THE USE OF OZONATION IN COMBINATION WITH LIME AND ACTIVATED SODIUM SILICATE IN WATER TREATMENT

Final Report

to the Water Research Commission

by

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EXECUTIVE SUMMARY

In South Africa the majority of the population use surface water for domestic purposes. Increasing population, industrialisation and the construction of water supply systems to serve all communities with drinking water is placing increasingly heavier demands on existing reserves and facilities.

Domestic and industrial pollution in surface water supplies, public awareness of drinking water quality and scientific investigations require that treatment methods to produce drinking water must be re-examined continuously. The effectiveness of conventional treatment process designed to primarily remove suspended matter and disinfect water with chlorine must be evaluated to see if drinking water of the desired quality can be produced at all times even if the raw water source is contaminated.

The treatment required to produce drinking water is a function of the source water quality and the desired quality to be distributed.

The use of ozone is well demonstrated and is used throughout the world in some 1000 treatment plants with capacities from as little as 10 m^3/h to as large as 30 000 m^3/h.

The power and usefulness of ozone in water treatment is apparent and is applied for specific purposes. Following are examples of such applications:

- Oxidation/Pre-ozonation
  - Oxidation of soluble iron and manganese
  - Removal of taste, odour and colour
  - Enhancement of particulate removal or "micellisation - demicellisation"
  - Oxidation of specific micropollutants such as some pesticides and phenolic compounds
  - Control of algae and algal blooms
- Biological Stabilisation
  - Ozonation before granular activated carbon to reduce the concentration of assimilable organic compounds by Biological Activated Carbon (BAC)
- Reduction of disinfection by-products (DBP) during disinfection

  In contrast to chlorination, trihalomethane compounds (THM's) are not formed by ozonation
- Disinfection

  Bacterial, viral and protozoa inactivation

From the practical point the main disadvantages of the use of ozone in water treatment are:

- No disinfection residual can be maintained
- Oxidation of organic material produces more biological assimilable compounds that could lead to microbiological aftergrowth
- Ozone is generated on site and cannot be stored
- Some ozone by-products may form which are mostly a function of the water quality being treated. As an example, bromoform ($CHBr_3$) could form if bromine present in the water forms hypobromous acid (HOBr) on ozonation which reacts with natural organics to form bromoform

In South Africa ozone is applied at only two large purification plants, viz. at Western Transvaal Regional Water Company for the removal of manganese by oxidation and at Umgeni Water's Wiggins treatment plant to treat eutrofied water.

Ozonation of water abstracted form the Upper Vaal River has never been performed and questions on the effect of ozone on the removal of suspended matter and algae still need to be answered. The use of hydrated lime and activated sodium silica treatment as practised by Rand Water for the destabilisation and flocculation of suspended matter in Vaal Dam water is unique. The effect of ozonation on removal of suspended organic and inorganic material in combination with hydrated lime and activated sodium silicate has never been studied before.

The purpose of this study was to evaluate the use of ozone in combination with activated sodium silicate and hydrated lime to determine the effect on:

- coagulation, flocculation and the removal of suspended matter
- removal or destruction of algae and other organisms
- fate of organic compounds in Klip River and Vaal Dam water during the treatment process

CONCLUSIONS

- Ozone affects the coagulation and flocculation of water when treated with activated sodium silicate and hydrated lime. Vaal Dam water was affected negatively and fewer fast settling macro particles were formed after pre-ozonation.

  Klip River water was affected positively and more fast settling macro particles were formed after pre-ozonation. Spontaneous flocculation took place when ozonating Klip River water.

- The zeta potential of natural occurring suspensions in Klip River and Vaal Dam water is changed by ozonation, making it less negative and therefore reduces the normal coagulant demand.

- Organic carbon compounds seem to play an important role in the improvement of coagulation and flocculation following ozonation.

- The organic quality of water is improved as the dissolved organic carbon (DOC) content as well as ultra violet light extinction at 254 nm of both Vaal Dam and Klip River water, are reduced. The fact that the percentage reduction in Vaal Dam water for these two determinants is greater than in Klip River water suggests that the nature of organic compounds plays a role.

- Ozone by itself, and in combination with hydrogen peroxide attacks algal cells and causes internal and external damage which kill the algae. Pre-oxidation improves the physical removal of algal cells by sedimentation and filtration.

- Ozone by itself, and in combination with hydrogen peroxide, reduces the number of micro-organisms by oxidation but not to the extent that it improves the overall removal efficiency of the treatment process.

- The test of aggregation can be used effectively to study subtle changes in water quality on coagulation and flocculation.

RECOMMENDATIONS

- Before considering the application of ozone for water treatment the following aspects should be considered carefully:
    - effect on coagulation and flocculation
    - effect on the organic matter present
    - effect on the concentration of assimilable organic carbon compounds in water.

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1. INTRODUCTION AND OBJECTIVES OF THE STUDY

1.1 INTRODUCTION

In South Africa the majority of the population use surface water for domestic purposes. Increasing population, industrialisation and the construction of water supply systems to serve all communities with drinking water is placing increasingly heavier demands on existing reserves and facilities.

Domestic and industrial pollution in surface water supplies, public awareness of drinking water quality and scientific investigations require that treatment methods to produce drinking water must be re-examined continuously. The effectiveness of conventional treatment process designed to primarily remove suspended matter and disinfect water with chlorine, must be evaluated to see if drinking water of the desired quality can be produced at all times, even if the raw water source is contaminated.

The consumer wants water that is aesthetically attractive i.e. it should be cool, clear, tasteless and colourless and he should also have the assurance that the water is safe to drink without any harmful effect. It is the water supplier's responsibility to provide water which is safe and wholesome and does not present a potential health threat to the end user. Therefore the water must be free of any pathogenic organisms or deleterious organic or inorganic chemical compounds.

The treatment required to produce drinking water is a function of the source water quality and the desired quality to be distributed.

Developments in treatment methods were first brought about through necessity to prevent the spread of disease. Dramatic proof of the value of treatment came in 1892 when a cholera epidemic ravaged Hamburg in Germany while the city of Altona escaped the effects, thanks to its water filtration systems. More cholera outbreaks led to the development of filtration plants in most cities of the world beginning in Western Europe and the United States.

Very soon it became clear that filtration by itself could not constitute the sole treatment process. This led to the development of the treatment plant comprising of several unit processes that could produce water to specific quality requirements.

Proper understanding of the chemical and physical mechanisms that take place during water treatment formed the basis for successful design and operation of modern treatment plants.

Initially water treatment was aimed at the removal of suspended matter by coagulation, flocculation, sedimentation and sand filtration, followed by disinfection. Chlorination was, and still is the most common method of disinfection.

During 1893 ozone was used for the first time for the full scale disinfection of drinking water in Oudshoorn, Netherlands. (AWWA, 1991). Although ozone was initially used for disinfecting purposes, it was realised quite early that improvements in taste and odour could be achieved at the same time.

As the power and usefulness of ozone in water treatment become apparent it was applied for more specific purposes. Following are examples of such applications:

- Oxidation/Pre-ozonation
    - Oxidation of soluble iron and manganese
    - Removal of taste, odour and colour
    - Enhancement of particulate removal or "micellisation - demicellisation"
    - Oxidation of specific micropollutants such as some pesticides and phenolic compounds
    - Control of algae and algal blooms
- Biological Stabilisation
    - Ozonation followed by filtration through granular activated carbon to reduce the concentration of assimilable organic compounds.
- Reduction of disinfection by-products (DBP) during chlorination.

  In contrast to chlorination, trihalomethane compounds (THM's) are not formed by ozonation.
- Disinfection

  Bacterial, viral and protozoa inactivation

The use of ozone is well demonstrated and is used throughout the world in some 1000 treatment plants with capacities from as little as 10 m^3/h to as large as 30 000 m^3/h.

From the practical point the main disadvantages of ozone are:

- No disinfection residual can be maintained
- Oxidation of organic material produces more biological assimilable compounds that could lead to microbiological aftergrowth
- Ozone is generated on site and cannot be stored (Katz, 1980)
- Some ozone by-products may form which are mostly a function of the water quality being treated. As an example, bromoform ($CHBr_3$) could form if bromine present in the water forms hypobromous acid (HOBr) on ozonation which reacts with natural organics to form bromoform

- Direct oxidation of bromine to bromate, which could have detrimental health effects at extremely low concentrations are possible. Because of limitations in available analytical and treatment methods, a provisional guideline value of 25 μg/ℓ for bromate in drinking water is recommended (World Health Organization, 1993).

Some instances where ozonation was introduced as an additional unit treatment process with the advantages observed, are given below:

- Laboratory tests performed by Richard and Jacq (1990) showed that it was possible to reduce the coagulant dosage, from 30 to 25 mg/ℓ aluminium sulphate in a specific water by ozone dosage. The combined effect of 30 mg/ℓ aluminium sulphate and 1 mg/ℓ ozone had the same effect on the removal of organic matter as 40 mg/ℓ aluminium sulphate by itself. Pre-ozonation by itself decreased the total organic carbon (TOC) content by 10 per cent while the ultraviolet light extinction decreased by 59 per cent. The removal of humic acids was improved from 25 per cent to 33 per cent. A 60 per cent reduction in the Total Trihalomethane Formation Potential (TTHMFP) was obtained in water treated with ozone combined with aluminium sulphate compared to the use of only the coagulant.

- Toui (1991) showed that manganese could be removed effectively from water by oxidation with ozone. The process was so efficient that by using ozone dosages of 1,0 mg/ℓ. the manganese concentration of the purified water was reduced to less than 0.01 mg/ℓ while manganese concentrations as high as 0,2 mg/ℓ were observed in the untreated water

- During October 1987 to October 1988 pilot scale tests were done on the Los Angeles Aqueduct Filtration Plant by Liang, Stolarik, Tate and Glaze (1991). They found that pre-ozonation improved turbidity removal through micro flocculation and that ozone reduced the formation of THM's

- Ozonation prior to sand filtration had an positive effect on the removal of algae. It seems as though the improvement in removal efficiency was not necessarily a function of algal morphology as this trend was observed with the larger *Asterionella* species as well as the small species such as *Cyclotella* with respective diameters of 40 - 100 μm and 10 - 40 μm. (Ginocchio 1982). In both cases the removal efficiency increased by at least 50 per cent.

1.2 OBJECTIVES

A number of sewage purification plants are situated in the Klip River drainage area which covers the southern Gauteng province. Although the stream receives large amounts of treated and untreated domestic and industrial effluent as well as diffuse pollution, there were signs that the mineral quality of the water has actually improved over the last years. This could be due to the increasing volume of Vaal Dam water, with a relatively low mineral content and an electrical conductivity of about 20 mS/m that reaches the stream as treated domestic sewage and therefore reduces the mineral content of Klip River water.

In contrast to a possible improvement in the mineral content it is believed that the organic and microbiological quality of the Klip River water has deteriorated as a result of insufficiently treated sewage reaching the river. Organic and microbiological contaminants from diffuse pollution will also add to this.(See figure 1 for raw water sources of Rand Water).

Ozone has been used successfully to treat water abstracted from the Vaal River by the Midvaal Water Company some 80 km below the Vaal River Barrage. At this treatment plant ozonation is used specifically to remove heavy metals such as manganese by oxidation and precipitation. However, the effect of ozonation on water abstracted from the Upper Vaal River has never been studied and questions on the effect of ozone in the removal of suspended matter and algae still need to be answered. The use of hydrated lime and activated sodium silica treatment as practised by Rand Water for the destabilisation and flocculation of suspended matter in Vaal Dam water is unique. The effect of ozonation on removal of suspended organic and inorganic material in combination with hydrated lime and activated sodium silicate has not previously been studied.

The purpose of this study is to evaluate the use of ozone in combination with activated sodium silicate and hydrated lime to determine the effect on:

- coagulation, flocculation and the removal of suspended matter
- removal or destruction of algae and other organisms
- fate of organic compounds in Klip River and Vaal Dam water during the treatment process

