ELECTROLYTIC OZONE GENERATION AND ITS APPLICATION IN PURE WATER SYSTEMS

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Abstract

Over the years manufacturers have become increasingly aware of the importance of water purity and its effect on the quality of the final product. One of the largest problems that confronts pure water system operators is bacterial recontamination shortly after the water purification equipment. There are several recommended methods of either preventing or removing such contamination but most have inherent disadvantages. The most innovative and effective method that has been adopted by leading pharmaceutical and. semi-conductor manufacturers, involves ozonation of the water in the system and reducing this prior to the first point of use with ultraviolet irradiation.

An efficient way of producing ozone is with an electrolytic ozone generator such as MEMBREL® that actually produces ozone from the water being treated. Ozone, and particularly electrolytically generated ozone, is ideally suited for pure water loops because only low concentrations are necessary to sanitise the system and there are no objectionable by-products or residue after the ozone has decomposed to oxygen.

Introduction

Irrespective of how well a plant has been designed and constructed, when no special measures have been taken, it is virtually impossible to avoid microbial contamination in a pure water network. This is especially the case when a system is not continually replenished with fresh makeup water such as over night or over the weekend when production is shut down and the water stands in a tank or circulates in a closed loop.

Only for specific applications do regulatory bodies require that certain criteria are met and request the operators of such plants to carry out validation tests. In all other cases operators are left to their own means and follow accepted guide fines to establish and maintain the integrity of their pure water systems.

Methods

There are several standard methods used by operators to disinfect their pure water systems, however, each of these has disadvantages that have a bearing on the water quality:

- **Shock disinfection** with chemicals such as peroxide or hyperchlorites.

  Disadvantages:

  a) Interruption of operation
  b) Work intensive
  c) Associated chemical problems
  d) Fluctuating water quality

- **Shock sterilisation** with steam.

  Disadvantages:

  a) Interruption of operation
  b) Costly installation 1 service
  c) Uncontaminated steam necessary
  d) Fluctuating water quality

- **Ultraviolet irradiation**

  Disadvantages:

  a) Risk of reduced disinfection
  b) Only localised effect
  c) Sterile filter beneficial
  d) Regular component replacement

- **Sterile filtration**

  Disadvantages:

  a) Bacterial growth is unaffected
  b) Regular replacement required
  c) Danger of bursting
  d) Expensive

Of the above mentioned standard methods shock disinfection with chemicals or shock sterilisation with steam seem to produce the best results providing that the service interruptions and fluctuating water quality can be tolerated.

An innovative and alternative method of disinfection of pure water loops, without any of the mentioned drawbacks, is by introducing ozone to the circulation flow. The advantages of using ozone are manifold:

> There are no objectionable by-products or residues when water is disinfected with ozone. In the absence of oxidizable substances ozone decomposes to form oxygen as soon as oxidizable substances are present traces of carbon dioxide will form. These substances do not pose a major problem in connection with the water quality.

Because the ozone does ultimately decay to form oxygen - the ozone molecule is only moderately stable and has a half fife time of something like 30 to 60 minutes at normal service conditions - there are no lasting problems with traces of disinfection chemicals.

Experience gained in the pharmaceutical industry has shown that very low ozone concentrations in the magnitude of 0. 1 to 0.2 mg/l are sufficient to keep germ counts below 1 c.f.u. per 100 ml. Figure 1 indicates microbial growth as a function of ozone concentration.

