

Commentary on Standards Development for Selection and Qualification of HSC- Resistant Materials in Subsea Service with Cathodic Protection

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AMPP values your input. To provide feedback on this standard, please contact: standards@ampp.org

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Foreword

AMPP technical reports are intended to convey technical information or state-of-the-art knowledge regarding corrosion. In many cases, they discuss specific applications of corrosion mitigation technology, whether considered successful or not. Statements used to convey this information are factual and are provided to the reader as input and guidance for consideration when applying this technology in the future. However, these statements are not intended to be recommendations for general application of this technology and must not be construed as such.

A major standard in the oil and gas industry for material selection today is ANSI⁽¹⁾/NACE MR0175/ISO⁽²⁾ 15156 Parts 1-3. It deals extensively with environmental cracking and its mitigation through material selection for equipment handling sour production environments containing H₂S, CO₂, chlorides, and/or sulfur. Unfortunately, it does not include material requirements for resistance to hydrogen stress cracking (HSC) for subsea applications and conditions that may involve exposure to seawater with cathodic protection (CP). There are several other standards that identify corrosion mechanisms and parameters for evaluation when selecting materials for pipelines, piping and equipment related to hydrocarbon production, transportation and processing, including utility and injection systems; however, they do not address detailed aspects of materials selection to avoid HSC in subsea applications under CP.

The above-mentioned lack of in-depth industry standards is somewhat surprising since exposure of materials to subsea conditions with CP and risks of HSC, as shown herein, have been documented in the literature for over 50 years. Risks associated with HSC have been elevated because of several component failures in high strength materials and recent near-miss, in-service incidents in bolting/fasteners/studs in drill-through equipment operating subsea under cathodic protection. The findings in this Technical Report (TR21524) were developed to support member-driven standardization activities that were initiated in AMPP to better define material requirements for HSC-resistant metallic materials for subsea service with cathodic protection.

This Technical Report is intended as a companion document to the AMPP standard MR21525 (Hydrogen Stress Cracking Resistant Metallic Materials for Use in Subsea Oil and Gas Production with Cathodic Protection), which is in development. It provides results, review and commentary on many investigations and includes important literature data, references, background information, service experience and related standards that were utilized in the development of the AMPP MR21525. Most of the information in this Technical Report covers findings from HSC field experience and HSC data from CP exposure tests or from cathodic charging experiments. It is important to note in the use of MR21525 and in the review of data contained herein that HSC can also be induced from hydrogenating environments and conditions other than from just from CP exposure. A non-exhaustive list of such conditions is presented later in this Technical Report.

Scope

As a companion document to MR21525, this Technical Report provides results, review and commentary on many investigations of HSC and includes important literature data, references, background information, service experience and related standards that were utilized in the development of the AMPP MR21525. Most of the information in this Technical Report covers findings from HSC field experience and HSC data from brine/CP exposure tests or from other cathodic charging experiments. It is important to note, in the use of MR21525 and in the review of data contained herein, that HSC can also be induced from hydrogenating environments and conditions other than from just from CP exposure alone. A non-exhaustive list of such conditions is presented later in this Technical Report.

Rationale

This report is important as a reference guide for those wishing to understand the background information and experience used in the development of the MR21525 standard and its elevated importance because of several component failures in high strength materials and recent near-miss, in-service incidents associated with HSC. These recent events were primarily in bolting/fasteners/studs in drill-through equipment operating subsea under cathodic protection, but as shown herein, HSC failures have also occurred in other subsea materials and components over decades of subsea service experience. The findings presented in this Technical Report were developed to support member-driven standardization activities that were initiated in AMPP to better define material requirements for HSC-resistant metallic materials for subsea service with cathodic protection.

⁽¹⁾ American National Standards Institute (ANSI), 25 West 43rd Street, 4th Floor, New York, NY 10036, www.ansi.org.

⁽²⁾ International Organization for Standardization (ISO), Chemin de Blandonnet 8, CP 401, 1214 Vernier, Geneva, Switzerland, www.iso.org.

Referenced Standards and Other Consensus Documents

The latest edition, revision, or amendment of the referenced standards in effect shall govern unless otherwise dated.

