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General principles of cathodic protection in sea water

Principes généraux de la protection cathodique en eau de mer

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Foreword

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The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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ISO 12473 was prepared by the European Committee for Standardization (CEN) (as EN 12473) and was adopted, under a special “fast-track procedure”, by Technical Committee ISO/TC 156, *Corrosion of metals and alloys*, in parallel with its approval by the ISO member bodies.

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Foreword

This European Standard has been prepared by Technical Committee CEN/TC 219 "Cathodic protection", the secretariat of which is held by BSI.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by July 2000, and conflicting national standards shall be withdrawn at the latest by July 2000.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

Annex A of this European standard is normative.

1 Scope

This European Standard covers the general principles of cathodic protection including the criteria for protection, environmental and design considerations and secondary effects of cathodic protection and is intended as an introduction to other European Standards in the general series "Cathodic Protection of Steel Structures in Sea Water".

This European Standard provides a link between the theoretical aspects and the practical applications of cathodic protection as contained in the European Standards:

prEN 12474:1997, *Cathodic protection for submarine pipelines.*

EN 12495:2000, *Cathodic protection for fixed steel offshore structures.*

prEN 12496:1997, *Galvanic anodes for cathodic protection in sea water and saline mud.*

prEN 13173:1998, *Cathodic protection for steel offshore floating structures.*

This group of European Standards does not cover cathodic protection of steel in concrete whether immersed or atmospherically exposed. These aspects are covered by prEN 12696-1:1997 and prEN 12696-2.

2 Normative references

This European Standard incorporates by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies.

EN ISO 8044, *Corrosion of metals and alloys – Basic terms and definitions (ISO 8044:1999).*

3 Terms and definitions

For the purposes of this European Standard the terms and definitions in EN ISO 8044 and the following apply:

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 in the electrolyte

3.4
anodic area
that part of a metal surface which acts as an anode

3.5
bond
metal conductor, usually of copper, connecting two points with the intention of making the points equipotential

3.6
calcareous deposits
minerals precipitated on the steel cathode because of the increased alkalinity caused by cathodic protection

3.7
calomel reference electrode

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

3.8
cathodic area

that part of a metal surface which acts as a cathode

3.9
cathodic disbonding

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

3.10
cathodic protection system

entire installation, including active and passive elements, that provides cathodic protection

3.11
cell

complete electrolytic system comprising of a cathode and an anode in electrical contact and with an intervening electrolyte

3.12
coating breakdown factor

coating breakdown factor is the anticipated reduction in cathodic current density due to the application of an electrically insulating coating when compared to that of bare steel

3.13
coating defect

discontinuity in the protective coating

3.14
coating resistance

electrical resistance between a coated metal and the electrolyte. It is determined largely by the size and number of coating defects and coating pores and is, therefore, indicative of the condition of the coating

3.15
conductor

substance in which electric current flows

3.16
continuity bond

bond designed and installed specifically to ensure electrical continuity of a structure

3.17
copper/copper sulphate reference electrode

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

3.18
corrosion interference

increase or decrease in the rate of corrosion, or the tendency towards corrosion, of an immersed structure caused by the interception of part of the cathodic protection current applied to another immersed structure

3.19
depolarization

removal of factors resisting the flow of current in a cell

3.20
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

3.21
drainage bond
bond to achieve electric drainage

3.22
driving potential
difference between the structure/electrolyte potential and the anode/electrolyte potential

3.23
electrical resistance of coating
see coating resistance

3.24
electronegative
qualification applied to a metallic electrode to indicate that its potential is negative with respect to another metallic electrode in the system

3.25
electro-osmosis
passage of a liquid through a porous medium under the influence of a potential difference

3.26
environmentally assisted cracking
brittle fracture of a normally ductile material in which the corrosive effect of the environment is a contributory factor

3.27
galvanic action
spontaneous electrochemical reaction which occurs in a system comprising a cathode and an anode in electrical contact and with an intervening electrolyte, resulting in corrosion of the anode

3.28
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

3.29
holiday
see coating defect

3.30
impressed current anode
anode in an impressed current installation

3.31
insulated flange
flanged joint between adjacent lengths of pipe in which the nuts and bolts are electrically insulated from one or both of the flanges and the gasket is non-conducting, so that there is an electrical discontinuity in the pipeline at that point

3.32
ion
atom, or group of atoms, carrying a charge of positive or negative electricity

3.33
isolating joint
electrically discontinuous joint or coupling between two lengths of pipe, inserted in order to provide electrical discontinuity between them

3.34
over polarization
when the structure to electrolyte potentials are more negative than those recommended for satisfactory cathodic protection. Over polarization provides no useful function and may even cause damage to the structure by excessive production of gases which may cause embrittlement or protective coating damage

3.35
polarization
change in the potential of an electrode as the result of current flow to or from that electrode

3.36
potential gradient
difference in potential between two separate points in the same electric field

3.37
protected structure
structure to which cathodic protection is effectively applied

3.38
protection current
current made to flow into a metallic structure from its electrolytic environment in order to effect cathodic protection of the structure

3.39
resistivity (of an electrolyte)
resistivity is the resistance of an electrolyte of unit cross section and unit length. It is expressed in ohm(s) metres (Ω m). The resistivity depends, amongst other things, upon the amount of dissolved salts in the electrolyte

3.40
scale precipitation
formation of insoluble chemical compounds on the surface of a cathodically protected structure. These are referred to as calcareous deposits (see 3.6)

3.41
silver/silver chloride reference electrode
reference electrode consisting of silver, coated with silver chloride, in an electrolyte containing chloride ions

3.42
slow strain rate test
this test involves the slow tensile loading of a specimen of a circular cross section under conditions of constant strain rate with the gauge area exposed to the test environment

3.43
standard hydrogen electrode
reference electrode consisting of an electro-positive metal, such as platinum, in an electrolyte containing hydrogen ions at unit activity and saturated with hydrogen gas at one standard atmosphere

