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Using oxidation–reduction potential to manage media filters treating sulfide-laden groundwater

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ABSTRACT

An evaluation studying the use of oxidation–reduction potential (ORP) for optimizing a 10,500 m^3/d (2.8 MGD) oxidizing media filter (OMF) process treating Floridan groundwater containing between 1.6 and 1.8 mg/L sulfide has been completed. One year after placing the OMFs on-line, colored water complaints were reported within the municipal water system. It was determined that the filter beds required regeneration as they were insufficiently oxidized, and the media's manganese dioxide coating was being released into the finished water. ORP, free chlorine residual, total manganese and turbidity measurements were recorded during filter run cycles before and after each regeneration event. Results showed that below 500 mV ORP was a more useful measurement for monitoring regeneration events within the media bed than chlorine residual which was not detectable. Results showed a significant increase in turbidity (>2 NTU) and total manganese (> 0.05 mg/L) when the ORP within the filter bed dropped below 400 mV. More frequent cycling of the filters was found to be an effective treatment option to maintain ORP values above 600 mV as an operational threshold.

Keywords: Filter regeneration; Greensand; Media filter; Oxidation-reduction potential; Sulfide; Sulfur; Manganese

1. Introduction

1.1. Oxidizing media filters

Oxidizing media filters (OMF) are used to treat iron, manganese and sulfide by combining oxidation and filtration in a single granular media filtration process [1,2,3]. Although there have been many studies evaluating OMFs to remove iron and manganese, less has been published with regards to sulfide removal. Lessard et al. [4] modified a greensand filter at the pilot scale to test the addition of a settling tank, use of sand and anthracite coated with manganese oxides, chlorination and aeration for iron and manganese removal. Results indicated that the presence of a high quantity of iron significantly improved the filter's removal of manganese. In another study, seven different types of filtration medias were evaluated for manganese removal, which demonstrated that greensand and proprietary medias were effective [5]. According to Hamilton et al. [3], manganese removal within a filter bed occurs through catalytic oxidation at the surface of manganese dioxide (MnO_2) coated media. Duranceau and Trupiano [6] piloted a greensand OMF for sulfur control. In this study, bleach was used to continuously regenerate the oxidizing media bed. A comparison was made between oxidation of sulfide by bleach addition and oxidation of sulfide by the piloted media bed. Results showed that the pilot OMF required less chlorine for complete sulfide oxidation and produced a finished water with less turbidity compared with bleach addition alone.

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Greensand filtration is a popular type oxidizing media filtration. In this process, the filtration media is coated with a layer of manganese(IV) dioxide (MnO_2) which can oxidize reduced species such as iron, manganese and sulfide. The reduced species that are originally dissolved in water oxidize and are trapped within the filter. Hence, the filter requires periodic backwashing to remove the oxidized inorganics, as well as periodic regeneration with a permanganate solution to maintain the effectiveness of the manganese dioxide coating. There are several alternative media choices to traditional greensand (glauconite), these choices rely on silica sand as the base of the media instead of natural glauconite [7], where the silica base is coated with a layer of manganese (IV) dioxide. One such alternative oxidizing media is Greensand Plus™, a synthetic media manufactured by Inversand Company (226 Atlantic Avenue Clayton, New Jersey 08312).

1.2. Oxidation–reduction potential

Oxidation–reduction potential (ORP), also known as redox potential, measures the capacity of an aqueous system to accept or release electrons from chemical reactions. When an aqueous system is in an oxidized state, the system will accept electrons. When a system is in a reduced state, the system will release electrons. Eq. (1) presents the oxidation of sulfide in the presence of an oxidizing environment (where sulfide can be S^{2-}, HS^- or H_2S). Here the formation of elemental sulfur (S^0) is desirable as this inorganic colloidal species can be trapped in the media filter and removed during routine backwash operations.

$$S^{2-} \rightarrow S^0 + 2e^- \tag{1}$$

The oxidation of sulfide to sulfur when using chlorine as an oxidant is instantaneous in nature [8]. The required molecular ratio of Cl_2 to sulfide for complete oxidation under laboratory conditions is approximately four [9]. Sulfide oxidation has been studied using other chemical oxidants. Levine et al. [10] evaluated using hydrogen peroxide catalyzed by iron to form elemental sulfur. Lamoureux [11] evaluated the use of ozone to oxidize sulfides prior to granular activated carbon treatment.

