Bench-Scale Evaluation of Chlorine-Ammonia Process for Bromate Control During Ozonation

Hongxia Lei, Dustin W. Bales, and Jon S. Docs

The David L. Tippin Water Treatment Facility (Facility), located in Tampa, is an advanced ozonation water treatment plant with a capacity of up to 120 mil gal per day (mgd), consisting of coagulation, flocculation, sedimentation, ozonation, and biofiltration. Its source water comes from the Hillsborough River. During the wet season (June-September), excess water is treated and pumped into a series of aquifer storage and recovery (ASR) wells. The ASR water is then pumped back out during the dry season (October-May) to supplement water supply. The high dissolved oxygen content of finished water pumped into the ASR wells frees bromide from the geological formation. The increased bromide from the ASR wells increases the total bromide in the water to a level where bromate formation during ozonation nears or exceeds the U.S. Environmental Protection Agency (EPA) maximum contaminant level (MCL) of 10μg/L on an annual average. Currently, pH is used as the primary control strategy. A decrease in pH inhibits bromate formation; however, pH depression prior to ozonation is operationally challenging and also costly at the Facility.

A bench-scale study of an alternative bromate control strategy, i.e., the chlorine-ammonia process, was performed to evaluate the efficacy of the process to reduce bromate formation. The study was conducted simulating full-scale conditions using Hillsborough River water. The chlorine-ammonia process involves first adding chlorine, and, after a 5-min delay, ammonia is added, quickly followed by ozonation. The process forms hypobromite from hypochlorite, which then reacts with the added ammonia to form bromamines. Bromate formation is hence effectively minimized as hypobromite is consumed and becomes less available for bromate formation during the ozonation process. The bromamines created can react with organics present in the water in a similar way to chloramines, providing a negligible amount of disinfection prior to conversion back to bromide. This bromate control strategy allows water treated by ozone at a higher pH, or with a longer ozone contact time if needed, for meeting *Cryptosporidium* inactivation requirements and assisting taste and odor reduction.

Background

Potassium bromate ($KBrO_3$) was identified as a possible carcinogen in the early 1980s. It was first reported that oral administration of potassium bromate led to renal cell tumors in rats (Kurokawa et al., 1982) and further research showed that it was a probable carcinogen to humans (Kurokawa, 1990). As a result of this research, the U.S. Environmental Protection Agency (EPA) added bromate to a list of contaminants for consideration of regulation in 1994. In 1998, EPA's Stage 1 Disinfection and Disinfection Byproducts Rule went into effect under the Safe Drinking Water Act, placing byproducts such as trihalomethanes and haloacetic acids under more stringent regulation (EPA, 1998).

Bromate is a disinfection byproduct (DBP) associated with ozonation. Ozone as a disinfection method is becoming more popular in the United States to meet higher disinfection requirements, as well as increase taste and odor control, going from 40 ozone installations in 1991 to close to 280 in 2012 (Leob et al., 2013; EPA, 1999). The increasing market penetration of ozone combined with the new EPA regulations made bromate minimization increasingly important.

The bromate formation mechanism during ozonation is well studied and primarily consists of three pathways. The first is a direct pathway involving molecular ozone; the second is a direct-indirect pathway involving first molecular ozone and then hydroxyl radicals from ozone decomposition; and the third is an indirect-direct pathway where the hydroxyl radicals react first, then the molecular ozone (Song et al., 1997; von Gunten and Hoigné, 1994; Haag and Hoigné, 1983). Von Gunten and Oliveras (1998) incorporated additional reactions and successfully confirmed the model based on laboratory experiments and

Hongxia Lei is the water quality assurance officer and Jon S. Docs is senior environmental scientist with City of Tampa Water Department. During this project, Dustin W. Bales was a graduate student at the University of South Florida and an intern with City of Tampa.

kinetic modeling. Based on bromate formation mechanism, a novel approach using a chlorine-ammonia process was developed using a bench-scale ozonation system and its efficiency evaluated at varying pH, ozone exposure, and chlorine concentrations (Buffle et al., 2004). Wert et al. (2007) confirmed the efficacy of the chlorine-ammonia process for bromate reduction in a pilot-scale ozonation system using Colorado River water and validated the pilot results with full-scale implementation.

