By Paul Overbeck

Ozone: More Is Not Always Better

Process Optimization and Control

Ozone is employed as the final treatment step in virtually every bottled water plant in North America and most non-mineral labeled bottled waters produced worldwide. The primary purpose for ozone treatment is oxidation and disinfection to assure an aesthetically superior, biologically safe and shelf stable product preferred by many consumers.

In short, a consumer would say, "it tastes better," and as the majority of human taste is governed by our olfactory sense, it goes without saying that "bottled water smells better too."

Many bottled water producers followed the adage, "if a little ozone is good then a lot is better" until recent U.S. EPA Stage 1 and 2 Disinfectants and Disinfection Byproducts Rule (D/DBP) regulation, which is followed by U.S. FDA, put many bottlers in fear of exceeding DBP standards for Bromate. Additionally, IBWA technical research showed that excessively high residual ozone could oxidize plastics used for bottles and closures, imparting off-tastes to the product water and compromising packaging.

Bromate formation chemistry and control strategies have received significant attention in the municipal drinking water treatment and bottled water industries. The International Ozone Association (IOA) has published about 60 papers on the subject at IOA conferences over the past five years.

Extensive pilot research and full-scale municipal treatment plant practices have shown that ozone-driven Bromate formation from Bromide ion present in the raw waters can be controlled by chemical intervention options and/or process optimization and control. Chemical interventions include pH adjustment, pre-oxidation with chlorine and/or complexing with ammonia. None of these are recommended for use with natural spring or mineral bottled waters; however, pH control is a good option for use with purified waters. Ozonation process optimization and control appears to be the most practical approach for the bottled water industry as adding chemicals can compromise the consumers' perception of product purity.

Optimization - Step One

The first step in process optimization is identification of the target organisms. Today, most water bottlers have followed IBWA recommendations to employ 1μ (micron) absolute filtration in the bottling line for the removal of parasitic cysts such as *Giardia* and *Cryptosporidium*, thereby reducing the load for ozone disinfection. Processes using reverse osmosis, ultrafiltration and nanofiltration also physically remove these parasites.

This leaves bacteria and viruses as targets for ozone inactivation.

Inactivation effectiveness of oxidizing biocides is a temperature-dependent function of residual concentration (mg/L) multiplied by the hydraulic retention time (minutes) as identified by EPA Concentration-Time (Ct) tables.

Table 1 presents EPA Ct values for virus inactivation at various temperatures, while Table 2 presents Ct Values for Inactivation of Bacteria by Ozone.

Municipal potable water providers are required to provide a minimum 4-log virus reduction and most bacteria species are easier to inactivate than viruses.

Table 1: Ct Values for Inactivation of Viruses by Ozone

	Temperature °C					
Inactivation	<1	5	10	15	20	25
2-log	0.9	0.6	0.5	0.3	0.25	0.15
3-log	1.4	0.9	0.8	0.5	0.4	0.25
4-log	1.8	1.2	1.0	0.6	0.5	0.3

Table 2: Ct Values for Inactivation of Bacteria by Ozone

E. coli	0.02 – 0.06 mg-min/L CT (2-log) AWWA
Streptococcus faecalis	0.01 – 0.025 mg-min/L CT (2-log) AWWA
Legionella pneumophila	0.3 – 1.1 mg-min/L CT (2-log) AWWA
Total Coliform	0.19 mg-min/L CT (6-log) LAAFP
HPC	0.19 mg-min/L CT (3-log) LAAFP*

* LA Aqueduct Filtration Plant.

Table 1 shows that a 4-log virus inactivation occurs at a Ct of 0.6 mg/L-min (0.3 mg/L DO_3 for two minutes) at 15° C. Yet many bottlers persist in maintaining ozone residuals ranging from 0.2 to 0.4 mg/L in tanks sized to provide a 6–12 minute hydraulic detention time.

While this Ct overkill provides ample disinfection of the bottle and its closure, these excessive (and unnecessary) ozone residuals at extended contact times promote the formation of Bromate in bromide containing waters.

Optimization - Step Two

Ozonation of water is typically carried out by dispersing ozone into water most typically by directing the gas into diffusers, static mixers or venturi injectors. Contact between the two phases is accomplished inside an ozone contactor, which can be circular towers (tanks), multi-compartment rectangular basins or pressurized pipelines, which are designed to allow gas to liquid mixing under specific hydrodynamic conditions.

Performance of ozone contactor hydrodynamics is strongly dependent on the configuration and the system operating conditions.

Historically, the bottled water industry has employed water flow moving counter current to fine bubble diffusers (FBD) gas flow in a single vessels ranging from 12 to 20 ft. height. In this design, the taller the vessel water column, the better the mass transfer due to hydrostatic pressure on the bubble rising from the FBD. The hydraulic volume in most vessels is equivalent to 6 to 12 minutes of the filler flow rate, though some have even greater capacity.

