

Oxidants and Scavengers vs. Sulfide

Part 1: Bleach vs. ClO₂

A. BACKGROUND

Introduction: Hydrogen sulfide (H₂S) is problematic in many types of systems. Sewer water, produced water, petroleum refineries and natural gas plants can contain dangerous concentrations of H₂S. A number of different chemicals can be used to either complex or oxidize H₂S. Almost all of these reactions are pH dependent.

In this work, the effectiveness of sodium hypochlorite (bleach) vs. that of ClO₂ as a sulfide scavenger are compared experimentally at pHs of 5 and 11.

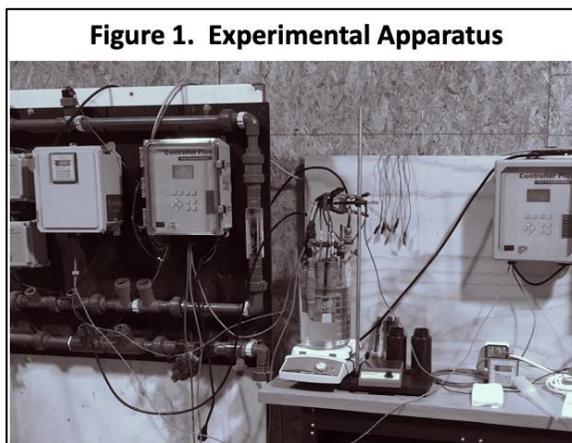
The objective of this work was to identify the stoichiometry of bleach vs ClO₂ vs sulfide

B. EXPERIMENTAL

Four liters of DI water were placed into a 5-L beaker. Several probes, including an Oxidation-Reduction Probe (ORP) and a pH probe were immersed in the water to be tested as shown in Figure 1.

The data from these probes was collected by a Walchem eController which was used to condition and store the probe data. The probes were calibrated prior to use.

The pH and ORP were recorded electronically every 30 seconds in this process, and either the oxidant or the sulfide was added every ~5 minutes (or longer) to give time for the reaction to occur to and the pH and ORP to reach equilibrium.



Two experiments were run. In Experiment 1, about 0.5 grams of Na₂S was added to 4-L of DI water and allowed to dissolve. In each case, the pH rose to almost 11. Then, small doses of chemical were added, and after about 5 minutes, either the oxidant concentration or the sulfide concentration was measured, where possible.

In Experiment 2, 4-L of DI water was buffered to a pH of about 5, by adding 50 mL of 0.1 N citric acid¹ and about 50 mL of 0.2 N Na₂HSO₄·12H₂O. Then, the oxidant was dosed to the 4-L solution. The ~ 0.5 g of Na₂S was added to 100 mL of DI water, and small this solution was added.

C. BLEACH

Background: The reaction chemistry of hypochlorite with sulfide is shown in Equations 1 and 2.¹

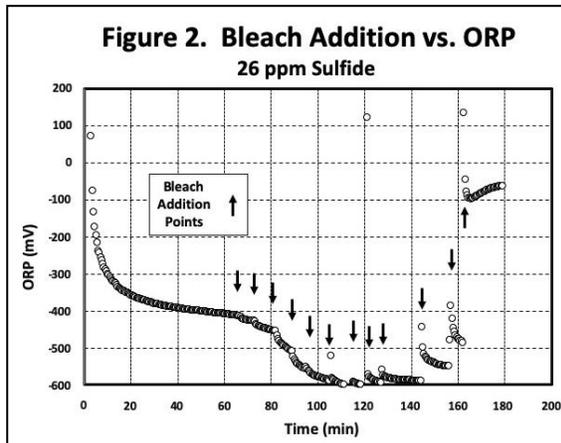
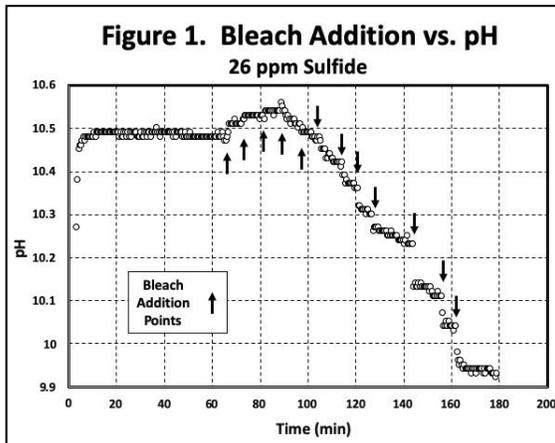


¹ Note: It has been suggested that citric acid is an antioxidant, and therefore is unsuitable as a buffer. The implication is that citric acid would consume any ClO₂ or other oxidant used in the test. The argument is absurd, as there are any number of products and patents where citric acid has been used to activate chlorite to produce ClO₂. A search of the USPTO using citric acid and ClO₂ as claims revealed 128 patents. While not all of the patents involve citric acid activation of chlorite to produce ClO₂, most of them do.

