INTERNATIONAL STANDARD

ISO 12473

Second edition
2017-10

General principles of cathodic protection in seawater

Principes généraux de la protection cathodique en eau de mer

Reference number
ISO 12473:2017(E)

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Contents

Page

Foreword ..... **v**

1 Scope **1**

2 Normative references **1**

3 Terms, definitions, abbreviations and symbols **1**

4 Application of cathodic protection in seawater **5**
- 4.1 General 5
- 4.2 Galvanic anode method 5
- 4.3 Impressed current method 6
- 4.4 Hybrid systems 6

5 Determination of level of cathodic protection **9**
- 5.1 Measurement of protection level 9
- 5.2 Reference electrodes 9
- 5.3 Potentials of reference electrodes 9
- 5.4 Verification of reference electrodes 9
- 5.5 Potential measurement 10

6 Cathodic protection potential criteria **10**
- 6.1 General 10
- 6.2 Carbon-manganese and low alloy steels 10
- 6.3 Other metallic materials 13
  - 6.3.1 General 13
  - 6.3.2 Stainless steels 13
  - 6.3.3 Nickel alloys 14
  - 6.3.4 Aluminium alloys 14
  - 6.3.5 Copper alloys 14

7 Design considerations **14**
- 7.1 Introduction 14
- 7.2 Technical and operating data 15
  - 7.2.1 Design life 15
  - 7.2.2 Materials of construction 15
- 7.3 Surfaces to be protected 15
- 7.4 Protective coatings 15
- 7.5 Availability of electrical power 16
- 7.6 Weight limitations 16
- 7.7 Adjacent structures 16
- 7.8 Installation considerations 16
- 7.9 Current demand 16

8 Effect of environmental factors on current demand **16**
- 8.1 Introduction 16
- 8.2 Dissolved oxygen 17
- 8.3 Sea currents 17
- 8.4 Calcareous deposits 17
- 8.5 Temperature 18
- 8.6 Salinity 18
- 8.7 pH 18
- 8.8 Marine fouling 18
- 8.9 Effect of depth 19
- 8.10 Seasonal variations and storms 19

9 Secondary effects of cathodic protection **19**
- 9.1 General 19
- 9.2 Alkalinity 19
- 9.3 Environmentally-assisted cracking 19

9.3.1 General 19
9.3.2 Hydrogen embrittlement 20
9.3.3 Corrosion fatigue 20
9.4 Chlorine 21
9.5 Stray currents and interference effects 21

10 Use of cathodic protection in association with coatings 21
10.1 Introduction 21
10.2 Coating selection 22
10.3 Coating breakdown 22

Annex A (informative) **Corrosion of carbon-manganese and low-alloy steels 24**

Annex B (informative) **Principles of cathodic protection 28**

Annex C (informative) **Reference electrodes 31**

Annex D (informative) **Corrosion of metallic materials other than carbon-manganese and low-alloy steels typically subject to cathodic protection in seawater 35**

Bibliography 37

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

This document was prepared by the European Committee for Standardization (CEN) (as EN 12473:2014) and was adopted, without modification, by Technical Committee ISO/TC 156, *Corrosion of metals and alloys*.

This second edition cancels and replaces the first edition (ISO 12473:2006), which has been technically revised.

General principles of cathodic protection in seawater

1 Scope

This document covers the general principles of cathodic protection when applied in seawater, brackish waters and marine mud. It is intended to be an introduction, to provide a link between the theoretical aspects and the practical applications, and to constitute a support to the other standards devoted to cathodic protection of steel structures in seawater.

This document specifies the criteria required for cathodic protection. It provides recommendations and information on reference electrodes, design considerations and prevention of the secondary effects of cathodic protection.

The practical applications of cathodic protection in seawater are covered by the following standards:

— EN 12495, *Cathodic protection for fixed steel offshore structures*;

— ISO 13174, *Cathodic protection of harbour installations (*ISO 13174*)*;

— EN 12496, *Galvanic anodes for cathodic protection in seawater and saline mud*;

— EN 13173, *Cathodic protection for steel offshore floating structures*;

— EN 16222, *Cathodic protection of ship hulls*;

— EN 12474, *Cathodic protection of submarine pipelines*;

— ISO 15589-2, *Petroleum, petrochemical and natural gas industries — Cathodic protection of pipeline transportation systems — Part 2: Offshore pipelines*.

For cathodic protection of steel reinforced concrete whether exposed to seawater or to the atmosphere, ISO 12696 applies.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 50162, *Protection against corrosion by stray current from direct current systems*

ISO 8044, *Corrosion of metals and alloys — Basic terms and definitions*

3 Terms, definitions, abbreviations and symbols

For the purposes of this document, the terms and definitions given in ISO 8044 and the following apply.

NOTE The definitions given below prevail on their versions in ISO 8044.

3.1
acidity
presence of an excess of hydrogen ions over hydroxyl ions (pH < 7)

3.2
alkalinity
presence of an excess of hydroxyl ions over hydrogen ions (pH > 7)

3.3
anaerobic condition

absence of free oxygen dissolved in the electrolyte

3.4
calcareous deposits

minerals precipitated on the metallic cathode because of the increased alkalinity caused by cathodic protection

3.5
cathodic disbondment

failure of adhesion between a coating and a metallic surface that is directly attributable to the application of cathodic protection

3.6
cathodic protection system

entire installation that provides cathodic protection

Note 1 to entry: It may include anodes, power source, cables, test facilities, isolation joints, electrical bonds.

3.7
coating breakdown factor

fc

ratio of cathodic current density for a coated metallic material to the cathodic current density of the bare material

3.8
copper/copper sulphate reference electrode

reference electrode consisting of copper in a saturated solution of copper sulphate

3.9
dielectric shield

alkali resistant organic coating applied to the structure being protected in the immediate vicinity of an impressed current anode to enhance the spread of cathodic protection and minimize the risk of hydrogen damage to the protected structure in the vicinity of the anode

3.10
driving voltage

difference between the structure/electrolyte potential and the anode/electrolyte potential when the cathodic protection is operating

3.11
electro-osmosis

passage of a liquid through a porous medium under the influence of a potential difference

3.12
environmentally assisted cracking

cracking of a susceptible metal or alloy due to the conjoint action of an environment and stress

3.13
groundbed

system of immersed electrodes connected to the positive terminal of an independent source of direct current and used to direct the cathodic protection current onto the structure being protected

3.14
hydrogen embrittlement

process resulting in a decrease of the toughness or ductility of a metal due to absorption of hydrogen

3.15
hydrogen stress cracking
HSC
cracking that results from the presence of hydrogen in a metal and tensile stress (residual and/or applied)

Note 1 to entry: HSC describes cracking in metals which may be embrittled by hydrogen produced by cathodic polarization without any detrimental effect caused by specific chemicals such as sulphides.

3.16
isolating joint (or coupling)
electrically discontinuous joint or coupling between two lengths of pipe, inserted in order to provide electrical discontinuity between them

3.17
master reference electrode
reference electrode, calibrated with the primary calibration reference electrode, used for verification of reference electrodes used for field or laboratory measurements

3.18
over-polarization
occurrence in which the structure to electrolyte potentials are more negative than those required for satisfactory cathodic protection

Note 1 to entry: Over-polarization provides no useful function and might even cause damage to the structure.

3.19
pitting resistance equivalent
PREN
indication of the resistance of a corrosion resistant alloy to pitting in the presence of water, chlorides and oxygen or oxidation environment, accounting for the beneficial effects of nitrogen

Note 1 to entry: For the purposes of this document, PREN is calculated as follows: PREN = % Cr + 3,3[(% Mo) + 0,5 (% W)] + 16 (% N).

3.20
potential gradient
difference in potential between two separate points in the same electric field

3.21
primary calibration reference electrode
reference electrode used for calibration of master reference electrodes is the normal hydrogen electrode (N.H.E.)

Note 1 to entry: The official reference electrode, standard hydrogen electrode (S.H.E.), which considers the fugacity coefficient for hydrogen gas and the activity coefficient for H^+ ions, is practically impossible to manufacture.

3.22
protection current
current made to flow into a metallic structure from its electrolytic environment in order to achieve cathodic protection of the structure

3.23
reference electrode
electrode having a stable and reproducible potential that is used as a reference in the measurement of electrode potentials

Note 1 to entry: Some reference electrodes use the electrolyte in which the measurement is carried out. Their potential varies according to the composition of this electrolyte.

3.24

resistivity (of an electrolyte)

resistivity is the resistance of an electrolyte of unit cross section and unit length

Note 1 to entry: It is expressed in ohm.metres (Ω.m). The resistivity depends, amongst other things, upon the amount of dissolved salts in the electrolyte.

3.25

saturated calomel reference electrode

reference electrode consisting of mercury and mercurous chloride in a saturated solution of potassium chloride

3.26

silver/silver chloride reference electrode

reference electrode consisting of silver, coated with silver chloride, in an electrolyte containing a known concentration of chloride ions

Note 1 to entry: Silver/silver chloride/ saturated KCl electrodes are electrodes currently used in the laboratory and for master reference electrode.

