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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 (SCC) occurring during downtimes and contiguous shutdown and start-up periods. This standard is directed toward preventing SCC by polythionic acids formed by the reaction of sulfide corrosion products with oxygen (air) and water. For practical purposes, it should be assumed that such acids can be formed by reaction of air and water with oxidizable sulfur species (sulfur, H_2S, metal sulfides).

Basic protection methods include avoidance of oxygen (air) entry, prevention of liquid water formation, and alkaline wash of surfaces to be exposed to prevent polythionic acid formation.

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 desulfurizing, hydrocracking, and reforming processes, in which the incidence of polythionic acid SCC has been comparatively high, it can be applied to other units using austenitic stainless steels and other austenitic alloys. The user must consider other factors such as the effect of the alkaline chemicals on catalysts. For the purposes of this standard, the term other austenitic alloys refers to those alloys of nickel, iron, and chromium which may be susceptible to polythionic acid SCC.

The techniques described in this standard are not designed to remove chloride deposits, but should minimize the possibility of chloride SCC by the wash solutions. Because units subject to polythionic acid SCC may contain chloride deposits, measures should be taken to remove these deposits.

This standard was originally prepared in 1970 by NACE Task Group T-8-19, revised in 1984 and 1993, and reaffirmed in 1997. It is published by NACE International under the auspices of Group Committee T-8 on Refining Industry Corrosion. This standard updates and supersedes all previous editions of RP0170.

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*, 3rd ed., Paragraph 8.4.1.8. *Shall* and *must* are used to state mandatory requirements. *Should* is used to state that which is considered good and is recommended but is not absolutely mandatory. *May* is used to state that which is considered optional.

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Contents

Section 1: General

1.1 If sulfide corrosion products are present on the surfaces of austenitic stainless steel and other austenitic alloy process equipment, there is a definite risk of polythionic acid stress corrosion cracking (SCC) when oxygen (air) and water are admitted during an outage. Tensile stresses, both residual and applied, are usually present in "cold" equipment. In the presence of polythionic acids, SCC may occur in stressed austenitic stainless steels and other austenitic alloys that are in a sensitized condition.

1.1.1 Polythionic acid SCC normally occurs with the standard (0.08% carbon max.) and high-carbon (0.10% max.) grades of austenitic stainless steels that have become sensitized either by weld fabrication or by operation in the sensitizing range of approximately 370° to 815°C (700° to 1500°F).

1.1.2 Low-carbon (0.03% max) and chemically stabilized grades (e.g., with titanium or columbium alloying additions) of austenitic stainless steels may also become sensitized by prolonged exposure in the sensitizing temperature range. Sensitization is more rapid in the presence of carbon (coke).

1.1.3 The resistance of chemically stabilized stainless steels and other austenitic alloys to polythionic acid SCC may be significantly improved by a thermal stabilization heat treatment.

1.2 The degree of sensitization and stress levels are generally not known. Therefore, austenitic stainless steel and other austenitic alloy process equipment on which sulfide corrosion products may be present should be protected using one or more of the following methods:

1.2.1 Exclusion of oxygen (air) and water by using a dry nitrogen purge.

1.2.2 Alkaline washing of all surfaces to neutralize any polythionic acids that may form. (Field experience has demonstrated that austenitic stainless steels and other austenitic alloys are effectively protected with properly applied alkaline solutions.)

1.2.3 Exclusion of water by using a dry air purge with a dew point lower than -15°C (5°F).

1.3 If process equipment remains unopened and "hot" (above the water dew point of the gas in the equipment), additional protection is unnecessary.

1.4 The internal surfaces of austenitic stainless steel and other austenitic alloy furnace tubes may be susceptible to polythionic acid SCC whether or not they have been thermally decoked and therefore should be protected. If thermally decoked, protection should be performed after decoking.

1.5 Protection of the external surfaces of austenitic stainless steel and other austenitic alloy furnace tubes should be considered when sulfur-containing fuels have been used for furnace firing.

Section 2: Nitrogen Purging

2.1 Process equipment may be protected by keeping it tightly closed and purging with dry nitrogen to exclude oxygen (air). Use of dry nitrogen is an effective means of lowering the water dew point temperature to less than ambient. Nitrogen purging provides optimum protection for catalysts.

2.2 If reactors are to be opened but furnaces are not, the furnaces may be purged with nitrogen and blinded. A small positive nitrogen pressure should be maintained.

2.2.1 Nitrogen should be dry and free of oxygen. (The user is cautioned that oxygen levels as high as 1,000 ppm have been found in commercial nitrogen.)

2.3 At the user's discretion, 5,000 ppm of ammonia may be added to the nitrogen to prevent SCC.

2.3.1 The addition of ammonia is generally unnecessary when purging with dry nitrogen, but may be advantageous when water and/or oxygen may be present.

