

## CHLORINE DIOXIDE – RECENT CORROSION STUDIES

### Overview

With the success of ClO<sub>2</sub> use in upstream water treatment, a few companies have raised concerns about the potential impact of ClO<sub>2</sub> corrosion on frac equipment. Several recently published studies, as are described below, should help reduce these concerns.

### Studies

In one study<sup>1</sup>, N80 carbon steel coupons exposed to 15% inhibited HCl for 5 minutes and subsequently to 50,000 ppm sodium chloride brine with 1-5 ppm ClO<sub>2</sub> for 1.5 hour, simulating a frac stage duration, showed no significant difference in corrosion rate compared to control samples without ClO<sub>2</sub> present. Corrosion was dominated by the presence of inhibited HCl and brine.

In another study<sup>2</sup>, the corrosion rate of N80 steel coupons exposed to 7.5% HCl made from either deionized water or produced water each containing ~5 to 40 ppm ClO<sub>2</sub> residual and 2.5 gpt corrosion inhibitor did not show a statistically significant difference in corrosion rate from the baseline comparison with no ClO<sub>2</sub> present. Inhibited tests however did show a statistically significant difference from baseline uninhibited tests. As expected, ClO<sub>2</sub> was shown to regenerate from residual chlorite ion in produced water used in making 7.5% HCl by dilution of more concentrated acid. However, even these higher concentrations did not impact the corrosion rate of the inhibited acid.

In a third instrumental based pilot scale study<sup>3</sup>, which simulated actual conditions used in a slick water frac stage (i.e. velocity, temperature, duration, fluid additives, proppants, in fresh and in produced water, with and without ClO<sub>2</sub> present) a variety of carbon and stainless steel alloys used in high pressure fracturing showed no statistically significant detrimental impact of maintaining 1 to 5 ppm ClO<sub>2</sub> residual in the fluids as shown in Figure 1 and Table 1. However, the study showed the general corrosive, erosive nature of the frac operations. It was found that corrosion rates were extremely

high during the inhibited acid phase of each stage. The corrosion performance of carbon steel in fresh water started out poor<sup>3</sup>. The addition of ClO<sub>2</sub> had minimal impact. However, the presence of brine increased the corrosion rate by more than 30–40 %. Corrosion increased at pH 5.8 or below and decreased above pH 6. While it is known that O<sub>2</sub> levels have significant impact on corrosion rate, the presence of ClO<sub>2</sub> did not increase O<sub>2</sub> levels. The corrosion rate of stainless steel alloys was consistently good even in the presence of ClO<sub>2</sub>. Pitting corrosion was not detected over the course of this study.

### Conclusion

It can be concluded from these studies that acidic solutions are the main contributor to corrosion in frac systems followed by salt from produced water. Frac iron systems just like salt water systems experience wet dry cycles that allow concentration of salts to significantly increase general corrosion and pitting<sup>5</sup>. Proper use of inhibitors can minimize corrosion but not eliminate it<sup>6</sup>. ClO<sub>2</sub> when properly generated and used at typical 1-5 ppm residual concentrations for disinfection of frac water is found to have minimal impact on the corrosive erosive nature of fracturing operations.