Eq. (2) presents the reduction of Mn(IV) oxide in the presence of a reducing environment (where manganese oxide can be any of a variety of manganese oxide chemical formulas – here MnO_2 is used). Here the formation of soluble manganese (Mn^{2+}) is undesirable as this inorganic can impart a color and metallic taste to water. When sulfur is the primary reductant additional byproducts of Mn(IV) oxide are sulfate and elemental sulfur [12].

$$MnO_2 + 2e^- \rightarrow Mn^{2+} \tag{2}$$

Maintaining an OMF in an oxidized state is essential for efficient and effective performance. A bleach or permanganate solution is often continuously fed to the filter during operation to maintain an oxidized state. Periodic regeneration events where an oxidation bed is soaked in a strong permanganate solution are also used to maintain filter efficiency.

1.3. Relationship between free chlorine levels and ORP values

Several studies have described the relationship between free chlorine levels and ORP levels. Suslow [13] notes, in a publication on using ORP for water disinfection monitoring, that water with a measurable amount of free chlorine would have ORP measurements of 650–700 mV if the water pH is between 6.5 and 7. The author notes that lowering the pH to 6.0 would raise the ORP, as more hypochlorous acid becomes available due to the equilibrium shift between hypochlorous acid and the hypochlorite ion (pK_a of 7.53). Similarly, increasing the pH would lower the ORP value, as more hypochlorite ions would be present [13]. A publication by Steininger and Pareja [14] presented experimental data that showed ORP curves for differing pH and free chlorine concentrations. Results showed that at constant free chlorine concentrations ORP increased with decreasing pH. Results also showed that when free chlorine concentration increased at a constant pH, ORP values also increased [14]. Other studies have shown that when no free chlorine concentration is detectable, ORP values are generally less than 400 mV [15,16]. When free chlorine starts to become measurable, ORP values increase rapidly to over 600 mV where there is 0.2 mg/L of detectable free chlorine and then start to plateau at over 700 mV when 2 mg/L or more of free chlorine is present. In a study assessing ORP/pH-based control strategies for chlorination and dichlorination of wastewater, a similar trend was found: ORP values were above 600 mV when free chlorine was measurable and then steeply dropped to below 500 mV when there was no measurable free chlorine residual [17].

1.4. Imperial Lakes water treatment plant

The Imperial Lakes water treatment plant (ILWTP) is located near Mulberry in Polk County, Florida. Historically water at ILWTP was treated by chlorinating with bleach, using tray aeration for partial sulfide and CO_2 removal and adding caustic for corrosion control. Currently, the plant has a permitted capacity of 2.8 MGD and uses an oxidizing media filtration process for removal of sulfides from three on-site, 18-inch diameter, 750 feet deep groundwater wells. The oxidizing media selected for use at the water treatment plant was Greensand Plus™. Polk County Utilities, a division of Polk County Government, provides potable water service to consumers within the county's service areas. The county selected to use an OMF instead of a more traditional treatment process (e.g., packed tower aeration) due to the plant being located directly adjacent to a residential community. The key water quality improvements the county sought when upgrading the facility was a reduction in turbidity, caused by elemental sulfur, and an improvement in reducing corrosivity within the system. The elemental sulfur is formed when naturally occurring sulfides in the groundwater were oxidized during chlorination, and implicated in corrosion of residential plumbing [6, 9,11]. For these reasons, the county chose the use of oxidizing media filtration for treatment of this water supply.

After approximately 1 year of operation, the county utility started to receive colored water complaints from residents. An investigation into the cause of the color found that an ineffective backwashing regimen and infrequent permanganate regeneration events had caused the oxidizing media beds to shift from an oxidizing environment to a reducing environment. The ineffective backwash regimen resulted in sludge layer half an inch deep containing 12,100 mg/kg of iron, 5,020 mg/kg of manganese and 321,000 mg/kg of sulfur that covered the top of the oxidizing media beds and caused entering chlorinated water to ineffectively oxidize the filters [18]. As a result, manganese was being released from the filter beds and entered the distribution system. In this research, the OMF beds at Imperial Lakes were monitored over two filter regeneration events to compare two measurement techniques, ORP and free chlorine residual. The goal of the research was to assess the efficacy of these two measurement techniques to monitor filter regeneration efforts and assess filter bed effectiveness. Specifically, the effectiveness of a filter bed to reduce turbidity and prevent the release of manganese from the filter media.

