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Organic wines that do not contain sulfites have established a niche market of their own-one which especially appeals to consumers who have asthmatic or allergic reactions to sulfites.



By Marne Coggan

THIS IS the second of a two-part series on ozone sanitation in wineries. In the Jan-Feb 2003 issue, the first article explained the properties of ozone, described how it is generated, and outlined winery safety and training issues. With that theory and background covered, we now can begin our exploration of winery uses for ozone, starting with a detailed look at barrel sanitation. From there, we'll examine other common applications like surface sanitation, clean-in-place (CIP) treatments for pipes, tanks and fill lines, and water treatment. We'll also look at newer uses including mold control in caves and cork storage rooms, building-wide ozone systems, and vineyard mildew and insect control.

Barrel Sanitation

David Mahaffey of Carlsen & Associates describes barrel sanitation as the killer application for ozone. Says Mahaffey, "It's because there aren't any good alternatives-nothing but ozone can sanitize barrels without tainting the wood, as chlorine chemicals will, or without extracting something out of the wood. Proxycarb will kill microbes in wood, but it is a soda ash-based product, and it strips out oak essence. That's what we winemakers spend all of the money on oak barrels to get.

"The best system for cleaning and sanitizing barrels is a two part process. The first part uses hot water at high pressure to dissolve tartrates and blast the barrel clean. The hot water also opens up the wood pores. Then the second stage is a cool rinse with ozonated water, which sanitizes and shrinks the pores in the oak. While larger wineries automate this process with barrel washing machines, smaller wineries do everything manually: Barrels are cleaned with hot water using a pressure washer, then a flashlight is used to illuminate the barrel to confirm that it is clean. After this, the cleaned barrel is rinsed with ozonated water from a hose connected to the ozone generator.

"We use ozone for barrel maintenance and keeping them neutral," says Felipe Martinez, Barrel Room Foreman at Kendall-Jackson's Oakville facility. "When a barrel is emptied, it gets rinsed on the floor, then it comes to our barrel washing machine. We do a minute and a half of hot water and three minutes with ozone. The ozone comes in with cold water, so besides sanitizing it cools down the barrels. It's working really good.

"Three factors-the type and age of the barrel, its microbial health, and the concentration of ozone in the treatment water-affect how long your ozone treatments should last. Higher concentrations of ozone in the treatment water will destroy a given level of microbes faster. And the larger quantities of microbes in problem barrels require longer treatments than the smaller quantities in healthy barrels. Says John McClain of McClain Ozone, "You just don't throw SO₂ at your barrels. You just don't throw ozone at them either. Determining barrel rinse times is based primarily on the concentration of ozone in the water, and the age and the degree of contamination of the barrel. The more ozone you can get into saturation in the water, the faster your



Damian Parker in a tank room at Joseph Phelps Vineyards.

rinse time. For example, at 10ppm, the rinse time for healthy barrel son a 4-head barrel washer is 30seconds. At 5ppm it would be one minute."

Mahaffey goes further. "In general, if a barrel is deemed healthy and the wines that come out of it are untainted, a treatment time of one and a half minutes is sufficient to sanitize the barrel. This is with the typical 2.0-2.5ppm concentrations produced by ozone machines in most cellars. Treatment times are longer if there is a perceived problem with a barrel. For example, if a barrel has a small elevation in the level of 4-ethyl phenol (4EP), the indicator for Brettanomyces, then the wash time can be extended to 4-5 minutes. The same 4-5 minute treatment would be appropriate for a barrel with any other problem-Acetobacter, Lactoba-cillus, Pedicoccus, anything where the wine has shown some problems."

Continues Mahaffey, "If you have a significantly damaged barrel with very high 4EP levels, a barrel which you'd consider retiring but would like to save because it's still young, give it a 4-5 minute treatment on three successive days. I've also used these extended ozone treatments to bring tainted oak uprights and ovals back to health. Of course, not every barrel on death's door can be fixed-ozone is not a panacea or a silver bullet. But it's probably worth trying the three-successive-day treatment regime on any problematic barrel-you can always retire it afterwards if it is still unhealthy."

