

Control of Metal Oxide Fouling in Reverse Osmosis

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Abstract

High levels of iron and manganese, along with large quantities of dissolved gases in the wells created concern for the viability of a conventional desalination design for the proposed City of Camarillo groundwater desalination facility. To identify viable pre-treatment process(es) for the control of metal oxide fouling in reverse osmosis, a 12-month pilot study was undertaken. The pilot study tested several pre-treatment alternatives, one of which was chlorine dioxide and filtration using dual media filters to remove both iron and manganese oxides.

The results of the pilot-scale testing indicated that chlorine dioxide and filtration using dual media filters is an effective pre-treatment process for preventing metal oxide fouling in reverse osmosis. Nearly 100% of iron and approximately 70% of manganese in the well water was oxidized and removed during the pre-treatment stages, and the remaining 30% of manganese did not appear to cause fouling of the reverse osmosis membranes. Chlorine resistant membranes were also tested along with standard brackish water membranes, during the pilot study. The test results indicated that standard brackish water membranes experienced damage from either the chlorine dioxide or low levels of impurities within the chlorine dioxide. No damage was seen, however, for the chlorine resistant membranes.

Keywords

Chlorine Dioxide; Fouling; Iron; Manganese; Metal oxide; Reverse Osmosis

INTRODUCTION

The city of Camarillo, CA, has been experiencing deteriorating water quality in some of their wells with increasing levels of iron, manganese, sulfates, and chlorides, which limit the City's ability to utilize their existing well supplies and increase their reliance on imported water supplies. Table 1 summarizes the historic water quality of the City's Well A.

Table 1: Historic Water Quality of Well A

Parameter	Unit	Average Value
Iron	mg/L	1.00
Manganese	mg/L	0.19
Sulfate	mg/L	851
Chloride	mg/L	172
Total Dissolved Solids (TDS)	mg/L	1773

Note: Average of water quality data from 8/3/1998, 6/3/2003, 5/21/2004, and 1/31/2007.

To further complicate the problem, the City's wastewater outfall is coming under control of total maximum daily load (TMDL) limits for chloride, total dissolved solids (TDS), and sulfate, essentially limiting the average concentrations in their well supplies to levels well below secondary maximum contaminant levels.

While it was clear to the City that reverse osmosis (RO) would be required to comply with TDS

and chloride limits for these wells, the increasing levels of iron and manganese, along with large quantities of dissolved gases in the wells created concern for the viability of a conventional desalination design.

The City contracted with CDM to conduct a 12-month pilot study to evaluate several pre-treatment processes for the control of metal oxide fouling in the RO. The pilot study evaluated oxygen quenching at the wells using sodium thiosulfate as a baseline alternative for conventional desalination. Three alternative oxidants were then evaluated for oxidation and filtration of the metal oxides prior to the RO. The alternatives included:

- Aeration and filtration using either dual media filters or microfiltration to remove iron oxides while allowing manganese to remain dissolved
- Chlorine dioxide (ClO_2) and filtration using dual media filters to remove both iron and manganese oxides
- Sodium hypochlorite and pyrolusite media filtration to remove both iron and manganese oxides

Purpose

This paper will present the results of pilot-scale testing of the chlorine dioxide and filtration pre-treatment alternative, which was tested from January 2, 2008 to January 31, 2008. The purpose of this pre-treatment evaluation was to test if iron and manganese could be oxidized by adding chlorine dioxide and removed through the granular media filtration while preventing fouling of or damage to the desalination process.

MATERIALS AND METHODS

The pilot study was conducted at the City's Well A. Chlorine dioxide was injected into Well A raw water (RW), upstream of the static mixer and the contact tank. Three overflow levels (full tank, 1/2 tank, and 1/3 tank) were used to vary the contact time (i.e., hydraulic residence time) for iron and manganese oxidations to occur. From the contact tank, the pre-treatment feed (PTF) water was pumped and filtered through the granular media filters (GMFs) operated in parallel. To test close to zero minutes of contact time, the contact tank was bypassed and the pre-treatment feed water was fed through the media filters using the pressure in Well A raw water pipe. The hydraulic loading rate through the media filters was varied by using two or three media filters. After media filtration, the pre-treatment product (PTP) water was fed through the cartridge filters, after which the antiscalant was injected, and the RO feed (ROF) water was then pumped to the RO membranes. Figure 1 presents a simplified schematic of the treatment process.