Figure 1 Coupon Average Corrosion Rate in 60/40 Blend Fluid <sup>3</sup>

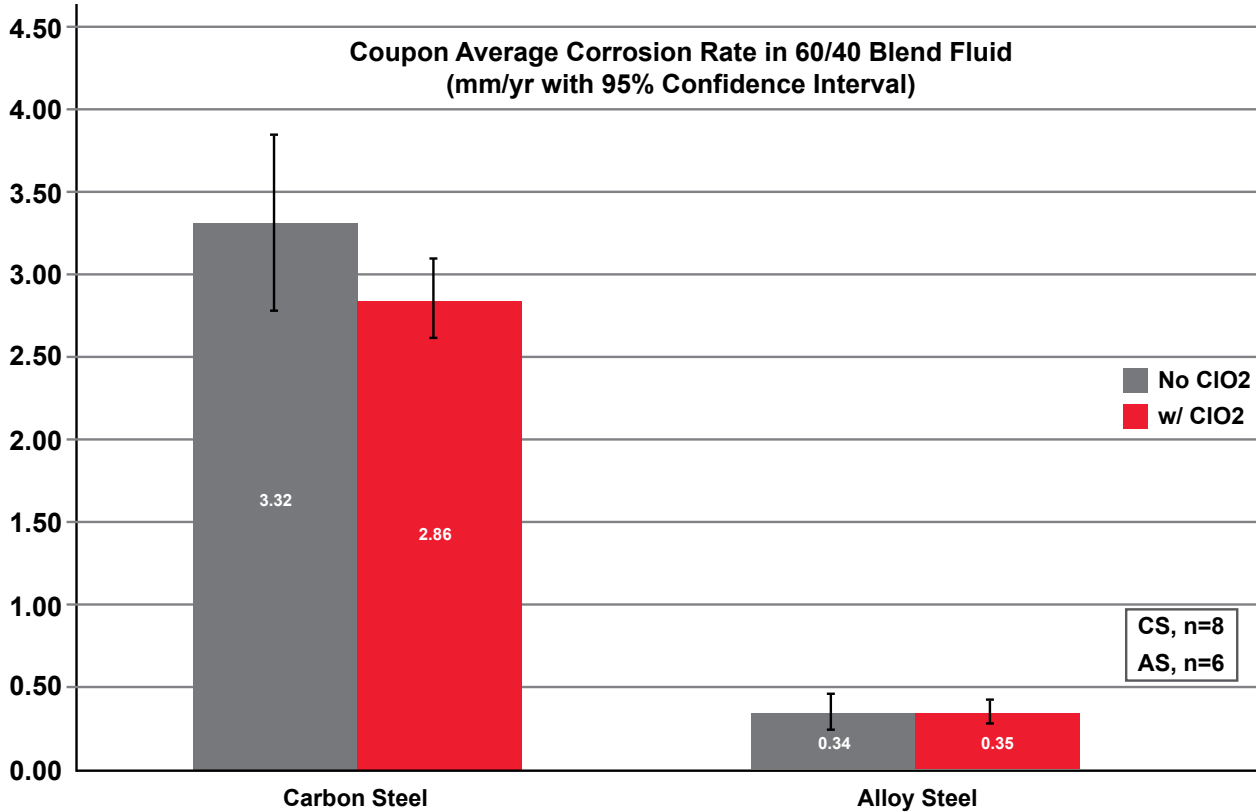


Table 1 Coupons Corrosion Rate (mm/yr) t-Test Statistical Analysis <sup>3</sup>

Corrosion Coupon 60/40 Blend Statistical Analysis t-Test: Two-Sample Assuming Unequal Variances Comparison of 60/40 Blend Mean Corrosion Rate on CARBON STEEL			Corrosion Coupon 60/40 Blend Statistical Analysis t-Test: Two-Sample Assuming Unequal Variances Comparison of 60/40 Blend Mean Corrosion Rate on ALLOY STEEL		
	No ClO2	With ClO2		No ClO2	With ClO2
Mean	3.32	2.86	Mean	0.34	0.35
Variance	0.62	0.13	Variance	0.02	0.01
Observations	8	8	Observations	6	6
Hypothesized Mean Difference	0.00		Hypothesized Mean Difference	0	
df	10.0		df	9	
tStat	1.49		tStat	-0.017	
P(T<=t) one-tail	0.08		P(T<=t) one-tail	0.493	
t Critical one-tail	1.81		t Critical one-tail	1.833	
P(T<=t) two-tail	0.17		P(T<=t) two-tail	0.986	
t Critical two-tail	2.23		t Critical two-tail	2.262	
SD	0.7858	0.3636	SD	0.1361	0.0939
CI (.05, SD, n=8)	0.6570	0.3039	CI (.05, SD, n=8)	0.1428	0.0985
Upper	3.9750	3.1652	Upper	0.4868	0.4437
Lower	2.6610	2.5573	Lower	0.2012	0.2467

## References

- <sup>1</sup> "ClO<sub>2</sub> Disinfection- No Significant Corrosion Impact in Fracturing", White Paper. Baker Hughes, 2018.
- <sup>2</sup> "ClO<sub>2</sub> Disinfection – No Significant Corrosion Impact in Acid Phase of Fracturing", Technical Bulletin E-00012. International Dioxide Inc., 02-20-18.
- <sup>3</sup> Monroe, Stephen. "Corrosivity of Chlorine Dioxide on Typical Oilfield Iron". Produced Water Society Seminar 2018, 13 February 2018, Marriott Sugar Land Town Center, Sugar Land, TX, Conference Presentation.
- <sup>4</sup> Fontana, Mars G. (1986) Corrosion Engineering. McGraw-Hill Book Co., NY, ISBN: 0-07-021463-8, Corrosion Ranges.
- <sup>5</sup> Fontana, Mars G. (1986) Corrosion Engineering. McGraw-Hill Book Co., NY, ISBN: 0-07-021463-8, Fig. 8-1 Corrosion of Ordinary Steel in the Sea.
- <sup>6</sup> Prues, W.et al., "Chemical Mitigation of Corrosion by Chlorine Dioxide in Oilfield Waterfloods." Material Performance, Vol 24, No.5, pp 45-50 (May 1985).
- <sup>7</sup> "Chlorine Dioxide in Fracturing Water Disinfection - Effectiveness Brings Competitive Scrutiny", White Paper L-0002 Rev 1. International Dioxide Inc., 11-30-16.
- <sup>8</sup> "Erroneous Claims from Competitors in the Market", White Paper L-0001 Rev 1. International Dioxide Inc., 11-30-16.

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