

Oxidants and Scavengers vs. Sulfide

Part 5: THPS 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.

Experimental: The objective of this work was to identify the stoichiometry of various chemicals vs sulfide. 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.

Experiments were done for each chemical at two separate pHs. 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 acid 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.

B. THPS

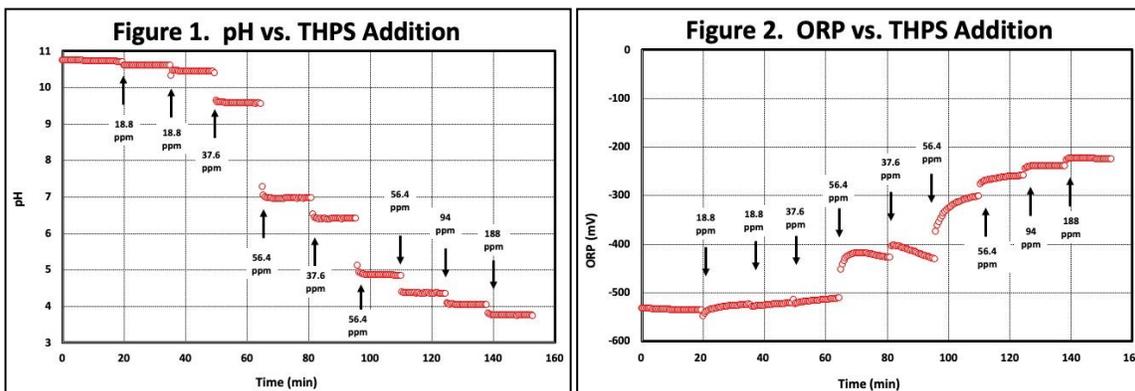
THPS is a biocide that has achieved some reputation in the oil patch as a sulfide scavenger. The reaction is shown in Equation 1.



THPS oxidizes rapidly to THPO (trishydroxymethylphosphine oxide). Both are effective biocides that readily biodegrade and have a low aquatic toxicity. A review of the available literature does not specify the ratio of THPS to sulfide, as the reduction in sulfide appeared to be a side benefit of its biocidal activity.

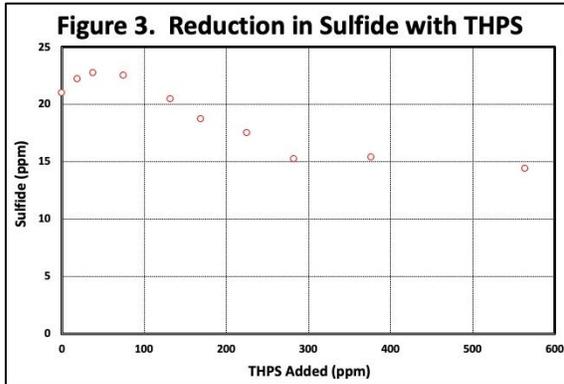
The structure appears to have places for 1 – 8 sulfides for each of the functional groups on the dimeric salt, although the rapid environmental oxidation of THPS to THPO makes this unclear.

Experiment 1. Unbuffered pH: About 0.5 grams of Na₂S was dissolved in 4-L of DI water. Duplicate sulfide tests showed a sulfide concentration of 21 ppm.



Small aliquots of 75% THPS were added, with the pH and the ORP being measured electronically every 30 seconds. The plots of pH and ORP are shown in Figures 1 and 2, respectively.

