4.18 Principles of Cathodic Protection

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Abbreviations

AC Alternating current
BS British Standard
DC Direct current
emf Electromotive force
EN European Norm
NACE National Association of Corrosion Engineers
SRB Sulfate-reducing bacteria

Symbols

E Potential
$E°$ Equilibrium potential
E_a Anodic potential
E_c Cathodic potential
E_{corr} Corrosion potential
I Current
I_a Anodic current
I_c Cathodic current
I_{corr} Corrosion current
I_{lim} Limiting current

IR Ohmic drop (equivalent to a voltage)
R Resistance
η Overpotential

4.18.1 Historical Background

In recent years, it has been regarded as somewhat passé to refer to Sir Humphry Davy in a text on cathodic protection. However, his role in the application of cathodic protection should not be ignored. In 1824, Davy presented a series of papers to the Royal Society in London,[1] in which he described how zinc and iron anodes could be used to prevent the corrosion of copper sheathing on the wooden hulls of British naval vessels. His paper shows a considerable intuitive awareness of what are now accepted as the principles of cathodic protection. Several practical tests were made on vessels in harbor and on sea-going ships, including the effect of various current densities on the level of protection of the copper. Davy also considered the use of an impressed current

device based on a battery, but did not consider the method to be practicable.

The first 'full-hull' installation on a vessel in service was applied to the frigate HMS Samarang in 1824. Four groups of cast iron anodes were fitted, and virtually perfect protection of the copper was achieved. So effective was the system that the prevention of corrosion of the copper resulted in the loss of the copper ions required to act as a toxicide for marine growth, leading to increased marine fouling of the hull. Since this led to some loss of performance from the vessel, interest in cathodic protection waned. The beneficial action of the copper ions in preventing fouling was judged to be more important than preventing deterioration of the sheathing. Cathodic protection was therefore neglected for 100 years, after which it began to be used successfully by oil companies in the United States to protect underground pipelines.[2]

It is interesting that the first large-scale application of cathodic protection by Davy was directed at protecting copper rather than steel. It is also a measure of Davy's grasp of the topic that he was able to consider the use of two techniques of cathodic protection, namely sacrificial anodes and impressed current, and two types of sacrificial anode, namely zinc and cast iron.

## 4.18.2   Electrochemical Principles

4.18.2.1   Aqueous Corrosion

The aqueous corrosion of iron under conditions of air access can be written as

$$2Fe + O_2 + 2H_2O \rightarrow 2Fe(OH)_2 \qquad [1]$$
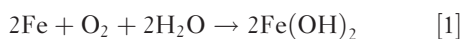
The product, ferrous hydroxide, is commonly further oxidized to magnetite (Fe_3O_4) or a hydrated ferric oxide (FeOOH), that is, rust.

It is convenient to consider separately the metallic and nonmetallic reactions in eqn [1]:

$$2Fe \rightarrow 2Fe^{2+} + 4e^- \qquad [2]$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad [3]$$
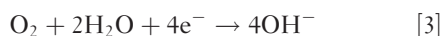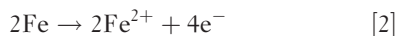
To balance eqns [2] and [3] in terms of electrical charge, it has been necessary to add four electrons to the right-hand side of eqn [2] and to the left-hand side of eqn [3]. However, simple addition and rationalization of eqns [2] and [3] yield eqn [1].

We conclude that corrosion is a chemical reaction [1] occurring by an electrochemical mechanism (eqns [2] and [3]), that is, by a process involving electrical and chemical species. **Figure 1** is a schematic representation of aqueous corrosion occurring at a metal surface.

Equation [2], which involves consumption of the metal and release of electrons, is termed an anodic reaction. Equation [3], which represents consumption of electrons and dissolved species in the environment, is termed a cathodic reaction. Whenever spontaneous corrosion reactions occur, all the electrons released in the anodic reaction are consumed in the cathodic reaction; no excess or deficiency is found. Moreover, the metal normally takes up a more or less uniform electrode potential, often called the corrosion or mixed potential (E_{corr}).

