

ClO₂ DISINFECTION – NO SIGNIFICANT CORROSION IMPACT IN ACID PHASE OF FRACTURING

Overview

Chlorine dioxide, ClO₂, has emerged as one of the best treatment technologies for the disinfection of water used in fracturing to recover oil and gas. However, fracturing systems are complex dynamic processes and corrosion is impacted by many variables: high water velocity, high proppant loading, chloride in produced water, atmospheric oxygen, acids used to open the fracture face as well as other additive chemistries all contribute to the corrosion of pumping and surface equipment.

Recently, claims of excessive corrosion have emerged from some service companies involved in this market. Newly published studies^{1,2} should help alleviate these concerns. The study described below investigated the impact of ClO₂ and chlorite ion, ClO₂⁻, on the corrosion of N80 carbon steel during the acid phase of the fracturing process with both fresh water and produced water. Chlorite ion, ClO₂⁻, is both the precursor of ClO₂ generation and an initial byproduct of disinfection reactions. The study was conducted at SET Laboratories in Stafford, TX. SET has extensive experience in evaluating corrosion in oilfield processes.

Methods

Short term, four hour, exposure screening tests were conducted to determine differences in corrosion rate of the HCl spearhead step of the fracturing process. The intent of this test was to determine if the presence of ClO₂ or ClO₂⁻ ion significantly alters the corrosive nature of the ~7.5% inhibited HCl used as a spearhead for each fracturing stage.

The bench-scale tests were conducted at ambient temperature in Hastaloy C autoclaves rated at 5000 psi design pressure. Nitrogen at 200 psig was added to minimize off gassing. Two N80 carbon steel coupons of ~ 28 sq cm surface area

were included in each test. The coupons were isolated from the autoclave walls and each other using Teflon™ mesh and prepared in accordance with standard practice for such testing. The acid test solution was made using 37% HCl. The acid was diluted to 7.5% use concentration by adding the appropriate volume of corrosion inhibitor and oxidant laden solution. The autoclave was closed for four hours at ambient temperature. Following the exposure period, the test coupons were removed, cleaned, bead blasted, weighed, and photographed in accordance with standard practice for such tests. Material loss from exposure and corrosion rate were calculated based on the average of the two coupons in each test. The test solutions were assayed for ClO₂ using Palin ChlordioX Plus (Amperometric) and standard Iodometric titration methods.

Two corrosion inhibitors were chosen for this investigation: TCA-6038 sourced from X-CHEM, a 20-30% Pyridine Benzyl Quaternary Ammonium Chloride in a methanol water mixture and CI-27 sourced from Baker Hughes, a proprietary mixture of methanol, fatty acids, polyoxyalkylenes, olefins, and 5-10% propargyl alcohol solution.