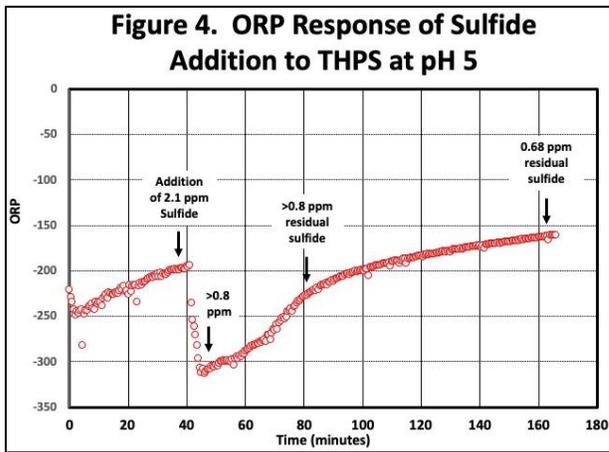
The THPS has a pH of about 3, which is why the pH dropped with each addition. Changes in ORP were somewhat less than that for oxidants, and although some of the sulfide was consumed, the ORP rose. Because oxidation was not the mechanism of reaction, no definitive conclusion could be made from this data.



Sulfide was measured several minutes after each addition of THPS. The plot of THPS added vs sulfide is shown in Figure 3. Although there was some reduction in sulfide, not all of the sulfide appeared to be complexed, or removed from solution.

It is not possible, from this data, to even approximate a THPS: Sulfide ratio.

Experiment 2. pH 5: THPS (1 mL) was dosed into 4-L of water. This equals 188 ppm. Then, aliquots of 0.5 g Na₂S in 100 mL DI water (850 ppm) were added. Figure 4 shows the response of ORP to the first addition of sulfide. The response after the first addition of sulfide was rather unexpected, and so no further sulfide was added.



The amount of sulfide added was well below the amount of THPS required to complex the sulfide. Therefore, a reading of zero sulfide was expected. Instead, the measurement was well above the upper limit of the test.

The data suggested that the reaction of THPS with sulfide at pH 5 was extremely slow, which was confirmed by the sulfide test results.

This raises questions about claims that THPS acts as a sulfide scavenger. Instead, it may be that the reduction in sulfide observed in downhole applications occurs as a result of suppression of sulfate reducing bacteria.

C. CHLORINE DIOXIDE (ClO₂)

Background: The reaction of ClO₂ with sulfide occurs via Equations 2 and 3.

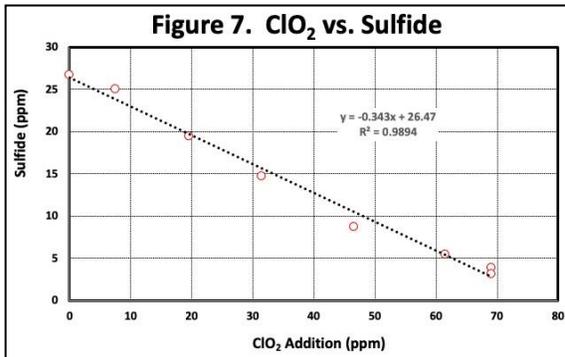
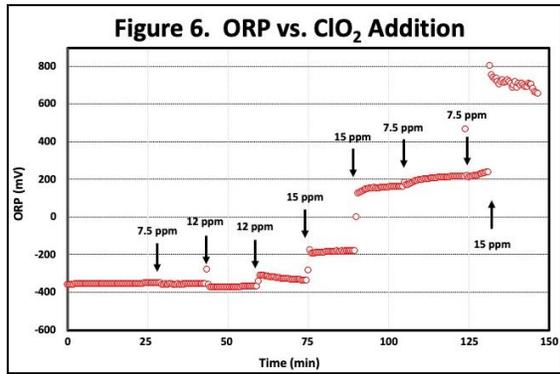
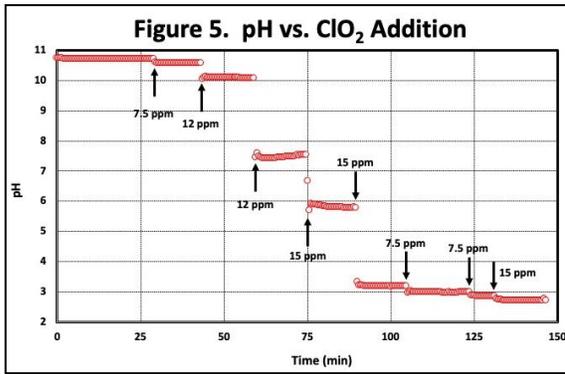


