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Effect of pipe corrosion scales on chlorine dioxide consumption in drinking water distribution systems

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ABSTRACT

Previous studies showed that temperature and total organic carbon in drinking water would cause chlorine dioxide (ClO_2) loss in a water distribution system and affect the efficiency of ClO_2 for *Legionella* control. However, among the various causes of ClO_2 loss in a drinking water distribution system, the loss of disinfectant due to the reaction with corrosion scales has not been studied in detail. In this study, the corrosion scales from a galvanized iron pipe and a copper pipe that have been in service for more than 10 years were characterized by energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD). The impact of these corrosion scale materials on ClO_2 decay was investigated in de-ionized water at 25 and 45 °C in a batch reactor with floating glass cover. ClO_2 decay was also investigated in a specially designed reactor made from the iron and copper pipes to obtain more realistic reaction rate data.

Goethite (α-FeOOH) and magnetite (Fe_3O_4) were identified as the main components of iron corrosion scale. Cuprite (Cu_2O) was identified as the major component of copper corrosion scale. The reaction rate of ClO_2 with both iron and copper oxides followed a first-order kinetics. First-order decay rate constants for ClO_2 reactions with iron corrosion scales obtained from the used service pipe and in the iron pipe reactor itself ranged from 0.025 to 0.083 min^{-1}. The decay rate constant for ClO_2 with Cu_2O powder and in the copper pipe reactor was much smaller and it ranged from 0.0052 to 0.0062 min^{-1}. Based on these results, it can be concluded that the corrosion scale will cause much more significant ClO_2 loss in corroded iron pipes of the distribution system than the total organic carbon that may be present in finished water.

1. Introduction

In United States, chlorine dioxide (ClO_2) was first used as a disinfectant to control taste and odor problems in the 1940s (Aieta and Berg, 1986; Gates, 1998). However, because of high chemical cost and failure and inefficiency of the generation equipment, ClO_2 has not become a widely used primary disinfectant in drinking water treatment facilities during the 1960s and 1970s (Aieta and Berg, 1986; Gates, 1998). Due to the concerns about disinfection byproducts resulting from the use of chlorine in drinking water treatment, ClO_2 is increasingly being considered as an alternative disinfectant for drinking water treatment. The selectivity and oxidation potential makes ClO_2 a desirable alternative to free chlorine. Its biocidal efficiency is equal to or superior to chlorine. Moreover, ClO_2 is effective over a wide pH range and is very effective for removing iron and manganese (Aieta and Berg, 1986; Gates, 1998).

Current applications of ClO_2 in drinking water treatment include the use of ClO_2 for secondary disinfection (Baribeau et al., 2002), nitrification control (McGuire et al., 2006), oxidation of the cyanobacterial hepatotoxin microcystin-LR

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(MC-LR) (Kull et al., 2006) and bromate control in the desalination process (Belluati et al., 2007).

New electrochemical generation systems use electrochemical cassettes and membrane technology to generate stock solution with approximately 500 mg/L ClO_2 from 25% sodium chlorite solution. The equipment is easy to install and safe to operate in the institutional plumbing system. Several studies have been conducted to evaluate the efficacy and safety of ClO_2 generated by this electrochemical process for controlling water-borne pathogens in hospital water systems (Srinivasan et al., 2003; Bova et al., 2004; Sidari et al., 2004). These studies showed that ClO_2 residual in hot water was significantly lower than in cold water. It is possible that faster reaction of ClO_2 with organic compounds in hot water and high organic load in the hot water contributed to such observations.

However, the loss of ClO_2 due to corrosion scales has not been studied in detail. Reactions between free chlorine and iron corrosion scales in distribution system have been reported to account for the significant free chlorine loss in the distribution system (Frateur et al., 1999; Hallam et al., 2002; DiGiano and Zhang, 2005). Loss of chlorite in cast-iron pipe loops (Eisnor and Gagnon, 2004) and full-scale drinking water distribution systems containing cast-iron pipes has also been reported (Baribeau et al., 2002).

Iron corrosion scales in water distribution systems have been investigated extensively because iron pipes are commonly used for distributing drinking water. The compounds usually found in iron corrosion scales include goethite (α-FeOOH), lepidocrocite (γ-FeOOH), magnetite (Fe_3O_4), siderite ($FeCO_3$), ferrous hydroxide ($Fe(OH)_2$), ferric hydroxide ($Fe(OH)_3$), ferrihydrite ($5Fe_2O_3 \cdot 9H_2O$), green rusts (e.g., $Fe^{II}_4 Fe^{III}_2(OH)_{12}(CO_3)$) and calcium carbonate (Sarin et al., 2001, 2004a, b; Tang et al., 2006). Previous studies showed that iron corrosion scales generally contain reduced iron, which can react with oxidative disinfectants (Sarin et al., 2001, 2004a, b). ClO_2 is a strong oxidant and will oxidize ferrous compounds in iron corrosion scales. The reactions of ClO_2 with corrosion scales will lead to undesirable losses in the disinfectant residual.

