Ozonation of Reverse Osmosis Permeate For Sulfide Control: Clearwater's New Water Treatment Plant Approach

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Figure 1. Rendering of the WTP #2 Site After Expansion

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The City of Clearwater (City) is currently expanding its Water Treatment Plant #2 (WTP #2) treatment capabilities through the addition of a reverse osmosis (RO) system. The upgraded plant will produce 6.25 mil gal per day (mgd) of finished water by blending 1 mgd of filtered fresh groundwater with 5.25 mgd of RO treated brackish water. The RO WTP #2 site is located on U.S. Highway 19 in a well-developed area of central Clearwater. It is a long and narrow site, bordered to the north and east by residential complexes and to the south by light commercial buildings. Figure 1 shows a rendering of the WTP #2 site after the expansion efforts.

The brackish raw water that will supply the RO system will be provided by 12 new wells. Overall, these wells will produce 6.56 mgd and have varying water quality. The water from the wells is expected to have an average total sulfide concentration of 1.4 mg/L; however, when the eight highest sulfide concentration wells (the expected number of wells required to provide the necessary amount of water) are averaged, the total sulfide concentration is 2.5 mg/L. Table 1 summarizes the average, minimum, and maximum concentrations for key constituents in the RO permeate water from pilot testing.

A portion of the total sulfides in the new wellfield will be present as hydrogen sulfide (H_2S), a naturally occurring gas found in Florida groundwater. The H_2S has a pungent odor at very low concentrations and can oxidize to form turbidity and color that further affects the aesthetics of drinking water; it can also corrode and damage copper pipes (Chastain, 2008; Duranceau, 2010). The City has water quality goals

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Table 1. Anticipated RO Permeate Water Quality

Constituent	Average (mg/L)	Minimum (mg/L)	Maximum (mg/L)
Total Sulfide	1.4	0.7	2.5
pH	6.3	6.0	7.0
Bromide	0.1	--	0.3

Table 2. FDEP Potential Sulfide Treatment Options

Potential for Impacts Without Total Sulfide Removal	Water Quality Ranges	Potential Water Treatment
Low	Total Sulfide < 0.3 mg/L Dissolved Iron < 0.1 mg/L[1]	Direct Chlorination[2]
Moderate	0.3 mg/L Total Sulfide 0.6 mg/L @ pH 7.2 or 0.3 mg/L Total Sulfide 0.6 mg/L @ pH 7.2	Conventional Aeration[3] (maximum removal efficiency ~40-50 percent) or Conventional Aeration with pH Adjustment[4,5] (maximum removal efficiency ~40-50 percent)
Significant	0.6 mg/L < Total Sulfide 3.0 mg/L @ pH 7.2 or 0.6 mg/L < Total Sulfide 3.0 mg/L @ pH 7.2	Forced Draft Aeration[3] (maximum removal efficiency ~90 percent) or Forced Draft Aeration with pH Adjustment[4,5] (maximum removal efficiency ~90 percent)
Very Significant	Total Sulfide > 3.0 mg/L	Packed Tower Aeration with pH Adjustment[4,5] (maximum removal efficiency >90 percent)

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 elemental sulfur and increased turbidity. Finished-water turbidity should not be more than two nephelometric turbidity units 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.
(FDEP, 2003)

