THE DEVELOPMENT AND EVALUATION OF NEW SOUTH AFRICAN OZONISER TECHNOLOGY FOR REMOVAL OF ENTERIC VIRUSES AND TASTES AND ODOURS PRESENT IN HARTEBEESPOORT DAM WATER

Report to the
WATER RESEARCH COMMISSION

by

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EXECUTIVE SUMMARY

Ozone is finding increased use in water treatment due to its remarkable properties as oxidant. It is used in a wide range of applications *viz* disinfection of bacteria and viral inactivation, removal of iron and manganese, oxidation of organic pollutants, destruction of odours and tastes, improvement of colour and many more. Ozone is often the only feasible method for many of these water treatment problems. Secondary uses e.g. treatment of industrial and sewerage effluent find equally wide application.

Historically, ozonation in South Africa was considered to be too expensive to find widespread use. Large capacity ozone generators have to be imported, with the associated problems of maintenance and spare parts. Deteriorating water quality in South Africa will no doubt benefit greatly from the properties of ozone if the equipment is available locally at competitive prices.

The main aim of this project was the development of South African ozonation technology, to make ozonation available locally. The technology is based on high-frequency surface corona discharge using proprietary materials. A range of ozone generator sizes of increasing production capacity was developed and commercialised. These range from output of 2 g/h of ozone, to 1 kg/h units in the prototype stage. Inherent modularity allow easy expansion to higher sizes. The units are now available for introduction into the marketplace.

Bad tastes and odours have been plagueing the Hartbeespoort Dam for decades due to large scale eutriphication and algae blooms. The removal of these odours with ozone was investigated as a secondary aim in this project. Results indicate that relatively high ozone doses, and specialised ozonation designs, will be required.

Hartbeespoort Dam will always be a candidate for the occurrence of enteric viruses, and the outbreak of associated disease, receiving large quantities of treated sewerage effluent. Ozone is a proven viral inactivant. The ozone demand of the water and the reaction rates of ozone with compounds in the water are important parameters for the design of an ozonation system for viral inactivation. These parameters were measured as part of this investigation to enable efficient design of future systems to combat viral contamination.

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1. INTRODUCTION

1.1 Ozonation

Authorities regulate water quality against standards stipulated by law. Standards are based on pollutant concentrations judged to be acceptable in terms of health, aesthetic appeal and possible environmental impact. Law, does not govern levels of certain pollutants, e.g. tastes and odours in drinking water, and treatment of these pollutants is generally controlled by end user acceptance. Generally, the applicable standard is determined by the end use of the water. Water standards refer to water pollutants consisting of various chemical compounds, elements and microbiological species. There are a large number of pollutants (determinants) to be considered. Apart from those compounds and elements occurring naturally in water, additional substances may occur due to pollution from e.g. mining, agriculture and industrial effluents. In these cases, authorities may issue additional criteria against which the quality of water can be referred. Some contaminants produce only aesthetic problems, while others are harmful and toxic to varying degree, to humans and animals, as well as the environment.

Pollution of water sources in South Africa has led to considerable deterioration of the water quality, surpassing the capabilities of conventional water treatment methods. Additional, highly effective methods of water treatment have become necessary, particularly with respect to treatment of organic chemical loading and high level disinfection.

The capabilities of ozone in this regard are well known. Major application areas for ozonation are:

- Destruction of microbiological species (disinfection)
- Organic compound oxidation
- Control of algae
- Removal of taste and colour
- Enhancement of microflocculation (control of turbidity and reduction of flocculant requirements)
- Removal of iron and manganese
- Biological stabilisation (reduction of bio-assimilable compounds)
- Only viable disinfectant for certain resistant virus types
- Ozone will not form trihalomethane (THM) compounds as obtained with chlorination

Since its first use for full scale disinfection in Oudshoorn, Netherlands [AWWA, 1991], a large number of ozone treatment plants have come into use all over the world, with water treatment capabilities of up to 30 000 m^3/h. The applications are not limited to drinking water treatment, but cover a wide range. Only some are listed below (advantages listed):

- Swimming pool water treatment (no chlorine discharge into environment)
- Small scale drinking water supply (rural populations)
- Cooling water circulation loops (less chemical usage and discharge to environment)
- Sewerage and industrial effluent plants (disinfection and reduction of organic loading)
- Industrial process water purification (allows water reuse)
- Industrial laundry machines (use of cold water, drastic reduction in washing powders and therefore release of phosphates into the environment)

There are potentially hundreds of ozone applications, too numerous to list, all with considerable benefit to the user, regulatory authorities and the environment.

Disadvantages of ozone are mainly, but not exclusively, related to the treatment of drinking water. Main disadvantages are:

- A disinfection residual cannot be maintained due to relatively short (<20 min) half-life of ozone in water.
- It is not possible to bottle ozone, and it has to be generated on site.
- Biologically assimilable compounds are formed after oxidation of organic materials leading to possible microbiological aftergrowth.
- Ozone can oxidise bromine to bromate, a possible hazard at low levels
- Certain ozonation by-products are potentially formed. As an example, ozonation of bromine in the water may form hypobromous acid (HOBr) which can react with organic species to produce bromoform ($CHBr_3$), a carcinogenic compound.
- Ozone was traditionally regarded as a high-technology, very expensive entity.

Ozone can be used as a stand-alone technology in very few water treatment applications, and it is usually added as a “polishing” step for the major purpose of disinfection, following several primary and secondary treatment processes. However, realisation of the other properties and advantages of dissolved ozone, as mentioned above, has led to modern

water treatment plants using three ozonation steps in the treatment process, notably in France and Germany.

The success of ozone in water treatment becomes clear when considering the fact that the cities of Montreal, Paris, Singapore, Brussels, Moscow, Helsinki, Zürich and Los Angeles, among others, use ozone in their water treatment plants. In South Africa, large-scale use of ozone has not yet fully realised. Ozone is used in the water treatment plants of Umgeni Water and Midvaal Water Company, while the water treatment plant at Windhoek in Namibia constitutes the only other large-scale ozonation plant for drinking water in Southern Africa. Entry barriers to the successful implementation of ozone in large-scale drinking water plants seem to be:

- High capital cost of not only generator equipment, but including air preparation systems and ozone injection systems e.g. deep U tube construction.
- Non-availability of local supply [M Krüger, 2004; Lombard et al 1992; Rencken, 1992]. Maintenance support and spare parts have to be acquired from overseas suppliers.
- Really urgent situations requiring ozonation have not yet occurred.

A considerable number of smaller ozone applications exist in the country, and user numbers grow daily as the water quality situation in the country worsens.

PARC Scientific (Pty) Ltd was prompted by this clearly defined need to embark on the development of local ozone generator and complimentary technology. The objective was to develop ozone generators that would be inexpensive, easy and inexpensive to maintain, and flexible and adaptable to various applications. Together with the generators, PARC would also found a broad base of ozone-related technology and expertise to support the establishment of ozonation in South Africa. The ozone generator technology can open the way for wide scale application of ozonation in South Africa. This report will describe the ozone generator technology that was developed, and the ongoing effort to further improve. The commercial value of the developments prohibits detailed descriptions and only the salient features and products that were developed will be discussed.

1.2 Tastes and Odours

The deteriorating water quality of the Hartbeespoort Dam results in extensive eutrification. High nutrient concentrations occur in feeder streams, and are introduced by effluents from up-stream sewerage plants. This causes colossal algae blooms, particularly in the summer months. Algal organisms such as microcystis and anabaena occur *en masse*, and cause the production of various toxic algal metabolites. In addition, bad tastes and odours are introduced into the water, giving rise to public complaint about water quality. Many of these compounds are detectable by smell and taste at very low levels. The compounds geosmin and 2–methylisoborneol (2-MIB), e.g. are detectable by smell and taste at concentrations of the order of nanogram per l (ng/l) [Gerber, 1983]. These two compounds are the most studied of the odour and smell producing metabolites and are probably the cause of the major proportion of complaints.

Literature indicates a wide range of findings on the efficiency of ozone in removing these compounds. Yasutake et al , 1987 reported almost 100 % removal of geosmin, and 80 – 90 % removal of 2-MIB with an ozone dose of 5 mg/l, using contact periods of between 10 and 20 min. Tatsumi, 1987, removed 85-100 % of geosmin and 2-MIB at an ozone dose of 2 mg/l, while Lalezory et al, 1987 reported a removal efficiency of only 50 % for geosmin at doses as high as 10 mg/l.

Locally, removal of odour causing compounds has been investigated by a number of authors. Inter alia, Geldenhuys, et al, 1996 reported a 45 % removal of geosmin with an ozone dose of 3.12 mg/l and improved this to 63 % by addition of hydrogen peroxide. Van der Walt, 1992 found 100 % removal of geosmin at a high ozone dose of 14 mg/l and a very high pH of 10, and 95 % removal of 2-MIB at the same conditions. The variance in results is due to different characteristics in the waters studied [Geldenhuys et al , 1999;Van der Walt, 1992.; Hoigne and Bader, 1976] with regards to pH, bicarbonate content, and organic loading. The first two parameters determine the dissociation rate of ozone to more reactive hydroxyl radicals, and the second the demand for - and consumption of applied ozone.

Whereas the removal of these compounds with ozone has been studied extensively, there is little information on the efficiency of their removal with ozone from Hartbeespoort Dam water. Results obtained for water at Brits Water Works indicate good removal efficiency but are not available for publication. This water is extracted from the Crocodile river about 30 km

downstream of Hartbeespoort Dam. The water flowing from the dam into the river exits the dam from a depth of several meters below the surface. This fact, and the effect of natural biological processes during the passage to Brits may change the nature of the organic loading of the water. Removal efficiency may therefore be different at Hartbeespoort Dam.

While this subject is of considerable importance, the steering committee suggested during the course of this project that the ozone generator development should be prioritised. The taste and odour removal studies were therefore scaled down to a series of simple, laboratory measurements. This report will summarise the methods and findings of ozonation of odour and taste causing compounds in Hartbeespoort Dam raw and filtered water, using batch ozonation methods in Section 4.

1.3 Enteric Viruses

Disinfection is one of the major application areas of ozone. Bacteria in water may be removed to less than detectable levels in relatively short contact time periods, with relatively low ozone dose [Kinman, 1975]. However, virus species are more resistant, and can only be inactivated by very specific ozone treatment. The work of French researchers in 1964 and 1967 led to the establishment of an ozonation rule, which will ensure 99.99% inactivation of viruses [Légeron, 1984]. The process, called true ozonation, has gained worldwide acceptance. According to these findings, maintenance of an ozone residual of at least 0.4 mg/l, for a contact time of 4 min (CT = 1.6 mg.min/l; C = ozone concentration, T =exposure time) is necessary to ensure this level of inactivation. At lower ozone residual levels, some resistant spores and cysts may survive. This ozone exposure is also the basis of the World Health Organisation (WHO) guideline for disinfection of potable water.

Resistant microorganisms like cryptosporidium and giardia have been the cause of concern in drinking water supplies [Najm, 1998]. Application of ozone at higher residual levels, and particularly for longer contact times was successful in the inactivation of these organisms (CT=1.5 mg.min/l for giardia and CT=5 – 10 mg.min/l for cryptosporidium)[Pryor and Rice, 1998].

Clearly, the establishment of a significant residual concentration of dissolved ozone is important in the process. In any water, some organic and other compounds react with ozone immediately upon its introduction. This initial absorption of ozone is a characteristic of the water and is called the ozone demand of the water. After the initial fast reactions with these

compounds, a residual amount remains, if sufficient ozone was injected. The residual decays with a half-time characteristic of the water. It is clear that the ozone demand of the water has to be satisfied before a residual becomes available for disinfection. Disinfection is mostly guaranteed when this is the case. This report will describe measurements of the ozone demand of Hartebeespoort Dam water in Section 5, since this parameter will be decisive for design purposes of possible future ozone installations on this water supply. Inactivation of real viruses was not investigated in this study due to prioritisation of the ozone generator development.

2. OZONE GENERATION TECHNOLOGY

2.1 Fundamental Principles

In essence, ozone is formed through the dissociation (molecular breakup) of oxygen (O_2) molecules into free oxygen radicals (O atoms), of which three recombine to form ozone (O_3). Oxygen can be dissociated with UV radiation in the shorter wavelength region (e.g. 180 nm), or with electrons in the energy range of 6 to 8 electron volt (eV). Both processes contribute to the formation of ozone in the atmosphere, or in lightning phenomena. Ozone generators operating with UV are commercially available, but are not energy efficient at higher ozone production rate. The methods employ very specific, relatively expensive UV tubes, which have a limited life span and have to be replaced at regular intervals. UV ozone generation is not regarded as competitive for larger scale ozone generation and will not be discussed further in this report.

Electrons of the energy mentioned are produced in electrical discharges, and specifically in the form of discharge known as corona discharge. Corona discharge in various forms constitutes the basis of ozone generation. In a corona discharge, gas (e.g. air or oxygen) is converted into a state of matter called cold plasma. High densities of electrons are generated in cold plasma, which dissociate the oxygen and ozone is produced.

Siemens, 1857 was the first to produce an apparatus to generate ozone from electrical discharges. The discharge mode used was called silent discharge and is still the mode used today. A silent electrical discharge is one form of corona discharge and these phenomena will be discussed briefly in Section 2.1.1.

The production of ozone in a silent corona discharge comprises the interplay of electrical discharge physics and plasma chemistry. This is indicated in the schematic of Figure 1 [Eliasson and Kogelschatz, 1991]

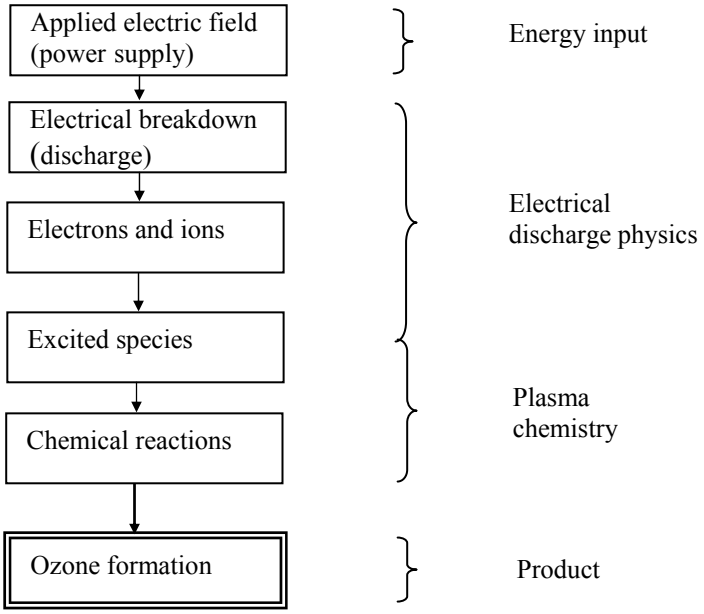

Figure 1: Interplay between discharge physics and plasma chemistry to produce ozone

The applied electric field constitutes the input of energy into the process, and will be discussed in Section 2.1.1, while its realisation forms the subject of Section 3.2. The physics of the discharge will be the subject of Section 2.1.1, while the plasma chemistry will be briefly discussed in Section 2.1.2.

