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Evaluation of oxidized media filtration for removing sulfides from groundwater

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ABSTRACT

An evaluation of oxidized media filtration processes for the removal of sulfides from groundwater supplies has been completed. Two different filtration processes were studied at the pilot scale: bleach (NaOCl) oxidation preceding electromedia filtration, and NaOCl oxidation preceding manganese (IV) oxide (MnO_2) filtration. Media filtration, historically used to remove iron and manganese from water supplies, was shown to effectively remove sulfide from groundwater where iron and manganese were not present in any appreciable quantities. Bleach oxidation prior to electromedia or manganese (IV) oxide filter media processes removed total sulfide to below detection levels (<0.1 mg/l) for groundwater supplies containing as high as 2.6 mg/l total sulfide. The use of bleach oxidation preceding media filtration produced finished water with low turbidity (<1.0 NTU), as compared to the more commonly used tray aeration and chlorination processes that produced significant turbidity (between 6–16 NTU as observed in this study). As compared to the more commonly employed treatment method of tray aeration and bleach processes for groundwater sulfide treatment, bleach consumption was found to be 30 percent less for the media filtration processes piloted in this study.

Keywords: Media filtration; Hydrogen sulfide; Oxidation; Groundwater treatment; Turbidity

1. Introduction

1.1. Overview and motivation

Reduced sulfur compounds, those that comprise total sulfide, are most often found in ground water and at the bottom of water impoundments where anaerobic conditions prevail. If left untreated, sulfides impact finished water quality, corrosivity, create undesirable taste and odor, and oxidize to form visible turbidity and color [1,2,3]. Hydrogen sulfide accelerates corrosion by reacting with metal ions to form nonprotective insoluble sulfides. It attacks steel, iron, galvanized and copper piping to form "black water" even when oxygen is not present, and can deteriorate asbestos-cement pipe in some waters through microbial reactions.

Hydrogen sulfide is commonly found in many potable groundwater supplies. Removing sulfur species, particularly hydrogen sulfide and sulfate, is an important aspect of potable water treatment. At present time, treatment methods employed to remove sulfide from groundwater supplies typically include tray aerators, packed towers or advanced oxidation processes such as ozone [3,4]. Although oxidized media filtration has historically been used for treating groundwater containing iron and manganese, the process has not been extensively studied for sulfide treatment. This paper presents the results of research that has been conducted to evaluate oxidized media filtration processes for the removal of sulfides from groundwater supplies. Two different filtration processes were studied at the pilot scale at existing groundwater treatment plants: NaOCl oxidation preceding electromedia filtration, and NaOCl oxidation preceding MnO_2 filtration.

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2. Aqueous sulfide characteristics

2.1. Hydrogen sulfide characteristics

Hydrogen sulfide (H_2S) is commonly found in gaseous form in groundwater and domestic wastewater. The gas gives off an obnoxious odor often compared to that of rotten eggs, which occurs as a result of anaerobic bacterial action on sulfates [3,4,5] As little as 0.5 mg/l of hydrogen sulfide in potable water is noticeable and the odor imparted by 1.0 mg/l of hydrogen sulfide can be considered offensive [5]. The minimum detectable taste of sulfide in water is approximately 0.05 mg/l.

Theoretically (and as shown in thermodynamic calculations), sulfate could be reduced to hydrogen sulfide inorganically. However, laboratory studies have shown that the inorganic reaction is only favorable at temperatures in excess of 250°C. These conditions are unlikely to be seen in a natural aquifer system, and thus the reduction of sulfate typically occurs through bacterial mediation. Sulfate reducing bacteria assimilate sulfur under conditions common to anaerobic aquifer systems that often have a source of organic carbon available, as low as 0.1 mg/l [6]. Bacteria reduce the sulfate ion (SO_4^{2-}) in a reaction with organic matter (CH_2O-R) that produces bicarbonate (HCO_3^-), hydrogen sulfide (H_2S), and undefined radicals (represented with R) as end-products, as depicted in Eq. 1. This reaction presented stoichiometrically is as follows:

$$2(CH_2O\text{-}R) + SO_4^{2-} + \text{Bacteria} \rightarrow 2(HCO_3^-) + H_2S + 2R \quad (1)$$

The genera most often responsible for sulfide production are *Desulfovibrio desulfuricans* and *Desulfotomaculum* which are known to accelerate the reduction of sulfate [6,7].

2.2. Speciation of hydrogen sulfide in water

Sulfide exists in three forms in the aqueous hydrogen sulfide system, hydrogen sulfide (H_2S), bisulfide ion (HS^-), and sulfide ion (S^{2-}). The sum of these three compounds is commonly referred to as total sulfide, with the concentration of total sulfide reported in equivalent units as mg/l S^{2-}. In this document total sulfide may be simply referred to as "sulfides". As shown in Fig. 1, in the pH range of 6.0 to 8.0 the predominant reduced sulfur forms are HS^- and H_2S; the sulfide (S^{-2}) form is negligible at ambient pH levels in groundwater. Other thermodynamically stable states of sulfur, both final and quasi, include sulfate (S^{+6}) and colloidal sulfur (S°) under oxidized water conditions. Consequently, of the thirty or more ionic and molecular sulfur species that exist, only five are thermodynamically stable under conditions found in drinking water, and include hydrogen sulfide [H_2S], bisulfide [HS^-], elemental sulfur [S°], bisulfate [HSO_4^-], and sulfate [SO_4^{2-}]. Other sulfur states that are found in nature, but are considered to be thermodynamically unstable in aqueous systems include polysulfides, polythionates, and thiosulfate [7,8].

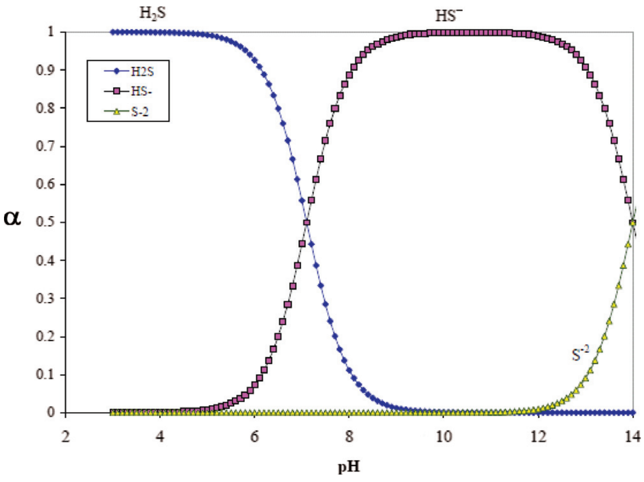

Fig. 1. Sulfide species distribution diagram.