2. Materials and methods

2.1. Groundwater quality and treatment description

Table 1 provides a summary of the groundwater quality that supplies the ILWTP. Fig. 1 presents a process flow diagram for the treatment plant, revealing that after water is pumped up from the groundwater source, sodium hypochlorite is added prior to entering two OMFs. Each filter contains three cells each having approximately 108 ft^2 of surface area. Water enters each filter and is then trifurcated before entering each of the three cells in each filter. After passing through the filters, a blended phosphate is added followed by an additional dose of sodium hypochlorite. Water is then transferred to a tray aerator prior to falling into the ground storage tank. High service pumps transfer water from the ground storage tank into the water distribution system. Additional sodium hypochlorite can be added at the water treatment plant's point of entry if necessary. As there are two OMFs, there is a total of six filter cells. The filtration rate for the entire system is 3,200 gpm (1,600 gpm/filter, 5 gpm/ft^2). Fig. 2 depicts a cross-sectional view of a filter cell. Each filter cell contains three sample taps. The bottom sample tap in each cell is in the middle of the oxidizing media layer. For monitoring considerations, the filter cells in each filter were assigned a designated letter. When viewing the filter from the side of the sample taps, the filter cells were labeled from left to right as Cell A, Cell B and Cell C.

Table 1
Raw groundwater quality from wells 1–3 at ILWTP

Water quality parameter	Value
Alkalinity, mg/L as $CaCO_3$	165–169
Bromide, mg/L	<0.2
Calcium, mg/L	40.0–43.9
Chloride, mg/L	9.3–9.5
Conductivity, μS/cm	392–407
Iron, mg/L	<0.005
Magnesium, mg/L	13
Manganese, mg/L	<0.005
pH	7.32–7.64
Sulfate, mg/L	1.88–2.47
Temperature, °C	23.7–25.5
Total dissolved solids, mg/L	79–136
Dissolved organic carbon, mg/L	1.17–1.39
Total sulfides, mg/L	1.6–1.8
Total suspended solids, mg/L	<0.5
Turbidity, NTU	0.04–0.39

2.2. Monitoring locations and water quality parameters

Water quality within the OMF was monitored both during operation and when the filter was not in operation between run cycles. Samples were collected from each of the six filter cells from the bottom most sample tap that is located approximately in the middle of the Greensand Plus™ oxidative media layer (Fig. 2). During filter operation, samples were collected every 2 min, and when the filters were at rest, samples were collected every 5 min. The four primary water quality parameters monitored were ORP, free chlorine residual, turbidity and total manganese. ORP measurements were made with the same probe throughout testing. ORP measurements were taken once every 2 min beginning when the well pump started and ending after 12 min. However, ORP measurements were taken every 5 min during the downtime between filter run cycles. The bottom sample tap on each cell

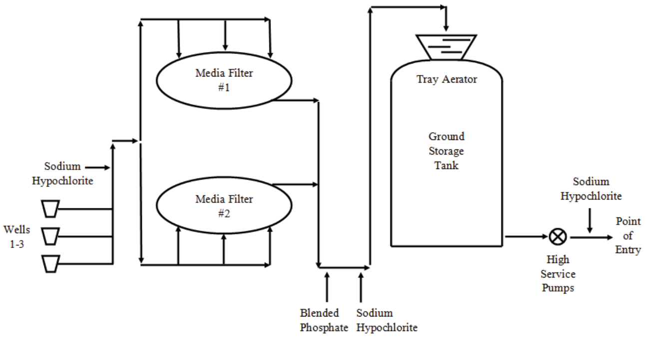

Fig. 1. ILWTP process flow diagram.

