

Cathodic Protection

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Abstract

Explains the technique of cathodic protection in conjunction with the galvanic series of metals and cell action, plus the history and development of cathodic protection. Touches upon thermodynamic considerations, and uses polarization curves to explain the rates of corrosion reaction and how these rates can be reduced by application of cathodic protection. Several practical applications of this technique are described.

Corrosion is said to occur when a material (usually a metal) combines with some element in its environment to produce a corrosion product that does not retain the useful properties of the original material. This process proceeds in a spontaneous manner and consequently by principles of thermodynamics must result in a decrease of energy in the corroding system.

Very few metals appear in nature in their metallic form, but rather as compounds such as oxides, sulfides, or chlorides. To win these metals from their ores requires the expenditure of considerable amounts of energy, so it follows that metals contain more energy than the compounds from which they were obtained. The corrosion process can be thought of as a reversion from the metal back to the original ore. The energy which is released in the corrosion process is called Gibbs free energy, and is expressed in calories or kilo calories per mole in most textbooks. Table 1 shows the free energy of formation of some oxides, expressed in kilo calories per mole of oxide at 27 C.

In Table 1, it can be seen that substances like silver have low free energies and sometimes appear as *native silver* in ores, and some like aluminum have such large free energies that their recovery from ores on a commercial scale has only been achieved in this century.

There is an important relation between Gibbs free energy and solution potential expressed by the equation $\Delta G = -nEF$ where E is the electrode (corroding element) potential, n is the number of electrons (chemical equivalents) in the reaction, and F is Faraday's number which relates the weight of metal going into solution with the coulombs of charge transferred. The principle consideration of this relationship for the nonelectrochemist is the relationship between energy and a measurable solution potential. The equation indicates that a metal with a large free energy will have a large negative solution potential.

Electrical potentials are similar in many respects to elevations in geography. The height of a mountain must be related to some bench mark. In this case it is usually the mean sea level. Electrical potentials are also related to an arbitrarily chosen reference electrode which consists of a piece of metal in a controlled environment that exhibits a

constant potential if no current is drawn from it during measurement. If pure metals are placed in aqueous solution of their salts under controlled conditions, each metal exhibits an electrical potential when compared to a reference electrode. These metals can be arranged into what is known as the electrochemical series with the electro-negative metals at the top and the electropositive metals at the bottom. A similar series can be made using commercial metals and alloys immersed in sea water. This series is called the practical or galvanic series and is reproduced in many corrosion texts. The electrical potentials are not usually measured with a great degree of accuracy since the relative positions of the metals and alloys in this series has the greatest practical importance. If two of these metals are coupled together in an aqueous solution, the metal higher in the series (more electronegative or active) will become the anode or corroding element in this cell and the metal that is lower in the series (electropositive or more noble) will become the cathode or noncorroding element. A metal that is the anode in one combination can become the cathode in another combination. A typical galvanic series in sea water is reproduced in Table 2.

The discovery of cathodic protection was brought about by the study of galvanic cells where it was noted that the cathode did not corrode, and it was correctly postulated as early as 1824 by Sir Humphrey Davy that the anode sacrificed itself to protect the cathode. He experimented with many combinations of metals in sea water and was able to protect copper ship sheathing using zinc plates and iron plates as anodes. Zinc was the most electronegative

TABLE 1 — Free Energy of Formation of Some Oxides

Silver oxide	2.55
Copper oxide	34.6
Lead oxide	45.0
Nickel oxide	51.4
Iron oxide	54.6 (at 227 C)
Zinc oxide	76.2
Magnesium oxide	136.5
Quartz oxide	197.3
Chromium oxide	236.7 (at 227 C)
Aluminum oxide	377.6

*Corrosion Service Co., Ltd., Toronto, Ontario, Canada.

TABLE 2 — Galvanic Series of Metals and Alloys in Sea Water

Active (Electronegative)	Magnesium
	Zinc
	Alclad 3S
	Aluminum 3S
	Aluminum 61S
	Aluminum 63S
	Aluminum 52
	Low Steel
	Alloy Steel
	Cast Iron
	Type 410 (Active)
	Type 430 (Active)
	Type 304 (Active)
	Type 316 (Active)
	Ni-Resist
	Muntz Metal
	Yellow Brass
	Admiralty Brass
	Aluminum Brass
	Red Brass
	Copper
	Aluminum Bronze
	Composition G Bronze
	90/10 Copper-Nickel
	70/30 Copper-Nickel — Low Iron
	70/30 Copper-Nickel—High Iron
	Nickel
Inconel	
Silver	
Type 410 (Passive)	
Type 430 (Passive)	
Type 304 (Passive)	
Type 316 (Passive)	
Monel	
Hastelloy C	
Noble (Electropositive)	Titanium

metal available at that time, and was therefore always anodic in combination with other metals. With the commercial production of magnesium, a metal is now available that is sufficiently electronegative to act as the anode when coupled to zinc. This metal is used in great quantities to provide galvanic (cathodic) protection to steel in aqueous immersion and in the soil.

