CORROSION PROTECTION OF METALS

Two methods of combating corrosion which are widely used in New Zealand are cathodic protection and chemical inhibitors. Both methods depend on controlling the charge on the metal surface, and this can be monitored by measuring the potential of the metal. The conditions needed to stop corrosion can then be predicted from an electrochemical phase diagram.

Cathodic protection is effected by forcing the potential to a negative region where the metal is completely stable. This can be done by using a sacrificial anode made from a more reactive metal, or using an external power supply to change the amount of charge on the metal surface. Cathodic protection is well suited to steel structures in marine or underground environments.

There is a class of chemical inhibitors which work by removing electrons from the metal, thereby pushing the potential into a positive region where an oxide film spontaneously forms. This results in a stable, passive surface with a very low corrosion rate. Industries apply this technology in processes where the inhibitor can be conveniently added without causing environmental or health problems.

INTRODUCTION

When iron or steel is exposed to atmospheric oxygen in the presence of water, the well-known rusting process takes place. The metal is degraded to form ferric rust, a red-brown compound, which is a sure sign of electrochemical oxidation of the underlying metal.

$$4Fe + 3O_2 + 2H_2O \rightarrow 4FeO.OH \qquad (1)$$

Nearly all metals, with the exception of gold and platinum, will corrode in an oxidising environment forming compounds such as oxides, hydroxides and sulphides. The degradation of metals by corrosion is a universal reaction, caused by the simple fact that the oxide of a metal has a much lower energy than the metal itself. Hence there is a strong driving force for the oxidation of metals. For example the familiar metal aluminium, which is used in aircraft, window frames and cooking utensils, is attacked by oxygen to form the oxide as follows:

$$4Al + 3O_2 \rightarrow 2Al_2O_3 \qquad (2)$$

This reaction is strongly exothermic, releasing -1680 kilojoules per mole of oxide. In fact the driving force of the reaction is so great that powdered aluminium will burn to produce very high temperatures, sufficient to melt steel.

It is important to realise that corrosive attack on a metal can only occur at the surface of the metal, hence any modification of the surface or its environment can change the rate of reaction. Thus we have a basis for designing methods to protect metals from corrosion. A

Table 1 - Corrosion protection techniques

Concept	Industrial Process
Removal of oxidising agent	Boiler water treatment
Prevention of surface reaction	Cathodic protection - sacrificial anode - impressed current Anodic protection
Inhibition of surface reaction	Chemical inhibitors pH control
Protective coatings:	
a. Organic	Paint Claddings
b. Metallic	Electroplating Galvanising Metal spraying
c. Non-metallic	Anodising Conversion coatings
Modification of the metal	Alloys - stainless steel - cupronickel - high temperature alloys
Modification of surface conditions	Maintenance to remove corrosive agents Design to avoid crevices Design to avoid reactive metal combinations

number of such methods have been developed, and they are set out in **Table 1**. The table shows a variety of different concepts by which the surface reaction rate can be reduced. Each of these has given rise to a number of technologies, the majority of which are represented in New Zealand industry. In some cases these industries are on a very large scale. For example paint manufacture is a major chemical industry which consumes large quantities of solvents, resins and pigments. Most paint products in New Zealand are used in corrosion protection. Other major industries involved in corrosion control include electroplating, anodising, galvanising and the production of corrosion resistant alloys.

In this article we will concentrate on two important methods of corrosion control used in New Zealand industry, namely cathodic protection and chemical inhibitors. Other types of corrosion control technology, such as electroplating and surface coatings, are covered elsewhere.

THE CHEMISTRY OF CORROSION REACTIONS

Corrosion reactions are electrochemical in nature. They involve the transfer of charged ions across the surface between a metal and the electrolyte solution in which it is immersed. There are two types of electrode reaction occurring at the metal surface: anodic and cathodic. Anodic reactions involve oxidation: electrons appear on the right hand side of the equation. For example metallic iron can produce ferrous ions by the anodic reaction:

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad (3)$$

In a solution with higher pH, the anodic reaction produces a surface film of ferric oxide according to reaction (4).

$$2Fe + 3H_2O \rightarrow Fe_2O_3 + 6H^+ + 6e^- \qquad (4)$$

Cathodic reactions involve electrochemical reduction: electrons appear on the left hand side of the equation. In corrosion processes the most common cathodic reaction is the electrochemical reduction of dissolved oxygen according to the equation:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad (5)$$

Hence the reduction of oxygen at an electrode will cause a rise in pH due to hydroxide ion production. This can be important in some corrosion processes as will be explained later.

