Using Reducing Agents to Eliminate Chlorine Dioxide and Chlorite Ion Residuals in Drinking Water

Mark H. Griese, Keith Hauser, Mona Berkemeier, and Gilbert Gordon

In an effort to determine the viability of various disinfection alternatives, the Evansville, Ind., Water and Sewer Utility is engaged in a pilot-plant investigation to compare chlorine dioxide and ozone pretreatment. As a result of increased speculation that the total residual concentration of chlorine dioxide and its inorganic species will soon be regulated, supplemental studies were performed to determine the effectiveness of various reducing agents for reducing or eliminating chlorine dioxide and chlorite ion residuals in finished water. The effectiveness of ferrous iron in achieving the desired reductions is examined along with promising results obtained with sodium thiosulfate. Specific difficulties encountered with the sulfur dioxide–sulfite ion method of chlorite ion reduction are also presented.

Interest within the water industry regarding chlorine dioxide (ClO_2) as an alternative disinfectant increased significantly with the promulgation of the 0.10-mg/L maximum contaminant level (MCL) for total trihalomethanes (TTHMs) in November 1979. Recommended by the US Environmental Protection Agency (USEPA) in 1983 as a suitable treatment technology for controlling THMs,[1] ClO_2 use in US plants was estimated to have tripled by 1986.[2]

Previous research conducted by the Evansville, Ind., Water and Sewer Utility confirmed the effectiveness of ClO_2 treatment for reducing THM formation.[3] That research resulted in a shift away from the utility's prechlorination practices and the implementation of raw water disinfection–oxidation using ClO_2. For the past seven years, this treatment alteration has proved effective in maintaining Evansville's TTHM level well below the promulgated MCL.

In the last several years, however, the role of ClO_2 in future water treatment applications has become increasingly uncertain. Numerous studies[4,5] have focused on the potential toxicological effects associated with the use of ClO_2 and the resultant inorganic by-product species of chlorite (ClO_2^-) and chlorate (ClO_3^-) ions. Because they are included on the drinking water priority list for disinfectants and disinfection by-products,[6] all three substances are targeted for future regulatory consideration by the USEPA. Their potential regulation, coupled with recent results published by Hoehn et al[7] that conclude that utilization of this alternative disinfectant may actually promote offensive odors at the consumer's tap, means that the acceptance of ClO_2 as a way of addressing more stringent disinfection by-product regulations appears doubtful.
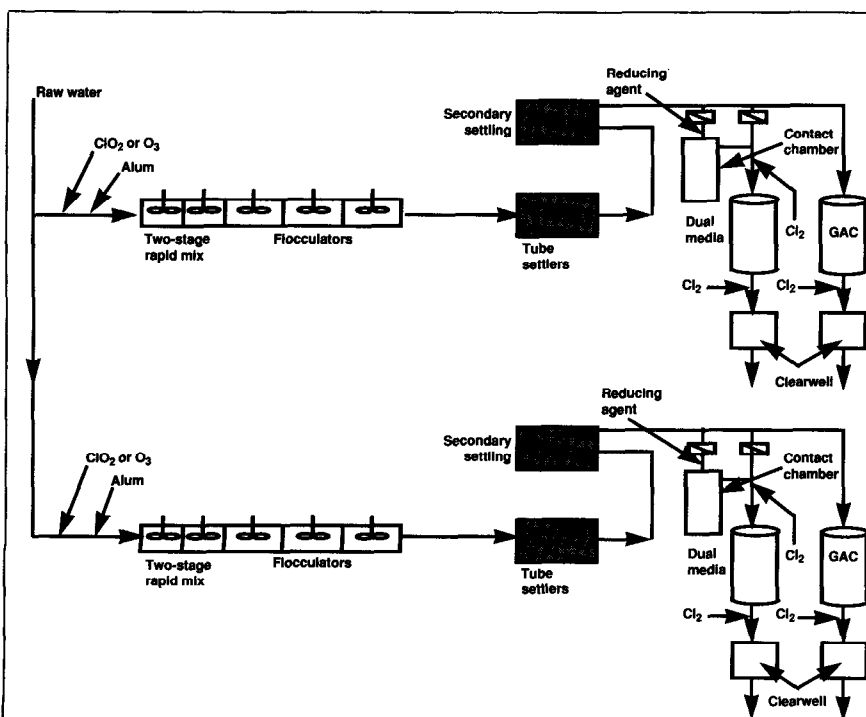

