GUIDELINES FOR THE SELECTION AND EFFECTIVE USE OF OZONE IN WATER TREATMENT

by

R Rajagopaul, NW Mbongwa and C Nadan

on behalf of

Umgeni Water

Report to the Water Research Commission on the project "Guidelines for the selection and effective use of ozone in water treatment"

WRC Report No 1596/01/08
ISBN 978-1-77005-740-1

August 2008

DISCLAIMER

Executive summary

The use of ozone as a pre-oxidant for water treatment is gaining momentum in South Africa. A case study has indicated that there are five waterworks in South Africa, where ozone is used successfully as a pre-oxidant for the treatment of raw waters with high levels of iron and manganese, colour through presence of humic acids, taste and odour, chlorophyll'a'. Because ozonation is energy intensive and also has the potential to form harmful disinfection by-products (DBP), the ozone option should be based on a systematic and rigorous approach.

Life cycle assessment in the selection of water treatment processes indicated that the most energy intensive process in a conventional water treatment chain is ozonation. Ozone production and operation accounted for about 35% of the total energy consumption of the treatment works (Friedrich and Buckley, 2002). The study further indicated that the operation stage is the most energy and material intensive stage in the life cycle.

The same study found that environmental burdens of producing potable water may be traced back to the consumption of electricity and that there was a need to increase electricity efficiency during operation (starting with the unit processes that consume the highest electricity).

In the short term, there is a need to lower potable water production costs so the safe drinking water is accessible to all. All efforts to cut unnecessary costs will be welcome, especially by water providers who have a fairly large proportion of consumers that only use the free 6000 litres per month.

A user friendly, practical guide, that summarises the rationale for the inclusion of pre-oxidation in the water treatment train, selection of an appropriate oxidant for the application, and operational strategies for the cost-effective use of ozone in water treatment, has been compiled. The guideline also assists in the selection of hardware that includes oxygen feed source and preparation, ozone generation, contacting and destruction.

The cost-effective operation of the ozonation process depends on four factors, viz, ozone production, ozone dose, ozone contacting and ozone destruction. This study focused on a holistic approach to the use of ozone in water treatment as an oxidant in the pre-treatment or intermediate stages of the water treatment train. The control and optimization of ozone dose based on raw water inflow quality was also investigated on a laboratory batch scale.

The main aim of the project was to develop a simple guideline for the cost-effective use of ozone in water treatment application. The following objectives were set to achieve the project aim:

- To conduct a comprehensive literature survey of international and local practices of ozone application to water treatment and develop a user friendly guide for the cost effective use of ozone in water treatment.
- To develop a means of determining the required ozone dose responding to changing raw water quality.

Laboratory scale work was conducted at the Wiggins Process Evaluation Facility (PEF) to develop analytical procedures for determining required ozone dose and develop a reliable means of controlling ozone dose.

A survey of South African ozone users for water treatment was conducted to establish a South African ozone perspective and operating philosophy. The principal users of ozone for water treatment included Umgeni Water's Wiggins Waterworks, Durban Recycle designed and operated by Veolia Water, Midvaal Water Company and Magalies Water's, Vaalkop Waterworks.

Products Emanating from the Project

At the inaugural project meeting, the Steering Committee suggested that the main product emanating from the research work, should be a user friendly guideline for the application of ozone to water treatment. Therefore the research on the project focused on the guidelines.

The guidelines serve as an ozone checklist for water treatment practitioners, faced with the prospect of specifying a suitable oxidant for either the pre-treatment or intermediate stage in the water treatment train. Guidelines, by nature, are by no means exhaustive or self sufficient. The matrix of conditions for individual applications may be different. A general rule of thumb is for a feasibility study incorporating the different oxidants available for water treatment application and related costs to be undertaken at a desktop level. From the outcome of the feasibility tests, on-site ozone demand trials need to be carried out before ozone requirements and design parameters are confirmed.

The structure of the guideline for ozone use in water treatment is as follows:

- *Criteria for selection. Why ozone?* This section deals with the commonly used oxidants in the water treatment industry and a summary of their main characteristics. A very brief description of some criteria to consider when selecting an oxidant is also given.
- *Design considerations:* This section deal with the basic information that the design engineer would require (viz. the ozone demand, points of application of ozone in the treatment process and contact time), with treatability tests (which are used to obtain the data to be used in the design process) and selection of materials of construction.
- *Ozone equipment selection:* A description of the choice of feed gas supply, methods of ozone generation (with the focus on corona discharge or UV technology), ozone contacting and ozone destruction is given in this section.
- *Operation strategies for cost-effective and safe operation of the ozone plant:* This section highlights some operational challenges associated with the unit processes that constitute the ozone system. Some local operational experiences are included in the relevant sections to guide the user towards good operational practice.

The concept of instantaneous ozone demand, for the prediction of required ozone dose was investigated and applied to local raw water conditions as a means of optimizing ozone dose, based on variable raw water quality. Ozone demand tests using the gas ozone test (GOT) procedure, are not accurate enough for ozone dose control when ozone is used for oxidation. Instantaneous ozone demand (ID) using the solution ozone test (SOT) technique was more reliable in predicting optimum ozone, based on reduction/removal of target micro-pollutants. An optimum ozone dose may be established on a laboratory scale for the particular raw water, based on the acceptable concentration of the micro-pollutant of interest in the final water. The ID can be directly related to residual ozone concentration. It is possible to control the ozone dose, based on raw water quality, by linking ozone dose to a set-point residual ozone concentration in the ozonated water.

A survey on ozone use in the South African water industry showed that ozone use locally is growing rapidly especially as a pre-oxidant in the pre-treatment and intermediate stages of the water treatment process train.

Ozone for final disinfection is not preferred over chlorine due to the short half life of ozone especially in water. Current DWAF regulations and guidelines for potable drinking water standards are based on accepted levels of chlorine residuals.

The plant survey conducted on the larger waterworks in South Africa that use ozone indicated the following:

- Ozone was used predominantly as an oxidant in the pre-treatment or intermediate stages of the water treatment process train.
- Ozone had a positive effect on the final water quality. However, in most cases, process monitoring data was unreliable or inadequate to quantify ozone benefits on down stream processes and chemical /operating costs.

The survey also highlighted some local challenges in the cost-effective operation of an ozone plant. The main challenges were in the operation and maintenance of the ozone plant.

- Most ozone plants were not operated optimally or cost-effectively due to a combination of reasons that included the following:
  - Maintenance issues were not resolved timeously.
  - There was no local or easily accessible expertise to handle technical problems that were beyond the operator or general maintenance personnel.
  - Changes in raw water conditions that effectively did not require ozone. The ozone plant was operated just to avoid start-up and other mechanical problems associated with frequent stoppages and long plant down times.
  - General process expertise in waterworks operations did not appear to be sufficient to operate a sophisticated ozone plant.
- Most waterworks did not have reliable on-line ozone analysers. This made process optimization and ozone removal target setting a huge challenge.

It is recommended that operations and maintenance personnel are adequately trained in the optimization of the ozone plant and troubleshooting ozone process problems. These relate mainly to the following aspects:

- Calibration and maintenance of analytical process control instrumentation including dewpoint analyser, ozone analyser (gas and liquid medium), gas flowmeters, and pressure gauges.
- A good practical understanding of the process control philosophy (including safety interlocks) inherent in a medium to large ozone installation.
- Collection of reliable process operating data including and continuous quality control monitoring that may be used to optimise ozonation and sustain cost-effectiveness of ozone.
- Conduct laboratory scale ozone instantaneous demand tests to check ozone dose and calibrate on-line ozone dose control in the full-scale plant.
- Use operational and quality control data to decide on the continuous operation of the ozone plant. There may be a significant energy and cost saving if the operation of the ozone plant is linked to raw and final water quality. Where there is no water quality or process enhancement incentive for the use of ozone, the ozone plant should only be operated at scheduled intervals for equipment maintenance reasons.

Further work is recommended for the collection of reliable full-scale process data that may be used to assess the long term advantages and disadvantages of ozone in the water industry. Interaction with water treatment personnel that use ozone for water treatment, indicated that Waterworks using ozone should be encouraged to co-operate with other ozone users in the industry and form an ‘Ozone User Forum’ where information with respect to ozone experience, new technology and data can be shared.

Further work in the use of instantaneous ozone demand for the control of ozone dose based on raw water quality should be considered. This can be investigated on a pilot plant scale leading to full-scale plant trials and application.

Acknowledgements

The financing of the project by the Water Research Commission and the contribution of the steering committee is gratefully acknowledged.

The steering Committee responsible for this project consisted of the following persons:

Dr G Offringa (Chairman)	Water Research Commission
Dr GE Rencken	VWS Envig
Mr D Nozaic	D Nozaic cc
Mrs Marina Krüger	Midvaal Water Co
Mr M Docrat	Umgeni Water
Mr V Botes	Umhlatuze Water
Mr P Thompson	Umgeni Water

Further assistance provided by the following institutions is also acknowledged:

Umgeni Water
Durban Water Recycling
Midvaal Water
Magalies Water

<u>The Project Team comprised the following:</u>

R Rajagopaul (Project Leader)
N Mbongwa (Researcher)
Late Christine Nadan (Researcher)

The Project Team and the Steering Committee pay tribute to the Late Christine Nadan and acknowledge, with gratitude and thanks, her valuable contribution to the project.

Table of Contents

List of Figures

List of Tables

1. Introduction

1.1. OZONE IN WATER TREATMENT: OXIDATION, DISINFECTION

Ozone, a powerful oxidizing agent is very unstable and has a relatively short half life in water compared to other oxidizing agents (Pontius, 1990). Ozone stability is affected by a number of factors, including temperature, ozone concentration, mass transfer, etc. (Quederin et al., 1996).

Ozone in water treatment has been effective in a number of applications, including (Geering, 1999):

- Bacterial disinfection and virus inactivation;
- Oxidation of iron and manganese;
- Color and odor removal;
- Elimination of algae and oxidation of organic substances;
- Micro-flocculation of organic substances.

Moreover, ozone has an advantage over chlorine as a disinfectant, as chlorine is know to form disinfection by-products e.g. trihalomethanes (THMs). In practice ozone is used as a primary disinfectant followed by chlorine as a final disinfectant due to poor ozone residual stability in water. Other advantages of ozone in water include enhancement in coagulation, settling and filtration, and the sparkling appearance of the ozone treated water.

1.2. MOTIVATION FOR THE RESEARCH

Nutrient loading in raw water sources in South Africa has necessitated the use of pre-oxidants in the affected water and waste water works in South Africa. Ozone is applied for its oxidative ability as well as its disinfection properties. There is also a rapidly expanding market in the small scale ozone systems that are being marketed for disinfection of pools, air purification and other applications.

Life cycle assessment in the selection of water treatment processes indicated that the most energy intensive process in a conventional water treatment chain is ozonation. Ozone production and operation accounted for about 35% of the total energy consumption of a full-scale conventional treatment works (Friedrich and Buckley, 2002). The study further indicated that the operation stage is the most energy and material intensive stage in the life cycle.

The study also reported that environmental burdens of producing potable water are traced back to the consumption of electricity and that there was a need to increase electricity efficiency during operation (starting with the unit processes that consume the highest electricity).

In the short term, there is a need to lower potable water production costs so that safe drinking water is accessible to all. All efforts to cut unnecessary costs will be welcome, especially by water providers who have a fairly large proportion of consumers that only use the free 6000 litres per month.

Project Focus / Scope
The cost-effective operation of the ozonation process depends on four factors, viz, ozone production, ozone dose, ozone contacting and ozone destruction. The Steering Committee suggestions with respect to the focus of the project were adopted. The suggestions included a study focused on a holistic approach to the use of ozone in water treatment as an oxidant in the pre-treatment or intermediate stages of the water treatment chain, guidelines for the use of ozone in water treatment with particular emphasis on the South African perspective. The control and optimization of ozone dose based on raw water inflow quality was also investigated on a laboratory batch scale.

1.3. OBJECTIVES

The main aim of the project was to develop a simple guideline for the selection and cost-effective use of ozone in water treatment applications. The following objectives were set to achieve the project aim.

- To conduct a comprehensive literature survey of international and local practices of ozone application to water treatment and develop a user friendly guide for the cost effective use of ozone in water treatment.
- To develop a means of determining the required ozone dose responding to changing raw water quality.

1.4. METHODOLOGY

The methodology for the project included the following:

- Extensive literature survey of the latest trends in the use of ozone, including hardware used in the ozonation process, both locally and internationally.

- A comprehensive survey of local ozone users was conducted. Four large ozone users were identified and operating data was collected from the participating waterworks to establish the benefits of ozone, cost implications, challenges experienced and possible solutions.

- The last component of the project was to develop a simple analytical tool that would assist in the optimization of ozone dose on the basis of raw water quality. Laboratory scale work was conducted at the Wiggins Process Evaluation Facility (PEF) to develop analytical procedures for determining the required ozone dose for a particular application and develop a reliable means of controlling ozone dose.

Three Waterworks in South Africa were selected for the laboratory scale trials based on the following criteria:

- ***Full-scale ozone plants*****:** The three Waterworks selected, viz, Wiggins Waterworks, Durban Water Recycling and Midvaal Water, had fully operational ozone plants.

- ***Raw water quality*****:** Each Waterworks had a different objective for using ozone. Wiggins Waterworks used ozone for the control of taste and odour problems, algae, iron and manganese removal. Durban Water Recycling employed ozone for colour reduction prior to final polishing through granular activated carbon.

***Raw water source*:** Wiggins Waterworks obtained its raw water from an impounded source, Inanda Dam. Midvaal Waterworks treats predominantly river water, while Durban Water Recycling Plant uses ozone at the tertiary treatment stage of the wastewater works.

2. Guidelines for Ozone use in Water Treatment

The guidelines serve as an ozone checklist for water treatment practitioners, faced with the prospect of specifying a suitable oxidant for either the pre-treatment or intermediate stage in the water treatment chain. Guidelines, by nature, are by no means exhaustive or self sufficient. The matrix of conditions for individual applications may be different. A general rule of thumb is for a feasibility study incorporating the different oxidants available for water treatment application and related costs to be undertaken at a desktop level. From the outcome of the feasibility tests, on-site ozone demand trials to be carried out before ozone requirements and design parameters are confirmed.

The structure of the guideline for ozone use in water treatment is as follows:

- ***Criteria for selection. Why ozone?*** This section deals with the commonly used oxidants in the water treatment industry and a summary of their main characteristics. A very brief description of some criteria to consider when selecting an oxidant is also given.

- ***Design considerations:*** This section deal with the basic information that the design engineer would require (viz. the ozone demand, points of application of ozone in the treatment process and contact time), with treatability tests (which are used to obtain the data to be used in the design process) and selection of materials of construction.

- ***Ozone equipment selection:*** A description of the choice of feed gas supply, methods of ozone generation (with the focus on corona discharge or UV technology), ozone contacting and ozone destruction is given in this section.

- ***Operation strategies for cost-effective use of ozone:*** Some of the aspects dealt with in this section include the effect of cooling water on ozone generation efficiency, moisture minimisation techniques for keeping moisture out of the ozone generator, control instrumentation and control strategies (viz. those based on raw water flowrate, residual ozone monitoring, raw water quality and control strategies using gas flowrate and generation power).

- ***Safety considerations in the handling of oxygen and ozone:*** this section draws attention to the importance of safety training of operators and highlights some of the ozone system safety features.

2.1. CRITERIA FOR SELECTION – WHY OZONE?

Ozone generation is an energy intensive process. In addition, the gas itself is hazardous in nature. Therefore, the selection of ozone for use in the water treatment process must be carefully considered and weighed against other options available. Ozone may be used on its own as a pre-oxidant or in combination with other compatible oxidants. This section is aimed at assisting one firstly in deciding whether a pre-oxidant is required and then gives the characteristics of some of the commonly used oxidants in the water treatment industry to assist one in choosing the most suitable type of oxidant.

2.1.1. Selection of a suitable oxidant for the application

There is no general procedure for the selection of an oxidant as each case is usually different from the other and each case is to be treated on its own (2). Traditionally, laboratory scale trials were carried out to determine the most suitable oxidant to use. Also, the analysis of historical data of tests which may have been conducted on the raw water is also useful is choosing an oxidant.

A simple decision making tree is presented in Figure 2.1 on the next page, indicating some of the questions that needs to be asked before deciding whether a pre-oxidant is required.

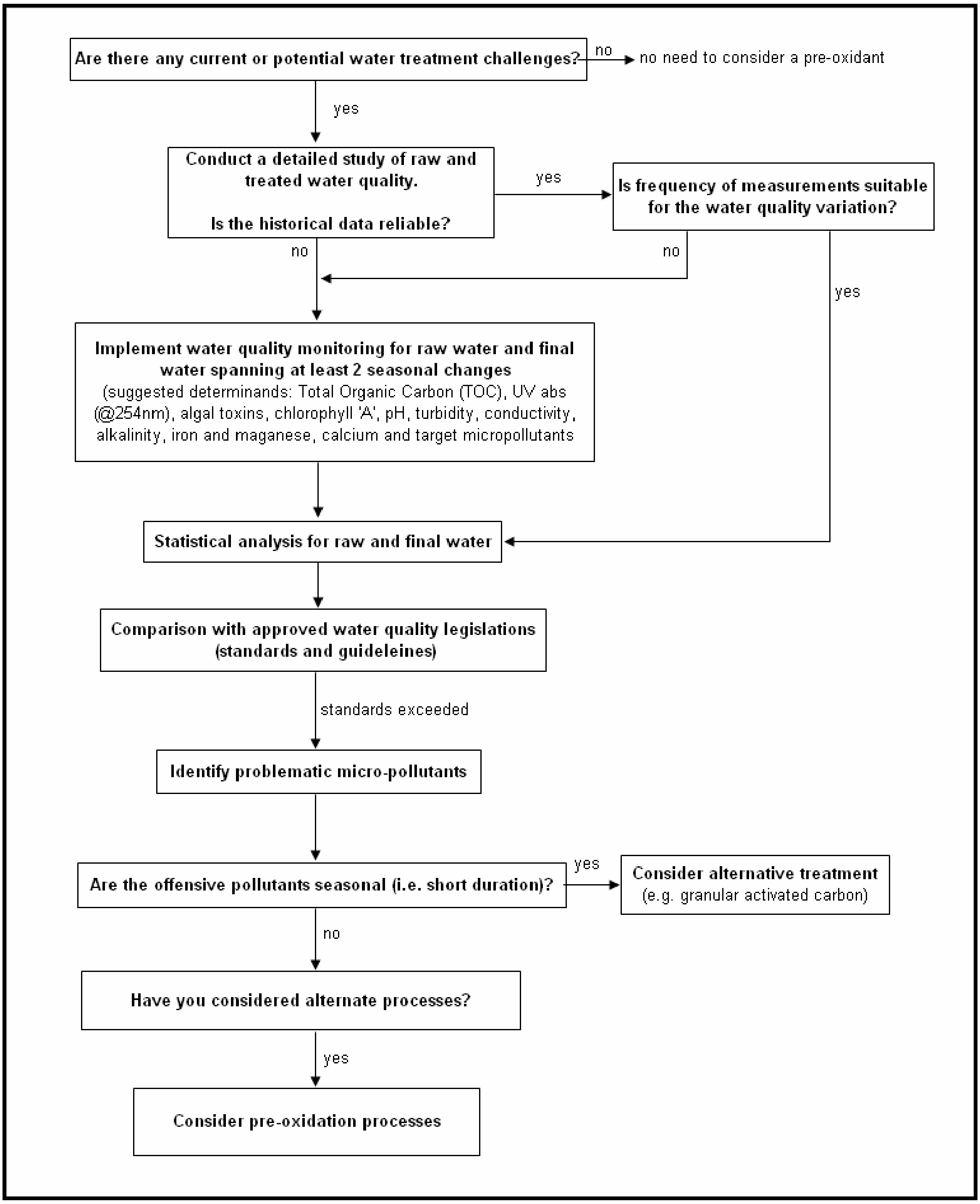


Figure 2.1: Decision making tree to be used to decide whether a pre-oxidant is required

2.1.2. Commonly used oxidants in the water treatment industry

Four main oxidants used in water treatment are:

- Chlorine
- Ozone
- Chlorine dioxide
- Potassium permanganate

The selection of the appropriate oxidant depends on the type and concentration of target micro-pollutants. The following gives a summary of the reaction characteristics of each type of oxidant for the removal/reduction of various micro-pollutants.

Table 2.1: Iron and manganese removal

Oxidant	Iron	Manganese	Interfering substance
Chlorine	Rapid reaction with uncomplexed Fe	Oxidation less efficient than for iron oxidation	Inefficient for complexed Fe and Mn.
Chlorine dioxide	Rapid oxidation for uncomplexed Fe	Rapid oxidation for uncomplexed Mn	Presence of DOC
Potassium Permanganate	Rapid oxidation for uncomplexed Fe	Rapid oxidation for uncomplexed Mn	Presence of DOC
Ozone	Can also oxidise Fe^{2+} complexes	Can also oxidise Mn^{2+} complexes	Presence of organic matter requires higher ozone doses.

Table 2.2: Colour removal

Oxidant	Colour	Interfering Substances
Chlorine	Satisfactory Colour reduction	Fulvic or humic acids Consume large amounts Of chlorine and form halogenated Compounds, TTHMs
Chlorine Dioxide	Not generally used for colour removal	Problematic generation / hazardous
Potassium Permanganate	Satisfactory colour reduction	Long contact times
Ozone	Preozonation intermediate or both, 3 -6 min contact time, Most promising, needs laboratory /pilot plant studies	Ozone required for colour removal can be very high, when colour is due to humic substances.

Table 2.3: Taste and odour control

Oxidant	Taste and Odour	Interfering Substances
Chlorine	Can be used in some cases.	Can form odours by itself and its by-products
Chlorine Dioxide	Not generally used	By-products can be toxic
Potassium Permanganate	May be effective at high concentrations	Relatively ineffective at oxidizing geosmin or MIB
Ozone	More effective than other oxidants. Most effective in removal of geosmin and MIB	Little effect on saturated odour forming compounds.

Table 2.4: Algae removal

Oxidant	Algae	Interfering Substances
Chlorine	Excellent algae reduction	TTHMs, May create secondary odour development
Chlorine Dioxide	Excellent algae reduction	May create secondary odour development
Potassium Permanganate	Requires relatively long reaction times (60 min)	
Ozone	Excellent algae reduction (5 min reaction time) Inactivation of certain zooplankton	High algae require pretreatment (flotation) before ozone.