The water from the Hillsborough River is dramatically different from the Colorado River. During the wet season, total organic carbon (TOC) could spike up to 45 mg/L due to the large amount of organic matter flushed out of the swamp and tributaries by heavy rains into the river. Color and other water quality characteristics vary seasonally as well, which poses a unique challenge in treating the Hillsborough River water. The purpose of this study was to evaluate the chlorine-ammonia approach for bromate control using the Hillsborough River water, and determine the optimal doses and the associated financial benefit. As illustrated in Figure 1 of the general treatment process at the Facility, pH is controlled at 4.5 for enhanced coagulation. After coagulation/flocculation, pH is raised to 6.5 by adding lime or $Ca(OH)_2$ (calcium hydroxide) before the bromide-containing water is treated by ozone. After ozonation, lime can no longer be used for pH adjustment as it will cause a turbidity issue. As a result, caustic soda or sodium hydroxide (NaOH) has to be added at two locations downstream of the ozone to further increase pH to around 7.8

before the water is sent to customers. This pH control strategy is costly as only limited amounts of lime can be used. Lime has a four-fold advantage over caustic soda as it costs half as much, and its bivalent nature makes it twice as effective. For this reason, the chlorine-ammonia process was investigated, as this will allow ozone to occur at higher pH without violating bromate MCL, which will result in more lime usage and less caustic soda consumption.

Materials and Methods

Reagents

The Indigo Stock Solution consisted of 0.770 g of ACS-grade potassium indigo trisulfonate and 1 millilitre (mL) of 85 percent high-performance liquid chromatography (HLPC)-grade concentrated phosphoric acid per 1 liter of solution. The stock was stored in an amber bottle for less than four months. The Indigo Reagent Solution consisted of 50 mL of the Indigo Stock Solution, 11.5 g of sodium phosphate monobasic monohydrate, and 7.0 mL of HPLC-grade concentrated phosphoric acid. It was stored in an amber bottle for less than one week. The 100-mg/L bromide stock was created by diluting 1000 parts per mil (ppm) bromide stock solution. The 400 ppm ammonia stock contained 1529 milligrams (mg) of ammonium chloride per liter of solution. Chlorine stock had a target concentration of 600 ppm, and was made by adding 11 mL of 5-6 percent hypochlorite stock solution to 1 liter of water. Chlorine stock solution concentration was tested weekly to determine if the concentration remained steady. All solutions were prepared with distilled deionized water (DDI water).

Ozone stock solution was created by dissolving a mixture of ozone and oxygen gas generated by an ozone generator operated at 50 percent capacity and 1 liter per min oxygen flow rate into DDI water using a coarse gas wash bottle. Off-gas was treated with a sodium thiosulfate solution for quenching. The gas wash bottle was placed in an ice bath prior to generation. The generator was run for 30 min to achieve a steady state solution.