4.18.2.2   Cathodic Protection

It is possible to envisage what might happen if an electrical intervention was made in the corrosion reaction by considering the impact on the anodic and cathodic reactions. For example, if electrons were withdrawn from the metal surface, it might be anticipated that reaction [2] would speed up (to replace the lost electrons) and reaction [3] would slow down, because of the existing shortfall of electrons. It follows that the rate of metal consumption would increase.

By contrast, if additional electrons were introduced at the metal surface, the cathodic reaction would speed up (to consume the electrons) and the anodic reaction would be inhibited; metal dissolution would be slowed down. This is the basis of cathodic protection.

Figure 2 shows the effect on the corrosion reaction shown in **Figure 1** of providing a limited supply of electrons to the surface. The rate of dissolution
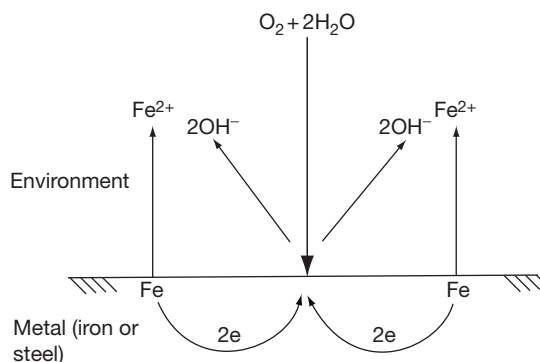

Figure 1 Schematic illustration of the corrosion of steel in an aerated environment. Note that the electrons released in the anodic reaction are consumed quantitatively in the cathodic reaction, and that the anodic and cathodic products may react to produce Fe(OH)$_2$.

slows down because the external source rather than an iron atom provides two of the electrons. **Figure 3** shows the effect of a greater electron supply; corrosion ceases since the external source provides all the requisite electrons. It should be apparent that there is no reason why further electrons could not be supplied, when even more hydroxyl (OH^-) ion would be produced, but without the possibility of a concomitant reduction in the rate of iron dissolution. Clearly, this would be a wasteful exercise.

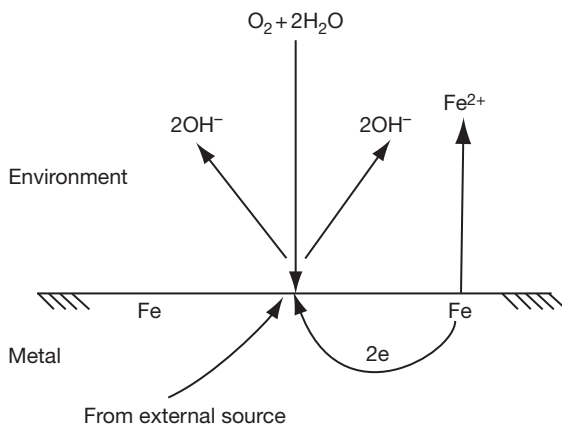The corrosion reaction may also be represented on a polarization diagram (**Figure 4**). The diagram

Figure 2   Schematic illustration of partial cathodic protection of steel in an aerated environment. Note that one of the anodic reactions shown in **Figure 1** has been annihilated by providing two electrons from an external source; an excess of OH^- ions over Fe^{2+} now exists at the surface.
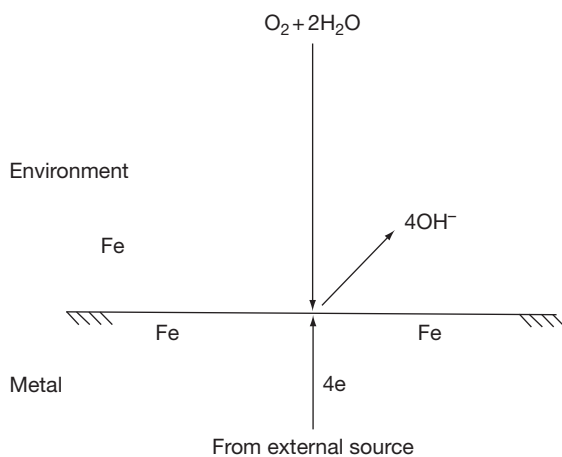
Figure 3   Schematic illustration of full cathodic protection of steel in an aerated environment. Note that both anodic reactions shown in **Figure 1** have now been annihilated, and there is an accumulation of OH^- at the surface.