In this study, the corrosion scales from a galvanized iron pipe and a copper pipe that have been in service for more than 10 years were characterized by energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD). The impact of corrosion scale materials on ClO_2 decay was investigated in DI (de-ionized) water at 25 and 45 °C in a batch reactor to simulate the application of ClO_2 in hot and cold water systems. In addition, ClO_2 decay was also investigated in a specially designed reactor made from the iron and copper pipes to obtain more realistic reaction rate data.

2. Materials and methods

2.1. Characterization of corrosion scale on iron and copper pipes

A 30-inch long, 4-inch diameter galvanized iron pipe and a 15-inch long, 2-inch diameter copper pipe that have been in service for at least 10 years were obtained from a local hospital water system and used for this study. The iron pipe was covered with deposits of corrosion products and heavily tuberculated as shown in Fig. 1a. The copper pipe was comparatively clean (Fig. 1b) and only a thin film of corrosion scale was detected by a scanning electron microscopy (SEM) image (Fig. 1c).

The scales were scraped from the top, middle and bottom layers of the tubercles close to the end of the iron pipe and ground into powder. The scales from the copper pipe were scraped from the copper pipe wall from both ends of the pipe. The elemental composition of the scales was analyzed by EDS using a Philips XL Series 30 scanning electron microscope and an X-ray energy dispersive spectrometer (Philip Analytical Inc., Natick, MA). The XRD patterns of the samples were obtained with a Philips X'PERT diffractometer (Philip Analytical Inc., Natick, MA) using a standard Ni-filtered Cu Kα radiation source operating at 40 kV and 30 mA X-ray patterns were analyzed using pattern processing software based on the latest Joint Committee on Powder Diffraction Standards (JCPDS) files. Powder samples were also sent to Materials Characterization Laboratory (Pennsylvania State University, University Park, PA) for X-ray photoelectron spectroscopy using a Kratos Axis Ultra X-ray photoelectron spectrometer (Kratos Analytical Inc., Chestnut Ridge, NY) with an X-ray source of monochromatic Al Kα (1486.6 eV).

2.2. Batch and pipe reactor experiment

A cell culture flask (Wheaton Science Products, Millville, NJ) capable of holding 2500 mL of liquid was used as the batch reactor (Fig. 2). A floating glass cover was used to prevent exchange of gases between the headspace and room air and to minimize the volatility of ClO_2. Single-port 45-mm red rubber stoppers with a 0.25-inch hole (Wheaton Science Products, Millville, NJ) were used on the side arms as a temperature monitoring port and a sample withdrawal port. The stoppers were sealed gas tight using a 45-mm inlet cap (Wheaton Science Products, Millville, NJ). The reactor and all parts were autoclaved prior to each experiment. The reactor was soaked overnight in 50 mg/L ClO_2 solution to satisfy disinfectant demand of the reactor material and rinsed with DI water before use.

The experiments were carried out at room temperature, which varied in a very narrow range of 25 ± 2 °C. Hot water temperatures were maintained by heating the flask on the hot plate with a temperature probe feedback. Temperature monitoring was performed using the temperature probe of the hot plate (PMC Industries Inc., San Diego, CA).

The corrosion scale material for these experiments was sampled from the entire scale of the corroded iron pipe and ground to powder without sieving before adding to the batch reactor. Commercial cuprite (Cu_2O) and Fe_3O_4 powder (particle size <5 μm; Sigma-Aldrich, St. Louis, MO) were also used in these batch reactor experiments.

