Avoiding Environmental Cracking in Amine Units

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Contents

Page

Figures

Avoiding Environmental Cracking in Amine Units

1 Scope

This recommended practice (RP) discusses environmentally assisted cracking of carbon steel equipment in amine treating units. Amine stress corrosion cracking and sulfide stress cracking of stainless steels in amine units is beyond the scope of this document, although there have been isolated reports of such problems. This RP provides guidelines for carbon steel construction materials including their fabrication, inspection, and repair to help assure safe and reliable operation. The carbon steels referred to in this document are defined by the ASTM designation system, or are equivalent materials contained in other recognized codes or standards. Welded construction is considered the primary method of fabricating and joining amine unit equipment. See terms 3.6 and 3.7 for the definitions of weld and weldment.

This document is based on current engineering practices and insights from industry experience. Older amine units may not conform exactly to the information contained in this RP, but this does not imply that such units are operating in an unsafe or unreliable manner. No two amine units are alike, and the specific strategies to avoid cracking in a unit will be customized to that unit. Each user company is responsible for safe and reliable unit operation.

Rotating equipment is specifically excluded from the API 945 scope. However, API 610 on centrifugal pumps does have a table that recommends PWHT of all welds in amine services.

2 Normative References

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any addenda) applies.

API 510, *Pressure Vessel Inspection Code: Maintenance Inspection, Rating, Repair, and Alteration*

API 570, *Piping Inspection Code: Inspection, Repair, Alteration, and Rerating of In-Service Piping Systems*

API Recommended Practice 572, *Inspection of Pressure Vessels*

API Recommended Practice 579-1/ASME FFS-1,*Fitness-for-Service*

API Recommended Practice 582, *Welding Guidelines for the Chemical, Oil, and Gas Industries*

API Standard 653, *Tank Inspection, Repair, Alteration, and Reconstruction*

API Recommended Practice 583, *Corrosion Under Insulation and Fireproofing*

API Technical Report 938-C, *Use of Duplex Stainless Steels in the Oil Refining Industry*

API Recommended Practice 956, *Hydrogen-Assisted Crack Growth in 2-$^1/_4$ Cr-1 Mo Steel*

American Welding Society (AWS), AWS D.10.10

NACE SP0472 [1] , *Methods and Controls to Prevent In-Service Environmental Cracking of Carbon Steel Welments in Corrosive Petroleum Refining Environments*

NACE No. 2/Near-White Metal Blast Cleaning SSPC-SP 10

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[1] Association for Materials Protection and Performance (AMPP), formerly NACE International.

NACE SP0296, *Detection, Repair, and Mitigation of Cracking in Refinery Equipment in Wet H_2S Environments*

NACE MR0103/ISO 17945,*Materials Resistant to Sulfide Stress Cracking in Corrosive Petroleum Refining Environments*

NACE Publication 8X194, *Materials and Fabrication Practices for New Pressure Vessels Used in Wet H_2S Refinery Service*

Welding Research Council (WRC), WRC 452

3 Terms and Definitions

The following terms and definitions apply to this document.

3.1
amine service
Minimum concentration of 2 weight percent amine in water-based solution.

3.2
fresh amine
An amine-water solution containing no H_2S and/or CO_2 (i.e. solution which has not been used in the unit and therefore not exposed to acid gas). Less commonly referred to as pure amine or virgin amine.

3.3
lean amine
An amine-water solution which has been regenerated to remove most of the H_2S and/or CO_2 but typically contains some trace levels of H_2S and/or CO_2.

3.4
postweld heat treatment (PWHT)
A thermal treatment performed on a weldment, typically to reduce hardness and/or residual stresses.

3.5
rich amine
An amine-water solution which has been exposed to H_2S or CO_2 in a contactor containing a significant amount of H_2S and/or CO_2 and has not been regenerated to remove H_2S or CO_2.

3.6
weld
The weld deposit.

3.7
weldment
The weld deposit, heat-affected zones (HAZ), and adjacent base metal zones subject to residual stresses from welding.

4 Background on Amine Units

4.1 Amine Units Process Description

In refineries and petrochemical plants, gas and liquid hydrocarbon streams can contain acidic components such as hydrogen sulfide (H_2S) and carbon dioxide (CO_2). Amine units operating at low and high pressures are used to remove such acidic components from process streams through contact with, and adsorption by, an aqueous amine solution.

Figure 1 is a simplified process flow diagram for a representative unit. The gas or liquid streams containing one or both the acidic components are fed to the bottom of a gas absorber tower or liquid contactor vessel, respectively. The lean (regenerated low acid) amine solution flows downward, counter to the acid laden hydrocarbon streams in the tower and absorbs the acidic components during the process. The purified gas or liquid stream flows upward and passes to the overhead system. The rich amine solution goes out of the bottom of the absorber (contactor) and is fed to a regenerator (stripper) tower, where the acidic components are removed by pressure reduction and by the heat supplied from a reboiler. The acidic components are removed overhead and sent to an incinerator, thermal oxidizer, or sulfur removal plant (usually called “sulfur recovery unit”), or another processing operation. The lean amine solution that leaves the bottom of the regenerator is cooled in a heat exchanger, then returned to the absorber or contactor to be used again for purification of the hydrocarbon streams. Since the amine is recycled back to the absorber (contactor), various salts and reaction products can accumulate and concentrate.

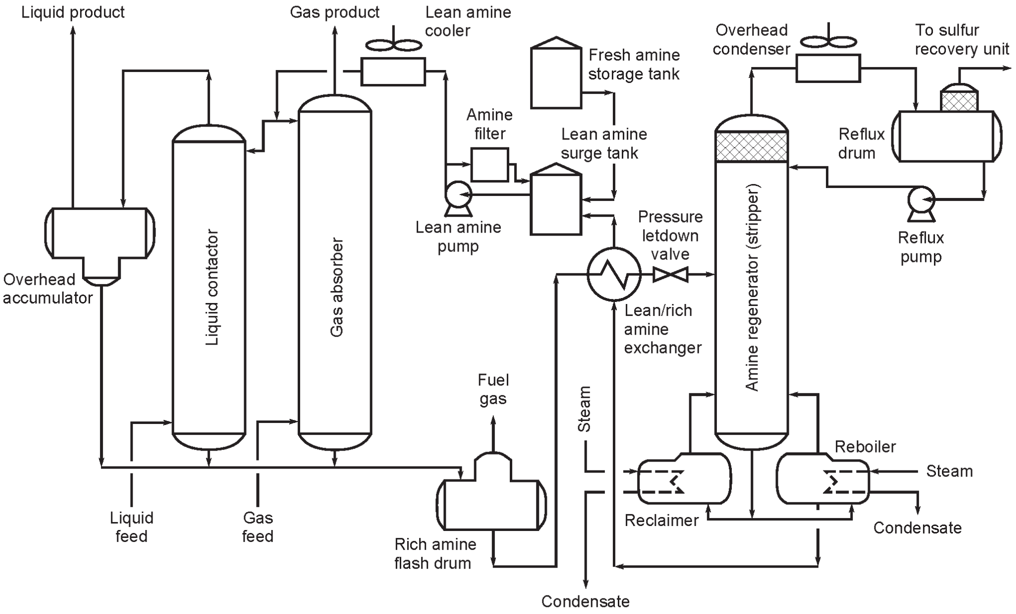


Figure 1—Simplified Process Flow Diagram of a Representative Amine Unit

4.2 Amine Solution Types

Various types of water-soluble amines have been developed for the purification of process streams. The most-commonly used amines are aqueous solutions of:

— Monoethanolamine (MEA),

— Diethanolamine (DEA),

— Methyldiethanolamine (MDEA),

— Diisopropanolamine (DIPA),

— Diglycolamine (DGA).

4.3 Problems in Amine Units

4.3.1 General

Metallurgical and corrosion problems in amine units can usually be traced to design, material selection or fabrication, operating practices, or solution deterioration. The problems fall into two major categories—environmental cracking and wall loss corrosion.

4.3.2 Environmental Cracking

Fresh amine solutions (solutions of amine and water, without H_2S or CO_2) have shown not to produce environmental cracking.

Conversely, both “lean” amine and “rich” amine can cause cracking of carbon steel equipment, due to four different mechanisms.

1) Sulfide stress cracking (SSC).

2) Hydrogen-induced cracking (HIC) associated with hydrogen blistering.

3) Stress-oriented hydrogen-induced cracking (SOHIC).

4) Alkaline stress corrosion cracking (ASCC). Note that amine stress corrosion cracking is termed amine SCC, not ASCC. However, amine SCC is one of several forms of ASCC.

The first three mechanisms (SSC, HIC, and SOHIC) are most prevalent in carbon steels that have been exposed to rich amine solutions containing wet H_2S, and more commonly associated with the lower sections of absorber or contactor towers. In contrast, ASCC is more common in carbon steel components that have been exposed to lean amine service, especially in high residual stress areas. Cracking can occur both with and without significant metal loss. Definitions of these cracking mechanisms and photomicrographs are presented in Annex A.

In rich amine services, cracking can occur due to sulfide stress cracking (SSC) in areas of high hardness and, to a lesser degree, residual tensile stresses. Cracks have also been reported in areas where high hardness levels were not detectable with standard field hardness measurement equipment. Weld-repaired areas can be particularly susceptible to cracking when excessively hard zones or regions of high residual stresses have not been effectively eliminated by the repair procedure. In addition, cracking has also been known to occur in base metal where arc strikes have occurred on the wetted internal surfaces.

In lean amine service, alkaline stress corrosion cracking (ASCC) can occur in carbon steels at slightly elevated temperatures in regions of high stress. This cracking is more often associated in areas of significant residual stress including the heat affected zone in weldments or opposite external welds for attachments, such as piping shoes, ladders, and lifting lugs. High residual stress is the major driver for cracking in lean amine, not high hardness.

Several serious cracking problems have been reported since the early 1950s. Some have been due to ASCC and some due to SSC. ASCC of carbon steel by amine solutions was first mentioned in a report published in 1951 by the NACE Technical Practices Committee 5C on Sub-Surface Corrosion by Alkaline Solutions [1]. The report noted that piping, regenerators (strippers), absorbers, and heat exchanger shells and heads made from carbon steel had cracked after six months to 10 years of exposure to 15 weight percent MEA in water at temperatures up to 300 °F (149 °C). The MEA contained unspecified amounts of both hydrogen sulfide and carbon dioxide. Complete stress relieving via PWHT was recommended as a solution to the problem.

In 1953, ASCC was reported in MEA solutions in gas treatment plants [2]. Requirements for cracking included the presence of both a high stress and a particular corrosive amine solution. The elimination of either factor was found to prevent cracking. Recommended preventive measures included maintaining the reboiler temperature and the regenerator pressure at the lowest practical levels, using reclaimers, and preventing air contact to minimize the corrosiveness of the amine solutions. Frequently, such process changes cannot be readily implemented, so stress relieving was recommended as an effective alternative.

Other instances of ASCC were reported in non-stress-relieved equipment operating in 20 weight percent MEA [3]. Affected equipment included two amine storage tanks, four absorber towers, one rich amine flash drum, one lean amine treater, and various piping locations. Cracking was found primarily at welds exposed to amine solutions where temperatures ranged from 127 °F to 200 °F (53 °C to 93 °C). The cracking was intergranular, and the crack surfaces were covered by a thin film of magnetite (Fe_3O_4). No cracking was found in postweld heat treated (PWHT) piping that operated at temperatures as high as 310 °F (154 °C). Although the exact reason for the extensive cracking was not clear, it was concluded that PWHT could be used to prevent the problem.