Note 2 to entry: Silver/silver chloride/seawater (Ag/AgCl/seawater) electrodes are electrodes currently used for field measurements in seawater.

3.27

slow strain rate test

test for evaluating susceptibility of a metal to environmentally assisted cracking (3.12 in this document) that most commonly involves pulling a tensile specimen to failure in a representative environment at a constant displacement rate chosen to generate nominal strain rates usually in the range 10^{-5} s^{-1} to 10^{-8} s^{-1}

Note 1 to entry: Slow strain rate testing may also be applied to other specimen geometries, e.g. bend specimens.

3.28

specified minimum yield strength

SMYS

minimum yield strength prescribed by the specification under which steel components are manufactured, obtained through standard analysis and representing a probabilistic value

Note 1 to entry: It is an indication of the minimum stress steel components may experience that will cause plastic (permanent) deformation (typically 0,2 %).

3.29

stray currents

current flowing through paths other than the intended circuits

3.30

structure to electrolyte potential

difference in potential between a structure and a specified reference electrode in contact with the electrolyte at a point sufficiently close to, but without actually touching the structure, to avoid error due to the voltage drop associated with any current flowing in the electrolyte

3.31

sulphate reducing bacteria

SRB

group of bacteria that are found in most soils and natural waters, but active only in conditions of near neutrality and absence of oxygen and that reduce sulphates in their environment, with the production of sulphides and accelerate the corrosion of structural materials

3.32
telluric currents
electrical currents induced by time varying changes in the earth's magnetic field

Note 1 to entry: They are able to flow in metallic conductors laid in the soil or in the sea.

3.33
zinc reference electrode
electrode consisting of pure zinc or zinc alloy specific for anodes in contact with the electrolyte in which the measurements are carried out

Note 1 to entry: Zinc reference electrodes are currently used for measurements in seawater carried out at permanent locations.

4 Application of cathodic protection in seawater

4.1 General

Metallic materials in aqueous environments such as seawater are susceptible to corrosion produced by electrochemical reactions. General information on corrosion of carbon-manganese or low alloy steels is given in Annex A.

Cathodic protection is an electrochemical corrosion prevention system based on the decrease of corrosion potential to a level at which the corrosion rate of the metal is significantly reduced (ISO 8044). For industrial structures, residual corrosion rates less than 10 µm/yr are typically achieved with a fully effective cathodic protection system.

Cathodic protection is achieved by applying a voltage able to supply sufficient current to the metallic surface to lower the potential. General information on the principles of cathodic protection is given in Annex B.

There are two methods whereby the protection current can be supplied to polarize the surface:

a) galvanic anode systems in which the current for protection is provided by a metal of more negative corrosion potential than the item to be protected i.e. aluminium, zinc and magnesium alloys for steel and iron for copper and copper based alloys,

b) impressed current systems in which direct current (normally produced from alternating current by a transformer rectifier) is used in conjunction with relatively inert anodes such as graphite, thin coatings of platinum or activated mixed metal oxides on metals such as titanium or niobium, lead alloys, silicon-iron, etc; in some cases a consumable anode such as scrap iron or steel is used.

4.2 Galvanic anode method

If two dissimilar metals are connected in the same electrolyte, a galvanic cell is produced. The open circuit voltage is the natural potential difference which exists between the two metals. If the circuit is closed, the potential difference drives an electrical current. The more negative electrode behaves as an anode and it releases electrons to the circuit and dissolves more rapidly while the more positive electrode behaves as a cathode and dissolves less readily. The use of galvanic anodes in cathodic protection is based on this phenomenon.

Assuming the structure to be protected is made of steel, aluminium or zinc alloy galvanic anodes can be used to form the cell, because these alloys are less noble (more electronegative) than steel. Anode attachment to the structure is made through a steel core on to which the anode material is cast. Thus the structure is in metallic contact with the anode material and also in electrolytic contact with it once the structure is immersed. This is represented in Figure 1, where it is seen that the electrons released by the dissolution of metal atoms are consumed in the cathodic reduction of oxygen on the structure and hydroxyl ions are produced at the structure surface.

4.3 Impressed current method

Most impressed current anodes are of a type that do not dissolve readily on anodic polarization but sustain alternative reactions which involve decomposition of the aqueous environment, or oxidizing of dissolved chloride ions in it, i.e:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{1}$$

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{2}$$

Figure 2 represents an impressed current cathodic protection system using an inert anode in seawater where in the secondary reactions hydrogen and chlorine are evolved.

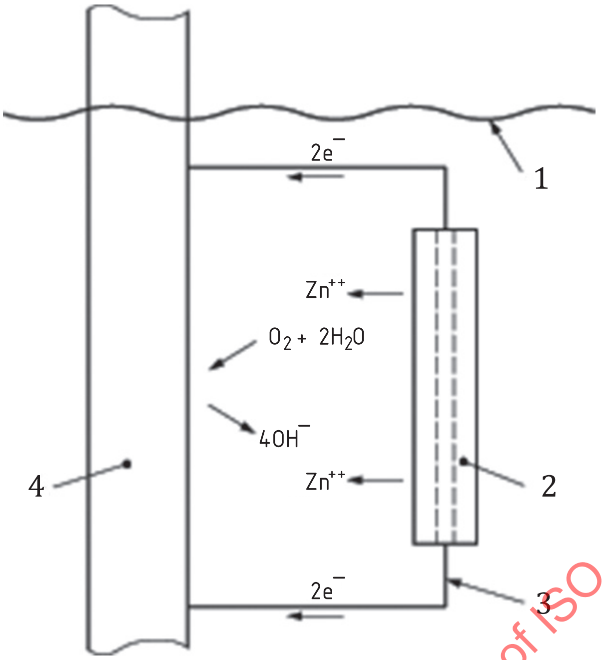
The advantages of the impressed current system are that it is possible to have a large adjustable driving voltage so that relatively few anodes need to be installed even to protect large uncoated structures in comparatively high resistivity environments. A comparison of galvanic and impressed current anode systems is given in Table 1.

4.4 Hybrid systems

These comprise a combination of galvanic anodes and externally powered impressed current anodes.

Because there can be a significant time between the initial immersion of a structure and the full commissioning of the impressed current system it is usual to fit sufficient galvanic anodes to polarize the critical region of the structure.

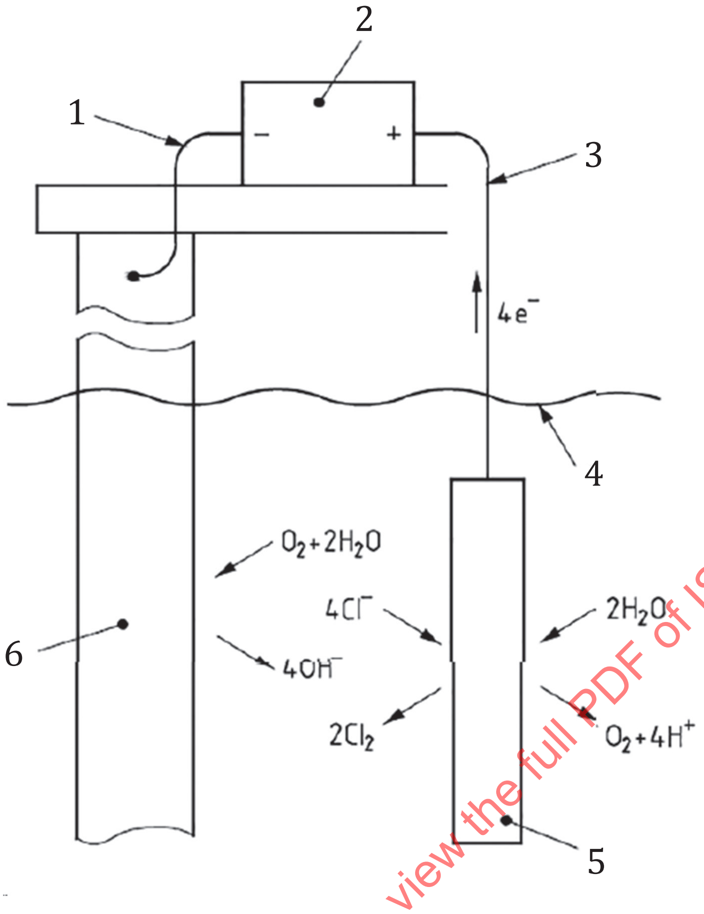
The galvanic anodes should also provide protection when the impressed current system is shut down for subsea survey and maintenance during the life of the structure.



Key

1	seawater
2	galvanic anode
3	anode attachment
4	protected structure in seawater

Figure 1 — Representation of cathodic protection using a galvanic anode on a structure in the seawater



Key

1	insulated cathode cable
2	power supply (dc)
3	insulated anode cable
4	seawater
5	impressed current anode
6	protected structure in seawater

Figure 2 — Representation of impressed current cathodic protection using inert anode in seawater

Table 1 — Comparison of galvanic and impressed current systems

	Galvanic systems	**Impressed current systems**
Environment	Use can be impracticable in soils or waters of high resistivity.	Use is not restricted by resistivity of soils or waters.
Installation	Simple to install.	Needs careful design otherwise can be complicated.
Power source	Independent of any source of electric power. Cannot be wrongly connected electrically.	External supply necessary. Care needs to be taken to avoid electrical connection in wrong direction.
Anodes	Bulk of anode material can restrict water flow and introduce turbulence and drag penalties.	Usually lighter and few in number. Anodes can be designed to have minimum effect on water flow.