A ClO_2 generator (Diox, Klenzoid Inc., Conshohocken, PA) provides a concentrated ClO_2 stock solution. The effluent solution was discarded until the generator achieved a ClO_2 concentration of approximately 500 mg/L. The ClO_2 concentration of the concentrated stock solution (fresh stock solution was prepared for each experiment) was monitored using the Hach Method 8138 (0–700 mg/L). The appropriate

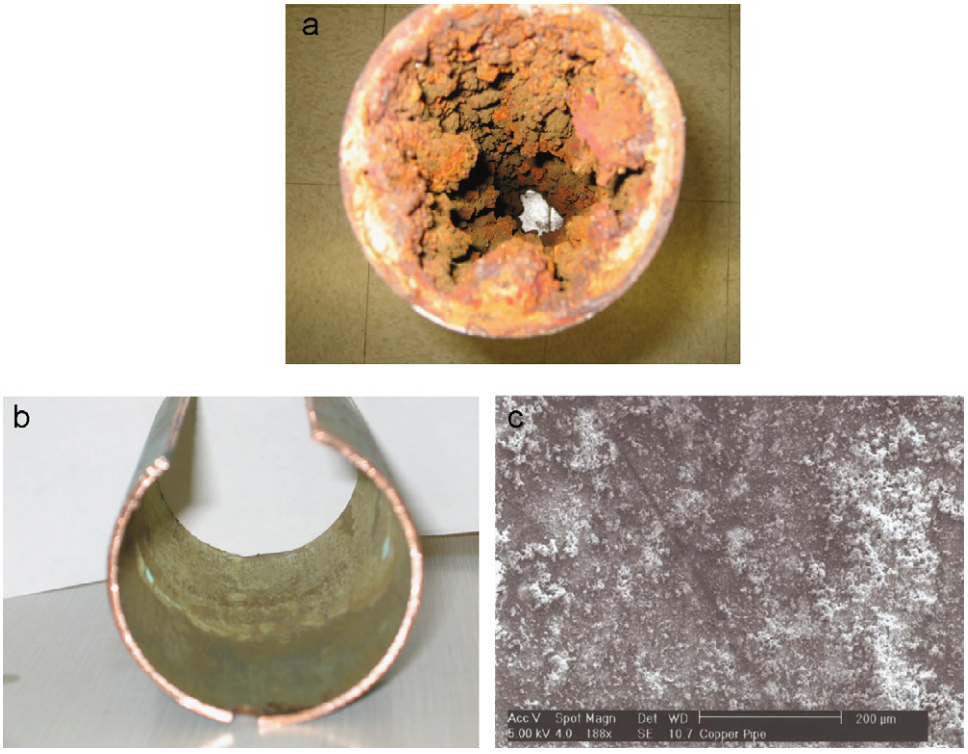

Fig. 1 – (a) Inner surface of the galvanized iron pipe, (b) inner surface of the copper pipe from a local hospital water system and (c) SEM image of the copper pipe wall.

amount of the ClO_2 stock solution was pipetted into the batch reactor to achieve the target ClO_2 concentration of 1.0 mg/L. The decay of ClO_2 was monitored after the addition of the corrosion scales using the Hach Method 10101-DPD Method for ClO_2 (0.00–5.00 mg/L) utilizing a glycine reagent and Hach DPD Free Chlorine Reagent (Hach Company, Loveland, CO). The colorimetric measurements were made using the Hach DR/2010 Spectrophotometer (Hach Company, Loveland, CO).

Samples for chlorite, chlorate and chloride analyses were collected at the beginning and at the end of each experiment. Chlorite, chlorate and chloride were measured by ion chromatography (DX-500, Dionex, Sunnyvale, CA) equipped with a suppressor and conductivity detector according to USEPA Method 300.1. Chlorite, chlorate and chloride concentrations produced through ClO_2 reaction with corrosion scales were determined as the difference between the final and initial concentrations to eliminate the interference due to the presence of these ions in the stock solution.

pH of the solution was buffered with 0.1 M phosphate buffer and it was adjusted by the addition of 0.1 M NaOH.

Copper and galvanized iron pipes were used to set up the experimental system shown in Fig. 3. Three holes were drilled in the corroded iron and copper pipes and a 0.25-inch plastic tubing was attached as sampling ports. The pipe reactor was flushed with tap water for 24 h before the experiment to re-wet the pipe surface and flush out any easily dislodged tubercles. The flow rate of 1.0 mg/L ClO_2 stock solution through the pipe was adjusted to achieve the retention time of 10, 20 and 30 min for sampling ports 1, 2 and 3, respectively. The ClO_2 residual at each sampling port was measured during the experiment until stable levels were achieved. These experiments were conducted in duplicate to provide statistical validity of the results.

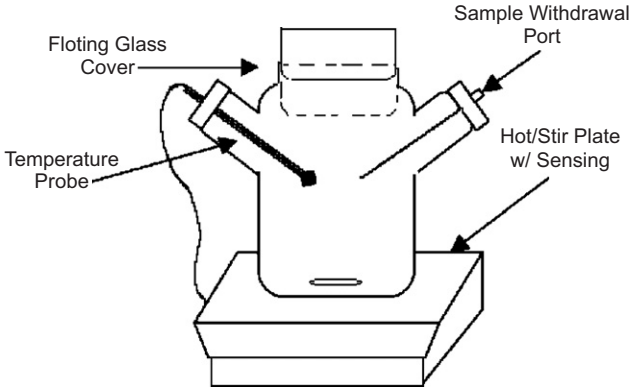

Fig. 2 – The batch reactor with the floating glass cover.