A major problem occurred in 1984, when an MEA absorber tower ruptured at a U.S. refinery. This failure initiated as SSC in the hardened area of the heat-affected zone of a rewelded shell seam and propagated by SOHIC through the base metal [4]. The weld repair had been performed 10 years earlier as part of a procedure to replace a shell course which had hydrogen blisters.

In 1986, extensive leaking of piping welds was reported in lean MEA service [5]. The leaking was attributed to ASCC. Most leaks occurred at piping welds that had been in lean amine service for 4 to 8 years. Cracks were found in the weld deposits, heat-affected zones, and areas of the base metal adjacent to heat-affected zones. Typically, the cracks propagated parallel to the weld. Shear-wave ultrasonic inspection confirmed the presence of cracks at many other welds in lean amine piping. None of the cracked piping welds had received PWHT.

As a result of these occurrences, in 1985 the NACE Group Committee T-8 on Refining Industry Corrosion, in cooperation with the API Subcommittee on Corrosion and Materials, sponsored an industry-wide survey of cracking problems in amine services [6]. The results of this survey indicated that cracking was most prevalent in MEA service, and that it occurred in all types of equipment at temperatures as low as ambient. PWHT of welds was identified as the single most effective means of preventing cracking. Additional data on stress corrosion cracking of carbon steel in DEA and DIPA services were reported in 1991 [7] and in DEA, DIPA, and MDEA service in 1993 [8].

Industry experience has shown that piping and equipment in rich amine service with H_2S do not typically experience ASCC. An exception has been ASCC in rich amine services due to steamouts of rich amine equipment without first doing a thorough water wash to remove all residual amine. Steamouts strip H_2S from the rich amine and provide the heat to drive ASCC.

In theory, carbon steel equipment and piping cannot be subject to both SSC and Amine SCC in one solution, because the two mechanisms are driven by the opposite electrochemical processes. SSC is a cathodic reaction (hydrogen reduction) cracking mechanism when the steel is in active state. Amine SCC is an anodic reaction (iron dissolution at grain boundaries) cracking mechanism when the steel is in active-passive state or passive breakdown state [14]. Generally, the higher the bisulfide content (from high H_2S loading) of the rich amine stream, the lower the solution pH, so that the carbon steel is more likely in the active state and subject to SSC. On the other hand, the lower the H_2S loading is, the higher the solution pH, so that the carbon steel is more likely in passive state and subject to amine SCC. In general, however, wet H_2S cracking and ASCC are somewhat mutually exclusive. In the regenerator tower where the rich amine is flashed and heated to strip adsorbed acid gases to produce lean amine, it is difficult to define where the transition occurs between wet H_2S dominated cracking versus ASCC dominated cracking.

4.3.3 Corrosion

Corrosion (metal loss) of carbon steel components in amine units is not caused by the amines themselves. Fresh amine is considered non-corrosive because 1) it is a weak filming inhibitor on its own merit, and 2) there is no corrodent such as bisulfide, heat stable salts (HSS), and it has not yet been introduced into the circulating solution. Metal loss usually results from dissolved acid gases, including hydrogen sulfide and carbon dioxide. Corrosion can also be caused by a variety of amine degradation products including heat stable salts, such as bicine.

In rich amine, typically the corrosion rate is higher than that of lean amine because of high conductivity and/or low pH, and the rate increases with increasing temperature. For example, rich amine with temperatures greater than 220 °F (104 °C) can result in acid gas flashing and increased localized corrosion when the pressure drop is high enough to cause flashing (such as downstream of a pressure letdown valve). Normally a high corrosion allowance is required for carbon steel or an upgrade to austenitic stainless steel under these conditions.

In lean amine, the corrosion rate is generally lower than that in rich amine, but an excess of heat stable salts above 2 weight percent may significantly increase corrosion rates on carbon steel.

Overstripping of lean amine (i.e. having too low of an H_2S content in H_2S removal units) has led to severe corrosion problems especially in the hot sections of the lean amine circuit. These case histories probably had additional factors contributing to the corrosion risks, such as somewhat high HSS contents, but to reduce the risk, many operators apply a minimum H_2S limit in addition to the maximum limits. The typical recommended minimum limits have ranged from ~100 to 800 ppmw H_2S. Other refiners have used values between 0.001 to 0.02 mol H_2S per mol amine as a minimum recommended limit. This is dependent on the refiner's experience and particular operation parameters and is also dependent on amine type/strength, HSS, velocity, and total dissolved solids. These limits vary considerably due to operational differences from refiner to refiner. In Tail Gas Treating units there are often environmental restrictions which require better stripping, resulting in lower H_2S contents than the 100 ppmw to 800 ppmw minimum recommended. Since it would be impossible in these units to produce H_2S contents above these minima and still meet environmental regulations, these limits are not applied to Tail Gas lean amine systems. Therefore, in these low H_2S Tail Gas Treating units, other corrosion control steps are necessary.

The cracking of carbon steel components in amine service is often related to the general corrosivity of amine solutions. This is because corrosion reactions are the source of atomic hydrogen, which causes hydrogen blistering and cracking by mechanisms such as SSC, HIC, and SOHIC, primarily of components in rich amine service (see Annex A). Similarly, corrosion reactions contribute to ASCC, primarily of equipment in lean amine service. It is not possible, however, to quantitatively relate cracking severity to corrosion severity. Nevertheless, efforts aimed at improving corrosion control may also reduce hydrogen-related cracking. (See Annex B for more information regarding corrosion in amine units.)

5 Guidelines for Construction Materials and Fabrication of New Equipment and Piping

5.1 Construction Materials

Carbon steel, with a nominal corrosion allowance, has been used for most equipment in amine units that remove hydrogen sulfide or mixtures of hydrogen sulfide and carbon dioxide containing at least 5 % hydrogen sulfide. Some problems have been experienced with erosion-corrosion (see B.3 and B.6.2) associated with circumferential welds in rich amine piping made of carbon steel. The problems are usually solved by reducing fluid velocity to less than 6 ft/sec (1.8 m/sec). However, when rich amine loading is above design limits (see Annex B for examples), even reducing the velocity may not reduce the corrosion rate.

Typically, the corrosion rate of carbon steel in rich amines is much more affected by service velocity compared with that in lean amine. Normally a maximum of 6 ft/sec (1.8 m/sec) for rich amine and maximum 20 ft/sec (6.0 m/sec) for lean amine may be applied for carbon steel piping and pressure vessels (inlet and outlet nozzle sections). However, these are initial guidelines and corrosion rates will also depend on amine loading, heat stable salts content, and temperature. Sometimes increasing the line diameter may be needed to reduce fluid velocity and the corrosion rate. The velocity limits should be decided by the purchaser or owner-operator. The selection of material is a tradeoff. In some cases, upgrading to austenitic stainless steel can allow the owner-operator to specify smaller diameter pipe which is often less expensive than larger diameter PWHT carbon steel, even though velocities are higher in the smaller diameter stainless pipe.

Austenitic stainless steels have been used in locations where the corrosion rate of carbon steel is excessive, or the PWHT of carbon steel is to be avoided. Such locations include those that contact hot/rich solutions with high acid gas loading, areas of high velocity, turbulence, impingement, vapor flashing, or two-phase flow, and most heat transfer surfaces operating above ~175 °F (80 °C). Austenitic stainless steels are usually employed extensively in amine units to remove carbon dioxide from hydrocarbon streams that contain very little or no hydrogen sulfide. For vessels and other fixed equipment, clad plate is preferred over solid stainless steel construction to avoid possible through-wall chloride stress corrosion cracking, although there are numerous cases where solid stainless has served reliably. Some owner-operators have specified solid stainless steel pressure vessels where control of external chloride stress corrosion cracking was achieved by external coatings such as organic paint coatings or thermally sprayed aluminum coatings. API Recommended Practice 583 gives additional guidance on prevention of corrosion under insulation, including SCC. For piping, solid austenitic stainless is generally used. Stainless alloys, such as Types 304L and 316L, have been used for regenerator reboiler tubes. In addition to these austenitic stainless steels, duplex stainless steels have been used for reboiler and reclaimer tubes. Duplex stainless steels have been used specifically in streams containing significant chloride levels which promote a chloride stress corrosion cracking and pitting risk in austenitic 300 series stainless steels.

Even higher alloys such as titanium tubes have been used in units handling CO_2, but they may embrittle due to hydride formation in service. This is especially true at tube-to-baffle interfaces when a carbon steel baffle is used with titanium tubes.

For pressure vessel plate or rolled and seam-welded pipe, carbon steels with a low level of inclusions, inclusion shape control, or both may provide improved resistance to hydrogen blistering, HIC, and SOHIC. These steels should be evaluated for potential use in equipment that handles rich amine solutions, and in the regenerator overhead, especially if cyanides are present. In some units, operating conditions in the bottom of amine absorbers or contactors are conducive to hydrogen blistering, HIC, or SOHIC despite relatively low temperatures. Carbon steels with a low level of inclusions or inclusion shape control may also be useful in these locations. However, it should be noted that these steels are not immune to blistering and cracking, so their potential use should be carefully considered. It should also be noted that continuous cast steels may be low in inclusion content, but impurities that are present might segregate at the plate mid-wall, which can cause high hardness or laminations at that location. For vessels and other fixed equipment, austenitic stainless steel cladding, lining, or weld overlay are more reliable methods of protection in areas where corrosion, cracking, or hydrogen blistering occurs.

For carbon steel piping, seamless manufacturing methods have reduced the amount of inclusions in the product compared with rolled and seam-welded product made from plate. In addition, the inclusions in seamless carbon steel piping are not elongated as much as in rolled plate product. Therefore, seamless carbon steel pipe can offer improved resistance to hydrogen blistering, HIC, and SOHIC. For new construction, seamless ASTM A106 Grade B carbon steel piping is generally preferred. For large diameter piping where seamless is not available, ASTM A671 or ASTM A672 is preferred.

One operator found ASCC in a high pressure lean amine circuit on thick, seamless CS pipe at multiple locations remote from welds. It is believed that the pipe mill cold bent the pipe by running it through straightening rolls after hot forming resulting in high residual stress fields. Attention should be given to any cold bending practices that results in excessive plastic deformation during the manufacturing or fabrication process for piping components. See A.6 for more details on this failure.

5.2 Fabrication

5.2.1 General

Certain fabrication practices can help reduce the likelihood of cracking in carbon steels in amine units. These practices include controlling weldment hardness levels and applying PWHT. Attention should be given to proper base metal and weld composition to assure satisfactory response to heat treatment. To control cracking problems effectively, proper consideration should be given to each of these factors. Refer to API Recommended Practice 582 and NACE SP0472 for guidance on weld fabrication. Some owner-users also require materials and fabrication for lean or rich amine service comply with NACE MR0103/ISO 17945 and NACE Publication 8X194.

5.2.2 Weldment Hardness Control

Proper control of weldment hardness in fabricated carbon steel equipment and piping can provide resistance to SSC in rich amine. NACE SP0472 defines practical and economical means of protection against this type of cracking, and outlines necessary controls on base metal, weld composition, and welding parameters to achieve weldments of acceptable hardness for the intended service.

As stated in NACE SP0472, the weld hardness of carbon steel equipment, including piping, should not exceed a Brinell hardness of 200, unless the purchaser has agreed to a higher allowable hardness.

However, it should be noted that a maximum Brinell hardness of 200 in the weld deposit provides no assurance of preventing SSC in the weld's heat-affected zone, or in base plate material where temporary attachments have been made or arc strikes have occurred. Other measures outlined in SP0472, including PWHT, should therefore be considered as a means of providing added cracking resistance to carbon steel weldments.

In the case of amine systems handling CO_2 only, there does not appear to be any benefit to limiting weldment hardness to 200 HB since amine containing carbonic acid produced by wet CO_2 does not cause environmental cracking. Hardness limits for such systems should be evaluated by each user based on past experience.

