

Oxidants and Scavengers vs. Sulfide

Part 2: Peracetic Acid (PAA) vs. ClO₂

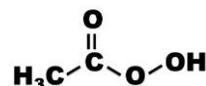
A. BACKGROUND

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.

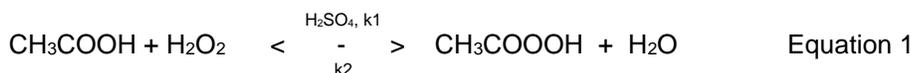
In this work, the effectiveness of a commercial product of Peracetic acid (16%) vs. that of ClO₂ as a sulfide scavenger are compared experimentally at pHs of 5 and 11.

About PAA: PAA is a clear, colorless pungent non-foaming liquid that has a pH < 2. It is miscible with water and is soluble in polar organic solvents.

Peracetic acid (PAA) has the structure shown. It is a stronger oxidant than either Cl₂ or ClO₂. Peracetic (also known as peroxyacetic acid), is a strong oxidant with a potential of 1.962 V (vs. SHE).¹ It is available in a variety of concentrations which can vary from about 5% to about 35%.



Commercial formulations of PAA contain significant amounts of H₂O₂. PAA is prepared by the reaction of hydrogen peroxide, H₂O₂, and acetic acid or acetic anhydride, and sulfuric acid is used to provide an acid catalyst.² Use of a sulfuric acid catalyst increases the rate of reaction. The concentration of PAA at equilibrium varies with the concentration of H₂O₂ and the molar ratio of acetic acid to H₂O₂. The concentration of the H₂SO₄ varies from 1 to 9%.³



This reaction is reversible, and proceeds to an equilibrium of reactants and products. Both forward and reverse reactions are fairly slow at room temperature, and a long time is necessary for equilibrium to establish. The reaction products may be allowed to react for up to 10 days in order to achieve high yields of PAA. A stabilizer or a sequestering agent is typically used during the production of PAA.

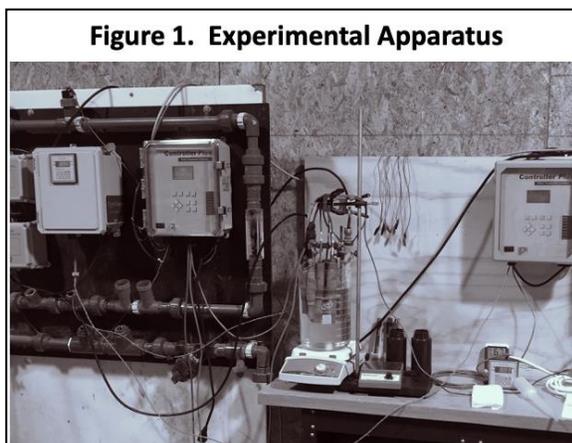
PAA is considerably less stable than H₂O₂. For example, H₂O₂ stored at concentrations > 30% have been shown to lose less than 1% of its activity in a year, while a 40% loses that much or more in a month.⁴ PAA was shown to degrade by 25-30% in 1 hour in tap water regardless of the demand.⁵ As the concentration of PAA decreased, the stability also decreased, e.g., a 1% of a solution lost half its strength in 6 days.⁶

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 Na_2S 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 acid and about 50 mL of 0.2 N $\text{Na}_2\text{HSO}_4 \cdot 12\text{H}_2\text{O}$. Then, the oxidant was dosed to the 4-L solution. The ~ 0.5 g of Na_2S was added to 100 mL of DI water, and small aliquots of this solution was added.

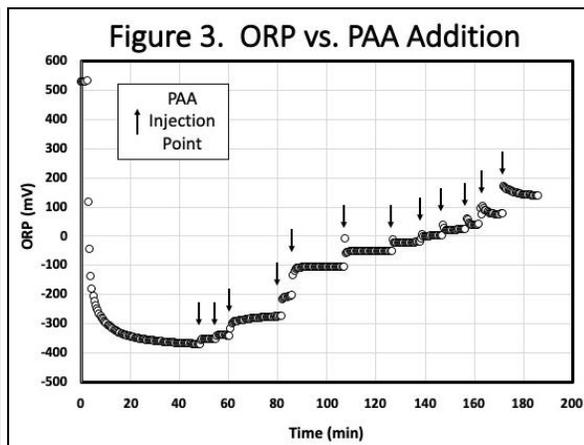
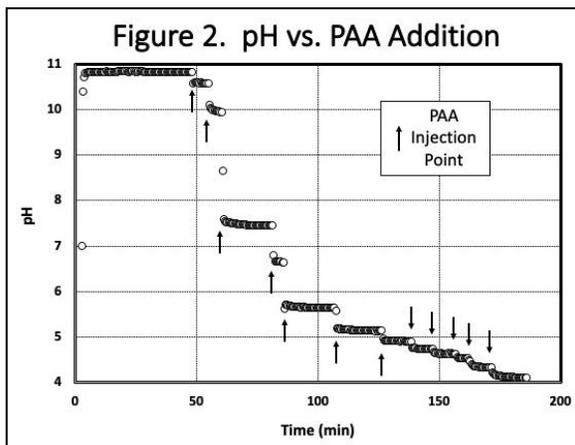
C. PERACETIC ACID