2.3.2 Ammonia is toxic, and fresh-air breathing equipment must be worn during installation and removal of blinds.

2.3.3 Copper-based alloys must be isolated from ammoniated nitrogen.

2.3.4 It should be determined that ammonia will not have an adverse effect on catalysts.

2.4 Nitrogen purging is preferable for protection of vertical tube heaters if alkaline wash solutions cannot be drained completely.

2.5 If steam is being used for purging or steam air decoking, steam injection should be stopped before the metal temperature cools to 56°C (100°F) above the water dew point. When depressured, but before cooling lower than 56°C (100°F) above the water dew point, the system should be purged with dry nitrogen. Some purge flow should be maintained until blinds are installed. A positive nitrogen purge pressure should be maintained on the system after blinding.

2.6 The user is cautioned that wearing fresh-air breathing equipment in nitrogen-purged equipment requires special precautions, in accordance with applicable safety procedures.

Section 3: Alkaline Wash Solutions

3.1 Sodium carbonate (soda ash) solutions should be used to protect austenitic stainless steels and other austenitic alloys from polythionic acid SCC. Solution pH should be greater than 9. These solutions may also contain an alkaline surfactant and corrosion inhibitor.

3.2 The recommended wash solution is 2 wt% soda ash. (Industry practice varies from 1 to 5 wt%, with a majority using 2 wt% solutions.) A 1.4 to 2 wt% soda ash solution provides a sufficient level of residual alkalinity on metal surfaces after the solution drains from the equipment. Additionally, this low concentration facilitates solution preparation.

3.2.1 The use of sodium hydroxide (caustic soda) is not recommended.

3.2.2 Experience with potassium carbonate is limited. No cracking has been reported by those who have substituted it for soda ash.

3.3 Because of successful past experience with solutions containing small amounts of chloride, it is not always necessary to provide chloride-free solutions.

3.3.1 Chloride concentration in the freshly mixed wash solution should be limited to 150 ppm. This nominal chloride limit is attainable with commercially available chemicals.

3.4 In special cases, flushing with ammoniated condensate may be necessary (Paragraphs 4.3 and 4.4). The solution should have a pH above 9 and a chloride content of less than 5 ppm.

3.5 The addition of an alkaline surfactant to the wash solution at 0.2 wt% concentration is recommended to promote penetration of coke, scale, or oil films. Heating of the wash solution to 49°C (120°F) may accelerate the penetration of oily films and residues.

3.6 Corrosion inhibitors have been used to decrease the possibility of chloride SCC by these alkaline solutions.

3.6.1 At the user's option, 0.4 wt% sodium nitrate may be added. (In laboratory tests, low concentrations of sodium nitrate have been found to be effective in suppressing SCC of austenitic stainless steel in boiling magnesium chloride solutions.) Caution: Excess $NaNO_3$ can cause SCC of carbon steel.

Section 4: Alkaline Washing

4.1 Austenitic stainless steel and other austenitic alloy equipment to be opened to the air is best protected with a soda ash solution (defined in Section 3). Soda ash solutions neutralize acids and, after draining, leave a thin alkaline film on the surface that can neutralize any additional acid formation. It is vital that this film is not washed off and that it remains in place as the equipment goes back on-stream.

4.1.1 The equipment must be alkaline washed before any exposure to air. It is very important that 100% of the equipment's internal surfaces be contacted.

4.1.2 The equipment should be soaked for a minimum of two hours. If deposits or sludges are present, the solution should be circulated vigorously (two hours minimum). Longer times are not detrimental in either case.

4.1.3 The circulating solution should be analyzed at appropriate intervals to ensure that pH and chloride limits are maintained.

4.1.4 It is essential that the alkaline wash is not followed by a water wash.

4.1.5 Each system must be evaluated individually and precautions taken to ensure that unvented gas pockets or cascading through downflow sections do not prevent complete surface contact.

4.1.6 If washing the outside of furnace tubes is necessary to remove deposits, a soda ash solution should be used because these surfaces may be subject to polythionic acid SCC. (See Paragraph 1.5.)

4.2 Hydrojetting of equipment should be conducted using a soda ash solution (defined in Section 3).

4.2.1 After hydrojetting, equipment should be kept dry and out of the weather. If this is not possible, the soda ash wash should be repeated as required to maintain a residual film of soda ash. Equipment shall be reinstalled with a soda ash residual film left on surfaces.

4.3 Hydrostatic testing of equipment should be conducted using a soda ash solution (defined in Section 3). Ammoniated condensate may be used if the equipment is not reopened or exposed to oxygen (air).

4.4 If sodium or chloride ions cannot be tolerated in the process system, the equipment should be washed with ammoniated condensate after being closed. If the unit is not started up immediately, the solution may be left in place or displaced with nitrogen or dry hydrocarbon. The unit must not be exposed to oxygen (air) after this procedure. Ammonia solutions do not leave a residual alkaline film after being drained.