3.44
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

3.45
sulphate reducing bacteria
group of bacteria found in most soils and natural waters, but active only in conditions of near neutrality and freedom from oxygen. They reduce sulphates in their environment, with the production of sulphides and accelerate the corrosion of structural materials

3.46
telluric currents
electrical currents induced by time varying changes in the earth's magnetic field. These currents flow generally in the earth or in the oceans. They are able to flow in metallic conductors laid in the soil or in the sea

3.47
transformer rectifier
transformer rectifier is a device that transforms the alternating voltage to a suitable value and then rectifies it to direct current. Direct current derived in this way is used as a power source for impressed current cathodic protection systems

4 Corrosion principles of buried or immersed metals

4.1 The nature of metallic corrosion

When a metal corrodes in contact with an electrolyte neutral atoms pass into solution by forming positively charged ions and excess electrons are left in the metal. The process for iron may be expressed as

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

Thus corrosion is accompanied by the flow of an electric current from metal to electrolyte due to the movement of positive ions into the electrolyte and of electrons into the metal. Any area to which current flows is referred to as an anodic area and the reaction is called an anodic reaction. The metallic ions may 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 equations show the most common reactions that occur at cathodes:

$$\mathrm{O}_2 + 2\,\mathrm{H}_2\mathrm{O} + 4e^{-} \rightarrow 4\,\mathrm{OH}^{-} \tag{2}$$

oxygen water electrons hydroxyl ions

$$2\mathrm{H}^{+} + 2e^{-} \rightarrow \mathrm{H}_2\uparrow \tag{3}$$

hydrogen ions electrons hydrogen gas

$$2\mathrm{H}_2\mathrm{O} + 2e^{-} \rightarrow \mathrm{H}_2\uparrow + 2\,\mathrm{OH}^{-} \tag{4}$$

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.

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

The ferrous hydroxide is readily oxidised by dissolved oxygen to form hydrated ferric oxide $\mathrm{Fe_2O_3{\cdot}H_2O}$:

$$4\mathrm{Fe(OH)}_2 + \mathrm{O}_2 \rightarrow 2\mathrm{H}_2\mathrm{O} + 2\mathrm{Fe}_2\mathrm{O}_3.\ \mathrm{H}_2\mathrm{O} \tag{6}$$

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

$$4Fe + 3O_2 + 2H_2O \rightarrow 2Fe_2O_3 . H_2O \qquad (7)$$

hydrated ferric
oxide (rust)

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 sulphate reducing bacteria may give rise to a further type of cathodic reaction in the corrosion of iron and steel. These microbes reduce dissolved sulphates to sulphides possibly through the reaction

$$SO_4^{2-} + 8H^+ + 8e^- \rightarrow S^{2-} + 4H_2O \qquad (8)$$

and the corrosion is characterised by the fact that it occurs

a) in the absence of air; and

b) sulphides are present in the corrosion products.

From the composition of the actual products formed it is probable that the corrosion mechanism involves cathodic depolarisation which may be represented by the simplified equation (9);

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

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

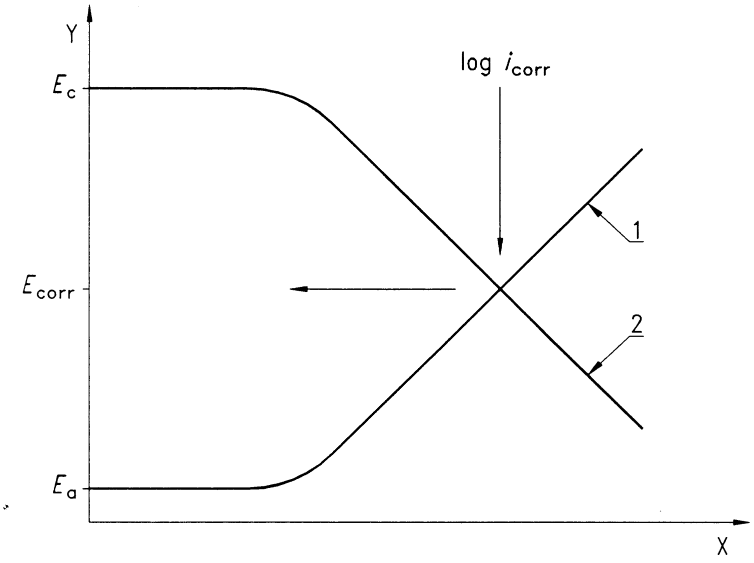
The sulphide ions produced by the reduction of sulphate can sometimes stimulate the anodic process of iron dissolution.

4.2 Polarisation

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 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 [eg equation (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.



Key :

x log *i*
y electrode potential
1 anodic kinetics
2 cathodic kinetics

Figure 1 — Polarisation diagram schematically representing the electrochemistry of aqueous corrosion

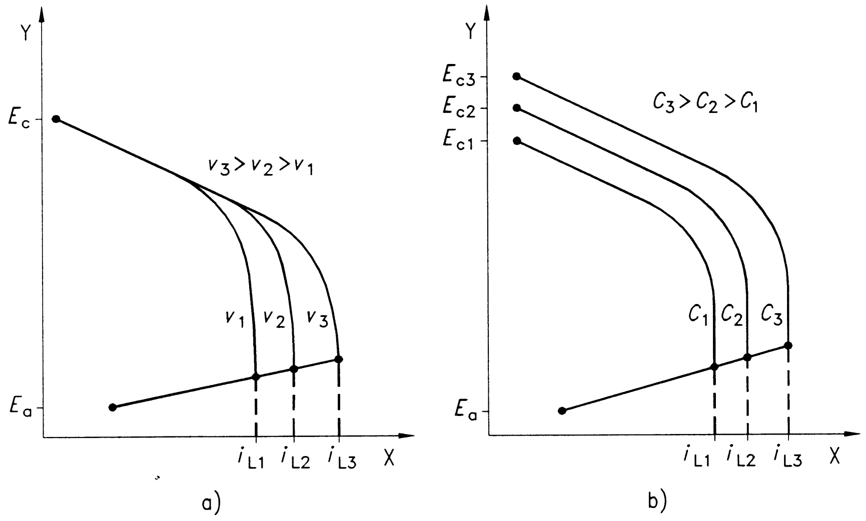
When corrosion takes place, the anodic reaction rate is exactly equal to the cathodic reaction rate. In environments of high conductivity (eg sea water or seabed mud) the corroding metal exhibits a single potential which lies between E_c and E_a. In figure 1 this condition occurs where the anodic and cathodic curves cross. The potential at this point is referred to as the corrosion potential, E_{corr}. It is the single potential exhibited by a corroding metal. The current, i_{corr}, 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_{corr}.