Theoretically, ozone generation should yield an energy efficiency of 400 g/kWh (grams of ozone formed per hour, per kW of power input) in oxygen. Current ozone generators reach efficiencies of about 120 g/kWh. It is clear that ozone generation, even at the theoretical optimum value, is very energy inefficient. This is because almost 66 % of the input energy is converted to heat, which has to be removed from the ozone generator. This will be discussed in Section 3.3.1.

2.1.1 Physics of electrical discharges

Figure 2 is a schematic representation of the configuration of one form of ozone generator. An alternating high-voltage waveform is applied to a high voltage electrode by a power supply unit. An air gap and a layer of dielectric material, the dielectric barrier, separate this electrode from a grounded electrode. A schematic example of an alternating high-voltage waveform is shown in Figure 3.

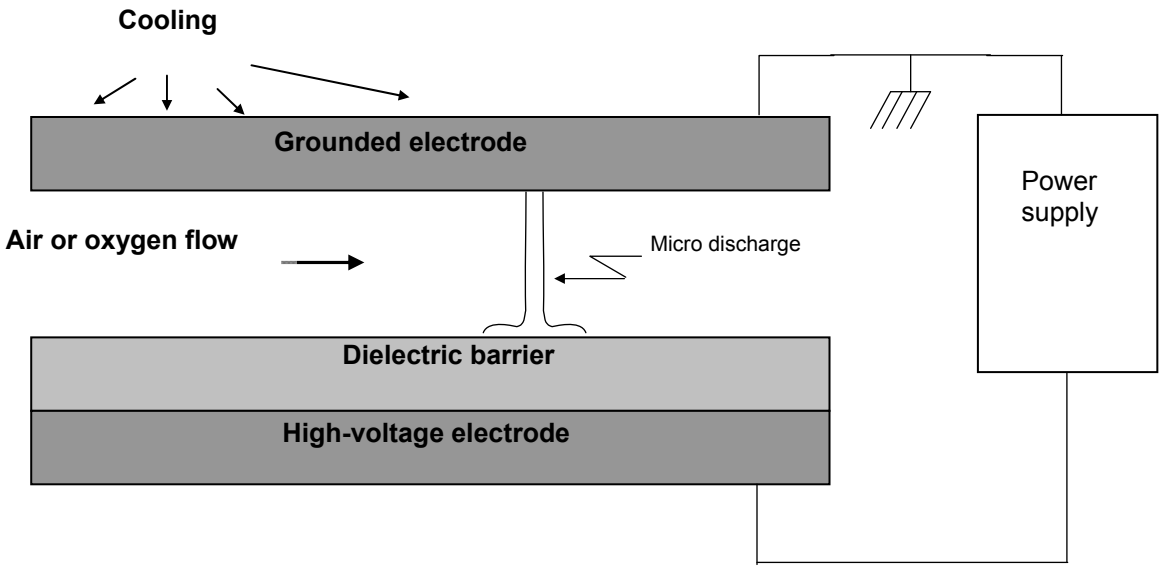

Figure 2: Schematic of a form of ozone generator

The figure shows the voltage applied to the high-voltage electrode as a function of time. Note that the voltage alternates between positive and negative values. As soon as the voltage reaches a certain level (V_c), an electrical discharge occurs in the air gap. In the absence of the dielectric barrier, an electric arc would have struck between the electrodes. In the presence of the barrier, the discharge is reduced to a glow, visible in the air gap. The discharge takes the form of numerous thin columns, called micro-discharges, of which one is shown in Figure 2.

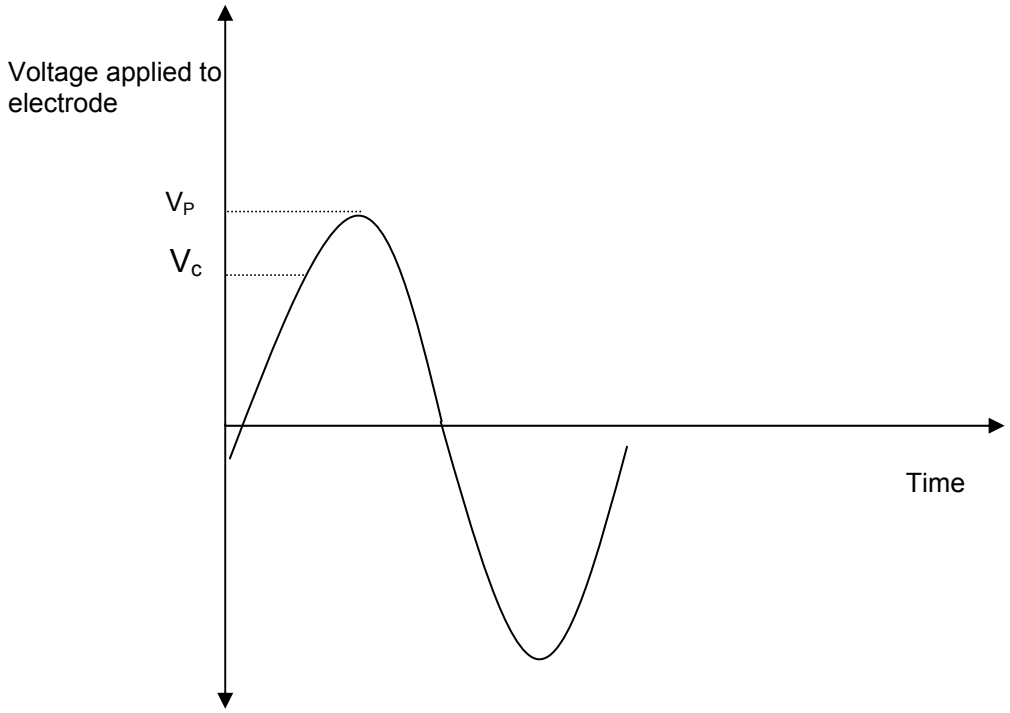

Figure3: Alternating high-voltage applied to electrodes

The micro-discharges each last for about 10 ns before being extinguished due to charge collection on the barrier. When the alternating voltage swings through to the negative cycle, the barrier is discharged and a new generation of micro-discharges is formed. The discharge is known as dielectric barrier discharge, or silent discharge, and is a form of corona discharge.

Voltage levels of up to 15 kV and more are used in conventional ozone generators, while the frequency of the voltage alternation vary between 50 and 5000 Hz in most commercial ozone generators.

Each micro-discharge column is a column of cold plasma. One property of cold plasma is that very high concentrations of free electrons are formed in the plasma. The electrons have relatively high energies, determined by the value of the applied high voltage (the applied electric field). Energy values up to 20 eV occur, including high densities of energy values in the crucial range of 6 to 8 eV. In addition to electrons, ions are formed, as well as a large variety of other excited molecular and atomic species. These species diffuse from the region of the micro-discharge column into the surrounding gas. Many of these species participate in

atomic and molecular reactions which eventually result in formation (or destruction) of ozone molecules. A detailed discussion falls outside the scope of this report, but excellent fundamental descriptions of the process are provided by Eliasson and Kogelschatz, 1991; Eliasson et al , 1987 and Pietsch, 1998.

Discharge physics provide a number of parameters to control the efficiency of ozone generation.

- The value of the voltage peak (V_p in Figure 3) determines the applied electric field and therefore controls the energy of the electrons. An optimum peak voltage range exists.

- The frequency of the applied voltage wave determines the concentration of micro-discharges, and therefore controls the number density of the electrons, and the rate of oxygen dissociation. Higher frequency implies higher ozone generation, but also an increase in heat dissipation.

- The air gap also determines the applied field, as well as the efficiency of cooling.

- The dielectric barrier thickness and its value of dielectric constant controls the applied field, determines value of corona onset (V_c) and limits the amount of energy that can be deposited in the air gap in the form of micro-discharges.

- The gas pressure determines the energy of the free electrons, as well as the concentration of oxygen molecules. It also determines the energy of ions in the discharge, which causes heat formation, and inefficient use of input energy.

Ozone generator design involves optimisation of these interrelated parameters with specific objectives in mind.

2.1.2 Chemistry of electrical discharges

Ozone may be generated in air or oxygen, with two different sets of chemical reactions. With pure oxygen in the air (or discharge) gap, ozone formation is a two step process [Eliasson et al , 1987] starting with the dissociation of oxygen molecules by energetic electrons:

$$e^- + O_2 \longrightarrow 2O + e^- \qquad (1)$$

followed by a three-body reaction:

$$O + O_2 + M \longrightarrow O_3 + M \quad (2)$$

Where M = O, O_2, or O_3 is a third body collision partner. These reactions are global representations of the chemistry in the discharge process. However, a large number of other reactions, involving all the other species formed in the discharge, also participate and contribute to ozone formation through secondary and tertiary pathways. Eliasson et al, 1987 recorded and modelled the interplay between 33 different reactions in oxygen. Apart from ozone formation reactions, there are also ozone destruction reactions viz:

$$O(^1D) + O_3 \longrightarrow 2O_2 \quad (3)$$

And

$$e^- + O_3 \qquad O + O_2 + e^- \quad (4)$$

Where $O(^1D)$ is one of the dissociation free radicals formed in the plasma. At high ozone concentration, this back-reaction limits the further formation of ozone. Ozone molecules diffusing or convecting into a micro-discharge will be dissociated according to reaction (4).

In air, containing 80 % nitrogen and 20 % oxygen, the presence of nitrogen and to a much lesser extent CO_2 play a role, and the reaction schemes become much more involved. Yagi and Tanaka, 1979 and Eliasson and Kogelschatz, 1991 provide reaction schemes involving 14, and 143 different reactions respectively, with 30 participating species. In addition to the oxygen dissociation reaction (1) there is also a nitrogen dissociation reaction in air:

$$e^- + N_2 \longrightarrow 2N + e^- \quad (5)$$

and various reactions occur between the additional nitrogen radicals, oxygen radicals, ozygen and nitrogen molecules and ozone. The more important reactions are formation of nitrogen oxides:

$$N + O_2 \longrightarrow NO + O \quad (6)$$

$$NO + O_3 \longrightarrow NO_2 + O_2 \quad (7)$$

$$NO_2 + O_3 \longrightarrow NO_3 + O_2 \quad (8)$$

$$NO_2 + NO_3 \longrightarrow N_2O_5 \quad (9)$$

These reactions are specifically shown because of their importance to the reliable operation of air-fed ozone generators. In the presence of moisture, further reactions occur involving the water molecule. Most important is the formation of HNO_3 (nitric acid). Nitric acid is formed as a vapour which condenses to form nitric acid aerosols, into which other impurities in the air may be incorporated. These aerosols deposit wherever air flow patterns in the ozone generator allow, and are extremely corrosive to construction materials. This is the root cause of the problems traditionally encountered when ozone generators are operated with moist air. This will be discussed in Section 3.1.2.

In the presence of moisture, electrons also dissociate the water molecule:

$$e^- + H_2O \longrightarrow OH + H \qquad (9)$$

The resulting hydroxyl radical (OH) is a very strong oxidant and takes part in competing reactions which lower the ozone molecule yield of the process. This will also be discussed in Section 3.1.2.

The chemistry of the discharge and the time constants of the reactions do not present any significant opportunities to optimise the ozone production, apart from equation 2 which indicates that ozone production is a three-body process. It should therefore be favoured by an increase in pressure [Pietsch, 1998,Uhlig et al, 1998]. Further, the chemistry allows insights into certain operational problems and their solution.

2.2 Dielectric Barrier Discharge

2.2.1 Volume discharge

The form of ozone generator shown in Figure 2 is known as a volume discharge generator. The dielectric barrier is intimately joined to the high-voltage electrode. An air gap separates the dielectric from the grounded electrode. Air or oxygen flows through the **volume** of this gap, where the micro-discharge cold plasma columns generate ozone. Gap distances vary between 0.5 and 3 mm, large gaps requiring higher voltage levels to operate. Water, oil, or air flowing across the outer surface cools the grounded wall of the generator. Sometimes the inner electrode is also cooled. Conventional ozone generators are built to the volume discharge configuration. In practice, the electrodes can be tubes (Wellsbach design) or plates (Lowther design). Considerable development and progress have been made in improving the generation efficiency of volume discharge ozone generators. The major thrust of most of the improvement lies in the dielectric barrier.

Considering the effects mentioned in Sections 2.1.1 and 2.1.2, two disadvantages of the volume discharge become apparent:

- Heat is dissipated in the volume of the air gap, and is not efficiently transported to the cooled walls. It is difficult to properly cool volume discharges.

- The gap is filled with micro-discharges. The airstream and diffusion processes transport ozone formed in the gap into these, where ozone molecules are destroyed (reaction 4, Section 2.1.2).
- Volume discharge requires relatively high voltage levels, adding to physical size and cost of power supply equipment.

Other disadvantages are more subtle, and relate to poor response to pressure increases, and a limited range of operational parameters (flexibility) [Masuda et al, 1988; Masuda et al, 1986].

Ozone yield of volume discharge ozone generators fed with oxygen is about two to three times higher than with air [Pietsch, 1998]

2.2.2 Surface discharge

Figure 4 shows another form of dielectric barrier discharge. The high-voltage electrode is a conductor in intimate contact with the dielectric layer. The conductor can be round or square in cross section. Corona discharge is initiated at the contact surface of the conductor and dielectric by a very specific mechanism [Kuffel and Zaengl, 1988] different from volume discharge. This mechanism causes the corona onset voltage (V_c in Figure 3) to be much lower than for volume discharge, and high-voltage levels as low as 1.5 kV may be used dependent on the layer thickness. Once initiated, microdisharge columns also extend from the conductor and spread over the surface of the dielectric. The discharge is in contact with the dielectric barrier. In practice, arrays of conductors are distributed across the surface of the dielectric in the form of strips on a flat dielectric, or wires wound around a tubular dielectric. The grounded electrode can be cooled as in volume discharge. The electrode structure is enclosed in a sheath, with air or oxygen flowing through the gap between the electrodes and the sheath. Ozone is formed in the microdischarges, and escapes into the flowing gas stream.

