regular monitoring may identify potential problems in the operational plant and thus prevents potentially hazardous events and costly corrections. Through regular monitoring, the advent of scaling or corrosion in pipelines and fouling of equipment are detected before serious impairment occurs. Especially relevant to the food and beverage industries is the potential contamination of the intake water (with reference to toxic chemicals or pathogenic organisms). Reduction of solid and liquid waste disposal may also be achieved.
- iii. Marketing: ISO 14000 accreditation may be beneficial when engaging upon a marketing strategy. According to a Gallup poll in America in 1990, it was found that 52 % of those surveyed stopped buying products with a poor environmental image (*Haklik, 1998*). ISO 14000 adds credibility to an EMS, since an independent auditor must issue certification.
- iv. Regulatory Compliance: Laws and regulations are becoming more stringent worldwide in order to protect the environment. If not addressed, financial and/ or criminal implications may result. The National Water Act (1998) addresses the requirements for South Africa (Refer to *Appendix C*). ISO 14000 requires evidence of working processes to maintain compliance with existing laws.

- v. **Social:** The reduction of pollution to natural resources and landfills benefit all of society, and indirectly benefits the associated company. The social responsibility of companies is constantly under scrutiny. By integrating the environmental function into the daily business operation, the company becomes environmentally pro-active. The creation of a sustainable planet demands the tracking of environmental performance and implementation of innovative technologies (*Zanardo, 1998*).

ISO 14001 requires that an organisation/ company develop an environmental management program describing all of its environmental objectives and targets, and how each will be achieved. The program must include the following (*Schiffman et al., 1997*):

- Specific plan detailing the actions required meeting each objective.
- Responsibility of personnel assigned to each objective.
- Time scale for target achievement.

5.1.2 The Principles of an EMS

An EMS is a continual cycle of planning, implementing, reviewing and improvement. *Figure 5.1* illustrates the five principles of an EMS.

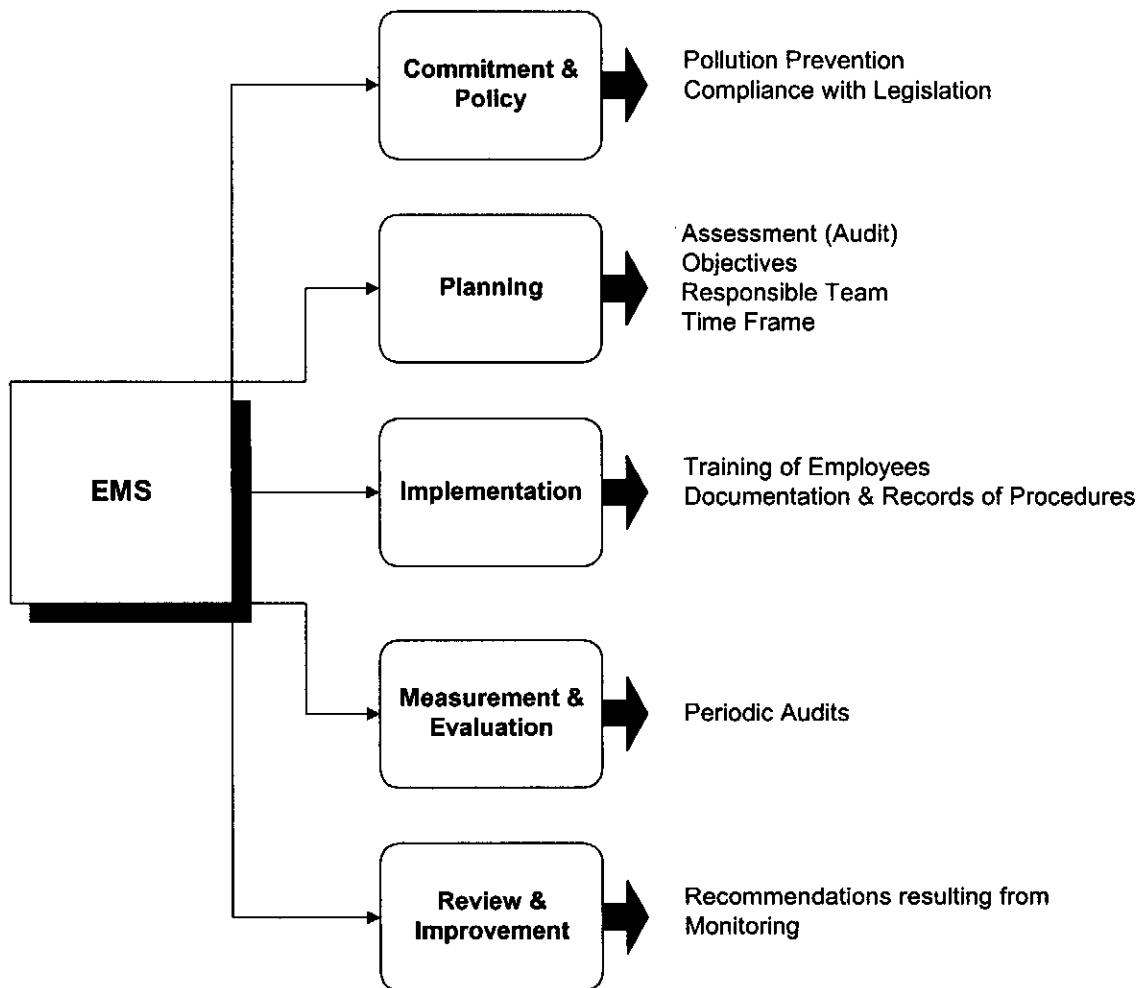


Figure 5.1 The Five Principles of an Environmental Management System (EMS)

An initial environmental review is fundamental to the establishment of an EMS. This review has been conducted over a two-year period at Rupert and Rothschild Vignerons and took the form a water-audit. According to *Schiffman et al. (1997)*, the following areas must be addressed when designing the environmental review:

- Legislative and regulatory requirements.
- Environmental aspects of the organisation's activities, products, or services.
- Performance compared with relevant internal criteria, external standards, regulations, codes of practice, and sets of principles and guidelines.
- Existing environmental management practices and procedures.

- Opportunities for competitive advantage.
- The views of the interested parties.
- Functions or activities of other organisational systems that can enable or impede environmental performance.

During the implementation phase of an EMS, consideration to the ISO 14001 documentation must be made and should address the following topics:

- The environmental policy, objectives and goals.
- Roles and responsibilities of employees.
- Operational control procedures.
- Monitoring equipment maintenance records.
- Training records.
- Audit results and reviews.
- Management reviews.

5.2 AN EMS FOR RUPERT AND ROTHSCHILD VIGNERONS

From the preceding discussion it is evident that an EMS is highly beneficial to an organisation, but requires extensive research, planning and support from management and employees. Having considered the status of an ISO 14001 EMS, Rupert and Rothschild Vignerons have ventured on an implementation strategy, co-ordinated by Dr. N. Barnardt.

Having assessed the water flow and environmental impact; suitable objectives, time attribution to their achievement, employee training and necessary alterations to the cellar were made possible. *Table 5.1* depicts proposed objectives for future wastewater quality, derived from the wastewater audit study.

Table 5.1 Proposed Wastewater Quality Objectives

Objectives	2001	2002	2003
COD [mg/L]	<4000	<3000	<2000
SS [mg/L]	<50	<40	<30
pH	6-8.5	6-8.5	6-8.5
Turbidity [NTU]	<100	<80	<50

These objectives are proposed to ensure the continuous improvement of Rupert and Rothschild Vignerons on their environment. Additionally, offensive odours and colour must be eliminated. These objectives were derived with consideration to treatment technologies; sustainable treatment technologies of wastewater will be discussed in *Chapters 6 and 7*.

The structure of the Rupert and Rothschild Vignerons EMS involves the environmental impact over the entire vineyard, wine making and distribution processes. An in-depth life cycle analysis of each stage of production is required. The environmental policy of Rupert and Rothschild Vignerons entails:

- Maintenance of records of environmental aspects of the processes in order to control their effects. Records will be made available to public on demand.
- Record and control winery wastes in order to determine the environmental effects. Progressive reduction of these wastes will be incurred via reviewed targets.
- Reduction of material and energy inputs where practical.
- Implementation of recycling procedures.
- Conservation of water resources, soils and ecosystems on the Fredericksburg Estate.
- Maintenance of the quality of surface and ground water.
- Adoption of environmentally sustainable methods of pest, disease and weed control.
- Annual review of performance objectives and targets by senior management.

- Ensurance of staff awareness and commitment to improved environmental performance.
- Compliance with legal and statutory environmental requirements.

Future planning and implementation phases of the proposed objectives, policies, and ISO 14000 accreditation, will be orchestrated by private companies.

5.2.1 Water Quality Management

The development of best practice guidelines for water quality management originating from the winery is essential when considering an EMS. A water management strategy for the vinification industry must be implemented following the hierarchy steps (adapted from the water management policy for mining and the role of best practice guidelines (*Pulles (1999)*):

- Step 1: Water quality management should be implemented at the source. The fundamental principle is to prevent, inhibit, retard or stop the hydrological, chemical and microbiological processes, which result in contamination of the water environment.
- Step 2: Should the water quality management measurements at source not prevent the discharge or disposal water containing waste, reuse and minimisation strategies should be implemented. This may include partial treatment of water in order to make it sustainable for reuse.
- Step 3: If both steps 1 and 2 do not prevent the discharge or disposal of waste containing water, water treatment strategies must be implemented.

5.2.2 Identification of Water Reclamation/Treatment Technologies for the Rupert and Rothschild Vignerons

"Reducing waste is one of the greatest challenges facing the chemical process industries today" (*Zinkus et al., 1998*). Water is the main waste

product generated by wineries, and the ability to reclaim wastewater would be a giant step towards overall waste reduction.

When considering the selection of a technology for reuse or reclamation the chemical aspects of organic, inorganic and biological constituents must be considered. According to *Zinkus et al. (1998)*, contaminants may be classified into six basic categories:

- Organics: Aliphatic and aromatic hydrocarbons, alcohols, aldehydes, ketones, esters, carboxylic acids.
- Dissolved Components: Components smaller than colloidal particles (0.1 micron) and are dispersed as individual molecules or ions.
- Suspended Solids: Particles that are larger than 0.1 micron that can be filtered.
- Biological Constituents: Pertains to bacteria, fungi, viruses, protozoa and pathogenic organisms
- pH: Hydrogen ion concentration of a wastewater stream as influenced by preceding list of compounds.

The contamination matrix at Rupert and Rothschild Vignerons pertaining to the wastewater is described in *Section 3.3.2*.

5.2.2.1 Overview of Water Treatment Technologies

Although a multitude of water treatment technologies exist, not all are appropriate for wastewater originating from wineries. As previously discussed, each winery is unique in terms of wine and wastewater production, cellar ethics and topography. Upon intrinsic wastewater audit analysis, suitable treatment technologies may be investigated (*See Section 2.4.2*). The following list provides information on treatment technologies as evaluated by *Zinkus et al. (1998)*, described with significance to winery wastewater:

- Biological Treatment: This employs a biological reactor that maintains a high concentration of suspended or attached micro-organisms. The

micro-organisms function to metabolise the organic compounds. Technology variations include aerobic, anaerobic and nitrification processes. Influent conditions should be as stable as possible, since excessive fluctuations in concentrations may be detrimental to the micro-population. Aerobic processes can generate significant quantities of bio-solids that require management and removal. Anaerobic processes on the other hand, generate methane and hydrogen sulphide, requiring off-gas handling. Another disadvantage of this type of treatment is that the effluent produced from the bio-treatment may require filtration and/or disinfection prior to reuse. According to *Zinkus et al.* (1998), degradable organics may be reduced by 90%, and is applicable for the reduction of BOD, COD, nitrogen and phosphorus, and phenol.

- Carbon Adsorption: The sorption phenomenon is a function of the type of medium, pH, temperature, contact time and concentration of contaminants. The presence of suspended solids may decrease the efficiency of the carbon, requiring pre-filtration. Certain organics including alcohols, acids and aldehydes, are not readily treated. According to *Zinkus et al.* (1998), 90 % of dissolved organics may be removed, while a 30-60 % reduction of BOD/COD may occur. Common applications of carbon include the removal of phenol and colour post-biological treatment.
- Chemical Oxidation: Chemical oxidation is the complete or partial conversion of organic compounds into carbon dioxide and water. Common oxidants include ozone, chlorine dioxide, peroxide, supercritical water and potassium permanganate. Advanced oxidation processes generate OH⁻ radicals. pH is an important criterion and generally pre-treatment of wastewater with a COD of more than 1000 mg/L is required to reduce the amount of oxidising chemical required. Chemical oxidation is effective for the treatment of organics (phenols, hydrocarbons), inorganics (sulphides, mercaptans) and biological contaminants (pathogens, bacteria) (*Zinkus*, 1998).
- Flotation: This is a process in which small gas bubbles are entrained in the wastewater by mechanical or diffused aeration. Dissolved air

flotation (DAF) and induced air flotation (IAF), are the two main types of flotation used in wastewater treatment. Bubbles rising through the liquid adhere to suspended particles, decreasing the specific gravity of the particle/bubble combination. This process induces the formation of froth, which is skimmed off the surface. This process is an effective means of removing suspended solids (organic, inorganic and biological). If high slugs of solids are present, pre-treatment may need to be considered. Also, chemical emulsions may need to be broken by pH adjustment. Suspended solids removal may be achieved by 75 %, and upon addition of chemicals, up to 90 % (*Zinkus et al.* 1998). The skimmed solids require de-watering and disposal treatment.

- Sedimentation: This process removes solids from wastewater based on the differentiation of densities. A sedimentation tank is designed to allow sufficient retention time, allowing the different phases to separate. Suspended solids removal of 10-50 % may be achieved by preliminary treatment, and by more than 70 % when used as unit process with coagulation and flocculation.

In order to achieve enhanced quality of the wastewater produced at Rupert and Rothschild Vignerons, two water treatment technologies were investigated. *Chapters 6 and 7*, respectively address the technologies of induced settling by the addition of coagulants, and chemical oxidation by employing ozone.

CHAPTER 6

COAGULATION-SEDIMENTATION AS A TREATMENT TECHNOLOGY FOR WINERY WASTEWATER

As illustrated in previous chapters, winery wastewater contains a range of colloidal material; micro-organisms, yeast cells, bentonite, anthocyanins and tannins, to name a few. The reduction of these colloids will result in a decreased pollution status. At present, a delta-settler serves to remove suspended particles from the wastewater produced at Rupert and Rothschild Vignerons. As previously mentioned, it is largely ineffective, only partly removing suspended particles from the wastewater, depending largely on the flow rate and chemical composition of the wastewater. The removal of colour compounds and other dissolve organic compounds are not induced by gravity alone. An investigation was conducted into the potential use of coagulants to induce settling, thereby increasing the wastewater quality. This Chapter discusses the potential viability and effect of commercial metal salt coagulants on the winery wastewater produced at Rupert and Rothschild Vignerons.

6.1 LITERATURE REVIEW

6.1.1 *Chemical Coagulation*

Coagulation and flocculation generally refer to the process by which metal salts are added to wastewaters in order to destabilize colloidal material, thereby inducing the aggregation of small particles with resultant floc formation. The coagulation process consists of three stages:

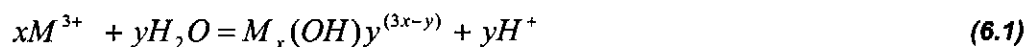
- i. Coagulant formation (if pre-hydrolysed coagulants are not used),
- ii. Particle destabilisation, and
- iii. Particle aggregation.

Four methods of colloid destabilisation exist:

- i. Compression of the diffuse layer.
- ii. Adsorption to produce charge neutralisation.
- iii. Enmeshment in a precipitate.
- iv. Adsorption to permit inter-particle bridging.

Coagulant formation and particle destabilisation are initiated by a rapid mixing stage where coagulants are added, hydrolysed and dispersed through the medium. Flocculation is defined by the mechanically or hydraulically induced inter-particle collisions aggregating particles and thus facilitating their separation (*Jiang and Graham, 1997*). The effectiveness of the process is determined by the coagulating agent, the coagulant dose, the solution pH and ionic strength, as well as the concentration and nature of the organic compounds (*Randtke, 1988*).

The formation of aggregates by hydrolysing metal salts of iron and aluminium are widely used in wastewater treatment. Conventional chemicals used for coagulation are mainly aluminium or iron based, including aluminium sulphate, ferric sulphate and ferric chloride. In aqueous solutions, the metal (M) ion hydrates and is hydrolysed to form monomeric and polymeric species: MOH^{2+} , M(OH)_2^+ , $\text{M}_2(\text{OH})_2^{4+}$, M(OH)_4^{5+} , M(OH)_3^0 (s) and M(OH)_4^- (*Dentel and Gosset, 1988*). In acidic conditions both Al^{3+} and Fe^{3+} remain in solution, but by increasing the pH or coagulant concentration, hydrolysis occurs to form the metal hydroxide M(OH)_3 (s). *Equation 6.1* illustrates the general hydrolysis reaction (*Stephenson and Duff, 1996*).



The resultant metal hydroxide polymers have a large surface area, an amorphous structure and a positive charge (*Randtke, 1988*). Their hydrophobic nature causes them to adsorb onto organic anionic particle

surfaces and become insoluble (*Dentel and Gosset, 1988*). Iron and aluminium tend to form insoluble complexes with polar molecules and oxygen containing functional groups such as hydroxyl or carboxyl groups (*Stumm and Morgan, 1962*). These groups provide a local negative charge, which reacts with the aluminium and iron cations. Charge neutralisation leads to colloid destabilisation, and subsequently, precipitation of metal cations and organic anions occur. This is termed sweep flocculation; the adsorption and bridging enmeshment of both particulate organics and inorganic solids to form large amorphous flocs. Dissolved organic compounds are removed primarily by sorption onto hydroxide surfaces (*Stephenson and Duff, 1996*).

6.1.1.1 The Effect of pH

Chemical coagulation is a phenomenon, which is highly pH dependent. The pH influences the polymeric metal species formed when metal coagulants are dissolved in water (*Stumm and Morgan, 1962*). *Randtke (1988)* summarised the influence of pH on chemical coagulation as a balance of two competitive forces:

- Between hydrogen ions and metal hydrolysis products for organic ligands.
- Between hydroxide ions and organic anions for metal hydrolysis products.

Should the pH be too low, the organic ligands favour the protons to the metal hydrolysis products, resulting in poor removal since some of the organic acids are not precipitated. Conversely, at a higher pH, the hydroxide ions compete with organic compounds for metal adsorption sites and the precipitation of metal hydroxides occurs by co-precipitation. Under alkaline conditions, the coagulating species becomes less positively charged, thus their attraction to anionic organic compounds are diminished (*Ching et al. 1994*). Therefore, little aggregation occurs at high pH (*Stephenson and Duff, 1996*).

6.1.1.2 Iron, Aluminium and Polyaluminium Chloride

Compared with $\text{Al}_2(\text{SO}_4)_3$ (alum), ferric chloride coagulates effectively over a broader pH range and forms a stronger, heavier floc. Furthermore, ferric chloride is less sensitive to overdosing, and does not contribute to aluminium residuals in the supernatant. However, liquid ferric chloride is an acidic, corrosive, dark brown material, which causes staining and necessitates special materials for construction (*Stephenson and Duff, 1996*).

It must be noted that the actual coagulant species are formed during and after these chemicals are mixed with the water to be treated. Thus Al^{3+} , Fe^{3+} , SO_4^{2-} and Cl^- are not primarily involved in the coagulation process (*Jiang and Graham, 1997*). An increased efficiency of inorganic Al/Fe (III) species is achieved by partially hydrolysing the Al/Fe (III) salts before adding them to the wastewater, thus pre-forming the actual coagulant species. The advantages of the preformed polymeric Al/Fe (III) coagulants are that they work efficiently over a wide pH range and are not sensitive to fluctuations in temperature or largely affected by the chemical composition of the wastewater. Polyaluminium chloride (PAC) is made by partial hydrolysis of an acid aluminium chloride solution using a specific reactor (*Jiang and Graham, 1997*).

For the above reasons, PAC coagulants were considered to be the best choice for winery wastewater, which exhibit large pH and chemical composition variation.

6.1.1.3 Coagulant Concentration

The optimum coagulant dosage depends on the nature of the wastewater, the pH and the coagulant. Coagulant dosage may be expressed as g coagulant/ g total carbon removed (*Stephenson and Duff, 1996*). *Alemark and Ekengren (1989)* recommended 3-6 mol of trivalent cation per g of influent COD. *Beulker and Jekel (1993)* found the optimum alum: TOC ratio for chlorine and oxygen bleached kraft to be 0.5 and 2.5 g alum/g TOC removed, resulting in a

60 % TOC removal at pH 5.5. *Lefebvre and Legube (1993)* found 2 g Fe/g TOC to be the optimum ferric chloride dose.

6.1.2 Sedimentation

Sedimentation refers to phase separation. Gravitational separation by sedimentation induces this phase separation. In this study, the settling of aggregated particles by coagulation is termed sedimentation. It should be noted that the term "coagulation" is often used to describe both colloid destabilisation and the resulting sedimentation of the aggregates.

6.1.3 Investigation into the use of Coagulation as Wastewater Treatment Technology

The use of chemical coagulation is widely employed in the treatment of ground water, pulp, tannery, municipal and textile wastewater. Chemical coagulation is frequently employed in parallel with ozonation. Turbidity is removed by ozonation through a combination of chemical oxidation and charge neutralisation. Colloidal particles that cause turbidity are maintained in suspension by negatively charged particles, which are neutralised by ozone. Ozone further destroys colloidal materials by oxidising the organic materials that occur on the surface of the colloidal particles (*Becker, 1996*). Partial ozone oxidation of organic compounds produces polar compounds. The efficiency of organic removal by coagulation is largely dependant on the polarity of the dissolved organics (*Stephenson and Duff, 1996*).

During the period of this project, only one study concerning the induced settling of winery wastewater was found, using chitosan as the coagulant. For the purpose of this study, the recent applications of coagulation on the wastewater originating from the textile, pulping and tannery industries are discussed briefly in order to demonstrate the choice of induced settling treatment for winery wastewater. A comparison between the use of chitosan and polyaluminium chloride (PAC) as choice coagulants of winery wastewater will be discussed.

6.1.3.1 Textile Wastewater

Textile wastewaters, as is the case of winery wastewater, are subject to high variability in composition. Colour compounds present the principle dilemma, and if not dealt with, presents a negative impact on the environment due to its turbidity and high polluting strength. *Lin and Lin (1993)* conducted a study on textile wastewater, employing ozone and chemical coagulation by use of polyaluminium chloride (PAC) for the purpose of COD and turbidity reduction. It was found that for low strength dye waste effluents (<500 mg/L COD, pH 10, 90 mg/L SS), ozonation was sufficient to totally eliminate the colour through a substantial turbidity decrease. However, for medium and high strength effluents (1000-2000 mg/L COD, pH 9-10, 130-250 mg/L SS) ozonation was not sufficient to reduce the turbidity and COD. In conjunction with PAC (dosage: 2.5 ml/ 4L), a COD reduction in the order of 70 % was attained (Refer to *Tables 6.1 and 6.2*).

Table 6.1 Ozone Specifications

Treatment	Concentration [g/hour]	Contact Time [min]	Total O ₃ Consumed [mg/L]
Ozone	20	10	833

Table 6.2 Effect of Ozone and PAC on High Strength Wastewater

Parameter	Raw Water [4L]	Ozonation [3.3 g O ₃]	PAC
pH	10		
COD [mg/L]	1800	1800	1000

Sarasa et al. (1998) similarly investigated the effects of ozone and chemical coagulation (Ca (OH)₂) on wastewaters containing azoic dyes. The COD was reduced by 25 % after ozonation, while it decreased by 50 % after ozonation and coagulation treatment. The TOC remained constant during ozonation, but was reduced by 42 % after coagulation. The colour (adsorbancy) decreased

gradually during ozonation and after the combined treatment, the reduction was 62 % (Refer to *Tables 6.3-6.5*).

Table 6.3 Ozone Specifications

Treatment	Concentration [mg/L]	Flow rate [L/min]	Contact Time [min]	Total O ₃ Consumed [mg/L]
Ozone	48	1.16	70	1156

Table 6.4 Coagulation Specifications

Treatment	Dosage [mg/L]	pH	Stir time [min]
Ca(OH) ₂	787	12	15

Table 6.5 Parameter Concentrations during Treatment

Parameter	Raw Water [4.5 L]	Ozonation [3.9 g O ₃]	O ₃ + Ca(OH) ₂
pH	6.4	9.0 ^a	8.7 ^b
COD [mg/L]	2460	1840	1216
TOC [mg/L]	620	572	362
Absorbency [A 400 nm]	2.598	1.473	0.992

^aPreviously adjusted to 10.3

^bPreviously adjusted to 12

6.1.3.2 Pulping Wastewater

Effluents from the pulping industry contain high concentrations of inhibitory and refractory organics. *Stephenson and Duff (1996)* investigated the potential use of chemical coagulation using metal salts for the treatment of pulp effluent. The COD concentration of the raw effluent was 2520-7930 mg/L, with a TOC of 1065-3560 mg/L. The experiments were conducted at 20°C, with a run time of 24 hours.

According to qualitative description, the addition of ferric chloride resulted in fine grey-brown floc, which tended to form large amorphous aggregates. The floc was found to exhibit poor settling characteristics with brown supernatant; while aluminium chloride coagulation resulted in a clear supernatant with fine, light brown flocs. Some flocs floated whereas others settled rapidly. The effects of four types of coagulants concerning the colour and total organic carbon (TOC) are demonstrated in *Table 6.6*.

Table 6.6 Optimum Removal Dosages in terms of TOC and Colour for $FeCl_3$, $FeSO_4$, $AlCl_3$ and $AlSO_4$ on Pulp Effluent

Coagulant	Dosage [g/L]	Colour Reduction [PtCo units]*	TOC Reduction [mg/L]
$FeCl_3$	10	5000 to 1000	2000 to 500
$FeSO_4$	7.5	5000 to 1000	2000 to 950
$AlCl_3$	10	5000 to 10	2000 to 1000
$AlSO_4$	10	5000 to 10	2000 to 1000

*Platinum Cobalt

Stephenson and Duff (1996) conducted a range of experiments with varying coagulant dosages on diluted effluent. It was found that the precipitation reactions were strongly influenced by the pH. In terms of reducing the TOC, colour and turbidity levels, the optimum adjusted pH were: 4.0-6.0 for $FeCl_3$, >7.4 for $FeSO_4$, 5.0-6.0 for $AlCl_3$ and 5.8-6.8 for $AlSO_4$.

6.1.3.3 Tannery Wastewater

Garrote et al. (1995) developed a two step coagulation process to treat tannery effluent using $FeCl_3$ and $Ca(OH)_2$. The characteristics of the effluent were: pH's between 8-9.3, SS concentrations of 270-338 mg/L, and COD concentrations of 2438-2617 mg/L. The treatment was conducted at pH 8.5 with dosages of 100-200 mg/L $FeCl_3$. Only the COD reduction was measured and found to reduce by 70-86 %.

6.1.3.4 Winery Wastewater

Coma et al. (1998) conducted a study on the use of chitosan, a coagulant used in the food industry. Effluent from red wine producing cellars in the Languedoc-Rousillon was used.

Table 6.7 illustrates the effect of the chitosan at different concentrations on the COD, SS and turbidity.

Table 6.7 Efficiency of Chitosan on Winery Effluent at Different Dosing Concentrations

Winery Effluent	Dosage [mg/L]	COD	SS	Turbidity
		Reduction %	Reduction %	Reduction %
Effluent A	20	20	90	80
	40	25	98	95
	60	46	98	98
Effluent B	20	70	92	98
	40	75	95	98
	60	60	90	95

The regulation of pH was not required since the optimum pH range of chitosan is 4-5. As depicted, the use of chitosan proved effective for the removal of SS and turbidity. For Effluent B, higher COD reductions were obtained in comparison to Effluent A.

During the period of this study (1996), the treatment cost was determined at $\pm 4\text{FF}/\text{m}^3$ ($\pm \text{R}4.00/\text{m}^3$) at a dosage of 30 mg/L.

6.2 INVESTIGATION INTO THE INFLUENCE OF PAC ON WINERY WASTEWATER

The objective of this research was to determine the effect of chemical coagulation by use of polyaluminium chloride for the removal of organic compounds (especially those contributing to colour and turbidity) and suspended solids from winery wastewater. In order to meet this goal, four objectives were identified:

- i. Determination of the effects of PAC on the quality of the wastewater.
- ii. Identification of coagulant dosage range.
- iii. Determination of effect of pH on the coagulation efficiency.
- iv. Determine the economic efficiency of coagulation using PAC's.

Although some researchers have employed ozonation as a pre-treatment to chemical coagulation, it should be noted that ozonation might also impart adverse effects. According to *Becker* (1996) ozonation of moderate to high DOC waters can have adverse effects on coagulation when metal coagulants are used. It was found that an increased optimum coagulant dose was required to reduce turbidity, thus leading to increased cost. For the purpose of this study, the effects of coagulation without prior ozonation were investigated to determine its potential application.

Different interpretations are found in chemical and engineering literature associated with the terms "coagulation" and "flocculation". This study applies the term coagulation, referring to the overall process of particle aggregation, including both particle destabilisation and particle transport.

6.2.1 Experimental Procedure

All experiments were carried out using wastewater obtained from Rupert and Rothschild Vignerons. The characteristics of the wastewater used for these experiments are illustrated in *Table 6.8*. An efficiency analysis was conducted

by means of assessing the concentrations of the COD, SS and turbidity prevalent before and after the treatment.

Table 6.8 Characteristics of Rupert and Rothschild Wastewater used for Experimentation

Parameter	Concentration
Conductivity [mS/m]	80-190
COD [mg/L]	2000-8000
SS [mg/L]	140-1000
Turbidity [NTU]	150-900

Experiments were carried out in 1 L measuring cylinders. Four types of PAC were used for the experiments: PAC I, II, III and IV, obtained from two individual manufacturers. The characteristics of the PAC's are illustrated in *Table 6.10*. The respective manufacturers supplied the reported aluminium concentrations in the coagulants. The wastewater was collected from the pit at Rupert and Rothschild Vignerons and stored at 4 °C prior to experimentation. All wastewater samples were filtered through a 3.55 µm filter to remove large suspended particles. The experimental conditions are outlined in *Table 6.9*.

Table 6.9 Experimental Conditions for Coagulation Experiments

Parameter	Value
Temperature	10-15 °C
Stirring Time	30 s, 80 RPM
pH	Upon adjustment: NaOH addition

Table 6.10 Description of Four Types of PAC Used for Coagulation

Name	Aluminium Content [% m/m]	Specific Gravity	Description
PAC I	± 14	1.25	Blend of polyaluminium chloride and organic polymer
PAC II	± 7.5	1.3	Polyaluminium hydroxysilicate chloride (pure inorganic product)
PAC III	6.6-14	1.28	Medium molecular weight cationic coagulant (blend of polyamine and PAC)
PAC IV	3-6	1.18	Low molecular weight cationic coagulant (blend of polyamine and PAC)

For the determination of the effect of dosage and pH on the efficiency of the coagulants, experiments were conducted at the pH of the raw water or adjusted by means of NaOH. For the selection of coagulant dosages, the aluminium content of the coagulants was considered in conjunction with dosages reported by literature.

The following experimental procedure was conducted for all experiments:

- i. Filtration through a 3.55 µm filter.
- ii. pH adjustment (some experiments were conducted at original pH).
- iii. Coagulant addition by micro-pipette.
- iv. Mechanical stirring (30 s, 80 RPM).
- v. Transfer to 1 L measuring cylinders.

6.2.2 Results and Discussion

Various experiments were conducted to ascertain the influence of dosage and pH on the reduction of COD, SS and turbidity. The values that are illustrated in the following figures were obtained by calculating the average percentage reduction observed for each of the respective dosages. For all values illustrated, at least two experiments had been conducted to calculate the average reduction induced by a particular dosage at a particular pH value.

Values that fell outside the scale of the figures (i.e. lower efficiency or no effect) will be discussed in parallel with the efficient dosages and pH ranges.

