MANAGEMENT OF HYDROGEN SULPHIDE GENERATION AT A KRAFT PAPER MILL

by

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DECLARATION

I, the undersigned, hereby declare that the work contained in this dissertation is my own original work and has not previously in its entirety or in part been submitted for a degree at any other university.

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By

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SUMMARY

A local integrated pulp and paper Kraft mill had come under pressure from the local communities and mill personnel to reduce the odours that were perceived to be generated at the Farm Dams and irrigation farm situated adjacent to the mill.

The typical odours associated with Kraft mills are due to the generation of four reduced sulphur compounds such as hydrogen sulphide (H_2S), methyl-mercaptan (CH_3SH), dimethyl-sulphide $(CH_3)_2S$ and dimethyl-disulphide $(CH_3)_2S_2$. These compounds are collectively referred to as Total Reduced Sulphur (TRS) components which are generated as a direct result of the Kraft pulping and chemical recovery process. These components can either be in the gaseous or aqueous phase depending on the characteristics of the effluent.

Gaseous and aqueous TRS profiling of the mill indicated that hydrogen sulphide (H_2S) was the main odour component generated and emitted from the Clarifiers and the Treated Effluent Transfer Sump (TETS) at the effluent treatment plant. The hydrogen sulphide (H_2S) emission levels were affected by process upsets, sludge removal frequencies, chemical composition of the effluent, Sulphate Reducing Bacteria (SRB) activity, pH and temperature fluctuations.

Treatment options such as pH control using slaked lime, dosing of biocides, addition of biomodifiers and/or a sulphate reduction inhibitor were investigated. The use of slaked lime, $Ca(OH)_2$, for pH control was not practical due to continuous pH fluctuations, increasing the pH would increase the scaling tendencies of the effluent and would also affect the soil cation-anion exchange properties of the irrigated farm land.

The use of non-oxidising biocides was effective in reducing SRB activity between 99.2% and 99.8% at dosages between 4 mg/l and 25 mg/l. However, the use of biocides was not considered as a long term treatment option due to the various disadvantages such as the stability of the biocides at fluctuating pH and temperatures, half-life, environmental accumulation, toxicity and costs.

The aqueous H_2S level was reduced by 79% using different combinations of biomodifiers (nitrates, nitrites, molybdenum). Increasing the dosages of the biomodifiers (> 500mg/l) would be required to increase the reduction of H_2S levels by more than 79%. The increased dosages would significantly increase the cost of the treatment programme. The accumulation of nitrates, nitrites and molybdenum could affect the soil texture, cation-anion exchange capacity, permeability, Sodium Absorption Ratio (SAR) and nutrient availability.

A more environmentally friendly and cost effective treatment was found using sodium nitrate (biomodifier) together with AQ (sulphate reduction inhibitor). The continuous dosing of 50 mg/l sodium nitrate together with 4 mg/l AQ would be effective in reducing the average aqueous H_2S levels (40 mg/l) by at least 92%. This treatment would also be compatible with aeration or oxidation procedures to further increase the removal of H_2S to achieve an aqueous H_2S level of <1 mg/l. Aeration or oxidation would also increase the dissolved oxygen and COD levels, increase the inhibition of SRB activity and oxidise any reduced sulphur.

The dosing of sodium nitrate and AQ to control the generation of H_2S is not patented in South Africa. It can, therefore, be used to treat the Kraft mill effluent without violating any intellectual property rights in South Africa.

KEYWORDS: Anthraquinone, Biocides, Biomodifiers, Effluent treatment plant, Hydrogen sulphide, Kraft mills, Odours, pH control, Slaked lime, Sulphate Reducing Bacteria (SRB), Total Reduced Sulphur (TRS)

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LIST OF ABBREVIATIONS

<	Less than
>	More than
≤	Equal to or less than
≥	Equal to or more than
AMP	Adenosine Monophosphate
APS	Adenosine Phosphosulphate
aq	Aqueous
AQ	9,10 Anthraquinone
AR	Analytical Reagent
ATSDR	Agency for Toxic Substances and Disease Registry (USA)
ATP	Adenosine Triphosphate
BOD	Biological Oxygen Demand
cfu/ml	colony forming unit per milliliter
CSIR	Council for Scientific and Industrial Research (South Africa)
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
E*h*	Electrical potential
g	Gaseous phase
GC-FPD	Gas Chromatography-Flame Photometric Detector
KLB	Kraft Liner Board
mV	Millivolt
NACE	National Association of Corrosion Engineers (USA)
NCASI	National Council for Air and Stream Improvement (USA)
NP	Newsprint
ORP	Oxidation Reduction Potential
PEL	Permissible Exposure Level
pK	Dissociation constant
PPi	Inorganic Pyrophosphate
R.S.I	Ryznar Stability Index
SAR	Sodium Absorption Ratio
SRB	Sulphate Reducing Bacteria
TETS	Treated Effluent Transfer Sump
TLV	Threshold Limit Value
TRS	Total Reduced Sulphur
UV	Ultraviolet

WHO	World Health Organisation (Switzerland)

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

A local integrated Kraft pulp and paper mill had come under pressure from the surrounding communities to reduce the foul odours that were perceived to be generated at the Farm Dams and irrigation farm situated adjacent to the mill (Dilsook, 2005). The mill generates approximately 27 000 m^3/d of effluent which is treated by clarification (solids separation) and then pumped into the Farm Dams before irrigation (Dilsook, 2005). The effluent is then irrigated over approximately 514 hectares of pastures according to the mill's Water Use license (Dilsook, 2005).

The typical odours associated with Kraft mills are due to the generation of four reduced sulphur gases, namely, hydrogen sulphide (H_2S), methyl-mercaptan (CH_3SH), dimethyl-sulphide $(CH_3)_2S$ and dimethyl-disulphide $(CH_3)_2S_2$. These gases are collectively referred to as Total Reduced Sulphur (TRS) components (Bonnin *et. al.*, 1990; Bordado and Gomes, 2003; Olendorf *et. al.*, 2000; Pinkerton, 1999). The TRS components are generated as a direct result of the Kraft pulping and chemical recovery process (Hagen and Hartung, 1997).

Gaseous and aqueous TRS monitoring of the mill indicated the effluent treatment plant to be the main source of H_2S generation (Dilsook, 2004). This was found to be caused by the reduction of sulphates to sulphides by anaerobic bacteria collectively known as Sulphate Reducing Bacteria (SRB) (Hoa *et. al.*, 1996), process upsets, pH and temperature fluctuations of the various incoming effluent streams (Dilsook, 2005, Rava *et. al.*, 2005). The main sources of sulphates in the effluent are the carry-over of black liquor into the bleach plant, excess by-product salt cake sewered from the chlorine dioxide generator and other liquor losses (Craig *et .al.*, 2001).

Desulphovibrio are the most common SRB found in paper mills (Korhonen and Lumme, 1978). Their growth rate is affected by the availability of an organic carbon source, inorganic sulphates, pH, temperature, salinity (Kosinska and Miskiewicz, 2005), COD/SO_4 ratio (Polanco *et. al.*, 2001; Kosinska and Miskiewicz, 2005) and redox potential (Czechowski and Rossmore, 1981; Postgate, 1984).

Hydrogen sulphide (H_2S) is the end product of sulphate reduction (Polanco *et. al*., 2001) which can either be released into the environment as dissolved sulphide species (H_2S, HS^-, S^{2-}) or as H_2S gas (Janssen *et. al.,* 1998).

This study was undertaken to investigate various options to reduce odours caused by H_2S at the mill's effluent treatment plant and irrigation farm.

1.2 OBJECTIVES OF THE STUDY

1.2.1 The objectives of this study were as follows:

- Identify the main sources of H_2S emissions
- Identify the main causes of H_2S production
- Control of SRB activity and H_2S production
- Propose a treatment programme

CHAPTER 2

LITERATURE REVIEW

2.1 TOTAL REDUCED SULPHUR (TRS) COMPONENTS

As stated in Chapter 1, the typical odours associated with Kraft mills are due to the generation of four reduced sulphur gases, namely, H_2S, CH_3SH, $(CH_3)_2S$ and $(CH_3)_2S_2$. These gases are collectively referred to as Total Reduced Sulphur (TRS) components (Bonnin *et. al.*, 1990; Pinkerton, 1999; Olendorf *et. al.*, 2000; Bordado and Gomes, 1998).

The TRS components have low odour thresholds (Vaczi, 1998; Bordado and Gomes 2003) and are emitted from point and diffuse sources at most Kraft mills (Rodden, 1996) and can be easily detected by mill employees and communities surrounding mills (Colella and Vanneste, 1992; Pote and Dwyer, 1999).

The human nose can detect hydrogen sulphide (H_2S) at levels lower than 1 ppm (Arthur and Anker, 2000). Olendorf *et. al.* (2000) reported the detection of H_2S levels as low as 0,0002 ppm which is well below the Permissible Exposure Limit (PEL) of 15 ppm for TRS components (Young, 2005). The toxicity of the TRS components at these levels is negligible, however, they are considered as a nuisance as the mills are faced with more stringent air emission limits (Bordado and Gomes, 2003).

The odour thresholds for the TRS components are summarised in Table 2.1 (Bonnin *et. al.,* 1990).

Table 2.1. Major TRS components and their odour thresholds

Compound	Odour description	Odour threshold (ppm)
Hydrogen sulphide	Rotten egg	0,0001 to 0,03
Methyl-mercaptan	Cabbage, garlic	0,0005 to 0,08
Dimethyl-sulphide	Rotten vegetable	0,0025 to 0,65
Dimethyl-disulphide	Putrification	0,003 to 0,014

2.1.1 Point source emissions

The potential point source emissions include the Kraft recovery furnaces, smelt dissolving tanks, lime kilns, brown stock washers, digesters, evaporators, condensate strippers, black liquor oxidation systems, tall oil recovery systems, black liquor storage tanks, turpentine recovery systems and condensate strippers (Gellman, 1972; Hagen and Hartung, 1997; Pinkerton, 1999; O'Connor *et. al.*, 2000). There are several options available for process modifications to reduce TRS emissions such as scrubbing, condensate stripping, non-condensable gas collection, incineration, absorption and adsorption (Bowker, 1999; Ramsay *et. al.*, 2001; Bordado and Gomes, 2003; Barbosa *et. al.*, 2004).

2.1.2 Diffuse source emissions

The potential diffuse source emissions include clarifiers, thickeners, wastewater treatment systems and on-site landfills (Collela and Vanneste, 1992; O'Connor *et. al.*, 2000; Bordado and Gomes, 2003). TRS emissions from diffuse sources are difficult to measure and quantify due to their fugitive nature, temporal variability and large area coverage (Pinkerton, 1999). Hydrogen sulphide (H_2S) is the main TRS component emitted from diffuse sources at Kraft mills (Bordado and Gomes, 2003; Dilsook, 2004).

