field report

BY BETH HAMM

DBP reduction using mixed oxidants generated on site

MIXED OXIDANTS GENERATED ON SITE HAVE A DEMONSTRATED TRACK RECORD OF REDUCING BOTH TOTAL TRIHALOMETHANES AND HALOACETIC ACIDS WITHOUT THE ATTENDANT PROBLEMS ASSOCIATED WITH BROMATES AND CHLORITES OR ISSUES REGARDING SAFE HANDLING.

The Safe Drinking Water Act (SDWA) was established by the US Environmental Protection Agency (USEPA) in 1974 to protect the quality of the nation's drinking water. Although the use of disinfectants in drinking water has drastically reduced disease, these disinfectants can react with material in the raw water and form disinfection by-products (DBPs) that are also hazardous to health.

Initially, the government focused on reducing formation of chloroform, bromodichloromethane, dibromochloromethane, and bromoform—all components of a category designated as total trihalomethanes (TTHMs). TTHMs have been found to cause liver, kidney, and central nervous system problems, as well as an increased risk of cancer. In 1979, USEPA set a TTHM limit of 100 µg/L for "large surface water systems," defined as systems serving more than 10,000 people.

The 1996 amendments to the SDWA attempted to further balance the risks between microbial pathogens and DBPs. The Stage 1 Disinfectants/DBP Rule (D/DBPR) lowered the permissible limit for TTHMs to 80 µg/L. It also established a new limit of 60 µg/L for the five haloacetic acids (HAA5), i.e., mono-, di-, and trichloroacetic acids and mono- and dibro-

Mixed oxidants, produced by generators such as this one, have the disinfection power of chlorine and have also been documented to inactivate even chlorine-resistant microorganisms.

moacetic acids. Chlorite and bromate are limited to 1.0 mg/L and 10 µg/L, respectively. These limits affect all public water systems that add a disinfectant, regardless of their size. The rule went into effect in January 2002 for large surface water systems and will go into effect in January 2004 for groundwater and small surface water systems (USEPA, 1998). Table 1 shows the maximum contaminant levels set by the D/DBPR for TTHMs, HAA5, chlorite, and bromate.

MIXED OXIDANTS

Onsite generation of a mixed-oxidant solution, which consists primarily of hypochlorous acid, uses a process similar to onsite generation of sodium hypochlorite. A brine solution is fed through an electrolytic cell, power is applied, and the resulting oxidant solution is created. The style of electrolytic cell and the operating parameters determine the formation of straight hypochlorite versus formation of mixed oxidants.

TABLE 1	MCLs for Stage 1 D/DBPR*	
DBP†	**MCL—*mg/L***	
TTHMs	0.080	
HAA5	0.060	
Chlorite	1.0	
Bromate	0.010	

*MCLs—maximum contaminant levels, D/DBPR—Disinfectants/Disinfection By-products Rule
†TTHMs—total trihalomethanes, HAA5—the sum of five haloacetic acids

Mixed oxidants have the disinfection power of chlorine, but they have also been documented by numerous agencies to inactivate even chlorine-resistant microorganisms, much like ozone or chlorine dioxide does. In addition, because only salt and water are used as feedstocks, the use of mixed oxidants does not raise concerns about hazardous chemicals or safety. Furthermore, the solution also leaves a durable chlorine residual in the distribution system.

Because of the presence of chlorine in the mixed-oxidant solution, the formation of TTHMs and HAA5 will still occur. However, anecdotal evidence from a number of installations shows DBP reductions ranging from 30 to 50%. Neither chlorite nor bromate has been detected in mixed oxidant–treated water. Depending on the level of precursors in the raw water, mixed oxidants may be a viable alternative for DBP reduction that also provides a chlorine residual without the safety and handling issues associated with traditional chlorination.

Mixed-oxidant chemistry. Manufacturers' claims of species other than chlorine in the mixed-oxidant solution have not been directly verified because

The biofilm-encrusted pipe sample (left) was disinfected by chlorine gas; the nearly spotless pipe (right) was exposed to mixed-oxidant treatment.

of the limitations of current analytical techniques and the complexity and interferences of multioxidant chemistry. Classical laboratory methods for detection of other oxidants do not function properly in the presence of a large chlorine matrix; thus, when these methods are used, studies on mixed oxidants have detected only chlorine (Gordon, 1998).

Although the chemistry of the mixed-oxidant solution is problematic, the biology is compelling. The mixed-oxidant solution exhibits several performance characteristics that show it contains more than just chlorine. The most dramatic evidence is the ability of

the mixed-oxidant solution to inactivate chlorine-resistant organisms (e.g., the *Cryptosporidium parvum* oocyst) or achieve substantially higher inactivation levels of other organisms at a lower concentration × time ($C \times T$) than is required with hypochlorite. Superior inactivation capability of a multitude of organisms using the mixed-oxidant solution has been demonstrated at a number of institutions, as described in the following section.