The driving energy for the corrosion process comes from the Gibbs free energy of the metal itself. The energy associated with a surface in contact with the electrolyte exemplifies itself by its solution potential, and with suitable measuring devices can be measured *in situ*. A metal surface in contact with an aqueous solution has on its surface areas that differ from one another in solution potential and are thus tiny anodes and cathodes. These differences are due to many causes such as residual stresses, impurities in the metal, grain orientation, differences in metal ion concentration, thermal effects, and so on. The anodes corrode and the cathodes do not. Cathodic protection is said to be achieved when the driving potential in a corroding cell is reduced to zero. This is achieved by forcing current to flow from the electrolyte to the surfaces of a corroding system in sufficient quantities to change the natural corrosion potentials that exist and reduce their differences to zero. Any change in potential at a metal surface due to the flow of current (natural corrosion currents or impressed currents) is referred to as polarization. Specifically then, cathodic protection is said to be achieved when the

potential of the cathodic areas on a corroding surface are polarized to become as negative as the open circuit potentials (unpolarized) of the anodic areas.

Polarization is the key to electrical protection and must be examined more carefully if a clear understanding of the control of corrosion processes is desired. In a galvanic cell using zinc and copper in sea water, zinc is the anode and copper is the cathode. If these two metals are not in metallic contact with one another, no current flows in the cell and the metals are *open circuited*. Using suitable measuring probes, the open circuit potential of the anode and cathode can be determined. When the metallic circuit is closed, a corrosion process commences and a corrosion current flows from the anode through the electrolyte to the cathode. This current flow causes polarization of these two surfaces which results in a reduction of potential difference between them. This process can be shown in an idealized fashion in what is called an Evans' Diagram (Figure 1).

The diagram in Figure 1 indicates the open circuit potentials of the cathode and anode and shows how polarization tends to bring these two potentials closer together as the current flow increases. If a galvanic cell is *short circuited*, as is usually the case in naturally occurring corrosion situations, the anode and cathode potentials come very close together indeed and are separated by the potential drop through the electrolyte caused by the passage of current (IR drop). In highly conductive electrolytes, the IR drop is small and the corrosion current is large. In poorly conducting solutions, the equilibrium condition would occur at smaller current flows with less polarization on the anodes and cathodes. Such a situation is described by the dotted line drawn between the polarization curves. In the diagram shown, the flow of corrosion currents affects the potential of both the anode and cathode equally and the corrosion process in this instance is said to be under mixed control. It is possible to have corroding systems where the principal change in potential due to the flow of current takes place on either the anode (anodic control, Figure 2) or the cathode (cathodic control, Figure 3).

Most corrosion processes in the soil are under cathodic control. This is very important when one considers the economic application of cathodic protection. If current from an outside source is impressed upon the corroding system, then the change in polarization is along the cathodic curve and if this polarization must increase until the open circuit potential of the anode is reached, the slope

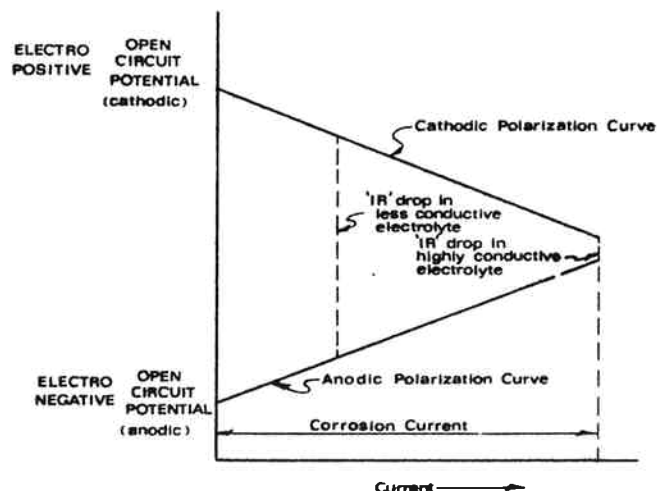


FIGURE 1 — Evans' diagram.