6.2.2.1 PAC I

For experiments with PAC I, the following dosages were used:

- 30 µL/L
- 200 µL/L
- 500 µL/L
- 600 µL/L
- 1000 µL/L

Figures 6.1-6.3 illustrate the efficient dosages and the respective reductions observed at the optimal pH range of 5-7 for PAC I. No settling occurred at a dosage of 30 µL/L (irrespective of pH adjustment). Although analyses were not performed, no visual coagulation or sedimentation was observed at 30 µL/L. In contrast, dosages of 200 µL/L -1000 µL/L induced sedimentation at pH 5, 6 and 7. At pH 3, some coagulation took place, however, the aggregated particles remained in suspension, with some sedimentation of larger flocs. At this pH, only the SS concentration was reduced by $\pm 50\%$ (dosage variation had no significant effect). At pH 5, 6 and 7, effective coagulation and sedimentation occurred. The COD was reduced by between 5-17 %. Higher dosages (500-1000 µL/L) in comparison to 200 µL/L, did not notably increase the COD reduction (Refer to *Figure 6.1*). In terms of the turbidity and SS, pH 5, 6 and 7 provided for efficient reduction. However, a slight drop in the turbidity reduction was observed at pH 6. This indicates that charge restabilisation occurred, preventing some colloids from settling. The turbidity was observed to decrease by 80-98 %, while 65-92 % reductions were observed for SS concentrations. A dosage of 200 µL/L proved effective for both turbidity and SS reduction; increased dosages did not markedly improve the quality of the wastewater. As observed in *Figure 6.3*, pH 7 favoured SS reduction (82-92 %).

The performance of PAC I may thus be summarised as follows:

- Superior performance at pH 5-7 in comparison to lower pH's.
- A dosage of 200 $\mu\text{L/L}$ is sufficient to improve the quality of the wastewater.
- High efficiency for turbidity removal.
- Reduces COD to a maximum of 17 %.
- Effectively reduces the SS concentration, with highest reductions at pH 7.

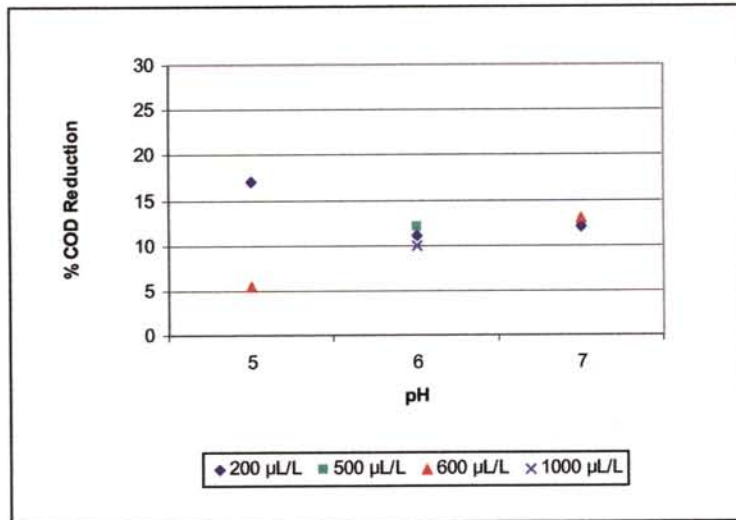


Figure 6.1 PAC I: Reduction in COD

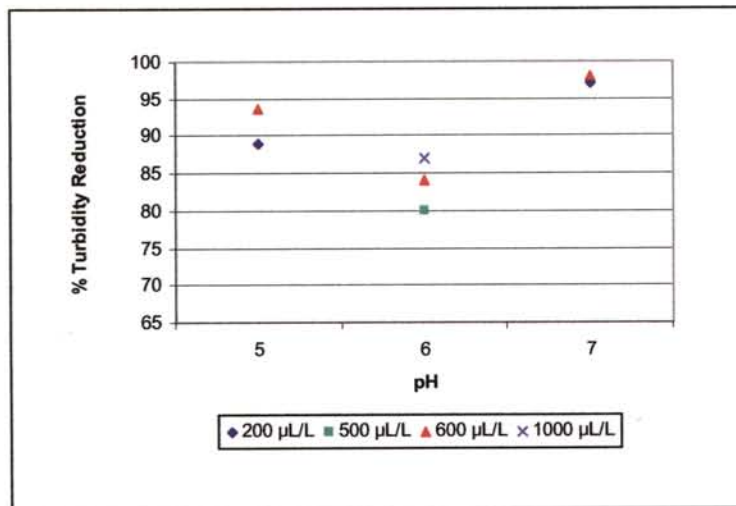


Figure 6.2 PAC I: Reduction in Turbidity

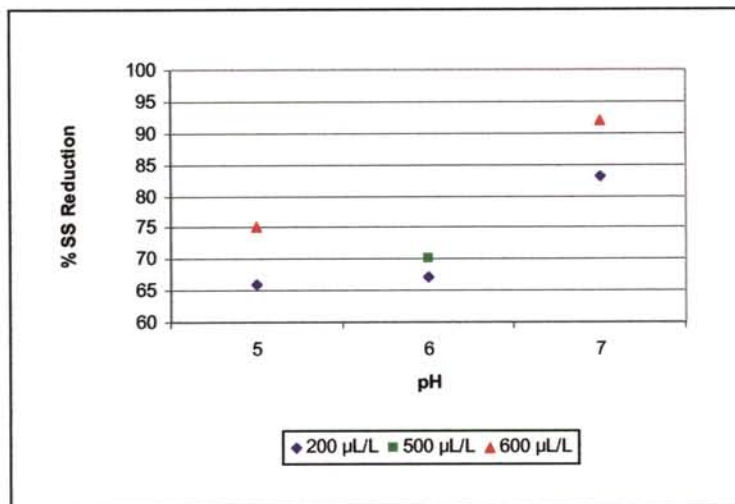


Figure 6.3 PAC I: Reduction in SS

6.2.2.2 PAC II

For experiments with PAC II, the following dosages were used:

- 500 µL/L
- 600 µL/L
- 700 µL/L
- 1000 µL/L
- 1500 µL/L

Similar findings in terms of the COD reduction were observed with PAC I and II. However, PAC II proved more effective at low pH (3.5) than PAC I. The COD was reduced by 10-15 % (Refer to *Figure 6.4*). No large variation in COD removal occurred upon dosage increase.

PAC II proved highly effective for turbidity reduction. For most experiments, reductions of 85-98 % were observed. Variation in pH did not influence the results. Substantial reductions (75-90%) were observed at the unadjusted pH of the wastewater (pH 3.5); thus considered economically feasible since no additional cost is incurred for pH adjustment. PAC II required a higher dosage than PAC I, which was expected since it contains less aluminium. It should also be noted that the most consistent reductions were observed at pH 3.5-5.5. In this pH range, a higher dosage improved turbidity reduction (Refer to *Figure 6.5*). The low pH of the raw water appeared to favour the reduction of SS (Refer to *Figure 6.6*). At pH 3.5, reductions of 60-90% were observed. A dosage of 700 µL/L-1000 µL/L increased the reduction in SS. For experiments conducted at a dosage of >1000 mg/L, the turbidity and SS did not decrease. This is attributed to charge restabilisation, as a consequence of over-dosing.

The performance of PAC II may thus be summarised as follows:

- Operational over a wide pH range, including the natural pH (unadjusted) of this winery wastewater.
- The optimal dosage range of 700-1000 $\mu\text{L/L}$. However, at 500 and 600 $\mu\text{L/L}$, good results were also achieved.
- Very high efficiency for turbidity removal (85-98%).
- Induced COD reductions in order of 10-15%
- Effectively reduces the SS concentrations (60-90%) with highest reductions at the natural pH of this winery wastewater (pH 3.5).

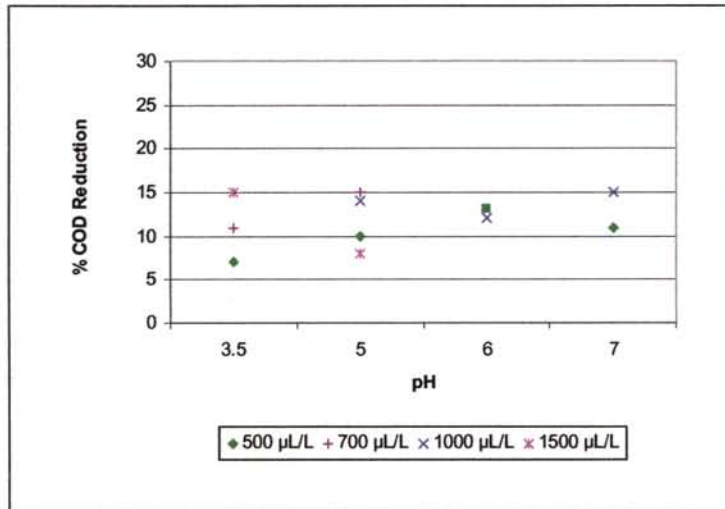


Figure 6.4 PAC II: Reduction in COD

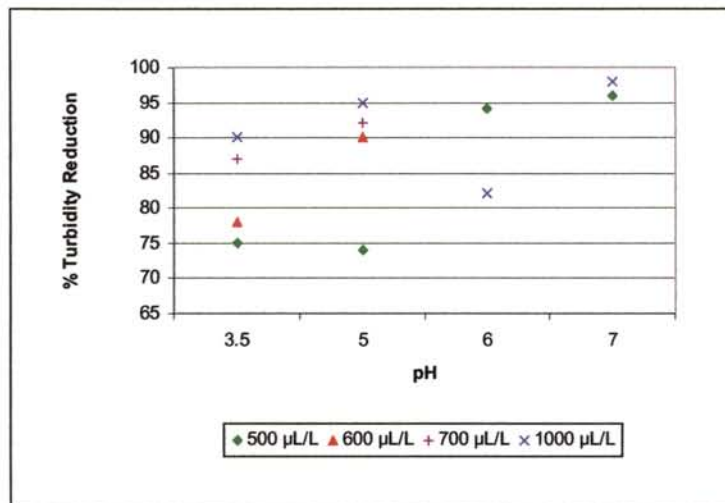


Figure 6.5 PAC II: Reduction in Turbidity

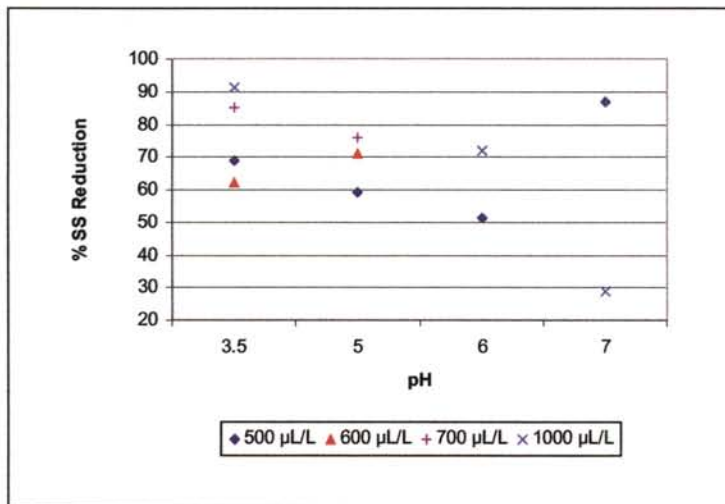


Figure 6.6 PAC II: Reduction in SS

6.2.2.3 PAC III

For experiments with PAC III, the following dosages were used:

- 200 µL/L
- 500 µL/L
- 600 µL/L
- 1000 µL/L

At a dosage of 200 µL/L, no COD reductions were observed. This dosage did, however, decrease the turbidity and SS by 80 % and 66 %, respectively (pH 6). Even though this coagulant is reported to contain 6.6-14 %, it was considered that higher dosages showed superior performance. As observed with type I and II, the COD reduction was in the order of 9-17 %. At 500 and 600 µL/L the most constant values of reduction were observed (Refer to *Figure 6.7*). High turbidity removal was observed at pH 3.8 and 5.5 (94-98 %). At pH 6 and 7, ± 80-84 % reductions were obtained. Experiments conducted with 500 and 600 µL/L showed the greatest consistency. With regard to SS removal, a low pH was not found to be favourable (pH 3.8). An 80-85 % reduction was noted at pH 5.5, while these values dropped to ±70 % at pH 6. At pH 7, the reduction improved again to ±85 % (Refer to *Figure 6.8*). It is hypothesised that at pH 6 the charge on some suspended particles is restabilised, thereby preventing settling. A zeta potential determination will clarify this phenomenon. As observed for the optimal COD and turbidity reductions, a dosage of 500-600 µL/L was shown to effectively improve the quality of the wastewater in terms of the SS concentrations (Refer to *Figure 6.9*).

The performance of PAC III may thus be summarised as follows:

- Superior performance at low pH and at the natural pH of winery wastewater.
- The optimal dosage range of 500-600 µL/L.
- Very high efficiency for turbidity removal (95-98%) at pH 3.8 and 5.5.

- Induces COD reductions in the order of 9-17%.
- A slight decrease in performance at pH 6.
- High SS reductions (80-85 %) at pH 5.5 and 7.

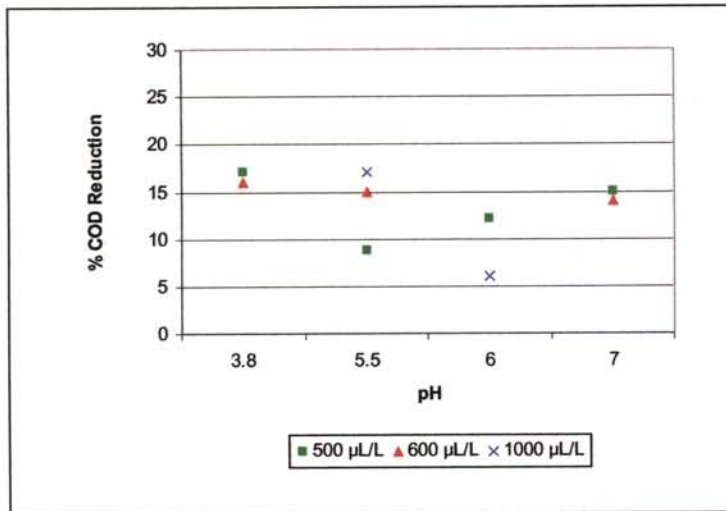


Figure 6.7 PAC III: COD Reduction

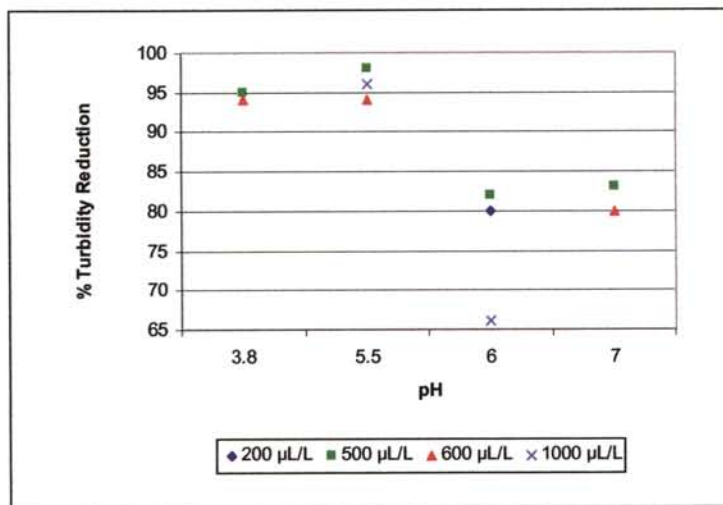


Figure 6.8 PAC III: Turbidity Reduction

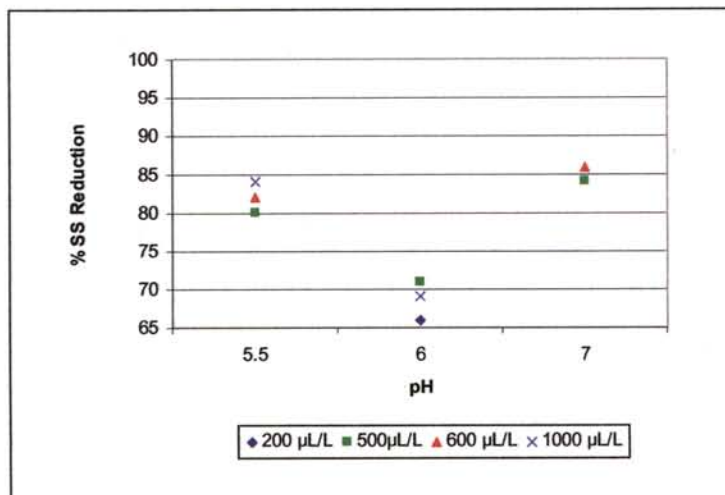


Figure 6.9 PAC III: SS Reduction

6.2.2.4 PAC IV

For experiments with PAC IV, the following dosages were used:

- 500 µL/L
- 600 µL/L
- 700 µL/L
- 1000 µL/L

Experiments were conducted at pH 3.8 and 5.5. As observed for PAC I, II and III, COD reductions of 5-15 % were achieved. Dosage variation was not observed to greatly influence the reductions (Refer to *Figure 6.10*). Turbidity reductions of 85-98 % were observed. Higher dosages (700-1000 µL/L) decreased the turbidity at both pH's (Refer to *Figure 6.11*). Similarly, at a dosage of 1000 µL/L, higher reductions in SS were achieved. This may be explained in that PAC IV contains a lower concentration of aluminium, thus requiring higher dosages than the other PAC's. Furthermore, for both turbidity and SS removal, experimentation at pH 3.8 appeared to produce the best results.

The performance of PAC IV may thus be summarised as follows:

- Excellent performance at low pH for turbidity and SS removal.
- The optimal dosage range is 700-1000 µL/L.
- Very high efficiency for turbidity removal (90-98%).
- Reduces the COD in the order of 5-15%.
- Very high SS reductions (85-92 %) were achieved at pH 3.8 (pH of winery wastewater).

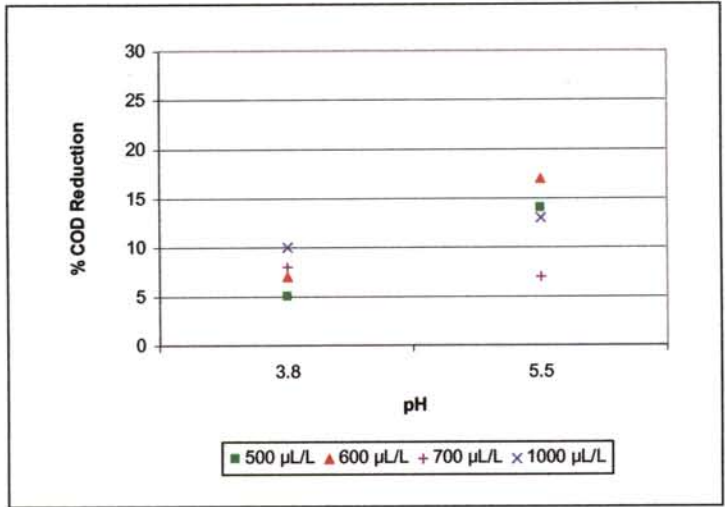


Figure 6.10 PAC IV: COD Reduction

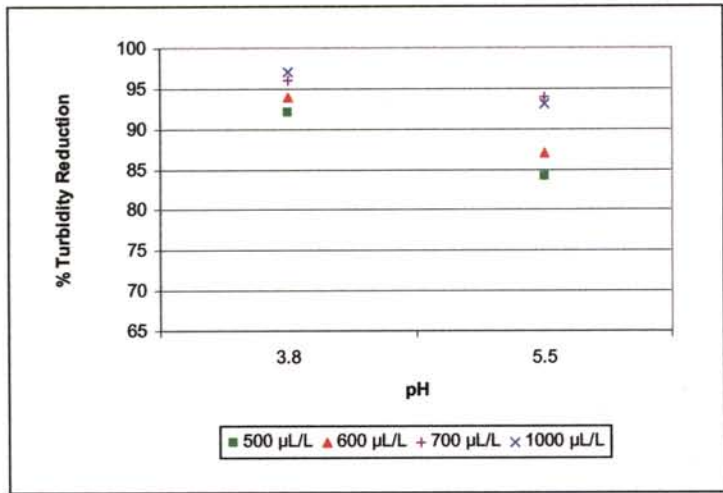


Figure 6.11 PAC IV: Turbidity Reduction

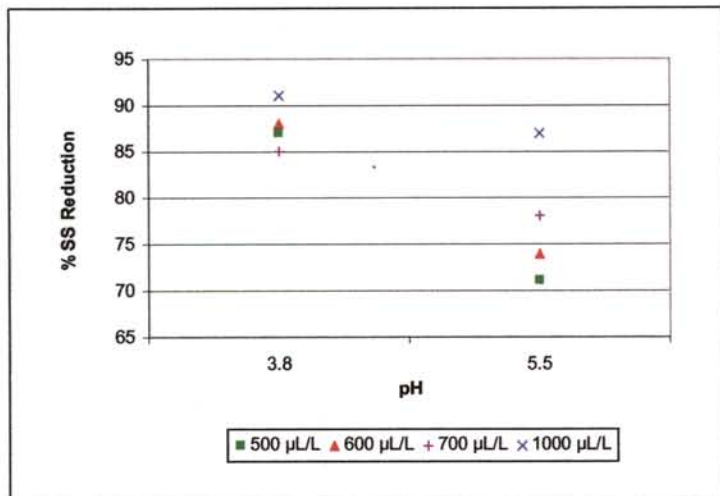


Figure 6.12 PAC IV: SS Reduction

6.2.2.5 Sedimentation Rate

The sedimentation rate for each of the coagulants was determined. The height of the interface was noted over time as sedimentation occurred after particle aggregation took place. The height of the interface corresponds to the volumetric measurement of a standard 1 L measuring cylinder. Sedimentation was considered to be complete once no further settling was observed, even though some particles may still have been suspended in the interface. *Figures 6.13-6.16* illustrate the sedimentation rates for the respective coagulants.

Coagulation of compounds present in the wastewater occurred almost instantaneously upon the addition of PAC I. The sedimentation rate occurred rapidly, following a linear gradient. After 7.5 min, the interface was ± 20 cm (2.6 cm/min). The rate declined as the volume of floc collected at the bottom of the measuring cylinder. Complete sedimentation occurred in approximately 12 minutes (Refer to *Figure 6.13*).

As seen in *Figure 6.14*, PAC II induced rapid initial sedimentation (2.2 cm/min), followed by a slower rate of 1.8 cm/min. Total sedimentation occurred in approximately 17 min.

The most rapid sedimentation rate was observed for PAC III. As seen in *Figure 7.15*, a 20 cm interface was observed after only 5 min (4 cm/min). However, complete sedimentation occurred over 25 min.

PAC IV exhibited the slowest sedimentation rate. During the first 10 min, sedimentation occurred at 1 cm/min. However, the rate declined substantially until complete sedimentation occurred after ± 45 min.

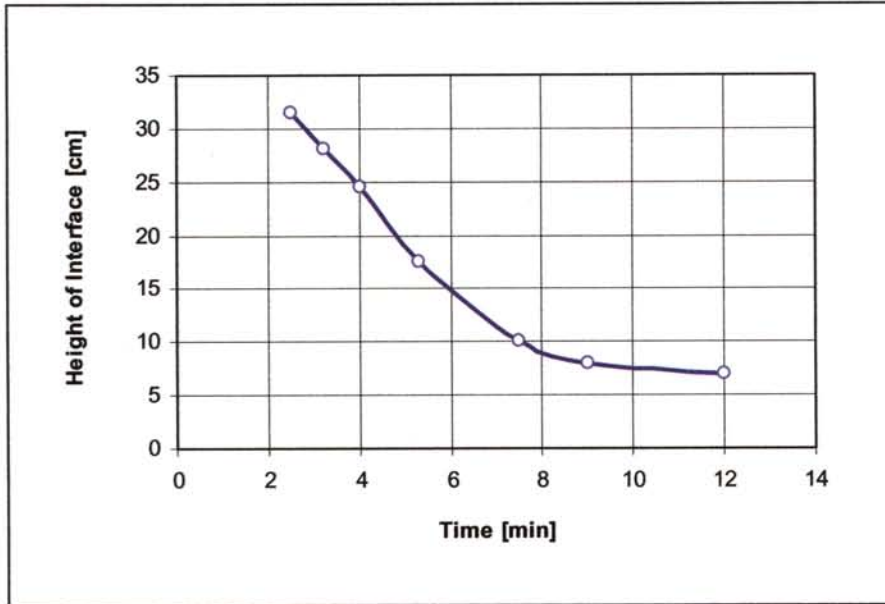


Figure 6.13 PAC I Sedimentation Rate

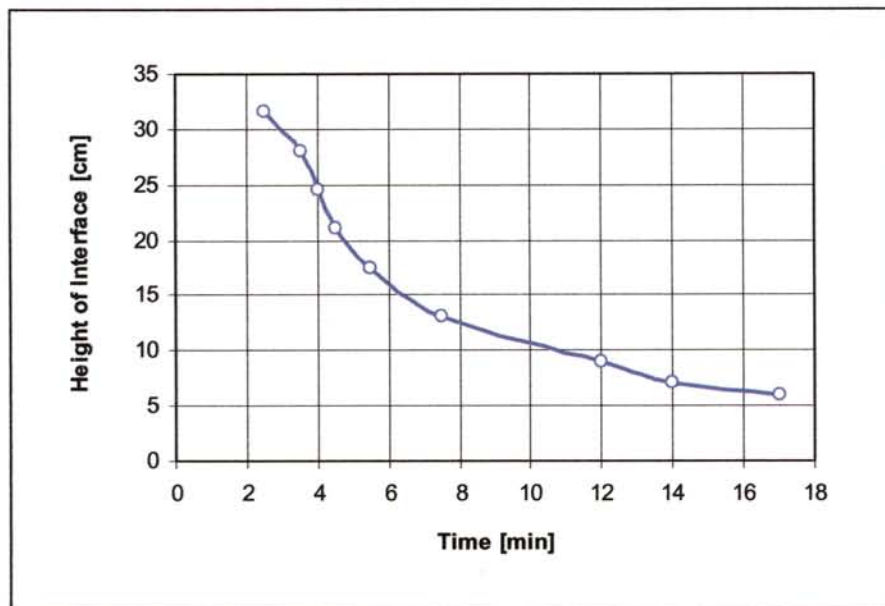


Figure 6.14 PAC II Sedimentation Rate

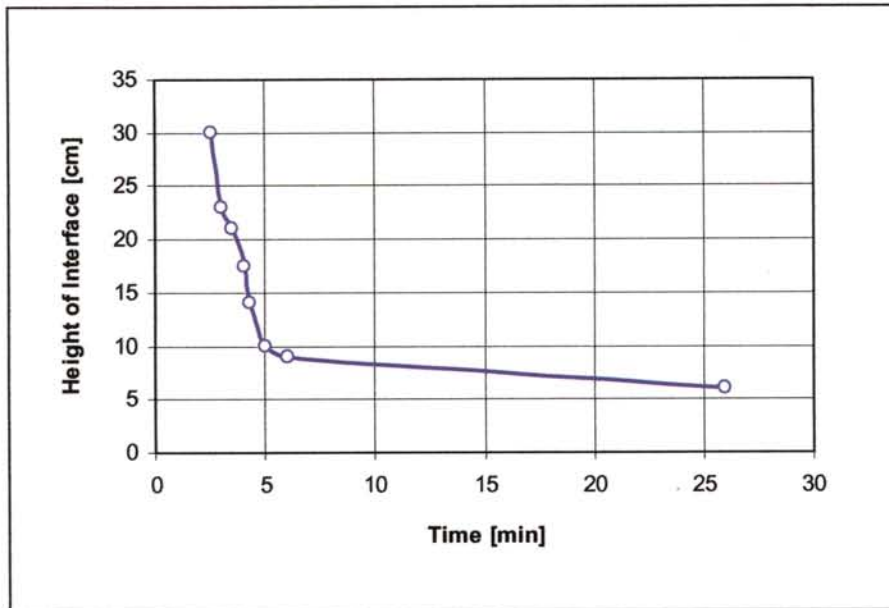


Figure 6.15 PAC III Sedimentation Rate

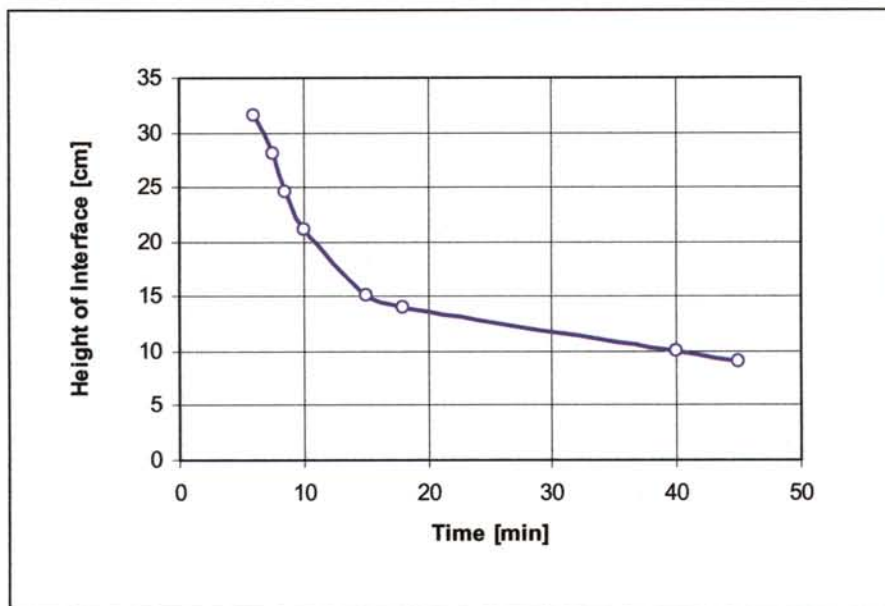


Figure 6.16 PAC IV Settling Rate

The sedimentation rates are an important consideration when designing a sedimentation tank or thickener. Coagulants that induce the most rapid sedimentation of colloids and suspended particles will reduce the cost of the thickener owing to a decreased residence time requirement.

6.2.2.6 Qualitative Description

The appearances of the settled solids (settled flocs) and supernatant were largely similar for the four coagulants. The visual observations are described in *Table 6.11*.

Table 6.11 Qualitative Description of the Sediment and Supernatant for the Four Coagulants

Coagulant	Supernatant	Settled Floc
PAC I	very clear (transparent)	compact dark floc mass
PAC II	very clear (transparent)	compact dark floc mass
PAC III	very clear (transparent)	brown flocs, less compact
PAC IV	clear	larger flocs, less compact

Figure 6.17 presents digital images of the aggregation of particles, the resultant floc sedimentation and the supernatant as observed for each coagulant type.


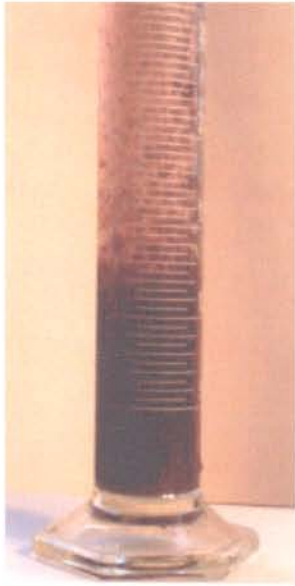




Particle Aggregation		Floc Sedimentation	
			
PAC I	PAC II	PAC III	PAC IV
			

Figure 6.17 Digital Photographs of Coagulation and Sedimentation

6.2.2.7 Comparative Study

Table 6.12 illustrates the comparison between chitosan and the four PAC coagulants for quality enhancement of winery wastewater.

