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

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ABSTRACT

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.

A user friendly, practical guide, that summarises the rationale for the inclusion of pre-oxidation in the water treatment train, selection of the 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.

INTRODUCTION

Ozone was first used in 1893 as a disinfectant. Before long it became apparent that ozone, a strong oxidizing agent, exhibited other properties that made its application to water treatment more advantageous in comparison with other oxidants. In South Africa, there's a rapidly growing market for ozone. While chlorine is still the final disinfectant of choice, ozone is gaining prominence as an oxidant at the pre-treatment and intermediate stages of the conventional water treatment train. Pre-ozonation is applied for the oxidation of soluble iron and manganese, control of algae and algal by-products, taste and odour, colour and other micro-pollutants such as pesticides and phenolic compounds. Intermediate ozonation is applied upstream of granular activated carbon filters to reduce the organic load on the GAC filters. Organic load can be reduced by as much as 40% through intermediate ozonation. Other advantages of ozone include inactivation of protozoa, immobilization of bacteria, viruses.

RATIONALE FOR PRE-OXIDATION

The need for a pre-oxidant has to be carefully evaluated. Figure 1 is a flowchart of a typical selection process.

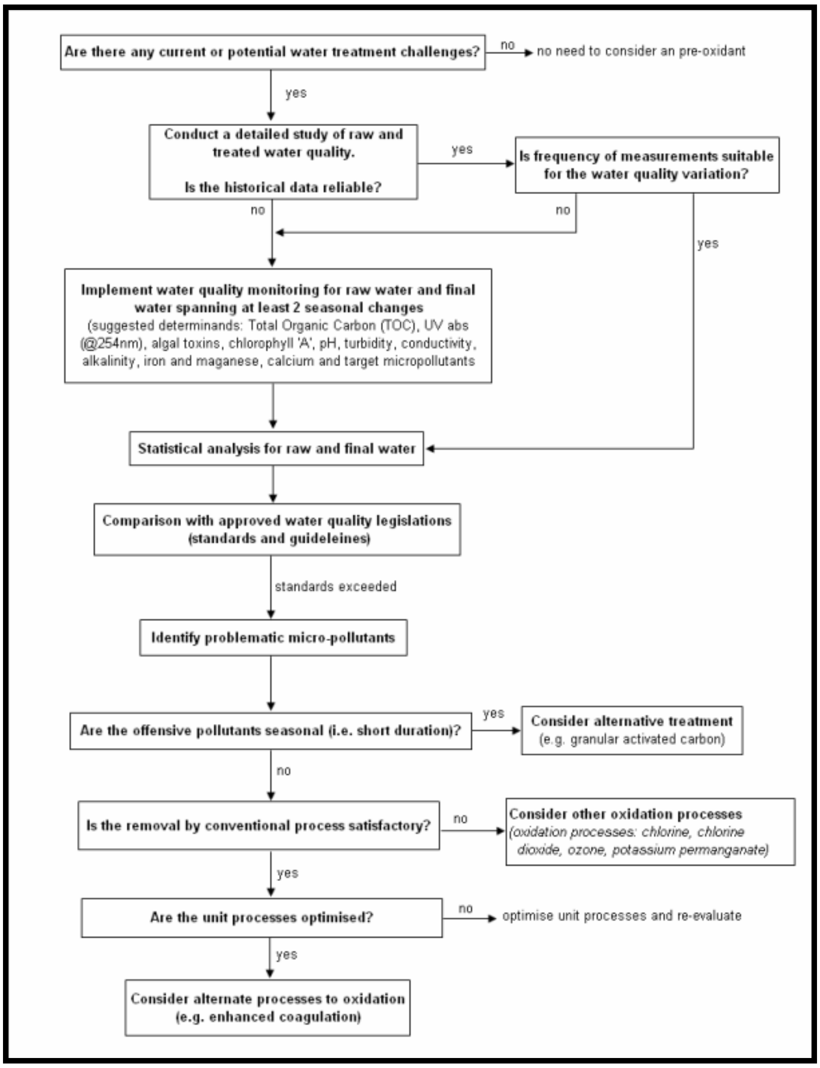

Figure 2: Flowchart showing selection process for pre-oxidation

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 (8). 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 advantages and disadvantages of each type of oxidant for various requirements.