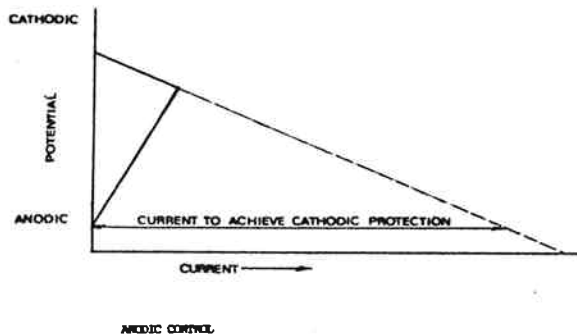


FIGURE 2 – Anodic control.

of the cathodic curve has an important effect on the applied current required to achieve protection and hence the cost of such a system. The dotted extension of the above diagram indicates the great variation of protective current required in different corroding systems. Cathodic protection can be made to work in most aqueous environments, but in some of the more aggressive ones (under anodic control), the current requirements are too large and the benefits are not economically justifiable. Table 3 gives typical current density required to protect some common structures:

In real corroding systems free from artificial control, the open circuit potential of the anode is difficult or impossible to measure or even calculate from electrochemical principles, therefore, the potential at which protection is achieved is often empirically determined. For steel pipes in the soil and steel immersed in sea water or fresh water, a potential of 850 mV measured between the structure and an adjacent copper-copper sulfate reference electrode has proven through long experience to indicate adequate protection. In cases of metal other than steel or in environments that are well out of the neutral pH range, the potential at which protection is achieved should be experimentally determined.

Pourbaix produced diagrams in which he plotted potentials against pH. He calculated boundaries on this diagram using thermodynamic considerations in which it is divided into regions of corrosion immunity and passivity. A somewhat simplified diagram for steel is shown in Figure 4.

The natural corrosion potentials of steel are found in the corrosion triangle on the upper left (Figure 4). Cathodic protection is achieved when one is able to push the potentials of the corroding system in the negative direction past the boundary between the corrosion and immunity areas. Note that as pH increases, more negative potentials must be achieved to cross this boundary. It is also important to note that it is theoretically possible to move from the region of corrosion to the region of passivity. In practice in certain environments, this can be achieved with most of the transitional metals and is called anodic protection. A discussion of this phenomenon is beyond the scope of this presentation.

In the practical application of cathodic protection, the criterion for protection must be established and the current required to achieve this potential must be calculated. At this juncture, an economic analysis of the preliminary design should aid in the decision of whether to rely upon galvanic anodes (magnesium or zinc) as a source of protective current or whether to design around a powered rectifier and an inert anode system. Galvanic anodes

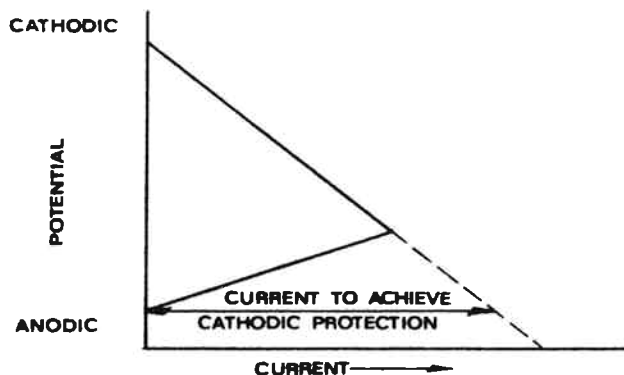


FIGURE 3 – Cathodic control.

represent prepaid power and are at least one hundred times more costly than power purchased from an electric power company. Their advantages lie in their simplicity, low maintenance, and the relatively small individual current output which lessen the risk of electrical interference with other structures. They are used in congested areas on well coated systems with small current requirements. Powered systems represent greater initial capital outlay since even for small systems, the minimum equipment required includes power supplies, a rectifier, and a prepared ground-bed, perhaps requiring land purchase or easements. These systems should be designed by a competent person and installed and energized under his supervision. The inert anodes, which are made of graphite silicon-cast iron or platinized titanium or niobium are vulnerable to various ills such as uneven corrosion patterns resulting in poor utilization of material, or gas blocking in which gases produced by electrolysis of soil water insulate the anode from the electrolyte and drying of the adjacent soil due to migration of water from the positive electrode (electroendosmosis). Cable insulating sheaths are vulnerable to mechanical damage which results in rapid corrosion of the highly anodic copper core. The cable insulation under some circumstances must exhibit great chemical resistance especially where they are contacted by nascent gases that are produced at the anodes. Complete deterioration of PVC and polyethylene sheath is not uncommon. All splices in the positive feeds should be cast in epoxy or made carefully by hand to an approved specification.

