

# Oxidants and Scavengers vs. Sulfide

## Part 3: Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>) vs. ClO<sub>2</sub>

### A. INTRODUCTION

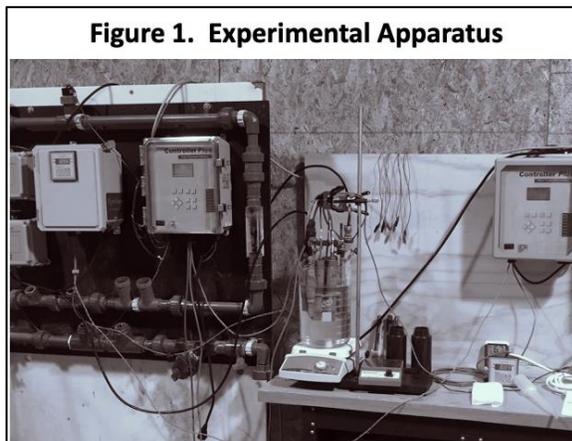
This is part 3 of a series of studies to determine experimentally the dosage of oxidant or chemical required to oxidize or scavenge sulfide.

### 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 Na<sub>2</sub>S 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 Na<sub>2</sub>HSO<sub>4</sub>·12H<sub>2</sub>O. Then, the oxidant was dosed to the 4-L solution. The ~ 0.5 g of Na<sub>2</sub>S was added to 100 mL of DI water, and small aliquots of this solution was added.

### C. HYDROGEN PEROXIDE

**Background:** The reactions of H<sub>2</sub>O<sub>2</sub> with sulfide are shown in Equations 1 and 2.

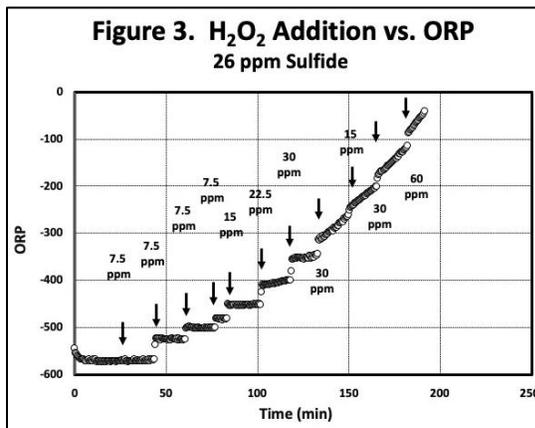
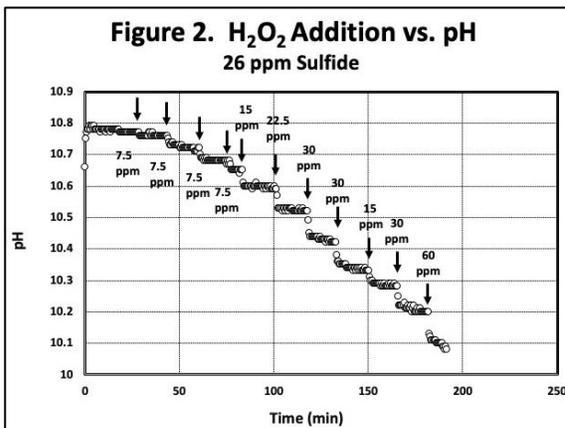


The theoretical reaction of H<sub>2</sub>O<sub>2</sub> with sulfide varies from about 1.1 to about 4.3. Which reaction predominates is a function of concentration, pH, and temperature.

**Experiment 1. Unbuffered pH:** Approximately 0.5 grams of Na<sub>2</sub>S was added to 4 L of DI water. The pH rose to 10.8 as the sulfide was dissolving. The sulfide concentration was measured in duplicate to be 26 ppm.

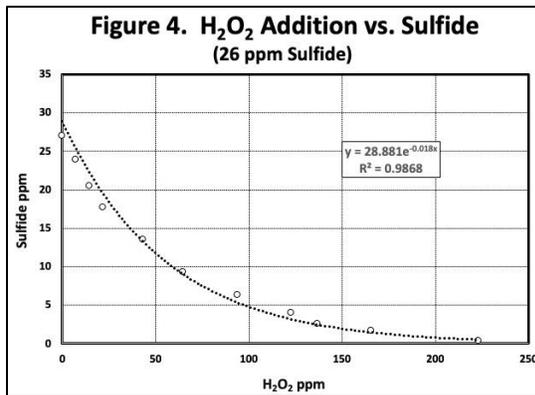
Then, 3% hydrogen peroxide was added in varying amounts, and the pH and ORP were recorded every 30 seconds. After a reaction time of about 5 minutes, sulfide was measured before the next addition of H<sub>2</sub>O<sub>2</sub>.

