

CATHODIC AND ANODIC PROTECTION APPLICATIONS IN THE PETROCHEMICAL INDUSTRY

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by

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Introduction

Most metals exposed to a liquid phase corrosive environment can be protected from aggressive corrosion attack using an electrochemical prevention technique, either cathodic protection (CP), anodic protection (AP) or potential adjustment protection (PAP). Which of these methods of protection is appropriate depends primarily on the metal/environment characteristics.

Whether or not a metal can corrode in a particular environment can be determined thermodynamically. For instance, Figure 1 is a diagram for steel in an aqueous environment which shows domains of immunity, corrosion and passivity with relation to the steel electrical solution potential and solution pH.

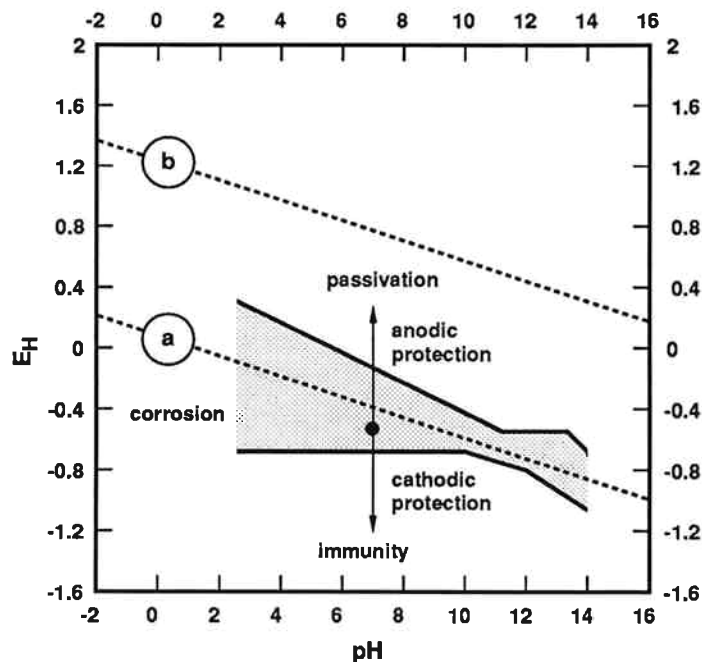


FIGURE 1 - EMP-pH DIAGRAM FOR STEEL IN WATER

Although the thermodynamic calculations which lead to the construction of this diagram can determine whether or not steel can corrode, they do not predict the rate of corrosion. On the otherhand at a given pH, it is certain that if the steel/environment potential is maintained in the immunity zone (eg. -0.80V, pH 3-9) then corrosion is thermodynamically impossible. Accordingly, if a steel surface is corroding actively and its solution potential is shifted electronegatively, as is the case with cathodic protection, then corrosion can be prevented. Conversely, for metals such as steel, nickel, titanium and stainless steels which exhibit active-passive behavior in some solutions the corrosion potential can be shifted in the anodic (electropositive) direction thereby producing a passive surface.

Cathodic Protection

Cathodic Protection is achieved by causing the metal/environment potential to be changed in the electronegative direction by the application of a DC current from the solution onto the metal as represented in Figure 2.

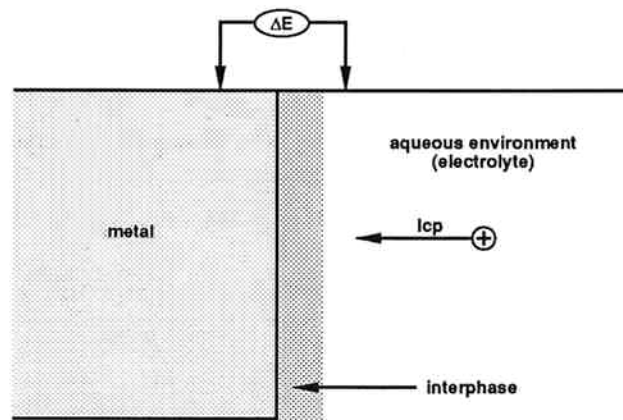
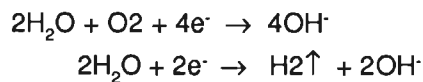


FIGURE 2

The change in potential results from polarization at the metal/electrolyte interphase owing to a slow step in one or both of the following charge transfer reactions for an aerated and de-aerated aqueous medium respectively.



The magnitude of current required to achieve satisfactory protection is very much dependent on the degree of aeration of the aqueous environment. The change of potential with the application of current is illustrated in Figure 3. There can be an infinite number of these potential/current density (polarization) curves between the completely aerated and deaerated cases. Other factors, such as temperature, agitation, pH and type of metal also affect the shape of the polarization

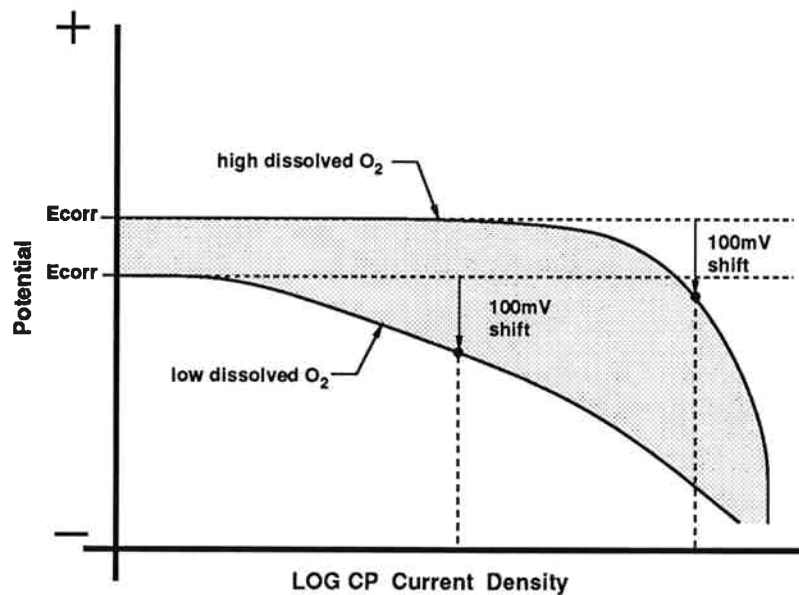


FIGURE 3 - POLARIZATION BEHAVIOUR WITH RESPECT TO DISSOLVED OXYGEN IN ELECTROLYTE

curve. In many cases however, a shift from the corrosion potential electronegatively by 100mV is sufficient to effectively control corrosion for most metal/electrolyte combinations. Depending on the environment the DC current density required to obtain the minimum 100mV shift normally ranges from 1mA/m² to 100mA/m².

