Article

Remediation of Sulfides in Produced Waters of the Oil and Gas Industry Using Hydrogen Peroxide

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Abstract: Produced waters are often treated in open lagoons where hydrogen sulfide (H_2S) can off gas, posing a risk to human health and the environment. The aim of this study was to optimize a treatment process using hydrogen peroxide (H_2O_2) to oxidize H_2S while minimizing off gassing. Samples of produced water from West Texas and laboratory-prepared waters utilizing sodium sulfide (Na_2S) or biogenic polysulfides were oxidized with H_2O_2 alone or in combination with copper or iron catalysts, sodium hydroxide (NaOH), or a commercial sulfide oxidizer, HydroPower Green™. Sulfur speciation was measured using Hach test kits for sulfide/sulfate/sulfite and Dräger tubes for headspace H_2S. HydroPower Green™ (HPG) helped to reduce H_2S in the headspace of water samples; some of this was pH related as NaOH also worked, but not as well as HPG. The dose of peroxide necessary to oxidize sulfides to sulfate is a function of the oxidation-reduction potential (Eh) of the water and total sulfide concentration as well as pH; approximately a 1–4:1 ratio of peroxide to sulfide concentration was needed to oxidize sulfidic waters of pH 7–10 with half-lives under 30 min. Both copper and iron catalysts reduce H_2O_2 demand and the half-life of H_2S. Peracetic acid (PAA) and copper (II) sulfate pentahydrate ($CuSO_4$, $5H_2O$) were explored as biocides for controlling sulfate-reducing bacteria (SRBs) that produce H_2S. An AquaSnap (Hygenia) test kit was employed to monitor relative microbial activity in a wetland porewater containing H_2S. Microbial regrowth occurred after a few days using the highest dose of PAA; these results showed that PAA was being used by bacteria as a carbon source even after the initial substantial reduction in the microbial activity. $CuSO_4$, $5H_2O$ at a dose of 1 ppm prevented microbial regrowth. The recommended treatment process from this research is determined by jar testing with H_2O_2, a base for pH control, a biocide, and possibly a metal catalyst or other co-oxidants in order to achieve oxidation of sulfides without H_2S release or the precipitation of metal carbonates or oxides.

Keywords: produced water; hydrogen sulphide; hydrogen peroxide; sulphate-reducing bacteria; HydroPower Green™

1. Introduction

In both oil and natural gas wells, water is present in varying proportions to the oil or gas. Water can be naturally occurring, and water is also injected into the reservoir for enhanced oil recovery. For every barrel produced, on average there are roughly five barrels of water co-produced [1]. Produced water is a complex mixture containing organic material such as dispersed oil (100 to 2000 mg/L), particulates (suspended solids), heavy metals, dissolved gases, radionuclides, and production chemicals [1,2]. Total dissolved solids (TDSs) in produced waters are usually high, such as 2600–310,000 mg/L [3]. Produced waters are often treated and reused on-site by oil companies, discharged into a deep disposal well, or transported off-site for further treatment and disposal [4]. The sheer

volume of water produced and the high concentration of constituents pose a challenge to the petroleum industry.

The most dangerous constituent of produced water is hydrogen sulfide (H_2S). According to the Bureau of Labor Statistics (BLS), H_2S caused 46 worker deaths between 2011 and 2017 [5]. H_2S is acutely toxic due to its binding to cytochrome C oxidase in mitochondria [6]. Breathing air with H_2S above 50 ppm can lead to loss of consciousness, respiratory paralysis, and even death [7,8]. H_2S in produced water is usually naturally occurring; H_2S forms in the oil and gas reservoirs by a microbial reduction in sulfate (SO_4^{2-}) and/or a thermochemical reduction in SO_4^{2-}. Reinjected reclaimed water may contain sulfur-reducing bacteria (SRBs) that further reinforce the souring of the well. The levels of total sulfides in produced water can thus be up to thousands of mg/L. This water may be stored in open lagoons where H_2S can off gas, posing a threat to birds that fly overhead as well as workers treating and monitoring the water.

H_2S gas in water speciates into H_2S (aq.), bisulfide ions (HS^-), and sulfide ions (S^{2-}) with an S oxidation state of –2 in all these species. This speciation is determined by pH (pK_a's of 7.02 and 13.9 for ionic strength of 0 [8]). Consequently, in most natural (pH between 6.5 and 8.5) waters, HS^- and H_2S dominate. The lower the pH, the more sulfide will be in the gas phase as H_2S and be released from the water into the air. This poses risks to human health and the environment.

The oxidation of sulfides in water mitigates the above-mentioned danger of H_2S gas being released into the air, where workers or organisms in the environment might be exposed. Oxidants often used include hydrogen peroxide (H_2O_2) and chlorinated compounds, including hypochlorite (ClO^-), permanganate (MnO_4^-), and air or molecular oxygen (dioxygen (O_2)). The solubility of air or O_2 in water is a function of temperature and has a greater solubility at low temperatures. O_2 solubility is negatively affected by the dissolved solid content in water, which is high in produced waters, so aerators are seldom cost-effective [9]. Chemical oxidation, or the use of liquid- or solid-bed scavengers, is a more common practice [10].

The chemical reactions involved in the treatment processes for produced waters in waste stabilization ponds are different than in desulfurization plants that have time on their side to remove the sulfur species. Desulfurization plants may use chemical or biological oxidations such as the Stretford, sulfolin, Lo-Cat, SulFerox, or Bio-SR processes to oxidize sulfides to elemental sulfur [11]. In fracking ponds/lagoons, precipitants are to be avoided because they can plug the oil-bearing formations if reinjection is the goal. There are many other issues to consider in the choice of treatment, for example, the effect on pH, whether organic chemical contaminants need to be oxidized, the toxicity of chemicals used and/or byproducts formed, cost, feasibility in terms of reaction times (e.g., half-life), reversibility of reactions, effect on bacterial growth, etc.