Figure 1: Municipal Multi-Chamber Ozone Contactor

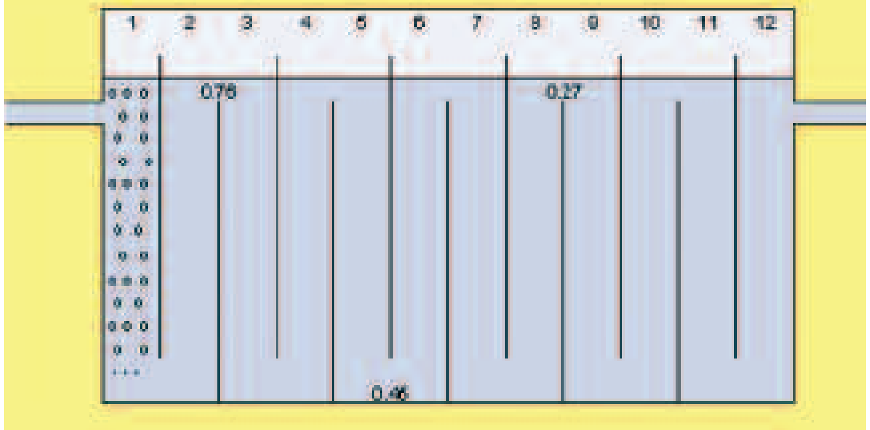


Figure 2: Injector-Nozzle Tank Recirculation

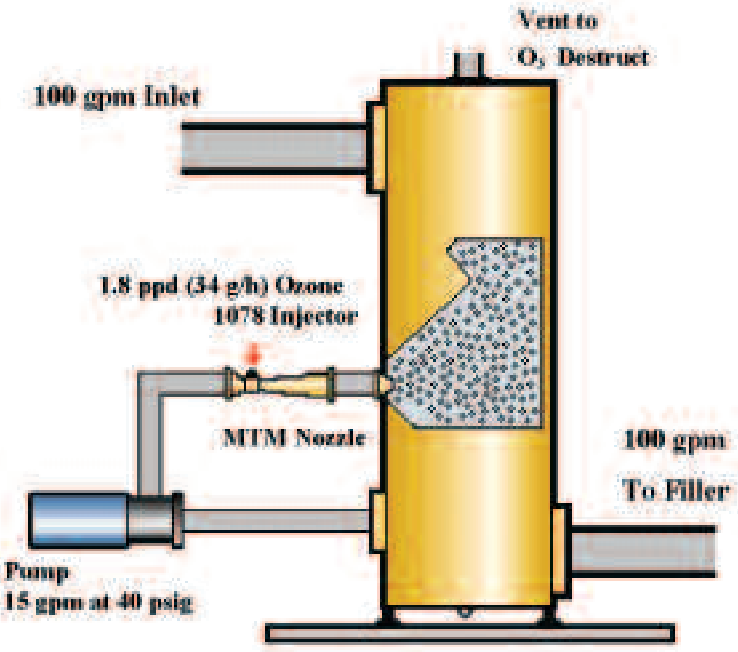
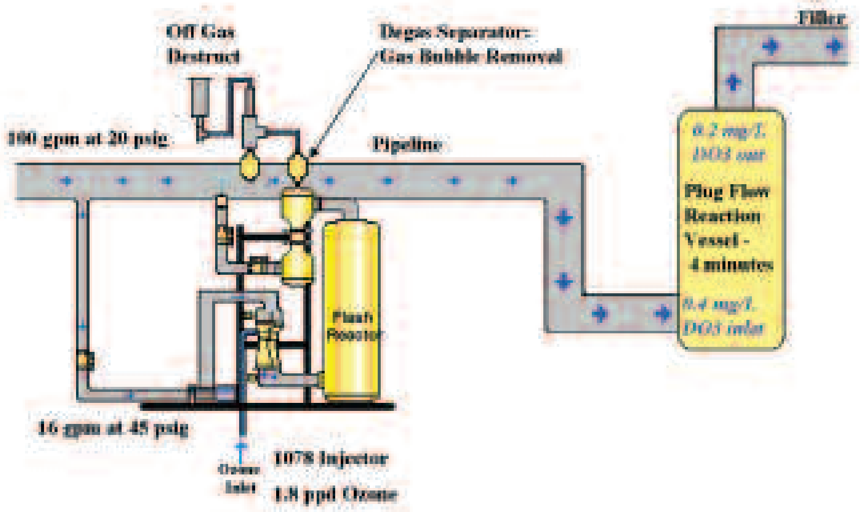


Figure 3: Side Stream Injection-Degassing with Plug Flow Retention



The hydraulic volume calculated (vessel diameter X water height) often is used incorrectly to determine the time component of the Ct disinfection calculation. For example, a hydraulic tank volume of 793 gal. (or 36 in. X 15 ft.) would appear to provide 7.9 minutes contact time at 100-gpm tank flow. However, this could only be the case if only a single-phase flow (liquid) was moving uniformly through the vessel.

