

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.¹ The Caustic Service Chart is currently published in the *NACE Corrosion Engineer's Reference Book*.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.

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*. The terms *shall* and *must* are used to state a requirement, and are considered mandatory. The term *should* is used to state something is good and is recommended, but is not considered mandatory. The term *may* is used to state something considered optional.

NACE International Standard Practice

Avoiding Caustic Stress Corrosion Cracking of Refinery Equipment and Piping

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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⁾ 945.³ 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

⁽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.

selection. Possible areas of concentrating include low-flow areas in heat exchangers, stagnant lines and equipment, and piping subjected to frequent wetting and vaporization.

2.4 The level of tensile stress required to produce cracking is a function of metal temperature and caustic concentration. The source of stress may be applied or residual. Sources of applied stress include the applied load and thermal stresses generated in service. Sources of residual stress include welding, bending, and forming. Residual welding stresses for non-PWHT welds approach material yield stresses⁸ and therefore often exceed applied stresses. For most all designs meeting common Codes, the applied stresses are not high enough to cause caustic SCC. Residual stresses can be alleviated by stress relief heat treatments, including PWHT.

2.5 CS welds (including groove welds, socket welds, and seal welds), cold-formed piping bends, and heat exchanger tube "U" bends in services that fall within area "B" and area "C" of the Caustic Service Chart shall be thermally stress relieved as outlined in Section 3.

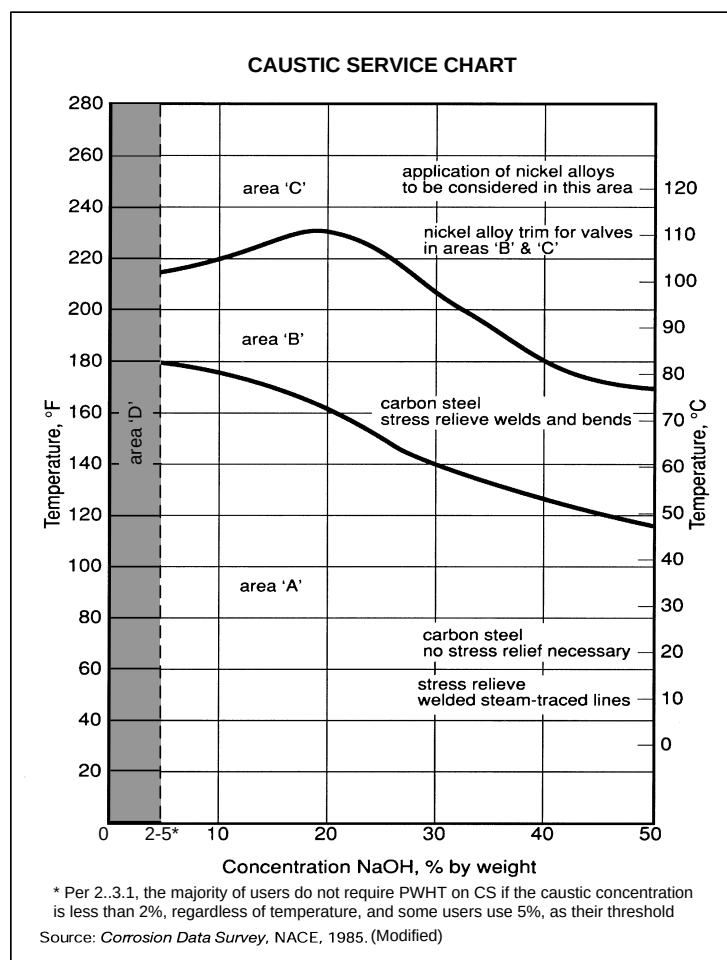


Figure 1: Caustic Service Chart²

(In accordance with paragraph 1.1.1, some contaminated caustics in area "A" can cause caustic SCC and may require stress relief.) See Figure 2 for 300 series stainless steels.

2.6 Heat-traced equipment and piping may have localized areas with metal temperatures at which caustic SCC may occur. If adequate temperature control cannot be ensured to maintain the metal temperature within area "A" of the Caustic Service Chart, thermal stress relief of CS welds and bends of traced components shall be performed. Because the risk of solidification often impacts the requirement for tracing, a caustic solidification curve is provided in Appendix B for reference.

2.7 Equipment and piping in caustic service which is to be steamed out without prior water wash shall also be thermally stress relieved. Note that some operators of non-stress-relieved equipment have found that water wash prior to steamout has been successful in preventing caustic SCC during steamout.

2.8 Caustic carryover has caused many caustic SCC failures in the industry. Possible carryover should be considered when the potential of caustic SCC and the need for mitigation is determined.