Figures 2 and 3 show the response of pH and ORP, respectively. The stair-step response of both pH and ORP are shown. Sulfide was tested after each addition of peroxide. The known concentration of H<sub>2</sub>O<sub>2</sub> was plotted against the sulfide concentration. Results are shown in Figure 4.



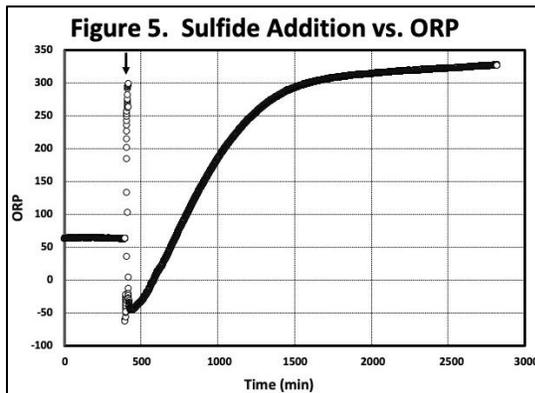
Note the photo. This was taken at the endpoint, suggesting at this high pH, H<sub>2</sub>O<sub>2</sub> takes the sulfide all the way to sulfate.

The concentration of H<sub>2</sub>O<sub>2</sub> required to reduce 26 ppm to zero was 223 ppm. This equates to 8.4 ppm H<sub>2</sub>O<sub>2</sub> per ppm sulfide.



**Experiment 2. pH 5:** This experiment was repeated three times because the results made no sense, initially. Approximately 180 ppm of H<sub>2</sub>O<sub>2</sub> was added to 4 L of DI water buffered to pH 5. Then, a small aliquot of sulfide solution was added. The amount of sulfide added was equivalent to 2.2 ppm. The results are shown in Figure 5.

The results show that at pH 5, in the absence of any catalyst such as iron, the reaction of hydrogen peroxide is extraordinarily slow.



This flies in the face of what is apparently common use of H<sub>2</sub>O<sub>2</sub> in produced water. One possible reason H<sub>2</sub>O<sub>2</sub> is effective is that produced water contains some iron.

#### D. CHLORINE DIOXIDE (ClO<sub>2</sub>)

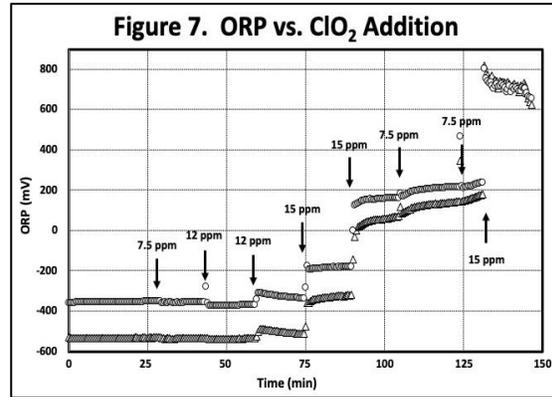
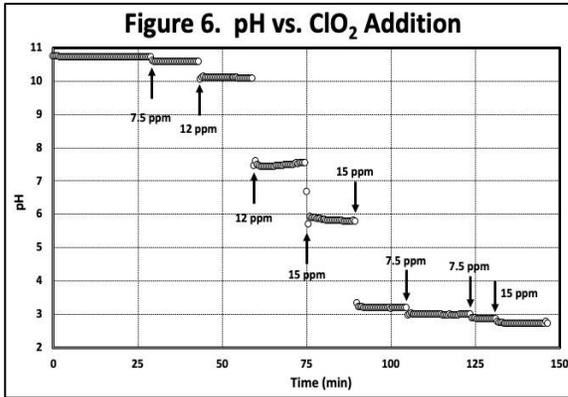
**Background:** The reaction of ClO<sub>2</sub> with sulfide occurs via Equations 3 and 4.



