CATHODIC PROTECTION

P E FRANCIS

CONTENTS

CATHODIC PROTECTION

P E FRANCIS

1 INTRODUCTION

The first practical use of cathodic protection is generally credited to Sir Humphrey Davy in the 1820s. Davy's advice was sought by the Royal Navy in investigating the corrosion of copper sheeting used for cladding the hulls of naval vessels. Davy found that he could preserve copper in sea water by the attachment of small quantities of iron or zinc; the copper became, as Davy put it, "cathodically protected".

The most rapid development of cathodic-protection systems was made in the United States of America to meet the requirements of the rapidly expanding oil and natural gas industry which wanted to benefit from the advantages of using thin-walled steel pipes for underground transmission. For that purpose the method was well established in the United States in 1945.

In the United Kingdom, where low-pressure thicker-walled cast-iron pipes were extensively used, very little cathodic protection was applied until the early 1950s. The increasing use of cathodic protection has arisen from the success of the method used from 1952 onwards to protect about 1000 miles of wartime fuel-line network that had been laid between 1940 and 1944. The method is now well established.

Cathodic protection can, in principle, be applied to any metallic structure in contact with a bulk electrolyte. In practice its main use is to protect steel structures buried in soil or immersed in water. It cannot be used to prevent atmospheric corrosion.

Structures commonly protected are the exterior surfaces of pipelines, ships' hulls, jetties, foundation piling, steel sheet-piling, and offshore platforms. Cathodic protection is also used on the interior surfaces of water-storage tanks and water-circulating systems. However, since an external anode will seldom spread the protection for a distance of more than two or three pipe-diameters, the method is not suitable for the protection of small-bore pipework.

Cathodic protection has also been applied to steel embedded in concrete, to copper-based alloys in water systems, and, exceptionally, to lead-sheathed cables and to aluminium alloys, where cathodic potentials have to be very carefully controlled.

2 PRINCIPLES OF CATHODIC PROTECTION

Corrosion in aqueous solutions proceeds by an electrochemical process, and anodic and cathodic electrochemical reactions must occur simultaneously. No nett overall charge builds up on the metal as a result of corrosion since the rate of the anodic and cathodic reactions are equal.

Anodic reactions involve oxidation of metal to its ions, e.g. for steel the following reaction occurs.

$$Fe > Fe^{2+} + 2e \qquad (1)$$

The cathodic process involves reduction and several reactions are possible. In acidic water, where hydrogen ions (H^+) are plentiful, the following reaction occurs.

$$2H^+ + 2e > H_2 \qquad (2)$$

In alkaline solutions, where hydrogen ions are rare, the reduction of water will occur to yield alkali and hydrogen.

$$2H_2O + 2e > H_2 + 2OH^- \qquad (3)$$

However, unless the water is deaerated reduction of oxygen is the most likely process, again producing alkali at the surface of the metal.

$$O_2 + 2H_2O + 4e > 4OH^- \qquad (4)$$

Reactions (1) and (2) are shown schematically in Fig 1 where anodic and cathodic sites are nearby on the surface of a piece of metal. We can change the rate of these two reactions by withdrawing electrons or supplying additional electrons to the piece of metal. It is an established principle that if a change occurs in one of the factors under which a system is in equilibrium, the system will tend to adjust itself so as to annul, as far as possible, the effect of that change. Thus, if we withdraw electrons from the piece of metal the rate of reaction (1) will increase to attempt to offset our action and the dissolution of iron will increase, whereas reaction (2) will decrease. Conversely, if we supply additional electrons from an external source to the piece of metal, reaction (1) will decrease to give reduced corrosion and reaction (2) will increase. The latter case will apply to cathodic protection. Thus, to prevent corrosion we have to continue to supply electrons to the steel from an external source to satisfy the requirements of the cathodic reaction. Note that the anodic and cathodic processes are inseparable. Reducing the rate of the anodic process will allow the rate of the cathodic process to increase.

These principles may be expressed in a more quantitative manner by plotting the potential of the metal against the logarithm of the anodic and cathodic reaction rates expressed as current densities. Typical anodic and cathodic curves are illustrated in Fig 2. The corrosion current, I_{corr}, and the corrosion potential, E_{corr}, occur at the point of intersection of the anodic and cathodic curves, i.e. where anodic and cathodic reactions rates are equal. If electrons are "pumped" into the metal to make it more negative the anodic dissolution of iron is decreased to a negligible rate at a potential E_I, whereas the rate of the cathodic current is increased to I_1. Hence, a current I_1 must be supplied from an external source to maintain the potential at E_1 where the rate of dissolution of the iron is at a low value. If the potential is reduced to E_2 (Fig 2) the current required from the external source will increase to I_2. Further protection of the metal is insignificant, however, and the larger current supplied from the external source is wasted. The metal is then said to be over-protected.

In aerated neutral or alkaline solutions the cathodic corrosion process is usually the reduction of oxygen. The kinetics of this cathodic process are controlled by the rate at which oxygen can diffuse to the surface of the metal, which is slower than the rate of consumption of oxygen by the cathodic reaction. Thus, the rate of this reaction does not increase as the potential of the metal is made more negative but remains constant unless the rate of supply of oxygen to the surface of the metal is increased by, for example, increase fluid flow rate. The influence of flow velocity on cathodic protection parameters is illustrated in Fig 3. A current of I_1 is initially required to maintain the metal at the protection potential E_1. However, if the flow rate is increased the limiting current for the reduction of oxygen is increased (dotted line) and the current required to maintain the metal at the protection potential is increased by ΔI. Thus, the current density required to maintain the correct protection potential will vary with service conditions. Clearly, cathodic current density is not a good guide as to whether a structure is cathodically protected. The correct protection potential must be maintained if corrosion is to be prevented.