Table 1 *(continued)*

	Galvanic systems	Impressed current systems
Control	Tendency for their current to be self adjusting.	Controllable. Control usually automatic and can be continuous.
Interaction	They are less likely to affect any neighbouring structures.	Effects on other structures situated near the anodes need to be assessed.
Maintenance	Generally not required. May be renewed in some circumstances.	Equipment designed for long life but regular checks required on electrical equipment in service. Continual power required.
Damage	Anodes are robust and not very susceptible to mechanical damage. Where a system comprises a large number of anodes, the loss of a few anodes has little overall effect on the system. Connections have to be able to withstand any forces applied to the structure. Electrical insulation of cables is not necessary.	Anodes lighter in construction and therefore less resistant to mechanical damage. Loss of anodes can be more critical to the effectiveness of a system. Complete electrical insulation of positive cables exposed to electrolyte is mandatory.

5 Determination of level of cathodic protection

5.1 Measurement of protection level

To determine whether a structure is adequately protected it is necessary to measure the metallic material/seawater potential. To achieve this, connections shall be made to both the structure and the electrolyte. The connection to the structure is a simple metallic one but for the connection to the electrolyte, a metal conductor has to be introduced into the electrolyte. This conductor introduces its own electrode potential, which inevitably becomes included in the measured value. This situation can be resolved by using a conductor of reproducible and defined electrode potential; this is called a reference electrode.

5.2 Reference electrodes

Most often, the reference electrodes used in the field are electrodes such as silver/silver chloride/seawater electrodes or high purity or anode alloy specification zinc electrodes. These electrodes are considered sufficiently accurate for most practical purposes even if the electrolyte is not fully defined and reproducible.

NOTE Saturated calomel electrode or silver/silver chloride/potassium chloride electrodes are not often used for monitoring and controlling cathodic protection systems in seawater, because they are insufficiently robust for field use. In addition, calomel electrodes are not considered acceptable for environmental reasons.

Details of the reference electrodes for marine applications are given in Annex C.

5.3 Potentials of reference electrodes

The potentials of various reference electrodes with respect to the normal hydrogen electrode are given in Table C.1 of Annex C.

5.4 Verification of reference electrodes

Reference electrodes used in the field shall be periodically checked with a master reference electrode having a valid calibration certificate. This master electrode shall be periodically (at least once a year) calibrated to a primary calibration reference electrode (N.H.E.).

Reference electrodes such as the saturated calomel electrode or various silver/silver chloride electrodes with different concentrations of KCl electrolyte may be used as master reference electrodes.

5.5 Potential measurement

Irrespective of the type of reference electrode used the measurement of the potential difference between the metal surface and the electrolyte can be affected by the potential drop produced by the protection current as it flows through the surrounding electrolyte to the structure. This effect, known as the IR drop, makes the measured potential more negative than the actual potential at the metal / electrolyte interface. The IR drop is dependent on electrolyte resistivity and is particularly relevant to buried structures.

IR drop errors are generally considered insignificant in marine applications especially when galvanic anodes are used. However potential measurements using “Instant Off” techniques or “coupon Instant Off” techniques (see EN 13509), or after switch-off of impressed current systems may be necessary in order to adequately demonstrate the achievement of the protection criteria, especially in brackish waters and close to impressed current anodes.

To determine the risks of overprotection (see 6.1) it is essential to measure the structure potential immediately after switching off the current source and before the metallic material depolarizes. This can be achieved with a fast sampling data logger or an oscilloscope.

If the measured potentials are fluctuating it may be due to either stray currents or telluric currents interference.

6 Cathodic protection potential criteria

6.1 General

The potential criteria required for the cathodic protection of the most often used metallic materials in seawater, brackish waters and saline mud are given in Table 2. Other requirements are provided by the standards covering specific applications. Other values can be used if proven reliable, justified and documented.

Some metallic materials are detrimentally affected by excessive negative potentials (overprotection) under some circumstances (as described in 9.2 and 9.3). In such cases, the protection criteria shall include a negative limit to prevent these detrimental effects (see Table 2).

The potential criteria and limit values related to the risks of overprotection are “polarized” and are expressed without IR errors.

If insufficient documentation is available for a given material, the specific negative potential limit relative to the metallurgical and mechanical conditions shall be determined by testing at the limit polarized potential.

Excessive negative potentials can also be detrimental to the adherence of coatings (as described in Clause 10).

6.2 Carbon-manganese and low alloy steels

When carbon steel in seawater is polarized to −0,80 V (measured with respect to Ag/AgCl/seawater reference electrode) or more negative potentials, the corrosion rate is reduced to an acceptably low level.

In the case of steels in contact with waters or mud containing critical levels of sulfate reducing bacteria (in anaerobic conditions at the metallic surface) the potential for protection shall be −0,90 V (Ag/AgCl/seawater reference electrode) instead of −0,80 V. Where there is the possibility of microbial corrosion, coatings should be used and in spaces with restricted access the use of biocides should be considered.

When surface temperature of steel is higher than 60 °C and when the temperature of the electrolyte in the vicinity of the steel surface is also high due to a low cooling effect by the environment (e.g. surfaces buried in the mud or surfaces in contact with warm seawater), the potential for protection shall be

−0,90 V (Ag/AgCl/seawater reference electrode). Between 40 °C and 60 °C the protection potential shall be interpolated between −0,80 V and −0,90 V (Ag/AgCl/seawater reference electrode).

As potential becomes more negative there can be blistering or cathodic disbondment of coatings (see Clause 10), an adverse effect on fatigue properties (see 9.3.3) and a risk of HSC (Hydrogen stress cracking) of high strength steels (see 9.3.2) due to hydrogen embrittlement. To prevent these detrimental effects the potential has to be limited.

For carbon-manganese and low alloy steels with a SMYS equal or lower than 550 N/mm^2, a negative limit of –1,10 V (Ag/AgCl/seawater reference electrode) prevents these various risks and is achieved on structures protected by zinc or aluminium galvanic anodes.

For steels with a SMYS higher than 550 N/mm^2 a negative limit of potential in the range −0,83 V to −0,95 V (Ag/AgCl/seawater reference electrode) is generally specified. For a given material, the specific negative potential limit relative to the metallurgical and mechanical conditions shall be determined by testing at the limit polarized potential. Information is available in[14].

NOTE Following cases of HSC (Hydrogen Stress Cracking) in high strength steels, used e.g. in the fabrication of jack up offshore drilling rigs, particularly in areas adjacent to welds, it has been established by slow strain rate tests that hydrogen damage to the steel was insignificant provided that the cathodic potentials were not more negative than −0,83 V (Ag/AgCl/seawater reference electrode)[16].

Figure 3 gives a summary of the effects of potential on steels in seawater expressed versus the reference electrodes normally used in seawater.

Table 2 — Potential criteria for the cathodic protection of various metals and alloys in seawater

Material	Minimum negative potential (V vs. Ag/AgCl/seawater)	Maximum negative potential (V vs. Ag/AgCl/seawater)
Carbon-manganese and low-alloy steels with SMYS equal or lower than 550 N/mm^2		
In aerobic environment	−0,80	−1,10
In anaerobic environment and/or steel temperature > 60 °C	−0,90	−1,10
High strength steels (SMYS higher than 550 N/mm^2)	−0,80	−0,83 to −0,95 (see Footnote [a])
Aluminium alloys (Al Mg and Al Mg Si)	−0,80 (negative potential swing 0,10 V)	−1,10
Austenitic steels or nickel base alloys containing chromium and/or molybdenum		
— (PREN ≥ 40)	−0,30	no limit if fully austenitic, if not see Footnote [c]
— (PREN < 40)	−0,50 (see Footnote [b])	no limit if fully austenitic, if not see Footnote [c]
Duplex or martensitic stainless steels	−0,50 (see Footnote [b])	see Footnote [c]

[a] The negative potential limit should be determined by testing of the high strength steel for specific metallurgical and mechanical conditions (see 9.3.2).

[b] For most applications these potentials are adequate for the protection of crevices although more positive potentials may be considered if documented.

[c] Depending on metallurgical structure, these alloys can be susceptible to Hydrogen Stress Cracking (HSC) and potentials that are too negative should be avoided (see 6.3.2 and 9.3.2).

[d] High strength nickel copper alloys can be subject to HSC and potentials that result in significant hydrogen evolution should be avoided (see 9.3.2).