AMPP/NACE/SSPC, www.ampp.org:

ANSI/NACE MR0175/ISO 15156 – Parts 1-3	Petroleum and Natural Gas Industries – Materials for Use in H ₂ S-Containing Environments in Oil and Gas Production
ANSI/NACE MR0175/ISO 15156:2003	Petroleum and Natural Gas Industries – Materials for Use in H ₂ S-Containing Environments in Oil and Gas Production
NACE MR0175-1980	Sulfide Stress Cracking Resistant Metallic Material for Oil Field Equipment
NACE MR0175-1975	Materials for Valves for Resistance to Sulfide Stress Cracking in Production and Pipeline Service
NACE SP0176	Corrosion Control of Submerged Areas of Permanently Installed Steel Offshore Structures Associated with Petroleum Production
NACE TM0111	Slow Strain Rate Test Method for Evaluation of Ethanol Stress Corrosion Cracking in Carbon Steel
NACE TM0177	Laboratory Testing of Metals for Resistance to Sulfide Stress Cracking and Stress Corrosion Cracking in H ₂ S Environments
NACE TM0198	Slow Strain Rate Test Method for Screening Corrosion-Resistant Alloys for Stress Corrosion Cracking in Sour Oilfield Service
NACE TM0284	Evaluation of Pipeline and Pressure Vessel Steels for Resistance to Hydrogen-Induced Cracking

API, www.api.org:

API Specification 20E	Alloy and Carbon Steel Bolting for Use in the Petroleum and Natural Gas Industries
API Specification 20F	Corrosion-resistant Bolting for Use in the Petroleum and Natural Gas Industries
API Standard 6A CRA	Age-hardened Nickel-based Alloys for Oil and Gas Drilling and Production Equipment
API Technical Report 21TR1	Materials Selection for Bolting

ASTM, www.astm.org:

ASTM A320	Standard Specification for Alloy-Steel and Stainless Steel Bolting for Low-Temperature Service
ASTM E1820	Standard Test Method for Measurement of Fracture Toughness
ASTM F1624	Standard Test Method for Measurement of Hydrogen Embrittlement Threshold in Steel by The Incremental Step Loading Technique
ASTM G148	Standard Practice for Evaluation of Hydrogen Uptake, Permeation, and Transport in Metals by an Electrochemical Technique

DNV, www.dnv.org:

DNV RP-B204	Welding of subsea production system equipment
DNV RP-B401	Cathodic protection design
DNV RP-F112	Duplex stainless steel – design against hydrogen induced stress cracking

EEMUA, www.eemua.org:

EEMUA 194	Guide to materials selection and corrosion control for subsea energy equipment
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ISO, www.iso.org:

ISO 21457	Petroleum, petrochemical and natural gas industries - Materials selection and corrosion control for oil and gas production systems
ISO 13628-1	Petroleum and natural gas industries — Design and operation of subsea production systems — Part 1: General requirements and recommendations

Standards Norway, www.standard.no:

NORSOK M-001	Materials Selection
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Introduction

In the oil and gas industry, a major standard for material selection is ANSI/NACE MR0175/ISO 15156 Parts 1-3. This standard deals extensively with environment cracking and its prevention for materials exposed to production environments containing H₂S, CO₂, chlorides, and sulfur. It included only limited guidance or material requirements for resistance to environmental cracking by hydrogen stress cracking – HSC, and none that apply to variable subsea conditions that involve exposure to seawater and cathodic protection (CP). ISO 21457 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 HSC in subsea applications with CP. EEMUA⁽³⁾ 194 is an industry accepted guideline used by many, as is NORSOK⁽⁴⁾ M-001, but still, specific requirements for selecting HSC-resistant metallic materials for subsea CP service are limited and found in various standards and technical papers. While HSC is a topic spanning over 50 years of investigation and service, there is a growing concern for risk of failures in high strength ferrous and non-ferrous materials in components and, in particular, in bolting, fasteners, and studs. In this Technical Report, these terms should be considered interchangeable or simply referred to as fasteners.