If the structure is over-protected and the potential is reduced to a potential region where reduction of water (reaction 3) can take place, further current will be required from the external source and current will be wasted. In Fig 3 reducing the potential from E_1 to E_2 will increase the current required from the external source from I_1 to I_2 as a result of an increased rate of reduction of water.

Excessive negative potentials can cause accelerated corrosion of lead and aluminium because of the alkaline environments created at the cathode. These alkaline conditions may also be detrimental to certain paint systems, and may cause loss of the paint film. Hydrogen evolution at the cathode surface may, on high-strength steels, result in hydrogen embrittlement of the steel, with subsequent loss of strength. It may also cause disbanding of any insulating coating: the coating would then act as an insulating shield to the cathodic-protection currents.

3 METHODS OF APPLYING CATHODIC PROTECTION

Cathodic protection may be achieved in either of two ways. By the use of an impressed current from an electrical source, or by the use of sacrificial anodes (galvanic action).

3.1 IMPRESSED CURRENT

The arrangement for protecting a buried pipeline is illustrated in Fig 4. The buried pipe receives current from a DC power source via an auxiliary inert electrode buried in the ground. The pipe becomes the cathode and the auxiliary electrode the anode. The auxiliary electrode sometimes consists of scrap iron. In this case the iron will dissolve from the anode by reaction (1) and the electrode is described as a consumable anode. If the anode is a noble metal or an electrochemically inert material, the surrounding environment will be oxidised and in water reaction

$$2H_2O > O_2 + 4H^+ + 4e \qquad (5)$$

will occur. In saline solutions, however, chlorine may be produced at the anode. This may present problems in confined spaces.

A range of materials have been used as non-consumable anodes for impressed-current systems. The sort of properties required by these anodes are

a. good electrical conduction,
b. low rate of corrosion,
c. good mechanical properties, able to stand the stresses which they may be subjected to during installation and in service,
d. readily fabricated into a variety of shapes,
e. low cost,
f. able to withstand high current densities at their surfaces without forming resistive barrier oxide layers, etc.

The following materials have been used as anodes: magnetite, carbonaceous materials (graphite), high silicon iron (14-18% Si), lead/lead oxide, lead alloys, platinised materials (such as tantalum, niobium, titanium). Platinum, with its high resistance to corrosion, would be an ideal anode material but has the major disadvantage of very high cost.

In practice, voltages up to 100 V and high current densities are possible on impressed-current anodes (see Table 1). Thus, large areas of a structure can be protected from a single anode and, because of the high driving voltage, the anode can be placed remote from the structure.

3.2 SACRIFICIAL ANODES

To understand the action of sacrificial anodes for cathodic protection it is necessary to have in mind the galvanic series of metals. The galvanic series for a few selected metals in sea water is shown in Table 2. When the tendency for metal to go into solution as metal ions increases (leaving an excess of electrons on the metal surface), i.e.

$$M > M^+ + e \qquad (6)$$

the metal becomes more electronegative. Thus, since zinc, aluminium and magnesium are more electronegative than steel they are increasingly able to supply electrons to the more electropositive steel when in electrical contact in water, and will effect cathodic protection of the steel surface. Clearly, if steel was coupled to copper ins ea water, steel would supply electrons to copper which would become cathodically protected, and the corrosion of the steel would be enhanced.

The cathodic protection of a steel pipe with sacrificial anodes is illustrated in Fig 5. Electrons are supplied to the steel pipe, via the electrical connection, and a corresponding amount of anode material goes into solution as metal ions, according to the laws of electrolysis. Some anode material is lost by self-corrosion, and the anodes are not converted to electrical energy with 100% efficiency. Zinc, aluminium and magnesium area the metals commonly used for sacrificial cathodic protection. Some anode properties are shown in Table 3.

The driving voltage of sacrificial anodes is now compared with impressed-current anodes, and sacrificial anodes must be located close to the structure being protected. Although almost any piece of zinc etc could provide cathodic protection over a short period of time, cathodic protection schemes are usually required to operate over periods of several years. Anodes can lose their activity and become passivated, developing a non-conducting film on their surfaces so that they no longer are able to supply current. This can be avoided by careful control of the concentrations of trace impurities in the anode materials, and by alloying. For zinc anodes the level of iron, for example, must be kept below 0.005% for satisfactory long-term operation of the anodes. To prevent passivation of aluminium anodes,alloying with, for example, indium has been found to be successful. The previously successful alloy with mercury is now disliked on environmental grounds.

4 DESIGN

4.1 PROTECTION POTENTIALS

In practice, the structure-to-electrolyte potentials are measured using a standard reference electrode based on copper/copper sulphate, silver/silver chloride, or pure zinc. The reference electrode should be very close to the surface whose potential is being measured. For steel in an aerobic electrolyte of nearly neutral pH a commonly accepted protection potential is -850 mV; when exposed to sulphate-reducing bacteria a potential of –950 mV would be required. Both values are referred to a copper/copper sulphate electrode. Results of a laboratory determination of the protection potential for steel are shown in Fig 6.

Some potential values for protection of other metals are shown in Table 4. Values for lead and aluminium must be carefully controlled to avoid damage by excess alkali which could build up at the surface of the metals if the protection potentials are too negative.