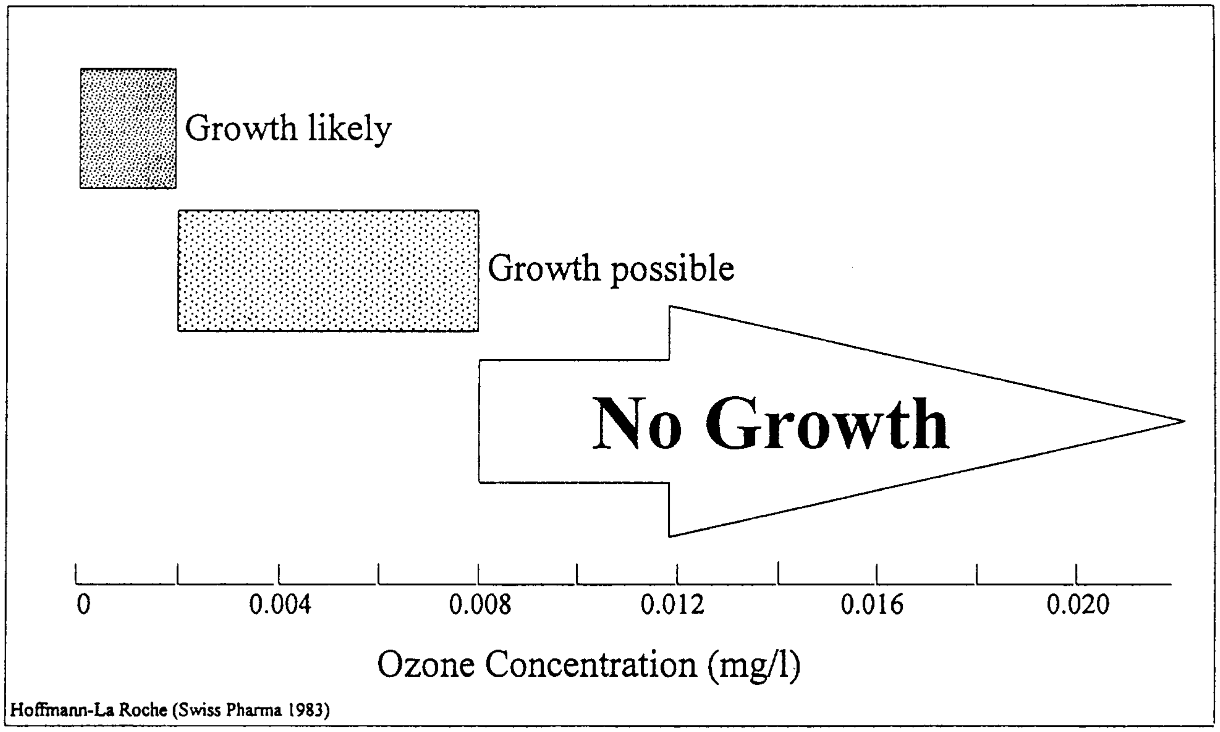

Figure 1: Microbial growth as a function of ozone concentration

Disinfection with ozone is a continual process and, in most cases, can be regulated by simple means. However, if required, the ozone production rate can be controlled by the process parameters in order to avoid incorrect dosing and to ensure optimised efficiency.

Owing to ozone's limited half life, it has to be produced in-situ when and where it is required. Although this means that extra investment must be made for a minor additional amount of infrastructure in the form of an ozone generator it avoids the transportation of potentially dangerous chemicals or the high running costs of a steam sterilisation unit.

The Electrochemical Oxidation Potential (EOP) **of ozone** is considerably higher than other disinfecting agents:

Disinfecting Agent	EOP (V)	EOP v. Chlorine
Fluorine	3.06	2.25
Hydroxyl-radical	2.80	2.05
Oxygen (atomic)	2.42	1.78
Ozone	**2.08**	1.52
Hydrogen dioxide	1.78	1.30
Hyperchlorite	1.49	1.10
Chlorine	1.36	1.00
Chlorine dioxide	1.27	0.93
Oxygen (molecular)	1.23	0.90

Ozone generation

The State of the Art method of producing ozone is by means of Dielectric Barrier Discharge using either dry air or dry oxygen as the feed gas. Synthetic ozone produced by these generators is ideal for drinking water disinfection waste water treatment, pulp bleaching, etc. but does have limitations when dealing with pure water systems.

A far more elegant way of producing ozone for this specific application without the inherent disadvantages associated with conventional processes, is with a MEMBREL® electrolytic ozone generator that splits water into its basic elements and then converts part of the liberated oxygen into ozone.

The main advantages of producing ozone with an electrolytic system are:

- There is no ionic contamination because the feedwater is being dissociated using a solid hydrated ion exchange membrane.
- The process water being disinfected is the source of oxygen for the generation of ozone - consequently, no outside contamination is introduced into the system being treated.
- The ozone is dissolved in the process water as soon as it is formed - this results in ozonation with the minimum amount of equipment.
- By operating the cell under pressure, relatively high ozone concentrations can be produced

This electrolytic system is fundamentally different method of dissociating water due to the fact that it uses a solid polymer membrane as the electrolyte instead of fluid - this feature in conjunction with suitably controlled intermediate anodic reaction makes it particularly suited for disinfecting pure water systems irrespective of their application. A basic cell is shown in figure 2.