Inactivation studies. *C. parvum oocysts*. Initial testing in 1996 was conducted at the University of Arizona in Tucson using the excitation method. Researchers achieved an approximate 2-$\log_{10}$ inactivation, whereas hypochlorite had no effect (Sterling, 1993).

In 1997, the University of North Carolina at Chapel Hill and the Centers for Disease Control and Prevention compared mixed oxidants and sodium hypochlorite for inactivation of the *C. parvum* oocyst via infectivity assays on neonatal mice. Mixed oxidants inactivated the organism by more than 3.6 $\log_{10}$ (>99.9%) at a concentration of 5 mg/L × 4 h. Hypochlorite at the same dosage and $C \times T$ achieved no inactivation whatsoever (Venczel et al, 1997).

In 2000, the University of Colorado in Colorado Springs demonstrated a 2–3-$\log_{10}$ inactivation using polymerase chain reaction amplification of fluorescent-labeled heat shock genes. The results in the report unequivocally indicated that treatment of live *C. parvum* oocysts with mixed oxidants for different periods inhibited expression of the heat-inducible Hsp70 gene, and the extent of the inhibition showed direct correlation with the duration and nature of the disinfection treatment. Again, hypochlorite had no effect whatsoever.

In 2000, researchers at the University of North Carolina at Chapel Hill presented their findings at the AWWA Water Quality Technology Conference. Mixed oxidants produced extensive

FIGURE 1   Comparison of DBP formation with use of chlorine versus mixed oxidants
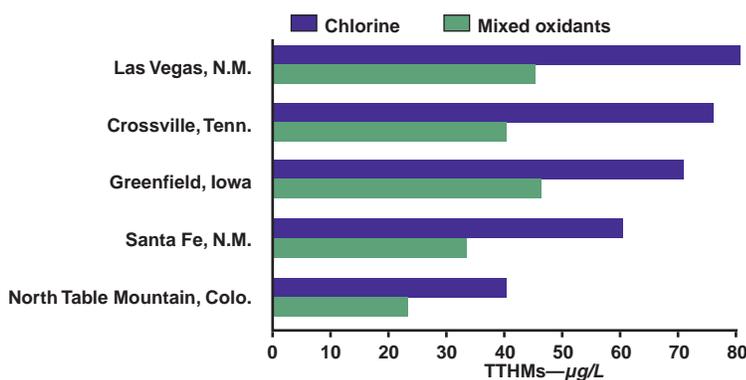
DBP—disinfection by-product, TTHMs—total trihalomethanes

(>4-log$_{10}$) inactivation of test bacteria, bacterial spores, and viruses within 1–10 min. The level of inactivation of *C. parvum* oocysts in 10 min ranged from 0 to >3 log$_{10}$, depending on the cell design, experimental conditions, and experiment (Sobsey et al, 2000).

Legionella pneumophila. At a dose of 2 mg/L and exposure of 10 min, mixed oxidants achieved total kill at pH 8.0, compared with bacteria concentrations > 2 cfu/mL with sodium hypochlorite (Barton, 1996). Subsequent studies showed that mixed oxidants achieved significantly higher inactivation than sodium hypochlorite was able to achieve (Bradford et al, 1997).

Pseudomonas aeruginosa. At a dose of 2 mg/L and exposure of 10 min, mixed oxidants achieved total inactivation, compared with bacteria concentrations of 1,200 cfu/mL remaining when sodium hypochlorite was used under the same conditions (Barton, 1996). Subsequent studies showed that mixed oxidants achieved 1.6–3.7-log$_{10}$ higher inactivation than sodium hypochlorite (Bradford et al, 1997).

Bacillus stearothermophilus. At a dose of 4 mg/L, exposure of 5 min, and pH of 8.0, mixed oxidants achieved total kill, whereas with sodium hypochlorite bacteria concentrations > 12 cfu/mL remained (Barton, 1996). Subsequent studies indicated that mixed oxidants achieved 1.5–2.5-log$_{10}$ higher inactivation than sodium hypochlorite (Bradford et al, 1997).

Escherichia coli. In 1996, the University of Arkansas Center of Excellence for Poultry Science at Fayetteville conducted a study at a major poultry plant approved by the US Department of Agriculture (USDA). The research explored the ability of mixed oxidants versus sodium hypochlorite to inactivate *E. coli* below the USDA's regulatory limit of 100 cfu/mL. Of the mixed-oxidant samples, 100% were below the limit, with an average value of 22 cfu/mL. By contrast, half of the hypochlorite samples were over the