BSEE⁽⁵⁾ and later NASEM⁽⁶⁾ studied failures in subsea threaded fastener, studs and bolts. These actions included a series of 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 2017.¹

This AMPP Technical Report provides:

- An extensive HSC literature review covering the 1950s through 2022,
- A summary of associated symposium and committee activities with respect to HSC conducted under the auspices of AMPP related to specification, selection, and qualification of HSC-resistant materials for subsea applications under CP that have taken place since the 2017 NAS meeting,
- An historical context for this standardization effort for a material requirement (MR) standard on materials for subsea service with CP with a short review of the original development effort for NACE MR0175-1975: “Materials for Valves for Resistance to Sulfide Stress Cracking in Production and Pipeline Service,” and
- A review of the technical literature to help define the materials used subsea and associated data that would help define available HSC-resistant metallic materials in subsea service with CP along with test methods for their evaluation and qualification.

⁽³⁾ The Engineering Equipment and Materials Users Association (EEMUA), 3 Hanbury Drive, London, E11 1GA, UK, www.eemua.org.

⁽⁴⁾ Standards Norway, P.O. Box 252, NO-1326 Lysaker, Norway, www.standard.no.

⁽⁵⁾ U.S. Bureau of Safety and Environmental Enforcement (BSEE), 1849 C Street, NW Washington, D.C. 20240, www.bsee.gov.

⁽⁶⁾ National Academies of Sciences, Engineering, and Medicine (NASEM), 500 Fifth St., N.W. Washington, D.C. 20001, www.nationalacademies.org.

Background

AMPP Conference and Standardization Activities

As a result of discussions at the previously mentioned NASEM meeting, a multi-year AMPP effort was initiated to engage the corrosion community in the issue of HSC in subsea materials, the need for further industry standardization and to openly discuss and disseminate information on environmental cracking in subsea fasteners and associated subsea equipment. The industry standardization needs specifically focused on the influences of metallurgy, material processing, design, and cathodic protection. The 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 NACE’s CORROSION 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 planned path-forward actions by NACE and its members in terms of publications and standardization.

Starting in the following year, NACE held a series of annual conference symposia on subjects related to environmental cracking of subsea materials and equipment. In 2019, this took the form of a research technical symposium titled “Subsea Materials versus Hydrogen Stress Cracking.” Ten presentations were made addressing: preliminary results from American Petroleum Institute (API) research on strength and hardness versus HSC of 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.

In 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 curtailed by the COVID-19 pandemic. CORROSION 2020 was cancelled after symposium papers were submitted; however, some of these papers were published online in 2020, while other authors chose to wait and present their papers 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 to better define acceptable materials and metallurgical processes to reduce the risk of HSC for subsea service. The consensus was for the development of AMPP standard documents from available testing and research results, and field experience to provide guidance and best practices to reduce the risk of HSC failures subsea. The discussion indicated that there is presently work being done on HSC within API⁽⁷⁾ (API Specifications 20E and 20F, and that described in Technical Report API 21TR1) associated with high strength steel and low alloy bolting. 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⁽⁸⁾ standards, some of which have already been addressed in the API 20E limits of HRC 34 for steel bolting for oil and gas components. Additionally, it was noted that there is a large variability in HSC susceptibility in seawater versus potential over the range of typical CP potentials (-850 mV to -1,150 mV SCE).

The consensus at 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 due to HSC have been reported, and have included:

- High strength or high hardness low alloy steels (non-fastener applications)
- Fasteners and equipment made from precipitation hardenable (PH) martensitic stainless steels
- Weldable martensitic 13Cr flowlines
- Forgings and wrought duplex stainless steel equipment, especially containing welds and cold worked duplex stainless steel, such as in control lines, and
- High strength precipitation hardened (PH) nickel-based alloys.

⁽⁷⁾ American Petroleum Institute (API), 200 Massachusetts Avenue NW, Suite 1100, Washington, DC 20001-5571, www.api.org.

⁽⁸⁾ ASTM International (ASTM), 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA, 19428-2959, www.astm.org.

It was also noted that use of high strength steels and stainless alloy in seawater may, in some cases, impose a risk of failure from anodic stress corrosion cracking, and at times HSC, at open circuit potentials if shielded from CP.