In aqueous solutions, hydrogen sulfide dissociates in water, and can be described by the equilibrium equations shown in Eqs. 2 and 3.

$$H_2S + H_2O \Leftrightarrow H_3O^+ + HS^- \qquad pKa_1 = 7.0 \qquad (2)$$

$$HS^- + H_2O \Leftrightarrow H_3O^+ + S^{2-} \qquad pKa_2 = {\sim}13.8 \qquad (3)$$

Eq. 2 illustrates that at a pH of 7.0, half of the dissolved sulfide species for any given concentration is bisulfide [HS^-], and half remains as hydrogen sulfide (gas). Since most ground waters are near a neutral pH of 7.0, only a portion of the total sulfide can be removed as a gas unless a change in pH is induced and the equilibrium of the system is shifted per LeChatelier's principle.

2.3. Chlorination of sulfides in groundwater

Chlorination of ground water containing hydrogen sulfide can result in the formation of elemental sulfur and colloidal polysulfides (which can impart a milky-white turbidity to the water), the removal of which can reduce copper corrosion rates in metallic distribution systems [8,9,10]. The oxidized form of sulfide, elemental colloidal sulfur, is considered a critical parameter needing to be taken into account in the research based in part to concerns of media fouling and because of the impact on oxidation chemistry.

2.4. Hypochlorite oxidation

Historically, chlorination has been used to remove residual sulfides after tray aeration and/or volatilization.

The decision to use chlorination for residual total sulfide removal has typically been one of convenience, whether the action be pre- or post-aeration, due to the fact that chlorine is commonly used as disinfectant in groundwater supplies. However, a secondary impact of using chlorine for the disinfection of groundwater containing sulfides is the formation of colloidal elemental sulfur turbidity [11]. Chlorination is typically performed using either chlorine gas or liquid bleach (sodium hypochlorite; NaOCl). In this study, chlorination of sulfides (operated in conjunction with a filtration process) was performed through the use of liquid bleach. When sodium hypochlorite is added to water, the chemical disassociates into sodium (Na^+) and hypochlorite (OCl^-), as shown in Eq. (4).

$$NaOCl \rightarrow Na^+ + OCl^- \tag{4}$$

The conjugate acid of the hypochlorite ion is hypochlorous acid (HOCl) which is a monoprotic acid with a pK of 7.5. For drinking waters that tend to be near neutral, both species will be present in significant concentration levels, and is represented by Eq. (5).

$$HOCl \leftrightarrow H^+ + OCl^- \tag{5}$$

HOCl and OCl^- both contribute to the oxidation of H_2S. This is shown in Eqs. 6 through 13, where the stoichiometry for the oxidation of hydrogen sulfide and bi-sulfide (HS^-) is shown. The stoichiometric equations for the oxidation of H_2S and HS^- to elemental sulfur are shown in Equations 6 through 9. As with Cl_2 oxidation, one mole of HOCl or OCl^- is required to convert one mole of a sulfide species (H_2S or HS^-) to elemental sulfur (S^0). In order to oxidize 1 mg/l of H_2S to elemental sulfur, it requires 2.08 mg/l of bleach (as Cl_2).

$$HOCl + H_2S \rightarrow S^0 + H^+ + Cl^- + H_2O \tag{6}$$

$$HOCl + HS^- \rightarrow S^0 + Cl^- + H_2O \tag{7}$$

$$Ocl^- + H_2S \rightarrow S^0 + Cl^- + H_2O \tag{8}$$

$$Ocl^- + HS^- \rightarrow S^0 + Cl^- + OH^- \tag{9}$$

Oxidation of H_2S to sulfate (SO_4^{2-}) is shown stoichiometrically in equations 10 through 13. Sulfate is the most oxidized form of sulfur, therefore, the conversion of hydrogen sulfide to sulfate is said to be the complete oxidation of hydrogen sulfide. As with Cl_2, four moles of HOCl or OCl- are required to oxidize one mol of H_2S to SO_4^{2-}. Stoichiometrically, 8.34 mg/l of bleach (as Cl_2) is required to completely oxidize 1.0 mg/l of H_2S. The advantage of complete oxidation is the avoidance of elemental sulfur turbidity [11].

$$4HOCl + H_2S \rightarrow SO_4^{2-} + 6H^+ + 4Cl^- \tag{10}$$

$$4HOCl + HS^- \rightarrow SO_4^{2-} + 5H^+ + 4Cl^- \tag{11}$$

$$4OCl^- + H_2S \rightarrow SO_4^{2-} + 2H^+ + 4Cl^- \tag{12}$$

$$4OCl^- + HS^- \rightarrow SO_4^{2-} + H^+ + 4Cl^- \tag{13}$$

Over time, free sulfur will oxidize to sulfate in the presence of an oxidant such as dissolved oxygen or hypochlorite. However, the typical residence time in drinking water systems does not allow for complete conversion before the turbidity formed during treatment is sent out for distribution. The conversion of H_2S to elemental sulfur is not instantaneous either, as studies have shown that after chlorination, turbidity continues to increase for several hours [11]. In practice, the chlorination of H_2S rarely yields complete conversion of sulfides to sulfate unless the pH is less than 3.5 and the water source is relatively pure, which is not practical for conventional municipal drinking groundwater systems [12].

3. Oxidizing media filters

3.1. Motivation for use of oxidizing media filters for sulfide removal

Oxidizing media filters, traditionally used for iron and manganese removal, have been evaluated solely for the use of H_2S treatment in this research project. A common type of media that was selected for this application is manganese greensand, which is impregnated with manganese (IV) oxide (MnO_2) and must be either continuously or intermittently regenerated. Feeding an oxidant (bleach or potassium permanganate) ahead of oxidizing media beds serve as a continuous regenerate for the filter media as long as an oxidant residual can be detected in the filter effluent.

3.2. Manganese (IV) oxide greensand filtration

Manganese greensand is an oxidizing filter media that is conventionally used to remove iron and manganese from aqueous streams. While it is widely known and recognized that manganese greensand will oxidize and remove hydrogen sulfide, there exist little literature on the use of this media solely for sulfides treatment. Most of the data that does exist is mainly a result of studies on the treatment of iron and manganese in waters which happen to have hydrogen sulfide in them. Other studies that have focused on the use of manganese greensand solely for H_2S treatment, such as the one by Brune and Perez, have used potassium permanganate as the bed regenerate [13,14]. During the conduct of this research effort, not one study could be identified where manganese greensand was used solely for H_2S

treatment while being regenerated with sodium hypochlorite (commonly known as bleach).