The extent of TRS emissions is highly mill specific (Bordado and Gomes, 2003) and depends on condensate re-use practices, pulp mill and recausticizing equipment types, sewer configurations and operating characteristics of the primary and secondary effluent treatment equipment (Pinkerton, 1999). The TRS levels and composition vary from each point in the Kraft mill and according to the age of the mill (Bordado and Gomes, 1998). Newer mills with high efficiency recovery boilers produce lower levels of TRS components (Bordado and Gomes, 1998).

2.1.3 Physiological effects of TRS components

The National Council for Air and Stream Improvement (NCASI) investigated the potential health effects of human exposure to the low concentrations of TRS components encountered within a mill environment. The results showed that concentrations above 250 ppm of H_2S are acutely toxic and potent inhibitors of cellular respiration, exposure to less than 15 ppm of H_2S is not generally associated with significant adverse health effects (Tatum, 1995). The

Threshold Limit Value (TLV) for H_2S is 10 ppm and the Permissible Exposure Limit (PEL) is 15 ppm (Hao *et. al.,* 1996; Young, 2005).

Methyl-mercaptan and dimethyl-disulphide appear to be less toxic than hydrogen sulphide. However, they produce similar health effects (Tatum, 1995). Based on known TRS mechanisms of toxicity, it is unlikely that adverse health effects would result from current exposure to TRS gasses within Kraft mills and surrounding communities (Tatum, 1995; Craig *et. al.*, 2001).

The physiological effects of human exposure to H_2S are summarised in Table 2.2 (Tatum, 1995; WHO, 2000; Young, 2005).

Table 2.2. Summary of the physiological effects of human exposure to H_2S gas.

H_2S (ppm)	**Physiological effects**
0,0005 to 0,01	Odour threshold
3 to 10	Odour obviously unpleasant
5 to 10	Eye irritation in some individuals
20 to 30	Odour strongly offensive
30	Odour becomes “sickening sweet”
50 to 100	Eye irritation and respiratory tract irritation
100 to 200	Odour fatigue
250 to 500	Prolonged exposure causes pulmonary edema with risk of death
500 to 1 000	Strong central nervous system (CNS) stimulation, respiratory arrest within minutes
1 000 to 2 000	Immediate collapse, respiratory paralysis, neural paralysis, death within minutes

Hydrogen sulphide has a characteristic rotten egg smell and can be detected by humans at less than 1 ppm (Arthur and Anker, 2000). However, at concentrations higher than 100 ppm the ability to smell the H_2S is lost due to paralysis of the olfactory nerves which can result in unconsciousness and possible death (WHO, 2000; Young, 2005). High concentrations can be obtained in an enclosed chamber with high turbulence from wastewater containing 1.5 mg/l dissolved sulphide at a pH of 7,0 (Hagen and Hartung, 1997).

Less information is available for the health effects of methyl mercaptan, dimethyl disulphide and dimethyl sulphide. Methyl mercaptan and dimethyl disulphide appear to be less toxic than hydrogen sulphide, but produce similar effects (Tatum, 1995). Exposure to very high

levels of methyl mercaptan results in respiratory arrest, coma and death (Tatum, 1995). Methyl mercaptan is reported to be 100 times less toxic than hydrogen sulphide and causes vomiting, dizziness, convulsions, pulmonary edema, wheezing, increased heart rate and unconsiousness (Tatum, 1995). Dimethyl sulphide appears to be considerably less toxic than the already mentioned TRS components (Tatum, 1995).

2.2 PROPERTIES OF HYDROGEN SULPHIDE

2.2.1 Aqueous hydrogen sulphide

Hydrogen sulphide (H_2S) is readily soluble in water and is a weak acid in solution exhibiting two dissociation reactions which are pH dependant. The dissociation reactions are: (1) dissociation of molecular H_2S to form the hydrogen sulphide ions (HS^-), (2) dissociation of the hydrogen sulphide ions (HS^-) to form the sulphide ions (S^{2-}) (Hagen and Hartung, 1997; ATSDR, 2004).

$H_2S_{(aq)} \leftrightarrow HS^-_{(aq)} + H^+_{(aq)}$ (Equation 1)

$HS^-_{(aq)} \leftrightarrow S^{2-}_{(aq)} + H^+_{(aq)}$ (Equation 2)

The distribution of sulphide ions as a function of pH is shown in Figure 2.1 (Nelson, 2004). Hydrogen sulphide (H_2S) is the dominant species at a pH of about 6,0 (Okabe *et. al.*, 1992). At a pH of about 7,0 the ratio of the concentration of H_2S to HS^- ions is approximately 1:1 (Okabe *et. al.*, 1992; Hagen and Hartung, 1997). As the pH increases above 7,0 the ratio of the concentration of H_2S to S^{2-} increases. Only above a pH of 12 does the concentration of the S^{2-} ions become significant (>50%) (Miller and Shand, 1998; Nelson, 2004; Dilsook, 2005).

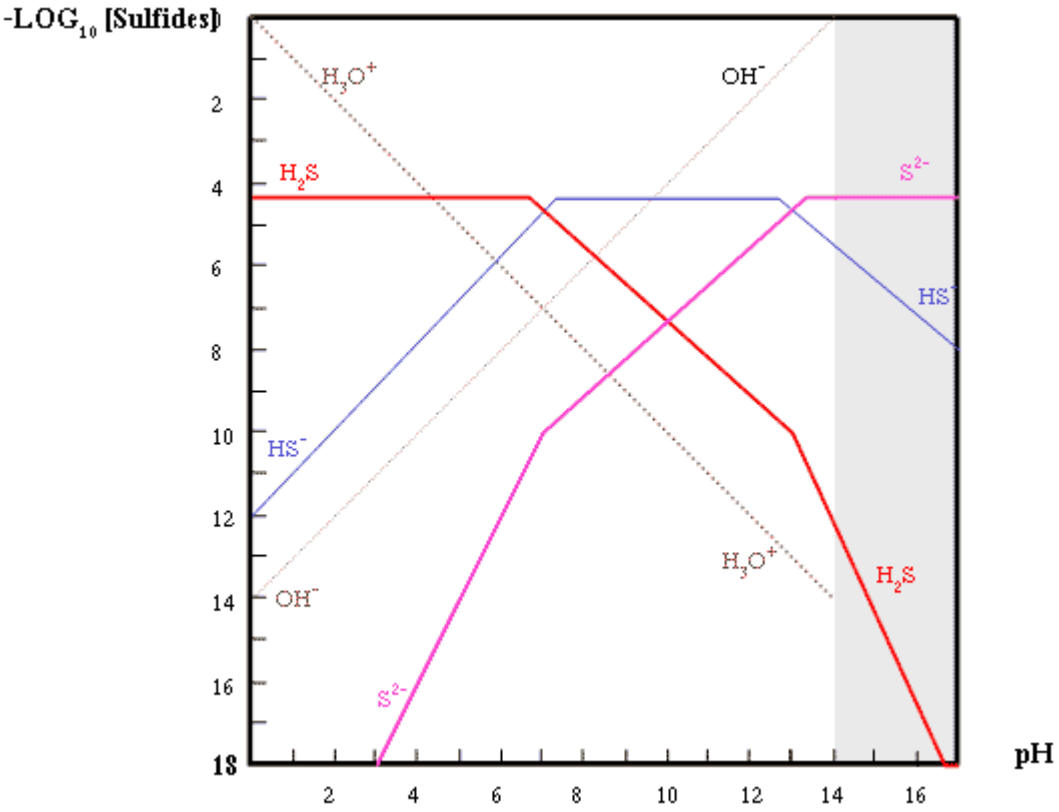

Figure 2.1: Distribution of sulphide ions as a function of pH (Nelson, 2004)

It is shown in Figure 2.2 (Nelson, 2004) that at a pH of 7,0 50% of the dissolved sulphides are present as H_2S and at a pH of 6.0, 90% of the dissolved sulphides are present as H_2S (Okabe *et. al.*, 1992). Less than 3% of the dissolved sulphides would form gaseous H_2S at a pH above 8,5 (Miller and Shand, 1998; Nelson, 2004). The distinction between the types of sulphide ions is important since *only* H_2S can escape from the solution and create odours (Hagen and Hartung, 1997) and corrosion problems (Groleau *et. al.*, 2002; Barbosa *et. al.*, 2004).

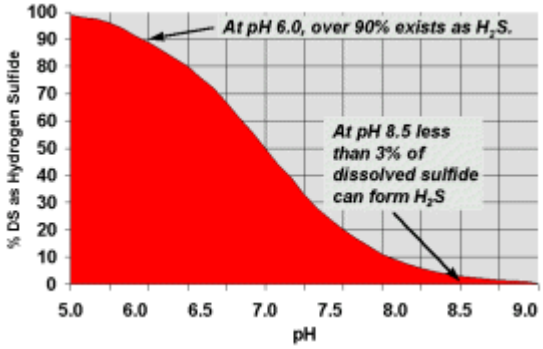

Figure 2.2: Solubility equilibrium of H_2S (Nelson, 2004)

It can be concluded that H_2S is slightly soluble in acidic solutions and that its solubility increases dramatically as the pH increases (Korhonen and Lumme, 1978). Therefore, maintaining the pH of the wastewater at a pH between 8,0 and 8,5 would significantly reduce the release of gaseous H_2S (Hagen and Hartung, 1997).

2.2.2 Gaseous hydrogen sulphide

Hydrogen sulphide (H_2S) degrades in the atmosphere by oxidation with oxygen (O_2) and ozone (O_3) to form sulphur dioxide (SO_2) and then ultimately sulphate compounds (SO_4^{2-}). Sulphur dioxide and sulphates are eventually removed from the atmosphere through adsorption by plants and soils or through precipitation (WHO, 2000).

Hydrogen sulphide can easily evaporate from water and the rate of evaporation depends on factors such as temperature, humidity, dissociation constants (pK), pH and concentration of certain metal ions. The Henry's law constant for dissolved H_2S was found to increase linearly with temperature thus indicating an increasing tendency to partition to the gas phase (Hao *et. al.,* 1996; WHO, 2000). Hydrogen sulphide will cross the air-water interface at pH levels ≤ 6 with kinetics similar to other unreactive gases such as oxygen (O_2), nitrogen (N_2), and carbon dioxide (CO_2) (WHO, 2000).

2.2.3 Effects of hydrogen sulphide released into the environment

Hydrogen sulphide (H_2S) is the end product of dissimilatory respiration (Polanco *et. al*., 1999) and can either be released into the environment as dissolved (aqueous) sulphides (H_2S, HS^-, S^{2-}) in wastewaters or as $H_2S_{(g)}$ in waste gases (Janssen *et. al.,* 1999).

H_2S has the following properties:

- It reacts with ozone in the atmosphere to produce acid rain (Janssen *et. al*., 1999).
- It is toxic to aerobic organisms because it reacts with heavy metal groups of the cytochrome systems (Atlas and Bartha, 1993, Lie *et. al*., 1999).
- It can kill nematodes, plants and animal populations in waterlogged soils (Atlas and Bartha, 1993).
- It has antimicrobial properties which can affect microbial populations in soil (Atlas and Bartha, 1993).
- It reacts with heavy metals to produce black metallic sulphide precipitates (Atlas and Bartha, 1993).