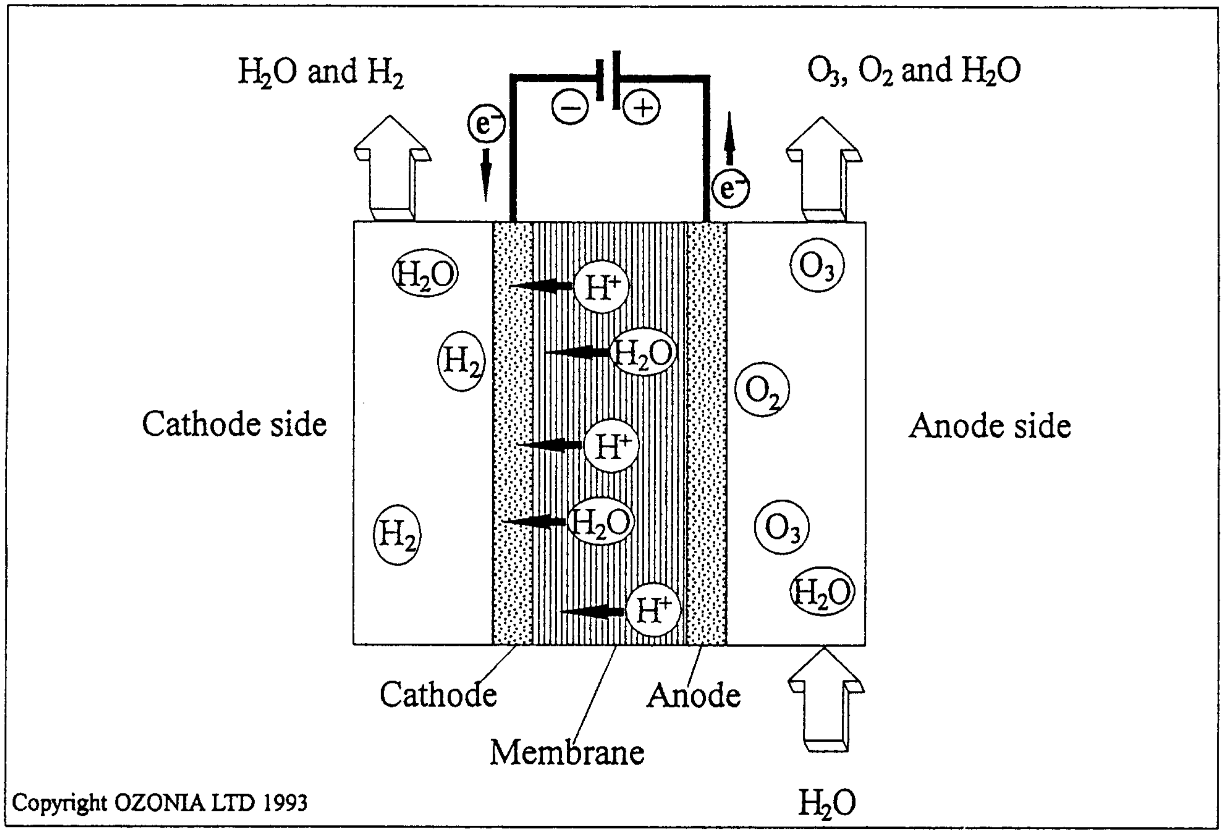

Figure 2: Basic electrolytic ozone generator cell

The membrane, which functions as both electrolyte and separator between anode and cathode, is contacted on both sides by the activated porous electrodes. The water fed to the anode side of the cell is dissociated at the interface between the anode and membrane as a result of the DC current being applied. To ensure that as much ozone as possible is produced, the anode must have an over potential above the decomposition and the ozone reaction potential and the catalytic layer must inhibit the formation of diatomic oxygen and encourage the formation of ozone.

<u>Integration</u>

Most modem pure water networks, are constructed as closed loop systems in which the water is pumped through one or more circulation loops to different consumer points. Depending on the application of the process water, there will be differing amounts and types of equipment installed in the system. Figures 3, 4 and 5 show typical flow diagrams for 3 different uses.

For all applications it was found best to install the ozone generation system in the loop return just before it re-enters the storage tank. The by-pass flow for the electrolytic system is tapped off before the loop's pressure retaining valve and reintroduced on the low pressure side - see figure 6.

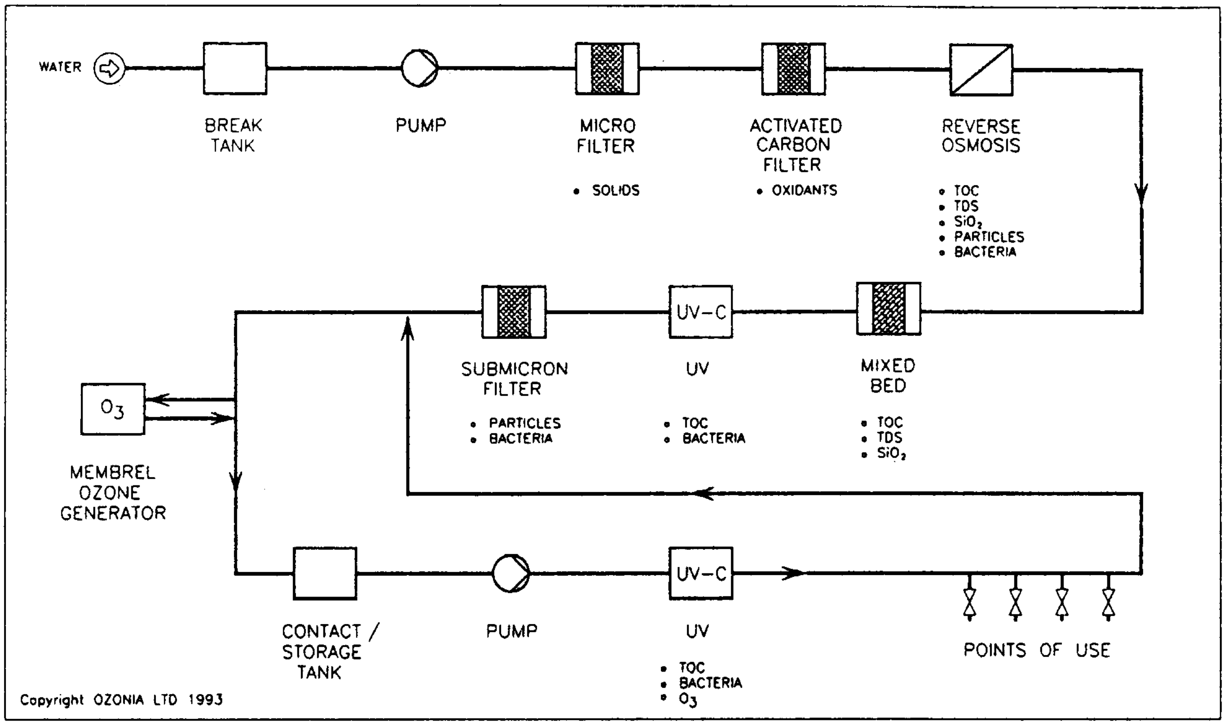

Figure 3: Typical arrangement for pharmaceutical application (not WFI)

