

Innovative Hydrogen Sulfide Treatment Methods: Moving Beyond Packed Tower Aeration

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The majority of water treatment plants within Florida that rely on groundwater at one time or another have required treatment to remove sulfide from their supplies. Except for isolated cases of source contamination because of synthetic and volatile organics, salinity or total dissolved solids (coastal influences), hydrogen sulfide, color, total organic carbon (disinfection byproduct precursor matter), and hardness represent contaminants of concern for groundwater purveyors in Florida. Of these contaminants, sulfide is the only federally non-regulated parameter that exists in dissolved and gaseous forms, is readily identified by consumers due to its “rotten egg” smell, and can impact quality (corrosivity; turbidity); therefore, removing this constituent from groundwater supplies is important.

In recent years, the use of packed tower air stripping and associated odor control systems have become more prominent in Florida, as traditional tray aeration and chlorination has become more difficult to implement because of newer, more stringent state regulations; however, packed towers have been shown to impact finished water microbiologically, and accompanying odor control systems are costly and can be operationally problematic. Consequently, water purveyors in Florida are interested in finding more affordable and alternative methods for treating sulfide.

In this current work, several alternative technologies were evaluated at the desktop, bench, and pilot scales. The desktop study included anion exchange, various oxidation methods, and alternative media filtration processes. Ferrate, mixed-oxidant, and bleach oxidation were evaluated at the bench scale. The processes tested at the pilot scale were chlorine bleach oxidation followed by either Electromedia® or manganese (IV) oxide (MnO₂) greensand filtration and included exploratory ferrate pilot work.

Motivation for the Work

Communities throughout the United States and its territories face a variety of environmental water supply and infrastructure challenges, and often find it difficult to comply with the increasing scope and stringencies of environmental regulations, not least of which are those imposed by the Environmental Pro-

tection Agency’s (EPA’s) Safe Drinking Water Act (SDWA). Consumers have become aware of regulatory violation through mandated public notification and Consumer Confidence Reports (CCRs), and they have always been aware of the appearance, taste, and odor of drinking water.

In addition to SDWA requirements, Florida utilities must also comply with FDEP Rule 62-555.315, Public Water System Wells—Security; Number; Capacity; Under the Direct Influence of Surface Water; Control of Copper Pipe Corrosion and Black Water; and Disinfection and Bacteriological Surveys and Evaluations. Rule 62-555.315 was promulgated to address corrosion and black water issues, and was made effective on August 28, 2003. The rule establishes sulfide treatment methods that are triggered by sulfide content.

Polk County Utilities Imperial Lakes & Turner Road Water Treatment Plants

Polk County Utilities (the county) has been in the process of expanding drinking water capacity to meet the demands of two of its Southwest Regional Service Area water treatment facilities. The expansion project will require the installation of at least one new groundwater well, as well as process modifications and/or refurbishment of existing facilities, which will require compliance with existing regulations—in particular, those outlined by Florida Department of Environmental Protection (FDEP) 62-555.315(5)(a).

These two facilities, the Imperial Lakes and Turner Road Water Treatment Plants, draw their water from the Upper Floridan Aquifer. Water quality data indicates that the source water is slightly alkaline with moderate hardness, typical of groundwater in Central Florida. The total hardness of the well water ranges between 80 and 150 mg/L (as CaCO₃), with an alkalinity between 80 and 155 mg/L (as CaCO₃). At an average pH of 7.2 to 7.8, the alkalinity is primarily in the form of bicarbonate.

Total dissolved solids ranges from 150 to 300 mg/L, containing less than 0.004 mg/L and 0.08 mg/L of lead and copper, respectively. Total sulfide in the raw water ranges from 1.4 to 2.6 mg/L (as S²⁻). Hydrogen sulfide will vary slightly seasonally, and is also a function of pumping rate. Existing treatment at the Imperial Lakes and Turner Road plants consists of traditional groundwater pumping, chlorina-

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tion (bleach), tray aeration, storage, and distribution; the finished water in the ground storage tanks can exceed 6 nephelometric turbidity units (NTU) at each plant, primarily because of elemental (colloidal) sulfur.

The county turned to the University of Central Florida (UCF) for help because of concerns that the treatment methods identified in FDEP 62-555.315(5)(a) (i.e. forced-draft aeration) would not fit adequately within the confines of the existing sites and would pose undue burden to neighboring residents. Both treatment sites were small and additional adjacent land acquisition opportunities were limited, so the county challenged UCF to develop a plan that would meet its needs while incorporating other considerations, such as minimizing the number of new chemical feed systems included in design, taking into account site constraints, minimizing aesthetic and secondary impacts to the neighboring communities, and also addressing master planning.

To meet the challenge, UCF first evaluated and screened a number of alternative sulfide removal technologies and methodologies, as others in Florida have researched such alternatives over the years. UCF then developed a testing plan and protocol that was designed to evaluate the following short-listed technologies: mixed-oxidants, ferrate, anion exchange, Electromedia® filtration and MnO₂ filtration. This article highlights a variety of treatment methods that were evaluated, and places particular emphasis on alternative and innovative filtration techniques.

