

Mastering the Fundamentals of Ozone: **monitoring & control**

In the March 2008 issue of Water Quality Products, the IOA column initiated a discussion on mastering the fundamentals of ozone: feed gas preparation, ozone generation, mass transfer, and monitoring and control. This month, we begin our discussion of the fourth basic element: ozone system monitoring and control.

For the purpose of this discussion, we will focus on ozone systems in which the ozone gas is dissolved into water and applied to the target application. This article will not cover gaseous ozone systems and applications.

Useful Power

Power without control is useless. At best, it is wasteful and inefficient to apply power without control; at worst, it can be dangerous. Evidence for this can

be found in many situations in everyday life. A car with a powerful engine, for example, must have monitoring (speedometer, gauges) and control systems (brakes, transmission, drive train, steering and suspension) to allow the driver to safely harness and direct the power of the engine. An overpowered and under-controlled car can be very dangerous.

The substantial oxidizing and disinfecting power of ozone must similarly be carefully monitored and controlled to ensure that the production of ozone matches the requirements of the application.

Inadequate ozone production may yield inadequate oxidation and disinfection. Too much ozone may damage the product or process equipment. Equally as important as ozone residual to achieving treatment goals is ambient (airborne) ozone levels in the workplace. Ambient ozone should also be monitored to limit worker exposure and automatically shut-down the system if necessary.

Monitoring

The first step in harnessing the power of ozone is accurate and reliable monitoring of ozone potential or concentration as well as airborne ambient ozone. Several technologies and methods are available for monitoring ozone ranging from simple colorimetric titra-

tion kits or paper test strips to electronic flow cell systems that continuously sample, measure and report dissolved ozone levels indirectly as oxidation-reduction potential (ORP) or directly as ozone concentration in real-time.

Colorimetric test kits provide a simple and economical means of spot-checking ozone concentration or ORP; however, these methods do not provide real-time information that can be automatically logged and applied to a control system.

Oxidation-Reduction Potential

ORP is the activity or strength of oxidizers and reducers in relation to their concentration in a solution. Oxidation-reduction potential is measured as the voltage potential at which oxidation/reduction occurs at the electrodes of an electrochemical cell. This voltage potential, typically expressed in millivolts (mV), is measured by a sensor with a platinum or gold surface that accumulates charge without reacting chemically. A voltage is generated, which is compared to a reference electrode similar to a pH probe. The more oxidizer available, the greater the voltage difference between the solutions. The measurement of ORP is similar to pH measurement in that both methods determine relative activity and are not direct measures of concentration.

ORP provides a relatively rapid and single-value assessment of water disinfection potential. It also provides robust performance in turbid or salt water; however, in complex and turbid solutions, ORP values can read far below expected values. One disadvantage of ORP is that it cannot be used as a direct indicator of dissolved ozone due to the

A closer look at the fourth basic element of ozone

ozone probes



effect of pH and temperature on the reading. In addition, the response time of ORP probes can be reduced in weak solutions or if the probe is saturated by over-injection of ozone.

Amperometric Ozone Measurement

Ozone concentration can be directly measured by ozone analyzer systems that utilize a flow cell with a membrane-covered amperometric sensor. The sensor is comprised of a gas-permeable membrane stretched over a gold cathode and a silver anode with an electrolyte solution.

Ozone diffuses from the sample through the membrane and reacts with the electrolyte solution to form an intermediate compound. The intermediate is reduced by a polarizing voltage, which produces a current between the cathode and the anode. The current is proportional to the concentration of ozone in the sample, and the result is detected and reported by the electronic analyzer.

Ozone analyzers provide fast, sensitive, accurate and precise monitoring of direct residual ozone concentration—especially in clean water applications. Ozone analyzer systems are robust and reliable. Many systems automatically compensate for changes in membrane permeability that occur with changes in temperature. Both ORP and amperometric analyzers require periodic calibration per the manufacturers instructions.

Ambient Ozone Detection

In addition to monitoring the dissolved ozone concentration in the process, airborne ambient ozone in the workplace should be monitored as well to ensure worker safety. Handheld and personal wearable ozone monitors and accumulated exposure badges are convenient and useful for spot-checking, monitoring and documenting employee exposure to ozone gas.

Ideally, each ozone application should include one or more fixed ambient ozone sensors that are hardwired to the control system. This configuration enables the system to be interlocked to alarm at the

OSHA long-term exposure limits and shutdown the ozone generator when the short-term exposure limit is reached.

Ozone Sensor Placement

Placement of dissolved and ambient ozone sensors must be carefully considered in the overall system design. Ideally, dissolved ozone sensors should be positioned as close to the point of application of ozone as possible to detect and compensate for potential decay in ozone in the course of mass transfer and distribution to the application point. Additional ambient ozone detectors should be positioned at the site of generation as well as at all points of likely release of ozone from solution (e.g., at the location of spray bars, filling equipment and open vats or flumes).

Other Parameters

Several other control parameters should be considered for monitoring and input into the control architecture:

- **Water flow rates.** Changes in water flow rates in the process can directly impact ozone concentration by effectively decreasing or increasing the effective ozone concentration.
- **Water temperature.** The decomposition of dissolved ozone varies with water temperature. The half-life of dissolved ozone at room temperature (21°C) is approximately 30 minutes, but at 37°C it is reduced to 5 minutes.
- **pH.** Dissolved ozone is most stable at neutral to acidic pH. The decomposition of dissolved ozone accelerates at basic pH levels, especially above pH 9.
- **Oxygen concentrator performance.** Poor feed gas quality can contaminate the oxygen concentrator and reduce its output. Reduced oxygen flow through the ozone reactor cell ultimately reduces ozone output and dissolved ozone concentration.
- **Feed gas flow rate.** Longer residence time of oxygen in the

ozone reactor cell increases concentration of the ozone gas output from the ozone generator.

- **Feed gas backpressure.** Increasing the feed gas pressure increases the residence time of oxygen in the ozone reactor cell and the concentration of ozone gas output.
- **Venturi vacuum.** The venturi vacuum is a product of the pressure differential across the injector system and must be matched to the output of ozone gas from the ozone generator. Too little vacuum may cause the formation of large entrained bubbles and reduce ozone mass transfer and dissolved ozone concentration. Too little vacuum can reduce residence time in the ozone reactor cell and ultimately affect the dissolved ozone concentration.
- **Ozone generator temperature.** The stability of gaseous ozone also varies with temperature. Excessive heat in the ozone reactor cell will decrease the concentration of ozone gas in the ozone generator output stream.
- **Ambient and cooling temperature.** The air temperature of the operational environment for air-cooled and cooling water for water-cooled ozone generators can impact the ozone generator internal temperature, which will impact ozone production rate and concentration and can effect consistent dissolved ozone concentration.

Accurate and reliable monitoring of dissolved and ambient ozone is critical to controlling the application of ozone in a process. Monitoring additional parameters can increase our understanding of factors that can ultimately affect the concentration of dissolved ozone in the process; however, monitoring ozone is only one half of the equation.

Next month, we will address the control of ozone systems in the final installment of this series. *wqp*