- It is corrosive to metals (cathodic depolarization) which can cause failures in various industries (Hardy, 1983; Hamilton, 1985; Lukanich, 1995; Lie *et. al*., 1999).
- It causes odour problems (Jobbagy *et. al*.; 1994; Sutton, 2004) which are greater in the summer than in the winter due to increased evaporation rates, anaerobic biological activity (Kasakura and Tatsukawa, 1995; Groleau *et. al*., 2002) and humidity (Ruth, 1986).

2.3 SULPHATE REDUCING BACTERIA (SRB)

2.3.1 Introduction

Sulphate Reducing Bacteria (SRB) are a diverse group of bacteria characterised by their anaerobic nature (O'Faherty and Colleran, 1995; Sutton, 2004; Kosinska and Miskiewicz, 2005) and their ability to use oxidised sulphur compounds such as sulfur (S^0), thiosulphate (S_2O_4), sulphite (SO_3^{-2}) or sulphate (SO_4^{-2}) as terminal electron acceptors (Postgate 1984; Balows *et. al*., 1992) for the dissimilation of organic material (Lukanich, 1995). The anion of choice is sulphate (Ballinger *et. al*., 2001) which has the highest sulphur oxidation state (+6) (Atlas and Bartha, 1993; Barbosa *et. al*., 2004) which makes the anion a very stable compound with a low redox potential (Matias *et. al*., 2005). The sulphate anion also acts as an oxygen source (Hagen and Hartung, 1997) which is non-volatile and non-toxic (Hao *et. al*., 1996).

Typical SRB genera include spore-formers *Desulphotomaculum* (Hamilton, 1985*;* Balows *et. al.,* 1992; O'Flaherty and Colleran, 1995) and non-spore formers *Desulphonema*, *Desulphobacter*, *Desulphococcus*, *Desulphobulbus, Desulphosarcina, Desulphovibrio*, (Postgate, 1984; Fauque *et. al*., 1991; Weimer *et. al.,* 1995) and *Thermodesulphobacterium* (Gawel, *et. al*, 1991; O'Flaherty and Colleran, 1995; Weimer *et. al.,* 1995). All the strains are gram negative except for *Desulphonema* which are gram positive (Postgate, 1984). *Desulphovibrio* are the most ubiquitious and most studied SRB genera (Birnbaum and Wireman, 1984; Postgate, 1984; Matias *et. al*., 2005).

SRB are capable of utilising various organic compounds with either complete oxidation to carbon dioxide (CO_2) and hydrogen sulphide (H_2S) or incomplete oxidation to acetate, CO_2 and H_2S (Lukanich, 1995; O'Flaherty and Colleran, 1995). They lack the enzymes needed to assimilate carbon dioxide (Atlas and Bartha, 1993), therefore, they metabolise volatile fatty

acids (electron donors) (Bak and Pfennig, 1987; Kim *et. al*., 2003) at a very fast rate (Polanco *et. al*., 2001).

The preferred carbon sources for SRB are low molecular weight compounds such as organic acids (Hao *et.al*., 1996). Typical organic acids (electron donors) are lactate, acetate, butyrate (Bratcova *et. al*., 2002), pyruvate, malate (Postgate, 1984, Hao *et. al*., 1996), alcohols or molecular hydrogen (Matias *et. al*., 2005). Molecular hydrogen can be used by some SRB as a sole energy source with acetate and carbon dioxide as the carbon source (Matias *et. al*., 2005). *Desulphovibrio* do not use acetate and only degrade lactate to acetate while *Desulphotomaculum* are acetate-utilizing bacteria (Hao *et. al*., 1996).

Desulphovibrio use lactate as the main carbon source (Postgate, 1984; Birnbaum and Wireman, 1984; Sutton, 2004) in the presence of inorganic sulphate ions (Weimar *et. al*., 1995). Lactate is oxidized by the enzyme lactate dehydrogenase to pyruvate which is then further metabolised to acetate and carbon dioxide with the generation of 2 ATP molecules (Czechowski and Rossmore, 1980).

Various other oxidisable simple carbon sources (Bratcova, 2002; Kim *et. al*., 2003) can also act as electron donors (Reis, 1992) and supply the hydrogen atoms required for the reduction of sulphate to sulphide (Czechowski and Rossmore, 1980; Sutton, 2004).

Desulphovibrio can tolerate pH environments between 4 and 10 and temperatures between 35º and 55ºC (Korhonen and Lumme, 1978). Their enzyme activity is most stable between pH 5,8 and pH 8,4 and temperatures between 40ºC and 42ºC (Czechowski and Rossmore, 1980).

SRB conduct their main metabolic oxidations within a redox span around an *Eh* of -150 to -200 mV. Their growth is accompanied by a drop in redox potential to the -250 mV range. There is also evidence that a drop in potential to the range of -200 mV is necessary for the initiation of SRB growth (Postgate, 1984).

Growth of *Desulphovibrio desulphuricans* on lactate can result in decrease of pH (Birnbaum and Wireman, 1984) due to acetic acid formation (Van Langenhove *et. al*., 1985). Growth on amine-containing compounds can result in the release of ammonia resulting in a pH increase (Birnbaum and Wireman, 1984). They can also increase the pH of their environment to neutral or slightly alkaline by the generation of bicarbonate (HCO_3^-) ions during the oxidation

of organic compounds (Hagen and Hartung, 1997; Bratcova *et. al*., 2002). The release of CO_2 and H_2S as gases will also increase the alkalinity (Hao *et. al*., 1996).

Desulphovibrio are the most common SRB genera found in paper mills (Korhonen and Lumme, 1978) and wastewater (Lukanich, 1995; O'Flaherty and Colleran, 1995). They have a high sulphate reduction rate (Gaylarde, 1992) with population doubling times as low as 3 to 6 hours (Okabe and Characklis, 1992). Their growth rate is affected by the availability of an organic carbon source, inorganic sulphates, pH, temperature, salinity, (Kosinska and Miskiewicz, 2005), COD/SO_4 ratio (Polanco *et. al*., 2001; Kosinska and Miskiewicz, 2005), COD/BOD concentration (O'Flaherty and Colleran, 1995) redox potential (Czechowski and Rossmore, 1981; Postgate, 1984) and solids residence time (Attal *et. al*., 1992; Djurle, 2004).

Bacillus, Pseudomonas species (Sobsey and Pfaender, 2002) and *Desulphotomaculum (Clostridium) nigrificans* (Anon., 1976; Postgate, 1984) are also able to release hydrogen sulphide from inorganic sulphate. However, these species do not play an important role in the dissimilatory reduction of sulphate (Atlas and Bartha, 1993).

The hyperthermophilic archaebacteria, *Pyrobacterium aerophilum* (Richardson, 2000), *Archaeoglobus fulgidus*, (Balows *et. al*., 1991; Fauque *et. al*., 1991; Lukanich, 1995, O'Flaherty and Colleran, 1995; Richardson, 2000) and *Thermodesulphobacterium* (Gawel, 1991) have been reported to release hydrogen sulphide from inorganic sulphate (Stetter *et. al*., 1987, Richardson, 2000). This indicates that dissimilatory respiration is not limited to eubacteria (Lukanich, 1995). The term SRB includes organisms that belong to both eubacterial and archaebacterial branches of the bacterial phylogeny (Tatnall, 1996).

2.3.2 Dissimilatory sulphate reduction

Dissimilatory sulphate reduction, also known as sulphate respiration (Hao *et. al*., 1996; Matias *et. al*., 2005) is an anaerobic process (Matias *et. al*., 2005; Mussman *et. al*., 2005) which *only* takes place in SRB as the sole source of energy (respiration) for cell growth (Anon, 1976; Balows *et. al*., 1992; O'Flaherty and Colleran, 1995).

The sulphate anion is a very stable compound with an extremely low redox potential and needs to be activated in order to be a suitable electron acceptor (Hamilton, 1985; Matias *et. al*., 2005; Balows *et. al.,* 1992). It is transported across the cytoplasmic membrane into the cell and activated by adenosine triphosphate (ATP) to form adenosine phosphosulphate (APS) and

inorganic pyrophosphate (PPi) (Fauque *et. al*., 1991; Atlas and Bartha, 1993; Matias *et. al*., 2005) as shown in Equation 3.

$ATP + SO_4^{2-} \rightarrow APS + PPi$ (Equation 3)

This activation reaction is catalysed by the cytoplasmic enzyme ATP sulphurylase (Mussman *et. al*., 2005).

The APS is then reduced by the enzyme APS reductase to adenosine monophosphate (AMP) and sulphite (Postgate, 1984; Fauque *et. al*., 1991; Balows *et .a*l., 1992; Matias *et. al*., 2005) as shown in Equation 4.

$APS \rightarrow AMP + SO_3^{2-}$ (Equation 4)

The sulphite is then reduced to sulphide by sulphite reductases (Matias *et. al*., 2005).

There are two types of sulphite reductases present in SRB which can be differentiated by the spin state of their siroheme iron (Fauque *et. al*., 1991; Balows *et. al*., 1992). The high spin dissimilatory enzyme group includes four sulphite reductase enzymes, namely, desulphoviridin, desulphorubidin, sulphite reductase P582 and desulphofuscidin. These enzymes all have high molecular masses and have different spectroscopic and molecular characteristics (Balows *et. al.,* 1992). The low spin sulphite reductase enzymes have low molecular masses and only one polypeptide chain (Fauque *et. al*., 1991).

There are two proposed pathways in the reduction of sulphite to sulphide. The first is the trithionate pathway which indicates sulphite is reduced via three two-electron reactions with trithionate and thiosulphate as free intermediates. This pathway is evident in the genus *Desulphotomaculum*. The second pathway (direct 6 electron reduction) indicates sulphite is reduced to sulphide without the formation of free intermediates (Matias *et. al*., 2005). This pathway is evident in the genus *Desulphovibrio* (Fauque *et. al*., 1991).

2.4 HYDROGEN SULPHIDE CONTROL TECHNOLOGIES

There are two approaches in reducing hydrogen sulphide concentrations in wastewaters:

1) Inhibition of hydrogen sulphide production by SRB
2) Removal of hydrogen sulphide produced by SRB

2.4.1 Inhibition of sulphate reduction

The sulphate transport system and ATP sulphurylase enzyme activity involved in cell growth can be reduced or inhibited by the following groups of compounds or mechanisms:

(a) *Sulphate reduction inhibitors*

These compounds have specific mechanisms which compete with the sulphate ion for the active site on the ATP sulphurylase enzyme. This results in the formation of an unstable sulphate analogue-AMP complex which easily hydrolyses to AMP. The sulphate analogue is then available to react again with the ATP sulphurylase enzyme (Weimer *et. al*., 1995; Lie *et. al.,* 1999). The repetitive reaction with the analogue results in the depletion of ATP in the cell, thus reducing the energy available for sulphate activation which eventually results in the inhibition of SRB growth (Newport *et. al.,* 1988, Weimer *et. al*., 1995; Cooling *et. al*., 1996; Ballinger *et. al*., 2001).