Table 2 *(continued)*

Material	**Minimum negative potential** (V vs. Ag/AgCl/seawater)	**Maximum negative potential** (V vs. Ag/AgCl/seawater)
Copper alloys		
without aluminium	−0,45 to −0,60	no limit
with aluminium	−0,45 to −0,60	−1,10
Nickel - copper alloys	−0,50	see Footnote [d]

[a] The negative potential limit should be determined by testing of the high strength steel for specific metallurgical and mechanical conditions (see 9.3.2).

[b] For most applications these potentials are adequate for the protection of crevices although more positive potentials may be considered if documented.

[c] Depending on metallurgical structure, these alloys can be susceptible to Hydrogen Stress Cracking (HSC) and potentials that are too negative should be avoided (see 6.3.2 and 9.3.2).

[d] High strength nickel copper alloys can be subject to HSC and potentials that result in significant hydrogen evolution should be avoided (see 9.3.2).

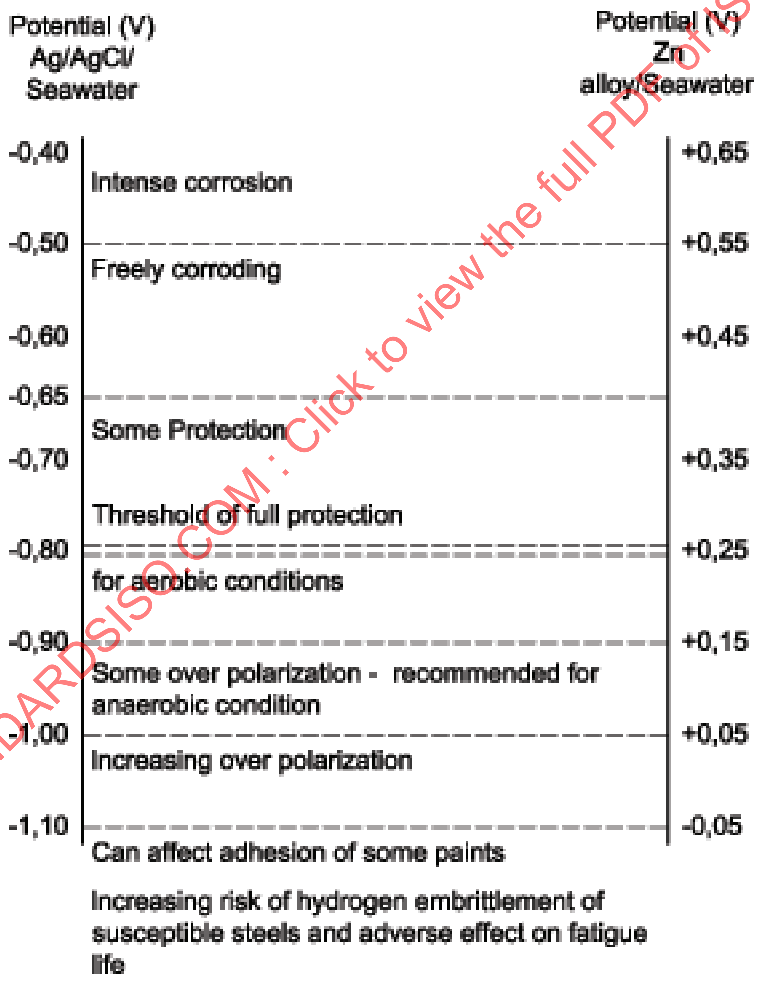


Figure 3 — Corrosion, cathodic protection and over-polarization regimes of steel expressed as a function of electrode potential

6.3 Other metallic materials

6.3.1 General

General information on corrosion of metallic materials other than carbon-manganese or low alloy steels typically subject to cathodic protection in seawater is given in Annex D.

6.3.2 Stainless steels

6.3.2.1 Role of microstructure

Austenitic microstructure is compatible with the range of potentials experienced in cathodic protection. Ferritic and martensitic microstructures can suffer from hydrogen embrittlement at too negative potentials in the form of HSC (Hydrogen Stress Cracking) which is a non-ductile mode of failure caused by an interaction between stresses, cathodic protection and a susceptible material (see 9.3.2).

6.3.2.2 Austenitic stainless steels

Austenitic stainless steels can be generally protected using a potential of −0,50 V (Ag/AgCl/seawater reference electrode) but for the more corrosion resistant stainless steels (PREN ≥ 40) a potential of −0,30 V (Ag/AgCl/seawater reference electrode) is accepted for most applications.

However, in view of the wide range of austenitic stainless steels available, other potentials should only be used if they are substantiated by documented service performance or appropriate laboratory tests.

Austenitic stainless steels are not vulnerable to HSC if over-polarized when their metallurgical structure is fully austenitic. However, limitations identical to duplex stainless steels (see 6.3.2.3) shall be observed when ferritic and/or martensitic phases are present, e.g. due to cold deformation or welding (see DNV RP B401[17]).

6.3.2.3 Duplex stainless steels

The positive limit for protection may be taken as that for austenitic stainless steels (see 6.3.2.2).

When cathodically protected, these alloys can be susceptible to hydrogen embrittlement in the form of HSC if their metallurgical structure is inappropriate, e.g. if they contain too much ferrite, coarse grain size or misaligned grains. Welds and their heat affected zones are the most likely locations for such unfavourable microstructures. The microstructure is appropriate if there is a good phase balance, i.e. a minimum of 40 % austenite in the microstructure, and the parent metal is correctly quenched after solution annealing. Welds and their heat affected zones will be equally resistant to cracking provided the content and distribution of austenite is satisfactory.

Duplex stainless steels known to have appropriate parent and weld metal microstructures will not normally be susceptible to HSC if their maximum negative potential in seawater is −1,05 V (Ag/AgCl/seawater reference electrode).

Where the microstructure of the material or the weld area is not in the optimum condition, a less negative potential limit should be used. If the design potential of the structure is more negative than −0,80 V (Ag/AgCl/seawater reference electrode) a special assessment shall be carried out to ensure that the risk of HSC is minimized [23],[9]. Such an assessment study shall consider all load contributions causing stress and strain. DNV-RP-F112 can be used to assess acceptable stresses and strains [13].

6.3.2.4 Martensitic stainless steels

The positive limit for protection may be taken as that for austenitic stainless steels (see 6.3.2.2).

If the design potential of the structure is more negative than −0,80 V (Ag/AgCl/seawater reference electrode) HSC constitutes a significant risk for martensitic stainless steels. A special assessment considering stresses and strains shall be carried out to ensure that the risk of HSC is minimized. Information is given in [23].

6.3.3 Nickel alloys

Cathodic protection of austenitic nickel alloys containing chromium and molybdenum as main alloying elements may be performed using the same protection criteria as for austenitic stainless steels (see 6.3.2.2).

Nickel copper alloys have been used for corrosion resistant purposes for a variety of uses in a marine environment including the cladding of risers, fasteners, propeller shafts and in water boxes. In most cases these items will be connected to large areas of steelwork at a potential in the range of −0,80 V to −1,10 V (Ag/AgCl/seawater reference electrode) but potentials of the order of −0,20 V (Ag/AgCl/seawater reference electrode) can be adequate for protection.

Failures of subsea bolts made of high strength nickel copper and nickel chromium iron alloys have been reported. The mode of failure has been attributed to hydrogen generated in the normal operations of sacrificial anodes and impressed current cathodic protection systems, causing embrittlement of the material.

At present it is not possible to recommend safe levels of cathodic protection for these materials but it would appear that slow strain rate tensile tests using hydrogen charged test pieces can be used for screening materials considered susceptible to hydrogen embrittlement.

6.3.4 Aluminium alloys

The potential of the aluminium magnesium and the aluminium magnesium silicon alloys in seawater is generally in the range of −0,70 V to −0,90 V (Ag/AgCl/seawater reference electrode) and they can be cathodically protected in seawater with a negative potential swing of 0,1 V from the corrosion potential.

The negative limit is usually taken as −1,10 V (Ag/AgCl/seawater reference electrode). More negative potentials need to be avoided particularly in stagnant conditions as the alkali generated can strongly attack aluminium to produce aluminate. Zinc and the aluminium anodes can be used for the protection of aluminium, except mercury containing aluminium anodes.

6.3.5 Copper alloys

The current densities required for the protection of copper alloys or iron/copper alloy couples could be significantly higher than those required for the protection of steel alone especially when the copper surface is oxide free. However, where the corrosion rate is solely controlled by the reduction of dissolved oxygen then the current density will not exceed the limiting current for oxygen reduction.

7 Design considerations

7.1 Introduction

The purpose of this clause is to outline some of the factors that can influence the design of a cathodic protection system. More detailed information is given in each of the respective standards.

When designing a cathodic protection system, it is important to ensure that the whole structure is adequately protected and that areas are not substantially over-polarized in order to avoid the possible adverse effects referred to in Clauses 9 and 10.

Using galvanic anodes, which are low voltage sources of current, a reasonably uniform distribution of current is not too difficult to achieve providing it is possible to distribute the anodes roughly in proportion to the exposed surface area. However difficulties can arise if the local steel area is high and restrictions are placed on the location of the anodes (e.g. in way of nodes, etc); in such circumstances it could be advantageous to use coatings.