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

On steel in sea water, 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 may be due to the dissolved oxygen concentration in the sea water and the water flow rate.

This may be represented on a polarisation diagrams (figure 2).

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



a)

b)

Key :

x log *i*
y electrode potential
a) shows the effect of velocity of the solution (V_X), and
b) shows the effect of the concentration of dissolved oxygen (C_X)

Figure 2 — Polarisation 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

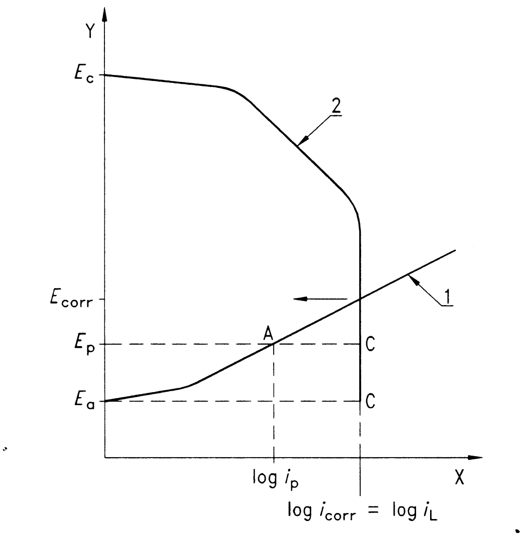
The solubility of oxygen in sea water is a function of temperature and salinity and therefore varies with water depth and geographic location.

5 Principles of cathodic protection

Figure 3 shows a schematic polarisation diagram for the steel corroding with oxygen reduction as the cathodic process. The corrosion potential is given by E_{corr}, and the corrosion rate, i_{corr} , is equal in magnitude to the limiting current, i_L, for oxygen reduction.

Suppose the potential could be lowered from E_{corr} to E_p, the anodic reaction rate would be lower at i_p, and the overall cathodic reaction rate would remain equal to i_L. However, 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 will decrease 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 $O_2 + 2\,H_2O + 4e^- \rightarrow 4\,OH^-$

Figure 3 — 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 $i(E_{corr}) - i(E_a)$ 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 range from relatively pure water, brackish and sea water, to soils and even to solutions of acids.

It should be emphasised that the method is electro-chemical and both the structure to be protected and the anode used for protection must be in metallic and electrolytic contact. Cathodic protection cannot therefore be applied for controlling atmospheric and similar forms of corrosion.

The forms of corrosion that can be controlled by cathodic protection include all forms of general corrosion, pitting corrosion, selective corrosion, crevice corrosion, environmentally assisted cracking, cavitation and bacterial corrosion.

To summarise :

- without cathodic protection the steel corrodes at a rate given by i_{corr} and i_L when oxygen reduction is the cathodic reaction;
- by lowering the potential to E_a, it is possible to stop corrosion completely, but this requires application of an external current equal to i_L;
- by lowering the potential to a value below E_{corr} but above E_a, the metal may be partially protected with some economy in current supplied;

- because the anodic polarisation, that is the relationship between the potential *E* and the current *i* is approximately logarithmic, a small initial negative shift in potential (or polarisation) can give a large benefit in terms of protection ;

- by moving the potential below E_a some of the current is used to electrochemically reduce water to hydroxyl ions.

6 The application of cathodic protection

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

a) sacrificial anode systems in which the current for protection is provided by a metal of more electro 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, and

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.

6.1 Sacrificial anode method

If two dissimilar metals are connected in the same electrolyte a galvanic cell is produced. The open circuit driving voltage derives from 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 sacrificial anodes in cathodic protection is based on this phenomenon.

Assuming the structure to be protected is made of steel, zinc alloy sacrificial 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 4, 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.

6.2 Impressed current method

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

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad (10)$$

and

$$2Cl^- \rightarrow Cl_2 + 2e^- \qquad (11)$$

Figure 5 represents an impressed current cathodic protection system using an inert anode in sea water where in the secondary reactions hydrogen and chlorine are evolved.

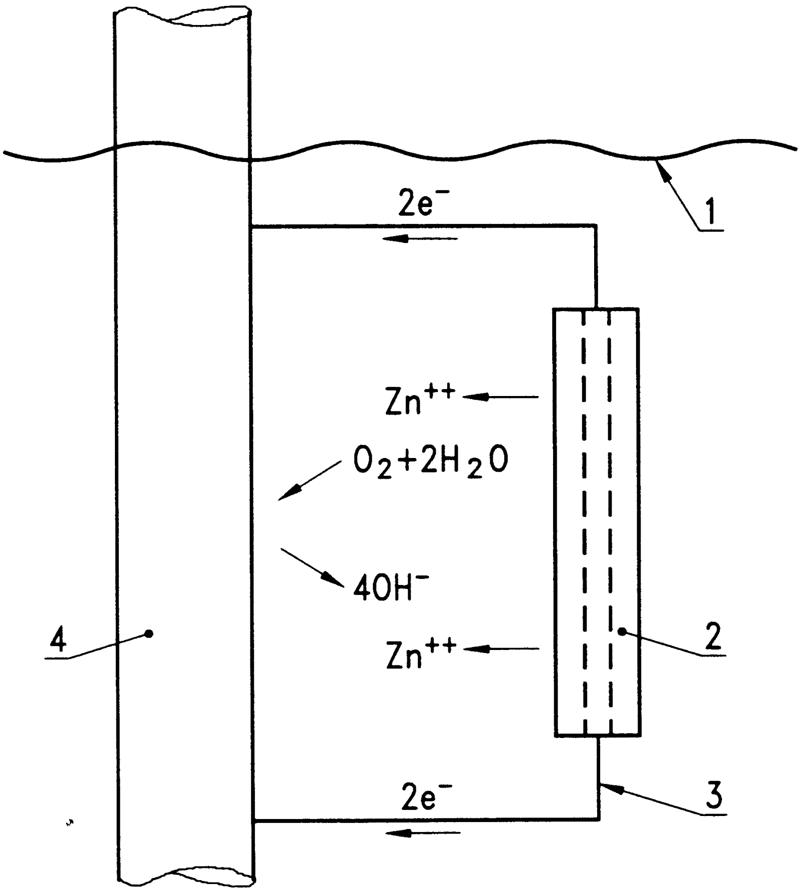
The advantages of the impressed current system are that it is possible to have a large adjustable driving voltage so that relatively few anodes need to be installed even to protect large uncoated structures in comparatively high resistivity environments. A comparison of sacrificial and impressed current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

