

Commentary On Standards Development For Selection And Specification Of HSC-Resistant Materials in Subsea Service with Cathodic Protection

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ABSTRACT

In the oil and gas industry, the major standard for material selection today is ANSI¹/NACE² (now AMMP³) MR0175/ISO⁴ 15156 Parts 1-3. This standard deal extensively with environmental cracking and its mitigation under exposure to sour production environments containing H₂S, CO₂, chlorides, and sulfur. Unfortunately, it does not include material requirements for resistance to environmental cracking under variable subsea applications and conditions that may involve exposure to seawater with or without cathodic protection (CP). Also, ISO 21457 and several other standards identify the corrosion mechanisms and parameters for evaluation when performing selection of materials for pipelines, piping and equipment related to hydrocarbon production, transport and processing, including utility and injection systems; however, they do not address in detail aspects of environmental cracking that can be associated with use of CP in subsea operations. This lack of attention in industry standards is somewhat surprising since exposure of materials to subsea conditions with cathodic protection and the potential for environmental cracking has been documented in the literature for over 50 years. Furthermore, there have been several component failures in high strength materials and recent near-miss, in-service incidents in drill-through equipment bolting/fasteners/studs operating subsea under cathodic protection. This paper comments on the member-driven standardization activities that have recently been initiated through AMPP to define hydrogen stress cracking (HSC) resistant metallic materials for subsea service with cathodic protection, the historical relationship to a material requirement standard – MR0175/ISO15156, and a recent review of published HSC literature and related standards that can support the current standardization efforts for HSC-resistant metallic materials in subsea CP service.

Key words: Hydrogen Stress Cracking, HSC, Sulfide Stress Cracking, Hydrogen Induced Stress Cracking, low alloy steels, nickel-based alloy, duplex stainless steel, martensitic stainless steel, austenitic stainless steel, MR0175, ISO15156, cathodic protection, subsea

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INTRODUCTION

In the oil and gas industry, the major standard for material selection today is ANSI/NACE MR0175/ISO 15156 Parts 1-3. [1] While this standard deals extensively with environment cracking and its prevention for materials under exposure to production environments containing H₂S, CO₂, chlorides, and sulfur, it does not include any guidance or material requirements for resistance to environmental cracking (such as hydrogen stress cracking – HSC, or otherwise) under variable subsea conditions that involve exposure to seawater with varying levels of cathodic protection (CP). ISO 21457 [2] provides further guidance for materials selection and corrosion control for oil and gas production systems but does not provide adequate coverage of the issue of environmental cracking in subsea applications with CP. EEMUA⁵ 194 [3] is an industry accepted guideline used by many, as is NORSOK⁶ M-001 [4], but requirements on the issue of selecting HSC-resistant materials for subsea CP service are limited. Exposure of materials to subsea conditions with CP and the potential for HSC is not a new subject, having over 50 years of service experience. However, there has been growing concerns for risk of failures in high strength materials and recent near-miss, in-service incidents in drill-through equipment bolting/fasteners/studs.

At the request of BSEE⁷, NAS⁸ studied the subject of subsea threaded fastener failures. This request was followed by a series meetings and discussions among representatives from oil and gas industry, material and equipment suppliers, and academia. In April 2017, NAS hosted a workshop in Washington, DC. on “Connector Reliability for Offshore Oil and Natural Gas Operations” from which a detailed report “High-Performance Bolting Technology for Offshore Oil and Natural Gas Operations” was published later in 2017. [5]

This paper provides documentation of NACE (AMPP) technical and standardization activities related to materials used in subsea applications that have taken place since the 2017 NAS meeting. It also provides an historical context to the present standardization effort for a material requirement (MR) on materials for subsea service with CP. This paper looks back to the original MR0175-1975: “Materials for Valves for Resistance to Sulfide Stress Cracking in Production and Pipeline Service” [6] and documents the published literature to define the materials used subsea and associated data with respect to HSC that may occur as a result of cathodic protection.

BACKGROUND - NACE (AMPP) ACTIVITIES SINCE THE 2017 NAS MEETING

As a result of discussions at the previously mentioned NAS meeting, a multi-year NACE (now AMPP) effort was initiated to engage the corrosion community in this issue and to openly discuss and disseminate information on environmental cracking in subsea fasteners and associated equipment specifically looking at the influences of metallurgy, material processing, design, and cathodic protection. The NACE/AMPP effort was initiated with an open forum titled “Environmentally Assisted Cracking of High Strength Steels and Alloys for Critical Service Subsea Bolting” held at the NACE 2018 annual conference. This forum presented information on critical service subsea bolting in drill-thru equipment, timeline of events & post-failure response; identification of failure mechanism & critical variables; industry standards; industry and independently sponsored research; and path forward actions by NACE and its members in terms of publications and standardization.