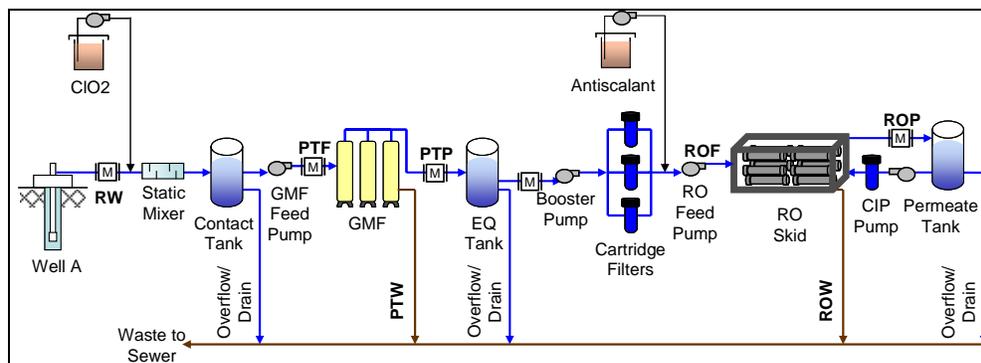


Figure 1. Schematic of Treatment Process

Granular Media Filters. Three 24-inch diameter pressure vessels, containing sand and anthracite media were used. Overall media depth in each filter vessel was 36 inches, with 30/70 split between sand and anthracite media.

Cartridge Filters. Three 20-inch long, 5 micron polypropylene cartridge filters were used.

Reverse Osmosis. Figure 2 presents a simplified schematic of the RO membrane system. The RO membrane system utilized two stages of low-pressure vessels in a 2:1 array with four elements per vessel. The first stage consisted of four 4-inch diameter vessels, simulating two parallel 8-element vessels (1A and 1B). The second stage consisted of two 4-inch diameter vessels simulating one 8-element vessel (Vessel 2). Chlorine resistant membranes (Model CRM, from Woongjin Chemical Co.) were used in Vessels 1A-1, 1A-2, and 2A. Standard brackish water membranes (Model BLR, also from Woongjin Chemical Co.) were used in Vessels 1B-1, 1B-2, and 2B.

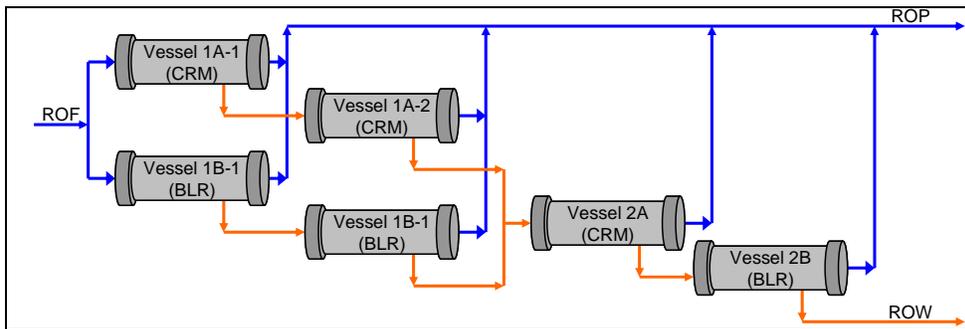


Figure 2. Schematic of Reverse Osmosis

In addition to the standard pre-treatment process of chlorine dioxide injection and granular media filtration, sodium thiosulfate feed upstream of the cartridge filters and caustic soda (NaOH) feed upstream of the chlorine dioxide feed point were also tested to evaluate the effects of quenching chlorine dioxide residual in the RO feed water, and of raising the pH of Well A raw water to pH 8, respectively.

The variables of the pilot-scale testing were: chlorine dioxide dose, chlorine dioxide contact time (CT), granular media filter loading rate (LR), pH adjustment, dechlorination, and the RO operating parameters. These test variables are listed in Table 2.