Table 6.12 Coagulant Comparisons in Terms of Quality Enhancement

Property	Chitosan	PAC I	PAC II	PAC III	PAC IV
% COD Reduction	20-70 ¹	5-17 ^{2a}	7-15 ^{3a}	9-17 ^{4a}	5-17 ⁵
% Turbidity Reduction	80-98 ¹	80-98 ^{2a}	75-98 ^{3b}	95-98 ^{4b}	84-98 ⁵
% SS Removal	92-98 ¹	65-92 ^{2b}	60-92 ^{3b}	80-82 ^{4c}	72-91 ⁵

¹ Variance due to dosage (20-60 mg/L) and wastewater origin (Coma *et al.* 1998)

^{2a} Dosage 200-1000 µL/L, pH range 5.0-7.0

^{2b} Dosage 200-500 µL/L, pH range 5.0-7.0

^{3a} Dosage Range 500-1500 µL/L, pH range 3.5-7.0

^{3b} Dosage Range 500-1000 µL/L, pH range 3.5-7.0

^{4a} Dosage Range 500-1000 µL/L, pH range 3.8-7.0

^{4b} Dosage Range 200-1000 µL/L, pH range 3.8-7.0

^{4c} Dosage Range 200-1000 µL/L, pH range 5.5, 7.0

⁵ Dosage Range 500-100 µL/L, pH range 3.8-5.5

From this table it is evident that both chitosan and PAC are suitable for the treatment of winery wastewater. Chitosan is, however, more efficient in COD reduction than the PAC's. This may be attributed to chitosan being a high-capacity adsorbent. Chitosan is derived from the polysaccharide chitin, found in the exo-skeletons of shrimp, crabs and other shellfish. Should turbidity and suspended solid reductions be strived for, PAC or chitosan may be considered. For the selection of the most suitable coagulant, economic aspects must be considered.

6.2.2.8 Economic Evaluation

Table 6.13 portrays the cost of the coagulants as provided by the individual manufactures. It should be noted that these figures are subject to variation depending on the order quantity and Rand (ZAR R):Dollar (US \$) exchange

rate. The price was calculated per m³ wastewater treated at a dosage of 200 mL/m³ for all four PAC coagulants. The additional cost of pH adjustment was not included in the calculations.

Table 6.13 Economic Performances of the Four Types of PAC Coagulants

Coagulant	Cost [R /kg]	Cost [R/L]	Cost @ 0.2 L/m ³ [R/m ³]
PAC I	6.20	7.75	R1.55
PAC II	4.00	5.2	R1.04
PAC III	32.65	41.79	R8.35
PAC IV	21.25	25.07	R5.01

According to *Coma et al.* (1998), chitosan treatment at 30 mg/L was in the order of 4 FF/m³ (French Franc) at the time of the investigation. However, it should be noted that in a recent article by *Rorrer* (2000), chitosan was quoted at 7\$/lb. Although it is not in the scope of this project to evaluate chitosan economics, it should nevertheless be noted that a wide range of chitosan derivations exists, with large variations in price.

In conclusion, PAC I and II are the most economically viable choices for chemical coagulation. These PAC coagulants may be further credited by their excellent performance in turbidity and suspended solids reduction, and rapid sedimentation rates.

6.3 FINAL REMARKS ON THE USE OF COAGULATION

Despite the multitude of interactive effects, some hypotheses were made. The contaminants, which were most easily removed by coagulant addition are thought to have functional groups which react with specific sites on the pre-hydrolysed aluminium. The selective removal of ionic compounds over neutral compounds was attributed by *Sinsabaugh et al.* (1986) to the formation of insoluble complexes with the positively charged coagulant. Removal of neutral compounds was attributed to enmeshment and sorption.

Sinsabaugh et al. (1986) showed that dissolved organics are removed through two distinct mechanisms:

- i. At low pH, the anionic organic molecules react directly to form insoluble complexes.
- ii. The adsorption of organics onto preformed metal hydroxide flocs, followed by sedimentation, is the more dominant mechanism at higher pH values and more elevated coagulant dosages.

The net results is that the removal of organics can occur over a wide range of pH's, and that a maximum removal will be obtained by combining the two mechanisms through pH adjustment (*Qureshi and Malmberg, 1985*). With reference to the COD, these mechanisms were considered to have induced the reduction of the dissolved organics in the wastewater. It is expected that the fraction of dissolved organics that did not precipitate, are comprised of low molecular weight compounds. Given the high coagulant dosages applied in the experiments, the residual dissolved organic compounds indicate a maximum limit of removal by aluminium rather than a limitation in availability of sorption sites.

The wastewater contains high levels of tannins, anthocyanins and colloidal particles. These high molecular weight compounds are responsible for the turbidity and suspended solid concentrations. Since colour compounds are generally highly anionic, they are expected to be readily neutralised by the cationic aluminium. The high turbidity removal was evidence of this. Particle aggregation of the high molecular weight compounds was highly effective. It is thought that charge destabilisation and particle enmeshment induced the rapid sedimentation of the aggregated compounds. However, should the dosage of the coagulant be too high, charge restabilisation occurs, causing the aggregated floc to be suspended and no settling takes place.

The prime objective in determining the dosage of coagulant is effectiveness and economy. Economically speaking, the minimum optimum dosage for the particular PAC should be determined through further investigation. It is

recommended that future experiments consider the magnitude of charge prevalent in the wastewater. The zeta-potential of the wastewater will indicate the point of zero charge; i.e. indicating the optimum pH and coagulant dose at which sedimentation occurs.

This study lead to the design and construction of a pilot-scale sedimentation tank (thickener). Further test work will be conducted at Rupert and Rothschild Vignerons employing this thickener with PAC as coagulant. *Figure 6.18* illustrates the sedimentation tank.

Having considered chemical coagulation, *Chapter 7* will focus on another chemical treatment technology, ozone. Although these two treatment technologies may be used in combination, the aim of this study was to consider their efficiency individually. A combination of these technologies is discussed in *Chapter 8*.

Figure 6.18 Sedimentation Tank (Thickener)

CHAPTER 7

EVALUATION OF OZONATION AS A POTENTIAL TREATMENT TECHNOLOGY FOR WINERY WASTEWATER

At the start of the investigation, ozonation of the wastewater produced at Rupert and Rothschild Vignerons was conducted by means of a venturi system. Ozone-winery wastewater dynamics had not been researched prior to the installation of the ozonation system. The effect of the ozone on the reduction of pollutants was not found to be satisfactory; however, several factors including mass transfer, retention time and system design were considered to be the factors limiting its efficiency. Ozone is used extensively in other applications of wastewater treatment (e.g. tannery, paper mill and textile wastewater) with positive results. It was thus, decided to research the potential of ozonation on winery wastewater. This chapter focuses on the applicability of ozone for the reduction of COD and turbidity in winery wastewater. Effects of ozonation in terms of the system conditions (pH), concurrent with the influence of mass transfer were examined.

7.1 LITERATURE REVIEW

In order to quantify the efficiency and applicability of gas-liquid contacting systems, the properties of the gas (in this case ozone) and liquid (in this case winery wastewater) have to be clearly understood. Previous chapters have defined the characteristics of the liquid and *Section 7.1.1* defines the characteristics of ozone and its kinetics.

7.1.1 Characteristics of Ozone

Ozone is generated when a high voltage is projected across a discharge gap in the presence of oxygen, or an oxygen-containing gas, such as air. The

word "ozone" is derived from a Greek word meaning "to smell". Ozone is a relatively unstable gas consisting of three oxygen atoms per molecule (O₃) and is one of the strongest oxidising agents known. Common oxidation treatments utilising ozone are those for the decomposition of cyanide, phenol, organic acids, cresol, xylol, aldehydes, mercaptans, hydrogen sulphide and iron. Complete oxidation of organic contaminants to nitrogen and carbon dioxide can be obtained with some compounds if sufficient ozone doses and reaction time are employed. However, most compounds form intermediate compounds that compete for the ozone and in some cases are difficult to oxidise. The physical chemistry of ozone is an important factor to consider when applied for wastewater treatment as a number of complex factors influence its solubility, reactivity, auto-decomposition and stability. The solubility of ozone increases as a function of pressure and decreasing water temperatures. Ozone is considered an excellent choice for oxidation since (Crawford and Cline, 1990):

- i. Speed of disinfection by ozone is much faster than disinfection by chlorine with no residuals in solution.
- ii. Ozone is an excellent biocide and decreases colour, turbidity and the chemical oxygen demand.

7.1.2 The Dissolution of Ozone into the Liquid

Ozone solubility follows Henry's law, which means that solubility is a direct function of partial pressure (Crawford and Cline, 1990). Equation 7.1 illustrates this relationship and shows how the solubility constant K_s is a function of absolute temperature:

$$[O_3] = K_s pO_3 \quad \text{Henry's Law} \quad (7.1)$$

where

- $[O_3]$ = ozone concentration (mg/L)
- K_s = solubility constant
- pO_3 = partial pressure of ozone

$$K_s = 1.29 \times 10^6 / T_{\text{kelvin}} - 3720.5$$

$$K_s = \frac{1.29 \cdot 10^6}{T_{\text{kelvin}} - 3720.5} \quad (7.2)$$

7.1.3 Kinetics of Ozone Transfer: The Physical Reaction

Ozonation is practiced by dissolving ozone into water to react with target contaminants or inactivate pathogenic organisms. Thus, an efficient mass transfer system is crucial. The overall rate of ozone mass transfer is affected by (Zhou and Smith, 2000):

- Operating Conditions
- Water Quality
- Facility Set-up

In order to predict the removal rate of an organic solute in an ozone contacting system, the amount of ozone transferred from the gas to the liquid phase must be quantified. The rate of ozone transfer (R) across the concentration boundary layer, in a control volume can be expressed as (Yuteri and Gurol, 1987):

$$R = k_L a \{ [O_3] - [O_3^*] \} \quad (7.3)$$

where $k_L a$ = mass transfer co-efficient for ozone

$[O_3^*]$ = dissolved ozone concentration in equilibrium with the partial pressure of ozone at the gas-liquid interface

$[O_3]$ = ozone concentration in the gas phase

The liquid mass transfer coefficient (k_L) is dependent on the diffusion coefficient (D_{ab}) and boundary layer thickness (δ); D_{ab} being the diffusion

coefficient of ozone (a) in an oxygen medium (b) in this study. Since the D_{ab} is not significantly changed by small changes in temperature and pressure, the boundary layer thickness presents the greatest opportunity for increased k_L . Velocity, shear forces and the geometry of the reactor in which ozonation takes place, directly influences the boundary layer thickness. Thus, a mass transfer system, which addresses these factors and thereby decreases the thickness of the boundary layer, will result in a higher k_L value, which in turn will increase the transfer rate of ozone to the liquid phase.

Danckwerts (1970) recognised that the occurrence of rapid chemical reactions may enhance the mass transfer from gas phase into liquid phase. The utilisation of $[O_3^*]$ is influenced by the solution composition and the gas reactivity. The process is thus comprised of two distinct steps:

- i. Physical transfer of ozone across the concentration boundary layer, and
- ii. Chemical oxidation in the aqueous phase.

7.1.4 Consumption of Aqueous Ozone: The Chemical Reaction

Following its transfer from the gas phase, ozone initiates a chain of oxidation reactions in the bulk liquid phase. In natural water and in water containing organic solutes, the rate of aqueous ozone consumption can be lumped into a first-order expression (*Yuteri and Gurol, 1987*):

$$r = k \cdot [O_3] \quad (7.4)$$

where $[O_3]$ = instantaneous bulk ozone concentration
k = specific ozone utilisation rate (reaction rate constant)
r = aqueous ozone consumption

While a portion of the molecular ozone reacts directly with the available solutes, another part may decompose to form hydroxyl radicals (*Yuteri and Gurol, 1987*). Direct oxidation is slow and highly selective, while the hydroxyl

radical oxidation is extremely fast and non-selective. Furthermore, the hydroxyl radicals and organic radicals produced by auto-decomposition become chain carriers and re-enter the auto-decomposition reaction to accelerate the reaction (Refer to *Figure 7.1*). A low solution pH favours direct oxidation, while high pH's and high concentrations of organic matter favour the auto-decomposition route (*Hoigne and Bader, 1975*).

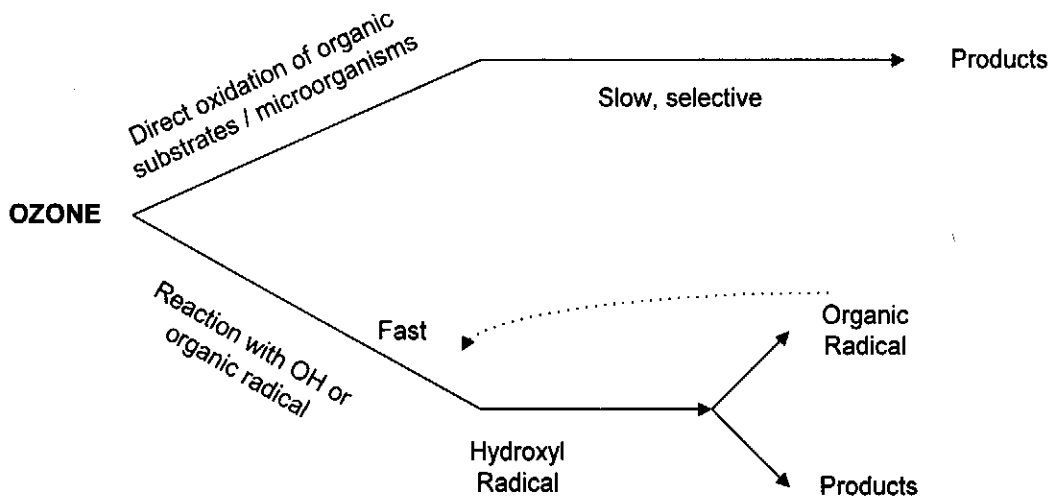


Figure 7.1 Reaction Pathways of Ozone in Wastewater (Adapted from Hoigne and Bader, 1975)

Ozone is thought to decompose as follows (*Ball et al., 1997*):



Ozonation reactions are complicated by the instability of the ozone molecule, hence the kinetics of ozone decomposition play an important role (*Whitlow and Roth, 1988*). In general, the half-life of ozone in water and wastewater decreases with increasing pH and organic content, ranging from less than a minute to several hours (*Yuteri and Gurol, 1987*). Although much research

has been done on ozonation reactions, the actual ozonation kinetics of heterogeneous ozone systems are largely uncertain due to its complexity (*Whitlow and Roth, 1988*). Heterogeneous systems are generally discussed in terms of the enhancement factor E. The E value measures relative rates of chemical reaction to ozone mass transfer, and is thus a function of both the reactivity of the wastewater toward ozone and k_L (*Zhou and Smith, 1997*). However, due to the intrinsic relationship of mass transfer and chemical enhancement, only the lumped mass transfer parameter can be measured for a process (Refer to *Equation 7.9*).

$$Ek_L a = \frac{Q_G H}{V} \ln \frac{C_{G,in}}{C_{G,out}} \quad (7.9)$$

where Q_G = gas flow rate (m^3/s)
 H = Henry's constant
 V = reactor volume (m^3)
 $C_{G,in}$ = concentration of ozone in gas phase (mg/L)

$Ek_L a$ varies according to the concentration of ozone in the off-gas ($C_{G,out}$), which in turn depends on the concentration of utilised ozone. In studies done by *Zhou and Smith (1997)*, it was found that $Ek_L a$ values decrease almost exponentially over the course of ozonation. It may thus, be concluded that the apparent rate of ozone mass transfer is not only a function of gas flow rate, but also depends on the oxidisability of the compounds in the wastewater. Thus, it is invalid to employ a constant mass transfer rate throughout the course of ozonation to predict the efficiency of ozone absorption.

Zhou and Smith (1997, 2000) reached the following conclusions pertaining to the physical and chemical reactions of ozonation of wastewaters:

- The reaction rate of ozone in wastewaters may be assumed to be pseudo-first order.

- The decomposition of ozone in the liquid phase will increase the driving force for ozone mass transfer from the gas phase into the liquid phase.
- Gas flow rate strongly affects surface area for ozone mass transfer, as does the gas diffuser and water type.
- The ozone absorption rate may be substantially enhanced by the occurrence of chemical reactions.
- Ozone absorption is influenced by the liquid film transport, thus making it imperative to include an enhancement factor due to chemical reactions to predict absorption efficiency.

7.2 LITERATURE REVIEW: APPLICATIONS OF OZONATION ON WASTEWATERS

The major advantage of ozone is that it can be applied directly in its gaseous state and thus, does not increase the volume of the wastewater or sludge. Storage and handling problems are also avoided, which are usually associated with conventional oxidants. Furthermore it reacts preferably with refractory substances. Ozone alone and in combination with ultraviolet light, hydrogen peroxide, catalysts, ultrasound or activated carbon has successfully been applied to a myriad of industrial discharges.

Ozone treatment has been found to increase the biodegradability of wastewaters. Ozone was effective for the reduction of colour of pulp mill effluents, but was ineffective in reducing the COD and TOC (*Zhou and Smith, 1997*). Ozonation is also considered one of the most effective methods to decolour textile wastewaters (*Gahr et al., 1994; Lin and Liu, 1994*). For olive wastewaters containing polyphenols, ozone was found to be an appropriate chemical oxidant at very high pH (± 12) (*Beltrán et al., 1998*). In alkaline solutions phenols dissociate to phenolate, which is predestined to electrophilic attack. According to *Langlais et al. (1991)* polyphenols react very rapidly with ozone through aromatic substitution and/or dipolar cycloaddition reactions. *Ball et al. (1997)* found that COD removal after ozonation of high pH wastewater (pH 11), was considerably higher than at pH 7 for textile wastewaters. The influence of pH is the result of the relationship between

oxidation potential and decomposition behaviour of ozone. The oxidation potential ranges from 2.08 volt at low pH's to only 1.4 volt in alkaline solutions (Gahr *et al.* 1994).

Pratt *et al.* (1990) studied the effect of ozone for kraft pulp decolourisation. It was found that a pH of 11 increased the reduction of coloured compounds by $\pm 10\%$ as compared to ozonation at pH 2.18. The effects of ozone concentration and flow rate were considered the principle role players. In this investigation (as with most others) ozone was introduced into the water by a bubble reactor. An 80 % decrease in colour was observed after 8 minutes of ozonation at a concentration of 15 mg/L at flow rate 1.08 L/min. With ozone concentrations of 32.4 mg/L at a flow rate of 2.11 L/min, an 80 % reduction was observed after 3.5 min. It was also observed that an increased COD reduction occurred at higher ozone dosages. Hostachy *et al.* (1997) similarly concluded that COD reduction was directly related to ozone dosage. In their study ozonation was carried out in a glass reactor with a mixing devise, employing ozone-catalyst technology. It was shown that the COD in pulp mill effluents could be reduced by 60% with an efficiency ratio of 1.2/1 (corresponding to an ozone demand of 1.2 kg per kg COD removed). Gahr *et al.* (1994) found that the elimination of 1 g reactive dyes from textile wastewaters required 0.25-0.4 g ozone for a 95% decolourisation and COD reduction of 5-20%.

In a report by Lin and Liu (1994), the COD of the textile wastewater (600-800 mg/L) was not reduced, but rather showed a slight increase. For their experiments, a multi-chamber bubble column reactor was employed. At an initial of pH 8.5 and exposure to 2400 mg ozone over 12 min (170 mg/L ozone concentration at gas flow rate of 1.67 L/min), ozonation proved an excellent means for decolourisation of textile wastewaters, but not for COD reduction.

Zhou and Smith (1997) studied the effects of ozonation on the wastewaters originating from the aerated lagoons of a kraft paper mill using bubble

contactors. For a wastewater volume of 4L at pH 7.62; with an initial COD of 485 mg/L, and colour of 943 TCU the following reductions were observed:

- At 30 mg/L ozone concentration (1-2 L/min) and 40 min retention time in the bubble column, 40% colour reduction, 10 % TOC reduction and 5 % COD reduction were achieved. At these conditions, 1800 mg ozone was required for the elimination of 96 mg COD (5% reduction).
- At 120 mg/L ozone concentration (1-2 L/min) and 40 min retention time in the bubble column, 80% colour reduction, 18 % TOC reduction and 16 % COD reduction were achieved. At these conditions, 7200 mg ozone was required for the elimination of 308 mg COD (16% reduction).

It was thus, concluded that ozonation was most effective for colour removal; that ozone adsorption fell within the fast or instantaneous kinetic regime; and that its rate was controlled by liquid film transport. According to *Zhou and Smith* (1997), "Improving the performance of ozonation should be directed to create gas bubbles as the smallest as practical".

In light of the findings from literature pertaining to ozone characteristics and limitations in view of ozone contacting, it was decided to consider an alternative mass transfer system.

7.3 LITERATURE REVIEW: GAS- LIQUID CONTACTING SYSTEMS

Ozone contacting configurations play a crucial role for maximum ozone utilisation and contact efficiency. For most of the literature studied, the use of bubble columns was most commonly employed, with the result that the mass transfer reaction was observed to be the rate-limiting factor (especially true when the chemical reaction was instantaneous due to hydroxyl radical activity). For efficient removal of organic pollutants by ozonation, the physical and chemical phenomena prevailing during the contact of a polluted liquid stream with a gaseous ozone-air mixture must be optimised.

Zhou and Smith (2000) investigated ozone mass transfer using a 2D laser particle dynamics analyser to measure bubble size distribution by bubble columns. It was found that a decreasing diffuser pore size increased efficient ozone transfer. However, small pore diffusers are easily clogged by particles in the wastewater. In consideration to this problem, it was suggested that venturi injectors be used, however, it was not investigated. According to *Zhou and Smith* (2000) "it is suspected that the advantages of this type of injector may become more significant, although more data on must be collected to confirm this expectation." An investigation into the enhancement of mass transfer due to the occurrence of chemical reactions was quantified. It was found that the rate of ozone adsorption could be shifted from a fast instantaneous regime to a slow one, since readily oxidised compounds are depleted in the later stage of ozonation.

In past studies done by *Zhou and Smith* (1997) into the use of ozone technology for the treatment of pulp mill effluent, the chemical reaction was found to exhibit a fast or instantaneous kinetic regime, and that the rate-limiting step was the mass transfer coefficient ($k_L a$). Most multiphase systems (especially gas-liquid systems) are characterised by the fact that mass transfer rates are limited by the transport of gas to the liquid phase and hence, the overall interfacial area available for mass transfer (*Kleingeld*, 2000).

In view of this, the use of a high intensity impinging stream jet reactor (σ configuration), developed at the Department of Chemical Engineering, University of Stellenbosch, was considered for the transfer of ozone into winery wastewater.

Gas-liquid contactors are compared with one another based on their respective mass transfer coefficients and interfacial areas. The calculation of these mass transfer parameters, however, is not always simple, especially in the case of a chemically enhanced absorption system. *Table 7.1* provides a general impression of the mass transfer coefficients for several conventional reactor types and the σ -jet reactor developed by *Kleingeld* (2000).

Table 7.1 Comparison of Mass Transfer Parameters for known Adsorption Reactors and Impinging Jets (Kleingeld, 2000)

Type of reactor	k_L (cm/s x 100)	a (m ² /m ³ x100)	$k_L a$ (s ⁻¹ x 100)
Packed Columns	0.4 - 6	0.1 - 17	0.04 - 120
Plate Columns	1 - 20	1 - 4	1 - 40
Bubble Columns	1 - 4	0.5 - 6	0.5 - 24
Spray columns	0.7 - 1.5	0.1 - 1	0.07 - 1.5
Venturi	5 - 10	1.6 - 2.5	8 - 25
Impinging Jets	3 - 6.6	0.9 - 20.5	2.5 - 95
σ -Jet Reactor	25 - 30	26 - 69	500 - 2500

From *Table 7.1* it is evident that the σ -jet reactor has a significantly higher $k_L a$. The impinging jets represent pilot scale reactors, and do not have the same configuration as the σ -jet reactor. Although the researchers of these reactors reported lower $k_L a$ values than that reported for the σ -jet reactor, it is nevertheless considerably higher than reports for other contacting systems. Thus, even on larger scale, the technology of impinging jets offer higher mass transfer rates. It should be noted, however, that these values serve only to illustrate the difference between configuration types, and are subject to high variation depending on the wastewater type and its behaviour towards the gas mixture.

It must be noted that a multitude of design parameters exist to explain mass transfer in gas-liquid contacting systems. Although not in the scope of this project, it was thought worthy to mention certain important design parameters:

- **Bubble Size:** Apart from bubbles being formed at an orifice or sparger, it can, however, generally be said that a balance between the rates of bubble break-up and coalescence determines the bubble size (distribution).
- **Interfacial Area:** Gas-liquid interfacial area plays an important role in the mass transfer rate, as can be seen from the expression for the

volumetric mass transfer coefficient, $k_L a$, the so-called drive force behind mass transfer.

- Gas-hold Up: Gas hold-up is a very important parameter characterising the hydrodynamics of a reactor and is mainly determined by the gas velocity, power input and physical properties of the liquid.
- Mass Transfer Coefficient: Since most gas-liquid contacting systems are characterised by the fact that mass transfer rates are limited by the transport of gas to the liquid, extensive literature on mass transfer, and prediction thereof by means of empirical correlations, exist.
- Volumetric Mass Transfer Coefficient: Correlations for the volumetric mass transfer coefficient ($k_L a$) are obtained by the product of the interfacial area and mass transfer coefficients.

A survey on the fundamentals of bubble columns and impinging stream (high-intensity contacting process) technology are presented with consideration to the enhancement of ozone mass transfer.

7.3.1 Bubble Columns

The features of bubble columns are (Lee and Tsui, 1999):

- Low to moderate mixing intensity
- Mixing is caused by the gas
- Large liquid hold-up
- Long liquid residence time
- Gas is considered to move in plug flow
- Variable extent of backmixing

A disadvantage of this configuration is that the gas-liquid interfacial area decreases if the ratio of column height to diameter exceeds 12, due to bubble coalescence (Lee and Tsui, 1999).

7.3.2 *Impinging Stream Technology*

The intensification of transfer processes in an impinging system may be attributed to (Kleingeld, 2000):

- An increase in the relative velocity between the penetrating particles and the opposed gas stream.
- An increase in the mean residence time of the particle in the system due to penetration and circulation in the opposing stream (translating into a decrease in the geometrical size of the system).
- An increase in shear forces between the two phases, resulting in a break up of bubbles and an increase in the interfacial area. Surface rejuvenation rates are also accelerated, resulting in higher mass transfer rates.
- Pressure pulsations and intense radial and axial velocity components in turbulent flow due to the collision of the opposing streams.

For these reasons the use of impinging jets for more efficient mass transfer of ozone into winery wastewater was considered. The reactor investigated was the so-called σ -shaped reactor, so called due to the fact that the design resembled four overlapping σ symbols; each rotated 90 degrees relative to one another. This design has two impingement zones, which allows more effective promotion and prolongation of turbulence. Due to the swirling motion of the liquid under the influence of centrifugal acceleration, this reactor produces high $k_L a$ values (Kleingeld, 2000). *Figure 7.2* illustrates the configuration of the σ -reactor.

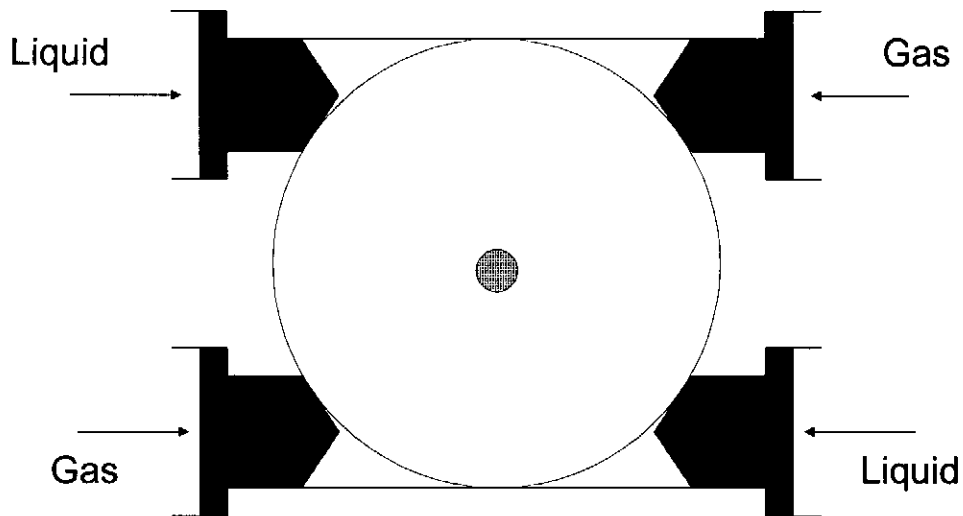


Figure 7.2 σ -Shaped Jet Reactor

The reactor is characterised by a small reactor volume (volume = 20 ml) supplied with nozzles, directed toward each other. The gas-liquid feed streams are jetted through the nozzles into the reactor volume, resulting in a highly turbulent mixture of phases. Under these conditions, mass transfer rates are improved dramatically (Kleingeld, 2000).

The reactor incorporates four impinging streams (two gas and two liquid nozzles). For gas injection, *Spraying Systems* TX-2 nozzles were used, while liquid injection was via *Spraying Systems* TG-1 nozzles. Only stainless steel nozzles were used due to their ability to withstand ozone. Ozone is highly aggressive, thus all rubber, plastics, neoprene and aluminium are unacceptable materials for use with ozone. The only acceptable materials are stainless steel, Hypalon, Teflon, silicone and concrete (Crawford and Cline, 1990).

The angle of impingement between ozone and wastewater streams is an important design consideration: each liquid spray must be directed slightly towards an opposing gas nozzle so as to shear off gas bubbles as they exit the nozzle, before colliding with another liquid stream or the reactor wall. The design strategy not only made provision for the shearing off of gas bubbles from their corresponding nozzles, but also for the head-on impingement of the

resulting two-phase streams. The circular reactor chamber also sustains efficient turbulence.

7.4 INVESTIGATION INTO THE USE OF OZONE FOR THE TREATMENT OF WINERY WASTEWATER

Although a considerable amount of research has been conducted on ozonation for the treatment of wastewater from several industries (paper mills, tanneries, textile plants and municipal wastewaters), research on winery wastewater has not been conducted to date. According to *Oeller and Weinberger (1997)* "Wastewater composition in terms of COD, DOC, pH's etc. is insufficient as a criterion for prognosis of the optimum conditions of ozone or other combined treatments. Since the optimum operating conditions which have been determined for a certain effluent are not transferable to another wastewater, systematic laboratory tests have to be conducted with a view to meeting the envisaged target values in each case". It was thus, aimed to determine the ozonation potential of winery wastewater while simultaneously investigating the optimum conditions as well as the influence of improved mass transfer as offered by the jet reactor.

The following section illustrates the experimental set-up and procedures that were followed. A preliminary investigation was conducted to ascertain the effect of ozone on winery wastewater using bubble columns. Further experimentation was conducted by use of impinging streams to determine the effect of an increased mass transfer coefficient on the reduction of COD and turbidity.

7.4.1 Ozonation via Bubble Columns

7.4.1.1 Experimental Set-up and Procedure

For the determination of the effect of ozone on winery wastewater, ozone was fed to two bubble columns in series. *Figure 7. 3* illustrates this set-up. Oxygen was fed to the ozonator for the generation of ozone by corona

discharge. The oxygen-air mixture was measured to contain ozone at 9 mg/L. The ozone production of the ozonator was determined by the standard potassium iodide (KI) procedure. The glass columns had a height of 24 cm and a diameter of 4.5 cm. The ozone was introduced into the wastewater by means of a sintered glass diffuser (17 mm diameter). The oxygen-ozone mixture was fed to the bubble columns at a flow rate of 2 L/min. The gas mixture was fed to the first bubble column, and then passed on to the second bubble column. The off-gas was discharged to the fume-hood.

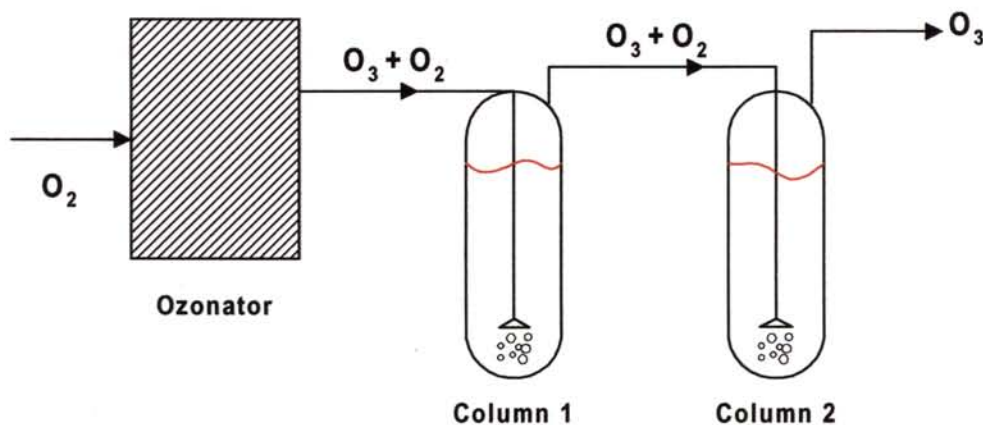


Figure 7.3 Bubble Column Experimental Set-Up

The experimental conditions are illustrated in *Table 7.2*.