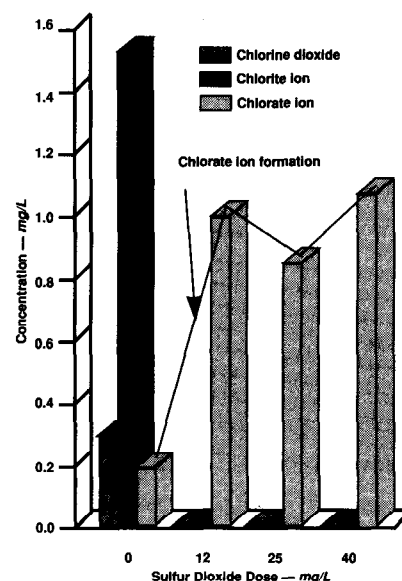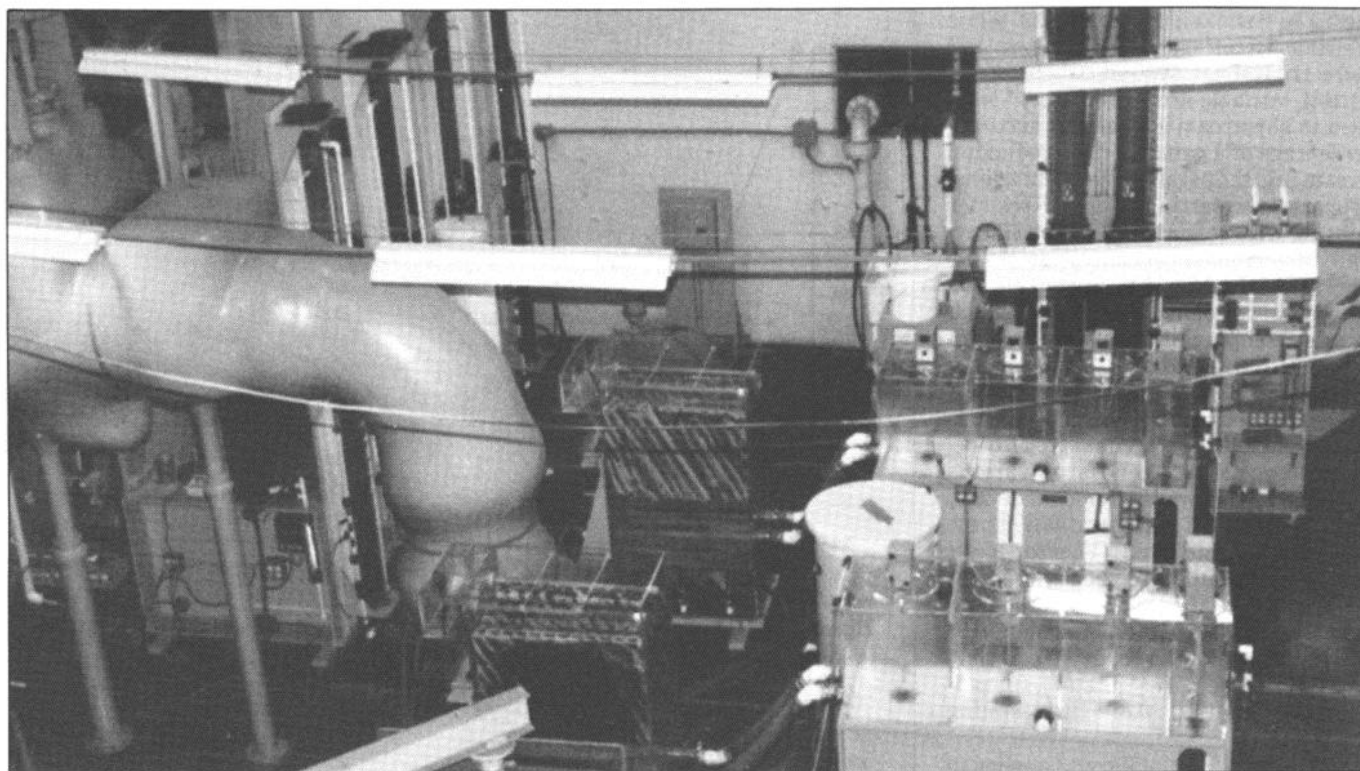**Figure 1.** Flow schematic of Evansville, Ind., pilot plant

Figure 2. Effect of applied sulfur dioxide on oxidant residuals in pilot-plant water treatment with chlorine dioxide

Additional research flexibility is provided by parallel treatment trains in Evansville's pilot plant.

To address these issues and to obtain data concerning those by-products associated with other disinfection alternatives, the Evansville utility initiated the current pilot-plant investigation.

Pilot-plant design

The majority of samples examined in the bench-scale phase were collected from a 2-gpm pilot plant constructed for the Evansville project (Figure 1). Designed and built by a contracted consulting firm,* the pilot plant closely simulates Evansville's conventional treatment train while providing the additional flexibility associated with parallel treatment trains, ozonation capabilities, and multiple filtration columns.

Conventional treatment. The conventional processes of coagulation and flocculation are accomplished in two parallel treatment modules. Constructed entirely of clear acrylic, each module contains two rapid-mix compartments and three flocculation chambers. Injectors and static mixers are provided prior to each of the rapid-mix compartments for chemical pretreatment. Independent mixing in each of the five basins permits tapered flocculation.

Sedimentation is accomplished by a two-stage process that incorporates both tube settlers and conventional gravity settling. The resultant 2–5-ntu settled water turbidities are representative of those produced in Evansville's full-scale treatment plant.

Although not utilized in the bench-scale portion of the project, four individual 4-in.-diameter filter columns complete the conventional treatment scheme of the pilot-plant system. Multiple filtration capability permits parallel testing of various filter media and comparisons of disinfection by-product removal, including that by granular activated carbon (GAC).