The comparison of the typical oxidants may be further explored on the basis of:

- Process requirements and complexity
- Operational requirements and complexity
- Safety, health, environmental and quality
- Budget costs (Capital, operational costs - chemical, electricity, scheduled component replacement, general maintenance)

Table 2.5 gives a brief comparison of various types of oxidants used in the water treatment industry. The aforementioned criteria to consider when selecting an oxidant are considered in the table below.

Table 2.5: Comparison of oxidants

(obtained from the website:** http://www.americanchemistry.com/s_chlorine/sec_content.asp?CID=1133&DID=4530&CTYPEID=109 **)

Disinfectant	Cost	Safety/handling
Chlorine Gas	- Highly effective against most pathogens - Provides "residual" protection required for drinking water - Operationally the most reliable - Generally the most cost-effective option	- Byproduct formation (THMs, Haloacetic Acids) - Special operator training needed - Not effective against Cryptosporidium
Chlorine dioxide	- Effective against Cryptosporidium - No formation of THMs, Haloacetic acids - Provides better taste and odor control than chlorination	- Byproduct Formation (chlorite, chlorate) - Requires on-site generation equipment and handling of chemicals - Generally higher cost than chlorine
Ozone	- Produces no chlorinated THMs, Haloacetic Acids - Fewer safety regulations - Effective against Cryptosporidium - Provides better taste and odor control than chlorination	- More complicated than chlorine or UV systems - No residual protection for drinking water - Hazardous gas requires special handling - Byproduct formation (bromate, brominated organics and ketones) - Generally higher cost than chlorine

2.2. DESIGN CONSIDERATIONS

The installation of an ozone system as a unit process in the water treatment train will have a significant impact on down stream processes, including coagulation flocculation, filtration and disinfection by-products. Generally, ozone has a beneficial effect on downstream processes and the inclusion of ozone is known to reduce construction costs of some down stream processes.

2.2.1. Data required for design

The major components of an ozonation system include preparation and treatment of the feed gas to the ozone generator, the ozone generator (incorporating the power supply unit and cooling water system), ozone dose strategy, ozone contacting and ozone destruction. As a starting point, a design engineer requires the following basic information:

(i) Ozone demand (maximum, average and minimum)

Total ozone demand consists of three factors (3)

- Decomposition of ozone to oxygen
- Conversion of ozone molecules to hydroxyl radicals – rapid at high pH
- Reaction with oxidizable constituents in the water

A fairly current and accurate knowledge of the ozone dose requirement for the water to be treated is most important for the design of the ozone generator and contacting system. The overall ozone demand is water quality specific and may vary widely with season and temperature (1).

(ii) Point/s of ozone application in treatment train

Ozone may be added at a single point or at multiple points in a process train. The treatment objectives generally dictate where ozone is dosed. The best point for ozone addition would be the one that satisfies the treatment objectives at the lowest cost. For instance, ozone dosing for controlling algal / chlorophyll 'a' may be dosed at two points, after DAF for algal reduction and between clarification and secondary coagulation for chlorophyll 'a' reduction. A brief description of pre-ozonation and intermediate ozonation is given below.

<u>Pre-ozonation:</u> Pre-ozonation refers to the addition of ozone to the raw water prior to coagulation. Pre-ozonation has the following advantages:

- Oxidation of inorganic compounds, iron, manganese, nitrite, cyanide and hydrogen sulphide.
- Oxidation of colour forming organic compounds
- Oxidation of synthetic compounds including pesticides and solvents
- Advanced oxidation of complex organic compounds (Methyl isoborneol (MIB), geosmin)
- Can reduce coagulant demand (Alum or ferric)
- Enhance micro-flocculation
- Reduce chlorine demand

Intermediate ozone: Ozonation of clarified water prior to filtration. Used when raw water quality is poor and ozone demand is high. Intermediate ozone has the following advantages

- Lower ozone demand – organic load reduced through
- Conventional treatment prior to ozone addition
- Improved filtration
- Improved aesthetic quality of water

(iii) Contact time (maximum, average, minimum)

Contact times depend on the treatment objectives. Ozone oxidation reactions with easily oxidizable organics require a shorter contact time, than disinfection with ozone. Therefore, contacting time for ozone disinfection will be controlled by disinfection requirement. For oxidation, contacting time is less important than the amount of ozone transferred during the contact time. The results of treatability tests, done on the effect of contacting time (6, 9 and 12 minutes) for the removal of the taste and odour compound, 2-methyl-isoborneol (MIB), indicated that MIB removal was fairly insensitive to contacting time (1).

An important finding (54) was that mixing intensity and rate of transfer can have a significant effect on contacting time. An in-line mixer and contacting system was able to achieve approximately the same colour removal with an equivalent ozone dose in 30 seconds, compared to a conventional contact column with 4 minutes detention time.

2.2.2. Methods of obtaining the data for design

There are a number of ways that important design data may be obtained. These include the following:

- Treatability studies with the same or similar water.
- Treatment plant experience on the same or similar water
- An educated guess based literature, discussions with other experienced professionals

As far as possible design data should be from plant experience on the same water, otherwise the design would be more conservative than if accurate data of the application requirements are available. A very conservative design may result in additional operating costs caused by inefficient operation. Given the importance of reliable process information and engineering data, it follows that treatability tests will form an integral part of the engineering design. The outcomes of the treatability tests would form the basis of the ozone facility design including process selection. The recommendations from the treatability study should provide sufficient information for the designer to size equipment, provide operational flexibility, in the most economically cost-effective manner.

Study objectives: What is ozone expected to achieve?

↓

Experiemental Plan:

- Apparatus
- Analytical techniques
- Process parameters to be varied
- Sampling location, number
- Scale of study:
  - *Bench scale: 0.5 - 1L samples*
  - *Pilot scale: 5 - 100 L/min*
  - *Demo plant: > 100 L/min*

↓

Study approach (based on objectives of the ozone application)

- Ozone dosing point
- Ozone dose
- Contact time
- Ozone by-products in water
- Downstream effects
- Site specific considerations
  - *Effect of the variability of raw water characteristics*
  - *Seasonal and annual raw water changes*
- Preliminary treatability study plan (no generic study plan)
- List of considerations
  - *Treatment characteristcs and parameters to be detrmined*
    - Ozone characteristics
    - Residual ozone vs transferred ozone
    - Effect of ozone application on downstream treatment
    - Ozone efficiency and effect at different locations in the treatment train
    - Special contcat considerations, in line mixing
  - *Testing periods and duration*
    - Seasonal changes in raw water
    - Testing at extreme raw water conditions
    - Testing duration: 6-10 weeks for initial testing and
    - >4 weeks for subsequent testing for seasonal/special occurences

↓

Parameters to be measured

- Ozone gas flow
- ozone feed gas concentration
- ozone off-gas concentration
- ozone residual
- ozone transfer efficiency
- Instantaneous ozone demand

↓

Treatment parameters to be measured are dictated by the planned ozone application e.g.

- color removal
- Iron and maganese oxidation
- Oxidation of taste and odour compounds
- Algae and chlorophyll 'A' oxidation
- UV absorbance at 254nm

2.2.3. Material selection for ozone systems

Ozone, as a powerful oxidizing agent, is by nature a corrosive chemical. Equipment that come in contact with ozone, both in the vapour phase and liquid phase (ozone dissolved in water), need to be carefully selected so that they are ozone resistant at best or known degree of corrosion at the least. Table 2.6 provides a summary of suggested materials of construction for the unit processes that make up the ozone system.

Table 2.6: Materials of construction for unit processes making up ozone system

Unit Process	Material of construction	Comment
Air feed	As for conventional compressors, dryers	For pipework to the ozone generators stainless steel 316
High purity oxygen feed gas	Stainless steel 316	Stainless steel 316L for welds
Ozone generators	Stainless steel 316L for welds	Stainless steel 316L for welds
Ozonised gas piping systems (dry)	Minimum stainless steel 304	Stainless steel 316L for welds
Ozonised gas piping system (wet)	Stainless steel 316	Stainless steel 316L for welds
Contact tanks	Civil contractor to advise	
Submerged concrete and water stops	Type 2 or type 5 Portland cement for water bearing structures	Hypalon or stainless steel gas seals
Gas space concrete, gas stops, gas sealing	Type 2 or type 5 Portland cement for water bearing structures	Stainless steel or terflon gas space seals
Ozone destruction systems	Stainless steel 316	Stainless steel 316L for welds
Electrical power cable protection	A PVC or stainless steel shroud to be provided as a shield between the electrical cable and ozonated water in the contactor.	

2.3. SELECTION OF OZONE EQUIPMENT

The major components of an ozone system for water treatment consist of the following:

- Air/oxygen feed
- Ozone generation
- Ozone dosing and contacting
- Ozone dose control
- Ozone destruction

Figure 2.2 below, shows the main components of a typical ozone plant.

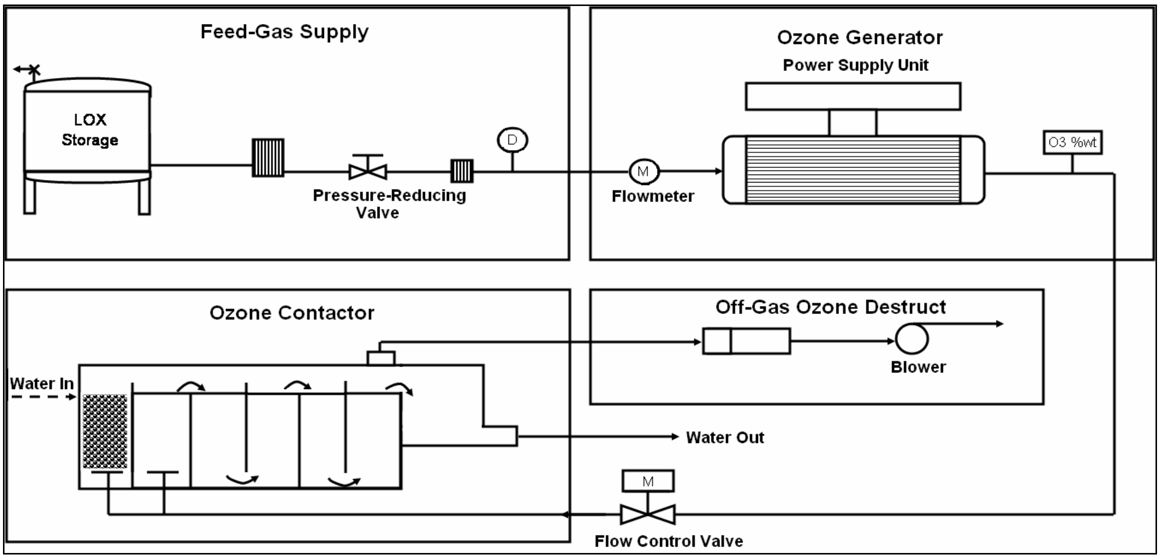


Figure 2.2: Major components of the generator system (Rakness, 1999)

2.3.1. Feed gas supply

There are several feed gas options that can be used in the generation of ozone. These include air, oxygen enriched air and high purity oxygen. Some systems use the mixture of air and high purity oxygen gas. The feed gas can be derived from atmospheric air on site or can be purchased from suppliers and stored on site. Each of these feed sources has attributes more suitable for particular ozone applications. Therefore feed gas selection should be made after careful consideration of factors which include:

- *Ozone requirement*: for smaller ozone plants, where the ozone requirements are low, it is generally more economical to use air as the feed gas supply. For larger plants, where more air would be sourced to meet the ozone requirements, it is generally inefficient to use air as the feed gas supply, as large amounts of dissolved air leads to problems such as air binding.
- *Aspects of the application*, including;
  - *Raw water with high ozone demand*: in this instance, oxygen would be the preferred feed source, as it would not be practical to use air when higher concentrations of ozone are required.
  - *Oxidation of easily oxidizable compounds*: in this instance, where less ozone would be required, air would generally be used as a source.
- *Operational and maintenance capabilities*: in situations where a strong operational and maintenance team is lacking, less maintenance intensive processes would be the preferred option. Liquid oxygen (LOX) systems are less complex than the air fed systems which use additional unit processes to sufficiently dry the feed gas.
- *Budgetary constraints*: cost estimates indicate that LOX-fed ozone systems have low capital and maintenance costs compared to air-fed systems (Rakness 2005).

- *Logistics*: environmental aspects such as the humidity of the air, transport costs, etc. would need to be considered when weighing the options of on-site generation of oxygen and the use of air as a feed gas.

Table 2.7: Advantages and disadvantages of various feed gas supply

Feed Gas	Advantages	Disadvantages
Air	More common More prevalent for small ozone systems	Problematic in dusty, high humidity conditions. Higher specific energy (kWh/kg O_3) Largest gas handling requirement Max O_3 concentration, 2.5% by weight.
High Purity Oxygen (LOX)	Simplest system Lowest specific energy (kWh/kg O_3) Least capital cost Most cost competitive with high efficiency generators	More popular Variable operational cost due to LOX purchase. Depending on location, transport costs may be prohibitive.
High Purity Oxygen (Cryogenic generation)	Suitable for large ozone applications	Capital intensive Complex to operate and maintain
High Purity Oxygen (Pressure swing adsorption, PSA, air separation)	Alternate to LOX in very small, small and medium ozone systems. Simple system	Energy costs and operating costs higher than for VPSA system
High Purity Oxygen (Vacuum swing adsorption, VSA, air separation)	Preferred over PSAs for larger ozone systems Lower operating and energy costs relative to PSA	High level of maintenance required

(i) On-site Oxygen Enrichment Processes

The two on-site oxygen enrichment processes, pressure swing adsorption (PSA) and vacuum pressure swing adsorption (VPSA) are similar in principle where water, hydrocarbons and nitrogen molecules are adsorbed under pressure while increasing the concentration of oxygen in the dry gas that passes through the system. The difference between PSA and VSA is in the complexity of equipment arrangement.

Pressure Swing Adsorption (PSA) System: The PSA system has less equipment and is suited for small ozone requirements. Energy and operating costs are higher than VPSA systems. Figure 2.3 is a schematic of a PSA system. The heatless desiccant dryer removes excessive moisture from the air stream. A molecular sieve adsorbs nitrogen, moisture and hydrocarbons allowing a dry oxygen enriched gas to flow into an oxygen receiver.

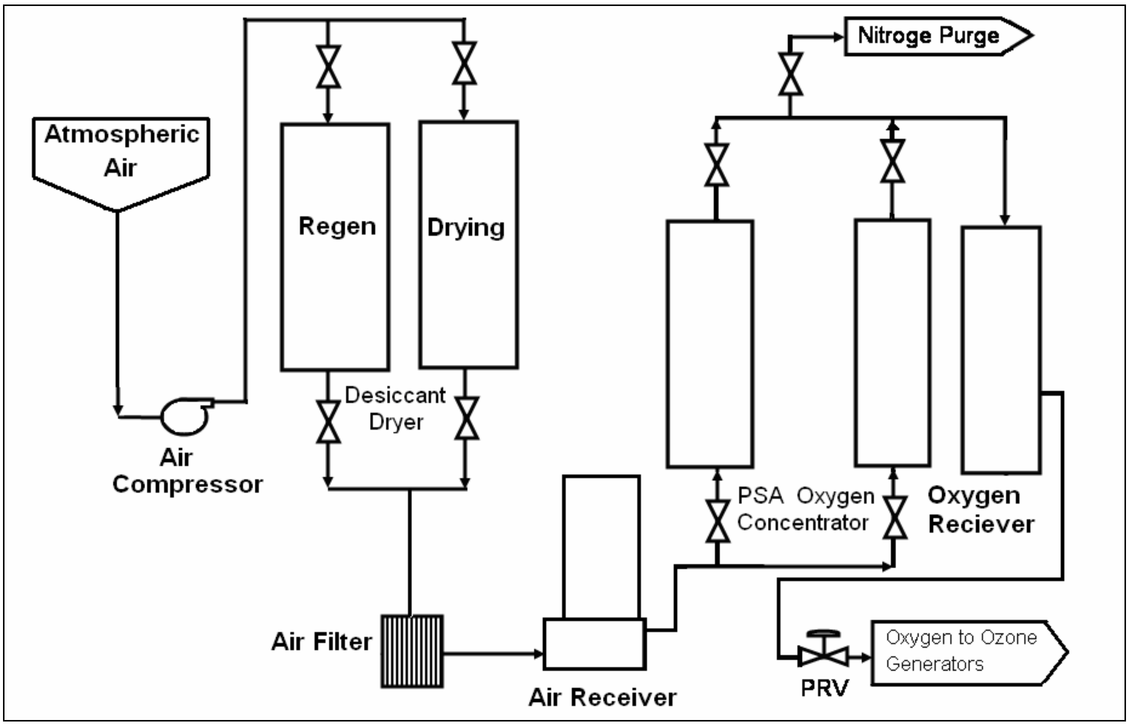


Figure 2.3: Pressure Swing Adsorption (PSA) system for generation of high purity oxygen feed (Rakness, 1999).

<u>Vacuum-Pressure Swing Adsorption (VPSA) System:</u> The VPSA system is a more complex equipment arrangement than the pressure swing adsorption system. The criteria for selection of an on-site VPSA system over LOX , is based on cost of LOX (Rands/ton) versus power production costs of the installed VPSA system in specific energy units, kW.day/ton and energy costs in kWh.

The VPSA system is similar to the PSA system, where moisture, hydrocarbons and nitrogen molecules are adsorbed into a molecular sieve media, allowing oxygen molecules to pass through. The adsorption stage, occurring under pressure, dries the gas and increases its oxygen content.

During the vacuum induced desorbtion stage, adsorbed moisture, hydrocarbons and nitrogen are purged from the molecular sieve and vented to atmosphere. Figure 2.4 shows a schematic of a VPSA system.

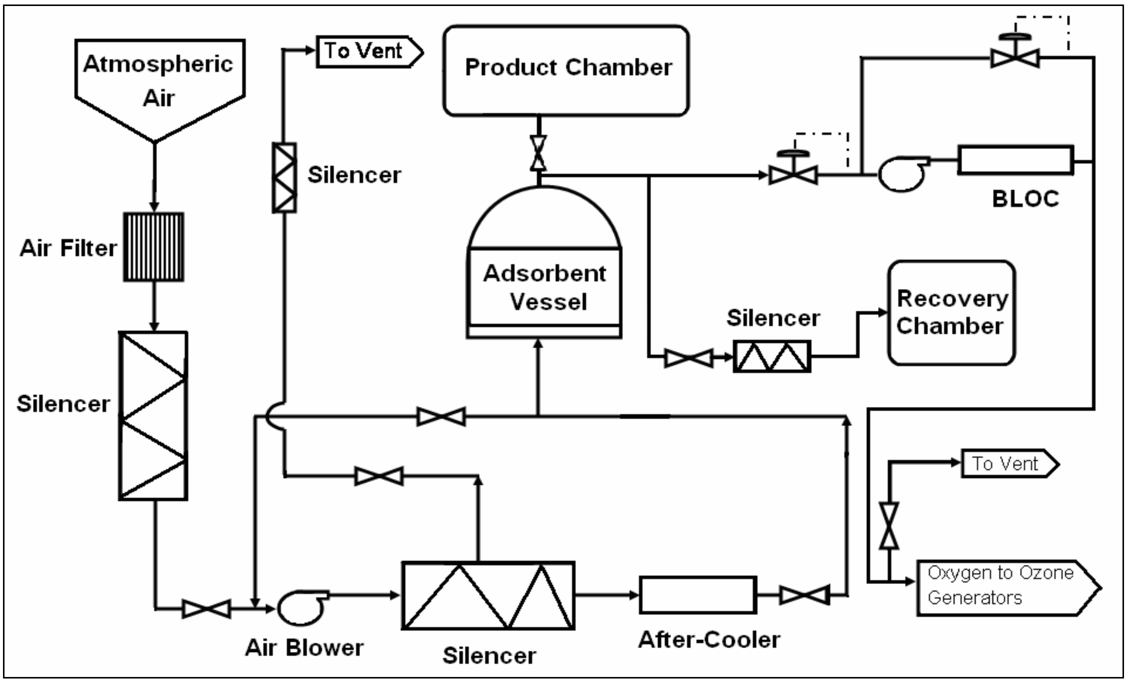


Figure 2.4: Vacuum Pressure Swing Adsorption (VPSA) system for generation of high purity oxygen feed (Rakness, 1999).

Some important factors that influence the choice of feed gas systems (air or oxygen) are tabulated in Table 2.8.

Table 2.8: Comparison between air-fed systems and oxygen fed systems

Feed Type	Air-fed systems	Oxygen-fed systems
Oxygen content	21 - 23 %wt.	95 to 98 %wt.
ozone concentration	1 to 4 %wt.	8 to 16 %wt.
Application	Confined space and where the use of high purity oxygen is hazardous. economical with low frequency generator	Compatible with high frequency generators. Large installations
Storage requirements	No air storage required Defrosting of ice on the pipeline is rare.	Liquid oxygen stored in vertical / horizontal tanks Tanks normally to store 15 days stock. Defrosting necessary Liquid oxygen (LOX) store at -98.1 ^{O}C. Alternative to vaporizers are water-bath vaporizers, which use cooling water from the generators. Tanks insulated to reduce temperature rise and liquid boil off. LOX boils off at a rate of 0.3 to 0.5 % of the tank capacity /day.
Gas flow	High air flow rate due to low oxygen content.	Low gas flow due to high purity oxygen.
Onsite site generation	Two types of air preparation systems *Low air-pressure system* *High-pressure system*	Two techniques for on-site production for high-purity oxygen. Vacuum-pressure swing adsorption (VPSA) Pressure swing adsorption (PSA) *Pressure swing adsorption (PSA) oxygen-fed ozone system*

In summary, oxygen fed ozone systems are lower in both capital and operating costs (2).

2.3.2. Ozone generation

Ozone is generated on site and used immediately after production, due to its instability and relatively short half-life (Pontius, 1990). Ozone is a naturally occurring allotrope of oxygen. The reaction for ozone formation is:

$$O_2 \quad + \quad Energy \quad \Leftrightarrow \quad O^- \quad + \quad O^- \qquad \ldots (2.1)$$

$$O^- \quad + \quad O_2 \quad \Leftrightarrow \quad O_3 \qquad \ldots (2.2)$$

(i) Methods of Ozone Generation

The main components of an ozone generation system are: power supply unit (PSU), ozone generator and a cooling water system. A suitable generation system is one that produces ozone in the required concentration range. Some methods of ozone generation are listed below, followed by a description of the most commonly used UV/corona discharge methods.