3. Results and discussion

3.1. *Characterization of corrosion scale*

The EDS measurements on powder samples from the galvanized iron pipe identified that iron was the major component element of the scale besides carbon and oxygen. XPS analysis showed that iron was present at 28% (atomic percent), carbon at 18% and oxygen at 48%. The top, middle

and bottom layers of the iron pipe corrosion scale were analyzed by XRD for the changes in compositions and the results are shown in Fig. 4. α-FeOOH, Fe_3O_4, hematite (α-Fe_2O_3) and elemental Fe were identified as the main crystalline components. All layers of the scales had a very similar set of peaks, but a few differences were discernible. Comparison of the peak heights for hematite suggests that it is mostly present in the top layer of the scale. Comparing the heights for Fe_3O_4 and elemental Fe peaks, it can be inferred that the content of Fe_3O_4 and elemental Fe increased from the top layer to the middle layer. The scale structure proposed by Sarin et al. (2004a, b) also included Fe_3O_4 as the dominant component in the shell-like layer of iron pipe corrosion scale. Based on these XRD results, it can be concluded that the crystalline ferrous compounds are mainly associated with Fe_3O_4. The lower peak intensity observed for the sample of the bottom layer indicates that the relative quantity of Fe_3O_4 is small and that α-FeOOH is the dominant component in this layer of the scale. Siderite was likely present in minor amounts since it is not stable when exposed to air. These results were similar to the results reported by other researchers (Sarin et al., 2001, 2004a, b; Tang et al., 2006). Green rust was not detected in the iron scale since it is not stable and can be further oxidized in contact with air to a more stable phase, like α-FeOOH or Fe_3O_4.

The EDS measurements on powder samples of the copper pipe scale identified copper as the major component of the scales besides carbon and oxygen. XPS analysis confirmed that copper was present at 10% (atomic percent), carbon at 19% and oxygen at 55%. XRD results showed that the crystalline phase of the copper corrosion scale primarily consists of Cu_2O, copper oxide and metallic copper (Fig. 5). Cu_2O was previously identified as a major corrosion product in copper pipes used in drinking water systems (Merkela et al., 2002). The same study also suggested that light brown Cu_2O film changes to light green malachite fibers ($Cu_2CO_3(OH)_2$) by slow oxidation process. Since malachite was not found in the XRD examination of the corrosion samples collected for this study, it is possible that the malachite concentration in the corrosion scale was too low to be detected by XRD.

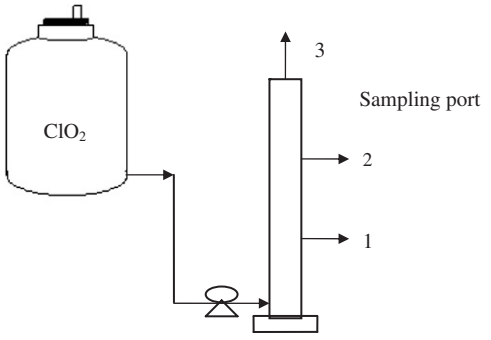

Fig. 3 – The pipe reactor setup.

3.2. *Reactions of ClO_2 with iron corrosion scale*

ClO_2 decay in DI water was first studied to verify the efficiency of the experimental system design with a floating glass cover to minimize ClO_2 loss due to the volatilization. The mass balance summarized in Table 1 verified that the floating glass cover successfully minimized ClO_2 loss from the reactor due to volatilization.

The results of ClO_2 interaction with 1.0 g/L of corrosion scale from the iron pipe at 25 and 45 °C are shown in Fig. 6.