The following compounds have been reported to be effective against SRB:

- Anthraquinones (Nagaoka, 1995; Cooling *et. a*l., 1996; Lie *et. al*., 1999; Pareek *et. al*., 2000; Harless *et. al*., 2000).
- Chromates (Wilson and Bandurski, 1958; Cypionka, 1989; Chen *et. al*., 1998)
- Fluorophosphates (Weimar *et. al*., 1995)
- Molybdate (Cooling *et. al*., 1996; Newport and Nedwell, 1988; Lie *et. al*, 1999; Pareek *et. al*., 2000; Ballinger *et. a*l., 2001; Okabe *et.al.,* 2003)
- Selenate (Wilson and Bandurski, 1958; Newport and Nedwell, 1988; Chen *et. al*., 1998)
- Tungsten (Cypionka, 1989; Lie *et. al*., 1999)

(b) *Biomodifiers*

In the absence of dissolved oxygen, nitrate (Hunniford and Davis, 1990; Norwood *et. al*., 2001; Bratcova *et. al*., 2002; Greene *et. al*., 2003) and nitrite (Seitz and Cypionka, 1986; Hitzman *et. al*., 1998) can act as alternative electron acceptors to a group of facultative aerobic denitrifying bacteria (nitrate reducers) (Norwood *et. al*., 2001). This can result in a population shift which suppresses SRB anaerobic activity (Bentzen *et. al*., 1995; O'Flaherty and Colleran, 1995) due to an increase in the redox potential of the environment (Ballinger *et. al*, 2001). The action of nitrates and nitrites is synergistic, thus by adding both, less of each compound is required for the suppression of SRB. Nitrites also act as hydrogen sulphide scavengers thus lowering the amount of hydrogen sulphide present (Hitzman, 1995).

The heterotrophic denitrifiers out-compete the SRB for the available nutrients due to their thermodynamic and physiological properties, (Hitzman *et. al*., 1998). The microbial competition for the organic carbon increases when the COD/SO_4^{2-} ratio is decreased (Polanco *et. al.,* 2001). The SRB are eventually left without sufficient carbon source and thus their growth and activity is inhibited (Ballinger *et. al*., 2001; Groleau *et. al*., 2002) and hydrogen sulphide is not produced (Hitzman *et. al*., 1998) due to the suppression of sulphate reduction (Seitz and Cypionka, 1986).

Denitrification is a stepwise process where nitrate is reduced to nitrogen gas (Lukanich, 1995; Richardson, 2000) via intermediates such as nitrite, nitric oxide and nitrous oxide (Bentzen *et. al*., 1995; Richardson, 2000; Groleau *et. al*., 2002). Reduction of nitrates to ammonia is not thermodynamically favourable for the denitrifiers (Hitzman *et. al*., 1998).

In the presence of high nitrate levels, *Desulphovibrio desulfuricans* and other SRB selectively utilise nitrate as the preferred electron acceptor instead of sulphate (Seitz and Cypionka, 1986; Mouche and Song, 1987; Marschall *et. al*., 1993) and reduce nitrates to ammonia (Seitz and Cypionka, 1986).

Paper mill wastewaters have high levels of sulphates (O' Flaherty and Colleran, 1995, Janssen *et. al*., 1999) but are deficient in nitrates and nitrites, thus nitrates/nitrites can be added to effluents resulting in a population shift from SRB to denitrifiers (nitrate utilizing bacteria) (Norwood *et. al*., 2001). Nitrates and nitrites can be added to an effluent in any desired form since the counter-ion is not critical (Hitzman *et. al*., 1998). Sodium and calcium salts are usually used due to their availability and low cost (Hitzman *et. al.,* 1998). Nitrates

can also stimulate the growth of a group of bacteria which oxidise sulphide to sulphate. Many genera of pseudomonads and bacilli can also reduce nitrates (Bentzen *et. al.*, 1995).

(c) Cell growth accelerators (Biostimulants)

Xeronine is a cell growth accelerator which re-activates reactions at the cellular level causing a shift in anaerobic fermentation to anaerobic respiration with more rapid growth and activity of facultative anaerobes (Pote and Dwyer, 1999). This shift allows for more nitrates to be used as terminal electron acceptors than sulphates, lowering the level of hydrogen sulphide produced (Parker, 1996; Miller *et. al.*, 1996). This process allows facultative anaerobes to have a greater growth rate than SRB (Parker, 1996). Multi-enzymatic biostimulants are not affected by limiting environmental conditions (Miller *et. al.*, 1996; McMillen, 1998; Pote and Dwyer, 1999).

(d) *Biocides*

Sulphate Reducing Bacteria (SRB) activity can be controlled using biocides (Greene *et. al.*, 2003). However, biocides are not specific against SRB and will kill aerobic, anaerobic and facultatively aerobic micro-organisms (Weimar *et. al.*, 1995). High dosages and repetitive dosages of biocides are required to kill SRB making this form of treatment very costly (Mouchè and Song, 1987). The biocidal properties are affected by pH, temperature, environmental conditions (Dilsook, 2005) and half-life (Harless *et. al.*, 2000).

The following compounds have been reported to be effective against SRB:

- Gluteraldehyde (Weimar *et. al.*, 1995; Reinsel *et. al.*, 1996; Cooling *et. al.*, 1996; McInerney and Bhupathiraju, 1992*;* Lie *et. al.*, 1999)
- Ozone and peroxides (Gawel *et. al.*, 1991)
- Quaternary ammonium salts and acrolein (Weimar *et. al.*, 1995)
- Sodium hypochlorite and chlorine (Cooling *et. al.*, 1996; Lie *et. al.*, 1999)
- Triazines, Isothiazolinones and 2-Mercaptobenzothiazole (Czechowski and Rossmore, 1981)

(e) *Oxygen*

SRB are oxygen tolerant (Okabe *et. al*., 2003) and can survive for hours or days when exposed to air (Tiller, 1983; Marschall *et. al*., 1993; Atlas and Bartha, 1993). However, no sulphate reduction occurs in the presence of oxygen (Fukui and Takii, 1990; Lukanich, 1995). SRB activity is inhibited at DO < 1 mg/l and an ORP < -100 mV (Hao *et. al,* 1996).

(f) *Hydrogen sulphide*

Relatively high levels of H_2S (550 mg/l to 2500 mg/l) can be toxic to SRB cells (Reis *et. al*., 1991; Lukanich, 1995; O' Flaherty and Colleran, 1995; Hao *et. al.,* 1996) by making cellular iron unavailable for use as ferredoxin and cytochrome C production and thus sulphate cannot be reduced (Postgate, 1984; Hao *et. al.,* 1996). Toxicity of H_2S to SRB increases as the pH increases (O' Flaherty and Colleran, 1995).

2.4.2 Removal of hydrogen sulphide produced by SRB

Some of the technologies available for the removal of hydrogen sulphide include:

- Hydrogen sulphide scavengers such as glyoxal or glyoxal in combination with gluteraldehyde or formaldehyde (Edmonson, 1987).
- Chemical oxidisers such as chlorine, hydrogen peroxide, potassium permanganate, ozone, (Joyce, 1990: Janssen *et. al*., 1999), oxygen and chlorine dioxide (Joyce, 1990).
- Precipitation of H_2S by metal salts such as ferrous and ferric sulphate, ferric chloride, aluminium sulphate, zinc chloride (Joyce, 1990), ferrous chloride and magnesium oxide (Miller and Shand, 1998).
- Aeration (Joyce, 1990; Janssen *et. al.,* 1999)

The above technologies were not investigated further due to the disadvantages summarised in Table 2.3.

Table 2.3. Hydrogen sulphide removal technologies (Edmondson, 1987; Dilsook, 2004)

Technology	**Disadvantages**
Hydrogen sulphide scavengers	• Expensive • Patented technology • Temperature and pH dependant
Chemical oxidisers	• Dangerous chemicals to handle • Dosages are pH dependant • Expensive • Not selective against SRB • May produce undesirable by-products
Precipitation with metal salts	• Corrosive chemicals • Increase mass and volume of sludge • Black precipitate formed by iron sulphide • Removes phosphates (nutrient for biological treatment) • pH adjustment of treated effluent may be required
Aeration	• New equipment required • Not possible in certain circumstances

CHAPTER 3

EXPERIMENTAL PROCEDURES

3.1 BACKGROUND

This chapter consists of six experimental phases based on the objectives, literature review and contract requirements.

- Phase 1: Identifying the main TRS components and sources of emission at the effluent treatment plant.
- Phase 2: Monitoring pH and temperatures of the clarifiers and effluent sumps, to determine, by computer modeling, the possibility of adjusting the effluent pH to 8.6 using slaked lime.
- Phase 3: Determining the chemical composition of the effluent sumps to identify the possible causes for the H_2S generation.
- Phase 4: Baseline monitoring of SRB in the effluent sumps.
- Phase 5: Reducing SRB activity in the effluent sumps by dosing biocides.
- Phase 6: Reducing H_2S levels using biomodifiers and sulphate reduction inhibitors.

3.2 EFFLUENT TREATMENT PLANT PROCESS

The process flow diagramme (PFD) shown in Figure 3.1 indicates the sampling points as well as the two main effluent streams entering the effluent treatment plant. These streams will be referred to as System 1 (Bleach effluent) and System 2 (General effluent).

