OPTIMISATION OF MINE SERVICE WATER DISINFECTION

WRC Report

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by

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Document 1

EXECUTIVE SUMMARY

INTRODUCTION

The South African gold mining industry uses some 510 Mℓ/d of fresh make-up water, discharges about 440 Mℓ/d of effluent, mainly to evaporation dams, and circulates roughly 5,500 Mℓ/d. More than 25 % of this volume is circulated as service water, which is used mainly for cooling of the working areas and to suppress dust. Since geothermal heat can raise the rock surface temperature as high as 55 °C, the service water is chilled to 4 °C. For various reasons mine workers have been found to drink the service water. At most mines, the service water is contaminated by faecal matter and faecal total coliform counts as high as 3 000/100 mℓ have been recorded. For this reason it is necessary to disinfect the service water. Chlorine was used traditionally to this end, but because of its reactivity with ammonia (*ca.* 5 mg NH_4-N/ℓ) in the water, the use of other disinfectants, such as chlorine dioxide and ozone, was investigated.

Disinfection studies conducted on the mine service water at the Kloof Gold Mine (where about 35 Mℓ/d is circulated) indicated a notable non-disinfective sink for oxidizing disinfectants such as chlorine, chlorine dioxide or ozone due to the nitrite ion present in water. The nitrite ion concentration in the water varies, but averages around 0,9 mg/ℓ. The oxidation of nitrite ion by chlorine dioxide would have to take place before it could disinfect the water effectively. This would mean a cost of about R2,5 million p.a., without any significant disinfection.

NITRITE ION BUILDUP

While nitrite ion oxidation serves to lessen the oxidant demand, it would be more advantageous to curtail nitrite ion buildup in the water.

Nitrite ion buildup could be due to:

(i) a source of nitrite ion that produces the ion at a higher rate than the normal bacterial processes could remove it; or

(ii) an inhibition of the normal bacterial processes.

An investigation into the use of explosives as a source of nitrite ion could not positively link their use to an increase in nitrite ion concentration.

The normal bacterial process of ammonia nitrification consists of two steps, i.e. the oxidation of ammonia no nitrite ion by species such as *Nitrosomonas*, and the subsequent oxidation of nitrite ion by species such as *Nitrobacter*. Both bacteria are obligate aerobic gram-negative autotrophs with a marked preference for attached growth. A comparison of the sand filter influent nitrite ion concentrations with the filter effluent (ratio $NO_2^-)_{out}$: $(NO_2^-)_{in}$ = 3.4 : 1; highlights the sand filters as a nitrite source and possibly as a growth area for the nitrifying bacteria. It is recognised that both these species are sensitive to inhibition by a wide variety of factors such as temperature, variable organic loading in the water, mercury(II), copper(II), arsenic(0), arsenic(III), chromium(IV), pH free ammonia, cyanide, etc. Nitrite ion buildup in a nitrifying system then could be explained by an inhibition of the action of *Nitrobacter*.

A comparison of the nitrite ion production in the mine service water with that in distilled water (with similar nutrient content) in an aerated batch reactor at 30 °C, shows a marked nitrite ion build-up in the service water. This points to a chemical component of the service water, rather than a physical property being responsible for the nitrite ion buildup. Measurements in the water circuit at the mine ruled out temperature and dissolved oxygen as inhibitive factors.

BENCH SCALE TESTS

Bench scale studies on the use of ozone for the treatment of the service water of the Kloof Gold Mining Company indicated that the ozone demand for the water varied between 5 and 10 mg/ℓ and that the total plate count could be reduced from 10^7 to 10/mℓ and the total coliforms could be reduced to 1 (or less)/100mℓ with only 5 mg/ℓ of ozone. It was therefore estimated that no more than 10 mg/ℓ of ozone would be needed. The applied dosage, however, would depend on the ozone transfer efficiency which had to be determined for various contacting systems on pilot scale.

PILOT SCALE OZONATION OF MINE WATER

For the pilot scale study, two Degrémont ozone generators were used which nominally generated 1 kg/h each. Ozone transfer was accomplished by means of either:

(i) an 8 m high (1.25 m dia.) concrete bubble column equipped with porous ceramic diffusers operated in counter-current mode;
(ii) by a deep U-tube or by a static mixer system, placed before an upflow sand filter.

MAIN FINDINGS

Ozone transfer efficiencies of 73-85 % for the static mixer system, 80-88 % for the bubble column and 96-99 % for the deep U-tube were obtained. The efficiencies tended to decrease with increasing ozone dosages.

Ozone was able to substantially reduce bacterial indicator numbers. An elimination of all coliforms and a reduction in total plate counts of 4 to 5 logs was always possible at ozone dosages of 7 mg/ℓ.

The ozone demand of the service water was found to be on average 7 mg/ℓ with maximum values reaching 10 mg/ℓ. On a 50 Mℓ/d scale, this would involve ozone generators with a capacity of 500 kg/d plus the allowance for losses. Costing was done on a 24 kg/h basis. This resulted in a cost figure of US$1.5 million for the whole plant including air preparation and dissolution. Amortization of the amount over 10 years at an interest rate of 16 % results in an annual cost figure of just over $300 000. The operational cost, mainly electricity and maintenance, would add another $75 000 to the annual ozonation budget bringing the total annual cost to just under $400 000. Ozone would have to be supplemented with another oxidant to ensure a residual disinfectant concentration through the service water system. This could add $40 000 to $80 000 to this option.

By comparison a dosage of 4 mg/ℓ of chlorine dioxide, which is insufficient to oxidize all the nitrite but which does result in a lowering of bacterial counts, would cost $1 million annually on a 50 Mℓ/d scale. Breakpoint chlorination with simultaneous nitrite oxidation would require about 45 mg/ℓ of chlorine which would also cost about $1 million annually.

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1.1 Introduction

It has been noted on many mines that the mine service water, i.e. the water used to cool the working areas and dampen the dust, is being drunk by the mine workers. This undesirable practise, although banned by mine managements generally, still persists and therefore the water needs to be disinfected.

The need for the disinfection of mine service water results from its poor microbiological quality. This quality is reflected in the presence of faecal- and other coliform bacteria in the water. Although these bacteria *per se* are harmless they indicate probable faecal contamination, which bears with it the spectre of enterically borne disease being spread through drinking water.

1.2 Motivation

The common disinfectants used are all oxidizing agents like chlorine, bromine, chlorine dioxide and ozone. Since the oxidation of bacterial matter, which is essentially organic, is kinetically slow relative to most of the inorganic oxidation reactions (Laidler, 1950) it follows that any inorganic reducing agent present in the water would have a pronounced effect on the disinfection of the water. It has been found that there are substantial concentrations of nitrite, a reducing agent, in the service water of the Kloof Gold Mining Company (see Table 2.2). This has had the effect that disinfection costs have been higher than would have been the case in the absence of nitrite.

An estimate of the saving that could be brought about by not having nitrite in the system runs at between R0,4 million/a, in the case of Cl_2 disinfection and R2,4 million/a in the case of

ClO_2 disinfection. An absence of nitrite will therefore improve the cost efficiency of water disinfection. There are two options available to lessen the cost effect of nitrite:

1) Removal of nitrite by the most economic method, eg O_3, with the further disinfection by a residuogenic disinfectant such as ClO_2 or

2) Removing or curtailing nitrite at its source.

The second option, if viable, is the better long term solution to the problem since it does not in effect add an additional cost component. Furthermore, it is likely that the answer obtained here may be applicable to other mines with a similar problem and it may even be extended to beyond the mining field to other water- and wastewater treatment fields.

It was found, however, that sufficient applicable data on nitrite build-up could not be found in the literature. In fact the phenomenon has not been widely reported, probably due to the common usage of determining and reporting the combined nitrite and nitrate concentrations.

In the light of the foregoing it has been decided to study the possible sources of nitrite in the Kloof Gold Mining Company's service water.

1.3 Reference

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CHAPTER 2

Background

2.1 Introduction

The Witwatersrand, where most of the South African gold mines are situated and indeed where ca 42% of the South African population is to be found, is located on a high plateau where the average rainfall amounts to 630 mm per annum (DWA,1986). Most of the water to this highly industrialized area is drawn from the Vaal river. The Vaal river catchment, where 77% of the mining activity of the RSA is found is designated the C catchment area by the Department of Water Affairs and Forestry, has a water availability and demand profile as described in Table 2.1. The shortfall in the water supply is to be made up by water imported via the Tugela-Vaal and the Lesotho Highlands projects increasing the flow by ca 2 000 million m^3/a. Because return flow remains an important factor in the water supply management of the area, the bulk of the effluent from the industrialized areas is also fed back into the Vaal River.A combination of these factors result in a paucity of both quantity and quality of the water supplied in this area. This results in a relatively high cost of the drinking water supplied in this area by the Rand Water Board, the Western Transvaal Regional Water Company and the Orange Free State Gold Fields Water Board. This also brought about stringent demands on the quality of effluents as enforced by the Department of Water Affairs and Forestry.

2.2 Service water in the gold mining industry

Water is used quite extensively on South African gold mines. The gold mining industry uses approximately 510 Mℓ/d of fresh make-up water, discharges about 440 Mℓ/d and recirculates

Table 2.1 Water demand and availability profile for the C catchment area in which the Kloof Gold Mining Company is situated. Values are projections in million cubic meters per annum by the year 2 000.

	Source	million m^3/a
Supply	Usable AAR1)	2 149
	Ground water	657
	Return flow	1 079
Total usable water supply		3 885
	Sector	million m^3/a
Demand	Industry	1 851
	Electricity	450
	Mining	343
	Agriculture total	1 480
	Nature conservation	41
Total water demand		4 165

1) AAR = average annual run-off.

roughly 5 500 Mℓ/d (Mackay *et al.*, 1991). During work underground it can be considered as one the most vital of all the resources. There it serves mainly two purposes:

i) It is used as drinking water for the mine workers. In the deeper South African mines the work areas can extend down as deep as 4 000 m below ground level. With many of these mines situated on the Witwatersrand which is at an average elevation of about 1 800 m above sea level, some of these working areas are more than 2 000 m below sea level. Under these conditions the combined effect of geothermal heat (with rock temperatures up to 60 °C being recorded) and high humidity (average 90-100% relative) make working conditions for the mine workers strenuous. The supply of chilled drinking water under these conditions by the mining companies makes both humanitarian and economic sense; indeed it may be vital.

ii) For the safety and well-being of both the mine workers and the equipment it is necessary to cool the working areas and dampen the dust down. This is achieved by importing quantities of relatively low quality water to the work faces. Water used for such purposes is termed service water.

The demands on the quality of mine service water is not very high, since the water is not meant to be consumed by humans. In the light of these factors, water in the service water circuit is circulated in the mine. This naturally results in salination of the service water. This common problem in the mining field may be somewhat ameliorated by the fresh ground water that is often encountered during mining operations. Due to the fluctuating water levels in the service water circuit, the excess water that is bled out of the system is not disposed of, but is stored in a holding dam. When the need arises fresh water of drinking water quality is added to make up for losses in the system.

Toilet facilities are supplied to the workers underground by the mining companies. Nevertheless, it has been found that *Escherichia coli* and other faecal coliform bacteria are present in the water (about 3 000 total coliforms/100 mℓ found in water at the Kloof Gold Mine at one stage, Pearson *et al.*, 1991), pointing to pollution of the water by the faeces of vertebrate animals; in this case, human beings.

The presence of the indicators of faecal contamination has resulted in many mining companies imposing strict regulations prohibiting the drinking of the mine service water. There is a very real fear of pandemic spread of enteric diseases within the workers corps on any particular mine. Referring to mathematical models of the spread of infectious diseases (Braun, 1987), it can be concluded that in the case where the source of infection is not removed the limiting value of the maximum number infected by the disease can rise so dramatically that effectively the whole workforce can eventually be paralysed. Such a spreading of infectious disease can have a severely debilitating effect on the production capacity of a mine as well as a very damaging effect on public relations and even have political repercussions.

A campaign designed to bring the danger of drinking the service water, as well as the regulations in this regard to the attention of the workers was launched. It was found, however, that these regulations regarding the drinking of the service water did not have the desired effect. Possibly two main reasons can be forwarded to explain this phenomenon:

i) Very often the stopes are far removed from the water cooling facility where the water is chilled to ca. 4 °C. Drinking water has to be transported to the stopes through several kilometres of uncooled passages, where the air temperature can be as high as 45 °C, in 50 mm metal pipes. The result is that the water reaches the stope at an unpalatable temperature (25 - 35 °C). In contrast the service water is transported to the stopes through a 300 mm pipe which delivers water to the stope at 14 - 18 °C.

ii) It is generally accepted within the mining community that there exists within the mine worker corps, an "underground worker" subculture for whom the drinking of this "dangerous water" is a matter of pride and status. If needs be, they will even drink this water surreptitiously.

The result has been that, supplementary to all other regulatory efforts, disinfection of the mine service water has become a matter of course and is considered standard practice on most mines.

Since the service water is being consumed by the workers, the disinfectant choice has been limited to those used in the drinking water field. The obvious choice was to use chlorine as disinfectant. It was recognized, however, that there is a substantial concentration of ammonia in the water (eg see Table 2.2). Ammonia reacts in various stoichiometries with

Table 2.2 The average water quality over the period 12/9/89 to 6/2/90 as reported by Pearson *et al* (1990). Concentrations expressed as mg/l.

Determinant	Month/Year of Sampling				
	9/89	10/89	11/89	1/90	2/90
Na^+	142	169	172	151	140
Ca^{2+}	49	123	107	115	141
Mg^{2+}	26	28	27	26	22
SO_4^{2-}	257	388	399	398	408
Cl^-	104	179	209	149	172
PO_4^{3-}-P	0,4	0,3	0,1	5,6	0,1
Alk ($CaCO_3$)	89	161	9	55	54
NO_3^--N	38	19	20	26	17
NO_2^--N	1,25	1,26	1,17	1,11	0,81
NH_3-N	5,18	4,41	3,51	4,00	2,87
Cl_2 demand	34	28	23	22	19
ClO_2 demand	11	11	7	7	7

$$NH_3 + Cl_2 \rightleftharpoons NH_2Cl + HCl \qquad (2.1)$$

$$NH_2Cl + Cl_2 \rightleftharpoons NHCl_2 + HCl \qquad (2.2)$$

$$NHCl_2 + Cl_2 \rightleftharpoons NCl_3 + HCl \qquad (2.3)$$

$$\underline{2NCl_3 + Cl_2 \rightleftharpoons N_2 + 7Cl_2} \qquad (2.4)$$

$$NH_3 + 2Cl_2 \rightleftharpoons \frac{1}{2}N_2 + 3H^+ + 2Cl^- \qquad (2.5)$$

chlorine (see equations 2.1 - 2.5) to form chloramine, chlorimine, nitrogen trichloride and nitrogen respectively (White, 1972), whereas the species that is thought to be responsible for disinfection, hypochlorous acid (HOCl) (Butterfield, 1948), is formed only in the absence of other reducing agents according to equation (2.6).

$$Cl_2 + H_2O \rightleftharpoons HOCl + HCL \qquad (2.6)$$

Chloramines are known to be several orders of magnitude weaker than chlorine as disinfectants (Butterfield, 1948). If effective disinfection is then to be achieved, it is necessary to keep chlorinating until chlorine (HOCl or its salt hypochlorite, OCl^-, depending on the pH) is once again the dominant species, through the process known as breakpoint chlorination. The breakpoint, per mg of NH_3-N, is achieved at

$$\frac{1}{14} * 2 * 71,7 = 10,13 \text{ mg } Cl_2$$

Given a current chlorine price of about R3,50/kg and a water usage of 50 Mℓ/d, the cost of breakpoint chlorination could amount to R658 000/a per mg NH_3-N/ℓ. This is however not the only chlorine reducing substance that may be found in water. That means that the total disinfection cost may be considerably higher.

It was against this background that the Kloof Gold Mining Company, which is part of the Gold Fields of South Africa group of mines, undertook a study to determine the economic alternatives to chlorine disinfection. The viable alternatives were considered to be chlorine dioxide (ClO_2) and ozone (O_3) since these do not react with NH_3 to any appreciable extent. In the course of this study it was determined that there is a significant oxidant consuming substance in the service water, which was identified as nitrite (see Table 2.2). The stoichiometry of the various oxidants with nitrite is shown in equations (2.7) - (2.9). At the

$$NO_2^- + Cl_2 + H_2O \rightleftharpoons NO_3^- + 2H^+Cl^- \qquad ...(2.7)$$

$$NO_2^- + O_3 \rightleftharpoons NO_3^- + O_2 \qquad ...(2.8)$$

$$NO_2^- + 2ClO_2 + H_2O \rightleftharpoons NO_3^- + 2HClO_2 \qquad ...(2.9)$$

Mass stoichiometries:

$Cl_2 : NO_2^- = 5,07:1$

$O_3 : NO_2^- = 3,43:1$

$ClO_2 : NO_2^- = 9,64:1$

time of writing the use of chlorine dioxide has been discontinued where it was used as disinfectant in one part of the service water circuit while chlorine was still being used in another part of the circuit. If it is assumed that the reaction of nitrite with chlorine dioxide (and with all the other oxidants) is kinetically dominant, the portion of the cost of disinfection ascribable to nitrite is shown in Figure 2.1. and the absolute cost in Figure 2.2.

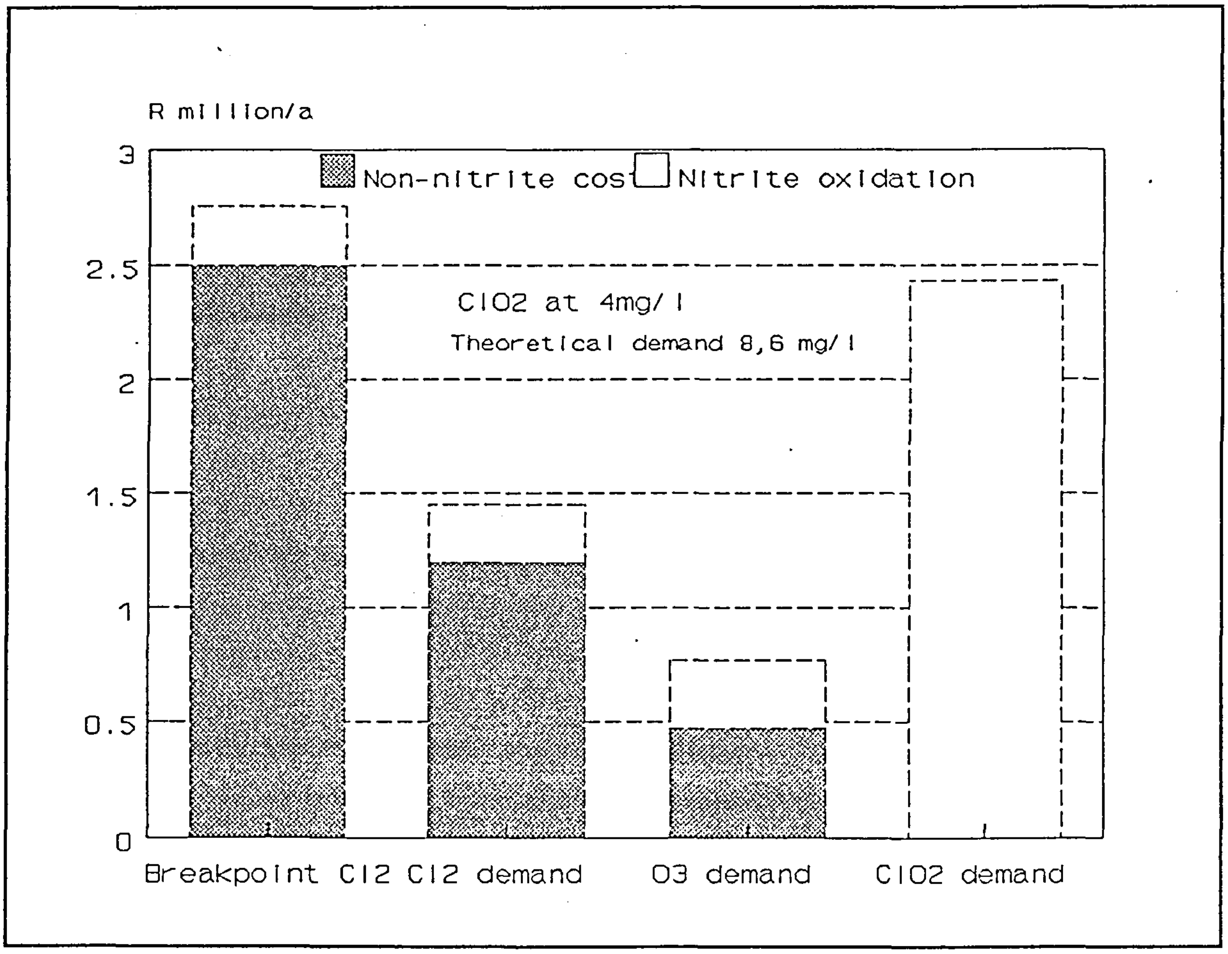

Figure 2.1 The portion of total disinfection cost attributable to nitrite on a 50 Ml/d water treatment plant with an average nitrite concentration of about 0,9 mg/l.