Thomas Chrisco, Production Manager at Kendall-Jackson's Oakville winery, echoes this. "With our problem barrels, we wash them good, leave them alone, wash them again, leave them alone. And we do this for three or four days. Our experience has been that this seems to work. Now, does it get rid of all of the Brett? No-you'll never do that. What we're doing is controlling the population-that's the goal."

Jon Johnson of Carlsen & Associates adds, "I don't tell people what to do-wineries need to establish their own SOPs. But I do tell them what other folks are doing, and I help and encourage them to do their own testing. You see, barrel treatment times can vary quite widely. The density of the wood, age of the barrel, and the amount of microbial presence is what determines how long is long enough. So experiment! The chemistry is out there to check for microbial levels, Brett, VA, etc. by swabbing and plating. See what you consider to be effective results for your own types of barrels with their unique microbial situation."

Mahaffey agrees. "Could higher ozone concentrations reduce the treatment time while still fully sanitizing the barrel? Possibly. But the only way to know for sure is to test."

How Effective Is Ozone in Barrels?

It's important to note that barrel sanitation with ozone is not barrel sterilization. Barrels have no discrete surface, more like a 4-5mm sponge, often with blisters. That amount of porosity provides far too many hidden nooks and crannies for ozone in any concentration or duration of treatment to completely eradicate all microbes. So ozone treatment of barrels is de-signed not to eliminate microbes, but to control them. This concept of microbial control is especially important when ozone is used to treat problem barrels, those with high populations of microbes which produce off-flavors or cause wine spoilage.

Says Matt Lowe of DEL Ozone, "Wineries haven't required a huge amount of data to adopt ozone. Their acceptance has been based on colleagues' opinions that Brett is being controlled when it wasn't before. Winemaking is an art that requires real living organ-isms, so winemakers don't really want truly sterile barrels. They're looking for some level of control. And they're get-ting it."

Until very recently, there has been no scientific research on the effects of ozonated water on barrel microflora or on oak flavors. But

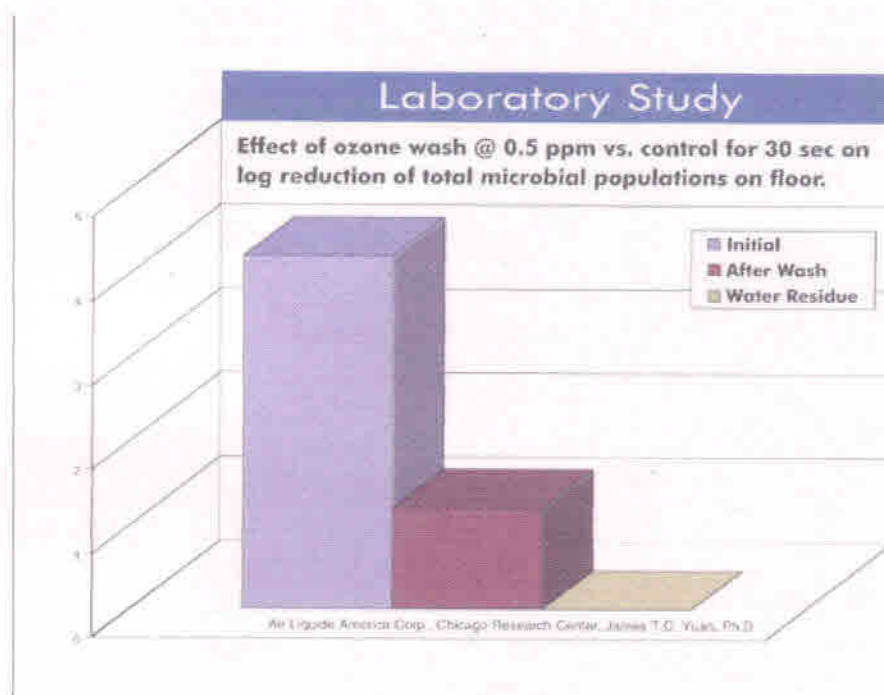
there is plenty of in-formal sensory evidence that winery ozone treatment does

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maintain and correct barrel health without degradation or loss of flavors from the oak. Recalls McClain, "When I first went to wineries advocating ozone, I was practically thrown out the door. That led to a whole lot of proving that ozone worked in barrels, and doing blind tasting of barrels to see that there was no impact. Now winemakers are believers."