Iron and Manganese Removal

Oxidant	Iron	Manganese	Interfering substance/disadvantages
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.

Colour Removal

Oxidant	Colour	Interfering Substances/disadvantages
Chlorine	Satisfactory Colour reduction	Fulvic or humic acids Consume large amounts Of chlorine and form halogenated Compounds, TTHM's
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 -6min 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.

Taste and Odour Control

Oxidant	Taste and Odour	Interfering Substances/disadvantages
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.

Algae Removal

Oxidant	Algae	Interfering Substances/disadvantages
Chlorine	Excellent algae reduction	TTHM's, 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 (5min reaction time) Inactivation of certain zooplankton	High algae requires pretreatment (flotation) before ozone.

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

1. Process requirements and complexity
2. Operational requirements and complexity
3. Safety, health, environmental and quality

4. Budget costs (Capital, operational costs - chemical, electricity, scheduled component replacement, general maintenance)

OXIDANT SELECTION

An appropriate oxidation process for the specific requirements of the application is selected based on the evaluation criteria and outcomes of the desktop study. The final selection may be based on the following main criteria:

- Cost including capital, operational, maintenance
- Meet overall removal efficiency as per legislation
- Local technical support

Having decided that ozone is the most suitable oxidant for the application, the next stage is the design consideration and equipment selection.

DESIGN CONSIDERATION AND EQUIPMENT SELECTION

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), ozone contacting and ozone destruction. As a starting point, a design engineer requires the following basic information:

1. Ozone demand (maximum, average and minimum)
2. Point/s of ozone application in treatment train
3. Contact time (maximum, average, minimum)
4. Effect of ozone on down stream treatment processes

AVAILABILITY OF RELIABLE PROCESS DATA

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

I. Treatability studies with the same or similar water.
II. Treatment plant experience on the same or similar water
III. An educated guess based on 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.

PROCESS SELECTION

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.

SELECTION OF OZONE EQUIPMENT

Figure 2 below, shows the main components of a typical ozone plant

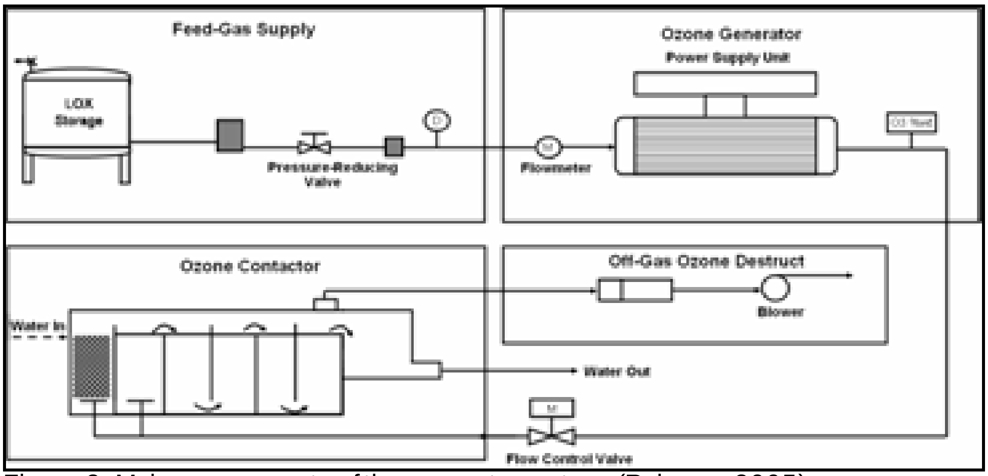

Figure 2: Major components of the generator system (Rakness, 2005)