There are two basic types of cathodic protection systems, namely sacrificial and impressed current. These designations are founded on the method of obtaining the DC cathodic protection current.

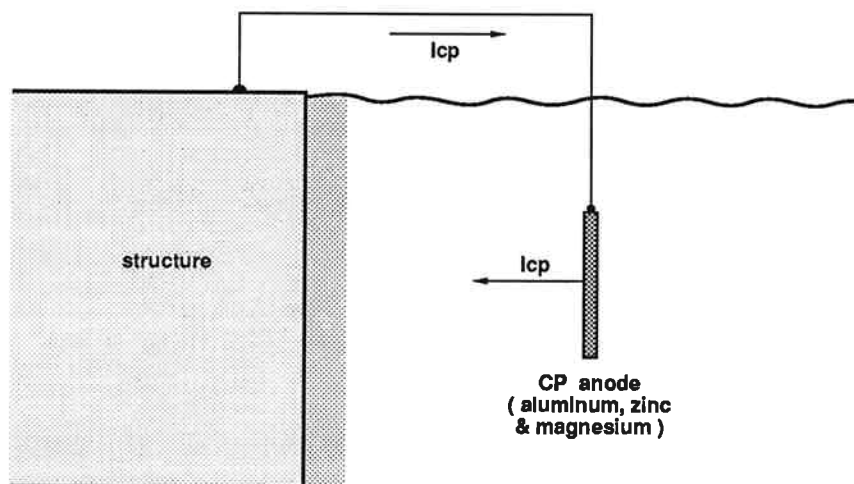


FIGURE 4 - SACRIFICIAL CATHODIC PROTECTION

In Figure 4, CP anode materials made of highly reactive metals such as aluminum, zinc and magnesium when connected directly to a steel structure will provide DC current as a result of the spontaneous corrosion of the anode material. Accordingly, these anode materials “sacrifice” themselves while providing cathodic protection.

The impressed current method, in Figure 5, utilizes an external power supply (eg. transformer/rectifier) to supply current via semi-inert anode materials such as graphite, high silicon iron or platinum.

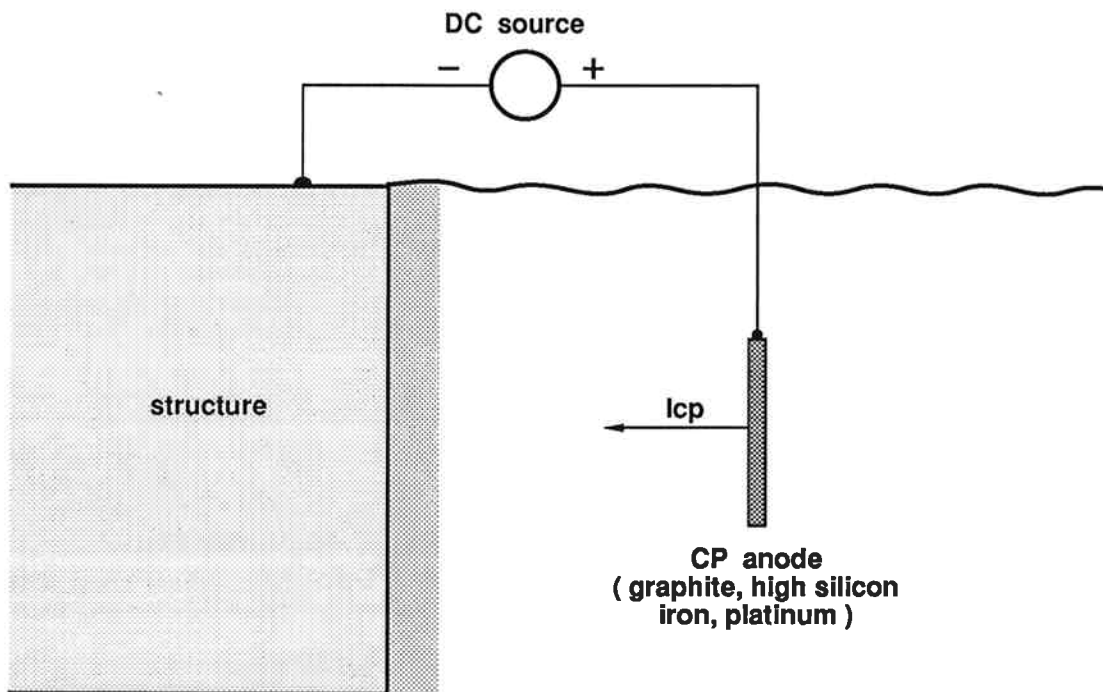
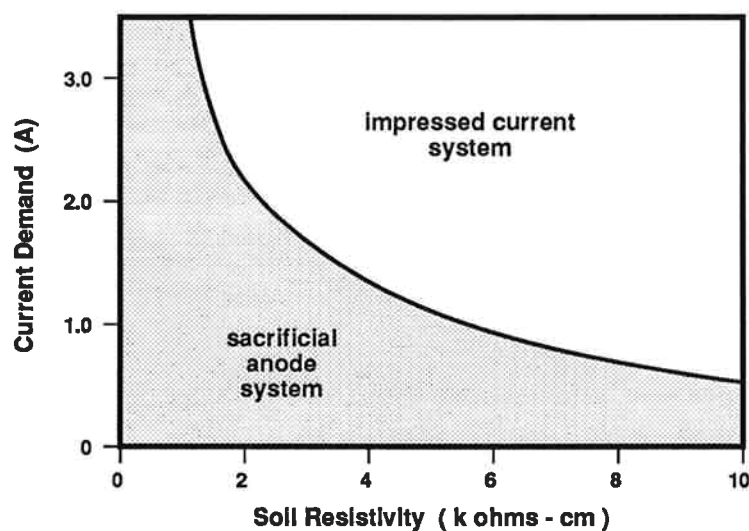


FIGURE 5 - IMPRESSED CURRENT CATHODIC PROTECTION

Choosing which CP system to use is determined primarily by the amount of current required (current demand) and the earth electrical resistivity. As the resistivity and current demand increases, as shown in Figure 6, the impressed current method becomes increasingly economically advantageous.