In a paper mill, cathodic protection can be used to protect the exterior surfaces of underground steel piping systems such as mill supply lines, wood yard fire lines, the underground lines from tank car unloading racks, trash racks and screens at water intakes, as well as the inside surfaces of various water and chemical storage vessels and some parts of paper making machinery where the electro-

TABLE 3 – Current Density Required to Protect Common Structures⁽¹⁾

Tank in hot sulfuric acid, static conditions: 50,000 mA/sq ft.
Pipelines and storage tanks, underground, static conditions: 1 to 3 mA/sq ft.
Fresh water pipelines, flowing: 5 to 10 mA/sq ft.
Water heaters (hot, fresh water)—slow flow: 1 to 3 mA/sq ft.
Reinforcing rods in concrete, static conditions: 0.1 to 0.5 mA/sq ft.

⁽¹⁾Corrosion Engineering, Fontana and Greene.

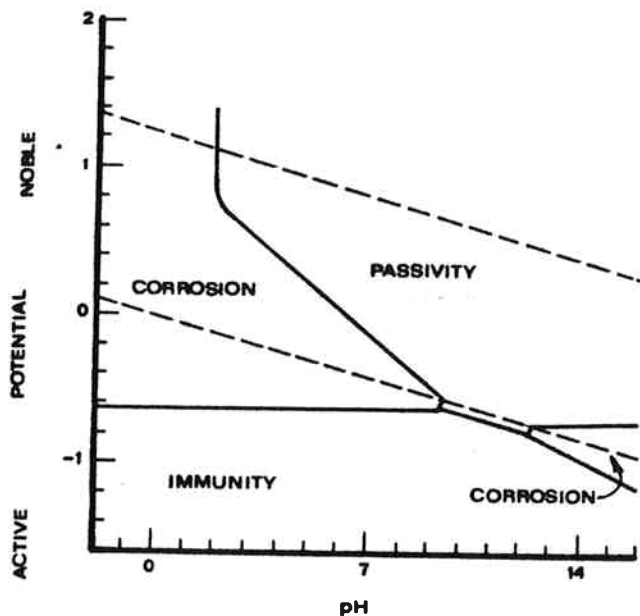


FIGURE 4 - Pourbaix diagram (simplified) for steel.

lyte is sufficiently conductive such that limited anode systems will adequately serve all surfaces.

In general, each system must be designed on its own merits. It is usual to perform a current requirements test to gain design parameters which usually involve the introduction of a temporary anode into the electrolyte which is powered from a direct current (DC) source and potential measurements are taken along the surface to be protected to determine the area affected by the test current. Usually, a number of such tests are undertaken and the data obtained extrapolated into an estimate of approximate anode configuration and the approximate total current requirements. The practicability of the anode system is then studied with a view to competition for space with both existing and contemplated structures and the likelihood of the anode system interfering adversely with other structures in the vicinity that are not part of the proposed protection scheme.

For example, supposing it was considered advisable to cathodically protect an underground portion of a natural gas supply line between a meter house and the boiler house. It is important that this pipe be electrically isolated from all other structures prior to the performance of a test to determine the current required for protection. The protective criterion for coated steel pipes in the soil has been established to be 850 mV when measured between a copper-copper sulfate reference electrode in contact with the soil directly above the pipe and the pipe metal. Because of the possible high resistances that can develop between the reference electrode and the soil contact, a high resistance voltmeter (greater than 100,000 ohms/volt) should be used.