Damian Parker, VP of Production at Joseph Phelps Vineyards, agrees. "Whenever we empty a barrel, we clean it on our Tom Beard machines, first with a hot-water wash of varying length, and then with a 1-minute ozone rinse. We do this every time, and we have close to 8,000 barrels. So I just laugh when I hear people say that ozone degrades the oak. I sure haven't seen it. But we only keep our barrels for five years. Maybe that's part of it."

Mahaffey concurs. "One of the first questions we had to answer was 'Is ozone going to adversely affect barrels?'. We did those duo- and trio-tastings, and with experienced tasters we could not ascertain any difference in ozone treated barrels, even with extended treatment."



The effectiveness of ozone in the surface sanitation at a concentration of 0.5ppm. Taken from laboratory analysis of the DEL Ozone AGW-0500 by Air Liquide America Corporation. (Graphic courtesy of DEL Ozone.)

And now, laboratory science has begun to verify that ozone sanitation does indeed destroy spoilage microbes in oak while not affecting the desirable flavors imparted to wine. Last fall, two graduate researchers working under Dr. Erin Dormedy at California State University Fresno released their preliminary findings in studies of ozone treatments of oak. (Caveat: These two laboratory studies had not been formally peer-reviewed at press time, and both have yet to test ozone treatments in actual barrels.) Using French oak blocks supplied by Inner stave and an ozone generator from Piper Environmental Group, researcher Steve Marko simulated two-minute barrel treatments with 1, 5 and 10ppm ozone in water. He found that the ozone had no statistically significant effect on the oak's volatile aroma compounds, including vanilla, smoky, and toasty oak notes. (Marko's sensitive equipment did find tiny changes, including some increases, in the concentration of oak aroma compounds in the ozonated blocks, but these were likely due to the variability of the oak itself.) Meanwhile, researcher Nicolas Cantacuzene used a generator donated by DEL Ozone to treat 1cm oak blocks infected with *Brettanomyces*. With ozone gas treatments, the Brett organisms were destroyed on the surface and inside the blocks. Tests on ozonated water treatments had not been completed at press time.

But Tom Beard, whose automated barrel cleaning and sanitizing machines allow wineries to use ozonated water in the cold rinse step, is cautious. Says Beard, "We

have rigged all of our elastomers and what not to stand up to the use of ozone. If our customers choose to use ozone, that's great; everybody I have spoken to who is using ozone with our barrel cleaning equipment is comfortable with it. But when wineries pay \$300-700 for oak barrels, they're buying oak essence. If ozone reduces the lifespan of the barrel by negating, reducing or altering the oak essence, then you're not doing anybody any favors. The barrel may be clean, but if you diminish what the barrel contributes to the wine, that's a problem. Studies of ozone on oak are ongoing, but long-term results aren't in yet. Until they are, we'll be ozone compatible and won't denigrate its use. But we won't advocate it either."

Surface Sanitation

Many wineries sanitize surfaces with ozonated water. It can be sprayed directly on floors, drains, walls, destemmer-crushers, tanks (inside and outside), fruit bins and any other wet-table, non-rubber, non-fiberglass equipment or surface in a winery. Typically, the equipment is first cleaned, then ozonated water is used as a final sanitizing rinse. This very effectively reduces microbial loads on the surfaces. (See chart above.)