Table 2: Operating Conditions

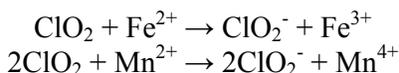
	Time	Operating	ClO ₂	Contact	GMF	NaOH	PTF	Sodium	RO
	Period	Hours	Dose	Time	LR	Feed	pH	Thiosulfate	Recovery
			(mg/L)	(min)	(gpm/sf)			Feed	(%)
A	1/02-1/07	115	1.8	36	4.7	No	7.3	Yes	74
B	1/08-1/11	87	1.7	38	4.6	No	7.3	No	74
C	1/11-1/13	66	1.7	36	5.1	Yes	8.1	No	76
D	1/14-1/15	23	1.8	38	3.0	Yes	8.1	No	75
E	1/16	18	0	38	3.0	No	7.1	No	74
F	1/17-1/22	116	2.1	38	3.0	No	7.3	No	74
G	1/23	23	1.9	17	3.2	No	7.3	No	74
H	1/24	20	1.8	15	4.5	No	7.3	No	74
J	1/25	25	1.6	10	4.6	No	7.3	No	74
K	1/28	29	1.3	6	5.6	No	7.4	No	74
L	1/29-1/31	64	0.9-1.4	0	4.5	No	7.3	No	74

RESULTS

Chlorine Dioxide Dose and Demand

The average chlorine dioxide dose was 1.7 mg/L, and the average chlorine dioxide residual measured in the RO feed water, after correcting for oxidized manganese interferences, was 0.24 mg/L. Therefore, the average chlorine dioxide demand was 1.5 mg/L.

The oxidation of iron and manganese with chlorine dioxide can be described by the following reactions:



The typical chlorine dioxide dose that has been reported for the oxidation of iron and manganese are 1.2 mg ClO₂/mg Fe²⁺ and 2.5 mg ClO₂/mg Mn²⁺, respectively (MWH, 2005). The average dissolved iron concentration in Well A raw water was 0.17 mg/L, all of which was oxidized by chlorine dioxide. The average dissolved manganese concentration in Well A raw water was 0.23 mg/L, but only 0.16 mg/L of it was oxidized by chlorine dioxide. Therefore, it appears that approximately 0.6 mg/L of chlorine dioxide, 40% of the total chlorine dioxide demand, was required to oxidize iron and manganese in the Well A raw water. It appears that the remaining 0.9 mg/L of chlorine dioxide, 60% of the total chlorine dioxide demand, was required to oxidize the organics in the Well A raw water. The average total organic carbon (TOC) in Well A raw water measured during this testing period was 1.6 mg/L.

Iron Oxidation

The total and dissolved iron data shows that the chlorine dioxide feed and granular media filtration is an effective pre-treatment process for removing iron. Figure 3 summarizes the average total iron and dissolved iron levels in the Well A raw water, pre-treatment feed water, RO feed water, and RO waste.

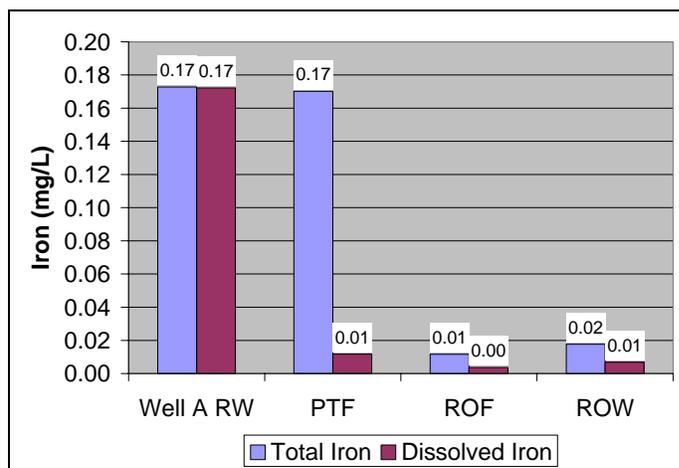


Figure 3. Average Iron Levels

The total and dissolved iron data for Well A raw water and pre-treatment feed water shows that chlorine dioxide oxidized nearly 100% of iron when chlorine dioxide was dosed.

The contact time had no effect on iron oxidation because chlorine dioxide reacts with iron nearly instantaneously. Although the contact time was reduced to nearly zero minutes by bypassing the contact tank during operating condition L, nearly 100% of iron was oxidized. The pH adjustment also had no effect on iron oxidation.