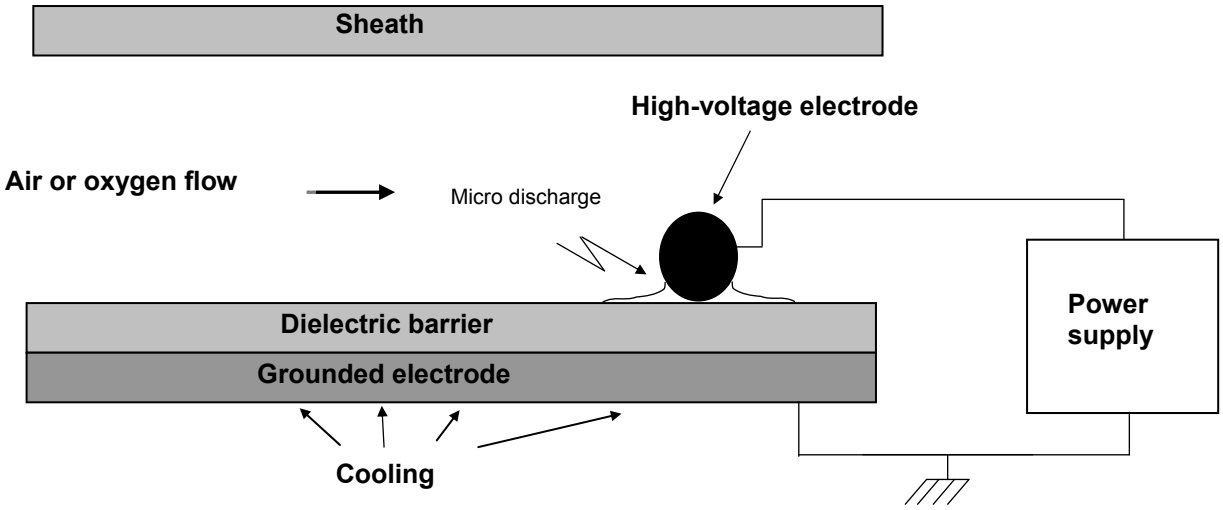

Figure 4: Surface discharge configuration

The use of surface discharge in ozone generation is relatively new, and was pioneered by Masuda et al, 1986 and Masuda et al , 1988. While the technique is being employed on smaller scale ozone generators, the author is not aware of its use in higher output generators. This application was one of the major motivations behind the current development.

The surface discharge has a number of advantages above the volume discharge configuration, which led to the choice of this configuration for the new development:

- The discharge occurs on the surface of the dielectric. Heat formed in the discharge is therefore relatively easy to remove through the heat conducting dielectric layer. Better heat removal enables the use of higher frequency, and therefore higher power deposition in the reactor.

- Ozone formed in the discharge diffuses to the discharge free zone above the discharge and cannot be destroyed in the corona.

- By correct selection of dielectric material, a thin layer can be established. This allows considerable reduction in the high-voltage level required (e.g. 3 kV as opposed to 10 kV), and more compact power supply. It also allows the use of a much higher frequency of

discharge (e.g. 20 kHz as opposed to 2 kHz and lower), again resulting in considerable size reductions, and higher power deposition.

- More subtly, surface discharge allows a wide range of operational parameters to be optimised for given ozone generation requirements. E.g. the ozone concentration can be doubled by an increase in pressure from 101 to 150 kPa [Masuda et al, 1998; author's own experience]. No such improvement is possible with conventional volume discharge.

- Ozone formation in surface discharge is not as susceptible as volume discharge to moisture conditions in terms of reduction in concentration. Ozone production is reduced by only 30 % at a relative humidity of 95 % in surface dishcarge [Masuda and Kiss, 1986; author's own experience].

Optimised surface discharge ozone generators can yield 5 times higher production rate with oxygen than with air [Pietsch, 1998; author's own experience]. Surface discharge ozone generators seem more susceptible to the effects of moisture than volume discharge, in terms of the corrosive effects of nitric acid formed in presence of moisture.

3. NEW DEVELOPMENT

3.1 Surface Discharge Realisation and Initial Investigations

The clear advantages of the surface discharge configuration prompted the development of the South African ozoniser technology, called the PURION technology. Surface discharge electrode systems used by others are of a very specific construction. Highly specialised alumina ceramic materials are used, with tungsten thick-film printed electrode strips. This requires specialised ceramic manufacturing techniques not available in South Africa, and would have to be established at costs that are unfeasible. The requirements for costly casting and extrusion dies would severely limit the flexibility of available electrode systems and sizes. Alternative ways to establish the technology were therefore required.

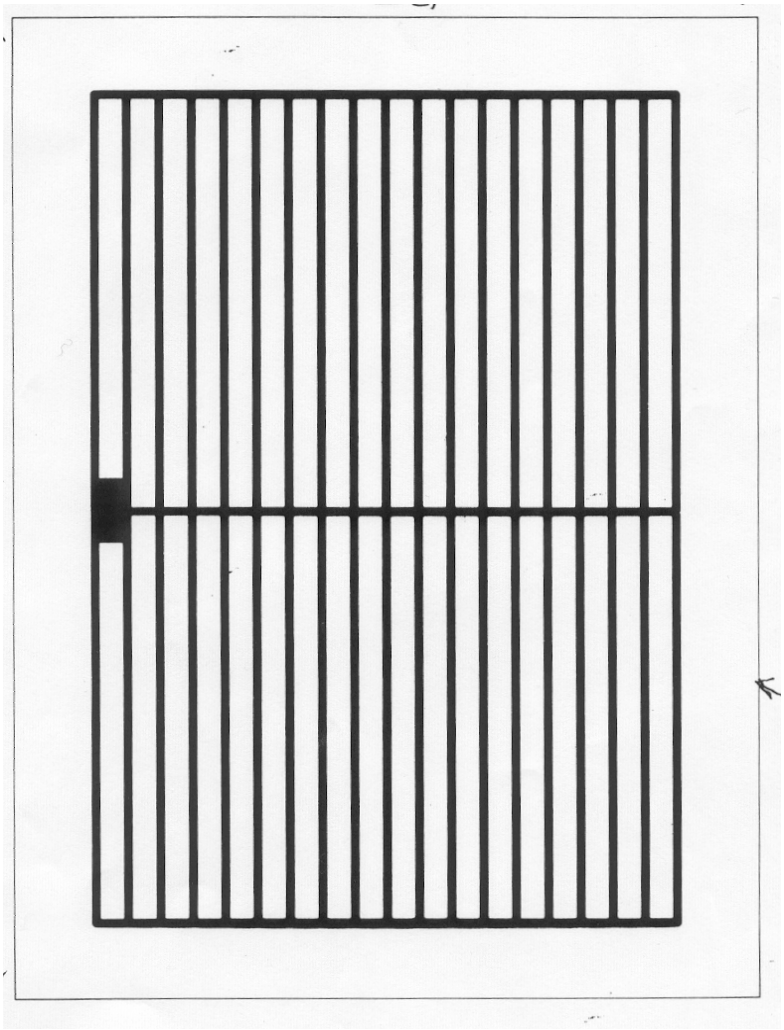

Figure 5: Strip copper electrodes etched onto high-purity alumina ceramic layer in the initial design stages.

One alternative was to have the electrodes manufactured from high-alumina (99.7%) ceramic sheets, onto which copper sheets are bonded, available off the shelf. This material is used in the manufacture of high temperature printed circuit boards, and can be imported. The copper was chemically etched into a strip electrode pattern as in Figure 5. The ceramic layer forms the dielectric barrier, and had a thickness of 0.6 mm. Manufacture of the systems proved very cumbersome and expensive, and the electrodes were limited to the sizes of sheets available.

A power supply to provide the high-voltage waveforms was available from previous work, and although intended for a totally different application could be used in the initial work that led to this project. During testing, it quickly became apparent that alternative electrode manufacturing techniques would have to be developed because:

- The ceramic layer was too thick (limited power input and high voltage requirement)
- The available sheet sizes would severely limit expansion and possible easier construction techniques.
- The copper strips quickly eroded from the action of ozone and nitric acids. Even nichrome and gold coatings were not resistant. The material also sputtered (removal of metal atoms from the surface) under the action of the corona discharge.

The following two sections will describe the development of the surface discharge electrodes and material selections of the PURION technology. Only the resulting products will be described, as their development entailed extensive experimentation, failures and successes over an extended time period, and these details fall outside the scope of this report. Furthermore, the products carry significant commercial value and trade secrets, which cannot be divulged in an open report.

3.1.1 Dielectric layer material selection and application

Optimisation of the surface discharge required a dielectric layer with the following properties:

- High dielectric strength (at least 10 kV/mm) , at temperatures from 0 to 100°C.
- High dielectric constant (allows higher capacitance and increased power input)
- High mechanical strength(against vibration and shock)
- High thermal conductivity (good heat removal)
- Good thermal expansion capabilities.
- Should maintain its integrity w.r.t all these properties even in a very thin layer (~300 µm).
- Chemical resistance to highly acid compounds.
- Easy to apply and shape into various geometries.
- Cheap to produce and apply.

After extensive research and experimentation, ceramic material was found that answered to all these requirements. The properties of the material are listed below:

Dielectric strength:	>2.5 kV/mm @ 200 µm
Dielectric constant:	6.6
Thermal conductivity:	840 W/(mºK)
Dielectric loss factor:	0.006

The material is imported, but is processed locally into the form used in the PURION technology. It is also applied locally to the metals ground electrode (tube). To obtain all the properties in one, a combination of constituents are used in the ceramic materials. This development comprised a major part of the research and holdups in the project. The material and its application are very inexpensive. This allows cheap manufacturing of electrodes, and a significant reduction in costs of maintenance- and spares. Electrodes will be inexpensive and easy to replace.

It was decided that the ground electrode configuration in the PURION technology should be tubular, i.e. the dielectric layer is applied to the outside of metal tubes, since these are obtainable in standard forms and in the ideal size range. Construction in tubular geometry is also easier. Figure 6 shows the dielectric layer applied to a ground tube, and a selection of complete electrodes.

Figure 6: Ceramic layer applied to the metal ground tube, and a selection of complete electrodes

3.1.2 Properties of the high voltage electrode and its construction

Simply winding a wire around the tube, on the dielectric layer, forms the high-voltage electrode. It is important that the wire remains in close contact with the dielectric. Considerable effort was expended into devising proper anchoring of the wire at the electrode ends.

The electrode is exposed to a very aggressive environment in the corona discharge. Ions in the discharge bombard the metal surface, at elevated temperatures, causing metal sputtering. Ozone is corrosive to most metals, and forms an extremely corrosive combination with the concentrated nitric acid (HNO_3) formed in presence of moisture (see Section 2.1.2). High purity stainless steel was eventually found to be the best option, after securing its availability in South Africa.

The number of turns of electrode wire is determined by the ozone output required, although no proportionality between the two parameters exist, and other considerations are applied. The power input from the power supply should *inter alia* be distributed over a length of wire that limits the power input per mm^2 of dielectric surface. This controls the heat deposition into the electrode and thus affects the ozone production. The property is used to control the temperature of the electrode.

Figure 6 shows the wire electrode on a number of different electrode sizes. The smaller electrode is used in the lower production generators, while the largest forms one of the electrodes in the prototype 1kg/h unit. A special machine was developed to wind the electrode wire with the correct spacing. Spacing is important in that as far as the electric fields from adjacent windings should not interfere with each other (confirmed through electric field modelling). This will “shorten” the micro-discharges and reduce the ozone production.

3.1.3 Effects of air moisture, chemical durability and air flow patterns

A feature of the surface discharge is that the electrode is “self-cleaning” to an extent. Electric fields are directed perpendicular to the wire, along the surface towards the adjacent electrode wire. “Electric wind” phenomena in the corona cause actual air velocity components (“winds”) in this direction, blowing contaminants formed in the corona (such as HNO_3) away from the surface. Figure 7 shows a typical example of the “self-cleaned” areas between wires, as opposed to contamination deposited on the ends.

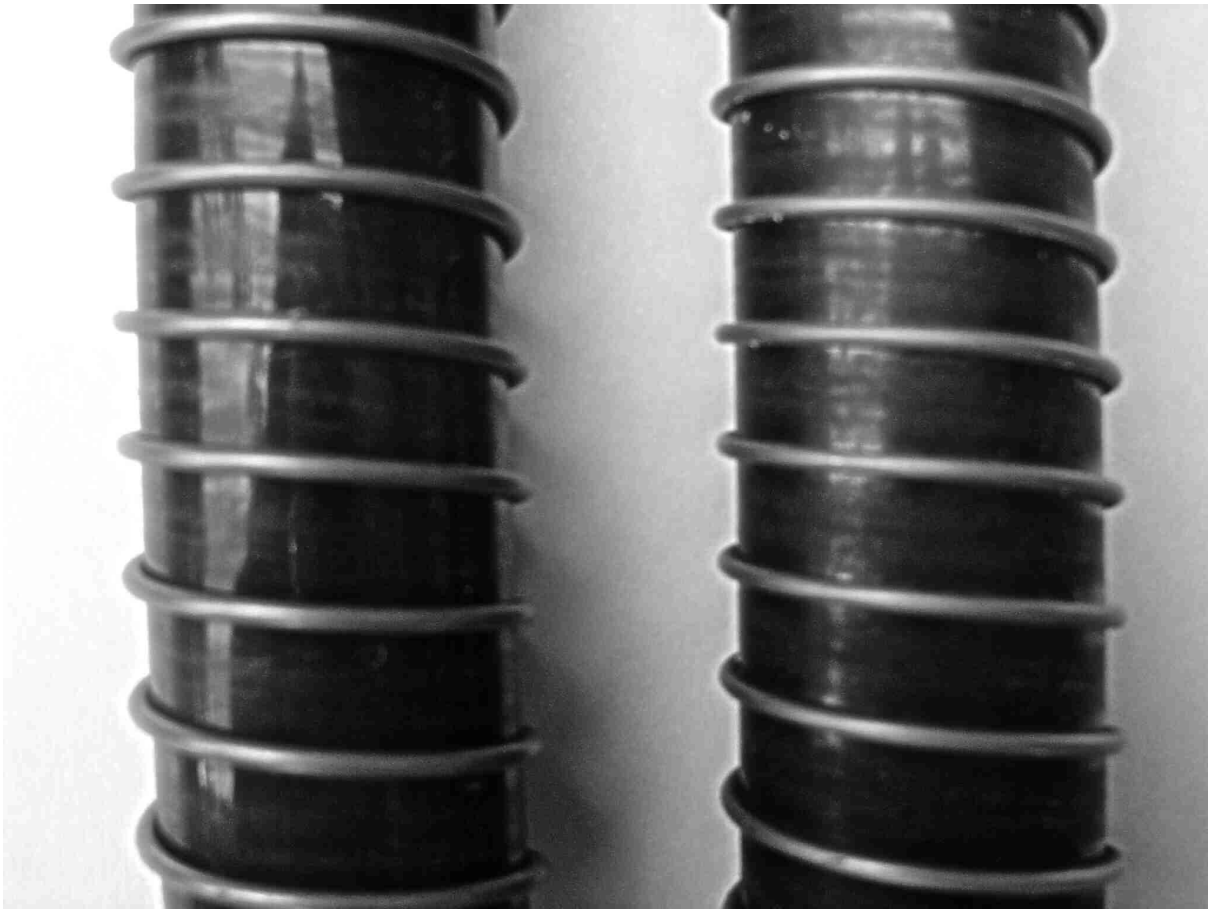

Figure 7: Self-cleaning of areas between electrode wires.