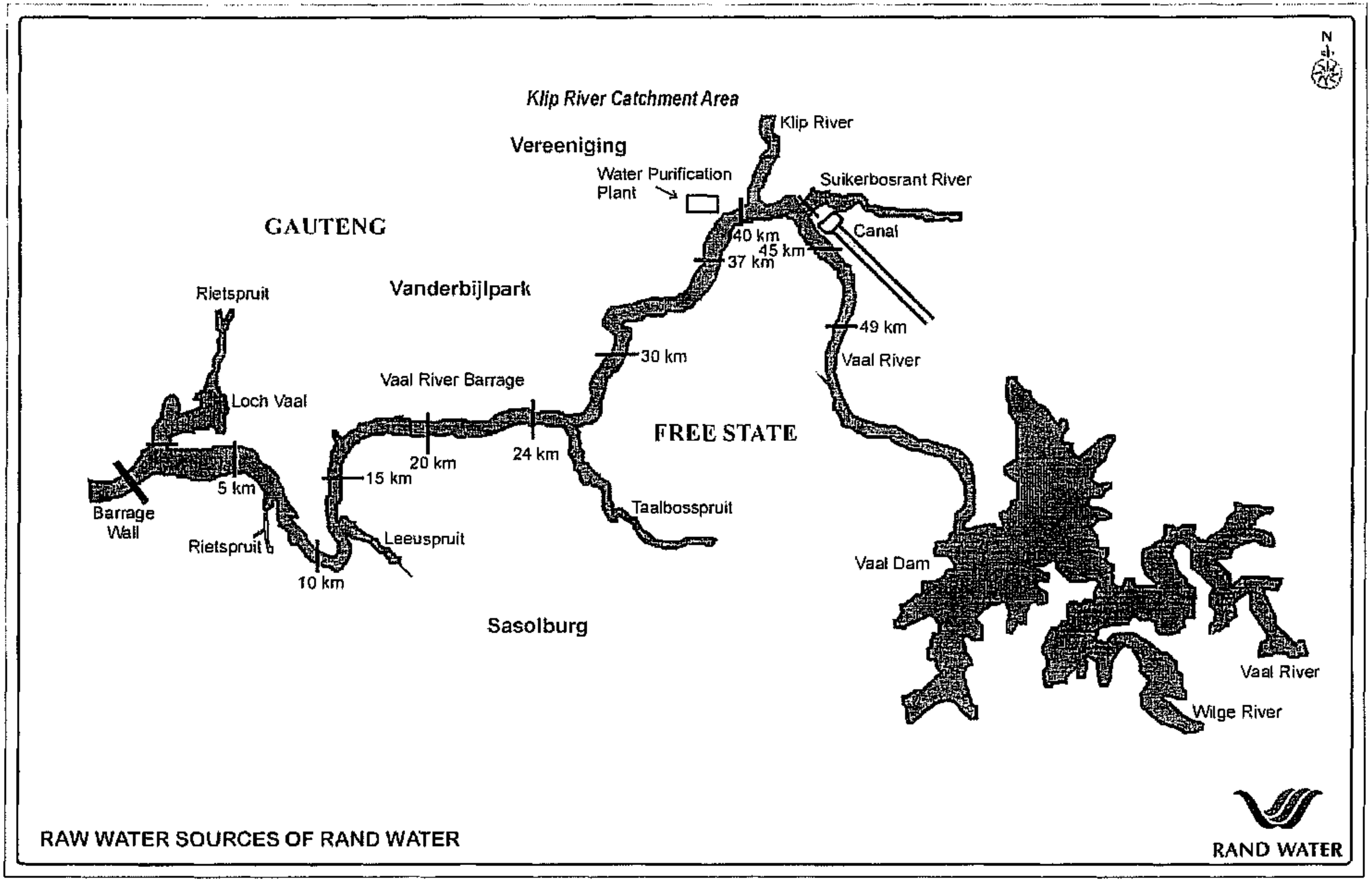

Figure 1.1 Map showing raw water sources of Rand Water

2. LITERATURE SURVEY

2.1 OZONE IN WATER TREATMENT

Ozonation used in drinking water treatment achieve a variety of treatment goals, and can be used in three ways: as a biocide, as classical oxidant and as a pretreatment for improving the performance of subsequent processes (AWWA 1991).The purposes of oxidation include the following:

1) Disinfection and algae control

2) Oxidation of inorganic pollutants -

   - Iron and manganese

3) Oxidation of organic pollutants -

   - Taste and odour producing compounds
   - Phenolic pollutants
   - Pesticides

4) Oxidation of organic macropollutants

   - Colour producing compounds
   - Increasing the biodegradability of organics
   - Reducing the trihalomethane formation potential (THMFP), total organic halide formation and chlorine demand

5) Improvement of coagulation

2.1.1 Pre-ozonation

2.1.1.1. Iron and Manganese Removal

Iron and manganese are two of the most abundant elements found in the earth's crust. The oxidised forms, Fe^{3+} and Mn^{4+}, are most prevalent, but it is the reduced forms, as in $FeCO_3$ and $MnCO_3$, that are present in water. The presence of iron and manganese in drinking water generates certain unpleasant side effects, mostly of aesthetic nature such as colour and precipitates in water and stains in clothing and plumbing fixtures. The growth of iron and manganese oxidising bacteria on the walls of water pipe lines lead to a general deterioration in the quality of water that is distributed.

The most common method used for removing these metals involves an initial oxidation step followed by a solid/liquid separation step to capture the resulting insoluble metal oxide. This can be done by settling or filtration.

Oxidation can be achieved by aeration at a suitable pH. This method is more effective for iron than manganese as the reaction rates favour the oxidation of iron. Other oxidants to be considered are chlorine, chlorine dioxide or potassium permanganate. Uncomplexed iron and manganese is removed effectively by these oxidants but dissolved organic matter may interfere with the process.

The following reactions show how iron and manganese are oxidised by ozone to insoluble compounds. (Hart, 1983).

$$2Fe^{2+} \xrightarrow{O_3 \searrow \quad \nearrow O_2} 2Fe^{3+} \xrightarrow{H_2O} Fe(OH)_3 \tag{2.1}$$

$$Mn^{2+} \xrightarrow{O_3 \searrow \quad \nearrow O_2} Mn^{4+} \xrightarrow{H_2O} \underset{\downarrow}{MnO_2} \tag{2.2}$$

There are many examples of treatment plants in Europe where iron and manganese removal by ozonation is practised. (Stoebner and Rollag (1981). In South Africa it is done at the Midvaal Water Company at Stilfontein where about 320 Mℓ/d is treated and ozonation is used primarily to remove manganese. This is a pollutant that comes from mining activities in the area and the concentration in the water as high as 3700 μg/ℓ can be reduced to less than 50 μg/ℓ at ozone doses of 1,4 mg/ℓ. (Lombard, Kruger and Willemse, 1992).

2.1.1.2 Taste and odour removal

A large proportion of consumer complaints received by water treatment organisations is related to taste and or odour. Many of these could be attributed to the presence of metabolites of various organisms such as actinomycetes and blue green algae. These compounds (of which geosmin and 2- methylisoborneol (MIB) give rise to the most complaints) are detectable at nanogram per litre concentrations. (Gerber, 1983).

The elimination of taste and odour causing compounds is dependent on the nature of the compound and either non-oxidative or oxidative processes are used. Non-oxidative processes will include stripping by aeration or adsorption onto activated carbon. Oxidation processes include aeration and the use of strong oxidants like chlorine, chlorine dioxide, potassium permanganate, ozone and advanced oxidation processes.

A study covering five compounds responsible for musty odours (2, 3, 6 - trichloroanisole [TCA], 2 - isopropyl - 3 - methoxy - prazine [IPMP], 2 - isobutyl - 3 - methoxy - pyrayine [IBMP], geosmin and MIB) has shown the relative efficiency of removing the different oxidants in organic free water (Lalezary, Pirbazori and McGuire 1986). This study showed that MIB was the most difficult to oxidise followed by geosmin, trichloroanisole. and the two pyrazines. It was also shown that ozone and permanganate were the most efficient of the oxidants at destroying the three unsaturated compounds.

With water containing large concentrations of organic matter it was observed that the action of ozone on the odour producing compound was variable and dependant on the treatment conditions. It has been shown that an increase in the odour level for some intermediate dosing rates are generally linked to the formation of alderhydes that gives the water a fruity taste. (Anselme, Suffet and Mallevialle 1988).

Conflicting results have been reported in the removal of taste and odour by ozonation. These results vary from 85 - 100 per cent removal of geosmin and MIB at 2mg/ℓ ozone (Tatsumi, 1987) to only 50 per cent removal at up to 10 mg/ℓ of ozone (Lalezory *et al,* 1987). Removal of 80 - 90 per cent MIB and nearly 100 per cent of geosmin was achieved by applying a 5 mg/ℓ ozone dose for a 10 - 20 minute contact period (Yasutake, Kato and Kono 1987).

In laboratory experiments it was found that geosmin concentration could be reduced by 45 per cent by dosing 3,12 mg/ℓ ozone and up to 63 per cent by dosing ozone combined with hydrogen peroxide at a O_3 : H_2O ratio of 2:1. (Geldenhuys 1996).

Differences in water quality may explain the different efficiencies that were achieved. According to Hoigne and Bader (1976), ozone may react following either one of two pathways, a direct reaction with moleculor ozone and indirect reaction of hydroxyl radicals. Hydoxyl radicals react with the tertiary alcohols, geosmin and MIB which are non-reactive towards molecular ozone. Therefore, water quality parameters such a pH and bicarbonate content, that influence the hydroxyl radical formation may have an effect on the differences in activity observed.

2.1.1.3 **Phenolic pollutants**

Phenolic compounds are all characterised by the presence of the OH^- group on the aromatic nucleus. These compounds are very reactive with ozone. The following two mechanisms on the oxidation of phenols by ozone have been described:

- At an acidic or neutral pH an electrophilic attack on the reactive carbons in the ortho and para positions take place
- At neutral or basic pH an electrophilic attack on the phenate ions or an $OH^{\cdot}$ radical mechanism that is initiated by hydroxyl ions on phenate ions

The oxidations products are diphenols and quinones as intermediate products, the products where breakdown of the ring has taken place and final oxidation products such as glyoxylic, oxalic and formic acids.

2.1.1.4 **Pesticides**

Numerous studies have been conducted to assess the action of ozone in pesticides. The chlorinated organic pesticides react slowly and are incompletely destroyed by direct oxidation. For instance, aldrine is transformed into dieldrine and heptachlor to heptachlorepoxide. It was found by (Prengle and Mauk,1978) that dichlorodiphenyl - trichloroethane (DDT) is effectively oxidised using a combination of ozone and UV light.

Organophosphorus pesticides are much more susceptible to direct ozonation. The principal reactions are:

- Oxidation of the $P = S$ bond to form a $P = O$ bond, and
- Splitting of the molecule at one of the bonds with the phosphorus atom, yielding simple esters of phosphoric acid

2.1.1.5 **Colour producing compounds**

True colour depends exclusively on the presence of dissolved species in the water and implies that these substances present in the water absorb light at the wavelength 400 - 800 nm.

This would suggest compounds with polyaromatic structure, substituted aromatic structures, carotenoides, humic acids, permanganate, manganese or iron. Fulvic acids produced in processes taking place in for instance swamps, play a major role in the colour that is produced, more important than humic acids, as they are more soluble. Eutrophic water which contains more chlorophyll and xanthic colouring matter will contain higher levels of humic acids.

Coloured water could be aesthetically unattractive and will influence the chlorine demand. Chlorination of these compounds produce organohalides.

Conventional water treatment processes comprising coagulation, flocculation, sedimentation and sand filtration would remove approximately 70 per cent of colour. Activated carbon can be used to remove even higher percentages by adsorption.

Of the oxidants, ozone is the most efficient. Ozonation also have positive effects on subsequent treatment processes in the removal, enhancing the removal by activated carbon and slow sand filtration of colour producing organics. For instance, in a specific case 20 - 60 per cent of the colour was removed by ozonation, this improved to 90- 95 per cent overall efficiency following activated carbon filtration. (AWWA 1991).

2.1.1.6 Biological Stabilization

The promotion of biological activity in a treatment plant can help to prevent uncontrolled growth in distribution systems. This is especially important for plants using oxidative treatment methods such as ozonation which can enhance the biodegradability of natural organic material. Greater biological stability may partially eliminate the need for maintaining disinfectant residue in the distribution system.

Slow sand filtration to some extent simulates natural processes observed in the environment. This unit process has the ability to reduce the organic content of water by biological activity and assimilation. Limitations of slow filtration such as the high sensitivity to variations of turbidity and algal concentrations in raw water and poor performance with regard to complexed minerals and organic micro pollutants and colour producing compounds, resulted in the improvement of rapid higher rate treatment technologies. Many of the dissolved organic compounds are not significantly reduced by conventional treatment methods. Biological methods can remove the biodegradable compounds that would otherwise be a nutrient source for bacteria present in a distribution system.

Where problems with high concentrations of biological assimilable organic compounds are experienced it will be prudent to incorporate such a step in the treatment process.

It has been established that ozone reacts with humic substances to reduce colour and the ultra violet light extinction at 254 nm. Ozonation of these compounds results in lower molecular weight carboxylic acids that are more easily biodegradable. (AWWA 1991).

The increase in biodegradability following ozonation has been demonstrated by many authors.(Sontheimer 1979).

Depending on the method used to measure the increase in biodegradebility, increases varying from 150 to 700 per cent have been observed. Ozone dosages required to improve the biodegradebility varied from 0,5 - 1,0 mg/ℓ O_3 and it seems unlikely that higher dosages will transform more of the organic compounds present. (AWWA 1991).

Successful biostabilisation can be obtained by ozonation followed by a biological process.

The use of granular activated carbon (GAC) as a medium to support biological growth is most common as the GAC also has good adsorptive properties while at the same time it provides the ideal physical structure for bacteria to colonise due to the porous structure.

Recent studies on treatment plant purifying Vaal Dam water using hydrated lime and a activated sodium silicate or ferric chloride showed a decrease in the assimilable organic carbon (AOC) and the biological biodegradable organic carbon (BDOC) through the treatment process.

Ozonation of the treated water increased the biodegradability of the organic compounds in the water. The same effect was also observed following the use of most water treatment chemicals such as activated sodium silica, hydrated lime, ferric chloride or chlorine. The values of both the f-factor, as an indication of concentration, and the μ-factor, indicating the availability of the assimilable organic carbon fraction increased more following ozonation compared to the use of other chemicals. This is due to the stronger oxidation effect of ozone that produces more assimilable fractions from larger molecules. (Grundlingh 1998).

2.1.1.7 Control of disinfection by-products

The use of ozone may cause changes in the concentration of disinfection by-products (DBP) in finished water. These changes may come about because ozone can either:

- immediately destroy or form by-products or new by-product precursors

- alter the nature of the water so that subsequent processes are better or worse at removing the by-products or the by-product precursors
- permit the use of lower doses of, or other disinfectants or change their point of addition (AWWA 1991)

Reckhow and Sibony (1986) showed that pH and alkalinity of water had major influences on how ozonation effected THM formation. At pH of four it seems as though THM precursors were destroyed while at a pH of about 8,5 - 9,0 precursors enhancement is observed and THM formation is stimulated significantly.

The critical pH is dependant on the alkalinity and the nature of the organic material. A shift in the ozonation mechanism is suggested by the effect of pH on the bicorbonate/ carbonate presence, from the non selective $OH^{\cdot}$ radical attack to the highly specific molecular ozone attack. It is possible that ozonation could change the relative rate at which THM's and total organic halides (TOX) are formed in water. (Hubbs and Holdren 1986).

