

Hydrogen sulfide and turbidity control using catalysed oxidation coupled with filtration for groundwater treatment

Audrey D. Levine, Blake J. Raymer and Johna Jahn

ABSTRACT

The presence of hydrogen sulfide in drinking water supplies can result in odour complaints, sulfur induced corrosion and black-water problems in distribution systems. Conventional approaches for hydrogen sulfide control are based on either air stripping to remove nonionized H₂S or oxidation to form sulfate. Residual hydrogen sulfide can react with chlorine or chloramines resulting in the generation of turbidity in the distribution system, potentially compromising disinfection effectiveness. A promising alternative is to employ hydrogen peroxide oxidation catalysed by iron to form elemental sulfur that can be removed by filtration. Bench and pilot-scale tests were conducted on a Florida groundwater to evaluate reaction kinetics and process efficiency. The use of in-line hydrogen peroxide oxidation catalysed by low dosages of ferric sulfate coupled with two-stage upflow filtration was capable of complete removal of hydrogen sulfide and associated turbidity. Additional benefits of this physical/chemical treatment approach include elimination of odour generation, reduction of chlorine demand and improved stability of the finished water.

Key words | colloidal sulfur, filtration, groundwater treatment, hydrogen peroxide, hydrogen sulfide, turbidity

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INTRODUCTION

Removal of hydrogen sulfide from water can be accomplished using a variety of approaches including: removal of gaseous hydrogen sulfide (aeration or degasification); conversion of hydrogen sulfide to elemental sulfur and removal of particulates (biological or chemical oxidation coupled with filtration); oxidation of hydrogen sulfide to sulfate; or removal of negatively charged forms of sulfur (sulfide and sulfate) through ion exchange. Incomplete oxidation of hydrogen sulfide can result in release of colloidal sulfur into the distribution system (Brune & Perez 1990), potentially compromising the effectiveness of disinfection by shielding microorganisms. Historically, tray aeration has been considered to be the least-cost approach for removal of hydrogen sulfide. However, less than half of the hydrogen sulfide can be volatilized at pH levels typical of groundwater. Over the past decade, in many locations, the encroachment of

development on treatment facilities has imposed a need for improved control of odours generated by conventional tray aeration systems.

In the light of increasing attention to groundwater quality and disinfection by-product formation, alternative approaches are needed to control hydrogen sulfide that minimize chlorine demand, turbidity and odour generation. Because many groundwater treatment systems rely on chlorine disinfection, chemical oxidation of sulfide is widely practised as a default control technology. However, reaction rates and associated by-products are influenced by pH, chemical dose and oxidant demand.

Oxidants that are appropriate for hydrogen sulfide control include chlorine, ferrate, hydrogen peroxide, permanganate and ozone. A summary of some generalized chemical reactions for removal of hydrogen sulfide is

Table 1 | Comparison of chemical reactions for oxidation of hydrogen sulfide^a

Oxidant	Oxidation reaction	Dose (mg per mg H ₂ S)
Chlorine	$\text{H}_2\text{S} + \text{Cl}_2 \rightarrow \text{S}^0 + 2\text{HCl}$	2.08
	$\text{H}_2\text{S} + 4\text{H}_2\text{O} + 4\text{Cl}_2 \rightarrow \text{H}_2\text{SO}_4 + 8\text{HCl}$	8.33
Ferrate	$4\text{H}_2\text{S} + 3\text{HFeO}_4^- + 7\text{H}^+ \rightarrow 3\text{Fe}^{+2} + \text{S}_2\text{O}_3^{2-} + 2\text{S}^0 + 9\text{H}_2\text{O}$	2.66
	$16\text{H}_2\text{S} + 20\text{HFeO}_4^- + 10\text{H}_2\text{O} \rightarrow 20\text{Fe}(\text{OH})_3 + 3\text{H}_2\text{S}_2 + \text{SO}_3^{2-} + 3\text{S}_2\text{O}_3^{2-} + 3\text{SO}_4^{2-} + 6\text{OH}^-$	4.44
Hydrogen peroxide	$\text{H}_2\text{S} + \text{H}_2\text{O}_2 \rightarrow \text{S}^0 + 2\text{H}_2\text{O}$	1.03
	$\text{HS}^- + 4\text{H}_2\text{O}_2 \rightarrow \text{SO}_4^{2-} + 4\text{H}_2\text{O} + \text{H}^+ \text{ (pH} > 8\text{)}$	4.11
Ozone	$\text{S}^{-2} + 4\text{O}_3 + 4\text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 4\text{O}_2$	5.64
Potassium permanganate	$3\text{H}_2\text{S} + 2\text{KMnO}_4 \rightarrow 3\text{S}^0 + 2\text{MnO}_2 + 2\text{KOH} + 2\text{H}_2\text{O}$	3.09
	$3\text{S}^{-2} + 8\text{KMnO}_4 + 4\text{H}_2\text{O} \rightarrow 8\text{MnO}_2 + 3\text{SO}_4^{2-} + 8\text{KOH}$	12.39