This is an important aspect in the resistance of the electrodes against the effects of moisture w.r.t corrosive destruction.

The dielectric layer has very good dielectric properties, and quality checking involves stressing the layer with voltages up to 10 kV, more than three times the operational value. However, the material is susceptible to corrosion by concentrated depositions of nitric acid aerosols. Where these appear close to the high-voltage electrode, local discharges of high intensity terminate on the deposits. The combination of high electric field and heat in these discharges then quickly corrodes the material away and arc breakthrough occurs, destroying the electrode. Figure 8 shows examples of the corrosive damage to electrodes.

Figure 8: Examples of corrosion damage to electrodes

A significant amount of research and time was expended to alleviate this problem through better distribution of the gas flow through the sheath. Along with problems in power supply design, this aspect was responsible for the longest time delay. It is believed that electrodes are now resistant to this effect, and can be operated at high moisture conditions.

3.2 Power Supply Development

An important component of the ozone generator is the power supply, which provides the energy input. The power supply generates the high voltage wave, explained in Section 2.1.1 and Figure 3. For sake of clarity, those descriptions were over-simplified. In reality, the waveform is much more involved, and can be any of a number of shapes. This is determined by the design of the power supply.

Power supply for ozone generation is a complex subject, and its description falls outside the scope of this report. A very good review is available in Vermaak, 2002 (a study which

evolved from this project). The major challenges to be overcome in the successful design of the power supplies were:

- The electrode with dielectric barrier forms a capacitor, and the electrode presents a capacitive load to the power supply. When corona discharge initiates, an additional resistive load originates for a certain period of the waveform.

- The capacitance of the electrode changes with temperature as the electrode heats up during operation. The resistive corona load is also variable w.r.t. temperature, pressure, air composition and electrode surface condition.

- Upon start-up, moisture may be condensed on the surface of the dielectric. The power supply should be able to vary the frequency of output until the condensation is driven off by heat.

- Should the dielectric material break down, an arc will occur between the electrode wire and the ground tube. The sudden high current associated with this “short circuit” can destroy the power supply, and has to be protected against.

- Should any of the connections to high-voltage electrode or ground tube be broken, an open circuit occurs, and the power supply will again be destroyed. Adequate protection is required against such an event.

At low frequencies, used in conventional ozone generators, these aspects do not cause significant problems. However, the surface discharge configuration allows high frequency operation for increased power input, and high-frequency power supplies are used. The encumbrances mentioned have severe effects at high frequency, and consumed considerable time and effort to resolve. Availability of reliable power supply units hampered progress of this project severely, and caused the most delay.

3.2.1 Switching topologies

Whereas a description of electronic circuitry is outside the scope of the report, some of the terminology used in the power supply development will be mentioned. Power supplies, which generate high frequency voltage output, are sometimes termed switch-mode power supplies.

Since the ozone generators require considerable electric current, the power supplies are also current supplies.

The configuration of the electronic components used in the circuits of the power supply, is called the switching topology, and this distinguishes the circuits. This pertains especially to the switching component (which causes the alternating output voltage) and the high-voltage transformer whereby the voltage output is stepped-up to the high voltage required for corona discharge. Sometimes more than one switching component is used, up to four.

In general, the AC voltage from the wall plug is rectified to DC, and this voltage is then switched to generate the high-frequency voltage signal. The signal is fed to the high-voltage transformer where it is stepped up to high level. All the circuits are designed such that the electric current, which flows into the electrode, resonates between the load (the electrode) and the circuit. This results in minimum energy input requirement during each voltage cycle.

To encompass all the variables, circuits can be designed with internal electronic controls. However, this increases the cost of the supply significantly, and was only introduced in the larger supplies where budgets allow. Innovative design strategies were used in the smaller supplies. The power supply units that were successfully developed are:

3.2.1.1.1 40 – 110 W power capacity, variable frequency, self optimising, single switch resonant supply

This forms the power supply unit to the smallest range of ozone generators developed in this project, and is used in a number of applications. The power supply is shown in Figure 9. It has no control circuitry other than internal self-regulating features and protection. The unit is protected against short circuits (e.g. when electrode fails) as well as open circuits (loose connections)

3.2.1.1.2 80 – 300 W power capacity, sine wave series resonant half-bridge converter

This power supply is shown in Figure 10. It is used in a range of ozone generators with larger ozone output, and is very energy efficient. The supply is also protected against short and open circuits. Due to the design of this supply, it is relatively easy to scale the output power to higher values for larger ozone production capacity.

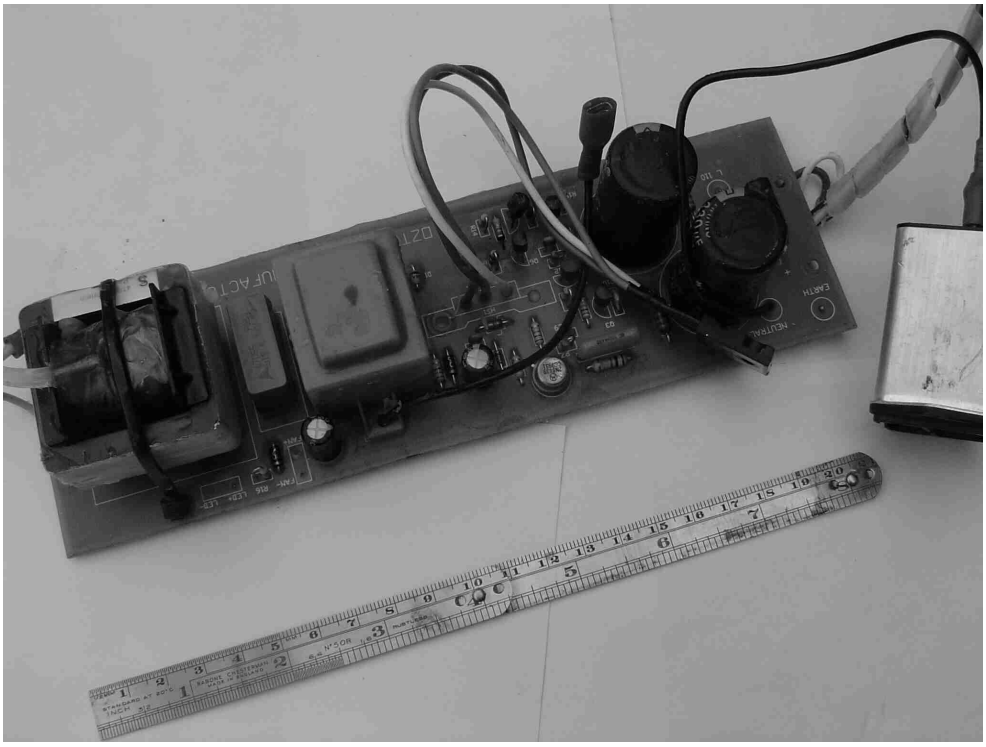

Figure9: 40 – 110 W power supply

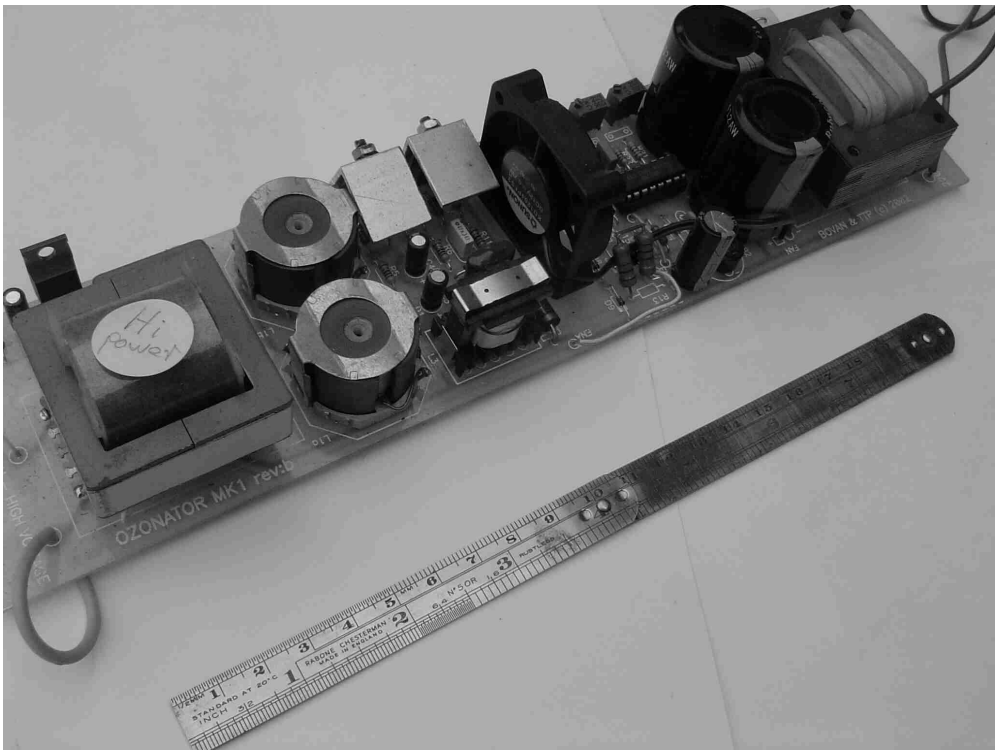

Figure10: 80 – 300 W power supply

3.2.1.1.3 300 – 600 W power capacity, half-bridge resonant converter

This power supply unit is used in ozone generators with considerably higher ozone output. It is also the power supply that is used when a number of generators are combined in modules to provide large ozone output (see Section 3.3.4.1). The power supply is shown in Figure 11.

3.2.1.1.4 16 kW power capacity full-bridge resonant converter

This unit is the largest power supply that was developed. It is capable of high power output and is employed in the largest ozone generators, up to 1 kg/h output. The unit drives several electrodes to generate the high ozone level. It features a number of built-in controls and diagnostics to protect the unit during start-up and operation, and will notify the operator of failures or problems. This unit will be discussed in more detail in Section 3.3.4. The power supply is shown in Figure 12.

3.3 Assemblies

Ozone generators were developed with various applications in mind, and were designed to address the requirements of these applications. These will be discussed in Section 3.2.