The potential difference *E* across the interface between a metal and a solution is the key factor controlling both the products of an electrode reaction and rate at which they are formed. The potential difference itself is caused by layers of charges at the surface: electrons in the metal and excess anions or cations in the solution, as shown in **Figure 1**. This arrangement of charges is known as the double layer or the Helmholtz layer. It is found not only on metal surfaces but also on other surfaces in contact with solutions such as colloids and proteins. The state of charging of the Helmholtz layer and hence the magnitude of the potential *E* can be changed as a result of using an external electrical current or by electrode reactions such as those shown in equations (3) to (5). For example, in the presence of a high concentration of oxygen, the cathodic reaction will remove electrons from the metal surface hence making the metal more positively charged and increasing the potential *E*.

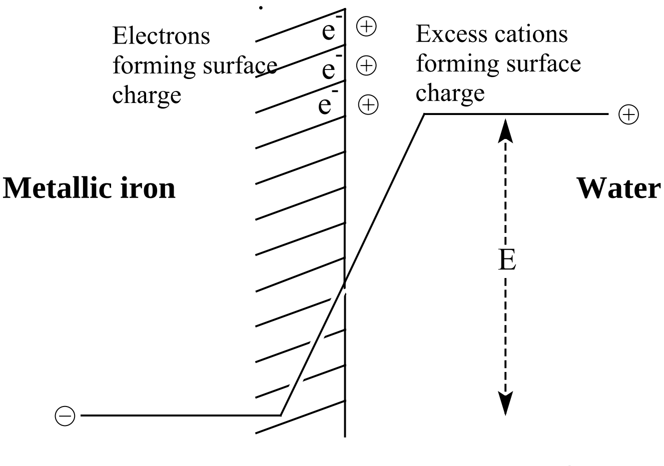

Figure 1 - Electric double layer at ametal surface
The surface charge on the metal (electrons) is equal and opposite to the excess charge in the solution (cations). The potential difference, E, at the surface is created by the double layer.

The role of the electrode potential *E* in defining the products of corrosion reactions can be readily seen in **Figure 2**. This figure shows the corrosion products as a function of electrode potential and pH for iron at room temperature in the presence of water as solvent. At negative potentials metallic iron itself is the stable form hence in this region no corrosion is possible, and this is referred to as the immunity condition. At higher potentials and acidic pH values ferrous ions will form giving rise to active corrosion. Ferric ions are produced only at high potentials above 0.7 V.