- Ultraviolet (UV) ozone generation
- Electrolytic generation:
- Radiochemical generation
- Corona discharge generation

<u>Corona discharge or UV</u>
The two most prevalent technologies for ozone generation are corona discharge (CD) and ultraviolet light (UV). Both technologies have advantages over one another (Teffeteller, 2000). However, CD is generally accepted as the preferred technology for potable water treatment. UV ozone generation offers initial economic benefits in non-potable water treatment, such as the spa industry.

Table 2.9: Comparison of ozone generation by UV and corona discharge (CD)

Parameter	Units	UV	CD
Maximum ozone production	g/KWh	1.94 (Using 185 nm bulb)	55 (from dry air)
*Concentration of ozone in output gas	g/m^3	1.8 (0.14 % wt)	12-60 (0.1 % to 4.8 % wt)
Energy required to generate 1 kg of ozone	KWh	44	6.8
Ozone production		Variable decline	Constant
Capital cost		Low	Moderate
Ozone stability		Very Low	High
Operating costs (Electricity)		High	Low

*The concentration of ozone gas is determined at a standard room temperature of 20°C and a standard pressure of 101 kPa. 1.0% by weight is equal to 12 g/m^3.

<u>Dielectric ozone generators</u>

The dielectric ozone generator is the most widely used system and is available in a range of sizes and configurations; including air-feed and oxygen feed units, with ozone concentrations ranging from 1 to 10 percent or higher. Ozone output can be controlled by adjusting the amount of gas that flows through the system or by changing the amount of electricity that is applied across the plates. Ozone generators with flat plate dielectrics are also capable of producing ozone at higher concentrations (up to 10 percent by weight) and offer users wider production ranges (60 to 70 % turn down capability) for greater operating flexibility. With higher ozone concentrations, relatively less feed gas is required, leading to lower operating costs.

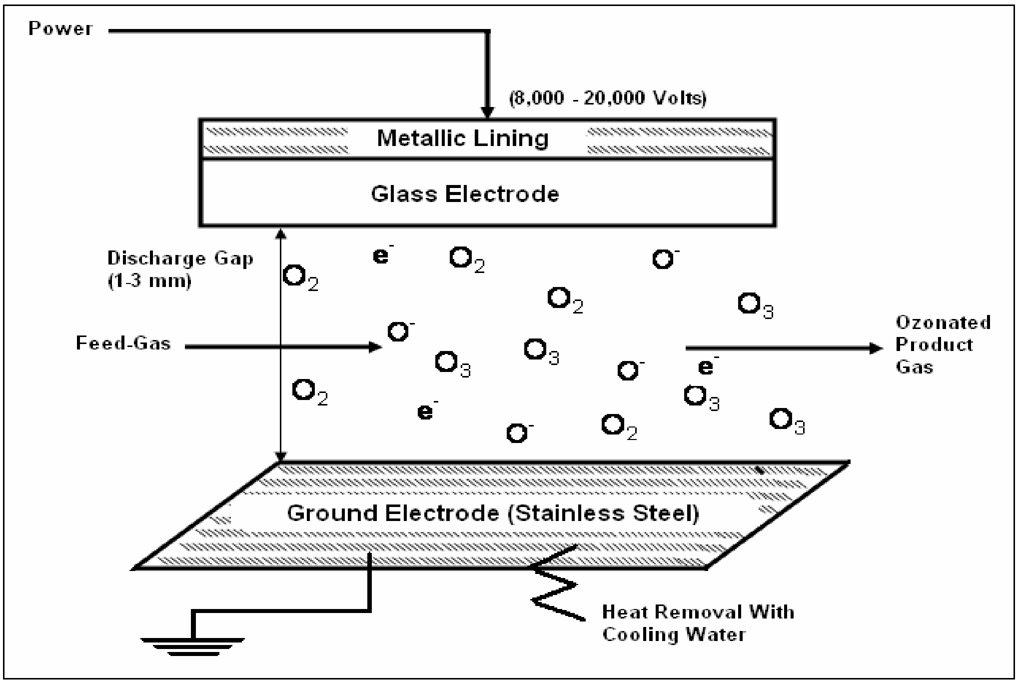


Figure 2.5: Dielectric ozone generator

Ozone is generated by passing dried, oxygen-containing gas through an electrical field. The electrical current causes the "split" in the oxygen molecules. There are three types of dielectric ozone generators:

- low frequency (50 to 100 Hz),
- medium frequency (100 to 1,000 Hz), and
- high frequency (>1,000 Hz).

Since 85% to 95% of the electrical energy supplied to a corona discharge ozone generator produces heat, heat removal is required.

The dielectric is at the heart of a corona discharge (CD) ozone system. The electrical charge is diffused over this dielectric surface, creating an electrical field, or "corona". Air preparation is critical to CD ozone systems.

The gas feeding the ozone generator must be very dry; minimum -26 ^{O}C (Rakness, 2005) because the presence of moisture affects ozone production and leads to the formation of nitric acid. Nitric acid is very corrosive to parts of a CD ozone generator, resulting in generator inefficiency and premature failure. The figure below shows that the relative ozone output decreases as dew point increases.

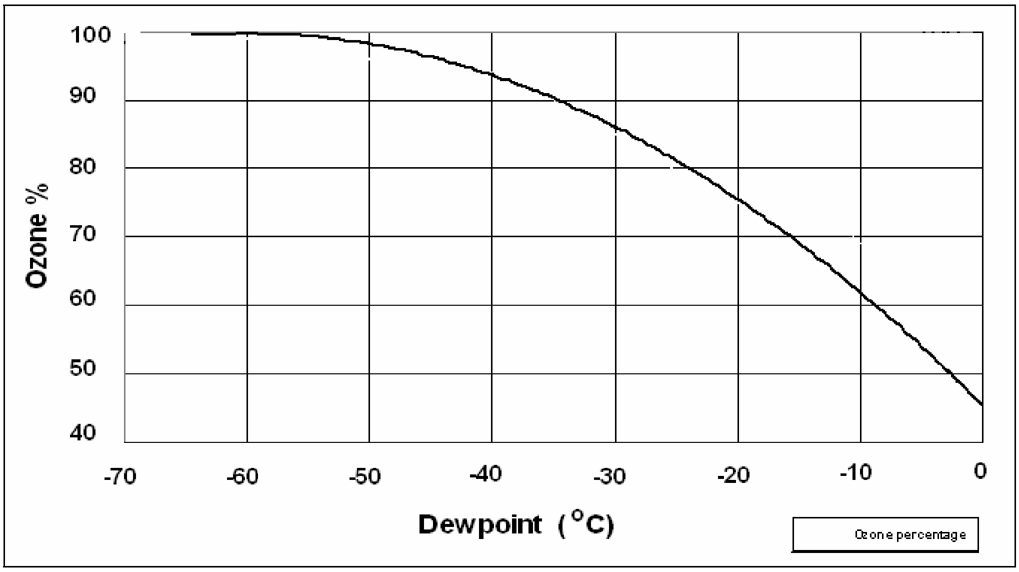


Figure 2.6: The relationship of the Relative Ozone Output and Air Dew point (www.ozoneapplications.com)

Ozone generation has undergone significant improvement in the past 15 to 20 years (2).

- Improvement in medium frequency ozone generators, have made it possible for increased ozone concentrations at lower oxygen flow without a rise in voltage levels that damage dielectrics.
- Ozone generator manufacturers have decreased discharge gap width, optimized dielectrics and PSUs to further increase ozone concentration and reduce energy consumption.

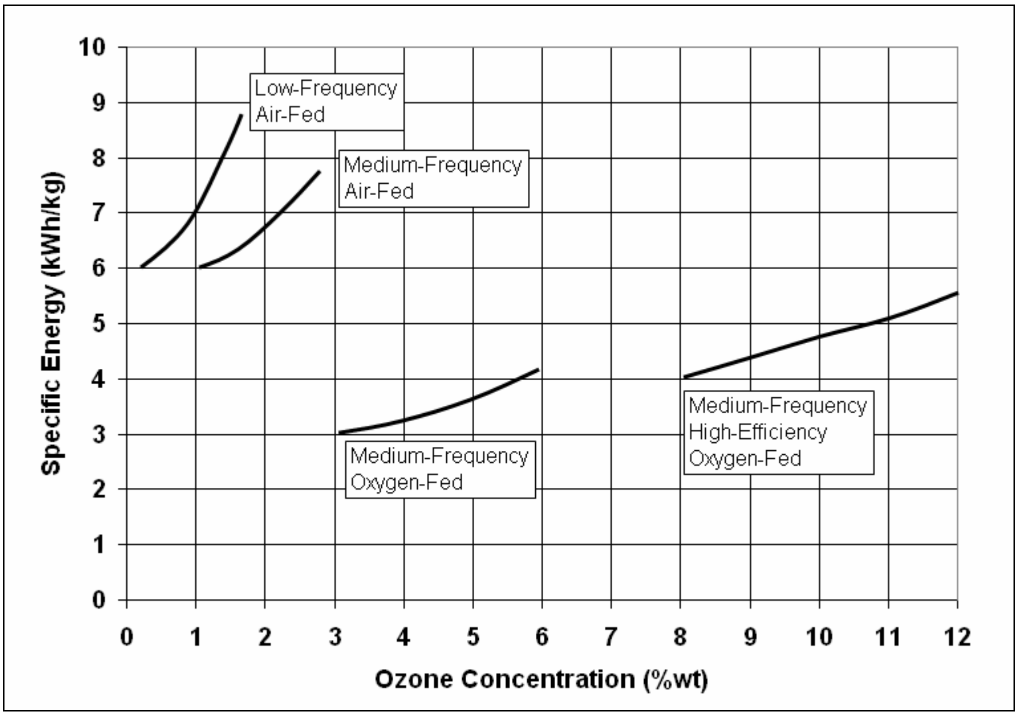


Figure 2.7: Ozone generator specific energy as a function of ozone concentration (Rakness, 1999).

Table 2.10: Comparison of characteristics of low, Medium and High Frequency generators (EPA Guidance Manual, 1999)

Characteristics	**Units**	**Low frequency (50-60 Hz)**	**Medium Frequency (up to 1000 Hz)**	**High Frequency (> 1000 Hz)**
Degree of electronic sophistication		low	High	High
Peak voltage	V	20	110	10
Turndown ratio		5:1	10:1	10:1
Cooling water required / mass of ozone produced	□/g	0.04 to 0.08	0.04 to 0.12	0.02 to 0.08
Typical application range	kg/day	< 200	Up to 900	Up to 900
Operating concentration wt-% in air wt-% in oxygen	%	 0.5 to 1.5 2.0 to 5.0	 1.0 to 2.5 2 to 12	 1.0 to 2.5 2 to 12
Optimum ozone production (as proportion of total generator capacity)	%	60 to 75	90 to 95	90 to 95
Optimum cooling water differential	^{O}C	-13 to -12	-15 to -13	-15 to -13
Power required Air feed Oxygen feed	kW-h/kg O_3	 18 to 26 9 to 13	 18 to 26 9 to 13	 18 to 26 9 to 13
Air feed system power requirements	kW-h/kg O_3	11 to 15	11 to 15	11 to 15

(ii) Advances in ozone generation technology

To meet the increased demand for more efficient ozone production with higher yields, ozone generator manufacturers have made significant technological improvements in their generators.

Ozone production efficiency of the conventional dielectric is limited by the poor heat transfer that is characteristic of the geometry of the cell design. Because of the nature of the conventional ozone dielectric cell, it is common to lose up to 10% of the glass dielectrics at startup or during cleaning from handling damage.

New technology features include the following:

- *The use of high-voltage stainless steel tube, lined with flint glass, as the outer ground electrode*. This allows for superior dielectric properties, greater accuracy and manufacturing consistency in both the high-voltage electrode and the glass lined ground electrode. The direct contact of the glass with the outer cell provides heat dissipation by conduction rather than convection. Heat is transferred to the cooling water side of the dielectric, resulting in lower operating temperatures. This helps reduce the natural tendency of ozone to disassociate at higher cell temperatures. The stainless steel electrode is removable. This eliminates the possibility of glass breakage during cleaning, a costly problem in conventional dielectric type generators.

- *For lower operating costs or higher concentrations of ozone, a dielectric cell has been developed with a secondary cooling system*. Unlike the standard cooling method, the secondary cooling system circulates water through the high-voltage electrode, too. With enhanced cooling, ozone concentrations of 10 - 16% are now possible, with almost the same power cost of non-enhanced Micro-Gap cells at lower output concentrations.

- *Modular generators for larger applications including municipal drinking water and wastewater applications are available.* These units can produce from 630 g to 29 kg O3/hr. (Carruthers, 1997). The ozone generator consists of a cylindrical vessel in which a number of stainless tubes are welded between two fixed plates in a compact arrangement. A coolant flows around the outside of the tubes to remove heat produced in the generation of ozone. The tubes serve as receptacles for calibrated high voltage electrodes with one tube and one high voltage electrode forming an ozone generating dielectric element. This method of construction prevents any possible contact of the coolant with the high voltage electrodes.

<u>Purion ozone generation technology in South Africa</u>
Ozone generators developed by PURION utilise corona discharge to create ozone. The discharge geometry is fundamentally different to other ozone generators in that a 'surface discharge' is generated occupying a flat area on the surface of the dielectric. Thin electrodes are fixed on the dielectric surface, and the corona discharge is formed on the surface. This has the advantage that ozone can escape the formation zone, and the discharge is easily cooled by water flow across the electrode counter surface. Unique dielectric materials are used, allowing very thin barriers and a concomitant reduction in the voltage required for corona discharge (2 to 3 kV), as well as very efficient cooling of the dielectric. The surface discharge allows the use of high frequency voltage application, with resulting higher ozone production efficiency, due to the superior cooling geometry. Novel high frequency power supply systems have been specially developed to drive the generator elements, allowing optimum matching of the supply output and the generator. Mathematical modelling of the corona discharge and ozone formation processes allows upscaling of the generator units to larger sizes.

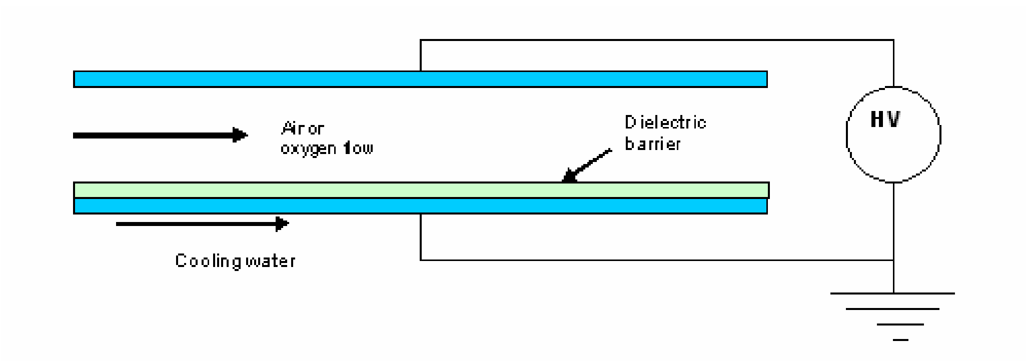


Figure 2.8: Schematic representation of the PURION ozone generator

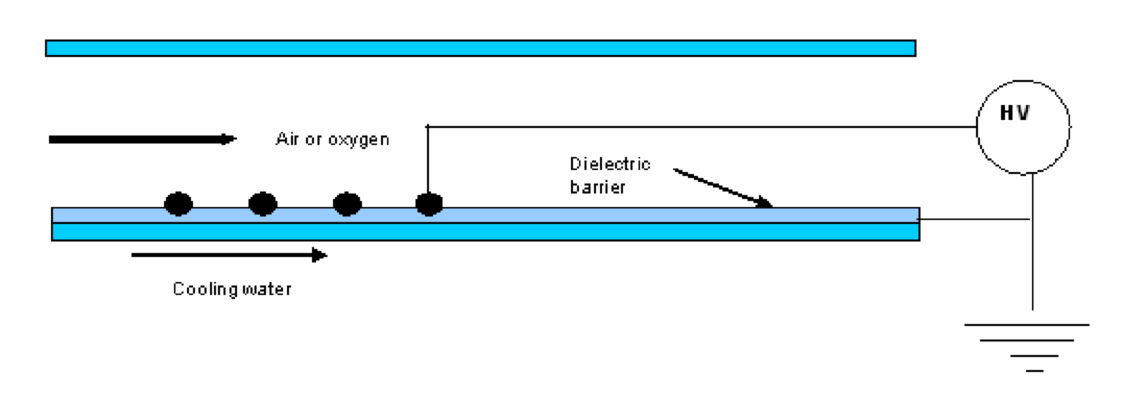


Figure 2.9: Schematic representation of PURION surface discharge technology

2.3.3. Ozone contacting

The mass transfer of ozone is affected by a number of parameters. These include temperature, pH and ionic strength, decomposition of ozone in gas and in water, concentration of ozone, volumetric gas/liquid ratio (V_g:V_L), etc. (Mazzi et al., 1995).

Transfer efficiency is an important parameter in the selection of an ozone contactor. Transfer efficiency is a measure of the quantity of ozone transferred into solution. It is determined by this mathematical expression:

$$Transfer\ Efficiency = \frac{O_3\ Dose - O_3\ residual - O_3\ in\ off\ gas}{O_3\ Dose} \qquad \text{… (2.3)}$$

Ozone contactor systems are responsible for the efficient transfer of ozone into the body of water to be treated. The four main ozone contactors are presented in Table 2.11.

Table 2.11: Comparison of ozone contactors

Ozone contactor	Description	Advantages	Disadvantages	Application
Static mixer	Helical or spiral flow mixing elements located inside a pipe tube.	Rapid ozone transfer (>99%) No moving parts Low Maintenance Low capex, opex	Requires pumping or higher head. Turndown capability limited to static mixer	Fe and Mn oxidation colour removal; taste and odour
Side stream venturi injector	Located outside the contactor Applicable to high ozone (10 -12 %) at low gas flow.	90% ozone transfer efficiency. Low maintenance costs than diffusers. Smaller contact tanks	Requires pumping Needs backflow prevention Turndown capability limited to venturi system	Fe and Mn oxidation; colour removal; taste and odour
Bubble diffuser	Diffusers consist of ceramic porous stones, stainless steel holders, and gasket seals.	85 to 95% ozone transfer efficiency	Not reliable for high ozone applications (12% wt) Particulate matter can block diffuser.	Primary disinfection; colour removal; taste and odour
Deep U tube	Two concentric vertical tubes of approximately 20m in depth. Ozone is injected in an orifice at the top of the inner tube and travels down with the water flow, exiting via the outer tube	High transfer efficiencies (95 to 99%). Relatively lower surface area requirements.	Limited operational experience Turn down capacities may be limited. Maintenance may be more difficult. Cost of drilling and excavation	colour removal; taste and odour; algae, chlorophyll'a'

In summary, literature review indicates that many types of contactors have been used for many applications but certain types of contacting systems have been more suited to particular applications (1).

2.3.4. Ozone Measurement

Accurate ozone measurement is very important for the safe and cost-effective operation of the ozone plant. However, the intrinsic nature of ozone makes ozone analysis, in the gas and liquid phase, difficult. Ozone decomposes in the gas phase but its decomposition is more rapid in aqueous phase. The volatility of the gas complicates the procurement of a representative sample. In addition, the stoichiometry of the reactions between ozone and many analytical reagents is uncertain.

Ozone measurement is also challenging due to its short half life and the two phases it is measured in (gas phase and liquid phase). In the gas phase, ozone concentrations are in the high range (typically 4 to 10% in an oxygen environment) and the very low range (in ambient atmosphere, as low as 0.01 mg/l). Ozone in the liquid phase, normally referred to as residual ozone in water, is in the 0 to 1 mg/l range. Ozone residual is the more problematic measurement.

Manual Gas Phase Measurement
The most common method for the determination of ozone in the gas phase is the iodometric titration method. A metered volume of gaseous ozone is bubbled into a solution of potassium iodide (KI). The iodine formed by the oxidation of KI is back titrated with standard sodium thiosulphate and the ozone concentration is calculated using the stoichiometry between ozone, sodium thiosulphate and potassium iodide. The approved method is available in standard methods for water and wastewater analysis (52).

Manual liquid Phase Measurement
The most reliable method for determination of residual ozone in water is a colorimetric technique, where a known volume of ozonated water is added to a know volume and concentration of potassium indigo trisulphonate. Ozone reaction with the potassium indigo trisulphonate results in a decrease in the intensity of the bright blue potassium indigo trisulphonate colour, quantified by absorbance measurements taken on a UV/VIS spectrophotometer. Without a properly designed sampling system, ozone measurements may be prone to errors.

On-line measurement – gas phase
A residual ozone analyzer is an effective tool for the control of ozone dosage. In this instance, the ozone production rate would be adjusted according to the residual ozone content of the contactor off gases. Generally, residual ozone concentration is used as a feed back signal to the ozonators to either increase or decrease ozone production.

Sophisticated on-line (gas phase) ozone measuring instruments are available. There are two general types of ozone analysers, one based on amperometry and the other is based on UV absorbance.

The analyser based on amperometry, has an electrochemical cell as a sensor, in which a gold cathode, silver anode and aqueous potassium bromide electrolyte are separated from the sample chamber by a gas permeable, water impermeable membrane. The overall reaction occurring at the cathode is:

$$O_3 \quad + \quad H_2O \quad + \quad 2e^- \quad \rightarrow \quad O_2 \quad + \quad 2OH^- \qquad \ldots(2.4)$$

and that at the anode :

$$Ag \quad + \quad KBr \quad \rightarrow \quad AgBr \quad + \quad K^+ \quad + \quad e^- \qquad \ldots(2.5)$$

The other type of ozone analyser, based on the principle of UV absorption, consists of two separate units, the ozomat WP (sample preparation) and the ozomat MP (ozone detection and microprocessing). The ozonated water sample enters the ozomat WP, where the flow rate and pressure is controlled by a levelling tank and ozone is stripped from the water sample in a desorption column packed with glass beads. The ozone (in air) then enters the ozone detection system, housed in the ozomat MP. Pressure and temperature measurements of the gas stream are taken before entering the sample cuvette, where ozone absorbs UV light proportional to the ozone concentration. The gas stream, after catalytic destruction of the ozone, flows into a reference cuvette, identical to the sample cuvette. Any impurities, in the gas stream, that absorb UV light, attenuate the intensity of the UV radiation immerging from the reference cuvette. The ratio of the UV light intensities from the sample cuvette (I) and the reference cuvette (I_0) is proportional to the ozone concentration according to the Beer-Lambert Law.