Sulfur and sulfate are formed in varying amounts, depending on temperature, concentrations of reactants, and pH. So, the theoretical stoichiometry can vary from 1.6 to 6.4 ppm OCl^- to ppm S^{2-} , depending on conditions.

Experiment 1. Un-buffered pH: To 4-L of DI water was added 0.560 grams of Na_2S . After suitable time and dilution, the sulfide concentration was measured to be 26 ± 0.5 ppm.

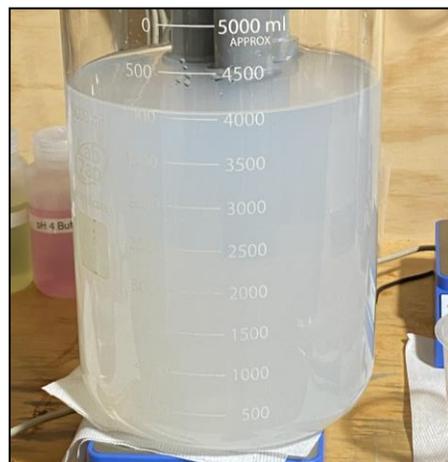
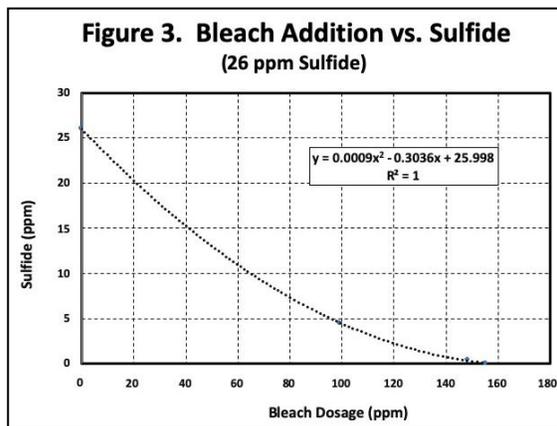
The pH and ORP response are shown in Figures 1 and 2, respectively.



This method of tracking the point at which all the sulfide is consumed appears valid, as long as the reaction occurs rapidly, i.e., shorter than the time frame between oxidant additions.

The photo shows either elemental sulfur, polysulfide, or some other white precipitate involving sulfur is being formed.

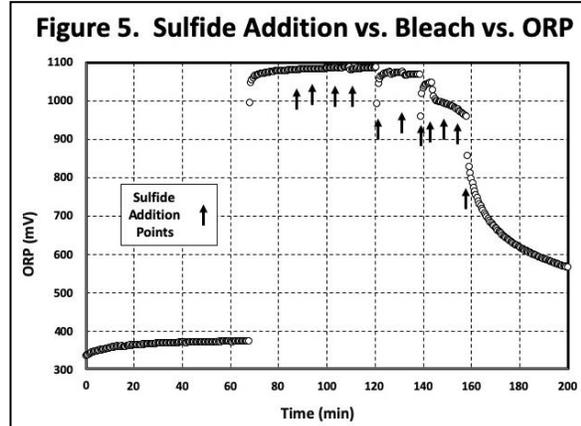
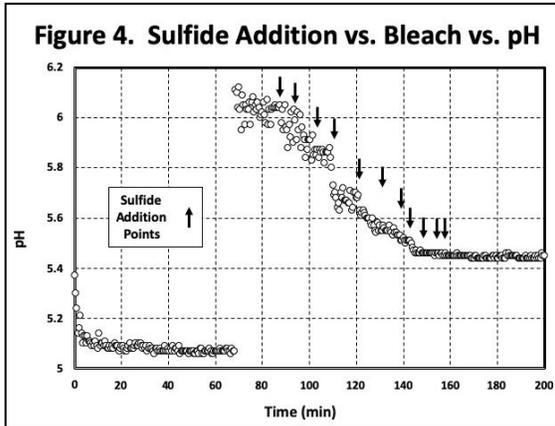
The plot of $[\text{Cl}_2]$ vs $[\text{S}^{2-}]$ is shown in Figure 3. At elevated pH, about 155 ppm of bleach (as Cl_2) was required to oxidize 26 ppm of sulfide or 6.0 ppm bleach per ppm sulfide. This is near the



upper end of the theoretical range.

Experiment 2. pH 5: To 4-L of DI water, ~ 12 mL of Chlorox bleach was added, along with the buffers to achieve pH 5. The initial chlorine concentration was measured to be 92 ppm.

