

Chemical Treatment To Mitigate Polythionic Acid SCC Without A Soda-Ash Wash: Laboratory And Plant Experience

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ABSTRACT

A novel oxidative chemical treatment method is already being used to neutralize pyrophoric metal sulfides present in Hydroprocessing reactor systems. It is hypothesized that this treatment will similarly neutralize the iron sulfides which contribute to the formation of polythionic acids. A simple laboratory test has been developed to test the effectiveness of the chemical treatment. Previous experimental studies into polythionic acid stress corrosion cracking (PTASCC) have typically immersed stainless steel specimens in Saman's solution, made by bubbling gaseous SO₂ and H₂S through the cell at controlled rates to produce a mixture of di-thionic through hexa-thionic acids along with sulfuric and sulfurous acids. In Saman's solution, it can be difficult to obtain cracking even with the standard sensitizing heat treatments suggested in ASTM A262¹. To circumvent these challenges, the current work uses standard U-bends (ASTM G30²), coated with an air-sprayed suspension of iron sulfide powder. Specimens are suspended in saturated air (100% RH) at 50°C. Similarly, slow strain rate testing (SSRT) specimens were produced and tested using similar methods to identify the effect of exposure to FeS and various SCC mitigation and elimination treatments. To date, results indicate that the test method is successful for achieving PTASCC; test exposures of the oxidative chemical treatment are currently in progress. Parallel to laboratory testing, trials the treatment on actual refinery Hydroprocessing equipment are in progress. A hydrotreating reactor and associated process equipment including feed/ effluent exchangers, fired heater and piping systems, previously treated with soda-ash wash during shutdowns was instead treated only with the oxidative chemical treatment for the current outage, and then opened to air. Internal inspections using standard API recommended methods under a complex risk based inspection program to examine for PTASCC did not reveal any evidence of cracking. The authors hope that these positive results, along with future work, may allow this method for PTASCC mitigation to be recognized in NACE SP0170³.

Key words: Polythionic acid, Stress corrosion cracking, stainless steel, sensitization

INTRODUCTION

Different refiners have a variety of procedures in place for hydroprocessing reactor and reactor system shutdowns, depending on the scope of the work to be performed during the downtime. If activities are to be performed inside the reactor (e.g. inspection, maintenance, catalyst changeout, etc.) such that the reactor must be opened to air, shutdowns must include steps to address the various hazards. These same steps must also be applied to associated process equipment related to the reactor system susceptible to similar hazards and damage mechanisms.

One well-known hazard comes from the active metal-sulfide catalyst surfaces. If exposed to air, even after a hydrogen strip or sweep operation (or similar contaminant removal method) to remove most of the residual hydrocarbon, the self-heating nature of the catalyst can result in ignition. Active catalyst is often referred to as being pyrophoric for this reason, although it is more accurate to describe the catalyst as self-heating⁴. To avoid potential combustion, catalyst unloading is conventionally performed under an inert nitrogen purge. A novel sodium-nitrite based oxidative chemical treatment, marketed as QuenchRX®[†] by Refined Technologies, Inc. (RTI)[†] has been demonstrated to successfully destroy catalyst metal sulfides by oxidation such that the nitrogen purge is no longer required⁵. Furthermore, the catalyst need not be classified as pyrophoric or self-heating waste.

Besides the potential for combustion, stress corrosion cracking potential exists. Typically, 300-series stainless steel equipment operating above about 750°F [399°C] (850°F [454°C] for some grades) is considered sensitized. When sensitized stainless steel encounters a corrosive, acidic solution, intergranular corrosion is likely to occur. In a sulfidizing hydroprocessing environment, the applicable acid is referred to as polythionic acid, which results from metal sulfide scales reacting with moisture and oxygen⁶. At the relatively high levels of residual stresses present in most stainless steel components, which are not typically stress relieved, intergranular corrosion from polythionic acid produces stress corrosion cracks, i.e. PTASCC. Typical practice is to apply a basic solution prior to or immediately after opening the equipment and exposing it to an oxygen containing atmosphere, to neutralize potential polythionic acids that may form. Soda ash (Na_2CO_3) is most commonly used, however potassium carbonate (K_2CO_3) and even tri-sodium phosphate (TSP) have been successfully used. These treatments are intended to leave a dry, basic film on the surface of the equipment that can immediately neutralize any polythionic acids which form if the surface is exposed to moisture. NACE SP0170³ contains additional details on protection of austenitic stainless steels from PTASCC during a shutdown of refinery equipment.