4.2 CURRENT DENSITY

The current density required to maintain the protection potential is very dependent on local conditions. Increased availability of oxygen at the surface of the metal will directly increase current density as illustrated previously in Fig 3. Increased availability of oxygen may occur because of increased concentration of oxygen in the environment, increased water flow or turbulence. Thus, current densities to structures in sea water, rivers, etc are likely to vary continuously. The pH of the environment will also be important. The presence of coatings, marine fouling, and calcareous deposits will have a profound effect on current density. Some typical values of current density for steel are shown in Table 5.

Having decided on the appropriate current density, the total anode current can be determined from the area of the structure. The size of the anodes can then be determined from data in Table 3 if a sacrificial anode scheme is to be employed, taking into account the working life of the protected structure or the period required between refits.

4.3 COATINGS

The provision of an insulating coating to the structure will greatly reduce the current demand for cathodic protection. When first applied, coatings will often contain flaws, and in service, further defects will develop over a period of time. The conjoint use of coatings and cathodic protection takes advantage of the most attractive features of each method of corrosion control. Thus, the bulk of the protection is provided by the coating and cathodic protection provides protection to flaws in the coating. As the coating degrades with time, the activity of the cathodic protection system develops to protect the deficiencies in the coating. A combination of coating and cathodic protection will normally result in the most economic protection system.

4.4 CALCAREOUS SCALES

In sea water, cathodic protection of bare steel is economic because of the formation of calcareous deposits. The alkali formed at the surface of a protected structure reacts with bicarbonate ions present in sea water to form carbonate ions (reaction 7) which, in turn, precipitate as insoluble calcium carbonate (reaction 8) on the surface of the metal

$$OH^- + HCO_3^- > CO_3^{2-} + H_2O \tag{7}$$

$$CO_3^{2-} + Ca^{2+} > CaCO_3 \tag{8}$$

4.5 CHOICE OF CATHODIC PROTECTION SYSTEM

In the design of a cathodic-protection scheme, a decision must be made as to whether the scheme should be a sacrificial anode or impressed-current system or a mixture of the two systems.

Sacrificial anode systems have the advantage of being

(a) simple to install,

(b) independent of any source of electric power,
(c) suitable for localised protection,
(d) less liable to cause interaction on neighbouring structures.

It is difficult to over-protect the structure and moderately easy to obtain a uniform electrode potential across the structure. The most severe limitation of the sacrificial anode is the small driving force which restricts its use to conductive environments or well-coated systems. To protect a large structure, such as a pipeline, with sacrificial anodes, a large number of them would need to be distributed along it, involving a multiplicity of electrical connections and considerable installation work.

The advantages of the impressed-current system include

(a) the large driving force available can protect a large, even uncoated, structure in high resistivity environments,
(b) comparatively few anodes are needed,
(c) the voltage may be adjusted to allow for environmental and coating changes.

The impressed-current system may allow considerable over-protection, however, and considerable variation of potential over the structure is difficult to avoid.

Generally, sacrificial anode schemes have found favour for small well-coated low-current-demand structures or for localised protection, with impressed-current schemes being utilised for large complex structures which may be bare or poorly coated. However, in North Sea offshore work, it has been found economic to provide galvanic protection to large uncoated platforms and similar structures where the cost of coating is prohibitive. In addition, the galvanic anodes offer easily installed robust systems which, being independent of a power source, provide protection immediately on “float-out” of the structure.

4.6 ANODE RESISTANCE

One of the most important parameters in the design of cathodic protection systems is the electrical resistivity of the environment. Resistivities encountered for pipeline environments vary from 1 ohm cm for brackish river water to greater than 500,000 ohm cm in non-porous granite (see Table 6). Measurement of the resistivity of the environment and calculation of the electrical resistance between the anodes and the structure due to the electrolyte must be made at an early stage in the design of the scheme to ensure that adequate current output will be obtained from the anodes over the design-life of the structure (by application of Ohm's Law).

Established methods for determining the resistivity of soils and water are available and will not be dealt within these notes. Exact calculation of the electrical resistances between anodes and structure due to the electrolyte is rarely possible.

Ground beds, as cathodic protection electrodes set in the earth are called, can be considered to lie in a semi-infinite electrolyte and the resistances of electrodes to infinite earth or sea water have been calculated for a number of anode shapes. Thus, if the anodes are remote from the structure, these anode resistances can be used, together with the difference between the required protection potential and the anode potential, to determine current output of anodes using Ohm's Law. If, however, the anodes are positioned close to the structure, then some correction to the resistance is required.

When current flows from a small anode to a large metal structure, the current density is at a maximum near the surface of the anode. Hence a major portion of the potential drop between anode and structure occurs in the vicinity of the anode. This factor probably enables values of anode-resistance to infinite-earth to be used reasonably successfully even when anode and structure are not well separated. A further consequence of this factor is that surrounding an anode with a backfill of conducting material greatly reduces the anode resistance in resistant soils.

In practice, the distribution of current to a structure is difficult to control. If we consider the protection of a pipe by an anode, it should be clear that there will be a higher current density at the point on the pipeline nearest the anode than elsewhere. The effect is illustrated in Fig 7. Clearly, to ensure that the ends of the pipe are protected, the centre of the pipe, nearest the anode, must be overprotected to some degree. The effect can be minimised by using several anodes spaced along the pipe, but this will greatly increase installation costs.