Ozone does not produce chlorinated organic by-products but small amounts of bromoform may be produced in the presence of bromide. This is the result of ozone's ability to oxidise bromide to bromine. The bromine, by forming hypobromous acid, similar to hypochlorous acid, reacts with organic matter to form bromoform (Doré and Legube 1988).

Ozone dosages used are normally lower that what is required to fully mineralize complex humic and fulvic precursor materials . Typical ozone dose - to - carbon ratios are below 1,2 mg O_3/mgC. At these levels ozonation of the humic and fulvic materials is not complete. However the ozonated humic material is different from the raw material and is characterised by mixtures of lower molecular weight, more polar products and higher molucular weight compounds similar to the raw material.

Aldehydes are produced by ozonation from a variety of unsaturated compounds. This also happens when humic acid or natural organic matter like unsaturated compounds are ozonated. These compounds could have a health effect and generate a fruity and orange like odour in treated water (Anselme 1988).

Schalekamp (1978) found that the concentration of aldehydes containing one to 14 - carbon atoms increased upon ozonation. The final concentration is dependent on ozone dose and the nature of the organic material. This is supported by the fact that precursor removal resulted in reduced aldehyde formation.

There is proof that ozonation increases the concentration of formaldehyde and acetaldehyde on the ozonation of a specific water, the concentration of these compounds were five times higher as obtained by chlorination.

2.1.1.8 Effects of the presence of algae in water

Eutrophication of impoundments often leads to algal blooms which could cause significant disturbances during the various stages of the conventional water treatment process.

These effects can vary from the presence of chlorophyll in water which will increase the disinfectant demand, to the occurrence of metabolites such as geosmin which may result in consumer complaints. Algal toxins, like the hepatotoxin. microcystin LR, produced by *Microcystis* and *Anabaena* sp are extremely toxic and the deaths of cattle drinking contaminated water have been reported. (Harding, 1996).

Hart, Fawell and Croll (1997) found that an oxidant will destroy the toxins and ozone was found to be the most effective of the oxidants normally used in water treatment.

The presence of algae in the water could also result in:

- poor coagulation and flocculation
- poor settling of floc
- shorter filter running times (AWWA, 1991)

If the algae are not removed effectively by the treatment process and appear in the distribution system the quality will further degrade as a result of microbial aftergrowth.

Contradicting observations on the effect of ozone on the removal of algae have been made.

Richard and Dalga (1993) reported that it was possible to decrease coagulant dosage levels when pre-ozonation was done at an optimum dose to reduce the zeta potential to zero.

By combining the optimal ozone dosage with the coagulant dosage it was found that the algal removal was at least a log factor better than with conventional treatment, 99,95 per cent removal vs 99,0 per cent removal. It was found that a one mg/ℓ increase in ozone could lead to a reduction of 20 mg/ℓ aluminium sulphate used as coagulant. On the contrary to the above, Rencken (1992) observed that ozonation impaired flocculation of algae, even at low dosages and resulted in an increase in coagulant demand.

In further research done by Freese, Juby and Trollip (1996) similar observations were made. They found that ozone and algal cell concentration, algal species and pH influenced the coagulant demand of the water, although for water containing predominantly *Microcystis* cells it was possible at certain ozone concentrations to obtain a reduction in coagulant demand. The coagulant demand of water containing predominantly *Anabaena* sp. cells was always found to increase after ozonation. The coagulant demand was found to increase proportionally with the *Microcystis* sp. cell concentration prior to ozonation (less than 200 per cent increases). After ozonation the increase in coagulant demand was as high as 600 per cent. In contrast, ozonation of water containing predominantly *Anabaena* cells resulted in much smaller increases in coagulant demand (below 50 per cent), although prior to ozonation, the presence of *Anabaena* sp. resulted in much higher coagulant demand than in the case of *Microcystis* sp. at similar cell concentrations.

2.1.1.9 Effects of ozone on particle destabilization

Effects of ozonation on coagulation may be used to refer to all the physicochemical phenomena involving the improvement of subsequent flocculation, flotation or direct filtration. These phenomena may take the form of a wide range of secondary effects induced by ozonation such as:

- A direct aggregation of particles, measurable as a shift in the particle size distribution to larger diameters and by increases or decreases in turbidity
- Formation of colloidal or suspended particles from dissolved material, usually indicated by a turbidity increase and improved TOC and DOC-removal afterwards
- Improved particle removal in filtration, thus lower coagulant demand (up to 50 per cent less) can be added and filter runs are extended
- Better settling rates of flocs
- There are various reports that seasonal benefits of pre-ozonation are most dominant in raw waters with elevated algae content, indicating either the direct action of ozone on algae cells or on the dissolved organic products produced by the algae (algogenic substances)
- Extended filter running times due to slower head loss build up
- There are, however, some observations, that the removal of dissolved organic carbon (DOC) may decline in coagulation by alum or ferric salts if preoxidation is performed with elevated ozone dosages. (Singer 1990)

These are all secondary reactions because they do not occur instantaneously with ozonation. It may take some time for these reactions to manifest themselves after a period of mixing or the addition of a coagulant. Although it is considered unlikely that a single mechanism is responsible for all the secondary phenomena, several of them may be attributed to the same primary effect. It is often found that these phenomena are related in some way to ozone-induced changes in the properties of the dissolved and particular matter. (AWWA 1991)

Since the first time the effect of pre-ozonation on the subsequent particle removals by various techniques such as rapid and slow filtration, coagulation/flocculation or flotation were observed, various terms were and are still being used to describe the unusual effects ozone has in this respect i.e. micellization/demicellization, microflocculation effect,ozone-induced particle destabilization, ozone as coagulant or coagulant aid. (Jekel 1992)

The mechanisms responsible for the effects of ozone on coagulation are mostly based on the presence of elevated levels of dissolved organic matter of natural or anthropogenic origin. Only in one instance is the effect of ozone attributed to the stripping of carbon dioxide followed by the super saturation and precipitation of calcium carbonate which results in particle aggregation. In most cases this proposed mechanism can be excluded. One major stumbling block in these investigations seems to be the lack of knowledge about the chemical characteristics of the organic matter measured as DOC, that could be humic or fulvic acids or derived from algal, or the unknown properties of the suspended matter.

The mechanisms, which could play a role in the destabilization of suspended matter where ozone is involved are given below. These possibilities are not presented in any order of preference.

- Increased association of oxidised metal ions with ozonated organic material. The interactions of dissolved organic substances and the coagulant (Al^{3+} and Fe^{3+}) are influenced by ozone, inducing an improvement or a decline in the overall efficiency of turbidity, metal or DOC removal. It is reasonable to assume that the carboxylic and phenolic functional groups in the natural organic matter form complexes with aluminium oxide and clay surfaces, and that the groups are therefore responsible for organic matter - aluminium surface associations. Ozonation could increase the degree of adsorption of natural organic material to aluminium hydroxide. A common deduction often made is that increases in carboxyl and phenolic content should lead to improved removal of DOC or DOC - coated clays by alum coagulation due to the increased formation of insoluble aluminium-humic compounds, the charge neutralisation from aluminium complexation on the increased adsorption of humic materials to aluminium hydroxide floc while this mechanism renders more of the DOC susceptible to coagulation, it may also lead to a higher coagulant demand.

- Improvement in calcium complexation by ozonated organic matter.

An increase in the number of carboxylic acid groups may also lead to an increase in the degree of calcium complexation. This could result in direct precipitation of the organic matter or increased particle destabilization by polymeric bridging. Absorbed strands of natural organic matter from two particles may form a bridge in binding with the same calcium atom.

- Losses of organic matter from the surface of clay particles.

It was found that the higher molecular weight organic fractions absorb most strongly to Al_2O_3 particles and are most capable of stabilising alumina and silica suspensions (Jekel 1983). Therefore it seems logic that any decrease of moleculor weight or increases in the hydrophilicity of the organic matter following ozonation will lead to the desorption from clay particles and the subsequent destabilisation. The alteration of the organic coating on the particles leads to the minimisation of the negative surface charges or by shrinking of the adsorbed organic layers which normally would have caused hindrance to inter particle contacts.

Since only a minor fraction of the organic material in water is associated with clay particles this mechanism only has bearing on turbidity removal.

- Polymerisation of organic matter.

Ozonation of natural organic material could lead to the formation of metastable organics such as ozonoides, ozone peroxides and organic radicals which continue to react long after the ozone has disappeared. If sufficient time is allowed and the concentration of the organics are high enough these compounds may come in contact with other stable or metastable compounds and undergo polymerisation reactions. These polymers can then

- precipitate spontaneously
- become more easily enmeshed by aluminium hydroxide
- associate more strongly with solid surfaces
- act as a bridging polyelectrolyte between particles
- or by virtue of its size attract less aluminium coagulant per carbon atom removed

- Breakup of metal - organic complexes.

The breakup of metal - organic complexes can be considered as an *in situ* production of a metal coagulant by the liberation of Fe^{3+} and Mn^{4+} atoms.

Ferric salts are widely used as coagulant while it has been found that hydrated Mn^{4+} species remove significant amounts of natural organic material by adsorption (Colthurst and Singer 1982).

- Reactions with algae

Ozone readily kills many types of algae followed by the liberation of biopolymers which could be considered to be the equivalent to natural organic coagulants improving the coagulation and settling or flotation of algal cells. (Ginocchio 1981)

The improved coagulation has in some instances been linked to concentrations of phytoplankton or is known to occur when high concentrations of algae were observed (Maier 1979). Liberation of surface active polymers may be responsible for the thick organic foam sometimes noted on contact chambers following ozonation. (Campbell and Pescod 1966).

Edwards and Benjamin (1991) showed that the ozonation could result in the stripping of carbon-dioxide from water resulting in the precipitation of calcium carbonate due to saturation and thus inducing particle destabilisation.

Knowledge of aqueous ozone chemistry indicates that the pH and alkalinity of water play an important role in the use of ozone as a coagulant and changes in these parameters are known to alter the rate of ozone decomposition that effects the relative degree of direct oxidation by moleculor ozone as compared to that of hydroxyl radicals. Polymerisation should occur more readily as a result of rapidly decomposing ozone at high pH and low bicarbonate levels via the radical mechanisms.

Oxidation of Fe^{2+} to Fe^{3+} should however be more efficient via the direct mechanism while iron itself may accelerate the decomposition of ozone and act as a catalyst between oxygen and organic material (Theis and Singer 1974).

The direct moleculor ozone attack should be more effective at killing stressed algal cells than the hydroxyl radicals as the probability of the latter to encounter larger particles are less.

3. MATERIALS AND METHODS

3.1 DESCRIPTION OF EQUIPMENT USED

3.1.1 Ozone generator

Ozonia type LN 103 - capacity 10g/h

3.1.2 Ozone contact chamber and bench scale treatment unit

All experiments involving the continuous addition of ozone and or coagulants were conducted in a small laboratory scale treatment unit. A schematic presentation of this plant is shown in Figure 2, and a photograph of the unit can be seen in Figure 3.

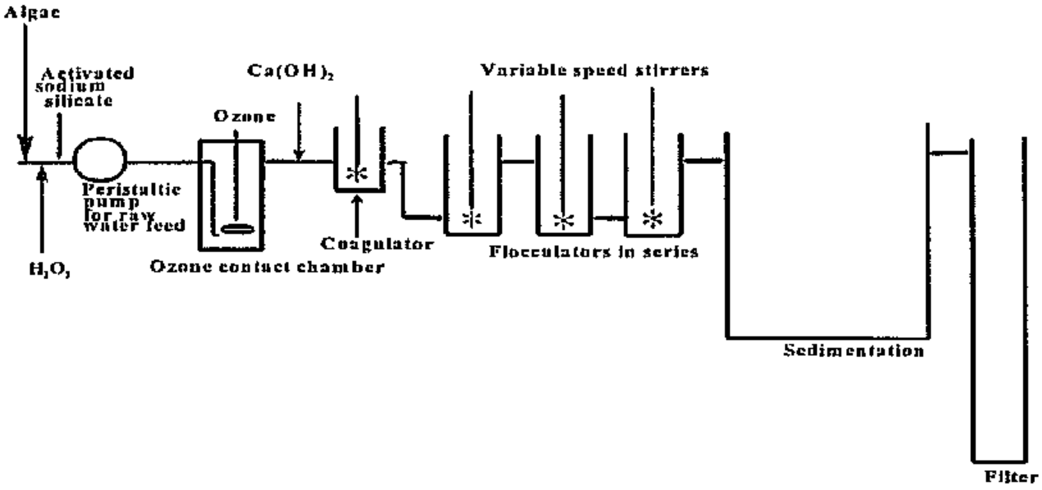

Figure 3.1 Schematic presentation of the bench scale treatment unit.

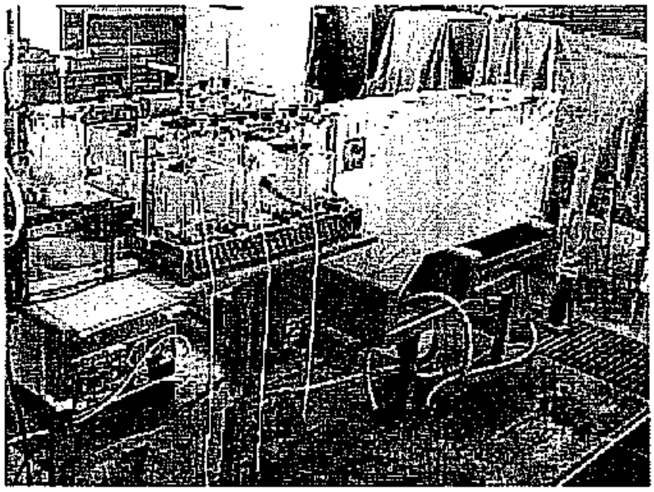

Figure 3.2 Bench scale treatment unit.