Because the nitrite-based treatment is effective at destroying metal sulfide scales on catalyst surfaces, it was hypothesized that it would also be effective at destroying sulfide scales on the pressure equipment surfaces. Once the metal sulfides are destroyed (oxidized), they will be unable to form polythionic acids even if the surface is exposed to moisture and oxygen. If confirmed, the sodium-nitrite treatment could potentially replace two time-consuming shutdown activities: nitrogen-purged catalyst removal and soda ash washing, while maintaining safety and equipment integrity. To test this hypothesis, a combination of field trials and laboratory experiments were performed, as described below.

FIELD EXPERIENCE

A number of field trials of the nitrite-based treatment have been performed with overall success. Initial trials were limited to carbon steel equipment and primarily confirmed the efficacy of the treatment at

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eliminating the pyrophoric or self-heating behavior of metal-sulfide catalysts in a commercial naphtha hydroprocessing unit. A second set of field trials using an earlier iteration of the application system was performed on 300-series stainless steel hydrotreater equipment with overall success. However, given the limited experience with the nitrite-based treatment at this time, the application also included the circulation and deposition of an alkaline salt on the surfaces of equipment. Although no cracking occurred during this second trial, it also did not rely entirely on the treatment to prevent cracking.

The third and most recent field trial is of primary interest to the refining community, as it was applied to 300-series stainless steel hydrotreater reactor, charge heater and feed/effluent section equipment without the auxiliary deposition of a neutralizing alkaline film following the treatment. In other words, this trial relied only on the action of the nitrite-based treatment to prevent both pyrophoric catalyst activity as well as PTASCC. Internal inspections performed at the end of the outage did not detect any cracking, and the unit was successfully restarted and has been operating since the trial without issue. The inspections included the standard API recommended inspection methods for the associated process equipment under a rigorous risk based inspection program.

This trial was performed using the current application process – that is, the system was first flushed using organic solvent with the intent of removing hydrocarbons and some of the more lightly-adhered coke deposits using RTI's QuickTurn RX Process[†]. The nitrite solution containing a small addition of amine oxide to provide a chemical dispersion mechanism and a pH buffer was injected into the system during shutdown over the period of 4-6 hours until the outlet targets for nitrite and amine oxide ion breakthrough were achieved. Monitoring is also used to confirm that the stoichiometric required oxidizing reactants were consumed in excess given the known metal sulfide mass present on the catalyst materials. Following the oxidation process the system was further flushed with an additional concentrated phosphate buffer solution. The purpose of the buffer component in the treatment solution and the subsequent post flush is to keep the pH at or below approximately 8. NaOH and NH₃ are biproducts of the treatment reaction. At the moderately high temperatures of application (maximum of 250°F [121°C]) the pH buffer intends to alleviate concern for caustic stress corrosion cracking and personnel exposure to materials with elevated pH as well as maintain NH₃ in solution.

EXPERIMENTAL PROCEDURE

An experimental approach was devised to test the claim that the nitrite-based chemical treatment would effectively destroy iron sulfide films on the surfaces of stainless steel. Various specialized laboratory tests have been developed which are related to PTASCC or more generally, intergranular corrosion and SCC. However, these tests largely seek to test the degree of sensitization (ASTM G108⁷), the resistance of material to sensitization or the effectiveness of a modification to the alloy itself (ASTM A262¹), or the intergranular corrosion action of a specific environment (e.g. Samans' work⁹). In contrast, the intent of the current work was to determine whether the nitrite-based treatment would effectively destroy iron sulfide and prevent PTASCC of sensitized material. To that end it was necessary to test specimens of uniform composition and sensitized to the same degree by a common heat treatment and exposed to iron sulfide, moisture, and oxygen with and without the nitrite-based treatment.

Materials, Heat Treatment, and Specimens

Two plates from different lots of the same heat (same chemical composition) were obtained in thicknesses that would permit the extraction of U-bend (0.1875-in [4.8 mm] starting plate thickness) and

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slow strain rate test (SSRT) specimens (0.500-in. [12.7mm] starting plate thickness). The chemical composition of this heat is shown in Table 1.

Table 1.
Chemical composition (in wt%) of Heat B61408 TP 304/304H dual-certified stainless steel.