2.9 CS is generally considered not suitable for use at conditions of concentration and temperature that fall within area "C" of the Caustic Service Chart, except at low concentrations depicted by area "D". Therefore, the application of nickel alloys should be considered at those conditions in area "C".

2.10 Threaded connections can contain highly stressed thread roots that can serve as crack initiation points in caustic service. Local evaporation can occur at points in threaded connections, which can lead to increased caustic concentration in some areas. The use of threaded connections should be avoided in caustic service when thermal stress relief of CS welds is specified to resist cracking.

2.11 Figure 2 shows the SCC susceptibility of austenitic stainless steel (SS) in caustic service. It provides temperature limits based on caustic concentration. Figure 2 should be used in conjunction with the Caustic Service Chart in Figure 1 to also evaluate the risk of SCC. Systems containing austenitic SS that might be exposed to caustic should be carefully evaluated to avoid localized caustic concentrations that can cause caustic SCC. Some users apply an additional safety margin of 33°C (60°F) below the delayed SCC failure curve to further reduce the potential of caustic SCC and as a measure of protection against chloride SCC, because chlorides may be present in some of these streams.

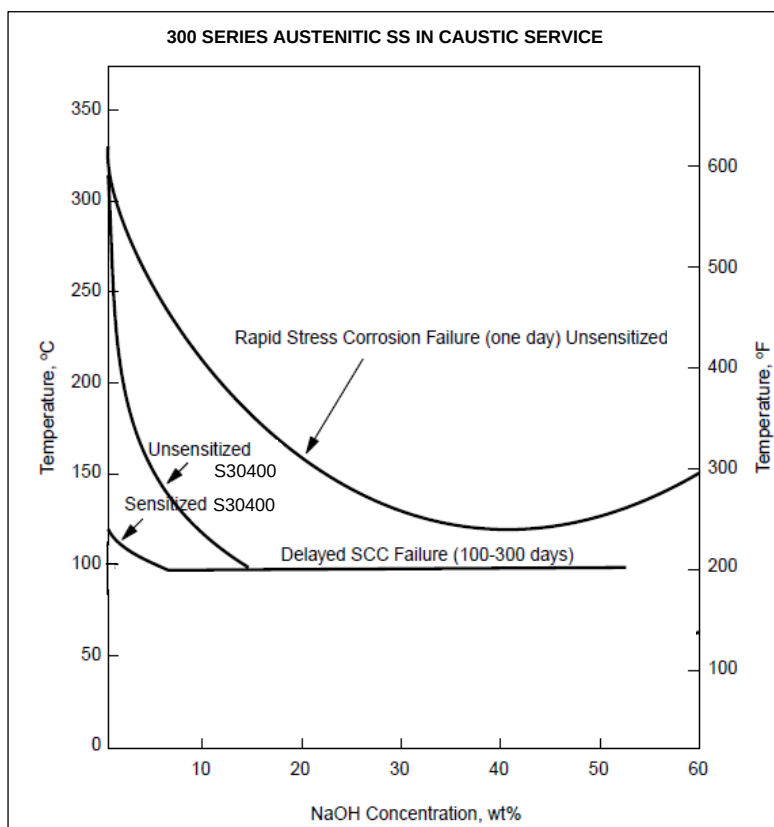


Figure 2: Caustic Service Chart for 300 Series Austenitic SS^{9,10}

2.12 Caustic SCC in austenitic SS is generally transgranular, but it has been found to be intergranular at higher temperatures.¹⁰ Caustic SCC in austenitic SS is often difficult to distinguish from chloride SCC. Caustic SCC of UNS S32100 is shown in Figures A6 and A7 in Appendix A.

2.13 Austenitic SS heat exchanger tube U-bends in caustic service should be heat treated regardless of operating temperature. This includes services with risk of caustic carryover, the formation of caustic deposits, or solutions from DNB.

2.14 Nickel and nickel-based alloys, such as alloys UNS⁽³⁾ N08800, N08825, N06690, N04400, N06600, N02200, and N02201 have historically been the material of choice for aggressive caustic service and possess excellent resistance to caustic SCC over the range of conditions shown in Figure 1.^{10,11,12} However, at operating conditions that promote the formation of molten caustic in the absence of free water (318 °C [604 °F] at atmospheric pressure), these nickel-based alloys can be susceptible to caustic SCC (molten caustic cracking). Images of caustic SCC of UNS N06625, N02201, and N08825 are shown in Figures A8 through A12 in Appendix A.