It is usual for the gas utility to provide electrical insulation at the meter set in the form of insulated unions or insulated flanges. If this insulation is effective, then the pipe-to-soil potentials should differ when the negative of the voltmeter is connected to either side of the insulator with the reference electrode remaining in a single location on the ground in the vicinity of the insulators. It is unlikely that any insulation will have been installed at the boiler house. After careful inspection to ensure that no part of the above ground piping upstream of the first available flange

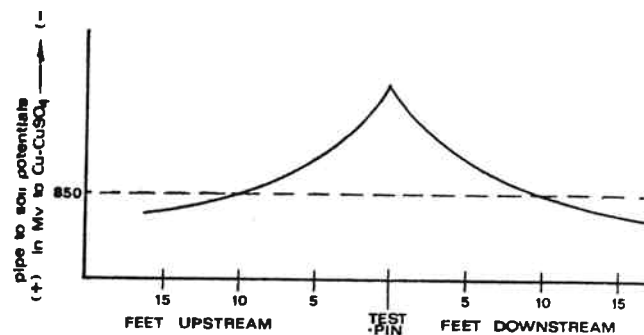


FIGURE 5 - Pipe-to-soil potential attenuation curve.

contacts any metal objects such as steel building columns, steel siding, electrical conduits, other pipes, etc., this flange can be insulated using a special flange insulation kit which includes plastic sleeves and washers. These are placed over the existing bolts which can be removed one at a time for this purpose. In addition to sleeving the bolt, plastic washers are placed under both the head and nut of the bolts and backed by a suitable steel washer to protect them from the damage during the tightening up. Each bolt treated in this manner should be tested with an insulation tester (500 V Megger or equivalent) to ensure proper isolation. When all bolts are so treated and providing the central gasket is made of a nonconducting material (it usually is), isolation of the pipe run can be achieved.

This piping should now show a good voltage response to the application of test currents. A steel rod about 5 feet in length should be driven into the ground about 10 feet away from the pipe somewhere near the center of the pipe run and 3 volts dc (2 D cells in series) should be applied between the pipe and the ground rod with the rod on the positive of the supply. The negative connection can be made to any convenient accessible location on the pipe. A milliammeter should be inserted into this circuit. The negative terminal of the high resistance voltmeter should be connected to the pipe under test at some suitable location other than that used for the current test and the positive terminal connected to the reference electrode which is placed on the ground directly over the pipe opposite the test pin. The pipe-to-soil potential is recorded at that location and a number of other locations upstream and downstream until readings are obtained that are below the 850 mV criterion. If these measured potentials are plotted using suitable scales, an attenuation curve as shown in Figure 5 will be obtained.

Experience has shown that a 4 to 5 foot driven ground rod when powered from a 3 volt battery will give out approximately the same current that could be expected from a magnesium anode installed in the same location. Our plots of pipe-to-soil potentials indicate that an anode will protect about 10 feet of pipe, therefore, a magnesium anode installed every 10 feet would provide cathodic protection for this pipe. A similar procedure can be used in determining the current required to protect the internal walls of a storage vessel, but considerable care would have to be taken in performing the tests, especially if the substances stored were caustic. The protective criterion should be separately established for each system by a controlled test program.

The extent of an anode system that is required to protect an interior surface of a storage vessel depends very greatly on the resistivity of the medium being stored and

whether or not a suitable dielectric coating has been applied to the tank. On extensive bare systems in the soil, the protective criterion that is striven for is seldom the 0.85 V to the Cu:CuSO₄ reference that is mandatory on well coated piping systems. Since polarization is made up of many different changes both at the surface of the metal and in the electrolyte adjacent to the metal surface, some of these processes take considerable time before a significant change in potential is observed. For this reason, it is usual to make a detailed pipe-to-soil potential survey of the structure prior to the application of test current, and then design a system that will cause an initial shift in potential in the negative direction of 150 mV. Cathodic protection current in the soil will not damage any structure that is electrically connected by means of a solid bond (accidental or deliberate) to the system being served, but if for any reason, a piping system that is electrically isolated from a cathodic protection system approaches or crosses a protected system, then adverse interference will be encountered and the isolated pipe could suffer accelerated corrosion attack in the vicinity of the crossing. Similarly, if cathodic protection is applied to pipes with mechanical

joints (which are common in some fire water systems), great care should be taken to ensure that each and every joint on these piping systems are bonded over with suitably sized copper bonds welded to the pipes. There are circumstances where limited cathodic protection schemes can be applied to well coated piping systems without adverse effects on mechanical joints or bell and spigot water pipe in the vicinity that does not form part of the protection scheme. These matters are usually taken into account when a system is being designed.

Cathodic protection is relied upon to protect thousands of miles of piping in the oil and gas industry and is a proven and necessary complement to coated pipe underground. It usually provides the only economic method of stopping leaks on old piping systems and should always be considered in conjunction with coating on underground pipe replacements. With a slight knowledge of this important conservation tool, a maintenance or design engineer will find many areas where the application of cathodic protection will give substantial economic returns. As with many specialties, the design and implementation of these systems should be left in the hands of experienced persons.