FEED GAS SUPPLY

There are several feed gases that can be used in the generation of ozone. These include air, oxygen enriched air and high purity oxygen. 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 have attributes more suitable for particular ozone applications. Therefore feed gas selection should be made after careful consideration of factors which include:

- Ozone requirements
- Ozone production
- Aspects of the application, including;
  - Raw water with high ozone demand
  - Oxidation of easily oxidizable compounds
  - Operational and maintenance capabilities
  - Budgetary constraints
  - Logistics

Table 1: 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 PSA's for larger ozone systems Lower operating and energy costs relative to PSA	High level of maintenance required

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

OZONE GENERATION

The main components of an ozone generation system are, power supply unit (PSU), ozone generator and cooling water system. A suitable generation system is one that produces ozone in the required concentration range.

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 PSU's to further increase ozone concentration and reduce energy consumption.

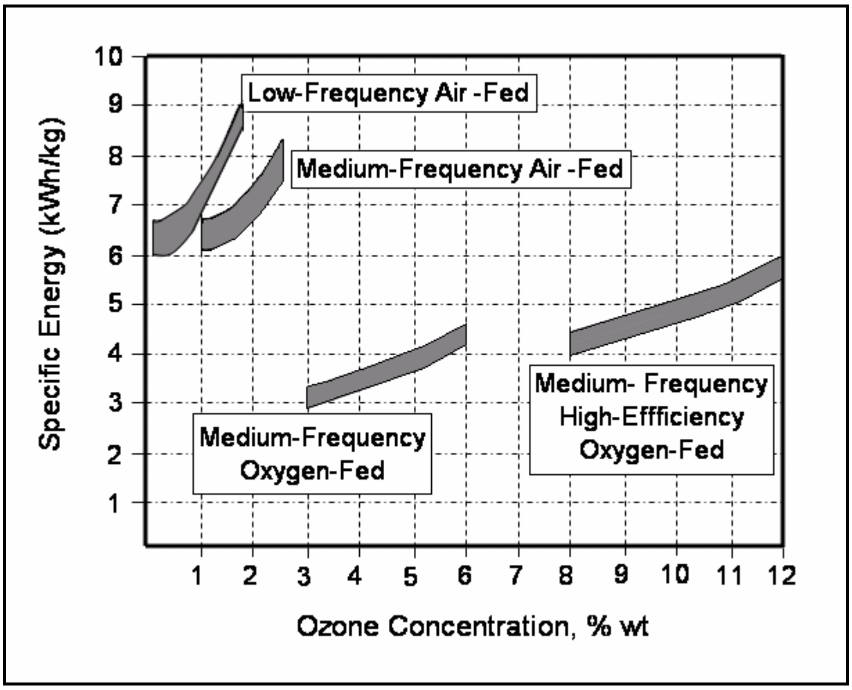

Figure 3: Specific energy profile for air-fed and oxygen fed ozone generators (Rakness, 2005)

OZONE CONTACTOR

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.

Table 2: 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 waterflow, 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).

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 used:

<u>Raw Water Flowrate</u>
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.

<u>Ozone Residual in water</u>
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.

Contrd 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).

OZONE DESTRUCTION

It is imperative that waste processes gase s containing ozone be returned to the atmosphere at concentrations that are safe for personnel, environment and equipment. Because the process off-gas contains ozone at concentrations that exceed the safe maximum allowable concentration, off-gas passe s through a destructor that essentially reconverts the ozone to oxygen.

There are essentially three types of ozone destructors:

1. Thermal destructors. These are energy intensive as they are normally operated between 300 and 350^0C. Heat recovery units are normally included, where the incoming off-gas is pre-heated.

2. Thermal catalytic destructors. These are more popular as they operate at lower temperatures (30^0C to 70^0C). 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 (Horst, 1982)

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. Generally, stainless steel 316 is preferred.