On-line Ozone Residual Measurement – liquid phase

Residual ozone concentration is an important control parameter that indicates whether or not adequate ozone is being dosed for the application. On-line residual analysers available are the membrane type analysers. The sensor is constructed of two metal electrodes, the gold working electrode and the counter electrode, immersed in an electrolytic solution and separated by a gas permeable membrane from the sample of interest. An electrical potential is applied between the electrodes to reduce the ozone that is driven through the membrane by a partial pressure gradient. An electrical current is produced, which is proportional to the concentration of the ozone in the sample.

Accuracy of residual ozone measurements depends to a large extent on proper installation with respect to the following critical factors:

- Low sample flows to the analyzer increases probability of tube blockages by solid settling in the small diameter sample tubes.
- Low flow also increases sample detention time and
- Gas accumulation and associated gas binding problems are also possible.

A piping arrangement that reduces the possibility of irregular and low flows into the sensor is shown in Figure 2.10.

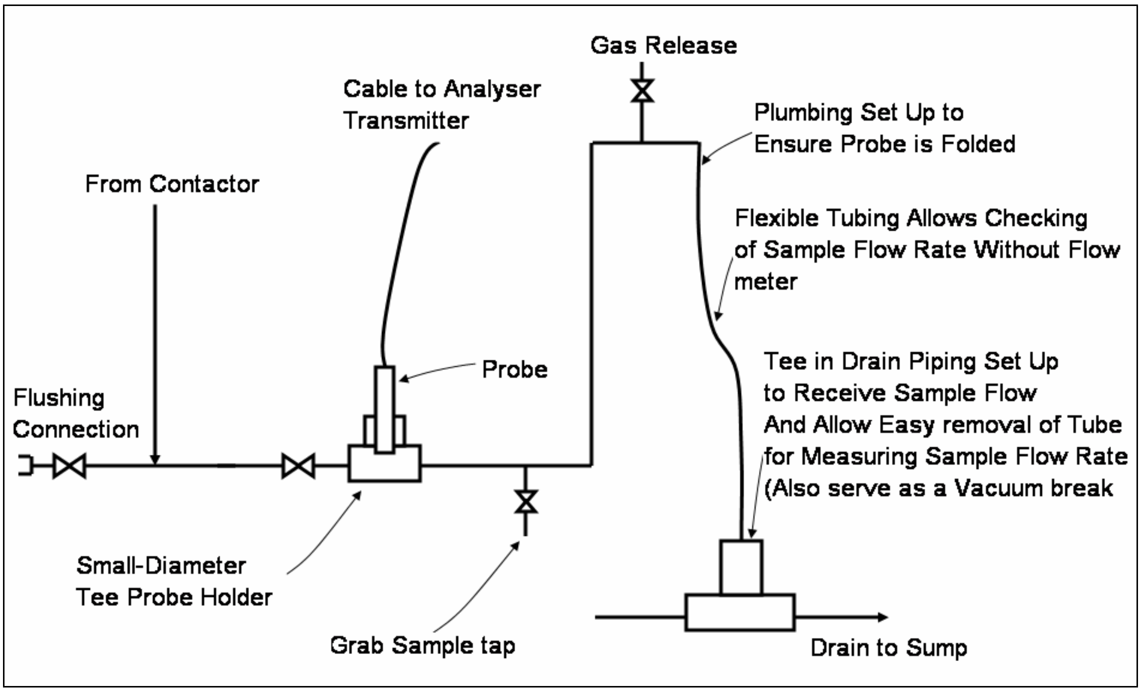


Figure 2.10: Online sampling for an on line ozone residual probe (Rakness, 1999).

Description of instrumentation

The main features of some ozone analyser systems are presented as Table 2.12.

Table 2.12: Main Features of the Ozone Analyser Systems

Ozone Analyser	MOCA Model 3600	Depolox 4	Ozomat MP	Ozonmat 8880	Dissolved Ozone Monitor 5122
Supplier : Make	Orbisphere Swiss	Wallace &Tiernan British	Anzeros German	Polymetron Swiss	E I T American
Local Agent /Branch	Branch Sandton	Klomac Agent	Turngro Agent	Kronhe Agent	DCM Instrumentation Agents
Backup Local Overseas	Complete maintenance backup including spares by Branch at Sandton.	Complete maintenance backup including spares by Agent in Durban	Complete maintenance backup including spares by Agent in Durban	Full maintenance provided including spares, in Durban and Johannesburg.	Full back-up will be provided by local Agent in Durban. Spares will require a max 2 weeks delivery period.
References	A list of customers (mostly UK), who purchased O_3 Analysers , was supplied in the operating manual	Instrument used in Umgeni Water for chlorine monitoring.	No known users in South Africa	Used in Umgeni Water for chlorine monitoring	No users in South Africa
Principle of Operation	Controlled potential amperometry Gas permeable/water impermeable membrane. 0.25V is applied to the cathode for ozone determination.	Controlled potential amperometry. reference electrode is separated with a membrane from sample. 0.25V applied to cathode.	Ozone is stripped from the aqueous sample. The UV absorbance of the ozone containing gas is proportional to the ozone concentration.	Controlled potential amperometry. No membrane Working potential 0.5V.	Amperometry Polymeric membrane Working potential is not specified.

Ozone Analyser	MOCA Model 3600	Depolox 4	Ozomat MP	Ozonmat 8880	Dissolved Ozone Monitor 5122
Minimum / Recommended flowrate	10 - 15 l/h	33l/h	100l/h	12l/h	33 - 132l/h 68 - 103 kpa
Lower/upper limits of zone measurement.	0.005 - 50 mg O_3/l	5 ranges between 0 and 10 mg/l	0 - 2 ug/l / 0 - 2 mg/l Detection limit : 2 ng/l	0 - 0.1mg/l / 0 - 1mg/l Sensitivity : <2 ug/l	0 - 20mg/l
Measuring cell **Materials**	Electrochemical cell consists of a gold cathode, silver anode and aqueous potassium bromide electrolyte. Membrane: 25.4 micron perfluoroalcoxy (PFA)	Potassium Chloride reference and counter electrodes and membranes	Cuvettes / UV Detector	Gold cathode Stainless steel anode Ag/AgCl/KCl	PVC , Gold/silver Electrodes
Response Time	90% signal change in 30 seconds at 25^0 c.	not specified	not specified	< 60 seconds	not specified
Interferences	Molecular chlorine	not specified	not specified	water sample to be free of undissolved matter	not specified
Calibration	Primary calibration in air. Can also be calibrated against a pre-determined result.	Against a lab determined result.	Primary calibration at factory. Can be set to a lab result. (Customer Factor)	Calibrated against a lab determined result	Calibrated against a lab determined result
Maintenance	No sensor maintenance	Full servicing from	During normal operation	Monthly calib check.	Sensor maintenance

Ozone Analyser	MOCA Model 3600	Depolox 4	Ozomat MP	Ozonmat 8880	Dissolved Ozone Monitor 5122
	schedule specified - dependent on operating conditions. Full service kit with consumables provided with instrument.	daily to 3 yearly.	only annual maintenance is necessary.	Weekly sample flowrate check. Replenish KCl reservoir. Periodic check gold electrode.	every 4 to 6 weeks requires replacing membrane and electrolyte.
Precision	1% (5% if calibrated in air)	0.2% of full scale	not specified	<5% of the measured value	0.1 mg/l
Approximate Budget Price (2007)	R 47 000	R52 000	R98 000	R40 000	R28 000
Outputs	Voltage : 0 - 5 VDC Current : 4 - 20 mA	0 - 20 ; 4 - 20 ; 0 - 10 and 0 – 5 mA	Not specified. Operational on 4 - 20 mA output.	2x (0/4 – 20 mA)	Current : 4 – 20 mA Voltage : 0 – 5 VDC

Experience with on-line ozone monitoring in the Wiggins Ozonation Plant, especially the measurement of residual ozone, has shown that the accuracy and reliability of ozone analyser measurements (residual ozone) are questionable especially under raw water conditions. It may, therefore, be necessary to evaluate the performance of ozone analysers, under different conditions, for purposes of selecting the correct one for a particular application. Zone sampling and measurement requires skilled personnel that have sound practical knowledge in the safe and efficient sampling and measurement of ozone.

Sampling

Accurate measurement of ozone depends, in the first instance, on a well planned, reproducible sampling system that incorporates the following:

- Safe handling - environmental and health, use of appropriate PPE, equipment
- Sample integrity – avoid contamination, dilution, degradation
- Adequate sample volume for analysis -
- Appropriate sample apparatus
- Analysis should immediately follow sampling due to the rapid degradation of ozone, especially in the water phase.
- Selection of a sampling point should consider safety, process chain of interest, purpose of sample. For example, to calculate the efficiency of a static mixer for ozone dissolution in the water feed, a gas sampling device is installed on the gas entry pipe into the static mixer and a liquid sampling cell is mounted at the outlet of the static mixer.

Ideally ozone measurement should be done on-site. Where this is not possible, suitable preservation techniques are employed. For example, for the determination of residual ozone using the potassium indigo trisulphonate method, a suitable volume of sample is added immediately into a volume of potassium indigo trisulphonate but may be read on a UV/VIS spectrophotometer, before 4 hours.

2.3.5. Ozone destruction

It is imperative that waste processes gases containing ozone be returned to the atmosphere at concentrations that are safe for personnel, environment and equipment. Due to the toxic nature of ozone, the off gas from the contactors passes through an ozone destructor.

The ozone destructor converts the ozone to oxygen before released to the atmosphere. Ozone exposure limits are guided by the maximum ozone concentration in ambient air as regulated by air pollution authorities or Government environmental agencies. The maximum eight hour exposure limit is 0.1 mg/l. Because the process off-gas contains ozone at concentrations that exceed the safe maximum allowable concentration, off-gas passes through a destructor that essentially reconverts the ozone to oxygen.

There are essentially two types of ozone destructors:

- Thermal destructors. These are energy intensive as they are normally operated between 300 and 350^{0}C. Heat recovery units are normally included, where the incoming off-gas is pre-heated.
- Thermal catalytic destructors. These are more popular as they operate at lower temperatures (30°C to 70°C). Many catalysts are based on palladium, manganese and nickel oxides. Catalyst life expectancy can be as high as 5 years for a properly operated system (55).

Ozone destruction can be effected through catalytic destruction, thermal destruction or both.

Table 2.13: Configuration, flow characteristics and operation of the ozone destructors

Parameter	Destructor
Destruction system configuration	Catalytic ozone destruction (COD) giving residual ozone of 0.02 mg/m^3. Destructor casing high-grade steel with gas heating, catalyst and PSU. Catalyst is poison by chlorine; therefore pre-chlorination should not be practiced. Thermal destruction is normally at high temperatures usually about 300°C.
Flow characteristics	Gas flow into the destructor is 5% lower than the feed gas flow into the contactor. The decrease in flowrate is due to gas dissolution into water. The off gas flow rate is affected by the water height in the contactor. Off gas concentration measurement is usually inaccurate due to dilution with air. This results in off-gas destructor operating at high operating cost. Off gas temperature is same as water in the off-gas exit point. Off gas has high moisture content high due to operating pressure and temperature. Off-gas condensate is drained to prevent damage to destructor heater and catalyst.
Methods of destruction	Gases are passed through the heater to vaporize the moisture as the off gas enters the catalyst. After the catalyst the gas is blown to atmosphere by an exhaust blower. Granular activated carbon (GAC) can destroy ozone but it is not used in ozone destructor units because GAC can ignite.

2.4. OPERATIONAL STRATEGIES FOR COST-EFFECTIVE USE OF OZONE

There are various operational control strategies that need to be implemented for the sustainability of cost-effective operation of an ozonation process. The first step is the planning of the ozone operation and performance optimization programme. The goal of optimizing ozone performance is to continuously achieve performance objectives at minimum operating cost (2).

Table 2.14: Adaptation of 'Ways to Optimise Ozonation' obtained from (2)

Intervention	Comment
An optimization team ideally comprising operations, maintenance and process engineering should be constituted.	There should be adequate buy-in and co-operation by all stake-holders, operations, maintenance and process engineer/technicians.
Identify a performance target/s that is: • Related to water quality • Easy to measure and • Provides instant feedback	General and operations related performance objectives may be insufficient. The performance criteria should be directly related to the measurable target, e.g. colour, Fe and Mn
Monitor performance using an indicator like a performance ratio.	Performance ratio is the ratio of measured performance and performance target. Performance ratio must be greater than 1 at all times. An operating safety factor may be built in, e.g. 1.2; 1.5 or any other value to ensure the ratio is greater than 1.
Ensure reliability of on-line analyzer measurements and use to calculate performance ratios.	Ensure analysers are correctly installed Planned maintenance and scheduled calibration
Verify accuracy of instrumentation for flow control and unit volume operating costs. E.g. flowmeter, power meter, ozone analyzer.	Inaccuracy of measuring (on-line) instruments due to poor maintenance is one of the main causes for poor plant performance.
Monitor optimization status on a spread sheet based monitoring programme.	An interactive spread sheet that updates data, calculates and reports optimization status would be useful
Implement optimization techniques as required.	Consider conducting a formal ozone facility evaluation Develop and discuss optimization ideas internally and with other utilities.

2.4.1. Operational strategies as applied to individual unit processes

In the perfect world, a properly designed plant with dedicated and trained operational staff that strictly adhere to good operating and maintenance practices will always perform optimally and cost-effectively. However, in the real world, new challenges are faced on an on-going basis, due to a number of reasons, primarily equipment failure and human error.

(i) Cooling water

Cooling water is required to remove heat due to excess energy used in ozone production. The water flow is calculated based on heat gain by the cooling water and ozone production rate. Cooling water flow through the PSU should be between 5 and 10% of water flow through the generator.

Since filtered water is generally used for cooling of equipment, the units should be designed and tested for the higher temperatures prevalent during the warm summer months. Umgeni Water experience was that during summer, the ozone generators did not start up as a result of the higher cooling water temperatures (5). The problem was resolved by re-programming the ozone controllers with the higher cooling water temperatures and operating the cooling water pumps manually. After stabilization the system is switched to automatic control.

Figure 2.11 below, illustrates the relation between cooling water temperature and the yield of ozone generation. This figure shows that an increasing cooling water temperature results in a decreasing ozone production. To limit the decomposition of ozone, the temperature in the discharge gap should not be higher than 25 °C. The general advice is that cooling water may increase 5°C to 20°C maximally. It is important that the temperature of the inlet air is not too high (www.Lenntech.com).

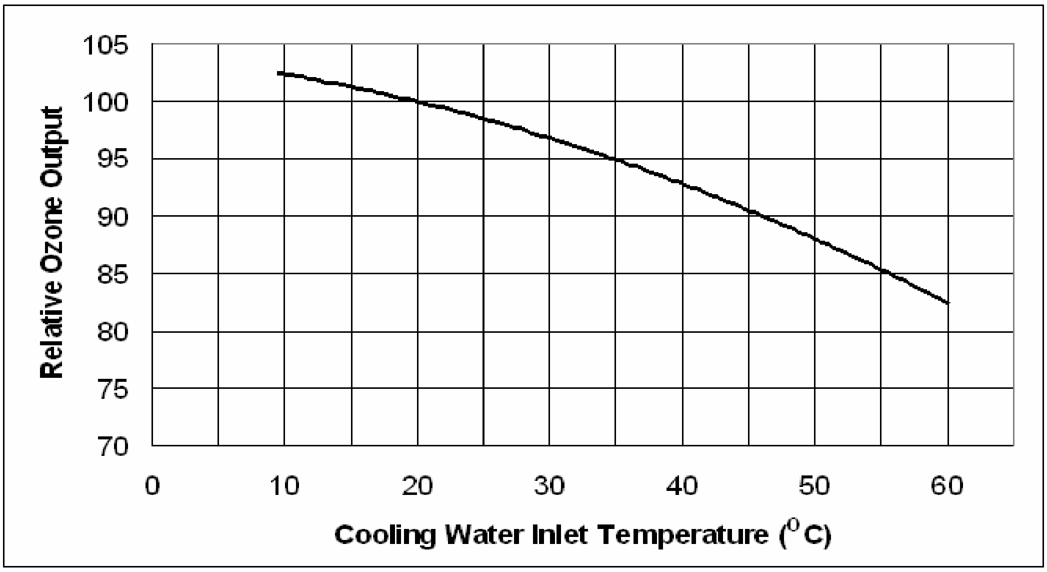


Figure 2.11: Influence of water cooling on ozone generation efficiency

(ii) Air preparation

It must be ensured that adequate cooling water is supplied, with minimum temperature fluctuations, to all air preparation equipment that require cooling. Dust and particulate matter in atmospheric air in the vicinity of the air blowers would require more frequent filter cleaning, as particulates will find their way into dryers and ozone generators. High humidity also places increased load on the dryers. The air preparation system should be operated through several cycles to ensure that the required dew point is achieved before entering the ozone generator.

(iii) Ozone generator

Ozone generators must be protected from the following:

- High dewpoint (> - 60°C)
- No air flow
- No cooling water
- Risk of moist air in the ozone generator.

Routine unit checks and data collection, scheduled maintenance, should include the following:

- Daily temperature, flowrate and pressure for both air and cooling water.
- Ozone concentration at the generator outlet.
- Check flow and pressure control devices on air and cooling water circuits and recalibrate sensors every month.
- Record high voltage temperatures every three months.
- Measure generator efficiency (kWh/kg ozone) annually. Drop in efficiency will determine how frequently the dielectric tubes are to be cleaned or replaced.

When ozone generators are operated at high moisture content, nitric acid develops within the generator and would then need to be shut down and cleaned. In addition, the generator efficiency is reduced and dielectrics could potentially break. It is therefore imperative that the generator operates under very dry conditions. Some moisture minimisation strategies are described below.

- Prior to start-up and following shut-down, traces of ozone in the system must be removed by purging with a high flow of dry air.
- When the generator is to be isolated for a long period, it is advisable to stop the cooling water flow and drain the generator before switching off, to prevent internal condensation. Startup should commence with about 12 hours of dry air flushing and initiation of the cooling water system.
- While the generator is in standby, a low flow of dry air is maintained on a continuous basis for as long as the generator is idle, in order to avoid condensation inside the generator.

(iv) Ozone contacting system

Normally the ozone gas stream to the contactor is equipped with the following instruments to control gas flow rate and overall ozone treatment performance.
Thermal flow meter - commonly used to measure contact gas flow. An orifice plate can be installed at the generator inlet to verify the accuracy of the thermal mass flow meter after the generator.
Motorized control valve and actuator valves - These must be sized correctly and capable of precise control over a broad range of gas flow. Butterfly valves and standard ball valves are generally insufficient for precise control. V-port ball or similar precision-control valves are used to control ozone gas flow.

The oxygen-ozone mixture dose should be monitored and controlled at all time since some operational problems may arise. The uncontrolled addition of air or oxygen may lead to:

- Filter air binding.
- Increase potential for corrosion
- And increase potential for biological re-growth in the distribution system.

For pre-ozonation applications, latest ozone practice is the contacting of ozone and water outside a relatively smaller contact tank. Ozone is added via a venturi, inline into a water stream just upstream of a suitably sized static mixer. The ozonated water then enters a contact tank, with retention time between 5 and 15 minutes.

The diffuser type ozone contacting system is problematic especially for a pre-ozone application. Settleable solids tend to block the diffusers, especially when the contactor has not been in service for a period of time. Blocked diffusers cause uneven bubble distribution in the contact tanks, resulting in poor ozone distribution.

Umgeni Water had serious problems with their old diffuser systems. The diffusers blocked frequently and low ozone transfer efficiencies (55 to 65%) were recorded. Significantly better ozone transfer efficiencies were obtained when the ozone contacting occurred before the contact tank, via a static mixer.

Selection of ozone resistant material for sealing joints in the contact tank is important as the fixing of leaks in the contact tank is generally costly and disruptive to the process.

Monitoring ozone transfer efficiency
Ozone contacting system may be monitored by measuring the ozone transfer efficiency. Ozone flowrate and concentration is measured on the gas feed into the contactor and the off-gas exiting the contactor. Residual ozone of the water at the outlet of the contactor is also measured. The ozone transfer efficiency is easily calculated by setting up an ozone mass balance across the contactor. A typical arrangement of ozone analysers in a contacting system is shown in Figure 2.12. By setting up a simple ozone mass balance equation across the ozone contacting system, the ozone transfer efficiency may be easily calculated using the following relationship.

Ozone $(\text{in})_{gas}$ = ozone $(\text{absorbed})_{gas}$ + Residual $\text{Ozone}_{(liquid)}$ + Ozone $(\text{out})_{gas}$

The ozone mass balance exercise will also assist in ensuring that ozone is optimised. This would enhance the ozone operation from a cost-effective and environmental perspective. Periodic contact efficiency tests (at least once in six months) will generally highlight problems due to blocked or broken diffusers, short-circuiting, ozone leaks.

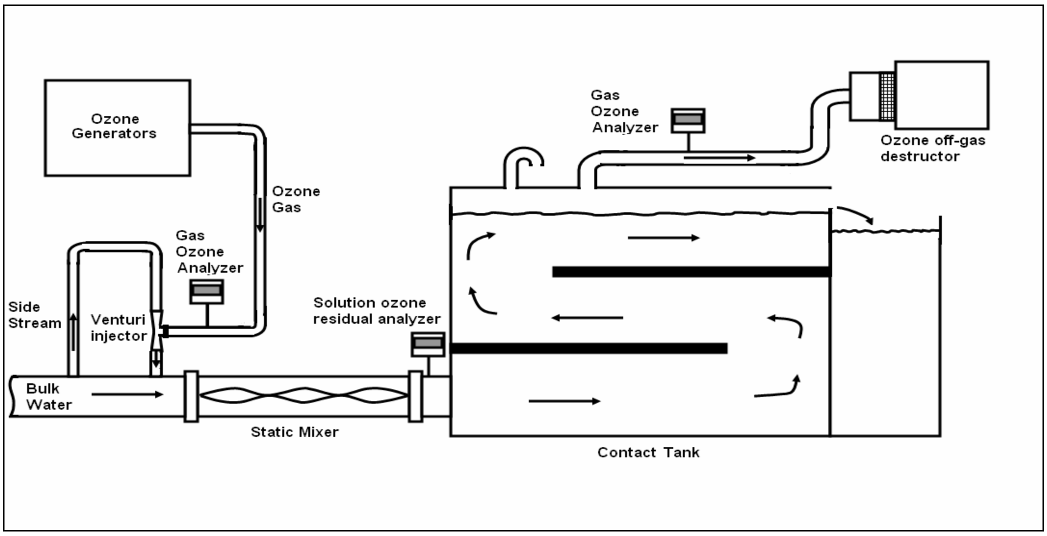


Figure 2.12: Typical ozone analyser positioning for automatic ozone dose control based on instantaneous ozone technique

(v) Ozone destructor

For the efficient operation of the ozone destructor, the following precautions need to be taken:

- No acidic or organic foams that form on the water surface of the contactor should enter the destructor. Suitable defoamers air water sprays should be used to control foam.
- Construction materials should be compatible to wet ozone.