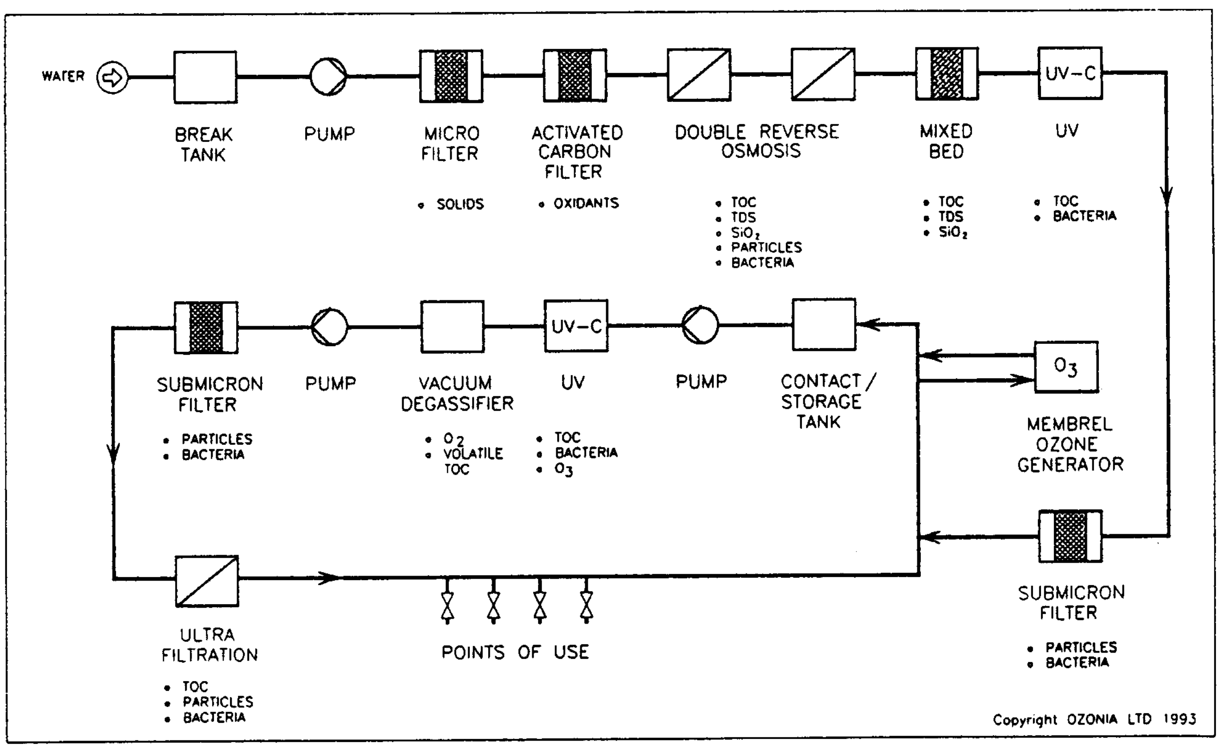

Figure 4: Typical arrangement for semi-conductor applications

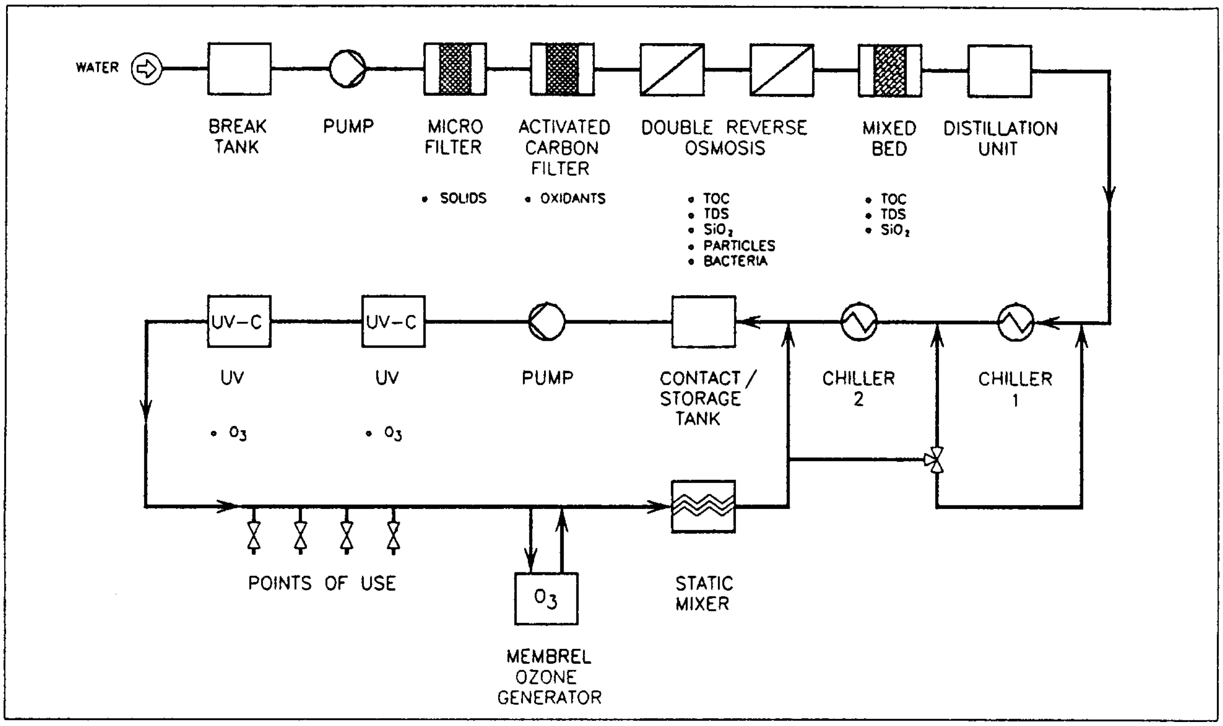

Figure 5: Typical arrangement for WFI production

For all applications it was found best to install the ozone generation system in the loop and return just before it re-enters the storage tank. The by-pass flow for the electrolytic system is tapped off before the loop's pressure retaining valve and reintroduced on the low pressure side - see figure 6.