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Hydrogen Sulfide Chemistry

Sulfide exists in three forms in the 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-} ; total sulfides herein are referred to as “sulfides”. Sulfides are commonly found in groundwater and impoundments where anaerobic conditions prevail.

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 (White 1972). The rotten egg odor of hydrogen sulfide may occur as a result of anaerobic bacterial action on sulfates. The minimum detectable taste of sulfide in water is approximately 0.05 mg/L.

The genera most often responsible for sulfide production are *Desulfovibrio desulfuricans* and *Desulfotomaculum*, which are known to accelerate the reduction of sulfate and can be a major source of sulfide production in anaerobic environments (Lim 1979). Other bacterially produced sulfur compounds creating swampy and fishy tastes and odors in distribution systems include *Dimethylpoly-*

sulfides and *Methylmercaptan*. Several types of *Pseudomonas* bacteria can also produce undesirable sulfur compounds (AWWA 1999).

In addition to odor, the presence of hydrogen sulfide in drinking water can impact taste, impact corrosion rates, and cause maintenance issues in water treatment plants and distribution systems. When treated with an oxidative method, converted sulfides can also contribute to the formation of turbidity and color in the finished water (Lyn 1992).

One primary concern with hydrogen sulfide is that it can accelerate corrosion by reacting with metal ions to form non-protective insoluble sulfides. Sulfide can attack steel, iron, galvanized, and copper piping to form “black water” even when oxygen is not present. Hydrogen sulfide has been found to promote a severe kind of pitting in copper piping. It has also been shown to damage asbestos-cement piping in some waters through microbial reactions (AWWA 1999).

In the pH range of 6.0 to 8.0, the predominant reduced sulfur forms are bisulfide (HS^-) and hydrogen sulfide (H_2S); the sulfide (S^{2-}) form is negligible at ambient pH levels in groundwater. Thermodynamically stable states, both final and quasi, include sulfate (S^{+6}) and colloidal sulfur (S^0) under oxidized water conditions. Consequently, of the 30 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^0], bisulfate [HSO_4^-], and sulfate [SO_4^{2-}] (Garrels and Naeser).

In aqueous solutions, hydrogen sulfide reacts with water, and can be described by the following equilibrium equations:

Equation (1) states 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), as shown in Figure 1. Since most groundwaters occur 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 occurs and the equilibrium of the system is artificially shifted. At pH values above 13, sulfur chemistry becomes very complex. Chlorination or oxygenation of groundwater 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 (Rubin 1974; Hausler 1979; Duranceau 1993).

FDEP Regulations Regarding Sulfide

Hydrogen Sulfide Removal

New revisions to FDEP Chapter 62-555 regarding hydrogen sulfide removal are now in effect for new wells. Table 1 presents H_2S removal requirements based on revisions to FDEP Chapter 62-555.315(5)(a). The new provisions pertain to public water system wells, with respect to various construction operation and maintenance items related to water quality. In an effort to control copper pipe corrosion and black water complaints, new permit provisions were developed under FDEP Chapter 62-555.315(5). Permit applications to connect a new or altered well to a community system after August 28, 2003 must adhere to the following provisions:

1. Include in the preliminary design report results for alkalinity, dissolved iron, dissolved oxygen, pH, total sulfide, and turbidity.
2. If total sulfide equals or exceeds 0.3 mg/L the applicant must perform the following:
 - i) Provide aeration to remove total sulfide. Recommended types of aeration treatment are provided in Table 1. The techniques listed next to each water quality level are recommendations only and not requirements; other treatment techniques used must achieve the same or better removal.
 - ii) Provide a preliminary design report demonstrating that secondary maximum contaminant levels (MCLs) for color and odor will not be exceeded in