Background: The reaction chemistry of PAA with sulfide is shown in Equations 2 and 3.⁷



Just like for bleach, elemental sulfur and sulfate may be formed in varying amounts, depending on a number of variables. So, the theoretical stoichiometry can vary from 2.4 to 9.5 ppm PAA to ppm S^- , 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 mixing, the sulfide concentration was measured to be 26 ± 0.5 ppm.



PAA was added in small aliquots, and the pH and ORP response are shown in Figures 2 and 3, respectively. It is clear that the PAA is acidic, as the pH drops significantly with each addition.

Once the sulfide reached a point slightly above 100 mV, the sulfide had been consumed. The sulfide concentration was measured a few minutes after each addition of PAA.

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 colloidal species of sulfur was formed.

Apparently, PAA reacts with sulfide, although the amount of PAA required to reduce sulfide to zero is high.

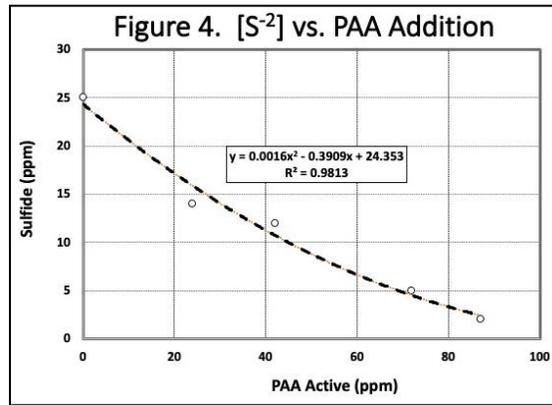
It appears that 87 ppm of PAA active is required to reduce the sulfide concentration from 23 to 2 ppm. Therefore, under these conditions, $87/23 = 3.8$ ppm of PPA active is required per ppm of sulfide.



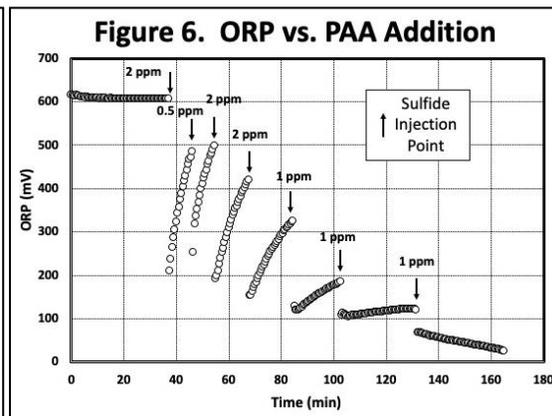
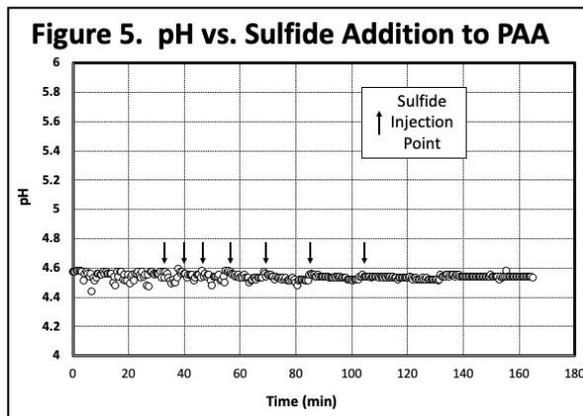
For this commercial 16% PAA product about 24 ppm of product was required per ppm of sulfide.

Experiment 2. pH 5: To 4-L of DI water was added pH 5 buffer solution and 58 ppm of PAA active. Then a solution of 100 mL of 830 ppm sulfide was made.