2.14.1 Molten caustic cracking was reported on an exchanger bellows expansion joint constructed of alloy UNS N06625 that operated at 399 °C (750 °F) in superheated steam service.¹³

2.14.2 Caustic SCC of an alloy UNS N08825 low point drain in a hydrotreater operating near 399 °C (750 °F) has also been reported. It is believed that the soda ash (sodium carbonate) solution used to neutralize the 300 series SS equipment for protection against polythionic acid SCC collected in the low point and was not drained prior to start-up. The soda ash solution disassociated into caustic as the unit was heated up, which then increased in concentration as the water boiled away.¹³

2.14.3 Rapid intergranular cracking of alloy UNS N06600 has been observed in steam environments that would have promoted the formation of molten caustic.¹⁰

Section 3: Thermal Stress-Relief Procedure Requirements to Mitigate Caustic SCC on CS

3.1 Thermal stress relief is an effective method for improving the SCC resistance of CS weldments and cold-formed piping bends in caustic service. An effective procedure consists of heating the weldments or bends to 635 ± 14 °C ($1,175 \pm 25$ °F)¹⁴ and holding at that temperature for one hour for each 25 mm (1.0 in), or fraction thereof, of metal thickness, with a minimum holding time of one hour. Each situation should be evaluated to determine whether this specified thermal stress relief is adequate for all other considerations in addition to caustic SCC prevention.

3.2 Investigations have shown that an inadequate heated band width during local PWHT can induce or inadequately relieve residual stresses in the weld region.¹⁵ The following local PWHT procedures, derived from AWS⁽⁴⁾ D10.10¹⁴ and WRC Bulletin 452,¹⁶ should be used along with the other requirements in AWS D10.10 and WRC Bulletin 452 for piping and vessels to minimize residual stresses and thereby increase resistance to caustic SCC.

3.2.1 Terminology used in the section includes soak band (SB), heated band (HB), and gradient control band (GCB). Definitions and further information on local PWHT are provided in Appendix C (nonmandatory).

3.2.2 The minimum HB and GCB widths for pipe should be as shown in Table 1:

Table 1
Minimum Recommendations for Local 360° Band PWHT on ASME⁽⁵⁾ B31.3 Piping¹⁷ (Note 1)

DN (NPS)	Minimum HB Width Centered Over the Weld (Note 2)	Minimum GCB Width Centered Over the Weld
≤ 50 (≤ 2)	280 mm (11.0 in)	330 mm (13.0 in)
100 (4)	370 mm (14.5 in)	465 mm (18.5 in)
150 (6)	435 mm (17.0 in)	575 mm (23.0 in)
≥ 200 (≥ 8) (Note 3)	HB = SB + $4\sqrt{Rt}$ (230 mm [9.05 in], minimum)	GCB = HB + $8\sqrt{Rt}$ (355 mm [14.0 in], minimum)

⁽³⁾ Metals and Alloys in the Unified Numbering System (latest revision), a joint publication of ASTM International and the Society of Automotive Engineers Inc. (SAE), 400 Commonwealth Dr., Warrendale, PA 15096.

⁽⁴⁾ American Welding Society (AWS), 550 N.W. LeJeune Road, Miami, Florida 33126.

⁽⁵⁾ ASME International (ASME), Three Park Avenue, New York, NY 10016-5990.

Note 1: Widths are for thickest piping schedules per AWS D10.10. Thinner pipe can reduce widths using AWS D10.10 Table 4.

Note 2: The HB width uses the HB2 formula per AWS D10.10 for smaller-diameter pipe but for ease of implementation and use consistent with WRC 452, the HB1 formula is used for the larger-diameter piping.

Note 3: ≥ 200 mm (8.00 in) pipe can have HB and GCB less than smaller-diameter piping, in accordance with AWS D10.10.

Where:

SB = 50 mm (2.0 in) + width of weld, mm (in)

R = pipe outside radius, mm (in)

t = pipe wall thickness, mm (in)

3.2.2.1 The GCB should be insulated using a 50 mm (2.0 in) minimum thickness insulation blanket.

3.2.2.2 In the case of flange welds, the entire flange (inside and outside) and a minimum of 230 mm (9.0 in) runout on the pipe from the weld should be insulated for pipes 200 DN (8 NPS) and smaller. For flange welds in pipes 250 DN (10 NPS) and greater, 230 mm (9.00 in) + $4\sqrt{Rt}$ should be insulated.