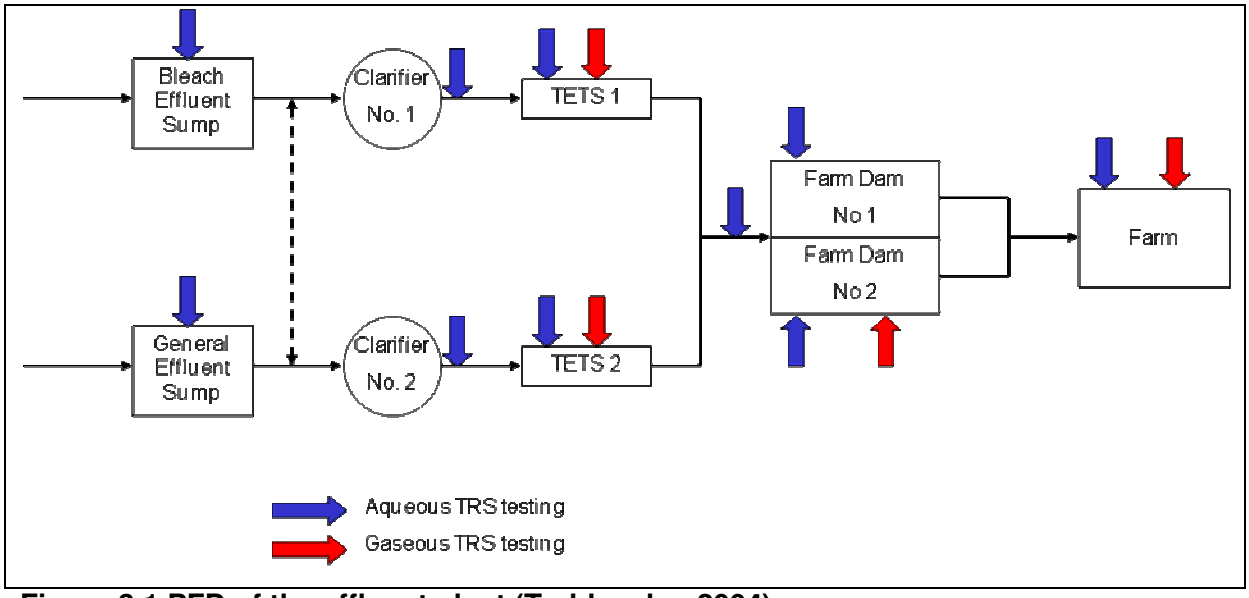

Figure 3.1 PFD of the effluent plant (Terblanche, 2004)

System 1: This system contains varying ratios of effluent coming from the different bleaching stages and demineralised water effluent coming in from the bleach plant. This combined effluent is referred to as the Bleach Plant effluent which is pumped to Clarifier 1 where the solids are removed by settling (clarification). The overflow is then pumped into the Treated Effluent Tank Sump 1 (TETS 1) where further settling takes place. The clarified effluent is then pumped across to the adjacent irrigation farm where it flows onto a deflector plate and then into Farm Dam 1.

System 2: This system contains varying ratios of effluent coming from the Kraft Liner Board (KLB) plant, Newsprint plant (NP), No. 1 and No. 2 Kraft digesters, No. 3 Kraft evaporator, No. 2 and No. 3 Uptake, groundwood rejects drain and groundwood floor drains. This combined effluent is referred to as the General Effluent which is pumped to Clarifier 2 where the solids are removed by settling (clarification). The overflow is then pumped into the Treated Effluent Tank Sump 2 (TETS 2) where further settling takes place. The clarified effluent is then pumped across to the adjacent irrigation farm where it flows onto a deflector plate and then into Farm Dam 2.

The TETS retention times are between 2,5 and 7,1 hours and are de-sludged every three months. Each TETS normally operates at 50% capacity level. The Clarifier retention times are between 4 and 6 hours and are de-sludged every 24 hours. The Farm Dam retention times are a few days and are de-sludged once a year. All retention times depend on incoming effluent flow rates.

3.3 SAMPLING

3.3.1 Aqueous and gaseous samples were taken from the Bleach effluent sump, General effluent sump, Clarifier 1, Clarifier 2, Treated Effluent Transfer Sump 1 (TETS 1), Treated Effluent Transfer Sump (TETS 2), Farm Dam 1, Farm Dam 2 and irrigation spray, to identify and quantify the aqueous and gaseous TRS components across the effluent treatment plant (Fig. 3.1).

3.3.2 Based on preliminary plant surveys and TRS profiling data, costs and logistics it was agreed with the mill management that future monitoring would be limited to TETS 2. Samples would be taken from TETS 2 for analyses every second week for a period of 7 months.

3.4 PHASE 1: TOTAL REDUCED SULPHUR (TRS) COMPONENT PROFILING

This phase of the study was carried out to identify the TRS components and emission sources across the effluent plant.

3.4.1 Aqueous samples (25ml) were collected in gas tight glass bottles, frozen and sent to Columbia Analytical Services (USA) for TRS profiling analyses by headspace GC-FPD.

3.4.2 Gaseous emissions where collected from the surface of each sampling point using air sampling domes (flux chambers) and Tedlar bags. The Tedlar bags were sent to SKC Laboratories (Boksburg, South Africa) for TRS profiling.

3.5 PHASE 2: MONITORING PROCESS pH AND TEMPERATURES

This phase was to determine the effect temperature and pH would have on TRS emissions from TETS 1, TETS 2, Clarifier 1 and Clarifier 2.

3.5.1 Temperature was measured using a certified liquid in glass thermometer.

3.5.2 pH was measured using a portable Beckman pH meter, gel-filled pH probe with automatic temperature compensation. Merck pH buffer solutions (4, 7, 10) were used to calibrate the instrument.

3.5.3 French Creek WaterCycle^{TM} computer software was used to determine the effect on scaling tendencies of the effluent water if the pH was increased to 8,6 using slaked lime.

3.6 PHASE 3: CHEMICAL COMPOSITION OF THE EFFLUENT

This phase of the study identified the main chemical constituents typically present, or absent, in Kraft mill effluents which contributed to the generation of H_2S.

3.6.1 Composite samples were collected in 1 000 ml plastic bottles.

3.6.2 Samples were chilled to 4ºC and analysed within 24 hours.

3.6.3 Pre-treatment and/or dilutions were carried out where required.

3.6.4 Chemical analyses were conducted using accredited methods where possible.

The constituents measured and the procedures used in this study are indicated in Table 3.1. All constituents indicated in Table 3.1, except those carried out on site at the mill, were sub-contracted to the analytical laboratories of Umgeni Water (KZN, South Africa) and the CSIR (Gauteng, South Africa) for analysis.

Table 3.1. Methodology and parameters measured

Constituent	**Unit**	**Procedure**
Calcium[(1)]	mg/l as Ca	Atomic Absorption Spectroscopy
COD[(2)]	mg/l as O_2	Dichromate digestion (Hach Method 8000)
Conductivity[(2)]	µS/cm	Hach conductivity meter (Hach Method 8160)
Dissolved oxygen[(2)]	mg/l as O_2	Hanna DO meter (HI 9142)
Hydrogen sulphide[(2)]	mg/l as H_2S	Hach HS-C test kit (Catalogue # 2537800)
Iron[(1)]	mg/l as Fe	Atomic Absorption Spectroscopy
Manganese[(1)]	mg/l as Mn	Atomic Absorption Spectroscopy
Molybdenum[(1)]	mg/l as Mo	Atomic Absorption Spectroscopy
Nitrates[(1)]	mg/l as NO_3	Ion Chromatography
Nitrites[(1)]	mg/l as NO_2	Ion Chromatography
ORP[(2)]	mV	Hanna ORP meter (HI 98201)
pH[(2)]	pH units	Inolab pH meter (WTW series pH720)
Sodium[(1)]	mg/l as Na	Ion Chromatography
Sulphates[(1)]	mg/l as SO_4	Ion Chromatography
Sulphides[(3)]	mg/l as H_2S	Iodometric titration
Temperature[(2)]	ºC	Liquid in glass thermometer (certified)

(1) analysed by Umgeni Water (2) analysed on site (3) analysed by the CSIR

Hydrogen sulphide in this study refers to dissolved HS^-, S^{2-} and/or H_2S in the test samples. The initial H_2S surveys were carried out using the Hach HS-C test method (Mouchè *et.al.*, 1987; Hagen and Hartung, 1997).

Data were compared to duplicate samples tested by the iodometric titration method (Table 3.1). The repeatability and accuracy between the two test methods were acceptable for continued monitoring of H_2S across the effluent treatment plant (Allison, 2005).

3.7 PHASE 4: BASELINE MONITORING OF SRB ACTIVITY

This phase of the study determined the SRB activity in the TETS 2 effluent water without the addition of treatment chemicals.

Iron Sulphite Agar (Oxoid CM 0079), supplemented with magnesium sulphate heptahydrate (AR grade) and sodium lactate (AR grade), was used as the growth medium (Postgate, 1984). The composition of the growth medium is shown in Table 3.2.

Table 3.2. Composition of the supplemented Iron Sulphite Agar (Oxoid CM 0079)

Nutrients	**Function**	**Concentration g/l**
Tryptone	Protein source	10
Sodium sulphite	Reducing agent	0,5
Iron (III) citrate	Iron source/Chelant	0,5
Technical Agar	Gelling agent	12
Sodium lactate (60%)	Organic Carbon source	3,5
Magnesium sulphate heptahydrate	Sulphate source	0,5

3.7.1 Agar tubes were prepared using the supplemented Iron Sulphite Agar (Table 3.2). The necessary decimal dilutions were made using sterile quarter strength Ringer's solution (Oxoid BR 52).

3.7.2 1 ml and 0,1 ml quantities of each dilution were transferred into sterile glass test tubes (150 x 16 mm). Molten agar (tempered at 46℃), was then poured up to the rim of the test tube.

3.7.3 The tubes were closed tightly and the contents were mixed by inverting 6 times. (Mara and Williams, 1970). Agar tubes were then incubated at 50ºC (Ballinger *et. al.*, 2001).

3.7.4 The agar tubes were checked daily for signs of black colonies (Mara and Williams, 1970) over a period of 72 hours (Tatnall *et. al.*, 1988; Harless, 2000).

3.7.5 Black colonies in tubes, preferably containing 10 to 20 colonies, were counted (de Bruyn and Cloete, 1992), multiplied by the dilution factor, and reported as colony forming units per millilitre (cfu/ml) (Tatnall *et. al.*, 1988).

3.7.6 Absence of growth after an incubation period of 3 days was reported as <10 cfu/ml. The incubation temperature and pH were based on the average operating temperatures and pH of TETS 2. The incubation period of 72 hours instead of 3

weeks, was chosen since thermophilic SRB grow faster at 50ºC than at 30ºC (Postgate, 1984) and the generation of H_2S is also much higher at 50ºC (Ballinger *et. al.*, 2001).

3.8 PHASE 5: CONTROL OF SRB ACTIVITY

This phase of the study determined the effect biocides had on reducing SRB activity.

3.8.1 Experiments were performed by filling 100 ml sterile glass bottles with effluent.
3.8.2 The samples were slug dosed with biocides having different active ingredients.
3.8.3 The bottles were tightly closed and incubated at 50ºC for 4 hours.
3.8.4 Agar tubes and dilutions were prepared as discussed in 3.7.
3.8.5 Untreated control samples were also tested.

Biocides of different chemistries were evaluated for the effectiveness against SRB. The respective active ingredients and dosages are shown in Table 3.3.

Table 3.3. Biocide active ingredients and dosages

Product	**Active ingredient**	**Dosage (mg/l)**
Biocide 1	s-Triazine (72%)	14
Biocide 2	Gluteraldehyde (25%)	7
Biocide 3	Isothiazolinones (1.5%)	13
Biocide 4	2,2-dibromo-3-nitrilopropionamide (20%)	4
Biocide 5	Methylene bisthiocyanate (10%)	4
Biocide 6	Sodium dimethyl-dithiocarbamate (40%)	25

Note: Dosages were based on the manufacture's recommendations

3.9 PHASE 6: CONTROL OF HYDROGEN SULPHIDE GENERATION

Part A: Use of biomodifiers

This phase of the study determined the effects the addition of nitrates, nitrites and molybdenum had on SRB activity and the generation of H_2S.