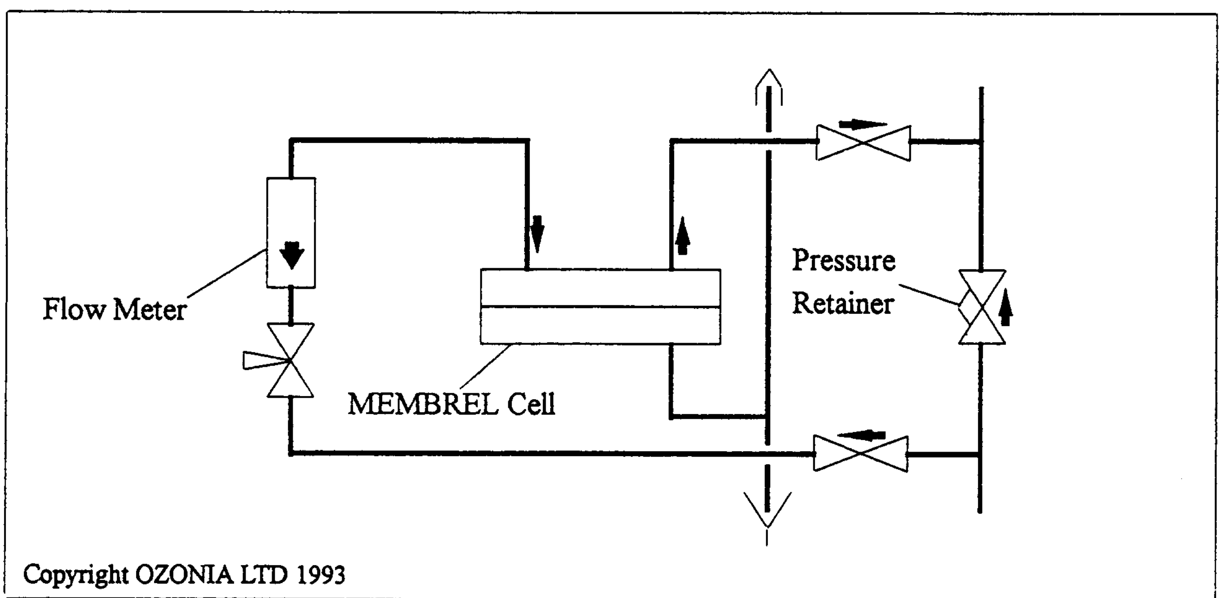

Figure 6: Ozone generator installation

Ozone effect

Ozone is a very strong oxidising agent with powerful disinfecting properties. It is bactericidal, viricidal, fungicidal and sporicidal - further, it is active against yeasts, parasites, etc..

One of the important factors to be taken into consideration when calculating the ozone dose is the organic content of the water being disinfected because if this is high the ozone demand win be correspondingly high and the ozone will be used also to reduce the organic content rather than just destroying micro-organisms. During periods when ozone is being used to oxidise both micro-organisms and organics the kill rate will be slow - once the TOC has been reduced to a minimum, the kill rate will increase accordingly. However, it is to be borne in mind that because cell death is caused by lysis and catoplasmic dispersion this will continually supplement the organic content of the water.

In order to simulate the effect of electrolytically produced ozone on normal water contamination, MacRae et al carried out tests on a mixed culture of **Staphylococcus Albus, Pseudomonas Diminuta, Flavobacterium Devorans** and **Coryneybacterium pyrogenes** which were seeded into a tank prior to ozonation. A count was taken for the total quantity of bacteria killed rather than the kill for each particular species:

System parameters			
	Volume of water	:	500 1
	Circulation rate	:	500 l/h
	Cell flow rate	:	100 l/h
	Cell current	:	10 A
	Ozone production	:	ca. 200 mg/h

Time	Count/ml	Log Count	Ozone mg/l
0	26000	4.4	0.00
20	2000	3.5	0.01
40	1900	3.3	0.01
60	650	2.8	0.02
80	28	1.5	0.02
100	0	-	0.03
120	0.2	-0.7	0.03

All species of bacteria inoculated could be detected in the initial plates. It was noted that all of the species were removed. See also figures 7 and 8.