Starting in 2019, NACE held a series of annual conference symposia on subjects related to environmental cracking of subsea materials and equipment. In that year, a research technical symposium was organized titled “Subsea Materials versus Hydrogen Stress Cracking”. Ten

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presentations were made addressing: preliminary results from API research on strength and hardness versus HSC for low alloy steel bolting; fracture mechanics approaches to address HSC in fasteners and other high strength materials including precipitation hardened (PH) Ni-based alloys; potential uses of cathodic protection and stress modeling versus HSC.

For 2020 and 2021, NACE annual conference technical symposia were organized under STG-32 (Oil and Gas Production—Metallurgy). The annual conference program schedule during these years was severely impacted by coronavirus. In 2020, conference symposium papers were submitted; some were published online in 2020 while some authors chose to wait and present in 2021 at what became a virtual conference.

In June 2021, following the AMPP virtual online conference, a web meeting among interested parties was held to discuss follow up actions aimed at initiating a standard writing effort for materials and metallurgical processed used versus HSC (with consideration of other environmental cracking mechanisms, if necessary) for subsea service. The consensus was for the development of a standard document(s) that take available technical findings, testing and research results, and field experience to provide guidance and best practices to reduce risk of environmental cracking failures subsea. The discussion indicated that there is presently work being done on HSC within API⁹ (API Specifications 20E and 20F, and that described in Technical Report, API 21TR1) associated with high strength steel and alloy bolting. [7-9] These documents indicate risk of HSC under CP (particularly if metallurgical processing is deficient) and use of Zn-plating (another source of hydrogen) is involved. It was also discussed that there are discrepancies in hardness limits for prevention of HSC depending on various API and ASTM standards some of which has already been addressed in the API 20E limits of HRC 34 for steel bolting. Additionally, it was noted that there is a large variability in HSC susceptibility in seawater versus CP potential over a range of potentials (-800 mV to -1,200 mV SCE).

The consensus of those attending the meeting was that the scope of AMPP standardization activities in this area should be broader than just bolting since cases of non-bolting subsea failures were reported with forgings, stainless values, 12Cr flow lines, annealed or cold worked duplex stainless control tubing and, failures in precipitation hardened (PH) nickel-based alloys. It was noted that use of stainless steels in seawater may, in some cases, impose a risk of failure from stress corrosion cracking or HSC at open circuit potentials if shielded from CP. Issues of metallurgical processing vs. cracking should be included in the standard in much the way that ANSI/MR0175/ISO15156 handles this area for resistance to sulfide cracking mechanisms. Therefore, the consensus was to pursue a Materials Requirement (MR) type standard.

Based on the input received from attendees at this meeting, two AMPP SC-08 committees were requested and authorized, these being:

- **TR21524 - Review of Material Requirement for Subsea Environmental Cracking and Sources of Information.** This committee will include an initial scoping study and the writing of a technical report over 6-12 month. It will include an outline for a new standard for subsea equipment vs environmental cracking, identification and review available literature and standards that may be utilized in its writing. This report will be utilized by a second follow-on committee that will be tasked with the drafting of a standard.
- **MR21525 - Material Requirement for Subsea Equipment Versus Cathodic Protection and Environmental Cracking.** This committee will take the input from the initial scoping study performed by TR21524 and their technical report and organize the drafting of a standard for defining service conditions, acceptable materials, and methods of metallurgical processing. This standard will document industry best practices and guidelines to reduce the risk of environmental cracking under subsea cathodic protection and environmental cracking.

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CONTEXT OF THIS EFFORT WITH RESPECT TO NACE MR0175

NACE standard MR0175 (1975 Edition) replaced NACE Publications 1F166 (Sulfide Cracking Resistant Metallic Materials for Valves for Production and Pipeline Service) and 1B163 (Recommendations of Materials for Sour Service. This latter document included Tentative Specifications 150 on valves, 51 on severe weight loss, 60 on tubular goods, and 50 on nominal weight loss. The new standard covered material requirements for resistance to sulfide stress cracking (SSC) applicable to equipment used in H₂S service covered by API Standards 6A and 6D (Production and Pipeline Valves). [10,11] Most importantly, efforts were made in the MR0175 standard to make sure that it was not construed as a guarantee that products conforming to the requirements contained therein will be resistance to SSC under all conditions. The same will be the case today with a new MR standard for materials for subsea service.