3.9.1 Experiments were performed by filling 100 ml sterile glass bottles with effluent.
3.9.2 Nitrate, nitrite and/or molybdenum were dosed to the samples as their aqueous sodium salts.
3.9.3 Dosages based on studies published by Howe *et. al*. (1967), Mouchè *et. al*. (1987), Hunniford *et. al*. (1990), Hitzman *et. al.* (1995), Craig *et. al*. (1996), Hitzman *et. al.* (1998) and Norwood *et. al*. (2001) were used.
3.9.4 Bottles were tightly closed and incubated at 50ºC for 72 hours.
3.9.5 ORP, pH and H_2S were then measured.
3.9.6 Untreated control samples were also tested.

Part B: Use of biomodifiers and sulphate reduction inhibitors

This phase of the study determined the effect the addition of sodium nitrate with 9,10 anthraquinone (AQ) had on the reduction and inhibition of H_2S generation when TETS 2 operated at 10%, 25% and 50% capacity level. The TETS never operated at a capacity level higher than 50% (Terblanche, 2004).

3.8.1 Experiments were performed by filling 100 ml sterile glass bottles with effluent.
3.8.2 Samples were then dosed with sodium nitrate[(1)] and 9,10 anthraquinone[(2)]
3.9.3 Dosages were based on studies published by Weimar *et. al*. (1995), Tatnall *et. al.* (1996), Harless *et. al.* (2000) and Ballinger *et. al*. (2001).
3.9.4 Bottles were tightly closed and incubated at 50ºC.
3.3.5 H_2S levels were measured after 24 hours.
3.9.6 Untreated control samples were also tested.

- [(1)] 50% solution of $NaNO_3$ and proprietary ingredients (Bulab® 2432)
- [(2)] 50% slurry of 9,10 anthraquinone and proprietary ingredients (Busperse® 9518)
  Particle size: 85% < 5 µm

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 TEMPERATURE AND pH MONITORING OF THE EFFLUENT

Temperature and pH were monitored to determine the stability of the effluent treatment plant processes and the effects any fluctuations would have on the aqueous and gaseous TRS levels.

4.1.1 Baseline temperature monitoring

The Henry's law constant for dissolved H_2S increases linearly with increasing temperature (Hoa *et. al.*, 1996; WHO, 2000) indicating an increasing tendency of H_2S to partition to the gas phase (Van Langenhoven *et. al.*, 1985).

The average operating temperatures of the Clarifiers were higher than the average operating temperatures of the TETS (Table 4.1). This was due to the effluent cooling down when pumped from the Clarifiers across to the respective TETS.

Table 4.1. Effluent temperature ranges

System	Minimum (ºC)	Maximum (ºC)	Average (ºC)
Clarifier 1	46	59	53
TETS 1	46	55	49
Clarifier 2	40	55	50
TETS 2	40	53	47

25 samples tested for each sampling point

System 1 (Clarifier 1 and TET 1) average operating temperatures were higher than System 2 (Clarifier 2 and TETS 2) due to the differences in processes. System 1 treated effluent from the Bleach plant and System 2 treated General effluent from the Kraft and Newsprint mills.

4.1.2 Baseline pH monitoring

The pH values fluctuated between very acidic conditions (pH < 7) to very basic conditions (pH > 7) (Table 4.2). System 1 stream operated mainly within an acidic pH range while System 2 stream operated mainly within the neutral to basic pH range (pH ≥ 7) (Table 4.2).

Table 4.2. Effluent pH ranges

System	Minimum pH	Maximum pH	Average pH
Clarifier 1	2,48	10,7	6,57
TETS 1	3,16	10,2	6,28
Clarifier 2	6,27	11,8	7,95
TETS 2	6,04	10,3	7,29

25 samples tested for each sampling point

4.2 TOTAL REDUCED SULPHUR (TRS) COMPONENT PROFILING

Aqueous and gaseous TRS components were monitored across the effluent treatment plant to identify which TRS component was the main cause of the odour and whether this component was emitted from the effluent treatment plant or from the irrigation farm.

4.2.1 Gaseous TRS profiling

Hydrogen sulphide (H_2S) can easily evaporate from water and the rate of evaporation depends on factors such as temperature, humidity, dissociation constants (pK), pH and concentration of certain metal ions (Hao *et. al.*, 1996; WHO, 2000). The equilibrium between gaseous and aqueous H_2S is governed by Henry's law (Hao *et. al.*, 1996).

Gaseous TRS profiling, using flux chambers and Tedlar bags, of the effluent treatment plant and irrigation farm indicated that the primary TRS component emitted was H_2S which was typical for Kraft mills (Olendorf *et. al.*, 2000). The highest H_2S emissions were measured at TETS 1 and the lowest H_2S emissions were measured at the irrigation farm (Table 4.3). The remaining TRS components, namely, dimethyl sulphide, dimethyl-disulphide and methyl-mercaptan were below the GC-FPD detection limit (< 1.9 ppb) and were reported as not detected.

Table 4.3. Gaseous H_2S levels across the effluent plant and irrigation farm (Dilsook, 2005)

Sampling point	**H_2S (ppb)[1]**	**H_2S (ppb)[2]**
TETS 1	9,97	757,97
TETS 2	<0,42	690,91
Farm Dam 2	2,01	6,66
Irrigation farm	1,40	2,61

1: Samples taken on 29/9/2004
2: Samples taken on 9/11/2004

The differences between the two sets of data (Table 4.3) was most probably due to the dumping of fouled condensate (high in sulphides) into the effluent during process upsets which increased the aqueous sulphide level of the effluent water (Olendorf *et. al.*, 2000) or black liquor (high in sulphides) coming in with the General effluent (System 1) (Dilsook, 2004). Aqueous sulphide levels above 1,0 mg/l would normally cause odour problems (Hao *et. al.,* 1996; Hagen and Hartung, 1997).

The decrease in H_2S levels (Table 4.3) from the TETS to the irrigation farm was most probably due to the following (Dilsook, 2005):

- stripping of H_2S by the pumping action of the effluent to the Farm Dams
- additional stripping caused by the deflector plates as the effluent entered the Farm Dams
- stripping of H_2S by the spraying action of the effluent onto the irrigation farm land

The H_2S values detected (Table 4.3) varied across the plant and were all above the odour threshold (0,0001 to 0,030 ppm) (Bonnin *et. al.,* 1990) but were below the permissible exposure limit (PEL) of 15 ppm for TRS components (Young, 2005). The toxicity levels were negligible (Vaczi, 1998; Bordado and Gomes, 2003), however, the levels detected would be considered as a nuisance by the mill personnel and surrounding communities (Collela and Vannester, 1992; Pote and Dwyer, 1999). Odour perception would also be affected by temperature and relative humidity (Ruth, 1986).

4.2.2 Aqueous TRS profiling

All four TRS components (Table 4.4) characteristic of Kraft mill odour, namely, hydrogen sulphide (H_2S), mercaptan (CH_3SH), dimethyl-sulphide $(CH_3)_2SH$ and dimethyl-disulphide $(CH_3)_2SH_2$ (Olendorf *et. al.*, 2000) were detected with H_2S being the primary TRS component.

Table 4.4. Aqueous TRS profile across the effluent plant (Dilsook, 2005)

Sampling point	**H_2S (mg/l)**	**CH_3SH (mg/l)**	**$(CH_3)_2SH$ (mg/l)**	**$(CH_3)_2SH_2$ (mg/l)**
System 1 effluent stream				
Bleach Effluent	< 0,420	< 0,13	3,43	2,51
Clarifier 1	33 400	499	1 550	478
TETS 1	1 040	2.95	659	84
System 2 effluent stream				
General Effluent	28	7,77	433	2,02
Clarifier 2	57 200	438	963	117
TETS 2	8 300	94,5	1410	71,4
Irrigation Farm				
Entering Farm Dams	500	< 0,13	997	147
Farm Dam 1	201	< 0,13	628	147
Farm Dam 2	169	< 0,13	701	62,2
Irrigation spray	322	< 0,13	335	21

Samples taken on 9/11/2004

The concentration of the aqueous TRS components were lower (Table 4.4) in System 1 stream than in System 2 stream. System 1 operated at a higher temperature (Table 4.1) and lower pH (Table 4.2) than System 2. The higher temperature and lower pH could have increased H_2S emissions which reduced aqueous TRS levels (Table 4.4).

The TRS profiling results indicated that H_2S was the main TRS odour component emitted from the effluent treatment plant (Clarifiers and TETS) and not from the irrigation farm (Table 4.3 and Table 4.4) as was initially reported by the mill personnel and local communities surrounding the mill (Dilsook, 2005).

4.3 COMPUTER MODELING FOR TETS 2 EFFLUENT WATER

The French Creek WaterCycle™ software (Palazzo, 2004) was used to model the effect of using slaked lime to increase the pH of the wastewater to 8,3 and above. The computer modeling indicated that at least 3 400 mg/l slaked lime would be required to increase the effluent average pH of 6,5 to 8,6.

The main disadvantages of pH adjustment using slaked lime would be (Palazzo, 2004):

- severe scaling tendencies of the effluent (Ryznar Stability Index < 0,7)
- difficult to control slaked lime dosing due to temperature and pH fluctuations
- pH above 7,5 would affect the irrigation farm soil properties, cation-anion exchange capacity and nutrient availability
- replacing gypsum with slaked lime for pH control would have to be investigated by a soil scientist
- implementation costs would be too high (> R 1,4 million)
- does not address the problem of SRB activity

Based on the above-mentioned disadvantages, the control of pH using slaked lime was not investigated further.

4.4 COMPOSITION OF TETS 2 EFFLUENT WATER

Chemical and microbiological analyses were conducted on the effluent to determine if the TETS 2 conditions were favourable for SRB activity (Table 4.5).