Experimental Methods

A 100-ml gastight syringe was used as the reactor vessel in all experiments. The syringe was placed inside of a water bath, which was maintained at 20°C. The syringe was connected to the outside of the water bath using 1/16-in. diameter 316 stainless steel tubing with a control valve for sampling and chemical dosing (Figure 2).
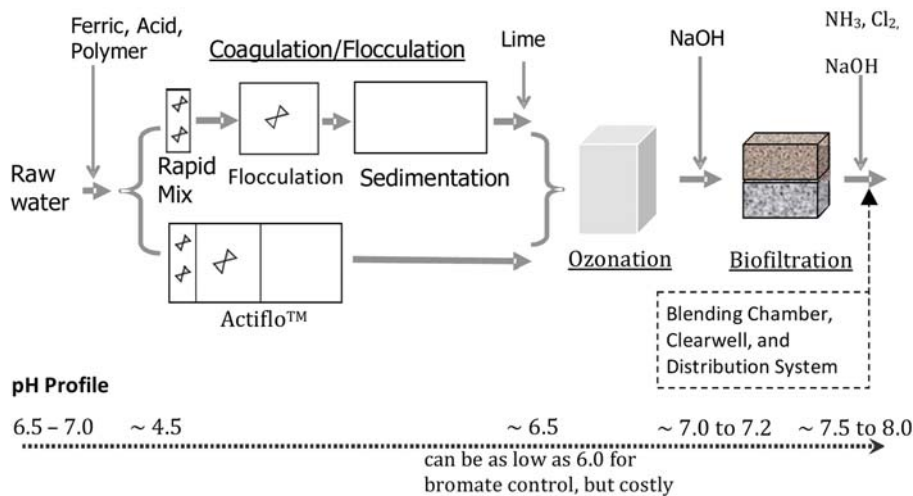
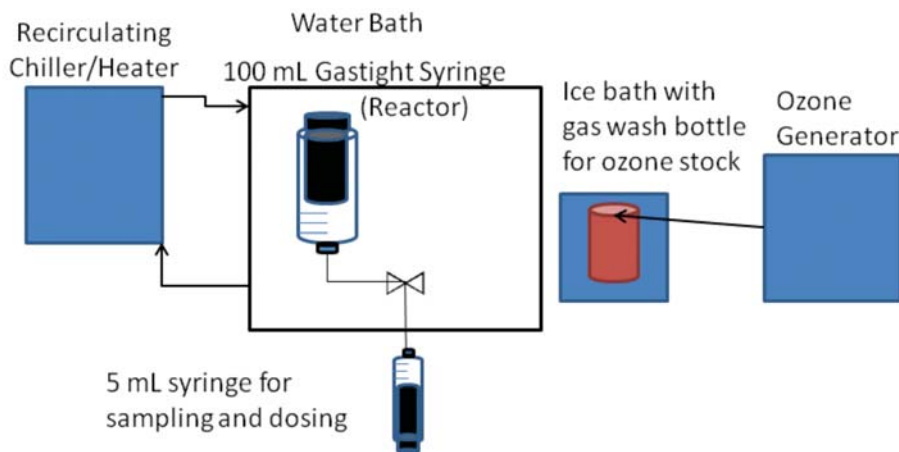

Figure 1. Current Treatment Process at the Facility.

Figure 2. Experimental Setup for the Bench-Scale Ozonation Apparatus.

Prior to each experiment, the pH of the test water was adjusted to pH 7 using hydrochloric acid or sodium hydroxide, followed by a bromide spike. Afterwards, the sample was placed in the reactor with the plunger removed. The syringe was filled to the top, and the plunger was then pushed in to ensure no air was in the syringe. A stir bar placed inside the reactor was stirred by a waterproof stir plate inside the water bath. The volume inside the reactor was adjusted to 85 mL. Some of the sample was retained in a 5-ml syringe for final volume adjustment. After approximately 10 min (allowing temperature to adjust from room temperature), chlorine was added in the appropriate dose using a 500-µl gastight syringe.

Approximately 1 mL of the retained sample in the second syringe was used to flush the chlorine from the tubing into the reactor. After 5 min, the ammonia was added in the appropriate dose and flushed into the reactor using the same syringes and process. One min after the ammonia dosing, 7-8 mL of ozone stock solution was added to the reactor. The stock was then flushed out of the tubing and the volume adjusted to exactly 100 mL using the 5-ml syringe. The 5-ml gastight syringes were used to pull ozone samples from the reactor. They were prefilled with 3 mL of indigo reagent solution. Samples were taken every min for the first 10 min, and less frequently after 10 min until the ozone concentration was 0.1 mg/L or below.

Analytical Methods

Dissolved ozone was measured with a spectrophotometer using a method similar to the Standard Method 4500-Ozone (Chiou et al., 1995; Bader and Hoigne, 1981) in order to be able to follow the rapid ozone decay. Bromate analysis was performed on an ion chromatography system using EPA Method 300C. The CT values (ozone concentration × contact time) were obtained by integrating the ozone decay curve generated in each experiment.

Experimental Design

Table 1 shows the labeling identification used for each condition and the associated pH, bromide concentration, chlorine concentration, and ammonia concentration. Three different chlorine concentrations were used with ammonia varying for each chlorine concentration.