As noted in A.5, controlling weldment hardness has no known effect on the prevention of amine SCC. However, PWHT at sufficiently long duration and sufficiently high temperature reduces residual stress in carbon steel weldments, thereby greatly reducing the risk of amine SCC. Guidelines for PWHT requirements are outlined in NACE SP0472. Controlled deposition welding (CDW) processes such as temper bead, half-bead, and multi-bead welding are not effective for ASCC mitigation since residual stresses are not reduced by controlled deposition welding.

Dissimilar metal welds between carbon steel and stainless steel should be avoided to alleviate potential hard zones and the inability of PWHT to relieve residual stresses at the bimetallic joint.

5.2.3 Postweld Heat Treatment (PWHT)

PWHT, as described in NACE SP0472, should be applied to new carbon steel equipment, including piping operating continuously or intermittently in lean or rich amine services. For stainless clad carbon steel plate and stainless weld overlay onto carbon steel where the amine will not contact the underlying carbon steel, there is no need for PWHT for cracking avoidance.

There is no need for PWHT of carbon steel in fresh amine service. However, some owner-users perform PWHT on carbon steel equipment in fresh amine service as an added caution and to simplify their specifications so that PWHT is performed for all amine services regardless of amine type or loading.

In the past editions of this RP, different amine types were believed to have threshold temperatures for when PWHT is recommended. These threshold temperatures versus amine type are included in Annex C. While these may still be technically correct, there is enough evidence to caution the owner-operator that ASCC may still occur below the previously stated threshold temperatures. Therefore, this Edition does not differentiate among amine type, concentration, or operating temperature and has no minimum threshold temperature. PWHT is now recommended for any amine service except fresh amine. Refer to 5.2.3.3 for correct PWHT parameters.

Industry experience has shown that infrequent exposure to amines from amine contamination of hydrocarbon streams has resulted in ASCC. Most commonly, absorber overhead systems can be subjected to amine carryover and stress corrosion cracking due to inadequate amine de-entrainment in the tower caused by irregular operation, such as foaming upsets. Some operators have chosen to PWHT carbon steel piping up to the first overhead drum, and the drum itself.

Although PWHT is now recommended, historically, some users did not specify PWHT of seamless piping in rich amine services with H_2S, based solely on the fact that ASCC did not typically occur in H_2S-rich systems without CO_2. In refining, most amine treating systems do not have significant amounts of CO_2 (except for steam methane reformers, fluidized catalytic crackers, and some cokers). In rich amine services without CO_2, the governing mechanism is wet H_2S cracking (e. g. sulfide stress cracking), not ASCC. Hence this requires controlling hardness in the weldment to acceptable levels. Multi-pass welding and thermal control per NACE SP0472 is one approach, but this requires minimizing residual elements (e. g. niobium and vanadium) to ensure the weld HAZ remains acceptably soft. The issue which stems from this approach relates to the definition of lean versus rich amine.

Mildly sour conditions can have rich amine which lacks sufficient H_2S loading to prevent ASCC. This document has therefore recommended PWHT to minimize the risk of both wet H_2S cracking and ASCC.

For lean amine systems, there have been recent reports of cracking failures even in carbon steel which has been PWHT. The main factor cited by refinery owner-operators is inadequate PWHT, most often when the PWHT temperature was too low, or the band width of the heated zone too narrow. In one case, the PWHT was conducted below 1094 °F (590 °C). Another contributing factor is that the sections of the lean amine systems from the regenerator tower and reboiler circuit through the tower bottoms to the lean exchanger cooler are much hotter than most of the rich amine circuits within the amine unit.

It is unclear what role, if any, electrochemistry plays in causing steel which has been PWHT to crack recently in these conditions. Lean amine cracking is an anodic reaction, causing iron dissolution in grain boundaries [14]. When passivity breaks down, the tendency to crack increases. FeS passive layers, formed by higher amounts of H_2S while still in the lean amine range may help prevent passivity breakdown. However, after a long period of use, the amine eventually needs to be changed or recycled. It may be that the passive layer is disrupted by the new, fresh amine solution and it is thought that this may lead to cracking. However, none of this fully explains why PWHT steel recently cracked, when years of experience showed no cracking under similar conditions. Austenitic or duplex stainless steel is a valid upgrade in these systems, and since they do not require PWHT they can be economical. Austenitic stainless Types 304L and 316L or duplex stainless alloy 2205 can be considered when stress relieving is difficult or impossible such as for tube-to-tubesheet welds. If using duplex stainless steel, API Technical Report 938-C and API Recommended Practice 582 welding and fabrication controls should be used.

Some equipment and components are challenging to PWHT and therefore are often exempted from PWHT. Examples include flare system headers, piping systems with in-line welded valves containing non-metallic internals, and field erected storage tanks.

For tanks, the following protocol has been used by some owner-operators to protect against ASCC, SSC, HIC, and SOHIC:

— Smaller shop fabricated tanks should be PWHT when practicable.

— Larger field-built tanks are difficult to PWHT successfully. Most operators do not attempt to PWHT larger tanks. When PWHT is performed, some operators have elevated the bottom with insulation to achieve sufficient heat flow into the weldment during a field PWHT.

— When tanks are not PWHT, flushing with clean water and then minimizing steamout and keeping the fluid temperature as low as possible is very important to minimize the risk of ASCC. (See historical temperature limits in Annex C.)

— When PWHT is not practicable for a tank, some users specify PWHT of the steam coil nozzle-to-insert plate prior to insertion and welding into the tank. In addition, some users specify an organic coating or lining in lieu of PWHT, especially in the critical chine area. The coating material must be chemically resistant to the amine at the tank service temperature. If the tank requires steamout, the coating must be resistant to the amine at the steamout temperature, or the tank needs to be flushed with water prior to steamout. Other users have applied metallic thermal spray coatings. It is not well documented how successful the organic or metallic coatings have been. The coating and liners are intended to isolate the environment from the steel, preventing cracking. If steam coils are present in the tank, the owner-operator will need to evaluate the risk and determine whether additional mitigation such as local PWHT or coatings are needed.

— Fresh amine tanks regardless of size are typically not PWHT, since industry has not seen issues with fresh amine causing ASCC.

5.2.3.1 PWHT of Socket-welded and Threaded Connections

5.2.3.1.1 Socket-welded Connections

Small-diameter socket-welded connections contain geometrical discontinuities that act as local stress raisers where cracks may initiate. Where PWHT is recommended for carbon steel equipment or piping containing socket-welded connections, the connections should also receive PWHT.

5.2.3.1.2 Threaded Connections

Threaded connections may contain highly stressed thread roots that can serve as crack initiation points in amine service. The use of threaded connections should be carefully evaluated in amine service where PWHT of carbon steel welds is required to resist cracking. Seal welded threaded connections should have at least two pass welds to minimize hard weld SSC issues. PWHT would be desirable but is often not performed.

5.2.3.2 PWHT versus Amine Types

Previous Editions of this RP have provided different acceptable temperature ranges for different amine types, calling for PWHT if the temperature exceeds certain values. This previous guidance on threshold temperature versus need for PWHT has been retained in Annex C for historical purposes.

Industry experience showed that MDEA has a higher threshold amine cracking temperature in carbon steel weldments than MEA. In general, experience showed that tertiary amines have been less aggressive at a given temperature than either secondary and primary amine molecules and this is discussed in Annex C. However, most owner-operators have decided to PWHT all NEW amine equipment exposed to lean amine (except for the limitations of tanks and other difficult-to-PWHT examples discussed above). Many operators also specify PWHT for all rich amine service equipment and piping.

In addition, there have been cases where a less-aggressive amine has been switched to a more-aggressive amine without a thorough review of the cracking consequences. This is another reason why many operators now PWHT all carbon steel in any amine service other than fresh amine.

5.2.3.3 PWHT Procedures and Temperatures

NACE SP0472 contains the detailed procedures for PWHT and the recommended temperature for PWHT in amine service. The latest edition of NACE SP0472 (at the time of this revision) requires 1175 °F ± 25 °F (635 °C ± 15 °C) for one-hour per inch, with one-hour minimum. American Welding Society (AWS) AWS D.10.10 and Welding Research Council (WRC) WRC 452 should be used for guidance to minimize residual stresses and deformation during PWHT. Alternative heat treatments at temperatures below 1100 °F (593 °C) should not be performed, because they do not adequately relieve residual stresses.

A PWHT range of 1175 °F ± 25 °F (635 °C ± 15 °C), which is higher than the minimum ASME Code PWHT temperature, is needed to reduce the residual stresses to an acceptable level to minimize amine SCC. The higher PWHT temperature is more effective in reducing residual stresses, and thus minimizes ASCC, HIC, and SOHIC. In addition, the higher PWHT temperature further reduces hardness of local brittle zones in weldments and thusly reduces SSC risk.

Note that for bare carbon steel, thick-walled, higher pressure amine vessels, the requirements which call for higher temperature, long duration PWHTs may cause difficulty in meeting carbon steel tensile strength requirements. For these cases, use of austenitic stainless cladding or weld overlay with standard ASME Code PWHT for the carbon steel base metal may be a better choice. The prospective vessel fabricator should be consulted to determine the best approach.

The user is cautioned to ensure that the PWHT temperatures and time requirements are strictly followed to ensure the weldment indeed sees enough thermal energy to allow the metal to soften and relieve residual stress. This has been cited as a potential reason why PWHT hasn’t always prevented ASCC, particularly in lean amine. While the ASME *Boiler and Pressure Vessel Code* allows carbon steel to be PWHT as low as 1100 °F (593 °C) without any additional increase in exposure time for general services, there have been various documented cases of ASCC from carbon steel with PWHTs performed around 1100 °F (593 °C).

The need for an additional PWHT for external welds deposited after the original PWHT (e.g. attaching pipe support shoes, lifting lugs, external surface repairs, arc strikes) requires consideration of PWHT based on the possibility of introducing tensile stress fields on the process exposed surface.

6 Inspection and Repair of Existing Equipment

6.1 General

The procedures in this section are guidelines for the inspection and repair of existing equipment used to handle amines. The objective is to maintain such equipment in a safe and reliable condition.

6.2 Inspection

The examinations listed in this section emphasize inspection of equipment for cracks. Inspection should be in accordance with API 510, API 570, and API Standard 653. The user should follow API 510, API 570, and API Standard 653 for inspection intervals.

The equipment inspection plan should consider ASCC and/or wet H_2S cracking based on its PWHT status and its operational (temperature) history and cracking susceptibility. For example, if the equipment had not been originally PWHT, there is more probability of cracking. Also, if the equipment was operated at a higher temperature than normal, there may be an increased probability of cracking.

The user also needs to take into account any subsequent repairs and determine if those were adequately PWHT or not. It is imperative that the area to be PWHT reach the specified temperature for the specified time. This is somewhat hard to determine on existing equipment when heat treat time-temperature charts are not available. In addition, field hardness tests are not a good indicator of cracking susceptibility. First, hardness does not measure residual stress which is the primary driver for ASCC. Tests showing the carbon steel is of acceptable hardness do not conclusively show that a weldment has been adequately stress relieved by PWHT. Tests showing high hardness are generally indicative of an inadequate PWHT, but caution must be used when evaluating field hardness results since it is very difficult to get accurate portable hardness readings, especially in the narrow HAZ.

Piping in lean amine service that is not PWHT could have some susceptibility to ASCC. While external inspection using ultrasonic methods can detect cracking in piping, most users do not inspect lean amine piping for cracks if it has been PWHT unless there is a history of ASCC. Also, most users do not routinely inspect rich amine piping for cracking if it has been PWHT because the likelihood of finding ASCC and wet H_2S cracking is extremely low. See 6.2.1.2 for further details on piping inspection.