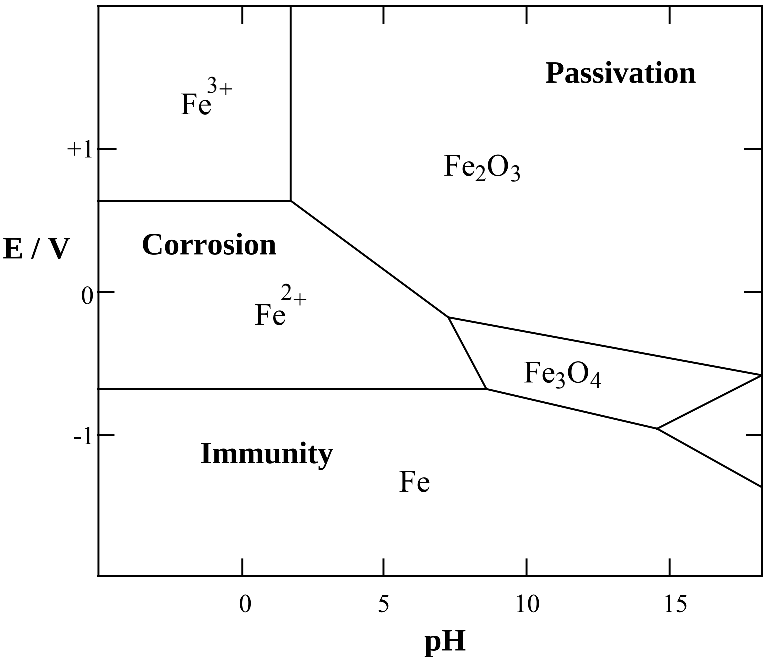

Figure 2 - Iron equilibrium diagram

Iron at 25°C in water. The diagram shows the stable forms of the element as a function of E and pH.

If the pH lies on the alkaline side of neutral then insoluble surface oxides will form. The oxide Fe_3O_4, known as magnetite or black iron oxide, is produced at low electrode potentials. Low potentials are found in relatively stagnant conditions with a low oxygen partial pressure as in soil or inside boilers which have been treated to remove oxygen. The characteristic black surface of iron under these conditions is due to magnetite. At more positive potentials the oxide formed is Fe_2O_3 and this is usually present as a thin adherent film. Since this oxide forms at the surface, its presence acts to block the surface reactions and hence corrosion rates are reduced. This is called passivation and the oxide film on the surface is known as a passive layer. The corrosion rate is very low in the passivation region of the diagram. Diagrams of the type shown in **Figure 2** are widely used in corrosion technology to predict the corrosion products which may be formed from a given metal under conditions specified by the axes of the figure. However the diagram does not tell the rate of corrosion which may be the most important information required in a practical situation.

In order to understand the rate of the corrosion process we must examine the electrochemical polarisation curves of the electrode reactions which take place on the metal surface. **Figure 3** shows the polarisation curve of iron in an acidic solution at room temperature. The rates of the electrode processes are controlled by the value of *E*. Thus, for a cathodic process in acidic solution producing hydrogen gas by the reduction of hydrogen ions, the more negative the electrode potential the greater the surface concentration of electrons and the faster the reaction rate.

$$2H^+ + 2e^- \rightarrow H_2(g) \qquad (6)$$

Since the reaction rate is proportional to the flow of electrons (measured as a current *I*) the diagram shows the magnitude of *I* as a function of *E*.