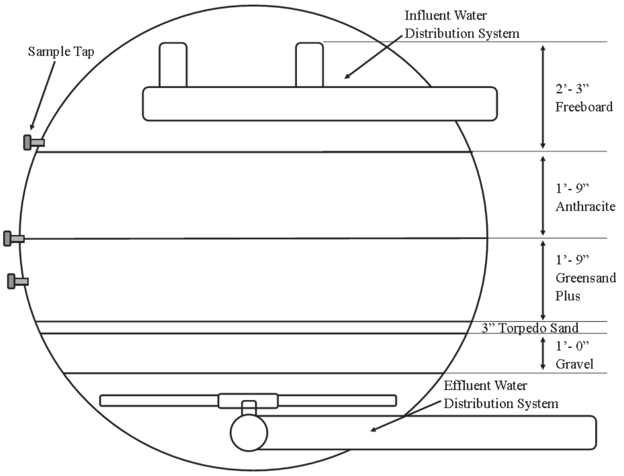

Fig. 2. Cross section of an oxidizing media filter cell.

Table 2
Monitored water quality parameters, associated standard method, monitoring equipment description and MDL

Water quality parameter	Standard method No.	Equipment description	MDL	Measurement location
Chlorine, free	8021[a]	HACH DR5000™ spectrophotometer	0.02 mg/L Cl_2	Field
Oxidation–reduction potential	2580B[b]	HACH HQ40d™ multimeter with MTC101 probe	0.1 mV	Field
Turbidity	2130B[b]	HACH 2100q portable turbidimeter	0.1 NTU	Field
Total manganese	3120B[b]	ICP plasma spectrometer	0.002 mg/L	Laboratory

[a] Hach, Loveland CO [19].
[b] Standard Methods [20].

was used to sample water from each cell. The bottom sample tap is located in the middle of the greensand media layer; hence sample values are thought to be representative of water that is in the middle of each of these layers. Table 2 presents the standard method used, a description of the equipment used, the minimum detection level (MDL) and the measurement location for each of these water quality parameters. A total of nine site visits were required to collect the measurements for the entire data set. Prior to each site visit, field equipment was calibrated and checked. ORP was found to be accurate to within ±10 mV throughout testing.

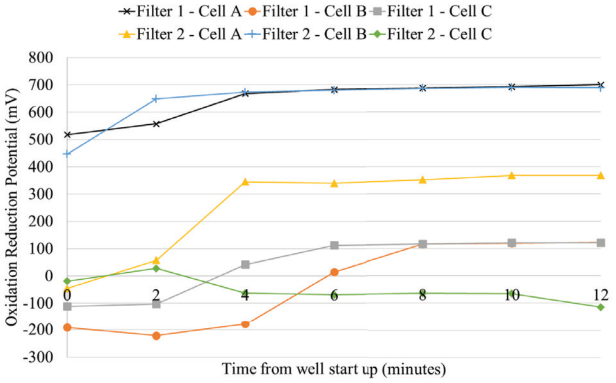

Fig. 3. ORP measurements during filter start-up and normal operation.

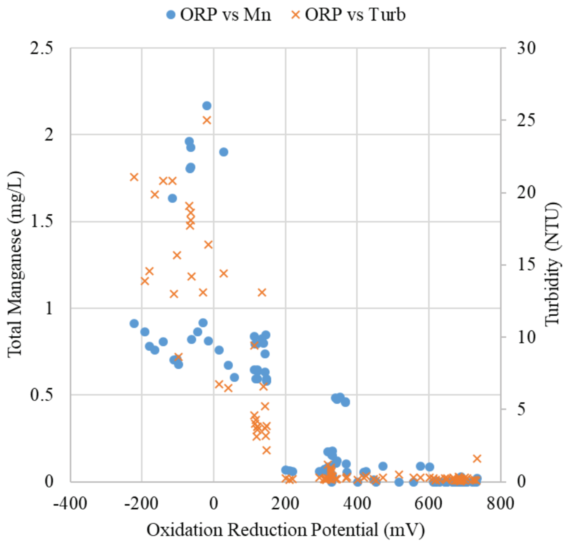

Fig. 4. ORP compared with manganese and turbidity measurements.

3. Results and discussion

The two OMFs used for sulfide treatment at ILWTP were monitored over a 10-month period to assess the effect of filter regeneration efforts to improve filter operation. Fig. 3 presents measured ORP values for each cell in both filter 1 and 2 during operation. There is a common trend in five of the six monitored cells shown in Fig. 3, the ORP increases over the first 4–6 min of filter operation. This increase is due to new well water that contains a dosed free chlorine residual being passed through the greensand layer and hence increasing the ORP of the filter bed. A similar trend occurs after the well pump is shut off, ORP values start to decrease in each of the cells until a well call when fresh water is pumped back into the cells and the ORP again increases.

