Avoiding Environmental Cracking in Amine Units

API RECOMMENDED PRACTICE 945
THIRD EDITION, JUNE 2003

REAFFIRMED, APRIL 2008

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Downstream Segment

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Avoiding Environmental Cracking in Amine Units

1 Scope

This recommended practice discusses environmental cracking problems of carbon steel equipment in amine units. Stress corrosion cracking of stainless steels in amine units is beyond the scope of this document although there have been isolated reports of such problems. This practice does provide guidelines for carbon steel construction materials including their fabrication, inspection, and repair to help assure safe and reliable operation. The 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 3.1 and 3.2 for the definitions of weld and weldment.

This document is based on current engineering practices and insights from recent industry experience. Older amine units may not conform exactly to the information contained in this recommended practice, but this does not imply that such units are operating in an unsafe or unreliable manner. No two amine units are alike, and the need to modify a specific facility depends on its operating, inspection, and maintenance history. Each user company is responsible for safe and reliable unit operation.

2 References

2.1 REFERENCED PUBLICATIONS

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2. G. L. Garwood, "What to Do About Amine Stress Corrosion," *Oil and Gas Journal,* July 27, 1953, Volume 52, p. 334.

3. P. G. Hughes, "Stress Corrosion Cracking in an MEA Unit," Proceedings of the 1982 U.K. National Corrosion Conference, Institute of Corrosion Science and Technology, Birmingham, England, 1982, p. 87.

4. H. I. McHenry et al., "Failure Analysis of an Amine Absorber Pressure Vessel," *Materials Performance,* 1987. Volume 26, No. 8, p. 18.

5. J. Gutzeit and J. M. Johnson, "Stress Corrosion Cracking of Carbon Steel Welds in Amine Service," *Materials Performance,* 1986, Volume 25, No. 7, p. 18.

6. J. P. Richert et al., "Stress Corrosion Cracking of Carbon Steel in Amine Systems," *Materials Performance,* 1988, Volume 27, No. 1, p. 9.

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8. R. J. Horvath, Group Committee T-8 Minutes, Sec. 5.10—Amine Units, Fall Committee Week/93, September 29, 1993. NACE International.

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10. H. U. Schutt, "New Aspects of Stress Corrosion Cracking in Monethanolamine Solutions" (Paper 159), *Corrosion/88,* NACE International, Houston, 1988.

11. M.S. Cayard, R.D. Kane, L. Kaley and M. Prager, "Research Report on Characterization and Monitoring of Cracking in Wet H_2S Service," *API Publication 939,* American Petroleum Institute, Washington, D.C., October 1994.

12. T. G. Gooch, "Hardness and Stress Corrosion Cracking of Ferritic Steel," *Welding Institute Research Bulletin,* 1982, Volume 23, No. 8, p. 241.

13. C. S. Carter and M. V. Hyatt, "Review of Stress Corrosion Cracking in Low Alloy Steels with Yield Strengths Below 150 KSI," *Stress Corrosion Cracking and Hydrogen Embrittlement of Iron Base Alloys,* NACE International, Houston, 1977, p. 524.

2.2 REFERENCED CODES AND STANDARDS

The following codes and standards are directly referenced (not numbered) in this recommended practice. All codes and standards are subject to periodic revision, and the most recent revision available should be used.

API

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*
RP 572	*Inspection of Pressure Vessels*
RP 574	*Inspection Practices for Piping System Components*
RP 579	*Fitness-for-Service*
RP 580	*Risk-Based Inspection*
RP 582	*Welding Guidelines for the Chemical, Oil, and Gas Industries*
Publ 2217A	*Guidelines for Work in Inert Confined Spaces in the Petroleum Industry*

NACE International[1]

RP0472	*Methods and Controls to Prevent In-Service Environmental Cracking of Carbon Steel Weldments in Corrosive Petroleum Refining Environments*
NACE No. 2/ SSPC-SP 10	Near-White Metal Blast Cleaning

2.3 OTHER CODES AND STANDARDS

The following codes and standards are not referenced directly in this recommended practice. Familiarity with these is recommended because they provide additional information pertaining to this recommended practice. All codes and standards are subject to periodic revision, and the most recent revision available should be used.

ASME[2]

B31.3	*Process Piping*
Boiler and Pressure Vessel Code, Section VIII, "Rules for Construction of Pressure Vessels," *and Section IX,* "Qualification Standard for Welding and Brazing Procedures, Welders, Brazers, and Welding and Brazing Operators"	

ASTM[3]

E 10	*Standard Test Method for Brinell Hardness of Metallic Materials*

NACE International

MR0103	*Materials Resistant to Sulfide Stress Cracking in Corrosive Petroleum Refining Environments*
TM0177	*Laboratory Testing of Metals for Resistance to Specific Forms of Environmental Cracking in H_2S Environments*
TM0284	*Evaluation of Pipeline and Pressure Vessel Steels for Resistance to Hydrogen-Induced Cracking*

2.4 SELECTED BIBLIOGRAPHY

The following selected publications provide additional information pertaining to this recommended practice.

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E. M. Berlie et al., "Preventing MEA Degradation," *Chemical Engineering Progress*, 1965, Volume 61, No. 4, p. 82.

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J. C. Dingman et al., "Minimize Corrosion in MEA Units," *Hydrocarbon Processing*, 1966, Volume 45, No. 9, p. 285.

R. A. Feagan et al., "Experience with Amine Units," *Petroleum Refiner*, 1954, Volume 33, No. 6, p. 167.

R. J. Hafsten et al., "API Survey Shows Few Amine Corrosion Problems," *Petroleum Refiner*, 1958, Volume 37, No. 11, p. 281.

G. D. Hall, "Design and Operating Tips for Ethanolamine Gas Scrubbing Systems," *Chemical Engineering Progress*, 1983, Volume 62, No. 8, p. 71.

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N. R Liebenmann, "Amine Appearance Signals Condition of System," *Oil & Gas Journal*, May 23, 1980, Volume 78, p. 115.

A. J. MacNab and R. S. Treseder, "Materials Requirements for a Gas Treating Process," *Materials Protection and Performance*, 1971, Volume 10, No. 1, p. 21.

A. J. R. Rees, "Problems with Pressure Vessels in Sour Gas Service (Case Histories)," *Materials Performance*, 1977, Volume 16, No. 7, p. 29.

F. C. Riesenfeld and C.L. Blohm, "Corrosion Resistance of Alloys in Amine Gas Treating Systems," *Petroleum Refiner*, 1951, Volume 30, No. 10, p. 107.