Table 4.5. Chemical and microbiological composition of the effluent

Analysis	Minimum	Maximum	Average	Number of samples
Calcium (mg/l as Ca)	8,80	132	64	12
COD (mg/l as O_2)	1 250	6 390	2 920	12
Conductivity (µS/cm)	2 360	4230	3 030	13
Dissolved oxygen (mg/l as O_2)	0,4	2,8	0,7	10
Iron (mg/l as Fe)	0,7	1,8	1,3	6
Hydrogen sulphide (mg/l as H_2S)	<1	310	40	21
Manganese (mg/l as Mn)	0,8	7,2	3,8	7
Molybdenum (mg/l as Mo)	<0,5	<0,5	<0,5	12
Nitrates (mg/l as NO_3)	3,6	43	0,6	12
Nitrites (mg/l as NO_2)	<0,5	<0,5	<0,5	12
o-Phosphate (mg/l as P)	0,5	2,8	1,4	5
ORP (mV)	-300	-250	-116	13
pH	6,04	10,3	7,29	25
Sodium (mg/l as Na)	223	925	521	13
Sulphates (mg/l as SO_4)	310	724	522	13
SRB (cfu/ml)	<10	940 000	2 200	25
Temperature (ºC)	40	53	49	25

The data in Table 4.5 showed that the effluent provided a suitable environment for SRB activity and the generation of H_2S for the following reasons:

- relatively high SRB population range
- presence of manganese could increase SRB growth rate (population duplication within 6 hours) (Medircio *et. al.*, 2007).
- an electron acceptor was available in the form of inorganic sulphates (Postgate 1984; Balows *et. al.,* 1992; Ballinger *et. al.,* 2001)
- an organic carbon source (Lukanich, 1995; O'Flaherty and Colleran, 1995) was available in the form of COD (Kim *et. al.,* 2003). The COD/SO_4 value for the effluent was between

4,0 and 5,6 (Table 4.5) which is higher than the theoretical value of 0,67 (Hao *et. al.*, 1996; Kosinska and Miskiewicz, 1999). The COD/SO_4 values of industrial wastewaters differ from one effluent to another. For example, the COD/SO_4 value for Baker's yeast production wastewater was reported to be between 3,3 and 4,0 and between 14 and 25 for industrial pig farming wastewater (Kosinska and Miskiewicz, 1999). Hao *et.al.* (1996) reported COD/SO_4 values between 0,7 and 1,5 depending on the type of carbon source available in the wastewater.

- anaerobic conditions due to the absence of dissolved molecular oxygen (Howe *et. al.*, 1967; Ballinger *et. al.*, 2001). DO <1mg/l and ORP < -100 mV (Hoa *et. al.,* 1996).
- low levels of molybdenum (<0,5 mg/l) was available for the production of SRB enzymes and co-factors necessary for SRB activity and growth (Chen *et. al.*, 1998)
- temperatures and pH were suitable for SRB activity (Korhonen and Lumme, 1978; Hao *et. al.*, 1996; Djurle, 2004).
- salinity was available in the form of sodium (Kosinska and Miskiewicz, 1999)
- o-Phosphates were available as a micro-nutrient for SRB activity (Ballinger *et. al.*, 2001; Kosinska and Miskiewicz, 2005)
- iron and manganese catalysed the generation of H_2S by SRB (Matsumura *et. al.,* 1992)
- high sulphate levels (Janssen *et. al.,* 1999) and low levels of nitrites and nitrates were typical of Kraft mill effluents (Norwood *et. al.*, 2001).

TETS 2 was only de-sludged every three months which most probably resulted in the formation of a sludge layer due to the build-up of suspended material and organic matter. The rate of sulphate reduction increases proportionally with the increase of suspended material (Hao, *et. al.*, 1992). Anaerobic conditions in the sludge layer lowered the amount of available dissolved molecular oxygen (< 1mg/l) (Howe *et. al.*, 1967; Ballinger *et. al.*, 2001) and the ORP (<-100mV) (Czechwski and Rossmore, 1981; Norwood *et. al.*, 2001).

It was concluded from the above and the data shown in Table 4.5 that the composition of the effluent was such that sulphates were indeed being reduced to H_2S (Fauque *et.al.*, 1991) by dissimilatory respiration (Matias *et. al.*, 2005; Mussman *et. al.*, 2005) which *only* occurs in SRB (Balows *et. al.*, 1992; O'Flaherty and Colleran, 1995) under anaerobic conditions (O'Flaherty and Colleran, 1995; Sutton, 2004; Kosinska and Miskiewicz, 2005).

4.5 REDUCING SRB ACTIVITY USING BIOCIDES

Non-oxidising biocides were tested as a short term measure to control SRB activity (McInerney *et. al.*, 1992; Greene, *et. al.*, 2003) and to reduce the generation of H_2S (Fauque *et. al.*, 1991) in TETS 2. Biocides containing different active ingredients were dosed at dosages recommended by the supplier (Table 4.6).

Table 4.6. Effect of biocides after a contact period of 4 hours at 50℃

Biocide	**Active ingredient**	**SRB (cfu/ml)**	**% Reduction**
Control	None	5 000	0
Biocide 1 (14 mg/l)	s-Triazine (72%)	30	99,4
Biocide 2 (7 mg/l)	Gluteraldehyde (25%)	40	99,2
Biocide 3 (13 mg/l)	Isothiazolinones (1.5%)	10	99,8
Biocide 4 (4 mg/l)	2,2-dibromo-3-nitrilopropionamide (20%)	40	99,2
Biocide 5 (4 mg/l)	Methylene bisthiocyanate (10%)	20	99,6
Biocide 6 (25 mg/l)	Sodium dimethyl-dithiocarbamate (20%)	10	99,8

The biocide selection tests (Table 4.6) showed that SRB activity could be reduced by 99,2% using Biocide 2 or Biocide 4 , 99,4% using Biocide 1, 99,6% using Biocide 5 and 99,8% using Biocide 3 or Biocide 6. Low levels of biocide were required to reduce SRB activity. The biocide efficacies were not affected by the level of SRB activity (SRB >100 cfu/ml).

Mouchè and Song (1987) reported that biocides were ineffective when SRB counts were higher than 100 cfu/ml and that high dosages of non-oxidising biocides would be required to reduce SRB activity. However, the results in Table 4.6 indicated that the biocides tested were effective in reducing relatively high SRB counts (5 000 cfu/ml) between 99,2% and 99,8% at relatively low dosages (4 mg/l to 25 mg/l).

The long term use of biocides to control SRB activity is not recommended due to the following:

- SRB re-growth due to rapid acclimation (Okabe *et. al.*, 1992)
- biocide half-life and chemical properties (Rava *et. al.*, 2005) would be affected by the fluctuating process temperatures (Table 4.1) and pH (Table 4.2)
- SRB levels fluctuated (Table 4.5) and biocides are not specific against SRB (Dilsook, 2004)

- higher and repetitive dosages of biocide would be required (Dilsook, 2004)
- SRB can become resistant to non-oxidising biocides (Dilsook, 2004)
- biocide break-down products could accumulate in the environment (Williams and Jacobson, 1999)
- implementation costs could be too high (Dilsook, 2004)

4.6 REDUCING HYDROGEN SULPHIDE LEVELS

4.6.1 Use of biomodifiers

Biomodifiers (nitrates, nitrites and/or molybdenum) were added to effluent samples from TETS 2 to induce a population shift from anaerobic SRB (Marschall *et. al.,* 1993; Bentzen *et. al.*, 1995) to the more aerobic denitrifying (nitrate-reducers) organisms (Hitzman *et. al.*, 1995). The effect of the biomodifers on ORP, pH and H_2S reduction is shown in Table 4.7.

Table 4.7. Effect of biomodifiers on ORP, pH and H_2S reduction after 72 hours at 50°C

Nitrates (mg/l)	**Nitrites (mg/l)**	**Molybdenum (mg/l)**	**ORP (mV)**	**pH**	**H_2S (mg/l)**	**H_2S reduction (%)**
Control	0	0	-300	6,69	8,5	0
25	0	0	-136	7,56	4,2	51
50	0	0	-131	7,89	4,2	51
100	0	0	-106	8,32	2,8	67
150	0	0	-70	8,44	2,2	78
200	0	0	-64	8,44	1,9	78
500	0	0	-60	8,54	1,8	79
25	25	0	-114	8,33	2,5	71
50	50	0	-101	8,71	2,0	76
100	100	0	-97	8,68	1,8	79
0	25	10	-126	8,22	2,8	67
0	50	10	-114	8,64	2,0	76
0	100	10	-90	8,85	1,8	79

The decrease in H_2S levels, increase in pH and increase in ORP could be ascribed to the following biochemical processes:

- nitrates were used as an alternative electron acceptor (Seitz and Cypionka, 1986; Mouchè and Song, 1987; Marschall *et. al.,* 1993) by SRB and denitrifying bacteria (Ballinger *et. al.,* 2001)
- pH increased due to the release of ammonia from amine containing compounds (Birnbaum and Wireman, 1984) and/or the dissimilation of nitrites and nitrates (Krekler and Cypionka, 1995)
- pH increased due to the formation of bicarbonate (HCO_3^-) ions generated during dissimilatory sulphate reduction in the presence of nitrate (Bratcova *et. al.,* 2002)
- pH increased due to the release of $CO_{2(g)}$ and $H_2S_{(g)}$ from the effluent (Hao *et. al*., 1996)
- nitrates were reduced to N_2 gas by denitrifiers when the COD/NO_3-N ratios were high (>0.64) (Polanco *et. al*., 2001, Craig *et. al*., 2001).
- increase in ORP due to the build-up of N_2 gas (Ballinger *et. al*., 2001) which suppressed sulphate reduction (Bentzen *et. al*., 1995; O'Flaherty and Colleran, 1995)
- nitrites reduced H_2S levels by scavenging the preformed H_2S (Hitzman *et. al.,* 1995; Hitzman *et. al.,* 1998) and inhibiting SRB activity (Ballinger *et. al*., 2001)
- denitrifiers used the preformed H_2S as a nutrient thus increasing the reduction of H_2S levels (Hitzman *et. al.,* 1995; Hitzman *et. al.,* 1998).
- denitrifiers used H_2S as an electron donor when the dissolved oxygen levels was < 1 mg/l (Polanco *et. al.,* 2001)
- synergism between nitrates/nitrites and nitrites/molybdenum (Hitzman *et. al.,* 1995; Hitzman *et. al.,* 1998) required lower dosages of biomodifiers. In excess of 3 000 mg/l molybdenum would be required to reduce H_2S without the addition of nitrite (Hitzman *et. al*., 1998).
- denitrifiers out-competed SRB for the available organic carbon source (Hitzman *et. al.,* 1995; Hitzman *et. al.,* 1998, Ballinger *et. al*., 2001) due to the decrease in COD/SO_4 ratio (Polanco *et. al*., 2001).

The H_2S generation was decreased by 79% (Table 4.7) with the following biomodifier additions.

- 500 mg/l nitrates
- 100 mg/l nitrates and 100 mg/l nitrites
- 100 mg/l nitrites and 10 mg/l molydbenum

However, higher dosages of biomodifiers would be required to reduce the aqueous H_2S levels (Norwood *et. al.* 2001) below the acceptable level of 1 mg/l to control H_2S emissions and odour (Hagen and Hartung, 1997; Ballinger *et. al*., 2001). Howe *et. al.* (1967) reported that 500 mg/l nitrate would inhibit H_2S generation, Bratcova *et. al.* (2002) reported that levels above 500 mg/l would be required to inhibit H_2S generation completely and Dilsook (2005) reported nitrate levels between 200 mg/l and 1 000 mg/l to inhibit H_2S generation.

The amount of biomodifiers required to inhibit the generation of H_2S would depend on the amount of carbon source available (Hitzman *et. al.,* 1998), optimum COD/SO_4^{2-} ratio, salinity (Kosinska and Miskiewicz, 1999), microbial population, pH, temperature, chemical composition of the specific effluent (Polanco *et. al*., 2001), ORP and carbonate alkalinity (Birnbaum and Wireman, 1984).

