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AN OVERVIEW OF NACE INTERNATIONAL STANDARD MR0103 AND COMPARISON WITH MR0175

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ABSTRACT

NACE MR0103 "Materials Resistant to Sulfide Stress Cracking in Corrosive Petroleum Refining Environments"[1] was developed by Task Group 231 to provide a standard set of requirements for materials used in sour petroleum refinery equipment. In the past, NACE MR0175[2], "Sulfide Stress Cracking Resistant Metallic Materials for Oilfield Equipment", was frequently referenced for this equipment, even though refinery applications were outside the scope of MR0175. The process used to develop MR0103 is described, followed by a review of the requirements in the standard accompanied by highlights of the differences between MR0103 and the previous and current versions of MR0175.

INTRODUCTION AND DOCUMENT HISTORY

In 1975, NACE issued standard MR0175, "Sulfide Stress Cracking Resistant Metallic Materials for Oilfield Equipment", to cover requirements for materials resistant to sulfide stress cracking (SSC) in sour oilfield environments. Although the scope of MR0175 includes only oilfield equipment and associated facilities (including gas production and treatment), the lack of similar standards for other industries has compelled many users in those industries to reference MR0175 for materials destined for "sour" applications. Although the process conditions that constitute the non-oilfield "sour" environments are often quite different from those defined in MR0175, the material and material condition requirements have proven to be fundamentally on target.

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In the late 1990's, the NACE T-1F-1 task group, now called Task Group (TG) 081, began working on a complete rewrite of MR0175 that included a number of fundamental changes. One of the most significant proposed changes was the expansion of the scope of the document to include chloride stress corrosion cracking (SCC), based upon the fact that most oil and gas production streams contain chlorides in sufficient levels to cause SCC in susceptible alloys. As such, the proposed rewrite included maximum temperature limits for all materials that are susceptible to chloride SCC. For example, the rewrite proposed that the temperature limit for S31600 (type 316 stainless steel) be set at 60°C (140°F) maximum. The proposed changes would mean that MR0175 would be less suitable for use in many applications, including those in petroleum refineries, where chloride ion concentrations tend to be low enough that chloride SCC isn't a common concern.

Initial discussion regarding the proposed changes to MR0175 and the potential development of a refinery-specific standard covering materials for sour environments occurred during the 1997 Fall Committee Week T-8 Information Exchange session. Further discussions, including review of drafts of proposed document sections, were held at subsequent T-8 Information Exchange sessions and at several Task Group (TG)T-8-25 ("Environmental Cracking") meetings. At Corrosion/2000, it was decided that a T-8-25 Work Group (T-8-25a) would be formed to develop a sulfide stress cracking document. This Work Group was eventually formed in June 2000 as TG (Task Group) 231 under the current NACE technical committee structure. TG 231 is administered by STG (Specific Technology Group) 34 "Petroleum Refining and Gas Processing" and sponsored by STG 60 "Corrosion Mechanisms".

The task group's writing approach was to borrow pertinent concepts and requirements from the current and proposed versions of MR0175, and modify them as needed to create a new standard that would meet the needs of the oil refining industry. For example, the resulting document utilized the alloy grouping philosophy that is used in what is now MR0175-2003[3], but did not implement environmental limits such as H2S partial pressures, temperature limits, pH restrictions, etc. Materials and material condition requirements are based upon a mix of MR0175-2002 and MR0175-2003 requirements and refinery-specific experience. Because of this approach, there are paragraphs in MR0103 that are identical to corresponding paragraphs in one or both versions of MR0175, whereas in other instances, the requirements in MR0103 have been modified to better suit the needs of the oil refining industry. The final result is a document that differs from previous and current versions of MR0175 in the following ways:

- 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 the refinery standard that are not listed in previous and/or current versions of MR0175.
- Materials and/or material conditions are included in previous and/or current versions of MR0175 that are not listed in the refinery standard.
- Because welding is prevalent in refinery piping and equipment, extra emphasis is placed upon welding controls in several material groups, most notably the carbon steels.