- When using a catalyst as part of the ozone destruction unit, procedures should be put in place to avoid water vapor and chlorine contact with the catalyst.

A study (Friedrich and Buckley, 2002) showed that of the total power consumed by the ozonation unit at Wiggins Waterworks, 72.4% was used in the thermal destruction unit (TDU). The study also showed that of the gases entering the TDU, a large proportion is made up of inert gases drawn from the atmosphere. Energy is therefore wasted by unnecessarily heating these gases. A reduction of gases entering from the atmosphere would thus decrease the energy demand of the TDU. A series of preliminary tests indicated that significant energy savings (up to 80%) may be realised by reducing the gas flow to the thermal destruct unit by partially closing the vacuum breaker on top of the contactors.

Based on these findings it is evident that an energy saving of up to 80% could be achieved on the TDU by reducing gas inflow. The installation of a low range ozone analyzer at the outlet of the destructor will assist in the optimization of ozone destructor operating temperature and in the reduction in air flow through the contactor via the extraction fan at the ozone destructor.

One of the ways to reduce the flow to the TDU is to extend a pipe from the vacuum breakers immersed slightly below the water level in the ozonator. This will create a water seal preventing air to flow to the TDU.

Closing the valves for those contactors not on-line will be effective in reducing the dilution of the off gas by the air and hence less energy required by the TDU. A further saving could be achieved by installing a variable speed controller on the fan drawing air to the TDU.

2.4.2. Safety interlocks and automatic control

The safe and efficient operation of the ozone plant is very dependent on the individual operation of the unit processes. The successful start-up of the ozone generators also includes process parameters or conditions necessary for the safety of equipment and operating personnel. Citing the Umgeni Water experience (5), between 50 and 60 conditions needed to be met before the automatic startup of an ozone generator. These include cooling water temperature, dew point, pressure, correct valve sequence, etc. The difficulty with the interlock operating software was that a general message was displayed when any of the conditions were not met, thus making trouble-shooting and corrective intervention long and tedious. The error messages have been improved to identify the problem area more closely.

2.4.3. Ozone control strategy

The sophistication of ozone dose control depends to a large extent on the specific outcomes for its application e.g. removal of iron and manganese, oxidation of micropollutants, ozonation prior to activated carbon, etc. For particular applications, some control systems will be more suitable than others. The following control strategies are generally used:

(i) Raw Water Flowrate

The ozone control philosophy most widely practiced in the water industry is based on a constant ozone dose. The required ozone dose is determined from laboratory batch or pilot scale tests on the water to be ozonated, based on ozone demand or the ozone dose required to reduce target micro-pollutants to acceptable levels. The change in raw water flowrate may be detected by a programmed logic controller (PLC) that can proportionally reduce ozone production by the generators, reduce gas flowrate or both, depending on the degree of change.

(ii) Ozone Residual monitoring in water

A dissolved ozone analyzer measures residual ozone concentration at a selected sampling point after ozonation. The ozone reading on the analyzer is compared to a pre-determined set-point and the ozone dose is adjusted accordingly. This technique allows for raw water quality fluctuations but is only applicable if the raw water flow is fairly constant. The accuracy of the on-line analysers must be confirmed regularly. Ozone sampling and measurement requires skilled personnel that have sound practical knowledge in the safe and efficient sampling and measurement of ozone.

An efficient sampling system is necessary for the accuracy of ozone residual measurements. The following sampling considerations are noteworthy.

- Minimum detention time in sampling line.
- Easy collection of grab sample without disturbing on-line instrument measurement.
- Ensure sufficient and consistent flow to an on-line instrument.
- Provide flexibility of measuring residual at different points within the ozone contactor.

It is imperative that the control response be coordinated with the rest of the plant, such as the need for chlorine to achieve disinfection compliance, etc. Even though SCADA screens are necessary, process oriented screens which display results for the entire ozone facility (information regarding dose, residual, etc.) and with facility for operators to make changes to set-points are also very useful (53)

(iii) Ozone production control

The gas flow and the generator power are used for ozone production control, with the generator power being easier to adjust. Good gas flow control can be achieved by using (53):

- high quality pressure regulating valves e.g. pilot operated PRVs
- high quality control valves e.g. segmented ball valves
- high quality valve actuators e.g. Digital Control (DC) operated actuators instead of analogue control (AC) operated actuators

The valves must be sized correctly for the entire operating range of expected gas flowrate.

(iv) Control Based on Raw Water Quality

Ozone dose may be adjusted based on the output of an analyzer that measures one or more of specific compounds or a sensor that measures a parameter representative of the waters combined organic concentration (for example, ultraviolet absorbance at 254 nm).

(vi) Ozone Dose Optimization and Control

For ease and simplicity of control, ozone dose is generally fixed. The optimum dose is determined on a pilot plant scale or laboratory batch scale and applied to the full-scale plant. The dose is maintained by linking the ozone production to the raw water flow through the plant such that the ozone production increases proportionally to the raw water flowrate. There is no compensation for the deterioration in raw water quality.

Some ozone users control the ozone dosage by monitoring the residual ozone concentration at the outlet of the contactor. The problem in this technique is the challenge in residual ozone measurement, especially on-line analytical instrumentation. Poor accuracy of residual ozone measurements at the low concentrations (typically <0.5 mg/l) were experienced at the Umgeni Water full-scale plant.

New state-of–the-art ozone analysers for both gas and liquid phase, with more selective and robust sensors, are available. Through the use of these more accurate analysers and other techniques like on-line UV absorbance @254 nm, ozone dose may be optimized on the basis of variable raw water quality.

Holistic approach to process optimization
Midvaal Water use Dissolved Air Flotation (DAF) and ozone as the main treatment processes for the removal of chlorophyll. However, chlorophyll removal efficiency is maximized through a holistic process optimization intervention and not just a particular unit process. A maximum permissible chlorophyll concentration in the final water is generally the criteria for process optimization.

The difficulty in setting the required ozone dose for chlorophyll removal is due to two main characteristics of the raw water, viz, specific algal groups and the concentration and type of other oxidizable material present in the raw water at that point in time. . Diatoms are generally more amenable to removal by DAF because of their buoyancy. Therefore, during periods when diatoms are the predominant algal groups, chlorophyll removal is dominated by DAF, while ozone might then play a role in the removal of the other Diatom related products, e.g. colour causing substances

Motile Green algae, on the other hand, are less successfully captured by DAF and thus increase the demand for ozone. Blue-green algae secrete substances in the water that cause taste and odour problems in drinking water. The success and optimum dose of ozone to decrease these substances also depend on the specific substance and the concentrations thereof and require optimisation of the subsequent treatment processes for the precipitation and removal by coagulation, flocculation and filtration.

Variations in the level and type of oxidizable inorganic and organic substances in the raw water would directly affect the amount of ozone available for the oxidation of the target micropollutant. Therefore, as an operational strategy, Midvaal Water uses a variety of quality indicators in the raw as well as in the final product to optimise the dose of ozone.

2.4.4. Operation Philosophy Based on Raw water Conditions

An ozone plant is generally operated on a 24 hour basis. The plant is designed on the basis that the raw water conditions that necessitated ozonation are always present. Another reason for continuous operation is the negative effects of intermittent shutdown and startup on the dielectric tubes and moisture buildup in the ozone generators.

Over the past three to four years, raw water to the Umgeni Water's Wiggins Waterworks that has the largest ozone plant in South Africa, improved significantly. Iron and manganese, colour, organics and turbidity had reduced to levels that do not require ozone. There was no quantifiable reason for using ozone other that for aesthetic reasons and intermittent spikes in raw water quality

2.4.5. Operator training

The ozone plant is a sophisticated combination of unit processes that differs significantly from the conventional water treatment plant. Although, part of the water treatment chain, the operating complexity of the ozone plant, requires personnel training at all levels.

Ozone training is generally provided by the ozone contractor as part of the ozone plant project budget. An operator training plan is developed and is ideally conducted through the various stages of the construction stage, including plant commissioning, optimization and during the first 6 to 12 hours into the process operation phase.

2.5. Safety Considerations in the Handling of Oxygen and Ozone

(i) Ozone Plant Safety

Ozone safety training forms an integral part of ozone training. Due to the hazardous nature of the process, it is imperative that operating personnel undergo intensive safety training before being allowed to operate the ozone plant.

An ozone installation poses a number of safety challenges that include human exposure to dangerous levels of ozone, high purity oxygen, electrical hazards and other hazards associated with a high energy industrial application.

(ii) Exposure to Oxygen

When high oxygen concentration is the feed to an ozone plant, oxygen safety plans are put into effect because of safety hazards that are associated with oxygen. The primary consideration for oxygen system includes the following (Rakness, 1999):

- Combustion or fire. Oxygen on its own is non-flammable but vigorously support combustion in the presence of fuel source.
- Freezing hazards associated with cryogenic LOX (-182.78 ^{O}C at 101 kPa)

Resources concerning oxygen installation and safety can be sourced from the Compressed Gas Association (Rakness, 1999). The safety concerns of handling of the LOX storage and the vaporizer can be referenced from the National Fire Protection Association (Rakness, 1999).

(iii) Exposure to Ozone

Ozone is an important component of the atmospheric layer. It absorbs ultraviolet radiation thereby reduces risk of skin cancer (Rakness, 1999). Ozone is also an excellent oxidizing agent and a disinfectant in the water treatment industry. The gas is colourless with pungent odor. Exposure to ozone at ground level is harmful to human healthy and the environment. Human detect (smell) ozone at low levels of 0.01 to 0.04 ppm_v, which is less than the maximum 8 hour recommended exposure limit of 0.1 ppm_v. This value of 0.1 ppm_v is used to set the first-alert sound and the visual alarm point in the ozone system.

2.5.1. Ozone Safety Features

The ozone generator is usually located in an enclosed building. The LOX and vaporizer are located outside the building. The Ambient ozone monitors are located near the ozone piping in low spots where ozone is likely to accumulate. Refer to Figure 2.13, shows the location of safety feature and the process units of the ozone system.

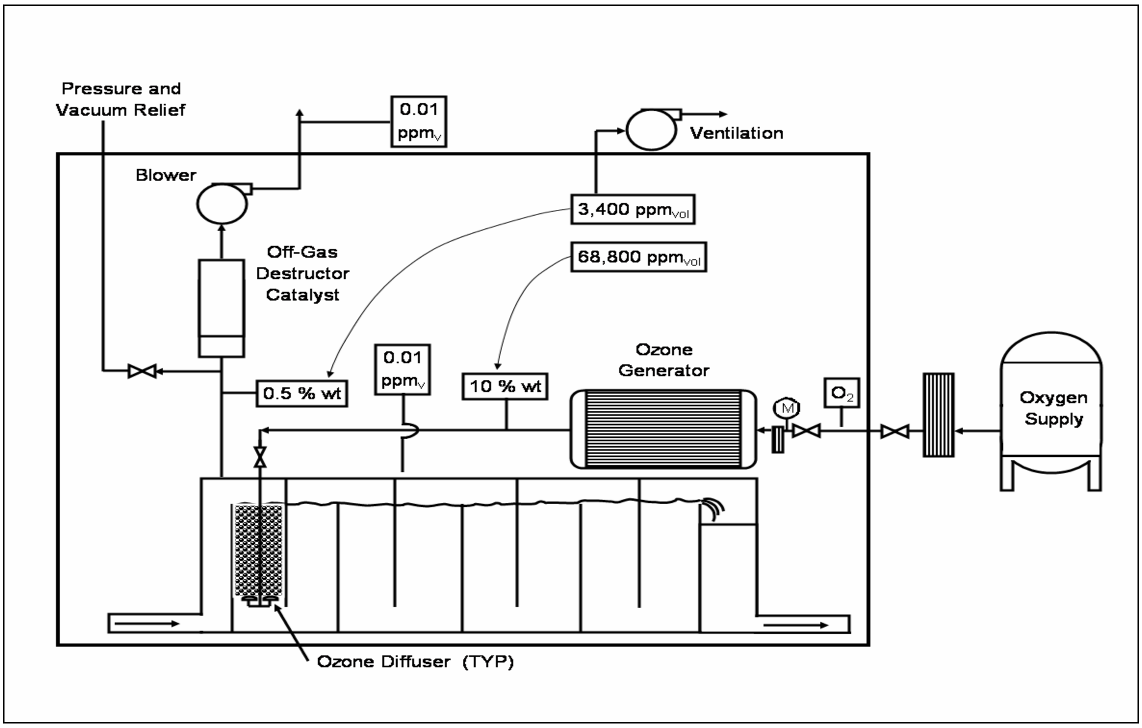


Figure 2.13: Ozone system layout with essential oxygen and ozone safety features (Rakness, 1999)

3. South African Plant Survey

3.1. INTRODUCTION

As part of the project, a detailed survey of the South African waterworks that use ozone was conducted. The main objectives of the survey were the following:

- To understand the basis for ozone application in the South African water industry.
- Ozone practice
- Impact of ozone in the overall process i.e. operation, maintenance, energy consumption, final water quality, etc.

The survey was conducted through a set of questionnaires sent to most users of ozone in the local water industry.

3.2. MAIN OZONE USERS IN THE SOUTH AFRICAN WATER INDUSTRY

While ozone is not widely used in the South African water treatment sector, its popularity is gaining momentum. The four main users of ozone are Umgeni Water, Midvaal Water and Veolia Water and recently Magalies Water.

3.2.1. Umgeni Water

Umgeni Water's Wiggins Water Works is situated in the central-costal region of Durban at KwaZulu Natal in South Africa. The Waterworks treats an impounded raw water source from Inanda Dam situated 40 kilometres away the northern region of Durban. Applied in the pre-treatment stage of the treatment chain, the main rationale for ozone use was for the control of algae, oxidation of iron and manganese.

3.2.2. Midvaal

Midvaal Water Company, situated in the North West Province, is a private company that draws its raw water from the Middle Vaal River. The plant uses ozone to treat high algae content in raw water and traces of iron and manganese from surrounding mines. The plant produces ozone from on-site generated oxygen and doses at the intermediate stage. An additional intermediate stage was implemented in 2008.

3.2.3. Durban Recycle

Durban Water Recycle Plant treats final effluent from the Southern Waste Waterworks, situated in the southern-costal region of Durban at KwaZulu-Natal. The Durban Water Recycling Plant uses ozone in the intermediate treatment stage primarily for colour reduction. Ozone in this plant is produced from liquid oxygen purchased from external supplier.

3.2.4. Magalies Water

Vaalkop water is situated in the North West Province in South African under the Brits Municipality. This plant receives its raw water from Vaalkop dam. Ozone in the plant is used for both oxidation and disinfection. Ozone is used to oxidize iron, manganese, organics, taste and odor. The plant is also equipped with Granular Activated Carbon (GAC) for the removal of organics and color. Ozone in the plant is also used for disinfecting the backwash water, sludge from sedimentation tanks and Dissolved Air Flotation (DAF).

3.3. SURVEY RESULTS

3.3.1. Basis for Ozone Selection

The three major users of ozone for water treatment, Umgeni Water (Wiggins Waterworks), Midvaal Water and Veolia Water (Durban Recycle) selected ozone on the basis of results from laboratory/pilot plant studies. Umgeni Water also conducted preliminary desktop feasibility before embarking on bench-scale and pilot plant work. Magalies Water (Vaalkop Waterworks) had desktop studies done on the experience of other users before deciding on how ozone will be implemented at their Treatment Works. All work on ozone studies and implementation were project managed by external Consultants. Final water quality was the over-riding factor over cost, in the final selection.
In all applications, ozone is used as an oxidant. At Wiggins Waterworks, ozone is used in the pretreatment stage (before coagulation, flocculation and DAF). The Midvaal Water Plant doses ozone at two points i.e. pre-ozone (before coagulation and flocculation) and at the intermediate stage (between the clarification and filtration processes). At the Durban Recycle Plant, ozone is added at the intermediate stage.

At the Vaalkop Waterworks ozone was dosed at the pretreatment and intermediate stages, with the purpose being twofold, viz. oxidation and disinfection (i.e. oxidation of Fe and Mn, partial oxidation of organics and taste and odour removal). Ozonation was also used as an aid for the subsequent granular activated carbon treatment step.

Table 3.1: General Information on South African Waterworks Using Ozone

	Name of treatment plant	**Wiggins Waterworks**	**Midvaal Water**	**Durban Water Recycle**	**Vaalkop Waterworks**
General Plant Information	District Municipality	Durban Metro	Private Company	Durban Metro	Brits
	Plant capacity, LM/d	350	320	47.5	30
	Treatment water source/s	Inanda Dam Nagle Dam	Middle Vaal River	Final effluent from waste waterworks	Vaalkop Dam
Rationale for using ozone as an oxidant	Description of raw water	Iron and manganese, colour, taste and odour	Mineralized Highly eutrophic Algae/ Chlorophyll, colour Turbidity in rainy Seasons, TOC, pathogens	Domestic sewage with 15% industrial effluents. High conductivity, colour and TOC	Combination of dam water and waterworks residual (filter backwash, clarifier desludge, scour) Algae, TOC, Cryptosporidium and Giardia detected.

3.3.2. Ozone Generation

From Table 3.2, ozone generators range in size from 9 kg/hr to 90 kg/hr units. Except for the Durban Recycle Plant, pre-ozone dose for the other waterworks were similar at an average dosage of 1.5 mg/l. Liquid oxygen was the preferred feed source for two waterworks.

Table 3.2: Ozone Generation, Dose and Feed Source

Waterworks	**Wiggins Waterworks**	**Midvaal Water**	**Durban Recycle**	**Vaalkop Waterworks**
Generator Output, kg/hr	3 x 30	3 x 8	2 x 12	2 x 9
Type				
Low frequency, Hz			50	
Medium frequency, Hz	600 to 800	900 to 1400		Medium frequency
Ozone dose **Pre-ozone, mg/l** **Intermediate, mg/l**	1.5	1.5 2.5	dependent on Inflow colour	1.5 target residual ozone of 0.5 mg/l
Ozonator feed source	Liquid Oxygen	On-site generated oxygen (PSA system)	Liquid Oxygen	Air
Challenges	LOX dew point analyzer unreliable. Too many interlocks Poor performance monitoring (ozone analyzer failure) Lack of dedicated specialized operator.	Ozone leaks; Control of generator pressure, dew point. Inadequate performance monitoring. Lack of dedicated specialized operator	No ozone monitoring, Inverters load shedding, broken tubes not detected.	Power supply Dew point

3.3.3. Ozone Contacting

Table 3.3: Ozone Contactors use in each plant

Waterworks	Wiggins Waterworks	Midvaal Water	Durban Recycle	Vaalkop Waterworks
Contactor type	Static Mixer	Diffusers	Diffusers	Static mixer For Pre-ozone Diffuser for intermediate
Contactor tank	Horizontal flow	U tube	Horizontal Flow	2 X horizontal flow contactors
Ozone contacting	Outside Tank	Inside Tank	Inside Tank	Inside Tanks
Contactor detention time, min	9 to 15	Pre-ozone: 2 Intermediate: 4	15	18 to 20
Ozone transfer efficiency	> 97%	Pre-ozone: ± 92 % Intermediate: ± 98 %	unavailable	unavailable
Challenges	Ozone leaks at joints in contactor. Unreliable ozone analysers	New diffusers in pre-ozone tank	Blockages in diffusers result in uneven ozone distribution. No ozone residual	unknown

The maintenance carried out on the contactors at each of these plants is given in Appendix C.

3.3.4. Ozone Dose Control

Table 3.4: Ozone dose control strategies

Waterworks	Wiggins Waterworks	Midvaal Water	Durban Recycle	Vaalkop
Ozone Dose Control	PLC Flow based	Manual PLC Flow based	Manual, PLC flow based	Manual PLC Flow based
Ozone Residual, mg/l	0.1	0.1		0.5 mg/l
Challenges	Unreliable residual ozone analyzer measurements	Changes in raw water conditions	Poor ozone distribution in contactor. No ozone analyzer in gas phase, no residual ozone measurement.	No reliable process data. Plant is still in the optimization stage.

3.3.5. Ozone Destruction

Table 3.5: Ozone Destruction technology used in each plant

Waterworks	Wiggins Waterworks	Midvaal Water	Durban Water Recycle	Vaalkop Waterworks
Ozone destruction	Thermal 350 ^{0}C	Thermal Catalytic	Thermal 350 ^{O}C	Thermal Catalytic (carulite granules)
Typical destructor exit ozone concentration	< 0.01 mg/L	<0.01 mg/L	< 0.01 mg/L	< 0.01 mg/L
Challenges	No ozone measurement at destructor outlet.	Destructor is bypassed when off gas ozone concentrations are very low.	Difficult to source alternate material for heat exchanger.	Unknown

3.3.6. Ozone Safety

Table 3.6: Safety consideration in the ozone generator systems

Waterworks	Wiggins Waterworks	Midvaal Water	Durban Recycle	Vaalkop
Safety Procedures In Place	Safety interlocks Ozone leak detection Minor ozone leaks Catastrophic leaks Contactor off-gas monitor Oxygen leakage	Induction programmes Identification signs of hazardous/ installation/ risks Written "safety Procedures" Routine monitoring programmes. Routine surveys on equipment safety	Training of operations personnel. Plant automation, trips and alarms: low or high pressure cooling water Safety training, breathing apparatus (BA sets) for any contingencies	Ozone leak detectors. BA sets Safety interlocks
Challenges	Ozone odour emanating from contact tank. Problem reduced when residual ozone analyzer probe was relocated inside the ozone contact tank.	Ozone vapors Management/ control of generator pressure	Relatively high ozone concentrations in off-gas near ozone contact tanks.	Unknown

3.3.7. Impact of Ozone

The impact of ozone could not be quantified due to the lack of quality operating data. This was primarily due to the following:

- Unoptimised unit processes
- Significant changes in raw water conditions
- Maintenance problems with respect to equipment breakdowns and
- Calibration of on-line analysers.
- Data not provided by respondents to ozone survey questionnaire.