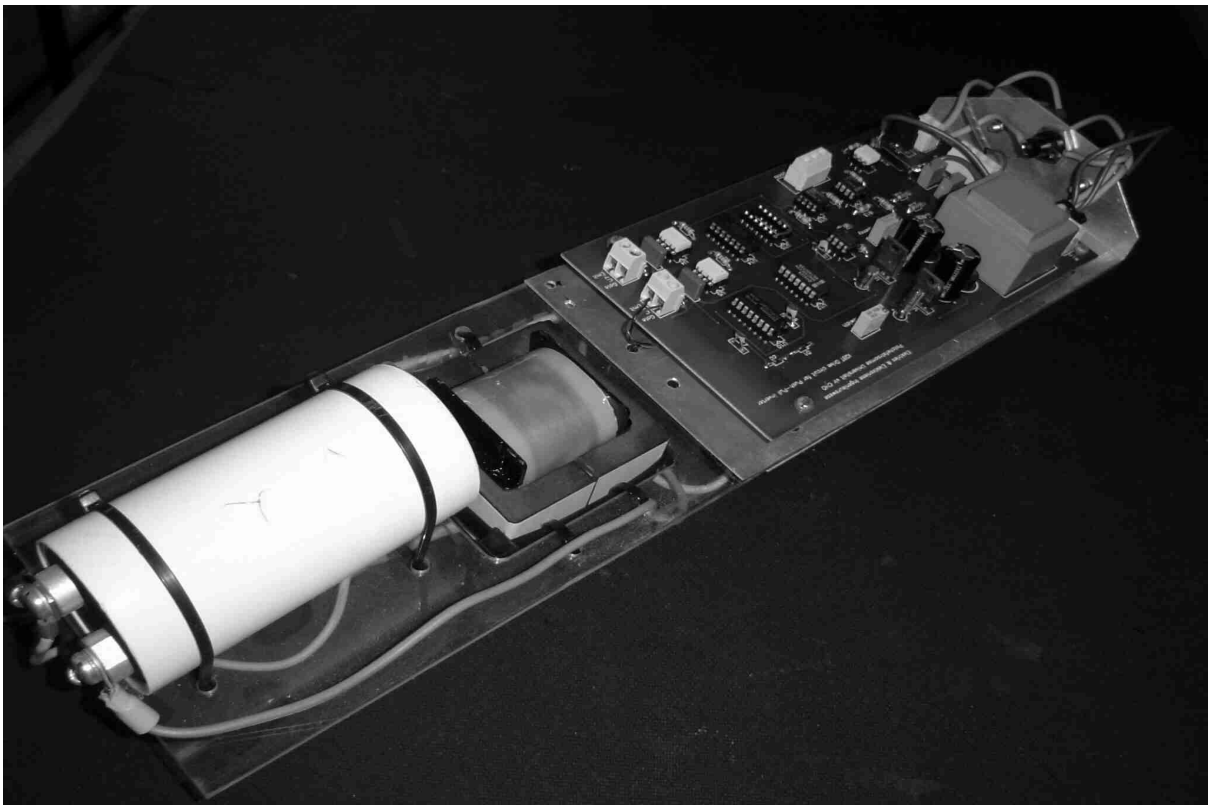

Figure 11: 300-600 W power supply

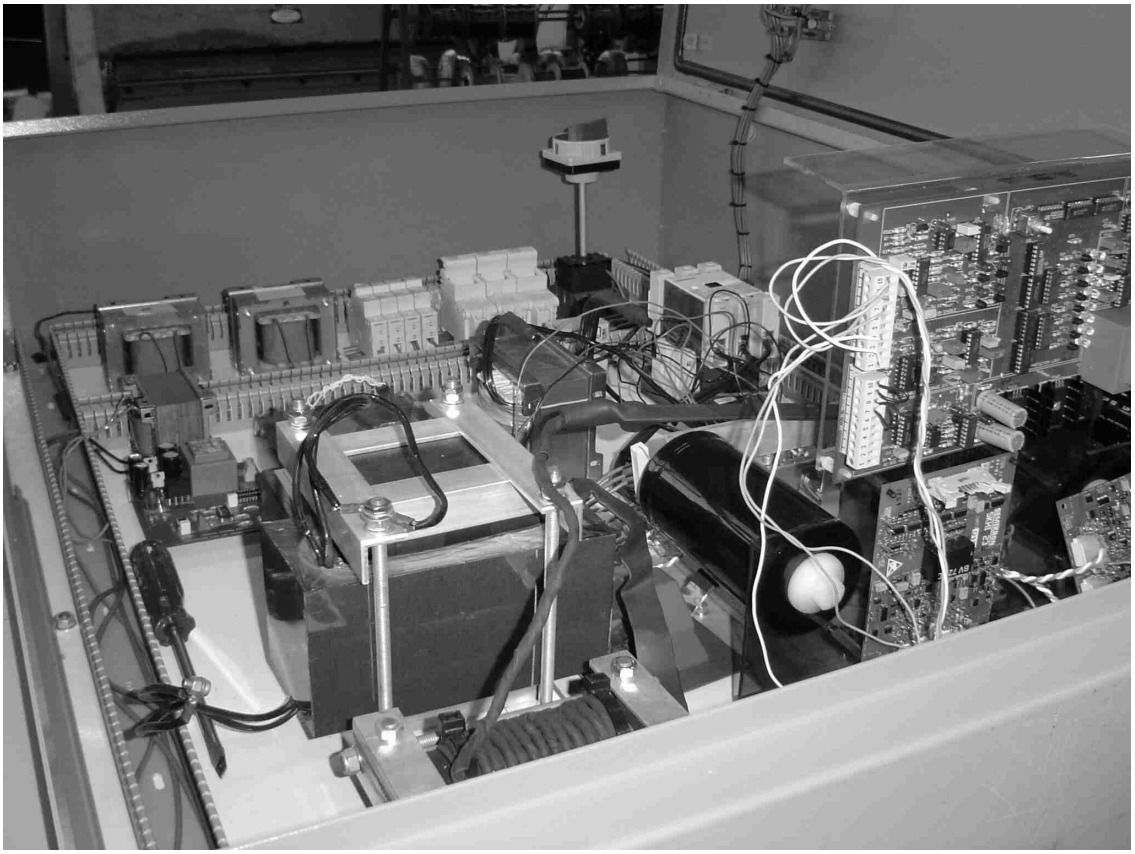

Figure 12: Power supply for prototype 1 kg/h ozone generator

Electrodes and power supplies are assembled into single stand-alone enclosures as integral units, or are mounted inside the enclosure of other systems. A number of parameters were considered when designing the units.

3.3.1 Water cooling vs air cooling

68 % of the energy input into ozone generators is expended as heat. For efficient ozone production, the heat must be removed from the discharge and reactor surfaces (see Section 2.2). Heat may be removed through cooling with water or air. Lower temperatures of the coolant enhance ozone production and high efficiency units use chilled water. The PURION ozone generators use the more efficient water cooling option. This was decided for two reasons:

- Any water purification application has water available for cooling, except where the water is very contaminated with solid materials. The electrode tubes are treated on the inside to be non-corrosive and non-scaling.

- With air-cooling, the electrode may at best be cooled to about 4 degrees ºC above the ambient air temperature. At high ambient temperatures this requires a large fan to accomplish, and cooling becomes inefficient, with resultant loss in ozone production. This effect was noticed on commercial air-cooled ozone generators.

- All higher output (> 6g/h on air) units must be water cooled, and it is easier to maintain standard construction techniques on all units if the same configuration is used.

Nevertheless, an air-cooled unit was also constructed and successfully operated. The air-cooled electrode structure is shown in Figure 13.

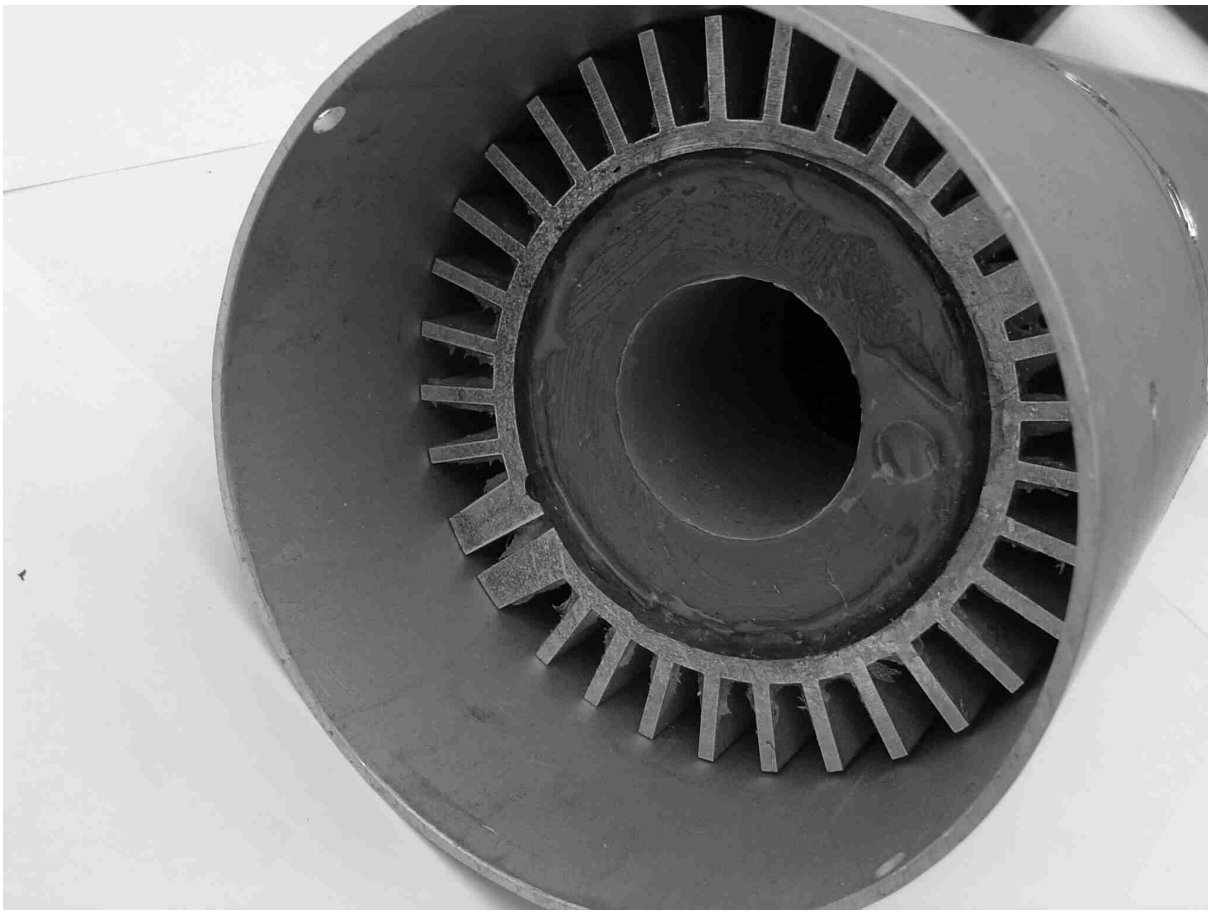

Figure 13: Air-cooled electrode structure

3.3.2 Air or oxygen operation

All PURION ozone generators are designed for operation with either air or oxygen as feed gas. In smaller applications, the cost of oxygen is prohibitive, and air operation is the only alternative. The units are inherently designed to be resistant to the moisture conditions of ambient air (see Section 3.1.3) however, it is always recommended to ensure low moisture, and to use oxygen where possible. The latter recommendation applies especially to the large output generators, where up to 5 times higher production is possible with oxygen (author's own experience).

The larger unit sizes are also ideally suitable for application with the state-of–the-art in oxygen concentrator technology. This allows oxygen to be generated on site, and does away with cumbersome and sometimes-hazardous liquid oxygen. The amount of oxygen used to produce a quantity of ozone is much less than the amount of air for a similar ozone quantity. It is easier to introduce this lesser quantity of gas into water and therefore leads to considerable size reductions in ozone / water transfer facilities. Preliminary calculations show that the increased cost in additional ozone generators to produce ozone from air is just offset by the cost of an oxygen concentrator.

3.3.3 Small and medium scale ozonators

The range of small scale ozone generators constructed on the PURION technology spans production rates from 1 to 3 g/h. The specification of these units are:

Production rate:	1 – 3 g/h air
	4 – 8 g/h oxygen
Ozone concentration:	0.5 % by weight air
	5 % by weight oxygen
Power consumption:	40 – 80 W
Air flow:	12 – 15 lpm
Oxygen flow	4 lpm

An example of this range is shown in Figure 14.

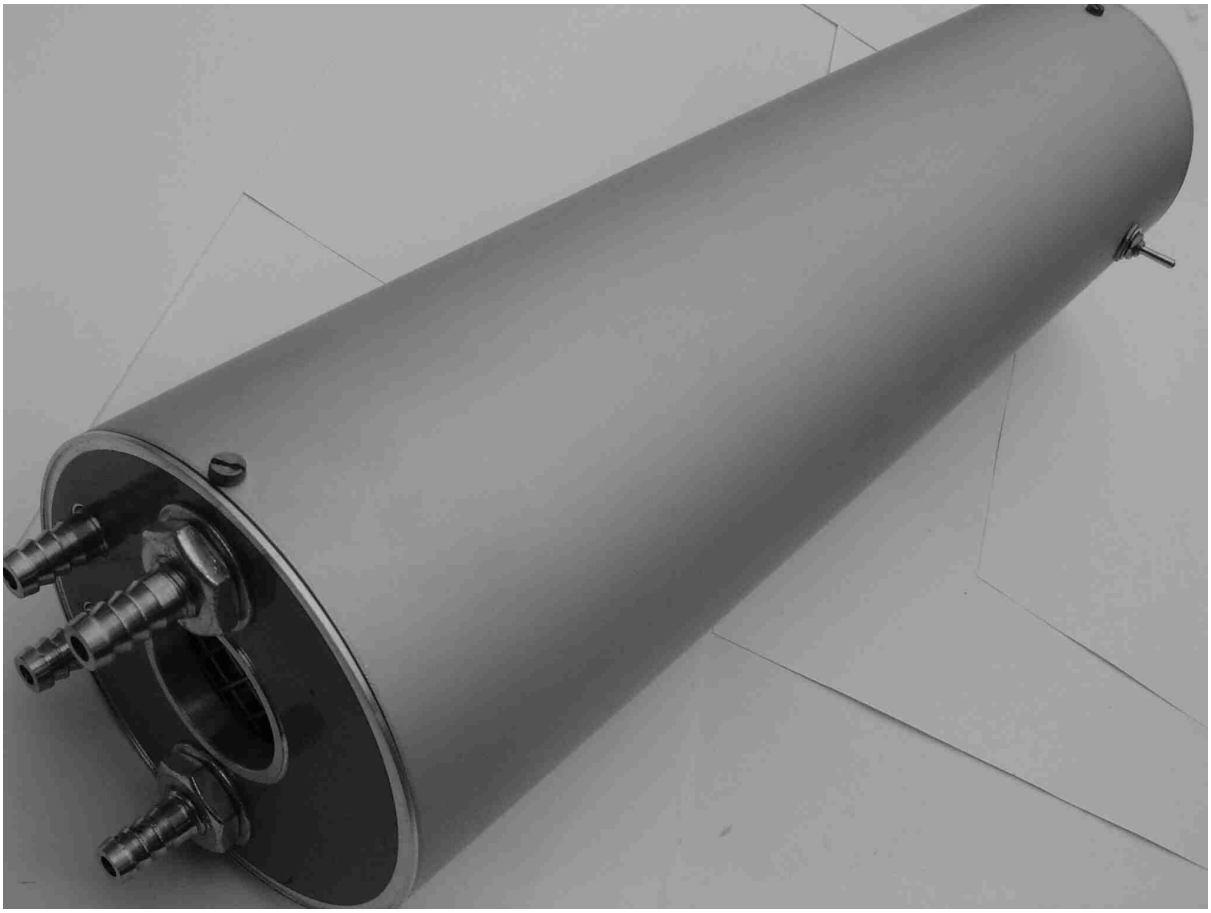

Figure 14: Example of a small-scale ozone generator

Medium scale ozone generators constructed on PURION technology spans production rates from 4 to 6 g/h. The specifications are:

Production rate:	4 – 6 g/h air
	16 – 30 g/h oxygen
Ozone concentration:	0.5 % by weight air
	5 % by weight oxygen
Power consumption:	160 – 300 W
Air flow:	15 – 20 lpm
Oxygen flow:	6 lpm

Typical results obtained with the medium scale ozone generators are indicated in Appendix I, where the effects of voltage, frequency, air flow and air pressure are shown for a specific generator. These results represent only a fraction of those obtained, and serves to illustrate

the performance of the technology, and the flexibility that exists to optimally adjust the operational parameters to a specific application. Note that the concentration of ozone almost doubles when the air pressure is increased to about 200 kPa, a result only possible with surface discharge.

3.3.4 Large scale ozonators

The largest generator constructed on the PURION technology is capable of producing 1kg/h of ozone when operated with oxygen. The production rate in air is still to be investigated, but is expected to between 222 and 200 g/h. The specifications of the large scale ozone generator are:

Production rate:	200 – 222 g/h air
	1 kg/h oxygen
Ozone concentration:	1.5% by weight with air
	5 – 9.5 % by weight with oxygen, variable through pressure
Power consumption:	16 kW
Air flow:	350 lpm
Oxygen flow	150 lpm

The prototype 1 kg/h ozone generator is shown in Figure 15. The power supply is housed in the box enclosure, and the electrode units are mounted in front.