A pH value of 7.0 was selected as an improvement of the pH of 6.5 currently implemented at the full-scale plant in order to lower the cost of caustic soda, in addition to the benefit of better bromate control. The testing

water was collected before ozonation from the full-scale plant. The water was analyzed for TOC (4.1 mg/L), bromide (73 µg/L), bromate (non-detect), calcium hardness (124 mg/L), ammonia (0.1 mg/L NH_3-N), UV-254 (0.06), and alkalinity (48 mg/L as $CaCO_3$).

Baseline conditions at pH 7.0 without any chlorine or ammonia addition and bromide spiked at 0, 100, 150, 200, and 250 µg/L and were studied first to establish the initial bromate formation without any optimization. Since the background bromide was 73 µg/L, the actual bromide concentrations were adjusted accordingly, as reflected in Table 1. The rest of the matrix varied ammonia for three distinct groups of chlorine concentrations using ratios similar to Wert et al. (2007) with bromide fixed at 273 µg/L, a number representative of the full-scale conditions during the dry season. Similarly, the initial ozone dose was selected to achieve a target CT in the range of 4 to 7 min·mg/L, typically encountered at the full-scale system.

Results and Discussion

The general relationship among bromate, bromide, and ozone demand is presented in Figure 3 based on three years of full-scale data from the Facility. The full-scale ozone contactor has internal baffles that separate the contactor into eight cells, with water going in from cell No. 1 and leaving from cell No. 8. Ozone demand is the difference between the ozone dosed and the ozone concentration in cell 5, which is typically close to non-detect. Clearly, bromate increases with either bromide concentrations or ozone demand. Ozone demand increases during high TOC and high color events (data not shown). While pH has a large effect on bromate production, it is not included in the graph because it is fixed to a tightly controlled range (6.2-6.5) to prevent bromate formation at the full-scale plant, making it difficult to see any relationship between pH and bromate formation. Before the water is treated by ozone, TOC ranges from 1-5 mg/L, cycling seasonally, with the highest range occurring during the rainy summer season and lowest during the drier winter. Flow rate also exhibits a seasonal trend, ranging from a dry season low of around 60 mgd to a wet season high of 100 mgd. Bromide conversion to bromate averages 1.8 percent during the dry season and 3 percent during the wet season.

Bromate formation in all conditions must be compared with the same CT in order to identify the best chlorine and ammonia dos-

ID (pH-NH_3-Cl_2-Br)	pH	Bromide Concentration (µg/L)	Chlorine (mg/L as Cl_2)	Ammonia (mg/L as NH_3-N)
7-0-0-200	7	273	0	0
7-0.1-.25-200	7	273	0.25	0.10
7-0.2-0.25-200	7	273	0.25	0.20
7-0.3-0.25-200	7	273	0.25	0.30
7-0.1-0.5-200	7	273	0.50	0.10
7-0.3-0.5-200	7	273	0.50	0.30
7-0.5-0.5-200	7	273	0.50	0.50
7-0.15-0.75-200	7	273	0.75	0.15
7-0.3-0.75-200	7	273	0.75	0.30
7-0.45-0.75-200	7	273	0.75	0.45
7-0.6-0.75-200	7	273	0.75	0.60