shows how the rates of the anodic and cathodic reactions (both expressed in terms of current flow I) vary with electrode potential E. Thus, at E_a, the net rate of the anodic reaction is zero and it increases as the potential becomes more positive. At E_c, the net rate of the cathodic reaction is zero and it increases as the potential becomes more negative. (To be able to represent the anodic and cathodic reaction rates on the same axis, the modulus of the current has been drawn.) The two reaction rates are electrically equivalent at E_{corr}, the corrosion potential, and the corresponding current I_{corr} is an electrical representation of the rate of the anodic and cathodic reactions at that potential, that is, the spontaneous corrosion rate of the metal. That is, at E_{corr} the polarization diagram represents the situation referred to above; namely, that when spontaneous corrosion occurs, the rate of electron release equals the rate of electron consumption, and there is no net current flow although metal is consumed, and meanwhile the metal exerts a single electrode potential.

To hold the metal at any potential other than E_{corr} requires that electrons be supplied to, or be withdrawn from, the metal surface. For example, at E', the cathodic reaction rate I'_c, exceeds the anodic reaction rate I'_a, and the latter does not provide sufficient electrons to satisfy the former. If the metal is to be maintained at E', the shortfall of electrons given by $(|I'_c| - I'_a)$ must be supplied from an external source. This externally supplied current serves to reduce the metal dissolution rate from I_{corr} to I'_a.

At E_a, the net anodic reaction rate is zero (there is no metal dissolution) and a cathodic current equal to I''_c must be available from the external source to maintain the metal at this potential. It may also be apparent from **Figure 4** that, if the potential is maintained below E_a, the metal dissolution rate remains zero ($I_a = 0$), but a cathodic current greater than I''_c must be supplied; more current is supplied without achieving a benefit in terms of metal loss. There will, however, be a higher interfacial hydroxyl ion concentration.

4.18.2.3   Oxygen Reduction

In illustrating the corrosion reaction in eqn [1], the oxygen reduction reaction [3] has been taken as the cathodic process. Moreover, in **Figures 1–4**, oxygen reduction has been assumed. While there is a range of cathodic reactions that can provoke the corrosion of a metal (since to be a cathodic reactant, any particular species must simply act as an oxidizing
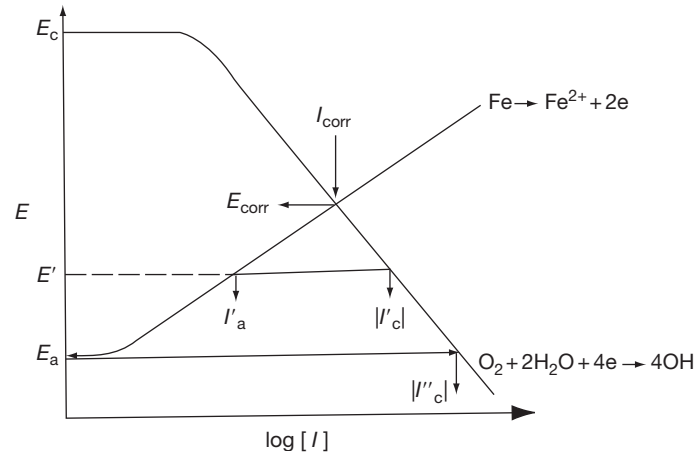
Figure 4 Polarization diagram representing corrosion and cathodic protection. A corroding metal takes up the potential E_{corr} spontaneously and corrodes at a rate given by I_{corr}. If the potential is to be lowered to E', a current equal to $(|I'_c| - I'_a)$ must be supplied from an external source; the metal will then dissolve at a rate equal to I'_a.

agent to the metal), the most common cathodic reactant present in natural environments is oxygen. It is for this reason that the oxygen reduction reaction has been emphasized here.