Finally, it was decided that issues of metallurgical processing as it pertains to limiting HSC susceptibility should be included in the standard in much the way that ANSI/NACE MR0175/ISO 15156 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 projects were requested and authorized, these being:

- TR21524 - Review of Material Requirement for Subsea Environmental Cracking and Sources of Information. This project included an initial scoping study and the writing of this Report. It also included an extended outline for a new MR standard for subsea equipment versus HSC and identification and review of available literature and standards that may be utilized in its writing. This work product was utilized by a second project team that was tasked with the drafting of a standard.
- MR21525 - Material Requirement for Subsea Equipment versus Cathodic Protection and Environmental Cracking. This project team is taking the input from the initial scoping study performed by the TR21524 project team and information presented in this Technical Report. The MR21525 project team is organizing the drafting of an MR standard for defining service conditions, acceptable materials, and methods of metallurgical processing for optimizing resistance to HSC. The intention of the MR21525 standard is to document industry best practices and guidelines to minimize the risk of HSC in metallic materials under subsea CP conditions.

Context of the AMPP Standardization Effort with Respect to That of Original NACE MR0175

NACE standard MR0175-1975 replaced prior 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. NACE standard MR0175-1975 covered material requirements for resistance to sulfide stress cracking (SSC) applicable to equipment used in H₂S service covered by API Standards 6A and 6D, e.g., production and pipeline valves. 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 would be resistant to SSC every and under all conditions. The same will be the case today with a new MR standard for materials for subsea CP 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 TM0177 (then only a uniaxial tension test method) was published and about five years later when standardized procedures for conducting SSC tests using C-ring, bent beam and double cantilever beam (DCB) fracture mechanics specimens would be included in TM0177. Furthermore, the test method standards for hydrogen induced cracking (HIC) – TM0284, and a slow strain rate test method, TM0198, 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 precipitation hardened [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 supporting role. Further details on the industry efforts that led to NACE standard MR0175-1975 are available in recent historical review papers developed by E. Caldwell et al. (2022) and B. Sherar et al. (2022).²⁻³

The above-mentioned situation described for the standardization environment at the time of MR0175-1975 is actually very similar to that of today for a proposed new standard MR21525 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 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) for SSC testing, TM0198 (smooth SSR for SCC testing of CRAs and its new Annex C addressing testing for HSC resistance of PH nickel-based alloys), and TM0111 (smooth and notched SSR) for ethanol SCC. However, none of these standards provide complete coverage of test conditions and procedures related to subsea service with exposure to cathodic protection and standardized procedures for material HSC evaluation and qualification. As in the case of MR0175/ISO 15156 for SSC/SCC, testing requirements for qualification and acceptance can be specified in a new MR for HSC-resistant metallic materials while methods and procedures for testing are contained in various test methods.

The provisions of NACE MR0175-1975 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 post weld heat treatment (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, NACE published revisions to MR0175 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.” 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 H₂S 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 ISO 15156) that was back-adopted as ANSI/NACE MR0175/ISO 15156 in 2003. This standard incorporated many aspects found in EFC⁽⁹⁾ Publication 16⁴ including concepts of additional variables to define more comprehensively sour serviceability limits in terms of H₂S partial pressure and pH for low alloy steels (Parts 1 and 2), and for corrosion resistant alloys H₂S partial pressure, pH, chlorides and sulfur (Part 3).

Furthermore, the expansion in scope of NACE MR0175 beyond valves that occurred after 1975 included the addition of various ferrous and non-ferrous materials. Completely new sections were also 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 for acceptable ferrous 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 H₂S) 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. Eventually, sour environment conditions were included based on inputs of partial pressure H₂S, in situ pH, chlorides and temperature followed by listings of acceptable materials for such conditions. Much of the effort to expand the standard that followed was based on extensive testing and balloting for inclusion of acceptably performing materials into the standard.

It is envisioned that the initial standardization effort in MR21525 for HSC-resistant materials for subsea service with CP may be able to proceed with a combination of documented field experience, the review of published test and research data, and existing information that already exists in other accepted industry standards in a similar manner in which the original MR0175 was developed. That said, due to the lack of unified hydrogen permeation (as per ASTM G148) and HSC test data over a range of materials and environments, it is still difficult to assess the relative severity of hydrogen charging from subsea CP exposure relative to other hydrogenating environments (e.g., sour service conditions). This topic is addressed later in this Technical Report.