The document was developed using the approved NACE work process. Various sections were drafted, reviewed at Corrosion and Fall Committee Week meetings, and then finalized based upon the feedback that was received. The "final" draft was sent out for formal letter ballot in mid-July 2002. This initial ballot resulted in 4 negative votes and 17 affirmative votes with comments. The document was modified to address the negative votes and other comments, and was sent out for reballot in January 2003. The reballot passed with a 97% affirmative vote after negative vote resolution. The MR0103 standard "Materials Resistant to Sulfide Stress Cracking in Corrosive Petroleum Refining Environments" was published in mid-April 2003.

Following is an overview of the document, including discussion of pertinent differences among MR0175-2002, MR0175-2003, and MR0103.

APPLICABILITY OF MR0175 AND MR0103

Both MR0175 and MR0103 include sections that describe the applicability of each of the Standards. Within each of these sections there are sub-sections that describe the material and environmental factors that affect susceptibility of materials to SSC and also provide guidelines to the user on how the Standard should be applied. It is extremely important to note that in both MR0175 and MR0103 the user is responsible for determining and judging 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. This difference between the upstream (oil and gas production) and downstream (refining and gas processing) environments was one of the principal reasons why NACE STG 34/TG 231 decided to write the MR0103 Standard. MR0103 is more focused on a broader range of sour environments conditions experienced in downstream process units.

The MR0175 definition of sour service environments in upstream processes is very well known and understood, having remained essentially unchanged for almost 30 years. In the 2003 version of MR1075 the environmental conditions likely to cause SSC are described in Paragraphs 1.4.1 and .4.2 with sample calculations in Appendix A. Simply summarized, these conditions consist of a partial pressure of H2S in the wet gas phase of a gas, gas condensate or crude oil equal to or exceeding 0.0003MPa abs (0.05 psia). For gas systems there is a low-pressure cut-off (i.e., total system pressure below which SSC is not expected to occur) of 0.45 MPa abs (65 psia) and for multiphase phase systems the low-pressure cut-off is 1.83 MPa abs (265 psia), (with other conditions applying).

The MR0175 definition of sour service has also been widely and successfully applied by users in many downstream facilities either directly in company specifications and practices or indirectly via the application of API equipment specifications such as API RP 610[4], 617[5] and 618[6]. However, for downstream applications many users, engineering contractors and suppliers have over the years developed their own practices on how and when MR0175 material requirements should be applied. These practices have ranged between:

- No application at all, irrespective of H_2S level since some downstream users have considered MR0175 strictly applicable to upstream applications,
- Application of MR0175 material requirements to any process containing H_2S, including trace levels in services with no free water present.

In the new MR0103 Standard an attempt has been made to develop consensus guidelines on what constitutes sour service in downstream units based on:

- User's plant experience and practices;
- Existing NACE and industry recommended practices and reports (i.e. NACE RP0296[7], 8X194[8], 8X294[9], API Publication 581[10]);
- 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, H_2S and HCN.

A significant difference between upstream and downstream sour environments is that in many refinery sour water environments dissolved ammonia is present which 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, embodied in MR0103, has resulted in the following guidelines *(with additional explanation in parenthesis)* on what constitutes a sour enough service in downstream units to justify the application of the Standard's material requirements (Note: the presence of a free water phase is a prerequisite for aqueous corrosion and SSC):

- >50 ppmw dissolved H_2S in the free water (recognition that significant levels of dissolved H_2S can result in SSC even in low pressure systems), or
- A free water pH < 4 and some dissolved H_2S present (recognition that in low pH environments significant charging of materials with atomic hydrogen can take place irrespective of H_2S level), or
- A free water pH > 7.6 and > 20 ppmw hydrogen cyanide ion (HCN) and some H_2S dissolved in the free water (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 H_2S in a process with a gas phase (based on historical MR0175 definition of sour service, without low-pressure cut-offs).