^aFrom Black & Goodson (1952), Hoffman & Fitzpatrick (1977), Dohnalek & Fitzpatrick (1983), Morse *et al.* (1987), Cadena & Peters (1988), Sullivan *et al.* (1988) and Sharma *et al.* (1997).

given in Table 1. As shown, reaction products consist of sulfate, elemental sulfur, bisulfite and/or polysulfides depending on the pH and reaction conditions. Typically, higher oxidant dosages are required to form sulfate than elemental sulfur. Formation of sulfate also consumes alkalinity and can increase the corrosivity of the finished water. The formation of elemental sulfur can result in increases in turbidity either at the treatment plant or within the distribution system.

Factors that influence the selection of an oxidant chemical include potential reaction by-products and chemical costs. While chlorine is the least expensive chemical on the list, its use for sulfide oxidation can also result in the formation of disinfection by-products such as trihalomethanes and haloacetic acids. Black and Goodson (1952) reported that sulfide oxidation using chlorine is a two-stage reaction in which the sulfide is first converted to elemental sulfur and then to sulfate. The reaction rate is a function of pH, temperature and chlorine concentration. At a pH of 7, the chlorine consumption rate was reported to be 2.1 moles of chlorine per mole of sulfide per minute (Black & Goodson 1952).

Other oxidant chemicals include ferrate, potassium permanganate and ozone. Ferrate is a highly reactive oxidant chemical that has been tested in wastewater applications (Sharma *et al.* 1997). Potassium permanganate is an effective oxidant; however, careful control of the chemical dose is necessary to prevent the generation of pink water due to excess manganese (Cadena & Peters 1988). Also, the manganese dioxide formed by the reaction can produce excess turbidity in the distribution system. Ozone is an effective chemical oxidant and disinfectant; however, its use can result in the formation of biodegradable organic material that can lead to biofilm growth in the distribution system (Escobar & Randall 2001). Hydrogen peroxide is widely used for control of hydrogen sulfide in wastewater, but limited operating data have been reported for potable water applications.

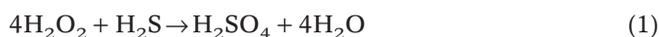
The objective of this paper is to evaluate the feasibility of using hydrogen peroxide for control of hydrogen sulfide in groundwater. In addition to testing hydrogen peroxide alone, low dosages of ferric sulfate were applied to catalyse hydrogen peroxide oxidation and to coagulate

colloidal sulfur particles. Bench-scale and pilot-scale studies were conducted using a Florida groundwater to elucidate reaction kinetics. Two-stage, continuously backwashed, upflow filtration was used to remove the particulate sulfur formed by the reaction.

BACKGROUND

The chemistry of hydrogen peroxide oxidation of hydrogen sulfide is well understood; however, other water quality variables may have an impact on the overall performance of hydrogen peroxide oxidation. Depending on the pH of the water and the dose of hydrogen peroxide, it is possible to convert hydrogen sulfide to either elemental sulfur or sulfate (Cadena & Peters 1988).

Several reaction pathways are possible when hydrogen peroxide is added to water containing hydrogen sulfide. At pH levels above 8, hydrogen sulfide is oxidized to sulfate.



The sulfate remains dissolved in the water and downstream filtration is not required. To accomplish this reaction in groundwater, it is often necessary to elevate the pH. However, for many groundwaters, increasing the pH can result in an increased potential for precipitation of mineral deposits within the distribution system (e.g. calcium carbonate).

At pH levels below 8, the dominant reaction is the conversion of hydrogen sulfide to elemental sulfur as shown in Equation (2):



By comparing these reactions, it is evident that the dose required for formation of elemental sulfur is 25% of the dose required for formation of sulfate. However, it may be necessary to include a filtration step to remove the colloidal elemental sulfur to prevent turbidity formation within the distribution system and potential reactions with iron or copper to form black water. Depending on the pH

of the water, a combination of reactions (1) and (2) can occur resulting in the formation of varying amounts of sulfate and elemental sulfur. It is also possible for sulfate to revert to elemental sulfur or sulfide within the distribution system due to biologically mediated sulfate reduction reactions.

Hoffman (1977) reported an optimal dose of hydrogen peroxide to be at a molar ratio of 2 moles of hydrogen peroxide per mole of hydrogen sulfide to accommodate competing oxidation reactions. Cadena and Peters (1988) reported that hydrogen peroxide oxidation could be modelled as a pseudo first-order reaction with an apparent reaction rate constant of 0.12 min^{-1} for oxidation of sulfide by hydrogen peroxide in wastewater at molar ratios greater than 2.4. Millero *et al.* (1989) reported similar values for reaction rate constants in natural waters and demonstrated that reaction rates increase with temperature and decrease at pH levels over 8, perhaps due to hydrogen sulfide dissociation or formation of sulfate.