Similar tests were conducted with 2.0 and 5.0 g/L of corrosion scales and the results are summarized in Table 2. A first-order kinetic expression provides a good fit of ClO_2 decay in DI water containing 1.0, 2.0, 5.0 and 10.0 g/L of pipe

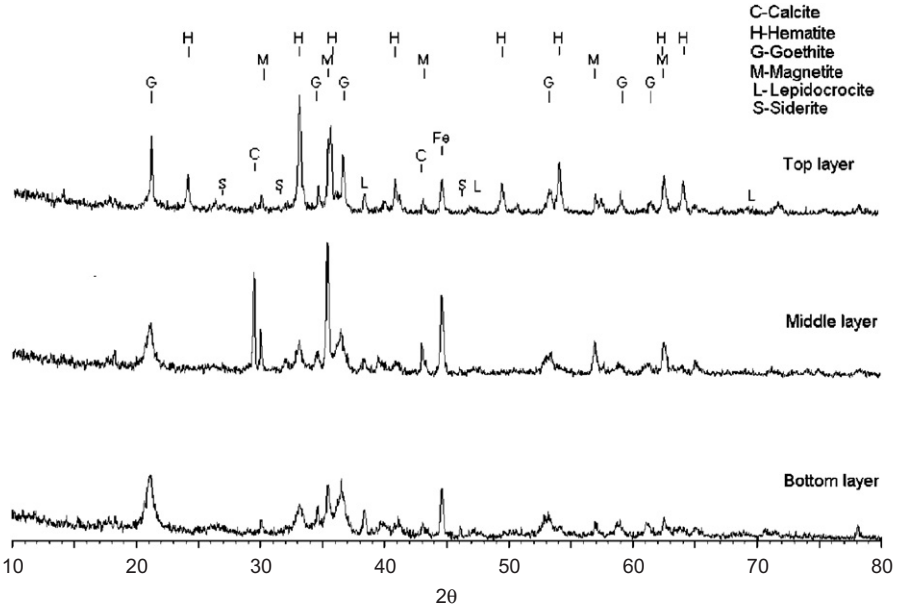

Fig. 4 – XRD patterns of the corrosion scale on different layers of the corroded iron pipe.

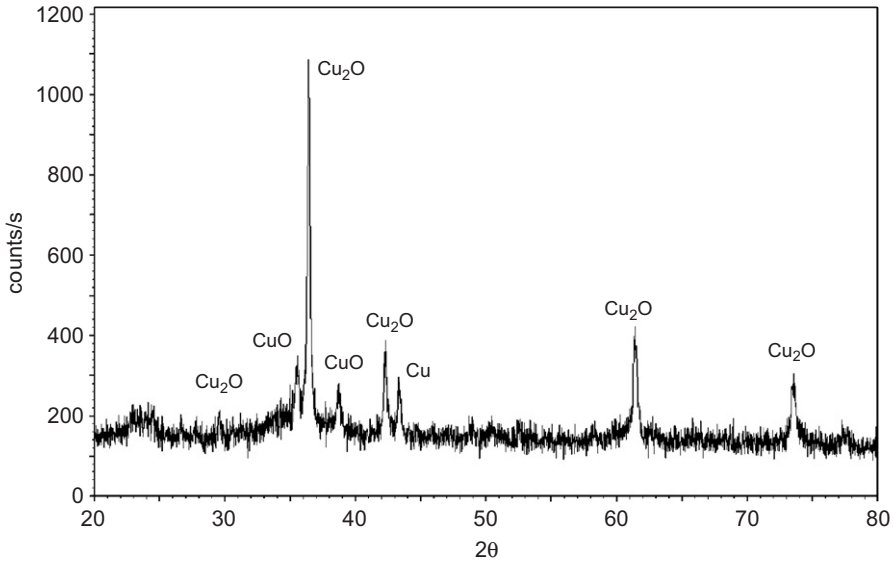

Fig. 5 – XRD patterns of the corrosion scale on the copper pipe.

Table 1 – Mass balance on ClO_2, chlorite, chlorate and chloride during the ClO_2 decay in DI water after 6 h (mg/L)

Test parameters	ΔClO_2	ΔClO_2^-	ΔClO_3^-	ΔCl^-	ClO_2 loss due to volatilization[a]
26 °C, pH 7.5	0.04[b]	0.02	0.01	0.02	−0.01
45 °C, pH 7.5	0.07	0.03	0.02	0.01	0.01
27 °C, pH 8.5	0.03	0.02	0.00	0.01	0
45 °C, pH 8.5	0.06	0.03	0.02	0.01	0

All concentrations are expressed as chlorine.
[a] ClO_2 loss due to volatility = $\Delta ClO_2 - \Delta ClO_2^- - \Delta ClO_3^- - \Delta Cl^-$.
[b] Cl mass = (atomic Cl mass/MWClO_2)*ΔClO_2, MW—molecular weight.

corrosion scale over the entire time period (Fig. 6 and Table 2) at 25 and 45 °C. The first-order reaction rate constant for ClO_2 consumption ranged from 0.025 to 0.083 min^{-1}. Temperature did not significantly affect the ClO_2 reaction rate with iron scales since the reaction of ClO_2 with reduced iron species was very fast.

