This article describes the suitability of ozone for the protection of purified water systems against microbiological contamination. It also describes the process of electrolytical ozone generation, as well as an ozone application with the aid of an example from the pharmaceutical industry.

Ozonization of Purified Water Systems

by Dr. Samuel Stucki, Dirk Schulze, Dieter Schuster, and Christian Stark

Purified Water Requires Good Protection

The use of drinking water as make-up to purified water is mandated by the FDA. Pretreatment and treatment steps for US purified processing are well known and accepted. Various methods can be used to avoid quality degradation during storage and distribution of the purified water - Table A.

Passive disinfection measures demand intervention in the production process and thus interrupt the output of purified water. Afterwards, the chemicals have to be flushed out of the system before production can be resumed. The effects of the disinfection process also should be measured by increased monitoring and should be observed closely.

Active disinfection measures are deliberately planned into the water treatment system and can be executed as a routine action. Their objective is to ensure a long-term reduction of microbial growth to suitably low levels.

Active disinfection measures can contribute considerably to the avoidance of the dreaded biofouling in water systems. Biofouling is defined, in the most general sense, as a change of the surface quality, i.e., the formation of a biofilm. It is caused by the accumulation (deposit and growth) of bacteria, fungi, and other organisms. This is not restricted to the actual water treatment system; it also can occur in the distribution system, the storage tanks, and the fittings.

In acute cases, disinfection with chemical agents is generally only partially successful since the microorganisms in a biofilm are extremely resistant to the commonly used concentrations of chemicals like peracetic acid, hypochlorite, or hydrogen peroxyde, particularly since these are applied only for a limited time. In contrast, experience has shown that the regular use of ozone results after only a few applications in the decomposition of the biofilm, and thus considerably improves the microbiological situation in a water treatment system. For this reason, ozone is equally suitable for use in newly installed systems and for the sanitation of existing water systems.

The Effects of Ozone

Ozone ($O_3$) was discovered in 1840 by Christian Friedrich Schönbein as a by-product of the oxygen ($O_2$) generated at the anode during electrolysis of sulphuric acid. Ozone is an allotropic version of oxygen with three atoms, and is, after fluorine, the second most powerful oxidant and disinfectant which can be used technically.

It is a gas with an oxidation potential of 2.07 eV and is up to 20 times more effective than chlorine. It has been used successfully for more than 100 years for the treatment of drinking water and industrial water. Ozone is an environmentally benign gas which can be produced in the required quantities close to the point of use and quickly breaks down into normal oxygen. In contrast to most other oxidants and disinfectants, ozone generates no undesirable or toxic by-products.

The effectiveness of ozone results from its powerful oxidizing effect on chemicals and microor-

Table A. Methods to avoid quality degradation during storage and distribution of purified water.

| Passive Disinfection Measures | • Sterilization with steam  
|                             | • Sanitization with hot water  
|                             | • Disinfection with chemicals such as:  
|                             | - hydrogen peroxyde ($H_2O_2$)  
|                             | - eau de Javel (NaOCl)  
|                             | - ozone ($O_3$)*  
|                             | - peracetic acid  
| Active Disinfection Measures | • Continuous addition of chemicals (such as chlorine)  
|                             | • Hot or cold storage and distribution  
|                             | • UV irradiation  
|                             | • Sterile filtration  
|                             | • Ozonization*  

* Ozone acts as both active (meanwhile production) and passive (demanding an interruption) measure.
Ozonization

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organisms – which is caused by the OH- share – in the water. The exposure time necessary for the elimination of microorganisms depends on their type and the ozone concentration. Ozone directly attacks the surfaces of the microorganisms and destroys their cell walls. The cells thus lose their cytoplasm and can no longer reactivate themselves.

A very low ozone concentration of less than 0.02 mg/l is sufficient for the disinfection of ultrapure water. This applies especially to the use of modern membrane and EDI devices and has been proven in practice.2

Ozone is metastable and decomposes in ultrapure water with a half-life of about 20 minutes. Since re-infection of distribution systems for ultrapure water can occur at any time, the disinfectant used for combating such infections must spread through the entire system and also provide protection in the distribution network. Figure 1 shows the microbicidal effects of ozone on various microorganisms as a function of the application time and the concentration.