The experimental unit had a capacity of 1000 cm^3 per minute and comprised two identical parallel treatment lines each consisting of:

- Coagulation with variable speed mixer:

  Dimensions of coagulator:
  Flash mixer : (98 x 98 x 45) mm
  Effective volume : 432 cm^3
  Retention time : 25,9 seconds
  Dimentions of blade : (65 x 25) mm
  Rotation speed of blade : variable from 250 - 500 r.p.m.

- Flocculator with three chambers in series fitted with variable speed drive. The flocculators were based on a design by Bratbury, Miller and Marais (1977)

  Dimensions of flocculation chambers : (200 x 500 x 130) mm
  Effective volume : 3900 cm^3
  Retention time : 234 seconds
  Flocculation blade : Static finger type with meshing paddle type stirrer

- Sedimentation tank with a retention time of four hours with a sludge withdrawal point at the bottom and V-notched overflow weir

- Carbonation chamber for pH correction and re-carbonation using carbon dioxide

- Single medium sand filter with 0,65 mm particle size, 600 mm deep and 100 mm diameter. Cleaning was done by upflowing water flow to create at least 30 per cent bed expansion to remove trapped suspended matter

- The flow of raw water and coagulant dosage into the plant was controlled with variable speed peristaltic pumps

- Ozonation of raw water was done prior to either of the treatment lines in a type of U-tube ozone contactor in a bore hole. Water mixed with ozone was pumped to the bottom of a stainless steel pipe, three metres deep and 42mm diameter, before flowing into the coagulator following degassing. The contact time achieved in these devices was about four and a half minutes at a flow of 1000 cm^3 per minute.

Table 3.1 Efficiency of ozone transfer into water at different ozone concentrations.

Ozone concentration in gas g/m^3	% Transfer efficiency
0,92	82,6
2,45	93,4
9,24	76,67

pH - 7,2, Temperature-18°C. Hydrostatic pressure-0,3 bar

The ozone transfer efficiency was calculated by comparing the ozone concentration in the feed gas to the contact chamber to the ozone concentration in respectively the water and the off gas from the contactor.

3.1.3 Continuous ozone measurement

An Orbisphere Model 3600 in line ozone detector, suitable to measure ozone concentrations in either gaseous or aqueous form, was used. This instrument made it possible to measure the ozone concentration in the gas feed to the contactor, off gas and residual ozone in the treated water.

Figure 3.3 gives an indication of the relationship between the ozone determinations done with the Orbisphere analyser and by iodometric titration. Since there was a good relationship the Orbisphere monitor was relied upon for the continuous measurements.

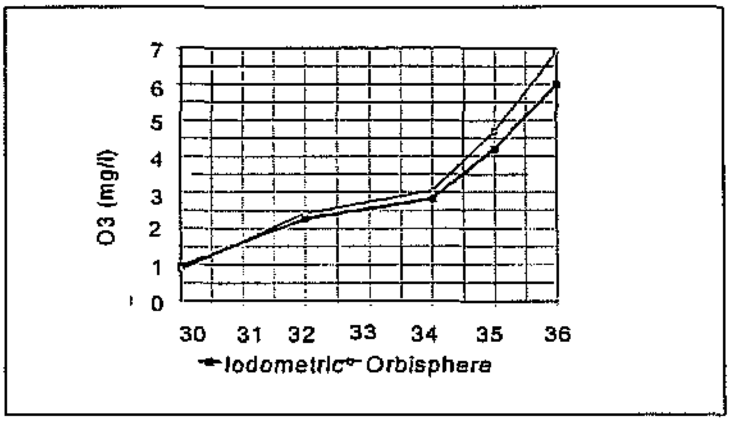

Figure 3.3 Relationship between ozone concentration in gas determined with the Orbisphere analyser and iodometric titration at different current settings of the ozone generator.

3.1.4 Batch type laboratory ozonation experiments

The ozonation of algal cultures was performed in batch experiments in glass gas flasks by bubbling the correct amount of ozone through the water to obtain the desired concentration.

3.2 TEST METHODS

3.2.1 Calibration of mixing devices

Mixing energy inputs are mostly described in terms of the well recognised mean velocity gradient (G-value) concept of Camp and Stein (1943).

$$G = \left\{\frac{P}{\mu V}\right\}^{½} \tag{3.1}$$

where G = root mean square velocity gradient (s^{-1})
P = total power dissipated (m^2 kg.s^{-3})
μ = viscosity of the fluid being mixed (m^{-1} kg. s^{-1})
v = volume (m^3)

The concept of G value is used for the design of coagulators and flocculators although it does not take the shape of the reactor or flow patterns into consideration.

When mixing is done mechanically accurate values for P can be determined only by measurement of the torque input into the fluid. The relationship between the measured torque in the mixer spindle is given by

$$G = \left\{\frac{2\pi trg}{v\mu}\right\}^{½} \tag{3.2}$$

where G = root mean square velocity gradient (s^{-1})
t = torque measure in the mixing spindle (g.cm)
r = rotation speed of the spindle (r.p.m.)
v = reactor volume (cm^3)
μ = absolute viscosity of water at 20°C (10^{-7} N.s.cm^{-2})
g = gravitational force (9,81 x 10^{-3} N.g^{-1})
π = 3,143

The direct measurement of energy input at laboratory scale levels creates problems as very small values are measured. For this purpose a small in-line torque meter as designed and built which made it possible to make torque measurements while experiments were in progress or to calibrate both coagulator and flocculator mixers for use. See Figure 3.4 for a photograph of the in-line torque measuring device.

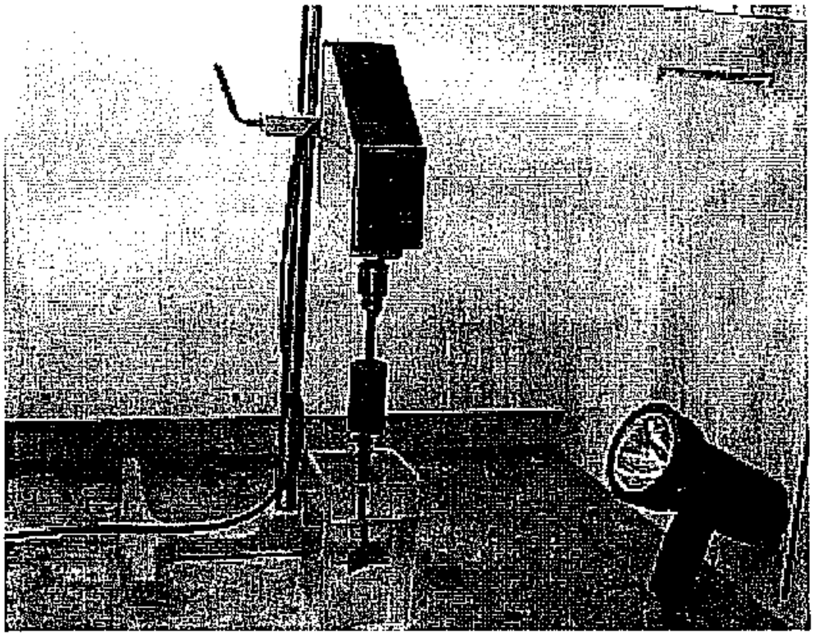

Figure 3.4 In-line torque measuring device.

The validity of the torque measurements were compared to those done by Botha (1995) on a device in which indirect torque measurements were made according to the design of Camp and Stein (1943).

This device is suspended on a low friction swivel on a long thin wire from the ceiling to avoid any outside influence and the effect of internal torque resistance. The rotational movement of the suspended beaker, in which the mixing paddle is turning, is balanced by a calibrated needle and tension wire arrangement.

In Table 3.2 below the comparative G values obtained by the two torque measuring devices for 2000 cm^3 of water in a square beaker are given.

Table 3.2 Comparative G values calculated at different rotating speeds on the in-line and indirect torque measuring devices.

Spindle Speed (r.p.m)	G value calculated from in-line torque measurement (Rand Water)	Gt value	G value calculated from indirect measurement (Botha)
50	28	725	28
100	57	1476	74
150	137	3549	128
200	217	5620	200
250	300	7770	268
300	400	10360	354
350	540	13986	474
500	1303	33750	

The Gt value is the product of the retention time in the coagulator in seconds and the G value. At a flow of 1000 cm^3 per minute through the coagulator the retention time is 25,9 seconds giving a Gt value of 13986 at 350 r.p.m.

The G values for the flocculator mixers, which consisted of a stationary set of blades and a rotating meshing set, were calculated in the same way. Tapered energy dissipation were obtained by driving the three paddles at progressively lower speeds. The G values of the successive flocculators can be seen in Table 3.3 below.

Table 3.3 The energy input into the flocculator blades at various rotating speeds.

Spindle Speed r.p.m.			G value (s^{-1})			Gt value		
Flocculator			Flocculator			Flocculator		
1	2	3	1	2	3	1	2	3
28	25	22	35	29	24	8190	6706	5616
34	30	26	46	39	31	10767	9126	7254
39	35	31	58	49	40	13572	11466	9360

Gt is the product of the G value and the retention time in seconds i.e. the G value of flocculator one at 28 r.p.m is 35 s^{-1}, multiplied by the retention time of 234 seconds at a flow of 1000 cm^3 per minute equals 8190.

3.2.2 Measurement of oxidant concentration

3.2.2.1 Ozone determination in gas phase

The iodometric titration method with sodium thiosulphate as described by International Ozone Association, Quality Assurance Committee, Revised Standardized Procedure 001/96 was used for the determination of ozone concentration in the gas phase. The ozone rich gas was bubbled through gas flasks containing known volumes of potassium iodide solution at known concentrations while the gas volume was measured with a gas flow meter.

The ozone concentration was then calculated from the amount of iodine released from the iodine solution, using starch as indicator for the titration.

These values were compared to those obtained with the Orbisphere in-line ozone monitor.

3.2.2.2 Ozone determinations using an on-line ozone monitor

The Orbisphere on-line monitor was used to determine ozone concentration in either the gas or water phase. This instrument was calibrated regularly by the agent.

3.2.2.3 Determination of the hydrogen peroxide concentration

In the experiments where hydrogen peroxide was used the concentrations were determined using the method described by Alliance Peroxide (1991).

3.2.3 Methods used to determine algae or associated determinants

3.2.3.1 Algal cell counts

Algal cell counts were prepared using standard Rand Water procedures as described in the Toxic algal monitoring protocol of the Hydrobiology Section (Adam, 1997). This method is according to APW-AWWA-WPCF. (Clesceri, Greenberg, and Trussell, 1989 and Greenberg, Clesceri and Eton, 1992).

3.2.3.2 Chlorophyll determinations

Chlorophyll determinations were carried out according to the revised Sartory (1982) method. This method has been accredited by the Hydrobiology Section, Rand Water (method number: 1.1.2.01.1) for Rand Water as Testing Laboratory number T0046.

3.2.3.3 Electron microscopic examination

Monoraphidium cultures were exposed to ozone and combinations of ozone and hydrogen peroxide after which the samples were preserved according to prescriptions given by the University of Potchefstroom before electron microscopic examination to determine whether any structural damage to the cells had been caused by the oxidants.

3.2.4 Methods used to determine microbiological determinants

The following accredited microbiological testing procedures were used.

- Standard plate count at 37°C after 48 hours incubation, according to EPA (1978)
- Total coliform count, according to EPA (1978)
- Determination of coliphages, according to APHA-AWWA-WPCF (Greenberg, Clesceri and Eton A. 1992)

3.2.5 Measurement of coagulation and flocculation efficiency

3.2.5.1 Test of aggregation

The test of aggregation gives an indication of the proportional distribution of size fractions of particles in a system. This test offers the possibility to determine the character of particles formed in different stages and under different conditions in the treatment system. Results of the test of aggregation may be used to evaluate the efficiency of a treatment plant and the suitability of various coagulants and mixing conditions. This test was based on work done by Polasek (1996).

The test of aggregation is based upon the formation of and settling rate of flocculated particles. According to this method the flocculated and other particles can be divided into:

- **Non-aggregated particles (*Pn*)** which are an indication of particles not affected by coagulants in the specific test and which cannot be separated by commonly used physical methods. The properties of these particles could be similar to that of colloidal material and do not settle. Centrifugation at $g = 5345$ may be used to separate these particles from water. The proportion of non-aggregated particles are given by

$$Pn = \frac{C_{F(0,01)}}{C_0} \qquad (3.3)$$

Where C_0 = concentration of particles, suspended matter or turbidity, in the original sample before treatment

$C_{F(0,01)}$ = amount of suspended matter that has a settling rate of less than 0,01 mm/sec and could be removed by centrifugation only

Pn should represent a large proportion (≈ 100%) of suspended matter in untreated water and a very small proportion (≈ 0,%) in well coagulated flocculated water.

- **Primary Particles *(Pp)*** which are those particles that are affected by coagulation and flocculation but have a very slow settling rate of less than 0,01 mm/sec. These particles have the potential of growing into micro and macro particles which will settle faster.

  The proportion of primary particles are given by the equation:

  $$Pp = \frac{C_{0,01} - C_{F(0,01)}}{C_0} \qquad (3.4)$$

  Where $C_{0,01}$ represents the fraction of particles with a settling rate of less than 0,01 mm/sec.

  Effectively the primary particles will be given by the difference between the extremely slow settling particles and those that will not settle at all, while primary particles will be the fraction of these particles compared to the original concentration (Co). As the primary particles are the first to form, this fraction should progressively decrease towards the end of the flocculation process.

- **Micro particles (*Pmi*)** are particles with a settling rate of between 0,01 and 0,13 mm/sec. and are formed as a result of the agglomeration of primary particles.

  The proportion of micro particles is given by the equation:

  $$Pmi = \frac{C_{0,13} - C_{0,01}}{C_0} \qquad (3.5)$$

Where $C_{0,13}$ represents the amount of particles that settle at a slower rate than 0,13 mm/sec. In well coagulated and flocculated water the fraction of micro particles should decrease towards the end of the flocculation process.