Common NDE methods used to detect cracking in amine service are:

— Internal Inspection—Wet fluorescent magnetic particle testing (WFMT, referred to in 6.4.1) or surface eddy current. Both techniques can detect surface breaking cracks. Either one can be performed during a shutdown.

— External Inspection—Phased array ultrasonic testing (PAUT). PAUT can be performed on-stream if the operating temperature isn't too high. Check with the PAUT equipment manufacturer to determine temperature limits. PAUT can also be performed during a shutdown.

If hydrogen blisters are identified during an internal visual inspection, consideration should be given to performing a selective ultrasonic inspection to identify blistered areas not apparent by visual inspection and to identify the presence of HIC and SOHIC.

6.2.1 Cracking Inspections

With ASCC, cracks and related defects initiate on the ID surface. With wet H_2S damage, cracks initiate either on the ID or slightly subsurface. Therefore, the primary inspection effort should be directed toward internal surfaces contacted by amine solutions, wherever practicable, (e.g. in vessels) using surface inspection techniques on the ID. When internal inspection is impossible or impracticable, (e.g. for piping) ultrasonic methods from the OD can be used.

6.2.1.1 Fixed Equipment Crack Inspections

Specific areas for inspection of vessels and other types of fixed equipment include:

a) Areas repaired by welding.

b) Longitudinal and circumferential weldments—both welds and HAZs.

c) Manway and nozzle attachment welds (including welds that attach reinforcing pads).

d) Attachment welds of internals (tray and downcomer welds, support attachment welds for distributors and vortex eliminators, bare base metal adjacent to cladding).

e) Heat-affected zones on internal surfaces opposite externally attached structural steel platforms, ladders, and the like; and arc strikes from welding or positive material identification (PMI).

f) Weld areas behind, or associated with, leaking panels of alloy strip-lined vessels which may also be susceptible to cracking.

g) Tube-to-tubesheet joints (either expanded or welded).

The items listed above may be adjusted based on the inspection program of each owner-operator along with the heat treatment condition of the item being considered for inspection.

6.2.1.2 Piping Crack Inspections

While piping is not typically inspected, when cracking is determined to be likely, the following list contains inspection focus areas.

a) Pressure containing welds, both longitudinal and circumferential.

b) Attachment welds associated with pipe shoes, support clips, or other non-pressure-containing attachments.

c) Attachment welds of reinforcing pads for nozzles.

d) Repair welds of any type, plus arc strikes.

The items listed above may be adjusted based on the inspection program of each owner-operator along with the heat treatment condition of the item being considered for inspection.

6.3 Examination Procedures and Methods

6.3.1 Wet Fluorescent Magnetic Particle Testing

Wet fluorescent magnetic particle testing (WFMT) is a very sensitive method for detecting surface-connected cracks and discontinuities.

WFMT requires surfaces that are grit blasted to a near-white finish that meets the requirements of NACE No. 2/SSPC SP 10. Abrasive blasting or high-pressure water jetting at a pressure of 70 MPa (10,000 psi) or higher may be used. The area prepared for inspection should normally be 4 in. to 6 in. (100 mm to 150 mm) on either side of the weld.

Light grinding may be needed to distinguish anomalies in weld profiles from indications of discontinuities, e.g. at the toe of welds.

Extensive field experience has demonstrated that detection of the fine amine cracks is greatly enhanced by subsequent polishing of the cleaned surfaces with flapper wheels or flexible abrasive sanding pads.

Considerable field experience has demonstrated that power wire brushing or grinding (e.g. power buffing) of the areas to be inspected in lieu of the surface preparation methods recommended above does not produce an acceptable surface for reliable detection of cracking in amine equipment, and therefore should not be used. Metallographic inspection indicates that power wire brushing or grinding smears metal on the surface that covers underlying cracking, greatly reducing the likelihood of its detection by WFMT.

6.3.2 Alternating Current Field Measurement and Surface Eddy Current

Alternating current field measurement (ACFM) and surface eddy current (EC) are electromagnetic techniques that can be used to detect surface-breaking cracks in ferromagnetic materials. These methods can be applied through thin coatings and do not require extensive surface preparation. They are best used as a screening tool for rapid detection of cracking along welds and heat-affected zones with little or no surface preparation. They can be used in lieu of WFMT but are less sensitive.

6.3.3 Ultrasonic Testing

Ultrasonic testing (UT), using either manual or automated methods, is very useful for crack detection in amine equipment. Various UT methods can also be used for sizing depth of cracks. See API Recommended Practice 956.

Depending on the surface temperature limitations, UT inspection can be performed onstream. Consideration should be given to the difficulty of detecting transverse cracking in the weld when using UT methods.

6.3.4 Radiographic Testing

Radiographic testing (RT) is typically not employed to detect cracks in amine equipment. ASCC can be very tight and present a challenge for RT.

6.3.5 Liquid Penetrant Testing (LP) and Dry Magnetic Particle Testing (MT)

Liquid penetrant testing and dry magnetic particle testing are not recommended inspection methods for ASCC or SSC. They do not reliably reveal the tight cracks that are characteristic of cracking in amine equipment.

6.3.6 Visual Examination

Visual examination of operating equipment in accordance with API 510 and API 570 should be part of the inspection process. Visual examination of uninsulated piping and vessels that are in operation can detect leaks at welds and other potential problem areas. For example, lean amine air coolers may leak at the tube-to-tubesheet joints. Oily areas behind the tubesheet can be a sign of leaks and cracks. Visual examination of insulation can help detect leaks in piping. The presence of a bubble in the paint over a weld, adjacent to a weld, or at any other area should be considered suspicious, because it can indicate the location of an extremely tight crack.

6.3.7 Surface Preparation—General

All methods of inspection rely on adequate surface preparation to enable reliable detection of cracking. The degree of surface preparation will vary considerably depending on the inspection technique that will be applied. Inadequate surface preparation will seriously reduce the effectiveness of any inspection technique.

Equipment should be thoroughly cleaned before internal inspections are performed. Amines are water soluble, and copious amounts of water should be used to wash the surfaces and remove any residual amine contamination. As noted in 4.3.2 and 5.2.3, some equipment has cracked during steamout due to the presence of amine. Therefore, if steamout is required for equipment cleaning, it should follow a thorough water wash to remove any residual amine. The equipment should be dried. In addition, loose scale, fouling deposits, and other material must be removed from all surfaces.

Limited laboratory data and field experience have indicated that in wet H_2S services, removal of protective scales from the internal surfaces of equipment by surface preparation to facilitate internal inspection might increase the likelihood of cracking when the equipment is returned to operation. This phenomenon is expected to be dependent upon the severity of the environment, specific start-up conditions, and the cracking susceptibility of the base metal or weldment.

Recent research conducted using a large-scale pressure vessel exposed to severe hydrogen charging conditions has confirmed that this is a viable concern [11]. Removal of the normally protective films on the steel surfaces led to a short period of higher-than-normal hydrogen flux during simulated start-up conditions and produced increased cracking that was confirmed by acoustic emission testing (AET), UT, and post-test metallographic sectioning of the test vessel.

Use of certain inhibitors applied directly to the cleaned surfaces after inspection was found to minimize the levels of hydrogen flux during simulated start-up conditions. Coatings, while not specifically addressed in this research work, may also be a suitable mitigation method. Notwithstanding the results of this research, industry experience has not indicated that surface preparation has subsequently led to significant additional cracking, especially in amine service. In other words, the benefits of properly de-scaling the steel surface prior to inspection to find cracks far outweigh the risk of removing protective scales in the brief periods post-startup.

6.4 Repair of Damaged Equipment

6.4.1 General

The repair methods listed in 6.4.2 and 6.4.3 primarily apply to vessels and large diameter piping and other piping components (e.g. valves). Small diameter piping [2 in. (50 mm) and smaller] can usually be replaced with new PWHT components at a lower cost than in situ repair and heat treatment.

6.4.2 Crack Removal by Grinding and Gouging

For all repairs, amine residuals and contaminants should be removed from equipment surfaces prior to grinding, gouging, welding, and PWHT. Flushing with copious amounts of water is usually effective. In some cases, additional cleaning with an inhibited acid solution, followed by water flushing, is required. Caution needs to be exercised when acid cleaning sulfide scales because of potential H_2S release.

Careful grinding is the preferred method for removing cracks and other discontinuities. The procedure requires careful control to avoid defect growth. During the grinding procedure, the area in question should be periodically checked (preferably by WFMT; see 6.3.1) to assure that all defects are eliminated. Since ASCC and wet H_2S cracks are tight and difficult to find with other techniques, WFMT is preferred.

Flame gouging and arc gouging methods can be used effectively as the first stage of crack removal, but they must be performed with care, since these procedures may also cause the defects to increase in size. In some cases, an outgassing heat treatment (bakeout) may need to be completed prior to gouging to avoid crack growth (see the section below for more details). After flame gouging or arc gouging, they should be followed by grinding and periodic WFMT to check for defect removal as discussed above.

API 579-1/ASME FFS-1 can be used to evaluate whether defects need repair and if cracks are ground out whether the excavation is acceptable or requires repairs.

6.4.3 Crack Repair by Welding

Prior to any welding, consideration should be given to heating to remove residual atomic hydrogen from the area to be welded (this is also called outgassing, bakeout, or dehydrogenation treatment). NACE SP0296 provides additional guidance on hydrogen bakeout treatments. This is most likely for equipment in rich amine service that has been subjected to a significant level of corrosion and hydrogen charging due to the presence of wet H_2S. Hydrogen outgassing typically is not needed for equipment in lean amine service, but some owner-operators do have a policy to use a hydrogen bakeout in this service.

The area to be weld repaired should be preheated as required (see API 510 and API Recommended Practice 582). When all repairs are completed, repaired areas should be examined using the same nondestructive test method that was initially selected (preferably WFMT; see 6.3.1). Other methods may be used to supplement the examination of the repairs as desired.

6.5 Postweld Heat Treatment of Undamaged or Repaired Equipment

PWHT is the most effective method of preventing cracking in amine services. In the great majority of cases, it has been quite effective, but it has not always been 100 % effective. This is especially true for thicker components where local PWHT is applied and the through wall temperature may not be evenly distributed. In such instances the process exposed surface may not achieve full PWHT temperature. However, in all reported cases it has reduced the amount of cracking failures when compared with non-PWHT carbon steel in the same unit and service.

Existing amine equipment that had not been PWHT could be considered for subsequent PWHT to minimize its susceptibility to cracking on a preventative basis or if there are welded repairs made. Typically, with the exception of smaller items that can be PWHT in a shop, most owner-operators do not retroactively PWHT existing equipment. Most would perform PWHT on repairs (even if not originally PWHT) or try to protect the repaired area with a coating and lining.

For equipment originally built using PWHT, weld repairs should be PWHT.

The decision to PWHT repairs on existing equipment must be made by each user company after the specific situation has been thoroughly evaluated. Factors of consideration should include, but are not limited to, personnel and equipment safety, age and condition of the unit, cost of heat treatment versus equipment replacement, and the intended frequency of future inspections. For in situ PWHT, the equipment and supporting structures must be evaluated to determine and assure their ability to withstand the heat treatment temperatures without permanent distortion or damage. All such evaluations must be based on a thorough understanding of the requirements of any codes, standards, or laws governing the operation of such equipment.

In all cases, equipment should first be washed and thoroughly cleaned before heat treatment is performed to prevent risk of amine SCC during the PWHT. Cleaning should include flushing with copious amounts of water and possibly a mild acid wash to neutralize traces of amine. All residual amine must be removed from the equipment before heat treatment to avoid ASCC. After the equipment has been properly cleaned, heat treatment may proceed. The procedure should be as specified in 5.2.3.