Table B lists many different sterilization and disinfection methods, together with the related problems for the treatment of purified water. Compared with the conventional disinfectants, ozone has the advantage that it not only eliminates the microorganisms, but also provides safe and continuous protection for the storage tanks and distribution systems. For this special application area, the ozone is best generated with the aid of an electrolytical process, which is described below.

Electrolytically Generated Ozone in the Purified Water Loop

Ozone can be generated at anodes with a high electrochemical overpotential. This can be achieved with the aid of very low temperatures (values of -20° to -60°C are mentioned in the literature)3 and/or by the use of anode materials which do not catalyze the formation of O₂. Lead dioxide (PbO₂) is one of the few suitable electrode materials with a high oxygen overpotential which can be used as an anode to generate ozone at room temperatures in the presence of suitable electrolytes (such as sulphuric acid or phosphate buffer solutions).1 However, in these electrolyte solutions the corrosion resistance of PbO₂ is insufficient for practical use. The lifetime of the anodes is too short and the loss of lead into the electrolyte can have unfavorable effects (contamination, deposits of lead on the cathode). In the past, the technical applications of electrochemical ozone generators failed primarily due to the low stability of the anodes.5 In addition, the efficiency of such cells for the generation of ozone is considerably lower than that of ozone generators which operate on the principle of a corona discharge in air or oxygen.

In 1985, Stucki et al. showed that lead-dioxide anodes used for ozone generation could have an unexpectedly high resistance to corrosion and could carry high currents if they are integrated into cells using a proton-conducting membrane as the electrolyte and are operated in purified water. This type of electrochemical cell is today called a Proton Exchange Membrane (PEM) cell. A typical feature of such a PEM cell is the very small distance (100 to 200 µm) between its anode and its cathode. It is thus possible to construct cells with a low electrical resistance through which high currents can be passed. The greatly reduced electrochemical corrosion of the electrodes in such cells has already been mentioned and was an important criterion for the successful introduction of this technology. Although they are so close together, the electrodes are separated by the gas-tight polymer membrane and thus permit electrochemical reactions which generate or consume gases. PEM were first described by General Electric...
at the end of the 1950s and were patented as part of the development of a new type of fuel cell. The idea of this patent was the use of a plastic membrane capable of passing ions as a solid electrolyte in an electrochemical cell. The PEM technology was originally developed for fuel-cell generators in space travel and was used in the Gemini spacecraft. The cells were equipped with cation-exchanger membranes, but the poor chemical stability of these membranes resulted in a restricted operating lifetime of the fuel cells.

The development, in the US at the beginning of the 1970s, of perfluorinated PEM membranes resistant to chemicals permitted the use of such membranes in various technically important electrochemical applications. The membrane material is a polymer with a structure similar to that of Polytetrafluoroethylene (PTFE) and is just as resistant as PTFE to chemicals. The polymer contains covalently linked sulphonic-acid groups which, in the presence of water, cause the polymer to swell and permit hydronium ions to move freely. Due to this property, the polymer can be used as a solid electrolyte. Such polymer membranes are today used industrially in chlor-alkali electrolysis. Subsequently, the PEM technology has been developed further for various electrolysis applications and for fuel cells, particularly for mobile applications.

Proton Exchange Membrane (PEM) Ozone Technology

PEM cells offer various advantages for the electrolytical production of ozone. First, the anode material used today is fully resistant to corrosion if no free anions exist in the medium – in other words, when used in purified water. PEM ozone cells have been operated for many years without degradation in purified water systems with outputs of one to several hundred cubic meters of water per hour. Second, PEM cells can be operated at very high current densities, permitting the construction of compact units with high performance.

Furthermore, the cells generate only oxygen and ozone; there are no by-products which could accumulate in the water. Since ozone is produced directly out of pure or ultrapure water, it should not be considered as an “added substance” regarding the FDA guidelines. This also applies to O₂ which is produced by the destruction of ozone via ultraviolet radiation. This technology is thus suitable for the production of ozone in purified water systems. A further advantage is that the ozone is produced directly in the purified water, and this considerably simplifies the devices for the injection of the ozone.