To 100 mL of DI water was added 0.515 grams of Na₂S. After suitable dilution, sulfide was



measured in duplicate to be 880 ppm. Then, the sulfide solution was dosed into the bleach solution a little at a time, and a minimum of 5 minutes was allowed before another small dose was added.

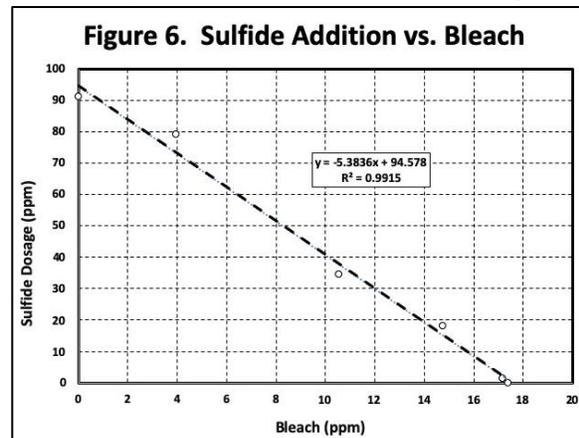
The pH and ORP response are shown in Figures 4 and 5, respectively.

Clearly, the response of the ORP has the opposite effect than the addition of bleach to DI water.

The results at pH 5 were essentially the same as results for pH 11. The reason for the change in the order of addition was solely safety considerations.

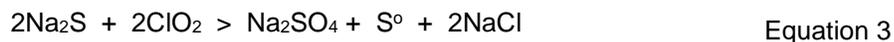
Free chlorine was measured by the Hach DPD method with appropriate dilutions at various times. In addition, sulfide was measured the same way, once the ORP began to drop precipitously and the chlorine residual neared zero.

The plot of sulfide vs chlorine concentration is shown in Figure 6. It took 17.4 ppm of sulfide to reduce 91 ppm of chlorine, or 5.2 ppm of chlorine per ppm sulfide. This is within agreement of the results of the pH 11 experiment and is within the theoretical range described earlier.



D. CHLORINE DIOXIDE (ClO₂)

Background: The reaction of ClO₂ with sulfide occurs via Equations 3 and 4.

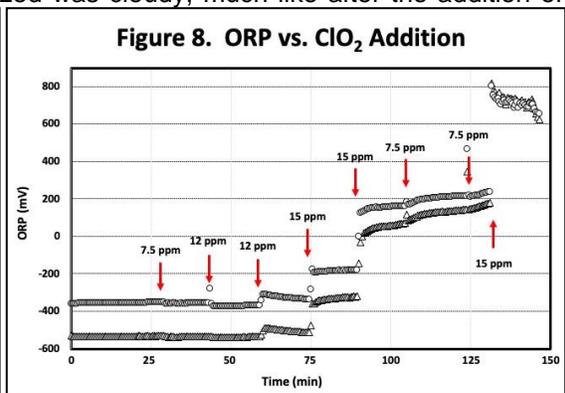
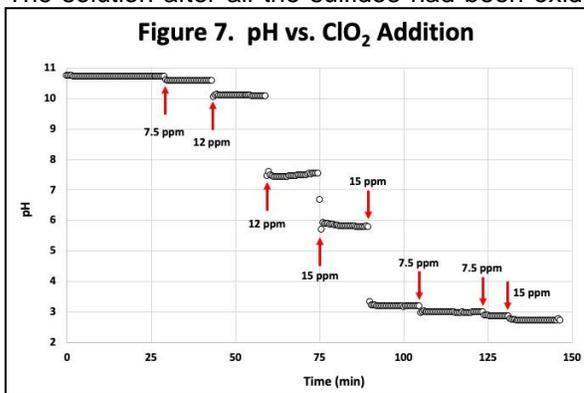


Elemental sulfur and sulfate may be formed in varying amounts, depending on a number of variables. The theoretical stoichiometry can vary from 2.1 to 3.4 ppm ClO₂ to ppm S⁰, depending on conditions. These results are close to those found by C.I. Smeck, who found a ratio of 2.7 – 4.0 of ClO₂/H₂S on a ppm/ppm basis.²

Experiment 1. Un-buffered pH: To 4-L of DI water was added 27 ppm of sulfide. The pH increased to almost 11.