Application of chlorine dioxide. Previous reports[2,8-12] have repeatedly emphasized the importance of optimized generation and effective application of ClO_2 in minimizing finished water ClO_2^- and ClO_3^- residual concentrations. To address these issues, a method was designed to provide an accurate and effective ClO_2 dosage (approximately 0–6

TABLE 1
Results of sulfur dioxide application to water treated with various chlorine dioxide dosages

ClO_2 Dose mg/L	Initial Oxidant Residuals—mg/L				Sulfur Dioxide Dose mg/L	Contact Time min	Final Oxidant Residuals—mg/L			
	ClO_2	ClO_2^-	ClO_3^{-*}	Total			ClO_2	ClO_2^-	ClO_3^-	Total
1.75	<0.1	1.05	0.17	<1.32	25	30	0	0	0.32	0.32
2.00	0	1.50	0.26	1.76	25	30	0	0	0.41	0.41
2.25	0.15	1.75	0.26	2.16	25	30	0	0	0.64	0.64
2.50	0.31	1.55	0.26	2.12	25	30	0	0	0.98	0.98

*Initial ClO_3^- residuals result from ClO_3^- present in the sodium chlorite feed stock and from the ClO_2 generation process.

TABLE 2
Effect of contact time on sodium thiosulfate reduction of chlorite ion in drinking water

Sample	Thiosulfate Dose mg/L	Final Adjusted pH	Residual Ion	Residual Concentration* mg/L		
				0-min Contact	30-min Contact	60-min Contact
1	15	6.3	ClO_2^-	0.90	0.81	0.56
			ClO_3^-	0.27	0.31	0.29
2	20	6.0	ClO_2^-	0.93	0.82	0.11
			ClO_3^-	0.23	0.30	0.26
3	25	6.0	ClO_2^-	1.19	0.25	0
			ClO_3^-	0.23	0.35	0.35

*Uncertainties in the ClO_2^- and ClO_3^- measurements are estimated to be ±0.02 mg/L.

*Camp Dresser McKee, Louisville, Ky.

mg/L) to Evansville's pilot plant while offering the efficiency of a larger and more traditional system. Chemical-resistant, variable-area flowmeters* were used to slipstream a small but accurate percentage of a generator's† production stream into the parallel treatment trains. Proper flow settings (millilitres per minute) were made based on the analytically determined concentration of this stream and the desired treatment dosage. A minimal residence time in the system ensured comparability between the generator effluent and the quality of the ClO_2 at the point of application.

Addition of reducing agents. Three kinds of experiments were conducted to determine the effectiveness of various reducing agents for the removal of ClO_2 and ClO_2^- residual concentrations. These experiments included (1) pilot-plant studies with sulfur dioxide (SO_2),‡ (2) bench-scale studies with SO_2, sodium metabisulfite,§ and sodium thiosulfate;** and (3) jar tests with reduced iron chloride (13.4 percent Fe^{2+} [3.2 M], 0.1 percent Fe^{3+} [<0.04 M], >0.8 M HCl resulting in pH < 0).††

Gaseous sulfur dioxide was applied in the pilot plant by use of an eductor-induced sulfonator system‡‡ and precision rotometers.§§ Not unlike the slip-streaming technique employed with ClO_2, this system permitted accurate application of various SO_2 dosages based on pound-per-day feed rates and proper millilitre-per-minute settings. To provide adequate time for complete ClO_2 and ClO_2^- removal, contact chambers were designed within the pilot-plant treatment scheme. Kinetic data recently reported by Gordon and co-workers[12] were used as the basis for the chamber design.

When difficulties were encountered during the pilot-plant studies of SO_2 reduction of ClO_2^- (discussed later), the experimental procedure was changed from pilot-plant studies to bench-scale and jar test experiments. This shift in procedure provided a high degree of treatment flexibility and permitted many more experiments to be performed within a given time period.

Freshly prepared stock solutions of sodium metabisulfite (1,500 mg/L) and sodium thiosulfate (2,500 mg/L) were used for the bench-scale studies. The preliminary, reduced-iron studies (discussed later) were carried out as jar tests because of concerns about potential changes in pH as a result of ClO_2^- reduction, air oxidation, and floc formation. The jar tests were performed using 1,000-mL samples collected from the pilot plant and the reduced iron chloride was applied using a freshly prepared stock solution (3,000 mg/L). The samples were mixed at 100 rpm for 20 s followed by continued mixing at 20 rpm for the total contact time desired. Clearly, the jar tests provided maximum reproduc-
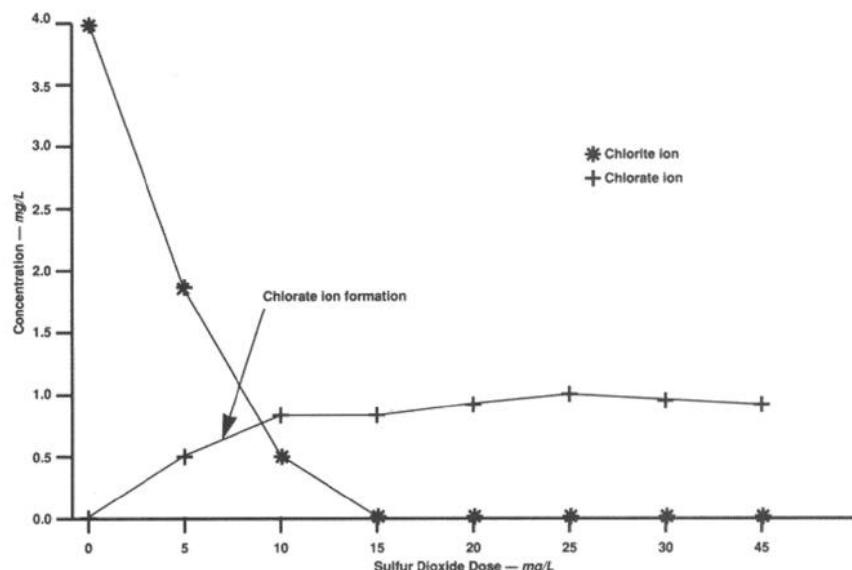