Table 7.2 Operating Conditions for Bubble Columns

Parameter	Value
Ozone Concentration in Inlet [mg/L]	9
Gas Flow Rate [L/min]	2
Gas Inlet Pressure [kPa]	10
Wastewater Volume in each Column [mL]	250

The wastewater used in these experiments originated from Rupert and Rothschild Vignerons; the properties of the wastewater are illustrated in *Table 7.3*. It should be noted that this wastewater originated predominantly from red

winemaking since Rupert and Rothschild Vignerons produce white and red wine in a ratio of 1:6. After collection the wastewater was stored at 4°C prior to experimentation.

Table 7.3 Properties of Wastewater from Rupert and Rothschild Cellar used for Ozonation via Bubble Columns

Property	Value Range
Conductivity [mS/m]	120-170
COD [mg/L]	2500-4000
SS [mg/L]	280-380
DOC [mg/L]	850-950
Turbidity [NTU]	50-280

The wastewater was filtered through a 3.55 µm filter to remove suspended particles. A volume of 250 ml wastewater was added to each bubble column. The ozone was allowed to react with the wastewater for 30 min. All data was measured after 30 min ozonation at 2 L/min gas flow rate. Irrespective of the initial pH of the wastewater, the pH was adjusted to 7 and 10.5, respectively.

7.4.1.2 Results and Discussion of Bubble Column Experiments

The results obtained concerning the COD and turbidity removal are illustrated in *Figures 7.4* and *7.5*. From these results it is clear that the pH has a marked influence on the reduction of COD and turbidity. Considering the results obtained from the 1st column, at pH 10.5, the COD was reduced by 38 % and the turbidity by 99.9 %. The un-reacted ozone passed from the 1st column to the 2nd column, reducing the original COD value by 21 %, and the turbidity by 99.9 %. During the experiments, it was observed that the colour of the wastewater changed from highly turbid to transparent after 5-7 min of ozonation under illustrated conditions. Although not sampled after 5 min, it was postulated that a high reduction in turbidity (>90%) had occurred within 5-7 min of reaction time.

At pH 7, the reduction in COD was observed to be 15% in the 1st column, and 6 % in the 2nd column. The reduction in turbidity was measured at 99 % and 98 % respectively in the two columns. The temperature escalated from \pm 6-17 °C after 30 min ozonation for reactions at pH 10.5, while at pH 7 the reaction temperatures were observed to escalate from \pm 6-11 °C, indicating that a higher degree of oxidation took place at pH 10.5.

Figure 7.6 is a digital presentation of the winery wastewater before treatment, after pH addition to 10.5, and after 30 min of ozonation.

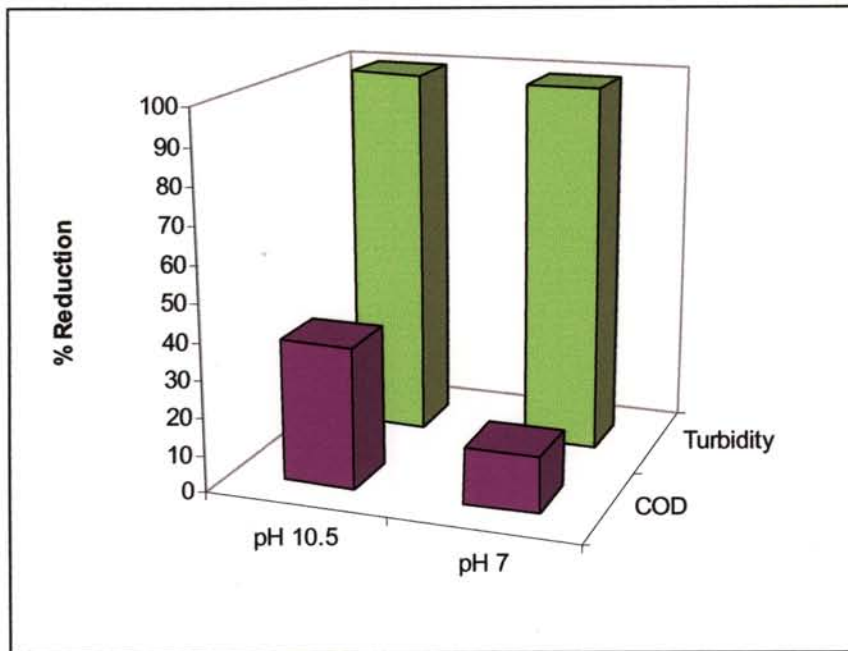


Figure 7.4 COD and Turbidity Decrease in Bubble Column 1 at pH 7 and 10.5

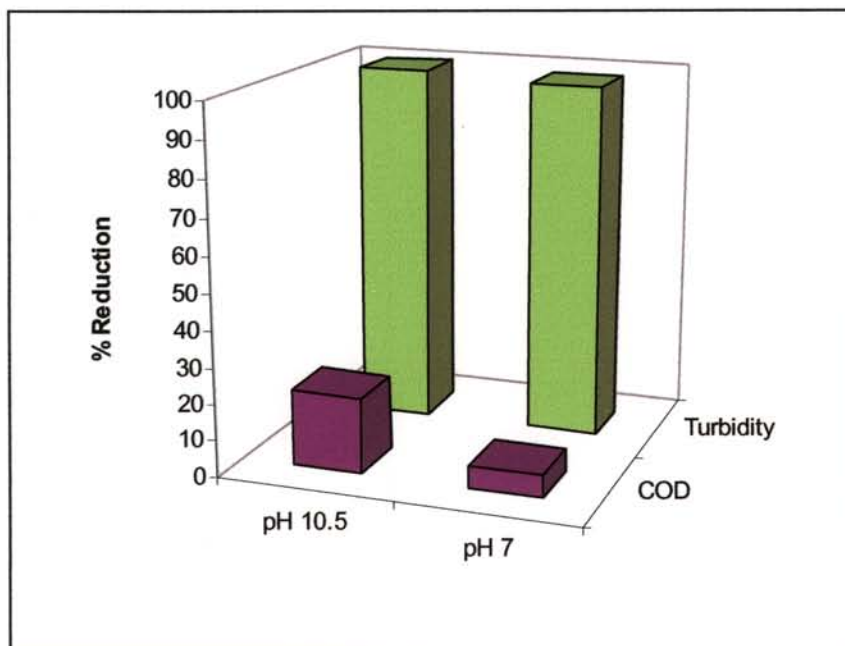


Figure 7.5 COD and Turbidity Decrease in Column 2 at pH 7 and 10.5

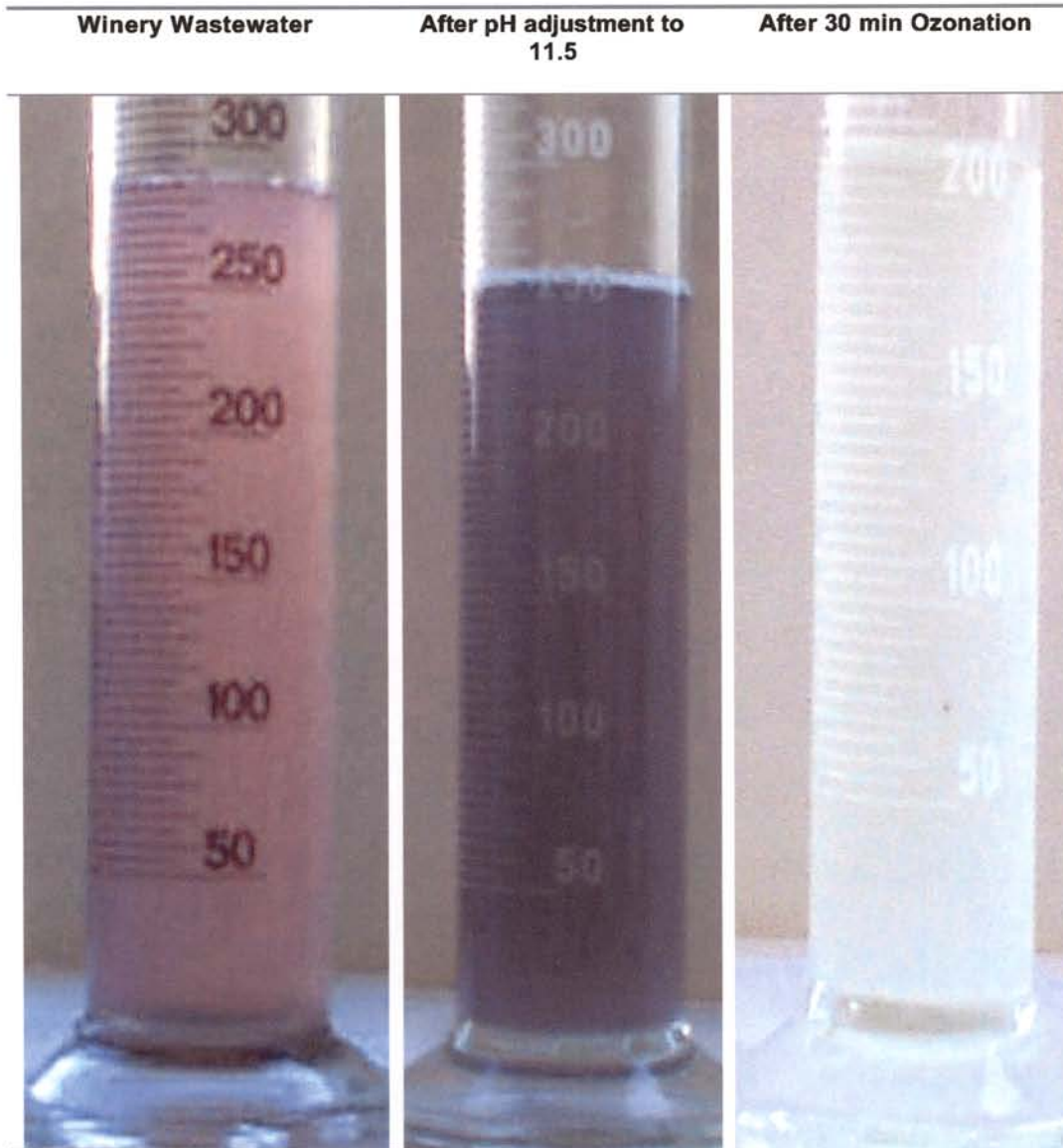


Figure 7.6 Digital Photographs of Wastewater Before and After Ozonation in a Bubble Column

It may thus, be concluded that at pH 10.5, the oxidation of organic compounds is faster than at pH 7. This indicates a higher reaction rate and lower degree of selectivity, indicating the presence of hydroxyl radicals at pH 10.5. Simultaneously, it demonstrates that certain organic compounds are more easily oxidised in alkaline conditions (particularly true of phenolic compounds). Similar findings concerning an alkaline pH and the COD removal efficiency from pulp and paper mill wastewater were reported by *Hostachy et al.* (1997). Ozonation decreased the pH for both investigated conditions. *Figure 7.7* illustrates the typical pH decreases observed. With reference to the odour; complete odour elimination was observed for all the ozonated samples.

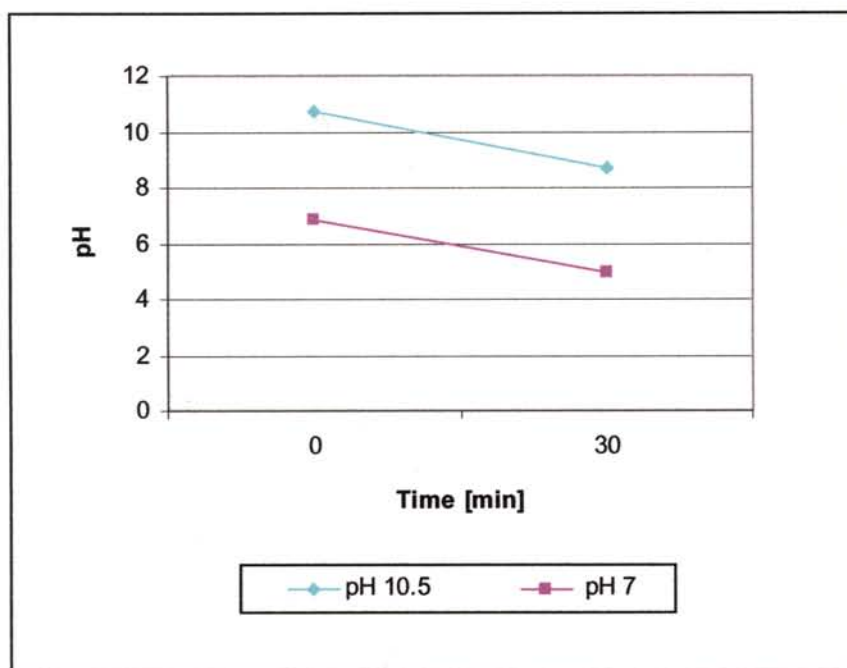


Figure 7.7 Typical pH Decreases Observed in Bubble Columns

For experiments conducted at pH 10.5, typical COD removals of 38% were achieved; the elimination of 800 mg COD required 540 mg ozone (ratio of 1 g COD/ 0.68 g O₃). This demonstrates an excellent case for ozone treatment of winery wastewaters when compared to the elimination ratios obtained for other wastewater types. In comparison, at pH 7 the elimination of 400 mg COD required 540 mg ozone (ratio of 1 g COD/ 1.35 g O₃).

7.4.2 Ozonation via Jet Reactor

7.4.2.1 Experimental Conditions and Set-Up

Similar to the experimentation with the bubble columns, oxygen was used as the feed gas to the ozonator. The oxygen-air mixture was introduced into the reactor via 10 mm silicone tubes, containing 9 mg/L ozone. The oxygen-ozone mixture was fed to the reactor at a flow rate of 5 L/min. The wastewater was contained in a drum and fed to the reactor via a centrifugal pump. The wastewater was introduced into the reactor via nozzles on opposing sides of the reactor as discussed in *Section 7.3.2*. The hydraulic residence time in the reactor at a liquid flow rate of 1.52-1.64 L/min was 0.73-0.78 s. *Figure 7.8* illustrates the experimental set-up. The following operational parameters were kept constant during the experimental runs:

- The gas and liquid pressures at the inlet to the reactor
- The gas and liquid flow rates

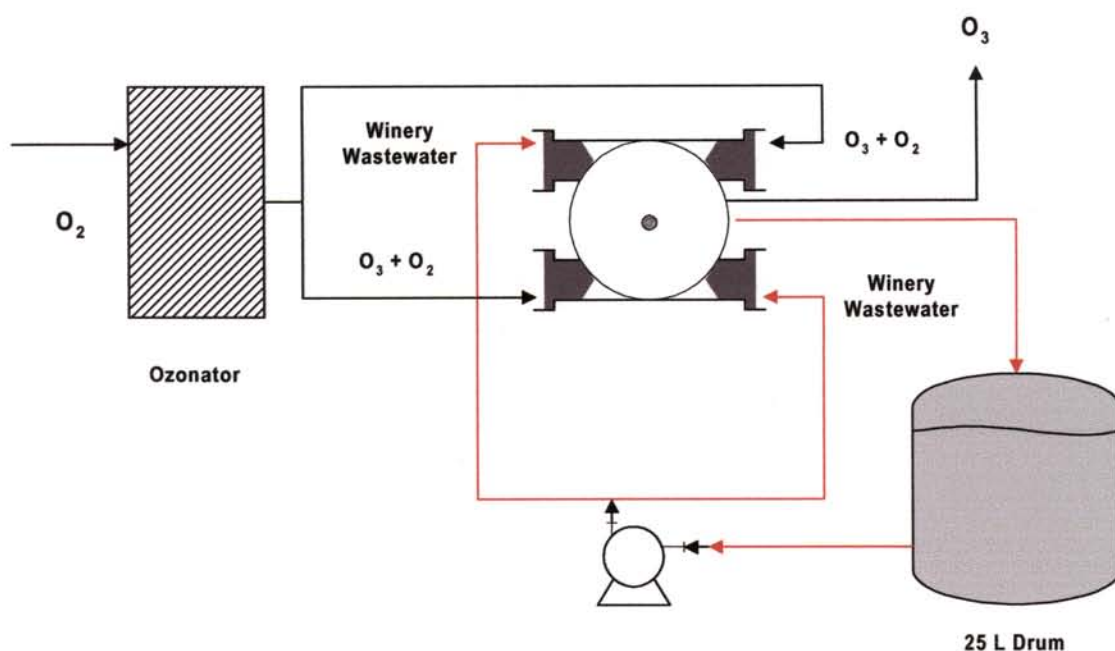


Figure 7.8 σ -Jet Reactor Experimental Set-up

The experimental conditions at which the runs were conducted are defined in Table 7.4.

Table 7.4 Jet Reactor Operating Conditions

Parameter	Value
Ozone Concentration [mg/L]	9
Gas Flow Rate [L/min]	5
Gas Inlet Pressure [kPa]	90-100
Liquid Flow Rate [L/min]	1.52-1.64
Liquid Inlet Pressure [PSIG]	60-70
Wastewater Volume [L]	23-24

Sampling of the wastewater exiting the reactor was done at consistent time intervals (15, 30, 60 min, etc.). These time intervals correspond to the time taken for ± 23 L of wastewater to pass through the reactor at ± 1.58 L/min. The corresponding amount of ozone charged to the reactor over time is illustrated in Figure 7.9. Thus, after one complete pass, 0.675 g ozone is charged, i.e:

15 min = 0.675 g ozone charged = 1 pass

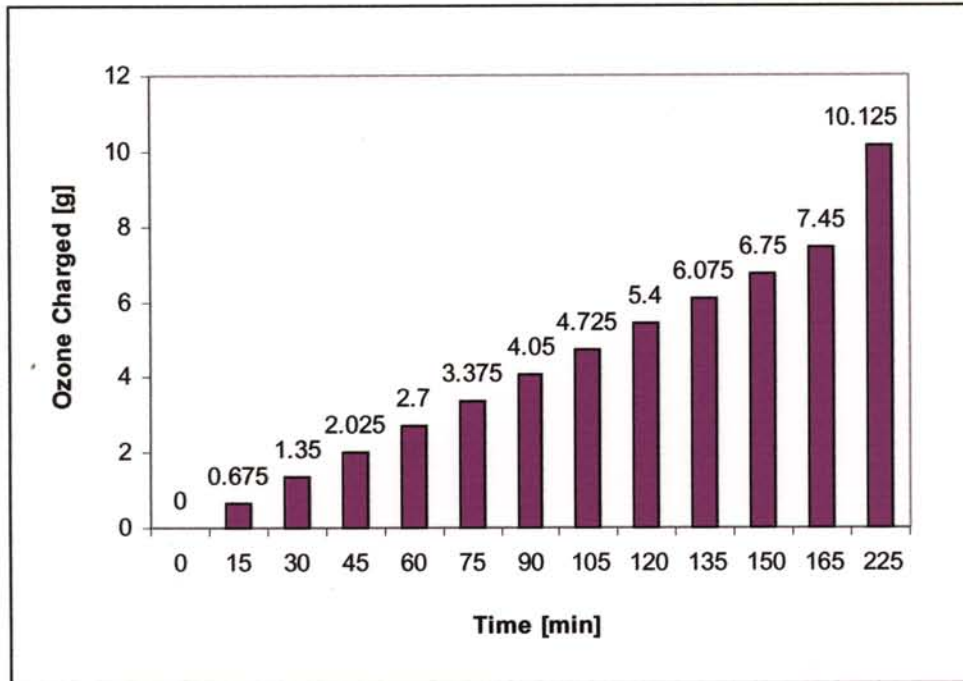


Figure 7.9 Ozone Charged [g] into Jet Reactor with Evolution of Time (Gas Flow Rate 5 L/min, ozone concentration 9 mg/L)

Contaminant reductions are plotted against the total amount of ozone charged to the reactor, thereby directly illustrating ozone utilisation.

The temperature of the wastewater exiting the reactor was measured by a thermometer. Since the reactor was viewed as a perfectly mixed tank reactor, the temperature in the reactor was assumed to be equal to the temperature of the exiting stream.

For the investigation of the effect of ozonation via the σ -shaped jet reactor, the pH of the wastewater collected from Rupert and Rothschild Vignerons was adjusted to 4.5, 7.5, 10.5 and 11.5. Owing to the large property variance of winery wastewater, all the wastewater used for the experiments fell within the property ranges illustrated in *Table 7.5*.

Table 7.5 Properties of Wastewater from Rupert and Rothschild Cellar used for Ozonation

Property	Value Range
Conductivity [mS/m]	120-190
COD [mg/L]	2000-4500
SS [mg/L]	200-380
DOC [mg/L]	800-1050
Turbidity [NTU]	150-450

Since the wastewater produced at Rupert and Rothschild Vignerons originates principally from red wine production, wastewater from a cellar producing only white wine was collected and ozonated to determine whether a difference in the rate of oxidation existed. The characteristics of the wastewater are portrayed in *Table 7.6*. Prior to ozonation, all wastewater samples were filtered through a 3.55 µm filter to remove large particles.

Table 7.6 Properties of Wastewater Originating from a White Wine Producing Cellar

Property	Value Range
Conductivity [mS/m]	120-170
COD [mg/L]	2000-2500
DOC [mg/L]	400-500
Turbidity [NTU]	100-150

7.4.2.2 Ozonation Influence on the pH

Figure 7.10 and 7.11 illustrate the typical effect of ozonation on the adjusted pH's over two time periods (0-60 min; 0-225 min) for various experimental runs. The pH of the wastewater decreased upon ozonation for wastewater for experiments with initial pH's above 7.5, but little to no decrease was observed for wastewaters with an initial pH of 4.5. In general, the pH decrease was not as substantial as observed for the reactions in the bubble column experiments, indicating a lower rate of oxidation. At pH's above 7.5, a more substantial decrease was observed. Over a period of 225 min, the pH generally continued to decrease. However, a marked decrease was observed after 15 min (i.e. after one pass). Owing to the fact that not all wastewater samples were identical in component concentration, some runs exhibited slight deviations.

The effect of the ozonation on the pH was considered to indicate that a higher degree of oxidation had taken place at high pH's, and that most of the oxidation had occurred after the 1st pass through the reactor (0.675 g ozone charge).

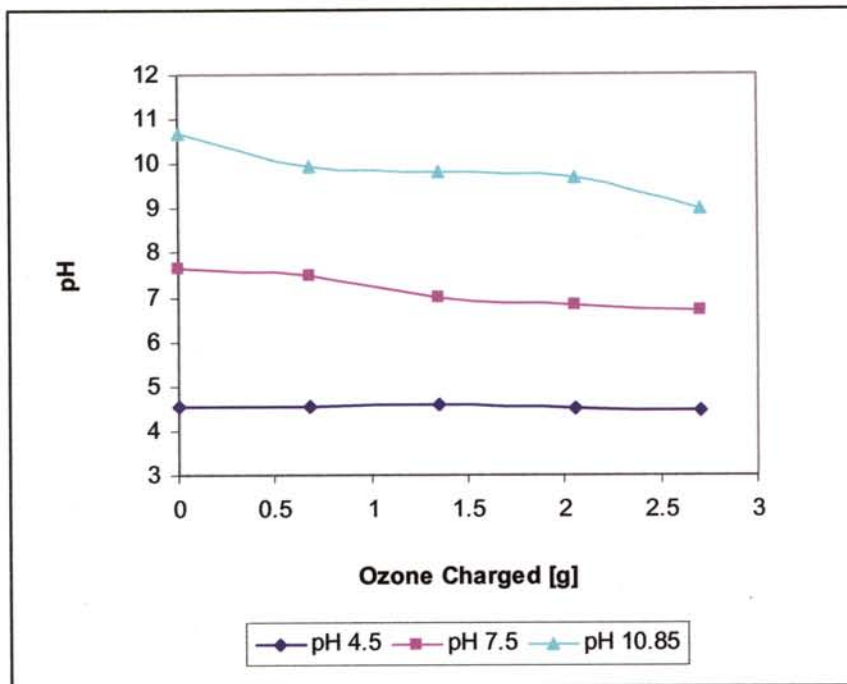


Figure 7.10 Effect of Ozonation on the pH of the Wastewater (0-60 min)

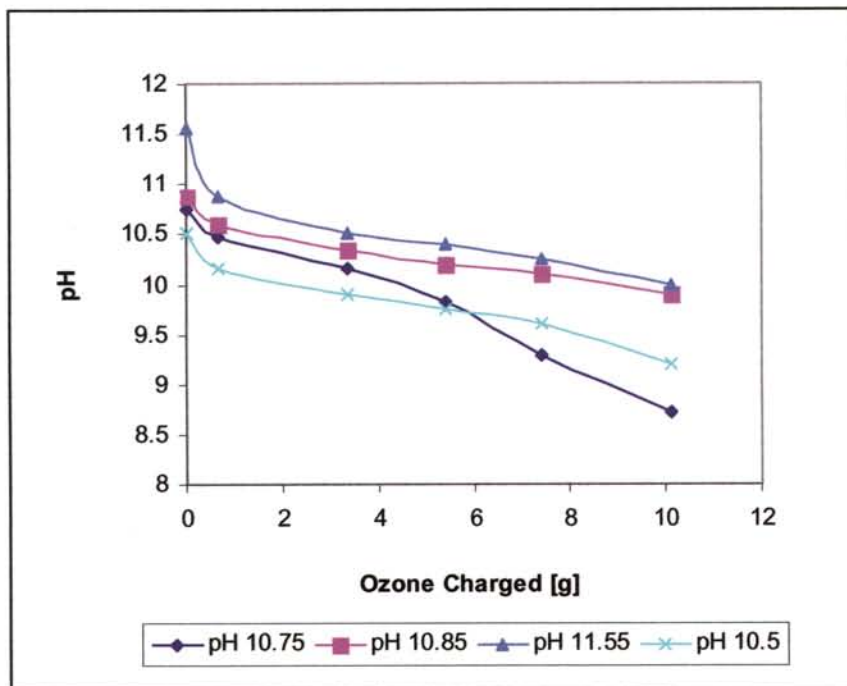


Figure 7.11 Effect of Ozonation on pH (0-225 min)

7.4.2.3 Ozonation Influence on the COD

With regard to the COD of the wastewater, no significant reductions are observed at pH's of 7.5 and below. Instead, the COD was frequently seen to increase after ozonation at these pH's. It is hypothesised that high molecular weight colour compounds decomposed to generate many small molecules such as aldehydes and simple organic acids. Hence, the COD decrease of the colour compounds was compensated by a COD increase of the generated products. Similar findings were reported by *Lin* and *Liu* (1994). Ideally, the wastewater should be analysed to verify the hypothesis.

For wastewaters at pH 7.5, more frequent occurrences of COD increase were observed. This may be explained in that a higher reduction in turbidity took place at pH 7.5 in comparison to pH 4.5; thus increasing the concentration of small molecules (Refer to *Figure 7.16*).

At low pH, oxidation reactions by ozone are considered to follow a slow kinetic regime, which is highly selective towards compounds (*Hoigne* and *Bader*, 1975). It was thus concluded that the oxidation reaction was slow and selective and concurrent with a short residence time, and further oxidation of the generated compounds did not take place. At pH's of 10.5 and above, this trend was less frequently observed, owing to the fact that the high pH's induced hydroxyl radical formation and subsequent fast, non-selective oxidation of generated compounds took place. *Figure 7.12* illustrates typical results pertaining to COD concentrations for the period of 0-60 min.

To investigate the effect of prolonged ozonation (± 15 passes through the reactor), wastewater samples at pH 10.5 and above were employed. Continued COD reductions were observed, however, the COD decrease became exponentially less over time (Refer to *Figure 7.13*). This indicated that the reactivity of the compounds in the wastewater decreased with time; the presence of highly reactive compounds diminished. It must also be

considered that a shift in the reaction pathway from hydroxyl radical formation to direct ozonation may occur with a decreasing pH; thus decreasing the oxidation rate of the compounds in the wastewater.

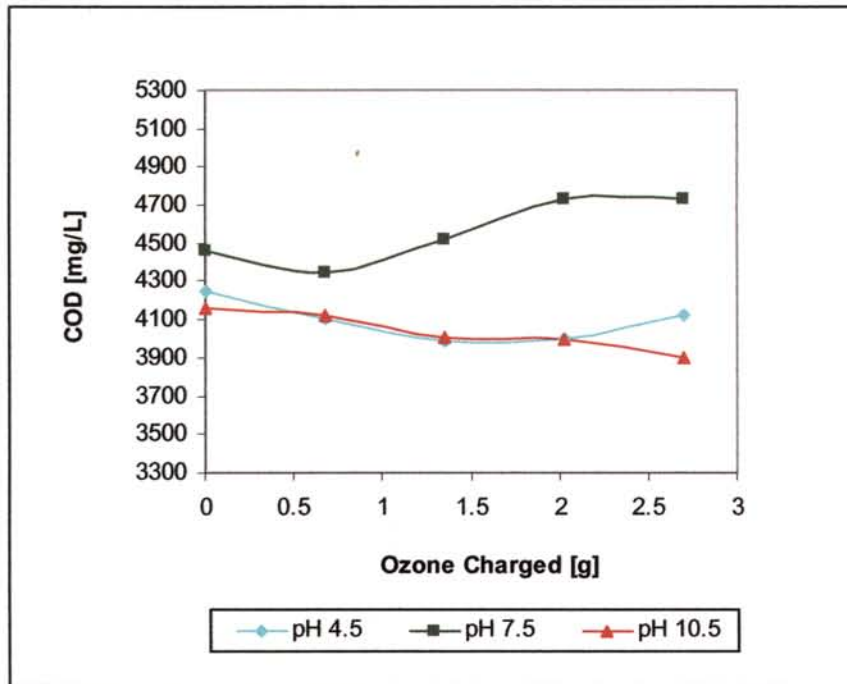


Figure 7.12 Effect of Ozonation on COD (0-60 min)

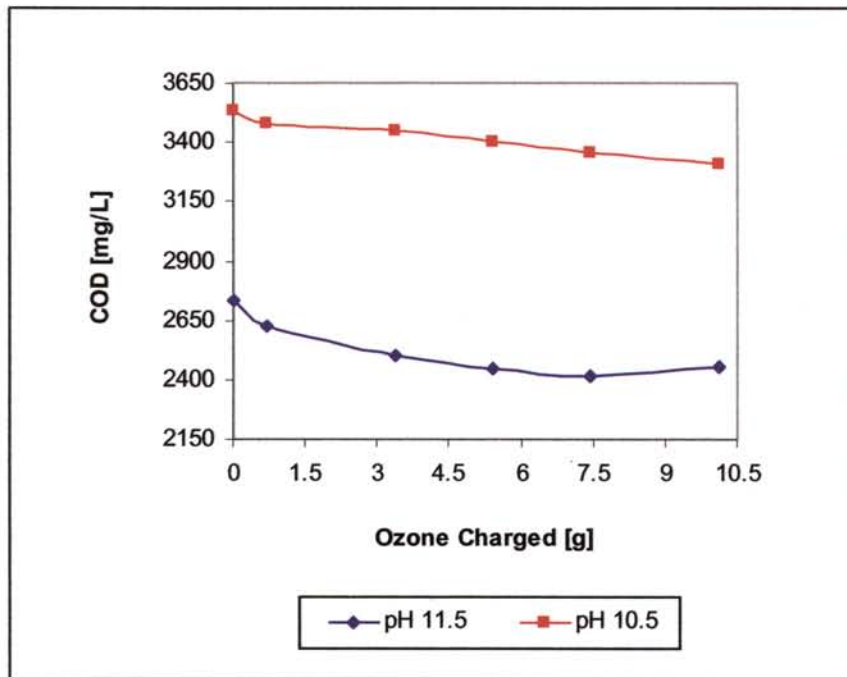


Figure 7.13 Effect of Ozonation on COD at High pH's (0-225 min)

7.4.2.4 Ozonation Influence on the DOC

DOC concentrations remained largely unchanged during ozonation at pH's of 7.5 and below. However, at pH 7.5, the DOC was seen to increase slightly. These results were consistent with the increase in COD, thus confirming that an increase in dissolved organic compounds (e.g. aldehydes and organic acids) had occurred (Refer to *Figure 7.14*).

