Standard Practice

Avoiding Caustic Stress Corrosion Cracking of Refinery Equipment and Piping

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Foreword

Caustic is used in many petroleum refinery applications in a wide range of concentrations and temperatures. This standard practice is intended to provide guidance to those designing, fabricating, and/or maintaining equipment and piping that are exposed to caustic environments.

Caustic stress corrosion cracking (SCC) of carbon steel (CS) equipment has been reported in industry since the 1930s, e.g., in riveted steam boilers. NACE has published guidance for handling sodium hydroxide (NaOH) in the form of a “Caustic Service Chart” since at least the mid-1960s. It is believed that the majority of the data used to produce the curves in the chart were developed by H.W. Schmidt, et. al.\textsuperscript{1} The Caustic Service Chart is currently published in the \textit{NACE Corrosion Engineer's Reference Book}.\textsuperscript{2} A modified copy of the chart is included as Figure 1 in this standard practice.

An informal review of current industry caustic-handling practices was completed in 1999. This standard practice incorporates the findings of that survey as they apply to refinery applications.

This standard practice was prepared by NACE Task Group (TG) 177 (formerly T-8-25), “Refineries, Environmental Cracking.” TG 177 was formed in 1998 to disseminate information on environmental cracking in refineries. Work Group (WG) 177a was formed from that TG to survey the industry on practices to mitigate caustic SCC and to develop a standard practice for avoiding caustic SCC of refinery equipment and piping. This standard practice was originally published in 2003, reaffirmed in 2008, and revised in 2015 under Specific Technology Group (STG) 34, “Petroleum Refining and Gas Processing.” TG 177 is administered by STG 34 and is sponsored by STG 60—Corrosion Mechanisms. This standard is issued by NACE under the auspices of STG 34.

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Section 1: General

1.1 This standard practice establishes guidelines to avoid caustic SCC of equipment and piping. It addresses applications that use “fresh” caustic.

1.1.1 In some services that involve contaminated caustic, SCC has been observed at conditions within area “A” of the Caustic Service Chart shown in Figure 1 (particularly when contaminated with sulfide compounds). The need for thermal stress relief should be considered when the service contains contaminated caustic.

1.2 The practices detailed below are specifically intended for handling aqueous solutions containing sodium hydroxide (NaOH). However, several companies extend these practices to include aqueous solutions of other strong alkali compounds such as potassium hydroxide (KOH) and lithium hydroxide (LiOH). Although amines form a high pH solution and may cause SCC, it is considered a different mechanism for the purposes of this standard and amine SCC is not addressed. A good reference on amine SCC is API(1) 945. Carbonate SCC is another “different” SCC mechanism occurring at high pH, which is not included in the scope of this standard. It is covered by NACE Publication 34108.4

1.3 Some proprietary caustic solutions are used in the industry, e.g., potassium carbonate/bicarbonate solutions for carbon dioxide removal in hydrogen manufacturing units. Some of these systems rely on postweld heat treatment (PWHT) to avoid SCC. These systems are outside the scope of this standard.

1.4 Other terms for caustic SCC used in past literature include caustic embrittlement, caustic cracking, and alkaline cracking.

Section 2: Cracking Mechanism and Prevention

2.1 Early cases of caustic SCC in CS were associated with steam boilers, more specifically, riveted boilers. In the riveted structures, cracks started in metal that was highly stressed. The majority of more recent industry cases of caustic SCC in CS equipment and piping are associated with non-stress relieved welds, typically in the heat-affected zone (HAZ) and adjacent base metal. Although rare, cracking also occurs away from welds if high tensile stresses are present.

2.2 Caustic SCC in CS is typically intergranular,5 although transgranular cracking occasionally occurs. These cracks are typically tight and filled with oxide. Often, multiple cracks are present. Cracking in weld metal is normally intergranular, following the ferrite constituent in the matrix. Caustic SCC in CS weld metal is shown in Figures A1 and A2 in Appendix A (nonmandatory). Caustic SCC in CS base metal is shown in Figures A3, A4, and A5 in Appendix A.

2.3 Concentration and Temperature Effects on Cracking Potential of CS

2.3.1 This standard practice reaffirms the recommended guidelines in the Caustic Service Chart (see Figure 1) for stress relief of CS to prevent caustic SCC. The chart shows when stress relief is recommended based on metal temperature and caustic concentration.

2.3.1.1 Caustic concentration greater than 5 wt% in the aqueous phase can produce SCC in CS.6 The majority of users do not require PWHT on CS if the caustic concentration is less than 2 wt%, regardless of temperature, and some users use 5 wt% as their threshold, as shown in area “D” of the Caustic Service Chart. Caustic SCC sometimes occurs in services with lower bulk fluid concentrations, usually in areas where local concentration effects occur. For these instances, caustic concentrations of 50 to 100 ppm in the bulk solution may cause cracking.7 Possible ways to prevent local concentrating effects are by avoiding departure from nucleate boiling (DNB)(2), keeping internal surfaces sufficiently free of caustic deposits, and avoiding formation of waterlines in components receiving high heat flux.5

2.3.1.2 Caustic SCC is known to occur over a wide range of temperatures in CS, from approximately 46 °C (115 °F) to boiling temperatures (depending on caustic concentration).

2.3.1.3 Possible concentrating effects in equipment and piping should be considered as part of an assessment to determine the potential of caustic SCC and the need for mitigation by either thermal stress relief or alternate material.

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(1) American Petroleum Institute (API), 1220 L St. NW, Washington, DC 20005-4070.
(2) Departure from Nucleate Boiling (DNB) is the point where steam bubbles no longer depart from the heating surface and instead a steam film forms around the heating element. In this condition the heating surface is no longer wetted and caustic can concentrate on the metal surface.