Figure 3. Effect of applied sulfur dioxide on a 4.0 - mg/L sodium chlorite standard in laboratory water
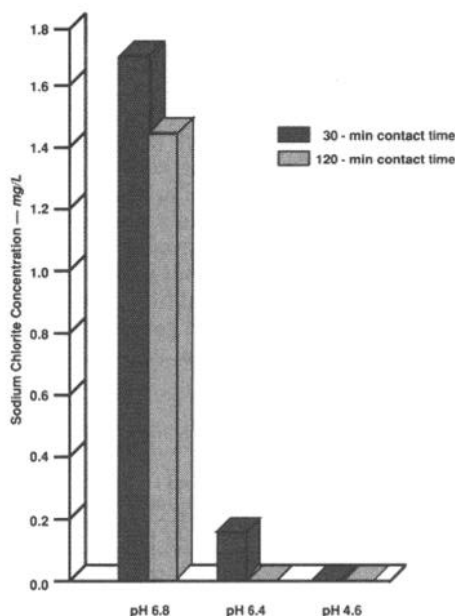

Figure 5. Sodium thiosulfate reduction of a 2.0 - mg/L sodium chlorite standard in laboratory water (thiosulfate dose — 10 mg/L)
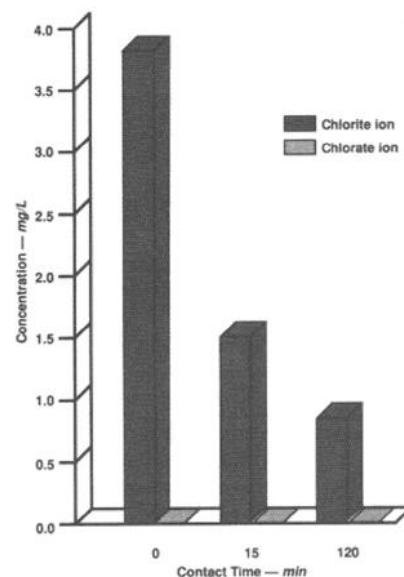
Figure 6. Sodium thiosulfate reduction of a 4.0 - mg/L sodium chlorite standard in laboratory water (thiosulfate dose — 40 mg/L; adjusted final pH — 6.1)

ibility under conditions similar to the actual operating conditions anticipated at Evansville.

Analytical procedures

Bench-scale analyses were performed using samples collected from the effluents of the pilot-plant secondary settling basins after approximately 200 min of ClO_2 contact time or from standard samples of sodium chlorite*** dissolved in laboratory water.††† The grab samples from the pilot plant were analyzed immediately for residual ClO_2, ClO_2^-,

and ClO_3^-; treated with the respective reducing agent for specific contact periods; and then reanalyzed for the same parameters. Any additional treatment
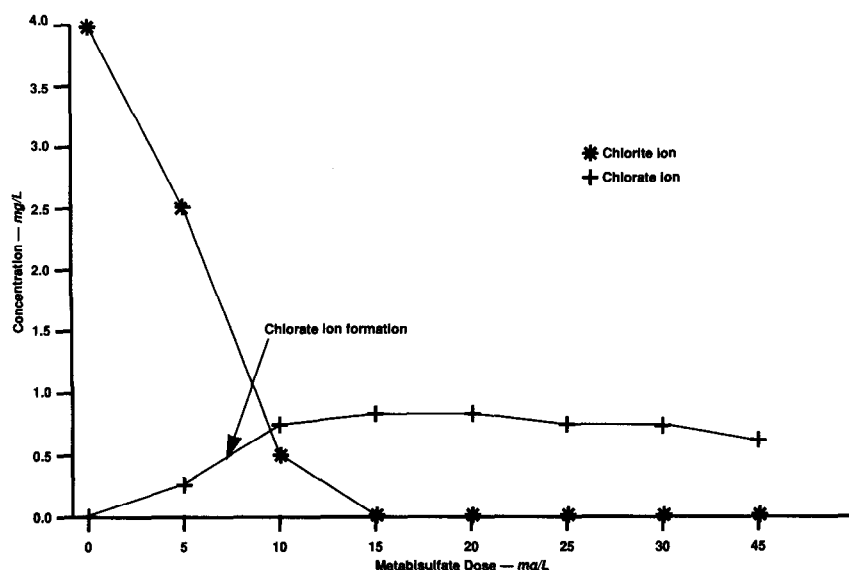
Figure 4. Effect of applied metabisulfate on a 4.0 - mg/L sodium chlorite standard in laboratory water

TABLE 3
Ferrous chloride reduction of chlorine dioxide and chlorite ion

ClO_2 Dose mg/L	Initial Oxidant Residuals—mg/L				Ferrous Chloride Dose mg/L	Contact Time min	Final Oxidant Residuals—mg/L			
	ClO_2	ClO_2^-	ClO_3^-	Total			ClO_2	ClO_2^-	ClO_3^-	Total
1.5	0	0.85	0.14	0.99	6.0	30	0	0	0.14	0.14
					5.0	60	0	0.06	0.14	0.20
2.0	<0.1	0.97	0.14	<1.21	9.0	30	0	0	0.13	0.13
					8.0	60	0	0	0.14	0.14
2.5	0.34	1.16	0.21	1.71	12.0	30	0	0	0.21	0.21
					11.0	60	0	0	0.21	0.21
3.0	0.41	1.50	0.22	2.13	15.0	30	0	0	0.25	0.25
					13.0	60	0	0	0.26	0.26
3.5	0.73	1.82	0.31	2.86	17.0	30	0	0	0.32	0.32
					16.0	30	0	0.13	0.36	0.49
4.0	0.79	1.83	0.32	2.94	18.0	30	0	0	0.36	0.36
					17.0	60	0	0.06	0.34	0.40

considerations unique to the individual reducing agents are discussed later in this article.

