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Introduction to NACE standard MR0103

Use these materials to reduce sulfide stress cracking in corrosive refinery environments

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Many process streams in petroleum refineries contain enough H₂S to cause sulfide stress cracking (SSC) in susceptible materials. Until recently, however, no industry standard was available that covered material requirements for sour refinery service. In April 2003, NACE International released MR0103, "Materials Resistant to Sulfide Stress Cracking in Corrosive Petroleum Refining Environments."¹ Several motivating factors led to the development:

- Although refineries sometimes specify materials compliant with NACE MR0175,² application practices varied widely among engineering contractors and users.
- Refinery "sour" environments are quite different from the sour environment definitions provided in MR0175.
- MR0175 was being revised to address chloride stress corrosion cracking, resulting in unnecessary environmental restrictions on some materials commonly used in refinery applications.

The MR0103 document uses borrowed concepts and requirements from various versions of MR0175 with modifications and additions as needed to create a new standard that meets industry needs. For example, MR0103 utilizes the alloy grouping philosophy that is used in what is now NACE MR0175/ISO 15156, but did not implement environmental limits such as H₂S partial pressures, temperature limits, pH restrictions, etc. Materials and material condition requirements are based on a mix of MR0175 requirements and refinery-specific experience.

There are several major differences between MR0103 and MR0175/ISO 15156:

- The refinery standard guidelines for determining whether an environment is "sour" are quite different from the sour environment definitions provided in previous and current versions of MR0175.
- The refinery standard does not include environmental restrictions on materials.
- Materials and/or material conditions are included in MR0103 that are not listed in MR0175/ISO 15156.
- Materials and/or material conditions are included in previous and/or current versions of MR0175/ISO 15156 that are not listed in MR0103.
- Because welding is prevalent in refinery piping and equipment, MR0103 places extra emphasis on welding controls in several material groups, most notably the carbon steels.

Applicability of MR0103. Both MR0175 and MR0103 include sections that describe applicability of each of the standards. Both describe material factors and environmental factors, and provide guidelines to the user on how the standard should be applied. Note that both standards require the user to specify whether the environmental conditions are such that the material requirements of the standard should be applied.

One of the key differences between the MR0175 and MR0103 standards lies in the guidelines addressing the environmental conditions under which SSC is likely to occur. MR0103 covers a broader range of sour environment conditions experienced in downstream process units. These guidelines are based on:

- User's plant experience and practices
- Existing NACE and industry recommended practices and reports (i.e., NACE RP0296,³ 8X194,⁴ 8X294,⁵ API Publication 581⁶)
- A fundamental understanding of atomic hydrogen generation in the sour service corrosion reaction and the subsequent rate of hydrogen flux into the process-contacted steel, i.e., combined effects of pH, H₂S and HCN.

A significant difference between upstream and downstream sour environments is that, in many refinery sour water environments, dissolved ammonia is present. This increases the pH, thereby increasing the solubility of H₂S, which in turn increases the bisulfide ion concentration and corrosivity. Ammonium bisulfide corrosion in these high-pH environments generates a relatively high rate of hydrogen flux.

Furthermore, the presence of cyanides at an elevated pH further aggravates the degree of atomic charging and hydrogen flux into the steel by poisoning the surface reaction that results in a stable and protective iron sulfide scale from forming.

The outcome of the consensus approach has resulted in the following guidelines on what constitutes a sour service in downstream units.

The fluid must contain a free water phase and:

- >50 ppmw dissolved H₂S in the free water (in recognition that significant levels of dissolved H₂S can result in SSC even in low-pressure systems), or
- A free water pH <4 and some dissolved H₂S present (in recognition that in low-pH environments, significant charging of materials with atomic hydrogen can take place irrespective of H₂S level), or
- A free-water pH >7.6 and >20 ppmw hydrogen cyanide ion (HCN) and some H₂S dissolved in the free water (in recognition that at high pH, the HCN ion is stable and results in significant charging of ferritic materials by poisoning the formation of a protective iron sulfide scale), or
- >0.0003 MPa abs (0.05 psia) partial pressure H₂S in a process with a gas phase (based on the historical MR0175 definition of sour service, without the 0.4 MPa abs [65 psia] minimum pressure requirement).