6.3 Hybrid systems

These comprise a mixture of sacrificial anodes and externally powered impressed current anodes.

Because there may 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 sacrificial anodes to polarize the critical region of the structure.

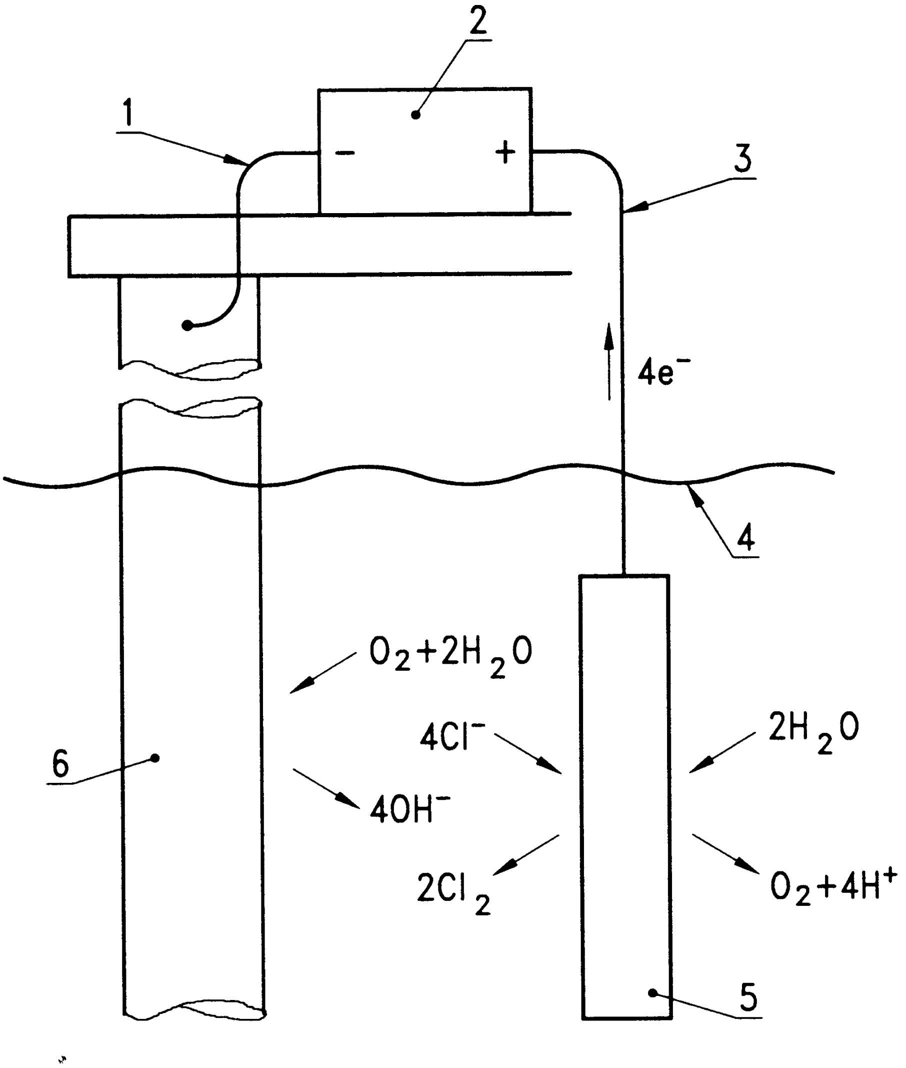
The sacrificial anodes should also provide protection when the impressed current system is shut down for subsea survey and maintenance during the life of the structure.



Key :

1 sea water
2 zinc alloy anode
3 anode attachment
4 protected structure in sea water

Figure 4 — Representation of cathodic protection using a zinc sacrificial anode on a structure in the sea water



Key :

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

Figure 5 — Representation of impressed current cathodic protection using inert anode in sea water

Table 1 — Comparison of Sacrificial and Impressed Current Systems

	Sacrificial systems	Impressed current systems
Environment	Use may be impracticable except in soils or waters of low resistivity.	Use is less restricted by resistivity of soil or water but may get Cl_2 in sea water.
Installation	Simple to install.	Needs careful design otherwise may 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 may restrict water flow and introduce turbulence and drag penalties.	Usually lighter and few in number. Anodes may be designed to have minimum effect on water flow.
Control	Tendency for their current to be self adjusting.	Controllable. Control usually automatic and may 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 must be able to withstand any forces applied to the structure.	Anodes lighter in construction and therefore less resistant to mechanical damage. Loss of anodes can be more critical to the effectiveness of a system.

7 Determination of level of cathodic protection

7.1 Measurement of protection level

To determine whether a structure is adequately protected it is usual to measure its solution potential. To achieve this connections must 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 in to 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.

7.2 Reference electrodes

Details of the reference electrodes for marine applications are given in annex A.

The types used for monitoring cathodic protection systems in sea water include the metallic zinc or silver/silver chloride (Ag/AgCl/sea water) electrodes as these are considered sufficiently accurate for most practical purposes.