Another key difference between the MR0175 and MR0103 Standards is the way the user is expected to use the guidelines on environmental conditions. In MR0175 the user is obligated apply the material requirements of the Standard when it is judged that the environmental conditions prescribed in the Standard have been exceeded; however, there is relatively little judgment required since the environmental conditions for SSC are tightly defined with sample calculations provided in Appendix A. In MR0103 the user is also obligated to determine whether the equipment falls within the scope of the standard; however, more judgment of the environmental conditions is permitted, and the user may supplement the environmental guidelines in the Standard with actual plant experience and risk based analysis to make a determination on applicability (API Publication 581 provides a methodology for such an analysis). However, when making this judgment the MR0103 user is expected to consider all plant operating scenarios including operational upsets, start-up/shutdown conditions etc.

MATERIALS OF CONSTRUCTION

Carbon Steels

Carbon steels are the workhorse materials in refineries, and as such they have received a great deal of attention in previous NACE activities. 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[11] (grades such as ASTM A105[12] forgings, ASTM A216[13] WCC and A352[14] LCC castings, ASTM A516[15] Grade 70 plate, ASTM A106 Grade B pipe) for piping and vessels. Unlike MR0175-2002 and MR0175-2003, MR0103 imposes no base metal hardness requirements on these materials due to the fact that these grades have maximum tensile strength requirements that effectively limit their bulk hardness. Other carbon steels are required to meet a 22 HRC maximum requirement.

MR0103 shares the following requirements with MR0175-2002 and MR0175-2003:

- 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 of Carbon Steels

Welding introduces the potential for creation of hard regions in carbon steels. As such, controls must be imposed to ensure that weldments will be soft enough to resist sulfide stress cracking in service.

MR0103 requires that welds in P-No. 1 carbon steel materials be performed per the methods outlined in NACE Standard RP0472 "Methods and Controls to Prevent In-Service Environmental Cracking of Carbon Steel Weldments in Corrosive Petroleum Refining Environments"[16]. RP0472 is a recommended practice document that was issued by the T-8 Unit Committee on Refinery Corrosion in 1972. Note that this document actually pre-dates MR0175, although the scope and requirements have changed somewhat since its initial release. RP0472 requires that the weld deposit meet a hardness limit of 200 HBW maximum. It allows control of heat-affected zone (HAZ) hardness by several different methods. Those methods include:

Post-weld heat treatment (PWHT): PWHT serves two purposes. As a tempering process, it reduces the hardness of the weld deposit and the heat affected zone (HAZ). As a stress relieving process, it reduces residual stresses in the weldment through stress relaxation. Both of these effects tend to reduce the probability of failure due to SSC. Although some of the ASME codes allow the option of using lower temperatures for longer times, this option is not recommended. Using lower temperatures for longer times may provide reduction in residual stresses, the primary concern of the ASME codes, but is less likely to reduce HAZ hardness, which is the primary factor in reducing susceptibility to SSC.

Base metal chemistry controls: This technique involves controlling of carbon content and/or carbon equivalent and levels of micro-alloying elements in base metals to such low levels that low hardness is virtually guaranteed in the weld deposit and HAZ regardless of welding process parameters. The carbon equivalent of a particular heat of material is calculated from the heat chemistry using the following equation:

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

NACE Committee Report 8X194 states that a maximum carbon equivalent of 0.43 is commonly specified for base materials when this technique is employed. Deliberate additions of micro-alloying elements (greater than 0.01% each of Cb, V, and Ti, or greater than 0.0005% B) are usually prohibited to ensure that hardenability will remain low.

HAZ hardness testing during welding procedure qualification: When this method is used, a procedure qualification record (PQR) specimen is created using either actual production material or a coupon of representative material with an actual carbon equivalent corresponding to the maximum carbon equivalent value that is to be applied to production base material. Welding variables (such as filler metal, preheat, current, voltage, travel speed, interpass temperature, etc.) are controlled and documented during the creation of the PQR specimen. The PQR tests include a hardness traverse performed using the 5-kgf or 10-kgf Vickers scale or the Rockwell 15N scale to demonstrate that the weldment hardness does not exceed 248 HV or 70.5 HR15N in the weld metal, HAZ and base metal.

