

Oxidants and Scavengers vs. Sulfide

Part 4: Chlorite Ion vs. ClO₂

A. INTRODUCTION

This is part 4 of an experiment to determine the relative stoichiometry of various oxidants and chemicals at oxidizing or scavenging sulfide.

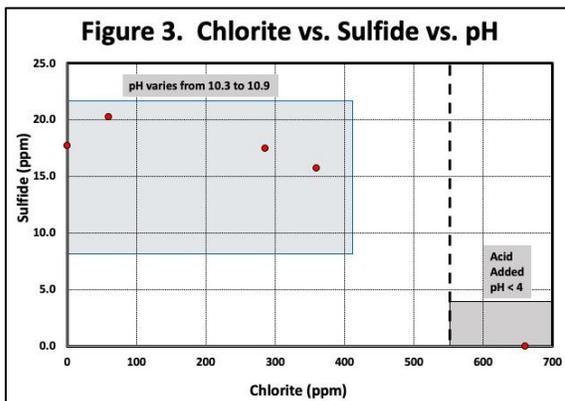
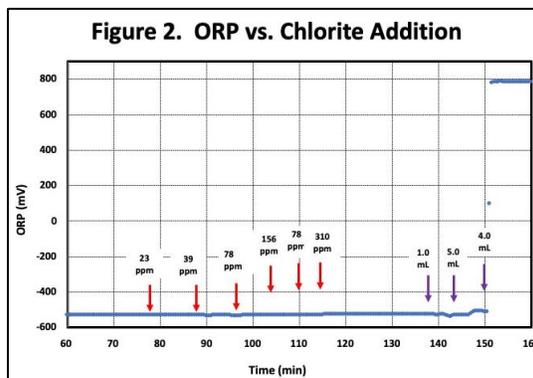
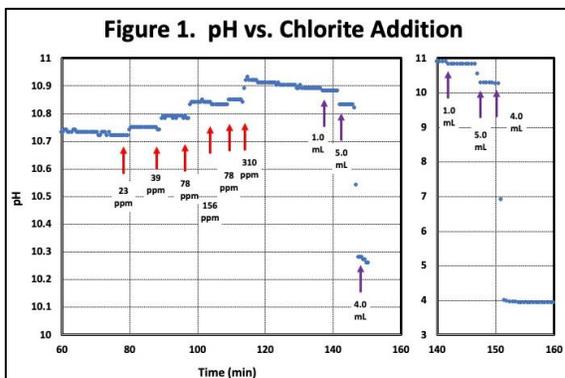
Experimental: The pH and ORP were recorded electronically every 30 seconds in this process, and either the oxidant or the sulfide was added every ~5 minutes (or longer) to give time for the reaction to occur to and the pH and ORP to reach equilibrium.

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, or both, were 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 aliquots of this solution was added.

B. SODIUM CHLORITE

Experiment 1. Unbuffered pH: To 4-L of DI water, about 18 ppm of sulfide was added.



The pH of the solution increased to 10.72 after the addition of Na₂S. The solution remained clear throughout the entire experiment.

The results suggested that there was minimal reaction between chlorite and sulfide at a pH of 10.

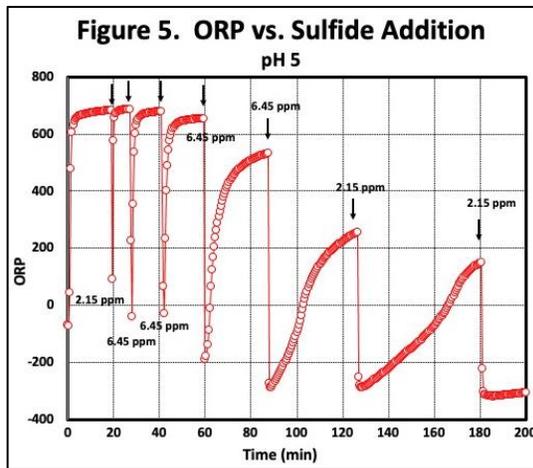
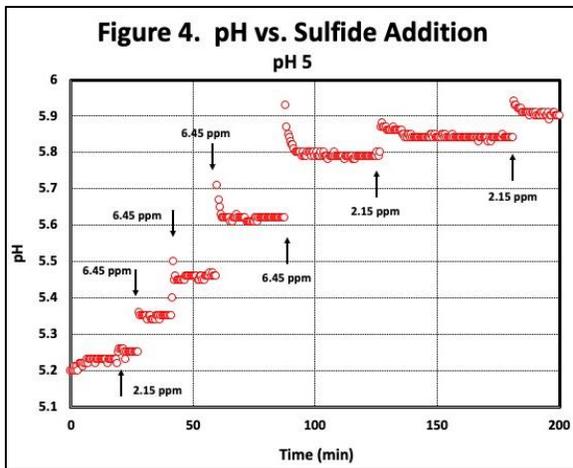
Therefore, after the addition of about 600 ppm of chlorite ion, and no reduction in pH or increase in ORP (Figures 1 and 2), acid was added to reduce the pH. After the addition of 10 mL of 0.1 N HCl, the pH had been reduced to a pH of about 4.