7.3 Potentials of reference electrodes

The potentials of various reference electrodes with respect to the standard hydrogen electrode are given in table A.1 of annex A. The calomel electrode is included as it is often used in the laboratory for checking the condition of reference electrodes used in the field. It is insufficiently robust for field use.

7.4 Potential measurement

Irrespective of the type of reference electrode used it is essential that it is placed very close to the metal surface as the measurement of the potential difference between the metal surface and the electrolyte can be considerably 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, has the effect of making 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. The resistance of any coatings will also have an effect.

8 Guidance for protection

8.1 General

This clause outlines some of the more important metals which may be protected by cathodic protection in sea water and gives guidance on the potentials recommended for protection. However, in view of the wide range of alloys and applications it is essential that these values are used for general guidance only and for more specific recommendations the European Standard covering the relevant application should be consulted.

A summary of the recommended potentials for protection of the various materials in sea water is given in table 2.

8.2 Steel

Loss of ions from the anode ceases when the corroding system is polarized to the open circuit potential of the anode.

It is not practical to polarize the steel to the E_a value as shown in figure 3. However, measurements have shown when the steel is polarized to -0,80 V (Ag/AgCl/sea water reference electrode) the corrosion rate has been suppressed to an acceptably low level. Consequently, this is the minimum negative level normally used for the cathodic protection of carbon steel in sea water.

In the case of steel immersed in solutions which contain active sulphate reducing bacteria (generally in anaerobic conditions) the potential for protection should be -0,90 V (Ag/AgCl/sea water reference electrode) instead of -0,80 V for mild steel.

With increasing negative potentials there may be a blistering of some coatings, an adverse effect on fatigue properties and a risk of hydrogen embrittlement of susceptible steels (see 11) and in view of these effects it is normal to limit the potential.

For mild steel a negative limit of -1,10 V (Ag/AgCl/sea water reference electrode) is generally accepted as the negative limit as this value would account for potentials that may be achieved on a bare structure close to aluminium sacrificial anodes.

In the case of high strength steels (yield strengths > 700 N/mm^2) due to a risk of hydrogen embrittlement it is more important to avoid over polarization (see clause 11). It has therefore been the practice to use potentials in the range -0,80 V to -0,95 V (Ag/AgCl/sea water reference electrode) for many applications.

Following cases of hydrogen assisted cracking in high strength steels used 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 small providing the cathodic potentials were not more negative than -0,83 V (Ag/AgCl/sea water reference electrode).

In view of this, consideration should be given to limiting the negative potential to -0,83 V (Ag/AgCl/sea water reference electrode). Where there is the possibility of microbial corrosion then coatings should be used and in spaces with restricted access the use of biocides should be considered.

Figure 6 gives a comparison between the reference electrodes normally used for a marine environment together with a summary of the effects of potential on steel in sea water.

Potential (V) Ag/AgCl/ Sea water		Potential (V) Zn/Sea water
-0,40		+0,65
	Intense corrosion	
-0,50	---	+0,55
	Freely corroding	
-0,60		+0,45
-0,65	---	
	Some protection	
-0,70		+0,35
	Threshold of full protection	
-0,80	====================================	+0,25
	for aerobic conditions	
-0,90	---	+0,15
	Some over polarization recommended for anaerobic condition	
-1,00	---	+0,05
	Increasing over polarization	
-1,10	---	-0,05
	Can affect adhesion of some paints Increasing risk of hydrogen embrittlement of susceptible steels and adverse effect on fatigue life	

Figure 6 — The corrosion, cathodic protection and over polarization regimes of steel expressed as a function of electrode potential

8.3 Other metallic materials

8.3.1 Aluminium alloys

Aluminium alloys have been used in the marine industry for many years mainly because of their combination of lightness with strength and corrosion resistance.

Aluminium is a very reactive metal with a high affinity for oxygen. However, due to the inert and protective nature of the oxide film which forms on the metal surface the metal is highly resistant to most atmospheres and to a wide range of chemicals.

There are two distinct groups of wrought aluminium alloys used in marine applications. One group consists of the non heat treatable medium strength aluminium magnesium alloys with magnesium contents in the range of 3,5 % to 4,9 %. The other alloys are the heat treatable aluminium magnesium silicon with magnesium contents of between 0,6 % and 1,2 % and silicon contents of 0,4 % to 1,3 %.

Aluminium alloy castings have not been used to any significant extent but the alloys need to have good castability, corrosion resistance and pressure tightness. The alloys with silicon contents in the range 10 % - 12 % are preferred for castability having good corrosion resistance and the alloys are often used in the "as cast" condition but those alloys with a magnesium content of between 0,15 % and 0,4 % can be heat treated.

In all cases the copper content is usually limited to 0,1 % in order to minimise pitting corrosion.

Although these alloys are selected for their corrosion resistance they can be cathodically protected.

The potential of the aluminium magnesium and the aluminium magnesium silicon alloys in sea water is generally in the range of -0,70 V to -0,90 V (Ag/AgCl/sea water reference electrode) and they can be cathodically protected in sea water 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/sea water reference electrode) as high negative potentials need to be avoided particularly in stagnant conditions as the alkali generated may strongly attack the aluminium to produce the aluminate. Zinc and the aluminium zinc indium and aluminium zinc tin anodes can be used for the protection of aluminium but mercury containing aluminium anodes should be avoided.

8.3.2 Stainless steel

Stainless steel is a generic name given to a whole range of alloy steels whose main attribute is their corrosion resistance. The resistance to various environments can be adjusted by altering the composition of the steel within wide limits. A common feature of all stainless steels is their high chromium content of at least 12 % which produces an oxide layer on the surface to make the steel passive in many environments.

The grouping of stainless steel is based on their micro-structure and the types available include: austenitic, ferritic, martensitic and duplex (a mixture of austenite and ferrite) but it is mainly the austenitic and duplex materials that are used for marine applications.