FIGURE 2 TTHM reduction at Greenfield Municipal Utilities, Iowa

TTHMs—total trihalomethanes
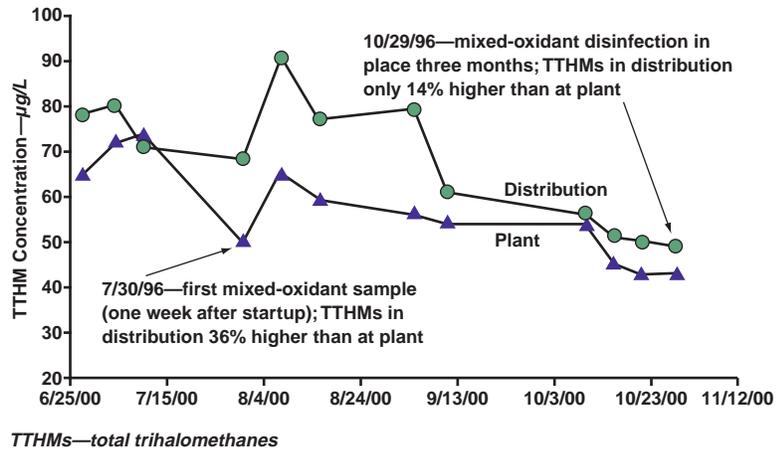
FIGURE 3 Comparison of dosage and residual for chlorine versus mixed oxidants
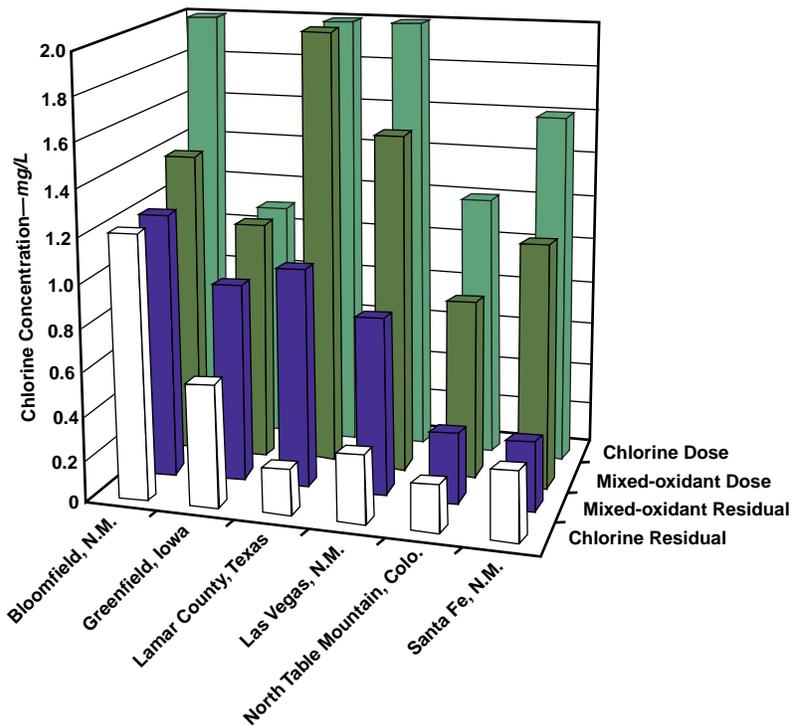
limit, with an average of 222 cfu/mL, more than twice the permissible level (Waldroup et al, 1996). Subsequent studies conducted in 2001 by the University of Georgia's Department of Poultry Science in Athens showed that mixed oxidants achieved a 2.4-log$_{10}$ greater inactivation of *E. coli* than hypochlorite did at the same dosage (Russell, 2001).

Salmonella typhimurium. Studies by the University of Georgia's Department of Poultry Science in 2001 showed mixed oxidants achieved a 2.1-log$_{10}$ greater inactivation at a 2-mg/L dose than hypochlorite was able to achieve at the same dosage (Russell, 2001).

Staphylococcus auereus. The University of Georgia studies indicated

TABLE 2   Microflocculation effects using mixed oxidants

Installation Site	Coagulant Consumption			Effluent Turbidity—*ntu*			TTHM* Levels
	Previous Doses	Current Doses	Percent Reduction	Previous Levels	Current Levels	Percent Reduction	Percent Reduction
Crossville, Tenn.	90 gpd (0.34 m³/d)	70 gpd (0.26 m³/d)	22	NA†	NA	NA	47
Greenfield, Iowa	14.7 mg/L	8.9 mg/L	40	0.107	0.065	39	>20
Las Vegas, N.M.	10.5 mg/L	7.5 mg/L	29	0.07	0.03	57	44
Midwestern site	Data not available	Data not available	Data not available	2.0	0.4	80	NA
Santa Fe, N.M.	90 mg/L	54 mg/L	40	0.60	0.18	70	>45

*TTHM—total trihalomethane
†NA—not applicable

that mixed oxidants achieved a 1.4-$\log_{10}$ greater inactivation than hypochlorite at a 2-mg/L dose (Russell, 2001).

