

Technical Memorandum

To: Utility Manager/Consulting Engineer
From: Dean Gregory
Date: August 15, 2008
Re: Use of ClO_2 for Mn oxidation/removal

Project Description and Findings

This memorandum summarizes the results of a bench-scale study of the impact of chlorine dioxide on manganese (Mn) oxidation and removal in raw water from a Pennsylvania water treatment facility. The raw water requires approximately 6 hours in the main transmission line to reach the plant during average flow conditions. In the past year the dissolved Mn level in the water entering the pipeline has ranged from approximately 0.05 – 0.15 mg/L, which is sufficient to cause aesthetic water quality issues (i.e. brown staining) in the treatment plant as well as in the distribution system. The goal of the city is to completely oxidize the dissolved manganese (Mn^{2+}) to its particulate form, $\text{MnO}_{2(s)}$, as the water enters the pipeline. Oxidizing the dissolved Mn completely as it enters the pipeline will 1) allow the particulate $\text{MnO}_{2(s)}$ to be removed effectively by the plant's coagulation-filtration processes, and 2) deprive the Mn-oxidizing bacteria, which represent a significant fraction of the biofilm population in the pipeline, of a their primary nutrient source (Mn^{2+}). The effectiveness of chlorine dioxide for Mn oxidation—particularly at the relatively low pH of this sample (6.0)—is well documented in the literature (Gregory and Carson, 2003; Knocke et al., 1990). Also, given the strength of chlorine dioxide as a general biocide, it is likely that establishing a residual in the pipeline would inactivate the biofilm and eventually “clean out” the main transmission line from the reservoir to the treatment facility, which could cause a temporary increase in the turbidity of the water entering the plant.

The objectives of this project were to 1) determine the chlorine dioxide doses required to completely oxidize dissolved Mn levels of 0.15 and 0.30 mg/L in raw water, and 2) characterize chlorine dioxide demand/decay, with and without dissolved Mn present.

The major findings of this project include:

Chlorine dioxide doses of 0.5 and 1.0 mg/L rapidly oxidized dissolved Mn levels of 0.15 and 0.30 mg/L, respectively, to $\leq 10 \mu\text{g/L}$ in raw water (Figure 1). These doses are only slightly higher than those predicted by the theoretical stoichiometry of the reaction ($2.45 \text{ mg ClO}_2/\text{mg Mn}^{2+}$ in demand-free water), which indicates the non-Mn demand in the raw water was minor. Given the low TOC level of the raw water (2.18 mg/L), this result was expected.

The decay rate of chlorine dioxide in the raw water is low in the absence of dissolved Mn (Figure 2). An applied dose of 1.0 mg/L, for example, would likely provide a residual for 3 – 4 hours. The

addition of dissolved Mn causes an increase in immediate demand proportional to the Mn level (approximately 2.5 mg ClO₂/mg Mn²⁺).

The addition of free chlorine—added as a blend with chlorine dioxide—did not significantly impact Mn oxidation, which was not surprising given the relatively low pH (6.0) of the sample.

Materials and Methods

Water quality. Table 1 provides water quality data for the raw sample from the WTF. The water was shipped overnight in a cooler to CDG laboratory facilities in Arvada, CO. The cooler contained artificial ice packs that kept the water chilled during shipment. Upon its arrival the water was immediately stored in a refrigerator until the bench-scale experiments were commenced.

Table 1. WTF raw water quality.

Constituent	Value
pH	6.05
Total Organic Carbon (mg/L)	2.18
Turbidity (NTU)	3.1
Total Mn (µg/L)	33
Dissolved Mn (µg/L) ¹	5
Temp. used for all experiments (°C)	15

¹ Mn²⁺ spikes of 150 and 300 µg/L were used for the Mn oxidation experiments.

Mn oxidation experiments. Due to the relatively low dissolved Mn concentration in the sample shipped from the treatment plant (5 µg/L), two 5-L batches of the raw water were drawn off and spiked with 150 and 300 µg/L Mn²⁺, respectively, to simulate more typical full-scale water quality conditions. A 1000 mg/L Mn²⁺ stock solution was prepared and used for this purpose. After the Mn²⁺ spikes were added the water was provided with a 48-h detention time to allow the dissolved Mn to equilibrate (at least partially) with the ambient natural organic matter (NOM) compounds.

One-liter samples of the Mn-spiked water, in amber glass bottles, were dosed with different amounts of chlorine dioxide and provided with a 20-minute detention period under slow-mix conditions prior to sampling for dissolved Mn. The ClO₂ doses ranged from 0.3 – 1.0 mg/L. Although a 20-minute detention time was used for all experiments, the actual rate of the ClO₂-Mn²⁺ reaction is on the order of seconds.

Manganese analyses. Manganese concentrations in the raw and oxidant-treated samples were measured using the Hach PAN method. Dissolved Mn samples were first filtered through a 0.45 µm

membrane and then through a 30-K molecular weight cut-off UF membrane (Millipore Corporation) prior to analysis. The primary purpose of the 0.45- μm step was to simply remove a majority of the Mn solids in order to decrease the fouling rate of the UF system. In this report, the term “dissolved Mn” refers to the total manganese remaining in the UF filtrate.