Table 1. Experimental Matrix Used for Bromide Concentrations of 273 µg/L and pH 7.
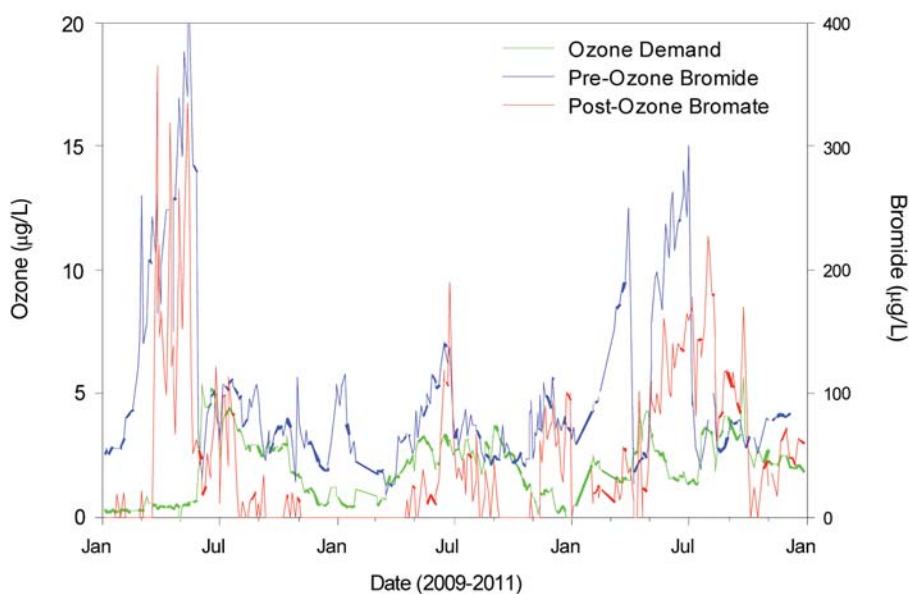
Figure 3. Full-Scale Ozone Demand, Bromide, and Bromate at the Facility: 2009-2011.

ID	Bromate	CT
7-0-0-200 #1	6.18	3.79
7-0-0-200 #2	5.23	5.26
7-0-0-200 #3	4.73	3.48
7-0-0-200 #4	7.42	6.36
7-0-0-200 #5	10.54	8.50

Adj Bromate =
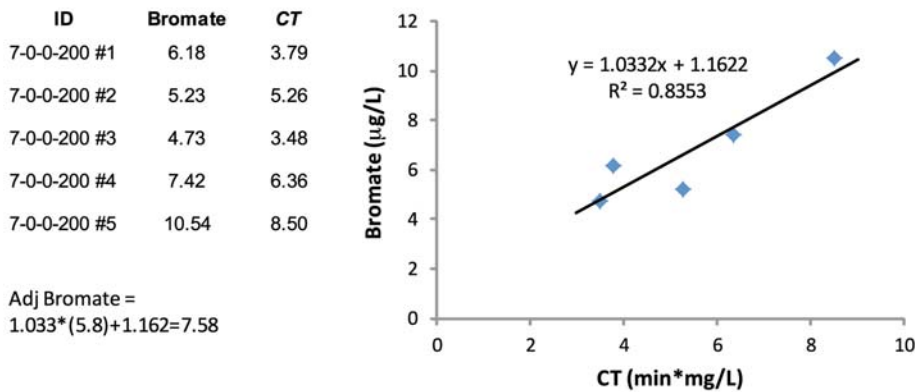1.033*(5.8)+1.162=7.58

$y = 1.0332x + 1.1622$
$R^2 = 0.8353$

Figure 4. Example of Adjusted Bromate Calculation.