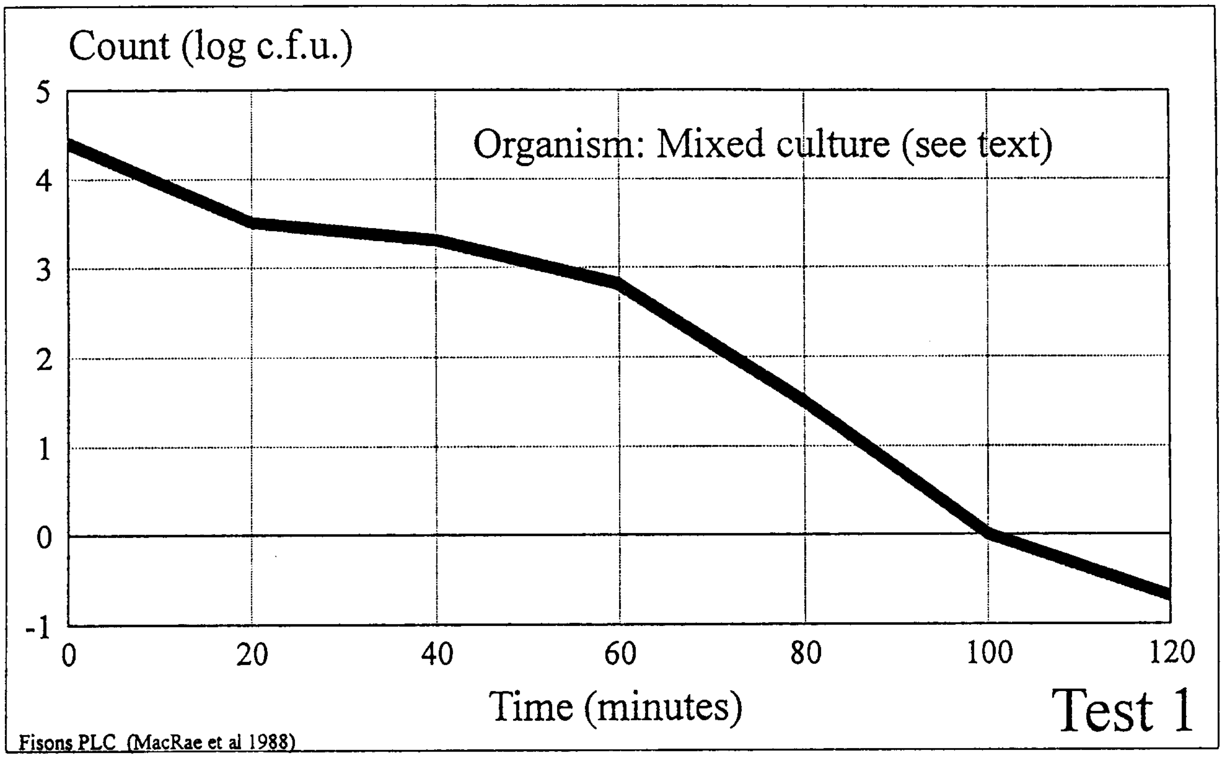

Figure 7. Reduction of micro-organisms with ozone

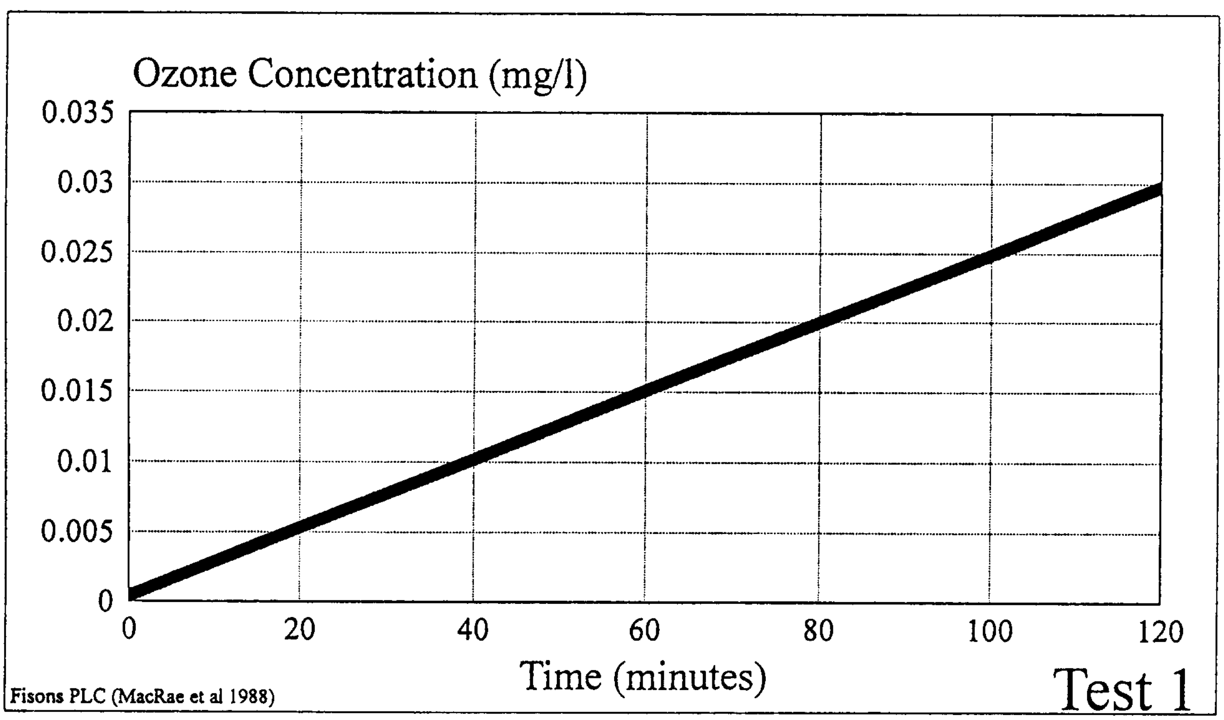

Figure 8: Residual ozone concentration

A second test was performed using the same mixture of cultures but with a higher ozone production rate:

bacteria killed rather than the kill for each particular species:

System parameters			
	Volume of water	:	500 1
	Circulation rate	:	500 l/h
	Cell flow rate	:	50 l/h
	Cell current	:	15 A
	Ozone production	:	ca. 300 mg/h

Time	Count/ml	Log Count	Ozone mg/l
0	41000	4.6	0.00
20	800	2.7	0.00
40	9.3	1.0	0.00
60	0	-	0.00
80	0	-	0.01
100	0	-	0.01
120	0	-	0.03

The water used for the second test had a higher temperature than the water used for the first test. Although some cooling did take place during the test period, the lack of detected residual ozone can be considered a result of the higher temperature reducing the half life - ozone did start to build up after 80 minutes when the temperature had reduced to 28'C. Even though the residual ozone content was below the detectable limit the bacteriological reduction was rapid and can be attributed to the synergistic effect of ozone and temperature. See figures 9 and 10. During testing it was noted that the **Staphylococcus Albus** and the **Pseudomonas Diminuta** appeared to have the greatest resistance to ozone while the other species were removed rapidly.