It was concluded from the results (Table 4.7) that the addition of biomodifiers did indeed shift the population from anaerobic conditions to more aerobic conditions as reported by a number of authors. The addition of biomodifiers (nitrates, nitrites, molybdenum) was not investigated further due to costs, the possible negative effects on the soil properties (cation-anion exchange capacity and nutrient availability) at the irrigation farm (Dilsook, 2004) and the possible patent infringements in South Africa (Allison, 2005).

4.6.2 Use of biomodifiers and sulphate reduction inhibitors

The reduction of aqueous H_2S levels at different capacity levels were investigated using sodium nitrate and 9,10 anthraquinone (AQ). The sodium nitrate was dosed as the biomodifier to provide an alternative electron acceptor for the denitrifying bacteria. The AQ was dosed as the sulphate reduction inhibitor to inhibit SRB dissimilatory respiration and the generation of H_2S. The percentage H_2S reductions at the different TETS 2 capacity levels are shown in Table 4.8.

Table 4.8. Reduction of aqueous H_2S levels

Initial H_2S (mg/l)	**Final H_2S (mg/l)**	**% Reduction**
$14^{(1)}$	<1	> 99
$50^{(1)}$	4	92
$200^{(2)}$	60	70
$310^{(3)}$	160	48

TETS 2 capacity levels: (1) 50% (2) 25% (3) 10%

The data in Table 4.8 show that the reduction of H_2S was less than 92% when TETS 2 was 10% and 25% full and higher than 92% when TETS 2 was 50% full. The TETS 2 effluent retention times were longer (> 4 hours) at the lower capacity levels. The longer retention times increased the settling rate of suspended material resulting in the formation of a thicker sludge layer (Dilsook, 2004). The build-up of sludge and organic matter provided the ideal ORP, pH and anaerobic conditions for the rapid reduction of sulphates to H_2S (Hao, *et. al.*, 1992; Norwood *et. al.,* 2001).

The product dosages required to reduce the aqueous H_2S (Table 4.8) were as follows:

- 25 mg/l sodium nitrate and 2 mg/l AQ:
  H_2S reduced from 14 mg/l to <1 mg/l (99% reduction at pH=7,08, TETS 50% full)
- 50 mg/l sodium nitrate and 4 mg/l AQ.
  H_2S reduced from 50 mg/l to 4 mg/l (92% reduction at pH=9,40, TETS 50% full)
- 50 mg/l sodium nitrate and 4 mg/l AQ:
  H_2S reduced from 200 mg/l to 60 mg/l (70% reduction at pH=6,59, TETS 25% full)
- 100 mg/l sodium nitrate and 8 mg/l AQ:
  H_2S reduced from 310 mg/l to 160 mg/l (48% reduction at pH=7,41, TETS 10% full)

The reduction in aqueous H_2S (Table 4.8) can be ascribed to the following mechanisms:

- loss of H_2S due to pH < 8,3 (discussed in section 2.2)
- population shift induced by the addition of sodium nitrate (discussed in section 4.6)
- inhibition of SRB dissimilatory respiration by the addition of AQ

The reactivity of the AQ is affected by solubility, redox potential, anaerobic conditions and particle size (Tatnall, 1996). The sub-micron colloidal particles of the AQ moved into the micro-colonies by Brownian motion and attached to the surfaces of the SRB where they partitioned into the cell membrane by SRB metabolism (Ballinger *et. al.,* 2001). Dissimilatory sulphate respiration was inhibited due to the uncoupling of the electron transfer from ATP synthesis caused by the AQ redox potential (Ballinger *et. al.,* 2001). The uncoupling resulted in insufficient energy charge for further sulphate activation and reduction (Cooling *et. al.,* 1996).

AQ are redox active molecules with negative midpoint potentials for the fully-oxidised to fully-reduced transitions (electrochemically reversible) which lies within the redox range of anaerobic respiration (-400 mV to -100 mV) (Cooling *et. al*., 1996).

SRB activity is initiated at -100mV (Hao *et. al*., 1996) and their main metabolic oxidations take place within a redox range of -150mV and -200mV (Postgate, 1984). The SRB are out-competed by methanogens at redox potential < -500mV (Norwood *et. al*., 2001).

Tatnall *et. al.* (1996) reported that the AQ particle size should preferably be less than 2.0 µm since particle size, and not surface area, affects AQ activity. Ballinger *et. al.* (2001) reported that the particle size should be less than 50 µm, preferably between 5 µm to 10 µm. Harless *et. al*. (2000) reported that the particle size should be 85% less than 0,45 µm in order to penetrate the cell membrane. AQ had a particle size of 85% less than 5 µm which fell within the range reported by Ballinger *et. al.* (2001) and would easily reach the SRB in the TETS 2 sludge layer.

The benefits of using sodium nitrate and AQ to control H_2S are as follows:

- synergism between nitrates and AQ require lower product dosages
- less impact of nitrates on the environment due to the lower dosages
- effective over a wide pH range (Ballinger *et. al*., 2001)
- no patent infringements in South Africa (Joseph and Van Niekerk, 2005)
- useful when biocides are not suitable for SRB control (Tatnall, 1996; Lie *et. al.,* 1999)
- AQ is non-reactive, non-ionic, hydrophobic with a low water solubility (Ballinger *et. al*., 2001; Mauldin *et. al*., 2002)
- AQ is environmentally friendly, biodegradable, non toxic to animals and plants (Cooling *et. al*., 1996)
- AQ is SRB specific and effective under anaerobic conditions (Tatnall, 1996)

The data (Table 4.8) showed that the generation of H_2S was controlled by dosing sodium nitrate as the biomodifier and AQ as the sulphate reduction inhibitor. The average aqueous H_2S measured at the TETS 2 was 40 mg/l (Table 4.5). Dosing 50 mg/l sodium nitrate and 4 mg/l AQ into the launder point between Clarifier 2 and TETS 2 would be sufficient to reduce the aqueous H_2S by at least 92%. The remaining aqueous H_2S (8%) could be removed by aeration or other oxidation procedures. The dosing would have to be continuous to maintain effective SRB inhibition and H_2S removal (Ballinger *et. al.,* 2001). Smaller particle sizes (< 5 µm) would also increase the activity of the AQ and decrease the dosages required (Tatnall, 1996).

CHAPTER 5

CONCLUSIONS

The conclusions are based on the initial objectives of this study and the laboratory scale investigations.

5.1 Main sources of hydrogen sulphide emissions

- All four TRS components typically associated with most Kraft mills, H_2S, CH_3SH, $(CH_3)_2SH$ and $(CH_3)_2SH_2$ were detected in the effluent water (aqueous TRS). Hydrogen sulphide (H_2S) was the only gaseous TRS detected in the atmosphere surrounding the mill.

- The main source of H_2S emissions was from the effluent plant and not from the irrigation farm as initially thought. The levels of H_2S detected across the effluent plant and the irrigation farms were all above the odour threshold (0,0001 to 0,030 ppm) but below the permissible exposure limit (PEL) of 15 ppm. The odours detected were considered as a nuisance by the mill personnel and surrounding communities.

5.2 Main causes of hydrogen sulphide emissions

- The differences between the gaseous TRS and aqueous TRS component levels at System 1 and System 2 effluents were due to the different types of effluent treated, fluctuations in the process temperature, pH and process upsets.

- Higher temperatures and lower pH's increased the emissions of gaseous TRS components. The relatively low levels of H_2S detected at the irrigation farm was due to the stripping of H_2S when the effluent was pumped from the effluent plant to the Farm Dams and the added stripping by the action of the deflector plates.

- The chemical and microbiological data showed that the TETS 2 effluent composition was typical of Kraft mills and that it was suitable for the rapid growth of SRB and the generation of H_2S.

The TETS 2 effluent contained high levels of SRB, COD/SO_4 ratio (4,0 to 5,6), available organic carbon source, sulphates, micro-nutrients, low levels of nitrates and nitrites. These conditions were all favourable for the reduction of sulphates to H_2S by SRB dissimilatory respiration.

5.3 Control of SRB activity and hydrogen sulphide emissions

5.3.1 pH control

- Computer modeling data indicated that increasing the average pH of the TETS 2 effluent from 6,8 to 8,6 using slaked lime would not be practical due to the following:
  - higher pH (>7,5) would affect the soil properties
  - increase scaling (R.S.I <0,7)
  - difficulty in controlling the pH due to process fluctuations
  - high implementation costs

5.3.2 Use of biocides

- The biocide selection tests indicated that SRB activity could be reduced by 99,2% using Biocide 2 (gluteraldehyde) or Biocide 4 (organobromine), 99,4% using Biocide 1 (s-triazine), 99,6% using Biocide 5 (organothiocyanate) and 99,8% using Biocide 3 (isothiazolinones) or Biocide 6 (dithiocarbamates). Low levels of biocide were required to reduce SRB activity. The biocide efficacies were not affected by the level of SRB activity.

- However, the use of non-oxidising biocides was not considered as a long term treatment option due to the various disadvantages such as the stability of the biocides at fluctuating pH and temperatures, half-life, environmental accumulation, toxicity and costs.

5.3.3 Use of biomodifiers

- The addition of biomodifiers (nitrates, nitrites, molybdenum) resulted in a population shift where denitrifying (nitrate reducers) micro-organisms out-competed SRB for the available organic carbon source and nutrients making the effluent conditions more aerobic.

- The more aerobic conditions inhibited SRB activity which in turn increased the pH and the ORP of the effluent, thus reducing the generation of H_2S levels by 79%.

- No stoichiometry was found between the level of aqueous H_2S in the effluent and the amount of biomodifiers required to reduce SRB activity and H_2S generation.

- Higher biomodifier dosages would be required to increase the reduction of aqueous H_2S by more than 79%. The increased dosages would significantly increase the cost of the treatment programme. The accumulation of nitrates, nitrites and molybdenum would affect the soil cation-anion exchange capacity, SAR, permeability and nutrient availability of the irrigated pastures.

5.3.4 Use of biomodifiers and sulphate reduction inhibitors

- The treatment option using sodium nitrate and AQ was found to be more environmentally friendly and cost effective.
- The average aqueous H_2S for TETS 2 (40 mg/l) indicated that continuous dosing of 50 mg/l sodium nitrate and 4 mg/l AQ would be effective in reducing the generation of H_2S by at least 92%. This treatment option would also be compatible with aeration or oxidation processes to increase the removal of H_2S above 92%. Aeration or oxidation would increase the dissolved oxygen, decrease the COD and further enhance the inhibition of SRB activity and oxidise any reduced sulphur.
- The use of sodium nitrate and AQ to control the generation of H_2S is not patented in South Africa. It can, therefore, be used to treat the Kraft mill effluent without violating any intellectual property rights in South Africa.

CHAPTER 6

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