4.7 DANGERS TO BE AVOIDED

Consideration must also be given to spark hazards created by the introduction of electric currents into structures situated in a hazardous atmosphere.

Any secondary structure residing in the same electrolyte may receive and discharge the cathodic-protection direct current by acting as an alternative low-resistance path. Corrosion will be accelerated on the secondary structure at any point where current is discharge to the electrolyte. This phenomenon is called “interaction”.

Interaction may occur, for example, on a ship that is moored alongside a cathodically protected jetty, or on a pipeline or metal-sheathed cable that crosses a cathodically protected pipeline.

Interaction may be minimised by careful design of the cathodic-protection system, in particular, by design of a scheme to operate at the lowest possible current density and by maintaining the greater separation between the protected structure and the secondary structure, and between the groundbeds or anodes and the secondary structure. It is an advantage of sacrificial-anode schemes that they are not prone to creating severe interaction problems and therefore are popular for protection in congested and complex locations.

Methods and procedures are available for overcoming interaction, and testing must be carried out in the presence of all interested parties, so that the choice of remedial measures may be agreed if and when the acceptable limit of interaction is exceeded.

Table 1 Properties of impressed-current anodes

Anode material	Max volts*	Typical anode current density A m^{-2}
Platinum / niobium	100	250 – 1500
Lead / silver / antimony	100	250 – 1000
High silicon iron	100	10 – 100
Graphite	-	200

* Dependent on the environment

Table 2 Galvanic series of some metals in sea water

Electropositive
Platinum
Titanium
Stainless steel
Monel
Copper
Lead
Iron, cast iron, or steel
Cadmium
Zinc
Aluminium
Magnesium
Electronegative

Table 3 Properties of sacrificial anodes

Anode material	Density g cm^{-3}	Potential volts $Cu/CuSO_4$	Amp-hrs per kg	Typical anode current density A m^{-2}
Zn	7.1	-1.10	780	0.5 – 2
Al	2.7	-1.15	2700	0.6 – 2.5
Mg	1.7	-1.55	1230	1.5 – 5.6

Table 4 Potential required for cathodic protection

Metal	Potential ($Cu/CuSO_4$)
Steel	-850 mV
Steel (sulphate reducing bacteria)	-950 mV
Copper alloys	-500 to –650 mV
Lead	-600 mV
Aluminium	-950 to –1200 mV

Table 5 Current densities required to protect steel

Environment	Current density $A\ m^{-2}$
Acidic solutions	350 – 500
Saline solutions	0.3 – 10
Sea water	0.05 – 0.15
Saline mud	0.025 – 0.05

Table 6 Average resistivities of some soils

Environment	Resistivity (ohm cm)
Brackish river water	1
Sea water	25
Town supply water	1000 – 1200
Alluvial soils	1000 – 2000
Clays	1000 – 5000
Gravel	10000 – 25000
Sand	25000 – 50000