Impressed current anodes can be considered as a point source of high current. This needs to be taken into account in the design in order to achieve adequate protection remote from the anodes without significant over-polarization local to the anodes. In order to achieve adequate distribution of protection, it might be advantageous to consider the use of dielectric shields local to the anodes or to install the anodes at some distance from the structure.

The information required to design a comprehensive cathodic protection system depends to a large extent upon the type, complexity and operational parameters of the structure. In general the information required includes:

a) technical and operating data of the structure;

b) current demand.

7.2 Technical and operating data

7.2.1 Design life

For many structures such as fixed offshore structures and pipelines the system should be capable of protecting the structure for its full design life, but for ships and other floating structures capable of being dry docked and which are protected with galvanic anodes, the design life of the system should coincide with an appropriate docking interval.

The design life of cathodic protection system should also include non-operational periods when the structure or vessel is exposed to seawater, such as building, testing, storage, transportation, installation, etc.

7.2.2 Materials of construction

The type of materials to be protected shall be considered as high strength steels, duplex stainless steels and certain non-ferrous alloys are susceptible to a reduction in their mechanical properties when subjected to excessive negative potentials (over-polarized) and the recommendations given in Clause 5 with regards to the maximum negative limit should be complied with.

This can influence the selection of the systems, the location of the anodes and the possible use of coatings or dielectric shields.

7.3 Surfaces to be protected

All external immersed surfaces (including those below the mean water level of fixed offshore structures) should be protected by cathodic protection. These include the main structure and any other appurtenances.

It is usual to refer to the superficial immersed area when the area of the cathode is being considered and this can be calculated from the full detailed and dimensional construction drawings. However, a corroded or weathered surface will be rough and the true surface area can be significantly greater. Due allowance should be made for elements of the structure which are buried and electrically continuous with the structure.

7.4 Protective coatings

While organic coatings are not entirely impermeable to oxygen and water they do restrict corrosion when applied to the surface of a metal. The bulk of the corrosion on a painted surface does not occur beneath the intact coating but at the base of holidays and pin holes. If cathodic protection is applied to a painted surface, the coating acts as a substantial resistive barrier to current flow and the current flows to the holidays or pin holes. In terms of cathodic protection the effect of coatings is to reduce the area of the exposed steelwork and thereby reduce the overall current required for protection and enhance the current distribution.

7.5 Availability of electrical power

The use of impressed current cathodic protection depends on the availability of a continuous supply of electrical power.

7.6 Weight limitations

In the case of fixed offshore structures, the float out weight can be very important and this can influence the type of system to be used. The use of a hybrid system can considerably reduce the weight compared with a full galvanic anode system.

7.7 Adjacent structures

The presence of other structures in the vicinity can result in corrosion by stray currents or a drainage on the structure to be protected. Insulation or bonding together with due allowance for the additional material to be protected should be considered.

7.8 Installation considerations

Galvanic anode installations could require a large number of anodes to be attached to the structure and because of stress concentrations there could be restrictions to the location where such anodes might be attached.

While it might be possible to use fewer impressed current anodes, the routing of cables feeding the anodes and reference electrodes can pose problems. Cables should be run through the structure wherever possible using appropriate cofferdam arrangements at penetrations to ensure water tightness.

Where cables are run through conduits attached to the structure then these should be properly designed to withstand all the conditions likely to be encountered.

Long unsupported cable lengths should be avoided to reduce the risk of cable damage during operation.

Where cables run through hazardous areas appropriate safety precautions shall be taken.

7.9 Current demand

As discussed in Clause 5, the criterion for protection is that the potential of the metal with respect to the electrolyte immediately adjacent to it should be at all positions more negative than the appropriate protective potentials for the particular metal.

The current required to achieve this will vary according to the type of structure to be protected and the environmental conditions prevailing.

Recommendations on current densities to be used for each practical application are given in the respective standards.

The various environmental factors that affect the current requirements are discussed in Clause 8.

8 Effect of environmental factors on current demand

8.1 Introduction

The chemical and physical characteristics of the environment and the rate at which they can change daily or seasonally need to be considered in assessing current density requirements. The principal factors affecting current density requirements in seawater are velocity of water movement, salinity, pH, temperature and water depth and their effects on the dissolved oxygen content, calcareous deposits and marine fouling.

This clause outlines the possible effect of these factors on the current density requirements.

8.2 Dissolved oxygen

One of the most important factors that have to be taken into account in the design of a cathodic protection system is that of dissolved oxygen in seawater.

It is considered that there is a direct correlation between the dissolved oxygen content and the corrosion rate in seawater and that the cathodic current density required to provide corrosion protection is proportional to the rate at which dissolved oxygen diffuses to the steel surface.

The dissolved oxygen content in seawater varies considerably with water depth and geographic location and since the solubility is a function of temperature and salinity it can also vary with the season.

8.3 Sea currents

As the rate of transport of dissolved oxygen to a steel surface is diffusion controlled, increased sea currents will increase the cathodic protection current density requirements for bare steel, particularly during the initial polarization before calcareous deposits or fouling have had time to build up. Sediment in the sea can scour the surface and increases the current density required for protection.

8.4 Calcareous deposits

Well-formed calcareous deposits reduce the rate of diffusion of dissolved oxygen in the seawater to the steel surfaces and thereby reduce the current density necessary to maintain cathodic polarization.

The major constituents of the calcareous deposits are $CaCO_3$ polymorphs, aragonite and calcite, and the magnesium compound $Mg(OH)_2$ (brucite) but the actual composition depends on such factors as pH, temperature, current density, water flow rate and seawater depth.

Seawater picks up CO_2 from the atmosphere and also from marine organisms near the ocean surface which results in a supersaturated condition of $CaCO_3$.

The equilibrium reactions of the carbon dioxide/carbonate and water may be expressed as follows:

$$CO_2 + H_2O \rightarrow H_2CO_3 \tag{3}$$

$$H_2CO_3 \rightarrow HCO_3^- + H^+ \tag{4}$$

$$HCO_3^- \rightarrow CO_3^{2-} + H^+ \tag{5}$$

With the addition of OH^- to the system through the cathodic processes then the reactions:

$$HCO_3^- + OH^- \rightarrow H_2O + CO_3^{2-} \tag{6}$$

$$CO_3^{2-} + Ca^{2+} \rightarrow CaCO_3 ppt \tag{7}$$

can occur with the precipitation at the cathodic areas.

Over the current density range where scales form they are predominantly calcium carbonate. With increasing current density, the scale becomes thinner and more compact and the protection improves. It is generally accepted that a high initial current density should be induced on unpolarized steel immediately upon immersion in order to promote rapid cathodic polarization and formation of a high protective calcareous deposit. However, at very high current density the deposit could have significant magnesium content. It is present primarily as $Mg(OH)_2$ but possible with some $MgCO_3$. $Mg(OH)_2$ is unstable in seawater and it does not normally precipitate below a pH of about 9,7. In general, deposits rich in calcium carbonate are more protective than those rich in magnesium.

8.5 Temperature

Temperature has a significant influence on seawater resistivity, dissolved oxygen and calcareous deposit formation.

As the temperature along with salinity of seawater has a significant effect on the resistivity of seawater and as this is directly related to the effective resistance of galvanic anodes, it should be taken into account in the design of cathodic protection systems.

The effect of temperature on the limiting current density is complex in that as the temperature increases the oxygen solubility is lowered but the diffusion constant for oxygen is increased. The net effect could result in a slightly increased current density requirement with increasing temperature. The situation is further complicated by the increased solubility of $CaCO_3$ with decreasing temperature. This will reduce the protective nature of the deposits and potentially increase the current density requirements for protection.

8.6 Salinity

The major effect of salinity on cathodic protection is its influence on seawater resistivity and in general, for a given temperature, the higher the salinity the lower will be the resistivity and the dissolved oxygen content.

Therefore an increased salinity is beneficial in that it reduces the dissolved oxygen level and the anode resistance.

Where impressed current systems are used, any dilution by fresh water can cause wide fluctuations in the power required and this could lead to damage of the rectifiers unless they are suitably protected.

8.7 pH

The pH of open seawater varies from about 7,4 to 8,4 and is highly buffered by a complex carbonate system. However, a small decrease in pH could occur near the sea bed due to the decomposition of organic materials. This decomposition consumes oxygen and therefore the corrosion rate should be reduced but lowering of the pH will retard calcareous deposit formation. On the other hand, alkali produced by the cathodic reactions will assist in the production of calcareous deposits and reduce the current density required for protection.

8.8 Marine fouling

Marine fouling takes place on marine structures to various degrees depending on the material, geographic location, depth and season.

Fouling adds weight and wave loading to a structure, increases maintenance costs and can degrade the coating. Marine fouling reduces the effective steel surface exposed to seawater, preventing diffusion of oxygen to the surface and hence reducing the current density required for protection. However, on the other hand, the fouling organisms can become entrapped in the calcareous deposits causing voids in the deposit on the death of the organism. The micro environment produced by the death of the organism can produce conditions conducive to high rates of corrosion.