Also consistent with the discussion on the COD concentrations, the DOC did not increase at high pH values (Refer to *Figure 7.15*). The most significant decrease was observed after the 1st pass, once again indicating that the most reactive dissolved organic compounds were oxidised instantaneously.

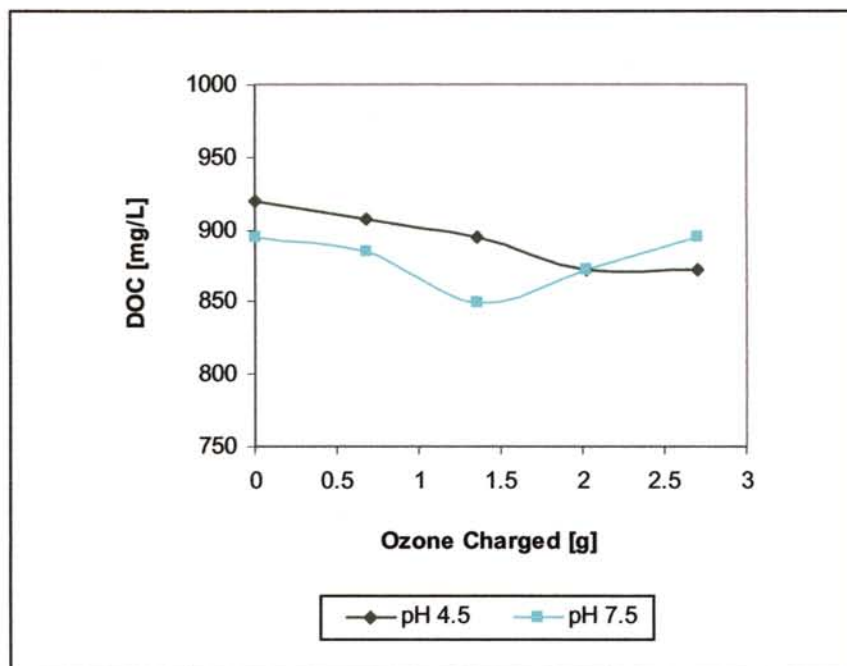


Figure 7.14 Effect of Ozonation on DOC at pH's 7.5 and 4.5

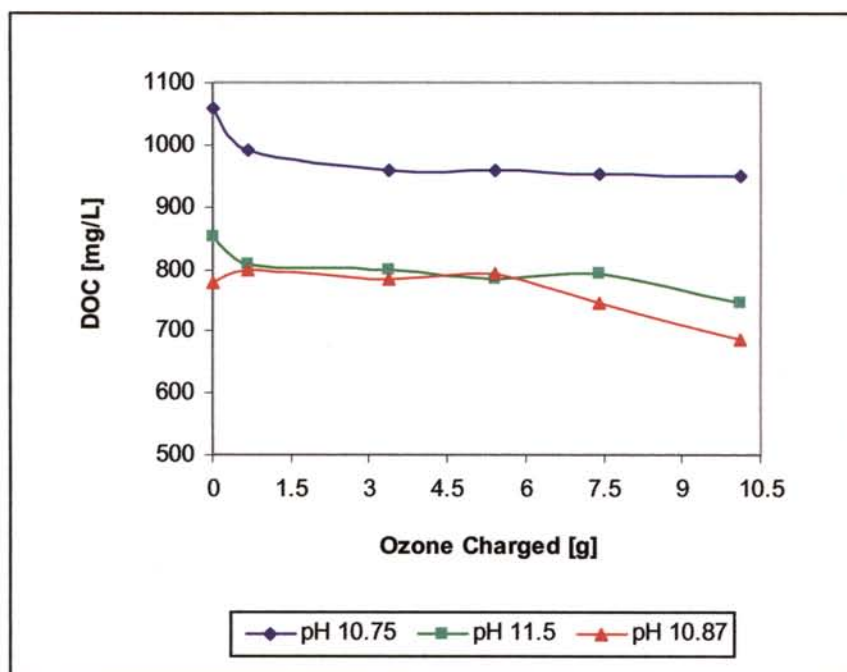


Figure 7.15 Effect of Ozonation on DOC at High pH's Over Extended Time

7.4.2.5 Ozonation Influence on Turbidity

In contrast to COD, significant turbidity reductions were observed at pH values of 7.5, 10.5 and 11.5 (Refer to *Figures 7.16* and *7.17*). The turbidity was, however, not significantly reduced at pH 4.5. It may thus, be concluded that pH is less critical for turbidity reduction in comparison to COD removal, however, increased turbidity reductions did occur at higher pH values.

As depicted in *Figures 7.16* and *7.17*, the largest reduction gradient was observed during the 1st pass. Further reductions were observed to plateau after 30 min (1.35 g ozone charged) for wastewater at pH 7.5, and at 105 min for wastewater at pH 10.5 and 11.5. From these observations the following conclusions were made:

- i. Colour and other compounds imparting turbidity may be divided into easily degradable and less degradable compounds (refractory colour compounds).
- ii. Easily degradable compounds are oxidised instantaneously, while refractory compounds require increased exposure to ozone (i.e. longer residence time).
- iii. "Instantaneous" oxidation at high pH's is a relative term, since even at high pH's the chemical reaction may require prolonged ozone contact.

The decreasing ozonation efficiency could be attributed to a lowered pH, and thus constant pH regulation should be considered to rule out the shift towards selective, slow oxidation.

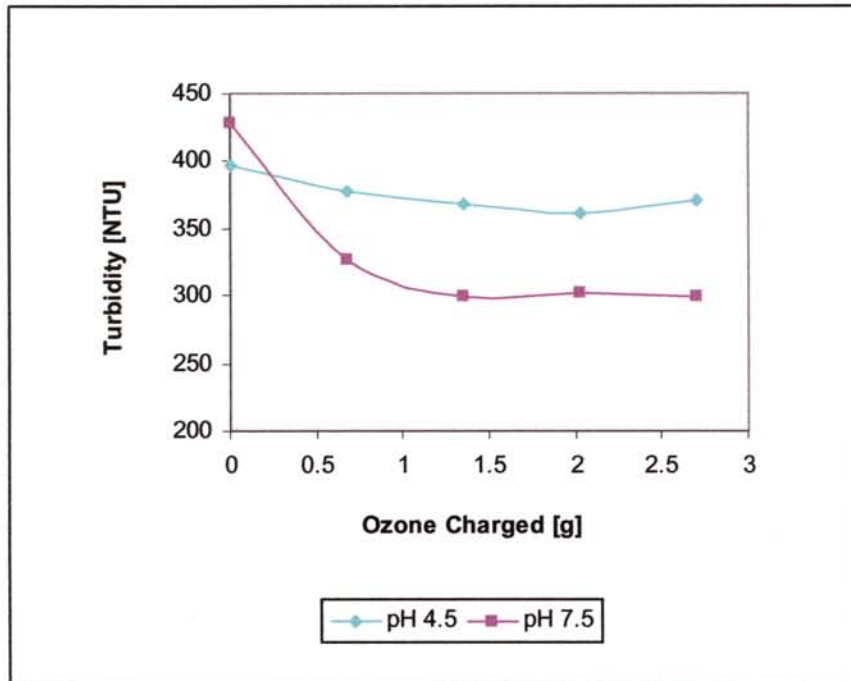


Figure 7.16 Effect of Ozonation on Turbidity at pH 4.5 and 7.5

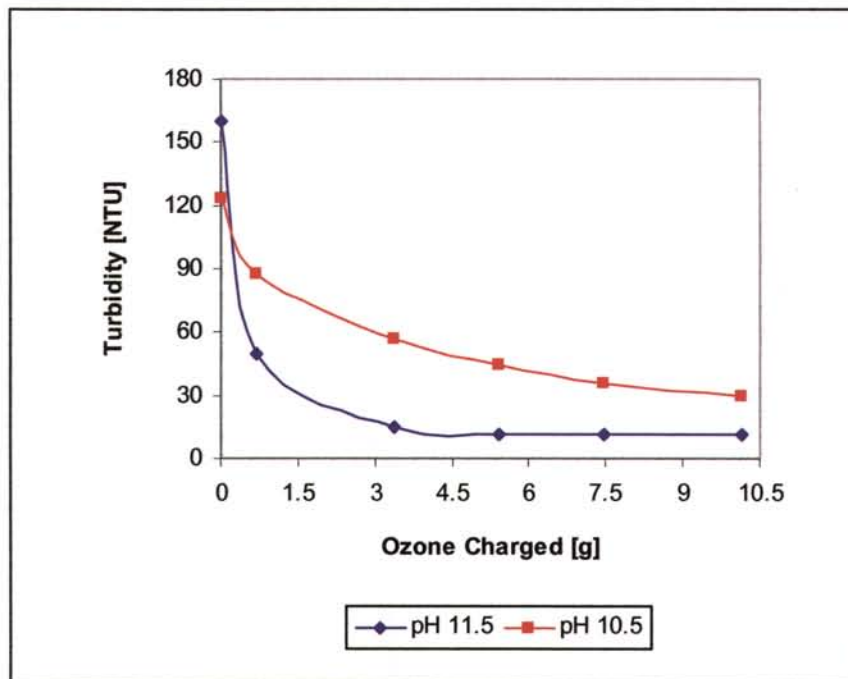


Figure 7.17 Effect of Ozonation on High pH Wastewater Over Extended Time

The trends in turbidity reduction at pH 4.5, 7.5 and 11.5 are illustrated in *Figure 7.18*. Typically a reduction in the order of 85 % was achieved for alkaline wastewaters. For neutral wastewaters, $\pm 30\%$ reductions were observed, while at low pH's (pH 4.5), only a 6.5 % improvement was observed. From this *Figure 7.18* it is clear that high pH's improve turbidity reduction.

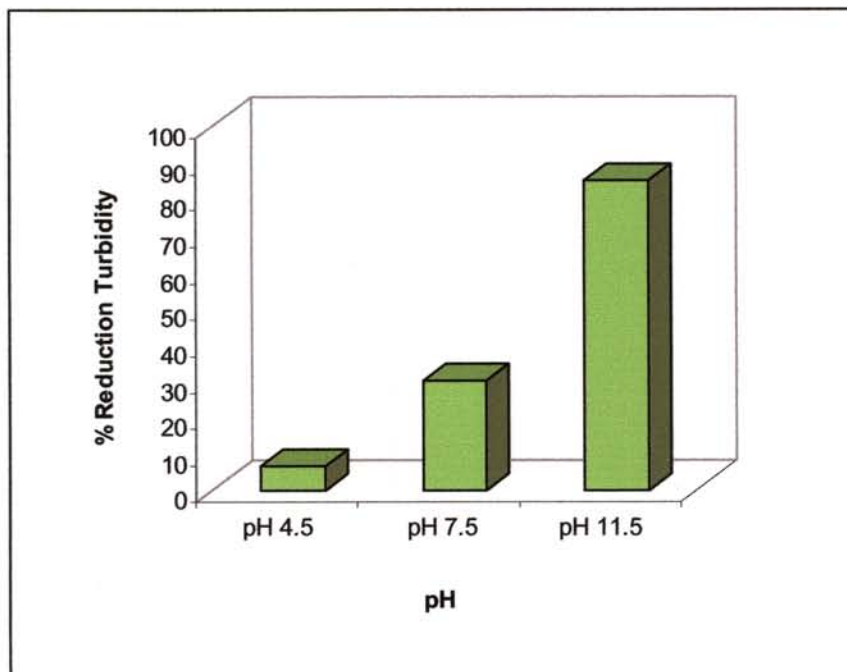


Figure 7.18 Typical Turbidity Reduction in Wastewaters Ozonated at Low, Neutral and High pH's

7.4.2.6 Ozonation Effects at pH 11.5

Figures 7.19-7.21 illustrate the effect of ozonation on the COD, turbidity and temperature of a wastewater sample at pH 11.5.

COD

A COD reduction of 8.5 % was observed over a 60 min period (4 % of which had been reduced after 15 min). After 225 min the total COD reduction was 10.8%.

As illustrated by *Figure 7.19*, the highest gradient of degradation occurred at the initial stage of ozonation (1st pass through the reactor). This was attributed to the presence of highly reactive organics. The oxidation of organics declined progressively up to a total of 7.5 g ozone charged (11 passes through the reactor). It was thus, concluded that COD reduction becomes dependent on the susceptibility of the organics to degradation with time. Thus, the mass transfer coefficient no longer plays the dominant role, but rather the rate of the chemical reaction in the liquid phase.

A resultant COD elimination of 5800 mg COD per 2700 mg ozone fed was observed (1 g COD_e/ 0.46 g O₃). This was considerably higher than ratios reported by other researchers (Refer to *Section 7.1.2*). It could be argued that winery wastewater is more susceptible to ozonation than tannery or paper mill wastewaters, however, the ratio COD removal to the corresponding ozone feed to the system as seen in the σ -reactor, was also higher than the ratio obtained in the bubble columns (1 g COD_e/ 0.68 g O₃).

It is thus, concluded that due to an increased mass transfer coefficient in the σ -jet reactor, more ozone is fed to the wastewater, and subsequently a higher concentration of COD is reduced for the amount of ozone charged. The physical transfer of ozone in the jet reactor thus, occurs at a fast enough rate to supply ozone for fast/instantaneous chemical reactions in the liquid.

Béltran et al. (1999) also found that at an elevated pH, certain compounds present in olive originating wastewater were oxidised instantaneously by hydroxyl radicals. However, during the presence of highly reactive

compounds such as polyphenols, the rate-limiting factor was the amount of ozone transferred into the wastewater. This is attributed to a poor mass transfer coefficient exhibited by the contactor (bubble column). As a consequence, higher amounts of ozone were charged to increase the mass transfer across the boundary layer, rendering the process unfeasible.

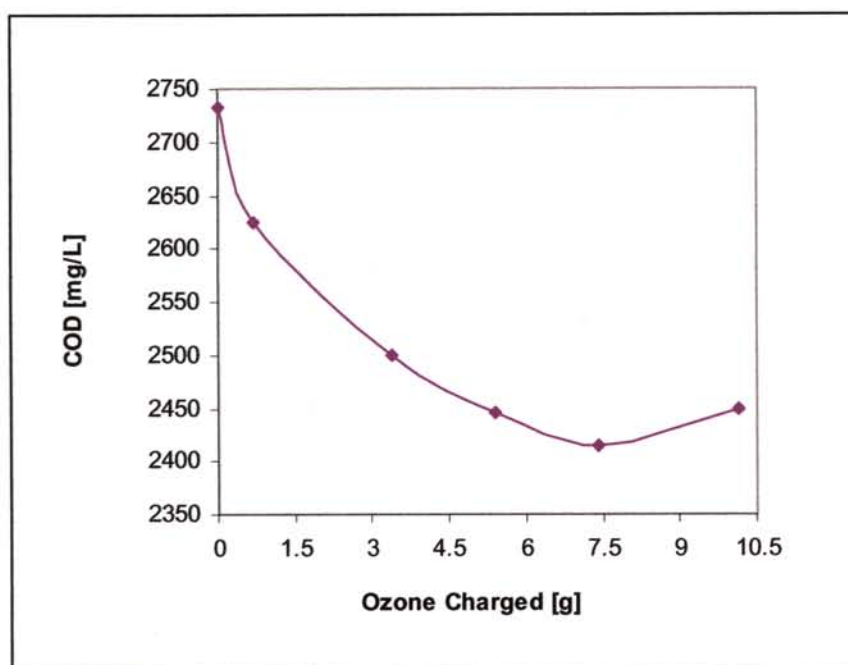


Figure 7.19 COD Reduction Observed for Wastewater at pH 11.5

Turbidity

A similar oxidation pattern was observed for the turbidity reduction (See *Figure 7.20*). Compounds influencing colour and turbidity (anthocyanins, tannins, polyphenolics) may also be grouped according to greater or lesser ease of degradation with reference to ozone. Upon investigation of the bleaching waters of paper mills, *Pratt et al.* (1990), also observed two categories of colour compounds. However, in contrast to organic compounds responsible for the COD, the colour compounds reach a plateau sooner. A sharp initial decline in turbidity occurs during the 1st pass and is further decreased in the 2nd pass, however, at a slower rate. It was concluded that compounds, which impart turbidity are generally more susceptible to

ozonation than organic compounds. However, as with organic compounds, less refractive colour compounds require an extended ozone contact time.

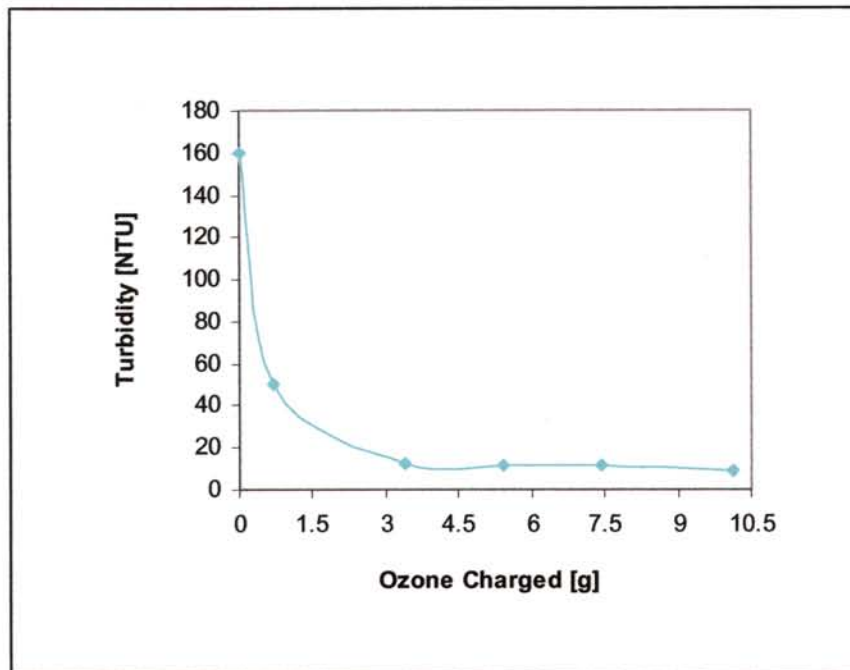


Figure 7.20 Rate of Turbidity Reduction Observed for Wastewater at pH 11.5

The temperature of the wastewater was seen to rise steadily, principally due to the energy dissipation of the ozonation reactions (Refer to *Figure 7.21*). The temperature rose steadily up to 100 min (± 7 passes through the reactor at 0.675 g charge per pass) before it plateau-ed. This correlates with the decreased ozonation activity observed for both the organic compounds and the colour compounds.

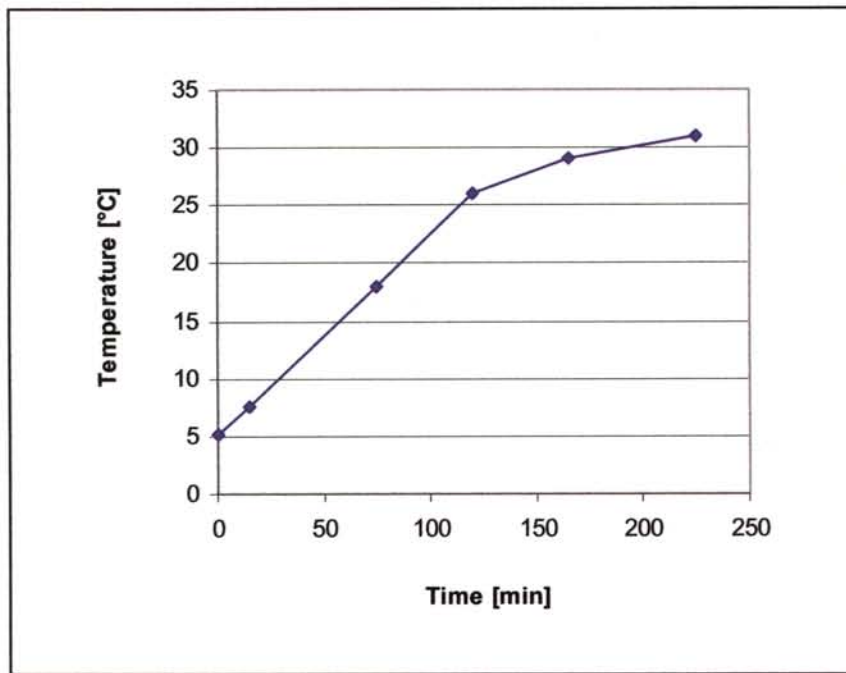


Figure 7.21 Effect of Ozonation on the Temperature of the Wastewater at pH 11.5

7.4.2.7 Ozonation Effects on Red and White Wine Originating Wastewaters

For comparative purposes, wastewater originating from a white wine producing cellar was collected, pH adjusted and ozonated, with interesting results.

Observations Pertaining to the Chemical Oxygen Demand (COD)

The COD of white wine wastewater was observed to decrease by 35% after 60 min (4 passes at 0.675 g O₃ per pass), while the COD of the red wine wastewater was only reduced by 8.5% over the same time frame and experimental conditions (Refer to *Figure 7.22*). The COD was consistently removed after each pass through the reactor, appearing to plateau during the 4th pass (2.7 g ozone charged to 25 L wastewater). Thus 20 875 mg COD was removed with a total ozone feed of 2.7 g (7.7 g COD_e/ 1 g O₃). This is considerably higher than the ratio obtained for the red wine wastewater of 2.15 g COD_e/ 1 g O₃.

Observations Pertaining to the Dissolved Organic Carbon (DOC)

Upon DOC analysis, it was confirmed that a higher percentage of dissolved organic compounds had been removed in the white wine wastewater, decreasing consistently after each pass through the reactor (Refer to *Figure 7.23*). Future experimentation is required to determine the effects of further ozonation on white wine wastewaters. For red wine wastewaters, the largest DOC elimination occurred during the 1st pass.

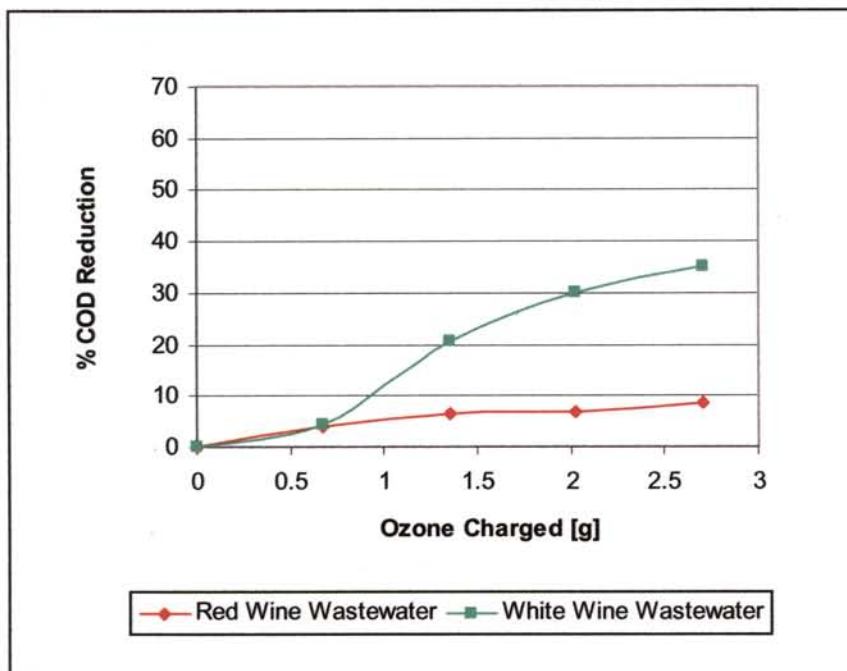


Figure 7.22 Reduction in COD Over 60 min for Red and White Wine Wastewater

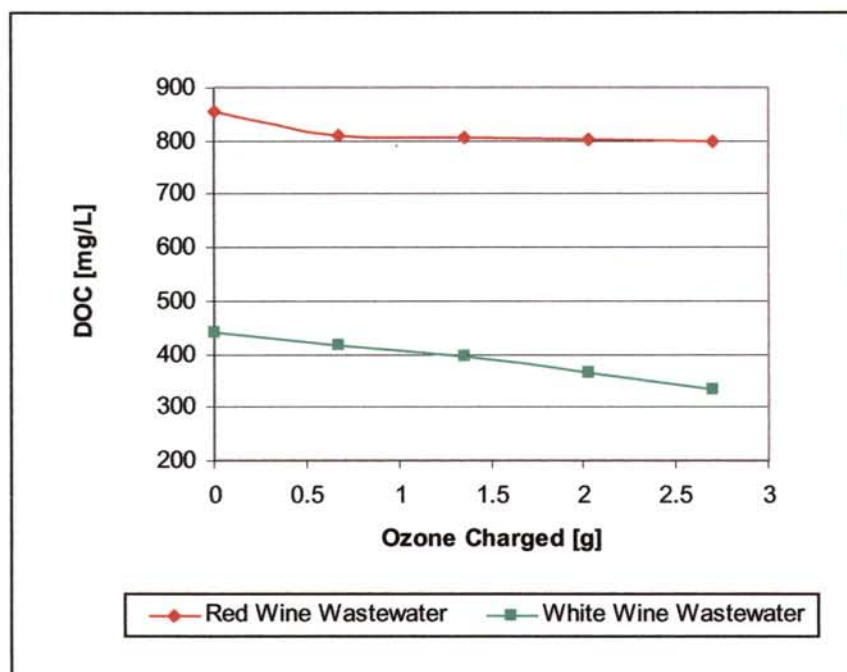


Figure 7.23 DOC Decrease Over 60 min for Red and White Wine Wastewater

Ozonation is thus, highly recommended for wastewaters originating from white wine production. The results may be explained in that red wine wastewaters contain a considerable amount of tannins and anthocyanins. Ozone has been shown to be extremely effective in reducing chromatophores, (*Crawford and Cline, 1990*) and it is considered that these are the target compounds, taking preference over dissolved organic compounds. For wastewaters containing low levels of chromatophores (white wine wastewaters), more ozone is available for organic reduction. However, it should also be noted that the type of organic compounds present in the wastewater under discussion, also play a vital role when considering their ozonation potential. An investigation into the types of organic compounds prevalent in red and white wastewaters should thus be conducted.

Pertaining to the COD and DOC results, the following conclusions were made:

- i. Compounds in white wine wastewater are highly susceptible to ozonation.
- ii. The chemical reactions in white wine wastewater follow a fast kinetic regime.
- iii. Mass transfer in the jet reactor occurs at a sufficient rate to supply ozone to the wastewater.
- iv. A larger concentration of the compounds in white wine wastewater, are easily degradable in comparison to red wine wastewaters.

Observations Pertaining to the Turbidity

As previously discussed, a rapid turbidity decrease is observed for the red wine wastewaters. The high gradient of reduction observed after the 1st pass was due to the degradation of easily oxidised compounds. In contrast, the colour imparting compounds in white wine wastewater appears to be less easily degraded. For both wastewater types the reduction in turbidity plateaus, indicating that further oxidation of coloured compounds require a longer contact time, indicating a limiting chemical reaction rate.

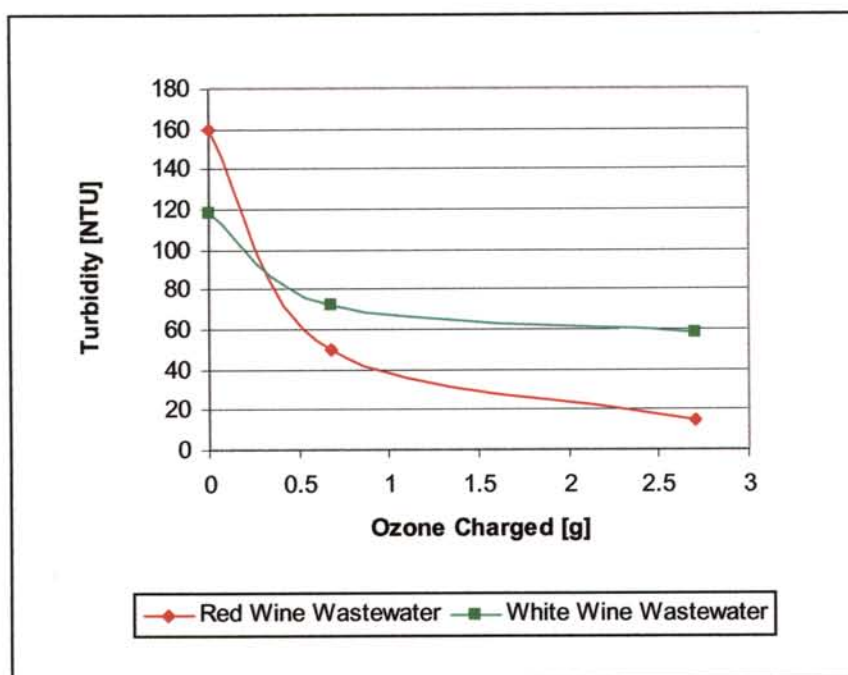


Figure 7.24 Turbidity Decrease for Red and White Wastewater

7.5 REMARKS ON REACTOR CONFIGURATION

This study has paved the way for the application of ozone treatment for winery wastewater. As proved true in most novel studies, once a foundation has been laid, extensive room for development exists. Also true, is the fact that once one problem has been solved, a next one emerges. It is no different for this investigation.

Although the original dilemma concerning an efficient mass transfer system has been addressed through the use of impinging stream technology, the requirement of a sufficient contact time emerges. Bubble column configurations have high contacting times, but low mass transfer rates; while the jet reactor allows sufficient mass transfer rates, but allows for low liquid residence times. Thus, a new problem statement in terms of increased residence time in jet reactors is derived.

Future work should concern the improvement of this design feature. The effect of an increased geometric size of the reactor may be investigated. However, an increase in the geometric size will decrease the mass transfer rate. Thus, the minimum required mass transfer rate must be determined in accordance to the required geometric size sustaining sufficient contact time.

Another consideration is the concentration of the ozone in the exiting gas. This should be determined throughout the period of ozonation by an automatic inline ozone analyser. It will provide additional information for an ozone mass balance determination, enabling the determination of the discussed enhancement factor. Although not measured, it is thought that a substantial concentration of ozone is present in the gas after reaction in the jet reactor. Should an optimum ratio between mass transfer efficiency and sufficient residence time in the reactor not be achieved, consideration to an additional reactor may be examined. In other words, the ozone gas mixture exiting the jet reactor is diverted to a second reactor that enables prolonged contact time. This will require minimal additional cost; but optimal ozone utilisation and efficiency.

7.6 CONCLUDING REMARKS AND RECOMMENDATIONS

As illustrated by the results from the investigation, it is evident that ozone is applicable to the treatment of winery wastewater. In comparison to biological treatment technologies, ozonation has the following benefits:

- Low maintenance.
- No labour requirement.
- Occupies small area.
- Batch treatment is possible.
- Complete elimination of odours.
- No harmful impacts on environment.
- No sludge accumulation
- Produces no toxic compounds or residual elements, as is the case with chlorine.

- No off-gas generation requiring additional treatment.

Although ozone cannot, at current, be recommended for complete organic degradation, it is considered a highly feasible treatment for the reduction of odour, turbidity and phenolic compounds. It is also considered to present extreme potential in multi-treatment design. However, it must be emphasised that significant research should take place before considering an installation. The physical and chemical reaction rates must be evaluated in order to realise optimum treatment conditions and a suitable reactor design. Although more research is required to firmly establish the effects on white wine originating wastewaters, it is nevertheless interesting to note the substantial improvement imparted by ozonation on these wastewaters.

As portrayed in this chapter, the mass transfer system is of vital importance, not only for effective contaminant reductions, but also from an economical point of view. The production of ozone from oxygen is highly energy consuming and cost intensive. Efforts should thus be directed towards increasing the ozone utilisation by the wastewater in order to achieve maximum elimination rates with the minimum ozone requirement. The strategy employed by researchers to increase the ozone concentration in the bulk gas for improved mass transfer, is not economically viable. For accurate cost evaluation, both the energy requirements of the pump (supplying wastewater to the reactor) and the ozone generator must be quantified.