After PWHT has been completed, the equipment should be carefully inspected again using preferably WFMT or alternatively UT to ensure no cracks have opened during the thermal cycle. Any cracks found should be ground out, and if fitness for service evaluation indicates the need for thickness restoration, they should be re-welded, PWHT and re-inspected.

ANNEX A
(informative)

Cracking Mechanisms

A.1 General

There are four basic cracking mechanisms that can affect carbon steel equipment in amine units. These are:

1) sulfide stress cracking (SSC),

2) hydrogen-induced cracking (HIC),

3) stress-oriented hydrogen-induced cracking (SOHIC), and

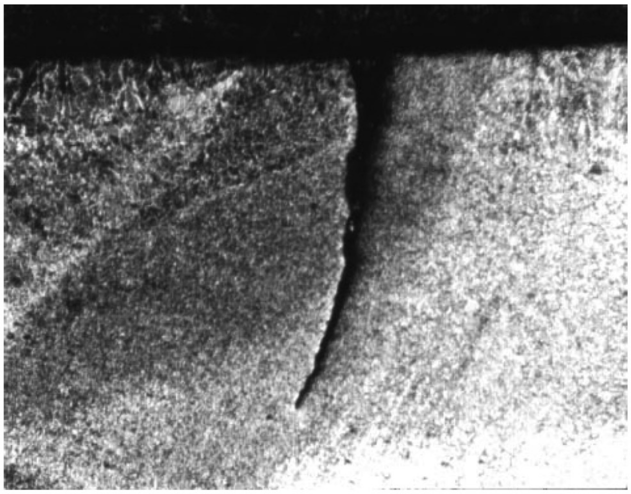
4) alkaline stress corrosion cracking (ASCC).

The first three, SSC, HIC, and SOHIC are forms of hydrogen-related damage. These forms of hydrogen-related damage are typically associated with the entry of atomic hydrogen into the steel. The atomic hydrogen is generated on the steel surface by a corrosion reaction. In amine systems, the corrosion of steel by hydrogen sulfide in an aqueous environment is usually responsible for hydrogen entry into the steel.

In contrast, ASCC is a type of cracking that can occur in amine systems is alkaline stress corrosion cracking. This is a form of anodic stress corrosion cracking and is not related to the three forms of hydrogen-related damage. The basic cracking mechanisms and methods for minimizing their occurrence in amine systems are discussed in A.2, A.3, A.4, and A.5.

A.2 Sulfide Stress Cracking

SSC is defined as the cracking of a metal under the combined action of tensile stress and corrosion in the presence of water and hydrogen sulfide. It is a form of hydrogen stress cracking (HSC). Corrosion of the steel by the hydrogen sulfide liberates atomic hydrogen at the metal surface. The hydrogen sulfide also “poisons” (prevents) the recombination of the atomic hydrogen into molecular hydrogen, thus promoting the adsorption of atomic hydrogen by the steel. The atomic hydrogen then diffuses through the steel and tends to accumulate at areas of high metal hardness and high tensile stress (either applied or residual) and embrittles the steel. Therefore, the SSC mechanism involves hydrogen embrittlement. The cracking mode is primarily transgranular in lower strength steels but can be mixed mode or even intergranular in localized hard regions and in higher strength (i.e. martensitic or bainitic) steels. Figure A.1 illustrates a sulfide stress crack that initiated in a hard heat-affected zone of a steel weldment.



NOTE Two-percent nital etch at 30X magnification.

Figure A.1—Sulfide Stress Cracking in an Existing Hardened Heat-Affected Zone of a Weld

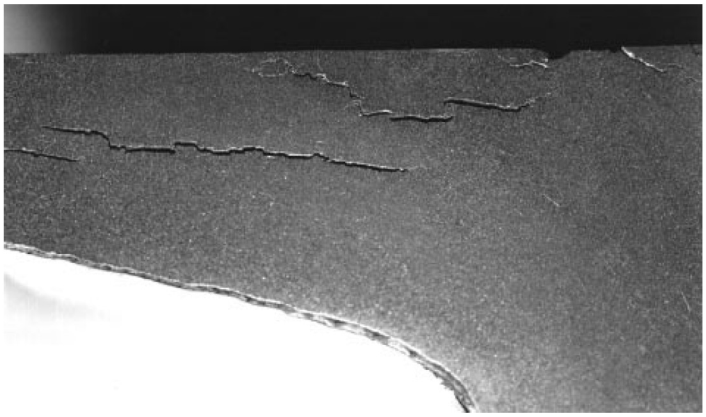
High metal hardness is primarily found in the weld deposit and weld heat-affected zones in the adjacent base metal. Hardness levels in these regions depend on the composition of the steel (i.e. weld deposit and base metal), strength level, and the welding and post-weld heat treating procedure that is employed. The hardness level of a weldment must be controlled below certain maximum values to minimize the likelihood of SSC [12].

High metal stresses of concern are primarily localized stresses from residual welding stresses and poor weld joint fit-up. The threshold stress for cracking and the severity of SSC is influenced substantially by the concentration of atomic hydrogen in the steel. The atomic hydrogen flux that permeates the steel is related to the level of corrosion activity at the steel surface, which is primarily a function of hydrogen sulfide concentration and pH of the aqueous solution. Other solution contaminants can influence the corrosion activity and hydrogen entry into the steel. The hydrogen flux is normally at its minimum in near neutral pH solutions and increases substantially at lower and higher pH values.

SSC can be minimized by limiting weldment hardness and by applying proper PWHT (see 5.2). SSC may be mitigated, but not prevented, through use of effective corrosion control procedures that reduce the rate of sulfide corrosion and hydrogen charging of the steel (see Annex B). Additionally, the likelihood of cracking during a weld repair of post-service equipment can be reduced by outgassing the weldment (see 6.4.2 and 6.4.3).

A.3 Hydrogen-Induced Cracking Associated with Hydrogen Blistering

Hydrogen blistering is defined as the formation of subsurface planar cavities, called hydrogen blisters, in a metal resulting from excessive internal hydrogen pressure. Growth of near-surface blisters in low-strength metals usually results in surface bulges. Hydrogen blisters form in carbon steels when atomic hydrogen, generated by corrosion of the steel surface, enters the steel, and diffuses to voids, laminations, and other internal discontinuities, such as at nonmetallic inclusions, where it collects as molecular hydrogen. Figure A.2 illustrates hydrogen blisters near the ID surface of a carbon steel flange. Steels with higher impurity levels, which tend to concentrate along planes parallel to the rolling direction of the plate, tend to experience more hydrogen blistering. As the internal pressure of molecular hydrogen increases, high stresses at the circumference of the blister can result in plastic deformation of the surrounding area. This might cause the blister to expand within its plane or, alternatively, might cause HIC.



NOTE Two-percent nital etch at 4.5X magnification.

Figure A.2—Hydrogen Blisters Near the ID Surface of a Carbon Steel Flange

HIC is defined as stepwise internal cracks that connect adjacent hydrogen blisters on different planes in the metal, or to the metal surface. No externally applied stress is needed for the formation of HIC. The driving force for the crack propagation is high stresses at the circumference of the blisters that are caused by the buildup of internal pressure in the blisters. Interaction between these high stress fields tends to cause cracks to develop that link blisters on different planes. The link-up of blisters on different planes in steels has been referred to as stepwise cracking to characterize the nature of the crack appearance. Figure A.3 shows typical HIC damage in carbon steel.

NOTE Two-percent nital etch at 5.5X magnification.

Figure A.3—Stepwise Hydrogen-Induced Cracking (HIC) in a Carbon Steel Specimen

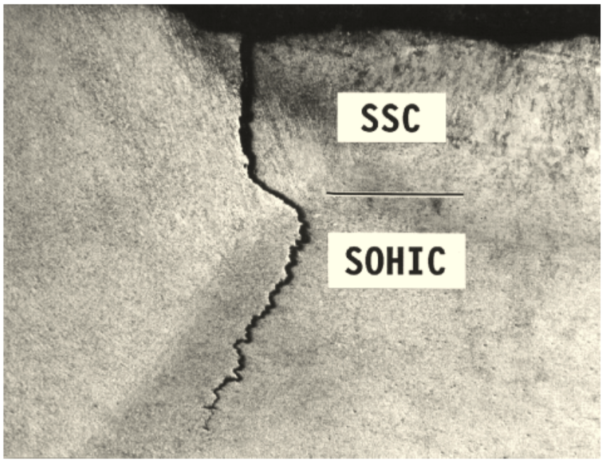
Blistering and HIC can be minimized by selecting a higher quality steel (often referred to as a “clean” steel) with low inclusion content. Increased resistance to blistering and HIC is usually achieved by lowering the sulfur content of the steel and controlling the sulfide inclusion morphology by calcium or rare earth element additions to produce spheroidal sulfide shapes. Plate heat treatments, such as normalizing or quenching and tempering above 1100 °F (583 °C) can increase base metal resistance to HIC, but stress reduction by PWHT in weldments has no significant impact on reducing blistering away from the welds. Using corrosion control procedures to reduce the sulfide corrosion and hydrogen charging also reduces the likelihood of blistering and HIC.

A.4 Stress-Oriented Hydrogen-Induced Cracking

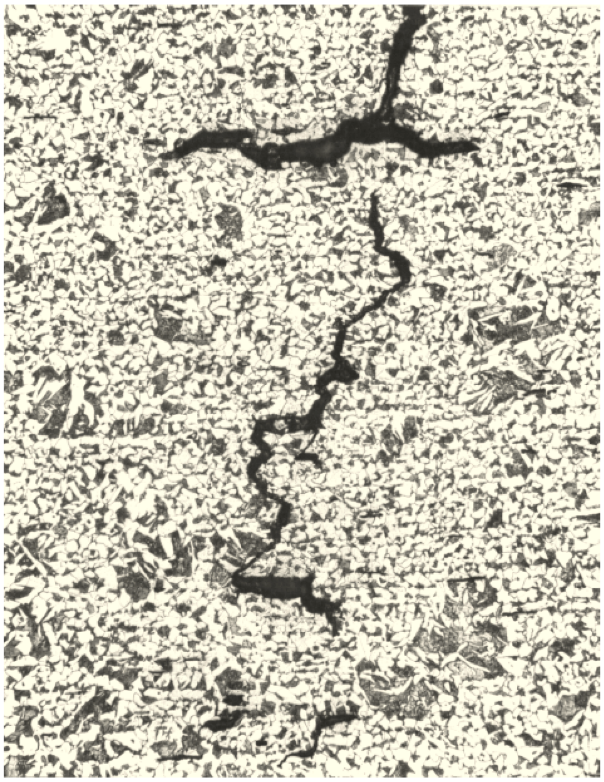
SOHIC is defined as a stacked array of small blisters joined by hydrogen-induced cracking, aligned in the through-thickness direction of the steel because of high localized tensile stresses. SOHIC is a special form of HIC that usually occurs in the base metal, adjacent to the heat-affected zone of a weld, where there are high residual stresses from welding. It can also occur at other high stress points, such as the tip of other environmental cracks (e.g. SSC) or geometrical anomalies (e.g. at the toe of a weld). The nearly vertical stacking of the small blisters and the interconnecting cracking are oriented in the through-thickness direction because they are aligned normal to the tensile stress at a typical pressure vessel weldment.