Von Baekmann, W. and Schwenk, W., Handbook of Cathodic Protection, Portoullis Press Ltd., 1971, p.351

FIGURE 6 - CATHODIC PROTECTION SYSTEM CHOICE

In petrochemical plants, CP first found application for the control of corrosion on underground process piping, particularly on feed stock or refined product piping. Presently, all petrochemical plants utilize cathodic protection on one or more of the following structures and equipment;

- underground piping
- heat exchangers/condensers
- cooler boxes
- water storage tanks
- effluent treatment facilities
- underground storage tanks
- dock structures
- surface storage tanks
- storage well casings

Underground Piping

Protection of underground piping is most often accomplished using distributed impressed current systems, wherein the anodes are positioned in close proximity to the piping as shown in Figure 7. When retrofitted to an existing piping system, as is often the case, the anodes are installed verti-

cally in augered holes or horizontally in an excavated trench.

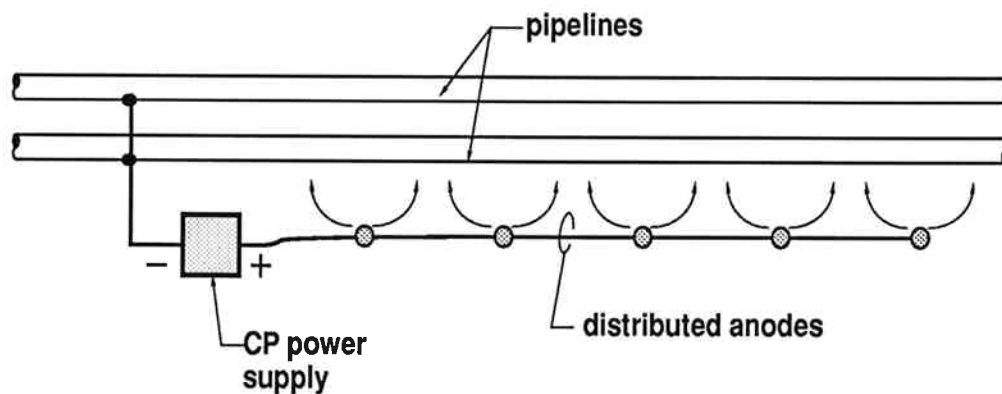


FIGURE 7 - CATHODIC PROTECTION OF A PIPING RUN

Heat Exchanger/Condensers

The heads and tubesheets of heat exchangers frequently require CP particularly when the tubing material is more noble than either the tubesheet or head box. Small exchangers handling fresh water are generally protected using small sacrificial disc anodes made of zinc or magnesium alloy as shown in Figure 8. Anodes are easily replaced when the exchanger is shut-down for inspection.

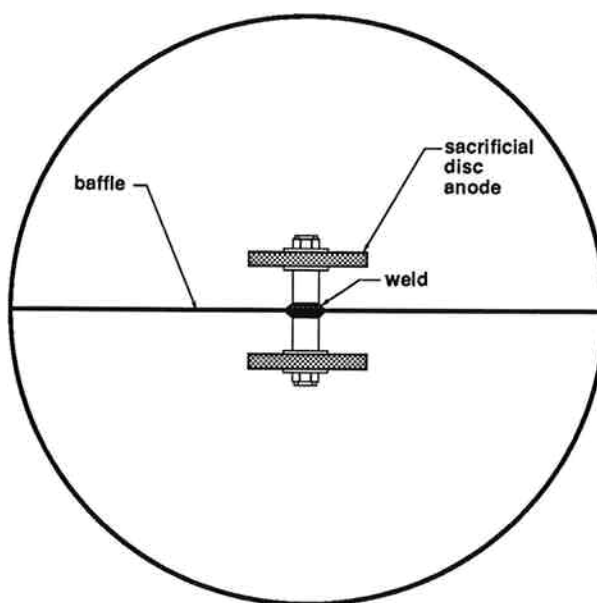


FIGURE 8 - CATHODIC PROTECTION OF HEAT EXCHANGER HEAD BOX

Cooler Boxes

Owing to the large bare surface area and high temperatures of the tubes, an impressed current system is required to protect cooler boxes. Typically this system consists of close spaced precious metal anodes (platinum, rare earth metal oxides, etc.) mounted on non-metallic racks. Close spacing of anodes is required because of the relatively closed packed arrangement of the tube bundle. A typical anode arrangement is shown in Figure 9.

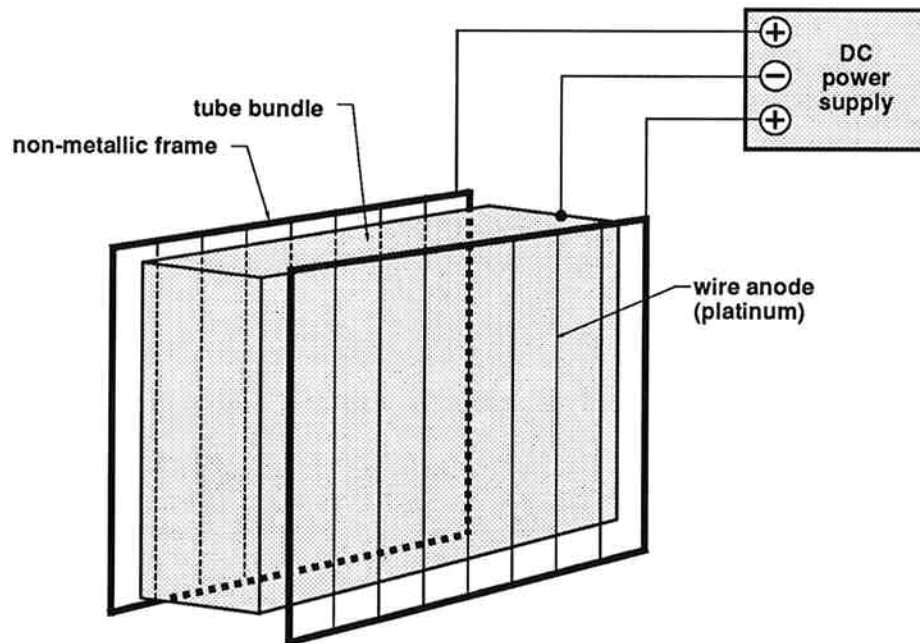


FIGURE 9 - CATHODIC PROTECTION OF A COOLER BOX AND TUBING

Water Storage Tanks

The choice of CP system for a water storage tank depends primarily on whether or not the internal surfaces are coated and secondarily on both flow rate and whether or not the tank is subject to freezing. Tanks which are well coated with epoxy or vinyl protective coatings can be inexpensively protected using sacrificial anodes as shown in Figure 10. Where the water is subject to freezing the sacrificial anode(s) are best mounted on non-metallic stand-offs on the bottom. The use of CP in combination with a high quality coating will extend the effective service life of the coating system several fold as well as prevent corrosion pitting at coating holidays.