CHAPTER 8

PROPOSED TREATMENT SYSTEM FOR RUPERT AND ROTHSCHILD VIGNERONS

In light of the findings from the investigations into the wastewater characteristics and efficiency of induced sedimentation and ozonation, the following treatment system unique to Rupert and Rothschild Vignerons is proposed:

- i. The installation of a sedimentation tank (thickener) on top of the delta-settler: Wastewater from the pit is pumped (via existing pumps) to the sedimentation tank with automated in-line injection of a polyaluminium chloride coagulant. The settled floc that collects at the bottom of the tank is passed a collection bin and dried. The supernatant, which flows over the top of the tank, is collected in a separate container and adjusted to a pH range of 11-12.
- ii. The pH-adjusted supernatant is pumped to a reactor for treatment by ozone.
- iii. The treated wastewater is then irrigated onto land.

This system does not increase the need for additional space, and also no additional cost is incurred for the system hydraulics as pumps and pipelines already exist, as does an ozonator. Additional cost is incurred for the sedimentation tank, pH adjustment requirement and ozone reactor design.

Before the recommended system is implemented at Rupert and Rothschild Vignerons, pilot plant test work on the designed thickener (as described in *Section 6.3*) must be conducted, and the results evaluated in combination with the results obtained from this study.

It is envisaged that the final system will produce wastewater quality that meets the requirements of the authorities, and also the objectives determined in the Environmental Management System (Refer to *Section 5.2*). It is envisaged that the employment of re-use and reclamation strategies, coupled with increased environmental awareness by employees, will allow the attainment of the objectives set for future years.

CHAPTER 9

CONCLUDING REMARKS AND RECOMMENDATIONS FOR FUTURE WORK

In conclusion, this chapter serves to highlight the conclusions drawn from the project conducted at Rupert and Rothschild Vignerons, and provides recommendations for future work.

9.1 OVERVIEW OF CONCLUSIONS

9.1.1 *Conclusions Drawn from the Auditing Procedure*

The following list of aspects summarise the auditing procedure:

- The process dynamics of the winery must be clearly defined and investigated.
- A sampling protocol forms the cornerstone of the audit.
- The characteristics of winery wastewater vary considerably as a function of cellar processes and practices employed.
- An individual assessment of the quality of the wastewater unique to each cellar must be determined.
- The intrinsic significance of the audit is the acquisition of knowledge into the degree of contamination, thereby enabling the setting of future objectives and the consideration to a sustainable treatment system.

9.1.2 Conclusions Drawn from the Coagulation Experiments

With reference to investigation of coagulation for induced sedimentation, the following conclusions were drawn:

- Polyaluminium chloride coagulants are highly effective for the removal of colloidal and suspended matter in winery wastewater.
- PAC is efficient over a broad pH range.
- Turbidity and suspended solids removal are achieved due to the high molecular weight of their imparting compounds.
- Colour compounds are negatively charged, and therefore readily neutralised by cationic aluminium.
- Compounds, which influence the COD, are not readily removed due to a low molecular weight.

9.1.3 Conclusions Drawn from Ozonation Experiments

- Winery wastewater is highly susceptible to ozonation.
- Ozonation effectively removes colour and odour from the wastewater.
- At high pH, the ozone reaction follows a fast kinetic regime owing to the formation of hydroxyl radicals.
- Substantial decreases in contaminants occur at high pH's in comparison to low pH's.
- The initial ozonation phase is characterised by the oxidation of degradable compounds such as phenols.
- A high rate of reduction occurs initially, decreasing due to decreasing pH and the presence of refractory compounds.
- The efficiency of ozonation is determined by the rate of mass transfer, coupled with the rate of the chemical reaction.
- Impinging stream jet reactors provide an efficient alternative to conventional contactors.
- The limiting reaction in bubble contactors is the mass transfer coefficient.

- For impinging stream jet reactors, the eventual limiting factor concerns the chemical reaction, indicating a prolonged liquid residence requirement.
- In order to compare the ozonation efficiency of wastewaters and contacting systems, the elimination of the contaminants must be quantified in relation to their ozone requirement. Thereby, an elimination-ozone requirement ratio is established.

9.2 PROJECT ACHIEVEMENTS

The main achievements of this study may be summarised as follows:

- The design of a successful wastewater audit.
- The devise of a sampling protocol.
- The identification of environmentally hazardous practices at the Rupert and Rothschild Cellar.
- The setting of future objectives concerning the wastewater quality at Rupert and Rothschild Vignerons.
- The proposal of a suitable treatment system for Rupert and Rothschild Vignerons.
- A pioneer study on the effects of ozonation on winery wastewater, achieving the crucial enhancement of the mass transfer reaction.
- A practical and economical preliminary evaluation of pre-polymerised metal salt coagulants for effective wastewater treatment.

In light of these achievements, the initial objectives of this project as discussed in *Chapter 1*, were reached.

9.3 RECOMMENDATIONS FOR FUTURE WORK

Following the investigation of the wastewater dynamics, the determination of eco-toxicology by winery wastewater irrigation should be conducted. According to *Muller and Heil* (1998), the following criteria should be addressed:

- i. Investigation of possible ground water pollution.
- ii. Degradation or persistence of detergents used in wineries; and the influence on the soil micro-population.
- iii. Definition of the maximum admissible quantity of wastewater to agricultural areas.

Since the studies conducted on coagulation and ozonation provided a basis for experimental conditions and experimental configuration, a myriad of future work may be realised. The most economic dosage for polyaluminium chloride should be ascertained. For this purpose, it is recommended that pilot-plant studies be conducted for dosage accuracy, as the polyaluminium chlorides are highly viscous. The efficiency of coagulation on white wine originating wastewaters may be similarly investigated. The future use of a zeta-potential meter is recommended to establish the point of zero charge (charge neutralisation), corresponding to the coagulant dosage and pH.

As discussed in *Chapter 7*, the optimal contact time in conjunction with high mass transfer rates in an ozonation reactor must be investigated. The increase in the geometric size of the employed jet-reactor is proposed, thus implicating scale-up and an element of re-design. The inclusion of an in-line ozone analyser will realise an in-depth study on ozone reaction kinetics and the determination of the enhancement factor E , obtaining a ratio for both the physical and chemical reactions. Simultaneously, a study on the economic viability and ozone efficiency should be done in terms of the power dissipation of the pump activity and ozone generation.

CHAPTER 10

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APPENDIX A

COMPLETE WATER & WASTEWATER AUDIT RESULTS 1999 & 2000

Table A.1 Water & Wastewater Audit Results from 1999 (1 March - 10 March)

SAMPLE No	1	2	3	4	5	6	7	8	9	10
Sample Point	F1	F2	F4	F6	F7	F8	F0	F2	F4	F6
Sample Date	01/03/99	01/03/99	01/03/99	01/03/99	01/03/99	01/03/99	10/03/99	10/03/99	10/03/99	10/03/99
Potassium as K mg/L		3.3	48				4.2	2.6		200
Sodium as Na mg/L							19	35		
Calcium as Ca mg/L	2.8	38					9.2	39		
Magnesium as Mg mg/L	6.7	10					4.5	8.4		
Ammonia as N mg/L										
Sulphate as SO4 mg/L			34	40		23	7.1	9.1		43
Chloride as Cl mg/L							32	60		
Alkalinity as CaCO3 mg/L	8	88	146	38			34	93	183	5
Nitrate plus Nitrite as N mg/L							0.12	6		
Ortho phosphate as P mg/L										
Iron as Fe mg/L	1	0.3				4.5	1.1	0.31		
Dissolved Organic Carbon as C mg/L	1	2.5					1.8	1.7		
Conductivity mS/m @ 25°C	29	49	75	84	90	88	20	45	72	109
pH (Lab)	5.5	7.3	7	4.9	6.3	6.1	7.5	7.4	7.5	4.6
Total Dissolved Solids mg/L (calc)										
Saturation pH (pHs 20°C)										
Total Hardness as CaCO3 mg/L	35	136					42	132		
SAR										
% Difference							1.39	1.34		
CATIONS meq/L							1.76	4.23		
ANIONS meq/L							1.74	4.17		
Total Dissolved Solids (180) ^o mg/L			334	1610	1537	1642			453	1394
Chemical Oxygen Demand mg/L			1091	8854	3350	3630			632	5257
Turbidity NTU						180	32	0.95		
Kjeldahl Nitrogen as N mg/L						29				
Total Phosphorus as P mg/L						5				
Suspended Solids mg/L			347	342	280	332			431	329

Table A.2 Water & Wastewater Audit Results from 1999 (10 March - 9 June10)

SAMPLE No	11	12	13	14	15	16	17	18	19	20
Sample Point	F7	F8	F9	F6	F7	F8	F6	F7	F8	F6
Sample Date	10/03/99	10/03/99	10/03/99	17/03/99	17/03/99	17/03/99	7/04/1999	7/04/1999	7/04/1999	9/06/1999
Potassium as K mg/L	127					227			273	
Sodium as Na mg/L	73					116			66	
Calcium as Ca mg/L	58					48			48	
Magnesium as Mg mg/L	18					16			18	
Ammonia as N mg/L						0.3				
Sulphate as SO4 mg/L	30		29			45				
Chloride as Cl mg/L						95			90	
Alkalinity as CaCO3 mg/L	155		158		178	283				
Nitrate plus Nitrite as N mg/L						0.5				
Ortho phosphate as P mg/L						0.7				
Iron as Fe mg/L	15				3.5	11				
Dissolved Organic Carbon as C mg/L									1725	
Conductivity mS/m @ 25°C	90	103	68	62	106	133	270	160	126	145
pH (Lab)	5.2	5.3	6.5	4.8	5.2	5.4	3.8	4.2		5.6
Total Dissolved Solids mg/L (calc)										
Saturation pH (pHs 20°C)										
Total Hardness as CaCO3 mg/L		219				186			194	
SAR									2.1	
% Difference										
CATIONS meq/L										
ANIONS meq/L										
Total Dissolved Solids (180)°mg/L	1005	1182	820	1042	1704	2187	12994	13780	1514	2022
Chemical Oxygen Demand mg/L	7510	3281	2166	3492	4762	5238	30710	4878	7090	4962
Turbidity NTU										
Kjeldahl Nitrogen as N mg/L		24								
Total Phosphorus as P mg/L		3.3								
Suspended Solids mg/L	2724	203	732	382	497	195	12994		729	233

Table A.3 Water & Wastewater Audit Results from 1999 (9 June - 5 October)

SAMPLE No	21	22	23	24	25	26	27	28	29	30
Sample Point	F7	F8	F6	F7	F6	F7	F8	F6	F7	F8
Sample Date	9/06/1999	9/06/1999	13/08/1999	13/08/1999	23/08/1999	23/08/1999	23/08/1999	5/10/1999	5/10/1999	5/10/1999
Potassium as K mg/L										
Sodium as Na mg/L										
Calcium as Ca mg/L										
Magnesium as Mg mg/L										
Ammonia as N mg/L										
Sulphate as SO4 mg/L										
Chloride as Cl mg/L										
Alkalinity as CaCO3 mg/L										
Nitrate plus Nitrite as N mg/L										
Ortho phosphate as P mg/L										
Iron as Fe mg/L		730								
Dissolved Organic Carbon as C mg/L					3000	1216	610			
Conductivity mS/m @ 25°C	145	145	275	188	86	193	70	355	155	155
pH (Lab)	7.1	6.6	5.6	7.3	4.3	7.7	6.6	11.8	5.2	5.1
Total Dissolved Solids mg/L (calc)					1563		516			
Saturation pH (pHs 20°C)										
Total Hardness as CaCO3 mg/L										
SAR										
% Difference										
CATIONS meq/L										
ANIONS meq/L										
Total Dissolved Solids (180) mg/L	1757	1816						1435	1539	1480
Chemical Oxygen Demand mg/L	3038	3019	3992	12588	10825	4504	2556	2500	8633	9950
Turbidity NTU										
Kjeldahl Nitrogen as N mg/L										
Total Phosphorus as P mg/L										
Suspended Solids mg/L	636	312	61	456			74	586	295	1442

Table A.4 Water & Wastewater Audit Results from 2000 (28 January - 23 February)

ORIGIN	Pit	Holding	Incoming	Holding	Incoming	Holding	Incoming	Tower	Incoming
SAMPLE No	1	2	3	4	5	6	7	8	
Time									
Sample Point:	F6	F7	F1	F7	F1	F7	F10	F1	
Sample Date	28/01/00	28/01/00	28/01/00	09/02/00	10/02/00	10/02/00	10/02/00	23/02/00	
Potassium as K mg/L	29	70	2	91					
Sodium as Na mg/L		87		209		106	1424		
Calcium as Ca mg/L		37	23	62	26	32	479	21	
Magnesium as Mg mg/L		12.3		20	7.5	10	309	6.1	
Ammonia as N mg/L									
Sulphate as SO4 mg/L	26					58			
Chloride as Cl mg/L				147		142			
Alkalinity as CaCO3 mg/L			53		59		163	52	
Nitrate plus Nitrite as N mg/L									
Ortho phosphate as P mg/L									
Iron as Fe mg/L				2.3	0.7	2.2	0.5	0.2	
Dissolved Organic Carbon as C mg/L	986	871	<1	1045		1151			
Conductivity mS/m @ 25°C	79	80	36	175	38	160	1040	35	
pH (Lab)	3.3	4.3	6.8	5	7.3	4.7	8.5	7.6	
Total Dissolved Solids mg/L (calc)	506	512	230	1120	243	1024	6656	224	
Saturation pH (pHs 20°C)			8.5		8.4		6.8	8.5	
Total Hardness as CaCO3 mg/L		143	57	237	96	121	2469	78	
SAR		3.17	0.00	5.91	0.00	4.19	12.47	0.00	
% Difference	37		13	290	62	35	3313	49	
CATIONS meq/L	0.74	8.43	1.20	16.16	1.91	7.03	111.27	1.55	
ANIONS meq/L	0.54	0.00	1.06	4.15	1.18	5.21	3.26	1.04	
Total Dissolved Solids (180)° mg/L	1061	791		1626		2230			
Chemical Oxygen Demand mg/L	3028	3068		3386		4732			
Turbidity NTU			0.7					4.1	
Suspended Solids mg/L	184	74		183		159			

Table A.5 Water & Wastewater Audit Results from 2000 (23 February - 25 February)

ORIGIN	Pit	Holding	Tower	Holding	Tower	Holding	Tower	Pit	Holding
SAMPLE No	9	10	11	13	14	15	16		
Time									
Sample Point:	F6	F7	F10	F7	F10	F6	F7		
Sample Date	23/02/00	23/02/00	23/02/03	25/02/00	25/02/01	25/02/02	25/2/00		
Potassium as K mg/L									
Sodium as Na mg/L	44	124	297		355		120		
Calcium as Ca mg/L	36	43	117		156				
Magnesium as Mg mg/L	9.4	11.3	59		77				
Ammonia as N mg/L									
Sulphate as SO4 mg/L	29	38							
Chloride as Cl mg/L	66	76			679		71		
Alkalinity as CaCO3 mg/L			181		316				
Nitrate plus Nitrite as N mg/L									
Ortho phosphate as P mg/L									
Iron as Fe mg/L	1.2	1.1							
Dissolved Organic Carbon as C mg/L	768	671			27	3390	466		
Conductivity mS/m @ 25°C	80	106	255	90	305	106	83		
pH (Lab)	4.4	5.1	8.7	4.4	8.6	3.6	4.8		
Total Dissolved Solids mg/L (calc)	512	678	1632	576	1952	678	531		
Saturation pH (pHs 20°C)			7.3		7				
Total Hardness as CaCO3 mg/L	129	154	535		707				
SAR	1.69	4.35	5.59		5.81				
% Difference	82	189	552		16		161		
CATIONS meq/L	4.48	8.47	23.61	0.00	29.56	0.00	5.22		
ANIONS meq/L	2.47	2.94	3.62	0.00	25.47	0.00	2.00		
Total Dissolved Solids (180)°mg/L	1503	1252				1744	989		
Chemical Oxygen Demand mg/L	2683	2656		3665		12510	1633		
Turbidity NTU									
Suspended Solids mg/L	565	248		244		625	109		

Table A.6 Water & Wastewater Audit Results from 2000 (25 February - 10 March)

ORIGIN	Holding	Pit	Holding	Tower	Pit	Pit	Pit
SAMPLE No	17	18	19	20	21	22	23
Time					11h00	11h30	12h00
Sample Point:	F7	F6	F7	F10	F6	F6	F6
Sample Date	25/2/00	02/03/00	02/03/00	02/03/00	10/3/00	10/3/00	10/3/00
Potassium as K mg/L							
Sodium as Na mg/L	69	169	164	58			
Calcium as Ca mg/L	40	33	42	49			
Magnesium as Mg mg/L	15.3	5.5	9.1	12			
Ammonia as N mg/L							
Sulphate as SO4 mg/L	57	40					
Chloride as Cl mg/L				110			
Alkalinity as CaCO3 mg/L							
Nitrate plus Nitrite as N mg/L							
Ortho phosphate as P mg/L							
Iron as Fe mg/L							
Dissolved Organic Carbon as C mg/L	1913		445		919	1211	926
Conductivity mS/m @ 25°C	95	86	94	70	190	180	220
pH (Lab)	3.8	6	6.5	8.3	5.1	5.5	5.6
Total Dissolved Solids mg/L (calc)	608	550	602	448	1216	1152	1408
Saturation pH (pHs 20°C)							
Total Hardness as CaCO3 mg/L	163	105	142	172			
SAR	2.35	7.18	5.98	1.93			
% Difference	427	1034		92			
CATIONS meq/L	6.26	9.45	9.98	5.96			
ANIONS meq/L	1.19	0.83	0.00	3.10			
Total Dissolved Solids (180)° mg/L	1687	2404	2435		3109	4203	3543
Chemical Oxygen Demand mg/L	7171	2704	2028		2684	3936	2584
Turbidity NTU							
Suspended Solids mg/L	544	420	149		202	649	176
							146

Table A.7 Water & Wastewater Audit Results from 2000 (10 March)

ORIGIN	Pit	Holding	Holding	Tank	Pit	Pit	Pit	Pit
SAMPLE No	25	26	27	28	29	30	31	Pit
Time	12h40	11h45	12h50		15h05	15h45	16h10	18h15
Sample Point:	F6	F7	F7	Caustic	F6	F6	F6	F6
Sample Date	10/3/00	10/3/00	10/3/00	10/3/00	10/3/00	10/3/00	10/3/00	10/3/00
Potassium as K mg/L								
Sodium as Na mg/L							188	
Calcium as Ca mg/L							38	
Magnesium as Mg mg/L							13	
Ammonia as N mg/L								
Sulphate as SO4 mg/L								
Chloride as Cl mg/L								
Alkalinity as CaCO3 mg/L								
Nitrate plus Nitrite as N mg/L								
Ortho phosphate as P mg/L								
Iron as Fe mg/L								
Dissolved Organic Carbon as C mg/L	1217	1094	1117	67	2361	2000	2056	2083
Conductivity mS/m @ 25°C	185	165	170	3550	155	140	150	122
pH (Lab)	5.5	5.3	5.3	12.6	5.4	5.2	4.9	4.5
Total Dissolved Solids mg/L (calc)	1184	1056	1088	22720	992	896	960	781
Saturation pH (pHs 20°C)								
Total Hardness as CaCO3 mg/L							148	
SAR							6.72	
% Difference								
CATIONS meq/L							11.14	
ANIONS meq/L							0.00	
Total Dissolved Solids (180)° mg/L	3055	2485	2537	16000	3529	2708	2524	2289
Chemical Oxygen Demand mg/L	4334	3738	3579	185	8571	7302	7143	7302
Turbidity NTU								
Suspended Solids mg/L	317			109	544	642	751	569

Table A.8 Water & Wastewater Audit Results from 2000 (10 March)

ORIGIN	Pit	Pit	Pit	Pit	Pit	Pit	Pit	Pit	Pit	Holding	Holding
SAMPLE No	33	34	35	36	37	38	39	40			
Time	18h45	19h30	20h42	21h30	22h00	22h40	15h00	18h25			
Sample Point:	F6	F6	F6	F6	F6	F6	F7	F7			
Sample Date	10/3/00	10/3/00	10/3/00	10/3/00	10/3/00	10/3/00	10/3/00	10/3/00			10/3/00
Potassium as K mg/L							180				
Sodium as Na mg/L			76				347				
Calcium as Ca mg/L			41				46				
Magnesium as Mg mg/L			14				12				0.25
Ammonia as N mg/L											
Sulphate as SO4 mg/L											
Chloride as Cl mg/L											72
Alkalinity as CaCO3 mg/L											
Nitrate plus Nitrite as N mg/L											
Ortho phosphate as P mg/L											
Iron as Fe mg/L											
Dissolved Organic Carbon as C mg/L	2083	2486	1966	1974	2256	3158	1045	1051			
Conductivity mS/m @ 25°C	129	142	134	107	149	108	183	191			
pH (Lab)	4.4	4.2	4.1	4.1	3.8	3.8	5.9	6.2			
Total Dissolved Solids mg/L (calc)	826	909	858	685	954	691	1171	1222			
Saturation pH (pHs 20°C)			160				164				
Total Hardness as CaCO3 mg/L			2.61				11.78				
SAR											
% Difference											11278
CATIONS meq/L			6.50				22.98	0.02			
ANIONS meq/L			0.00				0.00	2.03			
Total Dissolved Solids (180)°mg/L	2261	2734	2734	2351	1935		3827	4100			
Chemical Oxygen Demand mg/L	8016	8968	8095	7778			3849	3492			
Turbidity NTU											
Suspended Solids mg/L	582	857	1712	637			234	186			

Table A.9 Water & Wastewater Audit Results from 2000 (10 March - 15 March)

ORIGIN	Holding	Holding	Holding	Holding	Pit	Holding	Pit	Pit	Tank
SAMPLE No	40	41	42	43	44	45	46	47	48
Time	18h25	20h10	21h15	23h15	12h00	15H10	16H20	16H25	Lees
Sample Point:	F7	F7	F7	F7	F6	F7	F6	F6	
Sample Date	10/3/00	10/3/00	10/3/00	10/3/00	15/03/00	15/03/00	15/03/00	15/03/00	15/03/00
Potassium as K mg/L		182		219					
Sodium as Na mg/L		372		343				64	
Calcium as Ca mg/L		47		47				30	
Magnesium as Mg mg/L		12		12				12.5	
Ammonia as N mg/L	0.25								
Sulphate as SO4 mg/L				58				59	
Chloride as Cl mg/L	72			72				73	
Alkalinity as CaCO3 mg/L									
Nitrate plus Nitrite as N mg/L									
Ortho phosphate as P mg/L									
Iron as Fe mg/L									
Dissolved Organic Carbon as C mg/L	1051	1026	1064	1154					
Conductivity mS/m @ 25°C	191	193	175	177	132	103	87	100	249
pH (Lab)	6.2	6	6	5.6	6	4.3	5.1	4.3	3.6
Total Dissolved Solids mg/L (calc)	1222	1235	1120	1133	845	659	557	640	1594
Saturation pH (pHs 20°C)		167		167				126	
Total Hardness as CaCO3 mg/L		12.53		11.56				2.48	
SAR				636				61	
% Difference	11278			23.85				5.31	
CATIONS meq/L	0.02	24.17		3.24				3.29	
ANIONS meq/L	2.03	0.00		3751	1814	1772	1278	1502	4851
Total Dissolved Solids (180)°mg/L	4100	4083	3937	4484	2789	4622	3347	3506	19705
Chemical Oxygen Demand mg/L	3492	3968	3889	4484	2789	4622	3347	3506	19705
Turbidity NTU									
Suspended Solids mg/L	186	210	222	305	180	226	152	419	

Table A.10 Water & Wastewater Audit Results from 2000 (15 March - 17 July)

ORIGIN	Tower	Holding	Pit	Holding	Pit	Holding	Pit	Holding	Pit
SAMPLE No	49	50	51	52	53	54	55	56	
Time		12H28	12H00	12H20	12H00	12H00			
Sample Point:	F10	F7	F6	F6	F7	F6	F6	F6	F6
Sample Date	15/03/00	15/03/00	22/03/00	22/03/00	22/03/00	25/5/00	21/06/00	28/6/00	14/07/00
Potassium as K mg/L		87			126				
Sodium as Na mg/L	69	88	52		61				
Calcium as Ca mg/L	65	65	43		51		16.99		
Magnesium as Mg mg/L	20.4	19			17		9.53		
Ammonia as N mg/L									
Sulphate as SO4 mg/L			112		88		45.7	47	
Chloride as Cl mg/L	114	89			83		100	75	
Alkalinity as CaCO3 mg/L	163						183	183	
Nitrate plus Nitrite as N mg/L									
Ortho phosphate as P mg/L									
Iron as Fe mg/L					1.4		3.52	2.7	
Dissolved Organic Carbon as C mg/L	9.3	1961	1463		1140		1150	1078	
Conductivity mS/m @ 25°C	89	104	88	78	95	110	82	75	120
pH (Lab)	8	4.4	4.5	5.8	4.9	5.76	4.75	6.97	4.1
Total Dissolved Solids mg/L (calc)	570	666	563	499	608			1441	
Saturation pH (pHs 20°C)	7.6								
Total Hardness as CaCO3 mg/L	246	241	107		197				
SAR	1.91	2.47	2.18		1.89				
% Difference	22	333	89		135				
CATIONS meq/L	7.92	10.86	4.41		9.82				
ANIONS meq/L	6.48	2.51	2.33		4.17				
Total Dissolved Solids (180)° mg/L	527	1658	1301	1067	981	823	898	569	
Chemical Oxygen Demand mg/L	143	6693	5749	3772	4750	5180	5305	2045	4200
Turbidity NTU						196	781	200	
Suspended Solids mg/L			253	570	356	173	480	439	

APPENDIX B

ANALYSIS OF COOLING SYSTEM & TOWER WATER

During fermentation, heat is generated by the activity of the yeast, resulting in elevated tank temperatures. High temperatures are detrimental to the winemaking process for the following reasons:

- High temperatures encourage oxidation, microbial spoilage and instability.
- Under warm fermentation and storage conditions desirable aroma and flavour compounds, as well as alcohol, are volatilised.
- Above 38 °C the yeast becomes sluggish and may induce stuck fermentation.

Cooling is essential in wineries and its use extends from must and fermentation cooling to cold-stabilisation. At Rupert and Rothschild, cooling is achieved by means of double jacketed tanks with re-circulated refrigerant (glycol). Cooling water systems control temperatures and pressures by transferring heat from hot process fluids into the cooling water. To remove the heat from the wine, the refrigeration plant must provide a lower temperature than that of the wine, in order for heat transfer to take place. This heat transfer causes the refrigerant liquid, at lower pressure, to evaporate to a vapour in the heat exchanger or evaporator. The compressor, condenser and liquid feed valve recycle the vapour back to a lower pressure liquid. The refrigerant is retained in a closed circuit and recycled. The source water for the cooling plant is the incoming water from the borehole. Four main problems occur in cooling water systems:

- i. Corrosion - water tends to convert metals to their oxide states.
- ii. Scale - calcium and magnesium can form deposits.
- iii. Foul - suspended material is deposited.
- iv. Microbiological contamination - bacterial growth deposition.

The greatest cause of excessive concentration is evaporation. The conductivity increases because of evaporation. Pure water is driven off and the impurities (dissolved salts) remain behind. The concentration will continue until a point of saturation occurs and the salts will precipitate as scale. Unless the concentration ratio is controlled, saturated conditions will occur and scaling of heat exchanger tubes will follow.

The equilibrium saturation point of water for calcium carbonate, as well as for other salts is described by various indices, which provide an indication of the scale-forming or corrosive potential of water. If the water is super-saturated it will be scale forming, whereas undersaturation indicates corrosivity. To calculate the tendency of the water, calcium; alkalinity; total dissolved solids and pH values are required from both the incoming water and water from cooling tower. The corrosive/scaling properties of water can be manipulated by the addition of various chemicals. Heat transfer efficiencies can be reduced by as much as 25% because of calcium carbonate scaling. Tests have shown that 1.5 mm of calcium carbonate on the surface of a 25 mm cast iron plate has the same insulation properties as 100 mm of cast iron. To remove excessively concentrated water, conductivity control may be achieved by automating bleed-off streams. The system at Rupert and Rothschild is, however, manual, and water from bleed stream is discharged into the storm water.

The control of pH is critical. When the pH is below the critical range, the possibility of corrosion increases. Scaling may occur when the pH is above the recommended range. The effectiveness of many biocides also depends on the pH. The same conditions hold true for the alkalinity.

It should be emphasised that the original design of the cooling tower determines these critical ranges. The use of scale and corrosion inhibitors is also fundamental in the determination of acceptable ranges. If the scale inhibitor is adequate, then a total alkalinity of 300 ppm is acceptable. Hardness is usually associated with the tendency to form scale and should not be low (i.e. <100 mg/L) (Walsh, 1991).

A system is considered to be "in-balance" when the dissolved ions in the incoming water concentrate in equal ratios in the tower water. All soluble ions thus remain in

solution. The unequal concentration of ions in the tower water implies that ions are being lost and precipitation is occurring in the system. Since calcium is the only primary scale-forming agent that is lost at a high enough concentration to allow for monitoring, balances are conducted according to calcium and conductivity ratios.

B.1 COOLING TOWER ANALYSIS

The results from the cooling water tower analysis are presented in *Table B.1* and *Figure B.1*.

Table B.1 Analysis of Cooling Tower Water (F10) 2000

Sample Point	F10	F10	F10	F10	F10
Property	10-Feb	23-Feb	25-Feb	02-Mar	15-Mar
Sodium as Na [mg/L]	1424	297	355	58	69
Calcium as Ca [mg/L]	479	117	156	49	65
Magnesium as Mg [mg/L]	309	59	77	12	20.4
Chloride as Cl [mg/L]			679	110	114
Alkalinity as CaCO₃ [mg/L]	163	181	316		163
Conductivity [mS/m @ 25°C]	1040	255	305	70	89
pH [Lab]	8.5	8.7	8.6	8.3	8
Total Dissolved Solids [mg/L calc.]	6656	1632	1952	448	570
Saturation pH [pHs 20°C]	6.8	7.3	7	7	7.6
Total Hardness as CaCO₃ [mg/L]	2469	535	707	172	246
SAR	12.47	5.59	5.81	1.93	1.91

A cooling water system is considered to be "in-balance" when the dissolved ions in the incoming water concentrate in equal ratios in the tower water. All soluble ions thus remain soluble. The unequal concentration of ions in the tower water implies that ions are being lost and precipitation is occurring in the system. Since calcium is the only primary scale-forming agent that is lost at a high enough concentration to allow for monitoring, balances are conducted according to calcium to conductivity ratios.

Table B.2 Balance Determination Indicating Scale Formation (2000)

Date	Property	Incoming Water	System Water	Ratio	Result
10 Feb	Conductivity	38	1040	1:27.3	Scale
	Calcium	26	479	1:18.4	
	Cycles		±27		
Comment	Flow through bleed stream not sufficient, inhibitor not present				
23 Feb	Conductivity	35	255	1:7.2	Scale
	Calcium	21	117	1:5.5	
	Cycles		±7		
Comment	Concentration of inhibitor not sufficient				
25 Feb	Conductivity	37	305	1:8.2	Scale
	Calcium	25	156	1:6.24	
	Cycles		±8		
Comment	Inhibitor concentration not sufficient				
2 Mar	Conductivity	37	70	1:1.89	No scale
	Calcium	25	49	1:1.96	
	Cycles		± 2		
Comment	Flow through bleed stream excessive				
15 Mar	Conductivity	37	89	1:2.4	No scale
	Calcium	25	65	1:2.6	
	Cycles		±2		
Comment	Flow through bleed stream excessive				

In general, ± 5 cycles are adopted for cooling water to reduce water costs.

From the analyses it is clear that the system was out of balance on 10 February 2000, resulting in the precipitation of calcium carbonate. The bleed-stream was not sufficient and no use of inhibitor was applied. The tower was serviced on 14 February resulting in complete drainage of the sump and clean water was introduced. This explains the fact that the water in the tower exhibited a lower conductivity level on 25 February. Although the balance had improved, equilibrium had not yet been achieved, probably due to insufficient inhibitor dosage. This system should be monitored frequently to prevent scaling of heat exchangers. The bleed stream should also be evaluated to guarantee the removal of concentrated water at minimal

water wastage. A sensor in the bleed-off stream should be considered to monitor conductivity levels thus, automatically adjusting flow of concentrated water to storm water drain. The evaporation rate is directly related to the heat exchange ratio and the required temperatures of the cooling plant, thus it difficult to regulate manually.