Ozone (O_3 gas) is a strong oxidant that works better at lower pHs. However, there is a concern with its use; bromate, a suspected carcinogen, is formed in bromide-bearing water in the presence of O_3. However, Wang et al. [12] found that using H_2O_2 with O_3 can suppress the formation of bromate during ozonation, but the amount of bromate formation was found to vary depending on other water quality parameters, such as ammonia and organic matter or total organic matter (TOC). Bromate can be reduced/removed by adsorptive treatment processes, which may be impractical for treating large lagoons [12,13].
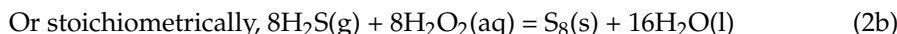
A relatively new technology is a hydrogen peroxide generator for oxidizing sulfides, which only requires water plus air. The HPNow peroxide generator (https://www.hpnow.eu/, accessed on 2 May 2024 [14]) produces a 1% (10,000 ppm) peroxide concentration in water with no chemical stabilizers added for the purpose of immediate water treatment. Sulfides in water can be oxidized to sulfates (see reactions 1 to 4 below).

The expected overall reactions of peroxide and sulfide in water are as follows:
Acid pH

$$H_2S + H_2O_2 \rightarrow S^0 + 2H_2O \tag{1}$$

Neutral pH
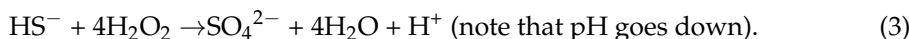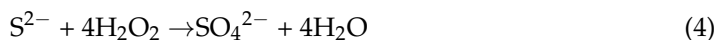
$$\text{First;} \quad H^+ + HS^- + H_2O_2 \rightarrow S^0 + 2H_2O, \tag{2a}$$

$$\text{Or stoichiometrically,} \quad 8H_2S(g) + 8H_2O_2(aq) = S_8(s) + 16H_2O(l) \tag{2b}$$
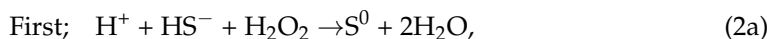
with a higher peroxide dose

$$HS^- + 4H_2O_2 \rightarrow SO_4^{2-} + 4H_2O + H^+ \text{ (note that pH goes down).} \tag{3}$$

Strongly Alkaline

$$S^{2-} + 4H_2O_2 \rightarrow SO_4^{2-} + 4H_2O \tag{4}$$

The concentration of S^{2-} is negligible at pH below 12 (i.e., reaction 4 is not important at pH < 12). Therefore, the reaction for peroxide oxidation is governed by that one under neutral pH (reactions 2a, 2b). The conversion of H_2S to bisulfide (HS-) is the rate-limiting step, and acid is a product, so a base, such as NaOH, can be added to speed the reaction, with the highest rate constant being at pH 8 [15]. At pH 9.5, the stoichiometry is expected to be 4.25 lbs H_2O_2 per lb of S^{2-}; for each weight part of H_2S, approximately 2.5 weight parts of NaOH are needed [16].

Table 1 shows the percentage of H_2S versus HS^- as a function of pH in distilled or tap water; the numbers may deviate in waters of high ionic strength and mineral or organic content. At pH ca. 9, the percentage of sulfide ions (S^{2-}) in their completely neutral sulfide (H_2S) form in a pond is approximately 1% [17]. So, there would be minimal off gassing of H_2S. The pH of produced waters is usually circumneutral (e.g., 6–7.5), and increasing the pH risks the precipitation of metal carbonates. Therefore, jar testing should be performed to determine the upper limit of pH during the treatment process.

Table 1. Speciation of sulfide as a function of pH in water (standard temperature and pressure (stp), low conductivity).

| pH of Water	Approx. % Sulfide as H_2S (Gas and Aqueous Phase in Closed Systems)	Approx. % Sulfide in Solution as Bisulfide Ion, HS^-
4	99	1
5	95	5
6	90	10
7	50	50
8	10	90
9	1	99

Fenton reactions require a low pH (reaction 1, below pH 7, which is the pK_1 for S^{2-}/HS^- speciation (vide supra)), which is dangerous in terms of the off gassing of H_2S. Since H_2S is heavier than air, there could be a concentrated "cap" of $H_2S(g)$ above the surface of a pond, making it dangerous for a treatment operator to monitor or treat the water.

Takenaka et al. [18] oxidized bisulfide (HS^-) at pH 9 with hydrogen peroxide and identified several intermediates and at least one unknown intermediate proposed, with ultimately all sulfur being oxidized to sulfate with an excess of peroxide.

The initial step in the oxidation of HS^- by H_2O_2 is the formation of hydrated elementary sulfur in the form of HOSH as follows:

$$HS^- + H_2O_2 \rightarrow HSOH + OH^- \tag{5}$$

The rate constant value for reaction 5 is 0.48 M^{-1} s^{-1} [19]. The composition of the reaction mixture dictates the fate of HOSH. There are two possibilities: (i) HOSH could be oxidized by excess H_2O_2 (reaction 6).

$$HSOH + 2H_2O_2 + 2OH\text{-} \rightarrow SO_3^{2-} + 4H_2O \tag{6}$$
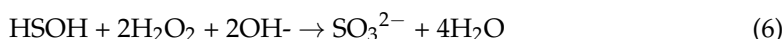
(ii) HOSH reacts with the unreacted HS^-, leading to the formation of polysulfide accompanied by the consumption of H^+ (reaction 7).

$$HSOH + HS_{x-1}^- \rightarrow HS_x^- + H_2O \text{ (x = 2-9)} \tag{7}$$
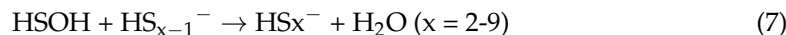
Subsequently, the polysulfides can react with H_2O_2 and other sulfur species, e.g., sulfite (reactions 8–13).

$$HS_x^- + (2x + 1)H_2O_2 + (2x - 1)OH^- \rightarrow xSO_3^{2-} + (3X + 1)H_2O \tag{8}$$