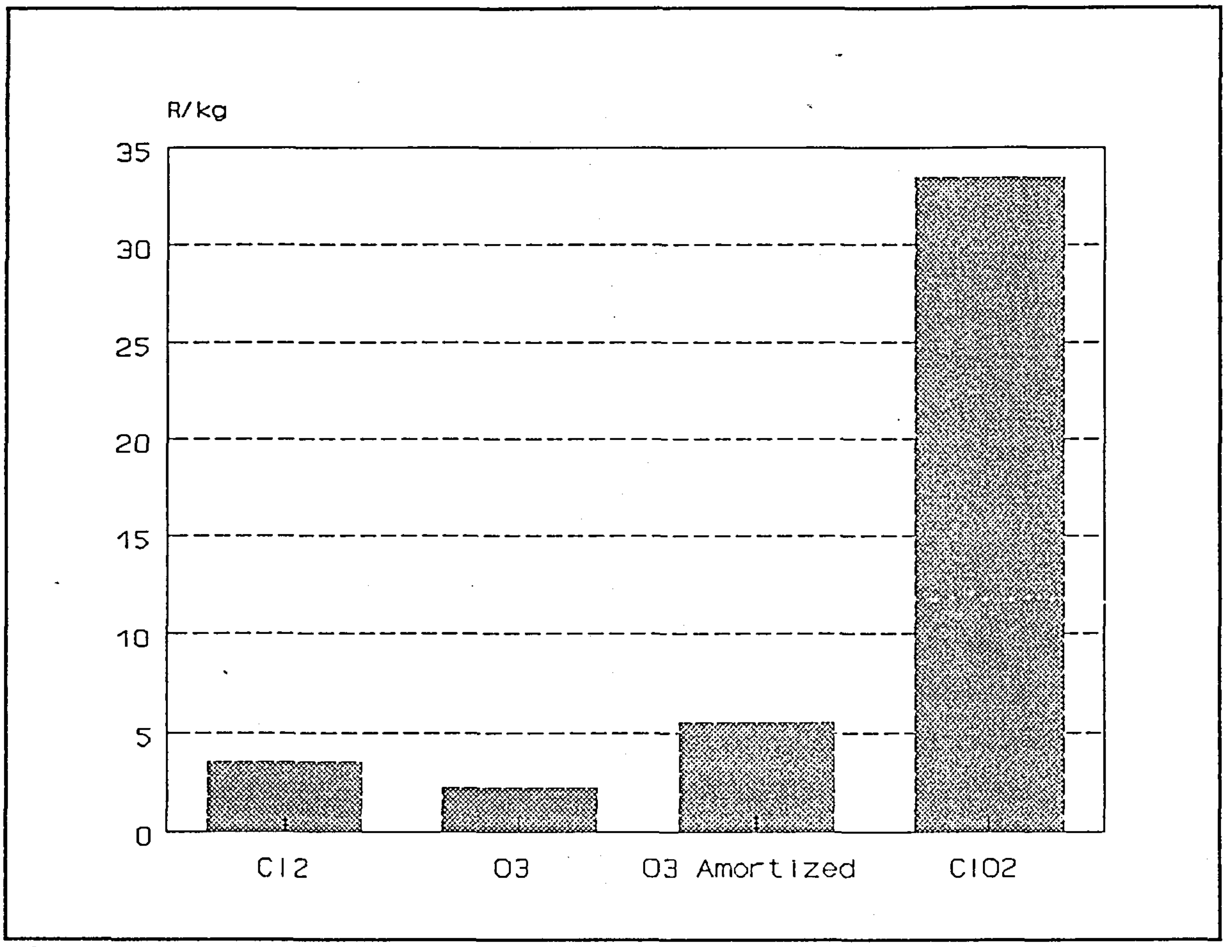

Figure 2.2 The cost of disinfection given various treatment options with conditions as in Figure 2.1.

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Chapter 3

Literature Review

3.1 Introduction

The existence of nitrite in water has been reported by a number of authors (Knowles *et al*, 1965; Painter, 1970; Curtiss *et al.* 1975; Watson *et al.*, 1989; Cunliffe, 1991). The conditions described in the literature cover water treatment situations from drinking water distribution to sewage treatment. No reference to nitrite in the mining situation has been found in the literature. It is therefore necessary to refer to non-mining related literature for references on nitrite build-up.

3.2 Nitrite chemistry in mine water.

The chemistry of nitrite formation, discussed in Chapter 4, is complex and references to the abiotic production of nitrite usually refer to laboratory preparations.

The oxidation of nitrite by oxidants common in the mining situation at Kloof Gold Mine include chlorine, some chloramines, chlorine dioxide, ozone, bromine and oxygen (Hueey, 1983; Valentine, 1985; Scully and White, 1991; Cunliffe,1991). The oxidation reactions, although thermodynamically favourable, proceed at varying rates (see Table 2.1), which causes the nitrite oxidation reaction to have to compete with other reductants for the oxidant (Haag and Lietzke, 1980; Scully and White, 1991).

Table 2.1 Observed kinetic constants in $M^{-1}s^{-1}$ for various reactions of chlorine.

Oxidant	Substrate	Forward(k_1)	Backward(k_{-1})
Cl_2 ($HOCl$)	NH_3	$1,2.10^4$	$3,0.10^{-5}$
	NH_2Cl	12,8	$6,5.10^{-7}$
	RNH_2	$6,8\ 10^5$	$1,6\ 10^{-6}$
	NO_2^-	11,3	
	Br^-	141	
Br_2 ($HOBr$)	NH_3	$2,6.10^7$	$1,5.10^{-3}$
	NH_2Br	$7,0.10^5$	43,1
	RNH_2	$5,1.10^7$	$1,6.10^{-4}$
	NH_2Cl	$5,0.10^3$	$2,0.10^{-4}$

The literature cited in Chapter 4, although not denying the possibility of inorganic (abiotic) nitrite production, tends to favour the oxidation of nitrite. The kinetics referred to above holds out the possibility of nitrite build-up, should the concentrations of other substances, such as ammonia and some organic amines, be favourable. It does however not pronounce on nitrite production *per se*. The presence of ammonia in the service water raises the possibility of microbiological (biotic) nitrite production.

3.3 Biotic nitrite production.

In a non sterile system devoid of extraneous toxins and in a steady state, no nitrite build-up should be in evidence since the combination of observed cell yield and substrate utilization rate favours the nitrite utilizing bacteria (Painter, 1970, Lo and Chen 1991). Furthermore, the oxidation of nitrite by a variety of oxidants is dynamically favourable. Probably partly due to these observations, partly due to no particular desire to investigate nitrite as a separate entity and partly due to the water quality guidelines never referring to nitrite as a separate parameter in measuring water quality (although it is implicated in methaemoglobinaemia in infants; SABS, 1984; USEPA, 1986; CWQG, 1987), very few studies of nitrite build-up were reported before 1970.

3.3.1 Genera

It is believed that the biotic oxidation of ammonia proceeds in two steps, i.e. i) the oxidation of ammonia to nitrite and ii) the oxidation of nitrite to nitrate(). The genera involved in the microbiological (biotic) oxidation of ammonia to nitrite are thought to be: *Nitrosomonas winogradsky*, *N. europaea*, *N. monocella*, *Nitrosococcus* and *Nitrosolobus multiformis*. The genera involved in nitrite oxidation are deemed to be: *Nitrobacter winogradsky*, *N agilis*, *Nitrococcus*, *Nitrocystis* and *Nitrospina* (Watson *et al.*,1989; Painter, 1970). Most nitrifying species are Gram-negative.

All species of ammonia oxidizers (often lumped under the name *Nitrosomonas*) are obligate chemolithotrophs which fix CO_2 to fulfil their energy and carbon needs. The oxidation of ammonia takes place in two steps: i) The oxidation of ammonia to hydroxylamine (NH_2OH), incorporating molecular oxygen and ii) The energy yielding oxidation of hydroxylamine to nitrite, possibly incorporating oxygen abstracted from water. The active substrate for *Nitrosomonas* is thought to be the un-ionized ammonia, NH_3 rather than NH_4^+ (Watson *et al.*, 1989).

Nitrite oxidizing species (lumped as *Nitrobacter*) are preferred chemolithotrophs fixing carbon dioxide to fulfil their carbon needs and using water as a terminal electron acceptor.

3.3.2 Inhibitors

Nitrite build-up as a deviation of the nitrification process has been studied by Randall and Buth(1984a, 1984b), Sato *et al.*(1985), Beg and Hassan(1987), Tyagi and Couillard (1988), and Gee *et al.*(1990). Later studies focus on the intentional inhibition of nitrite oxidation in order to gain economic advantage in the denitrification process (Turk and Mavinic, 1987; Turk and Mavinic, 1989; Suthersan and Ganczarczyk, 1990). These studies describe nitrite build-up in terms of the relatively greater inhibition of the second step of the biotic oxidation of ammonia. Factors that could lead to a nitrite build-up include:

1. Temperature

(Randall and Buth, 1984a and 1984b; Watson *et al.*, 1989; Antoniou *et al.*, 1990)

Assimilation of ammonia by *Nitrosomonas* as well as the assimilation of nitrite by *Nitrobacter* has been shown to be enzymatically linked. Common to all enzymatic (catalytic) reactions, nitrification can be expected to be temperature dependant. This temperature dependence has been observed in activated sludge systems and has been used in explaining a nitrite build-up in sewage treatment systems, either on its own or in conjunction with toxicity effects. With reference to the total nitrification reaction, the effective maximum specific growth rate has been expressed as being proportional to: exp{9980/T}, where T is the absolute temperature. A critical temperature between 12° and 14°C has been suggested, below which nitrite build-up is likely.

2. pH

(Kholdebarin and Oertli, 1977a; Antoniou *et al.*, 1990; Teichgräber, 1991)

The overall nitrification reaction can be expressed as:

$NH_4^+ + 2O_2 \quad NO_3^- + H_2O + 2H^+$

On equilibrium principles alone there would appear to be a pH effect, with the nitrification reaction being suppressed (by the principle of Le Chatelier) on a decrease of pH. A decrease in the activity of nitrifying bacteria has been observed at elevated pH but it is unlikely that this effect is entirely due to an increased OH^- concentration. An optimum pH range of 7-9 has been proposed for both organisms and a functional range of 4,5-10.

3. Free ammonia and free nitrous acid

(Randall and Buth, 1984b; Turk and Mavinic, 1987; Turk and Mavinic, 1989; Suthersan and Ganczarczyk, 1990)

Although free ammonia is considered to be the prime substrate for *Nitrosomonas*, it can be inhibited by free ammonia concentration of 10 mg/ℓ but the figure for inhibition of *Nitrobacter* may be as low as between 0,1 and 1 mgN/ℓ. For an ammonia-N concentration of 5 mg/ℓ the pH would have to be at least 9,28 to have a free ammonia concentration of 0,1 mg/ℓ ($pH=pK_a + \log([NH_3]/(C-[NH_3]))$). At a pH of 8,0 (about the upper quartile value for Kloof Mine) the NH_3-N concentration should be at least 376 mg/ℓ. Total ammonia concentrations > 9 300 mgN/ℓ may also be inhibitive to ammonia oxidation (i.e. to *Nitrosomonas*). Nitrite oxidation can be inhibited by nitrite concentrations above 173 mgN/ℓ but only at a pH<7,5. This raises the possibility that nitrous acid (HNO_2) may be involved since the pK_a of this acid is 5,5. A total absence of ammonia has an inhibitive effect on nitrite oxidation.

4. Chlorate/chlorite

(Belser and Mays, 1980; Turk and Mavinic, 1989)

At a concentration of 0,001 to 0,01mM (0,1 to 1 mg/ℓ) $NaClO_3$ has been reported to be inhibitive but concentrations as high as 532 mg/ℓ has been reported as "only mildly inhibitive". Even higher concentrations did not inhibit pure cultures of *Nitrosomonas* but in mixed cultures with *Nitrobacter* inhibition was observed. This led to the conclusion that ClO_3^- is reduced to ClO_2^- by *Nitrobacter* and that ClO_2^- is the inhibitory compound.

5. Other inorganic toxins

(Braam and Klapwijk, 1981; Beg and Hassan, 1987;; Sato *et al.*, 1988; Tyagi and Couillard, 1988)

The 50% inhibition concentrations (IC_{50}) for various toxins are reported as follows: As^0 - 1274 mg/ℓ, As^{3+} - 134-237mg/ℓ, Cr^{6+} - 56 mg/ℓ, F^- - 1185 mg/ℓ, CN^- - 0,67 mg/ℓ and Cu^{2+} - 0,01 to 0,5 mg/ℓ (decreasing with increasing NH_3-concentrations). The toxicity of these ions increase with a decrease in pH.

6. Organic toxins

(Collins *et al.*, 1975; Beg and Hassan 1987; Tang *et al.*, 1991)

Formalin (63 mg/ℓ), methanol (43 mg/ℓ), acetone (846 mg/ℓ), 2-chloro-6-(trichloromethyl)pyridine (2 mg/ℓ; causing a build-up of nitrite) and erythromycin (50 mg/ℓ) were observed to inhibit either the second or both nitrification steps. Chloramphenicol, oxytetracycline and sulfamerazine had no significant effects. Toxicity data for a number of organic compounds indicate increased toxicity for halogenated aromatic compounds (down to a few µM in the case of 2,4,6-trichloro phenol).

7. Hydraulic instability

(Kholdebarin and Oertli, 1977b; Watson *et al.*, 1989; Kugaprasatham *et al.*, 1991)

The predilection of nitrifying bacteria for attached growth was clearly demonstrated. *Nitrosomonas* appears to have a greater affinity for attached growth than *Nitrobacter* where they are often found embedded in slimy aggregates in zoogloea. *Nitrobacter* by contrast are more often found in cyst form. Short term changes in hydraulic conditions has an advantageous effect in that it increases the nutrient flux into the nitrifying biofilm. It has the disadvantage that should the turbulent intensity oscillate with an approximately 6-7 cm/s step, there could be a loss of nitrifying biofilm. It is therefore possible that nitrite oxidizing bacteria may be lost faster than the nitrite producing bacteria, causing nitrite build-up.

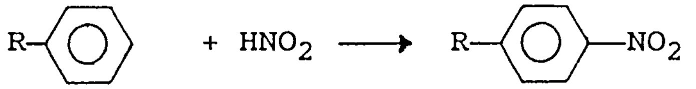
8. Population dynamics

(Kholdebarin and Oertli, 1977b; Gee *et al.*, 1990)

It was observed that *Nitrobacter* activity was highly dependant on the ratio between *Nitrobacter* and *Nitrosomonas* population. On the other hand the activity of *Nitrosomonas* was not affected by the ratio between the two groups of nitrifyers. It has been speculated that some enzymatic commensalism or biochemical energy-transfer phenomenon exists between the two genera. The oxidation of nitrite in the absence of ammonia was found to be highly unstable. This leads to the conclusion that with a non-steady state ammonia feed, conditions could arise where nitrite build-up will be possible.

3.4 Nitrite Toxicity.

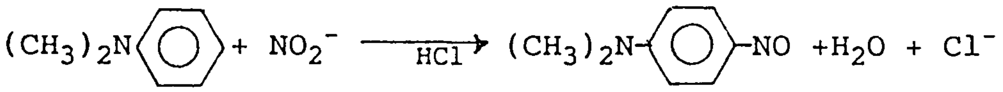
In section 3.2 reference was made to nitrite toxicity in terms of its implication in methaemoglobinaemia, which is also the reason for its being mentioned in the drinking water criteria cited. It must be recognized however that these criteria, when referring to the drinking water situation, refer to low organic content water (USEPA, 1986; CWQG, 1987). In water with high organic content and particularly where there are aromatics present, nitration reactions (eg. reaction[1])) are possible (Morrison and Boyd, 1976).



.....[1]

Where R could be any electron donating specie such as CH_3.

Of greater health impact are the electrophilic aromatic substitution nitrosation reactions, eg. [2], where the electrophile is ON^+ (or species such as H_2O^+-NO or NOCl which can easily transfer NO^+ to the ring)



...[2]

This nitrosation reaction will be facilitated by the presence of strongly activating moieties such as the dimethyl- or diethylamino or -OH groups in an aromatic ring. The reaction product of [2], *p*-nitroso-N,N-dimethylaniline is known as a powerful carcinogen and mutagen. This is true of most nitroso compounds.

It has been established (Suzuki *et al.* 1990) that nitro and nitroso compounds can form in water in the presence of nitrite. In the context of mine water this means that should nitrite production be left unchecked, the concentration of the carcinogenic nitroso compounds could build up in the service water. Such build-up could take place because the nitroso compounds are much less susceptible to oxidation than nitrite.

3.5 Method of determining biokinetic parameters.

The selection of the method used to ascertain the kinetic parameters for microbiological growth is open to debate. It is recognized that the water circuit in a mine will not necessarily conform to a simple batch reactor. Although certain sections of the mine, eg. piping, gullies, filters etc. may be better modeled as plug flow reactors (PFR's) the mine as a whole would probably be modeled better as a batch reactor if the water budget remains fairly constant, i.e. when the bulk of the water is recirculated rather than replaced. For the purposes of this study, a batch reactor was deemed sufficient since it provides an inexpensive way to determine biokinetic constants.

As pointed out by Braha and Hafner (1987) there is a parallel removal of both recalcitrant and easily removable substrates in a batch reactor or a CSTR accompanied by a continuous process of adaptation in the microbiota. In the case of a PFR there is a gradient in bacterial population along the length of the PFR. The concentration variation with time may cause different bacterial populations (as in the case of microbiological nitrification) to be in different growth phases (covering the spectrum from exogenous to endogenous) in a batch reactor, whereas in a PFR the change in concentration is accommodated in the population gradient. At every point the population in a PFR operating at steady state (that is when at a point in the reactor there is little or no change in the concentration at that point for a constant feed) is as close to optimal growth conditions as is allowed for by the substrate feed. It may therefore be expected that the biokinetic parameters obtained in a PFR will differ from those obtained in a batch reactor (Tucek and Chudoba, 1969; Gaudy and Gaudy, 1972) although Braha and Hafner (1987) maintains such differences are insignificant. For this reason the parameters obtained in this study cannot be used directly in a bacteriologically orientated mine service water model. The value of this study lies in the hitherto unreported observation regarding inhibition of the second stage of microbiological nitrification of ammonia. Clearly more research is indicated before this result can be reasonably applied to the "real world" mine situation.

3.6 Discussion

The nitrite build-up problem would seem to centre around finding the answer to the following questions:

1) Is there an abundant source of inorganic nitrite on the mine which produces nitrite faster than any of the oxidation processes can remove it?

2) Is there a source of ammonia on the mine which would serve as substrate for biotic nitrite production?

3) In the event of either or both 1) and 2) being true, are there any factors that could be involved in the inhibition of the second stage of nitrification?

Besides the obvious anaerobic conditions that could inhibit nitrification, the most obviously applicable conditions that could be investigated for causing nitrite build-up at the Kloof Gold Mine are: pH, temperature, inorganic toxins (such as arsenic which appears in some mines in the form of arsenopyrites), hydraulic instability and population dynamics.
Chlorite (ClO_2^-) which is a product formed during the use of

chlorine dioxide (ClO_2), which has been used experimentally on the mine, is also considered an inhibitor. In point of time it would appear however that the nitrite build-up problem at the mine may have preceded the use of ClO_2. The quantitative structure-activity relationships (QSAR) reported by Tang *et al.* (1991) point to the conclusion that the chlorine moiety in a molecule increases its toxicity to *Nitrobacter* appreciably. At the time the work on this project was started (March, 1990), no study specifically reporting on the toxicity of chlorine itself or of the chloramines had been found in the literature. This is surprising in the light of the observation by Strom and Finstein (1977) that during the chlorination of a drinking water supply, there was a build-up of nitrite. A recent paper by Cunliffe (1991) describes the chloramination of drinking water supplies in Australia. He found that there was an increase in NO_2^--N concentration after the cessation of chloramination and until *Nitrobacter* growth recommenced. From that study it would appear that when the chloramine residual drops below about 0,5 mg/ℓ then *Nitrosomonas* activity recommences and it is only several days later that *Nitrobacter* activity catches up.

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Chapter 4

An Investigation into the Abiotic Nitrite Build-up in Gold Mine Service Water.

4.1 Introduction

Service water in the South African gold mines is used largely for cooling, dust suppression and water jetting at the stope rock faces. In the mines, which are sometimes more than 3 000m deep, geothermal heat can raise the rock surface temperatures to as high as 55 °C. The service water is cooled to about 4 °C. The service water of which about 33 Mℓ/day is needed, is recirculated several times before discharge (Pearson *et al* 1989, Mackay *et al.*, 1991). Despite sanitation facilities provided, defecation sometimes occurs in the worked-out areas in the mine where water inadvertently comes into contact with the faeces. There is therefore an opportunity for this water to become highly contaminated with pathogenic organisms (such as typhoid and cholera), especially from migrant workers who have contracted these diseases while on leave at their homes in developing areas. At one of the larger gold mines an average total coliform count of 5 126 per 100 mℓ of service water has been found (Pearson *et al*, 1990).