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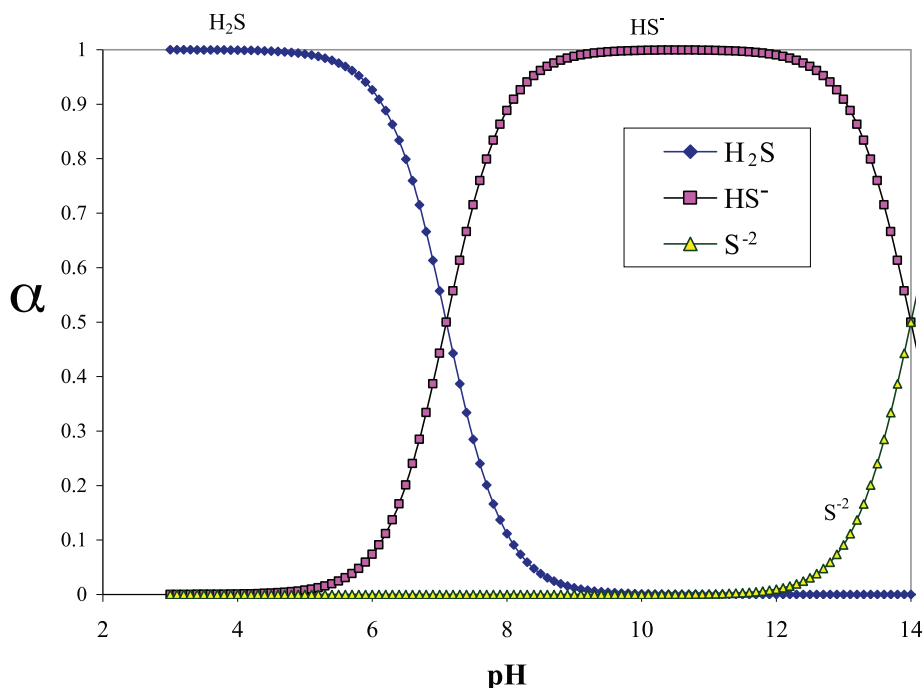
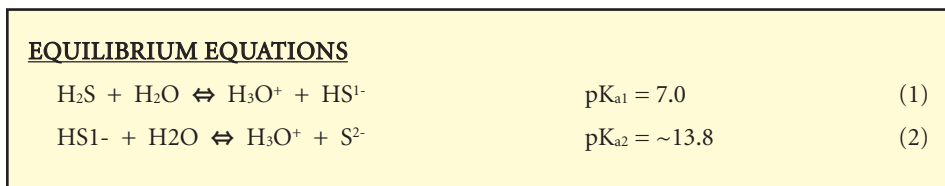


Figure 1. Sulfide Species Distribution Diagram

Table 1. FDEP Chapter 62-555.315(5)(a) Total Sulfide Treatment Recommendations

Potential for Impacts without Total Sulfide Removal	Source Water Sulfide Level	Potential Water Treatment Technique
Low	Total Sulfide (TS) < 0.3 mg/L; or Dissolved Iron (DI) < 0.1 mg/L ¹	Direct chlorination ²
Moderate	0.3 mg/L ≤ TS ≤ 0.6 mg/L @ pH ≤ 7.2	Conventional aeration ³ (maximum removal efficiency ≈ 40% to 50%)
	0.3 mg/L ≤ TS ≤ 0.6 mg/L @ pH > 7.2	Conventional aeration with pH adjustment (maximum removal efficiency ≈ 40% to 50%)
Significant	0.6 mg/L ≤ TS ≤ 3.0 mg/L @ pH ≤ 7.2	Forced Draft Aeration ³ (maximum removal efficiency ≈ 90%)
	0.6 mg/L ≤ TS ≤ 3.0 mg/L @ pH > 7.2	Forced Draft Aeration with pH adjustment ^{4,5} (maximum removal efficiency ≈ 90%)
Very Significant	TS > 3.0 mg/L	Packed Tower Aeration with pH adjustment ^{4,5} (maximum removal efficiency ≈ 90%)

1. High iron content raises concern if chlorination alone is used and significant dissolved oxygen exists in the source water. Filtration may be required to remove particulate iron prior to water distribution.
2. Direct chlorination of sulfide in water in the pH range normally found in potable sources produces S⁰_(s) and increased turbidity. Finished-water turbidity should not be more than two nephelometric turbidity units (NTU) greater than raw-water turbidity.
3. Increased dissolved oxygen entrained during aeration may increase corrosivity.
4. Reduction of alkalinity during pH adjustment and high dissolved oxygen entrained during aeration may increase corrosivity. Corrosion control treatment such as pH adjustment, alkalinity recovery, or use of inhibitors may be required.
5. High alkalinity will make pH adjustment more costly, and use of other treatment may be in order. Treatment that preserves the natural alkalinity of the source water may enhance the stability of finished water.

* Note – These recommendations are to be used as guidance and not as a requirement.

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the water supplier’s drinking water distribution system or in water customers’ potable water systems.

- iii) Odor compliance shall continue to comply with FDEP Chapter 62-296.320(2).

Hydrogen Sulfide Off-Gas Standards

Off-gas standards have not been set for hydrogen sulfide. FDEP Chapter 62-555 references FDEP Chapter 62-296 and FDEP Chapter 62-210 for objectionable odor guidelines. FDEP Chapter 62-210 defines objectionable odor as “any odor present in the outdoor atmosphere which by itself or in combination with other odors, is or may be harmful or injurious to human health or welfare, which unreasonably interferes with the comfortable use

and enjoyment of life or property, or which creates a nuisance.”

The Occupational Safety and Health Administration (OSHA) recommends 20 parts per million by volume (ppmv) threshold for hydrogen sulfide off-gas concentrations on-site for operators. While other sources cite 7.3 ppmv at the property boundary to avoid odor complaints, hydrogen sulfide can be discharged into the air untreated, or the air can be discharged following sulfide removal on-site.