Greensand is a common name for glauconite, a natural material that was first used as a water softening zeolite in the early 20th century. Deposits of the naturally occurring greensand can be found in the eastern parts of New Jersey, Delaware, Maryland, Virginia, and North Carolina [15]. Manganese greensand was first used for the removal of iron, manganese and hydrogen sulfide in the early 1950's. It is manufactured in a process which uses the ion exchange properties of its stabilized glauconite (greensand) substrate to form an active MnO_2 coating [16]. In the manganese greensand production process, naturally occurring grains of glauconite are washed and undergo a sieve graduation (18 by 60 mesh) resulting in an effective grain size of 0.3 to 0.35 mm and a uniformity coefficient of 1.60 or less. Once washed and sorted, the media is stabilized and then impregnated with manganese (IV) oxide [17].

The naturally occurring mineral glauconite is a finite resource; as such, demand for the product has put stress on product availability in recent years leading to spot shortages and long lead times. This has prompted companies to develop and produce synthetic substitutes for manganese greensand. One such substitute is "GreensandPlus", manufactured in Brazil by Fermavi Electrochemistry Ltd. and distributed in the United States by Inversand, Inc. [16]. Synthetic media differs structurally from manganese greensand in that it is not produced using a glauconite base. The synthetic media is manufactured by thermally fusing an active manganese (IV) oxide (MnO_2) coating onto silica sand, and is reported to contain 3.2 to 4.8 percent MnO_2 by weight and 96 to 98 percent quartz (SiO_2) by weight [18]. Physically, the synthetic media used in this study was a black, nodular granule with a screen grading of 18 by 60 mesh, and an effective size of 0.3 to 0.35 mm, with an apparent density of 88 pounds per cubic foot, a porosity of approximately 0.45, and a uniformity coefficient of less than 1.60.

As was the case in this study, anthracite is typically used in conjunction with the GreensandPlus™ when operated in a dual media configuration. The anthracite is provided as a pre-filtration layer to remove insoluble compounds, which helps to prevent clogging within the greensand media. Anthracite is a crushed coal, medium density filtration media. The anthracite used in this study originates from coal mined in Pennsylvania. The media has a mesh size of 14 by 30, an effective size of 0.6 to 0.8 mm, a uniformity coefficient of <1.7, and a density of 50 pounds per cubic foot. Anthracite has a lower density than greensand and will hydraulically classify, remaining above the greensand after backwash. The distributor recommends that the chlorine be fed at least 10–20 seconds ahead of the filter and that a Cl_2 residual be carried through the greensand filter in order to regenerate and protect the media's manganese (IV) oxide coating [18].

3.3. Electromedia® Filtration

Electromedia® I is a proprietary filter media that is produced by Filtronics, Inc. (Anaheim, California) that is typically used for iron, manganese and arsenic removal. The product is a granulated and naturally occurring, with an appearance similar to that of garnet. The media is a proprietary blend of minerals that are mined and processed in the United States; it is not a resin, plastic or silica product [19]. The electromedia filter is typically operated in a dual-media configuration and is stratified as follows: anthracite as a pre-filtration layer, then electromedia and then two grades of gravel support media to prevent the underflow drains from plugging. Unlike manganese greensand, Electromedia® does not require chemical regeneration. The manufacture claims that Electromedia® can be operated with a hydraulic loading up to 15 gallons per square foot minute, and requires 4 minute backwash cycles [19].

4. Experimental plan

4.1. Location of research

The genesis for this research study was the planned expansion of drinking water capacity for the Southwest Regional Service Area managed by Polk County Utilities (County) in central Florida, with facilities near Lakeland, Florida. The drinking water system for this service area is supplied by two interconnected water treatment plants; the Imperial Lakes (IL) Water Treatment Plant (WTP) and the Turner Road (TR) WTP. The IL and TR WTPs currently rely upon groundwater sources that contain total sulfide content ranging from 1.4 to 2.6 mg/l. At the IL and TR WTPs, the County currently employs a bleach disinfection and tray aeration process for groundwater treatment. The County complies with the provisions of the Environmental Protection Agency's Safe Drinking Water Act.

4.2. Existing water quality and treatment conditions

The raw water source for the IL and TR WTPs' is the upper Floridan aquifer, and water quality data indicates that the source water is slightly alkaline with moderate hardness, typical of groundwater in central Florida. A summary of representative raw water quality is presented in Table 1. The IL and TR water treatment plants both utilize a similar treatment process. Raw groundwater is pumped to the top of a ground storage tank (GST) where it is

Table 1
Raw water quality data

Raw water quality		
Parameter	Imperial Lakes	Turner Road
Total Sulfide (mg/l)	1.4–2.0	2.5–2.6
Sulfate (mg/l)	5.2–7.7	7.7–8.3
pH	7.4–7.6	7.4–7.6
Turbidity (NTU)	0.12–0.32	0.10–0.13
TOC (mg/l)	0.86–1.36	1.16–1.21
Iron (mg/l)	0.011–0.049	0.011–0.012
Manganese (mg/l)	0.003–0.005	<0.001
Total Hardness (mg/l as $CaCO_3$)	164–168	169
Alkalinity (mg/l as $CaCO_3$)	154–166	160–166

chlorinated and then fed to a tray aerator before falling into a GST for storage. Each site has a series of high service pumps which cycle on and off to meet demand. When the high service pumps are operating, treated water is withdrawn from the GST and is routed through a parallel set of hydo-pneumatic tanks before leaving the WTP and entering the distribution system. Chlorine is stored in bulk locally at both sites in the form of liquid bleach. Both sites also feed a small dose of caustic to the treated water for pH adjustment prior to entering the distribution system as a means of corrosion control. Fig. 2 features a schematic of a typical conventional groundwater treatment system. This schematic is representative of both the IL and TR WTPs; also, both of these sites feed their bleach at the top of the aeration trays and do not employ a post chlorine feed. The TR site is located at a lower elevation than the IL site. A pressure reducing valve (PRV) is used to maintain proper system pressure at the two sites. It should be noted that unlike a number of other similar central Florida groundwater treatment plants, chlorine is fed ahead of the tray aerator at both the IL and TR facilities due to the immediate proximity of residences that surround each water plant; it is more typical to aerate prior to the addition of chlorine when facilities are not in proximity of residents sensitive to odors.