Mine workers drink between 6 and 8 ℓ of water per shift (Pearson *et al.*, 1989). Chilled drinking water is supplied, but because of the large distances the water has to be transported to the work faces and despite all preventative engineering efforts, the water may reach the workers at an unpalatable temperature. For this reason many mine workers prefer to drink the service water, which was not treated to potable water standards but which generally reaches the work faces fairly well chilled. It has therefore become imperative to disinfect the service water on most mines in order to render it acceptable in microbiological terms.

During disinfection studies on the service water of the Kloof Gold Mining Company, which is part of the Gold Fields of South Africa Group of companies, it was recognized that, because of an approximate 1.5 mg/ℓ per cycle increase in the ammonia concentration in the underground circuit, breakpoint chlorination would become too costly (Pearson and McLaren, 1985). Further investigation (Pearson *et al.*, 1989, Van Leeuwen and van der Westhuizen, 1992) pinpointed nitrite in the service water as a major consumer of oxidizing disinfectants such as chlorine, chlorine dioxide and ozone. Nitrite in the service water, after filtration, was found to average around 0.98 mgN/ℓ (standard deviation 0.21mgN/ℓ) with a peak value of 11.9 mgN/ℓ. The recommended criteria for nitrite in potable water is 1 mg/ℓ (Kempster and Smith, 1989, McNeely, 1989). The magnitude of the problem in terms of disinfectant usage warranted a closer investigation into the origin of the nitrite.

The object of this study was to establish the contribution of the use of explosives to the nitrite in the service water and to establish a distribution pattern of nitrite in a typical section of the underground service water circuit.

4.2 Nitrite reactions with disinfectants

The occurrence of nitrite in water is well documented (Benefield and Randall, 1980, Krenkel and Novotny, 1980). Nitrite is an oxidized anionic form of nitrogen. Its conjugate acid, nitrous acid (HNO_2), is a weak acid with $pK_a = 5.22$ at 25 °C with redox potentials as given in equations [1] and [2] (Cotton and Wilkinson, 1972, Huheey, 1983, Glaze, 1987).

$$NO_3^- + 3H^+ + 2e^- \rightleftharpoons HNO_2 + H_2O \quad E^o=+0,94V \quad ....[1]$$

$$HNO_2 + H^+ + e^- \rightleftharpoons NO + H_2O \quad E^o=+1,00V \quad ....[2]$$

Nitrous acid can act as an oxidant toward e.g. iodide and ferrous ion and as a reductant toward stronger oxidants such as chlorine,

chlorine dioxide and ozone (equations [3] to [5]).

$$\begin{array}{lll} \mathrm{HOCl + H^+ + 2e^- \rightleftharpoons Cl^- + H_2O} & \mathrm{E^o=+1,49V} & \\ \underline{\mathrm{HNO_2 + H_2O \rightleftharpoons NO_3^- + 3H^+ + 2e^-}} & \mathrm{E^o=-0,94V} & \\ \mathrm{HNO_2 + HOCl \rightleftharpoons Cl^- + NO_3^- + 2H^+} & \mathrm{E^o=+0,55V} & ....[3] \end{array}$$

$$\begin{array}{lll} \mathrm{2ClO_2 + 2H^+ + 2e^- \rightleftharpoons 2HClO_2} & \mathrm{E^o=+1,28V} & \\ \underline{\mathrm{HNO_2 + H_2O \rightleftharpoons NO_3^- + 3H^+ + 2e^-}} & \mathrm{E^o=-0,94V} & \\ \mathrm{HNO_2 + 2ClO_2 + H_2O \rightleftharpoons NO_3^- + 2HClO_2 + H^+} & \mathrm{E^o=+0,34V} & ....[4] \end{array}$$

$$\begin{array}{lll} \mathrm{O_3 + 2H^+ + 2e^- \rightleftharpoons O_2 + H_2O} & \mathrm{E^o=+2,07V} & \\ \underline{\mathrm{HNO_2 + H_2O \rightleftharpoons NO_3^- + 3H^+ + 2e^-}} & \mathrm{E^o=-0,94V} & \\ \mathrm{O_3 + HNO_2 \rightleftharpoons O_2 + NO_3^- + H^+} & \mathrm{E^o=+1,13V} & ....[5] \end{array}$$

From the equations [3] to [5] above it is clear that the reaction of nitrite with the common oxidation disinfectants is thermodynamically favourable. The stoichiometry of the reactions together with current cost implications are set out in Table 1.

4.3 Chemistry of nitrite formation in water

No use of any nitrite compound was found at the Kloof Gold Mining Company to the extent that it could explain the observed nitrite levels. It would therefore be necessary to investigate the likely nitrite formation situations on the mine, of which the most apparent were those associated with the use of explosives.

Nitrite contains nitrogen formally in the +3 oxidation state. Although many laboratory scale nitrite preparation reactions are known (Cotton and Wilkinson, 1972) these often require the use of sophisticated apparatus and chemicals unlikely to be found in the rock excavation situation. Some of the gas phase reactions of nitrogen have, however, been shown to take place during the detonation of explosives (Hine and Jones, 1985). Rossi (1972) maintains that "oxides of nitrogen *[NO_x]* are converted to nitrogen dioxide *[NO_2]*, which reacts with the moisture in the mine atmosphere to form nitric *[HNO_3]* and nitrous *[HNO_2]* acid" (*italics ours*). Some of the relevant nitrite forming reactions (Cotton and Wilkinson, 1972, Huheey, 1983) are shown in equations [6] to [10].

Table 1. The stoichiometries and cost implications of the reactions of nitrite with chlorine, chlorine dioxide and ozone.

Oxidant	Ratio mg Oxidant: $mgNO_2^-$-N/ℓ	Current Cost per kg oxidant (R)	Cost of Nitrite oxidation (c/m^3.mgN)
Cl_2	5,07	3,20	1,62
ClO_2	9,64	35,00	33,74
O_3	3,43	5,50*	1,90

*= Including capital amortization cost over 15 years on a R5 m plant (delivering 15kg/h) at [prime overdraft rate - annual inflation], currently = 5%.

$$4NO + 2H_2O \rightleftharpoons 2HNO_2 + H_2N_2O_2 \quad E^o = -0,148V \quad ...[6]$$

$$H_2N_2O_2 + O_2 \rightleftharpoons 2HNO_2 \quad E^o = +0,325V \quad ...[7]$$

Reactions [6] and [7] would seem to indicate a thermodynamic equilibrium in favour of nitrous acid formation.

$$2NO + N_2O_4 + 2H_2O \rightleftharpoons 4HNO_2 \quad E^o = +0,04V \quad ...[8]$$

$$O_2 + N_2O + H_2O \rightleftharpoons 2HNO_2 \quad E^o = -0,11V \quad ...[9]$$

$$NO + NO_2 + H_2O \rightleftharpoons 2HNO_2 \quad ...[10]$$

Reaction [10] is known to be rapid with a kinetic constant of 1.56 atm^{-1}. NO_2 and N_2O_4 are known to be in equilibrium, with the enthalpy of dissociation for $2NO_2 = N_2O_4$ being $H^o_{298\ K} = 57$ $kJmol^{-1}$. This dissociation is complete above 140 °C so that under detonation conditions, where gas temperatures above 900 °C are encountered, reactions [8] and [10] are equivalent (Cotton and Wilkinson, 1972).

Nitrate formation is also encountered in the gas phase oxidation of nitrogen as indicated in reactions [11] and [12].

$$2N_2O_{4(g)} + O_{2(g)} + 2H_2O_{(g)} \rightleftharpoons 4NO_3^- + 4H^+ \qquad E^o = +0{,}38V \quad ...[11]$$

$$2HNO_2 + O_2 \rightleftharpoons 2NO_3^- + 2H^+ \qquad E^o = +0{,}25V \quad ...[12]$$

Reaction [11], like reaction [8] a nitrite forming reaction, is dependant on the partial pressure of N_2O_4 (or NO_2 at elevated temperatures) and they are therefore competing reactions, with reaction [11], the nitrate formation reaction, being thermodynamically favoured. Deviations from standard conditions, as well as subsequent side reactions, could cause the thermodynamic tendencies at standard conditions to be reversed, favouring nitrite formation. The situation is complicated by the observation that nitrous acid decomposes when warmed according to equation [13].

$$3HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O \qquad ...[13]$$

The decomposition product, NO, is involved in the equilibria [6] and [8]. The thermal decomposition of nitrogen dioxide, [14], which is complete above 600 °C also yields NO which is involved in the above equilibria.

$$2NO_2 \rightleftharpoons 2NO + O_2 \qquad ...[14]$$

From the above it is clear that, although nitrite (or nitrous acid) is easily oxidized, it is possible, given the right ambient atmospheric conditions such as low partial pressure in O_2, for nitrite to be formed and it would theoretically be possible to calculate a thermodynamic constant expressing the likelihood of nitrite formation from combustion gasses. However, the observation (Cotton and Wilkinson, 1972) that there is reasonable evidence to assume the presence of the $NO^\cdot$ and $NO_3^\cdot$ radicals, produced by a homolytic bond scission in N_2O_4, would have far reaching kinetic implications and could make such a theoretical thermodynamic calculation valueless. It would be more advantageous to assess the extent of nitrite production from empirical data.

4.4 Estimation of nitrite production

For the reasons mentioned above it is therefore neither easy nor useful to make a quantitative estimate of nitrite formation during and immediately after the detonation of explosives on the mine. It was established (Smith, 1990), however, that commonly between 2 and 3ℓ of NO_x gasses (at N.T.P) are released per kilogramme of explosive used. It was further established (Garcia and Harpalani, 1989) that about 33% of the NO_x gases consist of NO_2. The rest was designated as NO, although it is questionable in view of its reactivity towards oxygen (reaction [14], where the equilibrium lies far to the left below 160 °C, the temperature at which the actual measurement appears to have been made).

The maximum nitrite production can be estimated by assuming that about 1ℓ of NO_2 is formed per kg of explosive used and that all the NO_2 formed ends up as HNO_2, then the mass of nitrite nitrogen formed per kg of explosive is:

$$(1/22,4).14 = 0,625 \text{ g } NO_2^{-}\text{-N/kg explosive}$$

For an explosives usage of 7,5 t/d and assuming all the formed nitrous acid finds its way into the 33 Mℓ/d service water circulated, then the daily increase in nitrite (assuming no nitrite oxidation occurs) will be:

$$(0,625 \text{ kg}NO_2^{-}\text{-N/t} \ . \ 7,5\text{t}) \ / \ 33 \text{ M}\ell = 0,14 \text{ mg}NO_2^{-}\text{-N}/\ell$$

The stoichiometric chlorine demand for such nitrite production would be: 0,14 . 5,07 = 0,71 mg/ℓ. The average chlorine dosage used on the service water is about 4 mg/ℓ which means that the chlorine applied for disinfection should be able to oxidize 5 times the estimated nitrite production, more than can be expected even if all the NO_x were converted to NO_2^-. Since there is a persistent nitrite presence in the service water, either the nitrite production from explosives is much more than expected or the source of the problem is not directly related to explosives use.

4.5 Experimental

4.5.1. *Nitrite production at a stope*

A stope where the influent service water and the effluent water could be gauged and sampled and where those were the only contributions to the water budget, was found on the 23-level of the Kloof Gold Mining Company's No. 1 Shaft. The influent service water was gauged volumetrically and the effluent was gauged by a calibrated flume in the drainage gully. Samples were taken at hourly intervals for a 36 hour period in 250 ml poly-ethylene bottles with screw tops. These were brought to the surface at 8-hourly intervals and kept refrigerated until analysis.

4.5.2. *Nitrite production at various points in the underground service water circuit*

Grab water samples for ammonia and nitrite analyses were also taken at various points in the underground service water circuit (see Figure 1) namely:

i) The holding dam for chilled water at 23-level,
ii) The pipe line leading to the refrigeration plant at 32-level: a) at the first sampling point on 32-level and

b) just before the refrigeration plant,
iii) At the pump at the refrigeration plant,
iv) In the line leading from the refrigeration plant: a) just after the chlorine dosing point and b) about 200m from

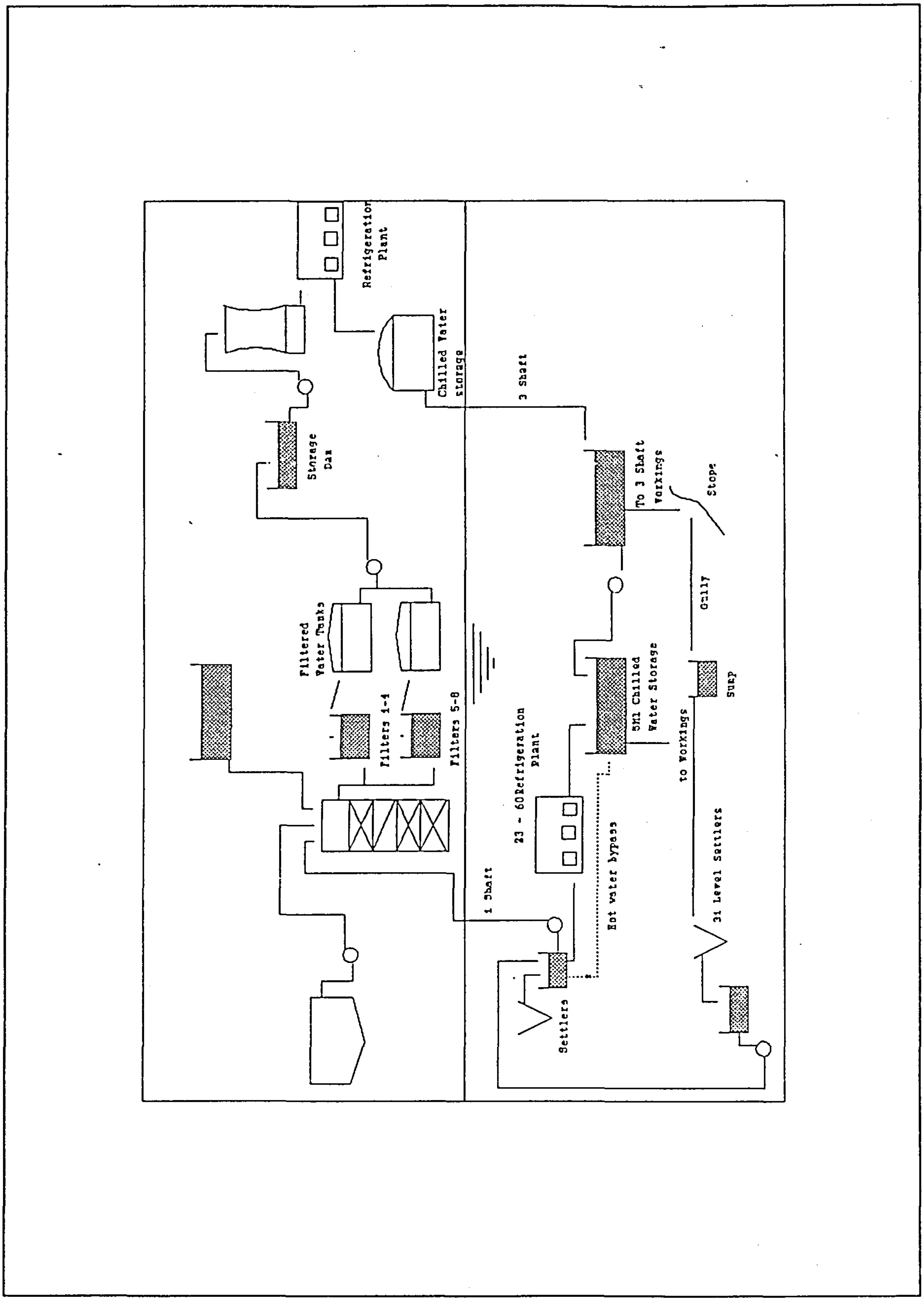

Figure 1a. Kloof Gold Mine service water circuit (based on Pearson *et. al.*, 1989)

the stope,

v) Service water fed to the stope,
vi) Water on the ground at the stope,
vii) Water in the gully draining from the stope,
viii) Water in a sump in the drainage gully,
ix) Water from the inflow to the settler at 32-level
x) Water from the outflow of the settler before being pumped to surface and
xi) Ground water seeping into a small pool at a disused stope.

Dissolved oxygen (DO) levels were measured at points iv)a), v), vii), viii) and x) with a YSI model DO meter with built-in temperature and pressure correction facility. The water sampled from the sampling points of the pipeline was channelled through a hose pipe that was primed with the water from the pipeline and then allowed to run into a container which was flushed by allowing the water to overflow the container while the pipe was kept submerged to prevent reaeration. The temperature at points iv), viii) and x) were measured with the same instrument.

Grab water samples were also taken at the outlet of the #7 filter in the line used for ozonation experiments during a period when there was no ozone being dosed. Samples were analyzed immediately for ammonia and nitrite.

Nitrite analyses were performed according to the method described in Standard Methods (1985) using a Bausch and Lomb Manual Spectrophotometer to measure the absorbance at 536nm.

Nitrate analyses were performed according to the cadmium reduction method described in Standard Methods (No 418C).

Ammonia was analyzed by the phenate method (No 417C) according

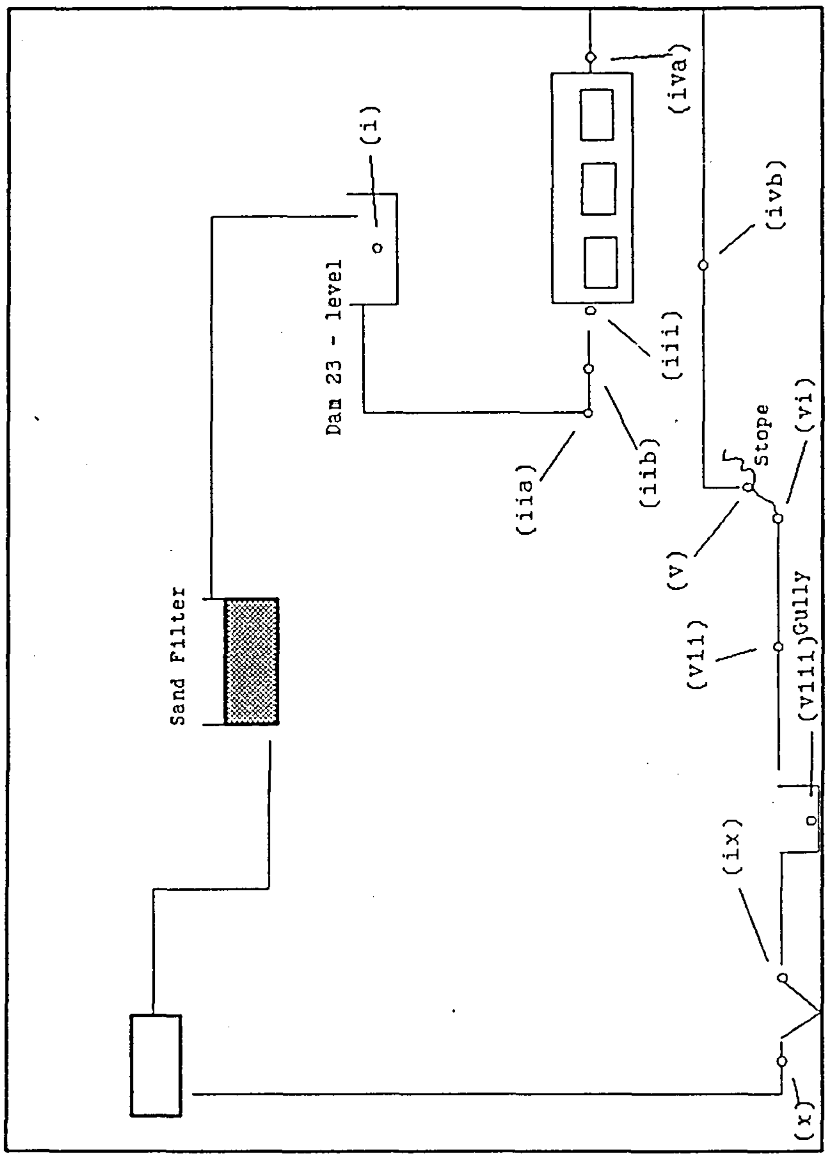

Figure 1b. Sampling points for determining nitrite production on 23- and 32-level.

to Standard Methods with absorbance measured at 630nm.

4.6 Results and Discussion

Mass balances for ammonia and nitrite over the stopes were performed and some evidence indicating microbiological reactions were evaluated.

4.6.1 *Mass balances over the stope*

The mass balance over the selected stope was calculated as the load out of the stope minus the load into the stope. The load was calculated as the concentration (in mg N/ℓ) times the flow (in ℓ/s). The results of this mass balance is depicted in Figure 2. During the period of blasting and until work at the stope recommenced, the inflow of water decreased from an average of 6 ℓ/s to 0,4 ℓ/s. During this period, when the outflow consisted largely of drainage from the workface, there was a nett decrease in nitrite concentration. In the period immediately after work commenced there was a nett increase in nitrite concentration. The nett nitrite loss over the whole sampling period amounted to 2,6g, despite the nett nitrite production during the 6 hours after the commencement of work of 2,61g. The nett nitrite loss over a 24 period was about 1 840 mg drained in about 7 000ℓ.