W. R. Schmeal et al., "Corrosion in Amine/Sour Gas Treating Contactors," *Chemical Engineering Progress*, March, 1978.

M. K. Seubert and G. D. Wallace, "Corrosion in DGA Treating Plants" (paper 159), *Corrosion/85,* NACE International, Houston, 1985.

3 Definitions

3.1 weld: The weld deposit.

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

4 Background

4.1 AMINE UNITS

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 absorption by, an aqueous amine solution. Figure 1 is a process flow diagram for a representative unit. The gas or liquid streams containing one or both of the acidic components are fed to the bottom of a gas-absorber tower or liquid-contactor vessel, respectively. The lean (regenerated) amine solution

[1]NACE International, 1440 South Creek Drive, Houston, Texas 77084-4906, www.nace.org.
[2]American Society of Mechanical Engineers, 345 East 47th Street, New York, New York 10017, www.asme.org.
[3]American Society for Testing and Materials, 100 Barr Harbor Drive, West Conshohocken, Pennsylvania 19428, www.astm.org.

flows counter to the contaminated hydrocarbon streams in the tower and absorbs the acidic components during the process. The purified gas or liquid stream passes to the overhead system. The rich (contaminated) amine solution 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, sulfur removal plant, or another processing operation. The lean amine solution that leaves the bottom of the regenerator is returned to the absorber or contactor to be used again for purification of the hydrocarbon streams.

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) and diethanolamine (DEA). Other amines, such as methyldiethanolamine (MDEA), diisopropanolamine (DIPA), and diglycolamine (DGA), are also used in various treating processes.

4.2 PROBLEMS IN AMINE UNITS

4.2.1 General

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

4.2.2 Environmental Cracking

Problems with environmental cracking occur when carbon steels are in regions of high hardness, high residual stress, or both. In particular, areas of high hardness in and adjacent to welds have been problematic. Cracks have also been reported in areas where high hardness levels were not detectable with standard field hardness–measurement equipment. The cracking of weld-repaired areas has also caused serious problems when excessively hard zones or regions of high residual stresses have not been eliminated by the repair procedure. In some instances, cracking has occurred in base metal at sites of internal arc strikes, or opposite external welds for vessel attachments, such as ladders.

Four different cracking mechanisms have been identified in carbon steel components in amine units:

a. Sulfide stress cracking (SSC).
b. Hydrogen-induced cracking (HIC) associated with hydrogen blistering.
c. Stress-oriented hydrogen-induced cracking (SOHIC).
d. Alkaline stress corrosion cracking (ASCC).

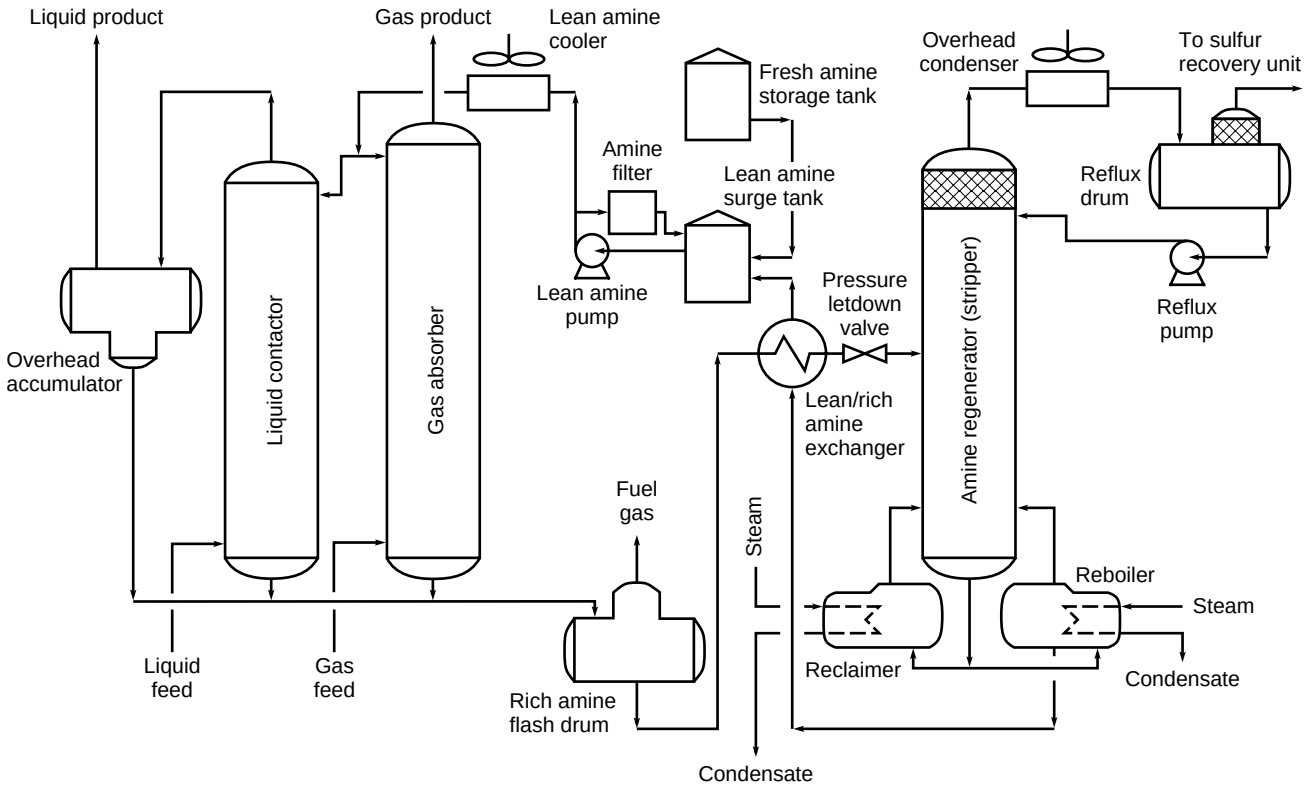


Figure 1—Process Flow Diagram of a Representative Amine Unit

The first three mechanisms are most prevalent in carbon steels that have been exposed to rich amine solutions loaded with H_2S, including 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. Cracking can occur both with and without significant metal loss. Definitions of these cracking mechanisms and photomicrographs are presented in Appendix A.

Several serious cracking problems have been reported over the past 50 years. 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 6 months to 10 years of exposure to 15-percent monoethanolamine in water (containing unspecified amounts of both hydrogen sulfide and carbon dioxide) at temperatures up to 149°C (300°F). Complete stress relieving 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 to the recommended practices.