Manganese Oxidation

The total and dissolved manganese data shows that chlorine dioxide feed and granular media filtration pre-treatment removed 55% to 80% of total manganese. On average, 70% of total manganese was oxidized and removed by pre-treatment. Figure 4 summarizes the average total manganese and dissolved manganese levels in the Well A raw water, pre-treatment feed water, RO feed water, and RO waste.

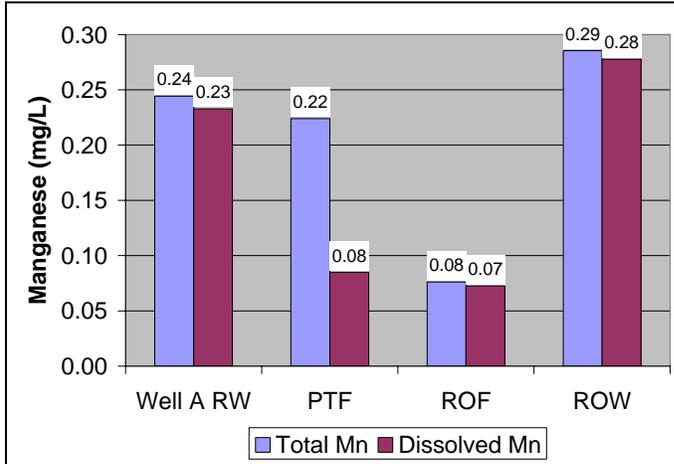


Figure 4. Average Manganese Levels

The total and dissolved manganese data for RO feed water shows that the manganese in the RO feed water was nearly all in the dissolved state. Further, it should be noted that the manganese levels in the RO feed water were nearly equivalent to the dissolved manganese levels upstream of the media filters (see Figure 4). The data indicates that approximately 0.07 mg/L of dissolved manganese that was not oxidized during the pre-treatment stage did not get oxidized in the RO, even in the presence of residual chlorine dioxide in the RO feed water. Although the chlorine dioxide oxidized only 70% of total manganese, the remaining 30% of total manganese that was dissolved in the RO feed water remained dissolved and was removed by desalination without causing particulate fouling of the RO.

The contact time had no apparent impact on manganese oxidation. On average, the same amount of manganese was oxidized with nearly zero minutes of contact time as with 37 minutes of contact time. Figure 5 shows the average manganese oxidation rates vs. contact time.

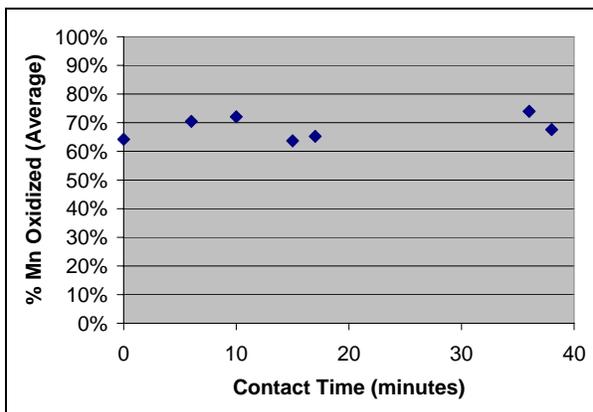


Figure 5. Average Manganese Oxidation Rates vs. Contact Time

It appears that raising the Well A raw water pH from 7.3 to 8.1 also did not improve manganese oxidation rate significantly (see Figure 6).

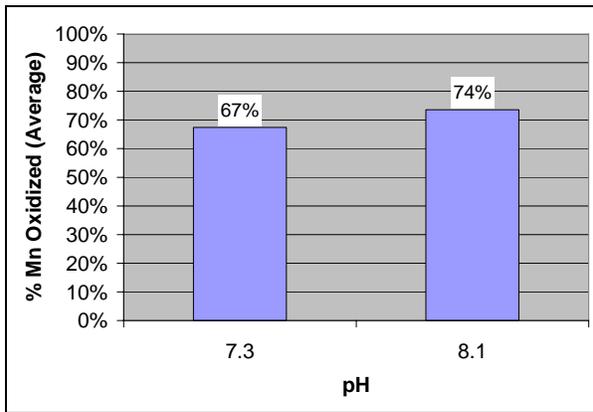


Figure 6. Average Manganese Oxidation Rates vs. pH

Granular Media Filters Performance

Table 3 summarizes the average fouling rates of the granular media filters. The differential pressure across the media filters increased by 1.5 psi/day at the hydraulic loading rate of 3.0 gpm/sf, and 3.6 psi/day at the hydraulic rate of 4.5 to 4.7 gpm/sf. The higher fouling rates require more frequent backwashes.