Construction and Principle of Operation of a PEM Ozone Cell

The proton-conducting electrolyte membrane is in direct contact with porous electrodes on both sides. The porosity ensures that any gases generated at the electrodes can be removed and that the water can reach the electrodes. The voltage applied to the cell causes the water to become disassociated at the anode:

![Diagram](https://example.com/diagram.jpg)

Figure 3. The flow diagram shows a water treatment system, followed by a storage tank and a distribution system which are actively sanitized with the aid of a PEM ozone generator.
Ozonization

\[ \text{H}_2\text{O} \rightarrow \frac{1}{2} \text{O}_3 + 2 \text{e}^- + 2 \text{H}^+ \] or

\[ \text{H}_2\text{O} \rightarrow \frac{1}{3} \text{O}_3 + 2 \text{e}^- + 2 \text{H}^+ \]

The resulting electrons are removed through the electrode. The protons pass through the electrolyte membrane to the cathode, where they recombine with the electrons supplied through the electrode:

\[ 2\text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2 \]

The reactions which form ozone (with three atoms) and oxygen (with two atoms) are competitive reactions. Their relative contributions to the total amount of released oxygen depend on various operating parameters and on the structure and composition of the boundary between the electrodes and the electrolyte membrane. At an optimum operating temperature of about 30°C, about 15% of the oxygen formed at the anode is released as ozone, and about 85% as oxygen. This corresponds to a current-efficiency of 15%.

For operation of the cell at an optimum current density, the voltage across the cell must be about 3 to 4 V. With a current-efficiency of 15%, the specific energy requirement is 67 to 90 kWh per kilogram of ozone. This is much higher than the specific energy requirement of an ozone generator operating on the principle of a corona discharge. However, for the ozone quantities typically needed in purified water technology, which lie in the range of 0.3 to 12 g/h, this higher power consumption is more than compensated by the proven advantages of the PEM cell technology.

Ozone in Industrial Applications

The effectiveness of the PEM process in the reduction of microbial growth and in the protection against external contamination makes ozone the preferred disinfectant for purified water systems in pharmaceuticals and life sciences. A further advantage is that it not only kills the microorganisms, but removes the endotoxin products of the decomposition process. It can be used equally well for the continuous disinfection of distribution lines and for one-off disinfection processes such as those necessary after maintenance or repair work on the system. While concentrations of 15 to 20 ppb are generally sufficient for continuous disinfection, a concentration of 50 to 60 ppb is necessary for full sanitization which is proven by general experience of the authors. Ozone generators with outputs of 0.3 to 4 g/h are today available to meet a wide range of system capacities. The PEM cell is a fully automatic, compact module, and is generally installed in a bypass line in the water circulation system. The ozone generated by the process of electrolysis dissolves directly in the purified water flowing through this bypass - Figure 3.

Design of a PEM Ozone Module

In addition to its integration into the water system, the performance of a PEM module also depends on its design, its regulation, and its power supply. In all cases, the design of an electrolytic ozone generator must take the specific requirements of the pharmaceuticals and life sciences into account. Among other things, it must permit complete draining of the water, it must be free of gaps and dead volumes, and the parts of the cell housing in contact with the water and the gaskets must be made of suitable materials. The housing can be made of stainless steel or Polyvinylidene Fluoride (PVDF), both of which are highly resistant to the corrosive effects of high ozone concentrations and comply with the FDA regulations. Since ozone is a highly potent oxidant, the compatibility of materials used for water purification systems generally have to be examined carefully. The above mentioned materials have proven their resistivity in more than 500 applications designed and carried out by the authors. Moreover, they are used in steam sterilized plants or hot storage tanks as well which also are highly corrosive.

A compact design which permits easy access to all components and compliance with safety requirements, such as the insulation of the electric terminals, will simplify installation and maintenance.

Whether ozone has to be removed before using purified water in the pharmaceutical industry depends on the application area. In sensitive areas, it is mostly removed by UV radiation. In other areas, for example where the water is used for rinsing, the half life time of ozone can be used.