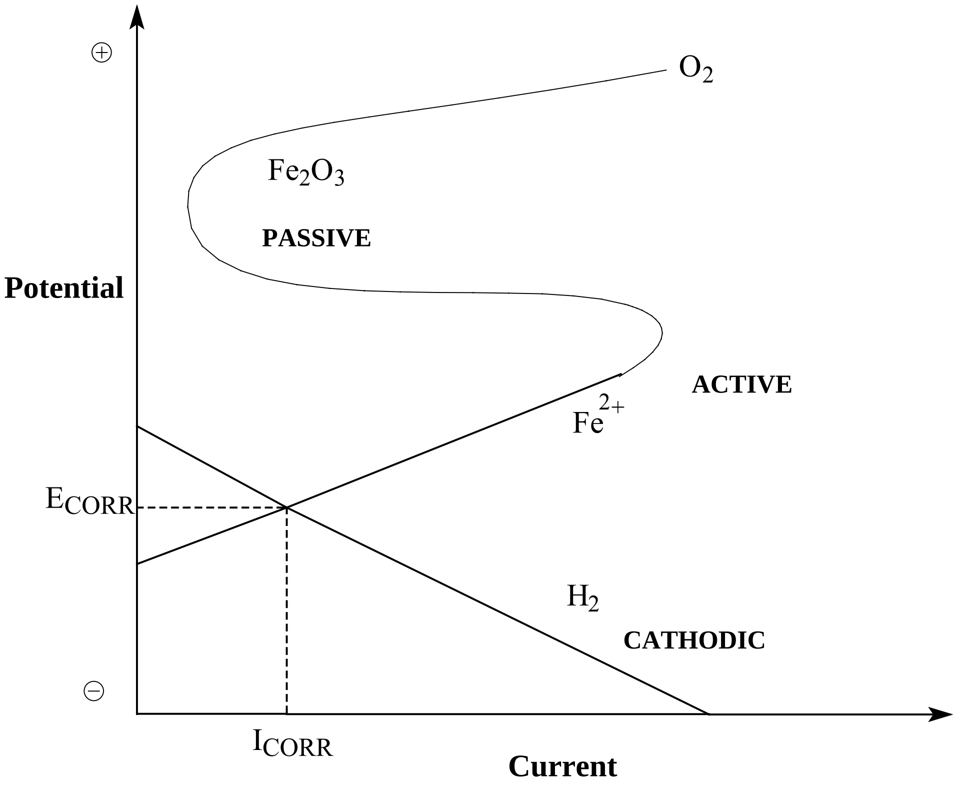

Figure 3- Polarisation of iron
The diagram shows how the potential, E, of the metal determines the electrochemical reaction rate and corrosion products.

Anodic reactions are accelerated by increasing potential in the positive sense as shown in the diagram. Ferrous ions are produced in the active state and this is the region in which corrosion will take place freely. At higher potentials the reaction passes into the passivation region (as shown in figure 2) and passivation occurs. This is observed as a very small current flowing in this region. The metal is protected by the passive film of ferric oxide on the surface. We see at very positive potentials that the passive electrode surface will act as an anode to oxidise water to oxygen gas, but this does not occur in normal corroding systems. To find the corrosion rate under normal conditions we look for the point on the diagram where the anodic and cathodic reactions intersect. At this point the rates of the anodic and cathodic reactions are equal and the system is behaving as a closed circuit with all the electrons produced in the anode reaction being consumed in the cathodic reaction. This is the situation for an electrically isolated structure made from the metal. The polarisation diagram can be used to predict changes of corrosion rate as will be discussed in the next section.

CATHODIC PROTECTION

The principle involved in cathodic protection is to change the electrode potential of the metallic article or structure so that it lies in the immunity region (shown in **Figure 2**).

Within this region the metal is the stable form of the element and corrosion reactions are therefore impossible. Cathodic protection may be regarded as the most elegant form of corrosion protection because it renders the metal completely unreactive. It can however be fairly expensive in the consumption of electric power or the extra metals involved in controlling the potential within this region. There are two major methods of applying cathodic protection to a metal structure and these will be discussed below.

In the case of iron or steel immersed in an aqueous solution the electrode potential should be about -700 mV (standard hydrogen electrode scale) or even more negative than this in order to ensure the structure remains in the immunity region. The metal surface under cathodic protection will be completely free from corrosion, but there may be some evolution of hydrogen gas according to equation (6). In seawater, calcareous deposits may form on the surface due to the increase in pH which occurs as a result of cathodic reactions. These deposits are composed of a mixture of calcium and magnesium basic carbonates, produced by precipitation from the localised zone of alkaline seawater close to the metal surface. Calcareous deposits of this type are found on the submerged steelwork supporting the Maui gas platform, which is located 30 km off the coast of Taranaki.

(a) Impressed Current

This technique is widely used for the protection of buried pipelines and the hulls of ships immersed in seawater. A d.c. electrical circuit is used to apply an electric current to the metallic structure. The negative terminal of the current source is connected to the metal requiring protection. The positive terminal is connected to an auxiliary anode immersed in the same medium to complete the circuit. The electric current charges the structure with excess electrons and hence changes the electrode potential in the negative direction until the immunity region is reached. It is important that the anode be completely separated from the cathode so that a true electric circuit is established with the current flow from the anode to the cathode taking place through the solution between those electrodes.