The resulting welding procedure specification (WPS) is written to contain restrictions to ensure that the PQR specimen is actually representative of production weldments. Those restrictions include the following:

- The procedure may only be used to weld a base metal of the same specification, grade, and class as that of the PQR specimen. In other words, a procedure qualified on ASTM A516 Grade 70 plate material could not be used to weld ASTM A516 Grade 60 plate material, ASTM A105 forgings, or ASTM A216 Grade WCC castings, even though all are within the same ASME Section IX P-No. 1 category.
- The maximum CE and micro-alloying element contents of production material must be controlled to values less than or equal to those of the PQR specimen.
- The heat input used during production welding must not deviate from the heat input used during creation of the PQR specimen by more than 10% lower or 25% higher. For the shielded metal arc welding (SMAW) process, the maximum bead size and the minimum length of weld bead per unit length of electrode used in creation of the PQR specimen can be imposed as an alternate requirement in the WPS.
- Preheat and interpass temperatures must be at least as high as those utilized in production of the PQR specimen.
- If preheat was not utilized for the PQR specimen, the maximum base metal thickness of production weldments must not be allowed to exceed the thickness of the PQR specimen.

Other restrictions apply to fillet welds, submerged-arc welding (SAW), gas metal arc welding (GMAW), flux-cored arc welding (FCAW) processes, welding procedures involving bead-tempering techniques and other techniques that are sensitive to weld-bead sequence, and materials containing intentional additions of microalloying elements such as Nb (Cb), V, Ti, and B.

This method may not be suitable for certain applications such as repair welding of castings. It is generally utilized for establishment of an acceptable welding procedure for a particular heat of material for a large job. An example would be the fabrication of a large vessel from a single heat of plate material which doesn't have chemistry restrictions that are adequate to guarantee low weldment hardness.

The wording regarding welding of carbon steels in MR0175-2002 and previous versions has always been somewhat subject to misinterpretation. Paragraph 5.3.1.2 from MR0175-2002 reads as follows:

> "5.3.1.2 Welding procedure qualifications on carbon steels that use controls other than thermal stress relieving to control the hardness of the weldment shall also include a hardness traverse across the weld, HAZ, and base metal to ensure that the procedure is capable of producing a hardness of 22 HRC maximum in the condition in which it is used."

This paragraph has often been misinterpreted to mean that if a welding procedure qualification performed on a P-No. 1 carbon steel included a hardness traverse with results meeting the 22 HRC maximum requirement, that the resulting procedure was acceptable for producing welds meeting MR0175 requirements in all P-No. 1 materials. Unfortunately, this is not the case, since the hardenability of P-No. 1 carbon steels varies quite widely depending upon the actual carbon and manganese contents as well as the levels of residual elements such as chromium, nickel, molybdenum, copper, and vanadium. The phrase “controls other than thermal stress relieving” in paragraph 5.3.1.2 is a vague reference to the need for control of chemistry and/or welding parameters that are above and beyond those required by the parent material specification and/or the ASME Section IX welding requirements. These extra controls ensure that as-welded hardness values will be acceptable.

The wording in the 2003 version of MR0175 has been modified to be somewhat more specific:

“5.3.1.2 Welding procedures for carbon steels and low-alloy steels may control welding variables to achieve a hardness of 22 HRC maximum in the weldment. The controls generally involve restricted base and filler metal chemical composition and welding parameters. The procedure qualification shall verify that the 22 HRC maximum hardness requirement is achieved in the weld deposit, HAZ, and base metal in the as-welded condition. The resulting welding procedure specification shall document the required controls to assure that the 22 HRC maximum hardness requirement will be achieved in production weldments.

5.3.1.3 Carbon steel and low-alloy steel weldments produced without restrictions on base and filler metal chemical compositions and welding parameters in accordance with Paragraph 5.3.1.2 shall be post-weld heat treated at a minimum temperature of 621°C (1,150°F) to produce a hardness of 22 HRC maximum.”