When corrosion occurs, if the cathodic reactant is in plentiful supply, it can be shown both theoretically and practically that the cathodic kinetics are semilogarithmic, as shown in **Figure 4**. The rate of the cathodic reaction is governed by the rate at which electrical charge can be transferred at the metal surface. Such a process responds to changes in electrode potential, giving rise to the semilogarithmic behavior.

Because oxygen is not very soluble in aqueous solutions (~10 ppm in cool seawater, for example), it is not freely available at the metal surface. As a result, it is often easier to transfer electrical charge at the surface than for oxygen to reach the surface to take part in the charge transfer reaction. The cathodic reaction rate is then controlled by the rate of arrival of oxygen at the surface. This is often referred to as mass transfer control. Since oxygen is an uncharged species, its rate of arrival is unaffected by the prevailing electrical field and responds only to the local oxygen concentration gradient. If the cathodic reaction is driven so fast that the interfacial oxygen concentration is reduced to zero (i.e., the oxygen is consumed as soon as it reaches the surface), the oxygen concentration gradient to the surface reaches a maximum and the reaction rate attains a limiting value. Only an increase in oxygen concentration or an increase in flow velocity will permit an increase in the limiting value. The cathodic kinetics under mass transfer control will be as shown in **Figure 5**.
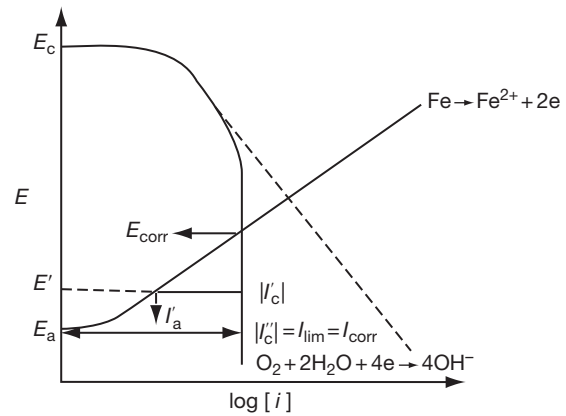

Figure 5 Polarization diagram representing corrosion and cathodic protection when the cathodic process is under mass transfer control. The values of E_{corr} and I_{corr} are lower than when there is no mass transfer restriction, that is, when the cathodic kinetics follows the dotted line.

Figure 5 demonstrates that, even when semilogarithmic cathodic kinetics is not observed, partial or total cathodic protection is possible. Indeed, **Figure 5** shows that the corrosion rate approximates to the limiting current for oxygen reduction (I_{lim}), and the current required for protection is substantially lower than when semilogarithmic cathodic behavior prevails.

4.18.2.4 Hydrogen Evolution

In principle, it is possible for water to act as a cathodic reactant with the formation of molecular hydrogen:

$$2H_2O + 2e^- \leftrightarrows H_2 + 2OH^- \qquad [4]$$
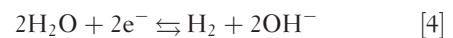
Indeed, in neutral solutions, the corrosion of iron with concomitant hydrogen evolution deriving from the reduction of water is thermodynamically feasible. In practice, this cathodic reaction is barely significant because the reduction of any oxygen present is both thermodynamically favored and kinetically easier. In the absence of oxygen, the hydrogen evolution reaction at the corrosion potential of iron is so sluggish that the corrosion rate of the iron is vanishingly small.