It has been reported that dissolved metals have catalytic effects on hydrogen sulfide oxidation rates (Chen & Morris 1972; Hoffman & Lim 1979). It has been proposed that a free radical is formed that promotes auto-oxidation (Morse *et al.* 1987):

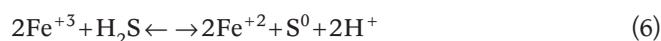


where M is the metal (e.g. nickel, cobalt, manganese, copper, iron, calcium or magnesium) and $\text{HO}_2 \cdot$ is the free radical.

As an alternative to oxidation, metals can be used to form metal-sulfide precipitates. For example, ferrous iron reacts with H_2S , HS^- or S^{-2} to form ferrous sulfide. The reaction with hydrogen sulfide is:



For ferric iron, the reaction may be written as:



and the ferrous iron can then react with additional hydrogen sulfide to form solid phase ferrous sulfide as described by Equation (5).

In the presence of excess iron, reaction kinetics are influenced by the sulfide concentration, pH and temperature. The presence of dissolved organics and phosphate is thought to decrease the reaction rates by competitive reactions with iron (Yao & Millero 1996; Poulton *et al.* 2002). At a constant pH, the reaction rate can be described as:

$$r = \frac{d[S_{tot}]}{dt} = k[S_{tot}]^a [Fe_{tot}]^b \quad (7)$$

where sulfur and iron concentrations are expressed in molar quantities and k is the reaction rate constant. Poulton *et al.* (2002) reported the exponent a as 1 and b as 0.5 for solid phase ferric oxides at a pH of 8.5.

At a constant pH with excess iron, the reaction can be expressed as a pseudo first-order reaction:

$$r = \frac{d[S^{-2}]}{dt} = k'[S_{tot}] \quad (8)$$

Rickard (1995) reported a pseudo first-order reaction rate constant (k') of 1.5 min^{-1} for the reaction in the presence of excess dissolved ferrous iron.

Alternatively, iron can combine with HS^- :



In this case, sulfide removal can be modelled as a second-order reaction (in the presence of excess iron):

$$r = \frac{d[\text{HS}^-]}{dt} = k_2'[\text{HS}^-]^2 \quad (10)$$

Rickard (1995) reported a reaction rate constant for this reaction of $1.3 \times 10^7 \text{ L}^2 \text{ mg}^{-2} \text{ s}^{-1}$ at 25°C .

METHODS

The potential for using hydrogen peroxide, ferric sulfate or hydrogen peroxide catalysed by ferric sulfate to remove

hydrogen sulfide was tested using groundwater from South/Central Hillsborough County, Florida. Currently, the County processes about $1.1 \text{ m}^3 \text{ s}^{-1}$ at its Lithia Water Plant using aeration, biological oxidation, chlorination, fluoridation and corrosion control. The source water is derived from a wellfield located in South/Central Hillsborough County. A summary of untreated water quality is given in Table 2. Hydrogen sulfide levels in the untreated water range from about 0.2 to over 3 mg l^{-1} , depending on the combination of wells in service at any time. The levels of dissolved iron are fairly low in this groundwater ($<0.02 \text{ mg l}^{-1}$).

For this project, bench-scale and pilot tests were conducted on the source water for South/Central Hillsborough County. The methods for each phase of testing are given below.

Bench scale tests

To assess the feasibility of using hydrogen peroxide as an oxidant for hydrogen sulfide, bench-scale tests were conducted using influent water from the Lithia Water Treatment Plant. For each test, a 20-litre water sample was transported to the University of South Florida Environmental Engineering Laboratory. Owing to the volatility of hydrogen sulfide and to maintain consistency between the tests, each sample was spiked with sodium sulfide to yield an initial sulfide concentration of about 3 mg l^{-1} . A summary of the bench-scale tests is given in Table 3.

Field tests of oxidation

Field tests were conducted using a 53-litre circular plastic tank operated under continuous flow conditions. Water entered at the bottom of the tank and exited at the top. Sample points were located at the inflow and outflow from the tank. Tracer tests were conducted initially to evaluate the mixing conditions. Based on the tracer studies, the reactor was modelled as a complete mix system.