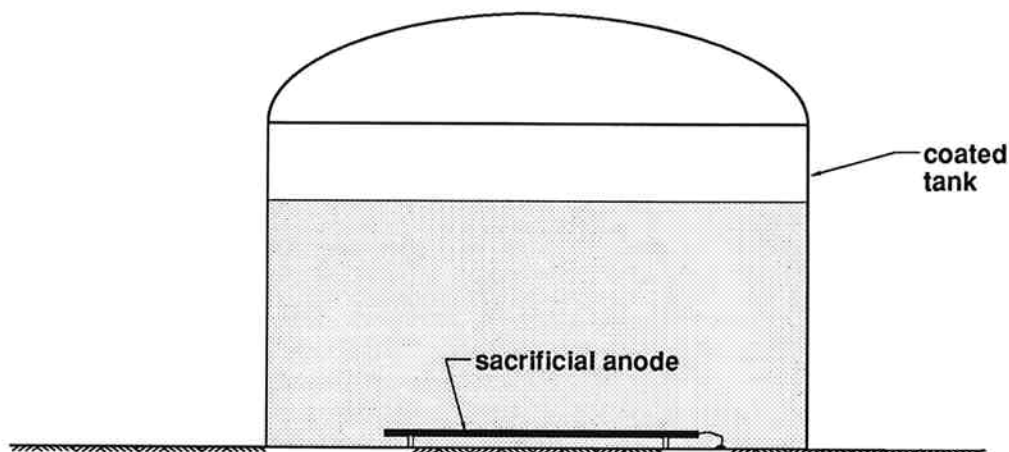


FIGURE 10 - CATHODIC PROTECTION OF A COATED WATER STORAGE TANK

Effluent Treatment Facilities

Rake arms and center wells of effluent clarifiers are commonly subject to aggressive corrosion, particularly when galvanically coupled to reinforcing steel in reinforced concrete side walls. In the latter case, the cathodic influence of the reinforcing steel must be accommodated and this requires the larger current capacity of an impressed current system. Typically, as shown in Figure 11, the anode materials are suspended in the effluent above the rake arm.

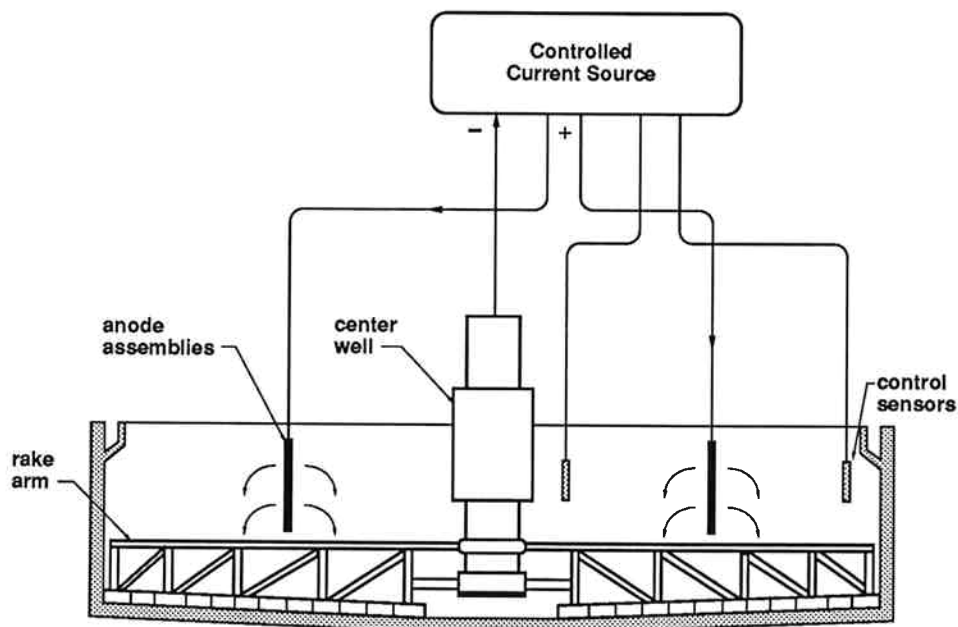


FIGURE 11 - APPLICATION OF CATHODIC PROTECTION TO EFFLUENT TREATMENT FACILITIES

Underground Storage Tanks

Newly installed underground storage tanks, if well coated, are routinely protected with sacrificial anodes as outlined in ULC Standard 603.1M. Existing tankage which is often poorly coated or bare is protected with a distributed impressed current system as specified in PACE guideline 87-