However, there was a clear relationship between the amount of corrosion scale present in the reactor and the first-order reaction rate constant. Fig. 7 shows that the rate constant increased with increasing scale concentration in the reactor. Such behavior indicates that the availability of corrosion scale in the batch reactor represents the rate-limiting step. The reaction order with respect to scale concentration was investigated using data collected with the initial ClO_2 concentration of 1.0 mg/L and the scale concentration of 1.0, 2.0, 5.0 and 10.0 g/L. The rate of ClO_2 decay is described by the pseudo-first-order expression

$$-\mathrm{d}\frac{[ClO_2]}{dt} = k[ClO_2],$$

where $k = k'[\text{scale}]^{\alpha}$. It is possible to identify the effect of scale concentration on the reaction rate by linearizing the expression for k:

$$\ln k = \ln k' + \alpha \ln[\text{scale}].$$

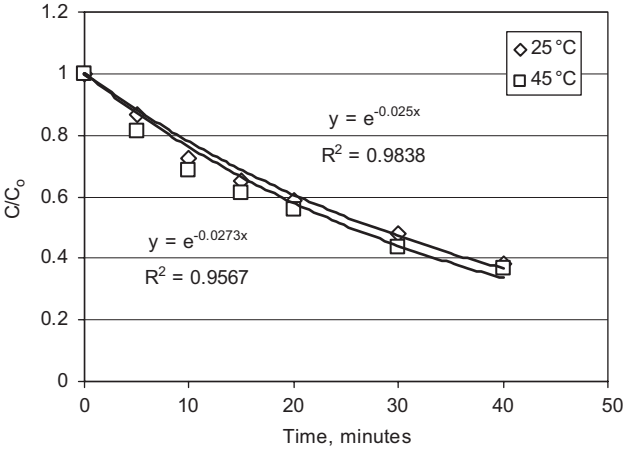

Fig. 6 – ClO_2 decay in DI water due to reaction with 1.0 g/L of corrosion materials from iron pipe at pH 7.5, 25 and 45 °C.

The reaction order with respect to scale concentration was determined by plotting ln k vs. ln [scale], as shown in Fig. 7. The slope of 0.83–0.85 indicates that the reaction is not exactly of the first order with respect to scale concentration. Based on these results with powder scale from iron pipe, it

Table 2 – Mean first-order rate constant for the reaction of ClO_2 with the iron corrosion scale, magnetite and cuprite

Scale concentration (g/L)	Temperature (°C)	Reaction rate constant (min^{-1})	R^2
1.0	25	0.0251	0.9783
	45	0.0273	0.956
2.0	25	0.0368	0.9913
	45	0.0408	0.977
5.0	25	0.0803	0.9746
	45	0.0829	0.9712
10.0	25	0.1748	0.9748
	45	0.1871	0.9555
1.0 g/L of Fe_3O_4	25	0.070	0.9557
	45	0.076	0.9635
2.0 g/L of Cu_2O	25	0.0052	0.9781
	45	0.0062	0.9745

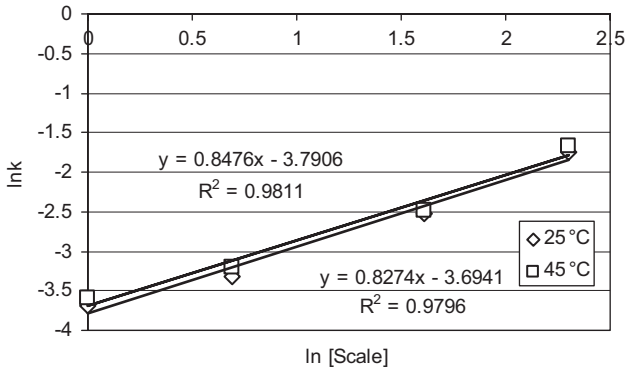

Fig. 7 – Impact of iron corrosion scale concentration on the chlorine dioxide decay constant at 25 and 45 °C.

can be concluded that the rate expression for ClO_2 consumption due to the reaction with the iron corrosion scale has the form

$$-\mathrm{d}\frac{[ClO_2]}{dt} = k'[ClO_2] \times [\text{scale}]^{0.84},$$

where k' varies from 0.021 to 0.027 min^{-1} $(g/L)^{-0.84}$.