The aim of the TR21524 project team is for this Technical Report to bring together HSC data and documented service experience and related information from various sources to assist in the initial development of MR21525 and help users of the MR standard understand the rational basis for the guidelines it contains.

⁽⁹⁾ European Federation of Corrosion (EFC), Avenue des Arts 56/4C, 1000 Brussels, Belgium, www.efcweb.org.

Review of Published Literature on Hydrogen Stress Cracking (HSC)

To properly scope or frame the task of writing an industry MR consensus standard, it is important to assess the published literature with respect to the industry's directions, needs and experience. In the case of an MR standard for HSC, the materials examined in laboratory tests, failure analyses and research over the years were key inputs. Another prerequisite is the definition of the use conditions, in this case, definition of CP conditions as they may vary from either type of CP used or seawater locations or seawater solutions used in laboratory tests. 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 generally in chronological order in each section, which helped to indicate the evolution of key learnings in various areas.

Defining The Hydrogen Charging Environments from Subsea Cathodic Protection

When it comes to development of an MR standard for subsea materials, there were important considerations found in NACE SP0176 for quantifying CP variables for subsea applications and for associated testing, as indicated below:

- Sacrificial anode CP (SACP) systems are the most prevalent method of CP used subsea. As shown in NACE SP0176, the typical anode selections are either zinc (providing cathodic potentials of -1,050 to -1,100 mV SCE) or Al-Zn-Id (providing -1,100 to -1,150 mV SCE). There are also sacrificial Al-Ga anodes that provide less electro-negative potentials in the range -800 to -950 mV (SCE) that offer an option for corrosion-resistant alloy (CRA) materials, provided they can be electrically isolated from other conventionally CP-affected portions of the system. CRAs that may require a more limited level of CP that also reduces hydrogen charging severity to very low levels such as that from Al-Ga anodes.⁵ From this viewpoint, the reasonable worst-case condition for defining severity of hydrogen charging (and HSC) severity for SACP systems is simply to define the most electronegative cathodic potential being used, which for SACP is typically around -1,150 mV SCE. It is the application of cathodic potentials of -850 mV SCE or those more electronegative where hydrogen production becomes the dominant electrochemical reaction on the cathode (i.e., the subsea structure, components, or bolting being protected). This results in the formation of atomic hydrogen on the metal surface that, due to its very small atomic size and other reasons, can be absorbed into the cathode (steel or CRA), diffuse to sites of high stress and/or low metallic bond energy and lead to higher levels of absorbed hydrogen and increasing risk of HSC as cathodic potentials become more electronegative.
- There are also CP systems that protect marine vessels and some subsea structures used in the drilling and production of oil and gas that utilize impressed current cathodic protection (ICCP) with current provided by electronic devices called rectifiers. These systems are generally controlled from the surface and designed to control and deliver similar levels of cathodic polarization as SACP systems. However, ICCP systems usually have the capacity to (either intentionally or unintentionally) deliver higher levels of CP, i.e., potentials more electronegative and associated higher currents than those of SACP systems. Therefore, ICCP has the capability to impose more severe conditions of hydrogen charging and potentially increased susceptibility to HSC if not properly calibrated or monitored. The two types of systems (SACP and ICCP) can interface such as when floating vessels and other systems are in electrical connection to risers and other subsea components. Therefore, calibration and monitoring of ICCP systems is required to reduce the risk of unexpected negative fluctuations in CP potential and higher than expected levels of CP current that can increase the risk of HSC.
- A third perspective on the severity of CP conditions with respect to HSC can arise from variable subsea conditions themselves. Electrochemical potential is really a way of defining the driving force for CP reactions, but not the rate of cathodic reactions (such as production of atomic hydrogen on the cathode). Therefore, it is important to keep in mind, once the CP potential reaches -850 mV SCE or at more electronegative potentials, the production of atomic hydrogen is the dominant CP reaction on the cathodic surface. Importantly, hydrogen charging from cathodic protection is controlled by the current density (and not potential) on the cathodic surfaces that the imposed CP potential provides. As shown in [Table 1](#) (adapted from Table A1 from NACE SP0176), CP current densities are generally highest during the initial phase of polarization after CP is initiated on the equipment. Over time, as protective calcareous deposits form on the cathodic surface, CP current generally decreases. Since hydrogen charging is related to current density, it is logical to assume that risk of failure from HSC may be greatest