¹ Claims have been made by some that citric acid is an antioxidant and therefore unsuitable for use in this way. Note that a search of the patent literature, 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, many of them do.

At this pH, chlorite became very reactive. There was sufficient chlorite to consume all the sulfide. Testing of the sulfide at the lowest pH showed there was no sulfide left. In addition, the solution remained clear during the entire test. No elemental sulfur was formed.

Sulfide was tracked with the methylene blue method to see if there was a proportional response. Results are shown in Figure 3.

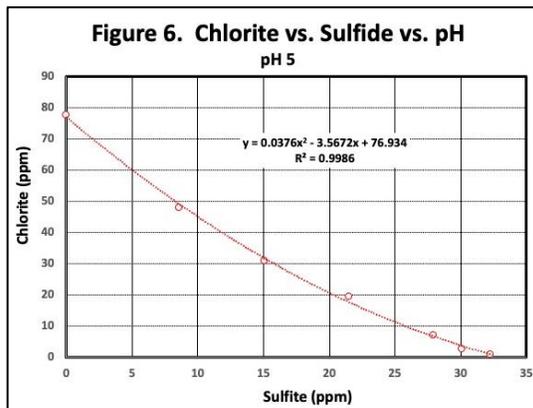
Experiment 2. pH 5: To 4-L of pH 5-buffered DI water was added 1.0 mL of PureCide E (31%



NaClO₂). This equaled 73.8 ppm chlorite ion.

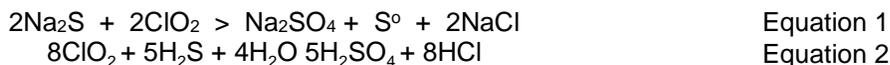
The response of pH and ORP are shown in Figures 4 and 5, respectively. The pH equilibrated rapidly, but the ORP response was slow. This suggests that upon the addition of sulfide, the ORP dropped, and then, over time, slowly increased as the sulfide reacted with chlorite ion.

Figure 6 shows a plot of the dosage of sulfide against the measured chlorite residual. It took 32.25 ppm sulfide to consume 73.8 ppm chlorite ion, or 2.3 ppm chlorite ion per ppm sulfide.



C. CHLORINE DIOXIDE (ClO₂)

Background: The reaction of ClO₂ with sulfide occurs via Equations 5 and 6.

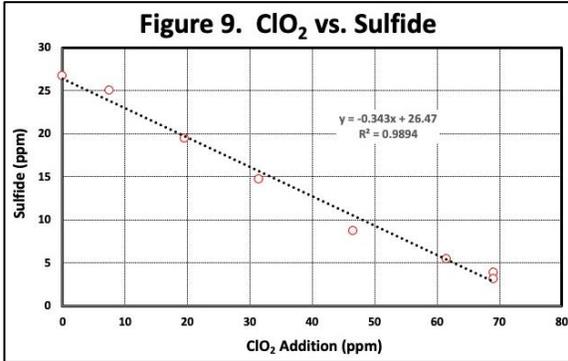
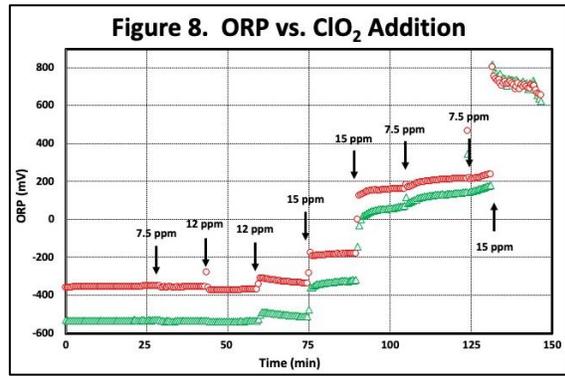
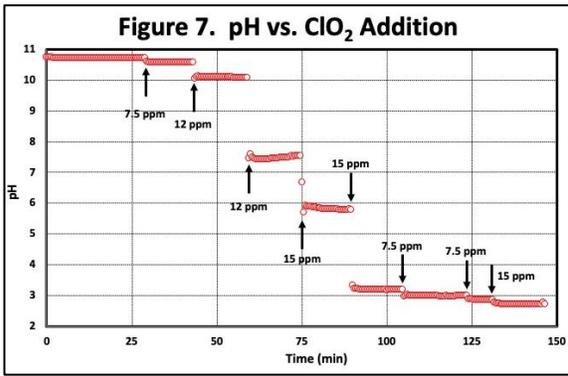