- **Macro particles (*Pma*)** given by the equation

$$\text{Pma} = \frac{C_0 - C_{0,13}}{C_0} \qquad (3.6)$$

represent the proportion of the suspended flocculated solids that settle faster than 0,13 mm/sec. This is given by the difference between the original concentration of suspended matter (Co) and that which showed settling rates of less than 0,13 mm/sec. ($C_{0,13}$).

Under ideal conditions, after coagulation and flocculation, all the suspended matter should be present as macro particles which will exhibit a high settling rate. If not present during the initial stages of flocculation the portion of macro particles should increase to 100% towards the end of the flocculation stage.

The concentration of the various fractions of suspended matter was obtained by turbidity measurements on a HACH 2000 ratio turbidity meter by withdrawing a volume of water by pipet at the correct depth after the appropriate settling time that corresponded to the required settling rate. Samples were withdrawn immediately after stopping the flocculator (time 0) and then 2 min. 33 sec. and 33 min. later at a position 20 mm below the water surface. This gave an indication of the following fractions:

Primary particles - settling rate $<0{,}01$ mm/sec.

Micro particles - settling rate between 0,01 and 0,13 mm/sec.

Macro particles - settling rate $>0{,}13$ mm/sec.

The non-aggregated fraction was measured as the residual suspended matter after centrifuging the last sample taken.

3.2.6 Test protocol

3.2.6.1 Laboratory treatment unit

The following procedures were followed throughout the experiments and on the laboratory scale treatment unit.

- Peristaltic pumps used to dose chemicals or to pump water were calibrated according to the specific requirements.

- The ozonator was switched on and allowed to stabilise to produce a consistent ozone stream. The temperature of the cooling water was kept constant at 10°C .

- Raw water treated with the coagulant was pumped through the parallel treatment lines for at least three hours to replace any stagnant water .

- The sand filter was cleaned by backwashing before samples were taken.

- At all times water treated in one leg of the treatment unit was used as a control while the oxidants, whether it be ozone or combinations of ozone and hydrogen peroxide, were dosed into the raw water going to the other line.

  Ozone was dosed before the contact chamber in the bore hole while the hydrogen peroxide was dosed just before the coagulants.

- Activated sodium silicate was always added before the hydrated lime at concentrations of 1,5 - 2,0 mg/ℓ as SiO_2.

  Clear saturated milk of lime solution was used to give a dosage of 60 - 65 mg/ℓ CaO.

- The water tested, obtained from the Klip River as an example of organically polluted water, and Vaal Dam water as an example of unpolluted water, was collected on the day before testing in 200ℓ drums.

- The ozone concentration in the water was measured continuously after 4 minutes contact time using the ozone analyser while the ozone concentration in the ozone rich feed gas was measured at regular intervals during the experiment with the same analyser by changing the gas flow or by iodometric titration.

  The amount of ozone absorbed by the water was calculated from these results.

Provision was also made to measure the ozone concentration in the off gas.

- Samples to measure determinants such as pH, turbidity and electrical conductivity were taken while the laboratory scale unit was running.

  The test of aggregation was done directly from the three flocculators and the proportion of the different particles calculated from that.

3.2.6.2 Batch ozonation of algal cultures

- When cultures of algal strains were exposed to ozone to test for survival it was done in a batch process.
- The required organism was cultured in suitable growth media until it had reached the required concentration where after it was suspended in clarified water obtained from the purification plant, prior to chlorination.
- A known amount of ozone was introduced into the suspension by regulating the time that ozone was bubbled through.
- Aliquots were then withdrawn at progressively increasing times to correspond to the required increasing ozone dosage.
- Where hydrogen peroxide was used it was added in the correct proportions at the same time as the ozone. The hydrogen peroxide concentration was calculated after the ozone concentration in the water was measured under stabilized conditions.
- The oxidants were neutralised by sodium thiosulphate which was placed in the sampling bottles beforehand.
- Determinations for algae were done as quickly as possible after the experiment had been performed.

4. DISCUSSION

4.1 EFFECT OF OZONE ON COAGULATION AND FLOCCULATION

The effect of ozone on coagulation and flocculation was investigated making use of the test of aggregation to give an indication of the success, or interference with, particle destabilisation and floc formation.

Both Vaal Dam and Klip River water were subjected to the tests as Vaal Dam is the major source of raw water to Rand Water and is relatively unpolluted. Klip River water on the other hand is highly polluted and contains high concentrations of organic compounds as large amounts of treated domestic and industrial effluent is discharged to this river. The Vaal River drains a sparsely populated rural area that does not contain many industries. Typical chemical and physicochemical analysis for these waters are given in Table 4.1 and 4.2.

Table 4.1 Typical chemical and physicochemical analysis of Vaal Dam water quality. 1993 to 1997.

	1993			1994			1995			1996			1997		
	Min	Ave	Max.	Min	Ave	Max	Min	Ave	Max	Min	Ave	Max	Min	Ave	Max
Conductivity (mS/m)$^+$	11	19	30	15	18	20	8,8	14	24	13	17	50	21	23	26
Turbidity (NTU)	21	200	340	19	140	180	75	125	190	41	125	200	38	56	84
pH$^+$	7,5	7,8	8,6	7,3	8,1	8,7	7,3	7,9	8,4	7,4	7,7	8,1	7,8	8,1	8,8
Alkalinity (as mg/ℓ $CaCO_3$)	43	65	105	45	56	65	36	50	75	42	53	175	66	75	93
Hardness (as mg/ℓ $CaCO_3$)	44	66	110	51	59	69	31	50	75	34	48	59	64	90	490
Calcium mg/ℓ	8,3	13	22	11	13	16	6,9	12	17	6,9	9,5	13	12	19	120
Magnesium mg/ℓ	3,2	6,9	12	5,0	6,3	7,1	3,1	5,2	8,0	4,0	5,9	8,5	8,1	10	49
Sodium mg/ℓ	5,8	12	20	8,1	11	16	2,2	7,8	16	4,6	7,1	10	12	19	120
Potassium mg/ℓ	2,0	3,9	7,7	2,8	4,0	5,2	1,6	2,8	4,6	2,6	3,8	4,7	3,1	4,6	19
Iron mg/ℓ	0,23	3,1	10	0,36	1,7	6,8	0,15	1,1	2,9	0,65	2,0	5,4	<0,05	1,0	2,2
Aluminium mg/ℓ	0,35	5,1	18	0,63	2,8	7,1	0,16	1,9	4,8	0,48	3,2	9,4	<0,1	1,8	4,5
Total Silica mg/ℓ	1,7	32	88	10	22	43	7,9	18	30	15	26	45	<1,0	19	36
Ammonia as N mg/ℓ	<0,05	0,12	0,42	<0,05	0,08	0,18	<0,05	0,1	0,25	<0,05	0,06	0,36	<0,05	0,21	1,1
Nitrite as N mg/ℓ	<0,05	0,11	0,25	0,05	0,09	0,19	<0,03	0,05	0,15	<0,03	<0,03	0,06	<0,03	0,04	0,23
Nitrate as N mg/ℓ	<0,1	0,46	1,5	<0,1	0,47	1,6	0,19	0,37	1,1	<0,1	0,36	0,68	<0,1	0,69	7,4
T/Kjeldahl Nitrogen as mg/ℓ N	<1,0	<1,0	4,7	<1,0	<1,0	1,5	<1,0	<1,0	2,3	<1,0	<1,0	<1,0	<1,0	1,2	17
Total Phosphate as mg/ℓ P	<0,3	0,43	3,5	<0,03	<0,3	0,5	<0,03	<0,3	0,31	0,03	<0,3	0,61	<0,3	<0,3	0,55
Sulphate mg/ℓ	<10	15	37	13	19	34	<10	14	25	<10	16	34	<10	21	510
Chloride mg/ℓ	<10	<10	18	<10	<10	13	<10	<10	13	<10	<10	18	<10	14	125
COD mg/ℓ	11	23	65	11	22	39	<10	16	32	14	24	45	16	29	52
DOC mg/ℓ	2,7	4,7	7,6	4,3	5,4	8,4	2,0	3,9	11	4,9	6,6	8,7	3,0	5,2	12

+ = Measured at 25°C
COD - Chemical oxygen demand
DOC - Dissolved organic carbon

< indicates less than detectable concentrations by the method used.

Table 4.2 Typical chemical and physicochemical analysis of Klip River water quality, 1993 to 1997.

	1993			1994			1995			1996			1997		
	Min	Ave	Max.	Min	Ave	Max	Min	Ave	Max	Min	Ave	Max	Min	Ave	Max
Conductivity (mS/m)$^+$	74	81	120	69	85	115	71	81	120	65	87	145	67	85	110
Turbidity (NTU)	3,9	17	61	3,1	14	41	2,3	15	44	2,2	14	45	1,9	19	78
pH$^+$	7,7	8,0	8,5	7,4	8,1	8,8	7,5	8,0	8,4	7,5	7,9	8,3	7,5	8,0	8,4
Alkalinity (as mg/ℓ $CaCO_3$)	72	110	140	74	120	150	79	115	140	68	120	155	66	120	145
Hardness (as mg/ℓ $CaCO_3$)	170	230	420	200	265	395	175	245	485	235	310	415	78	285	410
Calcium mg/ℓ	40	61	110	53	69	105	45	65	125	58	77	98	16	70	98
Magnesium mg/ℓ	14	19	35	17	22	32	15	21	42	20	27	37	9,2	27	41
Sodium mg/ℓ	52	58	83	36	60	105	38	59	69	28	53	72	12	61	84
Potassium mg/ℓ	11	15	23	9,7	15	20	10	15	19	7,7	12	17	3,9	15	20
Iron mg/ℓ	<0,05	0,06	0,36	<0,05	<0,05	0,16	<0,05	0,06	0,28	<0,05	0,05	0,18	<0,05	0,05	1,0
Aluminium mg/ℓ	<0,1	0,25	0,51	<0,1	0,25	0,64	<0,1	0,3	11	<0,1	<0,10	0,12	<0,1	0,11	2,3
Total Silica mg/ℓ	5,3	11	16	1,2	11	16	8,3	14	118	7,5	14	17	<1,0	15	28
Ammonia as N mg/ℓ	<0,05	0,07	1,6	<0,05	0,09	0,40	<0,05	0,19	0,69	<0,05	0,33	1,9	<0,05	1,1	11
Nitrite as N mg/ℓ	<0,1	0,10	0,47	0,05	0,07	0,15	0,05	0,13	0,36	<0,03	0,23	0,63	<0,03	0,33	1,3
Nitrate as N mg/ℓ	0,9	3,7	8,1	<0,1	3,5	6,1	2,1	4,1	6,8	<0,1	4,6	7,5	0,33	6,2	21
T/Kjeldahl Nitrogen as mg/ℓ N	<1,0	1,5	6,8	<1,0	1,1	3,6	<1,0	<1,0	2,5	<1,0	1,6	8,7	<1,0	2,3	7,7
Total Phosphate as mg/ℓ P	<0,3	1,1	3,1	<0,3	0,59	2,1	0,36	0,8	1,6	<0,3	0,82	1,9	<0,3	0,85	1,9
Sulphate mg/ℓ	60	160	365	145	190	420	100	175	435	72	210	330	< 10	205	285
Chloride mg/ℓ	25	63	105	36	67	87	42	66	79	34	67	180	< 10	63	115
COD mg/ℓ	23	37	88	20	33	56	19	32	53	19	31	51	29	40	55
DOC mg/ℓ	4,1	7,5	10	3,9	7,0	9,3	4,5	6,7	8,3	4,9	6,9	8,8	3,4	6,8	11

+ = Measured at 25°C
COD - Chemical oxygen demand < indicates less than detectable concentrations by the method used.
DOC - Dissolved organic carbon

During the experimentation the following treatment parameters were changed to see the effects:

1. Dosage of hydrated lime and sodium silica
2. Coagulation and flocculation energy
3. Ozone dosage

4.1.1 The effect of hydrated lime and sodium silicate as coagulants

In Table 4.3 the combined effect of increasing hydrated lime (expressed as mg/ℓ calcium oxide) and sodium silicate (expressed as mg/ℓ silicon dioxide) dosages on coagulation and flocculation can be seen. The turbidity measurements taken after the specified settling times to correspond to the Co, $CO_{0.13}$, $C_{0,01}$ and $C_F(_{0.01})$ fractions and the proportions of the different particles viz. *Pma, Pmi, Pp* and *Pn* are shown.

From the results it is clear that there is an increase in the proportion of macro particles formed with increasing sodium silicate dosages. A sharp improvement is seen at a dosage of between 1 and 3 mg/ℓ sodium silicate, as SiO_2, which seems to indicate that there would be an optimum dosage. Increased hydrated lime dosages did not have a too significant effect on the formation of the desirable floc that would settle rapidly and remove all suspended matter. Higher CaO dosages exceeding 65 mg/ℓ, interfered with the formation of macro particles and this proportion decreased relative to the fraction obtained at a CaO dosage of 50 mg/ℓ.

Based on these results the hydrated lime and activated sodium silicate dosages were respectively 50 mg/ℓ as CaO and 2 - 3 mg/ℓ as SiO_2 when treating Vaal Dam water. This is in agreement with the dosages used on the full scale treatment plant.

4.1.2 The effect of energy input on coagulation and flocculation

Flash mixing of coagulants with water is considered to be essential to achieve good coagulation and particle destabilisation. The equipment used was the same as used previously and capable of high mixing energy with G and Gt values of respectively 1303 sec^{-1} and 33750.

After the hydrated lime and sodium silicate dosages were optimised the effect of varying energy input into coagulation was determined. During the test the flocculation energy input was kept constant to G values of 35, 29 and 24 sec^{-1} for the three respective flocculators placed in series which provided for Gt values of 8190, 6786 and 5616 in the individual flocculators.

The best particle removal took place when the energy input into the coagulator was between 400 and 540 sec^{-1} corresponding to Gt values of 10360 to 13906.