3.2.2.3 If possible, the ends of the pipe should be closed to minimize convection currents.

3.3 The minimum heated band width for vessels should be as shown in Table 2:

Table 2
Minimum Recommendations for Local 360° Band PWHT on ASME Section VIII, Division 1 Vessels¹⁸

Minimum Soak Band	Minimum HB	Minimum GCB
SB = W + 2t or 100 mm (4 in), whichever is less	HB = SB + $4\sqrt{Rt}$	GCB = HB + $8\sqrt{Rt}$

Where:

W = weld width, mm (in)

R = pipe outside radius, mm (in)

t = pipe wall thickness, mm (in)

3.4 External attachment welds can generate residual stresses extending through the entire wall thickness, especially for wall thicknesses less than 25 mm (1.0 in). If an evaluation shows that the residual stresses do not extend through-wall, thermal stress relief of these welds may be considered optional. Otherwise, external attachment welds shall also receive thermal stress relief. Variables affecting the depth of residual stresses are welding heat input, base material thickness, and attachment weld size.

3.5 Mechanical stress-relief methods are not universally accepted as effective methods to mitigate caustic SCC. The peening stress-relief process should not be used for applications in caustic environments because of the limited success of this technique in corrosive services. Careful analysis of the stress conditions under all relevant design, loading, and operating conditions should be performed if other mechanical stress-relief methods (such as vibration) are considered.

3.6 Field fabricated API 650¹⁹ caustic tanks are typically impractical to PWHT. Therefore, care should be taken in the tank design to ensure the inlet nozzle design prevents hot caustic from being in contact with the shell of the tank, which could cause caustic SCC.

3.7 Organic or inorganic linings may be applied as a barrier against caustic SCC. Care should be taken to select a suitable coating that performs acceptably in the process environment and during shutdown operations, such as depressurizing and steamout. The coating must resist the maximum temperature exposures. Quality assurance of the coating installation is essential to provide the required initial level of protection. Periodic inspection and maintenance of the coating should be performed over the life of the equipment and piping to ensure continuing protection.

3.8 Small-diameter socket-welded connections can contain geometrical discontinuities that act as local stress raisers where cracks can initiate. For applications in which thermal stress relief is specified for CS equipment or piping, socket-welded connections should also receive thermal stress relief.

Section 4: Inspection and Repair Recommendations

4.1 Effective nondestructive examination (NDE) techniques for detection of caustic SCC in equipment include wet fluorescent magnetic particle testing (WFMT), alternating current field measurement (ACFM), and shear wave ultrasonic testing (UT). Shear wave UT is the most effective technique for external detection of internal caustic SCC in piping. All NDE shall be performed in accordance with industry-accepted standards and procedures.

4.2 Prior to making a welded repair or modification of CS equipment and piping in caustic service, the following should be considered:

4.2.1 The surfaces to be welded, including adjacent surfaces, should be free of oxide and caustic contamination. Caustic compounds in weld metal can result in weld defects and cracking.

4.2.2 If the equipment or piping was originally thermally stress relieved, the weld repair or modification to that equipment or piping shall also be stress relieved.

4.2.3 In-service welding (live-line or hot-tap welding) has a significant risk of immediate cracking. In-service welding should be considered only in combination with a thorough risk assessment.

4.2.4 Alternative welding methods such as temper bead welding and controlled deposition welding are not effective in mitigating caustic SCC. These methods do not sufficiently reduce residual stresses, and therefore shall not be considered in lieu of thermal stress relief.

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Appendix A: Caustic SCC Micrographs (Nonmandatory)

This appendix is considered nonmandatory, although it may contain mandatory language. It is intended only to provide supplementary information or guidance. The user of this standard is not required to follow, but may choose to follow, any or all of the provisions herein.

The micrographs in Figures A1 and A2 show caustic SCC in CS weld metal. The weld is a vertical butt joint made using the shielded metal arc welding (SMAW) process in a small shop-fabricated aboveground storage vessel (without PWHT). The vessel was used to store industrial NaOH at 20% concentration and a temperature of 35 to 46 °C (95 to 115 °F). Cracking was believed to have occurred during a single thermal excursion experienced during batch diluting of 50% NaOH. Figure A1 shows typical caustic SCC originating from the weld cap surface. In this case, none of the cracks had propagated deeper than the cap pass. Figure A2 shows the cracking within the rectangle depicted in Figure A1. The cracking was tight, filled with oxide, and typically followed the ferrite constituent in the weld metal.

