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

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Reference number
ISO 12473:2017(E)

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Foreword

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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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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.

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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)

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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

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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

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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.

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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

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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.

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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}

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

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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

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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.

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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.

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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.

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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:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad (1)$$

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad (2)$$

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.

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