Another key difference between MR0175 and MR0103 is that MR0103 allows the user to supplement the environmental guidelines in the standard with actual plant experience and risk-based analysis to determine whether the material requirements of the standard need to be applied. When making this determination, the user is expected to consider all plant operating scenarios, including operational upsets, startup/ shutdown conditions, etc.

Materials of construction.

Carbon steels. For the most part, refineries use carbon steels classified as P-No. 1 Group 1 or 2 in Section IX of the ASME Boiler and Pressure Vessel Code for piping and vessels.⁷ MR0103 imposes no base metal hardness requirements on these materials because these grades have maximum tensile strength requirements that effectively limit their bulk hardness. Other carbon steels must meet a 22 HRC maximum requirement.

MR0103 shares the following requirements with MR0175:

- Carbon steels must be in one of the following heat treatment conditions:
 - a. Hot-rolled
 - b. Annealed
 - c. Normalized
 - d. Normalized and tempered
 - e. Normalized, austenitized, quenched and tempered
 - f. Austenitized, quenched and tempered.
- Carbon steel materials that are cold worked to produce outer fiber deformation greater than 5% must be stress relieved to ensure that the material is below 22 HRC.

Welding carbon steels. Welding introduces the potential for creating hard regions in carbon steels. As such, controls must be imposed to ensure that weldments will be soft enough to resist SSC in service.

MR0103 requires that welds in P-No. 1 carbon steel materials be performed per the methods outlined in NACE Standard RP0472.⁸ RP0472 requires that the weld deposit meet a hardness limit of 200 HBW maximum. It requires control of heat-affected zone (HAZ) hardness by one of the following methods:

- Post-weld heat treatment
- Base metal chemistry controls, usually via a specified maximum carbon equivalent and limits on elements such as niobium, vanadium and boron. Carbon equivalent is defined as:

$$CE = \%C + \frac{\%Mn}{6} + \frac{(\%Ni + \%Cu)}{15} + \frac{(\%Cr + \%Mo + \%V)}{5}$$

- Custom welding procedure utilizing a combination of welding process controls, base metal chemistry controls (usually less restrictive than method 2 above) and a hardness traverse conducted on the procedure qualification specimen demonstrating that the hardness does not exceed 248 HV in the HAZ.

Alloy steels. MR0103 defines alloy steels as those with a chromium content of less than 10%. Total alloying element content can exceed 10%. In practical terms, alloy steels in MR0103 are those steels that contain alloying elements greater than the amounts allowed in carbon steels, but which do not contain enough chromium to be considered stainless steels.

Alloy steels with assigned P-Numbers in Section IX of the ASME Boiler and Pressure Vessel Code are required to meet the hardness requirements shown in Table 1.

Table 1. Low-alloy steel hardness requirements	
P-Number	Maximum hardness (HBW)
3	225
4	225
5A	235
5B	235
(except 9Cr-1Mo-V grades)	
5B	248
9Cr-1Mo-V grades (F91, P91, T91, WP91, Grade 91, C12A)	
5C	235
6	235
7	235

10A	225
10B	225
10C	225
P-No. 10F	225
P-No. 11	225

Alloy steels without P-Number assignments must meet a 22 HRC maximum hardness requirement, the same as in the various MR0175 revisions.

Welding alloy steels. MR0103 includes very specific information about welding alloy steels. It allows welding P-Number 3 and 4 materials without PWHT in cases where the practice is allowed per ANSI/NB-23.⁹ In other cases, PWHT is required. In all cases, with or without PWHT, a hardness traverse is required on the PQR specimen to demonstrate that the procedure will produce weldments with hardness values below 248 HV.

