Ozone Measurement Technology in Pure Water Systems

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Abstract

Ozonation is an effective technique for sanitizing ultrapure water and treatment systems and was introduced in the Semiconductor industry over 25 years ago[1]. With no permanent addition of material, unlike other chemical oxidants, its powerful oxidizing properties make ozonation an ideal treatment method. To assure adequate treatment levels as well as its removal downstream, measurements of dissolved ozone concentration are an essential part of the process.

Described here is a unique combination of dissolved ozone measurement technology and instrumentation that boosts the performance, reliability and maintainability of equipment for this specialized measurement. The theory of sensor operation as well as its benefits and limitations under various conditions are covered. Associated multi-parameter instrumentation enables the combination of ozone with other important measurements such as resistivity, conductivity, TOC, pH, flowrate and dissolved oxygen.

Introduction

Ozone, the unstable tri-atomic allotrope of ozone is a very strongly oxidizing gas that is injected into water to remove organics. Most importantly, ozone sanitizes the water, rapidly destroying any microbiological contamination and preventing associated particle generation[2]. It is an attractive alternative to energy-intensive heat sanitization. As shown in Table 1, dissolved ozone reverts back to harmless oxygen in a matter of minutes, depending on temperature, so it must be generated and measured right next to the process. Ozone leaves virtually no other breakdown products.

Temp (°C)	Half life (min)
15	30
20	20
25	15
30	12
35	8

Table 1 - Ozone Decay Rate

Ozonation is used to disinfect and sanitize ultrapure water as it passes through final filtering and distribution equipment. The goal is to control bacteria levels of the ultrapure water transported to the fab. Biological growth would generate organics and particles that would reduce product yields. Ozonation is typically applied prior to the UPW storage tank, in the distribution return piping, or directly into the storage vessel itself by diffusion[3]. Levels are maintained in the range of 5 to 60 ppb but are then eliminated using intense UV light. Ozone measurements are made to insure proper dosage control is maintained after injection and then to insure residual ozone is eliminated by the UV exposure. At this point any residual ozone becomes an unwanted contaminant. For these measurements, as shown in Figure 1, there are two points of measurement usually needed.

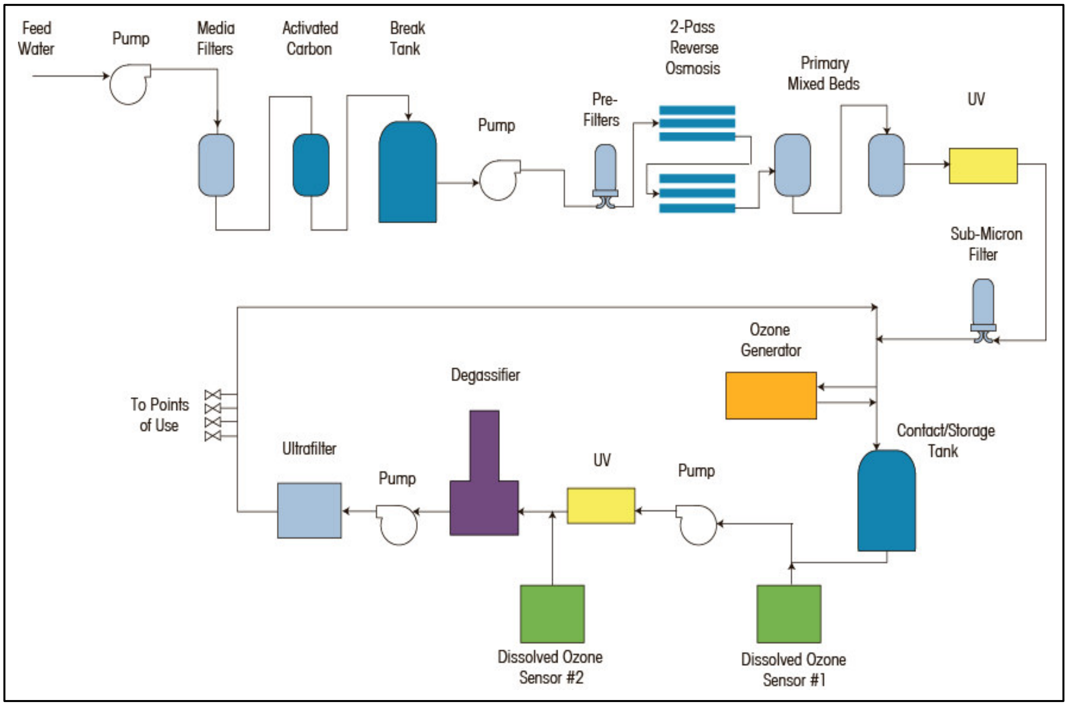

Figure 1 - Typical Ozone Measurement Points in a UPW Treatment System

Ozone Measurement

The above scenario for on-line monitoring and control has become standard practice where semiconductor UPW systems incorporate ozone treatment. Dissolved ozone instrumentation is available ranging from sophisticated high cost, maintenance-intensive equipment giving good performance to low cost, less reliable equipment with flow-sensitive readings. Described here is a recent development in ozone sensing technology that provides highly reliable measurements with infrequent, simple maintenance at reasonable cost. It is compatible with two multiparameter instrument platforms.