It is unlikely that precious metal impressed current anodes will be subjected to marine fouling during operation and although marine fouling of galvanic anodes could take place, it is probable that only the hard shell would mask portions of the anodes and reduce their effectiveness.

8.9 Effect of depth

Depth is likely to be associated with changes in temperature, solubility of oxygen and carbon dioxide flow rates and other environmental parameters. These should be considered and in particular the impact of these on the formation of calcareous deposits.

The effect of depth alone on cathodic protection current density requirements is not clear but it is unlikely that it will have a significant effect.

It would appear that there is little effect on the operation of aluminium and zinc anodes at depth.

At depth the hydrostatic pressure has been found to effect the hydrogen embrittlement of cathodically protected high tensile steels. In tests, the load to cause failure of notched high tensile steel specimens decreased with an increase in the hydrostatic pressure although the hydrogen permeation rate was not affected by the pressure increase.

8.10 Seasonal variations and storms

Changes in water temperature close to the surface and storms often associated with seasonal changes are likely to cause a disruption of the calcareous deposits and this could lead to an increase in current density requirements on structures close to the surface.

9 Secondary effects of cathodic protection

9.1 General

The application of cathodic protection can give rise to secondary effects such as the development of alkalinity and the generation of hydrogen on the protected structure and chlorine gas on the impressed current anodes.

The effects that can occur include those given in 9.2 to 9.5.

9.2 Alkalinity

Alkalinity can degrade oil based alkyd and oleo-resinous coatings by saponification (see Clause 10). Alkalinity favours the formation of calcareous deposits which can be beneficial since the current density needed to maintain cathodic protection is reduced. However, such deposits can cause a roughening of impellers or propellers which can then produce cavitation effects elsewhere in the system.

If the protected metal is amphoteric it could be attacked by the alkali. Aluminium is susceptible to this effect and cathodic protection should therefore be applied to it only if the potential is maintained within certain limits (see Clause 5). Aluminium pigmented paints can also be degraded by alkali in stagnant conditions.

In exceptional circumstances lead can also be attacked but the concentration of the alkaline in the electrolyte has to be high.

9.3 Environmentally-assisted cracking

9.3.1 General

Two of the basic design requirements for marine structures are that they possess adequate static strength and fatigue endurance. Both are impaired by environmentally assisted cracking and therefore it is necessary to consider the effect of cathodic protection on this phenomenon.

Environmentally-assisted cracking includes amongst others corrosion fatigue and hydrogen embrittlement and the application of different levels of cathodic protection can markedly affect the susceptibility and severity of materials to this phenomenon.

9.3.2 Hydrogen embrittlement

It is generally considered that as a result of the application of cathodic protection at the more negative potentials atomic hydrogen is produced and because of its small size can diffuse through a metal lattice whereas the much larger molecular hydrogen cannot.

The embrittling effects of hydrogen in steel are associated with the presence of hydrogen in the ferrite or martensite interfering with the plastic properties. Under these conditions, when the steel is strained at an appropriate rate and temperature it cannot plastically flow to locally accommodate a notch or stress raiser. As a consequence, a crack is generated and brittle fracture can ensue. For this to occur, the hydrogen needs to have time to diffuse to the site of dislocation movement to prevent plastic flow. Therefore hydrogen embrittlement is most likely to occur at slow strain rates. At low temperatures, the hydrogen diffusion rate could be too low for interaction with dislocation movement, while at high temperatures the hydrogen is ineffective in causing embrittlement.

HSC (Hydrogen Stress Cracking), consecutive to hydrogen embrittlement, is a non-ductile mode of failure caused by an interaction between stresses, cathodic protection and a susceptible material. A special assessment is often necessary to ensure that the risk for HSC is minimized. A major part of the assessment is to consider stresses and strains. All load contributions causing stress and strain shall be included.

9.3.3 Corrosion fatigue

Fatigue is a process of time delayed crack initiation and relatively slow crack propagation which can occur in metallic structures which are subjected to cyclic loading. Generally, the higher the cyclic stress the fewer the cycles to failure. The presence of fatigue or corrosion fatigue cracks can greatly reduce the static strength and load bearing capabilities of steel structures.

In general, fatigue cracks tend to initiate at various flaws, defects or stress raisers and in offshore steel jacket structures they invariably initiate at the toes of welds where the residual stress levels are the highest, as described in BS 7608.

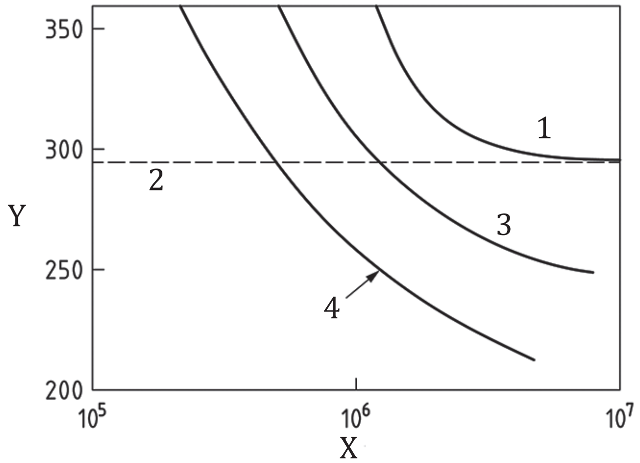
In the specific case of carbon and low alloy steels, these will exhibit a fatigue limit, in the absence of corrosion, which is a stress range below which fatigue cracking will not occur. This typically occurs at approximately 10^7 cycles as shown on a typical S-N curve (maximum dynamic stress vs. number of fatigue cycles before cracking) as illustrated Figure 4. Design codes of structures are based on this fatigue limit.

In the presence of a corrosive environment, cracking occurs in a shorter time than would be encountered as a result of the fluctuating stress alone. Where corrosion also occurs, the fatigue strength for the same number of cycles is significantly reduced and, importantly, there is no longer any fatigue limit.

Figure 4 illustrates the effect of a corrosive environment on the S-N curve.

The proper application of cathodic protection improves the fatigue resistance of materials exposed to seawater, even though it might not achieve the same level of fatigue resistance as measured in environments without any corrosive contamination. For this reason, where there is a risk of corrosion fatigue, it is essential that the cathodic protection should be applied in accordance with the criteria specified in this document. Structures codes dealing with fatigue do not take into account any possible corrosion.

However, excessive negative potentials can exacerbate the propagation rate of cracks (see 6.2).



Key

1 air
2 air fatigue limit
3 water
4 sodium chloride solution
X number of cycles
Y maximum stress (N/mm^2)

Figure 4 — Typical S-N curve for fatigue behaviour of steel in various environments

9.4 Chlorine

For an impressed current cathodic protection installation in a marine environment the anode reactions results in the electrochemical formation of chlorine. Seawater is normally slightly alkaline and the chlorine will form sodium hypochlorite and hypochlorous acid. Under stagnant conditions, the chlorine could be evolved as a gas and this could present a hazard to inspection and maintenance personnel.

Sodium hypochlorite can increase the corrosion rate of many alloys and this should be taken into account particularly where an impressed current system is proposed for stagnant conditions and where sodium hypochlorite can concentrate.

9.5 Stray currents and interference effects

Where a protected structure, or the anodes or groundbeds lie near to other immersed or buried metallic structures that are not fully insulated from earth, the metallic structure can pick up a proportion of the protective current due to potential gradients in the water or mud and return it to earth at other points where corrosion will take place.

The method in overcoming this effect depends on the circumstances but may include the use of drainage bonds, by isolating flanges or joints or by isolating structures by suitable coatings.

Requirements and recommendations specified by EN 50162 shall be used in seawater applications when applicable.

10 Use of cathodic protection in association with coatings

10.1 Introduction

While organic coatings are not entirely impermeable to oxygen and water they do restrict corrosion when applied to the surface of a metal. The bulk of the corrosion on a painted surface does not occur beneath the intact coating but at the base of holidays and pin holes. If cathodic protection is applied to a painted surface, the coating acts as a substantial resistive barrier to current flow and where the current flows, it is to the holidays or pin holes. In terms of cathodic protection the presence of a coating improves current distribution and reduces current demand and interference effects.

Where there is damage to the coating in the absence of cathodic protection, the metal is exposed to seawater which, in the case of steel, will be subject to corrosion. By applying cathodic protection, the exposed steel is polarized in the negative direction which increases the rate of the cathodic reaction but more importantly, reduces the rate of the anodic reaction. However, alkali is generated on the cathodically protected surface and this can result in the cathodic disbondment of the coating in way of any coating defects but the actual mechanism of disbondment due to alkali is not clear.

The conventional coatings of the oleo-resinous or alkyd types are attacked by alkali, i.e. they are subject to saponification and are not recommended for use in association with cathodic protection. Coatings containing aluminium have given variable behaviour and it is probable that they are attacked in stagnant conditions by the alkali generated at the cathode. The use of poly vinyl butyral shop primers has also caused loss of adhesion when combined with cathodic protection.