Table 4.3 Relative fractions of settleable particles produced by various dosages of hydrated lime and activated sodium silicate.

	SiO_2 dosage							SiO_2 dosage					
	0mg/ℓ	1mg/ℓ	2mg/ℓ	3mg/ℓ	4mg/ℓ	5mg/ℓ		0mg/ℓ	1mg/ℓ	2mg/ℓ	3mg/ℓ	4mg/ℓ	5mg/ℓ
CaO dosage - 50 mg/ℓ	Turbidity NTU						Fraction of the settleable solids						
C_0	131	128	127	125	125	128	*Pma*	-0,031	0,156	0,315	0,424	0,616	0.718
$C_{0,13}$	135	108	87	72	48	36	*Pmi*	-0,008	-0,807	0,652	0,561	0,36	0.257
$C_{0,01}$	136	4,7	4,2	1,8	3	3	*Pp*	0,992	0,036	0,032	0,013	0,023	0.022
$C_{F(0,01)}$	6	0,08	0,1	0,08	0,13	0,11	*Pn*	0,046	0,001	0,001	0,001	0,001	0.001
CaO dosage - 65 mg/ℓ													
C_0	129	124	123	125	125	127	*Pma*	0,008	0,057	0,106	0,392	0,464	0,606
$C_{0,13}$	128	117	110	76	67	50	*Pmi*	0	0,864	0,801	0,586	0,494	0,371
$C_{0,01}$	128	9,8	11,5	2,7	5,2	2,9	*Pp*	0,938	0,078	0,092	0,021	0,041	0,022
$C_{F(0,01)}$	7	0,08	0,14	0,08	0,11	0,09	*Pn*	0,054	0,001	0,001	0,001	0,001	0,001
CaO dosage - 80 mg/ℓ													
C_0	127	127	125	124	125	128	*Pma*	-0,024	0,150	0,16	0,476	0,52	0,602
$C_{0,13}$	130	108	105	65	60	51	*Pmi*	0,016	0,755	0,759	0,496	0,442	0,375
$C_{0,01}$	128	12,1	11,3	3,5	4,8	3	*Pp*	0,962	0,094	0,089	0,027	0,037	0,023
$C_{F(0,01)}$	5,8	0,11	0,12	0,11	0,13	0,11	*Pn*	0,046	0,001	0,001	0,001	0,001	0,001

Coagulation was done at a G value of between 400 and 450 Sec^{-} and Gt values of 10360 to 13906.

This assessment is made on the proportion of the various fractions of setteable particles present. In both the cases the fraction of primary particles (*Pp*) was the lowest while the micro particle (*Pmi*) fraction, that could produce the macro particles (*Pma*) was the highest.

This also lead to the best turbidity removal. See Table 4.4 and 4.5.

The improvement in the removal of settleable matter after coagulation and flocculation using 65 mg/ℓ CaO and 3 mg/ℓ SiO_2 at higher coagulation energy can be seen in Table 4.4.

Table 4.4 The effect of increasing energy input on coagulation, flocculation and the formation of settleable particles

Energy input G s^{-1}	57	217	400	540	1303
Fraction of the settleable solids					
Pma	0,328	0,379	0,325	0,246	0,328
Pmi	0,546	0,527	0,603	0,682	0,570
Pp	0,125	0,093	0,071	0,071	0,101
Pn	0	0	0	0	0

Table 4.5 The effect of coagulation energy on the removal of coagulated and flocculated settleable matter

Energy input G s^{-1}	217	400
Turbidity (NTU) after specific settling times		
0 min	125	121
10 min	14	18
20 min	14	12,5
30 min	12	10
40 min	11	9,3
50 min	11	9,3
60 min	11	8,5

4.1.3 The effect of various ozone dosages

Numerous tests were done on the bench scale treatment unit in which the effect of ozone on coagulation and flocculation was examined for both Vaal Dam and Klip River water.

The results obtained were displayed in tables and graphs of which table 4.6 and figure 4.1 are typical examples.

Table 4.6 Comparative proportion of settleable matter produced by hydrated lime and sodium silicate with and without ozone in Vaal Dam water.

Lime dosage	-	65 mg/ℓ Ca O
Sodium silicate dosage	-	3 mg/ℓ SiO_2
O_3 dosage	-	0,64 mg/ℓ
Fraction of settleable solid produced		
Flocculator 1		
	WITH - 0_3	WITHOUT - 0_3
Pma	0,260	0,322
Pmi	0,459	0,420
Pp	0,280	0,257
Pn	0,001	0,001
Flocculator 2		
	WITH - 0_3	WITHOUT - 0_3
Pma	0,517	0,553
Pmi	0,352	0,326
Pp	0,130	0,120
Pn	0.001	0,001
Flocculator 3		
	WITH - 0_3	WITHOUT - 0_3
Pma	0,662	0,704
Pmi	0,228	0,232
Pp	0,110	0,063
Pn	0,001	0,001

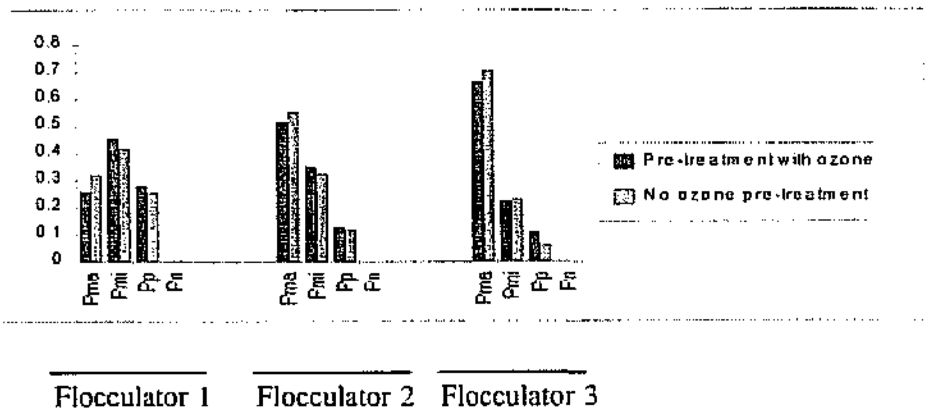

Figure 4.1 Proportional distribution of settleable particles formed by hydrated lime and sodium silicate with and without ozone in Vaal Dam water

Pma	-	Macro particles
Pmi	-	Micro particles
Pp	-	Primary particles
Pn	-	Non-Agregated particles

The changes in the relative fractions of settleable particles in water could give an idea of the success of coagulation and flocculation as well as the effect of ozonation. This is based on the premises that a higher proportion of macro particles will indicate successful coagulation. Based on the changes in the relative distribution of the various sizes of particles table 4.6 shows that ozonation could have detrimental effects on coagulation and flocculation. This may be observed in two ways:

1) The fraction of macro particles in ozonated water was lower than in the non-ozonated water

2) The ratio of macro particles at the end of the flocculation process compared to the micro particles in the untreated water was higher in the non-ozonated water than in the ozonated water.

Table 4.7 summarises all the data of flocculation experiments conducted on Vaal Dam water between April and July 1994. The results are arranged in order of increasing ozone dosage and compares the fraction (percentage) of macro particles (*Pma*) in the third flocculator, at the end of the process, to the fraction of micro particles (*Pmi*) present in the first flocculator.

This gives an indication of how successful the micro particles can be transformed into fast settling macro particles.

In 55 percent of cases the fraction of macro particles at the end of the flocculation process was smaller following ozonation.

Data in Table 4.7 are the results of a number of experiments performed at different ozone concentrations and show that the fraction of macro particles at the end of the flocculation process decreased relative to higher ozone doses. This would indicate interference with the flocculation which could only be attributed to ozonation.

Table 4.7 Effect of ozonation on the proportion of micro and macro- particles at the beginning and end of the flocculation process in Vaal Dam water. (Macro particles (*Pma*) measured at the end of the process and micro particles (*Pmi*) measured at the beginning.) Period April to July 1994.

Ozone dosage (mg/ℓ)	% *Pmi* after first flocculation	% *Pma* at end of process	Ratio *Pma/Pmi*	Average Ratio *Pma/Pmi*
0	42	74	1,76	
0	54	69	1,27	
0	51	70	1,37	
0	48	65	1,35	
0	55	62	1,12	
0	55	62	1,12	
0	55	64	1,16	1,307
0,65	55	62	1,12	
0,86	55	56	1,01	
1,44	57	42	0,7	
1,56	62	47	0,7	
1,80	64	41	0,6	
2,0	64	41	0,6	
2,4	62	49	0,79	0,79

Table 4.8: Water quality that prevailed while flocculation tests were done on Vaal Dam water. April to July 1994.

	Average	Minimum	Maximum
Conductivity mS/m$^+$	18	18	18
Turbidity (NTU)	165	150	165
pH$^+$	8,1	8,0	8,1
Alkalinity ($CaCO_3$)	55	55	60
Hardness ($CaCO_3$)	60	59	60
Calcium	14	13	14
Magnesium	6,2	6,2	6,3
Sodium	10	10	11
Potassium	4,0	3,9	4,4
Iron	1,9	1,9	3,2
Aluminium	3,3	2,9	5,9
Total Silica	28	24	34
Ammonia as N	0,10	0,09	0,1
Nitrite as N	0,15	0,13	0,15
Nitrate as N	0,52	0,38	0,52
T/Kjeldahl Nitrogen	<1,0	<1,0	<1,0
Total Phosphate as P	0,38	0,23	0,38
Sulphate	17	17	18
Chloride	11	10	11
COD	20	18	23
DOC	5,1	5,1	5,2

+ = Measured at 25°C
COD - Chemical oxygen demand
DOC - Dissolve organic carbon
Results in mg/ℓ where applicable
< Indicates less than detectable concentrations by the method used.

Table 4.9 Effect of ozonation on the proportion of micro and macro- particles at the beginning and end of the flocculation process in Vaal Dam water. (Macro particles (*Pma*) measured at the end of the process and micro particles (*Pmi*) measured at the beginning.) Period April to May 1995.

Ozone dosage (mg/ℓ)	% *Pmi* after first flocculation	% *Pma* at end of process	Ratio *Pma/Pmi*	Average Ratio *Pma/Pmi*
0	41	70	1,707	
0	43	79	1,83	
0	30	82	2,73	
0	54	28	0,519	
0	44	83	1,88	
0	49	29	0,59	
0	55	76	1,38	
0	39	76	1,94	
0	44	71	1,61	
0	51	51	1,0	
0	64	18	0,28	1,406
0,64	45	66	1,4	
0,76	41	67	1,63	
0,80	41	71	1,73	
0,87	60	11	0,18	
1,84	24	68	2,8	
2,73	55	9	0,16	
2,73	71	23	0,32	
2,99	55	39	0,70	
3,99	40	64	1,6	
6,2	62	17	0,27	
8,59	55	14	0,25	1,004

Data produced between April and May 1995 were arranged in similar fashion as to that in Table 4.7 and are shown in Table 4.9. In 60 per cent of the cases the fraction of macro particles at the end of the flocculation process were lower following ozonation.

The ratio between the percentage macro particles present in the last flocculator and the micro particles in the first flocculator were calculated. In the cases of the non-ozonated water the ratios were 1,307 and 1,406 for the respective periods and 0,79 and 1,004 for the ozonated water. This would indicate that the formation of fast settling macro particles did not take place as effectively where ozone was applied.

Table 4.10 Water quality that prevailed while flocculation tests were done on Vaal Dam water. April to May 1995.

	Average	Minimum	Maximum
Conductivity mS/m$^+$	15	13	16
Turbidity (NTU)	170	115	180
pH$^+$	8,0	7,5	8,0
Alkalinity ($CaCO_3$)	51	5,0	52
Hardness ($CaCO_3$)	56	54	57
Calcium	13	13	13
Magnesium	5,7	4,8	5,7
Sodium	9,7	8,0	12
Potassium	3,1	2,8	3,4
Iron	1,2	1,2	1,3
Aluminium	2,1	1,6	3,3
Total Silica	19	19	26
Ammonia as N	0,15	0,09	0,2
Nitrite as N	0,10	0,07	0,11
Nitrate as N	0,42	0,37	0,54
T/Kjeldahl Nitrogen	<1,0	<1,0	<1,0
Total Phosphate as P	0,17	<0,3	0,22
Sulphate	17	10	17
Chloride	<10	<10	<10
COD	13	10	19
DOC	3,4	3,4	4,1

+ = Measured at 25°C
COD - Chemical oxygen demand
DOC - Dissolve organic carbon
Results in mg/ℓ where applicable
< Indicates less than detectable concentrations by the method used.

Data on the presence of macro and micro particles in ozonated and non-ozonated flocculated Klip River water are presented in Table 4.11

Table 4.11 Effect of ozonation on the proportion of micro and macro particles at the beginning and end of the flocculation in Klip River water. (Macro particles (*Pma*) measured at the end of the process and micro particles (*Pmi*) measured at the beginning.) Period April to May 1995.

Ozone dosage (mg/ℓ)	% *Pmi* after first flocculation	% *Pma* at end of process	Ratio *Pma/Pmi*	Average
0	20	68	3,4	
0	34	68	2,0	
0	31	80	2,58	
0	50	60	1,2	
0	39	35	0,89	
0	22	9	0,14	1,78
1,9	19	23	1,2	
2,07	20	83	4,12	
2,07	28	91	3,2	
2,50	3	14	4,6	
2,89	17	87	5,11	
3,51	25	81	3,2	3,57

From the data it seems as though the Klip River water was more prone to flocculation when ozone was applied. This is bourne out by the fact that spontaneous visible flocculation often occurred when Klip River water was ozonated. This is evident in the greater presence of macro particles at the end of the flocculation period in relation to the micro particles in the non-ozonated water at an equivalent ozone doses exceeding 2.0 mg/ℓ. In 84 per cent of the cases the fraction of macro particles at the end of the flocculation process was larger following ozonation. This is the opposite to what was observed with Vaal Dam water.