Listeria monocytogenes. Results from the University of Georgia showed that compared with hypochlorite, mixed oxidants at a 2-mg/L dose achieved a 2.3-$\log_{10}$ greater inactivation (Russell, 2001).

Bacillus anthracis. Studies at the US Army Dugway Proving Grounds in Dugway, Utah, are in progress. Preliminary results indicate inactivation of *B. anthracis, Yersinia pestis* (plague virus), *Klebsiella terrigena, Francisella tularensis,* and *Vaccinia* (smallpox) (Wright et al, 2001).

DBP reduction. Another key indicator for the presence of oxidants other than chlorine in the mixed-oxidant solution is reduction in TTHMs and HAA5, as has been demonstrated at a number of water utilities that have replaced conventional chlorination with mixed-oxidant technology. Although this phenomenon is not seen at every site, no utility using mixed oxidants has observed DBP concentrations above the levels produced by chlorine. In fact, in the great majority of mixed-oxidant installations, both TTHMs and HAA5 are typically reduced by 30–50%, in contrast to levels formed with chlorine.

A number of mixed-oxidant sites have also tested for production of chlorites, chlorates, and bromates (Herrington et al, 1999; Yu & Mur-

phy, 1998; Mangold Environmental Testing, 1997). Neither chlorite nor bromate, both of which are regulated under the D/DBPR, has been detected in mixed-oxidant treated water. The only by-product that has been detected is chlorate, which is not a regulated substance and has no known adverse health effects. Chlorate formation is minimal and is produced in the range of 15 to 33 µg/L per 1-mg/L dose as free available chlorine (FAC), which is comparable to or less than the levels found in commercial bleach (Environmental Health Laboratories, 1995).

• Las Vegas, N.M., replaced chlorine gas with mixed oxidants for final disinfection and also added mixed oxidants in pretreatment where previously no disinfectant had been used. With chlorine gas, TTHM concentrations averaged 80 µg/L. Within three months after conversion to mixed oxidants, TTHM formation was reduced to 45 µg/L, a 44% reduction. This reduction was seen despite the fact that mixed oxidants were also being added to the clarifier, something that the utility could not do with chlorine gas because of excessive TTHM formation (Armijo, 2000).

• When disinfecting with chlorine, the Holiday Hills water treatment plant in Crossville, Tenn., averaged 75 µg/L of TTHMs and 79 µg/L of HAA5 in the first quarter of 2000. After conversion to mixed oxidants late in the year, the facility reduced both its

TTHM and HAA5 concentrations for the first quarter of 2001 to 40 µg/L, a decrease of 47 and 49%, respectively (Brownfield, 2001).

• Greenfield (Iowa) Municipal Utilities reported that switching to mixed oxidants resulted in a reduction in TTHM formation ranging from 20 to 40%. Initially TTHMs in the distribution system were ~36% higher than TTHM levels at the plant. After two months of treatment with mixed oxidants, TTHMs in the distribution system were only 14% higher than levels at the plant and were reduced even further as organic matter in the distribution system was eliminated (Duben, 1996).

• The Sangre de Cristo Water Company (Santa Fe, N.M.) also uses mixed oxidants in pretreatment and final disinfection. The facility was unable to pretreat with chlorine gas because of excessive TTHM formation. Despite the fact that mixed oxidants are injected preclarifier and in the clearwell, whereas chlorine was only injected at a single point, TTHMs have been cut from an average of 60 µg/L with spikes >80 µg/L to an average of only 33 µg/L, a reduction of ~50% (Herrington et al, 1999).

• North Table Mountain Water and Sanitation District (WSD) in unincorporated Jefferson County near Golden, Colo., converted its filtration and disinfection systems in two stages. The filtration system achieved significant reduction in the formation of TTHMs

(37%) and HAA5 (30%). Subsequent conversion to mixed-oxidant disinfection from chlorine gas achieved an additional 44% reduction in formation of both TTHMs and HAA5. The combined effect of the new filtration and mixed-oxidant disinfection was a total decrease of 64% for TTHMs and 61% for HAA5 (Jeschke, 2000a).

Figure 1 compares DBP formation with chlorine and with mixed oxidants at these five sites.

THEORIES FOR BEHAVIORAL DIFFERENCES

Laboratory testing and field installations have found that mixed oxidants and chlorine exhibit significant behavioral differences, although only chlorine can be measured in the mixed-oxidant solution. Several explanations have been proposed for the greater reduction in DBP formation achieved by mixed oxidants in contrast to hypochlorite. These theories include preferential action of nonchlorine oxidants, elimination of biofilm, improved chlorine residual at a reduced dosage, and microflocculation to remove precursors.