Ozone sensors are electrochemical devices very similar to dissolved oxygen sensors. They take advantage of the gas permeability of polymer membranes to separate the heart of the sensor from the sample. This separation enables a sensor to provide a controlled environment for the electrodes and electrolyte while allowing ozone to enter from the sample and react. It keeps the electrochemistry well contained. Figure 2 is a functional diagram of an ozone sensor.

The diffusion rate of ozone through a membrane is proportional to the partial pressure of ozone in the sample. Of course the membrane material and thickness also affect the diffusion rate, but they are fixed and those properties are normalized in calibration. The ozone which permeates the membrane reacts at the cathode, producing a current in direct proportion to the quantity of ozone. That current is the measurement signal which matches the ozone partial pressure and the concentration of ozone, at constant temperature.

To derive a concentration measurement from partial pressure with varying temperature, the signal must be temperature compensated. That is, the ozone concentration in water that a partial pressure represents, depends on temperature. The sensor’s RTD (resistance temperature detector) signal is used by the instrument microprocessor to temperature compensate the measurement. In addition, the instrument must compensate for the temperature-dependent diffusion rate of ozone through the membrane material.

Because ozone is so unstable, no calibration standards exist for this parameter. Ozone calibration is based on a colorimetric or other independent measurement and must be made very quickly before decay of ozone concentration in the sample can significantly affect the calibration.

Improved Ozone Sensor Design

Membrane ozone sensors have been around for many years but the design choices made in electrochemistry, membrane type, mechanics, and electronics can make a substantial difference in performance and maintenance requirements. Described here are these differences for an improved sensor design.

The electrochemical reactions occurring within this probe take place in many stages but the overall result is summarized in reactions 1 - 3 which occur when the sensor is energized with the appropriate polarization voltage.

Cathode

$$O_3 + H_2O + 2e^- \rightarrow 2OH^- + O_2 \qquad (1)$$

Anode

$$2Ag + 2Br^- \rightarrow 2AgBr + 2e^- \qquad (2)$$

Net

$$O_3 + H_2O + 2Ag + 2Br^- \rightarrow 2AgBr + 2OH^- + O_2 \qquad (3)$$

From this it can be seen that the electrical current flow is directly proportional to the ozone reduced at the cathode, giving a reliable linear signal. There is also consumption of bromide from the electrolyte as the anode is oxidized. However, with suitable design and operation in the ppb range, an extended operating life can be obtained. The maintenance interval for this type of sensor can be upwards of 6 months, depending on the concentration of ozone that is measured. The measuring instrument provides a carefully controlled polarizing potential. When the probe is not polarized, there is no consumption of the anode, giving it a long shelf life. A simplified cross-section diagram of the sensor is given in Figure 2. The actual sensor is a concentric design, with the insulator, anode and electrolyte built around the cathode in the center. The components and geometry are arranged such that a response time of 90% in 60 seconds is achieved.