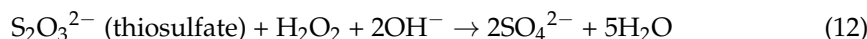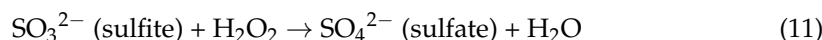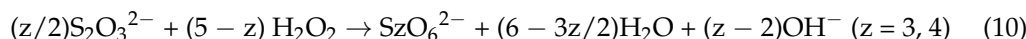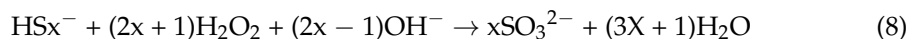$$(x - 1)SO_3^{2-} + HSx0- \rightarrow (x - 1)S_2O_3^{2-} + HS^- \tag{9}$$

$$(z/2)S_2O_3^{2-} + (5 - z)\,H_2O_2 \rightarrow S_zO_6^{2-} + (6 - 3z/2)H_2O + (z - 2)OH^- \text{ (z = 3, 4)} \tag{10}$$

$$SO_3^{2-} \text{ (sulfite)} + H_2O_2 \rightarrow SO_4^{2-} \text{ (sulfate)} + H_2O \tag{11}$$

$$S_2O_3^{2-} \text{ (thiosulfate)} + H_2O_2 + 2OH^- \rightarrow 2SO_4^{2-} + 5H_2O \tag{12}$$

$$S_zO_6^{2-} + (3z - 5)H_2O_2 + (2z - 2)OH^- \rightarrow zSO_4^{2-} + (4z - 6)H_2O \tag{13}$$
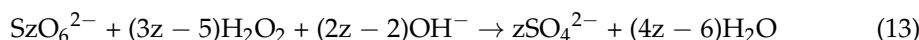
In this study, the use of a commercial oxidizer, HydroPower Green™ (HPG), was explored in combination with H_2O_2. HPG is an alkaline solution containing a phenolic and organo-zinc compound that in the presence of oxygen oxidizes hydrogen sulfide in water to sulfate and thiosulfate. The mechanism of oxidation is likely through a semiquinone radical intermediate [20].

Other constituents, such as residual oil hydrocarbons in produced wastewater, can be removed by adsorption [13] or mineralized with peroxide only with advanced oxidation, such as UV light [21]. UV peroxide is effective for oxidation. Complete oxidation of hydrocarbons will result in $CO_2 + H_2O$, and incomplete oxidation can result in alcohol, aldehyde, phenols, or organic acid being produced [21].

Control of Sulfate-Reducing Bacteria during Sulfide Treatment

Produced wastewater contains sulfur-reducing bacteria (SRBs) that can affect redox chemistry [22]. Water treatment by chemical oxidation produces higher redox species of sulfur, but SRBs perpetually reduce sulfur to hydrogen sulfide. Thus, the presence of SRBs can work against the goal of oxidizing sulfides in water. Hence biocides are often used in the treatment of produced waters. Glutaraldehyde, benzalkonium chloride, cocodiamine, and tetrahydroxymethyl phosphonium sulfate (TPHS) have been used as biocides to control SRBs [23–25]. The use of copper alone or in conjunction with organic biocides has also been shown to be effective in the control of SRBs [24,26].

Magnesium peroxide, a commercial product ORC® [27], and calcium peroxide with nitrate have also been used for microbial control [28]; NO_3^- ions fuel the growth of nitrate-reducing bacteria, which can then outcompete SRBs [29]. Nitrate inhibits sulfur-producing bacteria at a concentration at or above 0.7mM [30].

Peracetic acid (PAA) is a potent biocide and oxidizing agent with an oxidation potential of 1.96 V, which is slightly higher than that of H_2O_2 ($E° = 1.8$ V) [31]. PAA can be used along with a catalyst in advanced oxidation processes (AOPs) for breaking down organic contaminants [32]. PAA is a green alternative that is made with glacial acetic acid, sulfuric acid, and H_2O_2 and degrades to water, oxygen, and acetic acid. However, the acetic acid byproduct adds to the organic content of the treated water, which can result in microbial regrowth if under dosed, leaving no residual PAA in the effluent [33].

In theory, any organic biocide can be transformed (e.g., biodegraded, hydrolyzed, etc.) during water treatment and the carbon, nitrogen, and/or phosphorus from the molecule can end up becoming a source of nutrients for microbial regrowth. The use of biocides may affect the chemistry of the water, and the interactions between chemistry and biology must be understood. This study aimed to evaluate H_2O_2 to study its effectiveness in oxidizing sulfides with or without a copper or iron catalyst and with or without a

biocide treatment. PAA and a copper (II) sulfate pentahydrate ($CuSO_4$, $5H_2O$) solution (AquaDrop™, Ann Arbor, MI, USA) were explored in this study as biocides.

2. Methods

As a preliminary study to test the effectiveness of hydrogen peroxide (H_2O_2) from Sigma Chemical Company (St Louis, MO, USA) with and without a copper ($CuSO_4$, $5H_2O$) catalyst (AquaDrop™, Ann Arbor, MI, USA) on the oxidation of hydrogen sulfide in water, aqueous solutions of sodium sulfide (Na_2S) from Sigma Chemical Company (St Louis, MO, USA) were prepared by dissolving Na_2S in dechlorinated tap water with pH adjusted with 6N HCl to achieve pH 8–9. Na_2S is a base, so the pH was adjusted down to resemble natural waters. However, acid also oxidizes some of the sulfide, so the concentration of actual sulfide in water was measured using a Hach (Loveland, CO, USA) test kit (Method 8131) with a Hach DR 3900 spectrophotometer. The Hach DR 3900 spectrophotometer measures in units of mg/L. The reported copper concentrations are calculated based on the product information sheet rather than a direct measure of copper (Table 2). The product contains $CuSO_4$, $5H_2O$, but the concentration is in the metallic copper from the dissolution of the product. Copper test strips (Hach AquaChek 0–3 ppm) were used to check for the presence of copper and the relative abundance of copper in the solution based on the color of the test strip (Table 2).

Table 2. Setup for the sodium sulfide experiments.

Sample	Chemicals Added
Na_2S 30 mg/L (pH 9)	60 ppm H_2O_2 10 ppm copper
Na_2S 30 mg/L (pH 9)	30 ppm H_2O_2 50 ppm copper
Na_2S 30 mg/L (pH 9)	60 ppm H_2O_2 50 ppm copper
Na_2S 80 mg/L (pH 8)	30 ppm H_2O_2 1 ppm copper
Na_2S 80 mg/L (pH 8)	30 ppm H_2O_2
Na_2S 80 mg/L (pH 8)	60 ppm H_2O_2 1 ppm copper

The pH and concentration of sulfide were taken for each solution immediately after preparation or after adding any chemical treatment. The copper product was diluted in dechlorinated tap water prior to use as a treatment chemical because the product was acidic. The diluted copper solution had a pH of 7.