Martensitic stainless steels. Only specific alloys are listed as acceptable, with specific heat treatment and maximum hardness requirements. The martensitic stainless steel alloys most commonly used in sour applications are S41000, its cast equivalent, CA15 and CA6NM. These alloys are required to be double-tempered and meet maximum hardness requirements of 22 HRC, 22 HRC and 23 HRC, respectively.

Welding martensitic stainless steels. For S41000, CA15, and CA6NM, the base material is required to be in the double-tempered condition prior to welding. Weldments in S41000 or CA15 must be PWHT at 1,150°F (620°C) minimum to produce a maximum weldment hardness of 22 HRC. Weldments in CA6NM must be double-tempered per the same requirements as the base metal to produce a maximum weldment hardness of 23 HRC.

Precipitation-hardenable martensitic stainless steels. MR0103 includes wrought S17400, S15500, and cast CB7Cu-1 and CB7Cu-2 in the general section. These materials are all acceptable in either the double-H1150 or H1150M conditions. The maximum hardness requirements are the same as those specified in the MR0175 documents – 33 HRC maximum for the wrought grades, and 310 HBW (30 HRC) for the castings. S17400 or S15500 pressure-retaining bolting is required to be in the H1150M condition with a maximum hardness limit of 29 HRC. S45000 is allowed with a single-step precipitation-hardening treatment and a maximum hardness limit of 31 HRC.

Austenitic stainless steels. The acceptable austenitic stainless steel alloys are defined by a general composition requirement as shown in Table 2.

Element	Weight percent
C	0.10 max.
Cr	16.0 min.
Ni	8.0 min.
Mn	2.0 max.
Si	2.0 max.
P	0.045 max.
S	0.04 max.

General composition requirements allow use of many grades of stainless steel that are covered

under non-US standards and, as such, were technically unacceptable under MR0175-2002 and previous versions. Austenitic stainless steel materials are required to be in the solution-annealed or solution-annealed and thermally stabilized condition, must be free from cold work intended to enhance mechanical properties and must meet a maximum hardness requirement of 22 HRC. Free-machining alloys containing lead or selenium are not acceptable.

Specific austenitic stainless steel grades. MR0103 contains only one specific grade of austenitic stainless steel that doesn't fit into the standard austenitic stainless steel definition – S20910. This material is allowed in the solution-annealed, hot-rolled or cold-worked condition at 35 HRC maximum hardness. All of these conditions are listed in the general section, indicating that all are acceptable for general use.

Highly alloyed austenitic (superaustenitic) stainless steels. The highly alloyed austenitic stainless steels (commonly called superaustenitic stainless steels) are defined in MR0103 and MR0175-2003 as follows:

$$\%Ni + (2 \times \%Mo) >30 \text{ and } Mo >2\%$$

or

$$\text{Pitting resistance equivalent number (PREN)} >40\%$$

where *PREN* is determined as:

$$PREN = \%Cr + 3.3 \times (\%Mo + 0.5 \times \%W) + 16 \times \%N$$

These materials are acceptable per MR0103 in the solution-annealed or solution-annealed and cold-worked conditions with a hardness requirement of 35 HRC maximum.

Duplex stainless steels. MR0103 allows wrought and cast duplex stainless steels in the solution-annealed and liquid-quenched condition to 28 HRC maximum. The material must have a ferrite content of 35 – 65%, and heat treatments to increase strength or hardness are not allowed.

Welding duplex stainless steel. To ensure that production welds in duplex stainless steels possess the correct microstructure and hardness, MR0103 requires that the PQR and resulting WPS include the following:

- The PQR must include a Vickers hardness traverse demonstrating an average value of 310 HV maximum with no individual reading exceeding 320 HV.
- The PQR must include examination of the weld deposit and HAZ conducted in accordance with ASTM E562, demonstrating a ferrite content of 35 to 65 vol%.
- The PQR must indicate the heat input used during creating the PQR specimen. The WPS must restrict the heat input to the same value $\pm 10\%$.
- The PQR must list the PQR specimen thickness, and the WPS must restrict welding in production to components with wall thicknesses that do not deviate by more than 20% from that of the PQR specimen thickness.