The fluid dynamic profile caused by two-phase flow (water and gas) mixing promotes unstable flow patterns, resulting in both short-circuiting and extended retention. This phenomenon can be characterized by the vessel's Residence Time Distribution (RTD), a measurement of the many currents, that travel across the tank at different time intervals. Consequently, in most FBD designs a portion of the bottling flow may move through the vessel in less than 2 minutes, while other portions continuously mix, trapped in currents that result in hydraulic retention times exceeding those predicted by tank volume and water flow rates.

A vessel's RTD can vary with factors and processes that alter the contactor hydrodynamics including changes in contactor configuration, water or gas flow rates and water quality parameters. Short-circuiting and extended retention influence both organism inactivation and byproduct formation. Considered in total, the two-phase mixing in the detention vessel means one volume of water moving through the contactor is exposed to less ozone for some period of time resulting in a lower Ct, while another volume is exposed to more ozone over time for a greater Ct resulting in greater Bromate formation.

Municipal FBD systems are designed to conform to EPA Ct tables by using multi-chamber baffled basins (Figure 1) and, recognizing the uncertainty of two-phase flow, receive Ct credits only in chambers where ozone gas is not introduced (stages 2–12).

One recent design improvement for single flow through tall tower contactors to support development of a more uniform ozone residual is the use of a recirculating injector-nozzle system for gas to liquid mixing (Figure 2). In this design, a portion of the water at the bottom of the tank is pumped through an injector for introduction of ozone gas with the resulting two-phase flow mixing in the contactor via a high shear velocity nozzle to approximate a completely

stirred reactor.

While this design minimizes short-circuiting to provide a more uniform residual to the filler, a portion of the water is continuously re-ozonated. Logically, re-ozonation in this design will lead to higher Bromate formation in the re-ozonated stream (15 percent of total flow in Figure 2). This increase is offset by the improved RTD characteristics of the contactor in total. The improved RTD characteristics allow operators to reduce the water level in the vessel to limit residence time without impacting ozone mass transfer, disinfection and DBP goals.

An added plus is the stabilizing influence the fixed side stream water volume has on the rapid ozone equilibrium attainment in the vessels variable water flow and ozone dose operating conditions.

Another new process option providing the greatest control of ozone residual and efficient RTD is the side stream injection-degassing with plug flow retention system in Figure 3.

This pressurized process rapidly dissolves ozone in a small side stream and removes entrained gas bubbles before mixing (via nozzles) the high dissolved ozone side stream into the main flow prior to vessel retention. In this process, the uniform ozone residual produced in the pipeline passes under nearly "plug flow" conditions through the retention vessel as single-phase flow because the bubbles have been removed.

The bottler can now employ a smaller retention vessel, sized for the time needed to achieve the desired Ct value–say, 4 minutes–at the design fill rate and desired ozone residual for disinfection while minimizing Bromate formation.

Optimization - Step Three

With an improved RTD contactor, operators can focus on the control of ozone residual. Lower ozone overall Ct developed in the bottling process (contractor, piping and bottle) will form less Bromate in the finished water.

Injector-nozzle systems have not only shown more rapid and stable dissolved ozone residual attainment, but also the pressurized rapid mixing drives superior mass transfer performance. Together, this allows water treatment plants greater flexibility with control options including PID control loops to tightly control ozone dose and resulting O_3 residual, thereby minimizing Bromate formation.

A well calibrated dissolved ozone sensor and monitor installed on the outlet of the retention vessel can measure ozone residual and signal the ozone generator to increase or decrease ozone production. New ozone generators offer very linear output that enhances response time and Ct control.

Final Words

As a result, we can conclude that

- Bromate formation can be controlled by process optimization and control;
- Refinement of the ozone contactor reducing short-circuiting and overdosing can achieve desired Ct for target organism inactivation and Bromate reduction goals;
- Dissolved ozone instrumentation can automate process control; and
- Lower ozone overall Ct developed in the bottling process (contactor, piping and bottle) will form less Bromate in the finished water. WQP

About the Author

Paul Overbeck is the chairman of the International Ozone Association, Pan American Group. Paul received a Chemistry degree from the University of Minnesota, has about 30 years of water and wastewater treatment experience and has been involved in the ozone industry and ozone applications since 1982. Paul is also president of GDT Corp., a company specializing in high efficiency gas to liquid mass transfer. Prior to founding GDT, Paul was Chief Operating Officer for Osmonics Inc. - Phoenix Operations, now part of General Electric. He can be reached by E-mail at overbeck@gdt-h2o.com.

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