Other instances of ASCC were reported in non-stress-relieved equipment operating in 20-percent (by weight) monoethanolamine [3]. Affected equipment included two amine storage tanks, four absorber towers, one rich amine flash drum, one lean amine treater, and various piping. Cracking was found primarily at welds exposed to amine solutions where temperatures ranged from 53°C to 93°C (127°F to 200°F). 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 154°C (310°F). 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.

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].

4.2.3 Corrosion

Corrosion (metal loss) of carbon steel components in amine units is not caused by the amines themselves. It 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. The cracking of carbon steel components in amine service is often related to the general corrosivity of amine solutions. 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 Appendix A). Similarly, corrosion reactions can 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 Appendix B for more information regarding corrosion in amine units.)

5 Guidelines for Construction Materials and Fabrication of New Equipment

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 percent 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 were solved by reducing fluid velocity to less than 1.8 m/sec (6 ft/sec). Austenitic stainless steels have been used in locations where the corrosion rate of carbon steel is excessive. 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 approximately 110°C (230°F). 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. Clad plate is preferred over solid stainless steel construction to avoid possible through-wall penetration that results from chloride stress corrosion cracking. In some locations, solid stainless steel construction was used where control of external chloride stress corrosion cracking was achieved. Alloys, such as Types 304 and 316, have been used for regenerator reboiler tubes that handle little or no hydrogen sulfide. Titanium tubes have been used in units handling CO_2, but they may hydride in service.

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 damage despite relatively low temperatures. Carbon steels with a low level of inclusions or inclusion shape control might 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. Austenitic stainless steel cladding, lining, or weld overlay can offer alternative methods of protection in areas where chronic cracking or hydrogen blistering occurs.

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 RP 582 for guidance on weld fabrication.

5.2.2 Weldment Hardness Control

Proper control of weldment hardness in fabricated carbon steel equipment can provide resistance to SSC. NACE RP0472 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 RP0472, 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 RP0472, 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. Hardness limits for such systems should be evaluated by each user based on past experience.

As noted in Section A.5 controlling weldment hardness has no known effect on the prevention of ASCC. However, PWHT can reduce residual stress in carbon steel weldments, thereby effectively controlling ASCC.

5.2.3 Postweld Heat Treatment

5.2.3.1 General

PWHT is an effective method for improving the cracking resistance of carbon steel weldments in amine service. An effective procedure consists of heating to 593°C – 649°C (1100°F – 1200°F) and holding in this temperature range for 1 hour per 25 mm (1 in.) of metal thickness, or fraction thereof, with a 1-hour minimum holding time. PWHT below 593°C (1100°F) is not considered effective for crack prevention; therefore, it is not recommended. It should be noted that the allowable variation in the chemical composition of steels can be considerable, even within the same grade. In conjunction with welding variables, this can produce high hardnesses in heat-affected zones that might not be adequately softened by normal PWHT. Each situation should be evaluated to determine whether the proposed PWHT is adequate.

Investigations have shown that inadequate heated band width can result in residual stresses of up to 172 MPa (25 ksi) after heat treatment. The residual stresses are highest with large diameter piping, due to higher internal convection and greater dispersion of radiated heat from the pipe ID. The following guidelines have been provided to minimize residual stresses, and may be used to increase resistance to SSC, SOHIC, and ASCC.

a. The minimum heated band width should be as follows:

Nominal Pipe Size	Minimum Heated Band Width
19 to 25 mm ($^3/_4$ to 1 in.)	102 mm (4 in.)
38 to 76 mm ($1^1/_2$ to 3 in.)	152 mm (6 in.)
102 to 152 mm (4 to 6 in.)	203 mm (8 in.)
≥ 203 mm (8 in.)	$BW = 4.12\ (Rt)^1/_2 + 50.8$ mm (203-mm minimum) [$BW = 4.12\ (Rt)^1/_2 + 2$ in.] (8-in. minimum)

Where:

BW = Heated Band Width

R = Pipe Radius (Outside Diameter)

t = Pipe Wall Thickness

b. Insulate over the total heated band width and a 230 mm (9 in.) minimum runout on both sides, using at least 50 mm (2 in.) thick insulation blankets.

c. In the case of flange welds, insulate the entire flange inside and out, and a 230 mm (9 in.) runout of the pipe side of the weld.

d. If possible, close off the ends of the pipe to minimize convection currents.

PWHT should be applied to new carbon steel equipment, including piping in amine services, as described in 5.2.3.2 through 5.2.3.6.

5.2.3.2 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.

5.2.3.3 DEA Units

For DEA units, PWHT is recommended for all carbon steel equipment, including piping, exposed to amine at service temperatures of 60°C (140°F) and higher. The maximum operating temperature and the effects of heat tracing and steam-out 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 60°C (140°F). 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 steam-out due to the presence of amine [7]. Each user company should evaluate the need for PWHT of carbon steel at temperatures below 60°C (140°F), especially for equipment such as absorbers and contactors.

5.2.3.4 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 percent DIPA solutions [7]. This guideline does not apply to units containing a mixture of sulfolane and higher concentration DIPA (typically 50 percent), where no cracking has been reported.

5.2.3.5 MDEA Units

For MDEA units, PWHT is recommended for all carbon steel equipment, including piping, exposed to amine at service temperatures of 82°C (180°F) and higher. The maximum operating temperature and the effects of heat tracing and steam-out 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 88°C (190°F) [8].

5.2.3.6 Other Amine Units

In amine units other than MEA, DEA, DIPA, and MDEA, experience suggests that susceptibility to cracking is very low, especially at temperatures below 88°C (190°F). It seems that cracking susceptibility generally decreases in the order of primary amine, secondary amine, and tertiary amine. 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.

The cracking tendencies of amine solutions can be determined by careful inspection of operating facilities that are in actual amine service; appropriate laboratory tests can also be beneficial. Slow strain rate testing is a useful laboratory method to establish the tendency of amine solutions to promote cracking [5, 9, 10]. However, the test may provide conservative data; that is, it may indicate a tendency for stress corrosion cracking where it does not occur in actual service. If this test procedure is used, the test solutions should contain the acid gases (hydrogen sulfide and carbon dioxide) and other anticipated stream contaminants found in operating plants; where it is possible, tests should be conducted using actual plant solutions.

5.2.4 Socket-Welded Connections

Small-diameter socket-welded connections can 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.

5.2.5 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.

6 Inspection and Repair of Existing Equipment

6.1 GENERAL

6.1.1 General Guidelines

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.