For the field tests, untreated source water was pumped into the tank and mixed with treatment chemicals. Samples were collected at the outflow until steady state

Table 2 | Summary of water quality data for untreated groundwater in South/Central Hillsborough County 1999–2003

Parameter	Average	Range	Standard deviation
Water quality characteristics			
Alkalinity, mg l ⁻¹ as CaCO ₃	157	138–172	7.54
Colour, PCU	8	5–12	3.02
Conductivity, µmhos cm ⁻¹	457	425–554	28.25
Dissolved oxygen, mg l ⁻¹	0.53	0.24–1.05	0.21
Hardness, total, mg l ⁻¹ as CaCO ₃	202	182–226	13.77
Odour, TON	12	1–67	22.29
pH, standard pH units	7.39	7.08–7.83	0.17
TDS, mg l ⁻¹	263	247–277	9.79
Temperature	26	24.2–27.2	0.65
Turbidity, NTU	0.21	0.03–1.12	0.27
Corrosion potential			
Langelier index, pH units	0.04	- 0.18- + 0.28	0.18
Anions			
Bromide, mg l ⁻¹	0.06	0.04–0.09	0.02
Chloride, mg l ⁻¹	12	11.5–13.5	0.50
Fluoride, mg l ⁻¹	0.43	0.38–0.48	0.03
Sulfate, mg l ⁻¹	54	39.8–77.5	10.03
Minerals and nutrients			
Ammonia-nitrogen, mg l ⁻¹ as N	0.34	0.077–0.42	0.10
Phosphorus, mg l ⁻¹ as P	0.12	0.07–0.16	0.06
Iron, mg l ⁻¹	0.007	0.004–0.012	
Manganese, mg l ⁻¹	0.008	0.0081	
Calcium, mg l ⁻¹	52	41.87–59.23	5.32
Magnesium, mg l ⁻¹	17	15.45–19.01	1.59
Organic characteristics			
Total organic carbon, mg l ⁻¹	1.40	1.15–2.11	0.23
Ultraviolet absorbance at 254 nm, cm ⁻¹	0.051	0.035–0.084	0.01

Table 3 | Summary of bench-scale tests conducted on groundwater spiked with sodium sulfide

Test	Approach
Oxidation rate	Spike untreated Lithia influent water with sodium sulfide at ambient pH; add various dosages of hydrogen peroxide; monitor hydrogen sulfide concentration over time Adjust pH of untreated Lithia influent water to 8 with sodium hydroxide and spike with sodium sulfide; add various dosages of hydrogen peroxide; monitor hydrogen sulfide concentration and turbidity over time
Couple oxidation and coagulation	Use hydrogen peroxide in tandem with ferric sulfate: spike untreated Lithia influent water with sodium sulfide at ambient pH; add various dosages of hydrogen peroxide and a constant dose of ferric sulfate; monitor hydrogen sulfide concentration over time

conditions were reached (usually a minimum of three hydraulic detention times). Samples of influent and effluent were analysed on-site for pH, dissolved oxygen, turbidity, hydrogen sulfide and residual hydrogen peroxide. A summary of the field tests that were conducted is given in Table 4.

Pilot-scale oxidation and filtration tests

To evaluate the feasibility of using filtration to remove colloidal particles formed from oxidation of hydrogen sulfide, pilot-scale filtration tests were conducted using a two-stage, continuously backwashed, upflow filtration system. A schematic of the filter system is shown in Figure 1. The pilot unit was operated at a flowrate of 3 l s^{-1} . The first stage contained 2 m of sand with an

Table 4 | Summary of field testing of hydrogen peroxide oxidation of untreated groundwater at the Lithia Water Treatment Plant

Test	Conditions
Hydrogen peroxide oxidation	Vary molar ratios of hydrogen peroxide to hydrogen sulfide from 0.5 to 5
Reaction time	Vary flowrate to achieve hydraulic retention times ranging from 2 to 6 minutes
Use of ferric sulfate as a catalyst	Apply ferric sulfate and hydrogen peroxide in tandem to assess reaction rates

effective size of 0.9 mm. The second stage contained 1 m of sand with an effective size of 0.6 mm. The surface area of each filter was 1 m^2 .

In this filter, the water flows through a centre tube to a distribution spreader at the bottom of the filter. Then the water is forced up through the sand to an overflow weir and into the second unit. As the water moves up through the sand column, smaller and smaller floc particles are combined to form larger floc particles that are trapped in the voids of the filter. As the flow moves upwards, the sand moves down towards the bottom cone allowing the dirtiest sand to be removed by the continuous airlift. Sand moving up through the airlift passes through the sand washer. The differential head from the effluent weir and reject weir provides clean water to separate the trapped particles and the sand. The total headloss through the pilot unit is about 0.3–1 m (USEPA 1998).

After the first filter, the water is directed to the second-stage filter, which has a shallower bed and a smaller sand size (0.6 mm). The flow through the second filter is driven by the head of the first stage and no additional pumping is required. The second stage filter contains relatively fine sand to enhance removal of smaller particles and pathogens. Reject water from the second stage is returned to the first stage filter influent. The return of the reject water to the first stage enhances system performance, provides economical use of chemicals, and reduces total reject flow.