OPERATIONAL STRATEGIES FOR COST-EFFECTIVE OPERATION

Having designed built and commissioned the ozone plant, there are operational control strategies that need to be implemented for the sustainability of cost-effective operation of the process. The first step would be to plan the ozone operation and performance optimization programme. The goal of optimizing ozone performance is to continuously achieve performance objectives at minimum operating cost (2).

In the perfect world, a properly designed plant with dedicated and trained operational staff who 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.

Some inherent negative aspects associated with the use of ozone also need to be addressed.

Energy requirements: A significant disadvantage of ozone is that it is an energy intensive process. A recent study found that ozone production and operation accounted for 35% of the total energy consumption of a waterworks (1). The same study further indicated that the operation stage was the most energy and material intensive stage in the life cycle. The study also found that environmental burdens of producing potable water were traced to power consumption and that there was a need to increase electricity efficiency during operation (starting with the unit processes that consume the most electricity)..The looming crisis in South Africa, with respect to the sustainability of electrical power nationally, will greatly impact on the selection of water treatment processe s, especially, energy intensive processes like ozonation. This could weigh heavily on process selection, where power consumption may feature highly on selection criteria.

Disinfection by-products: Aldehydes and organic peroxides (some of the disinfection by-products which can be formed by the oxidation of many organic compounds in the raw water by ozone) are known to have adverse health impacts on both humans and animals (12). In addition, some studies have shown that pre-ozonation can increase the formation of certain halogenated disinfection by-products (DBPs) such as bromate (BrO_3^-), a potentially carcinogenic substance, which is formed in bromide-containing water (12, 2). There exists various ways of removing these (DSPs) (e.g. the use of GAC for the removal of aldehydes (12) or the removal of organics prior to ozonation using biological filters (2)), but the economic feasibility of these treatments need to be weighed against that of using alternative treatment processes to ozonation.

Cooling Water Temperature

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.

Air Preparation

Ensure adequate cooling water supply with minimum temperature fluctuations to all air preparation equipment that require cooling.

1. Dust and particulate matter in atmospheric air, in the vicinity of the air blowers, require more frequent filter cleaning, 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. (2).

Ozone generator

Ozone generators must be protected from the following:

- High dewpoint (> - 60^{0}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.

The ozone shutdown sequence must include initial purging with a high flow of dry air to remove traces of ozone in the system. 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.

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.

Ozone Contacting System

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.

Periodic contact efficiency tests (at least once in six months) will generally highlight problems due to blocked or broken diffusers, short-circuiting, ozone leaks, ozone analyzer, is an effective tool for optimization of the ozone destructor unit.

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 with 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.
- The power consumption of a t thermal destructor, normally operated between 300 and 350^{0}C, may be significantly reduced, if the volume of atmospheric air drawn by the destructor extraction fan, through the contactors, is optimized. Installing a low range ozone analyzer at the outlet of the destructor will assist in making decisions that include the following:
- Optimization of ozone destructor operating temperature.
- Reduction in air flow through the contactor via the extraction fan at the ozone destructor.

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 ling and tedious. The error messages have been improved to identify the problem area more closely.

<u>Ozone Dose Control</u>

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 fullscale 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 @254nm, ozone dose may be optimized on the basis of variable raw water quality.

<u>Operation Philosophy Based on Raw water Conditions</u>

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 below levels that do not require ozone. The situation is that there is no quantifiable reason for using ozone other than for aesthetic reasons and keeping the plant running.

<u>Operations Personnel Training</u>

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.

<u>Ozone Plant Safety</u>

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.

CONCLUSION

The main components of an efficiently operated ozone plant include the following:

- Well designed plant.
- Trained and highly motivated operators
- Proper operation and planned maintenance
- Efficient quality management plan
- Continuous learning and development.

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Acknowledgement

The paper emanated from a Water Research Commission (WRC) funded research project. Umgeni Water's support for the presentation of this paper is also acknowledged.