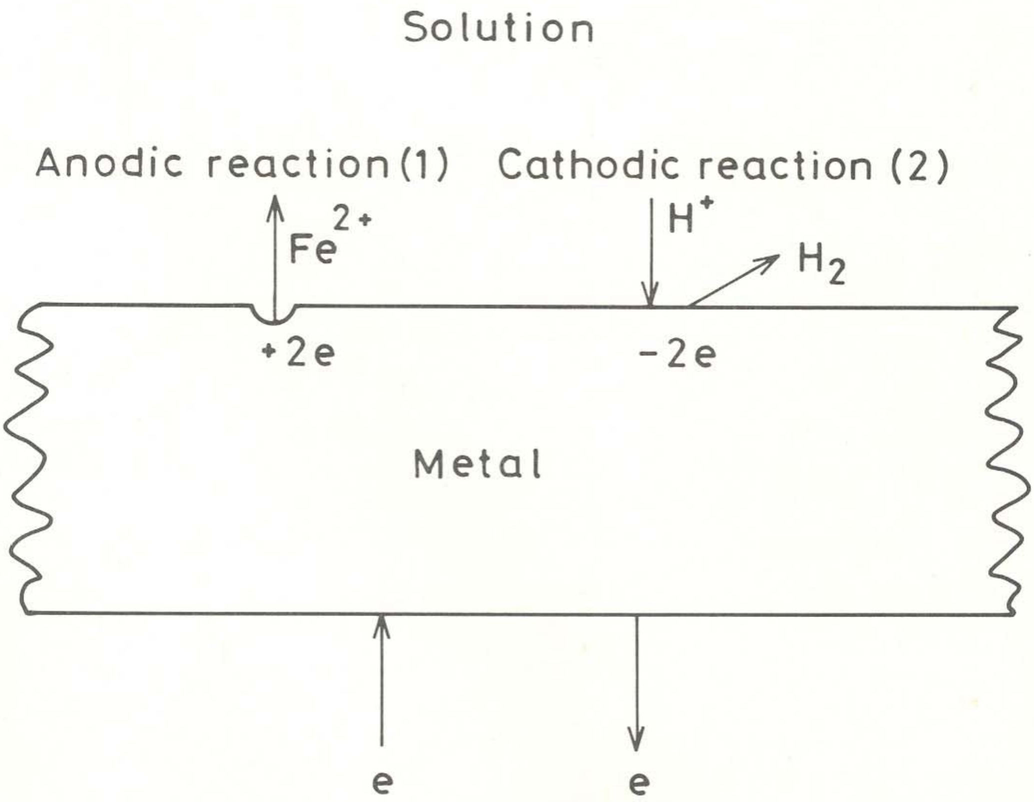


Fig 1 Anodic and cathodic reactions at a metal surface

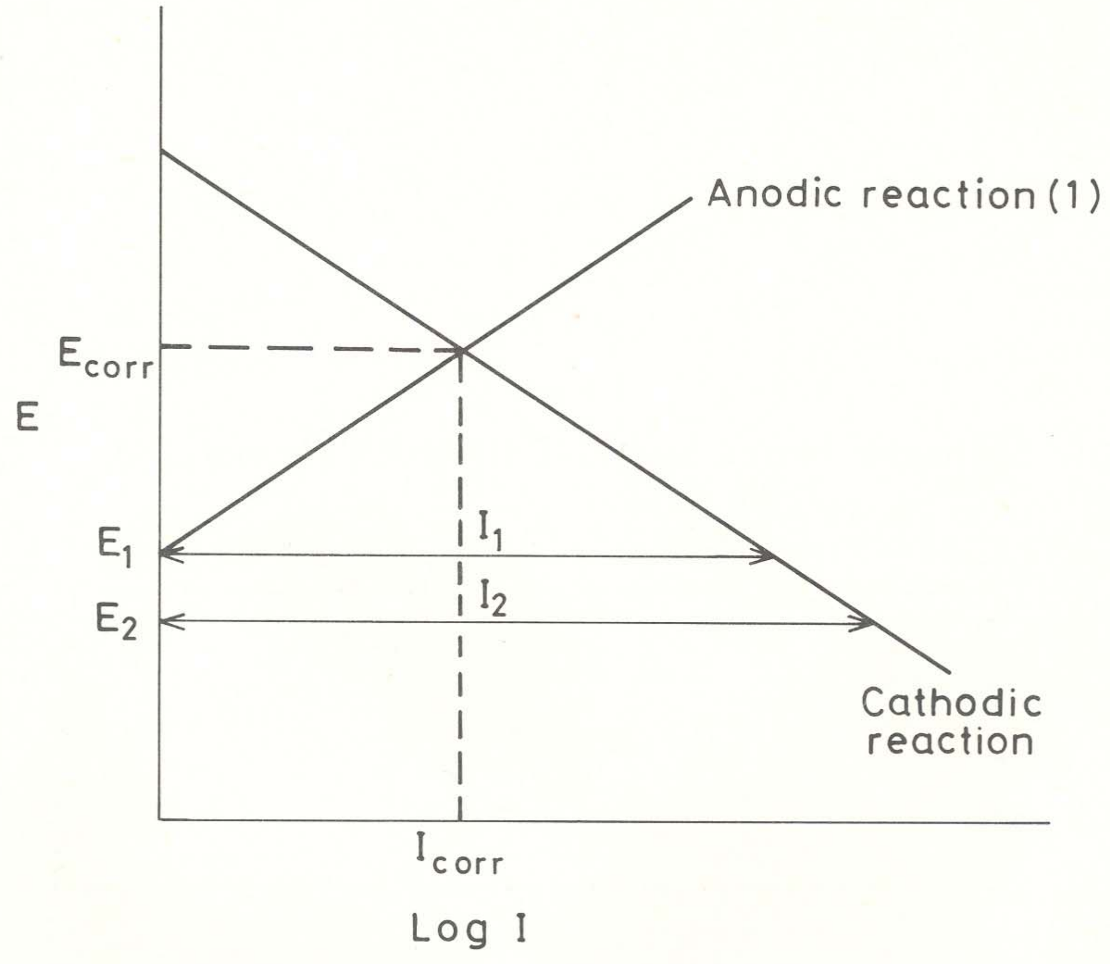


