

NACE MR0175 2015 and the stainless steel industry



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Stainless steel producers and distributors involved in the oil & gas industry are often required to supply materials that meet the requirements of ANSI / NACE MR0175 / ISO 15156 (referred to hereafter as NACE MR0175). This standard outlines the requirements for metallic materials for use in H_2S containing environments in oil and gas production. H_2S gas, which is present in some oil and gas production environments, is deadly in concentrations as low as 100ppm. In addition to being poisonous H_2S is corrosive and can lead to various forms of hydrogen related cracking. This article presents a brief overview of NACE MR0175 covering its origin, requirements for stainless steels and the relevance of this document within the regulatory framework.

By Ivan Gutierrez, Managing Director of Oil & Gas Corrosion

NACE MR0175: what is it & where did it come from?

NACE International is a professional organization for the corrosion control industry. The National Association for Corrosion Engineers (NACE) was founded in 1943 in Houston by 11 founding members and over the years it has become the corrosion authority with over 35,000 members in 130 countries publishing with a large number of standards, books and periodic publications. One of the main documents prepared by NACE is the standard NACE MR0175.

The history of NACE MR0175 starts in the late 1940s and early 1950s when in West Texas the oil and gas industry had the first challenges with gas fields containing H₂S (sour gas). Further failures were reported in Canada. NACE formed a committee to accumulate information and provide a solution. The following years were followed by several symposia and reports leading to 1F166 (sulfide cracking resistant materials for valves for production and pipeline service) was issued; this document originated the materials requirements for valves. 1F166 was the precursor of NACE MR0175, which was first published in March 1975 with the title "Materials for valves for resistance to sulphide stress

cracking in production and pipeline service". The purpose of NACE MR0175 was to share across the industry the lessons learned by operators that had developed technology and knowledge on how to deal with H₂S. The document was promptly adopted by the Railroad Commission of Texas (the State regulatory body) as a requirement for sour gas field operators. In 1975, the scope of the document was solely valves. A second revision was issued in 1978 and subsequently updates were published in the journal "Materials Performance". A review of the scope happened over the years due to factors such as the injection of seawater in North Sea wells leading to reservoir souring and material manufacture considerations such as the use of Thermo-Mechanically Controlled Processed (TMCP) steels that can suffer Hydrogen-Induced Cracking (HIC). At the same time, the European Federation of Corrosion had carried out work in parallel to develop reports 16 and 17 which covered similar issues. In 1995 it was proposed to combine the efforts of both organisations and this led to a new document being issued in 2003. NACE MR0175 and ISO 15156 have been identical documents since then. The document is split in three parts. The first part lists definitions, describes the requirements and recommendations that apply across the standard; the second part addresses carbon and low alloy steels and the third part focuses on corrosion resistant alloys. This third section includes stainless steels as well as nickel alloys, titanium and its alloys and other corrosion resistant alloys. The document is published every 5 years, and in between revisions technical circulars and technical corrigenda are published through the NACE website and the ISO 15156 maintenance panel site. Between 2009 and 2015 there were 7 technical circulars. The latest revision of the document is 2015 and a Technical Circular was issued on April 2016 that supplements the main document. The updating of NACE MR0175 is under the responsibility of its maintenance panel. This is composed of 15 material experts representing different geographical regions and providing a spectrum within the oil and gas industry (i.e. manufacturers, operators etc). The changes to the document can be derived from inquiries by the public,

ballots submitted to include new materials or changes to environmental limits or by collaboration work. Any proposed change to this document is reviewed by NACE TG299 (Oversight of Maintenance Panel) and submitted to ISO TC 67 WG 7. Changes are published in Technical Circulars which become an integral part of NACE MR0175. Any user can submit ballots, queries and interpretations of the document by contacting the maintenance panel through their website www.iso.org/iso15156maintenance. The maintenance panel meets twice a year in a meeting open to the public; the meetings coincide with the NACE Corrosion conference and with the EFC Eurocorr conference.

Stainless steels and NACE MR0175

As previously mentioned, NACE MR0175 is split in 3 main parts and it is part 3 which addresses corrosion resistant alloys. In clause 1 to clause 4 it provides general information such as definitions, the scope of part 3 and equipment exceptions. Clause 5 to clause 7 provide practical information regarding factors affecting cracking resistance of CRAs, qualification of CRAs and purchasing information, i.e. information to be exchanged between the equipment user, the equipment manufacturer and the material manufacturer. Clause 6 indicates that there are two ways to select a CRA for use in sour environments, users can select CRA materials using annex A of the document or by completing the qualification for a specific use. The qualification route involves laboratory testing or documented historical evidence. In this article we review the use of Annex A.