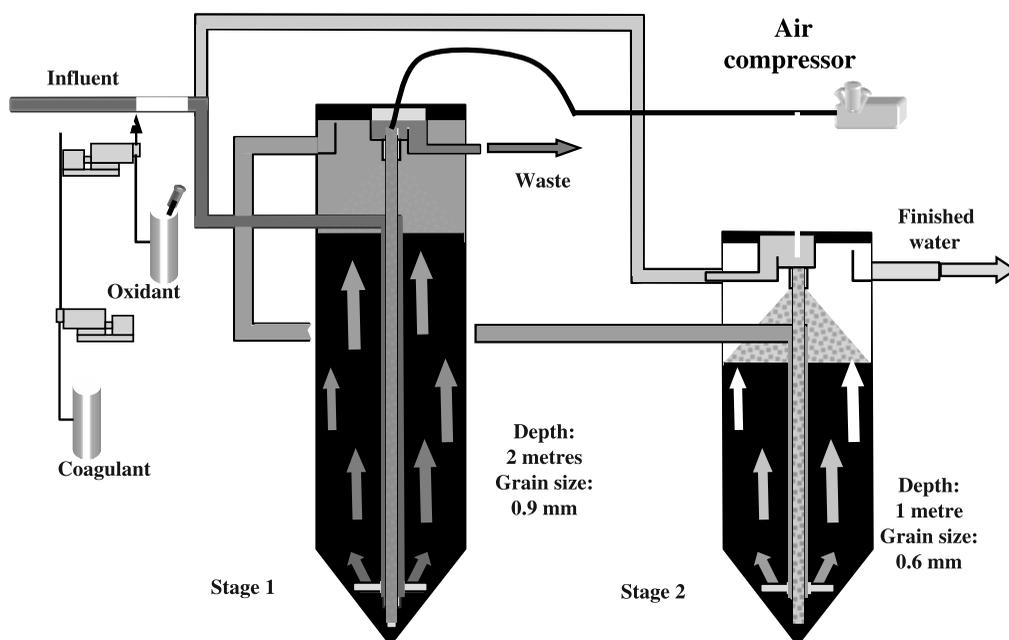


Figure 1 | Schematic of two-stage, continuously backwashed, upflow filtration process used for pilot testing of filtration at the Lithia Water Treatment Plant.

As in the first filter, the smaller floc particles combine in the smaller voids and are trapped within the filter, yielding a final effluent with much lower turbidity. Results from the first-stage operation provide insight into the potential performance of a conventional deep-bed sand filter.

The influent to the filter was connected to the source water for the treatment plant and the unit was operated at an average flowrate of 3 l s^{-1} , yielding a nominal hydraulic loading rate of 12 m h^{-1} . Chemicals were added upstream of the first filter using an in-line mixer. At a flowrate of 3 l s^{-1} , the chemical reaction time upstream of the filters was varied from about 0.4 min to 3.5 min. Following chemical addition, water flowed through the two filters in series and the effluent was discharged to a pond on-site. Typically the unit was operated continuously for 4 to 24 hours.

Turbidity, particle size and streaming current of the influent and effluent were monitored using on-line monitors (Hach Company 1996, 1999; Chemtrac Systems Inc. 1999). Grab samples were collected periodically for more detailed characterization of water quality and for evaluation of the effluent from the first filter. A summary

of the monitoring tests that were conducted during each run is given in Table 5.

RESULTS

Similar trends were observed for the bench-scale and field tests. Higher reaction rates were associated with use of hydrogen peroxide in the presence of dissolved iron than with either chemical alone.

Bench-scale tests

Reaction rates for oxidation of hydrogen sulfide using hydrogen peroxide were evaluated at different molar ratios of hydrogen peroxide:hydrogen sulfide. Pseudo first-order reaction rate constants are shown in Figure 2 as a function of the molar ratio of hydrogen peroxide to hydrogen sulfide. As shown, there was a linear increase in the rate constant of about 0.07 min^{-1} per molar increment of hydrogen peroxide. These results suggest

Table 5 | Routine monitoring parameters tested during pilot-scale filtration study of oxidized groundwater

Parameter	Sample location				Frequency/method
	Inflow	Filter 1	Filter 2	Reject	
Operational parameters					
Flow rate	×				Continuous in-line meter
Head loss		×	×		Periodic monitoring
Airflow		×	×		1 day ⁻¹
Reject 1 flow		×			1 day manual weir
Chemical dosing rates					Periodic monitoring
Water quality testing ^a					
Temperature	×				Periodically during run
Alkalinity					Periodic grab samples, field titration
Turbidity	×	×	×	×	Continuous in-line meter for inflow and effluent ^b Periodic grab samples; field test meter for Filter 1 and Reject
pH	×	×	×		Periodically during run
Particle count	×		×		Continuous in line particle counters ^c
Hardness	×	×	×	×	Periodic grab samples, field titration
Total iron	×	×	×	×	Periodic grab samples, field HACH test
Dissolved oxygen	×	×	×		Periodic grab samples; field meter and probe
Hydrogen sulfide	×	×	×		Periodic grab samples, field titration
Hydrogen peroxide		×	×		Periodic grab samples, field titration
TOC	×	×	×		Grab samples acidified and analysed at USF using Sievers TOC analyser

^aAnalytical methods from Standard Methods (1998) except where noted; ^bHACH Model 1720 C Low Range Process Turbidimeter; ^cChemtrac PC2400D.

that there are trade-offs between providing additional chemical contact time or additional chemical.