3.3.5 Modularity and packaging

A modular design philosophy was maintained from the outset with all units. The generators within a given size range are easily multiplexed to generate a larger quantity of ozone. This allows a redundancy to be built into a particular application; should one generator fail, all capacity is not lost. The design philosophy considers easy replacement of a unit, and a number of spare units will be provided with any system.

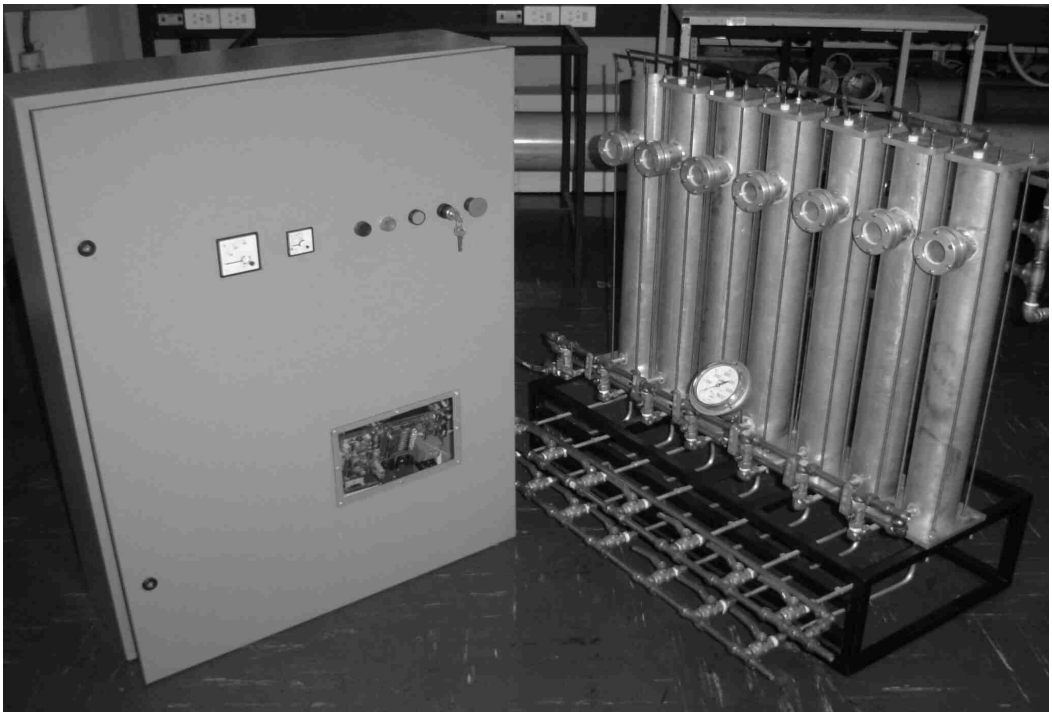

Figure 15: Prototype 1 kg/h ozone generator, with power supply at left, and generator modules at right.

The generators may also be used as stand-alone units where lower ozone production is required.

In the case of the large production generators (1 kg/h) the generator is built-up from a number of electrodes or reactors. Each electrode is individually provided with services of gas supply, ozone take-off and water cooling from manifolds. A single electrode can be isolated and replaced without prolonged downtime of the larger system. Loss of an electrode through failure will not cause the full unit to fail.

The 1kg/h generator represents one of the modules of a larger scale, multi-kilogram ozonation plant, where the this unit may be isolated for maintenance from the rest of the system if necessary. This modularity also provides the opportunity to turn-down the ozone production in periods where lower ozone dosing is required (e.g. during winter season).

3.3.6 Ozone applications and systems

The range of ozone generators was developed with a number of applications in mind. There are certainly many other applications where these units will be suitable due the adaptable nature of the designs. Three of the ozone systems developed or under development, with direct bearing on water quality in South Africa will be mentioned here.

3.3.6.1 Swimming pools

Swimming pool maintenance requires the dosing of large quantities of chlorine, as well as the release of chlorine into environmental water systems. This holds especially for the larger pools found e.g. at recreation resorts, often in environmentally sensitive areas. The successful and safe use of ozone for treatment of swimming pool waters is well documented [Rice and Bollyky, 1982, and various other papers in that publication]. In Germany, 64 % of all ozone plants installed in 1990 were in the swimming pool industry [Eichelsdörfer, 1992]. The PURION technology will be used for this purpose. Figure 16 shows a typical installation of one of the small ozone generators on a domestic pool. Systems for larger pools are currently under development.

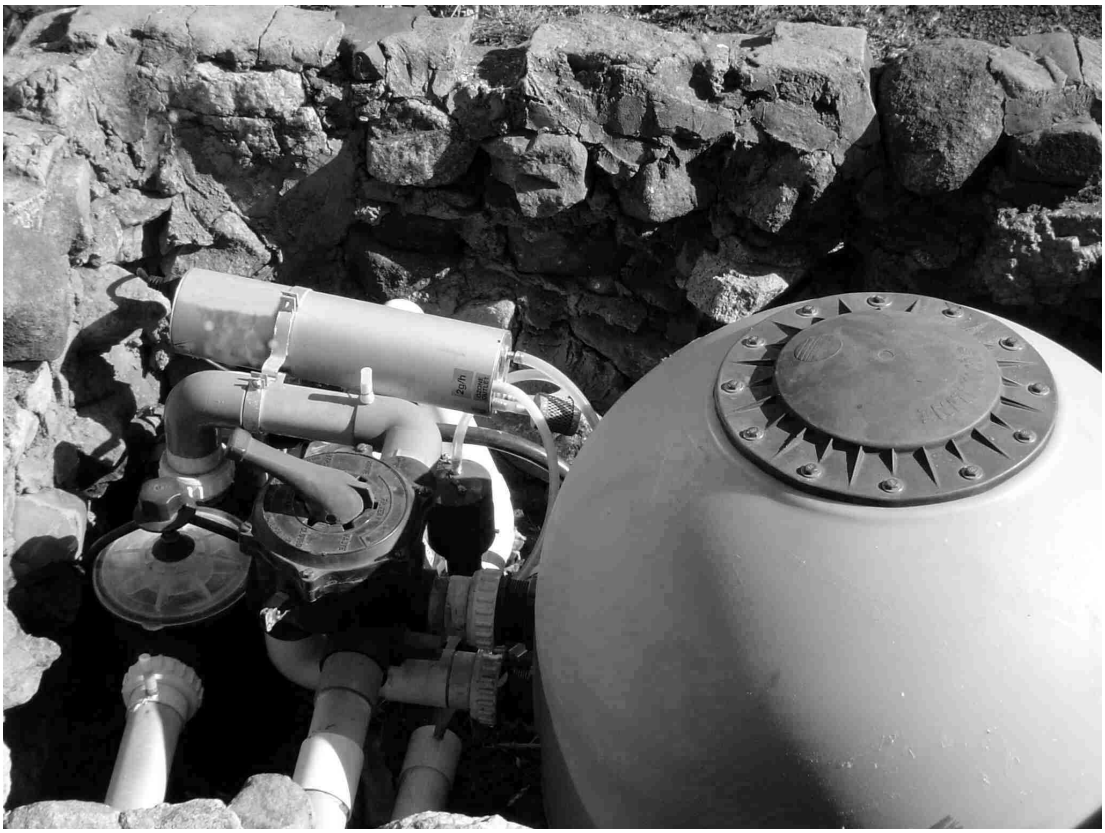

Figure 16: A small ozonator installed on a residential swimming pool

3.3.6.1.1 Mobile sterilisers / sanitizers

Sanitisation of working surfaces and floors in food processing plants, wineries, packaging plants, dairies and many other industries consume large quantities of water. The water is loaded with chemical disinfectants like chlorine, which eventually end up in environmental water sources. Hampson, 2000 showed that sanitisation with water ozonated to a high level is very effective, and leaves no chemical residues in the water. Potentially, the wash water may be re-used. Both features of this application hold considerable positive implications in terms of a reduction of chemicals released into the environment. Figure 17 shows a mobile sanitiser which was developed using the PURION ozone technology.

Figure 17: A mobile sanitising system using PURION ozone generation technology

3.3.6.1.2 General purpose systems

Ozone applications are very diverse, and it is out of the scope of this report to mention all of these. Many applications are generic and require the same basic ozonation system to benefit from the properties of ozone. Figure 18 shows two general-purpose systems that were built

using the PURION technology. The basic design of the systems is the same, and can be up-scaled to larger systems as required.

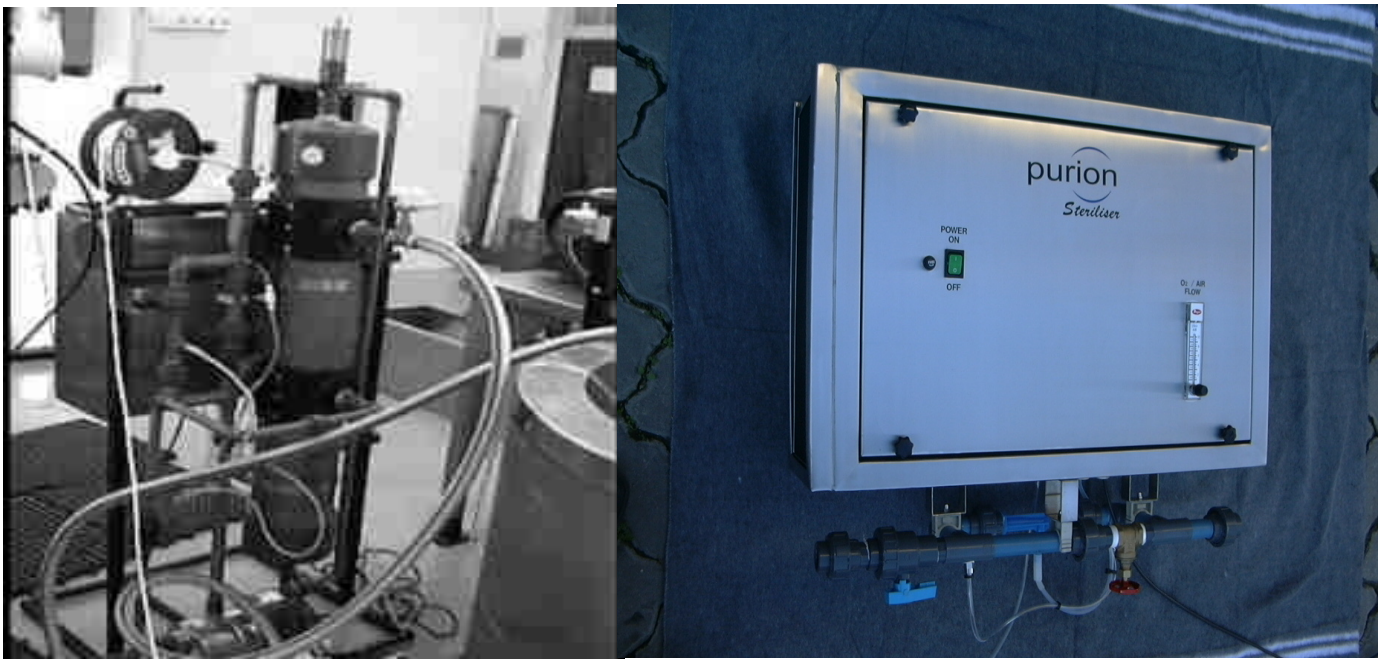

Figure 18: Two general-purpose ozonation systems using the PURION technology

3.4 Future Developments

The foundation has been laid for the establishment and manufacture of local ozone generator technology. There are a number of developments that can further improve the ozone generators. One of these involves the use of fast rising waveforms, where the voltage is applied to the electrode in about one hundred nanoseconds. This has been shown by Hosselet, 1973 to result in a seven-fold increase in the ozone/energy efficiency. It is believed that the combination of these voltage waves with the PURION dielectric technology will result in a very efficient ozone generator. This aspect and various others will be the subject of intense research and development in future.

4. REMOVAL OF TASTES AND ODOURS FROM HARTBEESPOORTDAM WATER

4.1 Strategy

Unacceptable tastes and odours occur periodically in the water of Hartbeespoort Dam. The phenomenon is seasonal, and although predictable to some extent, occurs randomly. This made it difficult to measure the effects of ozonation on the water. The problem was exacerbated by the delays in the development of reliable ozone generators and power supplies, which meant that ozone generators were unavailable when odour conditions

occurred. The ozone generator development aspect was prioritised after a steering committee decision.

Although not the ideal test, it was therefore decided to investigate ozonation for tastes and odour by adding odour-causing compounds to water samples, also called spiking. A continuous flow-through ozonation reactor was also built to investigate ozonation of tastes and odours (see Section 5) but was not used. Future experiments are planned using this equipment.

4.2 Methodology

4.2.1 Spiking of samples

40 l water samples were obtained from the waterworks at Hartbeespoort Dam. Samples were taken from the raw water supply, as well as after the sand filtration process, before addition of chlorine. Geosmin and 2-MIB were added to the samples by Thermtron Scientific, to obtain concentrations of 569 and 513 ng/l of geosmin and 2-MIB respectively in the raw water, and 13 and 262 ng/l respectively of geosmin and 2-MIB in the filtered water. The water samples were thoroughly mixed for a period of 18 h to ensure homogeneity, however, even with the precaution, the spiking process with geosmin in the filtered water was not successful. Concentrations obtained in the raw water are somewhat higher than those that exist when odour events occur (typically 100 ng/l).

4.2.2 Batch reactor experimental setup and analysis

Ozonation of the spiked water was performed in a batch reactor setup, as shown schematically in Figure 19. Sub-samples of 1.8 l were introduced into the flask, through which a known amount of ozone was bubbled. One of the smaller PURION ozone generators was used, producing 809 mg/l of ozone from an oxygen flow stream of 200 ml/min. The water was stirred vigorously using a magnetic stirrer for the duration of each test. A trap, filled with KI (potassium iodide) was fitted in the outlet of the flask to absorb ozone that was not absorbed in the water. The injection time of ozone into the water was varied to obtain different values of ozone dose. Injection times varied from 20 sec to 3 min. All samples were subjected to ozonation for 4 min. The true ozone dose transferred to the water was determined by measuring the quantity of ozone in the KI trap, using the iodometric method. At lower dose (up to 2 mg/l applied), no ozone was measurable in the trap, and the headspace above the water in the flask was sampled and analysed by the KI method to

determined transferred dose. Three water samples of 1.8 l each were treated at each ozone dose level. A third of each treated sample was collected, and the three sub-samples were mixed to obtain a composite sample representing the conditions at the given ozone dose. The samples were subsequently analysed through gas chromatography by Thermtron Scientific, using the SPME stripping technique developed by this company.