Although the intent has not changed, the paragraphs in MR0175-2003 now state the intended requirements much less ambiguously than in previous versions of MR0175.

Alloy Steels

MR0103 defines alloy steels as steels 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.

MR0175 has always limited the nickel content in carbon and alloy steel base metals and weld filler materials to 1% maximum. The main intent of the restriction was to limit the use of nickel in high-strength casing and tubular materials and in high-strength wellhead equipment. There has been a great deal of discussion over the years regarding the validity of the "nickel effect" concept - i.e., the theory that a nickel content above 1% reduces the resistance of a steel to SSC. Some tests have indicated that such steels are susceptible to SSC at bulk hardness levels below 22 HRC. Others have suggested that the reduced SSC resistance in these examples is due to the presence of a mixed microstructure containing untempered martensite caused by tempering above the lower critical temperature, which is relatively low in nickel-alloy steels[17]. Attempts to add alloy steels with more than 1% nickel to the general section by letter ballot have been unsuccessful.

The refinery industry has no need for the high-strength nickel-containing alloy steels. On the other hand, there is a need in some locations for materials with good impact toughness at low temperatures. Discussions at TG 231 meetings indicate that the 3½% nickel steels such as ASTM A333[18] Grade 3, A350[19] LF3, and A352 LC3 have been used for this purpose, and have demonstrated reliable performence in sour refinery environments for many years. As such, the nickel restriction was not included in MR0103.

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 (except 9Cr-1Mo-V grades)	235
5B 9Cr-1Mo-V grades (F91, P91, T91, WP91, Grade 91, C12A)	248
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 required in the various MR0175 revisions.

In MR0175 (2002 and 2003), low alloy steels are defined as a “steels with a total alloying element content of less than about 5%, but more than specified for carbon steel”. Low alloy steels are also restricted to a maximum nickel content of 1%. Note that according to these definitions, the 5 Cr-½ Mo steels are borderline, and the 9 Cr-1 Mo steels are unacceptable, as are the impact-tested nickel steels commonly used for low temperature service (such as LC3 and LF3).

Welding of Alloy Steels

MR0103 includes very specific information about welding of alloy steels. It allows welding of P-Number 3 and 4 materials without PWHT in cases where the practice is allowed per ANSI/NB-23[20]. 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.

MR0175-2002 required low-alloy steels to be PWHT at 1150°F (620°C) minimum to produce a maximum hardness of 22 HRC.

MR0175-2003 includes the same requirements for low-alloy steel weldments as for carbon steel weldments (requirements for both are covered in the same paragraph). Welding without PWHT is allowed. However, there are only certain circumstances where the construction codes will allow welding of particular alloy steels without PWHT, so the construction code restrictions would also need to be considered prior to utilizing this allowance.

Martensitic Stainless Steels

The requirements for martensitic stainless steel base metals are essentially the same in the two versions of MR0175 and in MR0103. 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, 22HRC, and 23 HRC, respectively.

Welding of Martensitic Stainless Steels

Descriptions of welding requirements for martensitic stainless steels differ somewhat among MR0175-2002, MR0175-2003, and MR0103, although it appears that the intent is the same in all of the documents. In all cases 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 1150°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.

MR0175-2002 included wrought S17400 in the general section in both the double-H1150 and H1150M conditions, with a hardness limit of 33 HRC maximum. Wrought S45000 was also listed in this section, with a single-step precipitation-hardening treatment and a maximum hardness limit of 31 HRC. The cast version of S17400, CB7Cu-1, was listed in section 9 in the double-H1150 condition with a maximum hardness limit of 310 HBW (30 HRC) for use only in non-pressure-containing, internal valve, and pressure regulator components.