To determine which of the cells in Fig. 3 is performing efficiently, a comparison of ORP to manganese concentration and turbidity was assessed for water exiting the greensand filter beds. Efficient operation with respect to sulfur treatment herein is defined as oxidizing sulfide to elemental sulfur while retaining turbidity in the filter so that water exiting the filter is below 2 NTU. Efficient operation with respect to total manganese herein is defined as the filter bed maintaining a sufficiently oxidized state so that water exiting the filter has a manganese concentration below 0.05 mg/L (this is the USEPA's secondary standard maximum contaminant level for manganese) [21].

Fig. 4 presents ORP measurements collected from the six greensand cells during multiple filter runs. Plotted against these ORP measurements are the resulting measured total manganese concentrations and turbidity values for each sample. Turbidity values and manganese concentrations remain below the aforementioned threshold values for 87% of samples when the measured ORP was equal to or above 400 mV. Hence, 400 mV was used as a minimum threshold for operators to assess filter bed health.

Free chlorine can also be used to assess filter bed health. Fig. 5 compares the same ORP measurements used to generate Fig. 4 to the free chlorine residual measurements of the same samples. Fig. 5 shows that a free chlorine residual is not consistently measurable until ORP values exceed approximately 500 mV and a notable increase in free chlorine levels occurs after an ORP value of 600 mV. These values are comparable with values found in literature when tested waters have a similar pH. Experimental testing did not show a clear plateau in ORP values at high free chlorine residuals. This is likely due to the measured free chlorine in the system never rising above 3.0 mg/L.

When a free chlorine residual of greater than 0.30 mg/L was present (which correlates to an ORP level of greater than 600 mV), turbidity was found to be below 2 NTU and total manganese was found to be below 0.05 mg/L for 94% of samples. Hence, when operators are assessing if a given filter cell is in an effective oxidative state, they can either measure ORP or test for a free chlorine residual. Testing for a free chlorine residual is often preferable as the measurement is quicker than that of ORP and is more readily available at most treatment plants.

ORP measurements are valuable when a filter cell registers an ORP value below 500 mV. During these conditions, ORP values are measurable where in contrast free chlorine residual measurements are below detectable levels. For instance, in Fig. 3 only two of the six filter ORP curves have measurable free chlorine results (filter 1 – Cell A and filter 2 – Cell B). The other four filter cells have no measurable amount of free chlorine and an increasing oxidation state would not be seen without ORP measurements. The value of ORP measurements is of particular importance when assessing filter regeneration events. For example, Fig. 6 presents ORP measurements during three filter run cycles for the same filter cell (filter 1 – Cell C). The bottom-most curve in Fig. 6 labeled 'Before Regeneration Events' depicts ORP measurements over a filter cycle before the filter 1 – Cell C was regenerated with sodium permanganate. The middle curve labeled 'Post First Regeneration Event' in Fig. 6 shows ORP measurements over a filter cycle after the filter was regenerated with sodium permanganate for the first time. There is a noticeable increase in ORP values throughout a filter run cycle when comparing the 'Before Regeneration Events' ORP curve to the 'Post First Regeneration Event' ORP curve. This shows that the regeneration had a positive effect on the filter cell. Similarly, the last ORP curve in Fig. 6 labeled 'Post Second Regeneration Event' shows ORP measurement after a second filter cell regeneration event took place. Again, an increase in ORP values throughout the filter run cycle when comparing the 'Post First Regeneration Events' ORP curve to the 'Post Second Regeneration Event' ORP curve indicates the second regeneration event improved filter health further. Fig. 6 also shows the 'Free Chlorine Residual Threshold'. Below the indicated threshold of 500 mV free chlorine residual is not detectable. Hence, free chlorine residual in this instance would not allow operators to assess if either the first or the second regeneration events were successful at improving the filter cell health. In this case, ORP measurements are more informative as they can verify that regeneration efforts are improving filter performance where free chlorine residual monitoring cannot.