in this initial period of CP. However, in some cases where HSC failures have been observed subsea, they have occurred later after significant time in service because of the time needed for hydrogen to diffuse and embrittle the metal at the high stress locations, or of operational events promoting a high level of imposed plastic strain (See section on duplex stainless steels as presented later in this report).

- CP current densities, however, can vary substantially from location to location and with water depth resulting from differences in water temperature, seawater turbulence/flow, dissolved oxygen content, and water salinity and resistivity. Lowest CP current densities (and presumably lowest levels of hydrogen charging and HSC) would be expected to occur in warm shallow seawater with low to moderate flow conditions (such as in the Gulf of Mexico). Under these conditions, calcium carbonate scale readily forms on cathodic surfaces, eventually limiting the CP current. Of critical importance is that the highest CP current densities are typically at low temperature and/or high flow conditions by virtue of dissolution or erosion of normally protective calcium carbonate scales. This situation tends to increase the CP current required to protect subsea equipment, resulting in more rapid anode depletion. There is also the risk that such conditions can result in higher-than-expected hydrogen charging conditions and resultant HSC susceptibility in deeper, colder seawater or if higher seawater current or erosional conditions exist than commonly experienced in warmer, shallow water conditions. Furthermore, another possible factor that is not yet totally accounted for is the effect of hydrostatic pressure on efficiency of hydrogen charging under deep water conditions. This topic will be discussed later in this report.

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

Table A1 Design Criteria For Cathodic Protection Systems								
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	0.29	4-12	Low	Varies	194 (18)	75 (7)	86 (8)	
GOM								
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)
North Sea								
Arabian Gulf	0.15	30	Moderate	Low	130 (12)	65 (6)	86 (8)	3.5 (37)
Southeast	0.23-0.30	12-18	High	Moderate	130 (12)	86 (8)	86 (8)	3.5 (37)
Australia								
Northwest					120(11)	65 (6)	65 (6)	
Australia								
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)	

- As mentioned previously herein, other situations in oil and gas service that can result in environmental cracking from causes other than simply CP. Examples of these situations are cited below:
 - Electroplating of metal surfaces that takes place during manufacturing and often used on threaded surfaces. This is shown by Townsend (1957)⁶ in Figure 1 for various coating/plated conditions on G41400 high strength steel (HRC 37) using hot dip Al-Zn, electroplated Zn, and hot dip Zn,
 - Corrosion taking place at more electropositive potentials than potentials associated with CP that occur near the open circuit potentials of exposed materials (usually associated with components freely corroding in seawater or shielded from CP). In the range of potentials in the range -700 to -400 mV SCE, corrosion can produce environmental cracking in high strength steels – Sandoz (1959)⁷ (See Figure 2), or anodic stress corrosion cracking in the case of stainless steels,

- Thread doping compounds that have materials (e.g., MoS_2) that contain and release species that are hydrogen recombination poisons may increase the efficiency of hydrogen charging, thereby accelerating the adsorption of hydrogen on the cathodic surface as addressed later herein, or
- 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 conductive well fluids (e.g., high density brine fluids) as addressed later herein or liberation of hydrogen from decomposition of formate fluids used in well completions - See Hills et al. (2009) and Lo Piccolo et al. (2012).^{8,9}