When caustic soda was used to raise the pH of Well A raw water from 7.3 to 8.1, the media filters were fouled at a much faster rate due to added fouling from scale build-up. The differential pressure across the media filters increased by as much as 13 psi/day at the hydraulic loading rate of 5.1 gpm/sf. Consequently, an acid soak and backwash was required to fully remove the scale which had built up on the media filters.

Table 3. Granular Media Filters Fouling Rate

GMF Loading Rate (gpm/sf)	Without pH Adjustment (pH 7.3)	With pH Adjustment (pH 8.1)
	Average GMF Fouling Rate (psi/day)	Average GMF Fouling Rate (psi/day)
3.0	1.5	4.8
4.5 to 4.7	3.6	--
5.1	--	13

The heaving fouling rate of the cartridge filters, discussed below, indicates that the media filters were only partially effective at removing the oxidized iron and manganese, even at the low filtration rates, averaging between 3 to 5 gpm/sf. This may have been the result of ineffective backwashing of the media filters, however, there was no clear trend of higher breakthrough toward the end of a filtration cycle.

Cartridge Filters Performance

It was evident that the granular media filters did not remove all oxidized iron or manganese based on the heavy fouling rate of the cartridge filters, which were replaced weekly (see Table 4). Also, high total iron level of 0.11 mg/L in the RO feed water, measured on January 14, 2008, was evidence of particulate iron break-through. The high silt density index (SDI) numbers, 4.2 and 5.0, measured two or more days after the cartridge filters replacement, as opposed to a low SDI number,

0.6, measured less than a day after the cartridge filters change-out, may also be evidence of particulate break-through.

Table 4. Cartridge Filter Fouling Rate

Sets	Date	No. of Hours Used	NaOH Used for pH Adjustment	Fouling rate (psi/day)
1	1/2 - 1/8	137	No	--
2	1/8 - 1/15	151	Yes	≥ 2.4
3	1/15 - 1/22	137	No	≥ 1.2
4	1/22 - 1/31	204	No	≥ 1.5

On average, the differential pressure across the cartridge filters increased by more than 1.2 psi/day when caustic soda was not used for pH adjustment. However, the fouling rate of the cartridge filters approximately doubled due to scale build-up when caustic soda was used to raise the pH of the Well A raw water.

The spent cartridge filters from this pre-treatment testing were dark brown overall when they were wet, but patches of black manganese were clearly visible when they were dry (see Figure 7). This compares well against the fouled cartridge filters from the aeration and filtration pre-treatment testing, which were uniformly rust colored without black manganese fouling (see Figure 8).



Figure 7. Cartridge Filters used during ClO₂ and Filtration Testing



Figure 8. Cartridge Filters used during DO and Filtration Testing

RO Membrane Performance Measured in Mass Transfer Coefficient

The first stage mass transfer coefficient (MTC) and the second stage MTC are shown in Figures 9 and 10, respectively. MTC is a measure of membrane performance, with fouled membranes demonstrating a drop or reduction in MTC.

$$MTC = \frac{\text{temperature_normalized_flux}}{\text{net_driving_pressure}}$$

The first stage MTC shows a slight upward trend during most operating conditions, with a slight downward trend during the latter stages of testing. Overall, the first stage MTC looks relatively flat, indicating that particulate fouling was not a significant concern during this stage of testing. The slight rise in MTC during the first 3 weeks of this pre-treatment testing, however, may be a concern, as it indicates that membrane damage could be occurring from chlorine dioxide or low levels of impurities in the chlorine dioxide.