Table 4.12 Water quality that prevailed while flocculation tests were done on Klip River water. August to October 1997.

	Average	Minimum	Maximum
Conductivity mS/m$^+$	85	83	89
Turbidity (NTU)	12	12	16
pH$^+$	7,8	7,8	7,8
Alkalinity ($CaCO_3$)	125	110	125
Hardness ($CaCO_3$)	305	260	310
Calcium	73	73	79
Magnesium	30	28	31
Sodium	66	61	68
Potassium	14	12	16
Iron	<0,05	<0,05	<0,05
Aluminium	<0,10	<0,1	<0,1
Total Silica	17	16	20
Ammonia as N	0,53	0,25	0,54
Nitrite as N	0,28	0,22	0,28
Nitrate as N	4,3	4,0	4,4
T/Kjeldahl Nitrogen	3,2	2,4	3,3
Total Phosphate as P	0,65	0,34	0,67
Sulphate	200	195	205
Chloride	56	55	71
COD	35	35	37
DOC	5,1	4,5	7,6

\+ = Measured at 25°C

COD - Chemical oxygen demand

DOC - Dissolve organic carbon

Results in mg/ℓ where applicable

< Indicates less than detectable concentration by the method used.

4.2 DESTABILISATION OF SUSPENDED MATTER BY OZONATION

In general it is believed that if suspended particles could be destabilised, flocculation would occur. This could be evident from visual flocs forming or be determined by observing changes in the zeta potential of the suspension. As the zeta potential approaches zero it would indicate a neutral suspension, or a charge close to zero, and spontaneous flocculation could take place at that point.

The zeta potential may be influenced by the addition of a coagulant such as ferric chloride or aluminium sulphate. In the following experiments the zeta potential of suspended matter of Vaal Dam and Klip River water was adjusted by the addition of ferric chloride while measurements were taken at increasing dosages. The dosage at which a zero zeta potential was observed, was recorded. Ozone was then applied at progressively higher dosages while the zeta potential was noted and the dosage required to obtain a zero zeta potential recorded.

Figures 4.2 and 4.3 show the increase of the zeta potential of Vaal Dam and Klip River water as function of ferric chloride dosages. The ferric chloride dosages are expressed as mg/ℓ Fe^{3+}, (1 mg/ℓ Fe^{3+} is equivalent to 3 mg/ℓ $FeCl_3$).

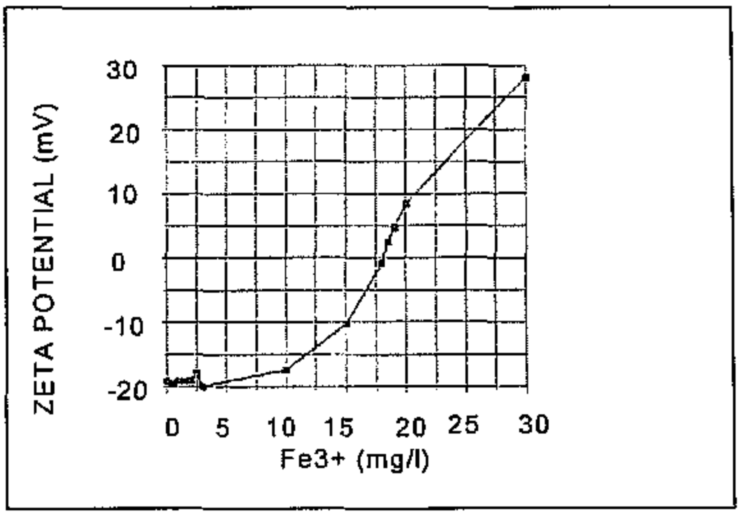

Figure 4.2 The effect of ferric chloride dosage on the zeta potential of Vaal Dam water (Dosage expressed as mg/ℓ Fe^{3+})

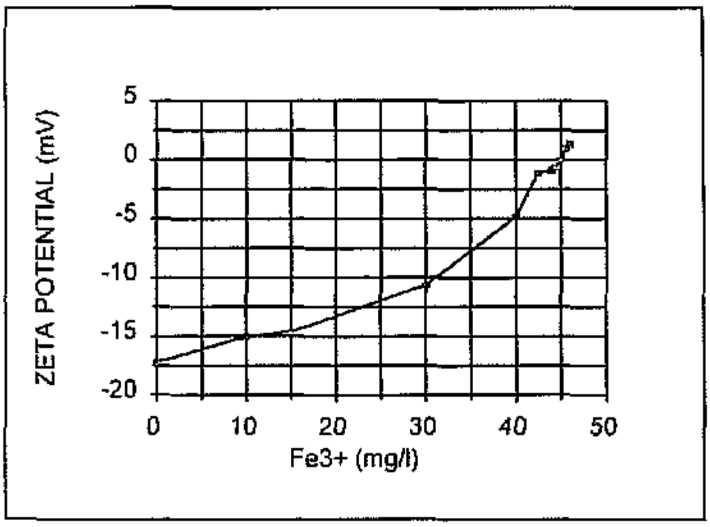

Figure 4.3 The effect of ferric chloride dosage on the zeta potential of Klip River water (dosage expressed as mg/ℓ Fe^{3+})

From the figures it can be seen that there was a difference in the zeta potential of the two waters at the start and that about twice the amount of ferric chloride was required to produce a zero zeta potential in Klip River water compared to Vaal Dam water.

The effect of ozonation on the zeta potential of the respective water samples was then tested. The results are shown in tables 4.13 and 4.14.

Table 4.13 The effect of ozone dosage on the zeta potential of Vaal Dam water

Ozone dosage (mg/ℓ)	Zeta potential in Vaal Dam water
0	-19,10
0,22	-19,10
0,37	-17,40
0,49	-18,10
1,03	-18,20
1,56	-17,50
2,28	-18,30
3,1	-18,80

Table 4.14 The effect of ozone dosage on the zeta potential of Klip River water.

Ozone dosage (mg/ℓ)	Zeta potential in Klip River water
0	-17,20
0,22	-15.90
0,42	-14,00
0,75	-12,80
1,01	-12,70
1,4	-9,04
2,46	-9,00
3,45	-11,80

From this data it can be seen that increasing ozone dosage had little effect on the zeta potential of Vaal Dam water. In the Klip River water it was increased from -17,20 to ≈ - 10,0. This supported the observation that ozonation could induce flocculation.

The effect of ozone to reduce the ferric chloride demand to obtain a zero zeta potential was then investigated for both Klip River and Vaal Dam water.

The results are presented in Tables 4.15 and 4.16.

Table 4.15 Decrease in ferric chloride dosage to achieve zero zeta potential in Vaal Dam water after ozonation.

Ozone dosage (mg/ℓ)	Fe^{3+} dosage (mg/ℓ)	Zeta potential	Decrease in Fe^{3+} dosage (mg/ℓ)	Decrease in Fe^{3+} dosage (%)
0	18	-0,8		
0,22	12	-0,1	6	3,3
0.37	12,5	0,7	5,5	30,6
0.49	19,5	1,5	-1,5	-8,3
1,03	19	1	-1	-5,6
1,56	18	0,3	0	0
2,28	19,5	1	-1,5	0
3,1	19	1,6	-1	-5,6

During these experiments the turbidity of Vaal Dam water was on average 170 NTU and the DOC values 3,6.

Table 4.16 Decrease in ferric chloride dosage to achieve zero zeta potential in Klip River water after ozonation

Ozone dosage (mg/ℓ)	Fe^{3+} dosage (mg/ℓ)	Zeta potential	Decrease in Fe^{3+} dosage (mg/ℓ)	Decrease in Fe^{3+} dosage (%)
0	45	0		
0,22	29,5	-0,4	15,5	34,4
0,42	41	0	4	8,9
0,75	47,5	0,2	-2,5	-5,6
1,01	44,5	0,1	0,5	1,1
1,4	42	0,2	3	6,7
2,46	45,5	0,5	0	0
3,45	43	0	2	4,4

During these experiments the turbidity of Klip River water was on average 12 NTU and the DOC values 5,1.

In both cases the ferric chloride dosage required to produce a zero zeta potential was determined. This was 18,0 and 45 mg/ℓ Fe^{3+} for respectively Vaal Dam and Klip River water. Ozone was then dosed at increasing concentrations and the amount of ferric chloride was then determined to obtain zero, or as close as possible, zero zeta potential in the water.

The difference between the effect achieved by the sole addition of ferric chloride compared to the ozone aided effect of ferric chloride was then calculated and expressed as the percentage difference.

See Figures 4.4 and 4.5.

From the results it is clear that zero zeta potential was reached at lower ferric chloride dosages when ozone was dosed first. This shows that ozonation could improve the action of ferric chloride as coagulant and therefore reduce the coagulant demand.

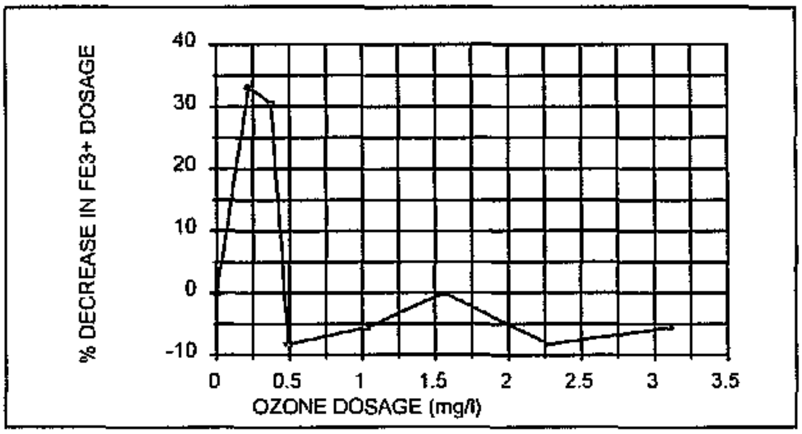

Figure 4.4 Percentage decrease in ferric chloride dosage realised to achieve zero zeta potential expressed as a function of ozone dosage in Vaal Dam water.

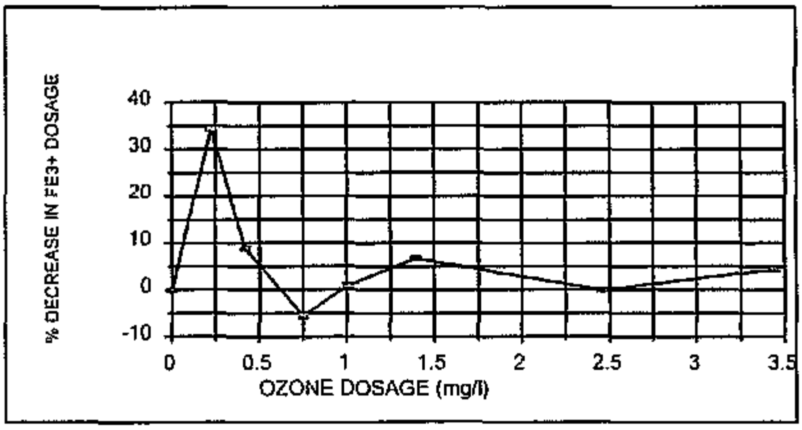

Figure 4.5 Percentage decrease in ferric chloride dosage realised to achieve zero zeta potential expressed as a function of ozone dosage in Klip River water

4.3 THE EFFECT OF OZONE ON THE REMOVAL OR DAMAGE TO ALGAL CELLS

The removal or damage to algal cells in water can be influenced by either the physicochemical action in the water or the direct damage to the algal cells by strong chemical oxidants such as chlorine or ozone.

4.3.1 Removal of algae by sedimentation and filtration

The effect of ozone on the physical removal of algae by sedimentation or filtration from water was studied by determining the removal of either natural occurring algae or specific algae species in the bench scale treatment unit.

The reduction in the concentration of algal pigment, measured as chlorophyll-*a*, was used as an indication of the numbers of natural occurring algae. Where the removal of specific algal species was determined, the number of cells was counted.

The following results were obtained where the algal removal efficiency of the various unit treatment processes were studied on the bench scale treatment unit, and represent the average of eight different experiments.

Table 4.17 Removal of algal pigments by various unit treatment processes with and without ozone.

	Per cent
Reduction by ozone only - dosage 1,2 mg/ℓ	11,1
Reduction by coagulation followed by sedimentation	66,5
and filtration	73,7
Reduction by ozone followed by coagulation and sedimentation	84,2
and filtration	90,7

From this it can be seen that under these conditions ozone by itself did not reduce the total chlorophyll value much. Good removal was obtained by sedimentation and flocculation without ozone. Ozonation improved the physical removal of algae by sedimentation and filtration by 17,7 and 17,0 per cent respectively.

The same pattern was observed when the actual number of algal cells removed in each unit treatment process was determined. See Table 4.17.

The algal species present in the water comprised of:

Melosira	59%
Centric diatoms	16%
Crucigenia	10%
Pennate diatoms	4,0%
Navicula	4,0%
Oocystis	3%
Chlamydomonas	1,0%
Trachelomonas	1,0%
Closterium	1,0%
Euglena	1%

Table 4.18 Removal of algal cells by various unit treatment processes with and without ozone.

	Per cent
Reduction by ozone only - dosage 1,2 mg/ℓ	1,4
Reduction by coagulation followed by sedimentation	69,8
and filtration	72,1
Reduction by ozone followed by coagulation and sedimentation	78,1
and filtration	87,6

The reduction in chlorophyll value as an indication of the removal of algal cells, influenced by ozone and ozone combined with hydrogen peroxide (peroxone) using activated sodium silicate and hydrated lime as coagulant, was examined. The results are given in Table 4.19. From this table it can be seen that the presence of oxidants enhanced the removal of chlorophyll containing cells by possibly improved coagulation and flocculation. As in the experiment using ozone only, see Table 4.18, the oxidation step only had a slight impact on the reduction of chlorophyll values.