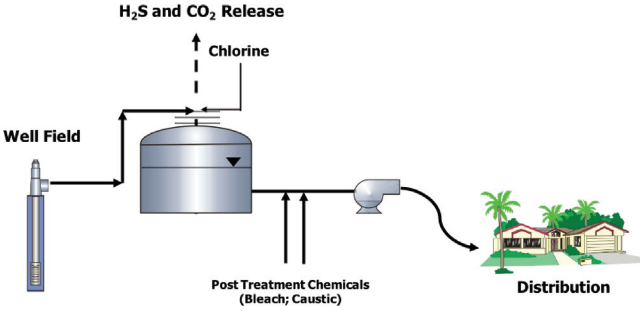

Fig. 2. Schematic of a conventional groundwater treatment system.

4.3. Pilot-scale filtration equipment

There were two filtration processes evaluated at the pilot-scale: bleach oxidation followed by Electromedia® filtration, and manganese (IV) oxide filtration continuously regenerated with bleach. Field evaluations at both sites (IL and TR WTP) began in February of 2009, and ran through September of that same year.

4.4. Electromedia® filter

The Electromedia® filter used in this study was supplied by Filtronics, Inc., Anaheim, CA. This pilot filter was shipped to Polk County pre-assembled with the media in place. However, the unit arrived with a crack in the clear plastic pressure vessel which allowed the media to spill out of the shipping container. The vendor, while on-site, provided a replacement vessel. The media was collected and reinserted into the pressure vessel of the pilot unit. The pilot skid was designed with two vertical 3 in. (I.D.) plastic pressure vessels. The first reaction vessel was baffled at the center for increased mixing, and the second vessel held the media bed, which was comprised of layers of anthracite and Electromedia®, followed by a layer of granular support media. The manufacture recommended hydraulic loading was 10 gpm/sf and a loading rate of 24 to 25 gpm/sf for backwash cycles. A bleach feed pump and a 1000 ml graduated cylinder was used for chemical feed purposes.

4.5. Manganese (IV) oxide filter

The pilot unit used for the manganese dioxide filter bed was supplied by Hungerford and Terry, Inc., (226 Atlantic Ave., Clayton, New Jersey) and was larger than that used for the Electromedia® bed. This unit used a vertical fiberglass pressure vesselthat was 6 inches in diameter (internal diameter (ID)) with bleach fed prior to entering the top of the filter bed. The pilot unit bed was filled with 27 pounds of anthracite and 88 pounds of synthetic media GreensandPlus™ (manganese dioxide) filter media, followed by 15 pounds of gravel support media. The bleach fed to this pilot unit was obtained from the TR and IL WTP's on-site day storage tanks. This bleach was diluted to a known concentration, stored in a 45 gal temporary "day tank" and fed with a modular peristaltic pump. The bleach concentration was determined by dilutions and the use of the Hach DPD colorimetric method.

4.6. Water quality

The primary water quality challenge for both of these WTPs is the hydrogen sulfide content (1.4 to 2.6 mg/l). The IL and TR WTPs both employ tray aeration as a

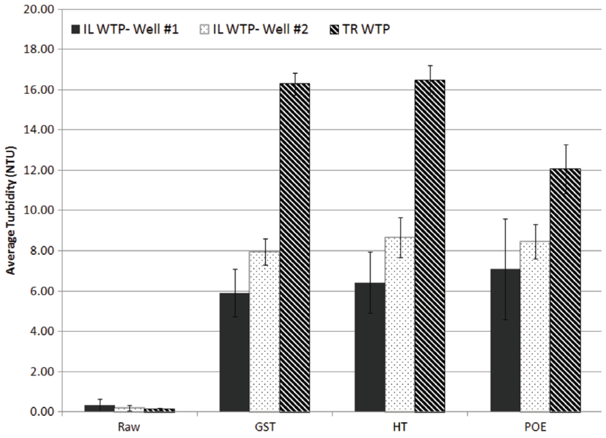

Fig. 3. Existing system average turbidity values (NTU).

primary method of hydrogen sulfide control. However, tray aeration is only partially efficient for H_2S removal and is inefficient for total sulfides removal [3]. Water treatment systems that utilize this process hence realize only partial sulfide removal from the use of tray aeration alone. For that reason, bleach, which is added for disinfection, must be applied in sufficient quantities to allow for sulfide oxidation; however, the use of bleach oxidation in the presence of natural organic material will lead to formation of disinfection by-products (DBPs) and the formation of elemental sulfur turbidity. Fig. 3 presents the existing average turbidity values of the IL and TR WTPs at the ground storage tank (GST), hydrotank (HT) and point-of-entry (POE) locations. This work was not intended to be an exhaustive water quality evaluation of the IL and TR WTPs; rather, the scope focused on examining process alternatives. Although a wider array of water quality parameters were measured (such as total organic carbon, hardness, iron, manganese, sulfate, total dissolved solids and heterotrophic plate counts), the primary parameters evaluated were pH, turbidity, total sulfide, and free available chlorine residual concentrations. A summary of the water quality methods used is provided in Table 2.

4.7. Sulfur turbidity

One of the end products of bleach oxidation of hydrogen sulfide is colloidal sulfur that is measurable as turbidity [11]. Lyn and Taylor’s work showed that not only does turbidity form very quickly after chlorination, but it continues to increase with time over a period of many hours. These findings were supported by the observations that were made at both the IL and TR WTPs. Compared to the raw water, these facilities both had elevated turbidity levels exiting the aeration trays. Treated water from the aeration trays cascades into a GST where it is stored, and turbidity continues to increase. Samples taken from the GSTs indicated that turbidity levels continue to increase after initial bleach dosing.

Table 2
Table of methods and equipment

Test	Location of test	Method description	Method detection limit
Hydrogen Sulfide	Field	SM 4500-S^{2-} F. Iodometric Method; 4500-S^{2-} D. Methylene Blue, LaMotte 4630 CC-PS	0.1 mg/l as S
Turbidity	Field	Hach Turbidimeter 2100N	0.01 NTU
Total Chlorine	Field	Hach Spectrophotometer DR/890	0.01 mg/l
Free Chlorine	Field	HACH DPD Method 8021, HACH Spectrophotometer DR/890	0.02 mg/l
pH	Field/Lab	Hana pHep; Accumet Research AR 50	0.01 pH Units
Temperature	Field/Lab	Hana pHep; Accumet Research AR 50	0.01°C
Conductivity	Field/Lab	Fisher Scientific Traceable Conductivity, Resistivity, and TDS Meter	0.01 µS/cm
Dissolved Oxygen	Field/Lab	YSI Model 58: Dissolved Oxygen Probe	0.01 mg/l
Alkalinity	Field/Lab	SM 2320 B. Titration Method, Accumet Research AR 50	20 mg/l as $CaCO_3$
Total Organic Carbon	Lab	Dohrmann Phoenix 8000: The UV-Persulfate TOC Analyzer	0.05 mg/l
Sulfate	Lab	SM 4500 $SO4^{2-}$ E. Turbidimetric Method, HACH Spectrophotmeter DR6000; Dionex DX-120 Ion Chromatograph	0.1 mg/l as SO_4^{2-}
Iron	Lab	Perkin Elmer Optima 2100DV ICP-OES	0.001 mg/l
Manganese	Lab	Perkin Elmer Optima 2100DV ICP-OES	0.001 mg/l
Calcium	Lab	Perkin Elmer Optima 2100DV ICP-OES	0.1 mg/l
Magnesium	Lab	Perkin Elmer Optima 2100DV ICP-OES	0.1 mg/l