The coating could also pick up moisture due to electro-osmosis where the liquid passes through pores in the coating due to potential differences across the coating. The water inside the blisters becomes alkaline due to the cathodic reaction and therefore corrosion will be hindered.

In practice it is not possible to achieve the same potential over the surface to be protected and in some cases the potential can be sufficiently negative for hydrogen gas to be evolved. This can affect the adhesion of the coating through a mechanical action.

Similarly, chlorine gas can be generated near anodes of impressed current cathodic protection systems and in stagnant conditions the chlorine can attack and discolour the paint adjacent to the anodes.

Access to all parts of the surface is required for the application of coatings before the item is buried or immersed when the degree of corrosion protection cannot be controlled.

On the other hand cathodic protection acts from a distance on bare areas and protection can be controlled after installation.

Coatings and cathodic protection should be considered as methods of corrosion prevention which are complementary and inter-dependent rather than competitive.

10.2 Coating selection

The most suitable form of coating depends on the type of structure and its environment. In the selection of a coating, the aim should be to achieve overall economy in the combined cost of the protected structure and of the initial and running costs of the protection schemes. Due regard should be paid to the design life of the structure and to the economics of repairing the coating should this become necessary. More information is given in the respective standards.

10.3 Coating breakdown

Coatings will deteriorate with time and there is likely to be mechanical damage through installation procedures, cleaning operations to remove marine growth and erosional effects of waves and current.

In order to take this into account at the design stage, it is usual to introduce coating breakdown factors. These factors are closely dependent on the actual installation and operational conditions and are not necessarily a measure of the extent of the visual breakdown but should be considered as relating to current requirements.

The coating breakdown factor (f_C) of a coating describes the anticipated ratio of cathodic current density for a coated metallic material to the cathodic current density of the bare material. When $fc = 0$ the coating is considered fully isolating but when $fc = 1$ the coating has no protective properties and the current density would be the same as for a bare metallic surface.

Recommendations on the factors to be used for a particular arrangement are given in the respective standards.

Annex A
(informative)

Corrosion of carbon-manganese and low-alloy steels

A.1 Nature of metallic corrosion

When a metal corrodes in contact with an electrolyte, cations appear in water and the corresponding negative charge is formed in the metal. This may be expressed as follows:

$$Fe \rightarrow Fe^{2+} + 2e^- \tag{A.1}$$

Thus corrosion corresponds to a flow of an electric current from metal to electrolyte due to the movement of cations into the electrolyte and of electrons into the metal. Any area to which current flows from the metal to the water is referred to as an anodic area and the reaction is called an anodic reaction. The metallic ions can react with negative ions in the electrolyte to give insoluble corrosion products (for example, rust in the case of steel). Such reactions do not materially affect the corrosion process except where insoluble corrosion products stifle further corrosion attack.

For the corrosion reaction to proceed, the overall electric neutrality has to be maintained. Therefore, the movement of electrons into the metal and positive ions into the electrolyte at the anodic areas has to be counterbalanced by the consumption of electrons at other areas, known as cathodic areas.

Various reactions can occur at cathodic areas and these are known as cathodic reactions.

The following formulae show the most common reactions that occur at cathodes:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{A.2}$$

$$2H^+ + 2e^- \rightarrow H_2 \uparrow \tag{A.3}$$

$$2H_2O + 2e^- \rightarrow H_2 \uparrow + 2OH^- \tag{A.4}$$

The first of these reactions occurs in the presence of dissolved oxygen and near-neutral conditions.

The second is favoured by acidity (excess of hydrogen ions) while the third is dominant at pH values greater than neutral.

In aerated near neutral conditions, the iron ions produced at the anode react with the hydroxyl ions formed at the cathodic sites to produce ferrous hydroxide.

$$Fe^{2+} + 2OH^{-} \rightarrow Fe(OH)_2 \tag{A.5}$$

The ferrous hydroxide is readily oxidized by dissolved oxygen to form hydrated ferric oxide $Fe_2O_3 \cdot H_2O$:

$$4Fe(OH)_2 + O_2 \rightarrow 2H_2O + 2Fe_2O_3, H_2O \tag{A.6}$$

Thus the overall reaction which proceeds through a series of intermediate steps may be written as:

$$4Fe + 3O_2 + 2H_2O \rightarrow 2Fe_2O_3, H_2O \tag{A.7}$$

In practice the rate of corrosion is often determined by the rate at which the cathodic reaction can be sustained.

In near neutral anaerobic waterlogged environments, sulfate reducing bacteria can give rise to a further type of cathodic reaction in the corrosion of iron and steel. These microbes reduce dissolved sulphates to sulphides through the reaction:

$$SO_4^{2-} + 8H^{+} + 8e^{-} \rightarrow S^{2-} + 4H_2O \tag{A.8}$$

and the corrosion is characterized by the fact that it occurs in the absence of air and when sulphides are present in the corrosion products.

From the composition of the actual products formed, it is probable that the corrosion mechanism involves cathodic depolarization which may be represented by the simplified Formula (A.9):

$$4Fe + 4H_2O + SO_4^{2-} \rightarrow 3Fe(OH)_2 + FeS + 2OH^{-} \tag{A.9}$$

Stimulation of the cathodic reaction depends on the bacteria possessing an enzyme (hydrogenase) to enable them to oxidize hydrogen found at the cathodic sites.

The sulphide ions produced by the reduction of sulfate can sometimes stimulate the anodic process of iron dissolution.

A.2 Polarization

Where corrosion occurs, the potential difference between the two electrochemical reactions on the surface provides the driving force for the reaction. As a result, both electrode reactions are changed from their equilibrium condition causing a net anodic reaction to occur in one case and a net cathodic reaction in the other. The two potentials approach one another because all or part of the potential difference is used in driving the individual reactions. For corrosion to occur spontaneously, not only does there have to be a difference between the two reaction potentials, but the potential of the cathodic process has to be more positive than that for the anodic process.

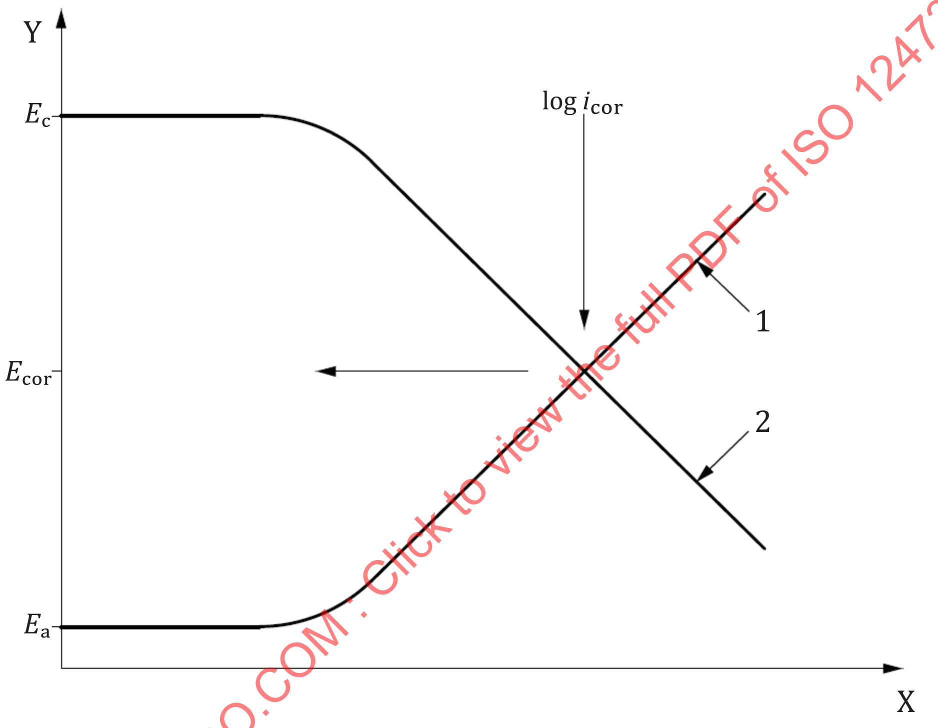
These circumstances are represented schematically in Figure A.1, which is a plot of electrode potential, E, against the logarithm of the reaction rate. Because anodic and cathodic reactions release and consume electrons, respectively, the anodic and cathodic reaction rates are represented by an electrical current, I. For simplicity, both reaction rates are plotted on the same axis, the direction of the current is ignored and only the magnitude is used to represent rate.

E_c is the equilibrium potential for the cathodic reaction where there is no net cathodic reaction rate. The negative changing curve from E_c shows that, as the potential becomes more negative, the cathodic reaction rate increases. Conversely, E_a is the equilibrium potential for the anodic reaction [e.g.

Formula (A.1)] and again at E_a there is no net anodic reaction. The positive changing curve from E_a shows that, as the potential becomes more positive, the anodic reaction rate increases.