Nickel alloys. Most of the acceptable solid-solution nickel alloys are covered by two compositional definitions:

$$9.0\% \text{ Cr minimum, } 29.5\% \text{ Ni} + \text{Co minimum, and } 2.5\% \text{ Mo minimum}$$

or

14.5% Cr minimum, 52% Ni + Co minimum, and 12% Mo minimum.

MR0103 also includes N06600 and N08800 with a maximum hardness requirement of 35 HRC. The wrought nickel-copper alloys N04400 and N04405, and ASTM A494 cast grades M35-1, M35-2 and M30C are included with a maximum hardness requirement of 35 HRC.

MR0103 allows use of a number of cold-worked nickel-chromium-molybdenum alloys for general use. These alloys are listed specifically by UNS number as: N06002 (35 HRC max.), N06022 (40 HRC max.), N06625 (35 HRC max.), N06686 (40 HRC max.), N06985 (39 HRC max), N08825 (35 HRC max.) and N10276 (35 HRC max.).

Precipitation-hardenable nickel alloys. MR0103 includes all of the precipitation-hardenable nickel alloys that are listed in MR0175-2003 with the same material condition and maximum hardness requirements. In addition, MR0103 added N05500 and N07750, both of which were acceptable according to MR0175-2002 and previous revisions, but were intentionally omitted from MR0175-2003. The conditions and hardness limits for N05500 and N07750 are the same as those listed in MR0175-2002.

Other Alloys. Requirements for cobalt-nickel-chromium-molybdenum alloys, cobalt-nickel-chromium-tungsten alloys and titanium alloys are identical to those in MR0175-2002 and MR0175-2003 with one exception. Laboratory test data for solution-annealed R31233 material indicate it has SSC resistance at hardness levels up to and including 33 HRC, so its hardness limit in MR0103 was set at 33 HRC maximum. The hardness limit for R31233 in all versions of MR0175 is 22 HRC maximum.

MR0103 does not address use of copper alloys or tantalum. Aluminum is only addressed for use in pistons and gaskets in Section 9 on Compressors and Pumps.

Fabrication. The fabrication section covers overlays; welding; cladding on carbon, alloy and martensitic stainless steels; identification stamping; threading and cold-deformation processes. With the exception of the cladding coverage on carbon, alloy and martensitic stainless steels, which is unique to the MR0103 document, these sections are essentially identical to, or very similar to, the corresponding sections in MR0175-2003. In MR0103, some of the information regarding welding and weld overlays in specific alloy groups has been incorporated into general sections covering those alloy groups.

The cladding section was included because many refineries use cladding to prevent corrosion and SSC in less-resistant base materials. To meet MR0103, cladding materials must be selected from sections 2 or 3 of MR0103, and must be applied by hot rolling, explosion bonding or weld overlaying. Some of the factors that influence clad component SSC resistance are listed for consideration by the end user. Because evaluating all of the relevant factors is outside the scope of MR0103, the end user is responsible for specifying whether the base metal must meet the requirements of MR0103.

Bolting. Bolting requirements in MR0103 are only slightly modified from those listed in MR0175-2002 and MR0175-2003. Two differences are the reference to special requirements for S17400 and S15500 when used for pressure bolting, and a warning statement indicating that zinc and cadmium coatings should not be used in sour environments because they enhance hydrogen generation on the surface, which can contribute to hydrogen cracking. The definitions for "exposed" and "nonexposed" bolting are the same as those in MR0175.

Plating, coatings, and diffusion processes. The requirements listed in this section are identical to those in the MR0175 documents. In essence, these types of coatings are acceptable provided they are not used in an attempt to protect an otherwise unacceptable base metal.