Overall, the reaction of ClO_2 with iron scale follows the first-order reaction kinetics with respect to ClO_2, but not exactly the first-order reaction with respect to scale concentration (Fig. 7). Such a finding implies a complex reaction mechanism, which is likely due to heterogeneous reactions and the fact that the corrosion scale is a mixture of iron compounds. Compared with the ClO_2 decay rate constant (0.0011–0.0044 min^{-1}) in drinking water due to reaction with organic matter (Zhang et al., 2006), the rate constant for the reaction of ClO_2 with the iron pipe corrosion scales (0.0251–0.0829 min^{-1}) is almost 20 times greater. Therefore, the major loss of ClO_2 in a water distribution system would be caused by the corrosion scales where heavy corrosion occurred. The decay rate of free chlorine with iron corrosion deposits was reported to range from 0.0027 to 0.034 h^{-1} in the batch reactor (Valentine et al., 2000), which is much smaller than the decay rate of ClO_2 observed in this study.

Chlorite analysis showed that 81–95% of ClO_2 was converted to chlorite (Table 3), which suggests that ClO_2 reacts with corrosion scale by a one-electron mechanism whereby ClO_2 oxidizes the ferrous compounds to ferric compounds.

3.3. ClO_2 consumption in pipe reactors

The results of the tests with iron and copper pipe reactors (Fig. 3) are shown in Fig. 8. During the first 2 h of the test in the iron pipe, there was no measurable ClO_2 at any of the three sampling ports, which means that ClO_2 was completely consumed in the first 10 inches of the pipe. After approximately 6 h, the mean ClO_2 residual at sampling ports 1, 2 and 3 reached stable levels. Using the first-order kinetic expression to fit the steady-state data, the mean reaction rate constant of 0.077 min^{-1} ($R^2 = 0.9661$) was obtained. It is clear that the reaction between ClO_2 and the corrosion scale was not limited by the concentration of the scale in the pipe

Table 3 – Mean mass change of ClO_2 and chlorite during the reaction of ClO_2 with the iron corrosion scale, magnetite and cuprite

Scale concentration (g/L)	Temperature (°C)	ΔClO_2	ΔClO_2^-	$\Delta ClO_2^-/\Delta ClO_2$ (%)
1.0	25	0.66	0.63	95
	45	0.66	0.62	94
2.0	25	0.76	0.72	95
	45	0.78	0.74	95
5.0	25	0.93	0.75	81
	45	0.97	0.82	84
1.0 g/L of Fe_3O_4	25	0.86	0.74	86
	45	0.91	0.81	90
2.0 g/L of Cu_2O	25	0.68	0.53	78
	45	0.76	0.65	86

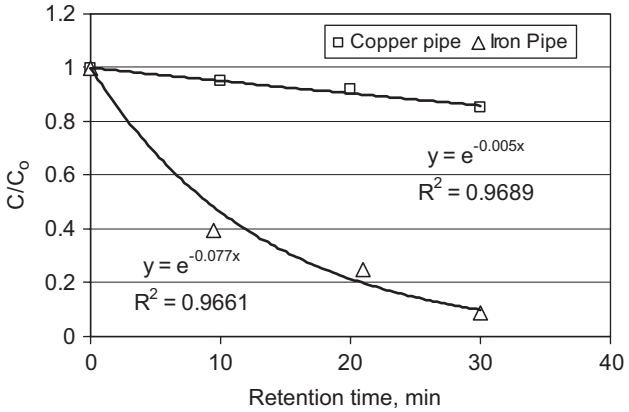

Fig. 8 – Steady-state ClO_2 residual profile in a used pipe.

reactor. A similar reaction rate constant was obtained in the batch reactor with an iron scale concentration of 5.0 g/L. The decay rate of free chlorine due to reactions with iron corrosion scale on the pipes (referred to as wall demand to differentiate from bulk decay) ranged from 0.07 to 0.26 h^{-1} (Hallam et al., 2002; DiGiano and Zhang, 2005), which is much smaller than that obtained for ClO_2 in this study. Such a behavior is to be expected since ClO_2 is a free radical that is very reactive with ferrous compounds (Moore et al., 2004).

ClO_2 consumption was much slower in the copper pipe than in the iron pipe. After approximately 6 h, the mean ClO_2 residual at sampling ports 1, 2 and 3 reached stable levels that could be modeled using the first-order kinetic expression. The first-order reaction rate constant for the copper pipe of 0.005 min^{-1} ($R^2 = 0.9689$) was obtained. These results suggest that the loss of ClO_2 by the reaction with corroded copper pipe is more than 10 times slower than in the case of corroded iron pipes.