Element	C	Mn	P	S	Si	Cr	Ni	Mo	Cu	N
Measured	0.06	1.01	0.034	<0.001	0.53	18.20	8.21	0.54	0.56	0.07
Specification A240 TP304H	0.04-0.10	2.00	0.040	0.030	0.75	18.00-19.50	8.00-10.50	0.75	0.75	0.10

Specimen blanks were extracted from the source plates and subjected to a heat treatment at 1175°F (635°C) for 72 hours. Notably this heat treatment is quite different from the typical sensitization heat treatment of 1250°F (675°C) for 1 hour, as suggested by ASTM A262¹. The heat treatment was selected to produce a sensitized microstructure that was expected to be most crack-prone, not simply with a high degree of sensitization measured in corrosion tests (e.g. double-loop electrochemical potentio-kinetic reactivation tests⁷). Nagashima et al. Similarly used a lower-temperature, longer-duration sensitization treatment of 1112°F (600°C) for 120 hours⁸.

Sensitization is a time and temperature dependent phenomenon related to the rate of chromium diffusion which increases with increasing temperature. Initially, chromium near the grain boundaries reacts with carbon to precipitate chromium carbides and deplete the surrounding matrix. During this first stage of sensitization, additional time at temperature results in more severe local chromium depletion in a solute-depleted zone (SDZ) adjacent to the grain boundary. Once the carbon has been consumed, additional time at temperature encourages chromium diffusion from the bulk grain to the SDZ. With sufficient time at temperature, stabilization will be achieved, where the chromium concentration in the SDZ has again become nearly equal to that of the bulk grain and intergranular corrosion does not occur. Samans recorded this and defined upper time-temperature-sensitization (TTS) limits for cracking in both polythionic acid and copper sulfate solutions⁹. Samans' TTS diagrams suggest that the 1175°F (635°C), 72 hour heat treatment is approximately centered in the "nose" of the sensitization region for a 0.06 wt% Carbon Type 304 stainless steel. The microstructure of the plates before and after heat treatment, etched electrolytically with 10% oxalic acid at 1 A/cm² for 90 seconds, is shown in Figure 1.

It was further recognized that the degree of cold work prior to sensitizing heat treatments would influence the stabilization behavior. Garcia et al. reported that more than approx. 20% cold work prior to sensitizing heat treatment encouraged chromium carbide precipitation along slip planes¹⁰. This encouraged anodic dissolution at more disperse locations, as opposed to being concentrated at SDZs near the grain boundaries. For this reason, the sensitizing heat treatment was applied prior to introduction of cold work into the test specimens. Following heat treatment, U-bend and SSRT specimen were machined to final dimensions from the blanks.

U-Bend Test Method

All U-bend tests were performed according to the guidelines provided in ASTM G30². The U-bend specimens were 5-in (127 mm) long by 0.75-in (19 mm) wide with two bolt-holes straddling the bend centerline at a distance of 4-in (102 mm) on center. The two-stage bending process recommended in ASTM G30² was used. The specimens were bent around a 1-inch (25 mm) mandrel during the first stage. The second stage included tightening the bolt and nut to the specimen and was performed just prior to exposing the specimens to the test environment. In order to increase the likelihood of cracking during the tests, two specimen thicknesses were selected to produce two different amounts of cold work. Half the U-bends were machined to a thickness of 0.0625-in (1.6 mm), while the other half were left at 0.1875-in

(4.8 mm). The bend extrados of each sample, regardless of thickness, was freshly polished to 600 grit before each test or before coating with FeS (within 30 minutes) using silicon carbide paper (600 grit). After polishing, the specimen was rinsed successively with acetone and deionized water and then immediately dried with compressed nitrogen.

After the final bend stage, the specimens were fastened to a specimen rack that was suspended in the vapor phase of a tall glass vessel. The vessel contained approximately 2 liters of deionized water to serve as a source of humidified air. The water temperature was maintained at 50°C and zero-air gas was sparged through the water to produce high humidity conditions (~100% RH) in the test vessel. The U-bend specimens were suspended above the water level with extrados facing down, such that condensed water droplets would collect and drip from the U-bend apex.