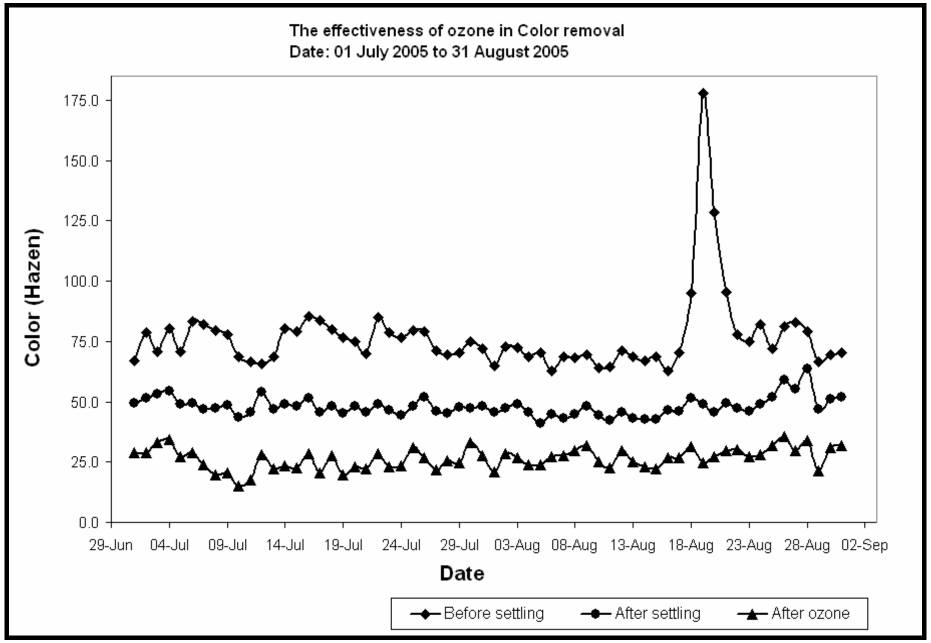
(i) Evidence of Ozone Benefits

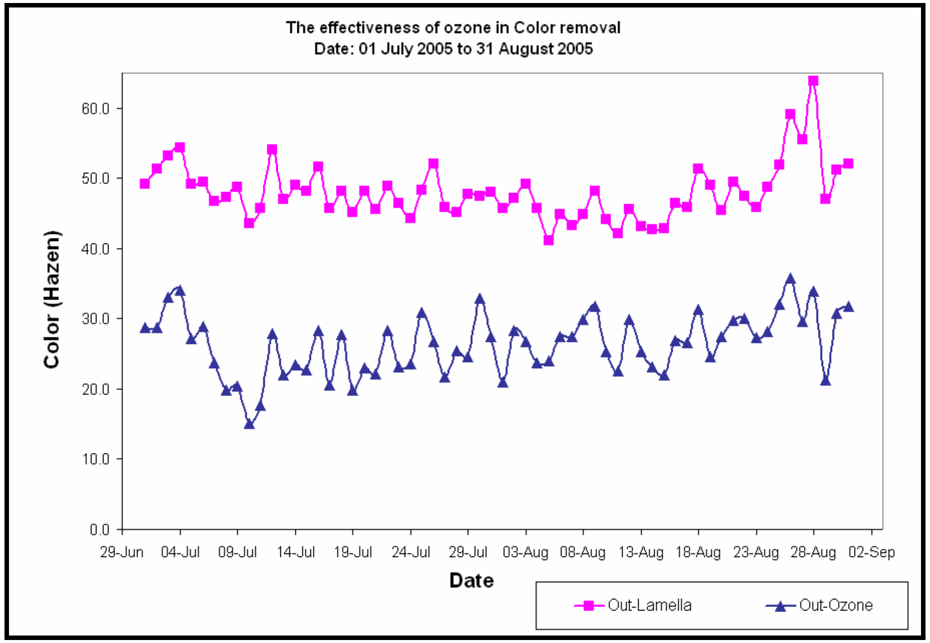
At Wiggins Waterworks a general enhancement in water quality was noted. There was a significant sparkle to the final water that included ozone in the pre-treatment stage. A significant increase in filter run time was noted with ozone use. The Waterworks also noted a decrease in disinfection chemicals with pre-ozonation. Vaalkop management stated that coagulant costs halved when ozone was used. Chlorine consumption was also reported to have halved with the use of ozone.

Midvaal Water reported significant benefits with the incorporation of ozone at the pre-treatment and intermediate stages of their treatment chain. 30% reduction in taste and odour causing compounds (2 methyl isoborneol), reduction in iron, manganese and chlorophyll'a' below target levels and 30% overall savings in chemicals, were reported. A 50% reduction in chlorine was also noted when ozone was used.

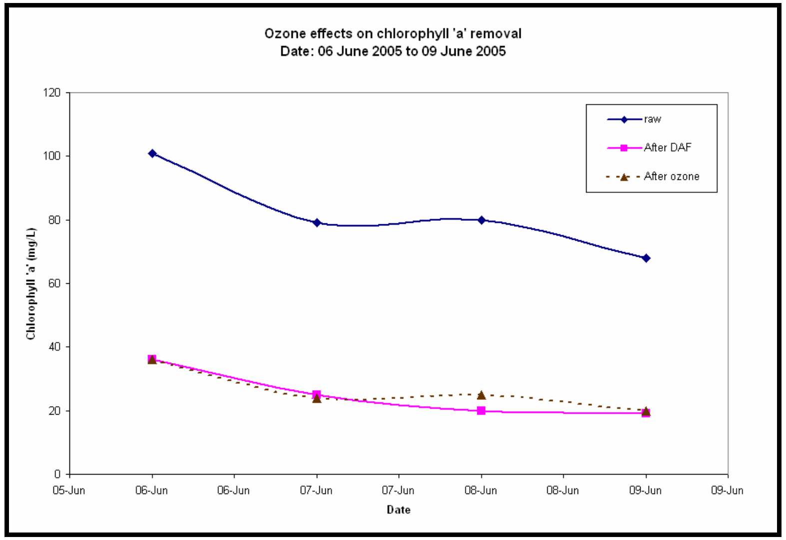
Durban Recycle Plant also reported that ozone was very effective in colour removal. Plant data indicated that 40% of the colour is removed by ozone. Chemical costs doubled when ozone was not dosed.

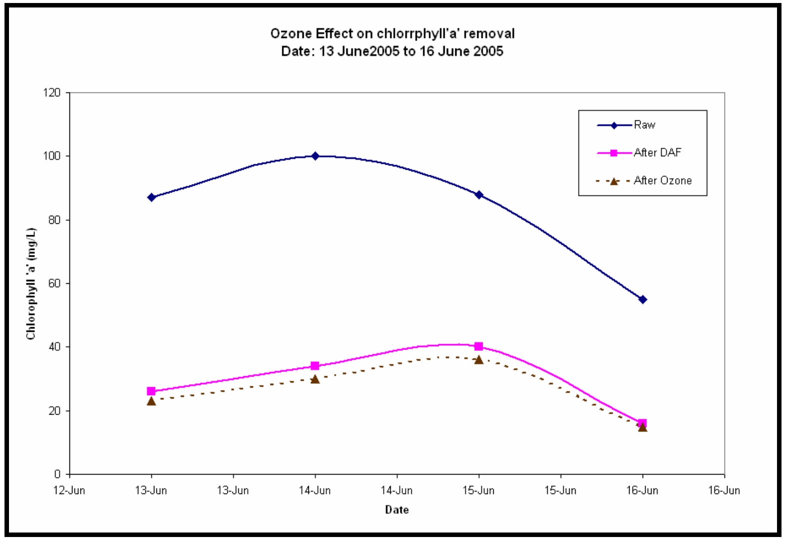
Figures 3.1 to 3.6 gives graphs showing the impact of ozonation on the reduction of chlorophyll 'a' and colour at Midvaal Water and Durban Recycle Plant, respectively.
Refer to Appendix A for pilot scale results obtained for the ozone demand for colour, Fe and Mn reduction.

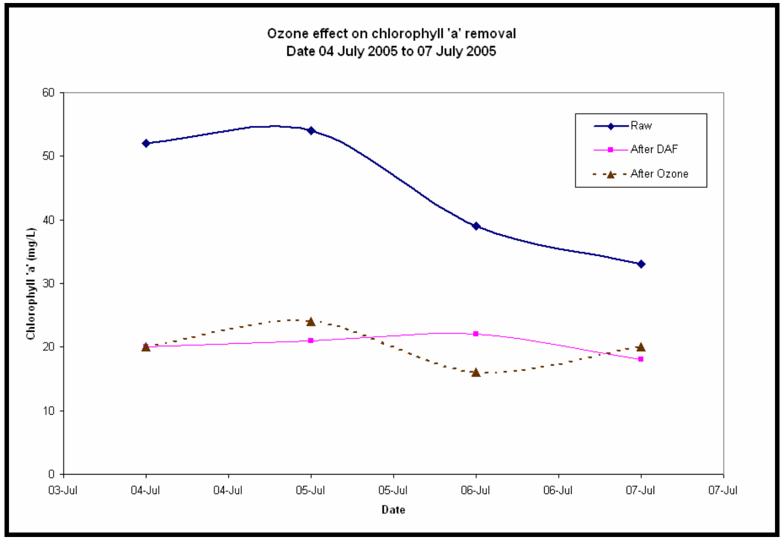


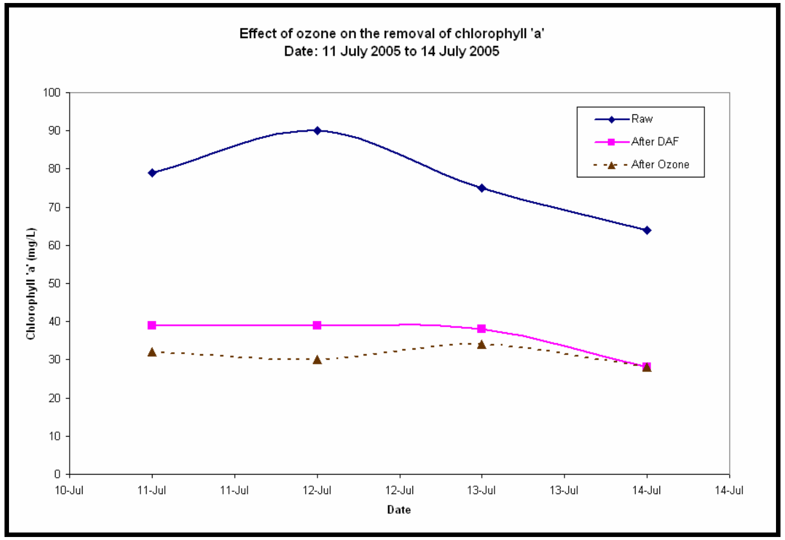


Figures 3.1 and 3-2: The effectiveness of ozone in colour removal at DWR









Figures 3.3 to 3.6: The effectiveness of removal of chlorophyll 'a' using ozone at Midvaal

Average ozone/micro-pollutant ratios

The average ratios of ozone required to the raw water micro-pollutant content (expressed as concentration of ozone required/concentration of target micropollutant) are tabulated in Table 3.7. The micro-pollutants considered were Fe, Mn, colour and chlorophyll'a'.

Ozone dose optimization for the removal of a target micropollutant may be achieved by dosing the ozone required for the reduction of the target micropollutant (to) below the maximum permissible concentration of the pollutant in the treated water, either at the end of the ozonation process or in the final water.

Variations in the type and concentration of background organic species greatly influence the ozone available for reduction of the target micropollutant. Ozone ratios would therefore vary as the raw water quality changes. The interpretation of the data presented in Table 3.7 should be used with due consideration to prevailing raw water conditions.

Table 3.7: Ratio of ozone required to amount of raw water pollutant

Pollutant	Concentration	Ozone required	Ratio
Fe, mg/L	0.24	1.5	6.2
Mn, mg/L	0.35	1.5	4.3
Chlorophyll 'a'	31	1.5	0.1
Colour, Hazens	21.7	1.8	0.1

4. Conclusions

- A user friendly, practical guide, that summarises the decision-making process for the inclusion of pre-oxidation in the water treatment train, selection of an appropriate oxidant for the application, and operational strategies for the cost-effective use of ozone in water treatment, has been compiled. The guideline also assists in the selection of hardware that includes oxygen feed source and preparation, ozone generation, contacting and destruction.

- A comprehensive survey on the ozone use in the South African water industry showed that ozone use locally is growing rapidly especially as a pre-oxidant in the pre-treatment and intermediate stages of the process chain. The survey also highlighted some local challenges in the cost-effective operation of an ozone plant. The main challenges were in the operation and maintenance of the ozone plant.

- The concept of instantaneous ozone demand, for the prediction of required ozone dose was investigated and applied to local raw water conditions as a means of optimizing ozone dose, based on variable raw water quality.

- Ozone demand tests using the gas ozone test (GOT) procedure, were not accurate enough for ozone dose control when ozone was used for oxidation.

- Instantaneous ozone demand (ID) using the solution ozone test (SOT) technique was found to be more reliable in predicting optimum ozone, based on reduction/removal of target micro-pollutants.

- An optimum ozone dose may be established on a laboratory scale for the particular raw water, based on the acceptable concentration of the micro-pollutant of interest in the final water. The ID can be directly related to residual ozone concentration. It is possible to control the ozone dose, based on raw water quality, by linking ozone dose to a set point residual ozone concentration in the ozonated water.

5. Recommendations

Operations and maintenance personnel should be adequately trained in the optimization of the ozone plant and troubleshooting ozone process problems. These relate mainly to the following aspects:

- Calibration and maintenance of analytical process control instrumentation including dewpoint analyser, ozone analyser (gas and liquid medium), gas flowmeters, and pressure gauges.

- A good practical understanding of the process control philosophy (including safety interlocks) inherent in a medium to large ozone installation.

- Collection of reliable process operating data including and continuous quality control monitoring that may be used to optimise ozonation and sustain cost-effectiveness of ozone.

- Conduct laboratory scale ozone instantaneous demand tests to check ozone dose and calibrate on-line ozone dose control in the full-scale plant.

- Use operational and quality control data to decide on the continuous operation of the ozone plant. There may be a significant energy and cost saving if the operation of the ozone plant is linked to raw and final water quality. Where there is no water quality or process enhancement incentive for the use of ozone, the ozone plant should only be operated at scheduled intervals for equipment maintenance reasons.

Further work is recommended for the collection of reliable data that may be used to assess the long term advantages and disadvantages of ozone in the water industry. Waterworks using ozone should be encouraged to co-operate with other ozone users in the industry and form an ‘Ozone User Forum’ where information with respect to ozone experience, new technology and data can be shared.

6. References

1. D. Barnes and F. Wilson, “Chemistry and unit operation in water treatment”, 1983, Applied Science Publisher LTD, England.
2. S. Carruthers, “Introduction to Ozone Generation”, 1997, available online at www.hydroponics.com
3. M. Gao and M. Hirata, "Ozone mass transfer in a new gas-liquid contactor-Karman contactor”, Vol. 42 (2), 2004, pp 145-149.
4. Urs van Gunten, “Ozonation of drinking water: Part I. Oxidation kinetics and production formation”, Vol 37(7), 2003, pp 1443-1467.
5. S. Hanft, “C-244 Ozone Generation: Technologies, Markets and Players”, 2004, available online at www.bccresearch.com/chem/244.html
6. Jones S.C, Sotiropoulos F., and Amirtharajah. A, “Numerical modeling of helical static mixer for water treatment”, Journal of environmental science, Vol. 128 (5), 2002, pp 431- 440.
7. S.Kawamura, “Integrated design and operation of water treatment facilities”, second edition, John Wiley & Sons; Canada,2000
8. U. Kogelschatz, E. Baldur, and E. Walter, “From ozone generators to flat television screens: history and future potential of dielectric-barrier discharges”, Pure Applied Chemistry, 1999, Vol 71(10), pp 1819-1828.
9. B. Langlais, D.A Reckhow and D.R Brink, “Ozone in water treatment-Application and Engineering”, Second edition, Lewis publishers, Chelsea, 1991
10. R.L Larocque, P.Eng, “Ozone application in Canada a state of the art review”, Vol21 (0191-9512/99), pp 119-125.
11. J. Le Pauloue and B. Langlais, “State of the art of ozonation in France”, 1999, Vol 21 (0191-9512/99), pp 153-162.
12. M.J, Pryor and S.D, Freeze, “The Treatment of Eutrophic Water using Pre and Intermediate Ozonation, Peroxone and Pica Carbon”, 2000, WRC Report No. 694/1/2000, ISBN 1868455882
13. Y.Magara, M. Itoh and T. Morioka, “Application of ozone to water treatment and power consumption of ozone generating systems”, 1995, Vol 29 (supplement 1), pp 175-182.
14. N. Matsumoto and K.Watanabe, “Foot prints and future steps of ozone applications in Japan”, 1993, Vol 21(0191-9512/99), pp 127-138.
15. G.J. Pietsch and V.I. Gibalov, “Dielectric discharge and ozone synthesis, Pure and Applied Chemistry”, 1998, Vol 70(6), pp 1169-1174.
16. F.P Pontius, “Water quality and treatment- a handbook of community water”, fourth edition, McGraw-Hill, United State of America, 1990
17. R.G. Rice, “Ozone in the United States of America-State-Of-The-Art”, 1999, Vol 21(0191-9512/99), pp 99-118.
18. J.Rueter and R. Johnson, “The use of ozone to improve solid removal during disinfection”, 1994, Vol. 14(2), pp 123-141.
19. Schulgen, B. F., Amirtharajah. A, and Jones S.C, “Effectiveness of static mixers for coagulation in water treatment industry”, 1996, AWWA Annual conference Denver, pp 121-147.
20. M.S. Siddiqui, G.L Amy and B.D. Murphy, “Ozone enhanced removal of natural organic matter from drinking water sources”, 1997, Vol 31(12), pp 3098-3106.
21. Y. Takeuchi, K.Mochidzuki, N.Matsunobu, R.K Motohashi and S. Toshimoto, “Removal of organic substances from water by ozone treatment followed by biological activated carbon treatment”, 1997, Vol 35(7), pp 171-178
22. T. Teffeteller, “Ozone Generators: Is ‘Apples to Apples’ Performance Evaluation Possible”, 2000, available online at www.wcponline.com/archive/jun00spot.htm

23. Tchobanoglous G., Burton L.F., Stensel H.D, "Wastewater engineering- Treatment and reuse", Fourth edition, McGraw-Hill, New York, 2003
24. C. Yurteri and M.D Gurol, "Ozone consumption in natural water: Effect of back ground organic matter", pH, and carbonate species, Ozone Science Engineering, 1988, 10:227:7.
25. W.J, Masschelein, "Ozonation Manual for Water and Wastewater Treatment", 1982, John Wiley and Sons Ltd., pp 28, 67
26. J. Katz, "Ozone and chlorine dioxide technology for disinfection of drinking water", Noyes Data Corporation, United State of America. , 1980
27. G.W, Miller, R.G. Rice, "European water treatment practices- their experiences with ozone", 1979, Civil engineering-ASCE, series on water resource no. 3.
28. NAVAZONE, 2002, "Ozone contactors in-line series", Liverron, CA 94551.
29. VERDER Ltd, "Verdemix-Dyanamic and static mixer, Solution in mixing technology", Hunslet, Leeds, MIX004-032000.
30. The Nursery paper, The national NIDO Project, 1997, ISSN: 1326-1495 (1997/008).
31. "The use of ozone in water and wastewater treatment-Proceedings", 1992, 2nd Southern African International Ozone Association Conference, ISBN 92-9095-001-3.
32. Wastewater technology fact sheet-Ozone disinfection, 1999, United States Environmental Protection Agency, Washington D.C; EPA 832-F-99-063.
33. GE Infrastructure Water and Process Technologies, available online at www.gewater.com
34. Lenntech Water Treatment and Air Purification, available online at www.Lenntech.com
35. Ozone Pure Water, Inc., available online at www.ozonepurewater.com
36. Ozone Solutions, Inc., available online at www.ozoneapplications.com
37. Ozonation of Wastewaters, available online at www.water.me.vccs.edu/courses/ENV149/ozonationb.htm
38. ProMinent Company Group, available online www.prominent.de
39. Prozone International, available online at www.prozoneint.com
40. Spartan Environmental Technologies Air and Water Treatment, available online at www.spartanwatertreatment.com
41. "Integration of CFD Modeling and Kinetic Study to Improve the Control Strategy of an Ozo Contactor", 2004, Biennial Conference and Exhibition, WISA, Cape Town.
42. G.E. Rencken, "Ozonation at Wiggins Water Purification Works", 1993, Durban, South Africa', Ozone Science and Engineering, Vol 16, pp. 247-262.
43. R. Lowndes, "Ozone Oxidation and Disinfection Environmental Benefits", 2005, Ozone News, Vol 33(6), pp. 17-19
44. Quederni, Q. Limvorapituk, R. Bes, and J.C Mora, "Ozone decomposition on glass and Silica", Ozone Science and Engineering, 1996, Vol 18(5)
45. F. Geering, "Ozone applications-The State-of-the-Art in Swirtland", Ozone Science & Engineering, 1999, Vol 21 (2), pp 187-200
46. A.L. Mazzie, RM. Meyer, L.J. Bollyky , (1995) Conference paper- Presented at International Ozone Association Pan American Group- 1995 Annual Conference
47. EPA Guidance Manual, Alternative Disinfectants and Oxidants, April 1999
48. K.L. Rakness, "Ozone in Drinking Water Treatment: Process Design, Operation and Optimization", 1st edition, American Water Works Association, United State of America, 1999
49. EPA Guidance Manual, Alternative Disinfectants and Oxidation, Chapter 3, April 1999
50. Compressed Gas Association, Inc. (CGA). Oxygen Product number CGA G-4. Compressed Gas Association, Inc.: Chantilly, VA. ,1996
51. National Fire Protection Association (NFPA). 2001. NFPA 50-Standard for Bulk Oxygen Systems at Consumer Site. National Fire Protection Association: Quincy, MA.
52. "Standard methods for the Examination of water and Wastewater", 20th Edition, Edited by L. S. Clesceri, A. E. Greenberg and A. D. Eaton, Pub. APHA-AWWA-WEF, 1998

53. Ozone News, Volume 35, No. 6. December 2007
54. Bellamy, W. D. et al. "Ozone demonstration and pilot evaluation for colour removal at Long Beach". Proc. AWWA Ann. Conf., Cincinnati, OH. 1990
55. Horst, M: Removal of the Residual Ozone in the Air After the Application of Ozone. In Ozone in Water treatment: Application and Engineering, edited by Langlias, B; Reckhow, DA; Brink, DR, AWWA (1991).