The saturation pH's in comparison to the pH, also supported the scaling characteristic of the cooling water. The pH and saturation pH should be in equal, however, the saturation pH's are lower, indicating scaling (see *Figure B.1.*)

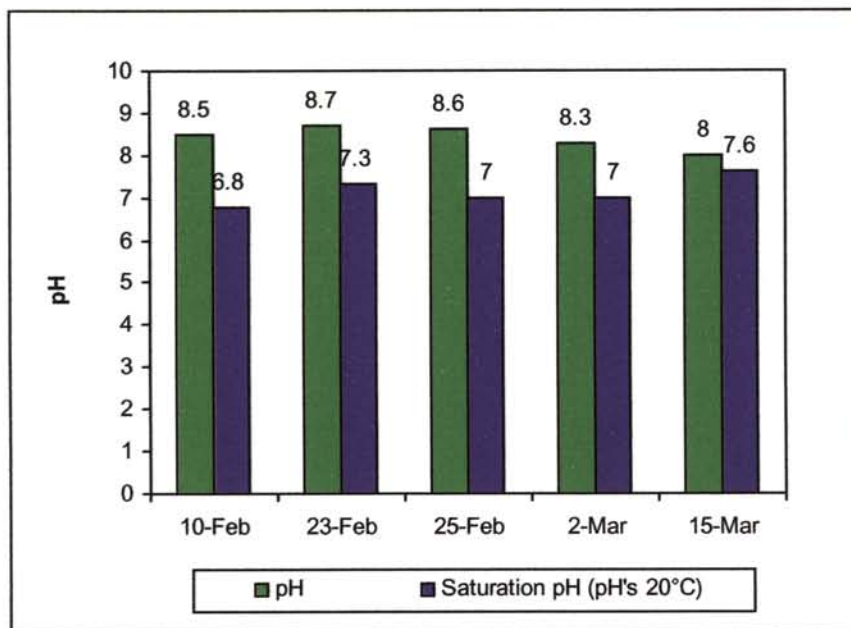


Figure B.1 pH and Saturation pH of Cooling Water (2000)

In conclusion, potential problems associated with cooling water are summarised in *Table B.3.*

Table B.3 Potential Water-Related Problems Associated with Process Water (South African Guidelines, 1996)

Process	Equipment Damage	Process Problems	Waste Disposal
Cooling Water	Corrosion/ Scaling	Foaming	pH
	Fouling	Sediments	TDS
	Blockages	Gas Production	COD
		Odours	SS
		Heat Exchange Impairment	

APPENDIX C

GOVERNMENT GAZETTE NO. 20526 8 OCTOBER 1999

GOVERNMENT NOTICE

DEPARTMENT OF WATER AFFAIRS AND FORESTRY

NO. 1191

8 October 1999

GENERAL AUTHORISATIONS IN TERMS OF SECTION 39 OF THE NATIONAL WATER ACT, 1998 (ACT NO. 36 OF 1998)

I, ARTHUR MICHAEL MULLER, in my capacity as Director-General of the Department of Water Affairs and Forestry, and duly authorised in terms of section 63 of the National Water Act, 1998 (Act No. 36 of 1998), do hereby authorise all or any category of persons to use water in terms of section 39(1) of the National Water Act, read together with section 21, in respect of the General Authorisations contained in the Schedule hereto.

DIRECTOR-GENERAL: WATER AFFAIRS AND FORESTRY

C.1 SCHEDULE

1. THE TAKING OF WATER FROM A WATER RESOURCE AND STORAGE OF WATER

[Section 21(a) and (b)]

Purpose of this authorisation

1.1. The authorisation permitted in terms of this Schedule replaces the need for a water user to apply for a licence in terms of the National Water Act for the abstraction or storage of water from a water resource, provided that the abstraction or storage is within the limits and conditions set out in this authorisation.

Exclusion

1.2. This authorisation does not apply-

- (a) to any determination as regards abstraction and storage in respect of a government water control area, a government water work, a catchment control area or an irrigation district as defined in the Water Act, 1956 (Act No. 54 of 1956) prior to its repeal;
- (b) to a person who does not have lawful access to any waterwork or water resource; and
- (c) to wetlands, the dewatering of mines or storage of water underground.

Compliance with National Water Act and other laws

1.3.(1) This authorisation does not-

- (a) apply to any water use under Schedule 1 of the National Water Act;
- (b) replace any existing authorisation that is recognised under the National Water Act; or
- (c) exempt a person who uses water from compliance with any other provision of the National Water Act unless stated otherwise in this notice, or any other applicable law, regulation, ordinance or by-law.

(2) In the case of the abstraction of water for industrial purposes the provisions of section 7 of the Water Services Act, 1997 (Act No. 108 of 1997), must be met.

(3) A person who uses water in terms of this authorisation is exempt from compliance with section 22(2)(e) of the National Water Act.

Area of applicability

1.4 This authorisation is applicable throughout the Republic of South Africa, except as excluded in paragraph 1.2.(a) above and the areas set out in-

- (a) Table 1.1 for surface water abstraction; and
- (b) Table 1.2 for groundwater abstraction.

Duration of authorisation

1.5. This authorisation will be valid for a period of five years from the date of publication of this notice, unless-

- (a) it is amended at any review period, which period shall be at intervals of two years from the date of publication of this notice;
- (b) the period is extended by a further notice in the *Gazette*; or
- (c) the water user is required to apply for a licence in terms of the National Water Act.

Definitions

1.6. In this authorisation unless the context indicates otherwise, any word or expression to which a meaning has been assigned in terms of the National Water Act shall have that meaning, and-

- (i) "**abstraction**" means taking water from a water resource;

- (ii) **"monitoring programme"** means a programme for taking regular measurements of the quantity and/or quality of a water resource, waste or wastewater discharge at specified intervals and at specific locations to determine the chemical, physical and biological nature of the water resource, waste or wastewater discharge; and
- (iii) **"storage"** means storing water not containing waste, in a watercourse or off-channel storage.

Abstraction and storage

1.7. A person who-

(i) owns or lawfully occupies property registered at the Deeds Office as at the date of this notice; or

(ii) lawfully occupies or uses land that is not registered or surveyed,

outside of the areas as excluded in paragraph 1.2.(a) above and as set out in Table 1.1 and Table 1.2, may on that property or land,

(a) abstract groundwater as set out in Table 1.3;

(b) abstract surface water at a rate of up to 25 litres per second-

(i) for the irrigation of up to 25 hectares of land, at 6 000 cubic metres per hectare per annum; or

(ii) for purposes other than irrigation, up to 100 cubic metres on any given day; and

(c) store up to 50 000 cubic metres of water.

Registration of water use

1.8.(1) A person who uses water in terms of this authorisation must submit a registration form obtained from the Department for the registration of the water use before commencement of-

- (a) abstracting more than 50 cubic metres from surface water or 10 cubic metres from groundwater on any given day; or
- (b) storing more than 10 000 cubic metres of water.

(2) On written acknowledgement of receipt of the application form by the Department, the person will be regarded as a registered water user.

(3) The registered user must comply with any regulation promulgated in terms of section 26(1)(c) of the National Water Act.

Precautionary practices

1.9.(1) The registered user must ensure that any dam complies with the requirements of Chapter 12 of the National Water Act.

(2) The registered user must follow acceptable construction, maintenance and operational practices to ensure the consistent, effective and safe performance of the abstraction and storage of water.

(3) Where water is stored in a watercourse, the registered user must take reasonable measures to ensure that the movement of aquatic species is not prevented, including those species which normally migrate through the watercourse.

Record-keeping and disclosure of information

1.10.(1) The registered user must ensure the establishment of monitoring programmes to measure the quantity of water abstracted and/or stored, as follows-

- (a) the quantity of groundwater or surface water abstracted must be metered or gauged and the total recorded as at the last day of each month;
- (b) in the case of irrigation and where no meter or gauge is used, the quantity of

water abstracted may be calculated according to methods set by the Responsible Authority; and

(c) the quantity of water stored recorded as at the last day of each month.

(2) Upon the written request of the Responsible Authority the registered user must-

(a) ensure the establishment of any additional monitoring programmes; and

(b) appoint a competent person to assess the water use measurements made in terms of this authorisation and submit the findings to the Responsible Authority for evaluation.

(3) Subject to paragraph 1.10.(2) above, the registered user must, for at least five years, keep a written record of all taking and storage of surface or groundwater which information must be made available upon written request to the Responsible Authority.

Inspections

1.11. Any property or land in respect of which a water use has been authorised in terms of this notice must be made available for inspection by an authorised person in terms of section 125 of the National Water Act.

Offences

1.12. Any person who contravenes any provision of this authorisation is guilty of an offence and is subject to the penalty set out in section 151(2) of the National Water Act.

<p>NOTE: Information regarding the drainage regions referred to in Tables 1.1, 1.2 and 1.3 can be obtained from the Department, upon written request.</p>

TABLE 1.1 Areas excluded from General Authorisation for surface water abstraction

Primary drainage region	Secondary/Tertiary/Quaternary drainage region and excluded resources	Description of main river in drainage region for information purposes
A	All catchments	Limpopo River
B	All catchments	Olifants River
C	C10, C20, C40, C50, C60, C70, C80 & C90	Vaal River
D	Orange River downstream of Gariep Dam	
	D13	Kraai River
E	Olifants River	
	E10A to K	Olifants River above the confluence with the Doring River
	E21	Groot River
G	G10	Berg River
	G21	Diep River
	G22	Eerste River
	G30	Verlorevlei River
	G40A to E	Bot River
	G40L & M	Klein River, Uilkraals River
H	H20A, B, D, E, F, G & H	Hex River
	H30	Kingna River
	H40	Breede River downstream of Brandvlei Dam to confluence with the Kingna River
	H60A, B & C	Tributaries of the Sonderend River upstream of the Theewaterskloof Dam
	H80A to E	Duivenhoks River
J	J12	Touws River
	J25	Gamka River
	J31 to 35	Olifants River
	J40C	Langtou and Weyers Rivers
K	K10	Little Brak River
	K20	Great Brak River
	K40C	Karatara River
	K50 & K60	Knysna, Keurbooms Rivers
	K70B	Bloukrans River
	K80A to F	Lottering, Storms, Sandrif, Groot, Tsitsikamma, Klippedrift Rivers
K90A to G	Kromme, Seekoei, Kabeljous Rivers	
L	L81	Baviaanskloof River
	L82	Kouga River

Primary drainage region	Secondary/Tertiary/Quaternary drainage region and excluded resources	Description of main river in drainage region for information purposes
	L90	Lower Gamtoos River
M	M10 M20 M30	Swartkops River Maitland River Van Stadens River
N	Sundays River downstream of Darlington Dam	
	Skoenmakers River downstream of Skoenmakers Canal Outlet	
	N11, N12 N12A, B & C	Sundays River upstream of Vanrynevelds Pass Dam Gats River
P	P10 P30 P40	Bushmans River Kowie River Kariega River
Q	Great Fish River, Little Fish River	
	Q41A, Q41B, Q41C, Q41D, Q44A, Q44B	Tarka River
	Q42A & B	Elands River
	Q43A & B Q44A & B	Vlekpoort River Lake Authur
R	R20 R30A, B, C & D R30E & F	Buffels River Kwenxura, Kwelera, Gonubie Rivers Nahoon River
S	S10 A to E S20A to C S32A to C S32D & E S32F S40A, B & C S50A, B & C S60A & B S60C & D S70C	White Kei River upstream of the Xonxa Dam Indwe River upstream of the Lubisi Dam Swart Kei River upstream of the Klipplaat confluence Klipplaat River upstream of Waterdown Dam Oxkraal River upstream of the Oxkraal Dam Thorn, Thomas Rivers Tsomo, Kwa-Qokwama and Mbokotwa Rivers Kubusi River upstream of Wiggleswade Dam Toise River Xilinx River upstream of the Xilinx Dam
T	T11A & B T20A & B T35A, B, C, D, F & G	Slang, Xuka Rivers Mtata River upstream of Mtata Dam Tsitsa, Pot, Mooi, Inxu, Wildebees, Gatberg Rivers
U	U20 & U40	Mgeni, Mvoti Rivers
V	V11	Upper Thukela River

Primary drainage region	Secondary/Tertiary/Quaternary drainage region and excluded resources	Description of main river in drainage region for information purposes
	V20 V60 V70	Mooi River Sundays River Bushmans River
W	W12 W21A W30	Mhlatuze River White Mfolozi River upstream of Klipfontein Dam Hluhluwe and Mkuzi Rivers
X	All catchments	Nkomati River

TABLE 1.2 Subterranean government water control areas excluded from General Authorisation for groundwater abstraction

Primary drainage region	Tertiary/Quaternary drainage region	Description of subterranean government water control area	Government Notice No.	Government Gazette Date
H	H30	Baden	136	1967-06-16
A	A30	Bo-Molopo	1324	1963-08-30
C	C30	Bo-Molopo	1993	1965-12-17
D	D41	Bo-Molopo	R634	1966-04-29
A	A24	Crocodile River Valley	208	1981-10-23
A	A21	Crocodile River Valley	18	1983-02-18
A	A21, A22	Kroondal-Marikana	180	1963-06-17
G	G10,G30	Lower Berg River Valley/Saldanha	185	1976-09-10
A,B	A60,B50,B31	Nyl River Valley	56	1971-03-26
G	G30	Strandfontein	2463	1988-12-09
M	M10,M20,M30	Uitenhage	260	1957-08-23
G	G30	Wadrif	992	1990-05-11
G	G20	Yzerfontein	27	1990-02-09
G	G30	Graafwater	1423	1990-06-29
A	A70	Dendron-Vivo	813	1994-04-29
A	A60	Dorpsrivier	312	1990-02-16
C	C24	Ventersdorp	777	1995-06-02

Table 1.3 Groundwater Abstraction Zones: Tertiary and Quaternary Drainage Regions

ZONE A No water may be abstracted from these drainage regions except as set out under Schedule 1 of the National Water Act	ZONE B 60 m ³ per hectare per annum may be abstracted from these drainage regions		ZONE C 300 m ³ per hectare per annum may be abstracted from these drainage regions		ZONE D 750 m ³ per hectare per annum may be abstracted from these drainage regions
A10C	A10A,B	J13 – all	A21D,L	T12,T13 – all	A21A,B
A24J	A21C,E,F,G,H,J,K	J21A	A22J	T20A,B,C	C22B,D
A32D,E	A22A,B,C,D,E,F,G,H	J22A,B,C,D,G	A23B,C,F,G,H,J,K,L	T31A,B,C,D,F,G,H	E10A,B,C
A63A	A23A,D,E	J23E	A24A	T33E,F,G	G10A,B,E,G
A71K,L	A24D,E,F,H	J24A,F	A24B,C,G	T34G,H	G21B
A80G,J	A31A,B,D,E,F,G,H,J	J31D	A31C	T35E,H,J,K	G22A,B,C,D,F
A92D	A32,A,B,C	J32E	A61D,E	T40F,G	G40A,B,C,D,E,G,H,J,L,M
D41C,E,F,H,K,M	A41A,B,C,D,E	J33A,B,C,D	A91B,C,D,E,F	T51A,B,D,E,F,G	G50A,B,E,F
D42 – all	A42,A50 - all	J34B,E,F	B11,B12 – all	T52M	H10B,C,E,G,J,K,L
D53D,E,F,G,H,J	A61A,B,C,F,G,H,J	J35B	B20A,D,G,H,J	T70D	H20B,C,D,E,F,G
D57C,D,E	A62 – all	J40A,C,D,E	B31A,B,C,D,E,F,G,H	T80,T90	H30C
D73C,D,E	A63B,C,D,E	K10A	B32A,B,C,G,J	U10A,B,C,D,M	H40K
D81A,B,C,D,E,F,G	A71A,B,C,D,E,F,G,H,J	L11 – all	B51C,H	U20L,M	H60A,B,C
D82 – all	A72 – all	L12B	B60A,B,C,D,H,J	U30A,B,D	H70D
E22D,E	A80A,B,C,D,E,F,H	L21,L22,L23	B71A,C,F,G,H	U40D,E,G,H,J	H80A,B,C,E,F
E23C,D,F,G,H,J,K	A91A,G,H,J,K	L30,L40,L50,L60	B72A,B,C,D,E,F,G,H	U50A	H90A,B,C,E
E24D,G,H	A92A,B,C	L70A,B,C,D,E,F	B73A	U70E	J12A

ZONE A No water may be abstracted from these drainage regions except as set out under Schedule 1 of the National Water Act	ZONE B 60 m ³ per hectare per annum may be abstracted from these drainage regions		ZONE C 300 m ³ per hectare per annum may be abstracted from these drainage regions		ZONE D 750 m ³ per hectare per annum may be abstracted from these drainage regions
E31 – all	B20B,C,E,F	M10C,D	B81A,B,C,D	U80 – all	J31A,B,C
E33A,B,D,E,H	B31J	M30 – all	B82A,B,C,D,E,F	V11A,B,E,G	J34A,C,D
F10A,B,C	B32D,E,F,H	N11,N12,N13,N14,N21,N22	C11A,B,C,D,E,F,G,H,J,K	V13A	J40B
F20A,B,C,D,E	B41,B42 – all	N23A,B	C12A,D,E,F,G,H,K,L	V20A,B,C,H	K10C,E
F30B,E,F,G	B51A,B,E,F,G	N24 – all	C13C,E,F,G,H	V31C,D,G,H,J,K	K30D
F40 – all	B52 – all	N30,N40 – all	C21A,B,C,D,E,G	V32 – all	K40A,B,C,E
F50D,F,G	B60E,F,G	P10,P30,P40 – all	C22C,E,F,K	V33A	K50,K60,K70,K80 – all
F60A,B,C,D	B71B,D,E,J	Q11,Q12,Q13,Q14,Q21,Q22,Q30 – all	C23B,C,D,E,F,G,H	V40B,D,E	K90A,B,C
J11G,J	B72J,K	Q41C,D	C24 – all	V50A,B,D	L70G
J21B,C,D,E	B73B,C,D,E,F,G,H,J	Q42,Q43,Q44 – all	C25A,D	V60A,B,C,D,E,F,G,H	L81,L82 – all
J22E,F,H,J,K	B81E,F,G,H,J	Q50,Q60,Q70,Q80 – all	C31A,B,C,D,E	V70A,B,C,D	M10A,B
J23A,B,C,D,F,G,H	B82G,H,J	Q91 – all	C32D	W11B,C	M20A
J24B,C,D,E	B83,B90 – all	Q92C,E,F,G	C33 – all	W12B,E	P20B
J32A,B,C,D	C11L,M	Q93B,C,D	C41A,B,D,E	W13A,B	T52L
L12A,C,D	C12B,C,J	R50B	C42A,B,C,D,E,F,G,H,J,K	W21A,B,D	T60D,E,G,H
	C13A,B,D	S10A,B,C,D	C60A,B,C,D,E,F	W21G,H,J	U20K
	C21F	S20A,B	C70A,B,J	W22A	U30C,E
	C22A,G,H,J	S31A,B,C	C81 – all	W31A	U40C,F
	C23A,J,K,L	S50A,B,C,D	C82A,B,C,D,E,F,G	W41A,B,C	U60C,D,E,F

ZONE A No water may be abstracted from these drainage regions except as set out under Schedule 1 of the National Water Act	ZONE B 60 m ³ per hectare per annum may be abstracted from these drainage regions		ZONE C 300 m ³ per hectare per annum may be abstracted from these drainage regions		ZONE D 750 m ³ per hectare per annum may be abstracted from these drainage regions
	C24B	T11A,B,D,E	C83A,B,C,D,E,F,G,H,J,K,L	W41D	U70C,D,F
	C25B,C,E,F	T20D,E,F,G	C92 – all	W42A,B,C,D,F,M	V50C
	C31F	T31J	D13A,B,C,D,E,F,K	W51A,B,C,D	W11A
	C32A,B,C	T32 – all	D16A	W52A,B,C	W12C,F,J
	C41C,F,G,H,J	T33A,B,C,D,H,J,K	D21D,E,F,G,H,L	W53A,B	W23C,D
	C42L	T34A,B,C,D,E,F,J,K	D22A,B,D,G,H,L	W54,W55 – all	W31J,L
	C43	T35A,B,C,D,F,G,L,M	D41A,G,L	W56A,B	W32A,B,F,H
	C51,C52 – all	T36 – ALL	E10D,E,F,G,H,J,K	W57J	W43F
	C60G,H,J	T40A,B,C,D,E	E21H,J,K	X11A,B,C	W45 – all
	C70C,D,E,F,G,H,K	T51C,H,J	E24A,L,M	X11H,J,K	W57K
	C82H	T52A,B,C,D,E,F,G,H,J,K	E40D	X12 – all	W70A
	C83M	T60A,B,C,F,J,K	G10C,D,F,H,J,K,L,M	X13A	
	C91,D12 – all	T70A,B,C,E,F,G	G21A,C,D,E,F	X14A,B,D,E,G,H	
	D13G,H,J,L,M	U10E,F,G,H,J,K,L	G22E,G,H,J,K	X21H,K	
	D14 – all	U20A,B,C,D,E,F,G,H,J	G30A,B,C,D,E,F,G	X22B,C,D,E,F,G,H,J,K	
	D15G,H	U40A,B	G40F,K	X23 – all	
	D18K,L	U60A,B	G50C	X24A,B,C,D	
	D23A,C,D,E,F,G,H,J	U70A,B	H10D,F,H	X31A,B,C,D,E,F,G,H,J	
	D24 – all	V11C,D,F,H,J,K,L,M	H20H	X32A,B,C,D,E,F	

ZONE A No water may be abstracted from these drainage regions except as set out under Schedule 1 of the National Water Act	ZONE B 60 m ³ per hectare per annum may be abstracted from these drainage regions		ZONE C 300 m ³ per hectare per annum may be abstracted from these drainage regions		ZONE D 750 m ³ per hectare per annum may be abstracted from these drainage regions
	D32,D33,D34,D35 – all	V12,V14 – all	H30A,B,D,E		
	D41B,D,J	V13B,C,D,E	H40B,C,D,E,F,G, H,J,L		
	D51,D52 – all	V20D,E,F,G,J	H50 – all		
	D53A,B,C	V31A,B,E,F	H60D,E,F,G,H,J		
	D54,D55,D56 – all	V33B,C,D	H70E,F		
	D57A,B	V40A,C	J23J		
	D58,D61,D62,D71 ,D72 – all	V60J,K	J25 – all		
	D73A,B,F	V70E,F,G	J33E,F		
	E21A,B,C,D,E,F,G ,L	W12A,D,G,H	J35A,C,D,E,F		
	E22A,B,C,F,G	W21C,E,F,K,L	K10B,D,F		
	E23A,B,E	W22B,C,D,E,F,G, H,J,K,L	K20A		
	E24B,C,E,F,J,K	W23A,B	K30A,B,C		
	E32	W31B,C,D,E,F,G, H,K	K40D		
	E33C,F,G	W32C,D,E,G	K90D,E,F,G		
	E40A,B,C	W41E,F,G	L90 – all		
	F30A,C,D	W42E,G,H,J,K,L	M20B		
	F50A,B,C,E	W44	P20A		
	F60E	W51E,F	Q41A,B		
	G30H	W52D	Q92A,B,D		
	G50D,G,H	W53C,D,E	Q93A		
	H10A	X11D,E,F,G	Q94 – all		
	H20A	X13J,K,L	R10,R20,R30,R40 – all		

ZONE A No water may be abstracted from these drainage regions except as set out under Schedule 1 of the National Water Act	ZONE B 60 m ³ per hectare per annum may be abstracted from these drainage regions		ZONE C 300 m ³ per hectare per annum may be abstracted from these drainage regions		ZONE D 750 m ³ per hectare per annum may be abstracted from these drainage regions
	H40A	X21A,B,C,D,E,F,G,J	R50A		
	H60K,L	X22A	S10E,F,G,H,J		
	H70A,B,C,G,H,J,K	X24E,F,G,H	S20C,D		
	H80D	X31K,L,M	S31D,E,F,G		
	H90D	X32G,H,J	S32,S40,S60,S70 – all		
	J11A,B,C,D,E,F,H,K	X33, X40 – all	S50E,F,G,H,J		
	J12B,C,D,E,F,G,H,J,K,L,M		T11C,F,G,H		

2 ENGAGING IN A CONTROLLED ACTIVITY, IDENTIFIED AS SUCH IN SECTION 37(1): IRRIGATION OF ANY LAND WITH WASTE OR WATER CONTAINING WASTE GENERATED THROUGH ANY INDUSTRIAL ACTIVITY OR BY A WATERWORK

[Section 21(e)]

Purpose of this authorisation

2.1. The authorisation permitted in terms of this Schedule replaces the need for a water user to apply for a licence in terms of the National Water Act provided that the

irrigation is within the limits and conditions set out in this authorisation.

Exclusion

2.2. This authorisation does not apply to a person who is not the lawful occupier of the land on which the wastewater irrigation takes place.

Compliance with National Water Act and other laws

2.3.(1) This authorisation does not-

- (a) replace any existing authorisation that is recognised under the National Water Act; or
- (b) exempt a person who uses water from compliance with any other provision of the National Water Act unless stated otherwise in this notice, or any other applicable law, regulation, ordinance or by-law.

(2) A person who uses water in terms of this authorisation is exempt from compliance with section 22(2)(e) of the National Water Act.

Area of applicability

2.4 This authorisation is applicable throughout the Republic of South Africa, except for any subterranean government water control area as defined in the Water Act, 1956 (Act No. 54 of 1956), prior to its repeal and set out in Table 2.1.

Duration of authorisation

2.5. This authorisation will be applicable for a period of three years from the date of publication of this notice, unless-

- (a) it is amended at any review period, which period shall be at intervals of one year from the date of publication of this notice;
- (b) the period is extended by a further notice in the *Gazette*; or

- (c) the water user is required to apply for a licence in terms of the National Water Act.

Definitions

2.6. In this authorisation, unless the context indicates otherwise, any word or expression to which a meaning has been assigned in terms of the National Water Act shall have that meaning, and-

- (i) **"biodegradable industrial wastewater"** means wastewater that contains predominantly organic waste arising from industrial activities and premises including-
 - (a) milk processing;
 - (b) manufacture of fruit and vegetable products;
 - (c) sugar mills;
 - (d) manufacture and bottling of soft drinks;
 - (e) water bottling;
 - (f) production of alcohol and alcoholic beverages in breweries, wineries or malt houses;
 - (g) manufacture of animal feed from plant or animal products;
 - (h) manufacture of gelatine and glue from hides, skin and bones;
 - (i) abattoirs;
 - (j) fish processing; and
 - (k) feedlots;

- (ii) **"commercial activity"** means those activities identified in the Standard Industrial Classification of All Economic Activities (5th Edition), published by the Central Statistics Service, 1993, as amended and supplemented, under the following categories-
 - a) 6: wholesale and retail trade,
 - b) 7: transport, storage and communication,
 - c) 8: business services,
 - d) 9: community, social and personal services,
 - e) 0: personal and other services;

- (iii) **"domestic wastewater"** means wastewater arising from domestic and commercial activities and premises, and may contain sewage;
- (iv) **"irrigation"** means the application of wastewater for the purpose of crop production, and includes the cultivation of pasture;
- (v) **"monitoring programme"** means a programme for taking regular measurements of the quantity and/or quality of a water resource, waste or wastewater discharge at specified intervals and at specific locations to determine the chemical, physical and biological nature of the water resource, waste or wastewater discharge;
- (vi) **"organic waste"** means waste of non-anthropogenic origin that is readily biodegradable in the environment and does not contain any substances that may accumulate in the environment;
- (vii) **"primary treatment"** means treatment of wastewater by a physical process, which may involve maceration, sedimentation, screening and grit removal;
- (viii) **"secondary treatment"** means treatment of wastewater by a biological process, through solar and other energy, bacteria, algae and a variety of aquatic biota, to remove organic matter;
- (ix) **"wastewater"** means water containing waste, or water that has been in contact with waste material.

Irrigation with wastewater

2.7. A person who-

- (i) owns or lawfully occupies property registered in the Deeds Office as at the date of this notice; or
- (ii) lawfully occupies or uses land that is not registered or surveyed,

outside of the areas as excluded in paragraph 2.4 above, may on that property or land-

(1) irrigate up to 500 cubic metres of domestic or biodegradable industrial wastewater on any given day, provided the-

- (a) electrical conductivity does not exceed 200 milliSiemens per metre (mS/m);
- (b) pH is not less than 6 or more than 9 pH units;
- (c) Chemical Oxygen Demand (COD) does not exceed 400 mg/l after removal of algae;
- (d) faecal coliforms do not exceed 100 000 per 100 ml; and
- (e) Sodium Adsorption Ratio (SAR) does not exceed 5 for biodegradable industrial wastewater.

(2) irrigate up to 50 cubic metres of biodegradable industrial wastewater on any given day, provided the-

- (a) electrical conductivity does not exceed 200 milliSiemens per metre (mS/m);
- (b) pH is not less than 6 or more than 9 pH units;
- (c) Chemical Oxygen Demand (COD) does not exceed 5 000 mg/l after removal of algae;
- (d) faecal coliforms do not exceed 100 000 per 100 ml; and
- (e) Sodium Adsorption Ratio (SAR) does not exceed 5 for biodegradable industrial wastewater.

Registration of irrigation with wastewater

2.8.(1) A person who irrigates with wastewater in terms of this authorisation must submit a registration form obtained from the Department for registration of the water use before commencement of irrigation if more than 10 cubic metres of wastewater are irrigated on any given day.

(2) On written acknowledgement of receipt of the application form by the Department, the person will be regarded as a registered water user.

(3) The registered user must comply with any regulation promulgated in terms of section 26(1)(c) of the National Water Act.

Location of irrigation with wastewater

2.9. Wastewater irrigation in terms of this authorisation is only permitted if the irrigation takes place-

- (a) above the 100 year flood line, or alternatively, more than 100 metres from the edge of a water resource or a borehole which is utilised for drinking water or stock watering; and
- (b) on land that is not or does not overlie a Major Aquifer (identification of a Major Aquifer will be provided by the Department, upon written request).

Record-keeping and disclosure of information

2.10.(1) The registered user must ensure the establishment of monitoring programmes to monitor the quantity and quality of the wastewater to be irrigated prior to commencement of irrigation, as follows-

- (a) the quantity must be metered and the total recorded weekly; and
- (b) the quality must be monitored monthly as at the last day of each month by grab sampling, at the point at which the wastewater enters the irrigation system for all parameters listed in subparagraph 2.7.(1).

(2) The methods for the measurement of specific substances and parameters in any wastewater must be carried out-

- (a) by a laboratory that has been accredited under the South African National

Accreditation System (SANAS) in terms of SABS Code 0259 for that method;
or

(b) as approved in writing by the Minister.

(3) Upon the written request of the Responsible Authority the registered user must-

(a) ensure the establishment of any additional monitoring programmes; and

(b) appoint a competent person to assess the water use measurements made in terms of this authorisation and submit the findings to the Responsible Authority for evaluation.

(4) Subject to paragraph 2.10.(3) above, the registered user must keep a written record of the following wastewater irrigation and related activities, for at least three years-

(a) the location and extent of the area under irrigation, demarcated on a 1:50 000 topographic map;

(b) details of the crop(s) and the area under irrigation;

(c) the irrigation management techniques being practised;

(d) quantity of wastewater irrigated;

(e) quality of wastewater irrigated;

(f) details of the monitoring programme;

(g) details of failure and malfunctions in the irrigation system and details of measures taken; and

such information must be made available upon written request to the Responsible Authority.

(5) Any information on the occurrence of any incident that has or is likely to have a detrimental impact on the water resource quality must be reported to the Responsible Authority.

Precautionary practices

2.11.(1) The registered user must follow acceptable construction, maintenance and operational practices to ensure the consistent, effective and safe performance of the wastewater irrigation system, including the prevention of-

- (a) waterlogging of the soil and pooling of wastewater on the surface of the soil;
- (b) nuisance conditions such as flies or mosquitoes, odour or secondary pollution;
- (c) waste, or wastewater, entering any surface water resource;
- (d) the unreasonable chemical or physical deterioration of, or any other damage to, the soil of the irrigation site; and
- (e) the unauthorised use of the wastewater by members of the public.