With repeated use, surface applications of ozonated water will remove biofilms. These are tough, resilient layers of microbes which adhere tenaciously to surfaces. Biofilms can be invisible or they can create a foggy haze on tank walls and cellar floors. First-time users of ozone sometimes measure post-treatment surface bacteria counts higher than pre-treatment counts. This is due to the destruction of the upper part of the biofilm by the initial ozone treatment, exposing the microbes below. Subsequent treatments quickly destroy those microbes, leaving the surface microbiologically sanitized as well as clean to sight and touch.

Phelps' Damian Parker is a fan of ozonated water for surface sanitation. "Ozone is not a panacea. It's not a cure-all. But if you use it, and you continually use it, your place will get cleaner and cleaner and cleaner. I don't just spray ozone once and the cellar is spotless. It doesn't work that way. Its effect is incremental but cumulative."

Continues Parker, "During harvest, using caustic cleaners is just a pain in the ass. So when the shoveling is done and the grunge has all been removed, we get inside the tank and do a simple hand-scrub with a telescopic pole and a white scrubby, but no cleaning solution at all. Then we rinse the tank out and put the ozone rinser in it for 5-10 minutes. You can tell by the off-gassing when the tank is clean. Ten minutes is more than enough. Also, our older barrel room had a mold problem in 1996-black specs on all of the walls. We took a power sprayer and cleaned the ceiling and walls, then went back and ozoned everything. That room has stayed clean ever since; we just knocked the population down to nothing."

But off-gassing issues and the susceptibility of common cellar components to degradation by ozone often makes ozone surface sanitation problematic. Lowe observes, "For some surface sanitation needs in wineries, ozone can replace current sanitizers. For others, ozone provides an additional point of intervention. However, if you spray ozonated water for 30-60 minutes in an enclosed space—a small room, a cave, a tank—it's unavoidable that some



Joe Mendez of Piper Environmental Group discusses tank sanitation with Brian Lenhart and Lynne Ryno, Oak Cellar Managers at Beringer's St. Helena facility.

ozone gas will become noticeably present in the air." Johnson adds, "Before you wash anything with ozone, make very sure that everything that might be sprayed, intentionally or accidentally, is compatible with it. For example, mild steel hit with ozone will be forever changed. You don't want to chemically damage equipment or cellar paraphernalia."

Joe Mendez of Piper Environment Group agrees, adding, "Ozone is not a great cellar surface sanitizer because of the off-gassing issues. If you're trying to sanitize an inside wall, for example, the best thing you can do is just coat it with quaternary ammonia and go away. If you want to sanitize a pneumatic press, a rubber-based bladder would be degraded by the ozone. But if you do choose to use ozone, apply just the amount that you need. Anything extra, any ozone that you smell, doesn't do you any good."



Dana DeLuvio at J Vineyards and Winery ready to move the ozone generator from the barrel room to the filler for CIP sanitation.

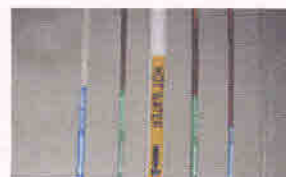
CIP-Clean In Place

Wineries have all kinds of equipment which cannot be taken apart to be cleaned. To sterilize these tanks, runs of pipe, hoses, bottling lines, fillers, etc., they must be cleaned in place (CIP). First, the CIP equipment is cleaned with soap and/or surfactants and thoroughly rinsed. For the sanitizing step, ozonated water is recirculated through the equipment using a closed loop of pipe or hose. The circulated ozone reacts with organic material in the CIP equipment. When there are no organics left to destroy, dissolved ozone will be detectable in water leaving the equipment. To ensure that sterility has been achieved, ozonated water is left to recirculate a few additional minutes after the effluent concentration of ozone matches the output of the generator.

