

THE DEVELOPMENT OF CORROSION INHIBITORS FOR MITIGATING ALKALINE CARBONATE STRESS CORROSION CRACKING

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ABSTRACT

Corrosion inhibitors have widespread use in the crude oil refining industry for corrosion protection and mitigation. Over the years, certain classes of inhibitors have been established as industry standards to confront specific corrosion mechanisms encountered throughout the refinery process. Although alkaline carbonate stress corrosion cracking (ACSCC) has been a well-documented corrosion mechanism found in the overheads of fluid catalytic cracking units (FCCU), gas separations units (GSU) and sour water strippers (SWS), there is a lack of inhibitor offerings to mitigate this type of mechanism. Traditional methods used to mitigate ACSCC include the use of post-weld treatments or costly metallurgy upgrades. With a limited number of examples highlighting the use of chemical abatement of such a corrosion mechanism, the present study describes the use of inhibiting compositions to mitigate stress corrosion cracking (SCC) in refinery processes, particularly due to environments high in carbonate (CO_3^{2-}) concentration. Herein, an optimized blend is shown to protect the metal surface against carbonate SCC and other corrosion mechanisms.

Key words: corrosion inhibitors, alkaline carbonate stress corrosion cracking,

INTRODUCTION

Organic corrosion inhibitors (CI) have widespread use in the crude oil refining industry for corrosion protection and mitigation.¹ An effective corrosion inhibitor is a chemical substance that is applied in low concentration into a stream which suppresses or mitigates a corrosion mechanism.^{2,3,4} Inhibitors can be classified into two classes: adsorption or film-forming with organic inhibitors falling under the adsorption class. In this type of inhibitor a self-assembled structure is formed, where an array of hydrocarbon tails extend away from the metal surface and the polar groups (e.g., N in amines) chemisorb onto the metal surface.² Over the years, certain classes of inhibitors have been established as industry standards to confront specific corrosion mechanisms encountered throughout the refinery process. Examples include, filming and neutralizing amines used in crude units to combat aqueous corrosion; polysulfides used in FCCU to combat hydrogen blistering, cracking and embrittlement; P-based chemistries to combat naphthenic acid corrosion.⁵

Intergranular cracking and failure of carbon steel piping and vessels made of carbon steel occurs in various refinery overhead streams or other systems. A well-documented corrosion mechanism affecting refinery units is alkaline carbonate stress corrosion cracking (ACSCC).⁶ This catastrophic corrosion mechanism manifest itself as surface-breaking cracks that typically develop at or near carbon steel welds under a combination of tensile stress and corrosion in an alkaline carbonate containing sour environment.⁶ These environments typically have a pH greater than or equal to 8.5 with a carbonate concentration of 1000 ppm or greater.⁷

Units affected by this type of mechanism include FCCUs and sour water strippers (SWS). These events have been documented in the main fractionator overhead systems of FCCU's, including the overhead condensers and accumulator, and in downstream areas such as the wet gas compressor knock out drums and the light end fractionation units of the GSU and all associated piping in these areas. There have also been some instances of ACSCC occurring in other refinery process units that handle and treat the condensed waters.^{6,7,8,9,10}

Traditionally, ACSCC has been mitigated by stress relief obtained through post weld treatment (PWHT) at temperatures of 621 °C (1150 °F).^{6,7} However, if heating is not done properly, the potential for ACSCC is not reduced. Other methods that have been used include nonmetallic coatings, resistant alloys, water washing, and metavanadate-based inhibitors.⁶ One example in the literature touts the use of imidazoline compounds, fatty amides, and fatty esters, individually or mixed, to inhibit ACSCC.¹¹ However, no other examples of the use of an organic inhibitor to mitigate this type of mechanism were found. Herein, an inhibiting composition comprising a dispersant and a corrosion inhibitor is shown to protect the metal surface against carbonate SCC and other corrosion mechanisms.

EXPERIMENTAL PROCEDURE

The inhibitors tested in this study are listed in Table 1 below. The inhibitors were evaluated using slow strain rate (SSR) testing to evaluate their performance towards mitigating ACSCC, linear polarization resistance (LPR) to evaluate their performance in an NH_4Cl rich environment, and wheel box testing to evaluate their performance in an H_2S rich environment.

Table 1. Corrosion Inhibitors Evaluated in this Study

Inhibitor	Test
Inhibitor A	SSR, LPR
Inhibitor B	SSR, LPR
Inhibitor C	SSR, WB, LPR
Inhibitor D	SSR, LPR
Inhibitor E	SSR, WB, LPR
Inhibitor F	SSR, WB, LPR

Slow Strain Rate (SSR) Testing

The performance of the inhibitors was evaluated using slow strain rate (SSR) testing of C1018 carbon steel coupons. The testing was performed generally in accordance with the methodology described in NACE TM0198-2016 "Slow Strain Rate Test Method for Screening Corrosion-Resistant Alloys for Stress Corrosion Cracking in Sour Oilfield Service." Sodium chloride (NaCl) was used in the test solution in order to hinder the re-passivation process at the crack tip and as a result, the propagation of intergranular SCC was accelerated sufficiently to occur within the timeframe of the SSR test. Table 2 summarizes the experimental conditions used in the SSR testing.

Table 2. Summary of Test Conditions

Experimental Parameter	Parameter
Passivation Medium	DI Water
Passivation Temperature	248 °F
Passivation Time	20 Hours
Chloride Concentration (Cl^-)	1,224 mg / L
Bicarbonate Concentration (HCO_3^{-1})	52,750 mg / L
Carbonate Concentration (CO_3^{-2})	12,058 mg / L
Starting pH	~9.0
Inhibitor Dose	200 mg / L
Nitrogen Pressure	200 psi
Extension Rate	1.0×10^{-6} in / s
Testing Temperature	250 °F

Slow Strain Rate Tests (SSRT) test specimens were manufactured from AISI 1018 mild / carbon steel and prepared in accordance with NACE T0198-2016. Slow strain rate tests were conducted on a total of 10 specimens; two specimens were exposed to an inert environment (nitrogen), two specimens were