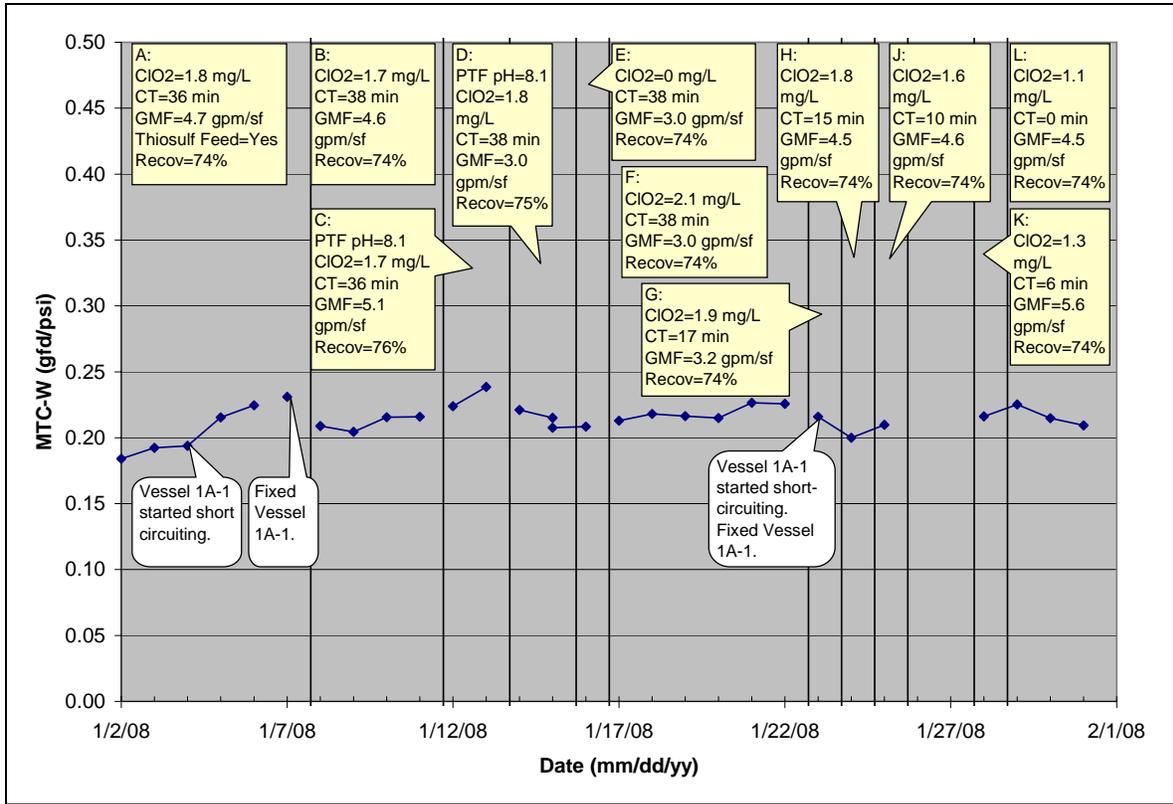


Figure 9. 1st Stage MTC_W at 25 °C

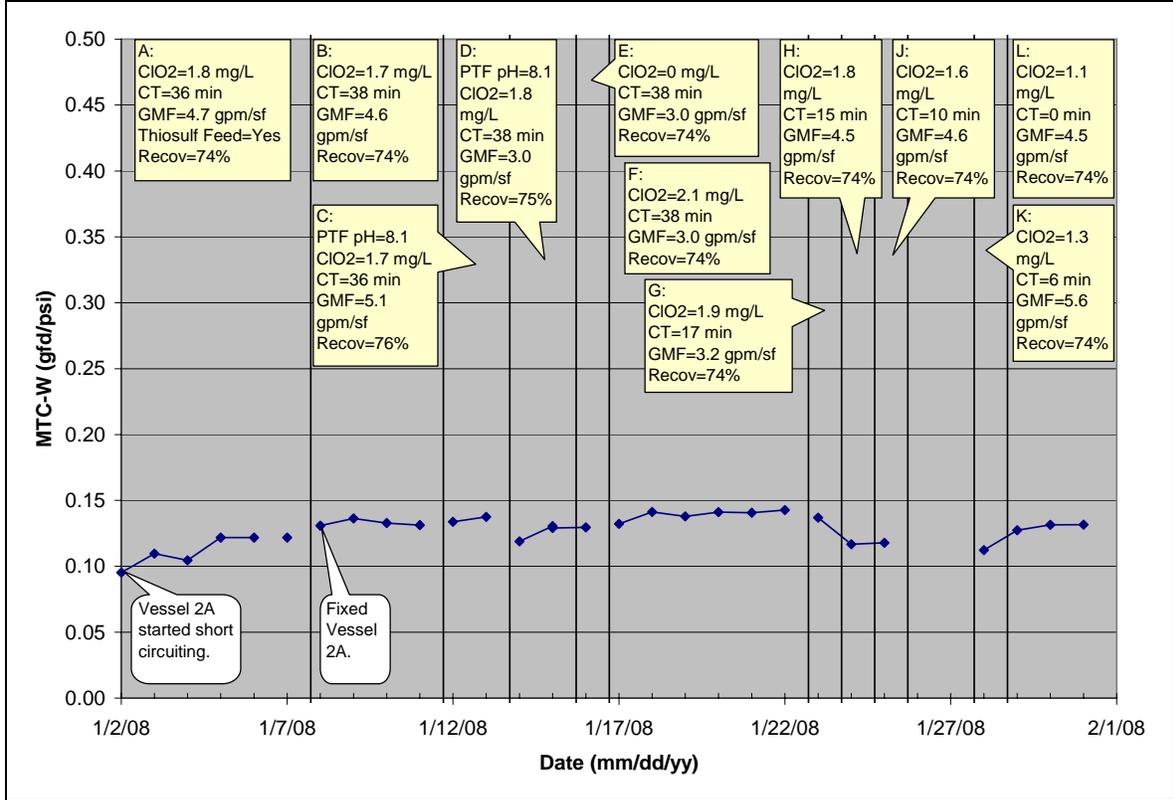


Figure 10. 2nd Stage MTC_W at 25 °C

RO Membrane Resistance to Chlorine Dioxide Measured in Permeate Conductivities

RO membrane damage could be determined by the permeate conductivities shown in Figures 11 and 12. Standard brackish water membranes (BLRs), used in Vessels 1B-1, 1B-2 