Elemental sulfur and sulfate may be formed in varying amounts, depending on a number of variables. The theoretical stoichiometry can vary from 2.1 to 3.4 ppm ClO₂ to ppm S⁼, depending on conditions. This is close to that found by C.I. Smeck, who found a ratio of 2.7 – 4.0.¹

Experiment 1. Un-buffered pH: To 4-L of DI water was added 27 ppm of sulfide.

Then, ClO₂ was added. The pH and ORP vs. ClO₂ addition are shown in Figures 5 and 6, respectively.

The solution after all the sulfide 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 being formed.

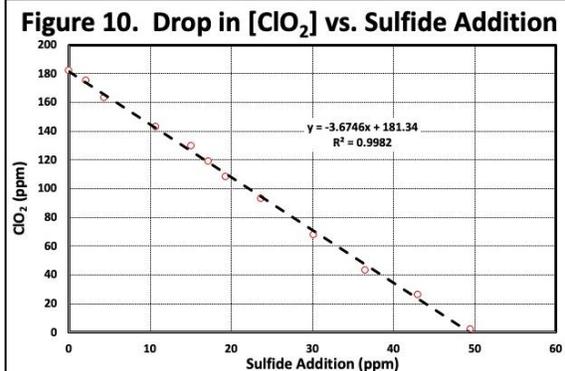
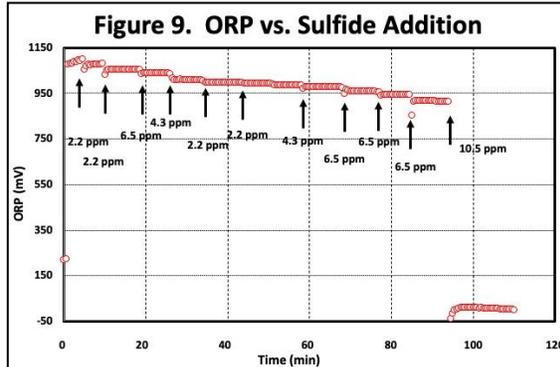
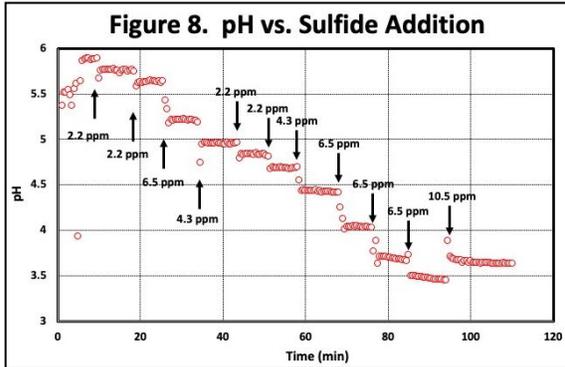


Sulfide was also measured 5 minutes after each addition of ClO_2 . A plot of ClO_2 addition vs sulfide measured in duplicate and averaged is shown in Figure 7. The last data point was ignored in this plot because the endpoint was overshoot, and its inclusion would have skewed the data. Therefore, the 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, aliquots of 860 ppm sulfide were added. Interestingly, both pH and ORP equilibrated almost immediately. This suggests the reaction of ClO_2 with sulfide occurs almost instantly. Figure 10 shows the reduction in ClO_2 with the addition of Sulfide.

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.

D. SUMMARY

Table 1 shows the results of this testing.

Chemical	Unbuffered pH (10.8)*	pH 5
THPS	-	-
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.

Even though THPS does not appear to scavenge sulfide, there is ample evidence that it is effective on some form of iron sulfides. Consequently, the combination of THPS with ClO₂ during hydraulic fracturing applications is promising.

E. REFERENCES

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