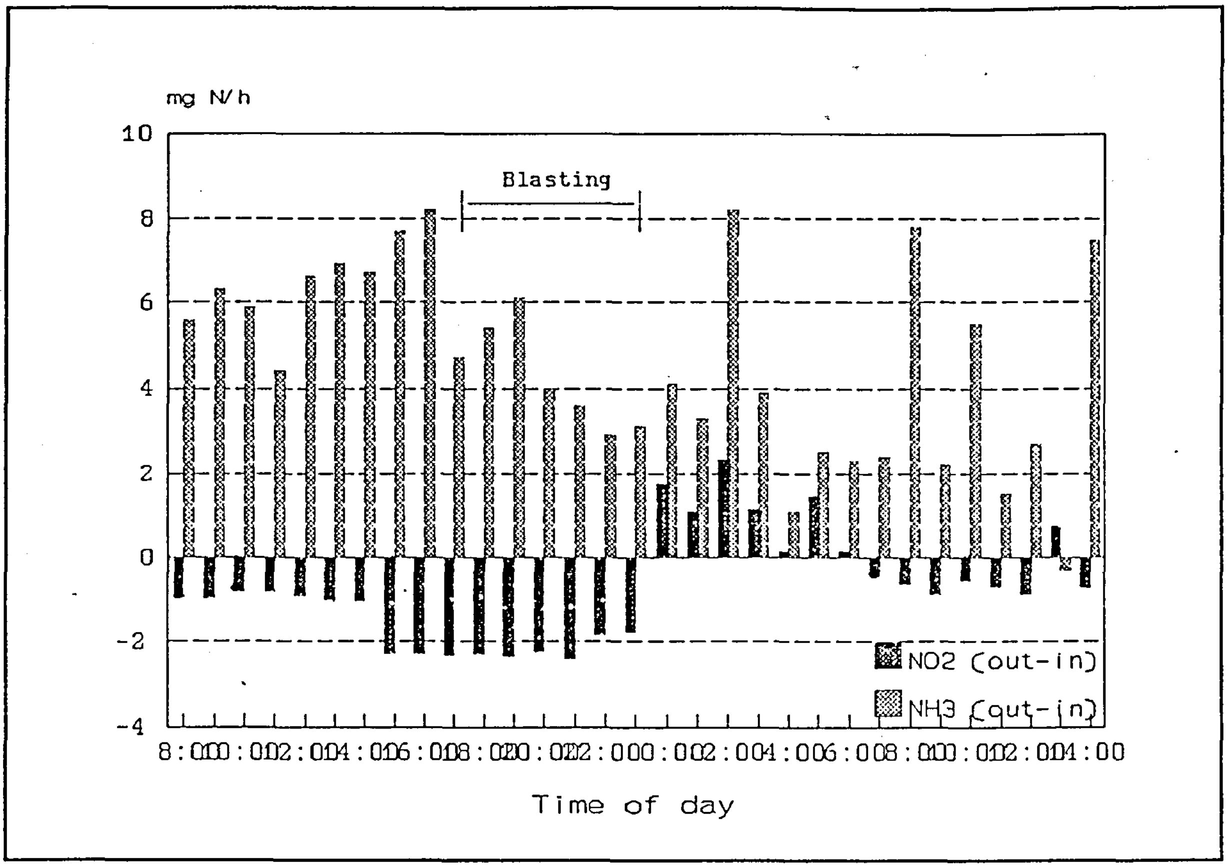

Figure 2 The nitrogen mass balance over a selected stope on 23-level of Kloof Mining Company's No. 3 shaft.

This would imply a daily NO_2^--N concentration decrease of about 0,3 mg/ℓ.

The nett ammonia load from the stope summed over the first 24 hours of the test period was about 34 g. The explosives used at this stope during the test period was 65kg, so that if the ammonia production at other stopes were identical, the daily increase in NH_3-N due to the use of 7,5t/d of explosives should be 0,12 mg NH_3-N/ℓ. This is considerably lower than the 1,5 mg/ℓ increase in NH_3-N observed by Pearson and McLaren (1985).

4.6.2 *Microbiological nitrification as an ammonia sink.*

The 1,5 mg/ℓ per cycle increase in ammonia established by Pearson and McLaren (1985) could not be kept under control by chlorination even at stoichiometric minimum ratio of 7,6:1, this would require a dosage of 11,4 mg/ℓ chlorine. The average dosage of 4 mg/ℓ would be therefore be inadequate to oxidize all the ammonia, leading to an unchecked build-up of ammonia, unless the ammonia is removed or converted by another mechanism. This raises the possibility of microbiological nitrification as an ammonia sink in the water. During the nitrification process where ammonia is oxidized to nitrite which is then oxidized to nitrate, DO would play an important part as can be seen from the formal equations [15] and [16] (Pelczar *et al.*, 1986):

$$2NH3 + 3O_2 = 2HNO_2 + 2H_2O \qquad \text{....[15]}$$

$$2HNO_2 + O_2 = 2HNO_3 \qquad \text{....[16]}$$

The DO level at various critical points on the mine is given in Table 2. The DO concentration was never lower than 4 mg/ℓ except at the overflow from the settler, where it was 0.5 mg/ℓ.

When insufficient alkalinity is present then the nitrification process could be inhibited due to too low a pH . It has however been established by Pearson *et al.* (1990) that the pH of the service water does not go below 5,9 at any of the point monitored in that study.

Table 2. Dissolved oxygen (DO) levels at various points on 32-level.

Point	DO (mg/ℓ)	Temperature(°C)
Refrigeration plant	5.5	14
Feed to stope	7.5	16
Gully draining stope	4.0	-
Sump in gully	5.5	27
Settler inflow	6.5	28
Settler outflow	0.5	28

4.6.3 *Ammonia and Nitrite profile on 23-level and 32-level*

The ammonia and nitrite concentration profile is presented in Table 3. At the time of sampling service water at the stope was used for lashing and drilling. The ammonia concentration in the water collected on the ground was drastically higher than that of the influent service water. The water drainage in the gully showed no clear tendency, as could be expected from the various activities as set out above. As no flow measurement could be done at the time of sampling it is not possible to calculate the loads at various points in the circuit. The ammonia and nitrite concentration in the service water varies considerably but the ratio of ammonia-nitrogen to nitrite-nitrogen at adjacent sampling points could be assumed

Table 3. The ammonia and nitrite concentrations measured at various points on 23-level and 32-level.

Point	NH_3-N mg/ℓ	NO_2^--N mg/ℓ
Holding dam on 23-level (i)	1.0	0.6
Line on 32-level (iia)	1.3	0.8
Line to 38-level refrigeration (iib)	0.3	0.1
Pump at 38-level refrigeration (iii)	0.8	0.8
Line from 38-level refrigeration (iva)	1.0	0.5
Line to stope (1km) (ivb)	0.9	0.3
Feed to stope (v)	0.6	0.8
Water on ground at stope (vi)	11.3	3.4
Ground water near stope (xi)	0.4	0.1
Drainage gully from stope (vii)	0.8	0.1
Sump in drainage gully (viii)	4.3	0.7
Settler inflow (ix)	0.6	0.8
Settler outflow (x)	1.9	0.8

to be comparable. This ratio would eliminate the plug flow concentration effects. It is significant that this ratio appears to decrease (Table 4) when adjacent units are considered. The relative increase in the NO_2^- concentration between the holding dam on 23-level and the stope and between the gully draining the stope and the settler could well indicate a bacterial nitrification process. The increase in nitritification (nitrite formation) in an aerated part of the system indicates an inhibition of bacterial activity other than by anoxic conditions. Since neither the DO concentration nor the temperature were lower than that reported in the literature as limiting the nitrification process (4mg/ℓ and 13°C respectively; Painter, 1977), it is unlikely that either of the above are responsible for the observed nitrite build-up.

Table 4. Ratio of ammonia nitrogen to nitrite nitrogen at various points on 32-level.

Point	Ratio
Holding dam at 23-level	1.7
Feed to 32-level refrigeration	1.7
Pump at 32-level refrigeration	1
Line from 32-level refrigeration	1.9
Feed to 32-level stope	0.8
Water on ground at 32-level stope	3.3
Gully draining stope	7.7
Sump in gully	6.6
Settler inflow	0.7
Settler outflow	2.3

If complete inhibition were to occur the ammonia not chemically oxidized to N_2 should appear as NO_2^--N. Since only about 4 mg/ℓ chlorine is dosed underground works, the ammonia available for nitrite formation per cycle should be: $1,5 - 4/7,6 \approx 1$ mg/ℓ. A dosage of 5 mg/ℓ ClO_2 should oxidize, according to stoichiometry, 5/9,6 mg/ℓ of nitrite nitrogen, leaving about 0,5 mg NO_2^--N/ℓ per cycle.

As shown previously, the normal processes (whether of chemical or microbiological nature) at the stope account for the removal of about 0.3 mg NO_2^--N/ℓ. From the literature (Painter, 1977) data it can be estimated that the rate at which nitrite is oxidized should, under normal circumstances in a continuous system, be in the order of 0.1 mg NO_2^--N/hour at 20 °C. This rate could double when the temperature is 30 °C. This means that the nitrite formed under the assumptions above should have been removed within one or two hours. The observed nitrite build-up could then only be ascribed to an inhibitive effect on the nitratification (i.e. the nitrate forming) reaction.

4.6.4 *Sand filters as nitrite producers.*

It has also been noticed that there has been an increase in nitrite concentration over the sand filters (Pearson *et al.*, 1989). The results obtained during this study agree with that observation. An average ratio of nitrite concentration after the filter to nitrite concentration before the filter of 3,4 (σ=0,8 with 13 degrees of freedom) was found compared to 3,8 found by Pearson *et al* (1989). It has been suggested by these authors that inhibition of microbiological nitratification is the reason for the nitrite build-up observed in the filters. They eliminated DO deficiency as an inhibitive factor but suggested temperature and ammonia concentration as inhibitive factors. The results obtained from the ammonia and nitrite profile on 32-level, where a wide spectrum of temperatures were encountered, while still observing a nitrite build-up, indicates that the temperature effect alone is not responsible for this phenomenon. Since there are so many variables that could be involved, this problem needs to be studied under controlled circumstances.

4.7 Conclusions and Recommendations

The combustion products of the explosives used on the mine even under thermodynamically favourable conditions do not significantly contribute to the nitrite concentration observed in the mine service water. The increase in ammonia concentration can be attributed to spillage or incompletely combusted explosive washed out by the service water.

The results of this study support the postulate that microbiological nitrification is an important process in mine service water.

The normal microbiological nitrification process of ammonia appears to be inhibited by factors other than DO or temperature but this needs to be demonstrated under controlled conditions.

4.8 Acknowledgements

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Chapter 5

An Investigation into the Biotic Production of Nitrite in Gold Mine Service Water

5.1 Introduction

It has been found necessary to disinfect the service water at many South African gold mines because this water is being drunk by many of the mine workers in spite of all the discouragement to do so (Pearson *et al*, 1990). Faecal contamination causes a risk of the water being contaminated by pathogenic organisms (such as typhoid and cholera). This problem can be amplified because of the need to recycle the service water several times before its discharge. During disinfection studies on the service water of the Kloof Gold Mining Company (Pearson *et al*, 1989, Van Leeuwen and Van der Westhuizen, 1992), it was found that nitrite exerted a significant demand for the oxidizing disinfectants such as chlorine and ozone in the service water.

This paper is aimed at elucidating the most probable conditions for nitrite build-up in the service water by a microbiological kinetics study in a controlled environment.

5.2 Biotic Nitrite Production

The production of nitrite as the first step in the microbiological nitrification of ammonia and its subsequent oxidation to nitrate has been extensively described in earlier literature (Knowles *et al.*, 1965, Kholdebarin and Oertli, 1977, Painter, 1977, Strom and Finstein, 1977, Benefield and Randall, 1980).

The biotic oxidation of ammonia is accomplished by, among others, the prokaryotes *Nitrosomonas europaea, N. monocella* and *Nitrosococcus*. The species *Nitrobacter winogradsky, N agilis* and *Nitrocystis*, among others, are thought to be involved in the subsequent oxidation of nitrite (NO_2^-) to nitrate (NO_3^-). Both these groups of organisms are gram-negative chemolithotrophs (Watson *et al.*, 1989). The identification of these organisms is tedious and was not considered essential for the purpose of this investigation.

The build-up of nitrite is not very common and has been ascribed to the breakdown in the microbiological oxidation of nitrite, which is the second step in the biotic mineralization of ammonia. More recent investigations (Suthersan and Ganczarczyk, 1986, Turk and Mavinic, 1989, Gee *et al.*, 1990a and 1990b) centre around the purposed inhibition of microbiological nitrite oxidation in order to provide a "shortcut" in denitrification during nutrient removal processes. In all the above research it was clearly demonstrated that the nitrite oxidation step is by far the more sensitive step in the nitrification process and is subject to the disruption by a number of inhibitive compounds.

5.2.1 *Possible Inhibitors*

The first step can be inhibited according to the Haldane substrate inhibition model (Haldane, 1965, Painter, 1977) by >2 500 mg/ℓ ammonia as well as by high concentrations (> 2 500 mg/ℓ) nitrite, chelating agents such as thiourea (0,7 mg/ℓ) and 2-chloro-6-trichloromethyl pyridine.

The oxidation of nitrite is inhibited by the simultaneous presence of ammonia (>9 000 mg/ℓ) and nitrite (>170 mg/ℓ) described by a modified Haldane model (Gee *et al*, 1990 b) as well as by cyanate, chlorate (ClO_3^-) and chlorite (ClO_2^-) among others. The inhibition level reported for chlorate varies between 0,001 mM (0,08 mg/ℓ; Lees, 1963) and 10 mM (835 mg/ℓ; Belser and Mayes, 1980). Hynes and Knowles (1983) found that chlorate was reduced to chlorite by *Nitrobacter* under both aerobic and anaerobic conditions and that chlorite was the more potent nitrite oxidation inhibitor. It is noteworthy that chlorite is a reduced form of chlorine dioxide, which is often used as a disinfectant for drinking water and has been used as such on the service water at the Kloof Gold Mine.

Optimum growth temperatures of 35 °C and 35-42 °C have been reported for *Nitrosomonas* and *Nitrobacter* species respectively at an optimum pH of 7,8 (Painter, 1977). It has been noticed though that there is a marked temperature dependence of the observed growth rate (μ) between 10 and 17 °C. This differing temperature dependence of μ of the nitrite-producing and μ of the nitrite-utilizing species can contribute to a nett build-up of nitrite (Randall and Buth, 1984).

Assuming these observations to hold true for mine service water, bench-scale investigations into the mechanics of nitrite build-up would centre around the inhibition of nitrifying bacteria. It has been shown that nickel(II), copper(II), arsenic(III), chromium(VI) and fluoride can act as inhibitors (Braam and Klapwijk, 1981, Randall and Buth, 1984, Beg and Hassan, 1987, and Sato *et al*, 1988). Of these chemical species, only nickel(II) appears in the mine service water to any significant extent - a peak of 2 mg/ℓ as compared to 3 mg/ℓ as observed by Randall and Buth (1984) in an activated sludge.

Since chlorine is being used as disinfectant at dosages less than 50% of breakpoint value, the effect of chlorine as well as other disinfectants currently used at the Kloof Gold Mining Company's No 1 shaft, was investigated. These include chlorine dioxide, ozone and bromine.

5.3 Microbiological Kinetics

While not in an endogenous growth phase, the rate at which the substrate, S, is being metabolized at time t, dS/dt, is directly proportional to the rate, dX/dt, at which the population, X, grows [1]. The value of the specific growth rate μ reaches a maximum value μ'.

$$\frac{dS}{dt} = \frac{-1}{Y}\frac{dX}{dt} = \frac{-\mu}{Y} X \qquad ....[1]$$

Where Y is the observed growth yield which is a measure of the amount of cell material formed per unit amount of substrate removed. The instantaneous growth rate, μ, can be related to the maximum growth rate, μ', the substrate concentration and the saturation constant K by the Monod equation [2].

$$\mu = \mu'\left(\frac{S}{K + S}\right) \qquad ....[2]$$

Combining equations [1] and [2] yields [3]:

$$\frac{dS}{dt} = - \mu'\left(\frac{S}{K + S}\right)\frac{X}{Y} \qquad ....[3]$$

Correcting equation [3] for the death and decay of bacteria by the term k', which is also proportional to the bacterial population at that instant in time, produces a differential equation [4], describing the substrate concentration profile:

$$\frac{dS}{dt} = - \frac{\mu'}{Y}\left(\frac{S}{K + S} - k'\right) X \qquad ....[4]$$

The kinetic constants in this equation are often determined either by directly solving equation [4] (Lawrence and McCarty, 1970) or by using various linearizing plots as well as simplifications of the kind K<<S or K>>S (Braha and Hafner., 1985, Braha and Hafner, 1987, Lewandowski, 1987). The combinations of two conditions in this case make the use of such techniques inadvisable:

i) The substrate concentrations (see Table 1) in mine service water are comparable to the saturation constants reported in the literature, which means the simplifications of the kind K>>S or K<<S are invalid.

ii) The action of two bacterial species is coupled by the production/utilization of nitrite, so the two steps in the nitrification process cannot be viewed independently.

Table 1. Typical composition of service water at the Kloof Gold Mine (Pearson *et al.*, 1990) over the period Sept. 1989 to Feb. 1990.

Determinant	Concentration (mg/ℓ)
Na	155
Ca	107
Mg	26
SO_4	370
P	0,13
Alkalinity	74 as $CaCO_3$

Imposing the conditions above on a batch reactor with initial concentrations A_0, N_0 and P_0 and concentrations A, N and P at any future time t for ammonia, nitrite and nitrate respectively, generates a set of simultaneous differential equations [5], [6] [7], [8] and [9] by the application of equations [4] and [2].

$$\frac{dA}{dt} = - \mu_m'\left(\frac{A}{K_a + A} - k'_m\right)\frac{M}{Y_m} \qquad \ldots.[5]$$

$$\frac{dN}{dt} = \mu_m'\left(\frac{A}{K_a + A} - k'_m\right)\frac{M}{Y_m} - \mu_b'\left(\frac{N}{K_n + N} - k'_b\right)\frac{B}{Y_b} \qquad \ldots[6]$$

$$\frac{dP}{dt} = - \mu_b'\left(\frac{N}{K_n + N} - k'_b\right)\frac{B}{Y_b} \qquad \ldots[7]$$

$$\frac{dM}{dt} = - \frac{M}{Y_m}\frac{dA}{dt} \qquad \ldots.[8]$$

$$\frac{dB}{dt} = - \frac{B}{Y_b}\frac{dN}{dt} \qquad \ldots.[9]$$

Where the bacterial cell concentration at time t of *Nitrobacter* or *Nitrobacter*-like nitrite oxidizing bacteria and of *Nitrosomonas* or *Nitrosomonas*-like nitrite producing bacteria is B and M respectively, with boundary values B_o and M_o at time $t=t_o$ respectively.

A correction for the mass of substrate used for cell maintenance must be applied. It can be assumed that this amounts to a constant fraction of the metabolized substrate and typically this fraction may be assumed to be 0,01 (Knowles *et al*, 1965). This means that the solutions A(t) and N(t) of equations (5) and (6) respectively must each be multiplied by 0,99.

5.4 Experimental Procedures

a) Analytical methods

Analyses were performed as described in the previous chapter.

b) Biotic Nitrite Production

A batch reactor was constructed from a 5ℓ bucket with a lid (see Figure 1). An inverted 250 mℓ poly-ethylene bottle, with a suitable hole cut into its bottom and filled about halfway with coarse, sterilized, ungraded river sand, retained by stainless steel mesh with 0,8 mm openings, was suspended in the bucket. Provision was made to circulate the reactor contents over the river sand by means of a peristaltic pump at a rate of c. 1 mℓ/min. The reactor content was maintained at a constant temperature (such as was demanded by the particular experiment) by means of a 100W immersion type fish tank heater or by means of a cryostatic unit circulating a cooling liquid through the reactor in 9 mm stainless steel tubing (in the case of sub-ambient temperature experiments).

Air was bubbled into the water above the sand by means of a commercial 15 mm ϕ sintered ceramic diffuser at a rate of a about 5 mℓ/min. The reactor was agitated by means of a 40 mm (5 mm ϕ) Teflon coated follower driven by a magnetic stirrer at about 120 r.p.m.