4.8. Total sulfide assessment

The analytical evaluation of hydrogen sulfide in water supplies is difficult due to the volatility of hydrogen sulfide gas. Hence, two methods were used in the measurement of total sulfide (as S_2^-): the methylene blue method and iodometric method. The methylene blue method is based on the reaction of sulfide, ferric chloride, and dimethyl-*p*-phenylenediamine to produce methylene blue [20]. The methylene blue method was used for primary analysis and total sulfide screening. In some cases (such as post treated water testing) the methylene blue test was used as an absence or presence test prior to use of a more sensitive test. In situations where sulfides were shown (through the methylene blue test) to be present, or in situations where sulfides were known to be present (i.e., raw water), the iodometric method was used to verify and determine a total sulfide concentration. The iodometric method is a back titration involving the oxidation of sulfide using iodine and then back titrating with sodium thiosulfate [20]. The methylene blue method was performed using two different test kits: a Hach Hydrogen Sulfide Test Kit-Model HS-WR, and a LaMotte 4630 H_2S test kit. Both kits evaluate total sulfide. The iodometric method was performed according to Standard Method 4500-S^{2-} F. Specific precautions were taken to avoid the volatilization of H_2S during testing and ensure that reagents were replaced and standardized regularly.

4.9. Post-treatment turbidity formation evaluation

A post-treatment evaluation was also conducted as part of the overall process evaluations in order to confirm relative treatment effectiveness. Turbidity was used as a simple water quality parameter for determining such effectiveness. As has been previously documented, once the water has been chlorinated in the existing IL and TR systems, it then passes over a series of aeration trays prior to cascading into a GST where it is stored. An additional study was conducted to evaluate the effect, if any, that tray aeration would have on turbidity formation following media filtration. Although the filtration method being tested would not need aeration for sulfides removal, tray aerators would be needed for CO_2 removal, and to increase the dissolved oxygen (DO) concentration for palatability concerns.

For this reason, a temporary pilot tray aerator was constructed to mimic a bleach, media and tray aeration process configuration. This also allowed for direct comparisons of the pilot configuration to the existing IL and TR WTP processes with regards to turbidity formation as a function of time. The "trays" were constructed using gutter downspout splash blocks with ridges for this study. A series of three splash blocks were arranged in a 30-gallon Rubbermaid garbage can in a zigzag pattern with water following from on tray to another. This effectively acted as a step/tray aeration system. The water exited the apparatus via a short PVC pipe extending downward from a hole cut into the center of the garbage can. The water samples for the turbidity formation study were collected at two locations: from the drain port at the bottom of the aeration trays mounted on top of the GST (existing systems), and from the drain port of the pilot aeration trays that follow the pilot filtration unit. These samples were collected in 1 l amber bottles. Each bottle was labeled for sampling at a specific time interval. At the specified time, the bottle was shaken and measurements were taken for turbidity, pH, conductivity and DO. Readings were taken at the same time intervals for both the existing and the pilot systems.

4.9.1. Bleach

Two brands of liquid bleach (sodium hypochlorite) were used in this study: store-purchased Clorox® bleach and the County's on-site bulk bleach stock (Ultra CHLOR™) that is supplied by Odyssey Manufacturing Co (1484 Massaro Blvd., Tampa, Florida). The Clorox® bleach was comprised of 6.15% sodium hypochlorite with a specific gravity of 1.1. The bulk stock bleach was 12.5 percent chlorine, and was at least 10.8 percent sodium hypochlorite by weight (10.3 percent Cl_2 by weight) with a specific gravity between 1.159 and 1.170.

5. Results and discussion

5.1. Electromedia® filter effective at sulfide control

Results of the Electromedia® filter test runs at the Imperial Lakes WTP are provided in Table 3. This pilot-filter was operated at several different bleach dose rates, and evaluations were made at a hydraulic loading rate of 10 gpm/sf. The target free chlorine residual was 1.0 mg/l for most of the testing. The target residual was obtained at the IL site with a bleach feed concentration of approximately 11.1 mg/l. A more comparative operating point residual of 2.33 mg/l (the County prefers a residual of 2.5 to 3.0 mg/l at POE) was reached with a slightly higher bleach feed concentration of 13.8 mg/l. In that same residual range, the County currently applies approximately 14 to 15 mg/l of bulk bleach at the IL WTP. Turbidity remained below 1.0 NTU during testing except for those times during filter bed startup. During start-up the turbidity could be upwards of 5.0 NTU but reached a steady operating state below 1.0 NTU within minutes of initiating flow.

The information illustrated in Fig. 4 was generated using data obtained from operation of the Electromedia® pilot-filter at the IL WTP well #2. This figure shows

Table 3
Electromedia® filter performance at the imperial lakes WTP

Cl_2 Feed concentration (mg/l)	Post treated total sulfide (mg/l)	Cl_2 (FAC) residual (mg/l)		Average turbidity (NTU)	
		Range	Average	Pre-Filtration	Post-Filtration
11.0	<0.10	0.28–2.18	0.85	0.76	0.28
11.1	<0.10	0.35–1.35	0.94	0.38	0.14
12.4	<0.10	1.24–2.16	1.78	0.68	0.25
13.8	<0.10	1.16–3.08	2.33	0.60	0.10

the breakpoint for raw water total sulfide removal as a function of the Cl_2 to sulfide molar ratio. This same figure also provides information regarding free chlorine residual formation as a function of the Cl_2 to sulfide molar ratio. Fig. 4 illustrates total sulfide removal with respect to two distinct operating zones: a "Demand Zone" where sulfides are exerting a demand on the bleach oxidant and a "Free Residual Zone" where sulfides are no longer present (for this work the method detection limit was 0.1 mg/l) and are in the presence of a free chlorine residual. These "zones" are operating regimes for the Electromedia® process. Total sulfide Cl_2 demand decreases from left to right in the demand zone (DZ) and free Cl_2 residual increases from left to right in the free residual zone (FRZ). In the DZ, 74% of the variation in the data could be explained by linear regression. At breakpoint there is a transition to the FRZ, whereupon 89% of the variation in the data could be explained by linear relationship.