1. The general anode arrangement for the latter case is illustrated in Figure 12.

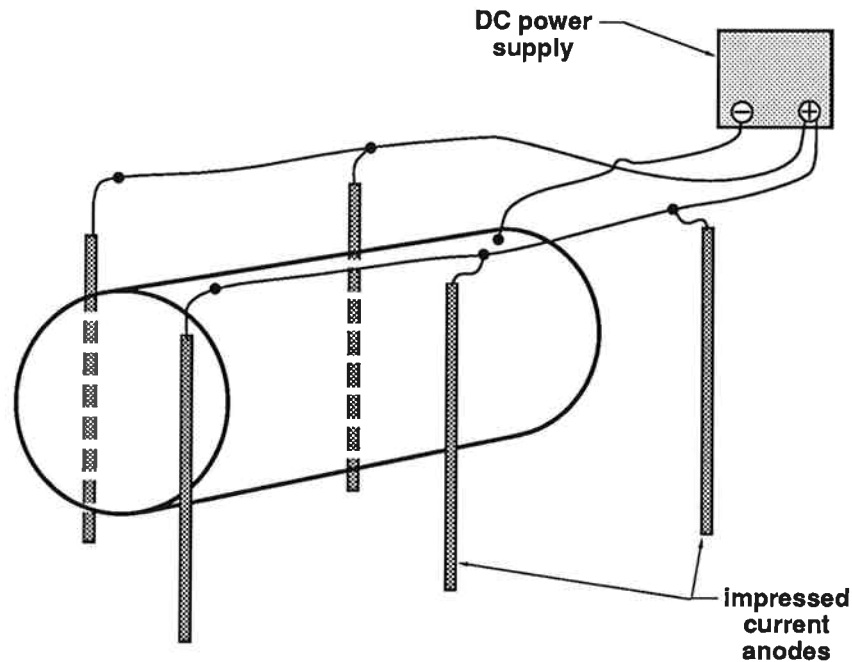


FIGURE 12 - CATHODIC PROTECTION OF AN EXISTING UNDERGROUND TANK

The anodes are installed horizontally on new tank installations and vertically when the CP system is retrofitted.

Dock Structures

Dock facilities because of the large surface area usually have high current requirements, and in low resistivity seawater environments sacrificial anodes are often utilized in the protection system. Typically the most severe corrosion appears just below the low mean water level regardless whether or not the structure is composed of pipe or sheet piles. Sacrificial CP is most appropriate on relatively shallow piling where the cost of attaching a sacrificial anode as in Figure 13 by underwater welding is modest. Deep sea water and fresh water docks are more cost effectively protected with impressed current systems.

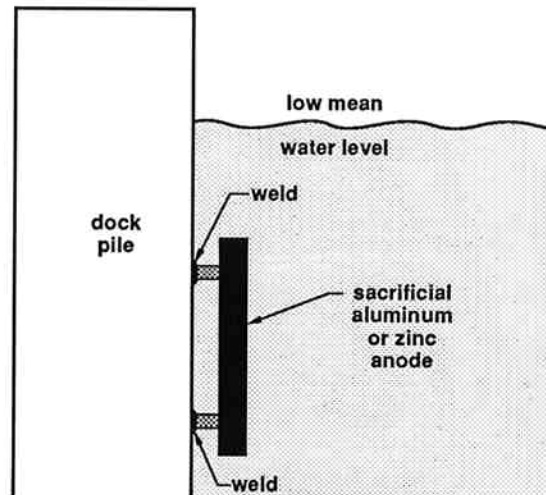


FIGURE 13 - CATHODIC PROTECTION OF A SHALLOW DOCK IN SEAWATER

Surface Storage Tanks

Many petrochemical plant storage tanks are reaching an age where external corrosion of tank bottoms is impacting on the serviceability of the vessels, even though the corrosion rate is often small. Characteristically most of the corrosion occurs on the outer one third of the tank bottom since this part of the bottom is exposed to the highest moisture conditions. Acid rain and poor drainage aggravate this situation. The relatively high current requirements, owing to the bare nature of the tank bottom plates, and moderate to high resistivity soil conditions usually dictate that an impressed current system be installed.

In order to achieve uniform current distribution to the worst areas, anodes are distributed around the periphery of the tank shell as indicated in Figure 14.

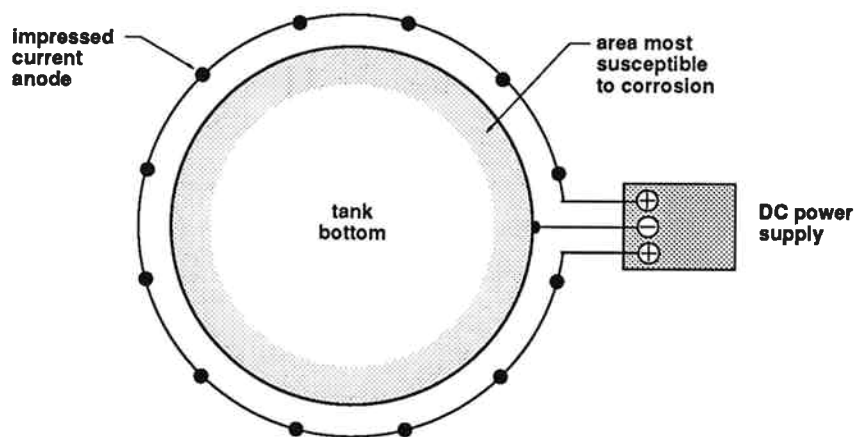
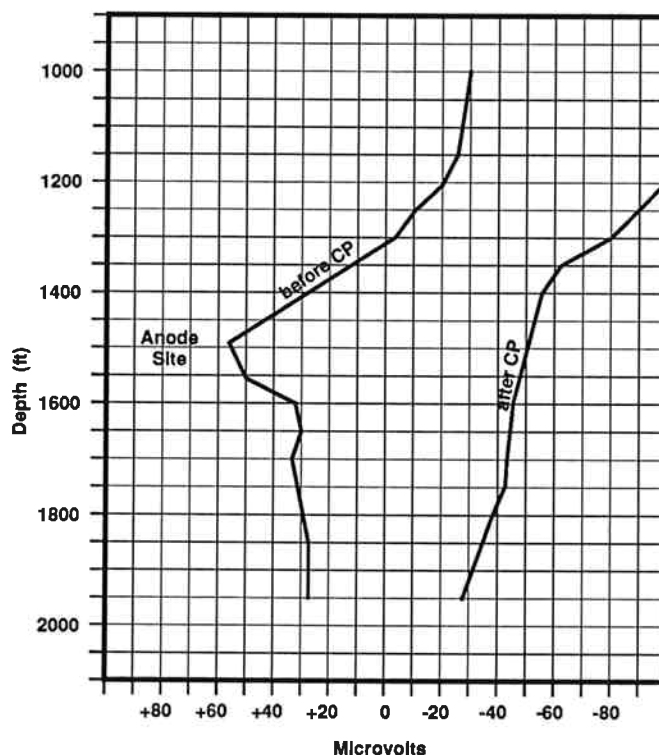


FIGURE 14 - TANK BOTTOM CATHODIC PROTECTION

In cases where the tank bottom is so badly corroded that it is beyond repair and a new bottom is to be installed, the old bottom plate can be modified to make it an impressed current anode for protecting the replacement bottom. This latter method is extremely cost-effective.