and 2B, show evidence of damage with a steadily increasing permeate conductivity in all three vessels (see Figure 11). The chlorine resistant membranes (CRMs), used in Vessels 1A-1, 1A-2 and 2A, did not show evidence of membrane damage during the testing period (see Figure 12).

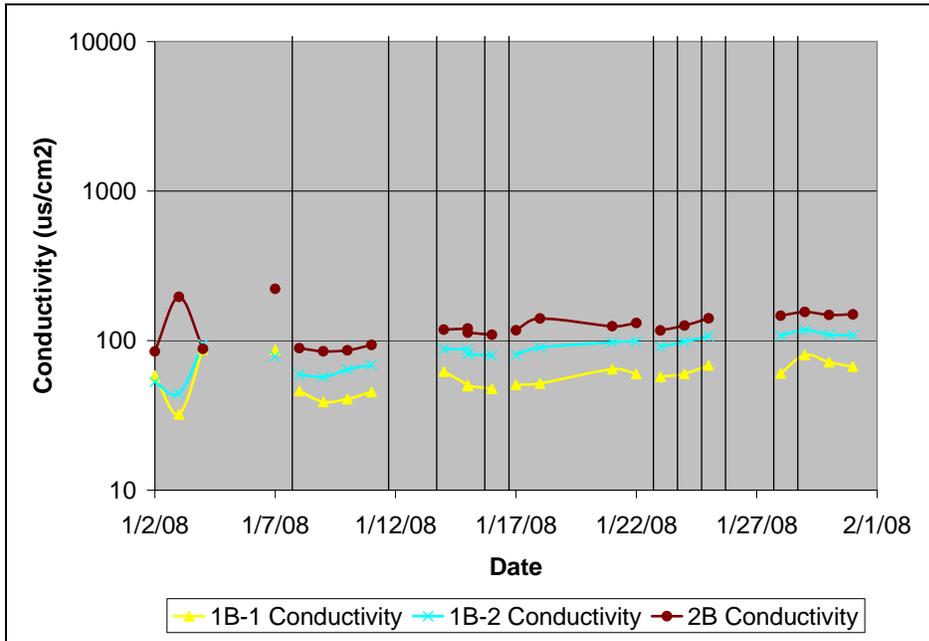


Figure 11. Permeate Conductivity for Standard Brackish Water Membranes (BLRs)