3.4. *Reactions of ClO_2 with model corrosion scales*

Fe_3O_4 and Cu_2O were identified as the major components of the corrosion scales collected form iron and copper pipes, respectively. These compounds will cause ClO_2 loss because Fe_3O_4 has one Fe(II) in each molecule that can be oxidized to Fe(III), while ClO_2 can oxidize cuprous to cupric compounds. The reactions of ClO_2 with Cu_2O and Fe_3O_4 were confirmed using commercially available Cu_2O and Fe_3O_4 powders with particle size below 5 μm. The reaction rate constant for ClO_2 reaction with 1.0 g/L Fe_3O_4 was 0.070 min^{-1} at 25 °C and it increased slightly to 0.076 min^{-1} as the temperature increased from 25 to 45 °C. These values are very close to the ClO_2 decay rate in the iron pipe (Fig. 8) and the reaction rate of ClO_2 with 5 g/L of iron corrosion scale in a batch reactor (Table 2). Therefore, it can be concluded that the reactions between ClO_2 and Fe_3O_4 in the corrosion scales are likely responsible for most of the ClO_2 loss in the iron pipes. Although Sarin et al. (2001) reported that soluble iron was released to bulk water primarily in the ferrous form, the amount of soluble ferrous ions is typically very small and cannot account for the significant ClO_2 loss observed in this study. Other studies showed that free chlorine loss in the distribution system is also dominated by the reactions with corrosion scale or materials deposited on the surface of the pipe (Valentine et al., 2000).

The corrosion scale on the copper pipe was so limited that it precluded direct experiments in the batch reactor. Because Cu_2O was identified as the main component of copper corrosion scale, 2.0 g/L of commercial Cu_2O powder was used to study the reactions between ClO_2 and corrosion scale in copper pipes. The results in Table 3 show that the reactions of ClO_2 with Cu_2O followed the pseudo-first-order kinetic expression. The reaction rate of ClO_2 with Cu_2O ranged from 0.005 to 0.006 min^{-1}, which is very close to the ClO_2 decay rate observed in the copper pipe (Fig. 8). The reaction rate constant increased to 0.0062 min^{-1} as the temperature increased from 25 to 45 °C. The similarity of reaction rate constants suggests that the ClO_2 loss in copper pipe is mostly caused by the reaction of ClO_2 with Cu_2O that is present in the corrosion scale.

It was found that 78–96% of ClO_2 consumed by the iron corrosion scales, Cu_2O and Fe_3O_4 was converted to chlorite (Table 3.), which suggests that ClO_2 reacts with these solids by a one-electron mechanism and oxidizes the ferrous and cuprous ions to ferric and cupric ions, respectively. Concentration of chlorate was negligible and chloride concentration resulting from these reactions could not be determined accurately due to the interference of chloride from corrosion scales. Since chlorite is also a weak oxidant, it can be further reduced to other chlorine species with excess ferrous ions (Hurst and Knocke, 1997; Henderson et al., 2001; Katz and Narkis, 2001), which may explain why the recovery of chlorite decreased as the concentration of corrosion scales increased. Loss of chlorite in full-scale drinking water distribution systems containing cast-iron pipes has already been reported (Baribeau et al., 2002). Chlorite can also react with soluble Fe^{2+} and thereby reduce the corrosion rate and red water (Eisnor and Gagnon, 2004).

4. Conclusions

Goethite (α-FeOOH) and magnetite (Fe_3O_4) were identified as the main components of iron corrosion scale. Cuprite (Cu_2O) was identified as the major component of copper corrosion scale. The reaction rate of ClO_2 with both iron and copper oxides followed a first-order kinetics. The estimated first-order reaction rate constant for ClO_2 reaction with iron corrosion scales and Fe_3O_4 ranged from 0.0251 to 0.0829 min^{-1}. The estimated first-order reaction rate constant for ClO_2 reaction with Cu_2O was much smaller and it ranged from 0.005 to 0.006 min^{-1}. Fe_3O_4 and Cu_2O were likely the main compounds in the scales that caused ClO_2 loss in this study through a one-electron-transfer mechanism. The loss of ClO_2 in the corroded iron pipe is most probably dominated by the reactions between ClO_2 and this ferrous compound present in the corrosion scale. Based on these results, it can be concluded that the corrosion scale will cause much more significant ClO_2 loss in corroded iron pipes of the distribution system than the total organic carbon that may be present in finished water. The application of ClO_2 in the water distribution system using cast-iron pipes is not recommended unless measures to prevent corrosion are fully implemented. Although ClO_2 loss caused by corrosion scale was much slower in the copper pipe than in the iron pipe, it may still be necessary to prevent the corrosion and unnecessary loss of disinfectant due to the corrosion scale in the copper pipe distribution system to maintain effective disinfectant residual.

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