2.1. Jar Testing of Produced Water Collected from a Natural Gas Well

A one-liter sample of produced water containing H_2S was collected from a natural gas well in West Texas (Permian basin) in March 2022. The water had the following water quality parameters: 940 mg/L H_2S; total dissolved solids (TDSs), 12,000 ppm; oxidation-reduction potential (redox), $E_h = -290$ mV; and pH 7.5. A hand-held Vivoson multipurpose probe was used to measure total dissolved solids (TDSs) and pH. An ORP meter (GainExpress-China, Hong Kong, China) was used for redox measurements. Aliquots of the water sample were put into Erlenmeyer flasks capped with rubber stoppers containing some headspace and stirred on a stir plate at a low speed while being treated with HPG and peroxide at different doses. Sulfides were measured by Hach Method 8131 using a colorimetric test kit and a Hach DR 3900 spectrophotometer. Sulfates were tested by Hach Method 10248. Measurements of redox potential (E_h) were carried out at room temperature (72–75 degrees Fahrenheit) and corrected for the potential of the reference electrode for the silver/silver chloride reference electrode. The setup is described in Table 3 below.

Table 3. Experimental setup for the jar tests.

Volume of Water Sample (mL)	Chemicals Added
25	1200 ppm H_2O_2 + 4 ppm FeCl3
50	HPG 100 ppm + 900 ppm H_2O_2
15	6000 ppm H_2O_2
10	3000 ppm H_2O_2

2.2. Jar Testing of a Biogenic Polysulfide Solution

A stock solution of biogenic polysulfides with a redox potential of −324 mV at pH 12 (polysulfides are only stable at high pH and concentration) was used to spike distilled water to various concentrations of sulfide for jar testing to determine the dose of H_2O_2 needed to oxidize the sulfides. H_2O_2 was sometimes added as a single application and sometimes added slowly over time to see if it made a difference.

The biogenic sulfur was collected in West Texas by bubbling natural gas containing hydrogen sulfide into a caustic trapping solution that formed polysulfides after being exposed to oxygen. Aqueous solutions of the polysulfides were prepared in various water matrices made in the laboratory (see setup in Table 3). HydroPower Green™ (HPG) was used as a pH control and to aid in oxidation. The dosing of HPG was on a volumetric basis in terms of percent solution and was also reported in ppm. H_2O_2 (using 50% strength stock solution) was added until sulfides read "not detected" by Hach Method 8131 using a colorimetric test kit and a Hach DR 3900 spectrophotometer; samples were diluted as needed within the sample cuvette to get within the range of detection (Table 4). Sulfates and sulfites were tested by Hach Methods 10248 and 10308, respectively, using a DR 3900 spectrophotometer.

Table 4. Setup for the oxidation experiments of biogenic sulfides in water.

Sample Conc. Total Sulfides	H_2O_2 Dose Added after pH Adjustment with HPG
1% solution (10,000 mg/L) pH12	1% (10,000 ppm) hydrogen peroxide (H_2O_2)
1% solution (10,000 mg/L) pH12	1% H_2O_2
6220 mg/L pH 11	1% H_2O_2
6220 mg/L pH 11	1% H_2O_2 added in increments over a 60′ period
1200 mg/L pH 11	0.05% (500 ppm) H_2O_2
1200 mg/L pH 11	0.05% (500 ppm) H_2O_2 added in increments over a 20′ period

Dräger tubes for hydrogen sulfide (1–200 ppm and 1–2000 ppm) were used to check the headspace of the samples. Samples remained capped after adding chemical treatment and before measuring sulfides and sulfates.

2.3. Effect of pH on the Kinetics of Oxidation at a High Peroxide: Bisulfide Dose

The biogenic polysulfide solution was used to spike tap water, which gave a pH of 6.5 with a concentration of 37 mg/L total sulfides. The water was divided into three 150 mL aliquots placed into 250 mL Erlenmeyer flasks with a stir bar in each, and they were stirred on a stir plate while being treated. Each flask was covered with a stopper to minimize losses from H_2S escaping and was opened briefly during testing for the aqueous phase and headspace H_2S. One sample had no pH adjustment and at pH 6.5, it was off gassing hydrogen sulfide; the headspace H_2S in the Dräger tube was about 10 ppm. The other two samples had a pH adjustment to 9.5 with either HPG or NaOH. The higher pH samples did not have detectable headspace H_2S (using Dräger tube 0–200 ppm).

2.4. Effect of Carbonates on Sulfide Oxidation with Hydrogen Peroxide and HPG or NaOH

A laboratory water sample with a complex matrix was prepared with or without high carbonate. Carbon dioxide was bubbled into the water to create different levels of total carbonates (e.g., bicarbonate and carbonate ions and metal carbonates that form upon carbonation of the water). The water matrix was prepared with 45 g/L of sodium chloride, 20 g/L of calcium chloride, 100 mg/L of magnesium chloride, 10 mg/L of barium hydroxide, and 1 g/L of crude oil. Samples of this water were then spiked with the polysulfide solution and different amounts of carbon dioxide as shown in Table 5.

Table 5. Experimental setup for the carbonate effect on sulfide oxidation.

Sample Matrix Variables	Treatment Process
Carbonate saturated	None (control)
Carbonate saturated	500 ppm HPG, 100 ppm H_2O_2
250 ppm carbonate	None (control)
250 ppm carbonate	250 ppm HPG, 750 ppm H_2O_2
No added CO_2	None (control)
No added CO_2	500 ppm H_2O_2

2.5. Use of PAA and Copper Biocides for Sulfate-Reducing Bacteria (SRBs)

The use of peracetic acid as a biocide to kill sulfate-reducing bacteria was explored by dosing a wetland water sample (Oakland County, Michigan, USA) with the chemical at doses of 10, 50, and 100 mg/L and measuring relative biological activity with Hygiena AquaSnap test swabs used with a Hygiena Ensure®Touch luminometer. Samples were stored in an incubator at 30 °C. The relative microbial activity was measured with Hygiena AquaSnap total and free ATP swabs into 50 mL samples of the water (the difference between the two indicates live microbial activity from intact cells) measured in relative light units (RLUs) with a luminometer. The assay utilizes luciferin–luciferase (substrate and enzyme, respectively) to create light utilizing energy from ATP. The use of copper pentahydrate was also explored as a biocide at 1 mg/L, and ATP measurements were taken over time. The samples were dosed only once. The control samples were untreated.