Treatment Alternatives for Sulfide in Water

There are many methods available to remove sulfide contaminants from drinking water supplies. A desk-top evaluation was con-

ducted to eliminate alternatives that would not achieve county goals. It included:

- ◆ Aeration (cascade tray aeration; forced-draft aeration; fine bubble aeration; volatilization)
- ◆ Oxidation (oxygen, chlorine, ozone, potassium permanganate, hydrogen peroxide, ferrate)
- ◆ Microbiological filtration
- ◆ Oxidation followed by membrane filtration, electromedia filtration or manganese greensand filtration
- ◆ Anion exchange (adsorption to media)

Sulfide removal technologies typically are based on sulfide equilibria, and include either: (1) a pH-dependent partitioning of hydrogen sulfide, (2) conversion to the thermodynamically stable state of sulfate, or (3) the controlled formation of elemental sulfur. The use of pH-dependent processes include cascade aeration, volatilization, forced-draft aeration, and fine-bubble aeration where the treatment is based on mass transfer of a gaseous form of sulfur from a water stream to an air stream.

Those processes based on the formation of sulfate involve electron transfer mechanisms and include oxidation and microbiological filtration. Membrane filtration applies to the removal of elemental sulfur. An overview of the basic advantages and disadvantages are provided for each identified method in Table 2.

Aeration

Aeration is a historical, common method of treatment for sulfides (Roe 1935; Flentje 1937; 1948). Since the type of sulfide species in water is dependent upon the pH, only that portion of the total sulfide that is present as hydrogen sulfide gas can be removed from water by aeration (tray, packed-tower, diffused air, or spray-nozzle methods). Beneficial effects of hydrogen sulfide treatment using aeration include:

1. The elimination of taste and odors.
2. A decrease in the corrosive effects of hydrogen sulfide on metals and concrete.
3. A reduction in the demand of chlorination disinfection.

For groundwater facilities not utilizing softening and filtration, sulfide removal typically is accomplished by cascade or tray aeration and volatilization in ground storage facilities; however, cascade tray aeration and volatilization are only partially effective in removing sulfide (approximately 15 to 25 percent total sulfide removal) and depend on pH and atmospheric conditions (more sulfide is removed on windy, warm days). Under high-flow conditions, tray aerators do not provide adequate sulfide removals for most groundwaters.

Packed towers utilize tower arrangements

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Treatment Method	Advantage	Disadvantage
1. Aeration		
-Cascade or Tray	Inexpensive	Insufficient removals; not effective; turbidity formation.
-Volatilization	Inexpensive	Control is difficult; not effective; sulfide bacteria regrowth.
- Forced-Draft	Effective treatment method and simple operation is attractive; documented experience	Increased capital costs; acid pretreatments must be employed; odor generation requires use of expensive scrubber systems; scrubber impact to POTW operations; aerated water can contain undesired microbiological constituents (thiothrix, pseudomonas aeruginosa).
-Fine Bubble	Moderate costs and amenable to GST retrofits	Insufficient removals at neutral pH levels; odor generator not easily treated; not typical in drinking water treatment
2. Oxidation		
-Oxygen	Minimal capital costs; simple process	Incomplete oxidation can create colloidal sulfur and polysulfides; design and control difficult; turbidity
-Chlorine	Minimal capital costs; controllable process	Incomplete oxidation; may increase DBPs; high dosages required, safety concerns, turbidity formation.
-Ozone	Controllable process; produces high quality finished water	Reaction chambers required; high operating and capital costs; may not be cost effective for small systems having greater than 2 mg/L total sulfide in raw water, turbidity formation
-Potassium Permanganate	Controllable process; inexpensive capital	Requires filters for residual MnO ₂ ; requires large chemical dose; expensive chemical; turbidity formation
-Hydrogen Peroxide	Controllable process; inexpensive capital	Requires optimum mixing and long detention/contact times; incomplete oxidation; large dosages needed; turbidity
-Ferrate	Powerful oxidant; inexpensive capital	Process has not been demonstrated at a large scale for drinking water treatment
3. Oxidation Filtration	Controllable process; effective; affordable	Typically used for iron and manganese control; sulfide is secondary benefit; discharge of waste streams; discoloration of basin equipment, breakthrough of permanganate if used can cause discoloration (pink)
4. Membrane Filtration	Controllable process; effective if controlled at optimum conditions	Expensive; requires colloidal sulfur formation to be complete prior to filtration step; irreversible fouling of membranes may occur
5. Microbiological Filtration	Natural process; chemical-free method; safe to operate	Detachment and clogging are issues; design and control difficult; not proven process for drinking water
6. Anion Exchange	Controllable; moderate cost compared to others	Biological fouling can foul resin; salt regeneration impacts discharge permits.

Table 2. Summary of Advantages-Disadvantages of Alternatives of Sulfide Removal from Water

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with plastic packing materials to increase the water/air effectiveness for stripping gaseous sulfide from the water. Packed towers rely on either structured or random-loosed packing materials, and are counter-current water air processes (hydrogen sulfide-laden water is introduced at the top of the tower and clean air is introduced at the bottom of tower, with clean water exiting the bottom of the tower and hydrogen sulfide-laden air exiting the top of the tower).