Storage Well Casings

Many petrochemical plants where the subsurface geology is suitable, have underground caverns for gas product storage. These storage caverns are connected to surface piping and process plants by a well casing. Increasing age, environmental concerns and a few isolated corrosion failures have focussed attention on the continued integrity of the steel casing. CP can be retrofitted to provide corrosion protection and its effectiveness must be judged using a downhole logging tool rather than structure-to-earth potential measurements. Care must be taken when protecting well casings to position the impressed current anodes in such a way as to ensure the distribution of adequate protection current density to the bottom. The voltage drop in the metal of the casing due to corrosion and CP currents is indispensable in evaluating system effectiveness. Typical downhole survey plots both before and after the application of CP is shown in Figure 15. At current flow direction reversals on a freely corroding casing an anode site is indicated. With CP applied and when all negative slopes are eliminated then the CP system has eliminated the corrosion activity.



Source: Dresser Atlas - Casing Evaluation Services
Catalogue, 1985, p.135

**FIGURE 15 - CASING VOLTAGE (POTENTIAL) PROFILES
BEFORE AND AFTER CATHODIC PROTECTION**

Summary

Of all the corrosion mitigation methods, CP is one of the easiest techniques to retrofit on a corroding structure and furthermore, has the advantage of attaining close to a zero corrosion rate result. Accordingly, when CP is properly designed, installed and maintained the practical service life of a structure can be extended indefinitely, usually at a cost which is a small fraction of the structure replacement cost and substantially less than that of other mitigation methods.

ANODIC PROTECTION

Introduction

A number of metals exhibit what is known as 'active-passive' transition when polarized in the electropositive direction as shown in Figure 16.

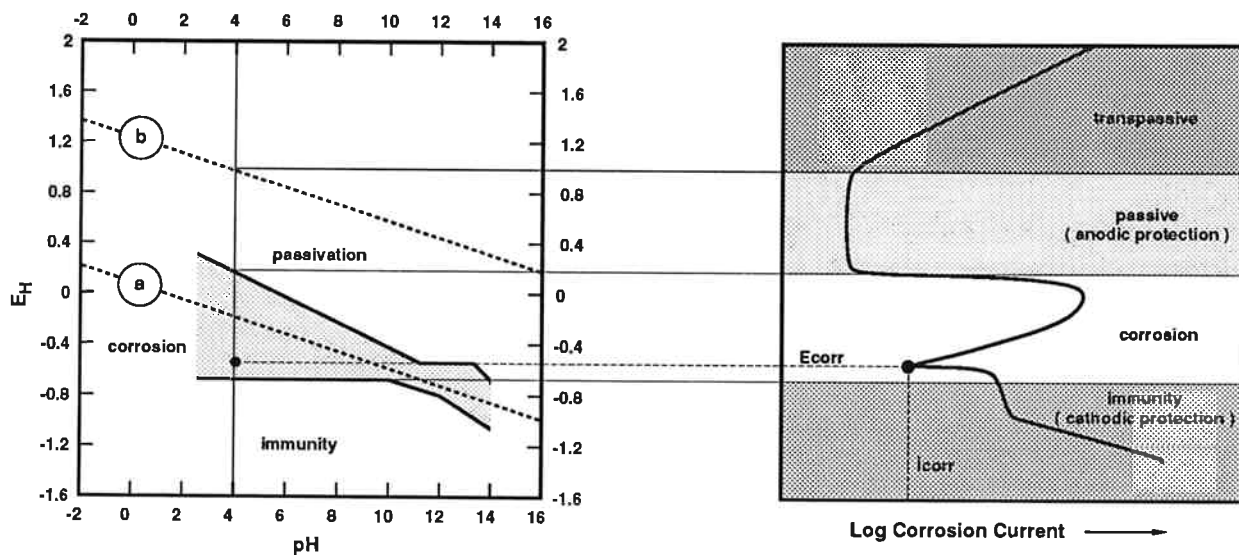


FIGURE 16 - POURBAIX DIAGRAM IN CONJUNCTION WITH AN ANODIC POLARIZATION CURVE

Here it can be seen that when the potential of the metal is moved in the electropositive direction by the application of a DC current the potential moves into a passive region indicating the formation of a passive surface film with a resulting decrease in corrosion current density and hence a lower corrosion rate. Increasing anodic polarization into the transpassive range may result in breakdown in the passive film with pitting type corrosion occurring.

Formation of the passive film is essentially a coulombic (total charge) effect and therefore the amount of current required to pass the primary passive potential is a function of time (eg. higher currents are required when the time period is short and vice-versa). Normally the current required to passivate the metal surface is an order of magnitude greater than the current required to maintain passivation.

The passive potential range and the current density required to achieve passivation is a function of the type of metal and electrolyte and to factors such as pH, temperature, degree of oxidation, etc. Mild steel, stainless steels, titanium and many other metals in the transition group exhibit “active-passive” behaviour.

A general anodic protection schematic for a tank or vessel is shown in Figure 17.