Nevertheless, hydrogen evolution is important in considering the cathodic protection of steel. Although hydrogen evolution takes little part in the corrosion of steel in aerated neutral solutions (see **Figure 6**), as the potential is lowered to achieve cathodic protection, it plays a larger, and eventually dominant, role in determining the total current demand. This too is demonstrated in **Figure 6** where, it must be remembered, the current supplied from the external source at any potential must be sufficient to sustain the total cathodic reaction, that is, both oxygen reduction and hydrogen evolution reactions at that potential. It will be seen that to lower the potential much below E_a entails a substantial increase in current and significantly more hydrogen evolution.

4.18.3   Methods of Applying Cathodic Protection

There are two principal methods of applying cathodic protection, namely the impressed current technique and the use of sacrificial anodes.
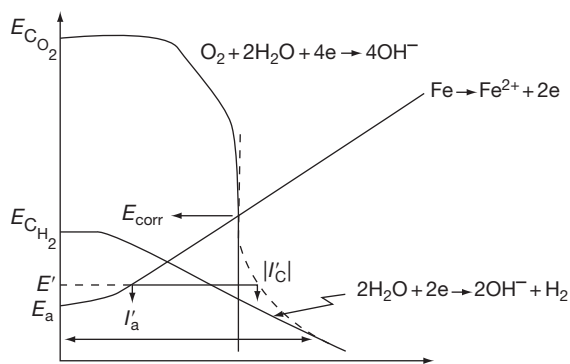
Figure 6   Polarization diagram showing the limited role hydrogen evolution plays at the corrosion potential of steel in aerated neutral solution, the larger role in determining cathodic protection currents, and the dominant role in contributing to current requirements at very negative potentials. The dotted line shows the total cathodic current due to oxygen reduction and hydrogen evolution.

The former includes the structure as part of a driven electrochemical cell, and the latter includes the structure as part of a spontaneous galvanic cell.

4.18.3.1   Impressed Current Method

Figure 7 illustrates the use of an external power supply to provide the cathodic polarization of the structure. The circuit comprises the power source, an auxiliary or impressed current electrode, the corrosive solution, and the structure to be protected. The power source drives a positive current from the impressed current electrode through the corrosive solution and onto the structure. The structure is thereby cathodically polarized (its potential is lowered), and the positive current returns through the circuit to the power supply. Thus, to achieve cathodic protection, the impressed current electrode and the structure must be in both electrolytic and electronic contact.

The power supply is usually a transformer/rectifier that converts AC power to DC. Typically, the DC output will be in the range 15–100 V and 5–100 A, although 200 V/200 A units are not unknown. Thus, fairly substantial driving voltages and currents are available. Where mains power is not available, diesel or gas engines, solar panels, or thermoelectric generators have all been used to provide suitable DC.

It will be seen that the impressed current electrode discharges positive current, that is, it acts as an anode in the cell. There are three generic types of anode used in cathodic protection, namely consumable, nonconsumable, and semiconsumable. The consumable electrodes undergo an anodic reaction that involves their consumption. Thus, an anode made of scrap iron produces positive current by the reaction
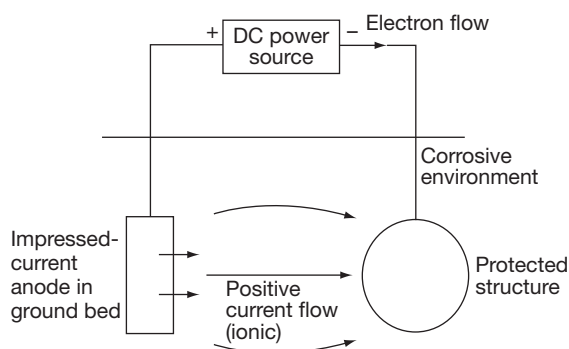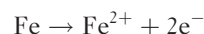
$$Fe \rightarrow Fe^{2+} + 2e^-$$

Figure 7   Schematic diagram of cathodic protection using the impressed-current technique.