Parallel tests were conducted to evaluate the use of hydrogen peroxide alone, ferric sulfate alone and a combination of the two chemicals on removal of hydrogen sulfide. Pseudo first-order reaction rate constants are

shown in Table 6 for a hydrogen peroxide:hydrogen sulfide molar ratio of 1.3. As shown, the slowest reaction rates were associated with the use of hydrogen peroxide alone. The rate of reaction with ferric sulfate was about twice the reaction rate for the hydrogen peroxide alone. Combination of ferric sulfate and hydrogen peroxide

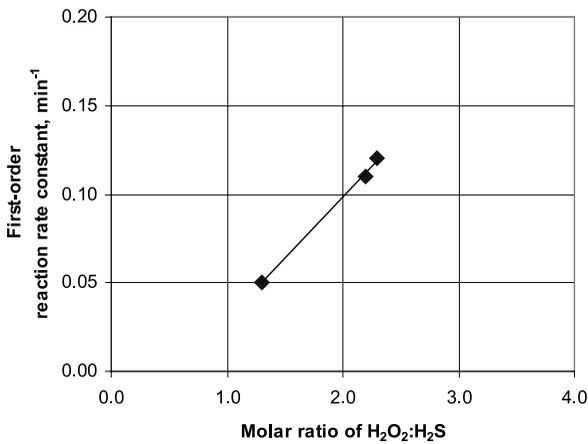


Figure 2 | Influence of the molar ratio of hydrogen peroxide to hydrogen sulfide on first-order reaction rate constants for removal of hydrogen sulfide in batch tests of groundwater spiked with hydrogen sulfide (correlation coefficient, r^2 , is 0.99).

yielded a reaction rate of four times the rate for hydrogen peroxide alone.

Field tests of hydrogen peroxide oxidation

The impacts of contact time and molar ratio of hydrogen peroxide to hydrogen sulfide on oxidation of hydrogen sulfide are shown in Figure 3. In general, the best removal of hydrogen sulfide was observed at a molar ratio of 2 moles of hydrogen peroxide per mole of hydrogen sulfide and a contact time of over 6 min. The tests were conducted under field conditions and a different combination of wells was in service for each of the test runs. Differences in

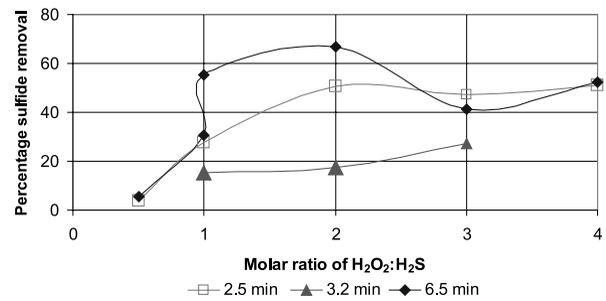


Figure 3 | Influence of molar ratio of hydrogen peroxide to hydrogen sulfide on removal of hydrogen sulfide from untreated source water at the Lithia Treatment Plant at three contact times under steady-state conditions.

water quality may explain some of the differences in observed reaction rates.

The reaction products were not quantified in this study; however, the generation of turbidity was used as an indicator of the formation of elemental sulfur particles. A comparison of steady-state turbidity levels associated with each dose and contact time is shown in Figure 4. In this case, the highest turbidity was associated with the contact time of 3.2 min at a molar ratio of 2 moles of hydrogen peroxide per mole of hydrogen sulfide. It should be noted that pH variations occurred during the field testing programming due to differences in the combination of wells in service. As noted above, lower levels of pH tend to preferentially form colloidal sulfur instead of sulfate.

Results from steady-state operation of the continuous flow reactor under different contact times were used to calculate apparent first-order reaction rate constants. A summary of calculated rate constants as a function of the

Table 6 | Comparison of first-order reaction rate constants for batch testing of hydrogen sulfide removal from influent water spiked with hydrogen sulfide^a

H ₂ O ₂ : H ₂ S, M/M	Fe: H ₂ O ₂ : M/M	Fe: H ₂ S: M/M	First-order reaction rate constant, min ⁻¹
1.3	0	0	0.05
0	NA	0.08	0.11
1.3	0.06	0.08	0.22

^apH 7.2, temperature 25°C.