Figure 4 shows the layout for a typical impressed current cathodic protection system. The function of the reference electrode is to monitor the electrode potential of the protected structure, in this case a buried pipeline, in order to ensure that the immunity region is reached. The reference electrode is designed to have a constant potential and no current passes through it. In the case of buried structures the most common reference electrode is $Cu/CuSO_4$ (saturated), with a potential of +316 mV (standard hydrogen scale). The d.c. rectifier acts as the power supply and is adjusted so that the potential of the structure is sufficiently negative to reach the immunity region, as indicated by the reference electrode. It is usual to apply a surface coating or wrapping to the pipeline before cathodic protection is used. This will result in a much smaller consumption of electricity since most of the structure will be effectively protected by the coating. Special anode materials have been designed to withstand applied currents for very long periods. They normally consist of platinised titanium or lead alloys connected to an insulated cable positioned some distance from the structure itself. The buried anodes are distributed at intervals along the pipeline, normally several kilometres apart and several hundred metres from the nearest point of the pipeline.

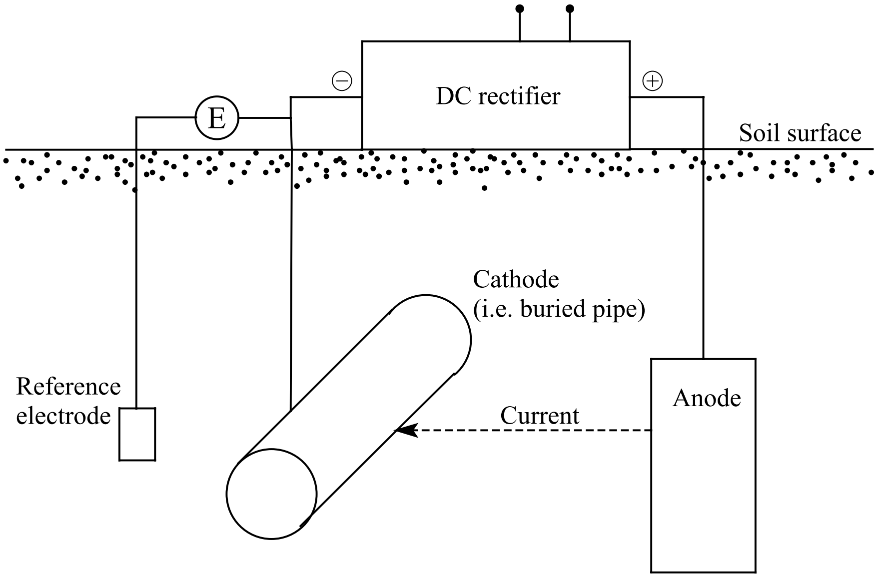

Figure 4 - Impressed current cathodic protection of a buried pipeline
A DC current passes between a buried anode and the pipeline. The pipeline is connected to the negative terminal, hence its potential becomes more negativ and it functions as the cathode.

Impressed current cathodic protection is a specialised technology and can be very effective if correctly designed and operated. Several warships operated by the Royal New Zealand Navy have impressed current systems for corrosion control. Other examples are the natural gas pipelines which distribute methane from the Kapuni and Maui fields. Impressed current cathodic protection is applied to gas pipelines in Auckland, with deep anode installations at the Auckland Domain and other points in the region.

(b) Sacrificial Anode

This technique is frequently used for ships in seawater and for offshore oil and gas production platforms such as the Maui gas platform operated by Shell BP Todd Oil Services Ltd. The principle here is to use a more reactive metal in contact with the steel structure to drive the potential in the negative direction until it reaches the immunity region. **Figure 5** illustrates the principle. Zinc is often used as the sacrificial anode. In the absence of zinc the corrosion potential E_{CORR} is given by the intersection of the anodic and cathodic curves. If a zinc electrode is now attached, it produces an anodic dissolution current at a more negative potential. The intersection with the cathodic curve now occurs at a more negative potential E_{PROT} in the region in which the steel itself has a negligible corrosion rate. In practice a reference electrode is used to check that the steel structure has indeed reached the immunity region. A potential of around -900 mV with respect to the Ag/AgCl reference electrode in seawater is the criterion for immunity of the steel. In the case of the Maui platform it was not feasible to apply surface coatings to the steel structure before it was installed, hence the corrosion protection of the 6,000 tonnes of steel forming the tower depends entirely on cathodic protection by sacrificial anodes made from the aluminium alloy "Alanode". Some 580 tonnes of this alloy has been used to produce several hundred separate anodes attached to the legs and braces of the tower under the sea so as to give complete and uniform protection to all parts of the steel structure. Regular monitoring of the potential of the steel is carried out using submerged reference electrodes of Ag/AgCl. Aluminium is a sufficiently reactive metal to provide the required corrosion protection, but a small proportion of indium, about 0.1%, is included in the alloy to provide efficient anodic action. Pure aluminium alone has such a resistant oxide film that its reactivity