Figure A.4 shows SOHIC propagating from the tip of a sulfide stress crack in a hard heat-affected zone of a weld. In this instance, cracking progressed by a classical SSC mechanism through the hard HAZ, but then propagated by SOHIC in the adjacent lower hardness base metal. Although SOHIC often occurs at the process-exposed surface, or connects to a surface-breaking flaw, it has been found to exist subsurface, with no connection to the ID surface. There is no evidence that hardness control of the weldment has any direct impact on reducing SOHIC. SOHIC has been found in steel with hardness less than 200 HB. However, hardness control might be of indirect benefit by reducing SSC, which can serve as an initiation point for SOHIC as illustrated in Figure A.4.

As with hydrogen blistering and HIC, use of higher quality HIC-resistant steels can reduce the likelihood of SOHIC. Laboratory tests have shown that these steels generally have a higher hydrogen flux threshold for SOHIC than conventional steels, but SOHIC readily occurred when the threshold was exceeded. Reduction of residual stresses by applying proper welding procedures and PWHT can reduce, but might not eliminate, the occurrence and severity of SOHIC. In severe hydrogen charging services, these practices might not provide adequate resistance to SOHIC, whereas the use of alloy clad, or weld overlaid equipment can provide the necessary resistance.



a) Top Panel



b) Bottom Panel

NOTE The top panel is a two-percent nital etch at 2X magnification. The bottom panel is a higher magnification view of the crack tip shown in the top panel (two-percent nital etch at 200X magnification).

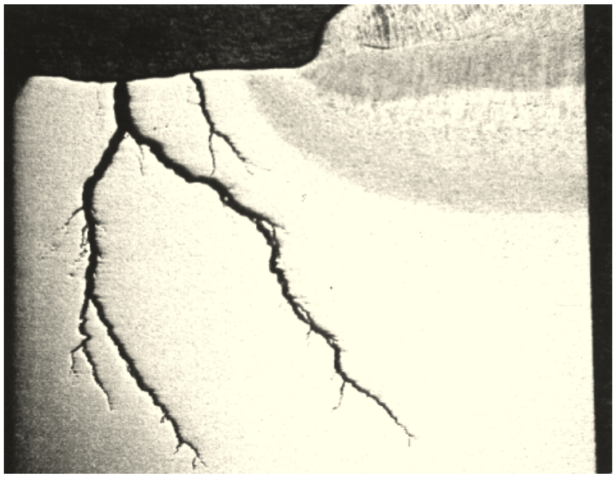
Figure A.4—Stress-Oriented Hydrogen-Induced Cracking

A.5 Alkaline Stress Corrosion Cracking (ASCC)

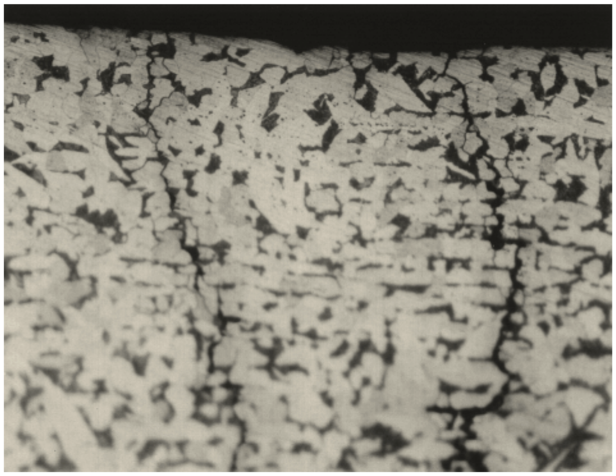
ASCC is defined as the cracking of a metal produced by the combined action of corrosion in an aqueous alkaline environment containing H_2S, CO_2, and tensile stress (residual or applied). The cracking is branched and intergranular in nature, and typically occurs in non-stress relieved carbon steels. In as-welded steels, cracks typically propagate parallel to the weld in adjacent base metal. In addition, cracking can occur in the transverse direction and can also occur in the weld deposit or heat-affected zones. Figure A.5 illustrates ASCC in the vicinity of a weld in an amine unit. This form of cracking has often been referred to as amine cracking when it occurs in alkanolamine treating solutions.

ASCC can occur over a wide range of temperatures, but susceptibility generally increases as the temperature increases. ASCC generally occurs in lean alkanolamine treating solutions containing H_2S and CO_2 with a pH in the 8 to 11 range, but its occurrence is highly dependent on the solution composition. The mode of cracking involves local anodic dissolution of iron at breaks in the normally protective corrosion product film on the metal surface. Laboratory tests have shown that cracking occurs in a relatively narrow range of electrochemical potential that corresponds to a destabilized condition of the protective film. This film destabilization occurs at very low ratios of the sulfide concentration to the carbonate/bicarbonate concentration in the alkanolamine solution and is possibly affected by various contaminants in the solution [9, 10, 13].

ASCC has occurred in a variety of steels. Field experience to date has not indicated any significant correlation between susceptibility to ASCC and steel properties. Hardness of the steel has virtually no effect on ASCC. Susceptibility to ASCC increases with increasing tensile stress level. Areas of deformation resulting from cold forming or localized high residual stresses in weldments are more prone to ASCC. Surface discontinuities, especially in and near weldments, often serve as initiation sites for ASCC because they act as localized stress raisers. Cracking has also occurred on internal surfaces of equipment opposite external welded attachments, such as those associated with lifting lugs and other attachments. ASCC can be effectively mitigated by PWHT and proper heat treatment after cold forming.



a) Top Panel



b) Bottom Panel

NOTE The top panel is a two-percent nital etch at 6X magnification. The bottom panel is a higher magnification view of the crack tip shown in the top panel. (Two-percent nital etch at 200X magnification).

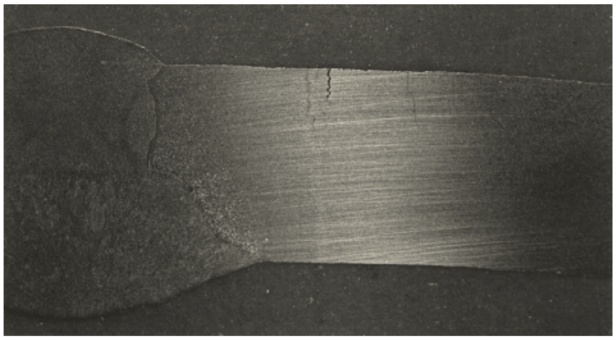
Figure A.5—Alkaline Stress Corrosion Cracking in the Vicinity of a Weld

A.6 Industry Experience

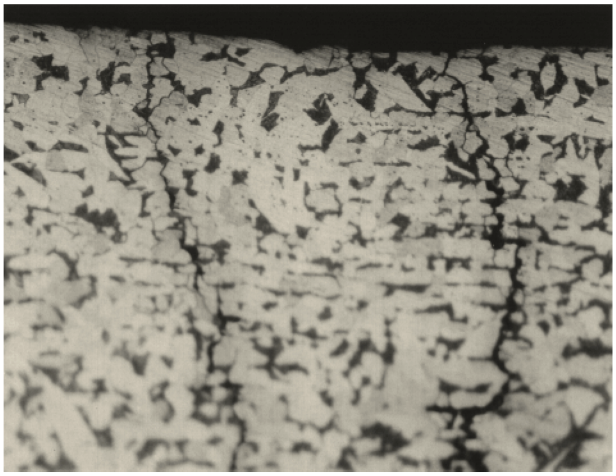
Several interesting examples of industry cracking problems reported to the API Task Group on Amine Cracking are included.

The first example involved ASCC in the overhead piping that was leading from the absorber column of an MEA unit. The line normally operated at 100 °F (38 °C) and carried a mixture of propane and butane. MEA was not usually present in the stream. However, MEA carryover may have occurred occasionally, and this appears to have been the cause of the problem. Figure A.6 illustrates the parallel cracks that developed near a weld in the

ASTM A106B pipe. The weld had not been stress relieved, and the material hardness at the cracks averaged 139 HB. The higher magnification photomicrograph clearly demonstrates the intergranular nature of the cracks.



a) Top Panel

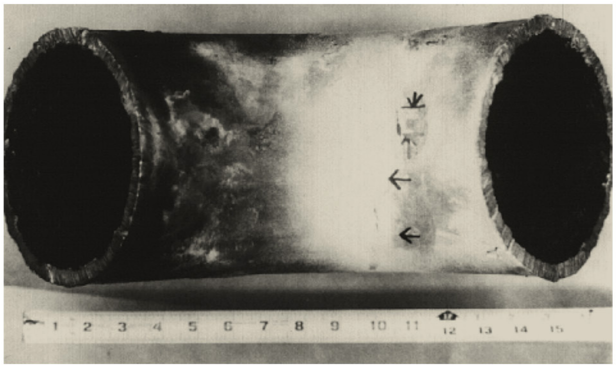


b) Bottom Panel

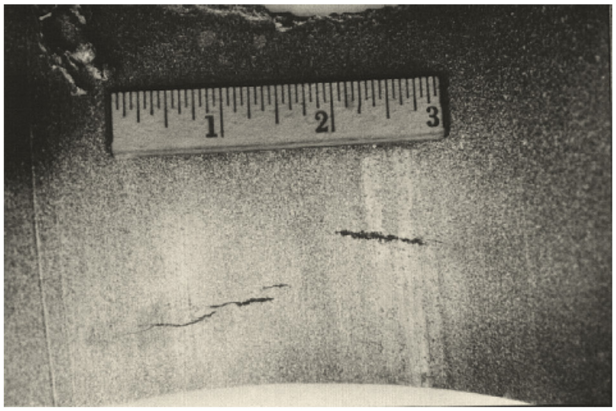
NOTE The top panel illustrates alkaline stress corrossion cracks in a pipe weld in an MEA unit; nital etched specimen at 6X magnification. The bottom panel illustrates the intergranular nature of the cracks; nital etched at 200X magnification.

Figure A.6—Alkaline Stress Corrosion Cracking in a Pipe Weld in MEA Service

The second example involved ASCC of a carbon steel elbow in the suction piping to the lean amine bottoms pump in a DEA unit. The elbow was made to ASTM A234 WPB specifications, and the piping class required stress relief after welding. The operating temperature of the component was approximately 150 °F (66 °C). Prior to cracking, the elbow had been heated by a torch to approximately 2000 °F (1093 °C) to relieve pump strain due to piping misalignment. This heating procedure resulted in high residual tensile stresses in the elbow that subsequently cracked in service. To relieve residual stresses caused by the heating procedure, a stress relieving operation should be performed as outlined in 5.2.3.3. Figure A.7 and Figure A.8 illustrate the intergranular cracking that initiated from the internal surface of the elbow and verify that amine cracking occurred in the line.



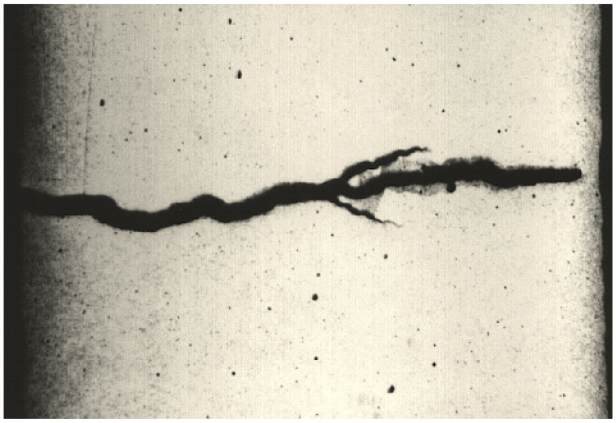
a) Top Panel



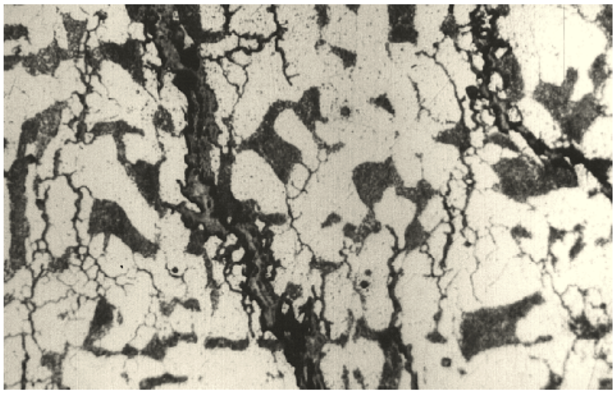
b) Bottom Panel

NOTE The top panel shows the location of circumferential cracks in a piping elbow from a DEA unit. The bottom panel confirms the cracks intiated on the ID surface.