The examinations listed in this section emphasize inspection of equipment for cracks. Inspection should be in accordance with API 510 and API 570.

Inspection of equipment in amine service should be conducted or supervised by experienced, certified inspectors who have comprehensive knowledge of the specific unit, its materials of construction, and its operating, maintenance, and inspection history.

6.1.2 Use

The procedures discussed in this section have been found to be effective in the inspection of amine unit equipment, but they are not the only means of achieving the desired inspection. New instrumentation and procedures are under development and should be evaluated as they become available.

6.1.3 Intent

This document is a recommended practice; therefore, none of the inspection methods or recommendations in this document are mandatory. Procedures that differ from government regulations (local or otherwise) should be evaluated carefully to confirm their compliance with such requirements. In areas where these procedures are superseded by jurisdictional regulations, those regulations shall govern. The responsibility for identifying and complying with legislative requirements rests with the user company.

6.1.4 Safety

Before entry, API Publication 2217A *Guidelines for Work in Inert Confined Spaces in the Petroleum Industry* should be consulted.

6.2 INSPECTION INTERVALS

The priority of equipment examination should consider the consequences of a leak or a failure on the surrounding area, operating conditions (temperatures, pressure, and contents), criticality of the equipment, and inspection and repair history. A methodology for a risk-based approach is outlined in API RP 580.

6.2.1 Initial Inspection

An initial examination should be made of any susceptible, non-PWHT equipment listed in 6.3. High priority equipment should be inspected by internal wet fluorescent magnetic particle testing (WFMT: see 6.4.1) at the next scheduled shutdown. A partial inspection of representative weldments with approximately 20 percent coverage may be performed first. Additional WFMT should be performed if cracking is detected by this initial examination.

If hydrogen blisters are identified during an internal visual inspection, consideration should be given to performing a selective ultrasonic (longitudinal) inspection to identify blistered areas not apparent by visual inspection. Blistered areas should be further examined to determine if HIC and SOHIC are present.

External ultrasonic shear-wave examination may be performed while the equipment is on stream. If the external inspection reveals cracking, or if the inspection history indicates past problems, the need for additional on-stream inspection, or the need for and timing of an internal inspection by WFMT, should be evaluated. In any case, an initial internal inspection for cracks in non-PWHT equipment should be made.

The maintenance and inspection records of PWHT equipment should be checked for past problems. Welds made on the equipment that have not received PWHT should also be inspected. This information should be used to determine the next date for internal and/or on-stream inspection for cracking.

Piping that has not received PWHT should also be considered for inspection. External inspection procedures, such as those listed for stationary equipment, should be applied to piping. Internal inspection of small diameter piping may be impractical (see 6.3.2). The user company must determine whether external inspection is sufficient to satisfy the criteria for safe operation.

6.2.2 Reinspection of Repaired Equipment

Equipment listed in 6.3 that has been repaired in accordance with 6.5 and 6.6, and that has not received PWHT, should be

considered for reinspection during the next scheduled shutdown. An examination should be performed as described in 6.4 and should primarily include weld repair areas, as well as spot checks of previously noted sound material.

6.2.3 Reinspection of Undamaged Equipment

Reinspection should be conducted at appropriate intervals on any of the equipment listed in 6.3 that has been found to be undamaged during previous inspection. The intervals can be set by experience, equipment criticality, and whether or not the equipment has received PWHT. Reinspection should include the examination of randomly selected areas. Reinspection intervals should be reevaluated if significant process changes occur, such as amine type, amine solution composition, flow rate increases and/or temperature increases.

6.3 EQUIPMENT AND PIPING THAT SHOULD BE INSPECTED

6.3.1 Equipment

Common equipment that should be considered for inspection includes: absorbers, accumulators, coalescers, columns, condensers, coolers, contactors, extractors, filter vessels, flash drums, heat exchanger shells/channels/tube bundles, knockout drums, reactivators, reboilers, reclaimers, regenerators, scrubbers, separators, settlers, skimmers, sour gas drums, stills, strippers, surge tanks, treating towers, and treated fuel gas drums.

Inspection of welded pressure-containing equipment associated with air coolers, such as header boxes, should be considered. Pump cases in amine service that have had weld repairs should be inspected for the presence of cracks.

Specific areas for inspection include those in and adjacent to longitudinal and circumferential welds; manway and nozzle attachment welds (including welds that attach reinforcing pads); attachment welds of internals (tray and downcomer welds, support attachment welds for distributors and vortex eliminators); areas repaired by welding; heat-affected zones on internal surfaces opposite externally attached structural steel platforms, ladders, and the like; and arc strikes. The weld areas behind, or associated with, leaking panels of alloy strip-lined vessels should also be inspected.

Cracks and related defects initiate internally. Therefore, the primary inspection effort should be directed toward internal surfaces contacted by amine solutions.

6.3.2 Piping

All process piping associated with amine units that have not been postweld heat treated should be considered for inspection to detect cracking. It might be more economical to replace small diameter piping than it is to inspect it, and this alternative should be evaluated. Specific areas to be inspected include those in and adjacent to the following locations:

a. Welds of pressure-containing piping.
b. Attachment welds associated with pipe shoes, support clips, or other non-pressure-containing attachments.
c. Weld arc strikes found on pipes.
d. Attachment welds of reinforcing pads for nozzles.
e. Repair welds of any type.

Stress corrosion cracks and related defects initiate internally. Therefore, the inspection should be directed toward internal surfaces that are contacted by amine solutions.

The following methods are useful for the external nondestructive inspection of piping:

a. Ultrasonic testing (see 6.4.3).
b. Radiographic testing (see 6.4.4).
c. Visual examination (see 6.4.6).

At times, it may be appropriate to remove selected pipe segments, cut them in half longitudinally, and use WFMT to inspect their internal surfaces.

6.4 EXAMINATION PROCEDURES AND METHODS

6.4.1 Wet Fluorescent Magnetic Particle Testing

Wet fluorescent magnetic particle testing (WFMT) is a very sensitive method for detecting surface-connected cracks and discontinuities. WFMT using an AC yoke is one of the primary methods recommended for internal inspection of pressure vessels in amine service.

Two modes of operation are available for the magnetizing - AC yoke and half-wave DC prods. The AC yoke mode achieves greater sensitivity in locating surface defects, and also reduces the effects of background interference. For these reasons, it is the recommended mode. The half-wave DC mode offers improved penetration of the magnetic field into the area that is being inspected, thereby permitting the detection of near surface defects in addition to surface defects. However, use of DC prods is not recommended because they can induce arc burns that could initiate future cracking.