Annex A of NACE MR0175 part 3 groups CRAs in several groups; the stainless steels of interest for this article are:

- Austenitic stainless steel (A.2)
- Highly alloyed austenitic stainless steels (A.3)
- Ferritic stainless steels (A.5)
- Martensitic stainless steels (A.6)
- Duplex stainless steels (A.7)
- Precipitation hardened stainless steels (A.8)

Each section presenting the group of materials above has a series of tables presenting the specific material requirements

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assure business continuity and optimise expenditure by managing the risks associated with materials and corrosion. Ivan has over 20 years' experience in metallurgy, materials and corrosion. He is a member of the National Association of Corrosion Engineers (NACE), a professional member of the Institute of Corrosion (MICorr) and the Society of Petroleum Engineers (SPE). He is recognised as an expert in sour service and is a member of Task Group 299 on the Oversight of Maintenance Panel for NACE MR0175 / ISO 15156. "Materials for use in H₂S-containing environments in oil and gas production"



for different applications, e.g. section A.2 has the following tables:

- Table A.2 — Environmental and materials limits for austenitic stainless steels used for any equipment or components
- Table A.3 — Environmental and materials limits for austenitic stainless steels used as valve stems, pins, and shafts
- Table A.4 — Environmental and materials limits for austenitic stainless steels used in surface applications for control-line tubing, instrument tubing, associated fittings, and screen devices

tubing, hardware (e.g. set screws, etc.), injection tubing, and injection equipment

Each one of the Annex A tables that present the material requirements has the format shown in Table 1.

Austenitic stainless steel (A.2)

The austenitic stainless steels listed in section A.2 include UNS S31603 (commonly referred as 316L). This material is used for many applications in the oil and gas industry. Since the publication of NACE MR0175/ISO 15156 there has been some questioning regarding the use of 316L. The changes in 2003 imposed limits stricter to austenitic stainless steels, this meant that many manufacturers would prefer to refer

Ferritic stainless steels (A.5)

Table A.17 lists the environmental limits of ferritic stainless steels. Some of the UNS numbers are listed in table D-5 of the document.

Martensitic stainless steels (A.6)

Martensitic stainless steels are listed in Tables A.18 to A.23. These include 410, 420 and the super 13Cr steels. Hardness limits and heat treatment conditions are clearly specified for each alloy based on their UNS number. These conditions are based on the information submitted during the ballot of each alloy.

Duplex stainless steels (A.7)

Duplex steels are listed in tables A.24 to A.26; these include 22cr (duplex),

“Founded in 1943 NACE has become the corrosion authority with over 35,000 members in 130 countries”

- Table A.5 — Environmental and materials limits for austenitic stainless steels used as seal rings and gaskets
- Table A.6 — Environmental and materials limits for austenitic stainless steels used in compressors and instrumentation and control devices
- Table A.7 — Environmental and materials limits for austenitic stainless steels used in gas lift service and for special components for subsurface applications such as downhole screens, control-line

to NACE MR0175 2002 for certification purposes rather than the latest revision of the NACE MR0175 / ISO 15156. In 2013 a technical circular reviewed the actual limits for 316L based on published research carried out by TWI and this technical circular is included in the main body of the 2015 document.

Highly alloyed austenitic stainless steels (A.3)

Tables A.8 to A.11 address highly alloyed austenitic stainless steels including 254SMO - also referred to as 6Mo - widely used in the offshore applications.

25Cr (super duplex) and other higher alloyed duplex steels. The alloys are organised based on their PREN (pitting Resistance Equivalent Number). For the sake of clarity, PREN is defined in NACE MR0175 (part 3, clause 6.3) as

$$\text{PREN} = \text{Cr} + 3.3(\text{Mo} + 0.5\text{W}) + 16\text{N}$$

Where:

Cr is the mass fraction of Chromium

Mo is the mass fraction of Molybdenum

W is the mass fraction of Tungsten

N is the mass fraction of Nitrogen

The requirements for duplex alloys include chemistry and heat treatment,

Table 1. Example of Annex A tables presenting material requirements

Material type / individual alloy UNS number	Temperature	Partial pressure H ₂ S	Chloride concentration	pH	Sulfur resistant	Remarks
In this section the materials are listed based on their type, UNS number or other characteristic such as PREN, specific chemistries listed by UNS number are included in Annex D	This section indicates the maximum temperature that the material can be used	This section indicates the maximum partial pressure of H ₂ S, this is calculated as the pressure of the system multiplied by the mol fraction	This section indicates the maximum content of chloride expressed as mg/l	This section indicates the limits of pH, i.e. the PH shall be (larger than or equal to a minimum value)	This section indicates if the material is resistant to elemental sulphur, if it states NDS it means no data has been submitted to determine if the material is acceptable for use in the presence of elemental sulfur	This section is reserved for any remarks indicated in the temperature, partial pressure, chloride, pH or sulfur resistance.