An electrolytic ozone generator has many operational advantages over conventional methods like silent discharge or UV radiation with a wave length of Lambda 185 nanometer because:

- it needs no high-voltage supply since it operates at only 4 VDC
- the ozone is produced directly from the water to be treated and no approved gas supply is needed
- there is no unwanted gas in the purified water
- the amount of ozone can be controlled easily

<table>
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<tr>
<th>Methods</th>
<th>Drawbacks</th>
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<td>Periodic disinfection with chemicals</td>
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<td>• Production has to be interrupted</td>
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<td>• Decomposition and flushing of remaining chemicals</td>
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<td>• Variations in the water quality</td>
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<td>Sterilization with steam</td>
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<td>• Production has to be interrupted</td>
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<td></td>
<td>• Sterile steam needed</td>
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<td>• Variations in the water quality</td>
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<td>Sterile filtration</td>
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<td>• Risk of breakthrough</td>
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<td>• Periodic sterilization and integrity tests necessary</td>
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<td>UV irradiation</td>
<td>• Effective only locally (in the beam)</td>
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<td></td>
<td>• No protection of the network</td>
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<td></td>
<td>• Sterile filter is necessary</td>
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<td>Hot storage</td>
<td>• High installation costs</td>
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<td></td>
<td>• High operating costs</td>
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<td>• Cooling at the point of use is generally necessary</td>
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Table B. Different sterilization and disinfection methods and related problems for the treatment of purified water.
with Faraday’s Law, the ozone production rate is directly proportional to the current flowing through the cell)
- external contamination is avoided
- it can be operated without additional safety measures (such as monitoring of the air in the room)

However, design details not only affect the FDA conformity and the reliable operation of the modules; they also are decisive for the ease of maintenance, and are thus an important cost factor. Microspherical anodes with a special surface coating ensure a long lifetime of the PEM module. Monitoring functions for such parameters as the flow of water, temperature, cell current and voltage, emergency power supply for the cell, and protection against short-circuits are integrated. There also is an option for external control with online measurement. Any faults which occur can thus be detected and rectified quickly, without the need for time-consuming fault-finding activities.

The power supply for a PEM cell must be very reliable, and at the same time, very efficient. Switched power supply units designed to meet the specific requirements are the best solution.

**Practical Use of Ozone - Experience at Infraserv Höchst in Frankfurt, Germany**

The industrial park Höchst, once the Frankfurt headquarters of Hoechst AG, is today occupied by more than 80 pharmaceutical, life-science, and chemical companies. It is operated by the company Infraserv Höchst, which provides the appropriate infrastructure for these companies. Since March 2000, this infrastructure includes the provision of purified water for production purposes for the 20 manufacturers of pharmaceutical products. After detailed studies, Infraserv decided, in agreement with its customers, to erect a new purified water distribution system behind the existing demineralization system for well water and drinking water. The purified water complies with the current requirements for Purified Water as laid down in the United States Pharmacopeia (USP) and European Pharmacopeia (EP).

**The Challenge: Distribution of Purified Water over a Distance of 14 km**

The central production of the purified water resulted in the technical challenge of distributing it throughout the industrial park, which has an area of four square kilometers. In order to maintain the quality of the water on its way to the consumers, microbial growth must be prevented in the entire system. This is no easy task since the distribution system for purified water is the largest of its kind in the world and has a total of 14 kilometers of sterile pipes. From the central water treatment system, the purified water is carried via a main loop to four separate storage tanks with capacities of 75 or 200 m³, which meet peak demands for water. Each of these tanks supplies five of the 20 companies via a sub-loop. The loops contain about 500 m³ of purified water at all times, even...
when there is no demand, and this water is circulated continuously to maintain the required microbiological quality. The actual consumption of purified water is about 250 m³/h. In addition, the storage tanks are equipped with special ozone injection devices and are designed for maximum hygiene. Thirteen sterile pumps provide the continuous circulation and the necessary turbulent flow in the system. Five redundant pairs of pumps ensure safe operation even if a pump fails. Most of the distribution system for purified water is mounted on pipe bridges or special pipeways.