WFMT requires surfaces that are cleaned to a near-white finish that meets the requirements of NACE No. 2/SSPC SP 10. Abrasive blasting or high-pressure waterjetting at a pressure of 70 MPa (10,000 psig) or higher may be used. The area prepared for inspection should normally be 100 – 150 mm (4 – 6 in.) on either side of the weld. However, the size of the area may vary depending on the location of arc strikes, exterior welds, and the like. The entire internal surface does not have to be prepared for inspection. Residual abrasive material and debris should be removed from the equipment before inspection.

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. This polishing should be performed on at least a representative percentage of the cleaned surface area in each piece of equipment, especially those with high priority.

Considerable field experience has demonstrated that power wire brushing 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 smears metal on the surface that covers underlying cracking, greatly reducing the likelihood of its detection by WFMT.

6.4.2 Alternating Current Field Measurement

Alternating current field measurement (ACFM) is an electromagnetic technique that can be used to detect and size surface-breaking cracks in ferromagnetic materials. The method can be applied through thin coating and does not require extensive surface preparation. It is best used as a screening tool for rapid detection of cracking along welds and/or heat-affected zones with little or no surface preparation. It can be used in lieu of WFMT. The sensitivity of ACFM to cracks decreases with the increase of the coating thickness and loose scale on the examination surface. ACFM can size crack length reliably. It can also accurately assess depths of non-branched, though-wall-oriented cracks. However, its crack depth sizing can yield erroneous results when ACFM is applied on high-branched, closely-spaced, or tilted (i.e. not exactly in the through-wall direction) cracks, such as amine stress corrosion cracks. ACFM data interpretation is much more complicated than WFMT. Highly skilled, experienced operators are essential to the success of ACFM inspection.

6.4.3 Ultrasonic Testing

Ultrasonic testing (UT), using either manual or automated methods, is very useful for crack detection in amine equipment. UT methods include longitudinal, shear wave, and crack-tip diffraction. Various UT methods can be used for detecting and sizing subsurface-connected cracks larger than approximately 3 mm (0.125 in.). Longitudinal UT is useful for evaluating in-plane cracking, such as hydrogen blistering. Shear wave UT is useful for evaluating through-thickness cracking, such as SSC, HIC, SOHIC, and ASCC. UT methods are non-intrusive, thereby facilitating inspection of equipment and piping from the external surface. Depending on the surface temperature limitations, UT inspection can be performed onstream.

UT will reveal discontinuities in welds. However, the effective use of this inspection method depends highly on the UT operator's knowledge, skill, and experience levels. Small, tight cracks might be overlooked by an inexperienced operator, or the cracks might be so tight or shallow that their UT signals are not easily identified.

Welds not fabricated in conjunction with a 100-percent weld quality inspection program might exhibit indications of discontinuities when examined by UT. This can result in having to evaluate minor weld discontinuities that may be of no consequence to vessel integrity.

UT is a valuable tool for inspecting operating equipment. If the limitations of the method are understood, inspections can be used to ensure continued safe operation of equipment without costly shutdowns.

6.4.4 Radiographic Testing

Radiographic testing (RT) is sometimes employed to detect cracks in amine equipment. However, unless the cracks are reasonably large or severe, radiographic inspection is not a very sensitive inspection method. This does not mean that radiographic inspection should be avoided; the method can reveal major defects relatively quickly, but if weld cracks are detected, a more extensive examination by UT should be considered. RT is a tool with limited applicability for inspecting piping in operation as flow characteristics might affect the quality of the radiographs.

6.4.5 Liquid Penetrant Testing

Liquid penetrant testing (PT) is not a recommended inspection method because it does not reliably reveal the tight fissures that are characteristic of cracking in amine equipment.

6.4.6 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. 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. Such cracks could weep and cause a bubble. An active, dripping leak obviously indicates a problem that warrants immediate attention.

6.4.7 Surface Preparation—General

All methods of inspection rely on a level of surface preparation to facilitate the reliable detection of cracking. The degree of surface preparation may vary considerably depending on the inspection technique that will be applied. Inadequate surface preparation can 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 5.2.3.3, some equipment has cracked during steam-out due to the presence of amine. Therefore, if steam-out is required for equipment cleaning, it should follow a thorough water wash to remove any residual amine. The equipment should be dried and loose scale, fouling deposits, and other material 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.

6.5 REPAIR OF DAMAGED EQUIPMENT

6.5.1 General

The repair methods listed in 6.5.2 and 6.5.3 primarily apply to equipment and large diameter piping. Small diameter piping [50 mm (2 in.) and smaller] can usually be replaced with new PWHT components at a lower cost than in situ repair and heat treatment.

6.5.2 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) to assure that all defects are eliminated.

Flame gouging and arc gouging (if used) must be performed with care, since these procedures may also cause the defects to increase in size. These methods can be used effectively as the first stage of crack removal. This should be followed by grinding and periodic WFMT to check for defect removal as discussed above.

If the defect depth is less than the corrosion allowance, an acceptable repair could consist of removing the defect by grinding, and feathering, or contouring the edges of the grind-out area by removing sharp edges and providing a smooth transition to the surrounding surface. Welding may not be necessary when this repair method is used.

If the defect depth is greater than the corrosion allowance, the evaluation and fitness-for-service methods methods specified in API 510, API 570 and RP 579, should be used to determine whether the vessel or piping with the locally thinned area is fit for continued service.

6.5.3 Crack Repair by Welding

Prior to any welding, consideration should be given to the need to remove (outgas) residual atomic hydrogen from the area to be welded. This is most likely for equipment in rich amine service that has been subjected to a significant level of corrosion and hydrogen charging. Outgassing should not be needed for equipment in lean amine service. An acceptable outgas procedure consists of heating the area to a metal temperature of 232°C – 316°C (450° – 600°F) and holding that temperature for 2 to 4 hours. Other similar procedures have also been used effectively.

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

6.6 POSTWELD HEAT TREATMENT OF UNDAMAGED OR REPAIRED EQUIPMENT

After existing amine equipment has been thoroughly inspected, consideration should be given to performing a stress-relieving heat treatment. If there is no history of cracking problems, and if thorough inspection has revealed no evidence of cracking in the equipment, heat treatment might not be warranted. However, PWHT is considered essential if any weld repairs are performed on equipment that originally received PWHT. If weld repairs are performed on equipment that did not originally receive PWHT, PWHT of repaired welds should be considered by using the guidelines in 5.2.3. PWHT is strongly advised for certain replacement equipment (see 5.2.3) and for any equipment that has a prior history of cracking.