Chlorine dioxide residuals were measured by using the amperometric method developed and described by Aieta et al.[8,13] Phenylarsine oxide was used as the titrant, and samples were purged using high-purity helium. Care was taken to prevent photolytic decomposition during this procedure by purging all samples in light-protective glassware.*

The residual concentrations of ClO_2^- and ClO_3^- were determined by ion chromatography with suppressed conductivity detection.† This method[14] is gaining acceptance as an attractive alternative to the titrimetric and colorimetric methods[12] predominantly used to test for these ions. The viability of this procedure for monitoring ClO_2^- and ClO_3^- in water treatment applications was reported in a recent study conducted by Thompson et al[15] and others.[16,17]

Except for the utilization of a more concentrated eluant (1.80 mM sodium carbonate and 1.70 mM sodium bicarbonate) and a smaller sample loop (25 μL), the isocratic elution procedures described by Pfaff and Brockhoff[14] were employed throughout the study. The increased eluant concentration provided a shorter analysis period without the interference of coelution, and the reduced sample-loop size provided excellent sensitivity while reducing the possibility of column overload. A calibration curve for each ion was generated by the analysis of four calibration standards containing both analytes. This calibration curve was verified daily by measurement of the calibration standard most representative of the concentrations being examined. A reagent water blank was also analyzed daily in order to ensure that no interference existed in the analytical system.

Results and discussion

Sulfur dioxide-sulfite ion. Recently, Gordon and co-workers[12] published a method for minimizing the ClO_2^- in drinking water. Based on their bench studies of the reactions in laboratory water, the authors reported that sulfur dioxide-sulfite ion (SO_2–SO_3^{2-}) is a potential agent for removing the ClO_2^- that forms as a result of ClO_2 treatment. Specifically, these investigators proposed that after the oxidant demand had been met in a water treatment facility where ClO_2 is used, excess SO_2–SO_3^{2-} could be added to remove any residual ClO_2 and ClO_2^-. Removal of the excess SO_2–SO_3^{2-} was achieved with postchlorination. This latter reaction was shown to be instantaneous[12,18] and, thus, would eliminate the potential health hazards that are associated with the presence of SO_2.

In view of these reported results, Evansville initiated bench-scale application of SO_2 to water samples treated with a variety of ClO_2 dosages. Representative data of this examination are given in Table 1.

Unexpectedly, the results of this phase of the study indicated that oxygenated water supplies containing ClO_2^- formed ClO_3^- when treated with SO_2. Although full reduction of residual ClO_2 and ClO_2^- was achieved, a marked increase in ClO_3^- concentration was consistently observed. This increase was independent of the SO_2–SO_3^{2-} dosage after the oxidant demand in the water samples had been met (Figure 2).

Suzuki and Gordon[19] have reported that during the reduction of ClO_2 with sulfur(IV) in the pH range 8.7–11.5, some ClO_3^- is formed. No experiments were reported at lower pH levels, however. The ClO_2^- formation observed at the Evansville utility in the pH range 4.0–8.5 may be explained by an examination of the two different mechanisms proposed for the reduction of ClO_2 by SO_2–SO_3^{2-}
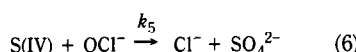
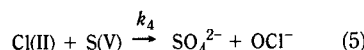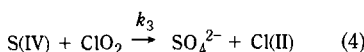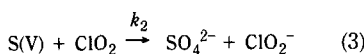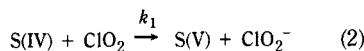---

*VWR Scientific Co., Chicago, Ill.
†Model 2000i, Dionex Corp., Sunnyvale, Calif.

[shown as sulfur (IV) in the following equations].

The first of these mechanisms involves discrete one-electron transfer processes. The overall reaction

$$2ClO_2 + S(IV) + H_2O \rightarrow 2ClO_2^- + SO_4^{2-} + 2H^+ \quad (1)$$
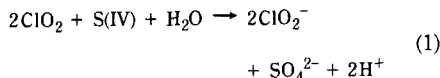
arises from the following simple electron transfer steps:

$$S(IV) + ClO_2 \xrightarrow{k_1} S(V) + ClO_2^- \quad (2)$$

$$S(V) + ClO_2 \xrightarrow{k_2} SO_4^{2-} + ClO_2^- \quad (3)$$

$$S(IV) + ClO_2 \xrightarrow{k_3} SO_4^{2-} + Cl(II) \quad (4)$$

$$Cl(II) + S(V) \xrightarrow{k_4} SO_4^{2-} + OCl^- \quad (5)$$

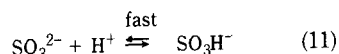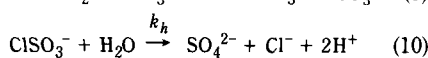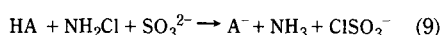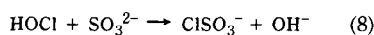$$S(IV) + OCl^- \xrightarrow{k_5} Cl^- + SO_4^{2-} \quad (6)$$