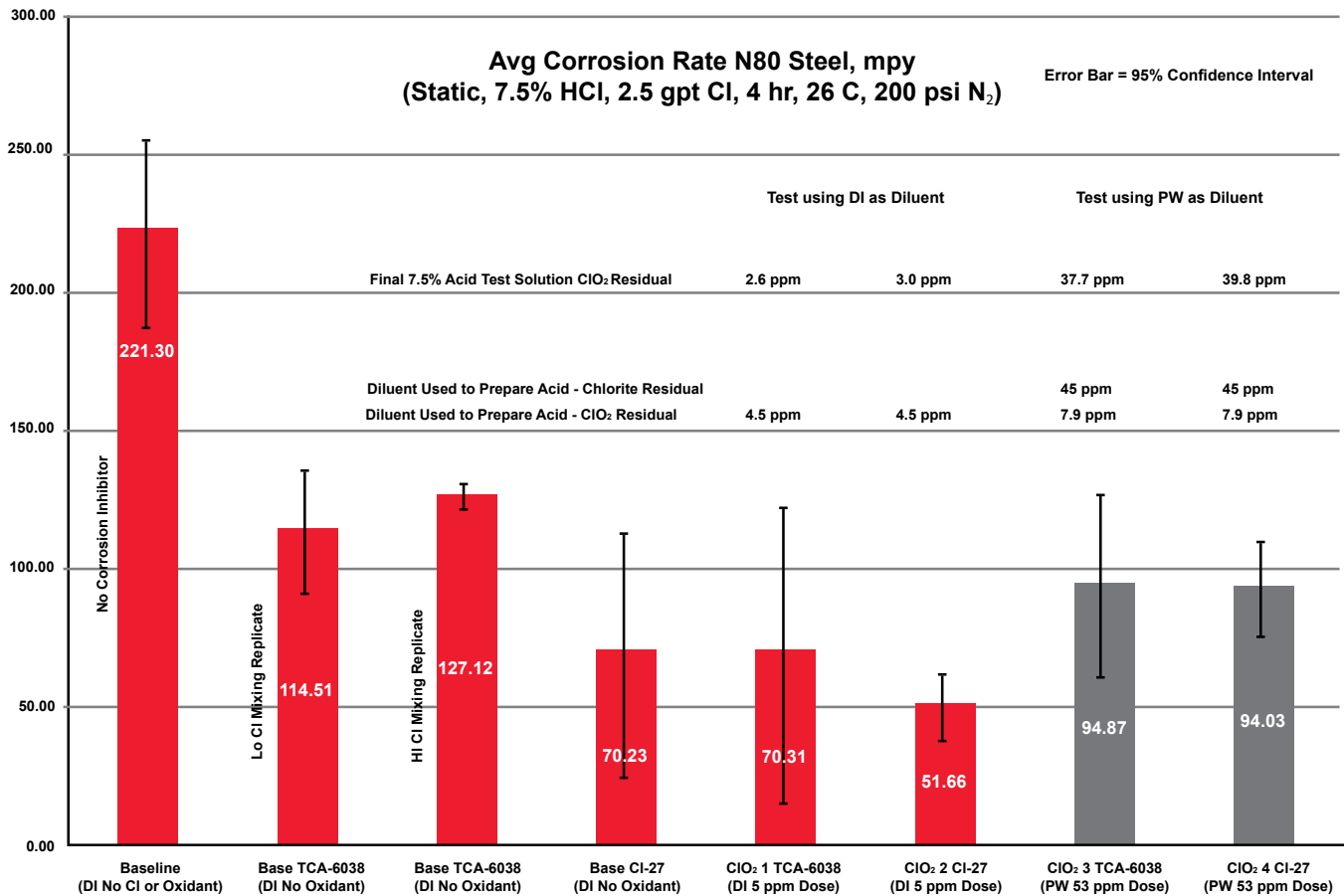
Produced water was provided by Fountain Quail from an active New Mexico fracturing site.

The dose levels of ClO₂ were chosen based on practical field application guidelines, 1–5 ppm ClO₂ residual at the working tanks feeding the blender. This level of residual ClO₂ was sufficient to provide a full bacterial kill in the water feeding the blender. The produced water used in this test exhibited a significant demand for ClO₂ and required dosing at ~50 ppm to achieve sufficient residual ClO₂.

Results and Discussion

The results shown in Figure 1 below reveal a negligible impact on corrosion rate due to the inclusion of ClO₂ or chlorite.

Figure 1: Results of the Corrosion Test



Conclusions

Laboratory experiments using concentrations and conditions similar to field applications for ClO₂ disinfection of frac water indicate that the acid phase fluid corrosion rate of N80 carbon steel coupons was not statistically altered by the presence of ClO₂. The corrosion rate of the coupons exposed to 7.5% HCl made from DI and produced water containing ~5 to 40 ppm ClO₂ residual and 2.5 gpt corrosion inhibitor did not show a statistically significant difference in corrosion rate from the baseline comparison with no ClO₂ present. Inhibited tests however did show statistically significant difference from the baseline uninhibited test. ClO₂ was found to regenerate from

residual chlorite ion in produced water when preparing 7.5% HCl by dilution of more concentrated acid. However even these higher ClO₂ concentrations did not impact the corrosion rate.

Reference

1. "ClO₂ Disinfection - No Significant Corrosion Impact in Fracturing", White Paper. Baker Hughes, 2018.
2. 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.

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International Dioxide

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International Dioxide

40 Whitecap Drive
North Kingstown, RI 02852
1-800-477-6071

idiclo2.com

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