The ferrous ions then enter the environment as a positive current carrier (although in practice the current will be carried in the environment by aqueous ions such as Na^+ and Cl^-. Since the dissolving anode must obey Faraday's law, it follows that the wasting of the anode will be proportional to the total current delivered. In practice, the loss for an iron anode is approximately $9\,kg\,A^{-1}\,year^{-1}$. Thus, consumable anodes must be replaced at intervals, or be of sufficient size to remain as a current source for the design life of the protected structure. This poses some problems in design because, as the anode dissolves, the resistance it presents to the circuit increases. More important, it is difficult to ensure continuous electrical connection to the dissolving anode.

Nonconsumable anodes sustain an anodic reaction that decomposes the aqueous environment rather than dissolves the anode metal. In aqueous solutions the reaction may be

$$2H_2O \rightarrow O_2 + 4H^+ + e^-$$

or in the presence of chloride ions

$$2Cl^- \rightarrow Cl_2 + 2e^-$$
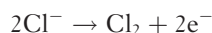
Anodes made from platinized titanium or niobium belong to this category.

Because these anodes are not consumed faradaically, they should not, in principle, require replacement during the life of the structure. However, to remain intact, they must be chemically resistant to their anodic products (acid and chlorine) and, where the products are gaseous, conditions must be produced that allow the gas to escape and not interfere with anode operation. This is particularly true of the platinized electrodes because they can operate at high current density ($>100\,A\,m^{-2}$) without detriment, but will then produce high levels of acidity ($pH < 2$) and large volumes of gas. Ground-bed design (the way in which the anode is installed) is therefore crucial.

Although the anodes are described as nonconsumable, they do suffer some loss of the thin ($\sim 2.5-10\,mg\,m^{-3}$) platinized coating. This loss, which unfortunately has become known as the wear rate although there is no question of the loss being due to mechanical wear, is usually small, related to the total current passed, and increased if the applied current has an AC component. Typically, values for the loss rate are $8\,mg\,A^{-1}\,year^{-1}$ for platinized titanium, which may be increased 10-fold if an AC component of $<100\,Hz$ is present. Negative-going current spikes, such as may be induced by a poorly designed thyristor switching device, even given otherwise clean DC, can produce a 100-fold increase in the rate of loss.

The semiconsumable electrodes, as the name implies, suffer rather less dissolution than Faraday's law would predict and substantially more than the nonconsumable electrodes. This is because the anodic reaction is shared between oxidizing the anode material (causing consumption) and oxidizing the environment (with no concomitant loss of metal). Electrodes made from silicon–iron, chromium–silicon–iron and graphite fall into this category.

Table 1 gives a brief summary of the behavior of some impressed current anodes, and protection by impressed current is discussed in more detail elsewhere.

4.18.3.2 Sacrificial Anodes

Using the impressed-current technique, the driving voltage for the protective current comes from a DC power source. The sacrificial anode technique uses the natural potential difference that exists between the structure and a second metal in the same environment to provide the driving voltage. No power source is employed. Moreover, the dissolution of the second metal, that is, the sacrificial anode, provides the source of electrons for cathodic polarization of the structure. Thus, while the impressed-current anode may be more noble or more base than the protected structure because the power source forces it to act as an anode, the sacrificial anode must be spontaneously anodic to the structure, that is, be more negative in the galvanic series for the given environment. Thus, in principle, zinc, aluminum, or magnesium could be used to protect steel, and iron to protect copper. **Figure 8** illustrates the use of a sacrificial anode for cathodic protection.

In practice, pure metals are never used as sacrificial anodes. There are a variety of reasons for this, which includes the need for

1. a reliable, reproducible and negative operating potential for the anode;
2. a high and reproducible capacity ($A\,h\,kg^{-1}$) for the anode;
3. uniform dissolution of the anode so that all metal is consumed usefully in providing cathodic protection and not wastefully by mechanical loss;
4. freedom from any loss of activity by the anode due to passivation.