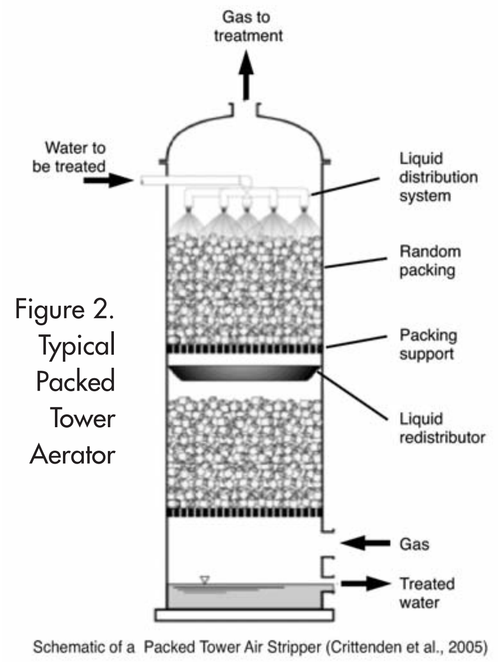

Figure 2. Typical Packed Tower Aerator

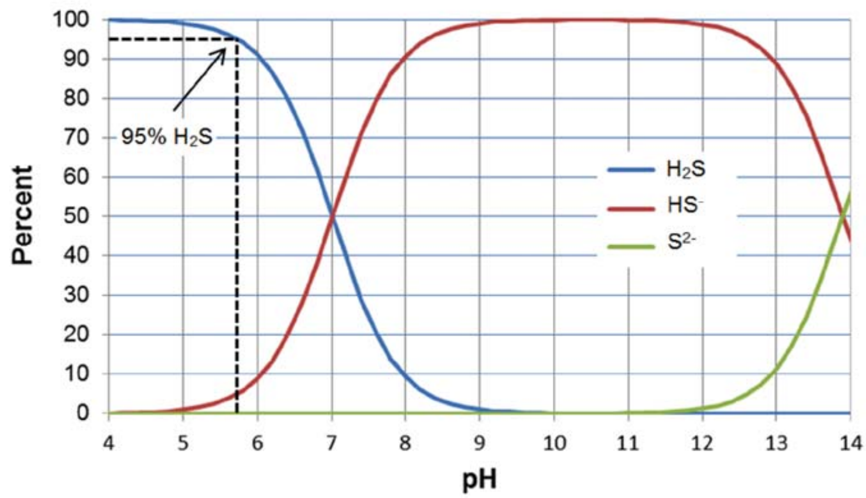

Figure 3. Hydrogen Sulfide Speciation versus pH

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that limit the concentration of total sulfides in its potable water system to 0.1 mg/L, and the Florida Department of Environmental Protection (FDEP) Rule 62-555.315(5)(a) sets removal requirements for wells used for public water supply. When the total sulfide of a water supply exceeds 0.3 mg/L, the FDEP requires treatment and provides a listing of potential treatment options, as shown in Table 2. Many of the potential water treatment options presented by the FDEP rule use aeration techniques to remove sulfides; however, these are recommendations and other appropriate sulfide removal processes are acceptable for satisfaction of the rule.

While the expansion of WTP #2 will include the use of RO, which is very effective at removing dissolved solids such as chlorides, it is ineffective for removal of gases, such as H_2S, as they pass readily through RO membranes. This means that even after RO treatment, the total sulfide concentration in the RO permeate is expected to fall between 0.6 mg/L and 2.5 mg/L; thus, the FDEP requires sulfide post-treatment and states that the potential for impacts on the distribution system without treatment is significant. With this in mind, two sulfide treatment options were analyzed for their feasibility, capital cost, and operating cost: packed tower aeration with pH adjustment versus ozonation via sidestream injection. The latter option would be the first large-scale municipal system in Florida to treat H_2S in RO permeate using ozone.

Table 3. Packed Tower Aerator/Scrubber System Capital Cost Estimate for RO WTP #2

	Quantity	Total Cost
Packed Tower each including: - Air supply fan with inlet filter - FRP vessel inlet transition piece - FRP degasifier tower - Instrumentation and controls - FRP I/C ductwork from degasifier towers to off-gas treatment system (with dampers)	2	$875,000
Scrubber: - FRP tower scrubber - Exhaust stack - Chemical feed system - Chemical recirculation pump - Instrumentation and controls	2	$400,000
Chemical Feed Systems: - Sodium bisulfite - Sulfuric acid - Piping	1	$50,000
Piping	1	$5,000
Sub-Total		$1,330,000
Contingency	15%	$200,000
TOTAL		**$1,530,000**

Packed Tower Aerators

A common method to remove sulfides from RO permeate is to use packed tower aerators. This technology transfers H_2S from the dissolved liquid phase to the gas phase through a mass transfer process (Crittenden, 2005; Chastain, 2008). A typical packed tower aerator, shown in Figure 2, consists of a column filled with plastic packing material used to increase the air-to- water interface. Blowers force air from the bottom of the tower, while water enters from the top.