At the IL WTP, the County maintains a chlorine residual between 2.5 and 3 ppm, depending on the temperature (that is, the summer requires a higher residual). According to the linear model, to achieve a 3 ppm free chlorine residual (using the Electromedia® process) a Cl_2 to sulfide molar ratio of 4.1 would be required. In practice, this system would be operated in the FRZ (i.e., the post-filtered water would carry a residual as required by law). Note that the chlorine demand for continuous regeneration operation of the MnO_2 filtration system can be estimated using Eq.(14).

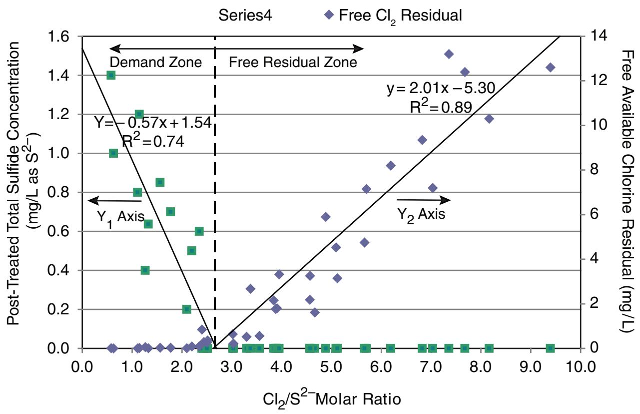

Fig. 4. Post-Treated sulfide and FAC residual as a function of Cl_2/S^{2-} molar ratio for electromedia® - IL WTP.

$$\text{mg/l } Cl_2 = (1 \text{ x mg/l Fe}) + (3 \text{ y mg/l Mn}) + (6 \text{ z mg/l } H_2S) + (8 \text{ w mg/l } NH_3) \quad (14)$$

where x, y, z and w are the amount of iron, manganese, hydrogen sulfide and ammonia in the water, respectively. For example, consider a similar source water having the following water quality: x=1.7 mg/l of iron, y=0.2 mg/l of manganese, z=1.9 mg/l of hydrogen sulfide, and w=0.1 mg/l of ammonia. The estimated bleach demand for this source water would be 14.5 mg/l Cl_2, as shown in Eq. (15).

$$\text{Demand} = (1 \cdot 1.7) + (3 \cdot 0.2) + (6 \cdot 1.9) + (8 \cdot 0.1) = 14.5 \text{ mg/l } Cl_2 \quad (15)$$

This estimate was found to be in general agreement with conditions experienced at the IL and TR water plants.

Clorox® bleach was used as the chlorine oxidant in the pilot test runs at the IL WTP. The calculations upon which the listed feed concentrations were determined relied upon the manufacture specified bleach strength. The Clorox® was stored on-site, replaced regularly, and was protected from the elements; however it was stored in unconditioned buildings which may have increased its degradation. This most likely means that these numbers are fairly conservative. Once testing began at the Turner Road WTP, the research team switched to the use of the county's on-site bleach stock. In these calculations, the actual bleach stock concentration was calculated and used to determine a more accurate chlorine dose concentration. Subsequent testing suggested that the data obtained from the former method may be conservative by as much as 10–60%. For the Turner Road WTP, data indicated that total sulfide removal (<0.10 mg/l) with sufficient free chlorine residual (0.97 mg/l FAC) was obtained with a feed concentration of 12.9 mg/l. However, if that dose concentration were to be calculated using

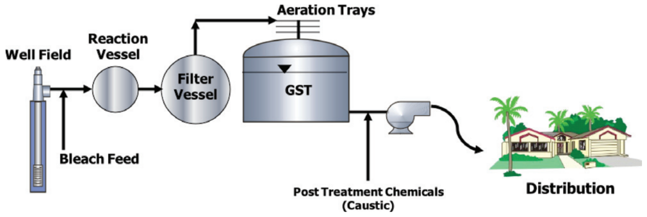

Fig. 5. Schematic of electromedia® filtration process.

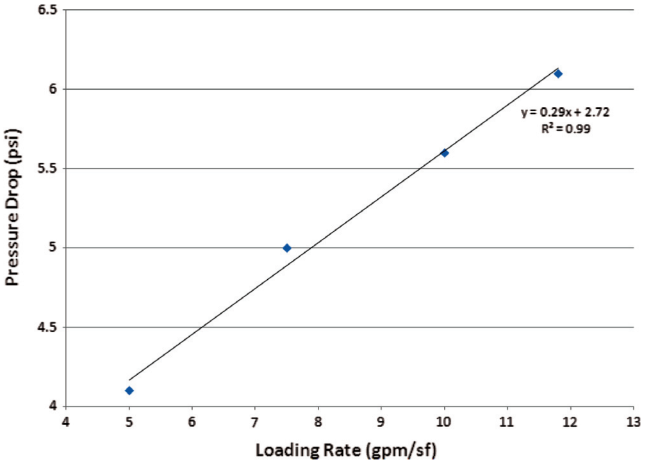

Fig. 6. Pressure drop across MnO_2 pilot filter bed as a function of hydraulic loading rate.

the initial method it would have given a dose concentration of 20.3 mg/l, an over-estimate of approximately 57%. This may be a worst case scenario, but it helps to explain why a similar dose concentration (to that used at the IL WTP) was effective at the Turner Road WTP even though there is greater sulfide content in the TR well water. It should also be noted that the Electromedia® pilot produced slightly higher turbidity at the TR WTP with an average post-filtration value of 0.8 NTU (compared to ~0.2 NTU at the IL WTP). Switching from the Clorox® to the county's Bleach stock also appears to have increased the turbidity of the finished water. Evaluation of the Electromedia® process at the Turner Road WTP was not as complete as that performed at the Imperial Lakes WTP because of hydraulic limitations of the TR site, which limited run time.

The schematic presented in Fig. 5 is representative of a full-scale manganese (IV) oxide process. Additional pumping will be required to carry the treated water from the filter vessels to the GST, and a backwash disposal and conveyance system would also be required that is not shown.