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 ClO<sub>2</sub> to ppm S<sup>0</sup>, depending on conditions. These results are close to those found by C.I. Smeck, who found a ratio of 2.7 – 4.0 of ClO<sub>2</sub>/H<sub>2</sub>S on a ppm/ppm basis.<sup>1</sup>

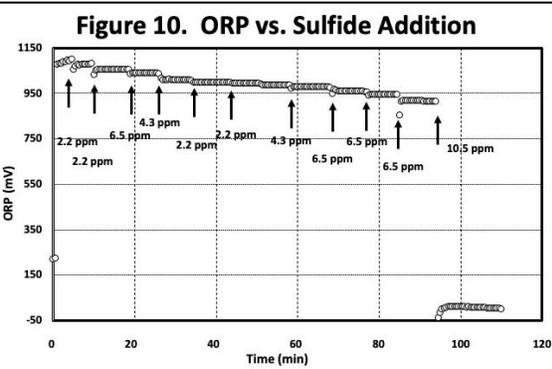
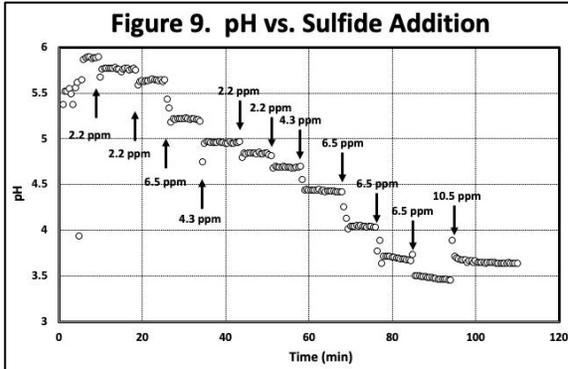
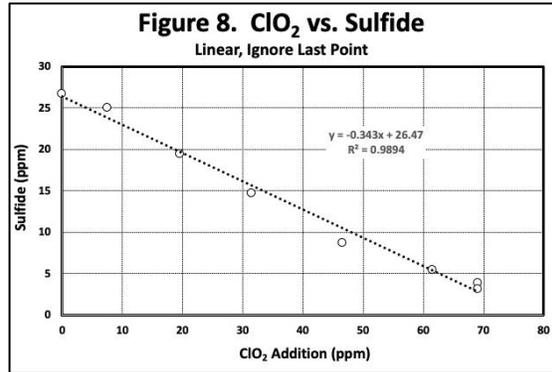
**Experiment 1. Un-buffered pH:** To 4-L of DI water was added 27 ppm of sulfide. The pH increased to almost 11.

Then, ClO<sub>2</sub> was added. The pH and ORP vs. ClO<sub>2</sub> addition are shown in Figures 6 and 7 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 ClO<sub>2</sub>. A plot of ClO<sub>2</sub> 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<sub>2</sub> to reduce sulfide to zero. This works out to a range of 2.9 – 3.4 ppm of ClO<sub>2</sub> 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<sub>2</sub>. 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<sub>2</sub> with sulfide occurred almost instantly (Figures 9 and 10, respectively).

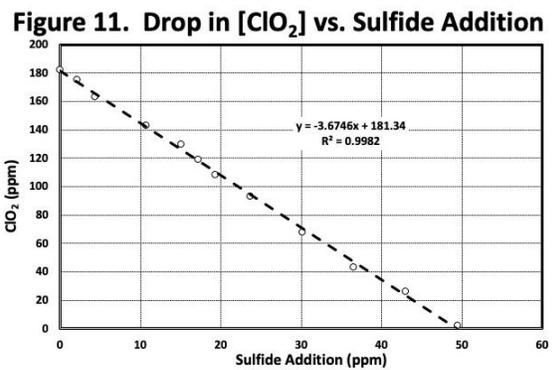


Figure 11 shows Sulfide (ppm) vs ClO<sub>2</sub> (ppm).

The data showed that about 3.7 ppm ClO<sub>2</sub> was required per ppm sulfide. This falls within the range of values found by Smeck.<sup>1</sup>

**E. SUMMARY**

Table 1 shows the results of this testing.

<b>Chemical (active)</b>	<b>Unbuffered pH (10.8)*</b>	<b>pH 5</b>
H <sub>2</sub> O <sub>2</sub>	~ 8.4	-
ClO <sub>2</sub>	~ 2.9 - ~ 3.4	~ 3.7

\* Adding 0.5 grams of Na<sub>2</sub>S 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 (ClO<sub>2</sub>), the pH remained > 10.

**F. REFERENCES**

<sup>1</sup> Smeck, C., "Treatment of Sulfide-Bearing Waters with Chlorine Dioxide," US Patent 4,077,879, March 7, 1978.