In sea water stainless steels are prone to pitting and crevice corrosion and pH, temperature and oxygen content can affect the behaviour. It has been established that the initiation of pitting and the resistance to crevice corrosion can be broadly related to the chromium, molybdenum, nitrogen and sometimes the tungsten contents of stainless steels.

In general providing the stainless steel has a pitting resistance equivalent number (PREN) of at least 40, where PREN = % Cr + 3,3 × % Mo + 16 × % N then it is unlikely to suffer from pitting or crevice corrosion in sea water at 20 °C. Therefore it is beneficial to apply cathodic protection to many of the stainless steels used in a marine environment.

8.3.2.1 Austenitic stainless steel

Many austenitic stainless steels can be protected using a potential of -0,60 V (Ag/AgCl/sea water reference electrode) but for the more corrosion resistant stainless steels it is considered that a potential of about -0,30 V (Ag/AgCl/sea water reference electrode) is adequate for most applications.

However, in view of the wide range of austenitic stainless steels available, potentials outside the range given in table 2 should only be used if they are substantiated by documented service performance or appropriate laboratory tests.

8.3.2.2 Duplex stainless steels

Because of their generally good corrosion resistance, duplex stainless steels are finding a wide field of application offshore and in particular in pipelines.

Duplex stainless steels are mainly resistant to general corrosion in sea water but may be susceptible to localized corrosion, in the form of pitting or, more probably, crevice attack at elevated temperatures. Therefore, some degree of cathodic protection is usually applied.

Crevice corrosion usually initiates and propagates, at potentials substantially less negative than those required for cathodic protection of carbon steel. In systems where carbon steel and duplex stainless steels are in electrical contact the two materials should be polarized to the same potential to mitigate any galvanic corrosion couples which may otherwise exist.

Consideration needs to be given to the effect of the more negative potentials when designing cathodic protection systems for duplex stainless steels. Duplex stainless steels in the usual quenched annealed condition have a microstructure containing 40 % - 50 % ferrite and 60 % - 50 % austenite. Although austenitic materials are compatible with the range of potentials experienced in cathodic protection, ferritic materials are known to suffer from hydrogen embrittlement at such potentials.

Duplex stainless steels are vulnerable to cracking if over-polarized as their metallurgical structure is inappropriate ie, it contains too much ferrite. Welds and their heat affected zones are the most likely locations for such unfavourable microstructures. However, providing there is a good phase balance ie, a minimum of 40 % austenite in the microstructure and the parent metal is in the quench annealed condition, it will not normally be susceptible to cracking in sea water at the recommended cathodic protection potentials and current densities. A negative limit of -1,05 V (Ag/AgCl/sea water reference electrode) is recommended although a more positive limit may be used where the microstructure of the material or the weld metal is not in the optimum condition. Welded material will be equally resistant to cracking provided the content and distribution of austenite in the heat affected zone is satisfactory.

The positive limit for protection may be taken as that for austenitic stainless steels (see 8.3.2.1)

8.3.2.3 Copper alloys

Copper and copper alloys find numerous applications amongst the appurtenances of marine structures, not only as corrosion resistant claddings but also in hydraulic and similar applications where small components are attached to structures. This is particularly common in subsea completion units and well closure assemblies.

Copper and copper alloys correctly selected have excellent corrosion resistance and minute traces of copper ions in the metal/sea water interface discourage the settlement or growth of marine life.

Cathodic protection is not generally required to prevent corrosion on copper or its alloys, however components attached to cathodically protected steel will receive protection and this may cause the loss of the "anti-fouling" properties of many copper based surfaces. This can be significant where heavy build up of marine growth can lead to substantial increase in weight and drag forces.

The current densities required for the protection of copper alloys or iron/copper alloy couples may 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.

8.3.2.4 Nickel based alloys

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/sea water reference electrode) but potentials of the order of -0,20 V (Ag/AgCl/sea water reference electrode) may 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.

Table 2 — Summary of potential versus silver/silver chloride/sea water reference electrode recommended for the cathodic protection of various metals in sea water

Material	Minimum negative potential volt	Maximum negative potential volt
Iron and steel		
aerobic environment	-0,80	-1,10
anaerobic environment	-0,90	-1,10
High strength steels	-0,80 (see note 1)	-0,95 (see note 1)
Aluminium alloys (Al Mg & Al Mg Si)	-0,80 (negative potential swing 0,10 V)	-1,10
Stainless steel		
Austenitic steel		
- (PREN ≥ 40)	-0,30	no limit
- (PREN < 40)	-0,60 (see note 2)	no limit
Duplex	-0,60 (see note 2)	(see note 3)
Copper alloys		
without aluminium	-0,45 to -0,60	no limit
with aluminium	-0,45 to -0,60	-1,10
Nickel base alloys	-0,20	see note 4

NOTE 1 For high strength steels susceptible to hydrogen assisted cracking the maximum negative potential should be more positive (less negative) than -0,83 V (Ag/AgCl/sea water reference electrode).

NOTE 2 For most applications these potentials are adequate for the protection of crevices although higher potentials may be considered.

NOTE 3 Depending on metallurgical structure these alloys can be susceptible to cracking and high negative potentials should be avoided (see 8.3.2.2).

NOTE 4 High strength nickel copper and nickel chromium iron alloys can be subject to hydrogen assisted cracking and potentials that result in significant hydrogen evolution should be avoided.

9 Design considerations

9.1 Introduction

The purpose of this clause is to outline some of the factors that may influence the design of a cathodic protection system. More detailed information is given in each of the respective European 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 11 and 12.

Using sacrificial anodes, which are low voltage sources of current, a reasonable 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 may arise if the local steel area is high and restrictions are placed on the siting of the anodes (e.g. in way of nodes etc) and it may be advantageous to use coatings.

Impressed current anodes may 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 may 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 parameter of the structure. In general the information required includes:

a) technical and operating data of the structure

b) current demand.

9.2 Technical and operating data

9.2.1 Design life

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

9.2.2 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 7 with regards to the maximum negative limit should be complied with.

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

9.3 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 may be significantly greater. Due allowance should be made for elements of the structure which are buried and electrically continuous with the structure.