For these reasons, alloying elements appear in all the commercial anodes, and very careful quality control

Table 1   Impressed-current anode materials

Material	Consumption rate or operating current density	Notes
Consumable:		
Scrap iron	~ 9 kg A^{-1} year^{-1}	Cheap: suitable for buried or immersed use
Cast iron	<9 kg A^{-1} year^{-1}	Cheap; buried or immersed use; carbon skeleton reduces consumption
Semiconsumable:		
Silicon cast iron (Fe–14Si–(3 Mo)	5–50 A m^{-2} (in freshwater or soil)	Buried or immersed use; consumption (<1 kg A^{-1} year^{-1}); Mo reduces consumption in seawater
Graphite	2.5–10 A m^{-2}	Consumption rate very much less than steel or cast iron (< 1 kg A^{-1} year^{-1}); chloride ions reduce consumption
Nonconsumable:		
Lead alloys:		
1. Pb–6Sb–1Ag	<50–200 A m^{-2} (in seawater)	PbO_2 film restrains consumption
2. Pt-activated	<50–500 A m^{-2} (in seawater)	PbO_2 film protective
Platinized Ti, Ta, or Nb	< 1000 A m^{-2} (consumption)	Discontinuities in Pt coat protected by oxide film on subtrate; sensitive (< 100 Hz) AC ripple in DC or negative current spikes causing electrode consumption; maximum operating potential with Ti substrate: 9 V
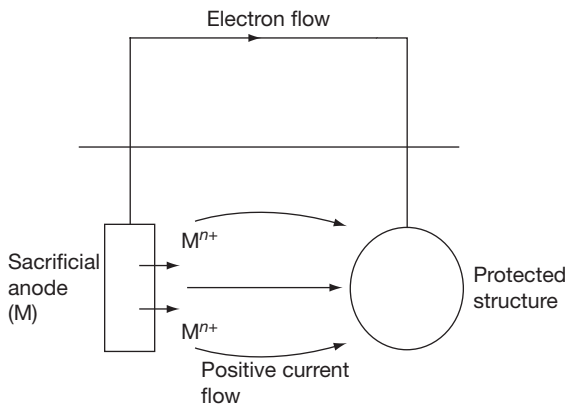
Figure 8   Schematic diagram of cathodic protection using sacrificial anodes. In practice, the anode, which will be mounted on a steel core, can be attached directly to the structure.

is required to keep disadvantageous tramp elements (notably iron and copper) below defined threshold levels. Many anode failures can be attributed to poor production quality control. A guide to minimum quality standards has been produced.[3]

Table 2 gives electrochemical properties for various generic anode types. It will be apparent that the driving voltages that are available from sacrificial anodes are substantially less than those available from power sources. At best, an anode will produce 1 V to steel, whereas an impressed current power source may produce up to 100 V.

A more detailed treatment of cathodic protection by sacrificial anodes is provided elsewhere in this book.

4.18.4   Proof of Protection

4.18.4.1   Steel

Figure 4 demonstrates that the rate of dissolution of iron (or any other metal) decreases as the potential is made more negative. **Figure 6** shows that the current required to reach any given potential below the corrosion potential (E_{corr}) will vary according to the composition of the corrosive solution. Thus **Figure 6** shows that, in the absence of oxygen, the current requirement would be low, but would increase to a value approximating to the limiting current in its presence. Moreover, since the limiting current can be increased by increasing the oxygen concentration or the solution flow rate, the current required for protection will change predictably with change in either of these parameters.[4] It follows that the current required to prevent corrosion completely (i.e., in principle to achieve E_a) will vary according to the environment and the environmental dynamics. As a consequence, there is no single current that will assure protection in all cases. Current supplied is not, therefore, an unequivocal indication of the effectiveness of protection.

