

# Oxidant Selection for the Treatment of Manganese (II), Iron (II), and Arsenic (III) in Groundwaters

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In order to comply with the United States Environmental Protection Agency's (U.S. EPA's) arsenic standard and the manganese and iron secondary maximum contaminant levels (MCLs) in water (10µg/L, 50µg/L, and 300µg/L, respectively), many Midwestern water utilities must add a strong oxidant before filtration to oxidize the reduced forms of arsenic, manganese and iron. Free chlorine and permanganate are the two most common chemical oxidants used to address arsenic, manganese, and iron issues. In Midwestern States, engineering practices have traditionally favored the use of permanganate as the oxidant of choice, followed by green sand filtration to remove manganese from source waters. Most water treatment plant personnel, however, find permanganate undesirable to use for a number of reasons, including: it stains everything it contacts, overdosing causes "pink" water, underdosing can cause manganese spikes, and handling issues. There is a real need to compare the effectiveness of chlorine and permanganate in manganese (and arsenic) removal systems, and, more importantly, to provide better guidance as to when each oxidant is most appropriate to address an iron, manganese, and/or arsenic problem. Observations from full-scale treatment plants will be used to illustrate the appropriate applications of chemical oxidants.

## Case A: Pre-Chlorination and Greensand Filtration (Ohio System)

Site A is a traditional iron removal filtration plant producing on average 4 million gallons per day (MGD) drawing from several well sites in the same semi-confined aquifer. Permanganate was used for the oxidation of iron and manganese until 1994. The system operator reported that the oxidant formed small flocs which required frequent backwash as well as various operational issues (e.g. staining, pink water, etc.). As a result, the plant switched to free chlorine addition to oxidize manganese and arsenic. The U.S. EPA, in cooperation with Battelle Memorial Institute, initiated a 6 month treatment plant water-monitoring study in 2004. Source water over the study period contained on average 140 µg/L and 1.8 mg/L of manganese and iron, respectively (Table 1). Following filtration, finished water contained only 2.2 µg/L manganese and 0.05 mg/L iron. The monitoring results, as well as plant operator feedback, illustrated that chlorine was an effective oxidant to address manganese removal requirements. Furthermore, the work showed that free

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chlorine performed as well as permanganate in more traditional green sand filter systems, while avoiding the negative secondary issues.

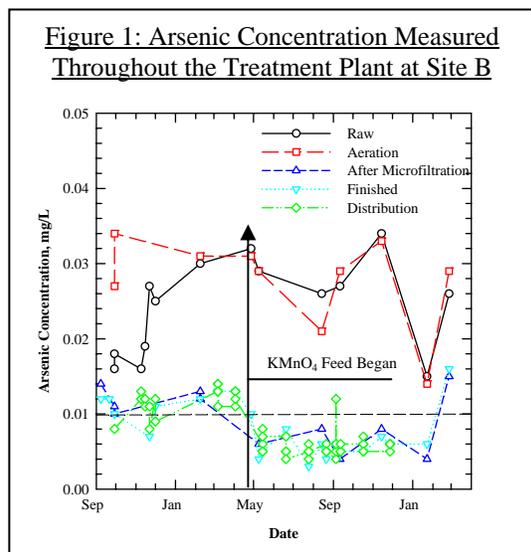
Parameter	Site A Raw	Site A Finished	Site B Raw	Site B Finished	Site C Raw	Site C Finished
Mn (µg/L)	141	2.2	51	<b>61</b>	130	<b>388</b>
As (III) (µg/L)	11.1	0.5	26.6	0.9	21.9	1.2
As (V) (µg/L)	1.5	0.6	8.2	6.3	3.5	2.3
Total As (µg/L)	16.6	1.5	39.1	8.5	27.5	5.9
Fe (mg/L)	1.83	0.054	4.19	0.02	2.38	0.19
NH <sub>3</sub> as N (mg/L)	NA**	NA**	6.2	2.1	1.2	NA**
pH	7.3	7.7	6.9	7.5	7.3	7.3
TOC	NA**	NA**	6.23	NA**	3.3	3.1

\*\* Data not Available

Case B: Permanganate Necessary to Meet Arsenic Standard does not Address Manganese

Site B is a microfiltration and softening plant located in Illinois with high total organic carbon (TOC), ammonia, manganese, iron, and arsenic in the source water (Table 1). Aeration is used for iron oxidation followed by chlorine addition for arsenic oxidation. Permanganate addition had been practiced, but handling issues were noted.