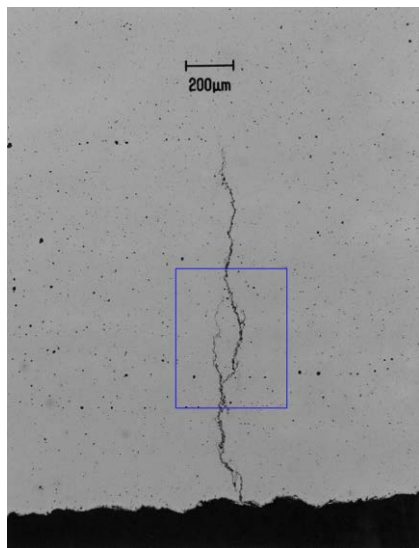


Figure A1: Caustic SCC in CS Weld Metal—Unetched

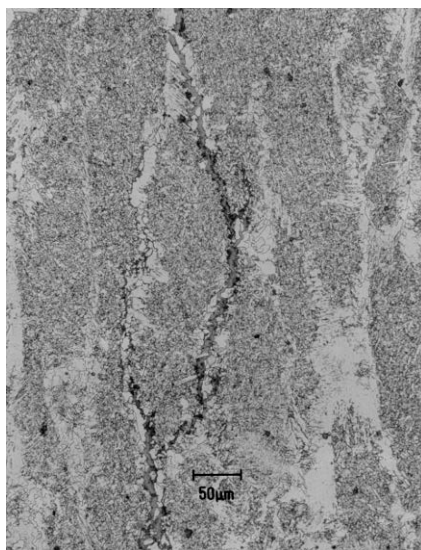


Figure A2: Caustic SCC in CS Weld Metal—Nital Etched

Figures A3 through A5⁽⁵⁾ show caustic SCC in CS base metal (photos courtesy of BP).

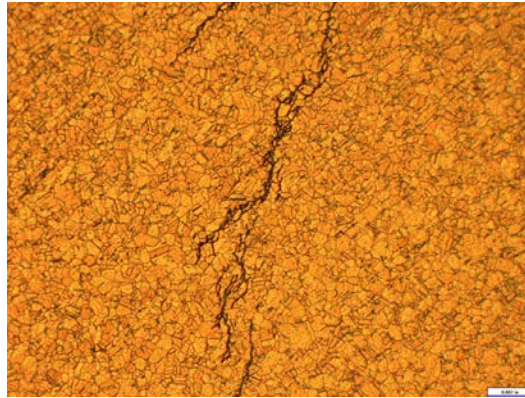


Figure A3: Caustic SCC in CS Base Metal—50X Magnification

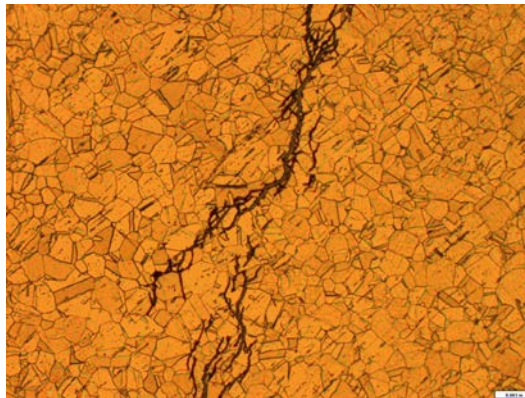


Figure A4: Caustic SCC in CS Base Metal—100X Magnification



Figure A5: Caustic SCC in CS Base Metal—200X Magnification

Figures A6 and A7 show photomicrographs of caustic SCC in an expansion joint bellows constructed of UNS S32100 operating in a steam environment.¹⁰

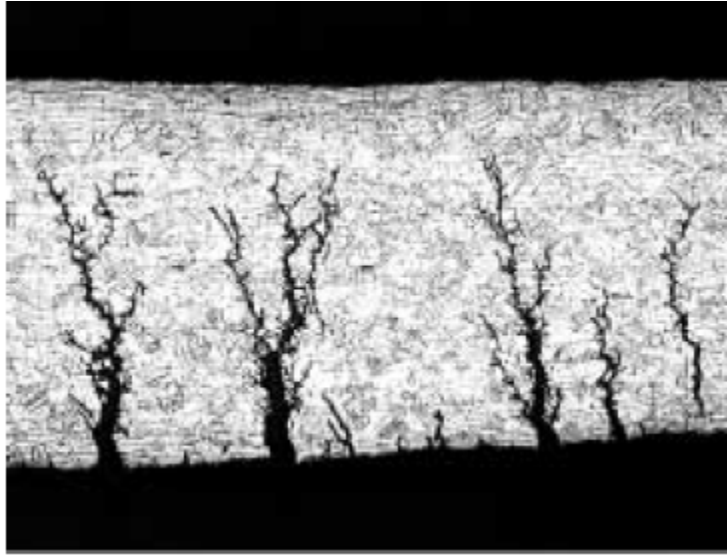


Figure A6: Photomicrograph of Caustic SCC in UNS S32100—Magnification 200X



Figure A7: Photomicrograph of Caustic SCC in UNS S32100—Magnification 500X

Figures A8 to A10 are micrographs showing caustic SCC in an expansion joint bellows constructed of nickel-based alloys in a 2.75 MPa (400 psig) steam superheater. In all cases the cracking was intergranular. (Photos courtesy of Flint Hills Resources.)