It must be realized what the situation was back in 1975 when MR0175 was published by NACE. At that time, there were no accepted and standardized H₂S-related test methods for SSC. Laboratory SSC data was being developed by various companies using various methods and procedures. It was not until two years after the publication of NACE MR0175-1975 when NACE standard test method NACE TM0177 (then only a uniaxial tension test method) [12] was published and about five years later when standardized procedures for conducted SSC tests using C-ring, bent beam and double cantilever beam (DCB) fracture mechanics specimens would be included into TM0177. Furthermore, the test method standards for hydrogen induced cracking (HIC) – TM0284 [13], and a slow strain rate test method TM0198 [14] for evaluation of corrosion resistant alloys (CRAs) for SCC in H₂S environments (and a recent annex that describes use of this procedure for evaluating HSC of PH nickel-based alloys) were still many years away. To make up for this lack of standardized methods of laboratory evaluation and qualification of materials, the initial MR0175 was based primarily on twenty-plus years of field experience with commonly utilized sour service materials with laboratory testing playing a secondary but an important supportive role.

The above-mentioned situation described for the standardization environment at the time of MR0175 is actually very similar to that of today for a proposed new MR standard today with a possible title – “Hydrogen Stress Cracking Resistant Metallic Materials for Subsea Oil and Gas Equipment Exposed to Seawater Under Cathodic Protection”. Today, there are several test methods available for evaluation of materials for HSC, some either generic methods for slow strain rate and fracture mechanics testing from ASTM (to be discussed later) that can be applied to HSC testing under applied cathodic protection or current, and those originally developed for SSC or SCC testing in sour or ethanolic environments, these being TM0177 (smooth tensile, C-ring, and DCB), TM0198 (smooth SSR and its new Annex C addressing testing for HSC resistance of PH nickel-based alloys), and TM0111 [15] (smooth and notched SSR). However, none of these standards provide complete coverage of test conditions, testing procedures related to subsea service with exposure to cathodic protection and standardized procedures of material evaluation and qualification. As in the case of MR0175/ISO15156, such testing requirements and acceptance criteria can be specified in a new MR.

The provisions of the MR0175 (1975 Edition) were organized based on material classifications supplemented by associated categories, HRC limits and recommended heat treat conditions for certain materials as used in valve components:

- Ferrous Metals: Carbon and Low Alloys Steels - HRC 22 max. limit with 629 C minimum PWHT temperature.
- Stainless Steels: Austenitic, Ferritic, and Martensitic HRC 22 max. limit, and Precipitation Hardened (PH) – HRC 27 max. limit.
- Cast iron and free machining steels: excluded from critical parts.

- Nonferrous Metals: Ni-alloys, Ni-Cu alloys, Ni-Cr-Fe alloys, Other High Alloys - HRC 35 max. limit.
- Cu alloys: no HRC limit but warning regarding accelerated corrosion.
- Fabrication: Trim applications and overlay, welds, identification stamping, flange cover and bonnet bolting, plating (not allowed for prevention of SSC), and bearings.

In 1978 through 1980, revisions to MR0175 were published by NACE that expanded the scope of the standard to the entirety of sour oil and gas operations as captured in a new title, “Sulfide Stress Cracking Resistant Metallic Materials for Oil Field Equipment”. [16] With the revised standard came additional provisions with definition of sour serviceability limits for sour gas and sour oil and multiphase conditions, based on a 0.05 psia (0.3 kPa) partial pressure H_2S with some low-pressure exclusions – gas service for pressures less than 65 psia (0.4 MPa), or oil/multiphase service at total pressure less than 265 psi (1.8 MPa). Eventually, nearly 20 years following the original standardization of MR0175, the concept of sour service limits evolved still further with a rewrite of MR0175 with the combined NACE/ISO edition in 2003 [17] and EFC¹⁰ Publication 16 [18] that incorporated the concepts of additional variables to define more comprehensively sour serviceability limits in terms of H_2S partial pressure and pH for low alloy steels (Part 2), and for corrosion resistant alloys H_2S partial pressure, pH and chlorides (Part 3).

Furthermore, the expansion in scope of MR0175 beyond valves that occurred through 1980, additional additions to ferrous and non-ferrous materials were made, and completely new sections were added related to wells, flow lines, gathering line, facilities, and field processing plants, and drilling, well servicing and control equipment. Tables were updated to provide separate listings of acceptable ferrous, stainless steel and non-ferrous materials, acceptable API and ASTM tubular goods, and materials for subsurface equipment. The provisions for acceptable materials conditions and processing were included either for general use (unrestricted direct exposure to H_2S or for specific uses /applications particularly if service experience indicated acceptable field performance where laboratory testing might be non-existent or, in some cases, indicate otherwise.