For this alternative, the design would require two packed towers, each capable of treating 5.25 mgd and two chemical scrubbers to treat the resulting off-gas of the degasifiers. A redundant system was chosen to ensure that the RO system would not need to be taken offline in the situation when a packed tower or a scrubber is taken out of service for repair, maintenance, or cleaning. During normal operation, the towers would be rotated in and out of service on a regular basis.

Sulfide is normally found in three different forms: H_2S, hydrogen sulfide ion (HS^-), and sulfide ion (S^{2-}). Depending on the pH, and with only H_2S removed through mass transfer to air, it is important for the water entering aerator systems to be slightly acidic (Crittenden, 2005; Chastain, 2008; Duranceau, 2010). As shown in Figure 3, in order to achieve the desired 95+ percent removal of total sulfide with an average permeate pH of

6.3, acid treatment is required to lower the pH and increase the total sulfide partition of H_2S prior to aeration.

The resulting off-gas from a packed tower is laden with H_2S, and to prevent odor issues, a chemical wet scrubber was chosen. Approximately 20,000 to 40,000 gal per day (gpd) of potable water would be mixed with sodium hydroxide and sodium hypochlorite, and recirculated through the scrubber several times to transfer the sulfide from the gas phase back into a liquid phase; it also oxidizes the H_2S to sulfur or sulfate. The resulting blowdown water is treated with sodium bisulfite to removed excess free chlorine and sulfuric acid to lower the pH before being disposed to the sanitary sewer. A wet scrubber was selected to treat the aerator off-gas over other options, such as a biological scrubber, to ensure reliable operation and minimize odor complaints from the nearby residents.

The construction cost for an aeration/scrubber system for WTP #2 was estimated to be approximately $1.53 million and is presented in Table 3. The operational costs were expected to be approximately $300,000 per year, and are shown in Table 4. The operation and maintenance (O&M) costs have been calculated for the average annual daily flow expected to be produced when the expansion is complete (~4.2 mgd of permeate).

The primary advantages for an aeration system are that it is a proven technology with many applications throughout the state, and it has a lower capital cost than an ozone system. However, disadvantages include: frequent cleanings of the aerators and scrubbers, which is necessary to prevent excessive biogrowth and to remove precipitated sulfur; disposal of blowdown water; the visual aesthetics of the system, as the 28-ft. tall aerator towers and 26-ft. tall scrubbers would very noticeable to the neighboring residents and are often associated with undesirable industrial facilities; and the need to store and feed additional chemicals. The proximity of the odor control system to the residences and offices also makes routine maintenance of the system more critical to avoid odor issues.

Ozone

Ozone is another technology that has been proven to be effective at removing H_2S from Florida groundwater supplies. Toho Water Authority, in central Florida, has used ozone for years, and the utilities of Orange County and Seminole County have recently installed, or are in the process of installing, ozone generators for the treatment of sulfide (Vanlandingham, 2012). Ozone is a powerful oxidant, and when it comes in contact with H_2S or HS^- the resulting products are oxygen gas and sulfate ion (SO_4^{2-}), thus effectively removing the objectionable H_2S gas and replacing it with benign levels of sulfate (Duranceau, 2010).

Ozone for municipal water treatment is typically produced by passing oxygen through a high-voltage dielectric. Liquid oxygen (LOX) is often used as an oxygen source and typical water utility ozone generators can produce 10 percent or greater ozone concentrations. In order to oxidize the average 1.4 mg/L of sulfide expected to be found in the 5.25 mgd of permeate flow and maintain an ozone residual of 0.2 mg/L, the design requires 214 lbs of ozone per day (ppd) with a ozone to sulfide ratio of 3.1:1. Two 220 ppd generators were selected to provide redundancy and would be housed in a separate structure to shelter the units from weather.