Sulfur(V) is formed in reaction 2 and terminated by reactions 3 and 5. The chlorine(II) radical is formed via a two-electron transfer process (Eq 4) and is terminated by reaction 5. The small ClO_3^- by-product formed is produced by an alternative termination of the chlorine(II) radical by reaction with ClO_2 or the ClO_2^- intermediate. The formation of ClO_3^- is given by the overall reaction in which both ClO_3^- and chloride ion are produced directly from ClO_2.

$$2ClO_2 + 2S(IV) + H_2O \rightarrow ClO_3^- + 2SO_4^{2-} + Cl^- + 2H^+ \quad (7)$$
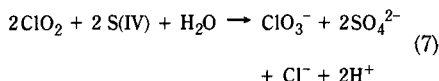
In other words, Eq 7 can be considered as an apparent disproportionation of ClO_2 accelerated by the presence of sulfur(IV), although the uncatalyzed disproportionation reaction in basic solution produces only ClO_2^- and ClO_3^-.

Another way of viewing the mechanism involves sulfur(IV)–oxychlorine species intermediates. There is considerable evidence in the literature that this type of species involves reactions of sulfur(IV) as a reductant and independently involves oxidation–reduction reactions of both ClO_2^- and ClO_2. More recently, Margerum and co-workers[18] have shown that similar intermediate species are required to account for the reduction of chlorine (Cl_2), hypochlorous acid (HOCl), hypochlorite ion (OCl^-), and the various inorganic chloramines. A typical set of reactions showing the formation of the chlorine–sulfur (IV)-containing intermediates is shown.

$$HOCl + SO_3^{2-} \rightarrow ClSO_3^- + OH^- \quad (8)$$

$$HA + NH_2Cl + SO_3^{2-} \rightarrow A^- + NH_3 + ClSO_3^- \quad (9)$$

$$ClSO_3^- + H_2O \xrightarrow{k_h} SO_4^{2-} + Cl^- + 2H^+ \quad (10)$$

$$SO_3^{2-} + H^+ \overset{fast}{\rightleftharpoons} SO_3H^- \quad (11)$$

$$CH_3NCl_2 + SO_3^{2-} + H_2O \xrightarrow{k_1} CH_3NHCl + ClSO_3^- + OH^- \quad (12)$$
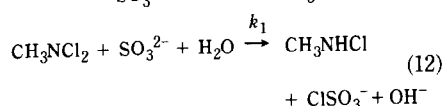
In this context, it should be noted that in the absence of oxygen, the overall rate of reduction of ClO_2^- by sulfur(IV) is reported by Gordon and co-workers[12] to be second order in sulfur(IV) species and first order in ClO_2^-. An increase in the rate of reaction brought about by hydrogen ion with a protonated sulfur(IV)–ClO_2^- intermediate of the composition $[O_2Cl - SO_3H]^{2-}$ is also reported.

In the absence of oxygen, this intermediate reacts directly with additional sulfur(IV) to produce sulfate and chloride ions. Gordon and co-workers[12] have shown that in the absence of oxygen, this mechanism totally accounts for the overall reaction rate and products and that no ClO_3^- is formed. However, as noted in Figure 2, the experiments reported here clearly show that in the presence of oxygen, ClO_3^- is also formed. The sulfur(IV)–ClO_2^- intermediate can be either further reduced by sulfur(IV) (resulting in the formation of chloride and sulfate ions) or oxidized by dissolved oxygen with the subsequent formation of ClO_3^- and sulfate ion. This oxidation process and ClO_3^- formation was further substantiated by $SO_2–SO_3^{2-}$ treatment of a sodium chlorite standard prepared with laboratory water (Figure 3).

The effect of applied aqueous sodium metabisulfite on 4.0-mg/L sodium chlorite standard solutions prepared in laboratory water is shown in Figure 4. The results with sodium metabisulfite were identical to those obtained with SO_2, thus indicating that equilibrium between the various sulfur species is achieved prior to the formation of the intermediates and their reaction to form chlorate.

Clearly, these reactions are complicated, and several different pathways result in both the reduction of ClO_2^- to chloride ion and the formation of ClO_3^- as an unwanted inorganic by-product. Because the removal of dissolved oxygen would be impractical under normal water treatment conditions, the potential benefits associated with the use of $SO_2–SO_3^{2-}$ for the reduction of disinfection by-products appear to be severely limited.

Sodium thiosulfate. Additional bench-scale studies were performed in order to evaluate sodium thiosulfate as a reductant for ClO_2^-. As is evident from the data presented in Table 2 and Figure 5, the degree of ClO_2^- reduction achieved with sodium thiosulfate depends greatly on sample pH and available contact time. These results clearly demonstrate the effective removal of ClO_2^- with little or no ClO_3^- formation.
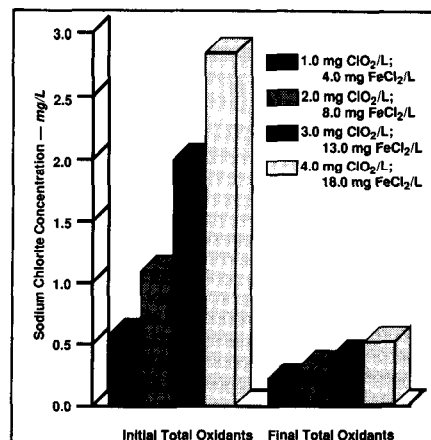