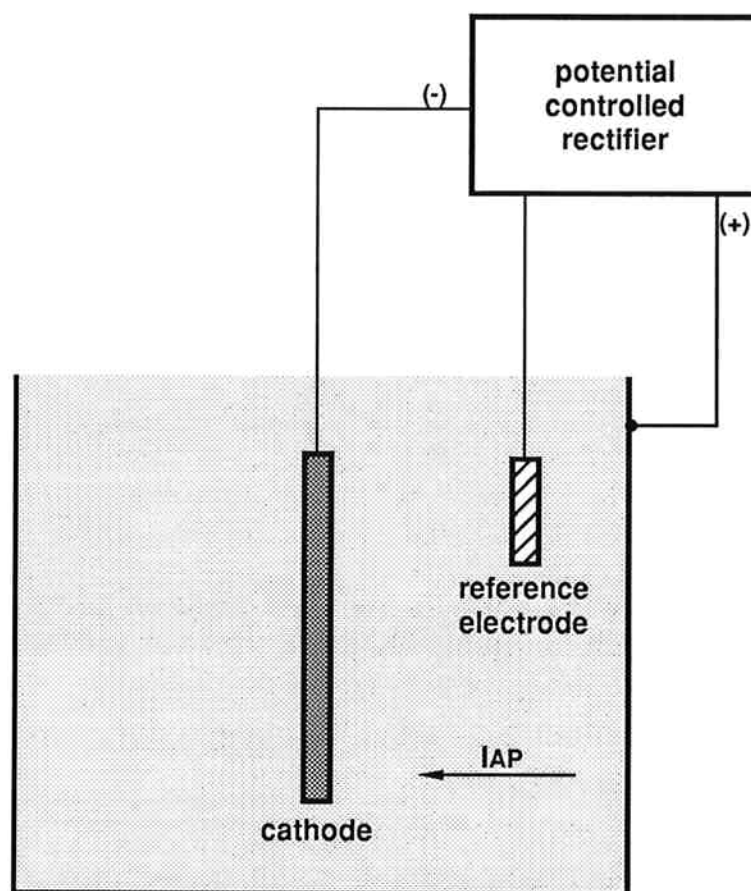


FIGURE 17 - SCHEMATIC OF ANODIC PROTECTION SYSTEM

The anodic protection current is supplied by a potential controlled power supply which is necessary in order to maintain the structure at a fixed potential in the passive range. It is usual to pre-determine the ideal set potential for operation either by laboratory testing or more preferably by running potentiostatic anodic polarization curves on coupons in the actual vessel.

The reference electrode is necessary to provide a feedback potential measurement for comparison to the set potential. The type of reference electrode is chosen for its compatibility with the liquid medium. Typical reference electrodes are platinum, calomel, silver-silver chloride, mercury-mercury sulphate and stainless steel.

Cathode materials are also chosen with respect to their durability in the liquid medium particularly since the cathode often passes through the vapour zone leaving it susceptible to aggressive atmospheric corrosion. Typical cathode materials are steel, chromium-nickel steel, Hastelloy C and platinum clad brass.

By far the largest application of anodic protection is for the protection of mild steel and stainless steel sulphuric acid storage tanks and to a lesser extent coolers and piping. Anodic protection has also been applied to mild steel in certain fertilizer solutions. Any situations in which a metal/solution combination produces active-passive behaviour is a potential candidate for the application of anodic protection if a corrosion problem arises.

Sulphuric Acid Equipment

Corrosion rates of steel or stainless steel in sulphuric acid service is a function of both temperature and acid concentration. Table 1 indicates the typical corrosion rate reduction which can be realized on 316 stainless steel in two concentrations of sulphuric acid by the application of anodic protection.

TEMPERATURE	93% H ₂ SO ₄		98% H ₂ SO ₄	
	UNPROTECTED	PROTECTED	UNPROTECTED	PROTECTED
70°C	32	<2		
100°C	552	28	46	<2

CORROSION RATE OF 316 STAINLESS STEEL IN M.P.Y.

TABLE 1 - CORROSION RATE OF 316 STAINLESS STEEL IN M.P.Y.

An anodic polarization curve for 316 stainless in 93% H_2SO_4 at 70°C is shown in Figure 18. Note that the current density required to achieve passivation is almost 10^4 microamps/cm² (10A/ft²). This potentiostatically derived polarization curve would indicate that an impractically large current capacity power supply would be required to get over the active-passive transition point. Fortunately smaller capacity units are feasible when operated galvanistically to take advantage of the coulombic effect. Current densities to maintain passivation are normally an order of magnitude less than the primary transition current.

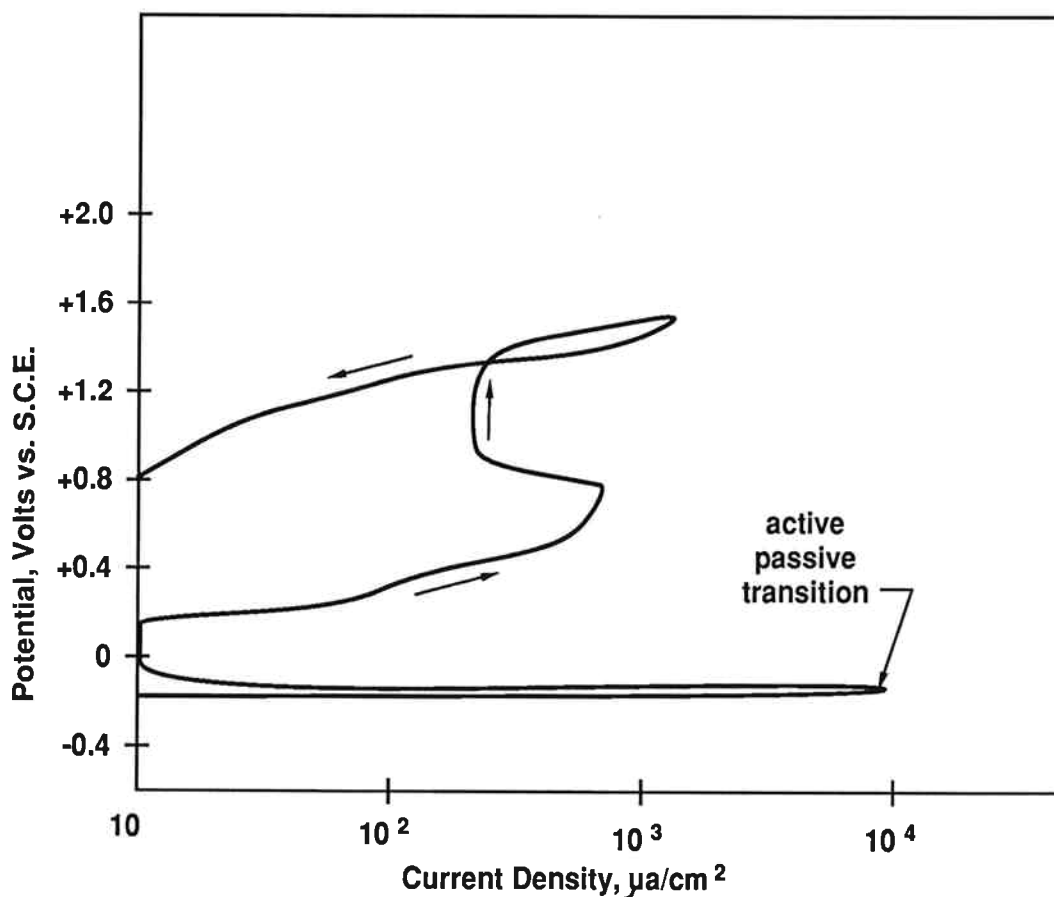


FIGURE 18 - POLARIZATION CURVE 316 STAINLESS STEEL
IN 93% H_2SO_4 AT 70°C

An interesting application of electrochemical protection involves the combined use of anodic and cathodic protection for corrosion mitigation in acid coolers as represented in Figure 19.