The biological culture was established anew for each experiment by circulating 5ℓ of mine service water through the reactor for 48h, within 24h of it being sampled at a point it enters the sand filters in the surface purification works at the Kloof Gold Mining Company's No 1 shaft. The service water was then drained and replaced in the reactor by a nutrient solution as described

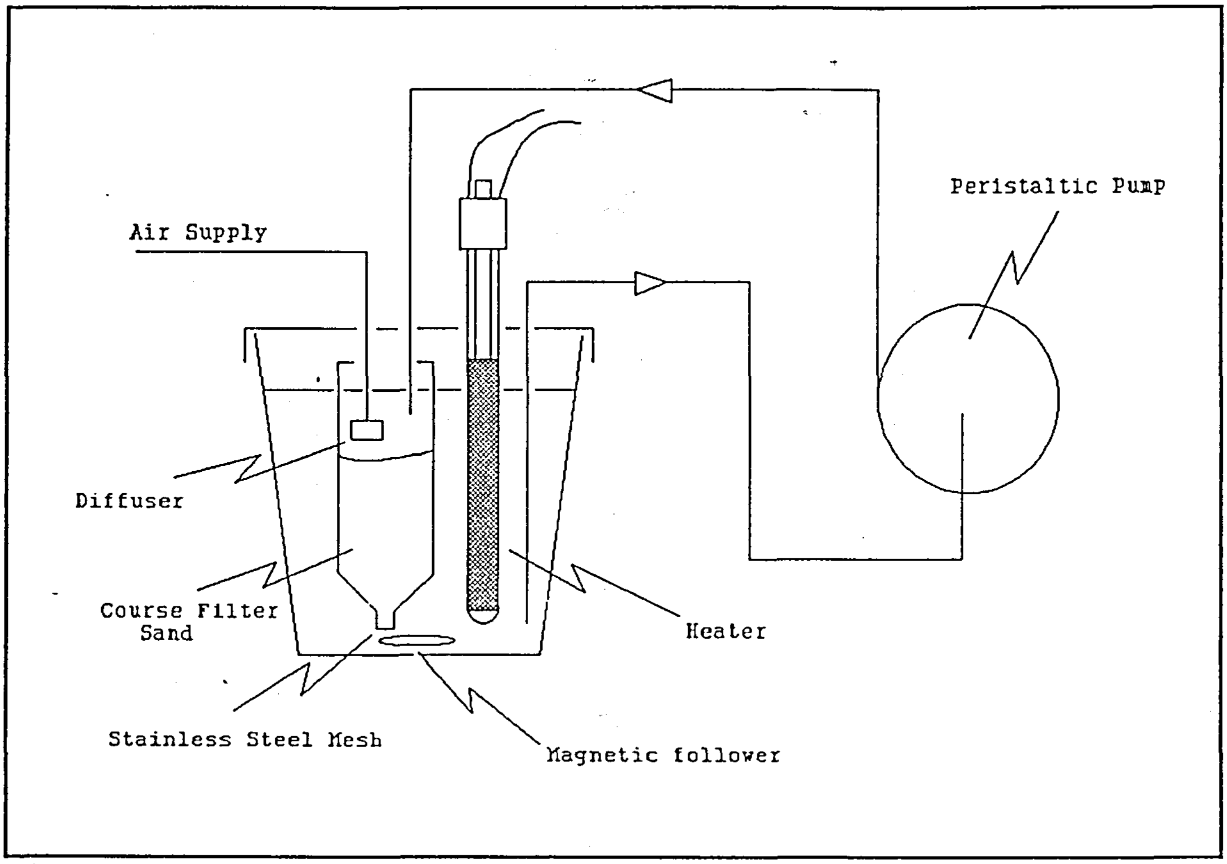

Figure 1 Diagram of the reactor used to determine the kinetic constants of the nitrifying bacteria in the gold mine service water. Detail in text.

by Randall and Buth (1984) containing 10 mg/ℓ NH_3-N. The pH of this solution was 7,8 ± 0,2. A series of 6 runs were done at a time and all 6 reactors were run on "pure" nutrient until it was established that all reactor substrate curves were within 10% of each other. After refreshing the nutrient solution,one reactor was set aside as a control reactor, while the other were dosed at various concentration levels with suspected bacterial inhibitors.

Chlorine solution was prepared by adding HCl (conc.) drop-wise to a 1:10 dilution of commercial NaOCl (3,5%) bleach, until the pH was between 6,5 and 7 and was then standardized using the DPD method in Standard Methods (1985).

Chlorine dioxide was prepared by adding a 5% excess of the stoichiometric amount of $NaClO_2$ to a chlorine solution as prepared above.

The other chemicals were obtained as the AR grade and dissolved in suitable volumes of distilled water.

The set of differential equations, [5] to [9], were solved numerically by using the Runge-Kutta-Fehlberg method (Burden and Faires, 1987) with a truncation error of the order of the third power of the step size. The kinetic parameters were chosen as that set of parameters that gave the best fit to the experimental data as measured by a least squares fit. The algorithm used was the derivative-free version of the Levenberg-Marquardt method described by Brown and Dennis (1972), which finds a local minimum of the objective function, defined as the sum of squared differences between the modeled and observed values at each corresponding datum point.

5.5 Results and Discussion

A study of the effect of suspended material in the water (Kholdebarin and Oertli, 1977), indicates that nitrification efficiency is enhanced by an increase in surface area of the suspended material, suggesting that nitrification preferably takes place at the solid /liquid interface and consequently that the nitrifying bacteria prefer attached growth conditions. Within the mine service water context this would imply that piping, channels and particularly sand filters would be areas of preferred growth. It is therefore likely that the nett decrease in nitrite concentration at the stope (Jooste and Van Leeuwen, 1992) is due to the natural course of the nitrification reaction by bacteria found on the ground and in the drainage channels.

The data expressed in Figure 2 indicates that the kinetics of nitrite formation is very different in mine service water compared to that in the pure nutrient solution. This is also reflected in the calculated values of μ' shown in Table 2. This indicates that a possible cause of nitrite build-up is microbiological inhibition in the mine service water.

Since both groups of organisms are aerobes, the dissolved oxygen level of the service water in the mine is critical for adequate growth. It has been established (Jooste and Van Leeuwen, 1992) that only at one point in the mine was a D.O. level of <1 mg/ℓ found but without a concomitant increase in nitrite concentration.

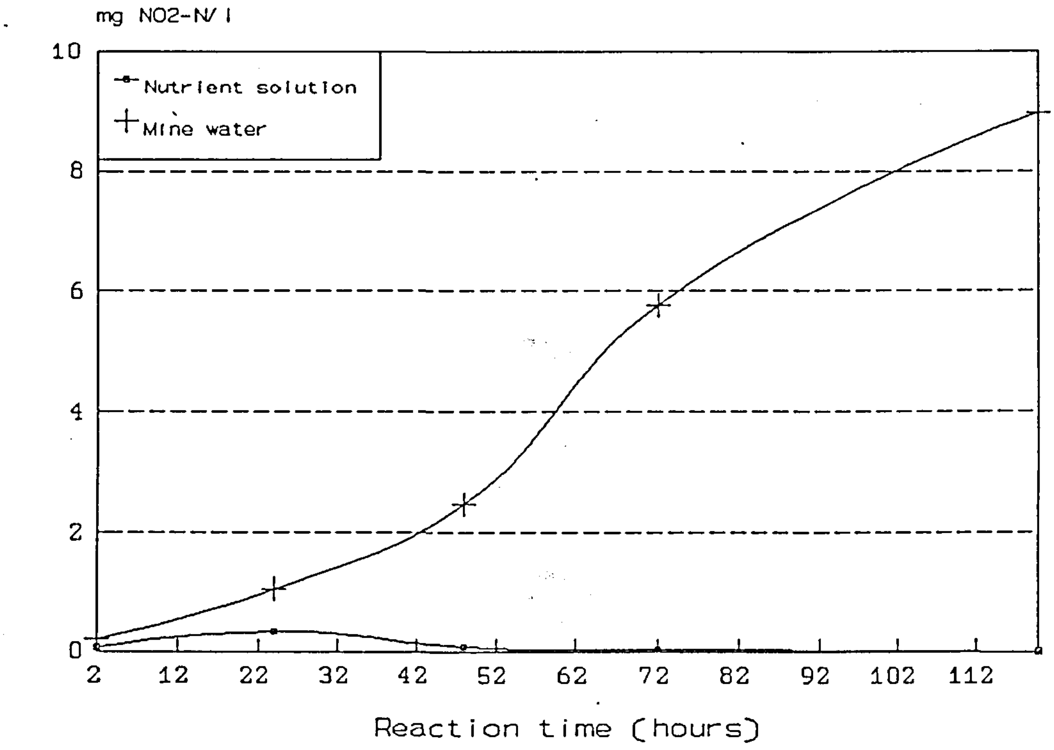

Figure 2. The nitrite concentration in mine service water compared to that in a nutrient solution.

The influent service water temperature at a particular stope was found to be about 5 °C and the drainage water was found to vary between 27 and 45 °C.

This temperature variation raised the possibility that a temperature effect (Randall and Buth, 1984, Antoniou *et al.*,

1990) could lead to a nitrite build-up. The tendency of the μ' values as a function of temperature reflected in Figure 3 predicts nitrite build-up above 17 °C (based on μ' values alone). The modeled growth yields (Y) at 30°C of *Nitrosomonas* and *Nitrobacter* are 0.08 and 0.01mg cells/mgN respectively and these values did not vary significantly with temperature. A combination of these factors in a substrate utilization equation (equation [1]) predicts a nitrite build-up effect below 17 °C, similar to that observed by Randall and Buth. The temperature dependence of the saturation constants (K_a and K_n) have not been determined explicitly.

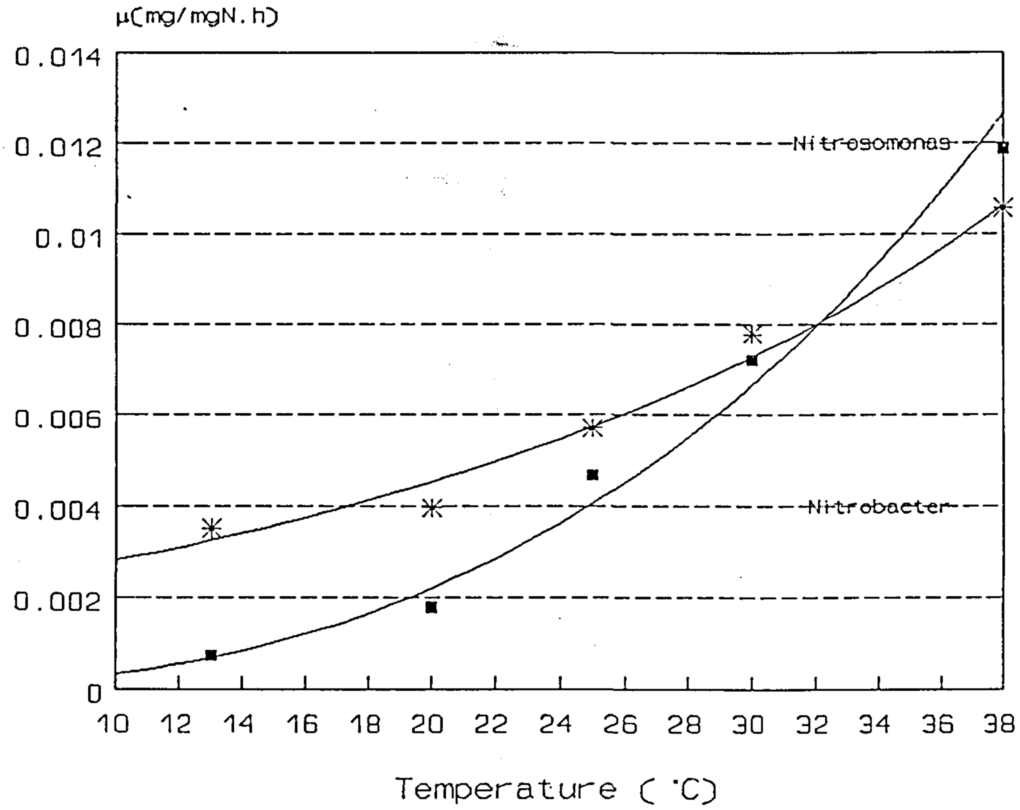

Figure 3. The maximum specific growth rate as a function of temperature for the nitrifying bacteria in the mine service water.

The chemical species that appeared to act as inhibitors together with the calculated μ' values, appear in Table 2. The μ' values determined at 20 °C have been corrected to 35 °C to correct for the temperature effect.

From the calculated values of μ' it is clear that there is a range of chlorine and chlorine dioxide dosing where nitrite build-up is favoured. Above a chlorine dosage of about 13 mg/ℓ and a chlorine dioxide dosage of about 6 mg/ℓ there appears to be complete inhibition of nitrification. Which chemical species are involved or what the mechanism of

Table 2. Specific maximum growth rate (μ') values for various inhibiting substances.

Species	Dosage mg/ℓ	$\mu'(h^{-1})$ *Nitrosomonas*	$\mu'(h^{-1})$ *Nitrobacter*
Cl_2 (35 °C)	0	0,030	0,010
	3	0,029	0,006
	4,4	0,030	0,004
	5	0,029	0,002
	8,8	0,028	0,001
	13,2	0,0003	0,0001
Cl_2 (20 °C)	0,5	0,030	0,010
	2	0,027	0,009
	5	0,024	0,007
	8	0,024	0,004
	10	0,024	0,002
	15	0,0003	0,0001
ClO_2	1	0,029	0,010
	3	0,029	0,007
	9	0,008	0,001
	12	0,0001	0,0001
Br_2 (35 °C)	1	0,030	0,010
	3	0,030	0,008
	10	0,025	0,003
CN^- (35 °C)	0,5	0,030	0,007
	1,5	0,026	0,002
	5,1	0,013	0,002
Ni^{2+}	1	0,027	0,009
	5	0,028	0,010
	10	0,025	0,005

inhibition is, has not yet been established. In the case of chlorine it is likely to be chloramines and in the case of bromine it is likely to be bromamines although this is yet to substantiated.

In order to estimate the effect of various chemical species in the mine service water circuit, it would be advantageous to model parts of the circuit as plug flow reactors (PFRs). This approach would hold true as far as the piping, drainage channels and sand filters are concerned. The integral form of equation [4] for a PFR is equation [10] (Braha and Hafner, 1987), where Θ is the mean bacterial age (sludge age).

$$\Theta = -\int \frac{Y}{\mu'}\frac{(K + S)}{S\ X}\,dS \qquad \ldots.[10]$$

$$X = (YS_o - X_o) - YS \qquad \ldots.[11]$$

By substituting the relation [11] between substrate elimination and bacterial growth (Braun and Berthouex, 1970) in equation [10] and integrating between the limits S_o and S, equation [12] is obtained.

$$\mu' = -\left(\frac{YK}{YS_o + X_o}\right)\ln\left(\frac{S}{S_o}\right) + \left(1 + \frac{KY}{YS_o + X_o}\right)\ln\left(\frac{Y(S_o - S)}{X_o} + 1\right) \ldots[12]$$

In the context of fixed growth, Θ could be interpreted as the residence time within the reactor. This equation is applicable for a single substrate, S. To extend the application to microbiological nitrification, it is assumed that the mass balance applicable to this situation is: (Nett nitrite produced) = (Nitrite formed) - (Nitrite oxidized). Assuming further that (Nitrite formed) = (Ammonia removed), i.e. the exogenous growth phase for the bacteria and recognizing that the equation [12] is applicable to the removal of a substrate, in this case ammonia or nitrite, then the expression used to calculate the nitrite formation potential, ß, is given in [13]:

$$ß = f(Y_m,A_o,M_o,K_a) - f(Y_b,N_o,B_o,K_n) \quad ....[13]$$

Where $f(x_i)$ refers to the values obtained by solving for the substrate concentration on substituting suitable parameters into equation [12].

In order to make the application "semi-dynamic" the function ß is calculated in hourly intervals, i.e. increased by 1. Application of the measured kinetic values to equation [12] and [13] yields the values depicted in Figure 4 and Figure 5. The values for the parameters have been assumed to be: Θ = 24h, Y_b = 0.02mg dry cells/mgN.day, Y_m = 0.06mg dry cells/mgN.day, M_o = B_o = 0.1 mg dry cells/unit area, K_a = 100 mgN/ℓ and K_n = 1 mgN/ℓ.

This suggests that for chlorine dosages (not residuals) between 3 and 13 mg/ℓ chlorine dioxide dosages between 2 and 8 mg/ℓ there is a possibility for nitrite build-up. The inhibitive effects of bromine appears to milder and it was found that the inhibitive effect disappeared after about 36 hours. In the case of both chlorine and bromine dosing, halo-amines would have been formed. Air stripping and further chemical reaction gradually caused halo-amine concentrations to drop and so reduce the inhibitive effect. However, on a further application of 5 mg/ℓ bromine in the reactor which had the 10 mg/ℓ dosage and with replenished nutrient, no recurring inhibition was observed. This would mean that the nitrite-oxidizing bacteria in the mine service water were probably able to adapt to the mild bromination applied here.

At the Kloof Gold Mining Company's surface water treatment works, it was observed that the sand filters are an important

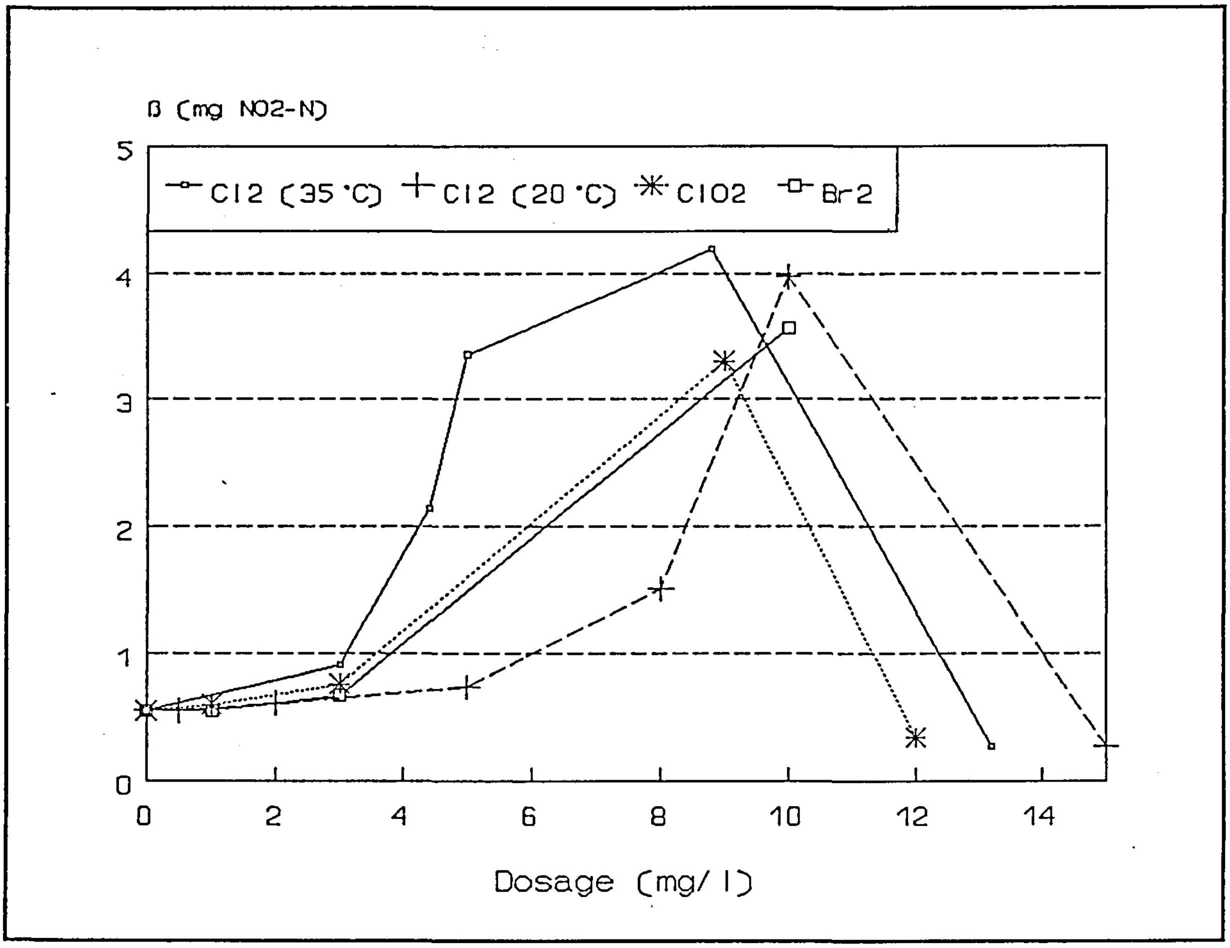

Figure 4 The nitrite formation potential for some halogen based disinfectants.

area where nitrite is produced (Pearson *et al.*, 1989). Nitrification at this point is understandable in view of the large surface area the sand provides for attached growth. Significant too, is the fact that chlorine dioxide is dosed before the water is filtered. McLaren (1992) confirmed that ClO_2 dosing has not solved the nitrite problem and that chlorine dosing at Kloof Mine has lead to significant build-up of chloramines during recycling. Chloramines are known to be stable