Material requirements:

In this section the tables include material requirements such as hardness limits, processing requirements (e.g. process route, heat treatment) as well as any footnotes in the main body of the table



The purpose of NACE MR0175 has always been to share across the lessons learned by operators that had developed technology and knowledge on how to deal with H_2S .

as well as cautionary notes on the formation of deleterious phases such as sigma phase and precipitates. It is also important to bring to notice another document which is commonly required during duplex steels procurements; DNV RP F112 presents the requirements for duplex steels to be used in subsea applications and under cathodic protection. These requirements are conceived to minimise the risk of hydrogen induced stress corrosion (HISC).

Precipitation hardened stainless steels (A.8)

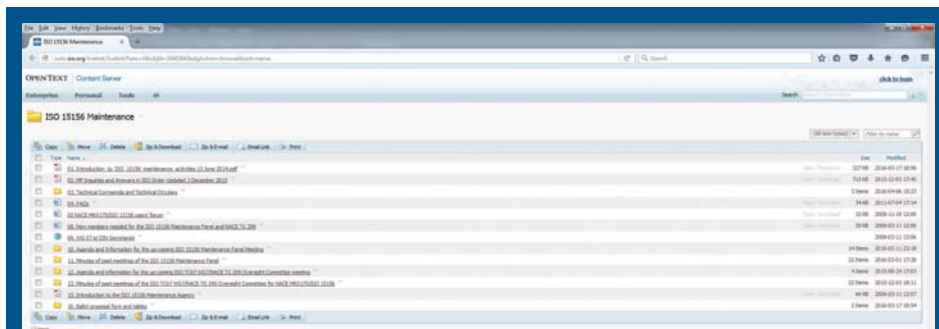
Tables A.26 to A.30 list the environmental limits, the material and processing requirements for precipitation hardness stainless steels, including UNS S17400, commonly referred as 17-4PH. This particular alloy has been associated with some in-service failures and has been under scrutiny over the last few years. The alloy has a satisfactory track record as a valve material and other

applications where the stress levels on the alloy component are not high; a comprehensive review of 17-4 PH in sour applications data was presented during the Corrosion 2014 (Paper No. 3816). The Technical Circular issued in April 2016 includes a remark on 17-4PH regarding the safe use limits on chloride and temperature which have not yet been clearly defined, this means that the user selecting this material needs to carry out further assessments; there is also a foot note that reads “The use of UNS S17400 is restricted to those applications where the sustained stress is no more than 50 % of the specified minimum yield strength (SMYS) or 380 MPa (55 ksi), whichever is less. The use of UNS S17400 is acceptable for wellhead valve trim where the stem is subjected to higher stress levels for very short periods of time during actuation; other or longer stress duration applications are prohibited above 50 % of the specified minimum yield strength (SMYS) or 380 MPa (55 ksi), whichever is less.”

Certification responsibility

Stainless steel manufacturers and distributors are regularly required to supply products ‘certified to NACE MR0175’; occasionally there are differences of interpretation regarding the certification issue, and this was addressed by the NACE MR0175 maintenance panel in the inquiry 2006-13. “QUESTION: Is it the intent of NACE MR0175/ISO 15156-2 that material manufacturers state on the Material Test Certificates that material conforms to the NACE standard even though no operating criteria are known? ANSWER: Certification requirements are outside the scope of the standard and there are no stipulations concerning certification in NACE MR0175/ISO 15156.

The compliance with the NACE/ISO standard of a material for use in H_2S -containing environments in oil and gas can only be assessed for the material in its final product form and this may differ metallurgically from that of the material supplied by the materials



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manufacturer. In addition, compliance with the standard also depends on the cracking mechanisms that have to be considered.

NACE MR0175/ISO 15156-2, Clause 9, Annex E (Informative) and NACE MR0175/ISO 15156-3, 7.2, Annex C (Informative) make some suggestions on how materials manufacturers and other suppliers might mark their materials to indicate the evaluation (testing) that they have carried out."

In all cases, communication between all

parties is necessary to agree material documentation requirements.

NACE MR0175 and the regulatory framework

The document is listed within the regulatory requirement in the USA in states such as Texas (Railroad Commission of Texas Statewide Rule 36) and in Code of Federal Regulations (30 CFR 250.901) among others. In the UK, the Health and Safety Authority lists NACE MR0175 in several

regulatory documents including the Well Construction Standards. Other countries that list NACE MR0175 within their regulatory framework include Denmark and Norway.

Concluding Remarks

ANSI / NACE MR0175 / ISO 15156 is a document listed within several regulatory requirements around the world, which provides guidance to select and use metallic materials in H₂S producing environments. It is a live document and users can submit clarifications and inquiries to its maintenance panel as well as take part of the meetings that steer the document. Stainless steel manufacturers and distributors need to establish and maintain communication channels with the equipment manufacturers and users in order to define the documentation requirements.

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