Figure 7. Total oxidant reduction achieved utilizing ferrous chloride treatment in pilot plant water *(FeCl₂ dosages apply only to final oxidants data)*
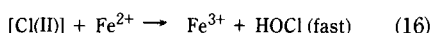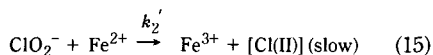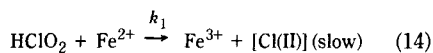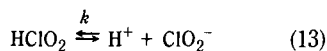
It should be noted that thiosulfate ion is less effective than SO_2 in forming mixed halogen–sulfur intermediates—but rather undergoes two-electron transfer reactions with the formation of dithionate and tetrathionate ion as intermediate species. In this case, the reaction appears to proceed through the chlorine(I), (HOCl), and dithionate ($SO_2O_3^{4-}$) species. Presumably, the final products are sulfate ion and chloride ion. Dissolved oxygen does not appear to interfere in these reactions.

Although the required dosages may make this reducing agent impractical for elevated ClO_2 concentrations (Figure 6), these results indicate that thiosulfate ion would be preferred over $SO_2–SO_3^{2-}$ or sodium metabisulfite for the reduction of ClO_2^- residuals without undesirable ClO_3^- formation.

Ferrous iron. A 1972 article by Ondrus and Gordon[20] reported the reduction of ClO_2^- by reduced iron (Fe^{2+}) under slightly acidic conditions. More recently, Aieta and co-workers[21] proposed that reduced iron might well be effective in the removal of ClO_2^- following the treatment of drinking water with ClO_2. Thus, a series of experiments was initiated to determine the effectiveness of reduced iron for eliminating unwanted ClO_2 and ClO_2^- residuals.

Initial and final oxidant levels were monitored after the samples were dosed with varied concentrations of ClO_2 (Table 3). The final total oxidant concentrations shown in Figure 7 were due almost exclusively to initial ClO_3^- concentrations originating from the ClO_2 stock solution. Chlorate ion concentrations were unaffected by the ferrous iron treatment. Only insignificant increases in ClO_3^- concentration were noted as a result of this treatment process.

The results reported here are readily explained in terms of the mechanism proposed by Ondrus and Gordon in 1972:

$$\text{HClO}_2 \underset{k}{\overset{k}{\rightleftharpoons}} \text{H}^+ + \text{ClO}_2^- \qquad (13)$$

$$\text{HClO}_2 + \text{Fe}^{2+} \overset{k_1}{\rightarrow} \text{Fe}^{3+} + [\text{Cl(II)}]\,(\text{slow}) \qquad (14)$$

$$\text{ClO}_2^- + \text{Fe}^{2+} \overset{k_2'}{\rightarrow} \text{Fe}^{3+} + [\text{Cl(II)}]\,(\text{slow}) \qquad (15)$$

$$[\text{Cl(II)}] + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{HOCl}\,(\text{fast}) \qquad (16)$$

The fate of the product HOCl is in the continued reaction with iron(II) and the formation of iron(III). Additional support for this explanation comes from comparison with a rate law,[20] which predicts that iron(II) at pH 6 should quantitatively remove ClO_2^- within minutes. This is supported by additional analyses performed in Evansville, which indicate that total removal is usually achieved in less than 15 min using a tenfold weight-to-weight excess of reduced iron.

Research in progress

Pilot-plant studies are being conducted to further investigate the use of iron(II) for the elimination of residual ClO_2 and ClO_2^-. Attention is being focused on the optimization of all applicable unit processes and the prefilter oxidation and subsequent removal of any remaining soluble iron. The impact of this removal process on filter head loss, filter effluent turbidity, and filter run length is also being examined.

Future phases of the project will include a comparative evaluation of GAC and iron(II) for the removal of ClO_2 and its inorganic species. Also examined will be a direct comparison of the ClO_2^-–iron(II) method of treatment with a treatment system using ozonation. Compounds and surrogates that will be evaluated during this phase of the project will include trihalomethanes, haloacetonitriles, haloacetic acids, chloral hydrate, chloropicrin, chloropropanone, total organic halide, total organic carbon, aldehydes, and ketones.

Summary and conclusion

The development of an economically feasible method of minimizing the residual oxidant level in drinking water treated with ClO_2 could significantly increase the viability of this alternative disinfectant as a means of addressing future disinfection by-product regulations. The authors used various methods to thoroughly investigate the application of a variety of reducing agents to water pretreated with ClO_2.

The SO_2–SO_3^{2-} method of ClO_2^- reduction produced unacceptable levels of ClO_3^- in oxygenated water. Although the SO_2–SO_3^{2-} could completely reduce all of the residual ClO_2 and ClO_2^-, ClO_3^- concentrations >1.0 mg/L were often produced. Experiments with sodium metabisulfite as the reducing agent showed similar results.

Sodium thiosulfate as a reducing agent for ClO_2^- appears to be unaffected by the presence of dissolved oxygen but is highly dependent on pH and contact time. The results indicated only minimal ClO_3^- formation. The use of this reducing agent substantially diminished ClO_2 and ClO_2^- residuals at pH values in the range of 4.5 to 6.5.