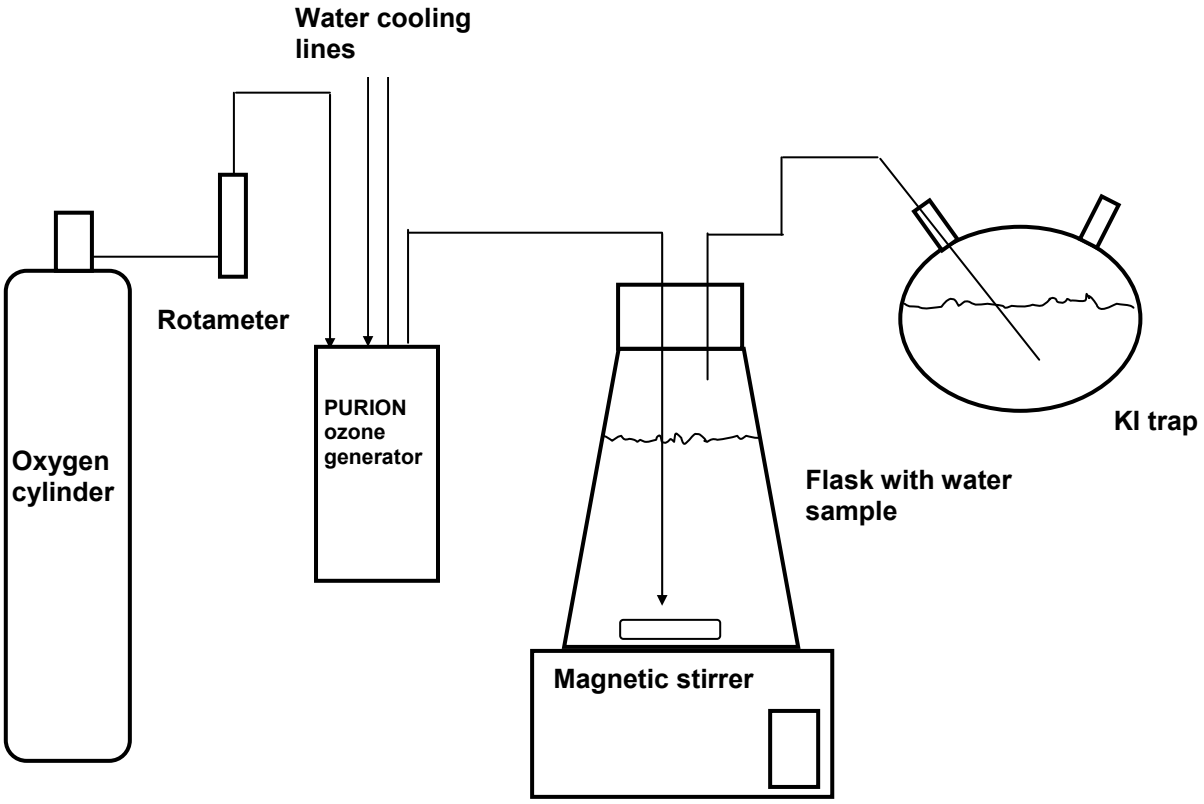

Figure19: Schematic of the experimental setup to investigate ozonation of tastes and odours

4.2.3 Results and discussion

The results of analysis are shown in Figure 20.

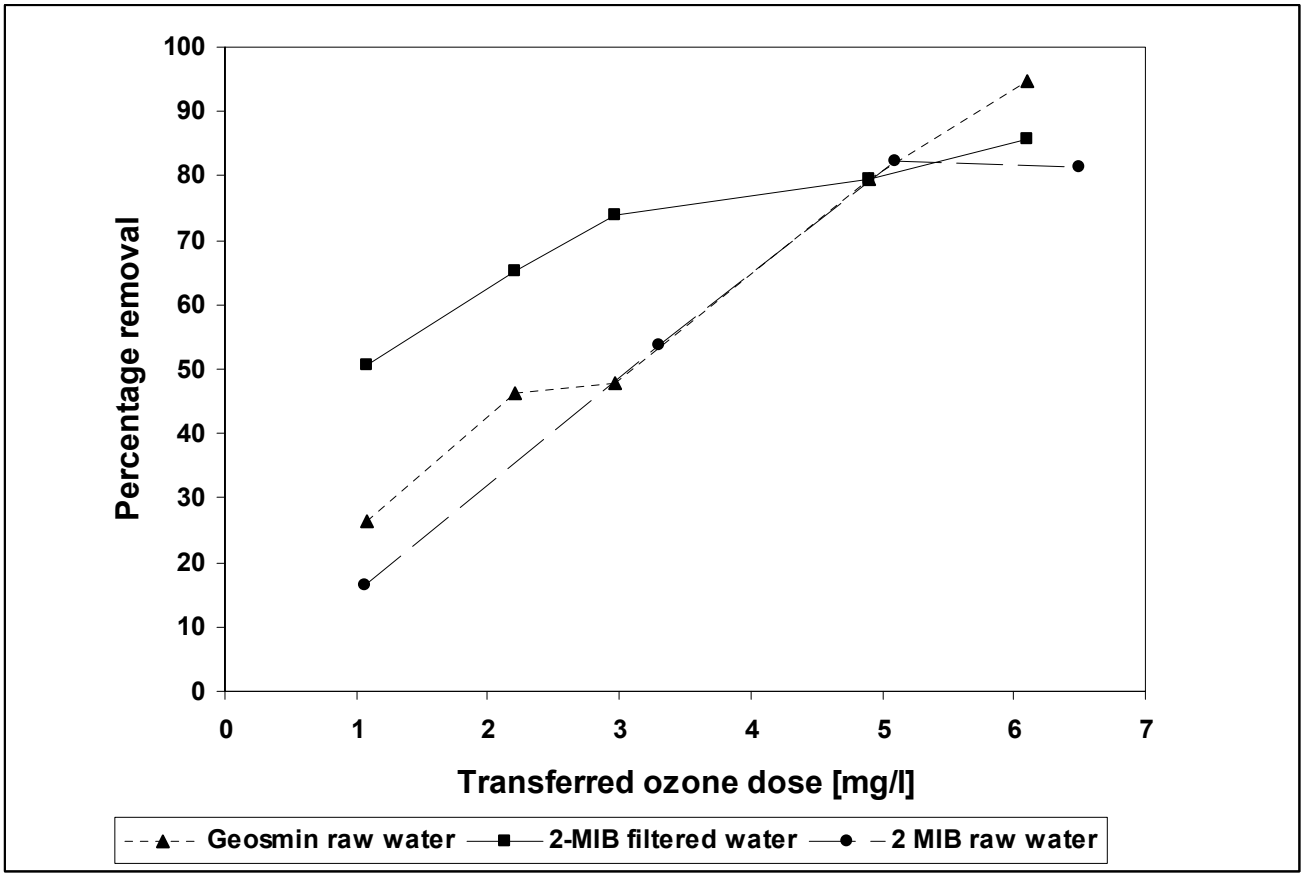

Figure20: Removal efficiency for geosmin and 2-MIB in raw and filtered water vs transferred ozone dose

Generally, ozone doses used in ozonation plants fall in the range of 0.5 to 3 mg/l [Chédal, 1984], for typical applications of disinfection, Fe and Mn removal, and raw water pre-ozonation. At the maximum of this range, the removal efficiency of geosmin in raw water was of the order of 40 %, and of 2-MIB up to 45%. This finding is in agreement with others (see Section 1.2) stating that these compounds are not easily oxidised by ozone. In filtered water, 2-MIB removal up to 75 % was found. This value for 2-MIB in filtered water is higher than reported, and will have to be corroborated by further studies.

At increased transferred ozone doses of 6 mg/l, geosmin removal up to 95% in raw water, and 2-MIB removal up to 80 % in filtered water were found. Levels in filtered water were below the detection limit due to the low initial value of 13 ng/l obtained with spiking. The results indicate that the compound can be removed by ozone at relatively high dose in

Hartbeespoort Dam water. The high required dose may be attributed to a high organic loading (see Section 5) as well as the presence of unknown compounds which compete in reactions with the applied ozone. These higher dose levels are normally only used in ozonation plants for specialised applications like removal of pesticides and detergents [Richard and Bréner, 1984]. Removal of odour causing substances from water should be regarded as a specialised application of ozone, in the consideration of the economics of high-dose ozonation.

5. OZONE DEMAND

5.1 Methodology

Methods to measure ozone demand include those described by Roustan et al, 1997; Hoigne and Bader, 1994 and Duguet, 2000. The various methods present a series of advantages and disadvantages, depending on the technique, available equipment and application. In this study, the continuous flow-through method of Duguet was used to determine ozone demand, since real-time dissolved ozone monitoring equipment was not available to follow the fast changes in this parameter that are inherent in the other methods.

The apparatus used for measurement of ozone demand (not only for this purpose) is shown in Figure 21. Water flowed continuously through the 2m high column at a low flow rate, with a residence time of 5 min. The column volume was 28 l. Ozone was injected continuously into the bottom of the column through a bubble diffuser. Ozone not dissolved or absorbed in the water escaped through a gas outlet line at the top of the column. Once steady state had been reached (ten minutes allowed) ozone was sampled from this line to determine the concentration of outlet gas. Dissolved ozone was measured at the top of the column using both the DDPD and the indigo trisulfonate method [Bader and Hoigne, 1981]. In the DDPD Method [CHEMetrics], the water sample is treated with an excess of potassium iodide (KI). Ozone oxidises iodide to iodine, which oxidises DDPD (a form of N,N-diethyl-p-phenylenediamine) to a purple coloured compound. The colour is compared to a set of standards

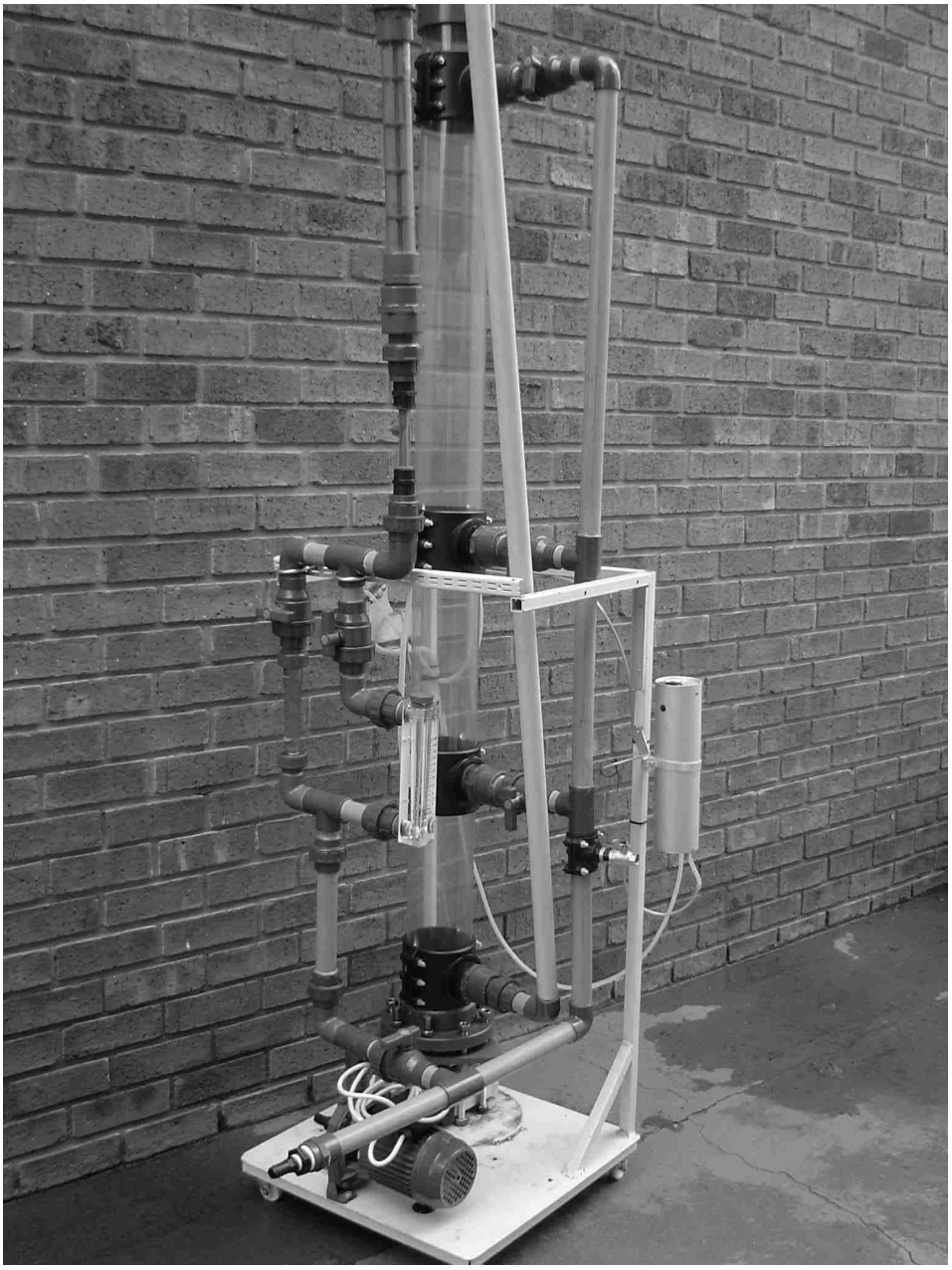

Figure 21: Apparatus used for continuous measurement of ozone demand

The transferred ozone dose was determined from the injected ozone concentration and the concentration in the gas outlet line. Solution of the set of mass balance equations for the liquid / gas system yields relationships between the transferred dose, ozone residual, and ozone reaction constant with compounds in the water. Applying different ozone injection rates varied the transferred ozone dose. Plotting the residual dissolved ozone concentration vs the transferred ozone dose allowed determination of the ozone demand, as well as the ozone reaction rate constant, as shown in the following section 5.2

5.2 Results and Discussion

Figure 22 shows the residual ozone concentration vs transferred ozone dose. The mass balance equations for the co-flowing liquid and gas streams indicate that the ozone demand is given by the intercept of the straight line through the X axis. The ozone demand from the measured graph is 0.6 mg/l. This value can be compared to raw water from the river Seine, which is reported to vary between 0.5 and 0.75 mg/l [Duguet, 2000].