Depending on the efficiency of the particular generators, one lb of ozone requires be-

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Table 4. Packed Tower Aerator/Scrubber System Operation Cost Estimate for RO WTP #2

	Unit Cost	Quantity	Total Cost
Power	$0.10/kWh	450,000 kWh/year	$45,000
Sodium Hypochlorite (12.5 percent)	$0.685/gal	210,000 gal/year	$145,000
Sulfuric Acid (98 percent)	$190/ton	5,300 gal/year	$8,000
Sodium bisulfite	$0.25/lb	15,000 lb/year	$3,500
Caustic (50 percent)	$4.2/gal	10,500 gal/year	$45,000
Cleaning Contract			$40,000
Scrubber maintenance			$12,000
Degasifier maintenance			$3,000
TOTAL			**$300,000**

Assumptions:
1. Power: $0.10/kWh: Aeration: 40 HP blower + 7.5 HP recirculation pump + 20 HP added head (compared to ozonation)
2. Sodium hypochlorite: $0.685/gal: bulk purchased cost by City of Clearwater for RO WTP#1
   a. Aerator dosage is based on a vendor quote
   b. Dosage equates to scrubber usage in a similar application and flow rate
3. Caustic: $0.33/lb: bulk purchased cost by City of Clearwater for RO WTP#1
   a. Aerator dosage is based on a quote from Siemens
   b. Dosage equates to scrubber usage in a similar application and flow rate
4. Sulfuric acid: $190/ton: quote from a local chemical provider
5. Aeration maintenance costs: $15,000 per year based on budget from operations of a similar system
   a. Degasifiers: $3,000 per year
   b. Scrubbers: $12,000 per year for City staff including quarterly cleanings with citric acid
6. Contract cleaning: based on previous project contractor quote for cleaning ($40k/degasifier)
   a. Frequency of one cleaning per year
   b. Cleaning costs include cleaning chemicals, onsite neutralization, and disposal to sanitary sewer
   c. Estimated freight for spent cleaning solution is $1,000 per cleaning

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tween eight and 12 lbs of LOX; therefore, under normal conditions, one 9,000-gal (85,600-lb) LOX tank would provide more than 30 days of storage. Redundant vaporizers would be operationally rotated to allow for adequate defrosting. The building and other areas near the ozone equipment will be monitored by ambient ozone monitors, and an alarm will sound if ambient ozone concentrations approach the regulated limits set by the Occupational Safety and Health Administration.

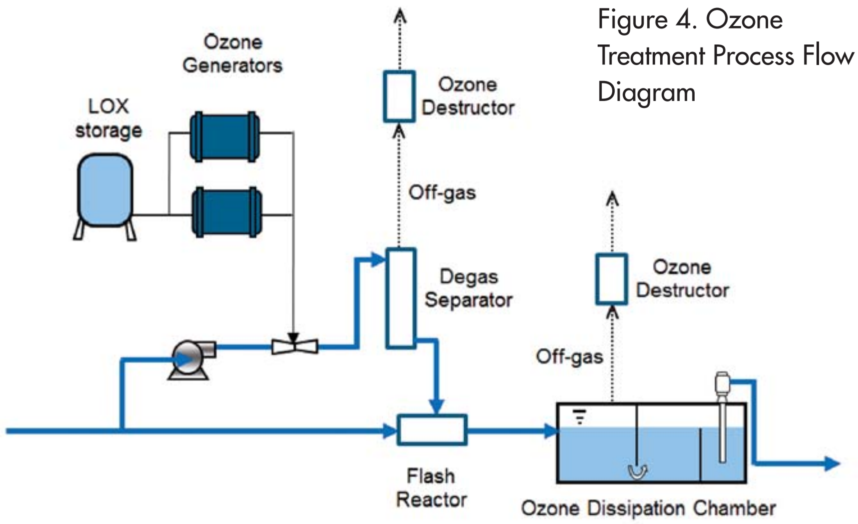

Figure 4. Ozone Treatment Process Flow Diagram

Table 5. Ozonation System Capital Cost Estimate for RO WTP #2

	Quantity	Total Cost
Ozone Generation System (Installed): - Two 220-ppd ozone generators - One LOX tank - Two ambient vaporizers - One nitrogen boost system - One side stream injection system - Two ozone destructors - One ozone control panel - Two high-concentration ozone monitors - Two off-gas ozone monitors - Two destructor outlet ozone monitors - Dissipation Chamber	1	$1,985,000
Building (Pre-cast Concrete)	1,500 sqft	$210,000
Sub-Total		$2,195,000
Contingency	15%	$329,000
TOTAL		**$2,524,000**