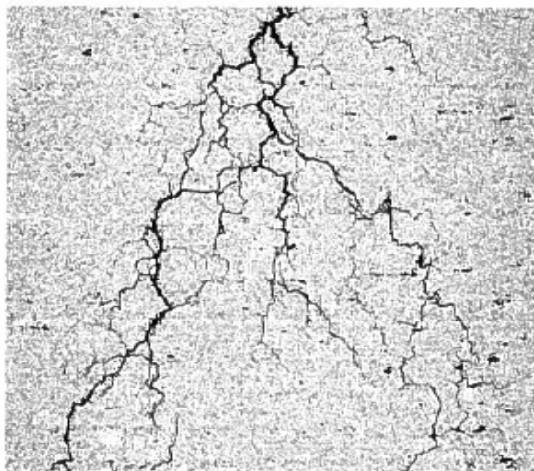


Figure A8: Photomicrograph of Caustic SCC in UNS N06625—Magnification 100X

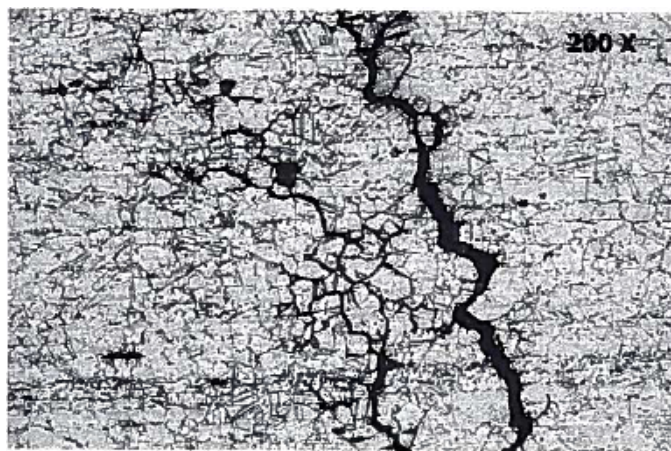


Figure A9: Photomicrograph of Caustic SCC in UNS N06625—Magnification 200X

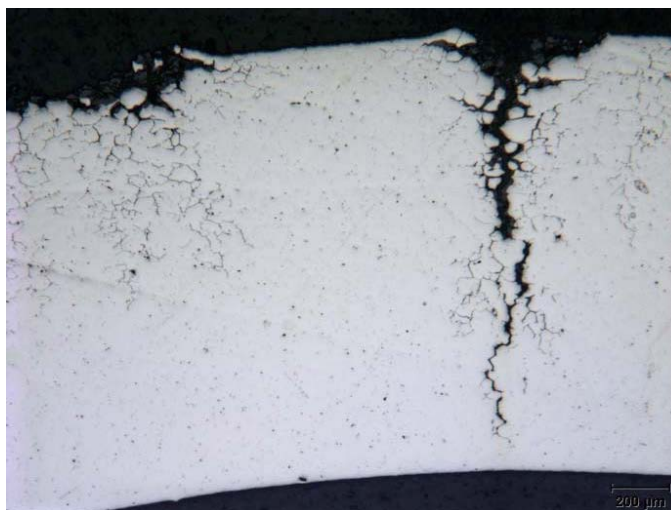


Figure A10: Caustic SCC in UNS N02201 Base Metal—50X Magnification

Figures A11 and A12 are micrographs showing caustic SCC in the base metal of an UNS N08825 half-coupling at a low point drain in a piping system.¹³



Figure A11: Photomicrograph of Caustic SCC in UNS N08825—Magnification 200X



Figure A12: Photomicrograph of Caustic SCC in UNS N08825—Magnification 200X

Appendix B: Caustic Solidification Curve (Nonmandatory)

This appendix is considered nonmandatory, although it may contain mandatory language. It is intended only to provide supplementary information or guidance. The user of this standard is not required to follow, but may choose to follow, any or all of the provisions herein.