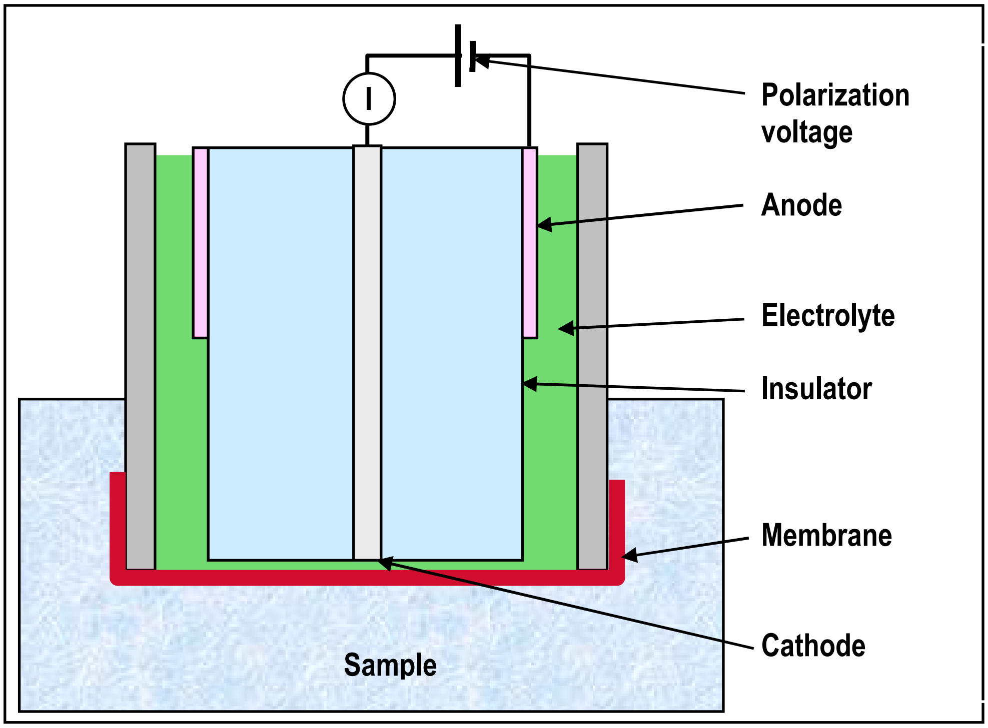

Figure 2 - Dissolved Ozone Sensor Components

The sensor is designed with modest ozone permeability which extends the sensor life and also reduces sensitivity to low flowrate. The ability to measure accurately at low sample flowrates is also enhanced by a flow housing design that directs the sample flow as a jet, directly at the membrane. This assures that the flow against the membrane is turbulent and will not be depleted of ozone. Operating with sample flowrates down to 100 mL/min, without compromising accuracy, can save a substantial amount of pure water on a continuous basis. For example, a probe requiring a 200 mL/min sample flowrate would consume nearly 53,000 liters (14,000 gallons) of water more per year than one that can operate at 100 mL/min.

When these improvements are all incorporated into a sensor design, the result is a long-lived assembly where membrane and electrolyte require only infrequent service. Service consists only of dropping in a low-cost pre-mounted membrane cartridge and replacing the electrolyte. No electrode polishing or other internal maintenance are required. Figure 3, left view, illustrates the simple three-piece probe design consisting of upper probe body, membrane body and cap sleeve.

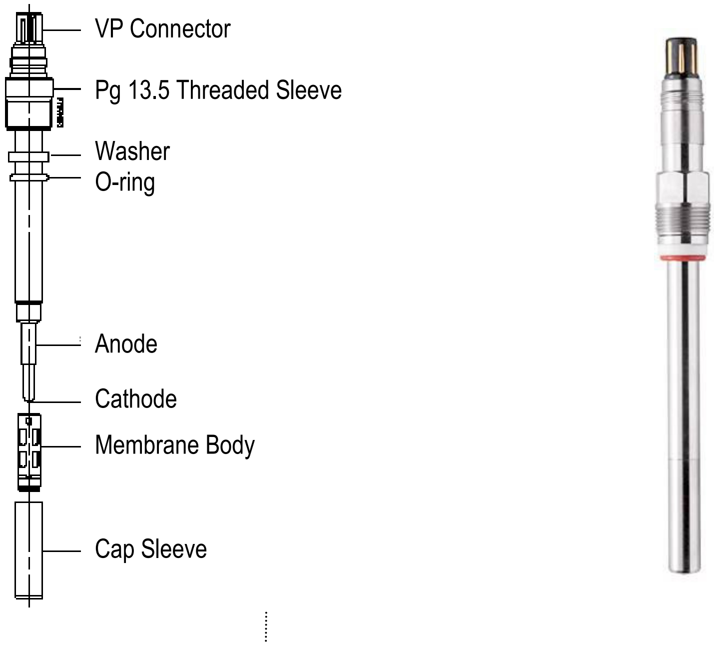

Figure 3 – Polarographic Dissolved Oxygen Sensor

Instrumentation

The measuring system was developed as collaboration between Metter-Toledo Ingold in Urdorf, Switzerland and Mettler-Toledo Thornton in Massachusetts. The probe is based on a robust steam sterilizable biotech DO (dissolved oxygen) sensor design but using different membrane, electrolyte and polarization voltage. The DO design has been proven under extreme process conditions for many years. The instrumentation complements the sensor design with extremely stable amplification, accurate temperature compensation, plus digital and multiple analog outputs.

The multi-parameter instrumentation can combine ozone measurements with additional parameters of conductivity, resistivity, pH, ORP, DO, flowrate, pressure and/or level in the same instrument. This can be especially convenient when the combination of measurements fills out the needs of a particular water treatment unit operation. Combined measurements are also very helpful in maximizing the number of measurements in a given panel space and in reducing instrumentation costs.