Figure A.7—Alkaline Stress Corrosion Cracking in an Elbow in DEA Service



a) Top Panel



b) Bottom Panel

NOTE The through-wall section of the elbow in the top panel illustrates extension of the branched crack from the ID surface on the left; unetched specimen at 12.5X magnification. The bottom panel confirms the cracks are branched, intergranular, and filled with oxide characteristic of alkaline stress corrosion cracking; nital etched at 500X magnification.

Figure A.8—Intergranular Alkaline Stress Corrosion Cracking in DEA Service

At the September 2019 API Task Group on Amine Cracking, four more examples were reported. The first example involved recent ASCC of carbon steel in a unit which had been relatively trouble-free for many years. This unit started up in 1971 using DEA at temperatures around 115 °F to 120 °F (46 °C to 49 °C). Most of the system was not PWHT, and it was reported that it was never steamed out. In 2005, the unit was converted to use MDEA and operated at a temperature of around 125 °F (52 °C). None of the equipment ever operated above 145 °F (63 °C). All repairs and all new sections installed after the mid-1980s had been PWHT. During a recent on-stream inspection, leaks were found in one PWHT and one non-PWHT section. Upon further inspection, several hundred lean amine welds were inspected. Roughly 90 % of the non PWHT welds were cracked and roughly 30 % of the PWHT welds were cracked. This included inspection of equipment built in 1971 and units added in 2004, 2005, and 2013. In all cases, the cracks arrested once they moved outside the residual stress field. The cracking was initially located with PAUT and followed up with metallographic analysis. It was noted that the PAUT did not locate the large number of transverse cracks found during destructive testing.

In addition, it was recently reported that a significant amount of ASCC failures in hot lean DEA above 212 °F (100 °C) and in warm lean amine service at 113 °F to 158 °F (45 °C to 70 °C) have been observed in European amine units. These included piping and equipment which had been PWHT, specifically a) lean amine tank, b) rich/lean amine heat exchanger shell, and c) lean amine air coolers with expanded or welded tube-to-tubesheet joints.

Another refiner reported an amine system without PWHT which went trouble-free for years until the amine was cleaned up. Only nine months after cleanup, there were ASCC failures. Over a three-year period, there were 50 clamps installed on piping leaks. Ultimately, there was a leak that severed the lean amine piping and released H_2S-laden gas into the atmosphere from the lean amine header. After replacement of the header with a new PWHT header, they had subsequent failures nine months later at pipe shoes and supports that were not PWHT.

In addition, another refiner reported ASCC failures after replacing their amines with fresh amine.

It was also noted at the September 2019 API Task Group on Amine Cracking meeting that there have been cases shown where the PWHT temperature has not reached the target temperature on the amine wetted surface. One case reported only got up to about 900 °F (482 °C), adding some uncertainty into the effectiveness of that PWHT. Given the industry experience over the last 50 years, PWHT clearly decreases the frequency of amine SCC, but it is not 100 % effective.

More recently, another refiner reported they had an instance of ASCC of seamless pipe in a high pressure lean amine line over 3000 psi (20.68 MPa) feeding a high pressure hydrocracking unit. The cracking occurred over about 30 years of service, and it seems to have been caused by residual stresses introduced in the pipe mill due to the use of straightening rolls after the pipe was formed. During failure analysis, the refiner found residual stress fields in the pipe wall, well away from welds. The cracking did not occur near welds, which had seen PWHT. The heavy wall thickness of this line is due to the very high pressure of the unit and is unusual for most lean amine systems which run at relatively low pressure and use thinner wall pipe. The refiner noted they haven’t seen the same issue on other units, but this is probably their highest pressure unit. For the replacement, they specified heat treatment of the pipe after forming.

ANNEX B
(normative)

Considerations for Corrosion Control

B.1 Scope

This annex provides information based on industry experience regarding corrosion control in amine units. The information does not present, nor is it intended to establish, mandatory practices for the design and operation of amine units. This information is intended to assist in the development of systems and procedures for individual company needs. Many companies safely operate amine units using practices different from those presented below. New or alternative practices should not be discouraged since they inevitably result in more effective amine unit technology for the industry.

B.2 General

In low-pressure systems, corrosion of carbon steel can be most severe in units that primarily remove carbon dioxide. Corrosion of carbon steel components has been less severe in units that remove only hydrogen sulfide, and in units that handle mixtures of carbon dioxide and hydrogen sulfide. In high-pressure units with high hydrogen sulfide partial pressure, corrosion of carbon steel can be severe. Corrosion in amine units that use MEA can be more severe than in those that use DEA, because MEA is more prone to degradation. However, amine solutions such as DEA that are normally not purified by reclaiming can also become quite corrosive.

MDEA has become a major alternative to DEA or MEA for the removal of acid gases. There are process advantages for MDEA over conventional amines. These advantages are acid gas selectivity, energy savings, and the ability to operate at higher concentrations than MEA or DEA. A typical MDEA plant can operate at up to 50 % concentration. MDEA units have been used to remove H_2S as well as H_2S/CO_2 and CO_2. Some acid gas removal units have been specifically designed to run on MDEA. These units may have special design features unique to these plants, such as a desorber column located upstream of the main stripper column. Other units have been converted from MEA or DEA with few, if any, equipment changes. See B.7.3.5 for precautions.

From a practical point of view, corrosion control procedures in amine units concentrate on: a) the removal of certain corrosive species from amine solutions by side-stream filtration, reclaiming, or both; b) the use of effective corrosion inhibitors; and c) the application of proven process schemes, equipment designs, and operating criteria, as outlined below. Corrosion (not necessarily cracking) has been most severe in units that primarily remove carbon dioxide, that is, where the hydrogen sulfide content of the acid gas is less than 5 % by volume. Corrosion (not necessarily cracking) has been less severe in low-pressure units that remove only hydrogen sulfide, or that handle mixtures of the two gases containing at least 5 % by volume of hydrogen sulfide.

B.3 Corrosion Locations

Attack is most pronounced at locations where acid gases are desorbed (flashed) from rich amine solution, and where temperatures and flow turbulence are highest. Typical problem areas include the regenerator tower reboiler, the lower section of the regenerator tower, the rich amine side of the lean/rich amine exchangers, amine solution pumps, the pressure let-down valve and downstream piping, and the reclaimer (where used). The overhead system of the regenerator tower can be affected where acid gases tend to concentrate. Severe hydrogen blistering can also be encountered in the bottom of the absorber or contactor tower. Vessel shell areas that face the incoming inlet opening can become severely corroded because the normally protective sulfide film is removed by stream impingement.

Corrosion of carbon steel components can take the form of uniform thinning, localized attack, or pitting, depending on location. Directionality in the pattern of attack can be attributed to excessive flow velocities and pressure drops. Corrosion can also be severe on heat transfer surfaces. Deposits often accelerate attack, especially on heat transfer surfaces. The localized overheating of reboiler and reclaimer tubes inside of baffle holes can cause groove-type corrosion. Preferential weld corrosion of carbon steel can also occur in hot, rich amine solutions.

Corrosion can be worse in lean amine systems where the H_2S is overstripped. The corrosion in these systems can be localized directly downstream of welds even at low velocities.

B.4 Filtration and Reclaiming

Precipitates such as iron sulfide can be removed from amine solutions by filtration, using cartridge-type filters. High-molecular-weight degradation products can be eliminated by adsorption, using a bed of activated carbon. Typically, 5 % or more of the circulating amine solution is passed through the filters. MEA solutions can be purified by reclaiming, or by semi-continuous steam distillation with soda ash or caustic that has been added to liberate the amine from the acid salts. When reclaiming is used, it is usually performed on a 1 % to 2 % slipstream of the circulating amine solution. DEA and MDEA solutions cannot be efficiently reclaimed because of boiling-point constraints. DIPA solutions can be reclaimed.

B.5 Corrosion Inhibitors

Over the years, a variety of corrosion inhibitors have been evaluated in amine solutions to reduce corrosion problems with various degrees of success. Corrosion inhibitors that have been and are being used include high-molecular-weight filming amines, inorganic and organic oxidizing salts, and chemical oxygen scavengers. Several proprietary multicomponent inhibitor packages are also available. These chemicals are designed for amine units that handle acid gases with or without hydrogen sulfide. Certain oxidizing inhibitors react with hydrogen sulfide and should not be used in amine units that remove hydrogen sulfide. As a rule, corrosion inhibitors based on filming amines have been relatively ineffective.

Some filming-amine inhibitors also contain sequestering agents that aid in keeping the circulating amine solution clean. However, sequestering agents also solubilize the protective iron oxide film that is normally present on steel exposed to lean amine solutions. This lowers the metal potential and can promote ASCC [5]. Oxidizing salts will increase metal potential and promote passivation of steel surfaces. If used in sufficiently high concentration, oxidizing salts may prevent ASCC.

B.6 Guidelines for Process and Equipment Design

B.6.1 General

To reduce energy costs and minimize sludge disposal problems, many amine units are now designed to handle higher solution loadings. Higher solution loadings can result in increased corrosion of carbon steel if proper precautions are not taken. Industry experience has shown the non-mandatory guidelines listed in B.6.2 to be useful in the design of such units. Other practices have been found to be equally suitable, based on experience in particular cases.

B.6.2 Guidelines

B.6.2.1 Minimize flow velocities in heat exchangers and piping in rich amine service. Velocities less than 6 ft/sec (1.8 m/sec) may be used if no other operating experience is available.

B.6.2.2 Place the rich solution on the tube side of lean/rich amine exchangers.

B.6.2.3 Avoid flashing of acid gases in lean/rich amine exchangers by locating the pressure let-down valve downstream of the last exchanger. This prevents acid gas from being released into the exchangers.

B.6.2.4 Reduce erosion-corrosion at inlet nozzles by using impingement plates or dummy rods.

B.6.2.5 Specify as low a pressure as possible for the regenerator tower and associated reboilers.

B.6.2.6 Use low-pressure steam [50 psig (345 kPa) or less] as the reboiler heating medium and maintain low reboiler temperatures to minimize amine decomposition [a limit of 300 °F (149 °C) may be used if no other data are available].

B.6.2.7 Use a square-pitch tube layout (or remove interior tubes) and proper baffle design to reduce vapor blanketing in reboiler bundles.

B.6.2.8 Locate the steam flow valve ahead of the reboiler to prevent condensate from flooding the tubes.

B.6.2.9 Use oversized pressure let-down valves to reduce erosion-corrosion caused by velocity effects. Let-down valves for high-pressure units should have hard-faced internals. Let-down valves in high-concentration carbon dioxide systems should be austenitic stainless steel.

B.6.2.10 Use corrosion resistant material for the section of piping immediately downstream of letdown valves to avoid corrosion/erosion by flashing of H_2S. Generally, Type 304L or 316L stainless steel has been acceptable.

B.6.2.11 Specify long-radius elbows and adequately sized process piping to minimize erosion-corrosion in transfer lines because of excessive flow turbulence. Stainless steel has been successfully used for two-phase flow piping in high concentration carbon dioxide systems.