Packed towers have higher stripping efficiencies than tray aerators and are an effective method for sulfide removal; however, the use of

packed towers has been shown to impact finished water negatively because of microbiological growth in the packing and release into the distribution system (Duranceau et. al. 2003).

Carbon dioxide is a smaller molecule than hydrogen sulfide and will be released at a faster rate than hydrogen sulfide (Garrels 1958). As the dissolved carbon dioxide and hydrogen sulfide gases are removed, the pH of the water flowing down over the packing increases, causing the ionization of hydrogen sulfide and carbonic acid and decreasing the removal efficiency of the tower; however, if carbon dioxide is present in concentrations of about 10 per-

cent (whether present initially or is added as a packed tower pretreatment method), the hydrogen ion concentration is raised to favor the release of hydrogen sulfide gas (Roe 1935). The use of carbonic acid for pH adjustment prior to packed tower aeration processes has been demonstrated to be an effective pretreatment method and can assist in corrosion control (Duranceau, Anderson and Teegarden 1999).

Fine bubble aeration is a limited process for sulfide removal and has not been utilized effectively for this specific contaminant primarily because of design limitations and cost. Volatilization would be relied on in place of fine bubble aeration, but volatilization is an unpredictable process and is limited by tank geometries and atmospheric conditions.

Oxidation

Oxidation of sulfides can be accomplished with oxygen, chlorine, hydrogen peroxide, ozone, potassium permanganate, hydrogen peroxide, and dipotassium ferrate. Historically, chlorine has been used to remove residual sulfides after tray aeration and/or volatilization, but chlorine oxidation results in the formation of colloidal sulfide turbidity (Lyn 1992). Stoichiometrically, 8.34 mg/L of chlorine is required to oxidize 1 mg/L of hydrogen sulfide to sulfate, but incomplete oxidation typically occurs under actual operating conditions.

Ozone oxidation is a beneficial process and has been demonstrated to be an effective, practical method for sulfide treatment of groundwater having nominal sulfide content. An ozone-to-hydrogen sulfide weight ratio of 5.65 mg/L to 1 mg/L is required for conversion from hydrogen sulfide to sulfate. Ozone oxidation for hydrogen sulfide is not cost-effective for groundwaters having total sulfide concentrations of 2.0 mg/L or greater.

Although this method has been implemented successfully by the Orlando Utilities Commission, the county was concerned about small-system applications, electrical costs, and

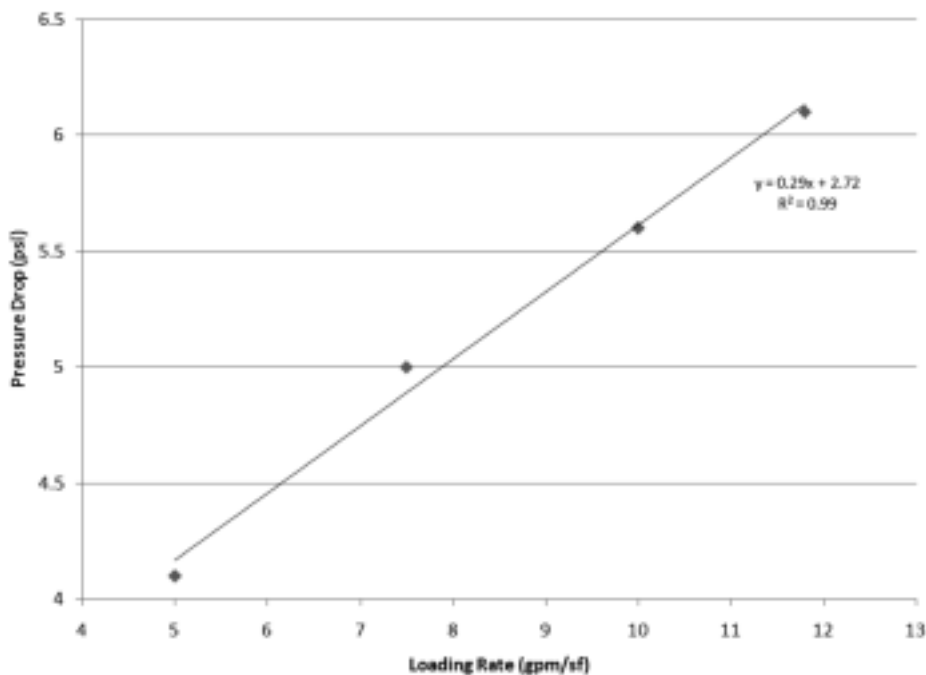


Figure 2. Pressure Drop across Filter Bed (MnO₂ Media)

sulfide loadings. Mixed-oxidants would be evaluated in lieu of ozone for the evaluation.

For conversion of hydrogen sulfide to sulfate using hydrogen peroxide oxidation, a stoichiometric ratio of 4.0 to 1.0 is required for water having a pH greater than 8.0 units, but the treatment method has not been demonstrated effectively for treatment of hydrogen sulfide in groundwater. Approximately 12.4 mg/L of potassium permanganate is required to oxidize 1.0 mg/L of hydrogen sulfide. Both peroxide and permanganate have been shown to provide complete removal of sulfide but yield both sulfate and colloidal sulfur as reaction products (Dohnalek 1983).