Operating Experience

As noted previously, there is extensive successful experience with the measuring technology and basic probe design. To confirm this in operation with the ozone version and multiparameter instrumentation, a comparison was run against an existing reference instrument at a southwestern U.S. semiconductor fab among other sites. The results of operation with data taken at five minute intervals are illustrated in Figure 4. A span difference in calibration was intentionally retained to prevent the data from falling on top of each other and not being visible in a plot. The responses tracked each other quite closely.

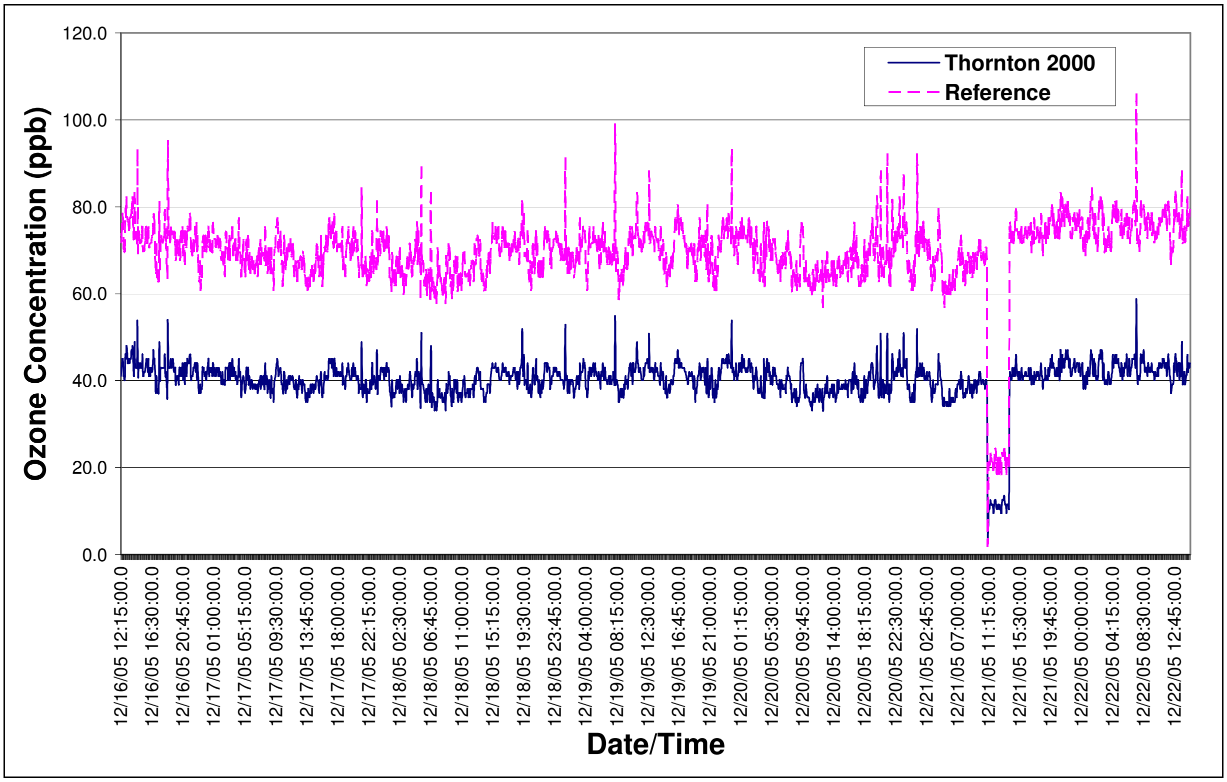

Figure 4 - Ozone Sensor Response Evaluation

Summary

The improvements in ozone measurement described here should go a long way toward reducing maintenance and operating costs for this type of instrumentation. The accompanying increased reliability of the measurement will also engender more confidence among operating personnel in reacting to water treatment system upsets and should improve their responsiveness in correcting them.

Bios

David Gray has over 30 years experience in the design and application of process analytical and control instrumentation. He has authored numerous articles and contributed to books on the measurement and control of conductivity/resistivity, pH, ORP, specific ion, and dissolved oxygen. He holds a B.S. degree in Chemical Engineering from Case Western Reserve University, is a senior member of ISA (Instrument Society of America) and a Task Group Chairman on the ASTM (American Society for Testing and Materials) D19 Water Committee.

Marc St. Germain has over 10 years experience in the design and application of both purification equipment and online instrumentation used for the production of high purity water. He has been a co-author and contributor to technical papers and articles on subjects relating to analytical measurement and online instrumentation used in the microelectronics industry as well as other high purity water markets. He holds a B.S. degree in Mechanical Engineering from Southeastern Massachusetts University and is a SEMI (Semiconductor Equipment and Materials International) member.

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