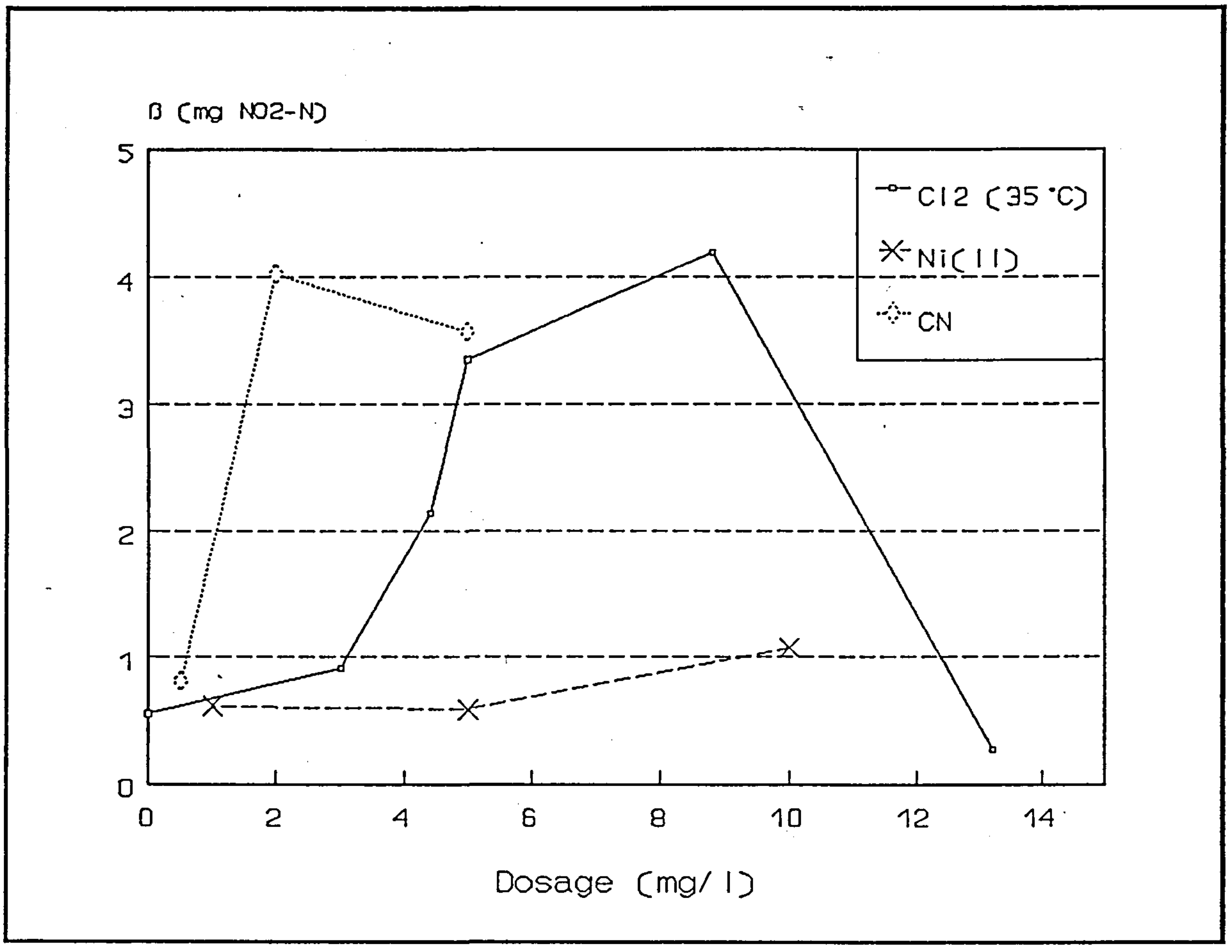

Figure 5. The nitrite formation potential for some non-halogens found in the gold mining context in comarison to chlorine.

compounds and are likely to build up under recycle conditions (White, 1972).

Although other species such as cyanide and nickel (II) also produced an inhibitive effect, it is probably not of great significance as a microbiological inhibitor in mine service water since inhibitive concentrations of >10 mg/ℓ were generally not encountered. It is possible though that such an effect might be observed in the effluent channels of the metallurgical works. The phenomenon of nitrite build-up may in fact be possible in any water treatment situation where chlorine or chlorine dioxide is used as disinfectant or oxidant at low dosages.

5.6 Conclusions and Recommendations

Appreciating the limitations of applying limited bench scale tests to a complex and dynamic situation such as a mine service water circuit, the selective inhibition of microbiological nitrite oxidation by the application of chlorine and/or chlorine dioxide may well merit further investigation as a model for nitrite build-up in mine service water. Water temperatures below 13 °C may add to this effect.

In situations where nitrite build-up due to selective inhibition of nitrification is encountered, the use of bromine should be investigated.

Where the use of bromine is not feasible, the use of an oxidant and non-lasting disinfectant, e.g. ozone, followed by the dosage of <4mg/ℓ chlorine as a residiogenic disinfectant could be used.

The mechanisms of selective inhibition as well as any synergistic/antagonistic effects still need to be investigated before any attention can be given to applying the results obtained here to a full scale application.

5.7 Acknowledgements

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CHAPTER 6

OXIDATION OF NITRITES IN MINE WATERS

Introduction

The South African gold mining industry uses some 510 ML/d of fresh makeup water, discharges about 440 ML/d of effluent, mainly to evaporation dams, and circulates roughly 5,500 ML/d (Mackay et al., 1991). More than 25% of this volume is circulated as service water, which is used mainly to cool the working areas and suppress dust. Since geothermal heat can raise the rock surface temperature as high as 55°C, the service water is chilled to 4°C. For various reasons mine workers have been found to drink the service water. At most mines, including the Kloof Gold Mining Company where this study was conducted, the service water is contaminated by fecal matter and fecal total coliform counts as high as 3,000/100 mL have been recorded (Pearson et al., 1990). For this reason it is necessary to disinfect the service water. Chlorine was used traditionally to this end, but because of its reactivity to the ammonia (ca. 5 mg NH_4-N/L) in the water, the use of other disinfectants, such as chlorine dioxide and ozone, was investigated.

Disinfection studies conducted on the mine service water, of which about 35 ML/d is circulated, indicated a notable non-disinfective sink for oxidizing disinfectants such as chlorine, chlorine dioxide or ozone is due to the nitrite ion present in the water. The nitrite ion concentration in the water varies, but averages around 0.9 mg/L (Pearson et al., 1989). The oxidation of nitrite ion by chlorine dioxide would have to take place before it could disinfect the water effectively. This would mean a cost of about R 2,5 million (about US $0.9 million) p.a., without any significant disinfection.

Ozone was considered for use as an oxidant for nitrite ion, which should cost only about R 0.9 million (US $0.35 million) p.a, but still be the major cost associated with service water disinfection.

A pilot scale study into the use of ozone was aimed at demonstrating its viability for oxidizing nitrite ion in order to reduce the disinfectant demand and at the same time to establish its disinfection efficiency on the mine service water. This paper describes the results of this study, the investigation into a possible source of nitrite ion buildup in the service water and what the impact of the method of disinfection could be on the nitrite ion buildup.

Background

Some pertinent reactions involved in the disinfection process and a possible nitrite ion buildup mechanism are discussed.

DISINFECTANT REACTIONS

The molar stoichiometries for the reactions of the commonly used disinfectants/oxidants with nitrite ion appear in equations [1], [2] and [3]. The mass stoichiometries calculated from these are given in equations [4], [5] and [6].

$$Cl_2 + NO_2^- + H_2O = NO_3^- + 2HCl \qquad [1]$$

$$O_3 + NO_2^- = NO_3^- + O_2 \qquad [2]$$

$$2ClO_2 + NO_2^- + H_2O = NO_3^- + 2HClO_2 \qquad [3]$$

$$\text{mg } Cl_2/\text{mg } NO_2^-\text{-N} = 5.07 \qquad [4]$$

$$\text{mg } O_3/\text{mg } NO_2^-\text{-N} = 3.43 \qquad [5]$$

$$\text{mg } ClO_2/\text{mg } NO_2^-\text{-N} = 9.64 \qquad [6]$$

Although these reactions are thermodynamically favorable (Huheey, 1983; Valentine, 1985; Scully and White, 1991), there are also other side reactions to be considered, as well as the relative kinetics of such reactions. Reaction [1] has a forward kinetic constant of 11.3 $M^{-1}s^{-1}$ compared with 1.2×10^4 for reaction [7] and between 1 and 4 $M^{-1}s^{-1}$ for reaction [8] (Isaac and Morris, 1980). Oxidation of nitrite ion, therefore, can only take place after ammonia has been largely oxidized. Amino acids, as well as other organic chemicals, can compete thereafter for the available chlorine.

$$Cl_2 + NH_3 = NH_2Cl + HCl \qquad [7]$$

$$Cl_2 + \text{Amino Acid} = \text{Chloramino-acid} + HCl \qquad [8]$$

The data above illustrates that the efficacy of these oxidizing disinfectants in a "real world" water environment cannot be estimated from thermodynamic considerations alone. These simultaneous reactions may have the effect that the actual effective stoichiometries may differ from the calculated stoichiometries and have to be determined empirically.

A POSSIBLE NITRITE ION BUILDUP MECHANISM

While nitrite ion oxidation serves to lessen the oxidant demand, it would be more advantageous to curtail nitrite ion buildup in the water.

Nitrite ion buildup could be due to i) a source of nitrite ion that produces nitrite ion at a higher rate than the normal bacterial processes could remove it, or ii) an inhibition of the normal bacterial processes.

An investigation into the use of explosives as a source of nitrite ion could not positively link their use to an increase in nitrite ion concentration (Jooste, 1992).

The normal bacterial process of ammonia nitrification consists of two steps, i.e., the oxidation of ammonia to nitrite ion by species such as *Nitrosomonas,* **and the subsequent oxidation of nitrite ion by species such as** *Nitrobacter.* **Both bacteria are obligate aerobic gram-negative autotrophs with a marked preference for attached growth. A comparison of the sand filter influent nitrite ion concentrations with the filter effluent [ratio $(NO_2^-)_{out} : (NO_2^-)_{in} = 3.4 : 1; \sigma = 0.8$], highlights the sand filters as a nitrite source and possibly as a growth area for the nitrifying bacteria. It is recognized that both these species are sensitive to inhibition by a wide variety of factors such as temperature, variable organic loading in the water, mercury(II), copper(II), arsenic(0), arsenic(III), chromium(VI), pH, free ammonia, cyanide, etc. (Kholdebarin and Oertli, 1977; Braam and Klapwijk, 1981; Randall and Buth, 1984, Antoniou, et al., 1990; Manem and Rittmann, 1992). Nitrite ion buildup in a nitrifying system then could be explained by an inhibition of the action of** *Nitrobacter.*

Using Monod kinetics (Benefield and Randall, 1980) corrected for bacterial death and decay, for a substrate S, the substrate concentration profile will be described by the differential equation [9]

$$\frac{dS}{dt} = -\frac{\mu'}{Y}\left(\frac{S}{K + S} - k\right)X \qquad [9]$$

where μ' is the maximum growth rate for the organism with population X feeding on substrate S (with half-saturation constant K) with an observed growth yield Y units of population per unit substrate consumed and dying off at rate k per unit time. At the same time it is assumed that the population growth is described by equation [10] (Benefield and Randall, 1980):

$$\frac{dX}{dt} = -\left(\frac{X}{Y}\right)\left(\frac{dS}{dt}\right) \qquad [10]$$

Based on the premise that the nitrite ion produced by *Nitrosomonas* **equals (residual nitrite ion + nitrite ion consumed by** *Nitrobacter*), **i.e., there are no other nitrite ion sinks or sources, a set of four simultaneous differential equations can be set up using equations [9] and [10] on ammonia and nitrite ion, respectively. This set of differential equations was solved numerically using the Runge-Kutta-Fehlberg algorithm to obtain a value for μ' as well as the other kinetic parameters.**

The solutions of the differential equations to determine these parameters were chosen in contrast to the graphical solutions to accommodate the dynamic equilibrium of the coupled nitrite ion-producing and nitrite ion-removal mechanisms which was operative in the batch reactors used. The kinetic parameters were chosen as that set of parameters that gave the best fit to the experimental data using the Levenberg-Marquardt derivative free least squares algorithm as described by Brown and Dennis (1972), which finds a local minimum of the objective function, defined as the sum of the squared differences between the observed and modeled values at each datum point (Jooste, 1992). Details of the results appear in Jooste and van Leeuwen (1993).

Experimental

The bench scale tests were performed at the University of Pretoria's Department of Chemical and Environmental Engineering and the pilot scale tests at the Kloof Gold Mining Company's premises.

BENCH SCALE TESTS

Bench scale studies on the use of ozone for the treatment of the service water of the Kloof Gold Mining Company indicated that the ozone demand for the water varied between 5 and 10 mg/L and that the total plate count could be reduced from 10^7 to 10/mL and the total coliforms could be reduced to 1 (or less)/100mL with only 5 mg/L of ozone. It was therefore estimated that no more than 10 mg/L of ozone would be needed. The applied dosage, however, would depend on the ozone transfer efficiency which had to be determined for various contacting systems on pilot scale.

PILOT SCALE OZONATION OF MINE WATER

For the pilot scale study, two Degrémont ozone generators were used which nominally generated 1 kg/h each. Ozone transfer was accomplished by means of either i) an 8-m high (1.25-m diameter) concrete bubble column equipped with porous ceramic diffusers operated in counter-current mode (Figure 1), ii) by a deep U-tube (Figure 2) or by a static mixer system, placed before an upflow sand filter.

BENCH SCALE NITRIFICATION

Bacterial investigations were conducted in a 5-L batch reactor and with a nutrient solution as described by Jooste and van Leeuwen (1993). Chlorine, chlorine dioxide, ozone and bromine analyses were performed according to *Standard Methods, 1985.*

Results and Discussion

Ozone transfer efficiencies of 73-85% for the static mixer system, 80-88% for the bubble column and 96-99% for the deep U-tube were obtained. The efficiencies tended to decrease with increasing ozone dosages (van Leeuwen and van der Westhuizen, 1992).

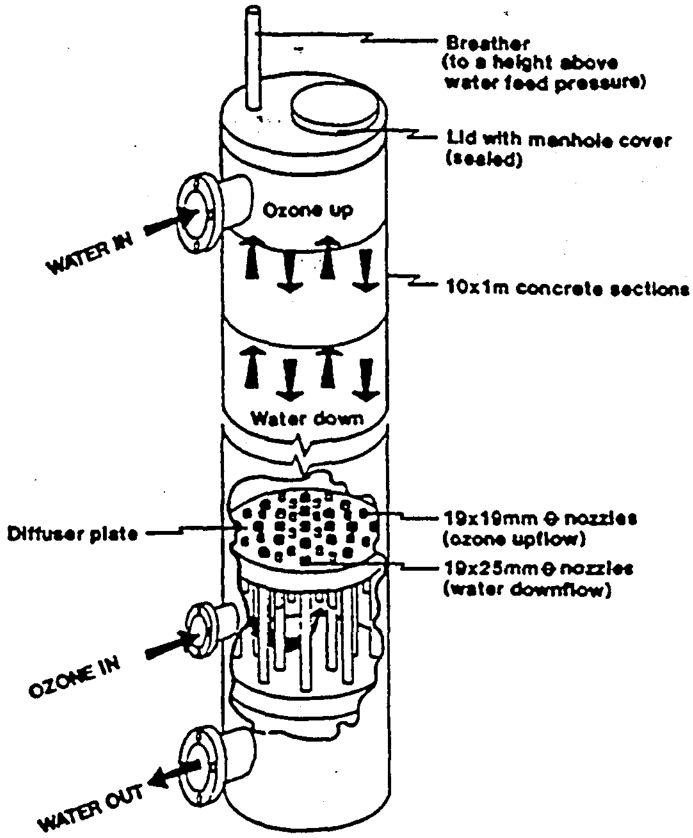

Figure 1. Detail of the concrete bubble column used as an ozone contacting system.

OXIDATION OF NITRITE ION BY OZONE

No nitrite ion could be detected after the contactors when ozone dosages exceeding the stoichiometric demand were applied. Remaining nitrite ion concentrations as a function of ozone dosage are shown in Figure 3. The slight tailing observed at low nitrite ion concentrations may be due to kinetically competitive reactions of ozone with organic compounds in the water. At the higher nitrite ion concentrations, the average ozone-to-nitrite ion ratio is 3/4, as predicted by stoichiometry.

The disinfective effect of ozone in the presence of nitrite is illustrated Figure 4. The kinetics of the disinfection mechanism would appear to be comparable with that of nitrite oxidation.

MICROBIOLOGICAL OXIDATION OF NITRITE ION

A comparison of the nitrite ion production in the mine service water with that in distilled water (with similar nutrient content) in an aerated batch reactor at 30°C, shows a marked nitrite ion buildup in the service water (Figure 5). This points to a chemical component of the service water, rather than a physical property being responsible for the nitrite ion buildup. Measurements in the water circuit at the mine ruled out temperature and dissolved oxygen as inhibitive factors.

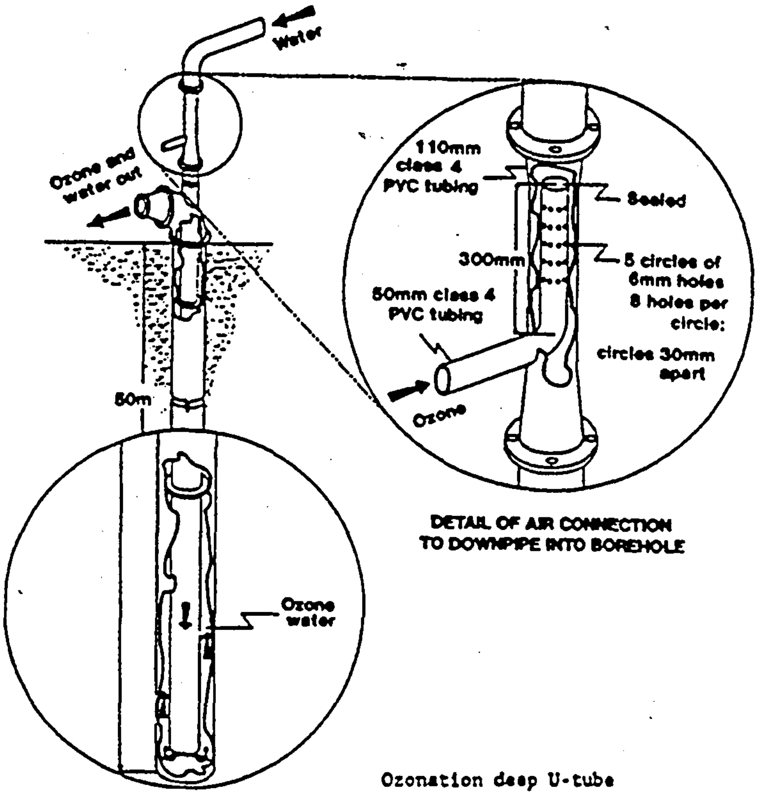

Figure 2. Detail of the deep U-tube used as an ozone contacting system at the Kloof Gold Mining Company.

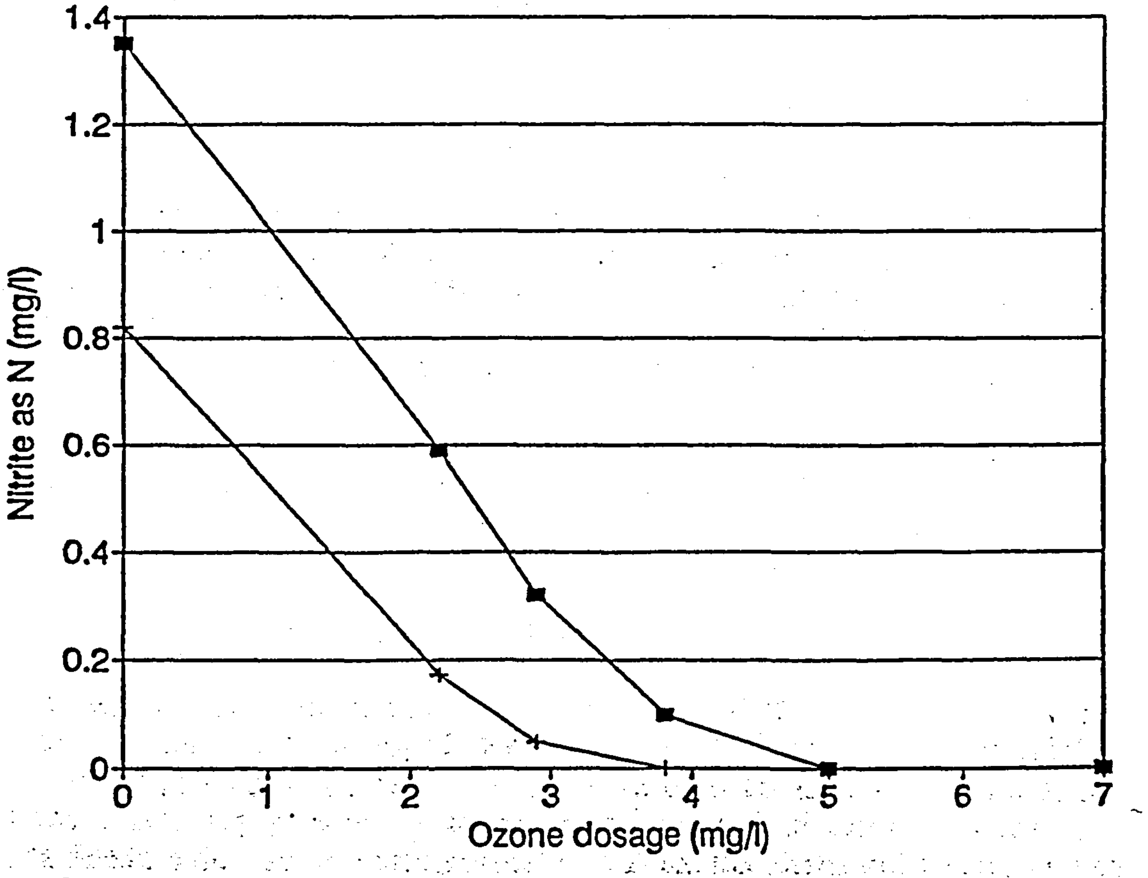

Figure 3. Residual nitrite ion concentrations as a function of ozone dosage applied to two different mine service water samples.