In addition to the tests on bacteria, MacRae also demonstrated that ozone was very effective against other micro-organisms:

Viruses	:	Ozone was proved to be a very powerful viricide - e.g., **Polio Virus** was inactivated in 2 minutes with an ozone concentration of 0.05 - 0.45 mg/l
Cysts	:	**Enteramoeba Hystolytica** were removed with a ozone concentration of 0.3 mg/1 for 2.4 minutes
Spores	:	Ten to fifteen times more resistant to ozone than vegetative cells because of the extra protection afforded by the spore coat
Fungi	:	**Candida Albicans** and a **Penicillium** were successfully sterilised
Parasites	:	**Schistosoma Mansoni** were sterilised after 3 minutes

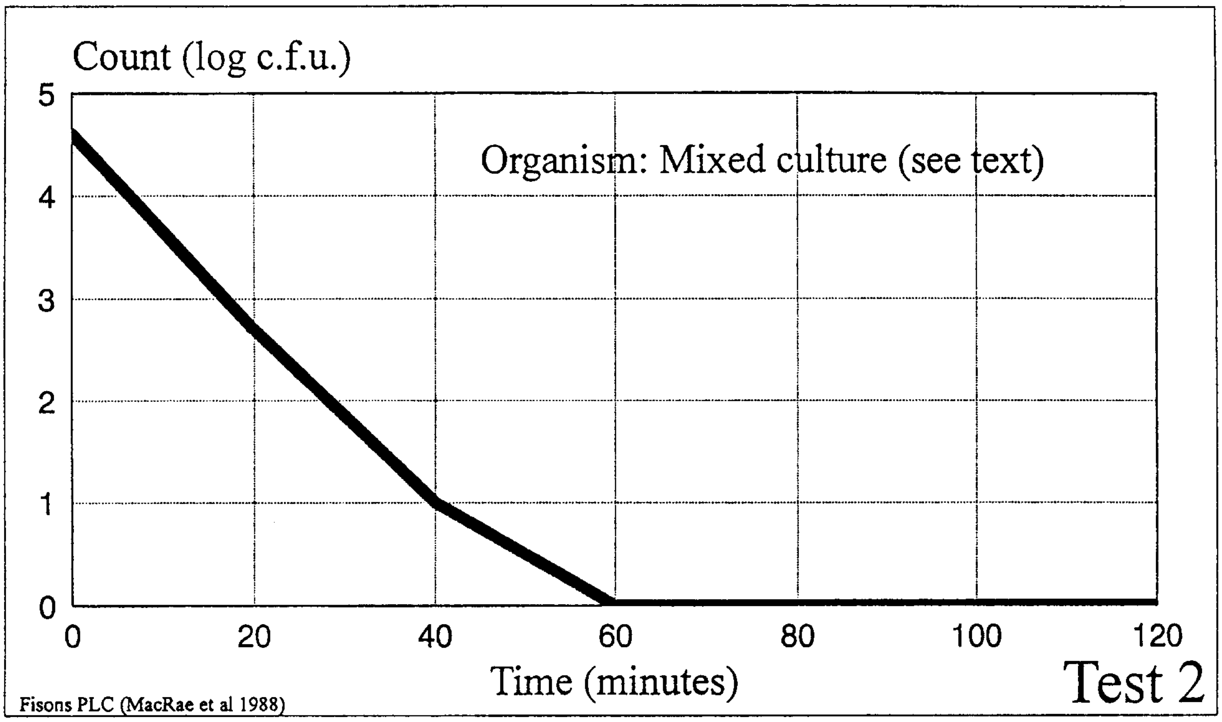

Figure 9: Reduction of micro-organisms with ozone

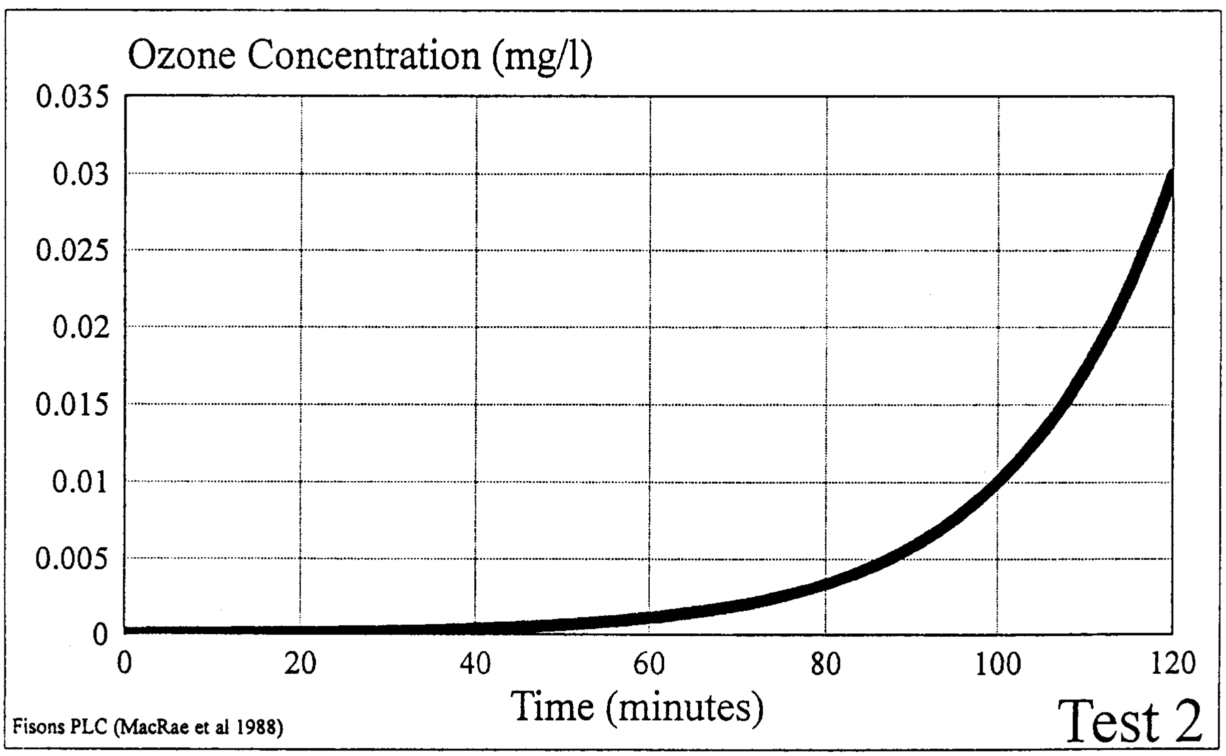

Figure 10: Residual ozone concentration during disinfection

Ozone destruction

Depending on the process or product in question, sometimes it is necessary to remove the ozone from the water prior to use. There are several methods of removing or reducing ozone (activated carbon filters, catalytic conversion units, thermal destructors, ultraviolet irradiation, etc.) but, because of the nature of the pure water and the associated systems, only ultraviolet irradiation comes into question.

Normal practice is to install a UV unit in the piping system shortly before the first point of use which is switched on shortly before starting the main process or commencing with production and then switched off when there is no demand for a longer period of time such as over night or over the weekend. The incorporation of an ultraviolet ozone destructor unit also offers operators the small added benefit gained from the fact that hydroxyl-radicals, with a high oxidation potential, are produced in the lamp unit.

