



NACE Standard RP0170-2004
Item No. 21002

Standard Recommended Practice

Protection of Austenitic Stainless Steels and Other Austenitic Alloys from Polythionic Acid Stress Corrosion Cracking During Shutdown of Refinery Equipment

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Foreword

This standard recommended practice provides methods to protect austenitic stainless steels and other austenitic alloys from polythionic acid stress corrosion cracking (PTA SCC) occurring during downtimes and contiguous shutdown and start-up periods. This standard is directed toward preventing stress corrosion cracking (SCC) by polythionic acids that are formed by the reaction of sulfide corrosion products with oxygen and water. For practical purposes, it should be assumed that such acids can be formed by reaction of oxygen and water with oxidizable sulfur species (sulfur, H₂S, metal sulfides).

Primary protection methods to prevent polythionic acid formation include appropriate material selection, avoidance of oxygen entry, alkaline washing of surfaces, and the prevention of liquid water formation. Regardless of the protection method selected, appropriate confirmation steps to validate compliance with the requirements of this standard are required by the user to ensure protection is provided.

This standard is intended primarily for petroleum refining industry materials and corrosion engineers as well as inspection, operations, and maintenance personnel. While the focus of this standard is on refining industry units such as desulfurizing, hydrocracking, and hydrotreating in which the incidence of PTA SCC has been comparatively high, it can be applied to other units using austenitic stainless steels and other austenitic alloys, such as crude distillation units and fluid catalytic cracking units, when the user may have a concern for PTA SCC. The user must consider other factors such as the effect of the alkaline chemicals on catalysts, as well as the appropriate means and protective equipment required for handling these chemicals. For the purposes of this standard, the term *other austenitic alloys* refers to those alloys of nickel, iron, and chromium that may be susceptible to PTA SCC.

The techniques described in this standard are not designed to remove chloride deposits, but should minimize the possibility of chloride SCC (Cl SCC) by the wash solutions.

This standard was originally prepared in 1970 by NACE Task Group T-8-19, revised in 1984 and 1993, and reaffirmed in 1997 by Group Committee T-8. It was revised in 2004 by Task Group (TG) 173 on Polythionic Acid SCC Prevention. TG 173 is administered by Specific Technology Group (STG) 34 on Petroleum Refining and Gas Processing. TG 173 is sponsored by STG 39 on Process Industry—Materials Applications, and STG 60 on Corrosion Mechanisms. This standard is issued by NACE International under the auspices of STG 34.

In NACE standards, the terms *shall*, *must*, *should*, and *may* are used in accordance with the definitions of these terms in the *NACE Publications Style Manual*, 4th ed., Paragraph 7.4.1.9. *Shall* and *must* are used to state mandatory requirements. The term *should* is used to state something good and is recommended but is not mandatory. The term *may* is used to state something considered optional.

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Section 1: General

1.1 PTA SCC refers to an intergranular form of cracking that can occur in sensitized austenitic stainless steels and other sensitized austenitic alloys.¹ Polythionic acid refers to the family of acids that have the form $H_2S_xO_y$, where x is generally considered to range from 1 to 5, and y may range from <1 to 6. Not all sulfur-containing acids are implicated in PTA SCC. Acids such as H_2SO_4 may exacerbate the mechanism and can result in intergranular corrosion, but by themselves do not cause it. The figures in Appendix A are examples of PTA SCC.

1.2 As in any SCC mechanism, the PTA SCC mechanism requires three primary contributing factors as described below. Addressing at least one of these factors can eliminate or reduce the probability of SCC.

1.2.1 Environment

Polythionic acid normally forms in refinery equipment by the reaction of oxygen and water with sulfide corrosion products usually present on the internal surfaces of equipment. When this combination of reactants occurs on sensitized austenitic stainless steel and other austenitic alloy process equipment, PTA SCC can occur, usually during an outage.

1.2.1.1 The most common source of oxygen for the formation of polythionic acid is opening equipment and exposure to the atmosphere. Other sources could be oxygen-containing cleaning solutions, impure nitrogen sources used for equipment purging, and/or blanketing gas that contains small amounts of O_2 .

1.2.1.2 Liquid water is a common product of shutdown operations, typically produced from condensation of steam used for hydrocarbon removal within equipment. Within heaters that require decoking, condensed steam from steam-air decoking, or water used to propel decoking pigs, may promote conditions necessary for PTA SCC. Other shutdown procedures like water washing are an obvious source. Less frequently, local ambient conditions, such as rainfall or regions with high humidity that may easily reach dew point conditions, may be the source of liquid water. Shutdown maintenance and inspection activities may introduce water into equipment from routine practices like hydrotesting or hydrojetting. Less obvious sources could include high-pressure water jet cutting, often used in major repairs of refractory-lined components in fluid catalytic cracking units (FCCU), and fluidized bed coking units.

1.2.1.3 The likelihood of PTA SCC is much greater in parts of refinery process units where the

environment is conducive to the formation of high-temperature iron or other metal sulfide scales. These high-temperature scales may then become wet in the presence of moist air during a unit shutdown, leading to the formation of PTA and ultimately PTA SCC if the material is sensitized.¹

1.2.1.4 A thermodynamic assessment may be used to determine the likelihood of forming metal sulfide scales in a system. Assessments have shown the difference between the likelihood of PTA SCC in hydroprocessing units and FCCU regenerators.²

Such assessments assume equilibrium conditions for the formation of iron sulfide are achieved. This is a conservative assumption, because in many cases it is unlikely that equilibrium will be reached, and that sufficient oxidizing potential with the austenitic material exists in such a way that chromium oxide (Cr_2O_3), rather than iron sulfide, scale forms. Provided a predominantly oxide scale is formed, the likelihood of PTA formation is low, even if the equipment is exposed to moist air after shutdown. This observation explains why PTA SCC on the outside of austenitic stainless steel and other austenitic alloy heater tubes is not a major concern, even when firing with a sulfur-containing fuel occurs, provided the firing conditions produce an oxidizing flue gas.

The theoretical thermodynamic assessment is supported by general industry experience as documented in the NACE REFIN•COR database.³ Overall, there are very few reported problems of PTA SCC in parts of refinery units that have predominantly oxidizing conditions prior to shutdown.

1.2.1.5 In hydroprocessing applications, the environments are much more reducing (no oxygen or CO_2 present) due to the presence of H_2S and hydrogen, leading to the formation of predominantly iron sulfide scales and high PTA SCC susceptibility if the austenitic material is sensitized.

1.2.1.6 Experience has shown that austenitic stainless steel and other austenitic alloy components in the reactor side of a FCCU are more susceptible to PTA SCC than in the regenerator side because the environment is much more reducing (i.e., more H_2S and less oxidizing species) in the reactor. However, partial-combustion FCCU regenerator systems may also be susceptible to PTA SCC because of the higher