Fig 2 Kinetics of anodic and cathodic reactions

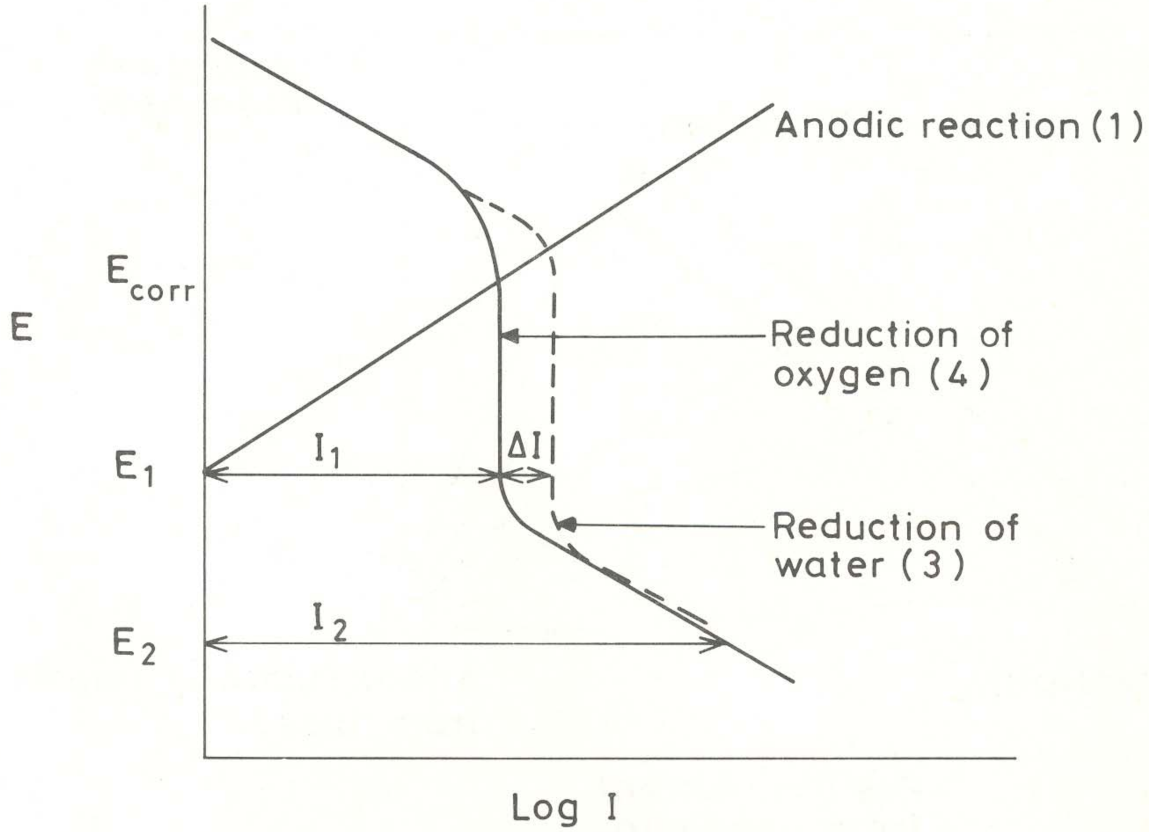