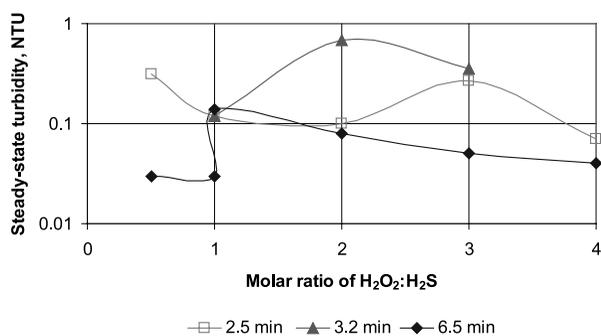


Figure 4 | Influence of molar ratio of hydrogen peroxide to hydrogen sulfide on turbidity formation from untreated source water at the Lithia Treatment Plant at three contact times under steady-state conditions.

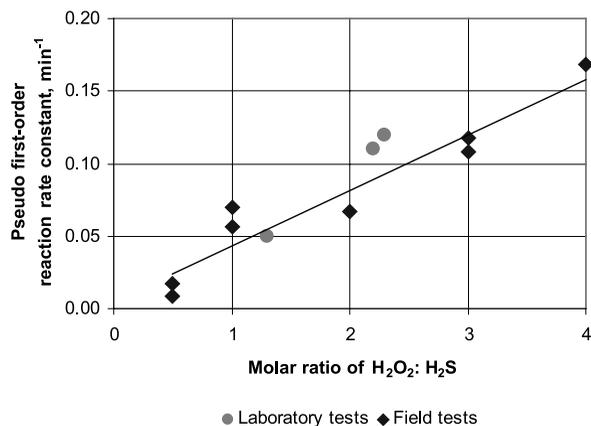


Figure 5 | Influence of molar ratio of hydrogen peroxide to hydrogen sulfide on pseudo first-order reaction rate constants for removal of hydrogen sulfide from untreated source water at the Lithia Treatment Plant. Laboratory data are also shown in the figure. The regression coefficient, r^2 , for the line is 0.92.

molar ratio of hydrogen peroxide to hydrogen sulfide is shown in Figure 5 in comparison to the laboratory generated data. As shown, there was a linear increase in the reaction rate with increasing ratio of hydrogen peroxide:hydrogen sulfide. For purposes of comparison, Cadena and Peters (1988) reported a first-order reaction rate constant of 0.12 min^{-1} at a molar ratio of 2.4.

Field tests of hydrogen peroxide oxidation catalysed by ferric sulfate

A comparison of the use of ferric sulfate in tandem with hydrogen peroxide for removal of hydrogen sulfide is

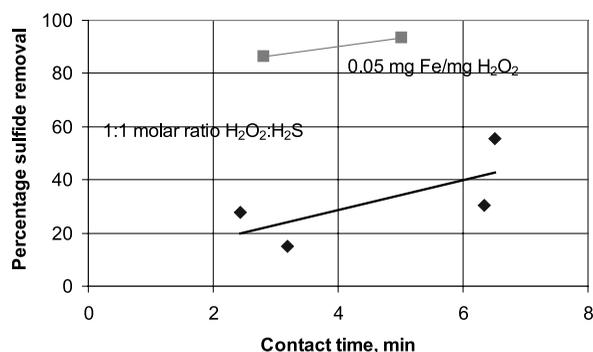


Figure 6 | Influence of contact time on removal of hydrogen sulfide from untreated source water at the Lithia Treatment Plant at a molar ratio of hydrogen peroxide to hydrogen sulfide of 1.1 under steady-state conditions.

shown in Figure 6, for a molar ratio of 1 mole of hydrogen peroxide to 1 mole of hydrogen sulfide at contact times ranging from 2.2 to 6.5 min. The addition of a low dose of ferric sulfate was effective at increasing the removal of hydrogen sulfide to over 80%, even at the shorter contact time. At a 1:1 molar ratio of hydrogen peroxide to hydrogen sulfide, and a ratio of 0.05 g iron per g H₂O₂ (0.03 M/M), the calculated first-order reaction rate constant was 2.2 min^{-1} compared with 0.04 min^{-1} for the same molar ratio of peroxide to hydrogen sulfide in the absence of iron. The observed rate of the field tests was about an order of magnitude higher than rates observed in laboratory tests (see Table 6). It may be possible to achieve the same result if adequate iron is present in the source water, thus providing concurrent removal of iron and hydrogen sulfide. Based on this study, at a hydrogen sulfide concentration of 3 mg l^{-1} , iron concentrations of about 0.15 mg l^{-1} would be appropriate. This level of iron is not uncommon for groundwater systems that contain hydrogen sulfide.