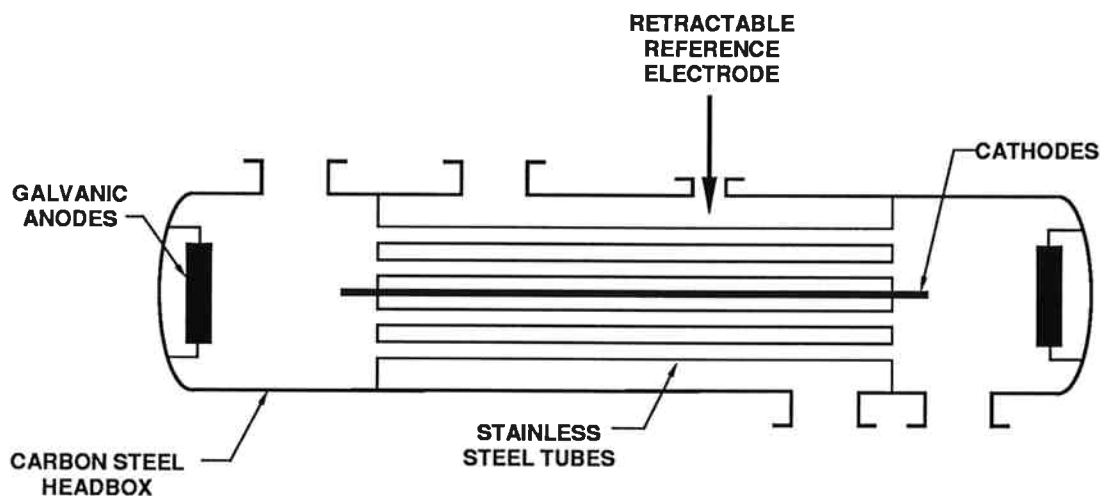


FIGURE 19 - ANOTECTION OF ACID COOLERS

Here the shell and tubes, made of 316L stainless steel and exposed to the acid are anodically protected where two Hastelloy rods, which are inserted in the place of two tubes, act as the cathodes. In addition, the carbon steel head boxes, exposed to cooling water, are protected with galvanic anodes. Piping carrying sulphuric acid can also be protected anodically.

Alkaline Process Equipment

Usage of AP in alkaline environments is almost entirely limited to the pulp and paper industry for the protection of digesters and storage tanks handling caustic kraft liquors (a mixture of sodium hydroxide and sodium sulfide). There is experimental evidence however, that mild steel can also be anodically protected in NaOH solutions at elevated temperatures.

Summary

Although AP can be retrofitted to control an existing corrosion problem, its major advantage is in allowing an equipment designer to choose a lower cost alloy or a lesser cost alternative. Table 2 indicates the comparative costs for a sulphuric acid storage facility having a 95,000L capacity.

	Mild Steel with AP	Mild Steel Lined	Stainless Steel
Tank Cost	1.70	1.70	4.57
AP System	0.94	--	--
Power	0.04	--	--
Maintenance	0.54	--	--
TOTAL COST	3.22	6.56	4.57

TABLE 2 - TANK COST ALTERNATIVES

An AP system affords the designer an opportunity to use a lower alloy material and to electrochemically induce the lower alloy to maintain passivity. Accordingly, AP has merit on new installations where the capital cost savings as indicated in Table 2 can be realized.

Summary

Both CP and AP electrochemical systems give a petrochemical plant process or maintenance engineer powerful corrosion control tools which can be applied to control corrosion on process equipment exposed to most liquid phase environments either at the construction stage or at a latter date by retrofitting. Most of the systems require external electrical power and must be operated continuously to be effective, which can sometimes be an added maintenance requirement. Recently however, remote monitoring equipment has been developed which facilitates system supervision thus allowing for automatic status checks either by the process operator or the system supplier. The latter method outlined in Figure 20 relieves the operator from having to become skilled in evaluating electrochemical system parameters.

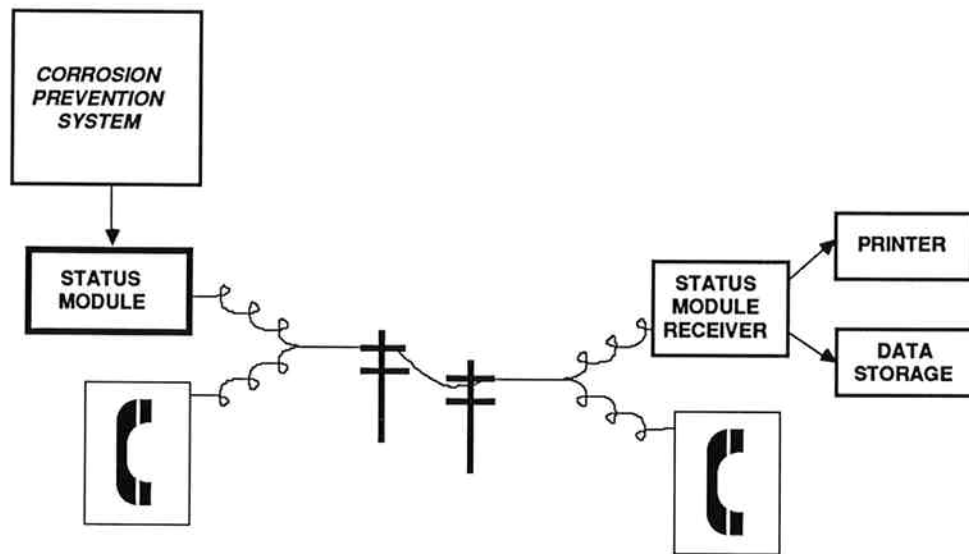


FIGURE 20 - REMOTE MONITORING OF AN ELECTROCHEMICAL CORROSION CONTROL SYSTEM

Accordingly, electrochemical systems have become as user friendly as a computer system will allow.