Microbiological Filtration

Aerobic bacteria such as *Beggiatoa* and *Thiothrix* will uptake reduced sulfide and convert the mass to sulfate. Although effective for sulfide removals, the organisms can slough off surfaces and cause turbidity downstream of storage facilities. No known controlled biofiltration process utilizing this method has been demonstrated cost effective for the removal of sulfides from a water stream for drinking water, although hydrogen sulfide-laden air streams have been treated with the use of biofilters.

Membrane Filtration

This method would involve the use of a synthetic membrane process for elemental sulfur removal. It is considered to be an experimental method and currently represents a high-cost alternative. Also, since an oxidation step is required to form elemental sulfur prior to removal by the membrane, only chlorine-tol-

erant membranes can be used and those that are used foul, which add to operating and membrane replacement costs. Control of this process is uncertain, and demonstrated use has not been shown; hence, this method is not considered to be favorable for sulfide removal at this time.

Anion Exchange

Similar to cation exchange, anion exchange can be used to remove negatively charged dissolved solutes such as total organic carbon and

sulfides, but with regard to sulfides, the removal efficiencies are variable and the resin can foul because of growth of sulfur-related bacteria. Also, salt regeneration of the resin is required, which will add cost and impact downstream wastewater discharges. Since the county was concerned about increasing the conductivity of discharges to its publicly owned treatment works, this option was not selected for field testing.

Discussion of Alternatives Removed from Consideration

Several treatment alternatives were evaluated, in varying degrees, in this study. Packed tower aeration, ozone, and anion exchange were evaluated through a desktop study. The most widely used, FDEP-recommended method of sulfides removal is the use of packed tower aeration. Since the FDEP Rule 62-555-315(5)(a) was implemented in 2003, packed tower and forced draft aeration systems have become the predominant choice of utilities looking to remove sulfides. In full-scale use, these systems have been shown to work reliably, although considerations should be made for the maintenance involved with operating them properly. Also, the wastewater generated from the odor scrubber will contribute to elevated conductivity levels in the municipal sewer system, which is a concern for the county.

Ozone is a powerful oxidant, and has been shown to effectively treat and remove sulfides from drinking waters. It is proven and is currently in use at full-scale operation at several

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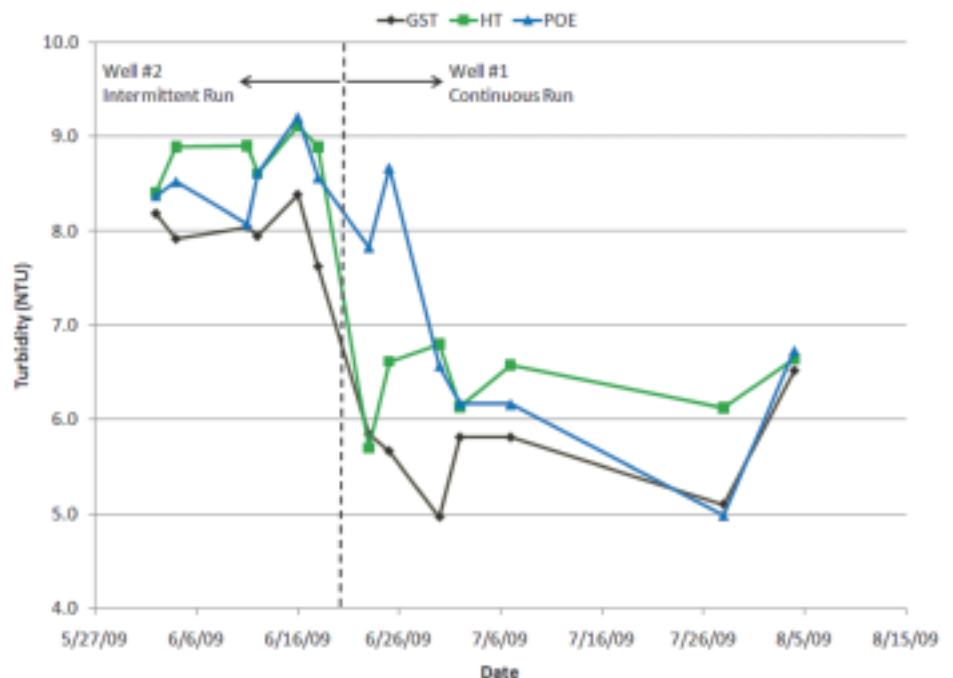