3. Results

3.1. Sodium Sulfide Experiments

As a preliminary study, the oxidation of sodium sulfide spiked in dechlorinated tap water pH adjusted with 6N HCl to achieve pH 8–9 was conducted with different doses of hydrogen peroxide (H_2O_2) with or without a copper catalyst. The setup and results are presented in Table 6. Note that the spiking of sodium sulfide does not result in the low redox conditions that would be present under natural conditions in environmental samples.

Table 6. Sodium sulfide aqueous solutions and treatment results.

Sample	Chemicals Added	Results Sulfide Concentration at Specified Reaction Times in Minutes
Na_2S 30 mg/L (pH 9)	60 ppm H_2O_2 10 ppm copper	16 mg/L at 5′
Na_2S 30 mg/L (pH 9)	30 ppm H_2O_2 50 ppm copper	7 mg/L at 5′
Na_2S 30 mg/L (pH 9)	60 ppm H_2O_2 50 ppm copper	4 mg/L at 5′ Not detected at 10′
Na_2S 80 mg/L (pH 8)	30 ppm H_2O_2 1 ppm copper	36 mg/L at 10′
Na_2S 80 mg/L (pH 8)	30 ppm H_2O_2 10 ppm copper	4 mg/L at 10′
Na_2S 80 mg/L (pH 8)	60 ppm H_2O_2 1 ppm copper	Not detected at 10′

Reaction times were kept short because it was found that over the span of several hours, sulfide in an untreated sample (control) escaped the vial possibly through the threads of the vial.

The data presented in Table 6 show that although the dose of H_2O_2 is the most important in oxidizing sulfide, the copper has an effect as a catalyst. The 80 mg/L sample that had ten times the copper dose as the other 80 mg/L sample with H_2O_2 held constant showed a difference (36 vs. 4 mg/L at 10′). A treatment of one part per million (ppm) of copper is suitable for water that will be discharged to surface waters or municipal systems, but 10 ppm copper would not be acceptable as it exceeds surface water quality and drinking water quality standards. Furthermore, samples that sat overnight treated with 10 ppm copper had visible copper precipitants in them. The higher doses of copper were used to demonstrate the effect of copper as a catalyst for H_2O_2-mediated oxidation. The following parameters have an effect on oxidation of sulfide concentration/copper concentration ratio, H_2O_2 concentration, pH, and time (duration of reaction).

3.2. Jar Testing of Produced Water Collected from a Natural Gas Well

A produced water from the West Texas Permian basin had the following water quality parameters: 940 mg/L H_2S; total dissolved solids (TDSs), 12,000 ppm; oxidation-reduction potential (redox), $Eh = -290$ mV; and pH 7.5. Samples of 10–50 mL in vials and jars were treated on a stir plate at a low speed with a magnetic stir bar while being dosed with chemicals. Final sulfide measurements were taken 30 min after the chemical was added. Working measurements (Eh) were carried out at room temperature (72–75 degrees Fahrenheit) and corrected for the potential of the reference electrode for the silver/silver chloride reference electrode. The setup of samples, including the dosing of treatment chemicals and the relevant water quality parameters, are listed in Table 7.

Table 7. Jar testing of produced water containing 940 mg/L H_2S(aq).

Volume of Water Samples (mL)	Chemicals Added	Result at 30 min
25	1200 ppm H_2O_2 + 4 ppm $FeCl_3$	10 mg/L sulfide $Eh = 0$ mV pH 7
50	HPG 100 ppm + 900 ppm H_2O_2	Non-detected sulfide, pH 9.5
15	6000 ppm H_2O_2	Non-detected sulfide $Eh = +153$ mV pH 6.5
10	3000 ppm H_2O_2	Non-detected sulfide, pH 7

Table 7 shows a water sample with 940 mg/L of sulfides that was oxidized with a 1:1 ratio of peroxide to sulfide when using the alkaline HydroPower Green™ product at 100 mg/L. In a treatment pond, if sulfur-reducing bacteria were still present, they could reduce the sulfate back to a sulfide, but a resulting pH of 9.5 would minimize the formation of H_2S gas. A dose of H_2O_2 more than three times the concentration of total sulfides without pH adjustment also completely oxidized the sulfides within a half hour. The iron (III) chloride ($FeCl_3$) may have worked as a catalyst to oxidize sulfides with H_2O_2 based on the assumption that the H_2O_2 dose to sulfide should have been at least 2:1. H_2O_2 and $FeCl_3$ slightly reduced the pH of the water sample, which started at pH 7.5. A higher dose (40 ppm) of $FeCl_3$ used with H_2O_2 caused precipitation of the iron. Thus, the jar tests help to optimize a treatment process and determine whether or not a precipitant will form. The water treatment of the sample did not address organic constituents because the water had no visible oil and had only trace hydrocarbons identified by GC/MS qualitatively. If produced water were to have a visible oily sheen, the water should be processed through an oil–water separator to remove as much oil as possible before using chemical treatment, as the organic constituents will create a demand for the peroxide. A review article by Alomar et al. [13] thoroughly covers the removal of organic constituents in produced water by adsorption and oxidation.

3.3. Jar Testing of a Biogenic Polysulfide Solution

A stock solution of biogenic polysulfides with a redox potential of −324 mV at pH 12 (polysulfides are only stable at high pH and concentration) was used to spike distilled water to various concentrations of H_2S for jar testing to determine the dose of hydrogen peroxide needed to oxidize the sulfides (reactions 1–13). The dosing of chemicals and the analysis of sulfide in the solution and other parameters, such as the pH of the final solution, are presented in Table 8. The polysulfides break down quickly into bisulfide ions upon dilution. The sulfides in pH 12 water were oxidized within twenty minutes using a dose of H_2O_2 equal to sulfide concentration (see Table 8). A Dräger tube with a range of 1–200 ppm H_2S showed no detections in the headspace of the vial containing the water sample. Under-dosing (e.g., sample ratio < 0.5 peroxide to sulfide) resulted in residual sulfide (incomplete oxidation), as expected. The samples had very low dissolved organic carbon (DOC) content, so there was no peroxide demand from constituents other than sulfide. Copper that was to be used as a catalyst at 1 ppm at a pH of 11 or greater came out of the solution, so data were not reported. $FeCl_3$ was tested, and it either came out of the solution or the dose and was not helpful and had a low peroxide dose.