The decision to heat treat 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.

Equipment should first be washed and thoroughly cleaned before heat treatment is performed. Cleaning should include flushing with copious amounts of water. All residual amine must be removed from the equipment before heat treatment. After the equipment has been properly cleaned heat treatment may proceed. The procedure should be as specified in 5.2.3. Alternative heat treatments at temperatures below 593°C (1100°F) should not be performed.

After heat treatment has been completed, the equipment should be carefully inspected again, by one of the acceptable methods. If no defects are found, the equipment may be returned to service. If defects are found after heat treatment, it must be decided if the equipment should be recleaned, repaired, or re-heat treated. In some cases it might be more economical to permanently remove the defective equipment from service and replace it with a new component that has received PWHT.

APPENDIX A—CRACKING MECHANISMS

A.1 General

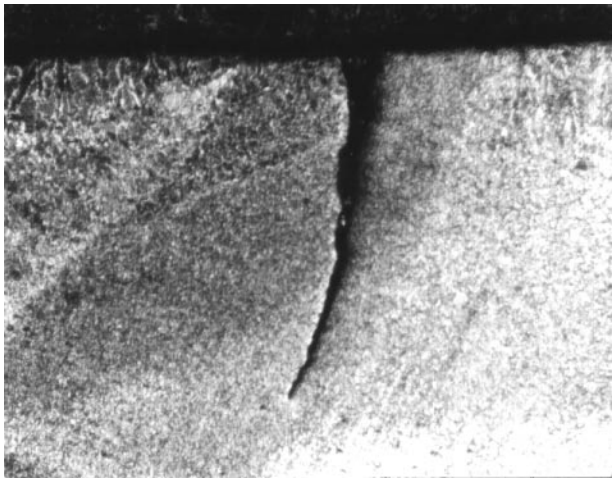
There are four basic cracking mechanisms that can affect carbon steel equipment in amine units. Three of these, namely sulfide stress cracking, hydrogen-induced cracking, and stress-oriented hydrogen-induced cracking, are forms of hydrogen-related damage. These forms of hydrogen-related damage are typically 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. The fourth 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 the following sections.

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 the recombination of the atomic hydrogen into molecular hydrogen, thus promoting the absorption 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.

High metal hardnesses are 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 postweld 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



Note: Two-percent nital etch at 30X magnification.

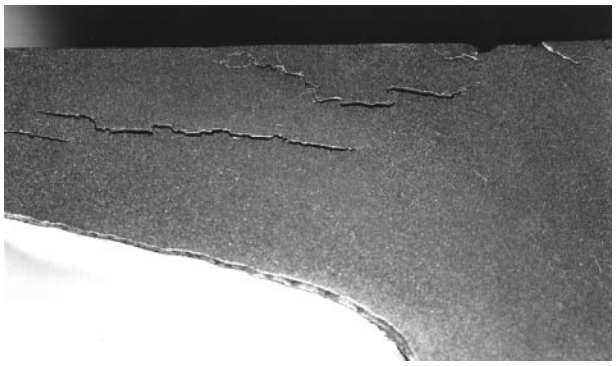
Figure A-1—Sulfide Stress Cracking in an Existing Hardened Heat-Affected Zone of a Weld

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 Appendix B). Additionally, the likelihood of cracking during a weld repair of post-service equipment can be reduced by outgassing the weldment (see 6.5.3).

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 direc-



Note: Two-percent nital etch at 4.5X magnification.

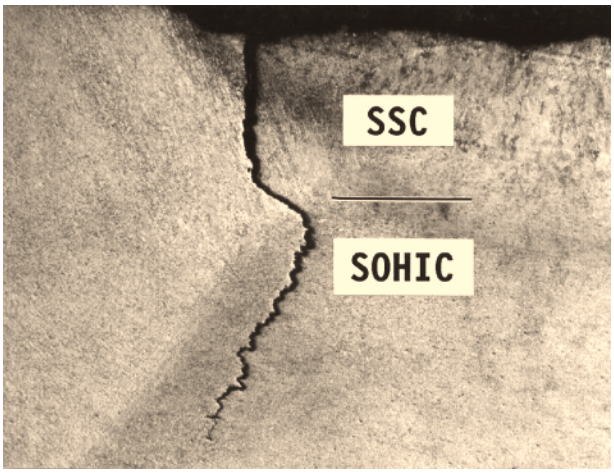
Figure A-2—Hydrogen Blisters near the ID Surface of a Carbon Steel Flange

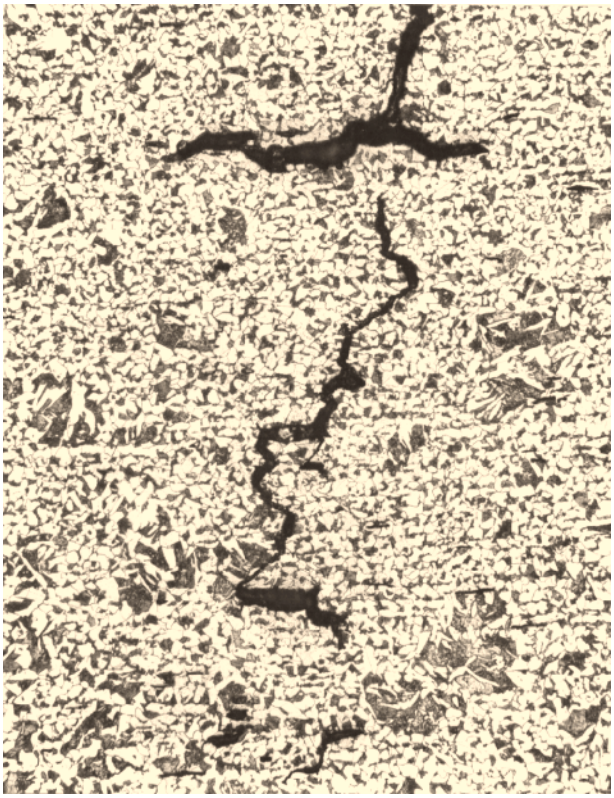
Note: Two-percent nital etch at 5.5X magnification.

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

tion 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.

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





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

the crack appearance. Figure A-3 shows typical HIC damage in carbon steel.