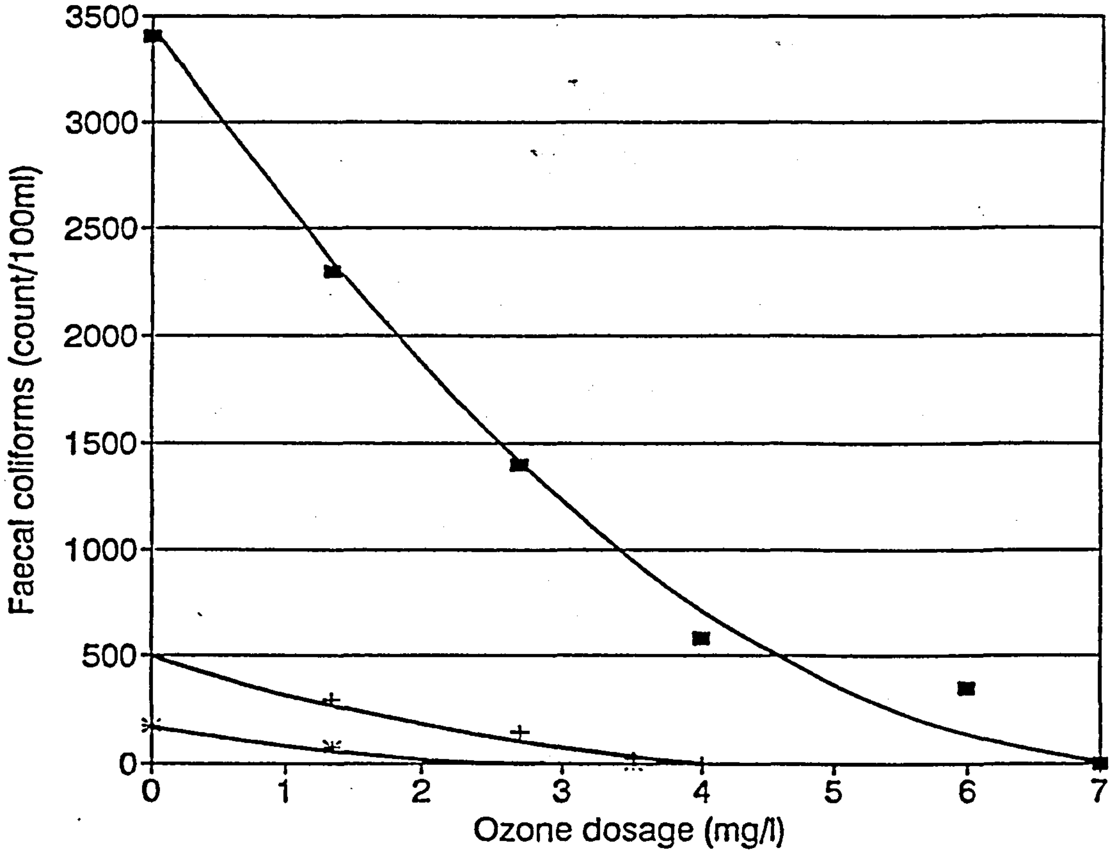

Figure 4. Bacterial counts as a function of ozone dosage applied to three different samples of mine service water.

Further systematic bench scale investigation into the substances known to be added to the mine service water revealed that it is possible to induce nitrite ion buildup in the reactor by the addition of some commonly used disinfectants such as chlorine, chlorine dioxide and bromine. The effect of disinfectants on the ratio of the normalized maximum growth rates (μ') of *Nitrosomonas* to *Nitrobacter* are described in Figure 6.

Dosages between about 3 and 12 mg Cl_2/L and 3 and 11 mg ClO_2/L were responsible for the inhibition of nitrite ion metabolism by *Nitrobacter*. This gives rise to a predicted nitrite ion buildup potential, ß, calculated as in equation [11] and depicted in Figure 7 for an ammonia concentration of 5 mg NH_4-N/L:

$$\beta = \text{nitrite ion produced} - \text{nitrite ion removed} \qquad [11]$$

The inhibitive effect of bromine disappeared in about 36 hours. No evidence of inhibition of *Nitrobacter* by ozone residue was found, possibly because of its short life span.

Ozone can be used as disinfectant in the mine water. The ozone residue, however, is short-lived, disappearing within 30 min and has to be used in conjunction with other disinfectants. Its advantage would be that it would reduce the required dosage of other oxidizing disinfectants, while not inhibiting microbiological nitrification.

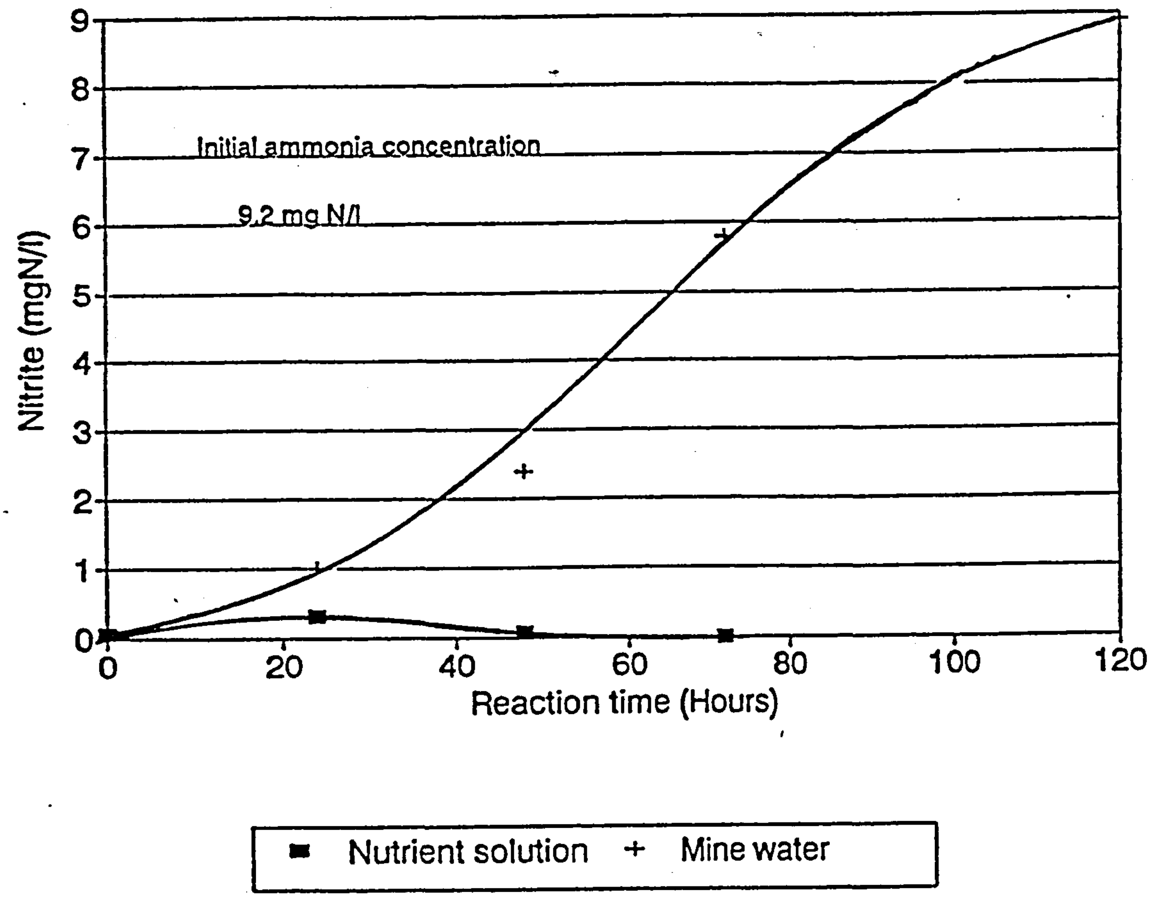

Figure 5. A comparison of the nitrite ion concentration profile of a nutrient solution compared with mine service water in a batch reactor.

The microbiological oxidation of nitrite ion should receive more attention. There is as yet no experimental evidence from the mine to show that the inhibition demonstrated in the bench scale tests is undoubtedly responsible for nitrite ion buildup in the mine water, but the evidence thus far indicates that the inhibition by chlorine, chlorine dioxide or their byproducts should be investigated.

Conclusions and Recommendations

1. A major cost component in disinfection of mine service water is the oxidation of biologically-produced nitrite.

2. Ozone can be used effectively to economically oxidize nitrite found in mine service water and so reduce disinfection costs.

3. The use of chlorine and chlorine dioxide in the mine water may be implicated in the nitrite build-up observed at the mine and should be investigated further.

4. The most effective type and placement of disinfectant and oxidant dosing points should be established to prevent recurrence of this problem.

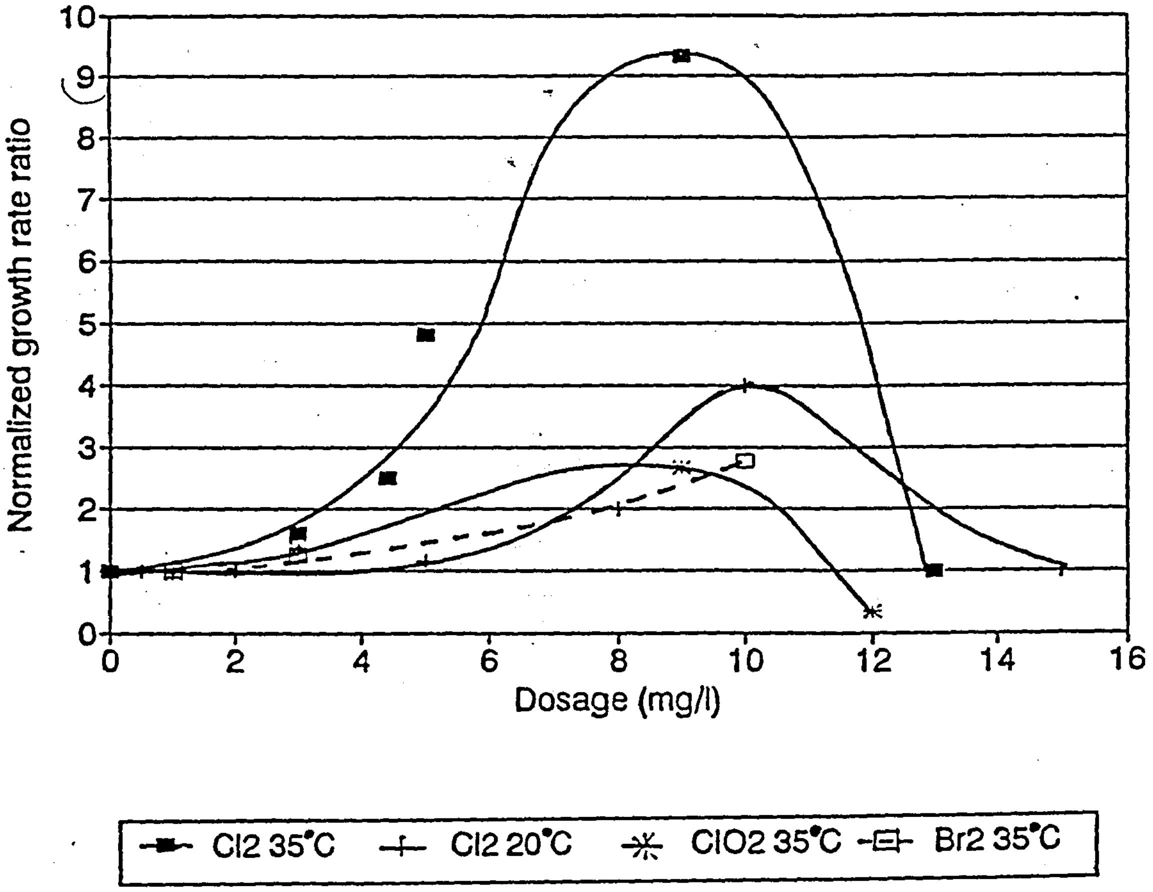

Figure 6. Ratio of the maximum specific growth rates of *Nitrosomonas* to *Nitrobacter*. Growth rates in both instances are normalized to the untreated system.

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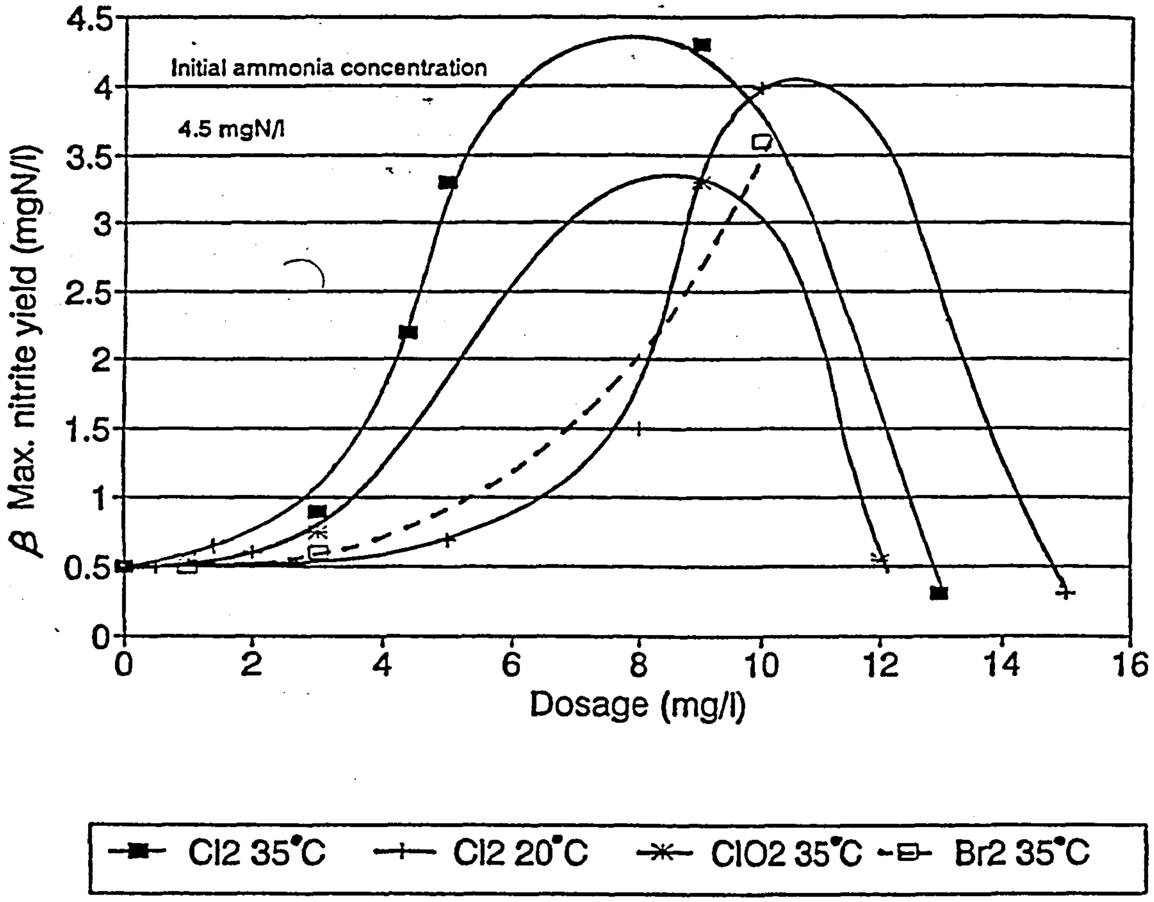

Figure 7. The calculated maximum nitrite-nitrogen concentration in a batch reactor with various dosages of oxidizing disinfectant.

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Key Words

Ozone; Nitrite Ion; Mine Waters; Potable Water; Gold Mine Potable Water Disinfection; Microbial Formation of Nitrite Ion; Chlorine; Chlorine Dioxide;

Résumé

Une composante majeure du coût de la désinfection des eaux de mine est l'oxydation des nitrites d'origine microbiologique. Ces nitrites peuvent être efficacement oxydés par l'ozone pour un taux de 3,6 mg d'O_3 par mg de N-NO_2. Proche de la stoechiométrie. Un emploi inapproprié d'oxydants pour la désinfection des eaux de mine peut conduire à l'augmentation de la teneur en nitrites. Des expériences en laboratoire ont montré que des taux de chlore de 3 à 12 mg/L, ou des taux de ClO_2 de 3 à 11 mg/L peuvent inhiber l'oxydation des nitrites par nitrobacter. Cet effet n'est pas observé dans le cas de l'ozone.

Zusammenfassung

Ein wesentlicher Kostenfaktor bei der Desinfektion von Grubenwasser ist die Oxidation des mikrobiologisch gebildeten Nitrits. Es kann - im stöchiometrischen Verhältnis 3,4 mg O_3 pro mg Nitrit-Stickstoff - sehr wirksam durch Ozon oxidiert werden. Durch den unsachgemässen Einsatz von Oxidationsmitteln bei der Desinfektion von Grubenwässern, kann es zur Oxidation von Stickstoff zu Nitrit kommen. Laborversuche zeigen, dass 3 bis 12 mg Cl_2/L bzw. 3 bis 11 mg ClO_2/L die Nitrit Oxidation durch *Nitrobacter* verhindern. Dieser Inhibierungseffekt konnte beim Einsatz von Ozon nicht beobachtet werden.

CHAPTER 7

OZONATION FOR REUSE OF GOLD MINE SERVICE WATER

INTRODUCTION

Gold mines need large quantities of service water mainly for removal of geo-thermal heat from the deep levels of the mines. A typical gold mine uses 30 to 50 Mℓ/d of service water, most of which is recycled after treatment and cooling. The water is a mixture of underground water, treated surface water and sometimes sewage effluent. Faecal pollution of the service water occurs in the open water circuits on the slopes where service water is used for dust suppression. Underground workers insist on drinking the chilled service water rather than the tepid potable water supplied. Gastro-intestinal and other diseases transmittable through water can be expected and the ominous threat of epidemics is always present unless the service water is properly disinfected.

The service water contains high concentrations of ammonia and nitrite which both, but particularly the ammonia, lead to a high chlorine demand. A particularly progressive mine in the water reuse field, Kloof Gold Mine, opted to use chlorine dioxide supplemented with underground marginal chlorination since the former does not react with ammonia. The nitrite in the service water, typically in concentrations of about 1 mg/ℓ by the time it reaches the treatment plant, results in a high chlorine dioxide demand and consequently high disinfection costs. Bench scale tests with ozonation indicated that ozone held the promise of more economical nitrite removal and disinfection. These results led to a pilot plant study of ozonation on site at Kloof Mine. This chapter is based on these results.

BACKGROUND

Nitrite is a reducing agent towards ozone, chlorine and chlorine dioxide. The redox reactions with these oxidants can proceed according to the following stoichiometry:

$$NO_2^- + O_3 \rightarrow NO_3^- + O_2$$

$$NO_2^- + HOC\ell_2 \rightarrow NO_3^- + H^+ + C\ell^-$$

$$NO_2^- + 2C\ell O_2 + N_2O \rightarrow NO_3^- + 2C\ell O_2^- + 2H^+$$

It should be noted that $HOC\ell$ is the product of the reaction as below.

$$C\ell_2 + H_2O \rightleftharpoons HOC\ell + H^+ + C\ell^-$$

The stoichiometric oxidant requirements for the oxidation of one mol nitrite to nitrate are therefore one mol ozone, two chlorine or two chlorine dioxide. The mass of oxidants required to oxidize 1 kg of nitrite-nitrogen to nitrate would therefore be 3.4 kg ozone, 5.1 chlorine or 9.6 kg chlorine dioxide.

EXPERIMENTAL

A pilot plant with a capacity of 150 m^3/h (3.6 Mℓ/d) was built at Kloof Mine. The pilot plant consisted of two ozone generators, three parallel ozone transfer units and one sand filter (See Figure 1).