9.4 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.

9.5 Availability of electrical power

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

9.6 Weight limitations

In the case of fixed offshore structures, the float out weight may be very important and this may influence the type of system to be used. The use of a hybrid system may considerably reduce the weight compared with a full sacrificial anode system (see 6.3).

9.7 Adjacent structures

The presence of other structures in the locality 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.

9.8 Installation considerations

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

While it may be possible to use fewer impressed current anodes the routing of cables feeding the anodes and reference electrodes may pose problems. It is recommended that the cables are 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.

In all cases long drops of cable should be avoided. Cables must not be led through spaces likely to contain gas from low flash point oil.

9.9 Current demand

As discussed in clause 8 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.

For long distance pipelines and particularly those that are well coated geomagnetic or telluric effects should also be considered as they can cause potential variations. The potentials generated in the coated pipeline may be reduced by installing insulating couplings in the line and may be less pronounced where sacrificial anodes provide the cathodic protection.

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 10.

10 Effect of environmental factors on current demand

10.1 Introduction

The chemical and physical characteristics of the environment and the rate at which they may change daily or seasonally need to be considered in assessing current density requirements. The principal factors affecting current density requirements in sea water 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.

10.2 Dissolved oxygen

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

It is considered that there is a direct correlation between the dissolved oxygen content and the corrosion rate in sea water 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 sea water varies considerably with water depth and geographic location and since the solubility is a function of temperature and salinity it may also vary with the season.

10.3 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 polarisation 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.

10.4 Calcareous deposits

Well formed calcareous deposits reduce the rate of diffusion of dissolved oxygen in the sea water to the steel surfaces and thereby reduce the current density necessary to maintain cathodic polarisation.

Calcareous deposits are minerals precipitated on the steel cathode because of the increased alkalinity caused by cathodic polarisation.

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 sea water depth.

Sea water 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:

$$CO_2 + H_2O \rightarrow H_2CO_3 \tag{12}$$

$$H_2CO_3 \rightarrow HCO_3^- + H^+ \tag{13}$$

$$HCO_3^- \rightarrow CO_3^{2-} + H^+ \tag{14}$$

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

$$HCO_3^- + OH^- \rightarrow H_2O + CO_3^{2-} \tag{15}$$

$$CO_3^{2-} + Ca^{2+} \rightarrow CaCO_3 \text{ ppt} \tag{16}$$

may occur with the precipitation at the cathodic areas.

Over the current density range where scales form they are predominantly calcium carbonate and with increasing the 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 polarisation and formation of a high protective calcareous deposit. However at very high current density the deposit may have a significant magnesium content. It is present primarily as $Mg(OH)_2$ but possible with some $MgCO_3$. $Mg(OH)_2$ is unstable in sea water 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.

10.5 Temperature

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

As the temperature along with salinity of sea water has a significant effect on the resistivity of sea water and as this is directly related to the effective resistance of sacrificial 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 may 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.

10.6 Salinity

The major effect of salinity on cathodic protection is its influence on sea water 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 may cause wide fluctuations in the power required and this may lead to damage of the rectifiers unless they are suitable protected.

10.7 pH

The pH of open sea water varies from about 7,4 to 8,4 and is highly buffered by a complex carbonate system. However, a small decrease in pH may 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.

10.8 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 may degrade the coating. Marine fouling reduces the effective steel surface exposed to sea water preventing diffusion of oxygen to the surface and hence reducing the current density required for protection. However, on the other hand, the fouling organisms may 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 may produce conditions conductive 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 sacrificial anodes may take place, it is probable that only the hard shell would mask portions of the anodes and reduce their effectiveness.

10.9 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 affect.

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.

10.10 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 may lead to an increase in current density requirements on structures close to the surface.

11 Secondary effects of cathodic protection

The application of cathodic protection may give rise to secondary effects such as the development of alkalinity and the generation of hydrogen and possibly chlorine gas.

The effects that may occur include the following:

11.1 Alkalinity

Alkalinity may degrade oil based alkyd and oleo-resinous coatings by saponification (see clause 12). Alkalinity favours the formation of calcareous deposits which may be beneficial since the current density needed to maintain cathodic protection is reduced. However, such deposits may cause a roughening of impeller or propellers which may then produce cavitation effects elsewhere in the system.

If the protected metal is amphoteric it may 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 8). Aluminium pigmented paints may 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.

11.2 Environmentally-assisted cracking

Two of the basic design requirements for structures, subsea installations and pipelines are that they must possess adequate static strength and fatigue endurance.

In the particular case of a fixed offshore platform the static strength must be more than sufficient to carry the normal weight of the structures and to withstand the loads imposed by extreme height waves (e.g. 100 year) while the static strength of high pressure oil and gas lines must be sufficient to withstand the high stresses imposed on the line. Both the static strength and fatigue endurance of offshore installations can be 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.

11.2.1 Corrosion fatigue

Fatigue is a process of time delayed crack initiation and relatively slow crack propagation which may occur in metallic structures which are subjected to cyclic loading. In the presence of a corrosive environment cracking occurs in a shorter time than would be encountered as a result of the fluctuating stress or the corrosive environment alone.

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.

The corrosion fatigue life in sea water of carbon manganese steels with yield strengths not greater than 400 N/mm^2 is about half the fatigue life in air as determined from curves obtained by plotting stress S to the number of cycles N to fracture. The application of controlled levels of cathodic protection restores the corrosion fatigue life to about the air value in small planar specimens. Tests on large welded tubular joints indicate that cathodic protection does not fully restore the corrosion fatigue life to the air value. This is because the life of planar specimens is dominated by crack initiation and growth of short cracks whereas the life of tubular specimens is dominated by the growth of much longer cracks.

11.2.2 Hydrogen embrittlement

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

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 must 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 may be too low for interaction with dislocation movement while at high temperatures the hydrogen is ineffective in causing embrittlement.