Appendix A

Inanda Dam Water

Samples for ozone demand tests were taken from the lower abstraction point where the concentration of Fe and Mn were higher. Table A-1 shows the water quality for Inanda Dam water during the testing period. The ozone demand for the Inanda Dam water was then calculated.

Table A-1: Inanda Dam Water Data

Determinant	Average Value	Units
pH	7.89	
Turbidity	2.00	NTU
Fe	0.24	mg/l
Mn	0.35	mg/l
Colour	19.1	H
Alkalinity	69.54	ppm

Figure A-1, shows that ozone demand increases with ozone dose.

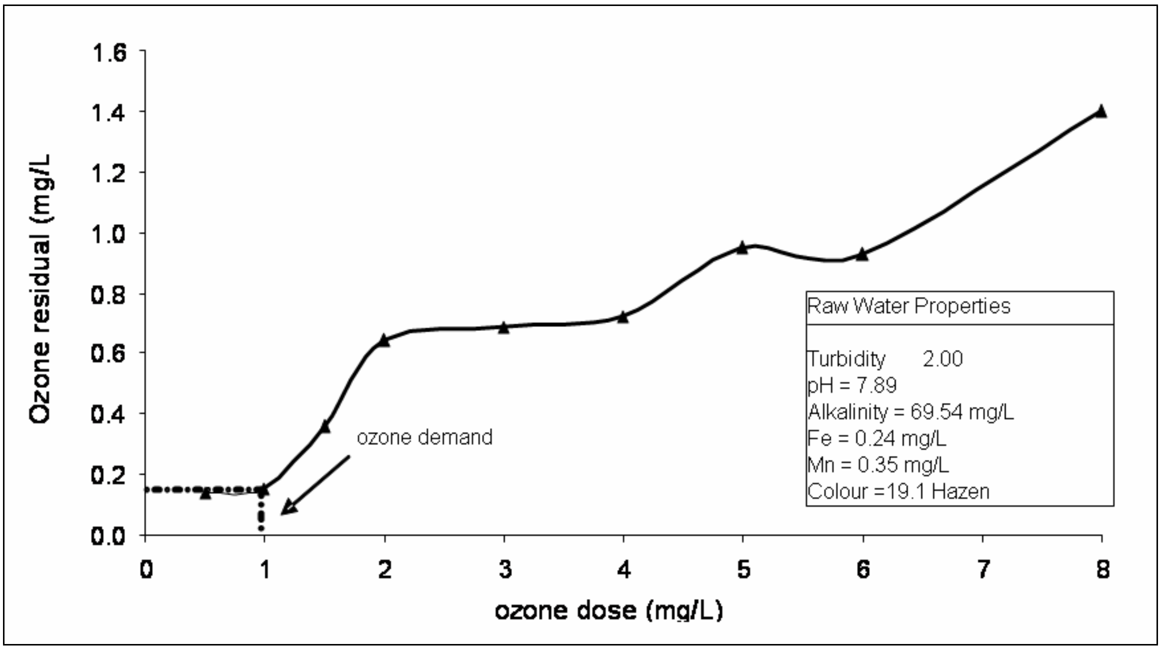


Figure A-1: Ozone demand at Inanda Dam

Figure A-2 shows the change in residual colour and residual ozone with incremental ozone doses in a sample of Inanda Dam water. The graph indicates that the ozone required to reduce colour to below 5 Hazen units (colour limit for potable water at Umgeni Water), almost coincides with the ozone demand.

However, the relationship between ozone demand and ozone required is not consistent or reproducible probably due to inaccuracies in the determination of ozone demand, especially at the lower ozone levels.

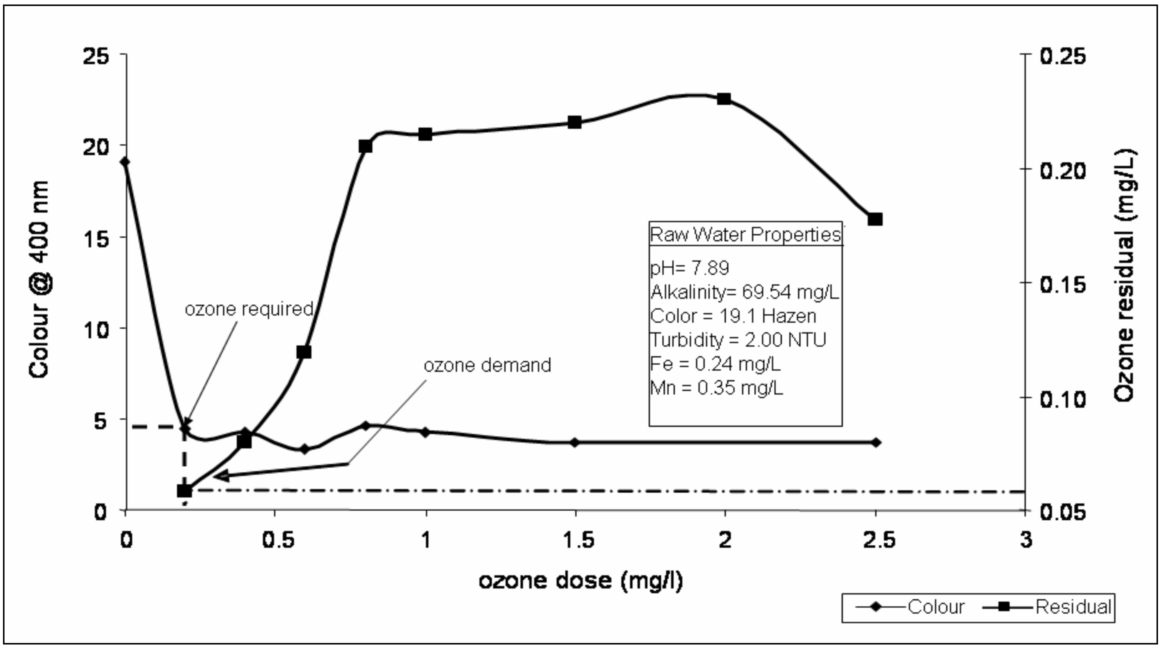


Figure A-2: Colour removal at Inanda dam

Figure A-3 indicates that the ozone demand and ozone required for iron removal appear to coincide. Again, as with colour removal, the relationship between ozone required and ozone demand is not consistent probably due to inaccuracies in ozone demand measurements at the lower ozone dosage levels.

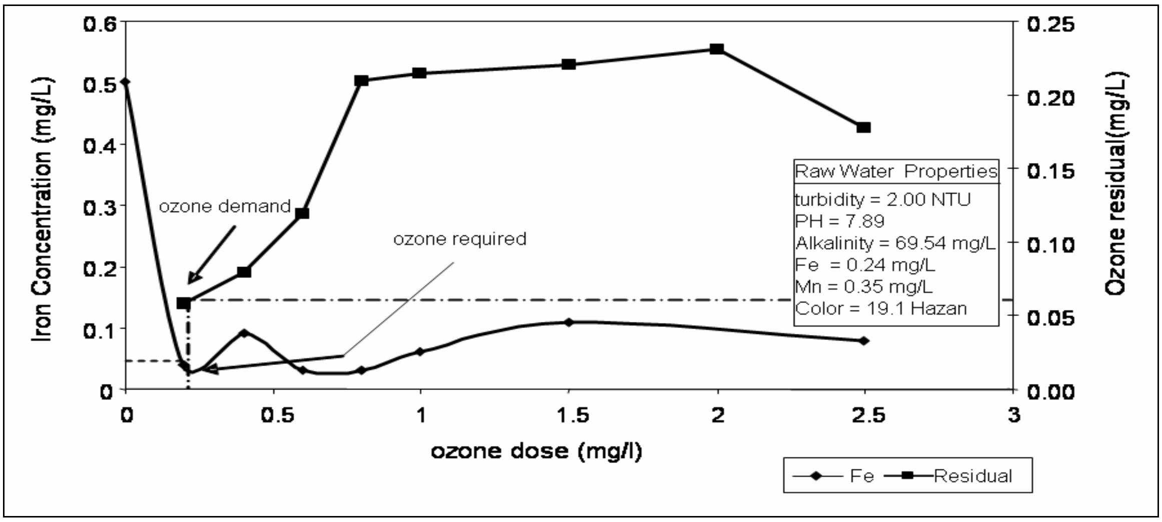


Figure A-3: Iron removal at Inanda dam

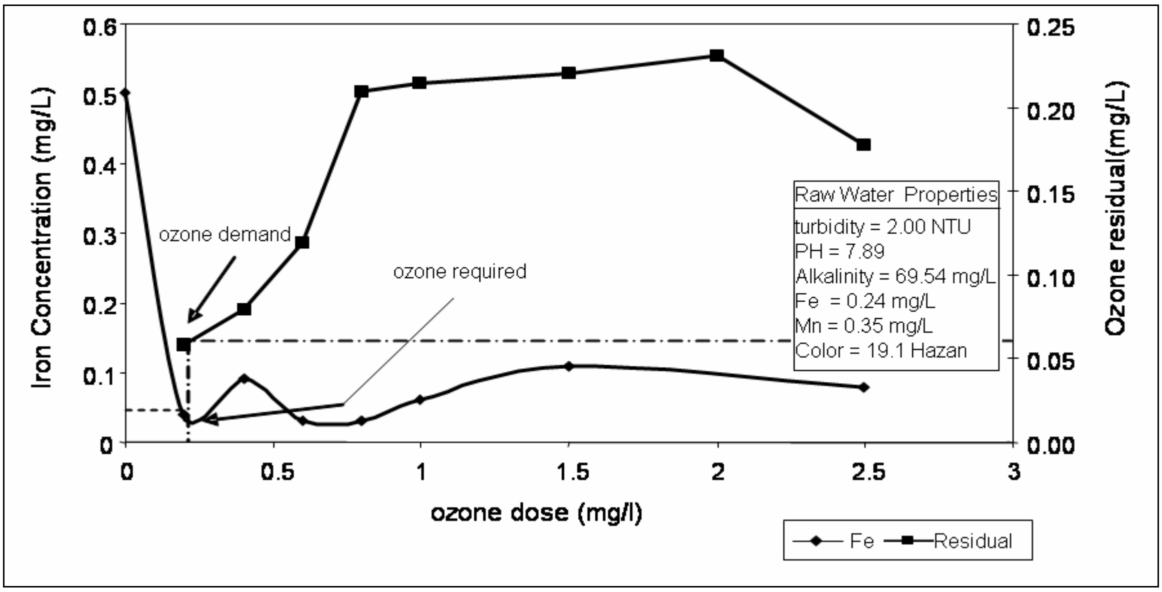


Figure A-3: Iron removal at Inanda dam

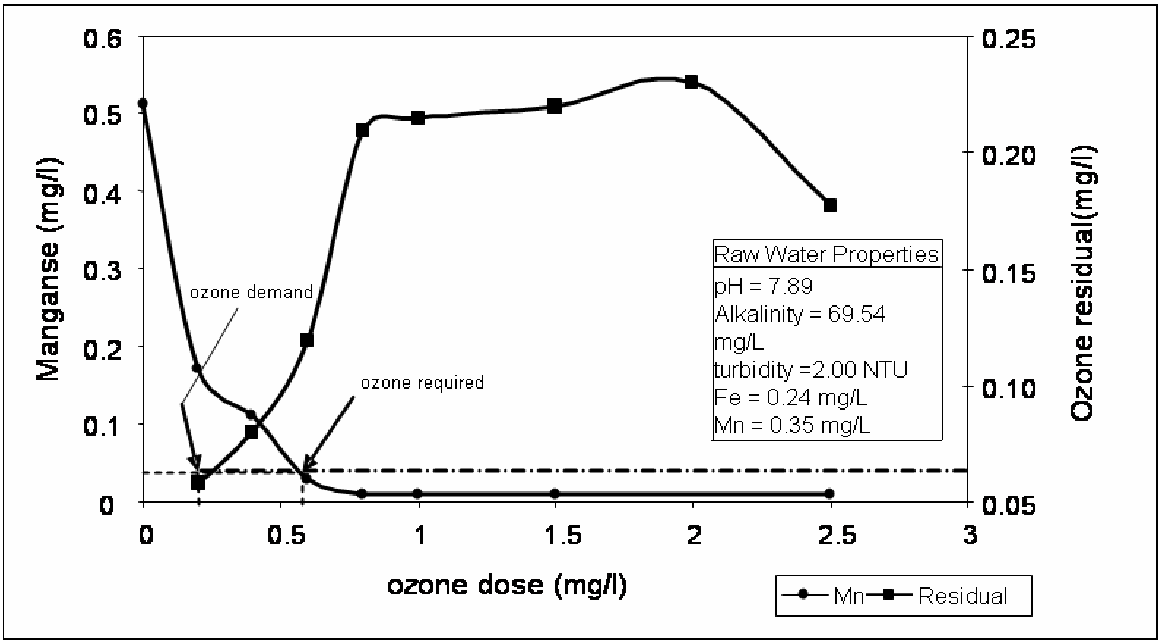


Figure A-4: Manganese removal at Inanda dam

It can be seen from the above figures (i.e. Figures A-1 to A-4) that the ozone demand is not easily quantifiable, especially at low ozone demand levels. In these situations, ozone required produces more consistent and reliable results. However, ozone required may vary, depending on the variability of the sample matrix and the concentration of the target micro-pollutant.

Ozone Demand Tests on Durban Water Recycle

Ozone demand tests were done on the water samples taken from the feed to the ozonators. Ozone required was the ozone dose that reduced the effluent colour (immediately after the ozonation stage) to less than a specified limit. Figure A-5 indicates that an ozone dosage of about 4.5 mg/l is required to reduce the colour to 10 Hazen units. Here the ozone demand was approximately 6.8 mg/l (7 mg/l - 0.21 mg/l).

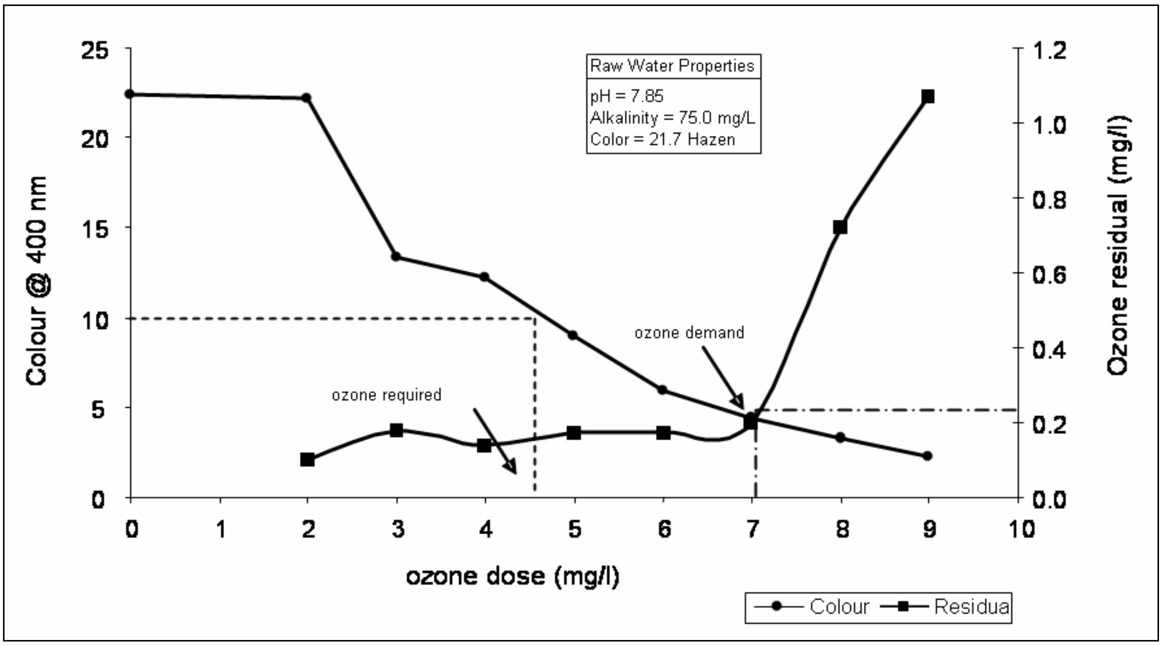


Figure A-5: Colour removal at Durban Water Recycle (DWR)

Relationship between Ozone Demand and Ozone Required

Comparison between ozone demand and ozone required for the reduction of iron, manganese and colour (Figures A-6 to A-8 indicate that there is no correlation between them based on the GOT method).

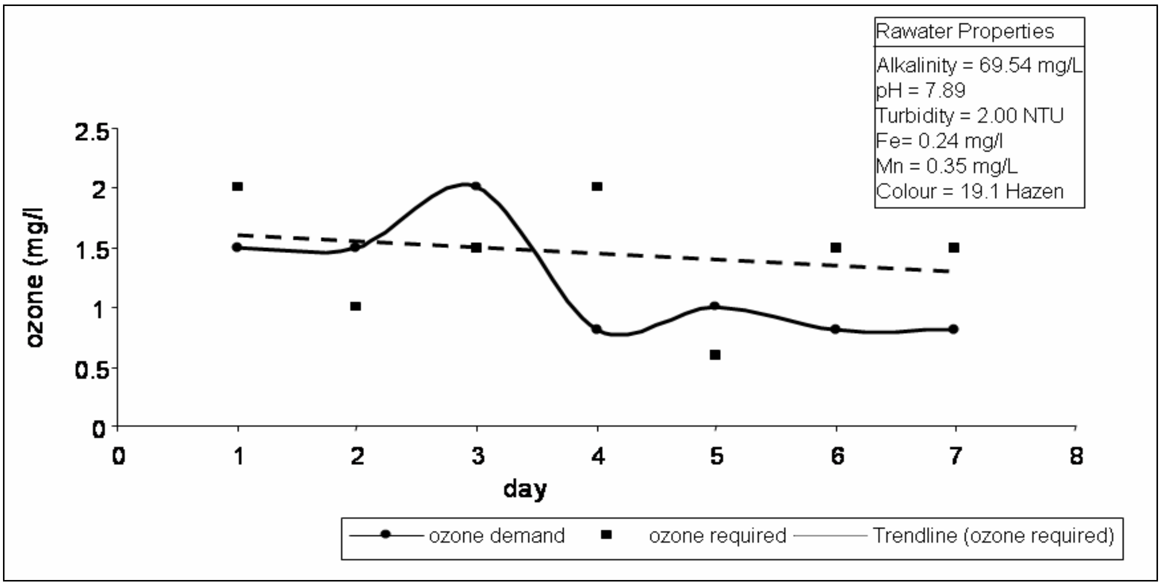


Figure A-6: Ozone demand vs. ozone required for Iron (Fe) removal

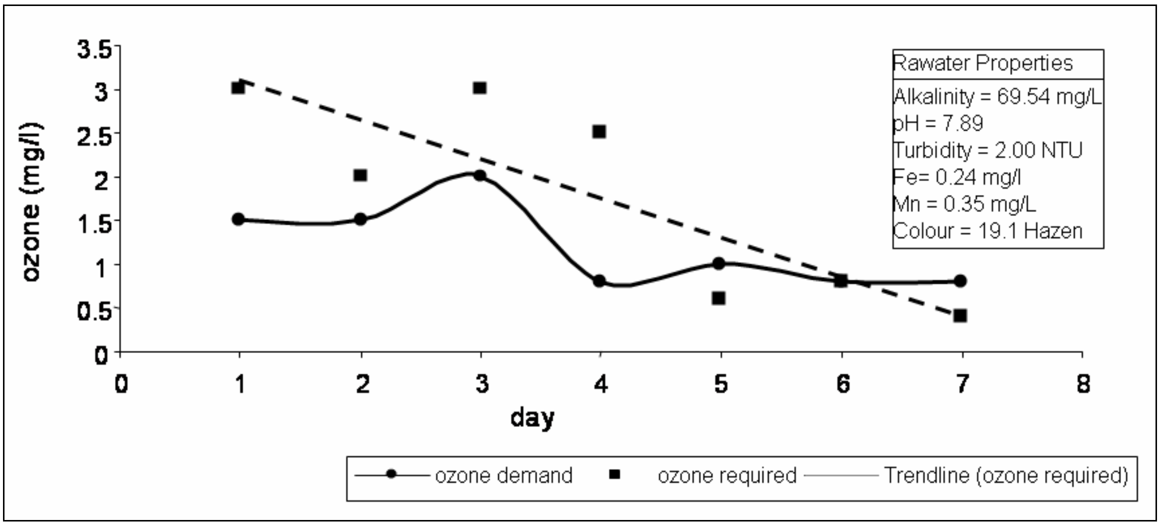


Figure A-7: Ozone demand vs. ozone required for Manganese (Mn) removal

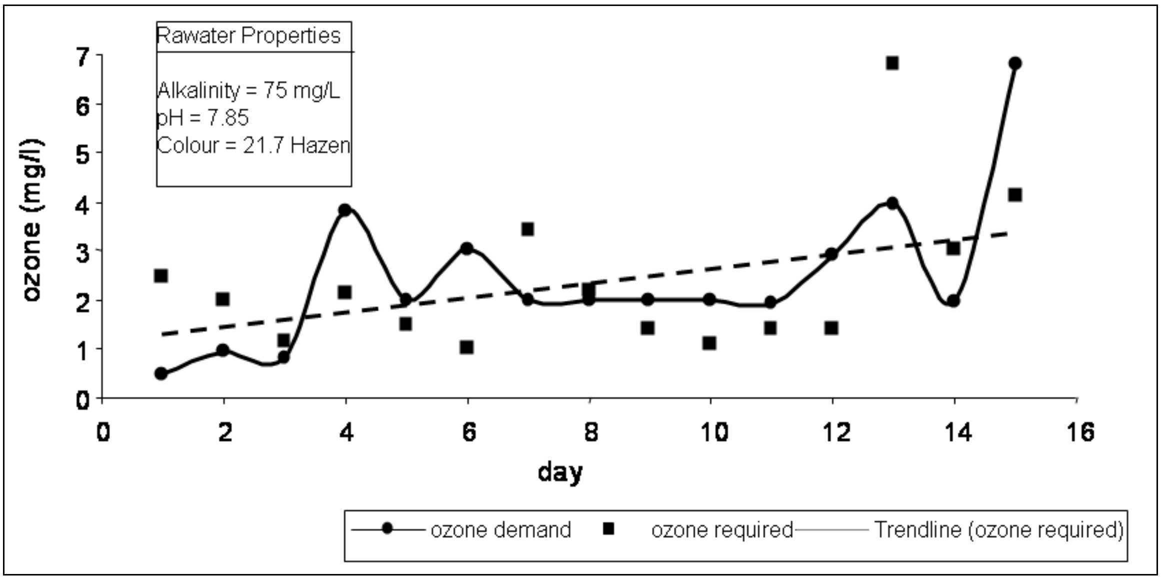


Figure A-8: Ozone demand at Durban Water Recycle (DWR) for colour removal

Recent literature has indicated the development of an instantaneous ozone demand (ID) that is determined by profiling the development of the residual ozone in less than 60 seconds. The method uses a simple 'solution ozone test' (SOT) procedure that determines the ID and the slower second phase ozone consumption represented by a pseudo first order rate constant of ozone decay, kc. ID may be used to control pre-ozonation and kc may be used to control post ozonation (disinfection) (KL Rakeness, 2005; Hyun-Je Oh et al., 2003).