It is likely that the present standardization effort for subsea service with emphasis on HSC resistant materials, may be able to proceed with a combination of documented field experience, the review of published test and research data, and information that already exists in other industry standards, such as from API and ASTM, in a similar manner in which the original MR0175 was developed. The question then comes, how to organize the standard with respect to which materials, applications and cracking mechanisms to be included at this early stage of this MR standard development.

REVIEW OF PUBLISHED LITERATURE

To properly scope or frame the task of writing an industry consensus standard on materials requirements for subsea equipment versus HSC, it is good to look to the published literature for advice with respect to industry’s interest, needs and experience. In the case of an MR standard, the materials examined in laboratory testing, failure analysis and research over the years will be key inputs. Another prerequisite will be the definition of the use conditions, in this case, definition of CP conditions. For this reason, a literature search was performed to identify what materials were examined and over what range of conditions. The information found in this initial study is provided in the following sections presented in chronological order that helps to indicate the evolution of key learnings in this area.

Defining The Hydrogen Charging Environments

When it comes to development of an MR standard for subsea materials, there are important considerations found in NACE (AMPP) SP0176 [19], for quantifying CP for subsea applications.

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- Sacrificial anode (SA) systems are the most prevalent method of CP used subsea. As shown in NACE SP0176, the standard anode selections are either Zinc or Al-Zn-Ir that typically provide cathodic polarization levels of -1,000 to -1,050 mV (Ag/AgCl) and -1,050 to -1,100 mV (Ag/AgCl), respectively. There are also sacrificial Al-Ga anodes with less electronegative potentials in the range -800 to -950 mV (SCE) that offer an option for CRA materials that may only require more limited levels of CP that reduce hydrogen charging. [20] From this viewpoint, the reasonable worst-case conditions for defining severity of HSC are simply to define the most negative cathodic potential, or -1100 mV (Ag/AgCl) or around -1150 Standard Calomel Electrode (SCE). It is the application of negative potentials of around -800 mV Ag/AgCl or more electronegative where hydrogen production becomes the dominant electrochemical reaction on the cathode (usually the subsea structure, components, and bolting). This results in the formation of atomic hydrogen on the metal surface that, due to its very small size, can be absorbed into the cathode (steel or CRA) and thus lead to the risk of HSC.
- There are also CP systems that protect marine vessels and structures used in the drilling and production of oil and gas that utilize impressed current (IC). These systems are usually controlled to deliver similar levels of cathodic polarization as SA CP systems; however, they have the capacity to (either intentionally or unintentionally) deliver higher levels of CP, i.e., potentials more electronegative than those of SA systems, and therefore have the capability to impose more severe conditions of hydrogen charging and susceptibility to HSC. The two types of systems (SA and IC) can interface such as when floating vessels are in electrical connection to risers and other subsea equipment.
- A third view of the severity of CP conditions can arise from variable subsea conditions. Electrochemical potential is really a way of defining the driving force for CP reactions. Another aspect of CP to keep in mind is that hydrogen charging from cathodic protection is really controlled by the charging current density on the cathode surface. As shown in Table 1 (adapted from Table A1 from NACE SP0176), CP current densities can vary substantially from location-to-location and with water depth resulting from differences in water temperature, seawater turbulence/flow, and water resistivity. Lowest CP current densities (and presumably lowest levels of hydrogen charging) tend to occur in warm shallow seawater with low to moderate flow conditions (like Gulf of Mexico) and where calcium carbonate scale readily forms on cathodic surfaces. Importantly, the highest CP current densities are at low temperature and high flow conditions by virtue of dissolution or erosion of normally protective calcium carbonate scales. Therefore, there is the possibility that hydrogen charging conditions and resultant HSC susceptibility can increase in deep water and/or high seawater current conditions than in warmer, shallow water conditions. Furthermore, studies of the effects of hydrostatic pressure (simulating deep water) on hydrogen charging have produced conflicting data and are discussed later.
- Another aspect of controlling HSC in high strength materials is realizing that hydrogen charging conditions can result from sources other than simply CP. Examples of these sources are: (a) electroplating of metal surfaces that takes place during manufacturing, (b) corrosion at potentials more electropositive near the open circuit potential for steel (usually associated with components freely corroding in seawater or shielded from CP), (c) the influence of coatings or thread doping compounds that have materials (e.g. MoS₂) that can locally accelerate the adsorption of hydrogen, or plating that have noble metal constituents can accelerate substrate corrosion on the metal surface, or (d) hydrogen charging from galvanic coupling between dissimilar metals (e.g. CRA and steel) that are in electrical contact in the presence of an electrolyte such as seawater or conductive well fluids.