The utilization of ferrous iron appears to be extremely effective for removing undesirable ClO_2 and ClO_2^- residuals in finished water. Both oxidants were eliminated from the water supply in minutes at pH 6.0–7.0, and preliminary results indicate that excess reductant may be easily controlled by prefilter chlorination. Coupled with control of ClO_3^- formation by optimizing ClO_2 generator efficiency, the use of ferrous iron following ClO_2 treatment will greatly minimize residual oxidant levels in the finished water.

References

1. *Fed. Reg.*, 48:40:8406 (Feb. 28, 1983).
2. AIETA, E.M. & BERG, J.D. A Review of Chlorine Dioxide in Drinking Water Treatment. *Jour. AWWA*, 78:6:62 (June 1986).
3. LYKINS, B.W. JR. & GRIESE, M.H. Using Chlorine Dioxide for Trihalomethane Control. *Jour. AWWA*, 78:6:88 (June 1986).
4. BULL, R.J. Toxicological Problems Associated With Alternative Methods of Disinfection. *Jour. AWWA*, 74:12:642 (Dec. 1982).
5. CONDIE, L.W. Toxicological Problems Associated With Chlorine Dioxide. *Jour. AWWA*, 78:6:73 (June 1986).
6. *Fed. Reg.*, 53:14:1892 (Jan. 22, 1988).
7. HOEHN, R.C. ET AL. Household Odors Associated With the Use of Chlorine Dioxide. *Jour. AWWA*, 82:4:166 (Apr. 1990).
8. AIETA, E.M.; ROBERTS, P.V.; & HERNANDEZ, M. Determination of Chlorine Dioxide, Chlorine, Chlorite, and Chlorate in Water. *Jour. AWWA*, 76:1:64 (Jan. 1984).
9. MASSCHELEIN, W.J. Experience With Chlorine Dioxide in Brussels: Generation of Chlorine Dioxide. *Jour. AWWA*, 76:1:70 (Jan. 1984).
10. LAUER, W.C.; LOHMAN, S.R.; & ROGERS, S.E. Experience With Chlorine Dioxide at Denver's Reuse Plant. *Jour. AWWA*, 78:6:79 (June 1986).
11. GATES, D. Improvements in Chlorine Dioxide Use: A Two-Step Method for Determining Residual Oxidants in the Presence of Other Chlorine Species in Finished Water. Proc. 1988 AWWA WQTC, St. Louis, Mo.
12. GORDON, G. ET AL. Minimizing Chlorite and Chlorate Ions in Drinking Water Treated With Chlorine Dioxide. *Jour. AWWA*, 82:4:160 (Apr. 1990).
13. *Standard Methods for the Examination of Water and Wastewater*. APHA, AWWA, and WPCF. Washington, D.C. (17th ed., 1989).
14. PFAFF, J.D. & BROCKHOFF, C.A. Determining Inorganic Disinfection By-products by Ion Chromatography. *Jour. AWWA*, 82:4:160 (Apr. 1990).
15. THOMPSON, A.L. ET AL. Chlorite and Chlorate Residuals in the Distribution System. Proc. 1988 AWWA WQTC, St. Louis, Mo.
16. JOYCE, R.J. & SCHEIN, A. IC: A Powerful Analytical Technique for Environmental Laboratories. *Amer. Envir. Lab.* (Nov. 1989).
17. PFAFF, J.D.; BROCKHOFF, C.A.; & O'DELL, J.W. Method 300.0: The Determination of Inorganic Anions in Water by Ion Chromatography. EMSL, USEPA (Dec. 1989).
18. FOGELMAN, K.D.; WALKER, D.M.; & MARGERUM, D.W. Non-Metal Redox Kinetics: Hypochlorite and Hypochlorous Acid Reactions With Sulfite. *Inorg. Chem.*, 28:986 (1989).
19. SUZUKI, K. & GORDON, G. Stoichiometry and Kinetics of the Reaction Between Chlorine Dioxide and Sulfur (IV) in Basic Solutions. *Inorg. Chem.*, 17:3115 (1978).
20. ONDRUS, M. & GORDON, G. The Oxidation of Hexaaquoiron(II) by Chlorine(III) in Aqueous Solution. *Inorg. Chem.*, 11:985 (1972).
21. AIETA, E.M. & ROBERTS, P.V. The Chemistry of Oxo-chlorine Compounds Relevant to Chlorine Dioxide Generation. *Water Chlorination, Environmental Impact and Health Effects*, Vol. 5 (R.L. Jolley et al, editors). Lewis Publ., Chelsea, Mich. (1985).
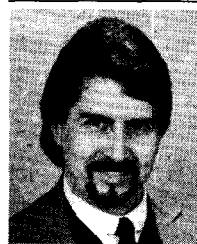
About the authors: *Mark H. Griese is manager of water quality and research, Evansville Water and Sewer Utility, P.O. Box 19, Evansville, IN 47740. He has served as on-site manager for two cooperative research efforts between the US Environmental Protection Agency and the Evansville utility involving chlorine dioxide application for disinfection by-product reduction. Griese is a member of AWWA and a graduate of the University of Southern Indiana at Evansville. Formerly a laboratory technician at the Evansville Water and Sewer Utility, Keith A. Hauser is currently a chemist with Chem-Lube Corp., 8010 E. 88th St., Indianapolis, IN 46256. Mona Berkemeier is a laboratory technician at the Evansville utility, and Gilbert Gordon is Volwiler Distinguished Research Professor, Department of Chemistry, 124 Hughes Laboratories, Miami University, Oxford, OH 45056.*