Figure 3. Average Daily Turbidity Trends: Imperial Lakes Water Treatment Plant

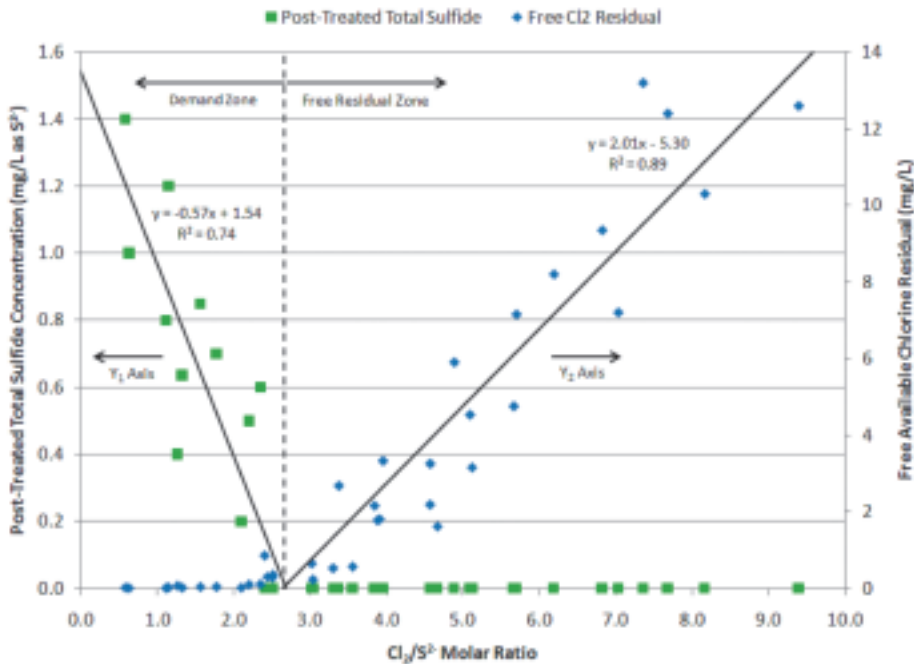


Figure 4. Total Sulfide Breakpoint Curve: Molar Ratio at Imperial Lakes Water Treatment Plant

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treatment facilities (Orlando Utilities Commission) in Florida, but ultimately it was removed from consideration because the county expressed a desire to find a process that would not require extensive investment in electrical and expensive process infrastructure and would minimize operational costs and labor.

Anion exchange is another promising treatment method for removal of hydrogen sulfide. While it has not yet been employed solely for sulfides removal at a full scale, bench and pilot scale studies have shown that it is effective. As discussed previously, an impact of using an anion exchange process is that salt must be brought on site for regeneration and subsequent disposal that will elevate conductivity levels for the municipal sewer system, which is of concern to the county. Regrowth associated with sulfide-reducing bacteria and other biological species may increase the likelihood of bio-fouling, causing operational problems when relying on anion exchange for sulfide removal (personal conversation with Audrey Levine of the EPA, Washington, D.C.).

Based on the information gathered and analyzed, UCF developed a testing plan and protocol that was designed to evaluate the following short-listed technologies: mixed-oxidants, ferrate, Electromedia® filtration and MnO₂ filtration.

Bench & Pilot Evaluations

UCF implemented field evaluations that included both bench and pilot scale testing

formats between February and September 2009 at each of the test sites. The proprietary mixed-oxidant MIOX® was studied at bench scale via jar testing activities. The mixed-oxidant was compared to bleach oxidation in on-site jar testing, and the two oxidants displayed similar performance, both in required dose and in finished water quality.

Ferrate was also evaluated at the bench scale via jar testing. Both ferrate and the mixed-oxidant were shown to be effective at sulfide conversion in this early testing.

Bleach oxidation preceding a proprietary Electromedia® filtration process and manganese greensand filtration continuously regenerated with bleach were studied at the pilot scale. The media used for greensand evaluation, GreensandPlus™, is synthetic product manufactured by thermally fusing a MnO₂ oxidizing layer onto a silica sand core. Ex-

ploratory ferrate testing was also performed at the pilot scale. Some of the results from those studies are shown in the accompanying figures.

Figures 2 and 3 represent pressure drop across the MnO₂ Greensand filter and turbidity response of the existing tray aeration operation at the Imperial Lakes Water Treatment Plant, respectively. The data for Figure 2 was obtained from operation (at 24-26°C) of the MnO₂ greensand filter at the Imperial Lakes Water Treatment Plant.

In Figure 3, the turbidity drops off after June 18. This shift coincides with changes that were made (ie. opening the PRV to the distribution system and switching to a smaller well) in order to allow for longer (continuous) run times. Since the two wells tested were located on the same site and provide similar water quality, it was reasoned that the GST was “flushed” as the continuous run operation reduced residence time in the GST and the sulfide turbidity was not fully forming in the GST but rather out in the distribution system.

The information illustrated in Figure 4 was generated using data obtained from operation of the Electromedia® pilot-filter at the Imperial Lakes Water Treatment Plant. This figure shows the breakpoint for raw water sulfides removal as a function of the Cl₂ to sulfide molar ratio. This same figure also provides information regarding free chlorine residual formation as a function of the Cl₂ to sulfide molar ratio.