Pre-chlorination had been used successfully as the sole chemical oxidant to address manganese and iron oxidation since permanganate was discontinued. However, the system configuration was unable to reduce arsenic levels below the new U.S. EPA standard of 10 µg/L. Given the elevated levels of natural ammonia in source water, chlorine was present as combined chlorine which lead to some concern that As(III), the form of arsenic in the source water, was not being effectively oxidized. In 2005, bench scale jar tests were performed on-site to evaluate the ability of hydrogen peroxide, chlorine, and potassium permanganate to oxidize arsenite [As(III)] to arsenate [As(V)]. Six one liter samples of aerated raw water were dosed with varying concentrations of either hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), sodium hypochlorite (NaOCl), or potassium permanganate (KMnO<sub>4</sub>), and agitated for 20 minutes (to simulate contact basin) in a jar test apparatus. After this treatment, the water was filtered with a 0.2µm membrane filter to simulate microfiltration. Dissolved oxygen, pH, and arsenic levels were measured before and after filtration.

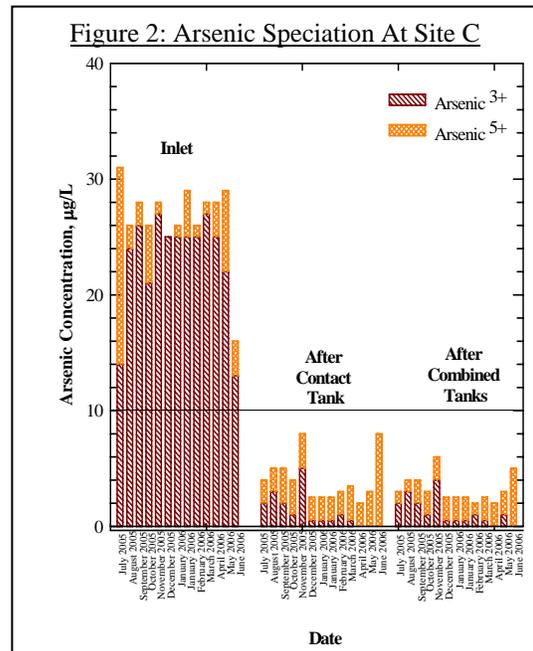


Jar test results suggested that the application of a sufficient dose of potassium permanganate before or just after aeration would allow the plant to produce final arsenic levels below the new arsenic MCL. Hydrogen peroxide was not an effective oxidant and chlorine was reasonably effective in oxidizing As (III) to As(V) for subsequent filtration and removal, but not effective enough to meet the MCL. Presumably, the elevated ammonia (6.2 mg/L) in the source water resulted in the formation of chloramines which are not effective at oxidizing As (III). Because of the jar test results, Site B began adding 0.5 mg/L of sodium permanganate (NaMnO<sub>4</sub>) after aeration, and within a month of operation increased the dosage to 0.7 mg/L. A target total chlorine residual before filtration of 0.05 to 0.70 mg/L (as Cl<sub>2</sub>) was adjusted based on TOC levels in raw water.