By contrast, it appears from **Figures 4** and **6** that a potential measurement would be more reliable: specifically, that E_a (the equilibrium potential for the

Table 2   Typical sacrificial anode compositions and operating parameters

Alloy	Environment	Operating voltage vs. Ag/AgCl/seawater (V)	Driving voltage[a] (V)	Capacity (Ah/kg)
Al–Zn–Hg	Seawater	−1.0 to −1.05	0.20–0.25	2600–2850
Al–Zn–In	Seawater	−1.0 to −1.10	0.20–0.30	2300–2650
Al–Zn–In	Marine sediments	−0.95 to −1.05	0.15–0.25	1300–2300
Al–Zn–Sn	Seawater	−1.0 −1.05	0.20–0.25	925–2600
Zn[b]	Seawater	−0.95 to −1.03	0.15–0.23	760–780
Zn[b]	Marine sediments	−0.95 to −1.03	0.15–0.23	750–780
Mg–Al–Zn	Seawater	−1.5	0.7	1230
Mg–Mn	Seawater	−1.7	0.9	1230

It is often important to control impurities and especially Fe, Cu, Ni, and Si, although a controlled Si concent is essential to some aluminum alloys.
[a]The driving voltage to bare steel, that is, protection potential of steel–anode operating potential.
[b]US Military Specification.

iron/ferrous-ion electrode given a suitably low ferrous ion concentration) would always represent the achievement of full protection for iron.

Almost without exception, all the accepted criteria for full cathodic protection of iron are based on a potential measurement. The various recommended practices published by the U.S. National Association of Corrosion Engineers (NACE) give six criteria for full protection.[5–11] The current British Standard Code of Practice[12] gives one. These are summarized in **Table 3**. Only the first three are useful; the remaining ones are of dubious value or expressions of pious hope.

The most widely accepted criterion for protection of steel at room temperature (the protection potential) in aerobic conditions is –0.85 V with respect to a Cu/CuSO$_4$ reference electrode. In anaerobic conditions, –0.95 V (versus Cu/CuSO$_4$) is the preferred protection potential because of the possible presence of active sulfate-reducing bacteria (SRB).

Various limitations on the most negative potential that may be imposed during cathodic protection are often quoted for high-strength steels (typically –1.0 V versus Cu/CuSO$_4$ for steels in the 700–800 MPa tensile strength range). The restriction is to limit the evolution of hydrogen at the structure and thereby prevent hydrogen absorption with the possibility of embrittlement of the steel, possibly leading to fracture. The consequence is that the useful window of potential in which the steel can operate is severely restricted, especially under anaerobic conditions.

It must not be assumed that the protection potential is numerically equal to the equilibrium potential for the iron/ferrous-ion electrode (E_a). The standard equilibrium potential ($E°$) for the iron/ferrous-ion is –0.440 V (versus the standard hydrogen electrode).

Table 3   Cathodic protection criteria: after British Standard Code of Practice[12] and NACE Recommended Practices[5–11]

1. $\leq$ −0.85 V w.r.t Cu/CuSO$_4$ with current applied but minimizing *IR* error
2. Negative shift $\geq$300 mV when current applied
3. Positive shift $\geq$100 mV when current interrupted
4. More negative than beginning of Tafel segment of cathodic polarisation (*E* – log *I*) curve
5. A net protective current in the structure at former anodic points
6. Polarize all cathodic areas to open circuit potential of most active anode areas

If the interfacial ferrous ion concentration when corrosion ceases is approximately 10^{-6} M, then according to the Nernst equation, the equilibrium potential (E_a) is given by

$$E_a = E° + \frac{2.303}{2F} RT \, \log(a_{Fe^{2+}})$$

where $a_{Fe^{2+}}$ is the activity or thermodynamic concentration of the ferrous cation, R is the gas constant, F is Faraday's constant, and 2 represents the number of units of charge transferred (i.e., the doubly charged ferrous ion). Thus, $E_a = -0.62$ V versus the standard hydrogen electrode or −0.93 V versus Cu/CuSO$_4$. This is a value substantially more negative than the accepted protection potential (−0.85 V).

A simple calculation based on the solubility product of ferrous hydroxide and assuming an interfacial pH of 9 (due to the alkalization of the cathodic surface by reaction [3]) shows that, according to the Nernst equation, at −0.85 V (versus Cu/CuSO$_4$), the ferrous ion concentration then present is sufficient to permit deposition of the hydroxide ion. It appears that the ferrous hydroxide formed may be protective,