Figure 4 illustrates the total sulfide removal in terms of two distinct operating regimes: a “Demand Zone” (DZ) where sulfides are exerting a demand on the bleach oxidant and a “Free Residual Zone” (FRZ) where sulfides are no longer present (for this work the method detection limit was 1.0 mg/L) and are in the presence of a free Cl₂ residual. Total sulfide Cl₂ demand decreases from left to right in the DZ and free Cl₂ residual increases from left to right in the FRZ. In the DZ, 74 percent of the variation in the remaining sulfide data could be explained by a linear regression of negative slope. At breakpoint there is a transition to the FRZ,

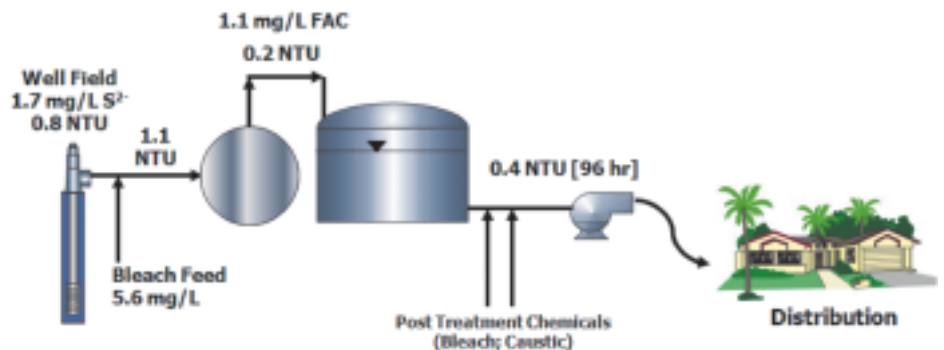


Figure 5. Summary of Pilot Scale Findings Using Bleach- MnO₂ Greensand Media Filtration

whereupon 89 percent of the variation in the free chlorine residual data could be explained by a linear relationship of positive slope.

At the Imperial Lakes Water Treatment Plant, the county maintains a chlorine residual between 2.5 and 3 ppm, depending on the temperature (that is, the summer required a higher residual). According to the linear model, to achieve a 3 ppm free chlorine residual (using the Electromedia® process) a Cl₂-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).

One of the issues water purveyors are faced with in traditional aeration/bleach oxidation processes is turbidity formation. Turbidity formation was found to be minimal when finished water from the filter pilot units was held in amber containers and measured after several days of detention time. This is shown in Figure 5. This turbidity is in comparison to the 6+ NTUs (average; finished water) measured along the existing treatment train. Figures 4 and 5 represent some of the findings from the pilot evaluations for the program; not all data is provided for brevity.

Ferrate was found to remove sulfide effectively to levels below the method detection limit (0.3 mg/L), but turbidity increased significantly (>10 NTU) after contact with the oxidant. This turbidity forms quickly (several minutes), is not colloidal in nature like that formed by bleach oxidation, and could be controlled by traditional filtration medias. Further work would be required to evaluate the benefits of advanced oxidation followed by sand filtration.

Preliminary results for the media filtration technologies have been promising, and it appears that the Electromedia® and MnO₂ Greensand filter options offer treatment performance equal to, or better than, conventional tray aeration/chlorination with respect to required bleach dose. These media filters could be engineered and placed into the existing process downstream of the well and prior to the tray aerator, offering an opportunity for a retrofit design far simpler than those systems implementing retrofit construction of packed towers and associated odor-control system for compliance with FDEP 555-620.315 on existing water treatment plant sites. The process would also have a lower vertical profile, which is an aesthetic quality conducive to the concerns of neighboring communities.

Post-treatment aeration with tray aerators would still be required for carbon dioxide removal and oxygen transfer for palatability considerations. The use of permanganate would not be needed for manganese greensand bed regeneration; the bed life is estimated at 10 years using a bleach oxidant for continuous regeneration.

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Consequently, the use of oxidation/filtration, typically used for iron and manganese removal, would offer the county flexibility and affordability for these two small systems; additional engineering activities would be required to determine the most appropriate path forward regarding implementation of this treatment process.

Summary

Reduced sulfide is a contaminant of concern for many water purveyors relying on groundwater supplies. If left untreated, sulfides impact finished water quality and corrosivity, create undesirable taste and odor, and oxidize to form visible turbidity and color.

Although there are several methods available that can remove sulfides from water supplies, it appears that forced-draft aeration and ozone have demonstrated their value successfully as a sulfides treatment method. Small systems, however, may not be able to implement such advanced forms of sulfides treatment easily, and increasing information on the use of packed tower aeration for sulfides control indicates that secondary impacts related to turbidity release to the distribution system and unintentional secondary impacts of scrubbed wastes on publicly owned treatment works are

significant in terms of cost of operations.

Consequently, packed tower aeration and ozone oxidation may not always be available for small systems to treat sulfide from groundwater. The work presented herein has shown that bleach oxidation followed by the use of Electromedia® or manganese greensand media filters, historically used for iron and manganese removal, show significant promise for use by water purveyors having significant (0.6 to 3.0 mg/L) levels of total sulfide in their groundwater supplies.

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