Without ozone, CIP sanitation must be done either by chemicals (usually chlorine or iodophore solutions), requiring multiple rinses afterwards to remove noxious residues, or by heat (usually high-temperature water or steam), which is very expensive to produce and creates a danger for cellar workers. In contrast, ozone achieves CIP sanitation at low cost, at ambient cellar temperatures, and without chemical residues. Further, hot water or steam causes the expansion and contraction of welds, one of the biggest causes of line degradation and repair. Heat also can bake on materials inside the lines, making them more difficult to clean. Since ozone is used in cold water, it avoids these and other problems of heat-based CIP sanitation.

Oded Shakked, winemaker at J Vineyards and Winery, uses ozonated water in a CIP system. "Once a week during bottling, we sanitize our filler with chlorinated TSP. But the other four out of five days we don't use chlorinated cleaners. Instead, we sterilize the filler with ozone. We use hoses to connect the filler to our ozone generator in a closed loop, and we run the whole thing at the end of the day. Then we shut it off, and the next morning the system's ready to roll. It's pretty slick."

While bottling lines would seem to be ideal for ozone CIP sanitation, two issues usually make them problematic. First, the filters, fittings and seals in bottling lines often are made of ozone-degradable materials. Granted, these components can



Cakebread Cellars' Centralized ozone system puts taps with ozonated water throughout the winery, right next to hot and

be replaced with ozone-resistant versions, but ozone-proof filters are generally more expensive. The other concern is nooks and crannies. Ozone dissolved in water will kill whatever it comes in physical contact with. But complex bottling lines often are rife with tiny hidden harbors, corners, cracks or voids. All of these are potential places for microbes to hide. Steam or high temperatures reliably reach these nooks-and-crannies, but ozonated water might not, even with lengthy circulation. (Gaseous ozone could potentially overcome this situation. See below.)

cold water taps. Ozonated water taps are even placed on catwalks for easy connections when sanitizing tanks.

But McClain argues that "Numerous wineries are currently using ozone to sanitize their bottling lines, and have been successfully for an extended period of time. Wineries have compared ozone and hot water, and reported ozone to be significantly better than hot water. What is important is that you get your lab personnel involved early to develop your SOPs for using ozone on your line and contact the bottling line manufacturer for their chemical CIP procedure. In fact, several bottling lines from the manufacturer can now be ordered with ozone CIP protocols."

Centralized Ozone Systems

When wineries rely on ozone so much that stationary ozone generators for barrel washing and ozone carts for CIP and surface sanitation aren't enough, the next step is to install building-wide ozone systems. McClain has installed centralized ozone systems at a number of wineries. He says, "Cakebread, for example, has bubble-free ozonated water on tap throughout their new winery. It's right there next to the hot and cold water at their crush pad. They can wash the crush equipment from that station. There also are taps for ozonated at cleaning stations in the winery, even up on the catwalks where they go to clean the tanks."



Ozone is an unstable molecule; warm temperatures and jostling travel through pipes cause it to decompose to oxygen, as will sitting in pipes for extended periods of time (e.g. overnight). So centralized ozone systems must be carefully designed to control these factors so that proper ozone concentrations are available at all times and in all locations throughout the winery. Some systems may require flushing each morning to get freshly ozonated water to peripheral taps. Others can maintain a continuous circulation of ozonated water through the system. Still other central ozone systems are designed to serve multiple applications- barrel washing, surface sanitation, water treatment, etc.-with separately controlled loops.

Gaseous Ozone

Up to now, we have described winery applications using water



When these caves were built, ozone gas lines were installed in the

with dissolved ozone. But ozone gas itself has interesting uses for wineries. One mentioned briefly above is CIP sanitation, since gaseous ozone will penetrate and sterilize the hard-to-reach nooks and crannies that ozonated water might miss.

ceiling to provide night time ozone treatments for controlling growth of mold and mildew.