5.2. Manganese (IV) oxide filtration reduces sulfide effectively

One of the objectives when evaluating the manganese (IV) oxide filter (MnO_2) process was to evaluate sulfur removal using this bed without the use of potassium permanganate regenerate. Consequently, a concept for the use of on-site chemicals to minimize the need for new chemical feed systems would be beneficial to the County in its future expansion of its facilities. Hence, bleach was used to the bed regenerate instead of potassium permanganate. Therefore, determination of the required Cl_2 feed concentration and pressure drop across the bed at varying hydraulic loading rates would be important to this component of the work. The evaluations of the manganese (IV) oxide filter were performed using on-site bulk bleach stocks. The hydraulic loading rates used in this evaluation were 5, 7.5, 10, and 11.8 gpm/sf. The hydraulic loading rate evaluations were conducted at IL. The TR testing was conducted at a loading rate 10 gpm/sf. A plot of the loading rate data is shown in Fig. 6. The pressure drop across a clean filter bed was show to range from approximately 4.1 to 6.1 psi for the range of hydraulic loading rates specified above. The data demonstrated good linearity, resulting in a correlation coefficient of 0.992.

The results of MnO_2 media evaluations at the IL WTP are shown in Table 4. The methylene blue method was used here to perform an absence/presence test on the post treated water. This data indicated no significant variation in performance at the different hydraulic loading rates for the conditions tested. Also, a feed dose of approximately 10 mg/l Cl_2 was observed for operation of

Table 4
Manganese (IV) oxide filter performance data-Imperial lakes WTP

Hydraulic loading rate (gpm/sf)	Cl_2 feed concentration (mg/l)	Post treated total sulfide (mg/l)	Cl_2 (FAC) residual		Average turbidity (NTU)
			2hr Range (mg/l)	Average (mg/l)	
5	5.2	<0.10	1.06–1.52	1.23	0.09
7.5	5.6	<0.10	0.80–1.41	1.15	0.06
10	5.4	<0.10	0.94–1.28	1.06	0.12
10	10.0	<0.10	3.42–3.90	3.59	0.10
11.8	5.3	<0.10	0.32–1.28	0.72	0.07

Table 5
Manganese (IV) oxide filter performance data-Turner road WTP

Hydraulic loading rate (gpm/sf)	Cl_2 feed concentration (mg/l)	Post treated total sulfide (mg/l)	Cl_2 (FAC) residual		Average turbidity (NTU)
			Range (mg/l)	Average (mg/l)	
10	13.2	<0.10	1.16–1.51	1.38	0.77
10	14.3	<0.10	–	3.05	0.20

the MnO_2 filter to achieve comparable FAC residual levels typically experienced by the existing system. However, it is noted that the bleach dose ahead of the MnO_2 filter is well below the 14–15 mg/l Cl_2 demand currently observed at the Imperial Lakes WTP. This suggests that the MnO_2 bed is providing some benefit in the oxidation of sulfide as is supported by observations made in Table 5. This Cl_2 dose is also lower than that required for the Electromedia® filter. As previously noted, the results for the Electromedia® testing at IL are most likely subject to some over-estimation because of the type of bleach initially used in those experiments. There is also a design difference between these two pilot skids. The Filtronics Electromedia® pilot skid has a built in contact chamber with a baffled static mixer ahead of which the bleach is fed, while the Hungerford and Terry MnO_2 filer pilot has its injection quill just ahead of the actual media bed with little to no contact time. The oxidation of sulfide is a relatively rapid reaction. The impetuous for the use of an oxidative MnO_2 filter, typically employed for iron and manganese removal, is that the filter media itself will provide some benefit in the sulfide oxidation reaction. In which case, the bleach oxidant acts equally as a regenerate as it does a sulfide oxidant (that is, the bed remains in an oxidative state). It is possible that a portion of the total sulfide is being converted to colloidal sulfur or sulfate by the bleach because of excess contact time ahead of the bed, which may negate some of the oxidative benefits that the MnO_2 media may provide. Regardless, the data would indicate that the combined effects of a bleach and oxidative media filtration process is effective for sulfides removal.

The results of media pilot testing at the Turner Road site are presented in Table 5. This data indicates that there is an increase in the bleach demand at the TR site as compared to the IL site. This is attributed to the increased raw water total sulfides levels at the Turner Road WTP, as the raw water concentration is 2.6 mg/l versus 1.6 mg/l at the Imperial Lakes WTP. Also, the 13.2 mg/l dose concentration required for the MnO_2 filter seems to be similar to the 12.9 mg/l dose concentration required with the Electromedia® filter. Given standard error and the slightly lower free available chlorine (FAC) residual for the Electromedia® system, the two numbers would be considered to be of the same magnitude.

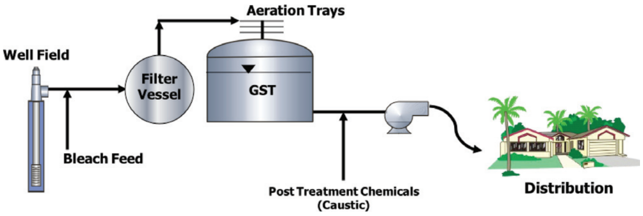

Fig. 7. Schematic of manganese (IV) oxide filter process.

The schematic presented in Fig. 7 is representative of a full-scale bleach and manganese (IV) oxide process. It should be noted that additional pumping will be required to carry the treated water from the filter vessels to the GST, and a backwash disposal and conveyance system would be required that is not shown.

5.3. Media filtration reduces post-filtration turbidity formation

During the pilot testing phase, it was noted that the existing IL and TR plants produced elevated turbidity (>6 NTU) in the GST. It was theorized that a majority of this turbidity was colloidal sulfur formed in the bleach oxidation process. The turbidity levels of the post-treated water from the pilot filters was significantly lower, less than 1.0 NTU in most cases. However, the data for the turbidity of the post-treated water was measured at time zero. In order to draw a more valid comparison between pilot and full-scale treatment systems, the turbidity formation over time would need to be observed. The elevated turbidity readings for the existing system were taken from the GST, hydro tanks, and POE. In order to evaluate the turbidity formation potential of the treated water from the pilot system, an attempt was made to simulate the existing plant treatment sequence (i.e., add simulated tray aeration). This arrangement would allow for the assessment of turbidity in the post-treated pilot water and allow for comparisons to the turbidity in the water being produced by the existing treatment process.