Chlorine dioxide demand/decay. A chlorine dioxide stock solution was produced using a CDG bench-scale chlorine dioxide generator. The solid sodium chlorite/chlorine gas process produces ClO_2 gas that is virtually 100 percent pure. The concentration of the stock solution was approximately 4000 mg/L throughout the period of experiments and was checked daily using the amperometric titration method (Standard Methods #4500- ClO_2 E).

For each demand/decay experiment chlorine dioxide residuals were measured over time from $t = 0$ to $t = 20$ min. Applied doses were 0.5 and 1.0 mg/L. The Lissamine Green B (LGB) method was used to measure chlorine dioxide residuals. Chlorite ion samples were collected approximately 4 hours after the application of chlorine dioxide. This detention time was used in order to allow equilibrium chlorite concentrations to be achieved, thus more closely simulating a full-scale process.

Results and Discussion

Dissolved Mn oxidation. Chlorine dioxide doses of 0.50 and 1.0 mg/L effectively oxidized dissolved Mn levels of 0.15 and 0.30 mg/L, respectively, to ≤ 10 $\mu\text{g/L}$ in raw water (Figure 1). Attaining a final dissolved Mn residual of ≤ 10 $\mu\text{g/L}$, despite the secondary MCL of 50 $\mu\text{g/L}$, is important because this 10 $\mu\text{g/L}$ standard has been identified and adopted by many utilities as the treatment goal for avoiding brown-water complaints in their distribution systems. The chlorine dioxide doses required were only slightly higher than those predicted by the theoretical stoichiometry of the reaction (2.45 mg $\text{ClO}_2/\text{mg Mn}^{2+}$ in demand-free water), which indicates the non-Mn demand in the raw water was not significant. Overall, these results suggest that operation of the chlorine dioxide system will be relatively straightforward, with the dose at any given time based primarily on the raw water dissolved Mn level plus an additional increment (0.4 mg/L, for example) to provide a longer residual in the pipeline.

Another noteworthy aspect of Figure 1 is that complete oxidation of dissolved Mn was achieved at a relatively low pH of 6.05. At this pH level, alternative oxidants such as permanganate and free chlorine 1) react slowly with dissolved Mn (if at all, in the case of chlorine) and 2) typically do not reduce dissolved Mn residual to less than 30 – 40 $\mu\text{g/L}$.

Chlorine dioxide demand/decay. Chlorine dioxide decay rates for two applied doses in the raw water are shown in Figure 2. For the dose of 1.0 mg/L, the decay rate is also shown in the presence of 0.3 mg/L Mn^{2+} . Overall, without dissolved Mn added, the chlorine dioxide demand was low and

typical for a raw water such as 's that contains a low TOC concentration (2.18 mg/L). For a typical water treatment dose of 1.0 mg/L, for example, the initial demand was only approximately 0.2 mg/L and after a 20-min. contact period a relatively high residual of 0.65 mg/L remained. The dissolved Mn spike of 0.3 mg/L increased the initial demand by about 0.7 mg/L, which is approximately equal to the theoretical stoichiometry of the reaction (2.45 mg ClO₂/mg Mn²⁺). The results in Figure 2 suggest that

Figure 1. Chlorine dioxide dose vs. dissolved Mn residual in raw water from a Pennsylvania reservoir. TOC = 2.18 mg/L, T = 15°C, pH = 6.05, detention time = 20 min.

1) a typical pre-oxidation dose for the WTF would be in the range of 0.5 – 0.7 mg/L when significant levels of dissolved Mn were not present; and 2) there is potential to obtain disinfection credit (Ct), if needed and if the detention time is available, from the application of chlorine dioxide to the raw water.

Figure 2. Chlorine dioxide demand/decay rates in raw water. Applied doses are shown. Temperature = 15°C, TOC = 2.18 mg/L, pH = 6.05. Mn²⁺ was spiked to the raw water in one experiment (blue trendline).

Chlorite ion formation. For the demand/decay experiments in which a 0.3 mg/L Mn²⁺ spike was used, chlorite ion residuals were measured approximately four hours after the application of chlorine dioxide to more closely simulate the equilibrium conditions that would be encountered during full-scale application. Results are shown in Figure 3. The chlorite residuals ranged from 61 – 68 percent of the applied chlorine dioxide dose, which is typical for many natural waters. It should be noted that, due to removal mechanisms such as coagulation, powdered activated carbon addition (if applicable), destruction by UV radiation, adsorption/reduction in the filtration process, and oxidation by free chlorine, full-scale chlorite ion residuals in finished water are generally lower than the residuals shown here. Full-scale chlorite ion concentration at the point-of-entry to the distribution system (where sampling is required) are typically about 50 percent of the applied chlorine dioxide dose.

Figure 3. Chlorite ion formation vs. chlorine dioxide dose in raw water. Samples were measured 4 hours after chlorine dioxide application T = 15°C, pH = 6.05, TOC = 2.18 mg/L.



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