When using peroxone the ratio of O_3 to H_2O was always kept to 2:1 expressed as mg/ℓ concentration.

It seems, as though the use of hydrogen peroxide, in addition to ozone, did not vastly improve the removal of chlorophyll or algal cells but that slightly better results were obtained in the Klip River water compared to Vaal Dam water.

Table 4.19 Effect of ozone and peroxone on the removal of chlorophyll-*a* from Klip River and Vaal Dam water.

	Oxidant applied				
	None	O_3	$O_3 + H_2O_2$	O_3	$O_3 + H_2O_2$
Treatment step	Percent removal from Klip River water			Percent removal from Vaal Dam water	
Oxidation	0	9	7	1	1
Sedimentation	68	73	71	42	60
Filtration	75	95	95	86	90

Ozone dosage 1,2 mg/ℓ; Hydrogen peroxide dosage 0,7 mg/ℓ; Contact time 4,5 minutes.

Table 4.20 shows the reduction in the number of a diatoms, *Monoraphidium,* removed by the various treatment processes with ozone and peroxone in Klip River and Vaal Dam water. From this it can be seen that the overall removal efficiency of this diatom species was slightly higher from Klip River water compared to Vaal Dam water and that the effect of peroxide is marginal.

Table 4.20 Effect of ozone and peroxone on the removal of *Monoraphidium* cells from Klip River and Vaal Dam water.

	Oxidant applied			
	O_3	$O_3 + H_2O_2$	O_3	$O_3 + H_2O_2$
Treatment step	Percent removal from Klip River water		Percent removal from Vaal Dam water	
Oxidation	3	3	1	1
Sedimentation	33	35	50	55
Filtration	82	83	75	78

Ozone dosage 1,2 mg/ℓ; Hydrogen peroxide dosage 0,7 mg/ℓ; Contact time 4,5 minutes.

4.3.2 **Oxidant damage to algal cells.**

Although it was clear that ozone had some effect on the algal cells, which could be observed by the reduction in chlorophyll concentrations in the bench scale treatment unit, the effect was not all that drastic. This could have been due to lack of contact time or too low an ozone concentration. To test the effect of different ozone concentrations, *Euglena* cells were exposed to increasing ozone dosages for fixed times. The effect was measured in the reduction in chlorophyll-*a* concentration, see Table 4.21.

Table 21 Percentage reduction in chlorophyll-*a* concentration at different ozone dosages.

Ozone dosage (mg/ℓ)	Percent reduction in chlorophyll
0,79	9,7
1,01	15,3
1,24	98,6
1,46	92,6
1,69	93,7

Since this exercise did not give any information about the damage to the algal cells an experiment was done in which the algal cells were exposed to ozone and peroxone. *Monoraphidium* cells were suspended in clarified water prior to chlorination and then exposed to concentrations of ozone and peroxone as shown below. The hydrogen peroxide concentration was maintained at half the ozone concentration.

O_3 mg/ℓ	O_3 / H_2O_2 mg/ℓ
0,19	0,19 / 0,1
0,76	0,76 / 0,38
1,40	1,40 / 0,7
2,04	2,04 / 1,0
2,6	2,6 / 1,3

After 10 minutes contact time the residual oxidant was neutralised with sodium thiosulphate. The effect of the oxidants were then examined by scanning and transmission electron microscope and the following observations made:

On the transmission electron micrographs it was clear that the following internal structures had been affected

Cell walls - swelling and an increase in elasticity resulting in separation from the cytoplasma

Cytoplasma - appeared more granular

Chloroplasts - grana became swollen and disintegrated

Nuclear membrane - became swollen

From this it seemed as though the ozone and hydrogen peroxide attacked the membrane systems in the cells, which resulted in the death of the cells.

The scanning electron micrographs showed that the surface of the affected algal cells had a shrivelled appearance in contrast to the smooth surface of the control samples.

Images of the algal cells are shown in Figures 4.6 to 4.8. The examples of the affected cells shown are at an ozone concentration of 2,04 mg/ℓ and combined with 1,02 mg/ℓ hydrogen peroxide. From these images it is clear that the combination of the oxidants had a greater effect than ozone alone and it was found that the surface damage became more obvious at higher oxidant concentrations.

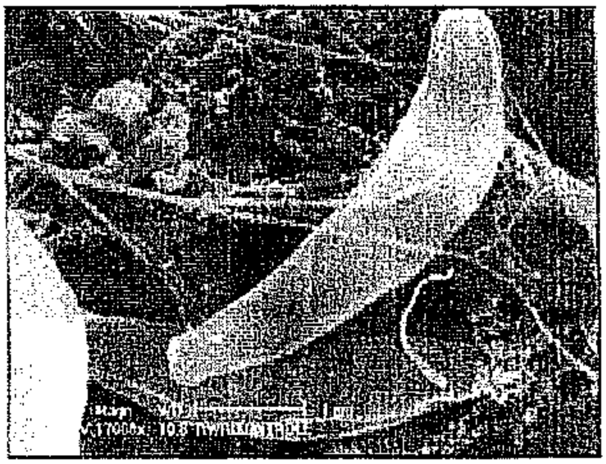

Figure 4.6 Appearance of a natural unaffected *Monoraphidium* cell.

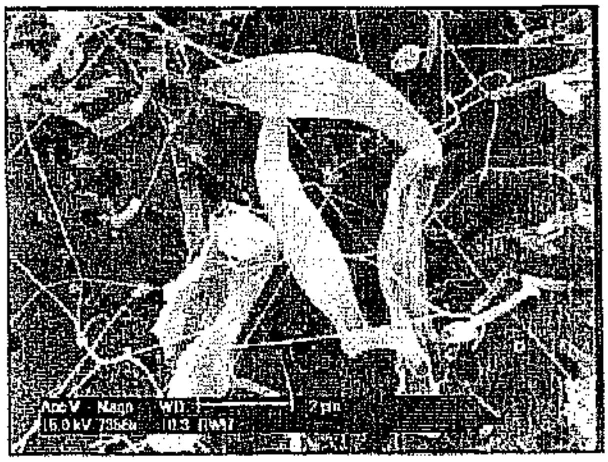

Figure 4.7 Evidence of damage to surface structures of *Monoraphiodium* cells exposed to 2,04 mg/ℓ ozone.

Figure 4.8 Evidence of damage to surface structures of *Monoraphidium* cells exposed to 2,04 mg/ℓ ozone and 1,02 mg/ℓ hydrogen peroxide.

4.4 THE EFFECT OF OZONE ON THE REDUCTION OF BACTERIAL NUMBERS

Vaal Dam water was spiked with a mixed bacterial culture containing coliform bacteria as well as coliphages. This water was then treated in the bench scale treatment unit using activated sodium silicate and hydrated lime. Ozone was dosed to one line at concentrations of between 1,8 and 2,9 mg/ℓ.

The effect of ozonation and the physicochemical treatment processes on the reduction of micro-organism numbers are given in Table 4.22.

Table 4.22 Effect of ozonation and physicochemical treatment on the removal of micro-organisms from Vaal Dam water.

	Initial numbers of organisms	Accumulative per cent removal				
		Oxidation	Sedimentation		Filtration	
		Only O_3	With O_3 +	Without O_3 -	With O_3 +	Without O_3 -
Standard Plate count/mℓ	200 000	14	93	87	97	96
Total coliform count/100mℓ	15 000	45	93	89	92	97
Coliphages/mℓ	86	91	100	100	100	100

Ozone dosage 1,7 mg/ℓ; Contact time 4,5 minutes.

From these data it can be seen that there is little difference between the overall removal efficiency whether pre-ozonation was applied or not, although oxidation reduced the numbers of the microbes to some extent.

The effect of ozone by itself and in combination with hydrogen peroxide was tested in Klip River water. As this water already contained high numbers of micro-organisms there was no need to add micro organisms. The results of these tests are summarised in Table 4.23.

Table 4.23 The effect of ozonation and peroxone and physicochemical treatment on the removal of micro-organisms from Klip River water

	Initial numbers of organisms	Accumulative per cent removal					
		Oxidation		Sedimentation		Filtration	
		O_3	$O_3 + H_2O_2$	O_3	$O_3 + H_2O_2$	O_3	$O_3 + H_2O_2$
Standard Plate count/mℓ	43 000	9	6	60	37	79	79
Total coliform count/ 100mℓ	1 800	27	21	81	79	95	91
Coliphage /mℓ	540	64	71	79	77	91	75

Ozone dosage 1,9 mg/ℓ; Hydrogen peroxide dosage 0,9 mg/ℓ; Contact time 4,5 minutes.

These data show that destruction of the micro organisms by direct attack varies in effectiveness with the bacteria phages being the most vunerable. The physicochemical removal plays an overwhelming important role, as in the case with Vaal Dam water, see Table 4.22.

By comparison, it was found that the removal efficiency of the Rand Water purification system for micro organisms, excluding disinfection, are:

Standard plate count; 87 percent, total coliforms; 84 percent and colipages; 78 percent (Geldenhuys 1978).

4.5 THE EFFECT OF OZONE ON GENERAL WATER QUALITY DETERMINANTS

From the experiments it became clear that ozonation or peroxone could have an effect on the biological quality, specifically the algal or chlorophyll values, of water. Removal of suspended matter is primarily a function of coagulation and flocculation, these processes could be affected adversely by the use of strong oxidants. Other inorganic water quality determinants such as the dissolved cations and anions were not affected by the treatment process unless these determinants were associated with suspended matter.

Oxidisable organic matter was affected by ozone as can be seen on the reduction of ultraviolet light extinction at 254 nm. See Table 4.24.

Table 4.24 The effect of ozone and peroxone on the extinction of ultra violet light at 254 nm in Klip River and Vaal Dam water.

	Oxidant applied			
	O_3	$O_3 + H_2O_2$	O_3	$O_3 + H_2O_2$
Treatment step	Per cent reduction in Klip River water		Per cent reduction in Vaal Dam water	
Oxidation	4	3	1	7
Sedimentation	15	27	60	53
Filtration	40	39	78	83

Ozone dosage 1,9 mg/ℓ; Hydrogen peroxide dosage 0,9 mg/ℓ; Contact time 4,5 minutes.

Although the dissolved organic carbon (DOC) content of Klip River water is higher than that of Vaal Dam water, there was a greater reduction in ultra violet light extinction, or absorption, compared to Klip River water.

In Vaal Dam water the absorption of ultra violet light at 254 nm with a path length of 50 mm decreased from 0,984 to 0,187 for ozone treatment and from 0,984 to 0,148 for the peroxone treatment. In Klip River water the respective figures are, from 0,330 to 0,198 for ozone and from 0,330 to 0,200 for the oxidants in combination.

This would indicate that fractions of the organic compounds present in Vaal Dam water, specifically those with unsaturated double bonds are more susceptible to attacks from strong oxidants than those present in Klip River water.

Removal efficiency of DOC from Klip River water was low, at only about 6,3 per cent when using ozone aided treatment and 7,6 per cent where ozone and hydrogen peroxide was used. In Vaal Dam water the respective figures were 27,7 per cent and 29,2 per cent.

Table 4.25 shows the DOC concentration of Klip River and Vaal Dam water before and after treatment.

Table 4.25 DOC concentration (mg/ℓ) and percent reduction in Klip River and Vaal Dam water through the treatment unit with ozone and peroxone.

	Klip River water		Vaal Dam water	
	DOC	Per cent reduction	DOC	Per cent reduction
Raw water	7,47		6,5	
O_3 + treatment	7,0	6,3	4,7	27,7
O_3, H_2O_2 + treatment	6,9	7,6	4,6	29,2

Ozone dosage 1,9 mg/ℓ; Hydrogen peroxide dosage 0,9 mg/ℓ; Contact time 4,5 minutes.

Note: Treatment includes:

- Coagulation with hydrated lime and activated sodium silicate
- Flocculation
- Sedimentation
- Sand filtration.

5. CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

- Ozone affects the coagulation and flocculation of water when treated with activated sodium silicate and hydrated lime. Vaal Dam water was affected negatively and fewer "fast settling" macro particles are formed after pre-ozonation.

  Klip River water was affected positively and more "fast settling" macro particles are formed after pre-ozonation. Spontaneous flocculation took place when ozonating the Klip River water at dosages above 2,2 mg/ℓ.

- The zeta potential of natural occurring suspensions in Klip River and Vaal Dam water is increased by ozonation, making it less negative for a narrow band of ozone concentrations and therefore reduces the normal coagulant demand.

- By ozonation the organic quality of water is improved as the dissolved organic carbon (DOC) content of both Vaal Dam and Klip River water, as well as ultra violet light extinction at 254 nm, are reduced. The fact that the percentage reduction in Vaal Dam water for these two determinants is greater than in Klip River water suggests that the nature of organic compounds play an important role.

- Ozone by itself, and in combination with hydrogen peroxide, attacks algal cells and causes internal and external damage that kills the algae. Pre-oxidation improves the physical removal of algal cells by sedimentation and filtration.

- Ozone by itself, and in combination with hydrogen peroxide, reduces the number of micro-organisms by oxidation but not to the extent that it improved the overall removal efficiency of the treatment process.

- The test of aggregation, by which it is possible to distinguish between particles with different settling rates, can be used effectively to study subtle changes in water quality, and the effects of different water treatment processes.

RECOMMENDATIONS

- Before considering the application of ozone for water treatment the potential advantages or disadvantages and the following aspects should be considered carefully:
  - ⋆ effect of ozone on coagulation and flocculation
  - ⋆ effect of ozone on the organic matter present
  - ⋆ effect of ozonation on the concentration of assimilable organic carbon compounds in water.
- Very little is known about the nature of the organic material in the relatively unpolluted Vaal Dam. The organic compounds in Vaal Dam and Katse Dam water should be characterised and the potential influence on water treatment processes and water quality determined.

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