In MR0175-2003, there are no precipitation-hardenable martensitic stainless steels listed in the general section. Wrought S17400, S15500, and S45000, as well as cast CB7Cu-1 and CB7Cu-2 are listed only in section 9 for certain uses in wellheads, christmas trees, valves, chokes, and level controllers. Heat treatment requirements and hardness limits are the same as those in MR0175-2002.

Austenitic Stainless Steels

The material requirements for the austenitic stainless steels in MR0103 are nearly identical to those in MR0175-2003. The acceptable alloys are defined by a general composition requirement as shown in Table 2:

Table 2: Composition Requirements for Austenitic Stainless Steels

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.

The use of general composition requirements allows the use of many grades of stainless steel which 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.

The compositional requirements in MR0103 vary slightly from those in MR0175-2003. MR0103 allows a maximum carbon content of 0.10%, which allows the use of the "H-grade" stainless steels. MR0175-2003 has a maximum carbon content requirement of 0.08% except for S30900 and S31000, which may contain up to 0.10% carbon. In addition, MR0175-2003 is somewhat ambiguous regarding sulfur content. In the compositional definition, sulfur is allowed up to 0.04%, but the statement "Free-machining austenitic stainless steel products (containing alloying elements such as lead, selenium, or sulfur to improve machinability) are not acceptable" gives the impression that no sulfur is allowed.

MR0175-2002 and previous versions listed specific grades of austenitic stainless steels, all of which were grades covered by UNS[21] numbers. This essentially precluded the use of materials covered by non-US standards even though they were equivalent or very similar to the materials listed in the standard.

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 of these conditions are acceptable for general use.

MR0175-2002 and MR0175-2003 list solution-annealed and hot-rolled material in the general section, but only allow the cold-worked material to be used for valve shafts, stems, and pins.

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 x %Mo) >30 and Mo >2%
or
Pitting Resistance Equivalent Number (PREN) >40%

where PREN is determined as follows:

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

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.

MR0175-2003 lists these materials in the general section in the solution-annealed condition only. Cold-worked material is allowed only for downhole tubular components, where the hardness requirement is 35 HRC maximum.

MR0175-2002 and previous revisions only listed specific alloys in this category. The maximum hardness limits on the various alloys and forms ranged from 94 HRB to 38 HRC.

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.

The requirements listed in MR0175-2003 are similar, except there are no hardness requirements listed for solution-annealed and liquid-quenched materials. A hardness requirement of 25 HRC maximum is imposed on hot isostatic pressure-produced S31803. Solution-annealed, quenched, and cold-worked duplex stainless steels are allowed for down-hole tubular components to 36 HRC maximum.

MR0175-2002 listed only specific grades of duplex stainless steels, some of which were only acceptable in the solution annealed condition, and others which were allowed in the cold-worked condition. Maximum hardness requirements ranged from 17 HRC to 36 HRC.

Welding of Duplex Stainless Steel

In order 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 hardness traverse conducted using 10 kgf Vickers encompassing the base metal, HAZ, and filler metal at the top and bottom of the weldment. The hardness may not exceed an average value of 310 HV 10, and no individual reading may exceed 320 HV 10.
- The PQR must include an analysis of the ferrite content of the weld deposit and HAZ conducted in accordance with ASTM E562. The measured ferrite content must be 35 to 65 vol%.
- The PQR must indicate the heat input used during creation of the PQR specimen. The WPS must restrict the heat input to the same value ±10%.
- The PQR must list the thickness of the PQR specimen, and the WPS must restrict welding in production to components with wall thicknesses which do not deviate by more than 20% from that of the PQR specimen thickness.

The only requirement provided for welding of duplex stainless steels in MR0175-2003 is that the PQR must assure that all regions of the weldment contain 30-70% ferrite. MR0175-2002 and previous versions did not address welding of duplex stainless steels.

Nickel Alloys

MR0103 covers the wrought solid-solution nickel alloys in much the same manner as MR0175-2003. Most of the acceptable alloys are covered by two compositional definitions as follows:

9.0% Cr minimum, 29.5% Ni + Co minimum, and 2.5% Mo minimum.	or	14.5% Cr minimum, 52% Ni + Co minimum, and 12% Mo minimum.