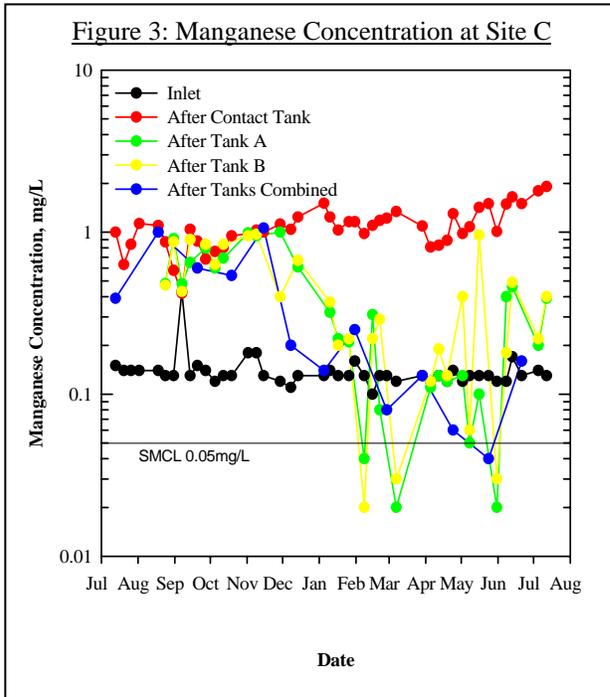
Once permanganate was added, the micro-filtration system was very effective in removing arsenic to levels below the MCL (Figure 1). Manganese levels in finished waters, however, remained above the secondary MCL and, on average, were higher than in raw ground water (Table 1). One possible reason for the elevated manganese is the TOC of the water. Carlson et. al (1999) reported that fine colloidal manganese (i.e., MnO<sub>2</sub> particles) might form in the presence of NaMnO<sub>4</sub> and high levels of dissolved organic material (DOM) in source water. Because of the high level of TOC in the source water (5.8 mg/L), it is possible that colloidal manganese was formed and passed through the filter system. Another possibility is that the permanganate dose was not optimized. The case study illustrates a situation where permanganate was necessary to meet a regulatory standard, but caused a problem in controlling manganese in treated water.

Case C: High TOC and DBP Formation Potential Requires Permanganate

Location C is an iron oxidation and filtration plant located in Minnesota that uses pressurized vessels and proprietary ceramic filtration media. In April 2005, a disinfection byproduct (DBP) formation test was conducted on the source water and found that, after 96 hours, the total trihalomethane (TTHM) level was 0.11mg/L, which exceeded the TTHM MCL (0.080mg/L) and existed almost completely as chloroform. The ammonia level of 1.2 mg/L was also elevated, and significantly increased the amount of chlorine necessary to fully oxidize the arsenic and manganese present and to maintain a free chlorine residual. To get around these problems, permanganate was added to oxidize As(III) in the source water (Table 1) and to avoid potential DBP issues.



During the one year U.S. EPA study period,  $\text{KMnO}_4$  dosage rates varied from 1.3 to 6.5 mg/L to optimize metals removal, and a minimum contact time of 20 minutes before filtration was maintained. Figure 2 shows the As(III) concentration dropped to  $1.0\mu\text{g/L}$  after  $\text{KMnO}_4$ , indicating effective oxidation of As(III) to As(V). As(V) concentrations after the contact tanks were low (average  $3.4\mu\text{g/L}$ ), indicating that the As(V) formed was adsorbed onto and/or co-precipitated with iron solids. The near complete precipitation of soluble iron from 2.38 mg/L to 0.19 mg/L (average) suggests that TOC levels did not adversely effect As(III) and Fe(II) oxidation.



As illustrated in Figure 3, manganese removal was inconsistent and often the finished water concentration exceeded the manganese secondary MCL. Jar tests indicated that increasing the  $\text{KMnO}_4$  dose to 4.5 mg/L would cause the formation of floc large enough to be removed during filtration, but this dose also caused episodes of pink water. Site C illustrates a situation when  $\text{KMnO}_4$  had to be used to avoid DBP formation issues and oxidize As(III), yet manganese levels in finished water were difficult to control.

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### Conclusion

The addition of chlorine, while in many cases not considered, was shown in some situations to be an effective method of oxidizing reduced forms of arsenic, manganese, and iron. In groundwaters with complicating factors, such as high ammonia or disinfectant byproduct formation potential, permanganate addition may be required. The addition of permanganate as a strong oxidant, however, does have significant drawbacks including difficulty in controlling manganese levels in finished water.

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### ***Notice***

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