Production Area	Water Resistivity ^(B) (ohm-m)	Water Temp. (°C)	Environmental Factors ^(A)		Typical Design Current Density ^(C)			Typical Design Slope ohm-m ² (ohm-ft ²)
			Turbulence Factor (Wave Action)	Lateral Water Flow	mA/m ² (mA/ft ²)			
					Initial ^(E)	Mean ^(F)	Final ^(G)	
Gulf of Mexico	0.20	22	Moderate	Moderate	110 (10)	54 (5)	75 (7)	4.1 (44)
Deep water GOM	0.29	4-12	Low	Varies	194 (18)	75 (7)	86 (8)	
U.S. West Coast	0.24	15	Moderate	Moderate	150 (14)	86 (8)	100 (9)	3.0 (32)
Cook Inlet	0.50	2	Low	High	430 (40)	380 (35)	380 (35)	1.0 (11)
Northern ^(D)	0.26-0.33	0-12	High	Moderate	180 (17)	86 (8)	120 (11)	2.5 (27)
North Sea Southern ^(D)	0.26-0.33	0-12	High	Moderate	150 (14)	86 (8)	100 (9)	3.0 (32)
Arabian Gulf	0.15	30	Moderate	Low	130 (12)	65 (6)	86 (8)	3.5 (37)
Southeast Australia	0.23-0.30	12-18	High	Moderate	130 (12)	86 (8)	86 (8)	3.5 (37)
Northwest Australia					120(11)	65 (6)	65 (6)	
Brazil	0.20	15-20	Moderate	High	180 (17)	65 (6)	86 (8)	2.5 (27)
West Africa	0.20-0.30	5-21	Low	Low	130 (12)	65 (6)	86 (8)	3.5 (37)
Indonesia	0.19	24	Moderate	Moderate	110 (10)	54 (5)	75 (7)	4.1 (44)
South China Sea	0.18	30	Low	Low	100 (9)	32 (3)	32 (3)	

Table 1 – Table A1 Design Criteria for Cathodic Protection Systems (from NACE SP0176).

REVIEW OF MATERIALS FOR SUBSEA APPLICATIONS

High Strength (HS) Carbon and Low Alloy Steels

High strength (HS) steels were the first material to be seriously examined for susceptibility to hydrogen embrittlement and HSC going back to the late-1950s. A publication in this area occurred in 1959 and describes the seminal work of Troiano – “Delayed Failure of High Strength Steels”. [21] While this paper was focused on the HSC of cadmium plated high strength steels used in the aircraft industry, it identified a new failure mechanism; that is, delayed embrittlement, cracking and failure by hydrogen dissolved in the HS steels, in this case, resulting from the plating process. It also demonstrated the deleterious effect of stress concentrations on HSC and the ability, to a certain degree, baking out hydrogen to restore normal material ductility.

Schuetz and Robertson (1957) authored a NACE Technical Committee Report covering hydrogen absorption and embrittlement fracture of various ferrous and non-ferrous alloys in sulfide and non-sulfide environments. [22] They concluded that dissolved hydrogen in the metal was the cause of embrittlement of both ferritic and martensitic steels, but they were not able to produce embrittlement in fully austenitic alloys. At the same time, Bruckner and Myles (1959) published their research that showed steels could be embrittled and exhibit cracking as a result of cathodic protection and that susceptibility to cracking was proportional to the level of dissolved hydrogen in the steel at electronegative potentials of at least -850 mV Cu/CuSO₄ (~925 mV SCE). [23]

In a practical sense, many constructional steels used in subsea construction are generally considered as low strength with yield strengths (YS) <80 ksi (550 MPa). As such, they can largely be categorized as unaffected by hydrogen picked up from normal sacrificial anode cathodic protection systems that control potentials in the range of -1000 to -1100 mV (SCE). The possible exception are welded joints that by virtue of joining process and thermal cycle contain locations of high hardness in weld metal and/or heat affected zones (HAZs) not addressed by weld procedure controls. Starting in the 1990s, with the quest for deeper water oil and gas production and development of higher-pressure offshore reservoirs, concerns were heightened for HSC under cathodic protection conditions with the use of higher strength steels – typically YS >100 ksi (690 MPa) and/or HRC >32. Concern in many areas started with HS steels used in bolts, fasteners, and studs in subsea systems, but also for welded components where weld procedures are needed to prevent the formation of hard weld zones.