These alloys are acceptable in the solution-annealed condition without any maximum hardness requirement. This set of compositional ranges covers many of the materials which were included in MR0175-2002 and previous revisions. However, the molybdenum requirements precluded N06600 and N08800, which are sometimes utilized in refineries and have demonstrated acceptable sulfide stress cracking resistance. As such, MR0103 also includes N06600 and N08800 with a maximum hardness requirement of 35 HRC, which matches the requirements for these materials in MR0175-2002. In addition, the wrought nickel-copper alloys N04400 and N04405, and ASTM A494[22] cast grades M35-1, M35-2, and M30C are included with a maximum hardness requirement of 35 HRC.

MR0103 allows the use of a number of cold-worked nickel-chromium-molybdenum alloys for general use. These alloys are listed specifically by UNS number as follows: 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.).

MR0175-2002 also included cold-worked nickel-chromium-molybdenum alloys in the general use section. MR0175-2003 only allows the use of the cold-worked grades for down-hole tubulars.

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

The 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 indicates 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 the 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 steels, alloy steels, and martensitic stainless steels; identification stamping; threading; and cold-deformation processes. With the exception of the coverage of cladding on carbon steels, alloy steels, 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. In order 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 the SSC resistance of clad components are listed for consideration by the end user. Because the evaluation of 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

The bolting requirements in MR0103 are only slightly modified from those listed in MR0175-2002 and MR0175-2003. There are a few editorial differences that provide clarification, but don't change the technical content. 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 the generation of hydrogen on the surface, which can contribute to hydrogen cracking.

Bolting was the subject of some good discussions during the generation and balloting of the document, especially regarding the subject of bolting that is under insulation. A number of refineries do not use special bolting grades (such as B7M) under insulation, and have not experienced problems even when gasket leaks have occurred. It is assumed that the lack of problems in these cases is due to the fact that insulation will not maintain enough pressure surrounding the bolting to result in the H_2S partial pressure reaching a level that will promote SSC. Consensus was never reached on this topic during discussions, and the paragraphs were balloted and passed with wording that is essentially identical to that in the MR0175 documents.

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 utilized in an attempt to protect an otherwise unacceptable base metal.

Special Components

This section covers special requirements for certain types of components which 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. ASTM A278[23] Class 35 or 40 gray cast iron and ASTM A395[24] ductile iron may be used for compressor cylinders, liners, pistons, and valves. Cast aluminum alloy ASTM B26[25] A03550-T7 may be used for pistons. Gaskets may be made from aluminum, soft carbon steel, and soft, low-carbon iron. Impellers may be produced from UNS G43200 and a modified version of UNS G43200 that contains 0.28 to 0.33% carbon provided it is double-tempered at 621°C (1,150°F) minimum to produce a maximum yield strength of 620 MPa (90 ksi).

CONCLUSIONS

From a practical standpoint it is expected that for downstream applications a broad range of users and authors of equipment standards will adopt the new MR0103 standard, in many cases replacing the current application of MR0175. It is expected that use of the environmental guidelines and material requirements of MR0103, together with NACE RP0472 for weld hardness control of P-No. 1 carbon steels, will be broadly applied to piping, valves, process contacted bolting, pumps, and compressors used in the sour service areas of the refinery process units listed in Table 3 in order to prevent SSC.

Table 3: Typical Refinery Equipment Susceptible to Sulfide Stress Cracking
(Note: this list is not all-inclusive)

Crude Unit – 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
Hydro-Processing Units	Feed System	Feed Surge Drums
	Reactor Effluent Section	High Pressure/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	Similar to FCCU
	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