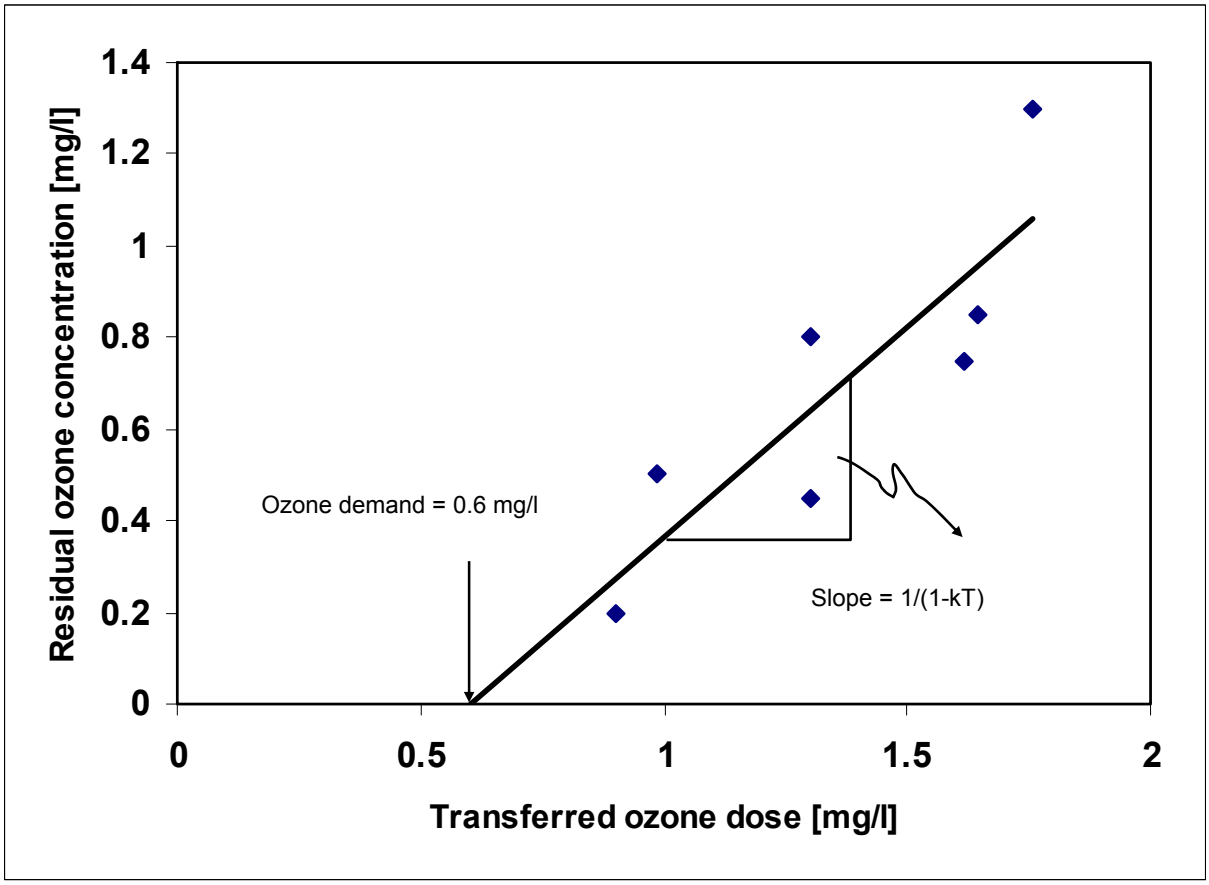

Figure 22: Ozone residual concentration vs transferred dose for filtered Hartbeespoort Dam water. The intercept with the X axis represents the ozone demand, while the slope gives the kinetic reaction constant (k value) for ozone.

The slope of the straight line is given by 1/(1+kT), where k is the kinetic reaction constant of ozone for the water, and T is the hydraulic residence time of the water in the column (5 min). The kinetic reaction constant was determined as k=0.02 min^{-1}. These values represent important input parameters for the design of an ozone mass transfer and contact system intended for viral inactivation. Further corroboration is proposed, to investigate the effects of fluctuations and seasonal changes.

6. CONCLUSIONS

6.1 Ozone Generator Technology

The program of research and development was successful in the establishment of South African based ozone generator technology. A number of important milestones in this process have been attained:

- All components are sourced and manufactured locally.
- A range of ozone generator sizes has been developed, that enables ozonation applications over a wide spectrum. Small systems, e.g. ozonation of residential swimming pools, or rural water purification can be addressed. The medium sized ozone generators will be used for larger applications e.g. cooling towers, or effluent treatment, while large, kg/h capacity systems are in the prototype stage. These are suitable for application in municipal water systems and other, large, ozone applications.
- The PURION technology that was developed is extremely flexible in design, allowing easy adaption of the generators to any specific application.
- This is enhanced by the inherent modular nature of the designs. Relatively easy replacement of faulty electrodes, without losing the full capacity of the unit for extended periods of time is a major advantage of the modular approach
- Modularity furthermore extends the usability of any of the power supplies or electrodes by employing a multiple of these units for a system with higher ozone output.

It is believed that the PURION ozone technology will make the use of ozone in South Africa possible and affordable across a wide range of applications, harnessing the remarkable properties and full potential of this oxidant for the benefit of cleaner water systems in the country.

6.2 Taste and Odour Removal

Although tests on taste and odour removal from Hartebeespoort Dam water were not prioritised in this study, a number of results were obtained. Ozonation tests on water samples spiked with the odour-causing compounds geosmin and 2-MIB corroborated the relatively low removal rates reported. However, application of high doses (6 mg/l transferred ozone dose) were successful in removing both contaminants with efficiency of 95% and 80 % respectively. The cost implication of these high required ozone doses, and highly efficient

ozone mass transfer techniques should be thoroughly considered in the design of ozone systems to adress taste and odour removal from these waters. A specialised design will be required.

6.3 Enteric Viruses

As for odours, this aspect was also not prioritised. No viral inactivation investigations were done. However, the measurements of ozone demand and kinetic reaction constant that were made contribute important values. This information is crucial for the optimised design of an ozone system intended for viral inactivation, because of the CT rule discussed in Section 1.3. Should an ozonation system for viral inactivation in the Hartbeespoort Dam become necessary, it is recommended that these parameters be corroborated through further measurements to also encompass the effects of fluctuations and seasonal variations.

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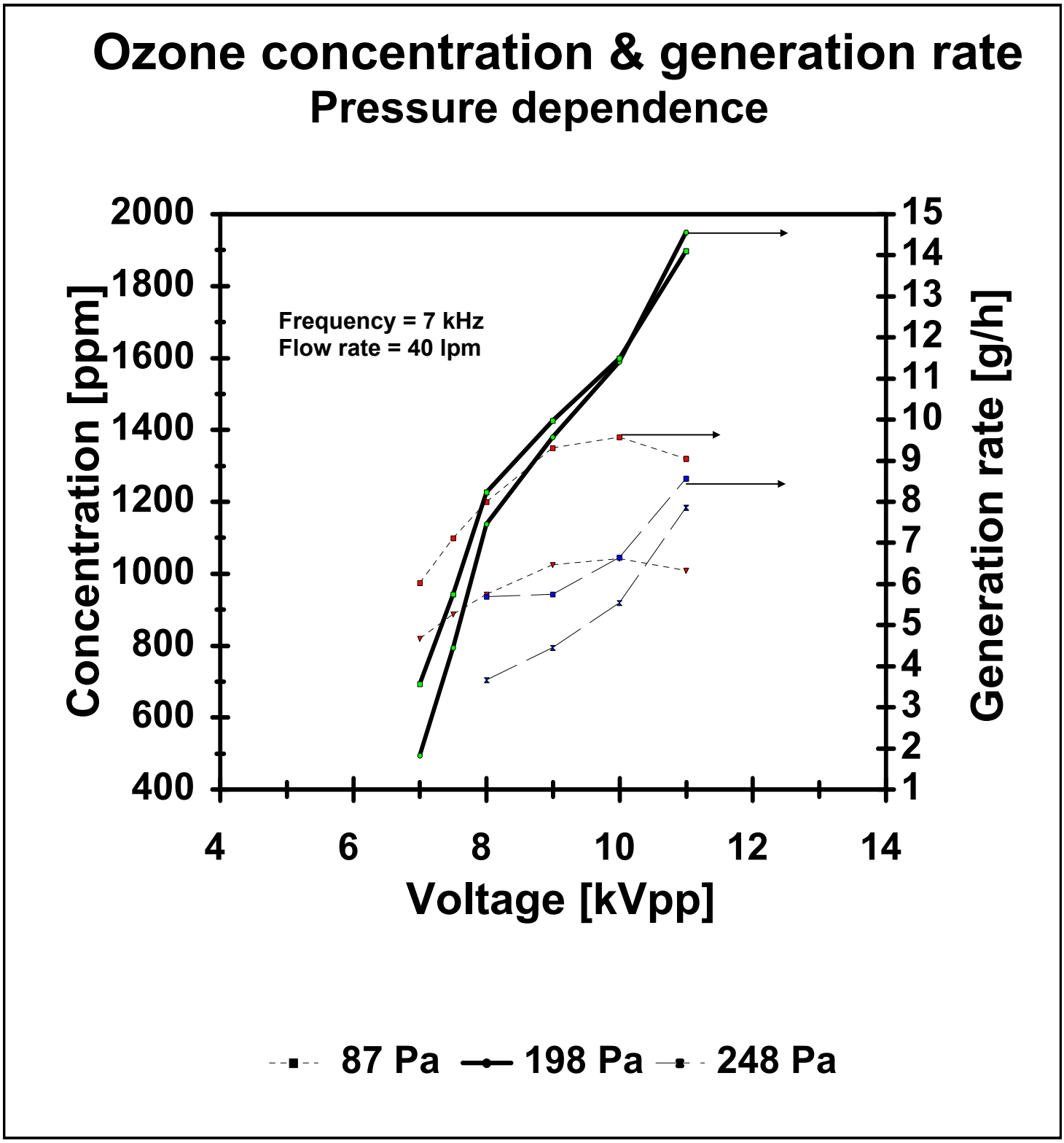
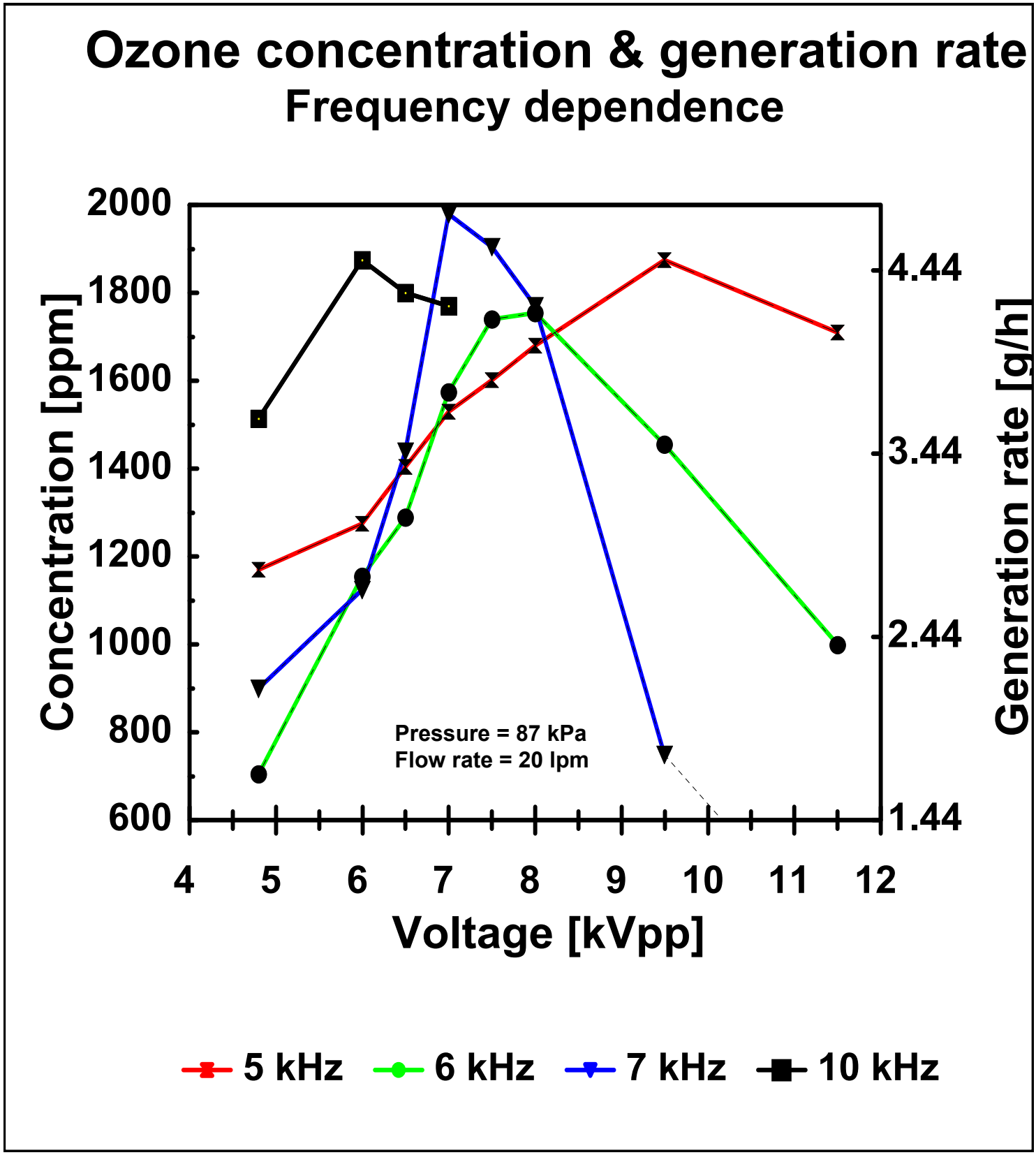
APPENDIX I

Typical results obtained with the PURION surface discharge technology




Ozone concentration & generation rate
Frequency dependence
Concentration [ppm]
2000
1800
1600
1400
1200
1000
800
600
Generation rate [g/h]
4.44
3.44
2.44
1.44
Pressure = 87 kPa
Flow rate = 20 lpm
4
5
6
7
8
9
10
11
12
Voltage [kVpp]
5 kHz
6 kHz
7 kHz
10 kHz