Another, somewhat covert use for ozone gas is barrel sanitation. Some wineries disconnect their generator's gas-destruct unit during barrel treatments, leaving actual bubbles of ozone gas in the water stream. Inside the barrel, these gas bubbles can penetrate into crevices, around blisters, and into pores, nooks and crannies far better than ozonated water. This same effect can occur even without disconnecting the gas-destruct unit when using water with very high concentrations of ozone. When the concentrated ozone solution hits the barrel walls, ozone gas bubbles out naturally. This creates a 'cloud' of ozone gas and water vapor inside the barrel which can penetrate deeper into the porous inner surfaces. Clearly, using ozone gas is a bad idea for manual washing of barrels in racks or on the cellar floor. However, it could work with well-sealed automatic barrel washers, especially those installed outdoors. But any winery choosing to use ozone this aggressively should take special care to establish sensible SOPs so that cellar workers' exposure to ozone gas will be carefully controlled and minimized.

Storage rooms and caves also can benefit from ozone gas treatment. Ozone gas can control the mold growth and sporulation fostered by the natural dampness of caves or the presence of volatile organics in barrel storage rooms. Corks stored in sealed rooms can be treated with ozone gas to reduce cork taint from trichloroanisol (TCA). Ozone gas levels of 5ppm show excellent effectiveness. (The eight hour worker exposure limit from OSHA is 10ppm.) But wherever ozone gas is used, serious engineering controls, air monitoring and SOPs must be maintained to prevent worker exposure to the gas.

McClain notes, "We've set up winery cork storage rooms which we treat with ozone gas for 30-90 minutes nightly. We turn the system on and have a flashing light on the outside while the room is above 0.1ppm. We calibrated the system until the desired concentration is achieved and there is no remaining ozone in the room when workers arrive in the morning. If the room was empty, ozonating it for 15 minutes could leave residual ozone in the air the following morning. With 20 sacks of corks in the room, however, we can run ozone for an hour and there'll be no ozone remaining the next morning."

But water treatment is the most important winery use of gaseous ozone. Incoming water, especially water from wells or ponds, can be treated with ozone gas to remove microbes, organics, iron and manganese without residual flavor or odor effects. Waste water also can be treated with ozone gas, allowing effluent to leave the winery devoid of any annoying odors, organic compounds (including alcohol) or microbes. However, Mendez cautions, "Be careful with very high bacterial or organic levels. This requires a lot of ozone, and high capital costs."

Ozone Frontiers

There are three wine industry applications where ozonated water isn't used now, but soon may be. One is long-term barrel storage, replacing SO₂ gas. It is theoretically possible to connect a daisy-chained circuit of empty barrels to an ozone generator in a CIP-like system. A continual, slow flow of ozonated water through the barrels would keep them hydrated and free of microbial contamination. Mendez also notes, "We're working on a similar system for safe, long-term barrel storage using ozone gas."

The second application is bottle washing. In Europe, where many wine bottles are recycled and reused, it is common for wineries to sanitize all bottles with ozonated water before they are filled. In the U.S., all bottled water containers and many soft drink and food containers receive pre-bottling sanitary rinses with ozonated water, although this practice is rare in the wine industry. But health concerns, valid or not, may soon prompt a government near you to require that wine bottles be sanitized with ozonated water before filling.

The final 'frontier' application for ozone is out in the vineyard—controlling mold, mildew and insects by spraying vines with ozonated water. The process involves hitting the vines with a real strong shot of ozone, in the 9ppm range. In addition to the hoped-for control of powdery mildew, the ozonated water treatments appear to be effective on

leaf hoppers and thrips, and especially on mites. Since ozone is non-residual and non-polluting, successful vineyard control of mildew would be a great boon to sustainable vineyard management, and the promising results from testing last summer ensure that research will continue in the coming season. However, thorough investigation will be needed on potential negatives, including effects on wine favor and vine health, and especially on unwanted kills of desirable insects or destruction of beneficial microbes like soil microrrhizae and native yeasts on berries.

In the O-Zone

Versatility with a punch! Ozone works on barrels, walls and floors, tanks and pipes, well and waste water, caves, and even the vineyard. And that's just today's list. More uses are sure to spring up as creative cellar masters and ingenious vendors find new ways to harness ozone's strong, residue-free sanitizing power. Stay tuned! 🍷

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