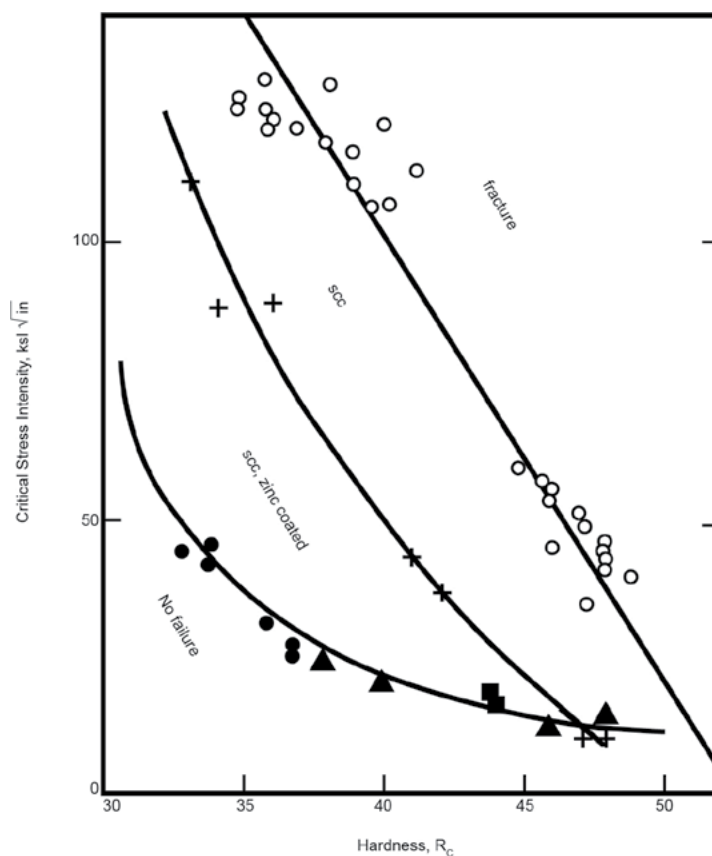


Figure 1: Critical Stress Intensities for Fracture in the Following Conditions:

○ Uncoated in Humid Air, + Uncoated in NaCl Brine, ● Hot Dip Al-Zn Coated in NaCl Brine, ▲ Electroplated Zn Coated in NaCl Brine, and ■ Hot-Dip Zn in NaCl Brine⁶

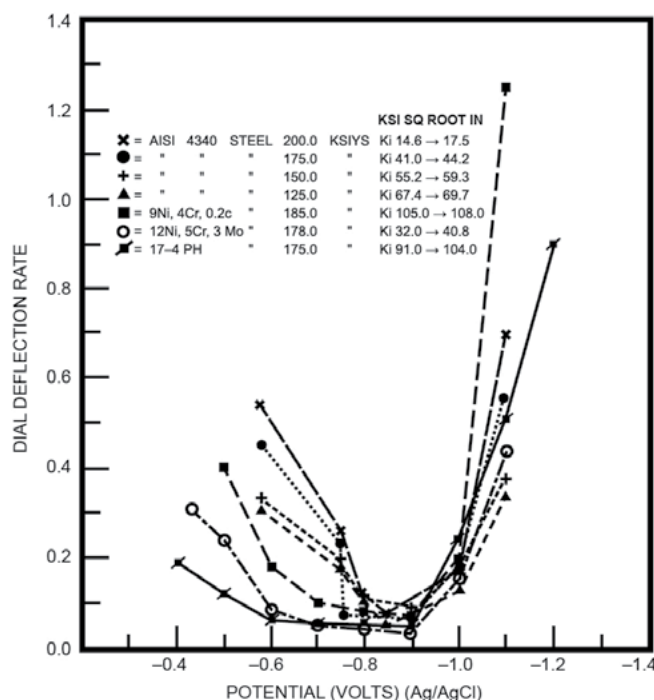


Figure 2: Effect of Applied Potential on Environmental Cracking Rate of Various High Strength, Low and High Alloy Steels, Conversion: mV (Ag/AgCl) +50 mV = mV SCE⁷

- It would be helpful to compare the relationship between hydrogen charging and environmental cracking in sub-sea conditions with CP with that for aqueous H₂S-containing sour environments. The work of Crolet and Maisonneuve (2000)¹⁰ was directed at creating a universal scale of hydrogen charging severity using hydrogen pressure (P_{H₂}) buildup data obtained from hollow carbon steel sensors. Their work showed

Aqueous sour environments with P_{H₂S} = 0.14 to 14.5 psia (1 to 100 kPa), the P_{H₂} buildup inside their sensors varied as follows:

- 44 to 116 psia (0.3 to 0.8 MPa) at pH 6.5,
- 1,600 to 3,600 psia (11 to 25 MPa) at pH 5.5, and
- >5,000 psia (> 34 MPa) at pH 4.5.