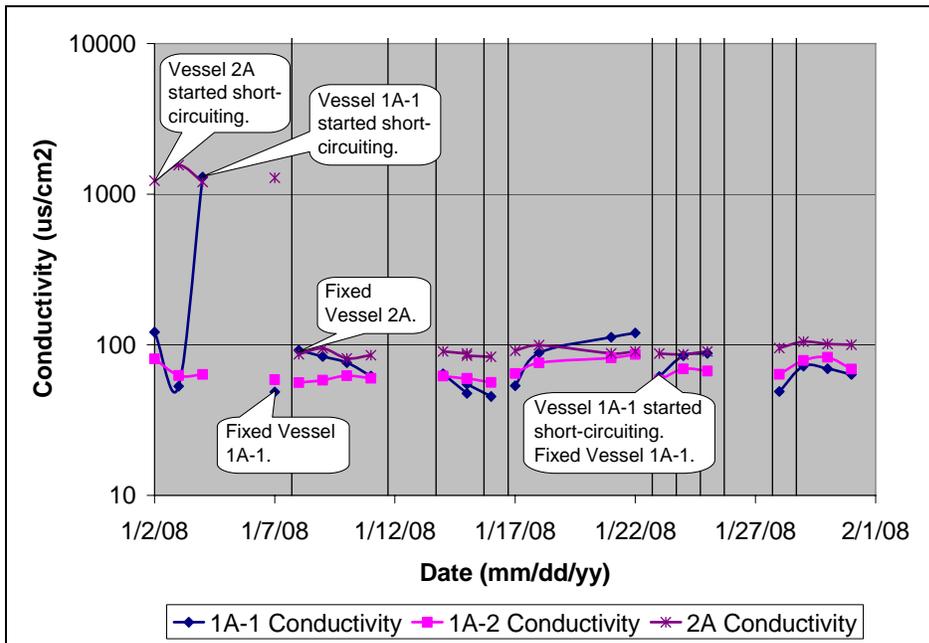


Figure 12. Permeate Conductivity for Chlorine Resistant Membranes (CRMs)

CONCLUSION

The estimated chlorine dioxide demand in Well A raw water ranged from 0.8 to 2.1 mg/L, with an average of 1.5 mg/L. Chlorine dioxide oxidized nearly 100% of iron and approximately 70% of manganese. The ability of chlorine dioxide to oxidize iron and manganese was not affected by contact time or raw water pH. The same quantities of iron and manganese were oxidized when the contact tank was bypassed as when 37 minutes of contact time was provided. Also, the same quantities of iron and manganese were oxidized at pH of 7.3 as at pH of 8.1.

Although only 70% of manganese was oxidized during the pre-treatment stages, the remaining 30% did not appear to cause fouling of the reverse osmosis (RO) membranes. It appears that when manganese was not oxidized at the first exposure to chlorine dioxide during the pre-treatment, it did not further oxidize downstream of the pre-treatment, regardless of the level of chlorine dioxide residual present in the RO feed water. All of the non-oxidized manganese remained dissolved and was successfully removed by the RO without causing particulate fouling.

Although chlorine dioxide with granular media filtration is an effective pre-treatment for the control of metal oxides in the RO, it appears to be problematic for several reasons. First and foremost, chlorine dioxide appears to have damaged the RO membranes, as was evident in the steadily increasing permeate conductivities and the gradually increasing MTC during the first three weeks of this pre-treatment testing. Although the chlorine resistant membranes (CRMs) appeared to be more resistant to chlorine dioxide than the standard brackish water membranes (BLRs), these membranes are a new product currently only produced by one manufacturer, and not in use in any full scale applications. For chlorine dioxide to be used in a full-scale plant with any membranes other than the CRMs, it is likely that dechlorination with sodium bisulfite or sodium thiosulfate would be required.

In addition to the RO damage, particulate iron and manganese appeared to be passing through the granular media filtration process, possibly due to ineffective backwashing of these filters, and fouling the cartridge filters. The cartridge filters should not be relied on for filtration, but were heavily loaded with particulate iron and manganese during this pre-treatment testing. Further, the fouling rate on the media filters was high, averaging 3 to 6 psi/day at a filtration rate less than 5 gpm/sf.

REFERENCES

MWH, J.C. Crittenden, et al (2005). *Water Treatment: Principles and Design*. 2nd ed. John Wiley & Sons, New Jersey, USA.