4.5 Upon completion of alkaline washing, all of the remaining alkaline solution must be drained from each low point in the system prior to returning the equipment to service. Failure to do so can result in concentration of carbonate and chloride salts by evaporation, which can also lead to SCC in austenitic stainless steels.

Section 5: Protection of Reactors

5.1 Reactors containing catalyst require special consideration. Personnel safety and protection of the catalyst may dictate the use of procedures that are less than optimum in terms of protection from polythionic acid SCC.

5.1.1 Nonregenerated catalysts frequently are pyrophoric. Such catalysts should either be kept wet or out of contact with oxygen (air) by the use of nitrogen purging.

5.2 Industry experience suggests that austenitic low-carbon and chemically stabilized weld overlays and chemically stabilized wrought internals in reactors are very resistant to polythionic acid SCC for reactor operating temperatures below 450°C (850°F).

5.3 Recommended procedures for protection of reactors that will be opened for entry and have a history of successful use in the field are as follows:

5.3.1 Catalyst unloading and loading may be conducted under nitrogen-blanketing conditions by personnel using appropriate fresh-air breathing equipment. Following unloading, the reactor should be purged with dry air and this purge should be maintained while the reactor is open. Purge air dew point temperatures from -15° to -46°C (5° to -50°F) have been used.

5.3.2 If the catalyst is to be discarded, the reactor may be filled with soda ash solution to wet both the catalyst and reactor parts. The solution strength should be increased to 5 wt% to compensate for the acidity of deposits held by the catalyst. Unloading may then be conducted in air while keeping the catalyst wet with soda ash solution to prevent pyrophoric ignition. The reactor should then be washed down with soda ash solution and dried prior to repairs or catalyst loading.

5.3.3 If the user wishes to eliminate the use of soda ash solutions and fresh-air breathing equipment while unloading the catalyst, the catalyst may be dumped, following wetting with good-quality fresh water (less than 50 ppm chloride), without nitrogen purging. This should be preceded by a careful investigation to determine that:

(1) Only chemically stabilized grades have been used when austenitic stainless steel materials have been specified.

(2) These alloy materials have not become sensitized as a result of either vessel fabrication procedures or the reactor's thermal history during operation.

This procedure involves some risk of polythionic acid SCC through either accidental use of unstabilized grades or misinterpretation of the thermal history of the reactor.

Bibliography

Alessandria, A.V., and N. Jaggard. *Stainless Steel in Petroleum Refining and Processes.* Proceedings API 40. Washington, DC: API, 1960, p. 111.

Backensto, E.B., and A.N. Yurick. "Stress Corrosion Cracking Studies of Austenitic Stainless Steels in Aqueous Ammonium Chloride Solutions." *Corrosion* 18, 5 (1962): p. 169t.

Beggs, D.V., and R.W. Howe. "Effects of Welding and Thermal Stabilization on the Sensitization and Polythionic Acid Stress Corrosion Cracking of Heat and Corrosion-Resistant Alloys." CORROSION/93, paper no. 541. Houston, TX: NACE International, 1993.

Brophy, A.J. "Stress Corrosion Cracking of Austenitic Stainless Steels in Refinery Environments." *Materials Performance* 13, 5 (1974): p. 8.

Couper, A.S. "Testing Austenitic Stainless Steels for Modern Refinery Applications." *Materials Protection* 8, 10 (1968): p. 17.

Couper, A.S., and H.F. McConomy. *Stress Corrosion Cracking of Austenitic Stainless Steels in Refineries.* Proceedings API 46. Washington, DC: API, 1966, p. 321.

Dravnieks, A., and C.H. Samans. *Corrosion Control in Ultra-forming.* Proceedings API 37. Washington, DC: API, 1957, p. 111.

Heller, J.J., and G.R. Prescott. "Cracking of Stainless Steels in Wet Sulfidic Environments in Refinery Units." *Materials Protection* 4, 9 (1965): p. 14.

Lendvai-Lintner, E. "Stainless Steel Weld Overlay Resistance to Polythionic Acid Attack." *Materials Performance* 18, 3 (1979): p. 9.

Piehl, R.L. *Stress Corrosion Cracking by Sulfur Acids.* Proceedings API 44. Washington, DC: API, 1964, p. 111.

Samans, C.H. "Stress Corrosion Cracking Susceptibility of Stainless Steels and Nickel-Base Alloys in Polythionic Acids and Copper Sulfate Solution." *Corrosion* 20, 8 (1964): p. 256t.

Stephens, C.D., and R.C. Scarberry. "The Relation of Sensitization to Polythionic Acid Cracking of Incoloy Alloys 800 and 801." CORROSION/88, paper no. 10. Houston, TX: NACE, 1988.

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