Table 8. Jar testing of a biogenic polysulfide solution.

Sample Conc. Total Sulfides	H$_2$O$_2$ Dose Added after pH Adjustment with HPG	Results
1% solution (10,000 ppm) pH12	1% (10,000 ppm)	Sulfide not detected at 20′ Sulfate = 10,100 mg/L Final pH 7
1% solution (10,000 ppm) pH12	1%	Sulfide not detected at 20′ Sulfate 9500 mg/L Final pH 7
6220 ppm pH 11	1%	Sulfide not detected at 20′ Sulfate 6100 mg/L Final pH 7
6220 ppm pH 11	1% H$_2$O$_2$ added in increments over a 60′ period	Sulfide not detected at 60′
1200 ppm pH 11	0.05% (500 ppm)	Sulfide 60 mg/L at 20′
1200 ppm pH 11	0.05% H$_2$O$_2$ added in increments over a 20′ period	Sulfide 150 mg/L at 20′ Final pH 10; Eh = −20 mV

3.4. Effect of pH on the Kinetics of Oxidation at a High Peroxide:Bisulfide Dose

Samples prepared from tap water and the biogenic polysulfide solution were tested with Drager tubes for H_2S with or without pH adjustment. The sample without pH adjustment had a pH of 6.5 and a headspace of H_2S in a Drager tube of about 10 ppm. The other two samples had a pH adjustment to 9.5 with either HPG or NaOH. The higher pH samples did not have detectable headspace H_2S (using a Drager tube of 0–200 ppm). The results of concentration over time for the three treatment types are presented in Figure 1. At the high H_2O_2 to bisulfide ion concentrations ratio of 4:1, pseudo-first-order kinetics were observed, as expected. The sample adjusted with HPG had a slightly lower starting concentration because the chemical oxidized a small amount of the sulfide in the water before adding peroxide. The HPG-treated sample also had slightly lower values throughout the time sequence. The samples were tested the next day and were not detected for sulfides.
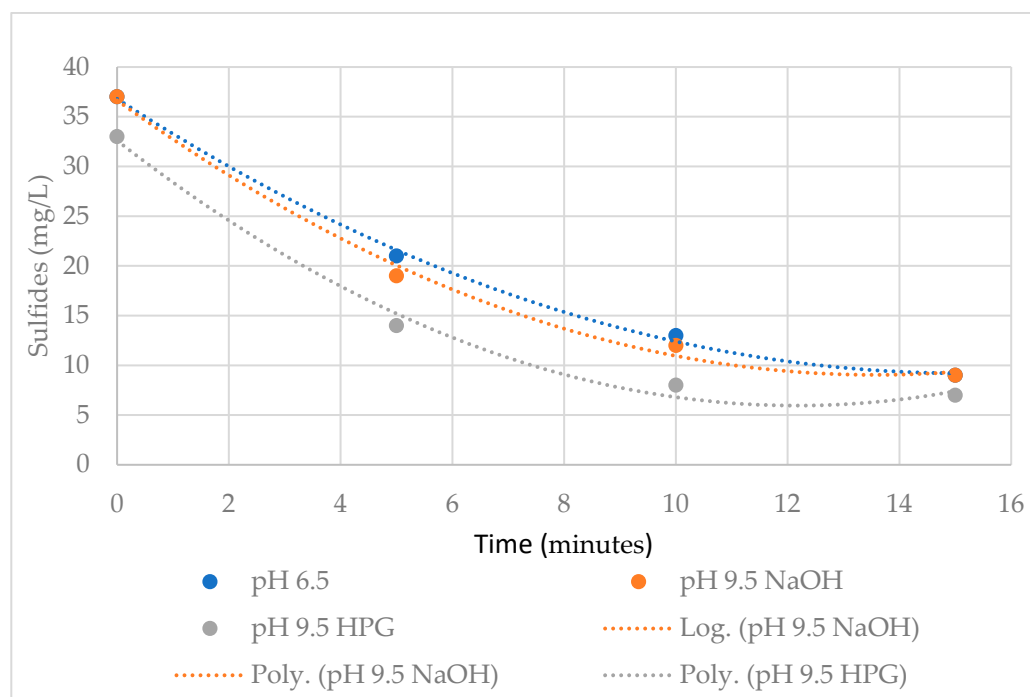

Figure 1. Aqueous concentration of sulfides (mg/L) over time after treatment with peroxide at a ratio of 4 parts of H_2O_2 concentration to 1 part HS^- concentration.

When a lower ratio of H_2O_2 to sulfide (1:1–2:1) is used at pH < 7.5, sulfide oxidizes to elemental sulfur (S^0 or cyclo-S_8) and sulfate [19]. There is a transition where the water turns from yellow (elemental sulfur) to sulfate (white to clear) when increasing the dose of peroxide. A 2:1 ratio was tried on a test sample at first, but the reaction stalled after five minutes. Thus, this experiment was conducted at a 4:1 ratio of H_2O_2 to bisulfide ion concentrations. Increasing the pH from 6.5 (blue line in Figure 1) to 9.5 (orange line in Figure 1) resulted in a slightly faster oxidation of sulfide. The transition to the elemental sulfur (S^0) resulting in yellow coloration (predominance of concentration of S^0 over that of SO_4^{2-} (reactions 1–4)) of the solution was observed at pH 6.5 but not at pH 9.5 as SO_4^{2-} concentration predominates at that pH.

Increasing the dose of H_2O_2 to shorten the reaction time will lead to a greater percentage of sulfate as a product. If a high amount of calcium is present, it could lead to gypsum precipitation. This did not occur in these test samples, which had low calcium content. Thus, jar testing can provide an optimum dose and pH.

3.5. Effect of Carbonates on Sulfide Oxidation with Hydrogen Peroxide and HPG or NaOH

The effect of carbonate on sulfide oxidation using H_2O_2 was tested by bubbling carbon dioxide into water to create different levels of total carbonates (e.g., bicarbonate and carbonate ions and metal carbonates that form upon carbonation of the water). Samples of this water were then spiked with the polysulfide solution and different amounts of carbon dioxide. The results are shown in Table 9.

Table 9. Oxidation of sulfides in the salty water matrix of different carbonate contents.