Preferential-acting nonchlorine oxidants. Chlor-oxygen species other than chlorine in the mixed-oxidant solution may be reacting with organic material in the water, reducing oxidant demand and eliminating some of the material that causes TTHM and HAA5 formation. These other species would be faster-acting and preferentially react with components in the water before the presence of chlorine in the mixed-oxidant solution could cause an adverse effect. Because these other species are short-lived and minute in comparison to the amount of chlorine present, they are not sufficient to achieve total removal. Thus, the remaining organic material reacts with the remaining chlorine, producing TTHMs and HAA5, although at reduced levels. This theory is speculative and has not been proven.

Biofilm elimination. There is significant anecdotal evidence of the ability of mixed oxidants to clean biofilm and algae from distribution systems

and clarifiers. Biogrowth that was able to survive with chlorine as a disinfectant is typically eliminated shortly after conversion to mixed oxidants. When a mixed-oxidant generator is first installed, flushing of the distribution system may be required to remove detached biosolids until the system has stabilized. The stabilization process usually takes one to two months, and then the lines remain free of biofilm or algae as long as mixed oxidants are used.

The ultimate effect is that reduced biogrowth decreases organic material that can react with chlorine, thus reducing DBP formation. Elimination of biofilms in distribution lines would mean that DBP levels in the distribution system would not be substantially higher than levels seen at the treatment plant. Data from a study conducted by H.R. Green Engineers demonstrate this effect (Duben, 1996). Over the three months of the study period using mixed-oxidant disinfection, the levels of TTHMs in distribution water dropped more rapidly than the levels at the plant. When the site first converted to mixed oxidants, TTHMs in the distribution system were 36% higher than levels at the plant. After three months of continuous operation, distribution system TTHMs were only 14% higher than at the plant. Overall, TTHM reduction in the distribution system was twice as great as at the plant. Figure 2 summarizes TTHM reduction at the utility.

Biofilm reduction with mixed oxidants has been observed at a number of other installations.

• At the Diana Water Supply Corp. in Diana, Texas, two line breaks occurred simultaneously. Both lines drew water from the same aquifer, but at that time the utility used chlorine gas to disinfect one line and mixed oxidants to disinfect the other line. The line disinfected with chlorine contained biofilm only 200 ft (61 m) from the disinfection station. The line break in the mixed-oxidant line occurred ~0.5 mi (0.8 km) from the disinfection station, so the expectation was an even

more contaminated line. However, the pipe exposed to mixed-oxidant treatment was spotless, as though it had never been used.

• The KOA Kampground in Great Falls, Mont., originally used hypochlorite for disinfection of both its swimming pool and potable water supply. The facility reported that conversion to mixed oxidants led to the removal of previously accumulated biofouling in the distribution system. Black slime that previously had formed in the showers when the facility was using hypochlorite disappeared. With hypochlorite, loss of distribution system pressure during frequent power outages resulted in biofouling in the pipelines, and the distribution system always needed to be flushed when pressure was regained. In contrast, since the campground switched to mixed oxidants, the distribution system requires no flushing, and no discoloration is evident after a power failure. With mixed oxidants, algal growth has not formed on the pool area surface, thus eliminating the need for an algaecide, a common requirement for outdoor pools disinfecting with hypochlorite (Crayton et al, 1997).

• The city of Las Vegas, N.M., also reported substantial improvements with mixed-oxidant chemistry. When the utility used chlorine gas, a 1.5–2 in. (38–51 mm) thick algae mat would grow in the clarifying basins. Staff had to drain the tanks every few weeks to scrub off the algae, which would peel off in sheets. The cleaning process took ~20 h. Since conversion to mixed oxidants, the facility has not seen any evidence of algae growth (Armijo, 2000).

• Hazlet, Sask., converted from sodium hypochlorite on its well site to mixed-oxidant generation. With hypochlorite, the facility experienced severe water quality issues and black film growth on the cistern ladder and walls. Within one month of conversion to mixed-oxidant disinfection, the black film on the cistern ladder and walls was nearly gone (Sletten, 2000).

• At a pilot-test site in the Midwest, mixed oxidants were fed to one

of the four standard clarifiers[1] at the plant. Within 8 h, biogrowth removal on tubes was observed, and within a week, solids on the tubes had turned dark brown and dropped off (Gould, 2000).

• Orange County Water District in Los Angeles, Calif., has developed novel techniques for evaluating biofilm formation and removal. Tests using mixed-oxidant solution and chlorine on selected biofilms were funded by the Defense Advanced Research Projects Agency. Initial results showed that mixed oxidants required a higher dosage than that required for chlorine to remove the biofilms. On further inspection, however, the mixed oxidant solution also removed the protein substrate that biofilms develop in order to attach to material surfaces; chlorine, on the other hand, did not remove the substrate. The initial conclusion was that it would be much more difficult and require more time for biofilms to reestablish themselves on mixed oxidant–treated membranes than on chlorine-treated membranes (Phipps & Rodriguez, 2001). Additional research is under way.