SOT Ozone Residual Decay Profile

A description of the Solution Ozone Test (SOT) is given in Appendix B.

Figure A-9 to A-11 show the Durban water recycle and Midvaal water samples that were ozonated at fixed initial doses of 2 mg/L, 3 mg/L and 3.5 mg/L, respectively. The figures show that ozone residual concentration drops sharply before 1 minute. After one minute the rate at which residual ozone decreases is slower. The fast decay of ozone in the sample within the first minute of ozone addition is due to the fast oxidation reaction while the slow decay of ozone after 1 minute of ozone addition is due to the slow disinfection reactions.

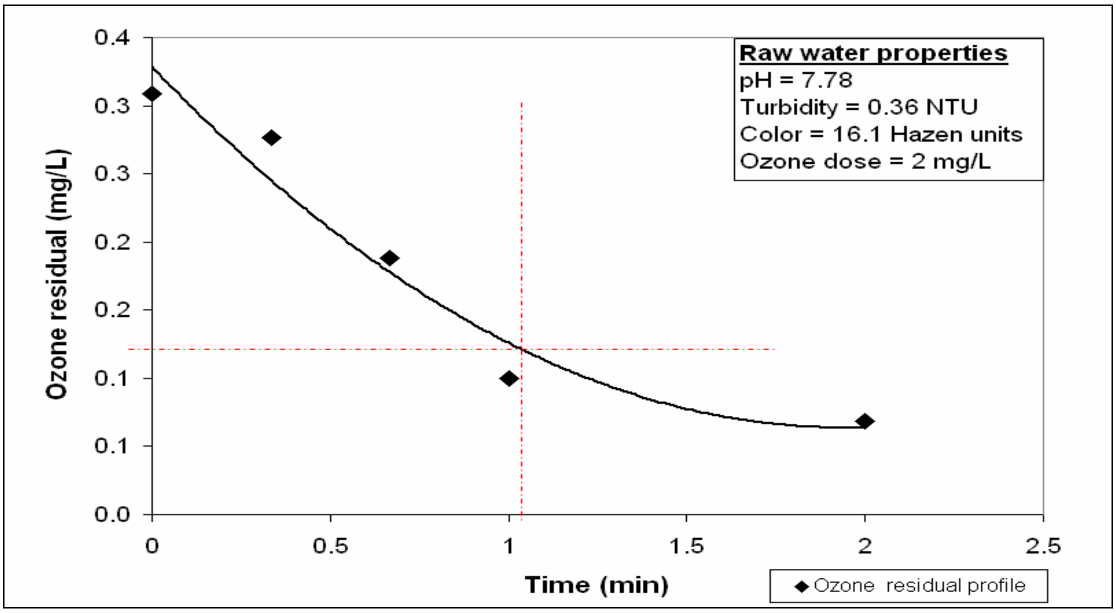


Figure A-9: Instantaneous Ozone Demand: Durban Water Recycle

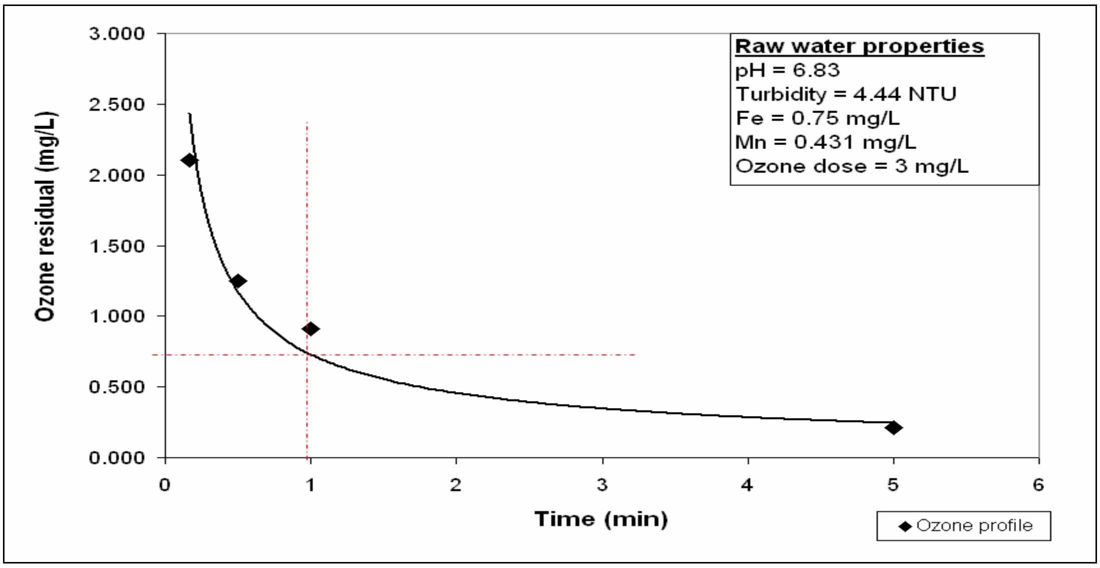


Figure A-10: Instantaneous Ozone Demand: Umzinto Dam

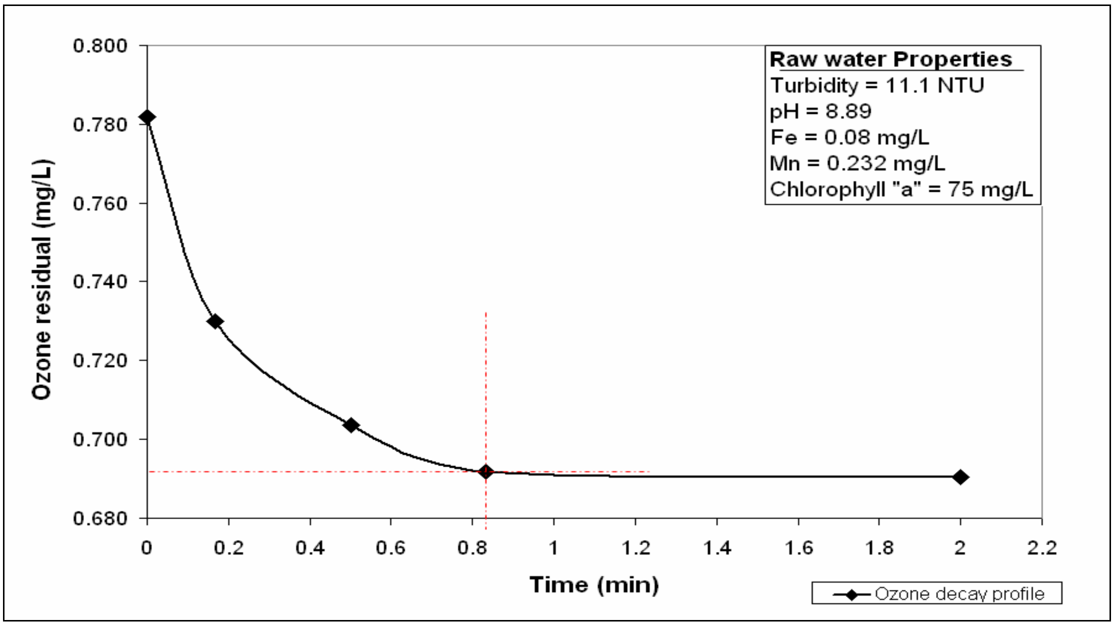


Figure A-11: Instantaneous Ozone Demand: Midvaal Water

Comparison between Instantaneous Ozone Demand (ID) and Target Micro-Pollutant

Figures A-12 and A-13 show the relationship between the target determinants or micro-pollutants and ID for incremental ozone doses in the Durban Water Recycling raw water and Midvaal raw water samples.

Figure A-12 indicates that instantaneous ozone demand (ID) increases linearly as with ozone dose. Figure A-12 also shows that ozone dose for optimum colour removal may be inferred from the ID profile.

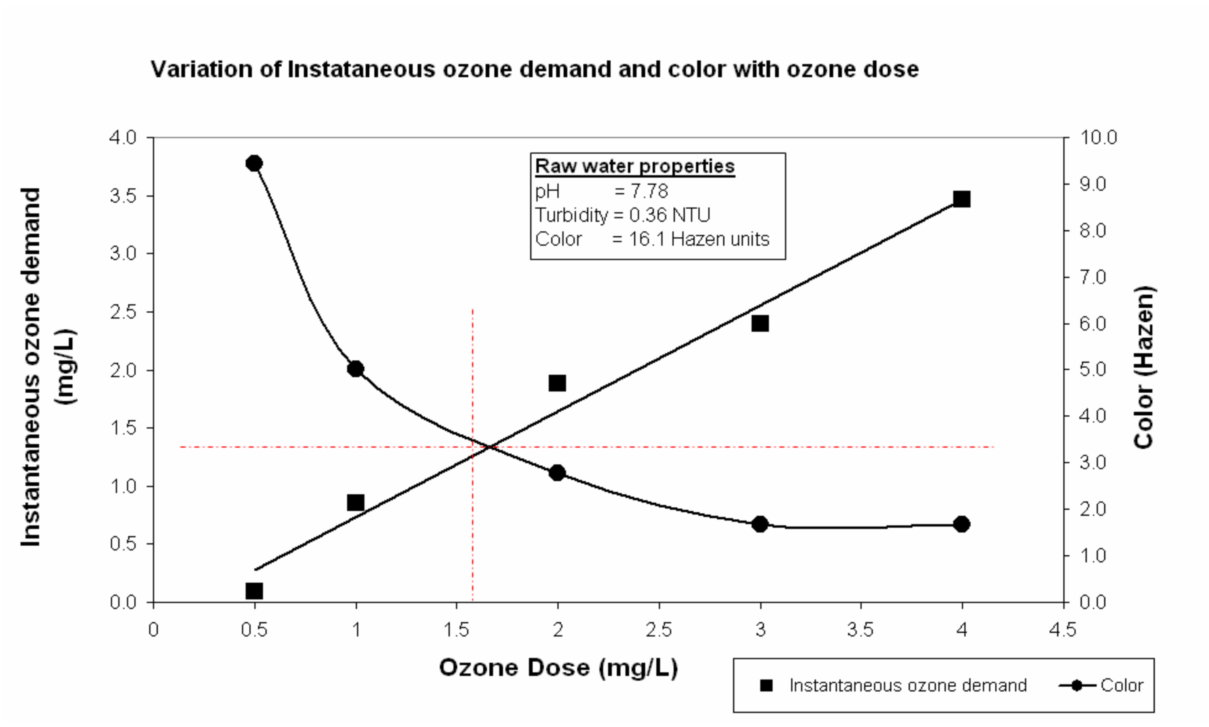


Figure A-12: Variation of Instantaneous Ozone Demand and Colour Removal with Ozone Dose: Durban Water Recycle

The response of instantaneous ozone demand, iron and manganese to the ozone dose has not been showed in this report. The levels of iron and manganese in the Wiggins water works were law for any conclusive experimental work.

Figure A-13 shows that the instantaneous ozone dose profile may be used to predict the required ozone dose for chlorophyll 'a' reduction.

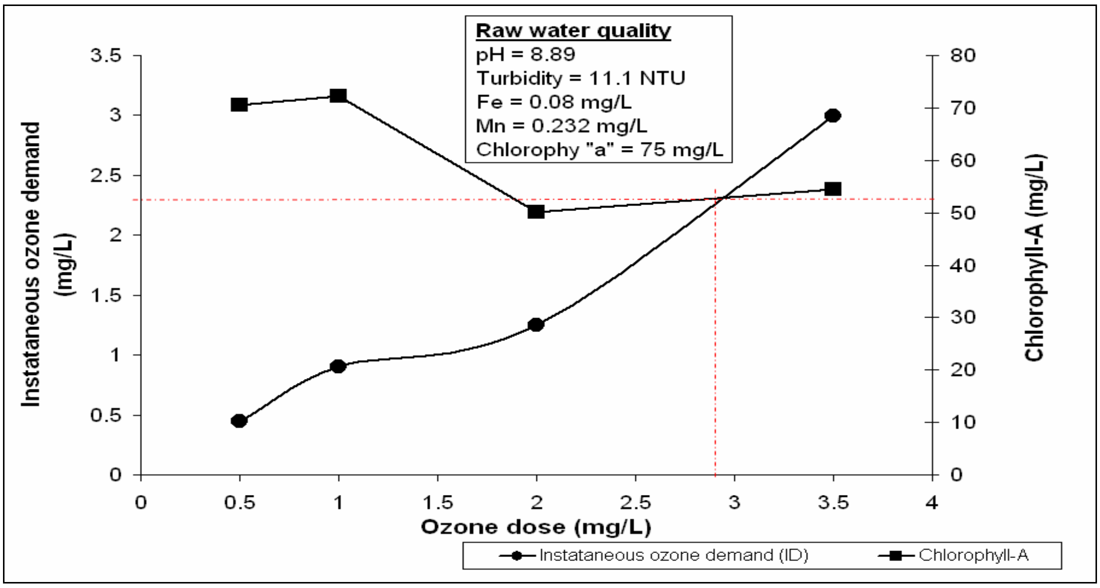


Figure A-13: Variation of Instantaneous Ozone Demand and Chlorophyll'a' Removal with Ozone Dose: Midvaal Water

<u>Summary of Findings</u>: An optimum ozone dose may be established on a laboratory scale for the particular raw water, based on the acceptable concentration of the micro-pollutant of interest in the final water. The ID can be directly related to residual ozone concentration. It is possible to control the ozone dose, based on raw water quality, by linking ozone dose to a set point residual ozone concentration in the ozonated water.

Appendix B

Determination of Ozone Demand

Gas Ozone Test (GOT)
Preliminary laboratory work focused on establishing relationships between the specific micro-pollutants and ozone dose, ozone demand, ozone residual and required ozone dose. The required ozone dose may be defined as the ozone dose corresponding to the targeted level or removal efficiency of the particular micro-pollutant.

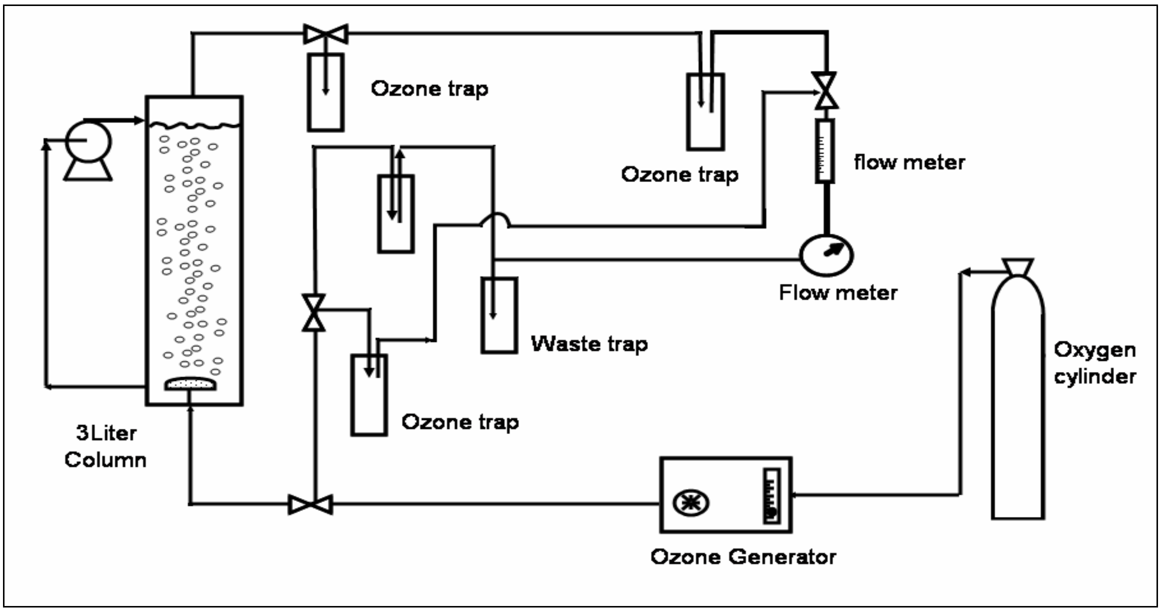


Figure B-1: Laboratory scale ozone apparatus for Gas Ozone Test (GOT)

Ozone Demand (Solution Ozone Test)
Kinetic studies have shown that the ozone oxidation reaction takes place within a minute of addition of ozone to the water sample. The oxidation reactions may be characterized by an instantaneous ozone demand which corresponds to an ozone residual, measured 1 minute after the addition of ozone. The advantage of the SOT method over the GOT method was that ozone residual may be measured at a fixed time interval after the addition of ozone into the sample. The apparatus shown in Figure B-2, allows the addition of a calculated volume of concentrated ozone in solution (of known concentration).

The water sample is mixed for 10 seconds after addition of ozone. Mixing is stopped and the first sample taken for residual ozone determination. Sampling for residual ozone determination continues at 10 second intervals until one minute. Thereafter samples are taken at one minute intervals until there is no significant change in residual ozone.

Samples of water from Umzinto Dam (Umgeni Water), Durban Water Recycling (DWR) and Midvaal Water collected and tested for ozone demand using the SOT method. Ozone dose was varied between 0.5 mg/L and 4 mg/L. Samples were analyzed for concentration of contaminants in raw water and in the ozonated water (after 1 minute of ozone addition).

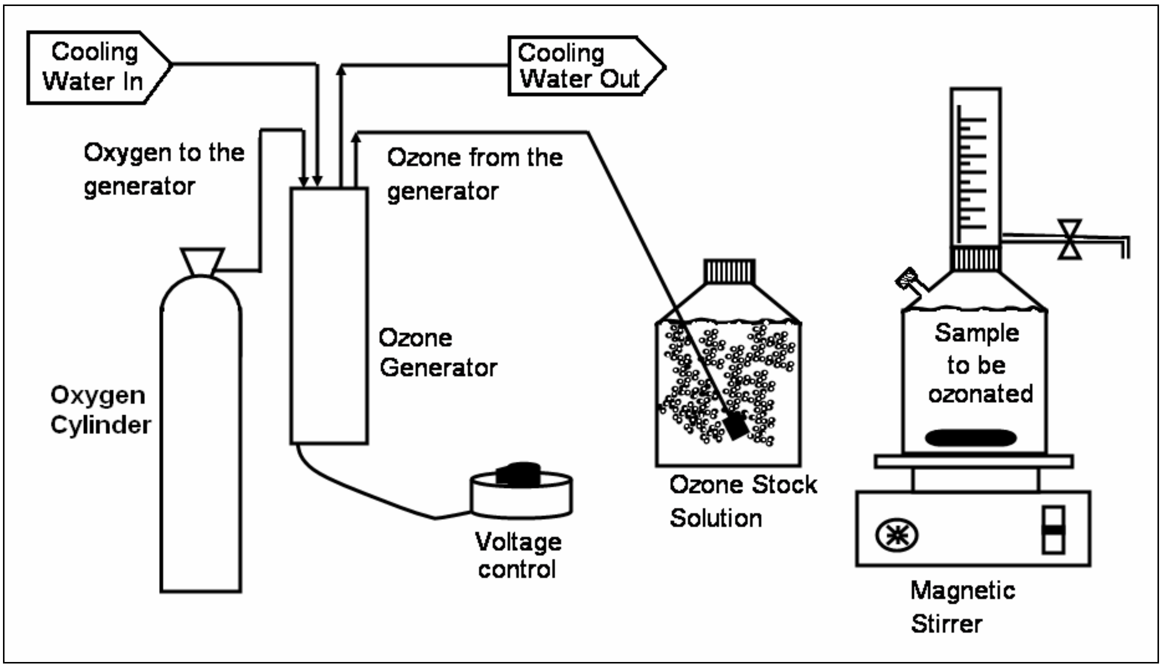


Figure B-2: Laboratory scale ozone apparatus for Solution Ozone Test (SOT)

Ozone demand tests using the gas ozone test (GOT) procedure are not accurate enough for ozone dose control when ozone is used for oxidation.
Instantaneous ozone demand (ID) using the solution ozone test (SOT) technique was more reliable in predicting optimum ozone, based on reduction/removal of target micro-pollutants.

Appendix C

MAINTENANCE

Table C-1: Maintenance requirement for ozone contactors

Waterworks	Wiggins Waterworks	Midvaal Water	Durban Recycle	Vaalkop
Routine Planned	As per supplier O&M manual	Daily, weekly, monthly & yearly inspections of all equipment	Ozone contactors checked annually during maintenance shut down. Rubber gaskets are checked fort-nightly to ensure no gas leaks from the contact tanks Daily operator checklist Of process operating data.	Negotiations with equipment Supplier For maintenance contract
Action		Repair of faulty equipment as and when required		
Breakdown	Revert to chlorine when ozone down. Or use powder activated carbon (PAC)	Repair of faulty equipment as and when required		

MATERIALS OF CONSTRUCTION

For all pipe-work and fittings in contact with ozone, stainless steel was the preferred material of construction.