| Table 2. Bromate Formation Under Various CT Values in Bench-Scale Experiments.						
ID (pH-NH$_3$-Cl$_2$-Br)	pH	Final Bromide Conc (μg/L)	Chlorine (mg/L as Cl$_2$)	Ammonia (mg/L as NH$_3$-N)	CT Adjusted Bromate (μg/L)	CT (min*mg/L)
7-0-0-200	7	273	0	0	7.58	5.8
7-0.1-.25-200	7	273	0.25	0.10	3.66	5.3
7-0.2-0.25-200	7	273	0.25	0.20	2.81	5.3
7-0.3-0.25-200	7	273	0.25	0.30	2.36	5.3
7-0.1-0.5-200	7	273	0.50	0.10	3.27	6.2
7-0.3-0.5-200	7	273	0.50	0.30	3.53	6.2
7-0.5-0.5-200	7	273	0.50	0.50	3.18	6.2
7-0.15-0.75-200	7	273	0.75	0.15	2.90	6.0
7-0.3-0.75-200	7	273	0.75	0.30	1.05	5.0
7-0.45-0.75-200	7	273	0.75	0.45	1.09	6.8
7-0.6-0.75-200	7	273	0.75	0.60	1.60	5.9
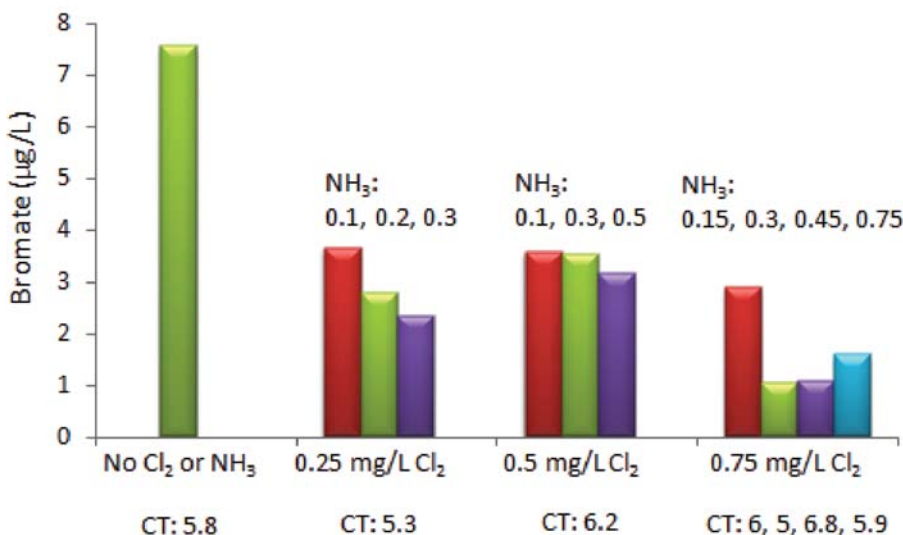
Figure 5. Bromate Formation at Varying NH$_3$:Cl$_2$ Ratios.

ing for bromate control. However, the actual CT achieved in the bench-scale experiments could be different depending on the ozone decay kinetics and initial ozone stock solution. To compare results between replications, bromate values had to be normalized using CT with linear regressions. An example of this process is illustrated in Figure 4. A CT inside the range of CTs for each replicate was used to predict the bromate at a target CT that can easily be compared to other sets. All the normalized bromate formation is presented in Table 2 as "CT-adjusted bromate" with its associated CT used for interpolation. Note that only interpolation was used, but not the extrapolation, because the relationship between CT and bromate formation is nonlinear, and thus extrapolation is inaccurate. As a result, only interpolation was used and limited by the CT range achieved under each condition and bromate numbers could not be always adjusted to the same CT.

After adjusting each data set to a target CT within the range, a CT-adjusted bromate value can be calculated; all the variations of the experiment can then be compared, to a certain extent. The groups at 0.25 mg/L and 0.5 mg/L Cl$_2$ all had CTs within a certain range, and were able to be adjusted to 5.3 min·mg/L and 6.2 min·mg/L, respectively. The data for 0.75 mg/L Cl$_2$ did not have consistent enough CTs to allow for this, so a CT for each condition had to be used. A higher CT leads to a higher bromate concentration. Because of this, set ID # 7-0.45-0.75-200 in Table 2 is likely a significantly better control measure compared to set ID# 7-0.3-0.75-200 due the nearly identical bromate value, but has a significantly higher CT value.

The least effective ammonia-chlorine dosing regimen (ID# 7-0.1-.25-200) resulted in an over 50 percent reduction in bromate formation. The most effective (the last three in Table 2) resulted in an 86 percent reduction in bromate formation. At typical plant conditions, this represents a near-zero risk of ever exceeding the MCL for bromate. Overall, having ammonia in excess causes an improvement in bromate prevention throughout all conditions, except when chlorine was dosed at 0.75 mg/L where no additional benefit was observed with 0.6 mg/L ammonia. The best bromate formation reduction was achieved when chlorine was dosed at 0.75 mg/L and ammonia at 0.45 mg/L (Figure 5).