Improved residual at a reduced dosage. The FAC residual from mixed oxidants is much more durable than the FAC residual from traditional chlorination. The mixed-oxidant FAC residual can endure for long distances and stays in the lines for a much longer period of time. This is likely related to the removal of substances such as biofilm, which creates oxidant demand within the distribution system. In addition to a more durable chlorine residual, treatment plants typically notice a reduction in the required dosage at the plant to maintain the same residual at the end of the line. After the distribution system has stabilized, most mixed-oxidant users report a 30% final reduction in dosage at the clearwell.

A secondary effect of the reduced dosage is a correlated reduction in DBP formation. Because chlorine require-

ments have decreased, there is less chlorine in the system that can react with organic matter. The end result is a correlated decrease in DBPs. The following sites have observed an improved residual at a reduced dosage, and the majority of them have also reported reductions in TTHM, HAA5, or both.

• Bloomfield, N.M., used chlorine gas in the clearwell at a dose of 2 mg/L to maintain a 1.2-mg/L residual at the end of the distribution system. With mixed oxidants, the facility has been able to reduce the dose ~30% to only 1.4 mg/L and still maintain the desired 1.2-mg/L residual at all points in distribution. In addition, the plant is immediately operational in the morning with no loss of residual overnight, whereas when chlorine gas was used, staff had to run the plant for hours each morning in order to get the residual up to the necessary level (Ruybalid, 1999).

• Greenfield Municipal Utilities in Iowa provides water to the neighboring community of Orient, 9 mi (14.5 km) away. When the utility used chlorine gas as a disinfectant, Orient had to boost the incoming water with additional chlorine in order to maintain the residual throughout its distribution system. When Greenfield converted to mixed-oxidant generation, the FAC residual continued throughout Orient's entire distribution system, enabling the community to discontinue boosting. In addition, within a few months of conversion, Greenfield reported a TTHM reduction of 20 to 40% (Herrington et al, 1997).

• When using chlorine gas, Lamar County Water Supply District in Brookstone, Texas, was unable to maintain the desired 0.2-mg/L residual at the end of its 25 mi (40 km) long distribution system. In contrast, mixed oxidants at the same dosage maintain a 1-mg/L residual at the end of the line (*American City & County,* 1997).

• Las Vegas, N.M., used chlorine gas at a dose of 2 mg/L to maintain a 0.3-mg/L residual in the distribution system. Use of mixed oxidants has

enabled the utility to reduce the dose by 15 to 30% (between 1.4 and 1.7 mg/L) and still maintain a higher chlorine residual of 0.8 mg/L in the distribution system. In addition, the facility reports a 44% reduction in TTHMs (Armijo, 2000).

• North Table Mountain WSD in Colorado previously dosed at 1.2 mg/L with chlorine gas in order to maintain a 0.2-mg/L residual in distribution. With mixed oxidants, the utility has reduced the dose 33% to 0.8 mg/L, which maintains a steady residual of 0.3–0.4 mg/L throughout distribution. The site also reports a 44% reduction in TTHM and HAA5 levels (Jeschke, 2000b).

• After switching to mixed oxidants, Santa Fe's Sangre de Cristo Water Company was able to decrease the chlorine dose by 31% (from 1.6 to 1.1 mg/L) and still maintain the same residual at all points in distribution. The facility also reports ~50% reduction in TTHM formation (Herrington et al, 1999).

Figure 3 compares the dosages and residuals at the six sites before and after conversion to mixed oxidants.

Microflocculation. Microflocculation is defined as enhanced flocculation producing either a reduction in coagulant demand for the same final (filtered water) turbidity or a reduction in final turbidity at the same coagulant demand. Processes have been developed first to determine whether microflocculation will occur and then to optimize the microflocculation effect. An improved clarification process will demonstrate reduced turbidity, reduced DBP formation, and reduced chemical addition for such chemicals as alum and polymer.

Enhancing the coagulation process essentially removes several of the precursors for DBP formation. A variety of installations using mixed oxidants in pretreatment report a microflocculation effect and a reduction in TTHMs and HAA5 not seen with traditional chlorination. The fact that these sites were unable to chlorinate in pretreat-

ment because of excessive TTHM formation further substantiates this theory. Although they are adding more oxidant overall because of dual injection points, they see an overall decrease in DBP formation. Table 2 shows microflocculation effects at five facilities using mixed oxidants.

• Crossville, Tenn., uses mixed oxidants in pretreatment and final disinfection. Finished water turbidity concentrations were always quite low (~0.1 ntu) even with chlorine gas, and use of mixed oxidants did not further reduce turbidity. However, since the treatment plant converted to mixed oxidants, alum consumption has dropped by 22%, and TTHM and HAA5 concentrations for comparative quarters have dropped 47–49% (Brownfield, 2001).