Table 6. Ozonation System Operation Cost Estimate for RO WTP #2

	Unit Cost	Quantity	Total Cost
Power	$0.10/kWh	625,000 kWh/year	$62,000
LOX	$0.05/lb	82,000 gal/year	$41,000
Maintenance			$25,000
TOTAL			**$128,000**

Assumptions
1. Power: $0.10/kWh: Ozonation: 60 HP generator + 60 HP injection system
2. LOX: $0.05/lb (local vendor quote) for 82,000 gallons/year (780,000 lbs/year or 2,150 lbs/day)
3. Ozonation maintenance costs estimates based on real costs incurred by Toho Water Authority
   a. Maintenance of ozone analyzers, UV lamp modifications, degas separator valve buttons replacement, heat exchanger spare plates and gaskets, cooling water strainers
   b. Replacement of catalyst for destruct
   c. Replacement of nitrogen boost motor
   d. Ozone meter cleaning and calibration

After the ozone is produced, it will be introduced to the permeate water by venturi injection into two 525-gpm sidestreams of the process water. The ozone laden sidestream passes through a degas separator that removes undissolved ozone and oxygen, after which the sidestream flow is reintroduced to the main water stream through a flash reactor. The ozone and water mixture is transferred to a dissipation chamber, where any remaining sulfides are oxidized and the ozone is off-gassed. The ozone collected by the dissipation chamber and degas separator is processed by a redundant set of catalytic ozone destruct units. Figure 4 diagrams the ozone generation and sidestream injection process flow.

An important aspect to consider when determining the feasibility of an ozone system for potable water treatment is the potential formation of regulated byproducts, such as bromate, aldehyde, and ketones; waters that are low in organic matter and bromide produce far less of these regulated compounds. Since reverse osmosis removes almost all organic matter, the formation potential of aldehyde and ketones is very low. Depending on the membrane used, some bromide may pass through into the permeate. Pilot testing of representative RO membranes found that the permeate bromide concentration can be expected to be approximately 0.1 mg/L, which is not expected to result in significant bromate formation during ozonation (Crittenden, 2005).

The estimated construction cost for an ozonation system for RO WTP #2 was estimated to be approximately $2.52 million and is presented in Table 5. The operational costs were expected to be approximately $128,000 per year and are shown in Table 6. The O&M costs have been calculated for the average annual daily flow expected to be produced when the expansion is complete (~4.2 mgd of permeate).

Advantages of the ozonation system include the absence of an additional waste stream, ozonation used to obtain the 4-log credit for virus inactivation as long as a residual is maintained, and lower O&M costs than a packed tower aeration system. Disadvantages for ozonation include higher capital cost than aeration, additional safety requirements, and a more complex treatment system.

Conclusion

The City of Clearwater's new WTP #2 will require a sulfide treatment system to meet City and FDEP water quality criteria. Aeration and ozone were both evaluated as potential options. Table 7 summarizes these options with their associated advantages, disadvantages, and costs.

Based on the estimated capital and O&M cost differences, the additional capital spent on ozone will be recovered (relative to aeration) in approximately five to seven years (a 3 percent annual increase in O&M costs and a 3 percent interest rate for capital investment were assumed). Taking this into account with other concerns, such as visual aesthetics and potential odor concerns, ozone was selected for sulfide removal for the City of Clearwater's reverse osmosis expansion of WTP #2. The project is currently expected to be completed in 2015.

References

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Table 7. Ozonation and Aeration Advantages and Disadvantages for Sulfide Removal

Aeration for Sulfide Removal	Ozonation for Sulfide Removal
Advantages	
- Simple process - Lower capital costs	- No waste streams - Use ozonation for 4-log virus credit - Lower operation costs - Higher reliability (less routine maintenance)
Disadvantages	
- Scrubber blowdown disposal - Blowdown neutralization with sodium hypochlorite and sodium bisulfate - Higher operation costs - High maintenance - Visual impediment and potential odor impacts to neighboring apartments	- More complex treatment process - Higher capital costs - Potential byproduct formation (minimized with TOC removal upstream to ozonation) - Safety requirements must be met
COSTS	
Capital: $1.53 million	Capital: $2.52 million
Operation: $300,000/year* ($0.20/1,000 gal)	Operation: $128,000/year* ($0.08/1,000 gal)

* Operation costs include power, chemicals, and maintenance only