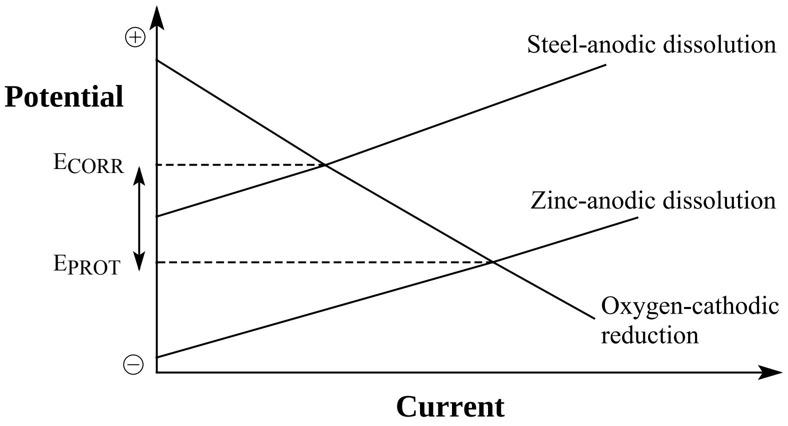

Figure 5 - Cathodic protection by a sacrificial anode
The addition of a sacrificial zinc anode to a steel structure shifts the potential from E_{CORR} to E_{PROT}, where steel is protected from corrosion (anodic current for steel falls to zero).

is insufficient to properly protect the steel structure.

CORROSION INHIBITORS

It is well known in surface chemistry that surface reactions are strongly affected by the presence of foreign molecules. Corrosion processes, being surface reactions, can be controlled by compounds known as inhibitors which adsorb on the reacting metal surface. The term adsorption refers to molecules attached directly to the surface, normally only one molecular layer thick, and not penetrating into the bulk of the metal itself. The technique of adding inhibitors to the environment of a metal is a well known method of controlling corrosion in many branches of technology. A corrosion inhibitor may act in a number of ways: it may restrict the rate of the anodic process or the cathodic process by simply blocking active sites on the metal surface. Alternatively it may act by increasing the potential of the metal surface so that the metal enters the passivation region where a natural oxide film forms. A further mode of action of some inhibitors is that the inhibiting compound contributes to the formation of a thin layer on the surface which stifles the corrosion process.

Table 2 shows some examples of common inhibitor systems classified by their modes of action. Adsorption inhibitors are used quite widely in many proprietary mixtures which are marketed to control corrosion. For example, radiator fluids in the cooling circuits of engines frequently contain amines such as hexylamine $C_6H_{13}NH_2$, or sodium benzoate. These act as inhibitors of the anodic reaction. Corrosion inhibitors are also used in the metal cleaning field. For example, it is possible to clean steel articles by immersion in sulfuric acid, H_2SO_4. The acid would normally attack the metal, causing corrosive loss. This can be minimised by adding antimony trichloride, $SbCl_3$, a specific inhibitor for preventing the corrosion of steel in acidic media. Oxides and foreign metals such as zinc will readily dissolve in the presence of $SbCl_3$, which acts only on the steel itself. Amine inhibitors are sometimes present in volatile corrosion inhibitors. These are used in packaging materials to prevent corrosion of steel articles during transport. A good example is the wrapping used on automobile engines and other machinery during their shipment to New Zealand.