(2) All reasonable measures must be taken for storage of the wastewater used for irrigation when irrigation cannot be undertaken.

(3) Suspended solids must be removed from any wastewater, and the resulting sludge disposed of according to the requirements of any relevant law or regulation, including-

- (a) "Permissible utilisation and disposal of sewage sludge" Edition 1, 1997. Water Research Commission Report No TT 85/97; and
- (b) "Guide: Permissible utilisation and disposal of treated sewage effluent", 1978. Department of National Health and Population Development Report No. 11/2/5/3 (obtainable from the Department upon written request).

(4) All reasonable measures must be taken to provide for mechanical, electrical, operational, or process failures and malfunctions of the wastewater irrigation system.

(5) All reasonable measures must be taken to collect stormwater runoff containing waste or wastewater emanating from the area under irrigation and to retain it for disposal.

Inspections

2.12. Any property or land in respect of which a water use has been authorised in terms of this notice must be made available for inspection by an authorised person in terms of section 125 of the National Water Act.

Offences

2.13. Any person who contravenes any provision of this authorisation is guilty of an offence and is subject to the penalty set out in section 151(2) of the National Water Act.

NOTE: Information regarding the drainage regions referred to in Table 2.1 can be obtained from the Department, upon written request.

TABLE 2.1 Subterranean government water control areas excluded from General Authorisation for irrigation with waste

Primary drainage region	Tertiary/ Quaternary drainage region	Description of subterranean government water control area	Government Notice No.	Government Gazette Date
H	H30	Baden	136	1967-06-16
A	A30	Bo-Molopo	1324	1963-08-30
C	C30	Bo-Molopo	1993	1965-12-17
D	D41	Bo-Molopo	R634	1966-04-29
A	A24	Crocodile River Valley	208	1981-10-23
A	A21	Crocodile River Valley	18	1983-02-18
A	A21, A22	Kroondal-Marikana	180	1963-06-17
G	G10,G30	Lower Berg River Valley/Saldanha	185	1976-09-10
A,B	A60,B50,B31	Nyl River Valley	56	1971-03-26
G	G30	Strandfontein	2463	1988-12-09
M	M10,M20,M30	Uitenhage	260	1957-08-23
G	G30	Wadrif	992	1990-05-11
G	G20	Yzerfontein	27	1990-02-09
G	G30	Graafwater	1423	1990-06-29
A	A70	Dendron-Vivo	813	1994-04-29
A	A60	Dorpsrivier	312	1990-02-16

Primary drainage region	Tertiary/Quaternary drainage region	Description of subterranean government water control area	Government Notice No.	Government Gazette Date
C	C24	Ventersdorp	777	1995-06-02

- 3 DISCHARGE OF WASTE OR WATER CONTAINING WASTE INTO A WATER RESOURCE THROUGH A PIPE, CANAL, SEWER OR OTHER CONDUIT; AND
DISPOSING IN ANY MANNER OF WATER WHICH CONTAINS WASTE FROM, OR WHICH HAS BEEN HEATED IN, ANY INDUSTRIAL OR POWER GENERATION PROCESS**

[Section 21(f) and (h)]

Purpose of this authorisation

3.1. The authorisation permitted in terms of this Schedule replaces the need for a water user to apply for a licence in terms of the National Water Act provided that the discharge is within the limits and conditions set out in this authorisation.

Exclusion

3.2. This authorisation does not apply to a person who discharges wastewater through sea outfalls, or to an aquifer, or any other groundwater resource.

Compliance with National Water Act and other laws

3.3.(1) This authorisation does not-

- (a) apply to any water use under Schedule 1 of the National Water Act;

- (b) replace any existing authorisation that is recognised under the National Water Act;
- (c) exempt a person from compliance with section 7(2) of the Water Service Act, 1997 (Act No. 108 of 1997); or
- (d) exempt a person who uses water from compliance with any other provision of the National Water Act unless stated otherwise in this notice, or any other applicable law, regulation, ordinance or by-law.

(2) A person who uses water in terms of this authorisation is exempt from compliance with section 22(2)(e) of the National Water Act.

Area of applicability

3.4 This authorisation is applicable throughout the Republic of South Africa, except for the areas set out in Table 3.1.

NOTE: Information regarding the drainage regions referred to in Table 3.1 can be obtained from the Department, upon written request.

TABLE 3.1 Areas excluded from General Authorisation for discharges to water resources

Primary drainage region	Tertiary drainage region	Description of main river in drainage region
B	B11, B12 B20 B31, B32 B41, B42 B60	Olifants River Wilge River Olifants River Steelpoort River Blyde River
W	W51, W52, W53, W54, W55, W56, W57	Usutu River
X	X11, X12, X13, X14 X21, X22, X23, X24	Nkomati River

Primary drainage region	Tertiary drainage region	Description of main river in drainage region
	X31, X32, X33 X40	

Duration of authorisation

3.5. This authorisation will be applicable for a period of five years from the date of this notice, unless-

- (a) it is amended at any review period, which period shall be at intervals of two years from the date of publication of this notice;
- (b) the time period is extended by a further notice in the *Gazette*; or
- (c) the water user is required to apply for a licence in terms of the National Water Act.

Definitions

3.6. In this authorisation unless the context indicates otherwise, any word or expression to which a meaning has been assigned in terms of the National Water Act shall have that meaning, and-

- (i) "**commercial activity**" means those activities identified in the Standard Industrial Classification of All Economic Activities (5th Edition), published by the Central Statistics Service, 1993, as amended and supplemented, under the following categories-
 - a) 6: wholesale and retail trade,
 - b) 7: transport, storage and communication,
 - c) 8: business services,
 - d) 9: community, social and personal services,
 - e) 0: personal and other services;

- (ii) **"complex industrial wastewater"** means wastewater arising from industrial activities and premises, that contains-
- a) a complex mixture of substances that are difficult or impractical to chemically characterise and quantify, or
 - b) one or more substances, for which a Wastewater Limit Value has not been specified, and which may be harmful or potentially harmful to human health, or to the water resource
- (identification of complex industrial wastewater will be provided by the Department upon written request);
- (iii) **"domestic wastewater"** means wastewater arising from domestic and commercial activities and premises, and may contain sewage;
- (iv) **"domestic wastewater discharge"** means a wastewater discharge consisting of 90% or more domestic wastewater, by volume, that is collected, treated and subsequently disposed of;
- (v) **"industrial activity"** means those activities identified in the Standard Industrial Classification of All Economic Activities (5th Edition), published by the Central Statistics Service, 1993, as amended and supplemented, under the following categories-
- a) 2: mining and quarrying,
 - b) 3: manufacturing,
 - c) 4: electricity, gas and water supply,
 - d) 5: construction;
- (vi) **"industrial wastewater discharge"** means a wastewater discharge consisting of more than 10% industrial wastewater, by volume, that is collected, treated and subsequently disposed of;
- (vii) **"intake"** is water taken from a water resource, and excludes water taken from any source that is not a water resource;
- (viii) **"monitoring programme"** means a programme for taking regular measurements of the quantity and/or quality of a water resource, waste or

wastewater discharge at specified intervals and at specific locations to determine the chemical, physical and biological nature of the water resource, waste or wastewater discharge;

- (ix) **"listed water resources"** are those water resources listed in Table 3.4 and include any tributary of a listed water resource, and any water resource draining the catchment area of a listed water resource;
- (x) **"wastewater"** means water containing waste, or water that has been in contact with waste material;
- (xi) **"wastewater limit value"** means the mass expressed in terms of the concentration and/or level of a substance which may not be exceeded at any time. Wastewater Limit Values shall apply at the last point where the discharge of wastewater enters into a water resource, dilution being disregarded when determining compliance with the Wastewater Limit Values. Where discharge of wastewater does not directly enter a water resource, the Wastewater Limit Values shall apply at the last point where the wastewater leaves the premises of collection and treatment.

Discharging of domestic and industrial wastewater into water resources

3.7.(1) A person who-

(i) owns or lawfully occupies property registered in the Deeds Office as at the date of this notice; or

(ii) lawfully occupies or uses land that is not registered or surveyed,

outside of the areas as excluded in paragraph 3.4 above, may on that property or land-

(a) discharge up to 2 000 cubic metres of wastewater on any given day into a water resource that is **not** a listed water resource referred to in Table 3.4, provided-

(i) the discharge complies with the General Limit Values set out in Table 3.2;

- (ii) the discharge does not alter the natural ambient water temperature of the receiving water resource by more than 3 degrees Celsius; and
- (iii) the discharge is not a Complex Industrial Wastewater.

(b) discharge up to 2 000 cubic metres of wastewater on any given day into a listed water resource referred to in Table 3.4, provided-

- (i) the discharge complies with the Special Limit Values set out in Table 3.2;
- (ii) the discharge does not alter the natural ambient water temperature of the receiving water resource by more than 2 degrees Celsius; and
- (iii) the discharge is not a Complex Industrial Wastewater.

(2) A person may discharge stormwater runoff from any premises, not containing waste or wastewater emanating from industrial activities and premises, into a water resource.

TABLE 3.2: Wastewater limit values applicable to discharge of wastewater into a water resource

SUBSTANCE/PARAMETER	GENERAL LIMIT	SPECIAL LIMIT
Faecal Coliforms (per 100 ml)	1 000	0
Chemical Oxygen Demand (mg/l)	75*	30*
pH	5,5-9,5	5,5-7,5
Ammonia (ionised and un-ionised) as Nitrogen (mg/l)	3	2
Nitrate/Nitrite as Nitrogen (mg/l)	15	1,5
Chlorine as Free Chlorine (mg/l)	0,25	0
Suspended Solids (mg/l)	25	10
Electrical Conductivity (mS/m)	70 mS/m above intake to a maximum of 150 mS/m	50 mS/m above background receiving water, to a maximum of 100 mS/m
Ortho-Phosphate as phosphorous (mg/l)	10	1 (median) and 2,5 (maximum)

SUBSTANCE/PARAMETER	GENERAL LIMIT	SPECIAL LIMIT
Fluoride (mg/l)	1	1
Soap, oil or grease (mg/l)	2,5	0
Dissolved Arsenic (mg/l)	0,02	0,01
Dissolved Cadmium (mg/l)	0,005	0,001
Dissolved Chromium (VI) (mg/l)	0,05	0,02
Dissolved Copper (mg/l)	0,01	0,002
Dissolved Cyanide (mg/l)	0,02	0,01
Dissolved Iron (mg/l)	0,3	0,3
Dissolved Lead (mg/l)	0,01	0,006
Dissolved Manganese (mg/l)	0,1	0,1
Mercury and its compounds (mg/l)	0,005	0,001
Dissolved Selenium (mg/l)	0,02	0,02
Dissolved Zinc (mg/l)	0,1	0,04
Boron (mg/l)	1	0,5

*** After removal of algae**

Registration of discharges into water resources

3.8.(1) A person who discharges wastewater into a water resource in terms of this authorisation must submit a registration form obtained from the Department for registration of the water use before commencement of the discharge.

(2) On written acknowledgement of receipt of the application form by the Department, the person will be regarded as a registered water user.

(3) The registered user must comply with any regulation promulgated in terms of section 26(1)(c) of the National Water Act.

Record-keeping and disclosure of information

3.9.(1) The registered user must ensure the establishment of monitoring programmes to monitor the quantity and quality of the discharge prior to the commencement of the discharge, as follows-

- (a) the quantity of the discharge must be metered and the total recorded weekly;
and
- (b) the quality of domestic wastewater discharges must be monitored monthly by grab sampling as set out in Table 3.3.

TABLE 3.3: Monitoring requirements for domestic wastewater discharges

DISCHARGE VOLUME ON ANY GIVEN DAY	MONITORING REQUIREMENTS
< 10 cubic metres	None
10 to 100 cubic metres	pH Electrical Conductivity (mS/m) Faecal Coliforms (per 100 ml)
100 to 1000 cubic metres	pH Electrical Conductivity (mS/m) Faecal Coliforms (per 100 ml) Chemical Oxygen Demand (mg/l) Ammonia as Nitrogen (mg/l) Suspended Solids (mg/l)
1 000 to 2 000 cubic metres	pH Electrical Conductivity (mS/m) Faecal Coliforms (per 100 ml) Chemical Oxygen Demand (mg/l) Ammonia as Nitrogen (mg/l) Nitrate/Nitrite as Nitrogen (mg/l) Free Chlorine (mg/l) Suspended Solids (mg/l) Ortho-Phosphate as Phosphorous (mg/l)

- (c) the quality of industrial wastewater discharges must be monitored weekly by grab sampling-
 - (i) for all substances which have been added to the water through any industrial activity;
 - (ii) for all substances which have been concentrated in the water through any industrial activity;

(iii) for all substances which may be harmful or potentially harmful to human health or to the water resource quality; and

(iv) as set out in paragraph 3.9(1)(b) above, if the wastewater contains any domestic wastewater.

(d) The methods for the measurement of specific substances and parameters in any wastewater must be carried out-

(i) by a laboratory that has been accredited under the South African National Accreditation System (SANAS) in terms of SABS Code 0259 for that method; or

(ii) as approved in writing by the Minister.

(2) Upon the written request of the Responsible Authority the registered user must-

(a) ensure the establishment of any additional monitoring programmes; and

(b) appoint a competent person to assess the water use measurements made in terms of this authorisation and submit the findings to the Responsible Authority for evaluation.

(3) Subject to paragraph 3.10(2) above, the registered user must, for at least five years, keep a written record of the following wastewater discharge and related activities-

(a) the quantity of wastewater discharged;

(b) the quality of wastewater discharged;

(c) details of the monitoring programme/s;

(d) details of failures and malfunctions in the discharge system and details of measures taken, and

such information must be made available upon written request to the Responsible Authority.

(4) Any information on the occurrence of any incident that has or is likely to have a detrimental impact on the water resource quality must be reported to the Responsible Authority.

Precautionary practices

3.10.(1) The registered user must follow acceptable construction, maintenance and operational practices to ensure the consistent, effective and safe performance of the discharge.

(2) All reasonable measures must be taken to provide for mechanical, electrical, operational, or process failures and malfunctions of the discharge system.

Inspections

3.11. Any property or land in respect of which a water use has been authorised in terms of this notice must be made available for inspection by an authorised person in terms of section 125 of the National Water Act.

Offences

3.12. Any person who contravenes any provision of this authorisation is guilty of an offence and is subject to the penalty set out in section 151(2) of the National Water Act.

TABLE 3.4: Listed Water Resources

	WATER RESOURCE
1	Hout Bay River to tidal water
2	Eerste River to tidal water
3	Lourens River to tidal water
4	Steenbras River to tidal water
5	Berg and Dwars Rivers to their confluence
6	Little Berg River to Vogelvlei weir
7	Sonderend, Du Toits and Elandskloof Rivers upstream and inclusive of Thee Waterskloof Dam

	WATER RESOURCE
8	Witte River to confluence with Breede River
9	Dwars River to Ceres divisional boundary
10	Olifants River to the Ceres divisional boundary
11	Helsloot and Smalblaar (or Molenaars) Rivers to their confluence with Breede River
12	Hex River to its confluence with Breede River
13	Van Stadens River to tidal water
14	Buffalo River from its source to where it enters the King Williams Town municipal area
15	Klipplaat River from its source to Waterdown Dam
16	Swart Kei River to its confluence with the Klipplaat River
17	Great Brak River
18	Bongola River to Bongola Dam
19	Kubusi River to the Stutterheim municipal boundary
20	Langkloof River from its source to Barkly East municipal boundary
21	Kraai River to its confluence with the Langkloof River
22	Little Tsomo River
23	Xuka River to the Elliot district boundary
24	Tsitsa and Inxu Rivers to their confluence
25	Mvenyane and Mzimvubu Rivers from sources to their confluence
26	Mzintlava River to its confluence with the Mvalweni River
27	Ingwangwana River to its confluence with Umzimkulu River
28	Umzimkulu and Polela Rivers to their confluence
29	Elands River to the Pietermaritzburg-Bulwer main road
30	Umtamvuma and Weza Rivers to their confluence
31	Umkomaas and Isinga Rivers to their confluence
32	Lurane River to its confluence with the Umkomaas River
33	Sitnundjwana Spruit to its confluence with the Umkomaas River
34	Inudwini River to the Polela district boundary
35	Inkonza River to the bridge on the Donnybrook-Creighton road
36	Umlaas to the bridge on District Road 334 on the farm Maybole
37	Umgeni and Lions River to their confluence
38	Mooi River to the road bridge at Rosetta
39	Little Mooi and Hlatikula Rivers to their confluence
40	Bushmans River to Wagendrift Dam
41	Little Tugela River and Sterkspruit to their confluence
42	M'Lambonjwa and Mhlawazeni Rivers to their confluence
43	Mnweni and Sandhlwana Rivers to their confluence
44	Tugela River to its confluence with the Kombe Spruit

WATER RESOURCE			
45	Inyamvubu (or Mnyamvubu) River to Craigie Burn Dam		
46	Umvoti River to the bridge on the Seven Oaks-Rietvlei road		
47	Yarrow River to its confluence with the Karkloof River		
48	Incandu and Ncibidwane Rivers to their confluence		
49	Ingogo River to its confluence with the Harte River		
50	Pivaan River to its confluence with Soetmelkspruit		
51	Slang River and the Wakkerstroom to their confluence		
52	Elands and Swartkoppie Spruit to their confluence		
53	All tributaries of the Komati River between Nooitgedacht Dam and its confluence with and including Zevenfontein Spruit		
54	Seekoespruit to its confluence with Buffelspruit		
55	Crocodile River and Buffelskloofspruit to their confluence		
56	All tributaries of the Steelpoort River down to its confluence with and including the Dwars River		
57	Potspruit to its confluence with the Waterval River		
58	Dorps River (or Spekboom River) to its confluence with the Marambanspruit		
59	Ohrigstad River to the Ohrigstad Dam		
60	Klein-Spekboom River to its confluence with the Spekboom River		
61	Blyde River to the Pilgrim's Rest municipal boundary		
62	Sabie River to the Sabie municipal boundary .		
63	Nels River to the Pilgrim's Rest district boundary		
64	Houtbosloop River to the Lydenburg district boundary		
65	Blinkwaterspruit to Longmere Dam		
66	Assegaai River upstream and inclusive of the Heyshope Dam		
67	Komati River upstream and inclusive of the Nooitgedacht Dam and the Vygeboom Dam		
68	Ngwempisi River upstream and inclusive of Jericho Dam and Morgenstond Dam		
69	Slang River upstream and inclusive of Zaaihoek Dam		
70	All streams flowing into the Olifants River upstream and inclusive of Loskop Dam, Witbank Dam and Middelburg Dam		
71	All streams flowing into Ebenezer Dam on the Great Letaba River		
72	Dokolewa River to its confluence with the Politzi River		
73	Ramadiepa River to the Merensky Dam on the farm Westfalia 223, Letaba		
74	Pienaars River and tributaries as far as Klipvoor Dam		
	RAMSAR LISTED WETLANDS:	PROVINCE	LOCATION
75	Barberspan	North-West	26°33 S 25°37 E
76	Blesbokspruit	Gauteng	26°17 S 28°30 E
77	De Hoop Vlei	Western Cape	34°27 S 20°20 E
78	De Mond (Heuningnes Estuary)	Western Cape	34°43 S 20°07 E

WATER RESOURCE			
79	Kosi Bay	Kwazulu-Natal	27°01 S 32°48 E
80	Lake Sibaya	Kwazulu-Natal	27°20 S 32°38 E
81	Langebaan	Western Cape	33°06 S 18°01 E
82	Orange River Mouth	Northern Cape	28°40 S 16°30 E
83	St Lucia System	Kwazulu-Natal	28°00 S 32°28 E
84	Seekoeivlei Nature Reserve	Free State	27°34 S 29°35 E
85	Verlorenvlei	Western Cape	32°24 S 18°26 E
86	Verloren Valei	Mpumalanga	25°14 S 30°4 E
87	Nylsvlei	Northern	24°39 S 28°42 E
88	Wilderness Lakes	Western Cape	33°59 S 22°39 E

4 DISPOSING OF WASTE IN A MANNER WHICH MAY DETRIMENTALLY IMPACT ON A WATER RESOURCE

[Section 21(g)]

Purpose of this authorisation

4.1. The authorisation permitted in terms of this Schedule replaces the need for a water user to apply for a licence in terms of the National Water Act for the disposal of waste, provided that the disposal is within the limits and conditions set out in this authorisation.

Exclusion

4.2. This authorisation does not apply to a person who is not the lawful occupier of the land on which the disposal takes place.

Compliance with National Water Act and other laws

4.3.(1) This authorisation does not-

- (a) replace any existing authorisation that is recognised under the National Water Act;
- (b) exempt a person from compliance with section 7(2) of the Water Services Act, 1997 (Act No. 108 of 1997);
- (c) exempt a person from compliance with the provisions of the National Building Regulations and Building Standards Act, 1977 (Act No. 103 of 1977) for construction, operation and maintenance of any structure used for the collection, treatment or disposal of waste; or
- (d) exempt a person who uses water from compliance with any other provision of the National Water Act unless stated otherwise in this notice, or any other applicable law, regulation, ordinance or by-law.

(2) A person who uses water in terms of this authorisation is exempt from compliance with section 22(2)(e) of the National Water Act.

Area of applicability

4.4 This authorisation is applicable throughout the Republic of South Africa, except for any subterranean government water control area as defined in the Water Act, 1956 (Act No. 54 of 1956), prior to its repeal and set out in Table 4.1.

Duration of authorisation

4.5. This authorisation will be applicable for a period of five years from the date of publication of this notice, unless-

- (a) it is amended at any review period, which period shall be at intervals of two years from the date of publication of this notice;
- (b) the period is extended by a further notice in the *Gazette*; or
- (c) the water user is required to apply for a licence in terms of the National Water Act.

Definitions

4.6. In this authorisation, unless the context otherwise indicates, any expression to which a meaning has been assigned in terms of the National Water Act shall have that meaning, and-

- (i) **"biodegradable industrial wastewater"** means wastewater that contains predominantly organic waste arising from industrial activities and premises, including-
 - (a) milk processing;
 - (b) manufacture of fruit and vegetable products;
 - (c) sugar mills;
 - (d) manufacture and bottling of soft drinks;
 - (e) water bottling;
 - (f) production of alcohol and alcoholic beverages in breweries, wineries or malt houses;
 - (g) manufacture of animal feed from plant or animal products;
 - (h) manufacture of gelatine and glue from hides, skin and bones;
 - (i) abattoirs;
 - (j) fish processing; and
 - (k) feedlots;

- (ii) **"category A mine"** means-
 - (a) any gold or coal mine;
 - (b) any mine with an extractive metallurgical process, including heap leaching;
 - or
 - (c) any mine where sulphate producing or acid generating material occurs in the mineral deposit;

- (iii) **"complex industrial wastewater"** means wastewater arising from industrial activities and premises, that contains-
 - a) a complex mixture of substances that are difficult or impractical to chemically characterise and quantify; or

b) one or more substances, for which a wastewater limit value has not been specified, and which may be harmful or potentially harmful to human health, or to the water resource-

(identification of complex industrial wastewater will be provided by the Department upon written request);

- (iv) "**domestic wastewater**" means wastewater arising from domestic and commercial activities and premises, and may contain sewage;
- (v) "**evaporation pond**" means a dam designed to collect and dispose of wastewater through evaporation, from which any concentrated waste or sludge must be removed and disposed of according to the requirements of any relevant laws and regulations;
- (vi) "**grey water**" refers to wastewater generated through domestic activities and premises, including washing, bathing and food preparation, but does not contain sewage;
- (vii) "**monitoring programme**" means a programme for taking regular measurements of the quantity and/or quality of a water resource, waste or wastewater discharge at specified intervals and at specific locations to determine the chemical, physical and biological nature of the water resource, waste or wastewater discharge;
- (viii) "**organic waste**" means waste of non-anthropogenic origin that is readily biodegradable in the environment and does not contain any substances that may accumulate in the environment;
- (ix) "**on-site disposal**" refers to the disposal of wastewater on individual properties not permanently linked to a central waste collection, treatment and disposal system, such as septic tank systems, conservancy tank systems, soakaway systems, French Drains and pit latrines;

- (x) **"primary treatment"** means the treatment of wastewater by a physical process, which may involve maceration, sedimentation, screening and grit removal;
- (xi) **"secondary treatment"** means the treatment of wastewater by a biological process, through solar energy, bacteria, algae and a variety of aquatic biota, to remove organic matter;
- (xii) **"wastewater"** means water containing waste, or water that has been in contact with waste material;
- (xiii) **"wastewater pond system"** means a dam or system of dams designed to collect wastewater and to conduct primary and secondary treatment, from which treated wastewater is disposed of.

Storage of domestic and/or biodegradable industrial wastewater for the purpose of re-use

4.7. A person who-

- (i) owns or lawfully occupies property registered in the Deeds Office as at the date of this notice; or
- (ii) lawfully occupies or uses land that is not registered or surveyed,

outside of the areas set out in Table 4.1, may on that property or land store up to 5 000 cubic metres of domestic and/or biodegradable industrial wastewater for the purpose of re-use.

Storage of domestic and/or biodegradable industrial wastewater for the purpose of disposal

4.8. A person who-

- (i) owns or lawfully occupies property registered in the Deeds Office as at the date of this notice; or
- (ii) lawfully occupies or uses land that is not registered or surveyed,

outside of the areas set out in Table 4.1, may on that property or land store domestic

and/or biodegradable industrial wastewater for the purpose of disposal of-

- (a) up to 10 000 cubic metres per property or land; or
- (b) up to 50 000 cubic metres in a wastewater pond system per property or land.

Disposal of domestic and/or biodegradable industrial wastewater

4.9. A person who-

(i) owns or lawfully occupies property registered in the Deeds Office as at the date of this notice; or

(ii) lawfully occupies or uses land that is not registered or surveyed,

outside of the areas set out in Table 4.1, may on that property or land dispose of wastewater as follows-

(a) up to 1 000 cubic metres of domestic and/or biodegradable industrial wastewater, on any given day-

(i) into a wastewater pond system; or

(ii) into an evaporation pond system;

(b) domestic wastewater or biodegradable wastewater into a wastewater irrigation system as set out under General Authorisation 2;

(c) wastewater to an on-site disposal facility for-

(i) grey water generated by a single household;

(ii) up to one cubic metre of biodegradable industrial wastewater on any given day; and

(iii) domestic wastewater to a communal septic tank serving no more than 50 households;

- (d) domestic wastewater generated by a single household not permanently linked to a central waste collection, treatment and disposal system, to an on-site disposal facility; and
- (e) stormwater runoff from any premises not containing waste or wastewater from industrial activities and premises.

Disposal of mine waste or residue

4.10. A person may dispose of mine residue into mine residue deposits provided-

- (a) the mine residue is not from a Category A mine;
- (b) the disposal is in accordance with Government Notice No. 704, dated 4 June 1999; and
- (c) the disposal is in accordance with SABS Code 0286.

Registration of wastewater storage

4.11.(1) A person who stores wastewater in terms of this authorisation must submit a registration form obtainable from the Department, for registration of the water use before commencement of storage if more than 1 000 cubic metres are stored for disposal or if more than 500 cubic metres are stored for re-use.

(2) On written acknowledgement of receipt of the application form by the Department, the person will be regarded as a registered water user.

(3) The registered user must comply with any regulation promulgated in terms of section 26(1)(c) of the National Water Act.

Registration of wastewater disposal

4.12.(1) A person who disposes of wastewater in terms of this authorisation must submit a registration form obtained from the Department, for registration of the water use before the commencement of the disposal if more than 50 cubic metres of

domestic wastewater or biodegradable industrial wastewater is disposed of on any given day.

(2) The responsible local authority must submit a registration form obtained from the Department, to register the water use for disposal of domestic wastewater in-

- (a) areas where more than 5 000 households are served by on-site disposal sites;
- (b) areas where the density of on-site disposal sites exceeds 10 per hectare; or
- (c) areas served by communal septic tanks.

(3) On written acknowledgement of receipt of the application form by the Department, the person will be regarded as a registered water user.

(4) The registered user must comply with any regulation promulgated in terms of section 26(1)(c) of the National Water Act.

Location of wastewater storage dams and wastewater disposal sites

4.13. Wastewater storage dams and wastewater disposal sites must be located-

- (a) outside of a watercourse;
- (b) above the 100 year flood line, or alternatively, more than 100 metres from the edge of a water resource or a borehole which is utilised for drinking water or stock watering; and
- (c) on land that is not, or does not overlie, a Major Aquifer (identification of a Major Aquifer will be provided by the Department upon written request).

Record-keeping and disclosure of information

4.14.(1) The registered user, with the exception of a local authority, must ensure the establishment of monitoring programmes to monitor the quantity and quality of the

wastewater prior to storage or disposal, as follows-

- (a) for the storage of wastewater, the quantity must be recorded monthly; or
- (b) for the disposal of wastewater, the quantity must be gauged or metered and recorded monthly.

(2) Upon the written request of the Responsible Authority, the registered user with the exception of a local authority, must-

- (a) ensure the establishment of any additional monitoring programmes; and
- (b) appoint a competent person to assess the water use measurements made in terms of this authorisation, and to submit the findings to the Responsible Authority for evaluation.

(3) Subject to paragraph 4.14(2) above, the registered user with the exception of a local authority must, for at least five years, keep a written record of the following wastewater storage or wastewater disposal and related activities-

- (a) the location of the storage dam or wastewater disposal site;
- (b) the quantity of wastewater stored or disposed of or re-used;
- (c) the quality of wastewater stored or disposed of, where applicable;
- (d) details of the monitoring programme;
- (e) details of failures and malfunctions of any wastewater disposal system or wastewater storage dam that the registered user is responsible for, and

such information must be made available upon written request to the Responsible Authority.

(4) Any information on the occurrence of any incident that has or is likely to have a detrimental impact on the water resource quality must be reported to the Responsible Authority.

Precautionary practices

4.15.(1) The registered user must follow acceptable construction, maintenance and operational practices to ensure the consistent, effective and safe performance of any

wastewater disposal system or wastewater storage dam.

(2) All reasonable measures must be taken to prevent wastewater overflowing from any wastewater disposal system or wastewater storage dam.

(3) All reasonable measures must be taken to provide for mechanical, electrical or operational failures and malfunctions of any wastewater disposal system or wastewater storage dam.

(4) Sewage sludge must be removed from any wastewater and the resulting sludge disposed of according to the requirements of any relevant law and regulation, including-

(a) "Permissible utilisation and disposal of sewage sludge" Edition 1, 1997. Water Research Commission Report No TT 85/97; and

(b) "Guide: Permissible utilisation and disposal of treated sewage effluent", 1978. Department of National Health and Population Development Report No. 11/2/5/3 (obtainable from the Department upon written request).

Inspections

4.16. Any property or land in respect of which a water use has been authorised in terms of this notice must be made available for inspection by an authorised person in terms of section 125 of the National Water Act.

Offences

4.17. Any person who contravenes any provision of this authorisation is guilty of an offence and is subject to the penalty set out in section 151(2) of the National Water Act.

NOTE: Information regarding the drainage regions referred to in Table 4.1 can be obtained from the Department, upon written request.

TABLE 4.1 Subterranean government water control areas excluded from General Authorisation for disposal of waste

Primary drainage region	Tertiary/ Quaternary drainage region	Description of subterranean government water control area	Government Notice No.	Government Gazette Date
H	H30	Baden	136	1967-06-16
A	A30	Bo-Molopo	1324	1963-08-30
C	C30	Bo-Molopo	1993	1965-12-17
D	D41	Bo-Molopo	R634	1966-04-29
A	A24	Crocodile River Valley	208	1981-10-23
A	A21	Crocodile River Valley	18	1983-02-18
A	A21, A22	Kroondal-Marikana	180	1963-06-17
G	G10,G30	Lower Berg River Valley/Saldanha	185	1976-09-10
A,B	A60,B50,B31	Nyl River Valley	56	1971-03-26
G	G30	Strandfontein	2463	1988-12-09
M	M10,M20,M30	Uitenhage	260	1957-08-23
G	G30	Wadrif	992	1990-05-11
G	G20	Yzerfontein	27	1990-02-09
G	G30	Graafwater	1423	1990-06-29
A	A70	Dendron-Vivo	813	1994-04-29
A	A60	Dorpsrivier	312	1990-02-16
C	C24	Ventersdorp	777	1995-06-02