The results of this turbidity study, using the manganese (IV) oxide filter, are presented graphically in Fig. 8 and Fig. 9. The data suggest that the oxidation/filtration technique reduced the turbidity formation over time in dark conditions where no sunlight was present. After a

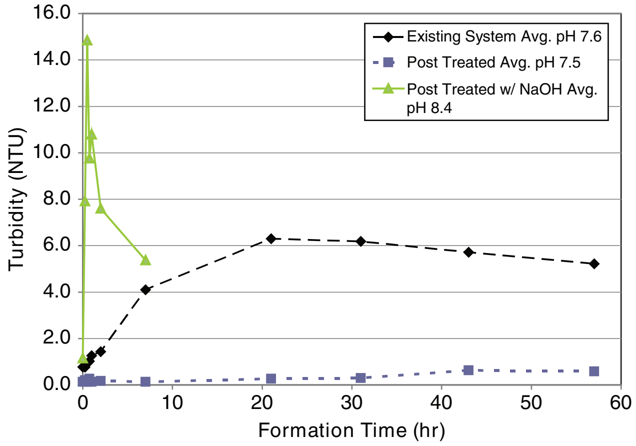

Fig. 8. Imperial Lakes Turbidity Study Data – Well #1.

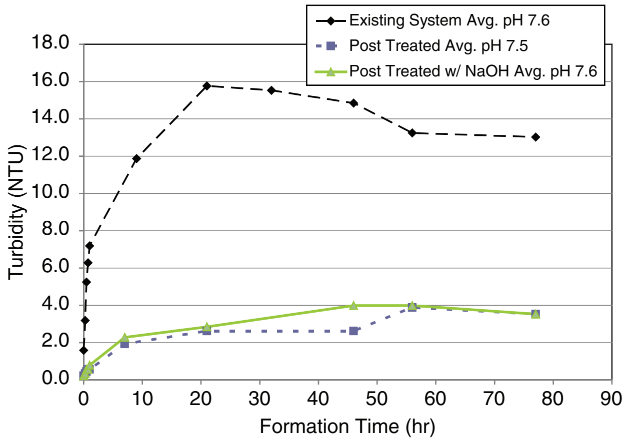

Fig. 9. Turner road turbidity study data.

20-h bleach contact time, the turbidity of the post media filtrate remained below 0.6 NTU. However, water from the existing IL water treatment system produced turbidity in excess of 6 NTU after a 20-h contact time. These results are reasonable because the average turbidity observed in the GST at the IL WTP was also in excess of 6 NTUs (illustrated in Fig. 3). The study demonstrated the effectiveness of MnO_2 filters for the oxidation of sulfides and subsequent supression of post-treated turbidity formation.

The addition of caustic to the post-treated water was shown to increase turbidity. In the IL experiments, a higher dose of NaOH was added which resulted in a greater increase in turbidity than experienced in the TR study. However, after approximately 30–50 minutes, the turbidity began to decrease. It is believed that this increased turbidity is caused by the formation of calcium carbonate, and that the decrease in turbidity is caused by the adherence of calcium carbonate to the amber bottle surface, or sedimentation, thus removing it from suspension. The turbidity formation of the post-treated water at IL remained below one over the duration of testing. Turbidity peaked at around 0.6 NTU after 43 hours of formation time. For the TR system, the turbidity of the post-treated water peaked at around 3.9 NTU after 56 hours of formation time.

In this pilot study, it was also noted that the finish water turbidity levels would rise at a greater rate when exposed to sunlight. It is postulated that calcium carbonate formed as the water was heated by the sunlight. Additional studies should be conducted to investigate this phenomenon. No additional work was conducted because the treated water was to be stored in tanks and distributed in pipes absent of sunlight.

5.4. Laboratory quality assurance and control

Quality assurance and control is a necessary component of laboratory analysis and quantitative measurement. Measures that were taken to assure quality included adherence to proper sample collection, storage and preservation procedures, observance of maximum storage periods as outlined in the Standard Methods, and proper maintenance of analytical equipment [20]. In order to provide a quality assessment, sample replicates and spikes were analyzed and evaluated. This data was used to establish quality control limits for continuous monitoring of analytical precision and accuracy. Precision was determined by performing duplicate analyses on samples during the study period.

In addition to duplicates, spikes were performed on the water samples in order to allow for accuracy monitoring. In some analyses, an analyte standard(s) was measured at the end of a given testing cycle as an additional gauge of accuracy and to ensure the testing equipment remained properly calibrated. The results from the sample spikes were used to determine percent recovery (%R). In laboratory analyses, duplicates and spikes were required for at least every fifth sample. The average variability of analysis was 1.5 percent, and the data indicated that the analyses yielded satisfactory reproducibility as duplicates analyzed exceeded quality control limits established for the laboratory; those that did not were rejected. Both sample spikes and standards were measured water quality analyses. Percent recovery numbers are said to be acceptable when they fall within the range of 80 to 120 percent; samples that did not fall within the range of acceptability were rejected. The average percent recovery for the analyses was 102 percent with a standard deviation of 7.1 percent.

6. Conclusions

Both chlorine bleach oxidation/filtration systems were shown to effectively remove sulfide without the accompanying finished water turbidity common to the existing method. This research has demonstrated that bleach oxidation followed by the use of manganese (IV) oxide or electromedia filters, historically used for iron and manganese removal, show promise for use by water purveyors having elevated (0.6 to 3.0 mg/l) levels of total sulfide in their groundwater supplies. Specific results obtained during the conduct of the study include:

- Media filtration, historically used to treat for iron and manganese, was shown to be effective for total sulfide treatment in water having low iron and manganese content. Bleach oxidation prior to media filtration (either electromedia or manganese (IV) oxide media) removed total sulfide to below detection levels (0.1 mg/l) for groundwater supplies containing as high as 2.6 mg/l total sulfide. The use of bleach oxidation ahead of media filtration produced finished water with low turbidity (<1.0 NTU) as compared to traditional tray aeration & chlorination processes (6–16 NTU, as observed in this study).
- Bleach consumption was reduced in the modified filtration process as compared to tray aeration processes alone. Both the modified filtration process and tray aeration process contained a bleach component. The values presented for the existing process assume a 15% degradation of the County's bulk bleach stock (~10.3% Cl_2 by wt.).
  - Existing IL WTP process: 14–15 mg/l Cl_2 (monthly averages June-August 09)
  - Existing TR WTP process: 17.5–18.5 mg/l Cl_2 (monthly averages June- August 09)
  - Manganese (IV) oxide filter, IL WTP: ~ 10 mg/l Cl_2
  - Manganese (IV) oxide filter, TR WTP: ~ 14 mg/l Cl_2
  - Electromedia filter, IL WTP: ~ 14 mg/l Cl_2

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