Sample Matrix Variables	Treatment Process	Results at 20′
Carbonate saturated	None (control)	pH 5.5; H_2S headspace 140 ppm; sulfide in water 10 ppm
Carbonate saturated	500 ppm HPG, 100 ppm H_2O_2	pH 7; headspace H_2S 100 ppm; water 4 ppm. Turbidity increase (fine particulates, likely barium)
250 ppm carbonate	None (control)	pH 6; H_2S headspace 100 ppm; sulfide in water 30 ppm
250 ppm carbonate	250 ppm HPG, 750 ppm H_2O_2	pH 7; H_2S headspace < 10 ppm; sulfide in water < 1 ppm
No added CO_2	None (control)	pH 8; H_2S headspace < 5 ppm; sulfide in water 10 ppm
No added CO_2	500 ppm H_2O_2	pH 7–8; headspace and sulfide in water < 1 ppm
No added CO_2	50 ppm HPG, 200 ppm H_2O_2	pH 9.5; H_2S headspace not detected; sulfide in water 0.02 ppm. Slight turbidity

Table 9 shows that carbonate, in this case created by bubbling carbon dioxide into a pH 8 water matrix, will decrease the pH, which increases the headspace H_2S and increases the dose of NaOH or alkaline solution containing both HPG and peroxide needed to eliminate H_2S. Metal carbonates and bicarbonates increase the propensity of unwanted solids formation. When the oxidized solution is close to saturation with respect to any metal carbonate, hydroxide, or sulfate, raising the pH will create fallout (precipitation). This highly salty solution, which is representative of produced waters, can tolerate a pH of 8–9 without fallout when carbonates are 250 ppm or less. The solution that had no additional carbonates (i.e., the only carbonate contribution is from the equilibrium with air) became turbid at pH 9.5, which is likely due to the barium. Barium and strontium carbonates/sulfides/sulfates have lower solubility than that of sodium or carbonate complexes.

3.6. Use of PAA and Copper Biocides for Sulfate-Reducing Bacteria (SRBs)

The effectiveness of peracetic acid as a biocide was tested at different doses (10, 50, and 100 ppm) over time on a wetland water sample collected in Oakland County, Michigan. The water contained 8–10 ppm sulfides determined by Hach Method 8131 and had a negative redox potential (−183 mV). The relative microbial activity was measured with Hygenia AquaSnap total and free ATP (the difference between the two indicates live microbial activity from intact cells) measured in relative light units (RLUs) with a luminometer.

Figure 2 shows that the PAA reduced microbial activity, as measured by the luminometer using the Hygenia AquaSnap test kit. However, after 96 h, the microbial activity rebounded with an increase in growth at the higher doses of treatment. In this study, the bacteria that rebounded are presumably selected for peracetic acid-resistant strains.
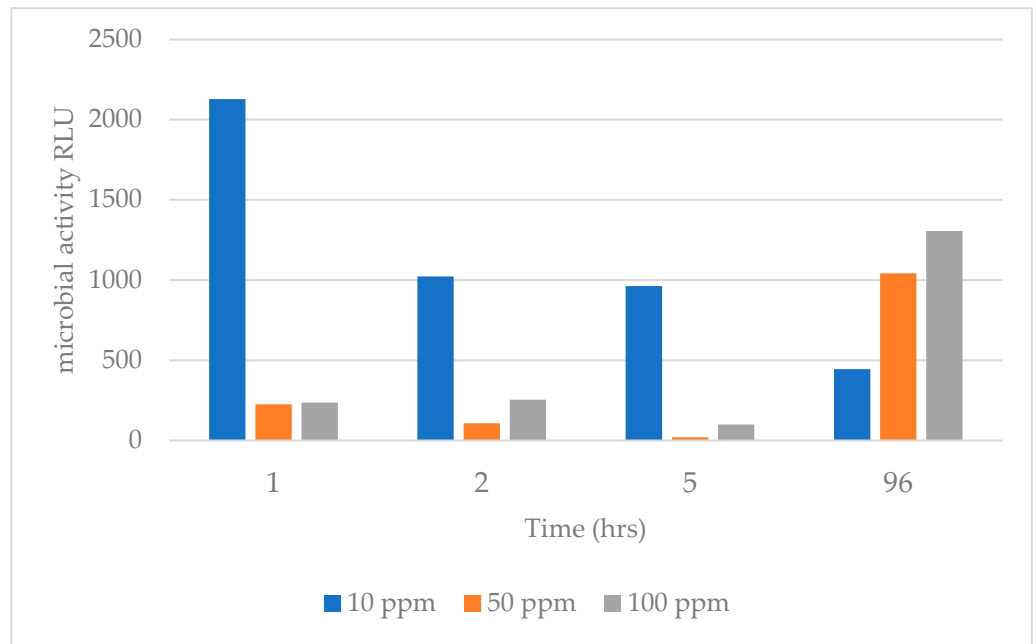
Figure 2. Microbial activity (ATP as relative light units) in pond water samples after treatment with peracetic acid at different doses.

Next, a pond water sample was treated with 1 mg/L of $CuSO_4$, $5H_2O$ solution. The microbial activity was quickly reduced and not detected (see Figure 3). An untreated sample (control) read 1149 RLU at t = 0.5 h.
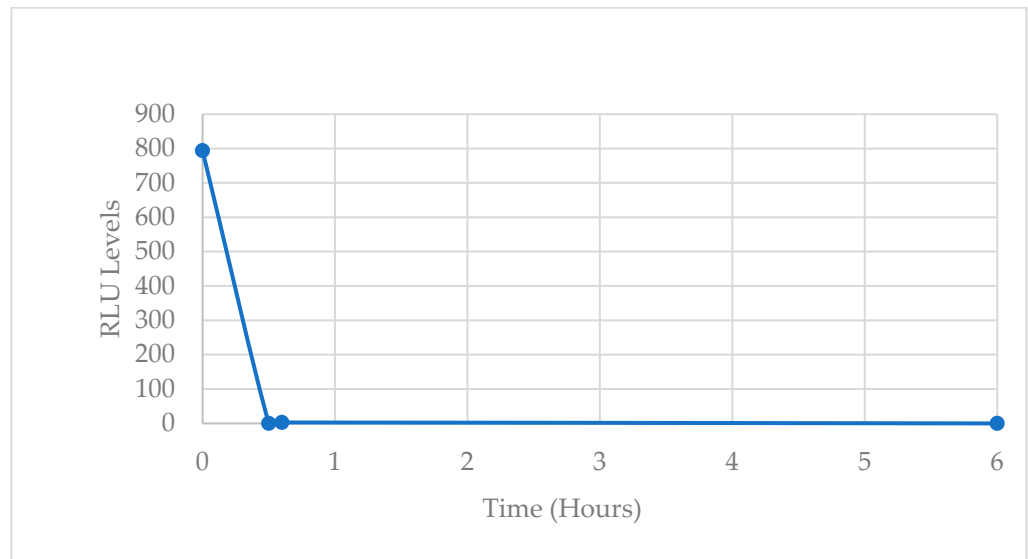

Figure 3. Microbial activity (ATP) in pond water (Sample 2) after treatment with 1 ppm copper in the form of copper pentahydrate.