The optimal chlorine and ammonia doses for bromate control presented is somewhat different from the results presented by Wert et al. (2007), apparently due to the difference in water quality parameters between the Col-

orado River in Nevada and Hillsborough River in Florida. The Wert study utilized Lake Mead water with the following characteristics: alkalinity (137 mg/L), total hardness (288 mg/L $CaCO_3$), TOC (2.59 mg/L), and pH (7.95). The optimal ratio found in that study was 0.5 mg/L NH_3 to 0.5 mg/L Cl_2, which was the highest concentration of both used in the study. This ratio produced less than 1 μg/L bromate at a CT of 4.41 min·mg/L. For comparison, the best ratio in this study is 0.45 mg/L NH_3 to 0.75 mg/L Cl_2, which produced 1.09 μg/L bromate at a CT of 6.8 min·mg/L. The results in this study demonstrated again the impact of source water and the necessity of running bench- or pilot-scale studies before full-scale implementation. However, results in Figure 5 do suggest that any of the chlorine and ammonia combinations investigated in this study would work well with at least 50 percent bromate reduction.

To determine the cost/benefit of switching to an increased ozonation pH, the buffer capacity of the water was determined by experiments (Figure 6), which was almost identical to the theoretical buffer curve. Currently, lime is used to increase the water's pH from 4.5 to 6.5 and caustic soda from 6.5 to 7.5. With the chlorine-ammonia bromate control approach, lime can be used to increase pH to 7.0 and caustic soda from 7.0 to 7.5. As a result of this alternative practice, based on Figure 6, lime usage would increase by about 21 percent of the total required pH increase, and caustic would decrease by 11 percent.

Because the Facility typically has no bromate concerns outside of the months of January-May, the decision was made to increase the ozonation pH prior to completion of the full-scale plant's ammonia and chlorine pre-ozonation dosing facilities, which will be completed in early 2014, when bromate will again be an issue. On May 22, 2012, the pH of ozonation was increased to 7.0; the change immediately resulted in cost savings in the following months. To determine the benefit of the change, costs for lime and caustic soda from the previous year were compared to the current year. Because of the bivalent nature of lime, combined with its significantly lower cost over caustic soda, the treatment plant has saved $495,500 in a four-month period compared to the same period of 2010 and 2011. The month-by-month costs can be seen in Figure 7. Once the capital improvement project is complete, allowing chlorine-ammonia approach to control bromate and ozonation occurring at pH 7.0 year round, the estimated annual chemical savings will be over $1 million.

Conclusions

Bromate control using the chlorine-ammonia process is very effective, resulting in a 50 percent reduction in bromate over the control group in the worst case and an 86 percent reduction in the best case. A ratio of around 1:2 $NH_3 : Cl_2$ with ammonia concentration of 0.45 mg/L appears to be the most effective. While the ideal ratio between chlorine and ammonia does vary and could be different for untested water quality matrices, this study has shown this approach is very tolerant. Under any of the studied conditions, bromate was reduced by at least 50 percent. This implies that if a utility doesn't have the resources to perform its own bench- or pilot-scale tests, this ratio could be directly applied and further optimized at the full-scale plant due to the efficacy of the process.