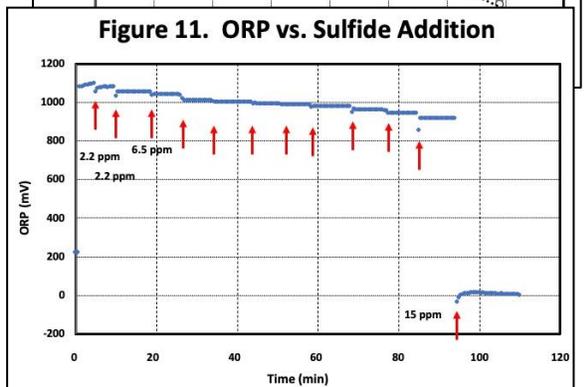
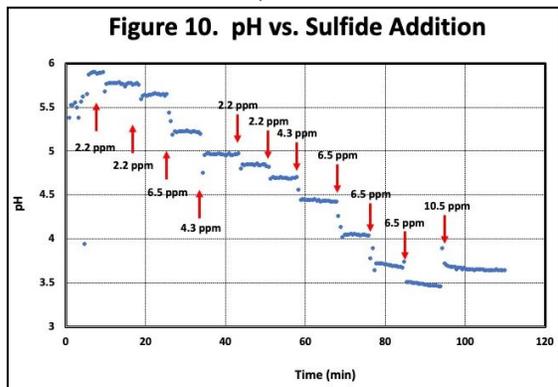
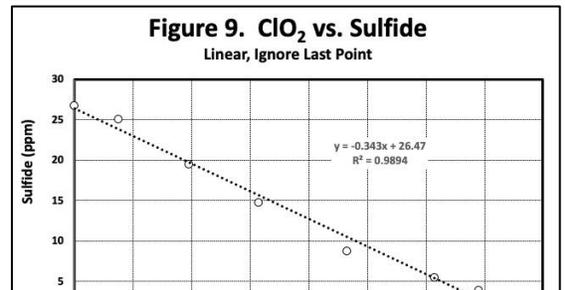
Then, ClO₂ was added. The pH and ORP vs. ClO₂ addition are shown in Figures 7 and 8, respectively.

The solution after all the sulfides had been oxidized was cloudy, much like after the addition of



bleach. It is clear that either elemental sulfur or some other sulfur form (polysulfide?) is formed.

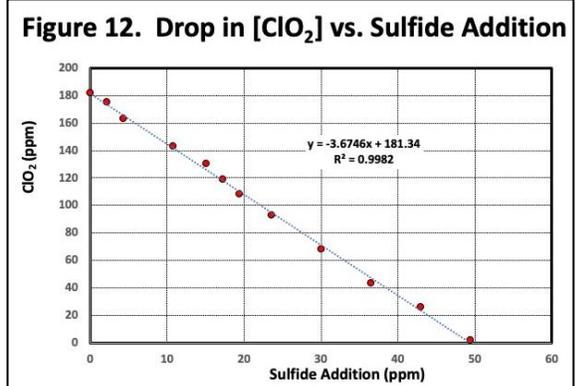
Sulfide was also measured 5 minutes after each addition of ClO_2 . A plot of ClO_2 addition vs sulfide measured in duplicate and averaged is shown in Figure 9. The last data point was ignored in this plot because the endpoint was overshoot, and its inclusion would have skewed the data. Therefore, the data was fitted to a



straight line, as shown.

It took somewhere around 77 – 91.5 ppm (if we include the last data point) of ClO_2 to reduce sulfide to zero. This works out to a range of 2.9 – 3.4 ppm of ClO_2 required to reduce sulfide to zero.

Experiment 2. pH 5: To 4-L of pH-5 buffered water was added 260 mL of 2800 ppm ClO_2 . This equates to about 182 ppm. Then, small aliquots of 860 ppm sulfide were added. Interestingly, both pH and ORP equilibrated almost immediately. This suggests the reaction of ClO_2 with sulfide occurred almost instantly (Figure 10 and 11, respectively). Figure 12 shows Sulfide (ppm) vs ClO_2 (ppm).



The data showed that 3.7 ppm ClO_2 was required per ppm sulfide and also falls within the range of values found by Smeck.

E. SUMMARY

Table 1 shows the results of this testing.

Table 1. Stoichiometry of Consumption of Sulfide		
Chemical	Unbuffered pH (10.8)*	pH 5
Bleach	~ 6.0	~ 5.2
ClO ₂	~ 2.9 - ~ 3.4	~ 3.7

* Adding 0.5 grams of Na₂S to DI water resulted in an immediate increase in pH to about 10.8. Unless the chemical added was acidic (PAA and THPS) or produced acids in the reaction (ClO₂), the pH remained > 10.

F. REFERENCES

- ¹ Black, A. and Goodson, J., "The Oxidation of Sulfides by Chlorine in Dilute Aqueous Solutions," Journal of the American Water Works Association, 44(4), 309(April, 1952).
Choppin, A. and Faulkenberry, L., "The Oxidation of Aqueous Sulfide Solutions by Hypochlorites," Journal of the American Chemical Society, 59, 2203(Nov. 1937).
- ² Smeck, C., "Treatment of Sulfide-Bearing Waters with Chlorine Dioxide," US Patent 4,077,879, March 7, 1978.