Leftover pond water that was untreated was diluted with tap water such that the starting ATP activity was lower. It was then treated with 1 ppm copper in the form of copper pentahydrate. The sample was kept longer (24 h) and showed no activity (Figure 4). A sample of the water without copper added (control) was 184 RLU at 24 h incubation.
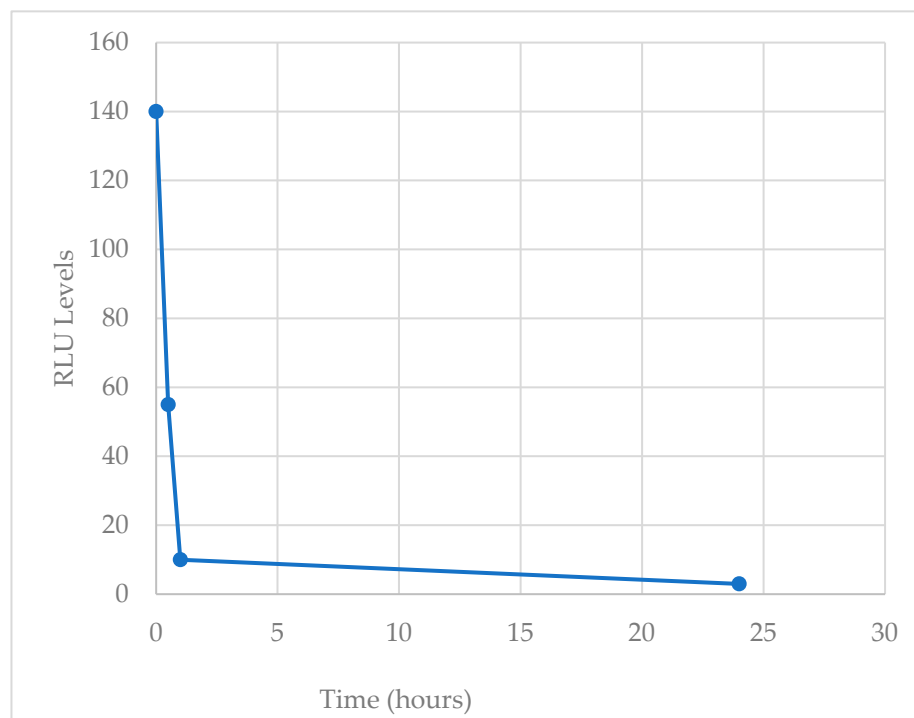
Figure 4. Microbial activity (ATP as RLUs) in unfiltered diluted pond water after treating with 1 ppm copper in the form of copper pentahydrate.

Open ponds containing sulfides at circumneutral pH will off gas toxic hydrogen sulfide. The use of hydrogen peroxide for sulfide oxidation results in a pH drop before the sulfides are completely oxidized because the acid–base chemistry is faster than the redox chemistry. Raising the pH prior to using hydrogen peroxide will reduce or eliminate off gassing but risks creating precipitants of metal carbonates and hydroxides. The oxidation of iron from Fe(II) to Fe(III) can also be problematic when using peroxide, so scale inhibitors should also be considered in the treatment process. Jar testing can optimize the dosing of chemicals and test for unforeseen problems. In one produced water from West Texas and laboratory-prepared water samples containing biogenic sulfides, the product HPG raised the pH and slightly improved the oxidation of sulfides. Raising the pH even slightly, if no precipitants form, resulted in shorter oxidation kinetics because the rate-limiting step is in converting the H_2S to HS^-.

H_2O_2 is not as cost-effective as using NaOCl with iron (Fe^{2+}) [34]. But, the new HPNow hydrogen peroxide generator [14] brings the cost down with on-site generation of H_2O_2. The use of OCl^{-1} increases the pH, can cause solids to precipitate, and can create toxic chlorinated organic compounds [35].

4. Conclusions

H_2O_2 can be used to treat sulfides in the water while keeping the H_2S gas levels down (i.e., preventing off gassing) by raising the pH as long as no solids form by enhancing the oxidation process with a catalyst or addition of other oxidants, such as commercial products, HydroPower Green™, and AquaDrop™ ($CuSO_4$, $5H_2O$), and by controlling sulfate-reducing bacteria with a biocide.

Between a pH of 6 and 8, the speciation of H_2S to HS^- shifts from 90:10 to 10:90. If an open water (e.g., a lagoon containing process wastewater or a frack pond) has a pH below 9 while it is being treated, a significant amount of hydrogen sulfide gas will be liberated. H_2O_2 reduces the pH, and a weakly caustic solution can be used to keep the pH from dropping during the treatment process. A commercial product, HydroPower Green™, worked for pH control and aided in the oxidation of sulfides in water. Jar testing must be

performed to make sure metal carbonates or iron oxide do not precipitate when dosing with chemicals. The dose of H_2O_2 necessary to oxidize sulfides is mainly a function of the oxidation-reduction potential (Eh) of the water and total sulfide concentration as well as pH; a ratio of approximately 1–4:1 of peroxide to sulfide concentration is needed to oxidize sulfidic waters, with shorter half-lives achieved at higher pH. Having oil or other organics in the water can consume some of the peroxide. Biocides should be added after peroxide has sufficient reaction time with sulfides.

A liquid form of $CuSO_4$, $5H_2O$ was shown to keep sulfide and bacteria levels down, suggesting it can be an effective biocide for controlling sulfate-reducing bacteria (SRBs). The use of peracetic acid as an antibiotic can kill SRBs but the bacteria may rebound if under-dosed, which is worse than not using it at all. One treatment option is to combine copper sulfate with other biocides, but compatibility should also be determined by jar testing.

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