• Iowa's Greenfield Municipal Utilities pretreats with mixed oxidants for removal of manganese. When conditions are optimal, the facility can eliminate the use of potassium permanganate, use 40% less alum, and decrease effluent turbidity by 39%. The site also reports TTHM reductions ranging from 20 to 40% (Herrington et al, 1997).

• In Las Vegas, N.M., use of mixed oxidants in pretreatment has resulted in a 29% reduction in alum demand and a 57% reduction in finished water turbidity. TTHM levels have dropped by 44% (Armijo, 2000).

• At the Midwest pilot-test site, mixed oxidants were used in pretreatment on a sidestream flow of water and in a full-scale test on one of the four existing upflow clarifiers. The engineer reported elimination of pinfloc from the clarifier effluent, noticeable improvement in effluent quality relative to the other clarifiers, and a positive effect on algae growth in the clarifier. In addition, total organic carbon dropped by 12%, providing further evidence for removal of precursors (Gould, 2000).

• The Sangre de Cristo Water Plant began using mixed oxidants for pre-

treatment at its 8 mgd (30 ML/d) surface water treatment plant in 1998. Before the change in treatment, turbidity levels were 0.6 ntu, which was above the 0.5-ntu limit. Plant flows had to be maintained at only 4 mgd (15 ML/d) during spring in order to control turbidity even to those levels. Upon conversion to mixed-oxidant generation, staff noticed the alum demand dropping. They initially reported a 39% reduction in alum demand, as well as a turbidity decrease to 0.25 ntu in summer and 0.01 ntu in winter. They are also able to maximize plant flows to 10 mgd (38 ML/d), even during springtime, with no adverse effect on turbidity concentrations because of a more rapid rate of floc formation (Herrington et al, 1999). Recent reports from the operating staff indicate a 60% reduction in alum demand from original dosages and even lower turbidity ratings.

CONCLUSION

Out of a number of disinfection alternatives, mixed-oxidant use is the only technology that offers safe operation, a chlorine residual as required by USEPA, and the potential for DBP reduction. As USEPA enforces implementation of new DBP limits, facilities will need to investigate the best technology for their sites and put manufacturer claims to the test.

Compared with other chlorine technologies, mixed oxidants provide significant advantages, including superior inactivation capability and reduced formation of DBPs, which indicate that the mixed-oxidant solution is more than just hypochlorite generated on site. There are a number of explanations for decreased TTHM and HAA5 formation, including preferential action of nonchlorine oxidants, elimination of biofilm, improved chlorine residual at a reduced dosage, and microflocculation to remove precursors. Only one of these explanations—preferential action of nonchlorine oxidants—is unproven, whereas the others are supported by

operational evidence from numerous field installations.

In implementation guidelines for the Stage 1 D/DBPR, USEPA describes a best available technology for users of chlorine, chloramines, and chlorine dioxide as "control of treatment processes to reduce disinfectant demand and control of disinfection treatment processes to reduce disinfectant levels" (USEPA, 2001). Mixed oxidants alone, without the use of any other chemicals or treatment techniques, have been shown to reduce both disinfectant demand and overall chemical usage. Although current analytical techniques can detect only chlorine in the mixed-oxidant solution, chlorine alone cannot account for the reduced dosages, higher residuals, and lower levels of DBPs that mixed-oxidant installations report.

Because mixed-oxidant solution is produced from sodium chloride salt (NaCl) and water (H_2O), it is clear that the other constituents in the solution are chlor-oxygen compounds. In hundreds of installations utilizing mixed-oxidant technology, not one has reported DBP formation higher than levels found with the use of chlorine. In fact, tests for by-products associated with the possible compounds in the mixed-oxidant solution usually showed lower TTHM and HAA5 formation than with chlorine or onsite hypochlorite generators. In addition, no chlorite or bromate has been found in mixed-oxidant treated water, and chlorate production is far below levels of concern and common to all hypochlorite solutions.

In summary, drinking water facilities, as well as wastewater facilities that follow California's water recycling criteria requirements for secondary reuse of their water (California Code of Regulations, 2001), can benefit from a treatment practice that provides superior disinfection, stable chlorine residual, no safety concerns, and lower DBP formation. The operational improvements of treatment with mixed

oxidants are well-documented and should be taken into consideration by any site designing or redesigning its disinfection process.

—Beth Hamm is a water utility consultant with Tetra Tech Inc., 800 Corporate Dr., Lexington, KY 40503, (859) 223-8000, e-mail hamme@tetratech.com. She has BS and MS degrees in chemistry from Cumberland College and Eastern Kentucky University, respectively. Hamm has 14 years of experience in the drinking water field. She is active in AWWA at the national and section levels and is a member of the AWWA National Disinfection Committee, the Coagulation and Filtration Committee, and the Operations Standards Committee.

FOOTNOTES

[1]Infilco Accelator, Richmond, Va.

REFERENCES

American City & County, 1997. Supplier Using Mixed Oxidants for Better Quality.