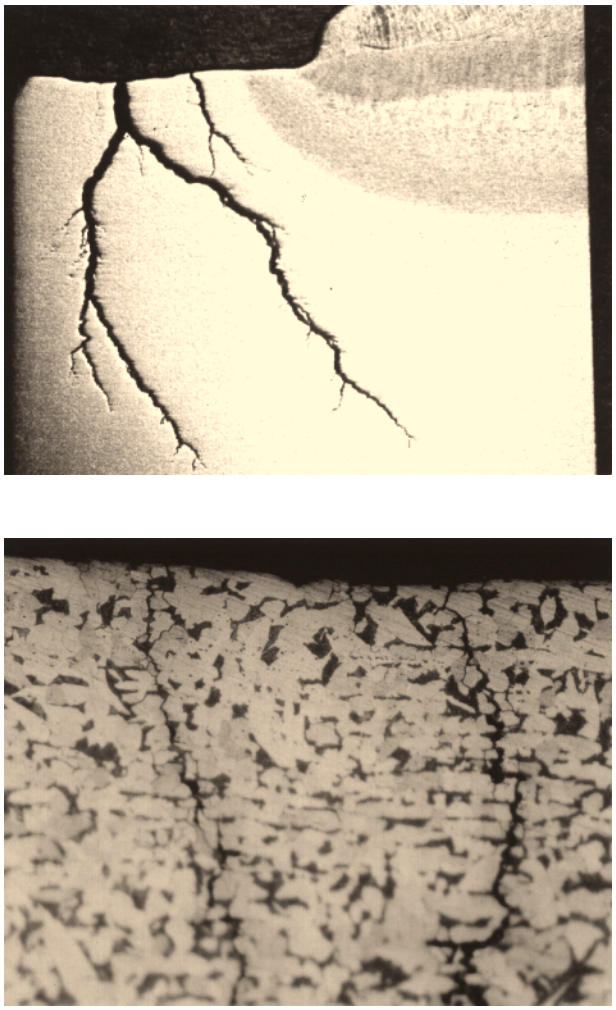
Blistering and HIC can be minimized by selecting a higher quality steel (often referred to as a clean steel) with low inclusion content. Increased resistance to blistering and HIC is usually achieved by lowering the sulfur content of the steel and controlling the sulfide inclusion morphology by calcium or rare earth metal additions to produce spheroidal sulfide shape. Base metal heat treatments, such as normalizing or quenching, and tempering above 593°C (1100°F), increase resistance to HIC. Using corrosion control procedures to reduce the sulfide corrosion and hydrogen charging also reduces the likelihood of blistering and HIC. Stress reduction by PWHT has no significant impact on reducing 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 as a result 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 only, 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 overlay equipment can provide the necessary resistance.



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. (2-percent nital etch at 200X magnification.)

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

A.5 Alkaline Stress Corrosion Cracking

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, but 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 appears to increase 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 a number of contaminants in the solution [9, 10, 13].

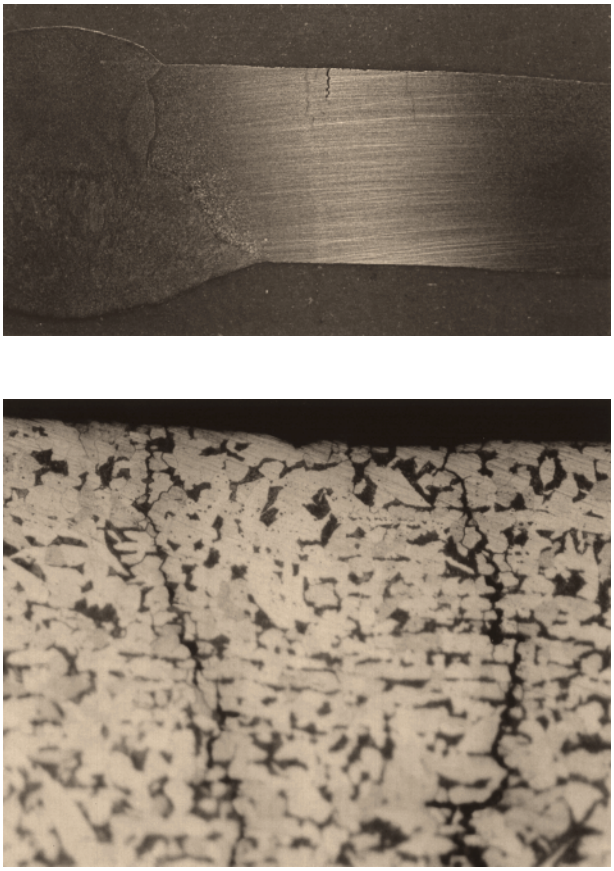
ASCC has occurred in a variety of steels. Field experience to date has not indicated any significant correlation between susceptibility to ASCC and steel properties. Hardness of the steel has virtually no effect on ASCC. Susceptibility to ASCC increases with increasing tensile stress level. Areas of deformation resulting from cold forming or localized high residual stresses in weldments are more prone to ASCC. Surface discontinuities, especially in the area of 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 controlled by PWHT and proper heat treatment after cold forming.

A.6 Recent Industry Experience

Two interesting examples of industry cracking problems were recently reported to the API Task Group on Amine Cracking.

The first example involved amine cracking (ASCC) in the overhead piping that was leading from the absorber column of an MEA unit. The line normally operated at 38°C (100°F), 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.

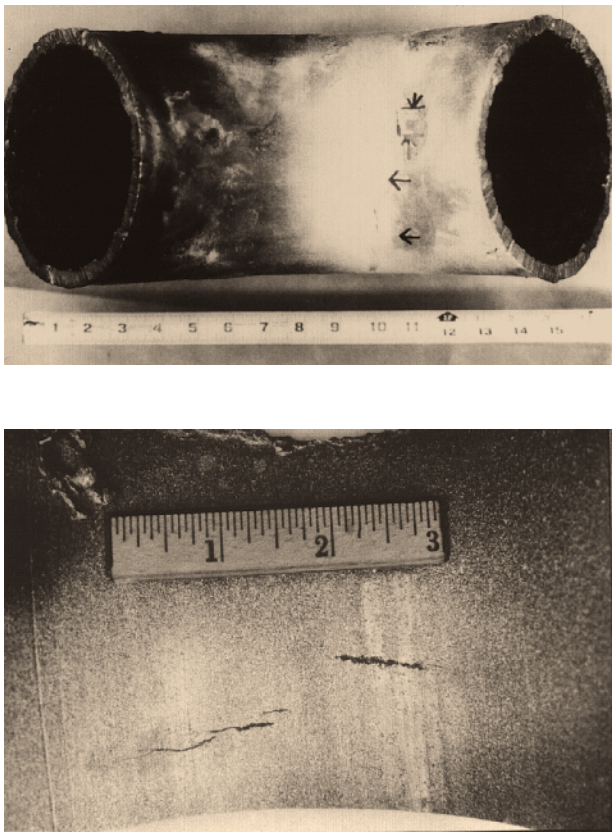
The second example involved ASCC of a carbon steel elbow in the suction piping to the lean amine bottoms pump