Filtration tests

For the filtration tests, the influence of chemical dosages and contact times on effluent turbidity was used as a measure of effectiveness. A summary of chemical dosages, contact times and average turbidity associated with each condition is given in Table 7. As shown, the turbidity of the source water varied considerably over the time period of

Table 7 | Summary of chemical dosages, contact times, hydrogen sulfide levels and average turbidity resulting from pilot-scale testing of oxidation/filtration of source water at the Lithia Water Plant

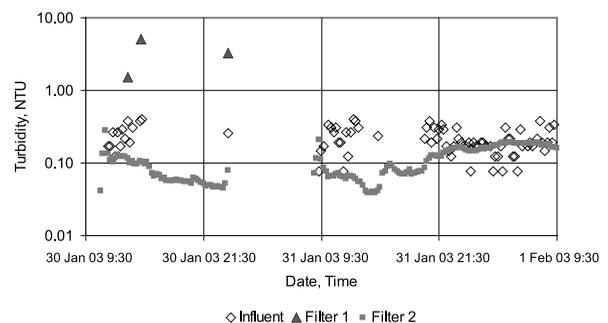
Dates	Dose, mg l ⁻¹ as Fe			Contact time, min	Initial hydrogen sulfide, mg l ⁻¹	Average turbidity		
	Ferric sulfate	Polyferric sulfate	Hydrogen peroxide, mg l ⁻¹			Source water	Filter 1	Filter 2
18 Dec 02	0.5		1.5	0.4	1.5	0.89		0.13
23 Dec 02	1		2.1	0.4	2.1	3.56	1.92	0.12
23 Dec 02 to 20 Dec 03	0.4 to 0.9		0.6 to 2.1	0.4	0.1 to 0.6	3.21	1.16	0.14
2–3 Jan 03	0		0.4	0.4	0.3 to 0.6	3.03	2.44	0.35
16–17 Jan 03	0.5		0.1	1.6	0.15 to 0.5	0.47	3.8	0.31
20–23 Jan 03	0.3		0.8	1.6	0.5 to 0.8	4.5		0.26
28 Jan 03	1.2		0.6	2.1	0.5 to 0.8	0.17		0.07
30–31 Jan 03		0.6	0.2	2.1	0.2 to 0.5	0.26	3.3	0.08
31 Jan 03		0.7	0.2	3	0.2 to 0.4	0.24		0.06
31 Jan 03–1 Feb 03	1.25		0.4	3	0.2 to 0.4	0.2		0.08

the testing because of differences in the wells in operation. In addition, the hydrogen sulfide levels of the source water were also variable. In each case, the hydrogen peroxide dose was set to reflect either a 1:1 or 2:1 molar ratio of hydrogen peroxide to hydrogen sulfide.

As shown in Table 7, independent of the characteristics of the raw water, it was not possible to obtain final turbidities below 0.1 NTU at contact times less than 2 min. For the shorter contact times, it appeared that the oxidation reaction was occurring within the first filter instead of upstream and there did not appear to be an adequate mechanism in place to promote aggregation of the elemental sulfur. However, once the contact time was increased to about 2 min, the two-stage filtration system was able to produce a water with effluent turbidities below 0.1 and in some cases below 0.05 NTU.

A comparison of influent and effluent turbidity for an extended run period is shown in Figure 7. In this case the unit was operated for a 24-hour period at a constant chemical dose. As shown, the performance of the system

was fairly consistent during this time period, even though there were variations in source water quality. In a full-scale system, the dose of hydrogen peroxide and iron would be controlled based on the hydrogen sulfide content of the source water instead of the manual adjustments that were used for this test programme.

**Figure 7** | Comparison of turbidity levels in influent to pilot filtration system (Lithia source water), effluent from filter 1 and effluent from filter 2. Chemical dosing information is given in Table 7.

For all of the test conditions, there was no residual hydrogen sulfide in the finished water. Dissolved oxygen levels were typically below 2 mg l^{-1} . If this treatment approach is selected, further testing would be required to optimize contact times, chemical dosages and to quantify reaction products.

CONCLUSIONS

This study focused on the use of hydrogen peroxide oxidation coupled with filtration for treatment of source water. The major conclusions from the study are listed below.

1. The use of hydrogen peroxide to oxidize hydrogen sulfide in the source water requires reaction times of over 20 min at molar ratios ranging from 0.5 to 4 moles of hydrogen peroxide per mole of hydrogen sulfide at ambient pH.
2. Hydrogen peroxide catalysed by iron coagulants is highly effective for converting dissolved hydrogen sulfide to particulate sulfur (most likely iron sulfide or colloidal sulfur) with contact times of less than 3 min. It may be possible to achieve the same result if iron is present in the source water.
3. Coupling of oxidation and filtration using hydrogen peroxide catalysed by iron-based coagulants is effective for producing water with turbidities below 0.1 NTU as long as adequate upstream chemical contact time is provided.

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