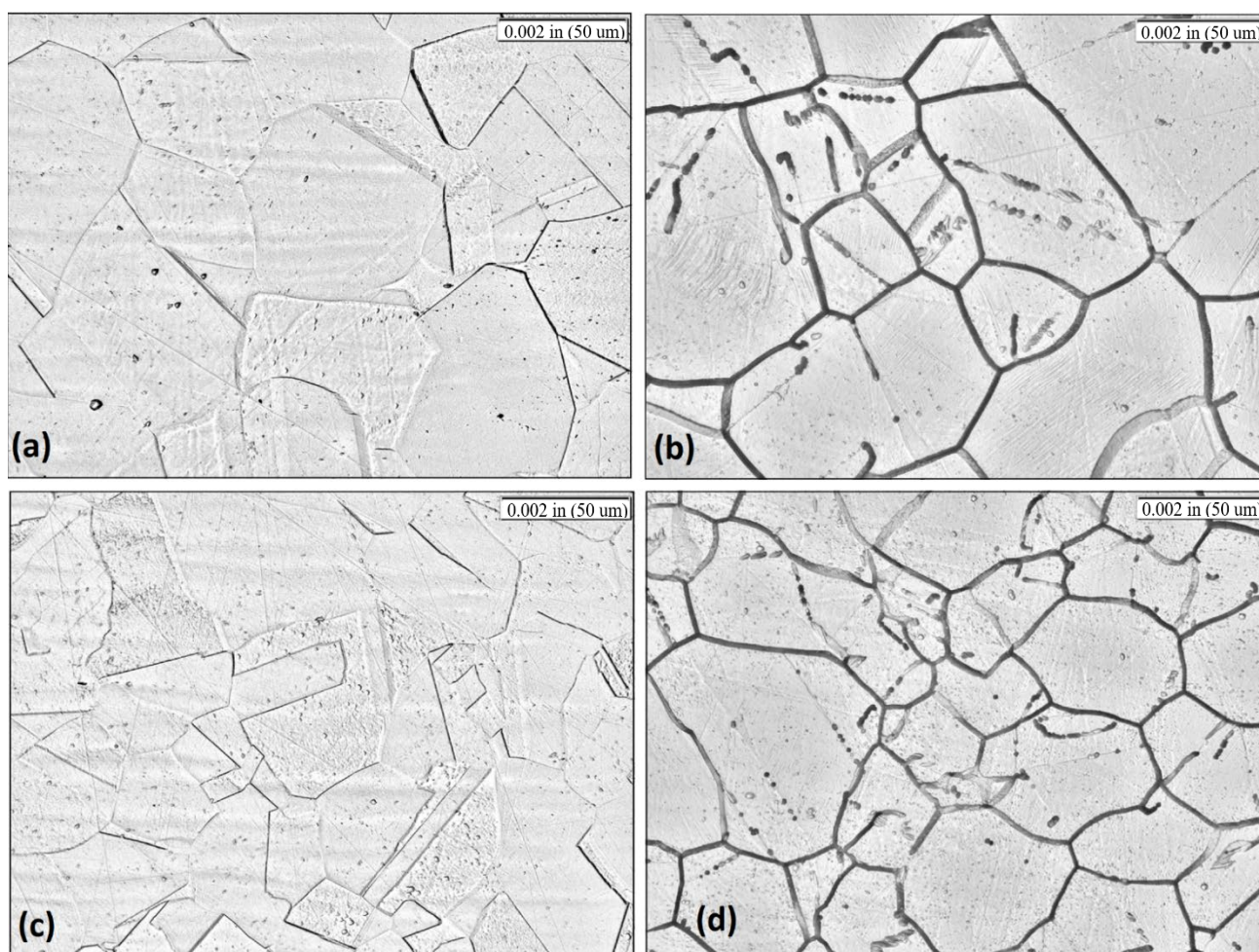


Figure 1: Microstructure of as received (a) and (c) plate material vs 1175°F (635°C)/72 hour sensitized (b) and (d) material. (a) and (b) show the 0.1875-in. (4.8 mm) plate; (c) and (d) show the 0.500-in. (12.7 mm) plate. All etched with 10% oxalic, 1A/cm², 90 sec.

SSR Test Method

All SSR tests were performed according to the guidelines provided in ASTM G129-00¹¹ using cylindrical tensile specimens at a constant extension rate of 10⁻⁶ in/s, unless otherwise noted. For the 1-inch gage length specimen, this corresponds to an initial strain rate of 10⁻⁶ s⁻¹. For each test, the SSR specimen