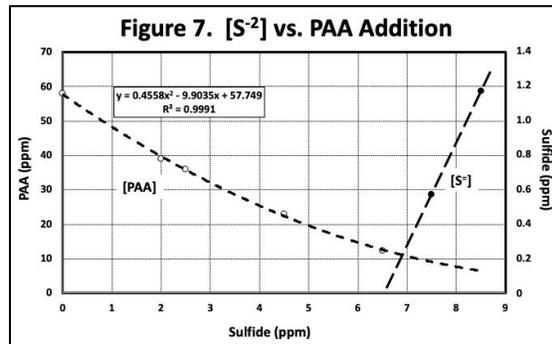
Aliquots of sulfide solution were added to the buffered PAA solution, and the ORP and pH were recorded electronically every 30 seconds in this process. Then aliquots of sulfide solution were added every 5 - 15 minutes to give time for the PAA to react with sulfide and the pH and ORP to reach equilibrium.



The pH and ORP response are shown in Figures 5 and 6, respectively.



The drop in PAA concentration was tracked over time, and plotted against the amount of sulfide dosed. The plot is shown in Figure 7. Toward the end of the addition of sulfide, the measured PAA began to increase slightly. At these points, the water was tested for sulfide, and a line drawn.

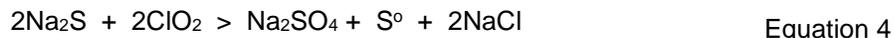


The point at which all the PAA was consumed was at about 6.8 – 6.9 ppm sulfide.

As the initial concentration of PAA was measured to be 58; the PAA/sulfide ratio was measured to be 58/6.8 or about 8.5 ppm of PAA per ppm of sulfide.

D. CHLORINE DIOXIDE (ClO₂)

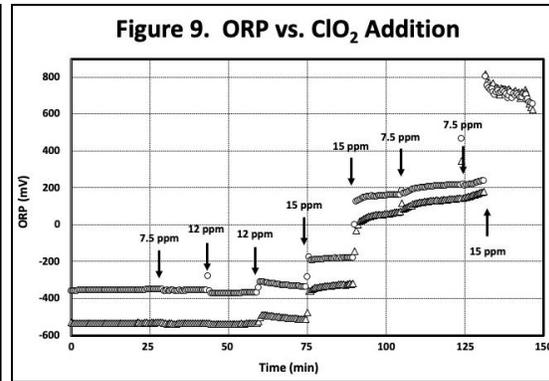
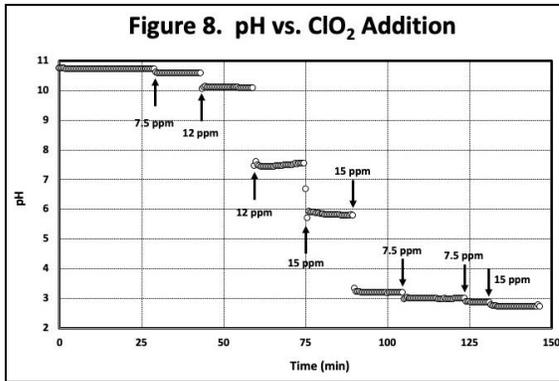
Background: The reaction of ClO₂ with sulfide occurs via Equations 4 and 5.



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.⁸

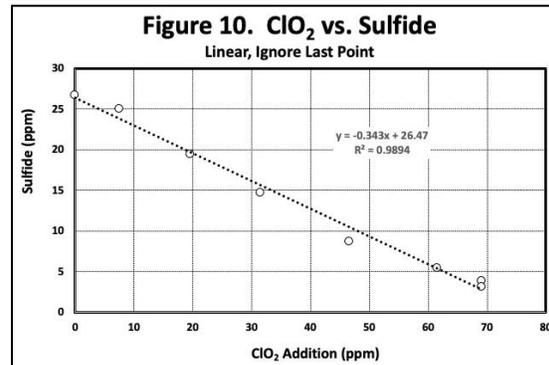
Experiment 1. Un-buffered pH: To 4-L of DI water was added 27 ppm of sulfide. The pH increased to almost 11.

Then, ClO₂ was added. The pH and ORP vs. ClO₂ addition are shown in Figures 8 and 9 respectively.