Armijo, F., 2000. Personal communication.

Barton, L.L., 1996. Disinfection of Simulated Cooling Water. University of New Mexico, Albuquerque.

Bradford, W. et al, 1997. Results of Tests Comparing the Disinfection Effectiveness of Mixed-oxidant Solution and Sodium Hypochlorite in Simulated Cooling Water. Los Alamos Technical Associates, Los Alamos, N.M.

Brownfield, J., 2001. Memorandum Regarding Crossville Data. S.O.S. Inc., Cleveland, Tenn.

California Code of Regulations, 2001. California Health Laws Related to Recycled Water: "The Purple Book." Excerpts From the Health and Safety Code, Water Code, and Titles 22 and 17 of the California Code of Regulations, Berkeley, Calif.

Crayton, C. et al, 1997. Final Report on the Validation of Mixed Oxidants for the Disinfection and Removal of Biofilms From Distribution Systems. Montana Water Resources Center, Montana State University, Bozeman.

Duben, M., 1996. Pilot Study Final Report: Mixed-oxidant Disinfection System at Greenfield, Iowa. Howard R. Green Co. Consulting Engineers, Des Moines, Iowa.

Environmental Health Laboratories, 1995. Analysis of Sample From a MIOX SAL-80 Cell. South Bend, Ind.

Gordon, G., 1998. Electrochemical Mixed-oxidant Treatment: Chemical Detail of Electrolyzed Salt Brine Technology. Miami University, Oxford, Ohio.

Gould, B., 2000. Midwestern Water System Claricone and MIOX Pilot Study Results. Lawrence A. Lipe & Assoc., Benton, Ill.

Herrington, R. et al, 1999. Performance of a Conventional Surface Water Plant Using Mixed Oxidants for Microflocculation and Final Disinfection. Proc. 1999 AWWA Ann. Conf., Chicago.

Herrington, R. et al, 1997. Pilot Study Report: Mixed-oxidant Disinfection System at Greenfield, Iowa. MIOX Corp., Albuquerque, N.M.

Jeschke, R., 2000a. Memorandum to the North Table Mountain Water and Sanitation District Board of Directors. Golden, Colo.

Jeschke, R., 2000b. Personal communication.

Mangold Environmental Testing Inc., 1997. Analysis of Sample From Greenfield Municipal Water Utilities. Greenfield, Iowa.

Phipps, D. & Rodriguez, G., 2001. Comparison of the Efficiency of Bacterial Removal and Reduction of Bacterial Viability by Mixed-oxidant Solution (MOS) and Chlorine (as NaOCl) on a Reverse Osmosis Membrane. Water Resources & Technol. Dept., Orange County Water District, Los Angeles.

Russell, S.M., 2001. A Comparison of MIOX Versus Bleach for Eliminating Pathogenic Bacteria Associated With Poultry Products. University of Georgia, Department of Poultry Science, Athens, Ga.

Ruybalid, C., 1999. Personal communication.

Sletten, L., 2000. Personal communication.

Sobsey, M.D. et al, 2000. Inactivation of *Cryptosporidium parvum* Oocysts and Other Waterborne Microbes by Oxidants Generated Electrochemically From Sodium Chloride From Portable Pen and Bench-scale Systems. University of North Carolina, Chapel Hill, N.C.

Sterling, C., 1993. Testing of the MIOX Electrolytic Disinfecting System for Inactivation of *Cryptosporidium* Oocysts. University of Arizona, Tucson, Ariz.

USEPA (US Environmental Protection Agency), 2001. Implementation Guidance for the Stage 1 Disinfectants/Disinfection Byproducts Rule. EPA 816-R-01-012, Ofce. of Water (4606), Washington.

USEPA, 1998. Stage 1 Disinfectants and Disinfection Byproducts Rule, EPA 815-F-98-010, Ofce. of Water (4607), Washington.

Venczel, L. et al, 1997. Inactivation of *Cryptosporidium parvum* Oocysts and *Clostridium perfringens* Spores by a Mixed-oxidant Disinfectant and by Free Chlorine. *Applied & Envir. Microbiol.,* 63:4:1598.

Waldroup, A.; Doyle, M.; & Scantling, M., 1996. Onsite Generation of Chlorine Solutions for Poultry Processing Applications. University of Arkansas, Center of Excellence for Poultry Science, Fayetteville, Ark.

Wright, J.D.; Dvorak, T.J.; & Harper, B.G., 2001. Interim Report: MIOX Disinfection Pen and the Mesosystems Mesostill Agents of Biological Origin (ABO) Disinfection Test. Life Sciences Div., W. Desert Test Ctr., US Army Dugway Proving Ground, Dugway, Utah.

Yu, C.H. & Murphy, J.K., 1998. Demonstration Testing of Onsite Electrolytic Generation of Disinfectants. EPRI-CEC, St. Louis, Mo.