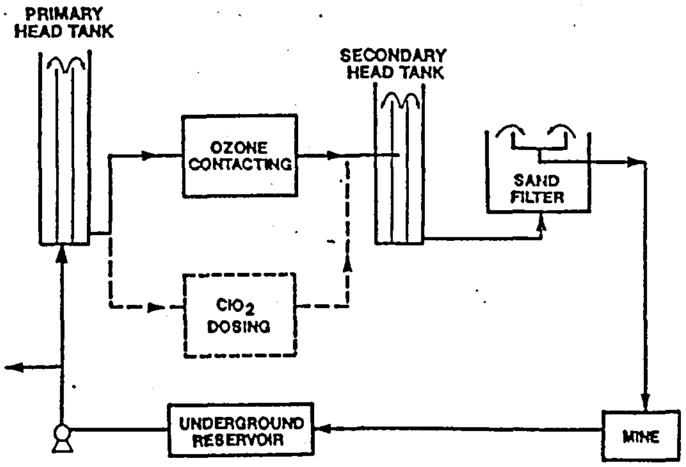

Figure 1 : Pilot and main plant layout

Ozone generators

Two Degrémont ozone generators capable of producing 1 kg ozone per hour each were operated on filtered air at 700 kPa. The typical ozone concentration generated was 10-15 g/m^3.

Ozone contactors

Three different contacting units were installed, i.e. a bubble column, a deep U-tube and an in-line mixer.

Bubble column

The bubble column was constructed from 1.25 m diameter precast concrete manhole segments to a height of 10 m (See Figure 2).

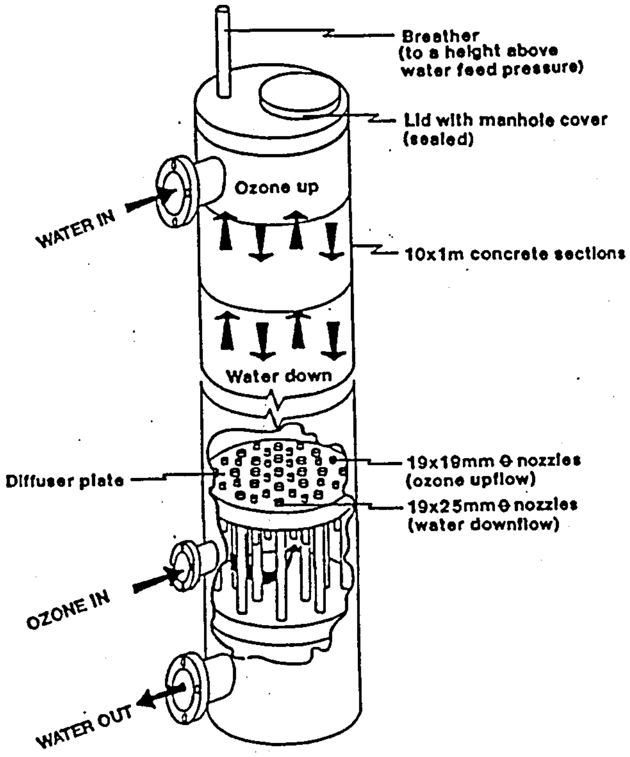

Figure 2 : Ozonation bubble column

A double concrete bottom provided an ozonated air inlet chamber from which the air could pass into the column through nineteen microporous ceramic diffusers (pore size 10-20 μm). Excess ozone and air was wasted through a breather pipe on the top of the column. The service water entered the column at the top, flowed downward through the column and through 19 PVC pipes of 38 mm diameter connecting the two bottoms into the water outlet chamber. This ensured counter-current contacting between the ozonated air bubbles and the service water through a 7 m path length. The differential head of about 4 m between the two water splitter head tanks made water flow rates of 70-150 m^3/h possible. The resulting water retention time in the column was between 3.4 and 7.4 min.

Deep-U-tube

The deep U-tube was constructed by drilling a 250 mm borehole to a depth of 50 m and pressure grouting a 200 mm inner diameter casing into this hole. A 110 mm outer diameter PVC pipe was positioned into the centre of the hole and connected to the incoming pipework (see Figure 3) to a depth of 50 m, later reduced to 25 m for testing purposes. Ozonated air was introduced into the water flowing down into the inner tube flowing co-currently down with the water and out with the water through the annulus between the pipes in the borehole. The design was similar to that described by Brodard & Mallevialle (1986).

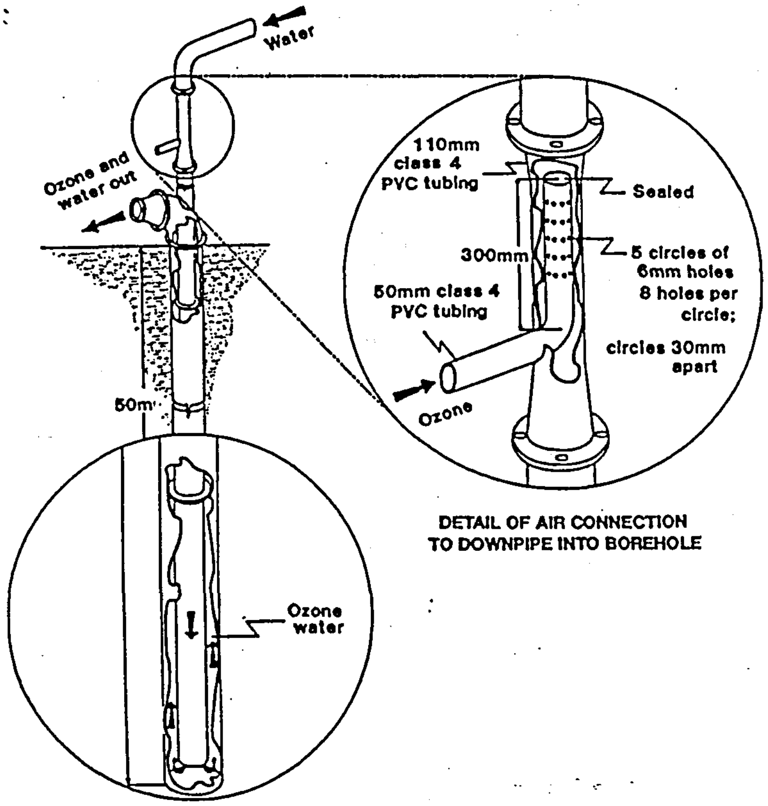

Figure 3 : Ozonation deep U-tube

The borehole could be operated at flow rates ranging from 30 to 50 m^3/h under the head differential between the two splitter towers and up to 70 m^3/h with the aid of a booster pump. The retention time in the deep U-tube ranged from 1.5 to 3.5 minutes.

In-line mixer

An in-line static mixing device for introducing ozonated air into the feed water stream to the concrete (bubble) column was installed 7 m above ground level. The water flow through the column was upwards, resulting in co-current contacting. The in-line mixer could be operated at flow rates ranging from 50 to 100 m^3/h with the aid of two booster pumps. The resulting water retention time in the column was between 5.4 and 10 minutes.

Oxygen enrichment

The bubble column and the deep U-tube were operated with higher ozone concentrations by supplementing the dried air feed to the generators with oxygen.

Corrosivity testing

Metallic corrosivity coupons were strategically positioned at points before and after ozonation to determine degree of attack and mass loss on steel due to ozone oxidation.

Analysis

Ozone concentrations in the inlet and outlet air streams to the ozone contactors and ozone residuals in the water streams exiting the contactors were measured according to the iodometric methods of the International Ozone Association (1987). A mass balance provided a method to calculate ozone transfer efficiencies.

RESULTS AND DISCUSSION

Transfer efficiencies, ozone residuals, residual stabilities, nitrite oxidation and bacterial inactivation are all presented as functions of the ozone dosage.

Transfer efficiency

The percentages of the introduced ozone which have been retained and utilised in the bubble column or the deep U-tube, or the static mixer system are shown in Figure 4. Efficiencies decreased with increasing ozone dosages as could be expected, as also found by Rakness et al (1988), but were variable because of changing ozone demand and a variation in ozone feed concentrations. The efficiency of the bubble column ranged from 80 to 88 %, that of the deep U-tube from 96 to more than 99 % and of the static mixer system from 73 to 85 %.

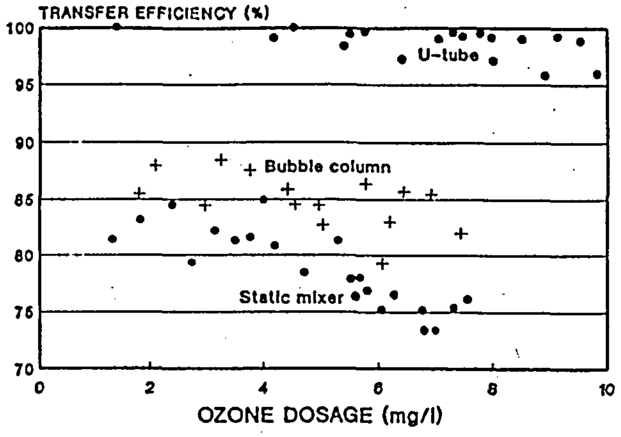

Figure 4 : Ozonation transfer efficiencies of the contacting units

U-tube (25 m)

Efficiencies decreased with the shortened downcomer pipes as could be expected, because of the reduced retention time and the lower pressure on the ozone bubbles. The efficiency of the reduced borehole ranged from 71 to 83 %, considerably lower than that of the deeper U-tube as shown in Figure 5.

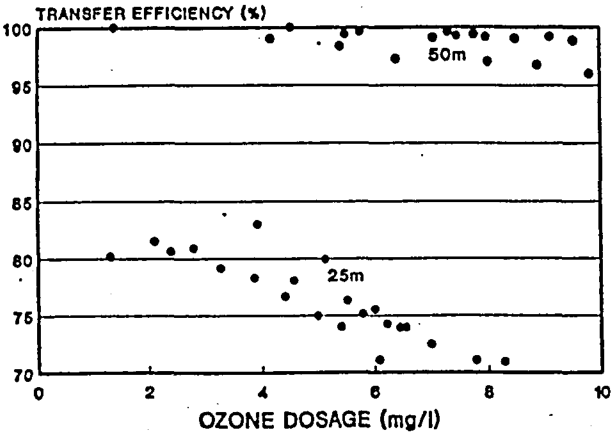

Figure 5 : Ozonation transfer efficiency of the deep U-tube at two depths

Ozone residuals

Ozone residuals in the water exiting the contactors would build up as a function of the ozone dosage. At least 3 or 4 mg/ℓ ozone had to be dosed to detect any residuals. Typical residual concentrations of strong oxidants after ozonation are shown in Figure 6. The oxidant residuals were unstable and decayed typically as shown in Figure 7. The measuring technique could not distinguish between ozone and secondary oxidants formed during ozonation.

Ozone residuals virtually disappear within half an hour, pointing to the need of supplementing ozone with another disinfectant to prevent reinfection of the service water.

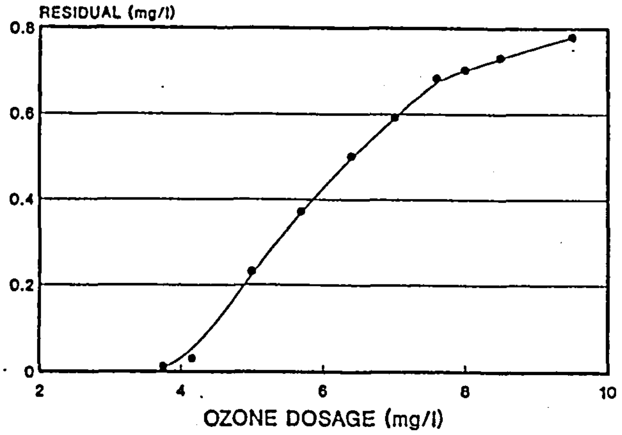

Figure 6 : Typical build-up of ozone residual as a function of ozone dosage

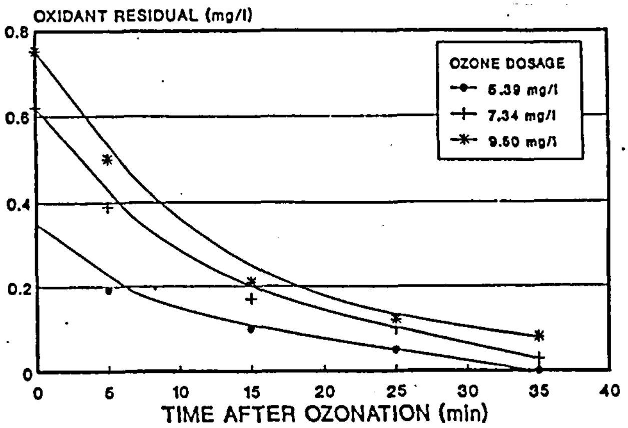

Figure 7 : Typical residual decay curves after different ozone dosages

Nitrite oxidation

Ozone oxidized nitrite rapidly so that no nitrite could be detected after the contacting units if ozone had been introduced in quantities exceeding the stoichiometric demand. Remaining nitrite concentrations as a function of ozone dosage are shown in Figure 8. Expect for some tailing-off at low nitrite concentrations, nitrite oxidation proceeded in a direct stoichiometric mass ratio of ozone: nitrite-nitrogen of 3.4. The tailing-off indicates that first (or second) order reaction rate limitations may have opened the opportunity for competitive oxidation reactions such as the oxidation of organic substances in the service water.

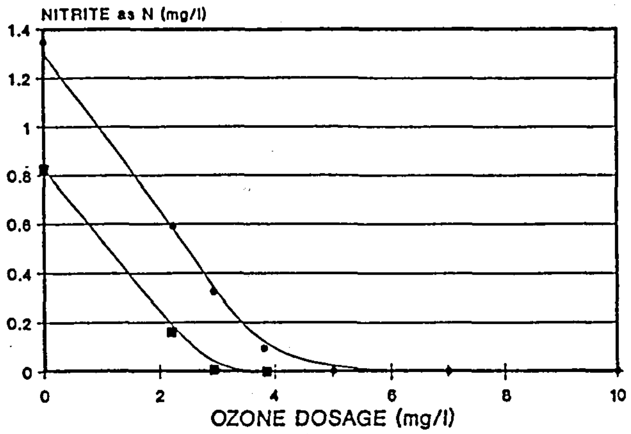

Figure 8 : Nitrite oxidation with ozone

Oxygen enrichment

Ozone could be generated in higher concentrations from air mixtures which are richer in oxygen. Ozone concentrations could be doubled up to 3.8 g/m^3 using 80 % oxygen.

Different oxygen concentrations have been injected into the dried air feed and subsequently into the bubble column and the deep U-tube with the resulting effect shown in figure 9.

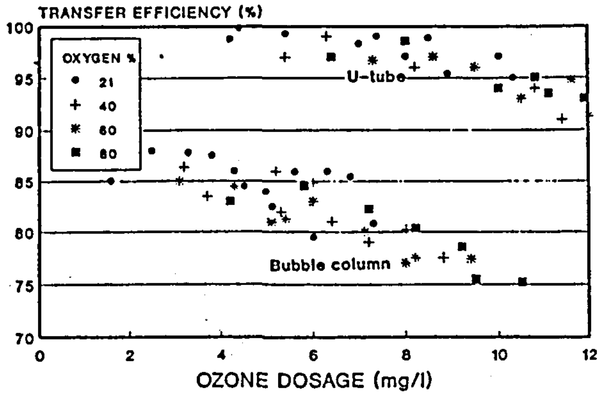

Figure 9 : Ozonation transfer efficiencies with oxygen enrichment

Corrosivity testing

The effect of ozone and chlorine dioxide addition on the corrosion rate of mild steel in service water, is shown in Figure 10.

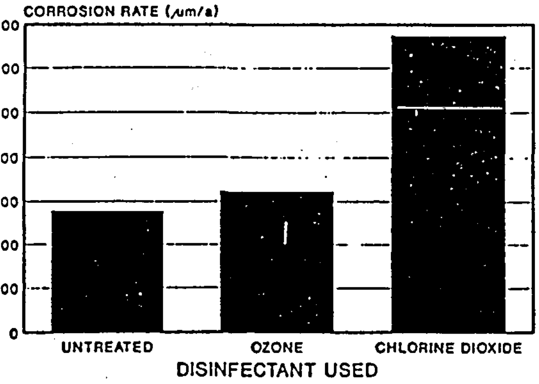

Figure 10 : The effect of ozone and chloride dioxide on corrosion

Ozone disinfection

Ozone was able to substantially reduce bacterial indicator numbers as shown in Figure 11. An elimination of all coliforms and a reduction in total plate counts of 4 to 5 logs was always possible at ozone dosages of 7 mg/ℓ.

An interesting aspect of the disinfection results is that the bacteria were inactivated in the presence of nitrite showing that disinfection kinetics must have been of the same order of magnitude as that of nitrite oxidation.

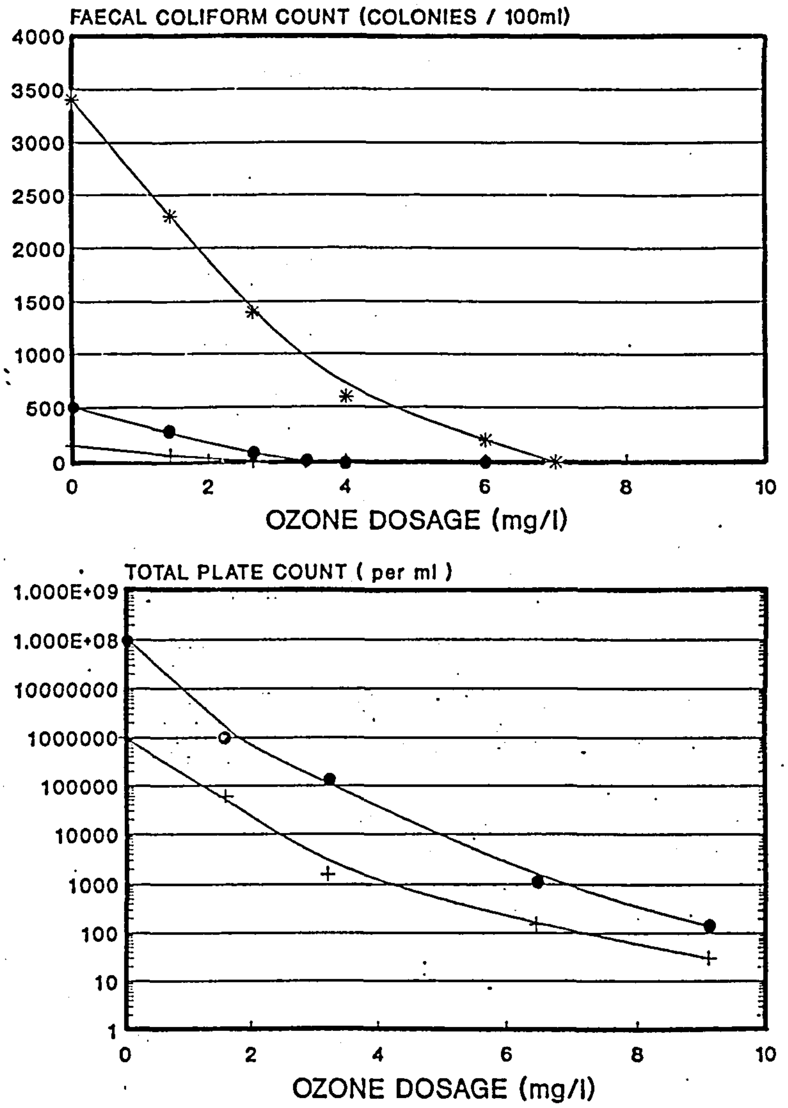

Figure 11 : The effect of ozone on bacterial indicators

COST IMPLICATIONS

The ozone demand of the service water was found to be on average, 7 mg/ℓ with maximum values reaching 10 mg/ℓ. On a 50 Mℓ/d scale, this would involve ozone generators with a capacity of 500 kg/d plus the allowance for losses. Costing was done on a 24 kg/h basis. This resulted in a cost figure of US $1.5 million for the whole plant including air preparation and dissolution. Amortisation of the amount over 10 years at an interest rate of 16 % results in an annual cost figure of just over $300 000. The operational cost, mainly electricity and maintenance, could add another $75 000 to the annual ozonation budget bringing the total annual cost to just under $400 000. Ozone would have to be supplemented with another oxidant to ensure a residual disinfectant concentration through the service water system. This could add $40 000 to $80 000 to this option.

By comparison a dosage of 4 mg/ℓ of chlorine dioxide, which is insufficient to oxidise all the nitrite but which does result in a lowering of bacterial counts, would cost $ 1 million annually on a 50 Mℓ/d scale. Breakpoint chlorination with simultaneous nitrite oxidation would require about 45 mg/ℓ of chlorine which would also cost about $ 1 million annually.

CONCLUSIONS AND RECOMMENDATIONS

1. Ozone was more efficiently introduced with a 50 m deep U-tube than a bubble column, while a static mixing device with co-current contacting was the least efficient.

2. Oxygen enrichment of feed air to the ozone generator increased ozone output but not ozone transfer efficiency.

3. Ozonation only marginally increased service water corrosivity while chlorine dioxide doubled corrosion rates.

4. The main factor contributing to the disinfection cost of service water is biologically formed nitrite. Prevention of nitrite build-up should be investigated.

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