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Chlorine Dioxide – Recent Corrosion Studies

Overview

With the success of ClO_2 use in upstream water treatment, a few companies have raised concerns about the potential impact of ClO_2 corrosion on frac equipment. Several recently published studies, as are described below, should help reducethese concerns.

Studies

In one study[1], 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_2 for 1.5 hour, simulating a frac stage duration, showed no significant difference in corrosion rate compared to control sampleswithout ClO_2 present. Corrosion was dominated by the presence of inhibited HCl and brine.

In another study[2], 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_2 residual and 2.5 gpt corrosion inhibitor did not show a statistically significant difference in corrosion rate from the baseline comparison with no ClO_2 present. Inhibited tests however did show a statistically significant difference from baseline uninhibited tests. As expected, ClO_2 was shown to regeneratefrom 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 corrosionrate of the inhibited acid.

In a third instrumental based pilot scale study[3], 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_2 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_2 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[3]. The addition of ClO_2 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_2 levels have significant impact on corrosion rate, the presence of ClO_2 did not increase O_2 levels. The corrosion rate of stainless steel alloys was consistently good even in the presence of ClO_2. Pitting corrosion was not detected over the course of this study.

Conclusion

It can be concluded from these studies that acidic solutions arethe 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[5]. Proper use of inhibitors can minimize corrosion but not eliminate it[6]. ClO_2 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 [3]

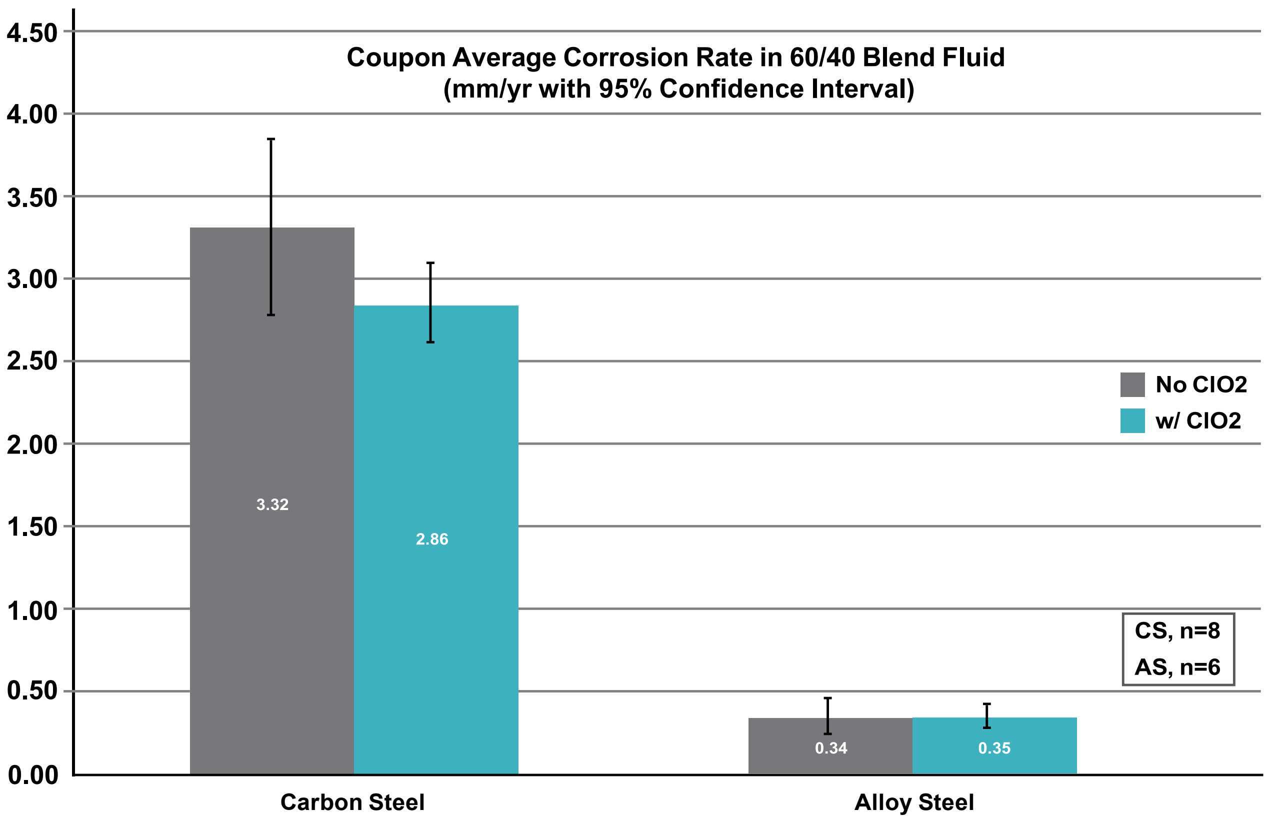

Table 1 Coupons Corrosion Rate (mm/yr) t-Test Statistical Analysis [3]

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

[1] "ClO_2 Disinfection- No Significant Corrosion Impact in Fracturing", White Paper. Baker Hughes, 2018.

[2] "ClO_2 Disinfection – No Significant Corrosion Impact in Acid Phase of Fracturing", Technical Bulletin E-00012. International Dioxcide Inc., 02-20-18.

[3] 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.

[4] Fontana, Mars G. (1986) Corrosion Engineering. McGraw-Hill Book Co., NY, ISBN: 0-07-021463-8, Corrosion Ranges.

[5] 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.

[6] 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).

[7] "Chlorine Dioxide in Fracturing Water Disinfection - Effectiveness Brings Competitive Scrutiny", White Paper L-0002 Rev 1. International Dioxcide Inc., 11-30-16.

[8] "Erroneous Claims from Competitors in the Market", White Paper L-0001 Rev 1. International Dioxide Inc., 11-30-16.

Note: The information contained in this publication is current as of May, 2018. Please contact International Dioxcide, Inc. to determine if this publication has been revised.

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