Special components. This section covers special requirements for certain types of components that often cannot be made from materials listed in the general materials sections of the document, such as bearings, springs, instrumentation and control devices, seal rings and

gaskets, snap rings and special process parts. The requirements listed in this section are identical to those in the corresponding sections of MR0175-2002 and MR0175-2003.

Valves. The valves section simply states that new and reconditioned valves, including internal components, must be manufactured from materials meeting the requirements of section 2 or 3.

Compressors and pumps. In general, compressors and pumps must be manufactured from materials meeting the requirements of section 2 or 3. However, this section provides a few alternative materials for cylinders, liners, pistons, valves, gaskets and impellers.

Several end users and engineering contractors are already specifying equipment per MR0103. Eventually, a broad range of users and authors of equipment standards is expected to adopt the new MR0103 standard for downstream applications, in many cases replacing the current application of MR0175. The environmental guidelines and material requirements of MR0103, together with NACE RP0472 for weld hardness control of P-No. 1 carbon steels, should be broadly applied to piping, valves, process contacted bolting, pumps and compressors used in the sour service areas of the refinery process units, as indicated in Table 3, to prevent SSC. **HP**

Table 3. Typical refinery equipment susceptible to sulfide stress cracking

(Note: this list is not all-inclusive)

Crude units – atmospheric and vacuum	Atmospheric tower overhead system	Coolers, accumulators
	Vacuum tower overhead system	Coolers, accumulators
	Light ends recovery section	Debutanizers, waste gas scrubbers, sour water collection system
Catalytic cracking units	Main fractionator overhead system	Overhead line, coolers/condensers, accumulators, coalescers, absorbers
	Wet gas system	Compressor suction drum, accumulators, coolers
	Light ends recovery section	Deethanizers, debutanizers, accumulators
Hydroprocessing units	Feed system	Feed surge drums
	Reactor effluent section	High/low pressure separators, trim coolers
	Fractionation section	Stripper towers, reflux drums
	Gas treating section	Amine absorbers, off-gas absorber, flash tower
	Recycle gas systems	Knock-out pots, condensers
Coker units	Coker fractionator overhead system, Coker light ends recovery section	Similar to FCCU
Other	Sour water recovery units	Sour water stripper column overhead system

Amine regenerator systems	Amine regenerator tower, accumulator drum, quench tower
Gas recovery plants	Similar to light ends recovery above
Sulfur recovery units	Acid gas knock-out drums, condensers, blow-down drums

LITERATURE CITED

¹ NACE Standard MR0103-2003, "Materials Resistant to Sulfide Stress Cracking in Corrosive Petroleum Refining Environments," Houston, Texas: NACE.

² NACE Standard MR0175-2003, "Metals for Sulfide Stress Cracking and Stress Corrosion Cracking Resistance in Sour Oilfield Environments," Houston, Texas: NACE.

³ NACE Standard RP0296 (latest revision), "Guidelines for Detection, Repair, and Mitigation of Cracking of Existing Petroleum Refinery Pressure Vessels in Wet H₂S Environments," Houston, Texas: NACE.

⁴ NACE Publication 8X194 (latest revision), "Materials and Fabrication Practices for New Pressure Vessels Used in Wet H₂S Refinery Service," Houston, Texas: NACE.

⁵ NACE Publication 8X294 (latest revision), "Review of Published Literature on Wet H₂S Cracking of Steels Through 1989," Houston, Texas: NACE.

⁶ API Publication 581 (latest revision), "Base Resource Document – Risk-based Inspection," Washington, DC: American Petroleum Institute.

⁷ ASME Boiler and Pressure Vessel Code, Section IX, Division I (latest revision), "Welding and Brazing Qualifications," New York, New York: ASME.

⁸ NACE Standard RP0472 (latest revision), "Methods and Controls to Prevent In-Service Environmental Cracking of Carbon Steel Weldments in Corrosive Petroleum Refining Environments," Houston, Texas: NACE.

⁹ ANSI/NB-23, "National Board Inspection Code," Columbus, Ohio: The National Board of Boiler and Pressure Vessel Inspectors.



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