References

- Bader, H.; Hoigné, J., Determination of ozone in water by the indigo method. Water Research 1981, 15, 449-456.
- Buffle, M.-O.; Galli, S.; von Gunten, U., Enhanced bromate control during ozonation: the chlorine-ammonia process. Environmental Science & Technology 2004, 38 (19), 5187-5195.
- Chiou, C. F.; Mariñas, B. J.; Adams,, J. Q., Modifed indigo method for gaseios and aqueous ozone analysis. Ozone Science and Engineering 1995, 17(3), 329-344.
- Environmental Protection Agency, EPA Guidance Manual: Alternative Disinfectants and Oxidants. 1999, http://water.epa.gov/lawsregs/rulesregs/sdwa/mdbp/upload/ 2001_01_12_ mdbp_alter_ chapt_3.pdf.
- Environmental Protection Agency, National primary drinking water regulations: disinfectants and disinfection byproducts. Federal Register 1998, 63 (241), 69390-69476
- Haag, W. R.; Hoigne, J., Ozonation of bromide-containing waters: kinetics of formation of hypobromous acid and bromate. Environmental Science & Technology 1983, 17 (5), 261-267.
- Song, R.; Westerhoff, P.; Minear, R.; Amy, G., Bromate minimization during ozonation. Journal American Water Works Association 1997, 89(6), 69–78.
- Kurokawa, Y.; Hayashi, Y.; Maekawa, A.; Takahashi, M.; Kokubo, T., Induction of renal cell tumors in F-344 rats by oral administration of potassium bromate, a food additive. Gann 1982, 73 (2), 335-338.
- Kurokawa, Y.; Maekawa, A.; Takahashi, M.; Hayashi, Y., Toxicity and carcinogenicity of potassium bromate--a new renal carcinogen. Environmental health perspectives 1990, 87, 309-35.
- Loeb, B. L.; Thompson, C. M.; Drago, J.; Takahara, H.; Baig, S., Worldwide ozone capacity for treatment of drinking water and wastewater: a review. Ozone: Science & Engineering 2012, 34(1): 64-77.
- von Gunten, U.; Hoigne, J., Bromate formation during ozonization of bromide-containing waters: interaction of ozone and hydroxyl radical reactions. Environmental Science & Technology 1994, 28 (7), 1234-1242.
- von Gunten, U.; Oliveras, Y., Advanced Oxidation of Bromide-Containing Waters: Bromate formation mechanisms. Environmental Science & Technology 1998, 32 (1), 63-70.
- Wert, E. C.; Neemann, J. J.; Johnson, D.; Rexing, D.; Zegers, R., Pilot-scale and full-scale evaluation of the chlorine-ammonia process for bromate control during ozonation. Ozone: Science & Engineering 2007, 29 (5), 363-372. ◊
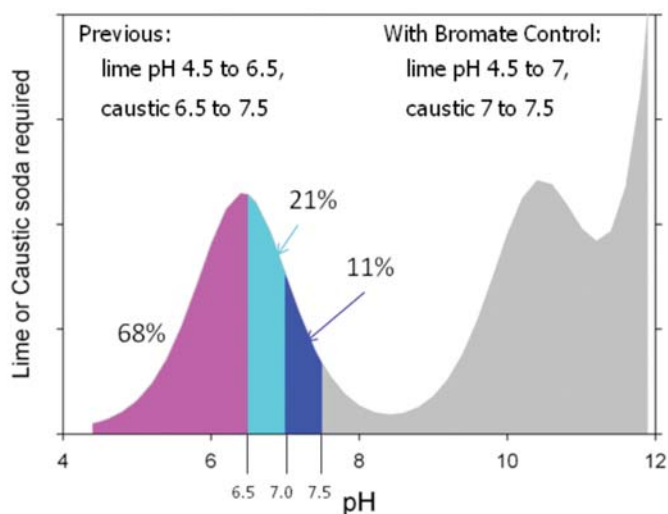
Figure 6. Buffer Capacity Curve Showing Percentages of pH Change by Lime and Caustic Soda.
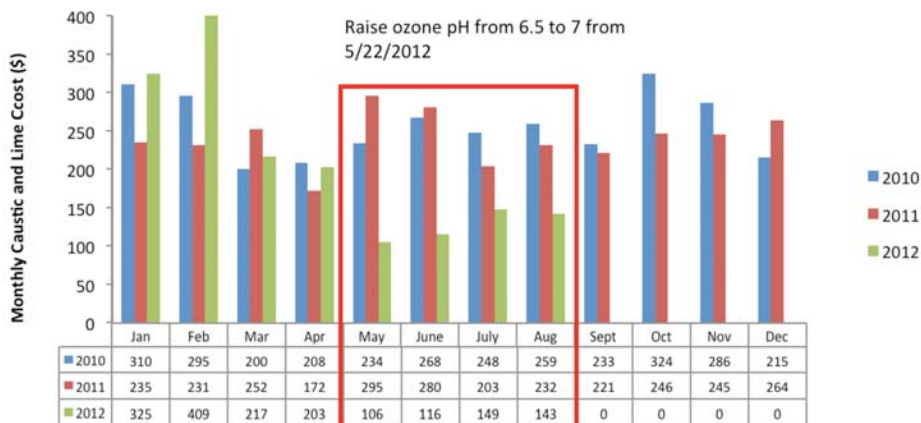

Figure 7. Combined Monthly Caustic Soda and Lime Costs at the Facility: 2010-2012.

www.fwrj.com