Elemental sulfur and sulfate may be formed in varying amounts, depending on a number of variables. The theoretical stoichiometry can vary from 2.1 to 3.4 ppm ClO₂ to ppm S⁰, depending on conditions. This is close to that found by C.I. Smeck, who found a ratio of 2.7 – 4.0.¹

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

Then, ClO₂ was added in small aliquots. The pH and ORP (two different probes) 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 being formed.

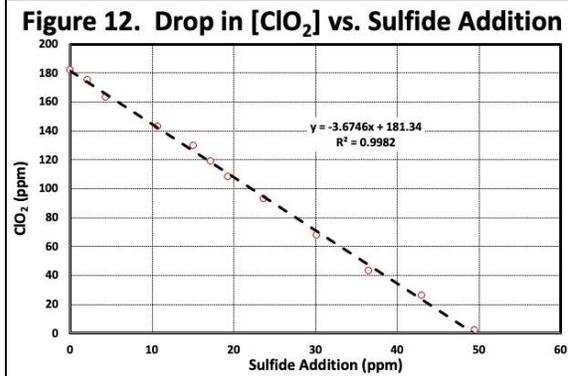
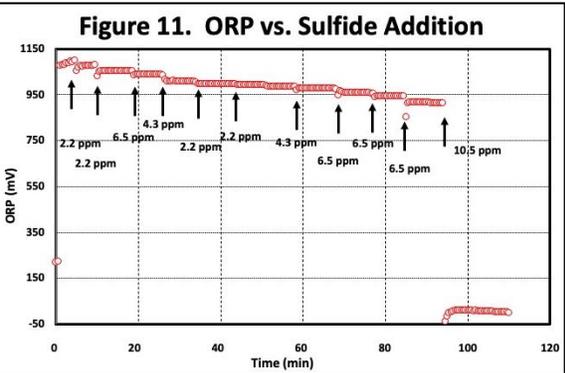
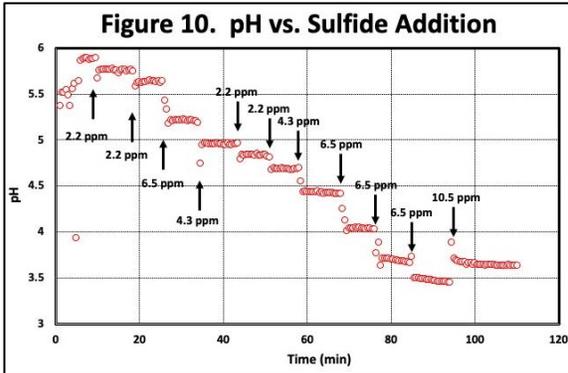


Sulfide was also measured 5 minutes after each addition of ClO_2 . A plot of ClO_2 addition vs sulfide measured in duplicate and averaged is shown in Figure 9. The last data point was ignored in this plot because the endpoint was overshoot, and its inclusion would have skewed the data. The data was fitted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

It took 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 (Figures 10 and 11, respectively). This suggests the reaction of ClO_2 with sulfide occurs almost instantly. Figure 12 shows the decrease in ClO_2 (ppm) 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
Sodium Chlorite	Little or very slow reaction	~ 2.3
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.

E. REFERENCES

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