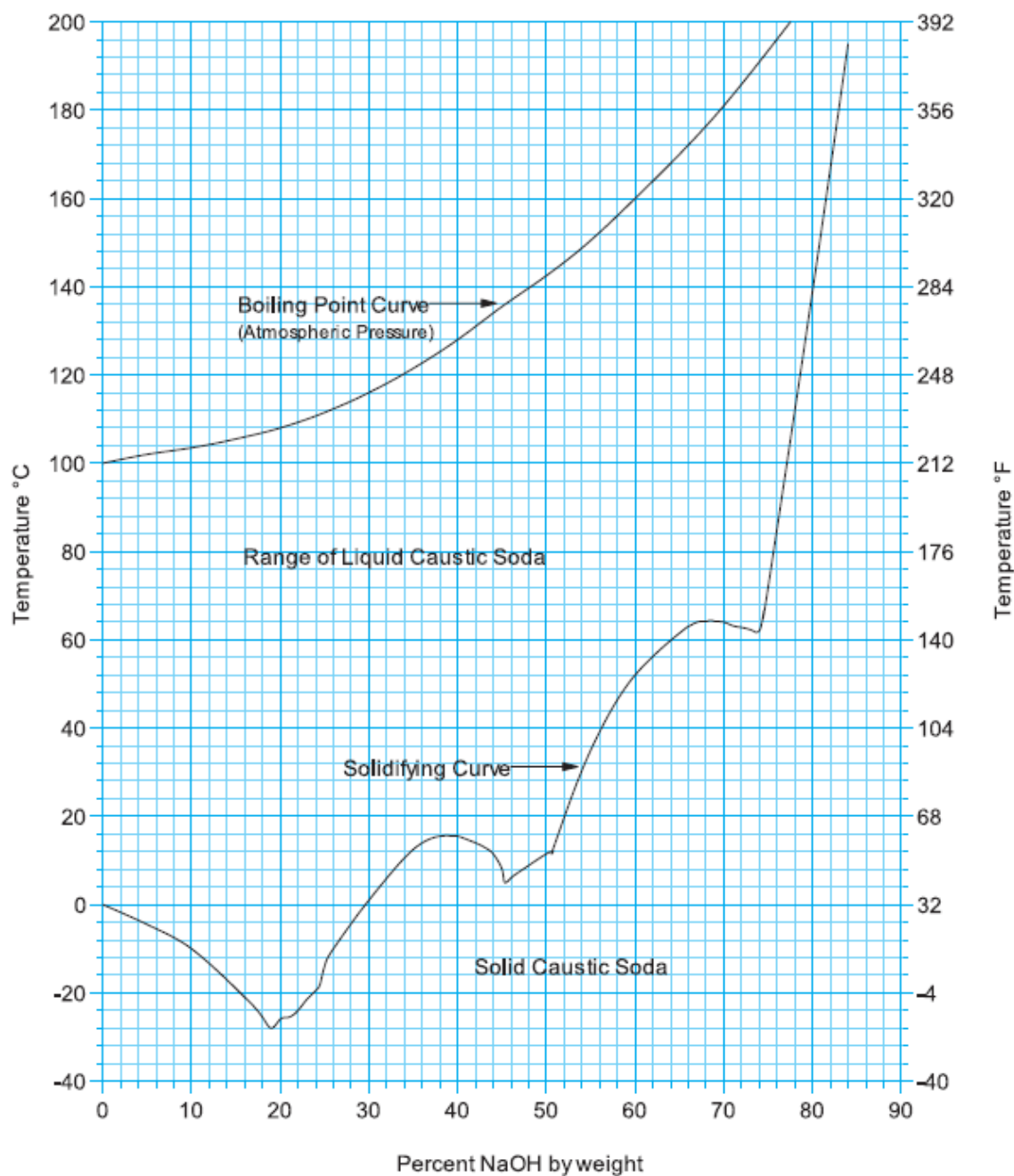


Figure B1: Boiling and Solidifying Temperatures of Aqueous Caustic Soda Solutions²⁰

Appendix C: Guidance on Local PWHT (Nonmandatory)

This appendix is considered nonmandatory, although it may contain mandatory language. It is intended only to provide supplementary information or guidance. The user of this standard is not required to follow, but may choose to follow, any or all of the provisions herein.

Terms used in Section 3 to define local PWHT for piping are from AWS D10.10 and are:

C1.1 Soak Band (SB)—The soak band consists of the through-thickness volume of metal, which is heated to the minimum, but does not exceed the maximum temperature. As a minimum, it should consist of the weld metal, HAZ, and a portion of the base metal adjacent to the weld being heated. The minimum SB width should be t or 2 in (50 mm), whichever is less, on either side of the weld, at its greatest width, where t = pipe wall thickness.

C1.2 Heated Band (HB)—The heated band consists of the surface area over which the heat source is applied to achieve the required temperature in the SB and limit induced stresses in the vicinity of the weld. It should consist of the SB plus any adjacent base metal necessary to both control the temperature and limit induced stress within the SB.