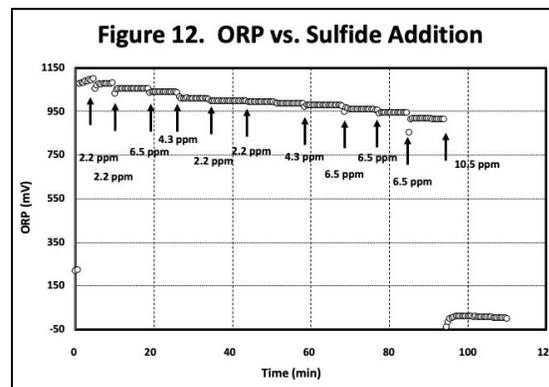
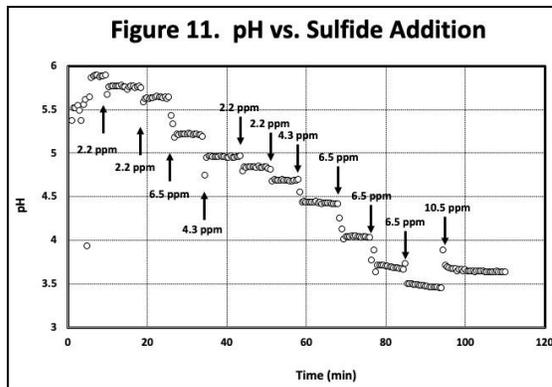


The solution after all the sulfides had been oxidized was cloudy, much like after the addition of bleach. It is clear that either elemental sulfur or polysulfide is formed.

Sulfide was also measured 5 minutes after each addition of ClO₂. A plot of ClO₂ 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.



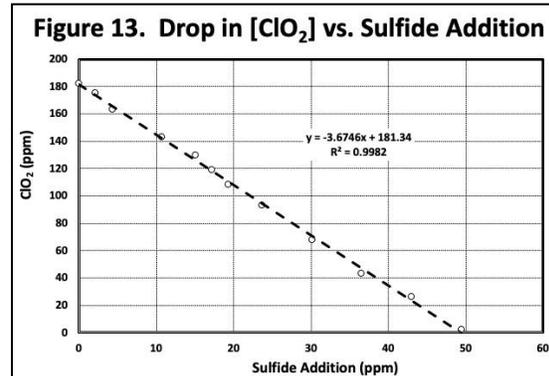
It took somewhere around 77 – 91.5 ppm (if we include the last data point) of ClO₂ to reduce sulfide to zero. This works out to a range of 2.9 – 3.4 ppm of ClO₂ required to reduce sulfide to



zero.

Experiment 2. pH 5: To 4-L of pH-5 buffered water was added 260 mL of 2800 ppm ClO₂. 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 ClO₂ with sulfide occurred almost instantly (Figure 11 and 12, respectively). Figure 13 shows Sulfide (ppm) vs ClO₂ (ppm).

The data showed that 3.7 ppm ClO₂ 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.

Chemical (active)	Unbuffered pH (10.8)*	pH 5
PAA	~ 3.8	~ 8.5
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 Cotillas, S., Sanchez-Carretero, A., Canizares, P., Saez, C., and Rodrigo, M., "Electrochemical Synthesis of Peroxyacetic Acid Using Conductive Diamond Electrodes," *Industrial & Engineering Chemistry Research*, 50, 10889(2011).
- ² Block S., "Disinfection, Sterilization, and Preservation," 4th edition, Lea & Febiger Publishers, Philadelphia, PA, 1991.
Zhao, X., "Preparation of Peracetic Acid from Acetic Acid and Hydrogen Peroxide: Experimentation and Modeling," *The Chinese Journal of Process Engineering*, 8(1), 35(February 2008).
- ³ Greenspan, F., "The Convenient Preparation of Per-Acids," *Journal of the American Chemical Society*, 68(5), 907(1946).
John, J. and Weymouth, F., "Manufacture and Uses of Peracetic Acid," *Chemical Industry*, 2, 62(1962).
Dul-neva, L., Moskvin, A., and Pavlov, S., "Kinetics of Formation of Peroxyacetic Acid," *Russian Journal of General Chemistry*, 75(7), 1125(2005).
- ⁴ Kitis, M., "Disinfection of Wastewater with Peracetic Acid: A Review," *Environment International*, 30, 47(2004).
- ⁵ Antonelli, M., Turolia, A., Mezzanotte, V., and Nurizzo, C., "Peracetic Acid for Secondary Effluent Disinfection: A Comprehensive Performance Assessment," *Water Science & Technology*, 12(68), 2638(2013).
- ⁶ Block, S., *Disinfection, Sterilization, and Preservation*, 4th Edition, Lea & Febiger Publishers, Philadelphia, 1991.
- ⁷ 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).
- ⁸ Smeck, C., "Treatment of Sulfide-Bearing Waters with Chlorine Dioxide," US Patent 4,077,879, March 7, 1978.