By comparison, their data for CP in a pH 6.5 NaCl brine condition at -1,100 mV SCE yielded a P_{H₂} of ~80 psia (~0.6 MPa), comparable to the sour condition at this pH, and much lower than P_{H₂} than for the aqueous sour solutions at pH 5.5 and especially that at pH 4.5.

Based on the above-mentioned comparison of the hydrogen pressure data from these tests, it is easy to understand that limiting hardness for carbon and low alloy steels to resist SSC at pH 3.5, as experience has shown, is in many cases HRC 22, but for seawater CP conditions (~pH 6.5), hardness limits to resist HSC would be generally higher due to the lower hydrogen charging severity for CP conditions, as shown by the work of Crolet and Maisonneuve.

Berkowitz and Heubaum (1984)¹¹ also compared hydrogen charging and environmental cracking severity in SSR tests for sour conditions with those from cathodic charging experiments for UNS G41300 steel. Data was presented for both sour and non-sour conditions plotting steady state hydrogen permeation current density versus applied cathodic current density (Figure 3).

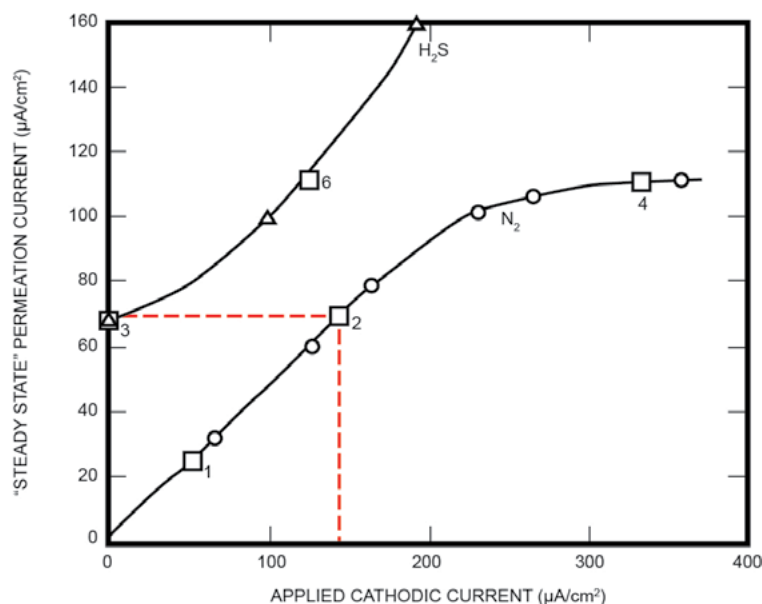


Figure 3: Steady State Permeation Current Density versus Applied Cathodic Current Density for (a) Sour Conditions (Upper Curve) and (b) Non-H₂S N₂-Purged Cathodic Charging Conditions (Lower Curve)¹¹

- These results showed that the steady state hydrogen permeation current from the sour test at open circuit conditions was ~80 $\mu\text{A}/\text{cm}^2$ whereas the non-sour tests (acid solution with NaAsO₂ with cathodic charging) required an applied cathodic current of ~150 $\mu\text{A}/\text{cm}^2$ to produce the same level of hydrogen permeation current. This connection is shown by the dashed lines in Figure 3.
- Then, their SSR time-to-failure and permeation data were compared based on steady state permeation current densities for various conditions (a condition of presumed equivalent hydrogen flux). The SSR data for either SSC or HSC from sour and non-sour tests, respectively, overlaid well on a plot of time-to-failure versus steady state permeation current density (See Figure 4). Therefore, resistance to fracture decreased with increasing hydrogen permeation current density no matter if the test was sour (H₂S feed) or non-sour (N₂ feed), and the point of “connection” between the severity of environmental cracking in the SSR tests for these two environments was when the steady state hydrogen permeation current density produced by these different types of exposures were the same.