Standard germicidal UV units, with low pressure mercury lamps with a high UV-C output at the wavelength of 254 nanometer, are ideal for reducing ozone in pure water loops to below the measurable limits. When dimensioning such lamps, special attention must be given to the fact that the UV dose delivered at the end of the lamp's service fife, and at maximum water flow, is sufficient to achieve the required level of ozone reduction. Figure 11 shows the ozone reduction rate at various UV doses.

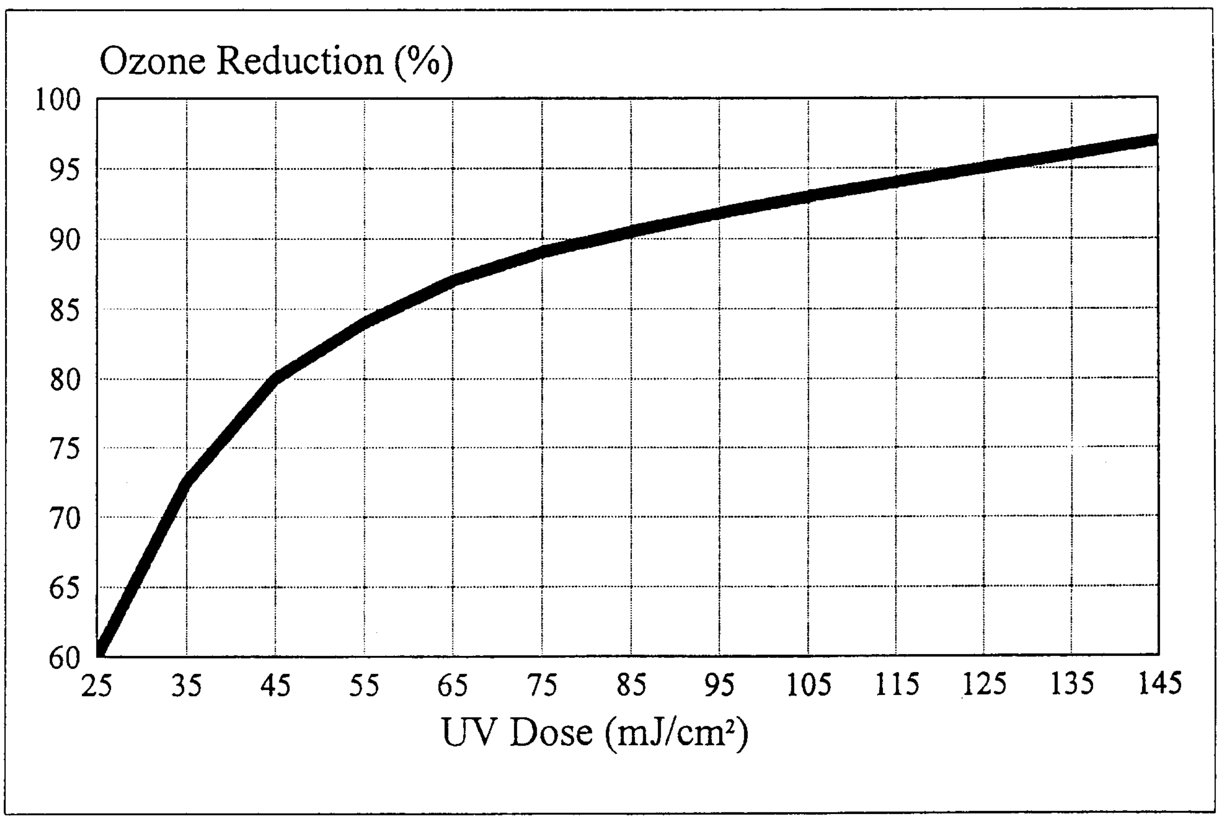

Figure 11: Ozone reduction with UV irradiation

Conclusion

Experience gained from numerous installations in various branches of industry and institutions indicate that the sanitisation of pure water systems with ozone is an easy and effective method not requiring specialised operator skills.

Because ozone disinfection is a continual process allowing very little chance of (re)contamination, many operators now rely solely on the ozone treatment and have dispensed with regular shock disinfection with either steam or other chemicals.

Keywords

Pure water, Ozone, MEMBREL®, Disinfection, Electrolytic Generation, Pharmaceutical, Semi-conductor, Water for Injection, Bactericidal, Viricidal, Fungicidal, Sporicidal, Ultraviolet Ozone Destruction.

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