B.6.2.12 Provide an amine reclaimer for MEA units.

B.6.2.13 Design the regenerator reboiler and amine reclaimer to assure that their tube bundles are fully immersed in process liquid at all times.

B.6.2.14 Provide inert-gas blanketing for storage and surge vessels to reduce oxygen degradation of amine solutions.

B.6.2.15 If a filter is used, size it for not less than 5 % of the amine circulation and less than 0.1 weight percent solids content.

B.6.2.16 Use a regenerator feed distributor design to limit corrosion-erosion at the inlet, especially where there is no stainless steel cladding.

B.7 Guidelines for Operation

B.7.1 General

Effective operating procedures should prevent buildup of potentially harmful degradation products and should keep the amine solution clean. Properly maintained solutions will reduce corrosion and may obviate the need for corrosion inhibitors. Industry experience has shown that the non-mandatory guidelines given in B.7.2 and B.7.3 are useful for preventing serious corrosion. However, as noted in B.6.1, other practices may be equally suitable, based on experience with specific units.

B.7.2 Overall Guidelines

B.7.2.1 Closely monitor corrosion inhibitors that are being field tested for the intended application.

B.7.2.2 If an amine reclaimer is incorporated in the unit, keep it in proper operating condition.

B.7.2.3 Use concentrations and grades of caustic soda or soda ash that are compatible with the reclaimer's construction materials. The use of low-chloride caustic is advisable with reclaimers that have austenitic stainless steel tubes.

B.7.2.4 Use only oxygen-free steam condensate to prepare amine solutions.

B.7.2.5 Analyze amine solutions periodically to monitor the concentration of heat-stable salts, carboxylic acids, and heat-stable compounds of carbon dioxide with alkanolamine (oxazolidones).

B.7.2.6 Inert blanketing of the fresh and lean amine tanks should be maintained to prevent contact with oxygen. Contact with oxygen may lead to degradation and subsequent increase of heat stable salts.

B.7.3 Guidelines for Specific Operating Units

B.7.3.1 General

Depending on the type of amine solution that will be used, specific operating guidelines, such as those given in B.7.3.2 and B.7.3.3, might apply.

B.7.3.2 MEA Units

For MEA units, reboiler temperatures maintained below 300 °F (149 °C) will help to minimize amine degradation and the corrosion of reboiler tubes. MEA concentrations above 25 % by volume, and acid gas loading above 0.35 mole per mole of amine, should be carefully evaluated with respect to the requirements for construction materials. The use of corrosion-resistant alloys may permit higher temperatures, amine concentrations, and gas loadings. Mitigate overhead piping and equipment corrosion by operating the regenerator so that 0.5 % amine is passed overhead. The presence of the amine prevents acidic corrosion in carbon-steel overhead systems. Alternatively, a corrosion-resistant alloy may prove useful.

B.7.3.3 DEA Units

The specific guidelines for DEA units are similar to those for MEA units, except that DEA concentrations and acid gas loadings may be higher. Recent experience has demonstrated successful operation of DEA units at concentrations of 40 % by volume, and acid gas loadings of up to 0.5 mole per mole of amine. Corrosion monitoring is advisable when operating with higher amine concentrations and gas loadings.

B.7.3.4 DIPA Units

Rich solutions of DIPA and DIPA with sulfolane generally do not corrode carbon steel because protective films are readily formed. Corrosion might occur where process conditions lead to flashing and/or boiling. Apparently, carbon dioxide flashing has been responsible for some contactor corrosion. A critical variable seems to be the carbon dioxide-to-hydrogen sulfide ratio, which was less than 1-to-8 when corrosion occurred. In carbon-dioxide rich DIPA systems, the corrosion of carbon steel is controlled by the metal wall temperatures and the degree of vaporization at the wall surface. If process conditions prevent temperature and vaporization control, Type 304 stainless steel will provide satisfactory resistance in place of the carbon steel.

B.7.3.5 MDEA Units

One of the original claims made about MDEA was that unlike MEA or DEA, it was not corrosive to carbon steel. Claims were also made that degradation would not be a problem because MDEA resisted degradation by CS_2 and COS. However, actual plant experience has shown mixed results. In H_2S and H_2S-rich units, corrosion of carbon steel has been low due to the protective iron sulfide scale. However, severe corrosion has been experienced in CO_2 or CO_2-rich units. Furthermore, while MDEA seems to resist CS_2 or COS induced degradation, it is highly sensitive to oxygen and thermal degradation.

Similar to DEA, the degradation products of MDEA cannot be reclaimed. For this reason, it is very important to prevent the formation of the degradation products by exclusion of oxygen from the system. MDEA systems with high levels of degradation products in circulation exhibit significant corrosion. To remove the degradation and suspended products, filtration should be used. For most units, both mechanical filtration and activated carbon filters are recommended. As in other amine units, high velocity and turbulence can cause localized erosion-corrosion. In MDEA units it is advisable to keep the velocity to under 6 ft/sec (1.8 m/sec). Oxidative-type inhibitors, common in CO_2 removal units, should not be used in MDEA units, especially for those converted from MEA.

Claims that MDEA units can be completely built with carbon steel equipment have not been validated in the field. Selective upgrading of materials for MDEA should be like other amine units. CO_2 removal units require the most upgrades. Typical equipment items that might require upgrades are the stripper tower, desorber tower (if one exists), lean/rich exchanger, and the stripper reboiler. When upgrading is required for towers or exchanger shells, they are normally lined with 300 series stainless steel. Low-carbon and stabilized grades of stainless steels (Types 304L, 316L, and 321) are preferred. Similarly, low-carbon or stabilized grades of tubes should be used for U-tube bundles to prevent sensitization during stress relief of bends.

B.7.3.6 DGA Units

Diglycolamine (DGA) systems are less corrosive than MEA systems. DGA corrosion characteristics are similar to other amine systems and depend on temperature, fluid velocity, concentration, and loading. Fluid velocity for carbon steel piping should not exceed 6 ft/sec (1.8 m/sec). In 40 % DGA that treats CO_2 and H_2S acid gases, at least 5 % H_2S in the CO_2/H_2S mix is required to avoid corrosion in the reclaimers. Type 304 stainless steel is resistant to higher velocities, temperatures, and CO_2 concentrations than carbon steel; however, the chloride level must be kept below 4000 ppm to prevent pitting of the stainless steel.

ANNEX C

(normative)

Historical Guidelines for PWHT for Various Amine Types

Earlier editions of API Recommended Practice 945 provided different temperature limits for where PWHT was recommended for the various amine types. These are included here for historical reference. Section 5.2.3 of this RP provides current PWHT guidance.

C.1 MEA Units

For MEA units, PWHT is recommended for all carbon steel equipment, including piping, regardless of service temperature. Cracking has been quite prevalent in non-PWHT carbon steel equipment at all normal operating temperatures.

C.2 DEA Units

For DEA units, PWHT is recommended for all carbon steel equipment, including piping, exposed to amine at service temperatures of 140 °F (60 °C) and higher. The maximum operating temperature and the effects of heat tracing and steamout on the metal temperature of components in contact with the amine should be considered.

Industry experience has shown that many reported instances of ASCC in DEA units have occurred in non-PWHT carbon steel equipment exposed to temperatures higher than 140 °F (60 °C). However, some cracking problems have been reported in DEA units at temperatures below this value. In some cases, equipment, including piping, has been known to crack during steamout due to the presence of amine [7]. Each user company should evaluate the need for PWHT of carbon steel at temperatures below 140 °F (60 °C), especially for equipment such as absorbers and contactors.

C.3 DIPA Units

For DIPA units, PWHT is recommended for all carbon steel equipment, including piping, regardless of service temperature. Cracking has been prevalent in non-PWHT carbon steel equipment at all normal operating temperatures exposed to 15 % to 20 % DIPA solutions [7]. This guideline does not apply to units containing a mixture of sulfolane and higher concentration DIPA (typically 50 %), where no cracking has been reported.

C.4 MDEA Units

For MDEA units, PWHT is recommended for all carbon steel equipment, including piping, exposed to amine at service temperatures of 180 °F (82 °C) and higher. The maximum operating temperature and the effects of heat tracing and steamout on the metal temperature of components in contact with the amine should be considered.

Industry experience has shown that cracking has not been prevalent in MDEA units. Only a few instances of cracking have been reported to date, and all but one of these occurred in equipment exposed to temperatures higher than 190 °F (88 °C) [8].

C.5 Other Amine Units

Therefore, each user company must evaluate the need for PWHT of carbon steel in such units. For licensed amine treating processes, the licenser should provide the operating company with guidance on PWHT requirements, based on laboratory testing, actual experience in other licensed plants, or both.

ANNEX D
(informative)

Request for New Information Concerning Problems with Environmental Cracking in Amine Units

The information contained in this RP is based on experience and engineering practices current at the time of its preparation. It is recognized that in the future, additional information will become available about problems that affect amine units and improved procedures to overcome them. Such information is of particular interest to the API Subcommittee on Corrosion and Materials, which is responsible for the preparation and periodic revision of this RP.

Figure D.1a and Figure D.1b show a report form that lists the basic information that should be provided when details of environmental cracking problems with amine units are forwarded. Additional information may be included in attachments to these data sheets. Please provide as many details as possible. General photographs of the equipment affected are of value. Photomicrographs of the construction material's microstructure are also of significant interest, particularly those that delineate the nature and location of any cracks present. Actual metal samples may also be forwarded.

The completed form or a legible facsimile should be sent to the following address:

API Staff, Recommended Practice 945 Task Group
API Subcommittee on Corrosion and Materials
c/o Standards Department
American Petroleum Institute
200 Massachusetts Avenue, N.W.
Washington, D.C. 20001
standards@api.org

API REPORT FORM:
ENVIRONMENTAL CRACKING PROBLEMS IN AMINE UNITS

Date ____________________
API File No. ____________________
Page ______ of ________

Name ____

Company Affiliation ____

Address ____
____
____

Country ____

Telephone __________________________FAX ___________________

E-mail ____

1. Type of amine unit (e.g. MEA, DEA, MDEA)
____
2. Location (e.g. refinery, chemical plant)
____
3. Acid gas being scrubbed (e.g. H_2S, CO_2)
____
4. Amine concentration (%)
____
5. Solution loading (moles acid gas per mole of amine)
____
6. Corrosion inhibitor, if used
____
7. Date of unit construction
____
8. Date of problem or failure
____
9. Equipment affected (e.g. vessel, exchanger, piping)
____
10. Location of problem (e.g. vessel shell, pipe weld)
____

Figure D.1a—Report Form for New Information Concerning Problems with Environmental Cracking in Amine Units

API REPORT FORM:
ENVIRONMENTAL CRACKING PROBLEMS IN AMINE UNITS

Date ____________________
API File No. ____________________
Page ______ of ________

Name ____

11. Metal temperature at location: (normal and maximum)
____

12. Construction material (ASTM designation or equivalent)
____

13. Material strength level (in ksi or MPa)
____

14. Wall thickness, pipe diameter, and schedule
____

15. Postweld heat treatment (PWHT) ______ YES ______ NO

16. PWHT time ____________ PWHT temperature ___________

17. Material hardness at location __________________________

18. Equipment steam out cleaned? _________ YES _______NO

19. Equipment water washed? _________ YES _______NO

20. Description of problem (include photographs and samples, if available)
____
____
____
____
____
____
____

21. Have other amines been used in equipment in the past?
_______ YES _______ NO
If yes, provide information about the type of amine and the conditions under which it was used:
____
____
____
____
____
____
____

Figure D.1b—Report Form for New Information Concerning Problems with Environmental Cracking in Amine Units

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