Fig. 7 presents ORP measurements collected during the downtime between filter run cycles. Measurements were initiated at the end of a filter run cycle when the well pump shut off (i.e., minute 0 in Fig. 7) and measurements were taken every 5 min until the well was turned back on for a new filter cycle (i.e., minute 35 in Fig. 7). Fig. 7 shows that when filter 2, Cell B, is at rest and fresh water with a dosed chlorine residual is not flowing through the filter cell, the ORP decreases over time. At 35 min, for example, the ORP approaches the threshold value of 400 mV under which turbidity and manganese concentration will start to increase in water exiting the filter. The decrease in ORP is measurable and a distinct trend can be seen. Free chlorine residual, however, is not measurable over this entire range and a distinct trend cannot be seen. Here again ORP is a more informative measurement. An operating alternative for the utility is to cycle the filters more frequently but for shorter durations during each run. This would help keep ORP values above a minimum threshold (this threshold could be 400 mV or a more conservative value) by passing fresh chlorinated water through the filters more often.

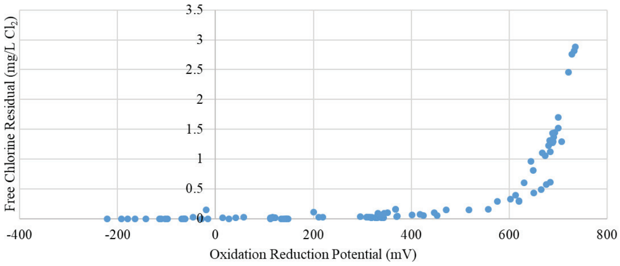

Fig. 5. ORP measurements compared with free chlorine measurements.

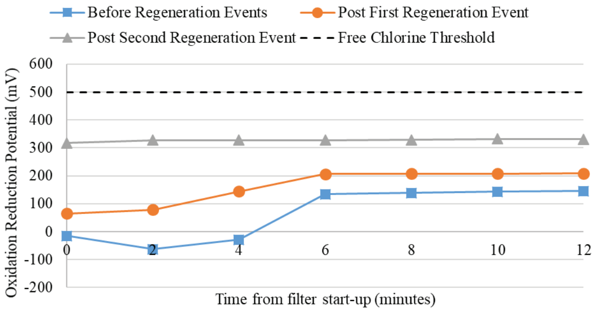

Fig. 6. ORP measurements before and after two regeneration events.

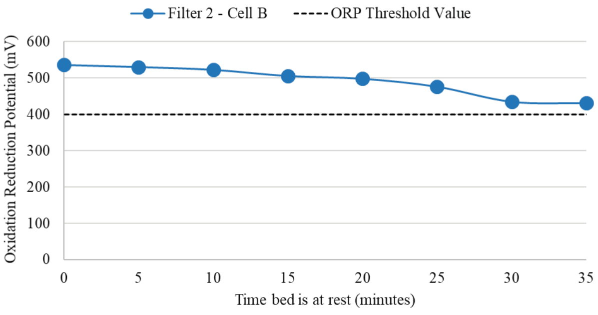

Fig. 7. ORP measurements when oxidizing media bed is at rest.

4. Conclusions

A Greensand Plus™ oxidizing media filtration system used to treat sulfide-laden groundwater was monitored over several run cycles before and after filter regeneration events with sodium permanganate. Results showed that turbidity and total manganese were below 2 NTU and 0.05 mg/L, respectively, 87% of the time when the ORP in the filter bed was measured to be at least 400 mV. This percentage increased to 94% when the ORP was measured to be at least 500 mV. Free chlorine residual was measurable when ORP values were greater than 500 mV. Hence, when assessing if a filter cell is in an effective oxidative state, either ORP or free chlorine residual measurements could be used. Here, testing for a free chlorine residual is often preferable as the measurement is quicker than that of ORP and is more readily available at most treatment plants.

When monitoring filter regeneration events with sodium permanganate, if the ORP of the monitored cell is below 500 mV, free chlorine measurements will not be informative as there will be no measurable residual. However, ORP will be measurable and can allow operators to assess the effectiveness of regeneration efforts. Similarly, when monitoring a cell during filter downtime, if the ORP of the cell is below 500 mV, ORP will be an informative measurement while free chlorine residual will not. Monitoring results during filter downtime show ORP values decline over time when the oxidizing filter beds are at rest. More frequent cycling of the filters was found to be an effective treatment option to maintain ORP values above 600 mV as an operation threshold to control Mn release.

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