**Continuous Ozonization with Electrolytic Cells**

In order to maintain the water quality during the storage and distribution process, the purified water is circulated continuously, and in addition, ozonized at various points in the distribution network. The electrolytic ozone generators used for this operate on the PEM principle described above. A prerequisite for ozonizing is that the conductivity of the purified water is less than 20 µS/cm. In the industrial park Höchst, the conductivity is normally less than 0.2 µS/cm. The electrolytic cells ozonize the purified water as it flows through them.

With a total of 34 electrolytic ozone cells, each with an output of 4 g, the system at the industrial park Höchst is the largest of its kind in the world. The permanent ozonization of the water is ensured by 15 ozone generation stations, each of which has several of the previously described electrolytic ozone cells connected in parallel. Some of the ozone generation stations are installed in containers at various locations throughout the park. Even when all connected consumers are drawing their maximum amount of purified water, the ozone concentration never drops below 20 ppb. If necessary, the entire system can be sanitized at an ozone concentration of up to 200 ppb without the need for additional equipment. The ozone is destroyed by ultraviolet radiators installed in the consumer companies. There are also 13 additional ozone generators installed locally in the consumer companies in order to protect the sub-loops.

The quality of the purified water is continuously monitored, in accordance with the requirements for a pharmaceutical water distribution system, by means of online and offline analysis. For example, the germ counts are tested once per month at 34 sample-extraction points, the samples being taken weekly. Since the installation of the system, there have been no problems.

**Control Technology Permits Online Monitoring**

The system is controlled by a central process controller consisting of two operating stations and five process stations. These are connected together by an industrial Ethernet which uses optical fibers as the connecting elements. The acceptance values of the consumers and the measured values with which the water quality is monitored online are used in the process control system to maintain the desired quality. The control system processes data from a total of 260 measuring points spread over an area of several square kilometers.

In the course of system operation, it became apparent that the capacity (500 m³/h) of the existing demineralization system, which is 40 years old is too large, since the actual consumption of purified water is only about 250 m³/h. A new treatment system is now being installed, sufficiently large to cope with peak demands, but not too large for the task. Due to the low Total Organic Carbon (TOC) content of the purified water, which means that only small amounts of ozone are needed, the full installed output of the ozone generators is not needed during normal operation: 20 to 30% of the installed output is sufficient to protect the system. Furthermore, the observed half-life time of the ozone is considerably longer than the expected value of 20 minutes.

**Summary**

Ozone is suitable for long-term protection of even very large systems for the storage and distribution of purified water. Due to its specific effects, which are described above, it makes hot storage and distribution of the water unnecessary. An intelligent process control system with low ozone concentrations ensures efficient protection against microbiological contamination; at the same time, the operating costs can be considerably reduced.

**References**

1. C.F. Schönbein, Poggendorf Annalen 50, 616 (1840).


Acknowledgement
Tables A and B and Figures 2-6 are courtesy of Christ Water Technology Group/Innovatec.

About the Authors
Samuel Stucki obtained his PhD in chemistry in 1973. He started his professional career as a researcher in electrochemical process technology at an industrial research center, where he carried out the fundamental investigations on electrochemical ozone production in the 1980s, which eventually led to the development of PEM ozone cells and their application in ultrapure water technology. He is currently head of a research department specializing in environmental technology at the Paul Scherrer Institut in Switzerland. Stucki has maintained his research interest in electrochemical ozone technology as a scientific consultant to Innovatec since 1995.

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Dirk Schulze studied mechanical engineering and business management. Since 1997, he is the Managing Director of the company Innovatec Geräetetechnik GmbH, located in Rheinbach. One of the main business sectors of the company is the development and production of ozone technology, and in particular, of components for the chemical and pharmaceutical industries, and of medical equipment. He has worked for the company since 1995 and has more than 13 years of experience in the sector of electrolytical ozone generation by means of PEM cells (about 500 units installed in the pharmaceutical industry throughout the world). He also has many years of experience concerning thermal methods as well as in the generation of ozone by corona discharge. As the result of his work in the development and design of ozone generation systems and in the applications of this technology, Schulze has in the last few years acted increasingly as a consultant in the design and configuration of ozone-protected systems for the cold storage and distribution of pure water.

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