REFERENCES

[1] NACE Standard MR0103-2003, "Materials Resistant to Sulfide Stress Cracking in Corrosive Petroleum Refining Environments" (Houston, TX: NACE).
[2] NACE Standard MR0175-2002, "Sulfide Stress Cracking Resistant Metallic Materials for Oilfield Equipment" (Houston, TX: NACE).
[3] NACE Standard MR0175-2003, "Metals for Sulfide Stress Cracking and Stress Corrosion Cracking Resistance in Sour Oilfield Environments" (Houston, TX: NACE).
[4] API Standard 610, "Centrifugal Pumps for Petroleum, Petrochemical and Natural Gas Industries" (Washington, DC: American Petroleum Institute)
[5] API Standard 617, "Axial and Centrifugal Compressors and Expander-compressors for Petroleum, Chemical and Gas Industry Services" (Washington, DC: American Petroleum Institute)
[6] API Standard 618, "Reciprocating Compressors for Petroleum, Chemical and Gas Industry Services" (Washington, DC: American Petroleum Institute)
[7] NACE Standard RP0296 (latest revision), "Guidelines for Detection, Repair, and Mitigation of Cracking of Existing Petroleum Refinery Pressure Vessels in Wet H2S Environments" (Houston, TX: NACE)
[8] NACE Publication 8X194 (latest revision), "Materials and Fabrication Practices for New Pressure Vessels Used in Wet H2S Refinery Service" (Houston, TX: NACE)
[9] NACE Publication 8X294 (latest revision), "Review of Published Literature on Wet H2S Cracking of Steels Through 1989" (Houston, TX: NACE)
[10] API Publication 581 (latest revision), "Base Resource Document - Risk-based Inspection" (Washington, DC: American Petroleum Institute)
[11] ASME Boiler and Pressure Vessel Code, Section IX, Division I (latest revision), "Welding and Brazing Qualifications" (New York, NY: ASME)
[12] ASTM A105/A105M (latest revision), "Standard Specification for Carbon Steel Forgings for Piping Applications" (West Conshohocken, PA: ASTM).
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[15] ASTM A516/A516M (latest revision) "Standard Specification for Pressure Vessel Plates, Carbon Steel, for Moderate- and Lower-Temperature Service" (West Conshohocken, PA: ASTM).
[16] NACE Standard RP0472 (latest revision), "Methods and Controls to Prevent In-Service Environmental Cracking of Carbon Steel Weldments in Corrosive Petroleum Refining Environments" (Houston, TX: NACE)
[17] R. N. Tuttle, "Selection of materials designed for use in a sour gas environment", in H_2S Corrosion in Oil and Gas Production ~ A Compilation of Classic Papers, eds. R. N. Tuttle, R. D. Kane, (Houston, TX: NACE, 1981), p. 161.
[18] ASTM A333/A333M (latest revision), "Standard Specification for Seamless and Welded Steel Pipe for Low-Temperature Service" (West Conshohocken, PA: ASTM).
[19] ASTM A350/A350M (latest revision), "Standard Specification for Carbon and Low-Alloy Steel Forgings, Requiring Notch Toughness Testing for Piping Components" (West Conshohocken, PA: ASTM).
[20] ANSI/NB-23, "National Board Inspection Code" (Columbus, Ohio: The National Board of Boiler and Pressure Vessel Inspectors).
[21] Metals and Alloys in the Unified Numbering System (latest revision), a joint publication of ASTM International (ASTM) and the Society of Automotive Engineers Inc. (SAE), 400 Commonwealth Drive, Warrendale, PA 15096
[22] ASTM A494/A494M (latest revision), "Standard Specifications for Castings, Nickel and Nickel Alloy" (West Conshohocken, PA: ASTM).
[23] ASTM A278/A278M (latest revision), "Standard Specification for Gray Iron Castings for Pressure-Containing Parts for Temperatures Up to 650°F" (West Conshohocken, PA: ASTM).
[24] ASTM A395/A395M (latest revision), "Standard Specification for Ferritic Ductile Iron Pressure-Retaining Castings for Use at Elevated Temperatures" (West Conshohocken, PA: ASTM).
[25] ASTM B26/B26M (latest revision), "Standard Specification for Aluminum-Alloy Sand Castings" (West Conshohocken, PA: ASTM).