Fig 3 Diffusion-controlled reduction of oxygen.

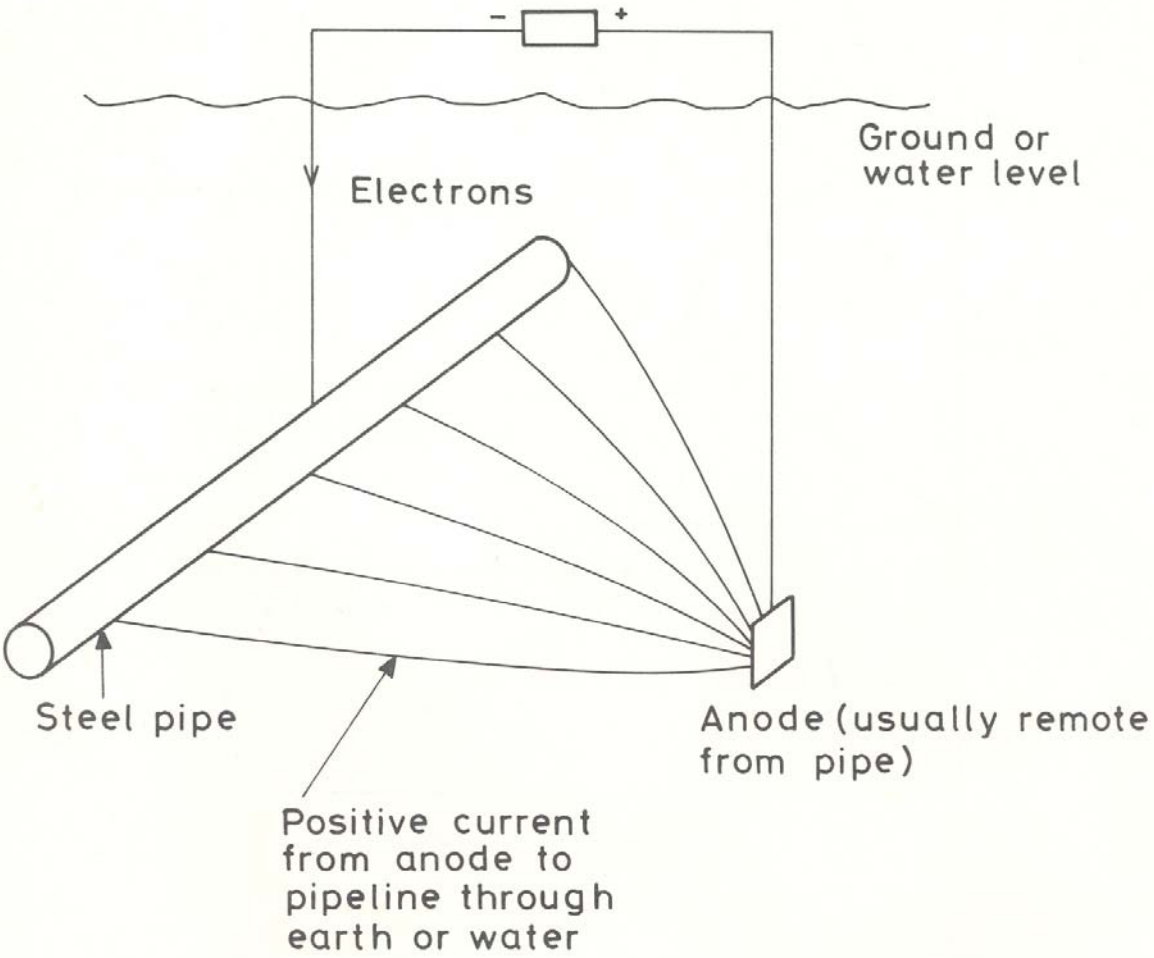
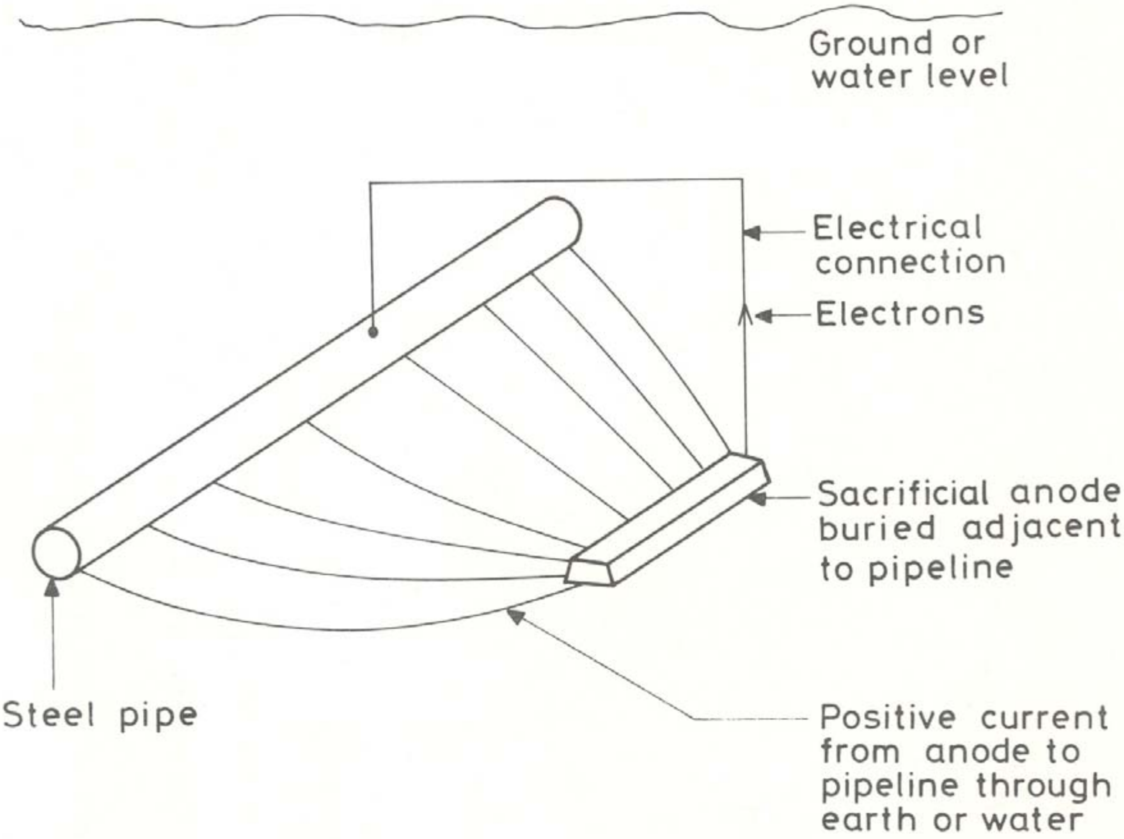