11.3 Chlorine

For an impressed current cathodic protection installation in a marine environment the anode reactions may result in the electrolytic formation of chlorine. Sea water is normally slightly alkaline and the chlorine will form sodium hypochlorite and hypochlorous acid. Under stagnant conditions, the chlorine may 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 may concentrate.

11.4 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 may 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 insulating flanges or joints or by insulating structures by suitable coatings.

12 The use of cathodic protection in association with surface coatings

12.1 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 sea water 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 may 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, ie 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 may 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 may be generated near anodes of impressed current cathodic protection systems and in stagnant conditions the chlorine may 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.

12.2 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 European Standards.

12.3 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) describes the anticipated reduction in cathodic current density due to the application of an electrically insulating coating. When $F = 0$ the coating is considered fully insulating but when $F = 1$ the coating has no protective properties and the current density would be the same as for a bare steel surface.

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

Annex A
(normative)

Reference electrodes

A.1 Reference electrodes

It is intended that a European Standard will be produced covering all aspects of reference electrodes. However, until such standard is available, the notes in this annex are applicable.

The reference electrodes as subsequently described are normally used for measuring structure/electrolyte potentials or as sensing electrodes for control systems.

Sufficiently accurate measurements can be obtained when the electrode has the following features:

a) it permits adequate current to be drawn to operate a millivoltmeter without significantly changing its potential;

b) it is not degraded or poisoned by the environment.

The reference electrodes used for monitoring marine cathodic protection systems are the silver/silver chloride/sea water electrode and the zinc/sea water electrode. While the copper/copper sulphate reference electrode is most suitable for making contact with soil and fresh water it is not recommended for use in sea water.

Zinc/sea water reference electrodes are cheaper and more robust than silver /silver chloride/sea water electrodes and can be used, unless a high degree of stability is required. Experience with zinc in clean sea water has shown variations between electrodes of ± 30 mV, and with a silver/silver chloride/sea water electrode, variations of ± 5 mV.

A.2 The silver/silver chloride/sea water electrode

This comprises metallic silver coated with silver chloride and a sparingly soluble salt. When placed in sea water the electrode achieves a stable potential, the value of which depends on the level of chloride present in the sea water. The electrochemical reaction for the silver/silver chloride electrode is as follows:

$$\text{AgCl (solid)} + e^{-} = \text{Ag (solid)} + \text{Cl}^{-} \text{ (solvated)} \qquad \text{(A.1)}$$

and the reaction is said to be reversible to chloride ions. The concentration of chloride ions in solution (i.e. in sea water) influences the electrode potential.

In order to achieve a long life in marine service, it is necessary to use a robust electrode with a thick layer of silver chloride. This may be produced by dipping the thinly coated electrode in molten silver chloride. The consistency of chloride concentration in sea water ensures a constant and consistent electrode potential.

Electrodes for marine service must also be protected from abrasion, fouling or other contamination by housing in a suitable structure, allowing contact with the sea water electrolyte to be maintained through perforated containers. They should be immersed in fresh sea water for several hours before use. The cable end should be insulated to prevent the electrode becoming short-circuited.

Variation of the salinity of the water will affect the potential of such an electrode. Dilution of the sea water, as may occur in estuaries, makes the electrode more positive. The change will not be greater than 60 mV for each 10-fold change in concentration so that, in many locations, the effect can be allowed for by adopting a slightly more negative protection potential. If, however, the effects on the measurements of variation of salinity are unacceptable, the element should be immersed in a solution of known concentration of potassium chloride in a non-perforated container, the electrode being separated from the environment by a porous plug. When not in use, this type of electrode should be stored in a solution of potassium chloride.

A.3 The zinc/sea water electrode

This electrode consists simply of metallic zinc in contact with sea water. Despite the many ionic species present in sea water and the alternative electrode reactions, the zinc/sea water electrode maintains a reasonably constant potential of ± 30 mV regardless of the variations in sea water. It is essential that the zinc should be sufficiently pure with an iron content not exceeding 0,0014 %. Both high purity zinc and anode specification zinc have been successfully used as reference electrodes.

Contamination of the electrode surface can affect its potential over long periods of time. This contamination problem may be overcome by ensuring that the surface of the zinc corrodes away at a controlled rate. The electrode should be isolated from its supports as direct electrical contact between the zinc and the protected structure will lead to polarisation of the electrode. The risk of polarisation can also be reduced by ensuring that the surface area of zinc exposed to the sea water is sufficiently large.

A.4 Electrodes for calibration purposes

The standard hydrogen electrode provides the datum for reference electrodes and is the electrode least sensitive to changes in electrolyte composition. The acid electrolyte is maintained under a blanket of hydrogen gas at one atmosphere and the electrolyte is held at 25 °C. The electrode which consists of a platinised platinum foil in an acid electrolyte of pH 1 is not, however, suitable for site use.

A more robust reference electrode is the saturated calomel electrode, which consists of mercury, mercurous chloride and saturated potassium chloride solution.

The calomel electrode is often used in the laboratory for checking the condition of reference electrodes used in the field but it is insufficiently robust for field use. The potentials of the various reference electrodes with respect to the standard hydrogen electrode are given in table A.1.

Table A.1 — Potentials of reference electrodes with respect to the standard hydrogen electrode (at 25 °C)

Electrode	volt
Silver/silver chloride/saturated KCl	+0,20
Silver/silver chloride/sea water	+0,25 (approx)
Calomel (normal KCl)	+0,28
Calomel (saturated KCl)	+0,24
Zinc/sea water (see A.3)	-0,78 (approx)

NOTE 1 The effect of temperature does not normally need to be taken into account during field testing.

NOTE 2 The potentials of reference electrodes are generally quoted with respect to the standard hydrogen electrode although the latter is only used in laboratories. The purpose of the table is to enable potentials measured with one reference electrode to be expressed in terms of another. For example, it will be seen that the zinc/sea water electrode is 1,03 V more negative than the Ag/AgCl/sea water electrode. A potential of -0,80 V measured with the Ag/AgCl/sea water electrode would thus be 1,03 V more positive (ie +0,23 V) with respect to a zinc/sea water electrode.

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