C1.2.1 The minimum recommend HB for PWHT is the larger of HB1 or HB2, as defined in Equations 1 and 2:

$$HB1 = SB + 4\sqrt{Rt} \quad (1)$$

$$HB2 = H_i \frac{\left[\frac{OD^2 - ID^2}{2} + (ID)(SB) \right]}{OD} \quad (2)$$

Where:

SB = soak band

R = pipe inside radius

t = pipe wall thickness

H_i = ratio of heat source area to heat loss area

OD = outside pipe diameter

ID = inside pipe diameter

C1.2.2 Use $H_i = 5$ for piping in the horizontal position up to 150 DN (6 NPS). Use $H_i = 3$ for piping in the horizontal position with pipe sizes over 150 DN (6 NPS). See Annex A of AWS D10.10 for further discussion of the H_i ratio.

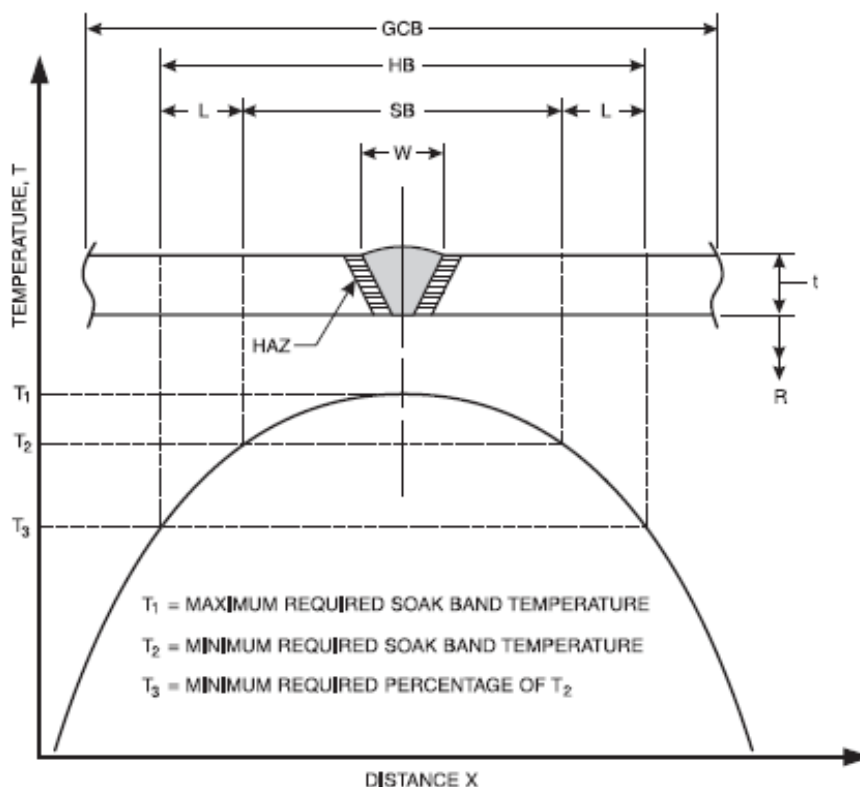
C1.3 Gradient Control Band (GCB)—The gradient control band consists of the surface area over which insulation and/or supplementary heat source(s) are placed. It should encompass the SB, HB, and sufficient adjacent base metal such that the maximum permissible axial temperature gradient within the heated band is not exceeded.

C1.3.1 The minimum gradient control band width and insulation characteristics should be as defined in Equation 3:

$$GCB = HB + 4\sqrt{Rt} \quad (3)$$

Use Equation 3 to calculate the minimum GCB width, with a minimum R-value for the insulation of 2° to 4° F-ft²-h/BTU.

Figure C1 provides a schematic diagram that uses the terms recommended for PWHT from AWS D10.10. The terms are defined as:



Nomenclature:

W = Widest width of butt or attachment weld.

HAZ = Heat-affected zone.

SB = Soak band (width of the volume of the material where the holding temperature equals or exceeds the minimum and equals or is below the maximum required. The minimum width is typically specified as W plus a multiple of t on each side of the weld).

L = Minimum distance over which the temperature may drop to a percentage of that at the edge of the soak band.

HB = Heated band (width of heat source).

GCB = Gradient control band (minimum width of insulation and/or gradient heat source).

t = Nominal thickness of piping, branch connection, nozzle neck, or attachment.

R = Inside radius of piping, branch connection, or nozzle neck.

Figure C1: Schematic Diagram for Description of Local 360° Band Heating¹⁴

WRC uses the same terminology, which is also used in Section 3 of this standard. The equations for vessels, based on WRC 452, are shown in paragraph 3.3.