Note: The top panel illustrates alkaline stress corrosion 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

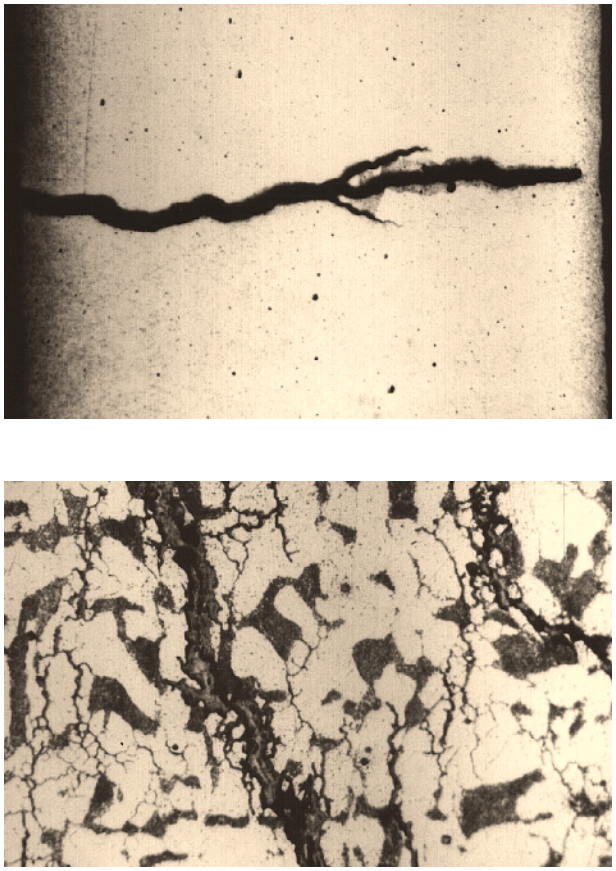
Figure A-6—Alkaline Stress Corrosion Cracking in a Pipe Weld in MEA Service

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 66°C (150°F). Prior to cracking, the elbow had been heated by a torch to approximately 1093°C (2000°F) 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 5.2.3.1. Figures A-7 and A-8 illustrate the intergranular cracking that initiated from the internal surface o f the elbow, and verify that amine cracking occurred in the line.



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

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



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

APPENDIX B—CONSIDERATIONS FOR CORROSION CONTROL

B.1 Scope

This appendix 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 least 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 percent 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: the removal of certain corrosive species from amine solutions by side-stream filtration, reclaiming, or both; the use of effective corrosion inhibitors; and 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 percent by volume. Corrosion (not necessarily cracking) has been least severe in low-pressure units that remove only hydrogen sulfide, or that handle mixtures of the two gases containing at least 5 percent 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.

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 percent or more of the circulating amine solution is passed through the filters. MEA solutions can be purified by reclaiming, or by semicontinuous 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 percent 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 in an attempt to reduce corrosion problems. Corrosion inhibitors that have been and are being used include high-molecular-weight filming amines, inorganic and organic oxidizing salts, and chemical oxygen scav-

engers. A number of 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. 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 1.8 m/sec (6 ft/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 is possible for the regenerator tower and associated reboilers.

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

B.6.2.7 Use a square-pitch tube layout (or remove interior tubes) 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 stainless steel.

B.6.2.10 Specify long-radius elbows and adequately sized process piping to minimize erosion-corrosion in transfer lines as a result of excessive flow turbulence. Stainless steel has been successfully used for two-phase flow piping in high concentration carbon dioxide systems.

B.6.2.11 Provide an amine reclaimer for MEA units.

B.6.2.12 Design the regenerator reboiler and amine reclaimer to assure that their tube bundles are fully immersed in process liquid at all times.

B.6.2.13 Provide inert-gas blanketing for storage and surge vessels to reduce oxygen degradation of amine solutions.

B.6.2.14 If a filter is used, size it for not less than 5 percent of the amine circulation and less than 0.1 weight percent solids content.

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.7.3 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 149°C (300°F) will help to minimize amine degradation and the corrosion of reboiler tubes. MEA concentrations above 25 percent by volume, and acid gas loading above 0.35 mole per mole of amine, should be carefully evaluated in regard 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 percent 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 percent 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 1.8 m/sec (6 ft/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 similar to 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 1.5 m/sec (5 ft/sec). In 40 percent DGA that treats CO_2 and H_2S acid gases, at least 5 percent 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.

APPENDIX C—REQUEST FOR NEW INFORMATION CONCERNING PROBLEMS WITH ENVIRONMENTAL CRACKING IN AMINE UNITS

The information contained in this recommended practice 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 recommended practice.

The following pages contain 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:

Chairman, Recommended Practice 945 Task Group
API Subcommittee on Corrosion and Materials
c/o Standards Department
American Petroleum Institute
1220 L Street, N.W.
Washington, D.C. 20005
standards@api.org

API REPORT FORM:
ENVIRONMENTAL
CRACKING PROBLEMS IN
ANIME UNITS

Date _____
API File No. _____
Page _____ of _____

Name _____

Company affiliation _____

Address _____
_____
_____

Country _____

Telephone _____ FAX _____

E-mail _____

1. Type of anime unit (e.g., MEA, DEA)
_____
2. Location (e.g., refinery, chemical plant)
_____
3. Acid gas being scrubbed (e.g., H_2S, CO_2)
_____
4. Anime concentration (%)
_____
5. Solution loading (moles of acid gas per mole of amine)
_____
6. Corrosion inhibitor, if used
_____
7. Date of unit construction
_____
8. Date of problem
_____
9. Equipment affected (e.g., vessel, exchanger, piping)
_____
10. Location of problem (e.g., vessel shell, pipe weld)
_____
11. Metal temperature at location: normal, maximum
_____

API REPORT FORM:
ENVIRONMENTAL
CRACKING PROBLEMS IN
AMINE UNITS

Date _____
API File No._____
Page _____ of _____

12. Construction material (ASTM designation or equivalent)
    _____
13. Material strength level
    _____
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:
    _____
    _____
    _____
    _____
    _____
    _____
    _____

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