When corrosion takes place, the anodic reaction rate is exactly equal to the cathodic reaction rate. In environments of high conductivity (e.g. seawater or seabed mud) the corroding metal exhibits a single potential which lies between E_c and E_a. In Figure 1 this condition occurs where the anodic and cathodic curves cross. The potential at this point is referred to as the corrosion potential, E_{cor}. It is the single potential exhibited by a corroding metal. The current, i_{cor}, is referred to as the corrosion current and it is an electrical representation of the corrosion rate. In practice, a corroding metal does not take up potential E_a or E_c, but spontaneously moves to E_{cor}.

While the shape of the individual E - log i curves can vary, with the prevailing environmental conditions, the manner in which the so-called polarization diagrams are interpreted in terms of E_{cor} and i_{cor} remain the same.



Key

X log i

Y electrode potential

1 anodic kinetics

2 cathodic kinetics

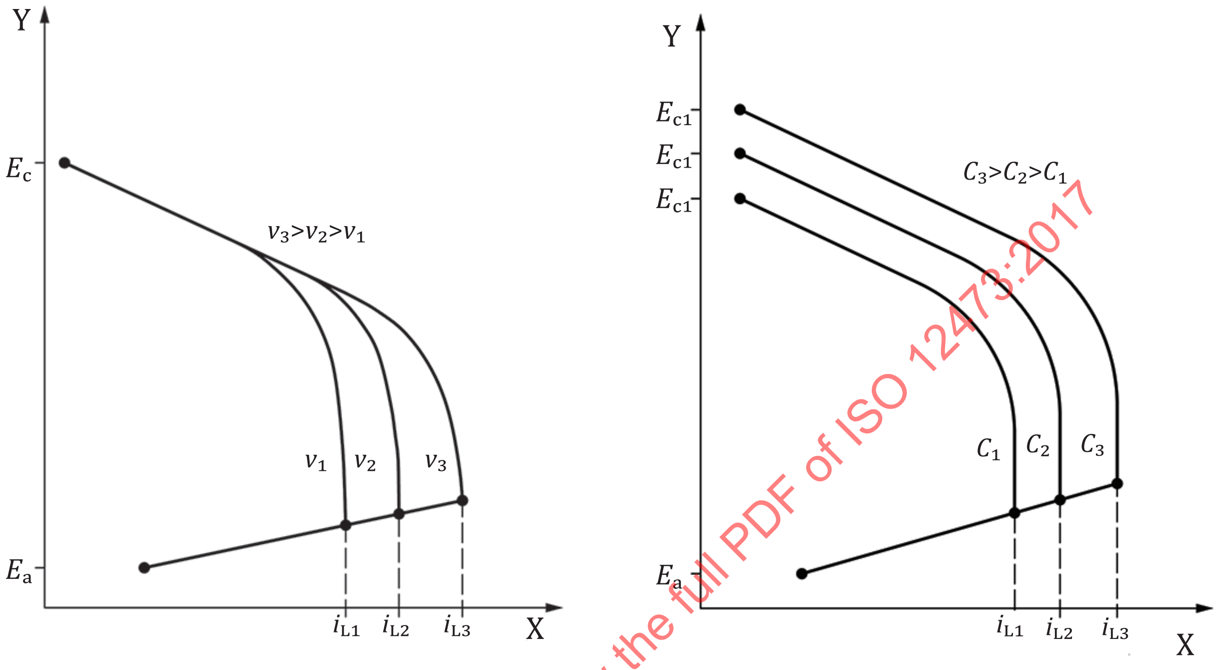
Figure A.1 — Polarization diagram schematically representing the electrochemistry of aqueous corrosion

On steel in seawater, the anodic process occurs more easily than the cathodic reaction but it is limited by the rate of the cathodic reaction. This is largely controlled by the rate of arrival of the oxygen at the metal surface, which could be due to the dissolved oxygen concentration in the seawater and the water flow rate.

This may be represented on a polarization diagram (see Figure A.2).

Increasing either the velocity and/or the oxygen concentration will have the effect of increasing the limiting current i_L.

The solubility of oxygen in seawater is a function of temperature and salinity and therefore varies with water depth and geographic location.



a) **Effect of velocity of the solution (V_x)**

b) **Effect of the concentration of dissolved oxygen (C_x)**

Key

X log *i*

Y electrode potential

Figure A.2 — Polarization diagram representing control of corrosion rate by sluggish cathodic kinetics (in this case it is controlled by the rate of arrival of oxygen at the surface) and the effect of increasing oxygen availability

Annex B
(informative)

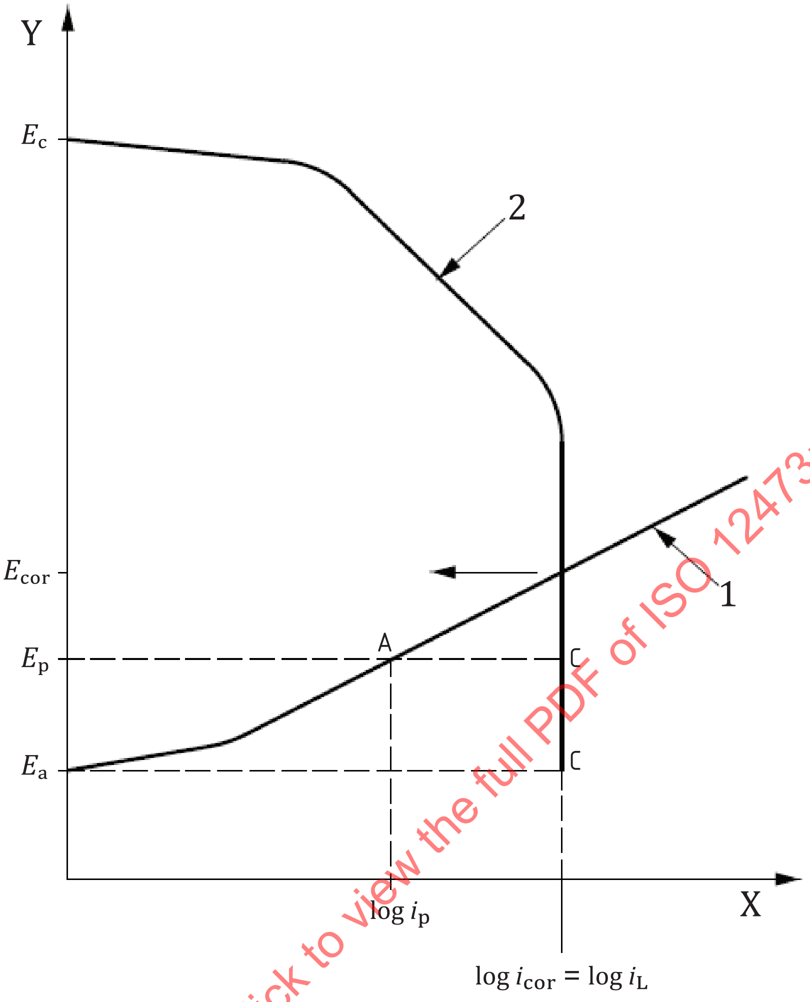
Principles of cathodic protection

Cathodic protection is used to reduce corrosion of a range of structural metals and alloys in aqueous environments including seawater at a level acceptable for their intended application.

Figure B.1 shows a schematic polarization diagram for such a steel corroding with oxygen reduction as the cathodic process. The free corrosion potential is given by E_{cor}, and the corrosion rate, i_{cor}, is equal in magnitude to the limiting current, i_L, for oxygen reduction.

When the potential is lowered from E_{cor} to E_p, the anodic reaction rate becomes lower than i_p, and the overall cathodic reaction rate remains equal to i_L. The cathodic reaction now receives its electrons from two sources (via the anodic process and from an external source of current). The anodic reaction provides electrons equivalent to i_p, and the additional current required (*C* minus *A)* is provided from an external supply.

If the potential is lowered to E_a the dissolution rate decreases to a negligible value and the cathodic reaction rate remains i_L. As there is no anodic reaction at this potential, the cathodic reaction now has to be sustained by the external electron supply alone, and it therefore takes more supplied current [equal to (i_L - 0)] to reach E_a than to reach E_p.



Key

X	log *i*
Y	electrode potential
1	anodic reaction Fe → Fe^{2+} + $2e^-$
2	cathodic reaction O_2 + 2 H_2O + $4e^-$ → 4 OH^-

Figure B.1 — Schematic diagram showing how corrosion can be reduced or stopped by applying cathodic protection

If the potential is depressed to below E_a, only secondary cathodic processes become energetically viable without affecting the free corrosion reaction.

The current required to reduce the corrosion rate to zero will be $i(E_{cor})$ - $i(E_a)$ and if the corrosion is solely due to the reduction of dissolved oxygen this will be equal to i_L, the limiting current for oxygen reduction.

The decreasing of the corrosion potential by applying a current is the basis of cathodic protection.

In principle cathodic protection can be used for a variety of applications where a metal is immersed in an aqueous solution of an electrolyte which ranges from relatively pure water, brackish and seawater, to soils and even to solutions of acids.

It should be emphasized that the method is electrochemical and both the structure to be protected and the anode used for protection have to be in metallic and electrolytic contact. Cathodic protection cannot therefore be applied for controlling atmospheric and similar forms of corrosion.