The second class of inhibitors are those which cause the potential of the metals to rise into

Table 2 - Corrosion inhibitors

Mode of action	Examples	
Adsorption	amines	RNH_2
	thiourea	NH_2CSNH_2
	antimony trichloride	$SbCl_3$
	benzoate	$C_6H_5COO^-$
Passivating	nitrite	NO_2^-
	chromate	CrO_4^{2-}
	red lead	Pb_3O_4
	calcium plumbate	Ca_2PbO_4
Surface layer	phosphate	$H_2PO_4^-$
	silicate	$H_2SiO_4^{2-}$
	hydroxide	OH^-
	bicarbonate	HCO_3^-
	hexametaphosphate	$Na_6(PO_3)_6$

the passivation region. They are all oxidising agents, containing elements in their higher oxidation states. For example nitrite, which is used as an additive in cooling fluid circuits for the control of corrosion of steel, is a mild oxidising agent which can raise the potential of steel into the passivation region. A traditional pigment used in paints is red lead, Pb_3O_4, containing lead in the tetravalent stale, and the formula can be written as plumbous plumbate $Pb(II)_2Pb(IV)O_4$. The plumbate ion is an active oxidising agent and serves to promote passivation of the underlying metal. The modern pigment calcium plumbate, often used in paint formulations, contains the same plumbate ion PbO_4^{4-} in a different compound. Likewise zinc chromate $ZnCrO_4$ is also widely used in corrosion control as a passivating inhibitor. The passivating inhibitors all share the common property of conferring protection on a metal by using its own natural oxide film.

The last category of corrosion inhibitors are those which form a surface layer of a foreign chemical compound provided by the inhibitor itself. For example phosphate is widely used as an additive in boiler water or cooling circuits and in pickling baths for metals. Phosphate produces a surface layer of ferric phosphate $FePO_4$ on steel which provides a measure of corrosion protection and is an excellent base for paints. Chromate is an extremely important industrial inhibitor in spite of its toxicity and unfavourable environmental problems. Chromate works in two ways, the high oxidation state Cr(VI) causes the metal to pass into the passivation region (see **Figure 2**) and the product of oxidation by chromate is chromic oxide Cr_2O_3 which itself forms an inert, relatively insoluble surface film. In practice chromate treatment of steels produces a mixed film of ferric and chromic oxides which is highly resistant to corrosion. An example of the use of chromate was the Marsden B thermal power station, now retired. Large quantities of cooling water are circulated in the plant and sodium chromate, added at a level of about 400 mg/L, was formerly used as a corrosion inhibitor. It proved to be very effective in protecting the steel; but changes in environmental regulations meant that it was no longer possible to permit discharge of chromium at a level above 5 µg/L. This ruled out the use of sodium chromate as an inhibitor at Marsden B and it was replaced by a new inhibitor system involving the use of an organic zinc phosphate mixture. Some of the other inhibitors listed in this category of surface film builders are very important industrially. The commercial inhibitor Calgon is a solution of sodium hexametaphosphate, a condensed phosphate polymer based on the unit $(-PO_3-)_n$.

Hexametaphosphate functions as a corrosion inhibitor because it has a high affinity for metal cations such as calcium, zinc, copper and ferrous ions. Under some conditions it acts to dissolve substances containing these cations and hence has a cleaning effect, assisting the removal of scale deposits. But at the surface itself an insoluble layer of a ferrous hexametaphosphate is deposited and will act as a corrosion inhibitor. Calgon therefore is used as an inhibitor in potable water systems (drinking water) because it is non-toxic and is widely used in large institutions such as hotels and hospitals. We must not neglect to mention the simple hydroxide ion as a corrosion inhibitor. In the presence of hydroxide, and hence high pH, metal oxides and hydroxides are insoluble, and these are effective in controlling corrosion. For example, the common building material ferroconcrete involves placing highly alkaline fresh concrete (pH above 12) in contact with steel reinforcing. The high hydroxide concentration ensures effective corrosion inhibition by passivation of the steel surface, and a strong bond is formed between the concrete and the steel.

CONCLUSION

Corrosion can be controlled effectively by cathodic protection or inhibitors, provided the chemical and electrical conditions are monitored in a scientific manner. The same can be said for all of the anti-corrosion technologies listed in **Table 1**. The costs of stopping corrosion can be quite high, but these costs must be faced by many industries if they wish to achieve a high level of performance. The key factor is the scientific knowledge on which the technologies are based.

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