Fig 4 Application of cathodic protection by an impressed current



$$Zn \longrightarrow Zn^{2+} + 2e$$
$$Al \longrightarrow Al^{3+} + 3e$$
$$Mg \longrightarrow Mg^{2+} + 2e$$

Fig 5 Application of cathodic protection by sacrifical anodes

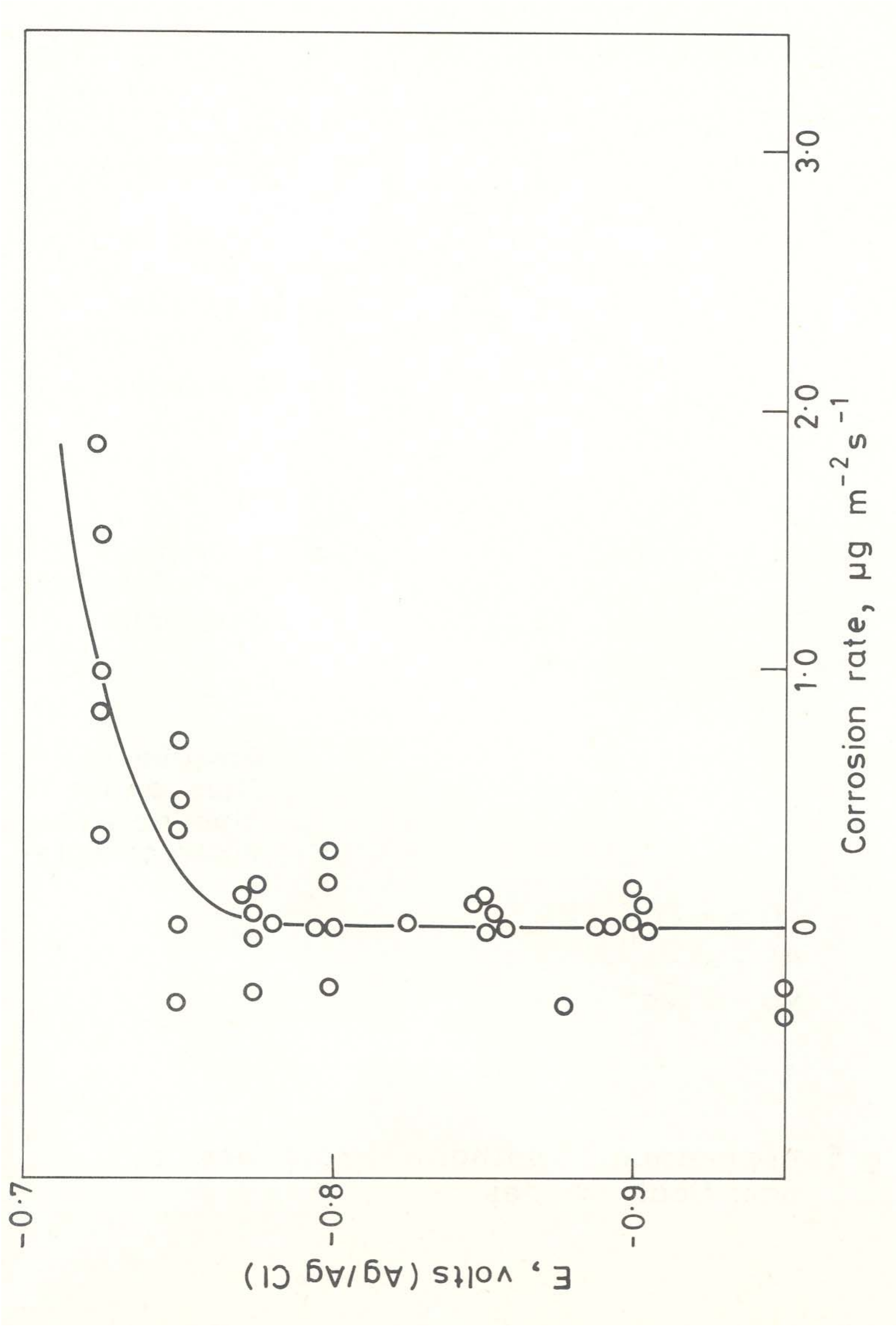


Fig 6. Determination of protection potential for steel in sea water

Fig 6 Determination of protection potential for steel in sea water.

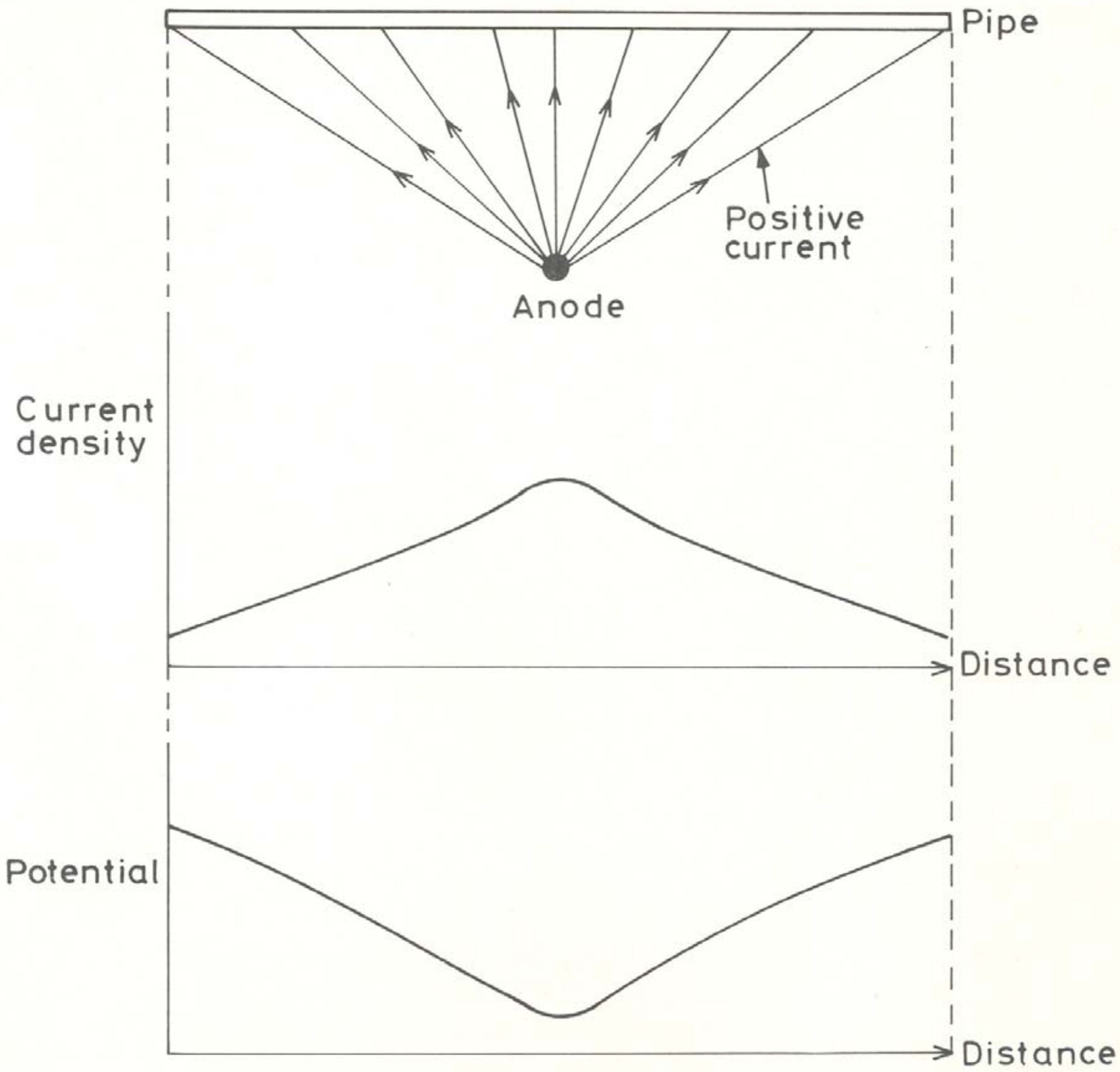


Fig 7. Current and potential distribution along a pipe